

First synthesis of a unique dilead Schiff base complex

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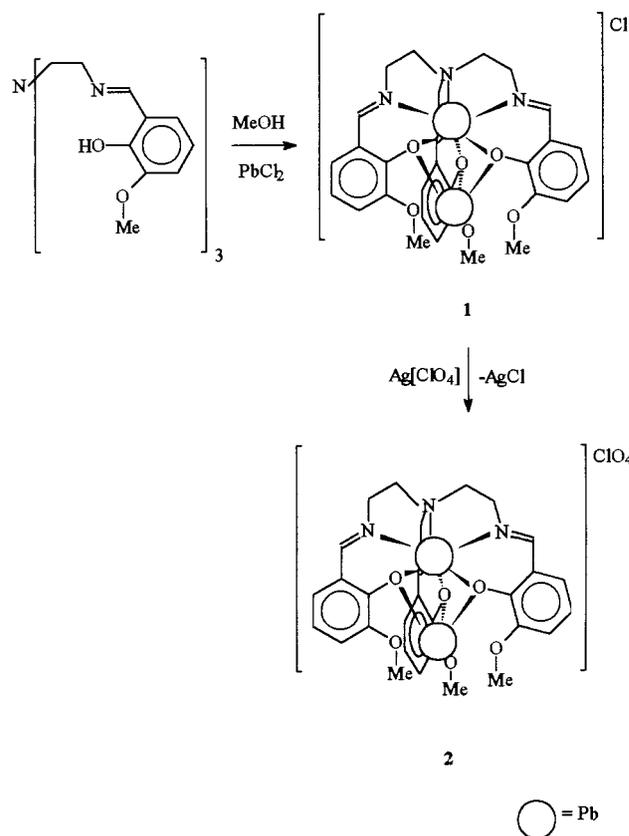
The reaction of the tripodal Schiff base ligand $N[\text{CH}_2\text{CH}_2\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_3(\text{OMe})\text{-3-(OH)-2}]_3$ (H_3L) with lead(II) chloride in methanol in the presence of a base led to the bimetallic complex $[\text{Pb}_2\text{L}]\text{Cl}$ **1** in good yield; the cation was characterised crystallographically as the perchlorate salt **2**, revealing dissimilar environments for the Pb(II) centres with one lead lying within the central cavity of (L^3)⁻ and the second bound externally to the three phenolate oxygens of the ligand.

Tripodal Schiff base ligands of general formula $N[\text{CH}_2\text{CH}_2\text{N}=\text{C}(\text{H})\text{C}_6\text{H}_3(\text{R})\text{OH-2}]_3$ have a well explored coordination chemistry with d- and f-block metals. Complexation of such trivalent metals by triply deprotonated ligands gives either octahedral complexes with $[\text{N}_3\text{O}_3]$ donor sets, or for some larger cations additional participation of the apical nitrogen atom gives a seven-coordinate monocapped octahedron with an $[\text{N}_4\text{O}_3]$ donor set.¹ The p-block metals have, in contrast, received less attention. We have previously demonstrated that polydentate Schiff base ligands support a range of unusual coordination polyhedra at Pb(II);^{2,3} here we report the preparation of a new bimetallic species $[\text{Pb}_2\text{L}]\text{Cl}$ **1**, where H_3L = tris[2-(3-methoxysalicylideneamino)ethyl]amine, characterised crystallographically as its perchlorate salt **2**.

The reaction of H_3L with an equimolar quantity of lead(II) chloride and triethylamine in refluxing methanol generates exclusively $[\text{Pb}_2\text{L}]\text{Cl}$ **1**, isolable in good yield from the reaction as an orange microcrystalline solid.† This contrasts with the corresponding reaction using the unsubstituted tripodal ligand $N(\text{CH}_2\text{CH}_2\text{N}=\text{CHC}_6\text{H}_4\text{OH-2})_3$ ($\text{H}_3\text{saltren}$) which gives exclusively $[\text{Pb}(\text{Hsaltren})]$.³ Anion metathesis of **1** using $\text{Ag}[\text{ClO}_4]$ or $\text{Pb}[\text{ClO}_4]_2 \cdot 3\text{H}_2\text{O}$ in methanol gives the perchlorate salt $[\text{Pb}_2\text{L}][\text{ClO}_4]$ **2** (Scheme 1).

