

Tris(oxamide oxime)nickel(II) Dichloride Hemihydrate

BY HELMUT ENDRES AND THOMAS JANNACK

Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg 1,
Federal Republic of Germany

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Abstract. $[\text{Ni}(\text{C}_2\text{H}_6\text{N}_4\text{O}_2)_3]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{C}_6\text{H}_{18}\text{N}_{12}\text{NiO}_6^{2+} \cdot 2\text{Cl}^- \cdot \frac{1}{2}\text{H}_2\text{O}$, $M_r = 492.9$, monoclinic, $C2/c$, $a = 16.574$ (6), $b = 9.700$ (3), $c = 15.956$ (5) Å, $\beta = 131.35$ (2)°, $Z = 4$, $d_c = 1.70$ Mg m⁻³; final $R = 0.055$ for 774 reflections. In the dark-blue complex, Ni is octahedrally coordinated by the oxime N atoms of three neutral oxamide oxime chelate ligands. The Cl⁻ ions are linked by H bridges with the oxime O atoms.

Introduction. We are presently investigating the structural variability of complexes of Ni, Pd, and Pt with oxamide oxime (diaminoglyoxime, oaoH₂) (Endres & Schlicksupp, 1979, 1980; Endres, 1980*a,b*, and references therein). Owing to a pronounced ability to form H bridges, unusual molecular and crystal structures are formed by these complexes, compared to the normal behaviour of 1,2-dione dioximato metal compounds. The title compound is obtained as dark-blue crystals, several mm³ in volume, from not-too-dilute ethanolic solutions of the starting materials. A solution of 1.2 g NiCl₂·6H₂O in 30 ml ethanol is added dropwise to a refluxing solution of 1.2 g oaoH₂ in ethanol. After cooling, a light-blue precipitate is filtered off and dissolved in slightly acidic (HCl) H₂O. The crystals form from the dark-blue solution on evaporation in air. In air containing traces of basic gases they decompose within a few days, otherwise they seem to be stable indefinitely. A similar sensitivity to bases is encountered in solution: if the blue acidic solution is neutralized or made slightly basic, it changes its colour to yellow, and an orange powder precipitates, which analyses as Ni(oaoH)₂.

Lattice parameters of the blue crystals were derived from the setting angles of 25 reflections, centred on a diffractometer (Syntex R3, monochromatic Mo K α radiation). Data collection (θ - 2θ scans, background-peak-background, $2\theta < 50^\circ$) yielded 774 observed independent reflections with $I > 3.0\sigma(I)$. An empirical absorption correction (ψ scans) as well as corrections for Lorentz and polarization factors were applied.

The Ni atom, occupying a twofold axis, was located from a Patterson synthesis; the other non-hydrogen atoms were found on Fourier maps. The temperature factor of the water O(4) was rather large, indicating

that a statistical occupation of its site was likely. Varying the site-occupation factor resulted in an occupation ratio of 0.51 (2). R was 0.061. The positions of the H atoms (except those of the H₂O) could be recognized on a difference map. They were refined with fixed temperature factors $B = 4$ Å². Refinement by full-matrix least squares with anisotropic temperature factors for the non-H atoms converged with $R = 0.055$ (maximum shift/error 0.8).*

Calculations were performed on a Nova 3 computer with *SHELXTL* (Sheldrick, 1979) and on an IBM 370/168 with the XRAY system (Stewart, Kundell &

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35245 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$, for H $\times 10^3$) and isotropic temperature factors equivalent to the refined anisotropic values

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
Ni	0	510 (2)	2500	0.026
Cl	3216 (2)	372 (3)	3892 (2)	0.046
O(1)	2168 (6)	1152 (10)	4955 (7)	0.049
O(2)	-1452 (6)	-1836 (8)	2335 (6)	0.038
O(3)	1372 (6)	2281 (8)	2138 (7)	0.046
O(4)	6302 (14)	1618 (18)	4074 (14)	0.063
N(1)	1254 (6)	304 (9)	4208 (7)	0.031
N(2)	-552 (7)	-926 (9)	2991 (7)	0.031
N(3)	1728 (10)	-467 (18)	5872 (9)	0.087
N(4)	-46 (11)	-2248 (16)	4517 (11)	0.077
N(5)	738 (7)	2227 (10)	2442 (8)	0.043
N(6)	556 (9)	4613 (12)	2096 (9)	0.059
C(1)	1085 (9)	-432 (15)	4735 (9)	0.042
C(2)	95 (9)	-1286 (13)	4033 (10)	0.042
C(3)	350 (8)	3425 (11)	2363 (9)	0.033
H(1)	246 (9)	109 (13)	472 (10)	
H(2)	-219 (8)	-101 (11)	187 (9)	
H(3)	208 (9)	196 (12)	275 (9)	
H(4)	234 (8)	8 (12)	615 (9)	
H(5)	166 (9)	-103 (12)	623 (10)	
H(6)	50 (9)	-268 (12)	521 (10)	
H(7)	-61 (10)	-266 (13)	409 (10)	
H(8)	-10 (8)	526 (12)	168 (9)	
H(9)	76 (9)	464 (14)	179 (10)	

Baldwin, 1970) and scattering factors from *International Tables for X-ray Crystallography* (1974). Unit weights were used for all reflections. The plot was drawn by *ORTEP* (Johnson, 1965).

