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Chirality in coordination polymers: homo- *vs.* hetero-chiral strand construction

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The functionalised cage amine complex, [1,8-bis(carboxymethylamino)sarcophagine]cobalt(III) (sarcophagine = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane), serves as a chiral supramolecular synthon in the formation of coordination polymers in which various metal(II) ions form labile links in the polymer strands. Both amorphous and crystalline polymers form, depending, amongst other factors, upon the stereochemistry at Co(III) and the nature of the metal(II) species. In the cases of Co, Ni, Cu and Zn as the linker species, polymers of 1 : 1 Co : M stoichiometry are obtained, whereas Mn is found to give both Co/Mn and Co/Mn_2 ‘monomer’ units. Crystal structure determinations are reported for the Co/Mn, Co/Mn_2, Co/Co and Co/Zn systems.

Introduction

The rational design of solid materials in which component units of significant molecular complexity are linked in a defined stereochemical manner through other, not necessarily simple, entities, requires a catalogue of appropriately functionalised chemical building blocks.[1,2] Such building blocks are characterised by kinetic inertness of certain components and the lability of others. Molecules which meet such requirements include the carboxymethylamino derivatives[3] of cage amines of the “sarcophagine” (hexaazabicyclo[6.6.6]icosane) type.[4] The cage of six nitrogen donor ligands provides a site where numerous different metal ions may be bound as an inert unit, while the pendent carboxymethylamino groups provide a reactive site allowing the formation of links, both labile and inert, between the cage entities. While any solid lattice formed by a cage amine complex involves some form of connection between the cage complex units, and indeed association *via* hydrogen-bonding to simple counter anions (in addition to overall charge attraction) is known to lead to control of such features as ligand conformation,[3,5] the addition of sophisticated pendent arms to the cage raises the prospects of both greater variety and greater control of the connections. In the present work, we provide justification for these assertions in describing the formation of coordination polymers based on carboxymethylamino–sarcophagine complexes linked by labile metal ions. A complication that arises in the construction of polymers from these species is the way in which the chiral cage units are combined.[6] Presumably, a linear polymer strand may contain a completely random array of enantiomeric “monomers”, an ordered array of units or blocks of units giving an overall achiral strand, or a chiral array made entirely of one enantiomer. In addition, coordination of the substituted “external” amino group should render it stable to inversion, so that chirality of the linker units is another factor for consideration. Interestingly, in the three systems giving rise to ordered, and therefore crystalline, arrays and presently characterised crystallographically, the polymerisation modes are all different.

Experimental

General

[Co((1,8-$NH_2CH_2CO_2H)_2$sar)]Cl_5 was prepared as described previously.[3] Its Δ enantiomer was synthesised identically using Δ-[Co($NH_2)_2$sar]$^{3+}$ as the precursor.[7] All other chemicals were from commercial sources and were used as supplied. All samples for elemental analysis were dried at 50 °C under vacuum (0.1 mmHg) for 4 hours. Microanalyses for carbon, hydrogen and nitrogen were carried out by The Australian National University Microanalytical Service. Analyses for metals (Co, Cu, Ni, Mn and Zn) were performed locally on 1% HCl solutions by ICP-AES. X-Ray powder-diffraction measurements were made on a Siemens “Kristalloflex” D5000 diffractometer.

Syntheses

In identifying each example as ‘M/M’ polymer’, the first metal to be quoted (Co^{III}) is encapsulated inside a hexamine cage ligand whilst the second divalent metal to be quoted is coordinated to the external $H_2NCH_2CO_2H$ functional group.

Polymers from Δ,Λ-[Co(($NH_2CH_2CO_2H)_2$sar)]Cl_5

Co/Zn polymer: $CoZnC_{18}H_{36}N_8Cl_3O_4\cdot 3H_2O$. [Co(($NH_2CH_2CO_2H)_2$sar)]$Cl_5$ (1.0 g, 1.5 mmol) was dissolved in water (20 mL). $ZnCO_3\cdot 2ZnO\cdot 3H_2O$ (0.51 g, 1.5 mmol) was added and the mixture was heated (80 °C) for 1 h before being filtered, and then left to stand at room temperature. After one week, orange crystals had formed. These crystals were collected by filtration and washed with water and ethanol. Yield: 0.78 g. Found: Co, 7.5; Zn, 9.4; C, 30.4; H, 5.5; N, 15.4; $ZnCoC_{18}H_{36}N_8Cl_3O_4\cdot 3H_2O$ (*cf.* X-ray model, structure **1** below, ≈3.5H_2O) requires Co, 8.26; Zn, 9.17; C, 30.31; H, 5.94; N, 15.71%. Crystals adequate for X-ray studies were obtained by slow evaporation at 50 °C of a hot, filtered aqueous solution.

Co/Cu polymer: $CoCuC_{18}H_{36}N_8O_4Cl_3\cdot 5H_2O$. [Co(($NH_2CH_2CO_2H)_2$sar)]$Cl_5$ (0.20 g, 0.29 mmol) was dissolved in water

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(*ca.* 5 mL) and heated to 80 °C. $CuCO_3{\cdot}Cu(OH)_2$ (0.069 g, 0.29 mmol) was added to the mixture, with effervescence visible. The mixture was heated (80 °C) for five minutes during which time the colour of the reaction mixture changed from orange to green. Unreacted $CuCO_3{\cdot}Cu(OH)_2$ was filtered out, the filtrate allowed to cool to ambient temperature and then left to stand overnight to give an amorphous green precipitate. This was collected by filtration and washed with water and copious quantities of ethanol, after which the solid was a fine green powder that was finally washed with diethyl ether. The solid was dried in air and then under vacuum. Yield: 0.16 g. Found: Co, 8.5; Cu, 9.3; C, 28.9; H, 5.8; N, 14.8; $CoCuC_{18}H_{36}N_8Cl_3O_4{\cdot}5H_2O$ requires Co, 7.88; Cu, 8.50; C, 28.92; H, 6.20; N, 14.99%.

