Complexes of Dibenzylsulfoxide with Lanthanide Nitrate

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Abstract

A new series of dibenzylsulfoxide (DBSO) compounds of empirical formula $[Ln(DBSO)_x(NO_3)_3]$ are reported, where $x = 3$ for $Ln = Pr$; $x = 2.5$ for $Ln = Nd$, Sm, Eu, Gd, Er and La; and $x = 2$ for $Ln = Dy$. The compounds were synthesized from a non-aqueous solvent and isolated as dibenzylsulfoxide salts. Infrared spectral data established coordination by the anion groups and also that coordination of DBSO is through the oxygen. Additional information based on the nature of bonding and geometrical structure was obtained from the electronic absorption spectra, X-ray diffraction analysis, molecular conductivities and molecular weight measurements (as well as magnetic susceptibility measurements). All these physical measurements indicate octahedral coordination. The 20% decrease in the metal ion radius across the lanthanide series and the competition between DBSO and nitrate groups for the coordination site affect the number of DBSO molecules bonded to a tripositive lanthanide ion.

Introduction

Complexes of several derivatives of sulfoxides as ligands have been reported by numerous authors [1]. Continuing our interest in sulfoxides as ligands [2], we began investigating the chemistry of the DBSO complexes of the lanthanide nitrates. The present work is an attempt to investigate and correlate the coordination chemistry of the 3d-type transition metal complexes and the lanthanide complexes, by using the title ligand.

In this paper, an account of preparation methods and a description of structural properties are given. Infrared data are used to show the presence or absence of the coordination number of the DBSO species and its variations as a function of the crystal radius of the cation.

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Experimental

Materials

Dibenzylsulfoxide was obtained from Aldrich Chemical Company, Inc., in technical grade form, and had to be recrystallized from 50% aqueous ethanol. The melting point for pure crystals is 132–134 °C. The lanthanide oxides were obtained from Semi-elements Inc., Saxonburg, Pa., U.S.A. in 99.9% purity or better.

Synthesis

The appropriate lanthanide oxide was converted to the lanthanide nitrate by dissolving approximately 0.25 g of the oxide in a minimum amount of water and adding 50% HNO_3 dropwise with stirring until the solution cleared. A small amount of oxide was added in excess. In some cases the application of heat was necessary in order to avoid an excess of acid (because the protons might block the reactive sites). The solution was then filtered and allowed to crystallize over a steam bath.

Crystals of the hydrated lanthanide nitrate were dissolved in a mixture of 4 ml of t-butanol and a stoichiometric amount of triethyl-orthoformate was stirred with a magnetic stirrer for at least 5 min at 30–40 °C, and then a stoichiometric amount of DBSO dissolved in warm t-butanol was added. The solution was covered and agitated for an additional hour. An equal volume of anhydrous ether was added and stirred into the mixture for 30 min at room temperature. The supernatant liquid was then decanted and the product was stirred in a minimum amount of anhydrous ether. The crystals were washed in successive portions of cold anhydrous ether until they formed a fine powder. The product was filtered and dried *in vacuo* over P_2O_5 at room temperature overnight. The yield was 90–98%.

Analysis

Carbon and hydrogen analysis for only a few complexes was performed by R.C. Johnson, Mic-Anal. Organic Microanalysis of Tucson, Ariz., U.S.A. The percent nitrate content was determined by gravimetric precipitation with nitron, as described by Welcher [3a].

The metal content was estimated by complexometric titration with EDTA, using xylenol orange as an indicator. This indicator permitted the direct titration of all the rare earth metals [3].

A known weight of the complex ($\approx 10^{-2}$ M) was dissolved in water and acetate buffer (pH 5, 10 ml). One drop of pyridine was added, followed by three drops of xylenol orange indicator. The solution was then titrated with 0.01 M EDTA until the color of the solution changed from red to yellow, then another drop of pyridine was added. If the pH of the solution dropped too much, the red color would reappear. The titration was completed to a permanent yellow end-point.

The total sulfoxide content was determined indirectly by following a procedure outlined by Douglas [4]. Standard solutions of potassium permanganate, sodium oxalate and ferrous sulfate were prepared following the prescribed methods of Kolthoff and Sandell [5], and Day and Underwood [6].

