ROBERTSON, G. B., TUCKER, P. A. & WHIMP, P. O. (1981). *Inorg. Chem.* **19**. In the press.

ROBINSON, S. D. & SHAW, B. L. (1965). *J. Chem. Soc.* pp. 4997–5001.

STALICK, J. K. & IBERS, J. A. (1970). *J. Am. Chem. Soc.* **92**, 5333–5338.

TUCKER, P. A., SCUTCHER, W. & RUSSELL, D. R. (1975). *Acta Cryst.* B**31**, 592–595.

WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 101–102. Cambridge Univ. Press.

ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

The Structure of *trans*-Diaquabis[(±)-hydrogen malato]cobalt(II) Dihydrate

BY ANASTAS KARIPIDES

Department of Chemistry, Miami University, Oxord, Ohio 45056, *USA*

Abstract. $[Co\{(\pm)\text{-}C_4H_5O_5\}_2(H_2O)_2].2H_2O$, $C_8H_{14}CoO_{12}.2H_2O$, triclinic, $P\bar{1}$, $a = 7.406$ (1), $b = 7.647$ (1), $c = 7.362$ (1) Å, $\alpha = 99.12$ (1), $\beta = 103.73$ (1), $\gamma = 63.72$ (1)°, $V = 362.5$ Å^3, $Z = 1$, $d_c = 1.82$, $d_m = 1.80$ Mg m^{-3}, μ(Mo $K\alpha$) = 1.31 mm^{-1}, $R = 0.026$ and $R_w = 0.044$ for 1250 counter-collected reflections. The sixfold coordination polyhedron around the Co^{2+} ion consists of α-carboxylate and hydroxyl O atoms from each of two hydrogen malate ligands and two water molecules (*trans* configuration). The molecular symmetry is $\bar{1}$.

Introduction. Suitable crystals of the title compound for X-ray diffraction were grown by evaporation of an aqueous solution of the salt which had been prepared from the reaction of cobalt(II) carbonate and (±)-malic acid. A crystal with approximate dimensions $0.15 \times 0.20 \times 0.20$ mm, which gave sharp optical extinction under crossed polarizers, was used. Unit-cell dimensions and X-ray intensity data were obtained using an automated diffractometer equipped with Zr-filtered Mo $K\alpha$ radiation. 1281 independent reflections out to 50° in 2θ were measured using the θ–2θ scan technique.

The raw intensity data were assigned estimated standard deviations and reduced to values of F_o and $\sigma(F_o)$. 1250 reflections had $F_o > \frac{1}{2}\sigma(F_o)$ and were used in the structure solution and refinement. The structure was solved using conventional heavy-atom methods. With $Z = 1$, the formula unit is required to have crystallographic $\bar{1}$ symmetry. There are two independent water molecules and one independent hydrogen malate in the asymmetric unit. Refinement was by a full-matrix least-squares procedure, although the H atom parameters were not varied. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight, w, was taken to be $|\sigma(F_o)|^{-2}$. The structure converged to a

conventional R index, $\sum||F_o| - |F_c||/\sum |F_o|$, of 0.026 and a weighted R_w index, $[\sum w(|F_o| - |F_c|)^2/ \sum w|F_o|^2]^{1/2}$, of 0.044. The goodness-of-fit was 1.49. In the last cycle of least-squares refinement the largest shift in any positional or thermal parameter was less than 5×10^{-3} times its own estimated standard deviation. A total of 106 parameters including one scale factor was refined yielding a data:parameter ratio of 11.8:1. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of F_o, sin θ/λ or Miller indices indicated no unusual trends. The final difference map was essentially

Table 1. *Fractional positional parameters and their standard deviations* ($\times 10^4$ *for nonhydrogen atoms*; $\times 10^3$ *for hydrogen atoms*)

The isotropic temperature factors, B_{eq} (in Å^2), for the nonhydrogen atoms were calculated from the anisotropic coefficients following the definition given by Hamilton (1959).

