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Ligand displacement for fixing manganese: relevance to cellular metal ion transport and synthesis of polymeric coordination complexes†

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A dinuclear manganese(III) complex (**1**) of an *N*-(carboxymethyl)-*N*-[3,5-bis(α,α-dimethylbenzyl-2-hydroxybenzyl)]glycine (HDA) ligand (**L**) binds a manganese(II) species through displacement of its solvating ligands by appropriately dispositioned carbonyl groups of a dinuclear complex {$[Mn_2(L)_2(OH)(OCH_3)][Mn(H_2O)_3(CH_3OH)_3]$, **2**, triclinic $P\bar{1}$, a = 13.172(3) Å, b = 15.897(3) Å, c = 19.059(4) Å, V = 3461.9(13) Å^3} leading to a trinuclear complex {**3**, monoclinic $P21/n$, a = 11.7606(8) Å, b = 21.3505(8) Å, c = 26.7827(17) Å, V = 6722.7(7) Å^3} with cyclization of two of the carboxy groups through the doubly-carboxy group coordinated Mn^{2+} ion. The reaction is discussed in terms of its significance as an illustration of how Mn^{2+} ions might be sequestered in biological systems. A similar solvato-ligand displacement reaction was used to synthesise coordination polymers of an HDA iron(III) complex involving polymerization through a bridging carboxylato group. Several isostructural polymers (**5–7**; for **5**: orthorhombic *Pbca*, a = 9.411(5) Å, b = 16.390(8) Å, c = 37.968(19) Å, V = 5856(5) Å^3) with different coordinated alcohols could be prepared indicating the potential synthetic uses of this method.

Introduction

Coordination complexes of manganese with organic ligands have attracted attention as potential materials for catalysis[1] and molecular magnetics.[2] For the latter, many oligonuclear complexes have been prepared that not only present unique structural motifs but also possess properties illustrating their importance as magnetic materials.[3] Moreover, mixed metal oligonuclear complexes of manganese with other cations such as those of the lanthanides have been investigated due to their significant and novel properties.[4] Additionally, manganese is one of the critical elements involved in life processes due to its variability both of oxidation state and coordinative form.[5] It is particularly notable for its presence (as an oligonuclear cluster) at the water splitting core of Photosystem II (PSII) in photosynthetic bacteria.[6] Apart from that role, manganese cations are present at the active sites of many important enzymes including superoxide dismutase[7] and catalase.[8] Coincidentally, manganese is also involved in mechanisms of bacterial pathogenicity[9] and in human disease states such as Parkinsonism and other brain disorders.[10] Because of these matters and also due to its ubiquity in biological systems, questions arise as to how it is fixed and transported in cellular media. Investigations of manganese transport have included X-ray crystal structural studies[11] to reveal, in depth, the fate of manganese in cells including its supply to important active sites like PSII.[12] High resolution X-ray studies have revealed that the chemical nature of the interactions between proteins and manganese ions is largely through coordination by carboxylate and imidazole side chains of, for instance, glutamate (or aspartate) and histidine amino acid residues.[13] In low valent complexes, two Mn^{2+} ions may be bridged in 1,3 fashion by carboxylate groups while enzymes containing manganese in higher oxidation states sometimes contain electronegative bridging groups such as oxide or hydroxide.[14] However, there is little information regarding how manganese cations are

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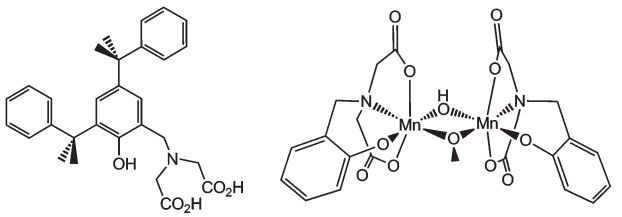
†Electronic supplementary information (ESI) available: CIFs for compounds **2**, **3**, **5–7**; additional figures of compounds **6** and **7**. CCDC 893592, 893593, 893594, 893595, 906345. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32547k



Scheme 1 The ligand *N*-[3,5-bis(α,α-dimethylbenzyl-2-hydroxybenzyl)] iminodiacetic acid (**L**) (left) and the dinuclear manganese complex $[(\mu_2\text{-OH})(\mu_2\text{-OCH}_3)\text{-}L_2Mn_2]^{2-}$ (right) described here (α,α-dimethylbenzyl groups removed for clarity).

initially fixed in the Mn^{2+} state (manganese and other transition metal cations are known to be transported in cells in divalent form[15]) although modes of binding in enzymes have been investigated.[16]

In this work we present X-ray structural studies of manganese complexes in which solvated Mn^{2+} ions are observed to have undergone ligand displacement reactions during the process of forming a trinuclear manganese complex from a dinuclear precursor. We also present structures of linear polynuclear coordination complexes of iron(III) prepared using a selective ligand displacement protocol deduced from the formation of the Mn_3 complex.

