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SYNTHESIS, STRUCTURE AND SPECTROSCOPIC PROPERTIES OF COMPLEXES OF RARE EARTH DITHIOCARBAMATES WITH 2,2'-BIPYRIDYL OR 1, 10-PHENANTHROLINE

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SYNTHESIS, STRUCTURE AND SPECTROSCOPIC PROPERTIES OF COMPLEXES OF RARE EARTH DITHIOCARBAMATES WITH 2,2'-BIPYRIDYL OR 1, 10-PHENANTHROLINE

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Two series of rare earth complexes with the general formula $[\text{RE}(\text{Me}_2\text{Dtc})_3(\text{bipy})]$ (RE = La, Pr, Nd, Sm, Yb, Y; Me_2Dtc = *N,N*-dimethyldithiocarbamate; bipy = 2,2'-bipyridyl) and $[\text{RE}(\text{Et}_2\text{Dtc})_3(\text{phen})]$ (RE = La, Pr, Nd, Sm, Lu, Y; Et_2Dtc = *N,N*-diethyldithiocarbamate; phen = 1, 10-phenanthroline) have been prepared and some of their chemical properties, IR spectra, electronic spectra and conductivity properties are reported. The structures of $[\text{Eu}(\text{Me}_2\text{Dtc})_3(\text{bipy})]$ and $[\text{Eu}(\text{Et}_2\text{Dtc})_3(\text{phen})]$ have been determined by single-crystal X-ray diffraction methods. $[\text{Eu}(\text{Me}_2\text{Dtc})_3(\text{bipy})]$ crystallizes in the tetragonal system, space group $I4_1/a$ with $a = 16.753(1)$, $c = 39.523(3)$ Å and $Z = 16$, while $[\text{Eu}(\text{Et}_2\text{Dtc})_3(\text{phen})]$ crystallizes in the monoclinic system, space group $P2_1/c$ with $a = 17.029(3)$, $b = 10.652(3)$, $c = 18.726(3)$ Å, $\beta = 96.41(4)^\circ$ and $Z = 4$. The central Eu(III) atoms are both octa-coordinated and in a distorted square antiprismatic geometry, each being coordinated to six sulphur atoms of three bidentate dithiocarbamates and to two nitrogen atoms of bipy or phen ligands. Spectrum analyses indicate that both Me_2Dtc and Et_2Dtc show similar coordination structures in all complexes.

KEYWORDS: Rare earth, dithiocarbamate, 2,2-bipyridyl, 1,10-phenanthroline, complex, crystal structure

INTRODUCTION

In recent years complexes of transition metal elements with dithiocarbamates have not only been studied thoroughly, but also have been widely used in the rubber industry, inorganic analyses and agriculture.¹ However, much less has been reported on corresponding rare earth derivatives. This is mainly because of difficulty of preparation and instability of the complexes towards moisture.^{2–4} In a previous paper⁵ we reported the preparation of dimethylsulfoxide-*N,N*-dimethyldi-

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thiocarbamate complexes of the rare earths, which confirms that rare earth dithiocarbamates form well-defined, stable adducts with dimethylsulfoxide. As a further study of this class of complexes, this paper reports the syntheses, structures and spectroscopic properties of $[\text{RE}(\text{Me}_2\text{Dtc})_3(\text{bipy})]$ and $[\text{RE}(\text{Et}_2\text{Dtc})_3(\text{phen})]$.

EXPERIMENTAL

Reagents

Dimethylammonium dimethyldithiocarbamate and diethylammonium diethyldithiocarbamate were prepared according to literature procedures.⁶ Hydrated rare earth perchlorates were prepared by dissolving rare earth oxides (AnalaR) in 50% perchloric acid. 2,2'-Bipyridyl and 1,10-phenanthroline were purchased from BJCRF (China). All other chemicals were of AnalaR grade and were used without further purification.

Synthesis

All complexes were prepared according to the following synthetic route: 0.1 mmol of $\text{RE}(\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$ and 0.3 mmol of $[\text{Me}_2\text{NH}_2]^+[\text{Me}_2\text{Dtc}]^-$ (or $[\text{Et}_2\text{NH}_2]^+[\text{Et}_2\text{Dtc}]^-$) were dissolved in 3 cm³ of acetonitrile, and then 0.1 mmol of 2,2'-bipyridyl (or 1,10-phenanthroline) dissolved in 2 cm³ of acetonitrile was added slowly. The mixture was left to stand for several hours. The complexes precipitated as crystals with yields of about 80%. Excess bipy or phen (two or three times) did not change the composition of the final products. Crystals suitable for X-ray diffraction were obtained in a similar way from more dilute solutions.

Crystal Structure Determination

A red, air-stable single crystal (both for $[\text{Eu}(\text{Me}_2\text{Dtc})_3(\text{bipy})]$ and $[\text{Eu}(\text{Et}_2\text{Dtc})_3(\text{phen})]$) was selected for data collection on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated CuK_α radiation (λ 1.54184 Å) at 21 °C, using the ω -2 θ scan technique. For $[\text{Eu}(\text{Me}_2\text{Dtc})_3(\text{bipy})]$, 3834 reflections were measured in the range $1 \leq \theta \leq 55^\circ$, of which 1923 reflections with $I \geq 3.0 \sigma(I)$ were used in the structure determination and refinement, while for $[\text{Eu}(\text{Et}_2\text{Dtc})_3(\text{phen})]$, 5022 reflections were measured in the range $1 \leq \theta \leq 57^\circ$, of which 3759 reflections with $I \geq 3\sigma(I)$ were used in the structure determination and refinement. Data were corrected for Lorentz and empirical absorption effects.

