Contribution from the Department of Chemistry,
University of Delaware, Newark, Delaware 19711, U.S.A.

Rare Earth Pseudohalide Complexes[1]

J. L. Burmeister, S. D. Patterson, and E. A. Deardorff

Received August 17, 1968

The synthesis and characterization of thiocyanate complexes of the type $[(n\text{–}C_4H_9)_4N]_3[M(NCS)_6]$ *for all of the tripositive rare earth ions except* Ce^{III}, Pm^{III}, Tm^{III}, *and* Lu^{III} *is described. The analogous selenocyanate and cyanate complexes were found to be very unstable, decomposing even in an inert atmosphere at low temperatures. Infrared spectral measurements indicate that the pseudohalides are N-bonded in all of the complexes. The thiocyanate complexes do not dissociate appreciably in poorly coordinating solvents such as nitrobenzene and acetonitrile. Visible spectral measurements in the latter solvent reveal striking differences in the number and intensity of the bands in the spectra of the thiocyanate complexes, relative to those in the spectra of the hexachloro complexes of the same metal ions. The enhancement of the intensity of the bands in the thiocyanate spectra is indicative, especially in the case of the hypersensitive pseudoquadrupolar transitions, of a marked deviation from* O_h *symmetry, and may be attributed to non-linear M-NCS linkages. The molar absorptivities of the bands are even larger than those of the corresponding bands in the spectra of the aquo ions,* $[M(H_2O)_9]^{3+}$, *which lack a center of symmetry. The* Pr^{III} *and* Ho^{III} *thiocyanate complexes were found to be photosensitive, the nature of the reaction being unknown.*

Introduction

Complex species involving rare earth metal ions, when compared with those of the d-type transition metals, are limited in number and notably stable only when derived from the strongest chelating agents, usually those with highly electronegative oxygen donor atoms.[2] It was therefore somewhat surprising to discover[3] that yttrium(III), possessing no 4d electrons and being intermediate in size between holmium(III) and erbium(III), forms a stable isoselenocyanate complex, $[Y(NCSe)_6]^{3-}$. This suggested the possibility of synthesizing a class of pseudohalide (NCS^-, $NCSe^-$, NCO^-) complexes of the tripositive rare earth ions. No such complexes have previously been isolated, although the stability constants for the formation of outer sphere ion pair $M(NCS)^{2+}$ and $M(NCS)_2^+$ complexes, where $M = Nd^{III}$ and Eu^{III}, have been determined[4] using a solvent extraction method, and the reactivity of some rare earth thiocyanate complexes toward ion exchangers has been studied.[5] Hart and Laming[6] have reported the synthesis of complexes of the type $M(dipy)_3(NCS)_3$, where $M = La^{III}$, Ce^{III} and Dy^{III}, and dipy is 2,2′-dipyridine. They were unable to determine the bonding mode of the thiocyanate groups, a feature of interest in the present study, insofar as the effect of the slowly decrasing size of the metal ions is concerned.

Experimental Section

Preparation of Complexes. Thiocyanate Complexes. Complexes of all of the tripositive rare earth ions, except Ce^{III}, Pm^{III}, Tm^{III}, and Lu^{III}, having the general formula $[(n\text{–}C_4H_9)_4N]_3[M(NCS)_6]$ were prepared by the same method. An ethanolic solution (9 mmole/15 ml.) of potassium thiocyanate, warmed to *ca.* 50° to effect complete dissolution, was slowly added to an ethanolic solution (3 mmole/5 ml.) of the appropriate rare earth(III) chloride hexahydrate [anydrous chloride, in the case of Pr^{III} and Nd^{III}]. The resulting solution was stirred at 50° for 0.5 hr., then allowed to cool to room temperature, whereupon the precipitated potassium chloride was removed by filtration. The filtrate was added to 10 ml. of an ethanolic solution containing 9 mmoles of tetra-n-butylammonium thiocyanate (prepared by the metathetical reaction of potassium thiocyanate and tetra-n-butylammonium bromide in ethanol, precipitation being effected by the addition of anhydrous ethyl ether after removal of the potassium bromide by-product by filtration). After stirring the resulting solution at 50° for 0.5 hr., its volume was reduced on a steam bath, and the remaining solution cooled to 0°. The process was repeated until crystallization occurred. The product was isolated by filtration, washed with cold ethanol and anhydrous ethyl ether, and dried *in vacuo*. The Pr^{III} and Nd^{III} complexes were precipitated by pouring the ethanolic solutions into 4 l. of anhydrous ethyl ether, isolated by filtration, washed with anhydrous ethyl ether, and dried *in vacuo*. The colors, yields, melting points, and microanalytical data for the complexes are shown in Table I.

