

Complexes of Ligands providing Endogenous Bridges. Part 1. The Syntheses and Crystal Structures of Barium and Lead(II) Complexes of Macrocyclic Schiff Bases derived from Heterocyclic Dicarboxyls and 1,*n*-Diamino-*n*'-hydroxyalkanes (*n,n*' = 3,2; 4,2; or 5,3) †

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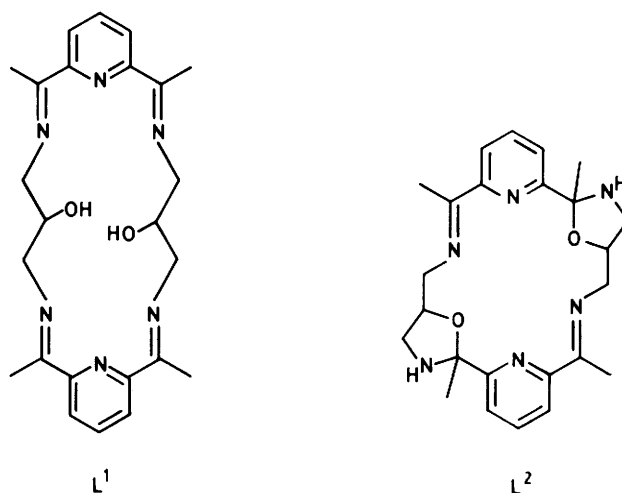
Barium and lead(II) complexes of tetraimine Schiff base macrocycles derived from the (2 + 2) condensation of heterocyclic dicarbonyls (2,6-diacetylpyridine and furan-2,5-dicarbaldehyde) and 1,*n*-diamino-*n*'-hydroxyalkanes (1,3-diamino-2-hydroxypropane, 1,4-diamino-2-hydroxybutane, and 1,5-diamino-3-hydroxypentane) are reported. The crystal structures of four complexes have been determined.

Tetraimine Schiff-base macrocycles derived from heterocyclic dicarbonyl 'head' units and 1,*n*-diaminoalkane 'lateral' units have proved to be versatile ligands for both mononuclear and binuclear metal complexes.¹ We have recently shown that the range of such ligands may be extended by the incorporation of functionalised pendant units into the lateral framework of the macrocycle.² The incorporation of the hydroxyl group into the lateral framework would give rise to a binucleating macrocycle having also the potential to use the hydroxyl group in endogenous bridging between the two incorporated metal atoms. This would provide, in the case of copper(II), a route to models for the bimetallobiosite in type III copper proteins where, from cumulative spectroscopic and EXAFS studies,³ an endogenous hydroxy bridge has been considered. We here report the metal-template syntheses of a series of tetraimine Schiff-base macrocycles derived from heterocyclic dicarbonyls and 1,*n*-diamino-*n*'-hydroxyalkanes and the X-ray crystal and molecular structures of four mononuclear complexes: the barium and lead(II) complexes of the macrocycles derived from 2,6-diacetylpyridine (dap) and 1,3-diamino-2-hydroxypropane (1,3-dhp); the barium complex of the macrocycle derived from furan-2,5-dicarbaldehyde (fdc) and 1,3-dhp, and the barium complex of the macrocycle derived from fdc and 1,5-diamino-3-hydroxypentane (1,5-dhp).

Results and Discussion

When equimolar amounts of the appropriate heterocyclic dicarbonyl and 1,*n*-diamino-*n*'-hydroxyalkane were refluxed in dry MeOH, EtOH, or tetrahydrofuran (thf), under normal (or high) dilution conditions yellow polymeric gums were isolated which did not provide satisfactory analyses. The addition of metal ions led to the isolation, in many instances, of metal complexes of macrocycles through utility of the metal-template effect.

Reaction of 1,3-Diamino-2-hydroxypropane with Heterocyclic Dicarbonyls.—(i) 2,6-Diacetylpyridine in the presence of Ba²⁺ salts. The reaction of dap with 1,3-dhp in the presence of Ba(ClO₄)₂ (2:2:1 molar ratio) in refluxing MeOH for 2 h led to the precipitation of a white powder. Recrystallisation from acetonitrile afforded colourless crystals of the mononuclear complex BaL¹(H₂O)₂(ClO₄)₂. The macrocyclic nature of L¹



was deduced by means of elemental analysis, i.r., ¹H and ¹³C n.m.r., mass spectrum, and by a single-crystal X-ray structure determination. The corresponding Ba(NCS)₂ complex was prepared by a similar route, albeit in lower yield.

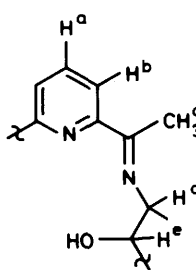
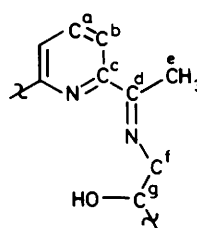
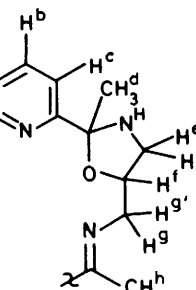
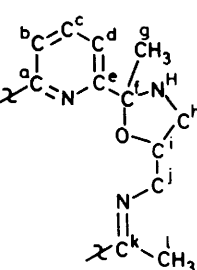
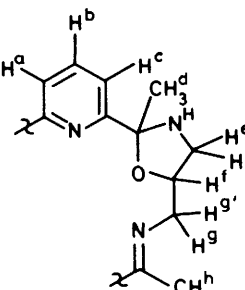
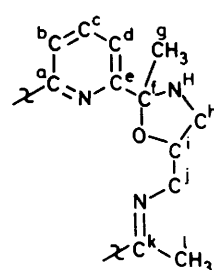
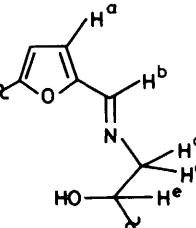
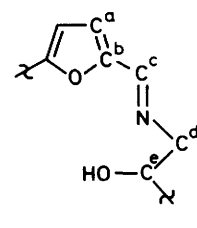
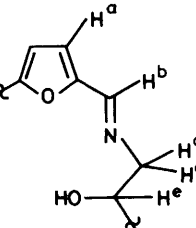
The i.r. spectra of the complexes are very similar when allowance is made for the variation in anions. Neither spectrum shows bands indicative of unreacted carbonyl or primary amine; both have present strong absorptions at 1 640 [ν(C=N)] and 3 450 cm⁻¹, due to the endogenous OH group. Single bands are observed at 1 090 and 625 cm⁻¹ in the perchlorate complex and are ascribed to non-bonded ClO₄⁻; two absorptions at 2 050 and 2 040 cm⁻¹ in the spectrum of the thiocyanate complex are indicative of the presence of two inequivalent, N-bonded NCS⁻ anions.⁵

Mass spectra were recorded for both complexes; the highest molecular weight peak in each case was at *m/e* 434, corresponding to free L¹. The ¹H and ¹³C n.m.r. confirm that the integrity of L¹ is maintained in solution and assignments of the chemical shifts are presented in Table 1.

(ii) 2,6-Diacetylpyridine in the presence of Pb²⁺ salts. In contrast to the reaction in the presence of Ba²⁺ salts the reaction of dap with 1,3-dhp in the presence of Pb(ClO₄)₂, or Pb(NCS)₂ (2:2:1 molar ratio), in refluxing MeOH for 3 h leads to the precipitation of the mononuclear complex of the macrocycle L². The macrocyclic nature of this ligand was deduced *via* elemental analysis, i.r., ¹H and ¹³C n.m.r., mass spectrum, and confirmed by a single-crystal X-ray structure

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. N.m.r. data

^1H N.m.r. (400 MHz, CD_3OD)		^{13}C N.m.r. [63 MHz, $(\text{CD}_3)_2\text{SO}$]		
		BaL¹(H₂O)₂(ClO₄)₂ a 7.87, t, 2 H b 7.69, d, 4 H c 2.30, d, 12 H d 3.92, m, 8 H e 4.57, m ^a		BaL¹(H₂O)₂(ClO₄)₂ a 139.58 b 123.83 c 154.93 d 165.54 e 16.04 f 57.40 g 68.56
		Ag₂L¹(ClO₄)₂·2H₂O^b a 7.86, t, 2 H b 7.76, d, 2 H c 2.31, s, 12 H d 3.83, m, 8 H e 4.88, br, 2 H		Ag₂L¹(ClO₄)₂·2H₂O a 139.77 b 124.11 c 149.61 d 163.03 e 15.38 f 59.04 g 68.96
		PbL²(NCS)₂·MeOH a/c 8.22, 8.31, d, 4 H b 8.35, t, 2 H d 1.94, s, 6 H e/e' 2.53, 3.75, q, 4 H f 4.35, m, 2 H g/g' 2.78, 4.49, m, 4 H h 2.56, s, 6 H		PbL²(NCS)₂·MeOH a 141.41 b 125.05 c 151.46 d 126.20 e 171.14 f 99.70 g 26.32 h 49.80 i 76.37 j 57.71 k 162.98 l 17.22
		SrL²(ClO₄)₂·H₂O a/c 8.12, 7.7, d, 4 H b 8.19, t, 2 H d 1.68, s, 6 H e/e' 2.54, 3.73, dd, 4 H f 4.72, m, 2 H g/g' 3.97, 3.22, dd, 4 H h 2.43, s, 6 H		BaL⁵(ClO₄)₂ a 6.76, s, 4 H b 8.00, d, 4 H c 4.13, ddd, 4 H d 3.73, d, 4 H e 4.42, t, 2 H
		BaL⁵(ClO₄)₂ a 115.51 b 152.48 c 151.06 d 65.48 e 69.68		

^a Partly obscured by solvent. ^b 250 MHz, $(\text{CD}_3)_2\text{SO}$.

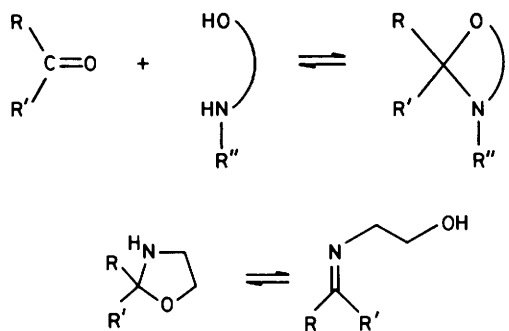
determination of $\text{PbL}^2(\text{NCS})_2 \cdot \text{MeOH}$, using crystals grown from MeOH.

The i.r. spectrum has a band at 1640 cm^{-1} [$\nu(\text{C}=\text{N})$] but instead of the absorption corresponding to the endogenous hydroxyl, a sharp band is present at 3275 cm^{-1} and attributed to a secondary amine $-\text{NH}$ group. Single bands at 1080 and 620 cm^{-1} for the perchlorate complex indicate that the anions are not co-ordinated. In the thiocyanate complex two absorptions at 2070 and 2050 cm^{-1} suggest the presence of two inequivalent anions being bonded *via* a S donor and N donor respectively.

