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Chemistry and Optical Properties of 4d and 5d Transition Metal Compounds. II. Synthesis and Optical Spectra of Acetatopentammineruthenium(III) and Pseudohalogenpentammineruthenium(III) Compounds

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A number of acidopentammineruthenium(III) compounds having C_{4v} micro-symmetry about Ru^{III} were prepared and characterized. Solution optical spectra below 50 kK were recorded, and charge-transfer, d–d, and internal transitions were observed. Tetragonal spin-orbit components of the charge-transfer $\pi(NCSe^-) \rightarrow Ru(xz,yz)$ transitions are only weakly antibonding, on the basis of band widths, relative to the ground state $\Gamma_{7t}(^2E_t)$. d–d transitions are assigned to $^2T_{1g}$, $^2T_{2g}{}^b$, and E_g. The latter are not split sufficiently to permit observation of their C_{4v} components. The observed spectrochemical series of L in $[Ru(NH_3)_5L]^Q$ is $NH_3 > NCO^- > OAc^- > SCN^- > SeCN^-$ on the basis of the energy of the first d–d band.

Introduction

A number of ruthenium(II) and ruthenium(III) compounds have been well characterized of late.[1,2] Taube and coworkers have also studied the oxidation-reduction processes of several of the compounds, especially ammines.[3,4] Convenient preparative procedures were also reported which led to $[Ru(NH_3)_5N_2]Cl_2$[5,6] and *trans*–$[Ru(NH_3)_4(NO)X]Cl_2$ ($X = Cl^-$, OH^-)[5] from $RuCl_3 . nH_2O$. The contents of this paper relate to the chemistry of ruthenium(III), linkage isomerization of SCN^- and $SeCN^-$ bound to Ru^{III}, and electronic excited states[7,8,9] of the complex ions.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer model 521 spectrometer, and optical spectra were obtained with a Cary 14. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee 37921.

A. *Preparations of Compounds.*

1. *Cyanato-N-Pentammineruthenium(III) Perchlorate and Iodide.* Chloropentammineruthenium(III) chloride (0.2 g) was dissolved in hot water (80°C, 20 ml), potassium cyanate (0.2 g) was added, and the solution was stirred and heated (80°C, 30 min.). The color of the solution changed to a deeper yellow during the first 10 minutes. It was cooled to room temperature, filtered into KI solution (3 *M*, 5 ml), and the precipitate was isolated and washed (ice water, ethanol, ether). The orange-brown $[Ru(NH_3)_5(NCO)]I_2$ (0.1 g) was dissolved in water (25 ml), and the solution filtered into a saturated solution of sodium perchlorate (5 ml). A pale yellow compound precipitate and was retained on a filter and was washed (ethanol, ether). It was identified as $[Ru(NH_3)_5(NCO)](ClO_4)_2$ (0.06 g, 21% yield).

Analyses: Calcd: N% = 19.65, Cl% = 16.60. Found: N% = 18.52, Cl% = 16.82.

2. *Thiocyanato-S-pentammineruthenium(III) Perchlorate.* Procedure (a) $[Ru(NH_3)_5]Cl_2$ (0.4 g) was dissolved in hot water (85°C, 40 ml), ammonium thiocyanate (2 g) was added, and the solution was heated (85°C, 45 min). It gradually turned from light yellow to red, and ammonia gas evolved from the solution. This hot solution was filtered into saturated sodium perchlorate solution (10 ml), and the purple compound precipitated immediately. The mixture was cooled (0°C, 30 min), and the compound was isolated and washed with sodium perchlorate solution (1 g/10 ml), ethanol, and ether. The solid (0.5 g, 82% yield) was redissolved in cold water (25° C, 100 ml), and filtered into saturated sodium perchlorate solution (25 ml). Violet-red, fine crystals of $[Ru(NH_3)_5(SCN)](ClO_4)_2$ formed immediately and were retained on a filter and washed (ice water, ethanol, ether). The solid weighed 0.35 g (58% yield). *This compound exploded when it was ground!*

Analyses: Calcd: N% = 18.95, S% = 6.53. Found: N% = 18.58, S% = 6.28.

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* Author to whom correspondence should be addressed.

