here give clear evidence for a change in sign of CD bands due to replacement of H by another substituent on an asymmetric nitrogen donor atom. Also although the asymmetric donor nitrogens make significant contributions to the intensity of individual CD bands, their contribution to the net rotatory strength of the compounds reported is quite small. By contrast, the contribution to the net rotatory strength from the configuration of chelate rings is relatively large.

Registry No. Ethylenediamine-*N,N′,N′*-triacetic acid, 688-57-3; potassium nitro(ethylenediaminetriacetato)cobaltate(III), 24651-89-6; silver nitro(ethylenediaminetriacetato)cobaltate(III), 39556-12-2; *N,N′*-dibenzylethylenediaminediacetic acid, 39556-13-3; $(+)_{546}$-[Co(en)$_2$ox]Br·H_2O, 31126-56-4; Na-$(+)_{589}$-[Co(ED3A)NO_2]·H_2O, 39556-15-5; Na[Co(ED3A)NO_2]·$2H_2O$, 39556-16-6; Ag[Co(BED3A)NO_2], 39556-17-7; Na-$(-)_{589}$-[Co(BED3A)NO_2]·$2H_2O$, 39561-41-6; *s*-[Co(DBEDDA)en]Cl·$4H_2O$, 39556-19-9; $CoCl_2 \cdot 6H_2O$, 7791-13-1; $(+)_{546}$-[Co(DBEDDA)en]Cl·$4H_2O$, 39556-20-2; Na-$(-)_{546}$-[Co(ED3A)NO_2]$^-$, 39561-40-5; Na-$(+)_{546}$-[Co(BED3A)NO_2]$^-$, 39556-18-8; $(-)_{546}$-[Co(DBEDDA)en]Cl, 39561-39-2.

Acknowledgments. Financial support for this research was provided by the University Science Development Program (GU3184) to C. W. M. and by The Pennsylvania State University to C. M. The authors thank Miss Judy Ferencz for preparation of optically active starting materials.

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Study of the Reaction of Some Cobalt Nitrosyl Complexes with Oxygen[1]

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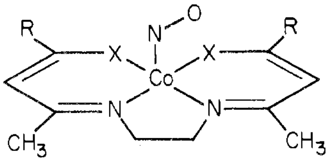
Received January 3, 1973

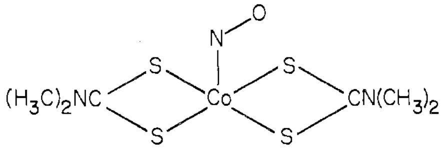
Several cobalt nitrosyl complexes, CoL_4NO, reacted with oxygen in the presence of nitrogen and phosphorus bases to yield the corresponding nitro compounds, $CoL_4(NO_2)B$, where L_4 is the tetradentate dianions *N,N′*-ethylenebis(acetylacetoniminate), *N,N′*-ethylenebis(monothioacetylacetoniminate), *N,N′*-ethylenebis(benzoylacetoniminate), *N,N′*-ethylenebis(salicylideniminate), and two bidentate dimethyldithiocarbamate anions. Exposing an acetonitrile solution of nitrosylbis(ethylenediamine)cobalt diperchlorate to oxygen resulted in the precipitation of $[Co(en)_2(CH_3CN)NO_2](ClO_4)_2$. The nitro products, $CoL_4(NO_2)B$ [where B = pyridine, $C_3H_7NH_2$, and $P(CH_3)_2(C_6H_5)$] and $[Co(en)_2(CH_3CN)NO_2](ClO_4)_2$ were isolated and characterized by elemental analyses and infrared, proton magnetic resonance, and electronic spectra. Kinetic studies revealed that the rates of reaction have a first-order dependence on the concentrations of oxygen and the cobalt nitrosyl complexes. The reaction rates increase with increasing base concentration but reach a limiting rate at high base concentrations. A possible mechanism for the reaction is proposed and discussed.

Introduction

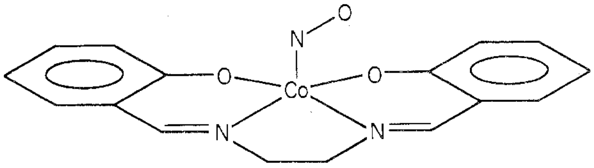
Recently, several authors[2-4] have reported that certain nitrosyl compounds are converted to metal-nitro products in the presence of oxygen. All that was reported was the nature of the products of these reactions. This paper describes in more detail the observations we reported[5] earlier on the reaction of several cobalt nitrosyl complexes with oxygen. The structures and symbols for the complexes are represented as follows.



Co(acacen)NO: R = CH_3, X = O
Co(benacen)NO: R = C_6H_5, X = O
Co(sacsacen)NO: R = CH_3, X = S



$Co(dtc)_2NO$



Co(salen)NO

Experimental Section

Solvents. Except for the solvents used in the kinetic studies, the solvents were obtained commercially and used without further purification. Deoxygenated solvents were obtained by bubbling N_2 through the solvent for at least 30 min before use. The solvents used in the kinetic studies were ACS reagent grade, and they were distilled prior to use.

Materials. The reagents[6] PPh_3, $P(C_6H_{11})_3$, $P(OPh_3)_3$, 4-NH_2py, imidazole, $Co(C_2H_3O_2)_2 \cdot 4H_2O$, and Na(dtc) were obtained commercially and used without further purification. The reagents PEt_3, PBu_3, $PEtPh_2$, PMe_2Ph, $P(OBu)_3$, py, 2-Me(py), 3-Me(py), 4-Me(py), 2,4,6-Me_3py, $C_3H_7NH_2$, (*i*-Pr)$_2$NH, Et_3N, 1-methylimidazole, and 1,2-dimethylimidazole were obtained commercially and distilled prior to use. The 4-CNpy was obtained commercially and recrystallized from ethanol before use. The nitric oxide (Matheson) was purified by passage through a Dry Ice-acetone bath and a tower of

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[1] (a) Abstracted from the Ph.D. thesis of S. G. Clarkson, Northwestern University, 1972. (b) Presented in part at the XIVth International Conference on Coordination Chemistry, Toronto, June 1972; see *Proc. Int. Conf. Coord. Chem.*, 14, 193 (1972).

[2] G. R. Clark, K. R. Grundy, W. R. Roper, J. M. Waters, and K. R. Whittle, *J. Chem. Soc., Chem. Commun.*, 119 (1972).

[3] (a) T. I. Shimyama and T. Matsumura, *Annu. Rep. Radiat. Cent. Osaka Prefect.*, 11, 50 (1970); (b) T. I. Shimyama and T. Matsumura, *Radioisotopes*, 20, 367 (1971).

