

Squaric Acid Salts of Bis(oxamide oxime)nickel(II):* the 1:1 Salt
 $[\text{C}_4\text{O}_4]^{2-} \cdot [\text{Ni}(\text{C}_2\text{H}_6\text{N}_4\text{O}_2)_2]^{2+}$ and the 1:2 Salt $[\text{C}_4\text{O}_4]^{2-} \cdot 2[\text{Ni}(\text{C}_2\text{H}_5\text{N}_4\text{O}_2)(\text{C}_2\text{H}_6\text{N}_4\text{O}_2)]^+$

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Abstract. Room temperature, Mo $K\alpha$, $\lambda = 0.71069 \text{ \AA}$. 1:1 salt: $M_r = 406.95$, monoclinic, $P2_1/c$, $a = 7.190 (1)$, $b = 8.272 (2)$, $c = 11.790 (3) \text{ \AA}$, $\beta = 102.99 (2)^\circ$, $V = 683.27 \text{ \AA}^3$, $Z = 2$, $D_x = 1.98 \text{ g cm}^{-3}$, $\mu = 14.9 \text{ cm}^{-1}$, $F(000) = 416$, final $R = 0.031$ for 2409 observed reflections. The structure consists of planar dipositive [bis(oxamide oxime)nickel(II)] cations and dinegative squarate anions with a loose axial interaction between Ni and squarate O atoms, $3.265 (2) \text{ \AA}$. 1:2 salt: $M_r = 699.84$, triclinic, $P\bar{1}$, $a = 7.326 (5)$, $b = 7.496 (9)$, $c = 10.782 (9) \text{ \AA}$, $\alpha = 96.54 (8)$, $\beta = 102.74 (6)$, $\gamma = 95.53 (8)^\circ$, $V = 569.24 \text{ \AA}^3$, $Z = 1$, $D_x = 2.04 \text{ g cm}^{-3}$, $\mu = 17.6 \text{ cm}^{-1}$, $F(000) = 358$, final $R = 0.076$ for 588 observed reflections. The crystals contain planar monopositive [(oxamide oximate)-(oxamide oxime)nickel(II)] cations and dinegative squarate anions. An extended H-bonding network exists in both structures.

Introduction. Complexes of oxamide oxime, $\text{HON}=\text{C}(\text{NH}_2)-\text{C}(\text{NH}_2)=\text{NOH}$ (diaminoglyoxime, oaoH_2) (Ephraim, 1889), with the metals of the Ni triad may occur as neutral molecules or as mono- or dipositive cations, as the degree of deprotonation of the oxime groups depends on the pH of the solutions. Ni complexes have been isolated hitherto as neutral (Endres, 1979; Endres, Jannack & Prickner, 1980) or as monopositive species (Endres, 1982). Treatment with acids resulted in a rearrangement of the $\text{Ni}(\text{oaoH})_2$ complex molecules. Either salts of the octahedral $[\text{Ni}(\text{oaoH}_2)_3]^{2+}$ dication as in the dichloride (Tschugaeff & Surenjanz, 1907; Endres & Jannack, 1980) were formed, or octahedral $\text{Ni}(\text{oaoH}_2)_2\text{X}_2$ complexes *via cis*-addition of two anions X^- (Endres, 1983). In the following we describe salts of the square-planar $[\text{Ni}(\text{oaoH}_2)_2]^{2+}$ and $[\text{Ni}(\text{oaoH})(\text{oaoH}_2)]^+$ cations which were obtained by the reaction of $\text{Ni}(\text{oaoH})_2$ with squaric acid. This acid (Cohen, Lacher & Park, 1959; West, Niu & Ito, 1963) forms polynuclear complexes with transition-metal ions (Habenschuss & Gerstein, 1974).

Experimental. 2.5 mmol solid $\text{Ni}(\text{oaoH})_2$ added portionwise to a solution of 5 mmol squaric acid (Fluka) in 50 ml warm water. The red-brown Ni complex changed color to pink. The slurry was kept at 353 K for 0.5 h, then the pink solid was filtered off and washed with water. It decomposes above 453 K. Elemental analysis was close to the composition $\text{Ni}(\text{oaoH}_2)_2 \cdot \text{C}_4\text{O}_4$: % found (calculated): C 22.8 (23.3), H 2.97 (2.97), N 26.9 (27.2), yield 60%. {In the filtrate the compounds $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} \cdot \text{C}_4\text{O}_4^{2-}$, $(\text{oaoH}_3)_2^+ \cdot \text{C}_4\text{O}_4^{2-}$, and $(\text{oaoH}_4)^{2+} \cdot 2\text{C}_4\text{O}_4\text{H}^-$ were isolated and characterized by X-ray structure determination.}

