

Cationic, neutral and anionic metal(II) complexes derived from 4-oxo-4*H*-pyran-2,6-dicarboxylic acid (chelidonic acid)

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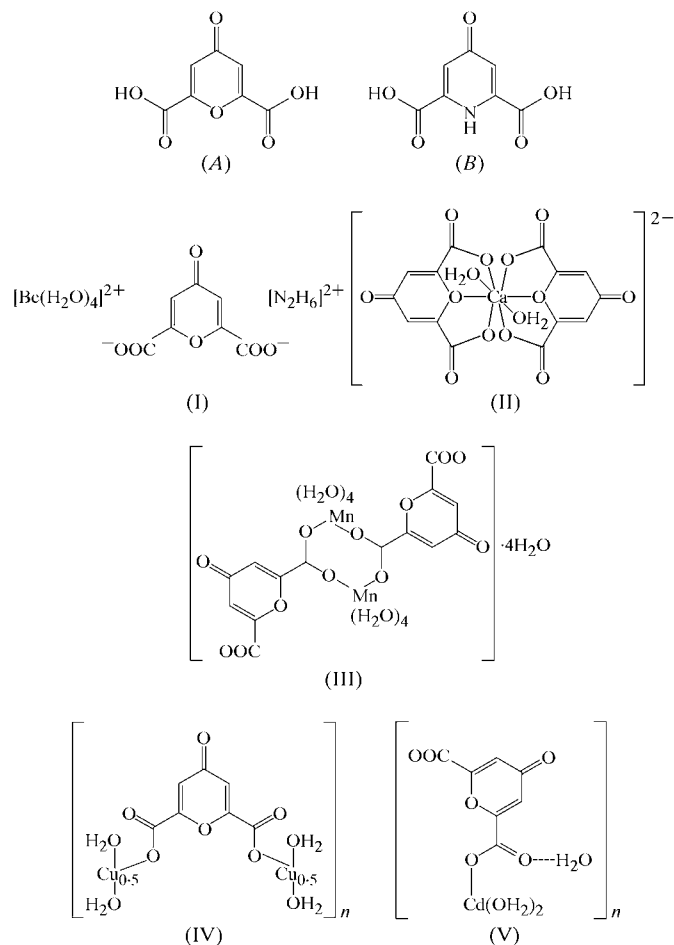
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The structures of five metal complexes containing the 4-oxo-4*H*-pyran-2,6-dicarboxylate dianion illustrate the remarkable coordinating versatility of this ligand and the great structural diversity of its complexes. In tetraaquaberyllium 4-oxo-4*H*-pyran-2,6-dicarboxylate, $[\text{Be}(\text{H}_2\text{O})_4](\text{C}_7\text{H}_2\text{O}_6)$, (I), the ions are linked by eight independent O—H...O hydrogen bonds to form a three-dimensional hydrogen-bonded framework structure. Each of the ions in hydrazinium(2+) diaqua(4-oxo-4*H*-pyran-2,6-dicarboxylato)calcate, $(\text{N}_2\text{H}_6)[\text{Ca}(\text{C}_7\text{H}_2\text{O}_6)_2(\text{H}_2\text{O})_2]$, (II), lies on a twofold rotation axis in the space group *P2/c*; the anions form hydrogen-bonded sheets which are linked into a three-dimensional framework by the cations. In bis(μ -4-oxo-4*H*-pyran-2,6-dicarboxylato)bis[tetraaquamanganese(II)] tetrahydrate, $[\text{Mn}_2(\text{C}_7\text{H}_2\text{O}_6)_2(\text{H}_2\text{O})_8] \cdot 4\text{H}_2\text{O}$, (III), the metal ions and the organic ligands form a cyclic centrosymmetric $\text{Mn}_2(\text{C}_7\text{H}_2\text{O}_6)_2$ unit, and these units are linked into a complex three-dimensional framework structure containing 12 independent O—H...O hydrogen bonds. There are two independent Cu^{II} ions in tetraaqua(4-oxo-4*H*-pyran-2,6-dicarboxylato)copper(II), $[\text{Cu}(\text{C}_7\text{H}_2\text{O}_6)(\text{H}_2\text{O})_4]$, (IV), and both lie on centres of inversion in the space group *P1*; the metal ions and the organic ligands form a one-dimensional coordination polymer, and the polymer chains are linked into a three-dimensional framework containing eight independent O—H...O hydrogen bonds. Diaqua(4-oxo-4*H*-pyran-2,6-dicarboxylato)cadmium monohydrate, $[\text{Cd}(\text{C}_7\text{H}_2\text{O}_6)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, (V), forms a three-dimensional coordination polymer in which the organic ligand is coordinated to four different Cd sites, and this polymer is interwoven with a complex three-dimensional framework built from O—H...O hydrogen bonds.

Comment

4-Oxo-4*H*-pyran-2,6-dicarboxylic acid (chelidonic acid), (A), is one of the constituents of the greater celandine *Chelidonium majus*, which exhibits a wide range of therapeutic



properties (Chevallier, 1996). It is also an inhibitor of dihydrodipicolinate synthase, a key enzyme in the biosynthesis of lysine *via* the diaminopimelate pathway (Borthwick *et al.*, 1995). A $\text{p}K_a$ value of about 2.4 for both carboxyl groups (Miyamoto & Brochmann-Hanssen, 1962) makes it a very effective chelating agent at physiological pH. However, while a number of metal complexes formed by the closely related

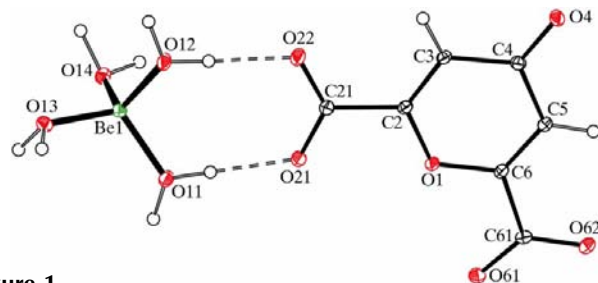


Figure 1

The independent ionic components of compound (I), showing the atom-numbering scheme and the two hydrogen bonds (dashed lines) within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

4-oxo-1,4-dihydropyridine-2,6-dicarboxylic acid (chelidamic acid), (*B*), have been structurally characterized (Devereux *et al.*, 2002; Burnett *et al.*, 2003; Zhou *et al.*, 2004; Cui *et al.*, 2006; Gao *et al.*, 2006), very few complexes derived from 4-oxo-4*H*-pyran-2,6-dicarboxylic acid have been structurally characterized. In pentaqua(4-oxo-4*H*-pyran-2,6-dicarboxylato)copper(II) monohydrate, the organic ligand is coordinated to the Cu atom *via* the ketonic O atom only and the coordination polyhedron around copper is completed by five water ligands. The carboxylate groups do not coordinate to copper, but participate in a complex hydrogen-bonding scheme which generates a three-dimensional framework structure (Manojlović-Muir *et al.*, 1999). In the dicyclohexylammonium salt of tributyl(4-oxo-4*H*-pyran-2,6-dicarboxylato)stannate(IV), the 4-oxo-4*H*-pyran-2,6-dicarboxylate dianion acts as a bridging ligand, *via* two different carboxylate groups, between planar tributyltin(IV) units, so forming a chain polymer (Ng *et al.*, 2000).

