Published in European Journal of Inorganic Chemistry 2010, issue 21, 3365-3371, 2010
which should be used for any reference to this work

The Adaptable Coordination Chemistry of 6-Chloro-2-(quinolin-2-yl)-2,4-dihydro-1*H*-benzo[*d*][1,3]oxazine Towards Zinc(II) and Mercury(II)

G. Attilio Ardizzoia,[a] Stefano Brenna,*[a] and Bruno Therrien[b]

[a] Dipartimento di Scienze Chimiche e Ambientali, Università dell'Insubria, via Valleggio 11, 22100 Como, Italy
Fax: +39-031-2386119, E-mail: stefano.brenna@uninsubria.it
[b] Service Analytique Facultaire, Université de Neuchâtel, Case Postale 158, 2009, Neuchâtel, Switzerland

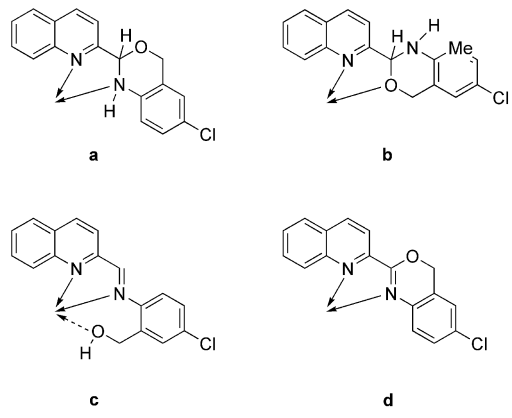
Keywords: Polydentate ligands / Coordination modes / N ligands / N,O ligands / Zinc / Mercury

The coordination chemistry of 6-chloro-2-(quinolin-2-yl)-2,4-dihydro-1*H*-benzo[*d*][1,3]oxazine (**L**H_2) towards zinc and mercury has been explored. The ligand exhibits high versatility and provides different environments to the metal centre as a function of its diverse coordination modes. In one of the isolated and characterized complexes, [Zn(**L**^{OH})Cl_2], the zinc centre is found pentacoordinated with the ligand present in an iminic "open" structure. The oxidized form, which contains the 4*H*-benzo[*d*][1,3]oxazine part (**L**), is also encountered in [Zn(**L**)Cl_2], whereas the crystal structure of the trinuclear compound [Hg_3(**L**H_2)$_2Cl_6$] shows the ligand **L**H_2 in its original arrangement.

Introduction

Heteropolydentate ligands represent an important tool that allows for the design of suitable coordination compounds.[1] Among others, 1,3-oxazine-based polydentate ligands have been demonstrated to be very useful. They showed high versatility together with remarkable properties when coordinated to transition metals, and their catalytic efficiency was usually proven to be higher when compared to the more extensively used 1,3-oxazolines. Singh et al. reported on vanadium and manganese complexes that contained bidentate *N*,*O*-oxazine ligands,[2] whereas the catalytic activity of palladium complexes with bidentate *N*,*P*-oxazine ligands has also been documented.[3] Moreover, the crystal structure of a zinc(II) complex that contains the same *N*,*P*-oxazine species has been described.[4] Commonly, strong donation from the metal centre to the π* orbitals of the oxazine ring has been invoked to justify these uncommon performances.[5]

This prompted us to investigate the coordination behaviour of the polydentate ligand 6-chloro-2-(quinolin-2-yl)-2,4-dihydro-1*H*-benzo[*d*][1,3]oxazine (**L**H_2). This ligand could in principle reveal a broad range of coordination modes, thereby providing the metal centre with a variety of coordination environments (e.g., *N*,*N*; *N*,*N*,*O*; *N*,*O*; see Scheme 1). We previously explored the coordination chemistry of species **L**H_2 towards copper(I) and copper(II) centres.[6] There, two different coordination modes were encountered, namely, an *N*,*NH* coordination by use of the quinolinic sp^2 nitrogen and the sp^3 nitrogen of the dihydrooxazine moiety, and a *N*,*N* coordination in which both the donor atoms were sp^2 nitrogen. Herein, we continue the investigation and report a study on the coordination chemistry of **L**H_2 towards zinc and mercury. In the course of this study, **L**H_2 displayed a further iminic "open" structure, with an *N*,*N*,*O* coordination to the zinc centre, thus resulting in a pentacoordinate species.



Scheme 1. Potential coordination modes of ligand **L**H_2 (**a**: *N*,*NH*; **b**: *N*,*O*; **c**: open *N*,*N* or *N*,*N*,*O*; **d**: oxidized *N*,*N*).

The reactivity of this complex in the presence of bases, together with an X-ray structure determination of the synthesized complexes, are presented. Finally, a parallel survey on mercury(II) complexes allowed for the isolation and characterization of a trinuclear Hg^{II} compound.

