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# Oxidation of Coordinated Nitric Oxide by Free Nitric Oxide

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Nitric oxide reacts with $Co(en)_2(NO)Cl_2$ to form *cis*-$Co(en)_2(NO_2)Cl_2$ and $N_2O$; likewise $Co(NO)(DMG)_2 \cdot CH_3OH$ (DMG = dimethylglyoximate anion) yields $Co(NO_2)(DMG)_2(py)$ in the presence of pyridine (py). Mechanisms which are consistent with the observed product stereochemistry are discussed. Reductive nitrosylation (*i.e.*, formation of $Co(en)(NO)_2^+$) can be achieved by limiting the Co(II):en ratio and using a noncoordinating base.

## Introduction

A methanolic solution of ethylenediamine (en) and $CoCl_2 \cdot 6H_2O$ absorbs nitric oxide (NO) to give a solution of $Co(en)_2(NO)(CH_3OH)^{2+}$, which can be precipitated as $Co(en)_2(NO)Cl_2$.[2] A crystallographic study[3] of the related salt $Co(en)_2(NO)Cl^+ClO_4^-$ has shown the NO to be coordinated in a bent fashion, with $\angle$Co-N-O = 136°. We find that $Co(en)_2(NO)(CH_3OH)^{2+}$ reacts with additional nitric oxide to yield $Co(en)_2(NO_2)Cl_2$ and $N_2O$; likewise $Co(NO)(DMG)_2 \cdot CH_3OH$ (DMG = monoanion of dimethylglyoxime) reacts to form the corresponding nitro complex, in the presence of base. This represents the first example of attack by free NO on coordinated NO uncomplicated by other concurrent oxidations.[4] As such it can be thought of as an example of catalysis, by cobalt, of the kinetically sluggish disproportionation $3NO \rightarrow N_2O + NO_2$.

## Experimental Section

**General Data.** Ethylenediamine was distilled from KOH (bp 117-118°). *cis*-$Co(en)_2(NO_2)Cl_2$ was prepared and purified as described by Werner.[5] All other purifications and manipulations were as previously described.[6] Infrared spectra (KBr disk) were measured on a Perkin-Elmer 137 spectrophotometer; pmr spectra in $D_2O$ or $CD_3OD$ were recorded within 15 min of dissolution on a Varian Associates HR-220 spectrometer. N-Deuteration is complete by this time in these solvents. The electronic spectra (6500-2000 A) were measured on a Cary Model 14 spectrophotometer in methanol and/or water. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

**I. Reactions with NO at 1 Atm. $Co(en)_2(NO)Cl_2$.** (a) Ethylenediamine (0.45 ml, 6.8 mmol) was slowly added to a solution of 3.4 mmol of $CoCl_2$ in 25 ml of methanol; a pale blue solid slowly precipitated from the red-orange solution. Within a 10-min period, 3.4 mmol of NO was added to the reaction flask using a gas buret; the solution color immediately turned to a deep red-brown and a small amount of yellow solid precipitated. After the solution was stirred for an additional 50 min, the yellow solid was filtered off and 50 ml of ethyl ether was rapidly added dropwise to the filtrate. The resulting chocolate-colored solid was filtered, washed with additional ethyl ether,[7] and dried under vacuum; yield 0.81 g (2.9 mmol, 85%). *Anal.* Calcd for $C_4H_{16}Cl_2CoN_5O$: C, 17.15; H, 5.77; Cl, 25.32; N, 25.01, O, 5.71. Found: C, 17.58; H, 5.77; Cl, 24.57; N, 24.29; O, 6.68. The infrared, pmr, and electronic spectra of the yellow solid were identical with those of $Co(en)_3Cl_3$.[8] *Anal.* Calcd for $C_6H_{24}Cl_3CoN_6$: C, 20.85; H, 7.01; Cl, 30.77; Co, 17.05. Found (yellow solid): C, 20.35; H, 8.12; Cl, 28.93; Co, 17.56.

