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Rare Earth Selenocyanate Complexes

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The synthesis and characterization of selenocyanate complexes of the type $[(n\text{–}C_4H_9)_4N]_3[M(NCSe)_6]$ *for the rare earth ions* Pr^{III}, Nd^{III}, Sm^{III}, Dy^{III}, Ho^{III}, *and* Er^{III} *is described. Infrared spectra measurements indicate that the selenocyanate groups are bonded through the nitrogen atom. The tendency of the complexes to dissociate in nitrobenzene decreases as the atomic number of the rare earth ion increases, the complexes being slightly less stable in this respect than the corresponding thiocyanate complexes. The complexes are reasonably stable when dry, but tend to decompose in moist air or in solution at room temperature. The magnitude of the molar absorptivities of the absorption maxima in the visible spectra of the complexes indicates pronounced deviations from* O_h *symmetry, possibly due to non-linear M–NCSe linkages. The wavelengths of the absorption maxima of the corresponding selenocyanate, thiocyanate and chloride complexes generally increase in the order* $-NCSe^- < -NCS^- < Cl^-$. *Attempts to prepare the analogous cyanate complexes by comparable synthetic procedures were unsuccessful.*

Introduction

Burmeister, *et. al.*,[1] have recently reported the synthesis and characterization of rare earth(III) thiocyanate complexes of the type $[(n\text{–}C_4H_9)_4N]_3[M(NCS)_6]$, but were unable to synthesize the corresponding selenocyanate and cyanate complexes. Encouraged by the known[2] stability of the $[Y(NCSe)_6]^{3-}$ complex and the considerable interest occasioned by the unusual visible spectra exhibited by the thiocyanate complexes,[1] we have continued our efforts along these lines, and now wish to report the successful synthesis and characterization of $[(n\text{–}C_4H_9)_4N]_3[M(NCSe)_6]$ complexes of selected rare earth(III) ions [Pr^{III}, Nd^{III}, Sm^{III}, Dy^{III}, Ho^{III}, and Er^{III}].

Experimental Section

Preparation of $[(n\text{–}C_4H_9)_4N]NCSe$. A solution of 50 mmol of potassium selenocyanate dissolved in 25 ml of Spectrograde acetone was slowly added to a solution of 50 mmol of tetra-n-butylammonium bromide dissolved in 50 ml of acetone. The resulting mixture was stirred for 0.5 hr., filtered, and the volume of the filtrate reduced to *ca.* 40 ml. on a steam bath. It was then poured into 4 l of ethyl ether (previously dried over sodium). After stirring the mixture for 0.5 hr., a white solid was obtained by filtration. This procedure is superior to that previously employed.[2]

Selenocyanate Complexes. The complexes may be synthesized by employing the anhydrous rare earth(III) chlorides as starting materials in place of the hexahydrates utilized in the earlier study.[1] Anhydrous ethanolic solutions of the appropriate anhydrous rare earth(III) chloride (3 mmol/25 ml) and potassium selenocyanate (9 mmol/25 ml) were mixed and stirred for 0.5 hr at –10°. The mixture was then filtered, allowing the filtrate to pass directly into an ethanolic solution, at –10°, of tetra-n-butylammonium selenocyanate (9 mmol/10 ml). The reaction mixture was stirred for 0.5 hr at –10°, then poured into 8 l of anhydrous ethyl ether, also at –10°. The product, which precipitates quite slowly, was isolated by filtration and dried *in vacuo*. The complexes are reasonably stable when kept dry in a tightly stoppered container, but tend to decompose quite rapidly in moist air or in solution at room temperature (*vide infra*). The colors, yields, melting points, and analytical data for the complexes are shown in Table I.

Cyanate Complexes. Attempts to prepare the corresponding cyanate complexes by analogous methods yielded completely different, albeit definite, results. The metathetical reactions between tetra-n-butylammonium bromide and potassium cyanate or silver cyanate in acetone yielded only unreacted starting materials. The reaction of stoichiometric amounts of anhydrous rare earth(III) chloride, silver cyanate, and tetra-n-butylammonium bromide in acetonitrile in the dark yielded, upon precipitation with ethyl ether, the white, very hydroscopic $[(n\text{–}C_4H_9)_4N][Ag(NCO)_2]$ complex. *Anal.* Calcd. for $C_{18}H_{36}N_3O_2Ag$: C, 49.77; H, 8.35; N, 9.67. Found: C, 49.17; H, 8.30; N, 9.33.

