

## A Neutron Diffraction Study of the Short Hydrogen Bond in a Tetradentate $\alpha$ -Amine Oxime Complex of Nickel(II)

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A single-crystal neutron diffraction study of the structure of 2,2'-(ethylenediamino)bis(2-methyl-3-butanone oximate)nickel(II) perchlorate,  $[\text{Ni}(\text{EnAO}-\text{H})]\text{ClO}_4$ , has provided information on the geometry of the short  $\text{O}\cdots\text{O}$  hydrogen bond. The monoclinic unit-cell dimensions are  $a = 9.692$  (1),  $b = 7.575$  (1),  $c = 25.586$  (3) Å, and  $\beta = 108.82$  (2)°, based on a neutron wavelength of 1.109 Å. The density of 1.552 (3)  $\text{g cm}^{-3}$  calculated for four formula units per cell agrees with the flotation density of 1.55 (1)  $\text{g cm}^{-3}$ . The space group is  $P2_1/c$ . The structure was solved from the neutron data by application of direct methods (*MULTAN*). A full-matrix least-squares refinement based on 2377 reflections with  $F_o^2 > 2.5\sigma(F_o^2)$  converged to give  $R(F) = 0.053$ . The perchlorate ion was refined with twofold disorder of the O atoms. The  $\text{Ni}^{\text{II}}$  ion is surrounded by a square plane of N atoms with an average Ni–N(oxime) distance of 1.842 (3) Å and an average Ni–N(amine) distance of 1.877 (2) Å. Because of the steric requirements of the tetradentate amine oxime ligand, the  $\text{O}\cdots\text{O}$  hydrogen bond is longer [2.478 (5) Å] than that observed in the previously reported bis(2-amino-2-methyl-3-butanone oximate)nickel complex [2.420 (3) Å].

### Introduction

Amine oxime metal complexes provide a unique opportunity to study  $\text{O}\cdots\text{O}$  hydrogen bonding in that, by proper choice of amine oxime ligand and metal ion, it is possible to vary the  $\text{O}\cdots\text{O}$  distance over a wide range. This range includes very short  $\text{O}\cdots\text{O}$  distances, such as that [2.420 (3) Å] observed in the bis(2-amino-2-methyl-3-butanone oximate)nickel(II) ion (Schlemper, Hamilton & LaPlaca, 1971), as well as much longer  $\text{O}\cdots\text{O}$  distances, such as that [2.699 (5) Å] observed in the dimeric 2,2'-(ethylenediamino)bis(2-methyl-3-butanone oximate)copper(II) ion (Gavel & Schlemper, 1977). The latter complex involves the same amine oxime ligand as that in the present study. The present study was undertaken to examine the effect of the ethylene bridge [not present in the Ni complex studied by Schlemper, Hamilton & LaPlaca (1971)] opposite the oxime hydrogen bond on the nature of the hydrogen bond, *i.e.* the  $\text{O}\cdots\text{O}$  distance and the location of the H atom in the bond.

### Experimental

#### Crystal data and data collection

The compound  $[\text{Ni}(\text{EnAO}-\text{H})]\text{ClO}_4$  was prepared as described by Murmann (1957, 1962). Yellow-green

crystals large enough for the neutron study were obtained by slow evaporation of an aqueous solution. The platelike crystal chosen for the neutron study had approximate dimensions of  $1.5 \times 3.5 \times 5.0$  mm.

The compound crystallizes in the monoclinic crystal system with  $a = 9.692$  (1),  $b = 7.575$  (1),  $c = 25.586$  (3) Å, and  $\beta = 108.82$  (2)°. The systematic extinctions, determined both from preliminary X-ray precession studies and neutron intensity measurements, are  $l = 2n + 1$  for  $h0l$  and  $k = 2n + 1$  for  $0k0$ , indicating space group  $P2_1/c$ . The density of 1.552 (3)  $\text{g cm}^{-3}$  calculated on the basis of four formulas per unit cell agrees well with that measured by flotation [1.55 (1)  $\text{g cm}^{-3}$ ]. The aforementioned cell dimensions were obtained by refinement with 19 carefully centered reflections on the neutron diffractometer using a neutron wavelength of 1.109 Å (Fair & Schlemper, 1977).

