

The Preparation of Ruthenium Nitrosyl Complexes Containing 2,2'-Bipyridine and 1,10-Phenanthroline

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Two types of reaction, conversion of coordinated nitrite to nitrosyl by acid and nitrosation by acidic solutions of free nitrite ion, have been used to prepare ruthenium nitrosyl complexes. The complexes prepared are of the types $\text{Ru}(\text{AA})_2(\text{NO})\text{X}^{2+}$ and $\text{Ru}(\text{AA})_2(\text{NO})\text{py}^{3+}$ (AA = 2,2'-bipyridine or 1,10-phenanthroline; X = Cl, Br, or NO_2 ; py = pyridine). The preparations and some chemical and physical properties of the complexes are presented and discussed.

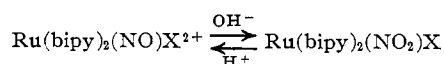
Introduction

The preparations of most ruthenium nitrosyl complexes ultimately begin with the compounds $[\text{Ru}(\text{NO})\text{X}_3]_n$ (X = Cl, Br, I) which are isolated from solutions containing RuO_4 , HX, and HNO_3 .¹ They can be converted into salts containing $\text{Ru}(\text{NO})\text{X}_3^{2-}$ by the addition of X^- . Both the salts and the starting compounds have been allowed to react with a wide variety of bases in displacement reactions, to give mixed-ligand complexes.¹ In these reactions the ruthenium-nitrosyl linkage remains intact under a wide variety of conditions in the presence of many different bases.

Bonding in ruthenium nitrosyl compounds is thought to involve mainly Ru(II) and NO^+ with appreciable back-donation from ruthenium to nitrosyl.² It is uncommon to find complexes which contain more than two back-bonding ligands in addition to NO itself. For example, even under forcing conditions $\text{Ru}(\text{NO})\text{Cl}_5^{2-}$ reacts to give only the disubstituted products $\text{Ru}(\text{NO})\text{A}_2\text{Cl}_3$ (A = py, $1/2$ bipy, $1/2$ phen).³

In a recent communication we reported that complexes of the type $\text{Ru}(\text{bipy})_2(\text{NO})\text{X}^{2+}$ can be prepared in two ways: (1) by prior coordination of NO_2^- followed by conversion to coordinated NO^+ in acidic aqueous solutions and (2) by the addition of stoichiometric amounts of nitrite ion to acidic solutions of the corresponding aquo complexes $\text{Ru}(\text{bipy})_2(\text{OH}_2)\text{X}^+$.⁴ It is significant that in both methods of preparation, the nitrosyl group is coordinated *after* the basic ligand framework has been established around the ruthenium.

It was also reported that the nitrosyl complexes, once formed, react with hydroxide ion to give the corresponding nitrite complexes $\text{Ru}(\text{AA})_2(\text{NO}_2)\text{X}$. The interconversion between the two forms is reversible



in aqueous solution and depends on the pH of the solution.⁴

Here we describe in greater detail the preparations

and some chemical and physical properties of a series of nitrosyl complexes of the types $\text{Ru}(\text{AA})_2(\text{NO})\text{X}^{2+}$ and $\text{Ru}(\text{AA})_2(\text{NO})\text{py}^{3+}$ [X = Cl, Br, NO_2 ; AA = 2,2'-bipyridine, 1,10-phenanthroline; py = pyridine]. The preparations and properties of the complexes are virtually the same regardless of whether 1,10-phenanthroline or 2,2'-bipyridine is used.

Experimental Section

Preparation of Ruthenium Complexes.—The complexes $\text{Ru}(\text{bipy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Ru}(\text{bipy})_2\text{Br}_2 \cdot 2\text{H}_2\text{O}$, $[\text{Ru}(\text{bipy})_2(\text{py})_2](\text{ClO}_4)_2$, $\text{Ru}(\text{phen})_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$, $\text{Ru}(\text{phen})_2\text{Br}_2 \cdot 2\text{H}_2\text{O}$, and $[\text{Ru}(\text{phen})_2(\text{py})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ were prepared essentially as described by Dwyer and coworkers.^{5,6} In some cases the waters of hydration can be removed by prolonged drying *in vacuo* over phosphorus pentoxide or by recrystallization from dichloromethane-ether.⁷ The perchlorate salts of the bis-pyridine complexes were converted to hexafluorophosphate salts by dissolving them in water and adding aqueous ammonium hexafluorophosphate.

