

Synthesis and Crystal Structure of $[\text{Nd}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)(\text{AlCl}_4)_3](\text{C}_6\text{H}_6)$ and Structural Comparison of $\text{Ln}(\eta^6\text{-arene})(\text{AlCl}_4)_3$

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Reaction of NdCl_3 with AlCl_3 and mesitylene in benzene gives complex $[\text{Nd}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)(\text{AlCl}_4)_3](\text{C}_6\text{H}_6)$ (**1**) which was characterized by elemental analysis, IR spectra, MS and X-ray diffractions. The X-ray determination indicates that **1** has a distorted pentagonal bipyramidal geometry and crystallizes in the monoclinic, space group $P2_1/n$ with $a = 0.9586(2)$, $b = 1.1717(5)$, $c = 2.8966(7)$ nm, $\beta = 90.85(2)^\circ$, $V = 3.2529(6)$ nm³, $D_c = 1.573$ g/cm³, $Z = 4$. A comparison of bond parameters for all the reported $\text{Ln}(\eta^6\text{-Ar})(\text{AlCl}_4)_3$ complexes indicates that the bond distance of $\text{Ln}-\text{C}$ is shortened with the increasing of methyl group on benzene and with the decreasing of radius of lanthanide ions.

Keywords η^6 -Arene complex, mesitylene, neodymium, lanthanide, X-ray diffraction

Introduction

Lanthanide elements have seven 4f orbitals. However, the 4f orbitals are supposed not to play a significant role in organolanthanide chemistry, because they have a limited radial extension and are shielded from the valence shell by the filled 5s and 5p orbitals. As a result, organolanthanide complexes have ionic characteristic and most of the complexes contain anionic ligands,

such as C_5H_5^- , $\text{C}_8\text{H}_8^{2-}$, C_9H_7^- , aryl, alkyl, etc. The complex with neutral arene (Ar) as a ligand in η^6 -fashion has not been reported until 1986. The first complex $\text{Sm}(\text{C}_6\text{Me}_6)(\text{AlCl}_4)_3$ was synthesized by Cotton under reducing Friedel-Crafts conditions.^{1,2} Then, the analogous complexes with less substituted arenes were published in turn, including $\text{Ln}(\text{C}_6\text{H}_6)(\text{AlCl}_4)_3$ ($\text{Ln} = \text{La}$, Nd , Sm),³ $\text{Sm}(\text{C}_6\text{H}_5\text{Me})(\text{AlCl}_4)_3$ ⁴ and $\text{Sm}(\text{C}_6\text{H}_4\text{Me}_2)(\text{AlCl}_4)_3$ ⁵ by the same method. Recently, a new method, without Al powder, has been successfully used in syntheses of $\text{Ln}(\text{C}_6\text{Me}_6)(\text{AlCl}_4)_3$,⁶ $[\text{Eu}(\text{C}_6\text{Me}_6)(\text{AlCl}_4)_2]_4$,⁷ $\text{Ln}(\text{C}_6\text{H}_4\text{Me}_2)(\text{AlCl}_4)_3$ ($\text{Ln} = \text{Pr}$, Er).⁸ Here, we would like to report the synthesis and molecular structure of the new complex with mesitylene $[\text{Nd}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)(\text{AlCl}_4)_3](\text{C}_6\text{H}_6)$ by the direct way. Structural trends in this kind of complexes are discussed.

Experimental

Since the complex described below was extremely air and moisture sensitive, all experiments were performed under pure argon using Schlenk techniques. All

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the solvents were predried with CaCl_2 and distilled from sodium benzophenone ketyl. Anhydrous NdCl_3 was prepared by a published procedure.⁹ AlCl_3 was sublimed prior to use. Mesitylene was predried with molecular sieves and distilled under reduced pressure. Analyses of Ln and Cl were accomplished using direct complexometric titrations with EDTA and the Volhard method, respectively. IR spectra were recorded on a BIO-RAD FTS-7 spectrometer as KBr pellet. MS spectra were recorded on a VG Quattro MS spectrometer using EI method.

