

Some Schiff base complexes of lead(II)

Jonathan Parr,* Andrew T. Ross and Alexandra M. Z. Slawin

Department of Chemistry, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK

The interaction of lead(II) salts with the Schiff bases *N,N'*-bis(salicylidene)ethane-1,2-diamine (H_2 salen) and tris[2-(*N*-salicylideneamino)ethyl]amine (H_3 salren) resulted in formation of the new complexes $[(Pb_3(salen)_2)](ClO_4)_2$ **1** and $[Pb(salren)]$ **2**. The crystal structures of both complexes have been determined: **1** is a hitherto unreported trimetallic lead species in which the ligand bonds to lead in two different modes; in **2** some sites on the ligand are not involved in bonding to the metal.

There has been much interest recently in the co-ordination chemistry of lead(II).¹ This is in part because of the inherently toxic nature of lead,² and because of its widespread utility in many areas of contemporary technology.³ Much of this work has been aimed toward finding powerful ligands to complex lead(II) specifically. In order to probe the nature of lead–ligand interactions and to assess the characteristics required for successful lead co-ordination we have undertaken studies of lead(II)–Schiff base complexes. Schiff bases represent a useful starting point as they are accessible synthetic targets, and are easily derivatised to allow variation in their properties, specifically their solubility, and donor atom type.⁴ Here we report complexes with *N,N'*-bis(salicylidene)ethane-1,2-diamine (H_2 salen) and tris[2-(*N*-salicylideneamino)ethyl]amine (H_3 salren), the condensation products of 2 and 3 equivalents of salicylaldehyde with ethane-1,2-diamine and tris(2-aminoethyl)amine respectively.

Results and Discussion

The interaction of lead(II) perchlorate with H_2 salen in hot methanolic solution gives $[Pb_3(salen)_2](ClO_4)_2$ **1** in high yield. Crystals suitable for X-ray analysis form from the reaction mixture on cooling. This complex shows an unusual trimetallic configuration (Fig. 1) where two $Pb(salen)$ units are linked by a bridging lead(II), which lies on a crystallographic two-fold axis. The linking lead(II) bonds to the four phenolic oxygens of the two salen ligands, and shows a geometry intermediate between trigonal bipyramidal and square-based pyramidal,⁵ with the fifth co-ordination site comprising the remaining lone pair. The two lead(II) centres within the pocket of the salen ligands are each bound to two phenolic oxygens and two imido nitrogens, and also exhibit an intermediate geometry. The somewhat unusual co-ordination of a second metal between the two $Pb(salen)$ subunits represents a unique environment for lead(II). It may be that the two phenolic oxygen atoms which would normally be considered hard donor sites are softened by initial co-ordination of the first lead(II), and thereafter they become more suitable donors than anything else available in solution. This is somewhat surprising in view of the almost 1 : 1 ligand : Pb stoichiometry of the reaction, although spectroscopic and microanalytical investigation of the bulk product confirms that this is the major product from the reaction. The lead–oxygen bond lengths for the unique lead are comparable with those for the others reported here. Selected bond lengths and angles are presented in Table 1.

The potentially heptadentate (N_4O_3) compound **2** H_3 salren is perhaps the most easily synthesised tripodal encapsulating polydentate compound known.⁶ It has been widely used in studies of the co-ordination chemistry of many elements,⁷ but until now, not with lead(II). The crystallographic analysis of the

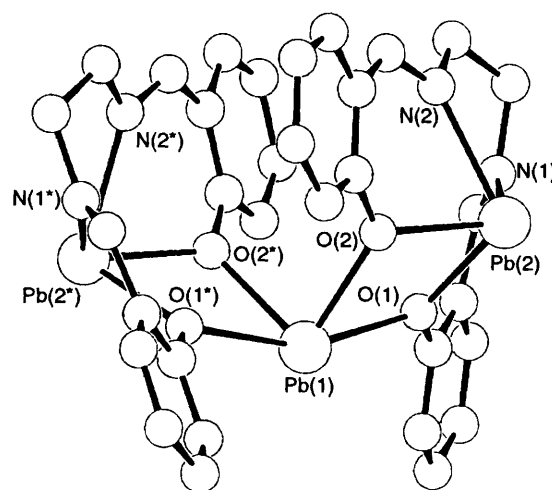
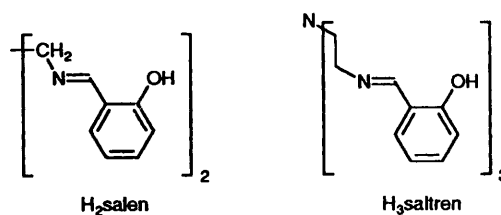


