References

CLEGG, W. (1981). Acta Cryst. A37, 22-28.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.

OLAH, G. A. & OSWALD, A. A. (1960). Can. J. Chem. 38, 1428-1430.

Acta Cryst. (1984). C40, 1152-1154

Tetraaquabis(hydrogen maleato)nickel(II), $[Ni(C_4H_3O_4)_2(H_2O_4)]$

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Abstract. $M_r = 360.9$, triclinic, $P\overline{1}$, Z = 1, a =b = 9.731 (2), c = 5.170 (2) Å, α = 7.309(3)105.97 (3), $\beta = 87.12$ (3), $\gamma = 117.05$ (2)°, V = $D_x = 1.911 \text{ Mg m}^{-3}$ $D_m = 1.890,$ $313.6 (4) Å^3$, (flotation in CHBr₃/toluene), Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 1.61 \text{ mm}^{-1}$, F(000) = 186, room temperature, R_w = 0.036 for 1336 reflections with $I \ge 2\sigma(I)$. The nickel ion is sixfold coordinated by oxygen atoms in a slightly distorted octahedron. The hydrogen maleate ion (HM) behaves as a unidentate ligand to the metal. A very short asymmetric intramolecular H bond [2.438 (3) A] connects the hydroxyl-group O atom of the non-ionized carboxyl group with an O atom of the ionized one, effectively closing a non-planar seven-membered ring. A three-center bifurcated donor H bond is observed.

Crystals of tetraaquabis(hydrogen Introduction. maleato)metal, $M(C_4H_3O_4)_2.4H_2O$ with M=Mn, Co, Zn, Ni, Fe have been investigated in the past by one of us (MPG) and co-workers but, except for Mn^{II}-(C₄H₃O₄)₂.4H₂O (Gupta & Mahanta, 1978), results of these studies have not been published. These crystals are isostructural and the purpose of the studies was to determine the effect of different metal ions on the geometry of the HM ion, as well as the scheme of hydrogen bonds in the crystals. However, as hydrogen atoms in the studies could not be properly located, the conclusions remained indecisive. Similar investigations by Antsishkina, Porai-Koshits & Guseinov (1974) equally remained inconclusive. The present work, therefore, reports on a new investigation of the nickel compound Ni($C_4H_3O_4$), 4H₂O. Crystals were grown from a solution of the compound in water by slow

SHELDRICK, G. M. (1983). SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. Univ. of Göttingen, Federal Republic of Germany.

VETTER, H.-J., STRAMETZ, H. & NÖTH, H. (1963). Angew. Chem. 75, 417-418.

WEISS, J. & EISENHUTH, W. (1967). Z. Naturforsch. Teil B, 22, 454-455.

evaporation. The solution was prepared by addition of maleic acid to nickel carbonate.

Experimental. 1375 reflections up to $\theta = 27^{\circ}$ measured, CAD-4 diffractometer, Μο Κα Enraf-Nonius radiation, graphite-crystal monochromator, ω/θ scan, scan angle $(1.0 + 1.5 \tan\theta)^\circ$, aperture of detection unit 2.0 mm. Lattice parameters from angle settings of 25 high-order reflections. 3 intensity and orientation control reflections measured every 2 h, no significant drift. Because of small size of crystal $(0.1 \times 0.1 \times$ 0.15 mm) and low μ no absorption correction. $-9 \le h \le 9$, $-12 \le k \le 11$, $0 \le l \le 6$. Earlier workers had used the space group $P\overline{1}$, but as intensity statistics showed an acentric distribution, we started the determination in P1. Structure solved by MULTAN (Germain, Main & Woolfson, 1971). Most likely E map with 200 terms revealed all non-hydrogen atoms. Data refined by least squares on F using Gauss-Seidel block method (Sparks, 1974), and Enraf-Nonius SDP package (Frenz, 1978), giving a weight to each reflection based on counting statistics. Even though decreased satisfactorily, no hydrogen atoms R could be found and the two HM ions had differences in geometries larger than was considered physically acceptable. Since there is no a priori reason to believe that the two HM ions, acting as unidentate ligands to the metal, would be significantly different, we changed the space group to $P\overline{1}$. Refinement proceeded smoothly and a difference Fourier map revealed all hydrogen atoms; their inclusion in further least-squares refinements, with fixed thermal temperature factors (2.5 Å^2) for H atoms, brought $R_{\rm w}$ to 0.036 and conventional R to 0.030, $w = 1/\sigma^2(F)$. Max. $\Delta/\sigma = 0.3$, max. peak, representing max. noise level, in final difference map, $0.3 \text{ e} \text{ Å}^{-3}$. Atomic scattering factors from International Tables for X-ray Crystallography (1974). Refined

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atomic coordinates* are given in Table 1, the numbering scheme of atoms in Fig. 1.