Preparation of $\text{Ru}(\text{bipy})_2(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$.—A 0.5-g sample of $\text{Ru}(\text{bipy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ was suspended in 30 ml of water and boiled for 15 min with vigorous stirring. The deep red solution was cooled and filtered, and 1.5 g of sodium nitrite was added. This solution was heated on a steam bath for 1 hr. The deep red crystals which formed were collected by filtration, washed with water and then methanol, air dried, and then dried over P_2O_{10} *in vacuo*; 78% yield. *Anal.* Calcd for $\text{RuC}_{20}\text{H}_{18}\text{N}_6\text{O}_5$: C, 47.52; H, 3.16; N, 16.53. Found: C, 46.88; H, 3.16; N, 16.25.

Preparation of $\text{Ru}(\text{phen})_2(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$.—The procedure was the same as for $\text{Ru}(\text{bipy})_2(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ except that a suspension of 0.5 g of $[\text{Ru}(\text{phen})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ in water was boiled initially for 45 min. The red-brown solid was obtained in 70% yield. *Anal.* Calcd for $\text{RuC}_{24}\text{H}_{18}\text{N}_6\text{O}_5$: C, 52.08; H, 2.89; N, 15.18. Found: C, 51.56; H, 3.07; N, 15.18.

Preparation of $[\text{Ru}(\text{bipy})_2(\text{NO})\text{NO}_2](\text{PF}_6)_2$.—A 0.5-g sample of $\text{Ru}(\text{bipy})_2(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ was suspended in 60 ml of methanol with vigorous stirring. A 4-ml amount of 70% hexafluorophosphoric acid was added slowly, dropwise. The initial red-brown solid was converted into a pale yellow-orange solid within a few seconds of addition of the acid. The yellow-orange solid was collected by filtration, washed with water and then methanol, and air dried. The product was recrystallized from acetonitrile-ether; 95% yield. *Anal.* Calcd for $\text{RuC}_{20}\text{H}_{16}\text{N}_8\text{O}_3\text{P}_2\text{F}_{12}$: C, 30.81; H, 2.05; N, 10.78; F, 29.27. Found: C, 31.13; H, 2.01; N, 10.89; F, 29.59.

Preparation of $[\text{Ru}(\text{phen})_2(\text{NO})\text{NO}_2](\text{PF}_6)_2$.—The procedure was the same as for $[\text{Ru}(\text{bipy})_2(\text{NO})\text{NO}_2](\text{PF}_6)_2$ except that $[\text{Ru}(\text{phen})_2(\text{NO}_2)_2] \cdot \text{H}_2\text{O}$ was used as the starting material. The pale green solid was obtained in 95% yield. *Anal.* Calcd for

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(3) M. B. Fairey and R. J. Irving, *J. Chem. Soc. A*, 475 (1966).

(4) T. J. Meyer, J. B. Godwin, and N. Winterton, *Chem. Commun.*, 872 (1970).

(5) F. P. Dwyer, H. A. Goodwin, and E. C. Gyarfás, *Aust. J. Chem.*, **16**, 42 (1963).

(6) B. Bosnich and F. P. Dwyer, *ibid.*, **19**, 2229 (1966).

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$\text{RuC}_{24}\text{H}_{16}\text{N}_6\text{O}_9\text{F}_{12}$: C, 34.74; H, 2.17; N, 10.13; F, 27.50. Found: C, 34.83; H, 2.15; N, 10.20; F, 27.58.

Preparation of $[\text{Ru}(\text{bipy})_2(\text{NO})\text{NO}_2](\text{ClO}_4)_2$ and $[\text{Ru}(\text{phen})_2(\text{NO})\text{NO}_2](\text{ClO}_4)_2$.—The same procedures were used as for the preparations of the hexafluorophosphate salts except that 70% perchloric acid was used. Both complexes were obtained in 95% yield. *Anal.* Calcd for $\text{RuC}_{20}\text{H}_{16}\text{N}_6\text{O}_{11}\text{Cl}_2$: C, 34.88; H, 2.33; N, 12.20; Cl, 10.31. Found: C, 34.68; H, 2.29; N, 11.93; Cl, 10.21. Calcd for $\text{Ru}_{24}\text{H}_{16}\text{N}_6\text{O}_{11}\text{Cl}_2$: C, 39.13; H, 2.17; N, 11.41; Cl, 9.46. Found: C, 39.07; H, 2.10; N, 11.10; Cl, 9.47.

