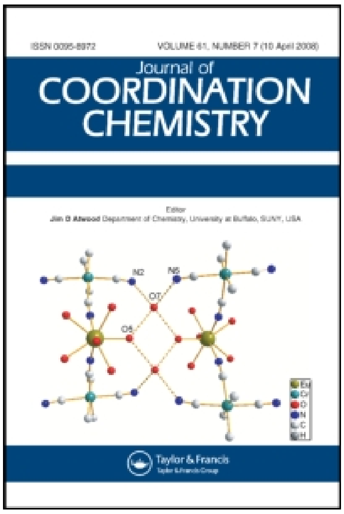

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SYNTHESIS, SPECTROSCOPIC PROPERTIES AND STRUCTURE OF *BIS*(DIMETHYLSULFOXIDE)*TRIS*(*N,N*-DIMETHYLDITHIOCARBAMATO)LANTHANIDE(III)

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SYNTHESIS, SPECTROSCOPIC PROPERTIES AND STRUCTURE OF *BIS*(DIMETHYL SULFOXIDE)*TRIS*(*N*,*N*-DIMETHYLDITHIOCARBAMATO)LANTHANIDE(III)

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The title complexes [Ln($Me_2Dtc)_3(DMSO)_2$)(Ln = La, Pr–Nd, Sm–Tb; Me_2Dtc = *N*,*N*-dimethyldithiocarbamate; DMSO = dimethylsulfoxide) have been synthesized, and the structure of [La($Me_2Dtc)_3(DMSO)_2$] has been determined by the use of single-crystal X-ray methods; the complex crystallizes in the monoclinic system, space group *Cc* with $Z = 4$, $a = 14.456(2)$, $b = 11.105(2)$, $c = 18.691(2)$Å, $\beta = 115.33(1)°$, $V = 2712.1(6)$Å^3. The structure was refined to $R = 0.022$ for 2493 independent reflections with $I \geqslant 3\sigma(I)$. The central La(III) atom is octacoordinated with dodecahedral geometry to six sulfur atoms of three Me_2Dtc ligands and to two oxygen atoms of two DMSO ligands. Spectroscopic properties of the complexes (IR and electronic spectra) are discussed.

KEYWORDS: lanthanide(III), *N*,*N*-dimethyldithiocarbamate, dimethylsulfoxide, complex, crystal structure

INTRODUCTION

Although the coordination of sulfur (a soft base) to a lanthanide (a hard acid) has been demonstrated to be stronger than has previously been expected and a few stable dialkyldithiophosphinato- and *O*,*O'*-dialkyldithiophosphato-lanthanide complexes have been characterized,[1–5] the synthesis of analogous *N*,*N*-dialkyldithiocarbamato complexes seems to be difficult and water must be excluded during preparation.[6–12] Considering the striking structural features and diversified applications of dithiocarbamato-metal complexes,[13] it is of both theoretical and practical significance to explore the field more fully. As a extension of our previous research on ion-association complexes of lanthanides with dithiocarbamates,[8–10] we have synthesized dimethylsulfoxide-*N*,*N*-dimethyldithiocarbamate (Me_2Dtc) mixed complexes of lanthanide elements, and find that this kind of ternary complex is more

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stable and can be prepared (using hydrated lanthanide salt), isolated and studied under ordinary laboratory conditions. The crystal and molecular structure of $[La(Me_2Dtc)_3(DMSO)_2]$ has been determined.

EXPERIMENTAL

Chemicals

Dimethylammonium dimethyldithiocarbamate ($Me_2Dtc \cdot H_2NMe_2$) was prepared according to literature procedures.[13] Hydrated lanthanide perchlorates were prepared by dissolving lanthanide oxides (AnalaR) in 1:1 perchloric acid. All other chemicals were AnalaR grade and were used without further purification.

