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Low-Temperature Crystal Structure of a Macrocyclic Tetradentate Nickel(II) Complex Having a Charge-Delocalized, Six-Membered Chelate Ring

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A low-temperature X-ray diffraction study of the neutral monomeric complex $[\text{Ni}\{((\text{PnAO})\text{-7H})\text{NO}_2\}]^0$, $[\text{Ni}(\text{C}_{13}\text{H}_{21}\text{N}_3\text{O}_4)]$, has been done to ascertain the extent of aromatization of the six-membered chelate ring containing the heteroatom (nickel). The complex crystallizes with four molecules in a monoclinic unit cell of symmetry $P2_1/a$ with $a = 14.118$ (7) Å, $b = 10.699$ (4) Å, $c = 10.542$ (4) Å, and $\beta = 103.70$ (2)° at 137 ± 3 K. Three-dimensional Patterson and Fourier methods followed by full-matrix least-squares refinement gave $R(F) = 0.063$ with 2901 data and 271 variables. The complex cation has square-planar coordination about the nickel atom with the metal atom and the 14-membered macrocycle being coplanar. The Ni-N bond lengths, angles involving amine nitrogens, and angles and distances within the six-membered chelate ring all are different from those in the related unoxidized complexes and clearly indicate electron delocalization in the chelate ring consistent with earlier conclusions based on NMR studies. The plane defined by the nitro group and the carbon to which it is attached makes an angle of 16° with the plane of the chelate system. The steric requirements of $((\text{PnAO})\text{-7H})$ with respect to the intramolecular hydrogen bond and metal chelation are nearly identical with those of its unoxidized precursor $((\text{PnAO})\text{-H})$ or of two coordinated AO ligands. The unusual reactivity of this neutral macrocyclic nickel(II) complex toward various electrophiles is felt to be a consequence of the unique electronic properties of the dinegative open-ended tetradentate ligand.

Introduction

The reactivity toward electrophiles of several macrocyclic nickel(II) complexes having charge-delocalized, six-membered chelate rings containing the metal ion has been reported.¹⁻³ One of such complexes, $[\text{Ni}\{((\text{PnAO})\text{-7H})\text{NO}_2\}]^0$, is obtained by oxidation of the corresponding aliphatic (amine oxime)-nickel complex ion $[\text{Ni}((\text{PnAO})\text{-H})]^+$.⁴ The aromatic nature

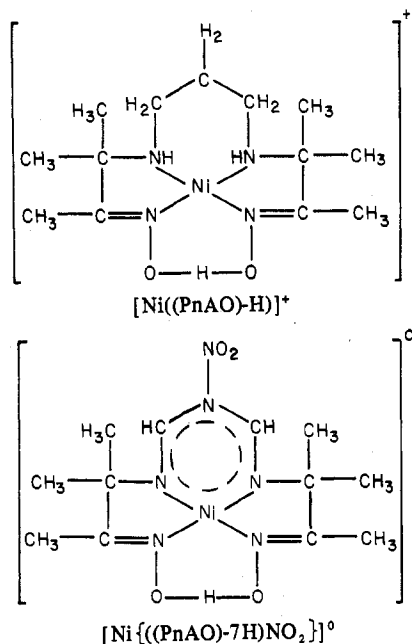
As part of our continuing project on crystal structures of compounds having a short intramolecular hydrogen bond, the present study reports a low-temperature X-ray structural analysis of $[\text{Ni}\{((\text{PnAO})\text{-7H})\text{NO}_2\}]^0$. The data were measured at low temperature in order to reduce errors due to thermal motions and to obtain higher order data. By studying the structure of this complex, it is possible to ascertain the magnitude of the structural changes resulting from the oxidation of $[\text{Ni}((\text{PnAO})\text{-H})]^+$, particularly those involving aromatization of the six-membered chelate ring. This study also allows a better understanding of the spectroscopic, thermodynamic, and chemical properties of the oxidized product.

Experimental Section

Crystal Preparation. The complex $[\text{Ni}\{((\text{PnAO})\text{-7H})\text{NO}_2\}]$ was prepared as described earlier.^{4,5} Crystals suitable for X-ray studies were obtained by slow evaporation of an anhydrous CH_3CN solution of the crystalline product.

Crystal Data. The neutral complex (2,2,3,9,10,10-hexamethyl-5,7-dioxa-6-hydra-1,4,8,11-tetraaza-13-nitrocyclotetradeca-3,8,11,13-tetraene)nickel(II), $[\text{Ni}\{((\text{PnAO})\text{-7H})\text{NO}_2\}]^0$, $[\text{Ni}(\text{C}_{13}\text{H}_{21}\text{N}_3\text{O}_4)]$, crystallizes in the monoclinic crystal system with four molecules in a unit cell with room-temperature cell dimensions $a = 14.146$ (3) Å, $b = 10.733$ (2) Å, $c = 10.659$ (2) Å, $\beta = 103.88$ (1)°, and $V = 1570.9$ Å³. These cell constants and their standard deviations were determined by a least-squares refinement⁶ of the angular coordinates of 15 reflections which were manually centered at room temperature on a Picker four circle diffractometer using Mo K α radiation. A measurement of density by flotation in a carbon tetrachloride-1,2,2-trichloroethane solution gave 1.55 g/cm³. A calculated density of 1.565 g/cm³ is obtained, assuming four molecules per unit cell. The systematic extinctions were for $h0l$, h odd, and for $0k0$, k odd, which are consistent with the monoclinic space group $P2_1/a$, a nonstandard setting of $P2_1/c$ (No. 14).⁷ A careful recentering of the setting angles of the same 15 reflections at low temperature (-136 ± 3 °C) gave significantly different lattice constants $a = 14.118$ (7) Å, $b = 10.699$ (4) Å, $c = 10.542$ (4) Å, $\beta = 103.70$ (2)°, and $V = 1547.1$ Å³.

