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Different complexation behavior of a proton transfer compound obtained from 1,10-phenanthroline and pyridine-2,6-dicarboxylic acid with In^{III} and Ce^{III}: Synthesis, crystal structures and solution studies

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Abstract

The different complexation methods of a proton transfer compound LH_2, $(phenH)_2(pydc)$ (phen = 1,10-phenanthroline; $pydcH_2$ = pyridine-2,6-dicarboxylic acid), are discussed and formation of $[In_2SO_4(pydc)_2(phen)_2(H_2O)_2]\cdot 5.5H_2O$ (**1**) and $\{[Ce(pydc)(pydcH)(H_2O)_2]\cdot 4H_2O\}_n$ (**2**) are reported. The complexes were synthesized by reaction of LH_2 with $In_2(SO_4)_3\cdot xH_2O$ and $Ce(NO_3)_3\cdot 6H_2O$, respectively. The characterization was performed using IR spectroscopy and X-ray diffraction. The complex **1** crystallizes in the space group $P\bar{1}$ of the triclinic system, with two molecules per unit cell. The unit cell parameters are $a = 11.9547(6)$ Å, $b = 12.8482(7)$ Å, $c = 16.1313(8)$ Å, $\alpha = 89.532(1)°$, $\beta = 72.007(1)°$ and $\gamma = 68.066(1)°$. The crystal system of the complex **2** is monoclinic with space group $P2_1/c$ and four molecules per unit cell. The unit cell parameters are $a = 14.0273(8)$ Å, $b = 11.2184(6)$ Å, $c = 12.9441(8)$ Å and $\beta = 102.177(5)°$. The complex **1** is a binuclear mixed-ligand system in which both phen and $(pydc)^{2-}$ have contributed to the molecular structure as tri- and bi-dentate ligands, respectively. The complex **2** is a polymeric system in which only one of the fragments of LH_2 has acted as a ligand. In both complexes **1** and **2** a large number of hydrogen bonds are observed. These interactions especially in case of complex **2** play an important role in the formation of self associated systems in the crystal lattices. Results of the potentiometric pH titration studies in aqueous solution strongly confirm the formation of In^{III} and Ce^{III} complexes in solution with stoichiometries very similar to those of the crystalline complexes **1** and **2**, respectively.

Keywords: Indium; Cerium; 1,10-Phenanthroline; Pyridine-2,6-dicarboxylic acid; X-ray crystal structure; Hydrogen bonds; Solution studies

1. Introduction

The different aspects of proton transfer systems have been studied by chemists in the recent years [1–5]. An interesting report in this area was investigation of the mechanism of proton transfer from intra-molecularly hydrogen-bonded acids and differences between nitrogen-to-oxygen and nitrogen-to-nitrogen proton transfer [6]. Some examples of proton transfer polymerization have been also reported [7,8]. In addition, the role of some effective factors such as pressure, environment and catalyst has been studied in some previous papers [9–11]. In recent years our research group has been involved in the study of proton transfer compounds and their complexes with different metal ions. We have already reported several proton transfer systems using 1,10-phenanthroline-2,9-dicarboxylic acid, $phendcH_2$, pyridine-2,6-dicarboxylic acid, $pydcH_2$, and 4-hydroxypyridine-2,6-dicarboxylic acid, $hypydcH_2$, as proton donor fragments, and 2,6-diaminopyridine, pyda, guanidine, G, and creatinine, creat, as proton acceptor fragments, which resulted in formation of proton transfer compounds,

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($pydaH_2$)(phendc) [12], ($pydaH_2$)(pydc) [13], (creatH)(pydcH) [14], $(GH)_2$(pydc) [15] and (GH)(hypydcH) [16]. The non-covalent interactions such as ion pairing, hydrogen bonding and π–π stacking are observed in these ionic compounds. We have particularly aimed to investigate 'hydrogen bonding' interactions, which have received a special interest in different fields because of their directional and precise nature [17–20]. We have also regarded the 'π–π stacking' interaction as a remarkable feature of some of our crystalline systems, as it has been considered as an effective factor on stability of biological and chemical systems [21–25]. Some of interesting metal complexes in which the non-covalent interactions play important roles in creation of the crystalline networks, were obtained from the proton transfer compound LH_2, $(phenH)_2$(pydc) (phen = 1,10-phenanthroline), that was reported by our research group previously [26]. The complex, $[Zn(pydc)_2][Zn(phen)_2(H_2O)_2]\cdot 7H_2O$ was an interesting case in which both $(pydc)^{2-}$ and phen participated in the complexation, but they did not form a single mixed-ligand complex and in fact two ionic complexes $[Zn(pydc)_2]^{2-}$ and $[Zn(phen)_2(H_2O)_2]^{2+}$ were formed simultaneously [26]. The other Zn^{II} complex prepared using LH_2 was $[Zn(phen)_3]_4\cdot(H(Hpydc)_2)(NO_3)_7\cdot 26H_2O$ in which only phen contributed to the complexation as a ligand, leaving $(H(Hpydc)_2)^-$ anion [26]. We succeeded also to prepare a mixed-ligand Cd^{II} complex of LH_2 with the formula $[Cd(pydc)(phen)_2]\cdot pydcH_2\cdot 4H_2O$, in which both ligands were linked to the central atom forming the first mixed-ligand complex of LH_2 [27]. On the other hand the Hg^{II} complex, $HgCl_2(phen)_2$ was the case that showed the participation of phen as the only fragment of LH_2 contributing to the complexation. It is noticeable that the latter is the only complex of LH_2 in which the $(pydc)^{2-}$ fragment has been removed completely and is not present in the crystal lattice [28].

In this paper we report a novel mixed-ligand complex, $[In_2SO_4(pydc)_2(phen)_2(H_2O)_2]\cdot 5.5H_2O$, and also the first complex of LH_2 in which only $(pydc)^{2-}$ has participated in the complexation, i.e. $\{[Ce(pydc)(pydcH)(H_2O)_2]\cdot 4H_2O\}_n$.