Approximately 30–50 mg of sample was dissolved in 50 ml of 0.5 N sulfuric acid and a few drops of phosphoric acid. An excess of 0.1 N $KMnO_4$ was added to oxidize the sulfoxide to a sulfone. After the reaction, the excess permanganate was reduced to Mn^{2+} by the addition of ferrous sulfate (0.06 N $FeSO_4 \cdot 7H_2O$). The clear solution was then titrated with $KMnO_4$ until a very slight pink color appeared.

Physical Measurements

Melting points for the complexes were obtained with a Thomas-Hoover Capillary Melting Point apparatus and were uncorrected.

The infrared spectra of the complexes were obtained from a Perkin-Elmer Model 283B recording spectrophotometer in the region 250–4000 cm^{-1}, using CsBr plates.

Conductance measurements were performed with an Industrial Instrument Model RC 16B2 conductivity bridge and a conventional cell calibrated with

aqueous KCl solution. All measurements were conducted with nitromethane at 25 °C. Molecular weight measurements were obtained using a Hewlett-Packard Model 301A vapor pressure osmometer. All determinations were done at 37 °C with a non-aqueous probe and nitromethane as the solvent. Standard solutions of benzil dissolved in nitromethane were used for a molecular weight calibration curve. X-ray diffraction patterns of the complexes were determined by the use of a General Electric Model XRD-5 and a direct reading diffractometer. A copper Kα radiation source was used in conjunction with a nickel filter ($\lambda = 1.54178$ Å at 33 KV and 15 mA). The sample holder was packed by the backpacking technique. The relative intensities were estimated by their relative peak heights.

The electronic absorption spectra of the complexes were obtained with two different recording spectrophotometers: a Hewlett-Packard Model 8450A (350–800 nm) and a Perkin-Elmer Model 559A (190–900 nm). Nitromethane solutions of colored complexes were used to record the visible spectra. Methylene chloride was the solvent for all complexes which absorb light in the ultraviolet region. The reflectance spectra of the solid compounds were obtained with a Beckman DU spectrophotometer over the wavelength range of 350–1000 nm. The reference standard used to obtain the reflectance spectra was U.S.P. magnesium carbonate.

Results and Discussion

The method used for the synthesis of the lanthanide nitrate complexes was that described by Bertan and Madan [7] for the tetramethyl sulfoxide complexes of the lanthanide nitrates, except for minor modifications. The complexes were found to be non-hygroscopic and air-stable. The yield for all DBSO complexes was in the range of 90–98%. The analytical data and some physical properties of these complexes are summarized in Table I; no coordinated

TABLE I. Analytical Data and some Physical Properties of the Lanthanide Nitrate Complexes of Dibenzylsulfoxide

Complex[a]	Theoretical (%)			Experimental (%)			Color	Yield (%)	Melting point (°C)
	M	NO$_3$	DBSO	M	NO$_3$	DBSO			
[Pr(DBSO)$_3$(NO$_3$)$_3$][b]	13.84	18.27	67.88	14.25	18.58	67.44	green	98	133
[Nd(DBSO)$_{2.5}$(NO$_3$)$_3$]	15.92	20.53	63.55	15.83	20.36	63.53	lavender	97	142
[Sm(DBSO)$_{2.5}$(NO$_3$)$_3$]	16.49	20.39	63.12	16.44	20.30	62.97	white	97	146
[Eu(DBSO)$_{2.5}$(NO$_3$)$_3$]	16.63	20.36	63.02	16.52	20.28	62.94	white	97	150
[Gd(DBSO)$_{2.5}$(NO$_3$)$_3$]	17.11	20.24	62.65	17.02	20.20	62.51	white	97	151
[Dy(DBSO)$_2$(NO$_3$)$_3$][c]	20.08	22.99	56.93	20.09	22.87	56.88	white	94	151-2
[Er(DBSO)$_{2.5}$(NO$_3$)$_3$][d]	18.00	20.02	61.98	18.06	19.97	61.81	pink	97	154
[La(DBSO)$_{2.5}$(NO$_3$)$_3$]	15.42	20.60	63.93	15.41	20.26	63.87	white	96	118

[a][DBSO = $C_{14}H_{14}SO$].   [b][Found: C, 48.50; H, 4.07. Calc.: C, 49.20; H, 4.16%].   [c][Found: C, 43.06; H, 3.66. Calc.: C, 42.60; H, 3.95%].   [d][Found: C, 45.58; H, 3.95. Calc.: C, 45.29; H, 3.80%].

water molecules were present. From the total analysis, it appeared that the lanthanide nitrate complexes are eight-coordinate. This was confirmed by taking physical measurements which agreed with our predictions.