---

[1] Presented, in part, at the X. International Conference on Coordination Chemistry, Nikko, Japan, September 12-16, (1967).

[2] T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel, and W. J. Randall, *Chem. Rev.*, *65*, 1 (1965).

[3] J. L. Burmeister and L. E. Williams, *Inorg. Chem.*, *5*, 1113 (1966).

[4] G. R. Choppin and J. Ketels, *J. Inorg. Nucl. Chem.*, *27*, 1335 (1965).

[5] J. P. Surls, Jr. and G. R. Choppin, *J. Inorg. Nucl. Chem.*, *4*, 62 (1957).

[6] F. A. Hart and F. P. Laming, *J. Inorg. Nucl. Chem.*, *27*, 1825 (1965).

Table I. Colors, Yields, Melting Points, and Analytical Data for the $[(n\text{-}C_4H_9)_4N]_3[M(NCS)_6]$ Complexes.

				Analyses, %							
			Melting	Theory				Found			
M^{III}	Color	% yield	point, °C[a]	C	H	N	S	C	H	N	S
Pr	pale yellow-green	91	156	53.34	8.95	10.36	15.81	53.45	9.16	10.41	15.92
Nd	pale blue-violet	87	160	53.16	8.92	10.33	15.77	53.07	9.10	10.43	15.82
Sm	pale orange	87	168	52.89	8.88	10.28	15.69	52.65	8.89	10.35	15.68
Eu	pale yellow-orange	65	165	52.82	8.86	10.26	—	52.40	8.40	10.20	—
Gd	pale orange	86	169	52.60	8.83	10.22	—	52.54	8.66	10.37	—
Tb	white	74	168	52.54	8.82	10.21	—	52.38	8.59	10.28	—
Dy	pale orange	90	171	52.37	8.79	10.18	15.53	52.19	8.82	10.16	15.55
Ho	pale orange	77	167	52.27	8.77	10.16	15.50	52.35	8.69	9.97	15.35
Er	peach	83	170	52.17	8.76	10.14	15.47	51.90	8.92	10.06	15.80
Yb	white	77	174	51.93	8.72	10.09	—	51.73	8.64	10.18	—
$[(n\text{-}C_4H_9)_4N]NCS$				67.94	12.07	9.32	10.67	67.85	12.01	9.31	10.52

[a] Uncorrected.

Table II. Molar Conductances of the $[(n\text{-}C_4H_9)_4N]_3[M(NCS)_6]$ Complexes[a]

	Λ_M, ohm^{-1} cm^2 mole^{-1}		
M^{III}	nitrobenzene[b]	acetonitrile	N,N-dimethylformamide[c]
Pr	82.4	472	414
Nd	77.8	457	420
Sm	76.6	468	362
Eu	—	—	341
Gd	—	—	394
Tb	—	—	424
Dy	72.7	430	372
Ho	66.7	440	416
Er	72.1	417	440
Yb	—	—	385
$[(n\text{-}C_4H_9)_4N]Br$	24.8	170	—
$[(n\text{-}C_4H_9)_4N]NCS$	38.8	181	—
$[(n\text{-}C_4H_9)_4]_2[Zn(NCSe)_4]$	58.2	284	—
$[(n\text{-}C_4H_9)_4N]_3[Fe(NCS)_6]$	83.7	527	—

[a] 10^{-3} *M* solutions at 25°C. [b] Phillips and Tyree [D. J. Phillips and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, *83*, 1806 (1961)] give the following ranges for molar conductances in nitrobenzene (25°, 10^{-3} *M*): 1:1, 20-30; 2:1, 40-60; 3:1, 60-90. [c] The molar conductance of a 3:1 electrolyte would be excepted to fall in the 200-260 range [J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, *J. Am. Chem. Soc.*, *83*, 3770 (1961)].

