

**Complexes of Ligands Derived from the Condensation of 2-Formyl- or 2-Acetylpyridine with Ethanolamine and the Formation of Two Rearrangement Products; X-ray Crystal Structures of  $Mn(L1)_2(NCS)_2$ ,  $[Mn(L1)(NCS)_2]_x$ ,  $[Cu(L1)(H_2O)_2(ClO_4)]_2(ClO_4)_2$ ,  $[Zn(L1)(H_2O)_2(ClO_4)]_2(ClO_4)_2$  and  $[Mn(L3)(L4)]_2(ClO_4)_4 \cdot 2EtOH$  ( $L1 = N$ -(2-hydroxyethyl)-2-pyridinecarboxaldimine,  $L3 = N$ -(2-hydroxyethyl)-methyl-2-pyridylketimine,  $L4 = (Z)$ -1,3-di(2-pyridyl)but-2-enone)**

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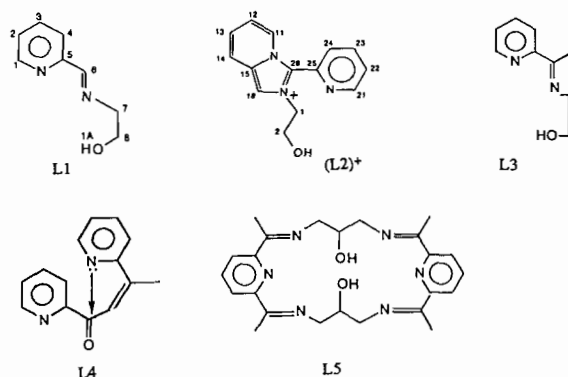
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### Abstract

Four structurally diverse complexes of  $L1$  ( $N$ -(2-hydroxyethyl)-2-pyridinecarboxaldimine) have been synthesised and characterised.  $Mn(L1)_2(NCS)_2$  is a monomer, orthorhombic, unit cell dimensions  $a = 9.786(4)$ ,  $b = 12.748(4)$ ,  $c = 17.615(6)$  Å,  $U = 2197(1)$  Å<sup>3</sup>;  $[Mn(L1)(NCS)]_x$  is a polymer, monoclinic,  $a = 16.718(8)$ ,  $b = 5.788(2)$ ,  $c = 28.135(11)$  Å,  $\beta = 91.61(3)^\circ$ ,  $U = 2721(2)$  Å<sup>3</sup>;  $[Cu(L1)(H_2O)_2(ClO_4)]_2(ClO_4)_2$  is a dimer, monoclinic,  $a = 15.132(11)$ ,  $b = 9.235(8)$ ,  $c = 23.030(17)$  Å,  $\beta = 102.32(5)^\circ$ ,  $U = 3144(4)$  Å<sup>3</sup>;  $[Zn(L1)(H_2O)_2(ClO_4)]_2(ClO_4)_2$  is also a dimer, monoclinic,  $a = 15.114(7)$ ,  $b = 9.428(3)$ ,  $c = 22.649(9)$  Å,  $\beta = 100.86(3)^\circ$ ,  $U = 3170(2)$  Å<sup>3</sup>. The formation of these complexes is discussed in relation to a proposed rearrangement scheme which accounts for the formation of a second, alternative product  $(L2)^+$  (2-(2-hydroxyethyl)-3-(2-pyridyl)-imidazo[1,5-*a*]-pyridinium cation). Use of an equivalent methyl ketone precursor in place of the aldehyde led to formation of  $L3$  ( $N$ -(2-hydroxyethyl)-methyl-2-pyridylketimine) *in situ*. The dimeric manganese complex  $[Mn(L3)(L4)]_2(ClO_4)_4 \cdot 2EtOH$  ( $L4 = (Z)$ -1,3-di(2-pyridyl)-but-2-enone) was structurally characterised, orthorhombic,  $a = 23.987(7)$ ,  $b = 12.697(3)$ ,  $c = 19.355(5)$  Å,  $U = 5895(3)$  Å<sup>3</sup>, and a possible rearrangement scheme to form  $L4$  is proposed.

### Introduction

We have described previously a number of tetramanganese complexes derived from the macrocyclic



ligand  $L5$  [1–3]. These complexes show interesting structural chemistry and are structural models for the oxygen-evolving complex (OEC) of photosystem II [4–7]. In this paper we report the investigation of the closely related non-cyclic ligands  $L1$  and  $L3$ . These both contain a flexible alkyl chain which terminates in an alcohol group.

Many related tridentate Schiff base ligands have been successfully employed to build clusters of copper(II) ions bridged by oxygen atoms. The incorporation of an ethanolamine fragment generally leads to the formation of  $[Cu_4O_4]$  cubane-type clusters [8–10]. However, a recent paper by Cros and Laurent proposed a binuclear structure for the copper(II) complex of the Schiff base derived from 2'-aminoacetophenone and ethanolamine, on the basis of the mass spectrum and the temperature dependence of the magnetic moment [11]. In comparison, when propanolamine is incorporated, binuclear copper(II) complexes are formed [10, 12–14]. In all of these examples the ligand alcohol group bridges at least two copper(II) ions. Therefore, it seemed that the new ligands  $L1$  and  $L3$  might also

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form clusters of transition metal ions bridged by the terminal alcohol group.

Free L1 is readily prepared as it is formed from a reactive aromatic aldehyde, however during the course of this work it was found that the chemistry of L1 is complicated by a rearrangement reaction to form (L2)<sup>+</sup> (see Fig. 4) [15]. In this paper some complexes of L1 are presented and discussed, and a possible scheme for the rearrangement to (L2)<sup>+</sup> is proposed. In an attempt to prevent this rearrangement reaction, which proceeds via loss of the aldehyde proton, the aldehyde precursor (2-pyridinecarbaldehyde) was replaced by the related ketone (2-acetylpyridine). This prevented the previous rearrangement but, in addition to forming the desired Schiff base L3, L4 formed via an aldol condensation (see Fig. 6).

## Experimental

### Preparation of Free L1

Initially this was prepared by the method of Johnson *et al.* [16]. 2-Pyridinecarbaldehyde (0.68 g, 6.4 mmol) dissolved in benzene (20 ml) was added to a mixture of ethanolamine (0.40 g, 6.5 mmol) and benzene (60 ml). The resultant mixture was brought to reflux and the azeotrope removed until no further water was produced. Evaporation of the remaining benzene under reduced pressure left a yellow oil which was pumped *in vacuo* overnight. Occasionally the oil solidified overnight to give white crystals. The oil was used promptly without further purification. Yield 0.95 g, 6.3 mmol, 99%.

L1 can also be obtained by simply adding equimolar amounts of 2-pyridinecarbaldehyde and ethanolamine together in a small volume of methanol. Evaporation of the solvent overnight followed by pumping *in vacuo* yielded the same yellow oil. The addition of one drop of 70% HClO<sub>4</sub> to this reaction had no effect on the reaction. Infrared spectrum: *inter alia* 3280(m,b), 2880(m,b), 1650(m), 1590(m) cm<sup>-1</sup>. Electronic spectrum (CH<sub>3</sub>OH): λ<sub>max</sub> = 273 nm, ε = 5600 l mol<sup>-1</sup> cm<sup>-1</sup>; λ<sub>max</sub> = 234 nm, ε = 10 000 l mol<sup>-1</sup> cm<sup>-1</sup>; λ<sub>max</sub> = 197 nm, ε = 17 500 l mol<sup>-1</sup> cm<sup>-1</sup>. NMR spectra (CDCl<sub>3</sub>): <sup>1</sup>H H1, 8.61(dd); H2, 7.30(m); H3, 7.71(m); H4, 7.90(dd); H6, 8.40(s); H7, 3.95(m); H8, 3.83(m) ppm. These were assigned using homonuclear decoupling experiments and <sup>1</sup>H-<sup>1</sup>H homonuclear two-dimensional correlation spectroscopy. <sup>13</sup>C Cl, 149.27; C2, 124.75; C3, 136.50; C4, 121.39; C5, 153.88; C6, 163.42; C7, 63.26; C8, 61.95 ppm. These assignments were confirmed using <sup>1</sup>H-<sup>13</sup>C heteronuclear two-dimensional correlation spectroscopy.

### Preparation of (L2)ClO<sub>4</sub> or (L2)(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>)

Several methods of obtaining (L2)<sup>+</sup>, that is the 2-(2-hydroxyethyl)-3-(2-pyridyl-imidazo[1,5-*a*]-

pyridinium cation, as either a perchlorate or *p*-toluenesulfonate salt, follow.

(a) Ethanolamine (0.29 g, 4.8 mmol) was brought to reflux in 15 ml of ethanol. Pyridinecarbaldehyde (0.5 g, 4.7 mmol) in 10 ml of ethanol was added dropwise followed by HClO<sub>4</sub> (0.67 g 70% HClO<sub>4</sub>, 4.7 mmol) in ethanol (10 ml). The resulting yellow solution deepened to a gold colour as it was refluxed for 2.5 h. After cooling and evaporation of the solvent (over a period of hours) yellow-brown crystals were filtered from the green-yellow solution. Further crops were obtained on evaporation of the solvent. Yield 0.32 g, 0.9 mmol, 40%.

(b) *p*-Toluenesulfonic acid (0.9 g, 4.7 mmol) in 10 ml ethanol was added to the pyridinecarbaldehyde (0.5 g, 4.7 mmol, in 10 ml of ethanol) solution, and the combination added dropwise to a refluxing ethanol (15 ml) solution of ethanolamine (0.29 g, 4.8 mmol). The red-gold solution was refluxed for 2.5 h after which it was yellow-brown. This solution slowly evaporated down to an oil which was pumped *in vacuo*. Addition of acetonitrile allowed some of the amine *p*-toluenesulfonate salt byproduct to be filtered off. Evaporation and pumping *in vacuo* left (L2)(*p*-toluenesulfonate) as a gold oil contaminated with some amine salt. Approximate yield (subtracting the amine salt as estimated from the NMR ratio) 0.34 g, 0.8 mmol, 34%.

(c) 2-Pyridinecarboxaldehyde (1 g, 9.3 mmol) dissolved in ethanol (20 ml) was slowly added to a refluxing ethanol solution of ethanolamine (0.58 g, 9.5 mmol in 30 ml). Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (3.41 g, 9.4 mmol) in ethanol (20 ml) was added and refluxing continued for 2.5 h. On cooling and evaporation of the solvent (over several weeks) a crystalline product was obtained. Yield 0.6 g, 1.8 mmol, 38%. Recrystallisation from methanol by diethylether diffusion yielded colourless crystals of X-ray quality [15].

Infrared spectrum: *inter alia* 3540(m), 1660(w), 1590(m), 1560(m), 1100(s,b). Electronic spectrum (EtOH): λ<sub>max</sub> = 315 nm, ε = 11 300 l mol<sup>-1</sup> cm<sup>-1</sup>; λ<sub>max</sub> = 204, ε = 36 000 l mol<sup>-1</sup> cm<sup>-1</sup>. Density (by flotation in CHCl<sub>3</sub>/CCl<sub>4</sub>): 1.52 g cm<sup>-3</sup>. NMR spectra (CDCl<sub>3</sub>): <sup>1</sup>H H1, 3.97(t); H2, 4.68(t); H11, 8.53(bd); H12, 7.20(bt); H13, 7.38(bdd); H14, 7.91(bd); H16, 8.35(s); H21, 8.95(bd); H22, 7.75(ddd); H23, 8.20(td); H24, 8.12(bd) ppm. These were assigned using homonuclear decoupling experiments. <sup>13</sup>C Cl, 53.93; C2, 61.79; C11, 124.14; C12, 119.97; C13, 126.88; C14, 119.84; C16, 116.46; C21, 152.70; C22, 128.04; C23, 139.87; C24, 128.68 ppm. The assignments of these complex spectra were confirmed using <sup>1</sup>H-<sup>13</sup>C heteronuclear two-dimensional correlation spectroscopy.

