ligands form a series of four diastereomers, which are denoted Λ-cis, Δ-cis, Λ-trans, and Δ-trans.[8] Experimentally, it is found that the CD spectra of the Λ-cis and Λ-trans forms are the same and that the CD of the Δ-cis and Δ-trans are opposite in sign and equal in magnitude.[8] These four diastereomers cannot be separated when one prepares $Tb(atc)_3$ since the analogous rare-earth complexes are exceedingly labile, and in solution phase one would expect that the four isomers would rapidly interconvert. As a result, if equal amounts of the four diastereomers were present in $Tb(atc)_3$, one would predict that no CPL should be observed.

However, it is well-known that six-coordinate lanthanide complexes are rare in solution and that much higher coordination numbers are possible.[11] In the present work, evidence has been obtained which points toward seven-coordination for the Tb(III) ion in the atc–substrate complexes. The atc ligands would be expected to have a large degree of steric bulkiness due to the presence of the camphor group, and solvent coordination to the metal would force the three ligands to interact more with each other than in the absence of the solvent. Since the ligands are inherently chiral, one would expect, therefore, to observe a stereospecific preference for a particular conformation that would minimize the interactions between the chelate rings. Such a preference would perturb the diastereomer interconversion and would result in the enrichment of one form over another; this would in turn lead to observable CPL.

The magnitude of the CPL suggests that the effects found in the present work are configurational in nature since the g_{lum} values are nearly an order of magnitude higher than values obtained in another work where the optical activity was due solely to conformational and vicinal effects.[9] This would then suggest that the sign of the CPL is related to the absolute configuration of the dominant diastereomer and that the class A and class B CPL line shapes represent the dominance of opposite configurations. We have recently observed that the sign of the CPL induced in the $^5D_4 \rightarrow {}^7F_5$ emission of $Tb(thd)_3$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedione) by chiral solvents correlates nicely with the absolute configuration of those solvents.[12]

We conclude, therefore, that the different CPL line shapes that have been obtained during the course of this work reflect increased steric interactions among ligands in the Tb(III) coordinative environment when one forms the adduct. In uncomplexed $Tb(atc)_3$ (obtainable, for example, in CCl_4), there is little need for extensive interligand interaction to take place while the Tb(III) ion remains six-coordinate. The expansion of the coordination number that takes place upon adduct formation must force the chelate to choose one stereoisomer over others, and in the cases of the pyridine and isobutylamine chelate adducts there may be two possible structures of comparable energy available. The superimposition of CPL of each of these does not lead to net cancellation, although the reason for this is not yet clear. Presumably, the lack of observed CPL for $Eu(facam)_3$ in a wide variety of solvents is a reflection of a lower degree of diastereomer preference.[7a] While the chirality due to the asymmetric atoms of the ligands cannot be altered in any way, it is certainly possible that the configurational isomerism of the chelate adduct will be able to dominate the observed CPL.

A few trends are observed in the g_{lum} values which indicate that the steric nature of the solvent plays an important role in the diastereomer perturbation. In the secondary amines, one notes a decrease in g_{lum} values as the size of one of the alkyl side chains increases, and one may conclude that the amine is binding less efficiently and therefore inducing less of a change at the Tb(III) ion. It is interesting to note that the largest effects are found with the most sterically bulky amines; tertiary amines make up almost all the class B solvents, and *tert*-butylamine led to the largest value of g_{lum} in the class A group.

Exactly why different diastereomers of $Tb(atc)_3$ should be enriched by the achiral solvents is not clear at the present time. In the case of $Eu(facam)_3$ only one CPL line shape was obtained when CPL could be detected,[7a] and these observations indicate that the process is more complicated than we have indicated. Further investigations are now under way to probe these effects in greater detail.

Acknowledgment. We are greatly indebted to Professor G. W. Everett, Jr. (University of Kansas), for providing the sample of acetylcamphor used to synthesize the Tb(III) chelate. Financial assistance by the Research Corp. (Cottrell Grant 8926) and the National Science Foundation (Grant CHE78-03402) is also gratefully acknowledged.

Registry No. $Tb(atc)_3$, 73663-66-8; *n*-propylamine, 107-10-8; isopropylamine, 75-31-0; *sec*-butylamine, 13952-84-6; ethylpropylamine, 20193-20-8; *tert*-butylamine, 75-64-9; diethylamine, 109-89-7; methylbutylamine, 110-68-9; methylhexylamine, 35161-70-7; methyloctylamine, 2439-54-5; *n*-butylamine, 109-73-9; benzylamine, 100-46-9; triethylamine, 121-44-8; tripropylamine, 102-69-2; tributylamine, 102-82-9; trihexylamine, 102-86-3.

