Formation of Amidotetra-amminenitrosylruthenium(II) and Nitropenta-ammineruthenium(II) from Nitrosylpenta-ammineruthenium(II) and Hydroxide Ion

By **F. Bottomley** * and **Janice R. Crawford**, Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada

In aqueous sodium hydroxide $[Ru(NH_3)_5NO]^{3+}$ was converted to $[RuNH_2(NH_3)_4NO]^{2+}$ and $[Ru(NH_3)_5NO_2]^+$. $[RuNH_2(NH_3)_4NO]X_2$ (X = Br or I) was isolated from solutions of $[OH^-] = 0{\cdot}5$M and $[Ru(NH_3)_5NO_2]X,H_2O$ (X = Cl, Br, or I) from solutions of $[OH^-] = 5$M. On setting aside or warming, $[RuOH(NH_3)_4NO]X_2$ (X = Br or I) were obtained; in solutions of $[OH^-] = 0{\cdot}5$—$1{\cdot}5$M the product was contaminated with $[Ru(NH_3)_5N_2]^{2+}$. The physical properties of $[RuNH_2(NH_3)_4NO]X_2$ and $[Ru(NH_3)_5NO_2]X,H_2O$ are reported.

NITROSYL complexes of ruthenium were for some years considered to be inert to reaction at the nitrosyl group. Recently reactions of a variety of ruthenium–nitrosyl complexes with nucleophiles (ammonia, hydrazines, hydroxylamine, azide, and hydroxide) have been investigated.[1-7] Of particular relevance to the work here are the reactions of pentacyanonitrosylruthenium(II), $[Ru(CN)_5NO]^{2-}$, anionobis(2,2′-bipyridyl)nitrosylruthenium(II), $[RuX(bipy)_2NO]^{2+}$, and anionobis(*o*-phenanthroline)nitrosylruthenium(II), $[RuX(phen)_2NO]^{2+}$ (X = Cl, Br, or NO_2) with hydroxide ion to form the corresponding nitro-complexes $[Ru(CN)_5NO_2]^{4-}$,[1] $[Ru(bipy)_2NO_2X]$, and $[Ru(phen)_2NO_2X]$.[2,3] For $[Ru(bipy)_2NO_2Cl]$ the reaction was reversible;[3] no information on reversibility is available for $[Ru(CN)_5NO_2]^{4-}$. We have shown previously that nitrosylpenta-ammineruthenium(II), $[Ru(NH_3)_5NO]^{3+}$, formed (dinitrogen)penta-ammineruthenium(II), $[Ru(NH_3)_5N_2]^{2+}$, with N_2H_4 or NH_3 and (dinitrogen oxide)penta-ammineruthenium, $[Ru(NH_3)_5N_2O]^{2+}$, with NH_2OH.[4] Also, we found $[Ru(NH_3)_5NO]^{4+}$ and hydroxide ion gave *trans*-hydroxytetra-amminenitrosylruthenium, *trans*-$[RuOH(NH_3)_4NO]^{2+}$.[4] This latter reaction is more complex than we supposed. In alkaline solutions $[Ru(NH_3)_5NO]^{3+}$ is converted into amidotetra-ammineruthenium, $[RuNH_2(NH_3)_4NO]^{2+}$, and nitropenta-ammineruthenium, $[Ru(NH_3)_5NO_2]^+$, and decomposition to $[RuOH(NH_3)_4NO]^{2+}$ is relatively slow. The results of an investigation of these reactions are presented here.

RESULTS

When sodium hydroxide was added to an aqueous solution of $[Ru(NH_3)_5NO]^{3+}$ the solution became yellow-orange and on increasing the hydroxide ion concentration, red. Addition of the appropriate potassium salt to a yellow-orange solution of $[Ru(NH_3)_5NO]^{3+}$ in $0{\cdot}5$M sodium hydroxide precipitated yellow crystals of $[RuNH_2(NH_3)_4NO]X_2$ (X = Br or I). The same procedure with a red solution of $[Ru(NH_3)_5NO]^{3+}$ in 5M sodium hydroxide gave brick-red crystals of $[Ru(NH_3)_5NO_2]X,H_2O$ (X = Cl, Br, or I).

