Ruthenium Complexes Containing Molecular Nitrogen

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Abstract: The first transition metal complexes containing molecular nitrogen, $[Ru(NH_3)_5N_2]^{2+}$, were prepared by the action of hydrazine hydrate on ruthenium(III) or ruthenium(IV) salts, or by the action of azide ion on aquopentaammineruthenium(III). A variety of Ru(II) and Ru(III) ammine complexes were obtained from these salts. The characterization, spectral properties, and reactions of $[Ru(NH_3)_5N_2]^{2+}$ salts are reported and discussed.

Transition metals, either in the form of complexes or in the metallic form, are known to play an important part in the fixation of molecular nitrogen. Several systems have been reported in which it was deduced that a complex containing molecular nitrogen was present[1-3] although none of these intermediates was isolated. We report here, in detail, the preparation and properties of nitrogenpentaammineruthenium(II)[4-6] salts, $[Ru(NH_3)_5N_2]X_2$ (X = Cl, Br, I, BF_4, PF_6). This formulation has been confirmed by single-crystal X-ray diffraction analysis.[7] Preliminary reports of this work have been presented elsewhere.[5,6] Since the completion of most of this work the preparation of two other complexes containing molecular nitrogen has been reported, $(Ph_3P)_2Ir(N_2)Cl$[8,9] and $(Ph_3P)_3CoN_2$.[10]

Experimental Section

Ruthenium trichloride was purchased from Englehard Industries. The infrared spectrum of the material was routinely checked for the presence of bands due to ruthenium nitrosyl complexes. No attempt was made to purify the material further, and hence all references to ruthenium trichloride refer to this material, which contains both Ru(III) and Ru(IV) species.[11,12] Ammonium hexachlororuthenium(IV) and potassium pentachloroaquoruthenium(III) were purchased from Englehard Industries and used as received. Aquopentaammineruthenium(III) methanesulfonate was prepared as described in the literature.[13]

All other materials were reagent grade. Solutions of sodium tetrafluoroborate and ammonium hexafluorophosphate were filtered before use. Solutions of N_2D_4 were prepared by repeated distillation of N_2H_4 in D_2O.

Nitrogenpentaammineruthenium(II) Complexes, $[Ru(NH_3)_5N_2]^{2+}$. Method 1. Ruthenium trichloride (1.0 g) was dissolved in water (12 ml), and hydrazine hydrate (10 ml) was added carefully over a period of 5 min. The initial vigorous, exothermic reaction was allowed to subside; the mixture was stirred overnight and filtered several times by gravity leaving a black residue. The appropriate anion (saturated aqueous solution) was added to the filtrate to precipitate the desired salt. The iodide, bromide, tetrafluoroborate, and hexafluorophosphate salts precipitated immediately; the chloride salt was obtained by allowing the solution to evaporate at room temperature. The product (0.5 g) was collected by filtration, washed with water, alcohol, and ether, and air dried.

Method 2. Similarly, when hydrazine hydrate (10 ml) was added to ammonium hexachlororuthenium(IV) (1.0 g), potassium pentachloroaquoruthenium(III) (1.0 g), or aquopentaammineruthenium(III) methanesulfonate (1.0 g) dissolved in the minimum quantity of water approximately 40% yields of nitrogenpentaammineruthenium(II) salts were obtained. Reaction times were 1 hr for $[Ru(NH_3)_5H_2O](CH_3SO_3)_3$ and 12 hr for $K_2[RuCl_5H_2O]$ and $(NH_4)_2[RuCl_6]$.

Method 3. Aquopentaammineruthenium(III) methanesulfonate (1.0 g) was dissolved in water (15 ml), and sodium azide (1.0 g) was added. The solution was adjusted to approximately pH 7 with methanesulfonic acid and gently warmed for 20 min. The mixture was filtered and cooled, and the product precipitated as in method 1, yield 0.80 g (83%). *Caution:* under certain circumstances it is possible to obtain explosive products from this reaction (see text). Analyses of the products are given in Table I.

The amount of nitrogen (N_2) obtained as a gas on heating of the compounds varied between 75 and 95% of the theoretical amount present. Conventional microanalytical techniques for total nitrogen frequently gave low values presumably due to loss of N_2.

