with nine[11] molecules of water per xenon, these crystals are "wet," not dried solids as in the case of americium perxenate. Further work will be necessary to check this unusual high degree of hydration.

Some preliminary work has been started with studying rare earth perxenates. For example praseodymium perxenate is a green insoluble solid. It "pops" when heated on a spatula. Its infrared spectrum is similar to that of americium perxenate. However, the hydration of this salt has not as yet been studied.

The solubility[9] of the perxenates decreases in the sequence Na^+ ($2.5 \times 10^{-2}\ M$) > Li^+ ($1.0 \times 10^{-3}\ M$) > Am^{3+} ($6.1 \times 10^{-5}\ M$) > Ba^{2+} ($2.3 \times 10^{-5}\ M$).

This study does not answer the problem of the oxidation of Am(III) in acid solutions by xenate or perxenate. A high yield (up to 80%) of Am(VI) has, however, been attained on the acid dissolution of the americium(III) perxenate prepared in basic solutions.

[11] A. Zalkin, J. D. Forrester, D. H. Templeton, S. Williamson, and C. W. Koch, *J. Am. Chem. Soc.*, **86**, 3569 (1964).

Contribution from the Department of Chemistry, Florida State University,
Tallahassee, Florida, and Euratom, Institut für Transurane, Karlsruhe, Germany

Environmental Effects on f–f Transitions.[1] I. Neodymium(III)

By G. R. CHOPPIN,[2a] D. E. HENRIE,[2a] and K. BUIJS[2b]

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The changes in the absorption spectrum (visible and near-infrared) of neodymium(III) have been studied in various media. It has been found that ligands may be divided into groups based upon their effect on the spectrum. The ligands within each group share certain chemical and physical characteristics suggesting that covalent effects are important for complexes of the rare earths. The use of spectral modifications to differentiate between inner- and outer-sphere complexes is discussed, and the behavior of the "hypersensitive" $^4I_{9/2} \longrightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition is discussed in relation to recent hypotheses concerning the origin of this effect.

Introduction

The correlation between structure and absorption spectra for complexes of the transition metals is rather well understood in terms of the ligand field theory. Regrettably, the same situation is not true for complexes of the lanthanide and actinide metals. It is well-known that the visible and near-infrared absorption spectra, consisting of narrow bands due to electronic transitions (Laporte forbidden) within the f^n configuration, are affected only slightly by changes in the environment of the metal ion. This is attributed to the shielding effect on the f electrons by the outer electrons of the ion.

The observed frequency changes are of the order of a few per cent,[3,4] while certain band intensities change by factors of 2 to 4.[5] Stark splittings due to a ligand field plus changing intensities give rise to marked variations in band shape. Moreover, interpretation of the spectra of rare earth ions in aqueous solutions is often greatly complicated by the simultaneous occurrence of several complex species. Only in the cases of well-defined complexes can certain conclusions be drawn from the absorption spectra concerning structure.

Recent theoretical work[6,7] has made variations in intensity more susceptible to interpretation. This study concerns the environmental effects on the spectrum of Nd(III) in an attempt to discover possible systematic effects connected with inner- and outer-sphere complex formation, anionic complexes attached to ion exchangers, and structural similarities of ligands. The variation in the intensity of the "hypersensitive" transition $^4I_{9/2} \rightarrow {}^4G_{5/2}$ is discussed in relation to the theory of Judd and Jørgensen[3] as to the origin of these effects. The neodymium acetate system is emphasized since by using the stability constants a more complete analysis was feasible. Other systems, where such an analysis is not at present possible, are discussed more qualitatively.

Experimental Section

The spectral measurements were made using a Cary Model 14 spectrophotometer and both 1- and 5-cm fused silica cells. All chemicals were reagent grade materials. The Nd(III) concentration in the aqueous solutions was approximately $0.015\ M$ for all systems but acetate, where the concentration was $0.067\ M$. The trinonylamine (TNA) was dissolved in ether (40% solution for Cl^- and SCN^-, 20% for NO_3^-). As anion-exchange resin, Dowex 1X1 was used. Saturated solutions of salts of the complexing anions, containing Nd(III), were run through a small column of Dowex 1X1 until the resin by visual estimation contained the appropriate amount of Nd(III). In cases where the complex is strongly held by the resin (such as with nitrate com-

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[1] This work was carried out jointly within the European Transplutonium Program under Contract 002/61/2 TPU B and with support of the U S. Atomic Energy Commission, Contract AT-(40-1)-1797.

