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Crystal Structure of ((*S*)-Malato)tetraaquamagnesium(II) Hydrate. Versatility of (*S*)-Malate–Metal Ion Binding

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The crystal structure of ((*S*)-malato)tetraaquamagnesium(II) hydrate, $[\mathrm{Mg}(S\text{-}\mathrm{C_4H_4O_5})(\mathrm{H_2O})_4]\cdot\mathrm{H_2O}$, 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 unit cell dimensions a = 11.403 (9) Å, b = 15.486 (10) Å, c = 5.954 (4) Å, and Z = 4. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to a conventional R index of 0.081 for 1248 reflections. The bidentate (*S*)-malate ligand chelates the magnesium(II) ion with an α-carboxylate oxygen atom and the hydroxyl oxygen forming a planar five-membered chelate ring. The irregular octahedral coordination polyhedron around the metal ion is completed by four water molecules. The β-carboxylate group is not bound directly to Mg(II) which differs from (*S*)-malate binding observed in all other 1:1 metal (*S*)-malate compounds. However, the β-carboxylate group is indirectly attached to the Mg(II) in an outer-sphere fashion through an intramolecular hydrogen bond from a coordinated water molecule. The conformation of the (*S*)-malate ligand is synclinal, and the range in Mg–O bond lengths is 2.045 (5)–2.125 (5) Å.

Introduction

As part of a continuing study of the structural characteristics of carboxylate–metal ion binding, we have been interested in the coordination chemistry of naturally occurring hydroxy acids such as (*S*)-malic acid, $\mathrm{HOOCCHOHCH_2COOH}$. The flexibility of (*S*)-malate binding to metal ions has been demonstrated from the crystal structural investigations of the 1:1 complexes of manganese(II),[1] zinc(II),[2] cobalt(II),[3] and calcium(II).[4] There has also been a report on the structure of a 2:1 oxomolybdenum(VI) complex.[5] In these instances the (*S*)-malate ligand is found to adopt different conformations as well as different modes of metal ion binding. Four-, five-, and six-membered chelate rings have all been observed. The carboxylate interactions encountered in such structures contribute to the understanding of the coordination chemistry of metal ions in biological systems. In particular, magnesium(II) ion is known to be required in many enzyme-catalyzed reactions, but accurate structural details of magnesium(II) complexes with simple biological metabolites are lacking. It is anticipated that oxygen atoms and carboxylate groups would be strongly implicated in the binding of such "hard" cations.[6] We report here the crystal structure of ((*S*)-malato)tetraaquamagnesium(II) hydrate which reveals a unique mode of (*S*)-malate binding and further establishes the versatility of (*S*)-malate–metal ion coordination.

Experimental Section

Well-formed colorless single crystals of the title compound were grown by evaporation of a solution prepared by dissolving magnesium carbonate in an aqueous solution of (−)-malic acid (Eastman). A crystal with approximate dimensions 0.22 × 0.34 × 0.40 mm, which gave sharp optical extinction under crossed polarizers, was mounted along the longest crystal dimension. Examination of indexed Weissenberg photographs revealed orthorhombic symmetry, and the observed pattern of systematically absent reflections, h odd for $h00$, k odd for $0k0$, and l odd for $00l$, uniquely indicated the space group to be $P2_12_12_1$. The unit cell dimensions were determined at 23 ± 2 °C from a least-squares refinement of the angular settings of 12 carefully centered reflections measured with a Picker FACS-I computer (PDP-8/L) automated diffractometer using Mo Kα radiation (λ 0.71069 Å).

Crystal data for $[\mathrm{MgC_4H_4O_5(H_2O)_4}]\cdot\mathrm{H_2O}$: orthorhombic; space group $P2_12_12_1$; a = 11.403 (9), b = 15.486 (10), c = 5.954 (4) Å; V = 1051.4 Å^3; Z = 4; d_m = 1.54 (1) (by flotation), d_c = 1.557 g/mL; $F(000)$ = 520; μ(Mo Kα) = 2.2 cm^{-1}.

