Seven-co-ordination in Metal Complexes of Quinquedentate Macrocyclic Ligands. Part 7.† Synthesis and Properties of some Manganese(II), Iron(III), Iron(II), Zinc(II), and Cadmium(II) Complexes of an N_3O_2 Macrocycle and the Crystal and Molecular Structure of {2,13-Dimethyl-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene}di-isothiocyanatomanganese(II)

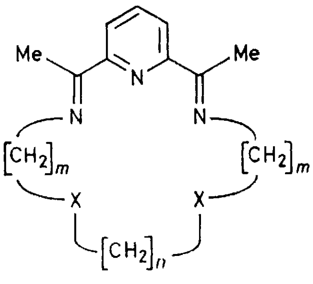
By **Michael G. B. Drew** * and **A. Hamid bin Othman**, Department of Chemistry, The University, Whiteknights, Reading RG6 2AD

Stephen G. McFall, Paul D. A. McIlroy, and **S. Martin Nelson**,* Department of Chemistry, Queen's University, Belfast BT9 5AG, N. Ireland

Reaction of 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine in methanol in the presence of a stoicheiometric amount of a salt of Mn^{II}, Fe^{III}, Fe^{II}, Zn^{II}, or Cd^{II} gives metal complexes of the 15-membered N_3O_2 macrocyclic ligand L^4 in good yield. Vibrational and electronic spectra as well as electrical-conductance data for solutions provide strong evidence for a seven-co-ordinate, approximately pentagonal-bipyramidal, structure in each case with the macrocycle occupying the pentagonal plane and the axial positions being filled by halide or pseudohalide ion. This is confirmed by a single-crystal *X*-ray structure determination of the title complex $[MnL^4(NCS)_2]$ which is triclinic, with $a = 13.834(4)$, $b = 7.403(2)$, $c = 10.645(3)$ Å, $\alpha = 91.0(1)$, $\beta = 71.3(1)$, $\gamma = 100.8(1)^\circ$, $Z = 2$, space group $P\bar{1}$. 1427 Independent reflections above background have been measured by counter methods and refined to R 0.075. Metal–nitrogen(macrocycle) distances are 2.244(9), 2.214(8), and 2.254(10) Å and the metal–oxygen distances are 2.296(8) and 2.270(7) Å. The metal–nitrogen(NCS) bond lengths are 2.254(13) and 2.277(13) Å with Mn–N–C bond angles of 130.4(10) and 126.1(9)°. From magnetic and Mössbauer measurements, the complexes of Fe^{III}, Fe^{II}, and Mn^{II} are shown to be high-spin. Electrochemical data for the iron and manganese complexes are reported; in the case of the iron complexes the oxidation state II is significantly stabilised relative to that in complexes of the analogous N_5 macrocycle.

EARLIER papers in this series [1–6] have reported the synthesis, properties, and, in several cases, the crystal and molecular structures of some complexes of Fe^{III}, Fe^{II}, Mn^{II}, Zn^{II}, and Mg^{II} with three quinquedentate N_5 macrocyclic ligands derived 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 macrocyles are abbreviated L^1, L^2, and L^3. In all the complexes of the 15- and 16-membered macrocycles L^1 and L^2 so far investigated the structures are approximately pentagonal bipyramidal with the macrocycle defining the equatorial plane and the axial positions occupied by a unidentate anion or water. Complexes of the 17-membered macrocycle L^3 differ in that the five ligand donor atoms do not lie on one plane, a distortion which results in one face of the macrocycle being more sterically crowded than the other. Thus, in $[MnL^3(NCS)_2]$ one $[NCS]^-$ ion is more strongly bound than the second, while in $[MnL^3(NCS)_2][ClO_4]$, for example, the sterically crowded axial site is unoccupied.[5] The co-ordination geometry of the latter complex is thus approximately pentagonal pyramidal and illustrates how an unusual stereochemistry can be imposed on a metal ion by the use of macrocyclic ligands of particular preferred conformations.

As a continuation of our studies on the effect of the nature and size of both the metal ion and macrocycle on the structure of the complexes formed, and on the effectiveness of different metal ions in promoting macrocycle synthesis, we now describe some complexes of Mn^{II}, Fe^{III}, Fe^{II}, Zn^{II}, and Cd^{II} of the 15-membered N_3O_2 macrocycle L^4; the results of the crystal and molecular-structure determination of one of these complexes, $[MnL^4(NCS)_2]$, are included. Some magnesium(II) complexes of the same macrocycle are described in Part 6.[7] A pentagonal-bipyramidal manganese(II) complex of a related, less flexible, N_3O_2 macrocycle has been reported



		X
L^1	$m = n = 2$	NH
L^2	$m = 2,\ n = 3$	NH
L^3	$m = 3,\ n = 2$	NH
L^4	$m = n = 2$	O

---

† Part 6 is ref. 7.

[1] S. M. Nelson and D. H. Busch, *Inorg. Chem.*, 1969, **8**, 1859; M. G. B. Drew, A. H. bin Othman, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, 1975, 2507.

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

[3] M. G. B. Drew, A. H. bin Othman, and S. M. Nelson, *J.C.S. Dalton*, 1976, 1394; M. G. B. Drew, A. H. bin Othman, P. D. A. McIlroy, and S. M. Nelson, *Acta Cryst.*, 1976, **B32**, 1029.

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

[5] M. G. B. Drew, A. H. bin Othman, S. G. McFall, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, 1977, 438.

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

[7] D. H. Cook, D. E. Fenton, M. G. B. Drew, S. G. McFall, and S. M. Nelson, *J.C.S. Dalton*, 1977, 446.

by Alcock *et al.*[8] as have the structures of some complexes of Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} of an open-chain N_3O_2 ligand by Wester and Palenik.[9]

RESULTS AND DISCUSSION

The complexes were prepared by similar procedures to those used previously for the synthesis of complexes of the N_5 series of macrocycles. This consisted of the Schiff-base condensation of equimolar quantities of 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine in methanol in the presence of an equimolar amount of the appropriate metal salt (see Experimental section for details). The macrocycle has been isolated only as its metal complexes; reaction in the absence of metal salt yielded only gums with properties consistent with an oligomeric product (or mixture of products) having residual unchanged carbonyl groups. The importance of the metal ion in promoting the cyclic condensation of the reactants and/or in stabilising the macrocycle once formed is thus apparent.