The structures were solved using direct methods followed by Fourier difference syntheses, and refined by full-matrix least-squares methods with anisotropic thermal factors for all non-hydrogen atoms; hydrogen atoms were located in calculated positions. All calculations were performed with the SDP package. Final $R = 0.058$, $R_w = 0.063$ were obtained for $[\text{Eu}(\text{Me}_2\text{Dtc})_3(\text{biPy})]$ and $R = 0.054$, $R_w = 0.062$ for $[\text{Eu}(\text{Et}_2\text{Dtc})_3(\text{phen})]$. Data collection and refinement parameters are summarized in Table I. Lists of anisotropic thermal parameters, H-atom parameters, and observed and calculated structure factors are available from the authors on request.

Table I Crystal data, data collection and refinement parameters.

	[Eu(Me ₂ Dtc) ₃ (bipy)]	[Eu(Et ₂ Dtc) ₃ (phen)]
Formula	C ₁₉ H ₂₆ N ₅ S ₆ Eu	C ₂₇ H ₃₈ N ₅ S ₆ Eu
Molecular weight	668.80	776.98
Crystal system	tetragonal	monoclinic
Space group	<i>I</i> 4 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>c</i>
Crystal size (mm)	0.2 × 0.25 × 0.3	0.2 × 0.25 × 0.35
Cell dimensions		
<i>a</i> (Å)	16.753(1)	17.029(3)
<i>b</i> (Å)		10.652(3)
<i>c</i> (Å)	39.523(3)	18.726(3)
β(Å)	90.00	96.41(4)
<i>V</i> (Å ³)	11092.8(21)	3375.3(22)
<i>Z</i>	16	4
<i>D</i> _{calc} (g cm ⁻³)	1.602	1.529
Radiation	CuK _α λ = 1.54184 Å	CuK _α λ = 1.54184 Å
<i>F</i> (000)	5344	1576
Data collection	ω-2θ	ω-2θ
2θ range(°)	2-110	2-114
<i>h</i> _{max} , <i>h</i> _{min} ; <i>k</i> _{max} , <i>k</i> _{min} ; <i>l</i> _{max} , <i>l</i> _{min}	17,0;17,0;42,0	18,-18;11,0;20,0
No. measured reflections	3834	5022
No. used in refinement (<i>I</i> ≥ 3σ(<i>I</i>))	1923	3759
μ(cm ⁻¹)	198.34	163.76
<i>R</i>	0.058	0.054
<i>R</i> _w (unit weights)	0.063	0.062
Maximum, minimum residual electron density/e Å ⁻³	0.67,-0.72	0.76,-0.88

Chemical and Physical Measurements

Carbon, nitrogen and hydrogen were determined using a Carlo Erba 1106 elemental analyser. IR spectra were recorded on a Nicolet 170 SX FT-IR instrument using KBr disks in the 4000–220 cm⁻¹ region. Electronic spectra in chloroform solution were obtained by using a Shimadzu UV-260 spectrophotometer. Conductivity measurements were carried out with a DDS-11A type conductivity bridge using 10⁻³M solutions at 25°C.

RESULTS AND DISCUSSION

All complexes were prepared in air using hydrated rare earth salts and were isolated in good yields as air-stable solids. Interestingly, the composition of the final products retained unchanging even if excess bipy or phen (two or three times) was added, suggesting that further replacement of any of dithiocarbamate ligand is not easy. Stable ternary complexes formed when bipy and phen were used as additional ligands, and they even stabilized rare earth dithiocarbamates to Yb and Lu. Physical and analytical data are summarized in Table II, which show that they have the general formula [RE(Me₂Dtc)₃(bipy)] and [RE(Et₂Dtc)₃(phen)]. The molar conductances indicate that all the complexes are non-electrolytes.⁷ All complexes are sparingly soluble in benzene, ether and hexane, soluble in ethanol, methanol, acetonitrile and dichloromethane, and very soluble in DMF, DMSO and chloroform.

Table II Analytical data, colours and molar conductance data for the complexes.