With this in mind, we report here the molecular and supramolecular structures of five metal complexes derived from 4-oxo-4*H*-pyran-2,6-dicarboxylic acid, namely tetraaquaberyllium 4-oxo-4*H*-pyran-2,6-dicarboxylate, (I), hydrazinium(2+) diaqua(4-oxo-4*H*-pyran-2,6-dicarboxylato)calcate, (II), tetraqua(4-oxo-4*H*-pyran-2,6-dicarboxylato)manganese(II) dihydrate, (III), tetraqua(4-oxo-4*H*-pyran-2,6-dicarboxylato)copper(II), (IV), and diaqua(4-oxo-4*H*-pyran-2,6-dicarboxylato)cadmium monohydrate, (V). Complexes (I), (III) and (V) were prepared straightforwardly by the reactions, in aqueous solution, of 4-oxo-4*H*-pyran-2,6-dicarboxylic acid with beryllium sulfate tetrahydrate, manganese(II) acetate and cadmium nitrate, respectively. Complex (IV) was similarly prepared using basic copper carbonate. Attempts to prepare the simple hydrazinium salt by a similar type of reaction consistently yielded only polycrystalline material

when conducted in doubly distilled water, but the same procedure in singly distilled water unexpectedly gave the anionic complex, (II), where the calcium component has presumably arisen from the water employed. Attempts to isolate crystals of this material from solutions containing hydrazine, calcium nitrate and 4-oxo-4*H*-pyran-2,6-dicarboxylic acid have been uniformly unsuccessful: polycrystalline samples of (II) have been readily obtained in this manner, in yields of around 65–70%, but no crystals suitable for single-crystal X-ray diffraction have been obtained by this route.

In each of compounds (I)–(V), the organic component is present in the dianionic form, $C_7H_2O_6^{2-}$. This entity occurs as

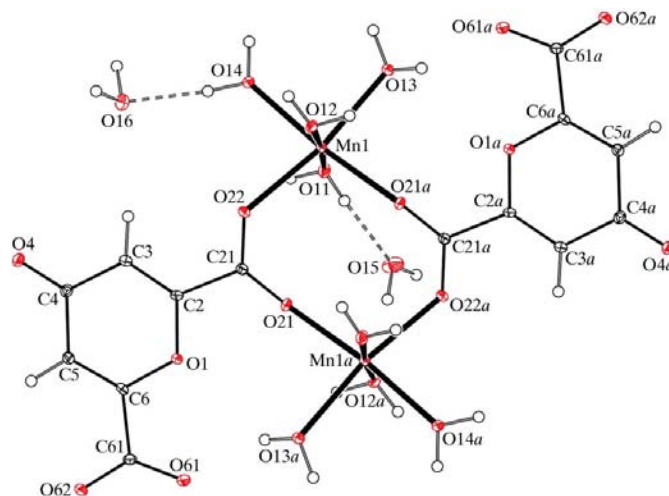


Figure 3

The dimeric aggregate in compound (III) and the two independent noncoordinated water molecules, showing the atom-labelling scheme and the hydrogen bonds (dashed lines) within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms labelled with the suffix *a* are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

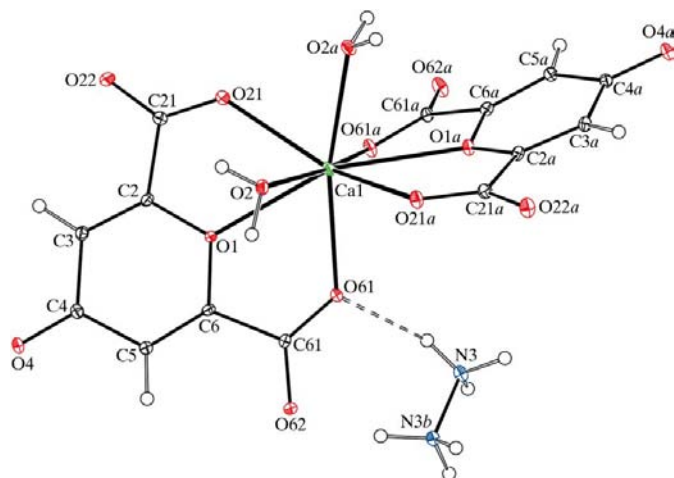


Figure 2

The independent ionic components of compound (II), showing the atom-labelling scheme and the hydrogen bond (dashed line) between the ions in the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms labelled with the suffixes *a* and *b* are at the symmetry positions $(1 - x, y, \frac{1}{2} - z)$ and $(-x, y, \frac{1}{2} - z)$, respectively.

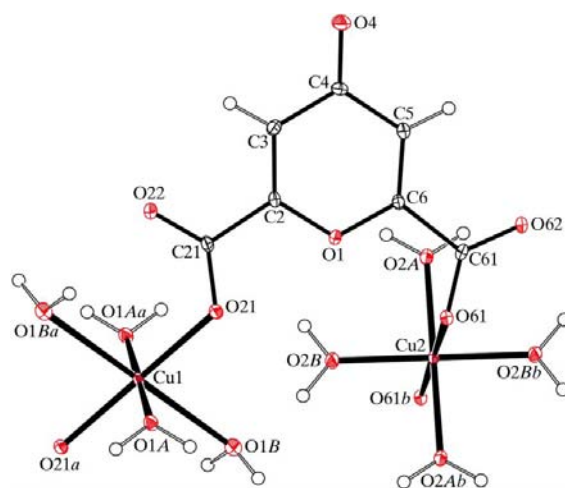


Figure 4

The independent components of compound (IV), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms labelled with the suffixes *a* and *b* are at the symmetry positions $(-x, -y, 1 - z)$ and $(1 - x, -y, -z)$, respectively.

isolated ions in compound (I), which is a hydrated salt in which the metal is present as a simple aqua ion, thus $[\text{Be}(\text{H}_2\text{O})_4]^{2+} \cdot \text{C}_7\text{H}_2\text{O}_6^{2-}$ (Fig. 1). In each of the coordination compounds (II)–(V), the 4-oxo-4*H*-pyran-2,6-dicarboxylate anion acts as a ligand towards the metal, and the coordination complexes are neutral in the cases of compounds (III)–(V) and anionic in compound (II). Compound (II) contains isolated mononuclear anions (Fig. 2), compound (III) contains isolated dimers which are neutral and centrosymmetric (Fig. 3), while both (IV) and (V) (Figs. 4 and 5) form coordination polymers, which are one-dimensional in the case of (IV) and three-dimensional in the case of (V). In all compounds, there is an extensive series of hydrogen bonds which link the metal-containing species. We note in particular here the contrast between the coordination polymer formed in the tetrahydrate, (IV), and the isolated mononuclear

