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<https://doi.org/10.1016/j.poly.2022.115737>

# Synthesis and characterisation of $\eta^6$ -arene(halogenidoaluminato)lanthanoid(II) and alkaline earth(II) complexes

Md Elius Hossain,<sup>[a]</sup> Zhifang Guo,<sup>[a]</sup> Jun Wang,<sup>[a]</sup> Glen B. Deacon,<sup>[b]</sup> Peter C. Junk<sup>[a]\*</sup>

[a] College of Science and Engineering, James Cook University, Townsville, Qld 4811, Australia

[b] School of Chemistry, Monash University, Clayton, Victoria, Australia

\* Corresponding author: peter.junk@jcu.edu.au

**Abstract:**  $\eta^6$ -Arene(iodidoaluminato)lanthanoid(II) complexes,  $\{[\text{Ln}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]_n\}$  [Ln = Sm, **1**, Eu, **2**, Yb, **3**;  $\text{C}_6\text{H}_5\text{Me}$  = toluene] have been prepared by reactions of *in situ* generated aluminium triiodide with the corresponding lanthanoid metals and 1,2-diiodoethane in toluene (molar ratio : 2:1:1). Compounds **1-3** are polymeric and the lanthanoid(II) atom of **1** and **2** is coordinated by an  $\eta^6$ -arene and three chelating  $\kappa$  (I, I') tetraiodidoaluminate ligands, two of which are also bridging ( $\text{LnI}_2\text{AlI}_2\text{Ln}$ ) and one is terminal. **3** is coordinated by an  $\eta^6$ -arene, one terminal chelating  $\kappa$  (I, I') and one chelating and bridging ( $\text{YbI}_2\text{AlI}_2\text{Yb}$ ) tetraiodidoaluminate ligand, and one monodentate tetraiodidoaluminate ligand, which is also bridging ( $\text{YbIAl(I)I}_2\text{Yb}$ ). These are the first X-ray crystal structures of arene(tetrakisiodidoaluminato)lanthanoid(II) complexes. The first reported alkaline earth(II) ( $\eta^6$ -arene)iodidoaluminate complexes, namely  $[\text{Ca}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]_n$  (**4**),  $\{[\text{Sr}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]_n \cdot n\text{PhMe}\}$  (**5**),  $[\text{Ba}(\eta^6\text{-C}_6\text{H}_5\text{Me})_2(\text{AlI}_4)_2]$  (**6**),  $[\text{Ca}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{AlI}_4)_2]_n$  (**7**) and  $\{[\text{Sr}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{AlI}_4)_2]_n \cdot 0.5n(\text{PhMe}_3)\}$  (**8**) have also been obtained in an arene (toluene or mesitylene) solution by a similar method. Complex **4** is isocoordinate with **3**, and **5** is isomorphous with **2**. Complex **7** has eight coordinate Ca similar to **4**, and complex **8** has nine coordinate Sr as in **5**. Mononuclear ten coordinate complex **6** is the first example of a monomeric  $\eta^6$ -arene sandwich complex

of barium. The Eu<sup>II</sup> bromidoaluminate complex  $\{[\text{Eu}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlBr}_4)_2]_n \cdot 0.5n\text{PhMe}\}$  (**9**) has been prepared from Eu metal, AlBr<sub>3</sub>, and BrCH<sub>2</sub>CH<sub>2</sub>Br in toluene and has a unit cell similar to **8** despite the different metal and arene.

**Keywords:** Divalent lanthanoids and Alkaline earths(II)  $\pi$ -arene complex; Aluminium tribromide, Aluminium triiodide, Iodido- and Bromido-aluminate complexes.

## Introduction

Lanthanoid(II/III) chloridoaluminate  $\eta^6$ -arene complexes  $[\text{Ln}(\eta^6\text{-arene})(\text{AlCl}_4)_n]$  ( $n = 2, 3$ ) have been known for over three decades [1-4]. Due to the high reactivity of these complexes, they are catalysts for polymerization of alkenes and dienes and butadiene polymerization [5]. The first structurally characterized lanthanoid chloridoaluminate  $\pi$ -arene complex  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Sm}(\text{AlCl}_4)_3]$  was synthesized by heating a mixture of samarium(III) chloride, aluminum chloride and hexamethylbenzene in toluene to reflux [1]. Other trivalent chloridoaluminatolanthanoid complexes were subsequently reported by a similar preparative method [6-11], and the only structurally characterised bromidoaluminatolanthanoid complexes are  $[\text{Gd}(\eta^6\text{-MeC}_6\text{H}_5)(\text{AlBr}_4)_3]$  [9],  $[\text{Dy}(\eta^6\text{-MeC}_6\text{H}_5)(\text{AlBr}_4)_3]$  [11], and  $[\text{Ln}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlBr}_4)_3]$  [ $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$ ] [12]. Moreover, Ln<sup>III</sup> halogenidogallate complexes  $[\text{Ln}(\eta^6\text{-arene})(\text{GaX}_4)_3]$  ( $\text{Ln} = \text{Ce}, \text{Yb}, \text{Dy}; \text{X} = \text{Cl}, \text{Br}$ ) have been prepared by the reaction of gallium(III) halides and lanthanoid(III) halides in the presence of alkylated benzenes [13]. A number of  $\eta^6$ -arene alkyltrihalogenidoaluminatolanthanoid(III) complexes  $[\text{Ln}(\eta^6\text{-arene})(\text{AlX}_3\text{R})_3]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}; \text{R} = \text{Me}, \text{Et}$ ) have been prepared by the reaction of  $\text{Ln}(\eta^6\text{-arene})(\text{AlX}_4)_3$  with the corresponding AlR<sub>3</sub> derivative [5a]. Although the chloroaluminate Ln<sup>III</sup> complexes have been explored extensively, only a few examples of the divalent analogues are known. The divalent chloridoaluminate  $\pi$ -arene complex  $[\text{Eu}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_2]_4 \cdot \text{C}_{10}\text{H}_{14}$  is the only reported Eu<sup>II</sup> halogenidoaluminate [14a], and its Mossbauer effect was studied in 1995 [14b]. The first polymeric divalent ytterbium  $\pi$ -arene chloridoaluminate complexes,  $\{[\text{Yb}(\eta^6\text{-C}_6\text{H}_6)(\text{AlCl}_4)_2]_n \cdot n\text{C}_6\text{H}_6\}$  and  $[\text{Yb}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)(\text{AlCl}_4)_2]_n$  were reported in 1998 [15], and the same year the group reported similar structures for samarium in  $[\text{Sm}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)(\text{AlCl}_4)_2]_n$  and  $\{[\text{Sm}(\eta^6\text{-C}_6\text{H}_6)(\text{AlCl}_4)_2]_n \cdot 0.5n\text{C}_6\text{H}_6\}$

[16]. The trichloridoiodidoaluminate complexes  $[\text{Sm}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlCl}_3)_2]_n$  and  $[\text{Sm}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_3)_2]_2 \cdot \text{C}_6\text{Me}_6$  were obtained by the reaction of  $\text{SmI}_2$  and  $\text{AlCl}_3$  in an arene solution, but their structures were complicated by disorder of iodide across all four positions [7b]. There have been no reported examples of tetrakisiodidoaluminato- $\pi$ -arene- or tetrabromidoaluminato- $\pi$ -arene-lanthanoid(II) complexes. The divalent metal centres of the precursors have a smaller charge to size ratio than their trivalent counterparts and the arene interaction is likely to be weaker [7b], hence isolation of these complexes is potentially synthetically challenging.