Ligands containing (2-hydroxyphenylmethyl)-iminodiacetic acid have been known for over sixty years[17] and they have been used extensively in preparation of coordination complexes especially with transition metal ions. Complexes prepared from these and similar ligands have been proposed as models of enzyme reaction centers.[18] We have previously investigated the structure-directing effects of iminodiacetic acid substituted phenols and characterised the supramolecular structures and properties of the resulting complexes (Scheme 1).[19] By varying the substituent structure of the phenol ligand, it has proved possible to vary the structures of the resulting complexes leading to several significant phenomena including cation–π binding of potassium counterions[19a] and formation of porous coordination complexes (*i.e.* MOFs).[19b] The cation–π effect was observed using a (2-hydroxyphenylmethyl)-iminodiacetic acid (HDA) ligand substituted with α,α-dimethylbenzyl groups.[19a] The structure of this ligand (**L**) is shown in Scheme 1 together with chemical structures of the basic dinuclear manganese complex (**1**) used here. In this work, the substituent α,α-dimethylbenzyl groups served to improve the solubility of **L**.

Results and discussion

Complex **1** contains the $[(\mu_2\text{-OH})(\mu_2\text{-OCH}_3)L_2Mn_2]^{2-}$ unit, which contains trivalent manganese stabilized by the electronegative ligand set including phenoxide and hydroxide/methoxide.[20] In this work, we could not obtain crystals of the dinuclear unit alone but we presume its existence in solution together with the solvated Mn^{2+}, which either cocrystallizes giving **2** or reacts with **1** leading to **3**. The presence of the bridging hydroxide is confirmed by a hydrogen-bonded water molecule in its vicinity. Dinuclear complexes of manganese with various ligands are known,[21,22] but in the case of **1** two peripheral carbonyl groups of the complex are oriented such that they can interact with a further species, here a solvated Mn(II) cation. The nature of the interaction depends on solution conditions and in the presence of base a complex system of hydrogen bonds (H-bonds) fixes a meridionally structured $[Mn(H_2O)_3(CH_3OH)_3]^{2+}$ in the proximity of the two aforementioned peripheral carbonyl groups. Fig. 1a shows the X-ray crystal structure of this trinuclear complex (**2**) and reveals H-bonds between each of two carboxylate groups of **1** and one of the aquo ligands of *mer*-$[Mn(H_2O)_3(CH_3OH)_3]^{2+}$. Additional H-bonds between other solvato ligands of *mer*-$[Mn(H_2O)_3\text{-}(CH_3OH)_3]^{2+}$, proximal methanol and the other oxygen atoms of the same carboxylate groups stabilize this complex. If no base is added during the reaction between **L** and manganese(II) acetate tetrahydrate then complex **3** (Fig. 1b) is obtained where two ligating solvent molecules of the previously H-bonded solvated Mn^{2+} atom have been displaced by the appropriately dispositioned carbonyl groups of complex **1**. In biological systems, manganese ions (probably $[Mn(H_2O)_6]^{2+}$) must at some point be free from interaction with protein and we propose that a process of ligand displacement similar to that apparent here from **2** to **3**, leading to fixing of Mn^{2+} by appropriately oriented carbonyl groups, may be analogous with processes occurring where manganese is initially sequestered. The 'fixed' manganese atom remains in its +2 oxidation state in both **2** and **3** and this is also consistent with biological systems where manganese is known to be transported in a divalent state. Once sequestered, Mn^{2+} is transferred *in vivo* by inter-protein interactions[13,15,23] although this would not preclude transport processes again involving small ligands such as aquo. Variable binding activity by carboxylate groups in enzymes has been noted *in vitro* by Lippard and coworkers.[16a]

2 is isolated from reactions containing hydroxide while **3** forms under slightly acidic conditions. Our proposed mechanism (Fig. 1c) for the formation of **2** from **3** thus includes replacement of aquo by carbonyl oxygen atoms as ligands which should be favoured under acidic conditions since protonation of water promotes its ability to act as a leaving group. Subsequent displacement of an alcoholato ligand is favoured by its proximity to the adjacent carbonyl group.