2. Experimental section

2.1. General methods and materials

IR spectra were recorded on a Perkin–Elmer 343 and 1720X spectrophotometers using KBr discs. 1,10-Phenanthroline, pyridine-2,6-dicarboxylic acid and $In_2(SO_4)_3\cdot xH_2O$ were purchased from Merck. $Ce(NO_3)_3\cdot 6H_2O$ was obtained from commercial suppliers. Doubly distilled deionized water was used throughout.

2.2. Potentiometric pH titrations

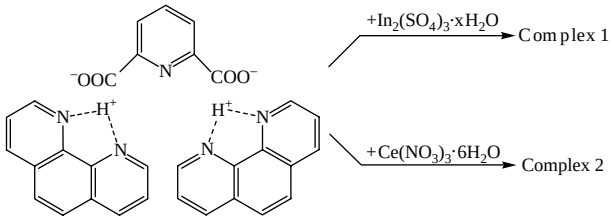
All potentiometric pH measurements were made on solutions in a 75-mL double-walled glass vessel using a Model 686 Metrohm Tiroprocessor equipped with a combined glass-calomel electrode. The temperature was controlled at 25.0 ± 0.1 °C by circulating water through the jacket, from a constant-temperature bath (MLW thermostat) . The cell was equipped with a magnetic stirrer and a tightly fitting cap, through which the electrode system and a 10-mL capacity Metrohm piston burrete were inserted and sealed with clamps and *O*-rings. Atmospheric CO_2 was excluded from the titration cell with a purging steam of purified nitrogen gas. The concentrations of phen and pydc were 5.12×10^{-3} and 2.50×10^{-3} M, respectively, for the potentiometric pH titrations of pydc and pydc + 2phen, in the absence and presence of order of 10^{-3} M metal ions. A standard carbonate-free KOH solution (0.099 M) was used in all titrations. The ionic strength was adjusted to 0.1 M with KNO_3. Before an experimental point (pH) was measured, sufficient time was allowed for the establishment of equilibrium. Ligands protonation constants and their metal complexes protonation, stability and hydrolysis constants were evaluated using the program BEST described by Martell and Motekaitis [29]. The value of $K_w = [H^+][OH^-]$ used in the calculations was $10^{-13.78}$ [30].

2.3. Synthesis of $[In_2SO_4(pydc)_2(phen)_2(H_2O)_2]\cdot 5.5H_2O$ (*1*)

A solution of $In_2(SO_4)_3\cdot xH_2O$ (28 mg, 0.047 mmol) in water (5 mL) was added to an aqueous solution (5 mL) of LH_2 (100 mg, 0.190 mmol). Light pink crystals of the complex suitable for X-ray analysis were obtained after 8 weeks. Anal. Calcd for $C_{38}H_{37}In_2N_6O_{19.5}S$: C, 39.63%; H, 3.21%; N, 7.30%. Found: C, 39.40%; H, 3.16%; N, 7.19%. IR(KBr): 3380–3497br, 3072m, 2941w, 2368w, 1725m, 1703w, 1664s, 1647s, 1591s, 1547s, 1526s, 1499m, 1461w, 1451w, 1430s, 1372m, 1279s, 1188s, 1150m, 1108m, 1076s, 1028s, 916s, 849s, 780s, 737s, 689s, 669s, 621m, 465m, 442m, 431m cm^{-1}.

2.4. Synthesis of $\{[Ce(pydc)(pydcH)(H_2O)_2]\cdot 4H_2O\}_n$ (*2*)

The complex was prepared by adding a solution of $Ce(NO_3)_3\cdot 6H_2O$ (41 mg, 0.095 mmol) in water (5 mL) to an aqueous solution (5 mL) of LH_2 (100 mg, 0.190 mmol). Yellow crystals of the complex were obtained after 1 week. Anal. Calcd for $C_{14}H_{19}CeN_2O_{14}$: C, 29.02%; H, 3.28%; N, 4.84%. Found: C, 28.86%; H, 3.22%; N, 4.75%. IR(KBr): 3250–3456br, 2359w, 1644m, 1623m, 1615m, 1584w, 1574m, 1670–1650br, 1469m, 1434s, 1388s, 1278s, 1191s, 1152w, 1078s, 1022s, 923s, 853s, 777s, 738s, 696s, 663s, 589w, 424w cm^{-1}.



Scheme 1.

3. Results and discussion

*3.1. Synthesis and characterization of [In$_2$SO$_4$(pydc)$_2$(phen)$_2$(H$_2$O)$_2$]·5.5H$_2$O (**1**)*

The procedure adopted in the synthesis of complex **1** is outlined in Scheme 1. The reaction of $In_2(SO_4)_3 \cdot xH_2O$ with the proton transfer compound LH_2, $(phenH)_2(pydc)$, in a 1:2 molar ratio was carried out and the crystalline complex **1** was obtained.

The IR spectroscopy has been widely used as a useful tool for investigation of interactions in such compounds. The IR spectrum of complex **1** shows a broad band at the region of 3380–3497 cm^{-1} that is due to the water molecules of the crystal. The most remarkable feature of the IR spectrum is the absorption band at 1647 cm^{-1} which refers to the stretching vibration of C=O bond [31].

*3.2. X-ray crystal structure of complex **1***

The molecular structure and the crystal packing diagram of complex **1** are illustrated in Figs. 1 and 2, respectively. Table 1 lists a summary of X-ray crystallographic data and Table 2 shows selected bond lengths and angles of this complex. A list of hydrogen bonds is also given in Table 3.

