Journal of Organometallic Chemistry, 376 (1989) 61–66
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20140

Synthesis and molecular structure of η^6-*m*-xylenesamariumtris(aluminum tetrachlorides)

Baochen Fan, Qi Shen * and Younhua Lin

Changchun Institute of Applied Chemistry, Academia Sinica 109 Stalin Street, Changchun (China)

(Received September 19th, 1988; in revised form March 28th, 1989)

Abstract

$AlCl_3$ activated by aluminum powder at 140 °C reacts with $SmCl_3$ in *m*-xylene to give a new neutral arene complex of samarium, $Sm(\eta^6\text{-}m\text{-}(CH_3)_2C_6H_4)(AlCl_4)_3$ (**1**). The crystal structure determination shows that **1** crystallizes in the monoclinic space group $P2_1/n$, with a 18.36(5), b 16.37(4), c 20.31(6) Å, β 114.11(2)°, V 5567.87 Å^3, $Z = 8$, $R = 0.071$. Two independent moieties with slightly different bond parameters occupy each unit cell.

Introduction

In the past, many studies have been reported on neutral arene complexes of transition metal elements (1). Such complexes having an actinoid centre U^{III} [2,3], U^{IV} [4,5] have also been synthesized and structurally characterized. But only recently, has attention been paid to the synthesis and characterization of η^6-arene complexes containing rare earth elements. In 1986 Cotton et al. reported the first η^6-arene complex of samarium $Sm(\eta^6\text{-}C_6Me_6)(AlCl_4)_3$ (**2**) [6]. Another example of η^6-arene organolanthanoids is $Gd(t\text{-}Bu_3C_6H_3)_2$ which is different from complex **2** both in its preparation and its bonding properties [7]. Up to now, **2** is the only example of a neutral arene complex of a rare earth element synthesized in solution. Here we report the preparation and the crystal structure of a homologous complex $Sm(\eta^6\text{-}m\text{-}(CH_3)_2C_6H_4)(AlCl_4)_3$ (**1**).

Results and discussion

Synthesis

The reaction of activated $AlCl_3$ with $SmCl_3$ in *m*-xylene gives a blood-red solution from which the only product isolated is a yellow crystal of Sm^{III} (**1**).

---

* Author to whom correspondence should be addressed.

0022-328X/89/$03.50

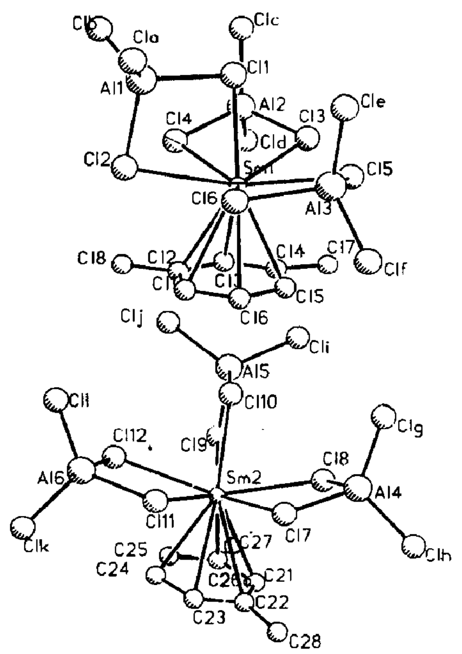

Fig. 1. The structure of Sm(η^6-*m*-$(CH_3)_2C_6H_4$)$(AlCl_4)_3$.

Attempts to isolate and characterize the red material in the solution were unsuccessful. Compound **1** is very air- and moisture-sensitive but is thermally stable up to 110 ° C. It is soluble in aromatic solvents but not in aliphatic ones. The synthesis of **1** shows that aromatic compounds with less substituents can also be used as ligands for preparing corresponding neutral arene complexes with samarium. So the chemistry of neutral arene complexes of lanthanoids has attained a broad prospect. Work on the preparation and characterization of this type of organolanthanoid having other aromatic ligands are presently under investigation.