### (L2)ClO<sub>4</sub>, Mn(L1)<sub>2</sub>(NCS)<sub>2</sub> and [Mn(L1)(NCS)<sub>2</sub>]<sub>x</sub>

L1 (0.5 g, 3.3 mmol) in ethanol (5 ml) was added dropwise to an ethanolic solution (5 ml) of manga-

nese(II) perchlorate (1.21 g, 3.3 mmol). A solution of sodium thiocyanate (0.54 g, 6.7 mmol) in 8 ml ethanol was added, followed by 5 ml of isopropanol. A mixture of products was obtained on rapid evaporation of the solvents. The yellow–brown solid formed was physically separated from some green oil. Crystals of  $(L2)ClO_4$  (1%) were obtained by vapour diffusion of diethylether into a methanol solution of the green oil. The acetonitrile-soluble portion of the yellow–brown solid yielded poor quality crystals by vapour diffusion of diethylether into the acetonitrile solution. A recrystallisation by the same method using methanol/diethylether gave yellow crystals (1%) identified as  $Mn(L1)_2(NCS)_2$  by a single crystal X-ray structure determination. The golden crystalline material left undissolved by acetonitrile was readily soluble in methanol and was recrystallised by vapour diffusion of diethylether to give clusters of yellow crystals of the polymer  $[Mn(L1)(NCS)_2]_x$ . Elemental analysis indicated the purity of this yellow crystalline polymer. *Anal.* Found: C, 37.8; H, 3.2; N, 1.74. Calc. for  $C_{10}H_{10}MnN_4OS_2$ : C, 37.4; H, 3.1; N, 17.4%. Yield c. 20% calculated for  $[Mn(L1)(NCS)_2]_x$ .

Infrared spectra for:  $Mn(L1)_2(NCS)_2$  *inter alia* 3440(m,b), 2070(s,b), 1645(w), 1590(m)  $cm^{-1}$ ;  $[Mn(L1)(NCS)_2]_x$  *inter alia* 3360(m,b), 2080(s,b), 1650(w), 1595(m)  $cm^{-1}$ .

#### $[Cu(L1)(H_2O)_2(ClO_4)]_2(ClO_4)_2$

A methanol solution (5 ml) of L1 (1 g, 6.7 mmol) was added dropwise to a solution of  $Cu(ClO_4)_2 \cdot 6H_2O$  (2.48 g, 6.7 mmol in 5 ml of methanol), causing a green colour to develop. A small amount of isopropanol was added and the solution evaporated to dryness. The resulting green solid was collected and washed with 20 ml of isopropanol, leaving a blue crystalline compound which was dried *in vacuo*. Yield 0.99 g, 1.1 mmol, 33%.

A crystal suitable for X-ray structural analysis was obtained from a similar preparation (70% scale) using 25 ml of a 1:1 mixture of dichloromethane:methanol as the reaction solvent. After most of the solvent had evaporated a little toluene was added and further evaporation allowed. The resulting blue crystals were filtered off and washed with methanol. *Anal.* Found: C, 20.2; H, 3.1; N, 5.8. Calc. for  $C_{16}H_{32}Cl_4Cu_2N_4O_{24}$ : C, 20.6; H, 3.4; N, 6.0%.

Infrared spectrum: *inter alia* 3310(m,b), 1650(w), 1605(m), 1100(s,b)  $cm^{-1}$ . Magnetic moment (293 K) = 1.88 BM. Electronic spectrum (MeOH):  $\lambda_{max} = 722$  nm,  $\epsilon = 40$  l mol $^{-1}$  cm $^{-1}$ ;  $\lambda_{max} = 285$  nm,  $\epsilon = 7500$  l mol $^{-1}$  cm $^{-1}$ ;  $\lambda_{max} = 204$  nm,  $\epsilon = 26$  700 l mol $^{-1}$  cm $^{-1}$ .

#### $[Zn(L1)(H_2O)_2(ClO_4)]_2(ClO_4)_2$

This complex was prepared in the same way as  $(L2)ClO_4$  except that the scale was halved and  $Zn(ClO_4)_2 \cdot 6H_2O$  (1.75 g, 4.7 mmol) was substituted for  $Mn(ClO_4)_2 \cdot 6H_2O$ . On cooling and evaporation of

the solvent over several weeks a pinkish white crystalline solid was obtained. This was collected by filtration and washed with a very small amount of methanol followed by chloroform. Further solvent evaporation from the filtrate resulted in a golden oil which, on pumping *in vacuo*, yielded hygroscopic crystals of  $[Zn(L1)(H_2O)_2(ClO_4)]_2(ClO_4)_2$  as colourless blocks which were suitable for single crystal X-ray structural analysis. *Anal.* Found: C, 21.1; H, 3.0; N, 6.0. Calc. for  $C_{16}H_{28}Cl_4N_4O_{22}Zn_2$ : C, 21.3; H, 3.1; N, 6.2%. Overall yield 0.78 g, 0.9 mmol, 38%.

Infrared spectrum: *inter alia* 3400(m,b), 1650(w), 1590(m), 1100(s,b)  $cm^{-1}$ . FAB-MS  $[Zn_2(L1)_2(H_2O)_2(ClO_4)_4H]^+$   $m/e = 861$  a.m.u. NMR spectra ( $CD_3CN$ ):  $^1H$  H1, 8.45(d); H2, 7.82(m); H3, 8.33(m); H4, 8.12(d); H6, 8.93(s); H7, 4.09(m); H8, 3.90(m); H1A, 4.621(t) ppm.  $^{13}C$  C1, 150.27; C2, 130.61; C3, 143.17; C4, 129.52; C5, 147.25; C6, 164.77; C7, 55.93; C8, 59.94 ppm.

#### $[Mn(L3)(L4)]_2(ClO_4)_4 \cdot 2EtOH$

2-Acetylpyridine (2 g, 16.5 mmol) in 5 ml of ethanol was added dropwise to a refluxing ethanol solution (60 ml) of ethanolamine (1.02 g, 16.7 mmol), followed by  $Mn(ClO_4)_2 \cdot 6H_2O$  (5.98 g, 16.5 mmol) in 10 ml of ethanol. The resulting gold solution was refluxed for 3 h, allowed to cool, then some solvent was removed under reduced pressure. On standing, brown crystals of  $[Mn(L3)(L4)]_2(ClO_4)_4 \cdot 2EtOH$  formed and were suitable for an X-ray structure determination. A further crop of yellow–brown powder was obtained. Yield 0.73 g, 0.5 mmol, 20%. Vapour diffusion of diethylether into an acetonitrile solution of the brown powder yielded crystals of  $[Mn(L3)(L4)]_2(ClO_4)_4 \cdot 2MeCN$  which had a different unit cell and crystal system to those crystals obtained from the reaction solution. However, X-ray structure determination showed that the molecular structure was very similar to that of the original product.

Infrared spectrum: *inter alia* 3440(m,b), 1645(m), 1620(m), 1600(m), 1100(s,b)  $cm^{-1}$ .

#### Crystallography

Data for all crystals were collected on a Nicolet R3m four-circle diffractometer using graphite-monochromated  $Mo K\alpha$  radiation ( $\lambda = 0.71069$ ). Unit cell parameters were determined by least-squares refinement of 14 to 22 accurately centered reflections in the range  $5 < 2\theta < 35^\circ$ . Crystal stability was monitored by recording three check reflections every 97 reflections, no significant variations were observed. The data sets were corrected for Lorentz and polarisation effects, and unless otherwise stated, an empirical absorption correction was applied, based on  $\Psi$ -scan data. Hydrogen atoms were inserted at calculated positions using a riding model with thermal parameters equal to  $1.2U$  of their carrier atoms. The

function minimised in the refinement was  $\sum w(|F_o| - |F_c|)^2$  where  $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ . All programs used in data reduction and final refinement were contained in the SHELXTL (version 4.0) package [17]; SHELXTL or SHELXS [18] programs were employed to solve the structures, and in some cases the intermediate refinement was performed using SHELX76 [19]. Atom coordinates for each structure are listed in Table 1.

*Crystal data for Mn(L1)<sub>2</sub>(NCS)<sub>2</sub>*

C<sub>18</sub>H<sub>20</sub>MnN<sub>6</sub>O<sub>2</sub>S<sub>2</sub>, irregular yellow block, dimensions 0.22 × 0.66 × 0.75 mm, orthorhombic,  $a = 9.786(4)$ ,  $b = 12.748(4)$ ,  $c = 17.615(6)$  Å,  $U = 2197(1)$  Å<sup>3</sup>, space group  $Pna2_1$ ,  $Z = 4$ ,  $F(000) = 972$ . Using 1.7°  $\omega$ -scans 1669 reflections were collected with  $4 < 2\theta < 45^\circ$  at 150 K; of these, 1526 were unique, and the 1356 having  $I > 3\sigma(I)$  were ultimately used in the structure refinement. A Patterson calculation [17] revealed the position of the manganese atom and the remaining non-hydrogen atoms were located from difference Fourier maps. Hydrogen atoms were inserted on all atoms except the alcohol oxygens O1 and O10. Anisotropic thermal parameters were assigned to all non-hydrogen atoms, except the carbon atoms of the pyridine rings, and the refinement converged with  $R = 0.0306$ ,  $R_w = 0.0395$ ,  $g = 0.00050$ . The final difference map showed no features greater than  $\pm 0.38$  e Å<sup>-3</sup>.

*Crystal data for [Mn(L1)(NCS)<sub>2</sub>]<sub>x</sub>*

C<sub>10</sub>H<sub>10</sub>MnN<sub>4</sub>OS<sub>2</sub>, irregular yellow plate, dimensions 0.16 × 0.35 × 0.5 mm, monoclinic,  $a = 16.718(8)$ ,  $b = 5.788(2)$ ,  $c = 28.135(11)$  Å,  $\beta = 91.61(3)^\circ$ ,  $U = 2721(2)$  Å<sup>3</sup>, space group  $I2/a$ ,  $Z = 8$ ,  $F(000) = 1304$ . Using peak top  $\omega$ -scans with a 0.5° scan width 4232 reflections were collected with  $4 < 2\theta < 45^\circ$ , index range:  $h$  0/19,  $k$  0/7,  $l$  -31/31, at 150 K. Of these, 1769 were unique, and the 1476 having  $I > 3\sigma(I)$  were ultimately used in the structure refinement. A Patterson calculation [18] revealed the structure 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 164 parameters converged with  $R = 0.0273$ ,  $R_w = 0.0394$ ,  $g = 0.0006$  (not refined). The final difference map showed no features greater than  $\pm 0.46$  e Å<sup>-3</sup>.