Preparation of $[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}](\text{PF}_6)_2$.—A 0.400-g sample of $\text{Ru}(\text{bipy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (0.83 mmol) was suspended in 30 ml of water and the solution was boiled with stirring for 15 min. The deep red-brown solution was filtered while hot and then cooled, and 2 ml of 2 M hydrochloric acid was added. A 5-ml sample of an aqueous solution containing 0.057 g of sodium nitrite (0.83 mmol) was added slowly, dropwise to the stirred solution over a 10-min period. After complete addition, the deep green-brown solution was warmed at 50° for an additional 10 min. A 4-ml amount of saturated ammonium hexafluorophosphate was slowly added to the solution giving a pale brown precipitate. The solid was collected by filtration, washed three times with small portions of cold water, and air dried. It was recrystallized by dissolving in the minimum amount of acetonitrile-methanol (1:1 by volume) and slowly adding the solution to ether in excess; 78% yield. *Anal.* Calcd for $\text{RuC}_{20}\text{H}_{16}\text{N}_5\text{ClOP}_2\text{F}_{12}$: C, 31.20; H, 2.00; N, 9.10; Cl, 4.61; F, 29.64. Found: C, 30.84; H, 2.00; N, 8.91; Cl, 4.54; F, 29.81.

Preparation of $[\text{Ru}(\text{phen})_2(\text{NO})\text{Cl}](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$.—The procedure was the same as for $[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}](\text{PF}_6)_2$ except that $\text{Ru}(\text{phen})_2\text{Cl}_2$ was used as the starting complex. A stoichiometric amount of sodium nitrite was used; 75% yield. *Anal.* Calcd for $\text{RuC}_{24}\text{H}_{18}\text{N}_5\text{O}_2\text{P}_2\text{F}_{12}$: C, 36.27; H, 1.95; N, 8.27; F, 27.92; Cl, 4.41. Found: C, 36.15; H, 2.23; N, 8.15; F, 26.82; Cl, 4.59.

Preparation of $[\text{Ru}(\text{bipy})_2(\text{NO})\text{Br}](\text{PF}_6)_2$.—A 0.400-g sample of $\text{Ru}(\text{bipy})_2\text{Br}_2$ (0.70 mmol) was suspended in 40 ml of water and the suspension was refluxed with stirring for 1 hr. The deep red-brown solution was filtered while hot and 2 ml of 10% hydrobromic acid was added. To the warm solution (50–60°) was added slowly, dropwise, 0.048 g of sodium nitrite (0.70 mmol) dissolved in 4 ml of water. After complete addition, the solution was pale yellow-green. A 4-ml sample of saturated ammonium hexafluorophosphate in water was added and the pale green solid which precipitated was collected by filtration, washed twice with cold water, and air dried. The solid was recrystallized from an acetonitrile-methanol mixture by careful addition to ether; 70% yield. *Anal.* Calcd for $\text{RuC}_{20}\text{H}_{16}\text{N}_5\text{OBrP}_2\text{F}_{12}$: C, 29.52; H, 1.97; N, 8.61; F, 28.04; Br, 9.84. Found: C, 29.75; H, 1.93; N, 8.78; F, 28.33; Br, 9.58.

Preparation of $[\text{Ru}(\text{phen})_2(\text{NO})\text{Br}](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$.—The same procedure was used as above except that $\text{Ru}(\text{phen})_2\text{Br}_2$ was the starting complex. We have been unable to obtain a pure sample of this complex as indicated by the analytical data. *Anal.* Calcd for $\text{RuC}_{24}\text{H}_{18}\text{N}_5\text{O}_2\text{BrP}_2\text{F}_{12}$: C, 33.45; H, 1.86; N, 8.13; F, 26.48; Br, 9.29. Found: C, 35.07; H, 2.00; N, 8.11; F, 22.56; Br, 6.62.