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Optical Spectrum of Hexaaquoruthenium(III) Ion and Its Conjugate Base

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Received September 6, 1979

The spectrum of $Ru(H_2O)_6{}^{3+}$ was measured and fitted to the Tanabe and Sugano matrices. The parameters obtained, $Dq = 2860 \pm 40$ cm^{-1} and $B = 640 \pm 40$ cm^{-1} assuming $C/B = 4$, were compared with a systematic survey of analogous ruthenium(III) and rhodium(III) complexes. The pK for the formation of $Ru(H_2O)_5OH^{2+}$ was found to be 2.4 ± 0.2 at 20 °C and $I = 1.0$ M by a spectrophotometric titration. The charge-transfer bands of $Ru(H_2O)_6{}^{3+}$ and $Ru(H_2O)_5OH^{2+}$ were interpreted in terms of the optical electronegativities of H_2O and OH^-.

Introduction

There are various reports in the literature containing data on optical spectra of ruthenium(III) complexes.[1-7] In most of these spectra the d–d transitions are obscured by strong charge-transfer ones. In ligands with high electronegativity,

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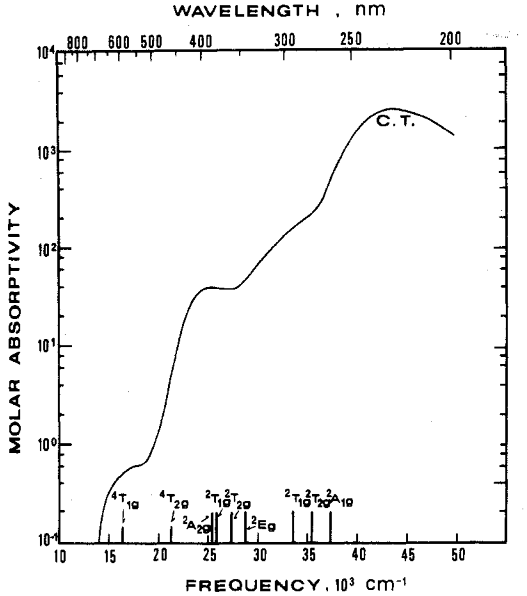

Figure 1. The spectrum of $Ru(H_2O)_6^{3+}$ in 1 M CF_3SO_3H. The stick diagram at the bottom is of calculated transitions with Dq = 2860 cm^{-1}, B = 640 cm^{-1}, and C/B = 4.0.

the charge-transfer bands occur at high energies so that the d–d transitions are clearly seen. This is true for the hexafluoro complex studied by Allen et al.[7] and for the hexaquo ion investigated here.

In the present work we give a systematic analysis of the spectrum of ruthenium(III) complexes according to the Tanabe–Sugano electrostatic matrices,[8,9] as well as an analysis of the charge-transfer bands in terms of Jørgensen's optical electronegativities.[10]

Experimental Section

$Ru(H_2O)_6^{3+}$ was prepared by modification of the procedure described by Kallen and Earley.[11] RuO_4 was obtained by $NaIO_4$ oxidation of $RuO_2 \cdot xH_2O$[12] (Aldrich or Merck-Schuchardt). In a typical experiment 0.2 g of $RuO_2 \cdot xH_2O$ were added to a solution of 1.6 g of $NaIO_4$ in 200 mL of distilled water. (In ref 12 acetone was used as a solvent.) The yellow RuO_4 gas was slowly swept with a stream of nitrogen into a stirred solution of 2 M HBF_4 containing an excess of tin powder. The red solution thus obtained, containing $Ru(H_2O)_6^{2+}$ was filtered and oxidized by bubbling oxygen for about 2 h until the color turned yellow. $Ru(H_2O)_6^{3+}$ was isolated from the solution by elution from Dowex 50W-X2 by 1 M CF_3SO_3H (Pierce or Merck-Schuchardt).[11]

In the spectrophotometric evaluation of the acid dissociation constant of $Ru(H_2O)_6^{3+}$ the acidic solution was partially neutralized with either NaOH or $NaHCO_3$ solutions. In order to avoid high local pH values, we mixed the solutions by addition of a $Ru(H_2O)_6^{3+}$ solution in 1 M CF_3SO_3H to dilute NaOH or $NaHCO_3$ solutions in a spectrophotometric cell; alternatively solid $NaHCO_3$ was added to the acidic solutions. The pH was measured before and after the recording of the spectrum. In all cases the pH did not change by more than 0.01 pH units during the spectrophotometric measurement. The spectra were measured by using a Cary-17 spectrophotometer.