Data Collection and Reduction. A distorted octahedral crystal with approximate dimensions $0.27 \times 0.13 \times 0.14$ mm showing the forms



of the oxidized complex in contrast to that of the parent unoxidized species was shown⁴ by both chemical and spectral data. Electrophilic substitution on the quasi-aromatic ring employing the usual type organic reactions has also been demonstrated by different experimental methods.⁵ However, no crystal structure study of any of the oxidized complexes having aromatic-like properties and containing the heteroatom (nickel) in the ring has been done.

- (1) C. J. Hipp and D. H. Busch, *Inorg. Chem.*, **12**, 894 (1973).
- (2) W. H. Elfring, Jr., and N. J. Rose, *Inorg. Chem.*, **14**, 2759 (1975).
- (3) J. P. Collman, *Adv. Chem. Ser.*, No. 37, 78 (1963).
- (4) E. G. Vassian and R. K. Murmann, *Inorg. Chem.*, **6**, 2043 (1967).
- (5) L. O. Urban and E. G. Vassian, *Inorg. Chem.*, **18**, 867 (1979).

- (6) All calculations were performed on the University of Missouri Computer Network operating an Amdahl 470/V7 and an IBM 3031 processor by using the following programs: ANGSET, angle setting program; SORTH, W. C. Hamilton's sorting program; HORSE, W. C. Hamilton's general absorption correction program; ORFEE, function and error program; FORDAP, Zalkin's Fourier synthesis program; NUCLS, R. Doedens and J. A. Ibers' least-squares program; and ORTEP, C. Johnson's thermal ellipsoid plot program.
- (7) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1969.

{111} and the faces $(\bar{1}00)$ and (100) was mounted on a copper pin with the crystallographic a axis close to the ϕ axis of a Picker diffractometer equipped with an Air Products and Chemicals (liquid nitrogen) Cryo-tip refrigerator, Model AC101A. The crystal was accurately centered to obtain the room-temperature lattice constants given above. It was then covered with a beryllium shroud and cooled to 137 ± 3 K, and the low-temperature cell dimensions were obtained (see Crystal Data). The construction of the cryostat hinders recentering after the crystal is cooled, especially with respect to height adjustment.

The intensities of 4469 reflections with $2\theta < 56^\circ$ in the quadrant hkl and $h\bar{k}l$ were measured by using a θ - 2θ scan employing Zr-filtered Mo $K\alpha$ radiation. Each reflection was scanned from $2\theta(\alpha_1) - 0.5^\circ$ to $2\theta(\alpha_2) + 0.55^\circ$ with a scan speed of $1.0^\circ (2\theta) \text{ min}^{-1}$. Background counts were measured for 10 s at each end of the scan range. Coincidence losses were minimized by adding an attenuator filter when the count rate exceeded 10 000 counts/s.

The intensities of two reference reflections $(00\bar{2}, 340)$ were measured every 75 reflections. During the course of data collection, these intensities were observed to increase in a linear manner by approximately 4% except for a group of about 900 reflections for which the increase was as high as 14%. The data were corrected for this variation, and Lorentz and polarization corrections were applied. The data were then corrected for absorption ($\mu = 12.7 \text{ cm}^{-1}$ for Mo $K\alpha$ radiation) with a transmission factor range from 0.736 to 0.806. Squared observed structure factors were obtained and averaged for symmetry-related reflections to give 3593 unique reflections, of which the 2901 having $I > 2\sigma(I)$ were used in the refinement procedure.

Solution and Refinement of the Structure. The position of the nickel atom was assigned from a Patterson map, and initial positions for all other nonhydrogen atoms were obtained from subsequent Fourier syntheses. Scattering factors for nickel, oxygen, nitrogen, carbon, and hydrogen atoms were taken from ref 8, as were correction terms $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to nickel. Full-matrix least-squares refinement⁶ employing isotropic thermal parameters and, at a later stage, anisotropic thermal parameters for all nonhydrogen atoms continued until all shifts in parameters were less than 10% of the estimated standard deviation for that parameter. A difference Fourier synthesis at this stage clearly indicated all hydrogen atoms. The positional coordinates of these hydrogen atoms were refined with fixed isotropic thermal parameters 1 \AA^2 larger than that for the atom to which they were attached and without varying nonhydrogen atoms. Three final least-squares refinement cycles on 271 variables (all nonhydrogen atoms varied anisotropically and only positional coordinates of hydrogen atoms varied) converged to the final R ($=[\sum ||F_o| - |F_c||] / \sum |F_o|$) value of 0.063 while the final R_w ($=[\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$) value was 0.082. The NUCLS refinement program⁶ minimizes $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factor amplitudes, respectively, and w is the weight for each reflection ($=4F_o^2/\sigma^2(F_o^2)$) and $\sigma(F_o^2) = [\sigma_{\text{counting}}^2 + (0.05F_o^2)^2]^{1/2}$. The standard deviation of an observation of unit weight was 2.35. These relatively high residual indices are apparently due to systematic errors in the data resulting from some movement of the crystal, despite the fact that the crystal was recentered three times during data collection. Perfect centering at low temperature was difficult to maintain due to the design of the low-temperature device, as mentioned earlier.

