

## Metal-induced Ring Contraction in a Macrocyclic Ligand; X-Ray Crystal Structure of a Cobalt Complex

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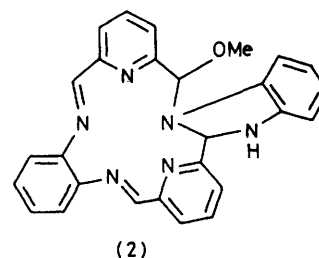
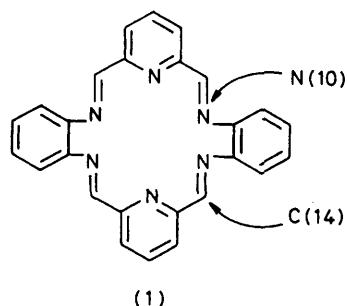
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*Summary* Replacement of alkaline earth metal ions from a conjugated hexadentate nitrogen analogue of [18]-annulene by some first row transition metal ions significantly smaller than the macrocycle cavity is accompanied by an intramolecular ring contraction yielding a 15-membered quinquedentate macrocycle of improved fit; the X-ray crystal structure of the cobalt complex has been determined.

AN important aspect of the co-ordination chemistry of multidentate ligands of limited flexibility concerns the mutual interplay of the geometrical preferences of the metal ion on the one hand with those of the ligand on the other.<sup>1</sup> Where a mis-match of these preferences occurs, for example, of metal ion stereochemistry and ligand conformation, an entatic state<sup>2</sup> leading to enhanced chemical reactivity may be generated. We report here on the chemical consequences of a mis-match in metal ion size and the cavity size of a non-flexible macrocyclic ligand.



The template synthesis, *via* the large alkaline earth metal ions, of the conjugated, hexadentate, macrocycle  $L^1$  (1) containing an 18-membered inner large ring has been described.<sup>3</sup> X-Ray analysis has shown that the complexed macrocycle has a near-planar hexagonal structure of fixed hole radius *ca.* 2.7 Å. It is not therefore expected to form stable complexes with metal ions of ionic radius much smaller than this value.

Treatment of the complex  $[Ba(L^1)_2][ClO_4]_2$  with an excess of a salt of the metal ions  $Mn^{II}$ ,  $Fe^{II}$ ,  $Co^{II}$ , or  $Zn^{II}$  (octa-co-ordinate ionic diameter 1.92, 1.84, 1.80, and 1.80 Å, respectively)<sup>4</sup> in refluxing MeOH for 1–3 days yielded a new series of crystalline complexes (Table) in 40–80% yield. I.r. spectra differ in two major respects from those of the complexes of  $L^1$ . All show a  $\nu(N-H)$  stretching vibration at 3260–3370  $cm^{-1}$  and a  $\nu(C=N)$  vibration of much reduced intensity at 1610–1630  $cm^{-1}$ . In addition to a peak at  $m/e$  414 (corresponding to  $L^1$ ) in the mass spectra, a strong peak at  $m/e$  446 (the highest mass peak observed) occurs. Moreover, the  $m/e$  32 peak is notably more intense than in the spectra of  $L^1$  complexes. These observations suggest that a molecule of MeOH has been added across one of the azomethine linkages of  $L^1$  during the metal ion replacement. The structure of a  $Co^{II}$  complex was determined by X-ray analysis. *Crystal data*:  $[CoL^2(HOMe)(OH_2)]_2[ClO_4]_2$ ,  $C_{28}H_{28}N_6Cl_2CoO_{11}$ ,  $M = 754.0$ , monoclinic,  $a = 15.548(11)$ ,  $b = 20.637(15)$ ,  $c = 11.537(10)$  Å,  $\beta = 111.5(1)^\circ$ ,  $U = 3445.2$  Å<sup>3</sup>,  $D_c = 1.45$ ,  $D_m = 1.44(2)$  g  $cm^{-3}$ ; space-group  $P2_1/a$ . 1951 reflections above background were measured on a G.E. XRD5 diffractometer and refined to  $R$  0.100.†

As shown in structure (2) ( $L^2$ ) the inner large ring of  $L^1$  has contracted from 18- to 15-member atoms as a result of covalent bond formation between N(10) and C(14) of  $L^1$  with formation of a 5-membered imidazoline ring. The ring contraction has left the  $Co^{II}$  atom in a pentagonal bipyramidal environment with the five nitrogen atoms of the

15-membered inner large ring making up the equatorial girdle (mean deviation of an atom from the  $CoN_5$  plane is 0.11 Å). The metal atom is bonded to a water molecule [ $Co-O$  2.22(2) Å] and a methanol molecule [ $Co-O$  2.19(2) Å] in the axial positions (see Figure). The  $Co-N(10)$  bond is very much longer [2.53(2) Å] than the other four [2.14(2)–2.24(2) Å] presumably because of the rigid asymmetric nature of the quinquedentate macrocycle. The angle between the plane containing the nine atoms of the fused benzimidazoline ring system and the  $CoN_5$  least-squares plane is  $64.3^\circ$  (Figure). Both perchlorate anions are disordered.

