An X-ray Structure Determination of Cobalt and Nickel Squarate Octahydrate,*
[M(H$_2$O)$_6$](C$_4$HO$_4$)$_2$.2H$_2$O (M = Ni, Co)

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Abstract. Ni^{2+}.2C$_4$HO$_4^-$.8H$_2$O, M_r = 428·93, monoclinic, $P2_1/c$, a = 10·288 (1), b = 6·372 (1), c = 12·852 (1) Å, β = 106·98 (1)°, V = 805·8 Å^3, Z = 2, D_x = 1·768 g cm^{-3}, Mo$K\alpha$, λ = 0·7101 Å, μ = 12·5 cm^{-1}, $F(000)$ = 444, T = 298 K, R = 0·027 for 2310 non-zero reflections. Co^{2+}.2C$_4$HO$_4^-$.8H$_2$O, M_r = 429·16, monoclinic, $P2_1/c$, a = 10·341 (3), b = 6·401 (2), c = 12·941 (3) Å, β = 106·87 (2)°, V = 819·7 Å^3, Z = 2, D_x = 1·739 g cm^{-3}, Mo$K\alpha$, λ = 0·7101 Å, μ = 10·4 cm^{-1}, $F(000)$ = 356, T = 298 K, R = 0·033 for 1585 non-zero reflections. The title compounds are isostructural; their crystal structures consist of layers of HC$_4$O$_4^-$ (HSQ$^-$) entities linked by hydrogen bonds along the b axis and layers of M(H$_2$O)$_6^{2+}$ octahedra separated from each other by non-coordinated water molecules.

Introduction. The anion of 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid), first synthesized by Cohen, Lacher & Park (1959), has been of much interest because of its cyclic structure and its possible aromaticity. The neutral transition-metal salts (NiC$_4$O$_4$.2H$_2$O and CoC$_4$O$_4$.2H$_2$O) were first prepared by West & Niu (1963) who proposed a structure consisting of chains of alternating metal and squarate ions. According to them, each squarate ion acts as a bidentate ligand to two metal ions, and the octahedral environment of the metal is completed by O atoms of two water molecules. In this paper the crystal structures of the acidic Ni/Co salts of 3,4-dihydroxy-3-cyclobutene-1,2-dione are described.

Experimental. The salts were prepared by an equimolar reaction between NiCl$_2$.6H$_2$O or CoCl$_2$.6H$_2$O and

squaric acid in water. On cooling a hot concentrated solution, the salts crystallized readily as well formed green or red transparent crystals.

From Weissenberg photographs the symmetry was found to be monoclinic, space group $P2_1/c$ (No. 14) for both compounds.

Structures were resolved by direct methods and difference Fourier syntheses; anisotropic weighted least-squares refinements on F. All H atoms located from difference syntheses and included in the refinement with isotropic thermal parameters. 151 parameters.

Nickel compound

Crystal 0·036 mm^3, Siemens Stoe AED 2 diffractometer, graphite-monochromated Mo$K\alpha$ radiation; lattice parameters and orientation matrix from 25 reflections, $15 \leq 2\theta \leq 25°$. Data collection of full three-dimensional data (8265 reflections; $-14 \leq h \leq 14$, $-9 \leq k \leq 9$, $-18 \leq l \leq 18$) for 2841 unique reflections, 2310 with $I > 1\sigma(I)$, $\omega-\theta$ scans, scintillation counter, $2 \leq 2\theta \leq 65°$ at the University of Karlsruhe. Absorption corrections using ψ-scan routine (max. 1·70, min. 1·17). R_{int} (from merging equivalent reflections) 0·017; three standard reflections, every 200 reflections measured, variations less than 3%. R = 0·027, wR = 0·023 with $w = [\sigma^2(F_o)]^{-1}$, S = 1·21; max. Δ/σ ratios 0·004 for non-H atoms, 0·016 for H; $\Delta\rho_{min}$ = −0·2, $\Delta\rho_{max}$ = 0·5 e Å^{-3}.