Physical Measurements. Infrared and visible-ultraviolet spectra and molar conductances were measured as previously described.[1] The tendency of the selenocyanate complexes to undergo rapid decomposition in acetonitrile solution prevented its use for the VIS-UV spectral measurements. Instead, ethanol solutions were prepared at *ca.* 0°, and the spectra measured at 10-12°. No decomposition was noted during

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[1] J. L. Burmeister, S. D. Patterson, and E. A. Deardorff, *Inorg. Chim. Acta*, 3, 105 (1969).

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

Table I. Colors, Yields, Decomposition Temperatures, and Analytical Data for the $[(n\text{—}C_4H_9)_4N]_3[M(NCSe)_6]$ Complexes

M^{III}	Color	% Yield	Decomposition Temperature, °C	Analyses, %							
				Theory				Found			
				C	H	N	Se	C	H	N	Se
Pr	pale green	69	117-119 [a]	43.29	7.27	8.41	31.62	43.56	7.54	8.23	31.40
Nd	pale blue	67	121-123	43.20	7.25	8.40	31.55	43.49	7.47	8.03	31.19
Sm	pink	64	107-110	43.02	7.22	8.36	31.42	43.02	7.24	8.22	31.37
Dy	pale pink	68	125-127	42.68	7.16	8.29	31.17	42.70	7.16	8.27	30.89
Ho	light grey	70	122-125	42.61	7.15	8.28	31.12	42.27	7.09	8.12	31.31
Er	pale pink	58	121-123	42.54	7.14	8.27	31.08	42.61	7.35	8.24	30.73
$[(n\text{—}C_4H_9)_4N]NCSe$		~100		58.77	10.44	8.06		58.99	10.38	7.92	

[a] Melts without decomposition.

Table II. Conductivity and Infrared Data for the $[(n\text{—}C_4H_9)_4N]_3[M(NCSe)_6]$ Complexes [g]

M^{III}	Λ_m [a] ohm^{-1} cm^2 $mole^{-1}$	δ_{NCSe} [b] cm^{-1}	ν_{CSe} [b] cm^{-1}	ν_{CN} [c]	
				Frequency cm^{-1}	A [d] $\times 10^{-4}$ M^{-1} cm^{-2}
Pr	84	425 m	613 s	2058	10
Nd	80	428 m	615 s	2058	12
Sm	81	425 m	614 s	2063	11
Dy	78	434 m	644 s	2047	16
Ho	73	433 m	642 s	2048	17
Er	69	435 m	646 s	2050	17
Y [e]	68	429 m	634 m	2068 [f]	5.0 [f]
$[(n\text{—}C_4H_9)_4N]NCSe$		436 w, 428 sh	534 w	2067 [e,f]	2.1 [e,f]

[a] 10^{-3} *M* nitrobenzene solutions at 25°. 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. [b] Nujol mulls. [c] 10^{-2} M nitrobenzene solutions. [d] Integrated absorption intensity, calculated per mole of coordinated selenocyanate. [e] Data taken from ref. 2. [f] Acetone solution. [g] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder.

the time required for the measurements. Dissociation of the complex ions in ethanol was found to be negligible, as indicated by the observation that the addition of tetra-n-butylammonium selenocyanate (0.1 *M*) did not result in any significant changes in the frequencies or intensities of the absorption maxima. In addition to the laboratories previously utilized,[1] some of the analyses were carried out by Micro-Analysis, Inc., Wilmington, Del. Selenium was determined gravimetrically after precipitation with hydrochloric acid and hydroxylammonium chloride.[3]

The conductivity and infrared data for the selenocyanate complexes are shown in Table II. The VIS-UV data for the Pr^{III}, Nd^{III}, Sm^{III}, Ho^{III}, and Er^{III} complexes are shown in Tables III through VII.