[4] M. Tamaki, I. Masuda, and K. Shinra, *Bull. Chem. Soc. Jap.*, 45, 171 (1972).

[5] S. G. Clarkson and F. Basolo, *J. Chem. Soc., Chem. Commun.*, 670 (1972).

[6] Symbols used are Ph = C_6H_5, py = pyridine, Et = C_2H_5, Bu = *n*-C_4H_9, Me = CH_3, Pr = *n*-C_3H_7, and *i*-Pr = *i*-C_3H_7.

KOH pellets. The oxygen (Matheson) and nitrogen (Matheson, prepurified) were used without further purification.

The quadridentate ligands acacenH_2,[7] benacenH_2,[8] and salenH_2[9] were prepared by modifications of the literature methods. The sacsacenH_2 was a generous gift from Dr. J. L. Corbin of Kettering Research Laboratories Inc.

Preparation of Cobalt Complexes. All the nitrosyl complexes were prepared in the absence of oxygen, in an atmosphere of nitrogen. The nitrosyl complexes Co(acacen)NO,[10] Co(benacen)NO,[10a] Co(salen)NO,[11] Co(dtc)$_2$NO,[12] and Co(en)$_2$NO(ClO$_4$)$_2$[13] were prepared by published methods. All the cobalt nitrosyl compounds are stable in air in the solid state.

Co(sacsacen)NO. A mixture of 1.0 g of sacsacenH_2 and excess Co($C_2H_3O_2$)$_2\cdot 4H_2O$ (1.25 g) was suspended in methanol (50 ml) at room temperature. Nitric oxide (purified as stated previously) was bubbled through the suspension. Within a few minutes the brick red suspension darkened to black. After 1 hr the bubbling of NO was ceased, and the solid was collected on a filter. The black product was washed with methanol (two 10-ml portions) and dried *in vacuo* at room temperature; yield 1.14 g (85%). *Anal.* Calcd for $CoC_{12}H_{18}N_3OS_2$: C, 42.00; H, 5.28; N, 12.24. Found: C, 41.68; H, 5.20; N, 11.95.

This compound exhibited a strong sharp absorption in the infrared spectrum (KBr disk) at 1638 cm^{-1} which was assigned to the N–O stretch, since the N–O stretch of known corresponding compounds occurs in this region (see Table I).

Reactions of the Cobalt Nitrosyl Complexes with Oxygen. All of the nitro products obtained by the reaction of the cobalt nitrosyls and base with oxygen are stable in the solid state and also fairly stable in solution.

Co(acacen)(NO$_2$)py. Air was bubbled through 30 ml of acetone containing 1.0 g of Co(acacen)NO and 4 ml of pyridine at room temperature. Passage of the air was continued until the solvent had completely evaporated, leaving a solid residue. The solid was dissolved in acetone (20 ml), and the solution was passed through a filter. The filtrate was reduced in volume by blowing air over it at room temperature. As the solvent evaporated, brown crystals formed. The product was collected on a filter, washed with diethyl ether, and air-dried; yield 0.99 g (76%). *Anal.* Calcd for $CoC_{17}H_{23}N_4O_4$: C, 50.25; H, 5.70; N, 13.79. Found: C, 49.92; H, 5.69; N, 13.47.

The ir spectrum (KBr disk) of the nitro product did not contain a band in the cobalt nitrosyl N–O stretching region (1600–1650 cm^{-1}), but new bands had appeared at 1312, 1208, and 812 cm^{-1}. The pmr spectrum of CDCl$_3$ solution of the product exhibited resonances characteristic of pyridine at τ 2–3.

Co(acacen)(NO$_2$)$C_3H_7NH_2$. This nitro compound was prepared in an analogous manner to that used for Co(acacen)(NO$_2$)py. *Anal.* Calcd for $CoC_{15}H_{27}N_4O_4$: C, 46.63; H, 7.04; N, 14.50; O, 16.56; Co, 15.25. Found: C, 46.75; H, 6.90; N, 14.49; O, 16.54; Co, 15.38.

Co(acacen)(NO$_2$)PMe$_2$Ph. A methanol solution (20 ml) of Co(acacen)NO (0.5 g) and 1 ml of PMe$_2$Ph was exposed to air for several weeks at room temperature. During this period all of the liquid evaporated leaving a dark residue. As was the case with other phosphorus bases and other cobalt nitrosyl complexes, a product could not be isolated unless all the liquid was first allowed to evaporate. Consequently, the product could not be purified by recrystallization. *Anal.* Calcd for $CoC_{20}H_{29}N_3O_4P$: C, 51.61; H, 6.28; N, 9.02. Found: C, 51.11; H, 6.32; N, 8.66.

The ir spectrum (KBr disk) of the nitro product did not have the original cobalt nitrosyl N–O stretching band, but it had new bands at 1318, 1220, and 814 cm^{-1}. The pmr spectrum of a CDCl$_3$ solution of the compound had a resonance at τ 7.87 and resonances characteristic of a phenyl group at τ 2.5–3.5. The uv-visible spectrum of an acetone solution of the product was almost identical in the 300–600-nm range as that of an acetone solution of Co(acacen)(NO$_2$)py containing excess PMe$_2$Ph.

Table I. Nitrosyl Stretching Frequencies and Some Co–N–O Bond Angles for Several Cobalt Nitrosyl Compounds

Complex	Co–N–O, deg	ν N–O, cm^{-1}
trans-[Co(en)$_2$(NO)Cl]$^+$	124[a]	1611[b]
Co(en)$_2$NO(ClO$_4$)$_2$		1663[b]
Co(dtc)$_2$NO	134[c]	1626[d]
Co(acacen)NO	122[e]	1654[f]
Co(benacen)NO	123[e]	1635[g]
Co(sacsacen)NO		1638[h]
Co(salen)NO		1624[i]
Co(dmgH)$_2$NO		1641[j]

[a] D. A. Snyder and D. L. Weaver, *Inorg. Chem.*, 9, 2760 (1970). [b] Reference 13. [c] Reference 12. [d] F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952). [e] R. Weist and R. Weis, *J. Organometal. Chem.*, **30**, C33 (1971). [f] Reference 10. [g] Reference 10a. [h] This work. [i] Reference 11. [j] Reference 4. dmgH is the dimethylglyoximate anion.

Co(benacen)(NO$_2$)py. Air was bubbled through an acetone suspension (15 ml) of Co(benacen)NO (0.35 g) and 2 ml of pyridine at room temperature. After 20 min of bubbling air through the solution, the solid had dissolved and the product was precipitated by the addition of pentane (50 ml). The reddish brown solid was collected on a suction filter, washed with pentane, and air-dried; yield 0.36 g (84%). *Anal.* Calcd for $CoC_{27}N_4O_4$: C, 61.13; H, 5.13; N, 10.56; O, 12.06. Found: C, 61.11; H, 5.44; N, 10.63; O, 12.01.

