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Stereochemistry of Carboxylate Complexes. Crystal Structure of $(-)_{589}$-Malatodiaquomanganese(II) Hydrate

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The crystal structure of $(-)_{589}$-malatodiaquomanganese(II) hydrate, $[Mn(C_4H_4O_5)(H_2O)_2]\cdot H_2O$, has been determined from three-dimensional single-crystal x-ray diffraction data collected by counter methods on a computer automated diffractometer. The compound crystallizes in the orthorhombic space group D_2^4-$P2_12_12_1$ with four formula units in a cell of dimensions $a = 9.219$ (7) Å, $b = 9.421$ (6) Å, $c = 10.536$ (7) Å. The structure was solved by Patterson and Fourier methods and refined by a full-matrix least-squares procedure to a conventional R index of 0.045 for 1167 independent reflections. Each manganese(II) ion is coordinated to one carboxylate oxygen atom and the hydroxyl oxygen from one ligand forming a five-membered chelate ring as well as two carboxylate oxygen atoms from two other different malate ligands. Two water molecules complete the irregular octahedral coordination around the metal. Four of the five oxygen atoms in the malate ligand are involved in coordination to three different Mn(II) ions forming an extensive polymeric network including hydrogen bonding to the single lattice water molecule. The malate conformation is antiperiplanar and the entire structure is compared to the structures of other malate complexes. The range in Mn–O bond lengths is 2.135 (3) to 2.230 (4) Å.

Introduction

Malate ion, $^-OOCCHOHCH_2COO^-$, is a multidentate dicarboxylate ligand which may coordinate metal ions in a variety of ways. As part of a continuing general study of the stereochemistry of metal–carboxylate complexes, we have been interested in establishing the relative variability in the mode of metal ion coordination by carboxylate ligands such as malate in the crystalline state.

The stereochemistry of the malate–metal interaction has been determined for the 1:1 compounds of calcium,[1] cobalt(II)[2,3] and zinc(II).[4] For each of the above ions x-ray crystallographic studies have revealed the malato ligand coordinates the metal through both carboxylate groups and the hydroxyl oxygen to form five- and six-membered chelate rings. Four-membered chelate rings are present as well in the calcium malate[1] crystal presumably needed to satisfy the eight-coordination stereochemistry requirement of the larger Ca(II) ion. For each of the indicated compounds (in addition to chelation) the malato ligand is bridged to one or more metal ions in a monodentate fashion forming polymeric units.

The manganese(II), zinc(II), and cobalt(II) 1:1 malate compounds all crystallize with the formula unit $MC_4H_4O_5\cdot 3H_2O$. The Co(II) and Zn(II) compounds are monoclinic while the Mn(II) crystals are orthorhombic. The obvious difference in crystal structure in the manganese(II) case does not imply the manganese–malate stereochemistry would necessarily be different from that in the zinc(II) and cobalt(II) compounds. But, if a change in the mode of coordination did occur, the crystal packing and structure would necessarily be altered. On this basis we undertook the x-ray crystal structure investigation of manganese(II) $(-)_{589}$-malate trihydrate to test the idea that the $(-)_{589}$-malato stereochemistry may differ in a series of complexes with similarly charged and sized metal ions.

Experimental Section

Short prismatic crystals of $(-)_{589}$-malatodiaquomanganese(II) hydrate were grown by slow evaporation from an aqueous solution prepared by dissolving manganese carbonate in $(-)_{589}$-malic acid (Eastman) in a 1:1 molar ratio. Small single crystals of the complex appear nearly colorless although clumps of larger crystals have a decided pink cast.

Examination of indexed Weissenberg photographs showed that the crystals belonged to the orthorhombic system. The observed systematic absence, h odd for $h00$, k odd for $0k0$, and l odd for $00l$, uniquely determined the space group to be $P2_12_12_1$. The lattice constants were determined at ambient room temperature from a least-squares refinement of the angular settings of 12 carefully centered reflections (2θ range 13 to 26°) on a Picker FACS-I automated diffractometer using Mo Kα radiation (λ 0.71069 Å).

Crystal Data for $[MnC_4H_4O_5(H_2O)_2]\cdot H_2O$: orthorhombic; space group $P2_12_12_1$: $a = 9.219$ (7) Å; $b = 9.421$ (6) Å; $c = 10.536$ (7) Å; $V = 915.1$ Å^3; $Z = 4$; $d_m = 1.75$ (1) g cm^{-3} (by flotation in a mixture of iodobenzene and pentachloroethane); $d_c = 1.748$ g cm^{-3}; FW = 241.06; $F(000) = 492$; μ(Mo Kα) = 15.3 cm^{-1}.

