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Complex array structures formed by metal complexes of *N*,*N′*-*p*-phenylenedimethylenebis(4-methylpyridin-2-one) †

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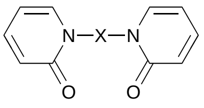
The syntheses of the 'extended reach' ligand *N*,*N′*-*p*-phenylenedimethylenebis(4-methylpyridin-2-one) (L) and of a range of its metal complexes with Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}, Y^{III}, and lanthanide ions have been accomplished. X-Ray studies showed that in the compound $\{[MnL_3](ClO_4)_2\}_n$ octahedrally co-ordinated manganese centres are connected by L bridges so as to form a three-dimensional array of contiguous rhomboidal 'boxes'. The analogous compounds with Co^{II}, Ni^{II}, Zn^{II} and Cd^{II} have the same structure. The polymeric compound $\{[Cu_4L_5Cl_8]\cdot 2MeOH\}_n$ forms a complex array of cross-linked chains containing both four- (distorted tetrahedral) and five-co-ordinate (distorted square pyramidal) copper centres in equal proportions.

The synthesis *via* self-assembly of metal complexes with extended and multidimensional structures is a major current research theme embracing a diversity of approaches.[1–12] Although many advances have been made in this fascinating field, and novel structures revealed, the accurate prediction of the types of extended polymeric structures that will be obtained still remains a continuing challenge, due to the complex interplay of the variables involved with respect to the metal centres, the types and geometries of the connecting ligands, and the competing non-covalent intra- and inter-molecular interactions.

As part of our research in this field, we have been exploring the use of 'extended reach' ligands based on spacer-linked pyridone donor units of general types **I** and **II**, where X represents a spacer group.[13–20] Ligands of this type bind to a wide range of metal ions and can be combined with a variety of connecting spacer units; the position of the O-donor atom can also be varied. The *p*-xylyl-bridged ligand, *N*,*N′*-*p*-phenylenedimethylenebis(pyridin-4-one), **III**, is particularly versatile in the range of polymeric arrays it can generate. It can form interwoven metallomacrocyclic networks,[18,19] link pairs of metal ions by μ-O atom bridges[19] and form complex arrays in which it bridges *via* metal co-ordination and also by hydrogen bonding.[20] These observations, and the formation of a triple helical bridge by the analogous linked pyridin-2-one ligand, **IV**, in $[Nd_2(2\text{-}OC_5H_4NCH_2C_6H_4CH_2NC_5H_4O\text{-}2)_3(NO_3)_6]$,[14] prompted a study with the 4-methyl-substituted analogue of **IV**, *N*,*N′*-*p*-phenylenedimethylenebis(4-methylpyridin-2-one) (**V**, L) and we report here the results of this work.



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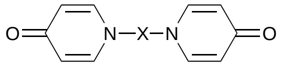

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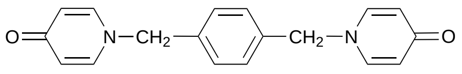

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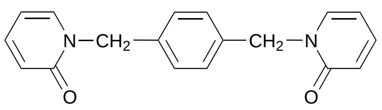

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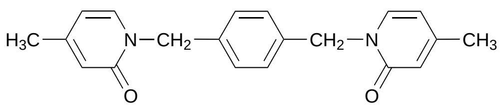

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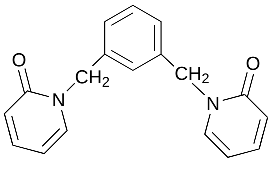

VI

Experimental

Preparations

***N*,*N′*-*p*-Phenylenedimethylenebis(4-methylpyridin-2-one) (L).** 4-Methylpyridin-2-one (3.27 g, 0.03 mol) was added to a solution of sodium butoxide (0.03 mol) in butanol (80 cm^3); α,α′-dibromo-*p*-xylene (3.95 g, 0.015 mol) was then introduced immediately. After gentle reflux, with stirring, for 6 h, the solution was filtered rapidly under suction and the filtrate allowed to cool slowly; white crystals of the desired product started to form instantly. The product was filtered off, washed with acetone and recrystallised from hot ethanol (52% yield), m.p. 242–246 °C. It crystallised with 0.25 H_2O of solvation (Found: C, 74.2; H, 6.2; N, 8.5. Calc. for $C_{20}H_{20}N_2O_2\cdot 0.25H_2O$: C, 73.9; H, 6.4; N, 8.6%). Mass spectrum (FAB, positive ion): *m/z* 321 $[MH^+]$; δ_H(500 MHz, $CDCl_3$) 2.16 (6 H, s), 5.07 (4 H, s), 5.98 (2 H, d), 6.40 (2 H, s), 7.11 (2 H, d) and 7.24 (4 H, s); δ_C(125 MHz, $CDCl_3$) 21.2, 51.2, 108.8, 119.6, 128.5, 136.1, 136.4, 151.1, and 162.6. The constitution of the ligand was also confirmed by the X-ray crystallographic results on the metal complexes (see below).