A final difference Fourier map revealed no peaks higher than 0.07 e \AA^{-3} except for four peaks (0.11 – 0.15 e \AA^{-3}) within less than 0.96 \AA of the nickel atom. All shifts in parameters for nonhydrogen atoms were less than $1/100$ th of the estimated standard deviation for that parameter, whereas for hydrogen atoms the shifts were as great as 10%.

Final atomic positional parameters are listed in Table I, while the final values of anisotropic thermal parameters for nonhydrogen atoms are in Table II. A listing of observed and calculated structure factor amplitudes is available as supplementary material.

Results and Discussion

Molecular Packing, Planarity, and Nitro Group. The crystals consist of discrete, neutral, monomeric units of the compound $[\text{Ni}\{\{(\text{PnAO})\cdot 7\text{H}\}\text{NO}_2\}]^0$, with no significant in-

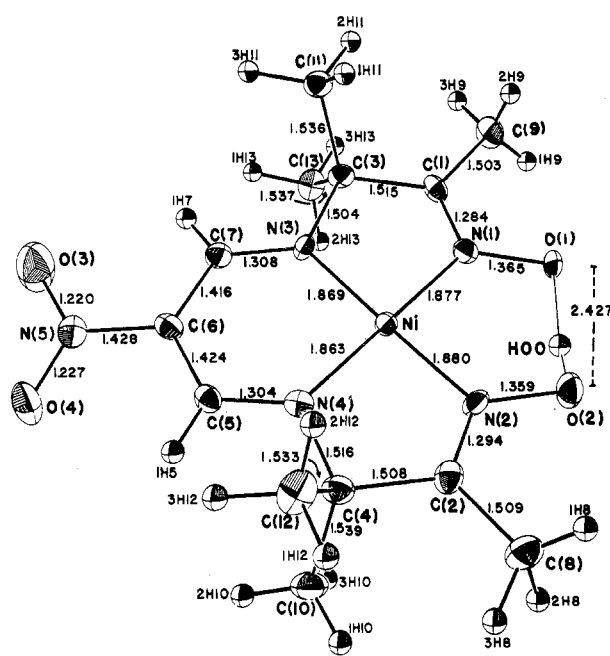


Figure 1. Bond distances and numbering system in $[\text{Ni}\{\{(\text{PnAO})\cdot 7\text{H}\}\text{NO}_2\}]^0$. In numbering hydrogen atoms the last number in the label corresponds to the carbon atom to which that hydrogen is attached. The standard deviations in the distances are as follows (Å): Ni-N, 0.004; N-C, 0.005–0.006; C-C, 0.006–0.007; N-O, 0.005–0.006.

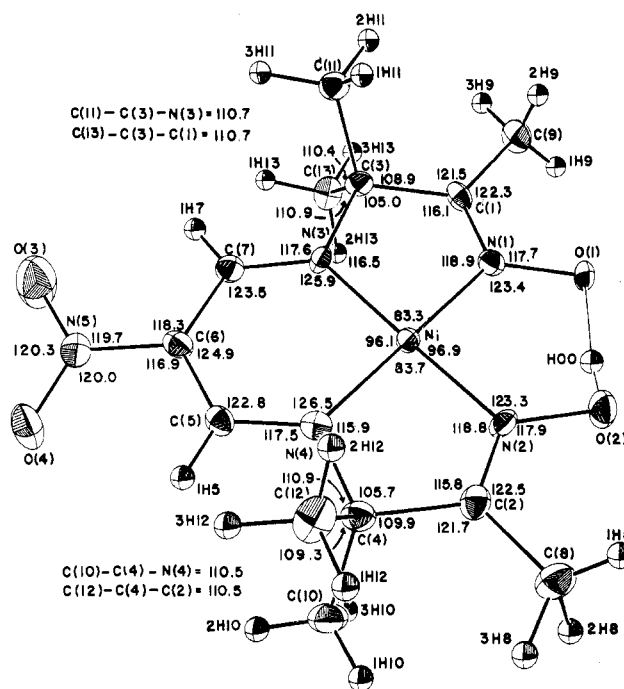


Figure 2. Bond angles in $[\text{Ni}\{\{(\text{PnAO})\cdot 7\text{H}\}\text{NO}_2\}]^0$. The standard deviations in the angles are as follows (deg): N-Ni-N, 0.2; Ni-N-C, 0.3–0.4; N-C-C, 0.4–0.5; C-C-C, 0.4; O-N-Ni, 0.3; O-N-C, 0.4; O-N-O, 0.5.

teractions (other than van der Waals contacts) between the molecules. The structure of one of these monomeric units along with bond distances and angles is displayed in Figures 1 and 2. Figure 3 demonstrates the manner in which the molecules are arranged within the unit cell. Table III contains calculated results relating to the planarity of various parts of the molecule.