(b) NO was bubbled[9] through a solution of 1.6 ml of en (24.0 mmol) and 12.0 mmol of $CoCl_2$ in 75 ml of methanol for 10-15 min. A yellow precipitate was filtered from the reaction solution and 125 ml of ethyl ether was added rapidly to yield $Co(en)_2(NO)Cl_2$. The solid was filtered and redissolved in a minimum amount of methanol. After filtration, 100 ml of ethyl ether was added dropwise to precipitate the product; 2.65 g of $Co(en)_2(NO)Cl_2$ (9.5 mmol, 79%) was isolated. The infrared spectrum was identical with that of $Co(en)_2(NO)Cl_2$ prepared above.

**$Co(en)_2(NO_2)Cl_2$.** When NO was bubbled through a solution prepared as in (b) above for 8-24 hr, initial gas uptake was rapid as in the preparation of $Co(en)_2(NO)Cl_2$. After 30-45 min, a pale red solid began to precipitate from the reaction solution and NO was absorbed more slowly. A total of 2.30-2.44 g of $Co(en)_2(NO_2)Cl_2$ (65-69% yield) was filtered from the solution, washed with 2-5 ml of methanol, and dried under vacuum. The pmr of the solid in $D_2O$ showed the presence of methanol ($\tau$ 6.65); integration of the methanol methyl and en methylene protons established a $CH_3OH$:$Co(en)_2(NO_2)Cl_2$ mole ratio of 0.3-0.5. *Anal.* Calcd for $C_4H_{16}Cl_2CoN_5O_2 \cdot 0.5CH_3OH$: C, 17.32; H, 5.82; Cl, 22.72; Co, 18.88; N, 22.44. Found: C, 17.47; H, 5.98; Cl, 21.92; Co, 18.82; N, 22.06. Recrystallization of the crude product from $H_2O$ with concentrated HCl yielded pale red, flocculent crystals; no methanol was detected in the pmr spectrum of the recrystallized material. *Anal.* Calcd for $C_4H_{16}Cl_2CoN_5O_2$: C, 16.23; H, 5.46; Cl, 23.95; N, 23.66. Found: C, 15.98; H, 4.95; Cl, 24.07; N, 23.39.

**$Co(NO_2)(DMG)_2 \cdot py$.** (a) Nitric oxide was bubbled through a solution of $Co(NO)(DMG)_2 \cdot CH_3OH$[10] (0.2 g, 0.57 mmol) in 10 ml of methanol for 12 hr. Removal of approximately 5 ml of solvent produced a crystalline solid with an infrared spectrum identical with that of unreacted starting material. The filtrate was taken to dryness and the resulting solid exhibited no nitrite bands in the infrared spectrum.

(b) The sample from (a) above was redissolved in 10 ml of methanol and 0.06 ml of pyridine (0.75 mmol of py) was added; NO was passed through this solution for 9.5 hr. After the solvent was removed under vacuum, the resulting solid was washed with ethyl ether and recrystallized from chloroform-ethyl ether. The infrared spectrum of the crystalline solid exhibited no NO stretch characteristic of $Co(NO)(DMG)_2 \cdot CH_3OH$ ($\nu_{NO}$ 1639 $cm^{-1}$)[10] but rather showed bands for py and DMG as well as absorptions at 1409, 1309, and 819 $cm^{-1}$, characteristic[11] of an N-bonded nitro complex. Pmr (integration) in $CDCl_3$: $CH_3$ from DMG, $\tau$ 7.70 (12); py, $\tau$ 1.74-2.80 (5). *Anal.* Calcd for $C_{13}H_{19}CoN_6O_6$: C, 37.68; H, 4.59; N, 20.28. Found: C, 37.21; H, 4.82; N, 18.98.

