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## Tetraaquabis(hydrogen maleato)nickel(II), $[\text{Ni}(\text{C}_4\text{H}_3\text{O}_4)_2(\text{H}_2\text{O})_4]$

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**Abstract.**  $M_r = 360.9$ , triclinic,  $P\bar{1}$ ,  $Z = 1$ ,  $a = 7.309$  (3),  $b = 9.731$  (2),  $c = 5.170$  (2) Å,  $\alpha = 105.97$  (3),  $\beta = 87.12$  (3),  $\gamma = 117.05$  (2)°,  $V = 313.6$  (4) Å<sup>3</sup>,  $D_m = 1.890$ ,  $D_x = 1.911$  Mg m<sup>-3</sup> (floatation in  $\text{CHBr}_3/\text{toluene}$ ),  $\text{Mo } K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 1.61$  mm<sup>-1</sup>,  $F(000) = 186$ , room temperature,  $R_w = 0.036$  for 1336 reflections with  $I \geq 2\sigma(I)$ . 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) Å] 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.

**Introduction.** Crystals of tetraaquabis(hydrogen maleato)metal,  $M(\text{C}_4\text{H}_3\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$  with  $M = \text{Mn}, \text{Co}, \text{Zn}, \text{Ni}, \text{Fe}$  have been investigated in the past by one of us (MPG) and co-workers but, except for  $\text{Mn}^{\text{II}}(\text{C}_4\text{H}_3\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$  (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  $\text{Ni}(\text{C}_4\text{H}_3\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ . Crystals were grown from a solution of the compound in water by slow

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

**Experimental.** 1375 reflections up to  $\theta = 27^\circ$  measured, Enraf–Nonius CAD-4 diffractometer,  $\text{Mo } K\alpha$  radiation, graphite-crystal monochromator,  $\omega/\theta$  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  $\mu$  no absorption correction.  $-9 \leq h \leq 9$ ,  $-12 \leq k \leq 11$ ,  $0 \leq l \leq 6$ . Earlier workers had used the space group  $P\bar{1}$ , 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 *R* decreased satisfactorily, no hydrogen atoms 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  $P1$ . Refinement proceeded smoothly and a difference Fourier map revealed all hydrogen atoms; their inclusion in further least-squares refinements, with fixed thermal temperature factors ( $2.5 \text{ \AA}^2$ ) for H atoms, brought  $R_w$  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,  $0.3 \text{ e \AA}^{-3}$ . 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<sup>II</sup> 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  $C_{2v}$  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 single-bonded C(sp<sup>2</sup>)–C(sp<sup>2</sup>) 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<sup>−</sup> groups of  $\alpha$ -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 Alsenoy & 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<sup>−</sup> 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 2.3 (1)° [C(1) O(1) O(2)] and 2.8 (1)° [C(4) O(3) O(4)]. The non-planarity of the HM ion lowers the symmetry of the C and O backbone

\* 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.

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 Lipsch & Cochran (1968):  $B_{eq} = 8\pi^2(U_{11}^0 U_{22}^0 U_{33}^0)^{1/3}$ , 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*.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}/B_{iso}(\text{Å}^2)$
Ni	0.0000	0.0000	0.0000	1.38
O(W1)	0.2302 (2)	0.0976 (2)	0.3126 (3)	1.90
O(W2)	−0.1768 (2)	0.0752 (2)	0.2523 (3)	1.87
O(1)	0.1420 (2)	0.2014 (2)	−0.1404 (3)	1.81
O(2)	0.1071 (3)	0.3797 (2)	0.2041 (3)	2.34
O(3)	0.2121 (3)	0.6675 (2)	0.3422 (4)	2.56
O(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,O(W1))	0.204 (4)	0.124 (3)	0.464 (5)	2.50
H(2,O(W1))	0.259 (4)	0.028 (3)	0.301 (5)	2.50
H(1,O(W2))	−0.156 (4)	0.151 (3)	0.292 (5)	2.50
H(2,O(W2))	−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(W2)	2.018 (1)	O(W1)–Ni–O(W2)	90.5 (1)

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

† 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)

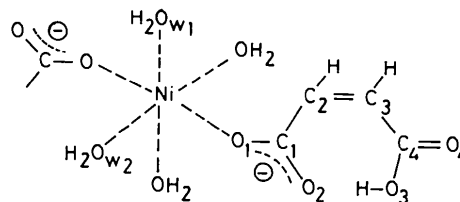


Fig. 1. Numbering scheme and shape of the complex tetraaqua-bis(hydrogen maleato)nickel(II).