The crystal used for the intensity measurements was bounded by seventeen faces: (001), (102), (100), (10 $\bar{2}$ ), (00 $\bar{1}$ ), ( $\bar{1}$ 02), ( $\bar{1}$ 02), (0 $\bar{1}$ 1), ( $\bar{1}$ 1 $\bar{2}$ ), ( $\bar{1}$ 11), (0 $\bar{1}$ 1), ( $\bar{1}$ 11), ( $\bar{1}$ 11), ( $\bar{1}$ 11), (112), (011) and (0 $\bar{1}$ 1), and was mounted with the  $b$  axis near, but displaced about 5° from, the  $\phi$  axis of the goniometer. The data were collected on the Missouri University Research Reactor using a PDP 11/40 computer-controlled Mitsubishi diffractometer modified and automated by the University of Missouri Physics Department electronic and machine shops. A full circle and the necessary electronics for computer control were designed and built by these shops. The computer software and time-share system were pro-

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vided by Gene Moun. The data were collected by the  $\theta$ - $2\theta$  step-scan technique with  $0.05^\circ$  ( $2\theta$ ) steps covering  $1.60^\circ$  for each peak. The incident beam was obtained from a Be monochromator crystal, a monitor counter was used to time the steps, and the diffracted beam was detected with a  $\text{BF}_3$  counter. 4496 reflections were measured out to  $2\theta = 92^\circ$ . Background correction, integration, and Lorentz correction were accomplished with a local program. The data were corrected by Gaussian numerical integration for absorption (calculated  $\mu = 1.99 \text{ cm}^{-1}$ ) with a transmission-factor range of 0.68 to 0.76. Two standards were measured after every forty reflections. No significant change was observed throughout the data collection. Equivalent and duplicate reflections were averaged to yield intensities for 3844 independent reflections. The average disagreement between equivalent reflection intensities was 4.6%. Of these 3844 reflections, 2377 with  $F_o^2 > 2.50$  were used in the structure solution and refinement.

### Structure determination

The structure was solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). A clear choice of phasing was possible based on FOM's. The resulting Fourier synthesis had clearly distinguishable peaks for all nonhydrogen atoms, except for the perchlorate O atoms. The perchlorate O atoms were located from subsequent difference Fourier syntheses after refinement of the other nonhydrogen atom parameters. Careful examination of the spherical shell at  $1.40 \text{ \AA}$  from the perchlorate Cl revealed considerable motion of these O atoms and the need for at least a twofold-disorder model. Consequently, the O atoms were first placed in two ideal tetrahedral groups about an ordered Cl atom. After group refinement, which included a relative occupancy factor for the two O tetrahedra and isotropic O temperature factors, the H atoms were located from a difference Fourier map. After refinement of the H atom positional parameters and anisotropic thermal parameters, the perchlorate O atoms were removed from the rigid groups and allowed to refine individually with isotropic temperature parameters and with occupancy factors fixed from the group refinement (0.48 and 0.52). This refinement gave final agreement factors of  $R = \sum |F_o^2 - F_c^2| / \sum F_o^2 = 0.078$  and  $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2} = 0.108$ , where  $w = 1/\sigma^2$  and  $\sigma = -0.0863F_o^4 + 0.64F_o^2$  for  $F_o^2 < 4.75$ ;  $\sigma = -0.00649 F_o^4 + 0.26 F_o^2$  for  $4.75 < F_o^2 < 24.0$ ; and  $\sigma = -0.000137F_o^4 + 0.112F_o^2$  for  $F_o^2 \geq 24.0$ . The goodness-of-fit parameter  $\{[\sum (F_o^2 - F_c^2)^2 / \sigma^2] / (\text{NO} - \text{NV})\}^{1/2}$ , where NO = number of observations and NV = number of variables, is 1.02. The shifts of the last cycle were all less than 10% of the corresponding standard deviations. An isotropic extinction parameter (Zachariasen, 1967) was included in the refinement and

Table 1. *Positional parameters for*  
 $[\text{Ni}(\text{C}_{12}\text{H}_{25}\text{N}_4\text{O}_2)]^+\text{ClO}_4^-$

Numbers in parentheses, in this table and elsewhere, represent estimated standard deviations for least-squares refinement.

