bonding scheme. There is a possibility of further hydrogen bonding in (II) [Table 5: O(6)···O*W* and N(4)···O*W*] but uncertainty in the positions of the H atoms of the water molecule prevents the assignment of further formal H-bonds.

In both (I) and (II), the Hg—S group is aligned about a centre of symmetry as in (*N,N*-diethyldithiocarbamato)methylmercury(II) (Chieh & Leung, 1976). In the latter, the intermolecular Hg···S distance is short (3·147 Å) while in (I) and (II) it is longer 3·67 (2) and 4·59 (3) Å respectively. The sum of the van der Waals radii for Hg and S is 3·35 Å (Pauling, 1960), so in (I) and (II) the interaction cannot be considered as secondary bonding as is the Hg···N(3) interaction. The orientation of the Hg—S groups about the centre of symmetry does, however, bear resemblance to the four-centred bridged intermediate proposed by Bach & Weibel (1976) and may provide additional support for such a mechanism of ligand exchange (equation 1).

All calculations were carried out on a Univac 1180 computer at the University of Cape Town.

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Bis(oxamide oximato)nickel(II)–Oxamide Oxime

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Abstract

$[Ni(C_2H_5N_4O_2)_2].C_2H_6N_4O_2$, $C_4H_{10}N_8NiO_4.C_2H_6N_4O_2$, $M_r = 411$, $P\bar{1}$, $a = 4{\cdot}982\ (1)$, $b = 12{\cdot}133\ (3)$, $c = 12{\cdot}871\ (4)$ Å, $\alpha = 67{\cdot}67\ (2)$, $\beta = 78{\cdot}84\ (2)$, $\gamma = 78{\cdot}14\ (2)°$, $V = 698{\cdot}5$ Å^3, $Z = 2$, $d_c = 1{\cdot}95$ Mg m^{-3}; final $R = 0{\cdot}050$ for 2055 reflections. The planar complex molecules form stacks along **a**, the normals of the planes being inclined at ~50° to the stacking axis. There are axial interactions between Ni and the amino groups of adjacent complex molecules within a stack. Free oxamide oxime, present in the *s-trans* form, links the stacks to sheets by forming H bridges to the complex molecules.

Introduction

We are presently investigating the structural variability of oxamide oxime (diaminoglyoxime, $oaoH_2$) complexes of Ni, Pd, and Pt (Endres & Jannack, 1980, and references therein). As we are interested in solids with highly anisotropic structures, we focus on the complexes of $oaoH_2$ with the metals of the Ni triad, for the α,β-dione dioximato complexes of these metals are known to prefer stacked structures in the solid state (Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977). The structural systematics outlined by these authors are often violated in complexes of $oaoH_2$, due to the reduced acidity of the oxime H atoms and to a pronounced capability to form intermolecular H bridges.

Experimental

The preparation of the compound is similar to that of $[Ni(oaoH_2)_3]Cl_2$ (Endres & Jannack, 1980) but with more dilute solutions: 600 mg $NiCl_2.6H_2O$ and 600 mg $oaoH_2$ are dissolved in 50 ml ethanol each, and the $NiCl_2$ solution is added dropwise to the refluxing solution of the ligand. The title compound is obtained as

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brick-red crystals by allowing the blue reaction mixture to evaporate in air.

Lattice constants were derived from the setting angles of 25 reflections centered on a diffractometer (Syntex *R*3, monochromatic Mo $K\alpha$ radiation). Data collection (θ–2θ scans background–peak–background, $2\theta < 60°$) yielded 2055 oberved [$I > 3{\cdot}0\sigma(I)$] independent reflections. An empirical absorption correction (ψ scans) and corrections for Lorentz and polarization factors were carried out.

Calculations were performed on an IBM 370/168 computer with the XRAY system (Stewart, Kundell & Baldwin, 1970) and scattering factors from *International Tables for X-ray Crystallography* (1974). Plots were drawn with *ORTEP* (Johnson, 1965).