Table III. Infrared Data for the Complexes.

Compound	C-X stretch,[a] $\nu_1(XCN)$, cm^{-1}	NCX bend,[a] $\nu_2(XCN)$, cm^{-1}	C-N stretch, $\nu_3(XCN)$ Frequency, cm^{-1}	A[b] × 10^{-4}, M^{-1}cm^{-2}
$Q_3[M(NCS)_6]$[c]				
M(III) = Pr	[d]	488, 485 m	2059[e]	13[e]
			2050[f]	14[f]
Nd	[d]	485, 481	2061[e]	13[e]
			2046[f]	17[f]
Sm	[d]	487, 483 m	2059[e]	13[e]
			2049[f]	19[f]
Eu	[d]	485, 475 m	2040 br[a]	[g]
Gd	[d]	483, 479 m	2045[f]	24[f]
Tb	[d]	485, 480 m	2050[f]	21[f]
Dy	[d]	484, 480 m	2052[e]	18[e]
			2053[f]	22[f]
Ho	[d]	486, 483 m	2053[e]	18[e]
			2045[f]	32[f]
Er	[d]	486, 483 m	2055[e]	18[e]
			2050[f]	32[f]
Yb	[d]	487, 483 m	2048[f]	30[f]
KSCN	749[h]	486, 471[h]	2068[i]	7.2[i]
$Q_3[Pr(NCSe)_6]$[c]	618 m	428 m 417 w	2055 br[a]	[g]
KSeCN	558[j]	424, 416[j]	2078[i]	4.9[i]
$Q_3[Er(NCO)_6]$[c]	1322 m	608 m	2155 br[a]	[g]
KOCN	1300, 1205[k, l]	636, 626[k]	2170[a, k]	[m]

[a] Nujol mull. [b] Integrated absorption intensity, calculated per mole of coordinated thiocyanate. [c] $Q = [(n\text{-}C_4H_9)_4N]^+$. [d] Obscured by absorption bands due to tetra-n-butylammonium ion. [e] 10^{-2} *M* acetonitrile solution. [f] 10^{-2} *M* methanol solution. [g] Not determined. [h] Data taken from L. H. Jones, *J. Chem. Phys.*, 25, 1069 (1956). [i] Ethanol solution, data taken from ref. 16. [j] Data taken from H. W. Morgan, *J. Inorg. Nucl. Chem.*, *16*, 367 (1961). [k] Data taken from T. C. Waddington, *J. Chem. Soc.*, 2499 (1959). [l] Doublet due to Fermi resonance between the overtone of the bending and the fundamental C-O stretching frequencies. The unperturbed C-O stretching vibration should have a value of 1254 cm^{-1} [A. Maki and J. C. Decius, *J. Chem. Phys.*, *31*, 772 (1959)]. [m] Solubility in organic solvents insufficient to permit measurement. Abbreviations: w, weak; m, medium; br, broad.

Selenocyanate Complexes. The use of the preceding method for the preparation of the selenocyanate complexes proved to be unsatisfactory. Upon prolonged standing in the cold, all solutions, except those of Pr^{III} and Nd^{III}, yielded a red decomposition product. Dilution of the Pr^{III} and Nd^{III} solutions with anhydrous ethyl ether yielded, respectively, pale green and pale blue crystals, contaminated with ionic selenocyanate. Products were obtained for the remaining rare earth ions shown in Table 1 from the reaction of 1 mmole of the rare earth chloride hexahydrate, 3 mmoles of tetra-n-butylammonium bromide, and an excess of potassium selenocyanate in cold nitromethane, followed by dilution with anhydrous ethyl ether. However, all of the selenocyanate complexes are extremely unstable, decomposing even under nitrogen at 0°. Characterization was therefore limited to infrared spectral measurements.