	x	y	z
Ni	0.2045 (2)	0.1407 (2)	0.3327 (1)
N(4)	0.2427 (2)	-0.0767 (2)	0.3052 (1)
N(1)	0.1523 (2)	0.3366 (3)	0.3648 (1)
N(3)	0.2714 (2)	0.0508 (3)	0.4049 (1)
N(2)	0.1625 (2)	0.2186 (2)	0.2612 (1)
C(3)	0.1865 (3)	0.1334 (4)	0.4385 (1)
C(4)	0.2811 (3)	-0.0510 (4)	0.2531 (1)
C(2)	0.2082 (3)	0.1217 (4)	0.2284 (1)
O(2)	0.0979 (4)	0.3757 (5)	0.2444 (1)
C(11)	0.2831 (4)	-0.1445 (4)	0.4007 (1)
O(1)	0.1132 (4)	0.4899 (4)	0.3369 (1)
C(10)	0.4460 (3)	-0.0306 (5)	0.2659 (2)
C(6)	0.1976 (3)	0.1812 (5)	0.1717 (1)
C(9)	0.2254 (4)	-0.2088 (4)	0.2145 (1)
C(7)	0.0421 (5)	0.0361 (6)	0.4291 (2)
C(1)	0.1497 (3)	0.3187 (4)	0.4147 (1)
C(12)	0.3412 (4)	-0.1775 (4)	0.3528 (1)
C(5)	0.1061 (5)	0.4614 (6)	0.4461 (2)
C(8)	0.2760 (6)	0.1357 (7)	0.4995 (2)
H3(C5)	0.0254 (29)	0.4254 (21)	0.4601 (11)
H2(C5)	0.0698 (23)	0.5716 (18)	0.4225 (5)
H1(C5)	0.1899 (22)	0.5065 (28)	0.4775 (7)
H1(C6)	0.2267 (18)	0.3175 (17)	0.1721 (4)
H2(C6)	0.0898 (13)	0.1906 (24)	0.1479 (4)
H3(C6)	0.2574 (21)	0.1121 (20)	0.1543 (5)
H1(C7)	0.0589 (14)	-0.0908 (14)	0.4487 (6)
H2(C7)	-0.0152 (10)	0.0164 (14)	0.3851 (5)
H3(C7)	-0.0278 (12)	0.1104 (15)	0.4465 (5)
H1(C8)	0.3709 (12)	0.2183 (19)	0.5065 (4)
H2(C8)	0.2114 (15)	0.1967 (21)	0.5237 (4)
H3(C8)	0.3072 (17)	0.0027 (18)	0.5133 (4)
H1(C9)	0.1094 (8)	-0.2244 (12)	0.2046 (4)
H2(C9)	0.2542 (12)	-0.1975 (14)	0.1771 (4)
H3(C9)	0.2727 (10)	-0.3300 (11)	0.2346 (4)
H1(C10)	0.5011 (8)	-0.1534 (12)	0.2822 (4)
H2(C10)	0.4700 (9)	-0.0015 (14)	0.2286 (4)
H3(C10)	0.4898 (8)	0.0724 (13)	0.2950 (4)
H1(C11)	0.1729 (9)	-0.2031 (9)	0.3901 (3)
H2(C11)	0.3523 (11)	-0.2034 (12)	0.4390 (3)
H1(C12)	0.4501 (7)	-0.1263 (12)	0.3623 (3)
H2(C12)	0.3415 (10)	-0.3182 (10)	0.3436 (4)
H(N4)	0.1419 (7)	-0.1351 (9)	0.2932 (3)
H(N3)	0.3755 (7)	0.1016 (9)	0.4195 (3)
H(OO)	0.1050 (7)	0.4489 (8)	0.2918 (3)
Cl	0.4062 (3)	-0.1552 (4)	0.0868 (1)
O(3)	0.2505 (19)	-0.1997 (26)	0.0690 (7)
O(4)	0.4149 (23)	0.0304 (28)	0.0859 (8)
O(5)	0.5051 (14)	-0.1745 (20)	0.1413 (5)
O(6)	0.4577 (11)	-0.2296 (16)	0.0455 (4)
O(3')	0.4617 (26)	-0.1379 (37)	0.0430 (10)
O(4')	0.4365 (22)	-0.3249 (28)	0.1113 (8)
O(5')	0.4817 (29)	-0.0494 (38)	0.1343 (11)
O(6')	0.2587 (14)	-0.1142 (21)	0.0745 (5)

converged with a value of  $g = 2.8(3) \times 10^{-4}$ . A final difference Fourier synthesis revealed the largest residuals in the vicinity of the perchlorate O atoms. Neutron atomic scattering factors (Bacon, 1972) were Ni (1.03), N (0.94), O (0.58), C (0.665), Cl (0.96),