Complex	Colour	C% Found (Calc.)	H% Found (Calc.)	N% Found (Calc.)	Λ_m^a (Scm^2 mol^{-1})
[La(Me ₂ Dtc) ₃ (bipy)]	White	35.23 (34.80) 34.77	3.86 (4.00) 3.88	10.51 (10.68) 10.60	25
[Pr(Me ₂ Dtc) ₃ (bipy)]	Pale green	(34.70) 34.79	(3.98) 3.83	(10.65) 10.47	25
[Nd(Me ₂ Dtc) ₃ (bipy)]	Pale blue	(34.52) 34.22	(3.96) 3.81	(10.60) 10.50	27
[Sm(Me ₂ Dtc) ₃ (bipy)]	Pale yellow	(34.20) 34.03	(3.93) 3.71	(10.50) 10.24	29
[Eu(Me ₂ Dtc) ₃ (bipy)]	Red	(34.12) 34.28	(3.92) 3.48	(10.47) 10.31	33
[Gd(Me ₂ Dtc) ₃ (bipy)]	White	(33.86) 33.81	(3.89) 3.61	(10.39) 10.29	27
[Tb(Me ₂ Dtc) ₃ (bipy)]	White	(33.77) 33.46	(3.88) 3.64	(10.36) 10.19	25
[Dy(Me ₂ Dtc) ₃ (bipy)]	White	(33.59) 33.44	(3.86) 3.75	(10.31) 10.16	24
[Ho(Me ₂ Dtc) ₃ (bipy)]	Pale yellow	(33.47) 33.12	(3.84) 3.61	(10.27) 10.10	31
[Er(Me ₂ Dtc) ₃ (bipy)]	Pink	(33.36) 33.10	(3.83) 3.59	(10.24) 10.23	38
[Tm(Me ₂ Dtc) ₃ (bipy)]	White	(33.28) 32.84	(3.82) 3.53	(10.21) 9.93	26
[Yb(Me ₂ Dtc) ₃ (bipy)]	Yellow	(33.08) 37.59	(3.80) 4.12	(10.15) 11.43	23
[Y(Me ₂ Dtc) ₃ (bipy)]	White	(37.67) 42.62	(4.33) 5.06	(11.56) 9.13	25
[La(Et ₂ Dtc) ₃ (phen)]	White	(42.45) 42.22	(5.01) 4.81	(9.17) 9.05	52
[Pr(Et ₂ Dtc) ₃ (phen)]	Pale green	(42.34) 42.30	(5.00) 4.94	(9.14) 9.18	44
[Nd(Et ₂ Dtc) ₃ (phen)]	Blue	(42.16) 42.06	(4.98) 4.90	(9.10) 9.05	39
[Sm(Et ₂ Dtc) ₃ (phen)]	Pale yellow	(41.83) 41.74	(4.95) 4.92	(9.03) 8.84	46
[Eu(Et ₂ Dtc) ₃ (phen)]	Red	(41.73) 41.58	(4.93) 4.82	(9.01) 8.91	41
[Gd(Et ₂ Dtc) ₃ (phen)]	White	(41.46) 41.40	(4.90) 4.70	(8.95) 9.09	47
[Tb(Et ₂ Dtc) ₃ (phen)]	White	(41.37) 41.17	(4.89) 4.68	(8.93) 8.92	53
[Dy(Et ₂ Dtc) ₃ (phen)]	White	(41.18) 41.39	(4.86) 4.75	(8.89) 9.03	48
[Ho(Et ₂ Dtc) ₃ (phen)]	Pale yellow	(41.05) 41.12	(4.85) 4.79	(8.87) 8.90	55
[Er(Et ₂ Dtc) ₃ (phen)]	Pink	(40.93) 40.90	(4.83) 4.60	(8.84) 8.88	60
[Tm(Et ₂ Dtc) ₃ (phen)]	White	(40.85) 40.37	(4.82) 4.59	(8.82) 8.78	58
[Yb(Et ₂ Dtc) ₃ (phen)]	Yellow	(40.64) 40.73	(4.80) 4.75	(8.78) 8.51	61
[Lu(Et ₂ Dtc) ₃ (phen)]	White	(40.54) 45.51	(4.79) 5.32	(8.75) 9.91	62
[Y(Et ₂ Dtc) ₃ (phen)]	White	(45.43)	(5.37)	(9.81)	59

^a In acetonitrile for [RE(MeDtc)₃(bipy)] and in chloroform for [RE(Et₂Dtc)₃(phen)].

Spectroscopic Properties

In the IR spectra the single band due to the $\nu(\text{C}=\text{N})$ stretching vibration of the present two series of complexes appears in the region $1492\text{--}1494\text{ cm}^{-1}$ for $[\text{RE}(\text{Me}_2\text{Dtc})_3(\text{bipy})]$ and $1481\text{--}1483\text{ cm}^{-1}$ for $[\text{RE}(\text{Et}_2\text{Dtc})_3(\text{phen})]$ respectively, and is shifted to higher wavenumber compared to the free ligands (1453 and 1469 cm^{-1}). One strong $\nu(\text{C}=\text{S})$ band in the region $978\text{--}986\text{ cm}^{-1}$ for $[\text{RE}(\text{Me}_2\text{Dtc})_3(\text{bipy})]$ and $992\text{--}1005\text{ cm}^{-1}$ for $[\text{RE}(\text{Et}_2\text{Dtc})_3(\text{phen})]$ respectively, indicates that the dithiocarbamates behave as bidentate ligands in these complexes.^{8,9} The bands at $3057\text{--}3061$, $1598\text{--}1594$, $1562\text{--}1560$, $769\text{--}771\text{ cm}^{-1}$ and $3044\text{--}3046$, $1622\text{--}1625$, $1589\text{--}1590$, $1569\text{--}1572$, $1516\text{--}1517$, $843\text{--}847$, $726\text{--}730\text{ cm}^{-1}$ are characteristic absorptions of 2,2'-bipyridyl and 1,10-phenanthroline, respectively.