The coordination geometry about the nickel(II) ion is square planar with the six-membered chelate bite angle about 139°

(8) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

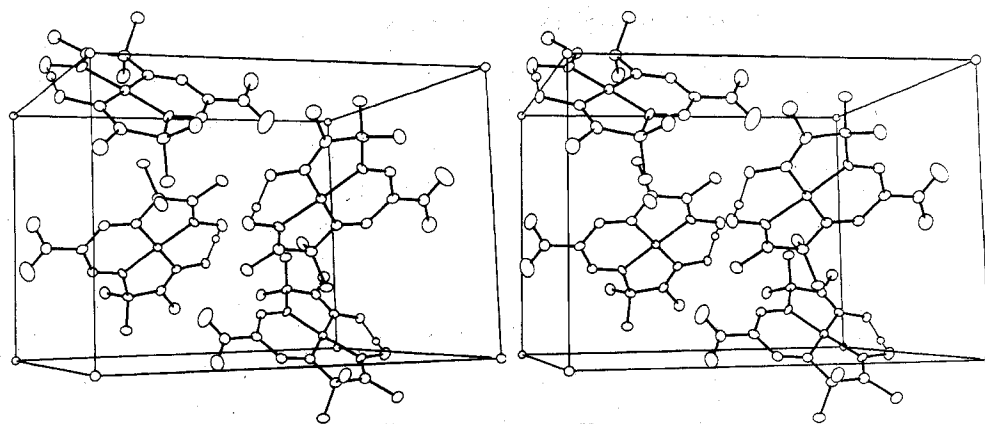


Figure 3. Stereoscopic view showing molecular packing in the centric monoclinic unit cell.

Table I. Atomic Fractional Coordinates^a for [Ni{(PnAO)-7H)NO₂}]⁰

atom	x	y	z
Ni	-0.1329 (1)	-0.0647 (1)	-0.2091 (1)
O(1)	0.0577 (2)	-0.1261 (3)	-0.0571 (3)
O(2)	0.0540 (3)	0.0190 (4)	-0.2352 (4)
O(3)	-0.5138 (3)	-0.1537 (5)	-0.2667 (5)
O(4)	-0.5151 (3)	0.0170 (4)	-0.3695 (4)
N(1)	-0.0401 (3)	-0.1487 (3)	-0.0807 (4)
N(2)	-0.0443 (3)	0.0281 (4)	-0.2792 (4)
N(3)	-0.2209 (3)	-0.1639 (3)	-0.1468 (3)
N(4)	-0.2263 (3)	0.0201 (4)	-0.3339 (4)
N(5)	-0.4701 (3)	-0.0696 (4)	-0.3064 (4)
C(1)	-0.0688 (3)	-0.2339 (4)	-0.0126 (4)
C(2)	-0.0779 (3)	0.1021 (4)	-0.3766 (4)
C(3)	-0.1777 (3)	-0.2573 (4)	-0.0425 (4)
C(4)	-0.1874 (4)	0.1095 (4)	-0.4210 (4)
C(5)	-0.3207 (3)	0.0114 (4)	-0.3516 (4)
C(6)	-0.3661 (3)	-0.0725 (4)	-0.2794 (4)
C(7)	-0.3160 (3)	-0.1581 (4)	-0.1846 (4)
C(8)	-0.0122 (4)	0.1737 (5)	-0.4449 (5)
C(9)	0.0012 (4)	-0.3107 (5)	0.0866 (5)
C(10)	-0.2215 (4)	0.2438 (5)	-0.4040 (5)
C(11)	-0.1982 (4)	-0.3914 (4)	-0.0938 (5)
C(12)	-0.2213 (4)	0.0713 (6)	-0.5647 (5)
C(13)	-0.2171 (4)	-0.2374 (5)	0.0800 (4)
H(OO)	0.050 (7)	-0.032 (9)	-0.184 (9)
1H5	-0.354 (6)	0.068 (7)	-0.412 (8)
1H7	-0.354 (6)	-0.209 (7)	-0.154 (8)
1H8	0.043 (7)	0.139 (8)	-0.449 (8)
2H8	0.004 (6)	0.253 (9)	-0.389 (8)
3H8	-0.045 (6)	0.241 (9)	-0.499 (8)
1H9	0.048 (7)	-0.263 (8)	0.133 (8)
2H9	0.023 (7)	-0.368 (9)	0.046 (8)
3H9	-0.034 (6)	-0.359 (8)	0.137 (8)
1H10	-0.191 (6)	0.297 (8)	-0.456 (8)
2H10	-0.289 (7)	0.249 (8)	-0.436 (8)
3H10	-0.207 (6)	0.269 (8)	-0.307 (8)
1H11	-0.167 (6)	-0.403 (8)	-0.164 (8)
2H11	-0.160 (6)	-0.451 (7)	-0.023 (9)
3H11	-0.275 (7)	-0.413 (8)	-0.124 (8)
1H12	-0.196 (6)	0.127 (8)	-0.620 (8)
2H12	-0.203 (7)	-0.012 (9)	-0.575 (8)
3H12	-0.295 (7)	0.073 (8)	-0.589 (9)
1H13	-0.289 (6)	-0.261 (8)	0.059 (8)
2H13	-0.210 (6)	-0.146 (8)	0.106 (8)
3H13	-0.187 (6)	-0.294 (8)	0.162 (8)