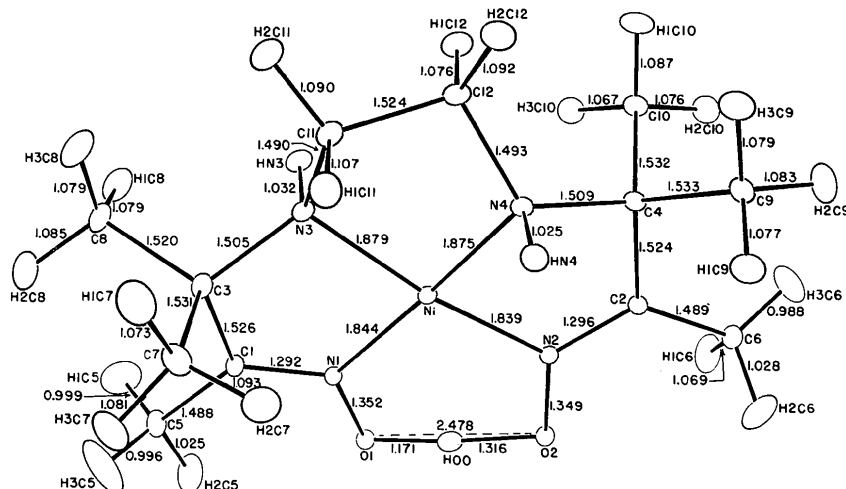


Fig. 1. Bond distances (Å) in the  $[\text{Ni}(\text{EnAO}-\text{H})]^+$  ion. The standard deviations are: Ni-N, 0.002–0.003; N-O and N-C, 0.003–0.004; C-C and O-O, 0.004–0.005; and C-H, N-H, and O-H, 0.006–0.010 Å.

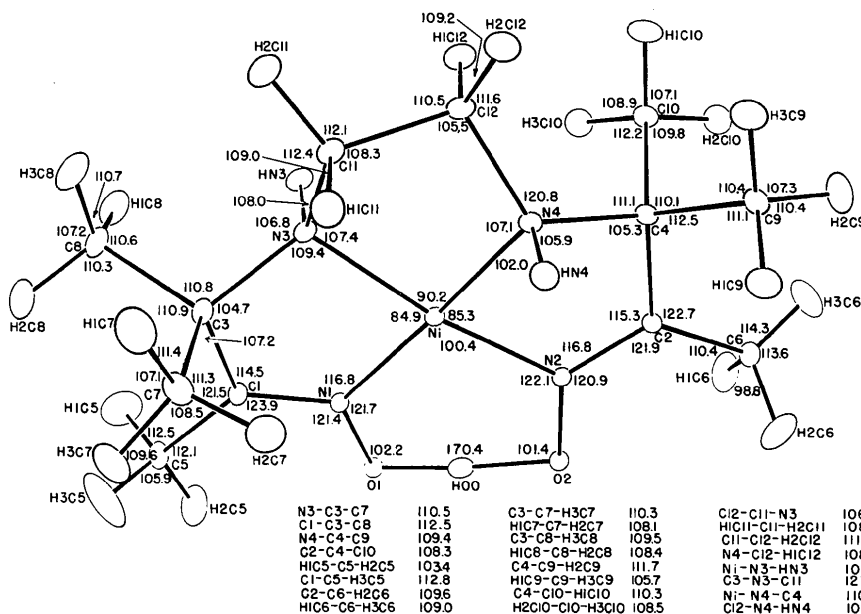


Fig. 2. Bond angles ( $^{\circ}$ ) in the  $[\text{Ni}(\text{EnAO}-\text{H})]^+$  ion. Standard deviations are 0.1–0.4 $^{\circ}$  for angles involving nonhydrogen atoms; 0.4–0.7 $^{\circ}$  for angles involving one H atom; and 0.5–1.0 $^{\circ}$  for angles involving two H atoms.

and H ( $-0.374 \times 10^{-12}$  cm). The final conventional  $R$  factor was 0.053.\*

The coordinates of the atoms are presented in Table 1.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33032 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

## Discussion

### Structure of the nickel complex

The structure of the nickel complex is almost identical to that observed for its nitrate salt (Ching & Schlemper, 1975). The Ni<sup>II</sup> atoms are in discrete complex cations with distorted square-planar coordination completed by the four N atoms of the tetradentate EnAO ligand (Figs. 1 and 2). The crystal structure (Fig. 3) is completed with disordered

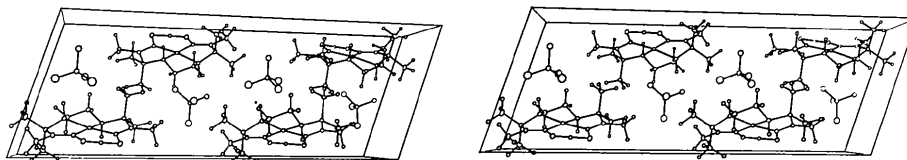


Fig. 3. Stereoscopic drawing of the contents of one unit cell. Two of the perchlorate groups are shown with one set of O positions and the other two with the alternative set. The view is nearly down the *b* axis.

