comparisons of the structures of cis disubstituted complexes that contain chelate rings to analogous complexes that do not, have yet to be reported. It will be of great interest to make such comparisons.

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Registry No. **1a**, 21948-42-5; **1b**, 29832-09-5; trimethyl phosphite, 121-45-9; triethyl phosphite, 122-52-1; triisopropyl phosphite, 116-17-6; tri-*n*-butylphosphine, 998-40-3.

Supplementary Material Available: Pseudo-first-order rate constants for reactions of (DTO)W(CO)$_4$ and (DTN)W(CO)$_4$ with L in DCE and CB at various temperatures (Table I) (5 pages). Ordering information is given on any current masthead page.

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Thermal Reactions of Metal Complexes under Quasi-isothermal and -isobaric Conditions. 4.[1] Solid-Phase Thermal Reactions of Ruthenium(II)–Pentaammine Complexes Containing Dinitrogen and Related Ligands

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A series of Ru^{II}–pentaammine complexes of the form [Ru(NH$_3$)$_5$(L)]X$_n$·mH$_2$O were prepared, where L = N$_2$, CO, NO$^+$, CH$_3$CN, CH$_3$NC, X = Cl$^-$, Br$^-$, I$^-$, n = 2, 3, and m = 0, 1. The thermal reactions of the complexes in the solid phase were investigated under quasi-isothermal and -isobaric conditions (Q conditions) and under open dynamic conditions (D conditions). It was found that the thermal reaction patterns of the complexes are considerably different from one another, depending upon the kinds of ligands (L). In the thermal reaction processes of [Ru(NH$_3$)$_5$(N$_2$)]X$_2$, the evolution of NH$_3$ precedes that of dinitrogen, indicating that the Ru^{II}–N$_2$ bond is unexpectedly stable in the solid state, whereas the bond has been found to be easily broken in aqueous media. The thermal reaction patterns of the CO, CH$_3$CN, and CH$_3$NC complexes are essentially similar to those of the dinitrogen complexes. [Ru(NH$_3$)$_5$(NO)]X$_3$ was converted into *trans*-[Ru(NH$_3$)$_4$X(NO)]X$_2$ when X was Cl$^-$ or Br$^-$, but into *cis*-[Ru(NH$_3$)$_4$I(NO)]I$_2$ when X was I$^-$. The cleavage temperatures of Ru^{II}–L bonds contained in the complexes [Ru(NH$_3$)$_5$(L)]Cl$_n$ increase in the order CH$_3$CN (191 °C) < N$_2$ (255 °C) < CO (286 °C) < CH$_3$NC (312 °C) < NO$^+$ (324 °C), which is parallel to the order of the strength of π back-bonding from Ru^{II} to L except for the case of the CH$_3$NC complex. The high cleavage temperature of the CH$_3$NC complex may come from the stronger σ bonding due to the –NC group rather than the π back-bonding.

Introduction

Since the (dinitrogen)ruthenium(II) complex [Ru(NH$_3$)$_5$(N$_2$)]Cl$_2$ was first isolated by Allen et al.,[3,4] studies have been devoted mainly to clarifying the possibilities of reduing the nitrogen molecule under mild conditions by the use of metal complexes.[5-8] Such attempts have not yet led to good results because of the strength of the N–N bond. Our interest concerns whether or not the dinitrogen complexes are stable in the solid state. We recently noticed two different papers on this topic: one stated that [Ru(NH$_3$)$_5$(N$_2$)]X$_2$ complexes are so unstable that they easily evolve the dinitrogen molecule in an anhydrous state[4] as well as in solution;[9,10] the other reported that the solid complexes do not expel the dinitrogen molecule even at 201 °C (for chloride), 183 °C (for bromide), and 155 °C (for iodide).[11] To settle the discrepancy, the present study was undertaken to learn the details of the solid-phase thermal reactions of [Ru(NH$_3$)$_5$(N$_2$)]X$_2$ (X = Cl$^-$, Br$^-$, I$^-$) under quasi-isothermal and -isobaric conditions.[1,12]

In [Ru(NH$_3$)$_5$(N$_2$)]Cl$_2$, the Ru–N$_2$ bond involves π back-bonding between the Ru dπ orbital and the pπ^* orbital of the N$_2$ ligand.[13] It therefore seemed of interest to extend the present study by considering the effect of other π-accepting ligands (L) on the thermal stability of [Ru(NH$_3$)$_5$(L)]X$_n$ complexes. Therefore, a series of Ru^{II}–pentaammine complexes containing a variety of π-accepting ligands other than dinitrogen were prepared and their solid-state thermal behaviors were investigated. In the present study, N$_2$, CO, NO$^+$, CH$_3$CN, and CH$_3$NC were selected as the π-accepting ligands.

Experimental Section

Preparation of Starting Materials. The starting complexes [Ru(NH$_3$)$_5$Cl]Cl$_2$[14] and [Ru(NH$_3$)$_6$]Cl$_3$[15] were prepared by a modification of

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Table I. Analytical Data for the Complexes Obtained

	% C		% H		% N	
complexes	found	calcd	found	calcd	found	calcd
$[Ru(NH_3)_5(N_2)]Cl_2$			5.12	5.30	33.59	34.39
$[Ru(NH_3)_5(N_2)]Br_2$			4.25	4.01	26.13	26.22
$[Ru(NH_3)_5(N_2)]I_2$			3.28	3.21	20.87	20.95
$[Ru(NH_3)_5(CO)]Cl_2$	4.28	4.21	5.17	5.26	24.80	24.56
$[Ru(NH_3)_5(CO)]Br_2$	3.27	3.21	3.87	4.01	18.91	18.73
$[Ru(NH_3)_5(CO)]I_2$	2.70	2.65	3.35	3.20	15.39	14.96
$[Ru(NH_3)_5(NO)]Cl_3 \cdot H_2O$			5.13	4.99	24.61	24.68
$[Ru(NH_3)_5(NO)]Br_3 \cdot H_2O$			3.96	3.59	17.34	17.73
$[Ru(NH_3)_5(NO)]I_3 \cdot H_2O$			2.85	2.77	13.92	13.67
$[Ru(NH_3)_5(CH_3CN)]Cl_2 \cdot H_2O$	7.60	7.60	6.37	6.33	26.35	26.59
$[Ru(NH_3)_5(CH_3CN)]Br_2 \cdot H_2O$	5.95	5.93	5.07	4.94	20.73	20.75
$[Ru(NH_3)_5(CH_3CN)]I_2$	4.97	4.99	3.84	3.74	17.60	17.47
$[Ru(NH_3)_5(CH_3NC)]Cl_2 \cdot H_2O$	7.60	7.60	5.82	6.33	26.60	26.59
$[Ru(NH_3)_5(CH_3NC)]Br_2$	6.17	6.20	4.77	4.65	21.79	21.72
$[Ru(NH_3)_5(CH_3NC)]I_2$	5.11	4.99	3.76	3.74	17.93	17.47

