Pentagonal-pyramidal Cadmium(II) and Mercury(II) Complexes of the Quinquedentate Macrocyclic Ligand 2,15-Dimethyl-3,7,10,14,20-pentaazabicyclo[14.3.1]eicosa-1(20),2,14,16,18-pentaene

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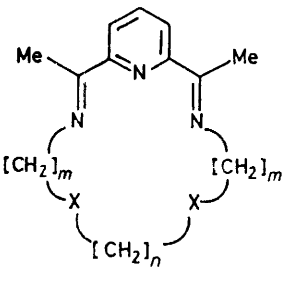
Reaction of 2,6-diacetylpyridine and 4,7-diazadecane-1,10-diamine in methanol in the presence of a stoicheiometric amount of cadmium(II) or mercury(II) halide gives metal complexes of the 17-membered title ligand (L^3) in good yield. Derivatives containing $[NCS]^-$ and/or $[ClO_4]^-$ anions have been prepared by metathetical reactions. The crystal and molecular structures of two of the complexes have been determined: $[CdL^3(Br)]Br\cdot0.5H_2O$ is orthorhombic, space group *Pccn*, with a = 11.059(5), b = 12.479(6), c = 31.114(15) Å, and Z = 8; $[HgL^3(Br)]_2[Hg_2Br_6]$ is triclinic, space group $P\bar{1}$ with a = 12.577(10), b = 10.485(9), c = 10.098(12) Å, α = 89.49(12), β = 100.98(12), γ = 106.15(14)°, and Z = 1. Diffractometer data for both crystals have been refined by full-matrix least squares (2 728 reflections to R 0.052, and 1 320 reflections to R 0.064, respectively). Both cations are six-co-ordinate with geometries best described as pentagonal pyramidal with the metal atom bonded to five nitrogen atoms of the macrocycle [Cd–N 2.428(7), 2.425(7), 2.335(7), 2.452(7), and 2.370(7); Hg–N 2.44(3), 2.25(5) 2.40(4), 2.44(5), and 2.40(3) Å] and to a bromine atom in an axial position [Cd–Br 2.582(1), Hg–Br 2.565(5) Å]. The remaining members of the two series of complexes are assigned similar six-co-ordinate structures on the basis of i.r. and electronic spectra together with electrical-conductance measurements in solution, with the exception of $[CdL^3(NCS)_2]$ which is seven-co-ordinate in the solid state. The structures are discussed in relation to those of metal complexes of related macrocyclic ligands.

PREVIOUS studies[1] have demonstrated the effectiveness of quinquedentate 'N_5' and 'N_3O_2' macrocyclic Schiff base ligands (L^1—L^4) in imposing unusual co-ordination geometries on a range of metal ions. For complexes of the 15- and 16-membered rings (L^1,L^2, and L^4) with Mg^{II}, Mn^{II}, Fe^{III}, Fe^{II}, and Zn^{II}, we have shown that the metal ion has a fairly undistorted pentagonal-bipyramidal geometry in which the macrocycle defines the pentagonal girdle and with the axial positions occupied by unidentate ligands. In all cases † examined by single-crystal *X*-ray methods the MN_5 or MN_3O_2 atom sets are coplanar to within 0.1 (L^1 and L^4) or 0.25 Å (L^2). Increase in ring size to 17 member atoms as in L^3 leads to deviations from this regular symmetry. Thus in $[MnL^3(NCS)_2]$ only four of the ring donor atoms are coplanar with the metal atom, the pyridine nitrogen atom being displaced from this plane by 0.92 Å.[2] This results in one face of the macrocycle being more sterically crowded than the other, and in certain derivatives, *e.g.* $[MnL^3(NCS)][ClO_4]$, one axial position appears to be unoccupied. It seemed possible that the folding of L^3 in its manganese(II) complexes is due to its being too large for the Mn^{2+} ion (Pauling radius 0.80 Å) when in the planar conformation. Consistent with this view is our failure to prepare (by the template method) complexes of L^3 with metal ions smaller than Mn^{2+}. In the complex $[AgL^3][ClO_4]$ containing the large Ag^+ ion (Pauling radius 1.26 Å) the macrocycle adopts a new conformation with approximate C_2 symmetry in which the pyridine nitrogen lies closest to the AgN_5 plane.



L	m	n	X
L^1	2	2	NH
L^2	2	3	NH
L^3	3	2	NH
L^4	2	2	O

It was of interest, therefore, to determine the co-ordination geometry and macrocycle conformation in complexes of L^3 with other metal ions of different size. We have had success in the synthesis of a series of complexes of L^3 with Cd^{II} and Hg^{II} (Pauling radii 0.97 and 1.10 Å respectively) and in this paper we describe some of their properties together with the crystal and molecular structure of one complex of each metal. A preliminary report of part of this work has appeared.[3]