Results and Discussion

The reaction at room temperature of **L**H_2 with $ZnCl_2$ (1:1) in methanol or acetonitrile results in the formation of a yellow solid. The infrared spectrum of the solid shows an

intense, large stretching band at 3319 cm^{-1}, firstly attributed to the N–H vibration. The very low solubility of this complex allowed NMR spectroscopic investigation only in [D_6]-DMSO: The ^{1}H NMR spectrum exhibits the typical roof pattern (quartet centred at δ = 4.98 ppm) of the CH_2O moiety as observed in the free ligand **L**H_2, together with a doublet at δ = 5.78 ppm (^3J = 2.92 Hz) assigned to the C*H* fragment. Consequently, according to elemental analysis and spectroscopic data, the compound was initially formulated as [Zn(**L**H_2)Cl_2], with the ligand **L**H_2 coordinated in the *N*,*NH* mode (Scheme 1, **a**) and the metal was assumed to be tetrahedral. Unexpectedly, the structure determination by means of X-ray single-crystal diffraction revealed a pentacoordination to the metal centre with the ligand present in the iminic (open) form (Scheme 1, **c**). The molecular structure of **1** with the corresponding atom labelling scheme is given in Figure 1 together with selected bond lengths and angles.

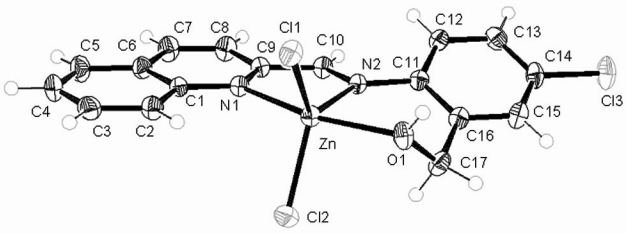
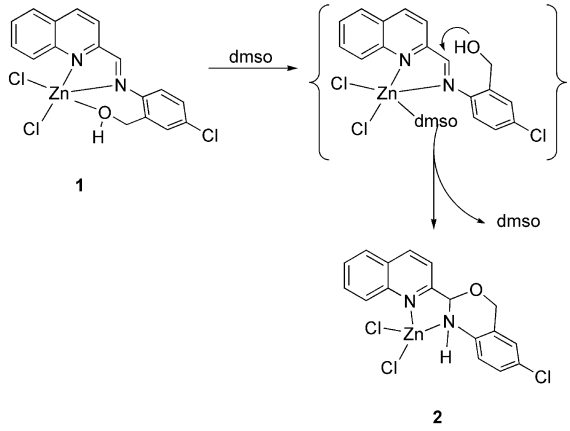


Figure 1. ORTEP drawing of **1** at 50% probability level ellipsoids. Selected bond lengths [Å] and angles [°]: Zn–N1 2.170(2), Zn–N2 2.148(2), Zn–Cl1 2.2742(10), Zn–Cl2 2.2418(11), Zn–O1 2.171(2), N1–C1 1.368(3), N1–C9 1.331(3), N2–C10 1.276(3), N2–C11 1.437(3), O1–C17 1.432(3); N1–Zn–N2 77.80(7), N1–Zn–O1 160.85(6), N2–Zn–O1 83.06(7), Cl1–Zn–Cl2 119.51(3), Cl1–Zn–N2 122.08(6), Cl2–Zn–N2 118.12(6).

The **L**H_2 molecule behaves in this case as an *N*,*N*,*O*-tridentate ligand and coordinates to the zinc centre by means of the two nitrogen atoms [Zn–N distances being 2.170(2) and 2.148(2) Å] and the oxygen of the pendant CH_2OH group [Zn–O distance: 2.171(2) Å]. Pentacoordination of zinc is not unusual and occurs especially in some structural motifs of enzymes active sites; however, to date only a few cases have been reported in the Cambridge Structural Database for compounds with a $ZnCl_2$ attached to two nitrogen atoms and an OH function.[7] In compound **1**, the Addison parameter[8] presents a value of τ = 0.65, thereby suggesting that the real coordination polyhedron is about halfway between a square pyramidal and a trigonal bipyramidal geometry, with a little preference for the latter. Two neighbouring molecules form in the solid state a weak hydrogen-bonded dimer (see the Supporting Information). The Cl1–O hydrogen-bond lengths are 3.079(2) Å with O–H···Cl1 angles of 159(3)°; the total distance between the two Zn atoms is 6.149(3) Å.

Herein, such a coordination mode can be rationalized if one considers the ring opening of **L**H_2, which is responsible for the formation of its new iminic arrangement (indicated hereafter for brevity as **L**^{OH}) in a process analogous to one already encountered for some pyridinyloxazolidine ligands.[9] Most probably, the presence of a rather acidic ion (due to the relatively small size) like zinc drives the ligand opening to the formation of a Zn–OH bond. The resulting complex is then better described as [Zn(**L**^{OH})Cl_2] (**1**). The adsorption at 3319 cm^{-1} in the infrared spectrum of **1**, firstly attributed to the N–H stretching of coordinated **L**H_2, is most correctly assigned to the O–H group.

To justify the ^{1}H NMR spectroscopic data discussed above, in which the presence of the ligand in the original closed form **L**H_2 is revealed, one should assume the occurrence of a process in which dimethylsulfoxide is involved (Scheme 2).



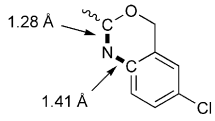
Scheme 2. Probable **1**→**2** interconversion mechanism mediated by DMSO.

