Lead(II) and Barium(II) Complexes of a potentially Octadentate Macrocyclic Ligand (H_4L), capable of providing Endogenous Alkoxy and Phenoxy Bridges. The *X*-Ray Crystal Structures of $[Pb(H_4L)][ClO_4]_2$, $[Pb_2(H_2L)][ClO_4]_2$, and $[(H_6L)(H_2O)_2][ClO_4]_2$†

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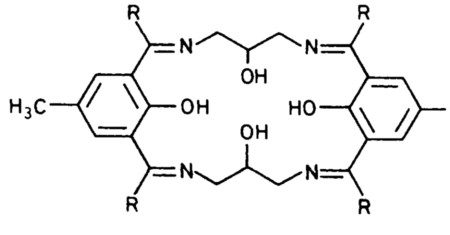
Condensation of 2,6-diformyl-4-methylphenol with 1,3-diamino-2-hydroxypropane in the presence of $Pb(ClO_4)_2 \cdot 6H_2O$ resulted in the sequential formation of three products which have been characterised by *X*-ray crystallography as mononuclear $[Pb(H_4L)][ClO_4]_2$ (**1**), binuclear $[Pb_2(H_2L)][ClO_4]_2$ (**2**), and a diaquo complex of the partly protonated macrocycle $[(H_6L)(H_2O)_2][ClO_4]_2$ (**3**) (where H_4L is a 20-membered, potentially octadentate, macrocyclic ligand, with an N_4O_4 donor set which is capable of providing endogenous phenoxy and alkoxy bridges). The use of $Pb(NCS)_2$ as a template agent, gave only the mononuclear complex $[Pb(H_4L)(NCS)_2] \cdot 2H_2O$ (**4**), under all conditions investigated. Similarly when $Ba(ClO_4)_2 \cdot 6H_2O$ or $Ba(NCS)_2 \cdot H_2O$ were used the only products were the mononuclear complexes $[Ba(H_4L)X_2] \cdot yH_2O$ [(**5**), X = NCS, $y = 2$; and (**6**), X = ClO_4, $y = 1$). These complexes were characterised by microanalysis, i.r., and ^1H and ^{13}C n.m.r. spectra. The mononuclear lead and barium complexes have been shown to have distinctly different co-ordination and this is ascribed to the relative sizes of the ions concerned.

Complexes of multidentate binucleating or polynucleating ligands which mimic the behaviour of the more complex biological polymetallic systems have been studied quite extensively in the last decade.[1] This may be attributed to increased recognition of the importance of polynuclear centres in biological catalytic processes and the potential application of such mechanisms to synthetic systems. A large number of enzymes requiring two or more metal ions for activity have been discovered and many of these appear to owe their catalytic activity to finely balanced metal–metal interactions.[2]

Tetraimine Schiff-base macrocycles formed by metal template or direct condensations of various heterocyclic dicarbonyls and 1,*n*-diaminoalkanes are well known ligands which can form mono- or bi-nuclear complexes with a wide variety of transition and non-transition metal ions. The versatility of these ligands can be enhanced by the incorporation of pendant alcohol groups which enable the macrocycles to form endogenous alkoxide bridges between the adjacent metal centres.[3] We have extended our previous study of polynucleating macrocycles with potentially bridging alcohol groups to include systems incorporating additional endogenous phenol groups. Since the introduction of 2,6-diformyl-4-methylphenol as a building block for the construction of binucleating ligands,[4] there have been many reports on the synthesis of transition-metal complexes with binucleating non-cyclic and macrocyclic Schiff-base ligands incorporating endogenous phenol groups. The presence of such bridging groups within the macrocyclic cavity should promote the binding of several metal ions, as well as mediating magnetic and electronic interactions between them. In this paper we report the metal template synthesis of a potentially octadentate tetraimine macrocyclic Schiff-base ligand derived from 2,6-diformyl-4-methylphenol and 1,3-diamino-2-hydroxypropane in the presence of lead(II) and barium(II) ions. The *X*-ray crystal structures of mononuclear $[Pb(H_4L)][ClO_4]_2$, binuclear $[Pb_2(H_2L)][ClO_4]_2$, and the diaquo complex of the protonated ligand $[(H_6L)(H_2O)_2][ClO_4]_2$ are also reported. These, and related complexes, provide entry into a series of potentially tetranuclear transition-metal complexes.[5] The structure of a barium complex of the macrocycle H_4L' has recently been reported,[6] and can be related to the structures of the complexes discussed below.



H_4L , R = H
H_4L', R = CH_3

Results and Discussion

Synthesis.—The Schiff-base condensation of two moles of 2,6-diformyl-4-methylphenol (dfmp) with two moles of 1,3-diamino-2-hydroxypropane (dahp) in the presence of Lewis acids such as Pb^{2+}, Ba^{2+}, and H^+ resulted in the formation of the 20-membered Schiff-base macrocycle (H_4L). This ligand has two phenol groups and two alcohol groups, all of which are capable of binding metal ions and also of acting as endogenous bridges between adjacent metal centres upon deprotonation. The presence of such bridging groups within the macrocyclic cavity enhances the versatility of the ligand and enables it to bind from one to four metal ions, as has been demonstrated in related ligand systems.[5]

Reaction of dfmp with dahp in the presence of $Pb(ClO_4)_2 \cdot 6H_2O$ in methanol yielded three products which have been characterised as mononuclear $[Pb(H_4L)][ClO_4]_2$ (**1**), binuclear

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

$[Pb_2(H_2L)][ClO_4]_2$ (**2**), and a salt of the protonated ligand $[(H_6L)(H_2O)_2][ClO_4]_2$ (**3**). The *X*-ray crystal structures of each of these compounds has been determined (see later). The initial product of the reaction is the binuclear complex (**2**). However, if the reaction mixture is allowed to stand for several days the mononuclear complex (**1**) and ligand salt (**3**) are obtained, and the proportion of (**3**) increases with time. Pure samples of (**1**) and (**2**) are quite stable and remain unchanged even after 48 h refluxing in methanol. It seems therefore, that loss of a metal ion from (**1**) or (**2**) requires the presence of acid in the solution in order for the accompanying protonation step to occur. Complex (**3**) can also be prepared directly, by reaction of dfmp and dahp in the presence of perchloric acid.

