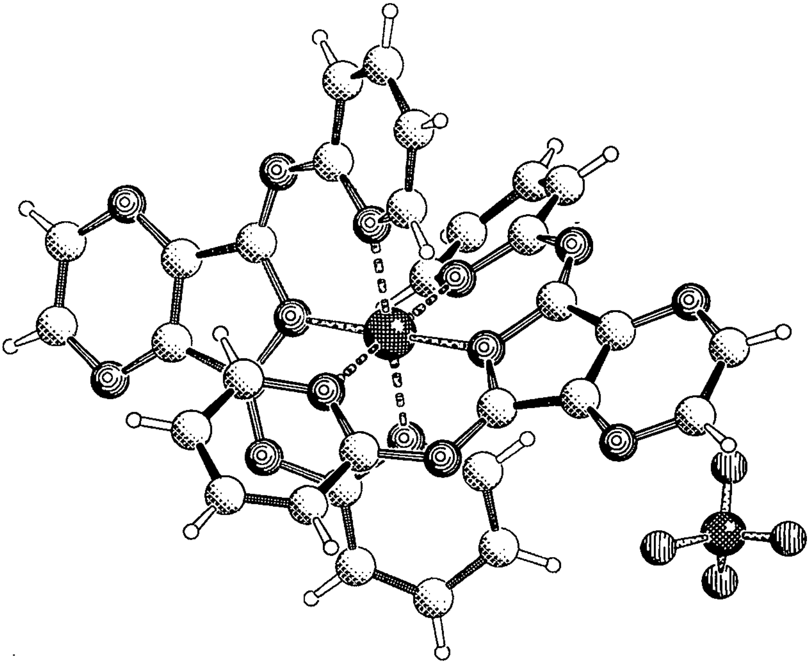
Coordination Behaviour of Some Pyrazine Based Nitrogen Donor Ligands with First Row Transition Metals:
Synthesis, Crystal Structure Analysis and Some Unexpected Results”



Maciej Posel

Janvier 1998

UNIVERSITÉ DE NEUCHÂTEL
FACULTÉ DES SCIENCES
INSTITUT DE CHIMIE

Coordination Behaviour of Some Pyrazine Based Nitrogen Donor Ligands with First Row Transition Metals: Synthesis, Crystal Structure Analysis and Some Unexpected Results"

Thèse Presenteé à la Faculté des Sciences par

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l'obtention du grade de docteur ès sciences

Institut de Chimie
Université de Neuchâtel

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IMPRIMATUR POUR LA THÈSE

Chimie de coordination de quelques ligands du type Pyrazine avec les métaux de transition: synthèses et structures cristallines

de M. Maciej Posel

UNIVERSITÉ DE NEUCHÂTEL

FACULTÉ DES SCIENCES

La Faculté des sciences de l'Université de Neuchâtel sur le rapport des membres du jury,

Mme H. Stoeckli-Evans (directrice de thèse),
MM. F. Stoeckli et T. Bartczak (Lodz Pologne)

autorise l'impression de la présente thèse.

Neuchâtel, le 25 mars 1998

Le doyen:

F. Stoeckli

Abbreviations:

°C	degree Celsius (centigrade)
Å	angstrom unit
Ac	acetyl (CH_3CO, not CH_3COO)
acac	2,4-pentanedionate, acetylacetonate
acacH	2,4-pentanedione, acetylacetone
aliph.	Aliphatic
anal.	analysis, analytical(ly)
anhyd.	anhydrous
approx.	approximate(ly)
aq.	aqueous
bppz	2,3-bis(2-pyridyl)pyrazine
bpy	2,2'-bipyridine
Bu	butyl (normal)
calc.	calculate
compd.	compound
conc.	concentrate
concd.	concentrated
cryst.	crystalline
d	doublet
$dipicH_2$	2,6-pyridinedicarboxylic acid, dipicolinic acid
DMF	*N,N*-dimethylformamide, Me_2NCHO
DMSO	dimethylsulfoxide
en	1,2-diaminomethane, ethylendiamine, $H_2NCH_2CH_2NH_2$
estd.	estimated
et al.	and others
Et	ethyl
etc.	et cetera
EtOH	ethanol
Fig.	Figure
g	gram

h	hour
Hacac	2,4-pentanedione, acetylacetone
i.e.	that is
inorg.	inorganic
IR	infra red
L	ligand
liq.	liquid
M	metal
m	multiplett
m.p.	melting point
ma	malonate
max.	maximum
Me	methyl
MeOH	methanol
min	minute (time)
mol	mole (the unit)
MS	mass spectroscopy
no.	number
org.	organic
ox	oxalate
pc	phthalocyanine
py	pyridine
pyz	pyrazine
s	strong
sol.	soluble
soln.	solution
t	tetragonal
Tab.	table
temp.	temperature
tppz	2,3,5,6-tetra(2-pyridyl)pyrazine
X	halogen

I. INTRODUCTION

Industry has focused its attention in recent years on developing a new generation of materials. These "new materials" are to be found in the fields of:

1. Polymers, in general with low dimensional structures,
2. Metal complexes (organic, inorganic and metal-organic)
3. Organic compounds.

This continued interest is because of their unusual and sometimes unexpected properties: electrical, magnetic and optical properties. Some of the most important compounds are coordination polymers which in the last 15 years have been studied very carefully {1-3}. This research has given a new series of compounds with potential application of their properties in e.g.: electrical conductivity, magnetism, and catalysis {4-6}. At the same time intense studies were performed on the correlation between the molecular structures of the polymers and the properties of these substances {7}. At the University of Neuchâtel Werner Marty developed the idea of using tetrasubstituted pyrazines as potentially bis(tridentate) chelating ligands to form, with the first row transitions metals, a special kind of coordination polymer called later "columnanes". In these polymers the bridging ligands are mutually perpendicular to one another in the polymer chain in Fig. 1.

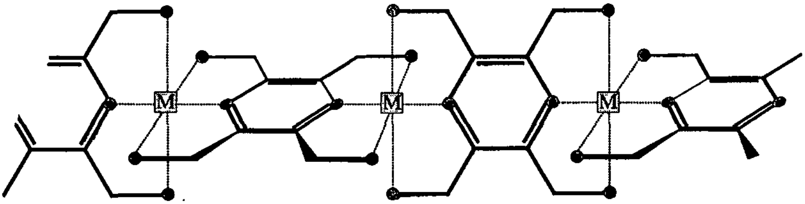


Fig. 1: Fragment of the polymer chain - "columnane".

The idea of using tetrasubstituted pyrazines as potentially bis(tridentate) chelating ligands was later heavily exploited - a whole series of polymers based on pyrazine derivatives were synthesised. The thesis of Pierre-Alain Marioni {8} was based on the ligand pyrazinetetracarboxylic acid (Fig. 2).

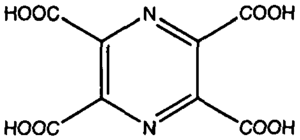


Fig. 2

Michel Ferigo {9} synthesized and used the new ligand 2,3,5,6-tetrakis(aminomethyl) pyrazine (Fig. 3);

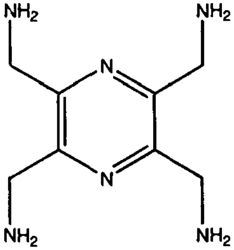


Fig. 3

Marion Graf used 2,3,5,6-tetra-(2-pyridyl)pyrazine (tppz) (Fig. 4) {10} continuing in this way the first attempts made by Goodwin and Lions {13}, who originally synthesized the ligand in 1959.

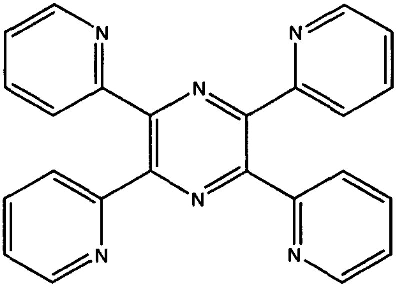


Fig. 4

She also studied the coordination behaviour of the ligand 2,4,6-pyrimidyl-1,3,5-triazine (tpymt) (Fig. 5)

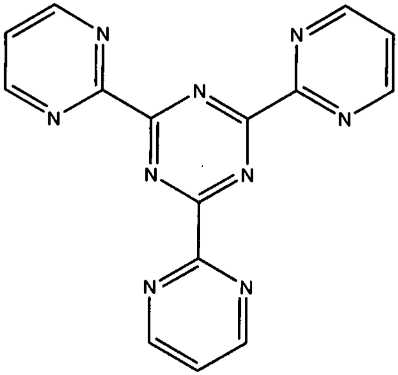


Fig. 5

Yi Wang {11} synthesized and used the ligands pyrazine-3,6-dimethyl-5,6-dicarboxylic acid, pyrazine-2,5-dipyridyl-3,6-dicarboxylic acid and pyrazine-2,3-dipyridyl-5,6-dicarboxylic acid.

Dr. Antonia Neels synthesized a series of polymers based on 2,5-bis(2-pyridiyl)pyrazine {12}(Fig. 6).

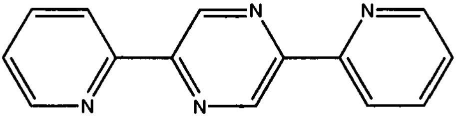


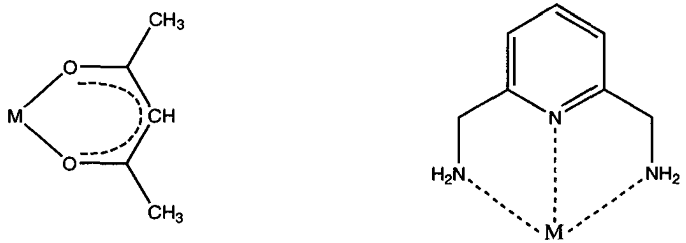
Fig. 6

All the authors mentioned above succeeded in synthesising coordination polymers and obtained very interesting results concerning their properties, especially magnetic.

This previous work indicated the necessity of continuing research in this direction, using the derivatives of pyrazine.

COMPLEXES

In general by a complex we understand a compound built from a central atom (or ion) and from another group of different atoms, molecules or ions. This second part is called the ligand; nowadays a ligand is defined as any molecule or ion that has at least one electron pair that can be donated. The section of inorganic chemistry investigating the properties of these compounds is called *coordination chemistry*. In the field of coordination chemistry one treats the central metal atom as a cation and the ligands as the Lewis bases (in the terms used in organic chemistry). There are different ways of classifying ligands and one way is to classify ligands structurally. The complexes where one metal atom - one central atom - is connected to only one atom of the ligand are called unidentate (or monodentate) e.g., in $Fe(CN)_6^{3-}$; when the ligand is bonded to two atoms we talk about bidentate complexes, with three atoms - tridentate etc. Generally in the case when the ligand is attached by more atoms we have polydentate complexes. The examples of complexes mentioned above are given in the Fig. 7.

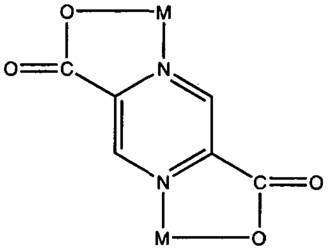


Example of a bidentate ligand

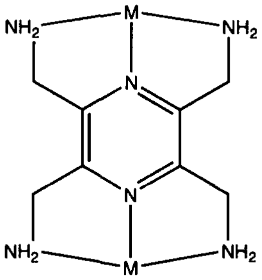
Example of a tridentate ligand

Fig. 7

Depending on the structure of the ligand we can also talk about mono-bidentate, bis-bi(or tri)dentate etc. Some examples of these ligands are given in Fig. 8.



Example of a bis-bidentate ligand



Example of a bis-tridentate ligand

Fig. 8

In this case the ligand is usually playing the role of a bridging group. In the case of unidentates the simplest bridging ligand can be, for example, a halogen atom - it forms bonds to different metal atoms. In our case, because we are using derivatives of pyrazine we are concerned with mono-bidentate, bis-bidentate and bis-tridentate ligands.

It is also necessary to mention that polydentate ligands, bound entirely to one metal atom are called chelates, and the whole group of complexes is called chelate complexes.

Another way of classifying ligands is by taking into account the nature of the bonding interactions between the central atom and the atoms in its neighbourhood. This leads to two classes of ligands:

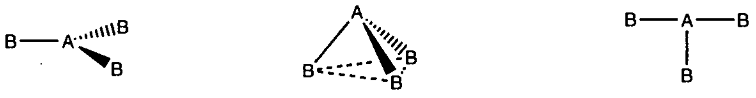
1. *Simple donor ligands*: theses are electron-pair donors to acceptor ions or molecules; which form complexes with all types of Lewis acids, metal ions, or molecules.
2. *π -bonding ligands*: form complexes almost exclusively with transition metals - the interaction is between the d-orbitals of the metal and the d-orbitals of the ligand.

COORDINATION NUMBERS (concerning the metallic center of the complexes)

In coordination chemistry the coordination number plays an important role - the proprieties of the metal, together with the coordination proprieties of the ligand itself determines the formation and the form of the complex obtained. The coordination number refers to the number of anions or atoms that are the first nearest neighbours to a cation in a complex. The most common coordination numbers are 2, 3, 4, 5, 6, less common are 7, 8, 9 and the higher coordination numbers are even more less common. Each coordination number corresponds to a geometrical arrangement in the space around the central atom (two or more geometrical arrangements are possible for each coordination number).

Coordination number 2: not very frequent, is found mainly in complexes of Cu^{I}, Ag^{I}, Au^{I} and Hg^{II} with two geometric possibilities, linear and bent.

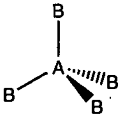
Coordination number 3: also not very frequent exhibits three possible types of geometrical arrangement; planar (9-1, Fig. 9), pyramidal (9-2, Fig. 9) and, very rare, a T-shaped form (it occurs in e.g., ClF_3 and BrF_3) (9-3, Fig. 9); examples of the three arrangements are given in Fig. 9.



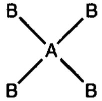
9-1 9-2 9-3

Fig. 9

Coordination number 4: frequently observed and a very important coordination number; exhibits three types of arrangements. The most important one, and typical for non-transition elements, but not only for them, is the tetrahedral fashion (10-1, Fig. 10). The second one, a square arrangement (10-2, Fig. 10) is observed in complexes of transition metals. The last one is irregular (e.g., SF_4).



10-1

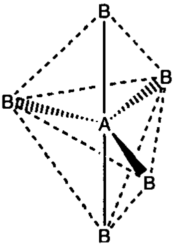


10-2

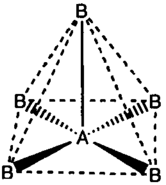
Fig. 10

Coordination number 5: two principal geometries are possible: trigonal bipyramidal (11-1, Fig. 11) and square pyramidal (11-2, Fig. 11). In the trigonal bipyramidal form the ligand atoms lie at the vertices of a trigonal bipyramid and for the second type the ligand atoms lie at the vertices of a square pyramid - hence the names of the two arrangements.

A very rare arrangement is planar pentagonal. This occurs in [$Te(S_2COEt)_3]^-$, where two ligands are bidentate and one monodentate.



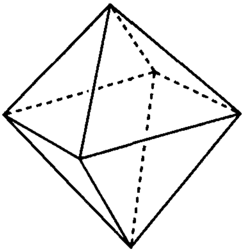
11-1



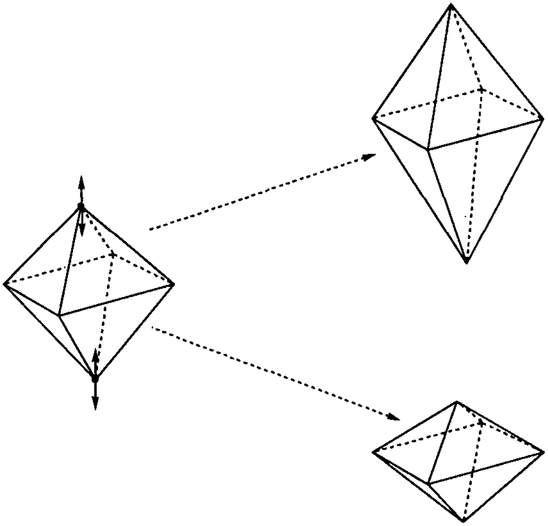
11-2

Fig. 11

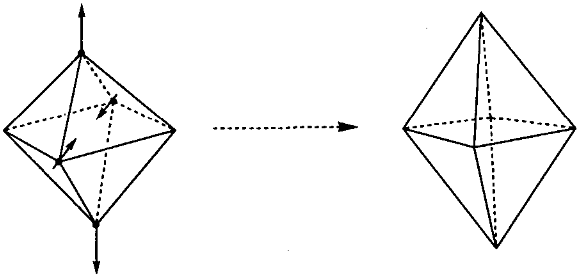
Coordination number 6: the most important and the most common coordination number, where the six ligand atoms lie at the vertices of an octahedron (12-1, Fig. 12) or a distorted octahedron. When elongation or concentration along a single C_4 axis occurs we have the tetragonal distortion (12-2, Fig. 12); deformation along two of the C_4 axes so that the no two are equal is called rhombic distortion (12-3, Fig. 12). The trigonal distortion occurs when we have elongation or concentration along one of the C_3 axes (12-3, Fig. 12).



12-1. Octahedral arrangement

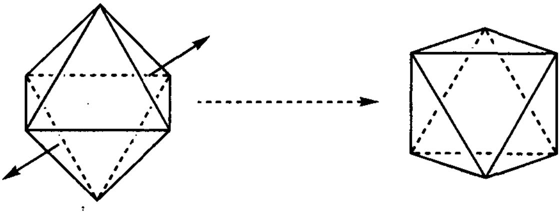


12-2. Tetragonal distortion of octahedral arrangement.



12-3. Rhombic distortion of octahedral arrangement.

12-4. Trigonal distortion of octahedral arrangement



There are also some other types of six-coordinate geometry such as trigonal prism, trigonal prismatic and antiprismatic, but they are not so common and will not be discussed in this work.

Coordination number 6 is the most important coordination number for this work. In almost all of the complexes synthesised here the metal atoms possess coordination number 6.

The higher coordination numbers, such as 7, 8 etc., are not so common in coordination chemistry and will not be discussed further.

SYNTHESIS OF THE PYRAZINE DERIVATIVES

The first documented synthesis of a pyrazine derivative was the synthesis of tetraphenylpyrazine, performed by Laurent {14} in 1844, from α-phenyl-α-(benzylideneamino)acetonitrile (PhCh=NCHPhCN). The next synthesis, done in a more "modern" way was, by Erdmann {15} in 1865 from the reaction of ammonia with benzoin. Up to today many different types of syntheses of pyrazines have been invented and described, for example in the work of Barlin {16}. Nowadays, the most general method used for the synthesis of substituted pyrazines is the condensation of α,β-dicarbonyl compounds with α,β-diamino compounds (Fig. 13):

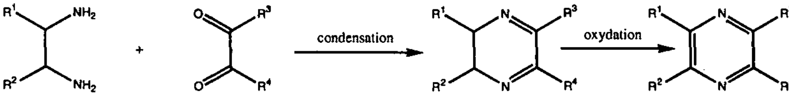


Fig. 13: Synthesis of the substituted derivatives of pyrazine (first method)

The second most popular method of obtaining substituted derivatives of pyrazine (used mostly for obtaining the 2,5-disubstituted and 2,3,5,6-tetrasubstituted pyrazines) is the self condensation of α-(primary amino) carbonyl compounds. This results in the formation of dihydropyrazines that are subsequently oxidised to the pyrazines themselves e.g., (Fig. 14.):

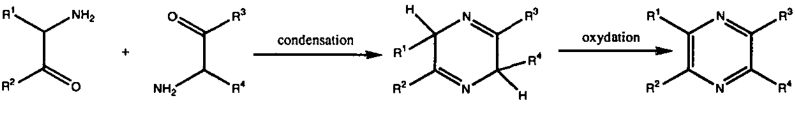


Fig. 14: Synthesis of the substituted derivatives of pyrazine (second method)

Other methods exists but for our purposes we adopted the first method mentioned above to obtain the first intermediate products, the pyrazine derivative, 2,3-dicyanopyrazine, which later served for obtaining the first ligand used in this work

POLYDENTATE LIGANDS

Ligand **L1**

A completely new ligand **L1**: 5,7-bis(2-aminopyridine)-5H-6,7-dihydropyrrolo[3.4-b]pyrazine; was chosen and synthesised for this work (Fig. 15):

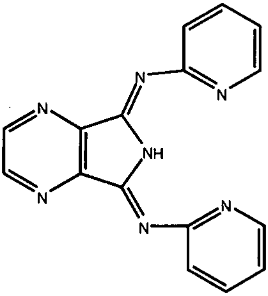


Fig. 15

This ligand is a potential mono-tridentate ligand and can serve for building complexes with a ligand to metal ratio such as 2 : 1, which are similar to the central fragment of the "columnane" polymers. The properties of the ligand and the complexes are compared with the properties of the 1,3-bis(pyridylimino)isoindoline ligand and its complexes. {23, 59, 61, 62, 65-68}

Ligand **L2**

The second ligand that we attempted to synthesise, **L2**, was similar to **L1** (Fig. 16).

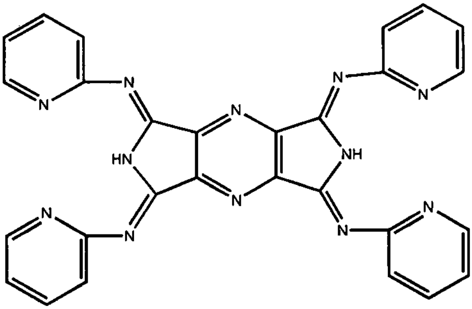


Fig. 16

The synthesis was similar but as a starting material, in the place of 2,3-dicyanopyrazine (the case of **L1**), we used 2,3,5,6-tetracyanopyrazine. This potential bis-tridentate ligand we hope could be used to obtain the "columnanes" polymers.

Other ligands

The third ligand is the already well known 2,3,5,6-tetra-(2-pyridyl)pyrazine (**tppz**) given in Fig. 3.

The next interesting ligand was based on the structure of the phthalocyanines but in place of benzene rings were placed the pyrazine rings (Fig. 17):

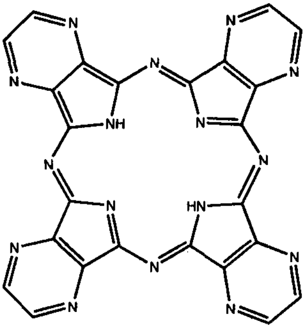
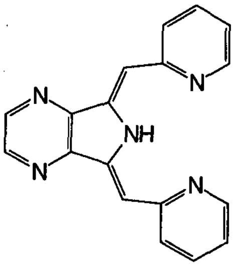


Fig. 17

So in this way all the ligands presented above could theoretically allow us to obtain a new series of chelate complexes with different transition metals. Later it was thought, that after a few modifications of the syntheses and the structure of the ligands themselves (for example, a small modification of the structure of **L1** could cause rotation of the pyridine rings and in this was a new coordination centre could be created), that from all of the ligands mentioned it should be possible to obtain coordination polymers and allow us to investigate their properties.

2. SYNTHESIS OF THE LIGANDS



Ligand **L1**: 5,7-bis(2-aminopyridine)-5H-6,7-dihydropyrrolo[3.4-b]pyrazine:

The synthesis of this product was not described in the literature, so it was necessary to apply a method used for obtaining 1,3-bis(pyridylimino)isoindoline. The first synthesis of the 1,3-bis(pyridylimino)isoindoline was given by Elvidge and Linstead {17} in 1952. The product was prepared from phthalimide through 1,3- Di-iminoisoindoline. Also examples of some nickel complexes of 1,3-bis(pyridylimino)isoindoline were given. The studies on this compound were continued later {18,19,20}. The investigation and some modification of the synthesis of 1,3-bis(pyridylimino)isoindoline were introduced by Siegl {21,22}, and Gagné et al. {23,24}. The first one step reaction for obtaining 1,3-bis(pyridylimino)isoindoline was given in 1952 by Clark, Elvidge, and Linstead {25} and was improved in later works of the same authors mentioned above {18-24}.

For our purposes we adopted and then modified the one step reaction described by Siegl {21}. As a starting material 2,3-dicyanopyrazine {26} was used. It was synthesised in the same way as given in Fig. 18.

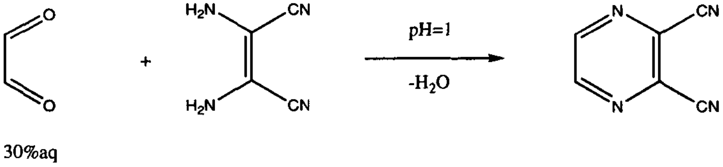


Fig. 18: Synthesis of 2,3-dicyanopyrazine

The nucleophilic addition of the aromatic amine (in this case the 2-aminopyridine) to the 2,3-dicyanopyrazine at 60°C in the presence of $CaCl_2$ gave the ligand **L1** (Fig. 19). Probably, as in the case of the synthesis of 1,3-bis(pyridylimino)isoindoline, the addition of a primary amine to 2,3-dicynopyrazine results in an intramolecular cyclisation to form a stable product **1**, to which a second molecule of the amine is added.

It has also been found that several alkaline salts facilitate the addition of primary aromatic amines to phthalonitrile under mild condition - the same method has been applied in the reaction for the formation of **L1**: $CaCl_2$ was used to facilitate the primary addition.

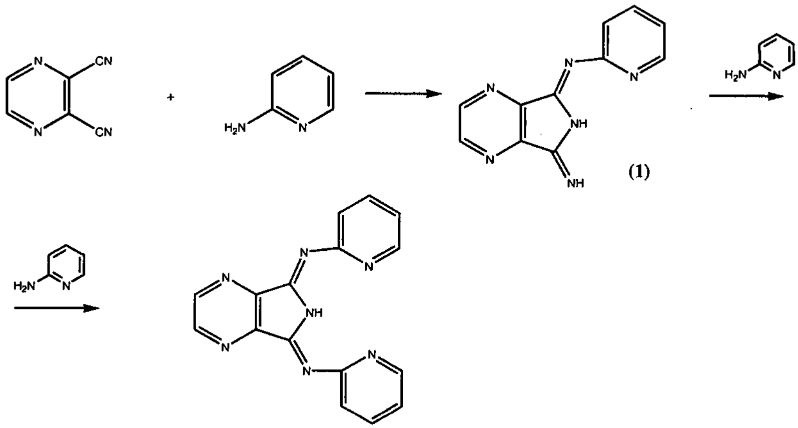


Fig. 19: Synthesis of ligand **L1**

The main product was then extracted with chloroform, then chromatographed over silica with chloroform as an eluent. It gave **L1** with the yield ~40%.

Characterisation of the ligand **L1**

The crystals used for analysis were obtained from the filtrate of the reactions of **L1** with the following metal salts: $Cu(BF_4)_2*xH_2O$, $Fe(ClO_4)_2*6H_2O$, $Co(ClO_4)_2*6H_2O$ and $Ni(ClO_4)2*6H_2O$. It was impossible to obtain crystals suitable for X-ray analysis by direct recrystallization, although many different solvents and solvent mixtures were used. In all cases the IR spectra and X-ray analysis of obtained crystals confirmed the same structure of **L1**.

The IR spectrum was taken in KBr disc. Different regions of strong absorption were assigned. Bands in the region 1400-1600cm^{-1} at 1378(s), 1435(s), 1477(w), 1554(s), 1581(s) correspond to the ν(C=C) and ν(C=N) stretching vibrations in the pyridine and pyrazine rings. A very strong band at 1641(s)cm^{-1}, corresponds to the C=N stretching vibrations in Py-C=N-Pz (substituted imine) fragment, and a band at 1139(s) cm^{-1} corresponds to the stretching vibrations C-N in the secondary amines. An intense band found at 790(m) cm^{-1} could be assigned to the corresponding C-H groups; absorption corresponding to the ring vibrations (1300-1600 cm^{-1}) and to the C-H out of plane deformations (600-1100 cm^{-1}) were also found. Mass spectrum, expected 301, observed 301. Also the elemental analysis is in agreement with the results found by means of X-ray structure analysis. The X-ray analysis of the obtained crystals allowed us to establish the structure of **L1**, presented in Fig. 20.

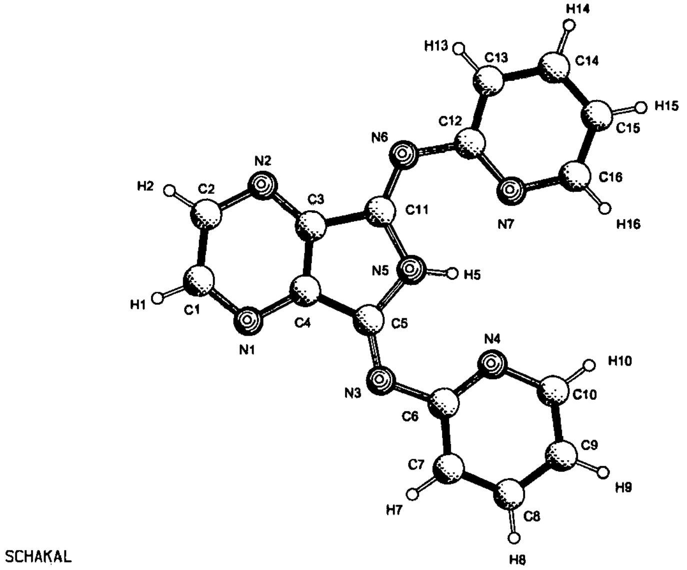


Fig. 20: SCHAKAL plot of **L1**

The product crystallised in the trigonal crystal system, space group R3c with a=b=29.757(1)Å, c=8.3849(7)Å, V=6429.8(7)Å^3, Z=18.

The molecule is almost planar: the dihedral angle between the pyrazine ring and the five membered pyrrole ring is 0.61°, between the pyrazine ring and C12- -C16-N7 pyridine ring 4.47°, and between the pyrazine ring and C6- -C10-N4 ring 3.26°. All the distances are typical for these types of bonds. {42}

Selected angles for **L1** are given below in Tab. 2.1.

Angle	Angle (°)	Angle	Angle (°)
C3-C11-N6	124.45(7)	C4-C5-N3	125.9(7)
C11-N6-C12	122.0(6)	C5-N3-C6	121.6(7)°
N6-C12-N7	121.0(6)	N3-C6-N4	120.(8)°
N5-H5-N4	119.7862(63)	N5-H5-N7	119.4568(54)

Tab. 2.1

Synthesis of the ligand **L2**

The synthesis of next ligand **L2** was based on a similar synthesis performed for obtaining 1,3,5,7-tetra-(2-pyridylimino)benzodipyrrole {22, 24}:

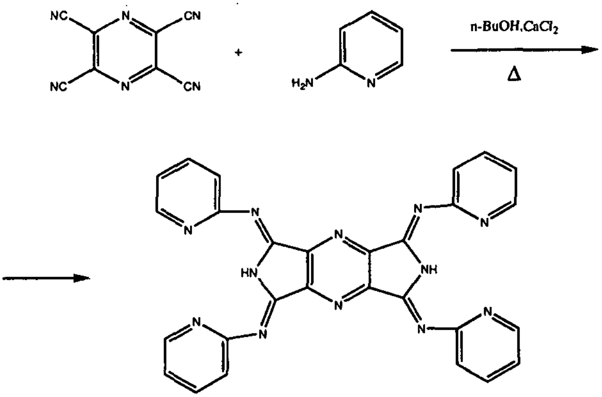


Fig. 21: Synthesis of ligand **L2**.

The synthesis gave a mixture of different products - the TLC indicated the presence of about 5 different products. Unfortunately it was impossible to isolate this ligand. It was therefore impossible to purify it and to use it for further analysis and reactions.

Synthesis of the ligand **tppz** *(see Fig. 4, page 6)*

The third ligand studied was 2,3,5,6-tetra-(2-pyridyl)pyrazine (**tppz**), synthesized for the first time by Goodwin and Lions in 1959 {13}. As it was already mentioned in the introduction, the Ph.D. thesis of Marion Graf is based on TPPZ {10}. In that work both conformational forms of the free ligand 2,3,5,6-tetra-(2-pyridyl)pyrazine and its properties are described and were investigated {34-40}. In our work we succeeded in repeating the synthesis of ligand and obtained after crystallisation both of the known forms of TPPZ: tetragonal and monoclinic. The results of the analysis of the crystals obtained are in full agreement with the published results {10}, therefore, further description of the synthesis and investigation of the properties is not necessary and was not be undertaken in this work.

Synthesis of the phthalocyanine derivatives

The last ligand that we attempted to synthesize was the phthalocyanine derivative. The benzene analogue has appeared in many publications {e.g., 27-33}.

The synthesis was carried out according to the synthetic method published by Wöhrle et al. in 1992 {41}. That reaction was catalysed by using a very strong base - in our case we used DBU - 1,8-diazabicyclo[5.4.0]undec-7-ene. The reaction was performed in the presence of metal salts to obtain in a one step reaction a metallized derivative (Fig. 22).

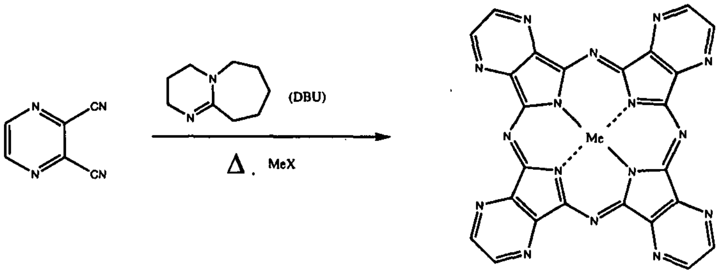


Fig. 22: Synthesis of phthalocyanine derivatives.

The following metal salts were used: $CuCl_2*2H_2O$, $CuCl_2$, $ZnCl_2$, $CoCl_2*6H_2O$ and $NiCl_2*6H_2O$. Each reaction resulted in the formation of a different product, in the form of powders. All the products are insoluble in almost all common organic solvents (they were only slightly soluble in DMF and DMSO), but were reasonably soluble in concentrated sulphuric acid. Until now no crystals were obtained from these solvents so that the X-ray analyses could not be carried out. The IR spectra seem to confirm the structures of the products proposed in Fig. 22, but the rest of the properties were not investigated in this work.

3. COORDINATION BEHAVIOUR OF LIGAND L1

COMPLEXES OF LIGAND L1
(5,7-BIS(2-AMINOPYRIDINE)-5H-6,7-DIHYDROPYRROLO[3.4-B]PYRAZINE)

3.1). Cobalt complex C1

The first metal complex of ligand **L1** synthesized during this work was a Co^{II} complex with a metal to ligand ratio of 1:2. The synthesis was quite simple: to a mixture of the **L1** with triethylamine in methanol, the solution of the metal salt: $Co(ClO_4)_2*6H_2O$ in methanol was added dropwise, at room temperature. On slow evaporation of the solvent black block-like crystals were obtained and analyzed by X-ray diffraction. This analysis allowed us to establish the structure of **C1**, presented in Fig. 23, as $[Co(L1)_2](ClO_4)*2CH_3CN$.

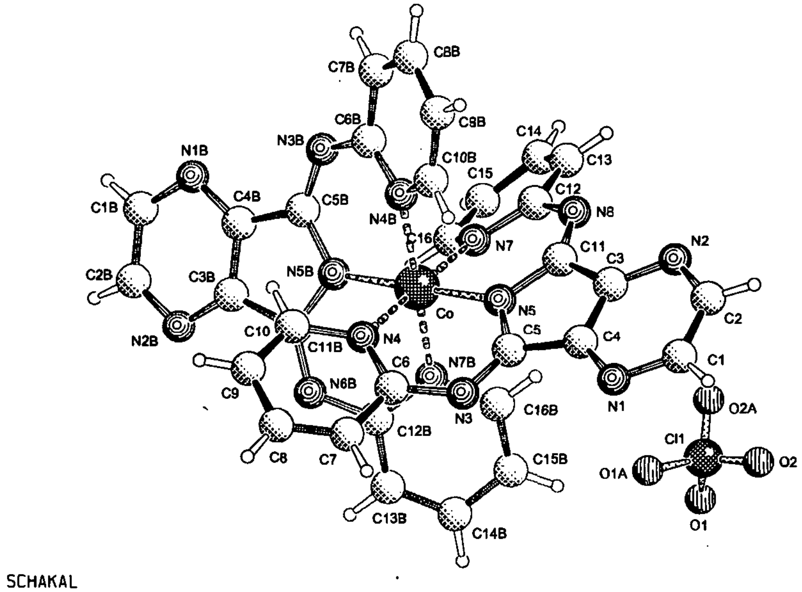


Fig. 23: SCHAKAL plot of complex C1

This product crystallized in the tetragonal crystal system, space group $I\bar{4}2d$, with a=b=19.976(2)Å, c=18.341(2)Å, V=7318.5(11)$Å^3$, Z=8, R1=0.0562, wR2=0.1486.