**Reaction of NO with $CoCl_2$ and en (1:3).** A 36.0-mmol amount of en (2.4 ml) was slowly added dropwise to a solution of 12.0 mmol of $CoCl_2$ in 75 ml of methanol. Bubbling NO through the solution for 10 hr yielded, after filtration, an orange-yellow solid which was shown by infrared, electronic, and pmr spectra to be $Co(en)_3Cl_3$ contaminated by minor quantities of nitro and nitrito complexes.

**Reaction of $Co(en)_2(NO)Cl_2$ with en.** To a slurry of 0.92 g of $Co(en)_2(NO)Cl_2$ (3.28 mmol) in 20 ml of methanol, 0.22 ml of en (3.34 mmol) was added dropwise. After 10 hr a salmon-colored solid was filtered from the solution, washed with methanol, and dried; the infrared spectrum of the solid was identical with that of the product obtained in the stoichiometric preparation of $Co(en)_2(NO)Cl_2$ (see below). Within 6 hr, a pale yellow solid precipitated from the filtrate; the infrared spectrum of the solid was that of $Co(en)_3Cl_3$.

**$Co(en)(NO)_2B(C_6H_5)_4$.** Successively, en (0.80 ml, 12.0 mmol)

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[1] Lubrizol Industrial Fellow.

[2] R. Feltham and R. Nyholm, *Inorg. Chem.*, 4, 1334 (1965).

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

[4] M. Rossi and A. Sacco, *Chem. Commun.*, 694 (1971).

[5] A. Werner, *Justus Liebigs Ann. Chem.*, 386, 1 (1912).

[6] D. Gwost and K. G. Caulton, *Inorg. Chem.*, 12, 2095 (1973).

[7] Anhydrous ethyl ether is required to prevent formation of an oil.

[8] J. Work, *Inorg. Syn.*, 2, 221 (1946).

[9] The exit bubbling rate has been established as approximately 150 $cm^3$/hr; this corresponds to ~15 bubbles/min through a Nujol bubbler.

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

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

and triethylamine (1.7 ml, 12.2 mmol) were added to a solution of 12.0 mmol of $CoCl_2$ in 75 ml of methanol. When the order of addition of amines was reversed, a small amount of white solid precipitated. In either case, bubbling NO through the reaction solution for 8–10 hr resulted in the formation of 0.3 g of $Co(en)_2(NO_2)Cl_2$ and a deep red solution. The infrared spectrum of the degassed reaction solution (methanol reference) showed four strong absorptions in the region 2000–1600 $cm^{-1}$: $\nu_{NO}$ 1864, 1840, 1798, and 1759 $cm^{-1}$. An additional 0.20 ml of en was added and the reaction solution was stirred for 15 min; the infrared spectrum in the nitrosyl region now showed only two of the stretches observed earlier: $\nu_{NO}$ 1867, 1788 $cm^{-1}$. The addition of 9.0 g of $NaB(C_6H_5)_4$ in 75 ml of methanol precipitated a mixture of $HNEt_3B(C_6H_5)_4$[6] and $Co(en)(NO)_2B(C_6H_5)_4$ ($\nu_{NO}$ 1866, 1792 $cm^{-1}$).[12]

**II. Stoichiometric Measurements.** All reactions were carried out at room temperature in 25 ml of methanol for 24 hr. Measurements were obtained on a vacuum manifold, *via* trap-to-trap fractionation of volatiles, as described earlier.[6] $Co(en)_2(NO)Cl_2$ was isolated by washing the insoluble products, after filtration, with 2–5 ml of methanol; 100 ml of ethyl ether was added to the combined filtrate and washings to precipitate the solid. Negative millimolar quantities indicate recovered reactants.

(a) **$4.0CoCl_2 + 8.1en + 4.0NO \rightarrow 0.3N_2O + 1.7Co(en)_2(NO)Cl_2$ + Salmon Precipitate (2.0 g-atoms of Co).** The infrared, electronic, and pmr spectra of the salmon solid (0.66 g, 17.64% Co) showed it to consist of predominantly $Co(en)_3Cl_3$. In addition to absorptions in the infrared spectrum for $Co(en)_3Cl_3$, there were three bands ($\nu_{ONO}$ 1410, 1095, 838 $cm^{-1}$) assignable[11] to a nitrito complex. After the salmon solid was recrystallized from water–ethanol, the infrared spectrum of the resulting yellow-orange needles was identical with that of $Co(en)_3Cl_3$.

