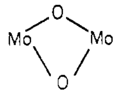

ring opening.

In order for the IER mechanism to operate on *trans*-dioxo ions a *cis*-dioxo intermediate state would be necessary. So in *trans*-dioxo systems, high activation energies are expected, resulting in a lower rate or in the intervention of another mechanism. Thus, in spite of the tendency for weakening the yl–metal bond in the trans ions due to the trans effect, the rate of yl-oxygen exchange is generally considerably slower than in cis ions.

It is significant that rapid electron exchange between $[VO_2(ox)_2]^{3-}$ and $[VO(ox)_2OH_2]^{2-}$ does not occur as evidenced by the lack of catalytic effect of the latter on the oxygen exchange of the former. This may be due to the different geometry since the V(V) complex is cis while with V(IV) the O and OH_2 are trans. Most *trans*-dioxo ions are d^2 ions, which strongly favors the trans configuration, making the cis form thermodynamically unstable.

Conclusions

The rate of yl-oxygen exchange of $VO_2^+(aq)$ with water in acid solution has a half-time of about 0.15 s at 0 °C. Complexation causes a lowering of the rate: $VO_2^+(aq) > [VO_2(ox)_2]^{3-} > [VO_2(EDTA)]^{3-}$. An internal rearrangement mechanism is suggested as the basic mechanism by which yl-oxygen exchange occurs for *cis*-dioxo complexes.

Acknowledgment. The authors express their appreciation to the University of Missouri Research Council for partial support of this work.

Registry No. O_2, 7782-44-7; VO_2^+, 18252-79-4; $VO_2(C_2O_4)_2^{3-}$, 56556-47-9; H_2O, 7732-18-5; SCN^-, 302-04-5; $VO_2(EDTA)^{3-}$, 68907-94-8.

Contribution from the Department of Chemistry,
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Bis[3-(hydroxyamino)-3-methyl-2-butanone oximato(2−)-*N*,*N′*]nickel. Structure and Properties of a $[Ni(DMG)_2]^0$-Related Complex

E. O. SCHLEMPER and R. KENT MURMANN*

Received July 21, 1982

A unique, planar, nickel complex, $[Ni(HAO)_2]^0$, $NiC_{10}H_{20}N_4O_4$, has been prepared, which formally contains Ni(IV) and two doubly deprotonated α-hydroxyamine oxime, 3-(hydroxyamino)-3-methyl-2-butanone oximate(2−) (HAO), ligands. It is extremely planar, deeply purple (ϵ = 3050 M^{-1} cm^{-1}, λ_{max} = 5410 Å), and quite soluble in organic solvents but slowly decomposes in solution. The X-ray study shows a monoclinic cell ($P2_1/c$) with a = 6.400 (2) Å, b = 9.333 (1) Å, c = 11.736 (1) Å, β = 90.37 (2)°, and Z = 2. The X-ray crystal structure shows it to be very similar to $[Ni(DMG)_2]^0$ with an extra CH_3 group on one of the ring carbons, which prevents one of the $-C{=}N{-}OH$ multiple bonds of the DMG complex. The molecule has a center of symmetry, intramolecular O–H···O hydrogen bonds, and two very short Ni–N bonds (1.804 (2) Å). Delocalized multiple bonding is indicated through the $O{-}N_{HA}{-}Ni{-}N_{HA}{-}O$ chain, (HA = hydroxyamine). The bonding in this molecule is discussed in terms of a five-atom conjugated chain (O–N–Ni–N–O) with π overlap utilizing p_z orbitals of two O and two N atoms and the d_{xz} orbital of Ni(II). It could as well be described as a square-planar, diamagnetic, deprotonated hydroxylamine oxime Ni(IV) complex. The ligand can be removed from the metal ion instantaneously with dilute acid and regenerated (~70%) with base, showing the ligand to be capable of independent existence and suggesting that other complexes of this ligand may be prepared.

Introduction

Nickel(II) complexes of aliphatic α-amine oximes are always[1] yellow-orange planar ions with small extinction coefficients ($\epsilon \approx$ 200 M^{-1} cm^{-1}, $\lambda_{max} \approx$ 4000 Å) in the visible region. During the preparation of two of these species with potentially tridentate ligands, it was noted that deep purple, water-insoluble nickel complexes were produced upon air oxidation in basic media. Spectral, elemental, and magnetic measurements showed the two purple products to be identical and indepenent of the reacting ligand.

