Six- and Seven-co-ordinate Manganese(II) Complexes of Schiff-base Ligands derived from the Condensation of 2,6-Diacetylpyridine with Ethanolamine (L^1) or Propanolamine (L^2); *X*-Ray Crystal Structures of $[MnL^1Cl_2]\cdot H_2O$ and $[\{MnL^2(NCS)_2\}_x]$†

Sally Brooker and Vickie McKee*
Department of Chemistry, University of Canterbury, Christchurch 1, New Zealand

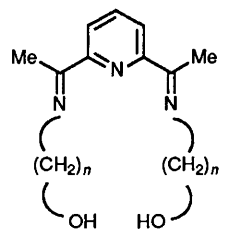
Four seven-co-ordinate manganese(II) complexes containing the ligand 2,6-bis[1-(2-hydroxyethylimino)ethyl]pyridine (L^1) have been synthesised by Schiff-base condensation of 2,6-diacetylpyridine and ethanolamine in the presence of Mn^{2+}. A six-co-ordinate complex containing 2,6-bis[1-(3-hydroxypropylimino)ethyl]pyridine (L^2) was obtained when the amine reagent was propanolamine. These complexes have been characterised by analytical, spectroscopic, magnetic, conductance, and single-crystal *X*-ray diffraction methods. Crystal data: $[MnL^1Cl_2]\cdot H_2O$ (**2**), triclinic, a = 8.322(6), b = 8.465(5), c = 12.935(9) Å, α = 72.82(5), β = 72.20(6), γ = 81.38(5)° $[\{MnL^2(NCS)_2\}_x]$ (**5**), monoclinic, a = 14.387(3), b = 10.045(2), c = 15.528(4) Å, and β = 115.10(2)°. The unusual seven-co-ordination observed is discussed in relation to the flexible non-cyclic ligands employed.

We have recently reported the structures of a number of tetramanganese(II) complexes[1–3] formed by the macrocyclic ligand L^3. In this paper we describe the structures and properties of a series of manganese(II) complexes of the related non-cyclic ligands L^1 and L^2.

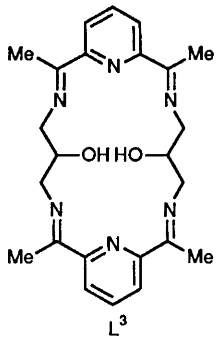
In the macrocyclic complexes the manganese atoms are all seven-co-ordinate, with the N_3O_2 donor set of the macrocycle forming a pentagonal plane and two exogenous donors as axial ligands; the same geometry is observed in the manganese(II) complexes of the small macrocycles L^4 (ref. 4) and L^5 (ref. 5) and the planar, resonance-stabilised ligands L^6 (ref. 6) and L^7(ref. 7). One aim of this work was to investigate whether seven-co-ordination would be maintained in the non-cyclic, flexible systems L^1 and L^2. Secondly, the tetramanganese(II) macrocyclic complexes are surprisingly stable towards oxidation and it was of interest to determine whether this would also be the case for the non-cyclic complexes. Finally, in the macrocyclic complexes the alcohol groups readily deprotonate and bridge two[3] or three[1,2] manganese atoms. Similar alkoxy bridging, leading to cluster formation, has been observed in transition-metal complexes of related ligands.[8] It therefore seemed possible that L^1 and L^2 would form alkoxy-bridged manganese clusters. Polynuclear, oxygen-bridged manganese complexes are currently under intense investigation as models[9] for the oxygen-evolving centre of Photosystem II in green plants.[10]