(b) **$4.0CoCl_2 + 8.1en + (12.0 - 1.5 = 10.5)NO \rightarrow 3.3N_2O + 2.9Co(en)_2(NO_2)Cl_2 + 1.0Co(en)_2(NO)Cl_2$.** The yield of $Co(en)_2(NO_2)Cl_2$ is 72%, similar to that from the reaction with excess NO at atmospheric pressure.

(c) **$Co(en)_2(NO)Cl_2$ in $CH_3OH$.** A 3.8-mmol amount of $Co(en)_2(NO)Cl_2$ was stirred in 25 ml of methanol for 24 hr. Filtration separated a trace of yellow solid with an infrared spectrum identical with that of $Co(en)_3Cl_3$. No detectable amount of evolved gas was isolated and 3.4 mmol of $Co(en)_2(NO)Cl_2$ was recovered from the filtrate (90% recovered yield).

(d) **$(3.9 - 1.1 = 2.8)Co(en)_2(NO)Cl_2 + (7.8 - 2.1 = 5.7)NO \rightarrow 2.8N_2O + 2.6Co(en)_2(NO_2)Cl_2$.**

(e) **$4CoCl_2 + 4NEt_3 + 4en + (12.0 - 3.6 = 8.4)NO \rightarrow 2.0N_2O + 0.9CH_3ONO + 0.8Co(en)_2(NO_2)Cl_2$ + Deep Red Solution.** The reaction solution was degassed for 1 hr prior to reaction with NO, allowing for equilibration of the two amines with $CoCl_2$. As detected in the infrared spectrum, $CH_3ONO$ could not be completely separated from $N_2O$. $Co(en)(NO)_2B(C_6H_5)_4$ was isolated by the dropwise addition of 3.0 g of $NaB(C_6H_5)_4$ in 25 ml of methanol to the deep red filtrate ($\nu_{NO}$ 1866, 1792 $cm^{-1}$; methanol reference).

## Results

$Co(en)_2(NO)(ClO_4)_2$ may be isolated[2] in high yields as violet-red crystals by the action of NO on $Co(ClO_4)_2 \cdot 6H_2O$ (1 mol) and en (2 mol) in methanol. Since the product is insoluble in this solvent, the yield is unaffected by excess NO. On the other hand, the original[2] preparation of $Co(en)_2(NO)Cl_2$ describes the need for removal of "impurities" by filtration and multiple recrystallizations. We find that a clean, high-yield synthesis of $Co(en)_2(NO)Cl_2$ requires that the amount of NO be stoichiometrically controlled (reaction 1). If the reaction is monitored using a gas buret, the absorption of the first mole of NO proceeds observably faster than the subsequent oxidation (see below).

$$CoCl_2 + 2en + NO \xrightarrow{CH_3OH} Co(en)_2(NO)Cl_2 \tag{1}$$

The "impurities" mentioned by Feltham and Nyholm are the result of oxidation of $Co(en)_2(NO)Cl_2$ by excess NO. When NO is passed through a solution containing a 2:1 molar ratio of en and $CoCl_2$ for 8–24 hr (as opposed to 15–20 min), the N-bonded nitro isomer ($\nu_{NO}$ 1393, 1321, 828 $cm^{-1}$) of $Co(en)_2(NO_2)Cl_2$ precipitates from the reaction solution in 65–70% yield. If the reaction is run at reduced pressure in a closed system, trap-to-trap fractionation of unreacted NO and $N_2O$ (the latter identified by infrared and mass spectra) confirms the stoichiometry in reaction 2; $Co(en)_2(NO)Cl_2$ is also isolated from this reaction.