Preparation of Other Complexes from Nitrogenpentaammineruthenium(II) Salts. The preparations of some of these complexes have been reported elsewhere,[14] but are given here for completeness. In some cases $[Ru(NH_3)_5N_2]^{2+}$ was not isolated from the reaction mixture.

Hexaammineruthenium(II) Iodide, $[Ru(NH_3)_6]I_2$. To nitrogenpentaammineruthenium iodide (0.54 g) in water (3 ml) was added concentrated aqueous ammonia (10 ml), and the resultant slurry heated until a clear yellow solution was formed. This, on cooling, deposited yellow crystals. These were collected by filtration, recrystallized from concentrated aqueous ammonia, and washed with water, alcohol, and ether. The complex was dried *in vacuo* at 78° over P_2O_5, yield 0.2 g (37%). *Anal.* Calcd for $H_{18}I_2N_6Ru$: H, 3.94; N, 18.38; I, 55.58. Found: H, 4.40; N, 18.57; I, 55.40.

By a similar method starting from nitrogenpentaammineruthenium(II) tetrafluoroborate (0.73 g) the analogous hexaammineruthenium(II) tetrafluoroborate salt was obtained, yield 0.55 g (77%). *Anal.* Calcd for $B_2F_8H_{18}N_6Ru$: H, 4.77; N, 22.28. Found: H, 4.77; N, 22.10.

Chloropentaammineruthenium(III) Chloride, $[Ru(NH_3)_5Cl]Cl_2$. To the filtered reaction solution described in method 1 for the preparation of $[Ru(NH_3)_5N_2]^{2+}$, 6 *N* hydrochloric acid (10 ml) was added and the resultant solution refluxed for 1 hr. The yellow product which separated was collected by filtration and recrystallized from a small quantity of water to which a few drops of concentrated hydrochloric acid was added. The hot solution was filtered into concentrated hydrochloric acid (5 ml), and the crystals obtained were collected by filtration, washed with water, alcohol, and ether, and dried, *in vacuo*, at 78° over P_2O_5. *Anal.* Calcd for $Cl_3H_{15}N_5Ru$: N, 23.98; H, 5.19; Cl, 36.39. Found: N, 23.12; H, 5.44; Cl, 36.10.

By exactly similar methods using hydrobromic or hydriodic acid, the complexes $[Ru(NH_3)_5Br]Br_2$ and $[Ru(NH_3)_5I]I_2$ were obtained. *Anal.* Calcd for $Br_3H_{15}N_5Ru$: N, 16.44; H, 3.88; Br, 56.33.

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[1] M. E. Vol'pin and V. B. Shur, *Nature*, **209**, 1236 (1966).

[2] H. Brintzinger, *J. Am. Chem. Soc.*, **88**, 4305 (1966).

[3] H. Brintzinger, *ibid.*, **88**, 4307 (1966).

[4] This compound was incorrectly named in earlier reports.[5,6]

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[6] C.I.C., 49th Canadian Chemical Conference, Saskatoon, Canada, 1966.

[7] F. Bottomley and S. C. Nyburg, *Chem. Commun.*, 897 (1966).

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[9] J. P. Collman, M. Kubota, J. Y. Sun, and F. Vastine, *ibid.*, **89**, 169 (1967).

[10] A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967).

[11] D. T. Sawyer, R. S. George, and J. B. Baggar, *J. Am. Chem. Soc.*, 81, 5893 (1959).

[12] J. F. Harrod, S. Ciccone, and J. Halpern, *Can. J. Chem.*, **39**, 1372 (1961).

[13] R. O. Harris, submitted for publication.

[14] A. D. Allen and C. V. Senoff, *Can. J. Chem.*, in press.