Preparation of $[\text{Nd}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)(\text{AlCl}_4)_3](\text{C}_6\text{H}_6)$

Anhydrous NdCl_3 (0.62 g, 2.5 mmol) and AlCl_3 (0.99 g, 7.5 mmol) were mixed in a Schlenk flask, to which benzene (40 mL) and mesitylene (2.0 mL, 1.5 mmol) were added by turn. The suspension was kept at 70°C with stirring until the color changed to blue green, then the solution was centrifuged to remove solids. The solution was concentrated to about 5 mL and crystallized at room temperature. Purple-red crystals were formed after several weeks. The crystals were isolated and washed by benzene and dried in vacuum. Yield: 0.596 g (47% based on mesitylene). The crystals decomposed at 83°C. IR (KBr, pellet, cm^{-1}): 3036(s), 1966(m), 1620(s), 1475(s), 1382(s), 1034(m), 841(m), 688(s). MS m/z (%): 603 ($\text{M}^+ - \text{AlCl}_3 - \text{Cl}$, < 1), 505 ($\text{M}^+ - 2\text{AlCl}_3$, < 1), 120 ($\text{C}_9\text{H}_{12}^+$, 100). Anal. $\text{C}_{15}\text{H}_{18}\text{Al}_3\text{Cl}_{12}\text{Nd}$. Calcd: Nd, 16.99; Cl, 50.12. Found: Nd, 16.78; Cl, 50.27.

Determination of the crystal structure of $[\text{Nd}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)(\text{AlCl}_4)_3](\text{C}_6\text{H}_6)$

A crystal of dimensions 0.36 × 0.44 × 0.24 mm was selected and sealed in a thin-walled glass capillary under argon for X-ray diffraction. All the intensity data were collected on a Nicolet R3 M/E automatic four-cycle diffractometer at room temperature using graphite-monochromated Mo K_α radiation ($\lambda = 0.071069$ nm). 6389 Reflections were collected in the range of $3^\circ \leq 2\theta \leq 50^\circ$, of which 3706 reflections with $I \geq 3\sigma(I)$ were considered to be observed. The intensity data were corrected for Lorentz and polarization factors but not for absorption. The structure was solved by Patterson techniques and refined by full-matrix least-squares technique with

anisotropic thermal parameters. All hydrogen atoms were not found and their coordinates were placed in calculated positions. Further refinement led to final convergence at $R = 0.0477$, $R_w = 0.0433$, where $W = [\sigma^2 |F_o| + g |F_o|^2]^{-1}$ ($g = 0.00020$). The detailed data were listed in Table 1 and the atomic coordinates listed in Table 2.

Table 1 Crystal data for $\text{Nd}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)(\text{AlCl}_4)_3(\text{C}_6\text{H}_6)$

Formula	$[\text{Nd}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)(\text{AlCl}_4)_3](\text{C}_6\text{H}_6)$
<i>MW</i>	848.8
Crystal system	Monoclinic
Space group	$P2_1/n$
Cell constants	
<i>a</i> (nm)	0.9586(2)
<i>b</i> (nm)	1.1717(5)
<i>c</i> (nm)	2.8966(7)
β (deg)	90.85(2)
<i>V</i> (nm^3)	3.25296(2)
<i>Z</i>	4
Density (g/cm^3)	1.573
μ (Mo K_α) (cm^{-1})	26.76
R^a	0.0477
R_w^b	0.0433
<i>F</i> (000)	1476

$$^a R = \Sigma(|F_o| - |F_c|) / (\Sigma|F_o|) \quad ^b R_w = \Sigma W^{1/2}(|F_o| - |F_c|) / \Sigma(|F_o|) W^{1/2}, \quad W = [\sigma^2 |F_o| + g |F_o|^2]^{-1}$$