Fig. 1 The crystal structure of complex 1

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

Complex 1			
Pb(1)–O(1)	2.488(5)	Pb(2)–O(2)	2.369(5)
Pb(1)–O(2)	2.298(6)	Pb(2)–N(1)	2.435(8)
Pb(2)–O(1)	2.285(6)	Pb(2)–N(2)	2.448(8)
O(1)–Pb(1)–O(1*)	159.2(3)	O(1)–Pb(2)–N(2)	104.2(3)
O(1)–Pb(1)–O(2)	68.5(2)	O(2)–Pb(2)–N(1)	117.0(2)
O(1)–Pb(1)–O(2*)	95.7(2)	O(2)–Pb(2)–N(2)	74.2(2)
O(2)–Pb(1)–O(2*)	84.1(3)	N(1)–Pb(2)–N(2)	66.4(3)
O(1)–Pb(2)–O(2)	70.8(2)	Pb(1)–O(1)–Pb(2)	106.6(2)
O(1)–Pb(2)–N(1)	73.6(2)	Pb(1)–O(2)–Pb(2)	110.3(2)
Complex 2			
Pb–O(5)	2.396(5)	Pb–N(2)	2.444(6)
Pb–O(15)	2.274(5)	Pb–N(12)	2.518(7)
O(5)–Pb–O(15)	79.6(2)	O(5)–Pb–N(2)	74.3(2)
O(5)–Pb–N(12)	142.5(2)	O(15)–Pb–N(2)	88.8(2)
O(15)–Pb–N(12)	71.6(2)	N(2)–Pb–N(12)	81.4(2)

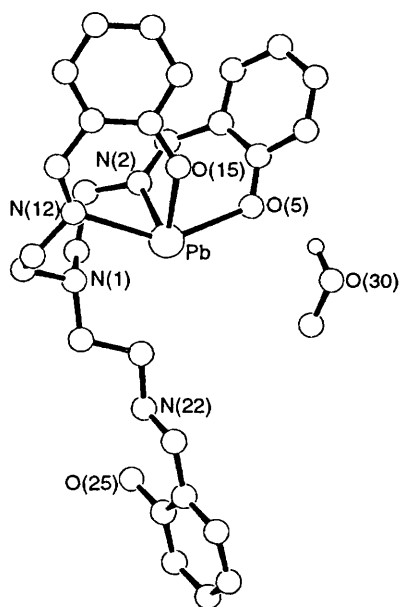


Fig. 2 The crystal structure of complex 2

complex [Pb(Hsaltren)] **2** reveals a neutral compound wherein the lead binds to two phenolate oxygens and two imido nitrogens in a geometry again intermediate between square pyramidal and trigonal bipyramidal (Fig. 2). The remaining apical amino nitrogen, the third imido nitrogen and the third phenolic oxygen do not interact with the lead centre. In the crystal lattice there is a molecule of methanol which forms a hydrogen bond with O(5), but is too distant to have a significant interaction with the metal centre. The geometry around the lead(II) centre is closely related to those seen in **1** (Table 1).