The dinuclear units in **2** and **3** have very similar forms and bond lengths about the two manganese atoms. The Jahn–Teller axis occurs in both cases between the coordinating carboxylate groups of the ligand (for bond lengths and angles see Fig. 1 caption) and is roughly perpendicular to the plane of the bridging hydroxo/alkoxo as is typical for $Mn^{3+}{}_2$.[21] The Mn–Mn distances in **2** and **3** are 2.9832(18) Å and 2.9661(12) Å, respectively. In **2**, the *mer*-$[Mn(H_2O)_3(CH_3OH)_3]^{2+}$ moiety is only slightly distorted as expected (which is typical for unsymmetrically substituted hexasolvatomanganese(II) complexes) and all the solvato groups are involved in a hydrogen bonding network. In **3**, one aquo and one alcoholato ligand have been

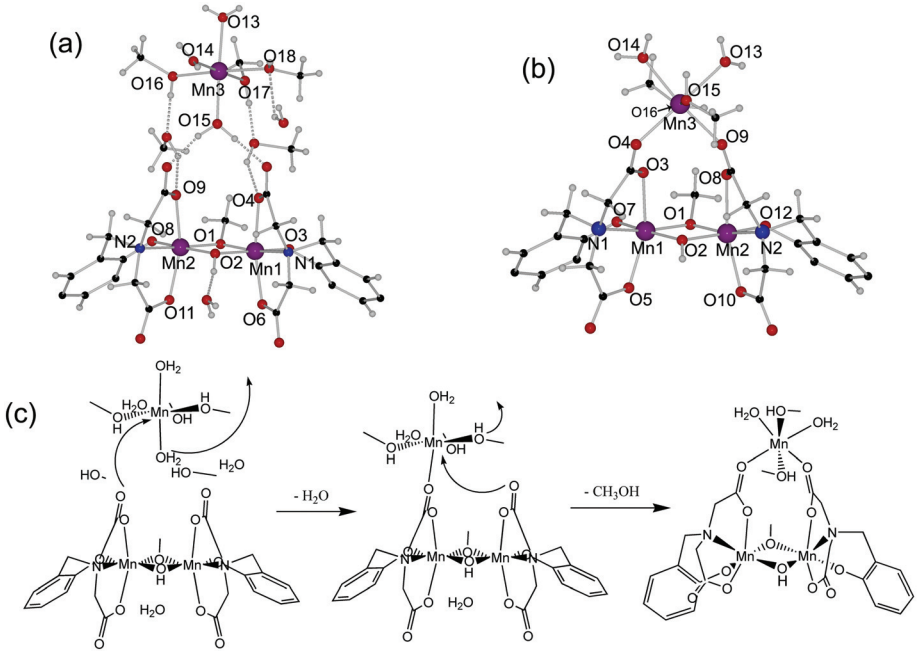


Fig. 1 (a) X-ray crystal structure of **2** showing the dinuclear unit interacting with *mer*-$[Mn(H_2O)_3(CH_3OH)_3]^{2+}$ through a hydrogen bonding manifold involving two additional molecules of methanol. Edge-on view is shown at the right. (b) X-ray crystal structure of **3** where the manganese atom remote from the dinuclear complex has been 'fixed' through carbonyl oxygen atom coordinate bonds. Edge-on view is shown at the right. (c) Proposed mechanism for transformation from **2** to **3** involving solvato ligand displacement from the incoming manganese atom (α,α-dimethylbenzyl groups removed throughout for clarity). Important bond lengths (Å) and angles (°): **2**: Mn1–N1 2.137(7), Mn1–O1 1.927(5), Mn1–O2 1.952(5), Mn1–O3 1.862(5), Mn1–O4 2.155(5), Mn1–O6 2.187(5), Mn2–N2 2.113(6), Mn2–O1 1.919(5), Mn2–O2 1.944(6), Mn2–O8 1.853(5), Mn2–O9 2.170(5), Mn2–O11 2.195(5), Mn3–O13 2.178(6), Mn3–O14 2.113(7), Mn3–O15 2.133(6), Mn3–O16 2.178(7), Mn3–O17 2.159(7), Mn3–O18 2.253(6), Mn1–O1–Mn2 101.7(2), Mn1–O2–Mn2 99.9(2); **3**: Mn1–N1 2.125(5), Mn1–O1 1.930(4), Mn1–O2 1.944(5), Mn1–O3 2.207(4), Mn1–O5 2.190(4), Mn1–O7 1.841(4), Mn2–N2 2.145(5), Mn2–O1 1.938(4), Mn2–O2 1.941(4), Mn2–O8 2.232(4), Mn2–O10 2.148(4), Mn2–O12 1.860(4), Mn3–O4 2.107(5), Mn3–O9 2.163(5), Mn3–O13 2.145(5), Mn3–O14 2.230(5), Mn3–O15 2.213(4), Mn3–O16 2.228(5), Mn1–O1–Mn2 100.16(18), Mn1–O2–Mn2 99.55(19), O4–Mn3–O9 93.14(18).