Metal complexes. The complexes obtained are listed in Table 1, together with the product yields and their analytical data (Microanalytical Laboratory, Imperial College).

$[ML_3][ClO_4]_2\cdot H_2O$ (M = Mn, Co, Ni *or* Zn), $[CdL_3][ClO_4]_2$ *and* $[ZnL_3][BF_4]_2$. A hot methanolic solution of the respective, hydrated metal salt (0.03 mmol in 3 cm^3) was added to a similar

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† We dedicate this paper to the memory of Geoffrey Wilkinson—an inspiring colleague and good friend.

Table 1 Microanalytical data for complexes of *N*,*N*′-*p*-phenylenedimethylenebis(4-methylpyridin-2-one) (L)

Complex	Colour	Yield (%)	Analysis (%)[a] C	H	N
1 $[MnL_3][ClO_4]_2\cdot H_2O$[b]	Colourless	72	58.5 (58.5)	5.1 (5.1)	6.7 (6.8)
2 $[CoL_3][ClO_4]_2\cdot H_2O$	Purple	92	58.0 (58.3)	5.1 (5.1)	6.8 (6.8)
3 $[NiL_3][ClO_4]_2\cdot H_2O$	Yellow	62	58.5 (58.3)	5.1 (5.1)	6.8 (6.8)
4 $[ZnL_3][ClO_4]_2\cdot H_2O$	Colourless	72	58.4 (58.0)	5.3 (5.0)	6.8 (6.8)
5 $[CdL_3][ClO_4]_2$	Colourless	78	56.6 (56.2)	5.0 (5.0)	6.3 (6.4)
6 $[ZnL_3][BF_4]_2$	Colourless	62	60.0 (60.1)	5.3 (5.0)	7.0 (7.0)
7 $[MnLCl_2]\cdot 0.5H_2O$	Colourless	78	52.6 (52.8)	4.5 (4.7)	6.2 (6.2)
8 $[CoLCl_2]\cdot 0.5H_2O$	Blue	43	52.4 (52.3)	4.4 (4.6)	6.0 (6.1)
9 $[Cu_2L_3(NO_3)_4]$	Green	56	53.6 (53.4)	4.4 (4.5)	10.6 (10.5)
10 $[Cu_4L_5Cl_8]\cdot 2MeOH$	Apple-green	45	55.1 (55.6)	4.7 (4.9)	6.7 (6.4)
11 $[Nd_2L_3(NO_3)_6]\cdot H_2O$	Lilac	45	43.9 (44.0)	3.5 (3.8)	10.1 (10.3)
12 $[Er_2L_3(NO_3)_6]\cdot H_2O$	Pink	56	42.4 (42.8)	3.3 (3.7)	9.8 (10.0)
13 $LaL_3(ClO_4)_3$	White	99	51.3 (51.5)	4.4 (4.3)	6.1 (6.0)
14 $NdL_3(ClO_4)_3$	Lilac	100	51.0 (51.3)	4.4 (4.3)	5.9 (6.0)
15 $SmL_3(ClO_4)_3\cdot H_2O$	White	86	50.6 (50.5)	4.5 (4.4)	6.0 (5.9)
16 $GdL_3(ClO_4)_3\cdot 3H_2O$	White	98	49.1 (49.0)	4.4 (4.5)	5.9 (5.7)
17 $DyL_3(ClO_4)_3\cdot 3H_2O$	White	100	48.8 (48.9)	4.4 (4.6)	5.8 (5.7)
18 $YL_3(ClO_4)_3\cdot 2H_2O$	White	85	52.1 (52.1)	4.7 (4.7)	6.2 (6.1)

[a] Calculated values in parentheses. [b] An X-ray diffraction study on a single-crystal sample gave the formulation $[MnL_3][ClO_4]_2$.

solution of L (0.1 mmol in 5 cm^3). The crystalline products which separated within several hours were collected, washed with methanol and air-dried.

$[MnLCl_2]\cdot 0.5H_2O$. A hot solution of $MnCl_2\cdot 4H_2O$ (0.1 mmol) in a mixture of methanol (1 cm^3) and acetonitrile (3 cm^3) was added dropwise to a hot solution of L (0.1 mmol) in acetonitrile (5 cm^3). Colourless microcrystals formed overnight.

$[CoLCl_2]\cdot 0.5H_2O$. A hot solution of $CoCl_2\cdot 6H_2O$ (0.1 mmol) in acetonitrile (3 cm^3) was added to a similar solution of L (0.1 mmol in 5 cm^3). The resulting clear, blue solution was gently heated for *ca*. 30 min and then allowed to cool. Fine, blue, feathery microcrystals formed within 2 d.

$[Cu_4L_5Cl_8]\cdot 2MeOH$. Hot methanolic solutions of copper(II) chloride dihydrate (0.1 mmol in 3 cm^3) and L (0.1 mmol in 5 cm^3) were mixed. Apple-green crystals suitable for X-ray analysis formed overnight.

