Pergamon

PII: S0277-5387(97)00033-8

Polyhedron Vol. 16, No. 16, pp. 2765–2770, 1997

0277-5387/97 $17.00+0.00

Tricoordinate complexes of lead(II) with innocent Schiff base ligands

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(Received 7 November 1996; accepted 14 January 1997)

Abstract—The interaction of lead(II) perchlorate hydrate with Schiff base ligands resulted in the formation of unexpected complexes wherein the ligand is coordinated in an "innocent" fashion. These compounds were characterised by ^{1}H NMR, IR and single crystal X-ray studies. These reveal an unprecedented binding mode for these ligands, where some of the apparently available binding sites are not used, and the lead(II) displays a low coordination number. © 1997 Elsevier Science Ltd

Keywords: lead(II) complexes; innocent Schiff base; crystal structures; low coordination number.

Preliminary results from a continuing investigation of lead(II) complexes with Schiff base ligands in this laboratory have recently been reported [1]. From these, it is clear that there is an unexpected wealth of new coordination chemistry available from the combination of these simple ligands with a well-known metal, and in this paper, a range of complexes that exhibit further unusual behaviour is described.

The complex formed from salen (*NN'*bis-(salicylidene)ethylenediimine) and lead(II) perchlorate hydrate is a dimer of [Pb(salen)] units linked by a bridging lead(II) [1]. In order to obtain a complex which would be mononuclear, a derivative of this ligand was prepared **1** (*NN'*-bis(3-methoxy-salicylidene)ethylenediimine) wherein the *ortho* positions on the aromatic rings are substituted with methoxy groups in the hope that this would discourage the formation of bridged species. In addition to this, compounds **2** (*NN'N''*-tris(3-methoxy-salicylidene)triethylenetriimine) and **3** (*NN'N''*-tris-(salicylidene)triethylenetriimine) were prepared, as three dimensional homologues of these ligands. Ligand **3** has been used previously to prepare complexes with a wide range of metals [2], including one with lead(II) acetate [1].

EXPERIMENTAL

General

Microanalyses were performed by the Loughborough University analytical service. ^{1}H NMR spectra were recorded at 250.13 MHz on a Bruker AM250, and at 89.55 MHz on a JEOL FX90. IR Spectra were recorded on a Perkin Elmer System 2000 NIR-FT Raman. Lead(II) perchlorate trihydrate, salicylaldehyde, *o*-vanillin, ethylenediamine, and tris(2-aminoethyl)amine were obtained from Aldrich and used without purification. Ligands were prepared by analogous methods to those given previously [1].

CAUTION—perchlorate salts are potentially explosive and must be handled with great care!

Preparation of complexes

1a. To a solution of **1** (0.10 g, 0.3 mmol) in 10 cm^3 of methanol was added dropwise a solution of lead(II) perchlorate hydrate (0.123 g, 0.27 mmol) in 5 cm^3 of acetonitrile. The solution gradually changed from canary yellow to orange during the addition. Solid **1a** separated from the solution on standing (isolated yield 0.18 g, 90% of yellow crystals), m.p. 305–7°C (decomp). (Found: C 29.3, H 2.9, N 3.7. Calc. for $C_{18}H_{18}N_4O_{12}Cl_2Pb$: C 29.4, H 2.5, N 3.8%).

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2a. To a solution of **2** (0.16 g, 0.3 mmol) in 10 cm^3 of methanol was added dropwise a solution of lead(II) perchlorate hydrate (0.12 g, 0.26 mmol) in 5 cm^3 of acetonitrile. **2a** crystallised from the reaction mixture on standing (isolated yield 0.15 g, 61%), m.p. 225–6°C. (Found: C 37.4, H 3.4, N 5.7. Calc. for $C_{30}H_{36}N_4O_{14}Cl_2Pb$: C 37.7, H 3.8, N 5.9%).

3a. To a solution of **3** (0.08 g, 0.18 mmol) in methanol (15 cm^3) was added dropwise a solution of lead(II) perchlorate hydrate (0.07 g, 0.15 mmol) in methanol (10 cm^3). Crystals of **3a** formed from the reaction mixture on slow evaporation (isolated yield 0.84 g, 64%), m.p. 241–3°C. (Found: C 37.4, H 3.3, N 6.6. Calc. for $C_{27}H_{30}N_4O_{11}Cl_2Pb$: C 37.5, H 3.5, N 6.5%).