Preparation of $[\text{Ru}(\text{bipy})_2(\text{NO})\text{py}](\text{PF}_6)_3$.—A 1.000-g sample of $[\text{Ru}(\text{bipy})_2(\text{py})_2](\text{PF}_6)_3$ (1.16 mmol) was suspended in 400 ml of water. The aqueous solution was refluxed for 3 hr with stirring, until the solution color had changed from orange to the deep red color of the aquated complex. During the last hour, the volume was reduced to 75 ml. The solution was cooled to 50° and 5 ml of 2 M hydrochloric acid was added. An aqueous solution containing 0.080 g (1.16 mmol) of sodium nitrite in 15 ml of water was added to the stirred solution changing its color from red to yellow. After the solution had cooled to room temperature, 4 ml of a saturated solution of ammonium hexafluorophosphate in water was added. The golden yellow product precipitated immediately. It was collected by filtration, washed several times with small portions of water, air dried, and then recrystallized

from acetone-ether; 78% yield. *Anal.* Calcd for $\text{RuC}_{25}\text{H}_{21}\text{N}_6\text{OP}_3\text{F}_{18}$: C, 31.34; H, 2.19; N, 8.77; F, 35.73. Found: C, 31.36; H, 2.28; N, 8.66; F, 35.08.

Preparation of $[\text{Ru}(\text{phen})_2(\text{NO})\text{py}](\text{PF}_6)_3$.—The same procedure was used as for $[\text{Ru}(\text{bipy})_2(\text{NO})\text{py}](\text{PF}_6)_3$ except that $[\text{Ru}(\text{phen})_2(\text{py})_2](\text{PF}_6)_2$ was the starting complex; 80% yield. *Anal.* Calcd for $\text{RuC}_{20}\text{H}_{21}\text{N}_6\text{OP}_3\text{F}_{18}$: C, 34.62; H, 2.09; N, 8.35; F, 34.07. Found: C, 34.45; H, 2.18; N, 8.49; F, 34.19.

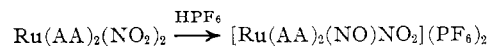
Preparations of Nitrite Complexes from the Nitrosyl Complexes. **Preparation of $[\text{Ru}(\text{bipy})_2(\text{NO}_2)\text{Cl}] \cdot \text{H}_2\text{O}$.**—A 0.15-g sample of $[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}](\text{PF}_6)_2$ was suspended with stirring in 10 ml of 1 M sodium hydroxide. The pale brown solid quickly reacted to give a red-brown solid. Stirring was continued for 15 min. The solution was filtered, and the collected brown solid was washed three times with cold water and then successively with dimethoxyethane and ether. After being air dried, it was dried *in vacuo* over P_2O_{10} ; 68% yield. *Anal.* Calcd for $\text{RuC}_{20}\text{H}_{18}\text{N}_5\text{O}_3\text{Cl}$: C, 48.48; H, 3.23; N, 14.14; Cl, 7.07. Found: C, 48.41; H, 3.46; N, 13.94; Cl, 6.96.

Preparation of $[\text{Ru}(\text{bipy})_2(\text{NO}_2)_2] \cdot \text{H}_2\text{O}$.—The procedure was the same as for $[\text{Ru}(\text{bipy})_2(\text{NO}_2)\text{Cl}] \cdot \text{H}_2\text{O}$ except that $[\text{Ru}(\text{bipy})_2(\text{NO})\text{NO}_2](\text{PF}_6)_2$ was the starting complex; 85% yield. *Anal.* Calcd for $\text{RuC}_{20}\text{H}_{18}\text{N}_6\text{O}_5$: C, 45.88; H, 3.44; N, 16.06. Found: C, 45.88; H, 3.16; N, 16.25.

Measurements.—Infrared spectra were recorded on Perkin-Elmer 421 and Beckman IR-12 spectrometers, ultraviolet-visible spectra on a Cary 14, and pmr spectra on Varian A-60 and HA-100 spectrometers. Magnetic susceptibility measurements were made using the Faraday technique as described by Hatfield, *et al.*⁸ Pascal's constants were used to make diamagnetic corrections.⁹

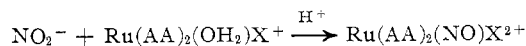
Results

Two types of reaction have been used in the preparations of the bis(2,2'-bipyridine) and bis(1,10-phenanthroline) nitrosyl complexes of ruthenium. In the first, nitrite initially is coordinated to ruthenium and is then converted into coordinated nitrosyl in the presence of acid



Since the nitrosyl complexes prepared by this route were obtained in 95% yield, the conversion from coordinated nitrite to coordinated nitrosyl is nearly quantitative. The conversion occurs in the presence of any strong protic acid, but the perchlorate and hexafluorophosphate salts are most easily isolated.

