delocalized scrambling (*i.e.*, passage of CO groups from one metal atom to the other *via* bridged intermediates) does not occur would be to prepare a molecule with nuclear spin labeling of the iron atoms. The practicality of this is now under study.

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Charge-Transfer Spectra and Stability Constants of Ion Pairs of Hexaammineruthenium(III) and Halide Ions

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Stability constants and extinction coefficients for ion pairs between ruthenium(III) hexaammine and chloride, bromide and iodide ions were measured spectrophotometrically. The absorption spectra of the ruthenium(III) hexaammine halide ion pairs were measured in solutions of varying sodium halide concentration. The stability constants at zero ionic strength K^0_{IP} and the molar extinction coefficients $\Delta\epsilon$ at the maxima of the absorption peaks were evaluated as follows: $K^0_{IP} = 16 \pm 1\ M^{-1}$, $\Delta\epsilon$ 255 M^{-1} cm^{-1} for Cl$^-$; $K^0_{IP} = 11 \pm 1\ M^{-1}$, $\Delta\epsilon = 300\ M^{-1}$ cm^{-1} for Br$^-$; $K^0_{IP} = 10 \pm 1\ M^{-1}$, $\Delta\epsilon$ 251 and 252 M^{-1} cm^{-1} for I$^-$. $\Delta H°$ and $\Delta S°$ were also measured for the formation of the ion pair with the chloride ion. The spectra were interpreted as charge-transfer transitions from the halide ions to the ruthenium ion. The spectrum of the iodide ion pair consisting of two maxima was described as a superposition of two gaussians and a slightly blue-shifted $Ru(NH_3)_6^{3+}$ spectrum. The difference between the two maxima, 6590 cm^{-1}, was interpreted as the $^2P_{3/2}$–$^2P_{1/2}$ doublet splitting of the iodide ion. For the bromide ion, a similar procedure gave a doublet splitting of 2250 cm^{-1}. The transition energies of the $Ru(NH_3)_6^{3+}, X^-$ ion pairs are compared to those of the analogous cobalt(III) complexes.

Introduction

Spectrophotometric investigations of ion pairs are possible in systems where a significant change in the absorption spectrum takes place upon the formation of the ion pair. Such a situation is likely to be obtained when a charge-transfer optical transition from the anion to the associated cation is possible.[1-3]

In our study of the base-catalyzed proton-exchange reactions of $Ru(NH_3)_6^{3+}$, its ion pair with hydroxide ion as well as the deprotonated species $Ru(NH_3)_5NH_2^{2+}$ was implicated in the exchange mechanism.[4] The formation of the latter species was indicated by the appearance of an additional absorption peak at 402 nm in basic solutions.[5] The problem of distinguishing between the absorption due to the ion pair and that due to the deprotonated species stimulated our interest in the spectra and stability of the ion pairs formed by $Ru(NH_3)_6^{3+}$. The results of a study of the ion pairs formed between $Ru(NH_3)_6^{3+}$ and halide ions are presented here.

Experimental Section

Materials. $Ru(NH_3)_6Cl_3$ (supplied by Johnson Matthey Chemicals) was either used without purification (batch no. 7) or recrystallized from 1 *N* HCl[6] (other batches). Identical results were obtained in either case. The other materials were of AR grade and were used without further purification.

Methods. $Ru(NH_3)_6Cl_3$ and NaI solutions were freshly prepared prior to each set of experiments. The pH of the iodide solutions was adjusted to 8 in order to reduce autoxidation of the iodide ion. The solutions were tested for traces of I_3^- ion by recording their absorbance near the absorption maxima of the triiodide ion at 226 and 352 nm.

Spectra of the $Ru(NH_3)_6Cl_3$–sodium halide mixtures were recorded as difference spectra with $Ru(NH_3)_6Cl_3$ solutions of identical concentration in the reference compartment. For the measurements of the entire absorption curves, including the short-wavelength region

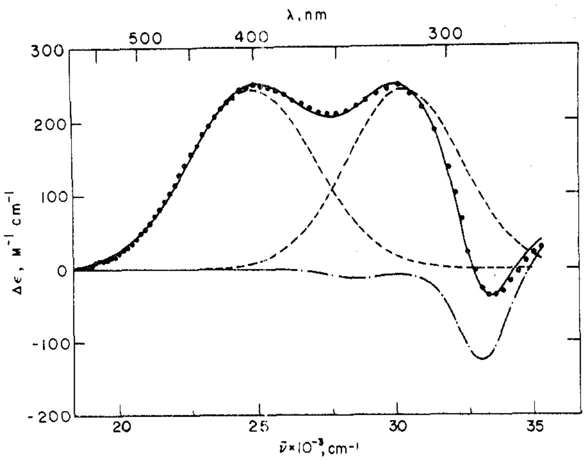

Figure 1. Difference spectrum of the Ru(NH$_3$)$_6$$^{3+}$,I$^-$ ion pair: points, experimental data; solid line, fitted curve; - - - -, fitted gaussian curves —·—·—, difference spectrum between shifted and not shifted spectra of Ru(NH$_3$)$_6$$^{3+}$.