^a Estimated standard deviations are given in parentheses.

larger than the five-membered bite angles. The nickel(II) atom and the coordinated nitrogen atoms are coplanar. All atoms of the 14-membered macrocycle are within ± 0.008 to ± 0.01 Å (except C(3) and O(1) which are -0.12 and 0.14 Å), from either a least-squares plane calculated through these 14 atoms (plane 1, Table III) or a plane calculated through the four corresponding nitrogen atoms (plane 3). As expected, C(8), C(9), and H(OO) are very close to the molecular plane,

whereas C(13) and C(11) are on opposite sides of the plane, as are C(10) and C(12). Each of the five-membered chelate rings is also planar with a maximum deviation of 0.03 Å for any atom defining the plane. Thus, aromatization of the PnAO⁵ leads to a flattening of the quadridentate ligand into a planar conformation similar to the ligand conformation in closely related PreH complexes^{9a} (where PreH¹⁰ corresponds to (PnAO)-H with a methyl group removed from both C(3) and C(4)) and in a nickel(II) complex of a highly unsaturated "N₄" macrocyclic ligand derived from diaminomaleonitrile.^{9b} This high degree of planarity is in contrast to any of the other α -amine oxime (AO, EnAO, and PnAO)¹⁰ complexes of nickel studied so far.^{11,12} In all of these compounds the planarity is restricted to the central metal atom and four coordinating nitrogens, but all the chelate rings are nonplanar. The chelate rings in a related macrocyclic nickel(II) complex,¹³ even with all sp^2 -hybridized nitrogen atoms, have been reported to exist in a nonplanar boat configuration.

The O(3) and N(5) atoms of the nitro group are at -0.05 and 0.19 Å from the molecular plane, whereas O(4) is 0.52 Å away. The plane defined by the nitro group and the carbon to which it is attached (plane 4) makes an angle of 16° with the plane of the molecule (plane 1) and $\sim 14^\circ$ with the plane of the six-membered chelate ring (plane 2). Such tilt of the nitro group either is insignificant on the NMR time scale or is only a solid-state effect, since the ¹H NMR spectrum⁵ is consistent with the identical environments of the two oxygen atoms based on a C_{2v} point group assignment for the molecule. All other chemically equivalent bond distances and angles are also internally consistent with C_{2v} point symmetry. The O(3)-1H7 and O(4)-1H5 distances are 2.37 (8) and 2.48 (8) Å, respectively, showing almost identical environments for the two ring protons which will consequently render the ¹H NMR of these protons equivalent.

The average nitro N-O distance (1.224 (6) Å) and O-N-O angle (120.3°) are comparable to those in *p*-nitropyridine *N*-oxide¹⁴ (1.227 (2) Å from neutron data, 1.227 (1) Å from high order X-ray data, and 1.235 (1) Å from X-ray data for

- (9) (a) O. P. Anderson and A. B. Packard, *Inorg. Chem.*, **18**, 1940 (1979); (b) M. McPartlin, P. G. Owston, R. Peters, T. Smith, and P. A. Tasker, Abstracts, 178th National Meeting of the American Chemical Society, Washington, D.C., Sept. 1979, No. INOR 19.
- (10) PreH = 3,3'-(trimethylenedinitrilo)bis(2-butanone oximate); AO = 2-amino-2-methyl-3-butanone oxime; EnAO = 2,2'-(1,2-diaminoethanediy)bis(2-methyl-3-butanone) dioxime; PnAO = 2,2'-(1,3-diaminopropanediy)bis(2-methyl-3-butanone) dioxime.
- (11) M. S. Hussain and E. O. Schlemper, *Inorg. Chem.*, **18**, 1116 (1979).
- (12) M. S. Hussain and E. O. Schlemper, *Inorg. Chem.*, **18**, 2275 (1979), and references therein.
- (13) P. W. R. Corfield, J. D. Mokren, C. J. Hipp, and D. H. Busch, *J. Am. Chem. Soc.*, **95**, 4465 (1973).
- (14) P. Coppens and M. S. Lehmann, *Acta Crystallogr., Sect. B*, **32**, 1777 (1976).