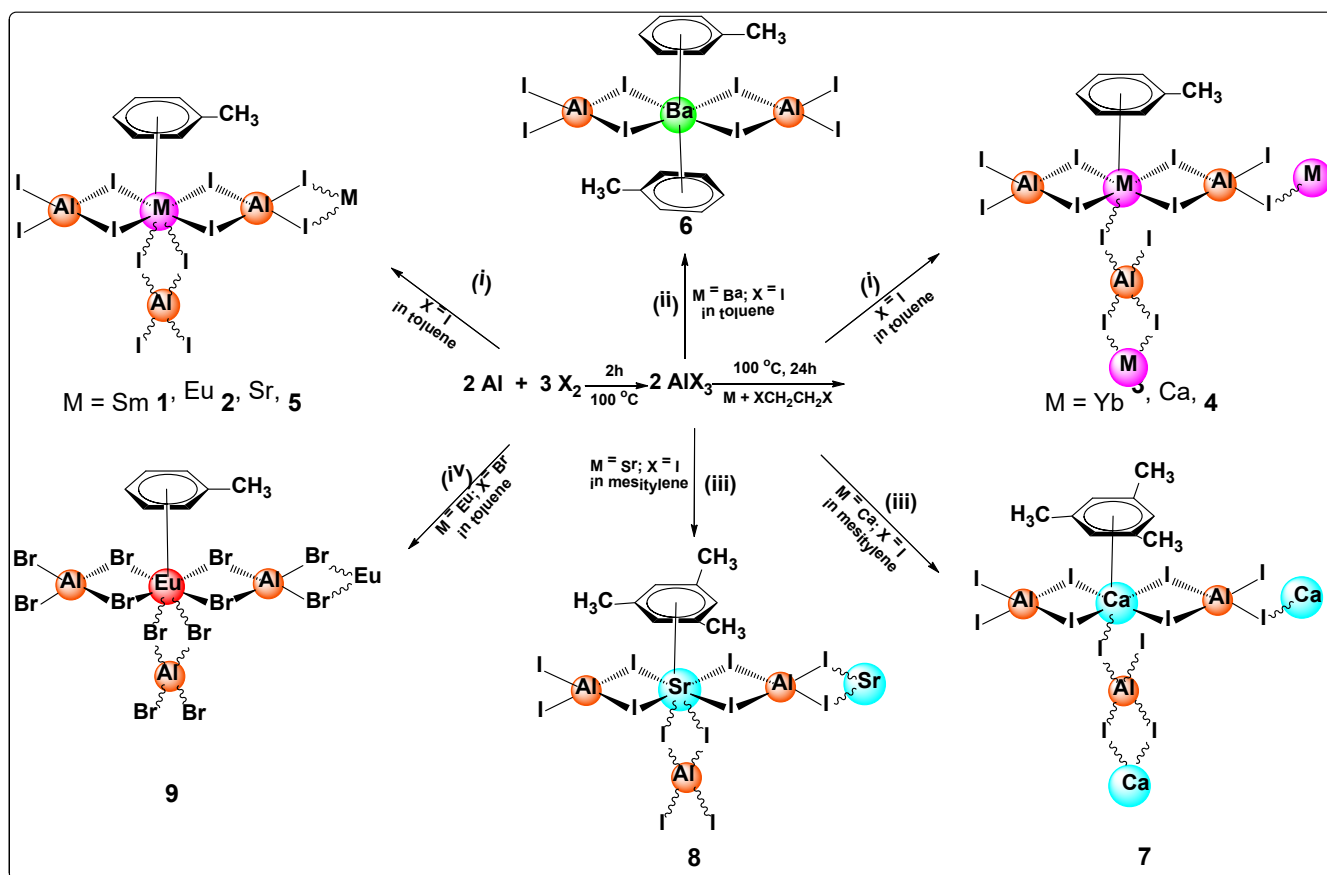
Recently our group reported the preparation of trivalent  $\pi$ -arene iodido-/bromidoaluminatolanthanoid(III) complexes,  $[\text{Ln}(\eta^6\text{-arene})(\text{AlI}_4)_3]$  and  $[\text{Ln}(\eta^6\text{-arene})(\text{AlBr}_4)_3]$ , by reactions of aluminium triiodide or aluminium tribromide with the corresponding lanthanoid metals and 1,2-diiodoethane or 1,2-dibromoethane in an arene (toluene or mesitylene) solution [12]. In the present work we explore iodidoaluminato- $\pi$ -arene lanthanoid(II) complexes and report the synthesis and X-ray crystal structures of the first tetrakis(iodidoaluminato)lanthanoid(II) complexes  $[\text{Ln}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]_n$  ( $\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$ ) and the first tetrabromidoaluminatoeuropium(II) complex  $[\text{Eu}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlBr}_4)_2]_n$ .

Divalent cations of the heavy alkaline earths  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  are large, polarisable, and electrophilic [17] with effective ionic radii of 1.12, 1.26 and 1.42 Å (C. N. = 8), respectively [18]. The first two of these alkaline earth metals are similar to the divalent Ln metals Yb, Sm and Eu with ionic radii of 1.14, 1.27 and 1.25 Å (C. N. = 8). A search of the Cambridge Crystallographic Database [19] confirmed there were no structural studies of alkaline earth(II)  $\pi$ -arene tetrahalogenoaluminate complexes, however, the tetrachloridogallatobarium complex  $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Ba}(\text{GaCl}_4)_2]_3$  has been synthesized by the reaction of gallium chloride, barium chloride and barium metal in benzene [20]. In this paper, we also report the first iodidoaluminate complexes of alkaline earths  $[\text{Ae}(\eta^6\text{-arene})(\text{AlI}_4)_2]_n$  ( $\text{Ae} = \text{Ca}, \text{Sr}$ ; arene = toluene or mesitylene) and  $[\text{Ba}(\eta^6\text{-C}_6\text{H}_5\text{Me})_2(\text{AlI}_4)_2]$  synthesised by a similar method to that for the  $\text{Ln}^{\text{II}}$  species.

## Results and Discussion

Divalent ( $\eta^6$ -arene)tetrakisiodidoaluminato- lanthanoid and –alkaline earth complexes were synthesised by heating a mixture of 5 molar equivalents of aluminium triiodide with 2.5 molar equivalents of the corresponding lanthanoid or alkaline earth metal and 2.5 molar equivalents of 1,2-diiodoethane in an arene (toluene or mesitylene) solution (Scheme 1). Aluminium triiodide was freshly prepared by heating a mixture of iodine with an excess of aluminium powder in the arene and was used *in situ*. Stoichiometric amounts of lanthanoid metal and diiodoethane were then added to the aluminium triiodide solution and the mixture was heated at 100 °C. After filtration and evaporation, crystallization at room temperature afforded the complexes  $\{\{\text{Sm}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2\}_n \cdot n\text{PhMe}\}$  **1**,  $\{\{\text{Eu}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2\}_n \cdot n\text{PhMe}\}$  **2** and  $\{\{\text{Yb}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2\}_n \cdot 0.5n\text{PhMe}\}$  **3**,  $[\text{Ca}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]_n$  **4**,  $\{\{\text{Sr}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2\}_n \cdot n\text{PhMe}\}$  **5**,  $[\text{Ba}(\eta^6\text{-C}_6\text{H}_5\text{Me})_2(\text{AlI}_4)_2]$  **6**,  $[\text{Ca}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{AlI}_4)_2]_n$  **7** and  $\{\{\text{Sr}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{AlI}_4)_2\}_n \cdot 0.5n(\text{PhMe}_3)\}$  **8**. The  $\text{Eu}^{\text{(II)}}$  bromidoaluminate complex  $\{\{\text{Eu}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlBr}_4)_2\}_n \cdot 0.5n\text{PhMe}\}$  **9** was also obtained in toluene (Scheme 1) by a similar method. Crystals of **1-9** are almost completely insoluble in aromatic solvents such as deuterobenzene, thereby precluding satisfactory NMR measurements. Furthermore, these compounds decomposed in polar solvents e.g. thf, in which the compounds are presumably ligated by the polar solvents in preference to arenes. All complexes are extremely air and moisture sensitive and are difficult to handle.

Due to extreme air sensitivity of the complexes and low percentage of C and H (only from toluene or mesitylene), % H microanalyses were often high and some % C values were somewhat deviant. However, the metal analyses on freshly prepared samples were closer to the expected values for the compositions found in X-ray crystallography (see below). Metal analyses were performed immediately after preparation, whereas C, H microanalyses required prior international travel and solvent loss/decomposition could occur in transit. Although single crystals of  $\{\{\text{Eu}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlBr}_4)_2\}_n \cdot 0.5n\text{PhMe}\}$  **9** were isolated, pure bulk material could not be isolated for microanalyses.



