is to be expected from a line, the origin of which is due to an exchange interaction.[29]

It would be interesting to compare the parameters determined in this experiment with the esr results on other dimeric copper compounds containing different ligands. Unfortunately, very little esr data are available. We note that our g values are approximately the same as all the others reported[23–27] within the experimental error. In addition, D and J in copper(II) cyanoacetate are only about 10–15% higher than in copper(II) acetate monohydrate. These relatively small changes in the magnetic parameters with respect to the considerably different nature of the ligand suggest that the interaction in both compounds is due to direct exchange. This is, of course, consistent with the presently accepted interpretation of the interaction in these compounds. A superexchange mechanism would probably be more ligand dependent. The observed differences in J, D, and E are explicable on the basis of small changes in the spatial arrangement of the complex. The fact that E is near zero in copper(II) cyanoacetate may be associated with the proposed polymeric structure which might tend to make the x and y directions equivalent.

Acknowledgments.—We thank the National Science Foundation for a departmental equipment grant, GP-2104, and for partial financial support under Grant GP-3498.

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CONTRIBUTION FROM THE SAVANNAH RIVER LABORATORY,
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The Hypersensitive Transitions of Hydrated Nd^{3+}, Ho^{3+}, and Er^{3+} Ions[1]

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Hypersensitive and normal absorption bands in the spectra of aqueous Nd^{3+} change in shape as the concentration increases from 0 to 12 M for the electrolytes HCl, LiCl, and $HClO_4$, or as the temperature increases in concentrated LiCl solutions. Based on a comparison with the absorption spectra of 9-coordinate Nd^{3+} and 8-coordinate Nd^{3+}, the shape changes in aqueous Nd^{3+} spectra are considered evidence of a change in the coordination number of the aquo Nd^{3+} ion from 9 in dilute solutions toward 8 in concentrated solutions. The oscillator strengths of the hypersensitive bands of Nd^{3+}, Ho^{3+}, and Er^{3+} in HCl, LiCl, and $HClO_4$ solutions increase at higher electrolyte concentrations and at a higher temperature. This increase in the oscillator strengths of hypersensitive bands is attributed to the action of an enhanced electric field gradient from the proximity of anions and hydrated cations to the lanthanide ions, as predicted from theory. The change to 8-coordination of Nd^{3+} in concentrated chloride solutions is taken to indicate that other normally 9-coordinate lanthanide ions undergo a similar change. Thus, in concentrated chloride, it appears likely that all lanthanide ions are 8-coordinate, possibly $Ln(H_2O)_8{}^{3+}$ ions. In strong chloride solutions, trivalent actinide ions are chloro complexes. The explanation for the successful group separation of lanthanides and actinides by ion exchange or solvent extraction from strong chloride media may depend upon the existence of lanthanide and actinide ions as different aqueous species.

Introduction

The hypersensitive transitions in the absorption spectra of lanthanide ions are those characterized by variations in the intensity of absorption bands in different media. Since the first theoretical calculations of spectral intensities by Judd[2] and Ofelt,[3] hypersensitive transitions have been the subject of several theoretical and experimental investigations.[4–8] Original theoretical studies[4] attributed hypersensitivity to the enhancement of quadrupole transitions by the dielectric inhomogeneities in the media. Judd[7] has suggested that a change in the symmetry of the field on the lanthanide ion is also a probable cause.

This study investigated the effects of strong chloride and perchlorate solutions on the hypersensitive transitions of Nd^{3+}, Ho^{3+}, and Er^{3+}. These ions represent both the light and heavy lanthanides, and their relatively high extinction coefficients simplify spectral measurements. Concentrated chloride solutions are the most successful media for the group separation of lanthanide and trivalent actinide ions by ion exchange[9–12] or solvent extraction.[13] The investigation of lanthanide

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[1] The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

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ions in chloride solutions was undertaken with the aim of illuminating a poorly understood chemical separation.

Previous work[14] has shown that the shapes of absorption bands of the lanthanide ions can be correlated with the coordination number and symmetry of the lanthanide ion in lanthanide β-diketonates. The change in band shape for the aquo Nd^{3+} ion was used to recognize changes in its coordination in this work.

Experimental Section

Stock solutions of lanthanide chlorides were prepared by dissolving chlorides purchased as 99.9% grade from Alfa Inorganics, Inc., Beverly, Mass. Solutions of perchlorates were prepared by repeatedly precipitating the hydroxides with aqueous ammonia, washing, and dissolving the hydroxide precipitates in perchloric acid. Stock solution concentrations were determined by titration. Concentrations of the solutions used in spectral studies were calculated by diluting the stock solution to a measured volume. Other chemicals and reagents were reagent grade.

Solid $NdCl_3 \cdot 6H_2O$ was prepared by vacuum drying $NdCl_3 \cdot xH_2O$ at room temperature. $Nd_2(SO_4)_3 \cdot 8H_2O$ was precipitated from a hot solution of $Nd(OH)_3 \cdot xH_2O$ in H_2SO_4. $Nd(BrO_3)_3 \cdot 9H_2O$ was prepared by mixing solutions of $Nd_2(SO_4)_3 \cdot 8H_2O$ and $Ba(BrO_3)_2 \cdot H_2O$, filtering off $BaSO_4$, and crystallizing the product from the filtrate. X-Ray powder patterns verified the identity of all three compounds.

