combined to predict the stability constants of many other complexes. Although the correlation is empirical, large deviations from the predicted values would suggest the replacement of groups other than water or would suggest steric interference.

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Aromatization of an Aliphatic Amine Oxime Nickel(II) Complex by Molecular Oxygen

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In basic aqueous media, molecular oxygen as well as other oxidizing agents oxidize an aliphatic tetradentate α-amine oxime complex of nickel(II), $[\mathrm{Ni(PnAO)\text{-}H}]^+$.[2] Four electrons are ultimately removed from the organic portion of the complex resulting in the diamine chelate ring becoming pseudo-aromatic in character. The product (in yields of 90% of theoretical) has the empirical formula $[\mathrm{Ni(PnAO)\text{-}6H}]^0$, is planar, and is stable at room temperature to replacement reaction by neutral or basic cyanide solutions. Its structure in solution and in the solid state is deduced by infrared and proton nmr studies.

During a study of the kinetic and thermodynamic stability of complexes of the tetradentate ligand PnAO,[3] it was noted that alkaline solutions of its nickel(II) complex slowly changed color and deposited crystals of a new complex on exposure to a CO_2-free atmosphere. It was demonstrated that $[\mathrm{Ni(PnAO)\text{-}H}]^+$ was oxidized by molecular oxygen in a nonreversible fashion. Since this was a novel reaction and one related to the unsolved problem of the oxidation of bis(dimethylglyoxamato)nickel(II) by molecular oxygen and other oxidizing agents, studies were carried out to ascertain the nature of the oxidized product.

The starting complex, $[\mathrm{Ni(PnAO)\text{-}H}]^+$, is one of a series of closely related compounds whose molecular structure has been reasonably well established[4] and some of the work to be presented confirms it as I. The resulting oxidized complex will be shown to have the molecular structure given by II. This paper reports studies to determine the stoichiometry of the reaction shown in Figure 1, its generality, and the structure and reactivity of the product.

Experimental Section

PnAO.—The preparative method used for EnAO[4] was modified using 1,3-diaminopropane. To a 10% excess of 2-chloro-2-methyl-3-butanone oxime in 400 ml of 0° absolute methanol was added 0.45 mole of 1,3-diaminopropane. It was maintained at 0–5° for 2 hr and at room temperature for 2 hr; then it was refluxed for 15 hr. The solvent was removed under vacuum and the solid was extracted with water. A large excess of a saturated solution of Na_2CO_3 followed by several milliliters of 10 *M* NaOH was added until a pH of 10–11 was reached. The white crystalline solid was collected, washed with cold water, and recrystallized from boiling methanol; yield, recrystallized, 53% of theory; mp 180–181°. *Anal.* Calcd for $C_{13}H_{28}O_2N_4$: C, 57.32; H, 10.36; N, 20.57. Found: C, 57.38; H, 10.28; N, 20.49.

$[\mathrm{Ni(PnAO)\text{-}H}]ClO_4$.—This was prepared by the addition of equivalent amounts of PnAO dissolved in dilute HCl and $NiCl_2 \cdot 6H_2O$ followed by sufficient NaOH solution to make the mixture permanently neutral. Addition of an excess of $NaClO_4$ solution gave small yellow crystals which were recrystallized twice from hot water; yield, 80% of theory. *Anal.* Calcd for $C_{13}H_{27}O_6N_4ClNi$: C, 36.35; H, 6.34; N, 13.04; Ni, 13.67. Found: C, 36.35; H, 6.35; N, 12.95; Ni, 13.69. $\epsilon_{\max}$ (water): 426 mμ, 130; 269 mμ, 7.8×10^3; 254 mμ, 7.5×10^3.