*Crystal data for [Cu(L1)(H<sub>2</sub>O)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>*

C<sub>16</sub>H<sub>28</sub>Cl<sub>4</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>22</sub>, blue block, dimensions 0.16 × 0.38 × 0.63 mm, monoclinic,  $a = 15.132(11)$ ,  $b = 9.235(8)$ ,  $c = 23.030(17)$  Å,  $\beta = 102.32(5)^\circ$ ,  $U = 3144(4)$  Å<sup>3</sup>, space group  $C2/c$ ,  $Z = 4$ ,  $F(000) = 1816$ . Using 2.2°  $\omega$ -scans 2278 reflections were collected with  $4 < 2\theta < 45^\circ$  at 150 K. Of these, 2049 were unique, and the 938 having  $I > 3\sigma(I)$  were ultimately used in the structure refinement. Direct methods

TABLE 1. Atomic coordinates ( $\times 10^4$ ) and temperature factors ( $\text{Å}^2 \times 10^3$ )

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sup>a</sup>
<b>Mn(L1)(NCS)<sub>2</sub></b>				
Mn	7498(1)	9956(1)	11700(1)	17(1)*
N(1)	6721(2)	8529(3)	11400(4)	19(1)*
C(1)	6063(2)	8325(3)	12030(5)	26(1)
C(2)	5656(3)	7407(3)	11791(5)	33(1)
C(3)	5929(3)	6690(4)	10880(5)	35(1)
C(4)	6611(3)	6885(4)	10236(5)	31(1)
C(5)	6982(2)	7812(3)	10510(4)	22(1)
C(6)	7694(3)	8074(3)	9817(5)	26(1)*
N(2)	8030(2)	8937(3)	10047(4)	24(1)*
C(7)	8721(3)	9156(4)	9282(5)	30(2)*
C(8)	8542(3)	9890(4)	8105(6)	37(2)*
O(1)	8008(2)	9442(3)	7188(4)	49(1)*
N(11)	8236(2)	11425(3)	11386(3)	19(1)*
C(11)	8929(2)	11620(3)	11887(5)	23(1)
C(12)	9308(2)	12558(3)	11698(5)	27(1)
C(13)	8961(3)	13339(4)	10956(5)	29(1)
C(14)	8241(2)	13155(4)	10422(5)	27(1)
C(15)	7898(2)	12195(3)	10663(5)	21(1)
C(16)	7139(3)	11959(3)	10112(5)	25(1)*
N(12)	6845(2)	11064(3)	10277(4)	22(1)*
C(17)	6104(2)	10873(4)	9660(5)	27(2)*
C(18)	6192(3)	10175(4)	8442(5)	31(2)*
O(10)	6670(2)	10639(3)	7434(4)	43(1)*
N(10)	6726(3)	10520(3)	13270(4)	28(1)*
C(10)	6229(3)	10819(3)	13936(5)	21(1)*
S(10)	5537(1)	11244(1)	14904(1)	28(1)*
N(20)	8312(2)	9387(3)	13137(4)	29(1)*
C(20)	8856(3)	9186(3)	13747(5)	22(1)*
S(20)	9609(1)	8903(1)	14638(1)	32(1)*
<b>[Mn(L1)(NCS)<sub>2</sub>]<sub>x</sub></b>				
Mn	4237(1)	558(1)	1274(1)	22(1)*
N(1)	2999(2)	1028(5)	1585(1)	30(1)*
C(1)	2717(2)	-51(8)	1964(2)	53(1)*
C(2)	1971(2)	468(8)	2146(2)	65(2)*
C(3)	1516(2)	2146(7)	1940(1)	51(1)*
C(4)	1792(2)	3290(7)	1547(1)	36(1)*
C(5)	2536(2)	2664(5)	1379(1)	25(1)*
C(6)	2862(2)	3733(5)	949(1)	25(1)*
N(2)	3563(2)	3205(4)	823(1)	23(1)*
C(7)	3859(2)	4226(5)	383(1)	27(1)*
C(8)	4351(2)	6366(5)	494(1)	28(1)*
O(1)	3858(1)	8188(4)	666(1)	27(1)*
N(11)	4420(2)	-2598(5)	1662(1)	29(1)*
C(11)	4582(2)	-4429(6)	1805(1)	22(1)*
S(11)	4838(1)	-7005(1)	2013(1)	28(1)*
N(21)	5330(2)	994(5)	896(1)	33(1)*
C(21)	5930(2)	877(5)	699(1)	24(1)*
S(21)	6783(1)	718(2)	422(1)	29(1)*
<b>[Cu(L1)(H<sub>2</sub>O)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub></b>				
Cu	7293(2)	6049(3)	-1095(1)	17(1)*
N(1)	6012(11)	6500(18)	-1435(7)	20(5)
C(1)	5293(13)	5594(22)	-1632(8)	13(5)

(continued)

TABLE 1. (continued)

Atom	x	y	z	$U^a$
C(2)	4442(15)	6178(25)	-1879(9)	24(6)
C(3)	4306(17)	7723(27)	-1929(10)	37(7)
C(4)	5024(14)	8498(24)	-1706(9)	23(6)
C(5)	5879(14)	7984(24)	-1470(9)	21(5)
C(6)	6680(13)	8890(26)	-1245(8)	15(5)
N(2)	7380(11)	8155(19)	-1033(7)	21(5)
C(7)	8219(14)	9056(26)	-800(8)	22(5)
C(8)	8485(13)	8975(25)	-129(8)	19(5)
O(1)	7830(9)	9523(16)	152(6)	22(5)*
O(2)	7160(10)	3956(17)	-1327(6)	31(6)*
O(3)	8605(9)	5745(15)	-811(6)	25(6)*
Cl(1)	8400(4)	6895(6)	-2307(2)	23(2)*
O(11)	7615(11)	6290(21)	-2123(6)	47(7)*
O(12)	9173(10)	7000(17)	-1810(6)	31(6)*
O(13)	8645(12)	6074(22)	-2764(7)	56(5)
O(14)	8119(12)	8365(19)	-2507(7)	49(5)
Cl(2)	5933(4)	1907(6)	-345(2)	20(2)*
O(21)	6791(9)	2023(17)	-516(7)	30(6)*
O(22)	5365(10)	3078(18)	-632(7)	37(6)*
O(23)	6091(12)	1974(20)	268(6)	50(7)*
O(24)	5527(11)	576(17)	-536(9)	50(8)*
[Zn(L1)(H <sub>2</sub> O) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ] <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>				
Zn	7313(1)	5990(1)	-1062(1)	17(1)*
N(1)	5958(2)	6566(4)	-1410(2)	19(1)*
C(1)	5246(3)	5729(5)	-1609(2)	25(1)*
C(2)	4413(3)	6279(5)	-1862(2)	30(2)*
C(3)	4302(3)	7730(5)	-1917(2)	31(2)*
C(4)	5037(3)	8612(5)	-1713(2)	28(1)*
C(5)	5845(3)	7980(4)	-1461(2)	19(1)*
C(6)	6665(3)	8832(4)	-1236(2)	18(1)*
N(2)	7391(2)	8220(3)	-1007(1)	15(1)*
C(7)	8193(3)	9091(4)	-801(2)	19(1)*
C(8)	8496(3)	8986(5)	-123(2)	19(1)*
O(1)	7835(2)	9591(3)	189(1)	18(1)*
O(2)	7150(2)	3948(3)	-1348(1)	33(1)*
O(3)	8679(2)	5790(3)	-784(1)	27(1)*
Cl(1)	8306(1)	6919(1)	-2282(1)	23(1)*
O(12)	8020(2)	8350(3)	-2429(1)	31(1)*
O(13)	9128(2)	6961(4)	-1836(2)	38(1)*
O(11)	7604(2)	6204(3)	-2038(1)	29(1)*
O(14)	8447(3)	6204(4)	-2809(2)	51(2)*
Cl(2)	5947(1)	1997(1)	-329(1)	27(1)*
O(21)	6827(2)	1991(4)	-509(2)	34(1)*
O(22)	5614(3)	598(4)	-385(2)	63(2)*
O(23)	5372(2)	2980(4)	-681(2)	53(1)*
O(24)	6058(3)	2399(6)	270(2)	79(2)*
[Mn(L3)(L4)] <sub>2</sub> (ClO <sub>4</sub> ) <sub>4</sub> ·2EtOH				
Mn(1)	902(1)	2341(2)	2656	40(1)*
N(1)	1349(5)	1290(11)	1941(7)	41(5)*
C(1)	1894(8)	1122(15)	1952(11)	58(5)
C(2)	2155(9)	285(16)	1523(11)	70(6)
C(3)	1792(8)	-303(17)	1085(12)	68(6)
C(4)	1259(8)	-147(16)	1093(11)	61(6)
C(5)	1016(8)	753(16)	1524(11)	61(6)
C(6)	427(7)	846(12)	1530(9)	38(4)

(continued)

TABLE 1. (continued)

Atom	x	y	z	$U^a$
C(7)	32(9)	373(18)	1074(13)	79(7)
N(2)	261(5)	1556(12)	2015(8)	54(6)*
C(8)	-332(9)	1911(18)	2065(12)	77(7)
C(9)	-404(9)	2501(17)	2798(13)	78(7)
O(1)	88(4)	2987(10)	2987(7)	56(5)*
N(10)	1154(6)	3801(10)	2097(8)	40(5)*
C(11)	931(8)	4025(15)	1491(11)	56(5)
C(12)	1085(8)	5054(15)	1147(11)	58(5)
C(13)	1456(7)	5681(13)	1445(9)	39(4)
C(14)	1648(6)	5411(13)	2052(9)	36(4)
C(15)	1494(7)	4470(13)	2374(9)	39(4)
C(16)	1750(9)	4011(18)	3024(13)	69(6)
C(17)	2446(8)	3921(15)	2973(11)	58(5)
C(18)	2646(10)	4639(17)	3351(12)	77(7)
C(19)	3266(10)	4881(22)	3471(16)	108(9)
C(20)	2255(7)	5267(15)	3733(11)	55(5)
C(21)	2352(12)	6044(19)	4224(16)	102(8)
C(22)	1822(9)	6457(18)	4507(12)	73(7)
C(23)	1346(10)	6104(18)	4330(12)	79(7)
C(24)	1312(7)	5345(14)	3797(10)	50(5)
N(20)	1754(7)	5017(16)	3553(12)	83(8)*
O(10)	1517(4)	3177(8)	3279(5)	35(4)*
Mn(2)	1678(1)	2168(2)	4127(2)	52(1)*
N(31)	1262(6)	3275(11)	4904(9)	54(6)*
C(31)	684(8)	3425(16)	4872(12)	69(6)
C(32)	468(11)	4128(19)	5306(14)	95(8)
C(33)	776(12)	4703(22)	5687(16)	106(9)
C(34)	1368(13)	4666(23)	5734(16)	112(10)
C(35)	1612(8)	3768(15)	5313(10)	54(5)
C(36)	2159(10)	3514(19)	5257(13)	84(7)
C(37)	2614(13)	4028(23)	5753(18)	130(11)
N(32)	2330(6)	2896(13)	4839(11)	77(7)*
C(38)	2867(13)	2433(25)	4766(18)	136(12)
C(39)	3010(13)	1821(27)	4168(18)	138(12)
O(30)	2501(6)	1509(10)	3809(9)	81(6)*
N(40)	1442(5)	752(11)	4738(7)	39(5)*
C(41)	1630(8)	447(15)	5353(10)	54(5)
C(42)	1542(7)	-494(13)	5650(10)	43(5)
C(43)	1231(7)	-1153(14)	5353(9)	40(4)
C(44)	988(7)	-923(15)	4696(10)	53(5)
C(45)	1106(6)	43(13)	4418(9)	34(4)
C(46)	812(7)	442(14)	3768(10)	45(5)
C(47)	189(7)	533(14)	3854(9)	48(5)
C(48)	-92(7)	-169(14)	3449(9)	45(5)
C(49)	-666(8)	-360(16)	3419(11)	68(6)
C(50)	323(6)	-762(12)	3071(9)	37(4)
C(51)	262(9)	-1552(16)	2588(11)	69(6)
C(52)	754(8)	-1977(17)	2284(12)	71(6)
C(53)	1269(9)	-1668(18)	2458(12)	76(7)
C(54)	1322(7)	-774(14)	2991(10)	48(5)
N(50)	846(6)	-415(10)	3235(8)	48(5)*
O(40)	1083(4)	1322(8)	3537(6)	35(4)*
Cl(1)	295(2)	2913(4)	9794(3)	64(2)*
O(11)	678(8)	2174(13)	9980(11)	115(8)*
O(12)	541(7)	3891(11)	9674(8)	83(6)*
O(13)	-96(8)	2975(13)	10329(9)	102(8)*
O(14)	3(7)	2556(13)	9222(9)	99(7)*