Crystallographic structure analysis and refinement

The structure of **1a** was solved by direct methods and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, the remainder isotropically. Hydrogen atoms were included but not refined. The final cycle of full matrix least-squares refinement was based on 2563 observed reflections ($I > 2.00\sigma(I)$) and 281 variable parameters to $R = 0.053$ [$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$]. The maximum/minimum residual electron density in the final ΔF map were -1.27 and 1.61 $e^-/Å^3$. The structure of **2a** was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. The final cycle of full matrix least squares refinement was based on 2393 observed reflections ($I > 3.00\sigma(I)$) to $R = 0.053$ [$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$]. The maximum/minimum residual electron density in the final ΔF map were -1.96 and 1.35 $e^-/Å^3$. The structure of **3a** was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. The final cycle of full matrix least squares refinement was based on 4115 observed reflections ($I > 3.00\sigma(I)$) to $R = 0.069$ [$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_c|$]. The maximum/minimum residual electron density in the final ΔF map were -1.67 and 1.39 $e^-/Å^3$. All calculations were performed using the teXsan crystallographic software package of the Molecular Software Corporation [9]. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

RESULTS AND DISCUSSION

Spectroscopic studies

Table 1 shows the ^1H NMR data obtained for ligands **1**–**3** and their complexes with lead(II) perchlorate **1a**–**3a**. The most significant feature of these data is that the ionisable phenolic protons of the ligand are still clearly present in the complexes, a result which is not consistent with the formation of compounds of the type expected. Previously, we have shown that the neutral complex formed from **3** and lead(II) is fluxional at room temperature, undergoing an exchange process which involves all three legs of the tripod, with a characteristically broad ^1H NMR spectrum [1]. At low temperature, a limiting spectrum is obtained wherein the one unionised phenolic proton can be seen. This indication, together with the overall simplicity of the remainder of the ^1H NMR spectra for **1a**–**3a**, led to the conclusion that the ligand is bound to the metal but is still unionised. It is significant also that the signal due to the azomethine proton becomes a doublet in the spectra of these complexes. Irradiation of the broad signal of the phenolic proton during collection of spectra for **1a** and **2a** leads to a sharpening of the observed azomethine peak and a loss of the coupling, and so this doubling is tentatively ascribed to a coupling with the unionised phenolic proton, whose environment is sufficiently modified over that in the free ligand upon coordination of lead(II) to allow a resolved coupling to be observed.

Table 2 shows selected IR data for the same compounds, of which the most informative data are the bands due to the C=N stretch. In each case, the peak shifts by about +15 cm^{-1} on going from the free ligand to the complex. There are also distinctive bands due to perchlorate seen in the complexes.

Table 1. ^1H NMR data for **1**-**3a**

	ArO*H*§	*H*C=N	Ar*H*	—OC*H*$_3$	—C*H*$_2$—
1*	14.50	9.01	7.38–7.57	4.51	4.62
1a*	14.20	9.24 (d, 8Hz)	7.30–7.80	4.71	4.38
2†	14.40	8.61	6.65–7.54	4.38	3.38–4.17
2a†	13.65	9.06 (d, 8Hz)	7.22–7.70	4.51	3.40–4.17
3‡	13.70	8.12	6.62–7.44	—	2.90–3.63
3a‡	10.99	8.58 (d, 9Hz)	6.87–7.64	—	2.96–3.45

Samples marked * were recorded in CD_3CN, † in d_6DMSO, ‡ in $CDCl_3$, all shifts reported as δ ppm, referenced to external TMS; § are broad resonances.

Table 2. Selected IR data (cm^{-1}) for compounds **1**–**3a**

Group	**1**	**1a**	**2**	**2a**	**3**	**3a**
CN	1630	1647(br)	1630	1645(br)	1633	1649
ClO_4		1091, 623		1096, 622		1090, 623

Figure 1 shows the crystal structure of **1a**, (*NN'*-bis(3-methoxysalicylidene)ethylenediimine)lead(II) perchlorate, the product of the reaction of **1** with lead(II) perchlorate. The potentially tetradentate ligand binds to lead through the two oxygens alone, a molecule of methanol completing the overall tricoordination at the metal centre. (Bond lengths and angles for **1a**–**3a** are given in Table 3). The metal is best described as having a trigonal pyramidal geometry, with the lone pair on the lead(II) oriented in the direction of the apex of the pyramid. This kind of shape is not unusual for heavier congeners of Group 14 in the M^{II} state [3]. Since the phenolic protons persist in the complexed form, they reside between the phenolic oxygen and the imine nitrogen [4]. The effect of this is to physically prohibit the lead from entering the usual ligand pocket defined by the two phenolic oxygens and the two imine nitrogens.