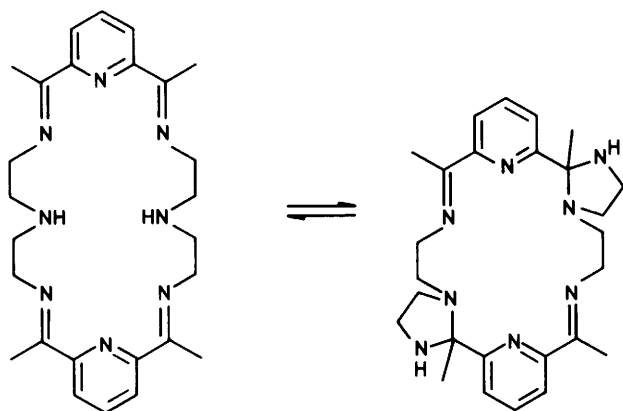
A mass spectrum of the thiocyanate complex has the highest molecular weight peak at m/e 434 corresponding to free L^2 . The ^1H and ^{13}C n.m.r. spectra (Table 1) confirm the integrity of the species in solution.

The macrocycle L^1 contains a 20-membered inner ring whereas L^2 has an 18-membered inner ring. The 20 \rightarrow 18 ring contraction can thus be viewed as a consequence of the nucleophilic addition of the two endogenous alcohol functions of L^1 , across adjacent azomethine bonds. The reversible reactions of β -aminoalcohols with carbonyl compounds leading to oxazolidines is well established (Scheme 1); however oxazolidines with no N-substituents ($\text{R}'' = \text{H}$) are potentially tautomeric with open-chain Schiff bases.⁶

Generalisations made concerning oxazolidine formation would suggest that in the present macrocyclic system any equilibrium would be displaced in favour of the Schiff-base macrocycle L^1 .⁷ It is noteworthy that the metal-controlled contraction produces a stabilised oxazolidine system; the 5-



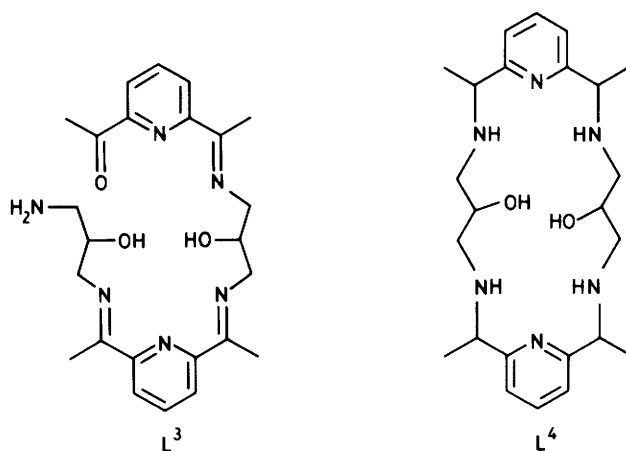
Scheme 1.



Scheme 2.

endo-trigonal ring closure producing such a system is formally disallowed.⁸ However, no such equilibrium is present in solution as evidenced by the ¹H and ¹³C n.m.r. study. The stability of the oxazolidine complex, and the thermodynamic driving force for the 20 → 18 ring contraction is attributed to a metal-ion control. There would be a mismatch of the cavity size of L¹ and the smaller Pb²⁺ ion (ionic radii: Pb²⁺, 1.18; Ba²⁺, 1.36 Å) and so the contraction would be facilitated by the requirement for a matching of the smaller cavity in L² with Pb²⁺. A related metal-induced contraction was reported by Nelson and co-workers⁹ during the reaction of dap with 2-azapentane-1,5-diamine in the presence of Ba²⁺ where a 24 → 18 ring contraction arises. Internal nucleophilic addition of two secondary amine functions in the lateral unit across adjacent azomethine bonds leads to expulsion of two imidazolidine rings (Scheme 2).

(iii) *2,6-Diacetylpyridine in the presence of Sr²⁺ salts.* The reaction of dap with 1,3-dhp in the presence of Sr(ClO₄)₂ (2:2:1 molar ratio) in methanol at reflux gave isolation of an intractable yellow gum; if this reaction is held at room temperature a bright yellow powder is obtained after 1 h. Analysis of this powder is consistent with the formulation SrL¹(ClO₄)₂·H₂O; however, there is a band at 1 690 cm⁻¹ in the i.r., indicative of unreacted carbonyl, together with bands at 3 425 cm⁻¹ (endogenous OH group) and 1 645 cm⁻¹ [ν(C=N)]. These suggest that the product is a complex of L³ in which the final condensation has not occurred to give ring closure. Dissolution of this complex in MeOH-MeCN (10:1), followed by stirring at room temperature for 3 d gave a white powder the i.r. spectrum of which no longer had a band at 1 690 cm⁻¹. The overall spectrum resembled that for PbL²(ClO₄)₂ and has the band at 3 280 cm⁻¹ attributable to a secondary amine -N-H stretch. This suggests that on ring closure a 20 → 18 ring contraction has occurred (ionic radii: Sr²⁺, 1.16; Pb²⁺, 1.18 Å) and this is confirmed by the ¹H n.m.r. spectrum (Table 1).



(iv) *Reduction of PbL²(NCS)₂.* Oxazolidines may be reduced to HOCH₂CH₂NHR (R = alkyl) using metal hydrides.¹⁰ The reaction of PbL²(NCS)₂ with excess NaBH₄ resulted in the isolation of the mononuclear Pb(NCS)₂ complex of the octadentate tetramine macrocycle L⁴. The i.r. spectrum of PbL⁴(NCS)₂ shows no absorptions attributable to the azomethine group, or to the oxazolidine NH; instead, absorptions at 3 375 and 3 225 cm⁻¹ may be assigned to the secondary alcohol and amine functions. A single vibration at 2 045 cm⁻¹ suggests that the NCS⁻ anions are equivalent and N-bonded. The mass spectrum has no parent ion but a highest molecular weight peak at *m/e* 442 corresponding to the free macrocycle. The ¹H n.m.r. spectrum is complicated by the presence of a number of isomers, which have not yet been separated, caused by the introduction of chiral centres at each imino-carbon.

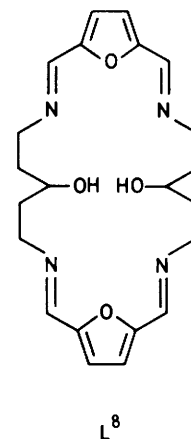
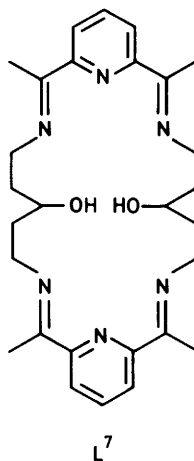
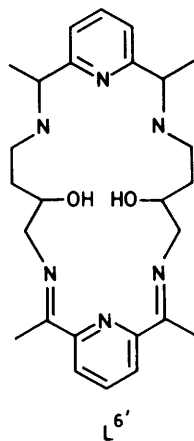
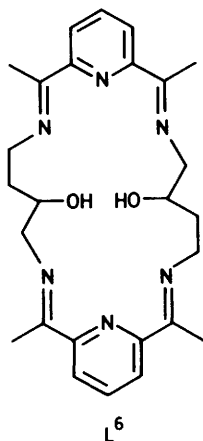
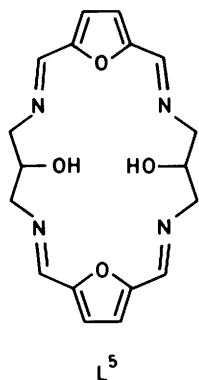
The reductions of metal complexes of tetramine Schiff bases is now an established route into the corresponding metal-free tetramines.¹¹ When Pb²⁺ complexes are reduced with NaBH₄ it is usual for the Pb²⁺ to be reduced to the metal and deposited from solution. In this respect the reduction of the oxazolidine complex to a tetramine complex is somewhat unusual.

(v) *Transmetalation reactions of BaL¹(H₂O)₂(ClO₄)₂ and PbL²(ClO₄)₂·H₂O.* The use of Mg²⁺ or Ca²⁺ as potential templating ions gave isolation of unidentifiable yellow products; the i.r. spectrum showed the presence of both carbonyl and imine stretches suggesting that non-cyclic Schiff-base polymers had been formed. This can be understood in terms of their ionic radii (Mg²⁺, 0.72; Ca²⁺, 1.00 Å) being too small for even the contracted macrocyclic cavity.

The reaction of equimolar amounts of BaL¹(H₂O)₂(ClO₄)₂ and Pb(ClO₄)₂ in refluxing MeOH or EtOH gave PbL²(ClO₄)₂ on cooling providing further evidence that the ring contraction is metal-induced and showing the viability of transmetalation reactions.

Transmetalation resulted when BaL¹(H₂O)₂(ClO₄)₂ and AgClO₄ were refluxed in dry MeOH; the complex Ag₂L¹(ClO₄)₂·2H₂O separated from solution as a white solid. The i.r. spectrum shows bands at 3 450 cm⁻¹ (endogenous alcohol) and 1 640 cm⁻¹ [ν(C=N)] and there is evidence for non-co-ordinated ClO₄⁻ as single bands are found at 1 100 and 625 cm⁻¹. Hydrogen-1 and ¹³C n.m.r. studies show that the integrity of the macrocycle is retained in solution (Table 1). Interestingly the same complex can be prepared by reaction of PbL²(ClO₄)₂ with two equivalents of AgClO₄. The transmetalation has occurred with ring expansion; analogous ring expansions have been noted with the ligand system of Scheme 2.⁹

(vi) *Furan-2,5-dicarbaldehyde in the presence of metal salts.* The reaction of fdc with 1,3-dhp in dry MeOH in the presence of



metal salts (Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+}) in 2:2:1 molar ratio gave intractable red-orange precipitates. Employment of dry EtOH as the solvent led to white precipitates but only in the case of Ba^{2+} were defined products recovered. Recrystallisation of the perchlorate complex from EtOH–MeCN (1:1) afforded colourless crystals of $BaL^5(ClO_4)_2$. The macrocyclic nature of L^5 was established from elemental analyses, i.r., 1H and ^{13}C n.m.r., and a single-crystal X-ray structure determination of $BaL^5(ClO_4)_2$. The i.r. spectra of the thiocyanate and perchlorate complexes are very similar when allowance is made for the anions; both have absorptions present at 3 450 (endogenous alcohol) and 1 640 cm^{-1} [$\nu(C=N)$]. A single absorption at 2 050 cm^{-1} in the spectrum of the thiocyanate complex indicates that both NCS^- anions are equivalent and N-bonded. The spectrum of the perchlorate complex shows splitting of both the ν_3 and ν_4 absorptions of ClO_4^- indicating co-ordination. Three bands are seen for each [1 145, 1 120, and 1 090; 642(sh), 640, and 630 cm^{-1}], suggesting that bidentate co-ordination has occurred. This contrasts with $BaL^1(H_2O)_2(ClO_4)_2$ where the perchlorate is not bound and a solvent-separated ion pair system exists. The complex was insufficiently volatile for mass spectrometry; 1H and ^{13}C n.m.r. confirm the integrity of the system in solution (Table 1) and show that the methylene protons (H^c and H^d) are inequivalent (geminal coupling $J_{dc} = 2$ Hz) and also coupled to H^e ($J_{ce} = 5$ Hz).

Reaction of 1,4-Diamino-2-hydroxybutane with 2,6-Diacetylpyridine.—The only successful templating agent in this condensation was $Pb(ClO_4)_2$, and then only when the reaction was carried out in a 1:1:1 molar ratio in refluxing MeOH. Elemental analysis of the product is consistent with the formulation $Pb_2L^6(ClO_4)_3(OH)$: the OH^- may result as a consequence of partial hydrolysis occurring in the presence of traces of moisture.¹²

The i.r. spectrum of the complex has sharp, intense bands at 3 450 and 3 575 cm^{-1} , attributable to the endogenous alcohol and the OH^- respectively. There is also a band at 1 650 cm^{-1} [$\nu(C=N)$] and single bands at 1 090 and 620 cm^{-1} indicating non-co-ordinated ClO_4^- . The complex is too involatile for mass spectrometry. The 1H n.m.r. is very complex; it is probable that there is more than one species in solution. Two possible diastereoisomers (L^6 and $L^{6'}$) could be formed during the reaction and each contains two chiral centres.