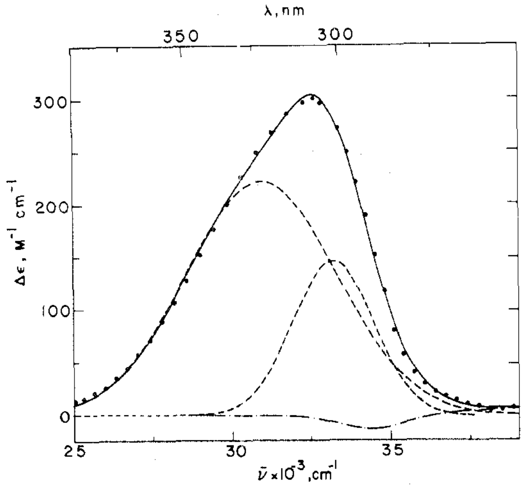

Figure 2. Difference spectrum of the Ru(NH$_3$)$_6$$^{3+}$,Br$^-$ ion pair. Curves are the same as in Figure 1.

where the absorption due to the halide ions gave a significant contribution, two absorption cells were used in each compartment. One cell in the reference compartment contained Ru(NH$_3$)$_6$Cl$_3$ solution and the other contained halide solutions. In the sample compartment one of the cells contained the mixture and the other distilled water.

The spectra were recorded on a Cary 17 spectrophotometer using quartz cells with 1.0-cm optical length. The temperature was controlled with a Colora thermostating bath; the temperature of the solutions was measured with a copper–constantan thermocouple prior to recording their spectra. The accuracy of the temperature was ±0.5°C.

Results

The solutions of ruthenium(III) hexaammine in the presence of halide ions were found to exhibit some extra absorption which could not be attributed either to the ruthenium(III) hexaammine ion or to the halide ions separately. This extra absorption was tentatively assigned to a charge-transfer (CT) spectrum of ion pairs of Ru(NH$_3$)$_6$$^{3+}$ and the halide ions. While in the case of iodide ion it appears as two extra peaks located at longer wavelengths than the Ru(NH$_3$)$_6$$^{3+}$ absorption, the extra absorption looks like a shoulder in the case of bromide ion and like a red shift in the case of the chloride ion. This extra absorption was observed more clearly by recording difference spectra, using the ruthenium hexaammine solutions without added halide salts as a reference solution. The shapes of the difference spectra for the chloride, bromide and iodide ions are shown in Figures 1–3.

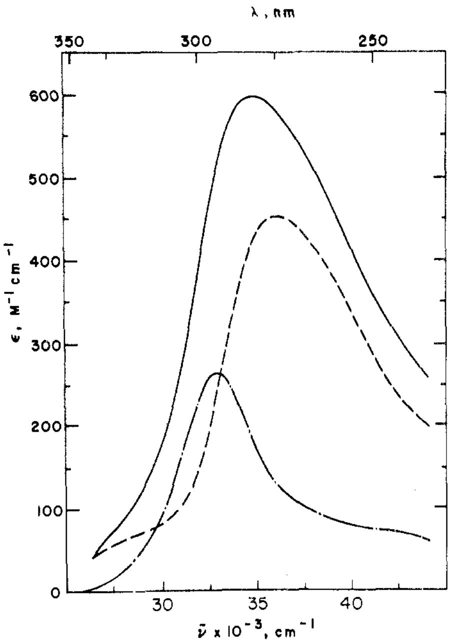

Figure 3. Spectrum of Rh(NH$_3$)$_6$$^{3+}$,Cl$^-$ ion pair: ——, spectrum of the ion pair; – – –, spectrum of the free Ru(NH$_3$)$_6$$^{3+}$ ion; —·—·—, difference spectrum of the ion pair.

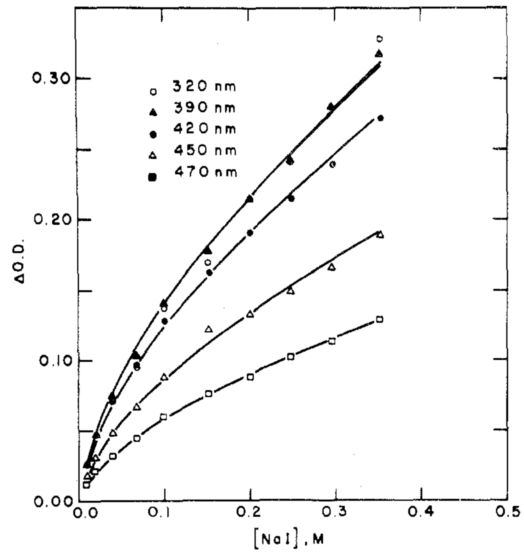

Figure 4. Difference absorbance, at various wavelengths, of Ru(NH$_3$)$_6$$^{3+}$ solutions, as a function of sodium iodide concentration. Ruthenium hexaammine concentration was 2.8 × 10^{-3} *M*; temperature was 24.7°. The solid lines are calculated with the fitted paramaters given in Table I.

