Conclusions

Norbornene adducts of the $S_3N_3^+$ cation are readily obtained by the reaction of $(NSCl)_3$ with an excess of norbornene in 1,4-dioxane followed by treatment of $C_7H_{10}{\cdot}S_3N_3Cl$ so formed with a chloride ion acceptor or silver salt. Although the structural data for one of these adducts indicate localized π-bonding at opposite ends of the S_3N_3 ring, it is likely that the structure of the unattached $S_3N_3^+$ cation will be significantly different from that of the adduct.[31] The structural weakness implied by the variations in S–N bond lengths in the adduct is reflected in the facile loss of the –NSN– bridge.

Acknowledgment. We are grateful to Dr. R. Yamdagni for assistance with the measurement of the ^{13}C and ^{14}N NMR spectra and Dr. M. J. Schriver (Dalhousie University) for providing the unpublished ^{13}C NMR data for $(C_7H_{10})_2{\cdot}NS_2^+$. We thank the NSERC (Canada), the National Science Foundation, and the State of Arkansas for financial support.

Supplementary Material Available: Listings of crystallographic parameters, thermal parameters, hydrogen atom parameters, and least-squares planes (5 pages); a table of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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[31] The structure of the norbornadiene adduct of the 8-π-electron system $Ph_2PN_3S_2$ shows substantial differences in ring conformation, bond lengths, and bond angles compared to that of $Ph_2PN_3S_2$.[6]

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Dioxygen Adducts of Nickel(II) and Cobalt(II) Dioxopentaazamacrocyclic Complexes: Kinetics, Stabilities, and Hydroxylation of the Ligands in the Nickel Dioxygen Complexes

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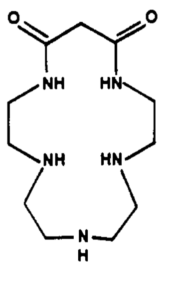
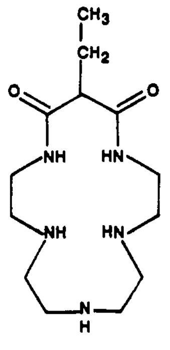
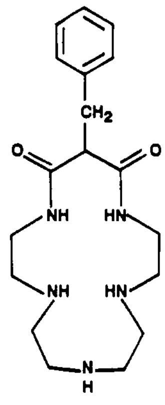
The macrocyclic ligands 1,4,7,10,13-pentaazacyclohexadecane-14,16-dione, 15-ethyl-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione, and 15-benzyl-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione have been prepared, and the stability constants of their Cu(II), Ni(II), and Co(II) complexes have been determined potentiometrically. The dioxygen affinities of the Ni(II) and Co(II) complexes have been measured as a function of partial pressure of dioxygen and temperature. The nickel(II) macrocycles form 1:1, superoxo-type dioxygen complexes, while the Co(II) complexes of the same ligands form 2:1 peroxo-bridged binuclear dioxygen adducts. Equilibrium constants (K_{O_2}), $\Delta H°$, and $\Delta S°$ of dioxygenation are reported. All dioxygen complex formation reactions are strongly exothermic with strongly negative entropy changes. Both nickel and cobalt dioxygen complexes undergo facile degradation in aqueous solution but have significant lifetime for determination of oxygenation constants by dioxygen sorption measurements. The cobalt(II) complexes have higher dioxygen affinities than the nickel(II) complexes with the same ligands. The rates of dioxygen complex formation and degradation have been measured qualitatively and semiquantitatively by UV–visible absorbance studies. The result of this investigation confirms the previous discovery of the formation of dioxygen adducts from nickel(II) complexes, but they are found to undergo irreversible degradation too rapidly to be employed for dioxygen separation or transport. All three Ni(II) dioxygen complexes studied hydroxylate the macrocyclic ligand at the electron-rich 15-carbon position, thus providing new examples of oxygen insertion (monooxygenase-like activity) by the activation of coordinated dioxygen.

Introduction


1 PNOH, L


2 PNOET, L'


3 PNOBZ, L''

The recent reports by Kimura et al.[1a-f] that the Ni(II) complexes of dioxopentaazamacrocyclic ligands form stable dioxygen adducts is of considerable interest in view of the fact that such complexes are the first nickel(II) dioxygen carriers to be described. The possibility that these Ni(II) macrocyclic complexes may be employed for the separation of dioxygen from air deserves further investigation, especially in view of the report[1a] that they may undergo several oxygenation and deoxygenation cycles. An even more unique characteristic is the reported endothermic nature of the formation of these nickel dioxygen complexes, which was suggested[1a] as the possible reason for their unusual properties.

In view of the novelty of these nickel(II) dioxygen complexes, it was considered worthwhile to carry out equilibrium and kinetic studies on their formation and to compare their properties with those of the corresponding cobalt dioxygen complexes involving the same ligands. The three ligands selected for this study seem particularly effective in forming stable nickel(II) dioxygen complexes: 1,4,7,10,13-pentaazacyclohexadecane-14,16-dione, PNOH (**1**), and its derivatives with ethyl and benzyl groups at the 15-position, to give 15-ethyl-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione, PNOET (**2**), and 15-benzyl-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione, PNOBZ (**3**), respectively.

Experimental Section

Materials. The malonic acid and substituted malonic acid esters employed in the following syntheses, diethyl malonate, diethyl ethylmalonate, and diethyl benzylmalonate, were obtained as pure substances from Aldrich Chemical Co. Tetraethylenepentamine was purified as described in the literature.[2]

1,4,7,10,13-Pentaazacyclohexadecane-14,16-dione, PNOH (1), was prepared by a modification of the method of Kimura et al.[1] ^1H NMR ($CDCl_3$–Me_4Si): δ 1.83 (s, 3 H, CH_2NHCH_2), 2.71–2.91 (m, 12 H,

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[1] (a) Kimura, E.; Machida, R.; Kodama, M. *J. Am. Chem. Soc.* **1984**, *106*, 5497. (b) Kimura, E.; Machida, R. *J. Chem. Soc., Chem. Commun.* **1984**, 499. (c) Kushi, Y.; Machida, R.; Kimura, E. *J. Chem. Soc., Chem. Commun.* **1985**, 216. (d) Kimura, E.; Anan, H.; Toike, T.; Shiro, M. *J. Org. Chem.* **1989**, *54*, 3998. (e) Kimura, E.; Sakonaka, A.; Machida, R. *J. Am. Chem. Soc.* **1982**, *104*, 4255. (f) Machida, R.; Kimura, E.; Kushi, Y. *Inorg. Chem.* **1986**, *25*, 3461.

[2] Jonassen, H. B.; Frey, F. W.; Schaafsma, A. *J. Phys. Chem.* **1957**, *61*, 504.