The ir spectrum (KBr disk) of the product did not exhibit the original nitrosyl N–O stretch, but it had new bands at 1325 and 826 cm^{-1}. The region around 1200 cm^{-1} was masked by ligand absorptions. A pmr spectrum of a CDCl$_3$ solution of the product showed resonances characteristic of pyridine.

Co(salen)(NO$_2$)py. Air was bubbled through a CHCl$_3$ solution (20 ml) of Co(salen)NO (0.5 g) and 2 ml of pyridine at room temperature. Bubbling of air was continued until most of the solvent had evaporated, which resulted in precipitation of the brown product. The solid was collected on a filter, washed with pentane, and air-dried; yield 0.58 g (76%). *Anal.* Calcd for $CoC_{21}H_{19}N_4O_4$: C, 56.00; H, 4.22; N, 12.43. Found: C, 55.97; H, 4.43; N, 11.96.

The ir spectrum (KBr disk) of the product had no N–O stretch in the 1600-cm^{-1} region, but new bands appeared at 1412, 1213, and 840 cm^{-1}.

Co(sacacen)(NO$_2$)py. A solution of 30 ml of acetone, 2 ml of pyridine, and 0.19 g of Co(sacacen)NO was exposed to the air for several hours at room temperature. During this time most of the solvent evaporated and a brown solid precipitated. The product was collected on a suction filter, washed with diethyl ether, and air-dried; yield 0.15 g (65%). *Anal.* Calcd for $CoC_{17}H_{23}N_4O_2S_2$: C, 46.57; H, 5.25; N, 12.78; O, 7.30; S, 14.63; Co, 13.44. Found: C, 45.84; H, 5.24; N, 12.04; O, 10.30; S, 12.60; Co, 13.04.

The ir spectrum (KBr disk) of the product did not exhibit the original nitrosyl N–O stretch, but new bands appeared at 1300 and 804 cm^{-1}. The region around 1200 cm^{-1} was masked by ligand absorptions. The solid was not sufficiently soluble for a pmr spectrum.

Co(dtc)$_2$(NO$_2$)py. An acetone solution (20 ml) containing 2 ml of pyridine and 0.5 g of Co(dtc)$_2$NO was exposed to air at room temperature for several hours. During this time most of the solvent evaporated and a green solid precipitated. The product was collected on a suction filter, washed with diethyl ether, and air-dried; yield 0.47 g (73%). *Anal.* Calcd for $CoC_{11}H_{17}N_4O_2S_4$: C, 31.11; H, 4.08; N, 13.19. Found: C, 30.95; H, 4.07; N, 12.97.

The ir spectrum (KBr disk) of the product exhibited no nitrosyl N–O stretch, but had new bands at 1308, 1214, and 816 cm^{-1}.

[Co(en)$_2$(CH$_3$CN)NO$_2$](ClO$_4$)$_2$. Exposure of an acetonitrile solution (10 ml) of Co(en)$_2$NO(ClO$_4$)$_2$ (0.5 g) to air resulted in precipitation of a solid within 30 min. After 1 hr the yellow-brown product was collected on a filter, washed with acetone and acetonitrile, and air-dried. The product was recrystallized from acetone; yield 0.46 g (86%). *Anal.* Calcd for $CoC_6H_{19}N_6O_{10}Cl_2$: C, 15.49; H, 4.12; N, 18.07. Found: C, 15.36; H, 4.48; N, 17.61.

The ir spectrum (KBr disk) of the product did not exhibit a nitrosyl N–O stretch. The regions around 1300 and 1200 cm^{-1} were masked by ligand absorptions, but a new band appeared at 828 cm^{-1}. There were also C≡N stretches at 2241, 2295, and 2330 cm^{-1}. The pmr spectrum of the solid in D$_2$O initially exhibited singlet resonances at τ 1.5 and 2.1 upfield from the HDO resonance. The resonance at τ 2.1 slowly decreased in intensity and a new permanent resonance

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(12) J. H. Enemark and R. D. Feltham, *J. Chem. Soc., Dalton Trans.*, 718 (1972).

(13) R. D. Feltham and R. S. Nyholm, *Inorg. Chem.*, **4**, 1334 (1965).

appeared at τ 2.6. The resonance at τ 2.6 was in a ratio of 3:8 to the resonance at τ 1.5. An aqueous pH 4 solution of $[Co(en)_2(CH_3CN)NO_2](ClO_4)_2$, after several hours, had the same uv-visible spectrum as that of *trans*-$[Co(en)_2(NO_2)H_2O]^{2+}$.[14]

Kinetic Studies. The rates of reaction of the CoL_4NO complexes with oxygen were followed by monitoring the change in optical density of the solution by means of a Cary 14 spectrophotometer equipped with a thermostated cell holder and a variable-speed recorder. The cell holder temperature was regulated so that the solution in the cell was at 25° (±0.2°). The procedure was to set the spectrophotometer at the wavelength which gave the greatest spectral change during the reaction and vary the speed of the recorder to accommodate the reaction rate. The reaction of Co(acacen)NO with oxygen in the presence of all nitrogen bases was followed at 380 nm, and the wavelengths used to study the other reactions are listed in Table II. All the reactions were carried out with at least a 20-fold excess of the base over the concentration of the complex. Since the concentration of the complex was generally $(1.5-2.8) \times 10^{-4}$ *M* and the Ostwald coefficient[15] for the solubility of oxygen in acetone gives a concentration of 2.4×10^{-3} *M* at 750 Torr and 298°K, the reactions were run under pseudo-first-order conditions with respect to the cobalt complex.

Plots of $\ln (A_t - A_\infty)$ [$\ln (A_\infty - A_t)$ for absorbance increases] *vs.* time, where A_t is absorbance at time *t* and A_∞ is absorbance at infinite reaction time, showed excellent linearity for at least 3 half-lives. The rate constants were reproducible to within ±10%.