Collection and Redution of the Intensity Data. Three-dimensional x-ray intensity data were collected from a crystal with approximate dimensions 0.28 × 0.31 × 0.31 mm on the diffractometer already mentioned. Zirconium-filtered Mo Kα radiation was used. The crystal was mounted along the c^* direction which was made coincident with the instrumental ϕ axis. All reflections out to 55° in 2θ were collected using the θ–2θ scan technique. A scan range from 1° below the Mo Kα_1 peak to 1° above the Mo Kα_2 peak was used. The scan rate was 1°/min. The background counting time was 20 sec at the start and end of each scan. During the data collection the intensities of three standard reflections were monitored after each 100 measurements and none showed any significant variation during the data collection. The raw intensity data were assigned estimated standard deviations and reduced to values of F_o and $\sigma(F_o)$ (assuming an "uncertainty factor", $p = 0.04$) in the manner previously described.[5] No absorption corrections were applied in view of the low absorption factors and the approximately equidimensional shape of the crystal. As a check

Table I. Positional[a] and Thermal Parameters[b] for $[Mn(C_4H_4O_5)(H_2O)_2]\cdot H_2O$

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Mn	0.23099 (8)	0.15856 (8)	0.11092 (6)	48.3 (7)	54.2 (7)	25.0 (5)	−0.6 (6)	−2.6 (6)	2.9 (6)
O(1)	0.2339 (5)	−0.0344 (3)	−0.0050 (3)	107 (5)	58 (4)	28 (2)	11 (4)	10 (3)	6 (2)
O(2)	0.2815 (6)	−0.2660 (4)	−0.0039 (4)	184 (7)	60 (4)	40 (3)	30 (5)	22 (4)	5 (3)
O(3)	0.2057 (5)	−0.0183 (4)	0.2443 (3)	103 (5)	51 (4)	34 (3)	−1 (4)	−0 (3)	−5 (3)
O(4)	−0.0001 (4)	−0.3237 (4)	0.4298 (3)	55 (4)	79 (5)	37 (3)	−1 (4)	3 (3)	9 (3)
O(5)	0.2347 (4)	−0.2743 (4)	0.4393 (3)	51 (4)	68 (4)	32 (2)	−2 (3)	−2 (3)	−9 (3)
O(6)	0.4674 (4)	0.1263 (6)	0.1450 (4)	62 (4)	203 (8)	85 (4)	−13 (5)	−15 (4)	77 (5)
O(7)	0.2311 (5)	0.3274 (4)	0.2475 (3)	123 (6)	99 (5)	45 (3)	−35 (6)	−2 (4)	−11 (3)
O(8)	0.4174 (4)	0.5190 (4)	0.1332 (3)	102 (5)	63 (4)	47 (3)	−0 (4)	2 (3)	−10 (3)
C(1)	0.2529 (5)	−0.1521 (5)	0.0505 (4)	63 (6)	70 (5)	31 (3)	−1 (6)	6 (4)	1 (4)
C(2)	0.2381 (5)	−0.1598 (5)	0.1970 (4)	67 (6)	61 (5)	21 (3)	−1 (6)	6 (3)	−1 (4)
C(3)	0.1213 (6)	−0.2628 (5)	0.2349 (4)	77 (6)	54 (5)	37 (4)	−16 (5)	−8 (4)	3 (4)
C(4)	0.1169 (5)	−0.2891 (4)	0.3790 (4)	52 (5)	44 (4)	38 (4)	−5 (4)	4 (4)	−7 (4)

[a] The estimated standard deviations in the least significant figures are given in parentheses here and in other tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table II. Positional Parameters for Hydrogen Atoms[a]

Atom	x	y	z
H(1)–O(3)	0.104	−0.003	0.240
H(2)–C(2)	0.348	−0.186	0.228
H(3)–C(3)	0.038	−0.212	0.200
H(4)–C(4)	0.126	−0.350	0.204
H(5)–O(6)	0.488	0.098	0.213
H(6)–O(6)	0.540	0.158	0.108
H(7)–O(7)	0.225	0.322	0.321
H(8)–O(7)	0.283	0.382	0.239
H(9)–O(8)	0.403	0.589	0.089
H(10)–O(8)	0.463	0.448	0.075

[a] Hydrogen atoms were assigned a fixed isotropic temperature factor of 5.0.

on possible variations in transmission factors, the intensity of the 008 reflection was measured at $\chi = 90°$ over a wide range of ϕ angles; no significant difference in intensity (<5%) was noted suggesting that absorption effects could be ignored. A total of 1167 reflections had $I > \sigma(I)$ and these were used in subsequent calculations.