Use of $Pb(NCS)_2$ in the template reaction resulted in the formation of only one complex, $[Pb(H_4L)(NCS)_2]\cdot 2H_2O$ (**4**), under all conditions tried. This complex has similar spectral features to (**1**) except that the i.r. spectrum suggests that the thiocyanate anions are bound to the lead atom.

Mononuclear complexes also resulted when Ba^{2+} was used as the template ion; $[Ba(H_4L)(NCS)_2]\cdot 2H_2O$ (**5**) and $[Ba(H_4L)(ClO_4)_2]\cdot H_2O$ (**6**) have been characterised. The inability of Ba^{2+} to form binuclear complexes, even with perchlorate as counter ion can be ascribed to its larger radius; the macrocyclic ring is too small to accommodate two Ba^{2+} ions.

I.r. Spectra.—The i.r. spectra provide evidence that cyclisation has occurred. In each case, the carbonyl and amine stretches of the reactants disappear and are replaced by imine bands in the region 1 620—1 660 cm^{-1}. Complexes (**1**), (**4**), (**5**), and (**6**) each exhibit two bands attributable to the ν(C=N) stretch (1 660 and 1 640; 1 650 and 1 640; 1 650 and 1 630; and 1 660 and 1 640 cm^{-1} respectively). This inequivalence of the imine groups suggests that the metal atom is co-ordinated to only two of the four imine groups. As might be expected, the binuclear complex (**2**) has only a single imine band, implying that all four imines are co-ordinated to the metal. In the case of the protonated macrocycle (**3**) there is a strong imine stretch at 1 645 cm^{-1} with a shoulder at 1 655 cm^{-1}, again indicative of two slightly differing environments for these functions.

The $\nu_3(ClO_4)$ vibration shows some splitting in each case, suggesting the perchlorate anions are involved in interactions which result in distortion from tetrahedral symmetry. For the lead complexes, the splitting is largest in the case of (**1**) (1 175 and 1 108 cm^{-1}) and can be accounted for by hydrogen bonding involving the perchlorate ions in this complex, as revealed by the crystal-structure determination. In (**6**) bands at 1 110 and 1 090 cm^{-1} are attributed to co-ordinated perchlorate. The position of the thiocyanate stretch at 2 045 cm^{-1} for (**4**) and 2 030 cm^{-1} for (**5**) suggests that this group is co-ordinated to the metal atom in both cases.

Description of the Structures.—Crystal-structure determinations have been carried out for complexes (**2**), (**1**), and (**3**). Perspective views of the cations are shown in Figures 1, 2, and 3 respectively; in each case the anion structures are unremarkable. Atomic co-ordinates are listed in Table 1, selected bond lengths and angles are given in Table 2.

The centrosymmetric, binuclear cation $[Pb_2(H_2L)]^{2+}$ of complex (**2**) is shown in Figure 1. The macrocyclic ring is approximately planar and the lead atoms are 1.32 Å out of the mean plane of their nitrogen and phenoxy donors. The metal ions are five-co-ordinate; each is bonded to the two bridging phenoxy groups, two imine nitrogen atoms, and one of the pendant alcohol groups. The Pb–O(alcohol) bond [2.77(1) Å] is considerably longer than the other bonds, suggesting a rather weak interaction. The geometry about the metal centres is quite irregular; this may be ascribed to the effect of the stereochemically active lone pair on each lead atom. The open face on each lead is, to some extent, blocked by the perchlorate anions [Pb′–O(11) 3.33(1), Pb′–O(13) 3.15 Å].

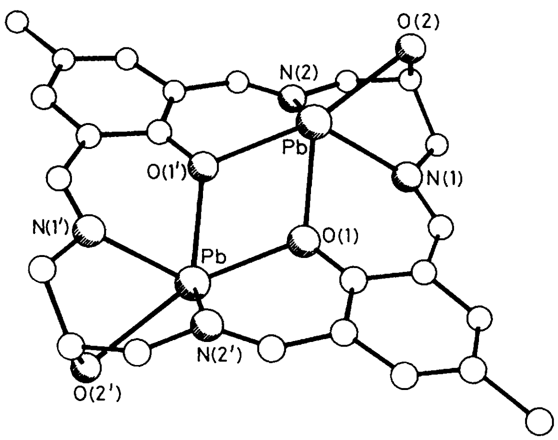


Figure 1. Perspective view of the cation of complex (**2**)

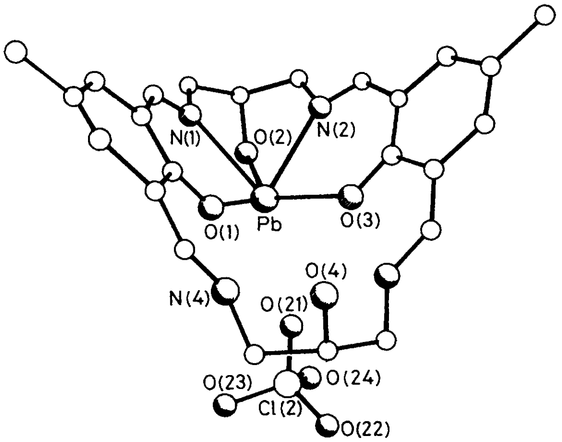


Figure 2. Perspective view of the cation of complex (**1**) showing the associated perchlorate anion

