Seven-co-ordination in Metal Complexes of Quinquedentate Macrocyclic Ligands. Part 5.† Synthesis and Properties of Pentagonal-bipyramidal and Pentagonal-pyramidal Manganese(II) Complexes and Crystal and Molecular Structure of {2,15-Dimethyl-3,7,10,14,20-penta-azabicyclo-[14.3.1]eicosa-1(20),2,14,16,18-pentaene}bis(isothiocyanato)manganese-(II)

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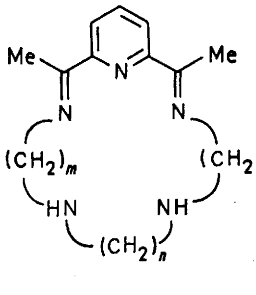
The Mn^{2+} ion acts as a template for the synthesis of complexes of the 15-, 16-, and 17-membered N_5 macrocycles (L^1, L^2, and L^3) formed from 2,6-diacetylpyridine and, respectively, 3,6-diazaoctane-1,8-diamine, 3,7-diazanonane-1,9-diamine, and 4,7-diazadecane-1,10-diamine. The complexes are of the type $[MnLX_2]\cdot xH_2O$ or $[MnLX(ClO_4)]\cdot xH_2O$ (X = Cl, NCS, or BPh_4; x = 0, 0.5, 2, or 6). All the complexes are high spin with $S = \frac{5}{2}$ ground states. From spectroscopic, magnetic, and other evidence it is concluded that the complexes of L^1 and L^2 have pentagonal-bipyramidal structures with the macrocycle defining the equatorial plane and the axial positions occupied by Cl^-, NCS^-, or H_2O. All the complexes of L^1 and L^2 are mononuclear except $[\{MnL(NCS)\}_n][ClO_4]_n$ which in the solid state are polymeric with the metal ions linked *via* NCS bridges which also transmit weak antiferromagnetic exchange. An *X*-ray structure determination of $[MnL^3(NCS)_2]$ shows that the complexes of the largest macrocycle have somewhat different structures from those of L^1 and L^2. Crystals of $[MnL^3(NCS)_2]$ are monoclinic with a = 12.007(8), b = 14.300(9), c = 13.227(9) Å, β = 100.51(6)°, Z = 4, space group $P2_1/n$. The structure has been solved by Patterson and Fourier methods and refined by full-matrix least squares to R 0.058 for 2 023 independent reflections above background measured by diffractometer. While the geometry of the co-ordination sphere is best considered as a distorted pentagonal bipyramid with the thiocyanate groups in axial positions, the macrocycle is distorted from planarity in that, while four nitrogens are coplanar with the metal ion, the pyridine nitrogen atom is 0.92 Å from this plane. Metal–nitrogen(macrocycle) distances are 2.385(6), 2.311(5), 2.354(6), 2.429(6), and 2.385(6) Å. The Mn–N bonds [2.174(7) and 2.294(7) Å] and the Mn–N–C angles [150.9(6) and 135.0(5)°] to the thiocyanates are significantly different and reflect the different environments of the two ligands. A further consequence of the folding of this macrocycle is that the more sterically crowded axial ligand is readily displaced, as in $[MnL^3(NCS)][ClO_4]$, to yield six-co-ordinate, presumably pentagonal-pyramidal, complexes.

We have previously reported [1-5] the preparation and properties of a number of seven-co-ordinate metal complexes containing the 15- and 16-membered N_5 macrocycles L^1 and L^2.‡ The macrocyclic ligands were synthesised from 2,6-diacetylpyridine and 3,6-diazaoctane-1,8-diamine (or 3,7-diazanonane-1,9-diamine) using a metal ion as template for the cyclic Schiff-base condensation. The ligands have been isolated only as their metal complexes. Metal ions so far found to be effective in the template synthesis of co-ordinated L^1 and L^2 include Fe^{III}, Fe^{II}, Zn^{II}, Cd^{II}, Hg^{II}, and Mg^{II}. Crystal structures of several complexes of each macrocycle have been determined: $[FeL^1(NCS)_2][ClO_4]$,[3] $[FeL^2(NCS)_2][ClO_4]$,[3] $[FeL^1(NCS)_2]$,[6] $[FeL^2(NCS)_2]$,[6] $[FeL^1(OH_2)_2]Cl[ClO_4]$,[7] $[ZnL^1(NCS)_2]$,[8] and $[MgL^1(OH_2)_2]Cl_2\cdot4H_2O$.[5] In all these cases the co-ordination geometry is approximately pentagonal bipyramidal (p.b.), the five nitrogen atoms of the macrocycle defining the pentagonal plane containing the metal. While distortions from planarity are relatively small in each case, they are measurably greater in the case of the larger macrocycle L^2, and are attributed mainly to the presence of a six-membered chelate ring, absent in L^1.

We are currently extending our studies to the template synthesis of complexes of other metal ions of varying radius and electron configuration and to new macrocycles of varying size. This paper describes the properties and structures of a series of manganese(II) complexes of macrocycles L^1 and L^2 and of the new 17-membered macrocycle L^3; it includes the results of an *X*-ray crystal- and molecular-structure determination of $[MnL^3$-



L^1 $m = n = 2$
L^2 $m = 2$, $n = 3$
L^3 $m = 3$, $n = 2$

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† Part 4 is ref. 6.
‡ Called B and C in previous papers.

[1] S. M. Nelson and D. H. Busch, *Inorg. Chem.*, 1969, **8**, 1859; S. M. Nelson, P. Bryan, and D. H. Busch, *Chem. Comm.*, 1966, 641.

[2] M. G. B. Drew, A. H. bin Othman, W. E. Hill, P. D. A. McIlroy, and S. M. Nelson, *Inorg. Chim. Acta*, 1975, **12**, L25.

[3] M. G. B. Drew, A. H. bin Othman, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, 1975, 2507.

[4] M. G. B. Drew, J. Grimshaw, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, 1976, 1388.

[5] M. G. B. Drew, A. H. bin Othman, S. G. McFall, and S. M. Nelson, *J.C.S. Chem. Comm.*, 1975, 818.

[6] M. G. B. Drew, A. H. bin Othman, and S. M. Nelson, *J.C.S. Dalton*, 1976, 1394.

[7] M. G. B. Drew, A. H. bin Othman, P. D. A. McIlroy, and S. M. Nelson, *Acta Cryst.*, 1976, **B32**, 1029.

[8] M. G. B. Drew and S. M. Nelson, *Acta Cryst.*, 1975, **A31**, S140.

(NCS)$_2$]. A few manganese(II) complexes of L^1 have been briefly reported by Alexander *et al.*,[9] and a brief account of a pentagonal-bipyramidal manganese(II) complex of a related macrocycle having an N_3O_2 donor set has recently appeared.[10]

RESULTS AND DISCUSSION

The complexes were synthesised by Schiff-base condensation in equimolar proportions of 2,6-diacetylpyridine with 3,6-diazaoctane-1,8-diamine (for L^1), 3,7-diazanonane-1,9-diamine (for L^2), or 4,7-diazadecane-1,10-diamine (for L^3), in the presence of $MnCl_2 \cdot 4H_2O$ in refluxing methanol for 12 h. Subsequent work-up of this reaction mixture yielded crystals of $[MnCl_2L] \cdot xH_2O$; derivatives containing other anions were obtained by the procedures given in the Experimental section. The crystalline complexes are stable in the solid state and in solution with the exception that those of macrocycle L^3 decompose in aqueous solution after several hours to give dark insoluble matter having i.r. spectra indicative of the presence of hydrolysis products.

