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Zinc(II) complexes of putative obligate tetrahedrally co-ordinating pro-ligands

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An attempt to impose tetrahedral geometry on zinc(II) through use of bis(salicylideneamino)biphenyl pro-ligands has produced hydrolytically sensitive complexes. The single-crystal structures of [ZnL(EtOH)] [H_2L = 6,6′-dimethyl-2,2′-bis(salicylideneamino)biphenyl] [monoclinic, space group $P2_1/c$, a = 11.654(2), b = 11.753(2), c = 18.878(3) Å, β = 98.97(2)°, Z = 4] and its pro-ligand H_2L [monoclinic, space group $I2/c$, a = 13.911(2), b = 13.759(2), c = 12.015(2) Å, β = 94.836(10)°, Z = 4] have been determined. The co-ordination geometry at zinc is slightly distorted trigonal bipyramidal.

In hydrometallurgy the solvent extraction of zinc(II) from ores dissolved in aqueous acidic sulfate media by a cation-exchange process is usually accompanied by extraction of iron(III).[1] Some discrimination or selectivity between these two metals can be achieved on the basis of kinetics, the rate of extraction of iron(III) being significantly slower. Improvement of the selectivity for zinc(II) might be achieved by use of a pro-ligand, H_2L, which discriminates in favour of tetrahedral co-ordination by deploying a preorganised set of perpendicular co-ordination planes. Having a complete d shell, zinc(II) has no crystal-field stabilisation to contribute to a preferred co-ordination geometry which therefore arises mainly from the steric requirements of the ligand.

Using orthogonal co-ordination planes to generate tetrahedral metal co-ordination environments, 2,2′-bi(benzimidazolyl) compounds **I** have recently been developed[2] as selective extractants for zinc(II) from chloride media. The metal–ligand complex is a 2,2′-bi(benzimidazolyl)-bridged dimer of the general form $[(ZnLCl_2)_2]$. Encouraged by these observations, we have investigated certain azomethine pro-ligands **II** which incorporate rotationally hindered biphenyl units with the potential to generate orthogonal N,O co-ordination planes for binding zinc(II) in tetrahedral N_2O_2 environments. We report our observations which are unexpected.

Results and Discussion

The crystal structure of the pro-ligand 6,6′-dimethyl-2,2′-bis(salicylideneamino)biphenyl (H_2L^2) (Fig. 1, Table 1) demonstrates the potential of the biphenylene-derived salicylideneamino ligands for promoting tetrahedral metal binding sites. The structure possesses crystallographic two-fold symmetry, with the rotation axis bisecting the biphenyl unit. The dihedral angle of 89.0° between the phenyl rings of the biphenyl unit indicates a role for steric repulsion in forcing their near-orthogonal disposition; it might be assumed that the 6,6′-methyl substituents contribute significantly to this effect but this may not be the case (see below). The torsion angle of 30.2° for C(16)–C(11)–N(1)–C(1) indicates that the link between the biphenylene unit and the nearly planar salicylaldimino unit is, however, somewhat twisted. This observation, coupled with the relatively short imine bond [C(1)–N(1) 1.282(3)], indicates there is little conjugation between the respective unsaturated systems and suggests that the compound may possess some flexibility about this linkage. The maximum deviation from the

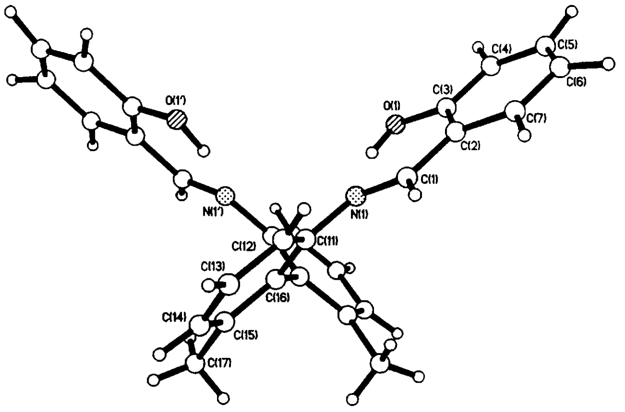
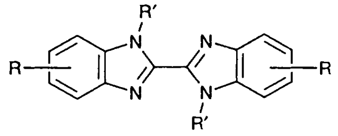


