

opportunity of separating the two effects in the cation [Fe₂(C₅H₅)₂(CO)₃(SC₂H₅)₃]⁺, the structure of the SbF₆⁻ salt of which has already been determined (English, Haines & Nassimbeni, 1977). It was anticipated that the crystal packing in the tetraphenylborate salt would be grossly different from that in the SbF₆⁻ salt due to the much greater size of the anion.

As can be seen from the packing diagram (Fig. 2), this is indeed the case; the complex has not crystallized in a centred space group as does the corresponding SbF₆⁻ salt and the structure is somewhat less compact than the SbF₆⁻ structure [average volume occupied by a non-hydrogen atom = 18.54 Å³ for the B(C₆H₅)₄⁻ salt, = 17.67 Å³ for the SbF₆⁻ salt].

However, a comparison of bond lengths and angles in the cations in the two structures reveals no major differences. A slight increase of 0.015 Å in the Fe—Fe length is observed for the B(C₆H₅)₄⁻ salt, with a concomitant increase in the Fe(1)—S—Fe(2) angle. The Fe(1)—S—Fe(2)—C(3) ring is also more puckered; the angles between the planes defined by Fe(1), Fe(2), S and Fe(1), Fe(2), C(3); and by Fe(1), S, C(3), and Fe(2), S, C(3) being 18.3 and 22.4° as opposed to the corresponding values of 15.6 and 19.2° in the SbF₆⁻ salt.

In conclusion, therefore, it can be stated with some certainty that systems where two Fe atoms are bound

together and where two bridging ligands symmetrically span the metal—metal bond are stereochemically quite rigid. Gross differences in the metal—metal length can be ascribed to changes of electron density on the metal atoms due to different bridging ligands or overall charge, as structural parameters in such systems seem insensitive to crystal packing.

All calculations in this study were performed on the University of Cape Town's Univac 1106 computer with the *SHELX* (Sheldrick, 1975) program system.

We thank Dr G. Gafner of the CSIR (Pretoria) for performing the data collection and the CSIR and the University of Cape Town for research grants.

References

- ADAMS, R. D., BRICE, M. D. & COTTON, F. A. (1974). *Inorg. Chem.* **13**, 1080–1085.
 BRYAN, R. F., GREENE, P. T., NEWLANDS, M. J. & FIELD, D. S. (1970). *J. Chem. Soc. A*, pp. 3068–3074.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 ENGLISH, R. B., HAINES, R. J. & NASSIMBENI, L. R. (1977). *J. Organomet. Chem.* **135**, 351–360.
 ENGLISH, R. B., HAINES, R. J. & NOLTE, C. R. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1030–1033.
 SHELDRIK, G. M. (1975). Private communication.

Acta Cryst. (1978). **B34**, 2306–2309

Bis(oxamide oximato)nickel(II)—Water—Dimethylformamide

BY H. ENDRES

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

(Received 16 February 1978; accepted 21 March 1978)

Abstract. Ni(C₂H₅N₄O₂)₂·H₂O·C₃H₇NO, FW 384.0, triclinic, *P*1̄, *a* = 8.116 (2), *b* = 9.902 (2), *c* = 9.856 (1) Å, α = 94.87 (2), β = 99.98 (1), γ = 100.98 (2)°, *V* = 760.08 Å³, *Z* = 2, *d*_c = 1.70 g cm⁻³. The structure was refined to *R* = 0.051 for 3734 reflections. There are two independent, centrosymmetric, planar complex molecules in the unit cell, one of them bound by hydrogen bonds to two water molecules. The water and the dimethylformamide do not coordinate to the metal.