Ligand **L1** itself coordinates in a monodentate manner. The complex, which is a bis-mono-tridentate arrangement, possesses crystallographic C_2 symmetry and the coordination sphere of the cobalt atom can be described as nearly perfectly octahedral (coordination number 6).

To simplify further investigations we have defined some planes and rings in the complex. Atoms C1-C2-N2-C3-C4-N1 built up the plane called *PZ*; in that pyrazine ring we define two planes: *PZN1* built up from atoms N1, C1, C4, and *PZN2* containing atoms N2, C2, C3. The pyrrole ring built up from atoms C3-C4-C5-N5-C11 will be called *PR*; the pyridine ring C6-C7-C8-C9-C10-N4 *PYN4*, second pyridine ring, C12-C13-C14-C15-C16-N7, *PYN7*. All the corresponding names are shown in Fig. 24.

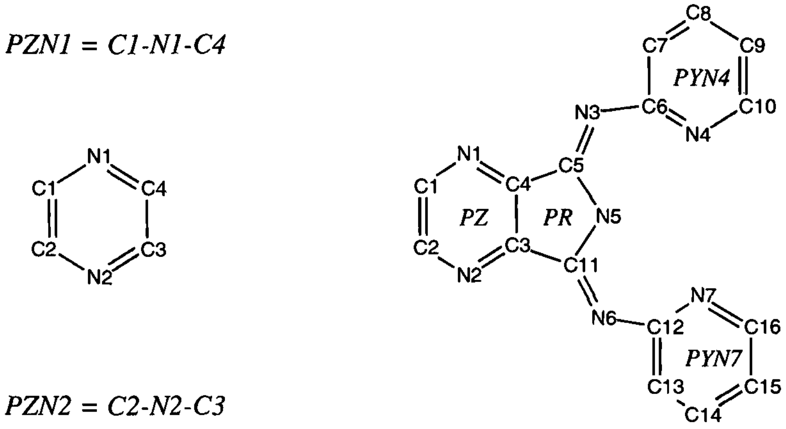


Fig. 24

The arrangement of the nitrogen atoms in the coordination sphere of Co atom is illustrated in Fig.25.

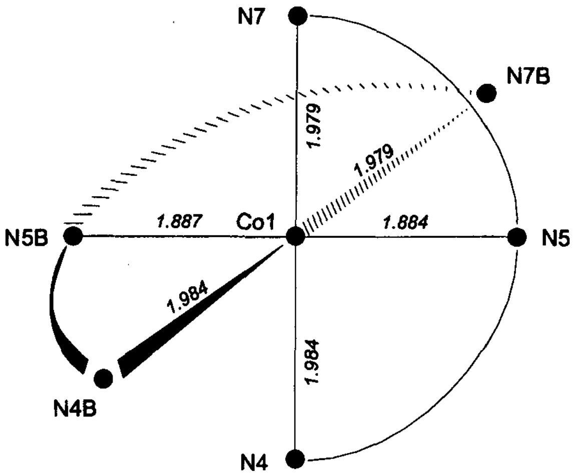


Fig. 25

Selected distances (Å) and for **C1** are given in Tab. 3.1:

Co(1)-N(4)	1.984(5)	Co(1)-N(5)	1.887(5)	Co(1)-N(7)	1.979(5)

Tab. 3.1

Selected angles (°) for **C1** are given in Tab. 3.2:

Angle	Angle (°)	Angle	Angle (°)
N(4)-Co(1)-N(4B)	92.5(3)	N(7)-Co(1)-N(4B)	89.0(2)
N(5)-Co(1)-N(4)	88.9(2)	N(5)-Co(1)-N(7B)	91.2(2)
N(5)-Co(1)-N(5B)	179.2(3)	N(7)-Co(1)-N(4)	177.7(2)
N(5)-Co(1)-N(4B)	90.6(2)	N(7)-Co(1)-N(7B)	89.6(3)
N(5)-Co(1)-N(7)	89.4(2)		

Tab. 3.2

The dihedral angle between the pyrazine ring *PZ* and the five membered pyrrole ring *PR* is 2.91(0.26)° - so comparing it with the same angle in the free ligand, which is 0.70(1.03)° we can say that this fragment of the complex is nearly coplanar, although slightly distorted. The dihedral angle between the pyrrole ring *PR* and the *PYN7* pyridine ring is 29.72(0.27)° (in the free ligand 4.40(0.45)°), between the pyrrole ring *PR* and *PYN4* ring is 28.93(0.27)° (in the free ligand 4.03(0.48)°). The pyridine rings are on opposite sides of plane in which lies the pyrazine ring. Such a large distortion is due to the steric requirements for coordination of **L1** to the cobalt atom.

The distances Co-N atoms in pyridine rings are almost the same (and typical for the M-N_{PY} bond lengths – 2.034-2.151Å). In the case of the central N atom in the pyrrole ring the bonds lengths are shorter indicating the stronger character of coordination with the Co atom (in the complex it is 1.887(5)Å when the standard bond length is 2.044Å). {42}

In this reaction $Co(ClO_4)_2*6H_2O$ was used, that is a Co^{II} salt; it is necessary to pay our attention to the fact that in the crystalline compound we have Co^{III}. It means that the metal was oxidized - it could happen already during the reaction with the ligand **L1** as a result of the presence of perchlorate. The second and rather more possible explanation is that the metal was oxidized during recrystallization that was not performed under nitrogen, just in the recrystallizer in air. There was no significant colour change of the solution during the reaction (the solution was at all time dark brown, the recrystallized powder was black-brown and the solution during recrystallization was also dark brown).

In the IR spectrum (KBr) different regions of strong absorption are assigned. The characteristic bands observed in the IR spectrum of the free ligand **L1** are shifted to lower wavelengths. The absorption bands characteristic for the presence of the ClO_4^- anion are observed: a very strong and wide absorption band in region of 1050-1100cm^{-1}, and a strong band at 623cm^{-1}.

3.2). Cobalt complex **C2.**

To the mixture of **L1** and triethylamine in dry methanol a solution of the metal salt $Co(BF_4)_2*xH_2O$ in dry methanol was added dropwise at room temperature. Slow evaporation of the solvent resulted in blue-black crystals that were recrystallized from a mixture of solvents, acetonitrile/methanol. The X-ray analysis allowed us to establish the structure of product **C2** as $[Co^{II}(L1)_2]*1/3CH_3CN$, and it is presented in figure Fig. 26.

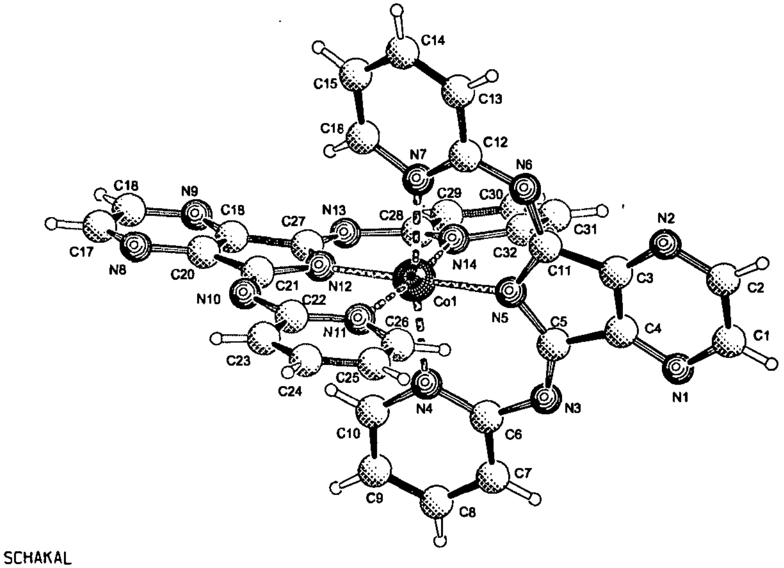


Fig. 26: SCHAKAL plot of **C2** molecule A

This product crystallized in the orthorhombic crystal system, space group Pccn, with a=19.118Å, b=24.816Å, c=18.69Å, V=8951.8Å^3, Z=12, R1=0.1366, wR2=0.1954.

Again ligand **L1** coordinates in a mono-tridentate manner, the coordination sphere of the cobalt atom can be described as nearly octahedral (coordination number 6). The asymmetric unit contains 1.5 molecules of complex and 1/3 of a molecule of solvent: acetonitrile. One molecule of complex possesses C_2 symmetry (molecule B). In both complex molecules (A and B) of product **C2** the distances C-C and C-N are normal within experimental error. The biggest differences in the two molecules can be observed in the length of the Co-N bonds because of symmetry of the molecule B.

Selected distances for **C2** are given in Tab. 3.2:

Molecule A		Molecule B	
Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
N(4)-Co(1)	2.211(12)	N(18)-Co(2)	2.184(12)
N(5)-Co(1)	2.061(11)	N(19)-Co(2)	1.993(12)
N(7)-Co(1)	2.205(11)	N(21)-Co(2)	2.148(12)
N(11)-Co(1)	2.198(11)		
N(12)-Co(1)	2.057(10)		
N(14)-Co(1)	2.225(11)		

Tab. 3.2

The simplified coordination spatial arrangement in both complex molecules (A and B) is schematically shown in figure Fig. 27.

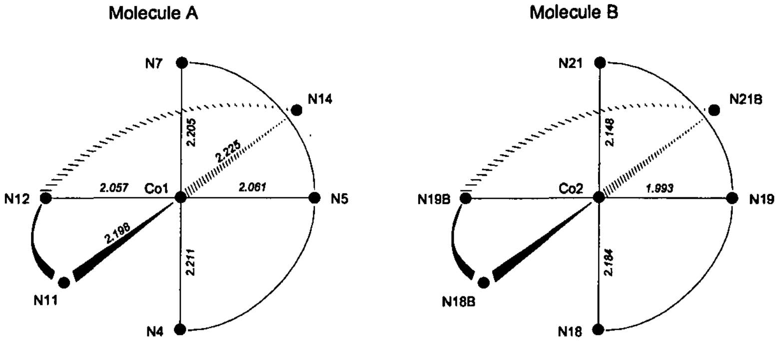


Fig. 27

The atoms N(5), N(12), N(19), N(19B) are the nitrogen atoms in the pyrrole rings. In molecule A we can observe slightly weaker coordination with atom Co1 - the distances between the central metal atom and coordinated nitrogen atoms are longer (~0.04Å) than in the case of molecule B, which may be due to the higher symmetry present in molecule B. The Co atoms in both molecules (A and B) have a distorted octahedral coordination sphere.

Selected angles (°) for **C2** are given in Tab. 3.3:

Molecule A		Molecule B	
Angle	Angle (°)	Angle	Angle (°)
N(4)-Co(1)-N(5)	86.0(4)	N(18)-Co(2)-N(19)	86.7(5)
N(4)-Co(1)-N(7)	171.4(4)	N(18)-Co(2)-N(21)	172.2(5)
N(4)-Co(1)-N(11)	91.7(4)	N(18)-Co(2)-N(18B)	85.9(6)
N(4)-Co(1)-N(12)	93.8(4)		
N(4)-Co(1)-N(14)	88.1(4)		
N(5)-Co(1)-N(7)	85.4(4)	N(19)-Co(2)-N(21)	86.5(4)
N(5)-Co(1)-N(11)	96.0(4)	N(19)-Co(2)-N(18B)	95.4(5)
N(5)-Co(1)-N(12)	178.6(4)	N(19)-Co(2)-N(19B)	177.1(6)
N(5)-Co(1)-N(14)	93.3(4)	N(19)-Co(2)-N(21B)	91.5(4)
N(7)-Co(1)-N(11)	88.9(4)	N(21)-Co(2)-N(18B)	91.0(4)
N(7)-Co(1)-N(12)	94.9(4)	N(21)-Co(2)-N(21B)	93.0(6)
N(7)-Co(1)-N(14)	92.8(4)		
N(11)-Co(1)-N(12)	85.4(4)		
N(11)-Co(1)-N(14)	170.6(4)		
N(12)-Co(1)-N(14)	85.3(4)		

Tab. 3.3

To simplify further investigations we have to define some planes and rings in the structure of **L1** in the complex. The atoms C1-C2-N2-C3-C4-N1 build up the plane called *PZ*; in that pyrazine ring we define two following planes: *PZN1* build up form atoms N1, C1, C4, and *PZN2* containing atoms N2, C2, C3. The pyrrole ring built up from atoms C3-C4-C5-N5-C11 will be called *PR*; the pyridine ring C6-C7-C8-C9-C10-N4 *PYN4*, second pyridine ring, C12-C13-C14-C15-C16-N7, *PYN7*.

The atoms C17-C18-N9-C19-C20-N8 build up the plane called *PZ2*; in that pyrazine ring we define the two following planes: *PZN8* build up form atoms N8, C17, C20, and *PZN9* containing atoms N9, C18, C19. The pyrrole ring built up from atoms C19-C20-C21-N12-C27 will be called *PR2*; the pyridine ring C22-C23-C24-C25-C26-N11 *PYN11*, second pyridine ring, C28-C29-C30-C31-C32-N14, *PYN14*.

In molecule B atoms C33-C34-N16-C35-C36-N15 build up the plane called *PZ3*; in that pyrazine ring we define two following planes: *PZN15* build up form atoms N15, C33, C36, and *PZN16* containing atoms N16, C34, C35. The pyrrole ring built up from atoms C35-C36-C37-N19-C43 will be called *PR3*; the pyridine ring C38-C39-C40-C41-C42-N18 *PYN18*, second pyridine ring, C44-C45-C46-C47-C48-N21, *PYN21*.

In molecule A the dihedral angles between the planes *PZN1* and *PZN2* is 2.20(3.16)°; between planes *PZN8* and *PZN9* 2.67(2.50)°. In molecule B the dihedral angle between planes *PZN15* and *PZN16* is 1.27(3.25)°. The smallest value obtained for the molecule B means that the pyrazine ring is less distorted although more distorted than in the free ligand where the corresponding value was 0.70(1.03)°.

In molecules A and B of **C2** the fragments containing the pyrazine and the pyrrole rings are almost planar. In molecule A the dihedral angle between *PZ* and *PR* is 1.03(1.10)°, between *PZ2* and *PR2* 1.91(0.88)°. In molecule B the difference is smaller, the dihedral angle between *PZ3* and *PR3* is 0.52(1.08)°. The smaller deformations are due to the presence of the symmetry element (C_2) present in molecule B.

The pyridine ring *PYN4* forms with the pyrrole ring *PR* a dihedral angle of 6.40(1.04)° while the *PYN7* ring forms with the same pyrrole ring an angle of 11.03(1.02)°. For *PR2* and *PYN11* the dihedral angle is 3.29(0.85)°, for *PR2* and *PYN14* 12.62(0.80)°. In molecule B the corresponding angles are: between *PR3* and *PYN18* 19.98(0.88)°, between *PR3* and *PYN21* 10.01(0.97)°. In the free **L1** ligand the same angles are 4.03(0.48)° and 4.40(0.45)°. The pyridine ring *PYN4* and *PYN7* are inclined to one another by 17.37(0.90)°, *PYN11* and *PYN14* by 15.07(0.72)°, *PYN18* and *PYN21* by 29.92(0.74)°. In the free ligand **L1** this angle is 2.88(0.47)°.

The IR spectrum (KBr disc) is very similar to the IR spectrum of the free ligand **L1** but characteristic absorption bands are shifted toward lower wavenumbers.

3.3). Cobalt complex **C3**

Product **C3** was obtained in the following way: to a solution of **L1** in dry methanol was added triethylamine and a small amount of Pyrex glass powder; to this mixture a solution of $Co(BF_4)_2*xH_2O$ in dry methanol was added dropwise. After slow evaporation of the solvent blue-black crystals were obtained. The crystal structure obtained after X-ray analysis revealed that **C3** was identical with the product **C1**.

3.4). Nickel complex C4

After using the Co^{II} salts for the reaction with the ligand **L1** we decided to use the salts of Ni^{II} for some further reactions. The first product obtained using Ni^{II} metal salts was complex **C4**. To a solution of the ligand **L1** in methanol with triethylamine was added a methanolic solution of $Ni(ClO_4)_2*6H_2O$. Slow evaporation of the solvent, did not give the crystals but a powder which on recrystallization from a mixture of acetonitrile/methanol gave black crystals. The X-ray analysis allowed us to establish the crystal structure of product **C4**, $[Ni^{II}(L1)_2]*$ $1/3CH_3CN$, which is presented in figure Fig. 28. There are two independent molecules (A and B) in the asymmetric unit and molecule B possesses crystallographic C_2 symmetry.

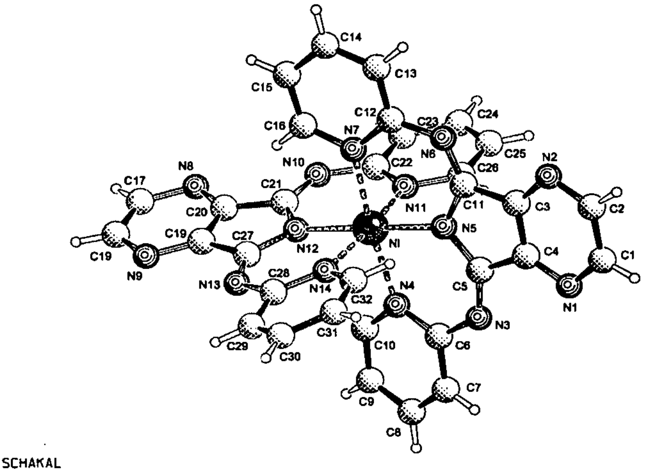


Fig. 28: SCHAKAL plot of **C4** molecule A

This product crystallized in the orthorhombic crystal system, space group Pccn, with a=19.044(12)Å, b=24.66(2)Å, c=18.80(2)Å, V=8827(10)$Å^3$, Z=12, R1=0.0534, wR2=0.0949, it is isomorphous with complex **C2**.

The ligand **L1** coordinates in a mono-tridentate manner, the coordination sphere of the nickel atom can be described as nearly octahedral (coordination number 6). The asymmetric unit contains 1.5 molecules of the complex and 0.5 a molecule of solvent: acetonitrile (exactly as in **C2**). One molecule of complex **C2** (B) possesses C_2 symmetry. In both molecules (A and B) the distances C-C, C-N are normal within experimental error.

Selected distances for **C4** are given in Tab. 3.4:

Molecule A		Molecule B	
Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
N(4)-Ni(1)	2.166(5)Å	N(18)-Ni(2)	2.148(5)Å
N(5)-Ni(1)	2.026(5)Å	N(19)-Ni(2)	2.017(5)Å
N(7)-Ni(1)	2.173(5)Å	N(21)-Ni(2)	2.135(6)Å
N(11)-Ni(1)	2.175(5) Å		
N(12)-Ni(1)	2.028(5)Å		
N(14)-Ni(1)	2.205(5)Å		

Tab. 3.4

The simplified coordination spatial arrangement in both molecules (A and B) is schematically shown in Fig. 29.

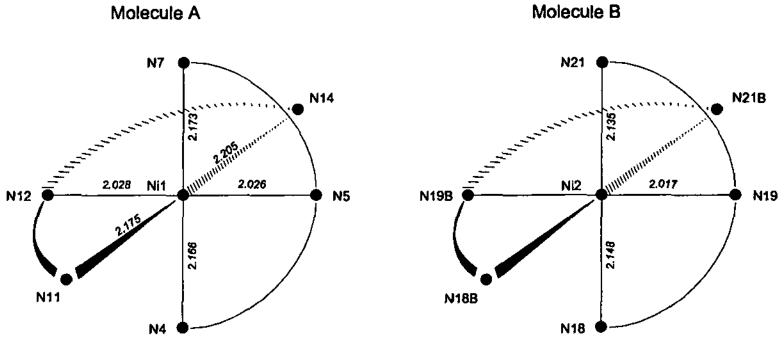


Fig. 29

We can conclude from the distances given above that the two Ni complexes present in the asymmetric unit are very similar. The differences between the corresponding bonds are rather small (smallest of the all complexes described till now).

The coordination polyhedron of the nickel atoms is a distorted octahedron.

Selected angles (°) for **C4** are given in Tab. 3.5:

Molecule A		Molecule B	
Angle	Angle (°)	Angle	Angle (°)
N(4)-Ni(1)-N(5)	87.0(2)	N(18)-Ni(2)-N(19)	86.7(2)
N(4)-Ni(1)-N(7)	173.3(2)	N(18)-Ni(2)-N(21)	173.0(2)
N(4)-Ni(1)-N(11)	91.3(2)	N(18)-Ni(2)-N(18B)	91.8(3)
N(4)-Ni(1)-N(12)	92.6(2)	N(18)-Ni(2)-N(19B)	91.3(2)
N(4)-Ni(1)-N(14)	88.4(2)		
N(5)-Ni(1)-N(7)	86.4(2)	N(19)-Ni(2)-N(21)	86.9(2)
N(5)-Ni(1)-N(11)	95.3(2)		
N(5)-Ni(1)-N(12)	178.5(2)	N(19)-Ni(2)-N(19B)	177.2(3)
N(5)-Ni(1)-N(14)	91.9(2)		
N(7)-Ni(1)-N(11)	89.2(2)	N(21)-Ni(2)-N(18B)	91.4(2)
N(7)-Ni(1)-N(12)	94.1(2)	N(21)-Ni(2)-N(19B)	95.2(2)
N(7)-Ni(1)-N(14)	91.9(2)	N(21)-Ni(2)-N(21B)	86.1(3)
N(11)-Ni(1)-N(12)	86.2(2)		
N(11)-Ni(1)-N(14)	172.8(2)		
N(12)-Ni(1)-N(14)	86.6(2)	N(19)-Ni(2)-N(21B)	95.2(2)

Tab. 3.5

Also in this case we can see that the most important bond angles are almost the same as in complexes **C1** and **C2**.

To simplify further investigations we have defined some planes and rings in the complex. The atoms C1-C2-N2-C3-C4-N1 build up the plane called *PZ*;

PZN1= N1, C1, C4; *PZN2* = N2, C2, C3; *PR* = C3-C4-C5-N5-C11, *PYN4* = C6-C7-C8-C9-C10-N4, *PYN7* = C12-C13-C14-C15-C16-N7

PZ2 = C17-C18-N9-C19-C20-N8, *PZN8* = N8, C17, C20; *PZN9* = N9, C18, C19; *PR2* = C19-C20-C21-N12-C27; *PYN11* = C22-C23-C24-C25-C26-N11, *PYN14* = C28-C29-C30-C31-C32-N14,.

In molecule B atoms C33-C34-N16-C35-C36-N15 build up the plane *PZ3;*

PZN15= N15, C33, C36; *PZN16* = N16, C34, C35; *PR3* = C35-C36-C37-N19-C43, *PYN18* = C38-C39-C40-C41-C42-N18, *PYN21*= C44-C45-C46-C47-C48-N21,

In molecule A the dihedral angles between the planes *PZN1* and *PZN2* is 0.81(1.29)°; between planes *PZN8* and *PZN9* it is 0.69(1.06)°. In molecule B the dihedral angle between planes *PZN15* and *PZN16* is 1.70(1.27)°. In the free ligand the corresponding value was 0.70(1.03)°.

In molecules A and B the fragment containing the pyrazine and the pyrrole ring is almost planar. In molecule A the dihedral angle between *PZ* and *PR* is 1.74(0.46)°, between *PZ2* and *PR2* 1.62(0.38)°. In molecule B the difference is smaller, the dihedral angle between *PZ3* and *PR3* is 0.72(0.47)°. The smaller deformations may be due to the presence of the symmetry element (C_2) in molecule B.

The pyridine ring *PYN4* forms with the pyrrole ring *PR* a dihedral angle of 6.81(0.44)° while the *PYN7* ring forms with the same pyrrole ring an angle of 10.43(0.43)°. For *PR2* and *PYN11* the dihedral angle is 1.73(0.36)°, for *PR2* and *PYN14* 12.78(0.33)°. In molecule B the corresponding angles are: between *PR3* and *PYN18* 9.38(0.43)°, between *PR3* and *PYN21* 21.19(0.38)°. In the free ligand **L1** the same angles are 4.03(0.48)° and 4.40(0.45)°. The pyridine rings *PYN4* and *PYN7* are inclined to one another by 17.23(0.37)°, *PYN11* and *PYN14* by 13.78(0.29)°, *PYN18* and *PYN21* by 30.55(0.31)°. In the free ligand **L1** this angle is 2.88(0.47)°.

IR spectrum (KBr disc) is very similar to the IR spectrum obtained for the free ligand **L1** and shows no significant differences with the spectrum of **C2** (the characteristic absorption bands are also shifted toward lower wavenumbers).

The next two complexes prepared using nickel salts are the same (chemically) as complex C4.

3.5). Nickel complex **C5**

The first nickel^{II} complex, **C5**, was prepared in the following manner – to a methanolic solution of ligand **L1** with triethylamine, heated to 70°C. a methanolic solution of the metal salt $Ni(ClO_4)_2*6H_2O$ was added dropwise. Then a solution of

tppz and NaCl in methanol was added dropwise. After the crystallisation by slow evaporation of the solvent black block-like crystals were obtained and analyzed by the X-ray diffraction.

The following structure has been established **C5** as [Ni(L1)$_2$] and is presented in Fig. 30:

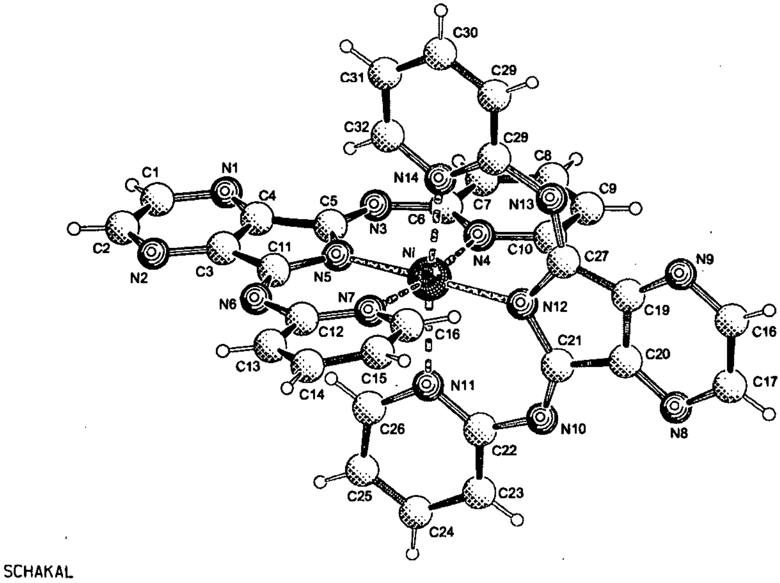


Fig. 30: SCHAKAL plot of **C5**

This product crystallized in the monoclinic crystal system, space group C 2/c, with a=14.669(10)Å, b=12.361(7)Å, c=31.98(2)Å, β=91.82(5)°, V=5795(6)Å^3, Z=8, R1=0.0686, wR2=0.1111.

Ligand **L1** coordinates to Ni^{II} in exactly the same manner as in complex **C4**, in a mono-tridentate manner. The coordination sphere of the nickel atom can be described as distorted octahedral (coordination number 6). The asymmetric unit contains in this case only two molecules of the ligand **L1** coordinated in a mono-tridentate manner with the Ni^{II} atom. In both complexes: **C4** and **C5**, the distances C-C, C-N are normal, within experimental error, for this type of bonds. The biggest differences can be observed in the lengths of the Ni-N bonds, which are longer than in complex **C4**.

Selected distances for **C5** are given in Tab. 3.6:

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
N(4)-Ni	2.158(4)	N(11)-Ni	2.204(4)
N(5)-Ni	2.024(4)	N(12)-Ni	2.022(9)
N(7)-Ni	2.213(4)	N(14)-Ni	2.153(4)

Tab. 3.6

Selected angles (°) for **C5** are given in Tab. 3.7:

Angle	Angle (°)	Angle	Angle (°)
N(12)-Ni-N(5)	177.1(2)	N(14)-Ni-N(11)	172.6(2)
N(12)-Ni-N(14)	86.6(2)	N(7)-Ni-N(11)	93.0(2)
N(5)-Ni-N(14)	95.1(2)	N(12)-Ni-N(4)	94.8(2)
N(12)-Ni-N(7)	91.8(2)	N(5)-Ni-N(4)	87.5(2)
N(5)-Ni-N(7)	85.9(2)	N(14)-Ni-N(4)	86.8(2)
N(14)-Ni-N(7)	91.0(2)	N(7)-Ni-N(4)	172.8(2)
N(12)-Ni-N(11)	87.0(2)	N(11)-Ni-N(4)	90.0(2)
N(5)-Ni-N(11)	91.4(2)		

Tab. 3.7

The simplified coordination spatial arrangement for both complexes, **C4** and **C5**, is schematically shown in figure Fig. 31.

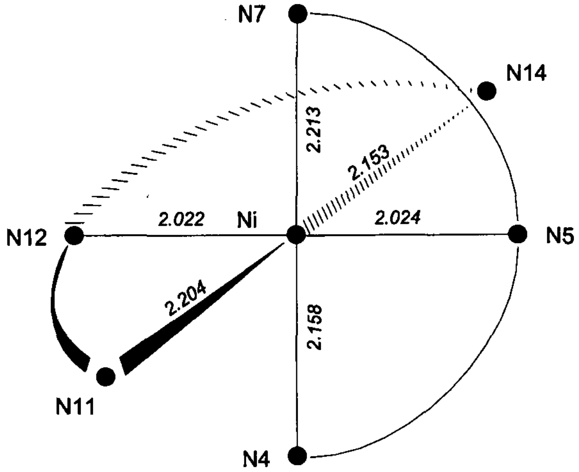


Fig.31

To simplify further investigations we have defined some planes and rings in the complex:

PZ = C1-C2-N2-C3-C4-N1, *PZN1* = N1, C1, C4; *PZN2* = N2, C2, C3; *PR* = C3-C4-C5-N5-C11, *PYN4* = C6-C7-C8-C9-C10-N4, *PYN7* = C12-C13-C14-C15-C16-N7 (all the corresponding names are shown in Fig. 30)

The dihedral angle between the pyrazine ring *PZ* and the five membered pyrrole ring *PR* is 1.19(0.34)° - so comparing it with the same angle in the free ligand, which is 0.70(1.03)° and complex **C1** which is 2.91(0.26)°, we can say that this fragment of the complex is coplanar. The dihedral angle between the pyrrole ring *PR* and the *PYN7* pyridine ring is 6.00(0.30)° (in the free ligand 4.40(0.45)°, in complex **C1** 29.72(0.27)°), between the pyrrole ring *PR* and *PYN4* ring it is 1.25(0.32)° (in the free ligand 4.03(0.48)°, in complex **C1** 28.93(0.27)°). The pyridine rings are on the opposite side of the plane in which lies the pyrazine ring and are inclined to one another by 6.68(0.31)° (in the free ligand 2.88(0.47)° in **L1**, in complex **C1** 53.93(0.24)°).

The IR spectrum (KBr disc) is very similar to the IR spectrum for the free ligand **L1** and shows no significant differences with respect to the spectrum for **C2** (the characteristic absorption bands are also shifted toward lower wavenumbers).

3.6). Nickel complex **C6**

The next product in the reaction with Ni^{II} salts is the complex **C6** prepared in the following way: to a methanolic solution of ligand **L1** and triethylamine, a methanolic solution of the metal salt $NiCl_2*6H_2O$ and NaCl was added at room temperature. After slow evaporation of the solvent a small amount of yellow needle like crystals were obtained.

The X-ray analysis showed that the product **C6** crystallized in the orthorhombic crystal system, space group Pccn, with a=19.016(2)Å, b=24.935(2)Å, c=18.830(2)Å, V=8928.4(12)$Å^3$, Z=12. That data are almost identical with those obtained for the analysis of **C4**. Comparison of the corresponding bond lengths angles, IR spectra confirmed that products **C4** and **C6** are the same although different metal salts were used.

3.7). Copper complexes **C7** *and* **C8**

Complex **C7** was obtained by adding to a methanolic solution of ligand **L1** and triethylamine a methanolic solution of the metal salt $Cu(ClO_4)_2*6H_2O$ and NaCl. The crystals which were obtained by slow evaporation of the solvent from the filtrate and where found to be the same as the crystals of product **C8**. Crystals of **C8** were obtained by the same reaction as for **C7** but another metal salt was used: $CuCl_2*2H_2O$. Only the structure of **C8** will be described here.

The crystal structure of **C8** obtained by X-ray analysis, $[Cu(L1)_2]*1½CH_3OH$ is illustrated in Fig. 32.

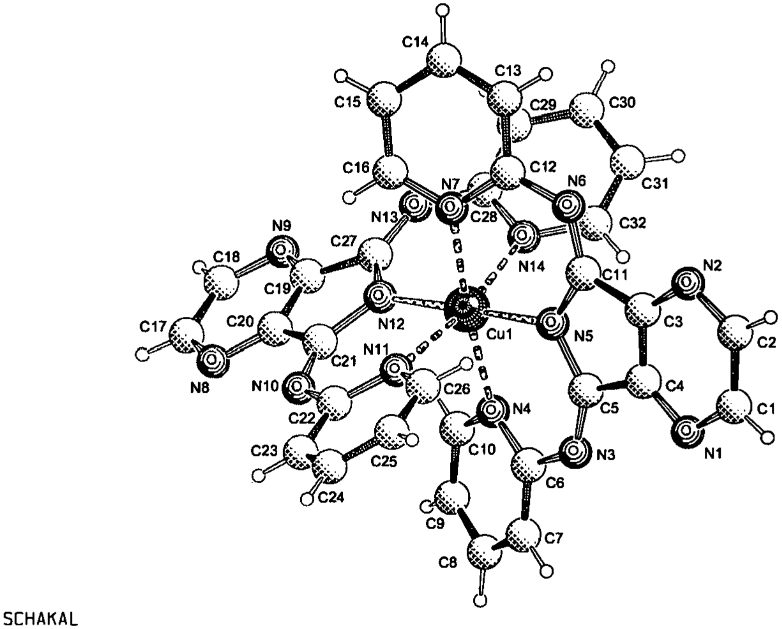


Fig. 32: SCHAKAL plot of **C8** (the 1½ molecules of the solvent, methanol, are omitted for clarity)

The rectangular yellow-brown crystals were classified to the monoclinic crystal system, space group P $2_1/c$, with a=10.626(4)Å, b=16.02(2)Å, c=19.760(9)Å, β=103.74(3)°, V=3267(4)$Å^3$, Z=4, R1=0.0999, wR2=0.2415.

The asymmetric unit contains two molecules of the ligand **L1** coordinated in a classical mono-tridentate manner with the Cu^{II} atom and 1.5 molecules of the solvent: methanol. Again the coordination polyhedron of the copper atom is distorted octahedron, all the corners, axial and equatorial, are occupied by nitrogen atoms.

The C-C and C-N distances are typical for these types of bonds and are, within the experimental error, in agreement with data given for the complexes described above.

Selected distances for **C8** are given in Tab. 3.8:

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
N(4)-Cu(1)	2.200(8)Å	N(11)-Cu(1)	2.256(8)Å
N(5)-Cu(1)	1.942(7)Å	N(12)-Cu(1)	1.950(7)Å
N(7)-Cu(1)	2.207(8)Å	N(14)-Cu(1)	2.293(8)Å

Tab. 3.8

Selected angles (°) for **C8** are given in Tab. 3.9:

Angle	Angle (°)	Angle	Angle (°)
N(4)-Cu(1)-N(5)	87.3(3)	N(5)-Cu(1)-N(14)	94.1(3)
N(4)-Cu(1)-N(7)	174.1(3)	N(7)-Cu(1)-N(11)	90.9(3)
N(4)-Cu(1)-N(11)	90.4(3)	N(7)-Cu(1)-N(12)	93.9(3)
N(4)-Cu(1)-N(12)	91.9(3)	N(7)-Cu(1)-N(14)	84.4(3)
N(4)-Cu(1)-N(14)	95.0(3)	N(11)-Cu(1)-N(12)	86.1(3)
N(5)-Cu(1)-N(7)	86.8(3)	N(11)-Cu(1)-N(14)	171.3(3)
N(5)-Cu(1)-N(11)	92.9(3)	N(12)-Cu(1)-N(14)	87.0(3)
N(5)-Cu(1)-N(12)	178.7(3)		

Tab. 3.9

The spatial arrangement about the copper atom is schematically presented in Fig. 33:

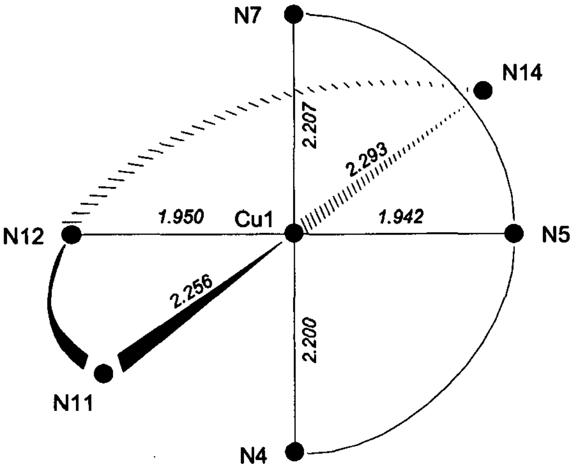


Fig. 33

The molecule of **C8** has no symmetry elements. The distances and angles given above indicate that the octahedral arrangement is less distorted than in the Ni^{II}, Co^{II} and Co^{III} complexes described previously.

