Contribution from the Department of Chemistry,
Boston University, Boston, Massachusetts 02215

# Preparation and Characterization of a New Series of Cis Nitrosylruthenium Complexes

STEVEN PELL and JOHN N. ARMOR*

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Synthesis of an entirely new series of cis nitrosyl complexes of the form *cis*-$[Ru(NH_3)_4(NO)X]^{n+}$, where $X = OH_2$, $OH^-$, $Cl^-$, $Br^-$, and $I^-$, was achieved by the direct, stereospecific attack of NO upon the corresponding *cis*-$[Ru(NH_3)_4X_2]^{m+}$ complexes. The reactions are clean and provide a direct route for the preparation of other nitrosyls. The uv-visible spectra of these new complexes have been recorded and compared with similar spectra for the corresponding trans series. The infrared spectra are noticeably different from those of the trans series with the cis complexes displaying the ir bands expected for the less symmetric isomer. Preliminary results for the interconversion of the cis to the trans isomer indicate that the isomerization does not proceed readily in the solid state or in acid solution, but the cis form does isomerize slowly in alkaline solution into the trans form. By comparing the $\nu$(NO) stretching frequencies for the cis and trans isomers, it appears that the cis ligands significantly influence the bonding of the nitrosyl ligand.

## Introduction

In the past, octahedral nitrosyl complexes of the form $RuX_4Y(NO)^{n+}$ have been identified as trans nitrosyl.[1-4] Detailed analyses of the infrared spectra of metal nitrosyls upon varying the trans ligand Y have been used to support arguments that nitrosyls exert a trans-labilizing influence.[2-4] X-Ray studies[5] have confirmed that the complexes are trans nitrosyls although some arguments[6] have arisen as to whether the metal-ligand bond trans to the nitrosyl is longer or shorter than the cis metal-ligand bonds. Very little comparative work has been presented for isomeric metal-nitrosyl complexes where the ligand trans to the nitrosyl is varied without altering the chemical composition of the complex. We shall present the preparation of an entirely new series of cis nitrosyl complexes. Their uv, visible, and infrared spectra are also reported and compared with the corresponding trans complexes.

## Experimental Section

**Nitric** oxide (Matheson) was purified by an exhaustive scrubbing procedure. Using an all-glass system, the reactant solution was degassed with argon. (The argon had been previously scrubbed through a tower of 0.2 *M* $Cr^{2+}$ followed by a tower containing 0.1 *M* NaCl.) By rotating a three-way stopcock, the gas flow was immediately switched to NO which had been previously scrubbed through the following series of towers: molecular sieve 5A at −40°, solid KOH, 8 *M* KOH, and 0.1 *M* NaCl. The NO emerging from the reactant solution was bubbled through a beaker of water to prevent back-diffusion of air into the system. The NO was removed by switching the gas flow back to argon. Nitric oxide directly from the cylinder has been used successfully in preparing ruthenium nitrosyls. Nevertheless, by scrubbing the contents of the cylinder, we remove any trace impurities which may produce temporary or permanent side products.

All uv-visible spectra were recorded on a Cary 14 recording spectrophotometer.

Infrared spectra were recorded on a Perkin-Elmer Model 180 spectrophotometer. In the 4000-600-$cm^{-1}$ region, the spectra were calibrated with a standard polystyrene film. The lower frequency region (<600 $cm^{-1}$) was calibrated using atmospheric water vapor.[7] All samples were suspended in KBr and recorded to 300 $cm^{-1}$.

$^{15}NO$ (99.5% enriched) was purchased from Mallinckrodt Nuclear.

Microanalyses were performed by Schwarzkopf Microanalytical Laboratories.

**$[Ru(NH_3)_5Cl]Cl_2$.** $[Ru(NH_3)_6]Cl_3$, purchased from Matthey Bishop, Inc., was dissolved in a minimum volume of water, filtered, and then reprecipitated by the addition of concentrated HCl. According to the procedure of Vogt, Katz, and Wiberly,[8] the chloropentaammine complex was then prepared by refluxing the hexaammine in 5 *M* HCl.

***cis*-$[Ru(NH_3)_4C_2O_4]_2S_2O_6$.** Following the procedure of Gaunder,[9] 0.82 g of $[Ru(NH_3)_5Cl]Cl_2$ (2.8 mmol) in 35 ml of water was saturated with argon. Five milliliters of concentrated aqueous $NH_3$ was added, and the solution was gently heated on a steam bath until dissolution was complete. Any solid residue which remained was removed by filtration. A solution of 2.2 g of $Na_2S_2O_6 \cdot 2H_2O$ (9.1 m*M*) dissolved in 10 ml of water was added to the light pink ruthenium solution. Argon was bubbled through the solution for 1.5 hr. The resulting yellow-brown solid of $[Ru(NH_3)_5OH]S_2O_6$ which remained was collected by filtration and used immediately. This hydroxo complex was added to 30 ml of a saturated solution of oxalic acid. After heating the solution on a steam bath for 10 min, the orange-yellow *cis*-$[Ru(NH_3)_4C_2O_4]_2S_2O_6$ precipitated. The oxalato complex was collected by filtration and washed with ethanol and ether.