Data Collection. Three-dimensional intensity data were collected out to 55° in 2θ by using zirconium-filtered Mo Kα radiation. The $\theta/2\theta$ scan mode with a fixed rate of 1°/min and a scan range of 2θ(Mo Kα_1) − 1.0° to 2θ(Mo Kα_2) + 1.0° were used. The background counting time was 40 s at the start and end of each scan. The intensities of two standard reflections were monitored after each 100 reflections to check on crystal and electronic instability. A uniform increase in intensity of 13% was observed during the time that approximately half of the reflections were collected, but no variation occurred in the intensities of the standards for the remainder of the data set. A suitable correction was applied to the affected part of the data. Absorption corrections were judged to be negligible in view of the small absorption coefficient and dimensions of the crystal. The raw intensity data were assigned standard deviations and reduced to values of F_o and $\sigma(F_\mathrm{o})$ by using $I = C - (t_\mathrm{c}/2t_\mathrm{b})(B_1 + B_2)$, $F_\mathrm{o} = (I/Lp)^{1/2}$, $\sigma(I) = [C + (t_\mathrm{c}/2t_\mathrm{b})^2(B_1 + B_2) + (pI)^2]^{1/2}$, and $\sigma(F_\mathrm{o}) = (2F_\mathrm{o})^{-1}(Lp)^{-1}\sigma(I)$. In these expressions C is the total count accumulated during the scan in time t_c, B_1 and B_2 are the background counts at each end of the scan each in a time t_b, and p is taken to be 0.04. A total of 1248 reflections had $I > \sigma(I)$, and these were used in subsequent calculations.

Solution and Refinement of the Structure[7]

The structure was solved by direct methods using MULTAN. The positions of all the nonhydrogen atoms were readily evident from an E map generated from the solution of the highest figure of merit and lowest residual. The absolute configuration of the (−)-malate ligand was fixed to be S.[3] After initial isotropic and then anisotropic refinement of the nonhydrogen atoms by a full-matrix procedure, a difference Fourier synthesis revealed the positions of all the hydrogen atoms. Each hydrogen atom was assigned an isotropic thermal parameter 1.0 Å^2 greater than the isotropic thermal parameter of the atom to which the hydrogen is attached. The entire structure was further refined by full-matrix least squares although the hydrogen atom parameters were not varied. A total of 136 parameters including one scale factor were refined yielding a data:parameter ratio of 9.2:1.

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Table I. Positional Parameters[a] for $[Mg(C_4H_4O_5)(H_2O)_4]\cdot H_2O$

atom	*x*/*a*	*y*/*b*	*z*/*c*
Mg	0.00509 (2)	0.0376 (1)	0.7602 (4)
O(1)	−0.0723 (4)	0.0751 (3)	0.4613 (7)
O(2)	−0.2278 (4)	0.1272 (3)	0.2804 (7)
O(3)	−0.1652 (4)	0.0799 (3)	0.8548 (7)
O(4)	−0.1101 (4)	0.2693 (2)	0.6950 (8)
O(5)	−0.2470 (4)	0.3297 (3)	0.9099 (8)
O(6)	−0.0415 (4)	−0.0913 (2)	0.7115 (8)
O(7)	0.0359 (5)	0.0148 (3)	1.0933 (7)
O(8)	0.0744 (4)	0.1608 (3)	0.7903 (9)
O(9)	0.1677 (4)	0.0013 (3)	0.6415 (9)
O(10)	0.6356 (6)	0.6352 (4)	0.8088 (10)
C(1)	−0.1755 (5)	0.1046 (3)	0.4544 (10)
C(2)	−0.2430 (5)	0.1089 (4)	0.6778 (10)
C(3)	−0.2971 (5)	0.1973 (4)	0.7297 (10)
C(4)	−0.2094 (5)	0.2711 (4)	0.7840 (10)
H(O3)	−0.190	0.097	1.010
H(C2)	−0.310	0.064	0.672
H1(C3)	−0.353	0.190	0.872
H2(C3)	−0.348	0.217	0.585
H1(O6)	0.005	−0.139	0.770
H2(O6)	−0.120	−0.105	0.685
H1(O7)	0.046	−0.048	1.110
H2(O7)	0.110	0.040	1.135
H1(O8)	0.010	0.200	0.755
H2(O8)	0.110	0.178	0.930
H1(O9)	0.228	0.040	0.685
H2(O9)	0.203	−0.050	0.586
H1(O10)	0.558	0.655	0.820
H2(O10)	0.660	0.638	0.650

[a] The estimated standard deviations in the least significant figures are given in parentheses in this and other tables.