Spectral measurements were made in a Cary Model 14 spectrophotometer, using 1- and 2-cm quartz absorption cells. The scanning speed of the spectrophotometer was 40 Å/min. Measurements were made at room temperature (~25°) and also at 42 ± 5° when an indication of the effect of elevated temperatures was desired.

Absorption intensity was determined by the planimeter measurement of the area under the absorption curve. These measurements could be reproduced to ±4% on separate dilutions of the stock solutions.

The absorption intensities, presented as oscillator strengths, were calculated from the reduced expression[6]

$$P = 4.31 \times 10^{-9}\left[\frac{9\eta}{(\eta^2 + 2)^2}\right]\int \epsilon(\nu)\mathrm{d}\nu$$

where η is the refractive index of the solution and $\epsilon(\nu)$ is the molar extinction coefficient at the wavelength ν. A refractive index value of 1.33 was used for all solutions.

The independence of oscillator strength for lanthanide ion concentration from 5×10^{-2} to 5×10^{-3} M was verified for the solutions measured. The lack of a concentration effect on the oscillator strength at 0, ~6, and ~12 M HCl was considered adequate verification for intermediate HCl concentrations.

The absorption spectra of solid compounds were measured on mulls that were prepared by grinding the dry solid and then regrinding it into a paste with paraffin oil. This paste was spread on a disk of filter paper; the proper thickness of the sample was determined by trial and error. A disk of filter paper, dampened with paraffin oil, was placed in the reference position. Absorption spectra of solids in the near-infrared region were obtained by restricting the slit width to 0.5 mm.

Results

Neodymium.—The absorption spectra of Nd^{3+} were measured in four regions of strong absorption for solid $Nd(BrO_3)_3 \cdot 9H_2O$, $NdCl_3 \cdot 6H_2O$, and $Nd_2(SO_4)_3 \cdot 8H_2O$ in HCl, LiCl, and $HClO_4$ solutions at anion concentrations as high as 12 M. The bands observed involve transitions from the $^4I_{9/2}$ ground state to the states $^2H_{9/2}$, $^4F_{5/2}$ (~8000 Å, referred to hereafter as Nd-I); to $^4S_{3/2}$, $^4F_{7/2}$ (~7500 Å, Nd-II); to $^4G_{5/2}$, $^2G_{7/2}$ (~5800 Å, Nd-III); and to $^2K_{13/2}$, $^4G_{7/2}$, $^2G_{9/2}$ (~5200 Å, Nd-IV). In all four bands, there is a distinct change in shape as the concentration of electrolyte is increased. All four bands of the spectrum of Nd^{3+} in solid $Nd(BrO_3)_3 \cdot 9H_2O$ closely resemble those of Nd^{3+} in dilute solutions, and the spectra of Nd^{3+} in solid $Nd_2(SO_4)_3 \cdot 8H_2O$ and $NdCl_3 \cdot 6H_2O$ resemble those of Nd^{3+} in concentrated chloride solutions (Figures 1–4). The changes in shape of the Nd-III band as the electrolyte concentration is increased are shown in Figure 5.

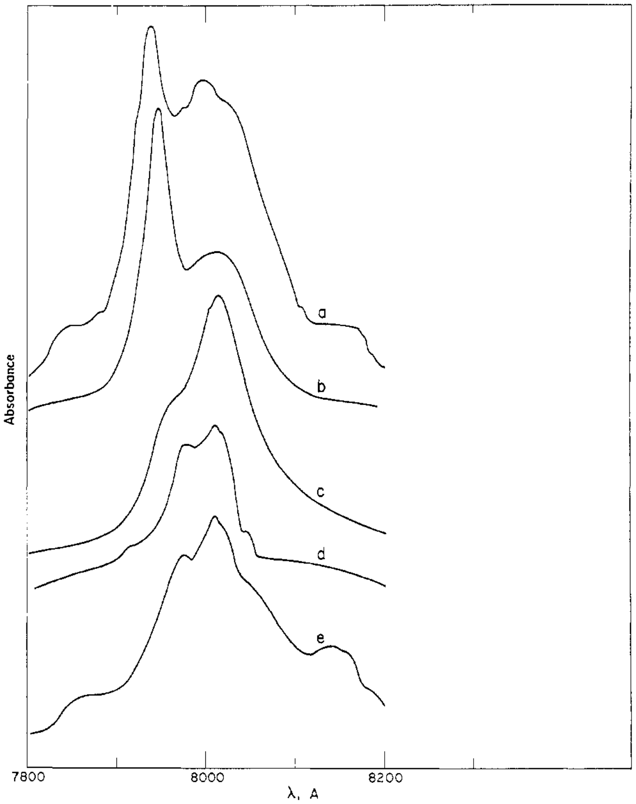

Figure 1.—Spectra of the Nd^{3+} $^4I_{9/2} \rightarrow$ $^2H_{9/2}$, $^4F_{5/2}$ transitions; a, solid $Nd(BrO_3)_3 \cdot 9H_2O$; b, 5.35×10^{-2} M Nd^{3+} in water: c, 5.35×10^{-2} M Nd^{3+} in 11.4 M HCl; d, solid $NdCl_3 \cdot 6H_2O$; e, solid $Nd_2(SO_4)_3 \cdot 8H_2O$.

The oscillator strengths calculated for each band are shown in Table I. Despite variations in the appearance of the bands as electrolyte concentration increases, the oscillator strengths for the Nd-I and Nd-II bands are constant within experimental error. The variation in the oscillator strengths for the Nd-III and Nd-IV bands identifies these as resulting from hypersensitive transitions. The oscillator strengths for Nd-III are shown in Figure 6; at high concentrations, the data define two curves, one for HCl solutions and a second for $HClO_4$ and LiCl solutions.