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(2) J.A. Stanko and T.W. Starinshak, *Inorg. Chem.*, *8*, 2156 (1969).

(3) J.E. Endicott and H. Taube, *Inorg. Chem.*, *4*, 437 (1965); T.J. Meyer and H. Taube, *Inorg. Chem.*, *7*, 2369 (1968), and references therein.

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(7) H. Hartmann and C. Bushbeck, *Z. Physik. Chem.*, *11*, 120 (1957).

(8) J.A. Stanko, Ph. D. thesis, University of Illinois, Urbana, Illinois, 1966.

(9) B.N. Figgis, J. Lewis, F.E. Mabbs, and G.A Webb, *J. Chem. Soc.*, (*A*), *4*, 422 (1966).

Procedure (b). By this method $[Ru(NH_3)_5(SCN)](ClO_4)_2$ was prepared from bromopentammineruthenium(III) bromide. The latter compound (0.2 g) was dissolved in hot water (85°C, 20 ml). Following the addition of ammonium thiocyanate (1 g), the solution was heated (85°C, 45 min). Its color changed from yellow to red after it was heated 10 minutes. The hot solution was filtered into saturated sodium perchlorate solution (5 ml), violet-red $[Ru(NH_3)_5(SCN)](ClO_4)_2$ precipitated immediately and the mixture was cooled (0°C, 30 min). The solid was isolated on a filter and washed with sodium perchlorate solution (1 *M*, 10 ml), ethanol, and ether. The reaction proceeded by 74% yield.

Procedure (c). Iodopentammineruthenium(III) iodide was used here and the steps are similar to procedure (b). The latter compound (0.3 g) was dissolved in hot water (85°C, 50 ml); following the addition of NH_4SCN (2 g), the solution was heated (85°C, 45 min), and ammonia gas evolved. The hot solution was filtered into saturated sodium perchlorate solution (10 ml), from which the violet-red complex precipitated immediately. This mixture was cooled (0°C, 30 min), and the solid compound retained on a filter and washed (ice water, ethanol, ether). $[Ru(NH_3)_5(SCN)](ClO_4)_2$ was obtained in 85% yield.

Procedure (d). By this series of reactions, which involve changes of oxidations state, $[Ru(NH_3)_5(SCN)](ClO_4)_2$ was prepared from $[Ru(NH_3)_5Cl]Cl_2$. The latter compound (0.3 g) was added to a solution of sulfuric acid (0.1 *M*, 25 ml). The mixture was stirred while in contact with zinc amalgam (2% Zn) and under helium atmosphere (50 min.). A deep orange-yellow solution was obtained and filtered. Ammonium thiocyanate (1 g) was added, and the solution gradually turned from orange-yellow to red at room temperature. A deep red solution was obtained after 30 minutes, which was filtered into a saturated solution of sodium perchlorate. A violet-red precipitate formed and was isolated. It was washed (ice water, ethanol, ether), and was identified as $[Ru(NH_3)_5(SCN)](ClO_4)_2$ (0.2 g, 74% yield).

3. *Selenocyanato–Se–pentammineruthenium(III) Hexafluorophosphate, Iodide, and Perchlorate.* Chloropentammineruthenium(III) chloride (0.3 g) was added to 25 ml of sulfuric acid (0.1 *M*) solution. The mixture containing zinc amalgam (2% Zn) was stirred under helium atmosphere for fifty minutes. A deep orange-yellow solution resulted and was filtered. KSeCN (0.3 g) was added to the solution. It gradually turned from orange-yellow to blue. A deep blue solution was finally obtained after 25 minutes standing at room temperature. It was filtered into a saturated solution of ammonium hexafluorophosphate, and the compound precipitated after the mixture was cooled (0°C, 30 min). It was washed with methyl alcohol (2 ml) and ether. The compound was then redissolved in cold acetone (0°C, 4 ml) and the solution was filtered. The acetone was removed from the dark blue solution under vacuum. Bright, fine crystals (0.2 g, 55% yield) were obtained and identified as $[Ru(NH_3)_5(SeCN)](PF_6)_2$.

Analyses: Calcd: N% = 14.45, Se% = 13.59. Found: N% = 13.95, Se% = 12.82.