Results and Discussion

The Acid Dissociation Constant of $Ru(H_2O)_6^{3+}$. The spectrum of $Ru(H_2O)_6^{3+}$ in 1 M CF_3SO_3H is shown in Figure 1. This solution is stable for more than a week at room temperature. Upon increasing of the pH of the solution, the spectrum is changing with the 225-nm peak disappearing while an absorption peak at 290 nm is formed starting at pH 1 and reaching a plateau at pH 4. The stability of the solutions was tested by acidification of the solutions with concentrated CF_3SO_3H and by checking the reversibility of the spectra. Above pH 4 the solutions were found to be stable only for a few minutes at room temperature, and after about an hour a brown precipitate formed, presumably due to a basic polymerized species. The reversibility of the spectra was better when the solutions were neutralized with $NaHCO_3$, since there was no contact of the Ru(III) with very high pH.

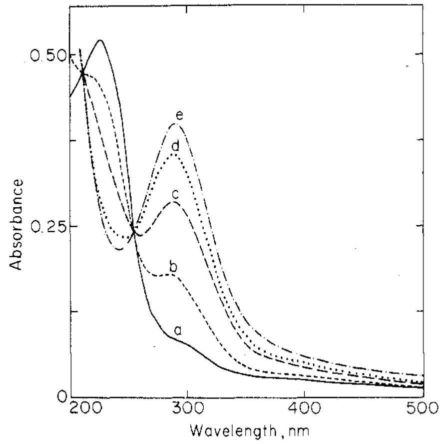

Figure 2. Spectra of aqueous Ru(III) at various pH values: (a) pH 1.53; (b) pH 2.1; (c) pH 2.45; (d) pH 2.99; (e) pH 3.74.

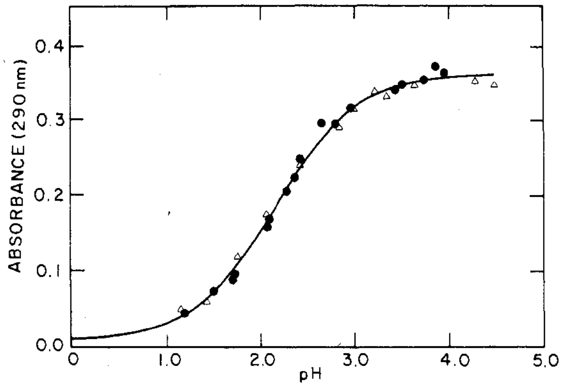

Figure 3. Spectrophotometric pH titration of the absorbance at 290 nm. The concentration of Ru(III) was 2.44 × 10^{-4} M. Optical path lengths were 1 cm. The neutralization was done by using solutions of either NaOH (●) or $NaHCO_3$ (△).

Typical spectra at various pH values are shown in Figure 2. Two isosbestic points can be seen at the UV part of the spectrum indicating an equilibrium between two species. Thus the following equilibrium is assumed to occur at the pH range 0–4:

$$Ru(H_2O)_6^{3+} \rightleftharpoons Ru(H_2O)_5OH^{2+} + H^+ \qquad (1)$$

A plot of the absorbance at 290 nm as a function of pH is given in Figure 3. The equilibrium constant of eq 1 obtained by a best fit procedure was $pK = 2.4 \pm 0.2$ and $\epsilon^{290} = 1650 \pm 100$ for $Ru(H_2O)_5OH^{2+}$. A pK value of 2.9 at 25 °C was reported very recently on the basis of cyclic voltammetry data.[13]

For comparison the acid dissociation pK for the water molecule in $Ru(NH_3)_5H_2O^{3+}$ was found to be between 4.2[14a]

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and 3.7.[14b] This follows the general trend of lower p*K* for hexaaquometal ions as compared to the aquopentaamine ions.[15]