To simplify further investigations we have defined some planes and rings in the complex. Atoms C1-C2-N2-C3-C4-N1 build up the plane called *PZ*;
PZN1 = C1-N1-C4, *PZN2* = C2-N2-C3, *PR* = C3-C4-C5-N5-C11, *PYN4* = C6-C7-C8-C9-C10-N4, *PYN7* = C12-C13-C14-C15-C16-N7;
PZ2 = C17-C18-N9-C19-C20-N4; *PZN8* = C17-N8-C20, *PZN9* = C18-N9-C19; *R2* = C19-C20-C21-N12-C27; *PYN11* = C22-C23-C24-C25-C26-N11, *PYN14* = C28-C29-C30-C31-C32-N14 (all the corresponding names are shown in Fig. 32).

The pyrazine rings in **C8** are slightly twisted. The dihedral angle between *PZN1* and *PZN2* is 4.08(1.69)°, and between planes *PZN8* and *PZN9* it is 1.26(1.61)°. Although these angles are larger than the angles in the free ligand **L1** (0.70(1.03)°) the pyrazine rings should be treated as planar. The dihedral angle between the pyrazine ring *PZ* and the pyrrole ring *PR* is 1.68(0.54)°, between *PZ2* and *PR2* it is 0.57(0.51)°. The same angle in the free ligand was 0.70(1.03)° and in complex **C1**, this angle is 2.91(0.26)° (which is the largest value observed), we can say that this fragment of the complex is coplanar. The dihedral angle between the pyrrole ring *PR* and the *PYN7* pyridine ring is 23.45(0.46)° (in the free ligand 4.40(0.45)°, in complex **C1** 29.72(0.27)°), between the pyrrole ring *PR* and *PYN4* ring is 14.50(0.47)° (in the free ligand 4.03(0.48)°, in complex **C1** 28.93(0.27)°). The dihedral angle between *PR2* and *PYN14* is 30.68(0.40)°, between *PR2* and *PYN11* it is 6.57(0.66)°. In **C8** we observe the largest twist of the pyrazine rings. It is probably due to the effect of space packing – the Cu atom has the highest (considered till now) atomic radius and it "enters" itself into the "teeth" (of the two pyridine rings) twisting them to give such a larger angle. The Cu^{II} atom with the coordination number 6 should achieve an octahedral space arrangement in its coordination sphere. At the same time the size of the metal atom entering between the pyridine rings has to cause its rotation around the C-N single bond by an angle that will allow them to enter. The rotation of the pyridine around the single C-N bond can also have an influence on the rest of the compound – it can also cause some tension that results in some deformations in the pyrrole and pyrazine rings.

The pyridine rings *PYN4* and *PYN7* are on the opposite side of the plane in which lies the pyrazine ring and are inclined to one another by 36.63(0.34)°, for *PYN11* and *PYN14* this angle is 37.17(0.45)° (2.88(0.47)° in **L1**).

The IR spectrum (KBr disc) is very similar to the IR spectrum for the free ligand **L1** and shows no significant differences with the spectrum of the complexes (the characteristic absorption bands are also shifted toward lower wavenumbers).

3.8). Zinc complex **C9**

Continuing our investigation of the coordination possibilities of ligand **L1** we performed the following synthesis to obtain the Zn^{II} complex – **C9**.

To a methanolic solution of ligand **L1** and triethylamine a methanolic solution of the metal salt $ZnCl_2$ and NaCl was added. After slow evaporation of the solvent orange block-like crystals were obtained. The X-ray analysis established the structure of **C9**, presented in Fig. 34, as $[Zn(L1)_2]*1/6CH_3CN$:

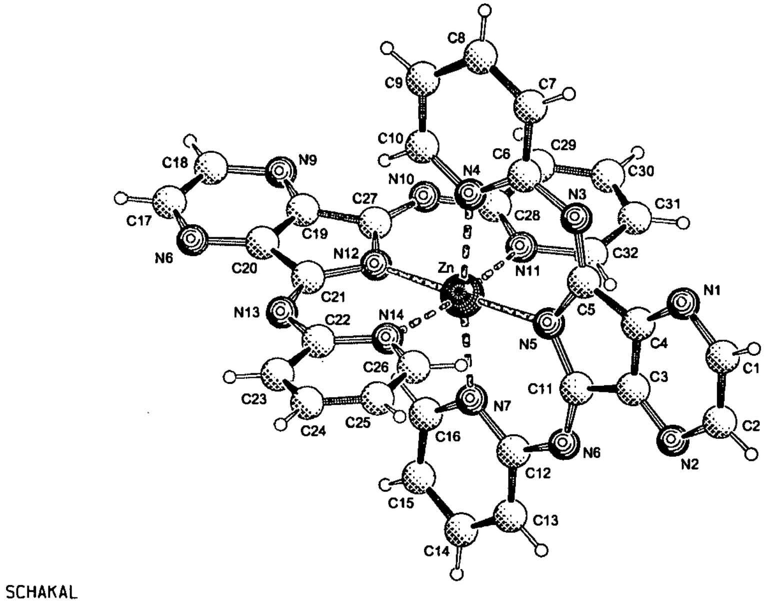


Fig. 34: SCHAKAL plot of molecule A of **C9** (the molecules of the solvent are omitted for clarity)

The product crystallized in the orthorhombic crystal system, space group P c c n, with a=19.099(2)Å, b=25.008(2)Å, c=18.931(2)Å, V=9042.4(14)Å^3, Z=12, R1=0.1285, wR2=0.2209.

Complex **C9** is isomorphous with the Co^{II} and Ni^{II} complexes **C2** and **C4**, respectively.

The asymmetric unit contains (as in the structures of **C2** and **C4**) 1½ molecules of complex and also 1/6 of a molecule of the solvent – acetonitrile. Molecule B of complex **C9** possesses C_2 symmetry. Again the coordination sphere of the metal atom can be described as nearly octahedral.

Selected distances for **C9** are given in Tab. 3.10:

Molecule A		Molecule B	
Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
N(4)-Zn(1)	2.276(11)Å	N(18)-Zn(2)	2.221(11)Å
N(5)-Zn(1)	2.072(11)Å	N(19)-Zn(2)	2.033(11)Å
N(7)-Zn(1)	2.229(11)Å	N(21)-Zn(2)	2.202(12)Å
N(11)-Zn(1)	2.243(11)Å		
N(12)-Zn(1)	2.056(11)Å		
N(14)-Zn(1)	2.247(10)Å		

Tab. 3.10

The simplified coordination spatial arrangement in both complex molecules (A and B) is schematically shown in Fig. 35.

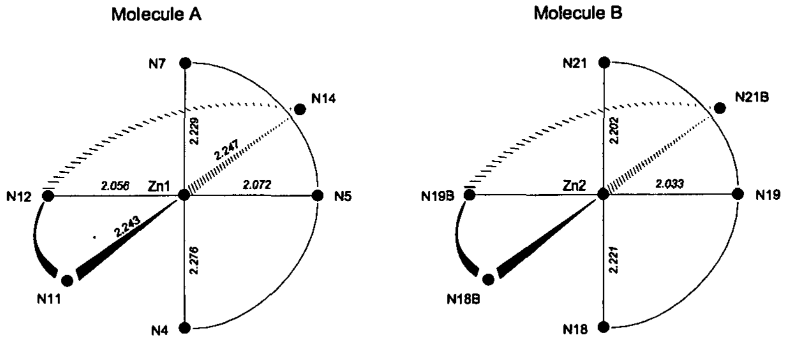


Fig. 35

Selected angles (°) for **C9** are given in Tab. 3.11:

Molecule A		Molecule B	
Angle	Angle (°)	Angle	Angle (°)
N(4)-Zn(1)-N(5)	85.1(4)	N(19)-Zn(2)-N(18)	84.8(4)
N(4)-Zn(1)-N(7)	170.0(4)	N(18)-Zn(2)-N(21)	169.3(5)
N(4)-Zn(1)-N(11)	88.0(4)	N(18)-Zn(2)-N(18B)	92.8(6)
N(4)-Zn(1)-N(12)	92.9(4)	N(18)-Zn(2)-N(19B)	93.4(4)
N(4)-Zn(1)-N(14)	92.3(4)	N(18)-Zn(2)-N(21B)	91.4(5)
N(5)-Zn(1)-N(7)	85.0(4)	N(19)-Zn(2)-N(21)	85.1(5)
N(5)-Zn(1)-N(11)	94.9(4)		
N(5)-Zn(1)-N(12)	178.0(4)	N(19)-Zn(2)-N(19B)	177.5(7)
N(5)-Zn(1)-N(14)	94.5(4)	N(19)-Zn(2)-N(21B)	96.8(5)
N(7)-Zn(1)-N(11)	91.5(4)		
N(7)-Zn(1)-N(12)	97.0(4)		
N(7)-Zn(1)-N(14)	89.8(4)	N(21)-Zn(2)-N(21B)	86.3(7)
N(11)-Zn(1)-N(12)	85.5(4)		
N(11)-Zn(1)-N(14)	170.6(4)		
N(12)-Zn(1)-N(14)	85.1(4)		

Tab. 3.11

To simplify further investigations we have defined some planes and rings in this complex. Atoms C1-C2-N2-C3-C4-N1 build up the plane called *PZ*; *PZN1* = C1-N1-C4, *PZN2* = C2-N2-C3, *PR* = C3-C4-C5-N5-C11, *PYN4* = C6-C7-C8-C9-C10-N4, *PYN7* = C12-C13-C14-C15-C16-N7;

PZ2 = C17-C18-N9-C19-C20-N8, *PZN8* = C17-N8-C20, *PZN9* = C18-N9-C19, *PR2* = C19-C20-C21-N12-C27, *PYN11* = C22-C23-C24-C25-C26-N11, *PYN14* = C28-C29-C30-C31-C32-N14;

PZ3 = C33-C34-N16-C35-C36-N15, *PZN15* = C33-N15-C36, *PZN16* = C34-N16-C35, *PR3* = C35-C36-C37-N19-C43, *PYN18* = C38-C39-C40-C41-C42-N18, *PYN21* = C44-C45-C46-C47-C48-N21

In molecule A the dihedral angles between the planes *PZN1* and *PZN2* is 1.14(2.42)° (in **C4** - 0.81(1.29)°; between planes *PZN8* and *PZN9* 0.97(3.23)° (in **C4** - 0.69(1.06)°). In molecule B the dihedral angle between planes *PZN15* and *PZN16* is

1.31(3.23)° (in **C4** - 1.70(1.27)°). In molecules A and B the fragments containing the pyrazine and the pyrrole ring are almost planar. In molecule A the dihedral angle between *PZ* and *PR* is 1.38(0.86)° (in **C4** - 1.74(0.46)°), between *PZ2* and *PR2* 1,74(1.12)° (in **C4** - 1.62(0.38)°). In molecule B the difference is smaller, the dihedral angle between *PZ3* and *PR3* is 0.31(1.09) (in **C4** - 0.72(0.47)°).

The pyridine ring *PYN4* forms with the pyrrole ring *PR* a dihedral angle of 12.34(0.79)° (in **C4** - 6.81(0.44)°) while the *PYN7* ring forms with the same pyrrole ring an angle of 1.05(0.81)° (in **C4** - 10.43(0.43)°). For *PR2* and *PYN11* the dihedral angle is 9.34(0.95)° (in **C4** - 1.73(0.36)°), for *PR2* and *PYN14* it is 6.53(0.97)° (in **C4** - 12.78(0.33)°). In molecule B the corresponding angles are: between *PR3* and *PYN18* 18.40(0.87)° (in **C4** - 9.38(0.43)°), between *PR3* and *PYN21* 10.46(0.91)° (in **C4** - 21.19(0.38)°). In the free ligand **L1** the same angles are 4.03(0.48)° and 4.40(0.45)°.

The pyridine rings *PYN4* and *PYN7* are inclined to one another by 13.10(0.73)° (in **C4** - 17.23(0.37)°), *PYN11* and *PYN14* by 13.92(0.82)° (in **C4** - 13.78(0.29)°), *PYN18* and *PYN21* by 25.64(0.66)° (in **C4** - 30.55(0.31)°). In the free ligand **L1** this angle is 2.88(0.47)°.

IR spectrum (KBr disc) is very similar to the IR spectrum for the free ligand **L1** and shows no significant differences with respect to the spectrum of **C2** (the characteristic absorption bands are also shifted toward lower wavenumbers).

3.9). Zinc complex **C10**

Complex **C10**, the next of the Zn^{II} complexes synthesized, was obtained in a similar way as **C9**. To the solution of ligand **L1** in acetonitrile/methanol the metal salt $ZnCl_2$ was added in a solid state. After the reaction the solvent was slowly evaporated giving orange crystals in the form of blocks.

The structure of the crystals obtained after X-ray analysis $[ZnCl(L1)(CH_3OH)]$ is quite different from the structures presented above. The asymmetric unit contains one molecule of the ligand **L1** coordinated in a tridentate mode with the Zn^{II} atom, one chlorine anion and a molecule of methanol. The chlorine anion and the oxygen atom from the solvent complete the coordination sphere of the zinc atom.

The plot of the crystal structure of **C10** is presented in Fig. 36.

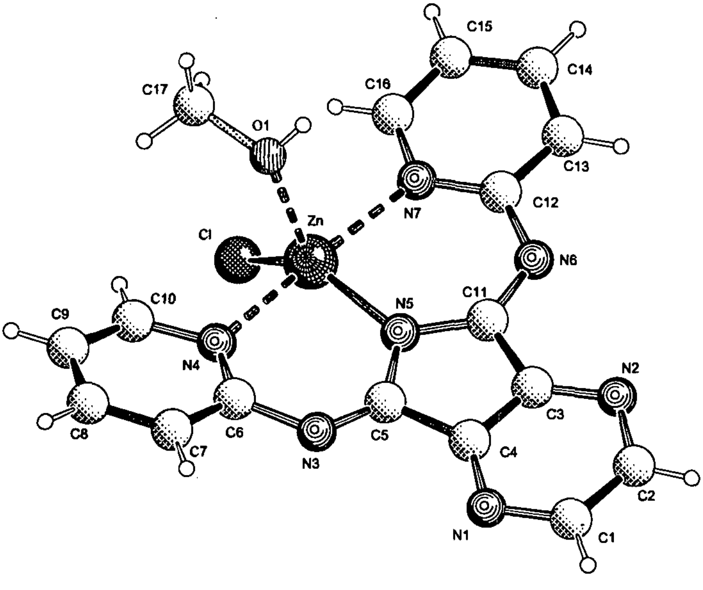


Fig. 36: SCHAKAL plot of **C10**

This product crystallized in the monoclinic crystal system, space group P $2_1/c$, with a=8.690(11)Å, b=17.49(3)Å, c=11.72(2)Å, β=103.36(10)°, V=1733(4)Å^3, Z=4, R1=0.0699, wR2=0.1435.

Selected bond lengths (Å) for **C10** are given in Tab. 3.12:

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
N(4)-Zn(1)	2.201(7)	Zn(1)-O(1)	2.099(7)

N(5)-Zn(1)	1.989(7)	Zn(1)-Cl(1)	2.272(5)
N(7)-Zn(1)	2.222(7)		

Tab. 3.12

Selected angles (°) for **C10** are given in Tab. 3.13:

Angle	Angle (°)	Angle	Angle (°)
N(4)-Zn(1)-N(5)	86.7(3)	N(5)-Zn(1)-O(1)	115.2(3)
N(4)-Zn(1)-N(7)	170.7(2)	N(5)-Zn(1)-Cl(1)	137.7(2)
N(4)-Zn(1)-O(1)	88.5(3)	N(7)-Zn(1)-O(1)	88.8(3)
N(4)-Zn(1)-Cl(1)	95.5(2)	N(7)-Zn(1)-Cl(1)	93.9(2)
N(5)-Zn(1)-N(7)	86.3(3)	O(1)-Zn(1)-Cl(1)	107.1(2)

Tab. 3.13

Schematic spatial arrangement of the zinc coordination sphere is presented on Fig. 37

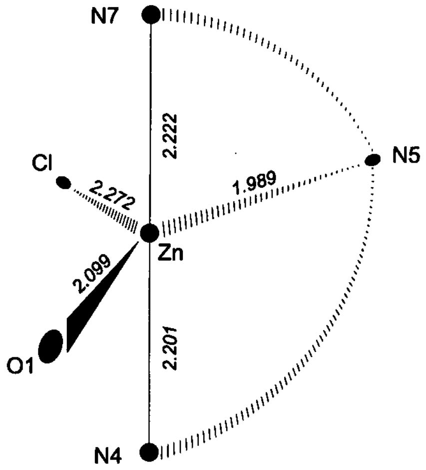


Fig. 37

The central metal atom, Zn^{II}, has the coordination number 5. As was described before for this coordination number two principal geometries are possible: trigonal bipyramidal and square pyramidal. In determining the type of coordination the geometrical parameter τ is used (defined by Addison *et al.*) {45}. τ is defined in the following equation:

$$\tau = \frac{(\beta - \alpha)}{60},$$

where β=the largest angle of the base

α=the second largest angle of the base

For an ideal square pyramidal coordination τ=0 (α=β=180°) while for the trigonal bipyramidal coordination τ=1 (α=120°, β=180°). In **C10** β= 170.7° and α=137.7° so τ=0.55. In this case we have an extremely distorted trigonal bipyramidal arrangement. In the coordination sphere of zinc the nitrogen N5 atom, chlorine atom and oxygen atom of the methanol occupy the equatorial positions, while the nitrogen atoms N4 and N7 of the ligand are in axial positions. The angle N4-Zn-N7 is 170.7(2)° close to 180°; the angles Cl-Zn-O1 (107.1(2)°), O1-Zn-N5 (115.2(3)°), N5-Zn-Cl (137.7(2)°) are close to 120° which are the conditions for obtaining a regular trigonal bipyramid.

For further investigations we defined some planes and rings in the complex. Atoms C1-C2-N2-C3-C4-N1 build up the plane called *PZ*, *PZN1* = C1-N1-C4, *PZN2* = C2-N2-C3; *PR* = C3-C4-C5-N5-C11; *PYN4* = C6-C7-C8-C9-C10-N4, *PYN7* = C12-C13-C14-C15-C16-N7

Deformation of the pyrazine ring in **C10** is comparable with the deformation in the free ligand **L1**. The dihedral angle between planes *PZN1* and *PZN2* in **C10** is 0.74(1.5)° whereas in **L1** it was 0.70(1.03)°. Also the fragment containing the pyrazine ring and pyrrole ring can be treated as planar, the dihedral angle between *PZ* and *PR* is 2.68(0.57)°. The pyridine rings *PYN4* and *PYN7* form with plane IN dihedral angles 18.39(0.44)° and 3.80(0.55)°, respectively.

The IR spectrum (KBr pellet) shows no significant differences with the spectrum of complex **C9**.

3.10). Ruthenium complex **C11**

Following the latest trends in chemistry we attempted to synthesize a complex of the ligand **L1** with ruthenium. To the solution of **L1** in a mixture of solvents: acetonitrile/methanol/water and triethylamine, we added dropwise, the metal salt $RuCl_3*xH_2O$ in the same mixture of solvents. Orange block-like crystals were obtained after a slow evaporation of the solvents from the filtrate. This allowed us to establish the crystal structure of the product **C11**, $[Ru(L1)_2]*1/4CH_3CN$, which is presented in Fig. 38.

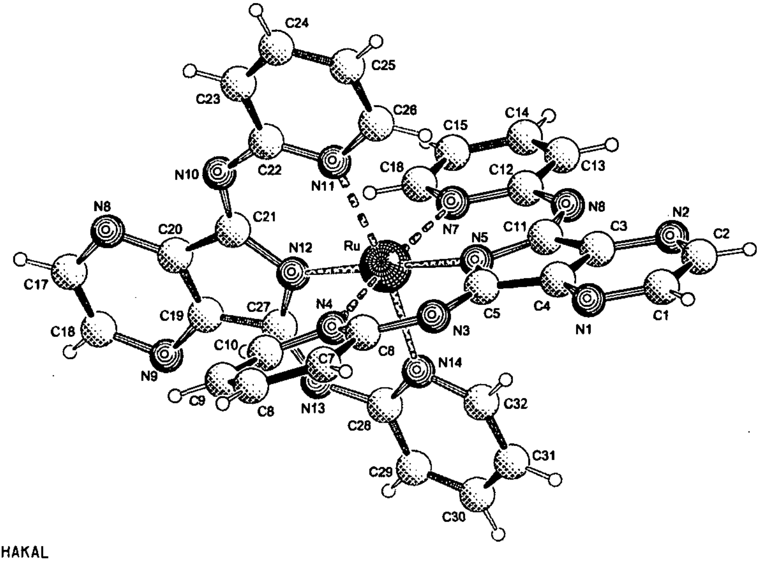


Fig. 38: SCHAKAL plot of **C11** molecule A (a molecule of acetonitrile is omitted for clarity)

The yellow rectangular crystals were analyzed by X-ray diffraction and allowed us to classify them to the orthorhombic crystal system, space group P c c n, a=19.095(2)Å, b=24.997(2)Å, c=18.930(9)Å, V=9036(5)Å^3, Z=12, R1=0.1447, wR2=0.3438.

Complex **C11** is isomorphous with the Co^{II}, Ni^{II} and Zn^{II} complexes **C2**, **C4** and **C9**, respectively.

The asymmetric unit contains (as in the structures of **C2**, **C4** and **C9**) 1½ molecules of complex and also 1/4 of a molecule of the solvent – acetonitrile. Molecule B of complex **C11** possesses C_2 symmetry. Again the coordination sphere of the metal atom can be described as nearly octahedral.

Selected distances for **C11** are given in Tab. 3.14:

Molecule A		Molecule B	
Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
N(4)-Ru(1)	2.275(13)Å	N(18)-Ru(2)	2.192(14)Å
N(5)-Ru(1)	2.057(12)Å	N(19)-Ru(2)	2.042(12)Å
N(7)-Ru(1)	2.214(12)Å	N(21)-Ru(2)	2.215(12)Å
N(11)-Ru(1)	2.259(11)Å		
N(12)-Ru(1)	2.065(12)Å		
N(14)-Ru(1)	2.245(12)Å		

Tab. 3.14

The simplified coordination spatial arrangement in both complexes is schematically shown in figure Fig. 39

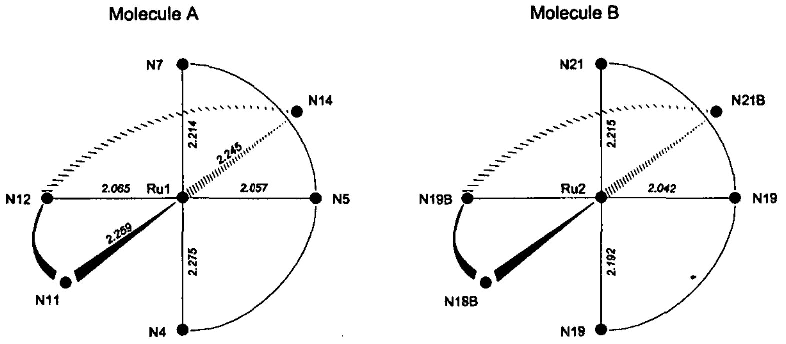


Fig. 39

Selected angles (°) for **C11** are given in Tab. 3.15:

Molecule A	Molecule B

Angle	Angle (°)	Angle	Angle (°)
N(4)-Ru(1)-N(5)	85.4(5)	N(18)-Ru(2)-N(19)	86.4(5)
N(4)-Ru(1)-N(7)	169.8(5)	N(18)-Ru(2)-N(21)	170.3(5)
N(4)-Ru(1)-N(11)	88.7(4)	N(18)-Ru(2)-N(18B)	85.8(7)
N(4)-Ru(1)-N(12)	93.1(5)	N(18)-Ru(2)-N(19B)	96.0(5)
N(4)-Ru(1)-N(14)	91.6(5)	N(18)-Ru(2)-N(21B)	91.4(5)
N(5)-Ru(1)-N(7)	84.5(5)	N(19)-Ru(2)-N(21)	84.6(5)
N(5)-Ru(1)-N(11)	95.8(5)		
N(5)-Ru(1)-N(12)	178.4(5)	N(19)-Ru(2)-N(19B)	176.8(8)
N(5)-Ru(1)-N(14)	94.3(5)	N(19)-Ru(2)-N(21B)	93.1(5)
N(7)-Ru(1)-N(11)	91.0(5)	N(21)-Ru(2)-N(21B)	92.8(7)
N(7)-Ru(1)-N(12)	97.0(5)		
N(7)-Ru(1)-N(14)	90.5(5)		
N(11)-Ru(1)-N(12)	84.6(5)		
N(11)-Ru(1)-N(14)	169.8(5)		
N(12)-Ru(1)-N(14)	85.2(5)		

Tab. 3.15

Also in this complex we can observe the distorted octahedral arrangement so typical for the coordination number 6, although distortion in this compound is the biggest one.

We defined some planes and rings in the structure of **L1** in the complex **C11**:

- in molecule A

PZ = C1-C2-N2-C3-C4-N1, *PZN1* = C1-N1-C4, *PZN2* = C2-N2-C3, *PR* = C3-C4-C5-N5-C11, *PYN4* = C6-C7-C8-C9-C10-N4, *PYN 7*= C12-C13-C14-C15-C16-N7
PZ2 = C17-C18-N9-C19-C20-N8, *PZN8* = C17-N8-C20, *PZN9* = C18-N9-C19, *PR2* = C19-C20-C21-N12-C27, *PYN11* = C22-C23-C24-C25-C26-N11, *PYN14* = C28-C29-C30-C31-C32-N14

- in molecule B:

PZ3 = C33-C34-N16-C35-C36-N15, *PZN15* = C33-N15-C36, *PZN16* = C34-N16-C35, *PR3* = C35-C36-C37-N19-C43, *PYN18* = C38-C39-C40-C41-C42-N18, *PYN21* = C44-C45-C46-C47-C48-N21

In molecule A the dihedral angles between the planes *PZN1* and *PZN2* is 1.43(2.18)° (1.14(2.42)° in **C9** and 0.81(1.29)° in **C4**); between planes *PZN8* and *PZN9* 3.30(3.81)° (0.97(3.23)° in **C9** and - 0.69(1.06)° in **C4**). In molecule B the dihedral angle between planes *PZN15* and *PZN16* is 1.36(3.61)° (1.31(3.23)° in **C9** and 1.70(1.27)° in **C4**).

In molecules A and B the fragment containing the pyrazine and the pyrrole ring is almost planar. In molecule A the dihedral angle between *PZ* and *PR* is 2.06(0.95)° (1.38(0.86)° in **C9** and 1.74(0.46)° in **C4**), between *PZ2* and *PR2* 2.61(1.32)° (1.74(1.12)° in **C9** and 1.62(0.38)° in **C4**). In molecule B the difference is smaller, the dihedral angle between *PZ3* and *PR3* is 0.91(1.27)° (0.31(1.09) in **C9** and 0.72(0.47)° in **C4**). The smaller deformations are probably due to the presence of the symmetry element (C_2) present in molecule B.

The pyridine ring *PYN4* forms with the pyrrole ring *PR* a dihedral angle of 11.19(0.95)° (12.34(0.79)° in **C9** and 6.81(0.44)° in **C4**) while the *PYN7* ring forms with the same pyrrole ring an angle of 1.48(0.93)° (1.05(0.81)° in **C9** and 10.43(0.43)° in **C4**). For *PR2* and *PYN11* the dihedral angle is 6.58(1.26)° (9.34(0.95)° in **C9** and 1.73(0.36)° in **C4**), for *PR2* and *PYN14* 8.37(1.26)° (6.53(0.97)° in **C9** and 12.78(0.33)° in **C4**). In molecule B the corresponding angles are: between planes *PR3* and *PYN18* 10.06(1.08)° (18.40(0.87)° in **C9** and 9.38(0.43)° in **C4**), between planes *PR3* and *PYN21* 19.47(0.99)° (10.46(0.91)° in **C9** and 21.19(0.38)° in **C4**). In the free ligand **L1** the same angles are 4.03(0.48)° and 4.40(0.45)°, respectively. The pyridine rings *PYN4* and *PYN7* are inclined to one another by 12.18(0.91)° (13.10(0.73)° in **C9** and 17.23(0.37)° in **C4**), planes *PYN11* and *PYN14* by 14.79(1.20)° (13.92(0.82)° in **C9** and 13.78(0.29)° in **C4**), and planes *PYN18* and *PYN21* by 26.88(0.80)° 25.64(0.66)° in **C9** and 30.55(0.31)° in **C4**). In the free ligand **L1** this angle is 2.88(0.47)°.

IR spectrum (KBr disc) is very similar to the IR spectrum for the free ligand **L1** and shows no significant differences with respect to the spectra of **C2**, **C4** and **C9** (the characteristic absorption bands are also shifted toward lower wavenumbers).

4. COORDINATION BEHAVIOUR OF tppz

THE CRYSTAL STRUCTURES OF THE COMPLEXES WITH THE LIGAND **Tppz**: *2,3,5,6-TETRA(α -PYRIDYL)PYRAZINE.*

4.1). Cobalt complex **C12** *of* **tppz**

In this work we also decided to investigate of the ligand **tppz**. This is a continuation of the work started in our group, here in Neuchâtel, by Dr. Marion Graf {10}. The first complex that we synthesized was a mononuclear complex of **tppz** with Co^{II}. To a mixture of the metal salt $Co(ClO_4)_2*6H_2O$ and **tppz** we added the solvent: 1-pentanol. Evaporation of the solvent resulted in the formation of black block-like crystals in the monoclinic crystal system, space group P $2_1/n$, with a=11.7869(13)Å, b=29.553(3)Å, c=14.0159(14)Å, β=101.280(11)°, V=4788.0(9)$Å^3$, Z=4, R1=0.0534, wR2=0.1199.

The asymmetric unit contains one molecule of the complex, two anions ClO_4^-, and two molecules of water. The established crystal structure, $[Co(tppz)_2](ClO_4)_2*2H_2O$, is presented in Fig. 40.

Two similar, but mononuclear complexes of cobalt were synthesized in the work of M.Graf {11}, $[Co(tppz)Cl(H_2O)_2]Cl$ and $[Co(TPPZ)(ma)H_2O)]*4H_2O$. In these complexes the three nitrogen atoms of **tppz** occupy the equatorial positions in the coordination polyhedron of the cobalt atom, the octahedral coordination sphere is completed by the oxygen atoms of water and malonate, or by the chlorine anions. For the malonate derivative the Co-O(malonate) distances are 1.964(8)Å and 2.077(7)Å; the Co-N distances are 2.092(8)Å for the central N pyrazine atom; 2.127(8)Å and 2.135(8) for the N pyridine atoms.

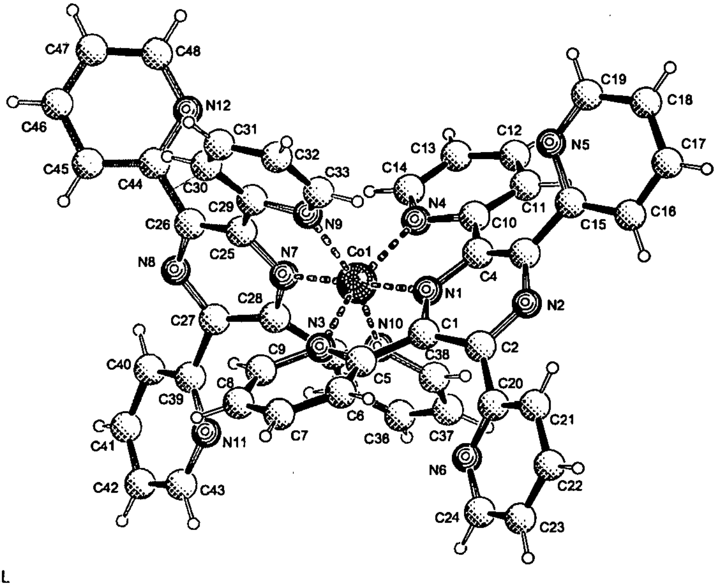


Fig. 40: SCHAKAL plot of the crystal structure of **C12** (the molecules of water and ClO_4^- anions are omitted for clarity).

In Fig. 41 the schematic spatial arrangement of the Co atom in **C12** is illustrated.

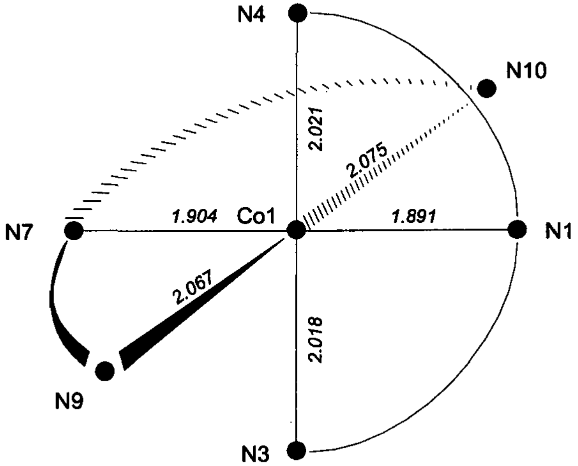


Fig.41

Selected bonds lengths for **C12** are given in Tab. 4.1:

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
Co(1)-N(3)	2.018(7)	Co(1)-N(9)	2.067(7)
Co(1)-N(1)	1.891(6)	Co(1)-N(7)	1.904(6)
Co(1)-N(4)	2.021(7)	Co(1)-N(10)	2.075(7)

Tab. 4.1

From that table it is clear that the Co-N(pyrazine) and Co-N(pyridines) bonds in both **tppz** molecules are significantly shorter than in the [Co(tppz)(ma)H_2O)]*4H_2O. Data for similar complexes with 2,2,':6,6'terpyridyl (terpy) are also available.

The Co-N(central) distances in [Co(terpy)$_2$]Br_2*3H_2O {43}are 1.89 and 2.10Å; in [Co(terpy)$_2$]Cl_3 {44} these distances are 1.863(7) and 1.853(7)Å (a little shorter) for the central N atoms and 1.921(7), 1.937(7)Å for the rest of the nitrogen atoms.

Selected angles (°) for **C12** are given in Tab. 4.2:

Angle	Angle (°)	Angle	Angle (°)
N(1)-Co(1)-N(3)	81.5(3)	N(3)-Co(1)-N(10)	95.8(3)
N(1)-Co(1)-N(4)	80.9(3)	N(4)-Co(1)-N(7)	100.7(3)
N(1)-Co(1)-N(7)	178.1(3)	N(4)-Co(1)-N(9)	94.5(3)
N(1)-Co(1)-N(9)	98.8(3)	N(4)-Co(1)-N(10)	88.1(3)
N(1)-Co(1)-N(10)	101.7(3)	N(7)-Co(1)-N(9)	80.2(3)
N(3)-Co(1)-N(4)	162.3(3)	N(7)-Co(1)-N(10)	79.4(3)
N(3)-Co(1)-N(7)	96.9(3)	N(9)-Co(1)-N(10)	159.5(3)
N(3)-Co(1)-N(9)	87.9(3)		

Tab. 4.2

To simplify this investigation we defined some planes in **C12**:

PZ = C1-C2-N2-C3-C4-N1, *PZN1* = C1-N1-C4, *PZN2* = C2-N2-C3, *PZ2* = C25-C26-N8-C27-C28-N7, *PZN7* = C25-N7-C28, *PZN8* = C26-N8-C27

The dihedral angles in *PZ* between the plane defined by atoms *PZN1* and the plane *PZN2* is 10.55(0.34)°; in the second pyrazine ring the dihedral angle between *PZN7* and *PZN8* is 10.42(0.52)°. Comparing these values with the value obtained for

[Co(tppz)(ma)H_2O)]*4H_2O which was 9.4(6)° we observe a bigger deformation of the pyrazine ring in **C12**. It is probably due to the presence of two molecules of **tppz** coordinated to the same metal atom and their spatial arrangement.