CH_2NHCH_2), 3.23 (s, 2 H, $COCH_2CO$), 3.39–3.44 (m, 4 H, $OCNHCH_2$), 8.09 (t, 2 H, CNHCO). Mp 170 °C (lit.[1] 179 °C).

15-Ethyl-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione, PNOET (2), was synthesized by a modification of the method of Kimura et al.[1] ^1H NMR ($CDCl_3$–Me_4Si): δ 0.96 (t, 3 H, CH_3), 1.91 (M, 2 H, CH_2), 2.13 (s, 3 H, CH_2NHCH_2), 2.65–2.80 (m, 12 H, CH_2NHCH_2), 3.01 (t, 1 H, COCHCO), 3.24–3.61 (m, 4 H, $CONHCH_2$), 7.72 (t, 2 H, CNHCO). Mp 203 °C (lit.[1] 203 °C).

15-Benzyl-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione, PNOBZ (3), was synthesized by a modification of the method of Kimura et al.[1a] ^1H NMR ($CDCl_3$–Me_4Si): δ 1.91 (s, 3 H, CH_2NHCH_2), 2.51–2.71 (m, 12 H, CH_2NHCH_2), 3.14 (m, 4 H, $CONHCH_2$), 3.25 (m, 1 H, COCHCO), 3.49 (m, 2 H, phenyl–CH_2), 7.17–7.25 (m, 5 H, phenyl), 7.45 (t, 2 H, CNHCO). Mp 204 °C (lit.[1] 202 °C).

The inorganic salts were reagent grade and were used without further purification: $NiCl_2·6H_2O$, $CoCl_2·6H_2O$, and $CuCl_2·2H_2O$ from J. T. Baker Chemical Co. and $Co(OOCCH_3)_2·4H_2O$ from Fisher Scientific Co. $^{18}O_2$ was obtained from Cambridge Isotope Laboratories, Woburn, MA, in 98% purity. Carbon dioxide free potassium hydroxide solutions were prepared with doubly distilled water and Baker Dilut-It ampules.

Oxygenation Constants. The equilibrium constants for the formation of 1:1 and 2:1 dioxygen complexes defined by eq 2 and 3 were measured by the volumetric gas uptake method described previously.[3]

$$M^{2+} + L \rightleftharpoons MH_{-2}L + 2H^+ \qquad K_{ML} = \frac{[MH_{-2}L][H^+]^2}{[M^{2+}][L]} \tag{1}$$

$$MH_{-2}L + O_2 \rightleftharpoons M(O_2)H_{-2}L \qquad K_{O_2}(1:1) = \frac{[M(O_2)H_{-2}L]}{[MH_{-2}L]P_{O_2}} \tag{2}$$

$$2MH_{-2}L + O_2 \rightleftharpoons M_2(O_2)(H_{-2}L)_2$$

$$K_{O_2}(2:1) = \frac{[M_2(O_2)(H_{-2}L)_2]}{[MH_{-2}L]^2 P_{O_2}} \tag{3}$$

The corresponding relationships for $P_{1/2}$, the dioxygen partial pressure corresponding to half-conversion of the oxygen-free complex to the oxygenated form are

$$P_{1/2}(1:1) = K_{O_2}^{-1} \tag{4}$$

$$P_{1/2}(2:1) = [MH_{-2}L(\text{initial})]^{-1}K_{O_2}^{-1} \tag{5}$$

It is noted that half-oxygen constants for the 1:1 dioxygen complexes are independent of concentration, while those of the 2:1 dioxygen complexes are concentration dependent. The oxygenation constants are expressed in terms of partial pressure of dioxygen in equilibrium with the dioxygen-saturated solutions, thus avoiding complications of changing solubilities of dioxygen with changes in temperature, ionic strength, and other solvent conditions.

Enthalpies of Dioxygenation, $\Delta H°$, were calculated from the temperature coefficient of the dioxygenation constants through the use of Van't Hoff plots.

Entropies of Dioxygenation, $\Delta S°$, were calculated from the standard relationships$_2$ $-\Delta G° = RT \ln K_O$ and $T\Delta S° = \Delta H° - \Delta G°$.

Equilibrium Measurements. Because of the complications resulting from the fact that some of the dioxygenation reactions are slow and some metal complex formation reactions are even slower and the added problem that some of the dioxygen complexes began to undergo irreversible degradation under the conditions at which equilibrium was measured, special precautions were taken to make certain that equilibrium had been reached when the oxygen uptake equilibrium data were recorded. The first precautions involved making certain that sufficient time had been allowed to reach equilibrium. For the more rapidly degrading solutions, this consideration involved a trade-off between the time required for equilibrium and the time during which an appreciable fraction of the dioxygen complex underwent degradation. For those systems less accuracy was achieved in measuring the oxygenation constants.

The second, and most convincing, criterion of equilibrium was to measure at least three equilibrium positions for each temperature investigated. The data would consist of three volumes of dioxygen absorbed corresponding to three different partial pressures of dioxygen at equilibrium. The test for equilibrium was the calculation of the same dioxygenation constant from the three sets of data.

Potentiometric Measurements. The potentiometric method employed for the determination of the stability constants of metal complexes of the macrocyclic ligands **1–3** is the same as that previously described.[4] The determinations were carried out on 3.5×10^{-3} M ligand and/or metal ion at 0.100 M ionic strength adjusted with KCl as the supporting electrolyte and at 25.0 °C. The Corning Model 150 pH meter, which was equipped with the standard glass electrode and calomel reference electrode, was calibrated to read hydrogen ion concentration directly. The log concentration product of water was determined as −13.78. All measured equilibrium constants are concentration constants and were obtained through potentiometric data reduction by the use of the program BEST.[4]

Table I. Protonation Constants

quotient	PNOH (1) this work[a]	PNOH (1) lit.[b]	PNOET (2) this work[a]	PNOET (2) lit.[b]	PNOBZ (3) this work[a]	PNOBZ (3) lit.[b]	DIEN[c]
$[HL^+]/[H^+][L]$	9.40	9.01	9.31	9.17	9.01	9.23	9.84
$[H_2L^{2+}]/[H^+][HL^+]$	8.22	8.69	7.98	8.00	7.43	7.91	9.02
$[H_3L^{3+}]/[H^+][H_2L^{2+}]$	2.29	<2	1.97	<2	2.03	<2	4.23
σ_{fit}	0.015		0.005		0.017		

[a] 25.0 °C, μ = 0.10 (KCl). [b] Reference 1; 35 °C, μ = 0.2 ($NaClO_4$). [c] Reference 5; 25.0 °C, μ = 0.10.