For the evaluation of the ion-pair formation constants and their molar extinction coefficients, difference spectra were recorded at various halide concentrations. Plots of observed absorbance differences (ΔOD) at various wavelengths as a function of halide concentration are given in Figures 4–6. Since in our measurements, concentrations of the halide ions were in a large excess over that of the ruthenium hexaammine, the absorbance difference is given by

$$\Delta\mathrm{OD} = \frac{\Delta\epsilon K_{\mathrm{IP}}[\mathrm{Ru(NH_3)_6}^{3+}]_0[\mathrm{X}^-]}{1 + K_{\mathrm{IP}}[\mathrm{X}^-]} \quad (1)$$

where $\Delta\epsilon$ is the difference between the molar extinction coefficients of the ion pair and its constituents, K_{IP} is the ion-pair formation constant, and the subscript zero denotes total concentrations. Our experiments were not done at a

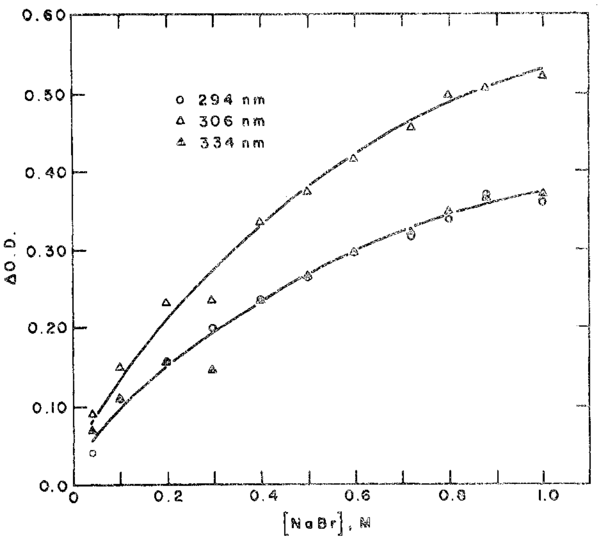

Figure 5. Difference abasorbance, at various wavelengths, of $Ru(NH_3)_6^{3+}$ solutions, as a function of sodium bromide concentration. Ruthenium hexaammine concentration was 2.0×10^{-3} *M*; temperature was 24.7°. The solid lines are calculated with the fitted parameters given in Table I.

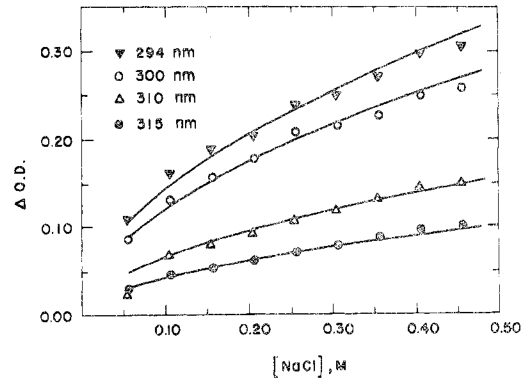

Figure 6. Difference absorbance, at various wavelengths, of $Ru(NH_3)_6^{3+}$ solutions as a function of sodium chloride concentration. Ruthenium hexaammine concentration was 2.0×10^{-3} *M*; temperature was 24.7°.

constant ionic strength. We have chosen to do so since maintaining a constant ionic strength requires the presence of another anion which may also form ion pairs with the $Ru(NH_3)_6^{3+}$ ion, and this makes the interpretation of the results more complex. Thus we have found that even bulky anions like ClO_4^- and $CH_3SO_3^-$ do form ion pairs with $Ru(NH_3)_6^{3+}$ (in agreement with the results found for the $Co(NH_3)_6^{3+},ClO_4^-$ ion pair[7]) and therefore compete with the formation of ion pairs with the halide ions.

Since, as a consequence of the variation in the ionic strength, K_{IP} was not constant during a particular set of measurements, the common procedures of evaluating K_{IP} and $\Delta\epsilon$ by a linearization of eq 1 could not be applied here. Therefore, using a nonlinear least-mean-squares computer program, the experimental data were fitted to eq 1 with the following Debye–Hückel type expression for the dependence of the ion-pair formation constant on the ionic strength, *I*[8]

$$\log K_{IP} = \log K^0_{IP} - \frac{6AI^{1/2}}{1 + GaI^{1/2}} + BI \qquad (2)$$

where

$$A = 1.825 \times 10^6 (DT)^{3/2} \qquad G = \left(\frac{8\pi Ne^2}{1000DkT}\right)^{1/2}$$

Table I. Parameters Obtained for the $Ru(NH_3)_6^{3+},X^-$ Ion Pairs[a]

Anion	λ_{max}, nm	$\Delta\epsilon_{max}$, M^{-1} cm^{-1}	K^0_{IP}, M^{-1}	B	a, Å
Chloride	294	255 ± 15[b]	15.8 ± 1[b]	0.78 ± 0.05[b]	4.4
		247 ± 16[c]	15.0 ± 1[c]	1.0 ± 0.1[c]	
Bromide	306	300 ± 21	11.1 ± 1	1.1 ± 0.1	4.6
Iodide	320	251 ± 17	9.8 ± 0.5	0.93 ± 0.05	4.8
	400	252 ± 17			

[a] $\Delta\epsilon_{max}$, K^0_{IP}, and *B* are the results of the fitting procedure using eq 1 and 2 to the experimental data at 24.7°. [b] Values for solutions with chloride ion concentrations up to 1.0 *M*. [c] Values for solutions with chloride ions concentrations up to 0.5 *M*.