$[Ru(NH_3)_5(SeCN)]I_2$ was prepared by filtering an aqueous solution of $[Ru(NH_3)_5(SeCN)](PF_6)_2$ into a saturated solution of potassium iodide. The dark blue compound precipitated and was washed with methyl alcohol and ether. It was clear from the infrared spectra that PF_6^- was displaced.

$[Ru(NH_3)_5(SeCN)](ClO_4)_2$ was prepared by filtering an aqueous solution of $[Ru(NH_3)_5(SeCN)](PF_6)_2$ into a saturated solution of sodium perchlorate. The light blue compound precipitated and was washed with methyl alcohol and ether.

4. *Acetatopentammineruthenium(III) Perchlorate and Iodide.* Chloropentammineruthenium(III) chloride (0.3 g) was dissolved in 20 ml of water, and the solution was heated to 60°C. Concentrated ammonium hydroxide solution was added (5 ml), the solution was further heated (60°C, 30 min), after which concentrated acetic acid (5 ml) was added while the solution was hot. It was cooled to room temperature, and filtered into a saturated solution of sodium perchlorate from which the light yellow compound precipitated. The mixture was cooled (0°C, 30 min), and the precipitate was isolated and washed (ice water, ethanol, ether). The compound (0.2 g, 44% yield) was identified as $[Ru(NH_3)_5(OAc)](ClO_4)_2$.

Analyses: Calcd: N% = 15.76, C% = 5.40, H% = 4.02. Found: N% = 15.55, C% = 5.29, H% = 4.02.

$[Ru(NH_3)_5(OAc)]I_2$ was prepared by filtering a cold aqueous solution of $[Ru(NH_3)_5(OAc)](ClO_4)_2$ into a saturated solution of KI. The yellow compound precipitated, was retained on a filter and washed with ethyl alcohol and ether.

Results and Discussion

A. *Reactions.* Ruthenium(III) pentammine complexes were prepared from aquopentammineruthenium(II), $[Ru(NH_3)_5(H_2O)]^{2+}$, and halopentammineruthenium(III), $[Ru(NH_3)_5X]^{2+}$, compounds. During the reaction between either NCS^- or $NCSe^-$ ions and $[Ru(NH_3)_5(H_2O](PF_6)_2$ the metal was found to undergo a change from Ru^{II} to Ru^{III} and resulted in the formation of $[Ru(NH_3)_5(SCN)]^{2+}$ and $[Ru(NH_3)_5(SeCN)]^{2+}$. The change in oxidation state is probably the result of atmospheric oxvgen reacting with $[Ru(NH_3)_5(H_2O)]^{2+}$ or $[Ru(NH_3)_5(XCN)]^{2+}$. However, it is known that Ru^{II} can be stabilized by the presence of coordinated ligands which have low-lying vacant orbitals ($d\pi$ or π^*) of appropriate symmetry, *e.g.*, *o*–phenanthroline, 2,2′–bipyridine, NO, CO, and N_2. The stabilization of Ru^{II} will be treated in the follow-up paper[10] to this work.

It was not possible to prepare $[Ru(NH_3)_5(SeCN)]^{2+}$ from $[Ru(NH_3)_5Cl]^{2+}$ in good yield. This is in contrast to what might be expected on the basis of the reaction between NCS^-, NCO^-, or OAc^- and the chloropentammine. The reason is that one encounters a solubility problem here, *i.e.*, $[Ru(NH_3)_5Cl](NCSe)_2$ before $NCSe^-$ ions had the opportunity of reacting with dissolved $[Ru(NH_3)_5Cl]^{2+}$. However, in solutions very dilute in both $NCSe^-$ and $[Ru(NH_3)_5(NCSe)]^{2+}$ and at 80°C, it was possible to obtain [Ru-

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[10] S.W. Lin and A.F. Schreiner, manuscript in preparation.

$(NH_3)_5(NCSe)]^{2+}$. However, the yield was low from the point of view of synthetic chemistry. It is advisable, in this respect, to prepare the compound from $[Ru(NH_3)_5(H_2O)]^{2+}$ (*vide supra*).