Ruby-red crystals of the 1:1 salt $[\text{Ni}(\text{oaoH}_2)_2]^{2+} \cdot \text{C}_4\text{O}_4^{2-}$ were obtained when the pink product was boiled several minutes in water and the filtered yellow solution was then allowed to evaporate at room temperature. Bright-red crystals of the 1:2 salt $\text{C}_4\text{O}_4^{2-} \cdot 2[\text{Ni}(\text{oaoH})(\text{oaoH}_2)]^+$ formed when the pink product was stirred at 353 K in water for several minutes and filtered. An equal volume of ethanol was added to the yellow filtrate, and the solution was allowed to evaporate at room temperature. This compound is rarely obtained, as the 1:1 salt will form under these conditions as well. Block-like crystals, lattice parameters from the setting angles of 25 reflections centered on a diffractometer (Syntex R3, monochromatic Mo $K\alpha$ radiation). Further experimental information in Table 1. Refinement based on F , $w = 1/\sigma^2(F)$, 'cascade-matrix' least squares on a Nova 3 computer, plots on a Tektronix plotter. *SHELXTL* program system (Sheldrick, 1981), scattering factors from *International Tables for X-ray Crystallography* (1974), anomalous dispersion included.

Both structures were solved by Patterson and Fourier methods. The limited data set for the 1:2 salt allowed refinement with anisotropic temperature factors only for Ni; the other atoms were refined isotropically. H positions could not be determined. The structure of the 1:1 salt was refined with anisotropic temperature factors for the non-H atoms, H atoms with individual isotropic temperature factors. Details are given in Table 1.

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

Discussion. Atomic coordinates of the 1:1 salt are listed in Table 2, those of the 1:2 salt in Table 3.* Fig. 1 shows the two ions of the 1:1 salt with bond distances and angles. Both ions lie on crystallographic inversion centers. Intramolecular H bridges exist. They are relatively long, 2.690 (2) Å, compared to 2.567 (4) Å in the neutral Ni(oaoH)₂ molecule (Endres, 1979), but correspond to the analogous bridge in [Ni(oaoH)-(oaoH₂)]Cl, 2.678 (4) Å (Endres, 1982). The oxime H(2) forms an H bridge to O(4) (at equivalent position $-x, -y, -z$) of the squarate dianion, O(2)···O(4) 2.532 (3) Å. Other H bridges involve the amino groups. The intermolecular bridges are indicated in Fig. 2. A further intermolecular contact is shown in Fig. 3.

[Ni(oaoH₂)₂]²⁺ is sandwiched between two squarate dianions, the dihedral angle between the molecular planes of cation and anion is 1.5 (3)°. The arrangement results in axial contacts of 3.265 (2) Å between Ni and squarate O(3) atoms, with N-Ni-O(3) angles of 78.9 (1) and 97.0 (1)°. The squarate anion is a nearly perfect square, with equal C-C distances, and complete electron delocalization may be assumed.

The constituents of the 1:2 salt are shown in Figs. 4 and 5, together with bond distances and angles. The squarate ion lies on an inversion center; the metal complex at a general position. Although the H-atom positions could not be determined, its composition implies that the compound has to be formulated as [C₄O₄]²⁻·2[Ni(oaoH)(oaoH₂)]⁺. The presence of the monpositive complex cation is also indicated by the occurrence of two different O···O separations, 2.57 (3) and 2.67 (3) Å, comparing well with those found in [Ni(oaoH)(oaoH₂)]Cl, 2.606 (4) and 2.678 (4) Å. Also reminiscent of the chloride is a short intermolecular O···O contact between oxime groups separated by a **b** cell translation, suggesting a strong H bridge: 2.53 (3) Å (chloride: 2.50 Å). H bonding to the squarate ions is effected by the amino groups, with N···O distances of the order of 2.9 Å. Due to the limited accuracy of this structure determination a more detailed discussion of bond distances would not be useful.