The X-ray analysis shows that both $(pydc)^{2-}$ and phen ligands have contributed to the molecular structure, forming a mixed-ligand complex. In a recent publication some similar mixed-ligand complexes have been reported, which contained 1,10-phenanthroline and pyridine-2,5-dicarboxylate as ligands [32]. The complex **1** is a binuclear system containing two metal fragments, which are linked through a bridge SO_4^{2-} group. Each indium atom is coordinated by one $(pydc)^{2-}$ and one phen fragment, which act as tri- and bidentate ligands, respectively, and also one oxygen atom of sulfate ligand, and one water molecule. Therefore, the coordination number is seven for each central atom and a distorted pentagonal bipyramidal geometry is observed around the indium atoms. The coordination surroundings of the two indium atoms, In(1) and In(2), are almost similar. With respect to the bond angles in the equatorial planes, the largest and smallest deviations from the ideal value of 72° around In(1) are observed for O(7)–In(1)–N(2) [75.84(10)°] and N(3)–In(1)–N(2) [71.27(10)°], and those of In(2) are observed for N(5)–In(2)–O(12) [76.13(8)°] and N(6)–In(2)–N(5) [71.57(9)°]. However there is a difference between

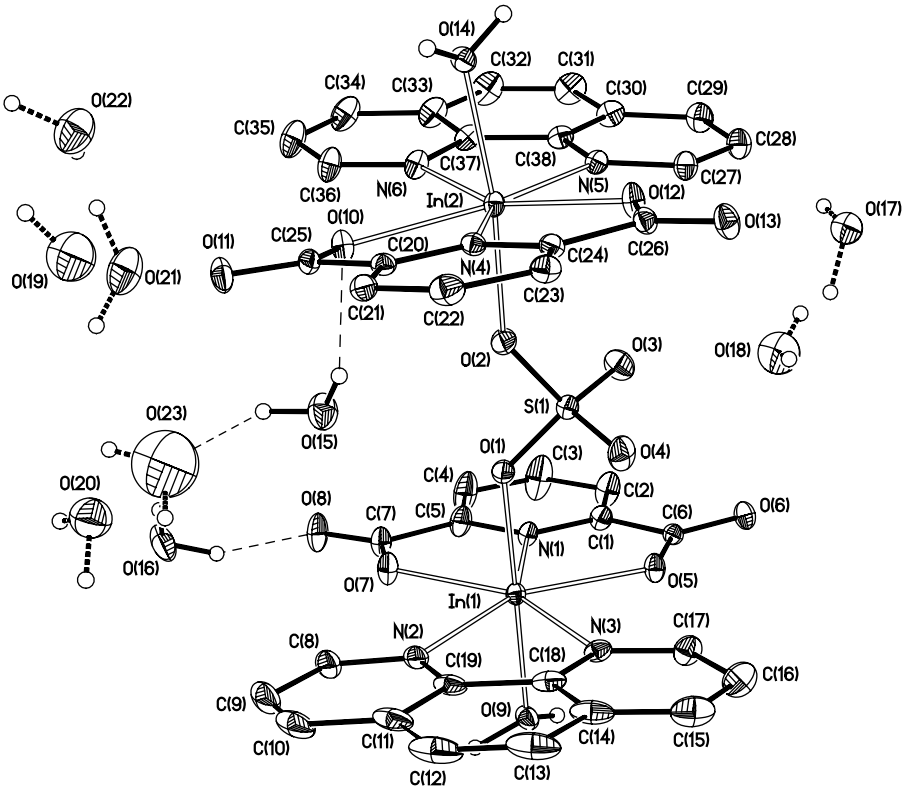


Fig. 1. Molecular structure of the complex **1**.

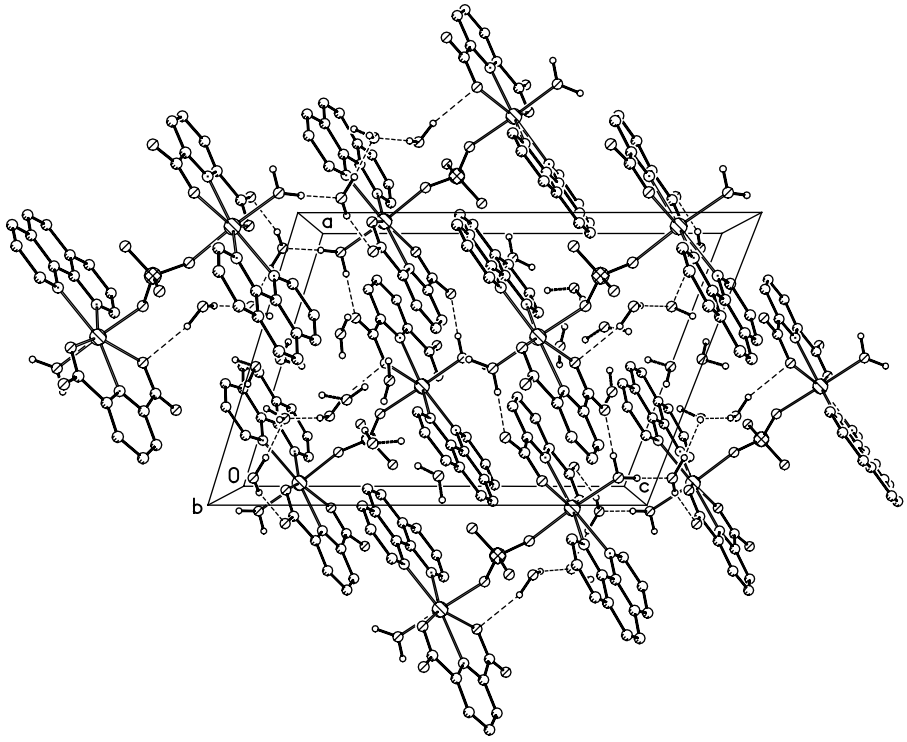


Fig. 2. Crystal packing diagram of the complex **1**.

axial angles, so that the angle between the axial bonds for In(1) is 175.94(9)°, rather than 171.69(9)° for In(2). The corresponding distances for metal–ligand bonds are almost the same for two indium atoms (Table 2).

