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Dichlorido(crown ether)lanthanoid(III) tetrachloroaluminate complexes☆

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ABSTRACT

Reactions between $LnCl_3$, $AlCl_3$ and a crown ether (18-crown-6 and dibenzo18-crown-6) in MeCN have led to the isolation of four new lanthanoid halide crown ether complexes, $[PrCl(\mu\text{-}Cl)(18\text{-crown-}6)]_2[AlCl_4]_2\cdot 2MeCN$ (**1**), $[YbCl_2(18\text{-crown-}6)][AlCl_4]\cdot MeCN$ (**2**), and $[LnCl(\mu\text{-}Cl)(dibenzo18\text{-crown-}6)\}_2][AlCl_4]_2\cdot 6.5MeCN$ (Ln = La, **3**, Pr, **4**). **1** was also obtained by unexpected halide transfer on addition of 18-crown-6 (18C6) to MeCN solutions of $[Pr(MeCN)_9][AlCl_4]_3$. Complexes **1**, **3** and **4** have dinuclear chloride-bridged nine-coordinate cations, and **2** has an eight coordinate mononuclear cation.

1. Introduction

The coordination chemistry of lanthanoids with crown ethers has received a large amount of attention since their discovery in the 1960s [1–3]. The lanthanoids are well suited for crown ether coordination chemistry due to the lanthanoid/crown ether size ratio. The radius of the cavity in 18-crown-6 (18C6) (1.34 – 1.43 Å) [4] is large enough to comfortably accommodate Ln^{3+} ions (ionic radii CN = 8; 1.160 Å (La) – 0.977 Å (Lu)) [5]. The lanthanoid/crown ether size ratio, combined with the oxophilic nature of the metal ions, makes them excellent candidates for host/guest systems provided by crown ethers [6].

Structurally, two classes are observed for trivalent lanthanoid complexes incorporating crown ligands. Firstly, there are *out of cavity* complexes, whereby the cavity size is too small to accommodate the Ln^{3+} ion but still interacts with it [7]. These types are exemplified by the smaller crown ethers *viz.* 15C5 and 12C4, which are not used in this study. The other distinct class is the *in cavity* complexes, whereby the cavity allows for encapsulation of the metal. These are observed with the larger cavity sizes of 18-crown-6 (18C6) and dibenzo-18-crown-6 (DB18C6) [3,7–16]. There are also several complexes exhibiting second sphere coordination, in that the crown ether forms hydrogen bonds with the water molecules that are coordinated to the lanthanoid [9,17].

The lanthanoid nitrate 18C6 systems exhibit several structural motifs with the change from La – Lu. There appears to be a progression from the *in cavity* monomer $[Ln(NO_3)_3(18C6)]$ [9,10,18] to the ionic $[Ln(NO_3)_2(18C6)]_3[Ln(NO_3)_6]$ [1d, 11], and then to the hydrogen bonded $[Ln(NO_3)_3(H_2O)_3]\cdot 18C6$ complexes [9,17–18] with some lanthanoids appearing in more than one class. The mixed chloride/nitrate monomeric complex $[LaCl_2(NO_3)(18C6)]$ was also reported with the ten coordinate La^{3+}cation perfectly residing in the cavity without much deformation of the crown [8]. Meanwhile, a number of $[Ln(NO_3)(X_4Cat)(18C6)]$ (X = Cl or Br) complexes were obtained by lanthanoid nitrates with 18C6 and tetrahalogenocatecholate (X_4Cat^{2-}) [19].

