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Refinement of Diaquabis(glycinato-*O,N*)nickel(II)

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Abstract. [Ni($C_2H_4NO_2$)$_2$(H_2O)$_2$], $C_4H_{12}N_2NiO_6$, $M_r = 242·86$, monoclinic, $P2_1/n$, $a = 7·616$ (1), $b = 6·601$ (1), $c = 9·247$ (1) Å, $\beta = 110·95$ (1)°, $V = 434·1$ (1) Å^3, $Z = 2$, $D_c = 1·858$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1·54184$ Å, μ(Cu $K\alpha$) = 3·10 mm^{-1}, $F(000) = 250$. The structure was refined with 823 independent reflections by full-matrix least squares with anisotropic temperature factors for all non-hydrogen atoms. Hydrogens were treated isotropically with their bond lengths constrained to fixed values. Final R factors are $R = 0·036$, $R_w = 0·035$. The crystal, which shows an antiferromagnetic transition at 0·88 K, is strongly stabilized by a net of hydrogen bonds which are potentially the most likely paths for superexchange interactions between Ni ions.

Introduction. Recent magnetic susceptibility measurements on diaquabis(glycinato-*O,N*)nickel(II) (NiDB) have shown an antiferromagnetic transition at 0·88 K (Calvo & Nascimento, 1981). The crystal structure of this compound was established by two-dimensional Fourier analysis several years ago (Stosick, 1945) but

the limitations inherent in this technique and the lack of computing facilities to perform least-squares refinements severely limited the accuracy of the results. The structure was reinvestigated from visually estimated three-dimensional photographic data and refined to an R factor of 0·095 but the positions of the hydrogen atoms could not be established with certainty and were therefore not reported (Freeman & Guss, 1968). The crystal structure is known to be stabilized by a net of hydrogen bonds. Since these hydrogen bonds are potentially the most likely paths for superexchange interactions between the Ni ions of the structure (see, for instance, Watanabe, 1962) a model for the transition mechanism would require accurate knowledge of the proton sites.

To obtain this information a diffractometric three-dimensional Fourier analysis and least-squares refinement of the NiDB complex was undertaken.

NiDB was synthetized as outlined by Stosick (1945) and detailed by Sen, Mizushima, Curran & Quagliano (1955). The material was purified by recrystallization and suitable crystals for X-ray analysis were obtained by slow evaporation from water solution at room temperature.

A fragment of irregular shape with maximum and minimum linear dimensions of about 0·20–0·25 mm

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was mounted on an Enraf–Nonius CAD-4 diffractometer. Cell dimensions and the orientation matrix for data collection were calculated by least squares from 25 centered reflections using graphite-monochromated Cu $K\alpha$ radiation. Diffraction intensities for reflections having θ in the range 1–75° were measured by the ω–2θ scan technique, using a variable scan speed between 2·85 and 20·0° min^{-1} determined by a fast prescan of 20·0° min^{-1}. Intensities of two strong standard reflections were essentially constant during the duration of the experiment. Of the 934 independent reflections measured the 823 having $I > 3\sigma(I)$ were used in the calculations. Data were corrected for Lorentz and polarization effects but not for absorption or extinction.

We chose a unit cell different from that of Stosick (1945) having a somewhat less acute β angle. The space group is No. 14 corresponding to the setting $P2_1/n$ with general positions x,y,z; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ and conditions for permissible reflections hkl none, $h0l\ h + l = 2n$ and $0k0\ k = 2n$.

All non-hydrogen atoms were found from a difference map phased on the Ni atom placed at the origin of the unit cell. Four cycles of full-matrix isotropic least squares with unit weights gave an R factor of 6·3%. The first six peaks of a difference map phased on this model corresponded to all the hydrogen atoms of the molecule. Further full-matrix refinement was then carried out with anisotropic temperature factors for non-hydrogen atoms and isotropic ones for the others. Positional parameters were constrained to the following interatomic distances: C–H = 1·04, N–H = 1·01 and O–H = 0·96 Å, with a common standard deviation of 0·01 Å. The function minimized by least squares was $M = \sum \omega (|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F)$, σ being determined from counting statistics. The final R factors were $R = 0·036$ and $R_w = 0·035$ and the largest parameter shift was less than 0·01 of its standard deviation. A final difference map was essentially flat.

The atomic scattering factors used were those given by Cromer & Waber (1974) and the anomalous-dispersion correction coefficients those given by Cromer & Ibers (1974). Most calculations were performed on a Vax computer with the $SHELX$ system
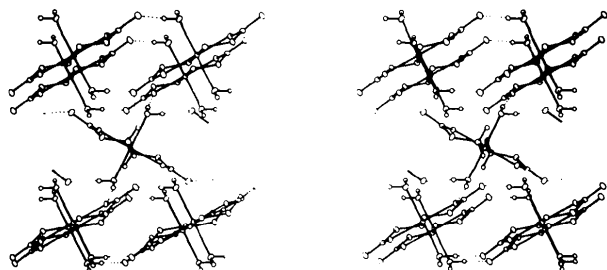
of programs (Sheldrick, 1976). The projection shown in Fig. 1 was calculated with the program $ORTEP$ (Johnson, 1965) incorporated in the $Enraf–Nonius$ $Structure\ Determination\ Package$.