Results and discussion

Synthesis

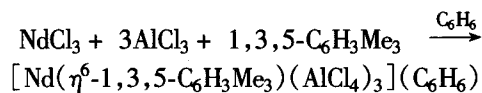
Friedel-Crafts reaction is a versatile method for the synthesis of neutral π -arene complexes of lanthanides. However, the method often gives tarry concomitantly with the desired products. The direct way, without Al powder, overcomes in part the shortcoming.⁶ Several arene complexes of lanthanide elements with C_6H_6 , $\text{C}_6\text{H}_5\text{Me}$, $\text{C}_6\text{H}_4\text{Me}_2$, C_6Me_6 have been synthesized by the two methods. However, the complex with mesitylene as a neutral ligand has not been reported so far. In order to understand the structural trend in η^6 -arene complexes of lanthanide elements, it is meaningful to synthesize the title complex. Attempt to prepare the complex with Friedel-Crafts reaction was failed, but only dark brown tarry was formed. However, the reaction of NdCl_3 with

Table 2 Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{nm}^2 \times 10^5$) with estimated standard deviations for $[\text{Nd}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)(\text{AlCl}_4)_3](\text{C}_6\text{H}_6)$

Atom	X	Y	Z	U_{eq}^*
Nd	4629(1)	6408(1)	6252(1)	52(1)
Cl(1)	5401(3)	5404(2)	7133(1)	72(1)
Cl(2)	4703(3)	8098(2)	6966(1)	81(1)
Cl(3)	7741(3)	7500(3)	7582(1)	106(1)
Cl(4)	4533(4)	6963(3)	8103(1)	116(2)
Cl(5)	5789(2)	4240(2)	6071(1)	59(1)
Cl(6)	7601(3)	6626(2)	6278(1)	72(1)
Cl(7)	8940(3)	4609(3)	5519(1)	98(1)
Cl(8)	8928(3)	4046(3)	6715(1)	95(1)
Cl(9)	4813(3)	8640(2)	5864(1)	76(1)
Cl(10)	5238(3)	6301(2)	5280(1)	77(1)
Cl(11)	7697(4)	8456(3)	5122(1)	114(1)
Cl(12)	4300(4)	8685(3)	4644(1)	120(2)
Al(1)	5659(4)	7015(3)	7501(1)	77(1)
Al(2)	7957(3)	4810(3)	6147(1)	65(1)
Al(3)	5580(4)	8131(3)	5187(1)	78(1)
C(11)	2174(10)	5588(9)	5758(4)	66(4)
C(12)	2344(10)	4778(9)	6111(4)	66(4)
C(13)	2223(10)	5129(10)	6567(4)	75(5)
C(14)	1875(10)	6240(10)	6675(3)	72(4)
C(15)	1707(9)	7008(9)	6323(3)	76(4)
C(16)	1816(10)	6702(9)	5865(4)	72(4)
C(17)	1486(12)	7531(11)	5475(4)	117(6)
C(18)	2509(10)	3537(9)	6003(4)	97(5)
C(19)	1573(11)	6589(12)	7156(4)	119(7)
C(21)	-558(22)	5182(14)	1706(5)	207(12)
C(22)	757(21)	5138(14)	1866(5)	252(13)
C(23)	1485(23)	4751(16)	1502(7)	180(11)
C(24)	1041(21)	4529(14)	1110(6)	159(10)
C(25)	-96(24)	4542(23)	994(10)	275(19)
C(26)	-1057(22)	4910(22)	1258(9)	259(17)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

AlCl_3 and mesitylene in the molar ratio of 1:3:1, without Al powder, gives only dark brown tarry just like the result by Friedel-Crafts reaction. Then, the reaction was studied under different conditions, including molar ratios, solvents, temperatures. At last, the desired purple title complex was successfully isolated in fair yield, when the molar ratio of NdCl_3 , AlCl_3 and mesitylene was decreased to 1:3:0.6.



MS spectra of $[\text{Nd}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)(\text{AlCl}_4)_3]\text{-}$

(C_6H_6) show no parent molecular ion peak, only some peaks at 603 ($\text{M}^+ - \text{AlCl}_3 - \text{Cl}$, 1), 505 ($\text{M}^+ - 2\text{AlCl}_3$, 1), 120 ($\text{C}_9\text{H}_{12}^+$, 100).