It was found that the three halopentammines $[Ru(NH_3)_5X]^{2+}$ (X = Cl, Br, I) reacted with thioyanate ion in aqueous solution and at elevated temperature. In each reaction the halogen was displaced by NCS^-, and the formation of $[Ru(NH_3)_5(SCN)]^{2+}$ resulted. The halopentammines reacted with NCO^- in a similar manner, displacing Cl^-, Br^-, and I^- to form $[Ru(NH_3)_5(NCO)]^{2+}$ in reasonably good yield. However, the reaction between acetate and $[Ru(NH_3)_5Cl]^{2+}$ produced the acetatopentammine in only low yield. For this reason, the acetatopentammineruthenium(III) cation was prepared from the high-yield reaction between acetate and aquopentammineruthenium(II) cation.

Attempts to directly synthesize the N—bonded isomer $[Ru(NH_3)_5(NCS)]^{2+}$ by using NCS^- and chloropentammineruthenium(III) dichloride or the ruthenium(II) pentammine, $[Ru(NH_3)_5(H_2O)](PF_6)_2$, in aqueous solution or ethanol were unsuccessful. However, thermal conversion (*vide infra*) of $[Ru(NH_3)_5(SCN)](ClO_4)_2$ to $[Ru(NH_3)_5(NCS)](ClO_4)_2$ in DMSO solution at elevated temperature (70°C) and prolonged time (70 hr) under N_2 atmosphere effected the formation of this linkage isomer (10% yield). A similar isomerization was recently carried out of $[Pd(AsPh_3)_2(SCN)_2]$ at 126°C, *i.e.*, a change from S—bonding to N—bonding resulted.[11]

The compositions of compounds were confirmed by elemental analysis, and molar conductance (Table I) are consistent with the formulations. The compounds have been found to be stable in air as solids and in aqueous solutions. Their rates of aquation are very slow, *e.g.*, several hours after making up solutions of them there are no apparent changes in their optical spectra. This is under further investigation to ellucidate the ligand substitution kinetics.

Table I. Molar Conductance Measurements of Aqueous Solution of Acidopentammineruthenium(III) Complexes

Complex	Conc. $(10^{-3}M)$	$\Lambda^*(Ohm^{-1})$	Charge Type
$[Ru(NH_3)_5OAc](ClO_4)_2$	0.555	220	2 : 1
$[Ru(NH_3)_5(NCO)](ClO_4)_2$	0.468	263	2 : 1
$[Ru(NH_3)_5(NCS)](ClO_4)_2$	0.194	276	2 : 1
$[Ru(NH_3)_5(NCSe)](Cl_4)_2$	0.555	254	2 : 1

* A stands for the molar conductance.

B. *Optical Spectra.* Change-transfer d—d transitions are of interest here. The band assignments are made on the basis of their intensities, energies, and the comparison of these quantities between related compounds. Spectral regions containing overlapping bands were decomposed into individual components assuming gaussian forms. The experimental data and the band assignmentes are shown in Table II. The parent hexammine is also included.

All the pentammine compounds studied here contain Ru^{III} in its strong-field configuration $4t_{2g}^5$. The one-electron spin-orbit coupling constant ζ_d is between approximately 500 K-1250 K.[12,13] For this reason one expects the coupled state Γ_7 rather than $^2T_{2g}$ to be the ground state in O_h microsymmetry. The ground state and a number of octahedral and tetragonal (C_{4v}) low energy excited states are shown in Figure 1. The O_h ground state, $^2T^a{}_{2g}$ $[t^5{}_{2g}]$, will split into ^2E_t and $^2B_{2t}$. is the C_{4v} ground state in view of (xz, yz) > xy due to π or $p\pi$ antibonding effects[14] of the acido ligand (on the z-axis), and Γ_{7t} will be the ground state Figure 1).