***cis*-$[Ru(NH_3)_4X_2]X$.** Following the procedure of Hartman and Buschbeck,[10] where $X^- = Cl^-$, $Br^-$, or $I^-$, the *cis*-$[Ru(NH_3)_4C_2O_6]_2$-$S_2O_6$ complex was dissolved in 30 ml of concentrated HX and heated on a steam bath for 10 min. Upon addition of ethanol to the cooled solution, the corresponding *cis*-$[Ru(NH_3)_4X_2]X$ precipitated. [The iodide salt, which precipitated immediately upon the addition of ethanol to the product solution, was used immediately.] It was collected by filtration and washed with methanol and ether. The purity of the complexes was confirmed by comparison with published uv-visible spectra.[10]

**Nitrosyl Complexes.** All of the cis nitrosyl complexes were prepared by dissolving the ruthenium complex in an excess of acid and saturating the solution with NO(g), followed by the addition of the sodium salt of the desired anion.

***cis*-$[Ru(NH_3)_4(NO)X]X_2$ ($X^- = Cl^-, Br^-, I^-$).** Using the *cis*-$[Ru(NH_3)_4X_2]X$ in dilute HX, the corresponding *cis*-$[Ru(NH_3)_4(NO)X]X_2$ precipitated (almost quantitatively) out of solution within $^1/_2$ hr of saturation with NO. The solid was filtered and washed with methanol and ether. *Anal.* Calcd for the chloro complex, $[Ru(NH_3)_4(NO)Cl]Cl_2$: Ru, 33.09; N, 22.91; H, 3.94; Cl, 34.82. Found: Ru, 33.16; N, 22.86; H, 4.11; Cl, 34.60. Calcd for the bromo complex, $[Ru(NH_3)_4(NO)Br]Br_2$: Ru, 23.04; N, 15.95; H, 2.73; Br, 54.62. Found: Ru, 22.97; N, 15.79; H, 2.93; Br, 54.28.

***cis*-$[Ru(NH_3)_4(NO)X]Y_2$ ($X^- = Cl^-, Br^-$; $Y^- = Cl^-, Br^-, I^-$).** The corresponding *cis*-$[Ru(NH_3)_4(NO)X]X_2$ was dissolved in a minimum amount of water and precipitated immediately with NaCl, NaBr, or NaI.

***cis*-$[Ru(NH_3)_4(NO)OH](ClO_4)_2$.** *cis*-$[Ru(NH_3)_4X_2]X$ ($X^- = Cl^-$,

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(1) J. R. Durig, W. A. McAllister, J. N. Willis, Jr., and E. E. Mercer, *Spectrochim. Acta*, 22, 1091 (1966).

(2) E. E. Mercer, W. A. McAllister, and J. R. Durig, *Inorg. Chem.*, 5, 1881 (1966).

(3) N. M. Sinitsyn and O. E. Zvyagintsev, *Dokl. Akad. Nauk SSSR*, 145, 109 (1962).

(4) M. B. Fairley and R. J. Irving, *Spectrochim. Acta*, 22, 359 (1966).

(5) N. A. Parpiev and G. B. Bokii, *Russ. J. Inorg. Chem.*, 4, 2454 (1959).

(6) R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, 9, 1053 (1970); J. T. Veal and D. J. Hodgson, *ibid.*, 11, 1421 (1972).

(7) L. R. Blaine, E. Plyer, and W. Benedict, *J. Res. Nat. Bur. Stand., Sect. A*, 66, 223 (1962).

(8) L. H. Vogt, J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, 4, 1157 (1965).

(9) R. G. Gaunder, Ph.D. Thesis, Stanford University, Aug 1969.

(10) H. Hartman and C. Buschbeck, *Z. Phys. Chem. (Frankfurt am Main)*, 11, 120 (1957).

$Br^-$) was dissolved in a minimum amount of water. A solution containing an equivalent amount of $Ag_2O$ dissolved in dilute $HClO_4$ was then added to the ruthenium solution.[11] The mixture was warmed for ~15 min at ~40°, cooled, and filtered. The filtrate was saturated with NO for 1 hr. After removing the NO(g) from the product solution, a pellet of NaOH was added. Upon the addition of $NaClO_4$, the pink complex precipitated (essentially quantitatively) out of solution. *Anal.* Calcd for $[Ru(NH_3)_4(NO)OH](ClO_4)_2$: Ru, 24.37; N, 16.87; H, 3.16; Cl, 17.08. Found: Ru, 23.67; N, 17.12; H, 3.65; Cl, 16.52.

***cis*-$[Ru(NH_3)_4(NO)OH_2](ClO_4)_3$.** The corresponding hydroxo complex, *cis*-$[Ru(NH_3)(NO)OH](ClO_4)_2$, was dissolved in a minimum volume of water. Upon the addition of a few drops of 0.1 *M* $HClO_4$, the pink solution became yellow. Addition of concentrated $HClO_4$ produced the yellow-orange aquo complex, which was washed with methanol and ether. The bromide salt was also prepared in the same manner using HBr instead of $HClO_4$.