TABLE 1

Analytical, electrical-conductance, and magnetic data for the complexes

		Analysis (%)											
		Found				Calc.				Λ [a]/S cm^2 mol^{-1}			$\mu_{eff.}$ [b]
Complex	Colour	C	H	N	Halogen	C	H	N	Halogen	H_2O	MeCN	$C_2H_4Cl_2$	B.M.
$[MnL^4(NCS)_2]$	Orange	46.0	4.7	15.9	14.5	45.7	4.7	15.7	14.4	212	77		5.91
$[FeL^4Cl_2][FeCl_4]$	Yellow	30.2	3.6	7.0	35.5	30.0	3.5	7.0	35.5				
$[FeL^4Cl_2][ClO_4]$	Yellow	35.5	4.1	7.9		35.9	4.2	8.4		576	161		5.92
$[FeL^4(NCS)_2][ClO_4]$	Red	37.6	3.6	12.4		37.3	3.9	12.8		356	163		5.93
$[FeL^4(NCS)_2]$	Blue	45.4	4.8	15.5	14.3 [c]	45.6	4.7	15.7	14.3 [c]	220	64	0.3	5.44
$[ZnL^4(NCS)_2]$	White	44.7	4.6	15.1	14.1	44.7	4.6	15.3	14.0 [c]	215	60		
$[CdL^4(NCS)_2]$	White	40.5	4.2	13.8	12.7	40.5	4.2	13.9	12.7	223	113		
$[CdL^4Br]Br{\cdot}H_2O$	White	31.6	4.2	7.4	28.4	31.8	4.1	7.4	28.3	240	136		
$[CdL^4Br]_n[Cd_2Br_6]_{n/2}$	White	22.2	2.8	5.0	39.0	22.0	2.6	5.1	39.0	783	214		

[a] For 10^{-3} mol dm^{-3} solutions at 25 °C. [b] At 20 °C, corrected for diamagnetism of ligands. [c] Sulphur analysis.

Analytical, magnetic, and electrical-conductance data are given in Table 1, and i.r. and electronic spectral data in Table 2. The formulations given for the complexes in the first columns of the Tables are justified, where possible, in the discussion below. The complexes are, for the most part, moderately soluble in water and in a variety of polar organic solvents. They appear to be indefinitely stable in the solid state and also in solution apart from exchange of axial ligand with solvent in most cases.

The evidence for the formation of the macrocycle comes from (*i*) the *X*-ray structure determination of $[MnL^4(NCS)_2]$ (see later), (*ii*) the i.r. spectra of the complexes which in all cases showed a strong band at *ca.* 1 650 cm^{-1} attributable to the imino-linkage C=N but no absorption at *ca.* 1 700 cm^{-1} nor at 3 100—3 300 cm^{-1} which would occur if residual carbonyl or primary amine groups were present, and (*iii*) the observation of a peak in the mass spectra of the cadmium(II) complexes (the spectrum of the perchlorate was not measured) at *m/e* 275 corresponding to $[L^4]^+$; no peaks of significant intensity were observed at higher *m/e* values. The i.r. spectra are all very similar to one another when allowance is made for the absorption due to axial ligands and/or counter ions. The spectra are also similar in important respects to those of the N_5 macrocycle L^1.[1,2,5]

Assuming that the macrocycle has a planar conformation in all cases as found directly for $[MnL^4(NCS)_2]$ and as previously shown, also by *X*-ray analysis, for complexes of Fe^{III},[1] Fe^{II},[3] Zn^{II},[4] and Mg^{II} [6] with L^1, it remains to establish the nature of the axial ligands in the various complexes. First, it may be noted that $[CdL^4(NCS)_2]$ is isomorphous with $[MnL^4(NCS)_2]$ and therefore presumably has a closely similar pentagonal-bipyramidal structure (see later) with *N*-bonded $[NCS]^-$ ions in the axial positions. The *X*-ray powder-diffraction patterns of the iron(II) and zinc(II) dithiocyanates are identical to one another but different from those of the complexes of Mn^{II} and Cd^{II}. However, despite the different unit cells in the iron(II) and zinc(II) complexes, the near identity of the i.r. spectra of all the four dithiocyanates, as well as the close similarity in properties to those of corresponding complexes of L^1 whose structures have been solved by *X*-ray methods,[3,4] is strong evidence for a common pentagonal-bipyramidal structure in all cases.

The complexes $[FeL^4X_2][ClO_4]$ (X = Cl or NCS) are 1 : 1 electrolytes in acetonitrile. In water the chloride is a 1 : 3 electrolyte indicating replacement of Cl^- ion by water. This replacement is incomplete in aqueous 10^{-3} mol dm^{-3} solutions of the thiocyanate. These conclusions are supported by the electronic spectra (Table 2) which are essentially the same in the solid state and in acetonitrile, whereas in water the strong charge-transfer band of the chloride at *ca.* 26 000 cm^{-1} is absent and that of the thiocyanate at *ca.* 18 000 cm^{-1} much diminished in intensity. In both complexes the $[ClO_4]^-$ is unco-ordinated as judged by the unsplit nature of the $[ClO_4]^-$ ν_3 and ν_4 bands at *ca.* 1 085 and *ca.* 620 cm^{-1} in the mull i.r. spectra. The asymmetric stretch ν_{asym} of the $[NCS]^-$ ion occurs as a strong band at 2 030 cm^{-1} in accord with co-ordination *via* the nitrogen atom; the positions of the symmetric stretch ν_{sym}, where identified, and the $[NCS]^-$ bending mode δ are also consistent with this conclusion.

In aqueous solution the series of bivalent metal-ion complexes $[ML^4(NCS)_2]$ (M = Mn, Fe, Zn, or Cd) are all

---

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

[9] D. Wester and G. J. Palenik, *J. Amer. Chem. Soc.*, 1973, **95**, 6505; 1974, **96**, 7565; U. Rychlewska, R. C. Palenik, R. W. King, and G. J. Palenik, *J.C.S. Chem. Comm.*, 1975, 799.

1 : 2 electrolytes and all show virtually the same electronic spectrum in the u.v. region (above *ca.* 30 000 cm^{-1}). We therefore propose that in aqueous solution the complexes exist as the seven-co-ordinate diaqua-cations $[ML^4(OH_2)_2]^{2+}$. In addition to the strong bands occurring above 30 000 cm^{-1}, attributable to the co-ordinated macrocycle, the complexes of Fe^{II} and Mn^{II} also exhibit a band at lower energy. These appear more strongly in the solid state. For the iron(II) complex this occurs at 14 400 cm^{-1} while for the manganese(II) complex a band occurs at *ca.* 24 000 cm^{-1} as a shoulder on the side of the more intensive u.v. absorption. We previously adduced evidence in the case of the N_5 macrocycles that these bands arise from metal-to-macrocycle charge transfer having its origin in overlap of metal d_{xz},d_{yz} orbitals with a low-lying p_π* antibonding orbital of the unsaturated segment of the macrocycle.[2] In 10^{-3} mol dm^{-3} acetonitrile solution all the four complexes show electrolytic behaviour intermediate between that expected for a 1 : 1 electrolyte and a non-electrolyte and it is concluded that the dissociation equilibrium (1) occurs in these solutions. The positions of the charge-transfer bands of the iron(II) and manganese(II) complexes are at higher wavenumbers, *i.e.* relative to their positions in the

$$[ML^4(NCS)_2] + MeCN \rightleftharpoons [ML^4(NCS)(NCMe)]^+ + [NCS]^- \quad (1)$$

solid-state electronic spectra. There can be no doubt that all the four dithiocyanates have neutral seven-co-ordinate structures in the solid state, as confirmed by *X*-ray diffraction analysis for one member of the series.