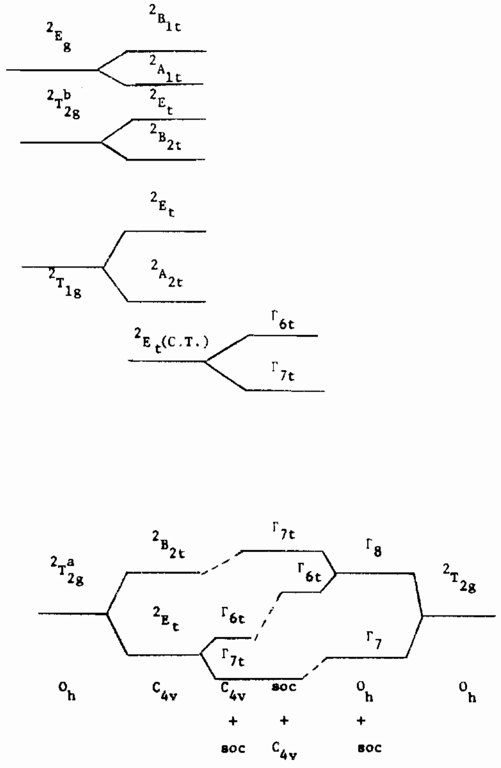

Figure 1. Several electronic states of t_2^5 complexes, $[Ru(III)(NH_3)_5X]^{n+}$. d—d states are ordered according to reference (24). Order of the tetragonal states is arbitrary above Γ_{6t}(C.T.)].

On the basis of all our current experience with ruthenium compounds, spin-forbidden transitions (absence of s.o.c. considerations) have ε_{max} values of about 20 or less. None of the transitions reported here are of that magnitude, for which reason only spin-allowed excitations are under consideration.

The first d—d excited state is $^2B_{2t}[^2T_{2g}{}^a]$ and derives from configuration $(xz, yz)^4(xy)^1$. ^2E_t will split further into Γ_{6t} and Γ_{7t} under the spin-orbit coupling interaction. With $\zeta_d(Ru^{III}) \cong 500$ K to 1250 K one can reasonably expect that $\Gamma_{7t}(^2B_{2t})$ be above ground state $\Gamma_{7t}(^2E_t)$ by about $3/2\zeta_d(\sim 1000\ K) + \delta_t(\sim 1500\ K) \cong$ 3 kK. It was not possible to establish the identities of these states in the infrared region, however.

(11) J.L. Burmeister and F. Basolo, *Inorg. Chem.*, *3*, 1587 (1964).

(12) $\zeta_{4d}(Ru^{III}) < 1180$ K on the basis of electron spin resonance data (8). Reference (9) has $\zeta = 500$ K on the basis of magnetic susceptibilities.

(13) For the Ru^{III} free ion, 1250 K is given for ζ_{4d}; B.N. Figgis, «Introduction to Ligand Fields», John Wiley and Sons, Inc., New York, 1966.

(14) H. Kamimura, *J. Phys. Soc. Japan*, *11*, 1171 (1956).

Table II. Optical Parameters[a, b] of Ruthenium(III) Ammine Complexes

X	Counter-Ion	λ_{max}	ν_{max} [a]	ε_{max} [a]	D(Debye^2)	f	Assignment [c]
NH_3	Cl^-	276	36.2	530	1.02	0.0174	II
NCO^-	ClO_4^-	227	44.0	331	0.368	0.00753	III
		284	35.3	231	0.632	0.0104	II
		345	29.0	2650	3.38	0.0463	I
OAc^-		222	45.0	436	0.920	0.0195	III
		296	33.8	1440	2.27	0.0362	I,II
SCN^-	ClO_4^-	204	45.0	13300	18.6[d]	0.394[d]	V
		278	36.0	209	0.191	0.00323	III
		321	31.1	401	1.45	0.0210	II
		496	20.2	3620	7.14	0.0678	I
Cl^-	Cl^-	228	43.8	144	0.206	0.00375	IV
		260	38.5	170	0.650	0.0112	III
		327	30.6	1690	2.24	0.0324	I,II
$SeCN^-$	ClO_4^-	213	46.9	8750	14.3[d]	0.315[d]	V
		330	30.3	811	1.67	0.0239	III
		455	22.0	325	1.20	0.0124	II
		586	17.1	2080	5.18	0.0417	I_2
		830	12.0	942	1.29	0.00733	I_1