With lanthanoid chloride 18C6 complexes isolated from protic solvents, water molecules progressively replace the chlorides of the inner coordination sphere as the Ln^{3+} ionic radii decreases [8]. This results in lanthanoid chloride 18C6 complexes with differing numbers of aqua ligands *viz.* $[LaCl_3(18C6)]$ [3], $[LnCl_2(H_2O)(18C6)][Cl]$ (Ln = La, Ce) [1e, 3, 12] and $[LnCl(H_2O)_2(18C6)][Cl]_2$ (Ln = Nd, Pr, Sm, Eu, Gd, Tb) [3,12–14]. Willey has reported the complex $[ScCl_2(18C6)][SbCl_6]$ (CN = 7 with one *unbound* crown ether oxygen atom), showing that it is possible to form mononuclear rare earth chlorido 18C6 cations [15]. A similar complex, namely $[ScCl_2(18C6)][FeCl_4]$ was also reported [20]. By using ^{45}Sc NMR spectroscopy, it was shown that adding greater than four equivalents of $FeCl_3$ per molecule of $ScCl_3$, a resonance attributable to a Sc^{3+} cation with no bound chloride atoms *viz.* $[Sc(MeCN)_n(18C6)]^{3+}$ [20] was detected. With the bulkier DB18C6 ligand the complex $[\{DyCl(\mu\text{-}Cl)(DB18C6)\}_2][\{Dy\text{-}Cl_3(\mu\text{-}Cl)(MeCN)\}_2]$ has a cation with two Y-shaped 'triangles' formed by the Cl^- atoms, sharing a common edge [7,16]. Similar dinuclear cations have also been observed in $[\{La(\mu\text{-}OH)I(DB18C6)\}_2][I][I_3]$ [21] and $[\{Ce(\mu\text{-}OH)I(DB18C6)\}_2][I_2]\cdot(H_2O)_3$ [7]. Other examples of lanthanoid DB18C6 structures are $[SmI_3(DB18C6)]$ [22] and $[PrCl_2(DB18C6)(H_2O)][SbCl_6]\cdot 0.5MeOH\cdot 0.5MeCN$ [23].

☆ We dedicate this paper to Professor Robert (Rab) Mulvey on the occasion of his 65th birthday and for his outstanding contributions to chemistry.

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We aimed to generate $[Ln(18C6)(solvent)_n]^{3+}$ systems by treatment of $LnCl_3$ with the Lewis acid $AlCl_3$ in the presence of 18C6 and DB18C6, utilising the halide abstraction pathway used to prepare $[Ln(MeCN)_n][AlCl_4]_3$ complexes [24]. Here we report the synthesis and characterisation of four new lanthanoid crown ether complexes highlighting incomplete halide transfer between the lanthanoids and aluminium, namely $[PrCl(\mu\text{–}Cl)(18C6)]_2[AlCl_4]_2\cdot 2MeCN$ (**1**), $[YbCl_2(18C6)][AlCl_4]\cdot MeCN$ (**2**), and $[LnCl(\mu\text{-}Cl)(DB18C6)]_2[AlCl_4]_2\cdot 6.5MeCN$ (Ln = La (**3**), Pr (**4**)).