Structure Determination and Refinement.[6] The position of the manganese atom was determined from a three-dimensional Patterson map. The remaining nonhydrogen atoms were successfully found from a succession of difference Fourier syntheses which were phased by the atoms already located. The configuration of the $(-)_{589}$-malato ligand was fixed to be (*S*) consistent with the absolute configuration determined in cobalt $(-)_{589}$-malate trihydrate.[2] The trial structure was refined by a full-matrix least-squares procedure assuming at first isotropic then anisotropic motion for the manganese, carbon, and oxygen atoms. At this point a difference Fourier synthesis revealed the positions of all hydrogen atoms. Each hydrogen atom was assigned an isotropic temperature factor of 5.0. The entire structure was further refined by full-matrix least-squares although the hydrogen atom parameters were not varied. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weight, w, applied to each observation was taken to be $1/\sigma^2(F_o)$. The structure refinement converged to a conventional R_1 index, $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0.045 and a weighted R_2 index, $(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, of 0.051. In the last cycle of least-squares refinement the largest shift in any positional or thermal parameter was 0.04 times its own standard deviation. The standard deviation of an observation of unit weight, defined by $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ was 1.84, where the number of observations (m) was 1167 and the number of variable parameters (n) was 118. An analysis of the function $w(|F_o| - |F_c|)^2$ vs. $|F_o|$ or $\sin \theta/\lambda$ revealed no dependence on these quantities indicating a correctly chosen weighting scheme. A final difference Fourier was featureless; the highest peak was 0.4 e Å^{-3} whereas the hydrogen atoms had been located on an earlier map as peaks of density 0.6–0.7 e Å^{-3}. The neutral scattering factors for manganese, carbon, and oxygen were taken from Cromer and Mann[7] while those for hydrogen were taken from Stewart, Davidson, and Simpson.[8] The scattering factors of Mn were corrected for the real and imaginary anomalous dispersion corrections given by Cromer.[7] A listing of the final observed and calculated structure factors as $10|F_o|$ and $10|F_c|$ electrons is available.[9] Final positional and thermal parameters are presented in Tables I and II.

Description and Discussion of the Structure

No symmetry conditions are imposed on the structure by the space group symmetry. A view of the sixfold coordination polyhedron, the atom numbering scheme, and the metal–ligand coordination is presented in Figure 1. Interatomic distances and angles are given in Table III. A carboxylate oxygen, O(1), and the hydroxyl oxygen, O(3), form a five-membered chelate ring Mn–O(1)–C(1)–C(2)–O(3). Two other coordination positions are filled by terminal carboxylate oxygen atoms O(4') and O(5'') from two different malato ligands. The sixfold coordination is completed by two oxygen atoms, O(6) and O(7), from water molecules. The sixfold coordination polyhedron is severely removed from idealized octahedral symmetry. This irregularity is manifested in the wide range of the Mn–O bond lengths and bond angles (Table III). The mean Mn–O bond length is 2.18 ± 0.03 Å which along with the observed spread is comparable to Mn–O bond distances found in the citrate,[10] acetate,[11] and ethylenediaminetetraacetate[12] compounds of manganese(II).

The crystal structure consists of polymeric units formed by the coordination of the terminal carboxylate oxygen atoms, O(4) and O(5), from each malato ligand to two different manganese atoms. Thus, each malate moiety is coordinated to three different manganese atoms as shown in Figure 1, and it follows that each manganese atom in the crystalline structure is attached to three different malato ligands.

The five-membered chelate ring Mn–O(1)–C(1)–C(2)–O(3) is shown in Figure 1 and exists in an uncommon conformation.[13] The four atoms O(1), C(1), C(2), and O(3) lie in the plane $-0.9774X - 0.1922Y - 0.0881Z + 2.044 = 0.0$ with deviations from this plane of +0.004, −0.003, −0.006, and +0.005 Å, respectively. The manganese atom is displaced by −0.43 Å from this plane. This conformation is different from that found in the other 1:1 metal–malate complexes where the more usual puckered chelate ring is present. For comparison, the dihedral angles in the malate five-membered chelate rings are summarized in Table IV.