Table I

Formula	NH$_3$ Calcd	NH$_3$ Found	N$_2$ Calcd	N$_2$ Found	H Calcd	H Found	Other Calcd	Other Found	Method of prepn[a]
$[Ru(NH_3)_5N_2]Cl_2$	30.07	29.89	9.89	8.68	5.30	5.69	Cl, 24.90	Cl, 24.80	1
$[Ru(NH_3)_5N_2]Br_2$	22.76	22.67	7.49	7.01	4.05	4.29	Br, 42.72	Br, 42.09	3
$[Ru(NH_3)_5N_2]I_2$	18.19	18.04	5.98	5.35	3.24	3.92	I, 54.27	I, 54.05	3
$[Ru(NH_3)_5N_2](BF_4)_2$	21.95	...[b]	7.22	6.43	3.90	4.10			3
$[Ru(NH_3)_5N_2](PF_6)_2$	16.89	...[b]	5.56	4.19	3.00	3.17	Ru, 20.04	Ru, 18.63	3

[a] See text. [b] Repeated analyses of $[Ru(NH_3)_5N_2](BF_4)_2$ for ammonia gave a value of 19.32%. Similarly $[Ru(NH_3)_5N_2](PF_6)_2$ gave 14.86%. Analyses of $[Ru(NH_3)_5Cl](PF_6)_2$ and $[Ru(NH_3)_6](PF_6)_3$ by the same Kjeldahl method gave values of only 88% of the theoretical ammonia value though microanalyses of the same compounds yielded the correct value. No explanation of this behavior can be offered.

Found: N, 16.92; H, 3.50; Br, 56.10. Calcd for $H_{15}I_3N_5Ru$: I, 67.19. Found: I, 67.60.

Bromopentaammineruthenium(III) bromide, $[Ru(NH_3)_5Br]Br_2$, was also obtained from a slurry of nitrogenpentaammineruthenium(II) bromide, $[Ru(NH_3)_5N_2]Br_2$ (0.3 g), in water (3 ml) by addition of fuming hydrobromic acid (4 ml). The solution was refluxed for 3 hr, then cooled to room temperature, and the crude product was recrystallized and dried as before, yield 0.2 g (59%). *Anal.* Calcd for $Br_3H_{15}N_5Ru$: Br, 56.33. Found: Br, 56.20.

(Dimethyl sulfoxide)pentaammineruthenium(II) Iodide, $[Ru(NH_3)_5(CH_3)_2SO]I_2$. To nitrogenpentaammineruthenium(II) iodide (0.55 g) in water (3 ml) was added dimethyl sulfoxide (1 ml). The resultant slurry was warmed until a yellow-brown solution formed, which was then cooled to room temperature. On addition of excess potassium iodide pale yellow crystals formed, which were collected by filtration and recrystallized quickly from a small quantity of water, washed with alcohol and ether, and dried *in vacuo* at 78° over P_2O_5, yield 0.3 g (57%). *Anal.* Calcd for $C_2H_{21}I_2N_5ORuS$: C, 5.75; H, 5.03; I, 49.70. Found: C, 5.02; H, 5.44; I, 49.20.

By a similar method nitrogenpentaammineruthenium(II) hexafluorophosphate gave (dimethyl sulfoxide)pentaammineruthenium(II) hexafluorophosphate, yield 0.3 g (49%) *Anal.* Calcd for $C_2H_{21}F_{12}N_5OP_2RuS$: C, 4.33; H, 3.89. Found: C, 4.89; H, 4.32.

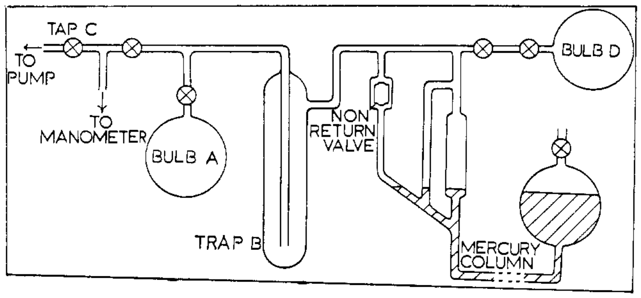

Figure 1. Apparatus for determination of nitrogen gas.

Bis(pyridine)tetraammineruthenium(II) Iodide, $[Ru(NH_3)_4(C_5H_5N)_2]I_2$. To nitrogenpentaammineruthenium(II) iodide (0.65 g) in water (4 ml) was added pyridine (1 ml), and the mixture was warmed until a dark red solution was formed (about 45 min). The solution was cooled in an ice bath and the bright yellow crystals that formed were collected by filtration and recrystallized from water. The product was dried *in vacuo* at 78° over P_2O_5, yield 0 25 g (31%) *Anal.* Calcd for $C_{10}H_{22}I_2N_6Ru$: C, 20.65; H, 3.79; I, 43.73. Found: C, 20.36; H, 3.83; I, 43.70.

