Table 3. *Distances* (Å) *and angles* (°) *of atoms possibly involved in hydrogen bonds*

O(1)···O(2^{i})	2·76 (1)	Pt–O(1)···O(2)	122·8 (4)
		Pt′–O(1)···O(2)	100·8 (4)
C(1)···O(6^{ii})	3·35 (4)	S(1)–C(1)···O(6)	91·1 (8)
C(2)···O(4^{ii})	3·42 (4)	S(1)–C(2)···O(4)	106·4 (8)
C(2)···O(7^{iii})	3·36 (5)	S(1)–C(2)···O(7)	88·1 (8)
C(3)···O(4^{iv})	3·46 (4)	S(2)–C(3)···O(4)	115·4 (9)
C(3)···O(3^{v})	3·27 (2)	S(2)–C(3)···O(3)	88·9 (6)
C(3)···O(5^{vi})	3·17 (3)	S(2)–C(3)···O(5)	114·7 (8)
C(4)···O(2^{i})	3·44 (2)	S(2)–C(4)···O(2)	115·8 (7)

Symmetry code: (i) $x-1, y, z$; (ii) $x, y-1, z$; (iii) $x+1, y-1, z$; (iv) x, y, z; (v) $1-x, 1-y, 1-z$; (vi) $x+1, y, z$.

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Bis[amino(methyl)glyoximato]nickel(II) Dihydrate: an Extended Interstack H-Bonding Network

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Abstract. Bis[2-(hydroxyimino)propionamide oximato]-nickel(II) dihydrate, $[Ni(C_3H_6N_3O_2)_2].2H_2O$, $M_r = 326\cdot95$, monoclinic, $P2_1/c$, $a = 3\cdot915\ (1)$, $b = 15\cdot559\ (3)$, $c = 9\cdot862\ (2)$ Å, $\beta = 96\cdot47\ (2)°$, $V = 597$ Å^3, $Z = 2$, $D_x = 1\cdot82$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $\mu = 15\cdot8$ cm^{-1}, $F(000) = 340$, room temperature, final $R = 0\cdot059$ for 1254 observed reflections. Planar complex molecules are stacked in columns along **a**; the interplanar separation is 3·34 (2) Å with the molecular planes inclined at 31·5 (5)° to the *a* axis. Each stack of molecules is linked with its four neighbouring stacks by H bridges involving the water molecules.

Introduction. Neutral bis(dioximato)metal complexes of Ni^{II}, Pd^{II} and Pt^{II} usually crystallize without the inclusion of solvent, with regular stacks of either the '*M*–*M*' or the '*M*–*L*' type (Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977). Owing to their pronounced capability of forming intermolecular H bridges, however, the bis(oxamide oximato)metal complexes [bis(diaminoglyoximato)metal complexes] always include H-bonded solvent or other molecules in the crystals. This leads to different structural patterns (Endres, 1978, 1979) and allows the synthesis of molecular metals by the inclusion of organic radicals (Endres, Bongart, Nöthe, Hennig, Schweitzer, Schäfer, Helberg & Flandrois, 1985). We have determined the structure of the title compound to compare it, especially with respect to H bonding, with the diaminoglyoxime and dimethylglyoxime (Godycki & Rundle, 1953) complexes.

Experimental. Powdery orange-red complex obtained by dropping ethanolic ligand solution containing aqueous ammonia into a boiling ethanolic solution of $NiCl_2.6H_2O$. Precipitate filtered off, washed with water, dried; suspended in water, diluted HCl added until slurry dissolved, filtered, allowed to evaporate at room temperature. Green product obtained loses HCl on drying, hence composition unknown; dissolved in water, solution put in one compartment of a diffusion cell with two compartments, separated by a sintered glass filter plate; other compartment filled with ethanol; red columns crystallized in ethanolic phase.