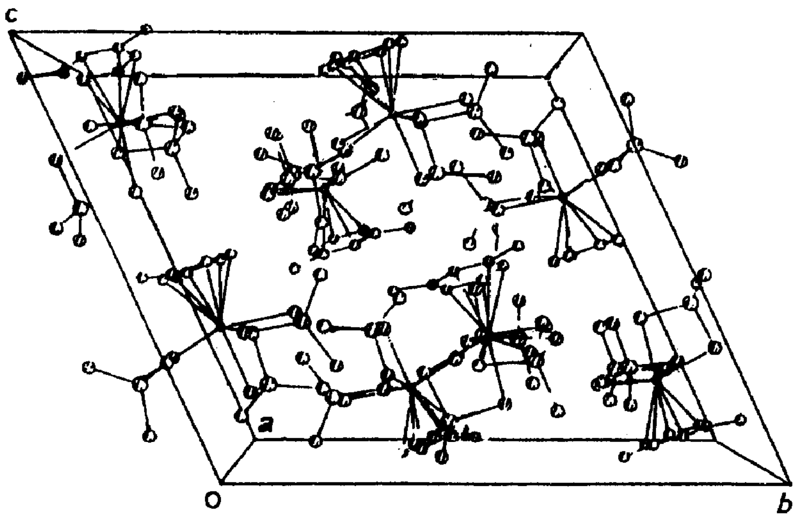

Fig. 2. The packing of Sm(η^6-*m*-$(CH_3)_2C_6H_4((AlCl_4)_3$ (**1**) in the unit cell.

Table 1

Selected bond lengths (Å)

Sm(1)–Cl(1)	2.79(2)	Sm(2)–Cl(7)	2.829(9)
Sm(1)–Cl(2)	2.842(8)	Sm(2)–Cl(8)	2.868(8)
Sm(1)–Cl(3)	2.835(7)	Sm(2)–Cl(9)	2.834(2)
Sm(1)–Cl(4)	2.823(7)	Sm(2)–Cl(10)	2.794(2)
Sm(1)–Cl(5)	2.841(8)	Sm(2)–Cl(11)	2.819(2)
Sm(1)–Cl(6)	2.826(8)	Sm(2)–Cl(12)	2.873(2)
Sm(1)–C(11)	2.92(3)	Sm(2)–C(21)	3.02(2)
Sm(1)–C(12)	2.94(4)	Sm(2)–C(22)	2.99(2)
Sm(1)–C(13)	2.92(5)	Sm(2)–C(23)	2.85(2)
Sm(1)–C(14)	2.88(4)	Sm(2)–C(24)	2.73(2)
Sm(1)–C(15)	2.86(3)	Sm(2)–C(25)	2.77(3)
Sm(1)–C(16)	2.88(3)	Sm(2)–C(26)	2.91(3)
Al(1)–Cl(1)	2.195(7)	Al(4)–Cl(7)	2.184(7)
Al(1)–Cl(2)	2.179(9)	Al(4)–Cl(8)	2.179(1)
Al(2)–Cl(3)	2.226(7)	Al(5)–Cl(9)	2.165(1)
Al(2)–Cl(4)	2.170(7)	Al(5)–Cl(10)	2.187(1)
Al(3)–Cl(5)	2.199(9)	Al(6)–Cl(11)	2.176(1)
Al(3)–Cl(6)	2.204(7)	Al(6)–Cl(12)	2.16(1)
C(17)–C(14)	1.61(4)	C(27)–C(26)	1.56(2)
C(18)–C(12)	1.53(4)	C(28)–C(22)	1.55(2)

Table 2

Selected bond angles (°)