The geometries exhibited by the three different lead(II) centres are compared in Fig. 3. They are all five-co-ordinate, and do not correspond to idealised trigonal bipyramids or square-based pyramids. These two shapes are related by the Berry rearrangement⁸ although the shapes of the compounds reported do not correspond to any intermediate point on the idealised pathway for this interconversion.⁵ They have a close similarity to those seen for the complexes reported by Raymond and co-workers.¹ However, those workers invoked long-range interactions between the lead and more distant donor sites, resulting in an overall six- or seven-co-ordination for the lead. In our compounds there is a similar array of close contact donor atoms but there are no distant donor sites that could contribute to a higher co-ordination number. In the solid state there is an intermolecular contact between the lead in **2** and O(15) (3.03 Å) and N(12) (3.44 Å) of an adjacent molecule. It seems reasonable to assume that this is a phenomenon that is present only in the solid state, as the fluxionality observed in the room-temperature NMR spectrum (see below) would seem to indicate that any extra co-ordination sites available on the lead would in solution be taken up by the third leg of the tripod. A well characterised example of an extended array leading to a higher co-ordination number in a lead(II) complex is reported by Dean *et al.*⁹

Proton NMR studies of complex **1** reveal a simple spectrum indicating a single environment for the two ligands (Table 2). This is in good agreement with the structural analysis which shows a highly symmetric configuration of the two ligands. Recording the spectrum at low temperatures does not change the result. Proton NMR studies of **2** at ambient temperatures reveal a single set of broad resonances, consistent with the whole molecule undergoing an exchange process (Fig. 4). However, on cooling to 225 K sharp resonances are seen. Two sets of peaks are observed in a ratio of 2:1. This is most clearly seen with the azomethine protons, which appear as two singlets

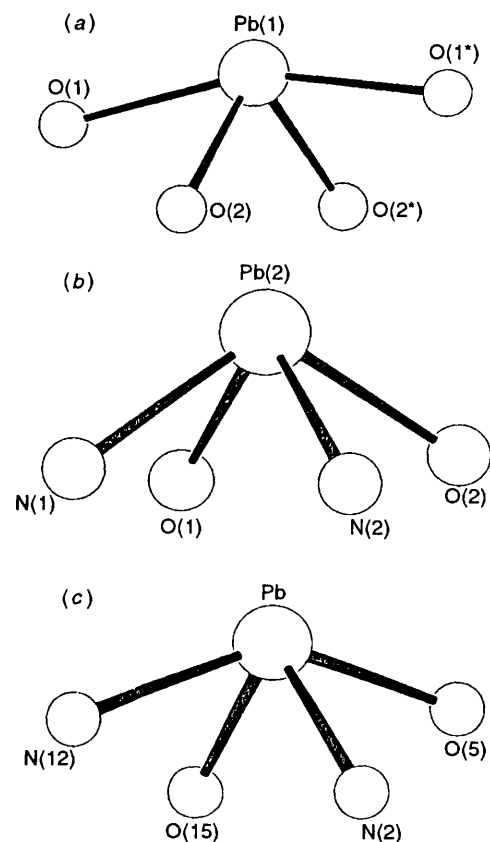


Fig. 3 The co-ordination environments of the three lead(II) centres: (a) Pb(1) in complex **1**, (b) Pb(2) in **1** and (c) Pb in **2**

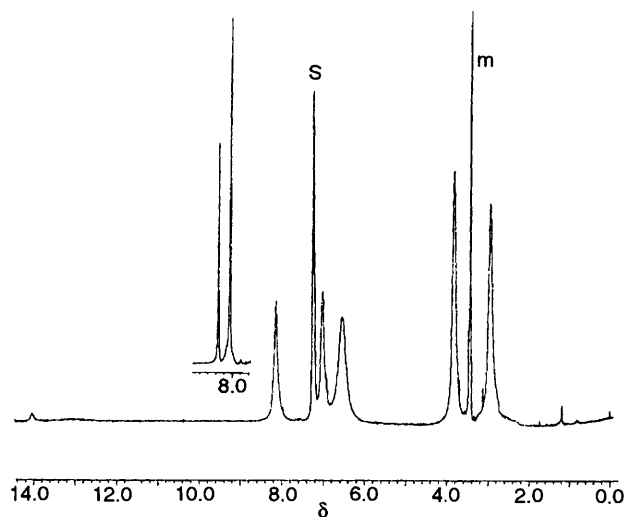


Fig. 4 Proton NMR spectrum (250 MHz) of complex **2** at 275 K (s = residual proton peak from CDCl₃, m = CH₃ from methanol). Insert shows azomethine proton region at 225 K

