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Di-n-butyl Sulfoxide Complexes of Lanthanide Perchlorates

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The synthesis and physical properties of crystalline lanthanide perchlorate di-n-butyl sulfoxide complexes ($Ln(ClO_4)_3 \cdot 6Bu_2SO$, where Ln = La–Nd, Sm–Lu, and Y) are reported. The i.r. spectra, the molar electrolytic conductances in nitromethane and acetonitrile and the X-ray powder patterns of the complexes were determined. The i.r. spectra reveal that all Bu_2SO's are coordinated to the metal ions, oxygen being the donor atom. A partial and weak coordination of perchlorate ions to the lanthanide ions of greater radius is also evidenced by i.r. spectral data. The electronic spectra of the neodymium complex indicate different environments in solid state and in acetonitrile and nitromethane solutions.

Introduction

Several complexes between trivalent lanthanide perchlorates and cyclic sulfoxides have been recently reported, while in the field of acyclic dialkyl sulfoxides, only dimethyl sulfoxide (dmso) complexes have been isolated.[1] The change from dmso to dialkyl sulfoxides with larger steric requirements and dissimilar basicities must allow the isolation of complexes of different stoichiometries and structures. The substitution of longer alkyl chains increases the donor properties of the sulfinyl group, so that di-n-butyl sulfoxide (Bu_2SO) is a stronger base than dmso.[2–4]

Di-n-butyl sulfoxide has been largely employed in solvent extraction of several metal ions. It provides a synergic enhancement of the extraction of trivalent lanthanides with 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione.[5–8] Equilibrium constants of the adduct formation of rare earth tris-(2-thenoyl-trifluoroacetonates) with Bu_2SO in carbon tetrachloride were determined.[9, 10]

No complexes of lanthanide ions with Bu_2SO as the only donor have, however, been reported. This study has been concerned with the synthesis and characterization of the complexes of Bu_2SO with lanthanide perchlorates.

Experimental

Preparation of the Complexes

The hydrated lanthanide perchlorates (2 mmol) were dissolved in a small amount of absolute ethanol and treated with 3 ml of an ethanolic solution containing 18 mmol of di-n-butyl sulfoxide (obtained from K&K Laboratories, Inc.), followed by 8 ml of ethyl orthoformate. Anhydrous diethyl ether was then added until turbidity occurred, the solution was warmed until clear and stored overnight at 0 °C. The resulting crystals were separated from the solution at low temperature. They were washed with a cold ethanol–ether mixture (1:4), followed by cold ether, and dried under vacuum over P_4O_{10}. The typical yield was 90%.

Analysis and Measurements

The metal and anion contents were estimated as reported previously.[11] Di-n-butyl sulfoxide was determined by potentiometric titration with perchloric acid in acetic anhydride.[12]

The infrared spectra, molar conductivities in acetonitrile and nitromethane solutions and X-ray powder patterns of the complexes were obtained as described in an earlier paper.[11]

The electronic absorption spectra of the neodymium compound in Fluorolube mull, acetonitrile and nitromethane solutions at (25.0 ± 0.5) °C were recorded with a Cary Model 17 spectrophotometer.

Results and Discussion

Analytical results (Table I) conform to the formula $Ln(ClO_4)_3 \cdot 6Bu_2SO$, where Ln = La–Nd, Sm–Lu, and Y. The complexes are crystalline, slightly hygroscopic and insoluble in non polar solvents.

The infrared spectra in the 1200–500 cm^{-1} region provide some information regarding the bonding in the complexes. There is a very strong band at about 990 cm^{-1}, which was assigned to the S=O stretching vibration (Table II). In the infrared spectrum of Bu_2SO this vibration appears at $\sim$1035 cm^{-1}.[13] The shift of the band to lower frequency in the complexes clearly

TABLE I. Melting Ranges and Analytical Data of the Compounds of General Formula $Ln(ClO_4)_3 \cdot 6\ Bu_2SO$.