Results and Discussion

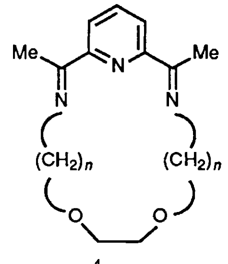
Synthesis.—Direct condensation of 2,6-diacetylpyridine (dap) with the appropriate amine in dry benzene has been used to prepare ligands of this type.[11] In the present cases, however this route was not very successful, largely due to the poor solubility of the aminoalcohols in benzene. Instead, the complexes were prepared directly, by refluxing dap and the aminoalcohol in methanol or ethanol in the presence of a manganese(II) salt. This route avoided potential difficulties due to the ready hydrolysis of the imine bond in the free ligands. The complexes investigated were $[MnL^1(H_2O)_2][ClO_4]_2$ (**1**), $[MnL^1Cl_2]\cdot H_2O$ (**2**), $[MnL^1(NCS)_2]$ (**3**), $[MnL^1(N_3)_2]$ (**4**), and $[\{MnL^2(NCS)_2\}_x]$ (**5**). No tendency towards air oxidation was noted for any of the complexes of L^1 in the solid state.



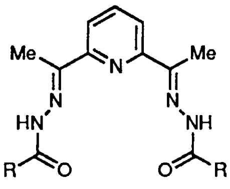
L^1 n = 2
L^2 n = 3



L^3



L^4 n = 2
L^5 n = 3



L^6 R = NH_2
L^7 R = Ph

Physicochemical Studies.—The i.r. spectra of the complexes were recorded as KBr discs. In each case formation of the Schiff-base linkage is confirmed by the replacement of the ν(C=O) stretch of dap at 1 700 cm^{-1} by an imine absorption at *ca.* 1 650 cm^{-1}. The spectra of (**3**)—(**5**) indicate the presence of co-ordinated thiocyanate or azide anions. For (**1**) the perchlorate asymmetric stretching vibration appears as a broad split band

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

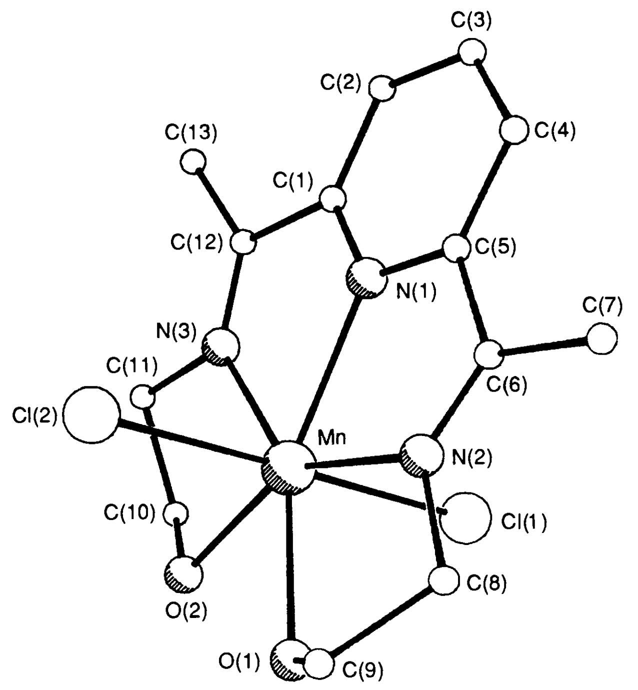

Figure 1. Perspective view of $[MnL^1Cl_2]$; the solvate water molecule has been omitted

Table 1. Selected interatomic distances (Å) and angles (°) for $[MnL^1Cl_2]$ (**2**)

Mn-N(1)	2.289(2)	Mn-N(2)	2.308(2)
Mn-O(1)	2.290(2)	Mn-O(2)	2.318(2)
Mn-N(3)	2.302(2)	Mn-Cl(1)	2.575(1)
Mn-Cl(2)	2.553(1)		
N(1)-Mn-N(2)	68.5(1)	N(1)-Mn-O(1)	139.3(1)
N(2)-Mn-O(1)	70.8(1)	N(1)-Mn-O(2)	140.8(1)
N(2)-Mn-O(2)	150.2(1)	O(1)-Mn-O(2)	79.8(1)
N(1)-Mn-N(3)	68.8(1)	N(2)-Mn-N(3)	137.2(1)
O(1)-Mn-N(3)	151.7(1)	O(2)-Mn-N(3)	72.5(1)
N(1)-Mn-Cl(1)	89.1(1)	N(2)-Mn-Cl(1)	89.8(1)
O(1)-Mn-Cl(1)	92.1(1)	O(2)-Mn-Cl(1)	86.1(1)
N(3)-Mn-Cl(1)	91.9(1)	N(1)-Mn-Cl(2)	91.8(1)
N(2)-Mn-Cl(2)	91.3(1)	O(1)-Mn-Cl(2)	87.7(1)
O(2)-Mn-Cl(2)	92.6(1)	N(3)-Mn-Cl(2)	87.6(1)
Cl(1)-Mn-Cl(2)	178.8(1)		