It is well known that the lanthanides form complexes most easily with oxygen donor ligands, so one would expect lanthanide sulfoxide complexes to form easily. However, upon examining the literature, most chemists found lanthanide complexes to be either six-, seven-, eight- and/or nine-coordinated, depending upon the size of the central metal ion [8]. These workers suggest that in many of these complexes, one or more of the three nitrate groups are present as bidentate. It can also be pointed out that as the size of the metal ion decreases, steric repulsion of ligands is increased and so, as a consequence, the number of ligands coordinated decreased by going from Pr^{3+} to Dy^{3+}, due to the well-known lanthanide contraction. The sharpness of the melting points indicate the purity of the respective complexes.

The infrared spectral data for the DBSO complexes of the lanthanide nitrates are given in Table II. The infrared spectra for all complexes were characterized by the lack of water bands and displacement of S=O stretching from 1030 cm^{-1} in the free ligand to approximately 988 cm^{-1} in the complexes. This is in good agreement with results previously reported by Cotton *et al.* [9], indicating coordination through the oxygen atom. Bonding via the oxygen atom of the sulfoxide group should definitely result in the draining of the electron density from the sulfoxide functional group double bond and, therefore, in a lowering of the force constant of the S=O bond, with a resulting decrease in the infrared stretching frequency of the S=O in the complexes compared to that of the free ligand. The IR data also indicate that only coordinated nitrate groups (symmetry C_{2v}) are present. The absence of the two infrared active bands of the nitrate ion (symmetry D_{3h}) in all these complexes at 720 and 1390 cm^{-1} is also a further proof that no ionic nitrate is present [10]. To determine the distinction between unidentate and bidentate nitrate groups by only the use of IR-spectra is difficult. The assumption that large values of $\Delta(\nu_4 - \nu_1)$ indicate the presence of a bidentate nitrato group cannot be proven without additional confirmation by the use of Raman spectral data [11]. Thus far, though, it is believed that these complexes contain one monodentate and two bidentate groups bonded to each central metal atom (to form a coordination number of eight, which is confirmed by subsequent physical measurements). The band shifts for all respective groups for the lanthanide nitrate complexes are shown in Table II. The complexes in our study have a C–S stretching vibration near 691 cm^{-1}. Srivastava and coworkers [12] reported that the C–S stretching

TABLE II. Infrared Spectral Data for the Dibenzylsulfoxide Complexes of the Lanthanide Nitrates (cm^{-1})[a]

DBSO	La	Pr	Nd	Sm	Eu	Gd	Dy	Er	Assignment
	1458(vs)	1460(vs)	1458(vs)	1455(vs)	1460(vs)	1460(vs)	1460(vs)	1460(vs)	$\nu_4(NO_3)$
	1280(vs)	1280(vs)	1285(vs)	1288(vs)	1289(vs)	1285(vs)	1291(vs)	1298(vs)	$\nu_1(NO_3)$
	178	180	173	167	171	175	169	162	$\Delta(\nu_4 - \nu_1)$
1082(m)	1068(m)	1068(m)	1070(m)	1080(m)	1073(m)	1070(m)	1080(m)	1070(m)	$\nu_2(NO_3)$
	1012(m)	1013(m)	1018(m)	1019(m)	1018(m)	1018(m)	1020(m)	1025(m)	$\nu(SO)$
1030(vs)	988(vs)	985(vs)	985(vs)	988(vs)	988(vs)	988(vs)	988(vs)	990(vs)	$\Delta\nu(SO)$
	42	45	45	42	42	42	42	40	$\nu_6(NO_3)$
	815(m)	812(m)	812(m)	812(m)	813(m)	812(m)	810(m)	812(m)	$\nu_3(NO_3)$
	729(m)	731(m)	832(m)	836(m)	739(m)	739(m)	740(m)	742(m)	$\nu_5(NO_3)$
	710(w, sh)	711(w, sh)	715(w, sh)	710(w, sh)	715(m)	711(w, sh)	710(w, sh)	715(w, sh)	$\nu_5(C_{2v})/\nu_6(C_{3v})$
	700	700	700	700	700	700	700	700	$\nu(C-S)$stretch.
683(s)	691(s)	691(s)	691(s)	691(s)	691(s)	691(s)	691(s)	691(s)	Ring breath.
	568(vs)	562(w)	565(w)		561(w)	561(w)	570(w)		$\nu(CSO)$(symm.)
468(s)	470(s)	471(s)	470(s)	470(s)	470(s)	470(s)	470(s)	470(s)	$\nu(CSO)$(asymm.)
	378(m)	378(m)	378(m)	378(m)	370(m)	368(m)	380(m)	380(w)	$\nu(M-O)$
	305(m)	308(m)	300(m)	305(m)	300(m)	305(m)	305(m)	300(m)	

[a]vs = very strong, s = strong, sh = shoulder, m = medium, w = weak.