When allowance is made for the presence of water and the variations in the nature of the anions present, the i.r. spectra of the complexes of a given macrocycle are very similar. All the spectra exhibited a medium-to-strong band at 1 630—1 650 cm^{-1} attributable to ν(C=N) and another at *ca.* 1 590 cm^{-1} due to the highest-energy pyridine-ring vibration. In some of the spectra ν(C=N) was split (see Table 2). In no case was any absorption observed at 1 700 cm^{-1} due to unchanged carbonyl groups of 2,6-diacetylpyridine. The spectra in the ν(N–H) region at 3 200—3 500 cm^{-1} were variable. From one to three bands of variable intensity and bandwidth were observed in different complexes, overlapping in some cases with water absorption. The complexity of the spectra in this region is almost certainly due to variations in the nature and extent of hydrogen bonding of the secondary amine groups and of water where present. The N–H stretching region apart, the overall similarity in the i.r. spectra of the complexes within each macrocycle series, and also of those of macrocycles L^1 and L^2 with those of corresponding complexes of Fe^{III} and Fe^{II},[1,4] is evidence for a basically common structural arrangement of the macrocycle in each case, *i.e.* the macrocycle is acting as a quinquedentate ligand.

I.r. absorption bands attributable to the polyatomic anions $[ClO_4]^-$ and $[BPh_4]^-$ are as expected for these ions in the ionic state and it is inferred, therefore, that they are not co-ordinated to the metal. Thus, for the perchlorates, the ν_3 and ν_4 vibrations occurred as unsplit bands at 1 090 and 620 cm^{-1} having bandwidths no greater than those observed in other complexes known to contain ionic $[ClO_4]^-$. In the case of the thiocyanates there are some significant variations in the positions of the ν_{asym} and δ vibrations; assignments of the latter mode were made by careful comparison of the spectra of NCS-containing complexes with those of other complexes of the same macrocycle (see Table 2). It was not possible to make unambiguous assignments of ν_{sym} in many cases because of the richness of the macrocycle spectra in the 700—850 cm^{-1} region. Of most significance, here, is the occurrence of ν_{asym} at appreciably higher wavenumber (2 090 cm^{-1}) in $[MnL^1(NCS)(ClO_4)]$ and $[MnL^2(NCS)(ClO_4)]$ than in the remaining thiocyanate complexes where ν_{asym} occurred at $<2\,065$ cm^{-1}. Absorption at 2 040—2 080 cm^{-1} for thiocyanato-complexes of bivalent metal ions is usually attributed to terminally *N*-bonded thiocyanate; in $[FeL^1(NCS)_2]$ and $[FeL^2(NCS)_2]$, for example, known from *X*-ray structure determinations to contain *trans*-isothiocyanate, ν_{asym} occurs at 2 065 and 2 067 cm^{-1}, respectively.[4] On the other hand, strong absorption at 2 080—2 120 cm^{-1} is indicative of a bridging M–NCS–M configuration.[11] We therefore propose that in the two thiocyanate perchlorates mentioned above the metal ions are NCS-bridged. Supporting evidence for this proposal is given later in this paper. For $[MnL^3(NCS)_2]$ there were two ν_{asym} vibrations (at 2 058 and 2 038 cm^{-1}). The results of the *X*-ray structure determination (see below) show that both $[NCS]^-$ ions are *N*-co-ordinated but that one is more strongly bound than the other.

Infrared spectra of the hydrates showed the expected absorption due to the stretching and bending modes of water at, respectively, 3 300—3 500 and *ca.* 1 620 cm^{-1}. Additionally, these complexes showed a broad medium-intensity band in the 500—600 cm^{-1} region. We assign these bands to rocking or wagging modes of water molecules co-ordinated to the metal.[4,12]

Summarising, the following provisional conclusions based on i.r. spectra may be drawn concerning the co-ordination sphere in the different complexes: (*i*) all the five nitrogen atoms of the macrocycles are co-ordinated; (*ii*) the complexes $[\{MnL^1(NCS)\}_n][ClO_4]_n$ and $[\{MnL^2(NCS)\}_n][ClO_4]_n$ are seven-co-ordinate polymers containing bridging thiocyanate; * (*iii*) $[MnL^3(NCS)][ClO_4]$ may be six-co-ordinate; * (*iv*) $[MnCl_2L^1] \cdot 6H_2O$ † and $[Mn(BPh_4)_2L^1] \cdot 2H_2O$ contain the mononuclear seven-co-ordinate cation $[MnL^1(OH_2)_2]^{2+}$; (*v*) the remaining hydrated complexes contain at least one co-ordinated water molecule; and (*vi*) the bis(thiocyanato) complexes are neutral mononuclear seven-co-ordinate complexes. Other properties are now described in relation to these provisional structural assignments.

Electrical Conductance.—Measurements of electrical

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* Crystals of these complexes could not be grown and therefore the proposed structures are unconfirmed. However, the existence of such polymers containing L^2 and of six-co-ordinate pentagonal pyramids containing L^3 have been confirmed by *X*-ray diffraction *via* the ions $[(CdBrL^2)_n]^{n+}$ and $[HgBrL^3]^+$.[13]

† This complex is isomorphous with $[MgCl_2L^1] \cdot 6H_2O$, known[5] from *X*-ray analysis to contain the pentagonal-bipyramidal complex ion $[MgL^1(OH_2)_2]^{2+}$.

[9] M. D. Alexander, A. Van Heuvelen, and H. G. Hamilton, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 445.

[10] N. W. Alcock, D. C. Liles, M. McPartlin, and P. A. Tasker, *J.C.S. Chem. Comm.*, 1974, 727.

[11] J. L. Burmeister, *Co-ordination Chem. Rev.*, 1966, **1**, 205; 1968, **3**, 225.

[12] J. R. Ferraro, ' Low-frequency Vibrations of Inorganic and Co-ordination Compounds,' Plenum, New York, 1971, p. 65.

[13] M. G. B. Drew, A. H. bin Othman, S. G. McFall, and S. M. Nelson, unpublished work.

TABLE 1

Analytical, conductance, and magnetic data for the manganese(II) complexes

Complex	Colour	Analysis (%) Found C	H	N	Halogen	Calc. C	H	N	Halogen	Λ [a] S cm^{-1} mol^{-1} Water	MeCN	$\mu_{\text{eff.}}$ [b] / B.M.	θ [c] / K
$[MnCl_2L^1]$ [d]	Brown	44.7	5.8	17.4		45.1	5.8	17.5		244	*e*	5.95	0
$[MnCl_2L^1]\cdot 6H_2O$ [d]	Yellow	35.6	6.8	13.7		35.5	7.0	13.8		244	*e*	5.98	
$[Mn(BPh_4)_2L^1]\cdot 2H_2O$	Yellow	75.7	6.7	6.9		75.5	6.7	7.0		*e*	260	5.97	
$[MnClL^1(ClO_4)]\cdot 2H_2O$	Orange	35.9	5.4	13.8		36.1	5.5	14.0		249	173	5.86	
$[MnL^1(NCS)_2]$	Orange	45.7	5.3	21.9		45.9	5.2	22.1		222	93	5.94	0
$[MnL^1(NCS)(ClO_4)]$	Orange	39.8	4.9	17.2		39.6	4.8	17.3		231	164	5.72	−13
$[MnCl_2L^2]\cdot 2H_2O$	Orange	42.6	6.4	15.4	15.6	42.8	6.5	15.6	15.8	236	43	5.95	
$[MnL^2(NCS)_2]$	Orange-yellow	46.9	5.5	21.3	13.9 [f]	47.2	5.5	21.4	14.0 [f]	230	60	6.03	0
$[MnL^2(NCS)(ClO_4)]$	Yellow	39.2	5.0	16.5		40.8	5.0	16.8		251	185	5.70	−13
$[MnCl_2L^3]\cdot 0.5H_2O$	Orange-yellow	46.7	6.6	16.1	16.5	46.8	6.5	16.1	16.3	242	123	5.91	
$[MnClL^3(ClO_4)]$	Orange-yellow	41.6	5.4	13.8		41.6	5.5	14.3		242	163	5.94	
$[MnL^3(NCS)_2]$	Yellow	48.2	5.8	20.7	13.3 [f]	48.3	5.8	20.8	13.6 [f]	276	122	5.95	0
$[MnL^3(NCS)(ClO_4)]$	Orange-yellow	42.2	5.2	16.3		42.1	5.3	16.4		261	150	5.90	0

[a] For 10^{-3} mol dm^{-3} solutions. [b] At 293 K; corrected for diamagnetism of ligands, estimated error ±0.10 B.M. [c] Weiss constant in $\mu_{\text{eff.}} = 2.84\,[\chi_m^1(T - \theta)]^{\frac{1}{2}}$. [d] Previously reported by Alexander *et al.*[9] [e] Insoluble. [f] Sulphur analysis.