[2] (a) Florida State University; (b) Euratom.

[3] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962.

[4] L. I. Katzin and M. L. Barnett, *J. Phys. Chem.*, **68**, 3779 (1964).

[5] C. K. Jørgensen and B. R. Judd, *Mol. Phys.*, **8**, 281 (1964).

[6] B. R. Judd, *Phys. Rev.*, **127**, 750 (1962).

[7] G. S. Oefelt, *J. Chem. Phys.*, **37**, 511 (1962).

TABLE I

Nd^{3+} OSCILLATOR STRENGTHS ($P \times 10^6$)

Transition	Energy range, cm^{-1}	H_2O[a] (μ = 1.0 *M*)	H_2O[b] (μ = 2.0 *M*)	Acetate 0.0285 *M*	Acetate 0.0570 *M*	Acetate 0.0855 *M*	Acetate 0.1140 *M*
$^4I_{9/2} \rightarrow {}^2G_{7/2}, {}^4G_{5/2}$	16,500–18,200	8.3	7.9	8.2	8.7	9.7	10.9
$^4I_{9/2} \rightarrow {}^2H_{9/2}, {}^4F_{5/2}$	12,000–13,000	7.7	7.6	7.2	7.4	7.4	7.4

[a] D. C. Stewart, Argonne National Laboratory Report ANL-4812 (1952). [b] This work.

plexes), the amount of Nd(III) to be used could also easily be calculated. The column was then washed with toluene and the resin transferred to a 0.5-cm rectangular absorption cell. A uniform distribution was obtained by centrifuging the resin under toluene in the absorption cell. The resulting sample was essentially free from scattering. A blank was prepared using the same procedure omitting the Nd(III). The spectra of the acetate complexes were measured in solutions with a constant ionic strength of 2.0 *M* using $NaClO_4$ as the inert electrolyte.

Results and Discussion

Acetate Complexes.—The effect of total acetate concentration on the oscillator strengths of two bands of Nd(III) is shown in Table I. It is readily seen that the transition to the levels $^2G_{7/2}$, $^4G_{5/2}$ is greatly intensified as the total acetate concentration is varied. The other transitions show smaller variations. The total oscillator strengths are due to contributions from at least three species: the hydrated ion [M], the first complex [ML], and the second complex $[ML_2]$. The equation

$$P_{\text{obsd}} = \frac{[M]}{C_M}P_M + \frac{[ML]}{C_M}P_{ML} + \frac{[ML_2]}{C_M}P_{ML_2} \quad (1)$$

can be rearranged as

$$\frac{C_M P_{\text{obsd}} - [M]P_M}{[ML]} = P_{ML} + \frac{[ML_2]}{[ML]}P_{ML_2} \quad (2)$$

The *P*'s denote the respective oscillator strengths and C_M the total concentration of neodymium ion. Using values of the stability constants β_1 and β_2, at an ionic strength of 2 *M* ($NaClO_4$),[8] the concentration of each of the M, ML, and ML_2 species can be calculated for various concentrations of total acetate and total neodymium (Table II). (The concentration of ML_3 was negligible in the solutions studied.) Since P_M is the observed oscillator strength of the hydrated cation in the absence of acetate, P_{ML} and P_{ML_2} can be determined by a plot of the left-hand side of eq 2 *vs.* $[ML_2]/[ML]$ (Figure 1). The values of P_M, P_{ML}, and P_{ML_2} for two transitions are listed in Table II. The most interesting point here is that for all bands but one the acetate ligands have essentially no effect on the intensity. (The transition to $^2H_{9/2}$, $^4F_{5/2}$ is representative of the behavior of most of the bands.) For the transition to $^2G_{7/2}$, $^4G_{5/2}$ the first ligand has little effect, while the second produces a greater than twofold enhancement.