Preparation

A solution of 0.18 mmol of $Ln(ClO_4)_3 \cdot nH_2O$ in 5 cm^3 of acetonitrile was added to a solution of 0.54 mmol of $Me_2Dtc \cdot H_2NMe_2$ and 0.36 mmol of DMSO in 5 cm^3 of acetonitrile. The mixture was stirred at room temperature for 10 min. Diethylether (5cm^3) was then added and the solution was left to stand over night. The complexes crystallized with yields of *ca* 70%.

Crystal Structure Determination

A single crystal of dimensions 0.40×0.40×0.40 mm was selected for data collection on an R3M/E diffractometer with graphite-monochromated MoKα radiation at 21°C, using the $\theta/2\theta$ scan technique. Some 2944 independent reflections were collected in the range $2 \leq 2\theta \leq 52°$, of which 2493 reflections with $I \geq 3\sigma(I)$ were used in the structure determination and refinement. Data were corrected for Lorentz-polarization and absorption effects.

The structure was solved by the Patterson method and subsequent Fourier synthesis techniques, and refined by full-matrix least-squares methods with anisotropic thermal factors for all non-hydrogen atoms and with hydrogen atoms in calculation positions; weighting scheme: $w = [1\text{-exp}(-5)(\sin\theta/\lambda)^2]/[\sigma^2(F) + 0.00015F^2]$; final $R = 0.022$, $R_w = 0.022$. The maximum and minimum residual electron densities in the final difference map were 0.43 and -0.25e Å^{-3}. All calculations were performed with the program SHELXTL. Data collection and refinement parameters are summarized in Table 1. Lists of anisotropic thermal parameters, H-atom parameters, and observed and calculated structure factors are available from the authors on request.

Other Measurements

Carbon, nitrogen and hydrogen analyses were determined using a Carlo Erba 1106 elemental analyser. The IR spectra were recorded on a Nicolet 170 SX FT-IR instrument using KBr disks in the 4000–220cm^{-1} region. Electronic spectra were obtained using a Shimadzu UV-240 spectrophotometer.

Table 1 Crystal data, data collection and refinement parameters.

Formula	$LaC_{13}H_{30}N_3O_2S_6$
Molecular weight	655.8
Crystal system	monoclinic
Space group	*Cc*
Crystal size (mm)	0.40x0.40x0.40
Cell dimensions	
a(Å)	14.456(2)
b(Å)	11.105(2)
c(Å)	18.691(2)
β(°)	115.33(1)
V(Å^3)	2712.1(6)
Z	4
D_{calc}(g cm^{-3})	1.61
Radiation	MoKα $\lambda = 0.71073$Å
F(000)	1320
Data collection	θ/2θ
Scan rate (°/min)	8
2θ range (°)	2–52
h_{max}, h_{min}; k_{max}, k_{min}; l_{max}, l_{min}	18,0;14,0;24,–24
No. measured reflections	3008
No. unique reflections	2944
No. used in refinement ($I \geqslant 3\sigma(I)$)	2493
μ(cm^{-1})	22.03
R	0.022
R_w	0.022
Largest shift/e.s.d.	0.076
S	0.913
Maximum, minimum residual electron density/e Å^{-3}	–0.25, 0.43

Table 2 Analytical data (theoretical values in parentheses).

Complex	Colour	C%	H%	N%
[La(Me_2Dtc)$_3$(DMSO)$_2$]	White	23.95 (23.81)	4.33 (4.61)	6.82 (6.41)
[Pr(Me_2Dtc)$_3$(DMSO)$_2$]	Pale green	23.82 (23.74)	4.46 (4.60)	6.58 (6.39)
[Nd(Me_2Dtc)$_3$(DMSO)$_2$]	Pale blue	23.97 (23.62)	4.59 (4.57)	6.42 (6.36)
[Sm(Me_2Dtc)$_3$(DMSO)$_2$]	Pale yellow	23.55 (23.40)	4.48 (4.53)	6.30 (6.30)
[Eu(Me_2Dtc)$_3$(DMSO)$_2$]	Orange red	23.37 (23.34)	4.46 (4.52)	6.39 (6.28)
[Gd(Me_2Dtc)$_3$(DMSO)$_2$]	White	23.21 (23.16)	4.48 (4.49)	6.35 (6.23)
[Tb(Me_2Dtc)$_3$(DMSO)$_2$]	White	23.32 (23.10)	4.44 (4.47)	6.30 (6.22)