TABLE 2

I.r. (cm^{-1}) [a] and electronic spectral data for the complexes

		[NCS]$^-$				Electronic spectra [b]		
Complex	ν(C=N)	ν_{asym}	ν_{sym}	δ	[ClO$_4$]$^-$	Solid [c]	Water [d]	MeCN [c]
$[MnL^4(NCS)_2]$	1 652s	2 058s, 2 075 (sh)	798w	482m		24.0 (sh)	42.0 (18 000), 32.8 (4 600), *ca.* 28.0 (sh) (170)	27.5 (sh) (300), 25.4 (140)
$[FeL^4Cl_2][FeCl_4]$	1 655s							
$[FeL^4Cl_2][ClO_4]$	1 650s				1 085vs, 620s	26.2	40.6 (21 000), 36.0 (7 100)	26.0 (5 200)
$[FeL^4(NCS)_2][ClO_4]$	1 650s	2 030s		500m	1 085vs, 622s	18.0	40.6 (20 000), 36.1 (6 900), 20.4 (2 800)	18.2 (14 500)
$[FeL^4(NCS)_2]$	1 640s	2 075s	795w	487m		14.4	42.9 (19 000), 34.0 (4 200), 16.4 (680)	15.2 (710)
$[ZnL^4(NCS)_2]$	1 658s	2 060s	795w	482w		*e*	42.4 (17 000), 34.5 (4 500),	*e*
$[CdL^4(NCS)_2]$	1 652	2 045		475, 488w		*ca.* 29.0 (sh), *ca.* 25.0 (sh)	42.0 (17 000), 34.2 (5 000)	*ca.* 28.5 (sh),
$[CdL^4Br]Br\cdot H_2O$	1 652s, 1 660(sh)					*ca.* 25.5 (sh)	41.8 (16 500), 34.1 (6 000)	*ca.* 28.5 (sh) (170)
$[CdL^4Br]_n[Cd_2Br_6]_{n/2}$	1 650s					*ca.* 25.5 (sh)	41.9 (15 500), 34.0 (4 000)	*e*

[a] s = Strong, vs = very strong, m = medium, and w = weak. [b] In 10^3 cm^{-1}; ε/dm^3 mol^{-1} cm^{-1} in parentheses for solutions. [c] Measured in the range 5 000—30 000 cm^{-1}. [d] Measured in the range 5 000—50 000 cm^{-1}. [e] The spectra showed no absorption other than the tail of the strong u.v. band at *ca.* 34 000 cm^{-1}.

The structure of the complexes of $CdBr_2$ is much less certain. In water $[CdL^4Br_2]\cdot H_2O$ and the complex of empirical formula $[(CdBr_2)_2L^4]$ show the same electronic spectrum as $[CdL^4(NCS)_2]$ in the same solvent and therefore probably exist as $[CdL^4(OH_2)_2]^{2+}$. Consistent with this the former complex is a 1 : 2 electrolyte in water. The latter complex has an equivalent conductance of nearly 800 S cm^2 mol^{-1} calculated on the formula $[(CdBr_2)_4L^4_2]$. By analogy with $[CdL^2Br]_n[CdBr_4]_{n/2}$ known from a single-crystal *X*-ray study [10] to contain a seven co-ordinate, bromide-bridged, polymeric cation, we suggest a similar structure for both $[CdL^4Br]_n[Br]_n$ and $[CdL^4Br]_n[Cd_2Br_6]_{n/2}$, the two complexes differing only in the nature of the counter ion. While small differences in the electronic spectra of the cadmium(II) complexes were noted they are not sufficiently clear either to support the above proposals on structure or to detract from them.

Magnetic Properties of the Complexes of Mn^{II}, Fe^{III}, *and* Fe^{II}.—Room temperature (293 K) magnetic moments of the complexes $[MnL^4(NCS)_2]$, $[FeL^4Cl_2][ClO_4]$, and $[FeL^4(NCS)_2][ClO_4]$ are close to the value of 5.92 B.M. predicted for high-spin d^5 systems.* The moment of the iron(II) complex is 5.44 B.M. at 293 K falling to 5.31 B.M. at 93 K, consistent with a $^5E_1''$ ground state (in D_{5h} symmetry). The orbital contribution, which seems quite large, could arise from the degeneracy of the d_{xz} and d_{yz} orbitals.

Mössbauer Spectra of the Iron Complexes.—Isomer shifts (relative to natural iron) and quadrupole splittings, where observed, are given in Table 3. At 293 K the complex $[FeL^4Cl_2][ClO_4]$ gave a doublet with small quadrupole splitting. At 77 K the spectrum appeared as a broadened single peak with a marked asymmetry towards lower velocities. The complex $[FeL^4(NCS)_2]$-$[ClO_4]$ also gave a broadened singlet with asymmetry on the low-velocity side at both 293 and 77 K. We have

---

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

[10] S. M. Nelson, S. G. McFall, M. G. B. Drew, A. H. bin Othman, and N. B. Mason, *J.C.S. Chem. Comm.*, 1977, 167.

noted similar effects previously[11] for the series of pentagonal-bipyramidal iron(III) complexes of the macrocycle L^1. A more detailed study of these complexes at 293, 77, and 4.2 K showed that the temperature-dependent spectra are due to paramagnetic-relaxation effects. For high-spin iron(III) compounds with axial symmetry the effective magnetic field at the nucleus splits the nuclear $\pm\frac{3}{2}$ state more than the $\pm\frac{1}{2}$ state.[12] If the higher-energy line is broadened the electric-field gradient (e.f.g.) is positive and *vice versa*. In the L^1 series of complexes it was shown[11] that the zero-field splitting changes sign as the nature of the axial ligand is varied in the sequence I^-, Br^-, Cl^-, $[N_3]^-$, $[NCS]^-$, being positive for I^-, Br^-, and Cl^- and negative for $[N_3]^-$ and $[NCS]^-$. For the complexes of the L^4 macrocycle considered here the data, while less complete, are sufficient to show that the sign of the zero-field splitting is negative for both the chloride and the thiocyanate. This result is consistent with the N_3O_2 macrocycle exercising a weaker equatorial ligand field than the N_5 analogue.