***cis*-$[Ru(NH_3)_4(^{15}NO)Br]Br_2$.** *cis*-$[Ru(NH_3)_4Br_2]Br$ (0.49 mmol, 20 mg) was dissolved in 18 ml of 0.02 *M* HBr. Using a vacuum line, the solution was degassed by the repetitive freeze-pump-thaw technique. Approximately 5 ml of $^{15}NO$ (at 1 atm) was introduced into the evacuated 25-ml flask. The flask was then sealed off and the contents stirred for 3 hr. The bromide salt was then isolated (almost quantitatively) by the addition of solid NaBr.

***cis*-$[Ru(ND_3)_4(NO)Br]Br_2$.** *cis*-$[Ru(NH_3)_4(NO)Br]Br_2$ (20 mg) was dissolved in ~15 ml of $D_2O$ and warmed at ~40° for 5 min. The deuterated bromide salt was precipitated from solution by the addition of NaBr.

Trans nitrosyl complexes were prepared as described in the literature.[12,13]

## Results and Discussion

**Uv-Visible Spectra.** The uv-visible spectra of the new series of cis nitrosyl complexes are described in Table I. For comparison, the complete uv-vis spectra of *cis*- and *trans*-$[Ru(NH_3)_4(NO)Cl]Cl_2$ are compared in Figure 1. Schreiner[14] has recently discussed the origin of the uv-visible bands for the *trans*-$[Ru(NH_3)_4(NO)X]^{2+}$ complexes. In general, he described the trans complexes, where $X^- = Cl^-$, $Br^-$, or $OH^-$, as having a broad band $[^1A_1 \rightarrow [^3T_1, {}^3T_2]$ and $t_2 \rightarrow \pi^*(NO)]$ with $\epsilon < 60$ in the 420-480-nm region, a band $[^1A_1 \rightarrow {}^1T_1]$ with $\epsilon < 300$, and an intense charge-transfer band in the uv with $\epsilon > 10^3$. For the series of cis nitrosyl complexes reported above, only two distinct bands are observed. There is a broad, weak transition in the 450-nm region ($\epsilon < 50$) and a more intense transition in the 350-nm region ($\epsilon \sim 10^2$) followed by an intense end absorption. The actual position and intensities of the cis complexes are quite different from those of the trans series, but the overall features are similar. The positions of the bands in the 350-nm region are strongly affected by the intense end absorptions, especially, as exhibited by the *cis*-$[Ru(NH_3)_4(NO)I]^{2+}$ complex.

**Table I.** Uv-Visible Spectra of Cis Nitrosyl Complexes

| Complex | Color of solid | $\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$) |
|---|---|---|
| *cis*-$[Ru(NH_3)_4(NO)Cl]Cl_2$ | Pink | 480 (19)[a]<br>345 ($1.26 \times 10^2$)[b] |
| *cis*-$[Ru(NH_3)_4(NO)Br]Br_2$ | Orange | ~500 (~5)[a]<br>347 ($1.65 \times 10^2$) |
| *cis*-$[Ru(NH_3)_4(NO)I]I_2$ | Green | ~295 sh ($10^2$) |
| *cis*-$[Ru(NH_3)_4(NO)OH](ClO_4)_2$[c] | Pink | 460 (21)[a]<br>330 ($1.7 \times 10^2$)<br>225 sh ($2.6 \times 10^2$) |
| *cis*-$[Ru(NH_3)_4(NO)OH_2]^{3+}$[d] | Yellow-orange | 435 (16)[a]<br>325 (87)<br>230 sh ($2 \times 10^3$) |

[a] Extremely broad. [b] Identical with that for *cis*-$[Ru(NH_3)_4(NO)Cl]Br_2$. [c] Made alkaline to pH >8. [d] Hydroxo complex made acidic to pH <2.

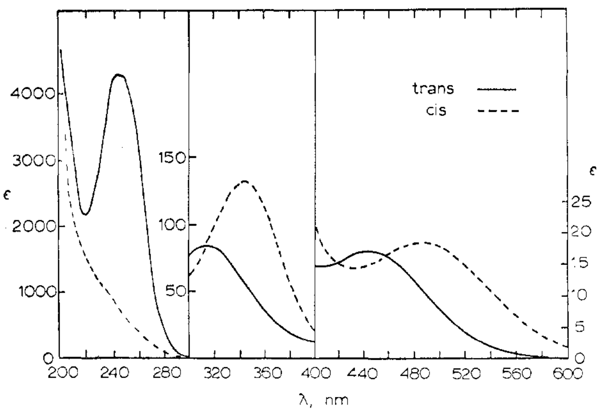

**Figure 1.** Uv-vis spectra of *cis*- (- - -) and *trans*-$[Ru(NH_3)_4(NO)Cl]Cl_2$ (——) in water at 25°. Ordinate ranges for the following spectral regions: (0–4) × $10^3$ $M^{-1}$ $cm^{-1}$, 200–300 nm; 0–150 $M^{-1}$ $cm^{-1}$, 300–400 nm; 0–25 $M^{-1}$ $cm^{-1}$, 460–600 nm.