Figure 2 shows the crystal structure of **2a** (*NN'N''*-tris(3-methoxysalicylidene)triethylenetriimine)lead (II) perchlorate. The ligand is a three dimensional analogue of **1**, and shows very similar behaviour, binding to the lead through the oxygen atoms only. In this case the tricoordination is attained without the coordination of a molecule of solvent. The ionisable protons which are still within the ligand pocket again prevent the lead from entering the ligand cavity. The geometry at the metal is trigonal pyramidal and the remaining lone pair on the lead(II) is in the hemisphere opposite the ligand plane. By coordinating to

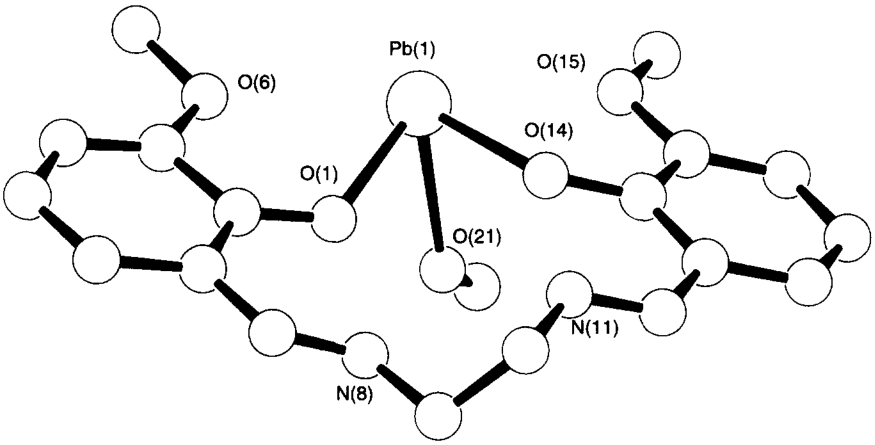

Fig. 1. The crystal structure of **1a**.

Table 3. Selected bond lengths (Å) and angles (°) for **1a**, **2a** and **3a**

1a			
Pb—O(1)	2.325(9)	O(1)—Pb—O(14)	74.8(3)
Pb—O(14)	2.304(10)	O(1)—Pb—O(21)	79.3(3)
Pb—O(21)	2.45(1)	O(14)—Pb—O(21)	73.2(5)
(Pb—O(6)	2.77)		
(Pb—O(15)	2.77)		
2a			
Pb—O(6)	2.34(1)	O(6)—Pb—O(16)	78.3(4)
Pb—O(16)	2.33(1)	O(6)—Pb—O(26)	78.6(5)
Pb—O(26)	2.34(1)	O(16)—Pb—O(26)	81.2(4)
(Pb—O(7)	2.97)		
(Pb—O(17)	2.72)		
(Pb—O(27)	2.85)		
3a			
Pb—O(6)	2.27(1)	O(6)—Pb—O(16)	73.8(5)
Pb—O(16)	2.29(1)	O(6)—Pb—O(26)	75.8(4)
Pb—O(26)	2.31(1)	O(16)—Pb—O(26)	81.0(4)