RESULTS AND DISCUSSION

Analytical data for the complexes are listed in Table 2. All of the complexes can be readily prepared using hydrated lanthanide salts without any precaution against instability or moisture. The composition of the complexes is independent of the stoichiometry of the reaction and excess DMSO does not replace any of the Me_2Dtc ligands.

X-ray Structure of [La($Me_2Dtc)_3(DMSO)_2$]

Final atomic positional and thermal parameters are given in Table 3 and selected bond lengths and angles in Table 4. Figure 1 shows the structure and numbering scheme for the complex molecule. Figure 2 shows the molecular packing arrangement in the unit cell.

As shown in the Figures, the complex molecules in the crystal are discrete. The central La (III) atom is octacoordined and has a distorted dodecahedron geometry. Three Me_2Dtc ligands are chelated through two corresponding sulfur atoms; two of them span *m* edges of the dodecahedron, while the other one spans an *a* edge. Two DMSO oxygen atoms bond at both ends of the base of a trapezium. Thus this complex is of "*mma*-type".[5] The configuration of the central metal of the present complex is different from that in [Ln($i$$Pr_2Dtp)_3(DMSO)_2$] and [Ln($i$$Pr_2Dtp)_3(DMA)_2$], which are of "*mmm*-type" structure and the two oxygen atoms are located side by side.[5] Similar configurations can be found in [La($Et_2Dtp)_3(Ph_3PO)_2$].[14]

The La–S bond lengths (2.964–3.008; average 2.989Å) are approximately the same; all S–C lengths are also approximately equal. Therefore, it is likely that the S = C double bond of the ligand is delocalized in the complex. La–S bond lengths are comparable with those in Na[La($Et_2Dtc)_4$] (2.97 Å)[7] and [La($i$$P_2Dtp)_3(DMA)_2$]

Table 3 Final atomic coordinates (× 10^5 for La, × 10^4 for others) and thermal parameters (Å^2 × 10^3).[a]

	x/a	*y/b*	*z/c*	U^b
La		24902(2)	0	35(1)
S(1)	-2381(3)	4111(3)	-1231(2)	53(1)
S(2)	2382(3)	4095(3)	1205(2)	60(1)
S(3)	-827(1)	2221(1)	1209(1)	54(1)
S(4)	-482(1)	4632(1)	724(1)	55(1)
S(5)	494(1)	4648(1)	-740(1)	53(1)
S(6)	925(2)	2194(1)	-1157(1)	66(1)
S(7)	943(1)	160(1)	746(1)	51(1)
S(8)	-940(1)	146(1)	-753(1)	53(1)
N(1)	-1245(10)	4253(12)	1750(7)	55(5)
N(2)	1251(9)	4222(10)	-1787(6)	43(4)
N(3)	-47(11)	-1834(3)	-13(8)	47(2)
O(1)	-1736(7)	2915(10)	-998(6)	49(3)
O(2)	1761(8)	3025(10)	1054(6)	53(3)
C(1)	-3377(11)	3769(16)	-2207(9)	73(4)
C(2)	-3089(12)	4062(18)	-732(10)	88(6)
C(3)	3252(12)	3887(15)	722(11)	67(5)
C(4)	3264(13)	4027(18)	2181(10)	84(6)
C(5)	-911(4)	3701(5)	1279(2)	43(2)
C(6)	-1584(9)	3478(14)	2216(7)	61(4)
C(7)	-1263(7)	5582(7)	1845(4)	77(3)
C(8)	900(4)	3782(4)	-1271(3)	47(2)
C(9)	1330(4)	5519(5)	-1842(4)	52(2)
C(10)	1627(13)	3606(15)	-2300(9)	72(5)
C(11)	18(11)	-629(4)	22(9)	38(1)
C(12)	818(15)	-2528(11)	690(9)	88(5)
C(13)	-788(9)	-2527(8)	-544(8)	55(3)

[a] Estimated standard deviation in parentheses. [b] Equivalent isotropic *U* defined as one third of the orthogonalised *Uij* tensor.