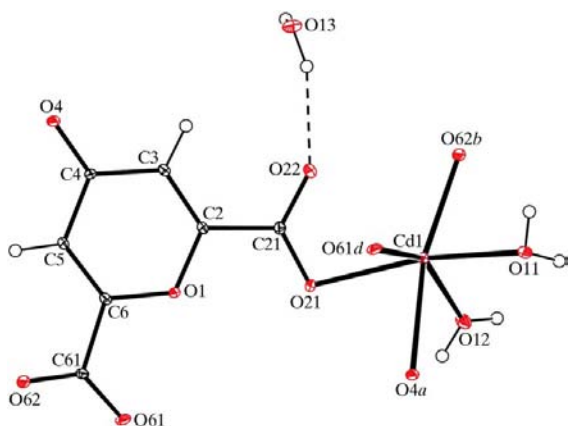


Figure 5
The independent components of compound (V), showing the atom-labelling scheme, the hydrogen bond (dashed line) within the selected asymmetric unit and the distorted octahedral coordination of the Cd atom. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms labelled with the suffixes *a*, *b* and *d* are at the symmetry positions $(-1 + x, y, -1 + z)$, $(-1 + x, 1 + y, z)$ and $(x, 1 + y, z)$, respectively.

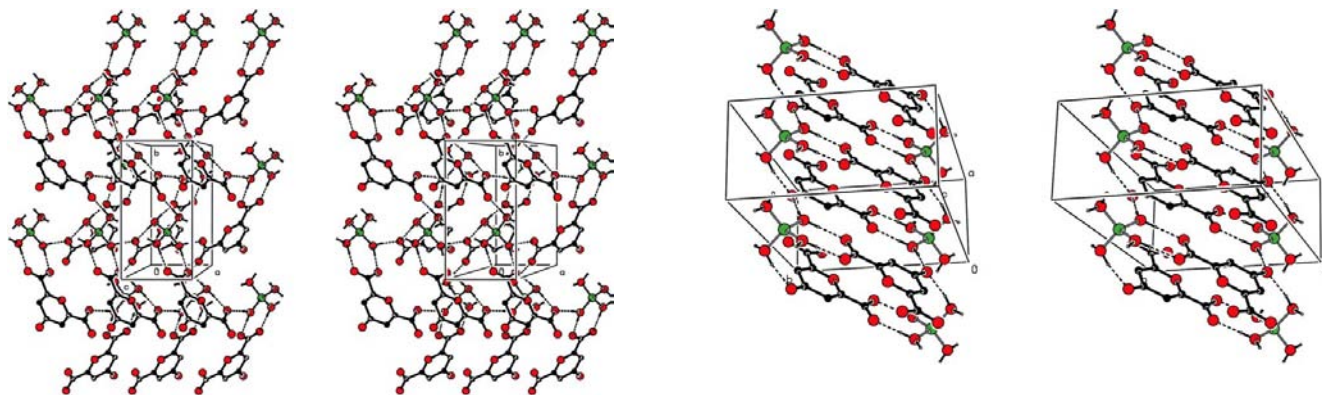


Figure 6
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded sheet parallel to (001). For the sake of clarity, H atoms bonded to C atoms have been omitted.

complexes formed in the corresponding hexahydrate (Manojlović-Muir *et al.*, 1999).

In compound (II), the 4-oxo-4*H*-pyran-2,6-dicarboxylate anion acts as a tridentate ligand to the Ca^{2+} cation, coordinating *via* a pair of carboxylate O atoms and also *via* the ring O atom (Fig. 2). In each of compounds (III) and (IV), the organic anion acts as a bidentate ligand bridging a pair of metal centres. However, in the Mn complex, (III), the anion utilizes two O atoms from a single carboxylate group acting as donor to a pair of symmetry-related Mn^{II} cations, and the resulting aggregate is centrosymmetric (Fig. 3). By contrast, in the Cu complex, (IV), the anion utilizes one O atom from each carboxylate group as donors to two independent Cu^{II} cations, each of which lies on a centre of inversion (Fig. 4). Finally, in the Cd complex, (V), the organic ligand utilizes three carboxylate O atoms and the ketonic O atom as donors to four different Cd atoms (Fig. 5).

The bond lengths within the organic ligands are remarkably constant across the series (I)–(V). The C–O distances in the carboxylate groups are fully consistent with complete ionization in every case. The metal–oxygen distances present only a few unexpected values. In the Ca complex, (II), the distance to the ring O atom [2.6231 (12) Å] is significantly longer than the distances to the adjacent carboxylate O atoms [2.4002 (13) and 2.4314 (13) Å], purely for geometric reasons. In the Cd complex, (V), the Cd–O(carboxylate) distances range from 2.242 (3) to 2.3284 (19) Å, with the distances to the water O atoms both within this range, but the distance to the ketonic O atom is significantly longer, at 2.419 (3) Å. The most striking distances occur for the Cu^{II} complex, (IV), where the six-coordination of the two independent Cu^{II} cations is subject to Jahn–Teller distortion giving, for both ions, the typical (4+2) coordination having local D_{4h} ($4/mmm$) point symmetry, with the two axial distances significantly longer than the four equatorial distances. However, for atom Cu1, the two axial sites are occupied by a pair of water molecules, while for atom Cu2, these sites are occupied by a pair of carboxylate ligands (Table 4).

Figure 7
A stereoview of part of the crystal structure of compound (I), showing the formation of the hydrogen-bonded chain of rings which links adjacent (001) sheets. For the sake of clarity, H atoms bonded to C atoms have been omitted.

The supramolecular structures of compounds (I)–(V) are all three-dimensional. In compounds (I)–(III), the three-dimensional frameworks are all built entirely from hydrogen bonds. Compound (IV) forms a one-dimensional polymer chain, and these chains are linked into a three-dimensional structure by hydrogen bonds, while compound (V) consists of the three-dimensional coordination polymer interwoven with a three-dimensional hydrogen-bonded framework.