Cobalt compound

Crystal 0·019 mm^3, Syntex $P\bar{1}$ diffractometer, graphite-monochromated Mo$K\alpha$ radiation, lattice parameters and orientation matrix from 14 reflections, $13 \leq 2\theta \leq 30°$. Data collection of 2177 reflections $(0 \leq h \leq 16, \quad 0 \leq k \leq 10, \quad -20 \leq l \leq 20)$, ω scan,

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* Squaric acid is 3,4-dihydroxy-3-cyclobutene-1,2-dione.

scintillation counter, $2 \le 2\theta \le 55°$ at the Max-Planck-Institut, Stuttgart. Absorption corrections (max. 1·30, min. 1·04). R_{int} (from merging equivalent reflections) 0·030. 1 standard reflection every 50 reflections measured, variation <3%. Number of unique reflections 1887, 1585 with $I > 0·5\sigma(I)$. $R = 0·033$, $wR = 0·032$ with $w = [\sigma^2(F_o)]^{-1}$, $S = 1·38$; max. Δ/σ ratio 0·015; $\Delta\rho_{min} = -0·2$, $\Delta\rho_{max} = 0·8$ e Å^{-3}.

All calculations were carried out with the program systems *SHELX*76 (Sheldrick, 1976), *XTL* (Syntex, 1971), *ORFFE* (Busing, Martin & Levy, 1971), *ORTEP* (Johnson, 1971). Form factor tables and f' and f'' values from *International Tables for X-ray Crystallography* (1974).

Discussion. Final coordinates and thermal parameters of both salts are given in Tables 1 and 2,* interatomic distances and bond angles are listed in Table 3.

The unit-cell contents of $[M(H_2O)_6](HC_4O_4)_2.2H_2O$ are presented in Fig. 1, the atom-numbering scheme and the structure of the HSQ$^-$ anions are shown in Fig. 2.

The structures consist of alternating layers of HSQ$^-$ and $M(H_2O)_6^{2+}$, HSQ$^-$ forming chains extending parallel to the b axis; the anions are not coordinated to the

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43481 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters* ($\times 10^4$; $\times 10^3$ *for* H *atoms*) *and their e.s.d.'s for* [Ni(H$_2$O)$_6$](HC$_4$O$_4$)$_2$.2H$_2$O

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2 \times 8\pi^2)$
Ni	0	0	0	1·67 (1)
C(1)	6050 (1)	495 (2)	4179 (1)	1·81 (4)
C(2)	5408 (1)	2428 (2)	8882 (1)	1·77 (5)
C(3)	4131 (1)	1533 (2)	3259 (1)	1·80 (5)
C(4)	5225 (1)	456 (2)	6396 (1)	1·71 (5)
O(1)	2798 (1)	93 (1)	5293 (1)	2·78 (4)
O(2)	5800 (1)	595 (1)	9090 (1)	2·48 (4)
O(3)	3011 (1)	2109 (1)	2671 (1)	2·77 (4)
O(4)	5745 (1)	2340 (1)	6589 (1)	2·38 (4)
O(5)	9569 (1)	2102 (1)	5464 (1)	3·20 (5)
O(6)	1742 (1)	1043 (1)	9705 (1)	2·39 (4)
O(7)	8976 (1)	665 (2)	8397 (1)	2·40 (4)
O(8)	8926 (1)	233 (1)	2763 (1)	2·74 (5)
H(1)	517 (2)	160 (3)	132 (1)	4·42 (4)
H(2A)	884 (2)	151 (3)	520 (1)	4·03 (4)
H(2B)	3 (2)	152 (1)	597 (2)	4·50 (4)
H(3A)	240 (2)	33 (3)	997 (2)	4·10 (4)
H(3B)	197 (2)	211 (3)	985 (1)	4·10 (4)
H(4A)	834 (2)	2 (3)	809 (2)	5·05 (5)
H(4B)	885 (2)	187 (3)	819 (1)	4·18 (4)
H(5A)	925 (2)	8 (3)	229 (2)	5·13 (6)
H(5B)	181 (2)	44 (3)	743 (2)	6·40 (6)

Table 2. *Atomic parameters* ($\times 10^4$; $\times 10^3$ *for* H *atoms*) *and their e.s.d.'s for* [Co(H$_2$O)$_6$](HC$_4$O$_4$)$_2$.2H$_2$O