TABLE 3

Mössbauer data (mm s^{-1}) for the iron complexes

Complex	Isomer shift [a]		Quadrupole splitting	
	293	77 K	293	77 K
$[FeL^4Cl_2][ClO_4]$	0.43	0.53	0.40	*b*
$[FeL^4(NCS)_2][ClO_4]$	0.58	0.98	*b*	*b*
$[FeL^4(NCS)_2]$	1.00	1.03	2.56	3.06

[a] Relative to natural iron. [b] Splitting not resolved but signal asymmetric to lower velocities.

TABLE 4

Cyclic-voltammetry data for the iron and manganese complexes in acetonitrile. The supporting electrolyte was 0.1 mol dm^{-3} $[NEt_4][ClO_4]$ unless otherwise stated; potentials in V *versus* the s.c.e.; sweep rate 0.08 V s^{-1}

Complex	First redox step			Second redox step		
	E_{p_c}'	E_{p_a}'	$E_0' = \frac{1}{2}(E_{p_c}' - E_{p_a}')$	E_{p_c}''	E_{p_a}''	$E_0'' = \frac{1}{2}(E_{p_c}'' - E_{p_a}'')$
$[FeL^4Cl_2][ClO_4]$	0.06	−0.05		−1.30	−1.20	−1.25
$[FeL^4Cl_2][ClO_4]$ *	0.04	−0.02	0.01	−1.30	−1.20	−1.25
$[FeL^4(NCS)_2][ClO_4]$	0.24	0.30	0.27	−1.25	−1.17	−1.21
$[MnL^4(NCS)_2]$	*ca.* 0.30	*ca.* 0.75		−1.37	−1.23	−1.30

* The supporting electrolyte was 0.1 mol dm^{-3} $[NEt_4]Cl$.

The isomer shifts and quadrupole splittings found for $[FeL^4(NCS)_2]$ at 293 and 77 K confirm the $S = 2$ ground state for the metal ion in this complex.[13]

Electrochemical Measurements.—Cyclic voltammetry carried out on 10^{-3} mol dm^{-3} solutions of $[FeL^4X_2][ClO_4]$ (X = Cl or NCS) in acetonitrile using 10^{-1} mol dm^{-3} $[NEt_4][ClO_4]$ as supporting electrolyte revealed two reduction waves (see Table 4). Both reductions were reversible in the case of X = NCS as judged by the small separation of the peak potentials of the cathodic and anodic waves, $E_{pc} - E_{pa}$ being close to the theoretical value[14] of 0.058 V for a one-electron process. Small departures from reversible behaviour were observed for the more positive wave (E_0') in the case of X = Cl. However, this wave became reversible when $[NEt_4]Cl$ was used as supporting electrolyte in order to suppress slight dissociation of the $[FeL^4Cl_2]^+$ cation. Experiments in which the sweep rate was varied established that the reduced species formed during the reduction at the more negative potential (E_0'') had lifetimes of less than 5 s. The more positive reduction is ascribed to addition of an electron to the iron(III) ion and the more negative reduction to addition of an electron to a low-lying antibonding orbital of the macrocycle. Comparison of the present results with those reported previously[2] for the L^1 macrocycle shows that the introduction of the oxygen atoms causes a displacement of both potentials to more positive values, the effect being greater (0.34 V) for the more positive redox process. Thus, the oxygen-containing ligand is appreciably more effective in stabilising the lower oxidation state of the metal. This is seen also in the storage stability in air of the two series of complexes, those of the N_3O_2 macrocycle being stable for long periods in solution whereas those of the N_5 analogue are converted into iron(III) species within minutes.

In Part 3[2] it was noted that there is a correlation in the magnitudes of the parameter, $F(E_0' - E_0'')$, the free-energy change associated with the removal of an electron from the metal in $[FeLX_2]$ (L = macrocycle) and the addition of an electron to the macrocycle in the same complex, with the energy of the charge-transfer band occurring in the visible spectrum of the iron(II) complex. This correlation is extended by the data obtained for $[FeL^4(NCS)_2]$. Thus, replacement of L^1 by L^4 causes $F(E_0' - E_0'')$ to increase from 127 to 143 kJ mol^{-1} and the energy of the charge-transfer band to increase from 163 to 173 kJ mol^{-1}. The reason for the greater energy of the electron transfer, common to both processes, in the case of the oxygen-containing complex probably lies in the greater electronegativity of oxygen over nitrogen which tends to resist the back co-ordination of electron density from the metal to the unsaturated segment of the macrocycle.

Cyclic voltammetry of 10^{-3} mol dm^{-3} solutions of $[MnL^4(NCS)_2]$ in acetonitrile also revealed two redox waves, one at 0.3—0.7 V and another at −1.30 V *versus* the standard calomel electrode (s.c.e.). The profile of the more positive wave, which was not reversible, suggested that it might be composed of two overlapping

---

[11] F. A. Deeney and S. M. Nelson, *J. Phys. and Chem. Solids*, 1973, **34**, 277.

[12] T. H. Moss, A. J. Bearden, and W. S. Caughey, *J. Chem. Phys.*, 1969, **51**, 2624.

[13] N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' Chapman and Hall, London, 1971.

[14] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.

waves. Since separate experiments showed that free $[NCS]^-$ ion (as Na[NCS]) in acetonitrile gives a reversible wave at 0.53 V *versus* the s.c.e. and since the conductance value for $[MnL^4(NCS)_2]$ in the same solvent indicates partial dissociation of $[NCS]^-$ ion, it seems likely that two redox processes are occurring at about the same potential, one due to the Mn^{II}–Mn^{III} couple and another due to $2[NCS]^-$–$(NCS)_2$. The peaks at 0.5—0.6 V of the cyclic voltammogram of the complex wave were enhanced by the addition of Na[NCS]. The reversible wave at −1.29 V is close in potential to that occurring in solutions of the corresponding iron complex (1—1.30 V) and is probably also due to a redox process involving the macrocyclic ligand. If our conclusions are correct the parameter $F(E_0' - E_0'')$ is appreciably greater for the complex of Mn^{II} than for Fe^{II}, an observation consistent with the higher energy of the metal–macrocycle charge-transfer absorption occurring in the electronic spectrum of the manganese(II) complex.

Crystal and Molecular Structure Determination of $[MnL^4(NCS)_2]$.—*Crystal data.* $C_{17}H_{21}MnN_5O_2S_2$, $M = 446.9$, Triclinic, $a = 13.834(4)$, $b = 7.403\ (2)$, $c = 10.645\ (3)$ Å, $\alpha = 91.0(1)$, $\beta = 71.3(1)$, $\gamma = 100.8(1)°$, $U = 1\ 013.3$ Å^3, $D_c = 1.46$, $Z = 2$, $D_m = 1.46(2)$ g cm^{-3}. Mo-K_α radiation, $\lambda = 0.710\ 7$ Å, $\mu = 9.03$ cm^{-1}. Space group confirmed as $P\bar{1}$ from the successful structure determination.