The geometry around sulfur atom is a distorted tetrahedral. The bond distances of S(1)–O(1) and S(1)–O(2) are longer than the other S–O bond lengths due to the bonding of O(1) and O(2) to the central indium atoms. Also the bond angles O(1)–S(1)–O(2) and O(3)–S(1)–O(4) are 101.3(1) and 113.8(2)°, respectively, which show a large deviation from regular tetrahedral angles. There are some uncoordinated water molecules in the crystal lattice, from

Table 1
Crystallographic data for complexes **1** and **2**

	Complex **1**	Complex **2**
Empirical formula	$C_{38}\ H_{37}\ In_2\ N_6\ O_{19.5}S$	$C_{14}\ H_{19}\ Ce\ N_2\ O_{14}$
Formula weight	1151.44	579.43
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2) [37] $Z=2$	$P2_1/c$ (no. 14) [37] $Z=4$
Unit cell dimensions	$a=11.9547(6)$ Å, $b=12.8482(7)$ Å, $c=16.1313(8)$ Å, $\alpha=89.5320(10)°$, $\beta=72.0070(10)°$, $\gamma=68.0660(10)°$	$a=14.0273(8)$ Å, $\beta=102.177(5)°$, $b=11.2184(6)$ Å, $c=12.9441(8)$
Unit cell volume	2169.75(19) $Å^3$	1991.1(2) $Å^3$
Temperature (K)	120(2)	153(2)
Absorption coefficient (mm^{-1})	1.199	2.364
Calculated density (mg/m^3)	1.762	1.933
$F(000)$	1154	1148
Crystal dimensions (mm^3)	$0.40\times0.30\times0.20$	$0.38\times0.30\times0.21$
R value	0.0440	0.0218
Rw value	0.0976	0.0511
Θ range for data collection	1.72–30.03°	2.35–29.64°
Limiting indices	$-16\le h\le16$, $-17\le k\le18$, $-22\le l\le22$	$-17\le h\le19$, $-15\le k\le15$, $-17\le l\le17$
Reflections collected/uniqe	25928/12498 [R(int) = 0.0184]	28759/5510 [R(int) = 0.0272]
Goodness-of-fit	1.019	1.083
Largest diff. Peak and hole	2.845 and -1.495 e $Å^{-3}$	1.021 and -0.640 e $Å^{-3}$

CCDC 259481 and 273009 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033). Deposited data may be accessed by the journal and checked as part of the refereeing process. If data are revised prior to publication, a replacement file should be sent to CCDC.

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**

In(1)–O(1)	2.127(2)	In(2)–O(2)	2.110(2)
In(1)–O(5)	2.277(2)	In(2)–O(10)	2.300(2)
In(1)–O(7)	2.243(2)	In(2)–O(12)	2.246(2)
In(1)–O(9)	2.157(2)	In(2)–O(14)	2.165(2)
In(1)–N(1)	2.304(2)	In(2)–N(4)	2.306(2)
In(1)–N(2)	2.338(3)	In(2)–N(5)	2.322(2)
In(1)–N(3)	2.341(3)	In(2)–N(6)	2.344(2)
S(1)–O(1)	1.517(2)	S(1)–O(3)	1.445(2)
S(1)–O(2)	1.494(2)	S(1)–O(4)	1.446(2)
O(1)–In(1)–O(5)	92.57(8)	O(2)–In(2)–O(12)	95.87(9)
O(1)–In(1)–O(7)	87.60(9)	O(2)–In(2)–O(10)	82.60(9)
O(1)–In(1)–O(9)	175.94(9)	O(2)–In(2)–O(14)	171.69(9)
O(1)–In(1)–N(1)	94.78(9)	O(2)–In(2)–N(4)	93.31(9)
O(1)–In(1)–N(2)	88.69(9)	O(2)–In(2)–N(5)	90.76(9)
O(1)–In(1)–N(3)	88.90(9)	O(2)–In(2)–N(6)	92.30(10)
O(5)–In(1)–N(1)	68.16(8)	O(10)–In(2)–N(4)	68.17(8)
O(5)–In(1)–N(2)	146.91(9)	O(10)–In(2)–N(5)	146.58(8)
O(5)–In(1)–N(3)	75.70(8)	O(10)–In(2)–N(6)	76.00(9)
O(7)–In(1)–O(5)	137.24(8)	O(12)–In(2)–O(10)	137.01(8)
O(7)–In(1)–N(1)	69.22(9)	O(12)–In(2)–N(4)	69.05(8)
O(7)–In(1)–N(3)	146.99(9)	O(12)–In(2)–N(6)	146.74(9)
O(7)–In(1)–N(2)	75.84(10)	O(12)–In(2)–N(5)	76.13(8)
O(9)–In(1)–O(5)	89.00(8)	O(14)–In(2)–O(10)	90.41(8)
O(9)–In(1)–O(7)	93.79(9)	O(14)–In(2)–O(12)	92.30(9)
O(9)–In(1)–N(1)	89.28(9)	O(14)–In(2)–N(4)	88.20(8)
O(9)–In(1)–N(2)	87.96(9)	O(14)–In(2)–N(5)	92.66(8)
O(9)–In(1)–N(3)	87.86(9)	O(14)–In(2)–N(6)	81.62(9)
N(2)–In(1)–N(3)	71.27(10)	N(5)–In(2)–N(6)	71.57(9)
O(2)–S(1)–O(1)	101.27(13)	O(3)–S(1)–O(4)	113.84(15)
O(3)–S(1)–O(1)	110.01(14)	O(4)–S(1)–O(1)	110.06(14)
O(3)–S(1)–O(2)	111.11(15)	O(4)–S(1)–O(2)	109.84(16)

which seven water molecules O(17)–O(23) are statistically disordered with partial occupancy of 0.5.

The non-covalent interactions connect the fragments of the crystal packing. The hydrogen bonds with D···A distances ranging from 2.569(3) to 3.062(3) Å make an extended network through the crystal lattice. Some of the uncoordinated water molecules contribute to the formation of this network through their hydrogen bonding interactions (Table 3). Another non-covalent interaction is π–π stacking among $(pydc)^{2-}$ and phen planes and also between two phen species due to the short distances of ≈3.3 Å, close to that of graphite layers, among the parallel planes of these aromatic rings.

