

The Ribbon Structure of *catena*- $\{\mu_4$ -(Dihydrogen mellitato)-bis[bis(oxamide oxime-*N,N'*)nickel(II)] Tetrahydrate, * $[\text{Ni}_2(\text{C}_{12}\text{H}_2\text{O}_{12})(\text{C}_2\text{H}_6\text{N}_4\text{O}_2)_2] \cdot 4\text{H}_2\text{O}$

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Abstract. $M_r = 1000.0$, triclinic, $P\bar{1}$, $a = 8.683$ (5), $b = 8.854$ (5), $c = 12.435$ (6) Å, $\alpha = 85.68$ (5), $\beta = 75.32$ (4), $\gamma = 72.24$ (4)°, $V = 880.7$ Å³, $Z = 1$, $D_x = 1.88$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 11.9$ cm⁻¹, $F(000) = 514$, room temperature, final $R = 0.103$ for 1767 observed reflections. Octahedrally coordinated Ni complexes with two bidentate oxamide oxime chelate ligands and two O atoms of different mellitic anions in *cis* positions, as it has always been found in this type of compound. Each carboxylic acid anion bridges four Ni atoms, which leads to a one-dimensional ribbon-like structure, empty spaces being filled by water molecules.

Introduction. Square-planar bis(1,2-dione dioximato)-nickel(II) complexes may add two acid molecules HX to form octahedral complexes $[\text{NiX}_2(\text{dioxime})_2]$ (*Gmelin's Handbuch der anorganischen Chemie*, 1969). This holds for the oxamide oxime complexes, $\text{Ni}(\text{oaoH})_2$, as well $[\text{oaoH}_2 = \text{HON}=\text{C}(\text{NH}_2)-\text{C}(\text{NH}_2)=\text{NOH}]$ (*Gmelin's Handbuch der anorganischen Chemie*, 1969; Endres, 1984; Endres & Schendzielorz, 1983b). $[\text{Ni}(\text{oaoH}_2)_3]^{2+}$ cations may also be formed (Tschugaeff & Surenjanz, 1907; Endres & Jannack, 1980) and, with squaric acid, salts of the square-planar $[\text{Ni}(\text{oaoH}_2)_2]^{2+}$ and $[\text{Ni}(\text{oaoH})(\text{oaoH}_2)]^+$ cations have been obtained (Endres & Schendzielorz, 1983a).

There is discussion in the literature as to whether the acid anions X in the octahedral $[\text{NiX}_2(\text{dioxime})_2]$ complexes occupy *cis* or *trans* positions (*Gmelin's Handbuch der anorganischen Chemie*, 1969). In all the $[\text{NiX}_2(\text{oaoH}_2)_2]$ complexes investigated so far by X-ray structure determination we have found *cis* coordination of the species X . Hence we suggest that this mode of coordination is a general one for $[\text{NiX}_2(\text{dioxime})_2]$ molecules. When polydentate acids are employed dinuclear or polymeric complex species may be expected. Thus we detected a helical chain structure in the reaction product of $\text{Ni}(\text{oaoH})_2$ with phthalic acid (Endres, 1984). Being interested in the structures and possible magnetic exchange interactions in such polymers, we undertook a systematic structural inves-

tigation of the addition products of polydentate aromatic carboxylic acids with $\text{Ni}(\text{oaoH})_2$. The results obtained with mellitic acid are described herein.

Experimental. Solid $\text{Ni}(\text{oaoH})_2$ added in portions to boiling aqueous solution of mellitic acid (purchased from EGA-Chemie) until dissolution stops; filtered hot, blue solution allowed to evaporate in gently warmed oven, mixture of light blue and blue-green crystals precipitated; blue-green crystals are title compound; light blue crystals of insufficient quality to complete structure analysis. (Preliminary results indicate a dinuclear complex with octahedrally coordinated Ni, bridged by one mellitic acid residue *via meta*-carboxylic groups.) Block-like blue-green crystal