The out-of-plane position of the lead ions is probably due to a mismatch between the size of the macrocyclic cavities and the radius of the metal ions. This configuration is stabilised by bonding of the metal to the alcohol group. Similar out-of-plane displacements have been observed for binuclear transition-metal complexes of related ligands.[7] The resulting configuration, with one lead atom above each face of the macrocycle, means that the macrocycle cannot fold to provide a more stable co-ordination geometry about one lead atom without forcing the expulsion of the second. This is likely to be the reason for the facile conversion of (**2**) to (**1**); one Pb atom is lost, two protons replace it and the ligand is free to fold. The resulting mononuclear cation is shown in Figure 2. The most striking difference between this structure and the binuclear complex is the folding of the ligand; the phenol groups are inclined at 100° to each other. Presumably the driving force for the formation of (**1**) from (**2**) is increased stability of the metal–ligand bonding. It is interesting to note, therefore, that the most significant change in the co-ordination sphere is a contraction of the Pb–O(phenol) distances. The Pb atom retains the same macrocyclic donor set as in complex (**2**) and is displaced from the mean plane of the imine and phenol donors by 1.26 Å. Again, as noted for (**2**), there is a rather open face on one side of the Pb atom. The vacant compartment of the macrocycle interacts weakly with a perchlorate anion; O(21)–Pb 3.16(1), O(21)–O(1) 3.14(2),

Table 1. Atomic co-ordinates (× 10^4) for $[Pb(H_4L)][ClO_4]_2$ (**1**), $[Pb_2(H_2L)][ClO_4]_2$ (**2**), and $[(H_6L)(H_2O)_2][ClO_4]_2$ (**3**)

Complex (**1**)

Atom	*x*	*y*	*z*
Pb	2 762(1)	1 942(1)	2 692(1)
O(1)	5 113(10)	1 623(7)	1 262(5)
C(1)	6 372(15)	777(10)	607(8)
C(2)	7 727(15)	1 029(10)	−100(8)
C(3)	9 072(16)	128(11)	−823(9)
C(4)	9 190(17)	−1 039(11)	−912(10)
C(5)	10 667(17)	−2 024(12)	−1 713(10)
C(6)	7 902(17)	−1 293(11)	−222(10)
C(7)	6 514(15)	−426(10)	530(8)
C(8)	5 256(18)	−862(11)	1 181(10)
N(1)	3 876(14)	−268(8)	1 932(8)
C(9)	2 859(17)	−979(12)	2 430(10)
C(10)	1 623(20)	−261(13)	3 465(11)
O(2)	583(13)	653(10)	3 465(9)
C(11)	2 297(21)	431(14)	4 172(11)
N(2)	3 221(14)	1 338(9)	3 918(8)
C(12)	4 185(19)	1 634(12)	4 310(9)
C(13)	5 247(16)	2 530(11)	4 245(8)
C(14)	6 283(16)	2 648(11)	4 740(8)
C(15)	7 346(16)	3 470(11)	4 769(9)
C(16)	8 395(18)	3 542(13)	5 323(10)
C(17)	7 355(15)	4 190(11)	4 271(8)
C(18)	6 377(14)	4 097(10)	3 747(8)
C(19)	5 280(16)	3 274(11)	3 736(8)
O(3)	4 380(11)	3 253(7)	3 268(6)
C(20)	6 578(14)	4 880(10)	3 239(8)
N(3)	5 842(12)	4 920(8)	2 694(7)
C(21)	6 081(19)	5 734(11)	2 186(11)
C(22)	7 232(17)	5 179(13)	1 083(11)
O(4)	8 700(15)	4 526(13)	906(10)
C(23)	6 590(19)	4 324(12)	424(10)
N(4)	6 545(14)	3 132(8)	471(7)
C(24)	7 726(16)	2 201(11)	−98(8)
Cl(1)	7 670(5)	−1 318(4)	2 872(3)
O(11)	6 013(18)	−1 367(13)	3 385(12)
O(12)	8 025(22)	−170(14)	3 030(14)
O(12′)	7 774(55)	−248(38)	3 696(33)
O(13)	8 196(34)	−2 002(19)	1 889(12)
O(13′)	7 207(61)	−492(43)	2 468(37)
O(14)	8 307(34)	−1 897(20)	3 271(18)
O(14′)	9 068(45)	−2 060(31)	2 303(26)
Cl(2)	1 865(5)	4 959(4)	2 027(3)
O(21)	3 005(13)	4 202(9)	2 106(8)
O(22)	2 389(13)	6 092(8)	2 103(8)
O(23)	1 797(22)	4 415(13)	1 104(11)
O(24)	308(14)	5 122(15)	2 818(11)

Complex (**2**)

Atom	*x*	*y*	*z*
Pb	−53(1)	6 183(1)	5 005(1)
O(1)	1 532(9)	5 021(4)	5 758(9)
C(1)	3 001(14)	5 026(7)	6 496(15)
C(2)	3 638(13)	4 543(7)	7 694(12)
C(3)	5 247(14)	4 578(8)	8 466(15)
C(4)	6 294(14)	5 040(7)	8 069(15)
C(5)	8 041(15)	5 032(8)	8 882(17)
C(6)	5 701(14)	5 509(7)	6 878(14)
C(7)	4 093(13)	5 537(7)	6 086(13)
C(8)	3 682(13)	6 064(7)	4 900(12)
N(1)	2 283(11)	6 304(5)	4 205(11)
C(9)	2 258(14)	6 845(7)	3 033(13)
C(10)	680(14)	7 316(6)	2 563(15)
O(2)	407(10)	7 593(5)	3 796(9)
C(11)	−649(14)	6 849(7)	1 623(14)
N(2)	−1 289(11)	6 256(5)	2 416(11)
C(12)	−2 720(15)	6 014(7)	1 791(16)
Cl	−1 377(4)	2 908(2)	1 545(4)
O(11)	−2 540(14)	3 345(8)	1 888(18)
O(12)	−1 982(14)	2 379(8)	414(13)
O(13)	−715(16)	2 424(7)	2 793(14)
O(14)	−134(13)	3 386(7)	1 374(14)
Complex (**3**)			
O(1)	1 964(25)	922(8)	2 858(7)
C(1)	2 063(34)	215(12)	2 938(11)
C(2)	2 681(38)	−313(11)	2 457(11)
C(3)	2 577(39)	−1 050(12)	2 567(12)
C(4)	2 173(42)	−1 375(14)	3 094(12)
C(5)	2 222(45)	−2 251(14)	3 215(13)
C(6)	1 518(37)	−934(12)	3 560(11)
C(7)	1 397(43)	−156(12)	3 502(10)
C(8)	471(41)	235(14)	3 973(12)
N(1)	218(33)	1 021(10)	3 922(9)
C(9)	1 010(36)	1 426(14)	638(11)
C(10)	2 873(37)	1 667(12)	938(12)
O(2)	2 413(27)	2 112(9)	1 468(7)
C(11)	4 094(43)	1 049(13)	1 185(12)
N(2)	3 268(29)	743(10)	1 783(8)
C(12)	3 311(42)	−11(12)	1 884(11)
Cl	1 453(14)	3 759(4)	376(3)
O(11)	1 781(27)	3 171(11)	−60(8)
O(12)	2 066(45)	3 575(10)	985(9)
O(13)	−433(41)	3 891(13)	404(12)
O(14)	2 475(37)	4 421(12)	185(8)
O(3)	842(38)	1 649(10)	2 077(10)