**Scheme 1.** Synthesis of compounds **1-9**

## X-ray Structures

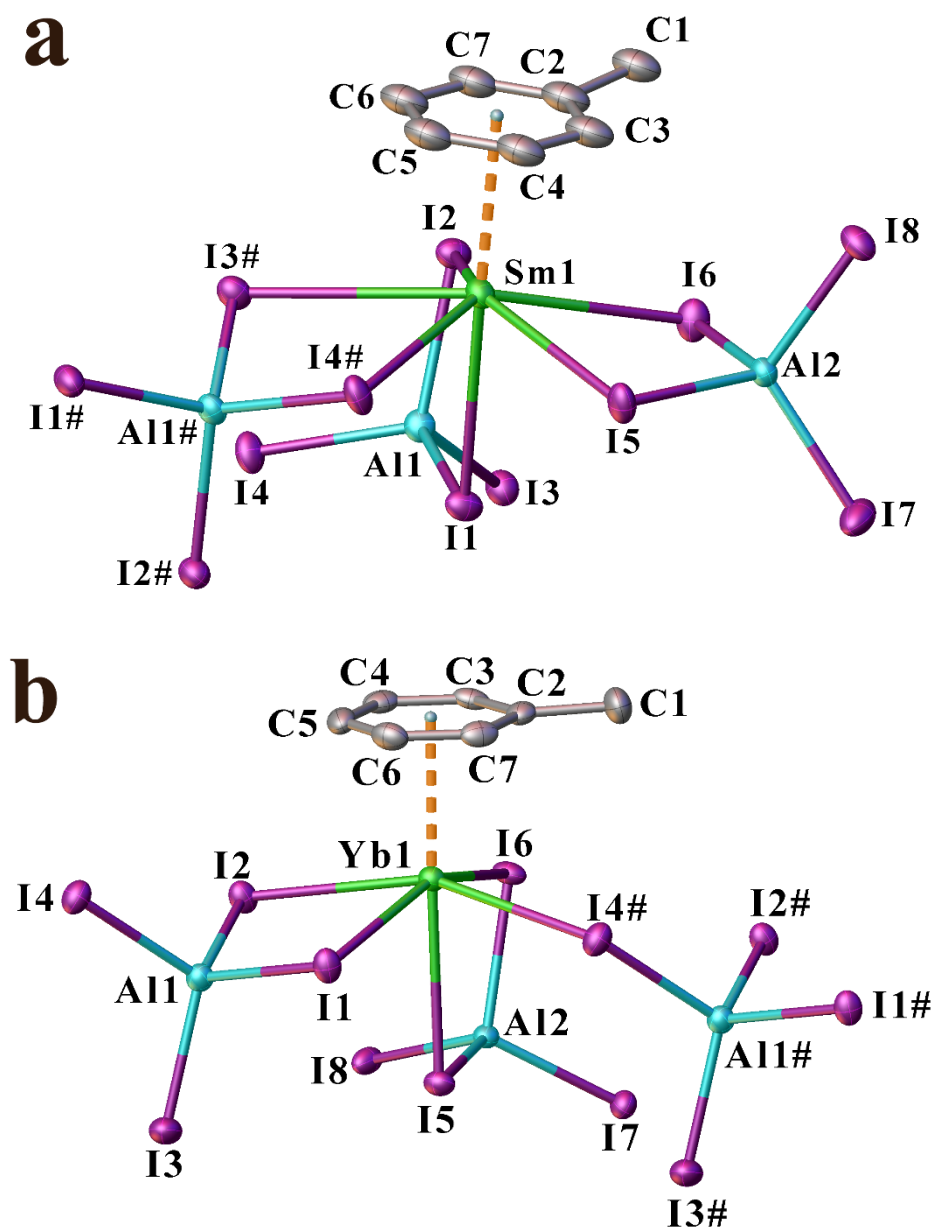
Representative structures of complexes **1-9** are shown in Fig 1-5. The M-C bond lengths and M-C-ring (centroid) are in **Table 1**, those for M-I/Br are in **Table 2**. Crystal data and refinement details are given in Table S1.

Single crystals of  $\{[\text{Ln}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]_n \cdot n\text{PhMe}\}$  ( $\text{Ln} = \text{Sm}$  **1**,  $\text{Eu}$  **2**) and  $\{[\text{Sr}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]_n \cdot n\text{PhMe}\}$  **5** are isomorphous and crystallize in the orthorhombic space group  $\text{P2}_1\text{2}_1\text{2}_1$  with a single molecule and one lattice PhMe in the asymmetric unit (**Fig 1**).  $\{[\text{Yb}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]_n \cdot 0.5n\text{PhMe}\}$  **3** and  $[\text{Ca}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]_n$  (**4**) crystallize in the monoclinic space group  $\text{C2/c}$ , and **3** has a single  $[\text{Yb}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]$  moiety and 0.5 molecules of lattice PhMe in the asymmetric unit, and **4** has 1.5 molecules in the asymmetric unit. Although **3** is not isomorphous with **1**, **2** and **5**, all complexes have similar monomeric repeating units (Fig. 1a, b), but with differing coordination numbers. Complexes **1**, **2** and **5** have polymeric structures in which the nine-coordinate  $\text{Ln}^{2+}/\text{Sr}^{2+}$  ions are coordinated by an  $\eta^6$ -toluene molecule (considered to be

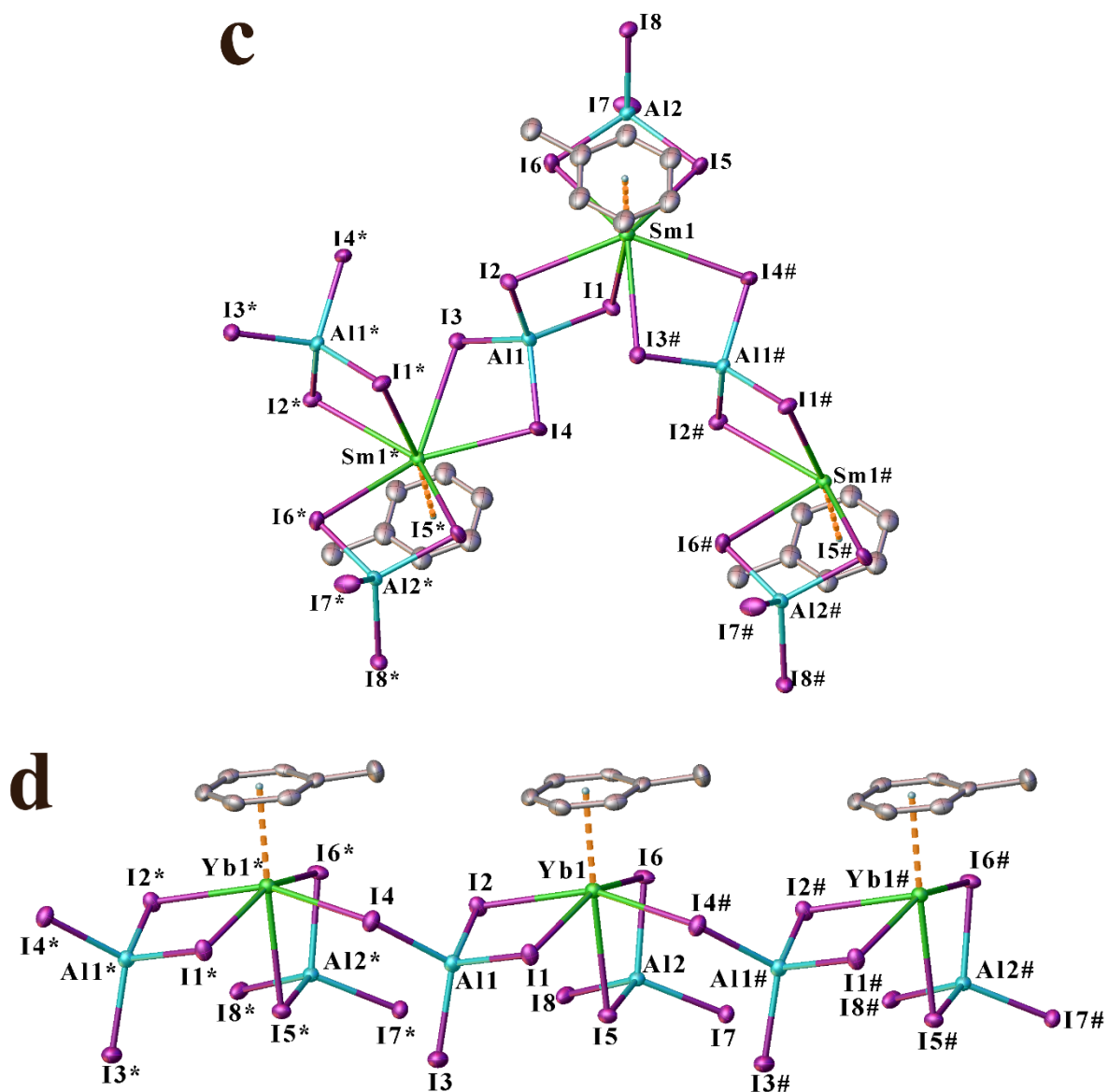
six electron donor occupying three coordination sites) in an axial position and three chelating  $\text{AlI}_4^-$  anions (through I1I2, I3#I4# and I5I6), of which the first two bridge to adjacent  $\text{Ln}^{2+}/\text{Sr}^{2+}$  ions through I3,I4 and I1#,I2# (Fig. 1c). The stereochemistry of the  $\text{Ln}^{2+}/\text{Sr}^{2+}$  ions can be described as distorted pentagonal bipyramidal if the centroid of the toluene ligand is considered the point of attachment. **3** and **4** have eight-coordinate  $\text{Yb}^{2+}/\text{Ca}^{2+}$  ions and are coordinated by two  $\text{AlI}_4^-$  anions (I1I2, I5I6), the former bridging to an adjacent  $\text{Yb}^{2+}/\text{Ca}^{2+}$  through I4, one bridging iodide (I4#) of a further  $\text{AlI}_4^-$  bridged through I1#,I2# to an adjacent  $\text{Yb}^{2+}/\text{Ca}^{2+}$ , and an  $\eta^6$ -toluene molecule (Fig. 1d). The stereochemistry is distorted octahedral, if toluene is considered attached by the centroid. The Sm-C bond lengths and the Sm-centroid distance (Table 1) are comparable with those of the samarium complex  $[\text{Sm}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_3)_2]_n$ , for which the Sm-C bond lengths and the Sm-centroid distances are 2.970(6)-3.063(6) Å and 2.655 Å, respectively [7b]. The Eu-C bond lengths and Eu-centroid distance (Table 1) are similar to values for the Sm complex, and they are longer than the average Eu-C value of  $[\text{Eu}(\eta^6\text{-C}_6\text{Me}_6)(\text{AlCl}_4)_2]_4 \cdot (\text{C}_6\text{H}_2\text{Me}_4)$  [2.999(23) Å and 2.676 Å] [14a]. **2** is the first polymeric ( $\pi$ -arene)tetrahalogenidoaluminatoeuropium(II) complex, the previous  $\text{Eu}^{\text{II}}$  tetrachloroaluminate being a cyclic tetramer [14a]. The average Sr-C and Sr-centroid distances in **5** (Table 1) are somewhat longer than corresponding Sm-C and Eu-C values of **1** and **2**, despite similar ionic radii [18], and indicative of weaker  $\pi$ -acceptor character. The difference between Yb-C values of **3** and those of **1** and **2** (ca. 0.1 Å, Table 1) is less than expected (0.16 Å) for the change in Ln element and coordination number [18], suggesting considerable crowding in **3**.