Using Schreiner's assumption[14] that the complexes can be considered as $d^6$ $Ru^{II}NO^+$, some comparison can be found in the LMCT[15] bands for *cis*- and *trans*-$[Co(en)_2(Cl)Br]^+$ ($d^6$). In the cobalt system,[16] the LMCT[15] band for the cis complex is at higher energy than that for the trans complex. Therefore, for the cis ruthenium nitrosyl the LMCT[15] in the uv might be expected at shorter wavelengths and perhaps hidden by the ligand localized transitions. At 278 nm where *trans*-$[Ru(NH_3)_4(NO)Br]^{2+}$ has a maximum, $\epsilon$ is $3.8 \times 10^3$ $M^{-1}$ $cm^{-1}$; $\epsilon$ for the corresponding cis complex is $5.7 \times 10^2$ $M^{-1}$ $cm^{-1}$. At 245 nm where *trans*-$[Ru(NH_3)_4(NO)Cl]^{2+}$ has a maximum with $\epsilon$ $4.3 \times 10^3$ $M^{-1}$ $cm^{-1}$, the corresponding cis complex has an $\epsilon$ of $1.3 \times 10^3$ $M^{-1}$ $cm^{-1}$.

**Infrared Spectra.** The frequencies of the cis bromo nitrosyls are given in Table II. The assignments made in this table are based on the $^{15}NO$ and deuterated samples and on the assignments made for the trans complexes.[2] Unlike the trans complexes, the cis nitrosyl complexes show a definite shoulder on the band ascribed to $\delta(NH_3)$, a weaker shoulder on the $\rho_r(NH_3)$ band, and a definite splitting of the $\nu(RuNO)$ band. The shoulders are expected for the less symmetric cis complexes, and the ir spectra are consistent with the present assignment of the isomers. The splitting of the $\nu(RuNO)$ band might also be expected for the less symmetric cis case; however, caution must be exerted here since the ammonia ligands might exert some influence on the position of the lower frequency bands.[17] Using $^{15}NO$, the bands, at

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(11) The $Ag_2O$ is not a requirement in the synthesis.

(12) K. Gleu and I. Buddecker, *Z. Anorg. Allg. Chem.*, **268**, 202 (1952).

(13) A. Werner, *Ber.*, **40**, 2614 (1905).

(14) A. F. Shreiner, S. W. Lin, P. J. Hauser, E. A. Hopcus, D. J. Hamm, and J. D. Gunter, *Inorg. Chem.*, 11, 880 (1972). We have prepared *trans*-$[Ru(NH_3)_4(NO)Cl]Cl_2$ by two separate methods: *via* $[Ru(NH_3)_4(NO)OH]Cl_2$[12] and by the direct reaction of NO with *trans*-$[Ru(NH_3)_4Cl_2]Cl$. The spectra which we obtained were identical: $\lambda_{max}$ ($\epsilon$, $M^{-1}$ $cm^{-1}$) 453 (17), 315 (90), 245 ($4.3 \times 10^3$). The spectrum is identical (within error) with that obtained by Schreiner—except for the intensity and position of the band at 315 nm. Schreiner reported a value 330 nm and $\epsilon$ 264 $M^{-1}$ $cm^{-1}$.

(15) LMCT = ligand to metal charge transfer. Caution must be exerted here since Schreiner assigned the band as ($p\pi(Cl) \rightarrow d_{x^2-y^2}, d_{z^2}$), yet it is of lower intensity compared to the cobalt system.

(16) K. Nakamoto, J. Fujita, M. Kobayaski, and R. Tsuchida, *J. Chem. Phys.*, **27**, 439 (1957).

(17) F. F. Bentley, L. D. Smithson, and A. L. Rozek, "Infrared Spectra and Characteristic Frequencies ~700-300 $cm^{-1}$," Interscience, New York, N. Y., 1968, p 6.

**Table II.** Assignment of Bands for Cis Nitrosyls[a]

| *cis*-[Ru(NH$_3$)$_4$(NO)Br]Br$_2$ | *cis*-[Ru(ND$_3$)$_4$(NO)Br]Br$_2$ | *cis*-[Ru(NH$_3$)$_4$($^{15}$NO)Br]Br$_2$ | Assignments |
|---|---|---|---|
| 3450 w | | 3460 b, w | |
| ~3250 s | 2435 s | ~3218 s | $\nu$(NH) |
| ~3150 sh, s | 2295 m | 3120 s, sh | $\nu$(NH) |
| 1934 s | 1933 s | 1896 s | |
| 1902 vs | 1901 vs | 1873 vs | $\nu$(NO) |
| 1590 b, w | 1138 w | ~1590 w, b | $\delta$(NH$_3$) |
| 1340 sh, w | 1030 sh | 1340 sh, w | |
| 1310 s | 1008 s | 1310 s | $\delta$(NH$_3$) |
| 850 m | 670 w | 850 m | $\rho_r$(NH$_3$) |
| 830 sh, w | | 830 sh, w | |
| | 623 m | | |
| 599 m | 580 w | 586 m | $\nu$(RuNO) |
| 589 w | 533 m | 579 m | |
| 481$^b$ m | 448$^b$ m | 483$^b$ m | $\nu$(Ru-NH$_3$) |

[a] Abbreviations used: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; b, broad. [b] This band also contains several ill-defined shoulders.