Introduction. Oxamide oxime (diaminoglyoxime), a possible chelating ligand with two additional potentially

coordinating sites at the two amino N atoms, has been known since 1889 (Fischer, 1889; Ephraim, 1889). A summary of the methods of its preparation and a discussion of the conformation of the free molecule were published by Ungnade, Kissinger, Narath & Barham (1963). Pearse & Pflaum (1959) reported spectroscopic investigations on several transition-metal complexes (Fe, Co, Ni, Cu). The coordination chemistry of this ligand has recently aroused new interest (Sarisaban, 1976), and the first X-ray structure analysis of an oxamide oxime (OAOH₂) complex has been published: Co(OAOH₂)₂·OAOH₂ (Bekaroglu, Sarisaban, Koray & Ziegler, 1977). The Co atom has a square-

bipyramidal coordination with the four oxime N atoms of two chelating OAOH molecules forming the base and amino N atoms of adjacent complexes at the apexes, thus forming chains in the crystal. The structure of another Co complex, $[\text{Co}(\text{OAOH}_2)_3]\text{Cl}_3$, where the Co is octahedrally coordinated by the bidentate ligands, is presently being investigated (Weiss, Nuber, Bekaroglu, Koray, Weidenhammer & Ziegler, 1978). I found the structural chemistry of this and related ligands interesting because the free amino substituents could be used as points of attack for chemical reactions, either to form new ligand systems [e.g. in a way similar to that reported by Lewis & Wainwright (1977) for 6,6'-dihydrazino-2,2'-bipyridyl-nickel(II) perchlorate] or to cross-link the monomer complex molecules to form polynuclear species.

The OAOH₂ was prepared according to Ephraim (1889). The solvent-free Ni complex precipitates as fine brown needles when a solution of 10 mmol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 100 ml H_2O , buffered with sodium acetate to pH ~8, is added dropwise to a boiling solution of 10 mmol oxamide oxime in 600 ml ethanol. As the crystals were too small for single-crystal investigations, media for recrystallization were sought (meanwhile larger crystals were grown by diffusion methods and are presently under investigation). The title compound is obtained by dissolving the complex in boiling dimethylformamide (DMF), filtering off the undissolved residue and evaporating slowly at room temperature (about three weeks). The red crystals are sucked off, washed with DMF and dried in air. They must not be washed with alcohol because they lose included DMF and collapse to an orange powder. This also happens when the crystals are heated to above 80°C.

Photographs (Cu $K\alpha$ radiation) showed the crystals to be triclinic. Lattice constants were calculated by least squares (Berdesinski & Nuber, 1966) from diffractometrically determined θ values of 75 reflections. Intensity measurements were performed on a computer-controlled single-crystal diffractometer (Siemens AED, Mo $K\alpha$ radiation, θ - 2θ scans, five-value method) up to $2\theta = 72^\circ$. Reflections with $I < 2.58\sigma(I)$ were regarded as unobserved; in later refinement cycles several reflections just above this limit were also discarded. 3734 observed intensities remained for calculations. They were corrected for Lorentz and polarization factors only.

The intensity distribution indicated that the Ni atoms occupy positions at (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. This was supported by the Patterson synthesis. As a heavy atom lies on (0,0,0), some of the Patterson vectors must be identical to atomic positions. This was checked by R -factor calculations, space group $P\bar{1}$ being assumed. Some of the non-metal atoms were located in this way; the others (except H) were found from Fourier syntheses. Isotropic refinement converged at $R =$

0.116, but the temperature factors of the atoms of the DMF molecule were rather high. Therefore, the non-centrosymmetric space group was considered, but refinement was worse. Thus $P\bar{1}$ should be correct, and the DMF is probably subject to slight positional disorder, as is also shown by the relatively high e.s.d.'s of the positional coordinates.

Refinement with anisotropic temperature factors resulted in $R = 0.057$, and H atom positions were sought on a difference map. All H atoms could be located, except for those of DMF, which is understandable because of the disorder. The H atoms were inserted in the refinement with fixed isotropic temperature factors equal to those of the carrier atoms in the last isotropic cycle. The last refinement cycles were performed by block-diagonal least squares and