Reaction of 1,5-Diamino-3-hydroxypentane with 2,6-Diacetylpyridine.—As in the previous section only lead was found to be effective in facilitating the formation of a macrocyclic product. The reaction of dap with 1,5-dhp in the presence of $Pb(ClO_4)_2$ (1:1:1 molar ratio) in refluxing MeOH for 2 h gave a white precipitate which analysed as $Pb_2L^7(ClO_4)_3(OH)$. The corresponding complex $Pb_2L^7(NCS)_4$ is prepared using the same approach. The macrocyclic nature of L^7 was deduced *via* elemental analysis, i.r., and in the case of the thiocyanate complex, a mass spectrum.

The i.r. spectra are similar, making allowance for the anions. Both have bands at 3 450 (endogenous alcohol) and 1 650 cm^{-1} [$\nu(C=N)$]. The i.r. spectrum of the perchlorate complex also has a band at 3 550 cm^{-1} (OH), and single bands at 1 090 and 620 cm^{-1} (non-co-ordinated ClO_4^-); for the thiocyanate complex three bands are found at 2 070, 2 025, and 2 000 cm^{-1} .

The mass spectrum of $Pb_2L^7(NCS)_4$ has a highest molecular weight ion at m/e 490 corresponding to L^7 ; the complexes were not soluble enough to permit recording of the n.m.r. spectra.

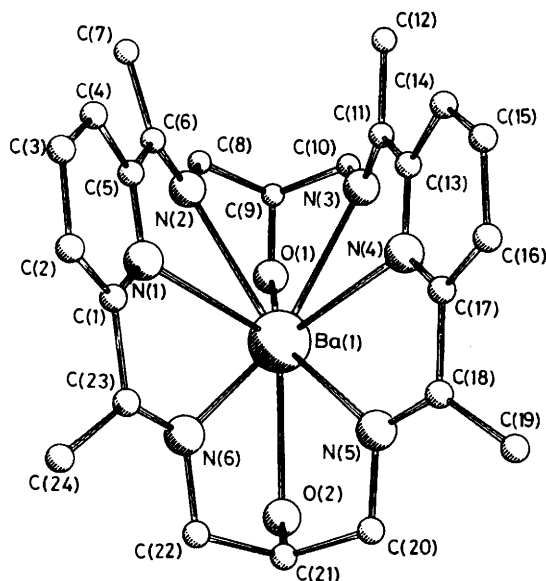
It is noteworthy that homobinuclear complexes of lead(II) have arisen with the last two ligands where the inner ring size has advanced to 22 and 24 respectively.

Reaction of 1,5-Diamino-3-hydroxypentane with Furan-2,5-dicarbaldehyde.—The reaction of an equimolar amount of fdc and 1,5-dhp in dry EtOH in the presence of $Ba(ClO_4)_2$ (2:2:1 molar ratio) gave an orange solution from which orange needles of $BaL^8(ClO_4)_2 \cdot EtOH$ grew. The macrocyclic nature of L^8 was established through elemental analysis, i.r., and 1H n.m.r. spectra, and by a single-crystal X-ray structure determination.

The solid-state i.r. spectrum of $BaL^8(ClO_4)_2 \cdot EtOH$ has a broad band at 3 375 cm^{-1} assigned to the O–H stretch of the endogenous alcohol groups, and two bands at 1 640 and 1 630 cm^{-1} both assigned to $\nu(C=N)$ absorptions. The presence of two imine bands may reflect the presence of co-ordinated and non-co-ordinated imine nitrogen atoms leading to an asymmetry of the complex. The spectrum also shows a splitting of the ν_3 and ν_4 modes of the perchlorate; each is split into three bands indicating bound, bidentate ClO_4^- . A Fourier-transform i.r.

Table 2. Selected bond lengths (Å), inter-atomic contacts (Å), and bond angles (°) for $\text{BaL}^1(\text{H}_2\text{O})_2(\text{ClO}_4)_2^*$

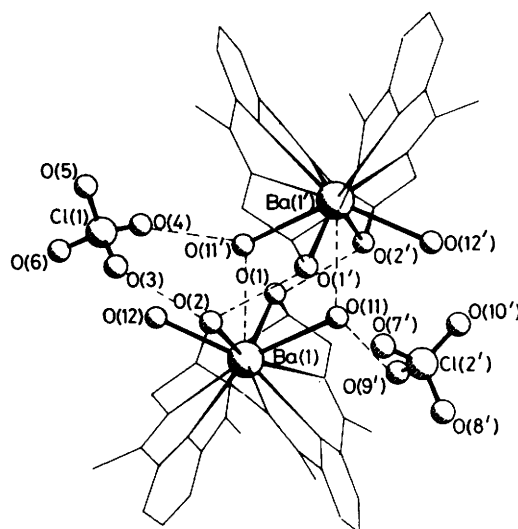
Ba(1)—O(1)	2.802(8)	Ba(1)—N(2)	2.963(8)	Ba(1)—O(2)	2.795(7)	Ba(1)—N(3)	2.914(10)
Ba(1)—O(11)	2.927(7)	Ba(1)—N(6)	2.926(8)	Ba(1)—O(12)	2.825(10)	Ba(1)—N(5)	2.918(9)
Ba(1)—N(1)	2.985(7)			Ba(1)—N(4)	2.923(8)		
Ba(1)···O(11)*	3.160(7)	O(6)···O(13)	2.626(23)	O(1)···O(2)*	3.025(11)	O(9)···O(11)*	2.979(13)
O(2)···O(3)	2.986(13)	O(10)···O(12)	3.169(18)	O(4)···O(11)*	2.999(15)	O(12)···O(13)	2.752(10)
O(11)—Ba(1)—O(12)	132.1(2)	Ba(1)—O(1)—C(9)	113.3(6)	O(1)—Ba(1)—O(2)	117.7(2)	Ba(1)—O(2)—C(21)	112.0(6)
N(2)—Ba(1)—N(5)	139.4(2)	Ba(1)—N(2)—C(8)	116.0(6)	N(3)—Ba(1)—N(6)	140.7(2)	Ba(1)—N(3)—C(10)	115.0(7)
N(1)—Ba(1)—N(4)	83.2(2)	Ba(1)—N(2)—C(6)	122.3(7)	N(3)—Ba(1)—N(4)	55.2(3)	Ba(1)—N(3)—C(11)	118.0(8)
N(1)—Ba(1)—N(2)	54.2(2)	Ba(1)—N(1)—C(1)	120.6(6)	N(4)—Ba(1)—N(5)	55.1(2)	Ba(1)—N(4)—C(17)	122.0(7)
N(1)—Ba(1)—N(6)	54.5(2)	Ba(1)—N(1)—C(5)	117.7(6)	N(5)—Ba(1)—N(6)	57.9(2)	Ba(1)—N(4)—C(13)	116.6(6)
N(2)—Ba(1)—N(3)	57.9(2)	Ba(1)—N(6)—C(23)	126.9(6)	O(1)—Ba(1)—N(3)	59.5(3)	Ba(1)—N(5)—C(18)	125.7(7)
O(1)—Ba(1)—N(2)	58.0(2)	Ba(1)—N(6)—C(22)	115.8(6)	O(2)—Ba(1)—N(5)	60.0(2)	Ba(1)—N(5)—C(20)	115.9(7)
O(2)—Ba(1)—N(6)	59.0(2)						

* Symmetry operation: a is $-x, -y, -z$.**Figure 1.** Molecular structure with atom labelling of the cation $[\text{BaL}^1]^{2+}$. For clarity the co-ordinated water molecules are not shown; neither are the perchlorate anions, nor the partial occupancy water molecule of crystallisation

spectrum of the complex in Me_2SO shows two absorptions at 1665 and 1643 cm^{-1} suggesting retention of asymmetry in solution; only one band is seen for ClO_4^- , at 1100 cm^{-1} , indicating that it is no longer co-ordinated and has perhaps been replaced by Me_2SO .

The ^1H n.m.r. spectrum [$(\text{CD}_3)_2\text{SO}$, 400 MHz] also indicated that asymmetric structure is maintained in solution. Resonances at 8.10 and 8.13 p.p.m. relative to SiMe_4 are assigned to imino protons and confirm the presence of inequivalent imino groups. Similar resonances at 6.90 and 6.91 p.p.m., ascribed to the furan ring protons, indicate inequivalence. The resonances due to the methylene protons of the ligand skeleton are very broad, possibly a consequence of the presence of diastereoisomers. A triplet at 1.06 and a quartet at 3.44 p.p.m. are assigned to the EtOH proton resonances. These do not give clear indication as to whether the EtOH is involved in bonding to the complex in solution as these resonances coincide with those expected for free EtOH in Me_2SO .

Descriptions of the Structures.—The structures of the four macrocyclic complexes are illustrated in Figures 1—5 with the

**Figure 2.** The weak dimerisation of $\text{BaL}^1(\text{H}_2\text{O})_2(\text{ClO}_4)_2$ across the crystallographic inversion centre at (0,0,0); primes represent atoms related by this symmetry. For clarity, the macrocycle is shown in skeletal outline only and only two of the four perchlorate anions are included; the partial occupancy water molecule is also omitted

atom labelling used in the corresponding Tables. Selected bond lengths and angles (together with estimated standard deviations) are given in Tables 2—5. Full listings of bond lengths and angles and details of planar fragments for all four structures are in the supplementary publication.

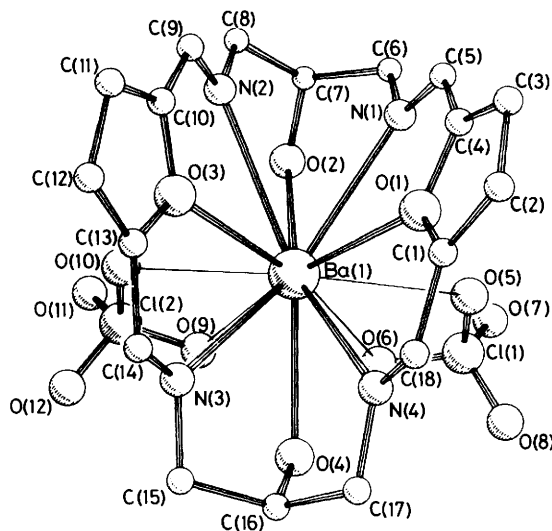
In the molecule $\text{BaL}^1(\text{H}_2\text{O})_2(\text{ClO}_4)_2 \cdot 0.16\text{H}_2\text{O}$ (Figure 1, Table 2), the macrocycle is substantially folded [137.2° between pyridyl fragments, $\text{N}(1)\text{—Ba}(1)\text{—N}(4)$ 83.2°] and, with the exceptions of the substituent hydroxyl groups, the macrocycle occupies one co-ordination hemisphere of the barium, with similar length contacts to all six nitrogen atoms. The other co-ordination hemisphere comprises five oxygen atoms: the two substituent hydroxyl groups, two water molecules and, at a greater distance, a water molecule [O(11)] of an inversion-related complex, thus giving rise to weak dimerisation across (0,0,0). The two perchlorate anions are not directly co-ordinated to the barium atom, but engage in extended hydrogen bonding to hydroxyl groups and to co-ordinated water molecules, thereby strengthening the dimerisation (Figure 2).