O(21)–N(3) 3.05(2), and O(21)–N(4) 3.05(2) Å. The pendant alcohol groups, which remain protonated, show evidence of hydrogen bonding to the perchlorate anions: O(12)–O(2) (under transformation 1 + *x*, *y*, *z*) 2.74(2), O(12′)–O(2) (under the same transformation) 2.68(2), and O(23)–O(4) (under *x* − 1, *y*, *z*) 2.91(2) Å.

The unsymmetric structure of complex (**1**) contrasts with the geometry reported[6] for a mononuclear barium complex of a related ligand $[Ba(H_4L')(ClO_4)_2]$. This latter complex possesses crystallographically imposed C_2 symmetry and the barium ion is co-ordinated to all four macrocyclic oxygen donors, two diagonally related imine nitrogen atoms, and two perchlorate anions. That this configuration does not occur in the mononuclear lead complex probably reflects the difference in ionic radii of the two ions (Pauling radii 1.21 and 1.35 Å for Pb^{2+} and Ba^{2+} respectively[8]); the lead ion is too small to span the diagonal imine–imine distance and adopt the same geometry as the barium ion. This being the case, the mononuclear barium complexes (**5**) and (**6**) would be expected to have similar symmetrical co-ordination geometry to that reported for $[Ba(H_4L')(ClO_4)_2]$ whereas complex (**4**) $\{[Pb(H_4L)(NCS)_2]\cdot 2H_2O\}$ would have a similar structure to (**1**). This suggestion is supported by the i.r. and n.m.r. data for these complexes.

Figure 3 shows the structure of the cation, $[(H_6L)(H_2O)_2]^{2+}$ which is derived from (**1**) by loss of the Pb^{2+} ion and addition of two protons. The cation has crystallographically imposed C_2 symmetry, the two-fold axis passing perpendicularly through the plane of the four nitrogen atoms. The macrocycle is folded so that the two π regions are almost parallel (the phenol rings are inclined at 7° to each other) and are separated by approximately 3.5 Å. This π interaction is probably responsible for the relative stability of (**3**) compared with (**1**) and (**2**). The configuration is very similar to that observed in $[Ba(H_4L')(ClO_4)_2]$. If this same arrangement were present in (**5**) and (**6**), it would provide a further stabilisation in the mononuclear barium complexes as compared to the lead compounds. The folding of the macrocycle

Table 2. Selected bond lengths (Å) and angles (°) for $[Pb(H_4L)][ClO_4]_2$ (**1**), $[Pb_2(H_2L)][ClO_4]_2$ (**2**), and $[(H_6L)(H_2O)_2][ClO_4]_2$ (**3**)

Complex (**1**)			
Pb–O(1)	2.318(7)	Pb–N(1)	2.482(9)
Pb–O(2)	2.710(12)	Pb–N(2)	2.479(14)
Pb–O(3)	2.356(10)		
O(1)–Pb–N(1)	74.5(3)	O(1)–Pb–O(2)	138.7(3)
N(1)–Pb–O(2)	66.7(3)	O(1)–Pb–N(2)	115.2(4)
N(1)–Pb–N(2)	70.9(4)	O(2)–Pb–N(2)	64.8(4)
O(1)–Pb–O(3)	76.5(3)	N(1)–Pb–O(3)	117.5(4)
O(2)–Pb–O(3)	134.1(4)	N(2)–Pb–O(3)	73.7(4)
Complex (**2**)			
Pb–O(1)	2.416(7)	Pb–N(1)	2.440(12)
Pb–O(2)	2.771(9)	Pb–N(2)	2.458(9)
Pb–O(1′)	2.434(7)		
O(1)–Pb–N(1)	72.3(3)	O(1)–Pb–O(2)	134.3(3)
N(1)–Pb–O(2)	62.4(3)	O(1)–Pb–N(2)	113.4(3)
N(1)–Pb–N(2)	79.4(3)	O(2)–Pb–N(2)	65.6(3)
O(1)–Pb–O(1′)	67.1(3)	N(1)–Pb–O(1′)	113.8(3)
O(2)–Pb–O(1′)	137.5(3)	N(2)–Pb–O(1′)	72.1(3)
		Pb–O(1)–Pb′	112.9(3)
Complex (**3**)			
O(1)–C(1)	1.268(26)	C(1)–C(2)	1.473(32)
O(1)–C(7)	1.471(33)	C(2)–C(3)	1.330(29)
C(2)–C(12)	1.429(33)	C(3)–C(4)	1.316(37)
C(4)–C(5)	1.575(35)	C(4)–C(6)	1.364(35)
C(6)–C(7)	1.388(30)	C(7)–C(8)	1.404(36)
C(8)–N(1)	1.410(30)	N(1)–C(9′)	1.484(32)
C(9)–C(10)	1.541(36)	C(9)–N(1′)	1.484(32)
C(10)–O(2)	1.437(29)	C(10)–C(11)	1.500(36)
O(2)–O(3)	1.920(28)	C(11)–N(2)	1.530(32)
N(2)–C(12)	1.356(28)	Cl–O(11)	1.428(20)
Cl–O(12)	1.434(21)	Cl–O(13)	1.368(30)
Cl–O(14)	1.444(24)		
O(1)–C(1)–C(2)	123.2(20)	O(1)–C(1)–C(7)	122.6(20)
C(2)–C(1)–C(7)	113.9(19)	C(1)–C(2)–C(3)	118.6(22)
C(1)–C(2)–C(12)	118.5(18)	C(3)–C(2)–C(12)	122.9(22)
C(2)–C(3)–C(4)	126.9(24)	C(3)–C(4)–C(5)	125.0(24)
C(3)–C(4)–C(6)	118.2(22)	C(5)–C(4)–C(6)	116.6(23)
C(4)–C(6)–C(7)	121.5(22)	C(1)–C(7)–C(6)	120.1(21)
C(1)–C(7)–C(8)	122.7(20)	C(6)–C(7)–C(8)	117.0(22)
C(7)–C(8)–N(1)	119.4(22)	C(8)–N(1)–C(9′)	120.2(20)
C(10)–C(9)–N(1′)	111.7(20)	C(9)–C(10)–O(2)	107.2(20)
C(9)–C(10)–C(11)	116.8(20)	O(2)–C(10)–C(11)	104.2(20)
C(10)–O(2)–O(3)	117.0(15)	C(10)–C(11)–N(2)	109.9(22)
C(11)–N(2)–C(12)	118.7(19)	C(2)–C(12)–N(2)	120.3(20)
O(11)–Cl–O(12)	113.5(12)	O(11)–Cl–O(13)	108.5(14)
O(12)–Cl–O(13)	107.3(17)	O(11)–Cl–O(14)	108.6(12)
O(12)–Cl–O(14)	107.2(14)	O(13)–Cl–O(14)	111.8(15)