TABLE 2

Infrared spectral data for the manganese(II) complexes

Complex	$\tilde{\nu}$/cm^{-1} N–H	C=N	ν_{asym}(NCS)	ν_{sym}(NCS) [a]	δ(NCS)	H_2O [b]
$[MnCl_2L^1]$	3 280	1 653				
$[MnCl_2L^1]\cdot 6H_2O$	3 240	1 653				550m, br
$[Mn(BPh_4)_2L^1]\cdot 2H_2O$	3 270	1 649				465m, br
$[MnClL^1(ClO_4)]\cdot 2H_2O$	3 280sh, 3 210	1 652				550m, br
$[MnL^1(NCS)_2]$	3 260, 3 248	1 650	2 058	782	480	
$[MnL^1(NCS)(ClO_4)]$	3 290, 3 280	1 650	2 090		470	
$[MnCl_2L^2]\cdot 2H_2O$	3 216	1 647, 1 640				560m, br
$[MnL^2(NCS)_2]$	3 285, 3 260, 3 240	1 642	2 060	830	476	
$[MnL^2(NCS)(ClO_4)]$	3 270	1 650, 1 645	2 090		472	
$[MnCl_2L^3]\cdot 0.5H_2O$	3 280, 3 250, 3 230	1 642, 1 636				475m, br
$[MnClL^3(ClO_4)]$	3 298, 3 266, 3 228	1 638				
$[MnL^3(NCS)_2]$	3 290	1 650, 1 630	2 058, 2 038	833, 790	492, 483	
$[MnL^3(NCS)(ClO_4)]$	3 300, 3 270	1 643	2 058	810	490	

[a] Tentative assignments. [b] Rocking or wagging mode of co-ordinated water.

TABLE 3.

Electronic spectra of the complexes (in 10^3 cm^{-1}; ε/dm^3 mol^{-1} cm^{-1} in parentheses for solutions)

Complex	State Solid	H_2O	MeCN
$[MnCl_2L^1]$	*ca.* 25.0br, 19.5 (sh)	*ca.* 28.5 (sh), (350), *ca.* 25.0 (sh), (150)	Insoluble
$[MnCl_2L^1]\cdot 6H_2O$	*ca.* 25.6 (sh)	*ca.* 28.5 (sh) (180), *ca.* 25.0 (sh) (150)	Insoluble
$[Mn(BPh_4)_2L^1]\cdot 2H_2O$	*ca.* 25.4 (sh)	Insoluble	24.4 (300)
$[MnClL^1(ClO_4)]\cdot 2H_2O$	*ca.* 21.0 (sh)	*ca.* 29.0 (sh) (170), *ca.* 25.0 (sh) (150)	*ca.* 27.4 (sh), (450), *ca.* 25.0 (300), 22.2 (sh)
$[MnL^1(NCS)_2]$	24.2, 19.0	*ca.* 28.5 (sh) (170), *ca.* 25.0 (sh) (150)	*ca.* 24.3 (180), *ca.* 22.0 (sh) (75)
$[MnL^1(NCS)(ClO_4)]$	26.6, 23.0	*ca.* 28.5 (sh) (180), *ca.* 25.0 (150)	*ca.* 27.0 (sh) (300), *ca.* 24.4 (sh) (240), *ca.* 22.0 (sh) (75)
$[MnCl_2L^2]\cdot 2H_2O$	*ca.* 28.5 (sh), *ca.* 23.8 (sh)	*ca.* 28.5 (sh) (130)	26.8 (220), *ca.* 24.7 (sh) (200)
$[MnL^2(NCS)_2]$	*ca.* 24.0 (sh)	*ca.* 28.0 (sh) (140)	*ca.* 26.3 (sh) (200)
$[MnL^2(NCS)(ClO_4)]$	*ca.* 27.0 (sh)	*ca.* 28.0 (sh) (140)	*ca.* 28.5 (sh) (300)
$[MnCl_2L^3]\cdot 0.5H_2O$	*ca.* 28.5 (sh), *ca.* 24.5 (sh)	*ca.* 28.0 (sh) (150)	*ca.* 28.2 (sh) (320)
$[MnClL^3(ClO_4)]$	*ca.* 28.0 (sh), *ca.* 24.5 (sh)	*ca.* 28.0 (sh) (160)	*ca.* 28.0 (sh) (320)
$[MnL^3(NCS)_2]$	*ca.* 25.0 (sh), 17.2	*ca.* 28.0 (sh) (170)	*ca.* 27.5 (sh) (300), 25.4 (140)
$[MnL^3(NCS)(ClO_4)]$	*ca.* 27.5 (sh), *ca.* 24.5 (sh)	*ca.* 28.0 (sh) (170)	*ca.* 28.0 (sh) (300), 25.3 (260)

conductance were made on 10^{-3} mol dm^{-3} solutions in water and in acetonitrile at 298 K. In each case molar conductances in water fall within the range of values characteristic of 2 : 1 electrolytes (Table 1). It may be concluded, therefore, that on dissolution the co-ordinated anionic ligands are virtually completely replaced by water. The seven-co-ordinate cation $[MnL(OH_2)_2]^{2+}$ is assumed to be the predominant solution species. In acetonitrile, on the other hand, molar conductances varied between values appreciably less than those expected for 1 : 1 electrolytes [dichlorides and bis(thiocyanates)], through values appropriate to 1 : 1 electrolytes (monoperchlorates), to values approaching 2 : 1 behaviour $\{[MnL^1(OH_2)_2][BPh_4]_2\}$. These results are consistent with the conclusions drawn from the i.r. spectra.

Electronic Spectra.—Measurements were made on solutions in water in the range 5 000—50 000 cm^{-1} and on solids and acetonitrile solutions in the range 5 000—33 000 cm^{-1}. In water the complexes of each macrocycle gave spectra which were virtually identical suggesting, for each series, a common absorbing species. Since the conductances indicate 2 : 1 electrolyte behaviour this species is almost certainly $[MnL(OH_2)_2]^{2+}$. Three regions of absorption were observed: a multicomponent band at *ca.* 40 000 cm^{-1} ($\varepsilon \simeq$ 20 000 $dm^3\ mol^{-1}\ cm^{-1}$), another at 32 000—35 000 cm^{-1} ($\varepsilon \simeq$ 4 800 $dm^3\ mol^{-1}\ cm^{-1}$), and a third consisting of one or two shoulders on the side of the latter at 25 000—30 000 cm^{-1} of apparent $\varepsilon \simeq$ 140—200 $dm^3\ mol^{-1}\ cm^{-1}$. The complexes $[MnCl_2L^1]\cdot 6H_2O$ and $[Mn(BPh_4)_2L^1]\cdot 2H_2O$ in the solid state exhibited closely similar spectra to those of their aqueous solutions. This supports our earlier conclusion that in these cases the axial ligands are water molecules. All the other complexes had solid-state spectra significantly different in the lowest-energy region from those of their aqueous solutions. They differed in exhibiting one, or sometimes two, bands, usually of greater intensity, at lower wavenumbers (see Table 3). It follows that in these cases one or more of the anions present (Cl^- or $[NCS]^-$) are co-ordinated. Because of the occurrence of these bands as relatively weak shoulders on the low-energy side of the 33 000 cm^{-1} absorption, it was difficult to define their positions and intensities with any precision. However, certain unambiguous conclusions could be drawn. Thus, the dithiocyanates must have different structures from the thiocyanate perchlorates in each case. Again, $[MnClL^1(ClO_4)]\cdot 2H_2O$ can be seen to be different from $[MnCl_2L^1]\cdot 6H_2O$, whereas $[MnCl_2L^3]\cdot 0.5H_2O$ and $[MnClL^3(ClO_4)]$ show very similar spectra. The spectra in acetonitrile solution were, in most cases, intermediate in profile between those in the solid state and in aqueous solution, suggesting, in agreement with the electrical-conductance data, that partial replacement by acetonitrile of anionic ligand and/or water from the co-ordination sphere has taken place.