Spectrophotometry. The Perkin-Elmer fast-scan Model 553 spectrophotometer employed was equipped with a 1.000 ± 0.001 cm quartz flow cell driven by a peristaltic pump. The volume of the cell and associated tubing was determined to be 20.0 mL. In preparation for a given run, the flow cell was thoroughly rinsed with distilled water and left filled. The solution was then made up by the direct weighing of a 20.0-mg sample of the PNOH ligand and dilution with 10.0 mL of 1.00 M KCl, 5.00 mL of 0.1008 M HCl, 3.00 mL of 0.021 71 M $NiCl_2$ or 0.021 92 M $CoCl_2$, and 62.0 mL of water. The total volume (including the 20.0 mL above from the flow cell) was 100.0 mL in each case. After the cell was closed, the peristaltic pump was started, and a steady stream of Ar gas was bubbled through the thermostated (25.0 °C), rapidly stirred test solution for at least 1 h. Just prior to the admittance of dioxygen, the solution pH was adjusted by means of a screw-type microburet with 1.00 M KOH and was spectrophotometrically checked for equilibrium. The spectrophotometer was then started in a repetitive scan mode at a rapid rate, and successive spectra were obtained at equally spaced intervals of time (e.g., 22–38 s/spectrum).

Product Analysis and ^{18}O Tracer Determination. In order to determine the oxidation products resulting from the attack of activated dioxygen on the ligands of the nickel dioxygen complexes, product analysis was carried out as follows. At 25 °C, 500 mg of the ligand and equimolar $NiCl_2·6H_2O$ were added to 100 mL of 0.1 M borax buffer solution (p[H] 10.3) under anaerobic conditions to form the pale purple complexes ($NiH_{-2}L$, where L = **1**, **2**, or **3**). Dioxygen was then bubbled through the solution for 24–48 h, producing color changes from the initial purple to dark brown and finally to yellow. For the workup, a 2.0-g sample of solid EDTA tetraacid was added to the reaction mixture, with stirring, whereupon the p[H] dropped to 3.5. The p[H] was increased to 11 by addition of 50% NaOH solution, and the color changed to green (Ni(II)–EDTA). About 90% of the solvent water was removed by evaporation, and the residual solution was extracted several times with chloroform. The oxidized ligand was obtained as a white solid by evaporation of the chloroform solvent and was analyzed by ^1H NMR, ^{13}C NMR, and mass spectral determinations. NMR studies of the reaction products showed the yields of hydroxylated ligands to be 85 ± 5%, based on the initial amount of ligand employed.

The ^{18}O tracer study of the ligand oxidation product was carried out in the same manner as described above, except that all traces of $^{16}O_2$ were removed from the initial solution by successive evacuation, followed each time by the introduction of argon. For the oxidation reaction the evacuated reaction chamber was connected to a flask containing $^{18}O_2$ (98%).

NMR Spectra. The proton and carbon-13 NMR spectra were recorded with a Varian XL-200 NMR spectrometer, and chemical shifts are reported in ppm relative to tetramethylsilane.

Mass Spectra. The mass spectra were obtained with a VG analytical 70S high-resolution double-focusing mass spectrometer with an attached VG analytical 11/250J data system. The operator was Dr. T. R. Sharp of the Departmental Research Services Facility.

Results

Protonation Constants. The protonation constants measured potentiometrically for the macrocyclic ligands **1–3** are listed in Table I and compared with those reported previously[1] under

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(3) Chen, D.; Martell, A. E. *Inorg. Chem.* **1987**, *26*, 1026.

(4) Martell, A. E.; Motekaitis, R. J. *Determination and Use of Stability Constants*; VCH Publishers: New York, 1989.

(5) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1974–1977, 1982, 1989; Vols. 1–6.

Table II. Metal Chelate Stability Constants[a]

	Cu(II)				Ni(II)			Co(II)		
quotient	PNOH	PNOET	PNOBZ	DIEN[b]	PNOH	PNOET	DIEN[b]	PNOH	PNOET	DIEN[b]
[ML]/[M][L]	13.02	13.08	12.39	15.9	6.91	6.77	10.5	4.62	4.66	8.0
[MHL]/[ML][H]	3.00	2.56	2.61	3.2	5.82	5.65		7.89	7.12	
[MH$_{-1}$L][H]/[ML]	−8.06	−8.14	−7.48		−7.45	−8.07		−7.57	−8.36	
[MH$_{-2}$L][H]/[MH$_{-1}$L]	−6.75	−7.08	−6.84		−8.39	−8.50		−8.33	−8.28	

[a] 25.0 °C, μ = 0.10 M (KCl). [b] Reference 5; 25.0 °C, μ = 0.10 M.

somewhat different conditions, as well as with the open-chain analogue diethylenetriamine, DIEN. It is noted that the first protonation constants of all of the macrocycles are lower than those of diethylenetriamine. This lower basicity may be due in part to the presence of additional electronegative atoms in the macrocyclic molecules and perhaps also to the lower degree of solvation of the macrocyclic ligands relative to the open-chain analogue, a factor which would inhibit somewhat the stabilization by hydration of the more protonated (more highly charged) form of the ligand, HL$^+$, relative to L. Although protonation reactions are generally very rapid (diffusion controlled) in aqueous solution, the protonation reactions of these macrocycles are very slow between p[H] 6 and 7.5, indicating considerable conformational rearrangement of the ligand in going from H_2L^{2+} to HL$^+$ and L or conversely in going from L to HL$^+$ and H_2L^{2+}. This effect is minimal with PNOH but is more pronounced with substitution. For potentiometric titration of PNOBZ as much as 10 min were required between additions of base to reach equilibrium. It is suggested that the amide groups are the focus of the rearrangements, which occur as the adjacent amino groups become protonated or deprotonated, and that the arrangement probably involves folding and unfolding of the ring to accommodate the making and breaking of intramolecular hydrogen bonds.

Stability Constants. In addition to stability constants of the ligands with the metal ions of interest, Ni(II) and Co(II), those of Cu(II) were also investigated for comparative purposes, and the results are listed in Table II. It is seen that all metal ions investigated react initially with all three ligands to form complexes designated as ML^{2+}, in which the three amino groups of the diethylenetriamine moiety are coordinated to the metal ion, but have stability constants 3–4 orders of magnitude lower than the corresponding chelates of the open-chain triamine, DIEN. While this is due in part to the lower basicities of the macrocyclic ligands (Table I), steric effects must also be involved because the drop in stability constants is much greater than would be expected from the differences of basicities alone. The amide groups are probably not involved as donor groups in these initial complexes, although there is the possibility that the metal ions are weakly coordinated by the amide carbonyl oxygens. This effect, if it occurs, would be quite weak and would not strongly influence the magnitudes of the stability constants.