When gently warmed or set aside at room temperature, the colour of the yellow-orange or red solutions of $[Ru(NH_3)_5NO]^{3+}$ faded slowly to pale yellow and addition of the appropriate potassium salt gave *trans*-$[RuOH(NH_3)_4NO]X_2$[8]

---

[1] E. J. Baran and A. Müller, *Chem. Ber.*, 1969, **102**, 3915.

[2] T. J. Meyer, J. B. Godwin, and N. Winterton, *Chem. Comm.*, 1970, 872.

[3] J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, 1971, **10**, 2150.

[4] F. Bottomley and J. R. Crawford, *Chem. Comm.*, 1971, 200.

[5] P. G. Douglas, R. D. Feltham, and H. G. Metzger, *Chem. Comm.*, 1970, 889; *J. Amer. Chem. Soc.*, 1971, **93**, 84.

[6] F. J. Miller and T. J. Meyer, *J. Amer. Chem. Soc.*, 1971, **93**, 1294.

[7] M. J. Cleare and W. P. Griffith, *J. Chem. Soc.* (*A*), 1970, 1117.

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

(X = Br or I). Although this complex was the major component of the pale yellow solutions, other complexes were present as well, depending on the experimental conditions. In highly alkaline solutions ($[OH^-] \geqslant 5{\cdot}0$M) fading of the red colour was accompanied by ammonia evolution, particularly on warming. Small quantities of *trans*-$[RuOH(NH_3)_4NO]^{2+}$ were obtained, but considerable decomposition to other unknown products appeared to have occurred. In solutions of lower alkalinity ($[OH^-] = 0{\cdot}5$—$1{\cdot}5$M], in addition to *trans*-$[RuOH(NH_3)_4NO]^{2+}$, $[Ru(NH_3)_5N_2]^{2+}$ [9] was obtained. We have not performed exhaustive experiments to determine the precise conditions for maximum yield of $[Ru(NH_3)_5N_2]^{2+}$, but a solution of $[Ru(NH_3)_5NO]^{3+}$ (0·025M) in sodium hydroxide (0·5M) set aside under argon at 5 °C for 48 h gave 30% $[Ru(NH_3)_5N_2]^{2+}$ (measured by the optical density at 220 nm [10]).

$[RuNH_2(NH_3)_4NO]X_2$ are air-stable, diamagnetic complexes which revert essentially quantitatively to $[Ru(NH_3)_5NO]X_3,H_2O$ in aqueous hydrohalogenic acid. Their i.r. spectra (Table) are similar to those of $[RuOH(NH_3)_4NO]X_2$.[11] There is not complete agreement in the literature on assignments for amminenitrosylruthenium complexes.[11,12] Those in the Table follow Cleare and Griffith.[12]

Infrared spectra (cm^{-1}) of $[RuNH_2(NH_3)_4NO]X_2$ and $[Ru(NH_3)_5NO_2]I,H_2O$

$[RuNH_2(NH_3)_4NO]X_2$		$[Ru(NH_3)_5NO_2]X,H_2O$					
X = Br	X = I	X = Cl	X = Br	X = I	X = I, ^{15}N	X = I, H = D	Assignment
3670w	3670						2νNO
		3500br,sh	3500	3500	3500	2482s	νOH
						2464s	
3260br	3240	3330br,s	3330	3330	3330	2350m	νNH
3180br,sh	3170		3240sh	3240	3240	2322m	
		3182br,s	3180	3190	3190		
1850sh	1860						νNO
1855vs	1837						
		1680br,sh	1680	1680	1680	1170br	δH_2O
1620br,m	1620	1635br,m	1626	1617	1614	1065m	$\delta_{deg}NH_3$
1570br,m	1570						δNH_2
1321w	1320	1259	1267	1278m	1277	977m	$\delta_{sym}NH_3$
1301m	1302			1257w	1257	963w	
1292m	1295						
1274w,sh	1279						
		1203br,vs	1203	1201	1169	1202br,vs	νNO_2
850br,m	835	820vw,sh	822	810	810		$\rho_r NH_3$
820sh	778	789m	784	780	777	585 [a]	
		628w	625	618	609		*b*
608m	607						νRuNO
595sh	592						
559m	552						δRuNO
		565br,w	555	540	535	540 [a]	*b*
485w,sh	455	455w	453	448	448	418w	$\nu RuNH_3$
465							

[a] The region from 600—450 cm^{-1} showed a very broad irregular absorption band. [b] See text.