The Analysis of the Optical Spectrum. $Ru(H_2O)_6^{3+}$ has a low-spin d^5 electronic configuration as is indicated by its room-temperature magnetic moment, $\mu_{eff} = 2.05\ \mu_B$[16] and its optical spectrum shown in Figure 1. The main features of the spectrum are a strong peak at 225 nm (44 400 cm^{-1}), a much weaker absorption with a peak at 392 nm (25 500 cm^{-1}), a shoulder with a very low intensity around 600 nm (16 000–17 000 cm^{-1}), and a very broad shoulder between 30 000 and 35 000 cm^{-1}, probably due to an overlap of several absorption peaks. From its intensity, the strong absorption peak of 225 nm is assigned to a charge-transfer transition. The high energy of this transition relative to other ruthenium(III) complexes such as $RuCl_6^{3-}$[5] or $Ru(NH_3)_6^{3+}$[2] is the reason that more d–d transitions can be seen. The shoulder at about 600 nm is assigned to the lowest energy spin-forbidden transition, $^4T_{1g} \leftarrow {}^2T_{2g}$, and the peak of 392 nm to the two lowest energy spin-allowed d–d transitions $^2A_{2g} \leftarrow {}^2T_{2g}$ and $^2T_{1g} \leftarrow {}^2T_{2g}$ which always have very similar transition energies. We have analyzed the spectrum by a diagonalization of the Tanabe and Sugano determinants[8,9] for a wide range of values of the parameters *Dq*, *B*, and *C*/*B*. We have looked for sets of these parameters that are consistent with peak positions of the $^4T_{1g}$ and $^2A_{2g}$ transitions in the range of 16 500 ± 700 and 25 400 ± 300 cm^{-1}, respectively. While the values of *Dq* in these sets were all in the narrow range of 2860 ± 40 cm^{-1}, the values of *B* were strongly dependent on the ratio *C*/*B*, being in the range of 640 ± 40 cm^{-1} for $C/B = 4.0$ and 590 ± 40 cm^{-1} for $C/B = 4.4$. The calculated d–d transitions based on these parameters are given in Figure 1. It is seen that the $^4T_{2g} \leftarrow {}^2T_{2g}$ transition is expected to be hidden under the tail of the spin-allowed transition centered at 392 nm.

d–d Transitions in Related Systems. In order to compare our results with crystal field parameters of related complexes, we fitted d–d transitions in ruthenium(III) and rhodium(III) complexes which have been reported in the literature to the diagonalized Tanabe and Sugano determinants.[8,9]

For $Ru(ox)_3^{3-}$ the four maxima reported[1] at 15 850, 20 400, 26 600, and 34 700 cm^{-1} with molar absorbances of 11, 28, 350, and 320 $M^{-1}\ cm^{-1}$, respectively, could be fitted in such a way that the first two transitions correspond to the two lowest spin-forbidden bands and the other two to the spin-allowed d–d transitions, with a set of parameters in the ranges of $B = 601–605\ cm^{-1}$, $C/B = 4.0–4.7$, and $Dq = 2745–2910\ cm^{-1}$, respectively. The error bar on *B* is increased considerably if one allows for a possible error in the transition positions. Since the spectrum of $Ru(ox)_3^{3-}$ was not given in ref 1, the error cannot be estimated. However, on the assumption of an error of ±250 cm^{-1} in the peak positions, a value of $B = 600 \pm 65\ cm^{-1}$ is obtained. A further increase in the error in the estimated *B* originates from the assumption of octahedral ligand field neglecting the trigonal perturbation.

For ruthenium(III) in a LiCl–KCl eutectic melt at 450 °C, Fung and Johnson[4] have performed a computer fit to Gaussian line shapes. The ligand field parameters they obtained by fitting their data to a linear expression of *B*, *C*, and *Dq* based on Tanabe and Sugano determinants,[17] $Dq = 1870\ cm^{-1}$, $B = 490\ cm^{-1}$, and $C/B = 4.67$, agree very well with the results of our direct fitting to the Tanabe and Sugano determinants: $Dq = 1872\ cm^{-1}$, $B = 483\ cm^{-1}$, $C/B = 4.61$. The only difference is our assignment of the 23 560 cm^{-1} transition to the third $^2T_{2g}$ level rather than $^2A_{1g}$.