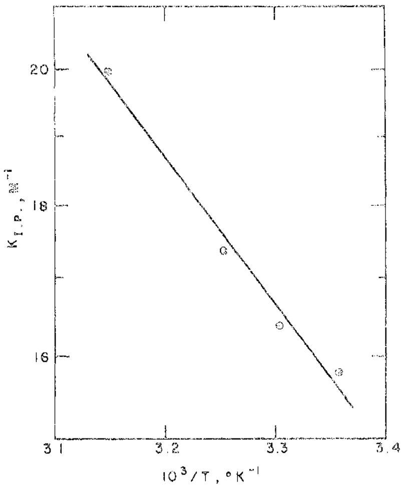

Figure 7. A semilogarithmic plot of the formation constant of the $Ru(NH_3)_6^{3+},Cl^-$ ion pair, at zero ionic strength, *vs.* the reprocical absolute temperature.

K^0_{IP} is the formation constant at zero strength; *D*, the dielectric constant of the solvent, was taken from the literature;[9] *a*, the distance of closest approach for the $Ru(NH_3)_6^{3+},X^-$ ion pairs was estimated on the basis of X-ray diffraction data[10,11] as 4.4, 4.6, and 4.8 Å for the chloride, bromide, and iodide ion pairs, respectively. A correction in the absorbance due to the small amounts of chloride ions which were introduced by the use of $Ru(NH_3)_6Cl_3$ salt was applied but was found to be about 2%, *i.e.*, smaller than the estimated experimental error in our absorbance measurements. A list of the best fit parameters is given in Table I. The standard deviation in the fitting procedure was about 8×10^{-3} absorbance unit for the Cl^-, Br^-, and I^- ion pairs.

The values of K^0_{IP} and $\Delta\epsilon$ obtained for the $Ru(NH_3)_6^{3+},Cl^-$ ion pair were similar in the two sets of experiments listed in Table I, where the maximum concentrations of NaCl were either 0.5 or 1.0 *M*. However, the *B* values obtained were significantly different. A possible reason for that is a contribution of a double ion pair at high NaCl concentrations. Preliminary experiments at NaCl concentrations up to 3 *M* indeed showed a further increase in the optical absorption indicating the existence of multiple ion pairs at this concentration range.

Theoretical curves calculated on the basis of the parameters listed in Table I are given as the solid lines in Figures 4–6.

The temperature dependence of the ion-pair formation constant was measured for the case of chloride ion. While the fitted $\Delta\epsilon$ and *B* did not vary with the temperature, the formation constant was found to increase upon increasing temperature. The semilogarithmic plot of the formation constant at zero ionic strength, K^0_{IP} *vs.* reciprocal temperature, is given in Figure 7 ; this plot gives $\Delta H^\circ = 2.3$ kcal mol^{-1} and $\Delta S^\circ = 14$ eu. The value of ΔH° is smaller than the value of 3.7 kcal mol^{-1} reported for ΔH° of the $Co(NH_3)_6^{3+},Cl^-$ ion

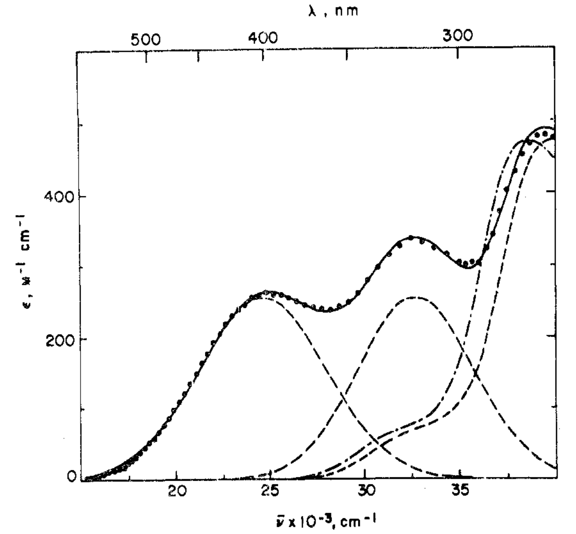

Figure 8. Spectrum of the $Ru(NH_3)_6{}^{3+},I^-$ ion pair: points, experimental data; solid line, fitted spectrum; - - - -, fitted gaussians and the shifted spectrum of the $Ru(NH_3)_6{}^{3+}$ ion; —·—·—, spectrum of the free $Ru(NH_3)_6{}^{3+}$ ion.