The electronic spectra of the present complexes exhibit two characteristic bands for bipy in the range $241\text{--}246$, $279\text{--}282\text{ nm}$ for $[\text{RE}(\text{Me}_2\text{Dtc})_3(\text{bipy})]$ and one band for phen in the range $266\text{--}268\text{ nm}$ in the UV region, whilst in the visible region, a number of f-f transitions, which are useful in assessing the covalency of the metal-ligand bond and determining the structure of the complex in solution, are found for Pr(III), Nd(III), Sm(III), Eu(III), Ho(III), Er(III) and Tm(III) complexes. A definite red shift is found for almost all these transitions compared with those of corresponding aqua-ions, and Sinha's parameter (δ), the nephelauxetic ratio (β) and the bonding parameter ($b^{1/2}$) have been calculated. The relative energy and J level assignment as well as the values of covalent parameters are given in Table III. Compared with $[\text{Ln}(\text{Me}_2\text{Dtc})_3(\text{DMSO})_2]$ ⁵ and $[\text{Ln}(\text{Et}_2\text{Dtc})_4]^{-3}$ the electronic spectra of the present complexes are interesting in the following respects. First, the covalent parameters of both RES_8 and RES_6L_2 (L = O or N) chromophores exhibit similar character suggesting that covalent bonding between metal and ligand is mainly effected by the relatively high polarizability of the sulphur atoms. Secondly, $[\text{RE}(\text{Me}_2\text{Dtc})_3(\text{bipy})]$, $[\text{RE}(\text{Et}_2\text{Dtc})_3(\text{phen})]$, $[\text{Ln}(\text{Me}_2\text{Dtc})_3(\text{DMSO})_2]$ and $[\text{Ln}(\text{Et}_2\text{Dtc})_4]^{-}$ present a similar spectroscopic pattern with small shifts of observed bands, thus indicating that ligand substitution has only a small effect on f-f transition properties. Thirdly, the f-f transitions of Eu(III) complexes are overwhelmed by the broad, strong CT band (see below) and only appear as shoulders; even so, the observation of the ${}^7F_0 \rightarrow {}^5D_0$ transition is very important to the discussion of the structure of Eu(III) complexes.¹⁰ This transition is forbidden in all symmetries higher than C_{nv} and fixes the symmetry of the two present Eu(III) complexes at C_{nv} or lower. In general, magnitudes of the nephelauxetic ratios (β) of the both series of complexes show an abrupt increase at Sm(III), suggesting less covalent character of the metal-ligand bond in the heavier rare earth complexes. This finding is consistent with conclusions reached by Pinkerton¹¹ with the NMR method.

The rather broad band of moderate intensity in the complexes $[\text{Eu}(\text{Me}_2\text{Dtc})_3(\text{bipy})]$ and $[\text{Eu}(\text{Et}_2\text{Dtc})_3(\text{phen})]$ appearing at about 443 nm may be attributed to charge-transfer (CT) transitions from the highest-filled molecular orbital of the ligands to the 4f orbitals of the metal ions.³ The same transitions should be expected for yellow Yb(III) complexes but they may be overlapped by the very strong intraligand transitions and could not be detected.

X-ray structures of [Eu(Me₂Dtc)₃(bipy)] and [Eu(Et₂Dtc)₃(phen)]

X-ray structure determinations confirm the coordination behaviour of the ligands assigned from above physical measurements. Final atomic positional and thermal parameters are given in Table IV, and selected bond distances and bond angles in

Table III Electronic spectroscopic data and covalent parameters for the complexes.

Complex	Frequency (cm ⁻¹) ^a	Assignment	Covalent parameters
[Pr(Me ₂ Dtc) ₃ (bipy)]	16705	³ H ₄ - ¹ D ₂	β = 0.9792
	20202	- ³ P ₀	δ = 2.1242
	20816	- ³ P ₁	b ^{1/2} = 0.1020
	21930	- ³ P ₂	
[Nd(Me ₂ Dtc) ₃ (bipy)]	11351	⁴ I _{9/2} - ⁴ F _{3/2}	β = 0.9863
	12345	- ⁴ F _{5/2} , ² H _{9/2}	δ = 1.3844
	13241	- ⁴ S _{3/2} , ⁴ F _{7/2} ^b	b ^{1/2} = 0.0828
	14633	- ⁴ F _{9/2}	
	15898	- ² H _{1/2}	
	16835	- ⁴ G _{5/2} ^b , ² G _{7/2}	
	18776	- ⁴ G _{7/2} , ² K _{13/2}	
	19223	- ⁴ G _{9/2}	
	20921	- ² G _{9/2} , ² (P,D) _{3/2}	
	21322	- ⁴ G _{11/2}	
	22989	- ² P _{1/2}	
[Sm(Me ₂ Dtc) ₃ (bipy)]	20855	⁶ H _{5/2} - ⁴ I _{9/2} , ⁴ M _{15/2}	β = 0.9980
	21505	- ⁴ I _{13/2}	δ = 0.1908
	23337	- ⁴ M _{19/2}	b ^{1/2} = 0.0316
	23981	-(⁶ P, ⁴ P) _{5/2}	
[Eu(Me ₂ Dtc) ₃ (bipy)]	17229	⁷ F ₀ - ⁵ D ₀	β = 0.9969
	21395	- ⁵ D ₂	δ = 0.3096
	25381	- ⁵ L ₆	b ^{1/2} = 0.0394
[Ho(Me ₂ Dtc) ₃ (bipy)]	12943	⁵ I ₈ - ⁵ I ₄	β = 0.9922
	15456	- ⁵ F ₅	δ = 0.7861
	18457	- ⁵ S ₂ , ⁵ F ₄	b ^{1/2} = 0.0624
	20509	- ⁵ F ₃	
	21008	- ⁵ F ₂	
	21295	- ³ K ₃	
	21872	- ⁵ G ₆ ^b , ⁵ F ₁	
	23764	-(⁵ G, ³ G) ₅	
[Er(Me ₂ Dtc) ₃ (bipy)]	15198	⁴ I _{15/2} - ⁴ F _{9/2}	β = 0.9985
	18369	- ⁴ S _{3/2}	δ = 0.1502
	19019	- ² H _{11/2} ^b	b ^{1/2} = 0.0274
	20383	- ⁴ F _{7/2}	
	22222	- ⁴ F _{5/2}	
[Tm(Me ₂ Dtc) ₃ (bipy)]	12550	³ H ₆ - ³ H ₄ ^b	β = 0.9961
	14443	- ³ F ₃	δ = 0.3915
	21436	- ¹ G ₄	b ^{1/2} = 0.0442
[Pr(Et ₂ Dtc) ₃ (phen)]	16545	³ H ₄ - ¹ D ₂	β = 0.9757
	20088	- ³ P ₀	δ = 2.4905
	20747	- ³ P ₁	b ^{1/2} = 0.1102
	21142	- ¹ I ₆	
	21863	- ³ P ₂	