An X-ray analysis of a single crystal, representative of the bulk samples, showed the neutral molecule to be very similar to $[Ni(DMG)_2]^0$ but with one additional methyl group on each ligand. The ligand also resembles the anticipated tridentate amine oxime ligand with bond breakage at the C–N bond of the diamine, presumably through oxidation.

This paper presents our investigation and conclusions on the method of preparation, the structure, the nature of the bonding, and the solution properties of this unique molecule. Also suggested are methods of metal ion exchange to give other metal ion complexes of the ligand that might have unusual properties.

Experimental Section

Preparation of the Complex.[2] The starting ligands were prepared from $(CH_3)_2C(Cl){-}C(CH_3){=}NOH$ and a diamine (either $NH_2C(CH_3)_2CH_2NH_2$ or $NH_2CH(CH_3)CH(CH_3)NH_2$) by refluxing the mixture having a 2:1 molar ratio of the two compounds in absolute methanol for 6 h. The product was isolated in the usual manner[2] and reacted with a slight excess of $NiCl_2$. The addition of Na_2CO_3 to free the amine and allow complexation gave a yellow-brown solution, which was filtered and aerated. The pH at this point was between 6.5 and 7.0. Gradually a deep purple solid formed, which was collected on a filter, washed with small quantities of ethanol, and recrystallized several times from acetone by the addition of water. Final crystallization is best accomplished thermally from acetone or CH_3CN. The yield averaged about 10% of the theoretical yield. Anal. Calcd for $NiC_{10}H_{20}N_4O_4$ (fw = 318.99): C 37.66; H, 6.32; N 17.57. Found: C, 37.79; H, 6.38; N, 17.54. The intensely purple diamagnetic complex is soluble in most organic solvents but is especially insoluble in water. It decomposes slowly in all solvents to a brown paramagnetic complex of unknown structure. The complex is changed to a colorless species

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[1] Murmann, R. K. *J. Am. Chem. Soc.* **1957**, *79*, 521; **1962**, *84*, 1349.

[2] Murmann, R. K. *J. Am. Chem. Soc.* **1958**, *80*, 4174.

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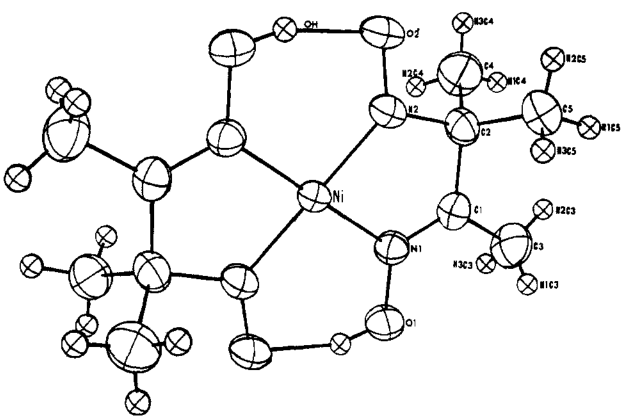

Figure 1. ORTEP drawing of $[Ni(HAO)_2]^0$ with the numbering system.

immediately upon addition of dilute acid and re-forms partially if the solution is then made neutral. Final crystallization for X-ray studies was accomplished by slowly cooling a saturated CH_3CN solution.

X-ray Data and Structural Solution. The dark purple crystal selected was semispherical, had a volume of about 4.3×10^{-3} mm^3, and showed no decomposition during the time of X-ray exposure. The space group and unit cell dimensions were determined from a least-squares refinement of the setting angles of 25 automatically centered reflections (2θ) between 20 and 40° on a Enraf-Nonius CAD4 diffractometer, using Mo $K\alpha_1$ radiation ($\lambda = 0.70926$ Å).

The crystals are in the monoclinic space group $P2_1/c$ (systematic absences $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$) with $a = 6.400$ (2) Å, $b = 9.333$ (1) Å $c = 11.736$ (1) Å, $\beta = 90.37$ (2)°, $V = 701.0$ Å^3, $d_c = 1.512$ (1) g/cm^3, $d_m = 1.51$ (1) g/cm^3, and $Z = 2$. The molecule therefore has a center of symmetry.

