

Contribution from the Department of Chemistry,
University of Missouri, Columbia, Missouri 65201**A Slightly Constrained O---O Hydrogen Bond. Crystal Structure of a Tetradentate α -Amine Oxime Complex of Nickel(II)**

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The crystal structure of 2,2'-(1,2-diaminoethane)bis(2-methyl-3-butanone oximate)nickel(II) nitrate monohydrate, $[\text{Ni}(\text{EnAO-H})]\text{NO}_3 \cdot \text{H}_2\text{O}$, has been determined from three-dimensional X-ray data collected with a scintillation counter. The orthorhombic unit cell dimensions are $a = 12.611$ (4), $b = 11.225$ (5), and $c = 13.043$ (5) Å. The density of 1.425 (2) g/cm³ calculated for four formula units per cell agrees with the flotation density of 1.41 (2) g/cm³. The space group is $P2_12_12_1$. A full-matrix least-squares refinement with 2214 independent reflections gave a final conventional agreement factor of 4.5%. The structure consists of discrete nearly square-planar nickel(II) complex positive ions, nitrate ions, and waters of hydration, interconnected by extensive hydrogen bonding. The coordination of the nickel is significantly distorted from square planar as a result of the steric requirements of the tetradentate ligand which is coordinated to the nickel through two amine nitrogens ($\text{Ni-N}(\text{amine}) = 1.838$ (5) Å) and two oxime nitrogens ($\text{Ni-N}(\text{oxime}) = 1.872$ (5) Å). The short intramolecular O1---O2 hydrogen bond (2.474 (6) Å) is apparently quite asymmetric with O2-H (0.80 (6) Å) and O1-H (1.68 (6) Å).

Introduction

Earlier studies have revealed short intramolecular hydrogen bonds in bidentate α -amine oxime (AO) square-planar Ni(II)^{1,2} and Pt(II)³ and octahedral Co(III)⁴ complexes as well as in a tetradentate α -amine oxime octahedral cobalt(III)⁵ complex. In the Ni(II) complex and the Co(III) complexes, the O---O hydrogen-bond distance (2.42–2.43 Å) was found to be among the shortest known while a longer O---O distance (2.48 Å) was observed with the larger Pt(II). The present study was undertaken to examine the effect on the hydrogen bond of having a shorter bridge between the amine nitrogens in a tetradentate α -amine oxime complex of a first-row transition metal. The ligand (Figure 1) chosen for this study, hereafter referred to as EnAO, has one less carbon in the bridge between the amine nitrogens than does the PnAO ligand previously studied with Co(III).⁵ This additional geometrical constraint was expected to result in a longer and less symmetric O---O hydrogen bond. The previously reported Ni(II) complex⁶ $[\text{Ni}(\text{EnAO-H})]^+$ was chosen for the X-ray study.

Experimental Section

A. Crystal Preparation. The complex $[\text{Ni}(\text{EnAO-H})]^+$ was prepared as described by Murmann⁶ and precipitated as $[\text{Ni}(\text{EnAO-H})]\text{NO}_3 \cdot \text{H}_2\text{O}$ by addition of NaNO_3 . Yellow-green crystals were then obtained by slow evaporation of aqueous solutions.

B. X-Ray Data. 2,2'-(1,2-Diaminoethane)bis(2-methyl-3-butanone oximate)nickel(II) nitrate monohydrate, $[\text{Ni}(\text{C}_{12}\text{H}_{25}\text{N}_4\text{O}_2)]\text{NO}_3 \cdot \text{H}_2\text{O}$, crystallizes in the orthorhombic crystal system with four formula units in a unit cell with $a = 12.611$ (4), $b = 11.225$ (5), and $c = 13.043$ (5) Å. These cell dimensions and their standard deviations were determined from a least-squares refinement⁷ of the setting angles of 23 reflections that had been carefully centered using a narrow vertical slit in front of the detector and a low takeoff angle on a Picker four-circle X-ray diffractometer with $\text{Mo K}\alpha_1$ radiation. A measurement of the density by flotation in benzene-chloroform solution gave 1.41 (2) g/cm³. A calculated density of 1.425 (1) g/cm³ is obtained, assuming four formulas per unit cell. The systematic extinctions were for $h00$, h odd, for $0k0$, k odd, and for $00l$, l odd, indicating that the space group is $P2_12_12_1$.