Most likely, dissolving [Zn(**L**^{OH})Cl_2] (**1**) in [D_6]DMSO caused the breaking of the Zn–OH bond through the coordination of a DMSO molecule to the zinc centre, thus generating a zinc complex that contains the ligand coordinated in the iminic form with a free pendant CH_2OH arm. The latter immediately underwent ring closing and converted into the most stable closed form of **L**H_2 coordinated in the *N*,*NH* mode. This species was effectively detected during the NMR spectroscopic investigation, as evidenced by the AB system assigned to the CH_2O moiety.

Conversely, the reaction of $ZnCl_2$ with **L**H_2 in the presence of a base (Et_3N) results in the formation of a pale yellow solid. The infrared spectrum shows a broad adsorption at about 3420 cm^{-1}, whereas in the ^{1}H NMR spectroscopy conducted in $(CD_3)_2CO$ an AB system attributed to the CH_2O moiety [centred at δ = 4.98 ppm (J_{AB} = 14.9 Hz)] is observed, and the C*H* proton appears as a doublet centred at δ = 5.77 ppm, the multiplicity of which originates from the coupling with the N–H proton (^2J = 2.8 Hz). The coordination to the zinc centre clearly forces the ligand in a sort of "blocked position", thus preventing the rotation along the C–C bond between the quinoline and the oxazine moieties. Furthermore, after treatment with D_2O and the consequent disappearance of the N–H coupling, the doublet becomes a singlet. On the basis of these observations, the yellow compound is formulated as [Zn(**L**H_2)Cl_2] (**2**).[10] Coloured zinc complexes (bearing colourless ligands) are quite rare, due the impossibility of

d–d transitions in a closed-shell ion such as zinc(II). However, a few examples are present in the literature, such as for the mixed-ligand complexes of phenanthroline or bipyridyl and 8-hydroxyquinoline or derivatives of 8-amino-2-methylquinoline.[11–13] As in our case, the yellow colour can be explained by assuming charge transfer from the metal to a low-energy empty molecular orbital of the ligand. On the contrary, the yellow colour of **1** can be likely attributed to π–π* transitions within the coordinated iminic ligand ($\mathbf{L}^{OH}$).

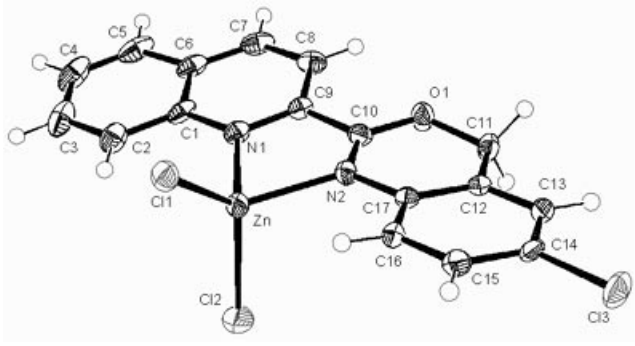
In species **2**, the ligand $\mathbf{L}H_2$ is coordinated in an *N*,*NH* fashion (i.e., in the same mode found in solutions of **1** in DMSO). It is worth noting that the same species **2** can also be isolated by treatment of the pentacoordinate species **1** with Et_3N in methanol or acetonitrile. Reasonably, the role of Et_3N in this reaction is the same as for DMSO as discussed above (i.e., blocking a coordination site on the zinc), thus hampering the coordination of the OH group and hence forcing the ligand closure. To support this assumption, the reaction was conducted by employing *N*-cyclohexyl-*N*-ethylcyclohexanamine instead of Et_3N. Because of the higher steric hindrance, $(C_6H_{11})_2NC_2H_5$ behaves essentially as a noncoordinating amine. Indeed, complex **1** (IR evidence) is quantitatively formed. The strict similarity among the ^{1}H NMR spectra of **2** and **1** (in DMSO) seems to suggest the leaving of coordinated DMSO from the intermediate species in Scheme 2 and the existence, also in DMSO (or in the presence of Et_3N), of the tetracoordinate species **2**. However, the presence in solution of penta- (or hexa-)coordinated zinc(II) species that bear ancillary DMSO (or Et_3N) ligands cannot in principle be excluded. Unfortunately, all attempts to grow single crystals of **2** failed, but in one of the several efforts, we isolated a crop of yellow crystals that were subjected to X-ray analysis. The molecular structure disclosed a marked difference between the two C–N distances in the oxazine portion of the ligand (see Scheme 3).



Scheme 3. Significant differences in C–N distances in the structurally characterized complex.

In fact, although the C–N distance of 1.412(3) Å agreed with a single C–N bond, the second C–N distance [1.281(3) Å] is significantly shorter and therefore is attributed to a double C=N bond. This could be rationalized by considering an oxidative dehydrogenation of the 2,4-dihydro-1*H*-benzo[*d*][1,3]oxazine portion of ligand $\mathbf{L}H_2$ to the corresponding 4*H*-benzo[*d*][1,3]oxazine derivative **L**, thus leading to complex [Zn(**L**)Cl_2] (**3**) (Scheme 4).