(Fig. 4). It seems likely therefore that at ambient temperatures there is an exchange process involving all three legs of the tripod and that this process is slowed sufficiently at 225 K to yield a limiting spectrum in which the azomethine peaks show their minimised linewidth. This suggests a free energy of activation of approximately 47 kJ mol⁻¹ for the process which interconverts these protons.¹⁰

Solid-state ²⁰⁷Pb NMR studies of complex **2** reveal a pattern centred on δ -855.3 with a significant degree of doubling for some of the signals. The chemical shift is well within the range of δ values reported for ²⁰⁷Pb NMR spectra,¹¹ although there are surprisingly few data for related lead(II) compounds for closer comparison. The doubling was also evident in solid-state

Table 2 Proton NMR data

Compound	δ			
	Aryl OH	CH=N	Aryl H	(CH ₂) _n
H ₂ salen	13.2 (br s)	8.35 (s)	7.20 (m), 6.85 (m)	3.93 (s)
1	—	9.95 (s)	7.2 (t), 6.9 (d), 6.6 (t), 6.2 (d)	3.8 (s), 3.4 (m), 3.2 (s)
H ₃ saltren	13.6 (br s)	7.8 (s)	7.2 (t), 6.95 (d), 6.55 (t), 6.1 (d)	3.5 (t), 2.8 (t)
2*	14.0 (s)	8.1 (s)	7.25 (s), 7.0 (s), 6.5 (s)	3.85 (s), 2.85 (s)

All spectra recorded in CDCl₃ solution and reported as ppm downfield of external SiMe₄. * All resonances at room temperature are broad (see text).

Table 3 Atomic coordinates for complex **1**

Atom	x	y	z
Pb(1)	1.0	-0.115 42(4)	0.75
Pb(2)	1.165 28(2)	0.057 27(4)	0.771 20(2)
Cl	1.154 2(1)	-0.311 1(3)	0.853 2(2)
O(1)	1.106 5(3)	-0.070 5(6)	0.687 2(4)
O(2)	1.054 9(2)	0.055 3(6)	0.810 2(3)
O(3)	1.089 2(4)	-0.312(1)	0.827 2(6)
O(4)	1.167 4(7)	-0.188 1(10)	0.882 2(7)
O(5)	1.162 1(4)	-0.404(1)	0.909 3(7)
O(6)	1.193 1(6)	-0.327(2)	0.794 3(7)
N(1)	1.188 6(4)	0.143 4(9)	0.643 0(5)
N(2)	1.125 2(4)	0.285 0(7)	0.750 0(5)
C(1)	1.128 3(4)	-0.125 8(9)	0.622 1(5)
C(2)	1.163 4(4)	-0.052 0(10)	0.567 5(5)
C(3)	1.182 8(4)	-0.112(1)	0.497 6(6)
C(4)	1.171 5(5)	-0.243(1)	0.483 6(6)
C(5)	1.135 4(5)	-0.318(1)	0.538 2(7)
C(6)	1.116 4(4)	-0.258 3(10)	0.605 3(6)
C(7)	1.183 3(4)	0.087(1)	0.578 5(6)
C(8)	1.204 9(5)	0.287(1)	0.649 1(7)
C(9)	1.153 8(6)	0.361(1)	0.687 3(7)
C(10)	1.079 7(5)	0.342 7(10)	0.787 1(6)
C(11)	1.041 2(4)	0.285 0(9)	0.848 4(5)
C(12)	1.030 3(4)	0.148 6(9)	0.858 5(5)
C(13)	0.992 8(5)	0.104 6(9)	0.918 9(5)
C(14)	0.964 0(4)	0.198(1)	0.969 1(6)
C(15)	0.974 2(5)	0.335(1)	0.959 4(7)
C(16)	1.013 1(5)	0.375 9(10)	0.898 8(6)

¹³C NMR studies, and these effects could be caused by the compound containing two molecules of **2** which are not crystallographically equivalent.¹² Whilst this was not the case for the structure reported here, a second structural determination carried out on a crystal of the same compound recrystallised using different solvents showed a different array* with a unit cell comprising two molecules of **2**. Although this second structure was poorly resolved, it was readily apparent that there were two independent molecules of **2**, as is supported by the cell volume.

There is clearly a variety of compounds accessible from the interaction of lead(II) with Schiff bases and we continue to investigate this area.