Ln	Melting Range (°C)	% Lanthanide		% Perchlorate		% Di-n-butyl Sulfoxide	
		Calcd	Found	Calcd	Found	Calcd	Found
La	75–83	9.84	9.86	21.14	21.4	69.01	68.9
Ce	90–95	9.92	9.93	21.13	21.5	68.95	69.6
Pr	96–100	9.97	9.98	21.11	21.3	68.91	68.8
Nd	99–102	10.18	10.11	21.06	21.0	68.75	69.0
Sm	104–107	10.57	10.54	20.97	21.0	68.46	69.4
Eu	100–106	10.67	10.77	20.95	21.2	68.38	68.0
Gd	100–107	11.00	11.04	20.87	21.1	68.13	67.3
Tb	106–112	11.11	10.98	20.85	20.9	68.05	68.2
Dy	105–112	11.33	11.42	20.80	21.1	67.88	67.4
Ho	106–111	11.48	11.52	20.76	21.0	67.76	66.9
Er	100–108	11.62	11.44	20.73	21.0	67.65	67.9
Tm	98–102	11.72	11.86	20.70	20.9	67.57	67.8
Yb	90–96	11.97	12.09	20.64	20.9	67.38	67.5
Lu	50–53	12.09	12.35	20.62	21.0	67.29	66.9
Y	102–106	6.53	6.57	21.92	22.1	71.55	71.1

TABLE II. Electrolytic Conductance Data and Characteristic Infrared Frequencies for the Compounds of General Formula $Ln(ClO_4)_3 \cdot 6\ Bu_2SO$.

Ln	Λ_m^a ($ohm^{-1} cm^2 mol^{-1}$)		Infrared Data (cm^{-1})							
	$MeNO_2$	MeCN	$\nu_{S=O}$	Ionic T_d ClO_4^-		Vibrational Modes of Coordinated Perchlorate Group				
				ν_3	ν_4					
La	145	340	979vs,br	1094vs,br	621m	1170m	1023m–w	918w	642w	614sh
Ce	148	343	984vs,br	1096vs,br	622m	1170w	1022w	918w	642w	614sh
Pr	151	325	984vs,br	1096vs,br	622m	1169w	1024sh	918w	642w	615sh
Nd	162	343	987vs	1097vs,br	622m	1167vw		917vw	642w	615sh
Sm	163	338	988vs	1098vs,br	622m	1165sh		918vw	641sh	614sh
Eu	168	348	990vs	1103vs,br	622m	1165sh		919sh	642sh	
Gd	164	338	992vs	1105vs,br	623m	1170sh			645sh	
Tb	175	362	993vs	1102vs,br	623m					
Dy	177	352	991vs	1102vs,br	621m					
Ho	181	352	991vs	1100vs,br	624m					
Er	178	363	994vs	1104vs,br	622m					
Tm	190	359	992vs	1101vs,br	622m					
Yb	196	365	992vs	1101vs,br	622m					
Lu	191	350	990vs,br	1097vs,br	622m					
Y	169	345	995vs	1105vs,br	623m					

[a] 1.00×10^{-3} *M* solutions at 25°C.

indicates coordination of the oxygen atom of the sulfinyl group to the lanthanide ion.

In the spectra of the heavier lanthanide complexes there is a single band at 625 cm^{-1} which, along with a strong and broad band at about 1100 cm^{-1}, indicates the retention of the T_d symmetry of the perchlorate ions.[14] In the spectra of the lighter lanthanide complexes, besides the bands due to ionic perchlorate group, there appear vibrational modes characteristic of a slight distortion of the anion,[15] indicating that some perchlorates are weakly coordinated to the lanthanide ions of greater radius. As one proceeds from lanthanum to the heavier lanthanides, these bands lose intensity gradually, disappearing completely at terbium (Table II). Anion coordination presumably becomes more difficult, due to steric crowding, as the central ion becomes smaller. Conductance studies in $MeNO_2$ show a similar trend. The molar conductivities

(Table II) gradually increase from values corresponding to 2:1 electrolytes to values intermediate between 2:1 and 3:1 electrolytes.[16]

In complexes containing oxygen bonded sulfoxide the metal–oxygen stretching mode is usually strongly coupled with the symmetric C–S stretching and C–S–O and C–S–C deformation vibrations of the ligand.[17] A broad band of medium intensity which occurs at 400–419 cm^{-1}, with a shoulder at about 385 cm^{-1}, can be assigned to ligand vibrations (probably mainly C–S–O deformations), since free Bu_2SO shows intense bands at 394 and 375 cm^{-1}.[18] An increase in the C–S–O deformation frequencies on complexation has been previously observed for dmso complexes of trivalent metals.[19,20]

Another characteristic band of medium intensity appears at about 180 cm^{-1} for the compounds of dysprosium to lutetium, while in the lighter lanthanides the band extended beyond the lower frequency limit of spectrometer range. The occurrence of this band at 204 cm^{-1} in the complex of yttrium (a lighter element) and its absence in the spectrum of the ligand support its assignment as mainly M–O(ligand) stretching vibration. The low frequency of this vibration is a consequence of the weak metal–ligand interaction in these rare earth complexes.