As the p[H] is increased, all three transition-metal ions displace hydrogen ions from the amide groups, making possible the expected strong coordination by the negatively charged amide nitrogens. In all cases, this reaction is seen to occur in two steps, with formation of an intermediate monodeprotonated complex, $ML^{2+} \rightleftharpoons MH_{-1}L^+ \rightleftharpoons MH_{-2}L$. In the case of Cu^{2+}, the second deprotonation is stronger than the first, so that the intermediate $MH_{-1}L^+$ is only a minor species in solution. All three metal ions also form intermediate protonated complexes, MHL^{3+}. Kimura et al.[1] assumed a much simpler model for complex formation and did not consider the possibility of forming the intermediates MHL^{3+} and $MH_{-1}L^+$. The result is apparent in the species distribution curves, obtained on the basis of Kimura's constants, which are much different from the species distributions reported here. The curves obtained by neglecting the formation of intermediates indicate that the ultimate complex Ni(II) species is completely formed at p[H] 8, while the more complete treatment illustrated in Figure 1 indicates that it is not the predominant form until the p[H] is above 9.

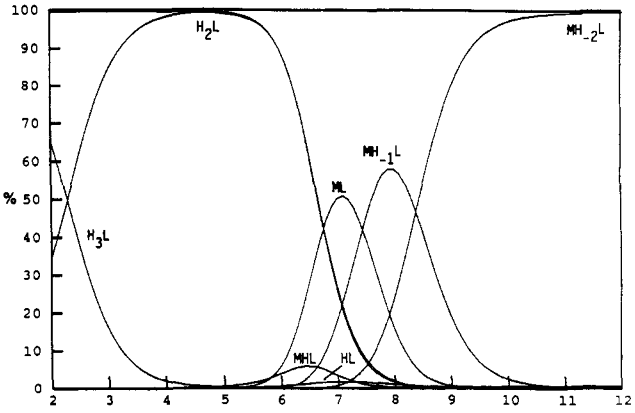

Figure 1. Species distribution curves for the system 3.5 × 10^{-3} M Ni(II) and PNOH at 25.0 °C and ionic strength 0.10 M (KCl). PNOH = L.

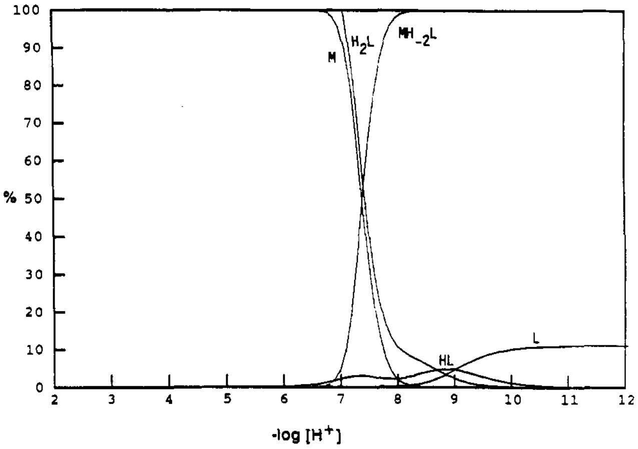

Figure 2. Species distribution curves for the system 0.0010 M PNOH, L, and 0.00090 Ni(II) assuming NiH$_{-2}$L to be the only complex species, at 35.0 °C and ionic strength 0.20 M (NaClO$_4$). Equilibrium constants from ref 1.

Potentiometric Measurements under Dioxygen. In contrast to the potentiometric data which resulted in the equilibrium constants in Tables I and II, potentiometric equilibrium curves could not be obtained for Co(II) and Ni(II) under dioxygen. Because of the sluggishness of the reactions of the macrocycles **1–3** with cobalt(II) and nickel(II) ions, each experimental point in the complex-forming buffer regions required considerable time, as expected from the anaerobic measurements. In the presence of dioxygen, however, before equilibrium was reached additional drifting of p[H] occurred and continued for long periods of time (several hours). This drifting, which is probably due to degradation of the dioxygen complexes formed, was especially rapid at low p[H] and was slower in the p[H] range 10–11.

Attempts were made to reproduce the titration data previously reported,[1] without success. For the 1:1 Ni(II)–PNOH system, a curve similar to that illustrated in Figure 2[1] was obtained with 20-min intervals between increments of base. However, quite different curves were obtained by allowing 40–80 min between p[H] readings (the resulting curves were displaced downward with distortion in shape), clearly demonstrating that such curves do not represent oxygenation equilibria but rather are indications of base uptake in a continuously changing system involving ox-

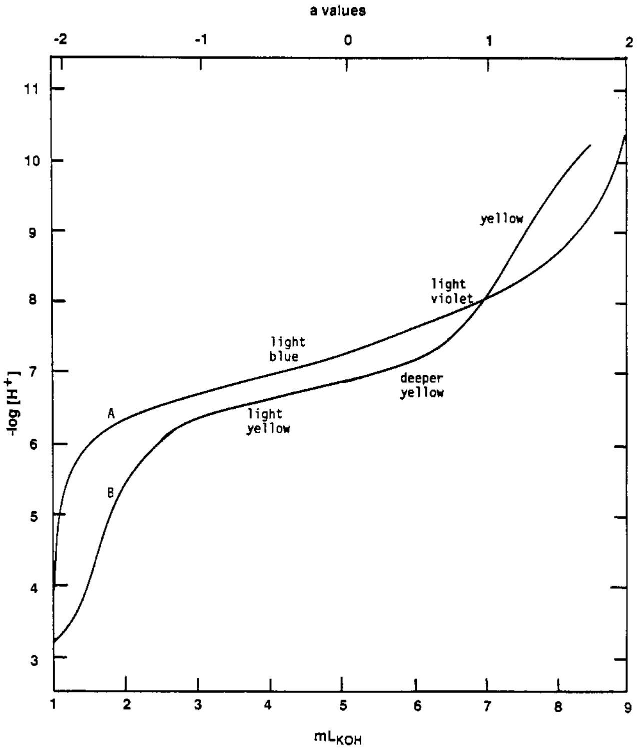

Figure 3. Potentiometric equilibrium curves for 1:1 molar ratio of PNOH and Ni(II) et 3.0×10^{-3} M concentration, 25.0 °C, and 0.10 M ionic strength (KCl): (A) potentiometric titration of anaerobic solution; (B) potentiometrric titration of the same solution after aeration for 2 h. a = moles of 0.1000 M KOH added per mole of ligand present.

ygenation equilibrium overlapping with irreversible degradation of the dioxygen complex formed to inert (non-oxygen carrying) products.

