

NEW MIXED LIGANDS COMPLEXES OF SAMARIUM(III) WITH DITHIOCARBAMATES AND 1,10-PHENANTHROLINE

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ABSTRACT

A new series of samarium(III) complexes with mixed ligands, dithiocarbamate and 1,10-phenanthroline were successfully synthesized using “*in situ*” method. Microelemental analysis data of the complexes are in agreement with the general formula, $\text{Sm}[\text{S}_2\text{CNR}'\text{R}'']_3\text{phen}$ ($\text{R}' = \text{methyl, ethyl; R}'' = \text{butyl, heptyl, isopropyl, isobutyl, benzyl and cyclohexyl; phen} = 1,10\text{-phenanthroline}$). Infrared spectra of the complexes showed that the thioureide $\nu(\text{C-N})$ band is in the regions $1450 - 1500 \text{ cm}^{-1}$. The unsplitting band of $\nu(\text{C-S})$ in the region $930 - 1000 \text{ cm}^{-1}$ indicates the bidentate nature of the chelated dithiocarbamate ligands. The ^{13}C NMR chemical shift of the carbon atom of the N-CS_2 group appeared in the range of $202 - 220 \text{ ppm}$. The crystal structure of $\text{tris}(N,N\text{-ethylbenzyl dithiocarbamate})(1,10\text{-phenanthroline})\text{samarium(III)}$ supports the elemental and spectroscopic data in which three dithiocarbamate and one phen ligands chelated to the central Zn atom in bidentate manner in a distorted dodecahedron environment.

Keywords: Samarium; dithiocarbamate; crystal structure.

ABSTRAK

Satu siri kompleks baru logam samarium(III) dengan ligan campuran ditiokarbamat dan 1,10-fenantrolin telah berjaya disintesis secara “*in-situ*”. Hasil analisis menunjukkan bahawa kompleks tersebut mempunyai formula am $\text{Sm}[\text{S}_2\text{CNR}'\text{R}'']_3\text{phen}$ ($\text{R}' = \text{metil, etil; R}'' = \text{butil, heptil, isopropil, isobutil, benzil and sikloheksil; phen} = 1,10\text{-fenantrolin}$). Spektrum inframerah kompleks menunjukkan jalur tioureida $\nu(\text{C-N})$ di sekitar $1450\text{-}1500 \text{ cm}^{-1}$. Jalur tunggal $\nu(\text{C-S})$ pada julat $930\text{-}1000 \text{ cm}^{-1}$ menunjukkan kemungkinan kelatan bidentat oleh ditiokarbamat. Anjakan kimia RMN C^{13} pada sekitar $202\text{-}220 \text{ ppm}$ adalah bagi atom karbon kumpulan N-CS_2 . Struktur hablur $\text{tris}(N,N\text{-etilbenzilditiokarbamat})(1,10\text{-fenantrolin})\text{samarium(III)}$ menyokong data analisis unsur dan spektroskopi di mana tiga molekul ditiokarbamat dan satu molekul phen terkelat kepada atom Sm secara bidentat dalam sekitaran dodekahedron terherot.

Kata kunci: Samarium; ditiokarbamat; struktur hablur.

Introduction

The chemistry of dithiocarbamate complexes have been reported to a great number of metal ions because of their striking structural features and diversified applications. They have been used extensively in the areas of analytical chemistry, agriculture, pharmaceutical industry and medicine [1-3]. Majority of them were synthesized with transition metals, however only a few have been reported on lanthanide elements due to their “*hard acid*” property and the dithiocarbamate ligands were “*soft bases*”. Majority of the dithiocarbamate complexes with lanthanide elements reported were prepared in an inert atmosphere, using anhydrous lanthanides salts and therefore the study on their applications were limited [4-6]. Su et al. (1997) have synthesized some complexes of lanthanides with mixed ligands of dithiocarbamate such as monomethyl, dimethyl and diethyl dithiocarbamate and 1,10-phenanthroline in an ordinary laboratory atmosphere without any special precaution [7]. An other method to synthesize similar complexes is by reacting $[\text{Ln}(\text{S}_2\text{CNR}'\text{R}'')_3]$ with 1,10-phenanthroline. However, the $[\text{Ln}(\text{S}_2\text{CNR}'\text{R}'')_3]$ complex can easily undergo hydrolysis and therefore require dehydrated solvents for the reaction..