The rest of the planes we define as follows:

PYN3 = C5-C6-C7-C8-C9-N3, *PYN4* = C10-C11-C12-C13-C14-N4, *PYN5* = C15-C16-C17-C18-C19-N5, *PYN6* = C20-C21-C22-C23-C24-N6.

In the second molecule of **tppz** in **C12**: C29-C30-C31-C32-C33-N9 = *PYN9*, C34-C35-C36-C37-C38-N10 = *PYN10*, C39-C40-C41-C42-C43-N11 = *PYN11*, C44-C45-C46-C47-C48-N12 = *PYN12*

Selected dihedral angles for **C12** are given in Tab. 4.3:

Planes	Angle (°)	Planes	Angle (°)
PZN1-PZN2	10.55(0.34)	*PZN7-PZN8*	10.42(0.52)
PZ-PYN3	21.43(0.34)	*PZ2-PYN9*	25.18(0.22)
PZ-PYN4	18.46(0.33)	*PZ2-PYN10*	22.91(0.23)
PZ-PYN5	37.13(0.20)	*PZ2-PYN11*	40.76(0.36)
PZ-PYN6	35.07(0.20)	*PZ2-PYN12*	44.74(0.35)
PYN3-PYN4	4.04(0.50)	*PYN9-PYN10*	5.13(0.06)
PYN5-PYN6	24.20(0.29)	*PYN11-PYN12*	44.43(0.28)
PYN4-PYN5	54.67(0.21)	*PYN9-PYN12*	67.77(0.32)
PYN3-PYN6	54.78(0.23)	*PYN10-PYN11*	61.73(0.32)

Tab. 4.3

All the pyridine rings are strongly inclined to the central pyrazine rings and to one another. This situation is similar in the complexes of M.Graf {10}. The dihedral angles between the planes *PYN3* and *PYN4*, and planes *PYN5* and *PYN6* are; 11.8(5)° and 41.3(4)°, respectively, for [Co(tppz)(ma)H_2O)]*4H_2O, 7.3(3)° and 51.5(3)° for [Ni(tppz)(ox)(H_2O)]*5H_2O, 13.5(1)° and 37.0(1)° for [Zn(tppz)Cl_2] respectively.{10}

4.2). Nickel complex **C13** *of* **tppz**

The next, very interesting compound synthesized during our work was the complex **C13**. The reaction of **tppz** with the metal salt $Ni(ClO_4)_2*4H_2O$ gave a green precipitate. This was recrystallized from a mixture of solvents containing acetylacetonate and green block-like crystals were obtained. The crystals were triclinic, space group P$\bar{1}$; a=12.724(5)Å, b=20.401(8)Å, c=20.857(9)Å, α=69.67(3)°, β=86.51(3)°, γ=72.96(3)°, V=4849(4)Å^3, Z=2, R1=0.1336, wR2=0.2153.

The total content of the asymmetric unit consists of

$[NiCl(acac)(tppz)(NiCl_3)]^-*[NiCl(acac)(tppzH)]^+*[NiCl(acac)(tppzH_2)]^{2+}*[NiCl_4]^{2-}$
$*H_2O*(acacH)$

In Fig. 42 a SCHAKAL plot of the crystal structure of **C13** is presented.

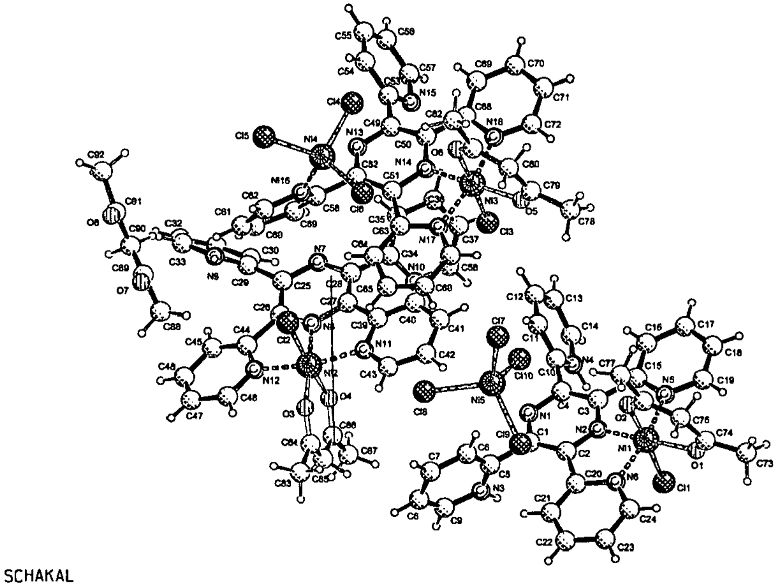


Fig. 42 SCHAKAL plot of the crystal structure of **C13** (a water molecule of crystallization is omitted for clarity)

In the structure we can see two molecules of the **tppz** forming mononuclear complexes with atoms Ni1 and Ni2. The selected bond lengths (Å) and angles (°) are given below:

The bond lengths (Å) for the Ni1 and Ni2 complexes are given in Tab. 4.4:

Ni1 complex		Ni2 complex	
Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
Ni(1)-N(5)	1.923(12)	Ni(2)-N(11)	1.934(12)
Ni(1)-N(2)	1.857(12)	Ni(2)-N(8)	1.839(12)
Ni(1)-N(6)	1.900(12)	Ni(2)-N(12)	1.939(12)
Ni(1)-O(1)	1.890(10)	Ni(2)-O(3)	1.883(10)
Ni(1)-O(2)	1.875(11)	Ni(2)-O(4)	1.896(11)
Ni(1)-Cl(1)	2.250(5)	Ni(2)-Cl(2)	2.232(5)

Tab. 4.4

The selected angles (°) for the Ni1 and Ni2 complexes are given in Tab. 4.5:

Ni1 complex		Ni2 complex	
Angle	Angle (°)	Angle	Angle (°)
N(2)-Ni(1)-N(5)	82.8(5)	N(8)-Ni(2)-N(12)	82.3(5)
N(2)-Ni(1)-N(6)	83.7(5)	N(8)-Ni(2)-N(11)	83.4(5)
N(2)-Ni(1)-O(1)	178.1(5)	N(8)-Ni(2)-O(3)	178.4(5)
N(2)-Ni(1)-O(2)	86.5(5)	N(8)-Ni(2)-O(4)	85.9(5)
N(2)-Ni(1)-Cl(1)	89.9(4)	N(8)-Ni(2)-Cl(2)	90.0(4)
N(5)-Ni(1)-N(6)	166.6(5)	N(11)-Ni(2)-N(12)	165.7(5)
N(5)-Ni(1)-O(1)	96.3(5)	N(12)-Ni(2)-O(3)	96.6(5)
N(5)-Ni(1)-O(2)	89.6(5)	N(12)-Ni(2)-O(4)	90.3(5)
N(5)-Ni(1)-Cl(1)	91.4(4)	N(12)-Ni(2)-Cl(2)	90.4(4)
N(6)-Ni(1)-O(1)	97.1(5)	N(11)-Ni(2)-O(3)	97.7(5)
N(6)-Ni(1)-O(2)	89.6(5)	N(11)-Ni(2)-O(4)	88.6(5)
N(6)-Ni(1)-Cl(1)	88.6(4)	N(11)-Ni(2)-Cl(2)	89.7(4)
O(1)-Ni(1)-O(2)	95.2(5)	O(3)-Ni(2)-O(4)	95.3(5)
O(1)-Ni(1)-Cl(1)	88.5(4)	O(3)-Ni(2)-Cl(2)	88.8(4)
O(2)-Ni(1)-Cl(1)	176.1(4)	O(4)-Ni(2)-Cl(2)	175.7(4)

Tab. 4.5

The selected and also the most interesting distances and angles indicate the spatial arrangement around the nickel atoms. There are a lot of spatial arrangements possible in the case of nickel atoms:

- Trigonal complexes like as $[Ni(NPh_2)_3]^-$
- Planar complexes (for four coordinate Ni^{II}) such as $Ni(CN)_4^{2-}$
- Tetrahedral complexes like $NiCl_4^{2-}$ (generally defined as NiX_4^{2-} NiX_3L^-, NiL_2X_2, where X represents a halogen atom and L a neutral ligand)
- Trigonal bipyramidal and square pyramidal complexes for nickel atoms with coordination number 5, such as $]Ni(CN)_5]^{3-}$
- Octahedral complexes for the maximum coordination number for nickel – 6, like $[Ni(NH_3)_6](ClO_4)_2$

Regarding the distances and the angles we can state that in these two complexes the coordination polyhedron is distorted octahedral where the central position is occupied by the Ni atom. The three equatorial positions are occupied by the nitrogen atoms of pyrazine and pyridine, the fourth equatorial position is occupied by an oxygen atom of acetylacetonate. The two axial positions are occupied by the second oxygen atom of the acetylacetonate and by a chlorine anion.

For both of the complexes the distances Ni-O are shorter than similar distances given in the work of M.Graf {10} for the binuclear complex $[Ni_2(tppz)(H_2O)_6](NO_3)_4*3H_2O$. Also the distances Ni-N (1.857(12)-1.939(12)Å) are shorter in our complex than in the above mentioned complex (1.998(7)-2.099(8)Å). In both complexes the pyrazine rings are distorted: the dihedral angle between the planes *PZN1* = C1-N1-C4 and *PZN2* = C2-N2-C3, is 2.85(2.39)°, between planes *PZN7* = C25-N7-C28 and *PZN8* = C26-N8-C27 it is 5.50(3.07)°. This means that the pyrazine rings are less twisted than in the complex **C12**.

The simplified spatial arrangement for Ni1 and Ni2 complexes is presented in Fig. 43.

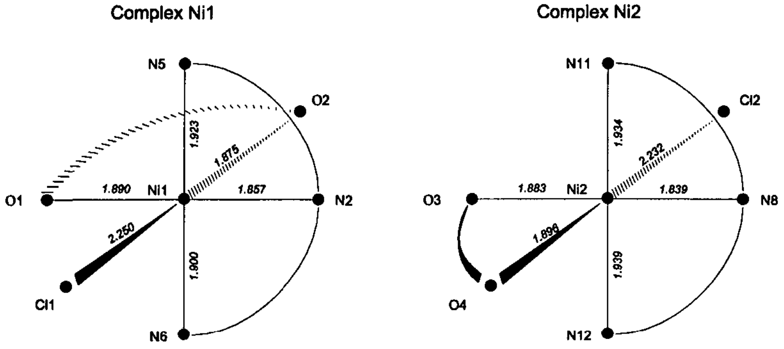


Fig. 43

For further consideration we have to define some planes:

Plane C1-N1-C4 = *PZN1*, C2-N2-C3 = *PZN2*, C25-N7-C28 = *PZN7*, C26-N8-C39 = *PZN8*, C49-N13-C52 = *PZN13*, C50-N14-C51 = *PZN14*,

PZ = C1-C2-N2-C3-C4-N1, *PYN3* = C5-C6-C7-C8-C9-N3, *PYN4* = C10-C11-C12-C13-C14-N4, *PYN5* = C15-C16-C17-C18-C19, *PYN6* = C20-C21-C22-C23-C24-N6

PZ2 = C26-C26-N8-C27-C28-N7, *PYN9* = C29-C30-C31-C32-C33-N9, *PYN10* = C34-C35-C36-C37-C38-N10, *PYN11* = C39-C40-C41-C42-C43-N11, *PYN12* = C44-C45-C46-C47-C48-N12

PZ3 = C49-C50-N14-C51-C52-N13, *PYN15* = C53-C54-C55-C56-C57-N15, *PYN16* = C58-C59-C60-C61-C62-N16, *PYN17* = C63-C64-C65-C66-C67-N17, *PYN18* = C68-C69-C70-C71-C72-N18

The pyridine rings *PYN5* and *PYN6* are coordinated to nickel Ni1 and inclined to one another by 1.22(0.94)°, the two pyridine rings not coordinated to Ni1, *PYN3* and *PYN4*, are inclined to one another by 73.04(0.95)°. The pyridine rings *PYN11* and *PYN12* are coordinate to nickel Ni2 and inclined to one another by 7.47(0.91)°, the two pyridine rings not coordinated to Ni2, *PYN9* and *PYN10*, are inclined to one another by 86.77(0.61)°. The rest of the selected dihedral angles for the complexes containing the Ni1 and Ni2 atoms are given below in Tab. 4.6:

Complex Ni1		Complex Ni2	
Planes	Angle (°)	Planes	Angle (°)
PZN1-PZN2	2.85(2.39)	*PZN7-PZN8*	5.50(3.07)
PZ-PYN3	81.35(0.69)	*PZ2-PYN9*	51.52(0.65)
PZ-PYN4	73.93(0.57)	*PZ2-PYN10*	67.76(0.54)
PZ-PYN5	5.39(0.92)	*PZ2-PYN12*	10.84(0.86)
PZ-PYN6	4.34(0.93)	*PZ2-PYN11*	5.65(0.85)
PYN3-PYN4	73.04(0.95)	*PYN9-PYN10*	86.77(0.61)
PYN5-PYN6	1.22(0.94)	*PYN11-PYN12*	7.47(0.91)
PYN4-PYN5	75.59(0.59)	*PYN9-PYN12*	53.95(0.67)
PYN3-PYN6	85.10(0.72)	*PYN10-PYN11*	70.38(0.54)

Tab. 4.6

The most interesting point of the structure of **C13** is the third complex where **tppz** is coordinated to two nickel atoms: Ni3 and Ni4. In this anion $[NiCl(acac)(tppz)NiCl_3]^-$ the ligand combines two different coordination modes. Compared with the known mono-tridentate chelating coordination to the Ni^{II}, an extra monodentate coordination is observed from a pyridine ring (*PYN16*) to a $[NiCl_3]^-$ anion (Ni4).

The selected bond lengths (Å) for the Ni3 complex are given in Tab. 4.7:

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
Ni(3)-N(17)	1.950(12)	Ni(3)-O(5)	1.889(9)
Ni(3)--N(14)	1.843(11)	Ni(3)-O(6)	1.892(10)
Ni(3)-N(18)	1.935(12)	Ni(3)-Cl(3)	2.246(4)

Tab. 4.7

The selected angles (°) for the Ni3 complex are given in Tab. 4.8:

Angle	Angle (°)	Angle	Angle (°)
N(14)-Ni(3)-N(17)	83.2(5)	N(17)-Ni(3)-Cl(3)	90.0(4)
N(14)-Ni(3)-N(18)	82.7(5)	N(18)-Ni(3)-O(5)	96.8(5)
N(14)-Ni(3)-O(5)	178.3(5)	N(18)-Ni(3)-O(6)	88.6(5)
N(14)-Ni(3)-O(6)	86.3(5)	N(18)-Ni(3)-Cl(3)	90.2(4)
N(14)-Ni(3)-Cl(3)	89.2(4)	O(5)-Ni(3)-O(6)	95.3(5)
N(17)-Ni(3)-N(18)	165.9(5)	O(5)-Ni(3)-Cl(3)	89.3(3)
N(17)-Ni(3)-O(5)	97.3(5)	O(6)-Ni(3)-Cl(3)	175.4(4)
N(17)-Ni(3)-O(6)	90.1(5)		

Tab. 4.8

From the data given above we see that the coordination mode of the Ni3 atom is the same as that for atoms Ni1 and Ni2; the coordination polyhedron is a distorted octahedron, the distances and angles for this arrangement are almost the same as those observed for Ni1 and Ni2.

The second coordination mode is different. The coordination polyhedron of atom Ni4 is tetrahedron: the three corners are occupied by Cl atoms (the bond lengths are almost the same and are given below) and the fourth position is occupied by nitrogen atom N16 from the *PYN16* ring. The bond length Ni4-N16 is 2.096(13)Å which is slightly longer than observed for the rest of Ni-N bonds in this product.

The spatial arrangement around atom Ni4 is schematically presented in Fig. 44.

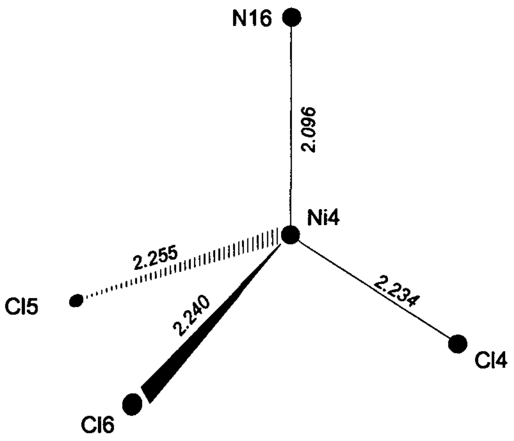


Fig. 44

The selected bond lengths (Å) for the Ni4 complex are given in Tab. 4.9:

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
Ni(4)-N(16)	2.096(13)	Ni(4)-Cl(6)	2.240(5)
Ni(4)-Cl(4)	2.234(5)	Ni(4)-Cl(5)	2.255(5)

Tab. 4.9

The selected angles (°) for the Ni4 complex are given in Tab. 4.10:

Angle	Angle (°)	Angle	Angle (°)
N(16)-Ni(4)-Cl(4)	105.3(4)	Cl(4)-Ni(4)-Cl(5)	109.5(2)
N(16)-Ni(4)-Cl(6)	109.5(4)	Cl(4)-Ni(4)-Cl(6)	115.0(2)
N(16)-Ni(4)-Cl(5)	101.5(4)	Cl(5)-Ni(4)-Cl(6)	114.8(2)

Tab. 4.10

In the asymmetric unit is also present a $[NiCl_4]^{2-}$ anion. Here also the nickel atom is tetrahedral, although the Ni5-Cl distances are larger than described above. However, the angles are more regular and the structure is very close to an ideal tetrahedron.

Selected bong lengths (Å) for the $[NiCl_4]^{2-}$ are given in Tab. 4.11:

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
Ni(5)-Cl(7)	2.259(6)	Ni(5)-Cl(9)	2.276(6)
Ni(5)-Cl(8)	2.301(5)	Ni(5)-Cl(10)	2.282(6)

Tab. 4.11

Selected angles (°) for the $[NiCl_4]^{2-}$ are given in Tab. 4.12:

Angle	Angle (°)	Angle	Angle (°)
Cl(7)-Ni(5)-Cl(8)	105.2(3)	Cl(8)-Ni(5)-Cl(9)	108.9(2)
Cl(7)-Ni(5)-Cl(9)	114.7(2)	Cl(8)-Ni(5)-Cl(10)	108.8(2)
Cl(7)-Ni(5)-Cl(10)	109.6(3)	Cl(10)-Ni(5)-Cl(9)	109.4(2)

Tab. 4.12

In the complex containing the Ni3 and Ni4 atoms the angle between the plane *PZ13* containing atoms C49-N13-C52 and plane *PZ14* containing atoms C50-N14-C51 is

4.87(2.08)°- this means that this pyrazine ring is more twisted than the *PZ* pyrazine ring (2.85(2.39)°), but less twisted than ring *PZ2* (5.50(3.07)°). The pyridine rings *PYN15* and *PYN16* are inclined to one another by 86.96(0.61)°, and rings *PYZ17* and *PYZ18* by 4.03(0.82)°. All the important dihedral angles are given below in Tab. 4.13:

Planes	Angle (°)	Planes	Angle (°)
PZN113-PZN14	4.87(2.08)	*PYN15-PYN16*	86.96(0.61)
PZ3-PYN15	63.25(0.57)	*PYN16-PYN17*	63.00(0.56)
PZ3-PYN16	59.72(0.52)	*PYN17-PYN18*	4.3(0.82)
PZ3-PYN17	7.08(0.81)	*PYN15-PYN18*	65.61(0.60)
PZ3-PYN18	7.06(0.84)		

Tab. 4.13

In the IR spectrum we found bands at 1479, 1407, 1360, 1283 cm^{-1}, typical for ν(C=C) and ν(C=N) vibrations.

4.3). Nickel complex **C14** *of* **tppz**

The next two complexes of **tppz** - **C14** and **C15** - were synthesized in the same reaction. To a suspension of **tppz** and **L1** in methanol/acetonitrile was added NaCl and the metal salt $Ni(ClO_4)_2*6H_2O$. After evaporation of the solvent the residue was divided into two parts and recrystallized from a mixture of the solvents containing acetonitrile (which gave the product **C14**) and the second part from a mixture of solvents containing acetylacetone (which gave the product **C15**).

Product **C14** (Fig. 45), $[(NiCl_2(tppz)NiCl)_2Cl]*ClO_4*H_2O$, black block-like crystals which crystallized in the monoclinic crystal system, space group A2/n, a=15.866(4)Å, b=14.843(4)Å, c=22.259(5)Å, β=98.84(2)°, V=5180(2)$Å^3$, Z=4, R1=0.0534, wR2=0.1199.

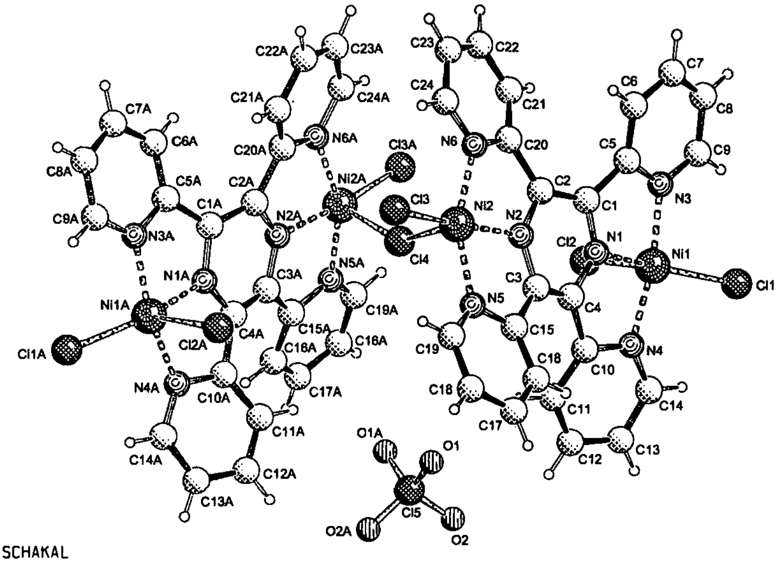


Fig. 45: SCHAKAL plot of the crystal structure of **C14** (water of crystallatization has been omitted for clarity)

The asymmetric unit of **C14** contains one molecule of **tppz** coordinated in a bis-tridentate manner with the nickel atoms, one molecule of water and ½ a molecule of the ClO_4^- anion. Atom Cl4 is situated on a special position, a 2-fold axis, and forms a chlorine bridge (Ni2-Cl4-Ni2A) between two complexes visible after the symmetry operations (Fig. 45).

For the first time we obtained here a bis-tridentate complex, coordination from both sides of the pyrazine ring has been obtained. The asymmetric unit contains one molecule of the tppz complex coordinated with two Ni^{II} atoms, ½ of the ClO_4^- anion and a molecule of water.

The selected bond lengths (Å) for **C14** are given below in Tab. 4.14:

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
Ni(1)-N(3)	2.003(4)	Ni(2)-N(6)	2.013(4)
Ni(1)-N(1)	1.978(4)	Ni(2)-N(2)	1.982(4)
Ni(1)-N(4)	2.024(4)	Ni(2)-N(5)	2.022(4)
Ni(1)-Cl(1)	2.2391(14)	Ni(2)-Cl(3)	2.2187(14)
Ni(1)-Cl(2)	2.491(2)	Ni(2)-Cl(4)	2.5087(10)

Tab. 4.14

The selected angles (°) for **C14** are given below in Tab. 4.15:

Angle	Angle (°)	Angle	Angle (°)
N(1)-Ni(1)-N(3)	79.5(2)	N(2)-Ni(2)-N(6)	79.6(2)
N(1)-Ni(1)-N(4)	79.8(2)	N(2)-Ni(2)-N(5)	80.0(2)
N(1)-Ni(1)-Cl(1)	157.13(12)	N(2)-Ni(2)-Cl(3)	171.34(12)
N(1)-Ni(1)-Cl(2)	94.34(12)	N(2)-Ni(2)-Cl(4)	85.67(11)
N(3)-Ni(1)-N(4)	158.0(2)	N(5)-Ni(2)-N(6)	156.5(2)
N(3)-Ni(1)-Cl(1)	98.43(12)	N(6)-Ni(2)-Cl(3)	99.14(12)
N(3)-Ni(1)-Cl(2)	95.85(12)	N(6)-Ni(2)-Cl(4)	94.83(12)
N(4)-Ni(1)-Cl(1)	97.75(12)	N(5)-Ni(2)-Cl(3)	99.25(12)
N(4)-Ni(1)-Cl(2)	93.08(13)	N(5)-Ni(2)-Cl(4)	95.13(13)
Cl(1)-Ni(1)-Cl(2)	108.51(5)	Cl(3)-Ni(2)-Cl(4)	102.99(5)

Tab. 4.15

On one side of **tppz** the Ni^{II} atom (Ni1) is coordinated with three nitrogen atoms from **tppz** (N1, N3, N4). The coordination sphere of Ni1 atom is completed by the chlorine atoms Cl1 and Cl2. The Ni1-Cl1 distance is 2.2391(14)Å where Ni1-Cl2 is 2.491(2)Å; the Ni2-Cl3 distance is 2.2187(14)Å whereas Ni2-Cl4 is 2.5087(10)Å. Considering these distances and the corresponding angles we can describe the coordination polyhedron of the Ni1 atom as a distorted trigonal bipyramid (schematically it is presented in Fig. 46). The second nickel atom, Ni2, is coordinated with three nitrogen atoms from **tppz** (N2, N5, N6) and one chlorine atom Cl3. The coordination polyhedron for this nickel atom is a distorted square planar arrangement.

From the tables we see that the bond lengths for both nickel atoms (Ni1 and Ni2) are almost the same, the largest difference being in the Ni-Cl bond lengths.

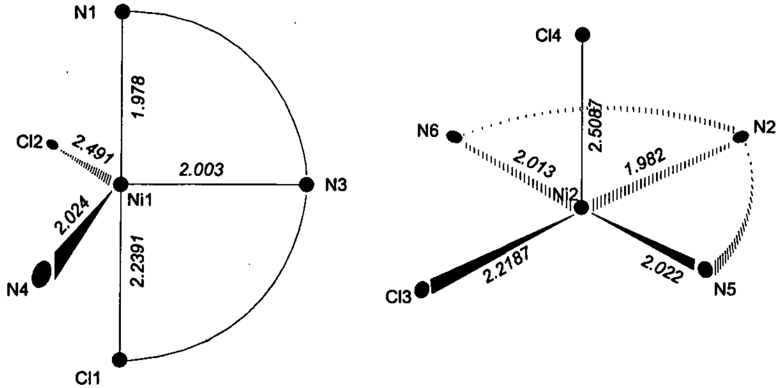


Fig. 46

This complex may be compared in someway (because of another type of coordination) with that synthesized and described by Marion Graf {57}. The following binuclear copper(II) and nickel(II) complexes were investigated in that work: [Cu_2(tppz)Cl_4]*5H_2O called in further part MG1, [Ni_2(tppz)$(H_2O)_6$]$(NO_3)_4$*2.5H_2O = MG2 and [Ni_2(tppz)$(H_2O)_6$]*(squarate)$_2$*5H_2O = MG3.

The geometry of the copper atoms in those complexes is described as square pyramidal or distorted square pyramidal. All the complexes have distorted pyrazine rings, in MG1 this ring is twisted by 9.9(9)°, in MG2 by 11.4(3)° and in MG3 by 11.2(6)°. In **C14** the deformation is smaller; the pyrazine ring is twisted by only 9.26(0.12)° (defined as dihedral angle between planes *PYN1* =C1-N1-C4 and *PYN2* = C2-N2-C3).

To simplify further considerations we have to define some planes:

Plane *PZN1* = C1-N1-C4, *PZN2* = C2-N2-C3, *PZ* = C1-C2-N2-C3-C4-N1, *PYN3* = C5-C6-C7-C8-C9-N3, *PYN4* = C10-C11-C12-C13-C14-N4, *PYN5* = C15-C16-C17-C18-C19, *PYN6* = C20-C21-C22-C23-C24-N6

The pyridine rings *PYN3* and *PYN4* are coordinated to atom Ni1 and inclined to one another by 13.07(0.14)°, the two pyridine rings *PYN5* and *PYN6* are coordinated to atom Ni2 and are inclined to one another by 9.83(0.20)°. In MG1 these angles were 12.7(2)° and 6.6(2)°; in MG2 9.9(4)° and 9.6(3)°; and in MG3 it is 5.3(2)°. In **C14** we have a smaller deformation of the pyrazine ring but the pyridine rings coordinated to the nickel atoms form larger angles with the central pyrazine rings. This is probably due to the steric requirements imposed by the coordination of the pyridine together with pyrazine rings.

The rest of the selected dihedral angles for complex **C14** is given below in Tab. 4.16:

Planes	Angle (°)	Planes	Angle (°)
PZN1-PZN2	9.26(0.12)	*PYN3-PYN4*	13.07(0.14)
PZ-PYN3	14.62(0.07)	*PYN5-PYN6*	9.83(0.20)
PZ-PYN4	24.17(0.10)	*PYN4-PYN5*	44.35(0.12)
PZ-PYN5	22.92(0.14)	*PYN3-PYN6*	31.29(0.11)
PZ-PYN6	17.44(0.12)		

Tab. 4.16

Atom Cl4 is located on a 2-fold axis and forms a chlorine bridge (Ni2-Cl4-Ni2A) between two complexes visible after the symmetry operations (Fig. 45).

In the IR spectrum the very strong band of the ClO_4^- is present at 1096, ν(C=C) and ν(C=N) at 1290, 1405, 1446, 1464cm^{-1}.

4.4). Nickel complex **C15** *of* **tppz**

The last product of the pyrazine complex series that we synthesized in this work is **C15**. It was obtained in the same reaction as that for complex **C14** but recrystallized from a different mixture of solvents. The molecular structure of **C15**, $[NiCl_2(tppz)]*(acacH)*\frac{1}{2}H_2O$ is presented in Fig. 47.

This product crystallized in black block-like crystals in triclinic crystal system, P $\bar{1}$ space group, with a=11.487(2)Å, b=11.920(6)Å, c=12.588(2)Å, α=112.28(2)°, β=93.455(12)°, γ=116.49(2)°, V=1371.5(7)Å^3, Z=2, R1=0.0569, wR2=0.1222.

We have defined the following planes in the structure:

plane *PZN1* = C1-N1-C4, *PYN2* = C2-N2-C3, *PZ* = C1-C2-N2-C3-C4-N1, *PYN3* = C5-C6-C7-C8-C9-N3, *PYN4* = C10-C11-C12-C13-C14-N4, *PYN5* = C15-C16-C17-C18-C19, *PYN6* = C20-C21-C22-C23-C24-N6

The asymmetric unit contains a mono-tridentate complex of **tppz** coordinated to the nickel atom; two chlorine atoms connected to the nickel atom, ½ a molecule of water and a molecule of one of the solvents used for recrystallization: acetylacetonate. The coordination octahedron of the nickel atom is a distorted trigonal bipyramid (τ=0.82 {45}). The Ni-Cl1 distance is 2.2370(14)Å, whereas the rest of the distances involving the Ni atom and atoms N5, N2, and N6 that occupy the rest of the corners lie between 1.968(4) and 2.038(4)Å)

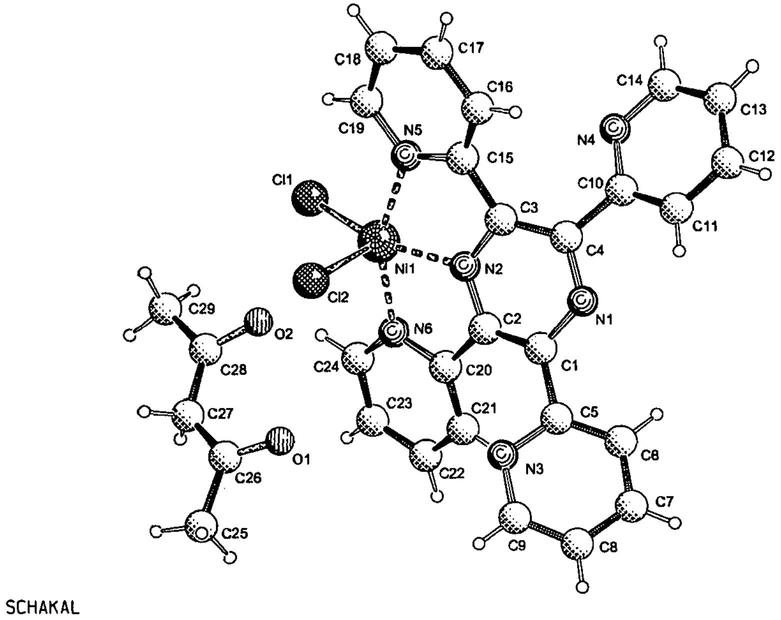


Fig. 47: SCHAKAL plot of the crystal structure of **C15**

Selected bond lengths (Å) for **C15** are given in Tab. 4.17:

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
Ni(1)-N(5)	2.038(4)	Ni(1)-Cl(1)	2.2370(14)
Ni(1)-N(2)	1.968(4)	Ni(1)-Cl(2)	2.432(2)
Ni(1)-N(6)	2.038(4)		

Tab. 4.17

Selected angles (°) for **C15** are given in Tab. 4.18:

Angle	Angle (°)	Angle	Angle (°)
N(2)-Ni(1)-N(5)	78.94(14)	N(5)-Ni(1)-Cl(1)	97.35(11)
N(2)-Ni(1)-N(6)	78.76(14)	N(5)-Ni(1)-Cl(2)	95.71(12)
N(2)-Ni(1)-Cl(1)	156.44(11)	N(6)-Ni(1)-Cl(1)	99.17(11)
N(2)-Ni(1)-Cl(2)	96.52(11)	N(6)-Ni(1)-Cl(2)	96.39(12)
N(5)-Ni(1)-N(6)	155.7(2)	Cl(1)-Ni(1)-Cl(2)	107.02(6)

Tab. 4.18

Some similar, mononuclear complexes of cobalt and nickel were synthesized in the work of M.Graf {11}, that was $[Co(tppz)Cl(H_2O)_2]Cl$, $[Co(tppz)(ma)H_2O)]*4H_2O$, and $[Ni(tppz)(ox)(H_2O)]*5H_2O$. For the malonate derivative the Co-O(malonate) distances are 1.964(8)Å and 2.077(7)Å; the Co-N distances are 2.092(8)Å for the central N pyrazine atom; 2.127(8)Å and 2.135(8) for the N pyridine atoms; for the oxalate derivative of the Ni complex the distances are: Ni-O(oxalate) = 2.063(5) and 2.003((5)Å, Ni-N(pyrazine) = 1.997(6)Å, Ni-N(pyridine) = 2.096(6) and 2.088(6)Å, Ni-O(water) = 2.094(5)Å. In both complexes the coordination spheres of Co and Ni atoms are distorted octahedrons.

In Fig. 48 the schematic spatial arrangement of the Ni atom in **C15** is illustrated.

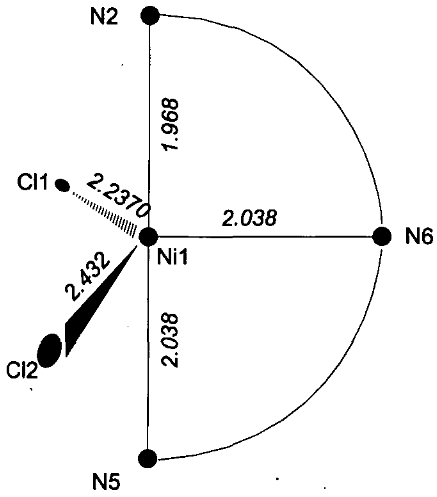


Fig. 48

From the tables it is clear that the bond Ni-N(pyrazine) and bonds Ni-N(pyridines) are similar to the bond lengths in the [Ni(tppz)(ox)(H_2O)]*5H_2O but shorter than in [Co(tppz)(ma)H_2O)]*4H_2O.

The dihedral angles in *PZ* between the plane the values obtained for [Co(tppz)(ma)H_2O)]*4H_2O that was 9.4(6)° and 9.0(4)° for [Ni(tppz)(ox)(H_2O)]*5H_2O, we observe a larger deformation of the pyrazine ring in **C15**.