In order to further explore the potentiometric titration results, it was decided to compare anaerobic titrations of a solution before and after oxygenation. Curve A and Figure 3 was obtained by careful potentiometric p[H] measurement of 1:1 Ni(II)-PNOH in a strictly anaerobic solution and required 24 h. The relatively flat buffer region obtained is the equilibrium curve that was used to calculate the equilibrium constants presented in Table II. The color of this anaerobic solution was characteristic of octahedral nickel(II) complexes, changing from nearly colorless to light blue and then to light violet as the a values increased. At the end of the titration, above p[H] 10, the solution was oxygenated and underwent the color changes expected for dioxygen complex formation and degradation (violet → pink → brown → orange, over a 2-h period). The solution was then acidified (all color vanished) to $a = -2$, pH ~3.2, thoroughly deaerated, and titrated again under argon. The system was now even more sluggish, and 2 days were required to obtain an equilibrium curve (curve B, Figure 3). The deep yellow color that developed and the completely different curve obtained indicated that the ligand had been oxidized and that a low-spin (square planar) Ni(II) complex had formed. The curve obtained, however, is an equilibrium curve and was employed for approximate calculations on the stabilities of the new complexes formed.

In view of the fact that curve B represents a mixture of ligands, it was analyzed with the use of the program BEST[4] on the basis of some of the assumptions that the original ligand was still present and that the oxidized ligand still contained the two original amide groups and the three amino nitrogens, with pK's the same as those of the original ligand. On this basis, the refinement of the data indicated that more than half of the original ligand had become oxidized and that the complexes formed are $NiHL^{3+}$, $NiH_{-1}L^{+}$, and $NiH_{-2}L$, with log Q values of $[NiHL]/[H][L][Ni]$ 14.4, $[NiH_{-1}L][H]^2/[NiHL]$ -13.0, and $[NiH_{-2}L][H]/[NiH_{-1}L]$ -9.8. While the σ_{fit} for this determination was quite good (0.015), the assumptions made to accomplish the calculations certainly indicate that these Ni(II) interactions with the oxidized ligand (to be elucidated below) should be considered only as rough approximations.

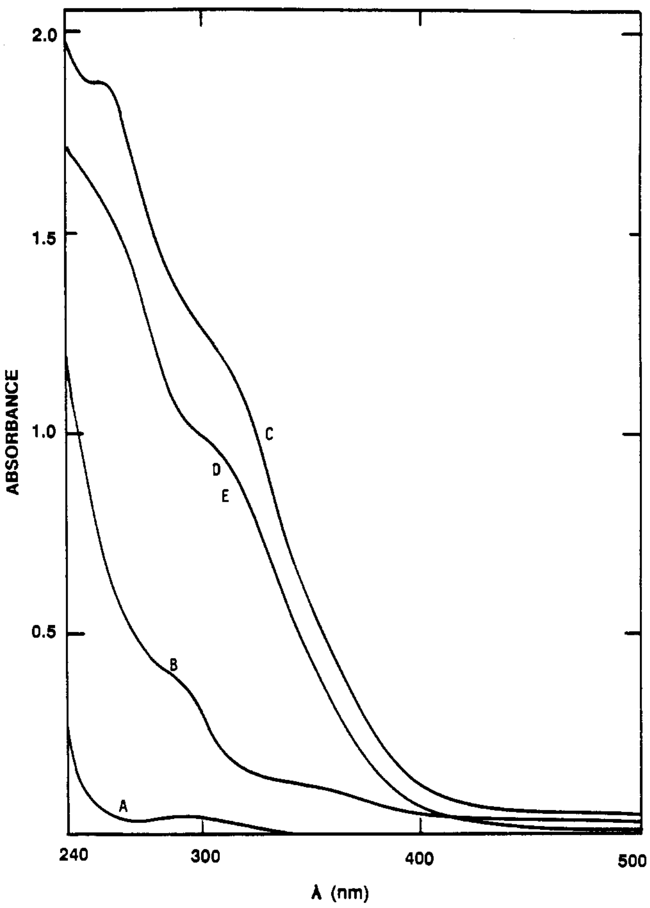

Figure 4. UV-vis absorbance spectra of a 1:1 molar ratio of Ni(II) to PNOH, 25.0 °C and μ = 0.10 M (KCl): (A) p[H] 2.20 under argon; (B) p[H] 10.21 under argon; (C) p[H] 10.21 under O_2 (1.5 h); (D) solution C at p[H] 10.19 under argon; (E) solution D at p[H] 10.19 under O_2.

Absorbance Studies. Absorbance measurements were made on the Co(II) and Ni(II) complexes of PNOH in order to obtain more information on the nature and rate of the oxidative degradation reactions of the complexes formed at high p[H]. The absorbance bands in Figure 4 demonstrate the changes that occur in the oxygenation of the Ni(II)-PNOH complex at p[H] 10.2. Curve A shows the weak anaerobic spectrum at low p[H] before the addition of base and is essentially that of the free aquo Ni(II) ion. Curve B, at p[H] 10.2, corresponds to the deprotonated Ni(II) complex, $NiH_{-2}L$. Introduction of dioxygen produces the large increase in absorbance indicated by curve C. The oxygenation reaction was nearly complete in 10 min, but the curve shown was obtained at 90 min. Acidification of the reaction mixture reproduced curve A, showing that all complexes present were more or less completely dissociated to free metal ion; however adjustment of p[H] to 10.2 under anaerobic conditions does not reproduce curve C but gives a spectrum D, which is much more intense than spectrum B and much weaker than curve C. Finally, reintroduction of dioxygen results in no further change in absorbance (curve E), showing that the end result of the first oxygenation produces a yellow Ni(II) complex that has no dioxygen affinity.

The absorbance spectra illustrated in Figure 5 show that the cobalt(II) complex of PNOH, $CoH_{-2}L$, oxygenates and degrades somewhat more rapidly than that of nickel(II). The absorbance curves in Figure 5 indicate that the maximum degree of cobalt dioxygen complex formation at p[H] 10.3 occurs in about 2 min and is followed by rapid conversion via metal-centered redox degradation to the inert Co(III) complex with a typical absorbance maximum at 530 nm. The complete conversion from the initial Co(II) complex to the final inert Co(III) complex took about 5