(continued)

TABLE 1. (continued)

Atom	x	y	z	$U^a$
Cl(2)	942(2)	7417(4)	9876(3)	71(2)*
O(21)	642(10)	6620(18)	9476(15)	175(13)*
O(22)	1466(7)	7095(17)	9951(11)	124(9)*
O(23)	677(9)	7457(15)	10552(10)	130(10)*
O(24)	918(9)	8428(14)	9614(10)	128(9)*
Cl(3)	3547(2)	1902(4)	1994(3)	67(2)*
O(31)	3690(9)	2449(13)	2582(10)	128(8)*
O(32)	3091(6)	2350(14)	1624(9)	94(7)*
O(33)	3437(9)	916(15)	2128(10)	136(10)*
O(34)	3992(7)	1926(18)	1599(14)	142(11)*
Cl(4)	2976(2)	7260(4)	1876(4)	78(2)*
O(41)	3260(8)	8231(16)	2107(10)	120(9)*
O(42)	2788(14)	6745(27)	2450(15)	264(20)*
O(43)	2562(11)	7438(22)	1538(23)	250(19)*
O(44)	3409(9)	6902(21)	1640(21)	219(18)*
O(60)	2682(8)	-330(16)	3196(10)	114(9)*
C(60)	2835(19)	-1210(33)	3633(17)	186(23)*
C(61)	2600(17)	-1075(25)	4288(22)	155(19)*
O(70)	-102(6)	4923(12)	3487(8)	70(6)*
C(70)	-178(12)	5731(19)	3009(15)	99(12)*
C(71)	-263(16)	5533(26)	2342(14)	161(19)*

<sup>a</sup>Starred item: equivalent isotropic  $U$  defined as one third of the trace of the orthogonalised  $U_{ij}$  tensor.

[17] revealed the structure and the remaining non-hydrogen atoms were located from difference Fourier maps. Anisotropic thermal parameters were assigned to the copper atom, and to all oxygen atoms except O23 and O24, the refinement on 157 parameters converged with  $R = 0.0793$ ,  $R_w = 0.1018$ ,  $g = 0.00213$ . The final difference map showed no features greater than  $\pm 1.06 \text{ e } \text{Å}^{-3}$ .

*Crystal data for [Zn(L1)(H<sub>2</sub>O)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>]/(ClO<sub>4</sub>)<sub>2</sub>*

$\text{C}_{16}\text{H}_{28}\text{Cl}_4\text{N}_4\text{O}_{22}\text{Zn}_2$ , colourless block, dimensions  $0.40 \times 0.56 \times 0.68 \text{ mm}$ , monoclinic,  $a = 15.114(7)$ ,  $b = 9.428(3)$ ,  $c = 22.649(9) \text{ Å}$ ,  $\beta = 100.86(3)^\circ$ ,  $U = 3170(2) \text{ Å}^3$ , space group  $C2/c$ ,  $Z = 4$ ,  $F(000) = 1826$ . Using  $1.7^\circ$   $\omega$ -scans 3066 reflections were collected with  $4 < 2\theta < 50^\circ$  at 150 K. Of these, 2785 were unique, and the 2260 having  $I > 3\sigma(I)$  were ultimately used in the structure refinement. Direct methods [18] revealed the structure 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 217 parameters converged with  $R = 0.0391$ ,  $R_w = 0.0500$ ,  $g = 0.00027$ . The final difference map showed no features greater than  $\pm 0.82 \text{ e } \text{Å}^{-3}$ .

*Crystal data for [Mn(L3)(L4)]<sub>2</sub>/(ClO<sub>4</sub>)<sub>4</sub>·2EtOH*

$\text{C}_{50}\text{H}_{60}\text{Cl}_4\text{Mn}_2\text{N}_8\text{O}_{22}$ , irregular brown block, dimensions  $0.18 \times 0.19 \times 0.25 \text{ mm}$ , orthorhombic,  $a = 23.987(7)$ ,  $b = 12.697(3)$ ,  $c = 19.355(5) \text{ Å}$ ,  $U =$

$5895(3) \text{ Å}^3$ , space group  $Pca2_1$ ,  $Z = 4$ ,  $F(000) = 2840$ . Using  $1.4^\circ$   $\omega$ -scans 4308 reflections were collected with  $4 < 2\theta < 45^\circ$ , index range:  $h$  0/26,  $k$  0/14,  $l$  0/21, at 170 K. Of these, 2447 were unique, and the 2260 having  $I > 3\sigma(I)$  were ultimately used in the structure refinement. Direct methods [18] revealed the structure and the remaining non-hydrogen atoms were located from difference Fourier maps. Anisotropic thermal parameters were assigned to all manganese, chlorine, oxygen and nitrogen atoms as well as to the carbon atoms of the ethanol molecules (C60, C61, C70, C71) and the refinement on 544 parameters converged with  $R = 0.0876$ ,  $R_w = 0.1146$ ,  $g = 0.00423$ . The remaining feature of  $+1.99 \text{ e } \text{Å}^{-3}$  was  $1.1 \text{ Å}$  from Mn2.

*Crystal data for [Mn(L3)(L4)]<sub>2</sub>/(ClO<sub>4</sub>)<sub>4</sub>·2MeCN*

$\text{C}_{50}\text{H}_{56}\text{Cl}_4\text{Mn}_2\text{N}_{10}\text{O}_{20}$ , irregular brown block, dimensions  $0.30 \times 0.30 \times 0.40 \text{ mm}$ , monoclinic,  $a = 10.391(7)$ ,  $b = 24.451(23)$ ,  $c = 11.558(6) \text{ Å}$ ,  $\beta = 92.31(5)^\circ$ ,  $U = 2934(4) \text{ Å}^3$ , space group  $P2_1/n$ ,  $Z = 2$ ,  $F(000) = 1408$ . Using  $2.8^\circ$   $\omega$ -scans 4172 reflections were collected with  $4 < 2\theta < 45^\circ$  at 180 K. Of these, 3815 were unique, and the 1325 having  $I > 3\sigma(I)$  were ultimately used in the structure refinement. A Patterson calculation [17] 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 the manganese atom and the two perchlorate groups and the refinement on 228 parameters converged with  $R = 0.1181$ ,  $R_w = 0.1460$ ,  $g = 0.00220$ . The remaining feature of  $+1.92 \text{ e } \text{Å}^{-3}$  was  $1.1 \text{ Å}$  from Mn.

Infrared spectra were recorded as KBr discs or Nujol mulls using a Pye-Unicam SP3-300 infrared spectrophotometer. A Varian DMS100 spectrophotometer was used to record electronic spectra over the range  $11\,111\text{--}50\,000 \text{ cm}^{-1}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a Varian XL300 Fourier transform spectrophotometer. Microanalyses were carried out by the Campbell Microanalytical Laboratory, University of Otago, Dunedin. Mass spectra were obtained by the FAB (fast atom bombardment) technique using a Kratos MS80 spectrometer.

## Results and Discussion

### Synthesis

L1 was prepared by Schiff base condensation of 2-pyridinecarbaldehyde and ethanolamine; metal complexes were then prepared either from the free ligand or by template reaction. L3 was prepared from 2-acetylpyridine and ethanolamine in a template reaction with Mn(II). The resulting manganese complex also contained the rearrangement product L4. Details of the synthesis are given in 'Experimental'. In each case, the progress of the reaction

could be followed by monitoring the changes in the infrared spectrum. The  $\nu(\text{C}=\text{O})$  stretch at *c.* 1700  $\text{cm}^{-1}$  in the pyridine precursors was replaced by the imine vibration at *c.* 1650  $\text{cm}^{-1}$ . The identities of the free ligand L1 and the rearrangement product (L2)<sup>+</sup> were established unambiguously using <sup>1</sup>H and <sup>13</sup>C two-dimensional NMR spectroscopy. The other complexes discussed have been structurally characterised by single crystal X-ray structure determinations.

#### Description of the Structures

Two manganese(II) complexes of L1 with thiocyanate were characterised; a monomer and a polymer. Contrary to expectations, no dimeric or tetrameric products were isolated. The monomer,  $\text{Mn}(\text{L1})_2(\text{NCS})_2$ , is shown in Fig. 1. Selected bond lengths and angles are given in Table 2. Two L1 ligands and two thiocyanate anions are bound to the manganese(II) atom in a geometry approaching octahedral. The distortion observed is due to the restricted angles enforced by the pyridineimine unit ( $72.7(1)^\circ$ ,  $72.6(1)^\circ$ ). The mean planes of the two pyridine rings are at  $75.2^\circ$  to each other. The two alcohol groups of the L1 ligands are not coordinated and the alkyl chains twist away from the central manganese atom; a distorted hydrogen bond links them (O1–O10 2.819 Å).

The second complex,  $[\text{Mn}(\text{L1})(\text{NCS})_2]_x$ , is polymeric (Fig. 2, Table 3). Again the six-coordinate manganese atom has distorted geometry due to the bound pyridineimine group ( $72.1(1)^\circ$ ) but only one L1 ligand is bound to each metal atom. The other angles are slightly closer to  $90^\circ$  as the donors have less constrained geometry. These donors are the nitrogen atom of a terminally bound thiocyanate group, one nitrogen atom and one sulfur atom from each of two 1,3-bridging thiocyanate groups, and the alcohol oxygen of an L1 ligand bound to the adjacent manganese atom. The 1,3-bridging thiocyanate and the

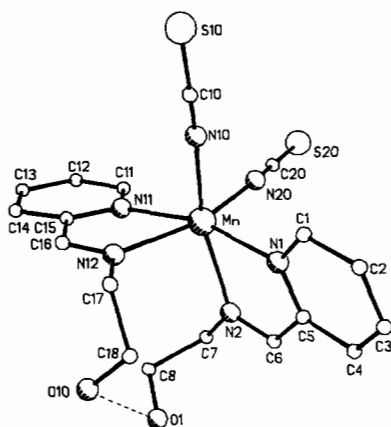


Fig. 1. Perspective view of  $\text{Mn}(\text{L1})_2(\text{NCS})_2$ .

