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# Syntheses and crystal structures of new suberato-bridged Mn(II) phen complexes: $\{[Mn(phen)_2]L_{2/2}\}_2\cdot H_2L\cdot 8H_2O$, $\{[Mn(phen)(H_2O)_3]_2L\}L\cdot 2H_2L\cdot 4H_2O$ and $\{[Mn(phen)_2(HL)]_2L\}\cdot H_2L$ ($H_2L = HOOC(CH_2)_6COOH$)

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## Abstract

Three suberato-bridged Mn(II) phen complexes $\{[Mn(phen)_2]L_{2/2}\}_2\cdot H_2L\cdot 8H_2O$ (**1**), $\{[Mn(phen)(H_2O)_3]_2L\}L\cdot 2H_2L\cdot 4H_2O$ (**2**) and $\{[Mn(phen)_2(HL)]_2L\}\cdot H_2L$ (**3**) have been synthesized and structurally characterized by single crystal X-ray diffraction methods. The $[Mn(phen)_2]^{2+}$ moieties in **1** are interlinked by bis-monodentate suberato ligands to generate $^1_\infty[Mn(phen)_2L_{2/2}]$ polymeric chains. Complex **2** features a nanoporous hydrogen bonded framework made up of suberate anions, suberic acid molecules and lattice water molecules with the bis-monodentate suberato bridged dinuclear $\{[Mn(phen)(H_2O)_3]_2L\}^{2+}$ complex cations residing in tunnels. The bis-monodentate suberato bridged dinuclear $\{[Mn(phen)_2(HL)]_2L\}$ molecules in **3** are assembled into a 3D framework with suberic acid molecules situated in the tunnels.

*Keywords:* Manganese; Suberato complexes; Coordination polymers; X-ray structures

## 1. Introduction

The past several years have witnessed considerable efforts directed toward the rational design and syntheses of coordination polymers with specific supramolecular architectures based on metal–organic coordination, hydrogen bonding as well as π–π stacking interactions, and it is well-known that organic bridging spacers play a very important role in construction of supramolecular systems [1–5]. Some polycarboxylates proved to be efficient rigid spacers to create nanoporous coordination polymers [5,6]. The application of dicarboxylates in the construction of coordination polymers has attracted much attention [7–21], as such dicarboxylate-based coordination polymers may possess special properties of technological interest; for example, Zn succinate with a distorted diamondoid network exhibits strong SHG effects [22]. Recently, we have extended our research to ternary mixed-ligand metal complexes with dicarboxylates as bridging ligands and heteroaromatic N-donor ligands as sources for π–π stacking interactions [23]. Synergetic coordination of dicarboxylates and hetroaromatic N-donor ligands to metal atoms has been shown to generate a variety of supramolecular motifs [24–35].

Here, we report the syntheses and crystal structures of $\{[Mn(phen)_2]L_{2/2}\}_2\cdot H_2L\cdot 8H_2O$ (**1**), $\{[Mn(phen)(H_2O)_3]_2L\}L\cdot 2H_2L\cdot 4H_2O$ (**2**) and $\{[Mn(phen)_2(HL)]_2L\}\cdot H_2L$ (**3**) with $H_2L$ standing for suberic acid (HOOC–$(CH_2)_6$–COOH).

## 2. Results and discussion

### 2.1. Syntheses

Our systematic synthetic experiments showed that the reaction products of freshly prepared $Mn(OH)_{2-2x}(CO_3)_x\cdot yH_2O$ precipitate, phenanthroline

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and suberic acid in mixed solvents of $H_2O$ and $CH_3OH$ are pH dependent. The reaction of equi-molar quantities of $Mn(OH)_{2-2x}(CO_3)_x\ yH_2O$ precipitate, phenanthroline and suberic acid was initially carried out in $CH_3CH_2OH/H_2O$, and a mixture consisting of the known $\{[Mn(phen)_2(H_2O)]_2L\}\{[Mn(phen)_2L]_2L\}\cdot 4H_2O$ [27] and a new complex $\{[Mn(phen)_2]L_{2/2}\}_2\cdot H_2L\cdot 8H_2O$ (**1**) were obtained by slow evaporation. To suppress the formation of the former complex and improve the synthetic yield of **1**, the reaction was then conducted in $CH_3OH/H_2O$ but all attempts were unsuccessful, which implied that the ethanolic medium is favorable for the formation of **1**. Astonishingly, the reaction of equimolar amounts of $Mn(OH)_{2-2x}(CO_3)_x\cdot yH_2O$ precipitate, phenanthroline and suberic acid in $CH_3OH/H_2O$ gave a very stable yellow filtrate (pH 5.6), which could be preserved even for over 1 year without any significant evaporation and no precipitation and crystallization took place. When the above methanolic filtrate was adjusted to pH 4.8 by adding powdered suberic acid, slow evaporation at room temperature produced firstly bulky crystals of $\{[Mn(phen)(H_2O)_3]_2L\}L\cdot 2H_2L\cdot 4H_2O$ (**2**) in high yield and then well-shaped crystals of $\{[Mn(phen)_2(HL)]_2L\}\cdot H_2L$ (**3**) after separation of **2**. If the methanolic filtrate was adjusted to pH 7.0 by dropwise addition of NaOH, the crystals of $\{[Mn(phen)_2(H_2O)]_2L\}\{[Mn(phen)_2L]_2L\}\cdot 4H_2O$ [27] was the sole product in good yield by slow evaporation at room temperature.

### 2.2. *Structure of* $\{[Mn(phen)_2]L_{2/2}\}_2\cdot H_2L\cdot 8H_2O$ (**1**)

Compound **1** consists of $^1_\infty[Mn(phen)_2L_{2/2}]$ polymeric chains, twisted suberic molecules and crystal water molecules. As illustrated in Fig. 1, each polymeric chain results from $[Mn(phen)_2]^{2+}$ moieties bridged by bis-monodentate suberato ligands, and the Mn atoms are each coordinated by two crystallographically distinct phen ligands and two symmetry-related suberato ligands to form a severely distorted $MnN_4O_2$ octahedron with the carboxylate O atoms at *cis* positions ($d(Mn-O) = 2.120(2)$ Å, $d(Mn-N) = 2.267(2)-2.341(2)$ Å, Table 2). Both phen ligands chelating the central Mn atom orientate nearly perpendicular to each other (dihedral angle: 86.92(4)°). Along the [0 1 0] direction, two polymeric chains are arranged in such a way that the suberato ligands are sandwiched between two symmetry equivalent and antiparallel phen ligands containing N(1) and N(2) atoms with a mean alkyl C-to-phen interplanar distance of 3.52 Å, indicating weak $C-H\cdots\pi$ interac-