Table II. Anisotropic Thermal Parameters^a for [Ni{(PnAO)-7H}NO₂]⁰

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.011 (1)	0.012 (1)	0.011 (1)	-0.000 (1)	0.001 (1)	0.002 (1)
O(1)	0.007 (2)	0.018 (2)	0.022 (2)	-0.001 (1)	-0.001 (1)	0.003 (1)
O(2)	0.012 (2)	0.028 (2)	0.024 (2)	-0.000 (1)	0.000 (1)	0.008 (1)
O(3)	0.028 (2)	0.059 (3)	0.057 (3)	-0.005 (2)	0.005 (2)	0.027 (3)
O(4)	0.019 (2)	0.039 (2)	0.026 (2)	0.005 (2)	-0.002 (2)	0.005 (2)
N(1)	0.014 (2)	0.013 (2)	0.018 (2)	0.002 (1)	0.002 (1)	-0.001 (1)
N(2)	0.013 (2)	0.013 (2)	0.016 (2)	-0.005 (1)	0.002 (1)	0.000 (1)
N(3)	0.010 (2)	0.015 (2)	0.011 (2)	-0.004 (1)	0.000 (1)	0.003 (1)
N(4)	0.017 (2)	0.013 (2)	0.011 (2)	0.001 (1)	0.003 (1)	-0.001 (1)
N(5)	0.016 (2)	0.021 (2)	0.019 (2)	-0.000 (2)	0.003 (2)	-0.002 (2)
C(1)	0.013 (2)	0.018 (2)	0.011 (2)	0.004 (2)	-0.001 (2)	-0.000 (2)
C(2)	0.015 (2)	0.017 (2)	0.016 (2)	-0.003 (2)	0.001 (2)	-0.003 (2)
C(3)	0.017 (2)	0.013 (2)	0.011 (2)	-0.001 (2)	0.001 (2)	0.004 (2)
C(4)	0.019 (2)	0.015 (2)	0.015 (2)	-0.000 (2)	0.001 (2)	0.002 (2)
C(5)	0.015 (2)	0.015 (2)	0.012 (2)	0.002 (2)	-0.000 (2)	-0.001 (2)
C(6)	0.017 (2)	0.013 (2)	0.014 (2)	0.003 (2)	0.000 (2)	-0.000 (2)
C(7)	0.016 (2)	0.015 (2)	0.015 (2)	-0.000 (2)	0.003 (2)	0.002 (2)
C(8)	0.025 (3)	0.021 (2)	0.025 (2)	-0.002 (2)	0.011 (2)	0.005 (2)
C(9)	0.018 (2)	0.025 (3)	0.017 (2)	0.003 (2)	-0.003 (2)	0.005 (2)
C(10)	0.026 (3)	0.013 (2)	0.030 (3)	0.002 (2)	0.010 (2)	0.004 (2)
C(11)	0.019 (2)	0.015 (2)	0.019 (2)	-0.001 (2)	0.000 (2)	0.002 (2)
C(12)	0.025 (3)	0.032 (3)	0.012 (2)	-0.007 (2)	0.004 (2)	0.002 (2)
C(13)	0.020 (2)	0.026 (2)	0.011 (2)	-0.002 (2)	0.005 (2)	0.002 (2)

^a Estimated standard deviations are in parentheses. The form of the anisotropic thermal ellipsoid is given by $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$.

Table III. Least-Squares Planes for [Ni{(PnAO)-7H}NO₂]⁰a. Deviations from Planes^a

plane 1 ($n = 14$): Ni (0.019), O(1) (0.138), C(2) (-0.037), Ni (0.058), N(2) (-0.020), N(3) (-0.050), N(4) (0.014), C(1) (-0.022), C(2) (-0.070), C(3) (-0.124), C(4) (-0.039), C(5) (0.075), C(6) (0.081), C(7) (-0.022), C(8) (-0.197), C(9) (-0.079), C(10) (1.212), C(11) (-1.476), C(12) (-1.292), C(13) (1.031), H(OO) (-0.039)

plane 2 ($n = 6$): Ni (0.036), N(3) (-0.167), C(5) (0.003), C(6) (0.033), C(7) (-0.019), N(4) (-0.036), N(5) (0.112), O(3) (-0.108), O(4) (0.398), Ni (0.141), N(2) (-0.022), N(3) (-0.017), N(4) (-0.036)

plane 3 ($n = 4$): N(1) (0.035), N(2) (-0.035), N(3) (-0.036), N(4) (0.036), Ni (0.019), O(1) (0.097), O(2) (-0.072), O(3) (0.024), O(4) (0.596), N(5) (0.256)

plane 4 ($n = 4$): O(3) (-0.0002), O(4) (-0.0002), N(5) (0.0006), C(6) (-0.002)

b. Equations of Planes^b

plane	A	B	C	D
1	0.193	-0.719	-0.667	1.684
2	0.178	-0.699	-0.692	1.761
3	0.207	-0.721	-0.661	1.654
4	0.157	-0.508	-0.847	2.116

c. Dihedral Angles between Planes

planes	angle, deg	planes	angle, deg
1-2	2.07	2-3	2.73
1-3	0.85	2-4	14.20
1-4	16.11		

^a Numbers in parentheses refer to the distance (Å) of the given atom from the calculated plane. The first n atoms in each case determine the given plane. ^b In the form $AX + BY + CZ = D$.