A crystal with dimensions *ca.* 0.25 × 0.50 × 0.6 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* several high-angle reflections). It was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered *X*-radiation was used to measure 1 904 independent reflections with $2\theta < 40°$ by the stationary-crystal–stationary-counter method. Backgrounds were taken for those reflections whose counts were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from a plot of backgrounds as a function of 2θ. Standard reflections measured at regular intervals during the course of the experiment showed no significant change in intensities. The standard deviation $\sigma(I)$ of the reflections was taken to be $[I + 2E + (0.03I^2)]^{\frac{1}{2}}$ where E is the estimated background of the reflections. 1 427 Reflections with $I > \sigma(I)$ were used in subsequent calculations. No extinction or absorption corrections were applied.

The positions of the Mn atoms were determined from a Patterson function and Fourier syntheses were used to determine the positions of the remaining atoms. The non-methyl hydrogen-atom positions were calculated assuming tetrahedral or trigonal positions and included in the refinement with isotropic thermal parameters. The structure was refined by full-matrix least squares, all the atoms being anisotropic except hydrogen, to R 0.075. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of values of F_o and $\sin\theta/\lambda$, was $w^{\frac{1}{2}} = 1$ for $F_o < 20$ and $w^{\frac{1}{2}} = 20/F_o$ for $F_o > 20$. Calculations were made on a C.D.C. computer at the University of London Computer Centre using the *X*-ray set of programs.[15] Atomic scattering factors were taken from ref. 16. The anisotropic temperature parameters are defined as

$$\exp\left(-2\pi^2 \sum_i\sum_j h_i h_j b_i b_j U_{ij}\right)\ (i, j = 1—3)$$

where b_i is the ith reciprocal cell dimension. The isotropic thermal parameter is $\exp[-8\pi^2 U \sin^2\theta/\lambda^2]$. The 477 zero reflections showed no large discrepancies. In the final cycle of refinement no shifts were $>0.4\sigma$. The final list of positions is given in Table 5, bond lengths and angles in Table 6. Structure factors and thermal parameters are given in Supplementary Publication No. SUP 22039 (7 pp.).*

TABLE 5

Atomic co-ordinates ($\times 10^4$ for Mn, N, C, S, O; $\times 10^3$ for H) with estimated standard deviations in parentheses

Atom	x	y	z
Mn	2 096(1)	1 579(2)	1 774(2)
N(1)	1 841(7)	3 881(14)	0 632(13)
C(1)	2 017(9)	4 116(16)	−0 492(16)
S(1)	2 234(3)	4 467(6)	−2 042(4)
N(2)	2 134(8)	−0 940(15)	2 941(12)
C(2)	2 599(9)	−0 967(16)	3 664(13)
S(2)	3 232(3)	−0 965(6)	4 680(4)
O(3)	0 525(5)	0 112(11)	1 617(7)
C(4)	0 688(9)	−1 527(17)	0 873(16)
C(5)	1 517(9)	−0 929(15)	−0 372(12)
N(6)	2 442(7)	0 046(12)	−0 107(10)
C(7)	3 346(9)	0 440(14)	−0 963(11)
C(8)	4 174(8)	1 555(14)	−0 449(10)
N(9)	3 798(6)	2 141(11)	0 769(9)
C(10)	4 430(7)	3 083(14)	1 387(11)
C(11)	3 881(9)	3 665(15)	2 734(11)
N(12)	2 886(8)	3 432(12)	3 003(9)
C(13)	2 206(10)	3 848(17)	4 304(11)
C(14)	1 138(11)	3 781(17)	4 209(12)
O(15)	0 859(6)	2 049(12)	3 685(8)
C(16)	−0 166(10)	1 585(22)	3 588(15)
C(17)	−0 228(12)	−0 154(26)	2 870(17)
C(20)	3 645(11)	−0 043(20)	−2 413(12)
C(21)	5 222(8)	1 867(15)	−1 105(13)
C(22)	5 912(10)	2 880(16)	−0 509(13)
C(23)	5 486(10)	3 445(15)	0 780(12)
C(24)	4 488(10)	4 402(18)	3 647(14)
H(51)	132(7)	−013(13)	−103(9)
H(52)	170(7)	−167(12)	−081(9)
H(41)	−015(11)	−187(20)	081(13)
H(42)	093(9)	−257(15)	136(11)
H(131)	248(9)	517(17)	433(11)
H(132)	207(7)	283(12)	513(8)
H(141)	129(6)	499(11)	344(8)
H(142)	064(7)	382(13)	511(9)
H(161)	007(9)	305(17)	279(12)
H(162)	−086(7)	141(11)	462(9)
H(171)	−085(12)	−040(19)	276(13)
H(172)	−018(7)	−103(14)	348(10)
H(21)	546(8)	154(14)	−207(11)
H(22)	666(11)	331(18)	−106(13)
H(23)	608(10)	415(18)	095(12)

Discussion of the structure. The structure of $[MnL^4$-

---

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

[15] '*X*-Ray' system of programs, ed. J. M. Stewart, University of Maryland, Technical Report TR 192, July 1970.

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

(NCS)$_2$], (1), is illustrated in Figure 1 together with the numbering scheme. The metal ion is in a pentagonal-bipyramidal (p.b.) environment with the macrocycle occupying the pentagonal girdle and the thiocyanate nitrogen atoms in the axial positions. The metal atom and the five donor atoms of the macrocycle are almost coplanar, the maximum deviation of a contributing atom from the MnN$_3$O$_2$ least-squares plane being 0.08 Å (Table 7). The conformation of the macrocycle in (1) may be compared with that of the N$_5$ macrocycle L^1 which has the same number of member atoms. (Much greater distortion from planarity occurs in complexes of larger N$_5$ macrocycles L^2 and L^3 which have been discussed elsewhere.[1,3,5])

TABLE 6

Bond lengths (Å) and angles (°) * for (1)