In addition to the polymeric nature of the structure there is an extensive network of hydrogen bonds utilizing the lone water of hydration, O(8), holding the polymeric units together. All six hydrogen atoms from the three water molecules are involved in hydrogen bonding and their parameters are summarized in Table V. The hydroxyl group is not involved in the hydrogen-bonding scheme. The lattice water is involved in four separate hydrogen bonds with hydrogen atoms H(6) and H(7) from two different water molecules and carboxylate oxygen atoms O(2) and O(4).

The three idealized conformations of a malato group are given below. In rotamer A the carboxylate groups are separated by the greatest distance thereby reducing the

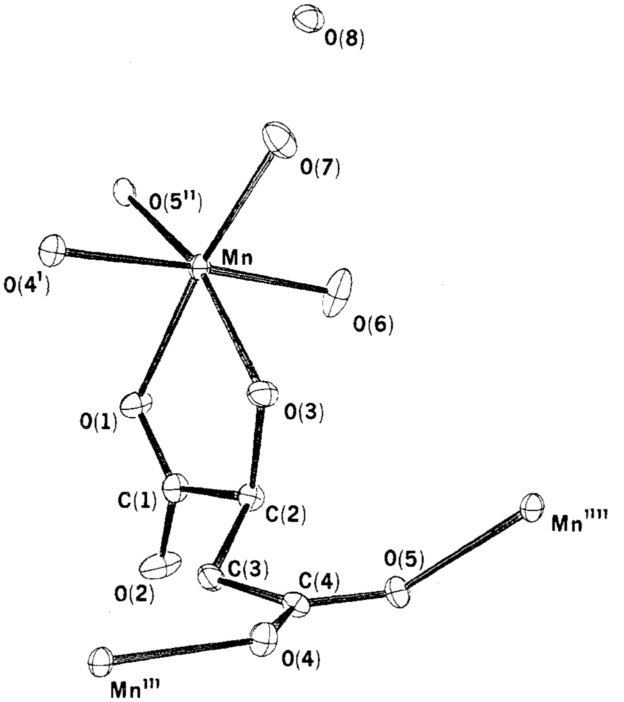


Figure 1. A view of the ligand-metal coordination and the atom-numbering scheme. The primed atoms are related to the corresponding atom positions given in Table I by the following symmetry transformations: O(4') $\bar{x}, {}^1/_2 + y, {}^1/_2 - z$; O(5'') ${}^1/_2 - x, \bar{y}, z - {}^1/_2$; Mn''' $\bar{x}, y - {}^1/_2, {}^1/_2 - z$; Mn'''' ${}^1/_2 - x, \bar{y}, {}^1/_2 + z$. Hydrogen atoms have been omitted for clarity.

Table III. Interatomic Distances and Angles

	Distances, Å		
Mn-O(1)	2.190 (3)	C(1)-O(2)	1.244 (6)
Mn-O(3)	2.192 (3)	C(1)-C(2)	1.551 (6)
Mn-O(6)	2.230 (4)	C(2)-O(3)	1.453 (6)
Mn-O(7)	2.145 (4)	C(2)-C(3)	1.504 (7)
Mn-O(4')	2.177 (3)	C(3)-C(4)	1.539 (6)
Mn-O(5'')	2.135 (3)	C(4)-O(4)	1.248 (6)
C(1)-O(1)	1.266 (6)	C(4)-O(5)	1.266 (6)
	Angles, deg		
O(1)-Mn-O(3)	74.2 (1)	O(4')-Mn-O(6)	176.0 (2)
O(1)-Mn-O(4')	88.0 (1)	O(4')-Mn-O(7)	94.3 (2)
O(1)-Mn-O(5'')	87.1 (1)	O(5'')-Mn-O(6)	93.5 (1)
O(1)-Mn-O(6)	87.9 (2)	O(5'')-Mn-O(7)	100.9 (1)
O(1)-Mn-O(7)	171.7 (2)	O(6)-Mn-O(7)	89.6 (2)
O(3)-Mn-O(4')	94.6 (1)	Mn-O(4')-C(4')	141.3 (2)
O(3)-Mn-O(5'')	161.2 (1)	Mn-O(5'')-C(4'')	127.5 (2)
O(3)-Mn-O(6)	84.1 (2)	Mn-O(1)-C(1)	118.1 (2)
O(3)-Mn-O(7)	97.7 (1)	Mn-O(3)-C(2)	117.1 (2)
O(4')-Mn-O(5'')	86.5 (1)	O(4)-C(4)-O(5)	123.7 (4)
O(1)-C(1)-O(2)	124.9 (4)	O(4)-C(4)-C(3)	119.2 (4)
O(1)-C(1)-C(2)	119.2 (4)	O(5)-C(4)-C(3)	117.0 (4)
O(2)-C(1)-C(2)	115.9 (4)		
O(3)-C(2)-C(1)	108.5 (4)		
O(3)-C(2)-C(3)	110.7 (4)		
C(1)-C(2)-C(3)	110.9 (4)		
C(2)-C(3)-C(4)	112.6 (4)		