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2 \times 8\pi^2)$
Co	0	0	0	2·13 (8)
C(1)	6035 (2)	506 (3)	4180 (2)	2·21 (8)
C(2)	5395 (2)	2421 (3)	8878 (2)	2·13 (8)
C(3)	4129 (2)	1536 (3)	3258 (2)	2·21 (8)
C(4)	5226 (2)	447 (3)	6396 (2)	2·13 (8)
O(1)	2817 (2)	79 (3)	5285 (1)	3·24 (8)
O(2)	5781 (2)	596 (2)	9084 (1)	2·84 (8)
O(3)	3010 (2)	2098 (3)	2672 (1)	3·16 (8)
O(4)	5742 (2)	2326 (2)	6590 (1)	2·76 (8)
O(5)	9558 (2)	2084 (3)	5484 (2)	3·71 (8)
O(6)	1778 (2)	1062 (3)	9726 (2)	2·92 (8)
O(7)	8951 (2)	707 (3)	8386 (1)	3·08 (8)
O(8)	8912 (2)	214 (3)	2756 (1)	3·16 (8)
H(1)	518 (3)	154 (5)	135 (2)	4·2 (6)
H(2A)	888 (3)	138 (6)	524 (3)	6·6 (9)
H(2B)	2 (4)	145 (6)	599 (3)	5·4 (8)
H(3A)	250 (3)	34 (5)	997 (3)	3·9 (5)
H(3B)	200 (3)	206 (5)	985 (3)	4·3 (6)
H(4A)	829 (4)	0 (5)	807 (3)	4·6 (7)
H(4B)	885 (3)	192 (5)	815 (3)	5·2 (8)
H(5A)	930 (3)	8 (5)	228 (3)	6·0 (9)
H(5B)	189 (4)	47 (6)	745 (3)	4·6 (8)

Table 3. *Bond lengths* (Å) *and bond angles* (°) *for* [M(H$_2$O)$_6$](HC$_4$O$_4$)$_2$.2H$_2$O

	$M = $Ni	$M = $Co		$M = $Ni	$M = $Co
M—O(5)	2·029 (1)	2·062 (2)	O(5)—M—O(6)	92·12 (3)	92·3 (1)
M—O(6)	2·047 (1)	2·085 (2)	O(5)—M—O(7)	89·13 (4)	90·7 (1)
M—O(7)	2·066 (1)	2·105 (2)	O(6)—M—O(7)	90·87 (4)	89·4 (1)
C(1)—C(2)	1·479 (1)	1·484 (3)	C(2)—C(1)—C(4)	88·47 (7)	88·6 (1)
C(1)—O(1)	1·240 (1)	1·246 (2)	C(1)—C(2)—C(3)	89·89 (9)	89·8 (2)
C(2)—C(3)	1·481 (1)	1·481 (3)	C(2)—C(3)—C(4)	88·35 (7)	88·4 (1)
C(2)—O(2)	1·239 (1)	1·238 (3)	C(3)—C(4)—C(1)	93·21 (8)	93·2 (2)
C(3)—C(4)	1·439 (1)	1·444 (3)			
C(3)—O(3)	1·235 (1)	1·238 (2)			
C(4)—C(1)	1·438 (1)	1·437 (3)			
C(4)—O(4)	1·308 (1)	1·310 (2)			

transition metal as in the neutral salts (Habenschuss & Gerstein, 1974). $M(H_2O)_6^{2+}$ lies on an inversion center while the squarate anions are situated in general positions. The HSQ$^-$ anions are linked in a *trans* arrangement to each other by asymmetric hydrogen bonds of length 2·603 (1) (Ni) and 2·592 (2) Å (Co), respectively. Detailed hydrogen-bond geometries are collected in Table 4.

From the basic structure of squaric acid (Semmingsen, Hollander & Koetzle, 1977), the hydrogen-bond network can be formed in two different ways resulting in either a *cis* or a *trans* chain arrangement, schematically represented below:


cis   *trans*
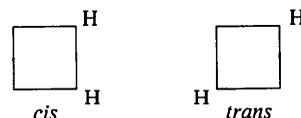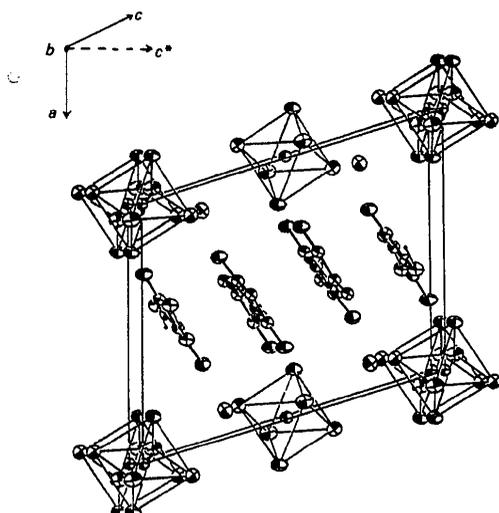
Fig. 1. The unit cell of [M(H₂O)₆](HC₄O₄)₂.2H₂O.
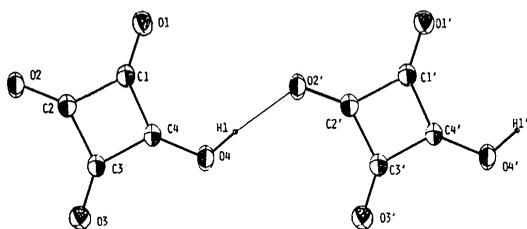
Fig. 2. The structure of the HSQ⁻ anions. In the numbering scheme the prime indicates units related by a center of symmetry.