Discussion. As Ni occupies a twofold axis, the asymmetric unit is represented by half the complex. Atomic coordinates are listed in Table 1. Ni is surrounded octahedrally by the oxime N atoms of three neutral oaoH₂ chelate molecules. The complex ion together with the adjacent Cl⁻ ions is shown in Fig. 1; bond distances and angles are given in Table 2. H bridges are formed from the oxime H atoms, the most acidic protons of the cation, to the Cl⁻ ions. All these bridges are intramolecular, and there are three for each Cl⁻, indicated in the figure. Relevant distances are summarized in Table 3, which also shows that the water molecule is likely to form H bridges to the complex ions. The H bridges form links between the cations by extending to O(2) and N(4) of one molecule and to N(6) of an adjacent one.

Table 2. Bond lengths (Å) and angles (°) in the cation

Ni—N(1)	2.074 (7)	N(3)—C(1)	1.369 (17)
N(2)	2.082 (12)	H(4)	0.95 (13)
N(5)	2.104 (12)	H(5)	0.86 (17)
O(1)—N(1)	1.417 (11)	N(4)—C(2)	1.33 (3)
H(1)	0.8 (2)	H(6)	0.95 (10)
O(2)—N(2)	1.427 (11)	H(7)	0.81 (12)
H(2)	1.22 (11)	N(5)—C(3)	1.293 (16)
O(3)—N(5)	1.42 (2)	N(6)—C(3)	1.348 (19)
H(3)	0.96 (10)	H(8)	1.04 (11)
N(1)—C(1)	1.27 (2)	H(9)	0.8 (2)
N(2)—C(2)	1.296 (15)	C(1)—C(2)	1.486 (17)
		C(3)—C(3')	1.49 (3)
N(1)—Ni—N(2)	75.5 (4)	C(2)—N(4)—H(6)	126 (10)
N(2')	97.0 (4)	H(7)	114 (11)
N(5)	91.6 (4)	H(6)—N(4)—H(7)	117 (12)
N(5')	97.2 (4)	C(3)—N(6)—H(8)	110 (8)
N(1')	169.0 (4)	H(9)	124 (10)
N(2)—Ni—N(2')	96.0 (5)	H(8)—N(6)—H(9)	107 (13)
N(5)	163.4 (4)	N(1)—C(1)—N(3)	125 (1)
N(5')	95.8 (5)	C(2)	116 (1)
N(5)—Ni—N(5')	75.3 (5)	N(3)—C(1)—C(2)	119 (2)
N(1)—O(1)—H(1)	102 (8)	N(2)—C(2)—N(4)	128 (1)
N(2)—O(2)—H(2)	100 (5)	C(1)	112 (1)
N(5)—O(3)—H(3)	109 (11)	N(4)—C(2)—C(1)	119 (1)
Ni—N(1)—O(1)	129.5 (8)	N(5)—C(3)—N(6)	126 (2)
C(1)	117.2 (7)	C(3')	114 (1)
O(1)—N(1)—C(1)	110.6 (9)	N(6)—C(3)—C(3')	120 (1)
Ni—N(2)—O(2)	130.1 (8)		
C(2)	117.8 (9)		
O(2)—N(2)—C(2)	111 (1)		
Ni—N(5)—O(3)	128.8 (8)		
C(3)	117 (1)		
O(3)—N(5)—C(3)	111 (1)		
C(1)—N(3)—H(4)	106 (9)		
H(5)	125 (7)		
H(4)—N(3)—H(5)	128 (10)		

Table 3. H bridges (Å) from Cl⁻ and H₂O to atoms of the complex ion

E.s.d.'s are of the order of 0.15 Å for distances involving H, otherwise 0.02 Å.

Cl—H(1)	2.46	Cl—O(1)	3.22
Cl—H(2)	1.85	Cl—O(2)	3.07
Cl—H(3)	2.17	Cl—O(3)	3.05
H ₂ O—O(2)	2.85		
H ₂ O—N(4)	2.97		
H ₂ O—N(6)	3.03	H ₂ O—H(8)	1.99

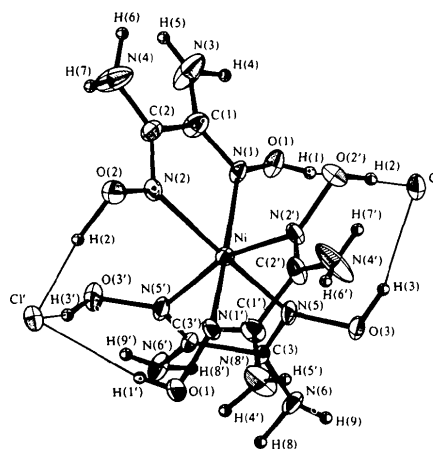


Fig. 1. The [Ni(oaoH₂)₃]²⁺ ion with its adjacent Cl⁻ anions. Thermal ellipsoids represent 25% probability. H atoms are drawn with arbitrary temperature factors.