Thus, the evidence from the properties so far considered indicates seven-co-ordinate structures for all the complexes of macrocycles L^1 and L^2, namely: $[MnCl_2L^1]$, $[MnL^1(OH_2)_2]Cl_2\cdot 4H_2O$, $[MnL^1(OH_2)_2][BPh_4]_2$, $[MnClL^1(OH_2)][ClO_4]\cdot H_2O$, $[MnL^1(NCS)_2]$, $[\{MnL^1(NCS)\}_n][ClO_4]_n$, $[MnClL^2(OH_2)]Cl\cdot H_2O$, $[MnL^2(NCS)_2]$, and $[\{MnL^2(NCS)\}_n][ClO_4]_n$. For complexes of the 17-membered macrocycle L^3, $[MnClL^3][ClO_4]$, $[MnL^3(NCS)][ClO_4]$, and, probably, $[MnClL^3]Cl\cdot 0.5H_2O$ appear to be six-co-ordinate. It will be shown below that $[MnL^3(NCS)_2]$ is seven-co-ordinate.

Origin of the electronic spectra. The two intense u.v. absorption bands of the manganese(II) complexes also occur in the spectra of analogous complexes of other metals,[1,4] although at slightly different energies. These are assigned to transitions of the co-ordinated macrocycle. The origin of the lowest-energy absorption at 19 000—30 000 cm^{-1} is uncertain. Since Mn^{II} with $S = \frac{5}{2}$ (see below) has no excited states of the same spin multiplicity as the ground state, this cannot be due to *d–d* transitions. Moreover, it is unlikely to be due to axial-ligand (Cl, NCS, or H_2O)-to-metal charge transfer since in corresponding complexes of the more easily reducible Fe^{III} the charge-transfer transitions occur at similar energies.[1,3] It is suggested that in the manganese(II) complexes this absorption may arise from metal-to-macrocycle (*i.e.* metal oxidation) charge transfer. Evidence for a similar assignment has been given previously[4] for the visible band in iron(II) complexes of macrocycles L^1 and L^2. This was considered as originating in overlap of metal d_{xy} and d_{yz} orbitals with vacant p_π^* orbitals of the tri-imine segment of the macrocycle. The higher energy of this charge transfer in the case of the manganese(II) complexes is consistent with the higher potential * for the oxidation of Mn^{II} to Mn^{III} than for the oxidation of Fe^{II} to Fe^{III}. Moreover, it is significant that in the case of both bivalent metal ions the energy of the charge-transfer band increases on replacement of L^1 by L^2; the opposite occurs in the case of the iron(III) complexes.[3]

Magnetic Moments.—All the complexes are high spin with $S = \frac{5}{2}$ ground states. Thus, with two exceptions, the room-temperature magnetic moments are close to the predicted value of 5.92 B.M.† The complexes $[\{MnL^1(NCS)\}_n][ClO_4]_n$ and $[\{MnL^2(NCS)\}_n][ClO_4]_n$ had significantly lower moments at 293 K (see Table 1) which decreased further as the temperature was reduced to 93 K. For these complexes the measured corrected susceptibilities (χ_m') obeyed the Curie–Weiss law; $\mu_{eff.} = 2.84[\chi_m'(T - \theta)]^{\frac{1}{2}}$ with the Weiss constant $\theta = -13$ K in both cases. The lower than predicted moments and the temperature dependence is evidence in support of an antiferromagnetic exchange interaction between the (magnetically non-dilute) paramagnetic centres, and are in accord with the i.r. spectra which suggested the occurrence of a thiocyanate bridge between Mn^{2+} ions linked in a polymeric chain. Recent work on di-μ-thiocyanato-dimeric complexes of Ni^{II} has demonstrated that weak intramolecular exchange coupling (giving in this case a net ferromagnetic effect) can occur.[14] In order to check that the complexes with normal room-temperature moments, particularly the dithiocyanates, are not antiferromagnetically coupled, variable-temperature (93—323 K) susceptibility measurements on five selected complexes were carried out. In each case, $\mu_{eff.}$ was found to be temperature independent, *i.e.* $\theta = 0$ (Table 1).

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* This was demonstrated by cyclic voltammetry; $[MnCl_2L^2]\cdot 2H_2O$ in acetonitrile showed a reversible one-electron oxidation wave at 0.58 V *versus* the standard calomel electrode.

† Throughout this paper: 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2.

[14] A. P. Ginsberg, R. L. Martin, R. W. Brookes, and R. C. Sherwood, *Inorg. Chem.*, 1972, **11**, 2884.

Crystal and Molecular-structure Determination.—Crystal data. $[MnL^3(NCS)_2]$, $C_{19}H_{27}MnN_7S_2$, $M = 472.53$, Monoclinic, $a = 12.007(8)$, $b = 14.300(9)$, $c = 13.227(9)$ Å, $\beta = 100.51(6)°$, $U = 2\,233.3$ Å^3, $D_c = 1.41(2)$, $Z = 4$, $D_m = 1.40$, $\mu(Mo\text{-}K_\alpha) = 8.18$ cm^{-1}, $\lambda = 0.710\,7$ Å, $F(000) = 988$. Space group $P2_1/n$ from systematic absences: $h0l$, $h + l = 2n + 1$, $0k0$, $k = 2n + 1$.

A crystal with dimensions *ca.* 0.50 × 0.75 × 1.00 mm was mounted with the b axis parallel to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions (*via* least-squares refinement of several high-angle reflections). The apparatus was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered X-radiation was used to measure 2 693 independent reflections by the stationary-crystal–stationary-counter method with $2\theta < 45°$ and for counts of 10 s. Individual backgrounds were recorded for those reflections whose counts were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of 2θ. Standard reflections were monitored during the course of the experiment but no significant changes in intensity were observed. No extinction or absorption corrections were applied. The standard deviations $\sigma(I)$ of the reflections were taken to be $[I + 2E + (0.03I^3)]^{\frac{1}{2}}$ where E is the estimated background of the reflection. 2 023 Reflections with $I > 2\sigma(I)$ were used in subsequent calculations.