Experimental

General

Microanalyses were performed by the University of Loughborough analytical service. Proton NMR spectra were recorded at 250.13 MHz on a Bruker AM250 spectrometer, the ²⁰⁷Pb NMR spectrum on a Varian Unity Plus 300 spectrometer at 62.70 MHz with a Doty Scientific magic angle spinning probe. Lead(II) perchlorate trihydrate, salicylaldehyde, ethane-1,2-diamine and tris(2-aminoethyl)amine were obtained from

* The sample was recrystallised from aqueous ethanol; triclinic, space group *P* $\bar{1}$, *a* = 16.310(6), *b* = 16.673(3), *c* = 10.986(2) Å, α = 107.65(1), β = 89.91(2), γ = 96.00(2)°, *U* = 2830 Å³, *Z* = 4 (two independent molecules).

Table 4 Atomic coordinates for complex **2**

Atom	x	y	z
Pb	0.420 64(2)	0.497 06(2)	0.104 58(2)
O(5)	0.322 1(4)	0.360 1(4)	0.133 0(3)
O(15)	0.357 8(4)	0.459 6(3)	-0.034 5(3)
O(25)	0.616 5(6)	0.616 0(5)	0.560 0(4)
O(30)	0.479 5(6)	0.233 6(5)	0.189 9(4)
N(1)	0.416 2(6)	0.662 6(5)	0.200 9(4)
N(2)	0.235 3(5)	0.545 7(4)	0.134 8(4)
N(12)	0.411 7(6)	0.639 9(5)	0.012 7(4)
N(22)	0.585 8(7)	0.573 6(5)	0.396 9(5)
C(1)	0.307 6(8)	0.662 4(6)	0.235 9(5)
C(2)	0.220 3(7)	0.638 4(6)	0.165 4(5)
C(3)	0.149 2(6)	0.496 1(8)	0.117 4(4)
C(4)	0.141 7(7)	0.403 7(6)	0.084 4(5)
C(5)	0.230 8(7)	0.342 2(5)	0.089 8(5)
C(6)	0.211 8(8)	0.257 2(6)	0.048 8(5)
C(7)	0.112 1(9)	0.235 3(6)	0.006 6(5)
C(8)	0.025 6(8)	0.294 4(7)	0.006 2(6)
C(9)	0.040 5(7)	0.377 8(6)	0.044 8(5)
C(11)	0.431 4(8)	0.740 7(6)	0.140 8(6)
C(12)	0.477 0(9)	0.714 0(6)	0.055 7(6)
C(13)	0.351 2(7)	0.658 1(6)	-0.055 3(5)
C(14)	0.282 6(7)	0.593 6(6)	-0.104 4(5)
C(15)	0.288 5(6)	0.498 5(7)	-0.090 3(5)
C(16)	0.217 2(7)	0.443 1(6)	-0.144 9(5)
C(17)	0.147 7(8)	0.479 6(8)	-0.209 1(6)
C(18)	0.142 3(8)	0.572 0(8)	-0.222 8(6)
C(19)	0.210 0(8)	0.629 1(7)	-0.171 4(6)
C(21)	0.507 3(8)	0.661 4(6)	0.271 7(6)
C(22)	0.518 2(9)	0.567 4(7)	0.313 3(6)
C(23)	0.671 5(9)	0.525 9(6)	0.404 9(5)
C(24)	0.739 9(7)	0.520 2(6)	0.487 4(5)
C(25)	0.707 6(8)	0.564 3(6)	0.562 8(6)
C(26)	0.767 5(9)	0.557 1(7)	0.642 0(6)
C(27)	0.862 1(8)	0.503 4(8)	0.644 9(6)
C(28)	0.896 6(8)	0.459 0(7)	0.570 1(7)
C(29)	0.834 5(9)	0.468 5(7)	0.492 5(6)
C(30)	0.525 6(9)	0.277 9(7)	0.262 7(6)

Aldrich and used without further purification. Lead(II) chloride was obtained commercially and used as received. The compounds H₂salen and H₃saltren were prepared according to literature procedures.⁷ **CAUTION:** perchlorate salts are potentially explosive and must be handled with great care.