Few complexes with a non-bridging amido-ligand have been isolated, and only for $[PtNH_2(NH_3)_4NO_2]Cl_2$ [13,14] was the i.r. spectrum reported. In the present case, the broad band at 1570 cm^{-1} may be assigned to the NH_2 bending mode. The frequency of νNO, 1837 cm^{-1}, for $[RuNH_2(NH_3)_4NO]I_2$ can be compared to 1917 cm^{-1} for $[Ru(NH_3)_5NO]I_3,H_2O$ and 1855 cm^{-1} for *trans*-$[RuOH(NH_3)_4NO]I_2$,[11] indicating *trans*-stereochemistry and a high π-electron donor capability for the amido-ligand.

$[Ru(NH_3)_5NO_2]X,H_2O$ were diamagnetic and stable to oxidation in solution or in the solid state. Analytical evidence indicated the water of crystallization content was variable and often less than one (see ref. 15). The complexes could not be dehydrated *in vacuo* over P_2O_5 at room temperature and they decomposed on heating. Their i.r. spectra (Table) were similar to that of $K_4[Ru(CN)_5NO_2]$,$2H_2O$ [1] in the region of the NO_2^- vibrations. In aqueous hydrohalogenic acid $[Ru(NH_3)_5NO_2]X,H_2O$ were converted essentially quantitatively to $[Ru(NH_3)_5NO]X_3,H_2O$, but in water, on setting aside, small quantities of *trans*-$[RuOH(NH_3)_4NO]^{2+}$ and $[Ru(NH_3)_5N_2]^{2+}$ formed also.

The electronic spectrum of $[Ru(NH_3)_5NO]^{3+}$ (bromide salt) in acid solution showed bands at 300 nm (ε 61·3) and 460 nm (ε 14·4) in reasonable agreement with the literature values.[16] In 15M sodium hydroxide solution $[Ru(NH_3)_5NO]^{3+}$ was completely converted to $[Ru(NH_3)_5NO_2]^+$, which showed a band at 368 nm (ε $7{\cdot}0 \times 10^3$) with a shoulder (on a high energy tail) at 272 nm (ε *ca.* 1×10^3). When the hydroxide ion concentration of solutions of $[Ru(NH_3)_5NO]^{3+}$ (1 or 6×10^{-4}M) was increased from 10^{-7} to 2M bands appeared at 281 and 368 nm and both bands increased in intensity to $[OH^-] = 0{\cdot}11$M, above which concentration the 281 nm band began to decrease, the 368 nm band continuing to increase to $[OH^-] = 2$M. The 281 nm band was assigned to $[RuNH_2(NH_3)_4NO]^{2+}$. Because of the difference in extinction coefficients it was never possible to observe all three complexes in the same solution. For $[OH^-] > 0{\cdot}1$M no isosbestic point was observed between the 368 and 281 nm absorption bands, and calculations based on the assumption only $[RuNH_2(NH_3)_4NO]^{2+}$ and $[Ru(NH_3)_5NO_2]^+$ were present did not give consistent results. This may be due to

---

[9] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, 1967, **89**, 5595.

[10] D. E. Harrison and H. Taube, *J. Amer. Chem. Soc.*, 1967, **89**, 5706.

[11] M. B. Fairey and R. J. Irving, *Spectrochim. Acta*, 1966, **22**, 359.

[12] M. J. Cleare and W. P. Griffith, *J. Chem. Soc.* (*A*), 1969, 372 and references therein.

[13] N. Sabbatini and V. Balzani, *Inorg. Chem.*, 1971, **10**, 209.

[14] F. Basolo and G. S. Hammaker, *Inorg. Chem.*, 1962, **1**, 1.

[15] F. Bottomley, following paper.