Table 3
Hydrogen bonds for complex **1**

D–H	*d*(D–H)	*d*(H···A)	⟨DHA	*d*(D···A)	A
O(9)–H(9B)	0.88	1.82	178	2.697(3)	O(11)[a]
O(9)–H(9C)	0.96	1.62	170	2.569(3)	O(16)
O(14)–H(14A)	0.91	1.73	175	2.642(3)	O(6)[b]
O(14)–H(14B)	0.95	−1.64	168	2.577(3)	O(13)[c]
O(15)–H(15B)	0.99	1.76	151	2.666(5)	O(23)
O(15)–H(15C)	0.99	2.16	151	3.062(3)	O(10)
O(16)–H(16B)	0.91	1.84	157	2.701(3)	O(8)[d]
O(16)–H(16C)	0.92	1.73	167	2.635(5)	O(23)[e]
O(22)–H(22C)	1.05	2.23	131	3.022(4)	O(13)[f]

[a] $x+1, y, z$.
[b] $x-1, y, z$.
[c] $-x+1, -y+2, -z+1$.
[d] $-x+2, -y+1, -z+2$.
[e] $-x+2, -y+1, -z+2$.
[f] $x, y-1, z$.

*3.3. Synthesis and characterization of {[Ce(pydc)(pydcH)(H$_2$O)$_2$]·4H$_2$O}$_n$ (**2**)*

The procedure of synthesis of complex **2** is shown in Scheme 1. The reaction of $Ce(NO_3)_3\cdot 6H_2O$ with the proton transfer compound LH_2, $(phenH)_2(pydc)$, in a 1:2 molar ratio leads to the formation of yellow crystals of complex **2**.

The IR spectrum of complex **2** illustrates a broad band at 3250–3456 cm^{-1} due to the stretching vibration of O–H bond. The stretching frequencies at 1615–1623 cm^{-1} show the absorption of C=O bonds [31].

*3.4. X-ray crystal structure of complex **2***

The numbering scheme, ORTEP, of complex **2**, and the array of hydrogen bonds in the crystal are shown in Figs. 3 and 4. A summary of crystallographic data and selected bond lengths and angles are reported in Tables 1 and 4, respectively. Table 5 lists the hydrogen bonding interactions of this complex.

The complex **2** is the first example of LH_2 complexes in which phen molecule is removed completely upon complexation. The $(pydc)^{2-}$ anion has a bridging role linking the fragments of the polymeric system through one of its carboxylate groups. The tridentate ligand $(pydcH)^{-}$ is also observed in the structure. Each central atom is connected to seven oxygen and two nitrogen atoms from $(pydc)^{2-}$, $(pydcH)^{-}$ and water molecules, which lead to a coordination number of nine for each cerium atom. The summation of bond angles, N1–Ce1–N2, N2–Ce1–O7 and O7–Ce1–N1 is equal to 359.94° and indicates that Ce1 is located in the center of N1N2O7 plane. The three oxygen atoms O1, O8 and O2W form a triangle and the other three, O3, O5 and O1W form another triangle. Considering the angles between the oxygen atoms, it is found that they are almost eclipsed. So a prism consisted of six oxygen atoms and three caps on its faces is proposed. Therefore, the coordination polyhedron should be a distorted tricapped trigonal prism. A similar structure with limited data and without non-covalent interactions was reported previously [33]. Some lanthanide complexes of pyridine-2,6-dicarboxylic acid with close relation to the structure of **2** were also reported [34,35]. An interesting example is a La^{III} complex, which is isostructure with complex **2** [36].

The non-covalent interactions have an important role in self-association of the crystal system. Hydrogen bonding is an interesting feature of the structure of this complex. The H-bonds with the D···A distances as short as 2.481(3) Å form an infinite network through the crystal. The interactions of uncoordinated water molecules increase

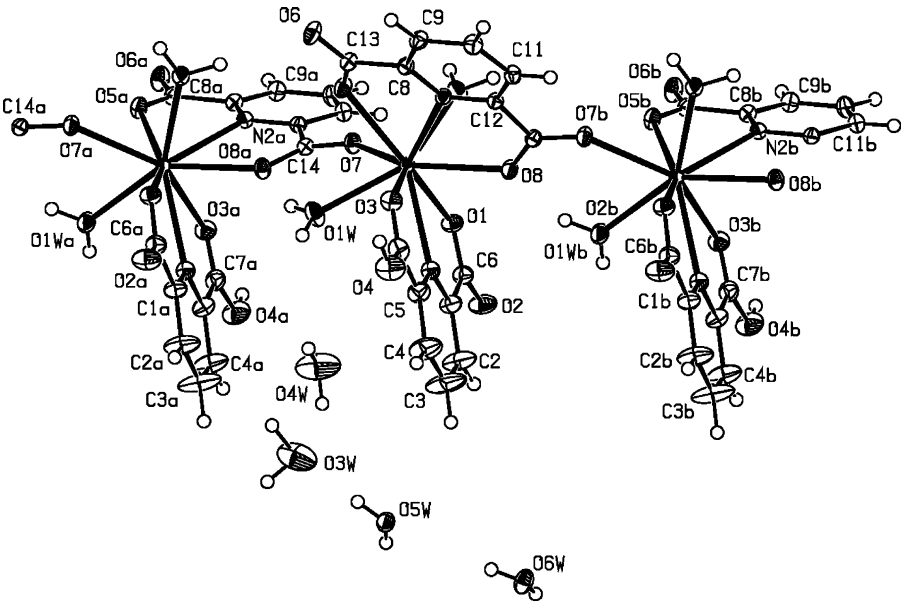


Fig. 3. Structure of the complex **2**.

the number of hydrogen bonds in the crystal lattice. The collection of all hydrogen bonds including those of coordinated water molecules and carboxylate oxygens results in formation of an impressive network through the whole crystal system. Fig. 4 shows the precise arrays of H-bonds of water and carboxylate oxygen atoms in the crystal lattice (all other atoms are omitted for clarity).