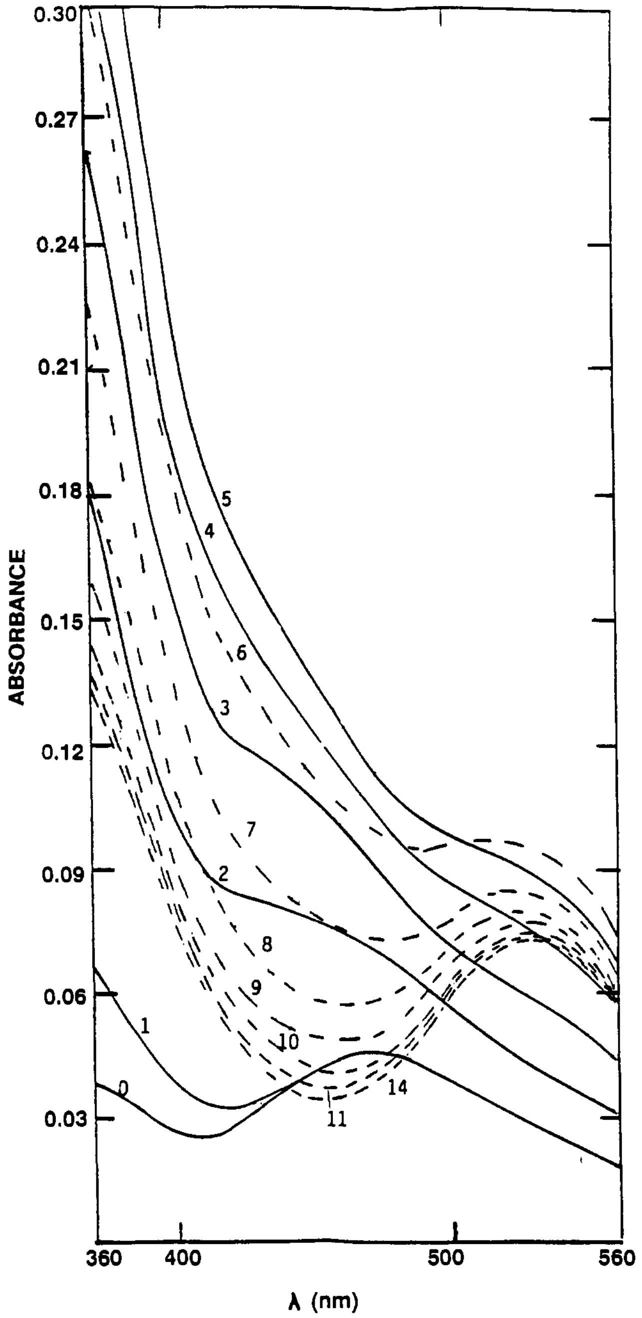

Figure 5. UV-vis absorbance spectra of a 3.0 × 10^{-4} M concentration of 1:1 molar ratios of PNOH and Co(II) at p[H] 10.30, 25.0 °C, and μ = 0.10 M (KCl). Curves were taken in the presence of dioxygen (except curve 0 taken under argon). Absorbances were measured at intervales of 22 s.

min. This reaction and the family of absorbance bands in Figure 5 resemble a similar oxidation of a cobalt(II) dipeptide complex to an inert cobalt(III) complex via dioxygen complex formation described by Harris et al.[6] It is noted that rapid degradation has been observed for many cobalt dipeptide dioxygen complexes having strongly coordinating negative nitrogen donors and that similar negative amide nitrogen donor groups are present in the Co(II) and Ni(II) macrocyclic complexes of PNOH, PNOET, and PNOBZ.

Dioxygen Sorption Measurements. It has been shown above that the potentiometric method cannot be used for determining oxygenation constants of these rapidly degrading systems because the measured quantity is hydrogen ion concentration (influenced by oxygenation). Thus the oxygenation reaction is linked to proton displacement through metal ion coordination, which is a slow process in the formation of complexes with these diamido macrocyclic ligands. Therefore it was decided to measure oxygenation quantitatively with the completely preformed complexes $MH_{-2}L$, at buffered high p[H], by the dioxygen sorption method previously described,[3] in which the volume of oxygen taken up and its partial pressure are measured as rapidly as possible.

Table III. Experimental Data Measured at Dioxygenation Equilibrium[a]

complex	t, °C	P_{O_2}, Torr	equilibrium O_2 sorption by carrier, mL	barometric pressure, Torr	vapor pressure H_2O, Torr
Co(II)–PNOH	5	142	1.90	761	7.0
0.0051 M	5	95	1.72	761	7.0
50 mL	5	73	1.63	761	7.0
	10	147	1.72	751	9.2
	10	120	1.61	751	9.2
	10	86	1.48	751	9.2
	15	146	1.54	761	13
	15	120	1.43	761	13
	15	97	1.33	761	13
Co(II)–PNOET	5	135	2.25	753	7.0
0.0051 M	5	93	2.12	753	7.0
50 mL	5	68	2.03	753	7.0
	10	132	2.05	757	9.2
	10	85	1.85	757	9.2
	10	57	1.71	757	9.2
	15	132	1.90	750	13
	15	75	1.66	750	13
	15	65	1.53	750	13
Co(II)–PNOBZ	20	131	2.05	756	18
0.0051 M	20	81	1.83	756	18
50 mL	20	65	1.70	756	18
	25	136	1.95	752	24
	25	100	1.81	752	24
	25	75	1.65	752	24
	30	143	1.73	750	32
	30	110	1.60	750	32
	30	85	1.45	750	32
Ni(II)–PNOH	5	117	5.55	756	7.0
0.0086 M	5	78	5.35	756	7.0
30 mL	5	54	5.15	756	7.0
	15	119	5.55	750	13
	15	80	5.30	750	13
	15	69	5.18	750	13
	25	117	5.50	752	24
	25	94	5.20	752	24
	25	71	4.93	752	24
Ni(II)–PNOET	15	45.0	5.400	756	13
0.0086 M	15	27.5	5.00	756	13
30 mL	20	55.0	5.40	762	18
	20	37.0	5.05	762	18
	25	73.0	5.50	764	24
	25	43.0	5.05	764	24
Ni(II)–PNOBZ	15	22.1	5.35	755	13
0.0086 M	15	27.3	5.50	755	13
30 mL	20	25.2	5.35	750	18
	20	38.0	5.55	750	18
	25	33.5	5.40	752	24
	25	45.0	5.60	752	24

[a] The Ni(II) complexes were measured in 0.050 M KCl and 0.050 M borate buffer solution at pH 9.4; the Co(II) complexes were measured in 0.050 M KCl and 0.050 M borate buffer solution at pH 9.0.

The experimental data obtained at dioxygenation equilibrium for the cobalt(II) and nickel(II) complexes of PNOH (**1**), PNOET (**2**), and PNOBZ (**3**) are presented in Table III. The dioxygen partial pressures for each temperature were selected so as to produce measurable values of dioxygen uptake. Also, the range of temperatures at 5-deg intervals was varied so as to produce easily measurable values of dioxygen adsorbed and partial pressure of dioxygen at equilibrium. Calculation of the partial pressure of dioxygen required knowledge of the barometric pressure as well as the vapor pressure of the solvent.

As noted above, the attainment of oxygenation equilibrium was of concern in the oxygen sorption measurements, because data needed to be recorded before an appreciable amount of degradation had taken place. In addition to the built-in precautions described in the Experimental Section, qualitative observations of the

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(6) Harris, W. R.; Bess, R. C.; Martell, A. E.; Ridgway, T. H. *J. Am. Chem. Soc.* **1977**, *99*, 2958.