Table 2. *Interionic contacts less than 3.8 Å*

C(8)—O(6)	3.62	C(5)—O(3')	3.72
C(8)—O(3')	3.60	C(5)—O(3)	3.59
C(8)—O(4')	3.57	C(5)—O(6')	3.48
C(8)—O(4)	3.32	C(5)—O(3)	3.49
C(8)—O(6)	3.30	C(5)—O(6')	3.39
Ni—O(5)	3.01	C(3)—O(6)	3.48
Ni—O(4')	3.33		
Ni—O(2)	3.57	C(4)—O(2)	3.74
Ni—O(5')	3.70	C(4)—O(1)	3.79
N(4)—O(2)	3.15*	C(2)—O(1)	3.18
N(4)—O(4')	3.68	C(2)—O(2)	3.76
N(4)—O(1)	3.70	O(2)—C(9)	3.67
N(4)—N(1)	3.71	O(2)—C(4)	3.74
N(1)—O(5)	3.39	O(2)—O(1)	3.78
Ni—O(9)	3.59	C(11)—O(1)	3.36
N(1)—O(5')	3.67	C(11)—O(4')	3.68
N(1)—O(6)	3.73	C(11)—O(6)	3.70
N(3)—O(6)	3.03*	C(11)—O(4)	3.75
N(3)—O(4')	3.11*	O(1)—C(6)	3.28
N(3)—O(5)	3.42	O(1)—C(12)	3.29
N(3)—O(3')	3.52	O(1)—C(9)	3.46
N(3)—Cl	3.79	O(1)—C(4)	3.79
N(2)—O(1)	3.48	C(10)—O(4')	3.38
N(2)—O(5)	3.50	C(10)—O(5)	3.50
N(2)—O(2)	3.59	C(10)—O(5')	3.53
C(9)—O(1)	3.46	C(10)—O(5)	3.65
C(9)—O(2)	3.56	C(6)—O(6')	3.52
C(9)—O(6')	3.74	C(6)—O(5')	3.66
C(9)—O(5)	3.78	C(6)—O(4)	3.74
C(7)—O(3)	3.58	C(12)—O(4)	3.27
C(1)—O(6)	3.58	C(12)—O(4')	3.33
C(1)—O(3')	3.66	C(12)—O(5')	3.37

\* Hydrogen bonds.

perchlorate ions which are involved in weak hydrogen bonding to the amine groups. In Fig. 3, two of the perchlorates are shown with one set of O positions and the other two with a second set of O positions. Although there are numerous interionic contacts less than 3.8 Å (ignoring H atoms), none of these are unusually short, as can be seen from Table 2. The closest contact between the Ni and the perchlorate O atoms is Ni—O(5) (3.01 Å). Interionic hydrogen bonding is limited to (1) a hydrogen bond from an amine group on one Ni complex to an oxime oxygen on an adjacent complex [N(4)—O(2), 3.150 (4) Å; H(N4)—O(2), 2.212 (7) Å; and N(4)—H(N4)···O(2), 151.7 (5)°] and (2) a hydrogen bond from the other amine group to a perchlorate O atom [N(3)—O(6), 3.03 (1) Å; H(N3)—O(6), 2.03 (1) Å; N(3)—H(N3)···O(6), 160.5 (7)°; or N(3)—O(4'), 3.11 (1) Å; H(N3)—O(4'), 2.27 (2) Å; N(3)—H(N3)···O(4'), 140.0 (7)°].

As in previous studies of Ni amine oxime complexes (Table 3) the metal—N(amine) distances are significantly longer than the metal—N(oxime) distances. The difference of 0.036 Å is almost identical to that observed in the X-ray study of the nitrate salt (Ching & Schlemper, 1975). Both of these exhibit shorter Ni—N distances than those observed with comparable bidentate (AO) ligands (Schlemper, Hamilton & LaPlaca, 1971). The shortening of about 0.03 Å is definitely significant and is probably indicative of stronger bonds with the tetradentate ENAO ligand.

Table 3. *Comparison of average bond distances with those from the X-ray study of [Ni(EnAO—H)]<sup>+</sup>NO<sub>3</sub>·H<sub>2</sub>O and the neutron study of [Ni(2AO—H)]<sup>+</sup>Cl<sup>-</sup>·H<sub>2</sub>O*

Distance	Present compound	[Ni(EnAO—H)] <sup>+</sup> NO <sub>3</sub> <sup>-</sup> ·H <sub>2</sub> O*	[Ni(2AO—H)] <sup>+</sup> Cl <sup>-</sup> ·H <sub>2</sub> O†
Ni—N(oxime)	1.841 (3) Å	1.838 (5) Å	1.866 (4) Å
Ni—N(amine)	1.877 (2)	1.872 (2)	1.908 (2)
N—O	1.350 (2)	1.356 (4)	1.340 (5)
C(sp <sup>2</sup> )—N	1.294 (2)	1.288 (2)	1.288 (2)
C(sp <sup>3</sup> )—N	1.499 (8)	1.505 (12)	1.492 (2)
C(sp <sup>2</sup> )—C(sp <sup>3</sup> )	1.488 (2)	1.484 (8)	1.490 (4)
C(ring)—C(ring)	1.524 (2)	1.510 (10)	1.513 (4)
C(sp <sup>3</sup> )—C(sp <sup>3</sup> )	1.529 (6)	1.535 (8)	1.526 (6)
O···O	2.478 (5)	2.474 (7)	2.420 (3)

\* This study involved the nitrate salt of the same Ni complex reported here (Ching & Schlemper, 1975).