Table 4. Crystal data for **1a**, **2a** and **3a**

	1a	**2a**	**3a**
Formula	$C_{19}H_{25}N_2O_{13.5}Cl_2Pb$	$C_{30}H_{36}N_4O_{14}Cl_2Pb$	$C_{28}H_{31.5}N_{4.5}O_{11}Cl_2Pb$
M	775.52	954.74	885.19
Crystal Size (mm)	0.1 × 0.1 × 0.47	0.25 × 0.20 × 0.10	0.15 × 0.18 × 0.06
Crystal System	Monoclinic	Orthorhombic	Triclinic
Lattice Type	Primitive	Primitive	Primitive
a (Å)	8.512(4)	21.027(2)	12.841(3)
b (Å)	28.972(5)	31.355(3)	14.935(4)
c (Å)	10.699(3)	10.832(2)	11.475(2)
α (°)			98.57(2)
β (°)			107.11(2)
γ (°)			112.96(2)
V (Å^3)	2624(1)	7141(1)	1847.6(8)
β (°)	95.98		
Space Group	$P2_{1/n}$ (#14)	$Pbca$ (#61)	$P1$ (#2)
Z	4	8	2
F(000)	1508.00	3776.00	870.00
$\mu(\mathrm{Cu}K_\alpha)$ (cm^{-1})	151.70	113.16	108.26
Scan Type	ω	ω	ω
$2\theta_{\max}$ (°)	120.3	120.2	120.3
Total reflections	4301	5938	5780
Observed ($I > 2.0\sigma I$)	2563	2393	4115 ($I > 3.00\sigma(I)$)
R	0.053	0.053	0.069
Rw	0.068	0.050	0.075

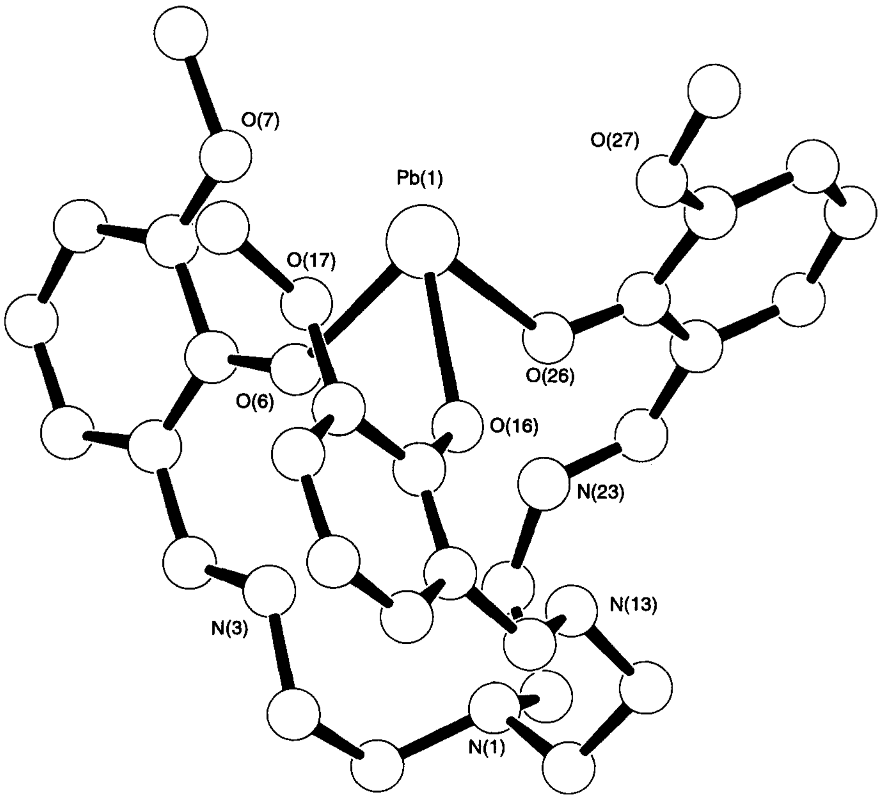

Fig. 2. The crystal structure of **2a**.