The position of the manganese atom was determined from a Patterson function and Fourier syntheses were then calculated to determine the positions of the remaining atoms. The structure was refined by full-matrix least squares with the non-hydrogen atoms given anisotropic thermal parameters of the form $\exp(-2\pi^2\text{-}\sum_i\sum_j h_i h_j b_i b_j U_{ij})(i,j = 1\text{—}3)$ where b_i is the ith reciprocal cell dimension. The non-methyl hydrogen atoms were refined with isotropic thermal parameters of the form $\exp[-8\pi^2 U \sin^2\theta/\lambda^2]$. Methyl hydrogen atoms could not be identified unambiguously from the difference-Fourier map and were not included in the structure-factor calculation. Atomic-scattering factors and anomalous-dispersion corrections were taken from ref. 15. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of F_o and $\sin\theta/\lambda$, was $w^{\frac{1}{2}} = 1$ for $F_o < 40$ and $w^{\frac{1}{2}} = 40/F_o$ for $F_o > 40$. Calculations were made on a CDC 7600 computer at the University of London Computer Centre using the programs described in ref. 16. The final R value was 0.058 for the 2 023 observed reflections with no shift $> 0.15\sigma$ in the last cycle. A difference-Fourier map showed no significant peaks. The reflections given zero weight showed no serious discrepancies. Final positional parameters are given in Table 4 and molecular dimensions in Table 5. Anisotropic thermal parameters and observed and calculated structure factors are listed in Supplementary Publication No. SUP 21933 (10 pp., 1 microfiche).*

TABLE 4

Atomic co-ordinates (× 10^4 except for H × 10^3) for (1) and isotropic thermal parameters (× 10^3) for the hydrogen atoms

Atom	x	y	z	U
Mn	2 191(1)	1 312(1)	4 291(1)	
N(1)	2 023(5)	0 833(5)	5 816(5)	
C(1)	2 286(5)	0 863(5)	6 706(6)	
S(1)	2 646(2)	0 912(2)	7 950(2)	
N(2)	2 059(5)	1 814(4)	2 626(5)	
C(2)	2 372(6)	1 542(5)	1 916(6)	
S(2)	2 807(2)	1 136(2)	0 905(2)	
C(3)	0 415(8)	3 009(8)	4 941(8)	
C(4)	1 386(7)	3 703(7)	5 197(8)	
C(5)	2 483(7)	3 281(7)	5 730(8)	
N(6)	3 041(4)	2 706(4)	5 065(4)	
C(7)	3 978(6)	2 975(5)	4 790(6)	
C(8)	4 545(5)	2 299(5)	4 245(5)	
N(9)	4 073(4)	1 449(4)	4 143(4)	
C(10)	4 531(5)	0 758(5)	3 678(5)	
C(11)	3 952(5)	−0 150(5)	3 634(5)	
N(12)	3 006(4)	−0 134(4)	3 983(4)	
C(13)	2 376(7)	−0 990(6)	4 076(7)	
C(14)	1 413(7)	−1 157(6)	3 181(8)	
C(15)	0 750(7)	−0 282(6)	2 762(7)	
N(16)	0 565(6)	0 379(4)	3 523(5)	
C(17)	−0 340(6)	1 037(6)	3 122(9)	
C(18)	−0 468(7)	1 760(8)	3 884(9)	
N(19)	0 584(5)	2 312(5)	4 172(6)	
C(20)	4 519(7)	3 930(6)	5 044(8)	
C(21)	5 521(6)	2 487(6)	3 839(6)	
C(22)	5 993(6)	1 788(7)	3 337(7)	
C(23)	5 518(6)	0 919(6)	3 244(6)	
C(24)	4 501(7)	−0 981(6)	3 245(7)	
H(31) *	−034(7)	333(6)	464(6)	83(28)
H(32)	046(7)	245(6)	552(7)	82(28)
H(41)	149(7)	399(6)	443(7)	91(30)
H(42)	107(7)	425(6)	572(7)	96(28)
H(51)	313(6)	383(5)	615(6)	74(24)
H(52)	233(5)	290(5)	639(6)	55(21)
H(131)	281(6)	−156(5)	426(6)	59(23)
H(132)	211(6)	−091(5)	475(6)	47(19)
H(141)	168(10)	−144(8)	256(9)	136(44)
H(142)	089(11)	−147(9)	371(10)	169(52)
H(151)	122(8)	021(7)	231(7)	106(32)
H(152)	−010(6)	−049(5)	233(5)	55(19)
H(16)	027(7)	−005(6)	398(7)	80(29)
H(171)	−006(6)	132(5)	242(6)	72(24)
H(172)	−102(6)	071(4)	280(5)	42(18)
H(181)	−116(7)	217(5)	354(6)	69(23)
H(182)	−057(9)	156(7)	451(8)	109(42)
H(19)	076(5)	253(4)	374(5)	19(19)
H(21)	581(6)	305(5)	399(6)	56(23)
H(22)	674(6)	187(5)	314(5)	57(20)
H(23)	580(6)	038(5)	282(6)	67(23)

* The first digit(s) of the hydrogen-atom numbering are identical with the atom to which they are bonded.

Discussion of the Structure.—The geometry of $[MnL^3(NCS)_2]$, (1), is shown in Figure 1, together with the atom-numbering scheme. The geometry of (1) is best considered as a distorted pentagonal bipyramid with the metal atom and the five nitrogen atoms of the macrocycle lying in the equatorial plane and the thiocyanate ligands in axial positions, an arrangement equivalent to that found for complexes containing macrocycles L^1 and L^2. However, as is apparent from the molecular dimensions in Table 5 and the least-squares

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[15] ' International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

[16] ' X-ray ' system of programs, ed. J. M. Stewart, University of Maryland Technical Report TR 67 58, July 1970.

planes in Table 6, the macrocycle is considerably distorted from planarity. The maximum deviation of a contributing atom from the least-squares plane of MnN_5 is 0.46 Å compared to distances of *ca.* 0.11 and 0.29 Å in iron(III) complexes of macrocycles L^1 and L^2, respectively.[3]

TABLE 5

Molecular dimensions (bond lengths in Å, angles in °)