To confirm this finding, the direct synthesis of **3** was performed. First, ligand $\mathbf{L}H_2$ was oxidized with $KMnO_4$ to form **L** following a procedure previously reported for dihydroisoquinolines.[14] Subsequently, species **L** was reacted with $ZnCl_2$ in a 1:1 molar ratio in methanol. From the resulting suspension a yellow solid was isolated, formulated as [Zn(**L**)Cl_2] (**3**) on the basis of analytical and spectroscopic data. In particular, the ^{1}H NMR spectroscopic investigation ([D_6]DMSO) revealed the presence of a singlet centred at δ = 5.56 ppm (CH_2) together with the set of quinoline protons, whereas the ^{13}C NMR spectrum showed a resonance at δ = 65.9 ppm attributed to the endocyclic CH_2 fragment and a resonance at δ = 150.08 ppm assigned to the *C*=N carbon. Eventually, the molecular structure of complex **3** was confirmed by single-crystal diffraction analysis and the structural information was in total agreement with those previously acquired. An ORTEP[15] drawing of **3** including the atom labelling scheme is given in Figure 2 together with selected bond lengths and angles.



Scheme 4. Dehydrogenation of 2,4-dihydro-1*H*-benzo[*d*][1,3]-oxazine to 4*H*-benzo[*d*][1,3]oxazine coordinated to a zinc(II) centre.

Figure 2. ORTEP drawing of **3** at 50% probability level ellipsoids. Selected bond lengths [Å] and angles [°]: Zn–Cl1 2.1911(7), Zn–Cl2 2.2162(8), Zn–N1 2.082(2), Zn–N2 2.050(2), N1–C1 1.367(3), N1–C9 1.324(3), N2–C10 1.281(3), N2–C17 1.412(3); N1–Zn–N2 80.18(8), Cl1–Zn–Cl2 118.43(3), Cl1–Zn–N1 116.26(6), Cl1–Zn–N2 118.10(6), Cl2–Zn–N1 111.97(6), Cl2–Zn–N2 105.56(6).

The molecular structure of **3** shows the zinc atom to be in a slightly distorted tetrahedral geometry. The geometrical parameters around the zinc atom are comparable to those found in analogous complexes [Zn($C_{10}H_8N_2$)Cl_2][16] and [Zn($C_{20}H_{20}N_2$)Cl_2].[17] Despite coordination of the imine nitrogen atom to the metal centre, the imine function preserves its C=N double bond character with a C–N distance of 1.281(3) Å. In the crystal packing of **3**, the molecules of **3** form a network through π-stacking interactions between parallel aromatic rings of adjacent complexes. Different types of π–π stacking interactions are involved in the multimeric system, the strongest being a face-to-face arrangement between quinoline moieties (see the Supporting Information). The centroid–centroid distances are 3.574 Å.

Oxidative dehydrogenation is rare for a ligand coordinated to a nonredox metal like zinc, and to the best of our

knowledge only a single example of such a reaction has been reported to date.[18] Therefore, we decided to better examine the dehydrogenation process, already encountered by us with copper(II) complexes that bear the same ligand.[6] In that case, the process involved the concomitant reduction of the two copper centres of the starting dimer $[Cu^{II}(\mathbf{L}H_2)Cl_2]_2$, thus giving $[Cu^{I}(\mathbf{L})Cl]$ and $[Cu^{I}(\mathbf{L}H_2)Cl]$ as a mixture of products. Here, due to the presence of two chlorido ligands bound to the zinc centre, the reduction of the metal is obviously excluded. Therefore, the only possibility to justify the oxidation of ligand $\mathbf{L}H_2$ into **L** is a reaction that requires molecular oxygen as oxidant. The synthesis of **3** from **1** and Et_3N was then performed under a constant stream of oxygen. As expected, it was not possible to isolate **2**, and all the spectroscopic data of the product are in total agreement with those of complex **3**.

Finally, we could reasonably assume that some adventitious oxygen was present during the slow growth of single crystals of **2**. As mentioned above, any subsequent attempt to grow single crystals of **2** failed, thus preventing the possibility of an additional comparison of the zinc complexes. However, crystallographic evidence of the *N*,*NH*-coordination mode (Scheme 1, **a**) of $\mathbf{L}H_2$ was obtained conducting the reaction between $\mathbf{L}H_2$ and $HgCl_2$.

The choice turned to mercury because of its marked different hard–soft properties with respect to zinc. The first alternative to zinc within Group 12 was represented by cadmium. Nevertheless, its use was excluded as a consequence of its toxicity (which reduces its attractiveness) and especially because, relative to zinc, its hard–soft character does not differ as markedly as it would be with mercury. In fact, due to its longer radius, Hg^{2+} has a lower charge density with respect to Zn^{2+}, thus showing a softer acidic character (absolute hardness[19] (eV): Zn^{2+} 10.8, Cd^{2+} 10.3, Hg^{2+} 7.7). The consequent less oxyphilic inclination could prevent ligand opening into the $\mathbf{L}^{OH}$ species.

The reaction was originally performed using a 1:1 molar ratio between $HgCl_2$ and $\mathbf{L}H_2$, with the aim of obtaining the $[Hg(\mathbf{L}H_2)Cl_2]$ derivative. Instead, quite unexpectedly, the trinuclear compound $[Hg_3(\mathbf{L}H_2)_2Cl_6]$, (**4**) is obtained in quantitative yields. Its infrared spectrum shows a stretching frequency at 3210 cm^{-1} assigned to the N–H group, the presence of which is afterwards corroborated by a broad resonance at δ = 6.33 ppm in the ^1H NMR spectrum in $(CD_3)_2CO$. The characteristic aliphatic signals of ligand $\mathbf{L}H_2$ appear as a singlet at δ = 5.92 ppm (C*H*) and as an AB system (CH_2O) centred at δ = 5.11 ppm. The ^{13}C NMR confirms the incidence of the closed form of the ligand coordinating in the *N*,*NH*-bidentate mode (Scheme 1, **a**; see also the Exp. Section).