Table 1. Atomic coordinates of the non-hydrogen atoms ($\times 10^4$)

	x	y	z
Ni(1)	0	0	0
N(1)	9162 (4)	9487 (3)	1568 (3)
O(1)	7500 (3)	9356 (3)	1723 (3)
C(1)	278 (5)	9210 (4)	2575 (4)
N(2)	9905 (5)	8762 (5)	3758 (4)
C(2)	2013 (5)	9386 (4)	2253 (4)
N(3)	3327 (5)	9111 (4)	3114 (4)
N(4)	2045 (4)	9770 (4)	1027 (3)
O(2)	3614 (4)	9955 (4)	624 (3)
Ni(2)	5000	5000	5000
N(5)	5026 (4)	3672 (3)	3571 (3)
O(3)	4505 (4)	2280 (3)	3546 (3)
C(3)	5608 (5)	4125 (4)	2495 (4)
N(6)	5693 (6)	3279 (4)	1381 (4)
C(4)	6113 (5)	5648 (4)	2658 (4)
N(7)	6689 (5)	6376 (4)	1685 (4)
N(8)	5915 (4)	6214 (3)	3852 (3)
O(4)	6338 (4)	7624 (3)	4136 (3)
O(5)	2379 (6)	5236 (5)	510 (4)
C(5)	717 (13)	3083 (9)	1604 (11)
C(6)	555 (11)	4895 (13)	3493 (8)
N(9)	1051 (5)	4476 (5)	2224 (4)
C(7)	1871 (9)	5522 (8)	1600 (8)
O(6)	7296 (5)	1148 (4)	3984 (3)

Table 2. Coordinates of the H atoms ($\times 10^3$)

	x	y	z
H(1)	655 (7)	985 (6)	15 (6)
H(2)	883 (8)	861 (6)	388 (6)
H(3)	70 (8)	873 (6)	438 (7)
H(4)	444 (8)	918 (6)	296 (6)
H(5)	651 (8)	100 (6)	627 (6)
H(6)	394 (7)	206 (6)	521 (6)
H(7)	519 (8)	220 (7)	130 (6)
H(8)	614 (8)	340 (7)	106 (6)
H(9)	680 (8)	739 (7)	177 (6)
H(10)	683 (8)	591 (6)	104 (6)
H(11)	717 (8)	62 (7)	340 (7)
H(12)	638 (8)	160 (7)	382 (7)

yielded $R = 0.051$.^{*} Atomic positions of non-hydrogen atoms are given in Table 1, those of the located H atoms in Table 2. Calculations were carried out on Siemens 301 (Anorganisch-Chemisches Institut, Heidelberg) and IBM 370/168 (Universitätsrechenzentrum, Heidelberg) computers with programs from the XRAY system (Stewart, Kundell & Baldwin, 1970). Scattering factors were those of Hanson, Herman, Lea & Skillman (1964).

Discussion. Fig. 1 shows a projection of the structure along c with the numbering scheme. Two centrosymmetric crystallographically-independent molecules

^{*} Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33480 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

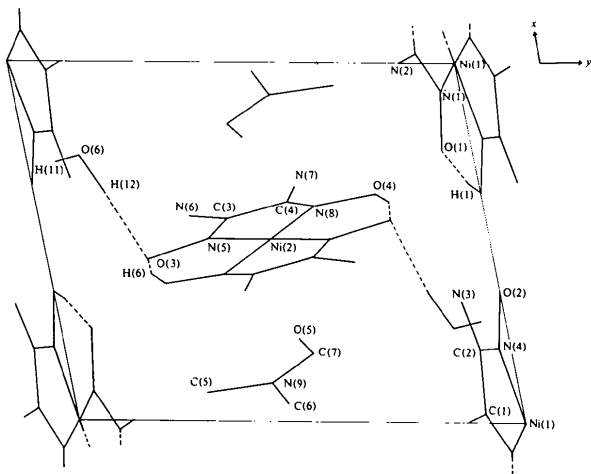


Fig. 1. Projection of the structure on to the ab plane, with the numbering scheme. Most of the H atoms are omitted for clarity.