Mn–N(1)	2.254 (13)	N(1)–Mn–N(2)	172.3(4)
Mn–N(2)	2.277 (13)	N(1)–Mn–O(3)	83.5(3)
Mn–O(3)	2.296 (8)	N(1)–Mn–N(6)	87.9(4)
Mn–N(6)	2.244 (9)	N(1)–Mn–N(9)	93.4(4)
Mn–N(9)	2.214 (8)	N(1)–Mn–N(12)	95.4(4)
Mn–N(12)	2.254 (10)	N(1)–Mn–O(15)	93.7(4)
Mn–O(15)	2.270 (7)	N(2)–Mn–O(3)	88.9(4)
N(1)–C(1)	1.151 (21)	N(2)–Mn–N(6)	90.6(4)
C(1)–S(1)	1.597 (17)	N(2)–Mn–N(9)	93.2(4)
Mn–N(1)–C(1)	130.4(10)	N(2)–Mn–N(12)	90.4(4)
N(1)–C(1)–S(1)	178.4(13)	N(2)–Mn–O(15)	83.4(4)
N(2)–C(2)	1.154 (21)	O(3)–Mn–N(6)	73.2(3)
C(2)–S(2)	1.594 (16)	O(3)–Mn–N(9)	144.6(3)
Mn–N(2)–C(2)	126.1(9)	O(3)–Mn–N(12)	145.1(3)
N(2)–C(2)–S(2)	178.7(13)	O(3)–Mn–O(15)	73.2(3)
O(3)–C(4)	1.450 (16)	N(6)–Mn–N(9)	71.5(3)
C(4)–C(5)	1.457 (16)	N(6)–Mn–N(12)	141.7(3)
C(5)–N(6)	1.454 (16)	N(6)–Mn–O(15)	145.9(3)
N(6)–C(7)	1.273 (13)	N(9)–Mn–N(12)	70.2(3)
C(7)–C(8)	1.525 (17)	N(9)–Mn–O(15)	142.2(3)
C(7)–C(20)	1.519 (17)	N(12)–Mn–O(15)	72.1(3)
C(8)–N(9)	1.331 (13)	N(12)–C(13)	1.469 (13)
C(8)–C(21)	1.370 (14)	C(13)–C(14)	1.505 (22)
N(9)–C(10)	1.343 (15)	C(14)–O(15)	1.425 (16)
C(10)–C(23)	1.371 (15)	O(15)–C(16)	1.431(17)
C(10)–C(11)	1.490 (15)	C(16)–C(17)	1.488 (24)
C(11)–C(24)	1.510 (21)	C(17)–O(3)	1.395 (16)
C(11)–N(12)	1.290 (17)	C(21)–C(22)	1.407 (19)
		C(22)–C(23)	1.399 (17)
C(4)–O(3)–C(17)	116.2(10)	N(9)–C(10)–C(23)	120.6(10)
Mn–O(3)–C(4)	108.1(6)	N(9)–C(10)–C(11)	114.4(9)
Mn–O(3)–C(17)	110.4(9)	C(11)–C(10)–C(23)	125.0(12)
O(3)–C(4)–C(5)	106.6(9)	C(10)–C(11)–N(12)	113.5(11)
C(4)–C(5)–N(6)	110.1(11)	Mn–N(12)–C(11)	120.1(7)
C(5)–N(6)–C(7)	125.1(10)	Mn–N(12)–C(13)	115.6(7)
Mn–N(6)–C(5)	113.7(6)	C(11)–N(12)–C(13)	121.6(11)
Mn–N(6)–C(7)	118.9(8)	N(12)–C(13)–C(14)	108.1(10)
C(8)–C(7)–N(6)	114.8(10)	C(13)–C(14)–O(15)	106.4(11)
C(8)–C(7)–C(20)	118.9(10)	Mn–O(15)–C(14)	111.8(6)
N(6)–C(7)–C(20)	126.3(12)	Mn–O(15)–C(16)	112.1(8)
C(7)–C(8)–N(9)	113.9(8)	C(14)–O(15)–C(16)	117.4(11)
C(7)–C(8)–C(21)	125.1(9)	O(15)–C(16)–C(17)	107.4(12)
N(9)–C(8)–C(21)	120.8(11)	C(16)–C(17)–O(3)	109.3(12)
Mn–N(9)–C(10)	119.7(6)	C(21)–C(22)–C(23)	117.4(10)
Mn–N(9)–C(8)	118.9(7)	C(22)–C(23)–C(10)	119.9(12)
C(8)–N(9)–C(10)	121.4(8)	C(22)–C(21)–C(8)	119.8(11)

* C–H distances are satisfactory.

Complex (1), like [FeL^1(NCS)$_2$], (2), and [FeL^1(NCS)$_2$]$^+$, (3), has a C_2 distortion from the p.b., the maximum deviation of an atom from the ML$_5$ girdle plane being slightly greater in (2) and (3), at 0.12 and 0.10 Å, respectively. However, there are significant differences in the deviations of the other atoms from this plane compared to those in (2) and (3). The most striking is that C(20) and C(24) are 0.53 and −0.61 Å from the plane compared to a mean of 0.08 Å in (2) and (3). This is for the most part due to the pyridine ring being rotated about the Mn–N(9) axis such that it intersects the MnN$_3$O$_2$ plane at an angle of 5.7°; in (2) and (3) the corresponding angles are 2.8 and 1.7°, respectively. This may be due to a greater difficulty in accommodating the larger

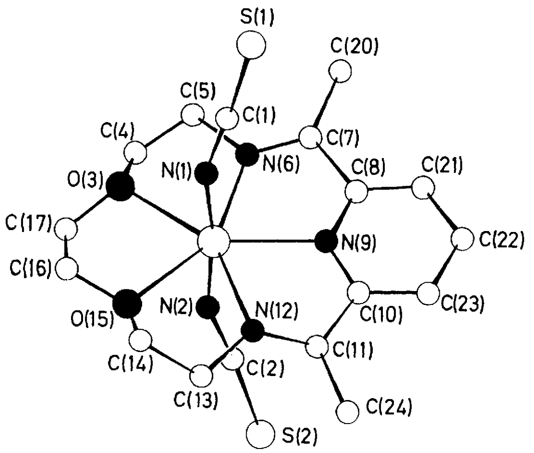


FIGURE 1 Structure of complex (1) and the atom numbering scheme

TABLE 7

Least-squares planes in the form $Ax + By + Cz = D$, where x,y,z are the crystallographic co-ordinates of the atoms. 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)	11.93	2.43	2.28	3.29
[Mn −0.00, N(1) −0.00, C(1) 0.01, S(1) −0.00, N(6) −0.39, C(7) 0.59, C(14) −0.05, O(15) −0.92]				
Plane 2: Mn, N(2), C(2), S(2)	8.68	−2.40	−5.50	0.46
[Mn 0.00, N(2) −0.00, C(2) 0.01, S(2) −0.00, O(3) −0.92, C(4) 0.02, C(11) 0.52, N(12) −0.43]				
Plane 3: Mn, N(3), N(6), N(9), N(12), O(15)	−5.60	6.28	−5.72	−1.22
[Mn 0.02, O(3) 0.07, N(6) −0.06, N(9) −0.00, N(12) 0.04, O(15) −0.08, C(7) 0.17, C(8) 0.12, C(10) −0.12, C(11) −0.21, C(13) −0.06, C(20) 0.53, C(21) 0.10, C(22) 0.01, C(23) −0.13, C(24) −0.61]				
Plane 4: N(9), C(8), C(10), C(21), C(22), C(23)	−5.17	6.64	−4.82	−0.91
[C(8) 0.01, N(9) 0.00, C(10) 0.00, C(21) −0.01, C(22) 0.01, C(23) −0.01]				
Plane 5: Mn, O(3), N(6)	−5.17	6.18	−6.00	−1.17
[C(4) −0.65, C(5) 0.03]				
Plane (6): Mn, O(15), N(12)	−6.17	6.31	−5.54	−1.28
[C(14) 0.63, C(13) −0.04]				
Plane 7: Mn, O(3), O(15)	−5.54	6.49	−5.18	−1.06
[C(16) 0.32, C(17) −0.41]				