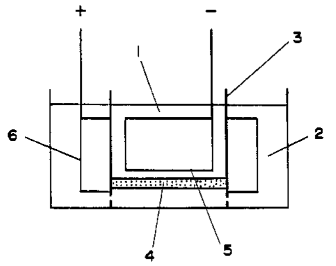

Figure 1. Sketch of the electrolytic cell for the preparation of the acetonitrile and methyl isocyanide complexes: (1) solution of $[Ru(NH_3)_5Cl](CF_3COO)_2$ and CH_3CN (or CH_3NC); (2) 1% NaCl solution containing a few drops of CH_3COOH; (3) negative part (glass filter); (4) diaphragm (fritted glass); (5) cathode (cylindrical platinum foil); (6) anode (cylindrical aluminum foil).

the known procedures. Methyl isocyanide (CH_3NC) was synthesized in a manner similar to that reported previously.[16]

Preparation of Complexes. $[Ru(NH_3)_5(L)]X_2$ (L = N_2,[17] CO;[18] X = Cl^-, Br^-, I^-) complexes were obtained by the methods in the literature.

$[Ru(NH_3)_5(NO)]X_3 \cdot H_2O$ (X = Cl^-, Br^-, I^-) were prepared according to a modification of the known method:[19] 1 g of $[Ru(NH_3)_6]Cl_3$ was dissolved in 50 cm^3 of 0.1 M HCl. NO was bubbled at ambient temperature into the solution for about 3 h. The resulting solution was then ice-cooled, and concentrated hydrochloric acid was added to completely precipitate the chloride $[Ru(NH_3)_5(NO)]Cl_3 \cdot H_2O$. The chloride thus obtained was collected by filtration, washed in turn with ethanol and ether, and dried in vacuo. The bromide and the iodide were obtained by metatheses of the chloride with NaBr and NaI, respectively. They were recrystallized from hot water.

$[Ru(NH_3)_5(CH_3CN)]X_2 \cdot nH_2O$ (X = Cl^-, Br^-, I^-; n = 0, 1). The products of the previously reported method of preparation[20] were contaminated with tetrahalogenozincates because zinc amalgam was used as the reducing agent. The procedures described below worked better:

A 0.5-g amount of $[Ru(NH_3)_5Cl]Cl_2$ was digested in a solution of CF_3COOAg (0.7 g) in water (5 cm^3). The mixture was filtered once to remove the AgCl produced. To the filtrate was added 1 cm^3 of acetonitrile, and the mixture was charged in the negative part of the electrolytic cell as depicted in Figure 1. Electrolysis (20–30 mA and ca. 6 V for 2 h) using aluminum and platinum foils as positive and negative electrodes, respectively, smoothly performed the reduction of the ruthenium(III) complex. The use of aluminum foil is particularly suitable for the electrolysis. During the electrolysis, yellow products initially deposited, which then completely dissolved by the end of reduction. The resulting solution was then cooled in an ice bath. The chloride and the bromide were obtained as follows: a small amount of concentrated hydrochloric or hydrobromic acid, ethanol (about 5 cm^3), and an appropriate amount of ether were in turn added dropwise to the above solution to produce the desired pale yellow complex $[Ru(NH_3)_5(CH_3CN)]Cl_2 \cdot H_2O$ or $[Ru(NH_3)_5(CH_3CN)]Br_2 \cdot H_2O$. On the other hand, the iodide $[Ru(NH_3)_5(CH_3CN)]I_2$ was readily obtained by adding NaI to the above solution. These complexes were collected by filtration, washed with ethanol and ether, and dried in vacuo.

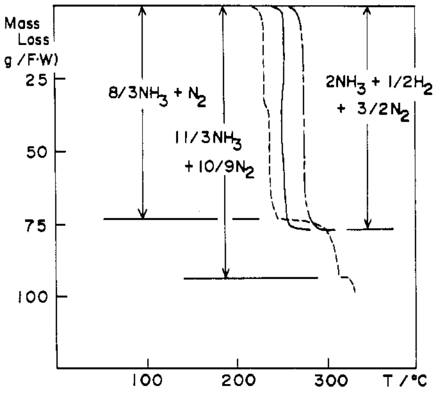

Figure 2. Q derivatograms of $[Ru(NH_3)_5(N_2)]X_2$: (—) chloride; (– – –) bromide; (- - -) iodide.

$[Ru(NH_3)_5(CH_3NC)]X_2 \cdot nH_2O$ (X = Cl^-, Br^-, I^-; n = 0, 1). The colorless methyl isocyanide complexes were prepared in a manner similar to that of the acetonitrile complexes except that methyl isocyanide was used in place of acetonitrile. The chloride has 1 mol of lattice water.

Table I summarizes the analytical data for the complexes obtained.

Isolation of Intermediate during Thermal Reactions. $Cs_2[RuCl_5(NO)]$. The grayish pink Q_2-product-(NO,Cl)[21] of $[Ru(NH_3)_5(NO)]Cl_2 \cdot H_2O$ (see the Nitrosyl Complexes part of Results) was dissolved in hot water, and grayish residues were filtered off. To the wine red filtrate were added appropriate amounts of CsCl. Pink precipitates thus obtained were collected by filtration, washed with ethanol and ether, and dried in vacuo. Anal. Calcd for $Cs_2[RuCl_5(NO)]$: N, 2.44. Found: N, 2.42.