Tetrakis(pyridine)diammineruthenium(II) Tetrafluoroborate, $[Ru(NH_3)_2(C_5H_5N)_4](BF_4)_2$. Nitrogenpentaammineruthenium(II) tetrafluoroborate (0.8 g) in water (8 ml) was added to pyridine (1 ml) and the mixture refluxed for 2 hr forming an orange solution. This was cooled and filtered, and an excess of sodium tetrafluoroborate was added to the filtrate. The bright yellow precipitate was collected by filtration, recrystallized from methanol-ether, and dried *in vacuo* over P_2O_5, yield 0.45 g (34%). *Anal.* Calcd for $C_{20}B_2F_8H_{26}N_6Ru$: C, 38.40; H, 4.16. Found: C, 38.60; H, 4.09.

By a similar method tetrakis(pyridine)diammineruthenium(II) hexafluorophosphate was obtained from nitrogenpentaammineruthenium(II) hexafluorophosphate (0.84 g), yield 0.70 g (59%). *Anal.* Calcd for $C_{20}F_{12}H_{26}N_6P_2Ru$: C, 32.39; H, 3.51. Found: C, 32.33; H, 3.63.

Both the above complexes are very soluble in ether, benzene, and chloroform.

Other methods of preparation for some of the above compounds have appeared in the literature.[15-17] Samples of these compounds were prepared and proved identical with those prepared from $[Ru(NH_3)_5N_2]^{2+}$.

Analyses. Carbon, hydrogen, and nitrogen analyses were performed by Dr. A. Bernhardt, Mulheim, West Germany, and by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Ammonia analyses were by conventional Kjeldahl methods and halide analyses by potentiometric titration.

Determination of Nitrogen Gas. A known weight of $[Ru(NH_3)_5N_2]^{2+}$ salt was introduced into bulb A (Figure 1). This was attached to the vacuum line, cooled in liquid nitrogen, and evacuated. The bulb was removed and heated over a Bunsen burner until no further change was observed. Bulb A was cooled and reattached to the vacuum line, and it and trap B were cooled in liquid nitrogen. Tap C was closed, and bulb A was opened to the line and the pressure noted. By repeatedly raising and lowering the mercury column the noncondensable gas was transferred to bulb D, of known volume, until no further pressure change could be observed. Bulb D was removed and attached to a second small vacuum line of known volume, where the pressure of the gas was measured. The bulb was then removed for insertion in a mass spectrometer. By this method both the volume and composition of the noncondensable gas could be measured.

Dimethyl sulfoxide solutions, 1 to 10 × 10^{-5} *M* in $[Ru(NH_3)_5N_2]I_2$, were used for the conductivity determination. These were prepared by diluting a 10^{-3} *M* stock solution. Similar procedures were used to prepare solutions of $[Ru^{III}(NH_3)_5I]I_2$, $[Ru^{III}(NH_3)_6]I_3$, and $(t\text{-}Bu)_4NI$. Fisher Scientific Co. "certified reagent" dimethyl sulfoxide was used. All measurements were made at 25° on an Industrial Instruments Inc. conductivity bridge, Model RC-16B2.

Infrared spectra in the KBr region were measured on a Perkin-Elmer "521" grating spectrophotometer as Nujol or hexachlorobutadiene mulls. The instrument was calibrated with polystyrene film between 4000 and 600 cm^{-1} and with water vapor between 600 and 250 cm^{-1}. Electronic spectra were measured on a Bausch and Lomb "505" spectrophotometer using 1-cm fused silica cells. Mass spectral measurements were made on an Associated Electrical Industries MS-2 mass spectrograph using an ionization potential of 75 ev. Proton magnetic resonance spectra were measured on a Varian A-60 instrument. Magnetic moments were measured by the Gouy method.

Results

The complexes of $[Ru(NH_3)_5N_2]^{2+}$ ion are stable, in the absence of water, for some weeks. Solutions in dry

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(16) K. Gleu and K. Rehm, *Z. Anorg. Allgem. Chem.*, 227, 237 (1936).