TABLE II

VALUES OF ($C_M P_{\text{obsd}} - [M]P_M)/[ML] \times 10^6$ FOR THE NEODYMIUM–ACETATE SYSTEM[a]

Total ionic strength = 2.0 *M*; C_M = 0.0666 *M*

pH	C_L, *M*	$[ML_2]/[ML]$	Upper levels involved in the transition $^2G_{7/2}, {}^4G_{5/2}$	$^2H_{9/2}, {}^4F_{5/2}$
3.52	0.0285	0.021	10.2 ± 2.8	4.6 ± 2.7
3.58	0.0570	0.051	11.8 ± 1.3	7.0 ± 1.2
3.64	0.0855	0.090	13.9 ± 0.7	7.7 ± 0.7
3.70	0.1140	0.140	15.9 ± 0.5	8.0 ± 0.5
Oscillator strength				
	$P_M \times 10^6$		7.9	7.6
	$P_{ML} \times 10^6$		9.5 ± 0.1	5.6 ± 0.3
	$P_{ML_2} \times 10^6$		46 ± 1	19 ± 3

[a] Error limits were estimated by assuming that [M] is known to ±5%. The stability constants (β_1 = 81.3, β_2 = 1107) were taken from ref 8.

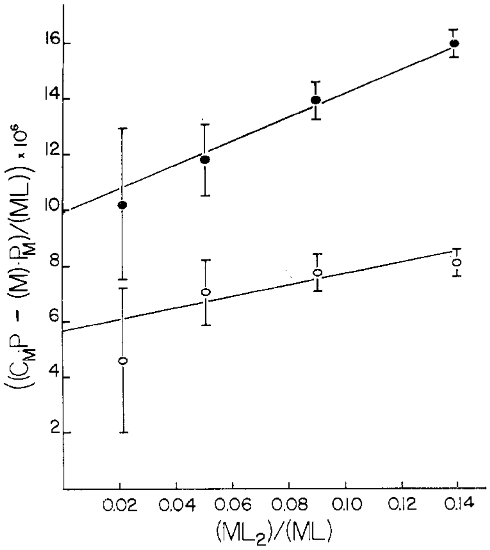

Figure 1.—Plot of $(C_M P_M - (M)P_M)/(ML) \times 10^6$ *vs.* $(ML_2)/(ML)$ for the Nd(III)–acetate system: ●, $^4I_{9/2} \rightarrow {}^2G_{7/2}, {}^4G_{5/2}$; O, $^4I_{9/2} \rightarrow {}^2H_{9/2}, {}^4F_{5/2}$.

It has been illustrated many times[3,5,9-14] that certain transitions in the lanthanides are extremely sensitive to changes in the environment of the ion. Jørgensen and Judd[3] have made a thorough study of the mechanisms which might account for this "hypersensitivity" and conclude that these transitions are most likely "pseudoquadrupole" in nature. An asymmetric distribution of the dipoles induced by the electromagnetic field in the environment about the ion causes the variation of the electric vector across the ion to be much greater than for the case of a homogeneous dielectric. This results in the enhancement of electric quadrupole transitions which normally are very weak.

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(8) I. Grenthe, *Acta Chem. Scand.*, **18**, 283 (1964).

(9) W. T. Carnall, P. R. Fields, and B. G. Wybourne, *J. Chem. Phys.*, **42**, 3797 (1965).

(10) T. Moeller and W. F. Ulrich, *J. Inorg. Nucl. Chem.*, **2**, 164 (1955).

(11) A. Sonnesson, *Acta Chem. Scand*, **12**, 1937 (1958).

(12) W. T. Carnall, *Anal. Chem.*, **34**, 786 (1962).

(13) W. T. Carnall, *J. Phys. Chem.*, **67**, 1206 (1963).

(14) I. Abrahamer and Y. Marcus, Israel Atomic Energy Commission Report IA-809 (1963).