Table II. Thermal Parameters[a] for $[Mg(C_4H_4O_5)(H_2O)_4]\cdot H_2O$ ($\times 10^4$)

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mg	36 (1)	21.1 (7)	106 (5)	4 (1)	−2 (3)	−4 (2)
O(1)	36 (3)	30 (2)	86 (11)	12 (2)	−2 (6)	−7 (4)
O(2)	42 (3)	31 (2)	120 (13)	6 (2)	−7 (6)	−7 (4)
O(3)	48 (4)	26 (2)	82 (11)	6 (2)	−2 (6)	4 (4)
O(4)	36 (3)	19 (2)	247 (16)	1 (2)	22 (7)	5 (5)
O(5)	68 (4)	21 (2)	261 (17)	−4 (3)	38 (8)	−35 (5)
O(6)	40 (3)	23 (2)	248 (17)	2 (2)	15 (7)	1 (5)
O(7)	83 (5)	40 (3)	110 (13)	14 (3)	−1 (7)	5 (5)
O(8)	49 (4)	22 (2)	308 (20)	6 (2)	−56 (8)	−22 (5)
O(9)	41 (4)	32 (2)	269 (17)	6 (3)	18 (7)	−25 (5)
O(10)	207 (9)	52 (3)	235 (20)	−56 (4)	98 (12)	−29 (7)
C(1)	39 (5)	13 (2)	92 (17)	−2 (3)	−18 (8)	−9 (5)
C(2)	35 (4)	19 (2)	137 (18)	1 (3)	−2 (8)	−11 (6)
C(3)	33 (4)	20 (2)	169 (19)	3 (3)	5 (8)	−12 (6)
C(4)	45 (5)	18 (2)	115 (17)	−2 (3)	−7 (8)	12 (6)

atom	*B*[b]	atom	*B*	atom	*B*
H(O3)	3.0	H2(O6)	3.6	H1(O9)	4.0
H(C2)	3.0	H1(O7)	4.2	H2(O9)	4.0
H1(C3)	3.1	H2(O7)	4.2	H1(O10)	7.3
H2(C3)	3.1	H1(O8)	4.0	H2(O10)	7.3
H1(O6)	3.6	H2(O8)	4.0		

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Isotropic temperature factors are given for hydrogen atoms in Å².

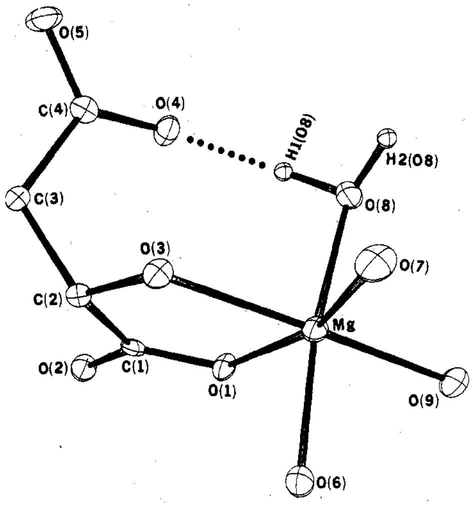

Figure 1. A view of the metal–ligand coordination polyhedron, the intramolecular hydrogen bond, and the atom-numbering scheme. Other hydrogen atoms have been omitted for clarity.

Table III. Interatomic Distances and Angles

	Distances, Å		
Mg–O(1)	2.070 (5)	C(1)–O(2)	1.246 (7)
Mg–O(3)	2.125 (5)	C(1)–C(2)	1.538 (8)
Mg–O(6)	2.086 (5)	C(2)–O(3)	1.449 (7)
Mg–O(7)	2.045 (5)	C(2)–C(3)	1.532 (8)
Mg–O(8)	2.073 (5)	C(3)–C(4)	1.553 (8)
Mg–O(9)	2.063 (5)	C(4)–O(4)	1.251 (7)
C(1)–O(1)	1.263 (7)	C(4)–O(5)	1.253 (7)