A set of three-dimensional intensity data was collected with the use of Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) from a graphite monochromator at $T = 22$ (1) °C. The θ–2θ step scan technique was used ($\theta = 1.5$–$25°$). Variable scan speeds were employed to maintain counting statistics of 3% up to a maximum of 120 s/scan. Crystal orientation was maintained by checking the centering of 3 reflections after the measurement of each 200 reflections. A new orientation matrix was determined on the basis of 25 reflections if any of these 3 was significantly off center. The intensities measured were $h,\pm k,\pm l$ (1.5–22°), $-h,\pm k,\pm l$ (1.5–14°), and $h,k,\pm l$ (22–25°). A total of 2751 reflections were recorded, of which 2068 had intensities above $1.5\sigma(I)$. The data were corrected for background, Lorentz–polarization factors and absorption ($\mu = 14.23$ mm^{-1}). The transmission factor ranged from 0.98 to 1.00 with an average of 0.993 as determined empirically from three φ scans measured at 10° intervals (0–360°). Three standards, monitored every 6000 s of X-ray exposure, showed no significant variation with time. After averaging, 1225 reflections remained, of which the 900 observations with $I > 1.5\sigma(I)$ were used for structural determination and refinement.

The scattering factors used were from ref 3. The structure was solved by Patterson and Fourier methods. The nickel lies on a center of symmetry $(0, {}^1/_2, {}^1/_2)$. After a few cycles of least-squares refinement of all non-hydrogen atoms, a difference Fourier map revealed all of the hydrogen atoms at reasonable positions. After inclusion of these $R(F) = 0.029 = \sum||F_o| - |F_c||/\sum|F_o|$, and $R(F)$ significantly increased when O(2) was converted to nitrogen, confirming that this atom is an oxygen. Full-matrix least-squares refinement using variable anisotropic temperature factors for all non-hydrogen atoms, variable isotropic temperature factors for H atoms, and variable positional parameters for all atoms except Ni gave $R(F) = 0.027$ and $R_w(F) = 0.034 = [\sum w(|F_o| - k|F_c|)^2/\sum wF_o^2]^{1/2}$. The least-squares program minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma(F_o))^2$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma_{\text{counting}}^2 + (0.05F_o^2)^2]^{1/2}$. There were 900 observations and 128 variables, and the esd of an observation of unit weight was equal to 0.965 in the last cycle. The largest parameter shift in the final cycle was equal to 0.40(esd); the largest difference Fourier peak amounted to 0.14 e/Å^3 and resided near the metal atom. No extinction correction was applied. $R = 0.040$ when all unobserved reflections were included. The structure factor amplitudes are available as supplementary material. Figure 1 shows a drawing of the molecule and the numbering system used. Table I gives the x, y, z coordinates of each atom in unit cell dimensions. Selected bond distances and angles are given in Table II. The hydrogen positions obtained from least-squares refinement were all reasonable (distances and angles), with the C–H distances ranging from 0.81 to 1.00 Å and averaging 0.92 (6) Å. A stereoscopic view of the unit cell and the anisotropic temperature factors for each atom are given in the supplementary material.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations

atom	x	y	z	B_{eq},[a] Å^2
Ni	0.0000 (0)	0.5000 (0)	0.5000 (0)	2.36
O(1)	−0.3631 (3)	0.6156 (2)	0.6087 (2)	3.63
O(2)	0.1342 (3)	0.2151 (2)	0.4959 (2)	4.03
N(1)	−0.2440 (3)	0.4961 (2)	0.5866 (2)	2.68
N(2)	−0.0012 (3)	0.3104 (2)	0.5298 (2)	3.10
C(1)	−0.3078 (4)	0.3775 (3)	0.6273 (2)	2.81
C(2)	−0.1735 (4)	0.2509 (3)	0.6005 (2)	3.03
C(3)	−0.5021 (5)	0.3645 (4)	0.6963 (3)	4.47
C(4)	−0.0813 (6)	0.1866 (4)	0.7084 (3)	4.96
C(5)	−0.2945 (5)	0.1404 (3)	0.5306 (3)	4.29
H1C3	−0.500 (7)	0.433 (5)	0.761 (3)	8.4 (11)
H2C3	−0.510 (6)	0.276 (4)	0.731 (3)	8.3 (11)
H3C3	−0.594 (6)	0.394 (4)	0.655 (3)	8.4 (11)
H1C4	−0.179 (5)	0.152 (3)	0.753 (2)	4.7 (7)
H2C4	−0.012 (4)	0.263 (3)	0.754 (2)	4.9 (8)
H3C4	0.005 (5)	0.113 (3)	0.688 (3)	5.8 (8)
H1C5	−0.415 (5)	0.106 (3)	0.573 (3)	5.5 (8)
H2C5	−0.226 (5)	0.063 (4)	0.518 (3)	5.0 (7)
H3C5	−0.344 (5)	0.184 (3)	0.463 (3)	5.4 (8)
HO	−0.305 (6)	0.689 (4)	0.571 (3)	7.2 (9)

[a] $B_{eq} = {}^1/_3 \Sigma_i \Sigma_j \beta_{ij} a_i{}^* a_j{}^* a_i a_j$.