Growing the structure of **4** from the one and half molecules in the asymmetric unit gives two layers of a one dimensional eight coordinate polymer with a similar structure to **3**, interspersed by a layer of seven coordinate monomers with the composition  $[\text{Ca}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]$ . The structure of  $[\text{Ca}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]$  monomeric units is shown in Fig. 2a with calcium coordinated by toluene, and two chelating  $\text{AlI}_4^-$  ions, and the packing of the polymer layers and the monomer layer is shown in Fig. 2b. Other views of the packing are shown in Fig S1. If the centroid of the arene is considered a single coordination site, the stereochemistry of Ca is distorted octahedral in the polymer chain and distorted square pyramidal in the monomer units. To the best of our knowledge, **4** is the first ( $\pi$ -arene)tetrahalogenidoaluminatocalcium(II) structure, the polymeric layers being isostructural with the ytterbium complex **3**. The structure of

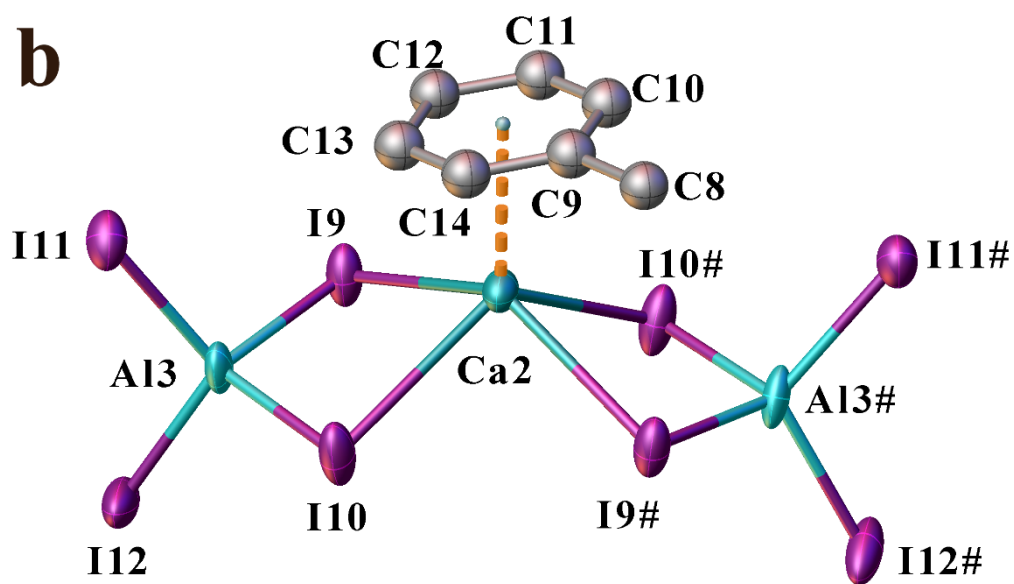
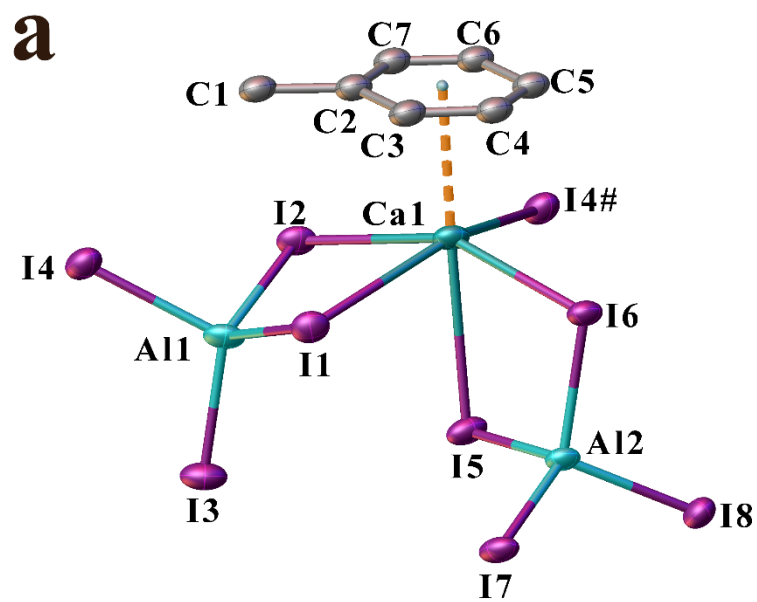
4 illustrates both the similarities of  $\text{Yb}^{2+}$  and  $\text{Ca}^{2+}$  coordination mainly due to their almost identical size (1.14 Å  $\text{Yb}^{2+}$  and 1.12 Å for  $\text{Ca}^{2+}$ ) [18], but also the differences that can occur [21]. The crystallographic data for complex 4 were not optimal leading to refinement issues and therefore the structure is reported for connectivity only, and bond length data are not provided in Table 1 and Table 2.

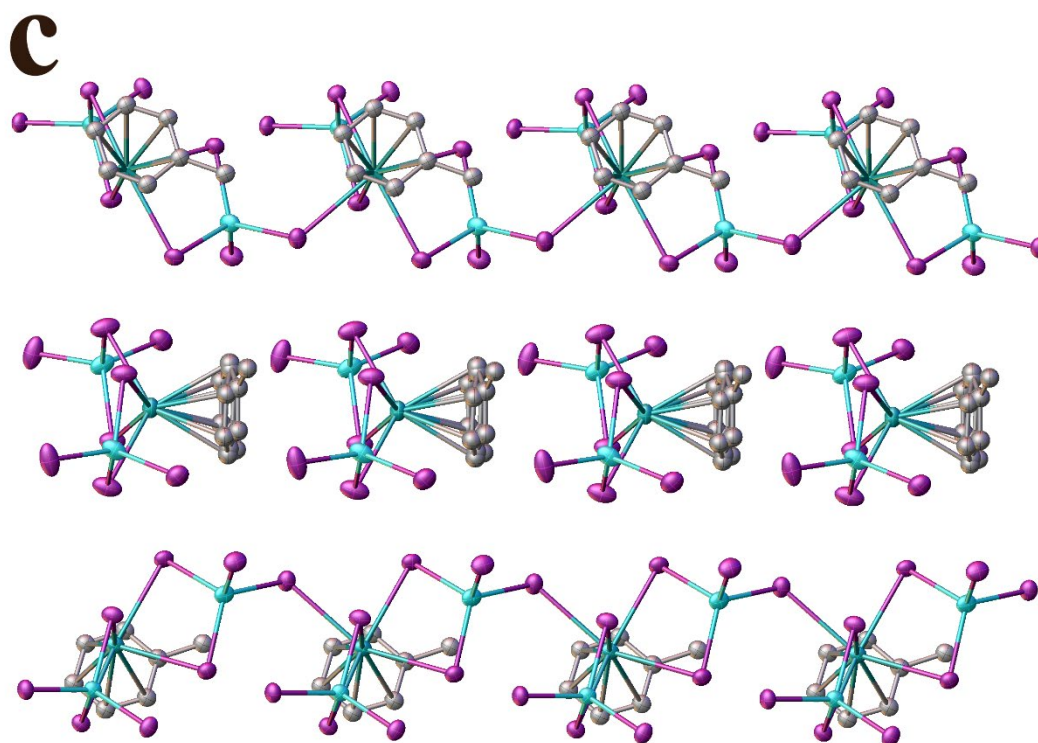






**Fig 1.** (a) A monomeric repeat unit of  $\{[\text{Sm}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]\}_n$  (representative of Sm, 1, Eu, 2, Sr, 5); (b) A monomeric repeat unit of  $\{[\text{Yb}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]\}_n$  3; (c) The connectivity of the 1-dimensional extended framework of  $\{[\text{Sm}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]\}_n$  (representative of Sm, 1, Eu, 2, Sr, 5); (d) The connectivity of the 1-dimensional extended framework of  $\{[\text{Yb}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]\}_n$  3. All the diagrams represented by 50% thermal ellipsoids. The lattice toluene molecules and hydrogen atoms have been omitted for clarity.