For the collection of intensity data a crystal of approximate dimensions $0.3 \times 0.3 \times 0.4$ mm bounded by 15 faces was aligned as described above on a Picker four-angle programmer system. Using the orientation matrix and cell dimensions from this refinement, the setting angles for all intensity measurements were calculated. The crystal was mounted with c^* coincident with ϕ for the intensity measurements. Intensity data were collected at a takeoff angle of 2.5° using $\text{Mo K}\alpha$ radiation filtered through a niobium β filter. The receiving aperture was 3×3 mm and was positioned 27 cm from the crystal. The data were collected by a θ - 2θ scan technique at a scan rate of 1.0°/min. The scan width was variable to account for the

α_1 - α_2 splitting and ranged from 0.95 to 1.22° in 2θ in the 0–50° 2θ region collected. Stationary-counter backgrounds were taken for 20 sec on each end of the scan. The count rate never exceeded 8000 counts/sec and was therefore in the linear range of the detector. The pulse height analyzer was set for about a 95% window, centered on the $\text{Mo K}\alpha$ peaks. The intensities of 6480 reflections were measured. Four standard reflections were measured every 50 reflections as a check on crystal and instrument stability. Because of instrument problems the data collection time was extensive, and the standard reflections all dropped in intensity in a nearly linear fashion by about 25%. The data were corrected for this decrease using the straight line generated from plotting the sum of the intensities of the standards vs. time.

Background and Lorentz-polarization corrections were made using the usual equations. Absorption corrections were made ($\mu = 10.9$ cm⁻¹) with the transmission factor ranging from 0.78 to 0.83. Equivalent and duplicate reflections were averaged, reducing the number of reflections to 2424, account being taken of the non-equivalence of Friedel pairs. For the 0–20° 2θ region all eight forms of hkl were measured. For 20–40° 2θ hkl , $h\bar{k}l$, and $\bar{h}kl$ were measured while for 40–50° only hkl and $h\bar{k}l$ were measured. When the data were averaged without accounting for the nonequivalence of Friedel pairs, the agreement factor ($= \sum |F^2 - F_{av}^2| / \sum F^2$) was 6.7%, but when Friedel pairs were separated, this agreement factor was reduced to 4.9%. Of these, 2214 which had $F_o^2 > 2.5\sigma(F_o^2)$, where $\sigma = [\sigma_{\text{counting}}^2 + (0.03F_o^2)^2]^{1/2}$, were used in the structure solution and refinement.

C. Determination of the Structure. The nickel atom was located by the Patterson method, and all other atoms were located from successive Fourier and difference Fourier syntheses. Refinement of positional and isotropic thermal parameters for all atoms except hydrogens converged with $R = \sum |F_o^2 - kF_c^2| / \sum F_o^2 = 0.126$ and $r = [\sum w(F_o^2 - kF_c^2)^2 / \sum wF_o^4]^{1/2} = 0.199$ where $w = 1/\sigma^2(F_o^2)$. In this and all refinements, the quantity $\sum w(F_o^2 - kF_c^2)^2$ was minimized. For C, N, and O scattering factors were taken from Ibers;^{8a} those of H, from Stewart;^{8b} and those of Ni, from Cromer and Waber.^{8c} Using the tabulated values^{8d} of $\Delta f'$ and $\Delta f''$ for Ni, the effects of anomalous dispersion were included in F_c .^{8e} Refinement with the nickel atom anisotropic reduced R to 0.120 and r to 0.190. Inclusion of hydrogen atoms in keeping with difference Fourier observations and in chemically reasonable positions with isotropic temperature factors about 1.0 Å² greater than that of the atom to which they were attached gave $R = 0.101$ and $r = 0.165$. Refinement with fixed hydrogen atoms and all other atoms anisotropic then gave $R = 0.068$ and $R = 0.130$. Inclusion of the hydrogen atom positional parameters (fixed thermal parameters) in the refinement converged with $R = 0.060$ and $r = 0.103$. This improvement is significant at the 99% confidence level.⁹ The conventional agreement factor was 0.045. The standard deviation of an observation of unit weight was 2.20. A comparison of F_o and F_c values for Friedel pairs supports the choice of enantiomers. A final difference Fourier had no peaks greater than 0.5 e/Å³. The observed and calculated structure factors are available.¹⁰ The hydrogen atom positions are given in Table I while

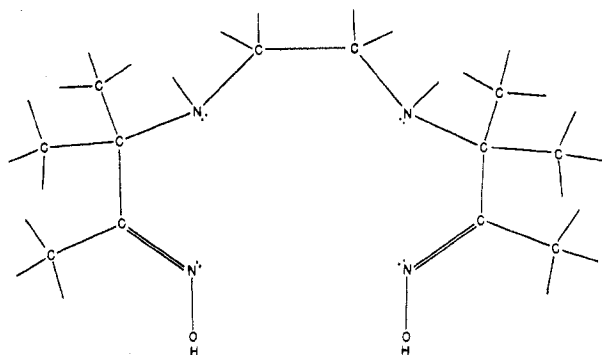


Figure 1. Neutral 2,2'-(1,2-diaminoethane)bis(2-methyl-3-butanone oxime)(EnAO).