Selected dihedral angles for **C15** are given below in Tab. 4.19:

Planes	Angle (°)	Planes	Angle (°)
PZN1-PZN2	10.28(0.58)	*PYN3-PYN4*	31.62(0.15)
PZ-PYN3	39.48(0.17)	*PYN5-PYN6*	5.69(0.36)
PZ-PYN4	25.65(0.30)	*PYN4-PYN5*	45.69(0.22)
PZ-PYN5	21.25(0.30)	*PYN3-PYN6*	62.24(0.17)
PZ-PYN6	23.10(0.28)		

Tab. 4.19

All the pyridine rings are strongly inclined to the central pyrazine rings and to one another. This is similar to the situation in the complexes published in the work of M.Graf {10}. The dihedral angles between planes *PYN3* and *PYN4*, and *PYN5* and *PYN6* are; 31.62(0.15) and 5.69(0.36)° in **C15**; 11.8(5) and 41.3(4)° for [Co(tppz)(ma)H_2O)]*4H_2O, 7.3(3)° and 51.5(3)° for [Ni(tppz)(ox)(H_2O)]*5H_2O, 13.5(1)° and 37.0(1)° for [Zn(tppz)Cl_2] respectively.{10}

The IR spectrum shows a wide band for the ν(CO) at 1650cm^{-1}, also the bands at 1474, 1418, 1382, 1301cm-1 were found n the ν(C=C) and ν(C=O) region.

5. UNEXPECTED RESULTS

5.1). Copper complex **U1** *of* **bpca** *(bis(2-pyridylcarbonyl)amide anion)*

During our work on the ligands described before we obtained some unexpected products that we will describe in the following section.

During the reaction of 2,3-bis(2-pyridyl)-5,6-dihydropyrazine and **tppz** with the metal salt $CuCl_2$ in methanol, we obtained the first unexpected product **U1**. The X-ray analysis of the crystals obtained from a filtrate after reaction established the structure of the product shown in Fig. 49, unfortunately a known compound. {46-56}
U1 crystallized in the form of blue needles, in the monoclinic crystal system, space group Pc, a=3.8069(12)Å, b=8.4498(10)Å, c=18.232(3)Å, β=93.40(2)°, V=585.4(2)$Å^3$, Z=2, R1=0.0457, wR2=0.0925.

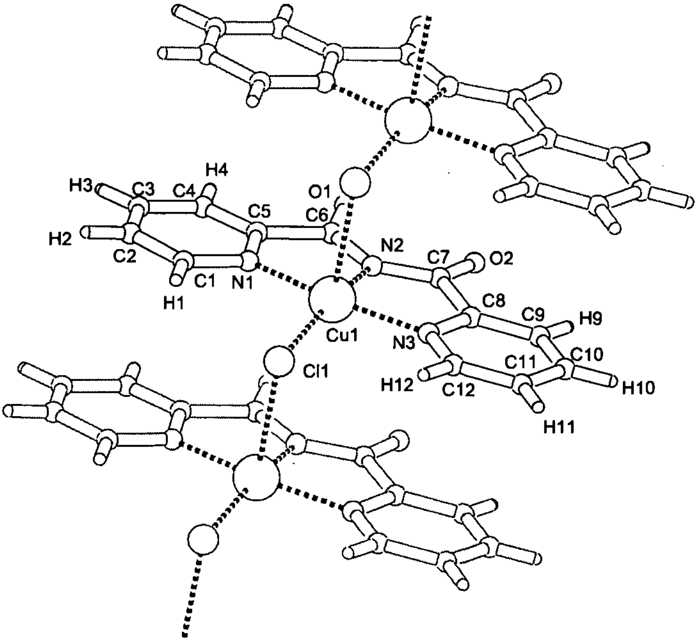


Fig. 49: Plot of the crystal structure of **U1**

Probably during the reaction under reflux the bonds of **tppz,** marked in Fig. 50 by the arrows, were broken giving in this way the ligand that coordinated with the metal salt.

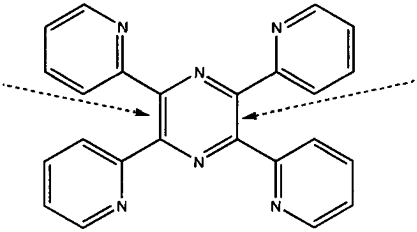


Fig. 50

In determining the type of coordination the parameter of geometry τ is used. τ has been defined by Addison *et al.* {45} on page 48. For the ideal coordination square pyramidal $\tau=0$ ($\alpha=\beta=180°$) while for the trigonal bipyramidal $\tau=1$ ($\alpha=120°$, $\beta=180°$). In complex **U1** $\beta= 165.6°$ and $\alpha=163°$ if so the $\tau=0.043$ which corresponds to a almost perfect square pyramidal coordination of the Cu atom.

The corners of the base of the square pyramid occupy three nitrogen atoms, N1, N2, N3, and one chlorine atom, Cl1. The axial position is occupied by chlorine atom Cl1' of a symmetry related complex molecule. In this way the separate complex molecules are connected together by a chlorine bridge to form a linear chain polymer.

The spatial arrangement around Cu atom is presented schematically in Fig. 51.

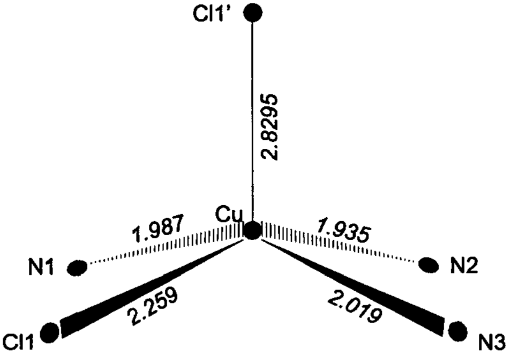


Fig. 51

The selected bond lengths (Å) of **U1** are given in Tab. 5.1:

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
Cu(1)-N(1)	1.987(9)	Cu(1)-Cl(1)	2.259(3)
Cu(1)-N(2)	1.935(9)	Cu(1)-Cl(1)'	2.8295(6)
Cu(1)-N(3)	2.019(9)		

Tab. 5.1

The selected angles (°) for **U1** are given in Tab. 5.2:

Angle	Angle (°)	Angle	Angle (°)
N(1)-Cu(1)-N(2)	81.4(4)	N(2)-Cu(1)-Cl(1)	165.6(3)
N(1)-Cu(1)-N(3)	163.0(4)	N(2)-Cu(1)-Cl(1)'	98.16(1)
N(1)-Cu(1)-Cl(1)	96.9(3)	N(3)-Cu(1)-Cl(1)	98.4(3)
N(1)-Cu(1)-Cl(1)'	93.26(1)	N(3)-Cu(1)-Cl(1)'	92.35(2)
N(2)-Cu(1)-N(3)	81.9(4)	Cl(1)-Cu(1)-Cl(1)'	96.21(2)

Tab. 5.2

We defined some planes to simplify further investigations: plane *PN2* = O1-C6-N2-C7-O2, *PYN1* = C1-C2-C3-C4-C5-N1, *PYN3* = C8-C9-C10-C11-C12-N3.

The dihedral angle between planes PN2 and PYN1 is 4.79(0.61)°, between PN2 and PYN3 2.12(0.63)°. The pyridine rings are inclined to one another by 3.13(0.55)° so they are almost in one plane.

Some similar structures of that ligand have already been published {46-56}, but till now no such polymer has been obtained in this way. Usually to synthesize these [bis(2-arylcarbonyl)amido] derivatives the ligand 2,4,6-Tris(2-pyridyl)-1,3,5-triazine (**tptz**) was used. In this way the $[Cu\{(NC_5H_4CO)_2N\}(NC_5H_4CONH_2)]ClO_4{*}H_2O$ (henceforth **1**) and $[Cu\{(NC_5H_4CO)_2N\}]ClO_4$ (henceforth **2**){46}. In **1** the copper (II) ion is in a distorted octahedral environment, in **2** it is a distorted trigonal bipyramidal environment. In **1** the Cu-N(pyridine) distances are:2.018(4) and 2.017(4)Å, in **2** 2.009(9) and 1.998(9)Å whereas in **U1** they are 1.987(9) and 2.019(9)Å. The distances Cu-N2 are 1.931(4), 1.944(7) and 1.935(9)Å for **1**, **2** and **U1**, respectively. The dihedral angle between the two pyridine rings in **1** is 8.7°, 3.7° in **2**and 3.13(0.55)° in **U1**.

Another two complexes were synthesized: [Cu{$(NC_5H_4CO)_2N$}$(NC_5H_4CONH_2)$][CF_3SO_3] (**3**) and [Cu{$(NC_5H_4CO)_2N$}(tptz)][CF_3SO_3] (**4**) {48}. In **3** the Cu-N(pyridine) distances are:2.022(5) and 2.016(4)Å, in **4** 2.047(8) and 2.055(8)Å where in **U1** they are 1.987(9) and 2.019(9)Å. The distances Cu-N2 are 1.935(4), 1.956(6) and 1.935(9)Å for **3**, **4** and **U1**, respectively. In1991 I.Castro *et al.* synthesized [$Cu_2(bpca)_2(H_2O)_2(C_4O_4)$] (**5**), where **bpca** = bis(2-pyridylcarbonyl)amide anion and $C_4O_4^{2-}$ is the dianion of squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) {51}. The Cu-N(pyridine) distances are 2.007(2) and 2.004(2)Å, and Cu-N2 1.922(2)Å. The pyridine rings of the **bpca** ligand are inclined to one another by 11.4°. The structure of [Cu{$(NC_5H_4CO)_2N$}$(H_2O)_2$]NO_3*$2H_2O$ (**6**) was published in 1990 {54}. The copper(II) ion in that complex is five coordinate and its coordination sphere is nearly square pyramidal (as in **U1**). In **6** the Cu-N(pyridine) distances are: 1.994(1) and 1.996(1)Å, whereas in **U1** they are 1.987(9) and 2.019(9)Å. The distances Cu-N2 are 1.938(1) and 1.935(9)Å for **6** and **U1**, respectively.

In the IR spectrum (KBr pellet) some of the bands, for example at 1716 and 1636cm^{-1}, are wide and cover some other characteristic bands that should be present in this region. Bands for ν(C=C), ν(C=N) are found in the region 1292 and 1027cm^{-1}, and ν(C-H) at 1358cm^{-1}.

5.2) Product **U2**

The second unexpected product, **U2**, was obtained during the reaction between the ligand **L1** and $Mn(ClO_4)_2$*$6H_2O$ in methanol in the presence of triethylamine. The solid obtained after the reaction was recrystallized from mixture of different solvents (also containing acetylacetone); finally the mixture of solvents: methanol/acetonitrile/water gave black-brown rectangular crystals. These crystals were monoclinic, space group P 2/c, a=12.5180(11)Å, b=7.8320(9)Å, c=12.635(2)Å, β=107.763°, V=1179.2(7)Å^3, Z=4, R1=0.0790

The X-ray analysis established the structure is presented in Fig. 52.

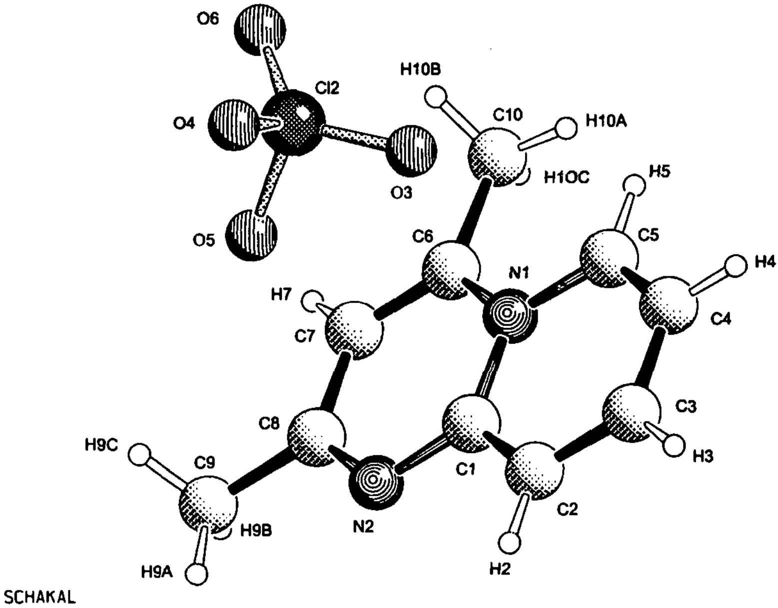


Fig. 52: SCHAKAL plot of the crystal structure of **U2**

The most probable way of obtaining **U2** is shown in Fig. 53:

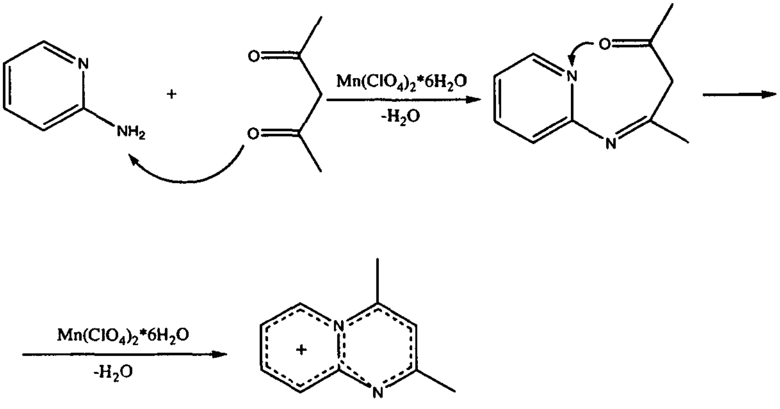


Fig.: 53

During the recrystallization from different solvents (containing also acetylacetone) in the presence of the Mn^{II} salt the free ligand **L1** decomposes. The double bond between the pyrrole ring and 2-aminopyridine fragment is broken and the liberated fragment (also probably the rests of 2-aminopyridine remaining after the synthesis of **L1**) reacts with the molecule of solvent – acetylacetone. Afterwards we have the cyclisation that finally gives **U2**. The bond lengths for this structure are rather typical – the C-C distances in the rings of the structure are between typical for aromatic structures (1.394(5)Å) and lie between 1.346(8) and 1.401(8)Å. The last value is slightly bigger but is still normal, within experimental error, for aromatic C=C bonds. The bonds N2-C8 (1.323(7)Å) and N2-C1 (1.333(6)Å) are also typical for a C=N double bond in aromatic rings similar to pyridine (1.339(5)Å). The bond lengths N1-C1 (1.379(6)Å), N1-C5 (1.385(7)Å), N1-C6 (1.381(7)Å) are typical for the double bonds C=N present in pyrroles (1.383Å). The difference in the bond lengths for these two nitrogen atoms is caused probably by presence of the positive charge located on the nitrogen atom N1. Actually this charge is dispersed on the two aromatic rings present in the structure. In this way we can talk about presence of the resonance structures in this compound. Also the angles confirm the regular structure of product **U2**. The positive charge is compensating for the presence of the counterion ClO_4^- in the asymmetric unit.

The distances C6-C10 (1.503(8)Å) and C8-C9 (1.495(8)Å) are typical for the for C-C bonds in C-Aryl compounds (1.505(5)Å).

Some selected bond lengths (Å) are shown below in Tab. 5.3:

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
C(1)-C(2)	1.410(7)	C(6)-C(7)	1.355(8)
C(2)-C(3)	1.352(8)	C(6)-C(10)	1.503(8)
C(1)-N(1)	1.379(6)	C(6)-N(1)	1.381(7)
C(1)-N(2)	1.333(6)	C(7)-C(8)	1.401(8)
C(3)-C(4)	1.379(9)	C(8)-C(9)	1.495(8)
C(4)-C(5)	1.346(8)	C(8)-N(2)	1.323(7)
C(5)-N(1)	1.385(7)		

Tab. 5.3

Selected angles (°) for **U2** are given in Tab. 5.4:

Angle	Angle (°)	Angle	Angle (°)
C(1)-C(2)-C(3)	120.5(5)	C(5)-N(1)-C(6)	121.4(4)
C(1)-N(1)-C(5)	119.5(4)	C(6)-C(7)-C(8)	120.3(5)
C(1)-N(1)-C(6)	119.1(4)	C(7)-C(8)-C(9)	121.5(6)
C(1)-N(2)-C(8)	118.9(5)	C(7)-C(6)-C(10)	122.5(5)
C(2)-C(3)-C(4)	120.1(6)	C(7)-C(6)-N(1)	118.1(5)
C(2)-C(1)-N(1)	118.5(5)	C(7)-C(8)-N(2)	121.1(5)
C(2)-C(1)-N(2)	119.0(5)	C(9)-C(8)-N(2)	117.4(5)
C(3)-C(4)-C(5)	120.2(6)	C(10)-C(6)-N(1)	119.3(5)
C(4)-C(5)-N(1)	121.2(5)	N(1)-C(1)-N(2)	122.5(5)

Tab. 5.4

The dihedral angle between the planes built up of atoms C6-C7-C8-N2-C1-N1 and C1-C2-C3-C4-C5-N1 is 1.16(0.27)°, so the two rings present in the structure are almost coplanar. In the IR spectrum we found the characteristic bands for the ClO_4^- it the region of 631, 1053 and 1094cm^{-1}, also typical bands are found for ν(C=C), ν(C=N), ν(C-C), ν(C-N) at 1629, 1607, 1581, 1301, 1164, 1141cm^{-1}.

5.3). Product U3

Product **U3** was obtained during the synthesis of 2,3-bis(2-pyridyl)-5-6-dicyanopyrazine. The main product of that reaction was recrystallized from a mixture of solvents containing acetylacetone. It resulted in yellow needle-like crystals; triclinic crystal system, space group $P\bar{1}$, a=5.1939(11)Å, b=8.070(2)Å, c=9.148(2)Å, α=106.82(2)°, β=96.08(2)°, γ=92.80(2)°, V=363.39(12)Å^3, Z=1, R1=0.732, wR2=0.1511.

The asymmetric unit contains only half of the full molecule, the second part is obtained by the symmetry operation around the symmetry center present in the middle of the C7-C7#1 bond; the molecule possess C_2 symmetry.

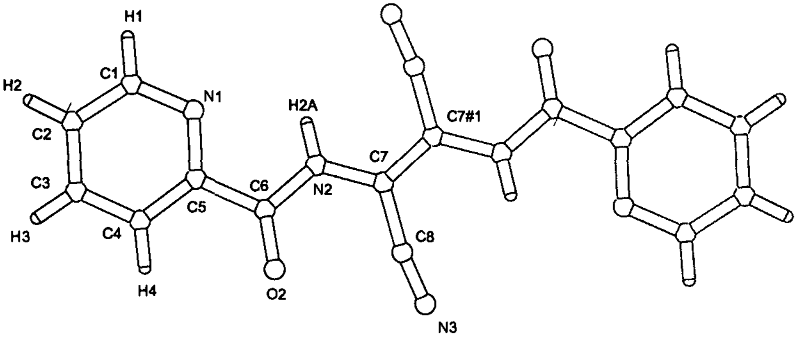


Fig 54: PLUTON plot of the crystal structure of **U3**

The probable way of obtaining product **U3** is shown on Fig. 55:

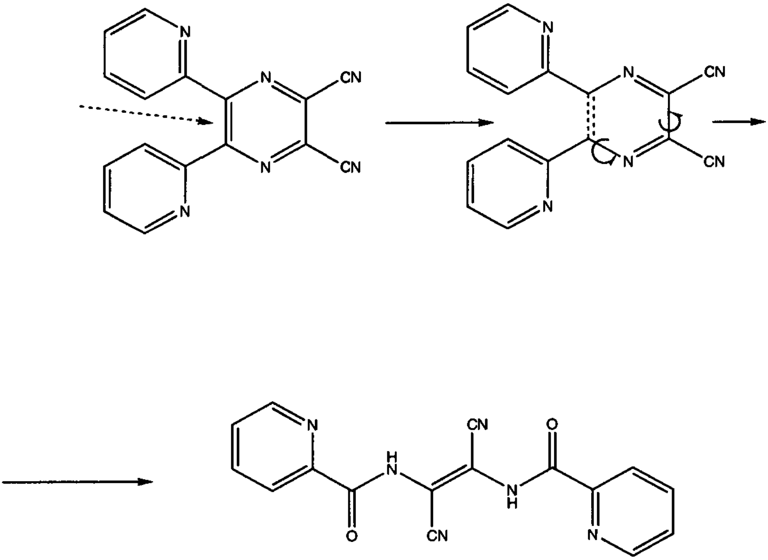


Fig.: 55

Multiple recrystallizations from different mixtures of solvents (containing also acetylacetone), at high temperatures, could cause brake and oxidation of one of the pyrazine bonds.

Selected bond lengths (Å) for **U3** are given in Tab. 5.5:

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
C(1)-N(1)	1.329(4)	C(6)-O(2)	1.216(3)
C(1)-C(2)	1.380(4)	C(6)-N(2)	1.364(3)
C(2)-C(3)	1.369(4)	C(7)-C(7#1)	1.352(5)
C(3)-C(4)	1.379(4)	C(7)-N(2)	1.392(3)
C(4)-C(5)	1.378(4)	C(7)-C(8)	1.437(4)
C(5)-N(1)	1.339(3)	C(8)-N(3)	1.135(4)
C(5)-C(6)	1.493(4)		

Tab. 5.5

From this table it can be seen that C-C bond lengths in the pyridine ring are slightly shorter (1.369(4)-1.380(4)Å) than given in the International Tables of Crystallography (1.394(5)Å); the C=N distance in the pyridine ring should be 1.339(5)Å and is 1.329(4)Å for C1-N1 and 1.339(3)Å for C5-N1 but still are within the experimental error. The C=O distance is 1.216(3)Å and is with agreement with the theoretical data. The distance between the atoms C7and C7#1 is 1.352(5) and it indicates us presence of the C-C double bond between these two atoms. The angles presented below confirm the described structure:

Selected angles (°) for **U3** are given in Tab. 5.6:

Angle	Angle (°)	Angle	Angle (°)
C(1)-C(2)-C(3)	118.8(3)	C(5)-C(6)-O(2)	123.5(2)
C(1)-N(1)-C(5)	116.4(2)	C(6)-N(2)-C(7)	124.1(2)
C(2)-C(3)-C(4)	118.9(3)	C(6)-C(5)-N(1)	116.9(2)
C(2)-C(1)-N(1)	123.7(3)	C(7)-C(8)-N(3)	171.7(3)
C(3)-C(4)-C(5)	118.2(3)	C(7)#1-C(7)-C(8)	117.8(3)
C(4)-C(5)-C(6)	119.1(2)	C(7)#1-C(7)-N(2)	122.6(3)
C(4)-C(5)-N(1)	123.9(3)	C(8)-C(7)-N(2)	119.6(2)
C(5)-C(6)-N(2)	114.3(2)	N(2)-C(6)-O(2)	122.2(3)

Tab. 5.6

The dihedral angle between the planes made up by atoms C1-C2-C3-C4-C5-N1 and C6-O2-N2-C7-C8-N3 is 9.69(0.17)° which means that the structure is not perfectly planar; this small deformation is due to the presence of the two carbonyl groups and two nitril groups in the carbon chain.

In the IR spectrum the characteristic band for the nitrile group was found at 2219cm^{-1}, for the C=O group at 1688, 1238, 1259cm^{-1}, N-H at 756cm^{-1}.

5.4) Product **U4**

The last unexpected but well-known product was **U4**, that is simply 2,3-Bis-(2-pyridyl)-pyrazine. Normally this product is obtained from 2,3-Bis-(2-pyridyl)-5,6-dihydropyrazine in mesitylene refluxed with palladium/charcoal catalyst. The full synthesis was described by Goodwin and Lions {13}. In our case we used the reaction 2,3-Bis-(2-pyridyl)-5,6-dihydropyrazine with CuCl$_2$ in ethanol. The reaction yielded 2,3-Bis-(2-pyridyl)-pyrazine, that structure of which is presented in Fig. 56.

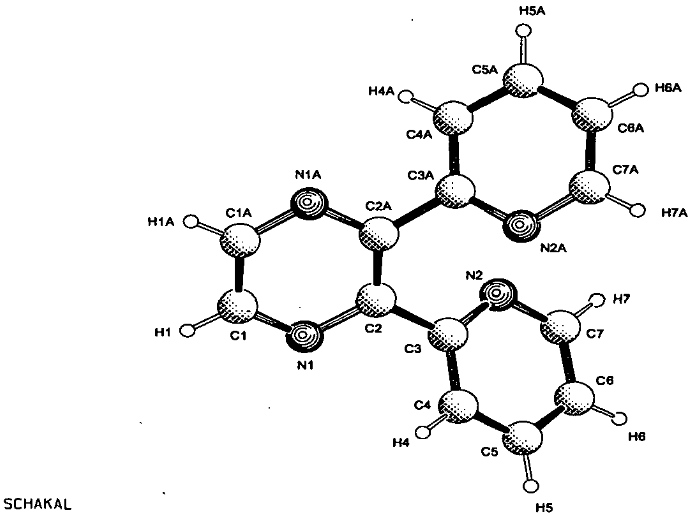


Fig. 56: SCHAKAL plot of the product **U4**

All the crystallographic data obtained for this product are in agreement with data accessible in the literature {58}.

6. CONCLUSIONS

This work was based on the new ligand **L1**: 5,7-bis(2-aminopyridine)-5H-6,7-dihydropyrrolo[3.4-b]pyrazine. Up till today no crystal structures of the complexes with this ligand were known. We succeeded in obtaining some interesting metal complexes of Ru^{II}, Cu^{II}, Co^{II}, Co^{III}, Zn^{II}, and Ni^{II}. These complexes were carefully investigated crystallographically. Generally for the reactions we used perchlorates, chlorides, carbonates, sulfates, or acetates of the different metals. Many reactions gave the same result for the same metal and were not repeated. The free ligand **L1** was very difficult to crystallize. Finally crystals of **L1** for analysis by X-ray crystallography were obtained accidentally from the filtrate after the reaction between **L1** and $Cu(BF_4)_2$. This was the only way to obtain suitable crystals for analysis; we also applied with success the reaction with other metal salts such as e.g.: $CuCl_2$, $Co(ClO_4)_2$, and $Fe(ClO_4)_2$. Complexes of **L1** were also very difficult to crystallize. The most effective method of obtaining crystals was by slow evaporation of the solvents from the filtrate of the reaction. Unfortunately from many reactions with different metal salts (we used salts of Ti^{IV}, Cr^{III}, Mn^{II}, Ag^{I}, W, Pt^{IV}, Hg^{I}, Hg^{II}, Tl^{I}, Pb^{II}, Cd^{II}, Zr^{II}, La^{III}, Rb^{I}, Pd^{II}, Sr^{III}) we obtained products in the form of powders, and it was impossible to recrystallize them to obtain crystals suitable for single crystal X-ray analysis. Attempts to recrystallize them will be continued in the future and at the same time we will try to determine the crystal structures using the possibilities offered by powder diffraction and Rietveld analysis.

The ligand **L1** is an almost planar molecule; the dihedral angles between the pyrazine and the pyrrole ring are no bigger than 1°; the pyridine rings are slightly twisted with respect to the plane of the pyrrole ring, but also not more than about 5°. In the complexes the deformation of the pyrazine ring and the dihedral angles between the pyrazine and pyrrole rings are much larger and this is probably due to steric requirements on complexation. The differences are not large – the largest deformation of the pyrazine ring is no bigger than 4.08(1.69)° in complex **C8** and for the rest of complexes does not exceed 2°. When we also take into account that the largest dihedral angle between the *PZ* and *PR* rings does not exceed 2° that part of the complex (*PZ* and *PR* rings) can be treated as planar. The pyridine rings present in the complex molecules are strongly inclined to the pyrrole ring. The highest values found are 13.78(0.29)° and 30.55(0.31)° in **C4**, and 29.72(0.17)° and 28.93(0.27)° in **C1**.

There are some similar products known for the benzene analogue 1,3-Bis(arylimino)isoindolines (Fig. 58) as ligand.{13, 17-24, 59-69}.

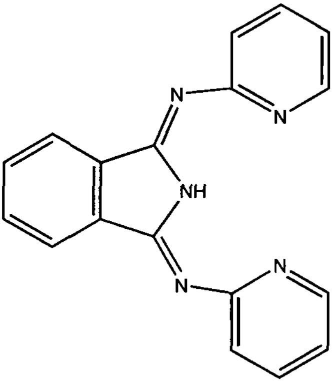


Fig. 58: plot of 1,3-Bis(pyridylimino)isoindoline

In a copper complex of that ligand {23} the Cu-N distances to the pyridine nitrogen atoms are ca. 2.020(3)Å, when those to the pyrrole nitrogen atom are 1.885(4)Å; for the complex presented in reference {63} the same distances are 2.050(5) Å and 2.056(5) Å for Cu-N(pyridine) and 1.904(5)Å for Cu-N(pyrrole). The pyridine rings are twisted by 6° and 9° with respect to the pyrrole ring. We also obtained two copper complexes, **C7** and **C8**, with ligand **L1**. In these complexes the Cu-N(pyridine) distances were 2.200(8) and 2.207(8)Å for **C7** and 2.250(8) and 2.293(8)Å for **C8**; the Cu-N(pyrrole) distances were 1.942(7) and 1.950(7)Å, respectively, and the pyridine rings are twisted by 1.68(.054) and 0.57(0.51)° , respectively, with respect to the pyrrole ring. In a similar nickel complex, 1,3-Bis(2'-pyridylimino)isoindolinato)nickel(II), {66} the distances are significantly shorter, 1.998(11) and 1.931(11)Å for Ni-N(pyridine) and 1.827(10)Å for Ni-N(pyrrole), than those obtained for nickel complex **C4**. There distances Ni-N(pyridine) were 2.166(5), 2.173(5), 2.175(5), 2.205(5), 2.148(5) and 2.135(6)Å, while the Ni-N(pyrrole) distances were 2.206(5), 2.028(5) and 2.017(5)Å; the pyridine rings are twisted by 6.81(0.44), 10.43(0.43), 1.73(0.36), 12.78(0.33), 9.38(0.43) and

21.19(0.38)° with respect to the pyrrole ring. In another nickel complex **C5**, the Ni-N(pyridine) distances were 2.158(4), 2.213(4), 2.204(4) and 2.153(4)Å; the Ni-N(pyrrole) distances were 2.024(4) and 2.022(9)Å; and the pyridine rings are twisted by 6.00(0.30) and 1.25(0.32)° with respect to the pyrrole ring

It would be worth trying in the future to modify ligand **L1**. Up till now we were able to profit only from the mono-tridentate possibilities of this ligand. Introducing (Fig. 59)

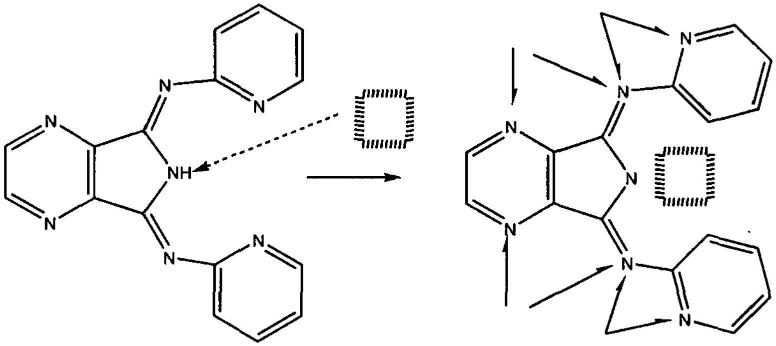


Fig. 59

an organic group in place of the hydrogen atom in the pyrrole ring, which would be large enough to turn the pyridine rings, could create theoretically, some more very interesting potential coordination sites (these "new" coordination sites are marked in Fig. 58 with arrows). This would give us the possibility of obtaining even more interesting complexes and perhaps some linear chain polymers. It will be very interesting to continue these investigations of **L1** in the form already presented, also it would be very interesting to obtain the modifications shown above and to try and obtain a polymer based on the modified form of **L1**. For the synthesis of **L1** we used 2,3-dicyanopyrazine and from that starting material we obtained our ligand. It is very characteristic for this compound that the possible coordination center (after multiple modifications) is only on one side of the pyrazine ring. In this way we obtained a very good mono-tridentate ligand, but it is still not symmetrical (the symmetry plane should contain the N atoms of pyrazine ring and be perpendicular to the pyrazine ring). Using 2,3,5,6-tetracyanopyrazine would allow us to obtain the new highly symmetric ligand (which is very similar to **L1** whose reaction properties are known) that is presented in Fig. 60.

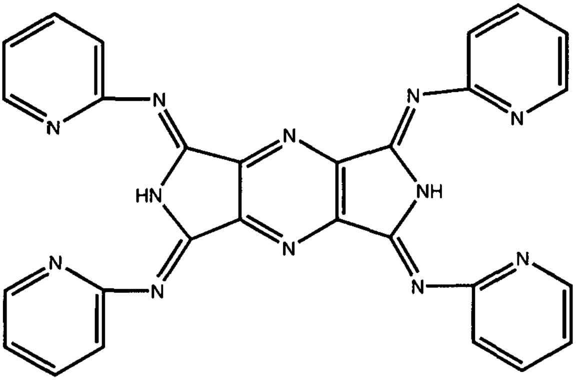


Fig. 60

In this way we would have a very good starting material for obtaining a new type of linear anisotropic coordination polymer.

The second ligand investigated was **tppz**, and complexes **C12**, **C13**, **C14**, **C15** were obtained. The pyrazine ring was distorted in all the complexes obtained. The largest distortion angle was 10.55(0.34)° in **C12**, and it was noted that this angle is always larger for the mono-tridentate complexes of **tppz** than for the bis-tridentate complexes. Also the dihedral angles of the pyridine rings, not coordinated with the metal in the mono-tridentate complexes, with respect to the pyrazine ring, are generally larger than the same angle for the pyridine rings coordinated to the metal (81.34(0.69) and 73.93(0.57)° / 5.39(0.92) and 4.34(0.93)°). This effect is due to the coordination from one side of the pyrazine ring that seems to release some tensions in the molecule on the opposite side of pyrazine ring. Generally the distances Metal-N(pyrazine) are shorter than the distances Metal-N(pyridine). In **C13** we obtained a completely new type of coordination, where in a mono-tridentate complex the nitrogen atom of one of the "free" pyridine rings coordinates with a nickel atom. This combination of two different types of coordination gives us the possibility of obtaining a completely new class of complexes and coordination polymers. In the future it would be worth trying to synthesize chain polymers using some other ligands as bridges between two complexes. As such a bridge even simple molecules such as pyrazine or squaric acid could be used.

The next ligand worth investigating could be the macrocyclic ligand, tetra-2,3-pyridinoporphyrazinate (Fig. 61), which is very similar to phthalocyanine.

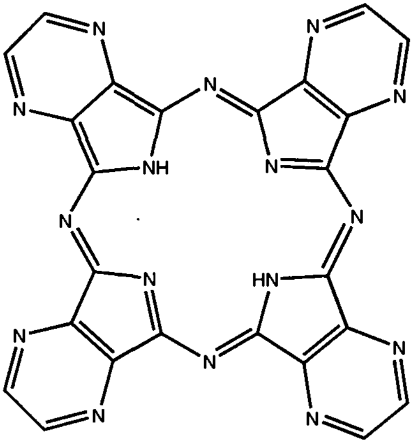


Fig. 61

Based on accessible literature {41} we tried to synthesize complexes of such a ligand with some different metal salts ($CuCl_2$ and $CoCl_2$, for example) in a direct reaction with 2,3-dicyanopyrazine in the presence of a very strong base DBU (1,8-diazabicyclo[4.3.0]undec-7-ene). All the reactions yielded dark black-blue powders, insoluble in almost all organic solvents. These powders were very slightly soluble in DMF and DMSO but very well soluble in concentrated sulfuric acid. During dissolution in hot acid we noticed that demetallization of the product took place – a very nice copper mirror was formed on the surface of the crystallizer. There was no decomposition of products during the same process at room temperature. From such macrocycles it may be possible to obtain a 3-D polymer network. This could lead to the formation of new components which may posses interesting properties for research and industry. Unfortunately, however, we did not yet obtain crystals suitable for X-ray analysis. In the future it may be possible to determine the structure of such compounds by using powder diffraction X-ray analysis.

It would be very interesting to investigate the physical and chemical properties of this kind of compound taking into account that the derivatives of phthalocyanines are used extensively as pigments, optical filters, materials for optical data storage, photo-inactivators for textile bleaching, and in medicine.