[a] Parameters are for separated components of overlapping bands (gaussian form) and are estimated as three significant figures without variance evaluation. [b] λ = wavelength (nanometer), ν = frequency (1 K = 1 cm^{-1}) of band maximum, ε = molar extinction coefficient defined by absorbance = $\varepsilon \times$pathlength (cm)$\times$molarity, D = dipole strength (debye^2), f = $((8\pi^2 mc\nu)/(3he^2))$ x D. [c] Transition I_1 is $\Gamma_{7t}[^2E_t) \rightarrow \Gamma_{7t}[^2E_t(C.T.)]$; I_2 is to $\Gamma_{6t}[^2E_t(C.T.)]$; I is to $^2E_6$(C.T.); II is to $[^2T_{1g}]$; III is to $[^2T_{2g}{}^b]$; IV is to $[^2E_g]$; V is $\pi(NCX) \rightarrow \pi^*(NCX)$. [d] Estimated from the red half of the band.

Out of excited configuration $4t_2{}^4 4e_g{}^1$ there arise eight O_h spin-doublets ($^2A_{1g}$, $^2A_{2g}$, ^2E_g (two), $^2T_{1g}$ (two), and $^2T_{2g}$ (two)). Electric-dipole transitions below 50 kK are potentially to $^2T_{1g}$, $^2T_{2g}{}^a$, and ^2E_g (Figure 1) under vibronic selection rules. Our solution spectra do not show any fine structure which might be attributable to either spin-orbit or C_{4v} components. Consequently octahedral notation is used in referring to d–d excited states.

In general, a very intense low-energy band was observed for each Ru^{III} pentammine (and a second one for $[Ru(NH_3)_5(SeCN)]^{2+}$). On the basis of intensities, band widths and energy shifts these bands are assigned to charge-transfer transition $L[e^4(p\pi \text{ or } \pi)] \rightarrow Ru[e^3(xz, yz)^1]$,[8,25] *i.e.*, $\Gamma_{7t}[^2E_t] \rightarrow {}^2E_t$ (C.T.) (Figure 1). Furthermore, it is the transition to theΓ_{6t} and Γ_{7t} components of ^2E_t. Γ_{6t} is expected at higher energy by the one-electron spin-orbit coupling constant of the hole,[15] or about $\zeta_{mo} \simeq 2/3 \zeta_{\pi X}$ (CNX^- or OAc^-) + 1/3 ζ_d (Ru).[16] Therefore, any band above Γ_{7t} by energy ζ_{mo} is suspect of being Γ_{6t}, since it is not known of what intensity the latter ought to be. Figure 2 is typical of the spectra reported here.

1. *Hexammineruthenium(III) Chlorides.* The first and apparently only band below 50 kK occurs at 36.2 kK. It is intense ($\varepsilon = 530$ and D = 1.02 debye^2) (Table II) as are numerous d–d bands of 4d and 5d compounds compared to those of 3d ones. The band is assigned to transition $\Gamma_{7t}[^2T_{2g}{}^a] \rightarrow {}^2T_{1g}$. The MCD mode of Faraday magneto-optical activity in a 30,000 Gauss field indicates the presence of two bands which may be Γ_6 and Γ_8 of $^2T_{1g}$. The band has high net rotational strength.[18]

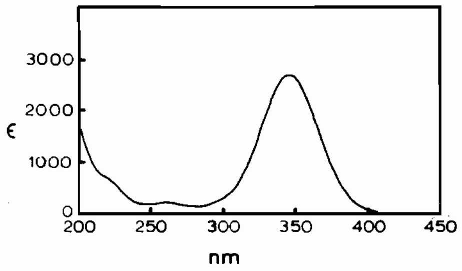

Figure 2. Solution optical spectrum of $[Ru(NH_3)_5NCO](ClO_4)_2$ in watertypical spectrum of $[Ru(III)(NH_3)_5X]^{Q+}$.

2. *Cyanatopentammineruthenium(III) Perchlorate.* Three distinct band maxima were observed (Table II and Figure 2). The characteristically intense charge-transfer band is at 29 kK ($\varepsilon = 2650$), and its dipole strength (3.38) is high. It is assigned to transition $\pi(NCO) \rightarrow (xz, yz)(Ru)$, $\Gamma_{7t} \rightarrow {}^2E_t$ (C.T.). No fine structure was evident, which is consistent with estimated $\zeta_{mo} \simeq 600$ K. There is another interesting feature about this band. Its full width at half-height (W) is only 3800 K. This implies that the nature of the excited state is weakly antibonding, which is consistent with the assigned fate of the electron.