Table II. Selected Bond Distances and Angles

Distances (Å)			
Ni-N(1)	1.869 (2)	N(1)-C(1)	1.275 (4)
Ni-N(2)	1.804 (2)	N(2)-C(2)	1.492 (4)
N(1)-O(1)	1.376 (3)	C(1)-C(2)	1.496 (4)
N(2)-O(2)	1.306 (3)	C(1)-C(3)	1.493 (5)
O(1)-OH	0.896 (43)	C(2)-C(4)	1.518 (5)
O(2)-OH	1.622 (44)	C(2)-C(5)	1.526 (5)
O(1)-O(2)	2.485 (4)		
Angles (deg)			
N(1)-Ni-N(2)	82.6 (1)	N(1)-C(1)-C(2)	114.9 (3)
N(1)-O(1)-HO	106.9 (2.8)	N(1)-C(1)-C(3)	122.9 (3)
Ni-N(1)-O(1)	123.6 (2)	C(2)-C(1)-C(3)	122.2 (3)
Ni-N(1)-C(1)	119.4 (2)	N(2)-C(2)-C(1)	104.5 (2)
O(1)-N(1)-C(1)	117.0 (2)	N(2)-C(2)-C(4)	109.1 (3)
Ni-N(2)-O(2)	127.3 (2)	N(2)-C(2)-C(5)	109.1 (3)
Ni-N(2)-C(2)	118.5 (2)	C(1)-C(2)-C(4)	110.9 (3)
O(2)-N(2)-C(2)	114.2 (2)	C(1)-C(2)-C(5)	110.9 (3)
O(1)-HO-O(2)	161 (4)	C(4)-C(2)-C(5)	112.0 (3)

Discussion

The structure consists of discrete molecules with nickel atoms on centers of symmetry. No intermolecular bonding of significance occurs, and metal–metal bonding like that in in $[Ni(DMG)_2]^0$ is not present.[4,5] The minimum Ni–Ni distance is 6.400 Å. The organic ligand closely resembles the well-known DMG but has an additional methyl group attached at C(2). The metal ion is coordinated to four nitrogen atoms at two distances, 1.804 (2) and 1.869 (2) Å. Two strong intramolecular hydrogen bonds exist with O–O distances of 2.485 (2) Å. The hydrogen appears to be unsymmetrically positioned between these oxygens:[6] O(1)–HO = 0.90 (4),

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(3) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(4) Godychi, L. E.; Rundle, R. E. *Acta Crystallogr.* **1953**, *6*, 487–495.

(5) The structure of $[Ni(DMG)_2]^0$ (R = 0.03) is given in: Lauher, J. W., personal communication (to be submitted for publication).

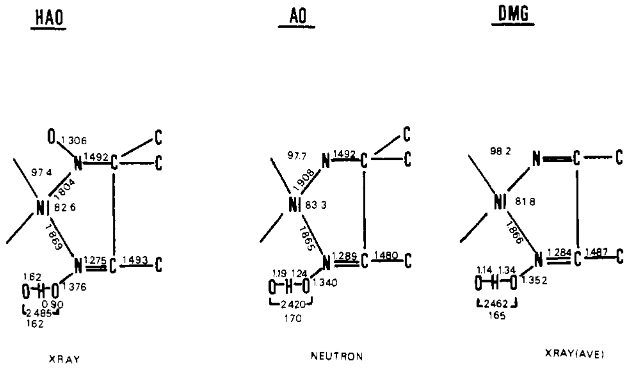


Figure 2. Comparison of bond distances and angles for Ni(II) complexes of HAO, AO, and DMG.

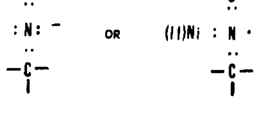
O(2)–HO = 1.62 (4) Å; ∠O(1)–HO–O(2) = 161.7 (4.3)°.

Except for two sp^3 methyl groups (C(4), C(5)) the heavy atoms of the entire molecule lie within 0.01 Å of a single plane. The least-squares planes, given in the supplementary material, show C(4) and C(5) to be on opposite sides with distances of −1.275 (3) and +1.248 (3) Å. The hydrogen-bonded hydrogen is also in this plane (0.07 (4) Å) within experimental error. The C(2), C(4), C(5) plane has a dihedral angle of 89.9° with the complex plane.