Co/Ni polymer: $CoNiC_{18}H_{36}N_8O_4Cl_3{\cdot}6H_2O$. $[Co((NH_2CH_2CO_2H)_2sar)]Cl_5$ (0.50 g, 0.75 mmol) was dissolved in water (10 mL). $NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O$ (0.28 g, 0.75 mmol) was added to the orange solution, strong effervescence being visible. The now brown mixture was heated on a steam bath for about 3 minutes, then filtered and left to stand for 24 hours. The yellow solid formed was collected by filtration, redissolved in hot water (50 mL), filtered, allowed to cool to room temperature and left to stand. After 1 week, an amorphous, yellow solid had formed. This was collected by filtration and washed with water and copious quantities of ethanol, after which the solid was a beige powder that was finally washed with diethyl ether. Yield: 0.30 g. Found: Co, 7.1; Ni, 7.0; C, 28.1; H, 5.8; N, 14.2; $NiCoC_{18}H_{36}N_8Cl_3O_4{\cdot}6H_2O$ requires Co, 7.57; Ni, 7.54; C, 27.77; H, 6.47; N, 14.39%.

Co/Co^{II} polymer: $Co_2C_{18}H_{36}N_8Cl_3O_4{\cdot}9H_2O$. $[Co((NH_2CH_2CO_2H)_2sar)]Cl_5$ (0.30 g, 0.45 mmol) was dissolved in water (30 mL). The pH of the solution was raised to approximately pH 8 by the dropwise addition of aqueous sodium hydroxide. $CoCl_2{\cdot}6H_2O$ (0.18 g, 0.75 mmol) was added and the mixture was left to stand at room temperature. Slow evaporation of the solvent at room temperature over a period of 8 weeks resulted in the precipitation of small orange crystals which, after a number of attempts, were obtained in a form adequate for X-ray studies. The orange crystals were collected by filtration and washed with water, ethanol and diethyl ether. Yield: 0.090 g. Found: C, 26.5; H, 6.2; N, 13.6; $Co_2C_{18}H_{36}N_8Cl_3O_4{\cdot}9H_2O$ (*cf.* X-ray model, structure **2**, ≈6.5H_2O) requires C, 26.53; H, 6.68; N, 13.75%.

Co/Mn^{II} polymer. *Method 1.* $[Co((NH_2CH_2CO_2H)_2sar)]Cl_5$ (0.85 g, 0.13 mmol) was dissolved in water (10 mL) and heated on a steam bath. $MnCO_3$ (0.020 g, 0.17 mmol) was added, causing some effervescence. The mixture was filtered and then concentrated to a volume ≈2 mL by evaporation at 50 °C. The solution was allowed to cool to room temperature to deposit orange/brown crystals suitable for X-ray studies. To establish the Mn : Co ratio, some of the crystals were removed damp from the mother liquor and simply crushed and dried between two pieces of filter paper before analysis. Found: Co, 7.7; Mn 8.7% (Mn : Co 1.21 *cf.* X-ray model, structure **3**, 1.25).

Method 2. This involved adopting the same procedure as before, except for addition of an excess of $MnCl_2$ after the addition of $MnCO_3$. Crystals were grown in the same manner as for the previous compound. The Mn : Co ratio given by the X-ray model (structure **4**) was 2 : 1.

Polymers from Δ-$[Co((NH_2CH_2CO_2H)sar)_2]Cl_5$

Starting with Δ-$[Co((NH_2CH_2CO_2H)sar)]Cl_5$ in place of its racemate, Co/Cu, Co/Ni and Co/Co polymers were obtained as powders using the procedure described above for the Co/Cu species involving reaction with excess metal(II) carbonate. Despite numerous subsequent efforts, visually crystalline materials were not obtained. The Co/Zn polymer appeared to be too soluble to crystallise from aqueous solution.

Δ-Co/Ni polymer. Analysis: Found: Co, 7.8; Ni, 7.6; C, 28.8; H, 5.7; N, 14.8. Calc. for $NiCoC_{18}H_{36}N_8Cl_3O_4{\cdot}5H_2O$, Co, 7.94; Ni, 7.90; C, 29.11; H, 6.24; N, 15.09%.

Δ-Co/Cu polymer. Analysis: Found: Co, 7.6; Cu, 7.7; C, 29.0; H, 5.9; N, 14.9. Calc. for $CuCoC_{18}H_{36}N_8Cl_3O_4{\cdot}5H_2O$, Co, 7.88; Cu, 8.50; C, 28.92; H, 6.20; N, 14.99%.

Δ-Co/Co^{II} polymer. Deposition of a yellow precipitate took several weeks. This was collected by filtration, and washed with water, ethanol and ether. During drying under vacuum, the material changed colour from yellow to beige. Found: C, 29.2; H, 6.1; N, 15.0; $Co_2C_{18}H_{36}N_8Cl_3O_4{\cdot}5H_2O$ requires C, 29.10; H, 6.24; N, 15.08%.

Structure determinations

(Materials as supplied, although crystalline, presented considerable difficulty in respect of isolation of single specimens, perhaps because of the nature of the complexes, being inter-/over-grown, polycrystalline aggregates, with some twinning more-or-less inherent in the specimens used.)

Full spheres of area-detector data were measured using a Bruker AXS CCD instrument at *ca.* 153 K, $N_{t(otal)}$ reflections being merged to N unique, R_{int} as specified after 'empirical'/multiscan absorption correction within the proprietary/preprocessing software, the 'observed' criterion applicable being $F > 4\sigma(F)$. Anisotropic thermal parameter forms were refined in a full matrix context for non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values where possible. Conventional residuals R, R_w (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$) on $|F|$ are quoted at convergence. Neutral atom complex scattering factors were employed within the Xtal 3.4 program system.[8] Pertinent results are given in the Figures and Tables below; individual variations in procedure/difficulties/idiosyncrasies are cited as '*variata*'. In the figures, non-hydrogen atoms are shown with 50% displacement envelopes, hydrogen atoms, where shown, having arbitrary radii of 0.1 Å; atom symbols are shown for atoms other than carbon, which are denoted by numbers only. In the following, L^{2-} is used to denote the doubly-deprotonated ligand $[(NHCH_2CO_2)_2sar]^{2-}$.