**Fig 2.** (a) A monomeric repeat unit of the polymeric layer of  $[\text{Ca}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{All}_4)_2]_n$  molecules of **4**; (b) A monomeric unit from the layer of discrete  $[\text{Ca}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{All}_4)_2]$  monomers; (c) The packing of the polymer layers (eight coordinate Ca) and the layer of discrete monomers of  $[\text{Ca}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{All}_4)_2]_n$  (seven coordinate Ca) of **4**. All the diagrams represented by 50% thermal ellipsoids. The lattice toluene molecules and hydrogen atoms have been omitted for clarity.

**Table 1** The bond distances of M-C(arene) and M-Centroid(arene) Å

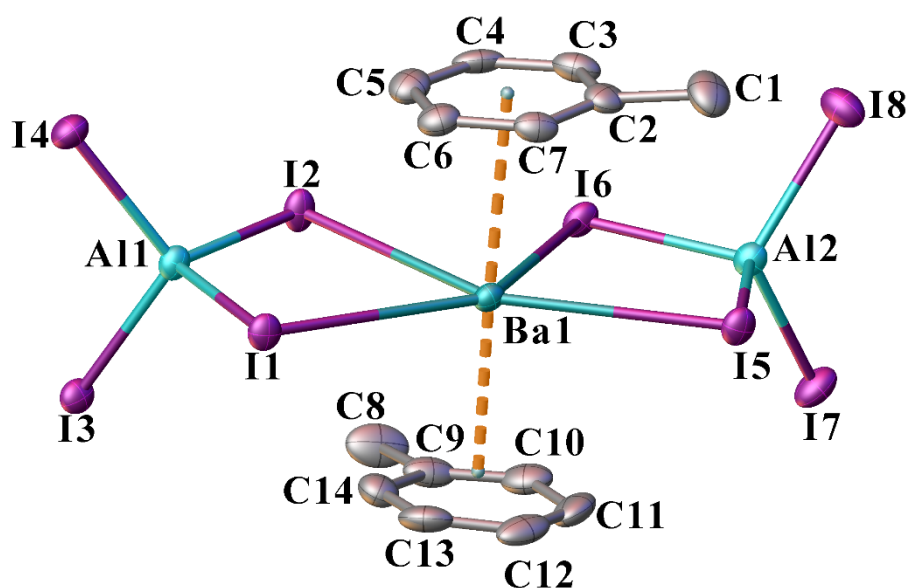
Complex	M1-C	M1-C <sub>avg</sub>	M1-C <sub>centroid</sub>
$\{[\text{Sm}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{All}_4)_2] \cdot \text{PhMe}\}_n$ <b>1</b>	2.971(14)-3.081(13)	3.027	2.688
$\{[\text{Eu}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{All}_4)_2] \cdot \text{PhMe}\}_n$ <b>2</b>	2.977(13)-3.079(11)	3.028	2.691
$\{[\text{Yb}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{All}_4)_2] \cdot 1/2\text{PhMe}\}_n$ <b>3</b>	2.900(9)-2.968(9)	2.923	2.570
$\{[\text{Sr}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{All}_4)_2] \cdot \text{PhMe}\}_n$ <b>5</b>	3.003(11)-3.138(9)	3.057	2.725
$[\text{Ba}(\eta^4\text{-C}_6\text{H}_5\text{Me})(\eta^3\text{-C}_6\text{H}_5\text{Me})(\text{All}_4)_2]_n$ <b>6</b>	3.232(9)-3.440(8)	3.386	3.088
$[\text{Ca}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{All}_4)_2]_n$ <b>7</b>	2.882(8)-2.956(7)	2.926	2.575

$\{[\text{Sr}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{AlI}_4)_2 \cdot 1/2(\text{PhMe}_3)]_n\}$ <b>8</b>	3.055(8)-3.165(8)	3.102	2.771
$\{[\text{Eu}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlBr}_4)_2 \cdot 1/2\text{PhMe}]_n\}$ <b>9</b>	3.004(4)-3.097(4)	3.037	2.696

**Table 2: M-X (I or Br) bond lengths (Å)**

X = I/Br	Sm 1	Eu 2	Yb 3	Sr 5	Ba 6	Ca 7	Sr 8	Eu 9
M1-X1	3.4060(15)	3.3851(13)	3.2319(12)	3.4080(11)	3.5578(9)	3.1908(11)	3.4952(12)	3.1436(9)
M1-X2	3.4113(16)	3.4230(14)	3.2224(9)	3.4266(12)	3.5894(10)	—	3.4062(12)	3.1701(7)
M1-X5	3.3583(16)	3.4082(14)	3.2910(9)	3.4601(11)	3.5206(9)	—	3.4243(16)	3.1927(7)
M1-X6	3.4359(15)	3.3681(14)	3.1440(9)	3.3650(11)	3.5069(9)	—	3.5947(11)	3.1661(13)
M1-X3/7#	3.6018(16)	3.6065(15)	—	3.6375(13)	—	—	3.4238(10)	3.1392(7)
M1-X4/8#	3.4656(16)	3.4594(15)	3.2830(9)	3.4929(12)	—	3.4252(14)	3.4161(11)	3.1477(7)
M-X (average)	3.4465	3.4417	3.2345	3.4149	3.5437	3.3080	3.4601	3.1599

Among all the divalent  $\pi$ -arene structures, only  $[\text{Ba}(\eta^6\text{-C}_6\text{H}_5\text{Me})_2(\text{AlI}_4)_2]$  **6** (Fig. 3) is a monomer, and it contrasts “ $(\text{Ba}[\text{GaCl}_4]_2)_3 \cdot 2\text{C}_6\text{H}_6$ ” [20], the only other barium  $\pi$ -arene sandwich structure which is oligomeric. **6** crystallizes in the monoclinic space group  $P2_1/c$ . Barium is bound by two chelating  $\text{AlI}_4^-$  ions and two toluene molecules and is ten coordinate if the arene rings are considered  $\eta^6$ -bound. Although the Ba-C contacts cover a 0.31 Å range in contrast to 0.03 Å for the  $\text{GaCl}_4$  species [20], a division into below and above 3.35 Å, thereby viewing the bonding of each ring as  $\eta^3$ , seems artificial with only a separation of 0.07 Å between closest bonded and non-bonded atoms. Moreover, the rings are co-linear with a near linear centroid-Ba-centroid angle (Table 3), consistent with  $\eta^6$ -toluene ligands. If the ring centroids are viewed as single points of attachment, **6** is the first reported distorted octahedral arene sandwich complex of barium. The average Ba-C bond length (Table 1) and Ba-centroid distance (Table 3) are suitably longer (considering ionic radii) [18] than those of **4** and **5**.



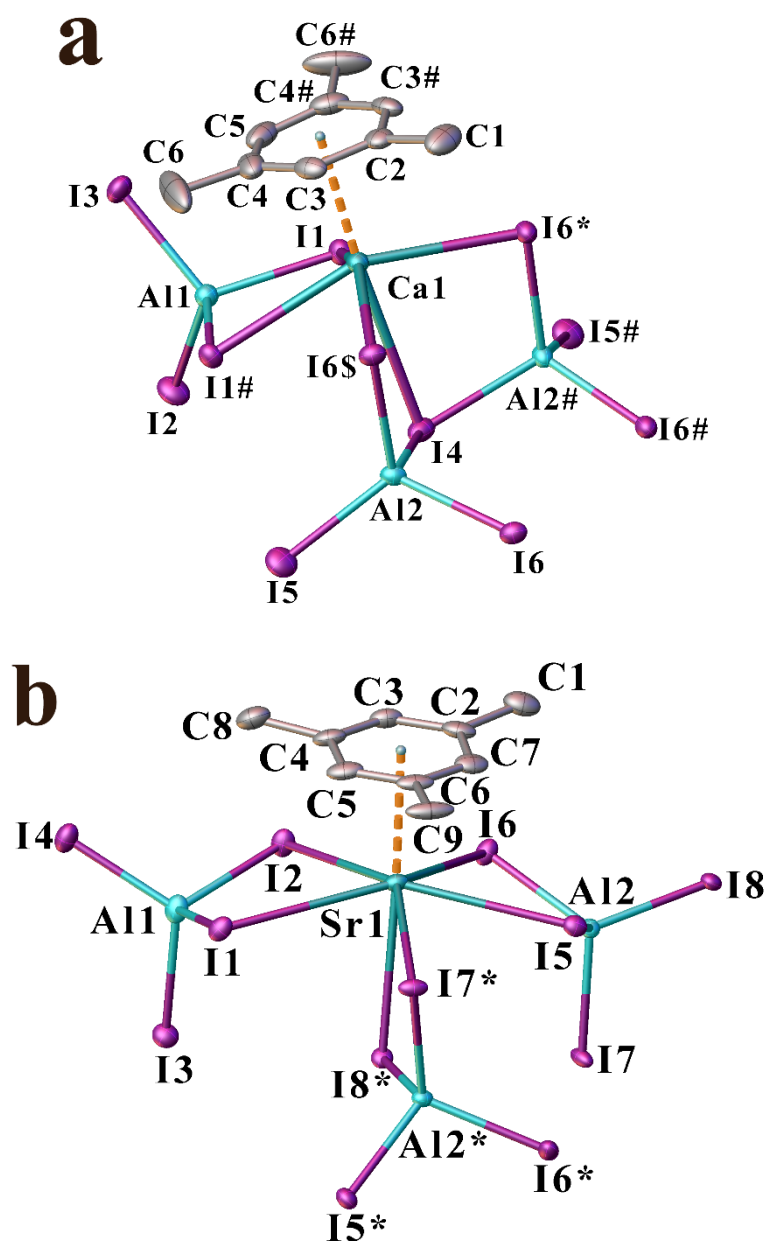
**Fig 3.** Molecular diagram of  $[\text{Ba}(\eta^6\text{-C}_6\text{H}_5\text{Me})_2(\text{AlI}_4)_2]$  represented by 50% thermal ellipsoids. The hydrogen atoms have been omitted for clarity.