Table I

	transitions fitted	*Dq*, cm^{-1}	*B*, cm^{-1}	C/B[a]
$RuCl_6^{3-}$[b]	$^4T_{1g}$, $^4T_{2g}$, $^2A_{2g}$ *c*	1840	520	4.0
	d	1870	490	4.67*
RuF_6^{3-}[e]	$^4T_{1g}$, $^4T_{2g}$, $^2A_{2g}$ *c*	2330	737	3.78*
	c	2330	697	4.0
	e	2200	550	4.75
$Ru(ox)_3^{3-}$[f]	$^4T_{1g}$, $^4T_{2g}$ *c*	2745	601	4.0
	c	2910	604	4.7
$Ru(H_2O)_6^{3+}$[c]	$^4T_{1g}$, $^2A_{2g}$ *c*	2860 ± 40	640 ± 40	4.0
	c	2860 ± 40	590 ± 40	4.4
$Ru(NH_3)_6^{3+}$[g]	$^4T_{1g}$, $^2A_{2g}$ *c*	3480 ± 60	580 ± 40	4.0

[a] Values of *C*/*B* are assumed except those with an asterisk where *C*/*B* is a free parameter. [b] Reference 4. $RuCl_6^{3-}$ was assumed to be the absorbing species in LiCl–KCl eutectic melt. [c] Present work. [d] Fitted in ref 4 to all seven transitions obtained by Gaussian analysis. [e] Reference 7. [f] Reference 1. [g] Reference 2.

For $Ru(en)_3^{3+}$ we failed to obtain a consistent fit with the positions of absorption peaks reported by Watt and Senoff.[3] The value of $Dq = 2950\ cm^{-1}$ reported by them is inconsistent with the value of *Dq* of about 3500 cm^{-1} for $Rh(en)_3^{3+}$ (see Table II). However, it is known that when this complex is obtained by an oxidation of $Ru(en)_3^{2+}$, there is some oxidation of the ligand to ethylenedimine,[19] which also absorbs at 22 500 cm^{-1}, as one of the peaks reported by Watt and Senoff for $Ru(en)_3^{3+}$. Difficulties in analyzing the spectrum of $Ru(en)_3^{3+}$ were reported also by Elsberno and Beattie.[20]

For $Ru(NH_3)_6^{3+}$ ion, the spectrum was fitted[2] to second-order perturbation energy expressions with the assumption of $C/B = 4.0$, obtaining $Dq = 3400\ cm^{-1}$ and $B = 580\ cm^{-1}$. Full diaganolization, assuming $C/B = 4.0$, gives a fit with $Dq = 3480 \pm 60\ cm^{-1}$ and $B = 580 \pm 40\ cm^{-1}$.

The diffused reflectance spectrum of K_3RuF_6 was reported by Allen et al.,[7] where several d–d transitions could be observed. While in their work they assumed $C/B = 4.75$, a better fit to their data is obtained with $C/B = 4.0$. If the value of *C*/*B* was allowed to vary as a free parameter, best fit was obtained with $C/B = 3.78$.

A summary of the ligand field parameters for the ruthenium(III) complexes is given in Table I. The evaluation of the parameters was done by fitting the calculated transition energies to the observed ones. In all cases the lowest band due to $^4T_{1g} \leftarrow {}^2T_{2g}$ transition was observed. In some cases the second spin-forbidden transition $^4T_{2g} \rightarrow {}^2T_{2g}$ was observed and in others the first spin-allowed transition $^2T_{1g}$, $^2A_{2g} \leftarrow {}^2T_{2g}$ was used for the fitting procedure. The difference in the diagonal elements between the two spin-forbidden exicted states of $^4T_{1g}$ and $^4T_{2g}$ is $8B$ while the difference between $^4T_{1g}$ and $^2A_{2g}$ or $^2T_{1g}$ is $3C + 2B$ and $3C + 3B$, respectively. Thus if one relies on the first two spin-forbidden transitions, a variation of *C*/*B* would affect *Dq* to a greater extent than *B*. The opposite happens when the fitting relies more heavily on the two transitions to $^4T_{1g}$ and $^2A_{2g}$.