	Angles, Deg		
O(7)–Mg–O(9)	97.5 (2)	O(8)–Mg–O(3)	92.4 (2)
O(7)–Mg–O(1)	162.9 (2)	O(6)–Mg–O(3)	95.7 (2)
O(7)–Mg–O(8)	90.5 (2)	O(1)–C(1)–O(2)	125.1 (6)
O(7)–Mg–O(6)	90.8 (2)	O(1)–C(1)–C(2)	117.9 (5)
O(7)–Mg–O(3)	87.3 (2)	O(2)–C(1)–C(2)	117.0 (5)
O(9)–Mg–O(1)	99.5 (2)	O(3)–C(2)–C(1)	108.0 (4)
O(9)–Mg–O(8)	86.4 (2)	O(3)–C(2)–C(3)	112.1 (5)
O(9)–Mg–O(6)	85.4 (2)	C(1)–C(2)–C(3)	114.5 (5)
O(9)–Mg–O(3)	175.0 (3)	C(2)–C(3)–C(4)	116.1 (4)
O(1)–Mg–O(8)	88.8 (2)	O(4)–C(4)–O(5)	125.4 (6)
O(1)–Mg–O(6)	92.3 (2)	O(4)–C(4)–C(3)	118.6 (5)
O(1)–Mg–O(3)	75.6 (2)	O(5)–C(4)–C(3)	116.0 (5)
O(8)–Mg–O(6)	171.8 (2)		

The function minimized was $\sum w(|F_o| - |F_c|)^2$, where the weight, *w*, applied to each observation was taken to be $[\sigma(F_o)]^{-2}$. The structure refinement converged to a conventional R_1 index, $\sum||F_o| - |F_c||/\sum|F_o|$, of 0.081 and a weighted R_2 index, $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, of 0.075. The error in an observation of unit weight was 2.03. In the final least-squares cycle no parameter varied by more than 0.02 of its estimated standard deviation. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $(\sin\theta)/\lambda$ or $|F_o|$ indicated no unusual trends. A final difference Fourier map was essentially featureless. The neutral scattering factors of all atoms were taken from Cromer and Waber and included corrections for the real and imaginary dispersion of the magnesium atom.[8] A listing of the final observed and calculated structure factors as $10|F_o|$ and $10|F_c|$ in electrons is available as supplementary material. Final positional and thermal parameters are given in Tables I and II.

Discussion

A view of the molecular structure and atom-numbering scheme is presented in Figure 1. Bond distances and angles are given in Table III. The sixfold coordination polyhedron is approximately "octahedral" albeit quite removed from idealized O_h symmetry. The magnesium(II) coordination polyhedron consists of four water molecules, O(6), O(7), O(8), and O(9), an *α*-carboxylate oxygen, O(1), and the hydroxyl oxygen, O(3). The *β*-carboxylate group is not coordinated to any magnesium ions. This feature is in sharp contrast to that found in other 1:1 metal (*S*)-malate compounds. In the zinc(II),[2] cobalt(II),[3] and calcium(II)[4] complexes the *β*-carboxylate group is directly attached to the metal ion forming, in addition, a six-membered chelate ring. In the manganese(II)[1] compound the conformation of the ligand is different, and although the *β*-carboxylate group does not bend back to chelate the Mn(II) ion, it is bound in a polymeric fashion to two other Mn(II) ions by single bridge bonds.

The observed bond distances and angles for the MgO_6 polyhedron given in Table III are similar to the values found previously.[9-14] The mean[15] Mg–O bond length is 2.08 ± 0.01 Å. The dimensions of the (*S*)-malate ligand also resemble

Table IV. Hydrogen-Bonding Parameters

hydrogen bond[a] D-H···A	interatomic dist, Å		D-H-A, deg
	D···A	H···A	
O(3)-H(3)···O(2)[b]	2.733 (6)	1.73	178
O(6)-H1(O6)···O(4)[c]	2.821 (6)	1.87	165
O(6)-H2(O6)···O(2)[d]	2.720 (6)	1.86	152
O(7)-H1(O7)···O(10)[e]	2.652 (7)	1.76	171
O(8)-H1(O8)···O(4)[f]	2.752 (7)	1.78	178
O(8)-H2(O8)···O(5)[g]	2.712 (7)	1.89	141
O(9)-H1(O9)···O(10)[h]	3.069 (9)	2.14	165
O(9)-H2(O9)···O(5)[c]	2.824 (6)	1.93	156
O(10)-H2(O10)···O(5)[i]	2.748 (8)	1.82	157