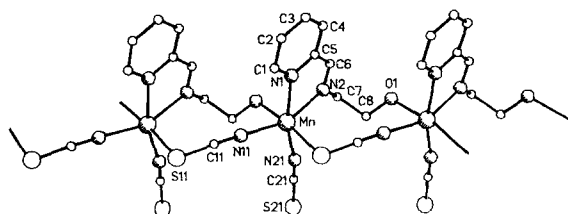
alcohol oxygen atom intermolecular bridge hold the linear polymeric chain together. The pyridine rings are parallel to each other at a separation of 3.97(1) Å. This complex is significantly different to the  $[\text{Cu}_2\text{O}_2]$  and  $[\text{Cu}_4\text{O}_4]$  clusters [8–14] because the alcohol group does not bridge two manganese ions, it binds only to the manganese atom of the next unit in the polymer. The observation that the monomeric and polymeric products could be separated and recrystallised cleanly from the same initial reaction suggests that there is little interconversion between the two structural types during recrystallisation. The mole ratio of one L1:one manganese(II) employed in the synthesis is probably the reason that the polymeric 1:1 complex predominates over the 2:1 monomeric complex.

The dimeric copper(II) and zinc(II) complexes of L1 are almost isomorphous. Hence, only the zinc cation is shown (Fig. 3, Table 4); the numbering scheme is the same for the copper complex (Table 5). Both compounds are dimeric with the monomer units linked by the alcohol groups (O1, O1'). In each case the metal ion has a geometry which approximates to octahedral; the donor atoms in the L1 plane are the two nitrogen atoms of L1 and two water molecules. Axial coordination by O11 of the perchlorate group is weak in both complexes (Zn–O11 2.342; Cu–O11 2.526 Å), however in the copper case this is accentuated by a Jahn–Teller distortion. This distortion is also evident in the axial Cu–O1' distance of 2.282 Å which is 0.3 Å longer than the average Cu (in the plane donor) bond lengths. In comparison the Zn–O1' distance of 2.105 Å is within the range of values 2.031–2.122 Å found for the nitrogen atoms of L1 and the water donors. There are numerous hydrogen-bonding interactions between the bound water molecules and the perchlorate groups. Again these complexes are different from those previously characterised [8–14] because the alcohol oxygen groups bind only to the copper (or zinc) atom of the second half of the dimer. That is, they hold the dimer together but they do not bridge two metal ions. Because there are no one-atom bridges, and the intermolecular alcohol bearing alkyl chains bind axially to the copper atoms, the Cu–Cu separation is large (5.6 Å). This leads to a room temperature magnetic moment of 1.88 BM for this copper(II) complex, which is in the range expected for uncoupled octahedral  $d^9$  ions (1.7–2.2 BM) [20]. The visible spectrum (MeOH) shows only one broad d–d transition at 722 nm,  $\epsilon = 40 \text{ l mol}^{-1} \text{ cm}^{-1}$ , which can be assigned to  ${}^2E_g \rightarrow {}^2T_2$ . Intense charge transfer or ligand transitions occur in the ultraviolet.

The (L2)<sup>+</sup> cation has two resonance forms shown with selected bond lengths in Fig. 4 [15]. The structure consists of a positively charged imidazo[1,5-*a*]-pyridinium ring with pyridine and hydroxyethyl substituents on the (five membered) imidazo ring.

TABLE 2. Interatomic distances (Å) and angles (°) for Mn(L1)(NCS)<sub>2</sub>

Mn–N(1)	2.296(3)	Mn–N(2)	2.277(4)
Mn–N(11)	2.300(3)	Mn–N(12)	2.292(3)
Mn–N(10)	2.174(4)	Mn–N(20)	2.136(4)
N(1)–C(1)	1.338(5)	N(1)–C(5)	1.344(5)
C(1)–C(2)	1.391(6)	C(2)–C(3)	1.365(7)
C(3)–C(4)	1.379(7)	C(4)–C(5)	1.377(6)
C(5)–C(6)	1.463(6)	C(6)–N(2)	1.269(5)
N(2)–C(7)	1.457(6)	C(7)–C(8)	1.517(7)
C(8)–O(1)	1.419(7)	N(11)–C(11)	1.339(5)
N(11)–C(15)	1.348(5)	C(11)–C(12)	1.382(6)
C(12)–C(13)	1.377(6)	C(13)–C(14)	1.390(6)
C(14)–C(15)	1.385(6)	C(15)–C(16)	1.473(6)
C(16)–N(12)	1.264(5)	N(12)–C(17)	1.459(5)
C(17)–C(18)	1.496(7)	C(18)–O(10)	1.425(6)
N(10)–C(10)	1.156(6)	C(10)–S(10)	1.636(5)
N(20)–C(20)	1.158(6)	C(20)–S(20)	1.628(5)
N(1)–Mn–N(2)	72.7(1)	N(1)–Mn–N(11)	164.8(1)
N(2)–Mn–N(11)	97.9(1)	N(1)–Mn–N(12)	96.4(1)
N(2)–Mn–N(12)	97.3(1)	N(11)–Mn–N(12)	72.6(1)
N(1)–Mn–N(10)	88.8(1)	N(2)–Mn–N(10)	161.5(1)
N(11)–Mn–N(10)	100.3(1)	N(12)–Mn–N(10)	85.0(1)
N(1)–Mn–N(20)	102.4(1)	N(2)–Mn–N(20)	89.9(1)
N(11)–Mn–N(20)	89.2(1)	N(12)–Mn–N(20)	161.1(1)
N(10)–Mn–N(20)	93.8(2)	Mn–N(1)–C(1)	127.7(3)
Mn–N(1)–C(5)	114.7(3)	C(1)–N(1)–C(5)	117.6(3)
N(1)–C(1)–C(2)	122.2(4)	C(1)–C(2)–C(3)	119.5(4)
C(2)–C(3)–C(4)	119.0(4)	C(3)–C(4)–C(5)	118.6(4)
N(1)–C(5)–C(6)	123.2(4)	N(1)–C(5)–C(6)	116.0(3)
C(4)–C(5)–C(6)	120.8(4)	C(5)–C(6)–N(2)	121.0(4)
Mn–N(2)–C(6)	115.4(3)	Mn–N(2)–C(7)	126.8(3)
C(6)–N(2)–C(7)	117.8(4)	N(2)–C(7)–C(8)	109.5(4)
C(7)–C(8)–O(1)	111.7(4)	Mn–N(11)–C(11)	128.1(3)
Mn–N(11)–C(15)	114.4(3)	C(11)–N(11)–C(15)	117.4(3)
N(11)–C(11)–C(12)	123.5(4)	C(11)–C(12)–C(13)	118.8(4)
C(12)–C(13)–C(14)	118.8(4)	C(13)–C(14)–C(15)	118.9(4)
N(11)–C(15)–C(14)	122.7(4)	N(11)–C(15)–C(16)	116.4(3)
C(14)–C(15)–C(16)	120.9(4)	C(15)–C(16)–N(12)	120.6(4)
Mn–N(12)–C(16)	115.4(3)	Mn–N(12)–C(17)	126.7(3)
C(16)–N(12)–C(17)	117.7(4)	N(12)–C(17)–C(18)	109.6(4)
C(17)–C(18)–O(10)	111.5(4)	Mn–N(10)–C(10)	168.9(4)
N(10)–C(10)–S(10)	178.9(4)	Mn–N(20)–C(20)	166.1(4)
N(20)–C(20)–S(20)	178.7(4)		

Fig. 2. Perspective view of [Mn(L1)(NCS)<sub>2</sub>]<sub>x</sub><sup>-</sup>.

Formation of an ionic compound is likely to be due to the poor leaving ability of the hydroxyethyl substituent. The angle between the mean planes of the imidazo[1,5-*a*]pyridinium ring and the pyridine ring is 43.2°. This large twist prevents the steric strain

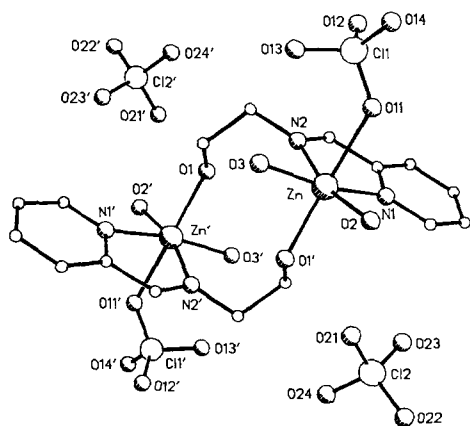
which a coplanar arrangement (with the hydrogen atoms very close to each other) would produce. The bond lengths show that the imidazo[1,5-*a*]pyridinium ring is not aromatic; double bonds are localised at C11–C12 and C13–C14 (Fig. 4(A)). This is also evident from the <sup>3</sup>*J* coupling constants shown in Fig. 4(B).

The cation of the [Mn(L3)(L4)]<sub>2</sub>(ClO<sub>4</sub>)<sub>4</sub>·2EtOH complex is shown in Fig. 5, and selected bond lengths and angles are given in Table 6. This dimeric complex consists of two six-coordinate manganese(II) ions each with a geometry approaching octahedral (Fig. 5, Table 6). The L3 ligand binds to the manganese atom via two nitrogen atoms and an alcohol group. The angle at manganese due to L3 binding is 72 ± 3°. The



TABLE 3. Interatomic distances (Å) and angles (°) for [Mn(L1)(NCS)<sub>2</sub>]<sub>x</sub>

Mn–N(1)	2.286(3)	Mn–N(2)	2.268(2)
Mn–N(11)	2.145(3)	Mn–N(21)	2.154(3)
Mn–O(1')	2.269(2)	Mn–S(11')	2.685(1)
N(1)–C(1)	1.332(5)	N(1)–C(5)	1.345(4)
C(1)–C(2)	1.395(6)	C(2)–C(3)	1.354(6)
C(3)–C(4)	1.380(5)	C(4)–C(5)	1.391(4)
C(5)–C(6)	1.475(4)	C(6)–N(2)	1.272(4)
N(2)–C(7)	1.470(4)	C(7)–C(8)	1.514(4)
C(8)–O(1)	1.431(4)	O(1)–Mn'	2.269(2)
N(11)–C(11)	1.164(4)	C(11)–S(11)	1.654(3)
S(11)–Mn''	2.685(1)	N(21)–C(21)	1.162(4)
C(21)–S(21)	1.647(3)		
N(1)–Mn–N(2)	72.1(1)	N(1)–Mn–N(11)	91.4(1)
N(2)–Mn–N(11)	157.1(1)	N(1)–Mn–N(21)	164.7(1)
N(2)–Mn–N(21)	93.4(1)	N(11)–Mn–N(21)	103.9(1)
N(1)–Mn–O(1')	97.1(1)	N(2)–Mn–O(1')	82.1(1)
N(11)–Mn–O(1')	84.3(1)	N(21)–Mn–O(1')	85.5(1)
N(1)–Mn–S(11')	88.0(1)	N(2)–Mn–S(11')	104.3(1)
N(11)–Mn–S(11')	90.5(1)	N(21)–Mn–S(11')	90.9(1)
O(1')–Mn–S(11')	172.8(1)	Mn–N(1)–C(1)	126.4(2)
Mn–N(1)–C(5)	115.8(2)	C(1)–N(1)–C(5)	117.6(3)
N(1)–C(1)–C(2)	122.2(4)	C(1)–C(2)–C(3)	119.6(4)
C(2)–C(3)–C(4)	119.4(4)	C(3)–C(4)–C(5)	118.1(3)
N(1)–C(5)–C(4)	123.0(3)	N(1)–C(5)–C(6)	115.3(3)
C(4)–C(5)–C(6)	121.6(3)	C(5)–C(6)–N(2)	119.5(3)
Mn–N(2)–C(6)	117.0(2)	Mn–N(2)–C(7)	124.7(2)
C(6)–N(2)–C(7)	118.2(3)	N(2)–C(7)–C(8)	110.4(2)
C(7)–C(8)–O(1)	110.9(2)	C(8)–O(1)–Mn'	123.3(2)
Mn–N(11)–C(11)	168.7(2)	N(11)–C(11)–S(11)	178.4(3)
C(11)–S(11)–Mn''	96.4(1)	Mn–N(21)–C(21)	169.9(3)
N(21)–C(21)–S(21)	179.7(3)		