TABLE III

ABSORPTION WAVELENGTHS (A) OF Nd(III) IN VARIOUS SYSTEMS

Anion	System	Transitions				
		$^4I_{9/2} \rightarrow {}^4S_{3/2}, {}^4F_{7/2}$			$^4I_{9/2} \rightarrow {}^4F_{5/2}, {}^2H_{9/2}$	
ClO_4	0.5 *M* $HClO_4$	7312 (41)	7398 (61)		7935 (100)	8002 (55)0
Cl	12 *M* LiCl		7417 (50)	7483 (59)		8009 (10)
	Dowex Cl^- complex		7405 (85)		7947 (100)	
	TNA Cl^- complex			7447 (78) 7494 (90)		8054 (97) 8112 (100)
SCN	10 *M* NH_4SCN	7333 (39)	7412 (67)	7480 (65)	7957 (100)	8009 (94)
	Dowex 1 SCN^- complex		7417 (48)	7505 (72)		8024 (100)
	TNA SCN^- complex			7470 (100)		8035 (75)
NO_3	10 *M* $LiNO_3$	7335 (63)	7385 (69)		7944 (100)	
	Dowex 1 NO_3^- complex	7310 (94)			7924 (100)	
	TNA NO_3^- complex	7319 (92)		7446 (54)	7959 (100)	
NO_2	2 *M* $NaNO_2$ (pH 4.9)	7328 (45)	7417 (66)		7946 (100)	
	Dowex 1 NO_2^- complex		7405 (67)		7957 (100)	
Ac	5 *M* NAOac	7340 (62)	7390 (71) 7419 (71)		7971 (100)	
	Dowex 1 OAc^- complex	7350 (52)	7410 (64)		7980 (100)	
CO_3	5 *M* K_2CO_3	7333 (71)	7405 (84)		7973 (100)	
EDTA	EDTA	7341 (56)	7384 (42) 7406 (48)	7451 (66)	7993 (100)	
OCN	7 *M* KOCN (pH 10.35)	7335 (63)	7411 (71)	7443 (65)	7981 (100)	

[a] Numbers in parentheses are relative peak heights.

The intensity of pure electric quadrupole transitions has a third-power dependency on the transition energy while for these enhanced transitions a first-power dependence is observed; hence, the nomenclature suggested by Jørgensen and Judd—"pseudoquadrupole" transitions.

The oscillator strengths for the acetate complexes provide some interesting evidence which seems to support this mechanism of intensity enhancement. If the environment about the ion were to become more asymmetric, the pseudoquadrupole transitions should become more intense relative to the other transitions. This is the case for the species ML_2, while the intensity of the pseudoquadrupole transition for the species ML is essentially the same as that for the aquo ion. The thermodynamic parameters for complex formation[8,15] indicate that the first acetate ligand is incorporated into the primary hydration sphere. Thus it seems likely that the environment about the ions in the aquo species and in the species ML must be similar, while the symmetry of the environment must be different (more asymmetric) for the ML_2 species. If the acetate ligand replaces only one water molecule in the primary hydration sphere, the Nd(III) ion would still be surrounded by almost the same arrangement of oxygen atoms. The significant change in symmetry of the second complex is not too surprising, as the presence of two acetate ligands could cause displacement of a relatively large number of water molecules due to steric effects and reduction of the charge on the cation. More recently, Judd[16] has suggested that the hypersensitivity may be due to the symmetry of the crystal field. While our results are also consistent with this mechanism, not much more can be said since the symmetries of the various species are unknown.

The transition $^4I_{9/2} \rightarrow {}^2P_{1/2}$ at 23.368 K (4279 A) shows an interesting effect as the acetate concentration is varied as shown in Figure 2. The nature of this effect suggests that a distinct peak may be assigned to the acetate complex. An estimated shift to lower energy corresponding to −20 K due to the first ligand and −60 K due to the second ligand can be obtained from this datum. This shift corresponds to a small increase in covalency of the metal–ligand bonds, apparently supporting Judd and Jørgensen's conclusion that covalency changes do not produce enhancement of the hypersensitive transitions since there is an increase in covalency for the species ML, relative to the aquo ion, but essentially no intensity enhancement occurs.