$[Cu_2L_3(NO_3)_4]$. This was obtained as a fine green powder using the same method as for $[CoLCl_2]\cdot 0.5H_2O$ but using copper(II) nitrate instead of cobalt(II) chloride.

$[M_2L_3(NO_3)_6]\cdot H_2O$ (M = Nd *or* Er). Hot methanolic solutions of the respective hydrated lanthanide nitrate (0.1 mmol in 2 cm^3) and L (0.1 mmol in 8 cm^3) were mixed and refluxed with stirring for 30 min. The solid product was collected by centrifuging.

$ML_3(ClO_4)_3\cdot nH_2O$ (M = La, Nd, Sm, Gd, Dy *or* Y). The method employed was essentially the same as that used for the lanthanide nitrate complexes but with a 5:1 L:Ln mole ratio.

Spectroscopy

Spectroscopic measurements were made as previously described.[21] Electronic spectra (cm^{-1}) of solids by reflectance: **2**; ${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}$ 7700, ${}^4T_{1g}(F) \longrightarrow {}^4A_{2g}$ 14 500, ${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ 18 530; **3**, ${}^3A_{2g} \longrightarrow {}^3T_{2g}$ 8000, ${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ 12 900, ${}^4A_{2g} \longrightarrow {}^4T_{1g}(P)$ 22 730 (sh on strong parity-allowed band at 27 000); **8**, ${}^4A_2 \longrightarrow {}^4T_1(F)$ multiplet at 5450, 6350 and 7700, ${}^4A_2 \longrightarrow {}^4T_1(P)$ 16 050, 16 800(sh); **9**, 13 250(br); **10**, 11 800(br).

X-Ray crystallography

A summary of the crystal data and of the data collection and refinement parameters for compounds **1** and **10** is given in Table 2. Data were collected at room temperature on a Siemens P4/PC diffractometer using graphite-monochromated Mo-Kα radiation (for **1**) and on a Siemens P4 rotating-anode instrument using graphite-monochromated Cu-Kα radiation (for **10**), in each case using ω scans. The data were corrected for Lorentz and polarisation effects but not for absorption.

The structures were solved by the heavy-atom method and the major occupancy non-hydrogen atoms refined anisotropically. In **1** the perchlorate anion showed evidence for disorder (high U_{ij} values) but this disorder could not be resolved into alternate partial-occupancy orientations for the oxygen atoms. In **10** a ΔF map revealed the presence of two 0.5 occupancy MeOH solvent molecules which were refined anisotropically. The C−H hydrogen atoms were placed at idealised positions (0.96 Å), assigned isotropic thermal parameters $U(H) = 1.2U_{eq}(C)$ and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares based on F^2, with computations carried out using the SHELXTL PC system.[22] Selected bond lengths and angles for **1** and **10** are listed in Tables 3 and 4 respectively.

Compound **10** crystallised as very fine, multiply twinned, fibrous needles and, despite several attempts, it did not prove possible to obtain a crystal free from some degree of twinning. This, coupled with the tendency of the crystals to ‘bend’, led to diffuse diffraction peaks and hence poor-quality data. Data for three different crystals were measured and the results presented correspond to the crystal that gave the lowest value of *R*. Although the final value of *R* is high, the structure and the superstructure are definitive.

CCDC reference number 186/593.

Results and Discussion

As our main objective was an investigation of the ability of compound **V** to form extended polymeric arrays we have concentrated on the isolation of crystalline compounds suitable for single-crystal X-ray analysis. The complexes isolated are listed in Table 1. The perchlorates of Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}, and Cd^{II} formed complexes of stoichiometry $[ML_3][ClO_4]_2$ and X-ray powder diffraction studies showed that they form an isomorphous series. Use of methanol as solvent gave good crystals in reasonable yields (60–90%) and a single-crystal X-ray analysis was carried out on a representative member of the series, $[MnL_3][ClO_4]_2$ **1**.

Structure of $[MnL_3][ClO_4]_2$ 1

The X-ray structural study on complex **1** confirms the 1:3 Mn:L stoichiometry and shows the presence of a C_i symmetric