In the second reaction the appropriate aquo complexes are nitrosated in the presence of stoichiometric amounts of nitrite ion in acidic solution



Stoichiometric amounts of nitrite ion must be used. If excess nitrite is used in the preparation of either $\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}^{2+}$ or $\text{Ru}(\text{bipy})_2(\text{NO})\text{Br}^{2+}$, the ultimate product is $\text{Ru}(\text{bipy})_2(\text{NO})\text{NO}_2^{2+}$. In the presence of excess nitrite in acidic aqueous solution $\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}^{2+}$ is converted into $\text{Ru}(\text{bipy})_2(\text{NO})\text{NO}_2^{2+}$ within a few minutes. The nitrosyl complexes were obtained most conveniently as their hexafluorophosphate salts which are only slightly soluble in water but

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show good solubility in acetonitrile and dimethylformamide and lesser solubility in other polar organic solvents.

When dissolved in water the complexes give pale yellow solutions, which immediately turn deep red-brown if hydroxide ion is added in excess. From reactions of $\text{Ru}(\text{bipy})_2(\text{NO})\text{NO}_2^{2+}$ and $\text{Ru}(\text{bipy})(\text{NO})\text{Cl}^{2+}$ with hydroxide, the corresponding nitrite complexes $\text{Ru}(\text{bipy})_2(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ and $\text{Ru}(\text{bipy})_2(\text{NO}_2)\text{Cl} \cdot \text{H}_2\text{O}$ have been isolated. The nitrite complexes are reconverted into the nitrosyl complexes within a few seconds by the addition of acids either to solutions or to suspensions of the complexes. The preparative and quantitative aspects of the reactions of the nitrosyl complexes with a variety of bases are currently under investigation.

The infrared stretching frequencies for coordinated nitrosyl and coordinated nitrite in the complexes are given in Table I. The nitrosyl stretching frequencies

TABLE I^a

Complex	ν_{NO}^b	NO_2^- bands, ^c cm^{-1}			
		ν_{as}	ν_{s}	δ_{ONO}	ρ_{NO_2}
$[\text{Ru}(\text{bipy})_2(\text{NO})\text{py}](\text{PF}_6)_3$	1950 vs
$[\text{Ru}(\text{bipy})_2(\text{NO})\text{NO}_2](\text{PF}_6)_2$	1942 vs	1450 vs ^d	1321 vs	817 s	612 w, br
$[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}](\text{PF}_6)_2$	1931 vs
$[\text{Ru}(\text{bipy})_2(\text{NO})\text{Br}](\text{PF}_6)_2$	1930 vs
$[\text{Ru}(\text{phen})_2(\text{NO})\text{py}](\text{PF}_6)_3$	1951 vs
$[\text{Ru}(\text{phen})_2(\text{NO})\text{NO}_2](\text{PF}_6)_2$	1943 vs	1428 vs	1319 vs	810 s	612 w, br
$[\text{Ru}(\text{phen})_2(\text{NO})\text{Cl}](\text{PF}_6)_2$	1932 vs
$[\text{Ru}(\text{phen})_2(\text{NO})\text{Br}](\text{PF}_6)_2$	1931 vs
$\text{Ru}(\text{bipy})_2(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$...	1332 vs	1304 vs	810 s	610 w, br
			1278 vs		
$\text{Ru}(\text{phen})_2(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$...	1318 vs	1304 vs	810 s	615 w, br
			1278 vs		
$\text{Ru}(\text{bipy})_2(\text{NO}_2)\text{Cl} \cdot \text{H}_2\text{O}$...	1325 vs	1270 vs	805 s	610 w, br

^a Abbreviations: vs, very strong; s, strong; w, weak; br, broad. ^b In acetone solution; $\pm 2 \text{ cm}^{-1}$. ^c In KBr pellets; $\pm 3 \text{ cm}^{-1}$. ^d This band is apparently coincident with a bipy band.

are relatively high when compared to those of other ruthenium nitrosyl complexes.¹⁰ The positions of the nitrite bands indicate that nitrite is nitrogen rather than oxygen bound.¹¹

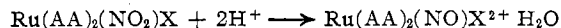
Magnetic susceptibility measurements were made for all of the nitrosyl complexes, and all were found to be diamagnetic. The observed molar susceptibilities, corrected for the diamagnetic contribution,⁹ were in the range of $(747\text{--}863) \times 10^{-6} \text{ emu/g-atom}$, and all samples probably contain paramagnetic impurities.