Table III. Internal $4f^2$ Transitions in the Praseodymium(III) Selenocyanate Complex [a]

Excited J Level [b]	λ_J [c]	ε_{max} [d]
$^1D_2$	597	8.1
?	506	9.8
$^3P_0$	483	15.8
$^3P_1$	471	14.4
$^3P_2$	447	26.3
?	332	31.9
?	310	46.5

[a] 10^{-2} *M* ethanol solution, with 10^{-1} *M* added tetra-n-butylammonium selenocyanate; 10^{-1} *M* ethanol solution of tetra-n-butylammonium selenocyanate used as reference. [b] Band assignments follow those of ref. 5 and L. I. Katzin and M. L. Barnett, *J. Phys. Chem.*, *68*, 3779 (1964). [c] Wavelength in nm of absorption maximum. [d] Molar absorptivity (M^{-1} cm^{-1}).

Table IV. Internal $4f^3$ Transitions in the Neodymium(III) Selenocyanate Complex [a]

Excited J level	λ_J	ε_{max}
$^4F_{9/2}$	684	4.2
?	593	7.8
$^4G_{5/2}$	588	11.6
$^2G_{7/2}$	585	15.6
?	583	17.3
?	581	17.3
?	572	11.0
$^2K_{13/2}$, $^4G_{7/2}$	525	12.3
$^2G_{9/2}$	513	11.1
$^4G_{9/2}$	478	11.9
$^4G_{11/2}$	460 sh	12.6
$^4D_{3/2}$	356	36.2
$^2I_{11/2}$	352	37.7
$^4D_{1/2}$	348	38.6
$^4D_{7/2}$	329	47.3

[a] Notations as in Table III.

Table V. Internal $4f^5$ Transitions in the Samarium(III) Selenocyanate Complex [a]

Excited J level	λ_J	ε_{max}
$^4G_{5/2}$, $^4F_{3/2}$	555 sh	8.7
?	499	14.0
?	478	16.8
$^4I_{13/2}$	469	18.3
?	441	21.0
?	437	21.6
^6P	403	32.8
?	375	39.0
?	344	62.9

[a] Notations as in Table III.

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(3) A. I. Vogel, « A Textbook of Quantitative Inorganic Analysis », 3rd ed., John Wiley and Sons, Inc., New York, 1961, pp. 508-9.

Table VI. Internal $4f^{10}$ Transitions in the Holmium(III) Selenocyanate Complex [a]

Excited J level	λ_J	ε_{max}
?	657	3.9
$^5F_5$	641	7.2
?	543	7.5
$^5S_2$, $^5F_4$	538	11.9
$^5F_3$	486	9.4
?	475	8.7
?	468	8.6
?	458	16.1
?	453	23.5
$^3K_6$	450	26.1
$^5G_5$	418	13.3
$^5G_6$	360	25.7
?	345	23.1
?	334	26.1

[a] Notations as in Table III.

Table VII. Internal $4f^{11}$ Transitions in the Erbium(III) Selenocyanate Complex [a]

Excited J level	λ_J	ε_{max}
$^4I_{9/2}$ ($^4F_{9/2}$)	653	6.4
?	650	6.4
$^4S_{3/2}$	543	5.0
?	528 sh	7.1
?	523	13.8
$^2H_{11/2}$	519	19.7
$^4F_{7/2}$	488	11.7
?	451	10.7
?	443	10.1
?	407	16.7
$^4F_{3/2}$	384 sh	26.5
$^2H_{9/2}$	380	42.3
$^4G_{11/2}$	377	56.9
$^2K_{15/2}$	364	41.0
?	325	92.4
?	288	191.2

[a] Notations as in Table III.

The VIS-UV spectrum of the Er^{III} complex is shown in Figure 1.

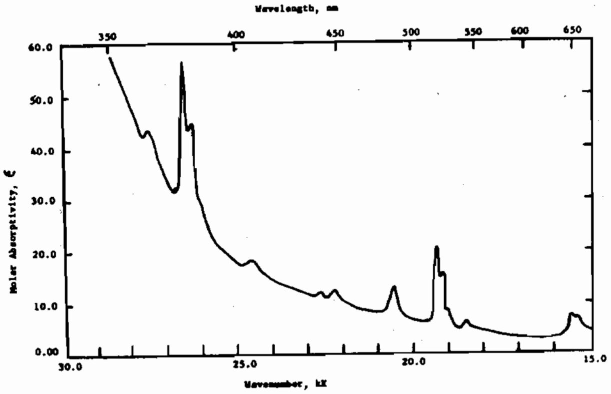

Figure 1. Visible spectrum of a 10^{-2} *M* ethanol solution of $[(n{-}C_4H_9)_4N]_3$ $[Er(NCSe)_6]$ (10^{-1} *M* in $[(n{-}C_4H_9)_4N]NCSe$).