Table III Continued

Complex	Frequency (cm ⁻¹) ^a	Assignment	Covalent parameters
[Nd(Et ₂ Dtc) ₃ (phen)]	11343	⁴ I _{9/2} - ⁴ F _{3/2}	β = 0.9866
	12333	- ⁴ F _{5/2} , ² H _{9/2}	δ = 1.3582
	13245	- ⁴ S _{3/2} , ⁴ F _{7/2} ^b	b ^{1/2} = 0.0818
	14590	- ⁴ F _{9/2}	
	15873	- ² H _{11/2}	
	16812	- ⁴ G _{5/2} , ² G _{7,2}	
	18762	- ⁴ G _{7/2} , ² K _{13/2}	
	19209	- ⁴ G _{9/2}	
	20956	- ² G _{9/2} , ² (P,D) _{3/2}	
	21478	- ⁴ G _{11/2}	
	23052	- ² P _{1/2}	
	[Sm(Et ₂ Dtc) ₃ (phen)]	18832	⁶ H _{5/2} - ⁴ F _{3/2}
20756		- ⁴ I _{8/2} , ⁴ M _{15/2}	δ = 0.4218
21432		- ⁴ I _{13/2}	b ^{1/2} = 0.0458
23343		- ⁴ M _{19/2}	
23969		-(⁶ P, ⁴ D) _{5/2}	
[Eu(Et ₂ Dtc) ₃ (phen)]	17229	⁷ F ₀ - ⁵ D ₀	β = 0.9958
	21395	- ⁵ D ₂	δ = 0.4218
[Ho(Et ₂ Dtc) ₃ (phen)]	15432	⁵ I ₈ - ⁵ F ₅	b ^{1/2} = 0.0458
	18443	- ⁵ S ₂ , ⁵ F ₄	β = 0.9939
	20467	- ⁵ F ₃	δ = 0.6137
	20991	- ⁵ F ₂	b ^{1/2} = 0.0552
	21240	- ³ K ₃	
	21863	- ⁵ G ₆ , ⁵ F ₁	
	23798	-(⁵ G, ³ G) ₅	
	[Er(Et ₂ Dtc) ₃ (phen)]	15188	⁴ I _{15/2} - ⁴ F _{9/2}
18309		- ⁴ S _{3/2}	δ = 0.2004
18997		- ² H _{11/2} ^b	b ^{1/2} = 0.0316
20342		- ⁴ F _{7,2}	
22124		- ⁴ F _{5/2}	
22573		- ⁴ F _{3/2}	
[Tm(Et ₂ Dtc) ₃ (phen)]		12463	³ H ₆ - ³ H ₄ ^b
	14393	- ³ F ₃	δ = 0.6036
	15051	- ³ F ₂	b ^{1/2} = 0.0548
	21459	- ¹ G ₄	

^aMeasured centre of observed band.^bHypersensitive band³.

Table V. Figures 1 and 2 shows the structures and numbering schemes for the complex molecules. In both molecules, the central Eu(III) is octa-coordinated and has a distorted square antiprismatic geometry. Three dithiocarbamate ligands are chelated through two sulfur atoms and bipy (or phen) through two nitrogen atoms to form an *ssss*-type¹² structure. Compared to [La(Me₂Dtc)₃(DMSO)₂],⁵ in these two complexes two nitrogen atoms are forced to adopt *cis* positions, while in [La(Me₂Dtc)₃(DMSO)₂], two oxygen atoms prefer to adopt *trans* positions. The bond distances of Eu-S are 2.824(1)-2.890(2) Å (mean 2.854 Å) for [Eu(Me₂Dtc)₃(bipy)] and 2.783(1)-2.914(1) Å (mean 2.854 Å) for [Eu(Et₂Dtc)₃(phen)]; Eu-N