RESULTS AND DISCUSSION

The complexes (Table 1) were prepared in methanol by the Schiff-base condensation of 2,6-diacetylpyridine with 4,7-diazadecane-1,10-diamine in the presence of the metal halide, and by metathetical reactions from initially formed products (see Experimental section). Reactions carried out in the absence of metal salt yielded only oils or gums having properties indicative of non-macrocyclic oligomeric products. The complexes reported here are all crystalline with low to moderate solubility in polar organic solvents and, in the case of many of the cadmium(II) complexes, in water also. No evidence for hydrolysis of the imine linkages was observed. Information on the structures of the complexes was inferred from the stoicheiometry and electrical-conductance data (Table 1), i.r. and electronic spectra (Table 2), and, for two of the complexes, $[CdL^3(Br)]Br\cdot0.5H_2O$ (1) and $[HgL^3(Br)]_2[Hg_2Br_6]$ (2), from

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† An exception is the dimeric complex ion $[(AgL^2)_2]^{2+}$ in which the two adjacent co-ordination spheres distort each other (S. M. Nelson, S. G. McFall, M. G. B. Drew, and A. H. bin Othman, *J.C.S. Chem. Comm.*, 1977, 370).

TABLE 1

Analytical and electrical-conductance data for the complexes

Complex	Analysis (%) Found C	H	N	Halogen	Calc. C	H	N	Halogen	Λ [a]/S cm² mol⁻¹ H_2O	MeCN
$[CdL^3(Cl)]Cl\cdot H_2O$	40.9	5.9	14.0	14.3	40.6	5.8	13.9	14.1	234	*b*
$[CdL^3(Br)]Br\cdot 0.5H_2O$	34.4	5.0	11.7	27.2	35.0	4.9	12.0	27.4	251	132
$[CdL^3(Cl)]_2[Cd_2Cl_6]$	30.3	4.0	10.8	21.5	30.6	4.1	10.5	21.2	467 [c]	*b*
$[CdL^3(Br)]_2[CdBr_4]$	29.1	3.9	9.6	33.7	28.8	3.8	9.9	33.8	352 [c]	212
$[CdL^3(Br)][ClO_4]$	34.3	4.5	11.6		34.4	4.6	11.8		273	153
$[CdL^3(NCS)_2]$	42.9	5.2	18.4		43.1	5.1	18.5		213	137
$[CdL^3(NCS)][ClO_4]$	37.8	4.7	14.5		37.8	4.8	14.7		232	161
$[HgL^3(Br)]Br$	30.8	4.3	10.5	30.2 [d]	30.8	4.1	10.6	30.3 [d]	*b*	131
$[HgL^3(Br)]_2[Hg_2Br_6]$	20.1	2.6	6.8	39.1 [d]	20.0	2.7	6.8	39.2 [d]	*b*	*b*
$[HgL^3(Br][ClO_4]$	29.9	4.0	10.3	29.3 [d]	30.0	4.0	10.3	29.4 [d]	*b*	161
$[HgL^3(I)]_2[Hg_2I_6]$	16.9	2.2	5.6	33.4 [d]	16.9	2.2	5.8	33.2 [d]	*b*	*b*

[a] For 10^{-3} mol dm^{-3} solutions at 25 °C, excepted where otherwise indicated. [b] Insufficiently soluble. [c] For 5×10^{-4} mol dm^{-3} solutions at 25 °C. [d] Mercury analysis.

TABLE 2

Infrared (cm⁻¹) and electronic spectral data for the complexes

Complex	ν(N–H)	ν(C=N)	$[NCS]^-$	$[ClO_4]^-$	Electronic spectra (10³ cm⁻¹) [a] Solid	H_2O	MeCN
$[CdL^3(Cl)]Cl\cdot H_2O$	3 215 2 175	1 644 1 628			33.5 28.5 (sh)	41.8 (14 100) 33.7 (4 800)	*b*
$[CdL^3(Br)]Br\cdot 0.5H_2O$	3 235 3 190	1 642			33.6 28.7 (sh)	41.8 (15 500) 33.6 (5 200)	41.8 (17 900) 33.4 (5 400)
$[CdL^3(Cl)]_2[Cd_2Cl_6]$	3 258 3 225 3 195	1 648 1 642			33.4 29.2 (sh)	41.8 (32 000) 33.6 (11 200)	28.6 (sh)
$[CdL^3(Br)]_2[CdBr_4]$	3 255 3 215	1 645			33.5 28.5 (sh)	41.8 (33 000) 33.7 (11 500)	41.8 (sh) 33.4 (10 700) 28.6 (sh)
$[CdL^3(Br)][ClO_4]$	3 270 3 225	1 643		1 085 [c] 618 [d]	33.5 28.8 (sh)	41.8 (12 100) 33.7 (4 700)	41.8 (18 100) 33.4 (5 600) 28.6 (sh)
$[CdL^3(NCS)_2]$	3 290 3 275	1 653 1 633	2 052 [e] 2 038 [e] 835 [f] 488 [g]		33.6 27.6 20.2 (sh)	41.8 (sh) 33.7 (5 200)	42.4 (21 200) 33.5 (5 600) 28.6 (sh)
$[CdL^3(NCS)][ClO_4]$	3 295 3 260	1 655 1 643	2 058 [e] 485 [g]	1 085 [c] 617 [d]	33.4 28.4 (sh)	41.8 (15 500) 33.6 (5 100)	42.0 (18 700) 33.6 (5 900) 28.6 (sh)
$[HgL^3(Br)]Br$	3 240 3 190	1 648			33.7 26.9br	*b*	41.5 (19 000) 33.9 (sh) 32.6 (sh) 28.7 (sh)
$[HgL^3(Br)]_2[Hg_2Br_6]$	3 295 3 265	1 652			33.8 26.8br	*b*	*b*
$[HgL^3(Br)][ClO_4]$	3 310 3 275	1 650		1 085 [c] 620 [d]	33.7 27.0br	*b*	41.7 (20 100) 33.7 (5 400) 32.6 (sh) 28.7 (sh)
$[HgL^3(I)]_2[Hg_2I_6]$	3 300	1 650			33.7	*b*	39.6 (34 200) 33.3 (18 700) 32.5 (sh) 28.7 (sh)