TABLE III. Conductance and Molecular Weight Data for the Lanthanide Nitrate Complexes of Dibenzylsulfoxide in Nitromethane

Complex	Concentration (mM)	Λ_m (ohm^{-1} cm^2 mol^{-1}) at 25 °C	Concentration (mM)	Apparent molecular weight at 37 °C	Actual molecular weight g/mole
[Pr(DBSO)$_3$(NO$_3$)$_3$]	3.00	9.49	10.00	1017.0	1017.90
	2.00	10.03	5.00	1003.1	
	1.00	13.47	2.02	998.4	
[Nd(DBSO)$_{2.5}$(NO$_3$)$_3$]	5.98	2.68	9.00	893.5	906.07
	3.98	3.21	3.60	893.2	
	2.00	5.44			
[Sm(DBSO)$_{2.5}$(NO$_3$)$_3$]	6.00	1.95	9.08	902.2	912.22
	3.96	2.51	3.64	900.5	
	2.02	4.23			
[Eu(DBSO)$_{2.5}$(NO$_3$)$_3$]	5.96	2.38	9.14	910.8	913.77
	4.00	2.59	3.58	908.4	
	2.00	4.17			
[Gd(DBSO)$_{2.5}$(NO$_3$)$_3$]	6.00	2.06	9.22	915.9	919.08
	4.00	2.51	3.88	915.9	
	2.00	4.02			
[Dy(DBSO)$_2$(NO$_3$)$_3$]	6.02	2.55	8.00	802.5	809.16
	4.02	2.87	3.24	800.2	
	2.02	5.02			
[Er(DBSO)$_{2.5}$(NO$_3$)$_3$]	6.00	2.38	9.18	921.5	929.09
	4.00	3.09	3.46	912.7	
	2.00	4.02			
[La(DBSO)$_{2.5}$(NO$_3$)$_3$]	6.02	3.57	9.00	886.2	900.73
	4.00	4.34	3.58	886.2	
	2.00	6.18			

absorption undergoes a slight positive shift on complexation from 685 to 700 cm^{-1} in their complexes. The positive shift in the C–S stretching frequency is an indication of the decrease in the double bond order of the SO group (pπ–dπ back-bonding) and an electron shift from the aryl group to the S atom of the ligand.

Conductivity data of these complexes are given in Table III. Geary [13] tabulated the molar conductances of various types of electrolytes in concentrations of approximately 10^{-3} M in nitromethane solvent and found that 1:1 is 75–95; 2:1 is 150–180; 3:1 is 200–260; and 4:1 is 290–330 ohm^{-1} cm^2 mol^{-1}. The choice of nitromethane solvent is based on its weak donor properties; consequently, all electrolytes are allowed to exhibit their relatively high conductivities. The molar conductance data for these complexes, consequently, indicate that they are non-electrolytes and neutral species. Our values ranged from 1.95–14.0 ohm^{-1} cm^2 mol^{-1}. This provides additional proof that nitrate groups are strongly bound to the metal ion [14]. This was also confirmed by the IR spectra. It can be stated that these complexes can undergo a slight dissociation with increased dilution (which could be proved by plotting

Λ_m versus $c^{1/2}$, excluded in this report). The molecular weight measurements for the lanthanide nitrate complexes, given in Table III, suggest that these complexes exist as one particle in CH$_3$NO$_2$, relative to the empirical formula. The Pr complex proved conclusively to be monomeric and undissociated in solution, while the rest of the lanthanide nitrate complexes may be non-monomeric in character with respect to stoichiometric and stereochemical requirements.

Although not reported here, the magnetic susceptibility data for our complexes fell within the expected theoretical range for free ions [15].