[16] J. N. Armor, H. A. Scheidegger, and H. Taube, *J. Amer. Chem. Soc.*, 1968, **90**, 5928.

intrusion of the high energy tail into the 280 nm region, coupled with the difficulty of estimating the contribution of the $[Ru(NH_3)_5NO_2]^+$ absorption at 272 nm to the $[RuNH_2(NH_3)_4NO]^{2+}$ absorption at 281 nm. The unfortunate ratio of extinction coefficients prevented measurement of ε for $[RuNH_2(NH_3)_4NO]^{2+}$. Hence the equilibrium constants for the reactions could not be determined. Attempts to obtain the constants from a potentiometric titration were unsuccessful, there being no breaks in the titration curve. $[Ru(NH_3)_5NO]I_3,H_2O$ was sparingly soluble in dimethyl sulphoxide, and formation of $[RuNH_2(NH_3)_4NO]^{2+}$ by reaction with 1,8-bis(dimethylamino)naphthalene was tried. However, no product could be isolated, probably because of the low concentration. The reaction could not be followed by spectroscopy since 1,8-bis(dimethylamino)naphthalene absorbed strongly at 280 nm.

Hydroxide ion in concentrations to 10M did not react with *trans*-$[RuOH(NH_3)_4NO]^{2+}$; neither did ammonia under conditions in which $[Ru(NH_3)_5NO]^{3+}$ gave $[Ru(NH_3)_5N_2]^{2+}$.[4] *trans*-$[RuBr(NH_3)_4NO]^{2+}$ and hydroxide ion formed *trans*-$[RuOH(NH_3)_5NO]^{2+}$ only.

DISCUSSION

Kinetic[17] and protonation[18] studies show conversion of $[Fe(CN)_5NO]^{2-}$ into $[Fe(CN)_5NO_2]^{4-}$ by hydroxide ion occurs in two steps with $[Fe(CN)_5NO(OH)]^{3-}$ as the intermediate. We found no evidence for similar intermediates, *e.g.*, $[Ru(NH_3)_5NO(OH)]^{2+}$ or $[RuNH_2(NH_3)_4NO(OH)]^+$. Such intermediates are likely to be unstable in view of the positive charges on the complexes, which would facilitate proton loss from the nitroxylic group. This explanation was given for the failure to observe a nitroxylic intermediate in the reaction between OH^- and $[RuCl(bipy)_2NO]^{2+}$.[3]

An important question is whether $[Ru(NH_3)_5NO]^{3+}$ or $[RuNH_2(NH_3)_4NO]^{2+}$ or both form $[Ru(NH_3)_5NO_2]^+$. $[RuNH_2(NH_3)_4NO(OH)]^+$ was not observed, implying either it does not exist or, if formed, protonation of the amido-ligand is easier than proton loss from the nitroxylic group. The latter explanation seems unlikely because of the charge on the complex. Neither $[RuOH(NH_3)_4NO]^{2+}$ nor $[RuBr(NH_3)_4NO]^{2+}$ formed a nitro-complex. Conversion of NO^+ to NO_2^- is drastically inhibited by complex formation, probably due to π-electron donation by the metal to the nitrosyl ligand,[18] and *trans*-π-electron donors such as OH^-, Br^-, or NH_2^- would inhibit further the conversion.

$[Ru(NH_3)_5NO_2]X,H_2O$ have i.r. spectra very different from $[Co(NH_3)_5NO_2]Cl_2$.[19] The water of crystallization in the ruthenium complexes and the NO_2^- ligand acting as a π-electron acceptor to a greater extent for ruthenium than cobalt[15] may influence the spectra. We assume νNO_2(asym) and νNO_2(sym) are contained within the band envelope at 1200 cm^{-1} (Table), as with $K_4[Ru(CN)_5NO_2],2H_2O$.[1] In this complex weak bands at 825 and 595 cm^{-1} were assigned to δONO and $\rho_w NO_2$ respectively.[1] For $[Co(NH_3)_5NO_2]Cl_2$ these vibrations appeared as strong bands at 835 and 595 cm^{-1}. In the present work weak bands at 618 and 540 cm^{-1} {609 and 535 cm^{-1} for $[Ru(NH_3)_5{}^{15}NO_2]I,H_2O$} are not assignable to NH_3 vibrations, but neither can then be assigned with certainty to the missing NO_2 vibrations.