Cl(1)–Sm(1)–Cl(2)	73.1(2)	Cl(7)–Sm(2)–Cl(8)	69.6(2)
Cl(1)–Sm(1)–Cl(3)	81.3(2)	Cl(7)–Sm(2)–Cl(9)	137.8(2)
Cl(1)–Sm(1)–Cl(4)	80.4(3)	Cl(7)–Sm(2)–Cl(10)	82.0(2)
Cl(1)–Sm(1)–Cl(5)	81.8(3)	Cl(7)–Sm(2)–Cl(11)	68.8(2)
Cl(1)–Sm(1)–Cl(6)	79.1(2)	Cl(7)–Sm(2)–Cl(12)	136.1(2)
Cl(2)–Sm(1)–Cl(3)	136.6(2)	Cl(8)–Sm(2)–Cl(9)	73.4(1)
Cl(2)–Sm(1)–Cl(4)	71.1(2)	Cl(8)–Sm(2)–Cl(10)	80.0(1)
Cl(2)–Sm(1)–Cl(5)	136.7(3)	Cl(8)–Sm(2)–Cl(11)	136.5(1)
Cl(2)–Sm(1)–Cl(6)	70.4(2)	Cl(8)–Sm(2)–Cl(12)	143.2(1)
Cl(3)–Sm(1)–Cl(4)	70.5(2)	Cl(9)–Sm(2)–Cl(10)	72.3(1)
Cl(3)–Sm(1)–Cl(5)	70.2(2)	Cl(9)–Sm(2)–Cl(11)	136.6(1)
Cl(3)–Sm(1)–Cl(6)	138.1(2)	Cl(9)–Sm(2)–Cl(12)	71.4(1)
Cl(4)–Sm(1)–Cl(5)	138.8(2)	Cl(10)–Sm(2)–Cl(11)	82.4(1)
Cl(4)–Sm(1)–Cl(6)	140.2(2)	Cl(10)–Sm(2)–Cl(12)	79.4(1)
Cl(5)–Sm(1)–Cl(6)	70.6(2)	Cl(11)–Sm(2)–Cl(12)	69.6(1)
Cl(1)–Al(1)–Cl(2)	100.2(3)	Cl(7)–Al(4)–Cl(8)	96.3(2)
Cla–Al(1)–Clb	117.5(1)	Clg–Al(4)–Clh	117.6(1)
Cl(3)–Al(2)–Cl(4)	95.9(3)	Cl(9)–Al(5)–Cl(10)	99.4(1)
Cl(5)–Al(3)–Cl(6)	96.1(3)	Cl(11)–Al(6)–Cl(12)	96.9(1)
Sm(1)–Cl(1)–Al(1)	93.8(3)	Sm(2)–Cl(7)–Al(4)	97.0(3)
Sm(1)–Cl(2)–Al(1)	92.8(2)	Sm(2)–Cl(8)–Al(4)	96.0(1)
Sm(1)–Cl(3)–Al(2)	95.8(3)	Sm(2)–Cl(9)–Al(5)	93.9(1)
Sm(1)–Cl(4)–Al(2)	97.4(3)	Sm(2)–Cl(10)–Al(5)	94.5(1)
Sm(1)–Cl(5)–Al(3)	96.4(3)	Sm(2)–Cl(11)–Al(6)	97.4(1)
Sm(1)–Cl(6)–Al(3)	96.7(3)	Sm(2)–Cl(12)–Al(6)	96.1(1)

Structure

The structure of 1 and the molecular packing in the unit cell are shown in Figs. 1 and 2. Important bond lengths and bond angles are listed in Tables 1 and 2. As shown in Fig. 1, there are two independent $Sm(\eta^6\text{-}m\text{-}(CH_3)_2C_6H_4)(AlCl_4)_3$ (**1a**, **1b**) moieties in the unit cell. Both of the coordination polyhedra of **1a** and **1b** can be described as distorted pentagonal bipyramids. The *m*-xylene molecule is apical. Two of the three $AlCl_4$ units (Al(2), Al(3) in **1a** and Al(4), Al(6) in **1b**) are placed in the equatorial plane, while the third $AlCl_4$ unit (Al(1) in **1a** and Al(5) in **1b**) spans one of its edges so that Cl(2) in **1a** and Cl(9) in **1b** are in the equatorial plane and Cl(1) in **1a** and Cl(10) in **1b** are at the other apex.

As shown in Tables 1 and 2, there are slight differences in the bonding parameters between **1a** and **1b**. The mean Sm–C and Sm–Cl distances are 2.90(4)Å, 2.83(8)Å for **1a**, and 2.88(2)Å, 2.84(3)Å for **1b**, respectively. The Cl–Sm–Cl bond angles for adjacent chlorine atoms, for example, the Cl(1)–Sm–Cl(2), Cl(3)–Sm–Cl(4), Cl(5)–Sm–Cl(6) bond angles in **1a** and Cl(9)–Sm–Cl(10), Cl(11)–Sm–Cl(12), Cl(7)–Sm–Cl(8) in **1b** are 73.1(2)°, 70.5(2)°, 70.6(2)° and 72.3(1)°, 69.6(1)°, 69.6(1)°, respectively. The differences may be ascribed to the different steric interaction caused by the different relative orientation of the methyl groups in *m*-xylene ring and by the equatorial chlorine atoms.