average N-O distances and $\sim 124^\circ$ for the O-N-O angles). These distances and angles are also similar to those observed in [Co(NH₃)en(NO₂)₃]¹⁵ (1.223 (10) Å and 118.4 (1.4)°) and are within two esd's of those in ionic nitrites such as NaNO₂¹⁶ (1.236 Å and 115.4°) and those in [Co((PnAO)-H)(NO₂)₂]¹⁷ (1.233 (9) Å and 118.9 (5)°). The C-N(nitro) distance (1.428

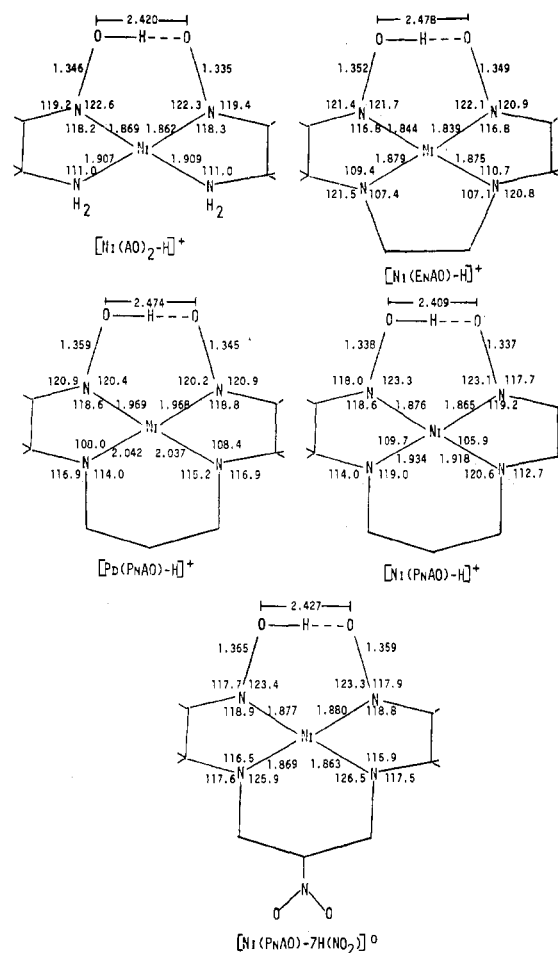


Figure 4. A comparison of the bond distances and angles in α -amine oxime and related complexes indicating the effects of aromatization on the six-membered chelate ring and the macrocycle. The standard deviations in the averaged distances are as follows (Å): Ni-N(oxime), 0.001-0.005; Ni-N(amine), 0.001-0.005; N-O, 0.002-0.007; O...O, 0.003-0.010. The standard deviations in the angles around the metal atom are 0.02-0.06° for [Ni((AO)₂-H)]⁺,¹⁹ [Ni((EnAO)-H)]⁺,¹⁸ [Pd((PnAO)-H)]⁺,¹¹ [Ni((PnAO)-H)]⁺,¹² and [Ni{((PnAO)-7H)-NO₂}]⁰ (present work).

- (15) K. G. Jensen, H. Soling, and N. Thorup, *Acta Chem. Scand.*, **24**, 908 (1970).
 (16) M. Ito, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **28**, 463 (1972).
 (17) R. K. Murmann and E. O. Schlemper, *Inorg. Chem.*, **12**, 2625 (1973).

(6) Å) observed in the present study is significantly shorter than that in *p*-nitropyridine *N*-oxide¹⁴ (1.454 (2) Å), suggesting some multiple-bond character in this bond. However, this does not result in the ONO plane being completely coincident with the aromatic ring.

Charge Delocalization over the Six-Membered Chelate Ring.

The angles and distances involving coordinated nitrogen atoms are compared in Figure 4. In the present complex two distinctly unequal pairs of Ni–N bonds were observed with the Ni–N(amine) bond length (average 1.866 (4) Å) significantly shorter (0.013 Å) than the Ni–N(oxime) bond (average 1.879 (4) Å). Distinct but opposite dichotomy of metal–nitrogen bond lengths was observed in closely related complexes. For example, the structures of nickel(II),^{12,18,20} cobalt(III),¹⁷ palladium(II),¹¹ and copper(II)¹⁹ complexes of AO, EnAO and PnAO all exhibited metal–nitrogen(amine) distances from 0.03 to 0.07 Å longer than the metal–nitrogen(oxime) distances, irrespective of the central metal atom or the steric requirements of the ligand. These observed systematic inequalities in metal–nitrogen bond lengths seem to be a function of the relative donor abilities of the two types of nitrogen atoms within the macrocycle. The fact that a distinct but reversed dichotomy is observed in the Ni(II)–N bond lengths in the present structure, in contrast to the unoxidized complexes, clearly indicates the existence of aromaticity in the six-membered chelate ring introduced as a result of oxidation. Such an aromaticity is also consistent with the angles around N(3) and N(4), which add to exactly 360°, suggesting sp² hybridization, compared to the sum of the corresponding angles (~340°) in unoxidized and related complexes. The C(5)–C(6) and C(6)–C(7) bond lengths are significantly shorter (~0.06–0.08 Å) than the average length (1.508 Å) of the C–C bond adjacent to a C=N bond. Similarly, N(3)–C(7) and N(4)–C(5) distances (average 1.306 (6) Å) are slightly longer than the average C=N distance (1.289 (6) Å). All these deviations from normality in the six-membered chelate ring in addition to the planar angles within the ring itself would be consistent with earlier conclusions based on NMR studies⁵ about electron delocalization in the chelate ring, resulting in its aromatic character toward various electrophiles.