Discussion. The Ni^{II} cation is at a center of symmetry, coordinated by six oxygen atoms forming a slightly distorted octahedron (Table 2). Four of the O atoms are donated by the water molecules [O(W1) and O(W2)] and two by the HM ions [O(1)]. The nickel–oxygen distances and oxygen–nickel–oxygen angles are normal.

Bond lengths and valence angles in the HM ion are given in Table 3. At first sight the HM ion has approximately $C_{2\nu}$ symmetry with the pseudo-mirror plane perpendicular to C(2)=C(3). As would be expected, C(1)-C(2) and C(3)-C(4), being singlebonded $C(sp^2)-C(sp^2)$ linkages, are short, while the carboxyl group O(3)C(4)O(4), being non-ionized, has significantly different C-O distances. The carboxyl group O(1)C(1)O(2) is ionized and again the C-O distances are different. Kanters, Kroon, Peerdeman & Schoone (1967) had observed that in the COO⁻ groups of α -hydroxy acids the C–O bonded to the cation is shorter than the other C–O. In the title compound O(1)is the only oxygen atom which takes part in the coordination octahedron around the metal and indeed C(1)-O(1) is shorter than C(1)-O(2). An alternative explanation, however, is that C(1)-O(2) is slightly elongated because O(2) takes part in an internal H bond (see below). Two arguments are in favor of this view. Firstly, the metal-coordinated C(1)-O(1) has a length (1.248 Å) very close to the value (1.245 Å) observed (Van Havere, Lenstra & Geise, 1980) in a number of malate salts for CO bonds not involved in metal coordination. Secondly, in magnesium bis(hydrogen maleate) hexahydrate (Gupta, Van Alsenov & Lenstra, 1984), none of the O atoms of the maleate moiety participates in the metal coordination and yet the CO bond lengths of the COO⁻ group are different (1.279 and 1.221 Å). In the latter compound the longer bond is also involved in an internal H bond. O(3)donates a hydrogen atom to O(2) in the HM ion and this intramolecular hydrogen bond effectively closes a seven-membered ring, which is not quite planar. The four C atoms are coplanar, the largest deviation being 0.006 (3) Å. Atoms in the seven-membered ring deviate from planarity: 0.025 (3) Å for C(4), 0.025 (3) Å for O(3) and 0.019(3) Å for C(2). C(2) is in the plane of its adjacent carboxyl group as is C(3). Dihedral angles between the least-squares plane of the four C atoms and the carboxyl planes are $2 \cdot 3$ (1)° [C(1) O(1) O(2)] and $2 \cdot 8$ (1)° [C(4) O(3) O(4)]. The non-planarity of the HM ion lowers the symmetry of the C and O backbone

Table 1. Positional parameters in fractions of the cell edges with e.s.d.'s in parentheses

Equivalent isotropic temperature parameters were calculated according to Lipson & Cochran (1968): $B_{eq} = 8\pi^2 (U_{11}^o U_{22}^o U_{33}^o)^{1/3}$, assuming equal volume of the 50% probability region. All anisotropic thermal parameters were physically acceptable.

H(j,x) with j = 1,2 is attached to atom x.