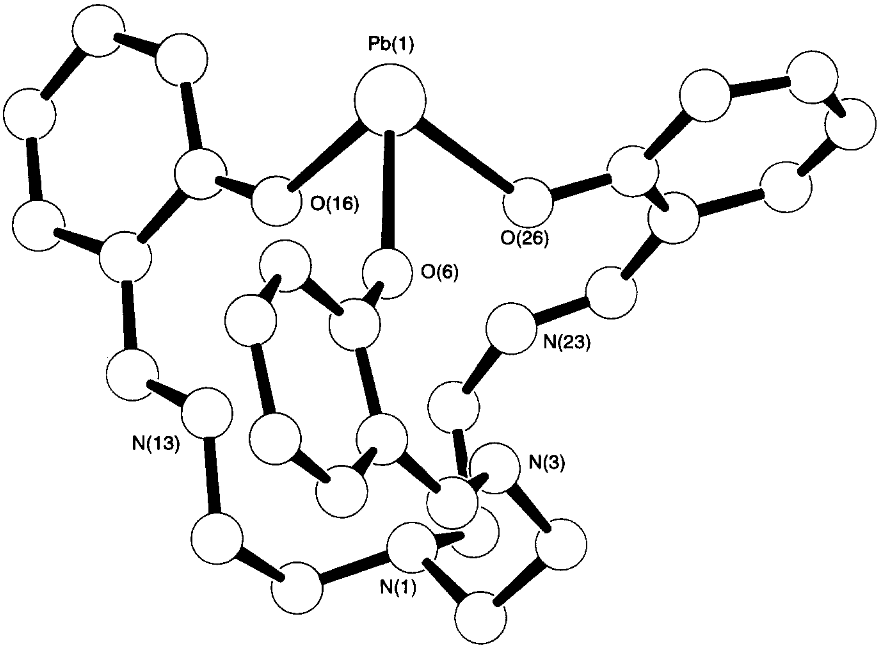

Fig. 3. The crystal structure of **3a**.

the three oxygen atoms, the lead(II) effectively closes the ligand cavity, as is usually seen for complexes with this type of ligand, but in this case, there are binding sites still available within.

Figure 3 shows the crystal structure of **3a** (*NN′ N″*-tris(salicylidene)triethylenetriimine)lead(II) perchlorate. This ligand is an unsubstituted version of **2**, and has been shown previously to form a neutral complex with lead(II) wherein two phenolate oxygens and two imino nitrogens bind to the metal. In this case, using perchlorate as the counter ions in the lead starting material, we obtain **3a**, where the ligand is innocent, binding lead through the three oxygens only. As with **1a** and **2a** the phenolic protons can be seen in the ^{1}H NMR of the complex, and again there is an exclusion of the lead(II) from the expected binding position. In all three cases, the structural studies are in agreement with the conclusions drawn from the ^{1}H NMR and IR data in that the molecules all have symmetric arrangements of the salicylidene subunits about the metal centres, which simplifies the observed spectra.

While it is proposed that the lead(II) in complexes **1a** and **2a** bind to the innocent ligands through the phenolic oxygens only, giving tricoordinate structures, it would be possible to argue that there is a bonding interaction between the metal centre and the oxygen of the *o*-methoxy function. In the case of **1a**, the average distance Pb—O(Me*O*, O(15), O(6)) is 2.77 Å, which is significantly longer than Pb—O(*O*Ph, O(1), O(14)) (ave. 2.31 Å) and Pb—O(Me*O*H, O(21)) (2.45 Å), although this is shorter than some distances reported for proposed Pb—O(ether) bonding interactions (for example, Pb—O in Pb(18-C-6) $(SCN)_2$ = 2.68–2.82 Å) [5]. A similar set of distances are seen in **2a** (ave. Pb—O(*O*Ph O(6), O(16), O(26)) = 2.33 Å; ave. Pb—O(Me*O*, O(7), O(27)) = 2.85 Å), and again the methoxy oxygens seem close enough for a bonding interaction. Comparison with **3a** reveal that the average Pb—O(Ph) bond lengths are very similar to those seen for Pb—O(*O*Ph) in **2a** (ave. Pb—O = 2.33 Å for **3a**, Pb—O(*O*Ph O(6), O(16), O(26)) for **2a** = 2.33 Å), which suggest that there is no fundamental difference in the bonding between the two complexes, and consequently this leads to the conclusion that there is no significant bonding interaction between the lead(II) centres and the methoxy oxygens.

Lead(II) can exhibit a wide range of coordination numbers in its compounds, with well characterised examples exhibiting coordination ranging from three [6] to ten [7]. The most commonly seen are those between tetra- and hexacoordinate, although because of the many crown ether complexes of lead(II) reported, complexes with higher coordination numbers are more often seen than those with smaller. Tricoordinate structures are rare, and few examples are seen beyond those with ligands designed to stabilise low coordination numbers [8]. The compounds reported here are therefore unusual, not only in being tricoordinate, but in having ligands which are in fact designed to give rise to complexes which have higher coordination numbers, rather than to stabilise lower ones.

Acknowledgements—One of use (A. T. R.) thanks the EPSRC for a studentship.

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