7. SUMMARY

We can compare some complexes of Bis(pyridylimino)isoindoline published in the Cambridge Crystal Structure Database {23, 60, 62, 63, 66, 67, 68, 69) with the complexes obtained in our work. The studies on these complexes were limited by the fact that the crystals suitable for the X-ray structure analyses were difficult to obtain. Generally the benzene derivatives were difficult to crystallize. We noticed the same phenomena during the studies of our pyrazine derivatives. Up till now there is no crystal structure even of a pure ligand Bis(pyridylimino)isoindoline present in CSD and we can compare our ligand **L1** (5,7-bis(2-aminopyridine)-5H-6,7-dihydropyrrolo[3.4-b]pyrazine) only with its complexes or complexes of **L1** itself.

Here we will consider the following complexes of Bis(pyridylimino)isoindoline:
HLg1 = 1,3-bis(2-pyridylimino)isoindoline
HLg2 = 1,3-bis((4-methyl-2-pyridyl)imino)isoindoline
HLg3 = 1,3-bis((5-methyl-2-pyridyl)imino)isoindoline
HLg4 = 1,3-bis((3-methyl-2-pyridyl)imino)isoindoline
DBM = dibenzoylmethane
2-Clpcyd = 2-chlorophenylcyanamide

FC1 a carbonate-bridged dimeric complex $(CuLg2)_2(\mu\text{-}CO_3)$ {23}
FC2 = a hydroxyl-bridged tetrameric complex $(CuLg2)_3(CuLgO)(\mu\text{-}OH)_3$ {23}
FC3 = [Cu(Lg3)((DBM)] {63}
FC4 = [Cu(Lg2)(OAc)] {67}
FC5 = $[Co^{III}(Lg1)(OCOPh)(OO\textit{t}\text{-}Bu)]$ {60}
FC6 = $[Co^{II}(Lg4)_2]$ {69}
FC7 = Nickel complex [Ni(Lg1)(2-Clpcyd)] {66}
FC8 = Manganese complex $[Mn(Lg4)_2]$ {62}
FC9 = Molybdene complex $[Mo_2(OAc)_3(Lg1)]$ {68}

We will also take into account the following of our products:

C1 = $[Co^{III}(L1)_2](ClO_4)*2CH_3CH$

C2 = $[Co^{II}(L1)_2]*1/3CH_3CN$

C4 = $[Ni(L1)_2]*1/3CH_3CN$

C5 = $[Ni(L1)_2]$

C8 = $[Cu(L1)_2]*1½CH_3OH$

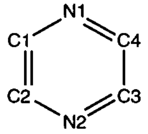
C9 = $[Zn(L1)_2]*1/6CH_3CN$

C10 = $[ZnCl(L1)(CH_3OH)]$

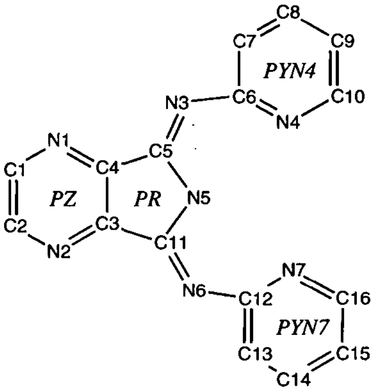
C11 = $[Ru(L1)_2]*¼CH_3CN$

To simplify investigations we define some planes and rings in the structure of ligand **L1**. The atoms C1-C2-N2-C3-C4-N1 build up the plane called *PZ*; in that pyrazine ring we define two planes: *PZN1* built up from atoms N1, C1, C4, and *PZN2* containing atoms N2, C2, C3. The pyrrole ring is built up from atoms C3-C4-C5-N5-C11 and will be called *PR*; the pyridine ring C6-C7-C8-C9-C10-N4 = *PYN4*, second pyridine ring, C12-C13-C14-C15-C16-N7 = *PYN7*. All the corresponding names are shown (in Fig. 24) below.

PZN1 = C1-N1-C4



PZN2 = C2-N2-C3



For the rest of the complexes only the corresponding numbers of the nitrogen atoms will be changed, and the number that concerns the pyrazine ring present in a complex (if there are more than one the second pyrazine ring will be called *PZ2*, the second pyrrole ring *PR2*, etc.)

Complex (metal)	Distance (Å) metal (M) - nitrogen (N) atom								
	Molecule **A**						Molecule **B**		
	M-N4	M-N5	M-N7	M-N11	M-N12	M-N14	M-N18	M-N19	M-N21
C1 ($\mathrm{Co^{III}}$)	1.984(5)	1.887(5)	1.979(5)	--	--	--	--	--	--
C2 ($\mathrm{Co^{II}}$)	2.211(12)	2.061(11)	2.205(11)	2.198(11)	2.057(10)	2.225(11)	2.184(12)	1.993(12)	2.148(12)
FC5 ($\mathrm{Co^{III}}$)	1.950(5)	1.845(5)	1.960(5)	--	--	--	--	--	--
FC6 ($\mathrm{Co^{II}}$)	2.188(4)	2.000(3)	2.200(4)	2.195(3)	2.001(3)	2.201(3)	--	--	--
C4 ($\mathrm{Ni^{II}}$)	2.166(5)	2.026(5)	2.173(5)	2.175(5)	2.028(5)	2.205(5)	2.148(5)	2.017(5)	2.135(6)
C5 ($\mathrm{Ni^{II}}$)	2.158(4)	2.024(4)	2.213(4)	2.204(4)	2.022(9)	2.153(4)	--	--	--
FC7 ($\mathrm{Ni^{II}}$)	1.931(11)	1.827(10)	1.998(11)	--	--	--	--	--	--
C8 ($\mathrm{Cu^{II}}$)	2.200(8)	1.942(7)	2.207(8)	2.256(8)	1.950(7)	2.293(8)	--	--	--
FC1 ($\mathrm{Cu^{II}}$)	2.012	1.881	2.026	2.018	1.889	2.025	--	--	--
FC2 ($\mathrm{Cu^{II}}$)	2.006	1.892	2.022	2.003	1.927	2.019	2.064 2.001	1.926 1.881	2.071 2.007
FC3 ($\mathrm{Cu^{II}}$)	2.050(5)	1.904(5)	2.056(5)	--	--	--	--	--	--
FC4 ($\mathrm{Cu^{II}}$)	1.992(6)	1.898(6)	1.998(6)	--	--	--	2.008(6)	1.896(6)	2.012(7)
C9 ($\mathrm{Zn^{II}}$)	2.276(11)	2.072(11)	2.229(11)	2.243(11)	2.056(11)	2.247(10)	2.221(11)	2.033(11)	2.202(12)
C10 ($\mathrm{Zn^{II}}$)	2.201(7)	1.989(7)	2.222(7)	--	--	--	--	--	--
C11 ($\mathrm{Ru^{II}}$)	2.275(13)	2.057(12)	2.214(12)	2.259(11)	2.065(12)	2.245(12)	2.192(14)	2.042(12)	2.215(12)
FC8 ($\mathrm{Mn^{II}}$)	2.284	2.152	2.325	2.274	2.141	2.295	2.278 2.289	2.137 2.145	2.285 2.310
FC9 ($\mathrm{Mo^{II}}$)	2.143(7)	2.120(7)	2.466(7)	--	--	--	--	--	--

Tab. 7.2

Selected dihedral angles (°)			Products							
			L1	**C1** (Co^{III})	**C2** (Co^{II})	**FC5** (Co^{III})	**FC6** (Co^{II})	**C4** (Ni^{II})	**C5** (Ni^{II})	**FC7** (Ni^{II})
MOLECULES	A	*PZN1-PZN2*	0.70(1.03)	2.92(0.82)	2.20(3.16)	--	--	0.81(1.29)	1.19(0.34)	--
		PZ-PR	0.54(0.43)	2.91(0.26)	1.03(1.10)	0.443	0.880	1.74(0.46)	0.31(0.53)	1.052
		PR-PYN4	4.03(0.45)	28.93(0.27)	6.40(1.04)	3.586	22.852	6.81(0.44)	1.25(0.32)	4.977
		PR-PYN7	4.40(0.45)	29.72(0.27)	11.03(1.02)	6.225	18.031	10.43(0.43)	6.00(0.30)	9.096
		PYN4-PYN7	2.88(0.47)	53.93(0.24)	17.37(0.90)	9.804	38.676	17.23(0.37)	6.68(0.31)	7.962
		PZN8-PZN9	--	--	2.67(2.50)	--	--	0.69(1.06)	--	--
		PR2-PZ2	--	--	1.91(0.88)	--	2.258	1.62(0.38)	--	--
		PR2-PYN11	--	--	3.20(0.85)	--	16.392	1.73(0.36)	--	--
		PR2-PYN14	--	--	12.62(0.80)	--	16.829	12.78(.033)	--	--
		PYN11-PYN14	--	--	15.07(0.72)	--	32.345	13.78(0.29)	--	--
	B	*PZN15-PZN16*	--	--	1.27(3.25)	--	--	1.70(1.27)	--	--
		PR3-PZ3	--	--	0.52(1.08)	--	--	0.72(0.47)	--	--
		PR3-PYN18	--	--	19.98(0.88)	--	--	9.38(0.43)	--	--
		PR3-PYN21	--	--	10.01(0.97)	--	--	21.19(0.38)	--	--
		PYN18-PYN21	--	--	29.92(0.74)	--	--	30.55(0.31)	--	--

Tab. 7.3

Selected dihedral angles (°)			Products						
			L1	**C8** (Cu^{II})	**FC1** (Cu^{II})	**FC2** (Cu^{II})		**FC3** (Cu^{II})	**FC4** (Cu^{II})
M O L E C U L E S	**A**	*PZN1-PZN2*	0.70(1.03)	4.08(1.69)	--	--		--	--
		PZ-PR	0.54(0.43)	1.68(0.54)	1.524	0.353		0.650	0.783
		PR-PYN4	4.03(0.45)	14.50(047)	9.314	1.900		5.970	3.376
		PR-PYN7	4.40(0.45)	23.45(0.46)	9.488	1.595		9.156	3.501
		PYN4-PYN7	2.88(0.47)	36.63(0.34)	18.151	3.140		3.331	6.436
		PZN8-PZN9	--	1.26(1.61)	--	--		--	--
		PR2-PZ2	--	0.57(0.51)	1.670	1.545		--	2.332
		PR2-PYN11	--	6.57(0.66)	1.080	3.234		--	4.276
		PR2-PYN14	--	30.68(0.40)	14.447	12.022		--	5.930
		PYN11-PYN14	--	37.17(0.45)	14.058	13.676		--	7.741
	B	*PZN15-PZN16*	--	--	--	--		--	--
		PR3-PZ3	--	--	--	0.95	1.071	--	--
		PR3-PYN18	--	--	--	11.399	6.717	--	--
		PR3-PYN21	--	--	--	13.642	11.433	--	--
		PYN18-PYN21	--	--	--	24.965	17.630	--	--

Tab. 7.4

Selected dihedral angles (°)			Products						
			L1	**C9** (Zn^{II})	**C10** (Zn^{II})	**C11** (Ru^{II})	**FC8** (Mn^{II})		**FC9** (Mo^{II})
M O L E C U L E S	A	*PZN1-PZN2*	0.70(1.03)	1.14(2.42)	0.74(1.50)	1.43(2.18)	--		--
		PZ-PR	0.54(0.43)	1.38(0.86)	2.68(0.57)	2.06(0.95)	0.520		7.60.
		PR-PYN4	4.03(0.45)	12.34(0.79)	18.39(0.44)	11.19(0.95)	3.606		11.189
		PR-PYN7	4.40(0.45)	1.05(0.81)	3.80(0.55)	1.48(0.93)	22.925		41.468
		PYN4-PYN7	2.88(0.47)	13.10(0.73)	20.63(0.42)	12.18(0.91)	26.241		33.267
		PZN8-PZN9	--	0.97(3.23)	--	3.30(3.81)	--		--
		PR2-PZ2	--	1.74(1.12)	--	2.61(1.32)	1.497		--
		PR2-PYN11	--	9.34(0.95)	--	6.58(1.26)	4.398		--
		PR2-PYN14	--	6.53(0.97)	--	8.37(1.26)	7.500		--
		PYN11-PYN14	--	13.92(0.82)	--	14.79(1.20)	9.190		--
	B	*PZN15-PZN16*	--	1.31(3.23)	--	1.36(3.61)	--	--	--
		PR3-PZ3	--	0.31(1.09)	--	0.91(1.27)	1.717	1.117	--
		PR3-PYN18	--	18.40(0.87)	--	10.06(1.08)	6.067	5.090	--
		PR3-PYN21	--	10.46(0.91)	--	19.47(0.99)	9.988	24.321	--
		PYN18-PYN21	--	25.64(0.66)	--	26.88(0.80)	10.938	28.914	--

From the comparison given in the above tables we can state that the distances between the central metal atom and the nitrogen atoms are larger in the complexes obtained in this work than for the benzene derivatives. Generally the differences are ca. 0.1Å for the bonds metal-N(pyrrole) and between 0.1 and 0.2Å for the distances metal-N(pyridine). The deformation angle (the angle in the pyrazine rings) lies between 0.70(1.03)° for the pure ligand **L1** and 4.08(1.69)° for complex **C8**. Also the differences in dihedral angles between the pyrrole ring and pyridine rings are significant and again these angles are larger for the compounds synthesized by us. There are only two exceptions: these angles are larger in complexes **FC8** and **FC9**, and it can be explained by the fact that both the Mn and Mo atoms present in **FC8** and **FC9**, respectively, have larger atomic radii than the metals present in our complexes. The larger values for the bond lengths and inclination angles of the pyridine rings, deformations of the pyrazine rings, in comparison with the known complexes of the benzene derivatives may be caused by the presence of the two nitrogen atoms in the pyrazine rings. The structure of the ligand for both types of complexes is almost the same, we have just introduced the pyrazine ring in place of the benzene ring. This causes the larger flexibility of this ring and the free electron pairs still present on the nitrogen atoms and lying in the plane of the ring may force the pyridine rings to be more inclined because of electronic steric reasons.

We can also compare structures of the complexes of **tppz** obtained in our work with the structures already published in Cambridge Crystal Structure Database. We will compare in tables the following compounds

C12 = $[Co^{II}(tppz)_2](ClO_4)_2{*}2H_2O$

C13 = $[Ni^{II}Cl(acac)(tppz)(Ni^{II}Cl_3)]^-$
$*[Ni^{II}Cl(acac)(tppzH)]^+{*}[Ni^{II}Cl(acac)(tppzH_2)]^{2+}{*}[Ni^{II}Cl_4]^{2-}{*}H_2O{*}\frac{1}{2}(acacH)$

C14 = $[[Ni^{II}Cl_2(tppz)Ni^{II}Cl)_2Cl](ClO_4){*}2H_2O$

C15 = $[Ni^{II}Cl_2(tppz)]{*}(acacH){*}\frac{1}{2}H_2O$

tetragonal form of tppz - *t*-tppz{76}

$tppzH_4$ {73}

$tppzH_2$ {77}

FC10 = $[Cu^{II}_2(tppz)(H_2O)_4](ClO_4)_4{*}2H_2O$ {40}

FC11 = $[Cu^{II}_2(tppz)Cl_4]{*}5H_2O$ {57}

FC12 = $[Cu^{II}(tppzH)Cl]_2(ClO_4)_2$ {40}

FC13 = $[Ni^{II}_2(tppz)(H_2O)_6](NO_3)_4{*}2\frac{1}{2}H_2O$ {57}

FC14 = $[Ni^{II}(tppz))(ox)H_2O]{*}5H_2O$ {10}

FC15 = $[Ni^{II}_2(tppz)(H_2O)_6](squarate){*}5H_2O$ {57}

FC16 = $Bis[Zn_2(\mu\text{-}tppz)H_2OCl(\mu\text{-}ZnCl)(\mu\text{-}ZnCl_2)(\mu\text{-}ZnCl_3H_2O)]$ {74}

FC17 = $[ZnII(tppz)Cl_2]$ {10,40}

FC18 = $[Co^{II}(tppz)(ma)H_2O]{*}4H_2O$ {10}

FC19 = $[Fe^{II}(tppz)_2][(dipic)_2Fe^{III}]_3{*}H_3O{*}11H_2O$ {75}

FC20 = $[Ru^{II}(tppz)(4,4'\text{-}(CH_3)bpy)Cl](PF_6)$ {34}

FC21 = $[Ir^{III}(tppz)Cl_3]$ {36}

To simplify our investigations we defined some planes as it is shown in Fig. 56:

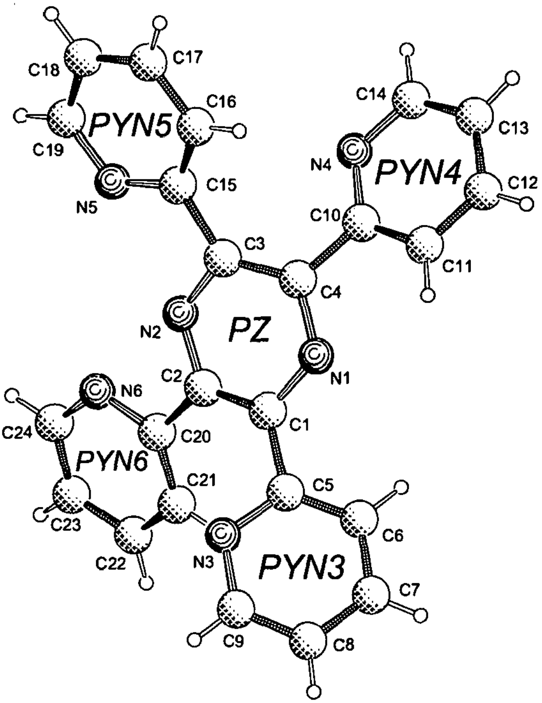


Fig. 56

Tab. 7.5

Bond (Å)	Complex (metal)							
	C12 (Co^{II})	**FC19** (Co^{II})	**C13** (Ni^{II})	**C14** (Ni^{II})	**C15** (Ni^{II})	**FC13** (Ni^{II})	**FC14** (Ni^{II})	**FC16** (Ni^{II})
M-NPY	2.018(7)	2.127(8)	1.923(12)	2.003(4)	2.038(4)	2.087(5)	2.088(6)	2.089(2)
M-NPZ	1.891(6)	2.092(8)	1.857(12)	1.978(4)	1.968(4)	2.026(5)	1.997(6)	2.009(2)
M-NPY	2.021(7)	2.135(8)	1.900(12)	2.024(4)	2.038(4)	2.094(6)	2.096(6)	2.089(2)
M-NPY	2.067(7)	--	1.934(12)	2.013(4)	--	2.059(6)	--	--
M-NPZ	1.904(6)	--	1.839(12)	1.982(4)	--	2.005(5)	--	--
M-NPY	2.075(7)	--	1.939(12)	2.022(4)	--	2.079(6)	--	--
M-NPY	--	--	1.950(12)	--	--	--	--	--
M-NPZ	--	--	1.843(11)	--	--	--	--	--
M-NPY	--	--	1.935(12)	--	--	--	--	--
P-NPY	--	--	2.096(13)	--	--	--	--	--

Tab. 7.6

Bond (Å)	**Complex** (metal)							
	FC10 (Cu^{II})	**FC11** (Cu^{II})	**FC12** (Cu^{II})	**FC17** (Zn^{II})	**FC18** (Zn^{II})	**FC20** (Fe^{II})	**FC21** (Ru^{II})	**FC22** (Ir^{III})
M-NPY	1.999(4)	2.020(4)	2.013(4)	2.094(4)	2.175(3)	1.94(1)	2.060(9)	2.032(5)
M-NPZ	1.962(3)	1.975(4)	1.943(4)	2.123(3)	2.1561(24)	1.87(1)	1.962(9)	1.917(8)
M-NPY	2.007(4)	2.025(4)	2.022(4)	2.116(4)	2.204(3)	1.96(1)	2.060(9)	2.031(5)
M-NPY	--	2.022(4)	--	2.117(4)	--	1.94(1)	--	--
M-NPZ	--	1.976(4)	--	2.145(3)	--	1.89(1)	--	--
M-NPY	--	2.023(4)	--	2.132(4)	--	1.96(1)	--	--

Angle (°)	***t*-tppz**	**TppzH$_2$**	**tppzH$_4$**	**C12** (Co^{II})	**FC19** (Co^{II})	**C13** (Ni^{II})			**C14** (Ni^{II})
PZN1-PZN2	0.020	0.000	0.000	10.55(0.34)	9.4(6)	2.85(2.39)	*PZN13-PZN14*	4.87(2.08)	9.26(0.12)
PZ-PYN3	59.396	16.601	38.440	21.43(0.34)	20.9(5)	81.35(0.69)	*PZ3-PYN15*	63.25(0.57	14.62(0.07)
PZ-PYN4	46.780	59.602	41.253	18.46(0.33)	18.9(4)	73.93(0.57)	*PZ3-PYN16*	59.72(0.52)	24.17(0.10)
PZ-PYN5	--	--	--	37.13(0.20)	--	5.39(0.92)	*PZ3-PYN17*	7.08(0.81)	22.92(0.14)
PZ-PYN6	--	--	--	35.07(0.20)	--	4.34(0.93)	*PZ3-PYN18*	7.06(0.84)	17.44(0.12)
PYN3-PYN4	60.456	59.960	60.494	4.04(0.50)	11.8(5)	73.04(0.95)	*PYN15-PYN16*	86.96(0.61)	13.07(0.14)
PYN4-PYN5	--	--	--	54.67(0.21)	32.3(4)	75.59(0.59)	*PYN16-PYN17*	63.00(0.56)	44.35(0.12)
PYN5-PYN6	--	--	--	24.20(0.29)	41.3(4)	1.22(0.94)	*PYN17-PYN18*	4.3(0.82)	9.83(.020)
PYN3-PYN6	--	--	--	54.78(0.23)	52.5(5)	85.10(0.72)	*PYN15-PYN18*	65.61(0.60)	31.29(0.11)
PZN7-PZN8	--	--	--	10.42(0.52)	--	5.50(3.07)	--	--	--
PZ2-PYN9	--	--	--	25.18(0.22)	--	51.52(0.65)	--	--	--
PZ2-PYN10	--	--	--	22.91(0.23)	--	67.76(0.54)	--	--	--
PZ2-PYN11	--	--	--	40.76(0.36)	--	10.84(0.86)	--	--	--
PZ2-PYN12	--	--	--	44.74(0.35)	--	5.65(0.85)	--	--	--
PYN9-PYN10	--	--	--	5.13(0.06)	--	86.77(0.61)	--	--	--
PYN10-PYN11	--	--	--	61.73(0.32)	--	70.38(0.54)	--	--	--
PYN11-PYN12	--	--	--	44.43(0.28)	--	7.47(0.91)(	--	--	--

Tab 7.8

Angle (°)	**FC13** (Ni^{II})	**FC14** (Ni^{II})	**FC15** (Ni^{II})	**FC16** (Ni^{II})	**FC17** (Zn^{II})	
PZN1-PZN2	11.4(3)	9.0(4)	10.9(1)	11.2(6)	11.568	11.568
PZ-PYN3	--	23.6(3)	24.1(3)	--	16.171	18.868
PZ-PYN4	--	17.5(3)	28.0(3)	--	26.622	22.793
PZ-PYN5	--	53.3(3)	22.6(3)	--	18.868	16.171
PZ-PYN6	--	30.8(3)	24.4(3)	--	22.793	26.622
PYN3-PYN4	9.9(4)	7.3(3)	9.8(4)	5.3(2)	41.099	41.566
PYN4-PYN5	46.6(2)	69.8(3)	--	54.4(1)	12.755	7.972
PYN5-PYN6	9.6(3)	51.5(3)	9.8(3)	5.3(2)	41.566	41.031
PYN3-PYN6	51.9(2)	50.7(3)	--	54.4(1)	7.972	12.755

The data in the second column for the product **FC17** corresponds to angles *PZN7-PZN8, PZ2-PYN9, PZ2-PYN10, PZ2-PYN11, PZ2-PYN12, PYN9-PYN10, PYN10-PYN11, PYN11-PYN12, PYN9-PYN12*, respectively.

Tab. 7.9

Angle (°)	**C15** (Ni^{II})	**FC10** (Cu^{II})	**FC11** (Cu^{II})	**FC12** (Cu^{II})	**FC18** (Zn^{II})	**FC20** (Fe^{II})		**FC21** (Ru^{II})	**FC22** (Ir^{III})
PZN1-PZN2	10.28(0.58)	0.000	9.9(4)	8.048	10.597	5.139	5.956	10.762	9.893
PZ-PYN3	39.48(0.17)	23.26	--	16.984	26.270	7.941	8.177	15.103	18.686
PZ-PYN4	25.65(0.30)	22.727	--	41.029	26.780	50.062	57.324	43.246	33.394
PZ-PYN5	21.65(0.30)	--	--	45.220	48.085	59.796	50.215	33.395	33.394
PZ-PYN6	23.10(0.28)	--	--	17.222	13.138	8.072	7.294	22.594	18.686
PYN3-PYN4	31.62(0.15)	34.335	6.6(2)	1.776	13.445	7.120	1.109	11.376	2.033
PYN4-PYN5	45.69(0.22)	--	47.2(2)	48.074	50.761	57.580	63.851	58.308	51.087
PYN5-PYN6	5.69(0.36)	--	12.7(2)	49.799	37.110	74.271	73.264	35.465	27.739
PYN3-PYN6	62.24(0.17)	--	32.9(2)	62.409	62.466	67.371	54.966	53.407	51.087

The data in the second column for the product **FC20** corresponds to angles *PZN7-PZN8, PZ2-PYN9, PZ2-PYN10, PZ2-PYN11, PZ2-PYN12, PYN9-PYN10, PYN10-PYN11, PYN11-PYN12, PYN9-PYN12*, respectively.

Tab. 7.10

Angle (°)	Mononuclear complexes						
	C12 (Co^{II})	C13 (Ni^{II})			**C15** (Ni^{II})	**FC12** (Cu^{II})	**FC14** (Ni^{II})
PZN1-PZN2	10.55(0.34)	2.85(2.39)	*PZN13-PZN14*	4.87(2.08)	10.28(0.58)	8.048	9.0(4)
PZ-PYN3	21.43(0.34)	81.35(0.69)	*PZ3-PYN15*	63.25(0.57	39.48(0.17)	16.984	23.6(3)
PZ-PYN4	18.46(0.33)	73.93(0.57)	*PZ3-PYN16*	59.72(0.52)	25.65(0.30)	41.029	17.5(3)
PZ-PYN5	37.13(0.20)	5.39(0.92)	*PZ3-PYN17*	7.08(0.81)	21.65(0.30)	45.220	53.3(3)
PZ-PYN6	35.07(0.20)	4.34(0.93)	*PZ3-PYN18*	7.06(0.84)	23.10(0.28)	17.222	30.8(3)
PYN3-PYN4	4.04(0.50)	73.04(0.95)	*PYN15-PYN16*	86.96(0.61)	31.62(0.15)	1.776	7.3(3)
PYN4-PYN5	54.67(0.21)	75.59(0.59)	*PYN16-PYN17*	63.00(0.56)	45.69(0.22)	48.074	69.8(3)
PYN5-PYN6	24.20(0.29)	1.22(0.94)	*PYN17-PYN18*	4.3(0.82)	5.69(0.36)	49.799	51.5(3)
PYN3-PYN6	54.78(0.23)	85.10(0.72)	*PYN15-PYN18*	65.61(0.60)	62.24(0.17)	62.409	50.7(3)
PZN7-PZN8	10.42(0.52)	5.50(3.07)	--	--	--	--	--
PZ2-PYN9	25.18(0.22)	51.52(0.65)	--	--	--	--	--
PZ2-PYN10	22.91(0.23)	67.76(0.54)	--	--	--	--	--
PZ2-PYN11	40.76(0.36)	10.84(0.86)	--	--	--	--	--
PZ2-PYN12	44.74(0.35)	5.65(0.85)	--	--	--	--	--
PYN9-PYN10	5.13(0.06)	86.77(0.61)	--	--	--	--	--
PYN10-PYN11	61.73(0.32)	70.38(0.54)	--	--	--	--	--
PYN11-PYN12	44.43(0.28)	7.47(0.91)(	--	--	--	--	--

Tab. 7.11

Angle (°)	Mononuclear complexes					
	FC18 (Zn^{II})	**FC19** (Co^{II})	**FC20** (Fe^{II})		**FC21** (Ru^{II})	**FC22** (Ir^{III})
PZN1-PZN2	10.597	9.4(6)	5.139	5.956	10.762	9.893
PZ-PYN3	26.270	20.9(5)	7.941	8.177	15.103	18.686
PZ-PYN4	26.780	18.9(4)	50.062	57.324	43.246	33.394
PZ-PYN5	48.085	--	59.796	50.215	33.395	33.394
PZ-PYN6	13.138	--	8.072	7.294	22.594	18.686
PYN3-PYN4	13.445	11.8(5)	7.120	1.109	11.376	2.033
PYN4-PYN5	50.761	32.3(4)	57.580	63.851	58.308	51.087
PYN5-PYN6	37.110	41.3(4)	74.271	73.264	35.465	27.739
PYN3-PYN6	62.466	52.5(5)	67.371	54.966	53.407	51.087

The data in the second column for the product **FC20** corresponds to angles *PZN7-PZN8, PZ2-PYN9, PZ2-PYN10, PZ2-PYN11, PZ2-PYN12, PYN9-PYN10, PYN10-PYN11, PYN11-PYN12, PYN9-PYN12*, respectively.

Tab. 7.12

Angle (°)	Binuclear complexes						
	C14 (Ni^{II})	**FC10** (Cu^{II})	**FC11** (Cu^{II})	**FC13** (Ni^{II})	**FC16** (Ni^{II})	**FC17** (Zn^{II})	
PZN1-PZN2	9.26(0.12)	0.000	9.9(4)	11.4(3)	11.2(6)	11.568	11.568
PZ-PYN3	14.62(0.07)	23.26	--	--	--	16.171	18.868
PZ-PYN4	24.17(0.10)	22.727	--	--	--	26.622	22.793
PZ-PYN5	22.92(0.14)	--	--	--	--	18.868	16.171
PZ-PYN6	17.44(0.12)	--	--	--	--	22.793	26.622
PYN3-PYN4	13.07(0.14)	34.335	6.6(2)	9.9(4)	5.3(2)	41.099	41.566
PYN4-PYN5	44.35(0.12)	--	47.2(2)	46.6(2)	54.4(1)	12.755	7.972
PYN5-PYN6	9.83(.020)	--	12.7(2)	9.6(3)	5.3(2)	41.566	41.031
PYN3-PYN6	31.29(0.11)	--	32.9(2)	51.9(2)	54.4(1)	7.972	12.755

Tab. 7.13

Bond (Å)	***Mononuclear complexes*** (metal)				
	C12 (Co^{II})	**C13** (Ni^{II})	**C15** (Ni^{II})	**FC12** (Cu^{II})	**FC14** (Ni^{II})
M-NPY	2.018(7)	1.923(12)	2.038(4)	2.013(4)	2.088(6)
M-NPZ	1.891(6)	1.857(12)	1.968(4)	1.943(4)	1.997(6)
M-NPY	2.021(7)	1.900(12)	2.038(4)	2.022(4)	2.096(6)
M-NPY	2.067(7)	1.934(12)	--	--	--
M-NPZ	1.904(6)	1.839(12)	--	--	--
M-NPY	2.075(7)	1.939(12)	--	--	--
M-NPY	--	1.950(12)	--	--	--
M-NPZ	--	1.843(11)	--	--	--
M-NPY	--	1.935(12)	--	--	--
P-NPY	--	2.096(13)	--	--	--

Tab. 7.14

Bond (Å)	**Mononuclear complexes** (metal)				
	FC18 (Zn^{II})	**FC19** (Co^{II})	**FC20** (Fe^{II})	**FC21** (Ru^{II})	**FC22** (Ir^{III})
M-NPY	2.175(3)	2.127(8)	1.94(1)	2.060(9)	2.032(5)
M-NPZ	2.1561(24)	2.092(8)	1.87(1)	1.962(9)	1.917(8)
M-NPY	2.204(3)	2.135(8)	1.96(1)	2.060(9)	2.031(5)
M-NPY	--	--	1.94(1)	--	--
M-NPZ	--	--	1.89(1)	--	--
M-NPY	--	--	1.96(1)	--	--

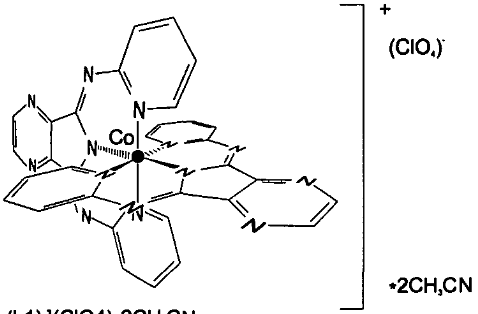
Tab. 7.15

Bond (Å)	**Binuclear complexes** (metal)					
	C14 (Ni^{II})	**FC10** (Cu^{II})	**FC11** (Cu^{II})	**FC13** (Ni^{II})	**FC16** (Ni^{II})	**FC17** (Zn^{II})
M-NPY	2.003(4)	1.999(4)	2.020(4)	2.087(5)	2.089(2)	2.094(4)
M-NPZ	1.978(4)	1.962(3)	1.975(4)	2.026(5)	2.009(2)	2.123(3)
M-NPY	2.024(4)	2.007(4)	2.025(4)	2.094(6)	2.089(2)	2.116(4)
M-NPY	2.013(4)	--	2.022(4)	2.059(6)	--	2.117(4)
M-NPZ	1.982(4)	--	1.976(4)	2.005(5)	--	2.145(3)
M-NPY	2.022(4)	--	2.023(4)	2.079(6)	--	2.132(4)

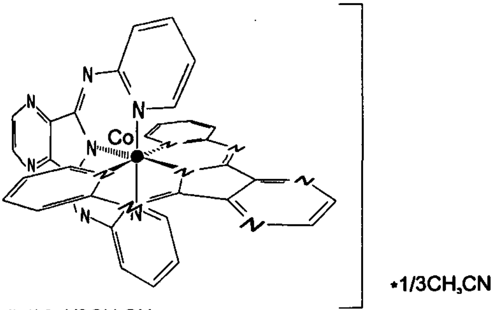
For complexes of **tppz** the distances between the metal atom and the coordinated nitrogen atom of the pyrazine ring are significantly shorter in the complexes **C12** (mononuclear bis-tridentate) and **C13** (mononuclear mono-tridentate) than in the rest of the complexes of the **FC** series. They are longer (although shorter than in the corresponding complexes given in the tables and not obtained in the present work – **FC** series) for the two other complexes **C14** (binuclear bis-tridentate) and **C15** (mononuclear mono-tridentate). These distances are also shorter than the metal-N(pyridine) distances and in complexes with the same metal atom they are also shorter in our complexes than in **FC** complexes.

The deformation angle of the pyrazine ring lies between 0° for the pure ligand 10.55(0.34)° for **C12** and 10.762 for **FC21**. The inclination angle depends on the type of coordination mode present in the complex. Generally there is no significant difference between the series of complexes obtained in this work (series **C**) and that accessible in the literature (series **FC**). Larger distortion angles were noted for the mono-tridentate complexes of **tppz** than for the bis-tridentate complexes. Also the dihedral angles of the pyridine rings, not coordinated with the metal in the mono-tridentate complexes, with respect to the pyrazine ring, are generally larger than the same angle for the pyridine rings coordinated to the metal.