Intramolecular Hydrogen Bond. The short intramolecular hydrogen bond O...O (2.427 (5) Å) is similar to that observed (2.420 (3) Å) for [Ni((AO)₂-H)]⁺²⁰ or (2.409 (10) Å) for [Ni((PnAO)-H)]⁺.¹² The positions of the hydrogen atom (H(OO)) in the intramolecular hydrogen bond as well as for all other hydrogen atoms were obtained from the least-squares refinement of the coordinates from a difference Fourier synthesis. The O(2) and H(OO) atoms are essentially coplanar with the rest of the molecule, whereas O(1) is 0.14 Å above the plane of the molecule (Table III). The refined hydrogen coordinates give the O(2)–H(OO) distance of ~0.80 Å and O(1)–H(OO) distance of 1.656 (9) Å, indicating nearly covalent bonding of H(OO) with one oxime oxygen and a weak bonding with the other, resulting in an appreciable asymmetry in the O–H...O bond. However, though the data were obtained at low temperature, the validity of the refined hydrogen atom position from all X-ray data (instead of only extensive high-order data)²¹ is questionable since similar asymmetry was

observed in the X-ray study²² of [Ni((EnAO)-H)]⁺, while a neutron diffraction study¹⁸ of the same cation resulted in hydrogen atoms more symmetrically disposed within the hydrogen bond.

The O...O bond distance is not significantly effected by aromatization of the six-membered chelate ring and the steric requirements of ((PnAO)-7H), with respect to the hydrogen bond in the nickel(II) complex, are identical with those of its unoxidized precursor ((PnAO)-H) or two-coordinated AO ligands.

Other C–H distances range from 0.85 (9) to 1.05 (9) Å and H–C–H angles are in the range 103–115°, except for those involving 1H5 and 1H7.

Conclusion

Probably the two most significant aspects of this structure are the apparent aromaticity of the heterocyclic ring containing the metal ion and the significant shortening of the metal–amine nitrogen bonds when compared to the unoxidized complex. These are obviously related to each other, but they also have a strong influence on the solution kinetic behavior of these complexes. Studies^{4,5} on the aqueous and nonaqueous solution behavior of the parent (H), the nitro, nitroso, and the chloro complexes show a highly enhanced kinetic stability over [Ni((PnAO)-H)]⁺ and related complexes. There is a rough inverse relationship between the basicity of the H-bonded complex and the dissociation rate in acidic media which may lead one to conclude that the rate is closely related to the opening of the chelate ring, i.e., the release of the oxime nitrogen. The complex of this study (and all of the other aromatized complexes with this ligand) is highly inert to substitution in acid or even by CN⁻.^{4,5} Furthermore, there is no evidence that the complexes are protonatable. Thus, when this study was begun, it was anticipated that the H bond would be extremely stable with a very short O...O distance. In reality, however, it is found that the hydrogen bond has parameters nearly identical with those of [Ni((PnAO)-H)]⁺ (in agreement with the proton NMR spectra). The conclusion reached is that the rate-controlling step in the irreversible dissociation of the ligand from this type of complex (open-ended tetradentate ligand) with a planar geometry involves opening of the diamine ring. Thus, the metal–nitrogen(amine) bond distances (or bond energies) are of primary concern in determining the rates.

Reactions of these complexes with CN⁻ seem to follow the same major path even though the CN⁻ most likely occupies a fifth coordination position before the rate-controlling step. The lability of the hydrogen in the hydrogen bond and the reversible release of the metal–nitrogen(oxime) bond precedes the rate-controlling metal–nitrogen(amine) bond breakage. However, with CN⁻ the thermodynamics may be responsible for the observed nonreplacement in the aromatized complexes. Since the free oxidized ligands have never been synthesized, the formation constants for the [Ni((PnAO)-7H)]⁰ complexes cannot be compared with those of the cyano complexes.

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Registry No. [Ni]((PnAO)-7H)NO₂, 68707-96-0.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

(18) C. K. Fair and E. O. Schlemper, *Acta Crystallogr., Sect. B*, **34**, 436 (1978).

(19) I. B. Liss and E. O. Schlemper, *Inorg. Chem.*, **14**, 3035 (1975).

(20) E. O. Schlemper, W. C. Hamilton, and S. J. LaPlaca, *J. Chem. Phys.*, **54**, 3990 (1971).

(21) (a) H. Hope and T. Ottersen, *Acta Crystallogr., Sect. B*, **34**, 3623 (1978); (b) *ibid.*, **35**, 370 (1978).

(22) J. C. Ching and E. O. Schlemper, *Inorg. Chem.*, **14**, 2470 (1975).