This feature, together with the trinuclear nature of compound **4**, was eventually confirmed by crystallographic analysis: In the complex, ligand $\mathbf{L}H_2$ is coordinated to the terminal tetrahedral mercury centres, whereas the central mercury atom is surrounded by four chloride anions in a square-planar geometry. Square-planar coordination geometries for Hg^{II} is rare, but have been observed previously.[20] The crystal structure of **4** is presented in Figure 3 together with selected bond lengths and angles.

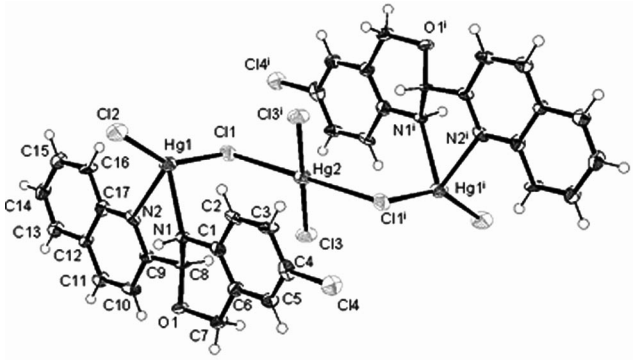


Figure 3. ORTEP drawing of **4** at 50% probability level ellipsoids. Selected bond lengths [Å] and angles [°]: Hg1–N1 2.514(10), Hg1–N2 2.426(8), Hg1–Cl1 2.352(3), Hg1–Cl2 2.324(3), Hg2–Cl1 3.114(3), Hg2–Cl3 2.283(3), N1–C1 1.458(14), N1–C8 1.448(11), N2–C9 1.324(15), N2–C17 1.365(14); Cl1–Hg1–Cl2 145.17(12), Cl1–Hg1–N1 100.6(2), Cl1–Hg1–N2 102.7(2), Cl2–Hg1–N1 106.9(2), Cl2–Hg1–N2 107.2(2), N1–Hg1–N2 68.0(3), Hg1–Cl1–Hg2 103.32 (11), Cl1–Hg2–Cl3 84.85(10) (i: $-x$, $2-y$, $2-z$).

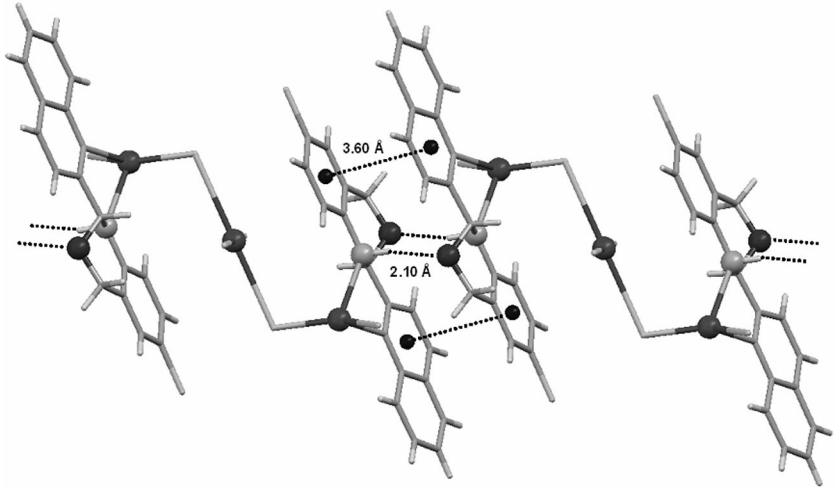


Figure 4. Main interactions in the crystal packing of **4**.

In the crystal packing of **4**, slipped-parallel π-stacking interactions are observed between adjacent complexes, which involve the chlorophenyl and pyridyl rings of the $\mathbf{L}H_2$ ligands: The centroid–centroid distance being 3.60 Å. The distance observed between the π–π interacting systems is in accordance with the theoretical value calculated for this stacking mode.[21] Moreover, the N–H function of $\mathbf{L}H_2$ forms a strong hydrogen bond with a neighbouring oxygen atom: The N···O distance is 3.00(1) Å with an N–H···O angle of 167.9°. These interactions are summarized in Figure 4.

Conclusion

In summary, we investigated the coordination chemistry of 6-chloro-2-(quinolin-2-yl)-2,4-dihydro-1*H*-benzo[*d*][1,3]-oxazine ($\mathbf{L}H_2$) towards zinc(II) and mercury(II). In the course of this study, the ligand revealed a broad range of coordination modes, thus providing the metal centre with a variety of coordination environments. Indeed, it was possible to isolate and fully characterize $[Zn(\mathbf{L}^{OH})Cl_2]$ (**1**), in which the *N*,*N*,*O* arrangement of the ligand provided a pentacoordination to the zinc centre. This open form of $\mathbf{L}H_2$ underwent a ring-closing reaction of the oxazine moiety in the presence of Et_3N or a coordinating solvent such as DMSO. Furthermore, it could take part to an oxidative dehydrogenation process induced by molecular oxygen, thereby generating the oxidized form of $\mathbf{L}H_2$ (**L**). This latter was unequivocally identified by means of X-ray analysis in the complex $[Zn(\mathbf{L})Cl_2]$ (**3**), whereas the synthesis and characterization of the trinuclear compound $[Hg_3(\mathbf{L}H_2)_2Cl_6]$ (**4**) confirmed the *N*,*NH*-coordination mode of the nonoxidized closed species $\mathbf{L}H_2$.