	x	У	z	$B_{eq}/B_{1so}(\dot{A}^2)$
Ni	0.0000	0.0000	0.0000	1.38
O(W1)	0.2302 (2)	0.0976 (2)	0.3126 (3)	1.90
D(W2)	-0.1768 (2)	0.0752 (2)	0.2523(3)	1.87
D(1)	0.1420 (2)	0.2014 (2)	-0.1404(3)	1.81
D(2)	0.1071 (3)	0.3797 (2)	0.2041(3)	2.34
D(3)	0.2121 (3)	0.6675 (2)	0.3422 (4)	2.56
D(4)	0-3977 (3)	0.8734 (2)	0.1886 (4)	2.49
C(1)	0.1706 (3)	0-3411 (2)	-0.0242 (4)	1.68
C(2)	0.2893 (3)	0-4659 (3)	-0.1657 (4)	1.94
C(3)	0.3524 (3)	0.6238 (2)	-0.0885 (5)	2.03
C(4)	0.3218 (3)	0.7297 (2)	0.1622 (5)	1.92
H(C2)	0.322 (4)	0.426 (3)	-0.335 (5)	2.50
H(C3)	0-423 (4)	0.676 (3)	-0.222 (5)	2.50
H(O3)	0.163 (4)	0.564 (3)	0.322 (5)	2.50
H(1,OW1)	0.204 (4)	0.124 (3)	0.464 (5)	2.50
H(2,OWI)	0.259 (4)	0.028 (3)	0.301 (5)	2.50
H(1,OW2)	-0.156 (4)	0.151 (3)	0.292 (5)	2.50
H(2,OW2)	-0.304 (3)	0.022 (3)	0.225 (5)	2.50

Table 2. The coordination of the nickel cation

Distances are in Å, angles* in degrees, e.s.d.'s in parentheses.[†]

Ni-O(1)	2.074 (1)	O(1)-Ni-O(W1)	92.3 (1)
Ni-O(W1)	2.078 (1)	O(1)-Ni-O(W2)	96.7 (1)
Ni-O(<i>W</i> 2)	2.018 (1)	O(W1)-Ni-O(W2)	90.5 (1)

* Other angles are either 180° or supplementary to those given.

 \dagger E.s.d.'s may be underestimated by a factor of three, because in the Enraf-Nonius *SDP* program series the uncertainties in the cell parameters are neglected.

Table 3. Bond lengths (Å) and valence angles (°) with e.s.d.'s in parentheses

O(1)-C(1)	1.248 (1)	O(1)-C(1)-O(2)	123.3 (1)
O(2) - C(1)	1.269 (1)	O(1)-C(1)-C(2)	116.5 (1)
O(3)–C(4)	1.292 (1)	O(2)-C(1)-C(2)	120.2(1)
O(4)–C(4)	1.216 (1)	O(3) - C(4) - O(4)	121.3 (1)
		O(3)-C(4)-C(3)	120.0 (1)
C(1)–C(2)	1.493 (1)	O(4) - C(4) - C(3)	118.7 (1)
C(2)–C(3)	1.330(1)	C(1)-C(2)-C(3)	130-5 (1)
C(3)–C(4)	1.496 (1)	C(2)-C(3)-C(4)	130.9 (1)
		C(1)-C(2)-H(C2)	114.0 (6)
C(2)–H(C2)	0.92 (1)	C(3)-C(2)-H(C2)	115.5 (6)
C(3)–H(C3)	0.96 (1)	C(2)-C(3)-H(C3)	113.5 (6)
		C(4)-C(3)-H(C3)	115.5 (6)
O(3)-H(O3)	0.88(1)	O(2)-H(O3)-O(3)	162.9 (1.0)
O(3)···O(2)	2.438 (1)	C(4) - O(3) - H(O3)	119.6 (7)



Fig. 1. Numbering scheme and shape of the complex tetraaquabis(hydrogen maleato)nickel(II).

^{*} Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39314 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

TETRAAQUABIS(HYDROGEN MALEATO)NICKEL(II)

Table 4. Hydrogen bonds in $Ni(C_4H_3O_4)_2.4H_2O_4$

Distances in Å, angles in degrees with e.s.d.'s in parentheses. D represents donor, A acceptor.

D	A A at	D-H	HA	$D \cdots A$	$D-H\cdots A$
O(W1) - H(1, OW1)	O(1) x, y, z + 1	0.80(1)	2.08(1)	2.876 (1)	178 (1)
O(W1) - H(2, OW1)	O(4) x, y - 1, z	0·78 (1)	$2 \cdot 12(1)$	2.872 (1)	163 (1)
O(W2)-H(2,OW2)	O(4) $x = 1, y = 1, z$	0.83 (1)	1.98 (1)	2.798 (1)	171 (1)
O(W2)—H(1,OW2)	O(2) x, y, z	0.65 (1)	2.33 (1)	2.812 (1)	132 (1)
	O(3) -x, 1-y, 1-z		2.37 (1)	2.894 (1)	139 (1)
O(3)—H(O3)	O(2) x, y, z	0.88(1)	1.59 (1)	2.438 (1)	163 (1)