Derivatographic Measurements. The thermal reactions of the complexes were traced under quasi-isothermal and -isobaric conditions (Q conditions) and open dynamic conditions (D condition) by using Q and D derivatographs, respectively.[1,12] The samples were used in 0.3- and 0.4-g amounts for Q and D derivatographies, respectively. The measurements by D derivatograph were carried out under constant flow of nitrogen at the heating rate of 2 °C min^{-1}.

Electronic Spectral Measurements. Electronic spectra of the samples freshly prepared in water were monitored on a JASCO UVIDEC-505 UV/vis recording digital spectrophotometer.

IR and Far-IR Spectral Measurements. IR spectra of the samples were measured by a KBr-disk method with a JASCO Model A-3 infrared spectrophotometer. Far-IR spectra were measured by a Nujol-mull

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(21) For convenience, throughout this paper, the term "Q products" is employed to express the products obtained under Q conditions. In addition, for example, Q-product-(N_2,Cl) and Q-product-(CO,Br) stand for Q products of the chloride of the dinitrogen complex ($[Ru(NH_3)_5(N_2)]Cl$) and of the bromide of the carbonyl complex ($[Ru(NH_3)_5(CO)]Br$). Hereinafter, all the products are abbreviated in a similar fashion.

Table II. IR and Far-IR Spectral Data (cm^{-1}) of the Dinitrogen Complexes

compds[a]	ν_{N-H}	$\nu_{N\equiv N}$	δ_{d,NH_3}	δ_{d,NH_4^+}	δ_{s,NH_3}	$\nu_{Ru\equiv N}$[b]	ρ_{NH_3}	ν_{Ru-N_2}	ν_{Ru-NH_3}
$[Ru(NH_3)_5(N_2)]Cl_2$									
original (pale yellow)	3312	2105	1622		1270		798	508	435
Q-product-(N_2,Cl)[c] (black)	3145			1400					
$[Ru(NH_3)_5(N_2)]Br_2$									
original (pale yellow)	3285	2114	1618		1266		788	499	423
Q-product-(N_2,Br)[c] (black)	3145			1400					
$[Ru(NH_3)_5(N_2)]I_2$									
original (pale yellow)	3297	2129	1605		1276		778	489	412
Q_1-product-(N_2,I)[c] (black)	3309		1608	1400	1277	1054	765		548
	3145								
Q_2-product-(N_2,I)[c] (black)								497[e]	
$[RuN(NH_3)_3I_2]I$[d] (brown)	3304		1602		1277	1054	753		549

[a] Original stands for the original complexes before heating. [b] See ref 22. [c] The compositions of the products were determined as follows: Q-product-(N_2,Cl), Ru + 2 NH_4Cl; Q-product-(N_2,Br), Ru + 2 NH_4Br; Q_1-product-(N_2,I), Ru + $^1/_2[RuN(NH_3)_3I_2]I$ + $^3/_2NH_4I$; Q_2-product-(N_2,I), Ru + $RuI_3N_{1/3}$. [d] Isolated as described in the Experimental Section. [e] Assigned to ν_{as,Ru_3N}.

Table III. IR and Far-IR Spectral Data (cm^{-1}) of the Carbonyl Complexes

compds[a]	ν_{N-H}	ν_{C-O}	δ_{d,NH_3}	δ_{d,NH_4^+}	δ_{s,NH_3}	$\nu_{Ru\equiv N}$	ρ_{NH_3}	δ_{C-O}	ν_{Ru-CO}	ν_{Ru-NH_3}
$[Ru(NH_3)_5(CO)]Cl_2$										
original (white)	3320	1920	1630		1280		808	583	542	448
					1232					
Q-product-(CO,Cl)[b] (black)	3145			1400						
$[Ru(NH_3)_5(CO)]Br_2$										
original (white)	3311	1934	1620		1280		798	582	533	440
					1246					
Q_1-product-(CO,Br)[b] (pale brown)	3370	1927	1620							
	3309	1907	1500[c]	1400	1289		773	599	570	443
	3248				1282		710[d]			
	3186				1261					
Q_2-product-(CO,Br)[b]	3145			1400						
$[Ru(NH_3)_5(CO)]I_2$										
original (white)	3304	1946	1614		1289		789	582	523	434
Q-product-(CO,I)[b] (brown)		1960				1230			555	
		1945								

[a] Original stands for the original complexes before heating. [b] The composition of the products were determined as follows: Q-product-(CO,Cl), Ru + 2 NH_4Cl; Q_1-product-(CO,Br), not determined in detail; Q_2-product-(CO,Br), Ru + 2 NH_4Br; Q-product-(CO,I), probably $[RuNI_2(CO)]$. [c] Assigned to δ_{d,NH_2}. [d] Assigned to ρ_{NH_2}.

method on a JASCO Model IR-F far-infrared spectrophotometer.

Raman Spectral Measurements. Raman spectra were measured in a powder state on a KBr disk with a JASCO Model R-500S laser-Raman spectrophotometer using an unfocused beam. The normal focused beam frequently caused undesired decomposition of the samples.

Magnetic Moments. Magnetic susceptibilities of the samples were measured by the Gouy method at room temperature. Effective magnetic moments (μ_{eff}) were corrected by the use of Pascal's constants for each component in the compounds.

Results

Under dynamic conditions (D conditions), a monotonous decrease in weight losses took place and any clear plateau was not observed in the TG curves of all the complexes, indicating that the complexes decompose gradually in a complicated manner without formation of any uniform product under D conditions. The D derivatograms are therefore omitted for simplification of the following discussion.

Dinitrogen Complexes. Derivatography. Figure 2 shows the Q derivatograms of $[Ru(NH_3)_5(N_2)]X_2$ (X = Cl^-, Br^-, I^-). The mass losses in the figure are expressed in terms of grams per formula weight (g/fw). In the Q derivatogram of the chloride, a sharp mass loss can be seen at 240–260 °C and then a plateau is obtained. The product obtained at this stage is called Q-products (N_2,Cl).[21] The Q derivatogram of the bromide is substantially the same as that of the chloride except that a sharp weight loss starts at 270–280 °C and then a plateau is obtained. The product at this stage is named Q-product-(N_2,Br). On the other hand, the Q derivatogram of the iodide shows a weight loss at 220–230 °C and the first plateau is obtained at the mass loss of 74 g/fw. Different from the chloride and bromide, another weight loss can be seen at 315–325 °C, the second tiny plateau being obtained at the mass loss of 93 g/fw. The products at the first and second plateaus are called Q_1- and Q_2-product-(N_2,I), respectively.