The asymmetric unit is completed by a partial occupancy water molecule (0.16 per barium) on an inversion centre at (0, 0,

Table 3. Selected bond lengths (Å), inter-atomic contacts (Å), and bond angles (°) for BaL⁵(ClO₄)₂ *

Ba(1)–O(1)	2.899(5)	Ba(1)–N(1)	2.972(6)	Ba(1)–O(3)	2.943(5)	Ba(1)–N(3)	3.008(6)
Ba(1)–O(2)	2.888(6)	Ba(1)–N(2)	3.082(6)	Ba(1)–O(4)	2.837(5)	Ba(1)–N(4)	3.024(6)
Ba(1)–O(5)	2.968(8)	O(2)···O(8) ^a	3.007(11)	Ba(1)–O(10)	2.875(7)	O(4)···O(12) ^b	2.858(11)
Ba(1)–O(6)	2.978(8)			Ba(1)–O(9)	2.979(8)		
O(1)–Ba(1)–N(1)	53.54(15)	O(5)–Ba(1)–O(9)	103.96(22)	O(3)–Ba(1)–N(3)	52.82(15)	O(6)–Ba(1)–O(10)	105.66(22)
O(2)–Ba(1)–N(1)	57.69(16)	Ba(1)–O(1)–C(1)	126.2(4)	O(4)–Ba(1)–N(3)	57.33(16)	Ba(1)–O(3)–C(10)	125.9(4)
O(2)–Ba(1)–N(2)	55.68(15)	Ba(1)–O(1)–C(4)	125.3(4)	O(4)–Ba(1)–N(4)	54.89(16)	Ba(1)–O(3)–C(13)	125.3(4)
N(1)–Ba(1)–N(2)	55.39(16)	Ba(1)–N(1)–C(5)	124.1(5)	N(3)–Ba(1)–N(4)	55.86(17)	Ba(1)–N(3)–C(14)	123.8(5)
O(3)–Ba(1)–N(2)	51.63(14)	Ba(1)–N(1)–C(6)	117.1(5)	O(1)–Ba(1)–N(4)	52.39(15)	Ba(1)–N(3)–C(15)	116.0(5)
O(2)–Ba(1)–O(4)	134.05(15)	Ba(1)–O(2)–C(7)	114.9(4)	O(1)–Ba(1)–O(3)	73.26(13)	Ba(1)–O(4)–C(16)	117.8(4)
N(1)–Ba(1)–N(3)	137.26(17)	Ba(1)–N(2)–C(8)	117.6(4)	N(2)–Ba(1)–N(4)	125.27(16)	Ba(1)–N(4)–C(17)	118.3(5)
O(5)–Ba(1)–O(10)	146.13(21)	Ba(1)–N(2)–C(9)	122.4(5)	O(6)–Ba(1)–O(9)	60.77(23)	Ba(1)–N(4)–C(18)	122.6(5)

* Symmetry operations: a is $\frac{1}{2} + x, y, \frac{1}{2} - z$; b is $-x, -y, -z$.

**Figure 3.** Molecular structure of BaL⁵(ClO₄)₂ with atom labelling

0.5) which is also hydrogen bonded to two perchlorate anions and to two co-ordinated water molecules, although stereochemistry would preclude their simultaneous formation and, when present, this water molecule is probably disordered close to the inversion centre. All the relevant hydrogen bonded distances are given in Table 2. Two further, similarly short distances, O(1)···O(11)^a and O(2)···O(11)^a must be consequential on the hydrogen-bonded network and cannot themselves be hydrogen-bonded contacts since they lie *trans* to C(9) and C(21) respectively. All other subtended angles are in the range 76–137° (mostly within 10° of 109°) so most hydrogen bonds will be fairly close to linear.

The monomeric unit (excluding the perchlorates but including the co-ordinated water molecules) has approximate *C*_{2v} symmetry. The co-ordination polyhedron of the barium can be analysed as either a square antiprism with two additional sites or as a cuboctahedron with two vacant sites. In either case, the mean angular displacement is only 3° from a regular polyhedron of *C*_{2v} symmetry. The barium atom lies > 1 Å from the pyridyl mean planes and the imine nitrogen atoms are each twisted to various extents (up to 0.5 Å), and in various directions [N(5) and N(6) towards the barium atom] away from the adjacent pyridyl planes. This results in a loss of coplanarity of the formally *sp*²-hybridised imino-nitrogen atoms and their immediate neighbours, particularly N(2) and N(3) with out-of-plane displacements of the nitrogen atoms by up to 0.20 Å.

The 1,3-diiminopropan-2-ol chelate ring adopts the inevitable boat conformation which permits hydroxyl group co-ordination. Remaining features of the geometry of the macrocycle are normal.

The closely related molecule BaL⁵(ClO₄)₂ (Figure 3, Table 3) has a similar geometry. The overall folding, measured in terms of the angle between furan ring planes (129.2°), is slightly less (by 8°) than the corresponding angle between pyridyl planes in BaL¹(H₂O)₂(ClO₄)₂ above, although the corresponding bond angle at barium [O(1)–Ba(1)–O(3)] is 10° smaller at 73.3°. The imino-nitrogen atoms deviate less from the adjacent furan planes. The barium atom is only about half the distance displaced from the furan and chelate planes, and more symmetrically so. The co-ordination around the imino-nitrogen atoms is again pyramidalised, with out-of-plane displacements of *ca.* 0.12 Å.

The co-ordinated water molecules in the previous molecule are replaced here by two approximately symmetrically bidentate perchlorate ligands. Each co-ordinated hydroxyl group is hydrogen bonded to a perchlorate oxygen atom of a different complex, one such pair of interactions being across an inversion centre and the other pair being to molecules related by *a*-glide symmetry operations. These together result in weak polymerisation in the *ac* plane. The remaining geometry of the molecule is normal.

The molecule PbL²(NCS)₂·MeOH (Figure 4, Table 4) is derived from the same macrocycle as is involved in BaL¹(H₂O)₂(ClO₄)₂ above; however, it has undergone a ring contraction in order to accommodate the smaller cation. Both hydroxyl groups have added across adjacent C=N double bonds to produce two hinged (by 33° and about the O···N line) oxazolidine rings incorporated in a macrocycle which has a ring size two fewer (at 18) than before the contraction.

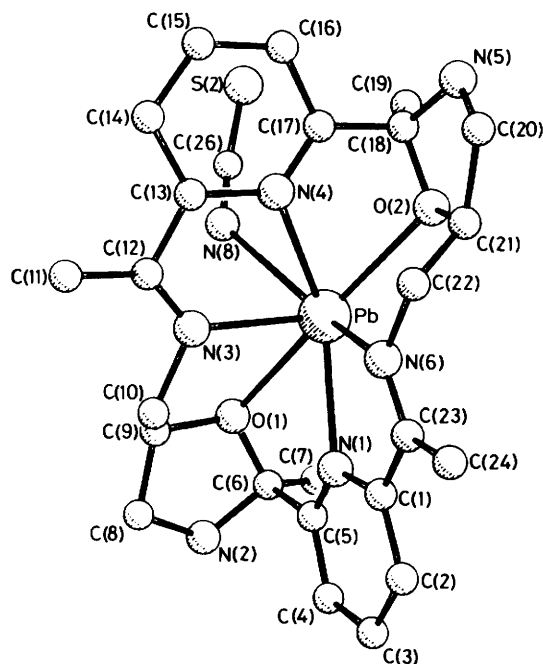
The highly buckled macrocycle fully occupies one co-ordination hemisphere of the lead atom with approximate *C*₂ symmetry. The oxazolidine oxygen atoms are almost precisely *trans* and the major non-coplanarity between adjacent chelate co-ordination planes (86°) occurs across these Pb–O bonds. The opposite hemisphere is filled by only an N-co-ordinated isothiocyanate and an anionic thiocyanate in which the closest contact is made to the sulphur. The positions of these two ligands conform to the approximate *C*₂ symmetry and the large angular space (122°) between them could be viewed as a consequence of a stereochemically active lone pair on the Pb²⁺ cation. Each pyridyl ring and its adjacent pyridylimino chelate plane are closely coplanar although the lead deviates by up to 0.5 Å. Each imine nitrogen is fairly coplanar with its immediate neighbours. Each thiocyanate group is linear and lies below a pyridyl fragment and the ionic thiocyanate lies precisely parallel to the pyridyl plane at a distance of 3.57 Å. The methanol of

Table 4. Selected bond lengths (Å), inter-atomic contacts (Å), and bond angles (°) for $\text{PbL}^2(\text{NCS})_2 \cdot \text{MeOH}^*$

Pb(1)–O(1)	2.634(5)	N(2)–C(8)	1.448(11)	Pb(1)–O(2)	2.702(5)	N(5)–C(20)	1.446(12)
Pb(1)–N(1)	2.587(6)	N(3)–C(10)	1.454(10)	Pb(1)–N(4)	2.569(6)	N(6)–C(22)	1.446(11)
Pb(1)–N(3)	2.469(6)	N(3)–C(12)	1.272(10)	Pb(1)–N(6)	2.532(6)	N(6)–C(23)	1.267(10)
Pb(1)–N(8)	2.889(8)	N(8)–C(26)	1.147(12)	Pb(1)···S(1)	3.415(3)	N(7)–C(25)	1.145(15)
O(1)–C(6)	1.436(9)	S(2)–C(26)	1.646(9)	O(2)–C(18)	1.432(10)	S(1)–C(25)	1.618(11)
O(1)–C(9)	1.427(9)	O(3)···N(5)	3.168(10)	O(2)–C(21)	1.435(10)	O(3)···N(7) ^a	2.834(13)
N(2)–C(6)	1.432(10)	O(3)···H(N5)	2.26	N(5)–C(18)	1.434(11)	H(O3)···N(7) ^a	1.95
O(1)–Pb(1)–O(2)	173.8(2)	Pb(1)–O(1)–C(6)	114.7(4)	N(8)–Pb(1)···S(1)	121.8(2)	Pb(1)–O(2)–C(18)	113.2(4)
N(1)–Pb(1)–N(4)	131.8(2)	Pb(1)–O(1)–C(9)	115.9(4)	N(3)–Pb(1)–N(6)	86.9(2)	Pb(1)–O(2)–C(21)	115.9(4)
O(1)–Pb(1)–N(1)	61.2(2)	Pb(1)–N(3)–C(10)	114.6(5)	O(2)–Pb(1)–N(4)	60.3(2)	Pb(1)–N(6)–C(22)	114.3(5)
O(1)–Pb(1)–N(3)	65.5(2)	Pb(1)–N(3)–C(12)	122.2(5)	O(2)–Pb(1)–N(6)	64.0(2)	Pb(1)–N(6)–C(23)	122.9(5)
N(1)–Pb(1)–N(6)	62.9(2)	Pb(1)–N(8)–C(26)	128.6(7)	N(3)–Pb(1)–N(4)	64.7(2)	Pb(1)···S(1)–C(25)	110.7(4)
Pb(1)–N(1)–C(1)	118.3(5)	S(2)–C(26)–N(8)	178.5(8)	Pb(1)–N(4)–C(13)	116.1(5)	S(1)–C(25)–N(7)	179.4(10)
Pb(1)–N(1)–C(5)	121.0(5)	O(3)···H(N5)–N(5)155		Pb(1)–N(4)–C(17)	122.2(5)	O(3)–H(O3)···N(7) ^a 164	