Oxygen Dependence on the Reaction Rate. The dependence of the reaction rate on the concentration of oxygen was determined by using the special cell depicted in Figure 1. A weighed amount of Co(acacen)NO was placed in cuvette E and a measured volume (usually 15 ml) of an acetone solution containing a known concentration of pyridine was put in bulb D. Tap A was closed and the cell was connected to a vacuum line, with a manometer, by joint B. The solution in bulb D was cooled to −78° in a Dry Ice–acetone bath. Then tap A was opened and the cell was evacuated. Tap A was then closed and oxygen gas was introduced into the line. Then tap A was opened and the pressure of oxygen in the line and the cell was determined by reading the manometer. Tap A was closed and the solution in bulb D was warmed to 25°. The cell was disconnected from the vacuum line and the solid was dissolved by tipping the cell so that the liquid spilled over into cuvette E. The cell was quickly inserted into the spectrophotometer, and the rate of reaction was monitored. Since Co(acacen)NO quickly dissolves in acetone, good kinetic data were obtained.

Oxygen Uptake Measurements. The oxygen consumption experiments were performed using the special cell shown in Figure 1. A weighed amount of Co(acacen)NO or $Co(en)_2NO(ClO_4)_2$ was placed in cuvette E and a volume of pyridine solution [acetonitrile for $Co(en)_2NO(ClO_4)_2$] was placed in bulb D. The solution was thoroughly degassed and frozen in liquid nitrogen. The cell was connected to an automatic Toepler pump which contained an amount of oxygen that had been estimated from *PVT* measurements assuming the ideal gas law. After allowing 20 min for equilibration, tap A was closed and the oxygen remaining in the line was collected and measured. The solid in cuvette E was dissolved after allowing the liquid in bulb D to melt. During the next hour the cell was agitated periodically to aid the reaction. Then the solution was transferred to bulb D and frozen in liquid nitrogen. The oxygen remaining in the cell was collected and measured. The amount of oxygen consumed was determined by subtracting the amount collected from the original amount.

Physical Measurements. The ir spectra were recorded on a Perkin-Elmer 337 grating spectrophotometer. The samples were prepared as KBr disks, as Nujol mulls, or in solutions in 0.2-mm CaF_2 matched cells. The electronic spectra were recorded on a Cary 14 spectrophotometer using matched quartz cells or in the special cell depicted in Figure 1. Proton nmr spectra were recorded on a Varian Associates Model T-60 spectrometer.

Table II. Wavelengths at Which the Reactions of the CoL_4NO Compounds with Oxygen and Base Were Monitored

Compd	Base	λ, nm
Co(acacen)NO	PEt_3	462
Co(acacen)NO	PBu_3	462
Co(acacen)NO	PMe_2Ph	475
Co(acacen)NO	$PEtPh_2$	530
Co(acacen)NO	$P(OBu)_3$	445
Co(benacen)NO	py	335
Co(benacen)NO	PBu_3	440
Co(salen)NO	py	340
Co(salen)NO	PBu_3	442
$Co(dtc)_2NO$	py	368
$Co(dtc)_2NO$	PBu_3	338
Co(sacsacen)NO	PBu_3	453

Table III. Oxygen Consumption in the Reaction of $Co(en)_2NO(ClO_4)_2$ and Co(acacen)NO with Oxygen in the Presence of a Base at Room Temperature

Compd	Mol of compd	Mol of O_2 consumed	Mol of O_2 consumed/ Mol of compd
$Co(en)_2NO(ClO_4)_2$[a]	1.38×10^{-4}	6.6×10^{-5}	0.48
$Co(en)_2NO(ClO_4)_2$[a]	1.64×10^{-4}	1.0×10^{-4}	0.60
$Co(en)_2NO(ClO_4)_2$[a]	8.11×10^{-5}	4.6×10^{-5}	0.57
Co(acacen)NO[b]	1.20×10^{-4}	6.4×10^{-5}	0.53
Co(acacen)NO[b]	1.16×10^{-4}	6.9×10^{-5}	0.60
Co(acacen)NO[c]	6.43×10^{-4}	3.3×10^{-4}	0.51
Co(acacen)NO[d]	1.06×10^{-4}	5.5×10^{-5}	0.52

[a] In acetonitrile; O_2 collected by Toepler pump. [b] In methanol; O_2 collected by Toepler pump. [c] In pyridine; O_2 consumption measured directly by method quoted in A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, 92, 55 (1970). [d] In pyridine; O_2 collected by Toepler pump.

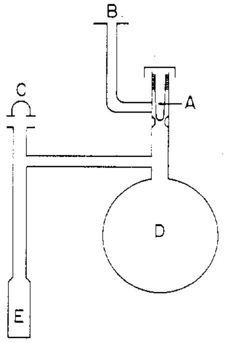

Figure 1. Diagram of the sample cell used to measure oxygen uptake, electronic spectra, and nitric oxide evolution: A, high-vacuum Teflon tap; B, O-ring joint for vacuum line connection; C, cap with O-ring joint; D, 100-ml round-bottom flask (bulb); E, quartz or glass cuvette.

Results

The results of the oxygen uptake experiments with Co(acacen)NO and with $Co(en)_2NO(ClO_4)_2$ are presented in Table III.

Prior to conducting kinetic studies, the stability of Co(acacen)NO in various solvents in the presence of oxygen was determined. In methanol, Co(acacen)NO reacts with oxygen, but at a reaction rate slower than when in the presence of the added bases used in this study. The compound decomposes in acetone and toluene in the presence of oxygen, but the rates of decomposition are very slow compared with the rates of reaction under investigation here.

The dependence of the reaction rate on the concentration of oxygen was determined in acetone as described in the Experimental Section. Assuming Henry's law, varying the partial pressure of oxygen above the solvent results in a variation of the concentration of oxygen in solution. Consequently, a plot of the observed rate constant *vs.* the partial pressure of oxygen is equivalent to using the concentration of oxygen in solution. Such a plot is shown in Figure 2.

All kinetic studies were carried out at 25°. Except for a few reactions in methanol and toluene, all reactions were carried out in acetone. The rates of reaction of the CoL_4NO compounds, except for Co(sacsacen)NO, with oxygen were all determined with both PBu_3 and pyridine as the added

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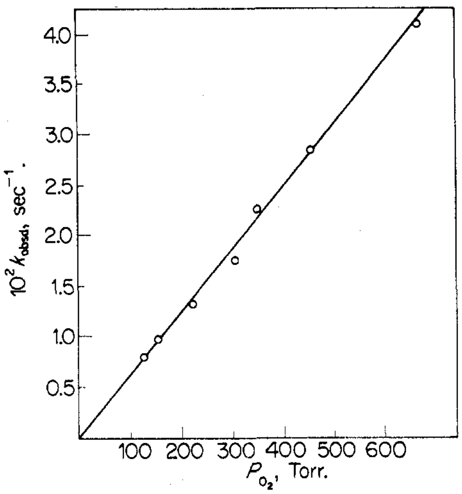


Figure 2. Plot of k_{obsd} *vs.* P_{O_2} for the reaction of Co(acacen)NO + py + O_2 in acetone at 25°. [Co(acacen)NO] = 2.0×10^{-4} *M*; [py] = 0.25 *M*.