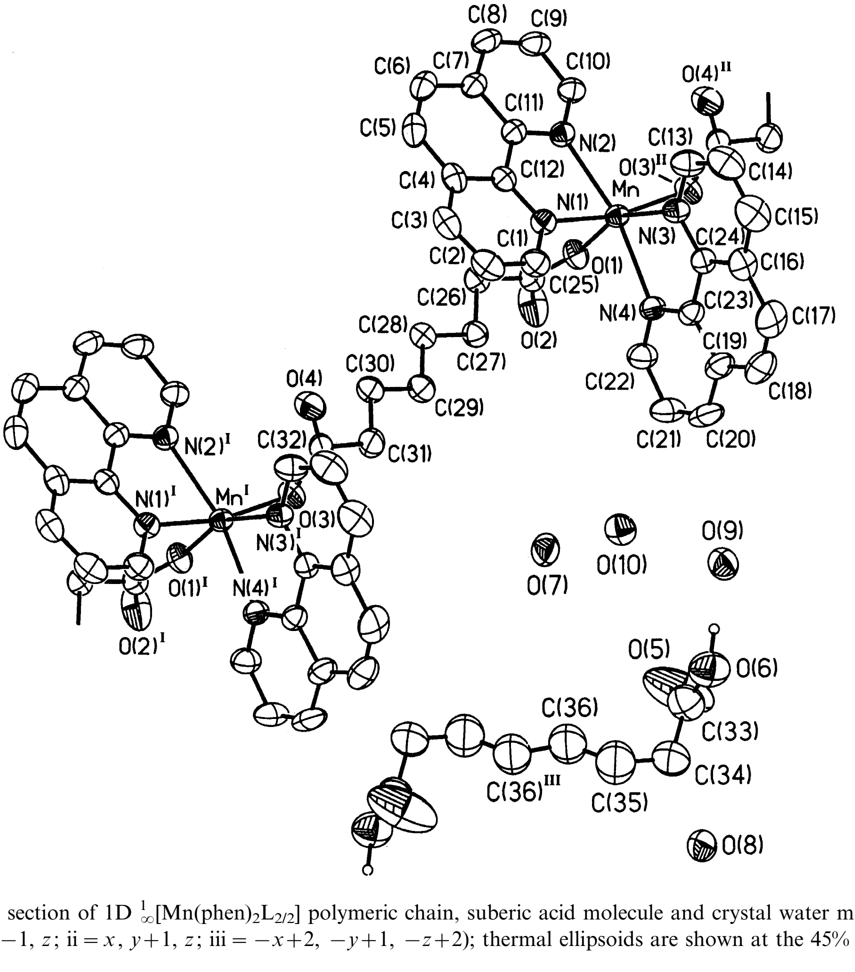

Fig. 1. ORTEP drawing of a section of 1D $^1_\infty[Mn(phen)_2L_{2/2}]$ polymeric chain, suberic acid molecule and crystal water molecules in **1** with atomic numbering scheme ($i = x, y-1, z$; $ii = x, y+1, z$; $iii = -x+2, -y+1, -z+2$); thermal ellipsoids are shown at the 45% probability level.

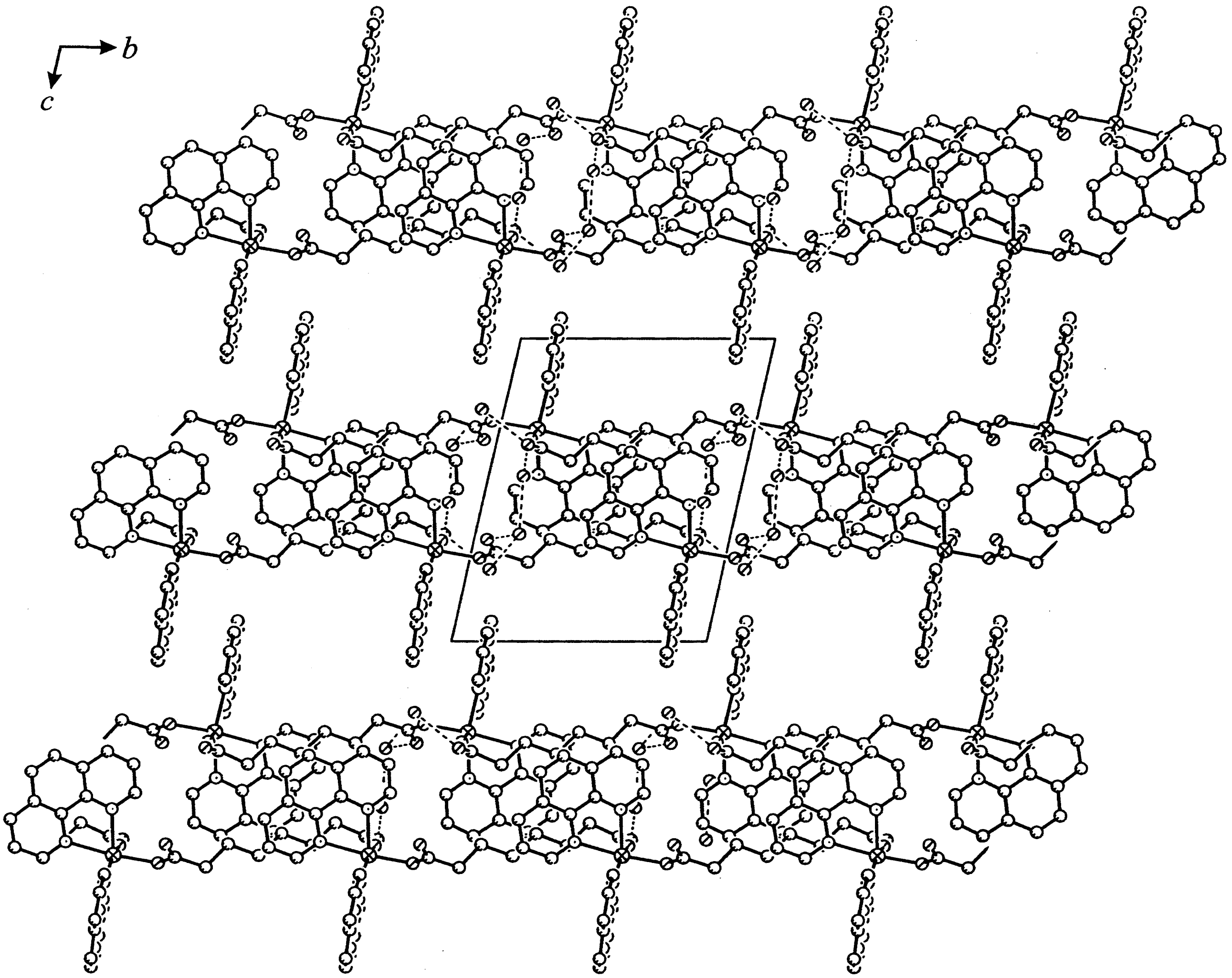

Fig. 2. 2D open supramolecular layer in **1** projected down to (1 0 0) (the twisted suberic acid molecules are omitted for clarity).

tions. With the help of such interactions, the polymeric chains are assembled to form supramolecular bi-chains with the phen ligands containing N(3) and N(4) atoms on both sides and orientated perpendicular to the bi-chains (Fig. 2). Interdigitation of the pendent phen ligands based on significant interchain π–π stacking interactions (mean interplanar distance: 3.44 Å) leads to 2D open layers parallel to (1 0 0) (Fig. 2). Through the extensive hydrogen bonds (Table 2), the lattice $H_2O$ molecules function as connectors between the open layers, forming a 3D framework with tunnels propagating along the [1 0 0] direction, and the twisted suberic molecules with $\bar{1}$ symmetry are located inside them and hydrogen bonded to the lattice water molecules.