Preparation of complexes

Complex 1. To a solution of H₂salen (0.10 g, 0.4 mmol) in hot methanol (5 cm³) was added with stirring a solution of Pb(ClO₄)₂·3H₂O (0.15 g, 0.37 mmol) in hot methanol (5 cm³). Stirring was continued under gentle heating for 5 min. The solution was then filtered hot and allowed to cool slowly to room temperature, whereupon complex **1** precipitated as a yellow crystalline solid (isolated yield 68%, m.p. 240–243 °C (decomp.)) (Found: C, 28.60; H, 1.80; N, 4.30. Calc. for C₃₂H₂₈Cl₂N₄O₁₂Pb₃: C, 28.40; H, 2.10; N, 4.15%).

Complex 2. To a solution of H₃saltren (2.06 g, 4.5 mmol) in methanol (150 cm³) was added PbCl₂ (1.25 g, 4.5 mmol). The mixture was refluxed for 30 min before the addition of an excess

of triethylamine (3 g). The solution was refluxed overnight and then allowed to cool to room temperature before being filtered. The product **2** formed as bright yellow-orange crystals over a period of 1 week (isolated yield 87%), m.p. 225–227 °C (Found: C, 49.05; H, 4.55; N, 7.95. Calc. for $C_{28}H_{32}N_4O_4Pb$; C, 48.35; H, 4.65; N, 8.05%).

X-Ray crystallography

Crystal data for complex 1. $C_{32}H_{28}Cl_2N_4O_{12}Pb_3$, $M = 1353.10$, orthorhombic, the molecule is disposed about a two-fold axis, space group $Pbcn$, $a = 20.569(4)$, $b = 9.990(5)$, $c = 17.372(6)$ Å, $U = 3569(3)$ Å³, $Z = 4$, $D_c = 2.52$ g cm⁻³, yellow block, dimensions 0.21 × 0.30 × 0.30 mm, $\mu(\text{Cu-K}\alpha) = 293.91$ cm⁻¹, λ 1.541 78 Å, $F(000) = 2496$.

All measurements were made at 20 °C on a Rigaku AFC7S diffractometer with graphite-monochromated Cu-K α radiation, ω -2 θ scan technique to a maximum 2 θ of 120.4°. 3047 Unique reflections were measured. The data were corrected for Lorentz and polarisation effects and an empirical absorption correction was applied¹³ resulting in transmission factors ranging from 0.63 to 1.00.

Crystal data for complex 2. $C_{27}H_{28}N_4O_3Pb\cdot CH_3OH$, $M = 695.79$, monoclinic, space group $P2_1/n$, $a = 12.220(3)$, $b = 14.674(1)$, $c = 15.203(2)$ Å, $\beta = 93.40(1)^\circ$, $U = 2721.4(7)$ Å³, $Z = 4$, $D_c = 1.70$ g cm⁻³, yellow prism, dimensions 0.32 × 0.45 × 0.70 mm, $\mu(\text{Cu-K}\alpha) = 125.38$ cm⁻¹, λ 1.541 78 Å, $F(000) = 1368$.

All measurements were made as for **1** to a maximum 2 θ of 120.2°. Of 4466 reflections measured, 4244 were unique ($R_{int} = 0.142$). The data were corrected as for **1** resulting in transmission factors ranging from 0.61 to 1.00.

Structure analysis and refinement. The structure of complex **1** was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in idealised positions (C–H 0.95 Å). The final cycle of full-matrix least-squares refinement based on 2134 observed reflections [$I > 3.00\sigma(I)$] converged to $R = 0.033$ [$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$]. The maximum and minimum residual electron densities in the final ΔF map were -1.29 and 2.02 e Å⁻³. The structure of **2** was solved by and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen associated

with O(25) was not located. The hydrogen associated with O(30) was located from a ΔF map and fixed. The final cycle of full-matrix least-squares refinement based on 3038 observed reflections [$I > 3.00\sigma(I)$] converged to $R = 0.032$. The maximum and minimum residual electron densities in the final ΔF map were -1.32 and 1.32 e Å⁻³. All calculations were performed using the TEXSAN package.¹⁴

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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