$$CoCl_2 + 2en + 3NO \rightarrow Co(en)_2(NO_2)Cl_2 + N_2O \tag{2}$$

The intermediacy of $Co(en)_2(NO)Cl_2$ in this reaction was verified by allowing a methanolic solution of authentic $Co(en)_2(NO)Cl_2$ to react with NO for 24 hr. Isolation of volatile and nonvolatile products confirms that excess NO oxidizes the intermediate nitrosyl complex (reaction 3).

$$Co(en)_2(NO)Cl_2 + 2NO \rightarrow Co(en)_2(NO_2)Cl_2 + N_2O \tag{3}$$

Likewise, free NO oxidizes $Co(NO)(DMG)_2$ to $Co(NO_2)(DMG)_2$ but only in the presence of base (*e.g.*, pyridine). The presence of additional base (en) in the oxidation of $Co(en)_2(NO)Cl_2$ does not enhance the oxidation to $Co(en)_2(NO_2)Cl_2$ but instead leads to the formation of $Co(en)_3Cl_3$; likewise, $Co(en)_3Cl_3$ is formed from the reaction of $Co(en)_2(NO)Cl_2$ and en.[13]

In an earlier report,[6] the apparently disparate behavior of en and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) as ligands in the reaction of Co(II) with NO was discussed. TMEDA facilitates reductive nitrosylation to give $Co(TMEDA)(NO)_2^+$ salts, while en gives six-coordinate mononitrosyls (*e.g.*, $Co(en)_2(NO)Cl_2$). We now find that by controlling the molar ratio of Co(II) and en *and* providing a noncoordinating proton acceptor ($NEt_3$), reductive nitrosylation does take place. Thus, a solution with a $CoCl_2$:en:$NEt_3$ 1:1:1 molar ratio in methanol reacts with NO to give $Co(en)_2(NO_2)Cl_2$ along with an equilibrium mixture of $Co(en)(NO)_2^+$ and $(Co(NO)_2Cl)_2$ (see Experimental Section). Ir spectra: $Co(en)(NO)_2PF_6$, $\nu_{NO}$ 1866, 1790 $cm^{-1}$ (tetrahydrofuran);[14] $(Co(NO)_2Cl)_2$, $\nu_{NO}$ 1842, 1757 $cm^{-1}$ (methanol).[6] Presumably $Co(en)_2(NO_2)Cl_2$ formation (*i.e.*, oxidation of $Co(en)_2(NO)Cl_2$) and reductive nitrosylation are competitive at low en concentrations. The resulting deficiency of en, from the formation of $Co(en)_2(NO_2)Cl_2$, establishes equilibrium 4

$$(Co(NO)_2Cl)_2 + 2en \rightleftharpoons 2Co(en)(NO)_2^+Cl^- \tag{4}$$

in solution. Addition of excess en displaces the equilibrium to the right; $Co(en)(NO)_2B(C_6H_5)_4$ is precipitated from the solution by the addition of $NaB(C_6H_5)_4$.

## Discussion

Clarkson and Basolo have demonstrated[15] that the bent Co–NO moiety is subject to electrophilic attack by molecular oxygen, presumably at the lone pair on nitrogen. Also, the electrophilicity of NO has been established[16] by its reactions with primary and secondary amines. Oxidation by free NO of the nitrosyl ligand in $Co(en)_2(NO)Cl_2$ and $Co(NO)(DMG)_2$ is therefore suggested to proceed by attack of NO at the coordinated $sp^2$ nitrogen of the nitrosyl.

The reaction may proceed with retention (eq 5) or scission (eq 6) of the Co–N bond. These differ primarily in whether

$$L_xCo(NO)^{q+} + 2NO \rightarrow L_xCo(NO_2)^{q+} + N_2O \tag{5}$$

$$L_xCo(NO)^{q+} + 2NO \rightarrow L_xCo^{q+} + N_2O + NO_2 \rightarrow L_xCo(NO_2)^{q+} \tag{6}$$

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[12] A. Sacco, M. Rossi, and C. Nobile, *Ann. Chim. (Rome)*, 57, 499 (1967).