1. Co/Zn polymer. $[Co(L)(ZnCl)]_{(\infty|\infty)}Cl_2{\cdot}3.5H_2O \equiv C_{18}H_{43}Cl_3CoN_8O_{7.5}Zn$; M = 722.3. Monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 11.959(1)$, $b = 14.731(1)$, $c = 17.536(2)$ Å, $\beta = 115.269(2)°$, $V = 2794$ Å^3. D_c $(Z = 4) = 1.71_9$ g cm^{-3}. $\mu_{Mo} = 18.0$ cm^{-1}; specimen: cuboid, *ca.* 0.20 mm; 'T'$_{min,max}$ = 0.74, 0.88. $N_t = 27661$, $N = 7086$ ($R_{int} = 0.038$), $N_o = 5374$; $R = 0.045$, $R_w = 0.048$; $|\Delta\rho_{max}| = 1.84(7)$ e Å^{-3}.

Variata. (x, y, z, U_{iso}) were refined for all hydrogen atoms, omitting those associated with the residue designated O(4), modelled as disordered over two sites, set at equal occupancy (0.25) after trial refinement.

2. Co/Co polymer. $[(CoL)\{Co(OH_2)_2\}]_{(\infty|\infty)}Cl_3{\cdot}6.5H_2O \equiv C_{18}H_{53}Cl_3Co_2N_8O_{12.5}$; M = 805.9. Monoclinic, space group $P2_1/n$ (C_{2h}^5, no. 14, variant), $a = 11.983(1)$, $b = 9.3804(8)$, $c = 14.720(1)$ Å, $\beta = 100.577(2)°$, $V = 1627$ Å^3. D_c $(Z = 2) = 1.64_5$ g cm^{-3}. $\mu_{Mo} = 13.4$ cm^{-1}; specimen: 0.15 × 0.05 × 0.05 mm; 'T'$_{min,max}$ = 0.78, 0.89. $N_t = 18154$, $N = 4119$ ($R_{int} = 0.023$), $N = 3293$; $R = 0.048$, $R_w = 0.048$; $|\Delta\rho_{max}| = 0.89(4)$ e Å^{-3}.

Variata. In the present cell and space group, both metal atoms lie disposed on crystallographic inversion centres, entailing, in the case of the locally chiral cage complex component, racemic disorder, resolvable in the $(CH_2)_2$ bridges, associated with, over a pair of centrosymmetrically related sites, one chloride and one water moiety, modelled as disordered, all disordered components having occupancies set at 0.5. Cl(1), lying near the ordered environment of Co(2), and interacting with that, is ordered; in respect of Cl(2) and O(03–08), there are various incompatibilities, *e.g.*, Cl(2) and C(4b,4b′) of the asymmetric unit may not have simultaneous occupancy (Cl(2)···C(4b,4b′) 1.703(7), 1.680(8) Å), while, among the water molecules, the same is true of O(03) and C(4a,4a′) (1.31(1), 1.50(1) Å), and between O(06)···O(07,08) (0.93(2), 1.01(3) Å), O(07)···O(08) (1.60(4) Å), simultaneously incompatible.

3. Co/Mn polymer (Method 1). $[0.675[\mathrm{CoL\{Mn(OH_2)_2Cl\}}]_{(\infty|\infty)}\mathrm{Cl_2} + 0.325[\mathrm{CoL\{Mn(OH_2)Cl_2\}\{Mn(OH_2)_2Cl\}}]_{(\infty|\infty)}\mathrm{Cl_2}]\cdot$*ca.* $8.3\mathrm{H_2O} \equiv \mathrm{C_{18}H_{57.35}Cl_{3.56}CoMn_{1.25}N_8O_{15.675}}$; $M = 898.0$. Monoclinic, space group $P2_1/c$, $a = 12.495(2)$, $b = 15.356(2)$, $c = 20.682(3)$ Å, $\beta = 106.232(2)°$, $V = 3810$ Å^3. D_c $(Z = 4) = 1.56_5$ g cm^{-3}. $\mu_{Mo} = 12.0$ cm^{-1}; specimen: 0.45 × 0.35 × 0.10 mm; ‘T’$_{min,max} = 0.62, 0.89$. $N_t = 37058$, $N = 9580$ ($R_{int} = 0.038$), $N_o = 7808$; $R = 0.064$, $R_w = 0.077$; $|\Delta\rho_{max}| = 0.96(4)$ e Å^{-3}.

Variata. See **4**.

4. Co/Mn polymer (Method 2). $[\mathrm{CoL\{Mn(OH_2)Cl_2\}\{Mn(0.5OH_2/0.5Cl)_2Cl\}}]_{(\infty|\infty)}\mathrm{Cl\cdot7.5H_2O} \equiv \mathrm{C_{18}H_{55}Cl_5CoMn_2N_8O_{13.5}}$; $M = 945.8$. Monoclinic, space group $P2_1/c$, $a = 12.303(2)$, $b = 15.336(2)$, $c = 20.730(3)$ Å, $\beta = 106.226(3)°$, $V = 3756$ Å^3. D_c $(Z = 4) = 1.67_2$ g cm^{-3}. $\mu_{Mo} = 15.2$ cm^{-1}; specimen: 0.30 × 0.15 × 0.10 mm; ‘T’$_{min,max} = 0.65, 0.91$. $N_t = 36797$, $N = 6588$ ($R_{int} = 0.054$), $N_o = 4829$; $R = 0.084$, $R_w = 0.10$; $|\Delta\rho_{max}| = 2.5(1)$ e Å^{-3}.

