

پژوهشی

## تهیه و مطالعه ساختار مولکولی



### با پراش پرتو X

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چکیده:  $\text{SmCl}_3(\text{THF})_3$  با  $\text{MeLi}$  در تتراهیدروفوران (THF) در حضور ترامتیل اتیلن دی آمین، TMEDA، کمپلکس  $\{[\text{Li}(\text{TMEDA})]_3[\text{Sm}(\text{CH}_3)_6]\} \cdot \text{THF}$  تشکیل می‌دهد. تجزیه عنصری، طیف IR و اندازه‌گیری مغناطیسی این کمپلکس مطالعه شده است. ساختار مولکولی این کمپلکس به روش پراش سنجی تک بلور پرتو X تعیین شده است. بلورهای این کمپلکس در سیستم بلوری سه گوشه (تری گونال) با گروه فضایی  $R\bar{3}c$  با شش مولکول در یاخته یک متبلور می‌شود. پارامترهای یاخته یک عبارت اند از:  $a = 16.684(10) \text{ \AA}$  و  $c = 24.946(10) \text{ \AA}$ . مقدار R برای  $2340^\circ$  بازتاب برابر  $0.43^\circ$  است.

واژه‌های کلیدی: ساختار مولکولی،  $\{[\text{Li}(\text{TMEDA})]_3[\text{Sm}(\text{CH}_3)_6]\} \cdot \text{THF}$ ، طیف IR، اندازه‌گیری مغناطیسی.

**PREPARATION AND MOLECULAR STRUCTURE OF  
TRIS[(N, N, N', N' - TETRAMETHYLETHYLENE -  
DIAMINE) LITHIUM] HEXAMETHYLSAMARATE(III),  
 $\{[\text{Li}(\text{TMEDA})]_3 [\text{Sm}(\text{CH}_3)_6]\} \cdot \text{THF}$**

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**Key Words :** *Preparation , Molecular Structure ,  $\{[\text{Li}(\text{TMEDA})]_3$ -  
 $[\text{Sm}(\text{CH}_3)_6]\} \cdot \text{THF}$ , IR Spectrum, Magnetic Measurement.*

**Abstract :** The  $\text{SmCl}_3(\text{THF})_3$  reacts with methyllithium in THF in the presence of tetramethylethylenediamine, TMEDA, to give  $\{[\text{Li}(\text{TMEDA})]_3[\text{Sm}(\text{CH}_3)_6]\} \cdot \text{THF}$ . The complex has been characterized by elemental analyses, IR spectrum and magnetic measurement. Molecular and crystal structure of this complex has been determined by a single crystal X-ray diffraction. The crystals are trigonal with  $a = 16.684(10)\text{\AA}$ ,  $c = 24.946(10)\text{\AA}$ , space group  $R\bar{3}c$ , and six molecules/unit cell. The final R value is 0.043 for 2340 reflections measured.

## INTRODUCTION

The organolanthanides of any type are usually thermally stable, but air and moisture sensitive. A variety of organo compounds of lanthanides are known, the main types being cyclopentadienides and cyclooctatetraenides and some

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compounds with M–C bonds are known [1–22]. Methyl derivatives and organosamarium complexes have been prepared and characterized recently [23]. In this research project  $[\text{Li}(\text{TMEDA})]_3[\text{Sm}(\text{CH}_3)_6] \cdot \text{THF}$  complex, has been prepared and characterized by a single-crystal X-ray diffraction method.

## EXPERIMENTAL

All the operations were carried out under a dry-box oxygen-free nitrogen atmosphere using standard *Schlenk* techniques. THF and N, N, N', N'–tetramethylethylenediamine, TMEDA, were dried and distilled by standard method before using. Infrared spectrum was recorded on a *Perkin–Elmer 393* instrument from Nujol mulls prepared in a dry-box. Sample for magnetic susceptibility measurement was sealed in calibrated tube inside a dry-box. Measurement was carried out at room temperature using a Gouy balance (Johnson–Mathey). Magnetic moment was calculated by following standard methods [24], and corrections for underlying diamagnetism was applied to the data [25].