[13] The high thermodynamic stability of $Co(en)_3Cl_3$ is demonstrated repeatedly in this study by its production in various side reactions.

[14] W. Hieber and K. Kaiser, *Z. Anorg. Allg. Chem.*, 362, 169 (1968).

[15] S. Clarkson and F. Basolo, *Inorg. Chem.*, 12, 1528 (1973).

[16] R. Longhi, R. Ragsdale, and R. Drago, *Inorg. Chem.*, 1, 768 (1962).

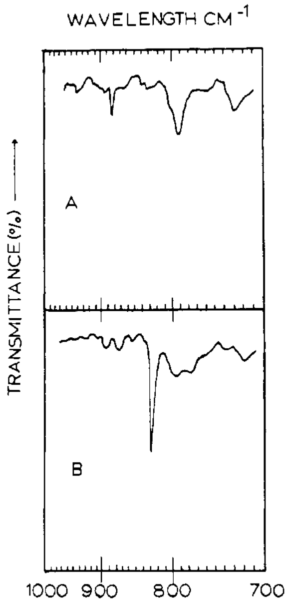
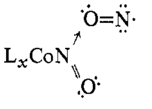
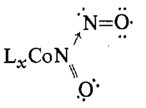


**Figure 1.** Infrared spectra (KBr disk) of (A) *trans*-Co(en)$_2$(NO)Cl$_2$ and (B) *cis*-Co(en)$_2$(NO$_2$)Cl$_2$·0.5CH$_3$OH.

free NO[17,18] attacks with oxygen (Ia), allowing retention of the Co-N bond, or with nitrogen (Ib). In the latter case, attack by a second NO molecule at either terminal oxygen generates a moiety which can collapse to free NO$_2$ and the easily dissociated ligand N$_2$O. The stability (see Experimental Section) of Co(en)$_2$(NO)Cl$_2$ in methanol solution for at least 24 hr makes autoxidation *via* a bridged hyponitrite complex[19] an unlikely pathway.



Ia



Ib

Based on the stereochemistry of the reactants and products and the reactivity of NO$_2$, we favor retention of the Co-N bond. Although the stereochemistry of Co(NO)(DMG)$_2$ and Co(NO$_2$)(DMG)$_2$·py is fixed by the rigidity of the two DMG ligands, Co(en)$_2$(NO)Cl$_2$ and Co(en)$_2$(NO$_2$)Cl$_2$ are not similarly constrained. A survey[20] of the infrared spectra in the 1000-600-cm$^{-1}$ region of a variety of *cis*- and *trans*-Co(en)$_2$XY$^{q+}$ isomers indicates that this region is useful in determining stereochemistry; cis isomers have two methylene vibrations near 900 cm$^{-1}$, while the more symmetric trans isomer has only one. Using this criterion (Figure 1), solid Co(en)$_2$(NO)Cl$^+$Cl$^-$ is assigned the trans configuration.[2,3] However, in solution, solvation occurs[2] with displacement of Cl$^-$, due to the strong trans effect of NO$^-$. The pmr spectra of Co(en)$_2$(NO)Cl$_2$ in methanol and water (Figure 2) indicate that the stereochemistry of solvolysis in methanol is different from what it is in water. Although the pmr spectrum of the en methylene protons in water shows a singlet, consistent with *trans*-Co(en)$_2$(NO)(H$_2$O)$^{2+}$,[21] the spectrum in methanol shows a symmetric multiplet, indicating the formation of *cis*-Co(en)$_2$(NO)(CH$_3$OH)$^{2+}$ or trigonal-bipyramidal Co(en)$_2$-