The ¹H NMR spectra of **1** and **2** in *d*₃-acetonitrile at room temperature each have broadened peaks indicating that at this temperature, the molecule is stereochemically non-rigid. They both show two distinct imine resonances in the ratio 2:1, suggesting a slow exchange process in which two legs of the tripodal ligand experience a different environment from the third. This situation is highly reminiscent of the fluxional behaviour of $[\text{Pb}(\text{Hsaltren})]$, which we have previously ascribed to an interchange involving all three legs of the tripod. Unfortunately, because of the insolubility of **1** and **2** in solvents of suitable melting point, we were unable to obtain VT NMR data over a sufficiently wide temperature range to throw any light upon the mechanism of this fluxionality.

The solid state structure of **2** has been determined by single crystal X-ray analysis.‡ The two lead(II) atoms in **2** [Fig. 1(a)] exist in dissimilar environments, whereby Pb(1) is bound by all of the nitrogen atoms and phenolate oxygens of L^{3-} and is seven-coordinate. This $[\text{PbL}]^-$ unit acts as a tridentate ligand to Pb(2) binding through the phenolate oxygen atoms O(6), O(16) and O(26) to give the dinuclear cation $[\text{Pb}_2\text{L}]^+$, which possesses pseudo-*C*_{3v} symmetry [Fig. 1(b)]. Complex **2** provides a rare example where all three phenolate oxygen atoms of a tripodal Schiff base ligand bridge two metal centres, a unique instance amongst main group elements. The central $[\text{Pb}_2\text{O}_3]$ core of **2** can be considered as a trigonal bipyramid, with Pb(1) and Pb(2) providing the apical vertices. Pb(2) has close contacts with an oxygen atom O(41) from the perchlorate counter ion

Scheme 1 The preparation of compounds **1** and **2**.

$[\text{Pb}(2) \cdots \text{O}(41)$ 3.19(1) Å] and the *o*-methoxy groups of L [$\text{Pb}(2) \cdots \text{OMe}$ 2.69(1)–2.78(1) Å]; the intermetallic distance $\text{Pb}(1) \cdots \text{Pb}(2)$ is 3.558(1) Å.

While the *o*-methoxy groups of L^{3-} have been identified as donor sites in heterodimetallic lanthanide complexes $[\text{LnLn}']\text{-}[\text{NO}_3]_3$ ($\text{Ln}, \text{Ln}' = \text{Gd}; \text{Ln} = \text{Yb}, \text{Ln}' = \text{Gd}$),⁵ we have previously discounted such bonding interactions in related Pb(II) complexes.² The Pb(1)–O and Pb(1)–N distances [2.518(3)–2.595(4) Å and 2.557(5)–2.651(4) Å respectively] are discernibly longer than in $[\text{Pb}(\text{Hsaltren})]$ [2.274(5)–2.518(7) Å] in which the lead(II) atom is bound by two phenolate oxygens and two imido nitrogens only;² additionally the Pb(2)–O lengths [2.339(3)–2.358(4) Å] are elongated compared with Schiff base complexes of lead(II) in which the central cavity of the ligand is occupied by the phenolic protons [2.27(1)–2.34(1) Å].² The Pb(1)–N(1) distance of 2.651(4) Å is comparable to the mean $\text{Pb}(1)\text{-N}_{\text{imine}}$ length of 2.60 Å, which seems to confirm that a genuine bonding interaction exists. The O–Pb(1)–O, N(1)–Pb(1)–N and chelating N–Pb(1)–O angles lie within a range 67.60(12)–71.82(11)°, the O–Pb(2)–O angles being slightly more open [74.96(13)–78.21(12)°]. All of the remaining X–Pb(1)–N angles (where X = phenolate O or N) between different chelate rings fall within a larger range, 103.2(14)–140.62(12)°.