$[\mathrm{Ni(PnAO)\text{-}6H}]^0$.—Oxygen gas was bubbled through a mixture of 1.0 g of $[\mathrm{Ni(PnAO)\text{-}H}]Cl$ and 15 ml of 1 *M* NaOH. After about 1 week the nearly colorless solution was removed and the orange crystals were collected. Extraction with ether removed insoluble impurities and after removal of this solvent it was recrystallized by the slow addition of water to an alcohol solution. A more rapid method involves adding solid KIO_3 (4–5 moles/mole of complex) to the $[\mathrm{Ni(PnAO)\text{-}H}]^+Cl^-$ dissolved in 2 *M* aqueous NaOH. Within a few minutes the orange product crystallizes and may be purified as above. Either method can give yields about 90% of theory. *Anal.* Calcd for $C_{13}H_{22}O_2N_4Ni$: C, 48.03; H, 6.82; N, 17.24; Ni, 18.06. Found: C, 48.00; H, 7.00; N, 17.05; Ni, 17.93. $\epsilon_{\max}$(ethanol): 486 mμ, 145; 385 mμ, 3.2×10^3; 336 mμ, 5.2×10^3; 256 mμ, 1.6×10^4.

All chemicals were of reagent grade, recrystallized where necessary. The water was distilled and deionized by a double-bed column. For visible–ultraviolet spectral measurements a Beckman DU instrument fitted with a constant-temperature (25.1 ± 0.05°) cell compartment was used. Infrared spectra were taken as Nujol mulls on a Perkin-Elmer Model 237B instrument. Proton nmr measurements were made on concentrated solutions in deuterated solvents at about 30° with a Varian A-60 nmr spectrometer. An internal standard, tetramethylsilane, was employed. Oxygen uptake measurements were made using a conventional Warburg apparatus at 25.10 ± 0.05°. Magnetic susceptibility measurements were made with a conventional Gouy apparatus at two field strengths at room temperature. The

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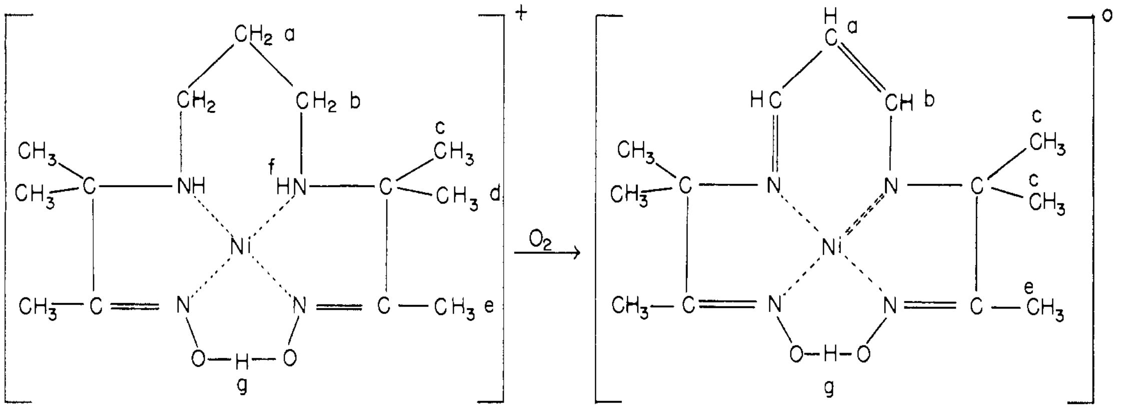
[1] Abstracted in part from the Ph.D. thesis of E. G. Vassian, University of Missouri, 1967.

[2] The designation [-H] is meant to imply the essentially complete ionization of an H^+ from the ligand of the complex.

[3] PnAO is an abbreviation for 2,2′-(1,3-diaminopropane)bis(2-methyl-3-butanone) dioxime.

[4] R. K. Murmann, *J. Am. Chem. Soc.*, **79**, 521 (1957); R. K. Murmann, *ibid.*, **80**, 4174 (1958).



[Ni(PnAO)-H]$^+$

I

[Ni(PnAO)-6H]^0

II

Figure 1.—Structural formulas for the starting material (I) and oxidized product (II).

field strength was calibrated with solid $Hg[Co(NCS)_4]$. The diamagnetic corrections were approximated from Pascal's constants. Analyses for C, H, and N were made by Galbraith Laboratories, Knoxville, Tenn., and the Ni analysis was carried out gravimetrically with DMG.