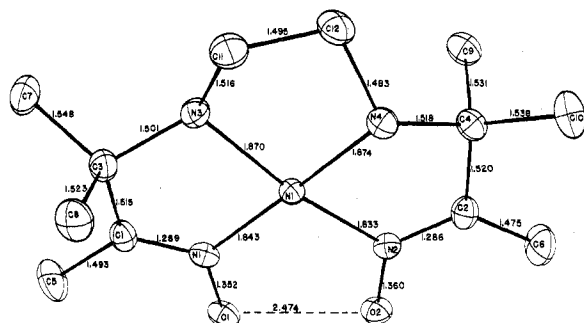


Figure 2. Perspective view of the 2,2'-(1,2-diaminoethane)bis(2-methyl-3-butanone oximate)nickel(II) ion, $[\text{Ni}(\text{EnAO-H})]^+$, showing bond distances: Ni-N, 0.005 Å; N-O, 0.007 Å; C-N, 0.007-0.009 Å; C-C, 0.009-0.011 Å. The thermal ellipsoids, except for hydrogen atoms, are drawn at the 5% probability level in all figures.

the final positional and thermal parameters of all other atoms are included in Tables II and III.

Discussion

A. Nature of the Structure. The crystal structure consists of discrete distorted square-planar nickel complex cations (Figures 2 and 3), nitrate anions (Figure 4), and waters of hydration. The distorted square plane about the nickel(II) consists of the four nitrogens of the tetradentate EnAO ligand. There are no unusually short intramolecular contacts as can be seen from Table IV where all interionic distances (ignoring hydrogens) under 3.8 Å are given. The shorter contacts are hydrogen bonds among the amine nitrogens, the nitrate oxygens, and the waters of hydration (Figure 5). These hydrogen bonds apparently stabilize the crystal structure.

The square plane about the nickel is distorted slightly toward tetrahedral geometry in that the trans N1 and N4 are below the best plane through the nickel and four nitrogens while the trans N2 and N3 are above the plane. This distortion is similar to but more pronounced than that observed for the tetradentate ligand in (-)-589-*trans*-dichloro(1,10-diamino-4,7-diazadecane)cobalt(III) nitrate.¹¹ The equation of this weighted least-squares plane and the deviations of all cation atoms except carbon hydrogens from the plane are given in

Table I. Hydrogen Atom Parameters^a

Atom	x	y	z	B, Å ²
H1	0.407 (6)	0.166 (6)	0.047 (7)	7.5
H2	0.361 (6)	0.242 (6)	-0.164 (6)	7.5
H3	0.360 (7)	0.026 (7)	0.167 (8)	8.0
H4	0.243 (7)	0.073 (7)	-0.183 (8)	8.0
H5	0.215 (5)	0.274 (6)	-0.079 (5)	8.0
H6	0.312 (6)	-0.019 (6)	0.001 (6)	5.5
H7	0.098 (8)	-0.271 (8)	0.072 (9)	6.5
H8	0.024 (7)	-0.242 (7)	0.031 (8)	8.5
H9	0.017 (7)	-0.198 (8)	0.123 (8)	8.5
H10	0.223 (7)	0.515 (8)	0.177 (7)	8.5
H11	0.169 (7)	0.412 (7)	0.243 (8)	8.5
H12	0.115 (7)	0.469 (8)	0.172 (9)	8.5
H13	0.286 (7)	-0.243 (8)	-0.012 (7)	8.0
H14	0.315 (7)	-0.204 (6)	-0.140 (7)	8.0
H15	0.207 (7)	-0.274 (7)	-0.103 (7)	8.0
H16	0.149 (6)	-0.089 (7)	-0.208 (7)	7.5
H17	0.083 (6)	-0.001 (7)	-0.153 (7)	7.5
H18	0.052 (6)	-0.146 (6)	-0.151 (7)	7.5
H19	0.399 (7)	0.243 (7)	0.114 (7)	7.0
H20	0.395 (7)	0.366 (7)	0.128 (7)	7.0
H21	0.449 (6)	0.330 (6)	0.032 (7)	7.0
H22	0.347 (7)	0.454 (7)	-0.080 (8)	8.0
H23	0.292 (6)	0.531 (7)	0.021 (7)	8.0
H24	0.200 (7)	0.485 (7)	-0.062 (6)	8.0
H25	0.654 (9)	0.214 (9)	0.259 (8)	11.0
H26	0.578 (7)	0.134 (8)	0.185 (8)	11.0
H27	0.061 (5)	0.154 (5)	0.190 (5)	6.0

^a Standard deviations from the least-squares refinement are included in parentheses in this and other tables. H1-H4 are methylene hydrogens, H5 and H6 are amine hydrogens, H7-H24 are methyl hydrogens, H25 and H26 are water hydrogens, and H27 is the oxime hydrogen.