The complex is extremely sensitive to air and moisture. It is only slightly soluble in aromatic solvents, therefore, NMR spectra for **1** can not be recorded.

Structure

The molecular structure of $[\text{Nd}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)(\text{AlCl}_4)_3](\text{C}_6\text{H}_6)$ was shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 3.

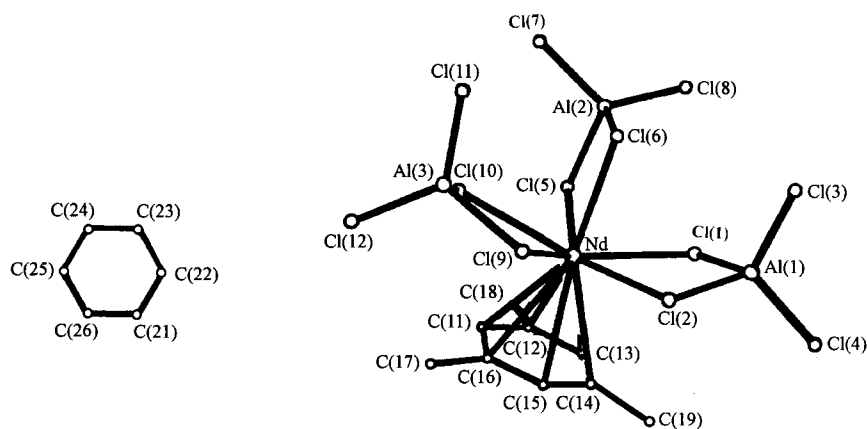


Fig. 1 Molecular structure of 1.

Table 3 Selected bond lengths (nm) and angles ($^{\circ}$) for $[\text{Nd}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)(\text{AlCl}_4)_3](\text{C}_6\text{H}_6)$

Nd—C(11)	0.2900(9)	Nd—Cl(10)	0.2887(2)
Al(3)—Cl(11)	0.2075(5)	Nd—C(12)	0.2930(10)
Al(1)—Cl(1)	0.2180(4)	Al(3)—Cl(12)	0.2085(5)
Nd—C(13)	0.2909(10)	Al(1)—Cl(2)	0.2191(4)
Al(3)—Cl(10)	0.2187(4)	Nd—C(14)	0.2933(9)
Al(1)—Cl(3)	0.2085(5)	Al(3)—Cl(9)	0.2188(4)
Nd—C(15)	0.2898(9)	Al(1)—Cl(4)	0.2067(5)
Al(2)—Cl(8)	0.2080(4)	Nd—C(16)	0.2926(9)
Al(2)—Cl(5)	0.2191(4)	Al(2)—Cl(7)	0.2075(4)
Nd—Cl(1)	0.2897(3)	Al(2)—Cl(6)	0.2190(4)
Nd—Cl(2)	0.2864(3)	Nd—Cl(5)	0.2825(3)
Nd—Cl(6)	0.2860(3)	Nd—Cl(9)	0.2854(3)
Cl(1)-Nd-Cl(2)	68.9(1)	Cl(1)-Nd-Cl(5)	72.7(1)
Cl(1)-Nd-Cl(6)	76.8(1)	Cl(1)-Nd-Cl(9)	134.7(1)
Cl(1)-Nd-Cl(10)	142.1(1)	Cl(6)-Nd-Cl(9)	82.0(1)
Cl(6)-Nd-Cl(10)	79.2(1)	Cl(6)-Nd-Cl(11)	147.5(2)
Cl(2)-Nd-Cl(5)	138.6(1)	Cl(2)-Nd-Cl(6)	84.6(1)
Cl(2)-Nd-Cl(9)	69.5(1)	Cl(2)-Nd-Cl(10)	137.0(1)
Cl(5)-Nd-Cl(6)	102.0(2)	Cl(5)-Nd-Cl(9)	136.4(1)
Cl(5)-Nd-Cl(10)	72.2(1)	Cl(1)-Al(1)-Cl(2)	96.5(2)
Cl(3)-Al(1)-Cl(4)	115.0(2)	Cl(5)-Al(2)-Cl(6)	99.4(2)
Cl(7)-Al(2)-Cl(8)	116.2(2)	Cl(9)-Al(3)-Cl(10)	96.0(2)
Cl(11)-Al(3)-Cl(1)	116.0(2)	Cl(9)-Nd-Cl(10)	69.0(1)