(17) R. O. Harris, Ph.D. Thesis, University of Toronto, 1963.

Table II. The Infrared Spectra[a] of $[Ru(NH_3)_5N_2]X_2$

$[Ru(NH_3)_5N_2]Cl_2$, cm^{-1}	$[Ru(NH_3)_5N_2]Br_2$, cm^{-1}	$[Ru(NH_3)_5N_2]I_2$, cm^{-1}	$[Ru(NH_3)_5N_2](BF_4)_2$, cm^{-1}	$[Ru(NH_3)_5N_2](PF_6)_2$, cm^{-1}	Assignment
3100–3350 (a)	3100–3350 (a)	3100–3350 (a)	3230, 3310, 3370	3225, 3306, 3375	ν_{HN}
2105	2114	2129	2144	2167	ν_{N-N}
1622	1618	1605	1630	1634	δ_{NH_3} deg
1270	1266	1276	1297	1298	δ_{NH_3} sym
798	788	775	768	~770[b]	ρ_{NH_3}
508	499	489	487	474	ν_{M-N_2}
454, 445 (sh)	458 (w), 432 (sh)	412	408	388	ν_{M-NH_3}
435	423				
			1100–1000 (a)	830 (a)	ν_{3}, BF_4^-, PF_6^- [c]
			519	551	ν_{4}, BF_4^-, PF_6^- [c]

[a] a = a region of broad absorption, w = weak, sh = shoulder. [b] Uncertain due to absorption of PF_6^-. [c] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 106, 115, 119. $[Ru(ND_3)_5N_2]I_2$ has absorption bands at 2308 (a) (ν_{ND}), 2124 (ν_{N-N}), 1160 (δ_{ND} deg), 933 (δ_{ND} sym), and 610 cm$^-$ (ρ_{ND_3}).

dimethyl sulfoxide are stable at room temperature for periods of up to 1 week, but solutions in water decompose slowly yielding red polynuclear ammine complexes.

The formulation of the complexes as $[Ru(NH_3)_5N_2]^{2+}$ is supported by the following evidence in addition to the analytical results given earlier.

The complexes are diamagnetic. Conductivity measurements showed $[Ru(NH_3)_5N_2]I_2$ to be a 2:1 electrolyte in dimethyl sulfoxide over the concentration range used (Figure 2). The infrared spectra (Figure 3, Table II) were similar to those of other ammine complexes of ruthenium.[14] In addition a strong sharp band in the region 2105–2170 cm^{-1} and a band at about 500 cm^{-1} were observed. The infrared spectrum of $[Ru(NH_3)_5N_2]I_2$ prepared as in method 1 (Experimental Section) using D_2O and N_2D_4 showed that the bands assigned to NH_3 vibrations had shifted as expected, but the band at 2129 cm^{-1} had shifted only 5 cm^{-1} (Table II). Proton magnetic resonance in both aqueous and dimethyl sulfoxide solution showed no high-field shift, which should be expected if the compounds were hydrides. No peaks were found other than those attributable to NH_3. Mass spectral analysis of the noncondensable gas evolved on dry heating revealed that it was N_2 of more than 99% purity. The coordinated nitrogen is relatively labile, as is shown by the variety of complexes obtainable using nitrogenpentaammineruthenium(II) as starting material. This is in contrast to the behavior of nitrosyl complexes of ruthenium in which the NO group is extremely difficult to replace.[18]

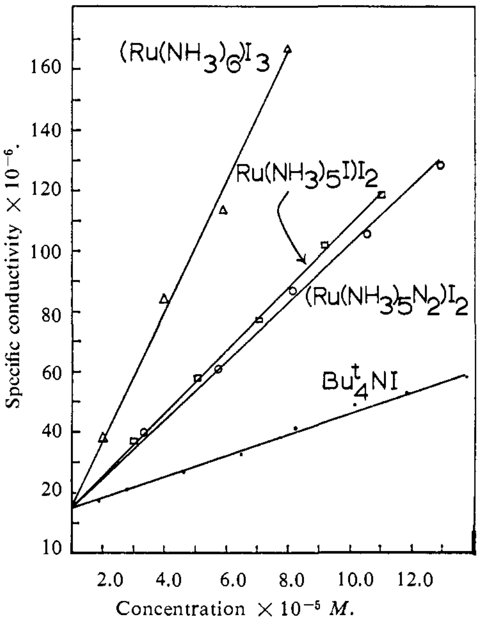

Figure 2. Conductivity of $[Ru(NH_3)_6]I_3$, $[Ru(NH_3)_5I]I_2$, $[Ru(NH_3)_5N_2]I_2$, and $(t\text{-}Bu)_4NI$.