Angle between planes 3 and 4: 5.7°.

manganese(II) ion in the macrocycle 'hole.' The equatorial Mn–N distances [2.214(8) Å] for the unique Mn–N(9) bond, with 2.244(9) and 2.254(10) Å for Mn–N(6) and Mn–N(12), are similar to those found for (2) and (3) demonstrating that metal–N_{eq} bonds in these complexes, in contrast to metal–N_{ax} bonds (see below), are not particularly sensitive to metal-ion size. Predictably the bonds in (1) are shorter than in the much more distorted complex $[MnL^3(NCS)_2]$ [5] of the larger macrocycle (2.311—2.429 Å). As found for other pentagonal-bipyramidal complexes of macrocyclic ligands, and particularly for the iron(II) complex (2),[3] the metal–N(9) distance is the shortest. In the seven-co-ordinate manganese(II) complex of a closely related macrocycle described by Alcock *et al.*[8] the Mn–N_{eq} distances are 2.22—2.30 Å, while in the seven-co-ordinate complex ion $[Mn(edta)(OH_2)]^{2-}$ (edta = ethylenediaminetetra-acetate) the bonds are longer (2.377 Å).[17] The Mn–O bonds in (1) [2.296(8) and 2.270(7) Å] are similar in length to the metal–N(3) and metal–N(15) bonds in (2) and (3). This contrasts with the situation in $[Mn(edta)(OH_2)]^{2-}$ where the Mn–O distances (2.212—2.261 Å) differ considerably from the Mn–N distance of 2.377 Å. The absence of notable response in the metal–donor atom distance in these complexes to alteration in the nature and charge of the metal or to change in donor atom from oxygen to (saturated) nitrogen is no doubt due to the cyclic nature of the ligand.

In contrast, metal–N_{ax} bond lengths in (1), (2), and (3) (2.265, 2.123, and 1.995 Å, respectively) vary in accord with the radii of the Mn^{2+}, Fe^{2+}, and Fe^{3+} ions. In $[MnL^3(NCS)_2]$ the Mn–N_{ax} distances are 2.174(7) and 2.294(7) Å. The shortness of the bond to the NCS ligand positioned on the open face of the folded macrocycle can be related to the fact that it is in a less sterically crowded site.[5]

The Mn–N–C bond angles in (1) are 130.4(10)° for Mn–N(1)–C(1) and 126.1(9)° for Mn–N(2)–C(2). The latter is the smallest metal–N–C angle yet observed in isothiocyanato-complexes, being *ca.* 3° smaller than the hitherto smallest known angle.[18] There appears to be a wide variation in the magnitudes of the metal–N–C angles in these macrocyclic complexes, ranging from 126° in (1) to 167° in (3). It is worth considering whether the variation is due to intermolecular contacts. There are a number of short contacts in (1) less than 3.60 Å listed in SUP 22039, indicating efficient packing of the molecules (see also Figure 2). In particular, we note that the S(2) ··· C(20) (*x*, *y*, 1 + *z*) and C(1) ··· C(23) (1 − *x*, 1 − *y*, −*z*) contacts of 3.36 and 3.51 Å, respectively, would both decrease if the Mn–N–C angles were increased. A dependence of metal–N–C angles on intermolecular contacts has previously been noted.[19] Against this it must be argued that the molecule, with the NCS ligands included, has C_2 symmetry despite differences in packing environments in the triclinic unit cell, suggesting that there is an intramolecular (presumably electronic) explanation for the small Mn–N–C angles in this complex. Using our program for calculating molecular symmetry we find that the r.m.s. deviation of the present molecule of 27 atoms from a molecule of C_2 symmetry is 0.14 Å with only two atoms, C(16) and C(17), having deviations much above this value. Without these two atoms the r.m.s. deviation for the remaining 25 atoms is 0.07 Å.

Both Mn–O–C–C–N five-membered rings have the asymmetric puckered conformation with one carbon atom approximately planar with the Mn, O, N (0.03 and 0.04 Å) and the other *ca.* 0.64 Å from it on the opposite side; in (2) one atom is 0.10 Å and the other 0.69 Å from the same side and similar values are found in (3). [In

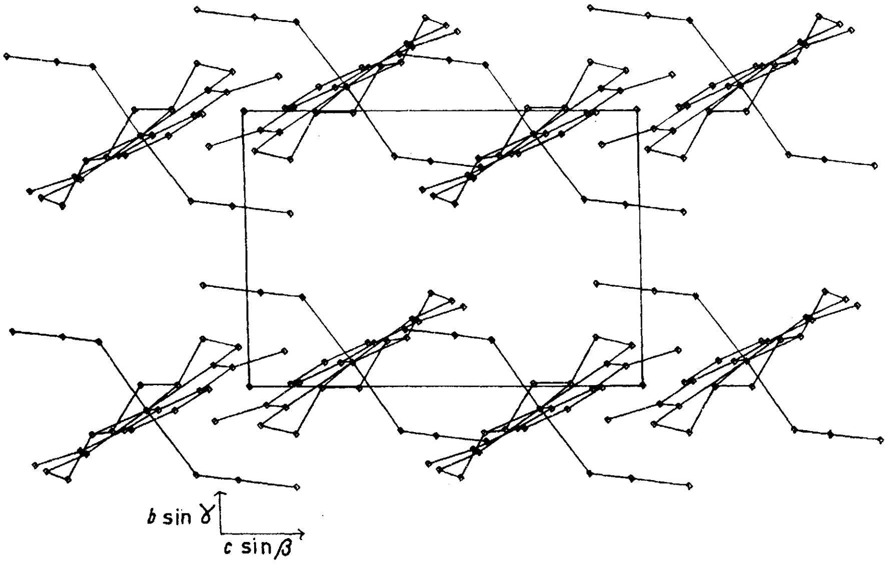


FIGURE 2 Unit cell of (1) in the *a* projection

---

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

[18] J. Korvenranta and A. Pajunen, *Suomen Kem.*, 1970, **B43**, 119.

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

all the structures, C(5) and C(13) are closest to the plane.] The remaining five-membered ring is more symmetrically puckered [C(16) 0.32, C(17) −0.41 Å from the Mn,O(3),-O(15) plane] than these two, but it is less symmetrical than in (2) and (3). Torsion angles for all the three five-membered rings are listed in Table 8.