Table IV. Dihedral Angles[a] in 1:1 Metal-Malate Complexes

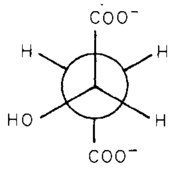
	Dihedral angle, deg			
i-j-k-l	Mn[b]	Co[c]	Zn[d]	Ca[e]
M-O(1)-C(1)-C(2)	13.8	−3.7	−4.0	−17.3
O(1)-C(1)-C(2)-O(3)	−1.2	−27.3	−26.8	−15.8
C(1)-C(2)-O(3)-M	−11.9	42.1	41.1	39.2
C(2)-O(3)-M-O(1)	14.2	−35.1	−34.7	−34.3
O(3)-M-O(1)-C(1)	−15.2	21.9	21.8	28.3
C(1)-C(2)-C(3)-C(4)	172.2	−64.9	−65.2	−70.7
O(3)-C(2)-C(3)-C(4)	−67.4	55.0	54.2	54.2

[a] A positive angle represents a clockwise rotation of the bond *kl* with respect to the bond *ij*, when viewed along the bond *jk*. [b] This work. [c] Calculated from coordinates given in ref 2. [d] See ref 4. [e] Calculated from coordinates given in ref 1.

Table V. Hydrogen Bonding Parameters

Hydrogen bond[a]	Interatomic distance, Å		Angle, deg
D-H···A	D···A	H···A	D-H-A
O(6)-H(5)···O(8)[b]	2.759 (6)	1.98	167
O(6)-H(6)···O(5)[c]	3.035 (5)	2.23	163
O(7)-H(7)···O(2)[d]	2.685 (6)	1.92	167
O(7)-H(8)···O(8)[e]	2.768 (6)	2.11	156
O(8)-H(9)···O(2)[f]	2.785 (6)	2.02	156
O(8)-H(10)···O(4)[g]	2.926 (5)	1.96	162

[a] Donor (D) and hydrogen atoms have the coordinates listed in Tables I and II. Superscripts *b-g* specify the symmetry-related positions of the acceptor (A) atoms. [b] $1 - x, y - {}^1/_2, {}^1/_2 - z$. [c] $1 - x, {}^1/_2 + y, {}^1/_2 - z$. [d] ${}^1/_2 - x, \bar{y}, {}^1/_2 + z$. [e] x, y, z. [f] $x, 1 + y, z$. [g] ${}^1/_2 - x, \bar{y}, z - {}^1/_2$.



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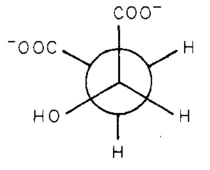

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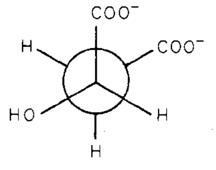

C

electrostatic and steric repulsion between the bulky negatively charged COO⁻ groups. This rotamer is expected to be favored in ionic structures and is the prevalent one observed in aqueous solutions of alkali metal malates using NMR spectroscopy.[14,15] On the other hand, conformer B is the principal species observed in an NMR study of the zinc(II) complex.[16] This conformation is favored by chelation of the hydroxyl oxygen and both carboxylate groups to the zinc(II), and is the one found in single crystals of (−)-malatodiaquozinc(II) hydrate from a crystal structure investigation.[4] This same malate conformation is found in the crystalline cobalt(II) and calcium complexes which, of course, have similar ligand–metal coordination. In the manganese(II) compound the rotamer observed is A. In contrast to the malate complexes of zinc(II), cobalt(II), and calcium the terminal carboxylate does not close to form a six-membered chelate ring with Mn(II). Quantitative comparison of the malate conformation in the various structures is indicated by the respective dihedral angles presented in Table IV. The bond lengths and bond angles (Table III) observed in the Mn(II) complex resemble those found in the other malate structures with the exception of the angle C(2)–C(3)–C(4). This bond angle has a value of 112.6 (4)° in the manganese(II) complex compared to 117.8 (3), 117.4 (6), and 116.4 (8)° in the cobalt(II), zinc(II), and calcium(II) derivatives. This angle is thus severely strained in the three malato complexes which involve a tridentate ligand and a six-membered chelate ring, but is considerably relaxed in the manganese(II) complex.