Formation of $[Ru(NH_3)_5N_2]^{2+}$ in alkaline solutions of $[Ru(NH_3)_5NO]^{3+}$ can be explained by liberation of ammonia on formation of *trans*-$[RuOH(NH_3)_4NO]^{2+}$, with subsequent attack by NH_3 on unreacted $[Ru(NH_3)_5NO]^{3+}$.[4]

EXPERIMENTAL

Ruthenium trichloride hydrate and potassium pentachloroaquoruthenate(III) were obtained from Johnson, Matthey and Mallory, Montreal, and used as received. $[^{15}N]$nitric oxide was purchased from Merck, Sharp, and Dohme Limited. All other chemicals were reagent grade. Hexa-ammineruthenium(II)dihalide, $[Ru(NH_3)_6]X_2$ ($X = Cl^-$ or Br^-) was prepared by literature methods.[20] Chloropenta-ammineruthenium(III)dichloride, $[Ru(NH_3)_5Cl]Cl_2$, was prepared by oxidation of $[Ru(NH_3)_6]^{2+}$ to $[Ru(NH_3)_6]^{3+}$ with hydrazine hydrochloride, the resultant solution of $[Ru(NH_3)_6]^{3+}$ being refluxed with 6M hydrochloric acid.[21,22]

Nitrosylpenta-ammineruthenium(II) $[Ru(NH_3)_5NO]X_3,H_2O$ (X = Cl, Br, *or* I).—$[Ru(NH_3)_5Cl]Cl_2$ (0·50 g) in water (6 ml) was converted to a solution of $[Ru(NH_3)_5H_2O]^{3+}$ by literature methods.[22] Nitric oxide was passed through the degassed solution for 12 h, the resultant orange solution filtered, and potassium chloride added until precipitation was complete. Yield, 0·34 g (62%). The complex was recrystallized by dissolving in water, filtering, and adding cold hydrohalogenic acid to precipitate the desired salt, which was washed with alcohol and ether and dried *in vacuo* over P_2O_5 (Found: H, 4·8; N, 23·8. Calc. for $H_{17}Cl_3N_6O_2Ru$: H, 5·0; N, 24·65. Found: H, 3·85; N, 17·5. Calc. for $H_{17}Br_3N_6O_2Ru$: H, 3·6; N, 17·75. Found: H, 2·6; N, 13·9. Calc. for $H_{17}I_3N_6O_2Ru$: H, 2·8; N, 13·65%). As noted above the electronic and i.r. spectra of the products agreed with the literature.[11,12,16] The νNO band in the i.r. spectra was found to be split into a doublet, as noted in ref. 16. νNO Cl^- salt: 1931, 1914vs; Br^-: 1928; 1913vs; I^-: 1930; 1917vs.

Amidotetra-amminenitrosylruthenium(II) *Dihalide*, $[RuNH_2(NH_3)_4NO]X_2$ (X = Br *or* I).—$[Ru(NH_3)_5NO]Br_3,H_2O$ (0·049 g) was dissolved in aqueous sodium hydroxide (0·5M; 3·2 ml). To the resultant solution, cooled in ice, potassium bromide was added until a precipitate formed. The solution was set aside in ice for 20 min and the resultant yellow *crystals* removed by filtration, washed with alcohol and ether and dried *in vacuo* over P_2O_5. Yield, 0·028 g (72%) (Found: Br, 42·55; H, 3·85; N, 22·25. Calc. for $H_{14}Br_2N_6ORu$: Br, 42·6; H, 3·75; N, 22·4%). The iodide was prepared by a similar procedure using $[Ru(NH_3)_5NO]I_3,H_2O$ and potassium iodide (Found: H, 3·1; I, 54·3; N, 17·8. Calc. for $H_{14}I_2N_6ORu$: H, 3·0; I, 54·15; N, 17·9%).

Nitropenta-ammineruthenium, $[Ru(NH_3)_5NO_2]X,H_2O$ (X = Cl, Br, *or* I).—$[Ru(NH_3)_5NO]Br_3,H_2O$ (0·135 g) was

---

[17] J. H. Swinehart and P. A. Roch, *Inorg. Chem.*, 1966, **5**, 573.

[18] J. Mašek and H. Wendt, *Inorg. Chim. Acta*, 1969, **3**, 455 and references therein.

[19] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 1967, **23A**, 2099.

[20] F. M. Lever and A. R. Powell, *J. Chem. Soc.* (*A*), 1969, 1477.

[21] F. Bottomley, *Canad. J. Chem.*, 1970, **48**, 351.