Table II. Atomic Positional Parameters

Atom	x	y	z
Ni	0.19168 (5)	0.11694 (6)	0.03258 (5)
O1	0.0469 (3)	0.0075 (4)	0.1662 (4)
O2	0.0761 (3)	0.2235 (4)	0.1941 (4)
O3	0.5231 (7)	0.5140 (6)	0.4360 (7)
O4	0.6011 (6)	0.3742 (6)	0.3676 (6)
O5	0.4502 (6)	0.4288 (7)	0.3153 (6)
O6	0.6340 (5)	0.1922 (6)	0.2129 (5)
N1	0.1119 (4)	-0.0068 (5)	0.0847 (4)
N2	0.1503 (4)	0.2384 (4)	0.1175 (4)
N3	0.2567 (4)	0.0002 (4)	-0.0481 (4)
N4	0.2645 (4)	0.2360 (4)	-0.0395 (4)
N5	0.5236 (6)	0.4402 (6)	0.3728 (6)
C1	0.1197 (4)	-0.1078 (6)	0.0384 (5)
C2	0.1986 (6)	0.3389 (5)	0.1098 (5)
C3	0.1859 (5)	-0.1066 (5)	-0.0585 (5)
C4	0.2875 (4)	0.3404 (5)	0.0310 (5)
C5	0.0596 (7)	-0.2151 (6)	0.0731 (7)
C6	0.1785 (8)	0.4427 (6)	0.1763 (7)
C7	0.2557 (6)	-0.2190 (6)	-0.0713 (7)
C8	0.1121 (6)	-0.0903 (6)	-0.1499 (6)
C9	0.3930 (6)	0.3177 (6)	0.0857 (6)
C10	0.2922 (6)	0.4569 (5)	-0.0309 (7)
C11	0.3033 (6)	0.0629 (6)	-0.1407 (6)
C12	0.3485 (5)	0.1769 (6)	-0.1007 (6)

Table V (plane 1). Both of the N(oxime)-N(amine) chelate rings are in the δ conformation while the N(amine)-N(amine) chelate ring is in the λ conformation. The puckering of the

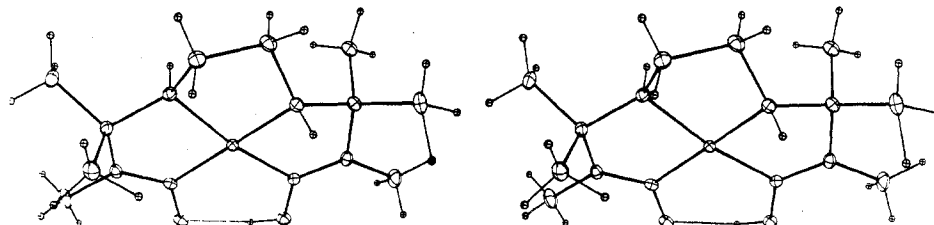


Figure 3. Stereoscopic view of the $[\text{Ni}(\text{EnAO-H})]^+$ ion. Hydrogen atoms are illustrated with small spheres. The atom labeling is shown in Figure 2.

Table III. Atomic Anisotropic Thermal Parameters

Atom	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.00532 (4)	0.00705 (5)	0.00420 (4)	-0.00023 (5)	-0.00041 (4)	-0.00005 (5)
O1	0.0066 (3)	0.0143 (5)	0.0057 (3)	-0.0021 (3)	0.0013 (3)	0.0002 (3)
O2	0.0072 (3)	0.0132 (5)	0.0070 (4)	0.0000 (3)	0.0020 (3)	-0.0020 (4)
O3	0.0221 (9)	0.0204 (8)	0.0215 (11)	-0.0015 (7)	-0.0034 (9)	-0.0114 (8)
O4	0.0161 (7)	0.0226 (9)	0.0126 (6)	0.0033 (7)	-0.0001 (6)	0.0019 (7)
O5	0.0158 (7)	0.0379 (13)	0.0095 (6)	-0.0055 (8)	-0.0035 (6)	-0.0029 (7)
O6	0.0146 (6)	0.0226 (8)	0.0117 (6)	-0.0023 (6)	0.0048 (5)	0.0002 (6)
N1	0.0053 (4)	0.0105 (5)	0.0055 (4)	-0.0005 (3)	-0.0003 (3)	0.0011 (4)
N2	0.0060 (3)	0.0088 (5)	0.0044 (3)	0.0003 (3)	0.0001 (3)	-0.0005 (3)
N3	0.0070 (3)	0.0084 (4)	0.0062 (4)	0.0003 (3)	0.0009 (4)	-0.0006 (4)
N4	0.0065 (3)	0.0090 (4)	0.0056 (4)	-0.0005 (3)	-0.0003 (4)	-0.0001 (4)
N5	0.0111 (6)	0.0125 (7)	0.0069 (5)	-0.0042 (6)	-0.0002 (5)	0.0014 (5)
C1	0.0075 (4)	0.0081 (5)	0.0069 (5)	-0.0007 (4)	-0.0016 (4)	0.0001 (6)
C2	0.0089 (5)	0.0081 (5)	0.0064 (4)	0.0002 (5)	-0.0009 (5)	-0.0007 (4)
C3	0.0072 (4)	0.0079 (5)	0.0075 (5)	0.0001 (5)	-0.0011 (4)	-0.0012 (4)
C4	0.0071 (5)	0.0093 (5)	0.0059 (4)	-0.0015 (4)	-0.0004 (4)	0.0001 (4)
C5	0.0148 (9)	0.0104 (7)	0.0143 (10)	-0.0063 (7)	0.0009 (8)	0.0007 (7)
C6	0.0160 (9)	0.0100 (7)	0.0133 (9)	-0.0008 (7)	0.0025 (8)	-0.0049 (6)
C7	0.0113 (6)	0.0088 (6)	0.0132 (9)	0.0016 (5)	-0.0009 (6)	-0.0029 (6)
C8	0.0100 (6)	0.0119 (8)	0.0073 (6)	-0.0004 (6)	-0.0022 (5)	-0.0003 (5)
C9	0.0082 (6)	0.0135 (7)	0.0081 (6)	-0.0022 (5)	-0.0006 (5)	-0.0003 (6)
C10	0.0142 (7)	0.0084 (6)	0.0109 (7)	-0.0030 (6)	-0.0001 (8)	0.0016 (6)
C11	0.0098 (6)	0.0129 (7)	0.0071 (6)	-0.0009 (6)	0.0035 (5)	-0.0017 (5)
C12	0.0081 (6)	0.0121 (7)	0.0068 (5)	-0.0021 (5)	0.0022 (5)	0.0003 (5)