2. Results and discussion

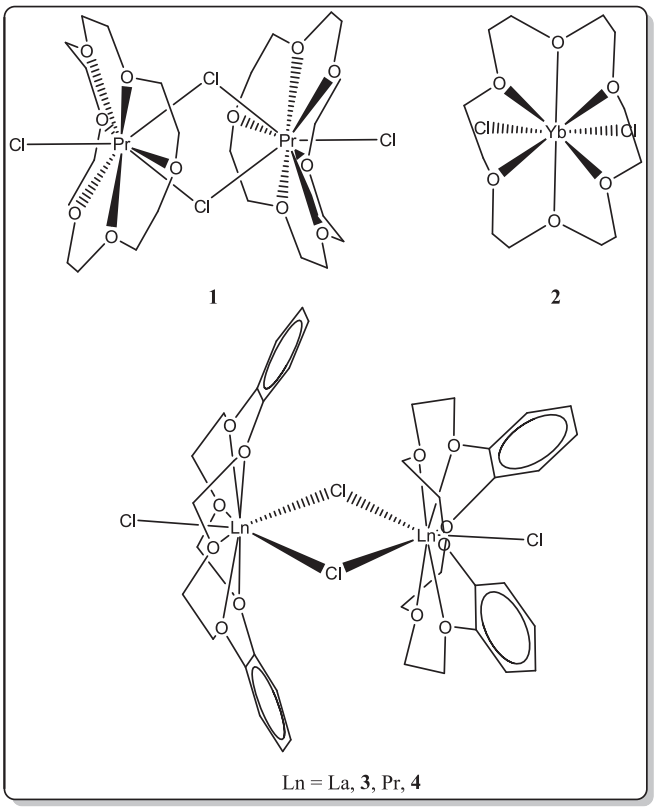
2.1. Synthesis and characterisation

Reactions of the complex $[Pr(MeCN)_9][AlCl_4]_3$ with 18-crown-6 (18C6) in MeCN resulted in reorganisation into $[PrCl(\mu\text{-}Cl)(18C6)]_2[AlCl_4]_2\cdot 2MeCN$ (**1**) (Scheme 1 eq.(**a**)). This rearrangement involves unexpected halide transfer from $[AlCl_4]^-$ to Pr upon addition of the crown ether. An identical product was obtained by the reaction of $PrCl_3$, $AlCl_3$ and 18C6 in MeCN (Scheme 1 eq.(**b**)). Utilisation of a smaller lanthanoid in a similar synthesis resulted in the isolation of $[YbCl_2(18C6)][AlCl_4]\cdot MeCN$ (**2**) (Scheme 1 eq.(**c**)). Incorporation of the bulkier dibenzo18-crown-6 (DB18C6) led to the isolation of complexes with dinuclear cations $[LnCl(\mu\text{-}Cl)(DB18C6)]_2[AlCl_4]_2\cdot 6.5MeCN$ where Ln = La (**3**), and Pr (**4**) (Scheme 1 eq.(**d**)). In carrying out the syntheses represented by eq. (b) to (d), sufficient $AlCl_3$ was added to abstract all Cl ligands from Ln, as in earlier syntheses of $[Ln(MeCN)_n][AlCl_4]_3$ (Ln = Pr, n = 9 or Yb, n = 8) complexes [24]. It is thus apparent that the relative Lewis acidities of Ln cations and $AlCl_3$ vary with co-ligands available. In the presence of crown ethers retention of chloride by lanthanoid cations is favoured. (See Scheme 2).

As satisfactory microanalyses could not be obtained for the moisture sensitive compounds, associated with both the cations and anions, bulk purity was established by lanthanoid metal analyses by complexometric methods with masking of Al. The IR spectra of complexes **1**–**4** are indicative of coordinated crown ether. The υ_{asym}(C—O—C) vibration is split into several bands as reported for metal complexation of crown ethers with various bands observed between 1139–1020 cm^{-1} [25]. Peaks are observed between 972 – 948 cm^{-1} for υ_{sym}(C—O—C) of the crown ether and are accompanied by a small frequency shift from the free ligand value (944 cm^{-1}) [25–26]. Bands attributable to the ring-breathing mode of the crown ethers are evident near 880 cm^{-1} [26]. Uncoordinated MeCN is also evident in complexes **1**, **2** and **4** with ν(CN) at 2291 and 2253–2251 cm^{-1} [27]. Vibrations attributable to MeCN in complex **3** occur at 2334 and 2305 cm^{-1} which is the region expected for coordinated MeCN. Since MeCN is present only as solvent of crystallization (see structure) the shift may be due to some weak interactions associated with the crystal packing.

In complexes **3** and **4,** several absorptions are evident for the aromatic group of the DB18C6 ligand. Two bands occurring at 1594 and 1505–1502 cm^{-1} in both complexes are indicative of C⋯C stretching modes of the aromatic group [28]. Additionally, there are several bands at 774, 754 and 750 cm^{-1} attributable to the C—H out of plane vibrations of the aromatic groups indicative of four adjacent H atoms [28]. In all complexes a vibration at 492 cm^{-1} is observed attributable to ν_{asym}(Al–Cl) of the non interacting $[AlCl_4]^-$ anions [29–30]. The ^{27}Al NMR spectra of complexes **1**–**4** show one resonance at 104 ppm similar to the $AlCl_4^-$ resonance observed for solutions of $AlCl_3$ in ethers (THF, diglyme and triglyme) [31]. The molar conductances of complexes **1**, **3** and **4** in MeCN correspond to values for a 1:2 electrolyte, whereas the value for complex **2** suggests a 1:1 electrolyte [32] as expected from the crystal structures (below).