Variata. Metal atom site occupancies were set at unity after trial refinement. Cl(21,22) were modelled as disordered in association with water molecules O(21,22) at similar sites, occupancies set at 0.5 after trial refinement. Difference map residues O(04–012) were modelled as water molecule oxygen atoms, site occupancies 0.5. Water molecule hydrogen atoms were not located. The data would support meaningful refinement of anisotropic displacement parameters for Co, Mn and Cl only. In **3**, the material obtained initially from Method 1, one of the Mn sites exhibited partial occupancy, also true of the modelling of associated Cl and water residues, the resultant model being described in terms of cocrystallised asymmetric units in which the second Mn site is either occupied or empty (resultant: 0.325(2)), with details of associated ligand components further elaborated in the Discussion.

CCDC reference numbers 169054–169057.

See http://www.rsc.org/suppdata/dt/b1/b107369a/ for crystallographic data in CIF or other electronic format.

Results and discussion

Although but a limited range of the possible systems has so far been investigated, it is clear that the formation of ordered (crystalline) coordination polymers from the Co(III) complex of bis(carboxymethylamino)sarcophagine is sensitive to both the stereochemistry of the Co(III) species and the nature of the bridge-forming metal ion. That crystal structure determinations, discussed ahead, were possible, on crystals of indifferent quality, for the Co/Mn, Co/Co and Co/Zn compounds derived from Δ,Λ-$[\mathrm{Co((NHCH_2CO_2)_2sar)}]^+$ shows that, in these cases, ordered arrays were readily formed. Powder diffraction measurements confirm this and also indicate that the analogous Co/Ni compound is crystalline, though no attempt to obtain crystals large enough for single-crystal diffraction study has yet been successful. Similarly, the powder diffractogram for the Co/Co compound obtained from optically active Δ-$[\mathrm{Co((NHCH_2CO_2)_2sar)}]^+$ shows it to be crystalline (though visually a powder) and, interestingly, the pattern is distinctly different to that of the racemic Co/Co crystals. Further complexity is evident from the fact that the powder pattern for the optically active Co/Ni compound indicates that it, unlike its racemic analogue, is not crystalline. Its diffractogram shows two very broad and weak peaks corresponding to d spacings ≈7.5 and 5.5 Å, essentially identical to those obtained for Co/Cu compounds from both the racemic and optically active precursor. This is all despite the fact that, with the exception of the (crystalline) Mn compound, all materials appear to have the 1 : 1 Co : M composition expected for coordination of the pendent groups of the cage complex (Fig. 1 shows an idealised representation). The analytical sensitivity is, nonetheless, not such as to exclude the possibility that the amorphous materials may comprise a wide range of species—linear oligomers of various chain lengths, cyclo-oligomers of various ring size, and other possibilities—though the variety of differences seen with just the present range of M(II) derivatives indicates that subtle factors must control the nature of the precipitated solids. Differences in solubility between the derivatives of the racemic and the active Co complex are not surprising,[9] although, at least in the case of the Co/Zn species, the magnitude of the difference is strikingly high. In the present work, we have sought to find aspects of the structures of crystalline complexes characterised through X-ray diffraction experiments that may offer a basis for understanding of the particular forms adopted by the polymers. In solution, we have only very limited information on the extent and nature of any association phenomena, since concentrations sufficient for spectroscopic changes to be observed result usually in very rapid precipitation. Electrospray mass spectrometry provides evidence of some association in solution but of course provides no information on the structures of these associates.

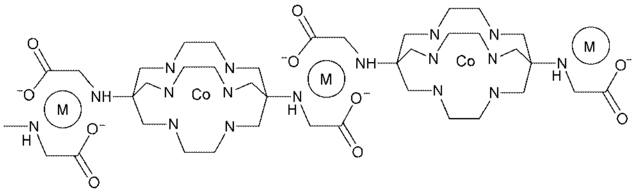

Fig. 1 An idealised representation of a linear polymer formed by chelation of pendent amino-acid substituents on a Co(III) cage amine complex.

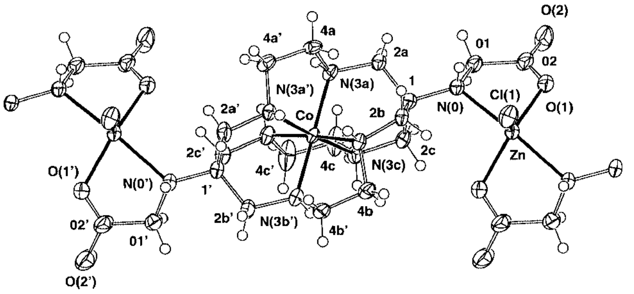

Fig. 2 A section of the Co/Zn cationic polymer of **1**.

The ‘simplest’ structure is that of the racemic Co/Zn compound (structure **1**, see Table 1), one formula unit devoid of crystallographic symmetry comprising the asymmetric unit in centrosymmetric space group C_{2h}^5, no. 14, set as $P2_1/c$. It is indeed polymeric (Fig. 2), infinite strands being formed by N,O-chelation of $\mathrm{ZnCl^+}$ units by a pair of pendent aminocarboxylate arms from separate *lel*$_3$-cage units, so that the repeat unit of this section of the polymer is $[\mathrm{\{Co(O_2CCH_2NH)_2sar\}ZnCl}]^{2+}$(with $\mathrm{Cl_2\cdot3.5H_2O}$), these strands being cross-linked through H-bonding interactions involving the additional chloride counter ions required by the overall stoichiometry, and water molecules. Along a given strand, the shortest separation between any pair of similar metal atoms, necessarily of the same chirality, is 11.959(1) Å (= a), a distance inconsistent with any significant electronic interaction, though minimum inter-strand Co···Co distances are shorter (8.782(1), 8.946(1) Å; corresponding to the separation of Co atoms in cages of opposite chirality), albeit still not indicative that a polymer of this type could be associated with metal–metal interactions of the encapsulated components.[10] The Co···Zn separation along the strands is 5.992(1) Å, again long in relation to possible interactions.