The mean M–Cl distances, 2.83(8)Å in **1a** and 2.84(3)Å in **1b**, are somewhat shorter than the 2.85(2)Å found in $Sm(\eta^6\text{-}C_6Me_6)(AlCl_4)_3$ [6]. This may be due to the increased steric congestion caused by the C_6Me_6 ligand. There are no clear differences between the average M–C distances, 2.90(4)Å for **1a**, 2.88(2)Å for **1b** and 2.89(5)Å for $Sm(\eta^6\text{-}C_6Me_6)(AlCl_4)_3$ [6].

Experimental

All operations were performed under argon. Hexane and *m*-xylene were refluxed and distilled over Na or CaH_2. Anhydrous $SmCl_3$ was prepared by a published procedure [8]. $AlCl_3$ was sublimed before use. IR spectra were recorded on an FTS-20E spectrometer as KBr pellets.

η^6-m-Xylenesamariumtris(aluminum tetrachloride) 1

$AlCl_3$ (400 mg, 3 mmol) and excess aluminum powder were heated at 130–140 °C for 30 min with stirring. After cooling to room temperature, 256 mg (1 mmol) of $SmCl_3$ and 30 ml *m*-xylene were added to the mixture. The suspension was then kept at 100 °C with stirring until there was a clear color change from yellow to blood-red. After centrifugation, *m*-xylene was removed appropriately and hexane was added until the solution turned slightly turbid. The resulting residue was crystallized at room temperature. Yellow crystals of **1** separated overnight. Several batches of the crystals were collected by decanting the liquid. Collection was discontinued when a red, tarry residue appeared. Yield of pure **1**: 0.28 g (16%). Anal. Found: Sm, 19.24; Cl, 55.59; Al, 9.93. $C_8H_{10}Al_3Cl_{12}Sm$ calcd.: Sm, 19.70; Cl, 55.81; Al, 10.61%. IR (ν_{max}, cm^{-1}): 3060s, 1615m, 1450s, 1380m, 1090m, 1030m, 810s, 680s.

X-ray crystallography

A single crystal (0.2 × 0.3 × 0.2 mm) of **1** was sealed in a thin-walled glass capillary under argon. The crystal data are as follows: $C_8H_{10}Al_3Cl_{12}Sm$, $MW =$

763.3, monoclinic space group $P2_1/n$, a 18.36(5), b 16.37(4), c 20.31(6) Å, β 114.11(2)°, V 5567.87 Å^3, $Z = 8$, $D_c = 1.82$ g cm^{-3}, μ(Mo-$K\alpha$) 16.98 cm^{-1}, $F(000) = 1452$.