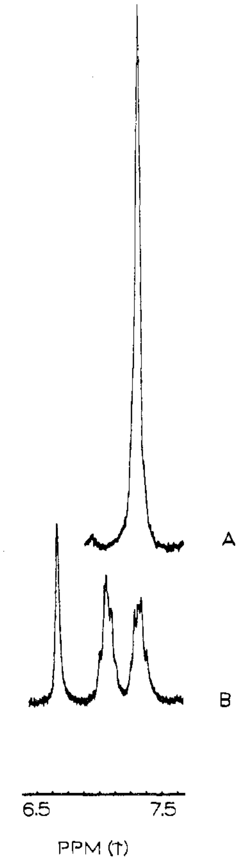


**Figure 2.** The 220-MHz pmr spectra of the methylene en protons for Co(en)$_2$(NO)Cl$_2$ in (A) D$_2$O and (B) CD$_3$OD solution (residual solvent protons appear at $\tau$ 6.7).

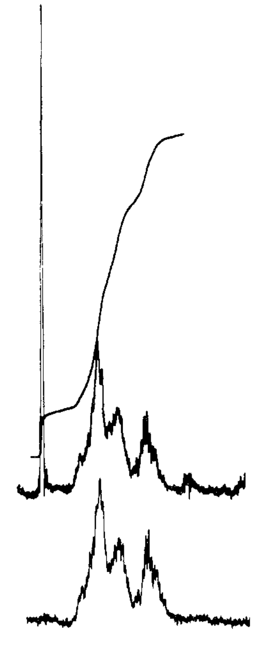


**Figure 3.** The 220-MHz pmr spectra of the methylene en protons for (A) *cis*-Co(en)$_2$(NO$_2$)Cl$_2$·0.5CH$_3$OH and (B) *cis*-Co(en)$_2$(NO$_2$)Cl$_2$ (sample A recrystallized from H$_2$O-HCl), both in D$_2$O solution.

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(17) The low concentration of NO dimer ($\Delta H = -2.45$ kcal/mol[18]) makes attack by (NO)$_2$ unlikely.

(18) C. Dinerman and G. Ewing, *J. Chem. Phys.*, **53**, 626 (1970).

(19) P. Gans, *J. Chem. Soc. A*, 943 (1967); B. Hoskins and F. Whillians, *J. Chem. Soc., Dalton Trans.*, 607 (1973).

(20) M. Baldwin, *J. Chem. Soc.*, 4369 (1960).

(21) C. Hawkins, "Absolute Configuration of Metal Complexes," Wiley-Interscience, New York, N. Y., 1971; J. Malin and H. Taube, *Inorg. Chem.*, 10, 2403 (1971).

$(NO)^{2+}$. Trigonal-bipyramidal nitrosyl complexes usually contain a linear Co-NO moiety[22] (*cf.* $Co(NO)(das)_2{}^{2+}$ with $\nu_{NO}$ 1852 $cm^{-1}$); however, the expected increase in $\nu_{NO}$ from 1635 $cm^{-1}$ (mull) is not seen in methanol. Therefore, the reactive nitrosyl complex in methanol is thought to be *cis*-$Co(en)_2(NO)(CH_3OH)^{2+}$, not the trans isomer as earlier[2] formulated based on electronic spectra.

The infrared spectrum (Figure 1) of $Co(en)_2(NO_2)Cl_2$, isolated from the NO oxidation of $Co(en)_2(NO)Cl_2$ in methanol, shows it to be the cis isomer; however it is solvated by methanol as shown by pmr data (Figure 3A) and elemental analysis. The $CH_3OH$:Co ratio of 0.3-0.5 suggests that methanol is not coordinated but instead is trapped in the solid lattice. This form of $Co(en)_2(NO_2)Cl_2$ is far more soluble in DMSO than an authentic sample of *cis*-$Co(en)_2(NO_2)Cl_2$. Recrystallization from HCl-$H_2O$ removes the lattice methanol but leaves the methylene resonances unchanged (Figure 3B); the pmr spectrum of the methylene protons both before and after recrystallization is identical with that of the authentic cis isomer.