*3.5. Solution studies of complexes **1** and **2***

In preliminary experiments, the fully protonated forms of pydc and phen, as the building blocks of the self-associated system, were titrated with a standard KOH aqueous solution, to obtain some information about their protonation constants, K_n^{H} ($K_n^{\mathrm{H}} = [\mathrm{H}_m\mathrm{L}]/[\mathrm{H}_{(m-n)}\mathrm{L}][\mathrm{H}]^n$, the charges are omitted for simplicity) calculated by fitting

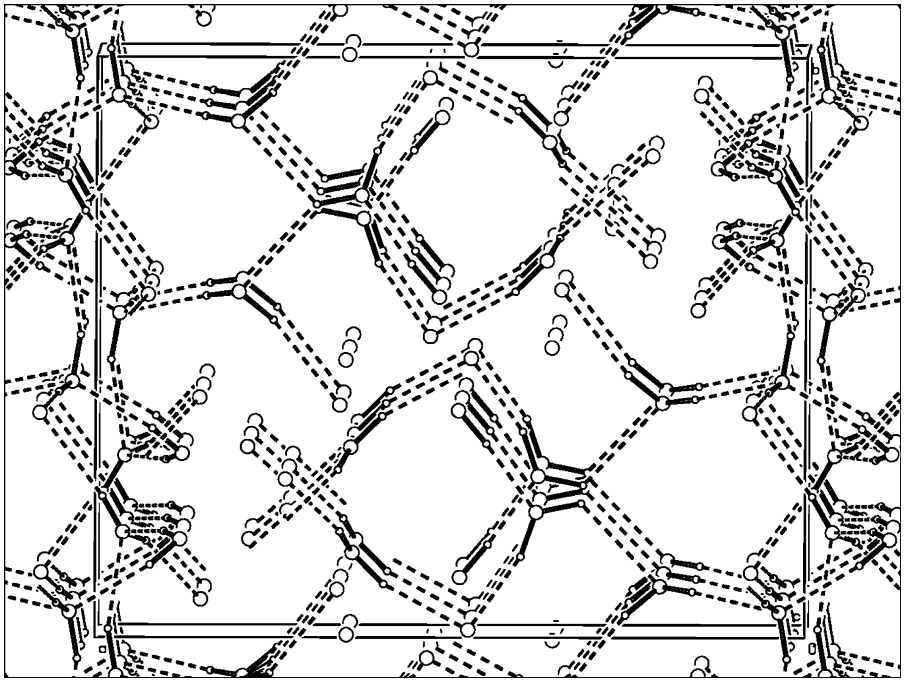


Fig. 4. Hydrogen bonding network of complex **2**, all atoms except those of water molecules and oxygens of carboxyl groups are omitted for clarity.

Table 4
Selected bond lengths (Å) and angles (°) for complex **2**

Ce(1)–O(1)	2.5006(14)	Ce(1)–O(1W)	2.4959(15)
Ce(1)–O(3)	2.5619(14)	Ce(1)–O(2W)	2.4652(14)
Ce(1)–O(5)	2.5339(14)	Ce(1)–N(1)	2.6377(17)
Ce(1)–O(7)	2.4924(13)	Ce(1)–N(2)	2.6376(15)
Ce(1)–O(8)	2.5500(13)		
O(1)-Ce(1)–O(3)	122.60(5)	O(8)–Ce(1)–N(2)	61.12(4)
O(1)-Ce(1)–O(5)	153.30(5)	O(8)–Ce(1)–O(3)	82.75(5)
O(1)-Ce(1)–O(8)	75.79(5)	O(8)–Ce(1)–N(1)	72.49(5)
O(1)-Ce(1)–N(1)	61.66(5)	O(1W)–Ce(1)–O(1)	98.32(5)
O(1)-Ce(1)–N(1)	61.66(5)	O(1W)–Ce(1)–O(3)	71.49(5)
O(1)-Ce(1)–N(2)	135.20(5)	O(1W)–Ce(1)–O(5)	78.39(5)
O(3)-Ce(1)–N(1)	61.20(5)	O(1W)–Ce(1)–O(8)	145.07(5)
O(3)-Ce(1)–N(2)	65.81(5)	O(1W)–Ce(1)–N(1)	74.52(5)
O(5)-Ce(1)–O(3)	81.89(5)	O(1W)–Ce(1)–N(2)	123.72(5)
O(5)-Ce(1)–O(8)	121.63(4)	O(2W)–Ce(1)–O(1)	80.28(5)
O(5)-Ce(1)–N(1)	139.42(5)	O(2W)–Ce(1)–O(3)	140.87(5)
O(5)-Ce(1)–N(2)	61.18(4)	O(2W)–Ce(1)–O(5)	86.13(5)
O(7)-Ce(1)–O(1)	75.74(5)	O(2W)–Ce(1)–O(7)	72.02(5)
O(7)-Ce(1)–O(3)	139.86(5)	O(2W)–Ce(1)–O(8)	72.25(5)
O(7)-Ce(1)–O(5)	78.24(5)	O(2W)–Ce(1)–O(1W)	141.62(5)
O(7)-Ce(1)–O(8)	137.24(5)	O(2W)–Ce(1)–N(1)	133.03(5)
O(7)-Ce(1)–O(1W)	70.54(5)	O(2W)–Ce(1)–N(2)	75.75(5)
O(7)-Ce(1)–N(1)	118.90(5)	N(1)–Ce(1)–N(2)	111.88(5)
O(7)-Ce(1)–N(2)	129.16(5)		
C(2)-C(1)–C(6)–O(1)	178.6(2)	C(4)–C(5)–C(7)–O(4)	3.6(3)
C(2)-C(1)–C(6)–O(2)	−1.2(4)	C(9)–C(8)–C(13)–O(5)	179.90(18)
C(4)-C(5)–C(7)–O(3)	−176.8(2)	C(9)–C(8)–C(13)–O(6)	1.3(3)
O(1)-Ce(1)–O(5)–C(13)	−154.35(14)	O(3)–Ce(1)–O(5)–C(13)	47.57(15)

the corresponding potentiometric data to the program BEST [29].

The protonation constants for pydc and phen and the equilibrium constants for the reaction of pydc and phen in aqueous solution were reported in our previous paper [26]. The stochiometry and stability of In^{III} and Ce^{III} complexes with pydc and phen were determined, no measurable interaction between Ce^{3+} and phen was observed. The results are summarized in Table 5.

