

Synthesis of a New Unsymmetrical Trinucleating Macrocycle incorporating both Phenolic and Pyridine Head Units: X-Ray Crystal Structure of $\{[\text{Pb}_2(\text{L1})(\text{Cl})](\text{ClO}_4)_2\}_x$

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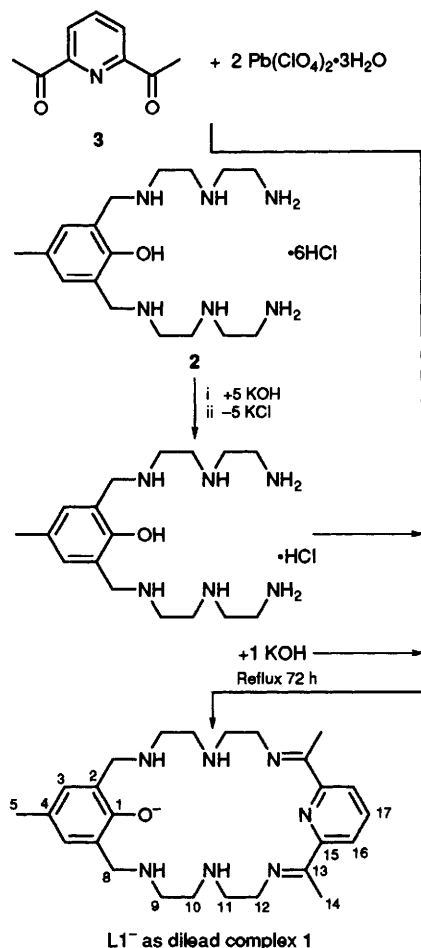
Dilead(II) and tricopper(II) complexes of the new unsymmetrical macrocycle L1⁻ are prepared; the structure of the chloride-bridged chain polymer $\{[\text{Pb}_2(\text{L1})(\text{Cl})](\text{ClO}_4)_2\}_x$, **1**, is described.

In contrast to the vast array of known mono- and bi-nucleating macrocycles,¹ macrocycles capable of encompassing three or more metal ions are rare. Very few large macrocycles prepared to date provide more than a single type of metal-binding site.^{2,3} Rather, research efforts have concentrated on 'symmetrical' macrocycles, primarily because of the relative ease of their synthesis.^{1,4-6} Our aim was to develop a new class of macrocycle that could bind three or more transition metal ions in close proximity to one another and provide two distinct types of metal-binding environment. This has been achieved with the successful template synthesis of the

unsymmetrical macrocycle L1⁻ (Scheme 1). The resulting macrocyclic dilead(II) complex, which is central to the synthesis of the desired trimetallic complexes, has been structurally characterised and is described herein.

The complex $\{[\text{Pb}_2(\text{L1})(\text{Cl})](\text{ClO}_4)_2\}_x$, **1**, was obtained as a pale-yellowish powder[†] in 54% yield from the reaction of the partially neutralised three-quarter macrocycle **2**, 2,6-diacetylpyridine **3**, and KOH in the presence of lead(II)

[†] Satisfactory elemental analyses were found for all new compounds.



Scheme 1 Synthesis of $\{[\text{Pb}_2(\text{L1})(\text{Cl})](\text{ClO}_4)_2\}_x$

perchlorate, in refluxing methanol (Scheme 1).⁷ The IR spectrum of this powder showed that cyclisation had occurred; an imine C=N stretch was present at 1627 cm^{-1} and amine N-H stretches at 3280 and 3240 cm^{-1} . No absorptions corresponding to unconverted carbonyl or primary amine were observed. Of the common solvents tried 1 was soluble only in dimethylformamide (it took time to dissolve in this solvent). Recrystallisation from dimethylformamide by vapour diffusion of diethyl ether yielded yellow blocks[‡] suitable for X-ray crystal structure analysis.[§] The ^1H NMR spectrum of the crystals confirmed that the two sets of aromatic protons

[‡] Conductivity, $\Lambda = 163\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ in DMF. ^{13}C NMR ($[\text{D}_2\text{H}_7]\text{DMF}$, referenced to external Bu^+OH), numbering scheme as in Scheme 1: δ 171.9 C(13); 163.0 C(15); 154.1 C(1); 141.2 C(17); 135.3 C(16); 127.0 C(3); 126.4 C(4); 125.6 C(2); (52.5, 51.9, 51.1, 50.1, 46.5) [C(8), C(9), C(10), C(11), C(12)]; (20.1, 18.4) [C(5), C(4)], assignments are tentative.