Table IV Final atomic positional and thermal parameters with e.s.d.'s in parentheses.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>Beq/ Å²</i> ^a
[Eu(Me₂Dtc)₃(bipy)]				
Eu	0.17705(6)	0.49121(6)	0.30920(3)	3.39(2)
S(1)	0.1374(3)	0.6368(3)	0.3415(1)	3.5(1)
S(2)	0.1387(3)	0.6247(3)	0.2673(1)	4.1(1)
S(3)	0.1696(4)	0.4330(3)	0.2422(1)	5.0(1)
S(4)	0.1510(4)	0.3234(3)	0.2996(2)	5.7(1)
S(5)	0.3253(3)	0.5692(3)	0.2961(2)	5.3(1)
S(6)	0.3206(3)	0.4305(4)	0.3405(2)	7.2(2)
N(1)	0.0247(9)	0.4764(6)	0.3128(3)	2.7(3)
N(2)	0.1198(9)	0.4577(8)	0.3675(4)	3.5(3)
N(3)	0.1081(9)	0.7590(8)	0.3005(3)	4.0(4)
N(4)	0.135(1)	0.2905(9)	0.2352(4)	6.1(5)
N(5)	0.446(1)	0.524(1)	0.3337(6)	8.4(6)
C(1)	-0.019(1)	0.486(1)	0.2859(5)	4.4(5)
C(2)	-0.103(1)	0.473(1)	0.2856(5)	4.4(5)
C(3)	-0.137(1)	0.450(1)	0.3152(6)	5.0(5)
C(4)	-0.091(1)	0.441(1)	0.3441(6)	5.4(5)
C(5)	-0.0114(8)	0.456(1)	0.3420(4)	3.0(3)
C(6)	0.038(1)	0.450(1)	0.3720(5)	3.8(4)
C(7)	0.009(1)	0.442(1)	0.4044(5)	4.8(5)
C(8)	0.057(1)	0.442(1)	0.4320(5)	4.9(5)
C(9)	0.140(1)	0.451(1)	0.4274(5)	5.0(5)
C(10)	0.166(1)	0.456(1)	0.3946(5)	4.3(4)
C(11)	0.1287(9)	0.6825(9)	0.3035(4)	3.0(4)
C(12)	0.101(1)	0.799(1)	0.2680(5)	6.5(6)
C(13)	0.095(1)	0.810(1)	0.3296(5)	4.9(5)
C(14)	0.150(1)	0.340(1)	0.2570(5)	4.1(4)
C(15)	0.117(2)	0.199(1)	0.2474(7)	7.8(7)
C(16)	0.136(2)	0.291(1)	0.1997(6)	8.3(8)
C(17)	0.373(1)	0.508(1)	0.3231(6)	5.1(5)
C(18)	0.488(2)	0.475(3)	0.359(1)	17(1)
C(19)	0.492(2)	0.586(2)	0.320(1)	14(1)
[Eu(Et₂Dtc)₃(phen)]				
Eu	0.24996(3)	0.02922(6)	0.13323(3)	1.73(1)
S(1)	0.2524(1)	0.2850(3)	0.1788(2)	2.70(6)
S(2)	0.3898(1)	0.1174(3)	0.2138(2)	2.39(5)
S(3)	0.1047(1)	0.0022(3)	0.1988(2)	2.77(6)
S(4)	0.2458(2)	-0.1435(3)	0.2488(2)	4.51(7)
S(5)	0.3569(1)	-0.1697(3)	0.0985(2)	3.31(6)
S(6)	0.1912(2)	-0.1509(3)	0.0336(2)	5.16(8)
N(1)	0.3141(5)	0.1337(9)	0.0310(5)	2.8(2)
N(2)	0.1534(4)	0.1385(9)	0.0343(4)	2.4(2)
N(3)	0.3960(5)	0.3642(8)	0.2321(5)	2.7(2)
N(4)	0.1036(5)	-0.1981(8)	0.2836(5)	2.5(2)
N(5)	0.2765(5)	-0.3556(9)	0.0284(5)	3.1(2)
C(1)	0.3926(6)	0.132(1)	0.0275(6)	3.8(3)
C(2)	0.4283(8)	0.190(1)	-0.0275(7)	4.9(3)
C(3)	0.3832(8)	0.251(1)	-0.0800(7)	5.1(3)
C(4)	0.3007(8)	0.255(1)	-0.0809(6)	3.9(3)
C(5)	0.246(1)	0.311(1)	-0.1361(6)	5.4(3)
C(6)	0.1679(9)	0.307(1)	-0.1358(7)	5.0(3)
C(7)	0.1323(8)	0.247(1)	-0.0788(6)	3.7(3)
C(8)	0.0520(7)	0.241(1)	-0.0767(7)	4.3(3)
C(9)	0.0244(7)	0.185(1)	-0.0209(7)	4.4(3)
C(10)	0.0754(6)	0.136(1)	0.0337(6)	3.5(3)
C(11)	0.1835(6)	0.194(1)	-0.0216(5)	2.4(2)