1933, 1901, 599, and 589 cm$^{-1}$ shift as expected. However, the deuterated sample does not behave as expected. While the bands at 3250, 3150, 1590, 1340, 1310, 850, 830, and 481 cm$^{-1}$ shift as expected, the bands at 599 and 589 cm$^{-1}$ also shift. For comparison, we have prepared the *trans*-[Ru(NH$_3$)$_4$(NO)OH]Br$_2$ in both the H and D forms. The infrared spectra corresponded exactly as previously reported.[2] In addition, we prepared [Ru(ND$_3$)$_5$NO]Br$_3$. As reported earlier, this complex also demonstrated a shifting of the band at 601 cm$^{-1}$ to 533 cm$^{-1}$ in addition to the expected shifts. These results suggest that the bands in the 600-cm$^{-1}$ region, previously assigned as $\nu$(RuNO), may be affected by the ammine frequencies. Mixing of vibrations in the lower energy region of the infrared is not unusual.[4,17]

In Table III, one can observe that the spectra for *cis*-[Ru(NH$_3$)$_4$(NO)Cl]X$_2$, where X$^-$ = Cl$^-$, Br$^-$, or I$^-$, are very similar. This is also true for *cis*-[Ru(NH$_3$)$_4$(NO)Br]X$_2$, where X$^-$ = Br$^-$ or I$^-$, and *cis*-[Ru(NH$_3$)$_4$(NO)OH$_2$]X$_3$, where X$^-$ = Br$^-$ or ClO$_4^-$. Therefore, the bands in the infrared spectra above 700 cm$^{-1}$ are not affected appreciably by the counterion.

Combining the data from Tables II-IV for *cis*-[Ru(NH$_3$)$_4$(NO)X]X$_2$, the spectra are virtually identical down to 600 cm$^{-1}$. This is in sharp contrast to the corresponding *trans*-[Ru(NH$_3$)$_4$(NO)X]X$_2$ where the $\nu$(NO) frequencies shift[2] from 1880 to 1870 to 1862 cm$^{-1}$ for X$^-$ = Cl$^-$, Br$^-$, and I$^-$ (1878 to 1891 to 1884 cm$^{-1}$, respectively in Nujol[4]). The variation of $\nu$(NO) with the trans ligand has been offered as a means of measuring the trans-directing[2,3,14] influence of the X group. This new series of cis nitrosyls demonstrates that when NH$_3$ is the ligand trans to the nitrosyl, there is only a slight variation in $\nu$(NO) for X$^-$ = Cl$^-$, Br$^-$, or I$^-$.

The position of the $\nu$(NO) does depend on the cis ligand to some extent. For X = NH$_3$, $\nu$(NO) occurs at 1913 cm$^{-1}$.[18] When X = H$_2$O or OH$^-$, $\nu$(NO) shifts more dramatically to 1928 or 1861 cm$^{-1}$, respectively. In order to assess the importance of the cis ligands, a more exacting study needs to be performed in the far-infrared region looking at the Ru-X bands.

In Table V, the strongest $\nu$(NO) frequencies for both the cis and trans nitrosyl complexes are presented. In all cases, the shift of $\nu$(NO) with respect to the [Ru(NH$_3$)$_5$NO]$^{3+}$ complex for the trans complexes is greater than for the cis complexes; however, the relative order of $\nu$(NO) is the same for both cis and trans complexes (OH$_2$ > NH$_3$ > halogen > OH$^-$). The effect of the cis ligands can be explained by the relative $\pi$-donor ability of the variable ligand. Except for hydroxide, a stronger $\sigma$ donor, the series does follow the expected variation in $\pi$-donor ability (NH$_3$ < halogen).[14,19]

**Table III.** Effect of Counterion on Ir Spectra of Cis Nitrosyls[a]

| *cis*-[Ru(NH$_3$)$_4$-(NO)Cl]Cl$_2$ | *cis*-[Ru(NH$_3$)$_4$-(NO)Cl]Br$_2$ | *cis*-[Ru(NH$_3$)$_4$-(NO)Cl]I$_2$ |
|---|---|---|
| 3450 w, sh | 3450 w, sh | 3450 w, sh |
| ~3260 s | 3260 s | ~3225 s |
| 3160 sh, s | 3160 sh, s | ~3140 sh, s |
| 1933 s | 1928 s | 1927 s |
| 1899 vs | 1900 vs | 1902 vs |
| ~1595 b, w | 1590 b, w | ~1595 b, w |
| 1340 sh, w | 1338 w | 1336 sh, w |
| 1310 s | 1308 s | 1308 s |
| 862 m | 850 m | 850 m |
| 840 sh | 830 sh, w | 830 sh, w |
| 604 m | 599 m | 599 m |
| 595 sh | 587 w | 581 w |
| 478$^b$ m | 478$^b$ m | 478$^b$ m |
| 325 m | 322 m | 320 m $\nu$(RuCl) |

[a] Abbreviations used: s, strong; m, medium; w, weak; sh, shoulder; b, broad. [b] This band also contains several ill-defined shoulders.

