Crystal Structures of Four Complexes of Quinquedentate Macrocyclic Ligands with Novel Co-ordination Geometries Containing Five-co-ordinate Silver(I), Six-co-ordinate Cadmium(II), Six-co-ordinate Mercury(II), and Seven-co-ordinate Cadmium(II)

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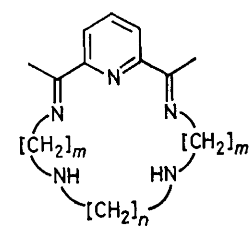
Summary Metal complexes of two 'N_5' macrocyclic ligands are five-co-ordinate (distorted pentagonal plane, M = Ag^{I}), six-co-ordinate (distorted pentagonal pyramid, M = Cd^{II} or Hg^{II}), or seven-co-ordinate (pentagonal bipyramid, M = Cd^{II}) depending upon the sizes of the metal ion and macrocycle.

PREVIOUS studies[1] have demonstrated the effectiveness of quinquedentate 'N_5' macrocyclic ligands (2,2,2-N_5) and (2,3,2-N_5) in pentagonal bipyramidal complexes of the type [M(macrocycle)X_2] (M = *e.g.* Mg^{2+}, Fe^{3+}, Fe^{2+}, or Zn^{2+}) in which the macrocycle defines the pentagonal girdle and the axial positions are occupied by unidentate ligands X. In extending the study we were interested in the structural effects of a wider variation in metal ion and macrocycle size. We now report the crystal and molecular structures of four complexes of the d^{10} ions Cd^{II}, Hg^{II}, and Ag^{I} (Pauling radii 0·97, 1·10, and 1·26 Å, respectively) with the 16- and 17-membered macrocycles (2,3,2-N_5) and (3,2,3-N_5).† The structures obtained exemplify the new co-ordination geometries (pentagonal pyramidal and pentagonal planar) in which one or both of the two axial sites are unoccupied and a new polymeric pentagonal bipyramidal structure based on bridging axial ligands.

The complexes were prepared from 2,6-diacetylpyridine and the appropriate tetramine by template methods similar to those described previously.[1] Satisfactory chemical analyses were obtained in all cases and the spectroscopic properties (u.v.-visible, i.r., mass, and ^{1}H n.m.r.) confirmed that ring closure had occurred during the syntheses. Crystal data for all four compounds were collected on a diffractometer and refined by full-matrix least-squares (Table).



N_5-Macrocycle
$m = 2, n = 2$ (2,2,2-N_5)
$m = 2, n = 3$ (2,3,2-N_5)
$m = 3, n = 2$ (3,2,3-N_5)

In (I), the polymeric cation $[Cd(2,3,2\text{-}N_5)Br]_n^{n+}$ is found in which the Cd^{2+} ion is seven-co-ordinate being bonded to five nitrogen atoms [2·36(2)—2·43(3) Å] and to two bridging Br^- ions [2·775(3) and 3·037(3) Å; ∠Cd–Br–Cd, 143·3(1)°] (Figure 1). The macrocycle is closely planar, the maximum deviation of a contributing atom from the N_5 plane being only 0·05 Å. However in contrast to complexes of smaller metal ions (Fe^{3+} or Fe^{2+}) of the same macrocycle, the metal in (I) is slightly displaced (0·13 Å) from this plane. This displacement and the two different Cd–Br distances are presumably a consequence of the Cd^{2+} ion being too large for the macrocycle hole.

The structures of the $[M(3,2,3\text{-}N_5)Br]^+$ cations [M = Cd (II) or Hg (III)] are very similar. Both are mononuclear with the metal atom bonded to five nitrogen atoms [in (II): Cd–N, 2·335(7)—2·452(7) Å; in (III): Hg–N, 2·25(5)—

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Table. Crystal data

	(I)[a]	(II)[a]	(III)	(IV)
Compound	$[Cd(2,3,2\text{-}N_5)Br]_{2n}$ $[CdBr_4]_n$	$[Cd(3,2,3\text{-}N_5)Br]$ $Br.H_2O$	$[Hg(3,2,3\text{-}N_5)Br]_2$ $[Hg_2Br_6]$	$[Ag(3,2,3\text{-}N_5)]$ $[ClO_4]$
Formula	$C_{32}H_{50}N_{10}Br_6Cd_3$	$C_{17}H_{29}N_5Br_2Cd$	$C_{34}H_{54}N_{10}Br_8Hg_4$	$C_{17}H_{27}N_5AgClO_4$
M	1391·47	591·47	2044·51	508·71
Class	Monoclinic	Orthorhombic	Triclinic	Monoclinic
a/Å	20·755(17)	11·059(5)	12·577(10)	11·643(10)
b/Å	19·889(12)	12·479(6)	10·485(9)	16·194(9)
c/Å	10·907(8)	31·114(15)	10·098(12)	24·206(11)
α/°	(90)	(90)	89·49(12)	(90)
β/°	95·90(11)	(90)	100·98(12)	117·70(9)
γ/°	(90)	(90)	106·15(14)	(90)
U/Å^3	4478·5	4293·9	1254·3	4058·2
Z	4	8	1	8
D_m	2·05(2)	1·85(2)	2·67(4)	1·65(2)
D_c	2·06	1·83	2·71	1·67
Radiation	Mo-K_α	Cu-K_α	Mo-K_α	Mo-K_α
Spacegroup	$I2/a$	$Pccn$	$P\bar{1}$	$P2_1/c$
μ/cm^{-1}	71·0	134·7	192·5	d
No. of independent reflections used in refinement	1732	2728	1320	1709
R	0·092[b]	0·052	0·064	0·099[c]

[a] The corresponding Hg^{II} compound is isomorphous. [b] Crystals were twinned with $hk0$ common. [c] In one of the molecules, the two six-membered rings are disordered. [d] Not applied.