The other bond distances of the molecule are compared with those of two similar complexes $[Ni(DMG)_2]^0$[4,5] and $[Ni(AO)_2\text{-}H]^+$,[7] in Figure 2. The bond angles and distances involving the coordinated oxime groups are very similar in the three cases. In the order HAO, AO, DMG, bond distances (in angstroms) and angles (in degrees) are as follows: Ni—N 1.869 (2), 1.865 (1), 1.866 (4); N—O 1.376 (3), 1.340 (2), 1.352 (5); C=N 1.275 (4), 1.289 (2), 1.284 (6); C(1)—C(3) 1.493 (5), 1.490 (2), 1.487 (7); ∠Ni-N(1)-C(1) 82.6 (1), 83.1 (1), 81.8 (2); ∠Ni-N(1)-O(1) 123.6 (2), 122.4 (1), 123.2 (4). However, the distances and angles associated with N(2) are not similar to those of a coordinated oxime nor to an amine group except for the N(2)–C(2) bond distance. That bond distance (1.492 (4) Å) is similar to that of the amine N–C bond in the AO complex, but the N(2)–O(2) distance is quite short (1.306 (2) Å), even shorter than that of the oxime group in the same molecule or in the AO or DMG complex. The angles around N(2) are Ni-N(2)-O(2) = 127.3 (2)°, Ni-N-(2)-C(2) = 118.5 (2)°, and O(2)-N(2)-C(2) = 114.2 (2)°, making the bonds to N(2) nearly trigonal planar.

The main feature of interest is the nature of the bonding between Ni and N(2). This bond distance is considerably shorter, 1.804 (2) Å, than that for the coordinated oxime, 1.869 (2) Å. Coupling this with the short N(2)–O(2) distance indicates considerable multiple bonding in these two bonds and thus through the five-atom system (O(2)–N(2)–Ni–N(2)–O(2)) as a result of the center of symmetry.

Using the convention of oxidation state, one may consider this molecule to contain spin-paired d^6 Ni(IV) and a diamagnetic reduced ligand having ionized two protons or as d^8 Ni(II) and a ligand having an uneven number of electrons and thus being paramagnetic when free:



The former, upon protonation to give the free ligand, produce –CH_2–N(H)OH (a substituted hydroxylamine), and Ni(IV). In the latter, since the complex is diamagnetic, coupling of the magnetic spins of the free-radical ligands must occur. Upon protonation, a free-radical ligand and Ni(II) would be expected. Neither approach is entirely satisfactory. With nickel(IV) one would have a square-planar d^6 situation, the first known to our knowledge, while Ni(II) requires a free-radical ligand, which would be expected to be unstable when uncomplexed. Thus acid dissociation would probably be irreversible, contrary to our observations.

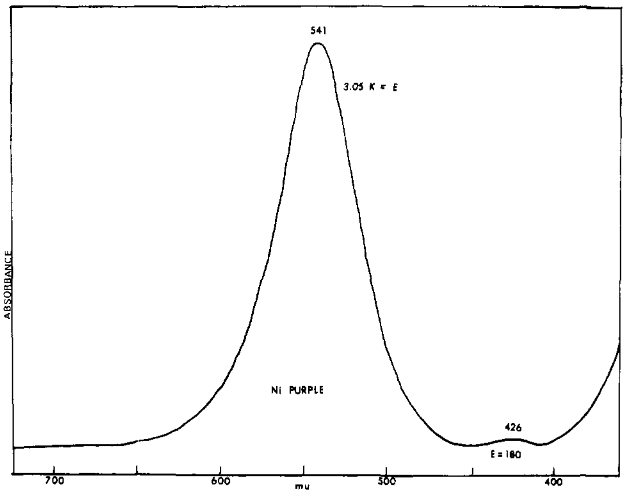


Figure 3. Absorption spectrum of $[Ni(HAO)_2]^0$ in CH_3CN, taken quickly from both directions and corrected to t_0.