[a] ε/dm³ mol⁻¹ cm⁻¹ given in parentheses for solutions. [b] Insoluble. [c] ν_3 vibration. [d] ν_4 vibration. [e] ν_{asym}(NCS). [f] ν_{sym}(NCS). [g] δ(NCS).

single-crystal *X*-ray studies. Since the structures of the two complexes are central to the discussion of the structures of the remaining complexes they will be considered first.

Crystal and Molecular Structures of (1) *and* (2).—*Crystal data.* (1) $[CdL^3(Br)]Br\cdot 0.5H_2O$, $C_{17}H_{28}Br_2CdN_5O$, $M = 591.5$, Orthorhombic, $a = 11.059(5)$, $b = 12.479(6)$, $c = 31.114(15)$ Å, $U = 4\,293.9$ Å³, $D_m = 1.85(3)$, $Z = 8$, $D_c = 1.83$ g cm⁻³, Cu-K_α radiation, $\lambda = 1.541\,8$ Å, $\mu = 134.7$ cm⁻¹, space group *Pccn* from systematic absences *hk*0 for $h + k = 2n + 1$, 0*kl* for $k + l = 2n + 1$, and *h*0*l* for $l = 2n + 1$.

(2) $[HgL^3(Br)]_2[Hg_2Br_6]$, $C_{34}H_{54}Br_8Hg_4N_{10}$, $M = 2\,044.5$, Triclinic, $a = 12.577(10)$, $b = 10.485(9)$, $c = 10.098(12)$ Å, $\alpha = 89.49(12)$, $\beta = 100.98(12)$, $\gamma = 106.15(14)$,° $U = 1\,254.3$ Å³, $D_m = 2.67(3)$, $Z = 1$, $D_c = 2.71$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, $\mu = 192.5$ cm⁻¹, space group $P\bar{1}$ from the successful structure determination.

For (1), 4 215 reflections with $2\theta < 140°$ were measured on an Enraf-Nonius CAD-4 diffractometer using the ω—2θ scan technique. During data collection the intensities of standard reflections decreased by 20%. A linear correction factor was employed. For (2), 2 318 reflections with $2\theta < 40°$ were measured on a G.E. XRD 5 diffractometer using the stationary-crystal–stationary-counter technique. No crystal decay was observed. For (1) 2 728 reflections with $I > 3\sigma(I)$ and for (2) 1 320 reflections with $I > 2\sigma(I)$ were used in subsequent calculations. For both crystals an absorption correction was applied using ABSORB[4] but no extinction correction was deemed necessary.

Structure determination. The positions of the heavy atoms in (1) were obtained by direct methods using the SHEL-X system, those in (2) from the Patterson map. Subsequent calculations on both structures were carried out using the '*X*-RAY '72' system on the C.D.C. 7600 computer at the University of London Computer Centre. Remaining atoms in both (1) and (2) were located from Fourier maps and refined by full-matrix least squares. In (1) hydrogen atoms were refined successfully except for four whose parameters were fixed. A water molecule was located and given an occupancy factor of 0.5. For (2) the data were not sufficiently precise and the percentage of heavy atoms present was too high to merit location of hydrogen atoms. In the refinements, data for (1) were given unit weights. For (2), $w^{\frac{1}{2}} = 1$ for $F_0 < 100$ and $100/F_0$ for $F_0 > 100$. In both cases values of $w\Delta^2$ for groups of reflections were independent of the values of F_o and $(\sin\theta)/\lambda$. Atomic scattering factors and corrections for anomalous dispersion were taken from ref. 5. For both structures a final difference-Fourier map showed no significant peaks and the shifts in the final cycle of refinement were less than 0.1σ. Final *R* values were 0.051 and 0.064 respectively. The zero-weighted reflections gave no serious discrepancies. Final positional parameters for (1) and (2) are given in Tables 3 and 4, and important molecular dimensions are in Table 5. Supplementary Publication No. SUP 22386 (27 pp.) * contains thermal parameters for both (1) and (2), hydrogen-atom parameters for (1), observed and