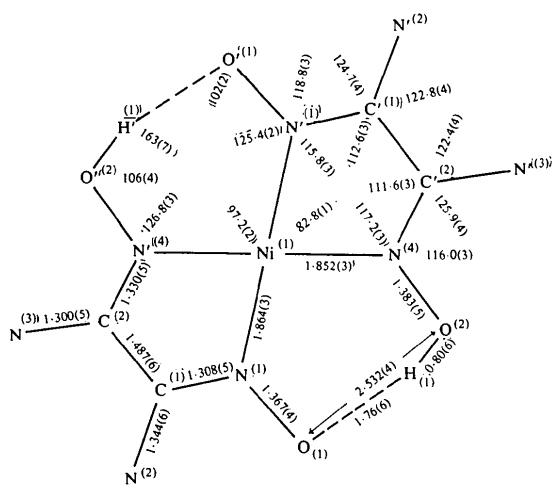


Fig. 2. Bond distances (Å) and angles (°) in molecule 1 (at 0,0,0), excluding amino H atoms.

are centered at (0,0,0) (molecule 1) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (molecule 2). The bond distances and angles (Figs. 2 and 3) in both molecules are identical. The hydrogen bonds between the oxime O atoms are not linear and are asymmetric. The water molecule is connected by a nearly linear hydrogen bond to O(3) of molecule 2. Geometric details are included in Fig. 3. The distances and angles involving H atoms not included in Figs. 2 and 3 are given in Table 4. The DMF molecule merely acts as a space filler and has no remarkable interactions with the complexes. The complexes are planar; deviations of the atoms from the respective planes are given in Table 3. The planes of the two independent molecules are nearly perpendicular (88°). The relative arrangement of the complexes is determined solely by packing criteria. There are no electronic interactions between them – an important contrast to the structure

Table 3. Deviations of atoms (Å) from least-squares planes

Plane equations are of the form $Px + Qy + Rz = S$.

Molecule 1 (at 0,0,0)

$$P = -0.0354, Q = 8.969, R = 2.874, S = 0.0$$

Ni(1)	0.000	N(2)	-0.027
O(2)	0.011	C(2)	0.026
N(1)	0.021	N(3)	-0.020
O(1)	0.007	N(4)	0.017
C(1)	0.021		(Centrosymmetric)

Molecule 2 (at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)

$$P = 7.294, Q = -2.762, R = 2.684, S = 3.608$$

Ni(2)	0.000	C(4)	0.004
N(5)	0.002	N(7)	-0.038
O(3)	0.000	N(8)	0.024
C(3)	0.013	O(4)	0.019
N(6)	0.010		(Centrosymmetric)

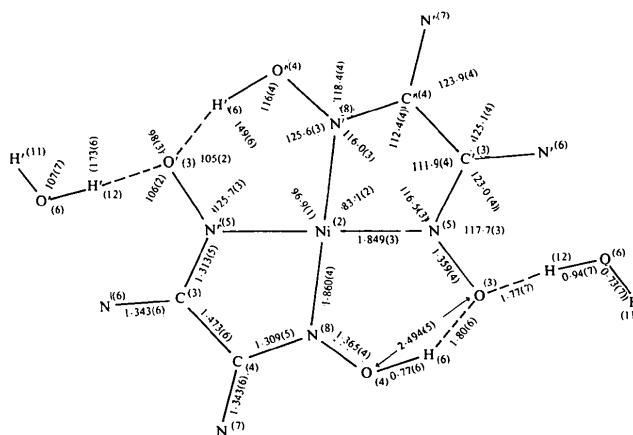


Fig. 3. Bond distances (Å) and angles (°) in molecule 2 (at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), excluding amino H atoms, and the water molecule.

Table 4. Bond distances (Å) and angles (°) involving H atoms not included in Figs. 2 and 3

N(2)—H(2)	0.89 (7)	N(6)—H(7)	1.06 (6)
N(2)—H(3)	0.82 (6)	N(6)—H(8)	0.53 (7)
C(1)—N(2)—H(3)	118 (5)	C(3)—N(6)—H(7)	121 (4)
H(2)—N(2)—H(3)	122 (6)	C(3)—N(6)—H(8)	124 (7)
C(1)—N(2)—H(2)	120 (4)	H(7)—N(6)—H(8)	112 (8)
N(3)—H(4)	0.94 (7)	N(7)—H(9)	0.99 (6)
N(3)—H(5)	0.63 (6)	N(7)—H(10)	0.80 (7)
C(2)—N(3)—H(4)	126 (4)	C(4)—N(7)—H(9)	120 (4)
C(2)—N(3)—H(5)	137 (6)	C(4)—N(7)—H(10)	113 (5)
H(4)—N(3)—H(5)	96 (7)	H(9)—N(7)—H(10)	126 (6)

of bis(oxamide oximato)cobalt(II)-oxamide oxime (Bekaroglu, Sarisaban, Koray & Ziegler, 1977), where the coordination of the Co atoms is tetragonal bipyramidal. In the Ni compound the amino substituents do not coordinate an adjacent metal, nor does the donating DMF molecule act as a ligand.