Attempts to isolate complexes of the smaller Ln^{3+} (e.g. Yb^{3+}) with DB18C6 proved to be unsuccessful, and presumably the folding of 18-crown-6 into a taco shape when encapsulating the smaller Yb^{3+} becomes too strained when the benzo-groups are incorporated into the



Scheme 2. Products of **1-4**.

$$2\ \{[Pr(MeCN)_9][AlCl_4]_3\} + 2\ (18C6) \xrightarrow{MeCN} \{[PrCl(\mu\text{-}Cl)(18C6)]_2[AlCl_4]_2\}\cdot 2MeCN\ \mathbf{1} + 4\ AlCl_3(MeCN)_n \quad \textbf{(a)}$$

$$2\ PrCl_3 + 2\ AlCl_3 + 2\ (18C6) \xrightarrow{MeCN} [PrCl(\mu\text{-}Cl)(18C6)]_2[AlCl_4]_2\cdot 2MeCN\ \mathbf{1} \quad \textbf{(b)}$$

$$YbCl_3 + AlCl_3 + (18C6) \xrightarrow{MeCN} [YbCl_2(18C6)][AlCl_4]\cdot MeCN\ \mathbf{2} \quad \textbf{(c)}$$

$$2\ LnCl_3 + 2\ AlCl_3 + 2\ (DB18C6) \xrightarrow{MeCN} [LnCl(\mu\text{-}Cl)(DB18C6)]_2[AlCl_4]_2\cdot 6.5MeCN \quad \textbf{(d)}$$

Ln = La, **3**, Pr, **4**

Scheme 1. Syntheses of **1-4**.

crown ether. The isolation of complex **2** illustrates the amount of distortion required by the crown ether to accommodate the small Yb^{3+} ion. Whilst we have demonstrated the ability of 18C6 to encapsulate the Yb^{3+} ion, the distortion required for DB18C6 would bring the two phenylene groups into close proximity which may place additional strain on the distorted conformation of the crown ether.

2.2. X-ray structures

Crystals of $[PrCl(\mu\text{-}Cl)(18C6)_2]_2[AlCl_4]_2{\cdot}2MeCN$ (**1**) suitable for X-ray analysis were grown from an MeCN solution stored at −30 °C. Complex **1** crystallises in the monoclinic space group $P2_1/n$ with a structure consisting of a nine coordinate Pr^{3+} cation, which is bound to six oxygen atoms of the crown ether, two bridging chlorides and one terminal chloride (Fig. 1), and it dimerises through an inversion centre. The chloride ligands form a Y-shaped 'triangle' about the Pr^{3+} ions with the two bridging chlorides and one terminal forming the Y-shape about the metal centres as previously described by Meyer for $[DyCl(\mu\text{-}Cl)(DB18C6)]_2[DyCl_3(\mu\text{-}Cl)(MeCN)]_2$ [7]. Two tetrahedral $AlCl_4^-$ ions in the lattice provide charge balance. Overall the best fit polyhedron can be described as a distorted tricapped trigonal prism with the trigonal prism being capped by Cl(1), O(2) and O(5) [33].

There is a distinct change in bond lengths between the terminal (Pr – Cl_{ter} 2.714(2) Å) and bridging chlorides (Pr – Cl_{br} 2.839(2) and 2.858(2) Å) as would be expected with similar changes between terminal and bridging Pr – Cl distances identified in $[PrCl_2(\mu\text{-}Cl)(tetraethyleneglycol)]_2$ [34]. The Pr – Cl_{ter} distance is comparable to those observed in the eight coordinate $[PrCl(H_2O)_2(18C6)][Cl]_2{\cdot}H_2O$ [3] and $[PrCl_2(DB18C6)(H_2O)][SbCl_6]{\cdot}0.5MeOH{\cdot}0.5MeCN$ [23]. The average Pr-O_{crown} distance of 2.583 Å is comparable to the average observed for $[PrCl(H_2O)_2(18C6)][Cl]_2{\cdot}H_2O$.[3] The Pr – O_{crown} distances range from 2.572 (4) to 2.590(7) Å, following the same trends in the related cation $[\{DyCl(\mu\text{-}Cl)(DB18C6)\}_2]^{2+}$ [16], albeit with a lengthening of Ln – O in line with differences in ionic radius between Pr and Dy (ca. 0.096 Å) [5].