Table 2. Selected interatomic distances (Å) and angles (°) for $[\{MnL^2(NCS)_2\}_x]$ (**5**)

Mn-N(1)	2.219(2)	Mn-N(2)	2.280(1)
Mn-N(3)	2.304(2)	Mn-N(21)	2.130(2)
Mn-N(31)	2.167(2)	Mn-O(1′)	2.282(2)
N(1)-Mn-N(2)	71.0(1)	N(1)-Mn-N(3)	71.2(1)
N(2)-Mn-N(3)	142.0(1)	N(1)-Mn-N(21)	163.9(1)
N(2)-Mn-N(21)	97.7(1)	N(3)-Mn-N(21)	120.0(1)
N(1)-Mn-N(31)	98.3(1)	N(2)-Mn-N(31)	89.5(1)
N(3)-Mn-N(31)	92.8(1)	N(21)-Mn-N(31)	92.8(1)
N(1)-Mn-O(1′)	85.4(1)	N(2)-Mn-O(1′)	93.6(1)
N(3)-Mn-O(1′)	86.4(1)	N(21)-Mn-O(1′)	84.0(1)
N(31)-Mn-O(1′)	175.7(1)	Mn-N(21)-C(21)	162.5(2)
Mn-N(31)-C(31)	160.1(2)		

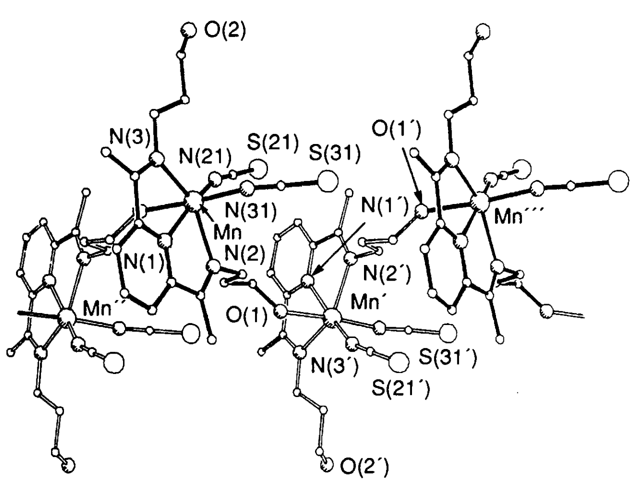

Figure 2. Perspective view of $[\{MnL^2(NCS)_2\}_x]$

at *ca.* 1 100 cm^{-1}; this is consistent with the presence of hydrogen bonding between the ionic perchlorate and the bound water molecule as has been confirmed by an *X*-ray crystal structure determination.

Room-temperature magnetic moments have been measured for each of the complexes. As might be expected, all the complexes show typical high-spin d^5 behaviour[12] with moments in the range 5.7—6.0 μ_B.

The complexes are all yellow or orange. Investigation of their electronic spectra in MeOH or dimethylformamide (dmf) solution reveals that the colour arises from a charge-transfer band at $\lambda_{max.}$ = 285—300 nm ($\varepsilon \approx 6\,000$ l mol^{-1} cm^{-1}) which tails into the visible region. Further intense bands occur at higher energy. Similar spectra are obtained for manganese(II) complexes of L^3.[13]

Conductivity measurements show that complexes (**3**), (**4**), and (**5**) are 1 : 1 electrolytes (in dmf, methanol, and dmf, respectively). Behaviour intermediate between that expected for a non-electrolyte and 1 : 1 electrolyte is observed for (**2**) in dmf. These results imply some dissociation of the anions on dissolution. As expected, complex (**1**) behaves as a 1 : 2 electrolyte.