Table IV. Thermodynamic Constants for Dioxygen Binding to Cobalt(II) and Nickel(II) Complexes in 0.05 M Borate Buffer Solution[a]

complex	stoichiometry of dioxygen complex	*t*, °C	log (K_{O_2}, mm^{-1})	$P_{1/2}$, mm	$\Delta H°$, kcal/mol	$\Delta S°$, eu
Ni(II)-PNOH	1:1	5	−0.95	8.9	−9	−40
		15	−1.2	15		
		25	−1.4	24		
Ni(II)-PNOET	1:1	15	−0.83	6.8	−10.9	−42
		20	−0.98	9.5		
		25	−1.10	13		
Ni(II)-PNOBZ	1:1	15	−0.57	3.7	−12.5	−46
		20	−0.71	5.1		
		25	−0.87	7.4		
Co(II)-PNOH	2:1	5	0.56	65	−15	−50
		10	0.33	92		
		15	0.14	140		
Co(II)-PNOET	2:1	5	0.98	21	−16.9	−56
		10	0.70	39		
		15	0.48	65		
Co(II)-PNOBZ	2:1	20	0.60	49	−18.6	−61
		25	0.43	73		
		30	0.18	130		

[a] The Ni(II) complexes were measured in 0.05 M KCl and 0.05 M borate buffer solution at pH 9.4; the Co(II) complexes were measured in 0.05 M KCl and 0.05 M borate buffer solution at pH 9.0.

characteristic absorbance of the dioxygen complexes were employed. When air was passed through a solution of the complexes $NiH_{-2}L$, under the conditions of the dioxygen sorption studies (p[H] 9.4), the color changed from purple to dark brown and then to yellow. For PNOH the dark brown color, characteristic of the dioxygen complexes lasted several (5–10) minutes. For the PNOET system it persisted for about 1 h, while for PNOBZ it lasted 4 h. The observations with the cobalt(II) complexes were analogous, with the changes occurring more rapidly (compare Figures 4 and 5), so that for all systems the rates of degradation of the dioxygen complexes varied in the order PNOH > PNOET > PNOBZ.

The values of log K_{O_2} and $P_{1/2}$ were calculated from the data in Table III with the aid of eq 2–5 and are listed in Table IV. The heats of oxygenation were determined from Van't Hoff plots. Entropies of oxygenation were obtained by the corresponding $\Delta G°$ and $\Delta H°$ values in the usual manner (see ref 3).

Degradation Product Analysis and $^{18}O_2$ Tracer Study. The oxidized ligand samples obtained from the product recovery described in the Experimental Section were analyzed by ^{13}C NMR spectroscopy. The spectrra of all three ligands had new strong resonances at 78.6, 80.5, and 87.7 ppm (relative to TMS) for PNOBZ, PNOET, and PNOH, respectively. These peaks are assigned to the group R–(C<)–OH, where R = benzyl, ethyl, and H, respectively, and < represents the ring structure from either side. For PNOH, the ^1H NMR spectrum showed a new single resonance at 4.5 ppm, which disappeared after addition of D_2O, so that it represents the active H of R–(C<)–OH. Mass spectral data of the degraded ligand samples gave the molecular ions 363 (PNOBZ), 301 (PNOET), and 273 (PNOH), all of which are 16 mass units above those of the original ligands. These data clearly indicate the insertion of an oxygen atom in the ligand at the 15-position. A preliminary communication announcing this ligand hydroxylation reaction has been published.[7]

In order to further confirm the oxygen insertion reaction, the degradation product analysis was carried out on the Ni(II)–PNOBZ complex in the same manner as the $^{16}O_2$ oxygenation products, but with $^{18}O_2$ as the only source of dioxygen. The mass spectral analysis gave a molecular weight of 365 (rather than 363 for the $^{16}O_2$ reaction), definitely demonstrating that the inserted oxygen came from the gaseous dioxygen via the dioxygen complex.

Discussion

In general, the oxygenation constants in Table IV show that the cobalt dioxygen complexes are of a different type (2:1) and are more thermodynamically stable (although kinetically more rapidly degraded) than the corresponding (1:1) nickel dioxygen complexes with the same ligand, a fact that is also reflected in the enthalpies of dioxygen complex formation. The stabilities of the dioxygen complexes of both metal ions seem to follow the normal pattern observed for all dioxygen complexes reported in the literature,[8] in that the driving force is a large negative $\Delta H°$, resulting from metal–dioxygen coordinate bond formation and an increase in the strengths of the metal–ligand coordinate bonds as the effective charge on the metal ion increases as a consequence of partial electron transfer to coordinated dioxygen.[9] In no case was the oxygenation reaction found to be endothermic, as reported previously.[1a] The large negative value of $\Delta S°$ resulting from the oxygenation process is also normal for dioxygen complex formation. The main contributions to the negative $\Delta S°$ values are the loss of translational entropy of free dioxygen and the loss of translational and vibrational freedom of the coordinated ligand as its coordinate bonds to the metal are strengthened and tightened up as the result of oxygenation. It is noted that the more favorable the $\Delta H°$ of oxygenation, the more unfavorable is the corresponding entropy change. This is now a familiar trend that has been observed for many coordination compounds; i.e., increasing the strength of the coordinates bonds causes an unfavorable entropy of reaction, which is due to loss of internal vibrational and rotational freedom in the complex relative to those of the less stable complex.

Another interesting effect that may be seen from the results in Table IV is that substitution at the 15-position of the ligand increases dioxygen affinity, although substitution does not significantly influence the stability constants[1] of the dioxygen-free complex. Generally, increases in metal chelate stability parallel increases in ligand basicity and corresponding increases in dioxygen affinity, as has been observed for many cobalt complexes.[9] On this basis one would expect dioxygen affinities to vary in the order PNOH > PNOET > PNOBZ, to parallel the trend in sums of the ligand protonation constants (Table I).

The reversal of this trend must be due to a special property of the dioxygen complex. It is notable that this effect, observed for both log K_{O_2} and $\Delta H°$ values, is especially pronounced for the benzyl derivative. It is suggested here that this substituent may help stabilize the 1:1 dioxygen complex by providing a hydrophobic environment, as indicated by the suggested configuration for the benzyl-substituted Ni(II) complex, illustrated by formula **4**.

It should be pointed out that Machida et al.[1f] reported the formation of a Ni(II) complex similar to **4**, in which the superoxide

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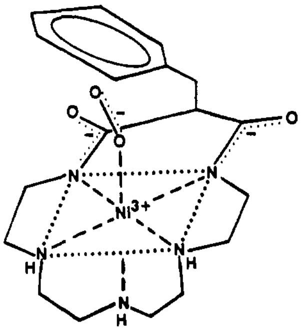
(7) Chen, D.; Martell, A. E. *J. Am. Chem. Soc.* **1990**, *112*, 9411.