In order to determine the stoichiometry and stability of the In^{III} and Ce^{III} complexes with the pydc–phen association in aqueous solution, the equilibrium

Table 5
Hydrogen bonds for complex **2**

D–H	*d*(D–H)	*D*(H···A)	⟨DHA	*d*(DA)	A
O1W–H1A	0.8600	1.8700	163.00	2.699(2)	O2[a]
O1W–H1B	0.9000	1.8500	158.00	2.705(2)	O8[b]
O2W–H2A	0.9800	1.7500	167.00	2.720(2)	O5W[c]
O2W–H2B	0.8600	1.8700	165.00	2.704(2)	O6W[d]
O3W–H3A	0.9300	2.1000	168.00	3.007(3)	O6W[b]
O3W–H3B	0.9900	2.1800	132.00	2.935(3)	O1[a]
O4W–H4A	0.8900	2.2100	122.00	2.793(3)	O3W
O4W–H4B	0.9100	1.7600	161.00	2.632(3)	O2[a]
O4–H4O	0.8400	1.6400	175.00	2.481(3)	O4W[a]
O5W–H5A	0.8400	2.0700	159.00	2.868(2)	O5[a]
O5W–H5B	0.8100	2.0400	172.00	2.844(2)	O6[e]
O6W–H6A	0.9100	2.0200	152.00	2.855(2)	O5W[f]
O6W–H6B	0.8400	1.8600	174.00	2.697(2)	O6[g]
C9–H9A	0.9500	2.6000	156.00	3.487(2)	O5W[d]

[a] $1-x, 1/2+y, 1/2-z$.
[b] $x, 1/2-y, -1/2+z$.
[c] $1-x, 1-y, 1-z$.
[d] $1+x, y, z$.
[e] $-1+x, y, z$.
[f] $x, -1+y, z$.
[g] $1-x, -1/2+y, 1/2-z$.

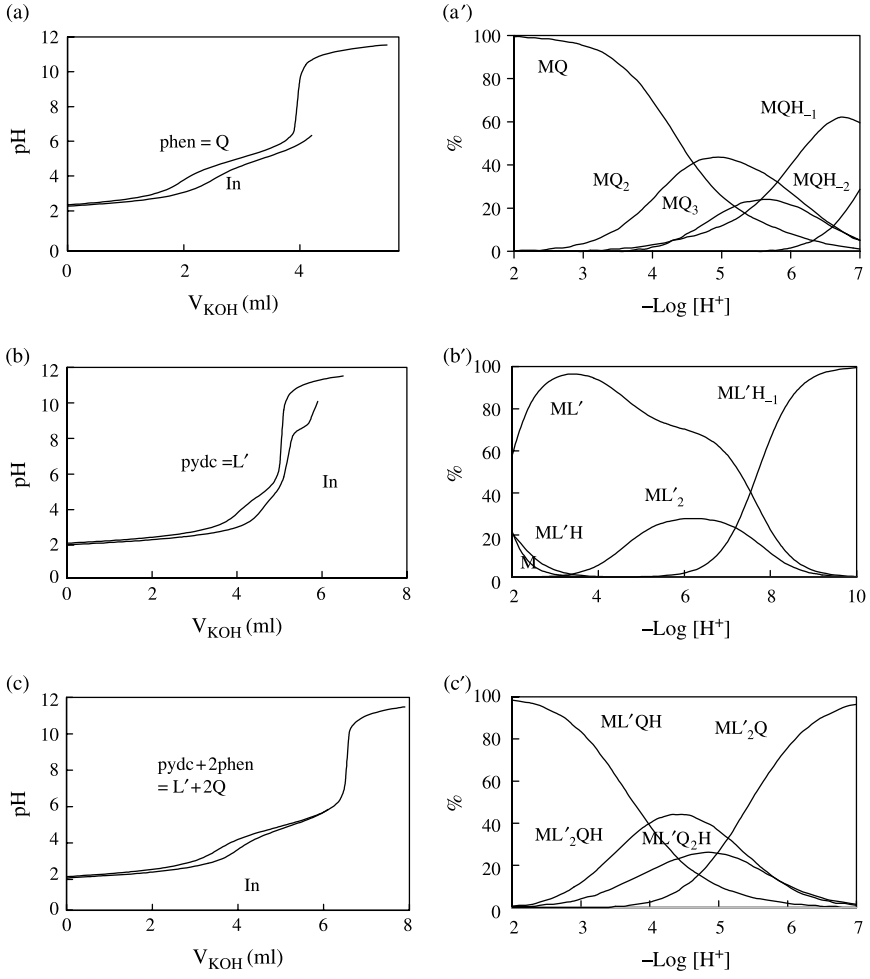


Fig. 5. Potentiometric titration curves for phen(Q)(a), pydc(L′)(b), and pydc–2phen (L′–2Q) (c) in the absence and presence of In^{3+} ion with KOH 0.099 M at 25 °C and $\mu = 0.1$ M KNO_3 and the corresponding distribution diagrams(a′, b′ and c′).