Experimental Section

Materials and Measurements: All reactions were carried out under purified nitrogen using standard Schlenk techniques. The solvents were dried and distilled according to standard procedures prior to use. $ZnCl_2$ and $HgCl_2$, 2-quinolinecarbaldehyde, 2-amino-5-chlorobenzyl alcohol, triethylamine and *N*-cyclohexyl-*N*-ethylcyclohexanamine (Aldrich) were used as purchased. Ligand $\mathbf{L}H_2$ was prepared according to a well-established procedure.[6] Infrared spectra were recorded with a Shimadzu Prestige 21 FTIR instrument, NMR spectra were acquired with a Bruker 400 Avance instrument and elemental analyses were obtained with a Perkin–Elmer CHN Analyser 2400 Series II instrument.

$[Zn(\mathbf{L}^{OH})Cl_2]$ (1): Ligand $\mathbf{L}H_2$ (330 mg, 1.11 mmol) was added to a solution of $ZnCl_2$ (150 mg, 1.10 mmol) in methanol or acetonitrile (10 mL), and the resulting yellow suspension was stirred for 2 h at room temperature. Then the solid was filtered, washed with diethyl ether and dried under vacuum; yield 371 mg (78%). IR (nujol): $\tilde{\nu}$ = 3119 cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO, 25 °C): NMR spectroscopic features were identical to those obtained in $(CD_3)_2CO$ for complex **2** (see text for explanation). $C_{17}H_{13}Cl_3N_2OZn$ (433.07): calcd. C 47.15, H 3.03, N 6.47; found C 46.89, H 2.94, N 6.36. Single crystals suitable for X-ray analysis were obtained by slowly cooling a hot saturated solution of **1** in ethanol to room temperature.

$[Zn(\mathbf{L}H_2)Cl_2]$ (2): Ligand $\mathbf{L}H_2$ (330 mg, 1.11 mmol) was added to a solution of $ZnCl_2$ (150 mg, 1.10 mmol) in methanol (10 mL), and the yellow suspension stirred for 2 h at room temperature. Then Et_3N was added (160 μL, 1.15 mmol) and the suspension was stirred for a further 2 h. The solid was filtered, washed with diethyl ether and dried in vacuo; yield 410 mg (86%). IR (nujol): $\tilde{\nu}$ = 3421 (br.) cm^{-1}. ^1H NMR [400 MHz, $(CD_3)_2CO$, 25 °C]: δ = 4.98 [d, ^2J(H,H) = 14.8 Hz, 1 H, H_a part of an AB system -CH_2O], 5.21 (d, $^2J_{H,H}$ = 14.8 Hz, 1 H, H_b part of an AB system -CH_2O), 5.85 (d, $^2J_{H,H}$ = 3.6 Hz, 1 H, C–*H*), 6.32 (br. s, 1 H, N-H), 6.91 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 7.07 (s, 1 H), 7.10 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 2.3 Hz, 1 H), 7.66 (t, $^3J_{H,H}$ = 7.0 Hz, 1 H), 7.81 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.02 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H), 8.09 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H), 8.46 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.76 (m, $^3J_{H,H}$ = 6.1 Hz, $^4J_{H,H}$ = 1.7 Hz, 1 H) ppm. ^{13}C NMR [100 MHz, $(CD_3)_2CO$, 25 °C]: δ = 68.2 (*C*H_2O), 84.7 (*C*H), 119.1, 119.9, 123.5, 124.3, 125.1, 127.2, 127.8, 128.1, 128.7, 129.6, 130.1, 137.9, 140.0, 147.5, 156.8 ppm. $C_{17}H_{13}Cl_3N_2OZn$ (433.07): calcd. C 47.15, H 3.03, N 6.47; found C 47.43, H 2.99, N 6.71.

Synthesis of Ligand L: Solid $KMnO_4$ (267 mg, 1.69 mmol) and [18]crown-6 (45 mg, 0.170 mmol) were added to a solution of ligand $\mathbf{L}H_2$ (500 mg, 1.68 mmol) in CH_2Cl_2 (20 mL). The suspension was stirred at room temperature for 12 h, then it was filtered through Celite to remove MnO_2. The filtrate was washed with H_2O (2 × 20 mL), the organic phase was dried with Na_2SO_4, filtered and the solvents evaporated to dryness. The residue was repeatedly washed with diethyl ether to give a light-yellow solid; yield 323 mg (65%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.55 (s, 2 H, -CH_2O), 7.06 (s, 1 H), 7.27 (s, 1 H), 7.31 (s, 1 H), 7.62 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H), 7.77 (t, $^3J_{H,H}$ = 6.9 Hz, 1 H), 7.87 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H), 8.26 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 8.31 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.41 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 66.5 (*C*H_2O), 120.5, 123.9, 124.0, 126.7, 127.5, 127.9, 128.9, 129.1, 129.9, 130.4, 132.6, 136.6, 137.7, 147.6, 150.1, 156.5 ppm. $C_{17}H_{11}ClN_2O$ (294.74): calcd. C 69.28, H 3.76, N 9.50; found C 69.51, H 3.98, N 9.33.