replaced in a *cis* configuration by carbonyl oxygen atoms of the **1** moiety. The two remaining aquo ligands lie *trans* to the coordinating carbonyl groups with the two methanolato ligands occupying sites above and below the carbonyl/water coordination plane with one of them undergoing an intramolecular H-bond with a carboxylate oxygen atom of the dinuclear unit (for bond lengths and angles see Fig. 1 caption).

The long range structures of complexes **2** and **3** are strongly influenced by hydrogen bonding involving basic ligands of the Mn^{2+} cation, solvent molecules and carboxyl groups of the HDA ligand. The bridging hydroxyl group of the dinuclear unit is also involved. Essentially, in both **2** and **3**, dinuclear units of **1** are respectively linearly polymerized through H-bonding between the carboxyl groups of the HDA and ligands and the ligands of the Mn^{2+} cation (see Fig. 2). Linear polymeric units are then joined through further H-bonding interactions. In **2**, this involves mutual H-bonds between carboxyl groups and solvato groups of the Mn^{2+} cation but additionally includes bridging between polymeric strands through hydroxo bridges mediated by solvent water molecules. For **3**, it appears that only mutual H-bonding between the bridging hydroxo groups of the dinuclear units is required. These interactions are summarized in Fig. 2. Apart from H-bonding there also exist C–H···pi interactions and there is obviously amphiphilic segregation within the structure with hydrophobic α,α-dimethylbenzyl groups contained in layers.

Having observed the potential solvent/ligand displacement reaction we considered that this process might be applied in a synthetic sense for preparation of coordination complexes of predictable structure or form if selective displacement analogous with the **1** system could be achieved. In previous work,[19d] one of us prepared the complex **4** which is a mononuclear complex of iron(III) with **L** containing coordinated solvent (water and methanol). This complex also provides the opportunity for determining whether there is any selectivity in the lability of the coordinated solvent. Under conditions that lead to crystallisation of a product we found that water is selectively displaced yielding a coordination polymer **5** (see Fig. 3a,b) through the expected displacement of coordinated solvent by a peripheral carbonyl group in a neighbouring mononuclear unit. Similarly to the case of **2**, acidic conditions lead to the displacement of aquo selectively over alcoholato ligands supporting our mechanism (Fig. 1c) involving initial displacement of aquo from **2**. Other alcohols including 1-propanol (**6**) and ethylene glycol (**7**) behave consistently leading to isostructural complexes (see Table 1). In the ethylene glycol complex there is an additional weak O–H···π interaction between the non-