means that each N_2O_2 compartment of the ligand is too small to accommodate a Pb^{2+} ion either within or above the cavity. Since the Pb^{2+} ion is too small to accept any other combination of donors, the most stable product is the ligand salt (**3**). The cavity formed by the folding of the macrocycle is occupied by two water molecules, each of which is held in place by a network of short hydrogen bonds [O(3)–O(1) 2.28(1), O(3)–O(2) 1.92(1), O(3)–N(2) 2.45(1), O(3)–O(1′) 2.39(1), O(3)–N(1′) 2.56, O(3)–O(3′) 2.20(1) Å].

N.M.R. Spectra. Proton and ^{13}C n.m.r. have been used to confirm that the solid-state structures described above are maintained in solution and, for the partially protonated complexes, to indicate likely sites of protonation. The spectral data, with assignments, are summarised in Table 3. The spectra fall into two groups; the first contains the mononuclear lead compounds (**1**) and (**4**), while the second comprises the more symmetrical set (**2**), (**3**), (**5**), and (**6**). Within each group, the spectra are broadly similar and, in each case, the n.m.r. data are quite consistent with the structural data.

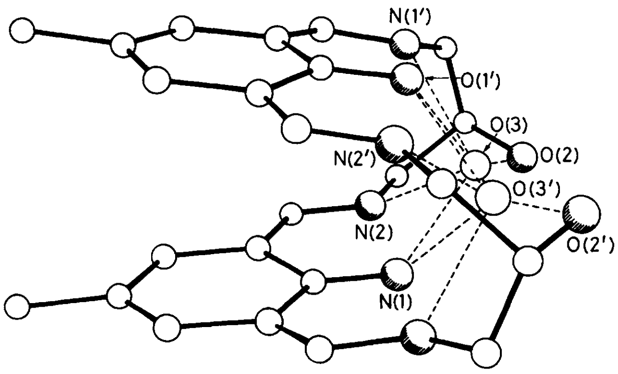


Figure 3. Perspective view of the cation of complex (**3**). Dotted lines represent hydrogen bonds

Complexes (**1**) and (**4**) are required by stoicheiometry to contain the fully protonated ligand H_4L and this is confirmed by their ^1H n.m.r. spectra. The signal due to the protons on C(8) and C(12) is a doublet which collapses to a singlet on shaking with D_2O. This indicates either protonation of N(1) and N(2), or hydrogen bonding of the imine nitrogen atoms to the protonated phenol groups O(1) and O(3). Similar effects are seen in the spectrum of (**3**), which contains the $[(H_6L)(H_2O)_2]^{2+}$ ion. The signal due to protons on C(8) and C(12) appears as a doublet with $J = 14$ Hz, which collapses to a singlet on shaking with D_2O. The magnitude of the coupling constant suggests that this effect is likely to be due to protonation of N(1) and N(2). The ^1H n.m.r. spectrum of (**2**) shows the C(8) and C(12) protons as a singlet. The only change which occurs on shaking with D_2O is resolution of the signal due to the proton on H(10) into a triplet. This is consistent with the formulation $[Pb_2(H_2L)]^{2+}$, in which the phenol groups are deprotonated and the alcohol groups are not.

The n.m.r. spectra of the mononuclear barium complexes (**5**) and (**6**) differ from the mononuclear lead complexes in that the former are simpler, indicating higher symmetry. The spectra of the barium complexes are consistent with structures similar to that found by Fenton and co-workers,[6] in which the metal is co-ordinated to all the oxygen donors and to two diagonally related imine nitrogens [*i.e.* N(2) and N(2′)] but not to the remaining imines [N(1) and N(1′)]. The ^1H n.m.r. signal due to the proton on C(12) is a singlet whereas that due to the proton on C(8) is a doublet which collapses to a singlet on shaking with D_2O.