Within the selected asymmetric unit of the hydrated salt, (I) (Fig. 1), the cation is linked to the anion by two nearly linear O–H...O hydrogen bonds (Table 1), where both acceptors are in the same carboxylate group. Ion pairs of this type are linked by six further O–H...O hydrogen bonds into a three-dimensional framework structure, whose formation is readily analysed in terms of simple substructures. The cation at (x, y, z) acts as hydrogen-bond donor *via* atom O11 to atom O61 in the anion at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$, *via* atom O13 to atoms O21 and O61 in the anion at $(\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$, and *via* atom O14 to atom O62 in the anion at $(1 + x, 1 + y, z)$, resulting in the formation of a complex sheet parallel to (001) generated by the 2_1 screw axes at $z = \frac{3}{4}$ (Fig. 6). Successive (001) sheets are linked by two further hydrogen bonds. The cation at (x, y, z) is linked *via* atoms O12 and O14, respectively, to atoms O4 in the anions at $(2 - x, 1 - y, 1 - z)$ and $(1 - x, 1 - y, 1 - z)$, both of which lie in the (001) sheet generated by the 2_1 screw axes at $y = \frac{1}{4}$. These two interactions together form a chain of alternating $R_4^4(18)$ (Bernstein *et al.*, 1995) and $R_4^4(22)$ rings (Fig. 7), whose propagation by the space group thus links each (001) sheet to the two adjacent sheets. Hence, all of the component ions are linked into a single three-dimensional structure.

In the salt (II), $N_2H_6^{2+} \cdot [Ca(C_7H_2O_6)_2(H_2O)_2]^{2-}$, the Ca atom forms part of an isolated anion, which lies across a twofold rotation axis in the space group $P2/c$. The hydrazinium cation likewise lies across a twofold axis. A combination of O–H...O and N–H...O hydrogen bonds (Table 2) links the component ions into a three-dimensional framework, but it is possible to identify a two-dimensional substructure built from anions only. The water atoms O2 at (x, y, z) and $(1 - x, y, \frac{1}{2} - z)$

are components of the reference anion across the axis $(\frac{1}{2}, y, \frac{1}{4})$. These two atoms act as hydrogen-bond donors *via* atom H2A to the ketonic atoms O4 at $(1 - x, 2 - y, -z)$ and $(x, 2 - y, \frac{1}{2} + z)$, respectively, which lie in the anions across $(\frac{1}{2}, -y, \frac{1}{4})$ and $(\frac{1}{2}, -y, \frac{3}{4})$, respectively. Similarly, the water atoms O2 at (x, y, z) and $(1 - x, y, \frac{1}{2} - z)$ act as hydrogen-bond donors *via* atom H2B to the carboxylate atoms O22 at $(-1 + x, y, z)$ and $(2 - x, y, \frac{1}{2} - z)$, which form parts of the anions across $(-\frac{1}{2}, y, \frac{1}{4})$ and $(\frac{3}{2}, y, \frac{1}{4})$, respectively. Propagation of these two hydrogen bonds by translation, rotation and inversion then generates a sheet of anions lying parallel to (010) and containing three types of

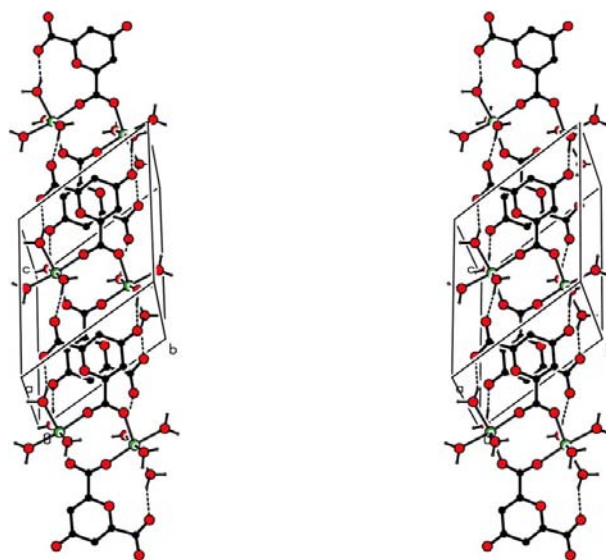


Figure 9
A stereoview of part of the crystal structure of compound (III), showing the formation of a hydrogen-bonded molecular ladder along [001]. For the sake of clarity, noncoordinated water molecules and H atoms bonded to C atoms have been omitted.

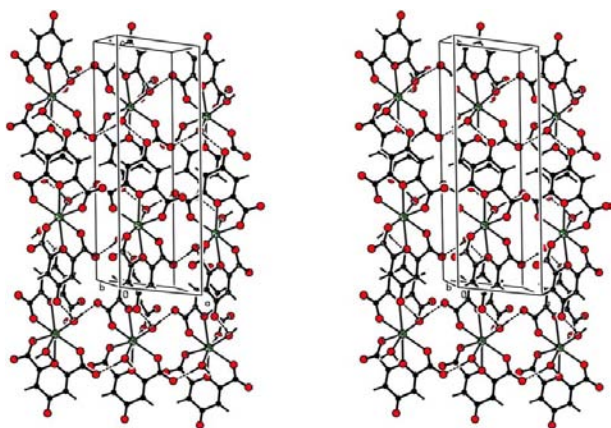


Figure 8
A stereoview of part of the crystal structure of compound (II), showing the formation of a hydrogen-bonded sheet of anions. For the sake of clarity, the cations and H atoms bonded to C atoms have been omitted.

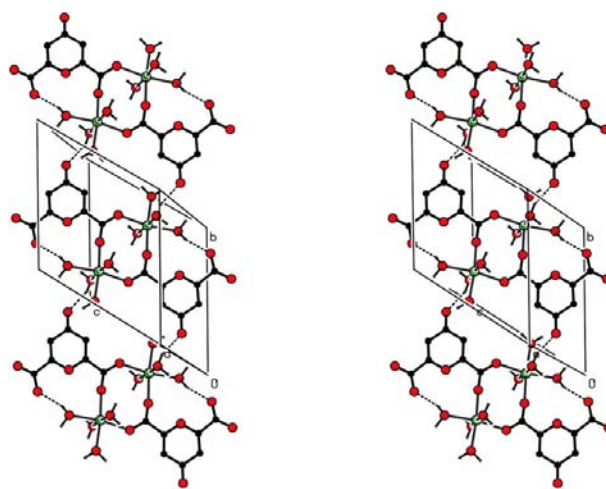


Figure 10
A stereoview of part of the crystal structure of compound (III), showing the formation of a hydrogen-bonded chain of fused rings along [010]. For the sake of clarity, noncoordinated water molecules and H atoms bonded to C atoms have been omitted.

ring (Fig. 8). A single sheet of this type passes through each unit cell. The hydrazinium cations lie within one of the larger rings, and each cation forms six N—H···O hydrogen bonds, four of which (involving atoms H3A and H3B) lie within the reference (010) sheet, while the other two, involving atom H3C, serve to link the reference sheet to the two adjacent sheets, so linking all of the ions into a single three-dimensional framework.