### 2.3. Structure of $\{[Mn(phen)(H_2O)_3]_2L\}L\cdot 2H_2L\cdot 4H_2O$ (**2**)

Complex **2** is built up of centrosymmetric dinuclear $\{[Mn(phen)(H_2O)_3]_2L\}^{2+}$ complex cations, suberate anions, suberic acid molecules and lattice $H_2O$ molecules. The complex cation centered at the crystallographic 1*b* position results from two $[Mn(phen)(H_2O)_3]^{2+}$ moieties bridged by the bis-monodentate suberato ligand, which is so twisted that the fragmental alkyl chain consisting of the middle six carbon atoms nearly lying in a plane is sandwiched between two antiparallel phen ligands (Fig. 3). The mean interplanar distance between the alkyl carbon plane and the chelating phen plane is 3.73 Å, indicating weak C–H···π interactions. The Mn atoms are each in a distorted octahedral environment defined by two N atoms of one chelating phen ligand and four O atoms of three aqua ligands and one suberato group. The Mn–O bond distances fall within the range 2.117–2.165 Å and the Mn–N bond lengths are averaged to 2.288 Å (Table 3). The linear and twisted suberic acid molecules are centered at the crystallographic 1*d* and 1*f* sites, respectively, and they are hydrogen bonded to aqua ligands (O(12), O(13a) and O(13b)) to generate chains extending along the [0 1 1] direction. The resulting chains are further connected through hydrogen bonds to the

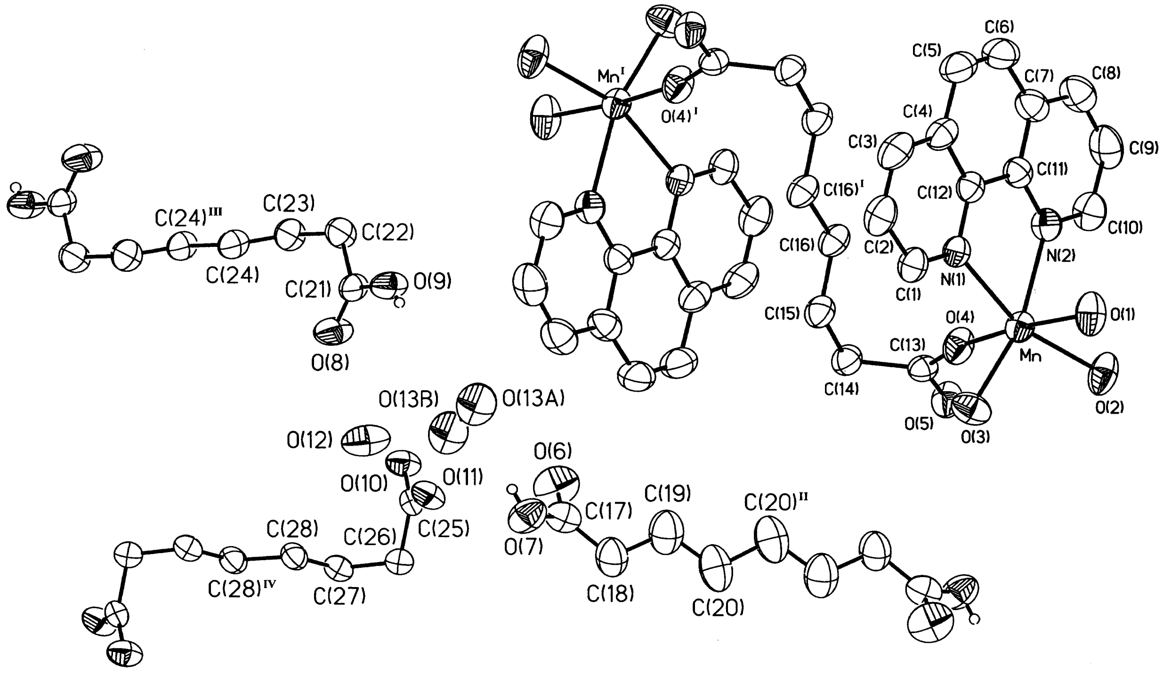

Fig. 3. ORTEP drawing of a centrosymmetric dinuclear $\{[Mn(phen)(H_2O)_3]_2L\}^{2+}$ complex cation, suberate anion, suberic acid molecules and crystal water molecules in **2** with atomic numbering scheme (i = $-x$, $-y+2$, $-z+1$; ii = $-x+1$, $-y+2$, $-z+2$; iii = $-x+1$, $-y$, $-z+1$; iv = $-x$, $-y$, $-z+2$); thermal ellipsoids are shown at the 45% probability level.