The geometry of all of the complexes is presumably cis since many of the starting complexes are known to be cis,^{5,6} and the nitrosation reactions are carried out under mild conditions. To verify the cis configuration for $\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}^{2+}$, the pmr spectrum of $[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}](\text{PF}_6)_2$ in acetone- d_6 was obtained. Although we have been unable to assign the spectrum completely, it is clearly inconsistent with a trans configuration.¹²

Discussion

Coordinated nitrite in $\text{Ru}(\text{AA})_2(\text{NO}_2)_2$ and $\text{Ru}(\text{AA})_2(\text{NO}_2)\text{Cl}$ is rapidly converted into coordinated nitrosyl

in the presence of excess acid. The conversion may occur by direct nitrosation of coordinated nitrite



It may also occur by prior acid-catalyzed aquation



followed by nitrosation of the aquo complex formed. The direct nitrosation path has been observed in the conversion of $\text{Fe}(\text{CN})_5(\text{NO}_2)^{4-}$ to $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ in acid solution,¹³ and it is probably the path for the ruthenium complexes as well. Also, $\text{Ru}(\text{bipy})_2(\text{NO})(\text{NO}_2)^{2+}$ does not lose nitrite even when dissolved in concentrated acids at room temperature for 1 hr.⁷ In the ruthenium complexes, acid-catalyzed aquation is apparently much slower than nitrosyl formation.

At room temperature in the absence of added acid, no reaction between excess NO_2^- and $\text{Ru}(\text{bipy})_2(\text{OH}_2)\text{Cl}^+$ to give $\text{Ru}(\text{bipy})_2(\text{NO}_2)\text{Cl}$ is observed after 1 hr.⁷ However, if a stoichiometric amount of sodium nitrite is added to an acidic solution of the aquo complex, nitrosation to give $\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}^{2+}$ is complete within a few minutes. Prior aquation to give $\text{Ru}(\text{bipy})_2(\text{NO}_2)\text{Cl}$, followed by acid conversion of coordinated nitrite to nitrosyl, does not occur. Rather, nitrosyl formation must take place by nitrosonium ion (or a nitrosonium ion precursor like HNO_2 or H_2NO_2^+) attack on the six-coordinate aquo complex. The position of attack by NO^+ may be at ruthenium with the displacement of coordinated OH_2 or at the oxygen of the coordinated water. Coordinated chloride and bromide ions are also displaced by NO^+ , but more slowly than water. In acidic solutions containing excess nitrite ion, $\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}^{2+}$ is converted into $\text{Ru}(\text{bipy})_2(\text{NO})\text{NO}_2^{2+}$ within a few minutes. Although the latter reaction indicates that a dinitrosyl intermediate like $\text{Ru}(\text{bipy})_2(\text{NO})_2^{4+}$ may exist, we have been unable to isolate it even from solutions of $\text{Ru}(\text{bipy})_2(\text{NO}_2)_2$ in 70% perchloric acid.⁷

Two general types of reactions have been described here which lead to ruthenium nitrosyl complexes. Both may have important consequences for the preparations of ruthenium and other metal nitrosyl complexes. Either reaction, acid conversion of coordinated nitrite to nitrosyl or nitrosation by acidic nitrite solutions, has the advantage that the ligand framework around the metal ion can be established before the metal-nitrosyl bond is formed. There is precedence for both types of reaction for other complexes. It has been reported that $\text{Ru}(\text{NH}_3)_6^{2+}$ forms $\text{Ru}(\text{NH}_3)_5\text{NO}^{3+}$ in aqueous nitrite-hydrochloric acid media¹⁴ and that $\text{K}_2[\text{Ir}(\text{NO}_2)\text{Br}_4]$ is converted into $\text{K}[\text{Ir}(\text{NO})\text{Br}_5]$ by hydrobromic acid.¹⁵ The generality of the reactions for 2,2'-bipyridine and 1,10-phenanthroline complexes of ruthenium is somewhat restricted since several potential cis ligands, including ammonia, iodide ion, and azide ion, react with both free and coordinated NO^+ .⁷ The reactions of

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(11) K. Nakamoto, J. Fujita, and H. Murato, *J. Amer. Chem. Soc.*, **80**, 4817 (1958).

(12) R. E. DeSimone and R. S. Drago, *Inorg. Chem.*, **8**, 2617 (1969).

(13) J. Masek and H. Wenat, *Inorg. Chim. Acta*, **2**, 455 (1968).

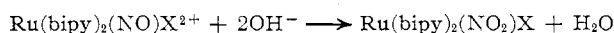
(14) F. M. Lever and A. R. Powell, *Chem. Soc., Spec. Publ.*, **No. 13**, 135 (1959).

