

## The Crystal and Molecular Structure of Bis(oxamide oximato)nickel(II) Dihydrate

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(Received 30 August 1978; accepted 8 December 1978)

### Abstract

The title compound,  $\text{Ni}(\text{C}_2\text{H}_5\text{N}_4\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{C}_4\text{H}_{10}\text{N}_8\text{NiO}_4 \cdot 2\text{H}_2\text{O}$ , FW 328.9, crystallizes in the monoclinic space group  $P2_1/n$ ,  $a = 3.969$  (1),  $b = 13.006$  (4),  $c = 11.512$  (3) Å,  $\beta = 99.45$  (2)°,  $V = 586$  Å<sup>3</sup>,  $Z = 2$ ,  $d_c = 1.863$  Mg m<sup>-3</sup>. The structure, including H, was solved by Patterson and Fourier methods and refined by a least-squares procedure to  $R = 0.037$  for 803 reflections. Extinction conditions are violated for two reflections. The centrosymmetric, planar molecules form stacks along  $a$ , the normals to the planes being inclined by 30° to the stacking axis. Square-bipyramidal coordination around Ni is completed by oxime N atoms of adjacent molecules, their distance to Ni being 3.478 (3) Å. The water bonds by H bridges to adjacent complexes of a stack, leading to a ladder-like structure.

### Introduction

Oxamide oxime (diaminoglyoxime,  $\text{OAOH}_2$ ), known since 1889 (Fischer, 1889; Ephraim, 1889), is interesting as a ligand, for the amino N atoms as well as the oxime N atoms should act as coordinating sites. A summary of the methods of preparation and a discussion of the possible conformations of the free ligand have been published (Ungnade, Kissinger, Narath & Barham, 1963), and spectroscopic investigations of some transition-metal complexes (Fe, Co, Ni, Cu) have been reported (Pearse & Pflaum, 1959). Recently the coordination chemistry of this ligand has attracted new interest (Sarisaban, 1976), and structural data of some complexes are available:  $(\text{OAOH})_2\text{Co}^{\text{II}} \cdot \text{OAOH}_2$  (Bekaroglu, Sarisaban, Koray & Ziegler, 1977),  $(\text{OAOH}_2)_3\text{Co}^{\text{III}}\text{Cl}_3$  (Weiss, Nuber, Koray, Weidenhammer & Ziegler, 1978) and the dimethylformamide (DMF) solvate of  $(\text{OAOH})_2\text{Ni}^{\text{II}} \cdot \text{H}_2\text{O}$  (Endres, 1978). In the following, the crystal growth and structure of DMF-free  $(\text{OAOH})_2\text{Ni}^{\text{II}} \cdot 2\text{H}_2\text{O}$  are described.

### Experimental

The  $\text{OAOH}_2$  ligand was prepared according to Ephraim (1889). Crystals of the title compound were

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grown by diffusion: large pieces of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  were put into a tube similar to a Schlenk tube, and a Schlenk frit was attached on top. The tube was filled with  $\text{H}_2\text{O}$  up to the bottom of the frit. Solid oxamide oxime, which dissolves very slowly in cold water, was placed on the frit. Then the frit was filled with  $\text{H}_2\text{O}$  and the whole arrangement left undisturbed in a vertical position. Two kinds of crystals formed in the lower tube: red-brown plates which were used in this structure determination, and long yellow needles. Later, when the solvent had partly evaporated, a third kind of crystals, light-brown columns, formed on top of the zone of red-brown and yellow products. Further investigations of these different modifications are in progress. After ten weeks the products were sucked off, washed with  $\text{H}_2\text{O}$ , and dried in the air. Only the red-brown crystals survived this procedure, the others broke into a powder.

A plate-like crystal with approximate dimensions  $0.2 \times 0.15 \times 0.05$  mm was mounted with epoxy glue on top of a glass capillary. Orientation matrix and lattice constants (see *Abstract*) were calculated from the setting angles of 15 reflections, centered on a computer-controlled four-circle single-crystal diffractometer (Syntex  $P2_1$ , Mo  $K\alpha$  radiation, graphite monochromator). Data collection ( $\theta$ - $2\theta$  scans, background-peak-background step-scan mode,  $5^\circ < 2\theta < 55^\circ$ ) yielded 808 observed unique reflections with  $I > 3\sigma(I)$ . They were corrected for Lorentz and polarization factors, and an absorption correction by numerical integration was applied. Statistical weights were assigned.

Calculations were carried out with programs of the *Structure Determination Package* (Enraf-Nonius) on a PDP11/45 computer (Department of Chemistry, Stanford University). Scattering factors were derived from *International Tables for X-ray Crystallography* (1974) and anomalous terms included. Plots were performed with the PDP11/45-Versatec plotter adaption of *ORTEP* (Johnson, 1965).