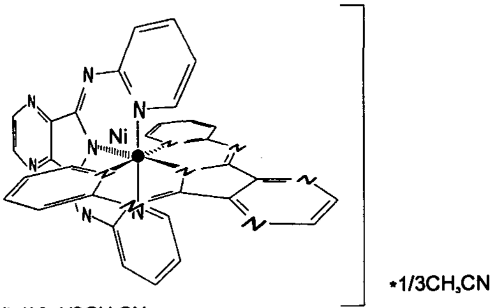
8. OVERVIEW OF SYNTHESIZED PRODUCTS



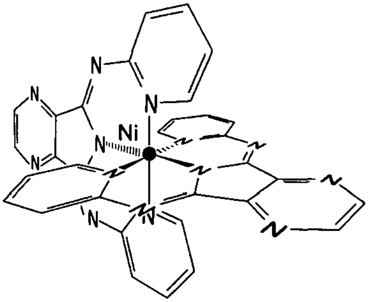
C1 = [Co(L1)$_2$](ClO4)•2CH$_3$CN



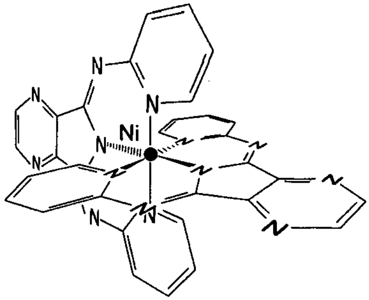
C2 = [Co(L1)$_2$]•1/3CH$_3$CN



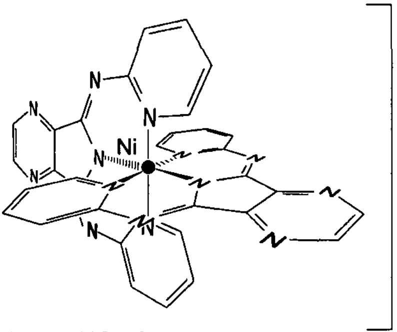
C4 = [Ni(L1)$_2$]•1/3CH$_3$CN



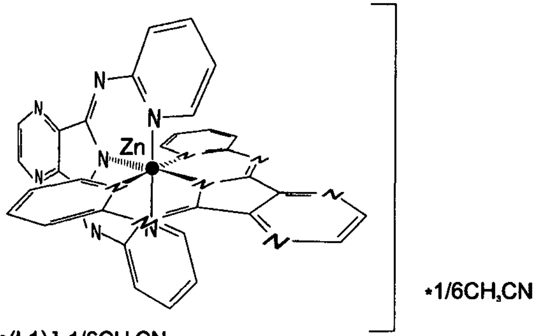
C5 = $[Ni(L1)_2]$



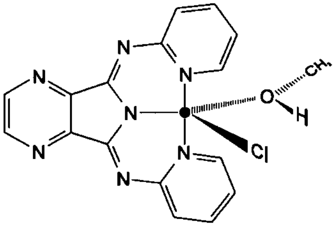
C6 = $[Ni(L1)_2]$



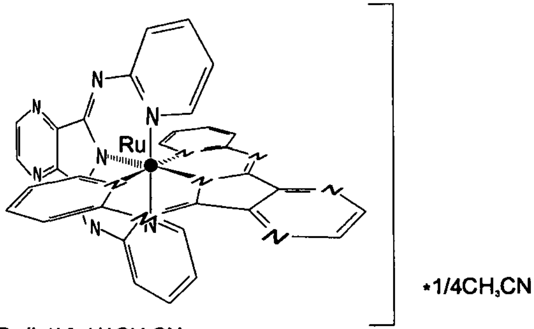
C7 = $[Cu(L1)_2]*1\frac{1}{2}CH_3OH$



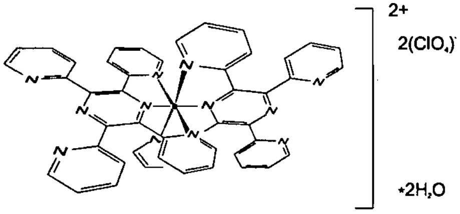
C9 = [Zn(L1)$_2$]•1/6CH$_3$CN



C10 = [ZnCl(L1)(CH$_3$OH)]

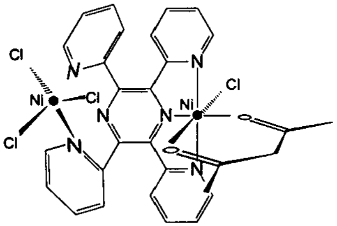


C11 = [Ru(L1)$_2$]•1/4CH$_3$CN

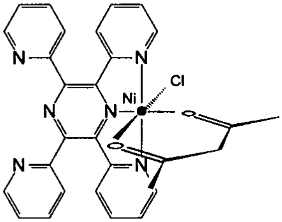


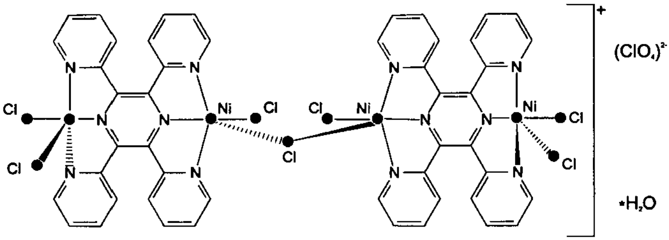
$C12 = [Co(tppz)_2](ClO_4)_2 \cdot 2H_2O$

Complex of Ni3 and Ni4

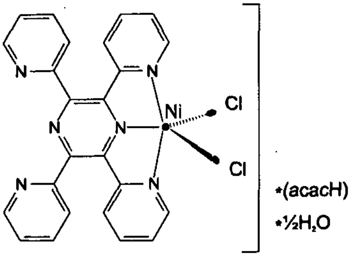


Complex of Ni1 and Ni2

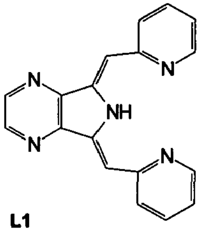




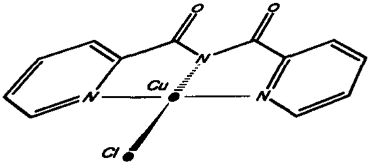
$C14 = [(NiCl_2(tppz)NiCl)_2Cl](ClO_4) \cdot H_2O$



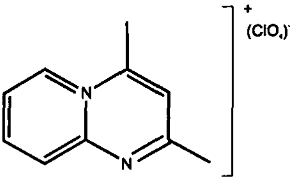
C15 = $[NiCl_2(tppz)]\bullet(acacH)\bullet½H_2O$



L1



U1



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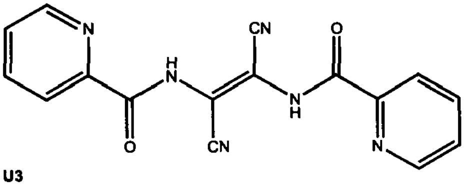
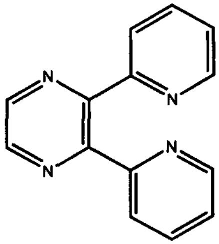


U3



U4

9. ANALYTICAL METHODS

Infrared spectroscopy (IR)

IR spectra were recorded on a PERKIN-ELMER FT-IR 1720 X spectrometer. Obtained powders were measured in the form of KBr pellets. The absorption bands are given in cm^{-1}, the spectra were taken in range between 4000 and $400cm^{-1}$. The abbreviations used for the intensities are: vs (very strong), s (strong), m (middle), w (weak), vw (very weak), br (bright), sh (shoulder).

Elemental analysis

The elemental CHN analysis were done by the laboratory for microanalysis of CIBA-GEIGY in Marly (CH-1723 Marly, Switzerland).

Mass spectroscopy (MS)

The spectra were recorded on HITACHI PERKIN-ELMER Nermag RC 30-10.

X-ray analysis

The measurements of the intensity data were performed on a STOE AED2 4-circle diffractometer with Mo-Kα radiation (graphite monochromated radiation).The structures were solved using direct methods or Patterson synthesis with the SHELXS-86 software. The rest of the calculations were performed using the SHLEXL-93 software The majority of the hydrogen atoms were included in calculated positions, the rest was located from difference maps. All the non-hydrogen atoms were refined anisotropically using weighted full-matrix least squares, on F^2. The plots of molecular structures were done using the following software. PLUTON, PLATON, SCHAKAL-92.

10. EXPERIMENTAL

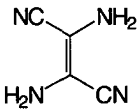
All the syntheses were performed using commercial products *purum* or *puriss* available from FLUKA, ALDRICH, or MERCK. Some of the products were purified before use (the process of purification is described either here or in the description of the synthesis): methanol was dried with $CaSO_4$, distilled over sodium, degasified and stored over Linde type 4A molecular sieve under nitrogen. Ethanol was refluxed for 4 hours with CaO, distilled over sodium, degasified and stored over Linde type 4A molecular sieve under nitrogen. THF was purified before using in the synthesis of the complexes: dried with CaO, distilled over sodium, degasified and stored over CaO under nitrogen; acetonitrile was dried with anhydrous $CaSO_4$, stirred and shaken with Linde A4 molecular sieve, distilled over P_2O_5 and stored over Linde A4 molecular sieve under nitrogen.

All the syntheses (if not indicated) were performed under nitrogen in a flask protected against moisture, light, and out-fitted with a reflux condenser.

INORGANIC COMPOUNDS AND LIGANDS

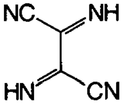
*Purification of diaminomaleonitrile (*DAMN*)*

The commercially available product is a brown powder or black crystalline solid. It has been found during our work that it is necessary to use a purer product for the reactions. Hence **DAMN** was purified with activated carbon from an ethanolic solution giving a pale orange product which was used for further reactions.



*Synthesis of the diiminosuccinonitrile (*DISN*)*

Charge: 0.03mol

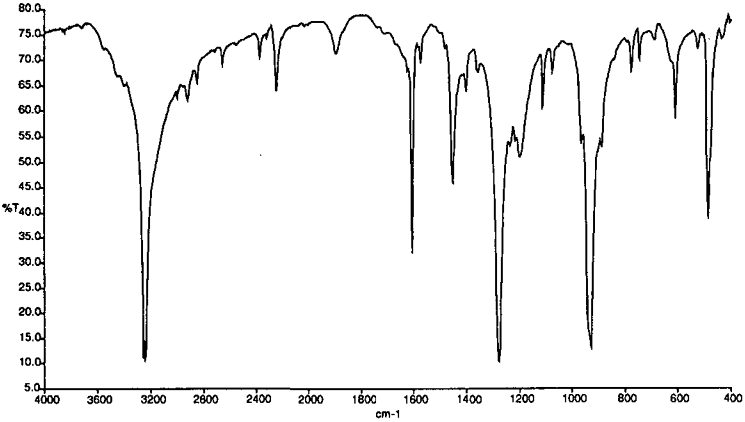


To a solution of 3.24g (0.03mol) of **DAMN** in 60ml of dry acetonitrile was added a suspension of 6.78g (0.03mol) of dichlorodicyanobenzoquinone in 15ml of acetonitrile and stirred for 2 hours at room temperature. Afterwards the precipitate that formed was filtered out and washed many times with acetonitrile. The filtrate was then evaporated under reduced pressure, the solid product was filtered off and washed a few times with dry acetonitrile. It was then dried in a vacuum desiccator over silica and under nitrogen to gave a beige product. The **DISN** obtained was used immediately for further reactions (storing for a longer time in air or light causes decomposition!)

Yield: 1.94g (65.92%) $C_4H_2N_4$ (98.1039g/mol)

mp.: 164.2-165°C

IR: (KBr pellet) cm^{-1}

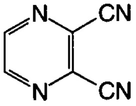


PEAKS:

3852, 3255, 3242, 3004, 2925, 2854, 2661, 2375, 2323, 2245, 1897, 1607, 1575, 1483, 1453, 1402, 1357, 1277, 1235, 1216, 1197, 1111, 1075, 965, 929, 888, 776, 746, 690, 610, 527, 487, 437

Synthesis of 2,3-dicyanopyrazine (2,3-Pyrazinedicarbonitrile, **DCPZ***)*

Charge: 0.025mol



12.5ml of deionized water in a round bottomed flask outfitted with a reflux condenser, was acidified with H_2SO_4 (tech.) to pH=1, then with vigorous stirring 2.7g (0.025mol) of the 2,3-diaminomaleonitrile were added; after it had dissolved (temp=50°C) a suspension of

5.8g (0.03mol) of a 30% aqueous solution of glyoxal was slowly added dropwise; an orange precipitate was obtained and the suspension was warmed up to 97°C and stirred at this temperature for 1.3hour. The suspension was then cooled to room temperature, the orange product was filtered off and washed several times with small amounts of deionized water. Immediately after the product was purified by dissolving in a mixture of diluted oxalic acid (~2-3% aqueous solution) and ethanol, heating it almost to the boiling point, with the addition of active carbon; the mixture was then boiled for 10min and filtered immediately. The pale yellow solution was left overnight in the refrigerator and the next day a crystalline white product was filtered off and washed several times with ethanol. The product was dried under vacuum in a desiccator over silica.

Yield: 2.8g (86%). $C_6H_2N_4$ (130.1087g/mol)

mp.: 131.6-131.8°C

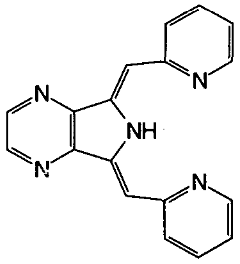
IR: (KBr pellet) cm^{-1}

PEAKS:

3425, 3105, 3075, 3056, 2929, 2818, 2708, 2359, 2296, 2245, 2103, 1977, 1862, 1748, 1645, 1564, 1551, 1525, 1413, 1387, 1270, 1224, 1178, 1143, 1121, 1082, 1053, 990, 972, 876, 865, 695, 613, 574, 537, 470, 446

Synthesis of the ligand **L1***:*

(5,7-bis(2-aminopyridine)-5H-6,7-dihydropyrrolo[3.4-b]pyrazine



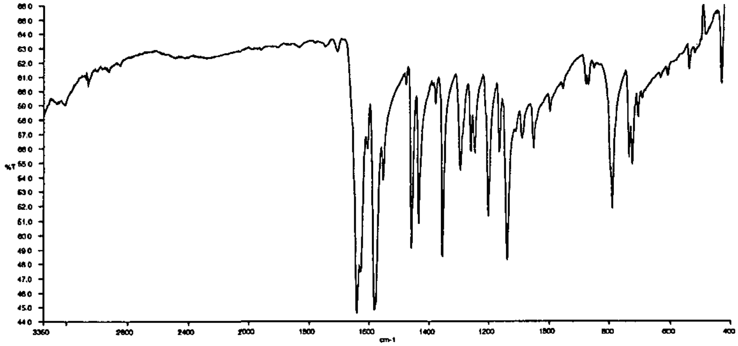
A round bottomed flask was charged with 0.65g (5mmol) of **DCPZ**, 0.06g (0.054mmol) of anhydrous $CaCl_2$ and 0.99g (10.5mmol) of 2-aminopyridine and 25ml of dry 1-buthanol. The mixture was heated for 48 hours at 60°C to give a green product. Afterwards the resulting solution was evaporated to dryness under reduced pressure, the residue was dissolved in ~40ml of deionized water. The product was extracted several times with chloroform (4*100ml), then the solution was again evaporated to dryness under reduced pressure and dried in a vacuum desiccator over silica.

Yield: 1.35g (89.6%) The greenish-brown product was chromatographed over silica (Kieselgel 60 particle size 0.063-0.200, 70-230 Mesh ASTM, MERCK) with chloroform as eluent; the yellow fraction was collected. After evaporated to dryness under reduced pressure the yellow product obtained was dried in a vacuum desiccator over silica.

Note: It was also possible to omit the extraction with chloroform but there is more work with the chromatographic column.

Yield:	0.5g (37%)		$C_{16}H_{11}N_7$ (301.3102g/mol)
calc.	C: 63.78%	H: 3.68%	N: 32.54%
found	C: 63.69%	H: 3.89%	N: 32.40%
mp.:	274.3-274.7°C		

IR: (KBr pellet) cm^{-1}



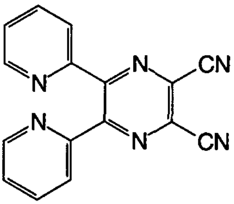
PEAKS:

3443, 3057, 1706, 1641, 1607, 1581, 1554, 1477, 1458, 1435, 1378, 1354, 1296, 1261, 1249, 1203, 1166, 1139, 1091, 1053, 998, 870, 790, 736, 725, 705, 538, 484, 431, 413

Note: Despite many attempts it was not possible to recrystallize the yellow product. The only crystals of the ligand were obtained from reactions of **L1** with metal salts: for e.g. $Cu(BF_4)_2$.

Synthesis of 2,3-bis(2-pyridyl)-5,6-dicyanopyrazine

Charge: 0.025mol

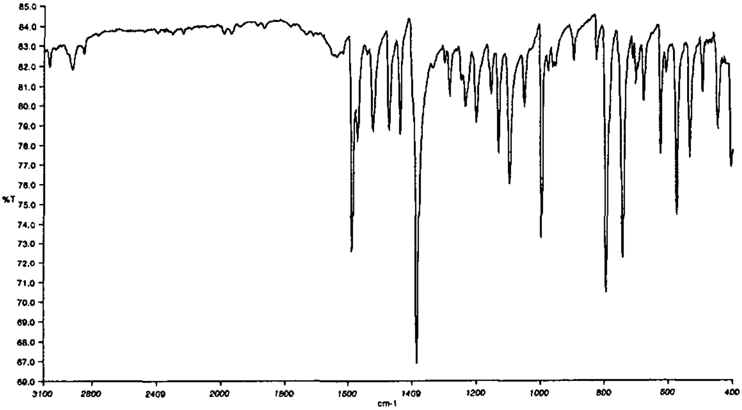


The synthesis was performed in almost the same way that was described in the thesis of Yi Wang, with some modifications. In a round bottomed flask, outfitted with a reflux condenser, 9.3663g (0.03mol) of 2,2'-pyridyl was dissolved in 15ml of dry ethanol and a solution of 2.7026g (0.025mol) of dimaleonitrile in 15ml of dry ethanol was added at 60°C with stirring. The mixture was refluxed for 3hours. After stopping the reaction, the mixture was filtered immediately (glass filter) to remove the orange-brown impurities. The filtrate was cooled down (no precipitate obtained), the solvent was then evaporated to dryness under reduced pressure to gave a brown product. Recrystallization from ethanol gave colourless crystals of 2,3-bis(2-pyridyl)-5,6-dicyanopyrazine. The other analytical results are the same as given previously:

Yield: ~0.8g (11%) $C_{16}H_8N_6$ (284.2797g/mol)

mp.: 180-181°C

IR: (KBr pellet) cm^{-1}

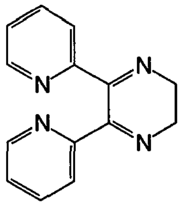


PEAKS: 3425, 3105, 3075, 3056, 2929, 2818, 2708, 2359, 2296, 2245, 2103, 1977, 1862, 1748, 1645, 1564, 1551, 1525, 1413, 1387, 1271, 1224, 1178, 1143, 1121, 1082, 1053, 990, 972, 876, 865, 695, 613, 574, 537, 470, 446

Note: A second product was also obtained: these orange-brown impurities were recrystallized from a mixture of methanol/acetonitrile/acetylacetone = 3/3/1 and gave a small amount of yellow needless - the properties are described under *Unexpected Results.*

Synthesis of 2,3-bis(2-pyridyl)-5,6-dihydropyrazine

Charge: 0.02mol

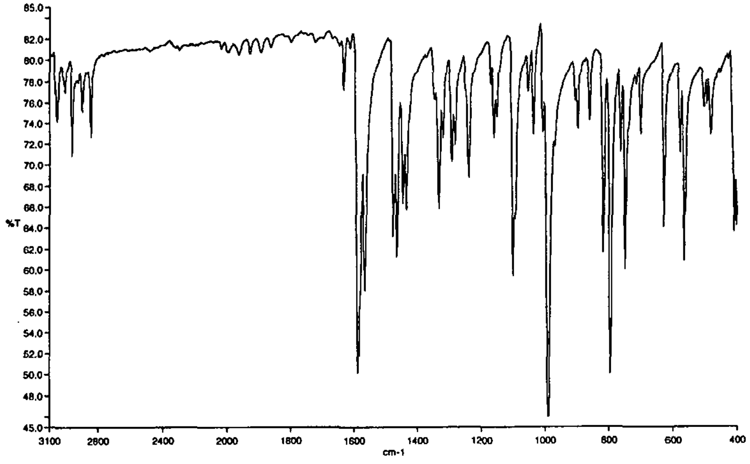


A round bottomed flask, outfitted with a reflux condenser and dropping funnel, was charged with a solution of 4.25g (0.02mol) of 2,2'-pyridyl in 20ml of dry ethanol, then a solution of 1.2g (0.021mol) of ethylenediamine was slowly added dropwise. The mixture was then refluxed for 2hours. After cooling the mixture was filtered to give a brown product which was washed many times with ethanol - giving a beige product. On recrystallization from ethanol colourless block-like crystals were obtained

Yield: 2.8g (59%) $C_{14}H_{12}N_4$ (236.2761g/mol)

mp.: 188°C

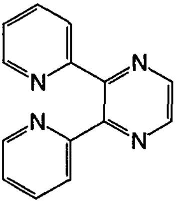
IR: (KBr pellet) cm^{-1}



PEAKS:

3425, 3053, 3003, 2960, 2896, 2843, 2299, 1963, 1928, 1894, 1862, 1722, 1632, 1613, 1588, 1566, 1476, 1464, 1446, 1435, 1332, 1319, 1291, 1281, 1238, 1169, 1159, 1150, 1099, 1051, 1035, 1006, 989, 903, 895, 859, 816, 794, 761, 747, 698, 626, 577, 564, 501, 492, 481, 407

Synthesis of 2,3-bis(2-pyridyl)pyrazine



Charge: 0.0085mol

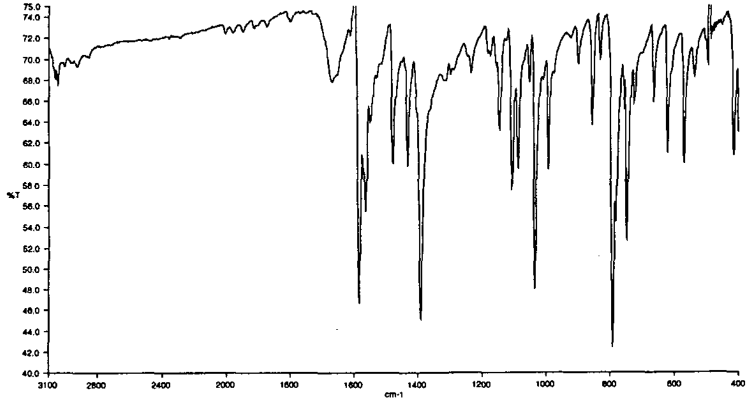
The synthesis was performed in two different ways: the first was the same as described by H.A.Goodwin and F.Lions but using 2g (0.0085mol) of the 2,3-bis(2'-pyridil)-5,6-dihydropyrazine in 22ml of mesitylene to which was added 0.25g of palladium/charcoal catalyst in 4ml of mesitylene. The mixture was refluxed for 24hours and left at room temperature for 2days. After it was once again refluxed for 2hours and then filtered when hot. After cooling to room temperature a brown precipitate appeared. The solid was filtered off, dried in a vacuum desiccator over silica and then recrystallized from ethanol.

Yield: 2.1g (product not purified) $C_{14}H_{10}N_4$ (234.2602/mol)

0.6g (30%) pale yellow crystals

mp.: 165°C

IR: (KBr pellet) cm^{-1}

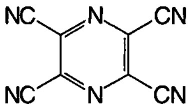


PEAKS:

3434, 3063, 3047, 2925, 2007, 1801, 1672, 1585, 1564, 1550, 1480, 1433, 1392, 1300, 1235, 1174, 1145, 1105, 1087, 1052, 1034, 992, 898, 854, 830, 790, 780, 747, 725, 665, 621, 569, 539, 496, 486, 415

Note: A second method of obtaining 2,3-bis(2'-pyridyl)pyrazine is described under *Unexpected Results*, and it gave exactly the same results as described above.

*Synthesis of 2,3,5,6-tetracyanopyrazine (***TCPZ***)*



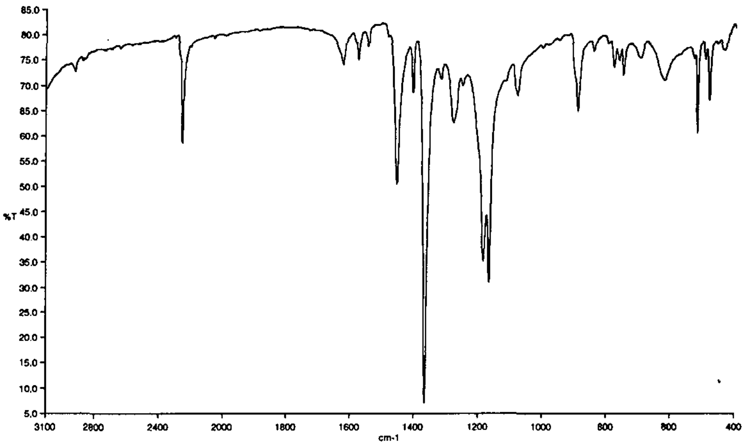
Charge: 0.005mol

The synthesis was performed in a similar way to that described by R.W.Bergland, D.R.Hatter, D.S.Donald, A.Cairncross, W.A.Sheppard, but some modifications were introduced: to 10ml of trifluoroacetic acid in a round bottomed flask, protected against moisture, outfitted with a reflux condenser and under nitrogen, a powdered mixture of 0.5031g (0.005mol) of **DISN** with 0.05406g (0.005mol) of **DAMN** was added in small portions over a period of 30mins (the temperature of the mixture was unchanged during the reaction). The mixture was then heated to 70°C and stirred at this temperature for 2.5hours (during stirring 4ml of the trifluoroacetic acid was added twice). Afterwards the mixture was cooled to room temperature, filtered, and the dark brown product obtained was washed many times with small amounts of the trifluoroacetic acid and later with deionized water to a give pale grey product.

Yield: 0.3885g (43%) C_8N_6 (180.1282g/mol)

mp.: 276-277°C

IR: (KBr pellet) cm^{-1}

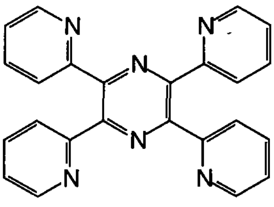


PEAKS:

3231, 2920, 2872, 2254, 1623, 1575, 1545, 1453, 1403, 1366, 1315, 1276, 1248, 1183, 1165, 1076, 887, 839, 776, 760, 746, 693, 618, 516, 492, 479, 431

*Synthesis of the 2,3,5,6-tetra(α -pyridyl)pyrazine (**tppz**)*

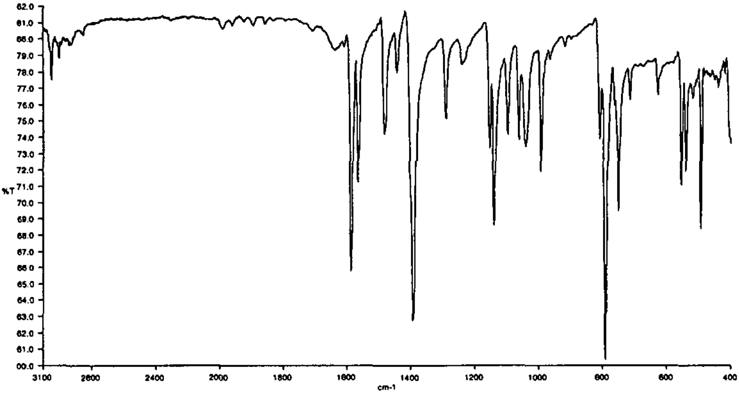
Charge: 0.047mol



In a round bottomed flask outfitted with a reflux condenser were mixed 10g (0.047mol) of α-pyridoin and 45g (0.584mol) of ammonium acetate which was then slowly heated to 160°C on an oil bath, and kept for 4hours at this temperature: an orange molten mixture was obtained. After cooling a yellow crystalline product was obtained, filtered off, washed many times with small amounts of water and ethanol, then dried in a vacuum desiccator over silica. The product was crystallized by the method published by H.A.Goodwin and F.Lions. The analytical data reported there are in agreement with obtained in this work.

Yield: 6.5g (36%) $C_{24}H_{16}N_6$ (388.4312g/mol) mp.: 285°C

IR: (KBr pellet) cm^{-1}



PEAKS: 3437, 3049, 3002, 1638, 1588, 1566, 1484, 1443, 1393, 1290, 1240, 1153, 1139, 1097, 1062, 1041, 992, 808, 790, 749, 714, 627, 553, 540, 518, 492, 438

SYNTHESIS OF THE COMPLEXES OF THE LIGAND **L1***: (5,7-BIS(2-AMINOPYRIDINE)-5H-6,7-DIHYDROPYRROLO[3.4-B]PYRAZINE:*

Complexes of Co^{II} and Co^{III}

Synthesis of the complex **C1** *(Co^{III})*

Charge: 0.0001mol

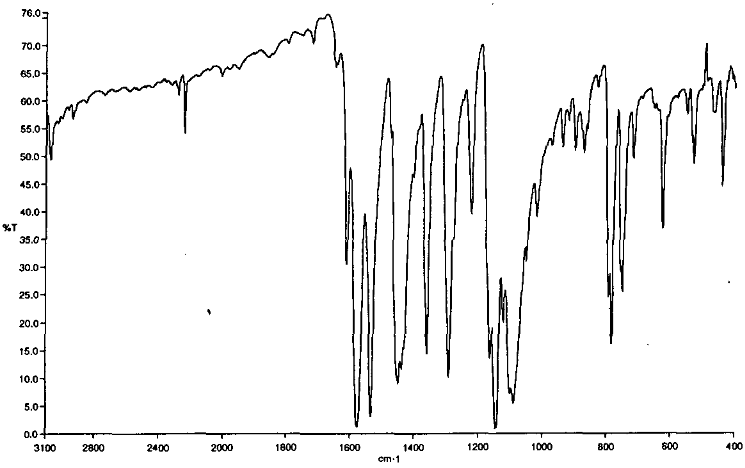
In a round bottomed flask, were mixed: 0.0646g (0.00021mol) of the ligand **L1** in 7ml of dry methanol and 0.1ml of triethylamine. Then a solution of 0.0366g (0.0001mol) of the metal salt: $Co(ClO_4)_2*6H_2O$ in 3ml of dry methanol was added. The mixture was stirred at room temperature for 48hours. The product obtained was filtered off and the filtrate left for crystallization by slow evaporation of the solvent but it gave no results. The main product, a black powder was dried in a vacuum desiccator over silica.

Yield: ~0.03g (36%) $[(C_{16}H_{10}N_7)_2Co]ClO_4\ 2(CH_3CN)$ (840.0931g/mol)

The black solid was used for recrystallization from a mixture of solvents: acetonitrile/methanol = 1/1, which gave a small amount of black block-like crystals.

calc.	C: 51.47%	H: 3.12%	N: 26.65%
found	C: 50.68%	H: 3.11%	N 26.18%:
mp.:	over 350°C		

IR: (KBr pellet) cm^{-1}



PEAKS:

3437, 3171, 3113, 3070, 2938, 2739, 2588, 2322, 2282, 2244, 2012, 1952, 1858, 1798, 1720, 1646, 1611, 1579, 1537, 1474, 1450, 1439, 1402, 1359, 1292, 1221, 1163, 1144, 1121, 1101, 1089, 1048, 1016, 970, 936, 917, 897, 868, 826, 792, 782, 754, 748, 715, 650, 623, 548, 533, 526, 486, 462, 437

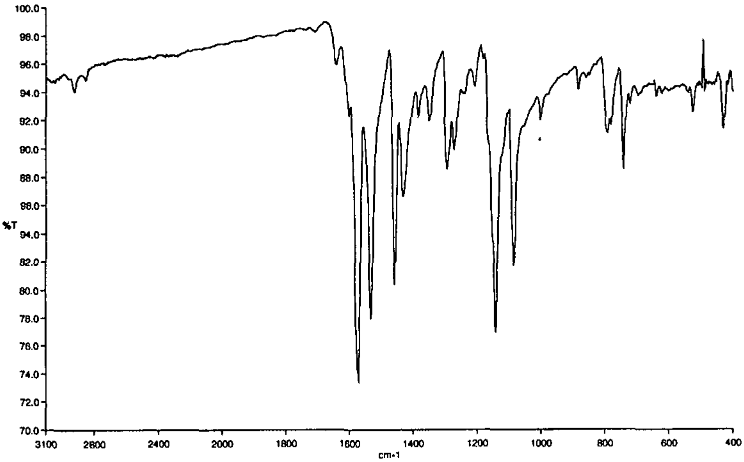
Synthesis of the complex **C2** *(Co^{II})*

Charge: 0.0001mol

A round bottomed flask was charged with 0.0603g (0.0002mol) of ligand **L1** in 18ml of dry methanol and 0.1ml of triethylamine. 0.0341g (0.0001mol) of the metal salt: $Co(BF_4)_2*xH_2O$ in 15 ml of dry methanol was slowly added dropwise. The resulting mixture was stirred at room temperature, under nitrogen for 4hours. A change of the colour from yellow to dark brown was noticed. After finishing the reaction the solution was filtered and the filtrate left to evaporate slowly, yielding blue-black crystals. The X-ray analysis and structure solution showed that the product obtained is different from complex **C1**.

Yield:	~0.008g (12%) crystals			$(C_{16}H_{10}N_7)_2Co$ (659.5378g/mol)
calc.	C: 58.28%	H: 3.06%	N: 29.73%	
found	C: 58.41%	H: 3.30%	N: 29.80%	
mp.:	over 350°C			

IR: (KBr pellet) cm^{-1}



PEAKS:

3434, 2924, 1643, 1573, 1533, 1459, 1433, 1385, 1349, 1294, 1271, 1207, 1141, 1085, 1001, 883, 791, 741, 525, 487, 429

Synthesis of the complex **C3** *(Co^{II})*

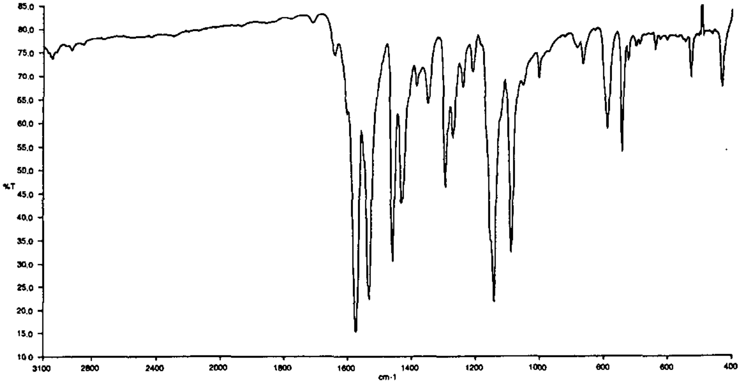
Charge: 0.0001mol

A round bottomed flask was charged with 0.0603g (0.0002mol) of the ligand **L1** in 18ml of dry methanol and 0.1ml of triethylamine and a small amount of pyrex glass powder. 0.0341g (0.0001mol) of the metal salt: $Co(BF_4)_2{*}xH_2O$ in 15ml of dry methanol was added dropwise. The mixture was stirred at room temperature, under nitrogen for 4hours. A change of the colour from yellow to dark brown was noticed. After finishing the reaction the mixture (almost a solution) was filtered and the filtrate left to evaporate slowly yielding blue-black crystals. The X-ray analysis and structure solution showed that product obtained was identical with complex **C1**.

Yield: ~0.005g (7%) crystals $[(C_{16}H_{10}N_7)_2Co]ClO_4$ (757.9881g/mol)

mp.: over 350°C

IR: (KBr pellet) cm^{-1}



PEAKS:

3435, 3047, 2925, 1711, 1642, 1574, 1535, 1459, 1432, 1386, 1349, 1295, 1271, 1240, 1209, 1142, 1088, 1051, 1001, 885, 865, 787, 742, 723, 699, 687, 639, 602, 545, 527, 488, 461, 431

Complexes of Ni^{II}

Synthesis of the complex **C4**

Charge: 0.0001mol

In a round bottomed flask light proved, under nitrogen it was mixed 0.0646g (0.00021mol) of the ligand **L1** in 7ml of dry methanol and 0.1ml of triethylamine. Then a solution of 0.0366g (0.0001mol) of the metal salt: $Ni(ClO_4)_2*6H_2O$ in 3ml of dry methanol, was added under nitrogen. The mixture was stirred at room temperature and light protected for 4 days. The product obtained was filtered off, and the filtrate left for crystallization by slow evaporation of the solvent. However, it gave no results. The main product: a metallic rust coloured powder was dried in a vacuum desiccator over silica.