* Symmetry operation: a is $x, y, 1+z$.**Table 5.** Selected bond lengths (Å), inter-atomic contacts (Å), and bond angles (°) for $\text{BaL}^8(\text{ClO}_4)_2 \cdot \text{EtOH}$

Ba(1)–O(1)	2.822(11)	Ba(1)–N(1)	2.998(15)	Ba(1)–O(13)	2.632(24)	Ba(1)–O(10)	3.006(21)
Ba(1)–O(2)	2.660(17)	O(2)···O(13)	2.89	Ba(1)–O(4)	2.711(15)	Ba(1)–N(4)	2.971(16)
Ba(1)–O(5)	2.867(14)	O(3)···O(13)	3.16	Ba(1)–O(9)	2.892(16)	O(4)···O(13)	2.74
Ba(1)–O(6)	2.993(16)						
O(1)–Ba(1)–N(1)	56.4(4)	Ba(1)–O(1)–C(4)	126.5(11)	O(1)–Ba(1)–N(4)	55.2(4)	Ba(1)–N(4)–C(22)	120.8(14)
O(2)–Ba(1)–N(1)	64.8(4)	Ba(1)–N(1)–C(5)	116.2(12)	O(4)–Ba(1)–N(4)	63.5(4)	Ba(1)–N(4)–C(21)	126.1(8)
O(2)–Ba(1)–N(4)	160.4(6)	Ba(1)–N(1)–C(6)	123.1(11)	O(4)–Ba(1)–N(1)	172.7(5)	Ba(1)–O(4)–C(26)	145.4(11)
O(1)–Ba(1)–O(13)	172.0(6)	Ba(1)–O(2)–C(8)	145.3(12)	Ba(1)–O(13)–C(23)	138.7(24)	Ba(1)–O(4)–C(19)	129.0(9)
				Ba(1)–O(1)–C(1)	126.8(10)		

**Figure 4.** Molecular structure with atom labelling of the cationic species $[\text{PbL}^2(\text{NCS})]^+$. The ionic thiocyanate and the solvent methanol of crystallisation are omitted for clarity

solvation is weakly hydrogen bonded to the protonated nitrogen N(5) of the oxazolidine ring and more strongly to the nitrogen N(7) of the anionic thiocyanate of a molecule one unit cell away along the c -axis. The hydrogen on the protonated

nitrogen N(2) which is not involved in hydrogen bonding is unevenly (0.75:0.25) disordered between two sites.

Although the full eight-co-ordinate polyhedron of the lead can be described as substantially distorted from either a bicapped trigonal prism or a dodecahedron, it does not approximate closely to any standard shape. There are two pairs of chiral carbon centres in the molecule [C(6) and C(18), C(9) and C(21)] and both members of each pair necessarily have the same configuration: thus, although each molecule is chiral, the crystal is racemic (space group is centrosymmetric). Bond lengths and angles in the macrocycle are normal.

The molecule $\text{BaL}^8(\text{ClO}_4)_2 \cdot \text{EtOH}$ (Figure 5, Table 5) is related to that of $\text{BaL}^2(\text{ClO}_4)_2$ in that the macrocycle has been enlarged by four carbon atoms, the two 1,3-di-iminopropan-2-ol fragments being replaced by 1,5-di-iminopentan-3-ol chains. The much larger macrocycle cavity results in a more planar skeleton than in the three previous complexes. The surface of the macrocycle is curved down by 57° (between furan rings) and accommodates a barium atom at one end of the cavity in an approximately planar (root mean square deviation 0.16 Å) five-co-ordinate environment, but with the barium lying 0.34 Å above the plane. However, the barium lies closely coplanar with the di-iminofuran fragment. The barium is further co-ordinated by a solvent ethanol molecule which lies above the second compartment and is in a position to form hydrogen bonds to hydroxyl groups and, *via* its own hydrogen, to the unco-ordinated furan oxygen, but not to the free imines. The co-ordination sphere is completed by two asymmetrically bidentate perchlorate ligands lying transversely above, and laterally below the macrocycle, in order to avoid steric interactions with the co-ordinated ethanol.

One 1,5-di-iminopentan-3-ol chain shows disorder of its three central carbon atoms between two conformations. The major component shows a boat conformation for the six-membered, metal-containing chelate ring, whereas the ordered ring has a

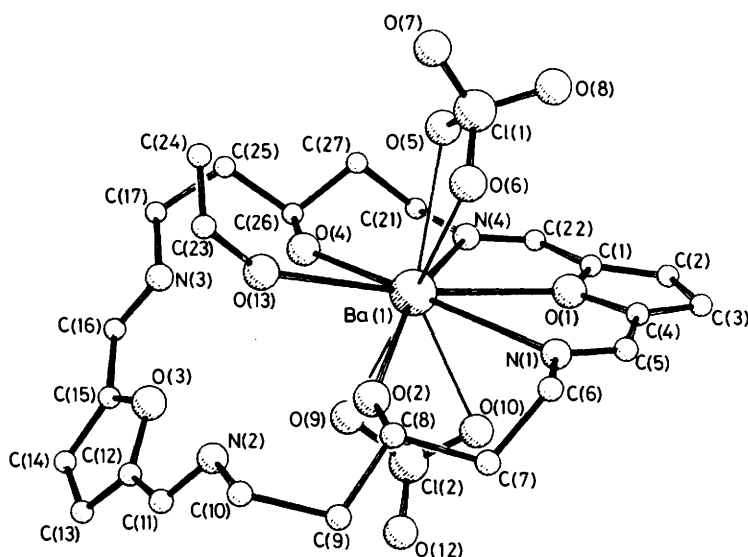


Figure 5. Molecular structure, with atom labelling, of $\text{BaL}^8(\text{ClO}_4)_2 \cdot \text{EtOH}$. Included are the central three atoms of the 1,5-di-iminopentan-3-ol chain [C(25)—C(27)] which have the higher occupancy; the minor disorder component is C(18)—C(20) and has a conformation which is approximately mirror-related to that of atoms C(9)—C(7). Atom O(11) is obscured by Cl(2)

chair conformation. The minor component of the disordered chain has a very twisted boat conformation. All other geometric features are normal.

Discussion of the Structures.—The molecules $\text{BaL}^1(\text{H}_2\text{O})_2(\text{ClO}_4)_2$ and $\text{BaL}^5(\text{ClO}_4)_2$ have strikingly similar conformations for the barium-macrocycle unit. The only significant geometric difference is the smaller value, by 10° , of the X—Ba—X bond angle (X = furan oxygen or pyridyl nitrogen) in the latter molecule although this is accompanied by an 8° lesser folding between the ring fragments, resulting in the greater out-of-plane displacements of the barium in the former molecule. The somewhat less encapsulating di-iminofuran fragment as compared to the di-iminopyridine units leads to Ba—N(imine) distances which are, on average, 0.09 \AA greater in the former case. The slightly lesser congestion around the barium in the furan-containing macrocyclic complex creates more space in the other co-ordination hemisphere, thereby permitting the direct co-ordination of the more bulky bidentate perchlorate ligands rather than the three water ligands (two close, one distant) in the pyridyl-containing macrocyclic complex. However, the effect must be marginal, particularly in view of the proven ability of perchlorate to vary the denticity of its mode of attachment.

It is clear that a 20-membered macrocycle is too large to accommodate a Ba^{2+} cation without conformational changes to reduce the cavity size defined by the heteroatoms. Indeed it has been shown⁹ that a planar, 18-membered macrocycle ideally accommodates a Ba^{2+} , although this macrocycle was produced from an originally 24-membered macrocycle containing secondary amine residues by a ring contraction to incorporate two imidazolidine rings in the macrocycle. Similarly, if a complex is produced between the smaller cation Pb^{2+} [as $\text{Pb}(\text{NCS})_2$] and the 20-membered, pyridine-containing macrocycle, a ring contraction to an 18-membered macrocycle occurs by the incorporation of two oxazolidine rings into the macrocycle. Presumably folding of the 20-membered macrocycle would be inadequate to reduce the cavity size sufficiently, and a planar 20-membered macrocycle is clearly insufficiently large to be binucleating with respect to Pb^{2+} , since it has been shown¹³ to be ideal to binucleate two smaller Cu^{2+} cations with a bridging hydroxyl function. However, the 18-membered macrocycle produced by ring contraction has still too large a

cavity to co-ordinate to Pb^{2+} in a planar manner; the macrocycle therefore buckles sufficiently to reduce the cavity size to optimum.

When expanding to the 24-membered macrocycle used in $\text{BaL}^8(\text{ClO}_4)_2 \cdot \text{EtOH}$, the macrocycle is still too small to binucleate two barium cations. It is known¹⁴ that essentially the same 24-membered macrocycle (with pyridine instead of furan and with methyl substituents) binucleates two Cu^{2+} cations, without hydroxyl bridges, but with substantial macrocycle folding and that a 22-membered macrocycle binucleates two Cu^{2+} cations with much reduced folding. It may be noted that a planar 24-membered macrocycle (L^7) does act as a binucleating ligand for Pb^{2+} . The ring contraction available to the 24-membered macrocycle is to a 20-membered macrocycle which, as we have seen, would still be too large to accommodate a Ba^{2+} cation without substantial folding. The Ba^{2+} is therefore incorporated at one end of the approximately planar macrocycle with a solvent molecule capping the second compartment.

The overall structure of $\text{BaL}^8(\text{ClO}_4)_2 \cdot \text{EtOH}$ resembles that of the complex comprising 2,6-pyrido-27-crown-9,* urea, and LiClO_4 (1:2:1 molar ratio) in which the Li^+ utilises donor atoms from one segment of the macrocyclic cavity and is co-ordinated to the oxygen atom of a neutral urea molecule which resides in the cavity.¹⁵ The urea molecule is in turn involved in the hydrogen-bonding interactions with the oxygen atoms of the crown ether.

Conclusions

When considering complex formation between a metal and a complexing macrocycle, the matching of macrocycle cavity size to metal radius is of prime importance. The macrocycle may be capable of modification by quantised changes in its cavity size by a ring-contraction procedure which may reduce the ring size by 2, 4, 6 or more atoms, depending on the chain length across which cyclisation takes place and the nature of the group which adds across the double bond. Asymmetric macrocycles may be able to reduce ring size by intermediate steps. After an

* 3,6,9,12,15,18,21,24-Octaoxa-30-azabicyclo[24.3.1]triaconta-1(30),-26,28-triene.

approximately correct cavity size is achieved, macrocycle folding provides a means of fine-tuning until optimum M-X (X = bonding atom) distances are reached. If the macrocycle is sufficiently large, it may act as a binucleating ligand. If none of these routes can provide an optimum cavity size, the metal may be asymmetrically incorporated in the macrocycle, perhaps with solvent or counter-ion interaction with the unused hetero-atoms.

Clearly the metal ion has fewer options available in adjusting to available macrocycle cavity size. However, given the circumstances, a metal may be able to respond to the environment provided by a macrocycle in a number of ways. Effective metal radius changes with oxidation state (where variable), spin state (for *d*-block metals), and cavity size can make a macrocycle selective for one metal over another. Finally, the geometry of the polyhedron provided by the heteroatoms defining a cavity may be selective with respect to some metals which have strong geometric preferences. In this connection, the presence of functional substituents on the macrocycle, such as hydroxyl groups or longer chains, could provide a more three-dimensional cage which might be more discriminating in its selectivity. Thus we have here many of the criteria which are known to be important in protein and enzyme action: encapsulating organic fragments with easily accessible and reversible conformational changes, and metal ions, the activity of which may be affected by those changes. Study of their interactions provides a means by which the active sites of proteins may be progressively more accurately modelled. Transmetallation reactions of the complexes described herein have given dinuclear copper(II) complexes.^{13,14} Such complexes have provided some optimistic parallels when the bimetallosite is oxyhaemocyanin.