Table 3

Atomic coordinates and thermal parameters of non-hydrogen atoms

Atom	x	y	z	U_{eq}
Sm(1)	0.3381(1)	0.7587(1)	0.1074(1)	0.056(1)
Cl(1)	0.1847(5)	0.7516(4)	0.1041(4)	0.071(4)
Cl(2)	0.3162(5)	0.5971(4)	0.1470(4)	0.069(4)
Cl(3)	0.2597(5)	0.8642(4)	−0.0114(4)	0.072(4)
Cl(4)	0.2616(5)	0.6650(4)	−0.0190(4)	0.071(4)
Cl(5)	0.3316(6)	0.9193(5)	0.1578(4)	0.087(5)
Cl(6)	0.3734(5)	0.7535(4)	0.2564(4)	0.075(4)
Cla	0.1840(5)	0.6144(5)	0.6331(4)	0.094(7)
Clb	0.1114(5)	0.5586(4)	0.0470(4)	0.088(6)
Clc	0.0832(4)	0.7649(5)	−0.1191(4)	0.089(5)
Cld	0.2446(6)	0.7736(5)	−0.1720(5)	0.12(1)
Cle	0.2542(5)	0.8982(5)	0.2931(5)	0.101(6)
Clf	0.4620(5)	0.9324(5)	0.3416(5)	0.113(7)
Al(1)	0.1944(5)	0.6218(5)	0.1337(4)	0.066(6)
Al(2)	0.2038(5)	0.7653(5)	−0.0915(4)	0.064(6)
Al(3)	0.3544(6)	0.8845(5)	0.2691(5)	0.075(7)
C(11)	0.496(2)	0.682(2)	0.159(2)	0.16(4)
C(12)	0.466(2)	0.671(2)	0.085(2)	0.11(3)
C(13)	0.449(2)	0.739(2)	0.039(2)	0.10(2)
C(14)	0.463(2)	0.817(2)	0.068(2)	0.09(3)
C(15)	0.493(2)	0.829(2)	0.142(2)	0.14(3)
C(16)	0.507(2)	0.761(2)	0.188(2)	0.17(4)
C(17)	0.455(2)	0.898(2)	0.020(2)	0.18(4)
C(18)	0.453(2)	0.585(2)	0.051(3)	0.22(4)
Sm(2)	0.8176(1)	0.7282(1)	0.0931(1)	0.064(1)
Cl(7)	0.8369(5)	0.8297(5)	0.2118(4)	0.080(5)
Cl(8)	0.7981(5)	0.8966(4)	0.0503(4)	0.090(8)
Cl(9)	0.7312(5)	0.7301(5)	−0.0588(4)	0.096(8)
Cl(10)	0.6563(5)	0.7494(5)	0.0640(4)	0.089(6)
Cl(11)	0.8156(5)	0.6361(4)	0.2096(4)	0.090(8)
Cl(12)	0.758(2)	0.567(2)	0.046(2)	0.09(3)
Clg	0.6895(6)	0.9805(5)	0.1405(5)	0.115(8)
Clh	0.6071(6)	1.5291(5)	0.3089(5)	0.124(9)
Cli	0.9316(8)	1.3594(8)	0.5994(6)	0.19(1)
Clj	0.9572(7)	1.1497(8)	0.5962(6)	0.18(1)
Clk	0.6405(5)	0.9348(5)	0.3105(4)	0.103(7)
Cll	0.3391(5)	1.5116(6)	−0.1462(5)	0.125(9)
Al(4)	0.8016(6)	0.9442(5)	0.1517(5)	0.083(9)
Al(5)	0.6169(7)	0.7476(7)	−0.0532(5)	0.110(9)
Al(6)	0.7710(5)	0.5227(5)	0.1510(5)	0.072(7)
C(21)	0.531(1)	1.290(1)	0.415(1)	0.10(2)
C(22)	0.509(1)	1.271(1)	0.342(2)	0.35(8)
C(23)	0.519(1)	1.182(1)	0.322(2)	0.13(1)
C(24)	0.551(1)	1.131(1)	0.375(2)	0.15(3)
C(25)	0.573(1)	1.150(1)	0.447(2)	0.17(4)
C(26)	0.564(1)	1.230(1)	0.468(2)	0.09(2)
C(27)	0.921(3)	0.755(4)	−0.046(2)	0.26(4)
C(28)	1.028(3)	0.821(4)	0.228(2)	0.05(4)

The X-ray intensity data were collected on a Nicolet R3m/E four circle diffractometer, using graphite-monochromated Mo-*Kα* radiation. A total of 7718 intensities within the range $3° < 2\theta < 45°$ were measured with ω–2θ scan mode. The intensities were corrected for the Lorentz polarization factor and for absorption to give 3461 unique reflections with $F_o^2 > 3\sigma(F_o^2)$.

The heavy atoms were located by Patterson technique. The light atoms were derived on successive Fourier synthesis. All positional parameters and temperature factors for non-hydrogen atoms were refined anisotropically. The final R value is 0.071.

Calculations were carried out by an Eclipse S/40 minicomputer with SHELXTL system of computer program. The atomic coordinates are listed in Table 3.

Supplementary material available. Tables of anisotropic thermal parameters for non-hydrogen atoms (2 pages) and a full list of bond lengths and angles 3 (pages) are available from the authors.

Acknowledgement

This work was supported by a grant from the Chinese National Foundation of Natural Science.

References

1 U. Thewalt, Gmelin Handbook of Inorganic Chemistry (8th Edition), Part 4, Organotitanium Compounds, Springer-Verlag, Berlin, 1984.
2 M. Cesari, U. Pedretti, A. Zazetta, G. Lugli, and N. Marconi, Inorg. Chim. Acta., 5 (1971) 439.
3 F.A. Cotton and W. Schwotzer, Organometallics, 6 (1987) 1275.
4 F.A. Cotton and W. Schwotzer, Organometallics, 4 (1985) 942.
5 G.C. Campbell, F.A. Cotton, J.F. Haw and W. Schwotzer, Organometallics, 5 (1986) 274.
6 F.A. Cotton and W. Schwotzer, J. Am. Chem. Soc., 108 (1986) 4657.
7 J.G. Brennan, F.G. Cloke, A.A. Sameh and A. Zalkin, J. Chem. Soc., Chem. Commun., (1987) 1667.
8 M.P. Taylor and C.P. Carter, J. Inorg. Nucl. Chem., 24 (1962) 387.