Table IV Continued

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>Beq/ Å^{2a}</i>
C(12)	0.2686(6)	0.194(1)	-0.0232(5)	2.6(2)
C(13)	0.3507(5)	0.267(1)	0.2110(5)	1.9(2)
C(14)	0.4814(6)	0.349(1)	0.2543(7)	3.8(3)
C(15)	0.5249(7)	0.359(1)	0.1891(8)	5.6(4)
C(16)	0.3664(7)	0.493(1)	0.2345(7)	3.7(3)
C(17)	0.3527(9)	0.532(1)	0.3093(9)	6.1(4)
C(18)	0.1468(5)	-0.123(1)	0.2478(5)	2.1(2)
C(19)	0.0175(6)	-0.185(1)	0.2833(7)	3.4(3)
C(20)	-0.0019(8)	-0.113(2)	0.3486(8)	5.8(4)
C(21)	0.1379(7)	-0.306(1)	0.3251(8)	4.5(3)
C(22)	0.1331(9)	-0.424(1)	0.280(1)	7.0(5)
C(23)	0.2759(5)	-0.238(1)	0.0510(6)	2.6(2)
C(24)	0.3492(7)	-0.433(1)	0.0358(8)	4.6(3)
C(25)	0.3915(9)	-0.421(2)	-0.0297(9)	7.2(4)
C(26)	0.2054(7)	-0.415(1)	-0.0100(7)	3.7(3)
C(27)	0.1522(8)	-0.472(1)	0.0411(9)	5.5(3)

$${}^a Beq = (4/3)[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

bond distances are 2.559(8), 2.569(4) Å and 2.562(5), 2.611(4) Å. It is interesting to note that they are almost equivalent, respectively, within experimental error, though the latter is obviously more sterically hindered. Moreover, when comparing the M-S bond distances of the present Eu(III) complexes with those of [La(Et₂Dtc)₄]⁻ (mean 2.97 Å)³ and [La(Me₂Dtc)₃(DMSO)₂] (mean 2.989 Å),⁵ we find that the present Eu(III) complexes correspond to about 0.04 Å less than the change in ionic radii (La = 1.160, Eu = 1.066 Å).¹³ This finding indicates that the coordination of bipy (or

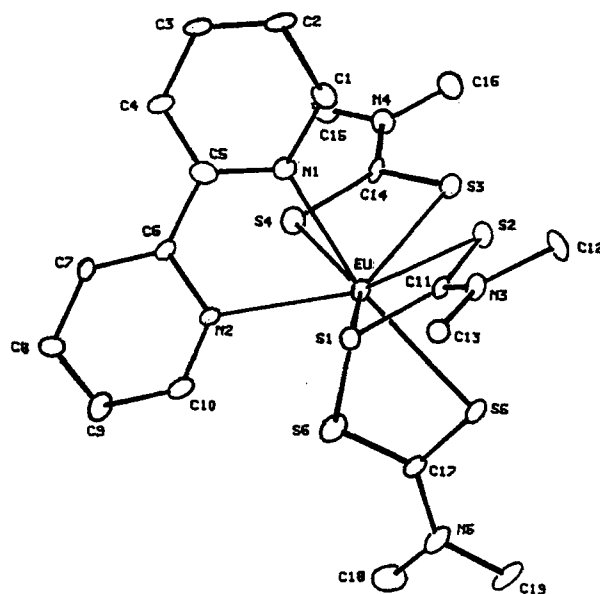


Figure 1 Perspective view of [Eu(Me₂Dtc)₃(bipy)] with the atom labelling scheme.

Table V Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses.