[a] Donor (D) and hydrogen atoms have the coordinates listed in Table I. Superscripts *b–i* specify the symmetry-related positions of the acceptor (A) atoms. [b] $x, y, 1 + z$. [c] $-x, y - {}^1/_2, {}^3/_2 - z$. [d] $-{}^1/_2 - x, -y, {}^1/_2 + z$. [e] $x - {}^1/_2, {}^1/_2 - y, 2 - z$. [f] x, y, z. [g] ${}^1/_2 + x, {}^1/_2 - y, 2 - z$. [h] $1 - x, y - {}^1/_2, {}^3/_2 - z$. [i] ${}^1/_2 - x, 1 - y, z - {}^1/_2$.

those found in previous determinations.[1-4] The C(2)–C(3)–C(4) angle is 116.1 (4)° which is near the values found in the Zn(II), Co(II), and Ca(II) compounds where the (*S*)-malate ligand is tridentate. Although (*S*)-malate in the Mg(II) complex is only bidentate, the conformation of the ligand is similar to that occurring in the Zn(II) complex so that the large value of the C(2)–C(3)–C(4) bond angle may be the result of modest steric strain created by the proximity of the two carboxylate groups. In manganese(II) (*S*)-malate the two carboxylate groups are trans and this bond angle is reduced to 112.6 (4)°. The dimensions of the water molecules are typical of that found in other hydrates[10] containing magnesium(II) ion. The average[15] O–H, Mg···H, and H···H lengths involving water molecules are 0.96 ± 0.01, 2.63 ± 0.04, and 1.57 ± 0.01 Å, respectively.

The crystal structure consists of isolated ionic $\mathrm{Mg}(S\text{-}\mathrm{C_4H_4O_5})(\mathrm{H_2O})_4$ units held together by an extensive network of hydrogen bonds which involve all of the water molecules including the lone lattice water of hydration, O(10), as well as the hydrogen from the hydroxyl group, O(3). The uncoordinated carboxylate group, O(4)–C(4)–O(5), is also heavily involved in the hydrogen-bonding scheme. Of particular interest is the presence of the rather strong intramolecular hydrogen bond O(8)–H1(08)···O(4). The pertinent hydrogen-bonding parameters are summarized in Table IV.

Although the β-carboxylate group is not directly bound to the magnesium(II) ion, it is coordinated to the Mg(II) in an outer-sphere fashion through the hydrogen bond O(8)–H1-(O8)···O(4) from the coordinated water molecule, O(8). This outer-sphere coordination through a hydrogen bond is reminiscent of the structural models proposed for the 1:1 and 1:2 nickel(II) and manganese(II) complexes of adenosine triphosphate.[16-19] In these instances on the basis of NMR shift data the paramagnetic metal ions, which are attached to the phosphate oxygens of ATP, are thought to bind the adenine ring indirectly through an intramolecular hydrogen bond from a coordinated water molecule. Attempts at establishing a similar water-bridged structure for MgATP, however, have failed since the effect of the diamagnetic Mg(II) ion is too small to record such interactions.[18] Although outer-sphere coordination[20] through an intramolecular hydrogen bond has been observed in the solid state with other metal ions,[22-25] to our knowledge this structure represents the first crystallographic evidence of magnesium(II) utilizing this mode of binding. It is apparent that in certain cases hydrogen bonding can compete effectively with a metal ion for coordination to a donor site.

The five-membered chelate ring Mg–O(1)–C(1)–C(2)–O(3) is essentially planar, which differs from the behavior of the corresponding five-membered chelate rings in all other 1:1 (*S*)-malate complexes, where buckling of the rings occurs to varying extents.[1] The five atoms Mg, O(1), C(1), C(2), and O(3) lie in the plane $0.3438X - 0.9296Y - 0.1327Z + 1.1660 = 0.0$ with deviations from this plane of +0.004, +0.003, −0.011, +0.015, and −0.012 Å, respectively. We anticipate that crystal packing may be largely responsible for the observed differences in the conformations of (*S*)-malate–metal ion chelate rings, but it would be of great interest to learn if any such differences survive in solution.

The ligand conformation is specified by the dihedral angles C(1)–C(2)–C(3)–C(4) and O(3)–C(2)–C(3)–C(4). In the magnesium(II) compound these angles are −69.0 and 54.5°, respectively, and thus fix the ligand conformation to be synclinal,[26] which is similar to that found in the zinc(II) complex (corresponding dihedral angles −65.2, 54.2°)[2] but differs from the antiperiplanar conformation found in the manganese(II) complex (corresponding dihedral angles 172.2, −64.4°).[1] In each instance given, a positive dihedral angle represents a clockwise rotation of the bond (C(3)–C(4) with respect to the bond C(1)–C(2) or O(3)–C(1) when the structure is viewed along the C(2)–C(3) bond.