Table 1 Metal atom environments, Co/Zn complex **1**. *r* (Å) are the metal–ligand atom distances, other entries in the matrices being the angles (°) subtended by the relevant atoms at the head of the row and column

(a) Co[a]

Atom	*r*	N(3a′)	N(3b)	N(3b′)	N(3c)	N(3c′)
N(3a)	2.000(3)	86.4(1)	90.6(1)	174.9(1)	89.4(1)	94.0(1)
N(3a′)	1.966(2)		92.7(1)	90.3(1)	174.8(1)	90.3(1)
N(3b)	1.973(3)			85.7(1)	90.5(1)	174.6(1)
N(3b′)	1.985(3)				94.1(1)	89.9(1)
N(3c)	1.981(3)					86.9(1)
N(3c′)	1.973(4)					

(b) Zn (italicised atoms are related by the unit *a* translation)

Atom	*r*	O(1)	Cl(1)	*N(0′)*	*O(1′)*
N(0)	2.225(3)	78.5(1)	98.07(8)	165.2(1)	97.1(1)
O(1)	1.982(3)		109.64(9)	97.3(1)	145.4(1)
Cl(1)	2.302(1)			96.70(8)	104.96(8)
N(0′)	2.239(3)				78.2(1)
O(1′)	2.002(3)				

[a] Torsion angles within the bonds (of the chelate rings): Co–N(3*x*,*x*′); N(3*x*)–C(4*x*), N(3*x*′)–C(4*x*′); C(4*x*)–C(4*x*′) are: (*x* = *a*) 18.0(3), 11.5(3); −44.0(3), −38.8(4); 55.0(4); (*x* = *b*) 21.8(2), 8.2(2); −47.0(3), −37.7(3); 55.0(3); (*x* = *c*) 20.5(3), 8.5(3); −45.0(4), −35.9(5); 53.7(5)°.

The polymer strand overall is devoid of crystallographic symmetry but the local environment about each metal site is quasi-2; within a given bimetallic strand, the cage units have a common chirality, as do the five-coordinate Zn(N,O-chelate)$_2$Cl 'linkers', where the two asymmetric N-donors have the same absolute configuration. More precisely, in chains built up from Λ-*lel*$_3$-*R,R,R,R,R,R*(N)-Co entities,[2,3,5] the asymmetric pendent N-centres, stabilised against inversion by coordination to Zn(II), have the *R* configuration, with the axial Cl atom of essentially square-pyramidal *trans*-ZnN$_2$O$_2$(Cl) being on the same side of the N$_2$O$_2$ plane as the H-atoms of the associated pendent N-centres. Each Co(III) cage unit is involved in H-bonding where two 'open' edges of the pseudo-octahedron are spanned in a familiar manner by chloride ions being 'chelated' by NH donors (Cl(2) $\cdots$ H(3b′,3c) 2.23(4), 2.39(5); Cl(3) $\cdots$ H(3a′,3b) 2.28(5), 2.39(3) Å), the third involving separate NH bond donation to a pair of (residues assigned as) water molecules (O(01) $\cdots$ H(3c′), O(04) $\cdots$ H(3a) 1.97(4), 2.27(4) Å). If the 'local' symmetry about the Co extends to the two Zn–Cl moieties, then the 2-axis thus defined, quasi-parallel to the Zn–Cl local axes, through the mid-point of C(4c)–C(4c′), is not coincident with that defined locally by the chloride chelation, the axis of which passes through the mid-point of C(4a)–C(4a′).

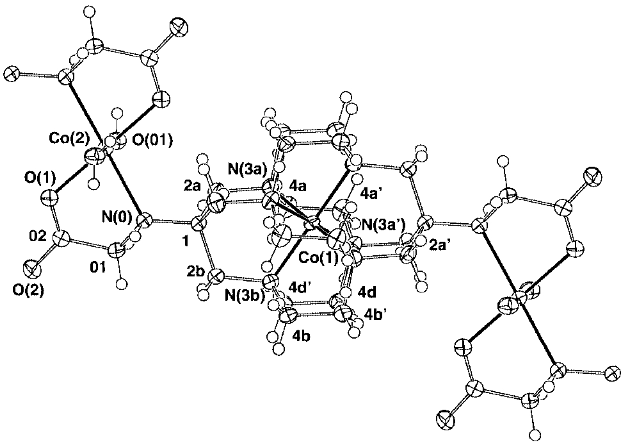

Fig. 3 A section of the Co/Co cationic polymer of **2**, inclusive of the resolved core (CH$_2$)$_2$ components of the Co sar string.

In attempting to understand the apparently large difference in solubility between Co/Zn compounds derived from the racemic and chiral Co-cage precursor, we have assumed that this must reflect, at least in part, differences in the lattice stability associated with the hydrogen-bonding interactions between homochiral polymeric strands seen in the overall achiral solid. For a single cage unit of any given strand, there is a local twofold symmetry resulting from the bridging of two 'open' octahedral edges by those chloride ions not coordinated to Zn, with the other edge having NH entities involved in separate interactions with water molecules. Each of the bridging Cl units may be considered to be of higher coordination, each being further involved in a hydrogen bond to the NH unit of the pendent arm of a separate cage complex (Cl(2) $\cdots$ H(0) (x, ½ − y, ½ + z), Cl(3) $\cdots$ H(0′) ($\bar{x}$, 1 − y, 1 − z) 2.51(4), 2.55(4) Å). In this way, a cage and hence one polymer strand is linked to two others of the opposite chirality. The two water molecules (O(01), O(4) (disordered)) involved in H-bonding to the third edge of a given cage also link it through further interactions to adjacent strands. N $\cdots$ N distances about the Co range between: 2.692(5)–2.716(4), mean 2.71(1) (en 'bites'), 2.793(4)–2.823(4), mean 2.80(1) (upper, lower triangle edges), 2.850(4)–2.906(5), mean 2.89(3) Å (interstrand).