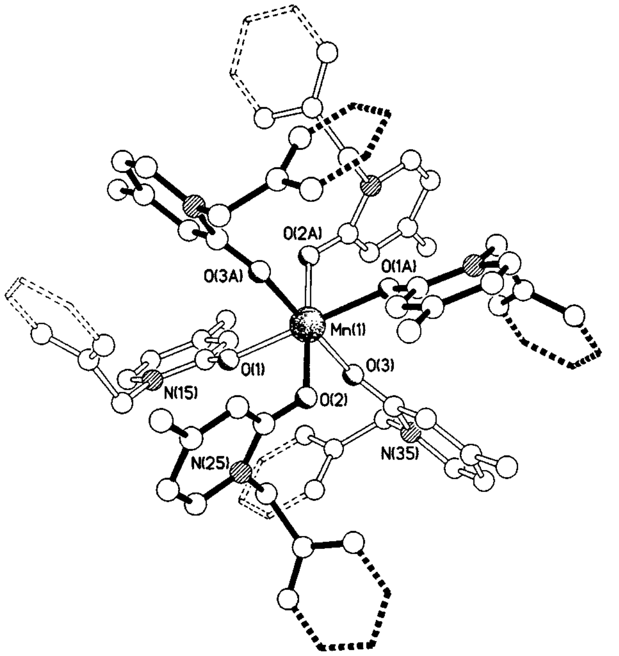

Fig. 1 The octahedral co-ordination geometry at manganese in complex **1**

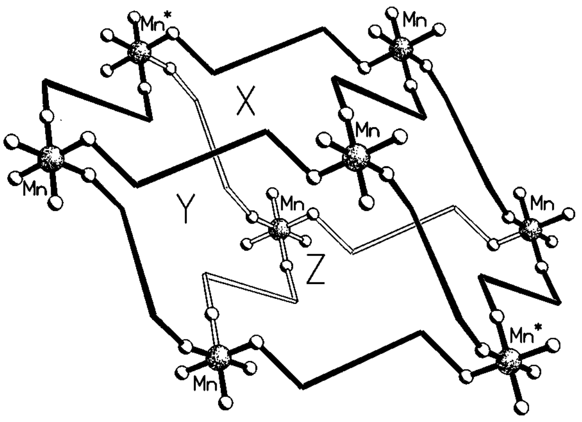

Fig. 2 Schematic representation of the rhomboidal arrangement of ligand-linked manganese centres in complex **1**; X, Y and Z refer to the top, left-hand side, and front faces respectively of the 'box', and the long 'bonds' correspond to the $CH_2 \cdots CH_2$ axes of the *p*-xylyl spacer of the L ligands

octahedral MnO_6 co-ordination geometry (Fig. 1). There are only small departures from O_h symmetry at the Mn; the acute angles at Mn range between 83.9(2) and 96.1(2)° and the Mn–O distances lie between 2.173(4) and 2.187(4) Å.

Each of the ligands L has a C_i symmetric *anti* geometry, adopting in one case an orthogonal relationship between the pyridone and the *p*-xylyl rings, whereas in the other two the geometry is skewed.‡ The L ligands bridge between symmetry equivalent manganese centres to form a rhombohedral array (Fig. 2) that is contiguous in all three lattice directions. The associated non-bonded $Mn \cdots Mn$ separations are 11.5, 11.9 and 12.7 Å, with 'interaxial' angles of 87, 96 and 123°. The geometries of the three principal faces of the rhomboid differ significantly (Fig. 3) as a consequence of the dissimilarity in the L ligand conformations (see above). Each box contains two perchlorate anions which are located at approximately one-third and two-thirds along the $Mn^* \cdots Mn^*$ body diagonal.

The rhomboidal arrangement described above is comparable to that observed for tris[*N*,*N*′-tetramethylenebis(imidazole)]-manganese(II) tetrafluoroborate **19**.[23] However in that complex an interpenetrating network is formed whereas this is not the case in **1**. A comparison of the ligand 'reach' values (donor atom–donor atom distances) shows that for *N*,*N*′-tetramethylenebis(imidazole) in **19** this distance (10.25 Å) is significantly longer than the range observed for L in **1** (8.4–9.3 Å).