The crown ether adopts a saddle-like conformation with the metal residing almost in the centre of the cavity made by the O1, O3, O4, O6 plane (0.601 Å from the plane) and the O2, O5 vector (0.491 Å from the vector). The crown ether collapses to accommodate the Pr^{3+}, which is evident by the angle between plane 1 (O1, O2, O5, O6) and plane 2 (O2, O3, O4, O5) of 125.71° showing slight distortion to ensure that the oxygen atoms are all bound to the Pr^{3+} ion. Distortion (or closure) of crown ethers is observed for all trivalent lanthanoid 18C6 complexes as the D_{3d} crown conformation distorts in order to accommodate the metal cation [14]. This angle closes from 129.74° in $[LaCl_3(18C6)]$ [16], through to 68.95° in $[Lu(CH_2SiMe_3)_2(18C6)][B(CH_2SiMe_3)Ph_3]{\cdot}CH_2Cl_2$ [35] owing to the reduction in size of the ionic radius of the Ln centre (1.216–0.977 Å) [5].

Complex **2** crystallises in the monoclinic space group $P2_1/c$, with two $[YbCl_2(18C6)][AlCl_4]{\cdot}MeCN$ molecules in the asymmetric unit. The X-ray crystal structure of complex **2** comprises an eight coordinate Yb centre, which is bound to six oxygen atoms of the crown ether and two chloride atoms (Fig. 2). The coordination polyhedron surrounding the Yb centre is best described as a distorted dodecahedron with O(2), O(3), O(5), O(6) in the A sites with Cl(1), Cl(2), O(1), O(4) occupying the B sites [33,36]. The cation is charge balanced by tetrahedral $AlCl_4^-$ ions in the lattice and the remaining voids are filled by uncoordinated MeCN molecules.

The Yb-O_{crown} distances range from 2.383(8) to 2.417(8) Å, following the trend of the lanthanoid contraction and change in coordination number from complex **1** (*ca.* 0.182 Å difference) [5]. The Yb – O_{crown} distances are comparable to those in eight coordinate $[YbCl_2(-H_2O)_2(12C4)][Cl]$ [37]. The Yb–Cl distances range from 2.549(3) to 2.568(3) Å which are comparable to the shortest lengths observed in $[YbCl_2(H_2O)_2(12C4)][Cl]$ [37]. The crown ether collapses quite drastically in order to accommodate the small Yb^{3+} ion. This provides spectacular results with the distortion of the crown ether in complex **2** to coordinate the Yb^{3+} cation resulting in a closure of the crown ether to

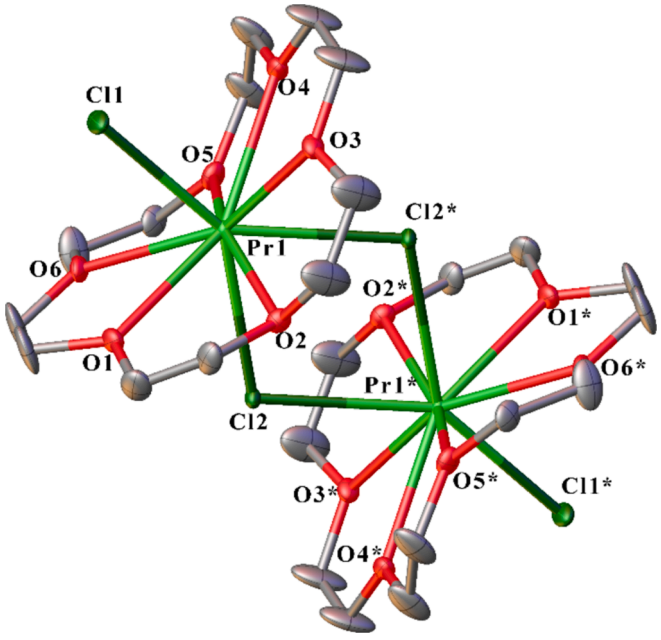


Fig. 1. The X-ray crystal structure of the cation in $[PrCl(\mu\text{-}Cl)(18C6)]_2[AlCl_4]_2{\cdot}2MeCN$ (**1**). Ellipsoids shown at 50% probability, hydrogen atoms were removed for clarity. Selected bond lengths (Å) and angles (°): Pr1-O1 2.576(3), Pr1-O2 2.578(3), Pr1-O3 2.575(4), Pr1-O4 2.588(4), Pr1-O5 2.589(4), Pr1-O6 2.592(4), Pr1-Cl1 2.714(2), Pr1-Cl2 2.839(2), Pr1-Cl2* 2.858(2), Cl1-Pr1-Cl2 144.30(4), Cl1-Pr1-Cl2* 143.18(4), Cl2-Pr1-Cl2* 72.52 (4). Symmetry code: *1-X,1-Y,1-Z.