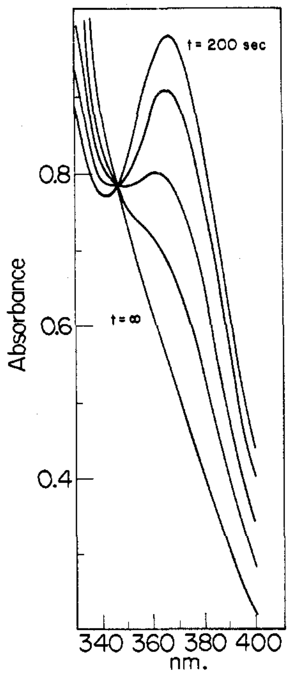


Figure 3. The uv-visible spectral changes of the reaction of 9.0×10^{-5} *M* Co[$S_2CN(CH_3)_2$]$_2$NO with 0.1 *M* py and 2.4×10^{-4} *M* oxygen in acetone at 25°.

base. Typical spectral changes for the reaction of Co(dtc)$_2$-NO with oxygen in the presence of pyridine are shown in Figure 3. In addition to PBu_3 and pyridine, the rate of reaction of Co(acacen)NO with oxygen was determined in the presence of several other bases. The results of the reactions of the CoL_4NO compounds with oxygen are presented in Table IV. Plots of the observed rate constants *vs.* the concentration of several representative bases are shown in Figures 4 and 5.

The cobalt nitrosyl complexes were stable in solution in the absence of oxygen, as evidenced by the constancy of their uv-visible spectra over a 24-hr period. Addition of base to an oxygen-free acetone solution of any CoL_4NO compound produced no detectable change in the uv-visible spectra of the solution over the 300-700-nm spectral range. This is perhaps due to the strong chromophoric effect that L_4 and NO have on the compound, dominating any perturbation caused by the axial base.

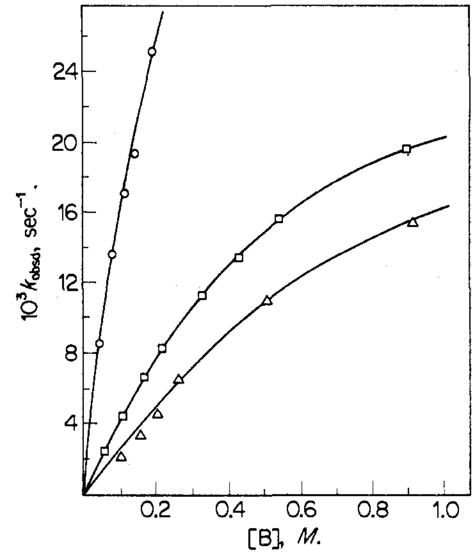


Figure 4. Plot of k_{obsd} *vs.* [B] for reactions of Co(acacen)NO with O_2 and B in acetone at 25°: △, B = py; □, B = 4-Me(py); ○, B = 4-NH_2py.

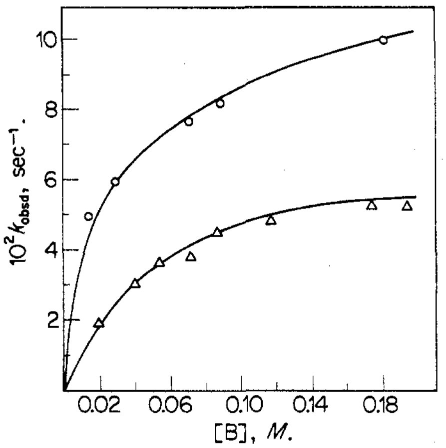


Figure 5. Plots of k_{obsd} *vs.* [B] for reactions of Co(acacen)NO with O_2 and B in acetone at 25°: ○, B = PMe_2Ph; △, B = PEt_3.

Discussion

The results of our studies show that certain cobalt nitrosyl complexes in solution containing added base react with oxygen to yield corresponding nitro compounds by reactions having the stoichiometries represented by

$$CoL_4NO + B + 0.5O_2 \rightarrow CoL_4(NO_2)B \quad (1)$$

$$Co(en)_2NO(ClO_4)_2 + CH_3CN + 0.5O_2 \rightarrow [Co(en)_2(CH_3CN)NO_2](ClO_4)_2 \quad (2)$$

Quantitative oxygen uptake studies on Co(acacen)NO clearly showed that 1 mol of cobalt nitrosyl complex reacted with 0.5 mol of oxygen molecules. The same results were observed for $Co(en)_2NO(ClO_4)_2$. Since the CoL_4NO complexes studied all reacted to yield $CoL_4(NO_2)B$, eq 1 is assumed to apply for all of these CoL_4NO compounds.

With the exception of Co(sacsacen)(NO_2)py, all of the $CoL_4(NO_2)B$ products gave good elemental analyses. The ir and/or nmr spectrum of some of the $CoL_4(NO_2)B$ compounds showed the presence of the L_4 ligand and the base. All the products had lost the starting nitrosyl N-O stretching band, and new bands had appeared in the 1300-, 1200-, and 800-cm^{-1} regions. These new bands are characteristic of a

Table IV. Experimentally Observed Rate Constants for the Reaction $CoL_4NO + B + 0.5O_2 \rightarrow BCoL_4NO_2$ in Acetone Solution at 25° and in Air at 1 Atm (B = Base)