TABLE 3

Positional parameters ($\times 10^4$) for (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cd	0 150(0)	0 561(0)	1 487(2)
Br(1)	0 202(1)	1 773(1)	2 159(0)
N(3)	−1 032(6)	−1 042(6)	1 627(2)
C(4)	−1 932(9)	−0 828(9)	1 973(4)
C(5)	−3 027(9)	−0 229(9)	1 792(4)
C(6)	−2 816(9)	0 920(9)	1 667(4)
N(7)	−1 933(6)	0 997(6)	1 317(3)
C(8)	−2 248(7)	1 006(7)	0 923(3)
C(9)	−1 242(7)	1 076(7)	0 606(3)
N(10)	−0 134(5)	0 945(5)	0 759(2)
C(11)	0 817(7)	1 080(6)	0 503(3)
C(12)	2 035(7)	1 047(7)	0 718(3)
N(13)	2 033(6)	1 080(7)	1 127(2)
C(14)	3 147(9)	1 127(11)	1 382(4)
C(15)	3 486(10)	0 184(12)	1 591(5)
C(16)	2 667(8)	−0 342(9)	1 913(3)
N(17)	1 567(6)	−0 761(6)	1 701(2)
C(18)	0 887(9)	−1 477(8)	1 988(3)
C(19)	−0 187(9)	−1 909(7)	1 741(3)
C(20)	−3 543(9)	0 971(11)	0 759(4)
C(21)	−1 427(10)	1 302(9)	0 172(4)
C(22)	−0 448(10)	1 420(8)	−0 095(3)
C(23)	0 693(10)	1 315(8)	0 075(3)
C(24)	3 146(8)	0 986(11)	0 441(3)
Br(2)	2 500 *	7 500 *	0 895(1)
Br(3)	7 500 *	7 500 *	0 807(1)
O	4 881(17)	−1 204(18)	0 531(6)

* Parameter fixed.

TABLE 4

Positional parameters ($\times 10^4$) for (2) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Hg(1)	2 666(1)	4 035(2)	2 100(2)
Br(1)	3 060(5)	5 993(5)	0 551(5)
N(3)	1 423(31)	2 086(36)	0 745(35)
C(4)	1 538(32)	2 013(37)	−0 698(36)
C(5)	2 681(40)	1 618(47)	−0 710(44)
C(6)	3 650(33)	2 647(39)	−0 124(36)
N(7)	3 743(32)	2 874(37)	1 432(36)
C(8)	4 115(32)	2 055(36)	2 094(35)
C(9)	4 270(52)	2 265(61)	3 692(58)
N(10)	3 701(33)	3 142(39)	3 950(38)
C(11)	3 838(32)	3 581(36)	5 088(37)
C(12)	3 260(31)	4 628(36)	5 221(34)
N(13)	2 810(39)	5 134(45)	4 279(45)
C(14)	2 464(39)	6 342(46)	4 425(42)
C(15)	1 255(46)	5 679(52)	4 033(51)
C(16)	0 480(51)	5 007(59)	2 509(57)
N(17)	0 720(26)	3 730(30)	2 174(29)
C(18)	−0 015(44)	3 216(52)	0 930(48)
C(19)	0 064(40)	1 940(47)	0 780(44)
C(20)	4 653(65)	1 002(73)	1 716(72)
C(21)	5 116(42)	1 854(48)	4 589(47)
C(22)	4 970(46)	2 219(53)	5 951(51)
C(23)	4 503(44)	3 120(50)	6 307(47)
C(24)	3 271(42)	5 155(48)	6 797(46)
Hg(2)	1 396(2)	−0 429(2)	4 981(2)
Br(2)	1 950(5)	−0 615(6)	2 744(5)
Br(3)	2 152(4)	−1 411(6)	7 083(5)
Br(4)	−0 942(4)	−1 841(4)	4 616(4)

TABLE 5

Molecular dimensions in (1; M = Cd) and (2; M = Hg) *

(*a*) Bonds (Å)	(1)	(2)
M−Br(1)	2.582(1)	2.565(5)
M−N(3)	2.428(7)	2.44(3)
M−N(7)	2.425(7)	2.25(5)
M−N(10)	2.335(7)	2.40(4)
M−N(13)	2.452(7)	2.44(5)
M−N(17)	2.370(7)	2.40(3)
(*b*) Angles (°)		
Br(1)−M−N(3)	110.4(2)	108(1)
Br(1)−M−N(7)	93.8(2)	99(1)
Br(1)−M−N(10)	131.9(2)	138(1)
Br(1)−M−N(13)	101.3(2)	103(1)
Br(1)−M−N(17)	99.5(2)	102(1)
N(3)−M−N(7)	73.3(2)	72(1)
N(3)−M−N(10)	105.7(2)	105(1)
N(3)−M−N(13)	139.2(3)	137(1)
N(3)−M−N(17)	74.5(2)	67(1)
N(7)−M−N(10)	67.4(3)	67(1)
N(7)−M−N(13)	130.4(3)	131(1)
N(7)−M−N(17)	147.7(2)	138(1)
N(10)−M−N(13)	67.5(2)	67(2)
N(10)−M−N(17)	120.3(2)	115(1)
N(13)−M−N(17)	75.6(2)	78(1)

* Remaining dimensions in the cations together with dimensions for the $[Hg_2Br_6]^{2-}$ anion in (2) are given in the SUP 22386.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

calculated structure factors for (1) and (2), molecular dimensions pertaining to light atoms [(1) and (2)] and the anion [(2)], and intermolecular distances >3.6 Å [(1) and (2)].