Discussion

The synthesis of the selenocyanate complexes makes possible some rather interesting comparisons with the thiocyanate complexes previously reported.[1] Based[4] (Table II) on the increased integrated absorption intensities of their νCN bands, the increased frequencies of their νCSe bands (both relative to the free ion values) and the single δNCSe band found above 400 cm^{-1} in their infrared spectra, the selenocyanates, like the thiocyanates, are most assuredly N-bonded. The Λ_m values (Table II) of both series of complexes decrease as the atomic number of the rare earth(III) ion increases, indicating, as would be expected, increasing stability, *i.e.*, decreasing dissociation, of the complex ions as the rare earth(III) ions decrease in size. Likewise, the Λ_m values of the thiocyanate complexes are generally slightly lower than their selenocyanate counterparts, indicating somewhat greater stability. It is interesting to note that the Λ_m value for the selenocyanate complex of yttrium(III), which is intermediate in size between holmium(III) and erbium(III), is quite comparable to the Λ_m values for the selenocyanate complexes of these ions. The decreased molar conductivities of the complexes of the heavier rare earths is accompanied by increased δNCSe and νCSe frequencies and more intense νCN bands.

The visible spectra of the selenocyanates (Tables III through VII, Figure 1) differ from those of the thiocyanates with respect to the number, wavelengths, and intensities of the absorption maxima. The fact that the selenocyanates generally exhibit a smaller number of absorption maxima is undoubtedly due to their lower solubility in ethanol (a concentration of 10^{-2} *M* was employed). Acetonitrile solutions of higher concentration (10^{-1} *M*) were utilized in the thiocyanate study, the size of the quartz cells being the same. The wavelengths of the absorption maxima of the corresponding selenocyanate, thiocyanate and chloride[5] complexes generally increase in the order $-NCSe^- < -NCS^- < Cl^-$.

Although the differences are quite small, they are beyond the limits of experimental error. Recognizing that several other effects[1] could also cause the observed shifts, it is true, nonetheless, that this is precisely the order expected[2,4] on the basis of the relative ligand field strengths of the three ligands.

The most striking differences, however, are found in the molar absorptivities of the absorption maxima. Those of the selenocyanate complexes are several times larger than those of the corresponding thiocyanate complexes. Although the very large values at the extreme low wavelength end of the spectra are undoubtedly due to the tail of a charge transfer band, this is not true over most of the visible wavelength range. What makes the ε_{max} values of the selenocyanates even more surprising, however, is the fact that the thiocyanate ε_{max} values are, in turn, much larger[1] than those of the chloride[5] and $M(H_2O)_9^{3+}$ complexes[5], the latter lacking a center of symmetry. It appears that the explanation[1] proposed for the thiocyanates is also applicable to the selenocyanates, namely, deviation from O_h symmetry due to non-linear metal-selenocyanate linkages, *i.e.*, $M{-}N\diagdown C\diagdown Se$.

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[4] J. L. Burmeister, *Coordin. Chem. Rev.*, *1*, 205 (1966); *3*, 225 (1968).
[5] J. L. Ryan and C. K. Jørgensen, *J. Phys. Chem.*, *70*, 2845 (1966).

This is of no little significance, since no X-ray strucral data for M–NCSe (or M–SeCN) linkages have yet been reported. Possible expansion of the coordination number due to the coordination of ethanol molecules may also be a contributory factor in the case of the selenocyanate complexes.

The reluctance of the cyanate ion to form complexes with the rare earth(III) ions is not understood, especially since numerous transition metal[6] and organometallic[7] isocyanates have now been reported.

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(6) See references cited in J. L. Burmeister and N. J. De Stefano, *Inorg. Chem.*, *8*, 1546 (1969).

(7) J. S. Thayer and R. West, *Advan. Organometal. Chem.*, 5, 115 (1967).