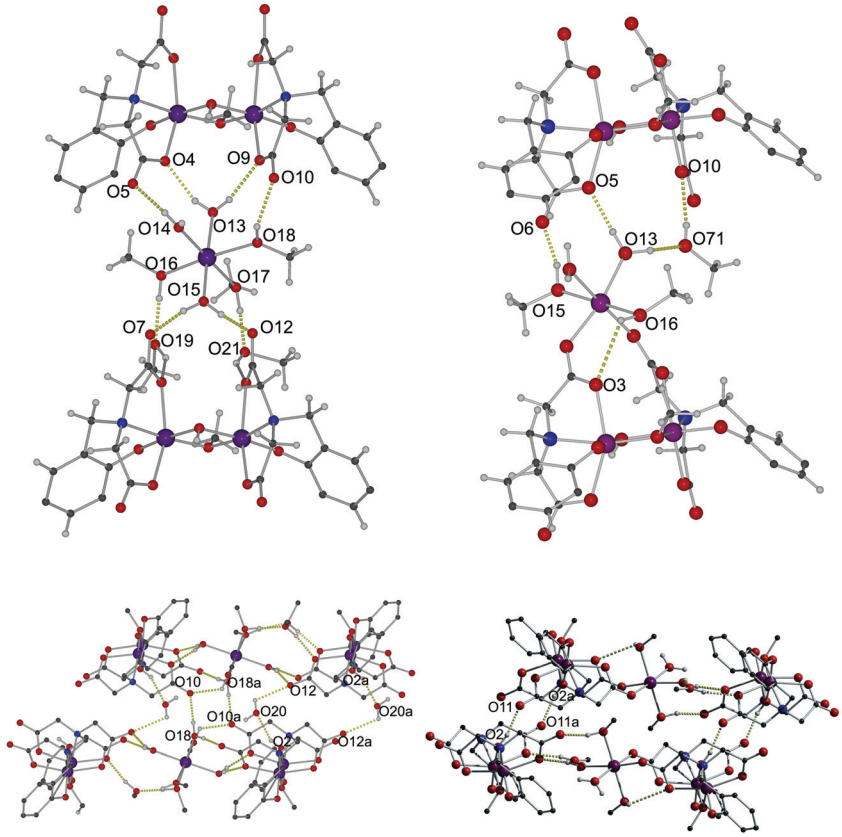


Fig. 2 Hydrogen bonding in **2** and **3**. (a) Structure of **2** showing its extensive hydrogen bond network forming a linear H-bond polymer. (b) Structure of **3** also revealing extensive hydrogen bonding forming linear chains of the complex. (c) H-bonds between linear chains involve the hydroxo bridge group and solvent water molecules. (d) In **3**, mutual H-bonding between chains occurs between hydroxo bridges and carbonyl oxygen atoms in adjacent chains (α,α-dimethylbenzyl groups removed throughout for clarity). Important H-bond lengths (Å) (and angles in degrees): **2**: O13–H13a···O4 2.718(8) (159(7)), O13–H13a···O9 2.784(7) (166(7)), O14–H14a···O5 2.685(9) (174(10)), O18–H18a···O10 2.627(8) (119.1), O16–H16···O19 2.698(9) (171(9)), O15–H15a···O7 2.709(8) (167(8)), O15–H15b···O12 2.693(8) (164(8)), O17–H17···O21 2.605(9) (177(10)), O14–H14b···O10 2.710(9) (174(11)), O2–H2···O20 2.722(8) (154(8)), O20–H20B···O12 2.727(9) (106(7)). **3**: O16–H16···O3 3.0533(7) (113(11)), O15–H15···O6 2.589(6) (163(6)), O13–H131···O5 2.780(6) (173(8)), O13–H132···O71 2.684(8) (155(7)), O71–H71···O10 2.834(7) (163.3), O2–H2···O11 2.710(6) (164(6)).