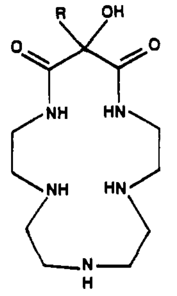
(8) Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984**, *84*, 137.

(9) Martell, A. E. *Acc. Chem. Res.* **1982**, *15*, 155.



4 Dioxygen complex of Ni(II)-PNOBZ

$Ni(O_2)H_{-2}L''$



5 Hydroxylated ligands

R = H, CH_3CH_2, $C_6H_5CH_2$

is replaced by a coordinated water molecule, by air oxidation of the Ni(II) complex of **3**. Presumably it was formed by the decomposition of the intermediate dioxygen complex, **4**. Its existence as a stable complex was considered due to the stabilizing influence of the macrocyclic ring; however, it was noted that considerable ligand degradation took place simultaneously, probably resulting from the oxidation by the coordinated superoxide group.

The differences in the rates of degradation of the Ni(II) dioxygen complexes described in the Results may be ascribed to the protective effects of the alkyl and aralkyl groups on the coordinated dioxygen, which may be considered formally as $Ni^{3+}–O_2^{\bullet-}$, stabilized by the microscopic hydrophobic environment. On the other hand, the Ni(II) complexes of the hydroxylated ligands **5** show no tendency to combine with dioxygen. Thus it seems that the highly polar, hydrophilic hydroxyl group in the oxidized ligands has a destabilizing effect on coordinated superoxide. Both observations, therefore, seem to be in accord with the concept that metal–superoxide complexes are stabilized by hydrophobic environments.

While the new Ni(II) dioxygen complexes are interesting in that another metal ion has been added to the list of metals whose complexes function as dioxygen carriers, they do not seem to offer any particular advantages over the oxygen carriers formed from other metal ions and in particular from the versatile Co(II) oxygen carriers. The main problems seem to be slow reactions of the nickel(II) complexes with dioxygen and a propensity toward degradation to inert complexes. The possibilities of using nickel dioxygen complexes as oxidants for organic substrates have not yet been explored, however, and they very well may be effective for the activation of dioxygen in redox processes.

The most significant result of this research is the discovery that Ni(II) sufficiently activates coordinated dioxygen to promote oxygen insertion into the ligand, which is also coordinated to the metal ion. Dioxygen complexes of nickel are themselves unusual in that very few have been reported previously. These complexes have a 1:1 metal:dioxygen ratio and are reasonably assumed to be of the superoxo type, which may be written formally as $Ni^{3+}{-}{-}{-}^{-}O{-}O^{\bullet}$. Oxidation of Ni(II) to the 3+ state requires a strong ligand field, provided by the negative deprotonated amide nitrogen donors **4**.

The ligand hydroxylation products, **5**, were obtained in high yields, indicating that for these nickel dioxygen complexes oxygen insertion into the ligand is the main reaction pathway. The hydroxylation of benzene to phenol under similar reaction conditions was reported by Kimura[1b,e,f] with a 40% yield based on the "amount of complex used". This report is somewhat ambiguous, in that it could mean that the hydroxylated product was estimated on the basis of the loss of the dioxygen complex or that the yield of phenol was based on the amount of dioxygen complex present rather than the amount of benzene employed. If the former, the benzene-hydroxylated yield was probably much less than 40% because there are other routes for dioxygen complex degradation (e.g., ligand degradation). If the latter, then the total hydroxylation yield (including ligand hydroxylation) is more than 100% of the amount of dioxygen complex employed. This possibility will be discussed below. In any case, the results of this study show that ligand hydroxylation is the major reaction pathway and occurs to a greater extent than aromatic substrate hydroxylation. In the absence of the aromatic substrate, it seems to be the only pathway for dioxygen complex degradation.

The ligand hydroxylation reaction may be visualized as occurring through the following reaction sequence:

$$Ni^{2+} + L \rightleftharpoons NiH_{-2}L + 2H^+$$

$$NiH_{-2}L \overset{O_2}{\rightleftharpoons} Ni^{III}H_{-2}L(O_2^-) \rightarrow Ni^{II}(H_{-2}LO) + O \text{ or } \tfrac{1}{2}O_2$$

Thus it seems that formation of the Ni(II) complex of the hydroxylation product results in the release of half of the dioxygen for further reaction with a substrate or as free dioxygen. In a recent oral presentation, Kimura[10] described aromatic hydroxylation by Ni(II) dioxygen complexes as an "intermolecular pathway", which would be competitive with ligand hydroxylation, termed an "intramolecular pathway", for the oxygenation process, and that the latter would mitigate the catalytic activity of the more useful intermolecular oxygenation process. It is certain that ligand hydroxylation forms a complex incapable of combining with and activating dioxygen, thus reducing the extent of substrate hydroxylation that can occur. It has not yet been demonstrated that the intermolecular reaction pathway is catalytic in nature of whether it is a mono- or dioxygenase type of reaction. The yields of 40% for the intermolecular reaction and 85% for the intramolecular pathway, however, suggest still another reaction sequence for substrate oxygenation, whereby the intermolecular oxygenation would be accompanied by the intramolecular reaction, as follows:

$$Ni^{III}H_{-2}L(O_2^-) + C_6H_6 \rightarrow Ni^{II}(H_{-2}LO) + C_6H_5OH$$

Further detailed studies of these systems are needed to sort out the possible reaction sequences and determine whether or not a catalytic oxygenation process can occur.

The results of this work may be summarized as follows: (1) the Ni(II) complexes of dioxopentaazamacrocyclic ligands form short-lived dioxygen adducts, as do their Co(II) analogues; (2) the dioxygen affinities of the Co(II) complexes are considerably higher than the corresponding Ni(II) complexes: (3) under ambient conditions the Ni(II) and Co(II) dioxygen complexes formed with these ligands degrade too rapidly to allow recycling of oxygenation and deoxygenation; (4) dioxygen complex formation is strongly exothermic and involves large negative entropy changes; (5) the Ni(II) dioxygen complexes hydroxylate the coordinated ligands at the 15-position (between the amide carbonyl groups); (6) degradation of the Co(II) dioxygen complexes results in the formation of inert Co(III) complexes of the unchanged ligands; (7) substitution of alkyl and aralkyl groups at the 15-position slows the rates of degradation of the dioxygen complexes of both Co(II) and Ni(II); (8) substitution of polar hydrophilic groups in the 15-position tends to inhibit Ni(II) dioxygen complex formation. These results, taken together with those of Kimura et al.,[1a,b,e,f] indicate that nickel dioxygen complexes probably constitute a fruitful area for the future study of model oxygenase systems.

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(10) Kimura, E. 200th National Meeting of the American Chemical Society, Washington, DC, Aug 28, 1990; Paper No. INOR0090.