In terms of the nature of coordination polymer units, the structure of the Co/Co compound, [{Co(O$_2$CCH$_2$NH)$_2$sar}-Co(OH$_2$)$_2$]Cl$_3$·≈6.5H$_2$O (structure **2**, Fig. 3) is quite different in that linker Co(II) units of an obligate achiral (meso) form join Co(III) cage species which, on average, are also achiral. The complex is again modelled in space group C_{2h}^5, no. 14, but in a cell of half the volume, no more extended array or different symmetry offering itself. The one-dimensional, formally cationic coordination polymer chains lie parallel to crystallographic *a* (11.983(1) Å, *cf.* 11.959(1) Å for **1**), the $P2_1/n$ (rather than $P2_1/c$) setting of the cell entailing a rather different relationship of the polymer to the symmetry elements of the space group. The environment of the linker metal, now Co(II) is six-coordinate, *trans*-CoN$_2$O$_4$, with two water molecules in the coordination sphere, harmonious with (the local *i* symmetry of) that metal being disposed at a crystallographic inversion centre. Opposed chirality of the associated pendent-arm N-donor centres is also entailed, and, further afield, of the two associated Co cage residues, an obviously untenable situation, since they are related by the unit *a* translation. The Co cage, in fact, is modelled as disposed with the metal atom on a crystallographic inversion centre also, with associated disorder resolvable in {*lel*-(CH$_2$)$_2$}$_3$ components of the cage framework, which is thus

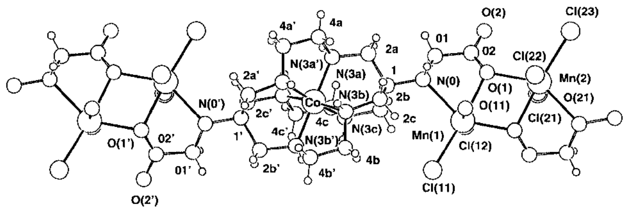

Fig. 4 A section of the Co/Mn_2 cationic polymer of **4**.

a Δ/Λ composite, with one pendent N-donor *R* and the other *S*. Thus, while the asymmetric unit strand of the Co/Zn compound consists of a sequence of ZnCl components linked by [(*S*-N,O){(*lel*$_3$)-Λ-cage}(*S*-N,O)] moieties, in the Co/Co compound, successive *trans*-$Co(OH_2)_2$ components are linked by [(*R*-N,O){(*lel*$_3$)-(Δ/Λ-cage}(*S*-N,O)] moieties, the statistics of the Δ/Λ disorder being indeterminate, except 50 : 50 in the gross. Here, Co(III)···Co(II) within the strand is $a/2$ = 11.983(1)/2 Å, comparable to Co···Zn in **1**. Interstrand Co···Co (minimum) is 8.7274(5) Å (= *b*). About the Co(II), Co–N(0), O(1), O(01) are 2.234(3), 2.057(2), 2.097(2) Å, with N(0)–Co–O(1), O(01), O(1)–Co–O(01) 77.3(1), 91.18(9), 89.52(9)°. About the Co(III), N···N distances range between 2.797(4)–2.804(4), mean 2.801(4) (upper, lower triangle edges) and 2.779(4)–2.789(4), mean 2.784(5) Å (between triangles 'bite'), the latter value approximating the mean of the two distinct interstrand types resolved in **1**. H-Bonding interactions are implicit, albeit with some less well-defined than in **1** because of the cage disorder. Cl(1) bridges two strands, linking Co(2) environments straightforwardly: Cl(1)···N(0), O(01) ($1 - x$, $2 - y$, $2 - z$) 3.382(3), 3.104(3) and Cl(1)···O(02) (½ − *x*, *y* − ½, 1½ − *z*) 3.146(3) Å, also contacting a pair of disordered water molecules (Cl(1)···O(05) ($1 - x$, $2 - y$, $2 - z$), O(06) (½ + *x*, 1½ − *y*, *z* − ½) 2.93(2), 3.139(8) Å). Cl(2) occupies a putative interstrand site: Cl(2)···N(3a) ($\bar{x}$, $2 - y$, $2 - z$), N(3b) 3.154(4), 3.109(3) Å, also having contacts to disordered water molecules: Cl(2)···O(3,4,5) (*x* − ½, 1½ − *y*, *z* − ½) 3.103(8), 2.965(7), 2.842(14) Å. N(3a) contacts Cl(2) (as above) and water O(03) 2.854(8) Å, N(3a′)···O(03,06,08) being 2.857(7), 2.746(8), 3.07(3) Å and N(3b′)···O(06,07) 2.938(9) 3.06(1) Å. Ligand and coordination geometries, imprecisely defined, are unexceptional.

The $Co/Mn_{(2)}$ system exhibits a further dimension of complexity. As with the other systems, suitable crystals were not readily obtained, structure determination of **3** initially being undertaken on material derivative of Method 1. The solution indicated that, in this case, there were two independent divalent metal sites, one exhibiting complete and the other partial occupancy. The conditions of synthesis were modified (Method 2) with the intent (successful) of achieving complete occupancy of both sites. The two structures are isomorphous; the stoichiometric result **4** derivative of Method 2 is simpler (Fig. 4, Table 2) and more readily apprehensible and we discuss it first.