† AO is a comparable bidentate ligand (Schlemper, Hamilton & LaPlaca, 1971).

Table 4. Deviations ( $\text{\AA}$ ) from least-squares metal-coordination plane

$$9.00x + 2.54y - 3.74z - 0.95 = 0$$

Present compound	$\text{NO}_3^-$ salt*	Present compound	$\text{NO}_3^-$ salt*
Ni	0.0052 (2)	C(5)	-0.49
N1	-0.088 (2)	C(6)	0.65
N(2)	0.092 (2)	C(7)	-2.08
N(3)	0.108 (2)	C(8)	0.01
N(4)	-0.101 (2)	C(9)	-0.25
O(1)	0.05	C(10)	1.99
O(2)	-0.03	C(11)	-0.27
C(1)	-0.35	C(12)	0.35
C(2)	0.38	H(O0)	0.04
C(3)	-0.57	H(N3)	1.12
C(4)	0.50	H(N4)	-1.11

\* These values are from the previously reported X-ray study (Ching & Schlemper, 1975).

Table 5. Perchlorate-ion bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Cl—O(3)	1.47 (2)	O(3)—Cl—O(4)	107 (1)
Cl—O(4)	1.41 (2)	O(3)—Cl—O(5)	125 (1)
Cl—O(5)	1.42 (1)	O(3)—Cl—O(6)	105 (1)
Cl—O(6)	1.42 (1)	O(4)—Cl—O(5)	95 (1)
Cl—O(3')	1.40 (2)	O(4)—Cl—O(6)	110 (1)
Cl—O(4')	1.42 (2)	O(5)—Cl—O(6)	114 (1)
Cl—O(5')	1.44 (3)	O(3')—Cl—O(4')	111 (1)
Cl—O(6')	1.40 (1)	O(3')—Cl—O(5')	114 (1)
		O(3')—Cl—O(6')	115 (1)
		O(4')—Cl—O(5')	99 (1)
		O(4')—Cl—O(6')	111 (1)
		O(5')—Cl—O(6')	106 (1)

The configuration of the chelate rings is the same as in the nitrate salt, *i.e.* the N(oxime)—N(amine) chelate rings are in the  $\delta$  conformation while the N(amine)—N(amine) ring is in the  $\lambda$  conformation. The deviation from square-planar coordination around the Ni atom can be seen in Table 4. This deviation is nearly the same as with the nitrate salt and is a minor distortion toward tetrahedral. Deviations of other ligand atoms from the metal coordination plane are similar but generally larger than for the nitrate salt.

#### The perchlorate ion

Presumably because of only weak interactions with the Ni complex, the O atoms of the nearly tetrahedral perchlorate groups are not well ordered and are vibrating rather freely. The final model chosen involves a twofold disorder so that approximately half (0.52) of the perchlorate groups in the crystal have one set of tetrahedral O positions around the Cl while the remainder have a second set of tetrahedral O positions. The resulting bond distances and angles for the

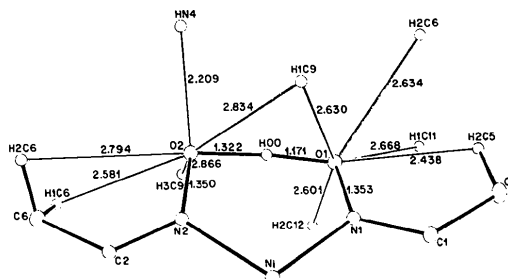


Fig. 4. The environments of the O atoms involved in the short hydrogen bond.

perchlorate ions are in Table 5. The second set of O atoms is significantly displaced from the first with the shortest distance between sets being 0.66  $\text{\AA}$  for O(3)···O(6'). The average Cl—O distance of 1.42 (2)  $\text{\AA}$  is in good agreement with other structural determinations. The range of O—Cl—O angles is rather large (95–125 $^\circ$ ). As indicated earlier, only weak hydrogen bonds with H(N3) involving O(4') and O(6) are involved in fixing the O positions.