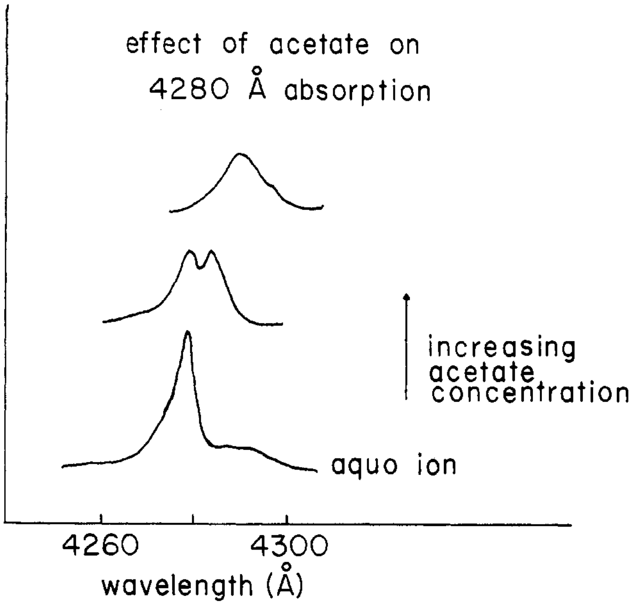

Figure 2.—Effect of acetate on 4280 A absorption of Nd(III).

Other Complexes.—In a more qualitative fashion we have studied the change in band shape in a variety of

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(15) I. Grenthe, *Acta Chem. Scand.*, **18**, 293 (1964).

(16) B. R. Judd, *J. Chem. Phys.*, **44**, 839 (1966).

ligand systems for the transitions $^4I_{9/2} \rightarrow {}^4S_{3/2}, {}^4F_{7/2}$ (~7400 A) and $^4I_{9/2} \rightarrow {}^2H_{9/2}, {}^4F_{5/2}$ (~8000 A). Table III lists the systems and the observed maxima and relative intensities. Figures 3–8 show the spectra of some of these systems to indicate how the spectral shapes vary. Invasion of the hydration sphere about a lanthanide ion by a ligand could be expected to affect the band shapes due to the changes in the relative intensities of the component lines in each band resulting from the alterations in the strength and symmetry of the field about the Nd(III) ion.

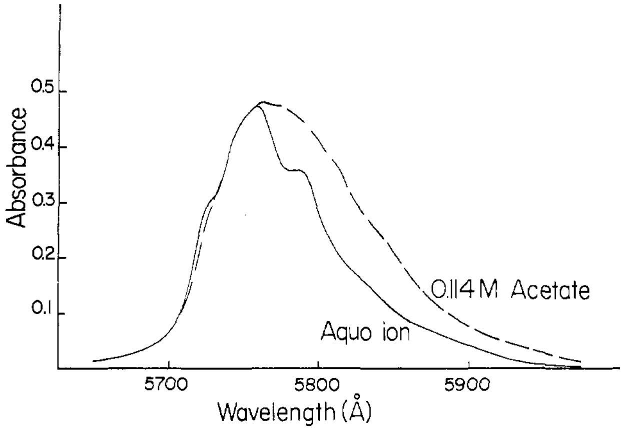

Figure 3.—Effect of acetate on $^4I_{9/2} \rightarrow {}^2G_{7/2}, {}^4G_{5/2}$ absorption of Nd(III).

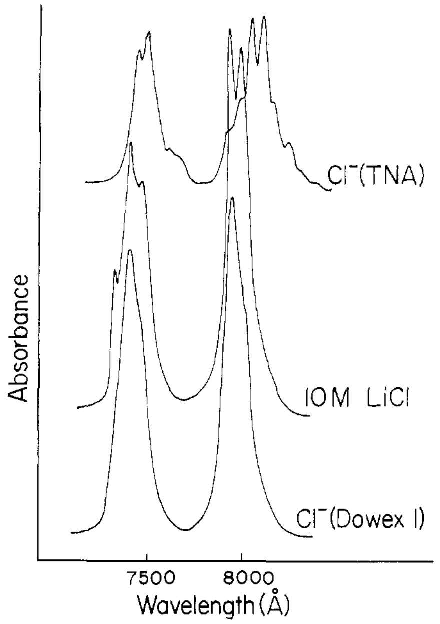

Figure 4.—Chloride complexes of Nd(III) (spectral region 7000–8500 A).