Mn–N(1)	2.174(7)	N(1)–Mn–N(2)	170.8(2)
Mn–N(2)	2.294(7)	N(1)–Mn–N(6)	88.2(2)
Mn–N(6)	2.385(6)	N(1)–Mn–N(9)	111.2(2)
Mn–N(9)	2.311(5)	N(1)–Mn–N(12)	89.8(2)
Mn–N(12)	2.354(5)	N(1)–Mn–N(16)	90.7(2)
Mn–N(16)	2.429(6)	N(1)–Mn–N(19)	92.3(3)
Mn–N(19)	2.385(6)	N(2)–Mn–N(6)	95.7(2)
N(1)–C(1)	1.163(11)	N(2)–Mn–N(9)	77.9(2)
N(2)–C(2)	1.142(11)	N(2)–Mn–N(12)	93.9(2)
C(1)–S(1)	1.625(9)	N(2)–Mn–N(16)	82.0(2)
C(2)–S(2)	1.627(9)	N(2)–Mn–N(19)	80.5(2)
Mn–N(1)–C(1)	150.9(6)	N(6)–Mn–N(9)	67.5(2)
Mn–N(2)–C(2)	135.0(5)	N(6)–Mn–N(12)	130.5(2)
N(1)–C(1)–S(1)	179.5(7)	N(6)–Mn–N(16)	152.5(2)
N(2)–C(2)–S(2)	178.9(7)	N(6)–Mn–N(19)	78.7(2)
		N(9)–Mn–N(12)	67.4(2)
C(3)–C(4)	1.522(13)	N(9)–Mn–N(16)	137.3(2)
C(4)–C(5)	1.502(12)	N(9)–Mn–N(19)	137.3(2)
C(5)–N(6)	1.453(12)	N(12)–Mn–N(16)	76.9(2)
N(6)–C(7)	1.302(10)	N(12)–Mn–N(19)	150.7(2)
C(7)–C(8)	1.448(10)	N(16)–Mn–N(19)	73.9(2)
C(7)–C(20)	1.524(11)		
C(8)–N(9)	1.338(9)	C(10)–C(23)	1.426(10)
C(8)–C(21)	1.400(10)	C(11)–N(12)	1.302(9)
C(21)–C(22)	1.377(13)	C(11)–C(24)	1.495(11)
C(22)–C(23)	1.364(13)	N(12)–C(13)	1.456(10)
N(9)–C(10)	1.334(9)	C(13)–C(14)	1.516(12)
C(10)–C(11)	1.469(9)	C(14)–C(15)	1.532(12)
C(15)–N(16)	1.428(12)	C(18)–N(19)	1.479(11)
N(16)–C(17)	1.462(10)	N(19)–C(3)	1.463(6)
C(17)–C(18)	1.472(10)		
C(4)–C(3)–N(19)	113.7(8)	C(21)–C(22)–C(23)	120.2(8)
C(3)–C(4)–C(5)	114.4(8)	C(22)–C(23)–C(10)	118.3(8)
C(4)–C(5)–C(6)	113.8(8)	C(10)–C(11)–N(12)	114.1(6)
Mn–N(6)–C(5)	121.7(5)	C(10)–C(11)–C(24)	118.8(6)
Mn–N(6)–C(7)	116.8(5)	N(12)–C(11)–C(24)	127.1(8)
C(5)–N(6)–C(7)	121.2(6)	Mn–N(12)–C(11)	119.6(4)
N(6)–C(7)–C(8)	116.8(5)	Mn–N(12)–C(13)	119.0(5)
N(6)–C(7)–C(20)	124.0(7)	C(11)–N(12)–C(13)	121.1(6)
C(8) C(7)–C(20)	119.2(7)	N(12)–C(13)–C(14)	113.6(7)
C(7)–C(8)–N(9)	115.3(7)	C(13)–C(14)–C(15)	115.2(7)
C(7)–C(8)–C(21)	124.3(7)	C(14)–C(15)–N(16)	115.0(8)
N(9)–C(8)–C(21)	120.3(7)	Mn–N(16)–C(15)	116.3(7)
Mn–N(9)–C(8)	118.1(4)	Mn–N(16)–C(17)	106.7(4)
Mn–N(9)–C(10)	117.9(4)	C(15)–N(16)–C(17)	111.7(6)
C(8)–N(9)–C(10)	121.1(6)	N(16)–C(17)–C(18)	111.5(7)
N(9)–C(10)–C(11)	116.1(6)	C(17)–C(18)–N(19)	111.2(8)
N(9)–C(10)–C(23)	120.6(6)	Mn–N(19)–C(3)	125.1(5)
C(11)–C(10)–C(23)	123.3(6)	Mn–N(19)–C(18)	109.9(5)
C(8)–C(21)–C(22)	119.4(8)	C(3)–N(19)–C(18)	108.9(7)
C(3)–H(31)	1.03(8)	C(14)–H(141)	1.02(12)
C(3)–H(32)	1.10(9)	C(14)–H(142)	1.12(14)
C(4)–H(41)	1.12(10)	C(15)–H(151)	1.14(10)
C(4)–H(42)	1.15(9)	C(15)–H(152)	1.12(6)
C(5)–H(51)	1.17(7)	N(16)–H(16)	0.98(9)
C(5)–H(52)	1.07(8)	C(17)–H(171)	1.11(9)
C(13)–H(131)	0.97(7)	C(17)–H(172)	0.98(6)
C(13)–H(132)	1.01(8)	C(18)–H(181)	1.05(8)
N(19)–H(19)	0.72(6)		
C(21)–H(21)	0.88(8)		
C(22)–H(22)	0.99(8)		
C(23)–H(23)	1.05(8)		

The geometry is best understood by considering the macrocycle in two parts. Four of the nitrogen atoms are approximately coplanar together with the metal atom (plane 4, maximum deviation 0.04 Å) and the unique

TABLE 6

Least-squares planes for (1) with equations in the form $Ax + By + Cz = D$, where x,y,z are the crystallographic fractional co-ordinates. Distances (Å) of the relevant atoms from each plane are given in square brackets

	A	*B*	*C*	*D*
Plane 1: Mn, N(1), C(1), S(1)	−8.66	9.90	2.16	0.33
[Mn 0.00, N(1) 0.00, C(1) 0.00, S(1) 0.00, C(7) −0.21, C(8) 1.07, C(15) 0.66, N(16) −0.32]				
Plane 2: Mn, N(2), C(2), S(2)	9.87	7.24	1.43	3.72
[Mn 0.00, N(2) −0.00, C(2) 0.01, S(2) −0.00, C(3) −0.43, C(4) 1.07, C(11) 0.59, N(12) −0.29]				
Plane 3: Mn, N(6), N(9), N(12), N(16), N(19)	−1.89	−4.59	12.50	4.20
[Mn 0.14, N(6) 0.31, N(9) −0.46, N(12) 0.26, N(16) −0.09, N(19) −0.16]				
Plane 4: Mn, N(6), N(12), N(16), N(19)	−3.55	−4.52	12.44	3.97
[Mn −0.01, N(6) 0.03, N(12) −0.02, N(16) 0.04, N(19) −0.04, N(9) −0.92, C(3) 0.67, C(4) 0.33, C(5) 0.79, C(7) −0.77, C(8) −1.34, C(10) −1.35, C(11) −0.79, C(13) 0.70, C(14) 0.01, C(15) −0.68, C(17) −0.44, C(18) 0.23, C(20) −1.08, C(21) −2.28, C(22) −2.75, C(23) −2.31, C(24) −1.09]				
Plane 5: C(5), N(6), C(7), C(8), N(9), C(10), C(11), N(12), C(13), C(20), C(21), C(22), C(23), C(24)	5.00	−3.91	10.27	5.76
[Mn −0.77, C(5) 0.08, N(6) −0.10, C(7) −0.02, C(8) −0.03, N(9) −0.04, C(10) −0.02, C(11) 0.00, N(12) −0.12, C(13) 0.00, C(20) 0.14, C(21) −0.04, C(22) −0.04, C(23) −0.03, C(24) 0.20]				
Plane 6: Mn, N(6), N(19)	−3.77	−4.58	12.38	3.89
[C(3), 0.70, C(4) 0.33, C(5) 0.77]				
Plane (7): Mn, N(12), N(16)	−3.30	−4.51	12.47	4.04
[C(13) 0.71, C(14) −0.01, C(15) −0.71]				
Plane 8: Mn, N(16), N(19)	−3.53	−4.18	12.54	4.06
[C(17) −0.46, C(18) 0.24]				

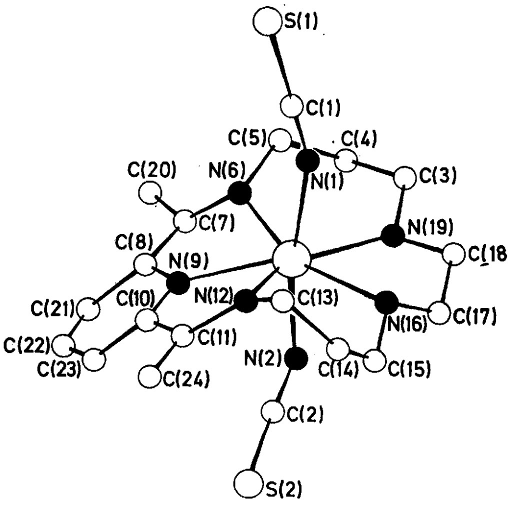

FIGURE 1 Geometry of (1) together with the atom-numbering scheme

pyridine nitrogen atom N(9) is 0.92 Å from the plane. The unsaturated part of the macrocycle [pyridine-ring atoms, C(5), N(6), C(7), C(20), C(13), N(12), C(11), C(24)] forms an approximate plane which intersects this MnN_4 plane at an angle of 41.8°. Surprisingly, the Mn atom is 0.77 Å from this plane; it is even 0.63 Å from the N(6), N(9), N(12) plane. Unlike complexes containing L^1 and L^2 macrocycles which have the C_2 distortion from the p.b.,[3,6] steric strain is relieved in the present co-ordination sphere *via* a C_s distortion. This is much less common [17] but one known example is [UO_2(macrocycle)].[18] The geometry is (as shown in Figure 2) distorted from the p.b. towards a capped trigonal prism (c.t.p.). In the rearrangement from the p.b. to the c.t.p., one atom, N(9), drops below the equatorial plane in the direction of an axial atom N(2). This axial atom forms a triangular face with N(16), N(19) and breaks edges with N(6), N(12). The atoms N(6) and N(12) form an additional edge and thus the c.t.p. is formed. The geometry of (1) is still much closer to a p.b. than a c.t.p. but all these distortions from the p.b. are observed. Thus angles involving N(9) are changed from 90°, *viz*. N(1)–Mn–N(9) [111.2(2)] and N(2)–Mn–N(9) [77.9(2)°]; N(2) moves towards N(16), N(19) [82.0(2), 80.5(2)] and away from N(6) and N(12) [95.7(2), 93.9(2)°]. Also N(6) and N(12) move closer together [130.5(2)] instead of exhibiting the 144° of the ideal p.b. As pointed out,[17] solid-state structures are often indicative of interconversion paths between the ideal polyhedra.