The next band at 35.3 kK is of characteristic spin-allowed d–d intensity ($\varepsilon = 231$) with oscillator strength 1.0×10^{-2} (Table II). Its location is at lower energy than the first d–d transition of the hexammine, [Ru-

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(15) C.K. Jørgensen, «Absorption Spectra and Chemical Bonding in Complexes», Pergamon Press, eNw York, 1962.

(16) Γ_{6t} and Γ_{7t} of ^2E_t(C.T.) in $t_{2g}{}^5$ halopentammines should be separated by the one-electron spin-orbit coupling constant of the halogen hole (15) with Γ_{6t} higher by ζ of the halogen (8). We assume the hole is about 1/3 Ru and 2/3 in the pi molecular orbital of NCX.

(17) The d—d state $^2T_{2g}$ is near $^2T_{1g}{}^a$. However, since it is even vibronically forbidden by electric-dipole selection rules, it is not considered in Figure 1.

(18) S.W. Lin, E.A. Hopcus, P.J. Hauser, and A.F. Schreiner, work in progress.

$(NH_3)_6]^{3+}$, as expected. The band is assigned to $^2T_{1g}$ (Figure 1).

The third band at 44 kK ($\varepsilon = 331$) is assigned to the second d–d transition type $^2T_{2g}{}^b$ discussed above. The band is broad and its oscillator strength is 7.53×10^{-3}.

3. *Thiocyanatopentammineruthenium(III) Perchlorate.* There is a striking but qualitatively expected difference between the locations of the $\pi(NCX) \rightarrow (xz, yz)(Ru)$ charge-transfer bands in going from NCO^- to NCS^-, *i.e.*, they are at 29.0 kK and 20.2 kK, respectively (Table II). This low energy 20.2 kK band of the thiocyanatopentammine is characteristically intense with $\varepsilon_{max} = 3620$ and dipole strength 7.14. However, its half-width is only ~ 2040 K. Again, the antibonding nature of ^2E_t is low, which is consistent with the assignment. The absence of any observed splitting of ^2E_t (C.T.) is also consistent with the estimated separation of $\zeta_{mo} \sim 800$ K between Γ_{6t} and Γ_{7t}.

The location of analogous d–d transitions in $[Ru(NH_3)_5(NCO)]^{2+}$ and N–bonded $[Ru(NH_3)_5(NCS)]^{2+}$ should be very near each other. However, it was found that the low energy transition at 31.1 kK ($\varepsilon = 401$) to $^2T_{1g}$ in the thiocyanato compound is ~ 4000 K lower than in the NCO analog. The second d–d band at 36 kK ($\varepsilon = 209$), assigned to $^2T_{2g}{}^b$ is ~ 8000 K lower than in the cyanatopentammine analog. This leads one to believe that the complex is the S–bonded isomer, $[Ru(NH_3)_5(SCN)]^{2+}$. There is additional evidence for this conclusion *i.e.*, d–d transitions of bromopentammine complexes of Ir^{III} and Rh^{III} are nearly of the same energy as those of the thiocyanato–S–pentammine compounds.[19] The same observations can be made about analogous ruthenium compounds based on present data and those of Hartmann and Buschbeck.[7,20] The conclusion is also consistent with all published empirical spectrochemical series.

Additional experiments support the assigned linkage isomerization. Schmidtke[19] observed that the N–bonded and S–bonded isomer of $[Ir(NH_3)_5(NCS)]^{2+}$ had $C \equiv N$ stretching frequencies at 2140 K and 2110 K, respectively. These relative locations are contrary to what is often observed,[11] but the optical data are consistent with his conclusion. We also carried out the thermal conversion of the above $[Ru(NH_3)_5(SCN)](ClO_4)_2$, having $\nu(CN) = 2065$ K, to what appears to be its N–bonded linkage isomer. From a DMSO solution of this original compound, when kept at 70°C for 70 hours, the complex was isolated which had an intense CN stretching band at 2120 K. Furthermore, the 850 K C–S stretching band became intense. Both features are consistent with a change from S–bonding to N–bonding.[19] The infrared spectrum excludes the possible presence of coordinated DMSO.