Identification of the Products. Table II contains the IR and far-IR spectral data for the original dinitrogen complexes and the products obtained during the thermal reaction processes. The IR data for Q-product-(N_2,Cl) and Q-product-(N_2,Br) suggest that both the products contain ammonium ion, but not dinitrogen ligand. Elemental and fluorescent X-ray analyses for the products indicate that they consist of Ru + 2 NH_4Cl and Ru + 2 NH_4Br, respectively. On the other hand, the lack of dinitrogen in Q_1- and Q_2-product-(N_2,I) is also supported by the absence of $\nu_{N\equiv N}$ and ν_{Ru-N_2} in the IR spectra. As for Q_1-product-(N_2,I), the appearance of a new band at 1054 cm^{-1}, which may be assignable to $\nu_{Ru\equiv N}$,[22] is important. Additionally, analytical data and fluorescent X-ray analyses implied that the product consists of Ru + $[RuN(NH_3)_3I_2]I$ + 2 NH_4I. Then, the compound $[RuN(NH_3)_3I_2]I$ was isolated from the black Q_1-product-(N_2,I) as follows: the product was dissolved in hot water, and black insoluble materials (fluorescent X-ray analysis evidenced that they contain Ru metal) were removed by filtration. To the filtrate were added appropriate amounts of NaI to yield brown precipitates. The precipitates were collected by filtration, washed with ethanol and ether, and dried in vacuo (Anal. Calcd for $[RuN(NH_3)_3I_2]I$: H, 1.65; N, 10.24. Found: H, 1.65; N, 9.89). The compound underwent subsequent solid-state reaction to produce the material having the composition of $RuI_3N_{1/3}$:[23]

$$[RuN(NH_3)_3I_2]I \rightarrow RuI_3N_{1/3} + 3NH_3 + {}^1/_2N_2$$

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[22] The band at 1054 cm^{-1} may be assigned to any one of $\nu_{Ru\equiv N}$, ν_{as,Ru_2N}, and ρ_{w,NH_2^-}. The possibilities of the last two can be discarded as follows: First, the possibility of ρ_{w,NH_2^-} is denied because attempts to deuterate the product did not cause the shift of the band. Second, Raman spectral measurements could not detect Raman-active ν_{s,Ru_2N} in the region 330–360 cm^{-1}.[24] The band may thus be attributed to $\nu_{Ru\equiv N}$.

Table IV. IR and Far-IR Data (cm^{-1}) of the Nitrosyl Complexes

compds^a	ν_{N-H}	$\nu_{N\equiv O}$	δ_{d,NH_3}	δ_{d,NH_4^+}	δ_{s,NH_3}	$\nu_{Ru\equiv N}$	ρ_{NH_3}	ν_{Ru-NO}	ν_{Ru-NH_3}
$[Ru(NH_3)_5(NO)]Cl_3 \cdot H_2O$									
original (orange)	3237	1910	1580		1329		855	609	480
					1310				
Q_1-product-(NO,Cl)^b (orange-yellow)	3260	1881	1550		1305		857	609	482
Q_2-product-(NO,Cl)^b (grayish pink)	3200	1902		1400				588	
$[Ru(NH_3)_5(NO)]Br \cdot H_2O$									
original (orange)	3255	1913	1590		1329		845	602	473
					1311				
Q_1-product-(NO,Br)^b (orange-yellow)	3255	1870	1585		1300		845	591	472
Q_2-product-(NO,Br)^b (grayish brown)	3172	1882		1400	1278			577	
$[Ru(NH_3)_5(NO)]I_3 \cdot H_2O$									
original (orange)	3227	1915	1600		1331		838	598	469
					1317				
Q_1-product-(NO,I)^b (green)	3231	1904	1613		1310		833	595	470
								580	
Q_2-product-(NO,I)^b (brown)	3310	1900	1600		1298	1055	780	590	458
	3227	1881			1286			573	
ref complexes									
trans-$[Ru(NH_3)_4Cl(NO)]Cl_2$^{c} (orange-yellow)	3260	1881	1560		1300		858	608	483
cis-$[Ru(NH_3)_4Cl(NO)]Cl_2$^{d} (pink)	3260	1899	1595		1310		862	604	478
								590	
trans-$[Ru(NH_3)_4Br(NO)]Br_2$^{c} (orange yellow)	3260	1870	1585		1300		845	591	472
cis-$[Ru(NH_3)_4Br(NO)]Br_2$^{d} (pink)	3260	1863	1588		1310		852	599	470
								589	
trans-$[Ru(NH_3)_4I(NO)]I_2$^{d} (green)	3240	1880	1563		1306		834	574	467
cis-$[Ru(NH_3)_4I(NO)]I_2$^{d} (green)	3220	1902	1580		1312		832	592	472
								581	
$(NH_4)_2[RuCl_5(NO)]$^{e} (pink)	3195	1887		1388				585	
$(NH_4)_2[RuBr_5(NO)]$^{e} (brown)	3165	1870		1390				572	

^{a}Original stands for the original complexes before heating. ^{b}Theproducts were identified as follows: Q_1-product-(NO,Cl), *trans*-$[Ru(NH_3)_4Cl(NO)]Cl_2$; Q_2-product-(NO,Cl), $(NH_4)_2[RuCl_5(NO)]$; Q_1-product-(NO,Br), *trans*-$[Ru(NH_3)_4Br(NO)]Br_2$; Q_2-product-(NO,Br), $(NH_4)_2[RuBr_5(NO)]$; Q_1-product-(NO,I), *cis*-$[Ru(NH_3)_4I(NO)]I_2$; Q_2-product-(NO,I), $[Ru(NH_3)_2I_3(NO)]$. ^{c}Cited from ref 26. ^{d}Cited from ref 25. ^{e}Cited from ref 27.