The cyclic voltammograms recorded between −2.0 and +1.5 V for (**1**), (**3**), and (**5**) were identical with the exception of the two thiocyanate oxidations at +0.6 and +1.2 V for (**3**) and (**5**) with an associated reduction at −0.9 V. Several irreversible reduction processes occurred between −1.5 and −2.0 V. No peaks could be assigned to metal oxidations. This is consistent with the observed stability of solutions of complexes (**1**)—(**4**). As (**5**) is a polymeric complex, metal-oxidation processes may produce peaks of low current which could be obscured by the large thiocyanate oxidation peaks.

Description of the Structures.—The structures of the four monomeric complexes (**1**)—(**4**) have been determined. A perspective view of (**2**) is shown in Figure 1, and selected bond lengths and angles are listed in Table 1. The manganese(II) atom has approximate pentagonal-bipyramidal geometry where the donors in the pentagonal plane are the three nitrogen atoms and two oxygen atoms of L^1 and the bound chloride ions are in the axial positions. The molecular structures of (**1**), (**3**), and (**4**) are essentially similar[13] to that of (**2**). The axial donors are the thiocyanate and azide anions in (**3**) and (**4**) respectively, whereas water is bound in preference to the perchlorate anions in (**1**). Hydrogen bonds between the bound water molecule and ionic perchlorate are observed in the latter complex [O(12″) ··· O(2) 2.78, O(16″) ··· O(2) 2.80, and O(15′) ··· O(2) 2.84 Å]. Co-ordination geometries, bond lengths and angles show little variation within the series but (**1**), (**3**), and (**4**) each have a crystallographic two-fold axis passing through Mn, N(1), and

C(3), which is absent in complex (**2**). In these examples the pyridinedi-imine unit provides an average angle at the manganese(II) atom of 68.7 ± 0.7° which results in a small distortion from regular pentagonal geometry (72°).

The structure of the manganese(II) complex of L^2 with thiocyanate, (**5**), has also been determined and is polymeric (Figure 2, Table 2). The manganese(II) ion has a geometry approximating to octahedral. The three nitrogen atoms of the pyridinedi-imine unit are held at angles of 71.0(1) and 71.2(1)°. Two thiocyanate groups are bound N-terminally to the manganese atom. The final site is occupied by the oxygen [O(1′)] of an alcohol chain from another unit; it is this intermolecular link which holds the polymer together. A sharp twist in this chain results in the mean planes of successive pyridine rings making angles of 76° with each other.

Conclusion

In spite of the variation in the nature of the anion, the four manganese(II) complexes of L^1 are very similar; each is seven-co-ordinate with pentagonal-bipyramidal geometry. This is in marked contrast to the nickel(II) complexes of L^1 where the molecular structure varies with changes in anion, and all the complexes have six-co-ordinate, pseudo-octahedral geometry.[14] This distinction demonstrates that the ligand itself does not enforce seven-co-ordination. The manganese(II) complexes show close structural resemblances to the manganese complexes of L^4 characterised by Nelson and co-workers[4] and to complexes derived from L^6 (ref. 6) and L^7 (ref. 7). Seven-co-ordination in complexes of L^4 (ref. 4) and L^5 (ref. 5) has been ascribed to the macrocyclic nature of the ligand and, in those of L^6 (ref. 6) and L^7 (ref. 7), to the resonance-stabilised planarity of the system. Undoubtedly, these factors are important in imposing pentagonal-bipyramidal geometry. However, the structures discussed above suggest that, in the particular case of a d^5 ion with no stereochemical preferences, the structural requirements leading to seven-co-ordination are less stringent. Two factors can be identified; first the rigid pyridinedi-imine section constrains three nitrogen donors to be planar and to occupy an arc of *ca.* 138°, leaving ample room for two further donors in the same plane. Secondly, the length of the alkyl chain is important as evidenced by the difference between the monomeric, seven-co-ordinate complexes of L^1 and the polymeric, six-co-ordinate complex of L^2. The ligand L^1 can form a pentagonal planar array of donors without undue strain but this is not the case for L^2 where the conformational requirements of the longer alkyl chain prevent formation of a regular pentagonal plane about the small manganese(II) atom.