The central metal Nd has distorted pentagonal bipyramidal geometry with mesitylene in one of the apical positions. The five chlorine atoms, Cl(1), Cl(2), Cl(5), Cl(9), Cl(10) are nearly located in a plane. The sixth chlorine atom Cl(6) occupies the other apical position. The average Nd—C bond length is 0.2916(9)

nm, which is shorter than 0.2926(5) nm in $\text{Nd}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlCl}_4)_3$ ⁴ and 0.2933(2) nm in $\text{Nd}(\eta^6\text{-C}_6\text{H}_6)(\text{AlCl}_4)_3$.³ The differences in Nd—C bonds might reflect the different interaction between various arenes and Nd metal in these analogous complexes. The more the methyl groups, the stronger the Nd—C bond. The bond

length of Nd—Cl is 0.2865(5) nm, which is comparable to 0.2857(1) nm in Nd(η^6 -C₆H₅Me)(AlCl₄)₃⁴ and 0.2852(7) nm in Nd(η^6 -C₆H₆)(AlCl₄)₃³, respectively. The Cl—Ln—Cl bond angles for adjacent chlorine atoms in the plane range from 68.9(1) to 72.7(1)° which are also comparable with 68.8 to 73.2° in Nd(η^6 -C₆H₆)(AlCl₄)₃ and 69.4 to 81.2° in Nd(η^6 -C₆H₅Me)(AlCl₄)₃.⁴

Structural trend in Ln(η^6 -Ar)(AlCl₄)₃

In order to get the best comparison, Table 4 summarizes the data for all the complexes and shows how the

average Ln—C distances change with the different central metals and arenes. The last two columns of Table 4 show the data normalized to the metal samarium. The average Ln—C bond distance parallels the metal radius which is expected by lanthanide contraction. The bond length of Ln—C_{ave} is shortened with the increasing of methyl group on the benzene ring. It seems that the more the methyl groups, the stronger the Ln—C bond. Ln—Cl bond distance increases with the increasing of methyl group. It was noticed that the average Eu—C bond length of Eu (II) complex is much longer. This may be attributed to that trivalent lanthanide ions are more electron withdrawing than divalent europium ion.

Table 4 Bond distances for Ln(η^6 -Ar)(AlCl₄)₃

Ln	Ln radius (nm) ^a	Arene	Ln—C _{ave} (nm)	Ln—Cl _{ave} (nm)	Ln radius minus Sm radius (nm)	Ln—C _{ave} minus Sm—C _{ave} (nm)	Ref.
Pr	0.1179	<i>m</i> -xylene	0.2949(20)	0.2872(5)	0.0047	0.0059	8
Nd	0.1163	benzene	0.2933(18)	0.2852(6)	0.0031	0.0024	4
		toluene	0.2926(5)	0.2857(1)	0.0031	0.0019	11
		mesitylene	0.2916(9)	0.2865(3)	0.0031		this work
Sm	0.1132	benzene	0.2909(7)	0.2829(1)	0		3
		toluene	0.2907(10)	0.2835(3)	0		4
		<i>m</i> -xylene	0.288(2)	0.2836(2)			
			0.290(3)	0.2826(7)			5
		HMB*	0.289(5)	0.285(2)		1,2	
Yb	0.1042	HMB	0.2865(39)	0.2785(10)	-0.0090	-0.0025	6
Eu(II)	0.109	HMB	0.2997(17)	0.3015(4)	-0.0042	0.0107	7

* HMB means hexamethylbenzene

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