[§] *Crystal data:* $\text{C}_{26}\text{H}_{38}\text{N}_7\text{O}_5\text{Cl}_3\text{Pb}_2$, yellow block, $0.3 \times 0.4 \times 0.4\text{ mm}$, monoclinic, space group $P2_1/c$, $a = 15.158(4)$, $b = 13.134(4)$, $c = 17.110(4)\text{ \AA}$, $\beta = 101.2(2)^\circ$, $U = 3342(2)\text{ \AA}^3$, $Z = 4$, $\mu = 1.04\text{ cm}^{-1}$. Data were collected at 180 K on a Nicolet R3m four-circle diffractometer using graphite monochromated Mo-K α radiation. 4920 Reflections were collected in the range $4 < 2\theta < 45^\circ$ and the 4365 independent reflections were used in the structural analysis. The structure was solved by Patterson methods (SHELXS-86⁸) and gave a final $wR_2 = 0.176$ and GOF = 0.95 for 214 parameters (lead and chlorine atoms anisotropic) after full-matrix least-squares refinement on F^2 (SHELXL-93 gamma release⁹) of all data [$wR_2 = 0.152$ and $R_1 = 0.087$ for the 2268 reflections with $I > 2\sigma(I)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

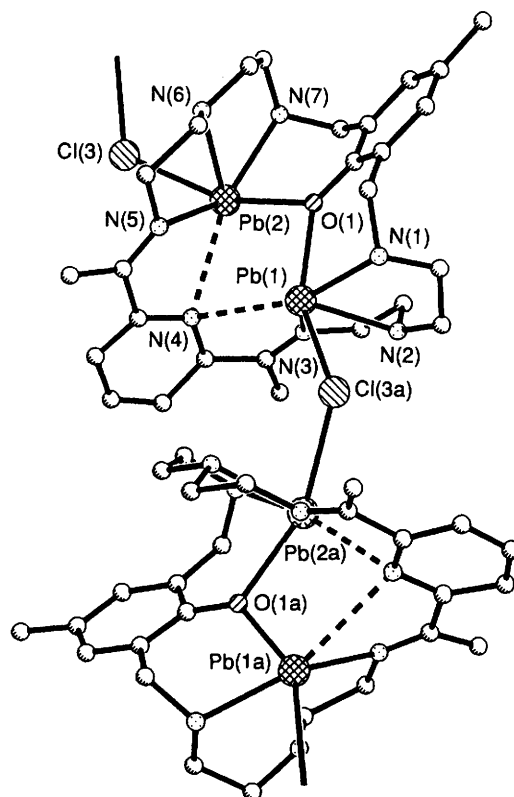


Fig. 1 Perspective view of the $[\text{Pb}_2(\text{L1})(\text{Cl})]_x^{2+}$ cation. Selected interatomic distances (\AA) and angles ($^\circ$): Pb(1)–N(1) 2.44(2), Pb(1)–O(1) 2.48(2), Pb(1)–N(2) 2.51(2), Pb(1)–N(3) 2.76(2), Pb(1)–Cl(3a) 2.965(8), Pb(2)–Cl(3) 2.832(8), N(1)–Pb(1)–O(1) 77.5(7), N(1)–Pb(1)–N(2) 70.3(8), O(1)–Pb(1)–N(2) 90.2(7), N(1)–Pb(1)–N(3) 128.6(7), O(1)–Pb(1)–N(3) 80.3(6), N(2)–Pb(1)–N(3) 64.1(8), N(1)–Pb(1)–Cl(3a) 74.2(5), O(1)–Pb(1)–Cl(3a) 151.6(5), N(2)–Pb(1)–Cl(3a) 79.1(6), N(3)–Pb(1)–Cl(3a) 117.0(5), O(1)–Pb(2)–N(6) 83.4(7), O(1)–Pb(2)–N(7) 70.7(7), N(6)–Pb(2)–N(7) 70.7(7), O(1)–Pb(2)–N(5) 90.4(6), N(6)–Pb(2)–N(5) 67.9(7), N(7)–Pb(2)–N(5) 138.1(7), O(1)–Pb(2)–Cl(3) 158.3(4), N(6)–Pb(2)–Cl(3) 75.6(6), N(7)–Pb(2)–Cl(3) 89.1(5), N(5)–Pb(2)–Cl(3) 86.5(5), Pb(2)–O(1)–Pb(1) 100.0(6), Pb(2)–Cl(3)–Pb(1b) 127.0(3).

were present in the ratio expected for L1^- , and the clean ^{13}C NMR spectrum was consistent with L1^- formation.