Table II. Gaussian Resolution of the Absorption Spectra of $Ru(NH_3)_6{}^{3+}$ Ion Pairs with Bromide and Iodide

Anion	λ_{max}, nm	$10^{-3}\bar{\nu}_{max}$, cm^{-1}	ϵ_{max}, M^{-1} cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}	Shift,[a] nm
Bromide	301	33.2	147	2980	0.7
	323	31.0	222	5570	
Iodide	318	31.5	245	5790	7
	402	24.9	244	6379	

[a] Shift of the contribution of the $Ru(NH_3)_6{}^{3+}$ spectrum to the spectrum of the ion pairs.

pair.[12,13] It is interesting to note that the temperature dependence of the ion-pair formation constant calculated using the Fuoss expression[14] leads to an apparent $\Delta H°$ of 1.2 kcal mol^{-1} and $\Delta S°$ of 10.7 eu which are of the same orders of magnitudes as our observed values.

As was mentioned above and can be seen in Figure 1, the difference spectrum of the $Ru(NH_3)_6{}^{3+},I^-$ ion pair exhibits two maxima. In addition one can see in the figure a negative difference absorption spectrum which becomes positive again at shorter wavelength. In our efforts to explain this phenomenon, we found that a good least-mean-squares computer fitting could be achieved if the observed spectrum of the ion pair was described as a superposition of two gaussians and a spectrum (designated as $\epsilon'_{Ru}(\bar{\nu})$) identical with the spectrum of $Ru(NH_3)_6{}^{3+}$ but slightly shifted toward shorter wavelength. Thus, the observed spectrum, $\epsilon(\bar{\nu})$, could be fitted to the expression

$$\epsilon(\bar{\nu}) = \epsilon^{(1)}{}_{max} \exp[-4 \ln 2(\bar{\nu}_1 - \bar{\nu})^2/(\Delta\bar{\nu}_1)^2] + \epsilon^{(2)}{}_{max} \exp[-4 \ln 2(\bar{\nu}_2 - \bar{\nu})^2/(\Delta\bar{\nu}_2)^2] + \epsilon'_{Ru}(\bar{\nu}) \qquad (3)$$

where $\Delta\bar{\nu}$ is the full bandwidth at half-maximum intensity. The difference and the full absorption spectra, along with the experimental points, are shown in Figures 1 and 8, respectively. In the case of the bromide ion the fitting of the spectrum to two gaussians (see Figures 2 and 9) also required the use of a slightly shifted spectrum of the $Ru(NH_3)_6{}^{3+}$ ion, though the resultant shift was very small (see Table II). For the chloride ion pair (Figure 3) the spectrum could not be fitted to gaussian absorption curves in any satisfactory manner. The results for the fitted parameters for the bromide and iodide ion pairs are given in Table II. Our observed absorption maxima are in agreement with the approximate values reported recently.[15] Similar absorption has been found also in solutions of $Ru(en)_3{}^{3+}$ and I^- and was assigned as CT transition from an outer-sphere iodide ion to the ruthenium complex.[16]

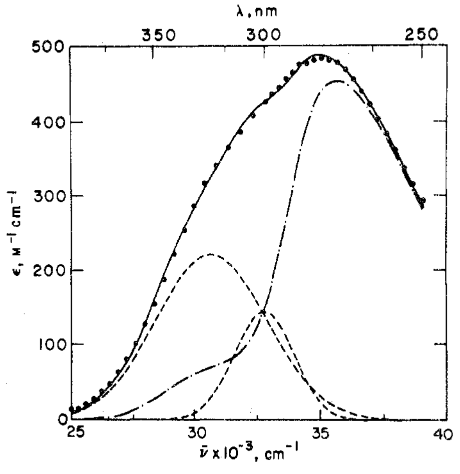

Figure 9. Spectrum of $Ru(NH_3)_6{}^{3+},Br^-$ ion pair. Curves are the same as in Figure 8. Due to the small shift, the shifted and unshifted spectra of $Ru(NH_3)_6{}^{3+}$ could not be drawn separately.

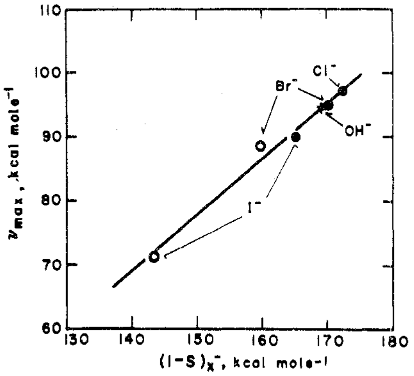

Figure 10. Linear plot of the charge-transfer absorption maxima of the $Ru(NH_3)_6{}^{3+},X^-$ ion pairs *vs.* the difference in the ionization potentials and solvation energies of the X^- ions: ○, CT transitions leading to halogen atoms in their $^2P_{3/2}$ states; ●, CT transitions leading to halogen atoms in their $^2P_{1/2}$ states. The values of the ionization potentials for the $^2P_{3/2}$ states were taken from ref 9. For the $^2P_{1/2}$ states, the doublet splittings of the gaseous halogen atoms[20] were added. Values of the solvation energies were taken from ref 23.