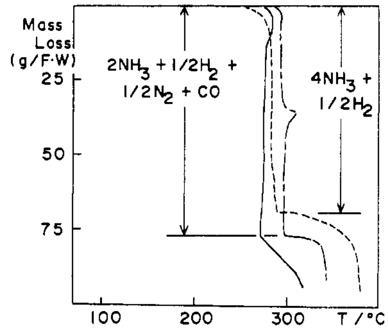

Figure 3. Q derivatograms of $[Ru(NH_3)_5(CO)]X_2$: (—) chloride; (- - -) bromide; (- · -) iodide.

The isolated compound may thus be considered to be $[RuN(NH_3)_3I_2]I$.

Carbonyl Complexes. Figure 3 depicts the Q derivatograms of $[Ru(NH_3)_5(CO)]X_3$ (X = Cl$^-$, Br$^-$, I$^-$). In the TG curve of the chloride, an acute weight loss is seen at 275–285 °C and then a break point is obtained at the mass loss of 77 g/fw. An unusual decrease in temperature during mass loss can be seen in the curve, reflecting that the reaction is considerably endothermic. The TG pattern of the chloride is essentially similar to that of $[Ru(NH_3)_5(N_2)]Cl$ except that the former's reaction temperature (275–285 °C) is higher than the latter's (240–260 °C). The IR data (Table III) and elemental analyses for Q-product-(CO,Cl) disclosed that the product consists of Ru + 2 NH_4Cl.

The Q derivatogram of the bromide illustrates that a steep and straight weight loss starts at 290–295 °C and then a small but clear plateau is obtained at the mass loss of about 35 g/fw; the second weight loss occurs at 310 °C, and then the second slant plateau is obtained at the mass loss of 77 g/fw. The products at the first and the second plateaus are called Q_1- and Q_2-product-(CO,Br). Visual observation of Q_1-product-(CO,Br) taken out from the crucible revealed that the product immediately turned from pale brown to dark brown. We were unable to determine the details of the product because the compound is unstable in the air. However, the appearance of the steep and straight TG curve plus the small but clear first plateau tells us that the product is not mixture, but single product. On the other hand, Q_2-product-(CO,Br) was found to simply consist of Ru + 2 NH_4Br.

The TG curve of the iodide shows the sharp weight loss at 250–280 °C and then a plateau obtained at the mass loss of 69 g/fw. The product at this stage is called Q-product-(CO,I). The IR data for the product show the peaks at 1960 and 1945, 1230, and 555 cm^{-1} assignable to ν_{C-O}, $\nu_{Ru\equiv N}$, and ν_{Ru-CO}, respectively. The fact that $\nu_{Ru\equiv N}$ appears at such a high wavenumber as 1230 cm^{-1} is probably due to the strong π donor nitride (N^{3-}) being stabilized by the coexistence of the strong π acceptor CO. From the mass loss and the IR data, the product may be expected to be $[RuNI_2(CO)]$, but the details could not be determined.

Nitrosyl Complexes. Figure 4 shows the Q derivatograms of $[Ru(NH_3)_5(NO)]X_3 \cdot H_2O$ (X = Cl$^-$, Br$^-$, I$^-$). As seen from the TG curve of the chloride, 1 mol of lattice water is first evolved at 100–150 °C and the first plateau is obtained. The second weight loss starts at 175 °C, the second wide plateau being obtained. The mass loss corresponds to the loss of 1 mol of ammonia (Anal. Calcd: 4.99. Found: 4.76). The product is named Q_1-product-(NO,Cl). The third weight loss is observed at 300–310 °C in the TG curve. The unusual decrease in temperature implies that the reaction is remarkably endothermic. No clear plateau is obtained, but a break point appears at the mass loss of about 97 g/fw. The product at the break point is called Q_2-product-(NO,Cl). Then the complex undergoes a complicated reaction above 325 °C. Table IV summarizes the IR data of the nitrosyl complexes.

Elemental analyses of the orange-yellow Q_1-product-(NO,Cl) suggest that it has the formula $[Ru(NH_3)_4Cl(NO)]Cl_2$ (Anal. Calcd for the formula: H, 3.93; N, 22.92. Found: H, 3.88; N, 23.25). Two configurations (*cis* and trans) are possible for the compound with respect to the position of Cl and NO. The trans configuration is reasonable for the compound because the elec-

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Table V. Cleavage Temperatures (T_c) of Ru^{II}–L Bonds, Differences ($\Delta\tilde{\nu}$) of Stretching Wavenumbers of Free ($\tilde{\nu}$(free)) and Coordinated ($\tilde{\nu}$(coord)) Ligands, and Band Maxima (λ_{max}) of MLCT Bands of $[Ru(NH_3)_5(L)]X_n$

L	X	T_c, °C	$\tilde{\nu}$(coord), cm^{-1}	$\tilde{\nu}$(free), cm^{-1}	$\Delta\tilde{\nu}$,[d] cm^{-1}	λ_{max}, nm
N_2	Cl	255	2105	2331[a]	−226	221
	Br	269	2114		−217	
	I	231	2129		−202	
CO	Cl	286	1929	2143[a]	−214	206
	Br	310	1938		−205	
	I	380	1946		−197	
NO^+	Cl	324	1910	2220[a]	−310	197
	Br	406	1913		−307	
	I	337	1915		−305	
CH_3CN	Cl	191	2247	2254[b]	−7	227
	Br	230	2249		−5	
	I	218	2250		−4	
CH_3NC	Cl	312	2073	2170[c]	−97	203
	Br	360	2090		−80	
	I	347	2094		−76	

[a] Cited from: Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds"; Wiley: New York, 1963; pp 187–202. [b] Cited from: Clark, R. E.; Ford, P. C. *Inorg. Chem.* **1970**, *9*, 227. [c] Cited from: Casanova, J., Jr.; Schuster, R. E.; Werner, N. D. *J. Chem. Soc.* **1963**, 4280. [d] $\Delta\tilde{\nu} = \tilde{\nu}(coord) - \tilde{\nu}(free)$.