Table 4 Selected bond lengths (Å) and bond angles (°).[a]

La-S(3)	2.990(2)	La-S(4)	2.964(2)
La-S(5)	3.002(2)	La-S(6)	3.008(2)
La-S(7)	2.978(1)	La-S(8)	2.994(1)
La-O(1)	2.448(8)	La-O(2)	2.535(9)
S(3)-C(5)	1.657(6)	S(4)-C(5)	1.754(6)
S(5)-C(8)	1.659(6)	S(6)-C(8)	1.775(5)
S(7)-C(11)	1.684(11)	S(8)-C(11)	1.744(11)
N(1)-C(5)	1.322(17)	N(2)-C(8)	1.358(15)
N(3)-C(11)	1.341(6)		
S(3)-La-S(4)	59.1(1)	S(3)-La-S(5)	132.8(1)
S(4)-La-S(5)	73.7(1)	S(3)-La-S(6)	167.7(1)
S(4)-La-S(6)	132.8(1)	S(5)-La-S(6)	59.3(1)
S(3)-La-S(7)	79.0(1)	S(4)-La-S(7)	129.3(1)
S(5)-La-S(7)	139.3(1)	S(6)-La-S(7)	89.2(1)
S(3)-La-S(8)	91.2(1)	S(4)-La-S(8)	139.8(1)
S(5)-La-S(8)	128.8(1)	S(6)-La-S(8)	79.6(1)
S(7)-La-S(8)	59.3(1)	S(3)-La-O(1)	89.1(3)
S(4)-La-O(1)	80.1(3)	S(5)-La-O(1)	82.2(3)
S(6)-La-O(1)	95.7(3)	S(7)-La-O(1)	129.7(3)
S(8)-La-O(1)	72.5(3)	S(3)-La-O(2)	91.7(3)
S(4)-La-O(2)	79.1(3)	S(5)-La-O(2)	79.2(3)
S(6)-La-O(2)	88.7(3)	S(7)-La-O(2)	74.5(2)
S(8)-La-O(2)	132.2(2)	O(1)-La-O(2)	155.3(4)
La-S(3)-C(5)	91.5(2)	La-S(4)-C(5)	90.5(2)
La-S(5)-C(8)	91.6(2)	La-S(6)-C(8)	89.2(2)
La-S(7)-C(11)	91.7(3)	La-S(8)-C(11)	90.0(2)
La-O(2)-S(2)	132.8(6)	La-O(1)-S(1)	131.8(5)
S(3)-C(5)-N(1)	124.9(7)	S(3)-C(5)-S(4)	118.8(3)
S(5)-C(8)-S(6)	119.9(4)	S(7)-C(11)-S(8)	119.1(2)

[a] Estimated standard deviations in parentheses.

(3.016Å),[4] and are about the sum of their ionic radii as presented by Shannon (3.00 Å).[5] However, the La-O bond lengths are slightly different (2.448, 2.535Å).