Although the parameter $(A_{7935} - A_{7970})/(A_{8000} - A_{7970})$ does not have any physical significance, it is most descriptive of the changes in line shape. The effects of Cl^-, SCN^-, NO_3^-, ClO_4^-, and acetate are shown in Figure 9. It is evident that only above 4 and 1 *M*, respectively, does the presence of Cl^- and SCN^- ion change the spectrum. However, using other methods, it has been established that even at a concentration of 0.1 *M* appreciable complex formation takes place in these solutions.[17] The small values of the thermodynamic parameters for the first Cl^-, SCN^-, and NO_3^- complexes of various lanthanide ions support the suggestion that at anion concentrations below 1 *M* a shell of water molecules separates the ion from the ligands (outer-sphere ion pairs). Jørgensen[18] reports a similar spectral behavior for the 4273 A ($^4I_{9/2} \rightarrow {}^2P_{1/2}$) absorption of Nd(III) in chloride solutions and also suggests outer-sphere complexing as the explanation. The question then arises as to why NO_3^-

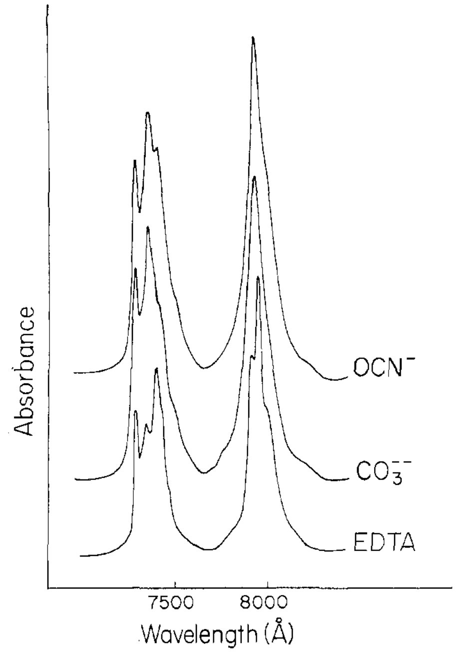

Figure 5.—Cyanate, carbonate, and EDTA complexes of Nd(III) (spectral region 7000–8500 A).

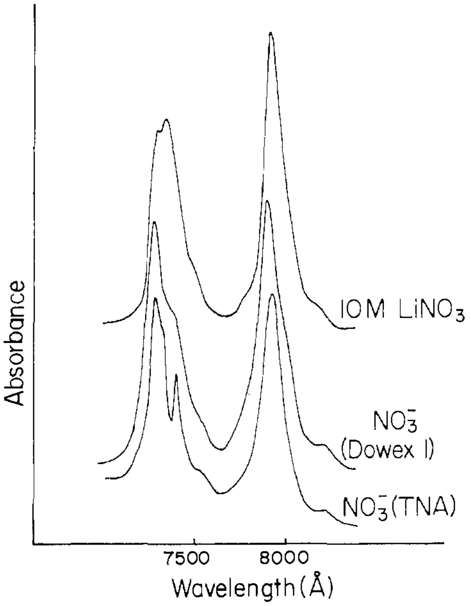

Figure 6.—Nitrate complexes of Nd(III) (spectral region 7000–8500 A).

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(17) G. R. Choppin and W. F. Strazik, *Inorg. Chem.*, **4**, 1250 (1965).

(18) C. K. Jørgensen, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.*, **30**, No. 22 (1956).