Discussion

A criterion for the assignment of a spectrum as a charge-transfer transition is a correlation between the transition energy and either the ionization potential of the donor or the electron affinity of the acceptor. For ions in polar solvents the change in solvation energy should also be taken into account. In our case the nature of the donor, which is the halide ion, is varied, while the acceptor, $Ru(NH_3)_6{}^{3+}$, is constant. Thus, the energy of the CT transition $M^{n+},X^- \rightarrow M^{(n-1)+},X$ is expected to be a linear function of the difference of the ionization potential and the (negative) solvation energies of the halide ions[17] $(I - S)_{X^-}$. This is seen to be the case in Figure 10.

It has been suggested[4,5] that the yellow color associated with the absorption maximum at 402 nm obtained for $Ru(NH_3)_6{}^{3+}$ ion in basic solutions is due to the formation of its deprotonated species $Ru(NH_3)_5NH_2{}^{2+}$. Another alternative is the ion pair with OH^- ion. However, the charge-transfer absorption maximum of the $Ru(NH_3)_6{}^{3+},OH^-$ ion pair can be roughly estimated from Figure 10: using a value of $(I - S)_{OH^-}$ = 168 kcal/mol, the absorption maximum is expected to be at 305 nm. This value, which is very far from the observed maximum at 402 nm, seems to rule out the ion-pair hypothesis and thus supports the assignment as a deprotonated species.

Charge-transfer transitions with halide ions as donors should have two excited states, having the halogen atoms in either $^2P_{3/2}$ or $^2P_{1/2}$ states. This $^2P_{3/2}$–$^2P_{1/2}$ doublet splitting was observed in the charge-transfer to solvent (CTTS) spectra of iodide in aqueous solution and bromide in acetonitrile and was found to be 7350[18] and 3000 cm^{-1} [19] for these two ions, respectively, as compared to 7603 and 3685 cm^{-1} [20] in the iodine and bromine gaseous atoms. In our case, two absorption peaks could be resolved for the $Ru(NH_3)_6^{3+},I^-$ and $Ru(NH_3)_6^{3+},Br^-$ ion pairs, separated by 6590 and 2250 cm^{-1}, respectively. It seems very probable that also in this case the origin of the separation is the halogen $^2P_{3/2}$–$^2P_{1/2}$ doublet splitting. It should be noted, however, that while, in the case of the iodide ion pair, the two peaks in the difference spectrum are clearly seen and therefore the resolution into the gaussians is very reliable, this is not the case for the bromide ion pair. Moreover, while two gaussians with almost equal intensities were obtained in the iodide case, the fitting procedure yielded two gaussians with very different intensities for the bromide ion pair, in contrast to the almost equal intensities in the CTTS spectrum of bromide in acetonitrile.[19]

The ion pairs between halide ions and $Ru(NH_3)_6^{3+}$ may be of two kinds: contact and solvent-separated ion pairs. It is interesting to note that our experimental formation constants are compatible with those calculated for both kinds of ion pairs using the Fuoss equation

$$K^0_{IP} = \frac{4\pi N}{3000} a^3 \exp[-z_1 z_2 e^2/DkTa] \qquad (4)$$

The calculated values assuming contact ion pairs and using the values for the distances of closest approach listed in Table I are 28, 26, and 24 M^{-1} for the Cl^-, Br^-, and I^- ion pairs, respectively. For the ion pairs with one water molecule separating the cation and the anion the calculated K^0_{IP} is 18 M^{-1} for the three halide ions. The reason for the insensitivity of the calculated K^0_{IP} to the distance a is that, for large values of a, the electrostatic energy becomes comparable to the thermal kT and the preexponential factor, which increases with a^3, begins to influence the behavior of K^0_{IP}.

It is impossible to distinguish between these two alternatives, just on the grounds of concentration dependence, since they differ only with respect to solvent molecules, the concentration of which does not change significantly during the variation of the concentration of the added halide ions. The absorption intensity, however, can give us some clue, since the solvent-separated ion pairs are expected to have a negligible absorption intensity due to the small electronic overlap. On the basis of our measured molar extinction coefficients, which are not very high, one still may consider a mixture of contact and solvent-separated ion pairs in which only the first species contributes to the CT absorption. The solvent-separated ion pairs will affect the results by competing with the formation of the contact ion pairs.