Final positional parameters and isotropic temperature factors are given in Table 1; non-hydrogen atoms are assigned equivalent isotropic temperature factors calculated following Hamilton (1959).*

Discussion. Atom labelling and intramolecular bond distances and angles between all non-hydrogen atoms are given in Fig. 2. The Ni ion is positioned on a crystallographic center of symmetry and is coordinated by two glycine residues, related to one another by the inversion center, and to the oxygen atoms of two water molecules related in the same way. The glycine residues act as bidentate ligands bonded to the cation through

Table 1. *Final positional coordinates and equivalent B values* (Å^2)

The B's are calculated following Hamilton (1959).

	x	y	z	B_{eq}
Ni	0	0	0	1·40 (3)
O(2)	−0·0457 (2)	−0·2743 (3)	−0·1154 (2)	1·87 (8)
O(1)	0·0995 (3)	−0·5073 (3)	−0·2074 (2)	2·40 (9)
N	0·2652 (3)	−0·0405 (3)	−0·0113 (2)	1·67 (9)
C(1)	0·1001 (4)	−0·3540 (4)	−0·1279 (3)	1·6 (1)
C(2)	0·2882 (4)	−0·2564 (4)	−0·0374 (3)	1·8 (1)
O(W)	0·0863 (2)	−0·1427 (3)	0·2170 (2)	1·92 (8)
H(C2)	0·347 (4)	−0·335 (5)	0·066 (2)	2·7 (8)
H'(C2)	0·381 (4)	−0·288 (5)	−0·093 (3)	2·1 (7)
H(N)	0·361 (5)	0·002 (7)	0·089 (3)	5 (1)
H'(N)	0·270 (6)	0·036 (9)	−0·102 (2)	4 (1)
H(W)	0·031 (5)	−0·272 (3)	0·211 (5)	4 (1)
H'(W)	0·216 (2)	−0·170 (7)	0·268 (5)	7 (1)

Fig. 1. Stereoscopic projection showing crystal packing and hydrogen bonding. Dashed lines show O–H···O contacts and dotted lines show N–H···O contacts.
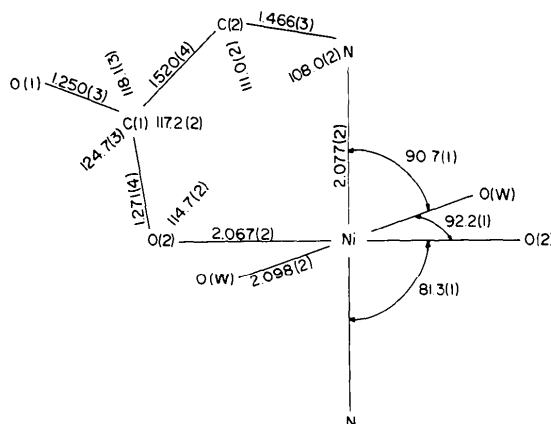

Fig. 2. Intramolecular bond lengths (Å) and angles (°).

Table 2. *Distances* (Å) *and angles* (°) *involved in hydrogen bonds*

A	B	C	A–B	B–C	∠A–B–C	A–C
O(1)···H(W)–O(W)			1·76 (1)	0·95 (1)	171·0 (1)	2·692 (4)
O(2)···H'(W)–O(W)			1·79 (1)	0·95 (1)	173·0 (1)	2·731 (4)
O(1)···H(N)–N			2·10 (1)	1·00 (1)	162·0 (1)	3·053 (6)

their amine nitrogens and O(2) oxygens of their carboxylate groups. The resulting coordination polyhedron is in a distorted octahedral configuration.

The O–C distances in the carboxylate group are somewhat different, as expected. It is interesting to note, however, that the interplay among these distances and the bond angles around C(1) is by no means arbitrary but follows closely the four systematic relationships described by Borthwick (1980).

The crystal structure is strongly stabilized by a net of hydrogen bonds. As pointed out by Stosick (1945) each of the water molecules of the complex forms two strong hydrogen bonds: one with oxygen O(1) of a neighboring complex and another with oxygen O(2) of a different neighboring complex. Also, one amine nitrogen forms a weaker hydrogen bond with oxygen O(1) of a neighboring molecule while the other one is close to O(1) of another neighbor molecule. As pointed out by Freeman & Guss (1968) this contact probably does not qualify as a potential hydrogen bond because of the unfavorable O–N distance [3·130 (5) Å] and N–H–O angle |137 (1)°|. Fig. 1 is a stereoscopic

projection down the mid-point of the unit cell, along a direction which minimizes overlap of the central molecule with its neighbors, showing the different types of hydrogen bonds formed by this molecule, including the short N–O contact which is probably not a hydrogen bond. For clarity not all hydrogen atoms and hydrogen bonds are displayed. Distances and angles about protons involved in hydrogen bonding are given in Table 2.

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Structure of (−)589-fac-Triammineglycinatonitrocobalt(III) Perchlorate

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Abstract. $[Co(C_2H_4NO_2)(NH_3)_3(NO_2)]ClO_4, C_2H_{13}Co-N_5O_4^+.ClO_4^-$, $M_r = 329\cdot5$, monoclinic, $P2_1$, $a = 10\cdot734$ (2), $b = 8\cdot441$ (1), $c = 6\cdot080$ (1) Å, $\beta = 95\cdot39$ (1)°, $V = 548\cdot5$ (1) Å^3, $Z = 2$, $D_x = 1\cdot99$ Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0\cdot7107$ Å, $\mu(Mo\,K\alpha) = 1\cdot91$ mm^{-1}. The structure was solved by Patterson–Fourier methods and refined to a final R value of 0·032 for 1955 observed reflections. The absolute configuration of the complex ion can be designated as *abc*-triammine-*ed*-glycinato-*f*-nitrocobalt(III).

Introduction. Three isomers of a new complex ion, $[Co(gly)(NH_3)_3(NO_2)]^+$ (gly: glycinate), were prepared and characterized by Fujinami & Shibata (1981). The optical resolution of the *fac*(NH₃) isomer was achieved by column chromatography and the last-eluted (−)589-