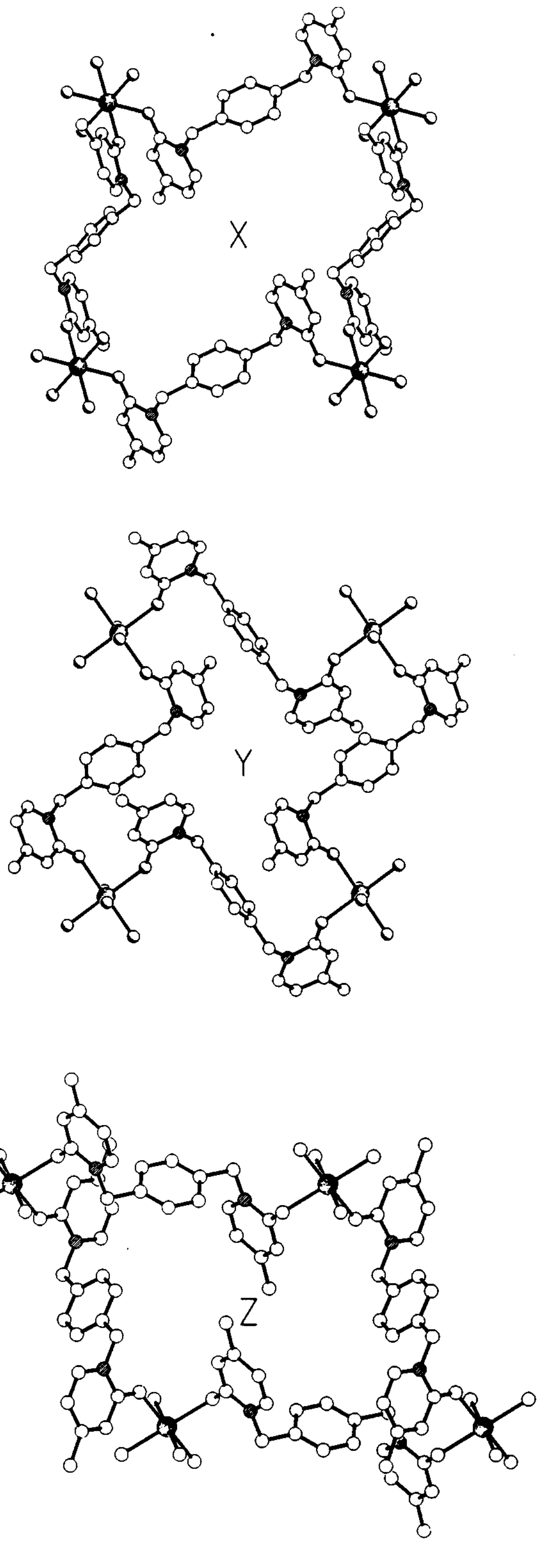

Fig. 3 The geometries of the three principal faces X, Y, and Z of the rhomboid illustrated in Fig. 2

These shorter lengths, coupled with the harsher steric constraints imposed by both the *p*-xylyl spacers and the methyl substituent on the pyridone ring, greatly reduce the potential free volume within the rhomboidal network and hence prevent interpenetration. Also the rhomboidal volume in complex **1** (1450 $Å^3$) is appreciably less than that observed for **19** (1950

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‡ The torsional twists about the C–N and C–C (aryl) bonds are, respectively: 82, 6°; 88, 67° and 76, 66° for the three independent L ligands.

Table 2 Crystal data and summary of data collection and refinement for compounds **1** and **10**

	1	**10**
Formula	$C_{60}H_{60}Cl_2MnN_6O_{14}$	$C_{51}H_{54}Cl_4Cu_2N_5O_6$
M	1214.98	1101.87
Crystal colour/habit	Clear plate	Apple-green needle
Crystal dimensions/mm	0.33 × 0.30 × 0.24	0.50 × 0.07 × 0.04
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	11.521(2)	9.250(3)
b/Å	11.664(1)	17.533(7)
c/Å	11.853(2)	17.668(7)
α/°	92.93(1)	115.84(3)
β/°	93.35(2)	95.67(3)
γ/°	113.62(1)	92.37(3)
U/Å^3	1452.0(4)	2555(2)
Z	1	2
D_c/ g cm^{-3}	1.389	1.432
μ/mm^{-1}	0.391	3.383
2θ Range/°	3.8–45.0	5.6–120
F(000)	633	1138
Measured reflections	3932	7524
Unique reflections (R_{int})	3712 (0.0768)	7524 (0.0000)
Observed reflections [$F > 4\sigma(F)$]	2368	4648
No. parameters refined	379	612
Mean, maximum Δ/σ ratio	0.001, 0.038	0.001, 0.022
Largest difference peak, hole/e Å^{-3}	0.628, −0.546	1.183, −0.600
$R1$	0.0783	0.1097
$wR2$	0.1885	0.4494

Table 3 Selected bond lengths (Å) and angles (°) for compound **1**

Mn(1)–O(1)	2.173(4)	Mn(1)–O(2)	2.187(4)
Mn(1)–O(3)	2.183(4)		
O(1)–Mn(1)–O(1A)	180.0	O(1)–Mn(1)–O(2)	83.9(2)
O(1)–Mn(1)–O(2A)	96.1(2)	O(1)–Mn(1)–O(3)	92.0(2)
O(1)–Mn(1)–O(3A)	88.0(2)	O(2)–Mn(1)–O(2A)	180.0
O(2)–Mn(1)–O(3)	90.8(2)	O(2)–Mn(1)–O(3A)	89.2(2)
O(3)–Mn(1)–O(3A)	180.0		

Å^3). It is interesting that in both of these structures the anions are located in pairs along one of the principal body diagonals.

The only interligand interaction of note is a π–π stacking interaction between the pyridone ring of one ligand and the *p*-xylyl ring of another (centroid–centroid separation 3.80 Å, mean interplanar separation 3.68 Å) which occurs within face Y of the rhomboid and, by virtue of the inversion centre within the *p*-xylyl ring, extends into an adjacent box.

The small departures from O_h symmetry at the manganese centre revealed by the X-ray study are reflected in the X-band EPR spectrum of powdered samples of the complex which exhibits several weak bands on either side of the main central band at $g = 2.00$. The distortions are, however, too small to be detected from the electronic spectra of the solid cobalt(II) and nickel(II) analogues (listed in the Experimental section).