Cyanate Complexes. Crystals of the cyanate complexes were obtained from the reaction of 1 mmole of the rare earth chloride, 3 mmoles of tetra-n-butylammonium bromide, and an excess of silver cyanate in nitromethane, followed by filtration, removal of the solvent under vacuum, and crystallization of the resulting oils under a layer of anhydrous ethyl ether. The products thus obtained melt at room temperature and are not converted to the crystalline solid upon recooling. They are sensitive to moisture and hydroxylic solvents, being irreversibly converted to a viscous liquid. Analyses indicated silver cyanate contamination.

Physical Measurements. Carbon, hydrogen, nitrogen, and sulfur microanalyses were performed by M-H-W Laboratories, Garden City, Michigan 48135, and the Alfred Bernhardt Microanalytical Laboratory, Mülheim, Germany. Molar conductances, at 25°, of $10^{-3}M$ solutions of the thiocyanate complexes and selected reference compounds were measured with an Industrial Instruments, Inc., Model RC-16B2 conductivity bridge and a cell with platinized electrodes. The results of these measurements are shown in Table II. Infrared spectra, in the 4000-400 cm^{-1} range, of complexes held in Nujol suspension between potassium bromide plates were measured on a Perkin-Elmer Model 337 grating spectrophotometer. A Perkin-Elmer Model 421 spectrophotometer was used to record high resolution solid state and solution spectra in the C-N stretching range (2200-2000 cm^{1-}). Matched 0.1 mm sodium chloride cells were employed for the solution measurements. The integrated absorption intensities, A (M^{-1} cm^{-2}), of the C-N stretching bands of the thiocyanate complexes were determined by Ramsay's method of direct integration.[7] The infrared data for the thiocyanate complexes, representative selenocyanate and cyanate complexes, and the ionic pseudohalides are shown in Table III. Visible spectra of acetonitrile solutions of the thiocyanate complexes were recorded on a Cary 14 spectrophotometer, using matched 1 cm quartz cells. Dissociation of the complex ions in this solvent was found to be negligible, as indicated by the molar conductances shown in Table II and the observation that the addition of tetra-n-butylammonium thiocyanate ($5\times10^{-2}M$) did not result in any significant changes in the frequencies or intensities of the absorption maxima. The visible spectral data for the Pr^{III}, Nd^{III}, Sm^{III}, Ho^{III}, and Er^{III} thiocyanate complexes are compared with data for the corresponding $[MCl_6]^{3-}$ complexes[8] in Tables IV through VIII. The visible spectrum of the Dy^{III} complex is shown in Figure 1.

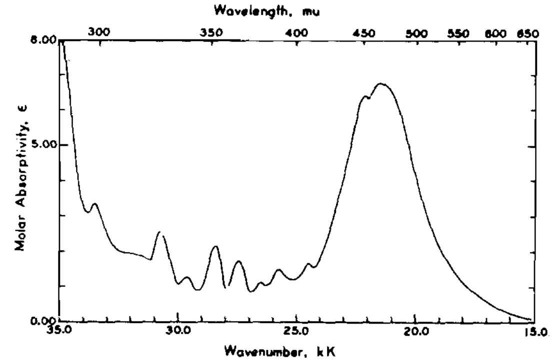


Figure 1. Visible spectrum of a $10^{-1}M$ acetonitrile solution of $[(n\text{-}C_4H_9)_4N]_3[Dy(NCS)_6]$.

Table IV. Internal $4f^2$ Transitions in Praseodymium(III) Complexes

	$[Pr(NCS)_6]^{3-}$ [a]		$[PrCl_6]^{3-}$ [b]	
Excited J Level [c]	λ_J [d]	ε_{max} [e]	λ_J [d]	ε_{max} [e]
$^1D_2$	594	3.5	592	0.09
$^3P_0$	484	6.1	485	0.94
$^3P_1$	473	6.0	475	0.40
$^3P_2$	448	13.5	450	0.34

[a] $10^{-1}M$ acetonitrile solution. [b] Data taken from ref. 8 (85% succinonitrile, 15% acetonitrile solvent). [c] Band assignments follow those of ref. 8 and Katzin and Barnett [L. I. Katzin and M. L. Barnett, *J. Phys. Chem.*, *68*, 3779 (1964). [d] Wavelength in mμ of absorption maximum. [e] Molar absorptivity ($M^{-1}cm^{-1}$).