Table 4. *Hydrogen-bond geometries for* [M(H₂O)₆]-(HC₄O₄)₂.2H₂O

Distances are in Å and angles in °.

	M=Ni	M=Co		M=Ni	M=Co
O(5)–H(2A)	0·81 (1)	0·81 (3)	H(2A)–O(5)–H(2B)	112 (2)	106 (4)
O(5)–H(2B)	0·78 (2)	0·79 (3)	H(3A)–O(6)–H(3B)	103 (2)	102 (3)
O(6)–H(3A)	0·80 (2)	0·85 (3)	H(4A)–O(7)–H(4B)	108 (2)	110 (3)
O(6)–H(3B)	0·74 (2)	0·70 (3)	H(5A)–O(8)–H(5B)	105 (2)	109 (3)
O(7)–H(4A)	0·78 (2)	0·81 (3)			
O(7)–H(4B)	0·81 (2)	0·83 (3)			
O(8)–H(5A)	0·78 (2)	0·83 (4)			
O(8)–H(5B)	0·85 (2)	0·91 (3)			
O(4)···O(2')	2·603 (1)	2·592 (2)	C(4)–O(4)–H(1)	115 (1)	118 (2)
O(4)–H(1)	0·89 (3)	0·92 (3)	O(4)–H(1)···O(2')	173 (2)	175 (2)
H(1)···O(2')	1·72 (2)	1·69 (2)			
O(1)···O(5)	2·729 (1)	2·742 (4)	O(1)···H(2A)–O(5)	174 (2)	174 (4)
O(1)···H(2A)	1·92 (1)	1·93 (2)	O(1)···H(3B)–O(6)	174 (1)	175 (3)
O(1)···O(6)	2·708 (1)	2·702 (4)	O(2)···H(3A)–O(6)	162 (2)	161 (4)
O(1)···H(3B)	1·97 (2)	2·02 (4)	O(3)···H(4A)–O(7)	168 (2)	167 (3)
O(2)···O(6)	2·756 (1)	2·758 (4)	O(3)···H(5B)–O(8)	157 (2)	155 (6)
O(2)···H(3A)	1·98 (2)	1·94 (6)	O(8)···H(4B)–O(7)	170 (2)	171 (4)
O(3)···O(7)	2·747 (1)	2·757 (3)	O(8)···H(2B)–O(5)	173 (2)	177 (5)
O(3)···H(4A)	1·98 (2)	1·96 (5)			
O(3)···O(8)	2·756 (1)	2·756 (4)			
O(3)···H(5B)	1·95 (2)	1·91 (4)			
O(8)···O(7)	2·734 (1)	2·732 (5)			
O(8)···H(4B)	2·00 (2)	1·91 (7)			

The structures of the related alkali-metal complexes LiHSQ.H₂O and KHSQ.H₂O have been determined by Semmingsen (1976) and Bull, Ladd, Povey & Shirley (1973). In these cases the HSQ⁻ anions are *cis* bonded in infinite chains and the hydrogen bonds are significantly shorter (2·34 Å for LiHSQ.H₂O and 2·47 Å for KHSQ.H₂O).

The angles within the four-membered-ring system agree well with those previously found in HSQ⁻ (Wang & Stucky, 1974).

The C—O distances show the expected bond-order–bond-length correlation. Within the ring, the double bond is delocalized about C(4)—OH.

Hydrogen bonds involve the remaining CO groups of HSQ⁻ and form relatively weak bonds to the free as well as to the coordinated water molecules in the coordination shell of the transition metal [2·71 (1)–2·76 (1) Å]. These M(H₂O)₆²⁺ octahedra show nearly O_h symmetry with distances listed in Table 3.

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