The 4-oxo-4*H*-pyran-2,6-dicarboxylate ligand in the Mn^{II} complex, (III), acts as a bridging ligand between two symmetrically related metal centres, thereby forming a cyclic centrosymmetric aggregate containing an $R_2^2(8)$ (Starbuck *et al.*, 1999) ring (Fig. 3), located for the sake of convenience across $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The four water molecules coordinated to the metal form three internal O—H···O hydrogen bonds, one to a carboxylate O atom and the other two to the uncoordinated water molecules. In addition, the noncoordinated water atom O15 at (x, y, z) forms an internal hydrogen bond to the coordinated water atom O12 at $(1-x, 1-y, 1-z)$. In each dimeric aggregate, therefore, there are 16 O—H bonds available for the formation of hydrogen bonds between the aggregates (Table 3), and these link the metal complexes into a three-dimensional framework structure of considerable complexity. However, the three-dimensional nature of the supramolecular structure can be readily demonstrated using just four of the independent hydrogen bonds between the aggregates, which give rise to three simple one-dimensional substructures. In the first of these substructures, water atom O12 at (x, y, z) acts as hydrogen-bond donor, *via* atom H12A, to ketonic atom O4 at $(x, y, -1+z)$, so generating by translation a molecular ladder running parallel to the [001] direction, in which the uprights are formed by an antiparallel pair of $C(8)$ chains, while the rungs of the ladder contain the $R_2^2(8)$ rings (Fig. 9). In addition, atom O12 at (x, y, z) also acts as

donor to atom O4 at $(1-x, 2-y, 1-z)$, this time *via* atom H12B, and propagation of this interaction by inversion generates a chain of fused rings running parallel to the [010] direction (Fig. 10). Finally, water atoms O13 and O14 at (x, y, z) act as donors to, respectively, carboxylate atoms O61 and O62 at $(-1+x, 1+y, -1+z)$, so generating by translation a

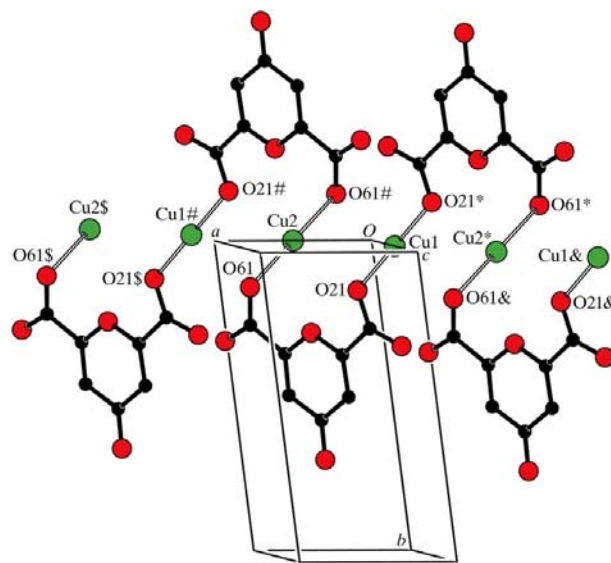


Figure 12

Part of the crystal structure of compound (IV), showing the formation of a chain of alternating cations and anions along [101]. For the sake of clarity, the water molecules and H atoms bonded to C atoms have all been omitted. O atoms marked with an asterisk (*), a hash sign (#), a dollar sign (\$) or an ampersand (&) are at the symmetry positions $(-x, -y, 1-z)$, $(1-x, -y, -z)$, $(1+x, y, -1+z)$ and $(-1+x, y, 1+z)$, respectively. Atoms Cu1# and Cu1\$ are at $(1, 0, -\frac{1}{2})$ and $(-1, 0, \frac{3}{2})$, respectively, and atoms Cu2* and Cu2\$ are at $(-\frac{1}{2}, 0, 1)$ and $(\frac{3}{2}, 0, -1)$, respectively.

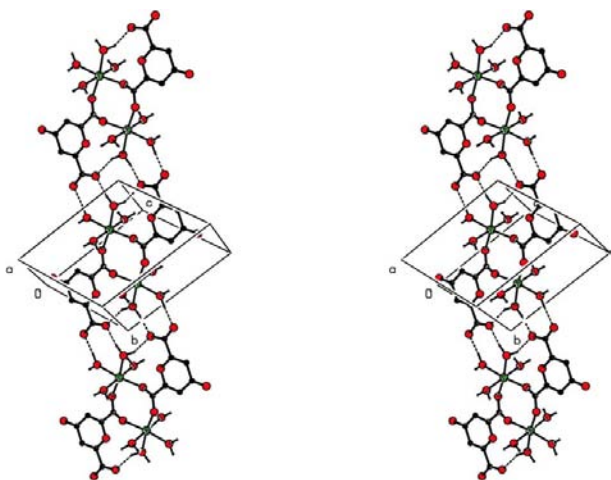


Figure 11

A stereoview of part of the crystal structure of compound (III), showing the formation of a hydrogen-banded chain of fused rings along [111]. For the sake of clarity, noncoordinated water molecules and H atoms bonded to C atoms have been omitted.

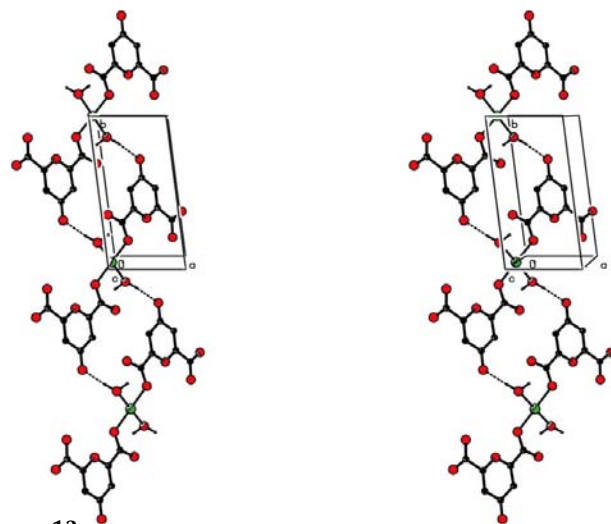


Figure 13

A stereoview of part of the crystal structure of compound (IV), showing the formation of a hydrogen-banded chain of spiro-fused rings along [010]. For the sake of clarity, atom Cu2, three of the water molecules and H atoms bonded to C atoms have been omitted.

metal-organic compounds

chain of fused rings running parallel to the $[1\bar{1}1]$ direction (Fig. 11). The combination of these $[001]$, $[010]$ and $[1\bar{1}1]$ chains suffices to generate a three-dimensional framework, whose structure is rendered considerably more complex by further hydrogen bonds involving both coordinated and noncoordinated water molecules (Table 3).