The compounds $[ML_3][ClO_4]_2$ (M = Mn, Co, Ni or Zn) tend to be slightly hygroscopic and the analytical results for the bulk samples (Table 1) were more consistent with the formation of a monohydrate than the solvent-free system found for the single crystal of **1**.

The unit cell and space group for $[ZnL_3][BF_4]_2$ **6** are the same as those observed for **1** indicating that this complex also adopts an analogous network structure. It is reasonable to conclude that the BF_4^- compounds of Mn^{II}, Co^{II} and Ni^{II} will also be of this type.

X-Ray quality crystals were not obtained for the chloride complexes of Mn^{II} **7** or Co^{II} **8**. In the case of **7**, the observation of a single broad band at $g = 2.00$ in its X-band EPR spectrum points to strong Mn · · · Mn interaction *via* chloride bridges as such interactions result in spectra which do not show the effects of zero-field splitting.[24] The absence of ν(Mn–Cl) bands >220 cm^{-1} is also consistent with the presence of chloride bridges.[25] The formation of chloride bridges between pairs of manganese centres is known[17] for the polymeric complex $[MnL'Cl_2]_n$, where L′ is *N*,*N*′-*m*-phenylenedimethylenebis(pyridin-2-one) **VI**. For **8** the solid-state electronic spectrum (see Experimental section) and the ν(Co–Cl) bands (at 300 and 338 cm^{-1}) both clearly demonstrate a distorted tetrahedral C_{2v}, co-ordination geometry for the cobalt centre, but, in the absence of definitive X-ray information, the long-range structure (chain[26] or discrete ring[15]) remains unknown.

The reaction between **V** and hydrated copper(II) chloride in methanol afforded crystals of an apple green compound **10** with an unusual Cu : L ratio of 4 : 5 and the structure of this complex is discussed below.

Structure of $[Cu_4L_5Cl_8]$·2MeOH 10

The X-ray analysis of complex **10** revealed an unusual polymeric structure containing both four- and five-co-ordinate copper centres in an overall 1 : 1 stoichiometry (Fig. 4). The geometry at the four-co-ordinate centre [Cu(37)] is approximately midway between square planar and tetrahedral, with O–Cu–O and Cl–Cu–Cl angles of 143 and 146° respectively. The other Cu has a distorted square pyramidal geometry, the basal plane comprising the two Cl atoms and the L oxygen atoms O(11) and O(15) whilst the apex is occupied by a third L oxygen atom, O(51), at 2.175(9) Å; *cf.* 1.955(9) and 1.960(9) Å for the two equatorial Cu–O bonds.

The asymmetric unit contains one complete, non-symmetric L ligand (A) and three 'half' L ligands (B, C, and D). Ligand A links the two independent copper centres (Fig. 4) and has a skewed 'open-book' conformation with torsional rotations about the N–C and C–C (aryl) bonds of 69, 77 and 82, 58° respectively. The other three have crystallographic inversion centres in their *p*-xylyl rings and therefore have *anti* geometries. Two of these ligands (B and C) have open-book conformations, with N–C and C–C (aryl) torsional twists of 86, 88 and 84, 84° for B and C respectively, whilst the third (D) is more skewed with respective twists of 81 and 66°.

Investigation of the extended structure (Fig. 5) reveals it to be comprised of a complex pattern of intersecting polymer chains, but with the absence of any macroring formation.

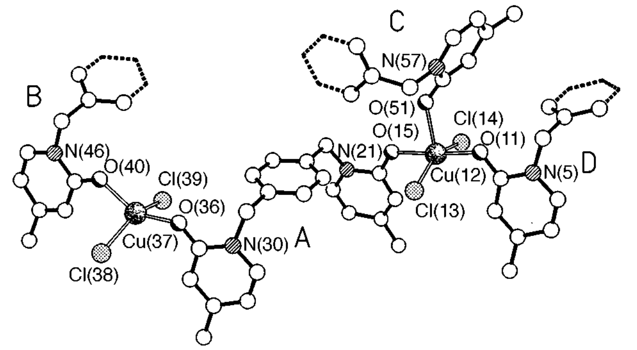

Fig. 4 The asymmetric unit in the polymer structure of complex **10**: A, B, C and D are the four independent linking L ligands

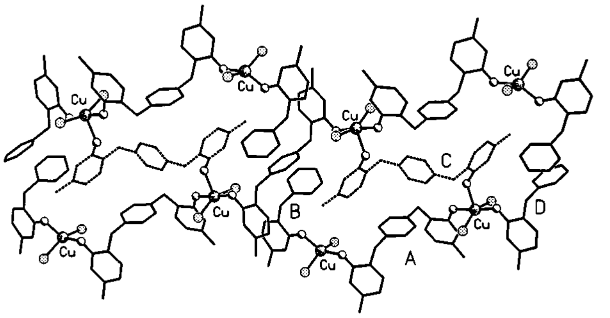

Fig. 5 Part of the extended, cross-linked polymer network present in the structure of complex **10**; A, B, C and D correspond to the ligands identified in Fig. 4

Depending on the pathway taken, many alternative chain sequences are achievable. Some contain equal numbers of four- and five-co-ordinate copper centres, whereas in another direction one containing only five-co-ordinate centres can be identified. Some sequences are linear extended chains whereas others produce coiled zigzag arrangements containing a (4, 5, 5, 5, 5, 4) sequence. The overall assemblage is essentially close-packed, being stabilised by weak π–π interactions.