The fourth and last band with dipole strength *ca.* 18.6 at 49.0 kK is very intense ($\varepsilon = 13{,}300$). It is most suspect of being SCN–internal in nature. It is of somewhat higher energy than observed (42.9 kK) in $[Rh(NH_3)_5(SCN)]^{2+}$,[22] however.

4. *Selenocyanatopentammineruthenium(III) Perchlorate.* Two sharp but intense bands were observed at 12 kK ($\varepsilon = 942$) and 17.1 kK ($\varepsilon = 2080$) which we assign to $\pi(NCSe) \rightarrow (xz,yz)(Ru)$ charge-transfer transition. Their full widths at half-height are small, *i.e.*, 940 K and 2080 K in the same order. They are assigned to Γ_{7t} (12 kK) and Γ_{6t} (17.1 kK) of ^2E_t inspite of their larger separation than estimated $\zeta_{mo} \sim 2500$ K.

The next two bands were found at 22 kK and 30.3 kK and are assigned to $^2T_{1g}$ and $^2T_{2g}{}^b$, respectively. Since these bands are of significantly lower energy than anticipated for the N–bonded compound, it follows that this is the selenocyanato–S–pentammineruthenium(III) cation.

The fifth and most intense band was found at 46.9 kK ($\varepsilon = 8750$). This is probably an $SeCN^-$ internal transition. However, its larger width (4740 K) indicates that the excited state is somewhat more antibonding than the lower energy $\pi(L) \rightarrow Ru$ transition. The band may contain a $Ru,xz, yz) \rightarrow \pi^*(NCSe^-)$ or $\sigma\ (NCSe^-) \rightarrow (z^2$ or $x^2 - y^2)(Ru)$ transition.

5. *Acetatopentammineruthnium(III) Perchlorate.* The compound has only two absorption maxima below 50 kK. The first one is at 33.8 kK ($\varepsilon = 1440$) and the second one at 45.0 kK ($\varepsilon = 436$) (Table II). Since the first d–d band of $[Ru(NH_3)_6]^{3+}$ is at 36.2 kK, it is concluded that the large 33.8 kK band of dipole strength 2.27 probably contains $^2T_{1g}[t_{2g}{}^4e_g{}^1]$.

The second band (45.0 kK) has extinction coefficient ($\varepsilon = 436$) and oscillator strength (0.0195) characteristic of $4t_{2g} \rightarrow 4e_g$ transitions. It is assigned to $^2T_{2g}{}^b$ (Figure 1 and Table II).

Summary

The preparations of a number of tetragonal ruthenium(III) ammines and some of their chemistry was described. Solution optical spectra were obtained below 50 kK. The intense lowest energy band in each compound is assigned to the charge-transfer transition $\Gamma_{7t} \rightarrow {}^2E_t$ and derives from p_π or $\pi(L) \rightarrow (xz, yz)(Ru)$. Γ_{7t} and Γ_{6t} components of ^2E_t were observed for $[Ru(NH_3)_5(SeCN)]^{2+}$. In conclusion it is observed that the spectrochemical series of ligands L in $[Ru(NH_3)_5L]^Q$ is $NH_3 > NCO^- > OAc^- > SCN^- > SeCN^-$ on the basis of decreasing energy of the first d–d band of each complex. It is the first time that $SeCN^-$ has been placed in the spectrochemical series of Ru^{III} compounds. Schmidtke's series (without $SeCN^-$) is consistent with the above sequence.[23] The Faraday magneto-optical activity of these compounds is presently being studied and will be the subject of another communication.

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(24) P. O'D. Offenhartz, «Atomic and Molecular Orbital Theory», McGraw-Hill Book Company, New York, 1970.
(25) The polarization of the similar low-energy, high-intensity band of $[Ru(NH_3)_5I]^{2+}$ was assigned to $\Gamma_7[^2E(C\,T.)]$ (ref. 8).