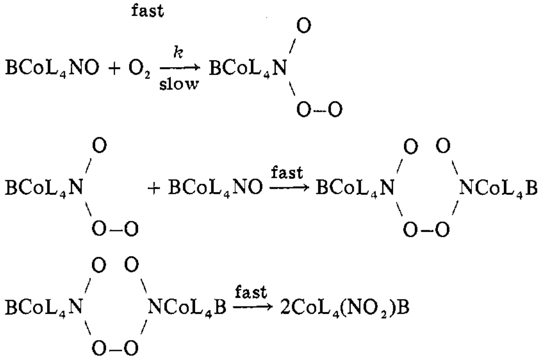
CoL_4NO + base	[B], *M*	$10^3 k_{obsd}$, sec^{-1}
Co(acacen)NO + py	0.05	1.42
Co(acacen)NO + py	0.15	3.60
Co(acacen)NO + py	0.26	6.63
Co(acacen)NO + py	0.51	11.1
Co(acacen)NO + py	1.01	16.0
Co(acacen)NO + 2-Me(py)	2.18	1.00
Co(acacen)NO + 2-Me(py)	6.36	1.20
Co(acacen)NO + 3-Me(py)	0.22	7.00
Co(acacen)NO + 3-Me(py)	0.43	10.6
Co(acacen)NO + 3-Me(py)	1.08	18.2
Co(acacen)NO + 4-Me(py)	0.05	2.40
Co(acacen)NO + 4-Me(py)	0.16	6.72
Co(acacen)NO + 4-Me(py)	0.32	11.1
Co(acacen)NO + 4-Me(py)	1.08	20.2
Co(acacen)NO + 2,6-Me_2py	1.29	3.35
Co(acacen)NO + 2,4,6-Me_3py	0.47	3.45
Co(acacen)NO + 4-NH_2py	0.032	9.37
Co(acacen)NO + 4-NH_2py	0.096	21.8
Co(acacen)NO + 4-NH_2py	0.191	38.5
Co(acacen)NO + 4-CNpy	0.10	0.80
Co(acacen)NO + aniline	1.71	1.16
Co(acacen)NO + imidazole	0.024	14.9
Co(acacen)NO + imidazole	0.048	27.0
Co(acacen)NO + imidazole	0.118	52.5
Co(acacen)NO + imidazole	0.141	59.4
Co(acacen)NO + (*i*-Pr)$_2$NH	2.74	0.69
Co(acacen)NO + Et_3N	3.5	0.00
Co(acacen)NO + $PrNH_2$	0.034	3.03
Co(acacen)NO + $PrNH_2$	0.068	4.85
Co(acacen)NO + $PrNH_2$	0.135	6.18
Co(acacen)NO + $PrNH_2$	0.474	8.20
Co(acacen)NO + CH_3CN	2.5	0.00
Co(acacen)NO + thiophene	2.1	0.00
Co(acacen)NO + PEt_3	0.017	20.1
Co(acacen)NO + PEt_3	0.052	36.6
Co(acacen)NO + PEt_3	0.086	44.6
Co(acacen)NO + PEt_3	0.173	51.8
Co(acacen)NO + PBu_3	0.044	30.0
Co(acacen)NO + PBu_3	0.087	41.7
Co(acacen)NO + PBu_3	0.218	51.0
Co(acacen)NO + $P(OBu)_3$	0.47	3.73
Co(acacen)NO + $P(OBu)_3$	0.93	4.82
Co(acacen)NO + $P(OBu)_3$	1.33	5.29
Co(acacen)NO + $PEtPh_2$	0.15	20.5
Co(acacen)NO + $PEtPh_2$	0.50	42.0
Co(acacen)NO + PMe_2Ph	0.018	52.0
Co(acacen)NO + PMe_2Ph	0.070	76.0
Co(acacen)NO + PMe_2Ph	0.181	99.4
Co(acacen)NO + PBu_3	0.042	5.50[a]
Co(acacen)NO + py	0.13	3.03[b]
Co(acacen)NO + py	1.01	22.2[b]
Co(acacen)NO + CH_3OH	24.7	0.31
Co(acacen)NO + PPh_3	2.0	0.00
Co(acacen)NO + $P(OPh)_3$	2.5	0.00
Co(acacen)NO + $P(C_6H_{11})_3$	3.3	0.00
$Co(dtc)_2NO$ + py	0.43	0.77
$Co(dtc)_2NO$ + py	4.29	5.83
$Co(dtc)_2NO$ + PBu_3	0.02	11.5
$Co(dtc)_2NO$ + PBu_3	0.05	16.1
Co(benacen)NO + py	0.27	7.00
Co(benacen)NO + py	1.31	20.6
Co(benacen)NO + PBu_3	0.007	23.4
Co(benacen)NO + PBu_3	0.03	64.0
Co(sacsacen)NO + PBu_3	0.018	2.08
Co(sacsacen)NO + PBu_3	0.10	10.0
Co(salen)NO + py	0.28	5.04
Co(salen)NO + py	0.85	12.6
Co(salen)NO + py	2.90	27.4
Co(salen)NO + PBu_3	0.003	23.3
Co(salen)NO + PBu_3	0.016	65.0

[a] Toluene solution. [b] Methanol solution.

coordinated nitro group.[16,17] Except for Co(sacsacen)(NO_2)-B, all the nitro products were stable in solution as shown by nonchanging uv-visible spectra. Acetone solutions of the product of the reaction among Co(sacsacen)NO, oxygen, and PBu_3, formulated as Co(sacsacen)(NO_2)PBu_3, became colorless in 30 min. The nature of this reaction is not known, but it can be responsible for the isolation of impure nitro products with this system.

Kinetic studies on reactions 1 and 2 show that the rates of reaction exhibit a first-order dependence on the concentrations of the cobalt nitrosyl compounds and on the concentration of oxygen. The rates of reaction also depend on the nature of the added base and on its concentration. With increasing concentration of base, the reaction rate increases but it appears to reach a limiting rate at high base concentrations. This behavior is suggestive of a rapid preequilibrium between the nitrosyl compound and the base. The kinetic data obtained are in accord with the sequence of reactions

$$CoL_4NO + B \underset{\text{fast}}{\overset{K}{\rightleftarrows}} BCoL_4NO \qquad (3)$$



(4)

(5)

(6)

Reaction 4 is designated as the rate-determining step, and its rate is first-order in oxygen concentration and in the concentration of the six-coordinated species $BCoL_4NO$. The concentration of this species depends on the concentration of B and of the substrate but reaches a saturation point at high concentrations of base. This accounts for the observation that the rates of reaction tend to level off at high concentrations of base. Since the rates of reaction are first-order in the cobalt nitrosyls, reactions 5 and 6 must be fast compared to reaction 4.

The proposed mechanism parallels that postulated for the gas-phase reaction between nitric oxide and oxygen.[18] In the gas reaction a NO_3 intermediate with a peroxy structure,[19] as opposed to a nitrate structure, is proposed. This corresponds to an oxygen attack on the nitrogen of the nitrosyl group forming a coordinated NO_3 group with a peroxy structure, as represented for the product of reaction 4. This intermediate then reacts with another $BCoL_4NO$ to form an unstable "N-O-O-N" linkage that decomposes to yield the final nitro product.

Assuming the proposed mechanism, it follows that the experimentally observed rate constant, k_{obsd}, has the expression

$$k_{obsd} = \frac{kK[B][O_2]}{1 + K[B]}$$

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[16] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Interscience, New York, N. Y., 1963, p 51.

[17] P. G. Douglas, R. D. Feltham, and H. G. Metzger, *J. Amer. Chem. Soc.*, **93**, 84 (1971).