^a The form of the thermal ellipsoids is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table IV. Interionic Distances

Distance	Value, Å	Distance	Value, Å
Ni-O3	3.80	C3-O4	3.67
O1-C11	3.25	C4-O6	3.74
O1-C6	3.58	C5-N5	3.78
O1-C10	3.69	C7-O4	3.38
O2-C12	3.30	C8-O5	3.48
O2-C5	3.58	C8-N5	3.54
O2-C7	3.74	C8-O4	3.74
N1-C11	3.79	C8-O6	3.76
N3-O3 ^a	3.14	C9-O3	3.58
N3-O4 ^a	3.28	C9-O6	3.74
N3-N5	3.66	C10-O6	3.52
N4-O6 ^a	2.91	C10-C7	3.70
C1-O4	3.73	C11-O3	3.50
C12-O3	3.25	C11-O6	3.61
C12-O6	3.41	O3-O6	3.42
O5-O6 ^a	3.16	N5-O6	3.63
O5-O6	3.77	N5-O6	3.75
O4-O6 ^a	2.90	O5-C9	3.32

^a Hydrogen bonds.

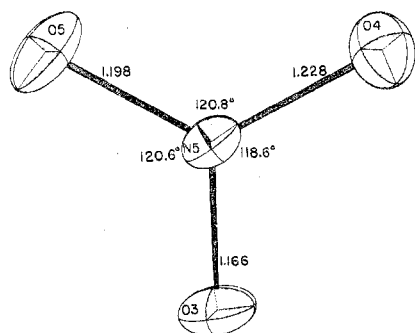


Figure 4. Bond distances and angles in the nitrate ion. Standard deviations: N-O, 0.008 Å; O-N-O, 0.8°.

EnAO chelate rings is probably responsible for the rather large deviation from square-planar coordination. Despite the puckering and large deviation of most of the atoms from the plane, the oxime oxygens and the associated hydrogen atom are nearly in the plane. The oxime nitrogen and oxygen atoms define a very good plane (Table V, plane 2) which nearly includes the nickel and the oxime hydrogen (H27).

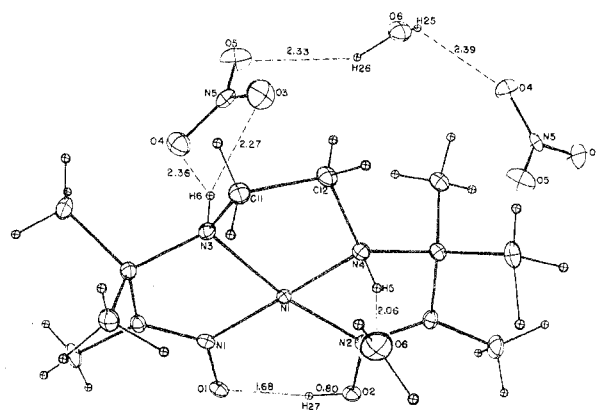


Figure 5. Interionic hydrogen bonding between the nickel complex, the nitrate ion, and the water of hydration. The intermolecular hydrogen bonds are illustrated as dashed lines.

Table V. Deviations from Least-Squares Planes

Atom	Distance, Å	Atom	Distance, Å
Plane 1: N1, N2, N3, N4, Ni			
$9.47X - 1.93Y + 8.31Z - 1.86 = 0$			
Ni	0.0003 (7)	C5	-0.27
N1	-0.083 (5)	C6	0.44
N2	0.080 (5)	C7	0.39
N3	0.173 (6)	C8	-1.87
N4	-0.140 (6)	C9	1.96
O1	-0.05	C10	-0.23
O2	0.02	C11	-0.28
C1	-0.17	C12	0.26
C2	0.28	H5	-1.00
C3	-0.38	H6	1.14
C4	0.46	H27	0.00