Spectra of $NdCl_3$ in 11 M LiCl at 42° showed a change in the shapes of all bands, compared to the band shape in these spectra at 25° (illustrated in Figure 7 for Nd-III). This shape change is the same as would be expected for an increase in LiCl concentration. The intensities of Nd-III and Nd-IV increased about 5% (Table I) while the intensities of Nd-I and Nd-II were

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(14) D. G. Karraker, *Inorg. Chem.*, **6**, 1863 (1967).

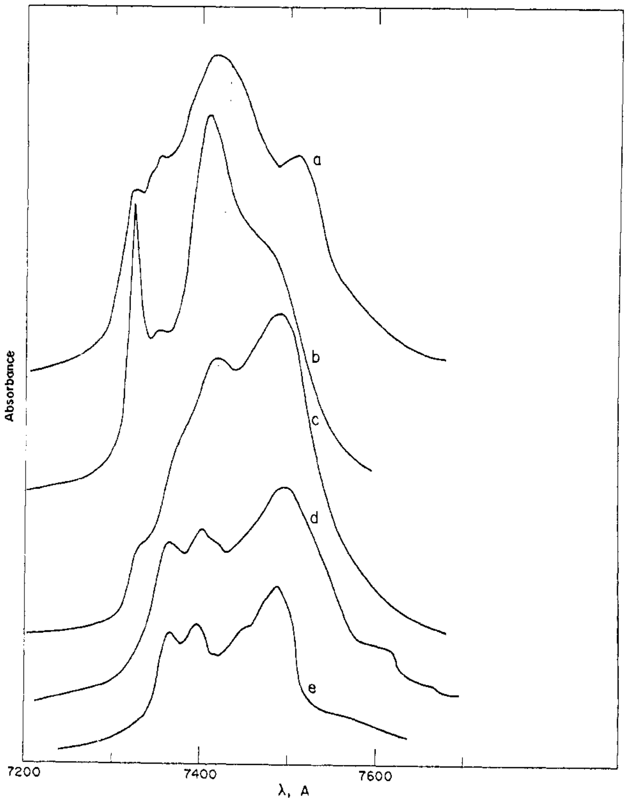

Figure 2.—Spectra of the Nd^{3+} $^4I_{9/2} \rightarrow {}^4S_{3/2}, {}^4F_{7/2}$ transitions: a, solid $Nd(BrO_3)_3 \cdot 9H_2O$; b, 5.35×10^{-2} *M* Nd^{3+} in water; c, 5.35×10^{-2} *M* Nd^{3+} in 11.4 *M* HCl; d, solid $Nd_2(SO_4)_3 \cdot 8H_2O$; e, solid $NdCl_3 \cdot 6H_2O$.

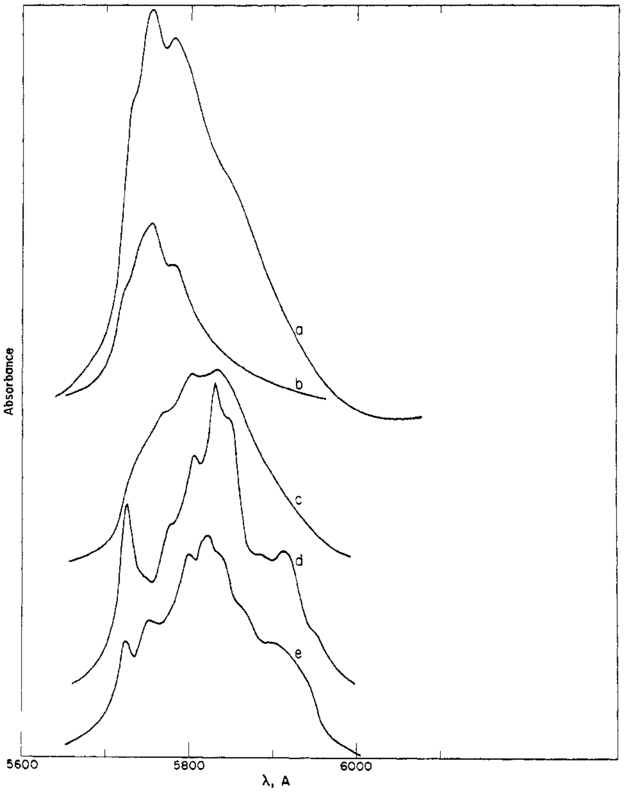

Figure 3.—Spectra of the Nd^{3+} $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transitions: a, solid $Nd(BrO_3)_3 \cdot 9H_2O$; b, 5.35×10^{-2} *M* Nd^{3+} in water; c, 5.35×10^{-2} *M* Nd^{3+} in 11.4 *M* HCl; d, solid $NdCl_3 \cdot 6H_2O$; e, solid $Nd_2(SO_4)_3 \cdot 8H_2O$.