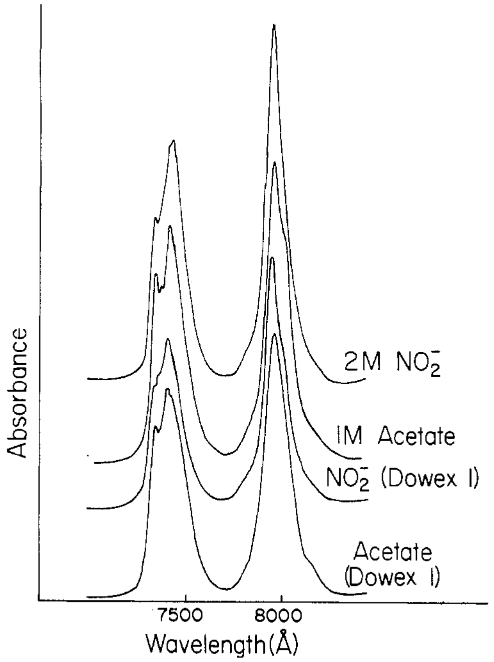

Figure 7.—Nitrite and acetate complexes of Nd(III) (spectral region 7000–8500 A).

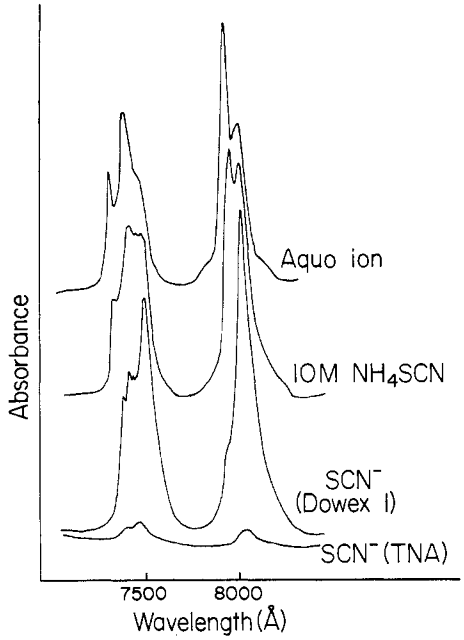

Figure 8.—Aquo ion and thiocyanate complexes of Nd(III) (spectral region 7000–8500 A).

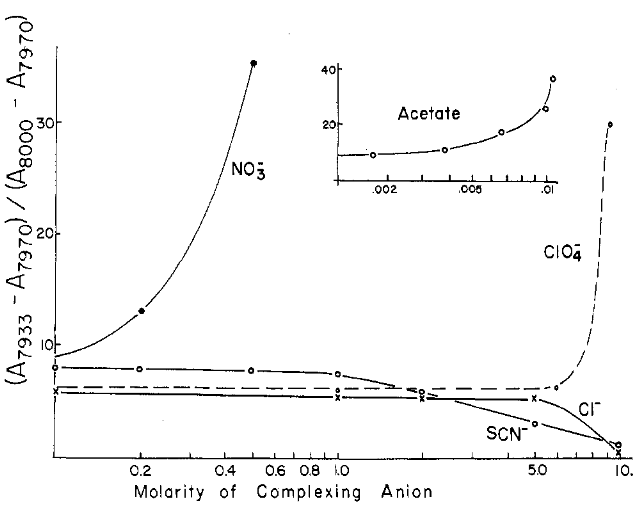

Figure 9.—Effect of selected ligands on line shape of $^4I_{9/2} \rightarrow {}^2H_{9/2}, {}^4F_{5/2}$ absorption.

affects the spectrum at very low concentrations, whereas Cl^- and SCN^- do not. The wavelength shifts in dilute NO_3^- media are practically nil, and the "hypersensitive" transition $^4I_{9/2} \rightarrow {}^2G_{7/2}, {}^4F_{5/2}$ shows a slight intensification relative to the other bands. In concentrated NO_3^- media, on the other hand, there is a definite red shift of the ^4F levels and the intensification is more marked. By comparing the effects of acetate and NO_3^- on the spectrum of Nd^{3+} one is led to the conclusion that the small spectral changes in dilute NO_3^- media are due to a small concentration of the "inner-sphere" neodymium nitrate complex in equilibrium with a much larger concentration of the "outer-sphere" complex. Concentrated chloride media have only a small effect on the $^4I_{9/2} \rightarrow {}^2G_{7/2}, {}^4G_{5/2}$ transition, apparently causing a slight decrease in its intensity relative to the other bands. These data lead us to suspect that Cl^- and SCN^- have much less effect due to a weaker interaction with the water molecules in the primary hydration layer of Nd(III).