The coordination geometry about Pb(1) in **2** is best described as a distorted monocapped octahedron, with the triangular faces defined by the three imine nitrogens and the three

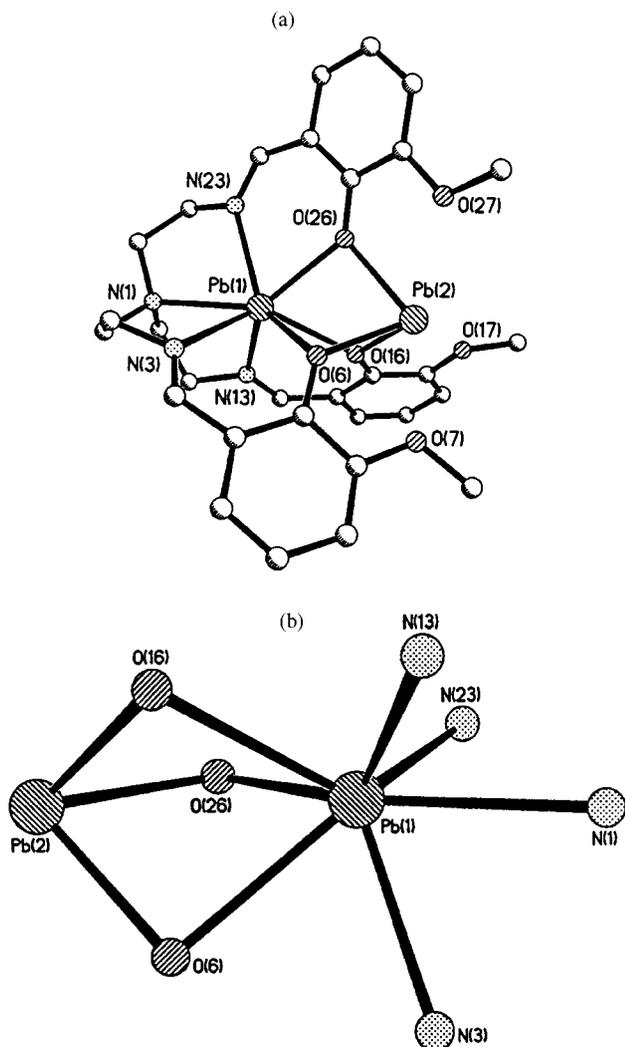


Fig. 1 (a) Structure of the cation in **2** (hydrogen atoms omitted for clarity), (b) core coordination environment. Selected bond lengths (Å) and angles (°): Pb(1)–O(6) 2.595(4), Pb(1)–O(16) 2.534(4), Pb(1)–O(26) 2.518(3), Pb(1)–N(1) 2.651(4), Pb(1)–N(3) 2.616(5), Pb(1)–N(13) 2.594(4), Pb(1)–N(23) 2.577(5), Pb(2)–O(6) 2.351(4), Pb(2)–O(16) 2.339(3), Pb(2)–O(26) 2.358(4); O(26)–Pb(1)–O(16) 71.82(11), O(26)–Pb(1)–N(23) 71.55(13), O(16)–Pb(1)–N(23) 123.13(14), O(26)–Pb(1)–O(6) 69.29(12), O(16)–Pb(1)–O(6) 67.60(12), N(23)–Pb(1)–O(6) 132.19(13), O(26)–Pb(1)–N(13) 135.96(13), O(16)–Pb(1)–N(13) 70.88(13), N(23)–Pb(1)–N(13) 111.7(2), O(6)–Pb(1)–N(13) 115.40(13), O(26)–Pb(1)–N(3) 117.63(14), O(16)–Pb(1)–N(3) 126.03(14), N(23)–Pb(1)–N(3) 109.2(2), O(6)–Pb(1)–N(3) 68.05(13), N(13)–Pb(1)–N(3) 103.02(14), O(26)–Pb(1)–N(1) 139.57(13), O(16)–Pb(1)–N(1) 140.62(12), N(23)–Pb(1)–N(1) 69.24(14), O(6)–Pb(1)–N(1) 135.70(13), N(13)–Pb(1)–N(1) 69.98(14), N(3)–Pb(1)–N(1) 68.01(14), O(16)–Pb(2)–O(6) 74.96(13), O(16)–Pb(2)–O(26) 78.21(12), O(6)–Pb(2)–O(26) 76.24(13).

