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Hexagonal Bipyramidal Alkaline Earth and Lead(II) Complexes of a Hexa-imine Macrocyclic Ligand*

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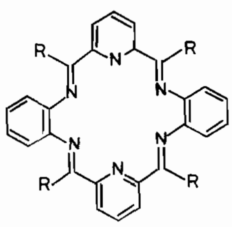
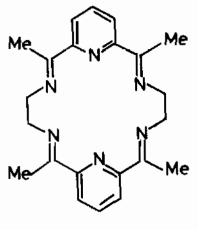
The Schiff base condensation of 2,6-diformylpyridine or 2,6-diacetylpyridine with linear polyfunctional di-primary amines in the presence of a suitable metal ion has been the basis of the synthesis of a variety of tetra- [1], penta- [2] and hexa-dentate [3] macrocyclic ligands. The isolation of the coordinated macrocycle in good yield is evidence for a template action, kinetic and/or thermodynamic, on the part of the metal ion in directing the condensation towards a cyclic rather than polymeric product. In reactions with short chain di-primary amines incapable of spanning the two carbonyl groups a cyclic '1 + 1' condensate is, of course, impossible and oligomeric/polymeric gums or oils are generally obtained. However, in such cases there is the possibility of formation of large 'double' rings by the cyclic condensation of two molecules of diamine with two molecules of dialdehyde or diketone.** Stotz and Stoufer [4] have described the synthesis in 40–45% yield of the 18-membered, potentially hexadentate, macrocycle L^1 by the reaction in dilute solution of 2,6-diacetylpyridine with *o*-phenylenediamine in the absence of metal ion, and also in the presence of Cu(II) ion under which conditions the macrocycle was isolated as the binuclear complex $[Cu_2L^1][NO_3]_4$. While no direct information on the structure of this complex was obtained, the presence of a weak metal–metal interaction was inferred from magnetic susceptibility and e.s.r. measurements.

This note is a preliminary report of the synthesis of metal complexes of the related macrocycle L^3 by the use of alkaline earth metal ions, and of lead(II), as templates and includes the results of X-ray structure determinations of a strontium(II) and a lead(II) complex.



L^1 : R = Me
L^2 : R = H



L^3

The complexes of L^3 (Table I) were prepared by reaction of 2,6-diacetylpyridine (0.02 mol) with 1,2-diaminoethane (0.02 mol) in the presence of a salt (nitrate, perchlorate, halide or thiocyanate) of Ca(II), Sr(II), Ba(II) or Pb(II) (0.01 mol) in refluxing methanol for periods varying from 1–12 h and by metathesis from initially formed product. Yields (see Table I) varied from 40–80% depending on the template salt employed. Macrocyclic products were not isolated from reactions carried out in the absence of metal ion (either under the above conditions or under the conditions described by Stotz and Stoufer [4] nor in the presence of salts of other metal ions *e.g.* Mg(II), Mn(II), Fe(II), Ni(II), Cu(II), Ag(I), Cd(II), Hg(II) (see below).

The formation of the 18-membered 'N' macrocycle L^3 in reactions employing an alkaline earth or lead(II) metal ion was inferred from the stoicheiometries and from i.r., ^1H *n.m.r.* and mass spectral data and from the X-ray crystal determinations of two members of the series, $[SrL^3Cl_2]\cdot 2H_2O$ and $[PbL^3(SCN)_2]$.

Crystal Data

$[SrL^3Cl_2]\cdot 2H_2O$, $C_{22}H_{30}O_2N_6SrCl_2$, $M = 568.5$, Orthorhombic, $a = 13.715(9)$, $b = 11.226(13)$, $c = 32.302\ (21)$ Å, $U = 4973.4$ Å^3, $D_m = 1.51$, $D_c = 1.52$, g cm^{-3}, $Z = 8$. Space group Fdd2.