It is believed that the hard acid-soft base (HASB) concepts should play an important role in the stability of the lanthanide dithiocarbamate complexes. We have recently synthesized the complexes of $[\text{Sm}(\text{S}_2\text{CNR}'\text{R}'')_3\text{phen}]$ by *in-situ* method in aqueous solution This paper describes the synthesis and characterization of a series of Sm(III) complexes with 1,10-phenanthroline mixed with various

dithiocarbamate ligands namely, ethylbutyldithiocarbamate (EBdtc⁻), heptylmethyldithiocarbamate(HMdtc⁻), ethylisopropyldithiocarbamate (EiPdtc⁻), methylisobutyldithiocarbamate(MiBdtc⁻), methylbenzyldithiocarbamate (MBzdtc⁻), ethylbenzyldithiocarbamate (EBzdtc⁻). The X-ray structure of tris-*N,N*-ethylbenzyldithiocarbamate(1,10-phenanthroline) is also presented.

Experimental

Reagents

A series of dialkylamine and ethanol (95%) were obtained from Fluka Chemical. Carbon disulphide and methanol (99.5%) from Ajax Chemical Ltd.

Acetonitrile(99.5%) from HmbG Chemical (99.5%) and dichloromethane(99.5%) from R & M Chemical (99.5%). Samarium(III) chloride was purchased from Merck. All the chemicals were used as supplied without purification.

Synthesis of dithiocarbamate complexes

The solution of potassium dithiocarbamate was prepared by using the technique employed by Su et al. (1996). Into 30 mL ethanolic solution of potassium hydroxide, a prescribed amounts of dialkylamine (30 mmol) and CS₂ (30 mmol) were added. The solution was stirred vigorously below 15°C for 30 minutes. 10 mmol solution of samarium trichloride was added drop wise into a 10 mmol 1,10-phenanthroline in 10 ml boiling water. The two solutions were mixed and heated for 10 minutes. The precipitate formed was filtered and washed with ethanol and later dried *in vacuo* over silica gel. All recrystallization of products were done from the mixture of chloroform, acetonitrile and methanol (1:2:3 v/v).

Physical measurements

The C, H N, and S microanalysis was carried out with a Fison EA 1108 CHN analyzer. Infrared spectra of all the compounds were recorded as KBr discs in using Perkin Elmer FTIR Model GX spectrophotometer in the frequency range 4000 – 500 cm⁻¹ and 500 cm⁻¹ - 200 cm⁻¹. ¹H and ¹³C NMR spectra were obtained using Joel JNM – LA400 spectrometer.

X-ray crystallography

Room-temperature diffraction data were collected on a Bruker SMART APEX area-detector diffractometer (Mo K α radiation, $\lambda=0.71073$ Å) on a crystal of size 0.50x0.19x0.05 mm over the range 1.76 < θ < 27.0. The structure was solved and refined by using the SHELXS-97 [8]. The final R (I>2/s(I)) and R_w values were 0.07 and 0.1820 respectively. All non-hydrogen atoms were refined anisotropically. The perspective view of the molecule was obtained using SHELXTL [9]. Selected bond distances and angles are listed in Table 4.

Result and Discussion

Microelemental analysis and physical properties data are given in Table 1. The elemental analysis data of the complexes are in agreement with the general formula M[S₂CNR'R'']₃phen [R' = methyl, ethyl; R'' = butyl, heptyl, isopropyl, isobutyl, benzyl and cyclohexyl; M = Sm(III); phen = 1,10-phenanthroline;].