Table V. Internal $4f^3$ Transitions in Neodymium(III) Complexes [a]

	$[Nd(NCS)_6]^{3-}$		$[NdCl_6]^{3-}$	
Excited J Level	λ_J	ε_{max}	λ_J	ε_{max}
$^4F_{9/2}$	685	1.1	686	0.05
$^2H_{11/2}$	629	0.5	—	—
?	603	2.0	—	—
$^4G_{5/2}$	589	14.1	590	5.6
$^2G_{7/2}$	586	22.5	—	—
?	578	13.1	—	—
$^2K_{13/2}$	528	6.6	—	—
$^4G_{7/2}$	526	6.7	534	0.72
$^2G_{9/2}$	513	5.7	517	0.27
$^4G_{9/2}$	478	6.5	—	—
$^2(P, D)_{3/2}$	473	6.4	—	—
$^4G_{11/2}$	463	6.7	—	—
?	461	6.7	—	—
$^2P_{1/2}$	432	4.3	434	0.11
$^4D_{3/2}$	359	5.9	358	1.0
$^2I_{11/2}$	352	5.9	—	—
$^4D_{1/2}$	345	1.8	—	—
$^4D_{7/2}$	330	3.4	—	—
?	301	3.3	—	—

[a] Notation as in Table IV.

---

(7) D. A. Ramsay, *J. Am. Chem. Soc.*, *74*, 72 (1952).

(8) J. L. Ryan and C. K. Jørgensen, *J. Phys. Chem.*, *70*, 2845 (1966).

Table VI. Internal $4f^5$ Transitions in Samarium(III) Complexes [a]

	$[Sm(NCS)_6]^{3-}$		$[SmCl_6]^{3-}$	
Excited J Level	λ_J	ε_{max}	λ_J	ε_{max}
?	590	0.86	—	—
?	587	1.3	—	—
$^4G_{5/2}$	578	0.96	562	0.02
$^4F_{3/2}$	527	2.0	531	0.01
?	474	6.0	478	0.04
$^4I_{13/2}$	467	5.9	465	0.025
$^6P_{5/2}$	422	2.5	422	0.15
?	418	2.3	—	—
^6P	404	4.7	410	0.67
?	376	6.7	—	—
?	346	16.0	—	—

[a] Notation as in Table IV.

Table VII. Internal $4f^{10}$ Transitions in Holmium(III) Complexes [a]

	$[Ho(NCS)_6]^{3-}$		$[HoCl_6]^{3-}$	
Excited J Level	λ_J	ε_{max}	λ_J	ε_{max}
?	658	0.46	—	—
$^5F_5$	643	0.79	648	0.17
?	545	1.0	—	—
?	542	1.5	—	—
$^5S_2$, $^5F_4$	538	2.1	542	0.35
?	490	1.0	—	—
$^5F_3$	486	1.3	488	0.12
?	474	1.3	—	—
?	466	1.4	—	—
?	460	8.7	—	—
?	454	7.3	—	—
?	449	10.5	—	—
$^3K_6$	448	19.9	454	9.6
?	432	0.56	—	—
$^5G_5$	419	1.2	421	0.32
?	415	0.83	398	0.1
$^5G_4$, $^3K_7$	411	1.11	383	0.06
$^5G_6$	361	8.0	362	3.1
?	345	0.92	—	—
?	336	0.89	—	—
?	288	6.5	—	—

[a] Notation as in Table IV.