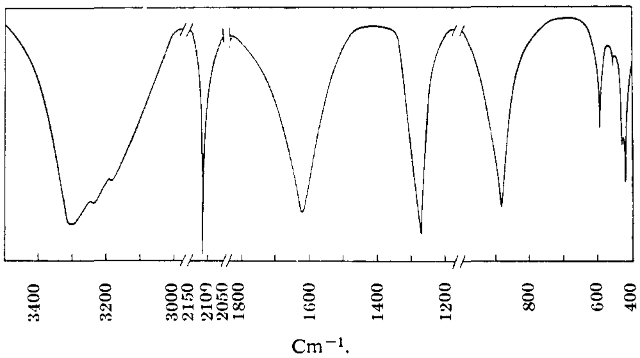

Figure 3. Infrared spectrum of $[Ru(NH_3)_5N_2]Br_2$.

Attempts were made for the analysis of coordinated nitrogen by reduction of the complex with sodium borohydride in basic solution followed by determination of the total ammonia by the Kjeldahl method. Although preliminary experiments showed that most of the coordinated N_2 could be converted to ammonia, more extensive experiments showed that only a total of six ammonia molecules per ruthenium could be obtained by this method instead of the expected seven. The mean value for ten determinations, 5.93 ± 0.07 molecules of ammonia per ruthenium, indicated that the low result was not due to loss of nitrogen gas, for which a random spread of results would be expected. Analysis of the residue after these experiments showed that it contained combined nitrogen; however, the quantity was insufficient to account for the seventh nitrogen. The infrared

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(18) B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, 7, 332 (1966).

spectrum of the residue showed no band attributable to coordinated N_2. Attempts to reduce the nitrogen with Devarda's alloy or with zinc powder were unsuccessful. The latter observation is in agreement with the reported preparation of a ruthenium nitrogen compound from $RuCl_3$ and $RuCl_3OH$ using zinc in tetrahydrofuran and nitrogen gas.[19] Similarly only 40% of the theoretical amount of N_2 could be obtained by heating the compound with concentrated sulfuric acid. These reactions indicate that the coordinated N_2 may undergo reactions other than displacement, and further work is in progress.

Of the three methods of preparation the one involving the reaction of N_3^- and $[Ru(NH_3)_5H_2O]^{3+}$ is to be preferred since it more easily leads to a pure product. The product from the reaction of hydrazine and ruthenium trichloride is sometimes contaminated with $[Ru(NH_3)_6]^{2+}$. The latter material is also obtained if the hydrazine–ruthenium trichloride reaction mixture is heated.

The preparation of $[Ru(NH_3)_5N_2]^{2+}$ from sodium azide and $[Ru^{III}(NH_3)_5H_2O]^{3+}$ resulted from attempts to prepare $[Ru^{III}(NH_3)_5N_3]^{2+}$ for comparison purposes. Gentle heating of the reaction mixture (method 3, Experimental Section) yielded only $[Ru(NH_3)_5N_2]^{2+}$. In the cold, if a precipitating anion, *e.g.*, I^-, was added shortly after the addition of sodium azide, it was possible to precipitate a red solid. This compound decomposed rapidly in the solid state to yield the off-white nitrogen compound. Examination of the infrared spectrum of the red solid showed it to have a broad band at about 2020 cm^{-1} which faded rapidly and was replaced by the $[Ru(NH_3)_5N_2]I_2$ band at 2129 cm^{-1}. Similarly the visible spectrum showed a band at approximately 463 mμ which decayed to yield a band at 221 mμ, the latter being due to $[Ru(NH_3)_5N_2]^{2+}$.[20] If, instead of adding I^- to the reaction solution, a large excess of N_3^- was added, a red precipitate could be obtained which did not decompose as rapidly as the material precipitated with I^-. This material had a paramagnetism of $\chi_m \times 10^6 = 1700$ cgs units, typical for a ruthenium(III) complex of this type,[15] which altered to a value of 1200 cgs units over a period of 12 hr. Attempts to characterize the red material further have failed due to its instability, but from the above results we concluded that it is $[Ru^{III}(NH_3)_5N_3]^{2+}$. Note well: During experiments designed to isolate the presumed $[Ru^{III}(NH_3)_5N_3]^{2+}$, the red material proved to be violently and unpredictably explosive.