The differences in ligand binding and conformations observed in metal (*S*)-malate compounds suggest that the selectivity and specificity normally encountered with metal ions in more complex biological systems may also be present in simpler systems.[27] We are pursuing research to examine if this discrimination in (*S*)-malate–metal ion binding extends to the solution state.

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Registry No. $[\mathrm{Mg}(S\text{-}\mathrm{C_4H_4O_5})(\mathrm{H_2O})_4]\cdot\mathrm{H_2O}$, 71341-66-7; $\mathrm{Mg}(S\text{-}\mathrm{C_4H_4O_5})\cdot 5\mathrm{H_2O}$ (salt), 71369-98-7.

Supplementary Material Available: A listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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(20) We should emphasize that the outer-sphere coordination through an intramolecular hydrogen bond postulated to occur in metal ATP complexes and observed here for magnesium (*S*)-malate involves an indirect metal–water–ligand interaction at one site *in combination* with a *direct* ligand contact at another site. The type of "outer-sphere" coordination

described by Sternglanz et al.[21] occurring in barium adenosine 5′-phosphate heptahydrate where a completely hydrated barium ion is attached to the adenosine 5′-phosphate moiety *only* through hydrogen bonds from coordinated water molecules is not analogous to the above situations. In fact, such indirect metal–water–anion interactions, where there is not other direct ligand metal binding, are not uncommon and occur usually whenever the anion contains suitable hydrogen bonding sites. For example, in $[Mg(H_2O)_6]H_2EDTA$[12] and $[Mg(H_2O)_6]Cr_2O_7{\cdot}2(CH_2)_6N_4$[13] the $Mg(H_2O)_6^{2+}$ ion is hydrogen bonded to dihydrogen ethylenediaminetetraacetate and hexamethylenetetramine, respectively, although no direct Mg(II) interactions with H_2EDTA or $(CH_2)_6N_4$ exist.

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Coordination Chemistry of Microbial Iron Transport Compounds. 17.[1] Preparation and Structural Characterization of Tris(*N*-methylthiobenzohydroxamato)cobalt(III), -chromium(III), -iron(III), and -manganese(III)

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The preparation and isolation of tris(*N*-methylthiobenzohydroxamato)cobalt(III), -chromium(III), -iron(III), and -manganese(III) are reported. The structures of these four compounds have been determined by single-crystal X-ray diffraction using automated-counter methods. The complexes are isostructural in the cis configuration, with the metal environment being a trigonally distorted octahedron, though the manganese complex displays considerable tetragonal distortion. The twist angle (the projection of the top trigonal face on the bottom one) averages 54.9° for the Co complex, 48.7° for the Cr, 42.9° for the Fe, and 46.0° for the Mn; these are 60° and 0° for octahedral and trigonal-prismatic structures, respectively. The M–S bond lengths average 2.203 (3) Å for Co, 2.367 (8) Å for Cr, and 2.445 (14) Å for Fe, while the M–O bond lengths average 1.935 (5), 1.976 (6), and 1.990 (5) Å, respectively. The axial (tetragonal axis) and equatorial bond lengths for the Mn–S bonds are 2.584 (1) and 2.339 (15) Å and for Mn–O are 2.132 (2) and 1.950 (9) Å, respectively. The average S–M–O chelate angles are 87.3 (3), 82.6 (1), 80.1 (2), and 80.6 (11)° for M = Co, Cr, Fe, and Mn. The changes in M–S bond lengths and trigonal twist angles of the complexes are ascribed to ligand field effects. The structure of $Cr(MTB)_3$ (MTB = *N*-methylthiobenzohydroxamate anion) was solved by direct phasing methods followed by full-matrix least-squares and Fourier techniques, while the other structures were refined by using atomic coordinates from the Cr complex. Green crystals of $Co(MTB)_3$ conform to the space group $P2_1/n$ with $a = 11.805$ (2), $b = 12.182$ (2), $c = 18.230$ (4) Å, and $\beta = 92.12$ (2)°; $V = 2620$ (2) Å^3; $Z = 4$; $\rho_{calcd} = 1.41$ and $\rho_{obsd} = 1.41$ (1) g cm^{-3}. Refinement using the 3862 reflections with $F^2 > 3\sigma(F^2)$, with all nonhydrogen atoms given anisotropic temperature factors, gave $R = 3.4\%$ and $R_w = 4.2\%$. Green crystals of $Cr(MTB)_3$ have $a = 11.698$ (4), $b = 12.080$ (3), $c = 18.851$ (6) Å, and $\beta = 93.81$ (3)°; $V = 2658$ (3) Å^3; $\rho_{calcd} = 1.38$ and $\rho_{obsd} = 1.36$ (1) g cm^{-3}. The 3207 reflections with $F^2 > 3\sigma(F^2)$ gave $R = 3.2$ and $R_w = 4.2\%$. Violet crystals of $Fe(MTB)_3$ have $a = 11.668$ (2), $b = 12.037$ (2), $c = 19.013$ (4) Å, and $\beta = 94.94$ (2)°; $V = 2661$ (2) Å^3; $\rho_{calcd} = 1.38$ and $\rho_{obsd} = 1.36$ (1) g cm^{-3}. The 3070 reflections with $F^2 > 3\sigma(F^2)$ gave $R = 3.3\%$ and $R_w = 3.8\%$. Green crystals of $Mn(MTB)_3$ have $a = 11.604$ (3), $b = 12.044$ (3), $c = 18.990$ (6) Å, and $\beta = 94.87$ (2)°; $V = 2644$ (3) Å^3; $\rho_{calcd} = 1.39$ and $\rho_{obsd} = 1.38$ (1) g cm^{-3}. The 3452 reflections with $F^2 > 3\sigma(F^2)$ gave $R = 3.5\%$ and $R_w = 3.8\%$.

