Alkaline Earth, Lead(II), and Cadmium(II) Complexes of a Nitrogen Analogue of [18]Annulene; X-Ray Crystal Structure of the Lead and Cadmium Complexes

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Summary Ca^{II}, Sr^{II}, Ba^{II}, and Pb^{II} are effective templates for the synthesis of a conjugated, 18-membered, hexadentate 'N_6' macrocycle; the crystal and molecular structures of a Pb^{II} complex, and of a Cd^{II} complex prepared by metal exchange, have been determined.

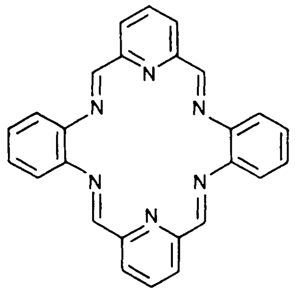
ALTHOUGH it has not previously been synthesised, the conjugated macrocycle L (**1**) containing the 18-membered inner large ring, has been the subject of theoretical calculations by Honeybourne[1] who predicted that (i) the six nitrogen atoms would define a hexagon with a face dimension of *ca.* 2·8 Å, (ii) when co-ordinated, the length of any

Table 1. Crystal data for the Pb^{II} and Cd^{II} complexes[a]

	$[PbL(OH_2)][ClO_4]_2(H_2O)$[b]	$[CdL(OH_2)(ClO_4)][ClO_4](MeOH)$[c]
Formula	$C_{26}H_{22}Cl_2O_{10}N_6Pb$	$C_{27}H_{24}Cl_2O_{10}N_6Cd$
M	856·3	775·8
Class	Monoclinic	Monoclinic
Spacegroup	$P2_1/a$	$P2_1/a$
a/Å	15·730(8)	15·733(10)
b/Å	11·990(11)	12·446(10)
c/Å	18·286(13)	18·152(11)
β/°	120·2(1)	121·7(1)
U/Å^3	2981·3	3024·6
D_c/g cm^{-3}	1·89	1·83
D_m/g cm^{-3}	1·90(2)	1·84(2)
Reflections above background	2058	1876
R	0·081	0·060

[a] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. [b] Both ClO_4^- ions are disordered (see text). [c] Both ClO_4^- ions are ordered.

metal–nitrogen bond would also be *ca.* 2·8 Å, and (iii) only large metal ions would fit into the central cavity of the macrocycle without considerable distortion from its D_{6h} microsymmetry.



(1)

We have now synthesised L (in the co-ordinated state) using the perchlorate salts of the large metal ions Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+} as templates for the '2 + 2' cyclic Schiff base condensation of two molecules of 2,6-diformylpyridine with two molecules of *o*-phenylenediamine (40—70% yield) in methanol or acetonitrile solution. No macrocyclic products were isolated from reactions carried out in the absence of metal ion nor by the use of Mg^{II}, Cd^{II}, Hg^{II}, or the transition metal ions Mn^{II}—Zn^{II}. Chemical analysis established the stoicheiometries of the complexes isolated to be $ML(ClO_4)_2$ (M = Ca or Sr), $PbL(ClO_4)_2.2H_2O$, and $BaL_2(ClO_4)_2$. (Derivatives containing other anions are readily obtained by metathesis.) I.r. spectra show the expected bands due to the co-ordinated imino (1620—1640 cm^{-1}) and pyridyl (1400—1600 cm^{-1}) groups and confirm the absence of the carbonyl and primary amine functions of the macrocyclic precursors. Parent ion peaks were not observed in the mass spectra which showed instead a strong peak at m/e 414 corresponding to the free macrocycle; no peaks of significant intensity were observed at higher m/e values. The structure of the Pb^{II} complex was determined by X-ray analysis. Crystal data are in Table 1 and selected bond distances in Table 2.

Table 2. Selected bond distances (Å) for the Pb^{II} and Cd^{II} complexes

Pb^{II} Complex		Cd^{II} Complex	
Pb–N(1)	2·76(4)	Cd–N(1)	2·70(3)
Pb–N(4)	2·85(3)	Cd–N(4)	2·79(3)
Pb–N(7)	2·79(3)	Cd–N(7)	2·66(3)
Pb–N(10)	2·76(4)	Cd–N(10)	2·60(3)
Pb–N(13)	2·65(3)	Cd–N(13)	2·52(3)
Pb–N(16)	2·69(3)	Cd–N(16)	2·50(3)
Pb–O (water)	2·45(3)	Cd–O (water)	2·24(3)
Pb . . .O[a] (perchlorate)	2·83(3)	Cd–O (perchlorate)	2·33(3)

[a] Nearest approach of an oxygen atom from the disordered perchlorate.