$[Zn(L)Cl_2]$ (3): Ligand **L** (325 mg, 1.10 mmol) was added to a solution of $ZnCl_2$ (150 mg, 1.10 mmol) in methanol (10 mL). The resulting yellow suspension was stirred at room temperature for 2 h, then it was filtered and the solid was dried under vacuum; yield 337 mg (71%). ^1H NMR (400 MHz, [D_6]DMSO, 25 °C): δ = 5.56 (s, 2 H, -CH_2O), 7.29 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 7.32 (d, $^3J_{H,H}$ = 2.3 Hz, 1 H), 7.40 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 2.4 Hz, 1 H), 7.71 (dt, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H), 7.85 (dt, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H), 8.07 (dd, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.0 Hz, 1 H), 8.14 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 8.33 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H), 8.51 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D_6]-DMSO, 25 °C): δ = 65.9 (*C*H_2O), 120.7, 125.0, 125.5, 126.6, 128.4, 128.6, 128.9, 129.3, 130.0, 130.8, 131.7, 137.4, 138.1, 147.4, 150.1, 157.2 ppm. $C_{17}H_{11}Cl_3N_2OZn$ (431.03): calcd. C 47.37, H 2.57, N 6.50; found C 47.72, H 2.39, N 6.31. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a saturated solution of **3** in DMF.

$[Hg_3(\mathbf{L}H_2)_2Cl_6]$ (4): Ligand $\mathbf{L}H_2$ (330 mg, 1.11 mmol) was added to a solution of $HgCl_2$ (300 mg, 1.10 mmol) in methanol (10 mL). The suspension was stirred at room temperature for 2 h and was filtered. The yellow solid was then washed with diethyl ether and dried in vacuo; yield 423 mg (82%). ^1H NMR [400 MHz, $(CD_3)_2CO$, 25 °C]: δ = 5.00 (d, $^2J_{H,H}$ = 14.8 Hz, 1 H, H_a part of an AB system -CH_2O), 5.22 (d, $^2J_{H,H}$ = 14.9 Hz, 1 H, H_b part of an AB system -CH_2O), 5.92 (s, 1 H, C–H), 6.33 (br. s, 1 H, N–H), 6.91 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 7.07 (s, 1 H), 7.14 (dd, $^3J_{H,H}$ =

Table 1. Crystallographic and structure-refinement parameters for complexes **1**, **3** and **4**.

	1	**3**	**4**
Chemical formula	$C_{17}H_{13}Cl_3N_2OZn$	$C_{17}H_{11}Cl_3N_2OZn$	$C_{34}H_{26}Cl_8Hg_3N_4O_2$
Formula weight	433.01	431.00	1407.96
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
Crystal colour and shape	yellow block	yellow block	yellow block
Crystal size	$0.19\times0.17\times0.12$	$0.21\times0.20\times0.16$	$0.15\times0.14\times0.13$
a [Å]	8.542(2)	12.9244(10)	9.4605(15)
b [Å]	8.571(2)	8.3419(7)	10.1435(16)
c [Å]	12.231(4)	15.1907(12)	11.2617(19)
α [°]	98.55(4)		67.339(18)
β [°]	101.41(4)	92.688(9)	71.352(18)
γ [°]	98.24(3)		78.669(18)
V [Å^3]	854.1(4)	1636.0(2)	941.6(3)
Z	2	4	1
T [K]	173(2)	173(2)	173(2)
$D_{calcd.}$ [g cm^3]	1.684	1.750	2.483
μ [mm^{-1}]	1.913	1.997	12.805
Scan range [°]	$2.44<\theta<26.00$	$2.02<\theta<26.06$	$2.04<\theta<26.17$
Unique reflections	3119	3176	3481
Reflections used [$I>2\sigma(I)$]	2555	2261	2474
R_{int}	0.0305	0.0521	0.0727
Final R indices [$I>2\sigma(I)$][a]	0.0259, wR_2 0.0634	0.0280, wR_2 0.0583	0.0472, wR_2 0.1141
R indices (all data)	0.0352, wR_2 0.0661	0.0505, wR_2 0.0552	0.0681, wR_2 0.1263
Goodness of fit	0.960	0.870	0.913
Max., min. $\Delta\rho$ [e Å^{-3}]	0.591, –0.464	0.533, –0.461	2.905, –4.522

[a] Structures were refined on F_o^2: $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_c^2)^2]^{1/2}$, in which $w^{-1} = [\Sigma(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

8.5 Hz, $^4J_{H,H}$ = 2.4 Hz, 1 H), 7.68 (dt, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H), 7.84 (dd, $^3J_{H,H}$ = 8.6 Hz, $^4J_{H,H}$ = 1.4 Hz, 1 H), 7.86 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 8.04 (dd, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,H}$ = 1.3 Hz, 1 H), 8.16 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 8.50 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H) ppm. ^{13}C NMR [100 MHz, $(CD_3)_2CO$, 25 °C]: δ = 67.3 (CH_2O), 84.5 (*C*H), 117.1, 119.5, 121.2, 122.6, 125.0, 127.3, 127.5, 128.2, 128.6, 129.2, 130.3, 137.4, 141.8, 146.7, 158.0 ppm. $C_{34}H_{26}Cl_8Hg_3N_4O_2$ (1408.00): calcd. C 29.00, H 1.86, N 3.98; found C 29.12, H 2.04, N 3.81.