### Structure determination and refinement

The systematic extinctions resembled those for space group  $P2_1/n$ , but  $\bar{1}04$  and  $\bar{1}06$  were nonextinct ( $I \approx$

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10 $\sigma$ ). Thus, solution of the structure was tried in space groups with extinction conditions  $0k0$ ,  $k$  odd, only: in centrosymmetric  $P2_1/m$  the structure could not be solved at all, but structure solution appeared successful in noncentrosymmetric  $P2_1$ , using Patterson and Fourier methods. Refinement with anisotropic temperature factors finally led to  $R = 0.042$ , but some difficulties were encountered: no convergence, when positional and thermal parameters were refined together, large deviations of bond distances and angles from the expected values, and unreasonable temperature factors. A plot revealed that the structure is actually centrosymmetric, and that the true space group has to be  $P2_1/n$ . The two forbidden reflections were removed, and refinement with anisotropic temperature factors was successful and without difficulties. It converged with  $R = 0.047$ , but with only half the number of parameters, as compared to refinement in space group  $P2_1$ . The strongest peaks in a difference Fourier synthesis could be identified as H atoms. They were inserted with fixed temperature factors of  $4 \text{ \AA}^2$ . After refining the parameters of the heavy atoms and then the coordinates of the H atoms,  $R$  dropped to 0.041. Then three reflections with structure factors just above the statistical threshold, and with much lower calculated ones, were rejected. Thus, final refinement was based on 803 observations. After six cycles of refinement of all the free parameters, a final  $R = 0.037$  was obtained (weighted  $R = 0.045$ , maximum shift/error = 0.06).\*

\* Lists of structure factors, anisotropic temperature factors, and deviations of the atoms from a least-squares plane have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34105 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates

	<i>x</i>	<i>y</i>	<i>z</i>
Ni(1)	0.0000 (0)	0.0000 (0)	0.0000 (0)
O(1)	0.2367 (9)	0.1261 (3)	0.2064 (3)
O(2)	-0.3264 (9)	-0.1979 (2)	-0.0061 (3)
O(3)	0.2011 (8)	-0.3385 (2)	-0.0032 (3)
N(1)	0.0733 (10)	0.0380 (3)	0.1571 (3)
N(2)	-0.0085 (10)	-0.0082 (3)	0.3474 (3)
N(3)	-0.3375 (11)	-0.1905 (3)	0.2299 (4)
N(4)	-0.1987 (9)	-0.1148 (3)	0.0592 (3)
C(1)	-0.041 (1)	-0.0227 (3)	0.2309 (4)
C(2)	-0.205 (1)	-0.1152 (3)	0.1730 (4)
H(1)	0.26 (1)	0.150 (4)	0.147 (4)
H(2)	0.07 (1)	0.045 (4)	0.366 (4)
H(3)	-0.10 (1)	-0.052 (4)	0.394 (4)
H(4)	-0.44 (1)	-0.239 (4)	0.198 (4)
H(5)	-0.34 (1)	-0.187 (4)	0.303 (4)
H(6)	0.36 (1)	-0.301 (4)	0.011 (4)
H(7)	0.04 (1)	-0.307 (4)	-0.005 (4)

### Description of the structure and discussion

Atomic coordinates are listed in Table 1. Ni occupies inversion centers at 0,0,0 and  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ . The OAOH moiety acts as a bidentate ligand *via* the oxime N atoms. As usual in  $\alpha, \beta$ -dione dioximato complexes, H bridges connect the O atoms of the two ligands, being 2.567 (4) Å apart. The H bridge is asymmetric and close to linear. Bond distances and angles within the complex molecule are shown in Fig. 1, those involving the water molecule are included in Fig. 2. Table 2 contains bond distances and angles involving amino H atoms. Fig. 3 shows an *xy* projection of the structure. The structure consists of stacks of planar Ni(OAOH)<sub>2</sub> molecules along the *a* axis. The normals of the molecular planes are inclined to the *a* axis at an angle of 30°. The resulting interplanar distance is 3.44 Å. The direction and amount of the tilt have adjusted so as to bring the Ni atom of a molecule perpendicularly above and below oxime N atoms of adjacent molecules (Fig. 2). Thus the coordination of the Ni may be described as tetragonal bipyramidal. Adjacent molecules of a stack are additionally linked together by H bridges from a water molecule to oxime O atoms [O(2)]. Thus, a

Table 2. Bond distances (Å) and angles (°) involving amino H atoms

N(2)—H(2)	0.78 (5)	N(3)—H(4)	0.80 (5)
N(2)—H(3)	0.90 (5)	N(3)—H(5)	0.85 (5)
C(1)—N(2)—H(2)	111 (4)	C(2)—N(3)—H(4)	124 (4)
C(1)—N(2)—H(3)	122 (3)	C(2)—N(3)—H(5)	121 (4)
H(2)—N(2)—H(3)	126 (5)	H(4)—N(3)—H(5)	114 (5)