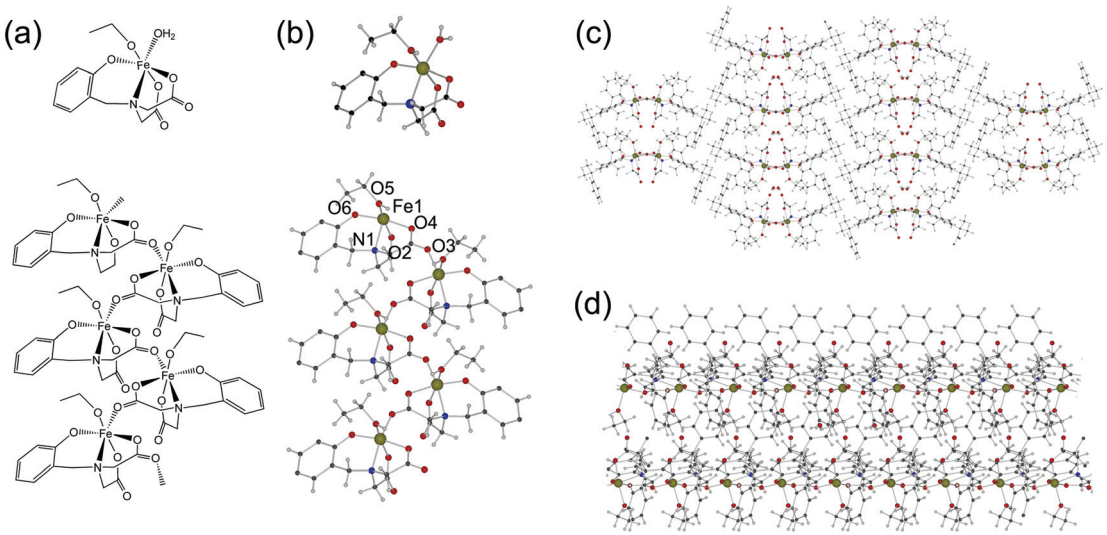


Fig. 3 Polymerization by selective displacement of coordination solvent in the mononuclear Fe^{3+} complex of **L**. (a) Schematic of monomer (**4**) and the resulting polymer (**5**). (b) Corresponding X-ray crystal structures of compounds shown in (a). Packing of the coordination polymer chains viewed along (c) the *a*-axis, (d) the *b*-axis. Important bond lengths and distances (Å): Fe1–N1 2.187(7), Fe1–O2 2.015(6), Fe1–O3 2.034(6), Fe1–O4 1.938(6), Fe1–O5 2.033(6), Fe1–Fe1A 5.840(3).

Table 1 X-ray crystallographic data and structure refinements for compounds **2**, **3**, **5–7**

	2	**3**	**5**	**6**	**7**
Formula	$C_{64}H_{92}Mn_3N_2O_{21}$	$C_{126}H_{157}Mn_6N_4O_{38}$	$C_{31}H_{36}FeNO_7$	$C_{32}H_{38}FeNO_7$	$C_{31}H_{37}FeNO_8$
M_r	1390.22	2665.21	590.46	606.50	607.47
Diffractometer	Bruker Apex II	Stoe IPDS	Bruker Apex	Bruker Apex	Bruker Apex
Crystal system	Triclinic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P\bar{1}$	$P21/n$	*Pbca*	*Pbca*	*Pbca*
T [K]	150	200	150	150	296
a [Å]	13.172(3)	11.7606(8)	9.411(5)	9.556(2)	9.467(10)
b [Å]	15.897(3)	21.3505(8)	16.390(8)	16.496(4)	16.4024(17)
c [Å]	19.059(4)	26.7827(17)	37.968(19)	38.041(9)	37.998(4)
α [°]	70.363(4)	90	90	90	90
β [°]	83.939(4)	91.494(8)	90	90	90
γ [°]	67.134(3)	90	90	90	90
V [Å^3]	3461.9(13)	6722.7(7)	5856(5)	5997(2)	5900.4(11)
Z	2	4	8	8	8
ρ_{calcd} [g cm^{-3}]	1.334	1.317	1.339	1.344	1.368
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	0.611	0.624	0.562	0.551	0.563
F (000)	1466	2790	2488	2568	2560
Reflections collected	31 865	39 608	43 338	43 888	32 741
Unique data	10 045	9629	6102	6245	6245
R_{int}	0.1734	0.0968	0.1358	0.0370	0.0636
Data with [$I > 2\sigma(I)$]	4622	4888	3625	5318	4108
Parameters/restraints	865/197	800/17	374/0	387/0	383/0
S on F^2 (all data)	0.982	1.011	1.007	1.106	1.036
wR_2 (all data)	0.2054	0.1224	0.1454	0.1078	0.1281
R_1 ($I > 2\sigma(I)$)	0.0744	0.0567	0.0659	0.0466	0.0510
Largest residuals [e Å^{-3}]	+0.961/−0.689	+0.927/−0.087	+0.777/−0.313	+0.506/−0.256	+0.467/−0.689

coordinated hydroxyl group of ethylene glycol and a phenyl ring in an adjacent chain.

Conclusions

In conclusion, we have shown a potential model for initial fixation of Mn^{2+} in biological systems by using a molecule (coincidentally a coordination complex) with carbonyl groups in the proper orientation to cause solvent displacement from solvated Mn^{2+}. Further, we have demonstrated that the ligand displacement by carboxylate carbonyl groups can be used to form stable polymeric coordination complexes. We are currently testing the reversibility of manganese fixation for **1** in order to better understand the process with respect to any therapeutic properties these and similar complexes might have. It may be also possible to generate polymeric coordination structures based on **2a** with higher dimensionalities such as in 2D (*e.g.* on surfaces) or in 3D (*e.g.* to form porous networks or MOFs) if appropriately structured ligands are prepared. We will report on those aspects of this system in due course.