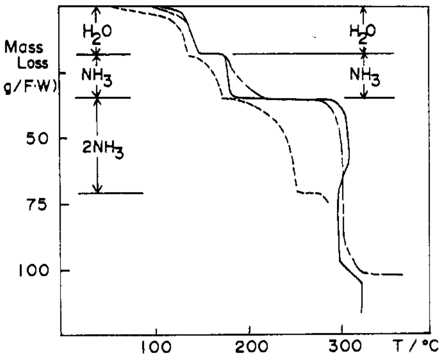

Figure 4. Q derivatograms of $[Ru(NH_3)_5(NO)]X_3{\cdot}H_2O$: (—) chloride; (– – –) bromide; (···) iodide.

tronic spectrum of the product has three λ_{max}'s at 453, 328, and 245 nm, which agree well with those (453, 330, and 245 nm) of the trans complex (cf. the cis complex has two λ_{max}'s at 480 and 345 nm).[24,25] The trans configuration of the product also receives support from comparison of the IR data (Table IV) of the product with those of the reference *cis*- and *trans*-$[Ru(NH_3)_4Cl(NO)]Cl_2$.[25,26] On the other hand, comparison of the IR data for Q_2-product-(NO,Cl) with those for the reference $(NH_4)_2[RuCl_5(NO)]$[27] indicates that the product consists of the ammonium salt. The attempt to isolate the ammonium salt from the product failed, but instead we succeeded in isolating the corresponding cesium salt as described in the Experimental Section.

As seen from the Q derivatogram of the bromide, 1 mol of water of crystallization is first evolved at 100–150 °C. The TG curve then shows the second smooth weight loss at 175–220 °C, and then the second plateau appears. The mass loss corresponds to 1 mol of ammonia (Anal. Calcd: 3.59. Found: 3.45), and the product at this stage is called Q_1-product-(NO,Br). The third sharp weight loss is observed at 280–325 °C in the TG curve, and then the third plateau appears. The product at this plateau is called Q_2-product-(NO,Br). By the analogy with Q_1-product-(NO,Cl), the orange Q_1-product-(NO,Br) was found to be *trans*-$[Ru(NH_3)_4Br(NO)]Br_2$. On the other hand, Q_2-product-(NO,Br) was confirmed to consist of $(NH_4)_2[RuBr_5(NO)]$ from the comparison of the IR data for Q_2-product-(NO,Br) and the reference $(NH_4)_2[RuBr_5(NO)]$.[27]

As seen from the TG curve of the iodide, after the release of lattice water at 60–140 °C, the second weight loss appears at 140–175 °C. The weight loss at this stage corresponds to 1 mol of ammonia (Anal. Calcd: 2.72. Found: 2.49). The reaction product is called Q_1-product-(NO,I). The third gradual weight loss is observed at 175–255 °C in the TG curve, the third plateau appearing at the mass loss of 2 mol of ammonia (Anal. Calcd: 5.53. Found: 5.83). The product at this stage is named Q_2-product-(NO,I). Judging from the results of Q_1-product-(NO,Cl) and Q_1-product-(NO,Br), we at first expected that the trans configuration is reasonable for Q_1-product-(NO,I). However, the expectation did not come true: the product is not *trans*- but *cis*-$[Ru(NH_3)_4I(NO)]I_2$. The fact that the release of the ammine in the cis position is favored over that of the ammine in the trans position is strange because the trans-labilizing effect of the NO ligand should be involved just as in the case of the chloride and bromide. Trans to cis isomerization might take place immediately after the formation of transient *trans*-$[Ru(NH_3)_4I(NO)]I_2$. The analytical data for Q_2-product-(NO,I) indicate that the product is $[Ru(NH_3)_2I_3(NO)]$ (Anal. Calcd: H, 1.10; N, 7.70. Found: H, 1.22; N, 7.41).

Nitrosyl is the best π-accepting ligand for ruthenium(II) ion so that the Ru^{II}–NO linkage is very stable; actually, the breakage temperatures of the Ru^{II}–NO bond are exceptionally high: 324 °C for the chloride, 406 °C for the bromide, and 337 °C for the iodide.

Acetonitrile and Methyl Isocyanide Complexes. The reactions of the acetonitrile complexes proceed in a manner similar to those of the dinitrogen complexes except that the cleavage temperatures (191 °C for the chloride, 230 °C for the bromide, and 218 °C for the iodide) are appreciably lower than those of the dinitrogen complexes (255 °C for the chloride, 269 °C for the bromide, and 231 °C for the iodide).

On the other hand, the reactions of the methyl isocyanide complexes are characterized in that the cleavage temperatures of the Ru^{II}–CH_3NC bond are so high (312 °C for the chloride, 360 °C for the bromide, and 347 °C for the iodide) that the cleavage of the bond leads to complicated decompositions of the compounds without formation of any pure intermediate.

Discussion

Evolution of Dinitrogen. As mentioned in the Introduction, there have been two different papers concerning the thermal stability of the dinitrogen complexes.[4,11] For the settlement of the discrepancy, it is necessary to decide which ligand (ammonia or dinitrogen) is preferentially evolved from the solid dinitrogen complexes. Then, isothermal experiments were carried out on the dinitrogen complexes. As an example, $[Ru(NH_3)_5(N_2)]Cl_2$ was isothermally heated at a fixed temperature near the initiation temperature (255 °C) of the weight loss. The IR spectra and the compositons of the samples were successively monitored at regular

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(24) Schreiner, A. F.; Lin, S. W.; Hauser, P. J.; Hopcus, E. A.; Homm, D. J.; Guter, J. D. *Inorg. Chem.* **1972**, *11*, 880.

(25) Pell, S.; Armor, J. N. *Inorg. Chem.* **1973**, *12*, 873.

(26) (a) Mercer, E. E.; McAllister, W. A.; Durig, J. R. *Inorg. Chem.* **1966**, *5*, 1881. (b) Fairey, M. B.; Irving, R. J. *Spectrochim. Acta* **1966**, *22*, 359.

(27) Durig, J. R.; McAllister, W. A.; Wilis, J. N., Jr.; Mercer, E. E. *Spectrochim. Acta* **1966**, *22*, 1091.