Results

The orange product, [Ni(PnAO)-6H]^0, has the following properties. It is essentially insoluble in water but soluble in acetone, CH_3OH, CCl_4, ether, $CHCl_3$, benzene, and dimethyl sulfoxide. In a 1:2.5 volume ratio of water–acetone a 3.3×10^{-3} M solution had a resistance of 4.69×10^4 ohms compared to the pure solvent (4.61×10^4 ohms) and a 2.4×10^{-3} M solution of [Ni(PnAO-H]ClO_4 (1.59×10^3 ohms) at 25° using a common cell. This shows that it is nonionic.

The bulk magnetic susceptibility at 27° shows both [Ni(PnAO)-H]ClO_4 and [Ni(PnAO)-6H]^0 to be spin-paired complexes; $10^6\chi_M = 10 \pm 8$.

Its molecular weight determined by the Rast method averaged 406 ± 100. As determined commercially by a thermoelectric method on a benzene solution its molecular weight was 314 ± 30. The molecular formula, [Ni(PnAO)-6H]^0, requires a molecular weight of 325 indicating the monomolecular nature of the complex.

The analysis gives atom ratios of C = 13.09, H = 22.69, N = 3.98, O = 2.05 (difference) based on Ni = 1.00. [Ni(PnAO)-6H]^0 requires C = 13, H = 22, N = 4, O = 2, and Ni = 1, which is as close an agreement as one can expect from these types of analyses.

Qualitative tests for Cl^-, ClO_4^-, NO_3^-, and NO_2^- were negative with [Ni(PnAO)-6H]^0 solutions.

Absorption of Oxygen

Figure 2 shows representative rates of oxygen absorption by [Ni(PnAO)-H]ClO_4. ΔP represents a lowering of pressure due to the loss of oxygen by reaction. Oxygen absorption did not stop completely even after long periods suggesting a second, much slower reaction which was not studied. Oxygen was absorbed more rapidly with increased [complex] and with increased [OH^-]. Because of the imprecision of kinetic measurements by the Warburg technique an evaluation of the form of the rate law was not attempted. Table I lists some representative results and control experiments.

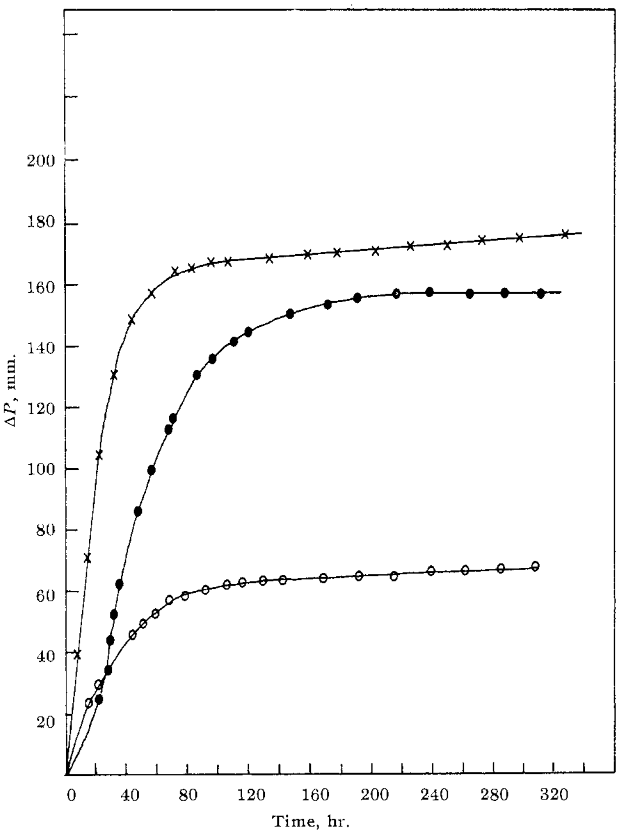


Figure 2.—Absorption of O_2 by basic solutions of [Ni(PnAO)-H]$^+$ at 25° and a 10.20-ml volume. Amount of complex: ×, 0.0377 g; ●, 0.0376 g; ○, 0.0152 g; ×, 1.0 M; ● and ○, 0.10 M OH^-.