The X-ray powder patterns of the compounds from cerium to lutetium and yttrium indicate that isomorphy occurs in the series. Lanthanum complex shows a slightly different pattern in the region of higher *d* values.

The electronic spectrum of the neodymium complex was examined. The band system corresponding to the ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$, ${}^2G_{7/2}$ transition has been termed "hypersensitive" band and its shape has been correlated with the coordination number and ligand geometry on the metal ion.[21] It is interesting to see if the partial coordination of the perchlorate ion could produce appreciable deviations from the expected six-coordination proportioned by the Bu_2SO molecules. The shape of the hypersensitive band of solid $Nd(ClO_4)_3 \cdot 6Bu_2SO$ (Figure 1A) compares reasonably well with the band shape of neodymium in some six-coordinate β-diketonates reported by Karraker.[22] However, such similarity is not conclusive, since the spectra of seven-coordinate complexes may show a general resemblance to the spectra of six-coordinate complexes.[22]

Conductance measurements in $MeNO_2$ and MeCN solutions of $Nd(ClO_4)_3 \cdot 6Bu_2SO$ ($0.001M$) indicate different electrolyte stoichiometry (Table II). The partial coordination of the anion observed in the solid state and in nitromethane solution did not occur in acetonitrile solution.

The hypersensitive band of the neodymium complex in these solvents was also recorded. A linear dependence of the integrated absorption intensity on concentration is observed over the approximate concentration ranges 0.04–$0.07M$ and 0.03–$0.15M$, for MeCN and $MeNO_2$, respectively. Differences in the shape of the bands (Figure 1) and a shift of the baricenter in solution spectra to higher wavenumber in respect to 17117 cm^{-1} (the baricenter in the solid state spectrum) evidence that the environment of the neodymium ion is not the same in these media. Moreover, the normal (nonhypersensitive) bands occurring in solution spectra are of about the same intensity as the corresponding bands in the neodymium(III) aqueous ions.[23] This means that the symmetry around the neodymium ions is not octahedral. The presence of an inversion center in the complex should cause a marked reduction in the extinction coefficients of the bands.[23]

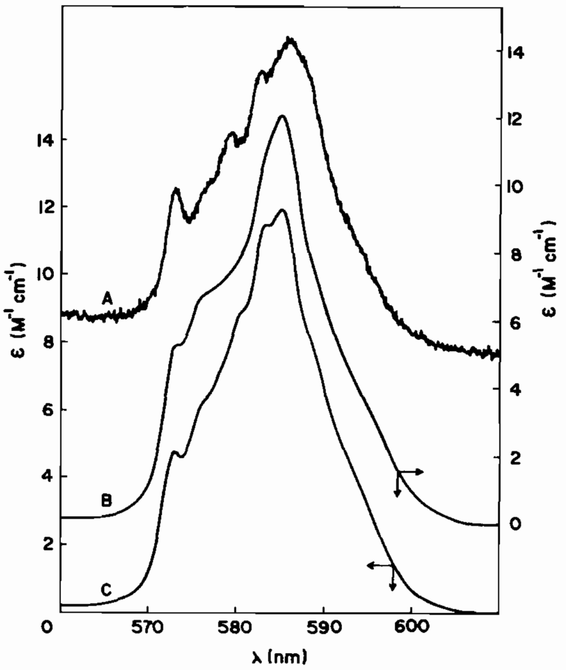

Figure 1. Electronic absorption spectra of $Nd(ClO_4)_3 \cdot 6Bu_2SO$ in the ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$, ${}^2G_{7/2}$ region: (A) solid complex on Fluorolube mull (y axis = arbitrary scale of absorbance); (B) $0.065M$ nitromethane solution; (C) $0.065M$ acetonitrile solution.

In dilute solutions, changes in shape, baricenter and intensity of the hypersensitive band are observed. By adding free ligand to these solutions, the spectra show a tendency to achieve the band features given in Figure 1 (curves B and C). Probably, several equilibria involving dissociation and solvolysis of the complex are occurring in solution, especially in MeCN which has a greater coordinating power than $MeNO_2$.[16] In fact, the infrared spectra of $0.01M$ solutions in both solvents show a band attributable to the S=O stretching vibration of uncoordinated sulfoxide molecules. In MeCN solution, this band can be observed even at higher concentrations (*e.g.* 0.065*M*), which shows the greater extent of solvolysis which occurs in this solvent.

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