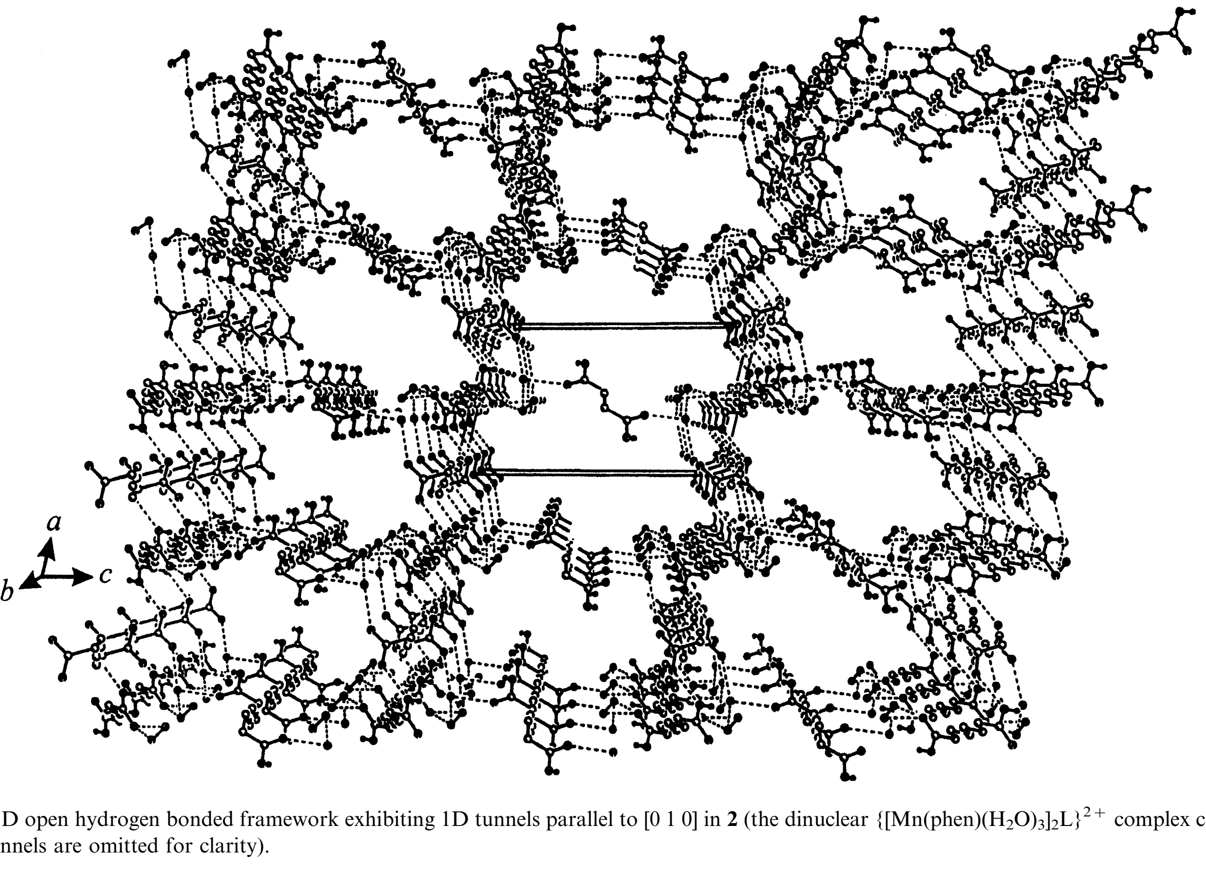

Fig. 4. 3D open hydrogen bonded framework exhibiting 1D tunnels parallel to [0 1 0] in **2** (the dinuclear $\{[Mn(phen)(H_2O)_3]_2L\}^{2+}$ complex cations in the tunnels are omitted for clarity).

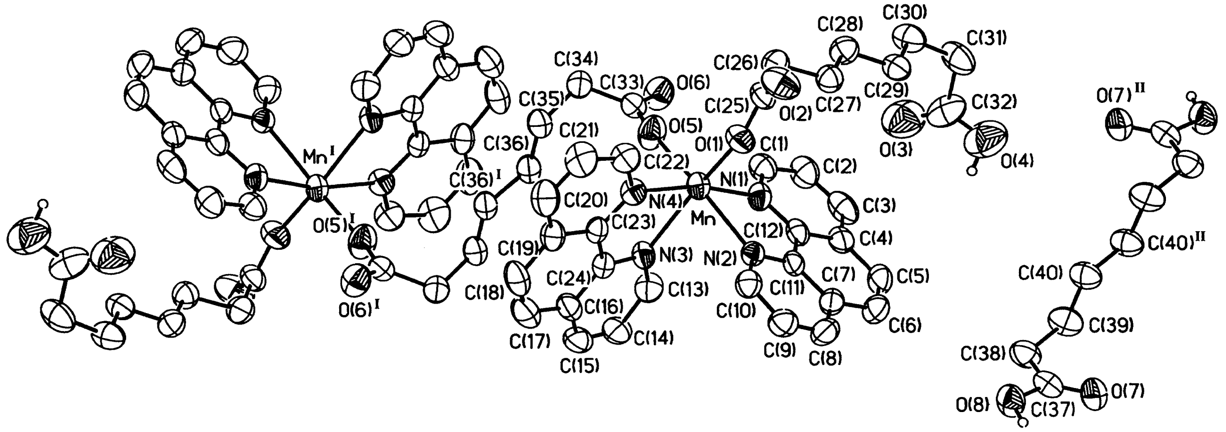

Fig. 5. ORTEP drawing of a centrosymmetric dinuclear {[Mn(phen)$_2$(HL)]$_2$L} complex molecule and suberic acid molecule in **3** with atomic numbering scheme (i = $-x+1$, $-y+2$, $-z+2$; ii = $-x+1$, $-y+1$, $-z$); thermal ellipsoids are shown at the 45% probability level.