	x	y	z	B_{eq}
Co	0	0	0	1.75
O(1)	1373 (2)	1283 (2)	−1150 (2)	2.13
O(2)	3651 (2)	2532 (2)	−608 (2)	2.28
O(3)	1589 (2)	971 (2)	2341 (2)	2.19
O(4)	3129 (3)	2420 (2)	5823 (2)	3.09
O(5)	2476 (4)	5524 (2)	5975 (2)	4.52
O(6)	−2555 (2)	2695 (2)	263 (2)	2.82
O(7)	2426 (3)	−996 (2)	5318 (2)	3.61
C(1)	2600 (3)	1877 (3)	−66 (3)	1.75
C(2)	2847 (3)	1819 (3)	2048 (3)	1.70
C(3)	2275 (3)	3890 (3)	2962 (3)	2.28
C(4)	2659 (3)	4012 (3)	5065 (3)	1.97
H(O3)	212	37	337	
H(O4)	333	258	709	
H(C2)	432	108	251	
H1(C3)	316	430	265	
H2(C3)	86	462	252	
H1(O6)	−370	270	23	
H2(O6)	−238	338	121	
H1(O7)	189	−22	628	
H2(O7)	236	−210	545	

flat. The neutral scattering factors of all atoms were taken from *International Tables for X-ray Crystallography* (1974) and included corrections for the real and imaginary anomalous dispersion of Co. In addition to local programs of the IBM 370/148 and HP 3000 computers, the following programs were used: *FORDAP* (Zalkin, 1980), *ORFLS* and *ORFFE* (Busing, Martin & Levy, 1962, 1964), and *ORTEP* (Johnson, 1965). The final positional parameters are given in Table 1.*

Discussion. A view of the structure with the atom-numbering scheme is shown in Fig. 1. Bond distances and angles are given in Table 2. The hydrogen malate moiety acts as a bidentate ligand and chelates the Co^{2+} ion through the carboxylate O(1) atom and the hydroxyl O(3) atom to form the five-membered chelate ring Co—O(1)—C(1)—C(2)—O(3). The β-carboxylic acid group is not coordinated to the metal ion. The irregular octahedral coordination polyhedron about the Co^{2+} has $\bar{1}$ crystallographic symmetry and consists of malate O(1), O(1^i) and O(3^i) atoms and water O(6) and O(6^i) atoms.

The dimensions of the malate moiety resemble those found in previous investigations (Karipides & Reed, 1976; Versichel, Van de Mieroop & Lenstra, 1978; Karipides, 1979; Lenstra & Van Havere, 1980). However, of more particular interest is the comparison of structural features in the title compound with malate–Co^{2+} coordination in the neutral salt, cobalt *S*-malate trihydrate (Kryger & Rasmussen, 1972). The neutral 1:1 racemic or optically active Co^{II} malates are readily prepared from the corresponding acid malate

salts on further neutralization with cobalt carbonate or hydroxide. Comparison provides some indication as to the differences which occur between hydrogen malate(1−) and malate(2−) coordination to a common cation. The conformations of the five-membered chelate rings as well as the malate ligands in the two compounds are summarized in Table 3.

In the racemic cobalt hydrogen malate the ligand conformation, which is specified by the dihedral angle C(1)—C(2)—C(3)—C(4) of −174·0° (Table 3), is antiperiplanar, which differs sharply from the synclinal conformation (dihedral angle −64·8°) in cobalt *S*-malate (Kryger & Rasmussen, 1972; Testa, 1979). This difference results because the β-carboxylate group in cobalt *S*-malate is also coordinated to the Co^{2+} ion and the synclinal conformation is favored for tridentate malate coordination (Karipides & Reed, 1976). The five-membered chelate ring Co—O(1)—C(1)—C(2)—O(3) in the acid malate salt is considerably closer to planarity than the corresponding extensively buckled ring in the neutral salt. It is apparent that considerable reorganization of the molecular structure occurs during the formation of a neutral cobalt malate from the corresponding acid malate salt.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35719 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
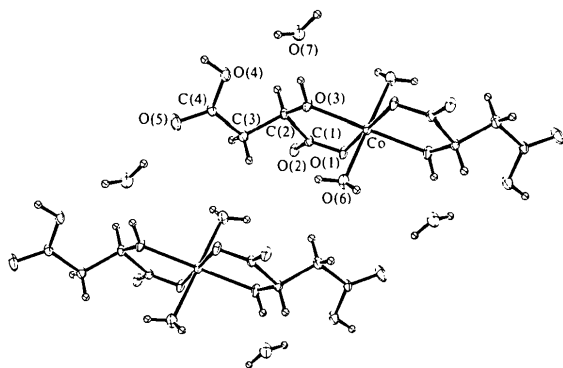
Table 2. *Bond distances* (Å) *and angles* (°)

The superscript (i) refers to the operation $-x,-y,-z$.