The preparation of pentaammine complexes of ruthenium(II) and -(III) from $[Ru(NH_3)_5N_2]^{2+}$ makes this material a useful synthetic intermediate. In many cases it was unnecessary to isolate $[Ru(NH_3)_5N_2]^{2+}$ from solution; for example, $[Ru^{III}(NH_3)_5Br]Br_2$ was obtained from the ruthenium trichloride–hydrazine reaction solution by treatment with HBr, and the same compound was obtained using $[Ru^{II}(NH_3)_5N_2]Br_2$ as starting material.

The infrared spectra of the compounds are given in Table II and a typical spectrum is illustrated by that of $[Ru(NH_3)_5N_2]Br_2$ in Figure 3. The number of bands due to ammonia vibrations is similar to those found in other ammine complexes.[14,21] The strong sharp band in the 2100-cm^{-1} region assigned to ν_{N-N} varies markedly with the anion, this band moving to higher frequency with increasing size of anion, and the band assigned to ν_{M-N} moving to lower frequency.

The following results were obtained in a preliminary study of the hydrazine–ruthenium trichloride reaction mechanism. The reaction mixture from hydrazine and ruthenium trichloride was filtered into excess sodium iodide after a reaction time of 2 min, yielding a brown-red solid. The infrared spectrum of this material showed, in addition to bands attributable to coordinated ammonia, a band at 2129 cm^{-1} (attributed to ν_{N-N}) and a broad band at 2090 cm^{-1}. The same procedure was performed after a reaction time of 1 hr and the spectrum showed a band at 2129 cm^{-1} having a broad shoulder centered at 2090 cm^{-1}. A similar procedure with the reaction between $[RuCl_6]^{2-}$ and hydrazine showed, after 2 min of reaction time, only a broad band at 2090 cm^{-1}. After 1 hr a spectrum similar to that obtained in the ruthenium trichloride–hydrazine reaction was obtained.

In the case of the reaction of $[Ru^{III}(NH_3)_5H_2O]^{3+}$ and hydrazine, a similar prodecure gave, after 2 min of reaction time, a material showing only one band at 2129 cm^{-1} in addition to ammine bands.

The complex $[Ru^{II}(NH_3)_5(CH_3)_2SO](PF_6)_2$ shows a strong band at 1042 cm^{-1} in the infrared, assigned to ν_{S-O}. The fact that this band is close to that obtained for free dimethyl sulfoxide (1045 cm^{-1}, chloroform solution[22a]) probably indicates that the dimethyl sulfoxide is bonded *via* the sulfur atom.[22b]

Discussion

The preparation of complexes containing molecular nitrogen poses two major questions. These are the nature of the bonding in these complexes and their mechanism of formation.

A detailed crystal structure analysis[4] of the compounds revealed that the M–N–N moiety is strictly linear. Because of a crystal disorder the exact M–N and N–N bond lengths could not be determined accurately. The results of the crystal structure analysis and the fact that the frequency of ν_{N-N} is reduced by 200 cm^{-1} from that in free nitrogen (2330 cm^{-1})[23] indicate that the bonding is analogous to that in metal carbonyls. Nitrogen is isoelectronic with carbon monoxide but is an even weaker Lewis base, and hence it would appear that the formation of a π bond by back-donation from the filled nonbonding metal orbitals to the empty antibonding π orbitals on nitrogen is even more important in nitrogen complexes than in carbonyls. Support for strong dπ–pπ back-bonding also comes from the fact that the NH_3 vibrations were observed at higher frequencies than those found in $[Ru^{II}(NH_3)_6]^{2+}$ and approach those found in $[Ru^{III}(NH_3)_5X]^{2+}$ compounds.[14,21]

The initial reaction between hydrazine and the ruthenium salts is vigorous, exothermic, and involves gas evolution. Hydrazine may decompose to yield nitrogen,

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(20) D. E. Harrison and H. Taube, private communication.