Spectroscopic Characteristics

Principal IR absorption bands together with band assignments for ligands and complexes are given in Table 5. The C–N stretching vibration of $Me_2Dtc \cdot H_2NMe_2$ appears at 1453 cm^{-1} and shifts to higher wavenumbers (1495–1498 cm^{-1}) on

Table 5 Principal IR bands (cm^{-1}).[a]

Compound	ν(C–N)	ν(C–S)	ν(S–O)	ν(M–S)	ν(M–O)
$Me_2Dtc \cdot H_2NMe_2$	1453s	962s,870s			
DMSO			1042		
$[La(Me_2Dtc)_3(DMSO)_2]$	1498s	979s	1000s	344w	401w
$[Pr(Me_2Dtc)_3(DMSO)_2]$	1497s	979s	999s	344w	403w
$[Nd(Me_2Dtc)_3(DMSO)_2]$	1497s	977s	998s	345w	404w
$[Sm(Me_2Dtc)_3(DMSO)_2]$	1495s	978s	999s	344w	405w
$[Eu(Me_2Dtc)_3(DMSO)_2]$	1498s	979s	1000s	345w	407w
$[Gd(Me_2Dtc)_3(DMSO)_2]$	1498s	983s	1002s	344w	409w
$[Tb(Me_2Dtc)_3(DMSO)_2]$	1497s	984s	1003s	344w	407w

[a] s: strong; w: weak.

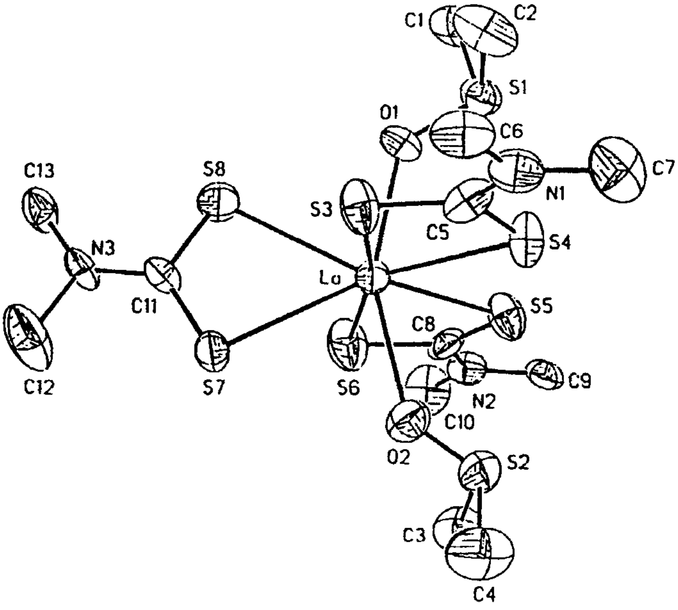

Figure 1 Structure and numbering scheme for the complex.

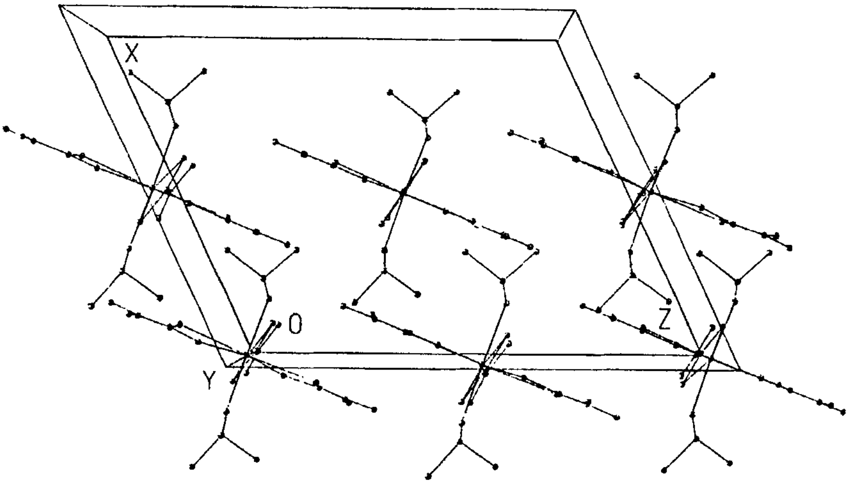

Figure 2 Molecular packing in the unit cell.