It can be seen from the parameters given in Table I that the general trend follows the usual spectrochemical series for *Dq* and the nephelauxetic effect for *B*. Using the semiempirical expressions given by Jørgensen[21]

$$10Dq = f(\text{ligand})\cdot g(\text{central ion}) \qquad (2)$$

$$1 - B/B_0 = h(\text{ligand})\cdot k(\text{central ion}) \qquad (3)$$

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Table II. Ligand Field Parameters of Rhodium(III) Complexes[a]

	Dq, cm^{-1}	*B*, cm^{-1}	*C/B*
$Rh(CN)_6^{3-}$ [b]	4490	229	(4)[c]
	4520	230	(5.5)
$Rh(en)_3^{3+}$ [b]	3460	422	(4)
	3510	424	(5.5)
$Rh(NH_3)_6^{3+}$ [b]	3410	428	(4)
	3455	431	(5.5)
$Rh(ox)_3^{3-}$ [b,d]	2730	356	8.04
	2620	426	(5.5)[e]
$Rh(H_2O)_6^{3+}$ [f]	2720	499	5.55
$RhCl_6^{3-}$ [f]	2070	344	5.60
Rh(III) in LiCl–KCl melt[g]	1930	372	4.34
	1990	338	(5.5)[h]
$Rh Br_6^{3-}$ [f]	1930	287	5.68

[a] The ligand field parameters were obtained by a fitting of the observed optical transitions to the Tanabe and Sugano determinants.[8,9] The three parameters were obtained in cases where three transition energies ($^3T_{1g}$, $^1T_{1g}$, and $^1T_{2g}$) are known. In cases where only two transition energies, $^1T_{1g}$ and $^1T_{2g}$, are known they were fitted to values of *Dq* and *B* while the ratio *C/B* was an assumed value. [b] Reference 18. [c] The values of *C/B* that are given in parentheses are assumed values. The choice of the assumed value of $C/B = 5.5$ was based on the values obtained for $Rh(H_2O)_6^{3+}$, $RhCl_6^{3-}$, and $RhBr_6^{3-}$. [d] Reference 1. [e] The calculated and experimental values of the $^3T_{1g}$, $^1T_{1g}$, and $^1T_{2g}$ transitions are 19 590, 24 450, and 30 650 cm^{-1} and 19 250, 25 100, and 30 300 cm^{-1}, respectively. [f] Reference 22. [g] References 17 and 23. [h] The calculated and experimental values of the $^3T_{1g}$, $^1T_{1g}$, and $^1T_{2g}$ transition are 14 600, 18 500, and 23 500 cm^{-1} and 14 800, 18 200, and 23 500 cm^{-1}, respectively.

Table III

complex	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	χ_{opt}[a]
$RuCl_6^{3-}$ [b]	349	3000	(3.0)
$Ru(H_2O)_6^{3+}$ [c]	225	2480	3.5
$Ru(H_2O)_5Cl^{2+}$ [c]	317	661	(3.0)
$Ru(H_2O)_5Br^{2+}$ [c]	385	536	2.8
$Ru(H_2O)_5OH^{2+}$ [d]	290	1650 ± 100	3.1

[a] Calculated on the basis of eq 7 with the assumption $\chi_{opt}(Cl^-) = 3.0$. [b] References 5 and 25. [c] Reference 11. [d] Present work.

. We can give a quantitative account of this trend. From the values of *f*(ligand) given by Jørgensen[21] and the *Dq* values (with $C/B = 4.0$) given in Table I, a value of $g(Ru(III)) = 27 \pm 2 \times 10^3$ cm^{-1} can be estimated. The deviation to this value is the largest (14%) for ruthenium(III) in LiCl–KCl melt. The value of *k* in eq 3 cannot be calculated since the free ion value of *B*, B_0 is not known. Yet a reasonable fit with the *B* values in Table I can be obtained with B_0 between 780 cm^{-1} ($k = 0.16 \pm 0.02$) and 860 cm^{-1} ($k = 0.22 \pm 0.02$).

Due to the similarities in the ligand field splitting parameters between Ru(III) and Rh(III), we analyze the spectra of analogous rhodium(III) complexes given in the literature. A summary of this analysis on the basis of diagonalization of the Tanabe and Sugano matrices is given in Table II. In cases where only two transitions were reported, the parameters *Dq* and *B* could be estimated only when values for the ratio *C/B* were assumed. As expected, the fitted *Dq* and *B* were less sensitive to the choice of *C/B* in the cases where the ratio *B/Dq* was smaller. On the basis of the fitted parameter of $Rh(H_2O)_6^{3+}$, $RhCl_6^{3-}$, and $RhBr_6^{3-}$, the ratio *C/B* seems to be close to 5.5. This value differs from the value $C/B = 6.5$ reported earlier,[22] where only the diagonal elements of the Tanabe and Sugano matrices were taken into account. Both *Dq* and *B* follow quite closely the empirical relations for the spectrochemical (eq 2) and nephlauxetic series (eq 3). The deviation was less than 8% for the *Dq* and less than 15% for *B* with the exception of the value of *B* for the $Rh(CN)_6^{3-}$ which deviates by 25% from that predicted by eq 3.