Fig. 1 Crystal structure of H_2L^2 viewed perpendicular to the two-fold axis bisecting the central bond [C(16)–C(16′)] of the biphenyl unit. Ligand bite distances are N(1)···N(1′) 3.60, N(1)···O(1) 2.59 and O(1)···O(1′) 4.77 Å



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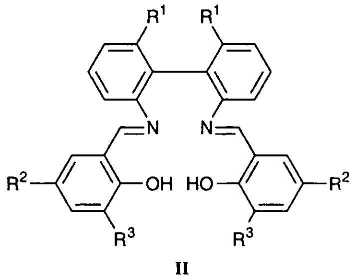

II

	R^1	R^2	R^3
H_2L^1	H	H	H
H_2L^2	CH_3	H	H
H_2L^3	H	C_9H_{19}	H
H_2L^4	H	C_9H_{19}	NO_2

J. Chem. Soc., Dalton Trans., 1996, Pages 2835–2838

Table 1 Selected bond lengths and angles for H_2L^2 and $[ZnL^2(EtOH)]$

H_2L^2			
N(1)–C(1)	1.282(3)	C(2)–C(3)	1.398(3)
N(1)–C(11)	1.418(3)	C(11)–C(16)	1.399(3)
O(1)–C(3)	1.346(3)	C(15)–C(17)	1.510(3)
C(1)–C(2)	1.447(3)	C(16)–C(16′)	1.507(4)
C(1)–N(1)–C(11)	121.5(2)	O(1)–C(3)–C(2)	121.2(2)
N(1)–C(1)–C(2)	121.4(2)	C(16)–C(11)–N(1)	116.9(2)
C(3)–C(2)–C(1)	121.8(2)	C(11)–C(16)–C(16′)	119.4(2)
$[ZnL^2(EtOH)]$			
Zn–N(1A)	2.121(10)	Zn–O(1S)	2.115(9)
Zn–O(1A)	1.910(9)	Zn–N(1B)	2.077(11)
Zn–O(1B)	1.976(8)	N(1A)–C(1A)	1.263(15)
N(1A)–C(11A)	1.364(13)	O(1S)–C(1S)	1.406(16)
C(1S)–C(2S)	1.470(18)	C(1A)–C(2A)	1.425(17)
C(3A)–O(1A)	1.303(12)	C(15A)–C(17A)	1.477(16)
C(16A)–C(16B)	1.460(13)	N(1B)–C(1B)	1.303(16)
N(1B)–C(11B)	1.384(14)	C(1B)–C(2B)	1.370(17)
C(3B)–O(1B)	1.317(13)	C(15B)–C(17B)	1.454(16)
O(1S)–Zn–N(1A)	84.7(4)	O(1A)–Zn–N(1A)	88.9(4)
O(1A)–Zn–O(1S)	117.2(4)	N(1B)–Zn–N(1A)	92.7(4)
N(1B)–Zn–O(1S)	119.0(4)	N(1B)–Zn–O(1A)	123.6(4)
O(1B)–Zn–N(1A)	171.2(4)	O(1B)–Zn–O(1S)	86.8(4)
O(1B)–Zn–O(1A)	96.7(4)	O(1B)–Zn–N(1B)	89.7(4)

least-squares plane of the salicylaldimino unit is no greater than 0.01 Å and this planarity is reinforced by a strong intramolecular hydrogen bond between the hydroxyl proton and the imino nitrogen [H(0) ··· N(1) 1.726(3) Å]. It is noteworthy that these units are expected to generate the rigid N,O-co-ordination planes for complexation. However, the dihedral angle of 73.8° between the N,O vectors from each salicylaldimino unit indicates that the compound is not fully preorganised to present these N,O-co-ordination planes in a truly orthogonal disposition and it might be expected that it promotes at best a distorted-tetrahedral metal co-ordination geometry.