[18] P. G. Ashmore, M. G. Burnett, and B. J. Taylor, *Trans. Faraday Soc.*, **80**, 685 (1962).

[19] S. W. Benson and W. B. DeMore, *Annu. Rev. Phys. Chem.*, **16**, 405 (1965).

and that then

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{kK[\text{B}][\text{O}_2]} + \frac{1}{k[\text{O}_2]}$$

Thus a plot of $1/k_{\text{obsd}}$ *vs.* $1/[\text{B}]$ should result in a straight line (see Figure 6) with a slope of $1/kK[\text{O}_2]$ and an intercept of $1/k[\text{O}_2]$. The equilibrium constant, K, can be estimated by dividing the intercept by the slope. Unfortunately it was not possible to determine K directly because only small spectral changes are observed when B is added to CoL_4NO. The reciprocal of the intercept yields $k[\text{O}_2]$. Two reciprocal plots are presented in Figure 6, and the constants estimated from the reciprocal plots are given in Table V.

A comparison of the rates of reaction of Co(acacen)NO with oxygen in the presence of the various bases reveals that the rate increases with increasing basicity of the base, in the absence of steric factors. A linear free energy plot of the log of k_{obsd} *vs.* the pK_a of the protonated base for a series of nonsterically hindered pyridines is shown in Figure 7. The more accurate experimental values of k_{obsd}, at a given base concentration, are used for this plot instead of the extrapolated pseudo rate constants $k[\text{O}_2]$. The linear plot has a slope of 0.2, indicating that the effect of increasing basicity on the reaction rate is small. However, reaction rates decrease markedly with increasing steric hindrance of the added base, *e.g.*, pyridine > 2-methylpyridine and propylamine > diisopropylamine > triethylamine.

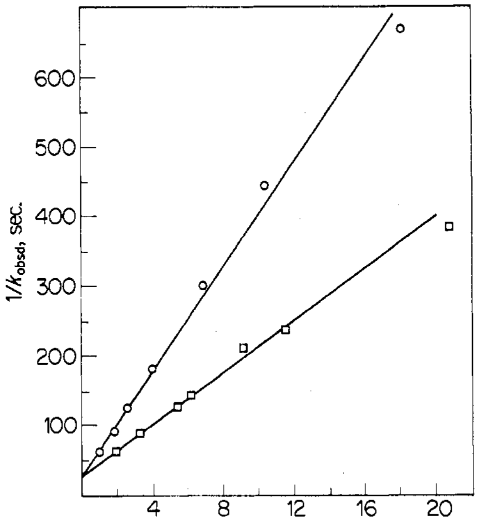

Figure 6. Plots of the reciprocal of k_{obsd} *vs.* the reciprocal of the concentration of B for the reaction of Co(acacen)NO with O_2 and B in acetone at 25°: ○, B = py; □, B = 4-Me(py).

Phosphorus bases also promote the reaction of CoL_4NO with oxygen to yield nitro products. The rate of reaction increases with increasing basicity of the phosphorus bases (Figure 8). Except for the anomalous fast reaction with added PMe_2Ph, the results are linear. Again steric factors are important since the presence of the basic phosphine, $\text{P(C}_6\text{H}_{11})_3$, does not cause a reaction to occur. Tolman[20] has stressed the importance of ligand size in the coordinating ability of phosphorus bases, and for a large number of such bases he has estimated sizes in terms of cone angles. The minimum cone angle of 179° for $\text{P(C}_6\text{H}_{11})_3$ is one of the largest, *e.g.*, PMe_3 = 118° and PPh_3 = 145°. Thus in spite of its proton basicity, $\text{P(C}_6\text{H}_{11})_3$ does not tend to coordinate

Table V. Estimates of Equilibrium Constants for Equilibria 3 and Pseudo Rate Constants for Reaction 4 for the Reactions of CoL_4NO with Oxygen in the Presence of Base in Acetone Solution at 25° and in Air at 1 Atm

Compd	Base	pK_a(BH$^+$)	$10^2k[\text{O}_2]$, sec^{-1} M	K, M^{-1}
Co(acacen)NO	py	5.27[a]	4.00	0.70
Co(acacen)NO	3-Me(py)	5.52[a]	4.00	0.79
Co(acacen)NO	4-Me(py)	6.00[a]	4.00	1.34
Co(acacen)NO	4-NH_2py	9.17[a]	10.0	2.86
Co(acacen)NO	Imidazole	6.95[b]	16.7	3.8
Co(acacen)NO	$\text{C}_3\text{H}_7\text{NH}_2$	10.59[c]	9.7	13.7
Co(acacen)NO	PEt_3	8.7[d]	6.67	23
Co(acacen)NO	PBu_3	8.4[d]	6.67	19
Co(acacen)NO	PEtPh_2	4.9[d]	5.75	5.4
Co(acacen)NO	P(OBu)_3	3.4[d]	0.8	1.87
Co(acacen)NO	PMe_2Ph	6.5[d]	11.1	37
Co(benacen)NO	py	5.27[a]	5.00	0.50
Co(benacen)NO	PBu_3	8.4[d]	10.0	45
Co(salen)NO	py	5.27[a]	5.00	0.40
Co(salen)NO	PBu_3	8.4[d]	14.0	57
$\text{Co(dtc)}_2\text{NO}$	py	5.27[a]	1.40	0.13
$\text{Co(dtc)}_2\text{NO}$	PBu_3	8.4[d]	2.10	0.73
Co(sacsacen)NO	PBu_3	8.4[d]	4.00	3.3

[a] K. Schofield, "Hetero-Aromatic Nitrogen Compounds," Plenum Press, New York, N. Y., 1967, pp 146–148. [b] "The Chemistry of Heterocyclic Compounds," Vol. 6, Interscience, New York, N. Y., 1953, p 15. [c] N. A. Lange, "Handbook of Chemistry," McGraw-Hill, 10th ed, New York, N. Y., 1969, p 1202. [d] Estimated from ΔHNP values by the method of C. A. Streuli, *Anal. Chem.*, 31, 1652 (1959).

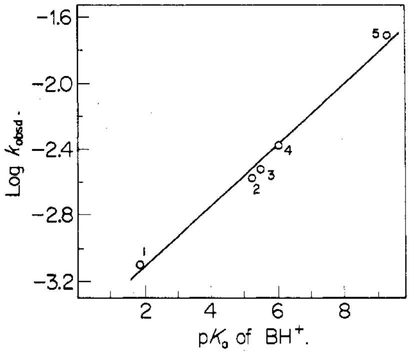

Figure 7. Linear free energy relationship of the basicity of the base (at 0.1 M B) with the rate of reaction of Co(acacen)NO with oxygen in acetone at 25°: 1 = 4-CNpy; 2 = py; 3 = 3-Me(py); 4 = 4-Me(py); 5 = 4-NH_2py.