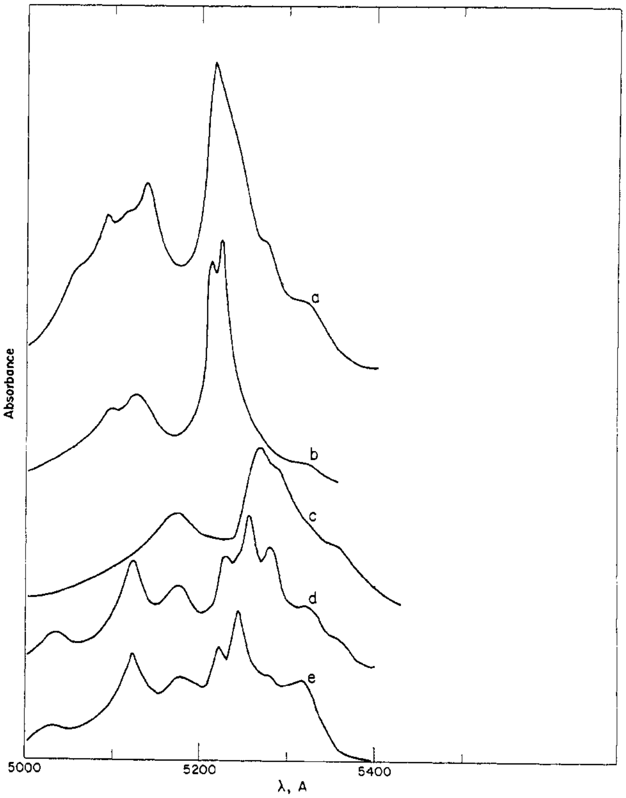

Figure 4.—Spectra of the Nd^{3+} $^4I_{9/2} \rightarrow {}^2K_{13/2}, {}^4G_{7/2}, {}^2G_{9/2}$ transitions: a, solid $Nd(BrO_3)_3 \cdot 9H_2O$; b, 5.35×10^{-2} *M* Nd^{3+} in water; c, 5.35×10^{-2} *M* Nd^{3+} in 11.4 *M* HCl; d, solid $NdCl_3 \cdot 6H_2O$; e, solid $Nd_2(SO_4)_3 \cdot 8H_2O$.

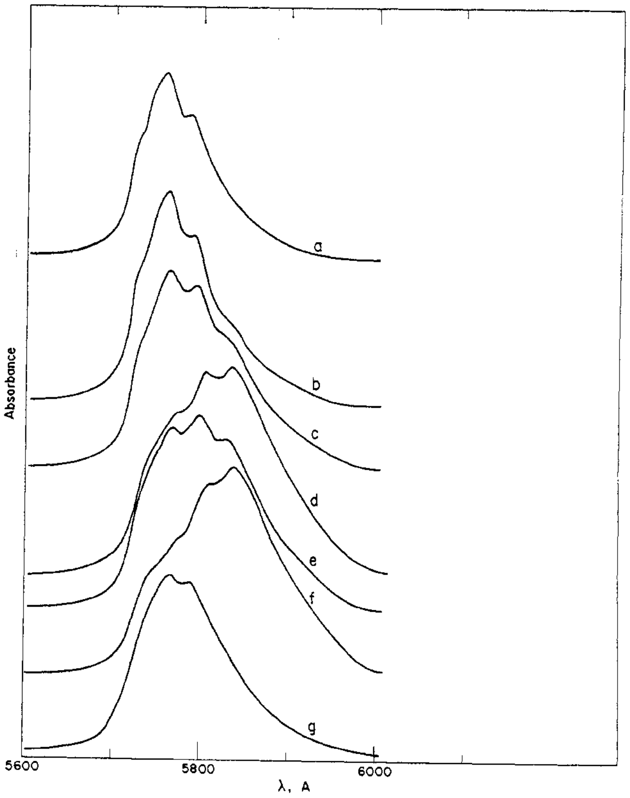

Figure 5.—Spectra of the Nd^{3+} $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transitions: a, H_2O; b, 5.7 *M* HCl; c, 8.6 *M* HCl; d, 11.4 *M* HCl; e, 11 *M* LiCl; f, 12.9 *M* LiCl; g, 11.2 *M* $HClO_4$.

TABLE I

OSCILLATOR STRENGTHS FOR SPECTRAL BANDS OF Nd^{3+}

	Upper level of transition			
	Nd-I, $^2H_{9/2}$, $^4F_{5/2}$	Nd-II, $^4S_{3/2}$, $^4F_{7/2}$	Nd-III, $^4G_{5/2}$, $^2G_{7/2}$	Nd-IV, $^2K_{13/2}$, $^4G_{7/2}$, $^2G_{9/2}$
	E range, cm^{-1}			
	12,195–12,723	13,158–13,700	16,667–18,182	18,657–20,000
Solution	$P \times 10^6$			
$NdCl_3$ in H_2O	6.74	6.42	7.70	5.45
5.7 *M* HCl			8.40	
8.6 *M* HCl			10.3	
11.4 *M* HCl	6.82	6.25	13.9	5.87
~13 *M* HCl[a]			16.1	
6 *M* LiCl			9.0	
9 *M* LiCl			10.8	
11 *M* LiCl (25°)	6.76	6.68	12.5	5.62
11 *M* LiCl (42°)	6.76	6.68	13.4	5.90
13.1 *M* LiCl	...	...	14.1	...
$Nd(ClO_4)_3$ in H_2O	6.9	6.4	7.90	6.0
5.3 *M* $HClO_4$	6.76	6.41	8.33	5.7
11.2 *M* $HClO_4$	6.8	6.3	12.3	5.8

[a] A 20% $C_2H_5OH-H_2O$ solution saturated with HCl at 5°. The HCl concentration varied over 12–14 *M* after warming to 25°.