There are very small voids between the chains and the disordered methanol molecules are included in these spaces. Throughout the array the shortest Cu···Cu distances are 8.0 Å, between pairs of four-co-ordinate centres, and 8.2 Å between pairs of five-co-ordinate centres; the shortest 4···5 separation is 9.1 Å.

It is interesting that the presence of the two types of copper(II) co-ordination geometry in complex **10** is not revealed by its solid-state EPR spectrum. The X-band EPR spectrum (Fig. 6) simply conforms to one of the standard 'axially elongated' type with components at $g_{\text{eff}} = 2.32$ and 2.10. This result, which presumably arises from an 'accidental' close superposition of the spectra of the two types of copper(II) centres, is a salutary example of the dangers of inferring copper(II) co-ordination geometry from such EPR spectra in the absence of definitive X-ray information. This is reinforced by the electronic spectrum of the solid compound which simply comprises a broad band centred on 11 800 cm^{-1}, and, again, provides no clear information about the unusual geometry revealed by the X-ray results.

The X-band EPR spectrum of $[Cu_2L_3(NO_3)_4]$ **9** also is of the 'elongated-axial' type with g values of 2.40 and 2.09 and showing copper nuclear hyperfine structure ($a = 110$ G; G = 10^{-4} T) on the $g_{\parallel}$ band. The stoichiometry of the complex suggests that it has a polymeric structure but it could only be obtained in powder form so we were unable to determine its true nature.

Lanthanide complexes 11–18

Our interest in lanthanide complexes of compound **V** was prompted by the ability of the related ligand **IV** to link pairs of lanthanide ions by triple helical bridges, as in $[Nd_2(2\text{-}OC_5H_4NCH_2C_6H_4CH_2NC_5H_4O\text{-}2)_3(NO_3)_6]$ **20**.[14] In particular, it was hoped that the use of a poorly co-ordinating anion, such as perchlorate, would prevent the 'capping' action of the nitrates in **20** and thereby permit the formation of 'infinite' chains of triple helically bridged metal centres. Ligand **V** readily forms complexes of types $M_2L_3(NO_3)_6$ and $ML_3(ClO_4)_3$ stoichiometrically analogous to **20** and to the desired 'rope-like' extended helical chain respectively. Unfortunately, crystals suitable for X-ray characterisation could not be obtained so, although the lanthanide compounds reported for record in Table 1 undoubtedly have polymeric structures, the details of their structures remain unknown.

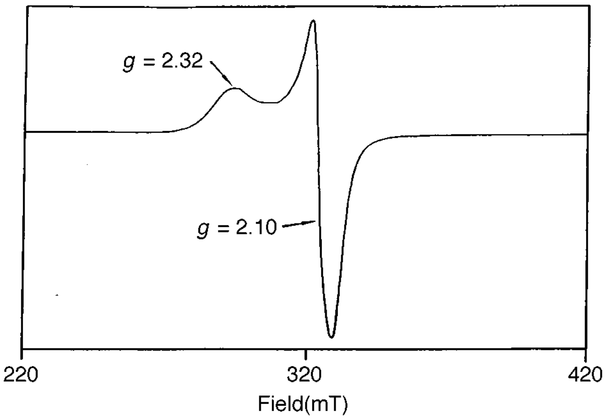

Fig. 6 X-Band EPR spectrum of a powdered sample of complex **10**

Table 4 Selected bond lengths (Å) and angles (°) for compound **10**

Cu(12)–O(11)	1.960(9)	Cu(12)–O(15)	1.955(9)
Cu(12)–O(51)	2.175(9)	Cu(12)–Cl(13)	2.289(4)
Cu(12)–Cl(14)	2.306(4)	Cu(37)–O(36)	1.921(8)
Cu(37)–O(40)	1.927(9)	Cu(37)–Cl(38)	2.217(4)
Cu(37)–Cl(39)	2.239(5)		
O(15)–Cu(12)–O(11)	174.4(4)	O(15)–Cu(12)–O(51)	85.8(3)
O(11)–Cu(12)–O(51)	88.9(4)	O(15)–Cu(12)–Cl(13)	89.0(3)
O(11)–Cu(12)–Cl(13)	90.6(3)	O(51)–Cu(12)–Cl(13)	105.9(3)
O(15)–Cu(12)–Cl(14)	93.2(3)	O(11)–Cu(12)–Cl(14)	89.7(3)
O(51)–Cu(12)–Cl(14)	100.6(3)	Cl(13)–Cu(12)–Cl(14)	153.5(2)
O(40)–Cu(37)–O(36)	143.1(4)	O(40)–Cu(37)–Cl(38)	95.9(3)
O(36)–Cu(37)–Cl(38)	96.9(3)	O(40)–Cu(37)–Cl(39)	95.1(3)
O(36)–Cu(37)–Cl(39)	93.5(3)	Cl(38)–Cu(37)–Cl(39)	145.9(2)