Crystal 0·15 × 0·15 × 0·34 mm, mounted on glass capillary. Lattice parameters from setting angles of 40 reflections (Siemens–Stoe AED2 diffractometer, monochromated Mo $K\alpha$ radiation). θ–2θ scans, $2\theta \leq 60°$. 1741 reflections measured. Index range −5,0,0 to 5,21,13. 2 check reflections every 3 h, intensity variation ±3·4%. Empirical absorption correction using ψ scans of 5 reflections with $11{\cdot}2° < 2\theta < 36{\cdot}4°$, min. transmission factor 0·66 (max. = unity). Equivalent reflections merged ($R_{\rm int} = 0{\cdot}041$) to 1254 observed independent reflections with $I \geq 1{\cdot}5\sigma(I)$. As $Z = 2$, Ni placed at origin. Non-H atoms from Fourier synthesis; some H atoms from difference Fourier maps. Methyl-H atoms not clearly visible unlike other H, probably due to disorder. Refinement by full-matrix least squares based on F. $w = 1/\sigma^2(F)$. Non-H atoms anisotropic. Located H atoms (no methyl H) with individual isotropic temperature factors. 108 parameters. $wR = 0{\cdot}056$, $R = 0{\cdot}059$, $S = 3{\cdot}08$. Max. $\Delta/\sigma = 0{\cdot}55$. Max. and min. $\Delta\rho$ +1·62 and −0·79 e Å^{-3}. *STRUCSY* (Stoe, 1984) program system on an Eclipse computer. Scattering factors including anomalous dispersion from *International Tables for X-ray Crystallography* (1974). Plots on a Tektronix plotter using *SHELXTL* (Sheldrick, 1983) on a Nova 3 computer.

Discussion. Atom coördinates are listed in Table 1.* Fig. 1 shows the numbering scheme and bond distances and angles in the centrosymmetric complex molecule, which possesses the usual intramolecular H bridges. The planar molecules are arranged in stacks along **a**, with an interplanar distance (referring to the least-squares plane through the non-H atoms) of 3·34 (2) Å. The normal to the plane is inclined at 31·5 (5)° to the *a* axis. This stacking mode, where the length of a crystallographic axis equals one metal–metal distance, has been termed the '*M–L*' form (Endres *et al.*, 1977). In contrast, solvent-free bis(dimethylglyoximato)-nickel(II) crystallizes in the '*M–M*' form, with the molecular planes perpendicular to the stacking direction and the repeat distance comprising two metal–metal separations (Godycki & Rundle, 1953).

The title compound resembles more the bis(oxamide oximato)nickel complex, which also crystallizes as a

Table 1. *Atom coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 ×10^3) *for non*-H *atoms*

$U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{\rm eq}$
Ni	0	0	0	17·6 (5)
N(1)	2918 (12)	314 (3)	1536 (5)	24 (2)
N(2)	920 (11)	−1105 (3)	708 (5)	20 (2)
O(1)	3769 (12)	1148 (3)	1934 (5)	30 (2)
O(2)	−350 (11)	−1819 (2)	102 (5)	29 (2)
C(1)	4119 (13)	−295 (4)	2331 (6)	19 (2)
C(2)	2972 (14)	−1163 (4)	1845 (6)	20 (2)
C(3)	4092 (15)	−1975 (4)	2551 (7)	28 (3)
N(3)	6244 (14)	−177 (3)	3475 (6)	28 (3)
O(3)*	615 (13)	1385 (3)	4436 (5)	35 (2)

* Water molecule.

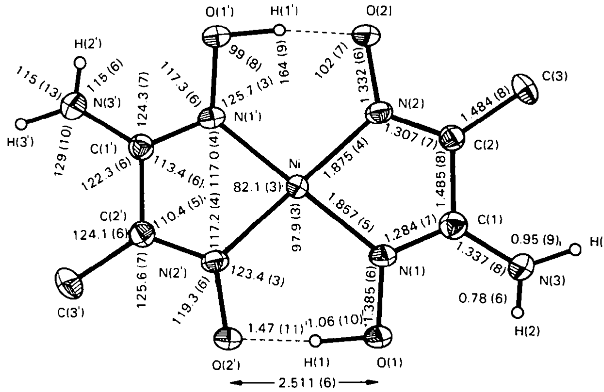

Fig. 1. The complex molecule with bond distances (Å) and angles (°). Methyl-H atoms at C(3) omitted. Thermal contours at 50% probability; H atoms as spheres with arbitrary radius.