These two structures show that squaric acid exhibits a reactivity with Ni(oaoH)₂, which is different from that of other carboxylic acids \bar{X} , which normally coordinate to the metal to form blue *cis*-octahedral [Ni(oaoH₂)₂X₂] complexes (Endres, 1983). In the squaric acid salts described above the anion does not coordinate to Ni (the loose Ni···O contact in the 1:1 salt can surely not be termed 'coordination'). It may be assumed that H

bridges play an important role in stabilizing the structures.

Table 1. *Experimental details*

	1:1 Salt	1:2 Salt
Crystal size	0.008 mm ³	0.003 mm ³
Data collection	$\theta/2\theta$	ω
$2\theta_{\max}$	70°	40°
Range of <i>hkl</i>	0,0,-9 to 11,13,18	0,-7,-10 to 7,7,9
Two standard reflections at intervals	200	100
Intensity variation	±2.8%	±4%
Reflections measured	3009	1064
Observed unique reflections [$I > 2.5\sigma(I)$]	2409	588
Merging <i>R</i>	0.031	0.030
Absorption correction	Yes	No
Min. transmission (max. = unity)	0.73	—
<i>R_w</i> , <i>R</i> , <i>S</i>	0.030, 0.031, 1.93	0.072, 0.076, 2.03
$(\Delta/\sigma)_{\max}$	0.15	0.01
$\Delta\rho$ max. (min.)	+0.43 (-0.47) e Å ⁻³	+0.74 (-0.65) e Å ⁻³

Table 2. [Ni(oaoH₂)₂]C₄O₄: atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10^3$)

U_{eq} is defined as $\frac{1}{3}$ trace \bar{U} , \bar{U} signifying the diagonalized \bar{U} matrix.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}(\text{Å}^2)$
Ni	0	0	0	16 (1)
N(1)	2318 (2)	-211 (2)	1091 (1)	19 (1)
N(2)	1237 (2)	-1407 (2)	-830 (1)	18 (1)
N(3)	5422 (2)	-1244 (2)	1447 (1)	24 (1)
N(4)	4009 (2)	-2924 (2)	-772 (1)	26 (1)
O(1)	2884 (2)	514 (2)	2183 (1)	29 (1)
O(2)	442 (2)	-2115 (1)	-1915 (1)	22 (1)
C(1)	3654 (2)	-1076 (2)	810 (1)	17 (1)
C(2)	2962 (2)	-1875 (2)	-341 (1)	17 (1)
O(3)	2192 (2)	1703 (2)	4512 (1)	33 (1)
O(4)	-2091 (2)	613 (2)	3283 (1)	27 (1)
C(3)	1002 (2)	775 (2)	4781 (1)	19 (1)
C(4)	-939 (2)	267 (2)	4224 (1)	19 (1)

Table 3. [Ni(oaoH)(oaoH₂)₂]C₄O₄: atomic coordinates ($\times 10^4$) and isotropic temperature factors ($\times 10^3$) (only Ni was refined anisotropically)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}(\text{Å}^2)$
Ni	1465 (5)	223 (5)	3829 (4)	18 (1)*
N(1)	3214 (27)	1128 (30)	5387 (18)	26 (6)
N(2)	1386 (26)	-2002 (27)	4470 (19)	24 (6)
N(3)	-300 (31)	-631 (33)	2289 (21)	36 (7)
N(4)	1489 (27)	2407 (27)	3143 (19)	20 (5)
N(5)	4860 (30)	149 (30)	7286 (21)	40 (7)
N(6)	2691 (26)	-3442 (28)	6279 (19)	21 (6)
N(7)	-2105 (28)	274 (28)	355 (20)	28 (6)
N(8)	290 (27)	3767 (28)	1279 (19)	30 (6)
O(1)	4165 (22)	2790 (25)	5826 (16)	29 (5)
O(2)	424 (20)	-3599 (20)	3899 (14)	21 (4)
O(3)	-1259 (23)	-2287 (24)	1923 (16)	32 (5)
O(4)	2619 (22)	4042 (22)	3662 (15)	30 (5)
C(1)	3440 (42)	-373 (47)	6065 (29)	30 (7)
C(2)	2444 (35)	-1990 (38)	5606 (25)	28 (7)
C(3)	-753 (36)	625 (40)	1520 (25)	25 (6)
C(4)	374 (35)	2339 (37)	1955 (24)	28 (7)
O(5)	5398 (22)	-2721 (24)	8790 (15)	34 (5)
O(6)	3006 (21)	-3369 (20)	10926 (15)	28 (4)
C(5)	5130 (34)	-3992 (35)	9460 (24)	33 (7)
C(6)	4141 (29)	-4255 (28)	10438 (20)	18 (6)

* U_{eq} defined as in Table 1.