Fig. 3. Perspective view of [Zn(L1)(H<sub>2</sub>O)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.

other donors, a pyridine nitrogen and two bridging oxygen atoms, are from the rearrangement product L4. The Mn<sub>2</sub>O<sub>2</sub> core is a rhombus; the internal angles at manganese are acute (76.5(4) and 73.8(4)°) whereas the internal angles at oxygen are obtuse (104.9(4) and 104.8(4)°). This matches the prefer-

ence of oxygen for tetrahedral angles (109.5°) and shows the irregular nature of the six-coordinate manganese(II) environment. The L3 pyridine rings (N1 → C5 and N31 → C35) and the L4 pyridine rings which share two atoms with the five membered ring (N50 → C54 and N20 → C24, respectively) lie above one another (*c.* 10° from parallel) at an average distance of 3.5 ± 0.2 Å, which indicates some π–π interaction. The L4 ligand is twisted at the saturated carbon of the five membered ring C16 (or C46), such that the mean planes of the respective pyridine rings lie at an angle of 89.9° (or 88.0°). C16 and C46 have distorted tetrahedral geometry; C16 is more distorted than C46, suggesting that the C16–O10 bond still maintains some double bond character (C16–O10 1.30(2), O10–C16–C15 117(2)°, O10–C16–C17 113(2)°, O10–C16–N20 114(2)°) at the expense of bonds to C17 and N20 (C16–C17 1.68(3), C16–N20 1.64(3) Å).

#### Formation of L1 and (L2)\*

Schiff bases such as L1 are formed via a series of equilibria. The precise mechanism is pH dependent

TABLE 4. Interatomic distances (Å) and angles (°) for [Cu(L1)(H<sub>2</sub>O)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>

Cu–N(1)	1.975(17)	Cu–N(2)	1.952(18)
Cu–O(2)	2.004(16)	Cu–O(3)	1.973(14)
Cu–O(11)	2.526(16)	Cu–O(1')	2.282(14)
N(1)–C(1)	1.370(25)	N(1)–C(5)	1.386(27)
C(1)–C(2)	1.400(28)	C(2)–C(3)	1.442(34)
C(3)–C(4)	1.311(31)	C(4)–C(5)	1.376(29)
C(5)–C(6)	1.474(29)	C(6)–N(2)	1.265(26)
N(2)–C(7)	1.517(26)	C(7)–C(8)	1.512(25)
C(8)–O(1)	1.388(26)	O(1)–Cu'	2.282(14)
Cl(1)–O(11)	1.455(18)	Cl(1)–O(12)	1.454(14)
Cl(1)–O(13)	1.410(20)	Cl(1)–O(14)	1.467(18)
Cl(2)–O(21)	1.439(16)	Cl(2)–O(22)	1.450(16)
Cl(2)–O(23)	1.381(15)	Cl(2)–O(24)	1.403(17)
N(1)–Cu–N(2)	82.2(7)	N(1)–Cu–O(2)	93.6(6)
N(2)–Cu–O(2)	169.0(6)	N(1)–Cu–O(3)	174.2(7)
N(2)–Cu–O(3)	94.0(6)	O(2)–Cu–O(3)	89.3(6)
N(1)–Cu–O(11)	88.8(6)	N(2)–Cu–O(11)	87.6(7)
O(2)–Cu–O(11)	82.2(6)	O(3)–Cu–O(11)	86.7(6)
N(1)–Cu–O(1')	98.8(6)	N(2)–Cu–O(1')	100.3(6)
O(2)–Cu–O(1')	90.3(6)	O(3)–Cu–O(1')	86.1(6)
O(11)–Cu–O(1')	169.7(6)	Cu–N(1)–C(1)	130.2(13)
Cu–N(1)–C(5)	110.4(13)	C(1)–N(1)–C(5)	119.3(17)
N(1)–C(1)–C(2)	119.7(18)	C(1)–C(2)–C(3)	121.1(20)
C(2)–C(3)–C(4)	114.7(21)	C(3)–C(4)–C(5)	126.6(22)
N(1)–C(5)–C(6)	118.5(19)	N(1)–C(5)–C(6)	116.3(18)
C(4)–C(5)–C(6)	125.3(20)	C(5)–C(6)–N(2)	112.9(20)
Cu–N(2)–C(6)	118.0(15)	Cu–N(2)–C(7)	127.6(13)
C(6)–N(2)–C(7)	114.2(18)	N(2)–C(7)–C(8)	110.8(17)
C(7)–C(8)–O(1)	113.4(16)	C(8)–O(1)–Cu'	124.8(11)
O(11)–Cl(1)–O(12)	111.5(9)	O(11)–Cl(1)–O(13)	111.8(11)
O(12)–Cl(1)–O(13)	109.1(10)	O(11)–Cl(1)–O(14)	104.3(11)
O(12)–Cl(1)–O(14)	108.4(9)	O(13)–Cl(1)–O(14)	111.6(11)
Cu–O(11)–Cl(1)	129.7(8)	O(21)–Cl(2)–O(22)	107.6(10)
O(21)–Cl(2)–O(23)	107.8(10)	O(22)–Cl(2)–O(23)	112.9(11)
O(21)–Cl(2)–O(24)	109.9(11)	O(22)–Cl(2)–O(24)	109.5(9)
O(23)–Cl(2)–O(24)	109.2(12)		

[21] and there exists an optimum pH for the maximum rate of formation of any particular imine. This is due to a switch of the rate determining step from acid-catalysed dehydration (Fig. 4, step 5) on the high pH side, to attack of the amine on the carbonyl group (Fig. 4, step 1) on the low pH side of the optimum pH. L1 can be formed quantitatively by several routes ('Experimental'). It appears that the optimum pH for L1 formation lies in the neutral or mildly acidic pH range. Schiff bases like L1 are known to be unstable with respect to hydrolysis. The rate of hydrolysis increases with acidity, allowing (L2)<sup>+</sup> formation to occur.

The structure of (L2)ClO<sub>4</sub> has been published [15]. Figure 4 outlines a possible mechanism for formation of L1 and (L2)<sup>+</sup> from 2-pyridinecarbaldehyde and ethanolamine based on those proposed for similar compounds [22]. (L2)<sup>+</sup> is formed when 2-pyridinecarbaldehyde and ethanolamine are reacted under acidic conditions (1:1 HClO<sub>4</sub> or *p*-toluenesulfonic acid:aldehyde) and, to some extent, in the

presence of metal ions. The role of acid is probably to destabilise L1 (i.e. enhanced hydrolysis), promoting (L2)<sup>+</sup> formation instead. (L2)ClO<sub>4</sub> has quite low solubility and crystallises out of ethanolic reaction solutions which contain mainly L1 and 2-pyridinecarbaldehyde rather than (L2)<sup>+</sup> (5:1) via the equilibria shown in Fig. 4. This conclusion is based on electronic spectra of ethanolic solutions; (L2)<sup>+</sup> has a characteristic absorption at 315 nm,  $\epsilon = 11\,300\text{ l mol}^{-1}\text{ cm}^{-1}$  which was readily distinguished from L1 ( $\lambda_{\text{max}} = 273\text{ nm}$ ,  $\epsilon = 5600\text{ l mol}^{-1}\text{ cm}^{-1}$ ;  $\lambda_{\text{max}} = 234\text{ nm}$ ,  $\epsilon = 10\,000\text{ l mol}^{-1}\text{ cm}^{-1}$ ), although 2-pyridinecarbaldehyde has absorptions at similar wavelengths to L1. On the other hand, (L2)(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>) is quite soluble and therefore no shift of the equilibrium due to precipitation occurs. After solvent removal an oil remains and some of the excess protonated amine precipitates as the *p*-toluene-sulfonate salt. NMR of the oil shows the presence of the amine salt and (L2)(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>) but no significant amounts of L1.

TABLE 5. Interatomic distances (Å) and angles (°) for  $[\text{Zn}(\text{L1})(\text{H}_2\text{O})_2(\text{ClO}_4)]_2(\text{ClO}_4)_2$ 

Zn–N(1)	2.122(3)	Zn–N(2)	2.107(3)
Zn–O(2)	2.031(3)	Zn–O(3)	2.051(3)
Zn–O(11)	2.342(3)	Zn–O(1')	2.105(3)
N(1)–C(1)	1.342(5)	N(1)–C(5)	1.346(6)
C(1)–C(2)	1.382(6)	C(2)–C(3)	1.381(7)
C(3)–C(4)	1.395(6)	C(4)–C(5)	1.383(6)
C(5)–C(6)	1.483(6)	C(6)–N(2)	1.262(5)
N(2)–C(7)	1.466(5)	C(7)–C(8)	1.521(5)
C(8)–O(1)	1.445(5)	O(1)–Zn'	2.105(3)
Cl(1)–O(12)	1.437(3)	Cl(1)–O(13)	1.447(3)
Cl(1)–O(11)	1.452(4)	Cl(1)–O(14)	1.421(4)
Cl(2)–O(21)	1.463(4)	Cl(2)–O(22)	1.410(4)
Cl(2)–O(23)	1.409(4)	Cl(2)–O(24)	1.389(5)
<hr/>			
N(1)–Zn–N(2)	78.8(1)	N(1)–Zn–O(2)	94.2(1)
N(2)–Zn–O(2)	165.1(1)	N(1)–Zn–O(3)	169.5(1)
N(2)–Zn–O(3)	91.8(1)	O(2)–Zn–O(3)	93.8(1)
N(1)–Zn–O(11)	88.1(1)	N(2)–Zn–O(11)	87.2(1)
O(2)–Zn–O(11)	79.3(1)	O(3)–Zn–O(11)	86.6(1)
N(1)–Zn–O(1')	98.6(1)	N(2)–Zn–O(1')	102.6(1)
O(2)–Zn–O(1')	91.4(1)	O(3)–Zn–O(1')	88.1(1)
O(11)–Zn–O(1')	168.9(1)	Zn–N(1)–C(1)	129.1(3)
Zn–N(1)–C(5)	112.5(3)	C(1)–N(1)–C(5)	118.3(3)
N(1)–C(1)–C(2)	121.9(4)	C(1)–C(2)–C(3)	119.7(4)
C(2)–C(3)–C(4)	119.0(4)	C(3)–C(4)–C(5)	117.8(4)
N(1)–C(5)–C(6)	123.3(4)	N(1)–C(5)–C(6)	115.1(3)
C(4)–C(5)–C(6)	121.6(4)	C(5)–C(6)–N(2)	119.9(4)
Zn–N(2)–C(6)	113.4(3)	Zn–N(2)–C(7)	127.7(2)
C(6)–N(2)–C(7)	118.5(3)	N(2)–C(7)–C(8)	111.0(3)
C(7)–C(8)–O(1)	111.3(3)	C(8)–O(1)–Zn'	124.2(2)
O(12)–Cl(1)–O(13)	108.5(2)	O(12)–Cl(1)–O(11)	108.4(2)
O(13)–Cl(1)–O(11)	109.9(2)	O(12)–Cl(1)–O(14)	109.7(2)
O(13)–Cl(1)–O(14)	110.7(2)	O(11)–Cl(1)–O(14)	109.6(2)
Zn–O(11)–Cl(1)	132.8(2)	O(21)–Cl(2)–O(22)	107.4(2)
O(21)–Cl(2)–O(23)	110.0(2)	O(22)–Cl(2)–O(23)	113.2(2)
O(21)–Cl(2)–O(24)	108.9(3)	O(22)–Cl(2)–O(24)	108.5(3)
O(23)–Cl(2)–O(24)	108.7(3)		