#### The short intramolecular hydrogen bond

The main purpose of this study was to compare the short hydrogen bond in this complex with that in similar complexes. In Table 6 the geometry of this hydrogen bond is compared with those found in other compounds with short O···H···O bonds not constrained by crystallographic symmetry, which have been studied by neutron diffraction. In this complex, the O···O distance of 2.478 (5)  $\text{\AA}$  is somewhat longer than the shortest observed O···O distances ( $\sim$ 2.40  $\text{\AA}$ ). This is because of the steric requirements of the tetradentate ligand (see discussion by Ching & Schlemper, 1975). In the nitrate salt studied by X-ray diffraction, the distance [2.476 (6)  $\text{\AA}$ ] was essentially identical with that in the present complex. In the X-ray study the H appeared to be 0.80 (6)  $\text{\AA}$  from one O atom and 1.68 (6)  $\text{\AA}$  from the other. From this neutron study the distances are 1.171 (8) and 1.316 (8)  $\text{\AA}$ . The longer distance is associated with O(2) which is involved in a weak hydrogen bond with H(N4) [O(2)—H(N4), 2.212 (7)  $\text{\AA}$ ]. The comparisons in Table 6 clearly indicate a gradual, but not completely regular, increase in asymmetry of the hydrogen bond with increasing O···O distance. This is most easily seen in the values of  $\Delta(\text{O—H})$ . An interesting comparison is with the recently studied Pt complex with bidentate amine oxime ligands (Schlemper & Fair, 1977) which has almost the same O···O distance [2.472 (5)  $\text{\AA}$ ], but a much larger difference in O—H distances. In that Pt complex, the O giving the longer O—H distance is involved in a relatively strong intermolecular hydrogen bond with a water H atom (O···H = 1.792  $\text{\AA}$ ). The shorter

Table 6. *Asymmetry of short O...O hydrogen bonds from neutron diffraction studies*

Compound	O...O	O—H	H...O	$\Delta(O-H)$	Reference
C <sub>7</sub> H <sub>5</sub> NO <sub>4</sub>	2.398 (3) Å	1.165 (5) Å	1.238 (5) Å	0.073 Å	Kvick, Koetzle, Thomas & Takusagawa (1974)
[Ni(C <sub>5</sub> H <sub>11</sub> N <sub>2</sub> O) <sub>2</sub> H] <sup>+</sup> Cl <sup>-</sup> ·H <sub>2</sub> O	2.420 (3)	1.187 (5)	1.242 (5)	0.055	Schlemper, Hamilton & LaPlaca (1971)
K <sup>+</sup> [C <sub>4</sub> H <sub>2</sub> ClO <sub>4</sub> ] <sup>-</sup>	2.403 (3)	1.199 (5)	1.206 (5)	0.007	Ellison & Levy (1965)
(NH <sub>2</sub> ) <sub>2</sub> CO·H <sub>3</sub> PO <sub>4</sub>	2.421 (3)	1.207 (6)	1.223 (6)	0.016	Kostansek & Busing (1972)
[H <sub>5</sub> O <sub>2</sub> ] <sup>+</sup> [C <sub>6</sub> H <sub>2</sub> (NO <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> ] <sup>-</sup> ·2H <sub>2</sub> O	2.436 (2)	1.128 (4)	1.310 (4)	0.182	Lundgren & Tellgren (1974)
C <sub>6</sub> (NO <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub> O <sub>2</sub> ·6H <sub>2</sub> O	2.44	1.18	1.27	0.09	Williams & Peterson (1969)
[Pt(C <sub>5</sub> H <sub>11</sub> N <sub>2</sub> O) <sub>2</sub> H] <sup>+</sup> Cl <sup>-</sup> ·3.5H <sub>2</sub> O	2.472 (5)	1.087 (7)	1.389 (7)	0.302	Schlemper & Fair (1977)
KHO(CH <sub>2</sub> COO) <sub>2</sub>	2.476 (2)	1.152 (3)	1.326 (3)	0.174	Albertsson & Grenthe (1973)
[Ni(EnAO—H)]ClO <sub>4</sub>	2.478 (5)	1.171 (8)	1.316 (8)	0.145	This work
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O	2.506 (4)	1.026 (7)	1.480 (7)	0.454	Sabine, Cox & Craven (1969)
NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	2.536 (3)	1.023 (5)	1.515 (5)	0.492	Barth, Catti & Ferraris (1976)
NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	2.577	1.028 (6)	1.553 (6)	0.525	Barth, Catti & Ferraris (1976)
InOOH	2.537 (3)	1.079 (7)	1.458 (7)	0.379	Lehmann, Larsen, Paulsen, Christensen & Rasmussen (1970)
H <sub>3</sub> PO <sub>4</sub> ·½H <sub>2</sub> O	2.563 (1)	1.017 (2)	1.556 (2)	0.537	Dickens, Prince, Schroeder & Jordan (1974)
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	2.595 (3)	1.016 (3)	1.583 (4)	0.568	Schroeder, Prince & Dickens (1975)
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	2.622 (3)	0.987 (5)	1.679 (4)	0.692	Schroeder, Prince & Dickens (1975)
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	2.626	0.987 (5)	1.653 (5)	0.676	Schroeder, Prince & Dickens (1975)