### *Preparation of Complex*

A suspension of 10.00g (14.66mmol) of  $\text{SmCl}_3(\text{THF})_3$  in 250mL of THF and 17.19g (147.92mmol) of N,N,N',N' – tetramethylethylenediamine, TMEDA, was treated at  $\cong -40^\circ\text{C}$  dropwise with 22.3mL of 1.7M solution of methyllithium in diethylether. The mixture was stirred and allowed to warm slowly to ambient temperature (1h). The cloudy yellow solution was filtered. Yellow crystals of  $\{[\text{Li}(\text{TMEDA})]_3[\text{Sm}(\text{CH}_3)_6]\} \cdot \text{THF}$  separated from the resulting light yellow solution upon standing overnight at refrigerator and then at  $-30^\circ\text{C}$ . The large single yellow crystals were filtered and dried and stored under nitrogen in sealed ampoules (yield  $\cong 68\%$ ). IR (Nujol mull, KBr,  $\text{cm}^{-1}$ ):

[Nujol: 3000–2860(vs), 1455(s), 1375(s), 1345(w,sh)]. 1290(s), 1285(m), 1260(m), 1180(m), 1160(m), 1130(s), 1105(s), 1060(s), 1035(s), 1020(s), 950(s), 910(w), 790(s), 770(w), 720(vw), 580(m), 520–380 (broad, not resolved).

Magnetic measurement:  $\mu_{\text{eff}} = 1.51\text{B.M.}$

### *Data Collection and Reduction*

A yellow crystal of  $\text{C}_{28}\text{H}_{74}\text{SmLi}_3\text{N}_6\text{O}$  having approximated dimensions of  $0.20 \times 0.20 \times 0.20\text{mm}$  was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Mo– $\text{K}\alpha$

radiation and a 12kW rotating anode generator. Cell dimensions were obtained from 24 reflections with  $2\theta$  angle in the range 40.00–50.00 degrees. Absorption corrections were made. The minimum and maximum transmission factors are 0.105599 and 0.171574. The crystals are trigonal with space group  $R\bar{3}c$ . The unit cell and crystal data are reported in Table 1.

#### *Structure Determination and Refinement*

Data were collected at  $-160^\circ\text{C}$ . The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated but not refined. The final cycles of full-matrix least-squares refinement was based on the number of observed reflection with  $I > 2.5\sigma(I)$  and corresponding parameters. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.650 and  $-1.0203\text{e}/\text{\AA}^3$ . The final R values were 0.043 and  $R_w = 0.035$  for 2340 reflections measured. Fractional atomic coordinates are given in Table 2, and anisotropic thermal parameters are available.

### RESULTS and DISCUSSION

The crystal consists of  $\{[\text{Li}(\text{TMEDA})]_3[\text{Sm}(\text{CH}_3)_6]\} \cdot \text{THF}$ , illustrated in Fig.1. Stereoview of the packing of this complex in the unit cell is given in Fig.2. The samarium atom is surrounded by six methyl groups in a slightly distorted octahedral arrangement (the symmetry of the molecule is  $D_3$ ) and the site symmetry of Sm is  $\bar{3}$ . The lithium atoms are located at the centers of tetrahedra made up of two methyl groups and the two nitrogen atoms of one TMEDA molecule. The Sm–C bond distance is  $2.639(5)\text{\AA}$  which is significantly shorter than the average Sm–C bond distances in  $\text{Sm}(\eta^6\text{-C}_6\text{Me}_6)(\eta^6\text{-AlCl}_4)_3$   $\{2.89(5)\text{\AA}\}$  [9] and  $\text{Sm}(\text{C}_6\text{Me}_6)_3$   $\{2.82(5)\text{\AA}\}$  [22] and significantly longer than the Sm–C(Terminal methyl) bond distance in  $(\text{C}_5\text{Me}_5)\text{SmMe}(\text{THF})$   $\{2.484(14)\text{\AA}\}$  [23]. Therefore, the Sm–C bond distance in this complex is reasonable.