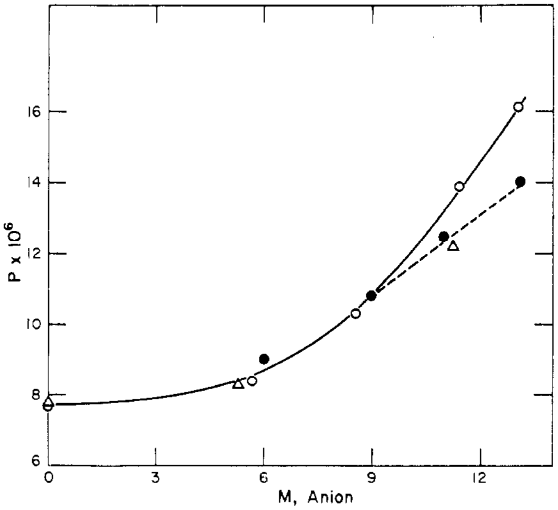

Figure 6.—Oscillator strength for Nd^{3+} $^4I_{9/2} \rightarrow {}^2G_{7/2}, {}^4G_{5/2}$ transition: ○, HCl; ●, LiCl; △, $HClO_4$.

unaffected, despite the change in band shape. The same measurements on a water solution of $NdCl_3$ showed a broadening of the Nd-I and Nd-II bands in the direction of longer wavelengths. The intensity change between 25 and 42° for both Nd-I and Nd-II was −2%, approximately the error of the measurement.

Holmium.—In preliminary measurements, spectra of $HoCl_3 \cdot xH_2O$ in water and in ~12 *M* HCl were compared over the 4000–7300-Å region. The major absorption band at ~4500 Å, due to the $^5I_8 \rightarrow {}^5G_6, {}^5F_1$ transition (Ho-I), was extremely hypersensitive; the band at ~5370 Å [$^5I_8 \rightarrow {}^5S_2, {}^5F_4$ (Ho-II)] was not hypersensitive; but some hypersensitivity was found in the bands at ~6420 Å ($^5I_8 \rightarrow {}^5F_5$) and ~4170 Å ($^5I_8 \rightarrow {}^5G_5$).

The absorption spectra of Ho^{3+} were measured in 0–12 *M* HCl, 9 *M* LiCl, 12 *M* LiCl, and ~12 *M* $HClO_4$ for the Ho-I and Ho-II transitions. As shown in Figure 8, the intensity of the Ho-I absorption band increased at higher electrolyte concentrations, but there was no change in its shape. The calculated oscillator strengths for spectral bands of Ho^{3+} are given in Table II.

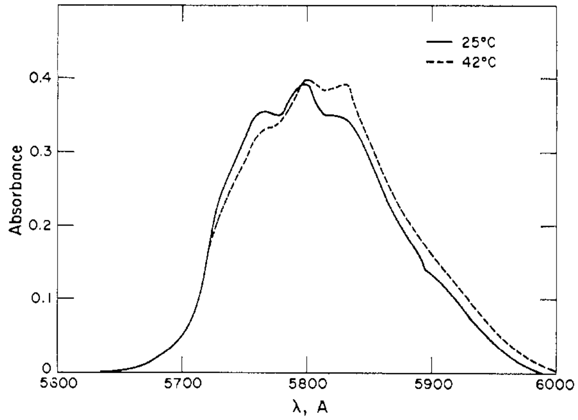

Figure 7.—Temperature effect on Nd^{3+} $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition in 11 *M* LiCl.

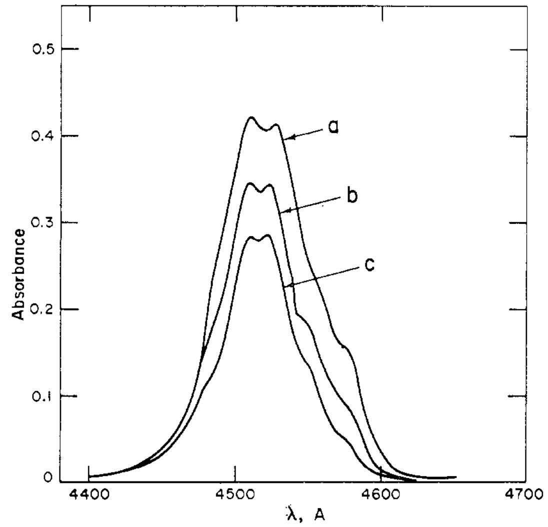

Figure 8.—The $^5I_8 \rightarrow {}^5G_6, {}^5F_1$ transition for Ho^{3+}: a, 3.5 × 10^{-2} *M* $HoCl_3$ in 11.4 *M* HCl; b, 3.5 × 10^{-2} *M* $HoCl_3$ in 8.6 *M* HCl; c, 3.5 × 10^{-2} *M* $HoCl_3$ in H_2O.

Spectra of Ho-I in both 9 *M* LiCl and 12 *M* LiCl at 42° showed a 5% increase in oscillator strength over that found at 25°. In the same solutions, the oscillator strength of Ho-II decreased 4% at 42° from 25°. The oscillator strengths of the Ho-I spectra from a water solution of $HoCl_3$ at 42 and 25° agreed within 1%.

Erbium.—The absorption spectra of Er^{3+} were measured in the regions of the hypersensitive transitions $^4I_{15/2} \rightarrow {}^2H_{11/2}$ (Er-I) and $^4I_{15/2} \rightarrow {}^4G_{11/2}$ (Er-II) in solutions of 0–11.4 *M* HCl, 12 *M* LiCl, and 11.2 *M* $HClO_4$. The oscillator strengths of the Er-I and Er-II bands increased in solutions of concentrated electrolytes (Figure 9). As found with Ho^{3+}, the band shape did not change. The oscillator strengths for these bands are given in Table III. The ratio of oscillator strengths for Er-I and Er-II is constant, 2.11 ± 0.02, in 0–11.4 *M* HCl.