FTIR Spectroscopy

The important IR peaks of the complexes are shown in Table 2. The $\nu(\text{C}=\text{N})$ modes appeared in the region of thioureide band (1450 – 1550 cm⁻¹), while $\nu(\text{C}=\text{S})$ modes appeared in the region 950 – 1002 cm⁻¹ [10]. The absence of any splitting to the $\nu(\text{C}-\text{S})$ bands that appeared in the range 965 - 972 cm⁻¹ indicates a bidentate nature of the chelation of the dithiocarbamate ligands [11,12]. The molar conductances between 40 and 55 m.ohm⁻¹ showed the complexes act as uninegatively charged bidentate species [7]. The highest $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{S})$ observed for Sm(EBdtc)₃phen may be due to the electron donating effect of the ethyl and benzyl group compare to the other groups [13].

TABLE 1 Analytical and physical data for Sm(S₂CNR'R'')₃phen complexes.

Complexes	Colour	Yield (%)	Melting point (°C)	Found (Calculated) (%)				
				C	N	H	S	M
Sm(EBdte) ₃ phen	White	70	134-136	40.28 (46.00)	6.71 (6.08)	6.71 (8.13)	30.69 (22.33)	16.30 (17.45)
Sm(HMdte) ₃ phen	White	64	115-116	48.91 (49.53)	7.32 (6.82)	6.72 (7.41)	18.65 (20.34)	14.56 (15.90)
Sm(EiPdte) ₃ phen	White	65	123-125	43.48 (43.97)	6.02 (5.66)	8.35 (8.55)	22.83 (23.48)	17.97 (18.35)
Sm(MiBdte) ₃ phen	White	72	115-116	43.32 (43.65)	6.26 (6.35)	8.45 (8.48)	23.12 (23.31)	17.81 (18.21)
Sm(MBzdte) ₃ phen	Cream	94	120-121	49.98 (50.83)	4.74 (4.38)	6.74 (7.6)	21.62 (20.88)	15.64 (16.32)
Sm(EBzdte) ₃ phen	White Yellow	88	119-121	49.19 (50.83)	5.17 (4.81)	7.69 (7.27)	20.65 (19.97)	16.70 (15.6)
Sm(EChdte) ₃ phen	White	91	122 - 123	48.40 (49.85)	6.69 (6.22)	6.69 (7.45)	19.98 (20.47)	15.30 (16.00)

TABLE 2 Infrared data for Sm(S₂CNR'R'')₃phen complexes.

Complexes	Frequency (cm ⁻¹)				
	ν(C-H)	ν(C [≡] N)	ν(C=S)	ν(Gd-N)	ν(Gd-S)
1. Sm(EBdte) ₃ phen	2929.31	1489.09	1001.45	363.84	353.08
2. Sm(HMdte) ₃ phen	2925.69	1474.95	985.84	363.7	359.04
3. Sm(EiPdte) ₃ phen	2973.16	1467.33	999.79	359.11	354.05
4. Sm(MiBdte) ₃ phen	2915.12	1476.49 1471.26	989.86	363.65	359.04
5. Sm(MBzdte) ₃ phen	2928.33	1451.68	959.66	356.05	350.56
6. Sm(EBzdte) ₃ phen	2927.91	1471s, 1451	959.39	361.51	354.18
7. Sm(EChdte) ₃ phen	2930.27	1450.72	997.28	358.24	353.01