Table 7. *Bond summation (Brown & Shannon, 1973) applied to the short hydrogen bonds in amine oxime metal complexes*

$$s_t = \sum_i s_i; s_t(O-H) = 0.50 (R_t/1.184)^{-2.2}; s_t(O-N) = 1.667 (R_t/1.241)^{-4.0}; R_t = \text{observed distance.}$$

Compound	$s_t [O(1)]$	$s_t [O(2)]$	$s_t (H)$	Reference
[Ni(AO) <sub>2</sub> —H]Cl·H <sub>2</sub> O	2.089 Å	2.031 Å	0.947 Å*	Schlemper, Hamilton & LaPlaca (1971)
[Pt(AO) <sub>2</sub> —H]Cl·3.5H <sub>2</sub> O	2.039	2.015	0.955*	Schlemper & Fair (1977)
[NiEnAO—H]ClO <sub>4</sub>	2.138	2.021	0.904	This work

\* Using 1.21 instead of 1.184, these values are essentially 1.00.

contacts with both O atoms in this structure are shown in Fig. 4.

Using the approach suggested by Brown & Shannon (1973), the bonding to the O and H atoms of the short hydrogen bonds in the three amine oxime complexes studied by neutron diffraction is compared in Table 7. All O—H contacts less than 3.00 Å are used to obtain the bond summations for the O atoms. A nearly constant value is obtained for both O atoms in all three complexes. For the H in the hydrogen bond, the value obtained in this study appears to be somewhat low. The results suggest that the asymmetry of the hydrogen bond is highly correlated with crystal packing around the O atoms.

Because of probable systematic errors in the thermal parameters due to the difficulty with the perchlorate O disorder, no attempt was made to fit the thermal parameters of the complex to a rigid-body model, as was done with the other two complexes. A cursory

examination (Fig. 1) of the shape of the O and H atom ellipsoids for the hydrogen bond suggests that the independent vibration of the H in the direction of the bond is significantly greater than that perpendicular to the bond. This would suggest a rather broad single minimum potential for the hydrogen bond as with the previously reported Ni complex and in contrast to the previously reported Pt complex.

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### Composés Organométalliques à Cycle Moyen.

## VII.\* Structure Cristalline et Moléculaire de la Diméthyl-6,6 Germa-6 Cycloundécane à $-40^{\circ}\text{C}$

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The structure of 6,6-dimethyl-6-germacycloundecanone has been determined by single-crystal X-ray techniques at  $-40^{\circ}\text{C}$ . The compound crystallizes in space group  $P2_1/n$  with  $Z = 4$ ,  $a = 9.662$  (2),  $b = 15.602$  (2),  $c = 9.768$  (2) Å,  $\beta = 117.65$  (2) $^{\circ}$ . The structure was solved by the Patterson method from diffractometer data. The least-squares refinement yielded an  $R$  of 3.2%. There is a tetrahedral coordination around the Ge atom with two methyl groups and a bidentate chain  $(\text{CH}_2)_4\text{-CO-}(\text{CH}_2)_2$ , giving rise to a ring  $[\text{GeC}_{10}]$ .

Les composés cycliques de taille moyenne (8 à 13 chaînons) sont caractérisés par une structure compacte. La gêne stérique importante qui en résulte conduit la molécule à adopter des conformations particulières. Aucune détermination structurale par rayons X n'a été réalisée à notre connaissance dans la série des cycloundécane de taille moyenne. Une approche structurale de ces cétones par étude en chromatographie en phase vapeur (Ledaal, 1967) et par effet de solvant en RMN

(Ledaal, 1968) indique cependant une orientation préférentielle du groupement carbonyle vers l'intérieur de la molécule. Plus récemment, une analyse conformationnelle par RMN à température variable a conduit Anet, Jacques, Henrichs, Cheng, Krane & Wong (1974) à proposer des conformations différentes (bateau-chaise et bateau-chaise-bateau) de celles du type 'couronne' généralement admises.

Une interaction entre l'oxygène du groupement carbonyle et l'hétéroatome, Si ou Ge, ayant été mise en évidence par spectroscopie photoélectronique (Guimon,

\* Partie VI: Mazerolles & Faucher (1973).