$[PbL^3(SCN)_2]$, $C_{24}H_{26}N_8S_2Pb$, $M = 689.4$, Monoclinic, $a = 8.517(9)$, $b = 29.700(13)$, $c = 10.351(9)$ Å, $\beta = 97.29(7)°$, $U = 2597.2$ Å^3, $D_m = 1.77$, $D_c = 1.76$ g cm^{-3}, $Z = 4$. Space group $P2_1/a$.

For both structures the independent reflections above background (959, 1576 respectively) were collected on a G.E. XRD 5 diffractometer and refined by full-matrix least squares (to R 0.064 and R 0.079, respectively).

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**Such '2 + 2' cyclic condensations are known to occur in high yield under certain circumstances even in cases where there is no geometrical constraint to the formation of the '1 + 1' cyclic product. See M.G.B. Drew, A. Rodgers, M. McCann and S. M. Nelson, *Chem. Commun.*, 415 (1978).

TABLE I. Yields, Analytical and Electrical Conductance Data for the Complexes.

Complex	Method of Preparation	Yield (%)	Analysis (%)						Λ^b (S cm^{-1} mol^{-1})
			Found			Calc.			
			C	H	N	C	H	N	
$CaL^3(ClO_4)_2$	T	55	43.0	4.2	13.6	43.1	4.3	13.7	325
$CaL^3(NCS)_2$	M	60	54.1	4.9	20.7	54.3	4.9	21.1	c
$CaL^3(BPh_4)_2\cdot 2H_2O$	M	80	76.7	6.7	7.4	77.2	6.5	7.7	260
$SrL^3(ClO_4)_2$	T	70	39.7	3.5	12.7	40.0	3.4	12.7	354
$SrL^3Cl_2\cdot 2H_2O$	M	50	46.5	4.8	14.4	46.4	5.3	14.9	307
$SrL^3(NCS)_2\cdot H_2O$	M	50	48.5	4.6	18.6	48.3	4.7	18.8	c
$SrL^3(BPh_4)_2\cdot 2H_2O$	M	75	74.3	6.4	7.2	74.0	6.2	7.4	262
$BaL^3(ClO_4)_2$	T	78	37.3	3.6	11.7	37.2	3.7	11.8	314
$BaL^3I_2\cdot 2H_2O$	M	90	33.6	3.7	10.6	33.7	3.6	10.7	c
$BaL^3(NCS)\cdot H_2O$	M	55	44.4	4.3	17.8	44.6	4.4	17.4	c
$BaL^3(BPh)_4\cdot 2H_2O$	M	60	70.8	6.2	7.6	70.9	6.0	7.1	251
$PbL^3(ClO_4)_2\cdot H_2O$	T, E	55	33.1	3.6	10.0	33.1	3.6	10.5	310
$PbL^3(NCS)_2$	T	42	41.4	3.7	15.9	41.3	3.8	16.1	c
$PbL^3(BPh_4)_2$	M	70	68.6	5.7	6.3	68.9	5.4	6.9	264

[a] T = template synthesis, M = metathesis from perchlorate complex, E = metal exchange from $BaL^3(ClO_4)$. [b] $10^{-3}M$ in acetonitrile. [c] Insoluble.

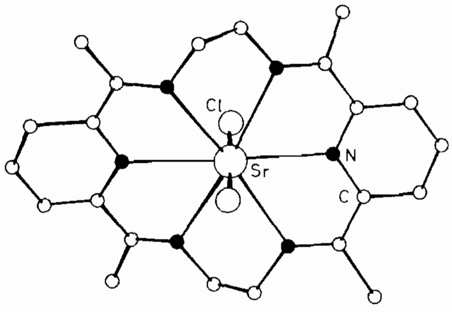


Figure 1. Structure of $[SrL^3Cl_2]$.