The final column shows that one oxygen molecule is used per molecule of [Ni(PnAO)-H]$^+$. The slightly higher value than 1.00 is due to the difficulty in estimating when the first reaction is over and reflects a

TABLE I

AMOUNT OF O_2 ABSORBED BY $[Ni(PnAO)\text{-}H]^+$

Expt no.	[Complex], moles $\times 10^{-5}$	$[NaOH]_i$, M	V_{gas}, ml	ΔP, mm[c]	Gas	$[O_2]$/[complex]
5	3.54	0.100	7.59	90.3	O_2	1.06
8A	6.45	0.0805	9.35	127	O_2	1.02
8B	8.75	0.100	8.05	199	O_2	1.00
10	3.68	1.00	7.54	92.1	O_2	1.05
3	8.80	1.00	7.30	237	O_2	1.08
19	8.78	1.00	10.20	174	O_2	1.11
1C	6.45	0.0805	12.57	0.0	N_2	...
7A-C	0.0	0.0805	8.41	0.0	O_2	...
7B-C[a]	0.0	1.00	6.89	0.0	O_2	...
8B-C[b]	0.0	1.00	8.05	42 (3000 hr)	O_2	...

[a] 0.0155 g (5.69×10^{-5} M) of PnAO present. [b] 0.0187 g (5.75×10^{-5} M) of $[Ni(PnAO)\text{-}6H]^0$ present. [c] After nearly level portion reached.

small contribution from the second slower reaction. Experiments 1C and 7B-C show that N_2 and PnAO are not involved in this reaction while 7A-C shows that the other reagents are not responsible for the O_2 uptake. Run 8B-C gives an estimate of the rate of O_2 uptake by the product under comparable conditions. Thus the oxidation proceeds slowly using 1 mole of O_2/mole of $[Ni(PnAO)\text{-}H]^+$. In all experiments containing complex and O_2 the product complex was at least 95% precipitated when the mole ratio was 1:1 and practically no color remained in solution.

The possibility exists that the complex ligand hydrolyzes in basic media giving NH_2OH which could then be oxidized. To check this NH_2OH was placed in the Warburg apparatus under the usual conditions. The pressure was found to increase as a function of time in direct contrast to the behavior of the complex. This was due to the liberation of N_2 according to

$$4NH_2OH + O_2 \longrightarrow 2N_2 + 6H_2O$$

That hydrolysis of the ligand to NH_2OH is improbable is also suggested by the fact that the nitrogen analysis of the product complex was not low. Another possibility is that O_2 is converted to H_2O_2. Tests on the supernatant solution after oxidation showed no H_2O_2. Tests for NO_2^- were also negative.

Using KIO_3 in basic aqueous media gave the same product (more quickly) as shown by infrared spectra. The oxidation state change was determined using this oxidant. The reaction was not complete even with an excess of KIO_3 and a correction had to be made.

$$n(IO_3^-) + m[Ni(PnAO)\text{-}H]^+ \longrightarrow n(I^-) + m[Ni(PnAO)\text{-}6H]^0$$

The complex was prepared from the ligand with a slight excess of $NiCl_2$ which was then treated with excess IO_3^-. After removal of $[Ni(PnAO)\text{-}6H]^0$ on a filter, the supernatant solution was treated with acid to liberate iodine which was separated with CCl_4 and titrated with standard sodium thiosulfate solution. Special care was taken to prevent loss of I_2 by volatilization and oxidation of I^- by air. Table II summarizes these results.