Table 1. Atom coordinates ($\times 10^4$) and isotropic temperature factors (Å² $\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*/U
Ni	1823 (3)	2131 (3)	2625 (2)	25 (1)*
C(1)	967 (18)	-822 (17)	3334 (11)	28 (4)
C(2)	447 (18)	-364 (18)	2263 (12)	30 (4)
C(3)	3085 (19)	3474 (18)	515 (12)	33 (4)
C(4)	4568 (18)	2182 (18)	610 (12)	31 (4)
C(5)	-1587 (16)	4581 (16)	3687 (10)	19 (3)
C(6)	-3314 (16)	4807 (16)	4371 (11)	19 (3)
C(7)	-4295 (17)	3903 (16)	4160 (11)	22 (3)
C(8)	5916 (17)	4108 (16)	4699 (11)	21 (3)
C(9)	-6819 (19)	3072 (19)	4400 (12)	32 (4)
C(10)	-3478 (18)	2810 (18)	3158 (11)	27 (4)
N(1)	1802 (15)	55 (14)	3569 (10)	30 (3)
N(2)	669 (15)	947 (15)	1873 (10)	34 (3)
N(3)	4231 (15)	1239 (15)	1496 (10)	32 (3)
N(4)	1838 (15)	3772 (14)	1335 (10)	29 (3)
N(5)	3102 (18)	4271 (17)	-494 (12)	54 (4)
N(6)	6108 (16)	1962 (16)	-84 (10)	42 (4)
N(7)	-221 (18)	-1320 (17)	1836 (12)	55 (4)
N(8)	697 (15)	-2123 (15)	3942 (10)	40 (4)
O(1)	2393 (13)	-449 (12)	4527 (7)	39 (5)*
O(2)	175 (16)	1344 (14)	830 (8)	55 (6)*
O(3)	5722 (12)	67 (13)	1587 (8)	41 (5)*
O(4)	407 (14)	4881 (14)	1154 (8)	53 (5)*
O(5)	-520 (13)	3292 (12)	3673 (7)	36 (5)*
O(6)	-1371 (14)	5741 (13)	3073 (9)	57 (5)*
O(7)	-3616 (18)	1390 (15)	3338 (10)	76 (7)*
O(8)	-2917 (17)	3324 (16)	2237 (10)	75 (7)*
O(9)	-7104 (16)	2000 (15)	5053 (8)	59 (6)*
O(10)	-7163 (13)	3335 (12)	3438 (8)	39 (5)*
O(11)†	5324 (14)	-2174 (13)	3021 (8)	49 (5)*
O(12)†	3705 (14)	-3992 (14)	2087 (8)	50 (5)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

† Water oxygen atoms.

* Mellitic acid = benzenehexacarboxylic acid, $\text{C}_{12}\text{H}_6\text{O}_{12}$.

Table 2. Bond lengths (Å) and angles (°)

Ni—N(1)	2.107 (12)	Ni—N(2)	2.059 (16)
Ni—N(3)	2.154 (11)	Ni—N(4)	2.082 (12)
Ni—O(5)	2.116 (9)	Ni—O(10 <i>b</i>)	2.030 (13)
C(1)—C(2)	1.501 (22)	C(1)—N(1)	1.303 (24)
C(1)—N(8)	1.378 (20)	C(2)—N(2)	1.274 (21)
C(2)—N(7)	1.363 (26)	C(3)—C(4)	1.462 (20)
C(3)—N(4)	1.260 (17)	C(3)—N(5)	1.392 (21)
C(4)—N(3)	1.357 (19)	C(4)—N(6)	1.361 (18)
C(5)—C(6)	1.486 (18)	C(5)—O(5)	1.229 (15)
C(5)—O(6)	1.265 (17)	C(6)—C(7)	1.413 (24)
C(6)—C(8 <i>a</i>)	1.446 (18)	C(7)—C(8)	1.359 (19)
C(7)—C(10)	1.519 (19)	C(8)—C(9)	1.494 (26)
C(8)—C(6 <i>a</i>)	1.446 (18)	C(9)—O(9)	1.243 (20)
C(9)—O(10)	1.293 (19)	C(10)—O(7)	1.296 (22)
C(10)—O(8)	1.237 (18)	N(1)—O(1)	1.404 (16)
N(2)—O(2)	1.453 (17)	N(3)—O(3)	1.416 (15)
N(4)—O(4)	1.387 (16)		
N(1)—Ni—N(2)	74.5 (5)	N(1)—Ni—N(3)	98.2 (4)
N(2)—Ni—N(3)	94.6 (5)	N(1)—Ni—N(4)	163.5 (5)
N(2)—Ni—N(4)	90.7 (5)	N(3)—Ni—N(4)	75.2 (4)
N(1)—Ni—O(5)	88.6 (4)	N(2)—Ni—O(5)	89.3 (5)
N(3)—Ni—O(5)	172.8 (5)	N(4)—Ni—O(5)	98.8 (4)
N(1)—Ni—O(10 <i>b</i>)	104.6 (5)	N(2)—Ni—O(10 <i>b</i>)	176.7 (4)
N(3)—Ni—O(10 <i>b</i>)	88.7 (5)	N(4)—Ni—O(10 <i>b</i>)	90.5 (5)
O(5)—Ni—O(10 <i>b</i>)	87.5 (4)	C(2)—C(1)—N(1)	113.1 (13)
C(2)—C(1)—N(8)	122.4 (16)	N(1)—C(1)—N(8)	124.3 (14)
C(1)—C(2)—N(2)	113.1 (16)	C(1)—C(2)—N(7)	119.1 (14)
N(2)—C(2)—N(7)	127.7 (15)	C(4)—C(3)—N(4)	118.5 (13)
C(4)—C(3)—N(5)	118.1 (12)	N(4)—C(3)—N(5)	123.3 (13)
C(3)—C(4)—N(6)	111.6 (12)	C(3)—C(4)—N(6)	124.6 (13)
N(3)—C(4)—N(6)	123.8 (12)	C(6)—C(5)—O(5)	120.3 (12)
C(6)—C(5)—O(6)	115.1 (11)	O(5)—C(5)—O(6)	124.3 (12)
C(5)—C(6)—C(7)	120.6 (12)	C(5)—C(6)—C(8 <i>a</i>)	123.8 (14)
C(7)—C(6)—C(8 <i>a</i>)	115.6 (12)	C(6)—C(7)—C(8)	124.2 (12)
C(6)—C(7)—C(10)	114.6 (12)	C(8)—C(7)—C(10)	120.7 (15)
C(7)—C(8)—C(9)	119.1 (12)	C(7)—C(8)—C(6 <i>a</i>)	119.9 (15)
C(9)—C(8)—C(6 <i>a</i>)	120.7 (12)	C(8)—C(9)—O(9)	118.7 (15)
C(8)—C(9)—O(10)	115.6 (14)	O(9)—C(9)—O(10)	125.6 (18)
C(7)—C(10)—O(7)	113.9 (12)	C(7)—C(10)—O(8)	121.0 (14)
O(7)—C(10)—O(8)	124.6 (15)	Ni—N(1)—C(1)	117.4 (10)
Ni—N(1)—O(1)	129.1 (10)	C(1)—N(1)—O(1)	113.0 (12)
Ni—N(2)—C(2)	120.7 (12)	Ni—N(2)—O(2)	127.3 (10)
C(2)—N(2)—O(2)	111.7 (14)	Ni—N(3)—C(4)	115.4 (8)
Ni—N(3)—O(3)	133.4 (8)	C(4)—N(3)—O(3)	109.3 (10)
Ni—N(4)—C(3)	117.8 (10)	Ni—N(4)—O(4)	123.3 (8)
C(3)—N(4)—O(4)	115.9 (12)	Ni—O(5)—C(5)	136.3 (9)
C(9)—O(10)—Ni(<i>a</i>)	129.8 (11)		