The structure of a manganese(II) derivative of L^5 (the macrocyclic equivalent of L^2) has been reported.[5] The complex is seven-co-ordinate, but the macrocycle is significantly folded so that the pyridine nitrogen atom is 0.92 Å out of the mean plane of the manganese and the other four donors of the pentagonal plane. In this example the macrocyclic nature of the ligand overcomes the steric strain involved in seven-co-ordination; with the open-chain ligand L^2, the alcohol groups do not co-ordinate to the central metal ion and a six-co-ordinate geometry results.

All of the solid complexes are stable in air and solutions of complexes of L^1 darken only slowly (several days) on exposure to the atmosphere. Solutions of (**5**), however, darken rapidly on exposure to air; this is interpreted as oxidation to an as yet unidentified manganese(III) product. The reluctance of the seven-co-ordinate complexes to undergo oxidation is similar to the behaviour of the related complexes of L^3 and appears to be associated with the seven-co-ordinate geometry, possibly reflecting a Franck–Condon barrier towards oxidation to manganese(III).

No complexes involving alkoxide bridges have been characterised in this work. This is in direct contrast to our observations with manganese(II) complexes of the binucleating macrocycle L^3.[1–3] A probable explanation of this difference lies in the ability of the macrocycle to maintain two metal ions in close proximity to each other and to the alcohol group, thereby promoting formation of an alkoxy bridge.

In spite of their monomeric nature, the complexes are of some interest with respect to the photosynthetic oxygen-evolving centre. Extended *X*-ray absorption fine structure (EXAFS) and *X*-ray absorption near-edge structure (XANES) studies of the chloro complex (**2**) are underway.[15] The unit-cell packing in this complex (all Mn-Cl vectors approximately aligned) is such that single crystal *X*-ray absorption data for it should assist with the interpretation of the data for oriented chloroplasts.[16]

Experimental

Preparation of Complexes.—$[MnL^1(H_2O)_2][ClO_4]_2$ (**1**). 2,6-Diacetylpyridine (1 g, 6.1 mmol) and $Mn(ClO_4)_2{\cdot}6H_2O$ (2.22 g, 6.1 mmol) in ethanol (50 cm^3) were brought to reflux. Ethanolamine (0.75 g, 12.2 mmol) in ethanol (10 cm^3) was added and refluxing continued for 10 h. A yellow powder formed after some solvent had evaporated and was collected by filtration. Further solvent evaporation led to the formation of yellow crystals suitable for a single-crystal *X*-ray structure determination. Yield 1.9 g, 3.53 mmol, 60% (Found: C, 29.2; H, 4.4; N, 7.9. Calc. for $C_{13}H_{23}Cl_2MnN_3O_{12}$: C, 29.0; H, 4.3; N, 7.8%). I.r.: 3 310s (br), 1 650m, 1 610m, 1 590m, and 1 100s (br) cm^{-1}. Magnetic moment (293 K) = 5.7 μ_B. Λ(MeOH) = 188 ohm^{-1} cm^2 mol^{-1} (lit. range for 1:2 electrolytes,[17] 160—220 ohm^{-1} cm^2 mol^{-1}).

$[MnL^1Cl_2]{\cdot}H_2O$ (**2**). Ethanolamine (0.38 g, 6.2 mmol, in 4 cm^3 methanol) was added to a refluxing methanol solution (35 cm^3) of dap (0.5 g, 3.1 mmol). This was followed by the addition of $MnCl_2{\cdot}4H_2O$ (0.61 g, 3.1 mmol) in methanol (15 cm^3). A pink solid precipitated from the brown solution but redissolved during the hour of refluxing. The solution was left to stand overnight, then the volume was reduced to 5 cm^3 by evaporation under reduced pressure. The resulting yellow solid was collected by filtration and washed with ethanol. Yield 0.60 g, 1.6 mmol, 52%. Recrystallisation by vapour diffusion of diethyl ether into a dmf–MeCN solution containing excess of LiCl resulted in yellow crystals suitable for an *X*-ray structure determination (Found: C, 40.0; H, 5.4; N, 10.7. Calc. for $C_{13}H_{21}Cl_2MnN_3O_3$: C, 39.7; H, 5.3; N, 10.7%). I.r.: 3 450s (br), 1 645m, and 1 585m cm^{-1}. Magnetic moment (298 K) = 5.9 μ_B. Λ(dmf) = 27 ohm^{-1} cm^2 mol^{-1} (lit. range for 1:1 electrolytes,[17] 65—90 ohm^{-1} cm^2 mol^{-1}).