The preparation of four-co-ordinate copper(II) complexes of 2,2′-bis(salicylideneamino)biphenyl (H_2L^1) and its 6,6′-dimethyl analogue H_2L^2 of the form $[CuL^1]$ and $[CuL^2]$ was reported by Lions and Martin[3] who argued that, because there is no possibility of the two benzene rings in the biphenyl unit being coplanar on co-ordination of the pro-ligand, the geometry of the complex must be pseudo-tetrahedral at copper. The determination of the crystal structure of $[CuL^1]$ revealed[4] such a severe distortion of a tetrahedron that it would be more reasonable to describe the co-ordination at copper in terms of a distorted square-planar geometry. Subsequent investigations of the related nickel(II) complexes by ^1H NMR spectroscopy indicated that, because they are effectively diamagnetic, the co-ordination geometry at nickel must be square planar, a conclusion which is reinforced by the preparation of a palladium(II) analogue.[5] The structure of the nickel(II) complex was not determined. However, the cobalt(II) atom in $[CoL^2]$ is in a highly distorted tetrahedral environment.[6] Zinc(II) complexes of certain 2,2′-bis(3-alkyl-salicylideneamino)biphenyls have been presumed[5] to be pseudo-tetrahedral in the absence of steric interactions. The extensive similarity between cobalt(II) and zinc(II) in the complexes which they form and in their structures might lead to the reasonable expectation that H_2L^2 would form a similarly distorted tetrahedral complex of zinc(II).

We have investigated the zinc(II) complexes of H_2L^1 and H_2L^2 in greater detail than previously. Crystallisation of $[ZnL^2]$ shows that the complex readily undergoes hydrolysis by adventitious water in dichloromethane and in acetone solution. The hydrolytic decomposition does not occur in dimethyl sulfoxide solution. The complex $[ZnL^1]$ is much less sensitive to hydrolysis in solution. Fast atom bombardment mass spectrometry on freshly prepared samples of both zinc(II) complexes established that they are monomeric. Computer-aided molecular modelling of both [ZnL] and $[Zn_2L_2]$ (L = L^1 or L^2) using the MOPAC package[7] showed that, in each case, formation of dimers analogous to those found[2] in complexes of the acid-functionalised bibenzimidazoles is predicted to be much less favourable energetically than formation of the monomer. The reason for this is seen to be intramolecular repulsion between 3-H (and 3′-H) on the biphenyl moiety and 6-H on the corresponding phenolate ring. The results of nuclear Overhauser effect (NOE) measurements on proton NMR spectra of the complexes lend some support to this conclusion. The calculations on the [ZnL] complexes indicate that a large distortion from a perfectly tetrahedral geometry at zinc is to be expected. They also indicate that the effect of the methyl groups in H_2L^2 in twisting the interannular bond is not significant. Models built on the basis of the calculated geometrical parameters (bond angles and lengths) in the four-co-ordinate monomeric [ZnL] disclosed ample space available for co-ordination of a further ligand in each case. We suggest that this may explain the sensitivity of $[ZnL^2]$ to hydrolysis mentioned earlier: dimethyl sulfoxide is a better donor than either dichloromethane or acetone and, once bound to zinc, effectively prevents hydrolysis.