Conclusions

The structure of the binuclear lead complex (**2**) has been shown to be similar to those reported for binuclear transition-metal complexes of related ligands.[7] The tendency of (**2**) to lose Pb^{2+} is explained by the larger radius of Pb^{2+} relative to first-row transition-metal ions. The mononuclear lead complexes (**1**) and (**4**) have distinctly different structures from those observed for barium complexes of H_4L and related ligands.[6] Again, this can be ascribed to the radius of the Pb^{2+} ion which is too small to adopt the co-ordination geometry shown by Ba^{2+}. The configuration of the protonated free ligand (**3**) closely resembles

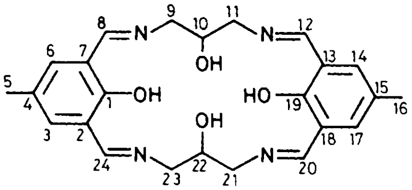
Table 3. Proton and ^{13}C n.m.r. spectra and assignments[a]

^{13}C N.m.r. Atom	Complex (2)	(3)	(5)	(6)
C(1)	162.3	176.4	167.1	167.3
C(2), C(7)	125.2	116.7	129.9, 126.0	131.8, 126.0
C(3), C(6)	139.8	145.5	132.9	132.9
C(4)	125.1	122.0	121.0	121.1
C(5)	19.4	19.1	20.0	20.0
C(8), C(12)	169.5	168.3	162.3	162.3
C(9), C(11)	63.5	55.5	63.6	63.7
C(10)	69.7	63.1	69.7	69.8

Atom	(1)	(4)
C(1), C(19)	170.6	170.3
C(2), C(18)	115.9	115.8
C(3), C(17)	146.4	146.2
C(4), C(15)	122.5	122.3
C(5), C(16)	19.1	19.2
C(6), C(14)	140.3	140.1
C(7), C(13)	125.1	124.9
C(8), C(12)	169.9	169.6
C(9), C(11)	65.1	65.1
C(10)	70.9	70.8
C(20), C(24)	165.6	165.4
C(21), C(23)	54.7	54.6
C(22)	64.3	64.2

^{1}H N.m.r. Atom	Complex (2)	(3)	(5)	(6)
H(3), H(6)	7.56(s)	7.43(s)	7.65(br s)	7.65(br s)
H(5)	2.45(s)	2.22(s)	2.36(br s)	2.36(br s)
H(8), H(12)	8.64(s)	8.70(d)[b]	8.69(d),[b] 8.72(s)	8.69(d),[b] 8.72(s)
H(9), H(11)	3.92(q), 4.27(br)	4.12—4.26(m)	3.80—3.86(m)	3.80—3.87(m)
H(10)	4.57(br s)[c]	4.42(br s)[c]	4.12(br s)	4.11(br s)

Atom	(1)	(4)
H(3), H(6), H(14), H(17)	7.44(s), 7.48(s)	7.46(s), 7.52(s)
H(5), H(16)	2.45(s)	2.23(s)
H(8), H(12)	8.43(s)	8.44(s)
H(20), H(24)	8.41(d)[b]	8.42(d)[b]
H(9), H(11)	4.16—4.28(m)	4.17—4.27(m)
H(21), H(23)	3.87—3.94(m)	3.86—3.94(m)
H(10)	4.64(br s)	4.63(br s)
H(22)	4.93(br s)[c]	4.38(br s)[c]



[a] All spectra recorded in $(CD_3)_2SO$. [b] Collapses to a singlet on D_2O shake. [c] Resolves to a triplet on D_2O shake.

that found in the barium complexes and shows evidence of stabilisation through π interactions.

The observed gradual replacement of Pb^{2+} ions by protons in the methanol reaction mixture (but not in ethanol, or in solutions of the pure complexes) is unexpected. That a metal ion template is not required in order to form the macrocycle is shown by the fact that **(3)** can be obtained using perchloric acid in place of a metal salt. However, the initial formation of **(2)** may indicate a kinetically favoured metal template effect yielding the planar binuclear complex which is slowly transformed into the thermodynamically preferred folded macrocyclic salt.

Experimental

Materials.—The solvents were dried by standard procedures. 2,6-Diformyl-4-methylphenol was synthesized using the literature procedure.[9] All other chemicals were analaR or reagent grade and were used without further purification. 1,3-Diamino-2-hydroxypropane was used as supplied by Aldrich.

Physical Measurements.—I.r. spectra of the solid samples were recorded as KBr discs on a Pye Unicam SP3-300 infrared spectrophotometer. Electronic spectra were recorded in dimethylformamide (dmf) solution on a Varian DMS 100 u.v.-visible spectrophotometer in the range 200—800 nm. Proton and ^{13}C n.m.r. spectra were recorded in $(CD_3)_2SO$ on a Varian XL-300 instrument.

Preparation of the Complexes.—(i) $[Pb_2(H_2L)][ClO_4]_2$. To a solution of $Pb(ClO_4)_2\cdot6H_2O$ (2 mmol) in dry methanol (20 cm^3) was added a solution of 2,6-diformyl-4-methylphenol (2 mmol) in hot dry methanol (20 cm^3). The reaction mixture acquired a pale yellow colour. It was stirred at ambient temperature for *ca.* 15 min and to it was added dropwise a solution of 1,3-diamino-2-hydroxypropane (2 mmol) in dry methanol (15 cm^3) with constant stirring over 10—15 min. The resulting bright yellow solution was stirred for a further 30 min and left at ambient temperature overnight. The bright yellow plates which separated were filtered off and washed with dry methanol (3 × 10 cm^3). The combined washings and filtrate, on standing at room temperature for *ca.* 24 h, gave a second crop of the complex. This was dried *in vacuo* at room temperature for *ca.* 24 h (yield 37%) (Found: C, 26.60; H, 3.10; N, 5.10; Pb, 38.80. Calc. for $C_{24}H_{26}Cl_2N_4O_{12}Pb_2$: C, 27.50; H, 2.50; N, 5.35; Pb, 39.50%). Crystals suitable for *X*-ray study were obtained by ether diffusion into a dmf–methanol (1:1) solution of the complex.

