

Synthesis and X-Ray Crystal Structure of $[\text{Eu}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_2]_4$; the First Cyclotetrameric Lanthanide(II) Complex with a Neutral π -Ligand

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The reaction of EuCl_3 , AlCl_3 and C_6Me_6 in toluene gives the Eu^{II} complex $[\text{Eu}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_2]_4$; X-ray crystal determination shows the molecule to be a cyclotetramer, in which the four $\text{Eu}(\text{C}_6\text{Me}_6)\text{AlCl}_4$ units are connected *via* four groups of $\eta^2\text{-AlCl}_4$.

Only two types of η^6 -arene complexes of lanthanide, $\text{Ln}(\eta^6\text{-arene})(\text{AlCl}_4)_3$ ^{1,2} and $[\text{Ln}(\eta^6\text{-Bu}^t_3\text{C}_6\text{H}_3)_2]$,³ were known so far. The former contains a lanthanide ion in oxidation state III and the latter in oxidation state 0. We were, therefore, interested to try to find out the reaction conditions for the synthesis of the η^6 -arene complex of divalent lanthanide.

We report here the synthesis and crystal structure of η^6 -arene complex of europium(II) $[\text{Eu}(\text{C}_6\text{Me}_6)(\text{AlCl}_4)_2]_4$ - $(\text{CH}_3)_4\text{C}_6\text{H}_2$ **1**. Stirring of EuCl_3 (1 equiv.), freshly sublimed AlCl_3 (1 equiv.) and C_6Me_6 (1.2 equiv.) in toluene at 60 °C for >72 h resulted in the formation of a deep-green suspension. After removal of the precipitate and crystallization at room

temperature, complex **1** was isolated as green crystals (17% yield) and identified by elemental analysis (Eu and Cl) and IR spectra† and by single-crystal X-ray analysis.‡

Complex **1** is extremely sensitive to air and moisture, but thermally stable and is only decomposed >140 °C. The complex displays a luminescence spectrum peak at 400 nm and an excitation spectrum peak at 247 nm, which were assigned to the characterized bands of Eu^{II}.^{4,5}

The molecular structure and atom-numbering scheme for **1** are shown in Fig. 1, together with selected bond distances. Complex **1** is a cyclotetramer composed of four Eu(C₆Me₆)(AlCl₄)₂ units. Each europium atom is coordinated by three groups of AlCl₄⁻ and one C₆Me₆ to form a distorted pentagonal bipyramid. The Eu^{II}-C distances range from 2.917(15) to 3.066(12) Å and average Eu^{II}-C 2.999(23) Å is comparable with the Sm^{III}-C 2.89 Å in Sm(C₆Me₆)(AlCl₄)₃ **2** if the difference of the ionic radii of Eu^{II} (1.09 Å) and Sm^{III} (0.964 Å) is considered. But Eu^{II}-C distance in **1** is significantly larger than Ln⁰-C 2.630(4) Å in Ln(η⁶-Bu₃C₆H₃)₂. Therefore, we can conclude that the nature of the arene-metal bonding in **1** and **2** is very similar.

Primary research work on how the unexpected reaction occurred shows that it is an especial reaction just for the case of europium and is unsuccessful for other lanthanide elements under the same conditions. It seems to correspond to reducing reactivity of Ln^{III}-Ln^{II}. GSMS spectra reveal that the reaction is very complicated, and after completion of the reaction, some new substances such as durene and pentamethylbenzene were found in the solution exclusive of original reacting substances. It means that C₆Me₆ not only was coordinating agent but also took part in the redox reaction. The neutral inserted molecule (Me₄)₄C₆H₄ in complex **1** was the product of

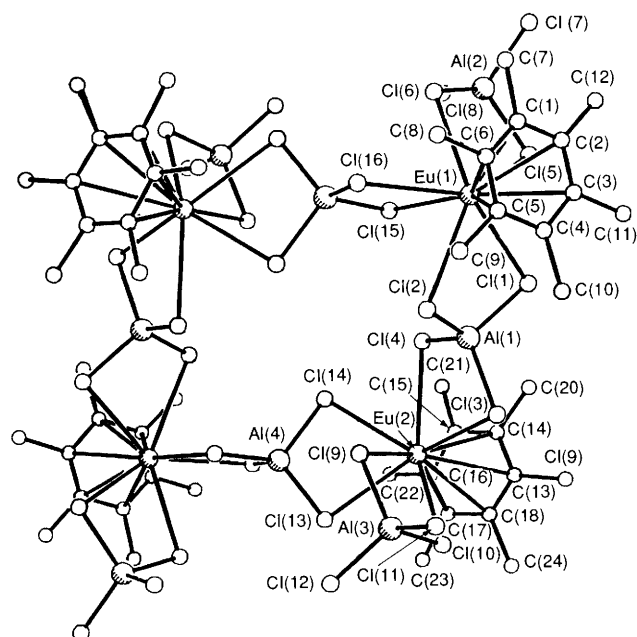


Fig. 1 Molecular structure of the [Eu(C₆Me₆)(AlCl₄)₂]₄. Selected bond lengths (Å): Eu(1)-C(1) 3.061(16), Eu(1)-C(2) 2.996(18), Eu(1)-C(3) 2.917(15), Eu(1)-C(4) 2.952(12), Eu(1)-C(5) 3.019(15), Eu(1)-C(6) 3.035(115), Eu(2)-C(13) 3.066(12), Eu(2)-C(14) 3.000(11), Eu(2)-C(15) 2.947(12), Eu(2)-C(16) 2.996(16), Eu(2)-C(17) 2.988(16), Eu(2)-C(18) 3.046(14).

the redox reaction. Unfortunately, knowledge of the mechanism of the reaction is limited and our next step is to find out more.

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† Elementary analysis (calculated values, %); and IR spectral data for **1**: C₅₈H₈₆Eu₄Al₈Cl₃₂, Eu 21.49(22.17), Cl 41.39(41.38). IR(KBr, cm⁻¹), 1620, 1555, 1495, 1470, 1383.

‡ Crystal data for **1**: C₅₈H₈₆Eu₄Al₈Cl₃₂, *M* = 2741.508, monoclinic, space group *P2₁/c*, *a* = 17.652(4), *b* = 15.918(4), *c* = 18.752 Å, β = 97.61(5)°, *V* = 5222, 6 Å³, *Z* = 2, *D_c* = 1.74 g cm⁻³ *F*(000) = 2668, (Mo-Kα) = 33.0 cm⁻¹. Data were collected on R3M/E diffractometer at 295 K using graphite monochromated Mo-Kα in ω-scan. The corrections were made for Lorentz and polarization effects. Least-squares refinement based on 4768 observed reflections led to a final *R* value of 0.049 (*R_w* = 0.046). The structure was solved by Patterson and Fourier methods. All non-hydrogen atoms were refined, except those in a disordered solvent fragment. This solvent fragment was modelled as tetramethylbenzene, with the methyl groups disordered over all six positions. The fragment located is not necessarily tetramethylbenzene. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.