TABLE II

OXIDATION OF $[Ni(PnAO)\text{-}H]^+$ WITH IO_3^-

Expt no.	[KOH], M	[PnAO], g	$[Ni(PnAO)\text{-}6H]^0$, g	% yield	0.100 N $S_2O_3^{2-}$, ml	E	E_c
3	1.0	0.2194	...	...	5.60	3.47	...
9	2.0	0.2006	0.2157	90.1	5.10	3.46	3.84
10	1.0	0.2062	0.2168	88.1	5.40	3.57	4.05
12	1.0	0.2082	0.2318	93.3	5.45	3.56	3.81

E represents the number of electrons lost per molecule of $[Ni(PnAO)\text{-}H]^+$ assuming complete reaction while E_c represents that value after correction for the amount not reacted. The average value of E_c of 3.90 ± 0.10 is in good agreement with that obtained from the O_2 uptake experiments, assuming in basic media, $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$.

Qualitative tests on the solution remaining after KIO_3 oxidation of $[Ni(PnAO)\text{-}H]^+$ showed no NO_2^-, NO_3^-, or H_2O_2.

Other oxidizing agents also generated the same new complex. $S_2O_8^{2-}$, PbO_2, and H_2O_2 were successful while I_2 in basic media was absorbed but produced other species.

The infrared spectra of both $[Ni(PnAO)\text{-}H]ClO_4$ and $[Ni(PnAO)\text{-}6H]^0$ show a broad band at 1780 and 1800 cm^{-1}, respectively. This band is diagnostic of the O–H–O group[5] in amine oxime and dioxime complexes of Ni(II) and other transition metal ions. Thus evidence is present for the presence of the oxime hydrogen bond in $[Ni(PnAO)\text{-}6H]^0$. The 31–3400-cm^{-1} band corresponding to the N–H stretching frequency is absent in $[Ni(PnAO)\text{-}6H]^0$ but present in $[Ni(PnAO)\text{-}H]ClO_4$. This suggests that no hydrogens are on the amine-type nitrogens in the former complex.

The oxidation with molecular oxygen is not reversible. When the O_2 was replaced by N_2 or the solution was placed under vacuum after the complex was oxidized, the original complex did not reappear. Further, reduction of $[Ni(PnAO)\text{-}6H]^0$ in basic media with S^{2-}, I^-, or Sn^{2+} was not attained.

The basic structure of $[Ni(PnAO)\text{-}6H]^0$ was determined by inspection of the proton nmr spectra in dimethyl sulfoxide-d_6, acetone-d_6, and CCl_4. The spectra were identical in these three solvents except for small peaks due to hydrogen impurities in the deuterated solvents. CCl_4 was less useful due to the limited solubility of the complex in this solvent.

Figure 3 shows representative pmr spectra of $[Ni(PnAO)\text{-}H]ClO_4$ and $[Ni(PnAO)\text{-}6H]^0$. The solvent proton impurities have been removed. Table III gives the chemical shifts at 60 Mc and the assignments according to the lettering scheme in Figure 1.

Several points on the nmr spectra merit comment. The spectra are completely consistent with planar, diamagnetic structures for both complexes. In $[Ni(PnAO)\text{-}H]^+$ the $-CH_2-CH_2-CH_2-$ group must be out of the plane of the metal and the four nitrogens creating a different environment for the c and d methyl groups. In $[Ni(PnAO)\text{-}6H]^0$, these methyl groups are

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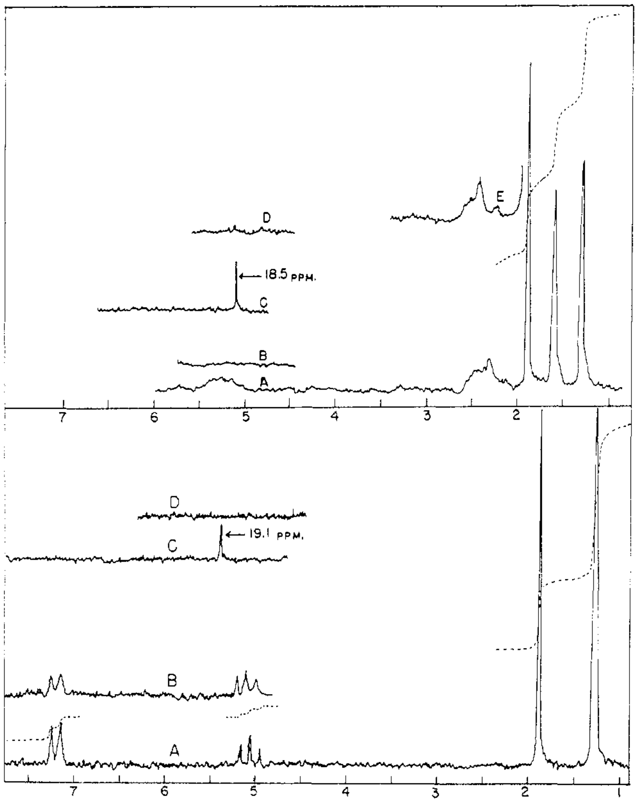
(5) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 195–197; also ref 4.