In both structures the metal atoms are eight-coordinate, the six nitrogens of the macrocycle defining the equatorial girdle and the monodentate anions occupying the axial positions. The structure of $[SrL^3Cl_2]$ is shown in the Figure. There is a crystallographically imposed C_2 axis running through the $SrCl_2$ moiety. Bond lengths are Sr–N 2.719(11), 2.744(10), 2.711(11) Å and Sr–Cl 2.915(8), 2.927(8) Å. In $[PbL^3(SCN)_2]$ the Pb–N(macrocycle bond distances range from 2.68(3) to 2.78(3) Å. One thiocyanate ion is N-bonded [2.42(4) Å] and the other S-bonded [3.22(3) Å]. The conformation of the macrocyle is similar in the two structures. While there are significant distortions of the ring from planarity (maximum deviation of a contributing atom from the SrN_6 and PbN_6 planes 0.39, 0.35 Å, respectively) the coordination geometry is best considered as hexagonal bipyramidal.

I.r., ^{1}H N.m.r. and Mass Spectra

Apart from variations due to the presence of different anions, and water in some cases, the i.r. spectra of the complexes are all very similar. In particular, they show the features at 1630–1650 cm^{-1} and 1400–1600 cm^{-1} characteristic of coordinated imino and pyridyl groups, respectively. None of the spectra exhibited any absorption at 3200–3400 cm^{-1} or at *ca.* 1700 cm^{-1} attributable to unreacted N–H or C=O groups. Parent ion peaks were not observed in the mass spectra (dithiocyanates) which gave instead a strong peak at m/e 374 corresponding to the uncoordinated macrocyle; no peaks of significant intensity were observed at higher m/e values. ^{1}H n.m.r. spectra of the dithiocyanates in DMSO-d_6 gave very similar patterns fully consistent with macrocycle formation. In each case three distinct regions of absorption were observed – at 8.2–8.4(m), 3.8–4.0(s) and 2.4–2.6(s) ppm. The integrated relative intensities were in excellent agreement with the required ratio of 3:4:6 consistent with assignment of the signals to protons of the pyridine ring, the methylene groups, and the methyl groups, respectively. These observations constitute strong evidence for the presence of the macrocycle L^3 in all the complexes and for its function as a hexadentate ligand. It remains to consider whether the anions, and/or water where present, are also coordinated. The X-ray analyses have shown that in $[SrL^3Cl_2]\cdot 2H_2O$ both Cl^- ions are axially coordinated and that a water molecule is hydrogen bonded to a Cl^- ion; in $[PbL^3$-

$(SCN)_2]$ a similar structure with axial SCN^- ions is found. By analogy, and on the basis of i.r. spectra, it seems probable that several of the remaining complexes have similar octa-coordinate structures. Thus, the dithiocyanate complexes of the alkaline earth metals show a single SCN^- asymmetric stretch at 2040–2060 cm^{-1} consistent with a *trans*-N-bonded structure [two ν_{asym} vibrations (2030, 2080 cm^{-1}) are seen in the spectra of $[PbL^3(SCN)(NCS)]$ consistent with the two bonding modes of the SCN^- ion in this complex revealed by the X-ray structure determination]. The anhydrous perchlorates show distinct splitting of the ν_3 and ν_4 ClO_4^- modes and it is concluded that in these cases both ClO_4^- ions are monodentately coordinated. The tetraphenylborate dihydrates exhibit a librational mode at 500–600 cm^{-1} suggesting that the water is bound in some way, probably to the metal in these cases. In contrast, the metal ion in the anhydrous $[PbL^3][BPh_4]_2$ is presumed to be hexa-coordinate. In acetonitrile solution all the soluble complexes are 2:1 electrolytes indicating ready replacement of coordinated anions by solvent.