[Eu(Me₂Dtc)₃(bipy)]			
Eu-S(1)	2.832(1)	S(1)-C(11)	1.692(14)
Eu-S(2)	2.855(1)	S(2)-C(11)	1.735(13)
Eu-S(3)	2.824(1)	S(3)-C9(14)	1.696(6)
Eu-S(4)	2.870(1)	S(4)-C(14)	1.707(16)
Eu-S(5)	2.854(1)	S(5)-C(17)	1.683(17)
Eu-S(6)	2.890(2)	S(6)-C(17)	1.714(10)
Eu-N(1)	2.569(4)	N(1)-C(5)	1.347(14)
Eu-N(2)	2.559(8)	N(2)-C(6)	1.383(4)
N(3)-C(11)	1.332(2)	N(4)-C(14)	1.339(13)
N(5)-C(17)	1.326(12)	C(5)-C(6)	1.451(15)
S(1)-Eu-S(2)	62.22(3)	S(4)-Eu-S(6)	80.70(5)
S(1)-Eu-S(3)	135.18(4)	S(4)-Eu-N(1)	76.22(8)
S(1)-Eu-S(4)	150.19(4)	S(4)-Eu-N(2)	81.21(6)
S(1)-Eu-S(5)	83.76(4)	S(5)-Eu-S(6)	60.99(5)
S(1)-Eu-S(6)	107.76(5)	S(5)-Eu-N(1)	156.79(7)
S(1)-Eu-N(1)	79.92(7)	S(5)-Eu-N(2)	126.2(1)
S(1)-Eu-N(2)	72.26(5)	S(6)-Eu-N(1)	140.28(8)
S(2)-Eu-S(3)	73.55(4)	S(6)-Eu-N(2)	81.30(8)
S(2)-Eu-S(4)	131.01(4)	N(1)-Eu-N(2)	63.6(1)
S(2)-Eu-S(5)	74.45(4)	N(1)-(15)-C(6)	117.2(4)
S(2)-Eu-S(6)	735.35(4)	N(2)-C(6)-C(5)	117.2(9)
S(2)-Eu-N(1)	83.35(8)	S(1)-C(11)-S(2)	118.0(1)
S(2)-Eu-N(2)	127.56(1)	S(3)-C(14)-S(4)	119.2(6)
S(3)-Eu-S(4)	62.06(5)	S(5)-C(1)-S(6)	118.2(5)
S(3)-Eu-S(5)	91.49(4)	S(3)-Eu-S(6)	108.50(5)
S(3)-Eu-N(1)	88.57(9)	S(3)-Eu-N(2)	138.77(9)
S(4)-Eu-S(5)	123.85(4)		
[Eu(Et₂Dtc)₃(phen)]			
Eu-S(1)	2.854(1)	Eu-S(2)	2.833(1)
Eu-S(3)	2.895(1)	Eu-S(4)	2.847(1)
Eu-S(5)	2.914(1)	Eu-S(6)	2.783(1)
Eu-N(1)	2.562(5)	Eu-N(2)	2.611(4)
S(1)-C(13)	1.725(4)	S(2)-C(13)	1.722(5)
S(3)-C(18)	1.724(5)	S(4)-C(18)	1.699(4)
S(5)-C(23)	1.718(5)	S(6)-C(23)	1.714(5)
N(1)-C(12)	1.366(6)	N(2)-C(11)	1.353(7)
N(3)-C(13)	1.328(6)	N(4)-C(18)	1.323(6)
N(5)-C(23)	1.324(7)	C(11)-C(12)	1.453(7)
S(1)-Eu-S(2)	62.68(3)	S(1)-Eu-S(3)	87.30(4)
S(1)-Eu-S(4)	112.97(5)	S(1)-Eu-S(5)	140.55(3)
S(1)-Eu-S(6)	148.29(4)	S(1)-Eu-N(1)	79.4(2)
S(1)-Eu-N(2)	76.9(1)	S(2)-Eu-S(3)	120.97(4)
S(2)-Eu-S(4)	84.27(5)	S(2)-Eu-S(5)	81.41(3)
S(2)-Eu-S(6)	143.43(4)	S(2)-Eu-N(1)	81.42(9)
S(2)-Eu-N(2)	130.98(9)	S(3)-Eu-S(4)	61.23(4)
S(3)-Eu-S(5)	127.36(4)	S(3)-Eu-S(6)	87.46(5)
S(3)-Eu-N(1)	144.64(9)	S(3)-Eu-N(2)	81.06(9)
S(4)-Eu-S(5)	76.65(5)	S(4)-Eu-S(6)	91.55(6)
S(4)-Eu-N(1)	153.8(1)	S(4)-Eu-N(2)	139.51(9)
S(5)-Eu-S(6)	62.35(4)	S(5)-Eu-N(1)	79.6(2)
S(5)-Eu-N(2)	121.72(9)	S(6)-Eu-N(1)	87.1(2)
S(6)-Eu-N(2)	71.4(2)	N(1)-Eu-N(2)	64.1(1)
N(2)-C(11)-C(12)	118.7(4)	N(1)-C(12)-C(11)	118.1(4)
S(1)-C(13)-S(2)	118.3(3)	S(3)-C(18)-S(4)	117.4(3)
S(5)-C(23)-S(6)	118.7(3)		

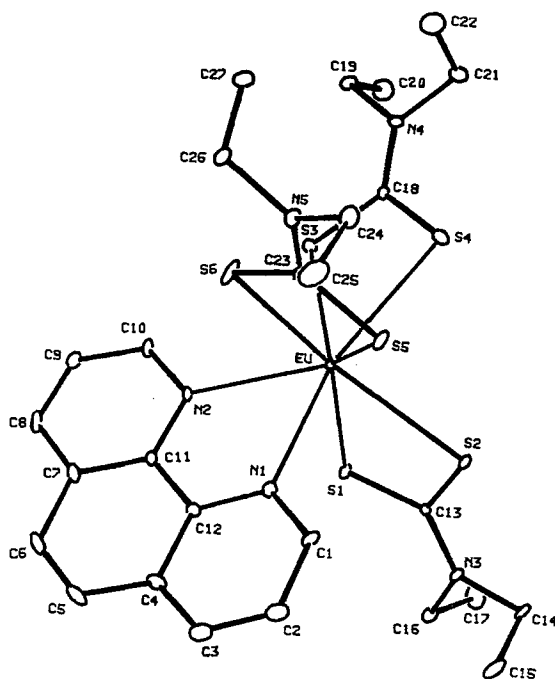


Figure 2 Molecular structure of $[\text{Eu}(\text{EtDtc})_3(\text{Phen})]$ with the numbering scheme.

phen) does not cause the increase in the M-S distance. This may be due to reduction of negative residual charge on the central ions by forming neutral ternary complexes,^{14,15} especially in the present complexes, bipy and phen permit easy electron delocalization. Therefore, these advantages perhaps are important for the stability of this class of complexes. Similar to that in the case of $[\text{La}(\text{Me}_2\text{Dtc})_3(\text{DMSO})_2]$, delocalization of S = C double bond is also found in the present complexes.

In conclusion, rare earth dithiocarbamates can react steadily with bipy or phen to form stable adducts $[\text{RE}(\text{Me}_2\text{Dtc})_3(\text{bipy})]$ or $[\text{RE}(\text{Et}_2\text{Dtc})_3(\text{phen})]$ whose compositions are independent of the stoichiometry of the reactions. In all complexes, dithiocarbamates behave as uninegative bidentate ligands. Electronic spectra shows covalent character in the RE-S bond and that it decreases with increasing atomic number.

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