coordination, revealing a slight increase in double bond character. The υ (C–S) band of $Me_2Dtc \cdot H_2NMe_2$ shows a doublet (962,870 cm^{-1}) while the complexes show only one strong band in the range 977–984 cm^{-1}. According to the literature,[15,16] the presence of a single υ(C–N) band at higher wavenumbers than in the free ligands, together with a single υ(C–S) band, suggests that in these complexes the dithiocarbamate ligand is bidentate. The υ(S–O) bands of the complexes appear in the range 998–1003 cm^{-1}, showing a slight shift towards lower wavenumbers as compared with the free ligands; this is consistent with oxygen coordination.[17] In the far-IR, new bands observed in the range 344–345 cm^{-1} and 401–409 cm^{-1} for the complexes are attributed tentatively to υ(Ln–S) and v(Ln–O) modes.[18,19]

The electronic spectra of Pr(III), Nd(III) and Sm(III) complexes show a number of bands in the range 350–900 nm which are assigned to f-f transitions. Compared with those of corresponding aqua-ions, a definite red shift is found for almost all transitions; this is related to the covalency of the metal-ligand bond, as assessed by Sinha's parameters (δ), the nephelauxetic ratio (β) and the bonding parameter ($b^{1/2}$).[20,21] The relative energy and J level assignments together with the values of covalent parameters are given in Table 6. The β value of less than one and the positive values of $b^{1/2}$ and δ support partial covalent bonding between metal and ligand.[22,23] Contrary to oxygen donor ligand complexes of lanthanide, the magnitudes of the covalency and bonding parameters decrease from Pr(III) to Sm(III), suggesting that the extent of the covalent character of the metal-ligand bond decreases with increasing atomic number. Similar conclusions were reached by Pinkerton using nuclear magnetic resonance methods.[24]

The rather broad band of moderate intensity, in the complex $[Eu(Me_2Dtc)_3(DMSO)_2]$, appearing at 430 nm may be attributed to electron-transfer from the highest-filled molecular orbital of the ligand to the 4f orbital of the reducible metal ion.[7]

Table 6 Electronic spectra data and associated parameters.[a]

Complex	Frequency[b] (cm^{-1})	Assignment	Covalent parameters
$[Pr(Me_2Dtc)_3(DMSO)_2]$	16722	$^3H_4$–$^1D_2$	$\beta = 0.9806$
	20284	–$^3P_0$	$\delta = 1.8764$
	21030	–$^3P_1$	$b^{1/2} = 0.0985$
	21978	–$^3P_2$	
$[Nd(Me_2Dtc)_3(DMSO)_2]$	11358	$^4I_{9/2}$–$^4F_{3/2}$	$\beta = 0.9849$
	12346	–$^4F_{5/2}$,$^2H_{9/2}$	$\delta = 1.5330$
	13263	–$^4S_{3/2}$,$^4F_{7/2}$[c]	$b^{1/2} = 0.0869$
	14599	–$^4F_{9/2}$	
	15873	$^2H_{11/2}$	
	16858	–$^4G_{5/2}$[c],$^2G_{7/2}$	
	18744	–$^4G_{7/2}$,$^2K_{13/2}$	
	19260	–$^4G_{9/2}$	
	20964	–$^2G_{9/2}$,$^2(P,D)_{3/2}$	
	21460	–$^4G_{11/2}$	
	23127	–$^2P_{1/2}$	
$[Sm(Me_2Dtc)_3(DMSO)_2]$	20894	$^6H_{5/2}$–$^4I_{9/2}$, $^4M_{15/2}$	$\beta = 0.9970$
	21459	–$^4I_{13/2}$	$\delta = 0.3009$
	22422	–$^4M_{17/2}$, $^4G_{9/2}$	$b^{1/2} = 0.0387$
	23364	–$^4M_{19/2}$	
	24125	–$(^6P,^4P)_{5/2}$	
	25974	–$^4L_{15/2}$	

[a] In acetonitrile. [b] Measured center of observed band, the value in cm^{-1} is the converted value.
[c] Hypersensitive band.[7]

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