To explain these observations it was necessary to determine whether or not  $(\text{L2})^+$  formation is reversible under these conditions. The electronic spectrum of  $(\text{L2})\text{ClO}_4$  in EtOH did not change over two months. Acidification to  $\text{pH} \approx 1$  did not change the absorption at 315 nm, although more acid did appear to cause aldehyde to be reformed (based on the electronic spectrum). Addition of base to  $\text{pH} \approx 14$  caused a white precipitate but, other than concentration effects, the electronic spectrum of the solution was unchanged. Therefore, under the reaction conditions employed,  $(\text{L2})^+$  formation appears to be irreversible. This implies that, in the free L1 forming reactions, any  $(\text{L2})^+$  produced should be detected in the products. No  $(\text{L2})^+$  is detected, possibly because the pH is close to the optimum for fast reaction to produce L1, and on the time scale employed (weeks rather than months)  $(\text{L2})^+$  did not form in significant quantity.

Transition metal ions (e.g. Mn(II), Fe(III)) will provide slightly acidic pH conditions favouring fast, reversible formation of L1. Because L1 and the transition metal complexes of L1 are very soluble, the equilibrium allows slow, irreversible  $(\text{L2})\text{ClO}_4$  formation over a period of months. When Zn(II) was present  $[\text{Zn}(\text{L1})(\text{H}_2\text{O})_2]_2(\text{ClO}_4)_4$  was formed although small amounts of  $(\text{L2})^+$  were detected in the remaining oil. The manganese complexes  $[\text{Mn}(\text{L1})_2(\text{NCS})_2]$  and  $[\text{Mn}(\text{L1})(\text{NCS})_2]_x$  have been isolated quickly (days) from reactions of Mn(II) and L1, with small amounts of  $(\text{L2})\text{ClO}_4$  also observed. In conclusion, it appears that in the presence of transition metal ions, L1 chemistry will be complicated by the formation of  $(\text{L2})^+$  to some extent.

The change to a ketone precursor prevented the rearrangement discussed above but, in addition to forming the desired Schiff base L3, L4 formed via an aldol condensation. Figure 6 shows a route by

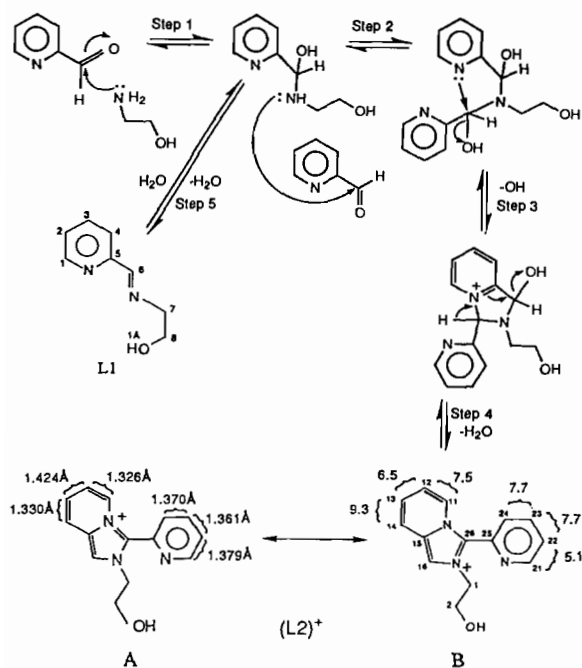


Fig. 4. A possible mechanism for the formation of L1 and  $(L2)^+$ . The two resonance forms of the  $(L2)^+$  cation are shown: A includes selected bond lengths (Å), B selected  $^3J$  coupling constants (Hz).

which L4 formation may occur. The first three steps are base-catalysed aldol-type reactions followed by a dehydration step, resulting in the  $\alpha\beta$ -unsaturated ketone (L4). On coordination, attack by the pyridine lone pair on the electron-deficient carbon of the carbonyl group (step 5) results in bond formation in the case of C46 (C46–N50 1.502 Å) but for C16 the

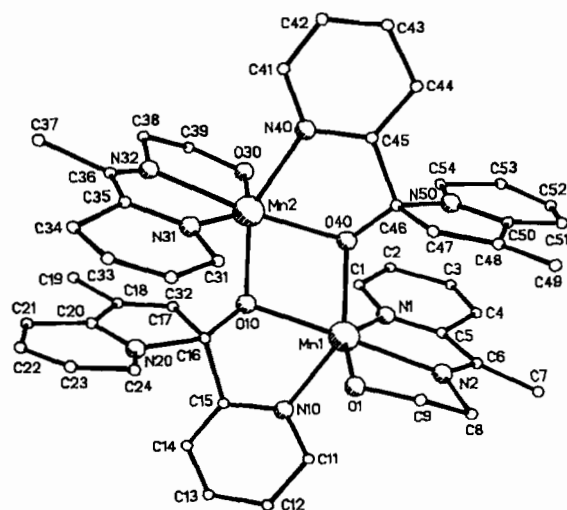


Fig. 5. Perspective view of the  $[Mn(L3)(L4)]_2^{4+}$  cation.

TABLE 6. Interatomic distances (Å) and angles ( $^\circ$ ) for  $[Mn(L3)(L4)]_2(ClO_4)_4 \cdot 2EtOH$

Mn(1)–N(1)	2.203(14)	Mn(1)–N(2)	2.211(15)
Mn(1)–O(1)	2.213(12)	Mn(1)–N(10)	2.230(13)
Mn(1)–O(10)	2.182(11)	Mn(1)–O(40)	2.185(11)
N(1)–C(1)	1.325(23)	N(1)–C(5)	1.324(25)
C(1)–C(2)	1.487(29)	C(2)–C(3)	1.427(30)
C(3)–C(4)	1.292(28)	C(4)–C(5)	1.530(29)
C(5)–C(6)	1.418(25)	C(6)–C(7)	1.427(29)
C(6)–N(2)	1.361(23)	N(2)–C(8)	1.495(25)
C(8)–C(9)	1.613(33)	C(9)–O(1)	1.380(25)
N(10)–C(11)	1.321(25)	N(10)–C(15)	1.294(21)
C(11)–C(12)	1.511(28)	C(12)–C(13)	1.327(26)
C(13)–C(14)	1.308(24)	C(14)–C(15)	1.398(24)
C(15)–C(16)	1.518(29)	C(16)–C(17)	1.676(29)
C(16)–N(20)	1.636(31)	C(16)–O(10)	1.295(24)
C(17)–C(18)	1.263(29)	C(18)–C(19)	1.539(33)
C(18)–C(20)	1.435(29)	C(20)–C(21)	1.389(34)
C(20)–N(20)	1.291(25)	C(21)–C(22)	1.481(35)
C(22)–C(23)	1.273(31)	C(23)–C(24)	1.413(29)
C(24)–N(20)	1.232(25)	O(10)–Mn(2)	2.117(11)
Mn(2)–N(31)	2.287(16)	Mn(2)–N(32)	2.281(18)
Mn(2)–O(30)	2.230(14)	Mn(2)–N(40)	2.225(14)
Mn(2)–O(40)	2.119(11)	N(31)–C(31)	1.403(25)
N(31)–C(35)	1.312(24)	C(31)–C(32)	1.330(33)
C(32)–C(33)	1.274(39)	C(33)–C(34)	1.424(41)
C(34)–C(35)	1.519(36)	C(35)–C(36)	1.356(31)
C(36)–C(37)	1.594(40)	C(36)–N(32)	1.198(31)
N(32)–C(38)	1.423(34)	C(38)–C(39)	1.436(48)
C(39)–O(30)	1.460(35)	N(40)–C(41)	1.330(24)
N(40)–C(45)	1.359(21)	C(41)–C(42)	1.342(26)

(continued)

TABLE 6. (continued)