**Table IV.** Ir Spectra of Additional Cis Nitrosyls[a]

| *cis*-[Ru(NH$_3$)$_4$-(NO)I]I$_2$ | *cis*-[Ru(NH$_3$)$_4$-(NO)OH](ClO$_4$)$_2$ | *cis*-[Ru(NH$_3$)$_4$-(NO)OH$_2$](ClO$_4$)$_3$ |
|---|---|---|
| ~3440 sh, w | | |
| ~3220 s | 3530 m | 3410 m, sh |
| ~3120 sh, s | 3260 s | 3210 s, b |
| | 3140 sh, s | |
| 1923 s | 1861 vs | 1928 s, sh |
| 1902 vs | | 1848 m |
| 1580 b | ~1600 w, b | ~1600 |
| 1335 sh, w | 1348 w | 1360 sh, w |
| 1312 s | 1305 sh, m | 1323 m |
| | 1293 s | 1295 sh, w |
| | ~1000 w, b | |
| | 1175, 1140, 1110, 1083, 940$^c$ | 1160, 1120, 1110, 1088, 940$^c$ |
| | 860 sh, m | |
| 832 m | 842 m | 848 m |
| | 635, 623$^c$ | 638, 625$^c$ |
| 592 m | 604 w | 598 m |
| 581 m | 588 sh, w | 592 sh, w |
| | 563 m | 568 w |
| | 543 s | |
| 472$^b$ m | 478$^b$ m | 475$^b$ m |
| | 468$^b$ m | |

[a] Abbreviations used: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; b, broad. [b] This band also contains several ill-defined shoulders. [c] Bands for ClO$_4^-$.

(18) Reference 2 reports 1903 cm$^{-1}$; however we have obtained reproducible values of 1913 cm$^{-1}$ by several different preparations. Reference 4 reports 1930 cm$^{-1}$ in Nujol.

(19) C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Vol. II, Oxford University Press, New York, N. Y., 1966, p 402.

**Table V.** $\nu$(NO) for Cis and Trans Nitrosyls ($cm^{-1}$)

| Complex | Trans | Cis | Δ, cis − trans |
|---|---|---|---|
| $[Ru(NH_3)_5NO]Br_3$ | 1913[a] | 1913 | 0[f] |
| $[Ru(NH_3)_4(NO)Cl]Cl_2$ | 1880[b,c] | 1899 | 19 |
| $[Ru(NH_3)_4(NO)Br]Br_2$ | 1870[b,c] | 1902 | 32 |
| $[Ru(NH_3)_4(NO)I]I_2$ | 1862[c] | 1902 | 42 |
| $[Ru(NH_3)_4(NO)OH]Br_2$ | 1845[d] | 1861 | 16 |
| $[Ru(NH_3)_4(NO)H_2O](ClO_4)_3$ | 1925[e] | 1928 | −3[f] |

[a] For the $Cl^-$ salt, ref 2 lists this band at 1903 $cm^{-1}$. Reference 4 lists this band at 1930 $cm^{-1}$ (in Nujol). Using the same preparation, we have repeatedly obtained values of 1913 $cm^{-1}$ for both the bromide and perchlorate salts. [b] Reference 2. [c] Reference 3 lists this band at 1893 and 1885 $cm^{-1}$ for the chloro and bromo complexes, respectively. [d] This work; reference 2 lists this band at 1840 $cm^{-1}$. [e] Reference 6, as the $Br^-$ salt. [f] Difference is within instrumental error.

The $\nu$(RuNO) does shift for both *cis*- and *trans*-$[Ru(NH_3)_4(NO)X]X_2$, where $X^- = Cl^-$, $Br^-$, or $I^-$. In the cis case, there is a splitting of this band which increases in proceeding from the chloro to the iodo complex.

Recently, an amido complex has been isolated,[20] $[Ru(NH_3)_4(NO)NH_2]X_2$. We believe that our assignment for *cis*-$[Ru(NH_3)_4(NO)OH](ClO_4)_2$ is correct (*i.e.*, that it is not an amido complex) because (1) the product was prepared from the tetraammine, (2) Bottomley[20] also reported that he was unable to isolate any amido complexes starting with the tetraammine nitrosyls, (3) both *cis*- and *trans*-$[Ru(NH_3)_4(NO)OH]X_2$ display sharp bands at 3530 $cm^{-1}$ indicative of coordinated[2] $OH^-$, and (4) acidifying the complex which we assign as the cis hydroxo with $HClO_4$ produced a complex unlike $[Ru(NH_3)_5NO](ClO_4)_3$.

**Preparation of Nitrosyl Complexes.** $[Ru(NH_3)_5NO]^{3+}$ has been prepared by saturation of acidic $Ru(NH_3)_6{}^{3+}$ or $Ru(NH_3)_5OH_2{}^{3+}$ solutions with NO(g).[21] It occurred to us that one could prepare both of the cis and trans isomers of $[Ru(NH_3)_4(NO)X]X_2$ by treating the tetraammine with NO. Using *trans*-$[Ru(NH_3)_4Cl_2]Cl_2$, a product was isolated having uv, visible, and ir spectra identical with those previously ascribed to *trans*-$[Ru(NH_3)_4(NO)Cl]Cl_2$. The previous preparation of the trans complexes involved refluxing the *trans*-$[Ru(NH_3)_4(NO)OH]X_2$ complex in HX. The trans hydroxo complex has been prepared from the pentahalonitrosylruthenate[2] in concentrated aqueous ammonia and by evaporation of the solution to dryness. The trans character of the X–Ru–NO system has been confirmed by X-ray analysis.[5]

Starting with *cis*-$[Ru(NH_3)_4X_2]X$, we have obtained compounds of similar elemental composition but different uv, visible, and infrared spectra. Retention of cis or trans character on substitution of pyridine into cis or trans $Ru^{II}(NH_3)_4X_2$, where $X = Cl^-$ or $H_2O$ has been reported by Ford.[22] More importantly the preparation of both cis and trans nitrosyls from the direct reaction of NO with the corresponding ruthenium tetraammine enforces the utility of this method of synthesis for the direct, clean, and quantitative preparation of ruthenium nitrosyls.