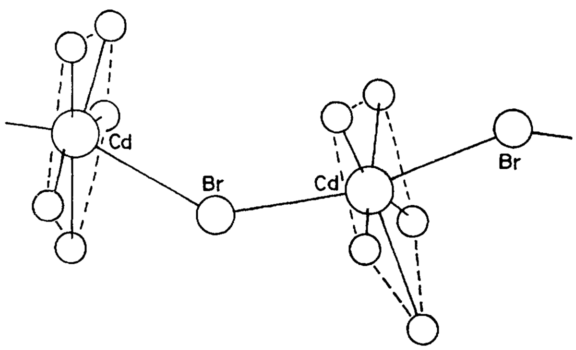


Figure 1. The structure of $[Cd(2,3,2\text{-}N_5)Br]_n^{n+}$ in (I). For clarity only the five donor nitrogen atoms of the macrocycle are shown.

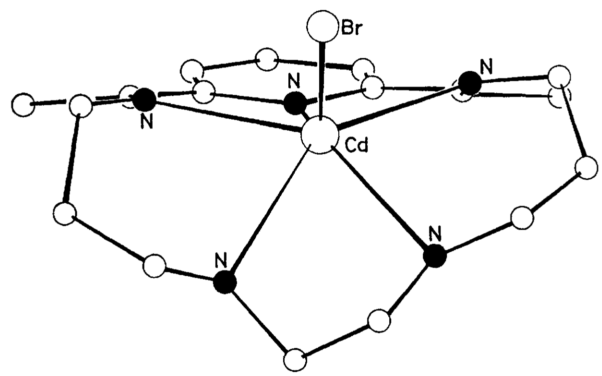


Figure 2. The structure of $[Cd(3,2,3\text{-}N_5)Br]^+$ in (II).

2·44(5) Å] and a bromine atom [Cd–Br, 2·582(1); Hg–Br, 2·565(5) Å]. The conformation of the macrocycle is such that the pyridine ring is bent down from the plane of the MN_4 unit. It is similar to that in $[Mn(3,2,3\text{-}N_5)(NCS)_2]$[2] but the angles of intersection of the planes [48·9° in (II) and 48·3° in (III)] are greater than in the Mn^{II} compound (41·8°). This folding of the macrocycle leads to one sterically crowded site which is unoccupied in (II) and (III) even by a water molecule [available in (II)] and the metal remains six-co-ordinate (Figure 2). In the Mn^{II} complex the smaller angle of fold is in keeping with the attachment of a seventh ligand $(NCS)^-$, though at a longer bonding distance than for the $(NCS)^-$ on the open face.

In (IV) there are two $[Ag(3,2,3\text{-}N_5)]^+$ cations in the asymmetric unit with similar geometries [Ag–N, 2·39(2)—2·51(3) and 2·37(3)—2·55(2) Å]; the ligands form distorted pentagonal planes with maximum deviations of a contributing atom from the AgN_5 plane of 0·94 and 0·95 Å, respectively (mean deviations 0·47 and 0·51 Å). It is interesting that the macrocycle conformation differs from that found in (II) and (III) where the pyridine nitrogen is displaced by 1·31 and 1·38 Å respectively from the plane of the other four nitrogens. This is not the case in (IV). Indeed the macrocycle in (IV) approximates to a C_2 distortion with the pyridine nitrogen closest to the AgN_5 plane. The absence of axial ligation in (IV) is unexpected particularly as there is no obvious steric barrier. No doubt this is due in part to the poor co-ordinating power of ClO_4^- (or H_2O) towards Ag^I. However attempts to form adducts with neutral nitrogen donor molecules were unsuccessful. On the other hand treatment with halide ion led to the decomposition of the macrocycle and precipitation of silver halide.

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[1] M. G. B. Drew, A. H. bin Othman, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, 1975, 2507; 1976, 1394; *Acta Cryst.*, 1976, **B32**, 1029; M. G. B. Drew and S. M. Nelson, *ibid.*, 1975, **A31**, S140; M. G. B. Drew, A. H. bin Othman, S. G. McFall, and S. M. Nelson, *J.C.S. Chem. Comm.*, 1975, 818. For other seven-co-ordinate structures including quinquedentate macrocyclic ligands see N. W. Alcock, D. C. Liles, M. McPartlin, and P. A. Tasker, *J.C.S. Chem. Comm.*, 1974, 727; V. W. Day, T. J. Marks, and W. A. Wachter, *J. Amer. Chem. Soc.*, 1975, **97**, 4519.

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