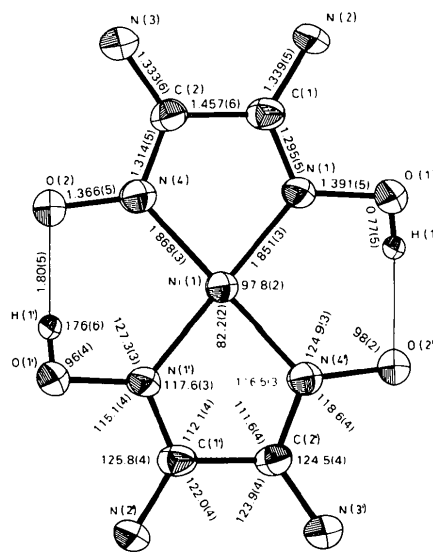


Fig. 1. The Ni(OAOH)<sub>2</sub> molecule with the numbering scheme, bond distances (Å) and angles (°). Amino H atoms are omitted for clarity. The bridging H is drawn with  $B = 1 \text{ \AA}^2$ .

ladder-like structure results. This structural feature has never been encountered before in  $\alpha,\beta$ -dione dioximato complexes. Details are shown in Fig. 2.

The maximum deviation from a least-squares plane through the non-hydrogen atoms of the complex molecule excluding O(2) is 0.024 Å. O(2) sticks out of this plane by 0.105 Å, probably due to the hydrogen-bonding interaction with the water molecule. The amino groups are not involved in any unusual intermolecular interactions. Such an interaction was found in (OAOH)<sub>2</sub>Co.OAOH<sub>2</sub> (Bekaroglu, Sarisaban, Koray & Ziegler, 1977), where the Co is in square-bipyramidal coordination involving amino N atoms of adjacent molecules at the apexes.

In (OAOH)<sub>2</sub>Ni.H<sub>2</sub>O.DMF (Endres, 1978), the DMF inclusion does not allow the occurrence of a stacked structure. Two water molecules are bound by H bridges to O atoms of one of the two complex molecules in the unit cell, and no linking of adjacent complex molecules occurs.

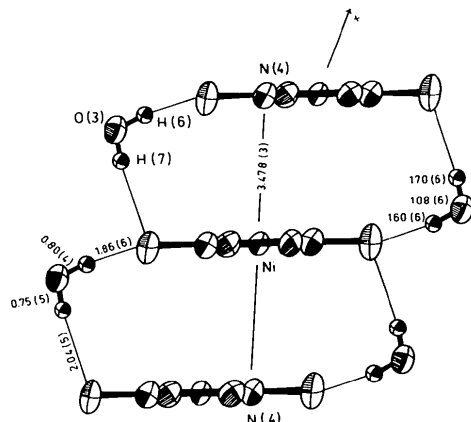


Fig. 2. Projection parallel to the molecular plane showing details of the bridging water molecule. Amino groups are omitted. H atoms are drawn with  $B = 1 \text{ \AA}^2$ .

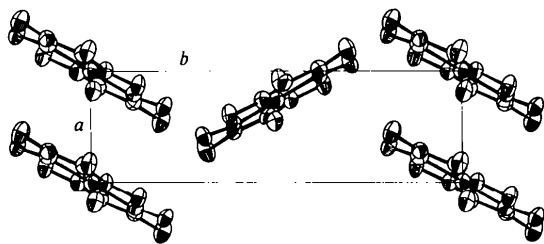


Fig. 3. Projection of the structure onto the  $ab$  plane. H atoms and the water molecules are omitted.

Following a discussion of crystal structures of  $\alpha,\beta$ -dione dioximato complexes of the Ni triad (Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977), the title compound is an  $M-L-M$  form, characterized by the slanted stacking. It could be argued that the yellow crystals mentioned in the experimental part exhibit a perpendicular stacking pattern ( $M-M$  form), resembling the only other case where the occurrence of an  $\alpha,\beta$ -dione dioximato nickel complex in both modifications is well established: in bis(ethylmethylglyoximato)nickel(II) (Sharpe & Wakefield, 1957; Bowers, Banks & Jacobson, 1972) where the  $M-M$  form is yellow and the  $M-L-M$  form is red.

This structure determination was carried out during a stay with the group of Professor W. A. Little, Stanford University, supported in part by the National Science Foundation (Grant No. DMR 76-82087-A02) and Office of Naval Research (Contract No. N0014-77-C-0631). The author is indebted to Professor K. O. Hodgson, Department of Chemistry, Stanford, for making available the diffractometer and computer facilities, which were procured in part through funds made available by the National Science Foundation Instrument Grant Program. A travel grant from Deutsche Forschungsgemeinschaft is acknowledged.

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