X-ray Crystallography: Crystals of complexes **1**, **3** and **4** were mounted on a Stoe Image Plate Diffraction system equipped with a φ circle goniometer, using Mo-K_α graphite-monochromated radiation (λ = 0.71073 Å) with φ range of 0 to 200°. The structures were solved by direct methods using the program SHELXS–97, whereas refinement and all further calculations were carried out using SHELXL-97.[22] The H atoms were located on a Fourier difference map or included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically using weighted full-matrix least-squares on F^2. In **4**, the residual electron densities greater than 1 e Å^{-3} are all located at less than 1 Å from the mercury atoms. Crystallographic details are summarized in Table 1. Figures 1, 2 and 3 were drawn with ORTEP-32.[15]

CCDC-765623 (for **1**), -765624 (for **3**) and -765625 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Hydrogen-bonded dimer of solid **1** (Figure S1) and π–π stacking interactions in complex **3** (Figure S2).

[1] D. Aguilà, E. Escribano, S. Speed, D. Talancón, L. Yermán, S. Alvarez, *Dalton Trans.* **2009**, 6610–6625, and references cited therein.

[2] K. Kandasamy, H. B. Singh, R. J. Butcher, J. P. Jasinski, *Inorg. Chem.* **2004**, *43*, 5704–5713.

[3] P. A. Evans, T. A. Brandt, *Tetrahedron Lett.* **1996**, *37*, 9143–9146.

[4] S. M. Lait, M. Parvez, B. A. Keay, *Tetrahedron: Asymmetry* **2004**, *15*, 155–158.

[5] R. F. Khairutdinov, K. Giertz, J. K. Hurst, E. N. Voloshina, N. A. Voloshin, V. I. Minkin, *J. Am. Chem. Soc.* **1998**, *120*, 12707–12713.

[6] G. A. Ardizzoia, S. Brenna, F. Castelli, S. Galli, N. Masciocchi, *Inorg. Chim. Acta* **2010**, *363*, 324–329.

[7] a) X.-X. Sun, C.-M. Qi, S.-L. Ma, H.-B. Huang, W.-X. Zhu, Y.-C. Liu, *Inorg. Chem. Commun.* **2006**, *9*, 911–914; b) A. Višnjevac, L. Tušek-Boži, M. Majerić-Elenkov, Z. Hameršak, H. Kooijman, E. De Clercq, B. Kojić-Prodic, *Polyhedron* **2002**, *21*, 2167–2177; c) J. K. Nag, P. K. Santra, C. Sinha, F.-L. Liao, T.-H. Lu, *Polyhedron* **2001**, *20*, 2253–2259.

[8] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.

[9] S. A. Cardile, M. C. Jennings, N. D. Jones, *Dalton Trans.* **2006**, 4672–4678.

[10] Ligand **L**H$_2$ in the form shown in Scheme 1(**a**) has a stereogenic centre in position 2 of the oxazine moiety. However, no attention was dedicated to a deeper understanding of any aspect related to chirality. Consequently, ligand **L**H$_2$ and the resulting complex **2** were always obtained as a racemic mixture.

[11] K. H. Reddy, Y. Lingappa, *J. Chem. Sci.* **1993**, *105*, 87–94.

[12] A. Furuhashi, H. Yokota, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3753–3754.

[13] X. L. Liu, Q. Y. Cheng, X. Yang, Z. W. Miao, W. Liu, F. M. Miao, *Chin. Chem. Lett.* **2001**, *12*, 563–564.

[14] A. T. Soldatenkov, A. V. Temesgen, N. M. Kolyadina, *Chem. Heterocycl. Compd.* **2004**, *40*, 537–560.
[15] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.
[16] M. A. Khan, D. G. Tuck, *Acta Crystallogr., Sect. C* **1984**, *40*, 60–62.
[17] H.-L. Cai, B. Liu, Z.-D. Lin, *Acta Crystallogr., Sect. E* **2008**, *64*, m1597.
[18] P. de Hoog, L. Durán Pachón, P. Gamez, M. Lutz, A. L. Spek, J. Reedijk, *Dalton Trans.* **2004**, 2614–2615.
[19] R. G. Parr, R. G. Pearson, *J. Am. Chem. Soc.* **1983**, *105*, 7512–7516.
[20] R. Haid, R. Gutmann, G. Czermak, C. Langes, W. Oberhauser, H. Kopacka, K.-H. Ongania, P. Brüggeller, *Inorg. Chem. Commun.* **2003**, *6*, 61–67.
[21] S. Tsuzuki, K. Honda, T. Uchimura, M. Mikami, K. Tanabe, *J. Am. Chem. Soc.* **2004**, *124*, 104–112.
[22] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.