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these and other substrates with coordinated nitrosyl is currently under investigation.

Coordinated NO^+ would also seem to be a likely leaving group in the acid-catalyzed aquation of metal nitrite complexes. However, this has been shown not to be the case in the acid-catalyzed removal of nitrite from $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$.¹⁶

All of the nitrosyl complexes reported here react rapidly in solution with hydroxide ion to give deep red-brown solutions of the corresponding nitrite complexes.⁷ Reconversion to the nearly colorless nitrosyl complexes occurs by making the solutions acidic. We have described in the Experimental Section the preparations of $[\text{Ru}(\text{bipy})_2(\text{NO}_2)_2] \cdot \text{H}_2\text{O}$ and $[\text{Ru}(\text{bipy})_2(\text{NO}_2)\text{Cl}] \cdot \text{H}_2\text{O}$ by reaction with hydroxide



In addition to the ruthenium chelate complexes reported here both $\text{Fe}(\text{CN})_5\text{NO}_2^-$ and $\text{Ru}(\text{CN})_5\text{NO}_2^{2-}$ react with hydroxide to give the corresponding nitrite complexes $\text{Fe}(\text{CN})_5\text{NO}_2^{4-}$,^{13,17} and $\text{Ru}(\text{CN})_5\text{NO}_2^{4-}$.¹⁸ Activation of coordinated nitrosyl to attack by bases

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seems to occur only when back-bonding ligands in addition to nitrosyl groups are coordinated to the metal. In other complexes, reactions with hydroxide or other bases result in ligand displacement and the metal-nitrosyl linkage is unreactive.¹

The relatively high infrared stretching frequencies for coordinated NO in these complexes are indicative that a high degree of positive charge resides on the coordinated nitrosyl. Values for ν_{NO} in acetone are from 1930 to 1951 cm^{-1} for the ruthenium chelate complexes and 1937 and 1930 cm^{-1} in mulls for $\text{K}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot \text{H}_2\text{O}$ and $\text{K}_2[\text{Ru}(\text{CN})_5\text{NO}]$, respectively.¹⁰ The high ν_{NO} values, diamagnetism of the complexes, and facile interconversion between coordinated nitrite and coordinated nitrosyl all indicate that the bipyridine and phenanthroline complexes contain essentially ruthenium(II) and bound nitrosyl with a high degree of positive charge.

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The Reaction of Tris(1,10-phenanthroline)iron(II) Ion with Chlorine(I) Species

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Hypochlorous acid reacts with $\text{Fe}(\text{phen})_3^{2+}$ by two paths, one which is dependent upon dissociation of the iron complex and one which is independent of dissociation. The reaction was studied at 15, 25, and 40° under pseudo-first-order conditions with the oxidant being in excess. At 25° and constant pH, plots of the pseudo-first-order rate constant as a function of $[\text{Cl(I)}]$ are linear with equal nonzero intercepts and slopes that increase with increasing $[\text{H}^+]$. The pseudo-first-order rate constant is given by

$$k_{\text{obsd}} = k_0 + \left[\frac{k_1[\text{H}^+]/K + k_2}{[\text{H}^+]/K + 1} \right] [\text{Cl(I)}]$$

At 25° $k_0 = (7.5 \pm 0.2) \times 10^{-5} \text{ sec}^{-1}$, $k_1 = (2.2 \pm 0.14) \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$, and $k_2 = (2.0 \pm 0.16) \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$. The rate constants were calculated using a value of 2.90×10^{-8} for the acid dissociation constant of hypochlorous acid at 25°.

Introduction

Hypochlorous acid reacts much more rapidly than does chlorine in solution with aquated iron(II).¹ However, preliminary work by Shakhashiri and Gordon indicates that oxidation of the tris(1,10-phenanthroline)iron(II) complex by hypochlorous acid is considerably slower than when chlorine is the oxidizing agent.²

The reaction of hypochlorous acid with tris(1,10-

phenanthroline)iron(II) ion in acid solution is autocatalytic; as the reaction proceeds, chloride ion formed as a product reacts with hypochlorous acid to produce chlorine appropriate to the equilibrium



Since tris(1,10-phenanthroline)iron(II) ion is stable in the pH region 2–9,³ we have attempted to eliminate chlorine interference by studying the reaction at high pH where chlorine is absent.

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