Experimental section

General

All chemicals were obtained from Tokyo Kasei Chemical Co. or Wako Chemical Co. and were used as received. FTIR spectra were measured using a Nicolet NEXUS 670 FT-IR spectrophotometer from samples prepared as KBr pellets. The ligand **L** *N*-(carboxymethyl)-*N*-[3,5-bis(α,α-dimethylbenzyl-2-hydroxybenzyl)]-glycine was prepared following a previously reported literature method.[19a] Elemental analyses were performed by the elemental analysis service of the University of Tsukuba.

X-ray crystallographic data collection and structure refinement

Diffraction data for **2**, **3** and **5**, **6** and **7** were collected using either Bruker Apex CCD diffractometers or a Stoe IPDS with sealed tube sources. For **2** and **3** data above 2θ = ~46.8° were removed due to the weakness of the high angle peaks. Narrow-frame exposures were employed. Cell parameters were refined from all strong reflections in each data set. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. Structure solution was carried out by direct methods and full-matrix refinement against F^2 (all data) using the SHELXTL package.[24] All non-hydrogen atoms were refined anisotropically. Water hydrogen atoms were located in the difference Fourier map and the coordinates allowed to freely refine, while the remaining hydrogen coordinates were constrained using a riding model with U_{eq} set to $1.2U_{eq}$ of the carrier atom ($1.5U_{eq}$ for methyl hydrogen). Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 893592 (**2**), 893593 (**3**), 893594 (**5**) and 893595 (**6**) 906345 (**7**).

2: Manganese(II) acetate tetrahydrate (0.115 g, 0.5 mmol) and **L** (0.112 g, 0.2 mmol) were dissolved in methanol (20 mL) and aqueous KOH (2 M; 3 mL) was slowly added to the stirred reaction mixture. Slow evaporation of the solution yielded green-grey crystals of **2** after 1 week. Yield: 61% based on

ligand. IR data (KBr): ν = 3403 [br, OH (str)], 2965 (w), 2954 (w), 2945 (s) [all C–H (str)], 1602 [m, C═O (str)], 1493 (s), 1465 (m), 1445 (s), 1412 (w), 1312 (s), 1234 (s), 1201 (m), 1157 (m), 978 (w), 921 (m), 867 (w) cm^{-1}. Elemental analyses: expected for $C_{64}H_{92}Mn_3N_2O_{21}$: %C 55.27, %H 6.67, %N 2.02, found %C 55.69, %H 6.53, %N 2.06.

3: A solution of **L** (0.120 g, 0.25 mmol) in ethanol (10 mL) was added to a solution of manganese(II) acetate tetrahydrate (0.095 g, 0.4 mmol) in a mixture of ethanol (10 mL) and water (2 mL). Green crystals of **3** were grown upon slow evaporation of the solvent. Yield: 37% based on ligand. IR data (KBr): ν = 3394 [br, OH (str)], 2950 (w), 2882 (w) [all C–H (str)], 1650 [m, C═O (str)], 1528 (s), 1463 (m), 1414 (m), 1402 (w), 1386 (w), 1314 (w), 1206 (w), 1086 (w), 1042 (w), 883 (w) cm^{-1}. Elemental analyses: expected for $C_{63}H_{76}Mn_3N_2O_{19}$: %C 56.87, %H 5.76, %N 2.11, found %C 57.35, %H 5.59, %N 2.16.

5: **L** (0.107 g, 0.2 mmol) and iron(III) chloride hexahydrate (0.100 g, 0.4 mmol) were together dissolved in ethanol (10 mL) yielding a solution of **4**.[19d] Acetic acid (2 mL) and water (10 mL) were added and the solution left to stand for 2 days whereupon blue crystals of the complex **5** formed. Yield: 80% based on ligand. IR data (KBr): ν = 3422 [br, OH (str)], 2973 (w), 2957 (w), 2926 (s), 2852 (w) [all C–H (str)], 1656 [m, C═O (str)], 1578 [m, C═O (str)], 1521 (s), 1507 (s), 1492 (s), 1464 (w), 1443 (s), 1382 (w), 1304 (w), 1027 (m), 940 (w), 907 (m), 829 (w) cm^{-1}. Elemental analyses: expected for $C_{31}H_{36}FeNO_7$: %C 63.03, %H 6.15, %N 2.37, found %C 63.30, %H 5.93, %N 2.42. If 1-propanol or ethylene glycol were used instead of ethanol, **6** or **7** were respectively obtained.

Acknowledgements

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