Co—O(1)	2·066 (1)	Co—O(3)	2·076 (1)
Co—O(6)	2·112 (1)	C(1)—O(1)	1·255 (2)
C(1)—O(2)	1·253 (2)	C(1)—C(2)	1·529 (2)
C(2)—O(3)	1·418 (2)	C(2)—C(3)	1·531 (3)
C(3)—C(4)	1·502 (3)	C(4)—O(4)	1·290 (2)
C(4)—O(5)	1·209 (2)		

O(1)—Co—O(3)	77·03 (5)	O(1) Co O(6)	91·85 (6)
O(3)—Co—O(6)	87·09 (6)	O(1^i)—Co—O(3)	102·97 (5)
O(1^i)—Co—O(6)	88·15 (6)	O(3^i)—Co—O(6)	92·91 (6)
Co—O(1)—C(1)	118·1 (1)	Co—O(3)—C(2)	117·9 (1)
O(1)—C(1)—O(2)	123·9 (2)	C(2)—C(1)—O(1)	119·0 (2)
C(2)—C(1)—O(2)	117·1 (2)	C(1) C(2)—C(3)	109·4 (1)
C(1)—C(2)—O(3)	107·6 (2)	C(3)—C(2)—O(3)	112·6 (2)
C(2)—C(3)—C(4)	114·8 (1)	O(4)—C(4)—O(5)	122·6 (2)
C(3)—C(4)—O(5)	121·8 (2)	C(3)—C(4)—O(4)	115·6 (2)

Table 3. *Conformations of chelate rings and malate moieties in* Co^{2+}*–malate compounds*

The torsion angles given below follow the convention of Klyne & Prelog (1960).

	[Co[(±)-	[Co(S-
i–j–k–l	C₄H₅O₅]₂].4H₂O	C₄H₄O₅)].3H₂O
Co—O(1)—C(1)—C(2)	−6·3°	−3·6°
O(1)—C(1)—C(2)—O(3)	2·3	−27·3
C(1)—C(2)—O(3)—Co	2·7	42·1
C(2)—O(3)—Co—O(1)	−4·4	−35·1
O(3)—Co—O(1)—C(1)	5·8	21·9
C(1)—C(2)—C(3)—C(4)	−174·0	−64·8
O(3)—C(2)—C(3)—C(4)	66·4	55·0

Fig. 1. A view of the crystal structure showing the coordination polyhedron, ligand conformation and mode of ligand–Co^{2+} binding.

Table 4. *Hydrogen-bond distances* (Å) *and angles* (°)

Donor (*D*) and hydrogen atoms have the coordinates listed in Table 1. Superscripts specify the symmetry-related positions of the acceptor (*A*) atoms.

(ii)	$x, y, 1 + z$	(v)	$x, y - 1, z$
(iii)	$x - 1, y, z$	(vi)	x, y, z
(iv)	$-x, 1 - y, 1 - z$		

	$D \cdots A$	$H \cdots A$	$\angle D - H \cdots A$
O(3)–H(O3)···O(7^{vi})	2·650 (2)	1·82	160
O(4)–H(O4)···O(2^{ii})	2·557 (2)	1·66	170
O(6)–H1(O6)···O(2^{iii})	2·784 (2)	1·97	164
O(6)–H2(O6)···O(5^{iv})	2·886 (2)	2·11	156
O(7)–H1(O7)···O(1^{ii})	2·995 (2)	2·08	166
O(7)–H2(O7)···O(5^{v})	2·763 (2)	1·88	173

Besides ionic interactions, the crystal structure is stabilized by an extensive network of hydrogen bonds which involve all the H atoms attached to O atoms in the structure. Hydrogen-bonding parameters are given in Table 4.

References

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

International Tables for X-ray Crystallography. (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794 (revised). Oak Ridge National Laboratory, Tennessee.

KARIPIDES, A. (1979). *Inorg. Chem.* **11**, 3034–3037.

KARIPIDES, A. & REED, A. T. (1976). *Inorg. Chem.* **15**, 44–47.

KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.

KRYGER, L. & RASMUSSEN, S. E. (1972). *Acta Chem. Scand.* **26**, 2349–2359.

LENSTRA, A. T. H. & VAN HAVERE, W. (1980). *Acta Cryst.* **B36**, 156–158.

TESTA, B. (1979). *Principles of Organic Stereochemistry*, pp. 86–87. New York: Marcel Dekker.

VERSICHEL, W., VAN DE MIEROOP, W. & LENSTRA, A. T. H. (1978). *Acta Cryst.* **B34**, 2643–2645.

ZALKIN, A. (1980). Unpublished.