This compound should be identical with the blue product obtained by Tschugaeff & Surenjanz (1907) by dissolving Ni(oaoH)₂·2H₂O in HCl and crystallizing. These authors formulated the compound as [Ni(oaoH₂)₃]Cl₂ and assumed, probably because of the unusual blue colour, that the ligand molecules coordinate *via* the amino N atoms. This structure determination shows that the oaoH₂ moieties coordinate in the normal way, *via* the oxime N atoms. The blue colour should be caused by the octahedral ligand field around Ni. A similar octahedral coordination by three neutral oaoH₂ molecules was found in [Co(oaoH₂)₃]Cl₃ (Bekaroglu, Sarisaban, Koray, Nuber, Weidenhammer, Weiss & Ziegler, 1978).

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Structure of Bis(*N,N*-dimethyldithiocarbamato)lead(II)

BY HITOSHI IWASAKI

The Institute of Physical and Chemical Research, Wako-shi, Saitama 351, Japan

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Abstract. $[\text{Pb}\{\text{S}_2\text{CN}(\text{CH}_3)_2\}_2]$, $\text{C}_6\text{H}_{12}\text{N}_2\text{PbS}_4$, $M_r = 447.6$, orthorhombic, *Fdd*2, $a = 21.073$ (7), $b = 27.422$ (9), $c = 4.214$ (4) Å, $U = 2435$ Å³, $D_x = 2.44$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 16.7$ mm⁻¹, $Z = 8$. The structure was refined to $R = 0.045$ by the block-diagonal least-squares method. The molecule has exact 2 symmetry. Four S atoms are coordinated to the Pb atom pyramidally, the two independent Pb–S distances being 2.779 (5) and 2.873 (6) Å.

Introduction. The crystal structure analysis of the title compound was undertaken as part of a series of studies on coordination compounds with metal–sulfur bonds. The compound was prepared by adding lead acetate to an aqueous solution of potassium *N,N*-dimethyldithiocarbamate. Pale-yellow needle crystals elongated along the *c* axis were grown from an acetone solution. They are extremely fragile and very easily cleaved into fibers.

A specimen of approximate dimensions 0.01 × 0.01 × 0.2 mm was mounted on a Rigaku four-circle automated diffractometer. Intensities of reflexions up to $2\theta \leq 55^\circ$ were measured with Mo *K*α radiation monochromated by a graphite plate. The measurement was made in the ω – 2θ scan mode with a scanning speed of 2° min⁻¹ in 2θ , and 788 independent reflexions with values of $|F_o|$ larger than three times the standard deviation were obtained. The intensities were corrected for Lorentz, polarization and absorption effects.

The structure was solved by the heavy-atom technique, and refined by the block-diagonal least-squares method with the weighting scheme $w = 0.5$ for $|F_o| < 80$, 1.0 for $80 \leq |F_o| < 250$ and $(250/F_o)^2$ for $|F_o| \geq 250$. The atomic form factors and the correction terms for anomalous scattering were taken from *Inter-*

national Tables for X-ray Crystallography (1974). The final *R* value was 0.045 without H atoms.* All the calculations were performed on a Facom 230-75 computer of this Institute using the UNICS 3 program system (Sakurai & Kobayashi, 1979).

Discussion. The atomic coordinates are shown in Table 1, and bond lengths and angles are listed in Table 2. The crystals consist of monomeric molecules composed of one Pb atom and two chelating carbamate ligands. The Pb atom lies on a crystallographic twofold axis, so that the molecule has exact 2 symmetry. The two carbamate ligands are coordinated through S atoms to the metal atom pyramidally, and in each chelate ring one Pb–S bond is significantly shorter than the other. The Pb atom is approximately on the plane of the ligand, the deviation being 0.58 (3) Å. The dihedral angle between the two ligand planes is 38 (1)°. These features are similar to those observed in the crystals of $[\text{Pb}(\text{S}_2\text{CNEt}_2)_2]$ (Iwasaki & Hagihara, 1972), $[\text{Pb}\{\text{S}_2\text{CN}(i\text{Pr})_2\}_2]$ (*iPr* = isopropyl; Ito & Iwasaki, 1980), and also of other dithioacid complexes of Pb (Hagihara & Yamashita, 1966; Hagihara, Watanabe & Yamashita, 1968; Ito, 1972), although the exact twofold symmetry of the present molecule is rather rare. The geometry within the ligand is normal.

The crystal structure is characterized by the stacking of molecules along the *c* axis (Fig. 1). Within this stack, each Pb atom is in contact at 3.361 (6) Å with two S

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