Conclusion

Developments in this field of research rest very heavily on the ability to determine the long-range structures of these complex arrays by X-ray diffraction methods. This, in turn, requires the formation of crystalline compounds of appropriate crystal quality, preferably on closely related sets of compounds, so that the contributing parameters can be fully assessed. However, as in the present study, it frequently proves difficult to achieve this 'ideal' situation and one must piece together information from less closely related individual examples.

The results described here with ligand **V** provide an instructive comparison with the p-xylylene-linked pyridin-4-one ligand **III**. Although both **III** and **V** form fused network structures, the three-dimensional array of contiguous rhomboidal 'boxes' formed by compound **1** contrasts markedly with the interpenetrating, polycatenated sheet structure formed by the same metal salt (manganese perchlorate) with ligand **III**.[18] Moreover, whereas ligand **III** when bonded to copper(II)[19] or to neodymium[20] forms interwoven superstructures, the copper(II) chloride complex, **10**, shows no such interweaving though it has a very complex multiple chain structure. Clearly, although the ligand 'length' and conformational flexibility of both **III** and **V** are similar, the position of the co-ordinating oxygen atom appears to be crucial in influencing the nature of the extended structure.

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References

1 J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier and D. Moras, *Proc. Natl. Acad. Sci. USA*, 1987, **84**, 2565.
2 R. Krämer, J.-M. Lehn, A. De Cian and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 703.
3 E. C. Constable, E. R. Heirtzler, M. Neuberger and M. Zhender, *Supramol. Chem.*, 1995, **5**, 197.
4 C. R. Woods, M. Benaglia, F. Cozzi and J. S. Siegel, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1830.
5 A. F. Williams, *Chem. Eur. J.*, 1997, **3**, 15.
6 B. F. Abrahams, S. R. Batten, H. Hamit, B. F. Hoskins and R. Robson, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1691.
7 L. R. MacGillivray, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1994, 1325.
8 P. Losier and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2779.
9 D. Venkataraman, S. Lee, J. S. Moore, P. Zhang, K. A. Hirsch, G. B. Gardner, A. C. Covey and C. L. Prentice, *Chem. Mater.*, 1996, **8**, 2030.
10 C. O. Dietrich-Bucheker and J.-P. Sauvage, *Bioorganic Chemistry Frontiers*, Springer, Berlin, 1991, vol. 2, 197.
11 J.-P. Sauvage, *Acc. Chem. Res.*, 1990, **23**, 319.
12 D. Cardenas, A. Livoreil and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1996, **118**, 11 980.
13 G. A. Doyle, D. M. L. Goodgame, S. P. W. Hill and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1993, 207.
14 D. M. L. Goodgame, S. P. W. Hill and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1993, 1019.
15 D. M. L. Goodgame, S. P. W. Hill, A. M. Smith and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1994, 859.
16 D. M. L. Goodgame, S. Menzer, A. M. Smith and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1994, 1825.
17 D. M. L. Goodgame, S. Menzer, A. M. Smith and D. J. Williams, *Inorg. Chem.*, 1994, **33**, 6409.
18 D. M. L. Goodgame, S. Menzer, A. M. Smith and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 574.
19 D. M. L. Goodgame, S. Menzer, A. M. Smith and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1995, 1975.
20 D. M. L. Goodgame, S. Menzer, A. M. Smith and D. J. Williams, *Chem. Commun.*, 1997, 339.
21 L. H. Carrad, D. M. L. Goodgame, S. P. W. Hill and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1993, 1003.
22 G. M. Sheldrick, SHELXTL, Version 5.03, University of Göttingen, 1995.
23 P. C. M. Duncan, D. M. L. Goodgame, S. Menzer and D. J. Williams, *Chem. Commun.*, 1996, 2127.
24 R. D. Dowsing, J. F. Gibson, D. M. L. Goodgame, M. Goodgame and P. J. Hayward, *Nature* (*London*), 1968, **219**, 1037.
25 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn., Wiley, New York, 1977, pp. 317–324 and refs. therein.
26 G. A. Doyle, D. M. L. Goodgame, S. P. W. Hill, S. Menzer, A. Sinden and D. J. Williams, *Inorg. Chem.*, 1995, **34**, 2850.

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