The two independent Cu^{II} ions in compound (IV) both lie on centres of inversion in the space group $P\bar{1}$, selected as those at $(0, 0, \frac{1}{2})$ for Cu1 and $(\frac{1}{2}, 0, 0)$ for Cu2. The 4-oxo-4*H*-pyran-2,6-dicarboxylate ligand lies in a general position, bridging the two Cu ions *via* a pair of carboxylate O atoms (Fig. 4). The action of the two independent inversion centres then generates a coordination polymer chain of alternating cations and anions, running parallel to the $[10\bar{1}]$ direction (Fig. 12). The role of the 4-oxo-4*H*-pyran-2,6-dicarboxylate ligand in (IV) is thus similar to that in the polymer formed with tributyltin(IV) units (Ng *et al.*, 2000), although in that instance the coordination polymer is anionic, whereas in (IV) it is neutral.

The coordination polymer chains are linked into a complex three-dimensional framework by no fewer than eight independent $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 5), but the three-dimensional nature of the supramolecular structure can most simply be demonstrated in terms of two one-dimensional hydrogen-bonded substructures involving just three of the hydrogen bonds. In the first of these substructures, water atom O1*B* at (x, y, z) acts as hydrogen-bond donor, *via* atom H12*B*, to ketonic atom O4 at $(x, -1 + y, z)$, and propagation of this interaction by translation and inversion generates a chain of spiro-fused $R_6^4(18)$ rings running parallel to the $[010]$ direction (Fig. 13). In the second hydrogen-bonded substructure, water atoms O2*A* and O2*B* at (x, y, z) act as donors to, respectively, atoms O62 and O61 at $(-1 + x, y, z)$. Propagation of these interactions by translation and inversion then generates a complex chain of $R_4^4(8)$ and $R_6^4(8)$ rings running parallel to the $[100]$ direction (Fig. 14). The combination of these $[100]$, $[010]$ and $[10\bar{1}]$ chains is sufficient to generate a three-dimensional framework, with further complexity generated by the remaining hydrogen bonds.

Compound (V) is a coordination compound, $[\text{Cd}(\text{C}_7\text{H}_2\text{O}_6)(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (Fig. 5), in which the Cd centre is coordinated by two water molecules, occupying *cis* sites, and four O atoms, one of them a ketonic O atom and three of them from

carboxylate groups, which themselves form parts of four different anionic ligands. The six-coordination of the Cd ion is markedly distorted from regular octahedral. The third water molecule is not coordinated to the Cd ion, but instead forms hydrogen bonds to O atoms in three different anions *via* one two-centre $\text{O}-\text{H}\cdots\text{O}$ interaction and one three-centre $\text{O}-\text{H}\cdots(\text{O})_2$ interaction (Table 6).

The Cd cations and the anions together form a three-dimensional coordination polymer, whose formation is very easily analysed in terms of two simple substructures, namely a

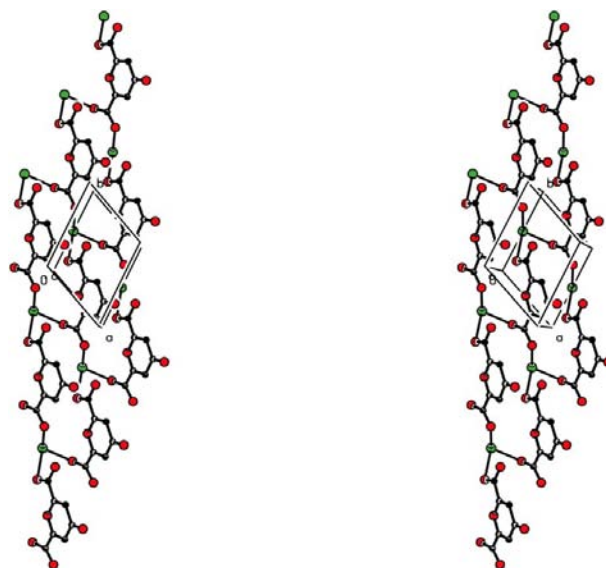


Figure 15
A stereoview of part of the crystal structure of compound (V), showing the formation of a coordination polymer sheet parallel to (001) . For the sake of clarity, the water molecules and H atoms bonded to C atoms have been omitted.

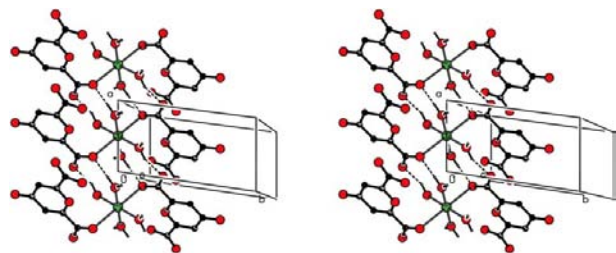


Figure 14
A stereoview of part of the crystal structure of compound (IV), showing the formation of a hydrogen-bonded chain of fused rings along $[100]$. For the sake of clarity, atom Cu1, two of the water molecules and H atoms bonded to C atoms have been omitted.

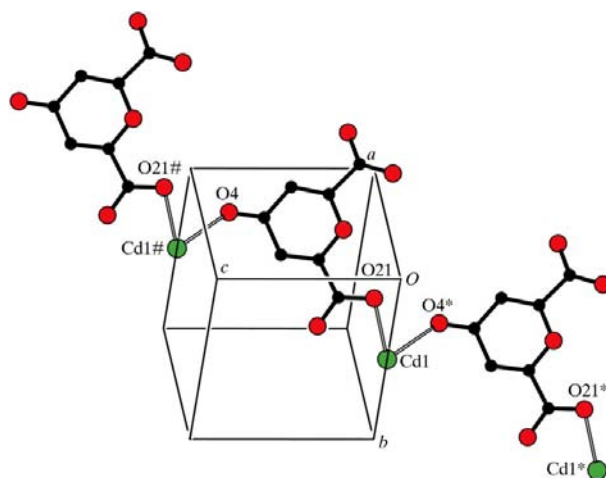


Figure 16
Part of the crystal structure of compound (V), showing the formation of a coordination polymer chain along $[101]$. For the sake of clarity, the water molecules and H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash sign (#) are at the symmetry positions $(-1 + x, y, -1 + z)$ and $(1 + x, y, 1 + z)$, respectively.

two-dimensional substructure involving only carboxylate coordination and a one-dimensional substructure based on the coordination of the ketonic O atom to the Cd ion. The reference Cd ion at (x, y, z) is coordinated not only by atom O21 at (x, y, z) , but also by atoms O61 and O62 in the anions at $(x, 1 + y, z)$ and $(-1 + x, 1 + y, z)$, respectively, and these interactions together generate a sheet parallel to (001) which takes the form of a (4,4) net (Batten & Robson, 1998) (Fig. 15). In the second substructure, the reference Cd ion is coordinated by ketonic atom O4 in the anion at $(-1 + x, y, -1 + z)$, so forming a $C(7)$ chain (Starbuck *et al.*, 1999) running parallel to the [101] direction (Fig. 16). The combination of these [101] chains and (001) sheets suffices to generate a single three-dimensional coordination polymer.