Plane 2: N1, N2, O1, O2

$$9.33X - 2.44Y + 8.30Z - 1.78 = 0$$

N1	-0.015 (5)	O2	-0.020 (5)
N2	0.016 (5)	Ni	-0.006
O1	0.020 (5)	H27	-0.003

Plane 3: N5, O3, O4, O5

$$5.49X + 7.10Y - 8.35Z - 2.89 = 0$$

N5	-0.002 (10)	O4	-0.002 (8)
O3	-0.001 (7)	O5	0.002 (6)

Table VI. Root-Mean-Square Components of Thermal Displacement along the Principal Axes (Å)

Atom	Axis 1	Axis 2	Axis 3
Ni	0.186 (1)	0.207 (2)	0.215 (2)
O1	0.195 (7)	0.243 (6)	0.311 (6)
O2	0.201 (7)	0.263 (6)	0.305 (6)
O3	0.251 (9)	0.424 (9)	0.501 (11)
O4	0.316 (9)	0.344 (9)	0.405 (9)
O5	0.244 (9)	0.369 (9)	0.505 (9)
O6	0.257 (8)	0.369 (8)	0.400 (8)
N1	0.205 (7)	0.212 (8)	0.266 (7)
N2	0.192 (7)	0.219 (7)	0.239 (7)
N3	0.211 (8)	0.237 (7)	0.250 (8)
N4	0.216 (7)	0.228 (7)	0.244 (6)
N5	0.222 (8)	0.252 (9)	0.341 (9)
C1	0.212 (9)	0.229 (9)	0.272 (9)
C2	0.218 (8)	0.237 (9)	0.274 (8)
C3	0.212 (8)	0.232 (9)	0.271 (9)
C4	0.216 (9)	0.227 (9)	0.263 (7)
C5	0.199 (10)	0.352 (12)	0.382 (11)
C6	0.212 (9)	0.332 (12)	0.391 (12)
C7	0.217 (9)	0.300 (9)	0.353 (12)
C8	0.225 (9)	0.276 (9)	0.304 (10)
C9	0.235 (9)	0.268 (10)	0.308 (9)
C10	0.211 (9)	0.310 (10)	0.349 (9)
C11	0.195 (11)	0.276 (9)	0.328 (10)
C12	0.205 (10)	0.267 (9)	0.304 (9)

Because of the asymmetric amine nitrogens which are not mirror related, the nickel complex is one of a pair of optical enantiomers. Large portions of the complex are nearly related by twofold symmetry about an axis through the nickel and the center of the C11 to C12 bond. The deviations from this twofold symmetry are however, in some cases, quite significant (see deviations from plane 1, Table V). The nitrate ion is strictly planar (plane 3, Table V).

The water molecule (O6) bridges the cation and anion through strong hydrogen bonds with the amine nitrogen (N4) of the cation (N4-O6 = 2.91 Å and with O4 and O5 of the nitrate ion (O4-O6 = 2.90 Å and O5-O6 = 3.16 Å). The nitrate ion also directly hydrogen bonds to the cation through amine nitrogen (N3) (N3-O3 = 3.14 Å and N3-O4 = 3.28 Å). The hydrogen atoms on N3 and N4 involved in these hydrogen bonds are on opposite sides of the complex coordination plane as are the corresponding water oxygen and nitrate oxygens.

The shapes and orientations of the thermal ellipsoids are shown in Figures 2-4 while the root-mean-square displacements along the principal axes are in Table VI. As can be seen from the figures the maximum vibrations of the terminal nonhydrogen atoms tend to be perpendicular to the bonds and the minimum vibrations nearly along the bonds as usually observed. The greatest thermal motion, as might be expected, is in the nitrate oxygens and the water.

B. Bond Distances and Angles. The bond distances for all atoms except hydrogens are given in Figures 2 and 4. Table VII contains the important bond angles, and Table VIII the distances involving hydrogens.

Corresponding Ni-N distances are significantly shorter than those² in [Ni(AO)₂-H]⁺ by about 0.03 Å. As previously observed, the Ni-N(oxime) distances (1.838 average) are shorter than the Ni-N(amine) distances (1.872 average). Comparable distances within the ligand are very consistent with those observed in other α -amine complexes of cobalt and nickel.¹⁻⁵ Of more interest are the rather distorted bond angles in the complex brought about by the steric requirements of the ligand. Even the angles around the nickel(II) atom are highly distorted from ideal square-planar values, with the largest deviation being the N1-Ni-N2 angle of 100.4 (2)°. This angle is significantly larger than the corresponding 97.34 (6)° angle in the [Ni(AO)₂-H]⁺ complex.⁵ This results in a corresponding increase in the O---O distance to 2.474 (6) Å