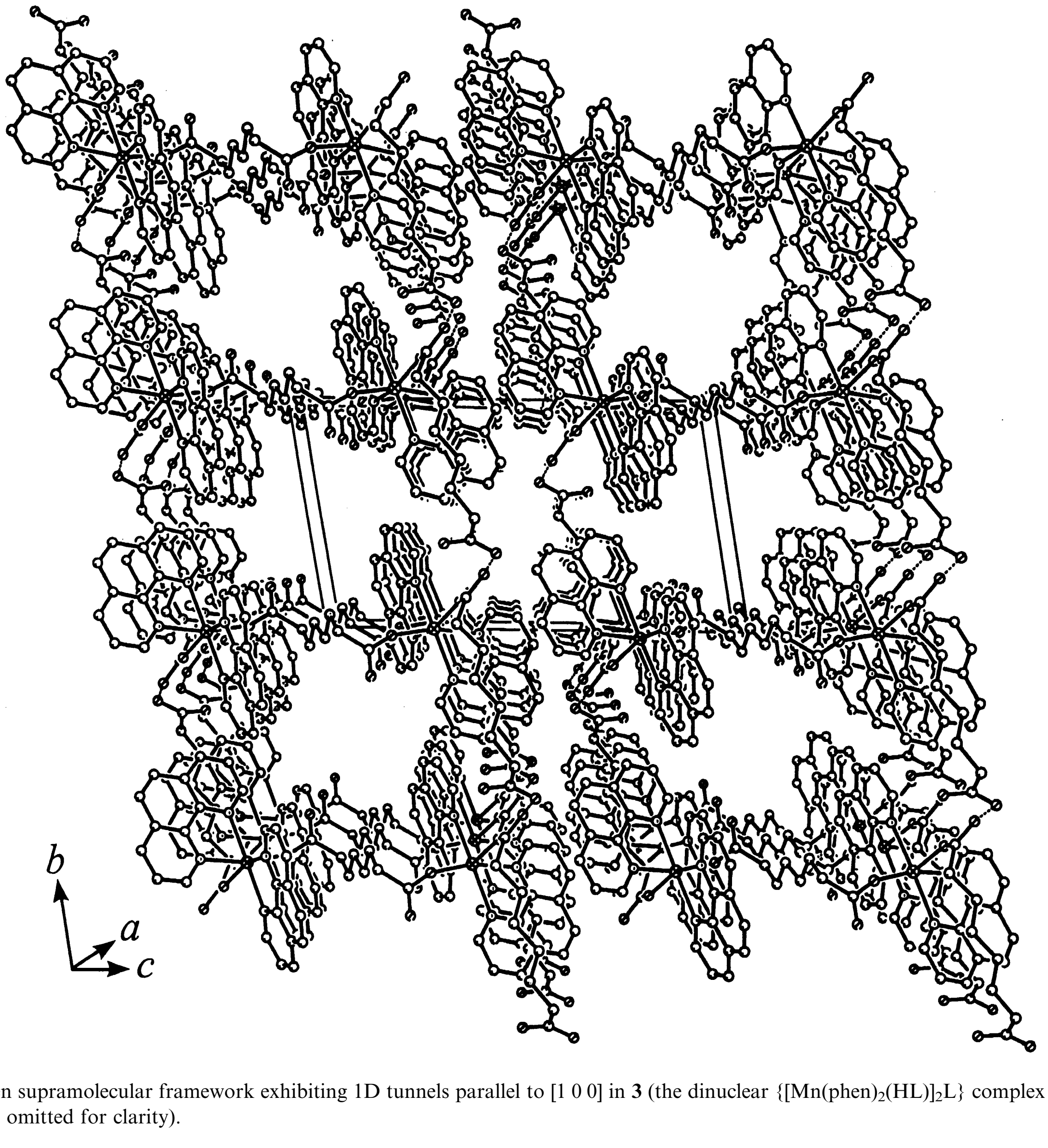

Fig. 6. 3D open supramolecular framework exhibiting 1D tunnels parallel to [1 0 0] in **3** (the dinuclear {[Mn(phen)$_2$(HL)]$_2$L} complex molecules in the tunnels are omitted for clarity).

Table 1
Summary of crystal data, data collection, structure solution and refinement details for **1**, **2** and **3**

| | **1** | **2** | **3** |
|---|---|---|---|
| Empirical formula | $C_{72}H_{86}Mn_2N_8O_{20}$ | $C_{56}H_{88}Mn_2N_4O_{26}$ | $C_{80}H_{84}Mn_2N_8O_{16}$ |
| Formula weight | 1493.37 | 1343.18 | 1523.44 |
| Description | yellow block | yellow block | Yellow block |
| Crystal size (mm) | 0.43 × 0.36 × 0.33 | 0.47 × 0.33 × 0.31 | 0.33 × 0.29 × 0.13 |
| Temperature (K) | 293(2) | 293(2) | 293(2) |
| Crystal system | triclinic | triclinic | triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| Unit cell dimensions | | | |
| $a$ (Å) | 10.577(2) | 9.697(2) | 10.036(3) |
| $b$ (Å) | 12.689(2) | 10.425(2) | 10.055(2) |
| $c$ (Å) | 15.896(3) | 17.147(3) | 18.737(6) |
| $\alpha$ (°) | 93.86(1) | 80.78(3) | 99.55(2) |
| $\beta$ (°) | 109.26(1) | 75.96(3) | 93.68(2) |
| $\gamma$ (°) | 111.58(1) | 84.56(3) | 97.55(1) |
| $V$ (Å$^3$) | 1829.1(6) | 1657.1(6) | 1841.3(9) |
| $Z$ | 1 | 1 | 1 |
| $D_{calc}$ (g cm$^{-3}$) | 1.356 | 1.346 | 1.374 |
| $F$(0 0 0) | 784 | 710 | 798 |
| Absorption coefficient (mm$^{-1}$) | 0.423 | 0.462 | 0.418 |
| Absorption correction | empirical | empirical | empirical |
| Transmission range | 0.694–0.906 | 0.680–0.706 | 0.753–0.831 |
| $\theta$ Range (°) | 1.39–27.50 | 1.24–27.50 | 1.11–27.49 |
| Refinement method | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ |
| Reflections collected | 9689 | 8982 | 9891 |
| Unique reflections ($R_{int}$) | 8335 (0.0452) | 7626 (0.0372) | 8441 (0.0561) |
| Data | 6037 | 4109 | 2996 |
| Parameters/restraints | 501/0 | 406/0 | 481/0 |
| Goodness-of-fit on $F^2$ | 1.044 | 1.020 | 1.213 |
| $R_1$, $wR_2$ [$I \geq 2\sigma(I)$] [a] | 0.0576, 0.1447 | 0.0507, 0.1186 | 0.0631, 0.1173 |
| $R_1$, $wR_2$ (all data) [a] | 0.0867, 0.1640 | 0.1096, 0.1554 | 0.1784, 0.2101 |
| Extinction coefficient | 0.0011(1) | 0.009(2) | 0.0051(7) |
| $\delta\rho_{max}$, $\delta\rho_{min}$ (e Å$^{-3}$) | 0.543, −0.541 | 0.499, −0.333 | 0.641, −0.527 |

[a] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

twisted suberate anions, which are centered at the crystallographic 1*a* positions, to form a 3D framework possessing tunnels running along the [0 1 0] direction (Fig. 4). The dinuclear complex cations fill the tunnels and are hydrogen bonded to the framework (Table 2). Unexpectedly, no π–π stacking interaction occurs in this complex.

### 2.4. Structure of {[Mn(phen)$_2$(HL)]$_2$L}·H$_2$L (**3**)

Similar to **1**, the Mn atoms in **3** are each in a distorted octahedral site surrounded by four N atoms from two chelating phen ligand and two O atoms from one bis-monodentate suberato group and one monodentate hydrogensuberato group, respectively. Two Mn atoms are bridged by one bis-monodentate suberato ligand to generate the dinuclear {[Mn(phen)$_2$(HL)]$_2$L} complex molecule (Fig. 5) centered at the crystallographic 1*d* position. The Mn–O bond distances are 2.053, 2.090 Å and the Mn–N bond distances vary from 2.275 to 2.322 Å (Table 4). The complex molecules exhibit two kinds of intramolecular C–H···π interactions, one of which occurs between the chelating phen ligand containing N(3) atom and the alkyl carbon plane defined by the middle six skeleton carbon atoms of the twisted suberato groups (interplanar distance: 3.74 Å), and the other takes place between the side phen ligand containing N(1) and the alkyl carbon plane defined by seven skeleton C atoms from C(25) to C(31) of the side hydrogensuberato (interplanar distance: 3.65 Å). Twisting of the bis-monodentate suberato ligand sandwiched between two crystallographically equivalent and antiparallel phen ligands may be ascribed to the requirement of weak intramolecular C–H···π interactions, while bending of the terminal carboxylic group from the rest of the hydrogen suberato ligand has to do with strong intermolecular O–H···O hydrogen bonds ($d$(O(4)–H···O(2)$^{iii}$) = 2.674 Å, Table 4). The dihedral angle of 77.2(1)° between both phen ligands within the complex molecule in the present compound is much smaller than the corresponding value in **1**.