The oscillator strengths of Er-I and Er-II in 12 *M*

TABLE II

OSCILLATOR STRENGTHS FOR SPECTRAL BANDS OF Ho^{3+}

	Upper level of transition	
	Ho-I, $^5G_6$, $^5F_1$	Ho-II, $^5S_2$, $^5F_4$
	E range, cm^{-1}	
	21,645–22,727	18,868–18,116
Solution	$P \times 10^6$	
$HoCl_3$ in H_2O	4.73	4.10
2.85 *M* HCl	5.06	...
5.7 *M* HCl	5.48	...
8.6 *M* HCl	6.35	...
11.4 *M* HCl	8.52	4.10
9 *M* LiCl (25°)	6.66	4.20
9 *M* LiCl (42°)	7.11	4.0
12 *M* LiCl (25°)	8.76	4.1
12 *M* LiCl (42°)	9.25	3.9
$Ho(ClO_4)_3$ in H_2O	4.82	
11.2 *M* $HClO_4$	7.06	

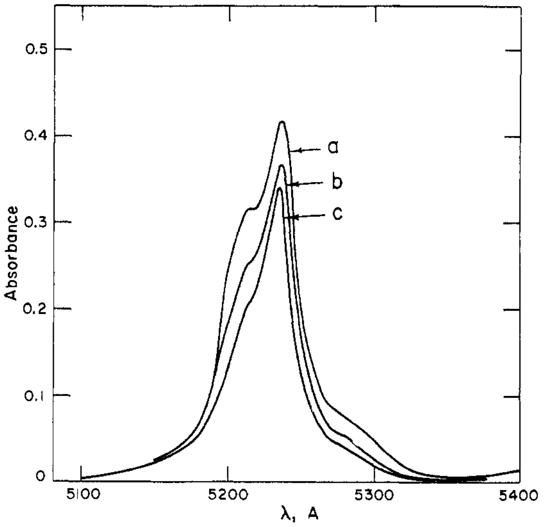

Figure 9.—The $^4I_{15/2} \rightarrow {}^2H_{11/2}$ transition of Er^{3+}: a, 4.74×10^{-2} *M* $ErCl_3$ in 11.4 *M* HCl; b, 4.74×10^{-2} *M* $ErCl_3$ in 8.6 *M* HCl; c, 4.74×10^{-2} *M* $ErCl_3$ in H_2O.

TABLE III

OSCILLATOR STRENGTHS FOR SPECTRAL BANDS OF Er^{3+}

	Upper level of transition	
	Er-I, $^2H_{11/2}$	Er-II, $^4G_{11/2}$
	E range, cm^{-1}	
	18,797–19,608	25,773–27,027
Solution	$P \times 10^6$	
$ErCl_3$ in H_2O	2.31	5.00
2.85 *M* HCl	2.52	5.30
5.7 *M* HCl	2.61	5.50
8.55 *M* HCl	2.98	6.27
11.4 *M* HCl	3.79	7.62
12 *M* LiCl (25°)	3.40	7.16
12 *M* LiCl (42°)	3.64	7.82
$Er(ClO_4)_3$ in H_2O	2.27	5.15
11.2 *M* $HClO_4$	3.20	6.42

LiCl at 42° showed an increase of 6.8 and 9%, respectively, compared to the absorption at 25°. The oscillator strength of $ErCl_3 \cdot xH_2O$ in water for the Er-I and Er-II bands was identical within ±1% at 42 and 25°.

Discussion

The experimental studies show two major effects—a change in the shape for all Nd^{3+} absorption bands as electrolyte concentration (or temperature) is increased, and an increase in the oscillator strengths for the hypersensitive bands of Nd^{3+}, Ho^{3+}, and Er^{3+} as electrolyte concentration or temperature is increased. The lack of a change in shape for the absorption bands of Ho^{3+} and Er^{3+} is considered significant, since spectral studies[14] on Ho^{3+} and Er^{3+} β-diketonates have shown that their absorption bands exhibit changes in shape that can be correlated with changes in the coordination of the metal ion.

The explanation proposed for these effects is that the change in the shape of Nd^{3+} bands indicates a change in the coordination number (CN) for the aquo Nd^{3+} ions from 9 to 8, and the enhancement of the absorption of the hypersensitive bands results from the action on these ions of an increased electric field produced by high electrolyte concentrations and elevated temperatures. The latter conclusion is in accord with theoretical studies[4,7] on the absorption intensities of the hypersensitive transitions of lanthanide ions.

Spedding and co-workers have found that the partial molal volumes,[15] heats of dilution,[16] and relative viscosities[17] of aqueous solutions of lanthanide chlorides are all consistent with the assumption that lanthanides La^{3+} to Nd^{3+} have one coordination number, lanthanides Gd^{3+} to Lu^{3+} have a lower coordination number, and intermediate lanthanides are a mixture of both species. Spedding's partial molal volume data agree with a CN 9 for lanthanide ions La^{3+} to Nd^{3+}, and a CN 8 for Gd^{3+} to Lu^{3+}. Nmr results[18] are also consistent with this interpretation. In agreement with this evidence, the shape of the spectral bands of Nd^{3+} in dilute solution is similar to the shape of the Nd^{3+} spectral bands in solid $Nd(BrO_3)_3 \cdot 9H_2O$, where the Nd^{3+} ion is known from a single-crystal X-ray study[19] to be coordinated to nine water molecules.