(ii) $[Pb(H_4L)][ClO_4]_2$. $Pb(ClO_4)_2\cdot6H_2O$ (2 mmol) was dissolved in dry methanol (20 cm^3) and 2,6-diformyl-4-methylphenol (2 mmol) in dry methanol (30 cm^3) was added. The pale yellow solution formed was refluxed for *ca.* 10 min and a solution of 1,3-diamino-2-hydroxypropane (2 mmol) in dry methanol (20 cm^3) added dropwise with stirring over *ca.* 10 min; the resulting solution was stirred at ambient temperature. After *ca.* 2 h a small amount of bright yellow $[Pb_2(H_2L)][ClO_4]_2$ formed, which on further stirring for 48 h gave a yellowish orange compound. This was filtered off, washed with dry methanol (3 × 15 cm^3), and dried *in vacuo* for *ca.* 24 h. Yield 95%.

The same compound was obtained by stirring/refluxing the reaction mixture in dry/wet ethanol for *ca.* 3 h. In ethanol as a solvent the formation of the binuclear complex, $[Pb_2(H_2L)][ClO_4]_2$, did not take place and only the mononuclear complex $[Pb(H_4L)][ClO_4]_2$ was formed in *ca.* 70% yield.

$[Pb(H_4L)][ClO_4]_2$ was also obtained as good crystals by keeping the filtrate from the complex $[Pb_2(H_2L)][ClO_4]_2$ at ambient temperature for a few days (Found: C, 34.80; H, 3.65; N, 6.85; Pb, 24.90. Calc. for $C_{24}H_{28}Cl_2N_4O_{12}Pb$: C, 34.20; H, 3.35; N, 6.65; Pb, 24.60%). Crystals suitable for *X*-ray study were obtained by ether diffusion into an acetonitrile solution of the complex.

(iii) $[(H_6L)(H_2O)_2][ClO_4]_2$. The filtrate from the preparation of **(2)**, upon standing at ambient temperature for 4 d, gave a mixture of two crystalline compounds: (*a*) yellowish orange crystals which analysed as $[Pb(H_4L)(ClO_4)][ClO_4]$ (yield *ca.* 30%) and (*b*) orange-red crystals which analysed as $[(H_6L)(H_2O)_2][ClO_4]_2$. The mixture was filtered, washed with dry methanol (3 × 5 cm^3), and the two compounds were separated physically (yield *ca.* 11%) (Found: C, 43.70; H, 4.55; N, 7.85. Calc. for $C_{24}H_{34}Cl_2N_4O_{14}$: C, 42.80; H, 5.05; N, 8.30%).

(iv) $[Pb(H_4L)(NCS)_2]\cdot 2H_2O$. Lead thiocyanate (1 mmol) and 2,6-diformyl-4-methylphenol were added to methanol (125 cm^3) and refluxed for *ca.* 20 min. To this pale yellow solution, with some undissolved $Pb(NCS)_2$, a solution of 1,3-diamino-2-hydroxypropane was added dropwise, while refluxing, over *ca.* 10 min and the colour of the reaction mixture changed to bright yellow. It was refluxed for 8 h and a yellowish orange solution formed which still contained a suspension of unreacted $Pb(NCS)_2$. This was filtered off and the volume reduced to *ca.* 50 cm^3. Upon standing at room temperature for *ca.* 24 h, an orange coloured compound separated out, was filtered off, washed with methanol (3 × 10 cm^3), and dried *in vacuo* (yield 63%) (Found: C, 41.10; H, 4.20; Pb, 26.80. Calc. for $C_{26}H_{28}N_6O_4PbS_2$: C, 40.90; H, 3.65; Pb, 27.15%).

(v) $[Ba(H_4L)(NCS)_2]\cdot 2H_2O$. To a solution of barium thiocyanate (1 mmol) in ethanol (20 cm^3) was added 2,6-diformyl-4-methylphenol (1 mmol) dissolved in hot ethanol (25 cm^3). The reaction mixture was refluxed for *ca.* 10 min, and a solution of 1,3-diamino-2-hydroxypropane (1 mmol) in ethanol (20 cm^3) was added dropwise with stirring at *ca.* 80 °C. The resulting orange coloured solution was stirred at room temperature for *ca.* 24 h. A small amount of orange coloured compound separated out and the solution was refluxed for a further 12 h (approximately) and concentrated to *ca.* 15 cm^3. Upon standing at room temperature overnight, a yellowish orange compound separated out. This was filtered off, washed with ethanol (3 × 10 cm^3), and dried *in vacuo* at room temperature for 24 h (yield 44%) (Found: C, 42.80; H, 4.70; N, 10.90. Calc. for $C_{26}H_{32}BaN_6O_6S_2$: C, 42.80; H, 4.40; N, 11.50%).

(vi) $[Ba(H_4L)(ClO_4)_2]\cdot H_2O$. Barium perchlorate (2 mmol) and 2,6-diformyl-4-methylphenol (2 mmol) were dissolved in refluxing dry ethanol (50 cm^3). The pale yellow solution formed was refluxed for *ca.* 10 min and a solution of 1,3-diamino-2-hydroxypropane (2 mmol) in dry ethanol (15 cm^3) was added dropwise with stirring over *ca.* 10 min. The reaction mixture acquired a yellowish orange colour. It was stirred at ambient temperature for 48 h and concentrated to *ca.* 10 cm^3. Upon standing, a yellowish orange solid separated out, was filtered off, washed with dry ethanol, and dried *in vacuo* over silica gel (yield 82%) (Found: C, 36.30; H, 4.20; N, 6.70. Calc. for $C_{24}H_{30}BaCl_2N_4O_{13}$: C, 36.45; H, 3.80; N, 7.10%).