In addition, the polymer framework is reinforced by an extensive series of hydrogen bonds (Table 6). These individually form chains parallel to [100], [010], [101], [201], [011] and [111], and their combination thereby forms a very complex three-dimensional hydrogen-bonded framework interwoven with the coordination polymer framework.

The range of structures reported here, together with those reported previously (Manojlović-Muir *et al.*, 1999; Ng *et al.*, 2000), indicate the remarkably versatile coordination behaviour of the 4-oxo-4*H*-pyran-2,6-dicarboxylate dianion, which has led here to the characterization of cationic, neutral and anionic complexes encompassing finite coordination species, both mononuclear and binuclear, as well as one- and three-dimensional coordination polymers.

Experimental

For the synthesis of compound (I), equimolar quantities (1 mmol of each component) of beryllium sulfate tetrahydrate and 4-oxo-4*H*-pyran-2,6-dicarboxylic acid were dissolved in doubly distilled water (20 ml). Slow evaporation at ambient temperature yielded, after 19 d, pale-yellow prismatic crystals of (I) (yield 94%). Analysis for (I) found: C 32.0, H 3.8%; $C_7H_{10}BeO_{10}$ requires: C 31.9, H 3.8%.

Compound (II) was unexpectedly obtained from the reaction between equimolar quantities (1 mmol of each component) of hydrazine hydrate and 4-oxo-4*H*-pyran-2,6-dicarboxylic acid in singly distilled water, followed by slow evaporation. Analysis for (II) found: C 36.0, H 2.9, N 5.8%; $C_{14}H_8CaN_2O_{14}$ requires: C 35.4, H 3.0, N 5.9%; IR (KBr, ν , cm^{-1}): 3460, 3299, 3064, 1616, 1402, 1349, 1109.

For the synthesis of compound (III), a solution of manganese(II) acetate (1 mmol in 5 ml of water) was added to a solution of 4-oxo-4*H*-pyran-2,6-dicarboxylic acid (1 mmol in 15 ml of water). Slow evaporation at ambient temperature gave, after 12 d, yellow rhomboid crystals of (III) (yield 53%). Analysis for (III) found: C 26.0, H 3.0%; $C_7H_{14}MnO_{12}$ requires: C 24.4, H 4.1%.

Compound (IV) was prepared by the portionwise addition of basic copper(II) carbonate (1 mmol, as a solid) to a hot (*ca* 350 K) solution of 4-oxo-4*H*-pyran-2,6-dicarboxylic acid (2 mmol in 40 ml of water). The solution was filtered hot and then allowed to cool to ambient temperature, when slow evaporation gave pale-green crystals of (IV) after 12 d (yield 80%). Analysis for (IV) found: C 26.1, H 3.2%; $C_7H_{10}CuO_{10}$ requires: C 26.5, H 3.2%.

For the synthesis of compound (V), aqueous solutions of cadmium nitrate (1 mmol in 5 ml of water) and 4-oxo-4*H*-pyran-2,6-dicarboxylic acid (1 mmol in 15 ml of water) were mixed at ambient

temperature. Subsequent slow evaporation at ambient temperature yielded, after 8 d, pale-yellow rhomboid crystals of (V) (yield 79%). Analysis for (V) found: C 24.4, H 2.1%; $C_7H_8CdO_9$ requires: C 24.15, H 2.3%.

In every case, the crystals were collected by filtration and then washed with ice-cold water (*ca* 5 ml) prior to analysis.

Compound (I)

Crystal data

$[Be(H_2O)_4](C_7H_2O_6)$	$V = 1096.75 (6) \text{ \AA}^3$
$M_r = 263.16$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 5.4331 (2) \text{ \AA}$	$\mu = 0.15 \text{ mm}^{-1}$
$b = 10.6173 (4) \text{ \AA}$	$T = 120 (2) \text{ K}$
$c = 19.1890 (5) \text{ \AA}$	$0.28 \times 0.24 \times 0.11 \text{ mm}$
$\beta = 97.771 (2)^\circ$	

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer	11511 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2504 independent reflections
$T_{\min} = 0.968, T_{\max} = 0.984$	2180 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	163 parameters
$wR(F^2) = 0.118$	H-atom parameters constrained
$S = 1.15$	$\Delta\rho_{\max} = 0.37 \text{ e \AA}^{-3}$
2504 reflections	$\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry ($\text{\AA}, ^\circ$) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O11–H11A···O21	0.86	1.74	2.6073 (16)	179
O11–H11B···O61 ⁱ	0.94	1.73	2.6501 (16)	165
O12–H12A···O22	0.86	1.74	2.6003 (16)	178
O12–H12B···O4 ⁱⁱ	0.89	1.73	2.6187 (16)	174
O13–H13A···O21 ⁱⁱⁱ	0.88	1.76	2.6353 (15)	171
O13–H13B···O61 ⁱⁱⁱ	0.89	1.75	2.6360 (15)	170
O14–H14A···O4 ^{iv}	0.89	1.79	2.6672 (16)	168
O14–H14B···O62 ^v	0.98	1.60	2.5788 (16)	177

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $x + 1, y + 1, z$.

Compound (II)

Crystal data

$(N_2H_6)[Ca(C_7H_2O_6)_2(H_2O)_2]$	$V = 854.88 (5) \text{ \AA}^3$
$M_r = 474.35$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 6.4669 (2) \text{ \AA}$	$\mu = 0.46 \text{ mm}^{-1}$
$b = 7.0797 (3) \text{ \AA}$	$T = 120 (2) \text{ K}$
$c = 18.8278 (6) \text{ \AA}$	$0.26 \times 0.18 \times 0.08 \text{ mm}$
$\beta = 97.372 (2)^\circ$	

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer	9031 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	1953 independent reflections
$T_{\min} = 0.909, T_{\max} = 0.964$	1876 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	141 parameters
$wR(F^2) = 0.116$	H-atom parameters constrained
$S = 1.20$	$\Delta\rho_{\max} = 0.68 \text{ e \AA}^{-3}$
1953 reflections	$\Delta\rho_{\min} = -0.54 \text{ e \AA}^{-3}$

Table 2
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2A...O4 ⁱ	0.84	1.89	2.7149 (18)	167
O2—H2B...O22 ⁱⁱ	0.90	1.77	2.6717 (19)	175
N3—H3A...O61	0.88	2.07	2.8091 (19)	142
N3—H3B...O62 ⁱⁱⁱ	0.96	1.74	2.679 (2)	166
N3—H3C...O21 ^{iv}	0.88	1.93	2.781 (2)	162

Symmetry codes: (i) $-x + 1, -y + 2, -z$; (ii) $x - 1, y, z$; (iii) $-x, y, -z + \frac{1}{2}$; (iv) $-x + 1, y - 1, -z + \frac{1}{2}$.