Structure solution and refinement

As the Patterson synthesis showed only one strong vector, $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, the centrosymmetric space group was likely. Of the two possibilities, two independent molecules centered at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, or one independent molecule centered at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$, the first was shown by the successful structure analysis to be correct. By plotting the Patterson peaks the free oaoH$_2$ molecules were recognized. Fourier syntheses revealed the positions of the other non-H atoms. With anisotropic temperature factors *R* became 0·058. A difference map yielded the H positions. They were inserted with fixed isotropic temperature factors $B = 4$ Å^2. Refinement of all the free parameters by full-matrix least squares converged with $R = 0{\cdot}050$ (maximum shift/error 0·5).*

Description of the structure and discussion

Atomic coordinates are listed in Table 1. There are two independent [Ni(oaoH)$_2$] molecules in the unit cell with Ni occupying inversion centers at 0,0,0 (molecule *A*) and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ (molecule *B*). Furthermore, the unit cell contains two independent free-ligand molecules. Their centers of gravity lie at the inversion centers $0,\frac{1}{2},0$ and $0,0,\frac{1}{2}$, respectively. The numbering scheme, and bond distances and angles in *A* and *B* are shown in Figs. 1 and 2. The free oaoH$_2$ is present in the *s-trans* form. The numbering scheme and the geometry are displayed in Fig. 3. The structures of the two complex molecules are practically identical, the molecules differing in their relative orientation in the unit cell. The same is true for the free oaoH$_2$. In the complex molecules the oaoH$^-$

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

	x	*y*	*z*	*U* (Å^2)
Ni(1)	0	0	0	142
O(1)	−1592 (9)	171 (4)	2212 (4)	264
O(2)	−2888 (9)	1188 (4)	−1988 (4)	233
N(1)	−2176 (10)	514 (5)	1134 (4)	194
N(2)	−2731 (10)	1009 (5)	−858 (4)	173
N(3)	−6231 (11)	1762 (5)	1557 (5)	237
N(4)	−7078 (12)	2205 (5)	−805 (5)	238
C(1)	−4433 (12)	1249 (5)	857 (5)	186
C(2)	−4814 (11)	1532 (5)	−342 (5)	175
H(1)	−115 (17)	59 (8)	−210 (7)	
H(2)	−800 (18)	214 (8)	138 (8)	
H(3)	−610 (17)	134 (8)	227 (8)	
H(4)	−837 (18)	254 (8)	−60 (8)	
H(5)	−725 (17)	242 (8)	−155 (8)	
Ni(2)	5000	5000	5000	153
O(3)	1316 (9)	3803 (4)	6981 (4)	251
O(4)	5814 (9)	4824 (4)	2777 (4)	245
N(5)	2416 (10)	3987 (5)	5862 (4)	179
N(6)	4469 (10)	4477 (5)	3864 (4)	188
N(7)	−696 (12)	2800 (5)	5811 (5)	272
N(8)	2092 (12)	3252 (5)	3457 (5)	266
C(3)	1382 (11)	3470 (5)	5347 (5)	152
C(4)	2673 (12)	3745 (5)	4152 (5)	174
H(6)	209 (17)	429 (8)	719 (8)	
H(7)	−137 (18)	265 (8)	647 (8)	
H(8)	−111 (17)	232 (8)	548 (8)	
H(9)	237 (17)	371 (8)	268 (8)	
H(10)	83 (18)	289 (8)	359 (8)	
O(5)	−3275 (10)	3956 (4)	−915 (4)	291
O(6)	−5253 (9)	1040 (4)	5917 (4)	250
N(9)	−1610 (11)	4805 (5)	−998 (5)	230
N(10)	−1612 (12)	3666 (5)	967 (5)	219
N(11)	−2787 (11)	188 (5)	5991 (5)	217
N(12)	−2004 (12)	1346 (5)	4041 (5)	219
C(5)	−908 (11)	4608 (5)	−22 (5)	178
C(6)	−1349 (12)	405 (5)	5024 (5)	206
H(11)	−400 (17)	428 (8)	−154 (8)	
H(12)	−175 (16)	390 (8)	172 (8)	
H(13)	−304 (17)	332 (8)	101 (8)	
H(14)	−605 (17)	76 (8)	660 (8)	
H(15)	−125 (18)	125 (8)	350 (8)	
H(16)	−377 (18)	165 (8)	409 (8)	

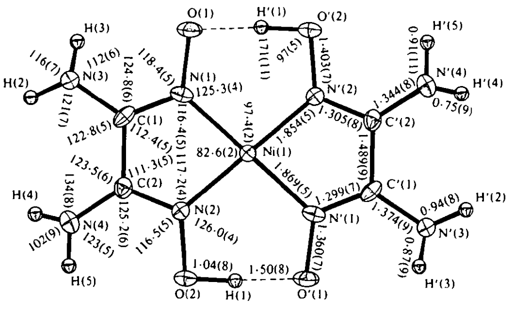

Fig. 1. Molecule *A* of [Ni(oaoH),], centered at 0,0,0, with bond distances (A) and angles (°).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35373 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