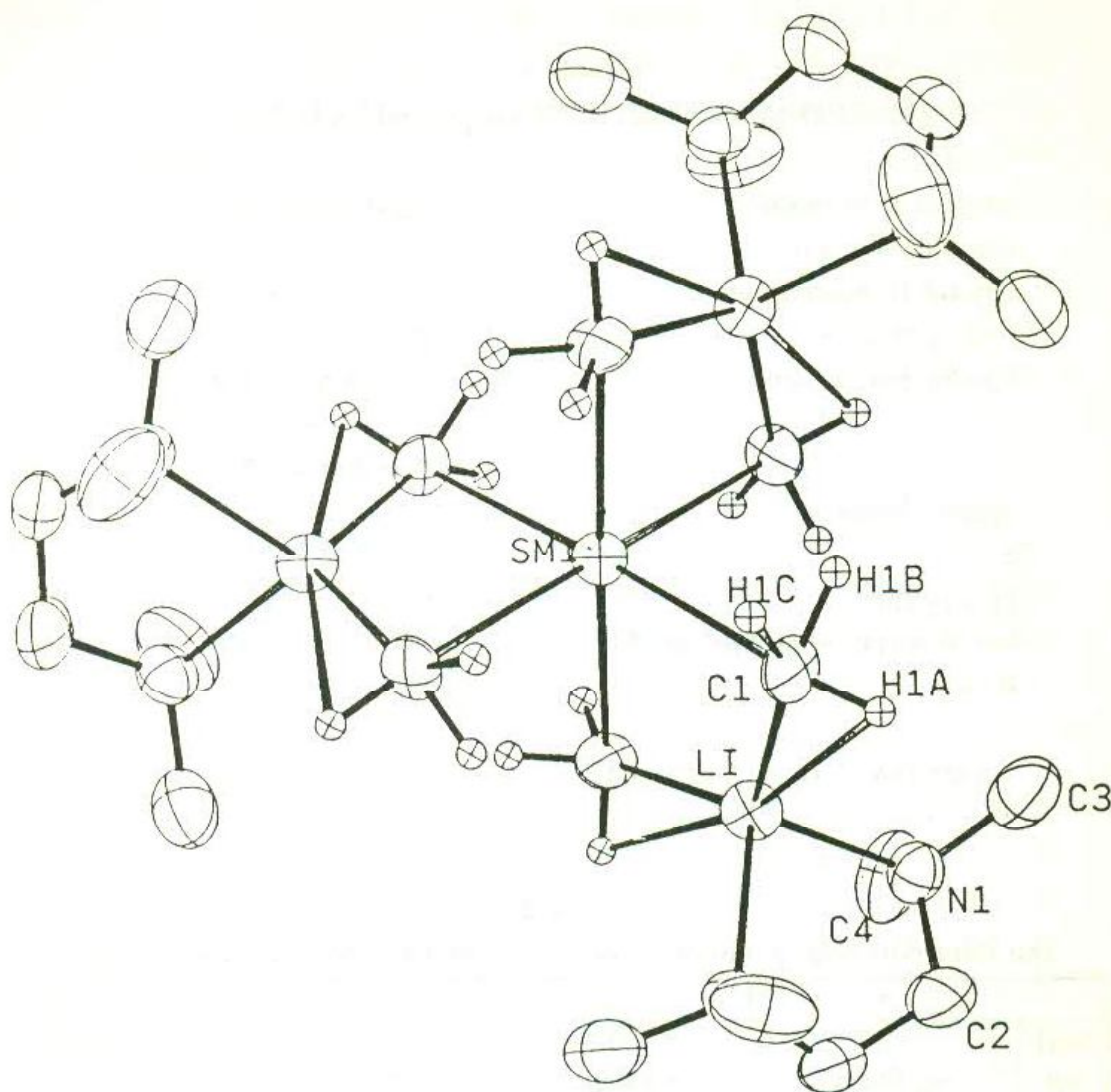
**Table 1**  
Crystal Data for  $\{[\text{Li}(\text{TMEDA})]_3[\text{Sm}(\text{CH}_3)_6]\} \cdot \text{THF}^*$

Empirical Formula	$\text{C}_{28}\text{H}_{74}\text{SmLi}_3\text{N}_6\text{O}$
Formula Weight	682.0
Crystal Dimensions(mm)	0.20 x 0.20 x 0.20
Crystal System	Trigonal
Lattice Parameters	$a = 16.684(10)\text{\AA}$ $c = 24.946(10)\text{\AA}$ $V = 6014(4)\text{\AA}^3$
Space Group	$R\bar{3}c$
z	6
$D_{\text{calc}}(\text{g/cm}^3)$	1.120
No of Reflections Measured	2340
R, $R_w$	0.043 , 0.035

\* TMEDA =  $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$

**Table 2**  
The final postionl parameters and Biso for the non – hydrogen atoms

	x	y	z	Biso
Sm1	0	0	3/4	2.471(22)
N1	0.2351(3)	0.3144(4)	0.71473(20)	3.3(3)
C1	0.1507(4)	0.0774(6)	0.69021(21)	3.5(5)
C2	0.3230(5)	0.3696(4)	0.7449(4)	5.8(5)
C3	0.1751(7)	0.3526(4)	0.72478(24)	5.2(6)
C4	0.2460(5)	0.3095(5)	0.6565(3)	5.7(6)
C5	0.029(3)	0.0490(9)	0.0410(4)	5.6(18)
C6	0.017(4)	0.0882(23)	0.0100(20)	8.3(28)
Li	0.1824(9)	0.1824(9)	3/4	2.5(7)



**Figure 1** An ORTEP view of  $\{[\text{Li}(\text{TMEDA})]_3[\text{Sm}(\text{CH}_3)_6]\} \cdot \text{THF}$

**Selected Bond Distances and Angles:**

$\text{Sm}-\text{C}(1) = 2.639(5) \text{ \AA}$ ,  $\text{Li}-\text{C}(1) = 2.155(11) \text{ \AA}$ ,  $\text{Li}-\text{N}(1) = 2.113(12) \text{ \AA}$