The dinuclear {[Mn(phen)$_2$(HL)]$_2$L} complex molecules and the linear suberic acid molecules build up the crystal structure of **3**. Along the [0 1 0] direction, the

Table 2
Selected bond lengths (Å) and angles (°) for **1**

| | | | | | |
|---|---|---|---|---|---|
| Mn–O(1) | 2.120(2) | Mn–N(1) | 2.341(2) | Mn–N(3) | 2.327(2) |
| Mn–O(3)$^{ii}$ | 2.120(2) | Mn–N(2) | 2.267(2) | Mn–N(4) | 2.296(2) |
| O(1)–Mn–O(3)$^{ii}$ | 90.82(8) | O(3)$^{ii}$–Mn–N(1) | 165.58(8) | N(1)–Mn–N(3) | 83.09(8) |
| O(1)–Mn–N(1) | 100.62(8) | O(3)$^{ii}$–Mn–N(2) | 99.36(8) | N(1)–Mn–N(4) | 94.69(8) |
| O(1)–Mn–N(2) | 91.42(8) | O(3)$^{ii}$–Mn–N(3) | 89.66(8) | N(2)–Mn–N(3) | 110.49(8) |
| O(1)–Mn–N(3) | 157.70(8) | O(3)$^{ii}$–Mn–N(4) | 94.84(8) | N(2)–Mn–N(4) | 165.61(8) |
| O(1)–Mn–N(4) | 86.03(8) | N(1)–Mn–N(2) | 71.84(8) | N(3)–Mn–N(4) | 71.72(8) |

*Torsion angles* (°)

| | | | |
|---|---|---|---|
| C(25)–C(26)–C(27)–C(28) | 175.9(2) | C(29)–C(30)–C(31)–C(32) | −179.2(3) |
| C(26)–C(27)–C(28)–C(29) | −178.1(2) | C(33)–C(34)–C(35)–C(36) | 43(1) |
| C(27)–C(28)–C(29)–C(30) | 178.3(3) | C(34)–C(35)–C(36)–C(36)$^{iii}$ | 173.7(9) |
| C(28)–C(29)–C(30)–C(31) | −179.3(3) | C(35)–C(36)–C(36)$^{iii}$–C(35)$^{iii}$ | 180 |

*Hydrogen bonding contacts*

| D–H···A | D–H | H···A | D···A | D–H···A |
|---|---|---|---|---|
| O(6)–H(37)···O(9) | 1.08 | 1.55 | 2.585 | 159 |
| O(7)–H(38a)···O(4) | 0.82 | 1.99 | 2.795 | 170 |
| O(7)–H(38b)···O(8)$^{v}$ | 0.87 | 2.06 | 2.879 | 157 |
| O(8)–H(39a)···O(2)$^{vi}$ | 0.91 | 1.88 | 2.787 | 179 |
| O(8)–H(39b)···O(4)$^{ii}$ | 0.81 | 2.35 | 3.094 | 154 |
| O(9)–H(40a)···O(10) | 0.85 | 1.88 | 2.716 | 169 |
| O(9)–H(40b)···O(3)$^{vi}$ | 0.80 | 2.03 | 2.827 | 176 |
| O(10)–H(41a)···O(2)$^{vii}$ | 0.79 | 1.91 | 2.694 | 171 |
| O(10)–H(41b)···O(7) | 0.82 | 1.99 | 2.768 | 159 |

Symmetry codes: i = $x, y-1, z$; ii = $x, y+1, z$; iii = $-x+2, -y+1, -z+2$; iv = $-x+2, -y+2, -z+2$; v = $-x+1, -y+1, -z+1$; vi = $x-1, y, z$; vii = $x-1, y-1, z$.

complex molecules are interconnected by intermolecular hydrogen bonds to form ladder-like ribbons, which are further assembled via intermolecular $\pi$–$\pi$ stacking interactions between the side phen ligands (mean interplanar distance: 3.40 Å) into 2D open layers parallel to (1 0 0). Through the weak interlayer C–H···O hydrogen bonds (Table 4), the resulting open layers are stacked to generate a 3D framework with tunnels extending along [1 0 0] direction (Fig. 6). The linear suberic acid molecules in the tunnels are centered at the crystallographic 1*e* positions and hydrogen bonded to the framework via both strong O–H···O and weak C–H···O hydrogen bonds (Table 4).

From the above structure description, we can deduce that the characteristic building blocks are the $^1_\infty$[Mn(phen)$_2$L$_{2/2}$] polymeric chains, divalent dinuclear {[Mn(phen)(H$_2$O)$_3$]$_2$L}$^{2+}$ complex cations and neutral dinuclear {[Mn(phen)$_2$(HL)]$_2$L} complex molecules in **1**, **2** and **3**, respectively. Within them, the suberate groups serve as bis-monodentate bridging ligands, which are twisted due to C–H···$\pi$ interactions between the alkyl skeleton carbon atoms and the chelating phen ligands. The structural motifs in these complexes can be derived from the dinuclear {[Mn(phen)$_2$L]$_2$L}$^{2-}$ anions or from the dinuclear {[Mn(phen)$_2$(H$_2$O)]$_2$L}$^{2+}$ cations existing in {[Mn(phen)$_2$(H$_2$O)]$_2$L}{[Mn(phen)$_2$L]$_2$L}·4H$_2$O reported by Casey et al. [27]. For example, either condensation of the {[Mn(phen)$_2$L]$_2$L}$^{2-}$ anions through the pendent monodentate suberato groups or replacement of the aqua ligands in the {[Mn(phen)$_2$(H$_2$O)]$_2$L}$^{2+}$ cations by bis-monodentate suberato ligands can generate the $^1_\infty$[Mn(phen)$_2$L$_{2/2}$] polymeric chains in **1**. Replacement of one chelating phen ligand at each end of the {[Mn(phen)$_2$(H$_2$O)]$_2$L}$^{2+}$ cation by two small H$_2$O molecules gives the corresponding dinuclear {[Mn(phen)(H$_2$O)$_3$]$_2$L}$^{2+}$ complex cations in **2**. On the other hand, substitution of monodentate hydrogensuberato (HL) groups for the monodentate suberato groups and the aqua ligands in the {[Mn(phen)$_2$L]$_2$L}$^{2-}$ anions and the {[Mn(phen)$_2$(H$_2$O)]$_2$L}$^{2+}$ cations, respectively, leads to formation of dinuclear {[Mn(phen)$_2$(HL)]$_2$L} complex molecules in **3**.