* Lists of structure factors and anisotropic thermal parameters for both salts, and H-atom parameters and bond lengths and angles involving H for the 1:1 salt have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38760 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

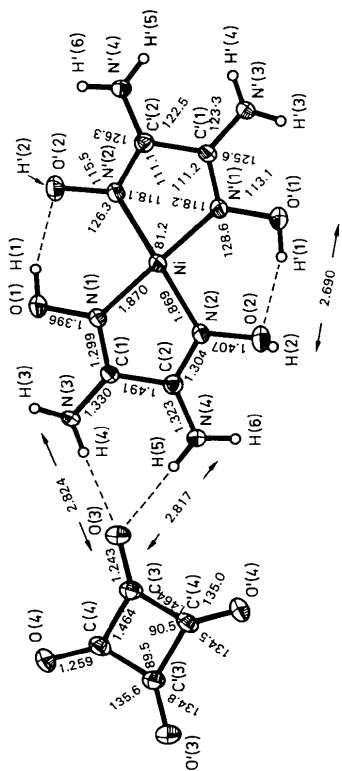


Fig. 1. Anion and cation in the 1:1 salt [Ni(oaoH₂)₂]²⁺·C₄O₄²⁻ with numbering scheme, bond distances (Å) and angles (°). Primed atoms are related to the corresponding unprimed ones by inversion through a center of symmetry (at 0,0,0 for the Ni complex; at 0,0,½ for the anion). Thermal ellipsoids at the 50% probability level. E.s.d.'s are 0.001–0.002 Å for lengths, 0.1° for angles.

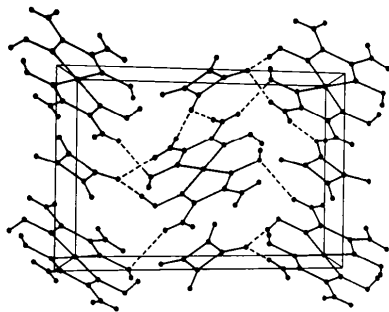


Fig. 2. Projection of the structure of the 1:1 salt along **a**; **b** points up the page, **c** to the right. Intermolecular H bridges are indicated by broken lines.

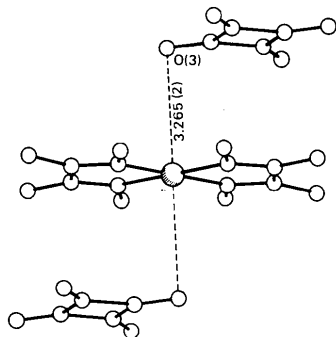


Fig. 3. View of the cation and two adjacent anions in the 1:1 salt.

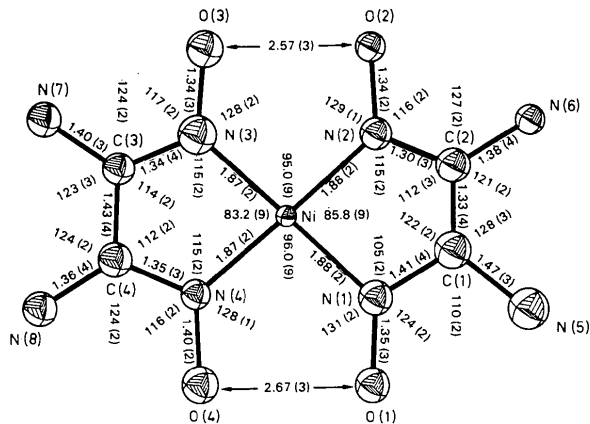


Fig. 4. The cation [Ni(oaoH)(oaoH₂)]⁺ in the 1:2 salt with bond distances (Å) and angles (°).

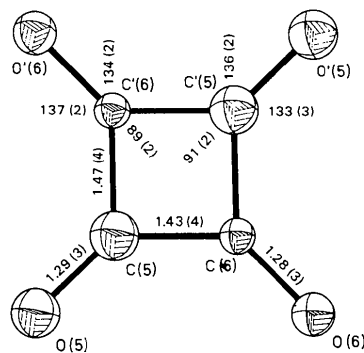


Fig. 5. The C₄O₄²⁻ anion in the 1:2 salt with bond distances (Å) and angles (°).

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