$[MnL^1(NCS)_2]$ (**3**). This complex was made as for $[MnL^1(H_2O)_2][ClO_4]_2$ but in methanol (30 + 10 cm^3) rather than ethanol. After refluxing overnight, NaNCS (1.0 g, 12 mmol) was added to the gold-coloured solution. After a further 15 min of reflux the solution was allowed to cool and the resulting yellow precipitate was collected by filtration. Further crops including yellow crystals suitable for single-crystal *X*-ray structural analysis were obtained after solvent evaporation. Yield 1.65 g, 3.93 mmol, 65% (Found: C, 42.7; H, 4.5; N, 16.8. Calc. for $C_{15}H_{19}MnN_5O_2S_2$: C, 42.9; H, 4.5; N, 16.7%). I.r.: 3 350s (br), 2 080m, 2 015s, 1 650m, and 1 590m cm^{-1}. Magnetic moment (293 K) = 6.0 μ_B. Λ(dmf) = 97 ohm^{-1} cm^2 mol^{-1} (lit. range for 1:1 electrolytes as above).

$[MnL^1(N_3)_2]$ (**4**). 2,6-Diacetylpyridine (0.5 g, 3.1 mmol) and $Mn(ClO_4)_2{\cdot}6H_2O$ (1.11 g, 3.1 mmol) were brought to reflux in methanol (55 cm^3). Ethanolamine (0.38 g, 6.2 mmol) in methanol (5 cm^3) was added and the orange solution refluxed for 30 min before addition of a suspension of sodium azide (0.39 g, 6.2 mmol) in methanol (20 cm^3). The clear orange-brown solution was refluxed for another hour after which time the solution was again orange. Orange needles crystallised as the

Table 3. Atomic co-ordinates (× 10⁴) for complexes (**2**) and (**5**)

$[MnL^1Cl_2]$ (**2**)				$[\{MnL^2(NCS)_2\}_x]$ (**5**)			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn	2 001(1)	3 959(1)	1 882(1)	Mn	308(1)	5 527(1)	7 410(1)
N(1)	1 126(2)	2 676(2)	3 766(2)	N(1)	664(1)	4 632(2)	8 822(1)
C(1)	−231(3)	3 310(3)	4 426(2)	C(1)	−23(1)	3 838(2)	8 930(1)
C(2)	−754(3)	2 633(3)	5 589(2)	C(2)	190(2)	3 219(2)	9 798(1)
C(3)	173(3)	1 249(3)	6 058(2)	C(3)	1 135(2)	3 460(2)	10 555(2)
C(4)	1 578(3)	582(3)	5 374(2)	C(4)	1 842(2)	4 274(2)	10 429(1)
C(5)	2 016(3)	1 331(3)	4 220(2)	C(5)	1 586(1)	4 857(2)	9 547(1)
C(6)	3 460(3)	719(3)	3 375(2)	C(6)	2 263(2)	5 791(2)	9 318(1)
C(7)	4 582(3)	−763(3)	3 745(2)	C(7)	3 276(2)	6 176(2)	10 098(2)
N(2)	3 627(3)	1 544(2)	2 357(2)	N(2)	1 901(1)	6 203(2)	8 459(1)
C(8)	5 007(3)	1 104(3)	1 440(2)	C(8)	2 451(2)	7 185(2)	8 150(2)
C(9)	4 523(4)	1 838(3)	361(2)	C(9)	3 111(2)	6 515(2)	7 726(2)
O(1)	3 978(3)	3 549(2)	290(2)	C(10)	3 545(2)	7 527(2)	7 269(1)
O(2)	1 514(2)	6 396(2)	579(1)	O(1)	4 109(1)	8 567(2)	7 920(1)
C(10)	475(4)	7 613(3)	1 114(2)	O(2)	−3 940(1)	5 408(2)	4 995(1)
C(11)	−1 018(3)	6 817(3)	2 037(2)	C(11)	−3 089(2)	5 074(3)	4 797(2)
N(3)	−340(3)	5 371(2)	2 775(2)	C(12)	−2 108(2)	5 215(2)	5 704(2)
C(12)	−1 117(3)	4 799(3)	3 807(2)	C(13)	−2 070(2)	4 236(2)	6 456(1)
C(13)	−2 804(3)	5 438(3)	4 434(2)	N(3)	−1 099(1)	4 339(2)	7 323(1)
Cl(1)	4 022(1)	5 577(1)	2 286(1)	C(14)	−1 020(1)	3 700(2)	8 066(1)
Cl(2)	−18(1)	2 413(1)	1 450(1)	C(15)	−1 850(2)	2 857(2)	8 125(2)
O(10)	3 496(3)	−2 702(2)	6 686(2)	N(21)	388(2)	6 197(2)	6 142(1)
				C(21)	574(2)	6 815(2)	5 608(1)
				S(21)	835(1)	7 727(1)	4 862(1)
				N(31)	−319(1)	7 401(2)	7 613(1)
				C(31)	−432(2)	8 538(2)	7 654(1)
				S(31)	−626(1)	10 129(1)	7 707(1)