TABLE 8

Dihedral angles (°) in (1)

Mn–O(3)–C(17)–C(16)	46.5
O(3)–C(17)–C(16)–O(15)	−59.2
C(17)–C(16)–O(15)–Mn	41.7
C(16)–O(15)–Mn–O(3)	−13.9
O(15)–Mn–O(3)–C(17)	−18.0
Mn–N(6)–C(5)–C(4)	−31.2
N(6)–C(5)–C(4)–O(3)	56.6
C(5)–C(4)–O(3)–Mn	−53.9
C(4)–O(3)–Mn–N(6)	28.2
O(3)–Mn–N(6)–C(5)	1.5
Mn–N(12)–C(13)–C(14)	−29.2
N(12)–C(13)–C(14)–O(15)	52.6
C(13)–C(14)–O(15)–Mn	−52.8
C(14)–O(15)–Mn–N(12)	28.4
O(15)–Mn–N(12)–C(13)	1.7

EXPERIMENTAL

Preparation of the Complexes.—2,6-Diacetylpyridine (Aldrich) was used as supplied, and 3,6-dioxaoctane-1,8-diamine was prepared by the method of Dwyer *et al.*[20]

Dichloro{2,3-*dimethyl*-6,9-*dioxa*-3,12,18-*triazabicyclo*-[12.3.1]*octadeca*-1(18),2,12,14,16-*pentaene*}*iron*(III) *Tetrachloroferrate*(III), $[FeL^4Cl_2][FeCl_4]$.—2,6-Diacetylpyridine (0.01 mol) in methanol (50 cm³) was added to $FeCl_2{\cdot}4H_2O$ (0.01 mol) in methanol (50 cm³) with stirring. To this blue solution was then added a solution of L^4 in methanol (50 cm³). The blue colour of the solution intensified. The solution was digested at 40—50 °C for at least 8 h and was then treated with an aqueous solution of $Na_2[S_2O_8]$ (3 g in 20 cm³). The colour changed from blue to brown. A solution of $FeCl_3$ (0.01 mol) and 11 mol dm⁻³ HCl (5 cm³) in methanol (50 cm³) was added and a yellow-green solid separated. This was washed with a little water, then ethanol, and was recrystallised to give yellow crystals in 43% yield (Found: C, 30.2; H, 3.6; Cl, 35.5; N, 7.0. $C_{15}H_{21}Cl_6Fe_2N_3O_2$ requires C, 30.0; H, 3.5; Cl, 35.5; N, 7.0%).

The complex $[FeL^4Cl_2][ClO_4]$ was prepared from the $[FeCl_4]^-$ salt above in 62% yield by addition of an excess of $Na[ClO_4]{\cdot}H_2O$ in acetone–methanol to an acetone solution of the $[FeCl_4]^-$ salt. The salt $[FeL^4(NCS)_2][ClO_4]$ was obtained from the dichloro-complex in 65% by addition of an aqueous solution of an excess of Na[NCS] containing a few drops of 60% $HClO_4$ to a hot aqueous solution of the dichloride. Red crystals separated on cooling. They were washed with cold water and recrystallised from warm aqueous methanol.

$[FeL^4(NCS)_2]$. 2,6-Diacetylpyridine (0.01 mol) and L^4 (0.01 mol) were added to a solution of $FeCl_2{\cdot}4H_2O$ (0.01 mol) and $Na_2[S_2O_4]$ (2 g) in methanol (200 cm³) and water (50 cm³). The reaction mixture was heated gently under reflux for 12 h and then filtered into a solution of Na[NCS] (20 g) and $Na_2[S_2O_4]$ (1 g) in water (100 cm³). The filtrate was reduced in volume to 100 cm³ by passing a stream of N_2 through it while maintaining it at 50 °C. Blue crystals of the product separated on cooling. They were further purified by recrystallisation from water containing a little $Na_2[S_2O_4]$. Yield 60%. This complex was also obtained in somewhat reduced yield by dithionite reduction of the iron(III) complexes in the presence of Na[NCS] as described previously for $[FeL^4(NCS)_2]$.

$[MnL^4(NCS)_2]$. 2,6-Diacetylpyridine (0.01 mol) in methanol (50 cm³) was added to a solution of $MnCl_2{\cdot}4H_2O$ (0.01 mol) in the same solvent (50 cm³). The mixed solutions were warmed to 50 °C and a solution of L^4 in methanol (50 cm³) was added with stirring. The mixture was digested for 4—8 h and then filtered. To the orange filtrate was added an excess of Na[NCS] in methanol. This gave an orange-brown solid on standing. It was recyrstallised from ethanol to give orange crystals in 55% yield.

$[ZnL^4(NCS)_2]$. 2,6-Diacetylpyridine (0.01 mol) in methanol (50 cm³) was added to $ZnBr_2$ (0.01 mol) in methanol (50 cm³). The solution was warmed to 50 °C and L^4 (0.01 mol) was added in methanol (25 cm³) followed by two drops of concentrated HBr. The solution was yellow at this stage. It was filtered and on standing the filtrate yielded a yellowish solid which was recrystallised from ethanol to give white crystals of the bromide complex in 40% yield. This complex was not investigated but was used to prepare the thiocyanato-complex by treatment of a methanolic solution with an excess of Na[NCS] in methanol. A cream precipitate formed on standing. This was separated and recrystallised from ethanol to give white crystals in 65% yield.

$[CdL^4Br]Br{\cdot}H_2O$. A solution of $CdBr_2{\cdot}4H_2O$ (0.01 mol) in aqueous methanol (300 cm³) was added to 2,6-diacetylpyridine (0.01 mol) in methanol (50 cm³) and warmed to 50 °C. A solution of L^4 (0.01 mol) in methanol (50 cm³) was then added. The reaction mixture was heated gently under reflux for 12 h and then filtered. The filtrate was reduced in volume at ambient temperature until the product started to separate. It was recrystallised from methanol.

$[CdL^4Br]_n[Cd_2Br_6]_{n/2}$. To a concentrated solution of the dibromide complex in methanol a solution of an excess of $CdBr_2{\cdot}4H_2O$ in methanol was added with vigorous stirring. A white solid separated immediately. Yield 85%. The complex $[CdL^4(NCS)_2]$ was prepared in a similar manner from the dibromide by addition of an excess of Na[NCS]. The crude product (65% yield) was recrystallised from methanol.

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

We thank the National University of Malaysia for a grant (to A. H. O.), the Department of Education of N. Ireland for postgraduate research awards (to S. G. McF. and P. D. A. McI.), and A. W. Johans for his assistance with the crystallographic investigations.

[6/1812 *Received, 27th September, 1976*]

---

[20] F. P. Dwyer, N. S. Gill, E. C. Gyarfas, and F. Lions, *J. Amer. Chem. Soc.*, 1953, **75**, 1526.