## 3. Experimental

All chemicals of p.a. grade were commercially available and used without further purification. The C, H and N microanalyses were performed with a Heraeus Rapid-CHNO elemental analyzer. The FT-IR spectra

Table 3
Selected bond lengths (Å) and angles (°) for **2**

| | | | | | |
|---|---|---|---|---|---|
| Mn–O(1) | 2.165(2) | Mn–O(3) | 2.157(3) | Mn–N(1) | 2.291(3) |
| Mn–O(2) | 2.135(2) | Mn–O(4) | 2.117(2) | Mn–N(2) | 2.284(3) |
| O(1)–Mn–O(2) | 84.3(1) | O(2)–Mn–O(3) | 102.1(1) | O(3)–Mn–N(1) | 92.2(1) |
| O(1)–Mn–O(3) | 92.2(1) | O(2)–Mn–O(4) | 89.7(1) | O(3)–Mn–N(2) | 164.0(1) |
| O(1)–Mn–O(4) | 173.9(1) | O(2)–Mn–N(1) | 161.7(1) | O(4)–Mn–N(1) | 102.4(1) |
| O(1)–Mn–N(1) | 83.7(1) | O(2)–Mn–N(2) | 93.9(1) | O(4)–Mn–N(2) | 90.5(1) |
| O(1)–Mn–N(2) | 90.7(1) | O(3)–Mn–O(4) | 88.3(1) | N(1)–Mn–N(2) | 72.5(1) |

*Torsion angles* (°)

| | | | |
|---|---|---|---|
| C(13)–C(14)–C(15)–C(16) | 71.5(4) | C(21)–C(22)–C(23)–C(24) | 67.1(5) |
| C(14)–C(15)–C(16)–C(16)$^{\mathrm{I}}$ | 175.9(3) | C(22)–C(23)–C(24)–C(24)$^{\mathrm{iii}}$ | 179.7(4) |
| C(15)–C(16)–C(16)$^{\mathrm{i}}$–C(15)$^{\mathrm{i}}$ | 180.00 | C(23)–C(24)–C(24)$^{\mathrm{iii}}$–C(23)$^{\mathrm{iii}}$ | 180 |
| C(17)–C(18)–C(19)–C(20) | 176.0(5) | C(25)–C(26)–C(27)–C(28) | −60.8(5) |
| C(18)–C(19)–C(20)–C(20)$^{\mathrm{ii}}$ | −175.0(6) | C(26)–C(27)–C(28)–C(28)$^{\mathrm{iv}}$ | 177.4(4) |
| C(19)–C(20)–C(20)$^{\mathrm{ii}}$–C(19)$^{\mathrm{ii}}$ | 180 | C(27)–C(28)–C(28)$^{\mathrm{iv}}$–C(27)$^{\mathrm{iv}}$ | 180 |

*Hydrogen bonding contacts*

| D–H···A | D–H | H···A | D···A | D–H···A |
|---|---|---|---|---|
| O(1)–H(29a)···O(6)$^{\mathrm{v}}$ | 0.88 | 1.88 | 2.735 | 163 |
| O(1)–H(29b)···O(11) | 0.89 | 1.79 | 2.664 | 168 |
| O(2)–H(30a)···O(9) | 0.81 | 1.96 | 2.748 | 166 |
| O(2)–H(30b)···O(10) | 0.94 | 1.71 | 2.634 | 169 |
| O(3)–H(31a)···O(5)$^{\mathrm{vi}}$ | 0.78 | 1.99 | 2.772 | 175 |
| O(3)–H(31b)···O(13a)$^{\mathrm{v}}$ | 0.93 | 1.78 | 2.634 | 152 |
| O(3)–H(31b)···O(13b)$^{\mathrm{v}}$ | 0.93 | 1.85 | 2.734 | 159 |
| O(12)–H(32a)···O(10) | 0.91 | 1.87 | 2.771 | 170 |
| O(12)–H(32b)···O(8) | 0.95 | 1.85 | 2.733 | 155 |
| O(13a)–H(33a)···O(6) | 0.87 | 1.85 | 2.717 | 177 |
| O(13a)–H(33b)···O(8) | 0.88 | 2.09 | 2.967 | 177 |
| O(13b)–H(34a)···O(12) | 0.88 | 1.77 | 2.653 | 178 |
| O(13b)–H(34b)···O(6) | 0.89 | 2.01 | 2.903 | 176 |
| O(7)–H(35)···O(11)$^{\mathrm{vii}}$ | 0.88 | 1.63 | 2.510 | 179 |
| O(9)–H(36)···O(5) | 0.87 | 1.60 | 2.477 | 179 |

Symmetry codes: i = $-x, -y+2, -z+1$; ii = $-x+1, -y+2, -z+2$; iii = $-x+1, -y, -z+1$; iv = $-x, -y, -z+2$; v = $x-1, y, z$; vi = $-x, -y+1, -z+1$; vii = $-x, -y+1, -z+2$.

were recorded from KBr pellets in the range 4000–400 cm$^{-1}$ on a Shimadzu FT-IR-8900 spectrometer.

### 3.1. Preparation of $\{[Mn(phen)_2]L_{2/2}\}_2\cdot H_2L\cdot 8H_2O$ (1)

Freshly precipitated $Mn(OH)_{2-2x}(CO_3)_x\cdot yH_2O$, which was obtained from dropwise addition of 3.0 ml $Na_2CO_3$ (1 M) to an aqueous solution of 0.11 g (0.66 mmol) $MnSO_4\cdot H_2O$ in 5.0 ml $H_2O$, followed by separation by centrifugation and washed with distilled water for several times until no detectable $SO_4^{2-}$ anions, was added to a stirred aqueous solution of 0.12 g (0.66 mmol) suberic acid in 10 ml $H_2O$. To the resulting mixture was added ethanolic solution of 0.13 g (0.66 mmol) phenanthroline monohydrate in 10 ml $CH_3CH_2OH$. The formed yellow solution was maintained at room temperature for several days and yellow precipitate deposited. After filtration, the yellow precipitate was re-dissolved in 20-ml ethanol. Slow evaporation afforded a mixture consisting of yellow bulky crystals and plate-like crystals. X-ray analyses indicated the former bulky crystals to be the known $\{[Mn(phen)_2(H_2O)]_2L\}\{[Mn(phen)_2L]_2L\}\cdot 4H_2O$ [27] and the latter to be a new complex $\{[Mn(phen)_2]L_{2/2}\}_2\cdot H_2L\cdot 8H_2O$ (**1**) as minor product, which was collected by handpicking for the pertinent characterizations. *Anal.* Calc. for $\{[Mn(phen)_2]L_{2/2}\}_2\cdot H_2L\cdot 8H_2O$ (**1**) (%): C, 57.91; H, 5.81; N, 7.50. Found: C, 57.63; H, 5.94; N, 7.82. IR (cm$^{-1}$): 3385m, 3249m, 3055w, 2939s (sharp), 2924m, 2847w, 1717m, 1645m, 1622w, 1556vs, 1516vs (sharp), 1495w, 1423vs (sharp), 1408s (shoulder), 1342m, 1315w, 1292vw, 1223m, 1190w, 1101m, 851vs (sharp), 777w, 731vs (doublet), 664vw, 627vw, 424m (sharp).