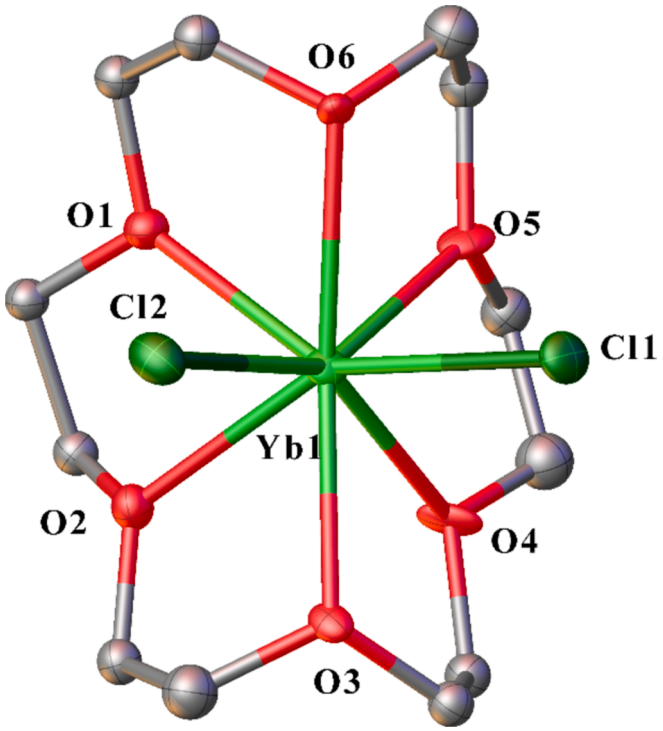


Fig. 2. The X-ray crystal structure of the cation in $[YbCl_2(18C6)][AlCl_4]{\cdot}MeCN$ (**2**). Ellipsoids shown at 50% probability, hydrogen atoms were removed for clarity. Selected bond lengths (Å) and angles (°): Yb1-O1 2.404(7), Yb1-O2 2.398(9), Yb1-O3 2.417(8), Yb1-O4 2.406(8), Yb1-O5 2.383(8), Yb1-O6 2.395(8), Yb1-Cl1 2.549(3), Yb1-Cl2 2.568(3), Cl1-Yb1-Cl2 95.47(10).

76.01°. The closure of the 18C6 is comparable to the angles observed in the reported complex $[Lu(CH_2SiMe_3)_2(18C6)][B(CH_2SiMe_3)Ph_3]\cdot CH_2Cl_2$ (68.95°) [35].

The isostructural complexes $[LnCl(\mu\text{-}Cl)(DB18C6)]_2[AlCl_4]_2\cdot 6.5MeCN$ where Ln = La (**3**), and Pr (**4**), crystallise in the *P*-1 space group from an MeCN solution at −30 °C. The overall structure of complexes **3** and **4** consist of a Ln^{3+} cation (where Ln = La, Pr) with three coordinated Cl atoms in the Y-shaped triangular geometry previously described [7]. The Ln^{3+} atom is also coordinated to six oxygen atoms of the DB18C6 unit, thus giving the Ln atoms an overall coordination number of nine (Fig. 3). Two chloride atoms are bridging to another Ln^{3+} to create a dinuclear cation. The best fit polyhedron can be described as a tricapped trigonal prism with Cl(1), O(2) and O(5) capping the trigonal prism on Ln(1), and Cl(4), O(9) and O(12) capping on Ln(2) (Fig. 3) [33]. Charge balancing of the cation is provided by uncoordinated tetrahedral $AlCl_4^-$ ions and the lattice voids host MeCN molecules.