The origin of the difference in the stereochemistry of these malate compounds is not related simply to electronic configuration or size. Certainly, the Mn(II) ion which is intermediate in size between the Ca(II) and Zn(II) ions is capable of accommodating tridentate coordination by the malate moiety. This is the case in the isomorphous crystalline citrate complexes of manganese(II)[10] and magnesium(II).[17] The tridentate citrate ligand chelates these metal ions with one end carboxylate oxygen atom as well as the hydroxyl oxygen and an oxygen atom from the central carboxylate group. There are both five- and six-membered rings in the structure essentially the same as those formed in both the cobalt(II) and zinc(II) malate compounds. Similarly, Mn(II) with a d^5 configuration, Co(II) (d^7), Ni(II) (d^8), Zn(II) (d^{10}), and Mg(II) (d^0) can and are known to form numerous isostructural compounds. In fact, in many cases the Mn(II) compounds resemble the corresponding Zn(II) complexes very closely. For example, Dahl and coworkers have shown that the Mn(II), Cu(II), and Zn(II) croconate complexes, $MC_5O_5(H_2O)_3$, are isomorphous and, of course, isostructural.[18,19] In particular, the molecular dimensions of the Mn(II) and Zn(II) croconates are practically identical.

The carboxylate–metal compounds under study are crystallized from aqueous solution. As can be anticipated such solutions of metal carboxylates, where water can compete effectively for the metal ion, would contain numerous species corresponding to the many possible equilibrium reactions. The structure which crystallizes from solution will depend on the energetics and dynamics characteristic of the interacting species as well as concentration, temperature, and pH. It is not unexpected then that in these systems there may be alternative ways to arrange the constituent species in the crystal and the free energy differences in such polymorphs may indeed be small. For Mn(II) and Zn(II) the 1:1 malate complexes were crystallized from 1:1 and 1:2 metal ion–malate ion solutions, respectively, by evaporation at ambient temperatures in air. It is not unlikely or surprising that under our experimental conditions the species present in solution prior to crystallization would differ in the two cases because of differences in the Mn(II)- and Zn(II)–malate equilibria. Although the details of the solution dynamics of Mn(II)- and Zn(II)–malate interactions are not known, it is of interest to note that a careful kinetic study of the Ni(II)–malate system[20] supports tridentate malate coordination to Ni(II) in solution. Clearly then, if conditions are altered, different species as well as structures may crystallize.[21] We are not certain that polymorphs of $MC_4H_4O_5(H_2O)_2 \cdot H_2O$ (M = Mn and Zn) exist where the mode of ligand coordination differs in each from that described. Although we have not characterized other crystalline forms of the 1:1 malate (trihydrates) our search at the present has not been all inclusive and the existence of polymorphs cannot be discounted.[21,22] Indeed, it would be surprising if polymorphs did not occur in such systems, although such existence would not indicate necessarily a change in ligand–metal coordination. Alternatively, different hydrates[23] may crystallize perhaps even with a change in the number of water molecules in the primary coordination sphere. Nevertheless, because the crystallization process is a sensitive function of many factors, it is important that simple generalization concerning the stereochemistry of a given metal–carboxylate interaction be made with caution.

This view is emphasized by noting that crystalline manganese(II) acetate tetrahydrate[11] is not isostructural with the crystalline tetrahydrate acetates of cobalt(II) and nickel(II).[24] In the latter crystals each metal ion is coordinated to four water molecules and two carboxylate oxygen atoms from two different acetate groups. In the $Mn(CH_3COO)_2 \cdot 4H_2O$ crystal there are two kinds of manganese environments. One Mn(II) is coordinated by six carboxylate oxygen atoms from six different acetate ions and the other Mn(II) by four oxygen atoms from four acetate ions and two water molecules.

Registry No. $[Mn(C_4H_4O_5)(H_2O)_2] \cdot H_2O$, 56994-99-1.

Supplementary Material Available: A listing of structure factor amplitudes, five pages. Ordering information is given on any current masthead page.

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