As the concentration of a concentrated electrolyte solution is increased, the shapes of Nd^{3+} bands become more similar to those for the Nd^{3+} ion in solid $NdCl_3 \cdot 6H_2O$ and $Nd_2(SO_4)_3 \cdot 8H_2O$. Based upon the X-ray structure of the isomorphous $GdCl_6 \cdot 6H_2O$,[20] $NdCl_3 \cdot 6H_2O$ has an 8-coordinate Nd^{3+} ion in $[Cl_2Nd(H_2O)_6{}^+]$ units. The shape of the Nd^{3+} spectra between $Nd(H_2O)_8{}^{3+}$ and $[Cl_2Nd(H_2O)_6{}^+]$ may be expected to show minor differences because of the field change as two chloride ions are substituted for water in the coordination sphere. The 8-coordination of Nd^{3+} in $Nd_2(SO_4)_3 \cdot 8H_2O$ is not certain. Early work[21] on the isomorphous $Sm_2(SO_4)_3 \cdot 8H_2O$ implied that the Sm^{3+} ion "probably occupied an eightfold position." Also, from a partial structure determination on $Nd_2(SO_4)_3 \cdot 8H_2O$,[22] the Nd^{3+} ion was reported to be 9-coordinate,

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(15) F. H. Spedding, M. J. Pikal, and B. O. Ayers, *J. Phys. Chem.*, **70**, 2440 (1966).

(16) F. H. Spedding, S. A. Csejka, and C. W. DeKock, *ibid.*, **70**, 2423 (1966).

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(20) M. Marezio, H. A. Plettinger, and W. H. Zachariasen, *Acta Cryst.*, **14**, 234 (1961).

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bonded to five sulfate oxygens and four water molecules. However, this structure has been criticized[23] as having two pairs of oxygen atoms unreasonably close and is therefore disregarded.

Thus, the comparison of the band shapes of the spectra of the Nd^{3+} ion between solutions and solid compounds suggests that the aquo Nd^{3+} ion changes from CN 9 in dilute solutions toward CN 8 in concentrated solutions. This effect, although qualitative, has been successful[14] in correlating the band shapes of several lanthanides with the coordination number or symmetry of the lanthanide ion.

The change in shape of the Nd^{3+} absorption bands has been explained by previous workers[24,25] by assuming coordination of the anion with the Nd^{3+} ion, even in $HClO_4$ solutions.[24] However, ion-exchange studies[10] on lanthanide and actinide ions in HCl solutions show that the affinity of lanthanide ions for cation-exchange resin increases a factor of 3 as the HCl concentration is increased from 6 to 12 *M*. Over the same range, the affinity of the resin for trivalent actinide ions decreases about a factor of 2; the trivalent actinides are present as chloro complexes.[26] The difference in ion-exchange behavior of the lanthanide ions is convincing evidence that complexing by chloride is not significant. A study of chloride complexes of lanthanide(III) ions has also established that the stability constants were less than unity, and the complexes were probably outer sphere; *i.e.*, the chloride ion does not penetrate to the first coordination layer surrounding the ion.[27] Similar changes in the shape of Nd^{3+} bands in HCl, LiCl, and $HClO_4$ solutions provide additional evidence that coordination of the anion is not involved.

A CN change for the Nd^{3+} ion from 9 to 8 in concentrated electrolyte solutions is reasonable, since Nd^{3+} must compete with H^+ or Li^+ ions for water of hydration. By simple stoichiometry, an 11 *M* HCl solution has 3.8 water molecules per hydrogen ion; if totally ionized, all H^+ ions could not reach their normal 4-coordination. A deficiency of water also exists in concentrated LiCl and $HClO_4$ solutions, and provides a strong driving force for decreasing the CN of Nd^{3+}. The competition among the cations for water of hydration is accentuated at elevated temperatures, since both lithium and hydrogen ions have a higher entropy of solution (3.4 cal/deg mole for Li_{aq}^+, 0.00 cal/deg mole for H_{aq}^+)[28] than the Nd_{aq}^{3+} ion (estimated, -44.5 cal/deg mole based on -44 cal/deg mole for Ce^{3+}), and thus they become relatively stronger competitors for water.

The decrease to a CN of 8 for Nd^{3+} in concentrated chloride solutions may be typical for other normally CN 9 lanthanide ions. The lack of a shape change in the absorption bands of Ho^{3+} and Er^{3+} indicates that these ions and other normally CN 8 lanthanides do not change coordination in concentrated electrolyte solutions. Thus, all lanthanide ions in concentrated chloride solutions probably exist as a single species, possibly $Ln(H_2O)_8{}^{3+}$. In the same solution, trivalent actinides are present mainly as monochloro complexes[29] of unspecified coordination. It is inferred that the existence of all lanthanide ions as similar species and actinide ions as similar, but different, species is an essential factor in the group separation of lanthanides from trivalent actinides. The lack of success of actinide–lanthanide group separations from solutions other than concentrated chloride, or thiocyanate,[30] shows that division of these groups as separate species in the aqueous phase is not easily achieved, at least under conditions that permit ion-exchange or solvent extraction operations.