Table VIII. Internal $4f^{11}$ Transitions in Erbium(III) Complexes [a]

	$[Er(NCS)_6]^{3-}$		$[ErCl_6]^{3-}$	
Excited J Level	λ_J	ε_{max}	λ_J	ε_{max}
?	658	0.82	—	—
$^4I_{9/2}(^4F_{9/2})$	653	1.1	657	0.23
$^4S_{3/2}$	546	0.75	549	0.18
?	533	1.9	—	—
?	523	5.2	—	—
?	522	8.7	—	—
$^2H_{11/2}$	521	10.0	524	6.0
?	492	1.2	—	—
?	488	1.6	—	—
$^4F_{7/2}$	487	1.6	490	0.20
$^4F_{5/2}$	470	0.99	461	0.37
$^4F_{3/2}$	386	2.5	454	0.09
$^2H_{9/2}$	382	6.2	409	0.1
$^4G_{11/2}$	378	11.0	380	9.6
$^2K_{15/2}$	366	2.5	—	—
$^2G_{7/2}$	358	1.0	—	—
?	351	1.3	—	—

[a] Notation as in Table IV.

Discussion

The thiocyanate complexes prepared are quite stable in the solid state and do not dissociate appreciably when dissolved in poorly coordinating solvents such as nitrobenzene and acetonitrile (see Table II). Dissolution in DMF, however, results in extensive dissociation.

The effect of coordination on the infrared absorption bands of the thiocyanate,[9] selenocyanate,[9] and cyanate[10-13] ions has been the subject of extensive investigations. Relative to the free ion values, the C-X (X = S, Se, O) stretching frequencies increase when the ions are N-bonded and decrease when X-bonded; the NCX bending frequencies increase or remain about the same when the groups are N-bonded, but at least one band of the multiplet is found at a decidedly lower frequency when X-bonded. In addition, the integrated absorption intensities of the thiocyanate and selenocyanate C-N stretching bands increase markedly upon N-coordination, but decrease upon S- or Se-coordination. The data shown in Table III clearly indicate that the pseudohalides are N-bonded in all of the complexes, emphasizing the class-(a)[14] or hard acid[15] character of the rare earth ions.

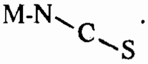
Relative to the values exhibited by the acetonitrile solutions, the C-N stretching bands of the thiocyanate complexes generally exhibit a decrease in energy and an increase in intensity when the complexes are dissolved in methanol. The integrated absorption intensities obtained for the methanol solutions are, in point of fact, the largest yet observed for the C-N stretching band of the thiocyanate group. As has been previously suggested by Pecile,[16] the enhancement of intensity may be attributed to hydrogen bonding interactions in the hydroxylic solvent.

A comparison of the visible spectra of the $[M(NCS)_6]^{3-}$ complexes with the visible spectra of the hexachloro complexes[8] of the same metal ions reveals pronounced differences in the number, intensity, and position of the absorption maxima (Tables IV-VIII). Although the thiocyanate complexes are considerably more soluble in acetonitrile than the chloro complexes are in the mixed succinonitrile-acetonitrile solvent employed by Ryan and Jørgensen,[8] the use of 10 cm cells in their study precludes an explanation of the differences in the number of bands observed which is based solely on concentration differences. More to the point is the greatly enhanced molar absorptivities of the bands in the thiocyanate spectra.

Several investigators[17] have noted that, although most of the Laporte forbidden electronic transitions within the f^n configuration are affected only slightly by environmental changes, the intensities of a few,

---

(9) J. L. Burmeister, *Coordin. Chem. Rev.*, *1*, 205 (1966); *3*, 225 (1968); and references contained therein.
(10) D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 262 (1965); 1286 (1965).
(11) A. Sabatini and I. Bertini, *Inorg. Chem.*, *4*, 959 (1965).
(12) A. H. Norbury and A. I. P. Sinha, *Inorg. Nucl. Chem. Letters*, *3*, 355 (1967); *J. Chem. Soc.* (A), 1598 (1968).
(13) J. L. Burmeister, E. A. Deardorff, and C. E. Van Dyke, *Inorg. Chem.*, *8*, 170 (1969).
(14) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), *12*, 265 (1958).
(15) R. G. Pearson, *J. Am. Chem. Soc.*, *85*, 3533 (1963).
(16) C. Pecile, *Inorg. Chem.*, *5*, 210 (1966).
(17) G. R. Choppin, D. E. Henrie, and K. Buijs, *Inorg. Chem.*, *5*, 1743 (1966), and references contained therein.