On the basis of the i.r. and mass spectra the  $Mn^{II}$ ,  $Fe^{II}$ , and  $Zn^{II}$  complexes (Table) are considered to have closely

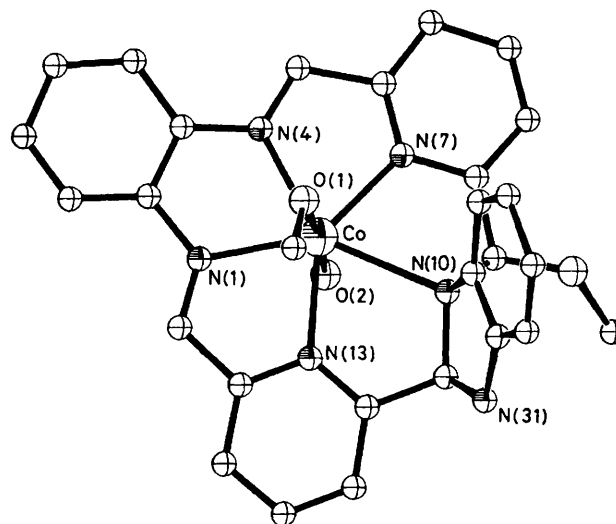


FIGURE. The structure of  $[CoL^2(OH_2)(HOMe)]^{2+}$ . Selected bond distances are:  $Co-N(1)$ , 2.16(2);  $Co-N(4)$ , 2.24(2);  $Co-N(7)$ , 2.14(2);  $Co-N(10)$ , 2.53(2);  $Co-N(13)$ , 2.18(2);  $Co-O$ (water), 2.22(2);  $Co-O$ (methanol), 2.19(2) Å.

TABLE. I.r. ( $cm^{-1}$ ) and magnetic data for the  $L^2$  complexes.

Complex	$\nu(N-H)$	$\nu(C=N)$	$\nu_{asym}[NCS]^-$	$\mu_{eff}/B.M.^a$
$[MnL^2(OH_2)(HOMe)][ClO_4]_2$	3340 <sup>b</sup>	1620(w)		5.82
$[MnL^2(NCS)_2]$	3260	1615(sh)	2060	5.81
$[FeL^2(OH_2)(HOMe)][ClO_4]_2$	3356	1622(w)		5.15
$[FeL^2(NCS)_2]$	3260	1615(sh)	2062	5.01
$[CoL^2(OH_2)(HOMe)][ClO_4]_2$	3370	1615(sh)		4.41
$[CoL^2(NCS)_2]$	3280	1620(w)	2080	4.37
$[ZnL^2(OH_2)][ClO_4]_2$	3340	1630(w)		

<sup>a</sup> At 293 K, corrected for diamagnetism of ligands. <sup>b</sup> 'Recrystallization' from  $CD_3OD$  gave  $\nu(N-D)$  at 2450  $cm^{-1}$ .

† 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.

related structures containing the same 15-membered macrocycle ( $L^2$ ). I.r. spectra suggest that the  $ClO_4^-$  ions are unco-ordinated and while some doubt must remain concerning the occupancy of the two axial positions in the diperchlorates, the dithiocyanates exhibit a single  $\nu_{asym}$  (NCS) vibration at 2060—2080  $cm^{-1}$  consistent with *trans*-N-bonded NCS<sup>-</sup> groups in a pentagonal bipyramidal structure.<sup>5</sup> All the transition metal complexes have high-spin d-electron configurations (Table).

From the results presented in this and in the preceding communication<sup>3</sup> it is clear that the  $Mn^{II}$ ,  $Fe^{II}$ ,  $Co^{II}$ , and  $Zn^{II}$  ions are too small for the  $L^1$  macrocycle cavity and that this is the reason for the rearrangement of  $L^1$  to  $L^2$ . The ring contraction can be seen as proceeding in two steps. The first is the addition of MeOH across one C=N bond as a result of the strain generated by the attempts of  $L^1$ , for example, by folding or other distortion,<sup>1</sup> to bond effectively *via* all six donors to a too-small metal ion. The gain in flexibility gained by the conversion of a double into a

single carbon-nitrogen bond (with loss in conjugation) then allows nucleophilic attack of the secondary amino group so formed at the imino carbon of the neighbouring azomethine group. This results in the expulsion of a stable imidazoline ring from the inner large ring of  $L^1$  and accompanying formation of a new smaller (quinquedentate) macrocycle well matched in hole size to the dimensions of the metal ions.

Confirmation for the conclusion that the ring contraction accompanying metal ion replacement is due to a mis-match in the size of the incoming metal ion and that of the central cavity of  $L^1$  and not to some stereochemical discrimination against a hexagonal environment<sup>6</sup> on the part of the transition metal ion is provided by the behaviour of the two  $d^{10}$  metal ions. The smaller ion  $Zn^{2+}$  (octa-co-ordinate ionic diameter 1.80 Å) effects the ring contraction while the  $Cd^{2+}$  ion (octa-co-ordinate ionic diameter 2.20 Å) does not.<sup>3</sup>

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<sup>2</sup> B. L. Vallee and R. J. P. Williams, *Proc. Nat. Acad. Sci. U.S.A.*, 1968, 59, 498.

<sup>3</sup> M. G. B. Drew, J. de O. Cabral, M. F. Cabral, F. S. Esho, and S. M. Nelson, preceding communication.

<sup>4</sup> R. D. Shannon, *Acta Cryst.*, 1976, A32, 751.

<sup>5</sup> M. G. B. Drew, A. H. bin Othman, S. G. McFall, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, 1977, 1173.

<sup>6</sup> It has been pointed out (G. E. Kimball, *J. Chem. Phys.*, 1940, 8, 188) that hydrid orbitals cannot be constructed towards the corners of the hexagonal bipyramid using only combinations of s-, p-, and d-orbitals.