The visible absorption spectra were measured in a number of solvents with no major solvent effect on the absorption shape or molar absorption coefficient, provided measurements were done quickly and were done in both directions. However, decomposition slowly occurs in all tested solvents at a rate roughly related to the coordinating ability of the solvent. At 25 °C the initial rates were as follows (in % decomposition/h unless otherwise noted): propylene oxide, 0.2; acetone, 3; CH_3CN, 20; dioxane, 3% decomposition/min. The visible spectrum in CH_3CN shows (Figure 3) an intense absorption at 5410 Å with a molar absorptivity of 3.05×10^3 M^{-1} cm^{-1}. A weak band also appears at 4260 Å with an apparent absorptivity of 180 M^{-1} cm^{-1}. Intense UV absorption is also apparent, but due to the sensitivity of this region to impurities and to the known complex decomposition in solution this region is not well-defined. The small, higher-energy transition (4260 Å) is characteristic of square-planar Ni(II) complexes, in both position and intensity, and is due to a d–d transition while the larger absorption is attributed to a π–π^* transition involved directly with the delocalized system.[8]

IR spectra are not very informative. No OH or NH stretches are seen above 3000 cm^{-1} while the weak OHO stretch appears as a broad peak centered at 1820 cm^{-1}, comparable to that in the other aliphatic α-amine oxime complexes of various metal ions.[9]

The proton NMR spectra were taken on a 90-MHz instrument in acetone-d_6 with Me_4Si as a standard. The sp^3 methyl protons were at 1.24 ppm while the sp^2 methyl protons were at 2.09 ppm with respect to Me_4Si in agreement with previous assignments,[10] and the intensity ratio was 1.9:1. No splitting of the sp^3 methyl peak could be discerned in agreement with the solid structural equivalence of these groups. The

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(6) Hussain, M. S.; Murmann, R. K.; Schlemper, E. O. *Inorg. Chem.* **1980**, *19*, 1448.

(7) (a) Schlemper, E. O.; Hamilton, W. C.; Laplaca, S. J. *J. Chem. Phys.* **1971**, *54* (9), 3900. (b) Schlemper, E. O. *Inorg. Chem.* **1968**, *7*, 1130.

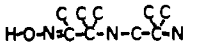
(8) Similar high extinction coefficients have been observed for π complexes of Ni(III) with tetraaza macrocycles but at higher frequencies.[15]

(9) Siripaisarnpipat, S. Ph.D. Thesis, University of Missouri, 1981, pp 174–189.

(10) Vassian, E. G.; Murmann, R. K. *Inorg. Chem.* **1967**, *6*, 2043 and ref 9 therein.

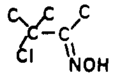
proton NMR spectra changed drastically with time due to decomposition and the formation of unknown paramagnetic Ni(II) species. While there was no shift in the Me_4Si peak upon addition of the complex to the solvent, it and all other peaks shifted significantly (about 0.3 ppm) in 30 minutes at 30 °C, and this change continued. This is due to the increase in bulk paramagnetism due to decomposition. The H-bonded hydrogen could not be seen in the usual 16–25-ppm downfield region with the concentrations possible. It is usually difficult to find, especially when it is unsymmetrical or is in the presence of paramagnetic impurities.

With respect to the mode of formation of this complex, the evidence suggests that the oxidation takes place on the complex, not on the free ligand since aeration of the ligand followed by metal ion addition produces no purple coloration. Furthermore, the unoxidized complex probably has a tridentate ligand of the type



$\mathrm{H{-}O{-}N{=}C(C){-}C(C)(C){-}N{-}C{-}C(C)(C){-}N}$

since only one



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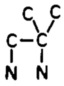
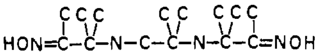
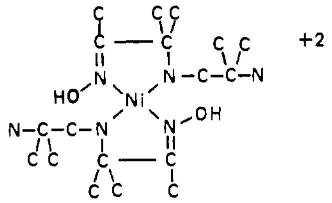


(at the unhindered end) probably due to steric hindrance. (Tetradentate ligands of the type



$\mathrm{HON{=}C(C){-}C(C)(C){-}N{-}C{-}C(C)(C){-}N{-}C(C)(C){-}C(C){=}NOH}$

or complexes of them have never been isolated with the two previously mentioned diamines, which give the purple complex.[11]) A binuclear planar Ni(II) complex of the tridentate ligand has been isolated whose crystal structure has been determined.[11] This binuclear complex, however, does not give the title complex upon reaction with molecular oxygen even in base. Thus the reactant complex is not known, but a reasonable candidate would be the *trans*-$(AO)_2$ complex with two free amine groups:



Oxidation at the coordinated amine–carbon bond could give the title complex, which would be stabilized by π bonding and electron pairing within the conjugated system. There is no convincing evidence to substantiate this mode of reaction, but it is reasonable and consistent with the known characteristics of the system.