For a mixture of those two species of ion pairs, contact (IP') and solvent-separated (IP'') ones, a rederivation of eq 1 gives the same general form, but K_{IP} is now the total ion-pair association constant for the formation of both IP' and IP''

$$K_{IP} = K_{IP'} + K_{IP''} = \frac{[IP'] + [IP'']}{[Ru(NH_3)_6^{3+}][X^-]} \qquad (5)$$

The apparent extinction coefficient difference $\Delta\epsilon$ has the meaning

$$\Delta\epsilon = \alpha\Delta\epsilon' + (1-\alpha)\Delta\epsilon'' \qquad (6)$$

where

$$\Delta\epsilon' = \epsilon_{IP'} - \epsilon_{Ru} - \epsilon_{X^-}$$

$$\Delta\epsilon'' = \epsilon_{IP''} - \epsilon_{Ru} - \epsilon_{X^-}$$

α is the fraction of ion pairs in the form of contact ion pairs

$$\alpha = \frac{[IP']}{[IP'] + [IP'']} = \frac{K_{IP'}}{K_{IP'} + K_{IP''}} \qquad (7)$$

if there is a mixture of the two species of ion pairs IP' and IP'', then, provided that $K_{IP'}$ and $K_{IP''}$ do not have accidentally the same temperature dependence, the experimental $\Delta\epsilon$ should be temperature dependent. Our measurements for the $Ru(NH_3)_6^{3+},Cl^-$ system yielded within experimental error the same $\Delta\epsilon$ at various temperatures. Since identical temperature dependence of $K_{IP'}$ and of $K_{IP''}$ is not very probable, this may serve as an indication that in our system there are either contact or solvent-separated ion pairs, but not a mixture of both, and the existence of the CT absorption indicates that only the first type is prevailing. The magnitude of our observed extinction coefficients for the $Ru(NH_3)_6^{3+}$ halide ion pairs is compatible with a symmetry-allowed CT transition, considering the expected low electronic overlap between the highest filled orbital on the halide ion and the lowest unfilled orbital on the $Ru(NH_3)_6^{3+}$ ion, even for contact ion pair species. It may be noted that even the extinction coefficients of the CT bands of the corresponding inner-sphere $Ru(NH_3)_5X^{2+}$ complexes, with the presumably much higher electronic overlap, about 2×10^3 M^{-1} cm^{-1}, are only one order of magnitude higher than the outer-sphere complexes investigated here.

It is interesting to compare the transition energies of the $Ru(NH_3)_6^{3+},X^-$ ion pairs with those of the analogous cobalt(III) complexes. Although the absorption maxima for the latter complexes could not be resolved,[12] lower limits for the CT absorption maxima can be estimated as 41,700 and 36,900 cm^{-1} for cobalt(III) hexaammine ion pairs with bromide and iodide, respectively. For the $Co(NH_3)_6^{3+},I^-$ ion pair an absorption maximum at 37,300 cm^{-1} has been observed,[21] but it seems that, by analogy with $Ru(NH_3)_6^{3+}$, a blue-shifted spectrum of the $Co(NH_3)_6^{3+}$ free ion should be included in the gaussian analysis; this will tend to shift the absorption maximum to even shorter wavelengths. Thus, taking this latter value of 37,300 cm^{-1} as a lower limit for the CT transition energy for the $Co(NH_3)_6^{3+}$ ion pair, the difference between the CT transition energies in the cobalt(III) and the ruthenium(III) ion pairs would be greater than 12,400 cm^{-1}. A comparison of these data with the oxidation–reduction potentials of the ruthenium(III) and the cobalt(III) hexaammine complexes may seem contradictory at first glance. In both the charge-transfer transition and the redox half-cell, the trivalent metal ion is reduced to its divalent state by an added electron. Yet while the ruthenium and the cobalt complexes differ considerably in their charge-transfer transition energies, both complexes have almost identical redox potentials of about 0.1 V.[22] A closer look, however, resolves this apparent discrepancy. The redox potential is an equilibrium property and the reduction products are ground-state, fully relaxed, divalent metal complexes, while according to the Franck–Condon principle the excited states of the charge-transfer transitions contain divalent metal complexes in the nuclear configuration of the trivalent ones. The Franck–Condon energy is expected to be higher for the cobalt complex since the added electron enters an e_g orbital which is a σ-antibonding orbital, and therefore a larger effect on bond distances is anticipated. Also in the case of the cobalt complex a low-spin electronic configuration of $t_{2g}^6e_g$ is obtained by the CT transition which has higher energy than the high-spin $t_{2g}^5e_g^2$ ground state of the $Co(NH_3)_6^{2+}$ ion. On the other hand, the low-spin electronic configuration t_{2g}^6 which is obtained by the CT transition in the ruthenium case has the electronic configuration of the ground state $Ru(NH_3)_6^{2+}$. Thus, both the excess Franck–Condon energy and the high-spin–low-spin energy difference in $Co(NH_3)_6^{3+}$ are likely to account for our estimated difference in the CT excitation energies in the $Ru(NH_3)_6^{3+},X^-$ and $Co(NH_3)_6^{3+},X^-$ ion pairs.

In conclusion, one may say that the absence of absorption lines in the visible region in the spectrum of the $Ru(NH_3)_6^{3+}$ free ion and the relatively low excitation energies for the CT transitions of its ion pairs make this complex an excellent ion for spectrophotometric investigations of ion pairs.