The X-ray data, not shown here for the DBSO complexes of the lanthanide nitrates, indicate two sets of structures for this series of complexes: one structure for the complexes of the smaller metal ions (Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III} and La^{III}) and the other structure for the larger lanthanide metal ions (Gd^{III}, Dy^{III} and Er^{III}). The intensity maxima, however, occur at almost the same values of 2θ (which gives an idea of the identical spacings between the lattice planes in the crystals). This suggests that isomorphism exists among all these compounds [16]. The difference observed from the X-ray spectra

TABLE IV. Visible Spectral Data for the Colored Dibenzylsulfoxide Complexes of the Lanthanide Nitrates in Nitromethane and Methylene Chloride Solvents (and Solid Reflectance Spectra)

Complex	Transitions (ref. 18)	Using CH_3NO_2 solvent		Using CH_2Cl_2 solvent		Using solid reflectance λ (nm) (E_{max})
		λ (nm)	E_{max} $(M^{-1} cm^{-1})$	λ (nm)	E_{max} $(M^{-1} cm^{-1})$	
$[Pr(DBSO)_3(NO_3)_3]$	$^3H_4 \rightarrow {}^3P_2$	600	5.01	590	4.00	
		552	8.17	552	9.12	558(–)[a]
		472	10.82	472	11.00	485(–)
	$^3H_4 \rightarrow {}^1D_2$	450	14.30	450	15.13	453(–)
$[Nd(DBSO)_{2.5}(NO_3)_3]$	$^4I_{9/2} \rightarrow {}^4G_{5/2}$	800	8.30	800	8.60	765(–)
		745	5.33	745	6.00	
		583	15.71	583	14.99	586(–)
	$^4I_{9/2} \rightarrow {}^2G_{7/2}$	525	3.32	526	3.95	530(–)
		513	1.60	513	1.92	
$[Er(DBSO)_{2.5}(NO_3)_3]$	$^4I_{15/2} \rightarrow {}^4G_{11/12}$	680	3.30	685	3.62	
		654	5.40	654	4.95	655(–)
		552	8.21	552	6.21	
	$^4I_{15/2} \rightarrow {}^2H_{11/2}$	522	14.50	522	14.40	525(–)
		490	2.19	490	3.00	385(–)

[a]Shoulder.

for the two sets) was due to the ability of the larger lanthanide ions to accommodate a close arrangement of the atoms [16, 17].

The hypersensitive bands observed for the colored lanthanide nitrate complexes of DBSO are shown in Table IV. For the $[Pr(DBSO)_3(NO_3)_3]$ complex, $^3H_4 \rightarrow {}^1D_2$ transitions appeared as a strong band at 450 nm and as a weak band at 472 nm in nitromethane and also in methylene chloride. For the $[Nd(DBSO)_{2.5}(NO_3)_3]$ complex, the hypersensitive transitions $^4I_{9/2} \rightarrow {}^4G_{5/2}$ and $^2G_{7/2}$ appeared as a strong band at 583 nm in nitromethane and also in methylene chloride, but were found at 595 nm in methanol, which proves solvolysis of this complex in this solvent. For the $[Er(DBSO)_{2.5}(NO_3)_3]$ complex, the hypersensitive transition $^4I_{15/2} \rightarrow {}^2H_{11/2}$ appeared at 522 nm in all solvents employed. The shape and intensity of these bands correspond with bands of the eight-coordinate $(CH_3)_3NHNd(hfaa)_4$ and $(CH_3)_3NHEr(hfaa)_4$ complexes, studied by Karraker [18]. He also found that, in each case, as the coordination number of the lanthanide ion decreased, so did the intensity of the hypersensitive bands in the visible spectrum.

Conclusions

There is a variability of the coordination number of ligands which is due to the differences in cationic sizes, electrostatic forces of attraction or repulsion and ligand lability, rather than bond orientation [19]. This also indicates competition between the nitrate ion and DBSO for the coordination sites. Forsberg

and Moeller [20] proved the ability of the anion to enter the coordination sphere in a decreasing order, $NO_3^- > Cl^- > Br^- > ClO_4^-$. Their work also showed that the radii of the lanthanide ions influenced the change in coordination number of the ligand in $[Ln(en)_y X_3]$ compounds, where X = anions and $y = 2-4$. It is also significant that the nitrate group has sufficient donor strength for the DBSO groups to 'make room' for it in the coordination sphere. So the additional space available for ligand coordination then becomes affected, and selectively in terms of ligand size results.

Acknowledgements

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