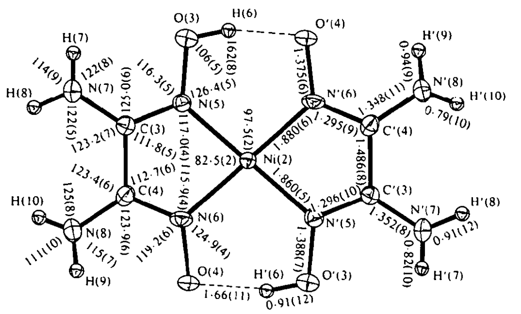

Fig. 2. Molecule *B* of [Ni(oaoH)$_2$], centered at ½,½,½, with bond distances (Å) and angles (°).

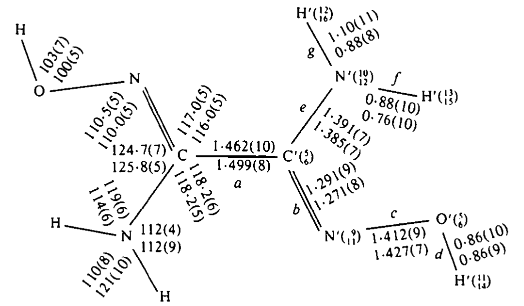

Fig. 3. Numbering scheme and geometry of the free oaoH$_2$ molecules. The upper lines describe the molecule centered at 0,½,0, the lower ones the molecule at 0,0,½. The distances may be compared with those found by Bekaroglu, Sarisaban, Koray & Ziegler (1977): (*a*) 1·494 (6), (*b*) 1·276 (9), (*c*) 1·408 (5), (*d*) 0·76 (15), (*e*) 1·380 (10), (*f*) 0·87 (11), (*g*) 0·73 (14) Å.

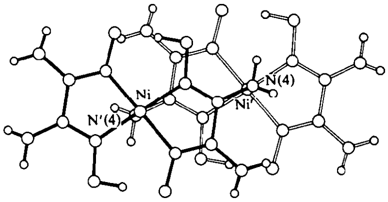

Fig. 4. Perpendicular projection of two molecules *A* of a stack. Stack *B* shows the same pattern.

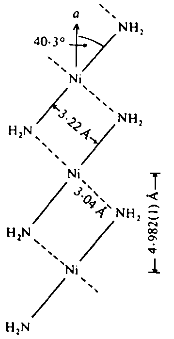

Fig. 5. Schematic projection of a part of a stack *A* parallel to the molecular planes. This figure also applies to stack *B*.

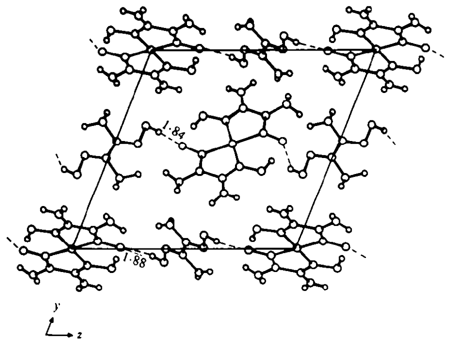

Fig. 6. Projection of the crystal structure on to the *yz* plane. The intermolecular H bridges are indicated.

species is present in the *s-cis* form and acts in the usual way as a bidentate ligand *via* the oxime N atoms. The H bridges are closed. This is often not the case in oaoH$_2$ complexes (Endres & Jannack, 1980). The H bridges are clearly asymmetric.