Discussion of the structure. Both structures contain the cation $[ML^3(Br)]^+$. Figure 1 shows the atom numbering scheme for $[CdL^3(Br)]^+$. In (1; M = Cd) [(1) and (2)] the anion is Br^- (there are two independent bromide ions on two-fold axes) and there is also a water molecule (with an occupancy of 0.5) in the asymmetric unit. In (2; M = Hg) there is one centrosymmetric $[Hg_2Br_6]^{2-}$ anion in the unit cell together with two equivalent cations. Both cations therefore have no imposed symmetry. Their geometries are very similar. The metal atom is six-co-ordinate being bonded to five nitrogen atoms of the macrocycle L^3 and a halogen atom. The conformation of the ligand in this six-co-ordinate cation is quite different from those found in seven-co-ordinate $[MnL^3(NCS)_2]$ (3) [2] and five-co-ordinate $[AgL^3]^+$ (4).[3]

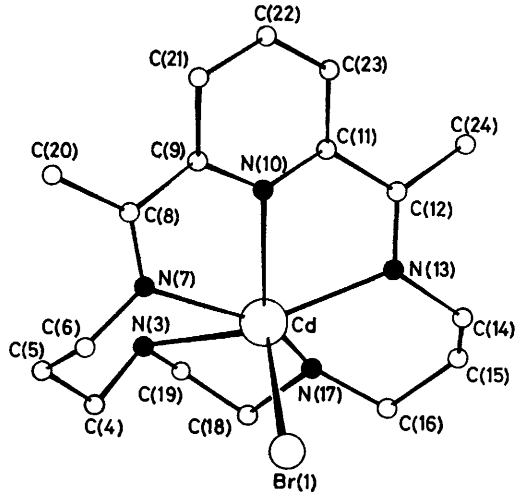

FIGURE 1 Atomic numbering scheme for the cation $[CdL^3(Br)]^+$

In (1) and (2) the two six-membered rings are symmetric chairs with the three carbon atoms on average 1.1—1.3 Å above the plane of the other three atoms in the MN_2 plane (Table 6). Both sets of three carbon atoms are on the bromine side of the MN_2 plane. By contrast, in (3) one six-membered ring has a flattened chair conformation (carbon atoms 0.70, 0.33, and 0.77 Å from the MN_2 plane) and the other has a skew-boat conformation. It was shown [3] that these conformations are due to the crowding found in the seven-co-ordinate complex. However, in (1) and (2) the ligand has more freedom of movement because of the large metal ion and the lower co-ordination number and both six-membered rings can adopt their most favourable conformation, the chair. The five-membered ring in (1) [and (2)] is more asymmetric than in the manganese structure with C(18) and C(19) 0.70 and −0.07 Å from the plane.

Despite the different conformations of the macrocycles, the geometry of the co-ordination spheres of (1) and (2) is not very different from that in (3). In that seven-co-ordinate complex the MnN_4 moiety is planar to within experimental error with the pyridine nitrogen atom 0.92 Å from the plane. In (1) and (2) the metal atom is well out of the N_4 plane [0.43 (1) and 0.50 Å (2)] on the side of the bromine atom. The angles between the MN_4 planes and the pyridine ring-atom planes are 49.7 (1) and 48.8° (2) compared to 41.8° in (3) (Table 6). In (1) and (2) the metal atom is far closer to the pyridine-ring plane (0.14 and 0.00 Å) than in (3) (0.77 Å).

TABLE 6

Least-squares planes for (1) and (2). Distances (Å) of relevant atoms from the planes are given in square brackets; atoms not contributing to the planes are marked with an asterisk [a]

Plane (A):
(1) [N(3) −0.24, N(7) 0.16, N(13) −0.15, N(17) 0.23, N(10) * −1.30, Cd * 0.43]
(2) [N(3) −0.15, N(7) 0.10, N(13) −0.09, N(17) 0.14, N(10) * −1.37, Hg * 0.50]

Plane (B):
(1) [Cd, N(3), N(7) 0.00, C(4) * 1.24, C(5) * 1.11, C(6) * 1.14]
(2) [Hg, N(3), N(7) 0.00, C(4) * 1.20, C(5) * 1.07, C(6) * 1.20]

Plane (C):
(1) [Cd, N(13), N(17) 0.00, C(14) * 0.97, C(15) * 0.92, C(16) * 1.12]
(2) [Hg, N(13), N(17) 0.00, C(14) * 1.11, C(15) * 0.87, C(16) * 1.07]

Plane (D):
(1) [Cd, N(3), N(17) 0.00, C(18) * 0.68, C(19) * −0.07]
(2) [Hg, N(3), N(17) 0.00, C(18) * 0.76, C(19) * 0.06]

Plane (E):
(1) [C(8) 0.05, C(9) −0.02, N(10) −0.08, C(11) −0.04, C(21) 0.01, C(22) 0.02, C(23) 0.00, C(12) 0.06]
(2) [C(8) 0.03, C(12) 0.10, C(9) −0.09, N(10) −0.11, C(11) −0.01, C(21) 0.15, C(22) −0.07, C(23) −0.01]

Angles (°) between planes (A) and (E): 49.7(1), 48.8(2)

[a] Equations of planes are given in SUP 22386.