**Stability of Cis Nitrosyls.** Several preliminary experiments have been performed to assess the possibility of cis–trans isomerization for the nitrosyl-tetraammine complexes of ruthenium.

(1) Solid samples of the pink *cis*-$[Ru(NH_3)_4(NO)Cl]Cl_2$ and the yellow *trans*-$[Ru(NH_3)_4(NO)Cl]Cl_2$ were placed on watch glasses and heated at 80°. After 3 days, the color and ir spectra of the two complexes were identical with those of the original samples.

(2) Dissolution of *cis*-$[Ru(NH_3)_4(NO)X]X_2$, where $X^- = Cl^-$ or $Br^-$, in water, gave a spectrum identical with that which was obtained for the same solution 7 days later. The *cis*-$[Ru(NH_3)_4(NO)OH](ClO_4)_2$ was dissolved in 0.1 *M* HBr. Concentrated HBr was added ($[HBr]_{final} \approx 8\ M$) and the solution was warmed on the steam bath for 1 hr. After only 1/2 hr, an orange solid began to form. The product had an ir spectrum identical with that of *cis*-$[Ru(NH_3)_4(NO)Br]Br_2$.

While the differences in the uv–vis and ir spectra are not appreciably different enough to offer an absolute statement regarding the exact amount of interconversion of cis to trans, one can estimate that in the solid state and in water the isomerization is extremely slow (if it occurs at all) and cannot be more than 15% trans.[23]

(3) Dissolution of *cis*-$[Ru(NH_3)_4(NO)Br^{2+}$, $3 \times 10^{-4}\ M$, in dilute NaOH (0.01 *M*) results in the shifting of the band at 345 nm to 330 nm, followed by the formation of a new band at 231 nm over a period of hours. The conversion can be accelerated by the addition of more NaOH. The final spectrum resembles that reported for *trans*-$[Ru(NH_3)_4(NO)OH]^{2+}$.

Upon heating an alkaline solution of *cis*-$[Ru(NH_3)_4(NO)Br]^{2+}$, the solution became lighter in color. After 1 hr, the addition of solid NaBr produced a solid having an ir spectrum identical with that of *trans*-$[Ru(NH_3)_4(NO)OH]Br_2$.

Dissolution of *cis*-$[Ru(NH_3)_4(NO)OH](ClO_4)_2$ in concentrated aqueous ammonia produced a solution having a spectrum which resembled that recorded for the cis hydroxo complex. [Note: No substitution of $NH_3$ for $OH^-$ was apparent from the uv–vis spectrum.] Upon heating the solution for 1 hr on the steam bath, the pink solution gradually acquired the yellow color of *trans*-$[Ru(NH_3)_4(NO)OH](ClO_4)_2$.

Thus, it appears that the cis complexes do isomerize slowly and almost completely to the trans form in warm, alkaline solutions. The stability of the cis complexes in neutral and acidic solutions as compared with their isomerization in alkaline solution is not unique. For example, both the cis and trans isomers[24] of $[Co(en)_2(H_2O)_2]Br_3$ are known to be stable in strong acid while the *cis*- and *trans*-$[Co(en)_2(H_2O)OH]Br_2$ isomers rearrange in alkaline solution. In addition, the rate of rearrangement of *trans*-$[Co(en)_2(NH_3)H_2O]^{3+}$ into the cis form increases with increasing pH.

## Summary

A new series of *cis*-nitrosyltetraammineruthenium complexes has been prepared. The color of the solids, the difference in their uv-vis spectra, the differences in their ir spectra, and the identical elemental analyses lead us to conclude that we have prepared an entire series of cis nitrosyls. Comparison of the ir spectra of the cis and trans isomers indicate that the cis ligands do influence the $\nu$(NO) frequency and in the same manner (aquo > ammine > halogen > hydroxide) as the trans nitrosyls. The synthetic route demonstrates the direct, stereospecific attack of NO upon the corresponding ruthenium complex. The solid cis complexes are quite stable. In acid or neutral solution, the

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(20) F. Bottomley and J. Crawford, *J. Chem. Soc., Dalton Trans.*, 2145 (1972).

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(22) P. Ford and C. Sutton, *Inorg. Chem.*, 8, 1544 (1969).

(23) Estimated by using the absence of the intense band in the uv at 278 nm for *trans*-$[Ru(NH_3)_4(NO)Br]^{2+}$.