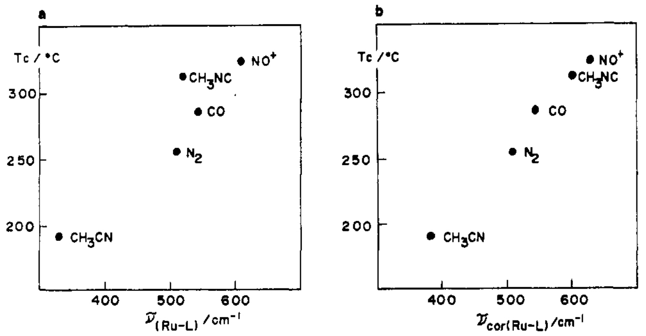

Figure 5. Relationship between (a) the observed stretching wavenumbers ($\tilde{\nu}_{\mathrm{Ru-L}}$) and (b) the corrected stretching wavenumbers ($\tilde{\nu}_{\mathrm{cor,Ru-L}}$) and the cleavage temperatures (T_c) of $\mathrm{Ru^{II}}$—L of $[\mathrm{Ru(NH_3)_5(L)}]\mathrm{Cl}_n$.

intervals. The results evidenced that the ammonia evolution precedes the dinitrogen evolution. From this, it may be concluded that the $\mathrm{Ru^{II}}$–$\mathrm{N_2}$ bond is unexpectedly stable in the solid state, whereas the bond has been found to be readily broken in aqueous media.[9,10]

Cleavage Temperatures (T_c) of $\mathrm{Ru^{II}}$–L Bonds. Table V summarizes the cleavage temperatures (T_c) of $\mathrm{Ru^{II}}$–L bonds contained in the complexes $[\mathrm{Ru(NH_3)_5(L)}]\mathrm{X}_n$. The table also contains the differences ($\Delta\tilde{\nu}$) of the stretching wavenumbers of free ($\tilde{\nu}$(free)) and coordinated ($\tilde{\nu}$(coord)) ligands (L) and the band maxima ($\lambda_{\max}$) of metal to ligand charge-transfer (MLCT) bands of $[\mathrm{Ru(NH_3)_5(L)}]\mathrm{X}_n$. As seen from the table, T_c's for the chlorides increase in the order $\mathrm{CH_3CN} < \mathrm{N_2} < \mathrm{CO} < \mathrm{CH_3NC} < \mathrm{NO^+}$. The order is approximately parallel to the increasing order of the ΔH values for the reaction of $[\mathrm{Ru(NH_3)_5(H_2O)}]^{2+}$ with $\mathrm{CH_3CN}$, $\mathrm{N_2}$, CO, and $\mathrm{CH_3NC}$.[28]

Figure 5a shows the relationship between the stretching wavenumbers ($\tilde{\nu}_{\mathrm{Ru-L}}$) of $\mathrm{Ru^{II}}$–L and the cleavage temperatures (T_c) of $\mathrm{Ru^{II}}$–L for the chlorides. Fairly good correlation can be seen between them. The $\tilde{\nu}_{\mathrm{Ru-L}}$ values were multiplied by the correlation factor f_{cor} by choosing $\tilde{\nu}_{\mathrm{Ru-N_2}}$ of the dinitrogen complex as the standard:[29]

$$\tilde{\nu}_{\mathrm{cor,Ru-L}} = f_{\mathrm{cor}}\tilde{\nu}_{\mathrm{Ru-L}}$$

where $\tilde{\nu}_{\mathrm{cor,Ru-L}}$ and $\tilde{\nu}_{\mathrm{Ru-L}}$ are the corrected and the observed stretching wavenumbers of Ru–L bonds. Figure 5b represents the relationship between $\tilde{\nu}_{\mathrm{cor,Ru-L}}$ and T_c. A linear correlation is obtained between them, which qulitatively reflects that T_c increases as the $\mathrm{Ru^{II}}$–L bond becomes stronger. In general, in the solid-phase thermal reactions, such a better correlation can never be obtained without Q derivatography.[30] Q derivatography has the excellent advantage that equilibrium between solid and gas phases is successfully achieved under an autogenerated quasi-isobaric condition.

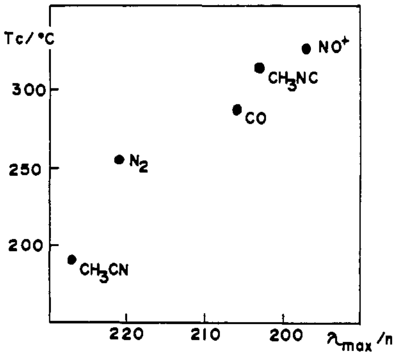

Figure 6. Relationship between the wavelengths ($\lambda_{\max}$) of metal to ligand charge-transfer (MLCT) bands and the cleavage temperatures (T_c) of $\mathrm{Ru^{II}}$—L of $[\mathrm{Ru(NH_3)_5(L)}]\mathrm{Cl}_n$.

Effect of π Back-Bonding on Thermal Stabilities of the Complexes. The presence of strong π back-bonding brings about the increase in the bond strength of $\mathrm{Ru^{II}}$ and π-accepting ligands. In fact, the study on the complexes containing very strongly π-accepting NO exemplified that the bond distance (180 pm) of $\mathrm{Ru^{II}}$–NO in $[\mathrm{Ru(NH_3)_5(NO)}]\mathrm{Br_3 \cdot H_2O}$ is abnormally short as compared with the normal distance (210 pm) of $\mathrm{Ru^{II}}$–$\mathrm{NH_3}$.[31]

The magnitude of the π back-bonding can qualitatively be manifested by the differences ($\Delta\tilde{\nu}$) given in Table V: the larger the differences are, the stronger the π back-bonding. The $\Delta\tilde{\nu}$ values in the table indicate that the magnitude of the π back-bonding increases in the order $\mathrm{CH_3CN} < \mathrm{CH_3NC} < \mathrm{CO} < \mathrm{N_2} < \mathrm{NO^+}$. From the value for the methyl isocyanide complexes, $\mathrm{CH_3NC}$ is conceivably not as strong of a π-accepting ligand as compared with dinitrogen, carbonyl, and nitrosyl. Nevertheless, the T_c values of the $\mathrm{R^{II}}$–$\mathrm{CH_3NC}$ bond are very high. This is probably because $\mathrm{CH_3NC}$ is a strong σ donor due to the –NC group. On the other hand, the –CN group of acetonitrile has a low ability as both σ donor and π acceptor so that the T_c's of the acetonitrile complexes are lowest among the present complexes.