Experimental

Microanalyses were carried out by the University of Sheffield Microanalytical Service. I.r. spectra were recorded as KBr discs using a Perkin-Elmer 297 spectrophotometer. Hydrogen-1 n.m.r. spectra were recorded using Perkin-Elmer R34 and Bruker 400-MHz spectrometers; ¹³C n.m.r. spectra were recorded using a Bruker WH 250 spectrometer. Mass spectra were recorded using a Kratos MS 25 spectrometer.

(a) *Complexes derived from 1,3-Diamino-2-hydroxypropane and 2,6-Diacetylpyridine.*—Preparation of the macrocyclic barium and lead complexes. 2,6-Diacetylpyridine and 1,3-diamino-2-hydroxypropane were used as supplied by the Aldrich Chemical Co. Ltd. The macrocyclic barium and lead complexes were prepared using the following general method.

2,6-Diacetylpyridine (0.01 mol) and the metal salt [Ba(ClO₄)₂, Ba(NCS)₂·2H₂O, Pb(ClO₄)₂·3H₂O, or Pb(NCS)₂] (0.005 mol) were dissolved in refluxing dry methanol or ethanol (150 cm³). To this was added a solution of 1,3-diamino-2-hydroxypropane (0.01 mol) in methanol or ethanol (50 cm³) dropwise over 15 min. The resulting solution or suspension was then refluxed for a further 3 h. The macrocyclic complexes deposited on cooling and were collected by filtration. Further batches of each complex were obtained by evaporation of the filtrate under reduced pressure. Samples for elemental analysis were dried *in vacuo* over silica gel.

BaL¹(ClO₄)₂·2H₂O. Colourless crystals (Found: C, 35.8; H, 4.3; Cl, 7.7; N, 10.6. C₂₄H₃₄BaCl₂N₆O₁₂ requires C, 35.7; H, 4.3; Cl, 8.8; N, 10.4%). Yields for several preparations 60–80%.

BaL¹(NCS)₂·2H₂O. White powder (Found: C, 43.2; H, 4.8; N, 15.4; S, 7.9. C₂₆H₃₄BaN₈O₄S₂ requires C, 43.1; H, 4.7; N, 15.5; S, 8.9%); m.p. 200 °C (decomp.). Yield 35%.

PbL²(ClO₄)₂·H₂O. Colourless crystals (Found: C, 33.5; H, 3.5; Cl, 8.8; N, 9.8. C₂₄H₃₂Cl₂N₆O₁₁Pb requires C, 33.6; H, 3.8;

Cl, 8.3; N, 9.8%). A mass spectrum could not be obtained due to the involatility of the sample. Yields for several preparations 80–90%.

PbL²(NCS)₂·MeOH. Pale yellow crystals (Found: C, 41.2; H, 4.8; N, 14.0. C₂₇H₃₄N₈O₃PbS₂ requires C, 41.1; H, 4.3; N, 14.2%); m.p. 200 °C (decomp.). Yield 85%.

Preparation of the strontium complexes. 2,6-Diacetylpyridine (2 mmol) and Sr(ClO₄)₂ (1 mmol) were dissolved in dry methanol (30 cm³). 1,3-Diamino-2-hydroxypropane (2 mmol) in methanol (20 cm³) was added dropwise over 10 min with stirring at room temperature (r.t.). After 3 h, SrL³(ClO₄)₂·H₂O precipitated from solution as a yellow powder and was isolated by filtration. A sample for elemental analysis was dried *in vacuo* over silica gel. The filtrate was left to evaporate slowly over a period of two weeks after which time, SrL²(ClO₄)₂·H₂O had crystallised from solution as colourless crystals. SrL²(ClO₄)₂·H₂O was also prepared by dissolving SrL³(ClO₄)₂·H₂O in methanol–acetonitrile (10:1) r.t. followed by slow evaporation of the resulting solution.

SrL³(ClO₄)₂·H₂O. Yellow powder (Found: C, 38.6; H, 4.3; Cl, 8.9; N, 11.2. C₂₄H₃₄Cl₂N₆O₁₂Sr requires C, 38.5; H, 4.5; Cl, 9.5; N, 11.2%). Yield 35%.

SrL²(ClO₄)₂·H₂O. Colourless crystals (Found: C, 39.1; H, 4.4; Cl, 9.7; N, 11.6. C₂₄H₃₂Cl₂N₆O₁₁Sr requires C, 39.0; H, 4.4; Cl, 9.6; N, 11.4%). Yield 60%.

Transmetallation reactions of BaL¹(ClO₄)₂·2H₂O and PbL²(ClO₄)₂·H₂O. (i) *Ring-closure reaction.* A solution of lead perchlorate (2 mmol) in methanol (25 cm³) was added to BaL¹(ClO₄)₂·2H₂O (2 mmol) suspended in refluxing methanol (25 cm³) and the resulting suspension was refluxed for 3 h. On cooling to r.t. PbL²(ClO₄)₂ precipitated from solution as a white powder. The sample gave a satisfactory elemental analysis and ¹H n.m.r. spectrum. Yield 70%.

(ii) *Ring-expansion reactions.* A solution of silver(I) perchlorate (2 mmol) in methanol (25 cm³) was added to PbL²(ClO₄)₂·H₂O (1 mmol) dissolved in refluxing methanol (25 cm³) and the resulting suspension was refluxed for a further 3 h. Ag₂L¹(ClO₄)₂·2H₂O was isolated by filtration of the hot reaction mixture. The same binuclear silver complex was also prepared by transmetallation of BaL¹(ClO₄)₂·2H₂O using the same procedure.

Ag₂L¹(ClO₄)₂·2H₂O. White powder (Found: C, 32.6; H, 3.6; Cl, 8.3; N, 9.6. C₂₄H₃₄Ag₂Cl₂N₆O₁₂ requires C, 32.6; H, 3.9; Cl, 8.0; N, 9.5%). Yields, 90% by transmetallation of BaL¹(ClO₄)₂·2H₂O or 80% by transmetallation of PbL²(ClO₄)₂·H₂O.

Reduction of PbL²(NCS)₂·2H₂O. The reduction of the macrocyclic ligand L² was effected using NaBH₄. Sodium tetrahydroborate (60 mmol, 50% excess) was added to a stirred suspension of PbL²(NCS)₂ (5 mmol) in ethanol (500 cm³). The reaction mixture was refluxed for 30 min and filtered hot through hyffosuperpel. The filtrate was evaporated to dryness under reduced pressure and the residue dissolved in water (50 cm³). The solution was cooled to 0 °C using an ice–salt bath and a few pellets of sodium hydroxide were added. The solution was left to stand at this temperature for 10 min (a period greater than this was found to lead to diminished yields) before extraction with chloroform (5 × 50 cm³). The combined extracts were dried over magnesium sulphate, filtered and evaporated, under reduced pressure, to leave a yellow oil. Addition of diethyl ether (dried over sodium) afforded a white powder which was isolated by filtration. The complex was purified by recrystallisation from chloroform–diethyl ether.

PbL⁴(NCS)₂·1.5H₂O. White powder (Found: C, 39.4; H, 5.1; N, 13.9. C₂₆H₄₁N₈O_{3.5}PbS₂ requires C, 39.4; H, 5.0; N, 14.1%); m.p. 148–150 °C (decomp.). Mass spectrum has a highest molecular weight peak corresponding to [L⁴]⁺ at *m/e* 442. Yield 60%.

Table 6. Atomic co-ordinates with e.s.d.s for $\text{BaL}^1(\text{H}_2\text{O})_2(\text{ClO}_4)_2^*$

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ba(1)	0.186 76(6)	0.119 70(5)	0.191 77(5)	C(3)	0.592 6(10)	0.548 8(8)	0.154 5(8)
Cl(1)	-0.302 1(3)	-0.100 5(2)	0.247 8(3)	C(4)	0.599 4(9)	0.444 0(8)	0.151 0(8)
Cl(2)	-0.003 3(3)	-0.367 6(2)	0.248 8(2)	C(5)	0.487 2(9)	0.335 9(7)	0.132 5(7)
O(1)	0.179 7(6)	-0.089 3(6)	0.116 2(7)	C(6)	0.489 5(9)	0.220 2(8)	0.118 4(8)
O(2)	-0.057 2(6)	0.123 7(5)	0.143 6(6)	C(7)	0.611 0(13)	0.224 8(11)	0.109 9(14)
O(3)	-0.276 9(9)	0.016 2(7)	0.227 2(9)	C(8)	0.381 8(10)	0.010 0(8)	0.087 0(9)
O(4)	-0.244 3(11)	-0.143 0(9)	0.197 8(11)	C(9)	0.308 6(10)	-0.082 9(8)	0.146 8(9)
O(5)	-0.437 0(13)	-0.170 1(9)	0.206 9(18)	C(10)	0.378 2(13)	-0.063 9(10)	0.275 2(10)
O(6)	-0.254 9(23)	-0.103 7(17)	0.363 7(14)	C(11)	0.501 3(10)	0.121 4(10)	0.394 6(8)
O(7)	0.101 8(10)	-0.349 8(11)	0.217 8(11)	C(12)	0.634 0(13)	0.117 1(14)	0.427 0(12)
O(8)	-0.070 2(10)	-0.488 8(8)	0.250 0(11)	C(13)	0.504 0(10)	0.222 0(9)	0.453 3(7)
O(9)	-0.090 2(9)	-0.329 7(8)	0.165 7(10)	C(14)	0.619 3(11)	0.305 2(10)	0.540 1(8)
O(10)	0.047 9(14)	-0.300 4(13)	0.350 1(10)	C(15)	0.612 9(11)	0.386 0(10)	0.599 2(9)
O(11)	0.082 6(6)	0.109 3(5)	-0.058 7(5)	C(16)	0.492 2(11)	0.386 9(9)	0.576 1(8)
O(12)	0.086 9(9)	-0.033 5(8)	0.340 0(8)	C(17)	0.381 1(10)	0.304 4(8)	0.484 9(8)
N(1)	0.371 6(7)	0.333 0(6)	0.123 7(6)	C(18)	0.248 8(10)	0.305 2(8)	0.452 2(8)
N(2)	0.387 6(7)	0.125 3(6)	0.110 1(6)	C(19)	0.225 2(14)	0.354 5(12)	0.541 2(10)
N(3)	0.391 9(9)	0.044 4(7)	0.325 2(7)	C(20)	0.034 3(10)	0.262 8(10)	0.313 3(10)
N(4)	0.386 8(7)	0.226 3(6)	0.423 8(6)	C(21)	-0.039 2(9)	0.237 4(8)	0.184 1(9)
N(5)	0.164 5(8)	0.261 0(7)	0.349 3(7)	C(22)	0.024 9(9)	0.330 8(8)	0.119 8(9)
N(6)	0.153 0(7)	0.336 4(6)	0.132 3(6)	C(23)	0.234 1(9)	0.431 1(7)	0.111 9(7)
C(1)	0.365 8(8)	0.436 5(7)	0.124 6(7)	C(24)	0.211 1(11)	0.537 9(9)	0.071 6(10)
C(2)	0.473 9(10)	0.547 7(8)	0.140 1(8)	O(13)	0.0000	0.000	0.5000

* Atoms Cl(1) and O(3)—O(6) comprise perchlorate (1); atoms Cl(2) and O(7)—O(10) comprise perchlorate (2). Atoms O(11) and O(12) are the co-ordinated water molecules and O(13) is the partial occupancy unco-ordinated water molecule, and is located on a crystallographic inversion centre; it therefore carries no e.s.d.s.