Here again, the complex is a one-dimensional polymer, one formula unit devoid of crystallographic symmetry comprising the asymmetric unit of the structure, and spanning a unit translation also in a C_{2h}^5, no. 14, monoclinic cell, but this time along *b*, rather than *a*, as in **1** and **2**. Here, as in the Co/Zn complex, all Co sar moieties, translation related within the polymer strand, are of the same chirality, set as Λ in that string definitive of the asymmetric unit, with the cage unit again *lel*$_3$; the pendent N configurations are perhaps not entirely securely, in view of the limited precision of the determination, assigned as *R*,*S*; the assignment for the more precisely determined, albeit disordered, **3** is *R*,*R*. The divalent metal atom bridge component in this case is binuclear; the environment of Mn(2) comprises a mixture of diastereoisomers. The two amino-acid residues each chelate one of the manganese atoms, but in this complex, the oxygen atom goes beyond the unidentate role found in the Co/Zn and Co/Co arrays to act as a bridge to the other manganese, the two manganese atoms thus being part of a four-membered $Mn(\mu\text{-}O)_2Mn$ ring derivative of the chelating amino-acid oxygen, defining, in combination with the chelated array, an 'equatorial' plane about each manganese. In consequence of the binuclear linkage between successive cages, the repeat unit of the polymer (*b*) (= 15.336(2) Å) is larger than in the Co/Zn, Co/Co adducts. The six-coordinate environment of Mn(1) is completed in a relatively uncomplicated way by the coordination of a pair of terminal chloride moieties, one equatorial (Cl(11)), one axial (Cl(12)), the latter opposed by the oxygen atom of a (presumed) water molecule for which hydrogen atoms were not resolved. The rather heterogeneous environment imposes some difficulty in assignment (*e.g.*, is O(11) derivative of water or hydroxide?) on the basis of geometry, and uncertainty in the proton count of course raises the prospect that the Mn atoms may not have retained their +II oxidation state. Nonetheless, dissolution of the solid in acid provides no evidence for the presence of Mn species in higher oxidation states and the presumed $Mn–OH_2$ bond length is perhaps rather longer than that observed in well characterised $[Mn(OH_2)_6]^{2+}$ species, *e.g.* classically, ammonium manganese Tutton salt, *ca.* 2.18 Å.[11]

About Mn(2), the amino-acid chelate sites are well-defined, as are equatorial O(1) and Cl(23) (terminal). In the lattice, a residue Cl(0) models comfortably as a fully populated counter ion to the polymer; assuming divalent manganese in association with water molecules, charge balance would sensibly require a further chloride bound to Mn(2), but, unlike Mn(1), this is not confined to one of the *trans* sites but disordered over both, together with the *trans* 'water molecule' as modelled, occupancies refined to 0.5 and constrained at that, with oxygen and chloride components independently resolvable and refinable. Relative to the $Mn(\mu\text{-}O)_2Mn$ plane, therefore, the axial chlorine (or water) at Mn(2) may be *cis*- or *trans*- (or *trans*- or *cis*-) evenhandedly *vis-a-vis* the well defined axial (Cl(12) + O(11)) array about Mn(1). The same *caveats* about the nature of the oxo moiety and the manganese valence state apply here, *a fortiori*. Lattice residues modelled as water molecules are ill-defined with high displacement parameters; the anionic chlorine, Cl(0), occupies a 'chelate' site relative to an adjacent polymer strand (Cl(0)···H(3a′,3b) ($2 - x$, $2 - y$, $2 - z$) 2.3, 2.2 Å (est.)), also contacting one of the better defined water molecules (Cl(0)···O(01) 3.16(2) Å). The final model for **4** is thus: $[\{Cl_2(H_2O)Mn\}(O_2CCH_2NH)(Co\ sar)(NHCH_2CO_2)\text{-}\{Mn(OH_2)Cl_2\}]_{(\infty|\infty)}Cl\cdot 7^1/_2H_2O$.

Although yielding a more precise refinement from a larger specimen, the model adopted for the material **3** first obtained (Method 1) is necessarily even more speculative, albeit interesting, essentially a similar complex but deficient in occupancy of the Mn(2) site, and modelled as a composite of a major component (*ca.* 0.675(2)) and a minor component (1 − 0.675(2)). In the model obtained, the major component corresponds to that of **4** minus {Mn(2) Cl(23) O/Cl(21,22)}, but with Cl(12) supplanted by water, the displaced Cl(12) component becoming a chloride ion fragment Cl(13) lying in the vicinity of the site of putative Cl(23) (Cl(13)···Cl(23) 1.543(5) Å). The minor component presents as the Method 2 species, **4**, as described above. The free anion, Cl(0), models as fully weighted, common to both, but the lattice water complement overall is augmented, in respect of occupancy of the void created by the loss of Mn(2) and associated atoms in the major component.

Conclusions

Although comparison of the M(II) linker systems presently characterised is complicated by differences in coordination geometry and/or full donor atom array, the failure of Mn(II) to readily form a bis(chelate) link may be no more than another illustration of the Irving–Williams series.[12] Mn(II) chelates with the same ligand would be expected to be less stable than those

Table 2 Manganese environments, Co/Mn (Method 2) complex **4** (presentation as in Table 1; italicised atoms are translation related)

(a) Mn(1)[a]

Atom	*r*	O(1)	*O(1′)*	Cl(11)	Cl(12)	O(11)
N(0)	2.365(7)	70.1(2)	144.4(2)	104.7(2)	92.4(2)	84.8(3)
O(1)	2.249(7)		74.6(2)	173.7(2)	85.7(2)	84.9(2)
O(1′)	2.163(6)			110.2(2)	89.1(2)	88.0(2)
Cl(11)	2.422(3)				98.3(1)	91.1(2)
Cl(12)	2.526(5)					170.6(2)
O(11)	2.310(7)					

(b) Mn(2)

Atom	*r*	*O(1′)*	O(1)	Cl(23)	Cl(21)[b]	O(22)[b]
N(0′)	2.408(8)	69.5(2)	143.5(3)	105.8(2)	92.1(2)	87.3(5)
O(1′)	2.253(7)		74.1(2)	110.5(2)	85.1(2)	87.8(5)
O(1)	2.182(6)			175.0(2)	86.7(2)	89.4(5)
Cl(23)	2.444(3)				96.7(2)	90.6(4)
Cl(21)	2.542(6)					172.6(5)
O(22)	2.19(2)					