C(42)–C(43)	1.260(24)	C(43)–C(44)	1.429(26)
C(44)–C(45)	1.370(25)	C(45)–C(46)	1.529(25)
C(46)–C(47)	1.506(23)	C(46)–N(50)	1.502(23)
C(46)–O(40)	1.368(20)	C(47)–C(48)	1.366(25)
C(48)–C(49)	1.398(26)	C(48)–C(50)	1.447(24)
C(50)–C(51)	1.378(27)	C(50)–N(50)	1.369(21)
C(51)–C(52)	1.424(30)	C(52)–C(53)	1.338(30)
C(53)–C(54)	1.540(29)	C(54)–N(50)	1.317(23)
Cl(1)–O(11)	1.362(19)	Cl(1)–O(12)	1.395(15)
Cl(1)–O(13)	1.398(19)	Cl(1)–O(14)	1.385(18)
Cl(2)–O(21)	1.463(26)	Cl(2)–O(22)	1.331(19)
Cl(2)–O(23)	1.455(21)	Cl(2)–O(24)	1.383(19)
Cl(3)–O(31)	1.375(20)	Cl(3)–O(32)	1.425(17)
Cl(3)–O(33)	1.306(19)	Cl(3)–O(34)	1.314(21)
Cl(4)–O(41)	1.478(21)	Cl(4)–O(42)	1.366(31)
Cl(4)–O(43)	1.210(34)	Cl(4)–O(44)	1.223(27)
O(41)–O(44)	1.947(36)	O(60)–C(60)	1.449(44)
C(60)–C(61)	1.396(55)	O(70)–C(70)	1.393(31)
C(70)–C(71)	1.330(40)		
N(1)–Mn(1)–N(2)	73.3(5)	N(1)–Mn(1)–O(1)	146.8(5)
N(2)–Mn(1)–O(1)	73.5(5)	N(1)–Mn(1)–N(10)	93.8(5)
N(2)–Mn(1)–N(10)	106.9(5)	O(1)–Mn(1)–N(10)	94.1(5)
N(1)–Mn(1)–O(10)	108.2(5)	N(2)–Mn(1)–O(10)	177.7(5)
O(1)–Mn(1)–O(10)	104.9(4)	N(10)–Mn(1)–O(10)	71.4(5)
N(1)–Mn(1)–O(40)	92.0(5)	N(2)–Mn(1)–O(40)	108.0(5)
O(1)–Mn(1)–O(40)	99.8(4)	N(10)–Mn(1)–O(40)	144.8(5)
O(10)–Mn(1)–O(40)	73.8(4)	Mn(1)–N(1)–C(1)	124.6(12)
Mn(1)–N(1)–C(5)	113.6(12)	C(1)–N(1)–C(5)	121.5(16)
N(1)–C(1)–C(2)	121.3(17)	C(1)–C(2)–C(3)	116.7(19)
C(2)–C(3)–C(4)	121.0(21)	C(3)–C(4)–C(5)	119.8(19)
N(1)–C(5)–C(4)	119.2(17)	N(1)–C(5)–C(6)	123.6(18)
C(4)–C(5)–C(6)	116.5(17)	C(5)–C(6)–C(7)	128.4(17)
C(5)–C(6)–N(2)	110.6(15)	C(7)–C(6)–N(2)	120.7(16)
Mn(1)–N(2)–C(6)	118.8(10)	Mn(1)–N(2)–C(8)	119.2(12)
C(6)–N(2)–C(8)	121.5(15)	N(2)–C(8)–C(9)	107.4(17)
C(8)–C(9)–O(1)	110.4(17)	Mn(1)–O(1)–C(9)	120.8(12)
Mn(1)–N(10)–C(11)	120.0(11)	Mn(1)–N(10)–C(15)	121.1(12)
C(11)–N(10)–C(15)	118.8(15)	N(10)–C(11)–C(12)	118.6(17)
C(11)–C(12)–C(13)	119.5(18)	C(12)–C(13)–C(14)	118.0(17)
C(13)–C(14)–C(15)	122.1(16)	N(10)–C(15)–C(14)	122.9(16)
N(10)–C(15)–C(16)	110.3(15)	C(14)–C(15)–C(16)	126.2(16)
C(15)–C(16)–C(17)	112.4(17)	C(15)–C(15)–N(20)	102.7(16)
C(17)–C(16)–N(20)	94.9(14)	C(15)–C(16)–O(10)	117.1(17)
C(17)–C(16)–O(10)	113.4(17)	N(20)–C(16)–O(10)	113.7(18)
C(16)–C(17)–C(18)	107.1(18)	C(17)–C(18)–C(19)	126.7(22)
C(17)–C(18)–C(20)	116.9(20)	C(19)–C(18)–C(20)	116.4(20)
C(18)–C(20)–C(21)	129.5(20)	C(18)–C(20)–N(20)	109.4(19)
C(21)–C(20)–N(20)	121.1(20)	C(20)–C(21)–C(22)	111.1(22)
C(21)–C(22)–C(23)	123.0(22)	C(22)–C(23)–C(24)	119.2(21)
C(23)–C(24)–N(20)	117.5(19)	C(16)–N(20)–C(20)	111.4(16)
C(16)–N(20)–C(24)	120.0(17)	C(20)–N(20)–C(24)	127.8(21)
Mn(1)–O(10)–C(16)	118.6(12)	Mn(1)–O(10)–Mn(2)	104.9(4)
C(16)–O(10)–Mn(2)	135.3(12)	O(10)–Mn(2)–N(31)	93.3(5)
O(10)–Mn(2)–N(32)	110.4(6)	N(31)–Mn(2)–N(32)	69.7(6)
O(10)–Mn(2)–O(30)	100.1(5)	N(31)–Mn(2)–O(30)	142.9(6)
N(32)–Mn(2)–O(30)	73.2(6)	O(10)–Mn(2)–N(40)	148.7(5)
N(31)–Mn(2)–N(40)	92.1(5)	N(32)–Mn(2)–N(40)	100.4(6)
O(30)–Mn(2)–N(40)	93.9(5)	O(10)–Mn(2)–O(40)	76.5(4)
N(31)–Mn(2)–O(40)	111.8(5)	N(32)–Mn(2)–O(40)	173.1(5)

(continued)

TABLE 6. (continued)

O(30)–Mn(2)–O(40)	104.9(5)	N(40)–Mn(2)–O(40)	72.9(5)
Mn(2)–N(31)–C(31)	119.1(13)	Mn(2)–N(31)–C(35)	114.3(12)
C(31)–N(31)–C(35)	126.4(17)	N(31)–C(31)–C(32)	116.7(20)
C(31)–C(32)–C(33)	121.7(26)	C(32)–C(33)–C(34)	126.6(28)
C(33)–C(34)–C(35)	112.0(24)	N(31)–C(35)–C(34)	115.9(18)
N(31)–C(35)–C(36)	117.2(19)	C(34)–C(35)–C(36)	126.5(21)
C(35)–C(36)–C(37)	121.1(22)	C(35)–C(36)–N(32)	122.8(22)
C(37)–C(36)–N(32)	116.2(22)	Mn(2)–N(32)–C(36)	116.0(15)
Mn(2)–N(32)–C(38)	113.2(17)	C(36)–N(32)–C(38)	130.3(23)
N(32)–C(38)–C(39)	121.3(28)	C(38)–C(39)–O(30)	109.3(25)
Mn(2)–O(30)–C(39)	120.5(16)	Mn(2)–N(40)–C(41)	128.7(12)
Mn(2)–N(40)–C(45)	116.3(11)	C(41)–N(40)–C(45)	114.6(14)
N(40)–C(41)–C(42)	126.1(17)	C(41)–C(42)–C(43)	119.3(18)
C(42)–C(43)–C(44)	120.8(17)	C(43)–C(44)–C(45)	116.7(16)
N(40)–C(45)–C(44)	122.4(15)	N(40)–C(45)–C(46)	115.5(14)
C(44)–C(45)–C(46)	121.7(15)	C(45)–C(46)–C(47)	113.0(15)
C(45)–C(46)–N(50)	107.4(13)	C(47)–C(46)–N(50)	100.7(13)
C(45)–C(46)–O(40)	108.6(13)	C(47)–C(46)–O(40)	116.5(14)
N(50)–C(46)–O(40)	110.0(14)	C(46)–C(47)–C(48)	112.2(15)
C(47)–C(48)–C(49)	128.6(17)	C(47)–C(48)–C(50)	106.8(15)
C(49)–C(48)–C(50)	124.5(17)	C(48)–C(50)–C(51)	130.5(16)
C(48)–C(50)–N(50)	110.3(14)	C(51)–C(50)–N(50)	119.2(15)
C(50)–C(51)–C(52)	118.0(18)	C(51)–C(52)–C(53)	123.3(21)
C(52)–C(53)–C(54)	117.5(19)	C(53)–C(54)–N(50)	115.0(16)
C(46)–N(50)–C(50)	110.0(13)	C(46)–N(50)–C(54)	123.0(15)
C(50)–N(50)–C(54)	126.9(15)	Mn(1)–O(40)–Mn(2)	104.8(4)
Mn(1)–O(40)–C(46)	130.0(10)	Mn(2)–O(40)–C(46)	124.0(10)
O(11)–Cl(1)–O(12)	111.9(10)	O(11)–Cl(1)–O(13)	107.2(12)
O(12)–Cl(1)–O(13)	110.9(10)	O(11)–Cl(1)–O(14)	109.1(11)
O(12)–Cl(1)–O(14)	111.8(10)	O(13)–Cl(1)–O(14)	105.8(11)
O(21)–Cl(2)–O(22)	108.0(13)	O(21)–Cl(2)–O(23)	106.6(14)
O(22)–Cl(2)–O(23)	109.0(13)	O(21)–Cl(2)–O(24)	115.3(14)
O(22)–Cl(2)–O(24)	111.4(13)	O(23)–Cl(2)–O(24)	106.2(12)
O(31)–Cl(3)–O(32)	114.0(12)	O(31)–Cl(3)–O(33)	111.7(12)
O(32)–Cl(3)–O(33)	109.2(12)	O(31)–Cl(3)–O(34)	105.5(14)
O(32)–Cl(3)–O(34)	108.7(13)	O(33)–Cl(3)–O(34)	107.5(14)
O(41)–Cl(4)–O(42)	107.8(16)	O(41)–Cl(4)–O(43)	112.7(16)
O(42)–Cl(4)–O(43)	105.0(22)	O(41)–Cl(4)–O(44)	91.7(15)
O(42)–Cl(4)–O(44)	114.0(22)	O(43)–Cl(4)–O(44)	124.3(26)
Cl(4)–O(41)–O(44)	38.9(8)	Cl(4)–O(44)–O(41)	49.4(12)
O(60)–C(60)–C(61)	109.5(32)	O(70)–C(70)–C(71)	121.7(24)

longer distance to N20 of 1.636 Å is better described as a strong interaction. These interactions allow better electron-donation by the bridging oxygens O10 and O40.

## Conclusions

No oxygen-bridged transition metal clusters were isolated using L1, but several other structural types have been identified. A different synthetic approach may, however, lead to the formation of the previously identified dimeric or tetrameric structural types [8–14]. For example, the copper and manganese complexes could be prepared under anhydrous conditions using only perchlorate counter ions. In

both cases the absence of water or thiocyanate ligands to complete the coordination sphere might promote the formation of clusters. Initially interest in the one-armed ligands focused on making complexes of L1. However, as discussed above, this system was complicated by the formation of (L2)<sup>+</sup>. In order to prevent this rearrangement, which proceeds via loss of the aldehyde proton (Fig. 4, step 4), the aldehyde was replaced by the ketone 2-acetylpyridine. This prevented the previous rearrangement but, in addition to forming the desired Schiff base L3, L4 formed via an aldol condensation (Fig. 6). In the preparation described in 'Experimental' the ketone was added to the solution of the amine (basic). Reversing the order of addition of these components does not appear to prevent L4

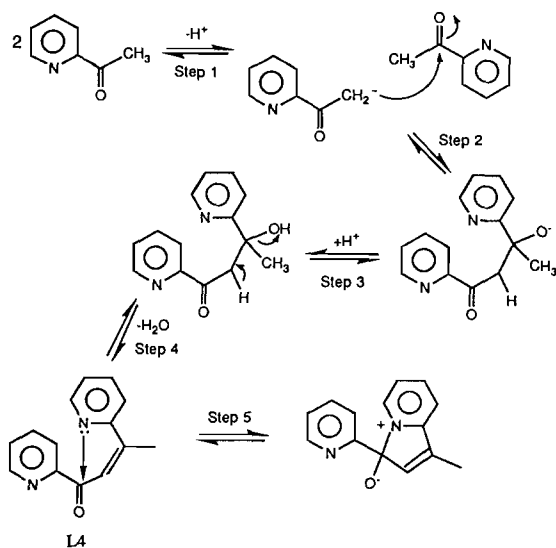


Fig. 6. A possible mechanism for the formation of L4.

formation and therefore it appears that in this system both acid and base catalysed aldol reactions readily occur.

#### Supplementary Material

Tables of anisotropic thermal parameters, hydrogen positions and listings of  $F_{\text{obs}}$  and  $F_{\text{calc}}$  structure factors are available from the authors.

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