$\text{N}(1)-\text{C}(2) = 1.488(9) \text{ \AA}$

$\text{N}(1)-\text{C}(3) = 1.453(12) \text{ \AA}$

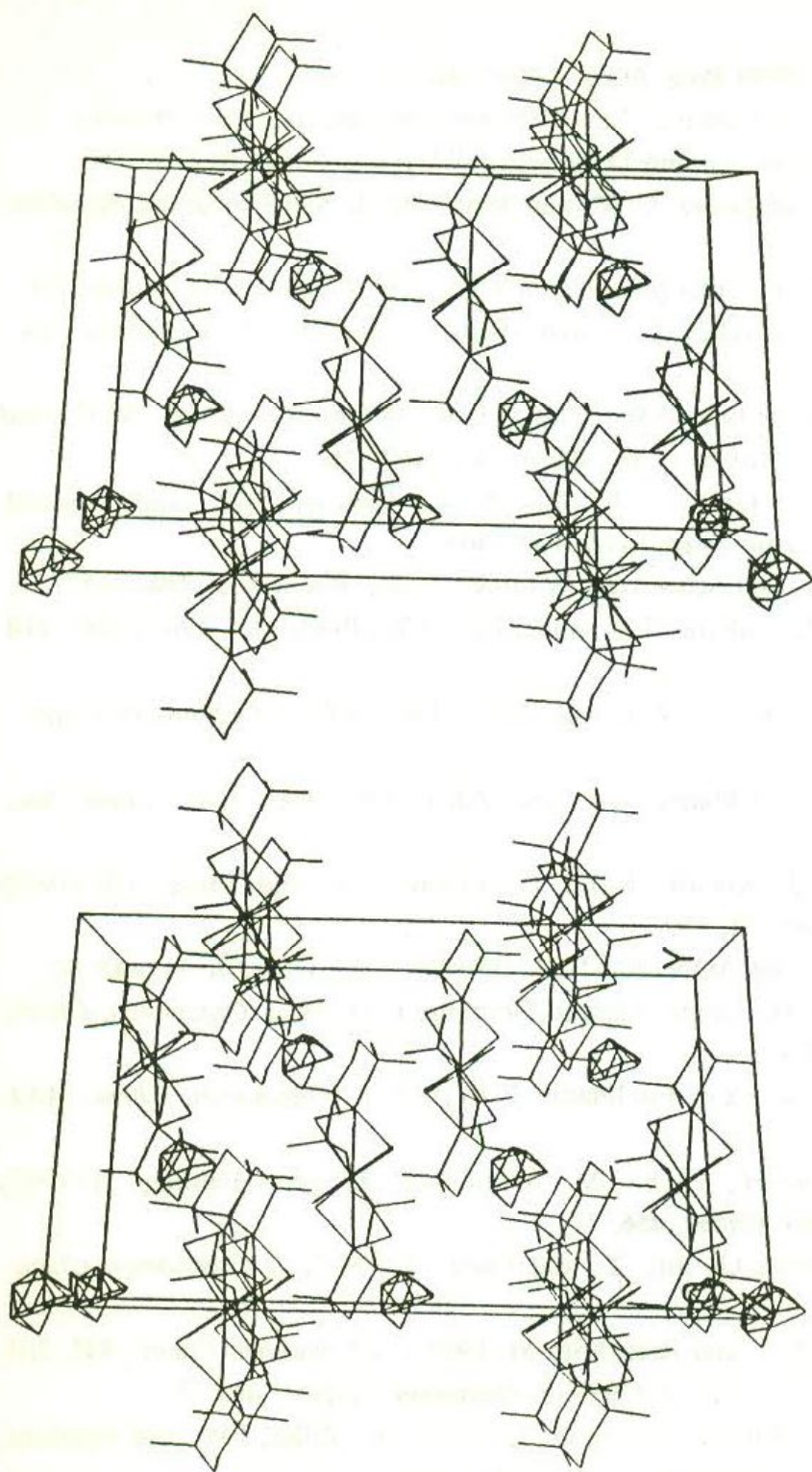
$\text{N}(1)-\text{C}(4) = 1.470(9) \text{ \AA}$

$\text{Sm}-\text{C}(1)-\text{Li} = 78.1(4)^\circ$ ,  $\text{Li}-\text{N}(1)-\text{C}(2) = 101.7(5)^\circ$

$\text{C}(2)-\text{N}(1)-\text{C}(3) = 108.9(5)^\circ$

$\text{C}(2)-\text{N}(1)-\text{C}(4) = 115.0(6)^\circ$

$\text{C}(3)-\text{N}(1)-\text{C}(4) = 109.0(5)^\circ$



**Figure 2** Stereoview of the packing of  $\{[Li(TMEDA)]_3[Sm(CH_3)_6] \cdot THF\}$  in the unit cell



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