s = strong, m = medium, b = broad, w = weak

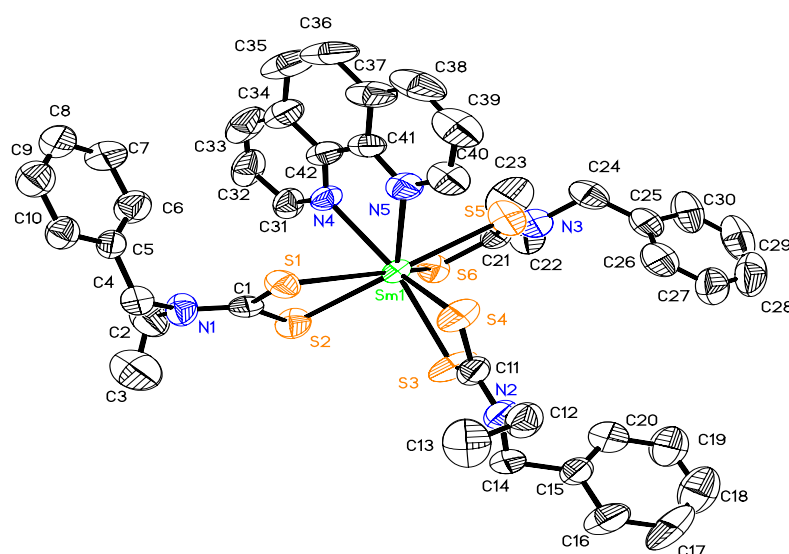
NMR Spectra

The selected NMR chemical shifts of the compounds are shown in Table 3. The chemical shifts of the phen group are between 7.33 and 9.60 ppm. Overlapping of the signals occur when R'' is also a phenyl and aryl groups. The important ¹³C chemical shifts of N-CS₂ moiety were observed between 208 and 217 ppm for all complexes except compound 3 and 7. The values are higher than those in M(sec-BuPrdte) where M=Zn, Cd, Ni, In, Sb and Bi (between 201-207 ppm) [14]. The down field shift of the NCS₂ moiety may be attributable to an increase of π-bond character or delocalization of electron along the C-N bond contributed by the unshared electron pair in the nitrogen atom [12], electron donating effect by the substituents and also the bidentate nature of the dithiocarbamate ligand..

A suitable crystal was obtained for compound (6), Sm[S₂CN(C₂H₅)(C₇H₇)]₃phen. The compound crystallized in orthorhombic system with space group P c c n. The crystal data and refinement parameters are given Table 4. The molecular structure of the compound (Fig. 1) supports the elemental and spectroscopic data given in Table 1, 2 and 3.

TABLE 3 Selected ^1H and ^{13}C NMR data (δ , ppm) for complexes

No	Formula	^1H NMR (Phen)	^{13}C NMR (NCS ₂)
1	Sm(EBdtc) ₃ phen	9.085 (d), 8.513 (d), 7.795 (s), 7.77 (d)	208.728
2	Sm(HMdtc) ₃ phen	8.31 (br), 7.856(d), 7.412 (t), 7.403(t)	213.908
3	Sm(EiPdtc) ₃ phen	9.61 (d), 8.40 (d), 7.90 (s), 7.80 (d)	-
4	Sm(MiBdtc) ₃ phen	8.273 (br), 7.839(d), 7.404 (s), 7.27 (d)	215.099
5	Sm(MBzdtc) ₃ phen	8.44 (d), 8.263 (d), 7.975 (s), 7.32(d)	216.8352
6	Sm(EBzdtc) ₃ phen	9.209(br), 8.376 (d), 7.909 (t), 7.27 (t)	215.941
7	Sm(EChdtc) ₃ phen	9.61 (d), 8.40 (d), 7.90 (s), 7.80 (d)	-

FIGURE 1. Molecular structure of Sm[S₂CN(C₂H₅)(C₇H₇)]₃phen (6) with displacement ellipsoids drawn with 50% probability level.