Table 7. Atomic co-ordinates with e.s.d.s for $\text{PbL}^2(\text{NCS})_2 \cdot \text{MeOH}^*$

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Pb(1)	0.269 93(2)	0.181 73(3)	0.135 3(2)	C(8)	0.386 4(5)	0.436 0(10)	-0.281 8(7)
S(1)	0.137 1(2)	-0.217 4(4)	-0.066 0(3)	C(9)	0.393 2(5)	0.420 2(9)	-0.153 9(7)
S(2)	0.528 5(2)	0.086 4(3)	0.367 3(2)	C(10)	0.344 5(5)	0.541 1(9)	-0.123 3(7)
O(1)	0.357 3(3)	0.241 0(6)	-0.135 2(4)	C(11)	0.415 6(7)	0.781 4(10)	0.067 3(8)
O(2)	0.182 0(3)	0.084 6(7)	0.166 8(4)	C(12)	0.366 6(5)	0.597 5(9)	0.074 3(7)
O(3)	0.148 1(4)	-0.219 8(9)	0.498 3(6)	C(13)	0.354 9(5)	0.532 6(9)	0.186 8(6)
N(1)	0.185 8(4)	0.222 5(7)	-0.203 6(5)	C(14)	0.392 0(6)	0.633 4(11)	0.283 9(8)
N(2)	0.354 4(4)	0.259 0(8)	-0.324 0(5)	C(15)	0.378 2(7)	0.560 9(13)	0.387 4(8)
N(3)	0.335 5(4)	0.492 9(7)	-0.009 8(5)	C(16)	0.327 4(6)	0.399 1(12)	0.388 2(7)
N(4)	0.304 9(4)	0.372 8(8)	0.189 2(5)	C(17)	0.290 9(5)	0.308 3(10)	0.285 4(6)
N(5)	0.174 3(5)	0.124 1(9)	0.345 0(6)	C(18)	0.234 7(5)	0.126 7(10)	0.283 7(6)
N(6)	0.125 5(4)	0.277 7(8)	-0.036 1(5)	C(19)	0.289 7(6)	-0.011 2(12)	0.328 7(8)
N(7)	0.097 3(7)	-0.265 2(14)	-0.300 1(9)	C(20)	0.101 8(6)	0.189 4(12)	0.262 8(7)
N(8)	0.453 1(5)	0.216 0(9)	0.144 7(6)	C(21)	0.103 7(5)	0.151 0(11)	0.143 5(7)
C(1)	0.103 8(5)	0.244 0(9)	-0.233 1(6)	C(22)	0.103 0(5)	0.310 1(10)	0.063 3(7)
C(2)	0.050 0(5)	0.235 8(11)	-0.347 1(7)	C(23)	0.074 0(5)	0.283 7(9)	-0.138 8(7)
C(3)	0.082 8(5)	0.200 9(12)	-0.429 9(7)	C(24)	-0.014 2(5)	0.328 6(12)	-0.172 8(8)
C(4)	0.167 3(5)	0.182 0(11)	-0.399 8(7)	C(25)	0.114 2(6)	-0.245 6(13)	-0.203 0(9)
C(5)	0.217 2(5)	0.193 1(9)	-0.285 0(6)	C(26)	0.484 4(5)	0.161 1(10)	0.235 6(8)
C(6)	0.309 7(5)	0.167 4(9)	-0.247 1(6)	C(27)	0.186 8(11)	-0.358 3(17)	0.504 8(12)
C(7)	0.311 1(5)	-0.026 3(10)	-0.236 2(7)				

* Atoms O(3) and C(27) constitute the methanol molecule of solvation. Atoms S(1), N(7), and C(25) constitute the unco-ordinated thiocyanate anion.

(b) *Complexes derived from 1,3-Diamino-2-hydroxypropane and Furan-2,5-dicarbaldehyde.*—Preparation of the macrocyclic barium(II) complexes. Furan-2,5-dicarbaldehyde (2 mmol)¹⁶ and the barium salt (1 mmol) (either perchlorate or thiocyanate) were dissolved in dry ethanol (30 cm³) at reflux temperature. A solution of 1,3-dhp (2 mmol) in ethanol (20 cm³) was added dropwise over 10 min. The immediate white suspension which resulted was refluxed for a further 30 min. The macrocyclic complexes were isolated by filtration and dried *in vacuo* at r.t. over silica gel.

$\text{BaL}^3(\text{ClO}_4)_2$. Colourless crystals (Found: C, 31.4; H, 3.0; Cl,

9.9; N, 7.9. $\text{C}_{18}\text{H}_{20}\text{BaCl}_2\text{N}_4\text{O}_{12}$ requires C, 31.2; H, 2.9; Cl, 10.2; N, 8.1%). Yield for several preparations 50–60%.

$\text{BaL}^3(\text{NCS})_2 \cdot \text{H}_2\text{O}$. Cream powder (Found: C, 38.5; H, 3.9; N, 12.6. $\text{C}_{20}\text{H}_{22}\text{BaN}_6\text{O}_5\text{S}_2$ requires C, 38.3; H, 3.5; N, 13.4%); m.p. 120 °C (decomp.). Yield 30–35%.

(c) *Preparation of Macrocycles derived from 1,5-Diamino-3-hydroxypentane.*—Either dap or fdc (4 mmol) and the metal salt [$\text{Ba}(\text{ClO}_4)_2$, $\text{Pb}(\text{ClO}_4)_2$, or $\text{Pb}(\text{NCS})_2$] (2 mmol) were dissolved in refluxing dry ethanol (50 cm³). 1,5-Diamino-3-hydroxypentane (4 mmol)¹⁷ in ethanol (20 cm³) was added and the

Table 8. Atomic co-ordinates with e.s.d.s for BaL⁵(ClO₄)₂

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ba(1)	-0.001 64(3)	0.209 48(2)	0.136 58(2)	C(1)	-0.163 4(5)	0.382 3(4)	0.137 8(4)
Cl(1)	-0.122 28(13)	0.093 00(12)	0.265 05(11)	C(2)	-0.180 0(6)	0.457 0(5)	0.161 6(5)
Cl(2)	0.137 12(15)	0.073 96(12)	0.051 71(13)	C(3)	-0.121 0(6)	0.471 5(5)	0.217 1(5)
O(1)	-0.097 3(3)	0.350 0(3)	0.175 0(3)	C(4)	-0.071 7(5)	0.405 0(4)	0.224 4(4)
O(2)	0.138 5(4)	0.181 4(3)	0.234 4(3)	C(5)	-0.002 1(6)	0.380 2(5)	0.269 7(4)
O(3)	0.057 6(3)	0.335 9(3)	0.041 4(2)	C(6)	0.100 5(6)	0.289 4(6)	0.309 2(4)
O(4)	-0.120 3(4)	0.110 5(3)	0.064 5(3)	C(7)	0.172 5(5)	0.251 2(5)	0.268 3(4)
O(5)	-0.112 2(6)	0.176 0(4)	0.261 7(5)	C(8)	0.213 3(5)	0.304 0(5)	0.213 6(4)
O(6)	-0.065 1(6)	0.066 2(5)	0.211 3(4)	C(9)	0.161 7(5)	0.384 8(4)	0.121 9(4)
O(7)	-0.095 3(6)	0.064 0(5)	0.330 6(4)	C(10)	0.111 5(5)	0.396 2(4)	0.059 4(4)
O(8)	-0.206 8(5)	0.075 7(6)	0.250 6(5)	C(11)	0.109 0(5)	0.451 7(5)	0.007 7(5)
O(9)	0.072 4(5)	0.053 0(4)	0.098 8(5)	C(12)	0.052 2(5)	0.423 5(5)	-0.045 3(5)
O(10)	0.141 5(5)	0.157 9(3)	0.051 4(4)	C(13)	0.022 0(5)	0.354 0(5)	-0.022 4(4)
O(11)	0.213 7(6)	0.039 5(6)	0.067 2(7)	C(14)	-0.035 0(5)	0.294 9(5)	-0.051 5(4)
O(12)	0.119 0(8)	0.049 5(4)	-0.017 1(4)	C(15)	-0.104 3(6)	0.171 1(5)	-0.048 5(5)
N(1)	0.029 9(4)	0.311 8(4)	0.262 0(3)	C(16)	-0.167 1(5)	0.143 2(4)	0.006 7(4)
N(2)	0.155 5(4)	0.319 0(4)	0.154 2(3)	C(17)	-0.225 6(5)	0.205 0(5)	0.037 2(5)
N(3)	-0.046 4(4)	0.231 0(4)	-0.017 6(3)	C(18)	-0.204 0(5)	0.330 5(5)	0.087 7(4)
N(4)	-0.177 4(4)	0.259 7(4)	0.083 5(3)				

Table 9. Atomic co-ordinates ($\times 10^4$) with e.s.d.s for BaL⁸(ClO₄)₂·EtOH *

Atom	x	y	z	Atom	x	y	z
Ba(1)	3 157(1)	1 126(1)	1 926(1)	C(5)	4 171(19)	995(10)	37(9)
Cl(1)	769(5)	2 301(3)	877(3)	C(6)	5 460(20)	1 998(11)	569(11)
Cl(2)	5 466(5)	-313(4)	2 517(3)	C(7)	6 656(20)	1 964(12)	1 198(12)
O(1)	2 641(11)	304(7)	592(6)	C(8)	6 402(22)	2 290(13)	1 924(11)
O(2)	5 493(15)	1 857(12)	2 221(8)	C(9)	7 704(19)	2 348(15)	2 475(13)
O(3)	5 283(11)	1 420(7)	4 539(6)	C(10)	7 553(22)	2 704(12)	3 196(12)
O(4)	2 003(9)	690(10)	3 105(8)	C(11)	7 288(19)	2 003(11)	4 191(11)
O(5)	522(15)	1 705(8)	1 328(9)	C(12)	6 646(23)	1 534(12)	4 711(13)
O(6)	2 186(10)	2 422(9)	984(9)	C(13)	7 152(23)	1 237(14)	5 353(13)
O(7)	125(17)	2 890(8)	1 065(11)	C(14)	6 071(24)	935(14)	5 645(11)
O(8)	285(20)	2 162(11)	163(7)	C(15)	4 952(23)	1 032(13)	5 126(10)
O(9)	4 856(20)	175(8)	2 965(8)	C(16)	3 540(21)	876(11)	5 093(12)
O(10)	4 953(19)	-159(12)	1 767(7)	C(17)	1 204(11)	832(4)	4 621(1)
O(11)	5 128(21)	-980(7)	2 694(11)	C(18)	549(34)	362(12)	3 943(5)
O(12)	6 798(9)	-249(12)	2 656(12)	C(19)	637(8)	697(2)	3 181(6)
O(13)	3 332(27)	1 996(14)	3 094(13)	C(20)	-207(15)	254(10)	2 552(10)
N(1)	4 514(15)	1 408(8)	598(7)	C(21)	394(4)	-393(1)	2 177(3)
N(2)	6 737(15)	2 262(10)	3 609(9)	C(22)	1 061(19)	-460(10)	1 041(13)
N(3)	2 610(13)	1 011(10)	4 533(8)	C(23)	3 245(27)	2 680(13)	3 231(24)
N(4)	1 215(18)	-110(9)	1 653(9)	C(24)	1 805(18)	2 885(17)	3 338(23)
C(1)	1 751(18)	-253(13)	438(10)	C(25)	319(13)	838(2)	3 839(4)
C(2)	1 804(21)	-505(13)	-251(12)	C(26)	919(15)	318(10)	3 324(10)
C(3)	2 722(22)	-79(14)	-569(13)	C(27)	-170(11)	202(7)	2 626(10)
C(4)	3 185(21)	416(12)	-34(11)				

* Atoms C(25)—C(27) comprise the major (0.58) disorder component of the disordered fragment: those of the minor (0.42) component are labelled C(18)—C(20).

reaction mixture was refluxed for a further 3 h. The lead(II) complexes precipitated from solution and were isolated by filtration. The barium complex was isolated as orange needles by slow evaporation of the reaction mixture. All samples were dried *in vacuo* over silica gel.