(24) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 274.

isomerization does not proceed to any great extent. However, in warm alkaline solutions, isomerization of the cis nitrosyl to the trans form is virtually complete. In addition, the characterization of these cis complexes has raised some interesting questions regarding the relative importance of cis ligands.

**Registry No.** *cis*-$[Ru(NH_3)_4(NO)Cl]Cl_2$, 38402-57-2; *cis*-$[Ru(NH_3)_4(NO)Br]Br_2$, 38402-58-3; *cis*-$[Ru(NH_3)_4(NO)I]I_2$, 38402-59-4; *cis*-$[Ru(NH_3)_4(NO)(OH)](ClO_4)_2$, 38402-60-7; *cis*-$[Ru(NH_3)_4(NO)OH_2](ClO_4)_3$, 38402-61-8; *cis*-$[Ru(ND_3)_4(NO)Br]Br_2$, 38402-62-9; *cis*-$[Ru(NH_3)_4(^{15}NO)Br]Br_2$, 38402-63-0; *cis*-$[Ru(NH_3)_4(NO)Cl]Br_2$, 38402-64-1; *cis*-$[Ru(NH_3)_4(NO)Cl]I_2$, 38402-65-2.

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Contribution from the Southern Regional Research Laboratory, New Orleans, Louisiana 70179,[1]
and the Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122

# Electrochemical Investigation of the Dichlorobis(2,2'-bipyridine)chromium(III) Complex[2]

DONALD M. SOIGNET*[3] and LARRY G. HARGIS

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Electrochemical reduction of dichlorobis(2,2'-bipyridine)chromium(III) proceeds in a one-electron step and is followed by a fast ligand disproportionation and water substitution reactions that produce an equimolar mixture of $[Cr(bipy)_3]^{2+}$ and $[Cr(bipy)(H_2O)_4]^{2+}$. When the reduction is performed in the presence of an equivalent of 2,2'-bipyridine, $[Cr(bipy)_3]^{2+}$ is the sole product. Formation of the tris complex is highly sensitive to the solution pH below pH 4 owing to protonation of the transient free 2,2'-bipyridine. Slow chemical or electrochemical oxidation of reduced solutions produces diaquobis(2,2'-bipyridine)chromium(III). Rapid chemical oxidation carried out in such a way that the initial oxidation product does not mix appreciably with the yet unoxidized solution yields tris(2,2'-bipyridine)chromium(III). The mechanisms by which these oxidations are accomplished are discussed.

## Introduction

There has been and continues to be substantial interest in the behavior of tris(2,2'-bipyridine)chromium(III) ion in solution.[4-9] Electrochemical studies of this complex ion in aqueous solutions have shown that under certain circumstances the attempted reduction of the complex resulted in the catalytic formation of a bis(2,2'-bipyridine)chromium(III) complex ion.[10,11] In a separate study of the tris-bipyridine complex, we reported briefly on the electrochemical behavior of a bis complex that was prepared *in situ via* the catalytic elimination of a bipyridine molecule.[12] From that brief study it appeared that the reduced complex was not behaving in a straightforward manner and that oxidation of the reduced solutions produced a substance quite different from the starting complex. We also noted some differences with the results of an earlier study of the bis complex that we were not able to satisfactorily resolve.[11]

This study was undertaken in an effort to gain a better understanding of the solution behavior of the bis complex and to resolve the apparent conflicts of earlier work with the preliminary results extending from our study of the tris complex. Our earlier success with the tris(2,2'-bipyridine)chromium(III) system[12] led us to believe that a similar electrochemical study of the bis complex would provide the answers and level of understanding we were seeking. The study is based on the polarographic and cyclic voltammetric behavior of the bis system at various stages of reduction, where the reductions were carried out by controlled-potential electrolysis at a mercury cathode.

## Experimental Section

**Apparatus.** Electrochemical measurements were made with a Beckman Electroscan 30[13] equipped with an integrator. The integrator output was collected by and displayed on a Scallette pulse counter, Model SC-355.[13] Rapid (2–500 V/sec) cyclic voltammetric experiments were performed with a laboratory-constructed instrument employing operational amplifiers according to the basic design of Huntington and Davis.[14] Data were recorded on a Tektronix Type 564[13] storage oscilloscope.

A single cell was employed for the controlled-potential electrolysis, polarographic, and cyclic voltammetric experiments. The design of the cell has been described previously;[12] however, it is worthwhile to point out that exclusion of trace amounts of air is exceedingly important.

The open-circuit $m$ and $t$ values of the polarographic capillary were 1.46 mg/sec and 3.50 sec, respectively, in 0.1 $M$ potassium chloride electrolyte at 25°. These gave a capillary constant of 1.59 $mg^{2/3}$ $sec^{1/6}$.

Prepurified argon, used for deoxygenation and subsequent blanketing of the solution, was passed successively through a vanadium(II) sulfate solution, two chromium(II) chloride solutions, and a 0.1 $M$ potassium chloride solution prior to passage through the sample in the cell. During the controlled-potential electrolysis experiments, after

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(1) One of the facilities of the Southern Region, Agricultural Research Service, U. S. Department of Agriculture.

(2) Presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., 1971.

(3) Address correspondence to this author at the Southern Regional Laboratory.

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