(21) W. P. Griffith, *J. Chem. Soc.*, 899 (1966).

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hydrogen, ammonia, or azide, or a mixture of any or all of these.[24] In the presence of transition metals, hydrazine yields nitrogen and hydrogen by a process which is essentially catalytic. For these reasons the mechanism of formation of $[Ru(NH_3)_5N_2]^{2+}$ is difficult to elucidate. A complete study of the reaction is in progress, and it is hoped that a more definite conclusion will be reached. At present it appears that when ruthenium(IV) is present the reaction proceeds *via* coordinated azide, this mechanism accounting for the band at 2090 cm^{-1}. In view of the results obtained with $[Ru^{III}(NH_3)_5H_2O]^{3+}$ and NaN_3 it would appear that the intermediate in the reaction is a $Ru^{III}–N_3$ species, the N_3^- being produced from hydrazine by reduction of Ru^{IV} to Ru^{III}. The reaction between $[Ru^{III}(NH_3)_5H_2O]^{3+}$ and hydrazine may proceed *via* coordinated azide or *via* some other adduct which decomposes to leave a bonded nitrogen molecule. No intermediate can be detected at present and hence no path can be suggested for this reaction. We have attempted to prepare $[Ru(NH_3)_5N_2]^{2+}$ from various ruthenium ammines and nitrogen gas under pressure. All such attempts have failed. The preparation of $[Ru^{II}(NH_3)_5N_2]^{2+}$ from $[Ru^{III}(NH_3)_5Cl]^{2+}$ using nitrogen and amalgamated zinc has recently been reported,[20] and Chatt has reported the formation of the same compound from the reaction of hydrazine and $(PR_3P)_3RuCl_3$.[25]

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The Crystal and Molecular Structure of Tetraethylammonium Bis-(3)-1,2-dicarbollylcuprate(II)[1]

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Abstract: The crystal structure of $(Et_4N)_2Cu(C_2B_9H_{11})_2$ has been determined from a single-crystal X-ray diffraction study. The two carbons of the icosahedral fragment were distinguished unambiguously from the borons. The coordination about copper deviates from the usual π-sandwich configuration by a slippage of the carborane moieties parallel to one another so that the primary coordination sphere of copper is six borons, three from each carborane cage ($\overline{\text{Cu–C}} = 2.57$ A, $\overline{\text{Cu–B}} = 2.20$ A). Although only the center is required crystallographically, the anion's molecular symmetry is within experimental error C_{2h}.

During the past 2 years Hawthorne[2–7] and coworkers have synthesized several carborane derivatives of transition metals. X-Ray crystal structure studies by Zalkin,[8,9] *et al.*, confirmed the π-sandwich structure postulated by Hawthorne for the iron and rhenium dicarbollyl derivatives. More recently Hawthorne and Warren[10] isolated a blue crystalline compound of copper from an aqueous, strongly basic solution of cupric chloride and (3)-1,2-dicarbollide anion.

In view of the fact that organocopper chemistry is very sparse and representative compounds, apart from the acetylides and olefins, are very unstable, the new carbametallic of copper is very unusual in its stability. There seems to be no analogous chemistry of copper, the only cyclopentadienide being triethylphosphinecyclopentadienylcopper $[C_5H_5CuPEt_3]$ which has been reported to be a σ complex.[11] To our knowledge no organometallic compounds of copper(II) have been reported.

Experimental Section

Dark royal blue platelets of the tetraethylammonium salt of $Cu(C_2B_9H_{11})_2{}^{2-}$ were kindly provided by Professor M. F. Hawthorne of this department. A single crystal 0.66 × 0.46 × 0.25 mm was selected using a polarizing microscope and mounted in a borosilicate capillary. The crystals are strongly dichroic. When viewed in transmission with polarized light propagating parallel to a^*, the crystals are blue if the electric vector is approximately parallel to

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