X-Ray Crystallography.—Crystal data for (**1**). $C_{24}H_{28}Cl_2N_4O_{12}Pb$, yellow, crystal dimensions 0.26 × 0.14 × 0.11 mm, triclinic, $a = 8.943(2)$, $b = 12.021(3)$, $c = 15.958(5)$ Å, $\alpha = 110.71(2)$, $\beta = 67.04(2)$, $\gamma = 88.56(2)°$, $U = 1\,451(1)$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.93$ g cm^{-3}, $F(000) = 824$. Using 2.3° ω scans at scan rate 2.93° min^{-1} and at room temperature, 3 694 unique reflections were collected in the range $4 < 2\theta < 45°$. 2 847 Reflections having $I > 3\sigma(I)$ were used in the structural analysis.

Crystal data for (**2**). $C_{24}H_{26}Cl_2N_4O_{12}Pb_2$, yellow, crystal dimensions 0.24 × 0.26 × 0.28 mm, monoclinic, $a = 8.879(3)$, $b = 17.076(4)$, $c = 9.858(2)$ Å, $\beta = 107.60(2)°$, $U = 1\,425(1)$ Å^3, space group $P2_1/n$, $Z = 2$, $D_c = 2.44$ g cm^{-3}, $F(000) = 984$. Using 1.6° ω scans at scan rate 3.91° min^{-1} and at 160 K, 2 509 unique reflections were collected in the range $4 < 2\theta < 50°$. 1 643 Reflections having $I > 3\sigma(I)$ were used in the structural analysis.

Crystal data for (**3**). $C_{24}H_{34}Cl_2N_4O_{14}$, orange, crystal dimensions 0.36 × 0.18 × 0.05 mm, orthorhombic, $a = 7.136(3)$, $b = 17.730(7)$, $c = 21.774(7)$ Å, $U = 2\,755(2)$ Å^3, space group *Pbcn*, $Z = 4$, $D_c = 1.62$ g cm^{-3}, $F(000) = 1\,408$. Using 2° ω scans at scan rate 2.93° min^{-1} and at 150 K, 1 364 unique reflections were collected in the range $4 < 2\theta < 40°$. 542 Reflections having $I > 3\sigma(I)$ were used in the structural analysis.

All three data sets were collected on a Nicolet R3m four-circle diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.7107$ Å). Crystal stabilities were monitored by recording three check reflections every 100 reflections and no significant variations were observed. The data sets were corrected for Lorentz and polarisation effects and data for (**1**) and (**2**) were also corrected for absorption.

The structure of the metal free compound (**3**) was solved by direct methods using the program SOLV.[10] Only the perchlorate anion and solvate water oxygen atom were refined anisotropically because of the paucity of the data. Hydrogen atoms were inserted at calculated positions using a riding model with thermal parameters set to 1.2 U of the carrier atom. The refinement converged with $R = 0.1132$, $R' = 0.1507$.

Both (**1**) and (**2**) were solved from Patterson calculations which revealed the positions of the lead atoms and the structures were developed from difference Fourier calculations. In each case all non-hydrogen atoms were refined anisotropically, the hydrogen atoms were inserted at calculated positions as described for (**3**). The refinement of (**1**) converged with $R = 0.0506$ and $R' = 0.0528$, for (**2**) the corresponding values were $R = 0.0379$ and $R' = 0.057$. One of the perchlorate groups in (**1**) showed some disorder. This has been modelled as a rotation about the O(11)–Cl(1) bond with 77% occupancy of the major orientation and 23% occupancy of the alternative sites.

All three structures were refined by blocked-cascade least-squares techniques. The function minimised in the refinement was $\Sigma w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ and $g =$ 0.000 14, 0.000 173, and 0.01 for (**1**), (**2**), and (**3**) respectively. All programs used for data collection and structure solution are contained in the SHELXTL (Version 4.1) package.[10]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

We wish to thank the New Zealand University Grants Committee for the award of a postdoctoral fellowship and the Punjabi University, Patiala for granting leave (to S. S. T.).

References

1 See, for example, R. H. Holm and J. M. Berg, *Acc. Chem. Res.*, 1986, **19**, 363; K. G. Strothkamp and S. J. Lippard, *ibid.*, 1982, **15**, 318; K. Wieghardt, U. Bossek, J. Bonvoisin, P. Beauvillain, J. J. Girerd, B. Nuber, J. Weiss, and J. Heinze, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1030.
2 See, for example, K. D. Karlin and Y. Gultneh, *J. Chem. Ed.*, 1985, **62**, 983; P. C. Wilkins and R. G. Wilkins, *Coord. Chem. Rev.*, 1987, **79**, 195; G. C. Dismukes, *Photochem. Photobiol.*, 1986, **43**, 99.
3 N. A. Bailey, D. E. Fenton, R. Moody, C. O. Rodriguez de Barbarin, I. N. Sciambarella, J. M. Latour, D. Limosin, and V. McKee, *J. Chem. Soc., Dalton Trans.*, 1987, 2519; S. Brooker, V. McKee, W. B. Shepard, and L. K. Pannell, *ibid.*, p. 2555.
4 N. H. Pilkington and R. Robson, *Aust. J. Chem.*, 1970, **23**, 255.
5 V. McKee and S. S. Tandon, *J. Chem. Soc., Chem. Commun.*, 1988, 385.
6 N. A. Bailey, D. E. Fenton, P. B. Roberts, and A. M. Walford, *J. Chem. Soc., Dalton Trans.*, 1987, 1965.
7 See, for example, R. R. Gagne, C. A. Koval, T. J. Smith, and M. C. Cimolino, *J. Am. Chem. Soc.*, 1979, **101**, 4571; H. Diril, H. R. Chang, X. Zhang, S. K. Larsen, J. A. Potenza, C. G. Pierpont, H. J. Schugar, S. S. Isied, and D. N. Hendrickson, *ibid.*, 1987, **107**, 6207; S. S. Tandon and V. McKee, unpublished work.
8 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, p. 52.
9 R. R. Gagne, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies, and A. K. Shiemke, *J. Am. Chem. Soc.*, 1981, **103**, 4073.
10 G. M. Sheldrick, SHELXTL User Manual (Revision 4), Nicolet XRD Corporation, Madison, Wisconsin, 1984.

Received 12*th January* 1988; *Paper* 8/00127H