Fig. 2. Geometrical details of the three-center bifurcated hydrogen bond. O(2) is at x, y, z and O(3) at -x, 1 - y, 1 - z. (Distances in Å, angles in deg.)

to roughly C_s with the mirror plane perpendicular to C(2)=C(3). O(2) and O(3) lie on the same side of the least-squares plane through the carbon skeleton with deviations of 0.026 (2) and 0.076 (2) Å, respectively. This disrotatory motion out of the central plane reduces the steric hindrance in one single HM moiety. A more efficient reduction in steric hindrance could have been introduced by a conrotatory motion of the two carboxyl functions leaving O(1) and O(3) on opposite sides of the central plane. The observed disrotatory fashion points to a combination of steric and electronic factors. A similar situation is observed in the structure of magnesium bis(hydrogen maleate) hexahydrate (Gupta, Van Alsenoy & Lenstra, 1984). In the latter compound none of the maleate O atoms is directly linked to the metal. In spite of the difference in packing and coordination the HM fragment has the same features in both structures. In both compounds an unsymmetrical internal H bond is observed, so that in the complete HM ion even the C_s symmetry is lost. Ab initio calculations of George, Bock & Trachtman (1983) have shown that an HM ion with an unsymmetrical H bond is about 5.6 kJ mol^{-1} more stable than one with a symmetrical H bond. This aspect of their calculations agrees with our findings. It should be noted, however, that George et al. assumed a planar HM ion, which is not observed here.

In the crystal the interactions are of the types metal-oxygen ionic linkages, van der Waals contacts and hydrogen bonds. All hydroxyl groups are involved in single donor-acceptor H bonds, with the exception of O(W2)-H(1,OW2) which is a donor in a three-center bifurcated H bond. The geometric features of this bond (Fig. 2) are in perfect agreement with the criteria put forward by Jeffrey (1982).

Water molecules O(W1) and O(W2) bind the anions into a three-dimensional network.

Of the 11 O···O contacts within 3.0 Å which could be regarded as possible H bonds only five are true H bonds, the rest being short O···O contacts. For example, there is a short distance [2.719 (3) Å] between O(W2) and O(1). However, as no H atoms have been found in the O(1)···O(W2) direction, this contact merely represents a short O···O contact in the nickel-oxygen octahedron.

Infrared spectroscopic studies on a crystal of the title compound have given no evidence for the existence of a free OH group. Therefore, as all H atoms have been found at positions which result in normal H-bond geometries, the H bonds given in Table 4 represent a complete and acceptable scheme.

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References

- ANTSISHKINA, A. S., PORAI-KOSHITS, M. A. & GUSEINOV, M. G. (1974). Akad. Nauk SSSR Chem. Ser. p. 237.
- FRENZ, B. A. (1978). The Enraf-Nonius CAD-4 SDP. In Computing in Crystallography, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 64-71. Delft Univ. Press.
- GEORGE, P., BOCK, C. W. & TRACHTMAN, M. (1983). J. Phys. Chem. 87, 1839-1841.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). Acta Cryst. A27, 368-376.
- GUPTA, M. P. & MAHANTA, B. (1978). Cryst. Struct. Commun. 7, 179–182.
- GUPTA, M. P., VAN ALSENOY, C. & LENSTRA, A. T. H. (1984). Acta Cryst. In the press.
- International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
- JEFFREY, G. A. (1982). In Molecular Structure and Biological Activity, edited by J. F. GRIFFIN & W. L. DUAX, pp. 135-150. Amsterdam: Elsevier Science.
- KANTERS, J. A., KROON, J., PEERDEMAN, A. F. & SCHOONE, J. N. (1967). *Tetrahedron*, 23, 4027–4033.
- LIPSON, H. & COCHRAN, W. (1968). The Determination of Crystal Structures, pp. 301 ff. London: Bell.
- SPARKS, R. A. (1974). Least-Squares Tutorial. Proc. Am. Crystallogr. Assoc. Meet., Berkeley, California, pp. 99 ff.
- Van Havere, W., Lenstra, A. T. H. & Geise, H. J. (1980). Acta Cryst. B36, 3117-3120.