Registry No. $Ru(NH_3)_6^{3+},Cl^-$, 53293-35-9; $Ru(NH_3)_6^{3+},Br^-$, 53293-36-0; $Ru(NH_3)_6^{3+},I^-$, 53293-37-1.

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Cryogenic Excited-State Fine Structure of $[Ni(NH_3)_6]A_2$ and Magnetic Circular Dichroism Temperature Dependence of $^3T_{1g}(t_{2g}{}^5e_g{}^3)$[1]

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Seven compounds of hexaamminenickel(II), $[Ni(NH_3)_6]A_2$, or the deuterated d_{18} analogs, $[Ni(ND_3)_6]A_2$, where $A^- = Cl^-, Br^-, I^-, ClO_4^-$, or PF_6^-, were studied by means of electronic absorption and magnetic circular dichroism (MCD) techniques at several temperatures (*ca.* 12–300°K). The absorption spectra in the d–d excitation region of six parity-forbidden bands permitted the observation of numerous vibronic progressions of the (NiN_6) skeletal normal modes and the symmetric stretching mode, $\nu_s(N-H)$, which are modes of the electronic excited states. These are progressions of a_{1g} or e_g built on t_{1u} and t_{2u} modes. The temperature-dependent MCD spectra through $^3T_{1g}(t_{2g}{}^5e_g{}^3)$ experimentally confirm the earlier suggestion that second-order spin-orbit coupling is important in the ground state $^3A_{2g}(t_{2g}{}^6e_g{}^2)$ so as to give this state angular momentum from the excited state $^3T_{2g}(t_{2g}{}^5e_g{}^3)$. Finally, the band position of $^3A_{2g} \rightarrow {}^1A_{1g}(t_{2g}{}^6e_g{}^2)$ is an excellent probe for the interaction between the lattice counterion and the complex ion $[Ni(NH_3)_6]^{2+}$.

Introduction

The most recent report[2] dealing with the nature of electronic excited states of the important parent complex ion hexaamminenickel(II), or $[Ni(NH_3)_6]^{2+}$, contained descriptions of vibronic structural features on two d–d excitations, $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^1A_{1g}$, between *ca.* 600 nm (16,670 cm^{-1}) and 430 nm (23,260 cm^{-1}). This was observed at 80°K for the Cl^- and ClO_4^- salts of the complex ion and complemented ambient room-temperature solution spectra measured previously by others.[3] The present paper reports on newly observed vibronic structure, measured between 12 and 80°K, with distinct vibronic progressions on $^3T_{2g}(t_{2g}{}^5e_g{}^3;\ {}^3F)$, $^3T_{1g}(t_{2g}{}^5e_g{}^3;\ {}^3F)$, $^1E_g(t_{2g}{}^6e_g{}^2;\ {}^1D)$, $^1A_{1g}(t_{2g}{}^6e_g{}^2;\ {}^1G)$, $^1T_{2g}(t_{2g}{}^4e_g{}^4;\ {}^1D)$, and $^1T_{1g}(t_{2g}{}^5e_g{}^3;\ {}^1G)$ which represent intra- as well as interconfigurational excitations. Some of the identifications of vibronic progressions were substantiated by preparing and studying the deuterated d_{18} complex, $[Ni(ND_3)_6](PF_6)_2$. In all, seven salts were studied, and the counterions were Cl^-, Br^-, I^-, PF_6^-, and ClO_4^-.

It was also possible experimentally to substantiate some suggestions made by Harding, Mason, Robbins, and Thomson[4] about the MCD spectrum of $[Ni(NH_3)_6]^{2+}$; *i.e.*, we measured the MCD spectra at 18 and 27°K of $[Ni(NH_3)_6]Cl_2$. The latter data contribute importantly to the understanding of excited-state structure of the hexaammine.

Experimental Section

1. Instrumentation. MCD spectra were obtained with a JASCO spectropolarimeter (Model ORD/UV/CD-5 with the SS-20 electronics modification). Low temperatures for MCD were attained by throttling vapors from a liquid helium reservoir past the sample. Near-ir, far-ir, and Raman spectra were measured on Perkin-Elmer 521, Perkin-Elmer FIS-3, and Jarrell-Ash 25-100 instruments (4880-Å Ar laser line), respectively. Low-temperature electronic absorption spectra were obtained by using an all-glass exchange-gas dewar and an all-glass dewar whose internal compartment and sample are cooled by throttling vapors from a liquid helium reservoir into it. Au-Co *vs.* Cu and constantan *vs.* copper thermocouples were used following their calibration. The matrices of the crystalline samples were either KBr disks or Kel-F mulls.

2. Compounds. The syntheses of $[Ni(NH_3)_6]A_2$ complexes, where $A^- = Cl^-, Br^-, I^-$, and ClO_4^-, are well known.[5] The syntheses of $[Ni(NH_3)_6](PF_6)_2$ and its d_{18} deuteration analog were devised as follows. $[Ni(NH_3)_6](PF_6)_2$ was prepared by the metathetical replacement reaction between $[Ni(NH_3)_6]Cl_2$ (in an ammoniacal