(c) Mn(1) (Method 1) **3**

Atom	*r*	O(1)	*O(1′)*	Cl(11)	Cl(12)[c]	O(11)
N(0)	2.404(3)	70.7(1)	149.1(1)	102.9(1)	93.2(1)	84.2(1)
O(1)	2.208(4)		78.9(1)	173.0(1)	85.1(1)	85.3(2)
O(1′)	2.148(3)			107.1(1)	89.4(1)	88.1(1)
Cl(11)	2.445(1)				98.4(1)	91.3(1)
Cl(12)	2.571(4)					170.4(1)
O(11)	2.238(4)					

[a] Mn(1) · · · Mn(2) is 3.523(2) Å; O(1) · · · *O(1′)* 2.674(9) Å. Mn(1)–O(1,1′)–Mn(2) are 105.3(3), 105.8(3)°. [b] Mn–Cl(22), O(21) 2.587(5), 2.16(2) Å; O(21)–Mn(2)–*N(0′)*, *O(1′)*, O(1), Cl(23), Cl(22)–Mn(2)–*N(0′)*, *O(1′)*, O(1), Cl(23) are 90.8(6), 83.5(6), 87.1(6), 98.2(6), 88.1(2), 88.6(2), 89.0(2), 89.9(2)°; Cl(21) · · · O(21), Cl(22) · · · O(22) are 0.39(2), 0.40(2) Å. [c] Refined as Cl(12): O(12) $x = 0.325(2) : 1 - x$, *i.e.* in the major component, site 12 is water; Mn(1)–O(12) is 2.185(6) Å, O(12)–Mn(1)–N(0), O(1), *O(1′)*, Cl(11), O(11) being 2.4(1), 88.6(2), 92.1(2), 94.7(2), 173.7(2)°.

of Co(II) or Zn(II), because of both effective nuclear charge and "ligand-field stabilisation energy" factors, though these might be counterbalanced to some extent by the fact that a ligand giving a five-membered chelate would be expected to favour the largest of any group of otherwise similar metal ions.[13] It is much more difficult to explain why the crystallisation of a polymer of the present type should be so sensitive to the nature of the linking cation, though it is clear from the present results (and others)[14] that the coordination chemistry of the proton (H-bonding) is a critical consideration which involves further the nature of counter anions, just as is true for numerous simpler structures involving cage amine complexes.[15]

The diamagnetic nature of the Co(III) cage limits the possibilities for magnetic interactions within these coordination polymers, and susceptibility measurements on the Co(II), Ni(II) and Cu(II) compounds showed them to behave as magnetically dilute systems.[16] The stability of the Co(III) state within the cage also limits possibilities for redox activity. It is possible, however, to substitute Co(III) by numerous more reactive transition metals and, assuming arrays similar to those characterised here can again be generated, stable solids with more interesting electronic and magnetic properties may result.[17]

References

1 G. F. Swiegers and T. J. Malefeste, *Chem. Rev.*, 2000, **100**, 3483 and references therein.

2 D. Braga, *J. Chem. Soc., Dalton Trans.*, 2000, 3705 and following articles.

3 P. S. Donnelly, J. M. Harrowfield, B. W. Skelton and A. H. White, *Inorg. Chem.*, 2000, **39**, 5817.

4 A. M. Sargeson, *Pure Appl. Chem.*, 1986, **58**, 1511; A. M. Sargeson, *Coord. Chem. Rev.*, 1996, **151**, 89.

5 (*a*) I. J. Clark, R. J. Geue, L. M. Engelhardt, J. M. Harrowfield, A. M. Sargeson and A. H. White, *Aust. J. Chem.*, 1993, **46**, 1485 and references therein; (*b*) S. Burnet, M.-H. Choi, P. S. Donnelly, J. M. Harrowfield, I. Ivanova, S.-H. Jeong, Y. Kim, M. Mocerino, B. W. Skelton, A. H. White, C. C. Williams and Z.-L. Zeng, *Eur. J. Chem.*, 2001, 1869.

6 For broader consideration of such issues, see F. R. Keene, *Coord. Chem. Rev.*, 1997, **166**, 121.

7 R. J. Geue, T. W. Hambley, J. M. Harrowfield, A. M. Sargeson and M. R. Snow., *J. Am. Chem. Soc.*, 1984, **106**, 5478.

8 S. R. Hall, G. S. D. King and J. M. Stewart, ed. *The Xtal 3.4 User's Manual*, University of Western Australia, Lamb, Perth, 1995.

9 S. F. Mason, *Molecular Optical Activity and the Chiral Discriminations*, Cambridge University Press, Cambridge, 1982, ch. 9.

10 For some related systems, see (*a*) P. A. Brayshaw, J.-C. G. Bünzli, P. Froidevaux, J. M. Harrowfield, Y. Kim and A. N. Sobolev, *Inorg. Chem.*, 1995, **34**, 2068; (*b*) J. M. Harrowfield, Y. Kim, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1995, **48**, 807.

11 H. Montgomery, R. V. Chastain and E. C. Lingafelter, *Acta Crystallogr.*, 1966, **20**, 731.

12 N. N. Greenwood and A. E. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1984, p. 1097.

13 R. D. Hancock, *Perspectives in Coordination Chemistry*, A. F. Williams, C. Floriani and A. E. Merbach, ed., VCH, Basel, 1992.

14 A. D. Burrows, R. W. Harrington, M. F. Mahon and C. E. Price, *J. Chem. Soc., Dalton Trans.*, 2000, 3845.

15 See ref. 3 and references therein.

16 P. S. Donnelly, A. K. Hall and J. M. Harrowfield, University of Western Australia, unpublished work.

17 K. R. Poeppelmeier, *Chem. Mater.*, 1998, **10**, 2577 and following articles.