The short Ni-N(HA) bond, short even when compared to the Ni-N(oxime) bond, which itself is generally shorter than Ni-N(amine) bonds,[12] reflects the unique character of this complex. To our knowledge no shorter Ni-N distance has been reported. On the basis of σ donation, L→M, the substituted hydroxylamine N should be more weakly bound and thus have a longer bond distance than that of the usual primary amine. The basicity of the oxime group is considerably less than of a primary amine, and it should have a relatively long bond distance. Both of these predictions are contrary to experimental fact, and it appears necessary to invoke in both cases considerable multiple π bonding using, at least partially, metal ion electrons. Further evidence of multiple bonding with the oxime ligand comes from the structure[13] where the hydrogen bond is protonated without significant weakening of the M–N oxime bond.

Table III. Ni-N Distances in $[Ni(HP)_2]^{2+}$ and $[Ni(P)_2]^{2+}$

	formal oxidn state	
	II	IV
Ni-N(oxime)	2.008	1.873
Ni-N(amine 1)	2.135	1.967
Ni-N(amine 2)	2.128	2.006

Considerable insight into the importance of multiple bonding, the apparent oxidation state, and the uniqueness of this M–N bond comes from a comparison with an octahedral AO complex[14] of a tridentate ligand whose structure had been determined in both the formal +2 and the formal +4 state. The tridentate ligand HON=C—C=N—C—C—N (HP), used in ref 14, is very similar to our starting ligand (before oxidation) but has a additional -C=N-. The hexacoordinated complex in the +4 state is deep purple and very inert to substitution even in strong acid. The average Ni–N distances for the two oxidation states are shown in Table III, and these values can be compared with those for the AO, HAO, and DMG complexes of Ni(II) in Figure 2.

The first observation is that in octahedral coordination both the oxime and amine M–N distances are longer than their counterparts in CN = 4 cases. This is expected, has often been observed, and reflects the steric and repulsive forces operating against the CN = 6 structure. The second observation is that increased formal oxidation state decreases the M–N distances about 0.13 Å (oxime and amine) with a slightly greater change with the oxime nitrogen due presumably to the ionization of H^+ from the oxime OH groups in the +4 state. Referring to Figure 2, we note that all of the bond distances associated with the coordinated oxime group are the same in the three complexes. A comparison of the bond angles results in the same conclusion. Since all evidence surrounding the AO and DMG complexes indicates that they have Ni in what we formally call the +2 oxidation state, we suggest that the metal ion in the title complex closely resembles them in its effective charge.

On the basis of the HP complexes of Ni(II) and Ni(IV), one should see a decrease in the M–N(oxime) distance in $[Ni(HAO)_2]^0$ of about 0.13 Å if it was in the +4 state, but within error there is none. Thus the shortness of the Ni–N-(HA) bond, 1.804 Å, cannot be due to a net loss of metal ion electrons (higher oxidation state), and since it is not expected from σ bonding (base strength), π bonding is most likely responsible. One also notes that the N–O bond is shorter by 0.04–0.07 Å than that for oxime groups and that the hydrogen-bonded hydrogen resides unsymmetrically between the oxygens on the oxime side. This suggests that there is N–O multiple bonding and that O(HA) is less basic than O(oxime). *Our conclusion at this time is that the complex should be considered a nickel(II) complex of a radical type ligand stabilized through metal–ligand π bonding.* The O–N–Ni–N–O system utilizes a nonlinear π system involving five atoms and eight paired electrons in five molecular orbitals of pri-

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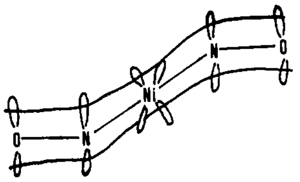
[11] Schlemper, E. O.; Murmann, R. K. *Inorg. Chem.* **1974**, *13*, 2424.

[12] Hussain, M. S.; Schlemper, E. O. *Inorg. Chem.* **1979**, *18*, 2278.

[13] The X-ray structure of $[Ni(PnAO)\text{-}6H]\cdot HClO_4\cdot H_2O$ is given in: Schlemper, E. O.; Vassian, E. G.; Murmann, R. K., unpublished results.

[14] Saarinen, H.; Korvenranta, J.; Nasakkala, E. *Acta Chem. Scand., Ser. A* **1980**, *A34*, 443–448.

marily p_z type for N and O and d_{xz} for the nickel atom.



This results in pairing of the odd electrons in the radical ligands and a low-energy metal–ligand electron-transfer band in the visible spectra.

For comparison a recent study[15] on an oxidized octahedral cyclam complex of nickel is interesting. The Ni–N bond distances average 2.003 (3) Å, which is consistent with the average distances in the +2 and +4 complexes of the HP ligand, 2.058 (4) Å, but closer to the average distance with the +4 oxidation state, 1.986 (4) Å.