phenolate oxygen atoms respectively, with the apical nitrogen atom N(1) capping the imine face. The *o*-methoxy substituents of L^{3-} increase the electron density at the phenolate oxygen atoms sufficiently to allow binding of a second Pb(II) centre; thus Pb(2) closes the ligand pocket around Pb(1), the mismatch in size leading to distortions in the overall geometry of the

encapsulated metal atom. While several authors have claimed the lone pair at Pb(II) centres of high coordination number to be stereochemically inactive, its precise steric requirements seem to be sensitive to several factors.⁶ Although Pb(2) can be described as having a distorted tetrahedral geometry in which the lone pair is in the hemisphere oriented away from Pb(1), the position of the lone pair at Pb(1) cannot be unequivocally defined.

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Notes and references

† Experimental conditions and instrumentation are as described elsewhere,^{2,3} H_3L was prepared from tris(2-aminoethyl)amine and *o*-vanillin.⁴ **CAUTION** perchlorate salts are potentially explosive and should be handled with care. $[Pb_2L]Cl$ **1**. A mixture of H_3L (2.42 g, 4.4 mmol) and lead(II) chloride (1.22 g, 4.4 mmol) in methanol (40 cm³) was heated at reflux for 30 min. Addition of triethylamine (3 cm³) gave a clear orange solution which was heated for a further 2 h, during which time a precipitate of triethylammonium hydrochloride formed. The solution was allowed to cool and filtered, orange microcrystals of **1** grew from the filtrate over one week. Yield 1.45 g, 66% based on Pb. Found (Calc. for $C_{30}H_{33}ClN_4O_6Pb_2$): C, 36.6 (36.2); H, 3.4 (3.3); N, 5.6 (5.6)%. IR(KBr disc): $\nu(CN)$ 1624s cm⁻¹. δ_H (250.1 MHz, CD_3CN): 8.28 (s, 2H, $CH=N$), 8.22 (s, 1H, $CH=N$), 6.96 (m, br, 6H, aryl), 6.57 (m, br, 3H, aryl), 3.88 (s, br, 9H, OCH_3), 3.70 (s, br, 6H, CH_2), 2.85 (s, br, 6H, CH_2). MS(FAB⁺): m/z 961 $[Pb_2L]^+$. $[Pb_2L][ClO_4]$ **2**. To a stirred solution of **1** (0.17 g, 0.17 mmol) in methanol (15 cm³) was added $Ag[ClO_4]$ (0.045 g, 0.22 mmol) in methanol (3 cm³). After 30 min the orange solid was collected by centrifugation, extracted into acetonitrile (10 cm³) and filtered through glass wool–Celite. Removal of the solvent *in vacuo* gave crude **2**, recrystallised from acetonitrile–diethyl ether as yellow microcrystals (49 mg, 28% yield). Found (Calc. for $C_{30}H_{33}ClN_4O_{10}Pb_2$): C, 34.1 (34.1); H, 3.2 (3.0); N, 5.3 (5.3)%. IR(KBr disc): $\nu(CN)$ 1630s, $\nu(ClO_4)$ 1097vs and 623m cm⁻¹. δ_H (250.1 MHz, CD_3CN): 8.55 (s, 2H, $CH=N$), 8.34 (s, 1H, $CH=N$), 7.13 (m, 4H, aryl), 6.99 (m, br, 2H, aryl), 6.71 (m, 2H, aryl), 6.60 (m, br, 1H, aryl), 4.00 (s, 3H, OCH_3), 3.90 (s, 6H, OCH_3), 3.64 (m, 6H, CH_2), 2.88 (m, 6H, CH_2).

‡ Crystal data and data collection parameters for **2**: $C_{30}H_{33}ClN_4O_{10}Pb_2$, $M = 1059.43$, monoclinic, space group $P2_1/c$, $a = 12.218(1)$, $b = 16.274(10)$, $c = 16.443(1)$ Å, $\beta = 91.04(1)^\circ$, $U = 3268.99(3)$ Å³, $Z = 4$, $\mu(Mo-K\alpha) = 10.431$ mm⁻¹, $T = 293$ K, $R1 = 0.0212$ for 4754 unique reflections. CCDC reference number 186/1127.

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