The Ln-O_{crown} bond lengths range from 2.473(4) – 2.693(4) Å in the La species, and 2.474(4) – 2.684(4) Å for the Pr complex. The La – O_{crown} bond lengths (average 2.603 Å) are similar to those observed in the nine coordinate complex $[La(\mu\text{-}OH)I(DB18C6)]_2[I][I_3]$ (average 2.650 Å) [21]. The Pr-O_{crown} lengths (average 2.594 Å) are similar to those of $[PrCl_2(DB18C6)(H_2O)][SbCl_6]\cdot 0.5MeOH\cdot 0.5MeCN$ (2.487–2.668 Å) [23] as well as those observed in complex **1** (average 2.583 Å) and similar derivatives such as $[PrCl_2(\mu\text{-}Cl)\text{-}(tetraethyleneglycol)]_2$ (2.525–2.675 Å).[34] The Ln–Cl bond lengths are reflective of both the ionic radius of the lanthanoid and the Cl environment. In complex **3**, the La–Cl_{ter} lengths are 2.686(2) and 2.688(2) Å whereas the La–Cl_{br} bond lengths are longer (2.863(2)-2.897(2) Å). The La–Cl_{ter} distances are comparable to that observed in $[(Li(\mu\text{-}Cl)_2(THF)_2)_2LaCl(THF)_2]$ (2.567 Å) [38] with the change between CN 9 and CN 8 taken into account (*ca.* 0.056 Å) [5]. The La–Cl_{br} distances (average 2.877 Å) are comparable with the shortest La–Cl_{br} distances observed in $[(Li(\mu\text{-}Cl)_2(THF)_2)_2LaCl(THF)_2]$ (2.760 Å) [38] allowing for the coordination number difference. In complex **4**, the Pr–Cl_{ter} bond lengths are 2.683(2) and 2.643(2) Å, and the Pr–Cl_{br} distance are 2.846(2)-2.862(2) Å. The Pr–Cl_{ter} bonds are shorter (by *ca.* 0.16 Å) than in nine coordinate $[PrCl_2(\mu\text{-}Cl)(tetraethyleneglycol)]_2$ (2.803 Å) [34], but are near the value for the complex $[PrCl_3(THF)_2]_n$ (2.633(1), 2.668(6) Å) [39–40] despite the difference in coordination number (9 and 7) The Pr–Cl_{br} values (average 2.857 Å) are shorter than those of $[PrCl_2(\mu\text{-}Cl)(tetraethyleneglycol)]_2$ (2.910 and 2.986 Å) [34] but slightly longer than those in complex **1** (average 2.849 Å). The La–Cl_{br} bond lengths of **3** are longer than Pr–Cl_{br} of complex **4** by an average of 0.02 Å, which is less than the change (ca. 0.037 Å) [5] in ionic radii associated with the lanthanoid contraction.