In the following discussion, the molecular plane is defined as the plane through Ni and the four oxime N atoms. The complex molecules form regular stacks along **a**. The normals of the planes are inclined at 49·7 (*A*) and 49·6° (*B*) to the stacking axis, in nearly opposite directions. The angle between the molecular planes of *A* and *B* is 80·6°. The interplanar distances along the stacks are 3·22 Å in *A* and 3·23 Å in *B*; hence, the amount of tilt and the interplanar distances are practically identical in both stacks. Fig. 4 shows a perpendicular projection of two molecules of *A*. It is evident that Ni lies nearly perpendicularly above and below the amino N of adjacent molecules of the same stack. The same observation holds for stack *B*. The Ni—NH$_2$ distances are 3·04 (1) Å in both stacks; the angles H$_2$N—Ni—N(oxime) range between 85·6 and 94·4°. A schematic projection parallel to the molecular planes is shown in Fig. 5. The amino N involved in the axial coordination, N(4) in *A* and N(7) in *B*, stick significantly out of the molecular plane towards Ni of the adjacent complex molecule. The deviation of N(4) from the molecular plane of *A* is 0·18 Å, compared with the maximum (mean) deviation of 0·06 Å (0·04 Å) of the other non-H atoms. The values in *B* are: deviation of N(7) 0·20 Å, maximum (mean) deviation of the other non-H atoms 0·06 Å (0·03 Å). This observation proves a bonding interaction between Ni and the axial NH$_2$ groups, and the coordination around Ni corresponds to an elongated tetragonal bipyramid. This stacking pattern is an example of one of the two typical arrangements of *α,β*-dione dioximato complexes of Ni. Pd, and Pt (Endres *et al.*, 1977), the *M–L* form.

The stacks are linked along *z* by H bridges to the free oaoH$_2$ molecules. Thus, sheets of alternating [Ni(oaoH)$_2$] and oaoH$_2$ piles are formed parallel to the *xz* plane. This is shown in Fig. 6, a projection of the structure on to the *yz* plane. The H bridges involve the most acidic H of the $oaoH_2$, the oxime H, and the most basic atom of the complex molecule, the oxime O which formally carries a negative charge.

This compound is a model for an idea outlined by us (Endres, 1979) and by Brown & Wrobleski (1979). Possible H bridges are supposed to stabilize a structure in which stacks of additional molecules run parallel to stacks of metal complexes. If the additional molecules are chosen to allow an electronic interaction along the stacks, interesting physical properties similar to the organic metals could result.

$[Co(oaoH)_2].oaoH_2$ (Bekaroglu, Sarisaban, Koray & Ziegler, 1977) has a very similar structure with a close axial interaction of Co with NH_2 groups of adjacent complex molecules within a stack, 2·639 (5) Å. The free $oaoH_2$ molecules are present in the *s-trans* form as well and link the stacks to sheets *via* H bridges. A comparison of bond lengths is included in Fig. 3.

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The Structure of Diammine(orotato)copper(II)

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Abstract

Crystals of $[Cu(C_5H_2N_2O_4)(NH_3)_2]$ are monoclinic, space group $P2_1/n$, with $a = 7{\cdot}217\ (5)$, $b = 7{\cdot}617\ (5)$, $c = 15{\cdot}148\ (11)$ Å, $\beta = 100{\cdot}73\ (6)^\circ$, $Z = 4$. The structure was refined to $R = 0{\cdot}042$ for 1853 symmetry-independent reflections. The primary coordination sphere around the Cu atom is square planar with the bidentate orotato anion and two ammonia molecules occupying the four coordination sites. The coordination sphere is extended to (4 + 2)-coordination geometry *via* intermolecular interaction involving the O(2) atoms of two stacking complex molecules and the $Cu—O(2^i)$ distance is 2·930 (4) Å. The conformation of the orotato anion differs only slightly from uncomplexed orotic acid, the C(6)—N(1)—C(2) angle being 4·8° smaller and the C(5)—C(6)—N(1) angle 3·7° larger. The crystal structure is dominated by columns of complexes along **a**. The stacking of the pyrimidine rings in these columns is fairly extensive. The stability of these columns is enhanced by the axial coordination of one exocyclic keto O atom to Cu. Interaction between the columns is primarily through hydrogen bonds.

Introduction

Orotic acid belongs to the class of pyrimidine derivatives, which are important components of nucleic acids and many enzymes with pronounced physiological action. Besides being biologically important the pyrimidines are interesting as ligands because the tautomerism between the ketonic and enolic forms makes multifaceted coordination possible.

There is general agreement that the preferred form for the pyrimidines at low and neutral pH is the ketonic (Tucci, Doody & Li, 1961). Coordination of metals at the hetero sites of the pyrimidine ring is thus less favourable than in other nucleic acid constituents, which have at least one ring N atom with an available lone pair. The situation is different in the enolic form, at higher pH, when the heterocyclic-ring N atoms are deprotonated and coordination is possible.

Three structures have been published for orotic acid compounds: the monohydrate of the Rb salt of 5-fluoroorotic acid (MacIntyre & Zirakzadeh, 1964), ammonium orotate monohydrate (Solbakk, 1971) and orotic acid monohydrate (Takusagawa & Shimada, 1973). Although some metal complexation works have

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