Gallagher[19] has shown that for aqueous solutions of $EuCl_3$ there are modifications in the "intensity" of the $^3F_0 \rightarrow {}^5D_2$ transition at concentrations below 1 *M*. This differing sensitivity as compared with the Nd(III) case is surprising, and a study of this with reference to the lanthanide series is presently being undertaken. A possible explanation is that the affected level in Eu(III) is at a higher energy (21.5 kK) than the sensitive level in Nd(III) (17.3 kK).

The effect of various anions is summarized in Table IV in a qualitative review, permitting the observation of certain trends which suggest that in solution the anions can be divided into a number of groups according to their influence on the two band groups at 7900 and 8000 A: group I: Cl^-, SCN^-; group II: NO_3^-; group III: NO_2^-, OCN^-, CH_3COO^-, $CH_3CH_2COO^-$, $(CH_3)_2CHCOO^-$, CO_3^{2-}; group IV: EDTA.

Group I is composed of anions of strong acids which contain no oxygen and form relatively weak outer-sphere complexes below 1 *M* anion concentration.

Group II (NO_3^-) is different from the group III anions in the strength of the corresponding acid. In addition, NO_3^-, at low concentrations, shows different effects on the positions of maxima.

The group III spectra are most similar to that of the aquo ion; the intermediate environment about Nd(III) is composed of oxygen atoms; the complexes are of the inner-sphere type.

Group IV (EDTA) forms a very strong complex by a multidentate ligand.

The spectra of the complex species on Dowex 1 are similar to the spectra in concentrated aqueous solu-

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[19] P. K. Gallagher, *J. Chem. Phys.*, **41**, 3061 (1964).

TABLE IV

INFLUENCE OF COMPLEXING ANIONS ON Nd(III) BANDS NEAR 8000 AND 7400 A

Anion	Change in ratio A_{max} (8000 A)/ A_{max} (7940 A)	Wavelength shifts of individual peaks compared with aquo ion	Effect on 7400 A band group
SCN^-	Solutions, Dowex 1, TNA: continuous decrease	Solutions and Dowex: 8000 A peak <0.3%	Increase intens. long wavelength peaks
Cl^-	Solutions: continuous decrease. Dowex 1 and TNA: irregular	Solutions: 8000 A peak <0.1%	Increase intens. long wavelength peaks
NO_3^-	Solutions, Dowex 1, TNA: continuous increase	Solutions and Dowex: 7940 A peak <0.2%	Increase intens. short wavelength peaks
NO_2^-	Solutions, Dowex 1: continuous increase	Solutions and Dowex: 7940 A peak <0.3%	Broadening central peak. Decrease others
CO_3^{2-}	Solutions: increase	Solutions: 7940 A peak < 0.5%	Slight wavelength shifts
OCN^-	Solutions: continuous increase	Solutions: 7940 A peak <0.6%	Broadening central peak. Decrease others
CH_3COO^-	Solutions, Dowex 1: continuous increase	Solution and Dowex: 7940 A peak <0.6%	Broadening central peak. Decrease others
EDTA	Uncertain[a]	Uncertain[a]	Decrease intens. central peaks, increase long wavelength peak

[a] The 7993 A band of EDTA complexes probably corresponds to the 7940 A band of the aquo ion, but this is not certain.

tions (except for the chloride complexes). This indicates that in these cases the picture of the ion-exchange resin as a very concentrated aqueous solution is correct. Ternary amines like TNA belong in general to a different class of solutions since they are nonaqueous. Consequently, it is not surprising that the spectra in TNA do not resemble closely their analogs in Dowex 1.

Summary and Conclusions

The data indicate that care must be exercised in attempting to distinguish between inner- and outer-sphere complexes by considering spectral modifications as illustrated here in the case of nitrate.

Our results also suggest that both changes in line shape and the intensities of hypersensitive transitions can be used as a qualitative indication of symmetry. The spectral distinctions between groups I, II, III, and IV which correlate with differences in complex type as well as acid strength are difficult to understand by electrostatic arguments alone. Our results would seem to support the conclusions of a recent paper by Katzin and Barnett[4] that covalent effects are important in lanthanide complexes.