Yield: ~0.0303g (46%) $(C_{16}H_{10}N_7)_2Ni$ (659.2946g/mol)

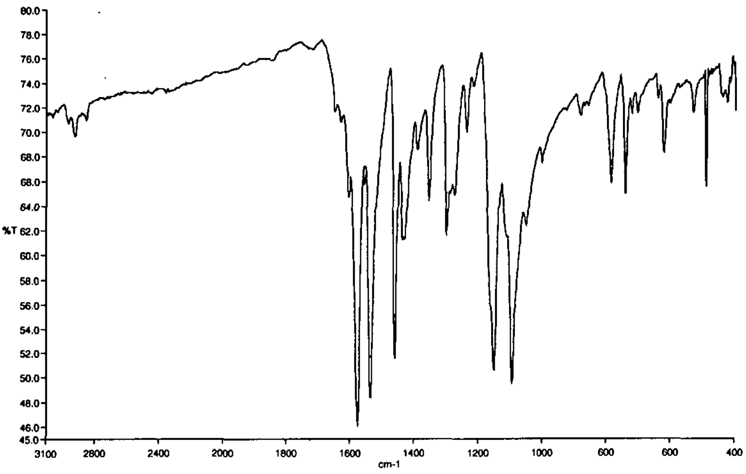
This solid was used for recrystallization from a mixture of solvents: acetonitrile/methanol = 1/1, which gave a small amount of black crystals in the form of blocks. Exactly the same reaction was repeated, stirring now for only 4hours, then the solution was filtered and the deep yellow (almost black) filtrate was left for crystallization. This resulted in the formation of black block-like crystals.

Yield: 0.024g (36%) crystals

calc.	C: 58.30%	H: 3.15%	N: 29.83%
found	C: 58.09%	H: 3.20%	N: 29.63%

mp.: over 350°C

IR: (KBr pellet) cm^{-1}



PEAKS:

3436, 3074, 2924, 1646, 1605, 1577, 1554, 1537, 1459, 1436, 1385, 1352, 1294, 1274, 1237, 1212, 1153, 1143, 1092, 1055, 1000, 883, 785, 742, 723, 699, 640, 527, 431

Synthesis of the complex **C5**

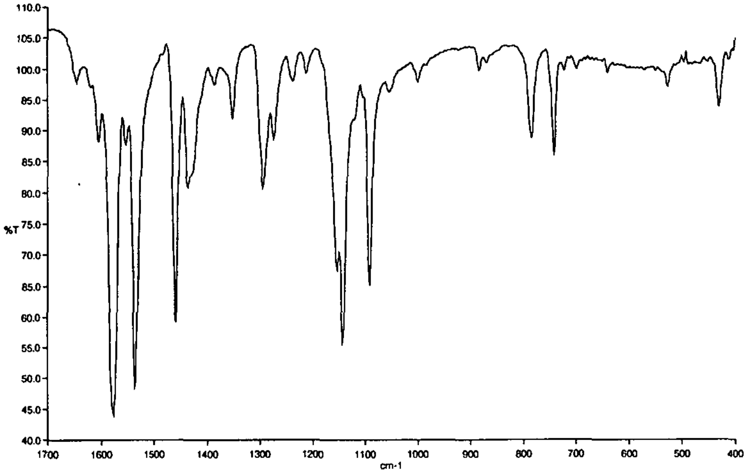
Charge: 0.00015mol

In a three neck reactor 0.0452g (0.00015mol) of ligand **L1** was dissolved in 15ml of dry methanol and 0.1ml of triethylamnie, the mixture was heated to 70°C and the yellow ligand was completely dissolved. Then 0.0365g (0.0001mol) of the metal salt $Ni(ClO_4)_2*6H_2O$ in 10ml of dry methanol, was slowly added dropwise. After 4hours of stirring at 70°C 0.0388g (0.0001mol) of **TPPZ** and 0.0485g (0.00084mol) of NaCl in 10ml of dry methanol, were slowly added dropwise. The resulting mixture was stirred at this temperature for 48hours. After stopping the reaction the suspension was filtered; the solid obtained was dried in a vacuum desiccator, and the filtrate was left for crystallization by evaporation. A small amount of black block-like crystals were obtained. The product is the same (chemically) as the complex **C4**, and this has been confirmed by X-ray analysis.

Yield: 0.0415g (42%) $(C_{16}H_{10}N_7)_2Ni$ (659.2946g/mol)

mp.: over 350°C

IR: (KBr pellet) cm^{-1}



PEAKS:

3434, 3074, 1646, 1605, 1577, 1554, 1537, 1459, 1436, 1386, 1352, 1294, 1274, 1238, 1212, 1154, 1143, 1092, 1055, 1000, 883, 785, 742, 722, 699, 641, 527, 488, 430, 412

Synthesis of the complex **C6**

Charge: 0.0001mol

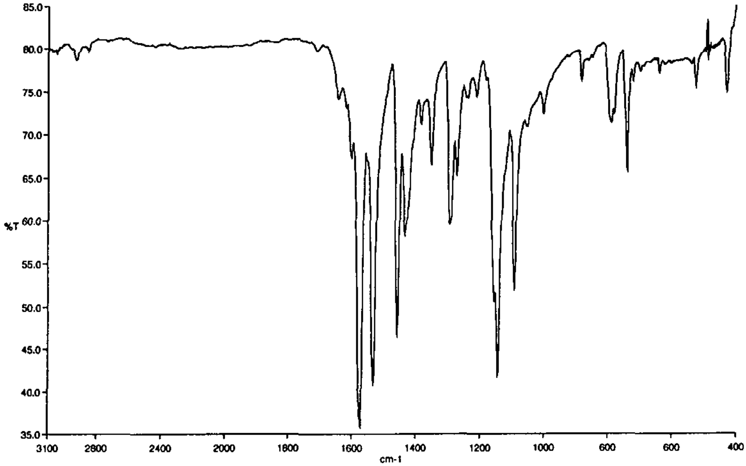
In a round bottomed flask were mixed 0.0646g (0.00021mol) of ligand **L1** in 10ml of dry methanol and 0.1ml of triethylamine. Then a solution of 0.0238g (0.0001mol) of the metal salt: $NiCl_2*6H_2O$ and 0.0467g (0.0008mol) of NaCl in 10ml of dry methanol was added under nitrogen. The mixture was stirred under nitrogen at room temperature and light protected for 4hours. After the light suspension obtained was filtered off, the filtrate was left for crystallization by slow evaporation of the solvent. The solid product: a small amount of a brown powder, was dried in a vacuum desiccator over silica. The X-ray analysis of the crystals obtained from the filtrate showed that the complex **C6** is the same (chemically) as the complexes **C4** and **C5.**

Yield: ~0.012g (18%) crystals (C$_{16}$H$_{10}$N$_7$)$_2$Ni 2/9(CH$_3$CN) (668.4174g/mol)

calc.	C: 58.30%	H: 3.12%	N: 29.80%
found	C: 58.31%	H: 3.33%	N: 29.82%

mp.: over 350°C

IR: (KBr pellet) cm^{-1}



PEAKS:

3436, 3046, 2925, 2280, 1645, 1603, 1573, 1534, 1458, 1435, 1385, 1353, 1294, 1273, 1238, 1211, 1155, 1143, 1091, 1002, 883, 790, 741, 722, 699, 640, 527, 488, 431

Synthesis of the complex **C7**

Charge: 0.0001mol

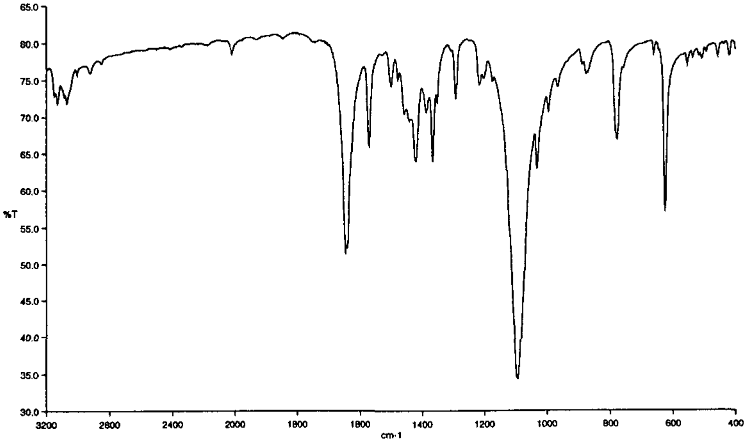
In a round bottomed flask were mixed 0.0646g (0.00021mol) of ligand **L1** in 10ml of dry methanol and 0.12ml of triethylamine. Then a solution of 0.0834g (0.0002mol) of the metal salt: $Cu(ClO_4)_2*6H_2O$ and 0.0486g (0.00083mol) of NaCl in 15ml of dry methanol were added under nitrogen. The mixture was stirred under nitrogen at room temperature and light protected for 4hours. After the product obtained was filtered off. The filtrate was left for crystallization by slow evaporation of the solvent, the solid product: a black powder was dried in a vacuum desiccator over silica. The solid obtained was used for recrystallization from a mixture of solvents: methanol/acetonitrile/acetylacetone = 3/3/1, which gave a mixture crystals - the main products after recrystallization were crystals of complexes of the metals used with acetylacetonate: blue blocks.

From the filtrate of the reaction a small amount of yellow-brownish blocks were obtained.

Yield: ~0.0180g (27%) $(C_{16}H_{10}N_7)_2Cu$ (664.1506g/mol)

mp.: over 350°C

IR: (KBr pellet) cm^{-1}



PEAKS:

3436, 3130, 3071, 2923, 2020, 1646, 1571, 1499, 1477, 1420, 1386, 1365, 1352, 1292, 1216, 1094, 1032, 996, 966, 876, 777, 660, 624, 553, 535, 507, 456, 419

Synthesis of the complex **C8**

Charge: 0.0001mol

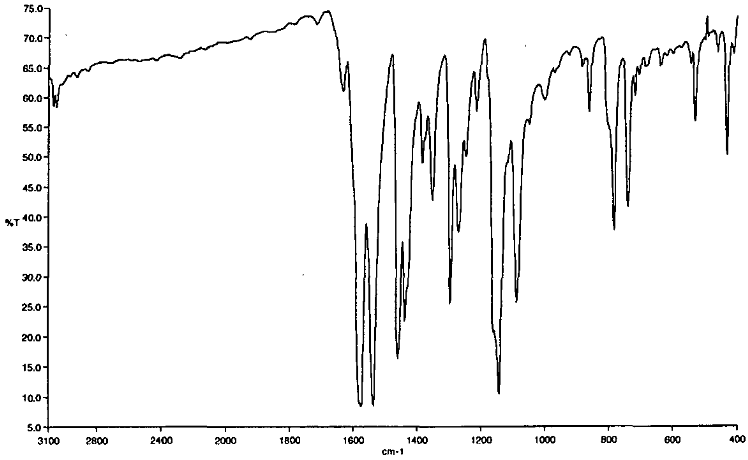
In a round bottomed flask were mixed 0.0646g (0.00021mol) of ligand **L1** in 10ml of dry methanol and 0.2ml of triethylamine. Then a solution of 0.0170g (0.0001mol) of the metal salt: $CuCl_2*2H_2O$ and 0.0467g (0.0008mol) of NaCl in 5ml of dry methanol, were added under nitrogen. The mixture was stirred under nitrogen at room temperature and light protected for 4hours. After the orange solution was filtered, and the filtrate was left for crystallization by slow evaporation of the solvent.

The X-ray analysis of the crystals obtained from the filtrate showed that the complex **C8** is the same (chemically) as complex **C7**.

Yield:	~0.009g (13%) crystals		$(C_{16}H_{10}N_7)_2Cu$ 1.5(CH_3OH) (712.2138g/mol)
calc.	C: 56.49%	H: 3.68%	N: 27.53%
found	C: 56.28%	H: 3.07%	N: 28.58%

mp.: over 350°C

IR: (KBr pellet) cm^{-1}



PEAKS:

3432, 3069, 3051, 2924, 1716, 1631, 1577, 1537, 1461, 1438, 1384, 1352, 1296, 1270, 1247, 1213, 1142, 1086, 1047, 998, 882, 860, 782, 740, 717, 704, 683, 638, 560, 543, 529, 488, 461, 432, 412

Complexes of Zn^{II}

Synthesis of the complex **C9**

Charge: 0.0001mol

In a round bottomed flask were mixed 0.0646g (0.00021mol) of ligand **L1** in 10ml of dry methanol and 0.2ml of triethylamine. Then a solution of 0.0136g (0.0001mol) of the metal salt: $ZnCl_2$ and 0.0467g (0.0008mol) of NaCl in 5ml of dry methanol was added. The mixture was stirred at room temperature and light protected for 4hours. A yellow light suspension was filtered off and the filtrate was left for crystallization by slow evaporation of the solvent. The small amount of yellow solid obtained was dried in a vacuum desiccator over silica.

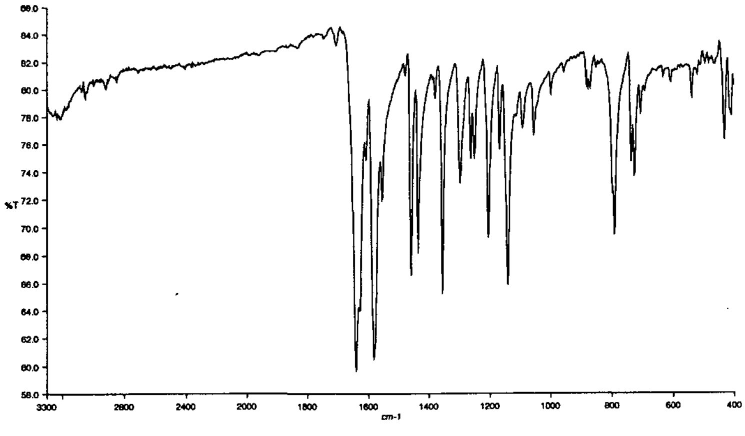
From the yellow filtrate orange block-like crystals were obtained.

Yield: ~0.0098g (15%) crystals $(C_{16}H_{10}N_7)_2Zn$ 1/6(CH_3CN) (672.8367g/mol)

calc. C: 57.72% H: 3.07% N:29.49% found C:57.67% H:3.14% N:29.66%

mp.: over 350°C

IR: (KBr pellet) cm^{-1}



PEAKS:

3434, 3213, 3058, 1705, 1641, 1607, 1582, 1554, 1477, 1459, 1435, 1378, 1355, 1297, 1261, 1249, 1203, 1167, 1139, 1091, 1053, 998, 871, 790, 736, 725, 705, 608, 538, 464, 431, 408

Synthesis of the complex **C10**

Charge: 0.00005mol

In a round bottomed flask were mixed 0.0301g (0.0001mol) of ligand **L1** in 4ml of dry methanol and 2ml of acetonitrile. Then 0.007g (0.00005mol) of the metal salt: $ZnCl_2$ was added. The mixture was stirred at room temperature and light protected for 4hours. After the yellow light solution was filtered and the filtrate left for crystallization by slow evaporation of the solvent.

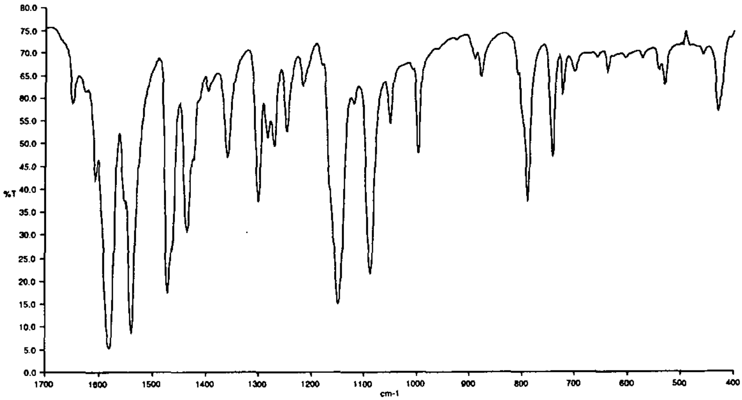
From the yellow filtrate orange crystals in form of blocks were obtained.

Yield: ~0.0068g (31%) crystals $(C_{16}H_{10}N_7)ZnCl(CH_3OH)$ (433.1871g/mol)

calc. C: 47.14% H: 3.26% N: 22.63% found C: 46.13% H: 3.27% N: 22.33%

mp.: over 350°C

IR: (KBr pellet) cm^{-1}



PEAKS:

3412, 3027, 2945, 2834, 1649, 1606, 1579, 1540, 1472, 1435, 1395, 1360, 1300, 1283, 1270, 1246, 1216, 1149, 1119, 1088, 1050, 998, 890, 878, 789, 742, 723, 701, 659, 638, 605, 574, 543, 531, 459, 430

Complexes of Ru^{III}

Synthesis of the complex **C11**

Charge: 0.0001mol

In a round bottomed flask it were mixed 0.0646g (0.00021mol) of ligand **L1** in 15ml of a mixture of solvents: acetonitrile/methanol/water = 4/1/3 and 0.1ml of triethylamine. Then a solution of 0.0207g (0.0001mol) of the metal salt: $RuCl_3{*}xH_2O$ in 14ml of the same mixture of solvents mentioned above was slowly added dropwise. The mixture was stirred at room temperature and light protected for 2hours. After the yellow-greenish solution was filtered, the filtrate left for crystallization by slow evaporation of the solvent.

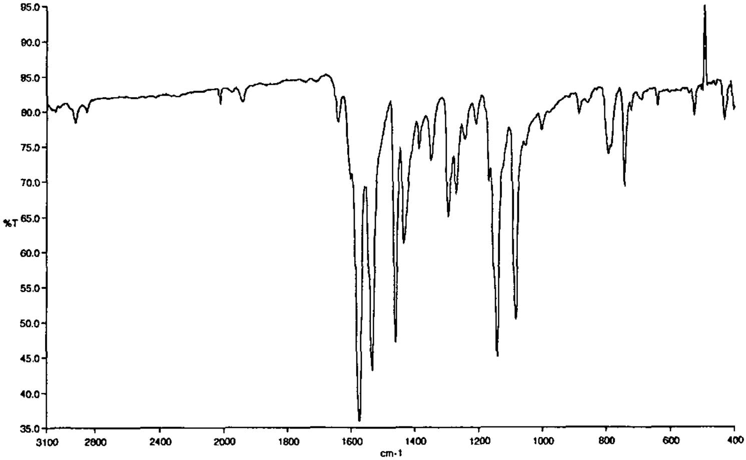
From the yellow-greenish filtrate orange block-like crystals were obtained.

Yield: ~0.028g (39%) crystals $(C_{16}H_{10}N_7)_2Ru$ 1/6(CH_3CN) (715.3588g/mol)

calc.	C: 54.29%	H: 2.89%	N: 27.74%
found	C: 57.64%	H: 3.30%	N: 29.38%

mp.: over 350°C

IR: (KBr pellet) cm^{-1}



PEAKS:

3434, 3046, 2924, 2854, 2025, 1943, 1642, 1602, 1576, 1536, 1461, 1434, 1386, 1348, 1294, 1270, 1242, 1208, 1166, 1141, 1083, 1001, 885, 792, 741, 722, 689, 638, 526, 456, 431

SYNTHESIS OF THE COMPLEXES WITH THE LIGAND **tppz**: *2,3,5,6-TETRA(α - PYRIDYL)PYRAZINE (***tppz***)*

Complex with Co^{II}

Synthesis of the complex **C12**

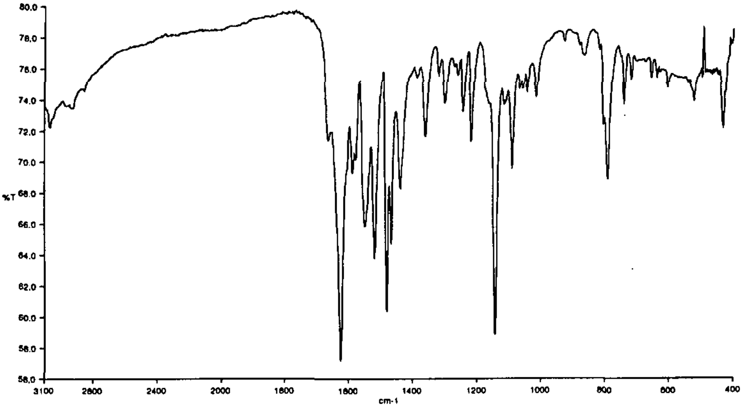
Charge: 0.0005mol

In a round bottomed flask, to a mixture of 0.0915g (0.00025mol) of the metal salt $Co(ClO_4)_2*6H_2O$ and 0.1942g (0.0005mol) of **tppz** was added 15ml of dry 1-pentanol. The mixture was stirred at 40°C for 1.5hr then heated to 70°C and stirred for 12hours (overnight). The next day a brown precipitate was filtered off, washed several times with ethanol and dried in a vacuum desiccator over silica. The filtrate was left for crystallization by evaporation of the solvent.

Yield: ~ 0.2g(crystals) (37%) $(C_{24}H_{16}N_6)_2Co(ClO_4)_2$ (1070.7268g/mol)

mp.: over 350°C

IR: (KBr pellet) cm^{-1}



PEAKS:

3436, 3068, 1626, 1589, 1550, 1520, 1482, 1468, 1440, 1361, 1320, 1299, 1260, 1243, 1217, 1142, 1114, 1089, 1061, 1042, 1013, 868, 791, 739, 718, 656, 604, 521, 431

Complex with Ni^{II}

Synthesis of the complex **C13**

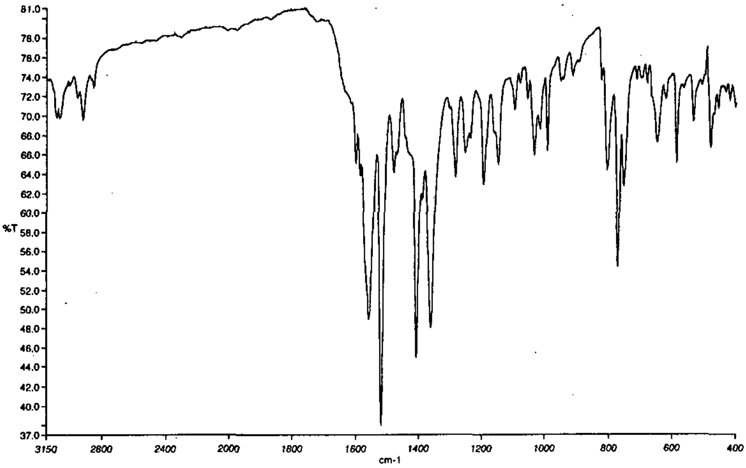
Charge: 0.0001mol

In a round bottomed flask to a mixture of 0.05599g (0.000225mol) of the metal salt $Ni(ClO_4)_2*4H_2O$ and 0.0486g (0.00083mol) of NaCl in 16ml of dry ethanol a solution of 0.0388g (0.0001mol) of **tppz** and 0.12ml of triethylamine in 16ml of dried methanol was slowly added dropwise. This mixture was stirred at room temperature for 4hours, filtered and the brown filtrate was left for crystallization. After evaporation of the solvent the dark brown product obtained was dissolved in a mixture of solvents: methanol/acetonitrile/acetylacetone = 3/3/1. After evaporation of the solvent the residue was dissolved in a mixture of the solvents: methanol/acetonitrile/trichloroethylene = 2/2/1 and this recrystallization gave a small amount of green block-like crystals.

Yield: 0.052g (24%) $C_{87}H_{75}N_{18}O_6Cl_{10}Ni_5$ ½$(C_5H_8O_2)(H_2O)$ (2202.7357g/mol)

calc.	C: 48.80%	H: 3.71%	N: 11.45%
found	C: 47.73%	H: 3.44%	N: 10.79%
mp.:	over 350°C		

IR: (KBr pellet) cm^{-1}



PEAKS:

3434, 3069, 2922, 1599, 1557, 15184, 1479, 1407, 1360, 1283, 1253, 1195, 1148, 1096, 1034, 992, 805, 771, 754, 648, 587, 534, 479

Synthesis of the complexes **C14** *and* **C15**

Charge: 0.0001mol

In a round bottomed flask were mixed 0.0388g (0.0001mol) of **tppz** (a suspension in 10ml of a mixture of solvents methanol/acetonitrile = 1/1) and 0.0301g (0.0001mol) of ligand **L1**, also a suspension in the same volume of the same solvent as above, and 0.0486g (0.00083mol) of NaCl in the same volume of solvent as above, and 0.0823g (0.000225mol) of the metal salt $Ni(ClO_4)_2*6H_2O$ again in the same volume of solvents as above. This mixture was stirred at ambient temperature for 4hr, filtered and the brown-greenish filtrate was left for crystallization. After evaporation of the solvent the residue was divided into two parts and recrystallized separately. The first part was recrystallized from a mixture of solvents: methanol/acetonitrile/= 1/1 and this crystallization gave a small amount black blocks: complex **C14**:

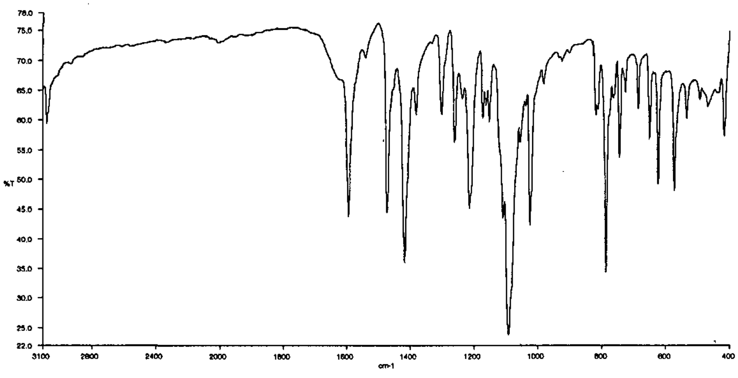
Yield: 0.025g (18%) $(C_{24}H_{16}N_6Ni2Cl_3)_2Cl(ClO_4)\ H_2O$ (1377.2569g/mol)

calc. C: 41.79% H: 2.63% N: 12.19%

found C: 40.76% H: 2.52% N: 11.85%

mp.: over 350°C

IR: (KBr pellet) cm^{-1}



Peaks:

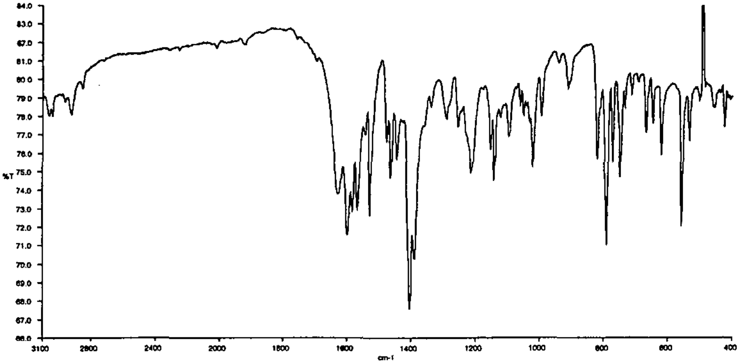
3436, 3052, 2923, 1628, 1599, 1583, 1568, 1529, 1478, 1464, 1446, 1405, 1390, 1290, 1255, 1213, 1153, 1141, 1096, 1021, 994, 910, 820, 790, 772, 748, 734, 713, 668, 647, 621, 557, 534, 456, 425

The second part was recrystallized from a mixture of the solvents: methanol/acetonitrile/acetylacetone = 3/3/1 and this crystallization gave a small amount of black blocks: complex **C15**.

Yield: 0.02g (32%) $(C_{24}H_{16}N_6)NiCl_2\ C_5H_8O_2\ 1/2H_2O$ (627.1516g/mol)

mp.: over 350°C

IR: (KBr pellet) cm^{-1}



PEAKS:

3439, 3075, 2014, 1595, 1542, 1474, 1418, 1382, 1301, 1260, 1236, 1214, 1172, 1162, 1151, 1108, 1091, 1055, 1037, 1024, 981, 923, 818, 787, 764, 745, 726, 686, 651, 624, 573, 534, 492, 468, 416

UNEXPECTED RESULTS

Synthesis of the product **U1**

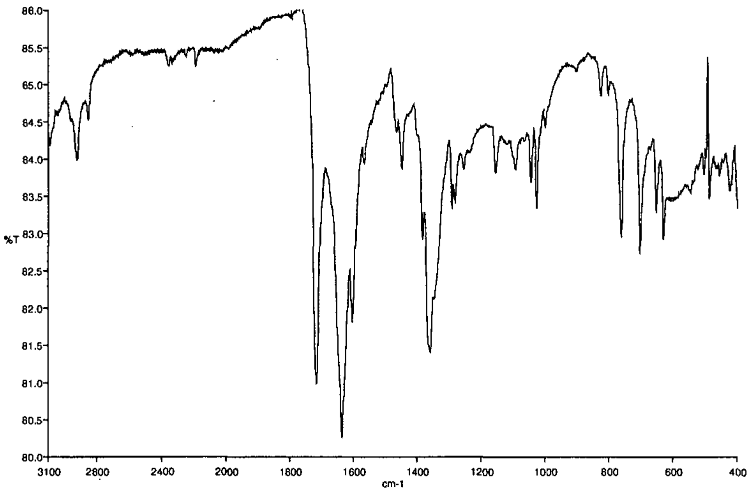
Charge: 0.0001mol

In a round bottomed flask were mixed: 0.0236g (0.0001mol) of 2,3-bis(2-pyridyl)-5,6-dihydropyrazine, 0.0389g (0.0001mol) of **TPPZ** in 10ml of dry methanol, which were heated up to 65°C, then 0.0269g (0.0002mol) of the metal salt $CuCl_2$ was added in one portion. The mixture was stirred at this temperature for 5hr, then the reaction was terminated and the solution filtered. The filtrate left was left to cool and eventually a small amount of blue block-like crystals appeared.

Yield: 0.003g (9%) $C_{12}H_8N_3O_2ClCu$ (325.2131g/mol)

mp.: over 350°C

IR: (KBr pellet) cm^{-1}



PEAKS:

3435, 1716, 1636, 1449, 1358, 1292, 1027, 762, 703, 631

Synthesis of the product **U2**

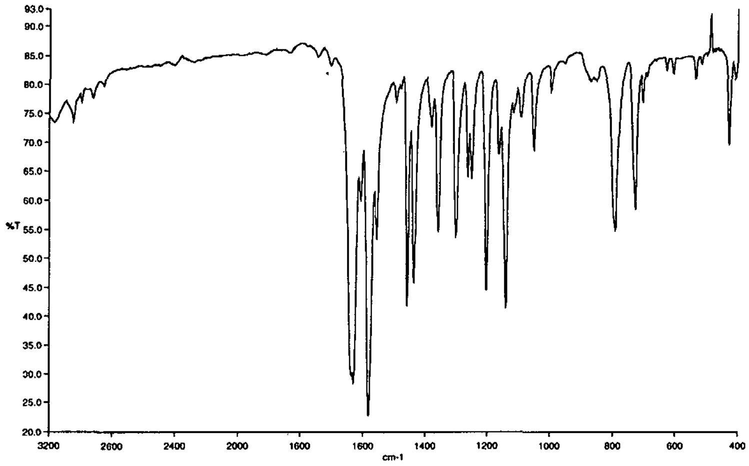
Charge: 0.0001mol

In a round bottomed flask were mixed: 0.0646g (0.0001mol) of ligand **L1** in 7ml of dry methanol and 0.1ml of triethylamine. Then a solution of 0.0362g (0.0001mol) of the metal salt: $Mn(ClO_4)_2*6H_2O$ in 3ml of dry methanol was added and the mixture stirred at room temperature under nitrogen for 4days. The mixture was filtered and the filtrate was left for crystallization, but no crystals were obtained. The solid left after evaporation of the solvent was recrystallized several times from different solvents (containing acetylacetone). Finally the mixture of solvents: methanol/acetonitrile/water = 1/4/3 was used and it gave a small amount of brown block-like crystals that were examined by X-ray analysis.

Yield: 0.0036g (14%) $C_9H_{10}N_3\,ClO_4$ (259.6488g/mol)

mp.: over 350°C

IR: (KBr pellet) cm^{-1}



PEAKS:

3411, 3166, 3047, 2996, 2923, 2854, 2286, 1748, 1705, 1629, 1607, 1581, 1556, 1494, 1458, 1437, 1380, 1358, 1301, 1263, 1251, 1204, 1164, 1141, 1118, 1094, 1053, 998, 871, 791, 727, 705, 631, 610, 539, 520, 430, 412

Synthesis of the product **U3**

Charge: 0.025mol

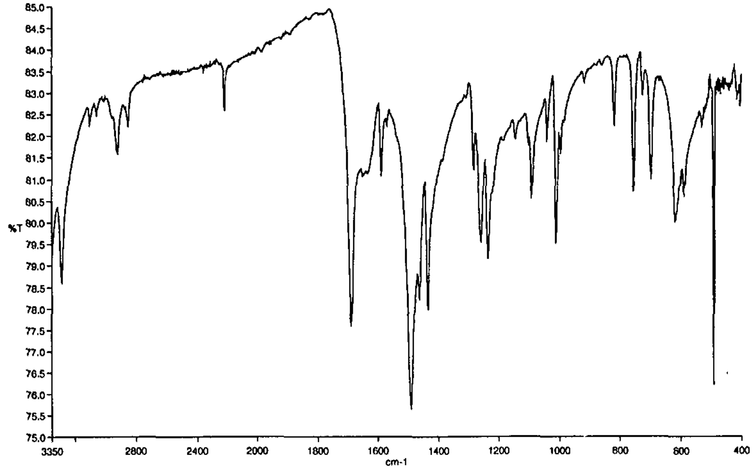
This synthesis was performed in almost the same way that was described in the thesis of Yi Wang (it is also the same synthesis for obtaining 2,3-bis(2-pyridyl)-5,6-dicyanopyrazine) with some modifications: in a round bottomed flask outfitted with a reflux condenser, 9.3663g (0.03mol) of 2,2'-pyridyl were dissolved in 15ml of dry n-buthanol and then a solution of 2.7026g (0.025mol) of diaminomaleonitrile in 15ml of dry n-buthanol was added at 60°C with stirring. The mixture was refluxed for 3hr. After stopping the reaction, the mixture was filtered immediately (glass filter) to remove an orange-brown precipitate. This orange brown precipitate was recrystallized from a mixture of the solvents methanol/acetonitrile/acetylacetone = 3/3/1 which resulted in the formation of yellow needle-like crystals.

Yield: ~2.5g(32%) $C_{16}H_8N_6O_2$ (316.2785g/mol)

From the filtrate colourless crystals of 2,3-bis(2-pyridyl)-5,6-dicyanopyrazine were obtained by slow evaporation of the solvent.

mp.: over 350°C

IR: (KBr pellet) cm^{-1}



PEAKS:

3436, 3288, 2923, 2219, 1688, 1589, 1490, 1435, 1283, 1259, 1236, 1091, 1040, 1011, 819, 756, 699, 619, 491

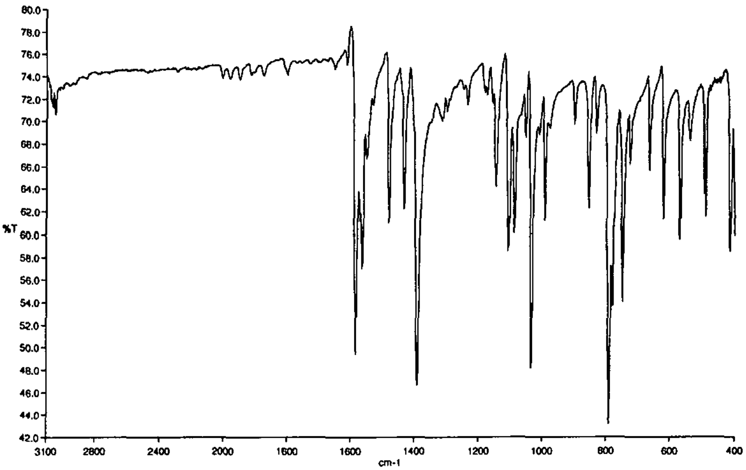
Synthesis of the product U4

Charge: 0.001mol

The second way of obtaining 2,3-Bis-(2-pyridyl)-pyrazine was as follows: in a round bottomed flask 0.1345g (1mmol) of $CuCl_2$ were dissolved under nitrogen in 10ml of ethanol, then 0.2363g (1mmol) of 2,3-Bis-(2-pyridyl)-5,6-dihydropyrazine in 7ml of ethanol were added also under nitrogen. After stirring for 2hr at ambient temperature the mixture was filtered and the filtrate left for crystallization. The product: 2,3-Bis-(2-pyridyl)-pyrazine was obtained in the form of yellow plates.

Yield: ~0.022g (9%) crystals $C_{14}H_{10}N_4$ (234.2602/mol)

IR: (KBr pellet) cm^{-1}



PEAKS:

3438, 3064, 3047, 2007, 1981, 1950, 1914, 1875, 1801, 1652, 1613, 1585, 1572, 1564, 1550, 1481, 1434, 1392, 1314, 1300, 1236, 1174, 1145, 1105, 1087, 1052, 1034, 992, 899, 854, 831, 791, 780, 748, 725, 665, 621, 569, 539, 492, 415

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