A comparison of the ligand field parameters of ruthenium(III) and rhodium(III) complexes given in Tables I and II indicates that the values of *Dq* for the same ligands are quite similar. Indeed, our estimated value of $g(Ru(III)) = 27 \pm 2 \times 10^3$ cm^{-1} is equal to $g(Rh(III)) = 27 \times 10^3$ cm^{-1} given by Jørgensen.[21] The values of *B* on the other hand are consistently higher for the ruthenium(III) probably due to both higher value of B_0 and smaller value of *k*.

Discussion of the Charge-Transfer Spectra. The spectra of $Ru(H_2O)_6^{3+}$ and $Ru(H_2O)_5OH^{2+}$ contain absorption peaks at 225 and 290 nm with extinction coefficients of 2480 and 1650 M^{-1} cm^{-1}, respectively, which were assigned to ligand to metal charge-transfer transitions. These spectra are compared with charge-transfer transitions of related complexes in Table III. One way to compare the spectra is to estimate the optical electronegativities by using the relations given by Jørgensen[10]

$$\bar{\nu}_{cor} = 30(\chi_{opt}(\text{ligand}) - \chi_{opt}(\text{metal})),\ 10^3\ \text{cm}^{-1} \qquad (4)$$

For the case of low-spin ruthenium(III) ions[10]

$$\bar{\nu}_{cor} = \bar{\nu}_{CT} - \tfrac{2}{3}D \qquad (5)$$

where *D*, the interelectronic repulsion parameter can be estimated by using the relation[10]

$$D = \frac{7}{6}\left(\frac{5}{2}B + C\right) \qquad (6)$$

Since the optical electronegativity scale is calibrated by assuming $X(Cl^-) = 3.0$ we can write

$$\bar{\nu}_{CT}(\text{ligand}) - \bar{\nu}_{CT}(Cl^-) = 30(\chi_{opt}\ (\text{ligand}) - 3.0) + \tfrac{2}{3}(D(\text{ligand}) - D(Cl^-)) \qquad (7)$$

The value of *D* can be assumed to be roughly the same for the series of $Ru(H_2O)_5X^{2+}$, X = Cl^-, Br^-, and OH^-, and is estimated by using the ligand field parameter for $Ru(H_2O)_6^{3+}$, given in Table I as $D = 4850$ cm^{-1}. For the $RuCl_6^{3-}$ complex a value of $D = 4000$ cm^{-1} is estimated. Values of optical electronegativities calculated by this way are given in Table III. The values of 3.5 and 2.8 calculated for H_2O and Br^-, respectively, coincide with the values given by Jørgensen.[10] The value $\chi_{opt} = 3.1$ for the hydroxide ion as a ligand coincides with that calculated by the same method using spectral data of $Ru(NH_3)_5OH^{2+}$.[24]

An estimate of $\chi_{opt}(Ru(III))$ on the basis of eq 4 for $RuCl_6^{3-}$, $Ru(H_2O)_5Cl^{2+}$, and $Ru(NH_3)_5Cl^{2+}$ gives values of 2.13, 2.06, and 2.08, respectively, in agreement with the approximate value of $\chi_{opt}(Ru(III)) = 2.1$ given by Jørgensen[10] and 2.15 given by Allen et al.[7] on the basis of the spectrum of RuF_6^{3-} and $\chi_{opt}(F^-) = 3.9$. Our data are consistent with the trend indicated by Jørgensen[10] of a slightly reduced χ_{opt}(metal) in complexes with less than six identical ligands. On the basis of our data for ruthenium(III) complexes we can conclude that the optical electronegativity scale is a reliable measure for ligand to metal charge-transfer transition energies.

Acknowledgment. The authors wish to thank Mrs. R. Panigel for assistance in performing some of the measurements.

Registry No. $Ru(H_2O)_6^{3+}$, 30251-72-0; $Ru(H_2O)_5OH^{2+}$, 73663-64-6; $RuCl_6^{3-}$, 21595-26-6; RuF_6^{3-}, 73663-65-7; $Ru(ox)_3^{3-}$, 25072-75-7; $Ru(NH_3)_6^{3+}$, 18943-33-4.

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