One phen and three ethylbenzylthiocarbamate ligands chelated to Sm(III) atom in bidentate manner via nitrogen and sulphur atoms respectively, in a distorted dodecahedron geometry. The cis bond angles of S2-Sm-S1, S3-Sm-S4, S5-Sm-S6 and N4-Sm-N5 are 62.42(7), 62.40(8), 61.68(7) and 64.0(3)^o respectively. The average C - S bond length is 1.71(3)^o and the mean S-C-S angle is 118.8(4)^o. The thioureide C - N bond distances of N1-C1, N2-C11 and N3-C21 [1.337(12); 1.321(11) and 1.327(12) Å respectively] are shorter than the other C - N bonds, indicating of partial double bond character (C[≡]N) as observed in the IR spectra data (1450 - 1500 cm⁻¹).

TABLE 4 Crystal data and structure refinement for Sm[S₂CN(C₂H₅)(C₇H₇)₃phen (6)

Compound	Sm(S ₂ CN(C ₂ H ₅)(C ₇ H ₇) ₃ phen
Empirical Formula	C ₄₂ H ₄₄ N ₅ S ₆ Sm
Formula weight	961.53
Temperature	273 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P c c n
<i>a</i>	19.825 (5) Å
<i>b</i>	42.721 (11) Å
<i>c</i>	10.652 (3) Å
α, β, γ	90 °
<i>V</i>	922 (4) Å ³
<i>Z</i>	8, 1.416 Mg/m ³
<i>D_c</i> /g cm ³	1.614 mm ⁻¹
<i>F</i> (000)	3912
Crystal size	0.50 x 0.19 x 0.05 mm
Refinement method	Full matrix least-square
θ range (°)	1.76 - 27.00°
Final R indices <i>I</i> > 2 σ (<i>I</i>)	R ₁ = 0.0735, wR ₂ = 0.1820
R indices (all data)	R ₁ = 0.0926, wR ₂ = 0.1904

TABLE 5 Selected bond distances (Å) and angles (°) for Sm[S₂CN(C₂H₅)(C₆H₇)₃phen

Sm1– S1	2.826(2)	Sm(1) - S(5)	2.822(3)
Sm1- S2	2.870(3)	Sm(1) - S(6)	2.885(3)
Sm- S3	2.805(3)	Sm(1) - N(4)	2.573(7)
Sm1 - S4	2.848(3)	Sm1 - N5	2.585(3)
S1 - C1	1.708(9)	S4 - C11	1.729(10)
S2- C1	1.713(9)	S5- C21	1.717(10)
S3 - C11	1.700(10)	S6 - C21	1.706(10)
N1 - C1	1.337(12)	N2 - C14	1.468(12)
N1 - C4	1.449(12)	N2 - C12	1.471(13)
N1 - C2	1.569(16)	N3 - C21	1.327(12)
N2 - C11	1.321(11)	N3 - C24	1.467(12)
N4-Sm1-N5	64.0(3)	S1-Sm1-S4	80.41(8)
N4-Sm1-S3	155.22(19)	N4-Sm1-S2	79.11(18)
N5-Sm1-S3	140.41(19)	N5-Sm1-S2	132.43(18)
N4-Sm1-S5	91.73(18)	S3-Sm1-S2	81.51(9)
N5-Sm1-S5	69.97(17)	S5-Sm1-S2	143.34(8)
S3-Sm1-S5	94.67(10)	S1-Sm1-S2	62.42(7)
N4-Sm1-S1	77.59(17)	S4-Sm1-S2	117.40(9)
N5-Sm1-S1	80.37(17)	N4-Sm1-S6	82.36(18)
S3-Sm1-S1	106.70(9)	N5-Sm1-S6	119.20(18)
S5-Sm1-S1	150.18(7)	S3-Sm1-S6	79.73(8)
N4-Sm1-S4	141.34(19)	S5-Sm1-S6	61.68(7)
N5-Sm1-S4	81.27(19)	S1-Sm1-S6	141.54(7)
S 3-Sm1-S4	62.40(8)	S4-Sm1-S6	132.11(7)
S5-Sm1-S4	91.84(9)	S2-Sm1-S6	81.84(8)

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