Compound (III)

Crystal data

[Mn₂(C₇H₂O₆)₂(H₂O)₈].4H₂O
M_r = 690.24
 Triclinic, *P*1̄
a = 7.4343 (2) Å
b = 10.1176 (3) Å
c = 10.2290 (3) Å
 α = 61.935 (2)°
 β = 78.219 (3)°
 γ = 69.061 (2)°
V = 633.49 (3) Å³
Z = 1
 Mo *K*α radiation
 μ = 1.11 mm⁻¹
T = 120 (2) K
 0.47 × 0.21 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
T_{min} = 0.625, *T_{max}* = 0.898
 14668 measured reflections
 2914 independent reflections
 2423 reflections with *I* > 2σ(*I*)
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.074$
S = 1.08
 2914 reflections
 181 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.45 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.40 \text{ e \AA}^{-3}$

Table 3
Hydrogen-bond geometry (Å, °) for (III).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O11—H11A...O15	0.83	1.85	2.6784 (19)	176
O11—H11B...O62 ⁱ	0.83	1.96	2.7846 (18)	175
O12—H12A...O4 ⁱⁱ	0.94	1.73	2.6670 (18)	174
O12—H12B...O4 ⁱⁱⁱ	0.82	1.95	2.7356 (18)	158
O13—H13A...O61 ^{iv}	0.91	1.81	2.7133 (18)	172
O13—H13B...O61 ^v	0.86	2.00	2.7866 (18)	151
O14—H14A...O16	0.89	1.86	2.7532 (19)	174
O14—H14B...O62 ^{iv}	0.88	1.82	2.6908 (18)	176
O15—H15A...O12 ^v	0.86	1.93	2.7930 (19)	173
O15—H15B...O13 ^{vi}	0.93	2.07	2.9814 (19)	166
O16—H16A...O22 ⁱⁱⁱ	0.88	2.00	2.8765 (19)	175
O16—H16B...O11 ^{vii}	0.95	2.13	3.0423 (19)	160

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

Compound (IV)

Crystal data

[Cu(C₇H₂O₆)(H₂O)₄]
M_r = 317.70
 Triclinic, *P*1̄
a = 4.9593 (6) Å
b = 9.8973 (14) Å
c = 10.4697 (12) Å
 α = 94.237 (9)°
 β = 94.955 (9)°
 γ = 97.353 (6)°
V = 505.88 (11) Å³
Z = 2
 Mo *K*α radiation
 μ = 2.21 mm⁻¹
T = 120 (2) K
 0.12 × 0.12 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
T_{min} = 0.777, *T_{max}* = 0.809
 6400 measured reflections
 2264 independent reflections
 2043 reflections with *I* > 2σ(*I*)
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.156$
S = 1.12
 2264 reflections
 167 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 1.42 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.42 \text{ e \AA}^{-3}$

Table 4
Selected bond lengths (Å) for (IV).

Cu1—O1A	1.970 (3)	Cu2—O2A	1.961 (3)
Cu1—O21	1.982 (3)	Cu2—O2B	1.906 (3)
Cu1—O1B	2.447 (4)	Cu2—O61	2.525 (3)

Table 5
Hydrogen-bond geometry (Å, °) for (IV).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1A—H11A...O21 ⁱ	0.88	1.86	2.743 (4)	176
O1A—H12A...O61 ⁱ	0.88	1.84	2.715 (4)	175
O1B—H11B...O4 ⁱⁱ	0.88	2.24	3.110 (6)	169
O1B—H12B...O4 ⁱⁱⁱ	0.88	2.01	2.790 (5)	147
O2A—H21A...O62 ^{iv}	0.88	1.83	2.672 (4)	160
O2A—H22A...O4 ^v	0.88	1.83	2.699 (5)	168
O2B—H21B...O61 ^{iv}	0.88	1.75	2.618 (4)	170
O2B—H22B...O1B	0.88	1.82	2.666 (5)	162

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $x - 1, y - 1, z$; (iii) $x, y - 1, z$; (iv) $x - 1, y, z$; (v) $-x + 1, -y + 1, -z$.

Compound (V)

Crystal data

[Cd(C₇H₂O₆)(H₂O)₂].H₂O
M_r = 348.53
 Triclinic, *P*1̄
a = 5.3262 (2) Å
b = 6.2885 (2) Å
c = 8.1008 (3) Å
 α = 97.733 (2)°
 β = 105.0554 (17)°
 γ = 110.4356 (18)°
V = 237.80 (2) Å³
Z = 1
 Mo *K*α radiation
 μ = 2.34 mm⁻¹
T = 120 (2) K
 0.10 × 0.04 × 0.04 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
T_{min} = 0.781, *T_{max}* = 0.912
 7006 measured reflections
 2108 independent reflections
 2108 reflections with *I* > 2σ(*I*)
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$
 $wR(F^2) = 0.042$
S = 1.15
 2108 reflections
 136 parameters
 3 restraints
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.58 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.98 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983), with 1003 Friedel pairs
 Flack parameter: $-0.002 (17)$

For compound (I), the space group *P*2₁/*n* was uniquely assigned from the systematic absences. For compound (II), the systematic absences permitted *Pc* and *P*2/*c* as possible space groups; *P*2/*c* was selected and confirmed by the successful structure analysis. Crystals of compounds (III)–(V) are all triclinic. The space group *P*1̄ was selected for compounds (III) and (IV), and *P*1 was selected for

Table 6

Hydrogen-bond geometry (Å, °) for (V).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O11—H11A...O13 ⁱ	0.82	1.99	2.805 (4)	172
O11—H11B...O21 ⁱⁱ	0.82	1.98	2.780 (3)	165
O12—H12A...O13 ⁱⁱⁱ	0.82	2.03	2.844 (4)	171
O12—H12B...O4 ^{iv}	0.82	2.04	2.827 (3)	162
O13—H13A...O61 ^v	0.82	2.42	2.950 (4)	124
O13—H13A...O4 ^{vi}	0.82	2.46	3.169 (5)	146
O13—H13B...O22	0.82	2.02	2.809 (4)	162

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

compound (V), and these selections were all confirmed by the subsequent structure analyses. All H atoms were located in difference maps and then treated as riding atoms. H atoms bonded to C atoms were placed in calculated positions, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms bonded to N or O atoms were permitted to ride at the locations deduced from the difference maps, giving N—H = 0.88–0.96 Å and O—H = 0.82–0.94 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ or $1.5U_{\text{eq}}(\text{O})$. The correct absolute configuration of the structure of compound (V) in the crystal selected for data collection was established by means of the Flack (1983) parameter.

For all compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3043). Services for accessing these data are described at the back of the journal.

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