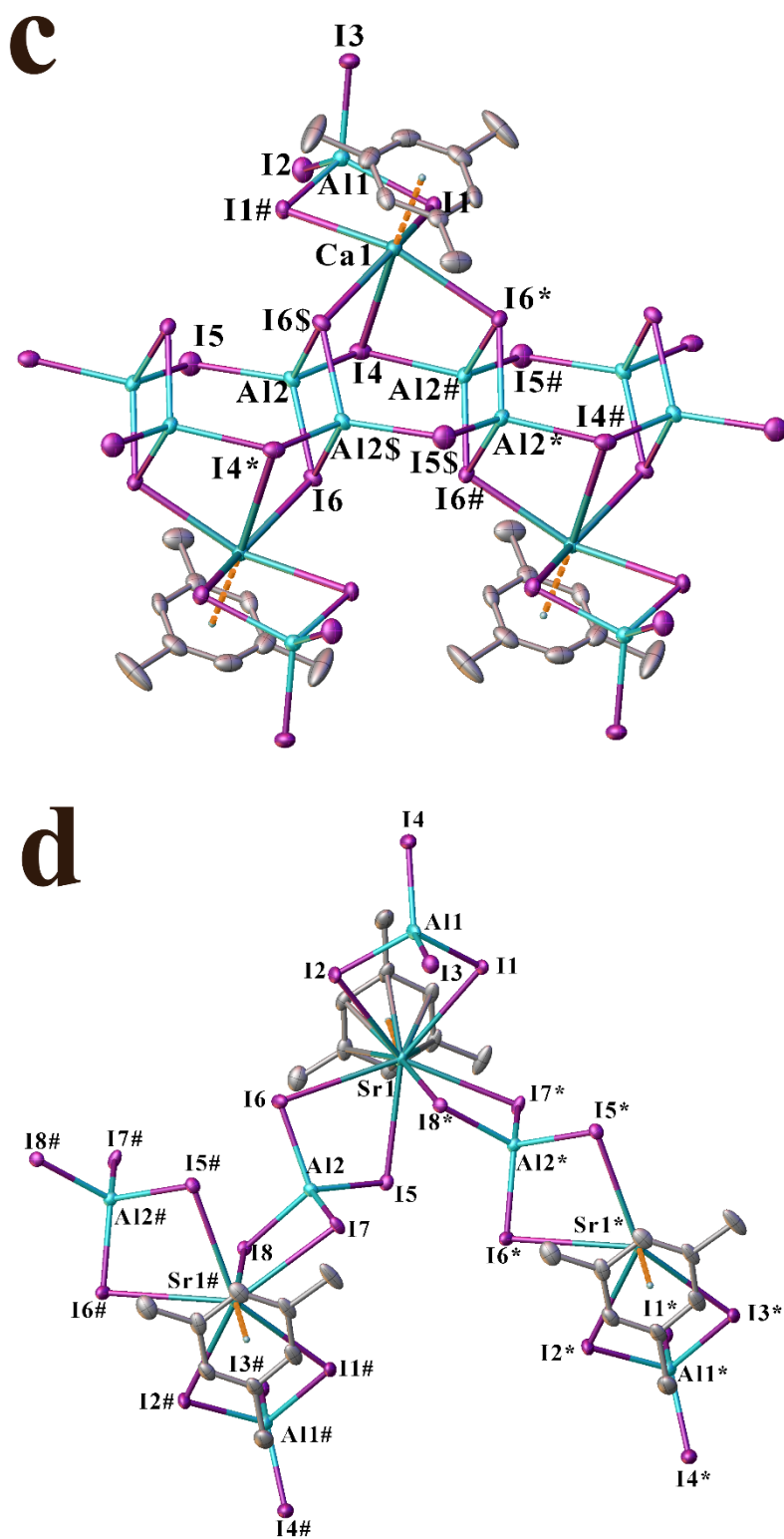
**Table 3** The Ba-C bond distances of  $[\text{Ba}(\eta^4\text{-C}_6\text{H}_5\text{Me})(\eta^3\text{-C}_6\text{H}_5\text{Me})(\text{AlI}_4)_2]_n$  **6**

Ba-C	Bond length (Å)	Ba-C	Bond length (Å)
Ba-C2	3.547(8)	Ba-C9	3.508(8)
Ba-C3	3.453(9)	Ba-C10	3.503(9)
Ba-C4	3.314(8)	Ba-C11	3.421(9)
Ba-C5	3.264(9)	Ba-C12	3.295(9)
Ba-C6	3.315(8)	Ba-C13	3.232(9)
Ba-C7	3.440(8)	Ba-C14	3.342(9)
Ba- centroid (C2-C7)	3.089	Ba-centroid (C9-C14)	2.647
centroid (C2-C7)-Ba centroid -(C9-C14): 178.20°			

The complex  $[\text{Ca}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{AlI}_4)_2]_n$  **7** (Fig. 4a) crystallises in the orthorhombic space group  $Pnma$ . Complex **7** has a polymeric structure in which the eight-coordinate  $\text{Ca}^{2+}$  ion is coordinated by five iodide donors from three  $\text{AlI}_4^-$  anions (I11I1#, I4, I6\$, I6\*) with an  $\eta^6$ -toluene molecule in an axial position (Fig. 3a). Al2 is disordered, and each of Al2 and Al2# has an occupancy of 0.5. Of the five iodide donors, two chelate to Ca, and one is single bridging iodide. Apart from the disorder, the coordination environment is similar to that of the polymeric chain of **4**. The complex  $\{[\text{Sr}(\eta^6\text{-$

$C_6H_3Me_3(AlI_4)_2\}_n$  **8** (Fig. 4b) crystallises in the monoclinic space group  $C2/c$ , has nine-coordinate  $Sr^{2+}$  and is isostructural with **5** despite having the bulkier mesitylene donor in place of toluene. Owing to the difference in steric and donor ability (which have opposing effects) between toluene and mesitylene, the average Sr-C and Sr-centroid distances in **8** (3.102 and 2.771 Å, respectively) are slightly longer than those of **5** (3.028 and 2.691 Å, respectively).