solution cooled slowly, but they proved to be twinned. A good single crystal for *X*-ray structural analysis was obtained after slow evaporation of the solvent. Yield 0.64 g, 1.65 mmol, 55% (Found: C, 40.0; H, 4.9; N, 32.2. Calc. for $C_{13}H_{19}MnN_9O_2$: C, 40.2; H, 4.9; N, 32.5%). I.r.: 3 190s (br), 2 045s, 1 655m, and 1 595m cm^{-1}. Magnetic moment (298 K) = 6.0 μ_B. Λ(MeOH) = 105 ohm^{-1} cm^2 mol^{-1} (lit. range for 1:1 electrolytes as above).

$[\{MnL^2(NCS)_2\}_x]$ (**5**). A methanol solution (50 cm^3) of dap (1 g, 6.1 mmol) and $Mn(ClO_4)_2 \cdot 6H_2O$ (1.56 g, 4.3 mmol) was refluxed for 5 min then propanolamine (0.92 g, 12.3 mmol) was added. After 1 h NaNCS (0.99 g, 12.3 mmol) was added to the orange solution and refluxing continued for 30 min. The initial yellow precipitate (the i.r. spectrum showed that this contained no NCS^-) was removed by filtration. Clusters of gold crystals suitable for *X*-ray analysis grew in the filtrate overnight. These were collected and washed with ethanol. Yield 0.75 g, 1.7 mmol (calculated on monomer molecular weight), 39%. I.r.: 3 480m (br), 3 290m (br), 2 080s, 1 640w, 1 620w, and 1 590m cm^{-1}. Magnetic moment (298 K) = 5.7 μ_B. Λ(dmf) = 79 ohm^{-1} cm^2 mol^{-1} (lit. range for 1:1 electrolytes as above).