(0.006 mm³) mounted at end of glass capillary, lattice parameters from setting angles of 25 reflections (Syntex R3 diffractometer, monochromated Mo K α radiation), θ - 2θ scans, $2\theta \leq 55^\circ$, 4047 reflections measured, 1767 observed independent reflections with $I > 1.5\sigma(I)$, hkl range of observed reflections $-10,-10,0$ to $9,11,15$, 2 check reflections at intervals of 100, intensity variation $\pm 13\%$, empirical absorption correction using ψ scans of 6 reflections, min. transmission = 0.42 (max. = unity), merging $R = 0.045$; Ni position from Patterson map, other non-H atoms from Fourier maps; not all H evident on difference Fourier map, hence no H included; Ni and O refined anisotropically, C and N isotropically; number of parameters = 190, refinement by cascade-matrix least squares based on F , $w = 1/\sigma^2(F)$, $R_w = 0.094$, $R = 0.103$, $S = 3.27$; max. $\Delta/\sigma = 0.06$; largest features in final difference Fourier map $+1.54$ and $-1.11 \text{ e } \text{\AA}^{-3}$ (close to Ni); *SHELXTL* program system (Sheldrick, 1981) on a Nova 3 computer, plots on a Tektronix plotter; scattering factors from *International Tables for X-ray Crystallography* (1974), anomalous dispersion included.

Discussion. Atomic coordinates are listed in Table 1,* bond distances and angles in Table 2. Fig. 1 shows a section of the crystal structure with the numbering scheme. The center of mass of the mellitic acid residue coincides with a crystallographic inversion center. The asymmetric unit consists of Ni with the two oaoH₂ ligands and half of the mellitic acid anion. Hence there are two Ni per anion. Although the H positions could not be determined, it may be assumed by analogy with other octahedral complexes of this type that the oaoH₂ ligand molecules are not ionized, leaving two positive charges per Ni^{II} species. The composition then implies that the mellitic acid residue is a tetraanion. For symmetry reasons the two remaining H atoms are probably bound to those carboxyl groups which do not coordinate to Ni.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39174 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

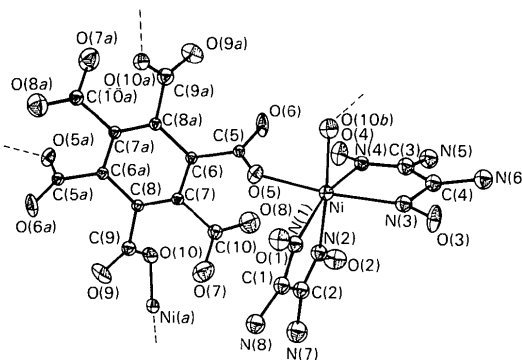


Fig. 1. Section of the crystal structure with the atomic numbering. Thermal contours at 30% probability. The polymer formation is indicated by dashed lines.