### 3.2. Preparation of $\{[Mn(phen)(H_2O)_3]_2L\}L\cdot 2H_2L\cdot 4H_2O$ (2) and $\{[Mn(phen)_2(H\text{-}L)]_2L\}\cdot H_2L$ (3)

An aqueous solution of 0.44 g (2.50 mmol) suberic acid in 20 ml $H_2O$ was mixed with a methanolic solution of 0.50 g (2.50 mmol) phenanthroline monohydrate in 20 ml $CH_3OH$. To this stirred mixture was added the freshly precipitated $Mn(OH)_{2-2x}(CO_3)_x\cdot yH_2O$ from

Table 4
Selected bond lengths (Å) and angles (°) for **3**

| | | | | | |
|---|---|---|---|---|---|
| Mn–O(1) | 2.090(4) | Mn–N(1) | 2.286(4) | Mn–N(3) | 2.322(4) |
| Mn–O(5) | 2.053(4) | Mn–N(2) | 2.304(4) | Mn–N(4) | 2.275(4) |
| O(1)–Mn–O(5) | 101.7(2) | O(5)–Mn–N(1) | 96.2(2) | N(1)–Mn–N(3) | 97.4(1) |
| O(1)–Mn–N(1) | 101.4(1) | O(5)–Mn–N(2) | 166.3(2) | N(1)–Mn–N(4) | 168.9(2) |
| O(1)–Mn–N(2) | 88.5(1) | O(5)–Mn–N(3) | 94.2(2) | N(2)–Mn–N(3) | 79.9(1) |
| O(1)–Mn–N(3) | 153.8(1) | O(5)–Mn–N(4) | 89.0(2) | N(2)–Mn–N(4) | 100.8(2) |
| O(1)–Mn–N(4) | 87.2(2) | N(1)–Mn–N(2) | 72.6(2) | N(3)–Mn–N(4) | 72.3(2) |
| *Torsion angles* (°) | | | | | |
| C(25)–C(26)–C(27)–C(28) | 176.4(5) | C(34)–C(35)–C(36)–C(36)$^{i}$ | −174.6(6) | | |
| C(26)–C(27)–C(28)–C(29) | −176.5(4) | C(35)–C(36)–C(36)$^{i}$–C(35)$^{i}$ | 180 | | |
| C(27)–C(28)–C(29)–C(30) | 179.6(5) | C(37)–C(38)–C(39)–C(40) | −70.0(6) | | |
| C(28)–C(29)–C(30)–C(31) | −174.4(5) | C(38)–C(39)–C(40)–C(40)$^{ii}$ | 179.2(6) | | |
| C(29)–C(30)–C(31)–C(32) | 75.2(7) | C(39)–C(40)–C(40)$^{ii}$–C(39)$^{ii}$ | 180 | | |
| C(33)–C(34)–C(35)–C(36) | −63.6(6) | | | | |

Hydrogen bonding contacts

| D–H···A | D–H | H···A | D···A | D–H···A |
|---|---|---|---|---|
| O(4)–H(41)···O(2)$^{iii}$ | 0.79 | 1.90 | 2.674 | 166 |
| O(8)–H(42)···O(6)$^{iv}$ | 0.84 | 1.75 | 2.584 | 170 |
| C(14)–H(14)···O(7)$^{v}$ | 0.93 | 2.44 | 3.230 | 145 |
| C(15)–H(15)···O(6)$^{vi}$ | 0.93 | 2.53 | 3.403 | 155 |
| C(15)–H(15)···O(6)$^{vii}$ | 0.93 | 2.50 | 3.350 | 152 |

Symmetry codes: i = $-x+1, -y+2, -z+2$; ii = $-x+1, -y+1, -z$; iii = $x, y+1, z$; iv = $x-1, y-1, z-1$; v = $x, y+1, z+1$; vi = $x-1, y, z$; vii = $x, y, z+1$.

dropwise addition of 4.0 ml $Na_2CO_3$ (1 M) to an aqueous solution of 0.43 g (2.50 mmol) $MnSO_4 \cdot H_2O$ in 5.0 ml $H_2O$, followed by separation by centrifugation and washed with distilled water for several times until no detectable $SO_4^{2-}$ anions. The greenish yellow suspension formed was adjusted to pH 4.8 by adding powdered suberic acid. The insoluble solid was filtered out and the orange filtrate was allowed to stand at room temperature. Pale yellow elongated bulky crystals of $\{[Mn(phen)(H_2O)_3]_2L\}L \cdot 2H_2L \cdot 4H_2O$ (**2**) (max. size: 5 × 3 × 1 mm; total amount: ca. 0.15 g) grew by slow evaporation for several weeks. After filtration, further evaporation at room temperature for several days gave two well shaped yellow crystals of $\{[Mn(phen)_2(HL)]_2L\} \cdot H_2L$ (**3**) (size: ca. 4 × 3 × 2 and 2.5 × 2 × 1 mm). *Anal.* Calc. for $\{[Mn(phen)(H_2O)_3]_2L\}L \cdot 2H_2L \cdot 4H_2O$ (**2**) (%): C, 50.08; H, 6.60; N, 4.17. Found: C, 50.25; H, 6.35; N, 4.39. IR ($cm^{-1}$): 3435s 3117s (broad), 2937s (sharp), 2856s (sharp), 1703vs, 1558vs, 1516s, 1497vw, 1423vs (sharp), 1344vw, 1308s, 1178w, 1128w, 1101w, 1057vw, 997w, 949vw, 922w, 854s (sharp), 781w, 725s (doublet), 625w, 548vw, 421w. *Anal.* Calc. for $\{[Mn(phen)_2(HL)]_2L\} \cdot H_2L$ (**3**) (%): C, 63.07; H, 5.56; N, 7.36. Found: C, 62.82; H, 5.49; N, 7.62. IR ($cm^{-1}$): 2918s (sharp), 2855m (sharp), 1709s (sharp), 1553vs (broad), 1514vs (sharp), 1493vw, 1415s (doublet), 1344s (sharp), 1229s, 1124w, 1099w, 853s (sharp), 730s (doublet), 635w (sharp).

### 3.3. *Crystal structure determination*

The reflection intensities of **1**, **2** and **3** were collected at 293 K on a Bruker P4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using the θ–2θ scan technique. SHELXS-97 [36] and SHELXL-97 [37] programs were used for structure determination and refinements. The structures were solved with direct methods and refined with full-matrix least-squares techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms associated with carbon atoms were generated geometrically, while the aqua and hydroxyl hydrogen atoms were located from the difference Fourier syntheses. Details of crystal data, collection and refinement of the three complexes are summarized in Table 1 and selected interatomic distances and bond angles in Tables 2–4.

## 4. Supplementary data

Supplementary data for the two structures are deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 199559–199561. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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