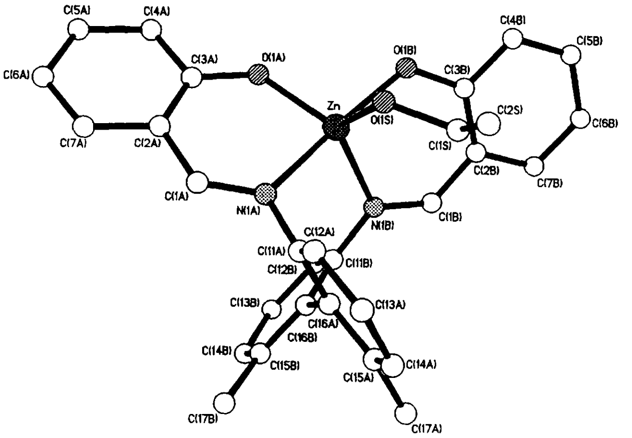

Fig. 2 Crystal structure of the neutral five-co-ordinate complex $[ZnL^2(EtOH)]$

The crystal structure of $[ZnL^2(EtOH)]$, shown in Fig. 2, establishes that there is indeed sufficient space to accommodate a further donor in the four-co-ordinate sphere of the [ZnL] complexes, in this case from ethanol. Selected bond lengths and angles for the complex are given Table 1; bond lengths in the metal co-ordination sphere are comparable with those of related zinc(II) systems,[8,9] although relatively few five-co-ordinate zinc(II) complexes of salicylaldimine systems have been structurally characterised.[9] The complex consists of discrete monomers in which the zinc atom is in a slightly distorted trigonal-bipyramidal environment of which N(1A) and O(1B) occupy the axial sites and O(1A), N(1B) and O(1S) describe the equatorial plane. The salicylaldimino units of the ligand present essentially planar six-membered chelate rings [maximum deviation for either least-squares plane 0.052 Å for C(1B)] which intersect with a dihedral angle of 49.0°. This represents a considerable 'flattening' of their disposition from that in free H_2L^2 and may arise from flexing about the C(11)–N(1) linkage in order to facilitate the approach of the solvent molecule. The dihedral angle of 74.3° between the rings of the biphenyl unit indicates that further distortion of the ligands occurs on co-ordination. This flattening of the biphenyl unit apparently originates from the near 90° bite angle imposed on the seven-membered twist-boat chelate involving N(1A) and N(1B) by the trigonal-bipyramidal zinc(II) centre. The overall effect in the complex appears to be a flattening and opening of the binding cavity of the ligand so that the ethanol ligand may be accommodated within the five-co-ordinate metal environment.

It appears that these systems possess sufficient flexibility to adapt to different co-ordination geometries and are therefore not rigid enough to impose a single defined geometry on the metal ion. Also, although the free pro-ligand features two approximately perpendicular co-ordination planes, the preorganised geometry of the $N_2O_2{}^{2-}$ donor set is not a particularly good fit for a relatively small 'tetrahedral' metal cation such as zinc(II). The mean distance between the centroid and the donor atoms in the free pro-ligand is 2.23 Å. Such a bonding cavity is too large for zinc(II) and the poor fit is reflected in H_2L^4 being a relatively weak extractant for zinc when deployed in the process (1). In kerosene solution (0.2 mol dm^{-3}) 50% transfer of zinc

$$Zn^{2+} + H_2L^4\,(org) \rightleftharpoons [ZnL^4]\,(org) + 2H^+ \quad (1)$$

from aqueous zinc sulfate solution (0.2 mol dm^{-3}) was observed at an equilibrium pH of 4.2 ($pH_{\frac{1}{2}}$) with an organic to aqueous ratio of 2.0. The unsubstituted analogue H_2L^3 appeared to be considerably weaker ($pH_{\frac{1}{2}} > 7$) although under the test conditions it was observed that it was unstable to hydrolysis of the imine. Addition of hydrocarbon-soluble monodentate compounds does little to lower the $pH_{\frac{1}{2}}$ for the above equilibrium. Consequently, the azomethine pro-ligands of type **II** are not potential candidates for the development of extractants to separate zinc from iron(III) in hydrometallurgical processes where relatively high acidity is required in the feed (pH < 2.3) to prevent precipitation of iron.

These studies suggest that while incorporation of a biphenyl unit into the pro-ligand backbone can generate one of the desired criteria for obligate tetrahedral co-ordination, the preorganisation of two mutually perpendicular bidentate arms, other design features are required for a system that will discriminate strongly in favour of zinc. Additional rigidity in the superstructure is needed to preclude the ready adoption of other co-ordination geometries and a reduction in the bite distances is required in order that the $N_2O_2{}^{2-}$ donor set is fully preorganised for a small tetrahedral ion, such as zinc(II).