A puzzling solvent extraction effect[31] is the extraction of representative lanthanides from 0.3 *M* HNO_3 by tributyl phosphate in direct order of atomic number, but from concentrated HNO_3 or HCl in reverse order. Although other factors influence solvent extraction selectivity, a change in CN for the "light" lanthanide ions could be a contributing cause to this effect.

The intensity changes in the hypersensitive bands of Nd^{3+}, Ho^{3+}, and Er^{3+} can be explained as due to the action of the increased electromagnetic field in the medium surrounding the ion, as suggested[4] by the theoretical mode for hypersensitivity. This model proposes that an enhancement of the variation of the electric vector of the electromagnetic radiation across the ion greatly increases the intensity of normally weak ($P \approx 10^{-11}$) quadrupole transitions.

The effect of solution concentration on oscillator strengths is consistent with the theoretical picture. The field on lanthanide ions is enhanced in concentrated solutions, as water in the secondary hydration layer is replaced with anions or hydrated cations. Both will increase the field on the ion, the anions by electrostatic interaction and the hydrated cations by reversing, in effect, the direction of the water dipoles from their direction in dilute aqueous solutions. Temperature effects in concentrated solutions probably result from entropy differences between the Li^+ ion and the lanthanide ions; this view is supported by the lack of a significant effect in dilute aqueous solutions.

Effects discovered in this work that invite theoretical clarification are the invariance of the oscillator strengths for the nonhypersensitive bands of Nd^{3+} while marked changes in band shape occur, the constant ratio of the oscillator strengths of the two hypersensitive Er^{3+} bands, and the effect of temperature on hypersensitivity.

The comparison of the band shapes in the spectra of

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lanthanide ions to indicate the coordination of the aqueous ion appears applicable to aqueous solutions. Although a strictly qualitative effect, there are published examples[24,25] where the coordination of the Nd^{3+} ion can be inferred from the shape of the absorption bands. Application to other lanthanide ions, and to other systems, might permit a better understanding of lanthanide coordination behavior.

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Parameter-Free Molecular Orbital Calculations

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A method is outlined for the calculation of electronic energy levels of transition metal complexes. The procedure is completely specified for a given choice of atomic wave functions and does not involve the use of arbitrary parameters for the evaluation of the matrix elements. The method is used to calculate the energies and molecular orbitals of four octahedral and seven tetrahedral chloro complexes. The results are evaluated in terms of Δ values, nephelauxetic B and β values, bond orders, overlap populations, stretching frequencies, and chlorine nqr results. The calculations substantiate increased covalency as a function of formal oxidation state by comparison of overlap populations with stretching frequencies and the correlation between calculated and experimental nephelauxetic β values. For different transition metals in the same oxidation state, an increase in covalent character with increasing atomic number is observed.

Introduction

In our recent publications,[2,3] we outlined a calculational procedure for estimation of the relative positions of the electronic energy levels of transition metal complexes. At that time, computational limitations necessitated the introduction of two parameters, R_σ and R_π, which were employed in the estimation of sums of two-center electrostatic interaction integrals. These two parameters were held constant for the series of fluoride complexes then under investigation. In this report, we shall indicate that not only was the assumption of constant R values a reasonable one, but also that it is possible to carry out the molecular orbital calculations without the introduction of these parameters. That is, for a proper basis set of atomic wave functions, we shall propose a calculational method which is completely specified. The procedure has been tested by application to four octahedral and seven tetrahedral chloride complexes of first-row transition metals. The accord achieved between experimental observables and the values calculated from the theoretical results are very satisfying and indicate that the calculational model holds promise for the elucidation of the electronic structures of metal complexes.

Matrix Elements of the Secular Determinant

The Diagonal Element.—As in our previous work,[2,3] the diagonal terms involving the metal wave functions, χ_i, are given by

$$(\chi_i|\mathcal{H}|\chi_i) = \epsilon_\chi(q_M) - \sum_{j=1}^{n} q_j(1/r_j|\chi_i\chi_i) \qquad (1)$$

where $\epsilon_\chi(q_M)$ is the orbital energy of the metal electron in the free ion of charge q_M, and the second term is the crystal field potential due to the ligand point charges, q_j. Both q_M and q_j are evaluated by means of the Mulliken electron population analysis[4] and it is required that self-consistency be established between the initial choices and final calculated values of q_M and q_j.

The ligand diagonal terms, exclusive of ligand–ligand interaction, have the form

$$(\phi_i|\mathcal{H}|\phi_i) = \epsilon_{\rho i1}(q_1) - q_M(1/r_M|\rho_{i1}\rho_{i1}) + \sum_{j=2}^{n} (1/r_j|\rho_{i1}\rho_{i1}) \qquad (2)$$

where $\epsilon_{\rho i1}$ is the orbital energy of the electron in the ith orbital of ligand 1 and of charge q_1, and the second and third terms constitute the crystal field potential due to the metal ion of charge q_M and the other ligands with charges q_j.

The concepts which led to the formulations given in eq 1 and 2 have been previously outlined.[2,3,5] It is worthwhile to note that while eq 1 and 2 are developed from consideration of the rigorous treatment of one-electron energies of closed-shell systems, the proposed method is semiempirical and deviates from rigor for the sake of computational simplicity. Furthermore, in our previous work we employed the commonly used simplification that the orbital energies, $\epsilon_{\chi i}$, could be obtained from the experimental values of the valence-state ionization energies (VSIE). This approximation has the undesirable feature that variations in the choice of the basis functions have no effect on the orbital

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(1) Abstracted in part from the thesis submitted by D. D. Radtke in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

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