Figure 6 illustrates the relationship between the wavelengths of band maxima ($\lambda_{\max}$) due to metal to ligand charge-transfer (MLCT) bands and T_c for the chlorides. A good correlation can be seen in the figure. The figure tells us that as π back-bonding becomes greater, MLCT bands shift to the shorter wavelength side except for the methyl isocyanide complex. In the case of the methyl isocyanide complex, however, the short wavelength of the band may be caused by σ bonding due to the –NC group rather than by π back-bonding.

Registry No. $[\mathrm{Ru(NH_3)_5(N_2)}]\mathrm{Cl_2}$, 15392-92-4; $[\mathrm{Ru(NH_3)_5(N_2)}]\mathrm{Br_2}$, 15246-25-0; $[\mathrm{Ru(NH_3)_5(N_2)}]\mathrm{I_2}$, 15651-39-5; $[\mathrm{Ru(NH_3)_5(CO)}]\mathrm{Cl_2}$, 23351-13-5; $[\mathrm{Ru(NH_3)_5(CO)}]\mathrm{Br_2}$, 23351-14-6; $[\mathrm{Ru(NH_3)_5(CO)}]\mathrm{I_2}$, 21884-94-6; $[\mathrm{Ru(NH_3)_5(NO)}]\mathrm{Cl_3 \cdot H_2O}$, 19469-59-1; $[\mathrm{Ru(NH_3)_5(NO)}]\mathrm{Br_3 \cdot H_2O}$, 96481-16-2; $[\mathrm{Ru(NH_3)_5(NO)}]\mathrm{I_3 \cdot H_2O}$, 96481-15-1; $[\mathrm{Ru(NH_3)_5(CH_3CN)}]\mathrm{Cl_2 \cdot H_2O}$, 96481-14-0; $[\mathrm{Ru(NH_3)_5(CH_3CN)}]\mathrm{Br_2 \cdot H_2O}$, 96481-13-9; $[\mathrm{Ru(NH_3)_5(CH_3CN)}]\mathrm{I_2}$, 34847-83-1; $[\mathrm{Ru(NH_3)_5(CH_3NC)}]\mathrm{Cl_2 \cdot H_2O}$, 96362-72-0; $[\mathrm{Ru(NH_3)_5(CH_3NC)}]\mathrm{Br_2}$, 96362-73-1; $[\mathrm{Ru(NH_3)_5(CH_3NC)}]\mathrm{I_2}$, 34842-68-7; $[\mathrm{Ru(NH_3)_6}]\mathrm{Cl_3}$, 14282-91-8; $[\mathrm{Ru(NH_3)_5Cl}]\mathrm{Cl_2}$, 18532-87-1; $\mathrm{Cs_2[RuCl_5(NO)]}$, 16449-91-5; $[\mathrm{RuN(NH_3)_3I_2}]\mathrm{I}$, 96362-74-2; Ru, 7440-18-8; $\mathrm{NH_4Cl}$, 12125-02-9; $\mathrm{NH_4Br}$, 12124-97-9; $\mathrm{NH_4I}$, 12027-06-4; $\mathrm{RuNI_2(CO)}$, 96362-75-3; *trans*-$[\mathrm{Ru(NH_3)_4Cl(NO)}]\mathrm{Cl_2}$, 29046-69-3; *trans*-$[\mathrm{Ru(NH_3)_4Br(NO)}]\mathrm{Br_2}$, 36400-25-6; $\mathrm{(NH_4)_2[RuBr_5(NO)]}$, 13815-01-5; *cis*-$[\mathrm{Ru(NH_3)_4I(NO)}]\mathrm{I_2}$, 38402-59-4; $\mathrm{Ru(NH_3)_2I_3(NO)}$, 96362-76-4.

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(28) Watt, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7351.

(29) From the familiar equation $\tilde{\nu} = {}^1/_2\pi(k/\mu)^{1/2}$ the following expression can be derived:

$$\tilde{\nu}_{\mathrm{Ru-N_2}}/\tilde{\nu}_{\mathrm{Ru-L}} = {}^1\!/_2\pi(k_{\mathrm{Ru-N_2}}/\mu_{\mathrm{Ru-N_2}})^{1/2}/({}^1\!/_2\pi(k_{\mathrm{Ru-L}}/\mu_{\mathrm{Ru-L}})^{1/2})$$

Rearrangement of the expression yields the following result. We set it to the correction factor (f_{cor}).

$$(\tilde{\nu}_{\mathrm{Ru-N_2}}/\tilde{\nu}_{\mathrm{Ru-L}})(k_{\mathrm{Ru-L}}/k_{\mathrm{Ru-N_2}})^{1/2} = (\mu_{\mathrm{Ru-L}}/\mu_{\mathrm{Ru-N_2}})^{1/2} = f_{\mathrm{cor}}$$

The use of the factor gives the corrected stretching wavenumbers ($\tilde{\nu}_{\mathrm{cor}}$) for $\mathrm{Ru^{II}}$—L:

$$f_{\mathrm{cor}}\tilde{\nu}_{\mathrm{Ru-L}} = \tilde{\nu}_{\mathrm{Ru-N_2}}(k_{\mathrm{Ru-L}}/k_{\mathrm{Ru-N_2}})^{1/2} = \tilde{\nu}_{\mathrm{cor,Ru-L}}$$

Thus, the $\tilde{\nu}_{\mathrm{cor,Ru-L}}$ values can be regarded as those corrected by choosing $\tilde{\nu}_{\mathrm{Ru-N_2}}$ as the standard.

(30) Actually, we were unable to obtain such a better correlation under open dynamic conditons (D conditions).

(31) Wyckoff, R. W. G. "Crystal Structures", 2nd ed.; Wiley: New York, 1965; Vol. III, p 803.