The metal atom is bonded to all six nitrogen atoms of the macrocycle [2·65(3)—2·85(3) Å] and to the oxygen atom of a water molecule [2·45(3) Å] in one axial position. The macrocycle is not quite planar; the four imino nitrogens form a plane with the two pyridine nitrogens displaced to one side and the metal atom to the other [Pb 0·30, N(7) −0·49, N(16) − 0·60 Å]. Thus, the structure is best described as a distorted hexagonal pyramid (Figure). One perchlorate group is severely disordered† with a smearing of electron density *ca.* 3·0 Å from the metal in a position approximately *trans* to the water molecule. All six N–Pb–O(H_2O) angles are less than 85° suggesting that a lone

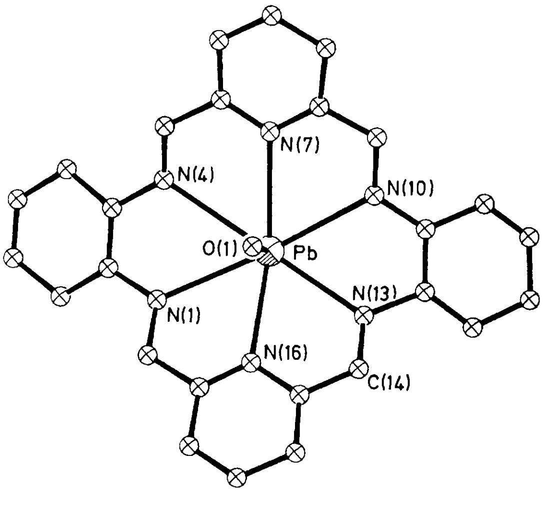


Figure. The structure of $[PbL(OH_2)]^{2+}$

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† Five tetrahedra with a total occupancy factor of 1·0 were required to explain the disorder. The second ClO_4^- anion is also disordered.

pair is stereochemically active in the other axial position and that its presence is the cause of the perchlorate ion disorder. In a hexagonal pyramid, as in a square pyramid, without an axially directed lone pair the L_{ax}–M–L_{eq} angles would be greater than 90° as a result of ligand–ligand repulsions (see also below).

I.r. spectra indicate that the ClO_4^- ions are co-ordinated in the Ca^{II} and Sr^{II} complexes but not in the Ba^{II} complex which contains two molecules of macrocycle per metal atom. On the assumption that the conjugated macrocycle maintains a near-planar conformation, as demonstrated for the Pb^{II} complex, it is therefore likely that the Ca^{II} and Sr^{II} complexes have hexagonal bipyramidal structures similar to those reported recently[3] for a related non-rigid macrocycle, and that the Ba^{II} complex has a (12-co-ordinated) sandwich-type structure. (Single crystal *X*-ray analysis revealed that this structure is highly disordered.)

The results can be rationalized in terms of metal ion radii and the dimensions of the macrocycle cavity. Honeybourne[1] has predicted a hole size of radius *ca.* 2·8 Å. A more realistic estimate based on the crystallographic results obtained for the Pb^{II} complex is *ca.* 2·7 Å. Thus it is not expected that Ba^{2+} (octa-co-ordinate ionic diameter 2·84 Å)[4] would sit within the macrocycle, a prediction in accord with the proposed sandwich structure for this complex. For the case of Ca^{2+}, Sr^{2+}, and Pb^{2+} (octa-co-ordinate ionic diameters 2·24, 2·52, and 2·58 Å)[4] the metal ions can now be readily accommodated in the 'N_6' plane. The Mg^{2+} and the first row transition metal ions (octa-co-ordinate ionic diameters 1·80—1·92 Å)[4] are clearly too small to be effectively bonded to all six nitrogen atoms of the planar macrocycle, thus accounting for their ineffectiveness as templates for its synthesis.

On size considerations alone the failure of d^{10} ions such as Cd^{II} (octa-co-ordinate ionic diameter 2·20 Å) as templates appears anomalous. However, we have found that the Ba^{2+} ion in $[BaL_2][ClO_4]_2$ may be exchanged in solution with Cd^{II} to yield the complex $[CdL(OH_2)(ClO_4)][ClO_4]\cdot MeOH$ shown by i.r. and mass spectra to contain the macrocycle L. It is isomorphous with the Pb^{II} complex (Tables 1 and 2). The macrocycle has a similar conformation to that in the Pb^{II} complex. In this case, however, the metal atom is displaced only 0·11 Å from the plane comprising the four imino nitrogens [Cd − 0·11, N(7) − 0·65, N(16) − 0·74 Å]. The metal ion has an approximate hexagonal bipyramidal geometry being bonded to a water molecule and a perchlorate oxygen atom in the axial positions. The presence of this perchlorate oxygen at 2·33(3) Å contrasts with the isomorphous Pb^{II} complex and lends weight to our view that the lone pair in this latter complex is stereochemically active. The lone pair prevents the close approach of the perchlorate ion which, consequently, having no preferred orientation, is disordered. There is some evidence that the Cd^{II} is somewhat too small for the macrocycle cavity. Not only are the Cd–N distances long in comparison with those found[5] in a smaller nitrogen macrocycle, but the data also indicate that the metal ion is asymmetrically positioned in the hexagonal hole, lying relatively closer to N(10), N(13), and N(16) (Table 2).

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[1] C. L. Honeybourne, *Tetrahedron*, 1973, **29**, 1549.

[2] The related macrocycle derived from 2,6-diacetylpyridine has been reported by R. W. Stotz and R. C. Stoufer, *Chem. Comm.*, 1970, 1962. However, no structural information is available. Steric interaction between the imino methyl groups and *o*-phenylene hydrogen atoms may render this ring non-planar.

[3] J. de O. Cabral, M. F. Cabral, M. G. B. Drew, A. Rodgers, and S. M. Nelson, *Inorg. Chim. Acta*, 1978, **30**, L313.

[4] R. D. Shannon, *Acta Cryst.*, 1976, **A32**, 751.

[5] M. G. B. Drew, S. G. McFall, and S. M. Nelson, *J.C.S. Dalton*, 1979, 575.