Table VII. Intraionic Bond Angles

Angle	Value, deg	Angle	Value, deg
N1-Ni-N2	100.4 (2)	N2-C2-C4	114.4 (5)
N1-Ni-N3	85.4 (2)	N2-C2-C6	124.4 (7)
N1-Ni-N4	171.4 (2)	C4-C2-C6	121.1 (7)
N2-Ni-N4	84.9 (2)	N3-C3-C1	105.0 (5)
N2-Ni-N3	170.5 (2)	N3-C3-C7	108.7 (6)
N3-Ni-N4	90.2 (2)	N3-C3-C8	109.6 (6)
Ni-N1-O1	122.3 (4)	C1-C3-C7	113.5 (6)
Ni-N1-C1	116.6 (5)	C1-C3-C8	108.6 (6)
C1-N1-O1	121.1 (5)	C7-C3-C8	111.2 (6)
Ni-N2-O2	122.4 (4)	N4-C4-C2	105.0 (4)
Ni-N2-C2	118.1 (4)	N4-C4-C9	108.7 (5)
C2-N2-O2	119.4 (5)	N4-C4-C10	110.4 (6)
Ni-N3-C3	110.5 (4)	C2-C4-C9	108.8 (6)
Ni-N3-C11	107.0 (4)	C2-C4-C9	113.3 (6)
C3-N3-C11	121.9 (6)	C9-C4-C10	110.5 (6)
Ni-N4-C4	109.9 (4)	N3-C11-C12	105.5 (6)
Ni-N4-C12	107.5 (4)	N4-C12-C11	107.4 (6)
C4-N4-C12	122.3 (5)	N2-O2-H27	105
N1-C1-C3	115.2 (6)	N1-O1-H27	101
N1-C1-C5	122.1 (7)	O2-H27-O1	169
C3-C1-C5	122.6 (7)		

Table VIII. Distances Involving Hydrogen Atoms

Distance	Value, Å	Distance	Value, Å
N3-H6	0.97 (8)	C9-H19	0.92 (7)
N4-H5	0.91 (7)	C9-H20	0.77 (8)
C5-H7	0.78 (9)	C9-H21	1.00 (8)
C5-H8	0.77 (9)	C10-H22	0.94 (9)
C5-H9	0.86 (9)	C10-H23	1.07 (8)
C6-H10	0.99 (9)	C10-H24	1.27 (9)
C6-H11	0.94 (9)	C11-H3	0.90 (9)
C6-H12	0.86 (9)	C11-H4	0.94 (9)
C7-H13	0.90 (9)	C12-H1	1.03 (8)
C7-H14	1.18 (9)	C12-H2	1.11 (8)
C7-H15	0.97 (8)	O6-H25	0.69 (10)
C8-H16	0.88 (8)	O6-H26	1.03 (9)
C8-H17	1.07 (7)	O1-H27	1.68 (6)
C8-H18	0.98 (8)	O2-H27	0.80 (6)

compared with 2.420 (3) Å in the AO complex. The trans N-Ni-N angles are also highly distorted due to puckering away from the square-planar configuration, largely a motion of the tetrahedral amine nitrogens to opposite sides of the square plane. The external angles between chelate rings subtended at the amine nitrogens (C4-N4-C12 = 122.3 (5)° and C3-N3-C11 = 121.9 (6)°) are highly distorted from tetrahedral values while the internal chelate ring angles subtended at the tetrahedral carbons C3, C4, C11, and C12 are significantly smaller than tetrahedral (105.0-107.4°). These ligand angle anomalies are apparently a necessity to achieve coordination of the ligand through all four nitrogens to the nickel in the nearly square-planar geometry.

Distances involving hydrogen atoms are poorly defined, but the average C-H distance (0.96 (9) Å) and the average N-H distance (0.94 (7) Å) are reasonable.¹² H-C-H, H-C-C, and H-C-N angles range from 90 to 124° with an average of 109° and an average deviation of 6°.

The nitrate ion, although planar, is quite distorted with N-O distances from 1.166 (8) to 1.228 (8) Å and O-N-O angles from 118.6 (8) to 120.8 (8)°. The apparent distances are undoubtedly too short because of the high thermal motion. A riding correction¹³ gives N-O distances of 1.28, 1.29, and 1.29 (1) Å. This is probably an overcorrection since the N-O distance in NaNO₃ is observed¹⁴ to be 1.241 (2) Å. A similar range of N-O distances (1.188-1.254 (6) Å) was observed¹¹ in (-)-589-trans-dichloro(1,10-diamino-4,7-diazadecane)cobalt(III) nitrate while an even larger range (1.11-1.29 (3) Å) was observed¹⁵ in nitratobis(acetone thiosemicarbazone)-nickel(II) nitrate monohydrate for the uncoordinated nitrate. As might be expected, the most strongly hydrogen-bonded oxygen (O4) is associated with the largest N-O distance.