The single crystal X-ray analysis reveals that 1 adopts a polymeric chain structure (Fig. 1). The two lead ions are in crystallographically independent but chemically similar coordination environments. They are bridged by the phenolic 'head' unit, so each lead ion occupies one 'side' of the macrocycle and is bound by a chloride ion, a phenolic oxygen atom, two amine nitrogen atoms, one imine nitrogen atom and weakly by the bridging pyridine nitrogen atom. The result is a distorted six-coordinate geometry about lead. There are also weak interactions with the perchlorate anions [Pb(1)–O(12) 3.38, Pb(1)–O(14) 3.13, Pb(2)–O(21) 3.31 Pb(2)–O(22) 3.88 \AA]. The chloride ion, Cl(3), bridges the lead ions in adjacent macrocycles; thus the chain has a $\{-\text{Cl}(3)-\text{Pb}(2)-\text{O}(1)-\text{Pb}(1)-\}_x$ backbone. The plane of the phenol ring intersects the plane of the pyridine ring at an angle of 113° , so the macrocycle is far from planar. This twist occurs so that the macrocycle may bind to the two lead ions. Bonds to the phenolic 'head' of the macrocycle are somewhat shorter than those to the pyridine 'head', as shown by the lead–imine bond lengths [Pb(1)–N(3) 2.76(2), Pb(2)–N(5) 2.64(2) \AA] in comparison with the longest lead–amine bond lengths [Pb(1)–N(2) 2.51(2), Pb(2)–N(7) 2.52(2) \AA]. However, despite the closer association of the lead ions with the phenolic 'head' unit, the pyridine nitrogen atom does interact weakly with the lead

ions, and in so doing it forms an unusual bridge [Pb(1)–N(4) 3.09, Pb(2)–N(4) 2.90 Å]. Pyridine rarely adopts a bridging mode of coordination, usually binding preferentially to a single metal ion. A search of the Cambridge Structural Database¹⁰ revealed that very few examples of bridging pyridine have been structurally characterised, and that there are no examples involving lead. Of the five relevant to this work^{11,12} only one involved a macrocyclic pyridine-containing ligand, and this was a mono-silver macrocyclic complex.¹² The common feature of all of these examples is that bonds to the bridging pyridine nitrogen are longer than other metal–nitrogen bonds in the complexes. This is also a feature in **1**. The formation of a weak bridging interaction is in this case facilitated by macrocyclic constraints, which hold the pyridine nitrogen atom in close proximity to the lead ions. L1[−] was designed to bind three transition metal ions so when templated on two large lead ions, which bind at the phenolic ‘head’ of the macrocycle, the pyridine nitrogen atom is left ‘available’ for such an interaction.

Transmetallation reactions of **1** with a wide variety of transition metal ions are now under investigation. Initial results indicate that trinuclear complexes are indeed formed when the large lead ions (radius 1.12 Å) are replaced by smaller transition metal ions (radii typically 0.65–0.82 Å). One recently isolated example of this is the emerald green tricopper(II) complex of L1[−], Cu₃(L1)(OH)(ClO₄)₄(H₂O).[¶] The IR spectrum shows that the macrocycle remains intact (C=N str. 1626, N–H str. 3239 cm^{−1}), and fast atom bombardment (FAB) mass spectrometry gives a cluster of peaks corresponding to [Cu₃(L1)(OH)(ClO₄)₃]⁺: the fragmentation pattern is consistent with the stepwise loss of perchlorate from this species. Thus, our aim of preparing new trinuclear complexes with metal ions in differing macrocycle environments has been achieved. We are now working towards a thorough characterisation of this tricopper complex, along with other novel trimetallic species derived from L1[−].

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[¶] Magnetic moment 2.2 μ_B per copper at 25 °C (Evans method, SiMe₄ in CD₃CN). UV–VIS (Me₃CN) λ_{d-d} 660 nm, ε = 330 dm³ mol^{−1} cm^{−1}.