Ppm downfield.

Figure 3.—Nmr spectra (60 Mc) of [Ni(PnAO)-H]ClO_4 (above). and [Ni(PnAO)-6H]^0 (below) in DMSO-d_6 relative to TMS Small peaks at 2.53 and 3.29 ppm due to H impurities in solvent have been removed. Curves C and D are offset 500 cps and have a sweep width of 1000 cps. Curves B and D are A and C, respectively, after the addition of D_2O. Curve E shows the methylene proton signal in water. Dotted lines are the integrated intensities.

Table III

Nmr Spectra in DMSO-d_6

(Downfield, Ppm Compared with TMS)

[Ni(PnAO)-H]ClO_4

Ppm	1.29	1.59	1.88	2.4^b	2.1^b	$5.2^{a,e}$	18.3^e
No. of H	6	6	6	(3–4)	(1–2)	2	1
Assignment (I)	d	c	e	b	a	f	g

[Ni(PnAO)-6H]^0

Ppm	1.29		1.89		5.07^c	7.21^d	19.1^e
No. of H	12		6		1	2	1
Assignment (II)	c		e		a	b	g

[a] Broad. [b] Broad multiplet. [c] Average triplet. [d] Average doublet. [e] Disappear on addition of D_2O.

identical suggesting that the a and b carbons are essentially in the plane of the rest of the complex. Both a and b type protons are in or near the aromatic region suggesting that pseudo-aromatic character is probable for that ring with the nickel ion participating in the ring *via* multiple bonding. Interpretation of the nmr spectra was facilitated by the changes noted upon addition of a small amount of D_2O. The OHO and NH protons are known to exchange the H's with D_2O rapidly resulting in the loss of the signals for that type of hydrogen. The decreased shielding of the oxime hydrogen in [Ni(PnAO)-6H]^0 suggests that the hydrogen bond is weaker. Although no thermodynamic studies have so far been possible, this is not in agreement with the increased kinetic stability of this complex.

Discussion

Although the transition state may involve a +4 or +3 oxidation state of Ni in the oxidation of [Ni(PnAO)-H]$^+$ to [Ni(PnAO)-6H]^0 the product contains only oxidized ligand in the sense that the H's are removed from the ligand. No evidence for intermediates was found which required the existence of a higher oxidation state for Ni. Presumably, however, the oxidizing agent associates at the metal ion axial positions and transfers electrons through the metal ion.

The molecular structure of the product has been determined using several techniques all of which lead to the common structure which retains the hydrogen bond and aromatizes the six-member ring. This ring has many of the characteristics of a heterocyclic aromatic ring.

Attempts to duplicate these results with a five-membered ring (EnAO[6]) or with other metal ions (Cu^{2+}, Fe^{2+}, Mn^{2+}) were unsuccessful which suggests that the driving force for the reaction is the resonance of the pseudo-aromatic ring which is allowed to form by virtue of the proper electron-transferring character of the coordinated metal ion.

The product molecule is extremely stable at least kinetically. Boiling with basic KCN solution or EDTA does not convert it to the new complex in 1 hr. In acidic media at elevated temperatures it is partially converted to a deep red positively charged complex whose structure is unknown. Attempts to isolate the metal-free ligand from [Ni(PnAO)-6H]^0 have so far been unsuccessful.

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(6) EnAO is an abbreviation for 2,2′-ethylenediaminebis(2-methyl-3-butanone) dioxime.