Experimental

The two pro-ligands (H_2L^1) and (H_2L^2) were prepared according to the method of Lions and Martin,[3] and fully characterised by analysis and spectroscopy. Proton NMR spectra were measured at 400 MHz using a Brüker AMX400 spectrometer, with δ values in ppm relative to internal $SiMe_4$. The FAB mass spectra were obtained on a JEOL JMS-SX-102 instrument.

Syntheses

6-Nitro-4-nonylsalicylaldehyde. Nitric acid (3.2 g, 0.05 mol) was added to a solution of 4-nonylsalicylaldehyde (12.4 g, 0.05 mol) in glacial acetic acid (15.0 g) at 20 °C. The mixture was stirred for 12 h and water (15 cm^3) was added. The solution was extracted with CH_2Cl_2 and the organic fraction washed acid-free with water, then dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* yielding the product as a brown oil (13.0 g, 89%). ^1H NMR ($CDCl_3$): δ 0.12–1.7 (m, 19 H, C_9H_{19}), 7.8–8.2 (m, 2 H, phenyl H), 10.2 (s, 1 H, CHO) and 11.1 (s, 1 H, OH).

H_2L^4. The above compound (3.07 g, 0.01 mol) was added in portions to a boiling solution of 2,2′-diaminobiphenyl (0.92 g, 5 mmol) in EtOH (30 cm^3). The mixture was refluxed for 30 min with stirring and then cooled. The resulting precipitate was collected, washed with EtOH and dried *in vacuo* yielding the product as an orange solid (2.46 g, 46%). ^1H NMR ($CDCl_3$): δ 0.2–1.7 (m, 38 H, C_9H_{19}), 7.2–8.0 (m, 10 H, phenyl H), 8.7 (d, 2 H, CHN) and 13.95 (s, 2 H, OH).

Table 2 Crystal data and refinement details

	H_2L^2	$[ZnL^2(EtOH)]$
Empirical formula	$C_{28}H_{24}N_2O_2$	$C_{30}H_{28}N_2O_3Zn$
M	420.49	529.91
Crystallographic system	Monoclinic	Monoclinic
Space group	$I2/c$	$P2_1/c$
a/Å	13.911(2)	11.654(2)
b/Å	13.759(2)	11.753(2)
c/Å	12.015(2)	18.878(3)
β/°	94.836(10)	98.97(2)
U/Å^3	2291.5	2554.1
D_c/g cm^{-3}	1.219	1.378
Z	4	4
$F(000)$	888	1104
μ(Mo-Kα)/cm^{-1}	0.77	9.7
Independent reflections (R_{int})	2016 (0.0151)	1272 (0.0585)[a]
No. parameters	147	137
Goodness of fit on F^2	1.005	—
R_1	0.0582[b]	0.0616[c]
(all data)	0.0948	—
R'	—	0.0570[c]
wR_2	0.1395[b]	—
(all data)	0.1562	—
Largest difference peak and hole/e Å^{-3}	0.239, −0.196	0.390, −0.448

[a] 1086 with $I > 3\sigma(I)$. [b] $I > 2\sigma(I)$. [c] $I > 3\sigma(I)$.

Zinc(II) complexes. A modification of the published[5] method was used, in that anhydrous powder $ZnCl_2$ was added to a solution containing the deprotonated (KOH) pro-ligand, KL^1 or KL^2, in methanol. The yellow solid isolated from the concentrated reaction mixture was recrystallised from methanol or ethanol. Yields were in the range 70–80%.