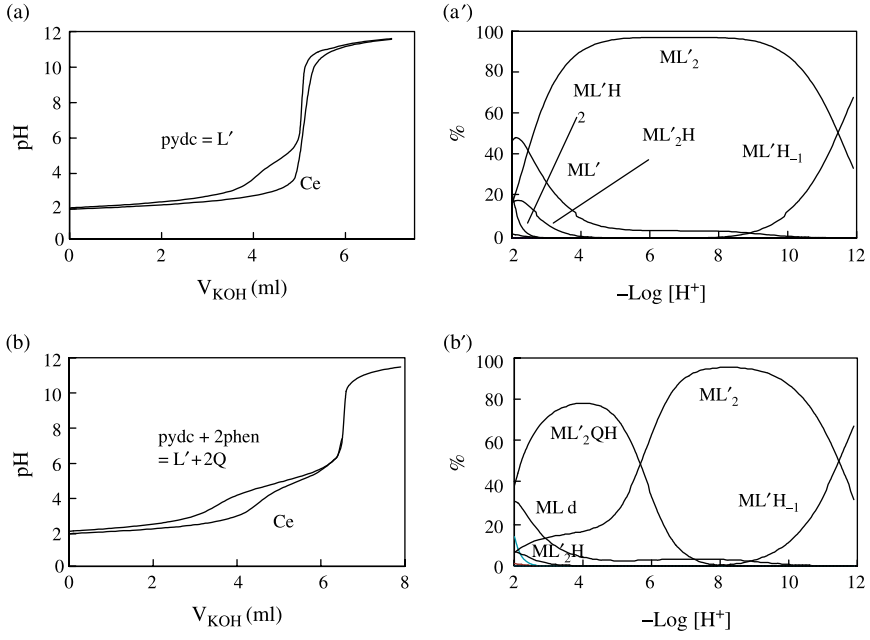


Fig. 6. Potentiometric titration curves for pydc(L′)(a), and pydc–2phen (L′-2Q) (b) in the absence and presence of Ce^{3+} ion with KOH 0.099 M at 25 °C and $\mu = 0.1$ M KNO_3 and the corresponding distribution diagrams(a′ and b′).

Table 6
Overall stability constant in pydc/phen/M^{3+}/H^+ binary and ternary systems

System	m	l'	q	h	Log β	Max (%)	At pH
Pydc	0	1	0	1	4.82	91.6	3.5
	0	1	0	2	6.96	57.9	2.0
Phen	0	0	1	1	5.02	99.9	2.0
In^{3+}-pydc	1	1	0	0	6.65	46.2	3.3
	1	1	0	1	8.26	9.9	2.0
	1	2	0	0	9.34	13.3	6.0
	1	2	0	1	11.57	Negligible	–
	1	1	0	−1	−0.83	47.9	10.5
Ce^{3+}-pydc	1	1	0	0	8.79	47.7	2.1
	1	1	0	1	9.47	2.0	2.0
	1	1	0	2	12.45	20.8	2.0
	1	2	0	0	14.56	97.0	6.0
	1	2	0	1	16.59	17.1	2.2
	1	1	0	−1	−0.09	Negligible	–
In^{3+}-phen	1	0	1	0	10.62	99.4	2.0
	1	0	2	0	13.64	43.6	5.0
	1	0	3	0	16.05	24.1	5.7
	1	0	1	−1	5.29	62.0	6.8
	1	0	1	−2	−2.02	–	–
In^{3+}-pydc-phen	1	1	1	0	17.36	Negligible	–
	1	1	1	1	26.33	98.4	2.0
	1	1	2	0	19.72	Negligible	–
	1	1	2	1	29.47	26.1	4.8
	1	2	1	0	25.12	99.4	>7.8
	1	2	1	1	30.25	44.1	4.2
Ce^{3+}-pydc–phen	1	2	1	1	22.66		4.0

potentiometric pH titration profiles of pydc, phen and their 1:2 mixture (i.e. pydc + 2phen) were obtained in the absence and presence of the metal ions, and the results are shown in Figs. 5 and 6. The cumulative stability constants for the resulting In^{3+} and Ce^{3+} ion complexes, β_{mlqh}, are defined by Eq. (1) (charges are omitted for simplicity)

$$m\mathrm{M} + l\mathrm{L}' + q\mathrm{Q} + h\mathrm{H} \rightleftharpoons \mathrm{M}_m\mathrm{L}'_l\mathrm{Q}_q\mathrm{H}_h$$

$$\beta_{mlqh} = \frac{[\mathrm{M}_m\mathrm{L}'_l\mathrm{Q}_q\mathrm{H}_h]}{[\mathrm{M}]^m[\mathrm{L}']^l[\mathrm{Q}]^q[\mathrm{H}]^h} \quad (1)$$

where M is metal ion, L′ is pydc, Q is phen and H is proton, and m, l, q and h are the respective stoichiometric coefficients. Since the ligand and complex activity coefficients are unknown, the β_{mlqh} values are defined in terms of concentrations. The errors are minimized using a high constant ionic strength (0.1 M KNO_3) and low ligand concentration (in the order of 10^{-3} M).

The cumulative stability constants were evaluated by fitting the corresponding pH titration curves to the program BEST and the resulting values for the most likely species in aqueous solutions are also included in Table 6. The corresponding species distribution diagrams for pydc, phen and their mixture in the presence of In^{3+} ion and those for pydc and pydc + 2phen with Ce^{3+} ion are shown in Figs. 5 and 6, respectively.

As it is seen from Table 6 and Figs. 5 and 6, the most likely species in the case of In-pydc(L′) and In-phen(Q) systems are: InL′, InL'_2, InL′H, InL′OH, InQ, InQ_2, InQ_3, InQOH and $InQ(OH)_2$. In the case of Ce-pydc(L′) system, the species CeL′, CeL'_2, CeL′H, CeL'_2H and CeL′OH were observed. In the case of pydc + 2phen mixture, the most likely indium adducts are InHL′Q, InL'_2Q, $InHL'_2Q$ and $InHL'Q_2$, while in the presence of cerium, only one tertiary species ($CeHL'_2Q$) was observed at low pH values. It is interesting to note that, among the above mentioned species existing in aqueous solution, the stoichiometries of the InHL′Q (98% at pH 2) and CeL'_2H (17.1% at pH 2.2) are in close agreement with those of the isolated $[In_2SO_4(pydc)_2(phen)_2(H_2O)_2]\cdot 5.5H_2O$ and $\{[Ce(pydc)(pydcH)(H_2O)_2\cdot 4H_2O\}_n$, respectively.

4. Conclusion

We have demonstrated that the proton transfer compound, LH_2 can be used as an appropriate starting material to synthesize a variety of interesting metal–organic compounds, showing different complexation behavior of this proton transfer system as discussed previously. Formation of Ce^{III} and In^{III} complexes in solid state are examples of contribution of one and two fragments of LH_2 to the complexation, respectively. Different non-covalent interactions such as ion-pairing, π–π stacking and hydrogen bonding play important roles in the construction of extended

networks in the crystal systems as can be observed in In^{III} and Ce^{III} complexes. The formation of two In^{III} and Ce^{III} complexes in solution with stoichiometries very close to those of the solid state is strongly supported by the results of the potentiometric pH titration studies in aqueous solutions.

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