All this suggests that the L^3 macrocycle is well suited to the six-co-ordinate structure; indeed, more so than to the seven-co-ordinate structure found in (3). Thus, it is not surprising that the axial vacancy in the pentagonal pyramid is not occupied by the water molecule available in (1).

Bond lengths in the two cations are unremarkable. It is interesting to note that in (1) as in (3) the M–N(py) bonds are the shortest of all the M–N bonds. A detailed comparison of the M–N bonds in (1) and (2) is not worthwhile because of the high standard deviations of the values for the latter structure.

There are very few structure determinations of molecules containing a Cd–Br bond, but one example is $[CdLBr_2]$ (L=*NNN'N'*-tetramethylethylenediamine) [6] in which Cd–Br is 2.752 Å. The distance in (1) is much shorter [2.582(1) Å] possibly because of the lack of steric crowding in the axial position, all Br–Cd–N angles being $>90°$. There are far more examples of Hg–Br bonds, *e.g.*, in $[Hg_2Br_4(bipy)]$ (bipy = 2,2'-bipyridyl) $Hg–Br_t$ (t = terminal) is 2.506 Å, $Hg–Br_b$ (b = bridging)

2.605 and 3.142 Å, and Hg–N 2.37 and 2.40 Å.[7] In $[HgBr_2(dioxan)_2]$,[8] Hg–Br is 2.433 Å and is 2.475 Å in the monotetrahydrofuran adduct of $HgBr_2$.[9] In (2) the Hg–Br_t distances in the anion are 2.491(6) and 2.511(6) Å. Thus, the present Hg–Br(1) bond length is as expected considering the increased co-ordination number of the metal. Another example of the $[Hg_2Br_6]^{2-}$ anion[10] has dimensions Hg–Br_t 2.513(5) and 2.522(4), and Hg–Br_b 2.731(4) and 2.717(4) Å. The present anion is different since the bridge is far from symmetrical having a short [2.649(6) Å] and a long bond [2.856(5) Å]. But both anions have essentially the same geometry, two distorted tetrahedra sharing an edge.

Intermolecular contacts in (2) are all greater than the sum of van der Waals radii. In (1) both bromine atoms and the water molecule may be participating in hydrogen bonding. Thus Br(3) · · · $N(3^{I})$ and Br(2) · · · $N(17^{III})$ distances are 3.53 and 3.47 Å with Br · · · H–N angles of 150 and 128°. Also, Br(2) and Br(3) are 3.29 and 3.42 Å respectively from $O(1^{III})$ and subtend an angle of 111° at that water molecule. However, this can hardly be a strong hydrogen-bonding scheme since the hydrogen atoms on O(1) were not located and indeed the occupancy of the site is only 0.5. Since the geometry of the cations in (1) and (2) is similar, it would appear that such a hydrogen-bonding scheme does not affect the conformation of the macrocycle. Packing diagrams for (1) and (2) are given in Figures 2 and 3.