Introduction

The siderophores are low-molecular-weight compounds which are manufactured by microbes in order to facilitate the uptake of ferric iron.[3,4] The insolubility of ferric hydroxide at physiological pH [$(Fe^{3+}) \simeq 10^{-18}$ M at pH 7 on the basis of $K_{sp} \simeq 10^{-39}$][5] and the essential nature of iron for microbial growth apparently engendered the production of a wide range of powerful sequestering agents—the siderophores. The common functional groups in these siderophores are hydroxamate, as in ferrichromes[6] and ferrioxamines,[7] and catecholate, as in enterobactin.[8] A potentially new type of chelate moiety belonging to the siderophore class of compounds came with the discovery that cupric and ferric complexes of *N*-methylthioformhydroxamic acid could be isolated from culture broths of *Pseudomonas fluorescens* grown on *n*-paraffin or sucrose as the only source of carbon.[9,10] The three siderophore chelate groups are shown in Figure 1.

We have reported the preparation and resolution of the thiobenzohydroxamato complexes of Cr(III), Fe(III), and Co(III),[11] where we predicted the compounds to have a cis geometry on the basis of their circular dichroism spectra and physical properties. Subsequently, Murray et al. have reported electrochemical and magnetic studies of tris(thiobenzohydroxamato)iron(III)[12] and the crystal structure of tris(*N*-methylthioformhydroxamato)iron(III),[13] which was found to have the cis geometry. Leong and Bell[14] have reported the synthesis and separation of the geometrical isomers of *N*-methylthioformhydroxamate complexes of Cr(III), Rh(III), and Pt(II). In a contradiction of Murray's report,[12] we have found that tris(thiobenzohydroxamato)iron(III) is high spin from 5 K to room temperature and, under suitable conditions, undergoes reversible electrochemical reduction.[15]

High-spin ferric iron and manganic ion are identical in ionic radius, while chromic and low-spin cobaltic ions are somewhat smaller.[16] The geometries of the metal(III) complexes are of interest both to characterize the coordination sites of the siderophore complexes and to determine the fundamentals of the coordination chemistry of the thiohydroxamate–transition-metal complexes, including the degree to which other complexes mimic the naturaly occurring ferric siderophores. The influence of the d-electron configuration on the coordination geometry within this isostructural series is a strong secondary interest. We report here the preparation and single-crystal structural analyses of tris(*N*-methylthiobenzohydroxamato)cobalt(III), -chromium(III), -iron(III), and -manganese(III).

Experimental Section

Sodium *N*-methylthiobenzohydroxamate was prepared by a method analogous to that used to prepare the N-unsubstituted acid salt.[17] The tetrahydrofuran adduct of chromic chloride, $CrCl_3{\cdot}3THF$, was