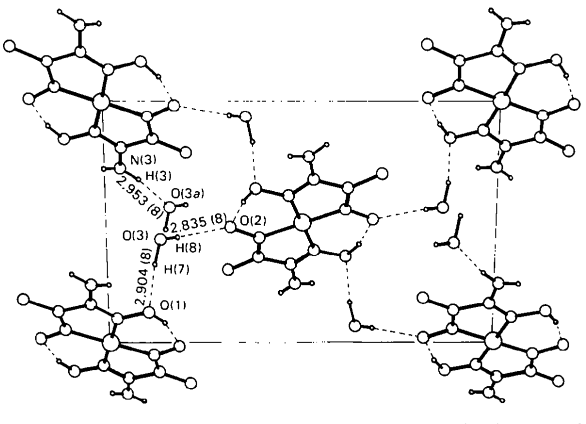

Fig. 2. Projection of the structure along a direction inclined at 20° to the *a* axis; *b* horizontal, *c* up the page. H-bonding interactions are indicated by broken lines. The O(3) and O(3*a*) water molecules are related by a unit translation **a**. Relevant heavy-atom distances (Å) are given. Distances and angles involving H are: H(7)–O(3) 1·00, H(8)–O(3) 0·68 Å, H(7)–O(3)–H(8) 110°; H(3)–O(3*a*) 2·01 Å, N(3)–H(3)–O(3*a*) 172°; H(7)–O(1) 1·95 Å, O(1)–H(7)–O(3) 159°; H(8)–O(2) 2·16 Å, O(3)–H(8)–O(2) 176° (e.s.d.s ~0·1 Å, 10°).

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42400 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

dihydrate and forms stacks of the '*M–L*' type (Endres, 1979). The intermolecular H-bonding network, however, is quite different: In the oxamide oxime complex the water molecules are linked by H bridges to adjacent complex molecules within a stack, leading to a ladder-like structure. In the title compound, however, the water molecules are H-bonded to the oxime O atoms of complexes of different stacks (Fig. 2). Each stack is thus linked to its four neighbours. A weaker H-bonding interaction exists between the amino group and the water molecule. Details of the distances are included in Fig. 2.

This investigation shows that the amino(methyl)-glyoxime nickel complex is similar to the oxamide oxime complex in its tendency to participate in intermolecular H bonding. Hence the complex is a promising candidate for the inclusion of other species in the crystal, possibly leading to molecular electron conductors, as is the case with oxamide oxime complexes (Endres *et al.*, 1985; Endres, 1984). Indeed, it forms a blue-black solid when co-crystallized with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ).

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Structure of Bis(isothiocyanato)(1,4,8,11-tetraazacyclotetradecane)nickel(III) Perchlorate

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Abstract. $[Ni(NCS)_2(C_{10}H_{24}N_4)]ClO_4$, $M_r = 474\cdot6$, triclinic, $P\bar{1}$, $a = 8\cdot559\,(1)$, $b = 9\cdot095\,(2)$, $c = 7\cdot517\,(1)$ Å, $\alpha = 110\cdot66\,(1)$, $\beta = 81\cdot42\,(1)$, $\gamma = 114\cdot95\,(1)^\circ$, $V = 496\cdot4\,(2)$ Å^3, $Z = 1$, $D_x = 1\cdot59$, $D_m = 1\cdot60$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot7107$ Å, $\mu(\text{Mo } K\alpha) = 1\cdot35$ mm^{-1}, $F(000) = 247$, room temperature, $R = 0\cdot041$ and $wR = 0\cdot053$ for 2645 observed reflections $[|F_o| > 3\sigma(F_o)]$. The Ni^{III} ion is surrounded octahedrally by a square-planar array of the four N atoms of 1,4,8,11-tetraazacyclotetradecane and by two N atoms of NCS$^-$ ions occupying the axial positions. The macrocyclic ligand adopts the most stable conformation with two five- and two six-membered chelate rings in *gauche* and chair forms, respectively. The average in-plane Ni—N and Ni—NCS distances are 1·972 (7) and 2·081 (3) Å, respectively.

Introduction. One dominant characteristic of tetraazacycloalkane ligands (*L*) is that they often form stable compounds of metal ions in unusually high oxidation states, such as Cu^{III}, Ni^{III}, Ni^{IV}, Ag^{II}, and Ag^{III} (Busch, 1978; Haines & McAuley, 1981; Nag & Chakravorty, 1980; Olson & Vasilevskis, 1971; Barefield & Mocella, 1973; Ito, Ito & Toriumi, 1981; Yamashita & Ito, 1984). The stability of the resulting complex depends on the sizes of the metal ion and of the cavity of the macrocyclic ligand. According to this guiding principle, a series of Ni^{III} complexes containing *L*, $[NiX_2L]ClO_4$ (X = Cl and Br; L = [13]aneN$_4$, [14]aneN$_4$, [15]aneN$_4$, *meso*-Me$_6$[14]aneN$_4$ *etc.*)[†] have been prepared and characterized by means of magnetic moments, ESR, X-ray photoelectron spectra (XPS) and

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[†] [13]aneN$_4$ = 1,4,7,10-tetraazacyclotridecane, [14]aneN$_4$ = 1,4,8,11-tetraazacyclotetradecane, [15]aneN$_4$ = 1,4,8,12-tetraazacyclopentadecane, *meso*-Me$_6$[14]aneN$_4$ = (7*RS*,14*SR*)-5,5,7,12,-12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

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