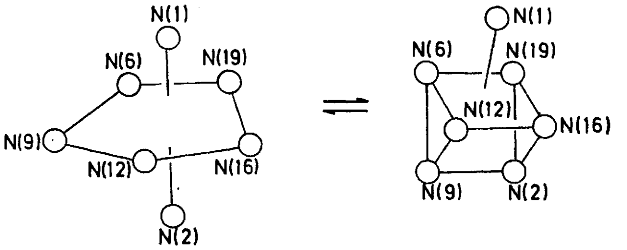

FIGURE 2 Polytopal rearrangement from a p.b. to a c.t.p. as illustrated by the co-ordination sphere of [$MnL^3(NCS)_2$]

As might be expected, the Mn–N(1) bond is much shorter [2.174(7) Å] than the more sterically crowded Mn–N(2) bond [2.294(7) Å]. It is interesting that axial bond lengths in [$MnL^4(NCS)_2$]* are 2.277(13) and 2.254(13) Å suggesting that the present Mn–N(1) bond is shorter because of the lack of crowding. It is indeed equivalent to that found in the octahedral polymer [$Mn(C_{10}H_{14}N_2O)_2(NCS)_2$] where Mn–NCS is 2.167(4) Å.[19]

The metal to thiocyanate bond angles are different and both much less than 180°, Mn–N(1)–C(1) being 150.9(6) and Mn–N(2)–C(2) 135.0(5)°. Variations in such angles are very often found [3,6] but in previous examples M–N bonds have been equal and decreases in M–N–C angles from 180° are usually concomitant with decreases in C–S bond lengths. In (1) however the C–S bonds are of equivalent length and it seems likely therefor that the difference in Mn–N bond lengths is the cause of the discrepancy. An alternative cause, intramolecular steric effects, is implausable as the $(NCS)^1$ group is less crowded than the $(NCS)^2$ group. The atom N(2) is 2.52, 2.61, and 2.55 Å from H(151), H(171), and H(19) respectively while the closest N(1) ··· H contact to H(132) is 2.87 Å. Surprisingly, the $(NCS)^2$ group is not positioned in the sterically most open position, C(2) being 2.47 Å from H(151). However, it could be an intermolecular effect in that there are three contacts between $(NCS)^2$ and C(14), C(24) in the molecule at $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ between 3.60 and 3.75 Å which would be decreased if the angle were increased. Such arguments are difficult to prove but a notable precedent has been provided [20] in which packing effects cause the M–N–C angle to vary.

The Mn–N(9) bond is the shortest of the equatorial bonds at 2.311(5) Å, the others ranging between 2.354(6) and 2.429(6) Å. Whether this is due to its uncrowded site (being well out of the p.b. girdle) or to some bonding pattern (being the unique pyridine nitrogen atom) is uncertain. Certainly, in [$MnL^4(NCS)_2$] [21] this bond is also the shortest $Mn-N_{eq}$ bond by *ca*. 0.03 Å. In both [$MnL^4(NCS)_2$] and the other known p.b. structure of Mn^{II}, [Mn(macrocycle)$(ClO_4)_2$],[10] both with N_3O_2 donor sets in 15-membered rings, equatorial bond lengths range between 2.22(1) and 2.30(1) Å for N and O; so it is apparent that the bond lengths in (1) are longer than usual because of the larger size of L^3 and possibly also because of its folded conformation. A similar range of bond lengths was found for [$Mn(OH_2)(edta)$]$^{2-}$ with Mn–N bonds of 2.352(4) and 2.402(4) Å and this was ascribed to the constraints forced on the co-ordination sphere by the edta ligand (ethylenediaminetetra-acetate).[22]

TABLE 7

Torsion angles (°) in the three saturated rings of (1)

Mn–N(6)–C(5)–C(4)	−63.4
N(6)–C(5)–C(4)–C(3)	72.4
C(5)–C(4)–C(3)–N(19)	−66.4
C(4)–C(3)–N(19)–Mn	54.7
C(3)–N(19)–Mn–N(6)	−35.5
N(19)–Mn–N(6)–C(5)	38.5
Mn–N(19)–C(18)–C(17)	−38.8
N(19)–C(18)–C(17)–N(16)	60.6
C(18)–C(17)–N(16)–Mn	−47.6
C(17)–N(16)–Mn–N(19)	19.1
N(16)–Mn–N(19)–C(18)	9.9
Mn–N(16)–C(15)–C(14)	74.6
N(16)–C(15)–C(14)–C(13)	−38.5
C(15)–C(14)–C(13)–N(12)	−39.0
C(14)–C(13)–N(12)–Mn	75.4
C(13)–N(12)–Mn–N(16)	−33.9
N(12)–Mn–N(16)–C(15)	−33.8

As indicated by the least-squares planes (6,7) and the torsion angles (Table 7), the two six-membered rings have

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* L^4 is the 15-membered N_3O_2 macrocycle in which the secondary amine groups of L^1 have been replaced by ether oxygen.

[17] M. G. B. Drew, *Progr. Inorg. Chem.*, in the press.

[18] M. N. Akhtar and A. J. Smith, *Acta Cryst.*, 1973, **B29**, 275.

[19] F. Bigoli, A. Braibanti, M. A. Pellinghelli, and A. Tiripicchio, *Acta Cryst.*, 1973, **B29**, 39.

[20] D. V. Naik and W. R. Scheidt, *Inorg. Chem.*, 1973, **12**, 272.

[21] M. G. B. Drew, A. H. bin Othman, S. G. McFall, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, submitted for publication.

[22] B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, 1964, **3**, 27.

different conformations which are a necessary consequence of the puckered conformation of the five-membered ring containing N(16), N(19) and the C_s distortion of the unsaturated part of the macrocycle. Because of the former, C(3) and C(15) [bonded to N(19) and N(16)] are positioned on opposite sides of the girdle, respectively above and below, and because of the latter C(5) and C(13) [bonded to N(6) and N(12)] are both positioned above the girdle (see plane 4, Table 6). Therefore the six-membered ring Mn, N(6), C(5), C(4), C(3), N(19) has the chair conformation and Mn, N(12), C(13), C(14), C(15), N(16) has the skew-boat conformation.

Gollogly and Hawkins [23] calculated the conformational preferences for the chelate rings formed by propane-1,3-diamine in octahedral complexes.* The conformation of lowest energy is a symmetrical chair with the next lowest being the skew boat. In the six-membered rings found in the L^2 complexes, the chair conformation is found with the three carbon atoms being equivalent distances (1.1—1.2 Å) from the Mn, N, N plane, while in (1) the conformation is very much flattened with C(3), C(4), and C(5) being 0.70, 0.33, and 0.77 Å from the plane. It has been shown [23] that this latter variation can be predicted by taking into account axial–equatorial contacts. However, there is nothing striking about such values in this structure. For while N(2)–Mn–N(19) is 80°, the C(3), C(4), and C(5) atoms are on the opposite side of the girdle plane from N(2) towards N(1), and as we have seen non-bonded contacts involving $(NCS)^1$ with the chair are 0.35 Å longer than those involving $(NCS)^2$.