Table IX. Short O---O Hydrogen Bonds in Related Compounds

Compd	O1---O2, Å	O2-H, Å	O1-H, Å	Ref
[Ni(EnAO-H)]NO ₃ ·H ₂ O	2.474 (6)	0.80 (6)	1.68 (6)	This work
[Ni(AO) ₂ -H]Cl·H ₂ O	2.420 (3)	1.187 (5)	1.242 (5)	2
[H ₅ O ₂] ⁺ [C ₆ H ₂ (NO ₂) ₃ SO ₃] ⁻ ·H ₂ O	2.436 (2)	1.128 (4)	1.310 (4)	20
Co(PnIO-H)(CH ₃) ₂ ^b	2.461 (8)	0.99 ^a	1.53 ^a	16
CoDMG(CH ₃)(H ₂ O) ^b	2.486 (4)	1.11 (4)	1.38 (4)	17
CoDMG(Ph ₃ P)Cl ^b	2.50 (1)	Asymmetric ^a		18
[CoDMG(NH ₃)Cl]·H ₂ O ^b	2.49 (1)	Asymmetric ^a		18
Co(PnAO-H)(NO ₂) ₂	2.432 (3)	1.19 ^a	1.26 ^a	5

^a H atom positions taken unrefined from difference Fourier syntheses. ^b Co(PnIO-H)(CH₃)₂ = dimethyl[3,3'-(trimethylenedinitrilo)bisbutan-2-one oximato]cobalt(III), CoDMG(CH₃)(H₂O) = aquomethylbis(dimethylglyoximate)cobalt(III), CoDMG(Ph₃P)Cl = *trans*-chlorobis(dimethylglyoximate)(triphenylphosphine)cobalt(III), and [CoDMG(NH₃)Cl]·H₂O = *trans*-chlorobis(dimethylglyoximate)(ammine)cobalt(III) monohydrate.

C. The Short Intramolecular Hydrogen Bond. The short intramolecular O1---O2 hydrogen bond (2.474 (6) Å) is somewhat longer than those observed in most other complexes of this type. A neutron diffraction study of bis(2-amino-2-methylbutanone oximate)nickel(II) chloride monohydrate [Ni(AO)₂-H]Cl·H₂O² has revealed an O---O distance of 2.420 (3) Å. With that same bidentate α -amine oxime ligand occupying a square plane in a *trans*-dichloro octahedral Co(III) complex [Co(AO)₂-H]Cl₂⁴, an O---O distance of 2.421 (3) Å has been observed by X-ray diffraction. In a *trans*-dinitro octahedral cobalt(III) complex [Co(PnAO-H)(NO₂)₂] with a ligand differing from that used in this study only by the presence of a propylene rather than ethylene bridge opposite the short hydrogen bond, an O---O distance of 2.432 (3) Å was observed.⁵ However, in dimethyl[3,3'-(trimethylenedinitrilo)bis(butane-2-one oximate)]cobalt(III),¹⁶ where the tetradentate ligand differs from that in the *trans*-dinitro cobalt(III) complex in that the amines have been replaced by imines, the O---O distance is 2.461 Å. O---O distances in other related compounds are included in Table IX.

Of greater interest are the locations of the hydrogen atoms in these short intramolecular hydrogen bonds. In those complexes^{1,2,4,5} with O---O distances of 2.42–2.43 Å, the hydrogen is apparently nearly centered between the oxygens, but in this work and in several recently studied cobalt complexes^{16–18} with O---O distances greater than 2.46 Å, the hydrogen atom appears to be nearly covalently bonded to one oxygen and more weakly bonded to the other (Table IX). In the present study the distances are O2–H27 (0.80 (6) Å) and O1–H27 (1.68 (6) Å) from the least-squares refinement, in agreement with the location of the hydrogen atom from a difference Fourier based on all other atoms including the other hydrogens. This abrupt change from a nearly symmetric single potential to a very asymmetric single potential is somewhat surprising, but the O---O distance of 2.47 Å is the critical value indicated by Pimentel and McClellan¹⁹ where both symmetric and highly asymmetric potentials are observed. A more recent neutron study²⁰ of [H₅O₂]⁺[C₆H₂(NO₂)₃SO₃]⁻·H₂O, however, indicates that significant asymmetry exists even with O---O distances as short as 2.436 (2) Å. The O–H distances in that compound are 1.128 (4) and 1.310 (4) Å. When compared with an O---O distance of 2.420 (3) Å and O–H distances of 1.187 (5) and 1.242 (5) Å found² for [Ni(AO)₂-H]Cl·H₂O, a more gradual transition in O–H distances with increasing O---O distances might occur than previously observed.¹⁹ An examination of the environment of O1 and O2 (Table IV) shows that they have nearly identical neighboring contacts and that neither is involved in any other hydrogen bonding. Because of this apparent equivalence of the two oxygen atoms, a double-well potential with equal occupancy might have been expected with a resulting disorder of H27 on either side of the center of the O1---O2 hydrogen bond. The O–H---O angle of 168.7° is nearly identical with that found² by neutron

diffraction in [Ni(AO)₂-H]⁺ of 169.9° which has a nearly symmetric hydrogen bond. A neutron diffraction study of the present structure is planned to verify and improve the accuracy of the hydrogen atom location.

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Supplementary Material Available. A listing of structure factor amplitudes ($\times 10$) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 \times 148 mm, 24 \times reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 115 16th St. N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC50170E-10-75.

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