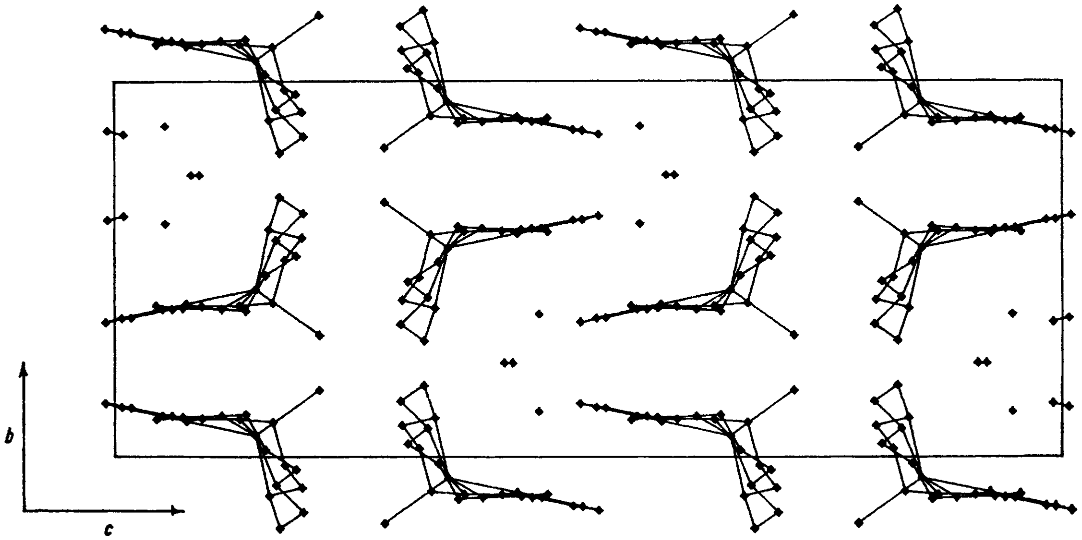

FIGURE 2 The unit cell of (1) in the *a* projection

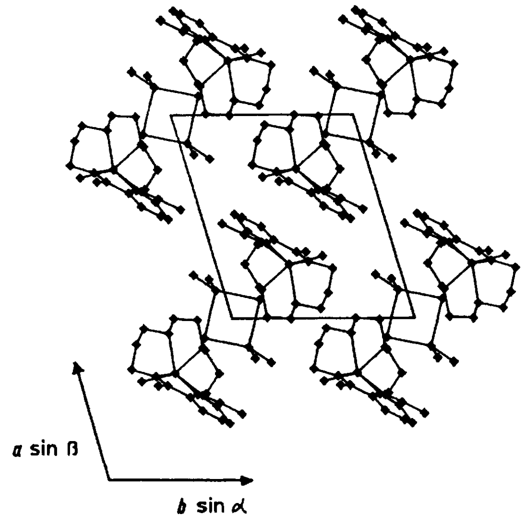

FIGURE 3 The unit cell of (2) in the *c* projection

Properties of the Complexes.—Infrared spectra. All the complexes displayed the features (see Table 2) expected for Schiff-base formation. This, coupled with the absence of any ν(C=O) absorption at *ca.* 1 700 cm^{-1}, is evidence that the Schiff base is macrocyclic in all the complexes, as confirmed for two of them by *X*-ray analysis.

In the perchlorates the ν_3 and ν_4 modes of $[ClO_4]^-$ occur as unsplit bands (Table 2) from which we conclude that the metal is six-co-ordinate in these cases as in the two complexes whose structures have been solved. In the two thiocyanates the $[NCS]^-$ absorptions (Table 2) suggest co-ordination *via* the nitrogen atom; the dithiocyanate is isomorphous with $[MnL^3(NCS)_2]$ known by *X*-ray analysis to be seven-co-ordinate with two non-equivalent *N*-bonded $[NCS]^-$ groups.[2]

Electronic spectra and electrical-conductance measurements. In water, in which all the complexes having simple counter anions are 2 : 1 electrolytes (Table 1), all the cadmium(II) complexes give the same spectrum, consisting of two intense absorptions in the u.v. (Table 2) attributable to transitions of the co-ordinated macrocycle in the species $[CdL^3(OH_2)_n]^{2+}$ where *n* is probably 2.

The spectra of the solids and of their solutions in MeCN differ in exhibiting a third, weaker, absorption at 27 000—29 000 cm^{-1}. The presence of this band, probably charge transfer in nature, is sufficient to indicate that at least one of the halide or pseudo-halide anions present is co-ordinated. From a consideration of (*i*) the known structures of (1) and (2), (*ii*) the close similarity, with one exception, of all the spectra whether in the solid state or in MeCN, and (*iii*) the 1 : 1 electrolyte behaviour (Table 1) of the salts containing simple counter ions, there can be little doubt that all the complexes, apart from $[CdL^3(NCS)_2]$ in the solid state, contain the six-co-ordinate complex ion $[ML^3(X)]^+$ (X = halide). The complex $[CdL^3(NCS)_2]$ is exceptional in showing a band at 20 200 cm^{-1} in the solid, which is not apparent in MeCN. Since this complex is seven-co-ordinate in the solid state, this discrepancy in the spectra is readily accounted for by extensive dissociation in MeCN into $[CdL^3(NCS)]^+$ and $[NCS]^-$ ions.

General Conclusions.—Cadmium(II) and mercury(II) halides are effective as templates for the condensation in good yield of one molecule of 2,6-diacetylpyridine with 4,7-diazadecane-1,10-diamine to yield complexes of the 17-membered quinquedentate Schiff-base macrocyclic ligand L^3. Evidence from i.r. and electronic spectra and electrical-conductance measurements has been presented which points to a six-co-ordinate geometry for the complexes except $[CdL^3(NCS)_2]$ which is seven-co-ordinate. *X*-Ray structure determinations carried out on $[CdL^3Br]Br{\cdot}0{\cdot}5H_2O$ and $[HgL^3Br]_2[Hg_2Br_6]$ confirm this six-co-ordinate geometry and further show that the macrocycle is folded such that the pyridine nitrogen is displaced below the approximate plane formed by the other four nitrogens and with the metal atom displaced above this plane towards the axially co-ordinated bromide ion. With the exception noted above, the other axial position is unoccupied so that the overall co-ordination geometry approximates to a pentagonal pyramid.