Pb₂L⁷(ClO₄)₃(OH). White powder (Found: C, 27.9; H, 3.5; Cl, 9.2; N, 6.6. C₂₈H₃₉Cl₃N₆O₁₅Pb₂ requires C, 27.6; H, 3.2; Cl, 8.7; N, 6.9%). Yield 95%.

Pb₂L⁷(NCS)₄. White powder (Found: C, 33.8; H, 3.4; N, 12.4. C₃₂H₃₈N₁₀O₂Pb₂S₄ requires C, 33.8; H, 3.4; N, 12.3%); m.p. 270—272 °C. Mass spectrum, [L⁷]⁺ at *m/e* 490. Yield 55%.

BaL⁸(ClO₄)₂·EtOH. Orange needles (Found: C, 36.2; H, 4.3; Cl, 8.8; N, 6.9. C₂₄H₃₄BaCl₂N₄O₁₃ requires C, 36.3; H, 4.3; Cl, 8.9; N, 7.1%). Yield 55%.

(d) Preparation of the Macrocyclic Complex derived from 1,4-Diamino-2-hydroxybutane.—2,6-Diacetylpyridine (2 mmol) and lead(II) perchlorate (2 mmol) were dissolved in dry methanol (50 cm³) at reflux temperature. A solution of 1,4-diamino-2-hydroxybutane (2 mmol) in methanol (20 cm³) was added dropwise over 15 min and the reaction mixture was refluxed for 3 h. Pb₂L⁹(ClO₄)₃(OH) precipitated from solution and was isolated by filtration. The sample was dried *in vacuo* over silica gel. White powder (Found: C, 26.1; H, 3.0; Cl, 8.4; N, 6.5. C₂₆H₃₅Cl₃N₆O₁₅Pb₂ requires C, 26.2; H, 3.0; Cl, 8.9; N, 7.1%). Yield 75%.

Crystal Data.—BaL¹(H₂O)₂(ClO₄)₂·0.16H₂O, C₂₄H_{34.32}BaCl₂N₆O_{12.16}, *M* = 809.69, crystallises from acetonitrile as

colourless polyhedra; crystal dimensions $0.66 \times 0.34 \times 0.20$ mm; triclinic, $a = 12.097(14)$, $b = 12.524(10)$, $c = 12.721(15)$ Å, $\alpha = 86.27(8)$, $\beta = 112.74(8)$, $\gamma = 115.64(7)^\circ$, $U = 1.590(3)$ Å³, $Z = 2$, $D_m = 1.65$, $D_c = 1.691$ g cm⁻³; space group $P\bar{1}$ (C_i , no. 2), graphite-monochromated Mo- K_α radiation ($\bar{\lambda} = 0.71069$ Å), $\mu(\text{Mo-}K_\alpha) = 14.83$ cm⁻¹, $F(000) = 833.28$.

Three-dimensional X-ray diffraction data were collected in the range $3.5 < 2\theta < 50^\circ$ on a Nicolet R3m diffractometer by the omega-scan method. The 3 632 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were placed in calculated positions (C-H 0.97, O-H 1.0 Å, C-C-H 111°); their contributions were included in structure factor calculations ($B = 10.0$ Å²) but no refinement of positional parameters was permitted. The hydrogen atoms on co-ordinated water O(12) were found to be disordered and were given 0.67 occupancy at each chosen site. A partial occupancy water molecule was detected on an inversion centre at (0, 0, 0.5); an occupancy of 0.16 was assigned on the basis of acceptable thermal parameters; the hydrogens were not located. Refinement converged at $R = 0.0520$ with allowance for anisotropic thermal motion of all non-hydrogen atoms (with the exception of the oxygen atom of the partial occupancy water molecule) and for the anomalous scattering of barium.

$\text{PbL}^2(\text{NCS})_2 \cdot \text{MeOH}$, $\text{C}_{27}\text{H}_{34}\text{N}_8\text{O}_3\text{PbS}_2$, $M = 789.94$, crystallises from methanol as pale yellow plates; crystal dimensions $0.50 \times 0.45 \times 0.14$ mm; triclinic, $a = 16.586(17)$, $b = 7.828(6)$, $c = 12.255(8)$ Å, $\alpha = 84.57(6)$, $\beta = 109.48(6)$, $\gamma = 102.80(8)^\circ$, $U = 1.463(2)$ Å³, $Z = 2$, $D_m = 1.72$, $D_c = 1.794$ g cm⁻³; space group $P\bar{1}$ (C_i , no. 2), graphite-monochromated Mo- K_α radiation ($\bar{\lambda} = 0.71069$ Å), $\mu(\text{Mo-}K_\alpha) = 59.90$ cm⁻¹, $F(000) = 780$.

The data were collected and processed (4 479 independent reflections) and the structure solved and refined ($R = 0.0359$) as for the barium complex above. Hydrogen atoms were detected and included in structure factor calculations [C-H, N-H 0.96, O-H 0.91 Å, X-C-H 111° (X = C or O), C-O-H 110° , $B = 5.0$ Å²]. The hydrogen atom on N(2) was disordered (0.75:0.25) between two sites. Anisotropic thermal motion was allowed for all non-hydrogen atoms, anomalous scattering for lead and sulphur.

$\text{BaL}^3(\text{ClO}_4)_2 \cdot \text{C}_{18}\text{H}_{20}\text{BaCl}_2\text{N}_4\text{O}_{12}$, $M = 692.58$, crystallises from methanol as colourless plates; crystal dimensions $0.50 \times 0.184 \times 0.524$ mm; orthorhombic, $a = 15.50(8)$, $b = 16.97(9)$, $c = 18.84(8)$ Å, $U = 4.955(42)$ Å³, $Z = 8$, $D_m = 1.80$, $D_c = 1.857$ g cm⁻³; space group $Pbca$ (D_{2h}^{15} , no. 61), graphite-monochromated Mo- K_α radiation ($\bar{\lambda} = 0.71069$ Å), $\mu(\text{Mo-}K_\alpha) = 18.86$ cm⁻¹, $F(000) = 2.736$.

The data were collected ($6.5 < 2\theta < 50^\circ$) on a Stoe Stadi-2 diffractometer and processed (2 519 independent reflections) and the structure solved and refined ($R = 0.0357$) as for the complex above.

$\text{BaL}^6(\text{ClO}_4)_2 \cdot \text{EtOH}$, $\text{C}_{24}\text{H}_{34}\text{BaCl}_2\text{N}_4\text{O}_{13}$, $M = 794.75$, crystallises from ethanol as colourless needles; crystal dimensions $0.49 \times 0.09 \times 0.09$ mm; monoclinic, $a = 9.960(5)$, $b = 18.387(12)$, $c = 18.102(13)$ Å, $\beta = 99.85(5)^\circ$, $U = 3.266(4)$ Å³, $Z = 4$, $D_m = 1.60$, $D_c = 1.616$ g cm⁻³; space group $P2_1/c$ (C_{2h}^5 , no. 14), graphite-monochromated Mo- K_α radiation ($\bar{\lambda} = 0.71069$ Å), $\mu(\text{Mo-}K_\alpha) = 14.43$ cm⁻¹, $F(000) = 1.600$.

The data were collected and processed (1676 independent

reflections) and the structure solved and refined ($R = 0.0591$) as for the first barium complex above. One of the pentan-3-ol chains showed disorder in its central section [atoms C(18)—C(20)] and geometric constraints were applied to both disorder components by comparison with the geometry of the second, ordered chain: the disorder refined to 0.42:0.58. Hydrogen atoms were located and positioned on all carbon atoms but not on the three oxygen atoms; they were given isotropic thermal parameters which were 10% greater than the equivalent isotropic thermal parameter of the attached carbon atoms. Anisotropic thermal parameters were permitted for all but the disordered atoms.

Tables 6—9 list atomic positional parameters with estimated standard deviations for the four structures. Scattering factors were taken from ref. 18; unit weights were used throughout all refinements. Computer programs used were SHELXTL,¹⁹ implemented on a Nova 3 computer, and those of the Sheffield X-ray system.

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References

- 1 S. M. Nelson, *Inorg. Chim. Acta*, 1982, **62**, 39; *Pure Appl. Chem.*, 1980, **52**, 2461.
- 2 D. E. Fenton and G. Rossi, *Inorg. Chim. Acta*, 1985, **98**, L29.
- 3 N. C. Eickman, R. S. Himmelwright, and E. I. Solomon, *Proc. Natl. Acad. Sci. USA*, 1979, **76**, 2094; G. L. Woolery, L. Powers, M. Winkler, E. I. Solomon, and T. G. Spiro, *J. Am. Chem. Soc.*, 1984, **106**, 86 and refs. therein.
- 4 M. R. Rosenthal, *J. Chem. Educ.*, 1973, **50**, 331.
- 5 A. H. Norbury and A. I. P. Sinha, *Q. Rev. Chem. Soc.*, 1970, **24**, 69.
- 6 J. W. Cornforth, in 'Heterocyclic Compounds,' ed. R. C. Elderfield, Wiley, New York, 1957, vol. 5, ch. 6.
- 7 E. D. Bergmann, E. Gil-Av, and S. Pinchas, *J. Am. Chem. Soc.*, 1953, **75**, 358.
- 8 J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 1976, 734.
- 9 M. G. B. Drew, J. Nelson, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1678.
- 10 E. D. Bergmann, D. Lavie, and S. Pinchas, *J. Am. Chem. Soc.*, 1951, **73**, 5662.
- 11 K. F. Dancy, D. E. Fenton, S. Moss, G. Jones, and R. Price, *Synth. Commun.*, 1986, **16**, 795.
- 12 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Wiley-Interscience, New York, 1972.
- 13 N. A. Bailey, D. E. Fenton, I. T. Jackson, R. Moody, and C. O. Rodriguez de Barbarin, *J. Chem. Soc., Chem. Commun.*, 1983, 1463; V. McKee and J. Smith, *ibid.*, p. 1465.
- 14 R. Moody, Ph.D. Thesis, University of Sheffield, 1985.
- 15 D. N. Reinhoudt, personal communication, 1985.
- 16 A. F. Oleinik and K. Yu. Novitskii, *J. Org. Chem. USSR*, 1970, 2643.
- 17 I. Murase, M. Hatano, M. Tanaka, S. Ueno, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2404.
- 18 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
- 19 G. M. Sheldrick, SHELXTL system for solution of X-ray crystal structures, University of Göttingen, 1983, revision 4.

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