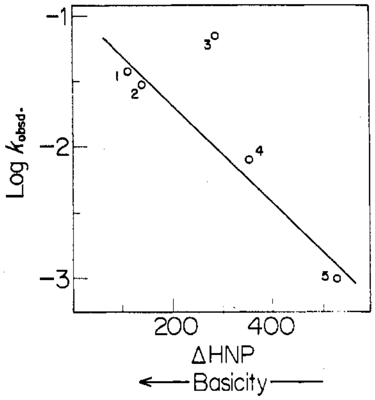

Figure 8. Linear free energy relationship of the basicity of the base (at 0.05 M B) with the rate of reaction of Co(acacen)NO with oxygen in acetone at 25°: 1 = PEt_3; 2 = PBu_3; 3 = PMe_2Ph; 4 = PEtPh_2; 5 = P(OBu)_3. Values of ΔHNP are the differences in half-neutralization potentials of the phosphorus bases from that of *N,N'*-diphenylguanidine taken as a standard, all measured toward a protonic acid in nitromethane solution (C. A. Streuli, *Anal. Chem.*, 32, 985 (1960)).

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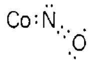
(20) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

to cobalt in these systems and its presence does not promote the reaction with oxygen. That PMe_2Ph is a more effective reagent than expected from its proton basicity is not understood. However, it had also been noted previously[21] that PMe_2Ph has a greater tendency than does PBu_3 to coordinate with cobalt in its Schiff base complexes.

Noteworthy are the rate data summarized in Table V which show only a 20-fold variation in pseudo rate constants for the reactions of CoL_4NO with oxygen in the presence of different bases, and the values of the equilibrium constants vary by a factor of about 50. However, the added bases vary as much as seven orders of magnitude in proton basicity. For the same added base, changes in the chelating groups L_4 also have a small effect on the rates of reaction. That the rates of reaction are not greatly altered by changes in the ligands coordinated to the cobalt of the cobalt nitrosyls suggests that the nitrosyl groups in all of these systems are very similar. This follows from the proposed mechanism which involves an electrophilic attack on the nitrogen of the nitrosyl group. One might have expected the electron density on the nitrosyl group to increase greatly with large increases in the basicity of the ligands coordinated to cobalt. This in turn would enhance electrophilic attack on the nitrosyl nitrogen and markedly increase the rate of reaction. However, contrary to this, the experimental facts show that the rates of reaction change only by a factor of about 20.

The suggestion that the nitrosyls are all similar in the substrates investigated is supported by the narrow range (1611-1654 cm^{-1}) of N-O stretching frequencies for the CoL_4NO compounds (Table I). This is in contrast to the wide range (1500-2000 cm^{-1}) of N-O stretching frequencies known to occur for metal nitrosyls.[22]

Further support that the nitrosyls in these systems are similar may come from the observation that they have similar M-N-O structures. The crystal structures of Co(acacen)NO,[23] Co(benacen)NO,[23] $[Co(en)_2NOCl]ClO_4$,[24] and Co$(dtc)_2$NO[12] were determined by means of X-rays and found to have Co-N-O bond angles of about 120° (Table I). A simple interpretation of a bent metal nitrosyl system is that it contains a formally NO^- ligand and that the N atom is sp^2 hybridized. Thus a Lewis dot structure for NO^- coordinated to Co(III) in these systems would be



The N atom with its pair of nonbonding electrons can then behave as a nucleophile toward the electrophile oxygen for the reactions reported in this investigation. It also follows that other electrophilic reagents should attack the nucleophilic N atom in bent M-N-O systems, and investigations to test this hypothesis are in progress.

In conclusion, the point to be emphasized is that metal nitrosyls with bent M-N-O structures may react by electrophilic attack on the N atom, whereas linear M-N-O structures are known[25] to react by nucleophilic attack on the N atom. It follows that compounds with M-N-O of intermediate structures or with structures which readily rearrange[26] may exhibit "amphoteric" behavior (undergo both nucleophilic and electrophilic reactions).

Registry No. Co(acacen)NO, 24323-14-6; Co$(dtc)_2$NO, 36434-42-1; Co(benacen)NO, 39836-72-1; Co(sacsacen)NO, 39732-97-3; Co(salen)NO, 36915-19-2; $Co(en)_2NO(ClO_4)_2$, 39721-22-7; py, 110-86-1; 2-Me(py), 109-06-8; 3-Me(py), 108-99-6; 4-Me(py), 108-89-4; 2,6-Me_2py, 108-48-5; 2,4,6-Me_3py, 108-75-8; 4-NH_2py, 504-24-5; 4-CNpy, 100-48-1; $C_6H_5NH_2$, 62-53-3; imidazole, 288-32-4; $(i\text{-}Pr)_2NH$, 108-18-9; $PrNH_2$, 107-10-8; PEt_3, 554-70-1; PBu_3, 998-40-3; $P(OBu)_3$, 102-85-2; $PEtPh_2$, 607-01-2; PMe_2Ph, 672-66-2; CH_3OH, 67-56-1; CH_3CN, 75-05-8; O_2, 7782-44-7; Co(acacen)(NO_2)py, 39019-72-2; Co(acacen)$(NO_2)C_3H_7NH_2$, 39721-24-9; Co(acacen)$(NO_2)PMe_2Ph$, 39721-25-0; Co(benacen)(NO_2)py, 39721-26-1; Co(salen)(NO_2)py, 39721-27-2; Co(sacacen)(NO_2)py, 39721-28-3; Co$(dtc)_2(NO_2)$py, 39721-29-4; $[Co(en)_2(CH_3CN)NO_2](ClO_4)_2$, 39721-30-7.

Acknowledgment. The authors thank Professor Ralph G. Pearson and Dr. Bruce C. Lane for helpful discussions. This work was supported in part by a grant from the National Institutes of Health.

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[21] L. G. Marzilli, P. A. Marzilli, and J. Halpern, *J. Amer. Chem. Soc.*, 93, 1374 (1971).

[22] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, p 201.

[23] R. Weist and R. Weis, *J. Organometal. Chem.*, 30, C33 (1971).

[24] D. A. Snyder and D. L. Weaver, *Inorg. Chem.*, 9, 2760 (1970).

[25] J. H. Swinehart, *Coord. Chem. Rev.*, 2, 385 (1967).

[26] J. P. Collman, P. Farnham, and G. Dolcetti, *J. Amer. Chem. Soc.*, 93, 1788 (1971).