The folding of L^3 in these complexes contrasts with the planar conformation of the smaller macrocycles L^1,L^2, and L^4 in (seven-co-ordinate) complexes not only of other metals [1] but also of cadmium(II) [3,11] and mercury(II) [3] and is presumably the reason for the lower co-ordination number. However, it has also been shown that the sterically crowded axial site can be occupied by a unidentate ligand of small steric demands and good co-ordinating capacity such as (*N*-bonded) $[NCS]^-$ as in the complex $[CdL^3(NCS)_2]$. Comparison of the structures of the six-co-ordinate cations of (1) and (2) with that of the seven-co-ordinate (3) {isomorphous with $[CdL^3(NCS)_2]$} suggests that the accommodation of the extra unidentate ligand, with accompanying decrease in the angle of fold of the ring, is at the expense of a readjustment of the macrocycle conformation from that preferred. Thus, in (1) and (2) the six-membered rings have the chair conformation while in (3) they have the flattened chair and skew-boat conformations. Reference to the completely different conformation of L^3 in the five-co-ordinate complex $[AgL^3][ClO_4]$ [3] has already been made. Thus L^3 can adopt three different conformations suitable respectively to a five-, six-, or seven-co-ordinate complex.*

It is difficult to decide whether the five-co-ordinate structure is due to the larger size of the Ag^+ ion or to some electronic factor. That the electronic configuration of the metal ion can have a dominant influence on macrocycle conformation is well illustrated by the distorted-octahedral structure deduced [14] for the complex $[NiL^3(NCS)][ClO_4]$ (prepared by a metal-exchange procedure from $[AgL^4][ClO_4]$). However, Cd^{II} and Hg^{II} have spherically symmetrical electronic configurations and Cd^{II}, in particular, is known in a variety of stereochemical environments so such effects are unlikely to be important here.

EXPERIMENTAL

Preparation of the Complexes.—2,6-Diacetylpyridine was used as supplied and 4,7-diazadecane-1,10-diamine was prepared as described by Brubaker and Schaefer.[15]

$[CdL^3(Br)]Br{\cdot}0.5H_2O$ (1) *and* $[CdL^3(Br)]_2[CdBr_4]$. 2,6-Diacetylpyridine (0.01 mol), 4,7-diazadecane-1,10-diamine (0.01 mol), and $CdBr_2{\cdot}4H_2O$ (0.01 mol) in methanol (400 cm^3) were heated under reflux for at least 6 h during which time the colour of the mixture became yellow-orange. The resulting solution was filtered while hot and concentrated by slow evaporation. There were two separate stages in the crystallisation of product from this solution. The first, which started during the initial cooling of the filtrate, yielded pale cream crystals of $[CdL^3Br]Br{\cdot}0{\cdot}5H_2O$ in 25—30% yield. The filtrate from this solution on further concentration yielded white nugget-shaped crystals of $[CdL^3Br]_2[CdBr_4]$ in 45—55% yield. These were recrystallised from methanol. The former, less soluble, complex could also be obtained from the latter by addition of $CdBr_2{\cdot}4H_2O$ to a methanolic solution.

$[CdL^3(Cl)]Cl{\cdot}H_2O$ *and* $[CdL^3(Cl)]_2[Cd_2Cl_6]$. These were prepared in an analogous manner to the corresponding bromides, using $CdCl_2{\cdot}2.5H_2O$ in place of $CdBr{\cdot}4H_2O$. The two products separated in two stages as before. Both complexes are more soluble than the bromides and they were recrystallised from ethanol, in the presence of added $CdCl_2{\cdot}2.5H_2O$ in the case of the salt of the complex anion. The combined yield was 60—70% in the ratio of *ca.* 2 : 3.

$[CdL^3(Br)][ClO_4]$. To a methanol–water (1 : 1) solution of $[CdL^3(Br)][CdBr_4]$ was added an excess of $Na[ClO_4]{\cdot}H_2O$ The white crystalline product separated in 90% yield on standing.

$[CdL^3(NCS)_2]$. This complex was obtained in 59% yield by the addition of a three-fold excess of Na[NCS] to an ethanolic solution of (1).

$[CdL^3(NCS)][ClO_4]$. To a methanolic solution of the above dithiocyanate was added a three-fold excess of $Na[ClO_4]{\cdot}H_2O$. The white crystalline product separated in 91% yield on concentration.

$[HgL^3(Br)]Br$, $[HgL^3(Br)]_2[Hg_2Br_6]$ (2), *and* $[HgL^3(Br)][ClO_4]$. 2,6-Diacetylpyridine (0.01 mol), 4,7-diazadecane-1,10-diamine (0.01 mol), and $HgBr_2$ (0.01 mol) were allowed to react in refluxing methanol for 3—5 h. The product isolated depended on the subsequent treatment. If the

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* These types of C_s and C_2 distortion for quinquedentate ligands of a similar type when placed in six- and five-co-ordinate structures respectively are also found in methyl [2,2′-(pyridine-2,6-diyl)bis(ethylidynenitrilo)dibenzenethiolato(2—)-*NN′N″SS′*]-thallium(III) [12] and 2,6-diacetylpyridine-bis(2-thiobenzaldimino)-zinc(II).[13]

hot reaction mixture was filtered into a concentrated solution of $Na[ClO_4]\cdot H_2O$ in methanol then $[HgL^3(Br)][ClO_4]$ separated on standing. If the hot filtrate was allowed to stand without addition of $Na[ClO_4]\cdot H_2O$ the complex (2) separated. The resulting filtrate then yielded $[HgL^3(Br)]Br$ on further concentration. The combined yield of mercury-containing complexes was 50—70% in different preparations.

$[HgL^3(I)]_2[Hg_2I_6]$. This complex was prepared similarly to its bromide analogue. No other macrocyclic derivative was obtained in this preparation.

Physical measurements were carried out as described in earlier papers in this series.[1]

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