Production of *cis*-$Co(en)_2(NO_2)Cl_2$ from a methanolic solution of $Co(en)_2NO(CH_3OH)^{2+}$ is most simply explained by ligand oxidation with retention of the Co-N bond. On the other hand, formation of labile Co(II) would be expected to produce a mixture of cis and trans products; the free $NO_2$ produced concurrently could attack ethylenediamine[23] or, more probably, the solvent.[24] Neither is observed. Although we find no evidence for production of *trans*-$Co(en)_2(NO_2)Cl_2$ in the reaction under study, its formation and subsequent isomerization to the less soluble[5] cis isomer cannot be rigorously excluded. However, when the ligand oxidation was carried out at 0° for only 1 hr, in order to minimize isomerization, the isolated product was still entirely cis.

## Conclusions

By varying the ratio of en to Co(II), three different reactions of NO have been characterized: 3:1, formation of $Co(en)_3Cl_3$ *via* oxidation; 2:1, oxidation of the intermediate nitrosyl complex to the nitro complex; 1:1, reductive nitrosylation in the presence of base. The reactivity of NO parallels that of $O_2$ (ligand and/or metal oxidation); however, the ability of NO and $NO_2$ to function as ligands limits its versatility. Although the exact role of pyridine in the oxidation of $Co(NO)(DMG)_2$ is not known, the possibility of ligand oxidation by excess NO in the preparation of nitrosyl complexes, especially when the nitrosyl may be characterized as $NO^-$, must be considered.

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**Registry No.** NO, 10102-43-9; *trans*-$Co(en)_2(NO)Cl_2$, 42741-15-1; $Co(en)_3Cl_3$, 13408-73-6; *cis*-$Co(en)_2(NO_2)Cl_2$, 14221-34-2; $Co(NO_2)(DMG)_2 \cdot py$, 42741-17-3; $Co(NO)(DMG)_2$, 36509-25-8.

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[22] J. Enemark and R. Feltham, *Proc. Nat. Acad. Sci. U. S.*, 69, 3534 (1972).

[23] F. Falk and R. Pease, *J. Amer. Chem. Soc.*, 76, 4746 (1954); A. Comyns, *Nature (London)*, 172, 491 (1953).

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# Solvent and Alkyl Substituent Effects on the Kinetics of Base Exchange in Alkylbis(dimethylglyoximato)cobalt(III)-Trimethyl Phosphite Complexes[1]

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The rate of dissociation of $P(OCH_3)_3$ from the methylatobis(dimethylglyoximato)cobalt(III)-$P(OCH_3)_3$ complex, $CH_3Co(dh)_2$-$P(OCH_3)_3$, was observed using nmr techniques in solvents of varying dielectric constant, and the rate at 100° was found to decrease by a factor of about 2 over the range of solvents from toluene to nitrobenzene. Replacement of protons in the OHO bridges of the planar ligand system by deuterium results in no observable change in the $P(OCH_3)_3$ dissociation rate. Substitution of axial $CH_3$ by haloalkyl groups results in a decrease in rate, which, however, does not follow the expected inductive order. Replacement of $CH_3$ by $(CH_3)_3SiCH_2$ results in an increase in rate. The relative ordering of dissociation rates in bromobenzene at 110° is $CH_2Si(CH_3)_3 > CH_3 > CH_2F > CHF_2 > CH_2Cl > CF_3 \approx CHCl_2 \approx CH_2Br > CHBr_2$. The ratio of fastest to slowest rate in the series is about 200. The base dissociation is thus shown to be subject to a strong trans effect due to alkyl group substitution.

The kinetics of ligand substitution and exchange in bis(dimethylglyoximato) complexes of cobalt(III) have been extensively studied.[2-5] It is evident that alkyl substituents on the axis normal to the planar ligand system strongly labilize the trans position. We have studied the kinetics of base ex-

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