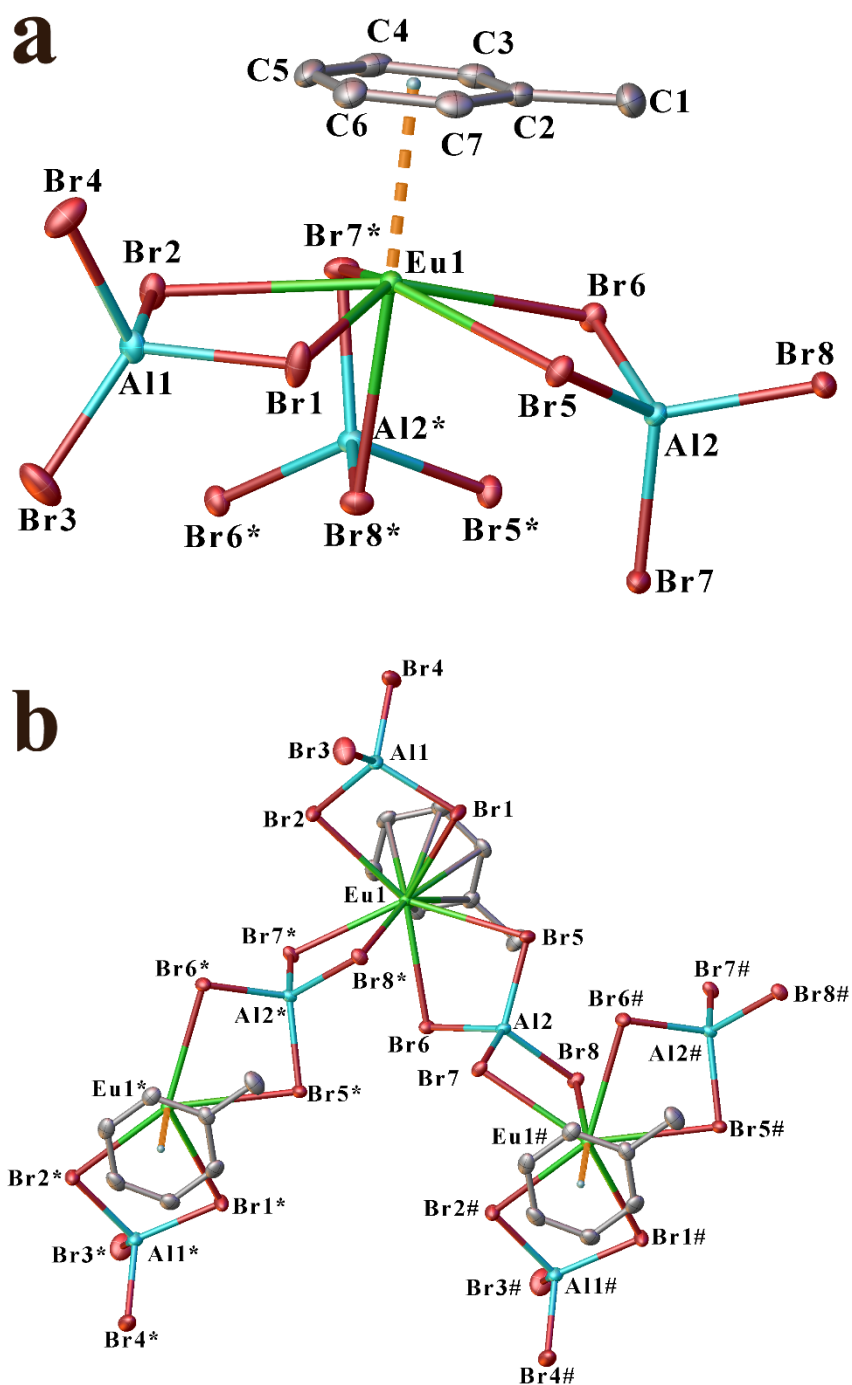
**Fig 4.** (a) A monomeric repeat unit of  $\{[\text{Ca}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{AlI}_4)_2]\}_n$  **7**; (b) A monomeric repeat unit of  $\{[\text{Sr}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{AlI}_4)_2]\}_n$  **8**; (c) The connectivity of the 1-dimensional extended framework of  $\{[\text{Ca}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{AlI}_4)_2]\}_n$  **7**; (d) The connectivity of the 1-dimensional extended framework of  $\{[\text{Sr}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\text{AlI}_4)_2]\}_n$  **8** represented by 50%

thermal ellipsoids. The lattice toluene molecules and hydrogen atoms have been omitted for clarity.

The M-I bond lengths (Table 2) show some degree of variation (0.15-0.3 Å) except for **6** (0.09 Å) which has less M-I bonds. Otherwise, the smallest variation is associated with the small Yb<sup>2+</sup> ion. It is not possible to correlate the changes with structural features, as for example, the longest bonds include both terminal and bridging AlI<sub>4</sub><sup>-</sup> ligands, but all involve Al-I-M bonds. The decrease in <Ln-I> from Ln = Sm, Eu to Ln = Yb (0.21 Å) is greater than expected from ionic radii differences [18] offsetting the opposite relationship with Ln-C bond lengths (above). From Ca to Sr the change is either as expected or somewhat less. From Sr to Ba, the change is much less than expected from ionic radii changes, but this is associated with a major structural change, which evidently increases crowding.

The tetrabromidoaluminate complex {[Eu(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>Me)(AlBr<sub>4</sub>)<sub>2</sub>]<sub>n</sub>·0.5nPhMe} **9** crystallizes in the monoclinic C2/c space group with one toluene and three [AlBr<sub>4</sub>]<sup>-</sup> (Br1Br2, Br5Br6, Br7\*Br8\*) ligands (**Fig. 5**), one AlBr<sub>4</sub><sup>-</sup> is chelating and the other two are chelating and bridging. Compound **9** is isomorphous with the reported [Sm(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>Me)(AlCl<sub>3</sub>l)<sub>2</sub>]<sub>n</sub> (structure actually solved as [Sm(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>Me)(Al<sub>2</sub>Cl<sub>7.3</sub>l<sub>0.7</sub>)] [7b]) from a comparison of unit cell data. The stereochemistry of the Eu<sup>2+</sup> ion is close to pentagonal bipyramidal. The average Eu-C bond distances and the Eu-centroid values of are similar to those of **2** [Eu-C: **2** 3.028 Å, **9** 3.037 Å; Eu-C<sub>(centroid)</sub> **2** 2.691 Å, **9** 2.696 Å], but the average Eu-Br bond length (3.160 Å) is significantly shorter than <Eu-I> **2** (3.442 Å), consistent with the differing ionic radii of the halides [18]. It is also of interest that the Eu-Br bond lengths show very much less variation than the Eu-I bond lengths of **2** or indeed of any of the iodidoaluminate complexes (Table 2), suggesting that bromide ions are perhaps the most comfortable steric fit.





**Fig 5.** (a) A monomeric repeat unit of  $\{[\text{Eu}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlBr}_4)_2]\}_n$ ; (b) The connectivity of the 1-dimensional extended framework of  $\{[\text{Eu}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{AlBr}_4)_2]\}_n$  represented by 50% thermal ellipsoids. The lattice toluene molecules and hydrogen atoms have been omitted for clarity.

## Conclusions

Lanthanoid(II) and alkaline earth metal(II)  $\eta^6$ -arene tetrahalogenidoaluminate complexes **1-9** were synthesised by a convenient one pot procedure from lanthanoid/

alkaline earth(II) metals with a straightforward isolation procedure. The divalent iodidoaluminate complexes of lanthanoids **1-3** and alkaline earths **4-8**, and the bromidoaluminate europium complex **9** are the first structurally characterised compounds of this kind. The structures and bonding parameters for the lanthanoid complexes are comparable to the alkaline earth complexes of similar ionic radii, except in the case of **3** and **4**, where one component of the structure of **4** is similar to **3**, but another component is different. These complexes illustrate the structural diversity attainable within the iodidoaluminate complexes of divalent lanthanoids and alkaline earths.

## **Experimental**

### **General**

The lanthanoid and alkaline earths compounds described here are highly air and moisture sensitive, and were prepared and handled with vacuum-nitrogen line techniques and in a dry box in an atmosphere of purified nitrogen. Lanthanoid metals were from Santoku/Molycorp/Eutectix, and alkaline earths metals were from Sigma. Large chunks were filed in the drybox before use. All other chemicals were purchased from Sigma Aldrich. Toluene was pre-dried over sodium metal and distilled over sodium before being stored under an atmosphere of nitrogen. IR spectra were recorded as Nujol mulls between NaCl plates using either a Perkin Elmer 1600 Series FTIR instrument or a Perkin Elmer Spectrum RX I FTIR Spectrometer within the range 4000-600  $\text{cm}^{-1}$ . Microanalyses were determined by the Elemental Analysis Service, London Metropolitan University, and all the samples were sealed in tubes under nitrogen. Metal analyses were performed by complexometric titration using EDTA after digestion with dilute HCl, buffering with hexamine, and masking Al with a 5% aqueous solution of sulfosalicylic acid. Crystals were immersed in crystallography oil, and were measured on the MX1 beamline at the Australian Synchrotron. Crystal data and refinement details are given in Table S1.

### **Preparation of iodidoaluminate complexes in toluene**

A mixture of excess Al (0.162 g, 6.0 mmol) and  $\text{I}_2$  (1.90 g, 7.5 mmol) in a Schlenk flask charged with toluene (40 mL) was heated with stirring for 2 h at 100 °C. The solution turned to colourless from red indicating the consumption of all iodine. After cooling the solution to room temperature, stoichiometric amounts Ln/ alkaline earths metals filings

and ICH<sub>2</sub>CH<sub>2</sub>I were added to the solution under a nitrogen atmosphere in the glove box. The mixture was heated at 100 °C for 24 h, filtered and allowed to crystallize over 2 days at room temperature.

**{[Sm( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>Me)(AlI<sub>4</sub>)<sub>2</sub>]<sub>n</sub>·nPhMe} (1):** Sm filings (0.375 g, 2.5 mmol) and ICH<sub>2</sub>CH<sub>2</sub>I (0.704g, 2.5 mmol) were added to the aluminium iodide solution. Red crystals (0.85g, 24%). IR (Nujol,  $\nu$ /cm<sup>-1</sup>): 3023 (w), 2731 (m), 1569 (w), 1307 (m), 1234 (w), 1126 (w), 969 (w), 723 (w); anal. calc. for C<sub>14</sub>H<sub>16</sub>Al<sub>2</sub>I<sub>8</sub>Sm (%): C 11.98, H 1.15, Sm 10.71, found: C 3.91, H 1.71, Sm 10.34 (loss of one toluene of crystallization: C 4.11, H 0.61; Sm 11.46%).