e.g., the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transitions of neodymium(III) (Table V) and the $^4I_{15/2} \rightarrow {}^4G_{11/2}$ transition of erbium(III) (Table VIII), are extremely sensitive (« hypersensitive »). Jørgensen and Judd[18] have suggested that these transitions are probably pseudoquadrupolar in nature. If an asymmetric distribution of dipoles is induced by the electromagnetic field in the environment about the ion, the variation of the electric vector across the ion is much greater than for a symmetric distribution of dipoles. As a result, the hypersensitive pseudoquadrupolar transitions, which are normally very weak, are enhanced. The transitions are termed pseudoquadrupolar because their intensities exhibit a first-power dependence on the transition energy, rather than the third-power dependence of pure electric quadrupole transitions. Oscillator strength measurements for the aqueous neodymium(III)-acetate system support this mechanism of intensity enhancement. Alternatively, Judd[19] has assigned the hypersensitivity principally to a change of point symmetry, the explanation being presented within the framework of crystal field theory. Both mechanisms imply, in the present study, that the environment of the metal ions in the solutions of the thiocyanate complexes is less symmetric than that existing in the solutions of the chloro complexes. Indeed, all of the bands in the thiocyanate spectra are generally more intense than even the corresponding bands in the spectra of the aquo complexes,[8] $[M(H_2O)_9]^{3+}$, which lack an inversion center. The apparent deviation from O_h symmetry in the thiocyanate complexes may be due to non-linear metal-thiocyanate linkages, *i.e.*,  $\mathrm{M{-}N{\diagdown}C{\diagdown}S}$. Although linear M-NCS linkages are more common, non-linear isothiocyanate linkages are not unknown,[20] *e.g.*, $[Co(NCS)_4]^{2-}$(∠M-NC ca. 120°), *trans*-$[Ni(py)_4(NCS)_2]$(∠M-NC 165^2), and *cis*-$[Ni(tren)(NCS)_2]$(∠M-NC 163°, 156°).

The bands in the thiocyanate spectra are, in general, shifted to slightly higher energies, and it is tempting to try to interpret this in terms of the greater ligand field strength of the N-bonded thiocyanate group. Unfortunately, several other effects could also cause the observed shift, *e.g.*, symmetry-dependent stabilization of the ground levels, a change in the relative transition probabilities from the lowest Stark levels, different vibronic structure in the line groups, etc. The great difference in stability between the yttrium(III)[3] and holmium(III) selenocyanate complexes provides a graphic illustration of the inadequacy of attempting to describe the bonding in these complexes solely in terms of simple electrostatic interactions. Despite the fact that the metal ions are virtually identical in size, the yttrium(III) complex (m.p. 159°) is stable indefinitely in the solid state, whereas the holmium(III) complex decomposes even under nitrogen at 0°. The rare earth ions therefore occupy a bonding position intermediate between the d-type transition metal ions, where covalent interactions with ligands are of considerable importance, and the metal ions of Groups IA and IIA, in whose complexes electrostatic intereactions are of primary importance.

The praseodymium(III) and holmium(III) thiocyanate complexes were found to be photosensitive, becoming bright yellow in color when exposed to the fluorescent lighting in the laboratory. The color change is an irreversible surface phenomenon. Although the melting points of exposed samples were found to have been lowered by as much as 30°, no significant differences were observed in the infrared spectra of the original and irradiated samples. Efforts to determine the nature of the reaction are currently in progress.

Acknowledgment. This research was supported in part (S.D.P.) by the University of Delaware Research Foundation and in part (E.A.D.) by the National Science Foundation (grant no. GP-8327).

---

(18) C. K. Jørgensen and B. R. Judd, *Mol. Phys.*, *8*, 281 (1964).
(19) B. R. Judd, *J. Chem. Phys.*, *44*, 839 (1966).
(20) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961), and references contained therein.