Discussion

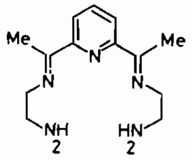
The formation of the 18-membered macrocycle L^3 in the presence of alkaline earth metal ions, but not apparently in the presence of various transition and post-transition metal ions, is unusual and contrasts with results found for other (smaller) 'nitrogen' macrocycles derived from 2,6-diacetylpyridine [1, 2]. In fact, the complexes described here appear to be the first in which the 'hard' alkaline earth metal ions are bound to a macrocyclic ligand containing only 'soft' (unsaturated) nitrogen donors. The ineffectiveness of Mg^{2+} (and the first row transition metal ions) as a template ion and the increasing yields obtained with increase in the size of the heavier metal ions of this group is almost certainly a reflection of the compatibility or otherwise in the sizes of the metal ion (see Table II) and the macrocycle cavity. Our failure to isolate complexes of *e.g.* the electronically spherically symmetrical Cd^{2+} or Hg^{2+} (ionic radii, 1.07 and 1.14 Å, respectively) which are comparable in size to Ca^{2+} (ionic radius, 1.12 Å) is, at first sight, surprising. The two structure determinations reveal that the macrocycle cavity has a diameter of not less than 5.4 Å. Thus, the metal–nitrogen distance will be $\geqslant$2.7 Å irrespective of the size of the metal ion (assuming an approximately planar MN_6 unit). Reference to the known structures [5] of related 17-membered macrocyclic complexes of Cd(II), Hg(II) and Ag(I) shows that the metal–nitrogen distances are significantly shorter (Cd–N 2.33–2.46Å; Hg–N 2.25–2.45 Å; Ag–N 2.37–2.55 Å) than this value. That the macrocycle cavity is large even for Pb(II) (ionic radius, 1.31 Å), which does form a stable complex, is dramatically shown by the fact that the Pb–N (thiocyanate) distance, for which there is no constraint, is only 2.42(4) Å. Thus, the question is not so much that metal ions such as Cd(II), Hg(II) and Ag(I) do not form stable complexes with L^3 but rather that Ca^{2+} does. We suggest that the answer lies in the differing natures of the metal–ligand interactions. Thus, the binding energy is expected to fall off much more rapidly for a predominantly covalent interaction (M = *e.g.* Hg) than for a predominantly electrostatic interaction (M = *e.g.* Ca) as the M–N distance is increased beyond the preferred value. A Ca–N distance of 2.64 Å in another macrocyclic complex has recently been reported [3].

TABLE II. Ionic Radii of Octa-co-ordinated Metal Ions (A)^a.

Mg^{2+}	0.90	Mn^{2+}	0.93
Ca^{2+}	1.12	Cd^{2+}	1.07
Sr^{2+}	1.25	Hg^{2+}	1.14
Ba^{2+}	1.42	Ag^{+}	1.30
Pb^{2+}	1.31		

^{a}Data from R. D. Shannon and C. T. Prewitt, *Acta Cryst., B25,* 925 (1969).

Evidence in support of the view that the non-isolation of the transition metal and post-transition metal complexes of L^3 is due to their intrinsic thermodynamic instability (because of the size factor discussed above) rather than to some kinetic barrier to their formation in the template process is provided by the results of some metal exchange reactions. When $BaL^3(ClO_4)_2$ was treated with $Pb(ClO_4)_2\cdot 3H_2O$ the known complex $PbL^3(ClO_4)_2\cdot H_2O$ was obtained in high yield. However, analogous replacement reactions using Mn(II), Cd(II) or Ag(I) salts yielded complexes of the ring-opened ligand L^4



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The facile hydrolysis of the macrocycle after replacement of the alkaline earth cation contrasts with the high hydrolytic stability of the alkaline earth complexes themselves which can be recovered unchanged from aqueous media.

Attempts to prepare a Ba(II) complex, by the template method, of the macrocycle L^1 described by Stotz and Stoufer [4] have so far proved unsuccessful. However, analogous Ca(II), Sr(II) Ba(II) and Pb(II) complexes of the fully conjugated macrocycle L^2 have been successfully synthesized.

A fuller account of this continuing investigation will be reported in due course.

References

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4 R. W. Stotz and R. C. Stoufer, *Chem. Commun.*, 1682 (1970).

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