$[ZnL^1]$ (Found: C, 65.7; H, 4.5; N, 5.8. $C_{26}H_{18}N_2O_2$-Zn·MeOH requires C, 66.5; H, 4.5; N, 5.7%): ^1H NMR ($CDCl_3$): δ 6.60 (1 H, t, $H^{5'}$, *J* 7.0), 6.87 (1 H, d, $H^{3'}$, *J* 8.5), 7.11 (1 H, m, $H^{6'}$), 7.24 (1 H, dd, H^5, *J* 7.7, 1.4), 7.33 (2 H, m, $H^{4'}$, H^6), 7.45 (1 H, dd, H^3, H^4, *J* 7.7, 1.4 Hz) and 8.25 (1 H, s, H^7); FAB mass spectrum *m*/*z* 455 (51, $M^+ + H$) and 392 (47%, HL^+); IR (KBr) 1612, 1494 and 1220 cm^{-1}.

$[ZnL^2]$ (Found: C, 68.0; H, 5.4; N, 5.3. $C_{28}H_{22}N_2O_2Zn$·2EtOH requires C, 68.0; H, 5.3; N, 5.3%): ^1H NMR [$(CD_3)_2SO$]: δ 2.10 (3 H, s, CH_3), 6.43 (1 H, t, $H^{5'}$, *J* 7.7), 6.55 (1 H, d, $H^{3'}$, *J* 8.5), 6.92 (1 H, d, H^3, *J* 7.7), 7.13–7.23 (2 H, m, $H^{4'}$, H^5), 7.24 (1 H, dd, H^6, *J* 7.7, 2.1), 7.32 (1 H, d, H^4, *J* 8.5 Hz) and 8.30 (1 H, s, H^7); FAB mass spectrum *m*/*z* 483 (57%, $M^+ + H$) and 421 (HL^+); IR (KBr) 1611 and 1238 cm^{-1}.

X-Ray crystallography

Data collection. Yellow crystals of H_2L^2 (dimensions 0.38 × 0.37 × 0.35 mm) and $[ZnL^2(EtOH)]$ (0.22 × 0.22 × 0.18 mm) were mounted on quartz fibres and data were collected at ambient temperature on a Philips PW1100 four-circle diffractometer with Mo-Kα radiation (λ = 0.710 69 Å) in the ranges θ 3–25 and 3–23° respectively using scan widths of 0.90° and a fixed scan speed of 0.05° s^{-1} by the method described previously.[10] In each case, three reference reflections measured at 5 h intervals showed no significant changes in intensities. Crystal data and refinement details are given in Table 2.

Structure solution and refinement. H_2L^2.[11] The structure was solved by direct methods. Fourier-difference syntheses revealed the positions of all the non-methyl hydrogens in the structure for which a common isotropic thermal parameter refined to

0.075 Å^2. The methyl hydrogens were included in idealised positions (C–H 0.96 Å) and assigned thermal parameters 1.5 times that of the carbon atom to which they are attached. In the final cycles of full-matrix least-squares refinement on F^2 $\{w^{-1} = \sigma^2(F_o^2) + (0.647P)^2$ where $P = [\max(F_o^2,0) + 2F_c^2]/3\}$ all non-hydrogen atoms were given anisotropic thermal parameters.

[ZnL^2(EtOH)].[12] The positions of the metal atom and one nitrogen were deduced from a Patterson synthesis. A series of Fourier syntheses revealed the positions of the atoms of the azomethine ligand, which were distinguished from their pseudo-symmetric ghost images by identifying appropriate vectors in the Patterson map. The co-ordinated ethanol was located from a subsequent Fourier-difference synthesis. The phenylene rings in the structure were constrained to refine with idealised geometries (C–C 1.395 Å, C–C–C 120°). All hydrogen atoms in the complex were included in idealised positions (C–H 1.08 Å) and assigned fixed isotropic thermal parameters of 0.08 Å^2. After isotropic refinement of all non-hydrogen atoms an empirical absorption correction[13] was applied (maximum 1.050, minimum 0.856). In the final cycles of full-matrix least-squares refinement on F, individual weights of $1/\sigma^2(F)$ were assigned to each reflection and anisotropic thermal parameters were given to the zinc, nitrogen, oxygen atoms of the complex and to all atoms of the ethanol molecule.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/82.

Acknowledgements

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