[22] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *Inorg. Synth.*, 1971, **12**, 2.

dissolved in the minimum quantity aqueous sodium hydroxide (5M; 13 ml) with stirring. The red solution was set aside at 5 °C for 48 h and the brick-red *crystals* which formed removed by filtration, washed with alcohol and ether and air-dried. Yield 0·086 g (90%). Alternatively, potassium bromide was added to the red solution, without cooling, until precipitation of the *amorphous* red complex was complete (Found: H, 5·25; Br, 22·95; N, 23·9. Calc. for $H_{17}BrN_6O_3Ru$: H, 5·2; Br, 24·2; N, 24·45%). The chloride and iodide salts were prepared similarly except that the iodide precipitated without cooling (Found: H, 6·15; Cl, 13·05; N, 29·55. Calc. for $H_{17}ClN_6O_3Ru$: H, 6·0; Cl, 12·4; N, 29·4. Found: H, 4·55; I, 32·7; N, 22·6. Calc. for $H_{17}IN_6O_3Ru$: H, 4·55; I, 33·65; N, 22·3%). Considerable difficulty was experienced in obtaining reproducible analyses, presumably because of the variable water of crystallization.

trans-*Hydroxytetra-amminenitrosylruthenium Dihalide*, $[RuOH(NH_3)_4NO]X_2$ (X = Br *or* I).—$[Ru(NH_3)_5NO]Br_3,H_2O$ (0·084 g) was dissolved in aqueous sodium hydroxide (1·5M; 6 ml), the solution filtered and warmed gently until it became pale yellow. Potassium bromide was added until precipitation was complete. The product was redissolved in the minimum quantity of 1·5M sodium hydroxide, filtered, reprecipitated, the precipitate washed with alcohol and ether and dried *in vacuo* over P_2O_5. Yield, 0·035 g (52%) (Found: H, 3·35; Br, 42·5; N, 18·55. Calc. for $H_{13}Br_2N_5O_2Ru$: H, 3·5; Br, 42·5; N, 18·6. Found: H, 2·85; I, 54·25; N, 14·95. Calc. for $H_{13}I_2N_5O_2Ru$: H, 2·8; I, 54·0; N, 14·9%). The i.r. spectra of the products agreed closely with the literature.[11] The electronic spectrum showed one band, $\lambda_{max.}$ 328 nm, ε 223. $[RuOH(NH_3)_4NO]Br_2$ was converted into $[RuBr(NH_3)_4NO]Br_2$ [11] by heating in aqueous hydrobromic acid.

Reaction of $[Ru(NH_3)_5NO_2]I,H_2O$ *with Acid.*—$[Ru(NH_3)_5NO_2]I,H_2O$ (0·045 g) was dissolved in aqueous hydrochloric acid (0·3M; 9 ml). To the solution potassium iodide was added and the resultant precipitate of $[Ru(NH_3)_5NO]I_3,H_2O$ removed by filtration. Yield, 0·050 (71%). The i.r. spectrum of the product was identical to that of $[Ru(NH_3)_5NO]I_3,H_2O$ prepared as described above.

Reaction of $[RuNH_2(NH_3)_4NO]Br_2$ *with Acid.*—$[RuNH_2(NH_3)_4NO]Br_2$ (0·027 g) was dissolved in aqueous hydrobromic acid (2M; 9·3 ml). The solution was set aside at 5 °C for a few min and the resultant orange precipitate of $[Ru(NH_3)_5NO]Br_3,H_2O$ removed by filtration, washed with alcohol and ether and dried *in vacuo* over P_2O_5. Yield, 0·029 g (87%). The i.r. spectrum of the product was identical to that of $[Ru(NH_3)_5NO]Br_3,H_2O$ prepared as described above.

I.r. spectra were measured (as Nujol or hexachlorobutadiene mulls) on a Beckman IR 12 instrument, electronic spectra on a Bausch and Lomb spectronic 505; magnetic moments were by the Gouy method; microanalyses were by A. Bernhardt, West Germany.

We thank Dr. D. G. Brewer of this department for helpful discussions, Johnson, Matthey and Mallory, Montreal, for the generous loan of ruthenium salts and the National Research Council of Canada and the University of New Brunswick Research Fund for financial support.

[2/546 *Received, 8th March,* 1972]