Acta Cryst. (1978). B34, 2309–2311

Sodium Acetylphosphonate Acetic Acid Solvate

BY PETER G. JONES AND OLGA KENNARD*

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

(Received 22 March 1978; accepted 29 March 1978)

Abstract. $\text{Na}^+\text{C}_2\text{H}_4\text{O}_4\text{P}^-\cdot\text{C}_2\text{H}_4\text{O}_2$, $M_r = 170.04$, monoclinic, $P2_1/c$, $a = 9.576$ (5), $b = 7.290$ (10), $c = 13.885$ (6) Å, $\beta = 120.87$ (2)°, $U = 832.0$ Å³, $Z = 4$, $D_x = 1.357$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 3.2$ cm⁻¹. The structure was refined to $R = 0.038$ for 2288 unique reflexions. A network of non-bonded interactions links the different residues in the extended crystal structure.

Introduction. Acetylphosphonic acid, $\text{CH}_3\text{—CO—PO}(\text{OH})_2$, is an analogue of pyruvic acid, and has been shown to be an effective reversible inhibitor of the enzyme complex pyruvate dehydrogenase (Harrison, Perham & Slater, unpublished; cited by Ambrose & Perham, 1976). An improved synthesis of acetylphosphonic acid (as its monosodium salt) has recently been designed (Dixon, Norris, Giddens & Sparkes, 1978) so that it might be better characterized and its

- References**
- BEKAROGLU, Ö., SARISABAN, S., KORAY, A. R. & ZIEGLER, M. (1977). *Z. Naturforsch. Teil B*, **32**, 387–392.
- BERDESINSKI, W. & NUBER, B. (1966). *Neues Jahrb. Mineral. Abh.* **104**, 113–146.
- EPHRAIM, J. (1889). *Chem. Ber.* **22**, 2305–2306.
- FISCHER, E. (1889). *Chem. Ber.* **22**, 1930–1936.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
- LEWIS, J. & WAINWRIGHT, K. P. (1977). *J. Chem. Soc. Dalton Trans.* pp. 734–739.
- PEARSE, G. A. & PFLAUM, R. T. (1959). *J. Am. Chem. Soc.* **81**, 6505–6508.
- SARISABAN, S. (1976). PhD Thesis, Technical Univ. of Istanbul.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- UNGNAD, H. E., KISSINGER, L. W., NARATH, A. & BARHAM, D. C. (1963). *J. Org. Chem.* **28**, 134–136.
- WEISS, J., NUBER, B., KORAY, A. R., WEIDENHAMMER, K. & ZIEGLER, M. (1978). *Acta Cryst.* B34, Submitted.

properties checked. The final stage of the synthesis involved recrystallization from aqueous acetic acid/diethyl ether, the product forming as an acetic acid adduct. This acetic acid could not be removed, and the possibility that the adduct was covalent, *i.e.* that the —CO— group had become $\text{—C}(\text{OH})(\text{OAc})\text{—}$, could not be excluded. A crystallographic investigation was therefore undertaken to determine the nature of the adduct.

100 mg of the adduct were dissolved in a mixture of 0.2 ml water and 1.0 ml glacial acetic acid, and diethyl ether was layered onto the solution. Large colourless crystals, in the form of rectangular blocks, appeared after a few days. Since the adduct is somewhat hygroscopic, crystals were sealed in Lindemann tubes with the mother liquor. A crystal 1.0 × 0.4 × 0.4 mm, elongated along **b**, was used to collect data on a Syntex $P2_1$ diffractometer using Cu $K\alpha$ radiation and a graphite monochromator. 1401 reflexions were measured in the range $0 < 2\theta < 116^\circ$; after application

* External Staff, Medical Research Council.