The discovery of this DMG-like complex opens several interesting new areas of study involving metal ion replacement. The observation that the complex color immediately disappears with even dilute acid and reappears (~70%) upon rapid neutralization suggests that the ligand has some independent stability and can re-form complexes. (There is still the possibility that protonation destroys the chromophore without dissociation of the ligand from the metal ion.) When dissociation and recombination is accomplished in the presence of an excess of another metal ion, i.e. Cu(II), new species are formed that contain the new metal ion. Purification and isolation of these complexes have not yet been accomplished.

Conclusions

A new planar nickel complex has been formed by the air oxidation of a tridentate amine oxime complex. It is formulated as a Ni(II) complex of an unstable radical ligand that achieves stability by π bonding utilizing an O=N=Ni=N=O delocalized bond system. This results in an extremely short Ni–N(HA) bond distance and a very planar complex.

Acknowledgment. Financial support from the National Science Foundation (Grant CHE81-06795) and from the University of Missouri Research Council is gratefully acknowledged.

Appendix

For those having a special interest in this type of structure, we have recently learned of an unpublished structure of bis(diiminosuccinonitrilo)nickel(II), which also apparently has delocalized π bonding including a nickel atom with an average Ni–N distance 1.829 (2) Å.[16]

Registry No. $[Ni(HAO)_2]$, 84432-86-0.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic temperature factors, and least-squares planes and a stereoscopic view of the unit cell (8 pages). Ordering information is given on any current masthead page.

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[15] Zeigerson, E.; Bar, I.; Bernstein, J.; Kirschenbaum, L. J.; Meyerstein, D. *Inorg. Chem.* **1980**, *21*, 73.

[16] Lauher, J. W., unpublished results. Correspondence should be addressed to Dr. Lauher at the Department of Chemistry, State University of New York.

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439,
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Metrical Characterization of Tridentate Tetrahydroborate Ligation to a Transition-Metal Ion. Structure and Bonding in $Hf(BH_4)_4$ by Single-Crystal Neutron Diffraction

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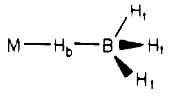
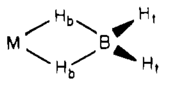
This paper reports the molecular structure of the transition-metal tetrahydroborate complex $Hf(BH_4)_4$ by single-crystal neutron diffraction at 110 K. The compound crystallizes in the cubic space group $P\bar{4}3m$ (T_d^1, No. 215) with a unit cell of dimensions a = 5.827 (4) Å. Full-matrix least-squares refinement gave a final value of $R(F_o^2)$ = 0.103 for 71 unique reflections with $F_o^2 > \sigma(F_o^2)$. The molecular structure consists of monomeric $Hf(BH_4)_4$ units having rigorously T_d symmetry and tridentate tetrahydroborate coordination. Important bond distances are Hf–B = 2.281 (8) Å, Hf–H(bridging) = 2.130 (9) Å, B–H(bridging) = 1.235 (10) Å, and B–H(terminal) = 1.150 (19) Å. Important bond angles are Hf–H(bridging)–B = 80.6 (6)°, H(bridging)–B–H(bridging) = 105.8 (6)°, and H(bridging)–B–H(terminal) = 112.9 (10)°. It is seen that the internal BH_4^- metrical parameters do not differ significantly from those in $Hf(CH_3C_5H_4)_2(BH_4)_2$, in which the tetrahydroborate ligands are coordinated in an unsymmetrical bidentate fashion. However, Hf–B is 0.27 (1) Å longer and Hf–H(bridging, average) 0.035 (9) Å shorter in the latter molecule.

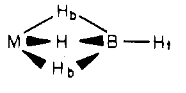
Transition-metal, lanthanide, and actinide complexes of the tetrahydroborate ligand, BH_4^-, exhibit a number of interesting and unusual properties.[2] These include coordination through metal–hydrogen–boron multicenter bonds (A, B, or C), very low barriers to intramolecular bridge–terminal (H_b–H_t) hydrogen interchange, covalent properties reminiscent of organometallic compounds such as η^3-allyls, and, in some instances, catalytic activity. That BH_4^- and CH_4 are isoelec-



A



B



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[1] (a) Argonne National Laboratory. (b) Northwestern University.

[2] (a) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263–293. (b) Wegner, P. A. In "Boron Hydride Chemistry"; Muetterties, E. L., Ed.; Academic Press: New York, 1973; Chapter 12. (c) James, B. D.; Wallbridge, M. G. H. *Prog. Inorg. Chem.* **1970**, *11*, 99–231.

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