Crystallography.—*X*-Ray crystallographic data were collected on a Nicolet R3m four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 69Å). The cell parameters were determined by least-squares refinement of 14 to 22 accurately centred reflections in the range $5 < 2\theta < 35°$. Crystal stability was monitored by recording three check reflections every 97 reflections and no significant variations were observed. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections were applied, based on ψ-scan data. Hydrogen atoms were inserted at calculated positions using a riding model with thermal parameters equal to 1.2*U* of their carrier atoms. The function minimised in the refinements was $\Sigma w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + gF_o{}^2]^{-1}$. Final atom co-ordinates are given in Table 3. All programs used in data reduction and final refinement are contained in the SHELXTL (version 4.0) package;[18] SHELXTL or SHELXS[19] programs were employed to solve the structures, and in some cases the intermediate refinement was performed using SHELX 76.[20]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Crystal data for $[MnL^1Cl_2] \cdot H_2O$ (**2**). $C_{13}H_{21}Cl_2MnN_3O_3$, irregular yellow block, crystal dimensions 0.55 × 0.75 × 0.80 mm, triclinic, space group $P\bar{1}$, a = 8.322(6), b = 8.465(5), c = 12.935(9) Å, α = 72.82(5), β = 72.20(6), γ = 81.38(5)°, U = 827(1) Å^3, Z = 2, $F(000)$ = 406.

Using 1.6° ω scans at a scan rate of 5.86° min^{-1}, and a background to scan ratio of 0.3:1, 4 037 reflections were collected with $4 < 2\theta < 55°$, index range *h* 0—11, *k* −11 to 11, *l* −17 to 17, at 150 K. Of these, 3 776 were unique, and the 3 208 having $I > 3\sigma(I)$ were ultimately used in the structure refinement. A Patterson calculation[19] revealed the complete structure. Anisotropic thermal parameters were assigned to all non-hydrogen atoms and the refinement on 199 parameters converged with R = 0.0363, R' = 0.0561, g = 0.000 37, and a maximum least-squares shift/error ratio of 0.06:1. The final difference map showed no features greater than ±0.70 e Å^{-3}.

Crystal data for $[\{MnL^2(NCS)_2\}_x]$ (**5**). $(C_{17}H_{23}MnN_5O_2S_2)_x$, irregular yellow block, crystal dimensions 0.38 × 0.38 × 0.48 mm, monoclinic, space group $P2_1/n$, a = 14.387(3), b = 10.045(2), c = 15.528(4) Å, β = 115.10(2)°, U = 2 032.1(9) Å^3, Z = 4, $F(000)$ = 932.

Using 1.2° ω scans at a scan rate of 5.33° min^{-1}, and a background to scan ratio of 0.5:1, 4 877 reflections were collected with $4 < 2\theta < 54°$, index range *h* 0—16, *k* 0—11, *l* −17 to 17, at 173 K. Of these, 4 447 were unique, and the 3 478 having $I > 3\sigma(I)$ were ultimately used in the structure refinement. The data were corrected for extinction effects. A

Patterson calculation[18] revealed the position of the manganese atom and the remaining non-hydrogen atoms were located from difference Fourier maps. Anisotropic thermal parameters were assigned to all non-hydrogen atoms and the refinement on 245 parameters converged with $R = 0.0308$, $R' = 0.0393$, $g = 0.000\,346$, and a maximum least-squares shift/error ratio of 0.02 : 1. The final difference map showed no features greater than ± 0.3 e Å^{-3}.

Other Measurements.—Infrared spectra were recorded as KBr discs using a Philips Scientific SP-300 spectrometer. A Varian DMS 100 spectrophotometer was used to record electronic spectra over the range 11 111—50 000 cm^{-1}. Room-temperature magnetic moment measurements were carried out using a Newport Instruments Gouy balance. Microanalyses were carried out by the Campbell Microanalytical Laboratory, University of Otago, Dunedin. A Wayne Kerr Universal Bridge B224 in conjunction with a conductivity cell (platinum electrodes) of cell constant 0.251 was used for measurements of electrical conductance. Electrochemical data were obtained using a PAR model 273 potentiostat/galvanostat and a model 175 Universal Programmer. A single-compartment cell containing a glassy carbon disc working electrode (area = 0.07 cm^2), platinum-wire auxilary electrode, and a silver wire pseudo-reference electrode was used and *in situ* ferrocene enabled the measured potentials to be referenced to the saturated calomel electrode (s.c.e.). All cyclic voltammograms were recorded in dmf—0.1 mol dm^{-3} tetraethylammonium perchlorate using 1 mmol dm^{-3} complex. In this electrolyte $E^{\circ\prime}$ (ferrocenium–ferrocene) = 0.3 V *vs.* s.c.e.

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