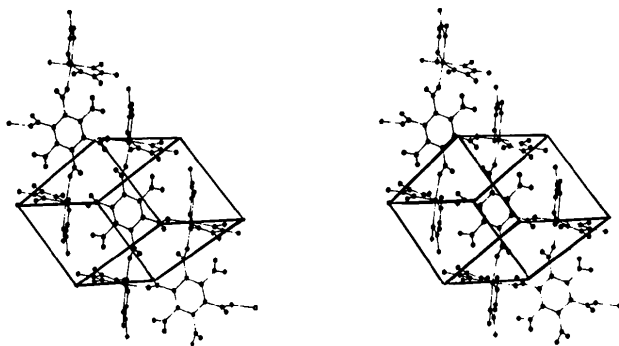


Fig. 2. Stereoview of part of a one-dimensional ribbon extending parallel to *a*. The mellitic acid tetraanions have their midpoints at crystallographic inversion centers $x, 0.5, 0.5$ with $x = -0.5, 0.5, 1.5$, respectively. View direction is perpendicular to the planes of the benzene rings.

Each Ni atom is coordinated in an essentially octahedral geometry by four oxime N atoms of two oaoH₂ molecules, and two carboxyl O atoms of different (but crystallographically equivalent) mellitic acid anions. These O atoms occupy *cis* positions, as is always found in octahedral $[\text{NiX}_2(\text{oaoH}_2)_2]$ complexes (Endres, 1984; Endres & Schendzielorz, 1983b).

Each mellitic acid anion bridges four Ni centers. This results in a one-dimensional ribbon-like structure extending parallel to *a* (Fig. 2). Empty space left by this arrangement is filled with water molecules.

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Structure of Bis(9-methylhypoxanthine)silver(I) Nitrate Dihydrate, $[\text{Ag}(\text{C}_6\text{H}_6\text{N}_4\text{O})_2](\text{NO}_3)\cdot 2\text{H}_2\text{O}$

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Abstract. $M_r = 506.2$, triclinic, $P\bar{1}$, $a = 9.985$ (3), $b = 14.655$ (4), $c = 6.606$ (2) Å, $\alpha = 107.26$ (3), $\beta = 95.92$ (3), $\gamma = 96.71$ (3)°, $V = 907.0$ (7) Å³, $Z = 2$, $D_x = 1.84$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54182$ Å, $\mu(\text{Cu } K\alpha) = 10.01$ mm⁻¹, $F(000) = 508$, room temperature, $R = 0.066$ for 2532 observed reflections. The Ag⁺ ion is linearly bonded to the two 9-methylhypoxanthine ligands through the N(7) sites. The structure of the metal-bridged base–base pair is in the *syn* configuration with respect to the N(7)–Ag–N(7) bond and stabilized by a water bridge between the carbonyl O atoms O(6).

Introduction. Shin & Eichhorn (1980) have shown that the Ag⁺ ion reacts with polyinosinic acid to form a 1:2 complex at low pH, with no proton release, and they have proposed a double-helix structure with N(7)–Ag⁺–N(7) bonding. Structurally, two arrangements with N(7)–metal–N(7) bonding are possible, as shown in Fig. 1. Of the (I) *syn* and (II) *anti* configurations, the type (I) structure has, in fact, been exemplified in the crystal structure of $[\text{Ag}(9\text{-methylhypoxanthine})_2](\text{ClO}_4)\cdot \text{H}_2\text{O}$ (Gariépy &

Beauchamp, 1980). We have determined the crystal structure of the nitrate salt of Ag⁺–9-methylhypoxanthine in the hope of finding the type (II) structure.

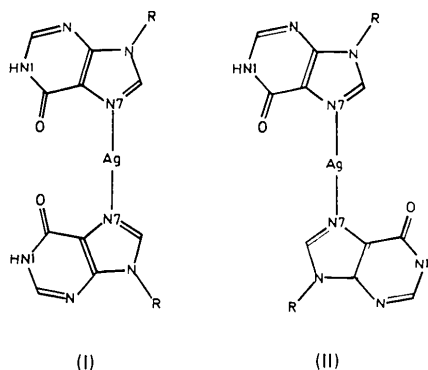


Fig. 1. A schematic representation of the two possible structures with N(7)–Ag–N(7) bonding for the 1:2 Ag–polyinosinic acid system: (I) *syn* and (II) *anti* configurations of the ligands with respect to N–Ag–N.