Particularly striking in the chair arrangement is the Mn–N(19)–C(3) angle which is a massive 125.1(5),° 9° more than the corresponding angle in the skew boat. The N(6)–Mn–N(19) angle is 78.7(2)°, larger than any other but still much less than the 90° predicted [23] for the isolated chair. The skew-boat ring has C_2 symmetry with Mn, N(12), N(16), and C(14) approximately planar and C(13), C(15) on opposite sides of this plane. This conformation, while of higher energy, is inevitable in this complex. Unlike the chair ring, the Mn–N bonds in the skew boat are significantly different and presumably affected by steric strain. The conformation is identical with that predicted by Gollogly and Hawkins.[23] The five-membered ring has the asymmetric puckered geometry with C(17) $-$ 0.46 and C(18) 0.24 Å from the Mn, N(16), N(19) plane.

Intermolecular contacts, not involving hydrogen, less than 3.75 Å are listed in the Supplementary Publication. There are only eight of these, none being significantly less than the sum of van der Waals radii. The packing diagram in the *a* projection is shown in Figure 3.

General Conclusions.—The Mn^{2+} ion is effective as a template for the Schiff-base condensation of 2,6-diacetylpyridine with three different tetra-amines yielding complexes of the quinquedentate 15-, 16-, and 17-membered N_5 macrocyclic ligands. The evidence of various physical properties leads to the conclusion that the complexes of the two smaller macrocycles L^1 and L^2 are seven-co-ordinate. Also, the similarity in properties of the manganese(II) complexes of L^1 and L^2 with those of other metal ions known from crystallographic studies to be pentagonal bipyramidal strongly suggests that the conformation of either macrocycle does not alter appreciably on change of central metal ion.

The structures of the complexes of the 17-membered macrocycle L^3 are different in two important respects. The first is, as shown by the *X*-ray structure determination of $[MnL^3(NCS)_2]$, that this macrocycle is severely folded. It is not yet clear whether the non-planarity arises from an intrinsic preferred conformation of the ring or whether it is due to a mismatching of the sizes of the Mn^{2+} ion and the macrocycle ' hole '. It may be significant that we have so far been unsuccessful in synthesising complexes of L^3 with the metal ions Fe^{3+}, Zn^{2+}, and Mg^{2+}, all of which are smaller than Mn^{2+}, while with the larger ions Cd^{2+}, Hg^{2+}, and Ag^+ macrocyclic complexes have been obtained.[13]

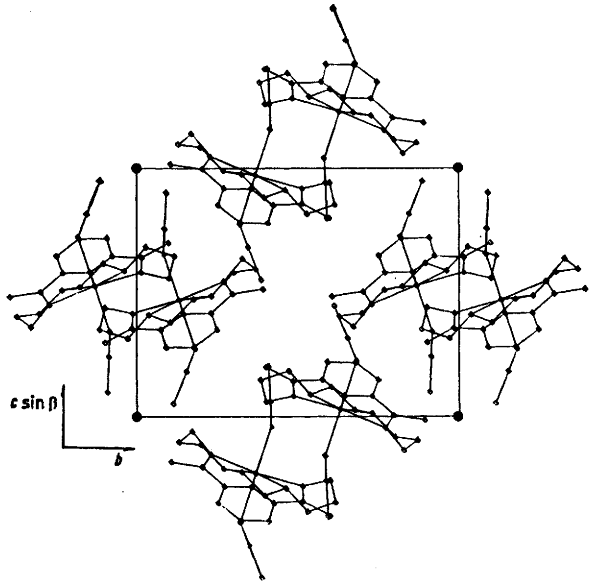

FIGURE 3 Unit cell of (1) in the *a* projection

The second structural difference of the manganese(II) complexes of L^3 from those of L^1 and L^2 follows from the first. The folded conformation of L^3 leads to one of the axial positions being sterically crowded. Where a potential axial ligand has good co-ordinating ability and small steric requirements such as *N*-bonded $[NCS]^-$ both axial positions can be occupied giving a seven-co-ordinate complex. However, the two Mn–N(NCS) bond distances are different, the $[NCS]^-$ ion concave to the macrocycle fold being more weakly bound. When one $[NCS]^-$ ion is replaced by the larger, more weakly co-ordinating, $[ClO_4]^-$ ion the sterically crowded axial position is left unoccupied and a six-co-ordinate complex results. Although we have no *X*-ray data for this

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* These show an N–M–N angle of *ca.* 90°, but despite this the results have some relevance here.

[23] J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1972, **11**, 156.

complex, i.r. spectra provide no evidence for any serious alteration in macrocycle conformation. A pentagonal-pyramidal structure is therefore proposed. As far as we are aware this is the first example of this structural class. The complex $[MnClL^3(ClO_4)]$ {and possibly, also, $[MnCl_2L^3]\cdot 0.5H_2O$} presumably has a similar structure.

In contrast to $[MnL^3(NCS)][ClO_4]$, the corresponding complexes of the same stoicheiometry containing the essentially planar macrocycles L^1 and L^2 are seven-co-ordinate. In these there is no steric reason for a lower co-ordination number and seven co-ordination is preserved by a bridging function on the part of the single $[NCS]^-$ ion present.

EXPERIMENTAL

Preparation of the Complexes.—2,6-Diacetylpyridine (Emmanuel) and 3,6-diazaoctane-1,8-diamine (Eastman) were used with further purification. 3,7-Diazanonane-1,9-diamine and 4,7-diazadecane-1,10-diamine were prepared as described by Brubaker and Schaefer.[24]

2,6-Diacetylpyridine (0.04 mol) in methanol (200 cm^3) was added to $MnCl_2\cdot 4H_2O$ (0.04 mol) in methanol (400 cm^3). To this virtually colourless solution was added a solution of the tetramine (0.04 mol) in 200 cm^3 methanol with stirring. The mixture, now red-orange, was gently heated under reflux for 12 h. Solvent was then removed and the residue extracted with cold ethanol to leave a brown or black tarry gum which was discarded. The ethanol extract yielded yellow or orange crystals on standing. These were recrystallised from ethanol ($[MnCl_2L^1]\cdot 6H_2O$), 1,2-dichloroethane ($[MnCl_2L^2]\cdot 2H_2O$), or ethanol–diethyl ether ($[MnCl_2L^3]\cdot 0.5H_2O$). Yields were variable but usually within 40—70%.

The bis(thiocyanates) were prepared by addition of an excess of Na[NCS] in ethanol to a cold ethanolic solution of the appropriate dichloride. In the cases of $[MnL^2(NCS)_2]$ and $[MnL^3(NCS)_2]$ the red-orange products separated immediately. They were isolated and recrystallised from methanol; $[MnL^1(NCS)_2]$ separated more slowly and was recrystallised from ethanol. Yields were >80%. The $[MnL(NCS)][ClO_4]$ and $[MnClL][ClO_4]\cdot xH_2O$ complexes were prepared from the corresponding bis(thiocyanates) or dichlorides in methanol (thiocyanates) or ethanol (chlorides) by addition of an excess of $Na[ClO_4]\cdot H_2O$. Yields were 50—80%.

The complex $[MnL^1(OH_2)_2][BPh_4]_2$ precipitated in *ca.* 80% yield from an ethanol solution of $[MnL^1(OH_2)_2]Cl_2\cdot 4H_2O$ on addition of an excess of $Na[BPh_4]$ in water; $[MnCl_2L^1]$ was obtained from the hexahydrate by heating at 333 K for 12 h.

Physical Measurements.—These were carried out as described in earlier papers in this series.[2,4]

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[6/732 *Received*, 14*th April*, 1976]

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[24] G. R. Brubaker and D. P. Schaefer, *Inorg. Chem.*, 1971, **10**, 811.