**{[Eu( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>Me)(AlI<sub>4</sub>)<sub>2</sub>]<sub>n</sub>·nPhMe} (2):** Eu filings (0.379 g) and ICH<sub>2</sub>CH<sub>2</sub>I (0.704g, 2.5 mmol) were added to the aluminium iodide solution. Light yellow crystals (0.59g, 17%). IR (Nujol,  $\nu$ /cm<sup>-1</sup>): 2952(s), 2724(w), 2667(w), 1602 (w), 1299(w), 1261(w), 1154(w), 1029(w), 823(w), 769(w), 727(m); anal. calc. for C<sub>14</sub>H<sub>16</sub>Al<sub>2</sub>I<sub>8</sub>Eu (%): C 11.96, H 1.15, Eu 10.81, found: C 3.28, H 2.98, Eu 10.43 (loss of one toluene of solvation: C 4.11, H 0.61; Eu 11.57%).

**{[Yb( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>Me)(AlI<sub>4</sub>)<sub>2</sub>]<sub>n</sub>·0.5nPhMe} (3):** Yb filings (0.432 g, 2.5 mmol) and ICH<sub>2</sub>CH<sub>2</sub>I (0.704g, 2.5 mmol) were added to the aluminium iodide solution. Red crystals (0.77g, 22%). IR (Nujol,  $\nu$ /cm<sup>-1</sup>): 2921(s), 2726(w), 2670(w), 1587(m), 1302(w), 1258(w), 1169(w), 1078(w), 846(w), 770(w), 722 (m); anal. calc. for C<sub>10.5</sub>H<sub>12</sub>Al<sub>2</sub>I<sub>8</sub>Yb (%): C 9.13, H 0.88, Yb 12.54, found: C 4.09, H 1.74, Yb 12.08 (loss of 1/2 toluene of solvation: C 4.04, H 0.60; Yb 12.97%).

**[Ca( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>Me)(AlI<sub>4</sub>)<sub>2</sub>]<sub>n</sub> (4):** Ca pieces (0.1 g, 2.5 mmol) and ICH<sub>2</sub>CH<sub>2</sub>I (0.704g, 2.5 mmol) were added to the aluminium iodide solution. Light yellow crystals (1.46 g, 32%). IR (Nujol,  $\nu$ /cm<sup>-1</sup>): 2923(s), 2727(w), 2673(w), 1610(w), 1302(w), 1264(w), 1170(w), 1080(w), 831(w), 767(m), 722(m); anal. calc. for C<sub>7</sub>H<sub>8</sub>Al<sub>2</sub>CaI<sub>8</sub> (%): C 6.99, H 0.67, Ca 3.33, found: C 7.15, H 0.70, Ca 3.29.

**{[Sr( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>Me)(AlI<sub>4</sub>)<sub>2</sub>]<sub>n</sub>·nPhMe} (5):** Sr pieces (0.219 g, 2.5 mmol) and ICH<sub>2</sub>CH<sub>2</sub>I (0.704g, 2.5 mmol) were added to the aluminium iodide solution. Light yellow crystals (0.92 g, 27%). IR (Nujol,  $\nu$ /cm<sup>-1</sup>): 2926(s), 2727(w), 2667(w), 1605 (w), 1302(w), 1261(w), 1153(w), 1081(m), 799(m), 769(m), 727(s); anal. calc. for C<sub>14</sub>H<sub>16</sub>Al<sub>2</sub>I<sub>8</sub>Sr (%): C 12.54, H 1.20, Sr 6.53, found: C 11.59, H 1.31, Sr 6.48.

**[Ba( $\eta^4$ -C<sub>6</sub>H<sub>5</sub>Me)<sub>2</sub>(AlI<sub>4</sub>)<sub>2</sub>] (6)**: Ba pieces (0.343 g, 2.5 mmol) and ICH<sub>2</sub>CH<sub>2</sub>I (0.704g, 2.5 mmol) were added to the the aluminium iodide solution. Light yellow crystals (0.79 g, 23%). IR (Nujol,  $\nu$ /cm<sup>-1</sup>): 2923 (s), 2720(w), 2670(w), 1592(w), 1302(w), 1261(w), 1166(w), 1081(w), 1026(w), 840(w), 755(w), 723(m); anal. calc. for C<sub>14</sub>H<sub>16</sub>Al<sub>2</sub>BaI<sub>8</sub> (%): C 12.09, H 1.16, Ba 9.87, found: C 11.91, H 1.22, Ba 9.79.

### **Preparation of iodidoaluminate complexes in mesitylene**

A mixture of excess Al (0.162 g, 6.0 mmol) and I<sub>2</sub> (1.90 g, 7.5 mmol) in a Schlenk flask charged with 40 mL of mesitylene was heated with stirring in oil bath for 2 h at 100°C. The solution turned to colourless from red indicating the consumption of all iodine. After cooling the solution to room temperature, stoichiometric amounts of alkaline earths metals filings and ICH<sub>2</sub>CH<sub>2</sub>I (0.704 g, 2.5 mmol) were added to the solution under a nitrogen atmosphere in the glove box. The mixture was heated overnight at 100°C giving a colourless solution, which was filtered and allowed to crystallize at room temperature generally for two days.

**[Ca( $\eta^6$ -C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>)(AlI<sub>4</sub>)<sub>2</sub>]<sub>n</sub> (7)**: Ca pieces (0.1 g, 2.5 mmol) and ICH<sub>2</sub>CH<sub>2</sub>I (0.704g, 2.5 mmol) were added to the aluminium iodide solution. Light yellow crystals (1.28 g, 42%). IR (Nujol,  $\nu$ /cm<sup>-1</sup>): 2925(s), 2724(w), 2670(w), 1593(w), 1305(w), 1261 (w), 1166(w), 1093(w), 1034(w), 867(w), 800(w), 722 (w); anal. calc. for C<sub>9</sub>H<sub>12</sub>Al<sub>2</sub>CaI<sub>8</sub> (%) C 8.79, H 0.98 Ca 3.26; found C 5.45, H 3.31. Ca 3.31, (Loss of 40% of mesitylene C 5.49, H, 0.61' Ca 3.39%).

**{[Sr( $\eta^6$ -C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>)(AlI<sub>4</sub>)<sub>2</sub>]<sub>n</sub>·0.5n(PhMe<sub>3</sub>)} (8)**: Sr pieces (0.219 g, 2.5 mmol) and ICH<sub>2</sub>CH<sub>2</sub>I (0.704g, 2.5 mmol) were added to the aluminium iodide solution. Light yellow crystals (0.79 g, 23%). IR (Nujol,  $\nu$ /cm<sup>-1</sup>): 2924(s), 2730(w), 2670(w), 1592(w), 1302(w), 1261(w), 1163(w), 1093(w), 1030(w), 861(s), 834(s), 806(w), 723(w); anal. calc. for C<sub>13.5</sub>H<sub>18</sub>Al<sub>2</sub>I<sub>8</sub>Sr; (%) C 12.13, H 1.36; Sr 6.55, found C 11.78, H 1.73. Sr 6.82.

**{[Eu( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>Me)(AlBr<sub>4</sub>)<sub>2</sub>]<sub>n</sub>·0.5nPhMe} (9)**: A mixture of AlBr<sub>3</sub> (1.6 g, 6.0 mmol), Eu filings (0.304 g, 2.0 mmol) and BrCH<sub>2</sub>CH<sub>2</sub>Br (0.6 g, 6 mmol) was taken in a Schlenk flask charged with 40 mL toluene. The mixture was heated overnight at 100 °C giving a dark cloudy solution, which was filtered to remove the unreacted solid. The solution was kept at room temperature for crystallisation and dark red crystals covered with muddy solution were obtained next day. Crystals suitable for X-ray study were

separated and identified by X-ray crystallography. No pure material could be isolated for elemental analysis.

#### Appendix A. Supplementary data

CCDC 2142752 contains the supplementary crystallographic data for compound **1**, 2142753 contains the supplementary crystallographic data for compound **2**, 2142754 contains the supplementary crystallographic data for compound **3**, 2142755 contains the supplementary crystallographic data for compound **4**, 2142756 contains the supplementary crystallographic data for compound **5**, 2142757 contains the supplementary crystallographic data for compound **6**, 2142758 contains the supplementary crystallographic data for compound **7**, 2142759 contains the supplementary crystallographic data for compound **8**, 2142760 contains the supplementary crystallographic data for compound **9**. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

#### **Acknowledgements**

This research was supported by Australian Research Council (DP190100798), Part of the research were undertaken on the MX1 beamline at the Australian Synchrotron, part of ANSTO [22]. MEH is grateful for the award of an International Postgraduate Research Scholarship.

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