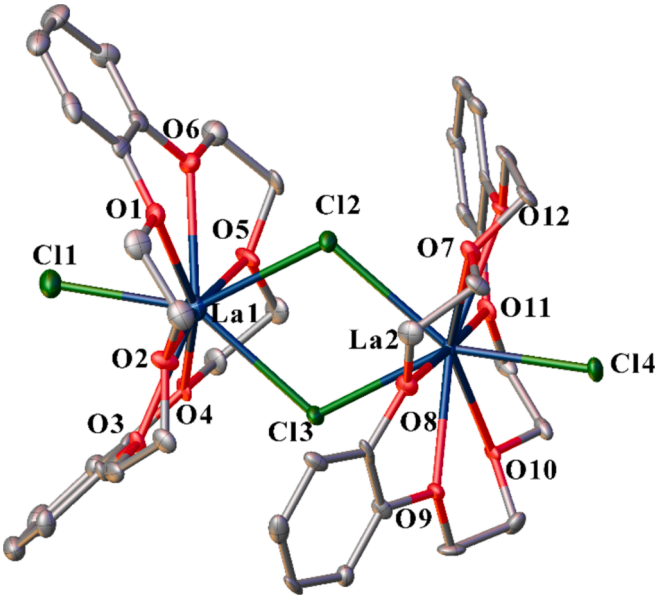


Fig. 3. The X-ray crystal structure of the cation in $[LaCl(\mu\text{-}Cl)(DB18C6)]_2[AlCl_4]_2\cdot 6.5MeCN$ (**3**) (representive of La, **3**, Pr, **4**). Ellipsoids shown at 50% probability, hydrogen atoms were removed for clarity. Selected bond lengths (Å) for **3** and **4** respectively: Ln1-Cl1 2.688(2) 2.683(2), Ln1-Cl2 2.863(2) 2.859 (2), Ln1-Cl3 2.866(2) 2.859(2), Ln1-O1 2.644(4) 2.612(4), Ln1-O2 2.483(4) 2.464(4), Ln1-O3 2.614(4) 2.615(4), Ln1-O4 2.601(4) 2.648(5), Ln1-O5 2.473 (4) 2.474(4), Ln1-O6 2.605(4) 2.632(4), Ln2-Cl2 2.880(2) 2.862(2), Ln2-Cl3 2.897(2) 2.846(2), Ln2-Cl4 2.686(2) 2.643(2), Ln2-O7 2.653(4) 2.567(4), Ln2-O8 2.615(4) 2.553(4), Ln2-O9 2.676(4) 2.684(4), Ln2-O10 2.597(4) 2.625 (4), Ln2-O11 2.581(4) 2.587(4), Ln2-O12 2.693(4) 2.670(4), Cl1-Ln1-Cl2 144.64(5) 145.36(6), Cl1-Ln1-Cl3 145.29(5) 145.18(6), Cl2-Ln1-Cl3 70.06(5) 69.45(5), Cl2-Ln2-Cl3 69.41(5) 69.59(5), Cl2-Ln2-Cl4 145.11(5) 145.56(5), Cl3-Ln2-Cl4 145.45(5) 144.83(5).

The crown ethers in **3** and **4** exhibit several interesting characteristics. Firstly, the difference between the planes of the phenylene groups are approximately 78°, unlike those of $[\{DyCl(\mu\text{-}Cl)(DB18C6)\}_2][\{DyCl_3(\mu\text{-}Cl)(MeCN)\}_2]$ [16], $[\{La(\mu\text{–}OH)I(DB18C6)\}_2][I][I_3]$ [21] and $[\{Ce(\mu\text{–}OH)I(DB18C6)\}_2][I_2]\cdot(H_2O)_{3.3}$ [7] where the phenylene groups are close to coplanar. In each case the crown ether collapses slightly to accommodate the metal (measured between the planes O(1, 2, 5, 6) and O(2, 3, 4, 5), as well as the planes O(7, 8, 11, 12) and O(8, 9, 10, 11), with the closure of the La complex at 118.75 and 121.87° whilst in the Pr analogue these are 115.19 and 119.22°. In both of these complexes, the planes collapse towards the each other instead of away as observed in complex **1** and $[\{DyCl(\mu\text{-}Cl)\text{-}(DB18C6)\}_2][\{DyCl_3(\mu\text{-}Cl)(MeCN)\}_2]$ [16].

The unusual orientation of the crown ether appears to be a result of intramolecular C—H…Ar interactions (Fig. 4). The crown ether coordinated to Ln(2) collapses towards the other crown ether due to interactions between C(3)–H(3B)…$Ar_{Centroid}$ (2.763 Å) and C(13)–H(13B) …$Ar_{Centroid}$ (2.672 Å) (Table S1). This is also supported by a deformation of the crown ether backbone at the C(3) and C(13) positions. The dibenzo groups also provide weak intermolecular π – π stacking to link symmetry equivalent dinuclear cations to produce a two dimensional polymeric array of cationic $[\{LnCl(\mu\text{-}Cl)(DB18C6)\}_2]^{2+}$ units (Fig. 4). The distance between the interacting phenylene groups range from 3.414(8) – 3.670(9) Å which are comparable to the π – π stacking observed in $[Cu_2(bpy)_2(H_2O)(OH)_2(SO_4)].4H_2O$ (mean distance = 3.450 Å) [41] and $[(ZnCl_2)_3(tdapb)]$ (3.60 – 3.85 Å) [42] (bpy = 2, 2′-bipyridine, and tdapb = 1,3,5-tris[*p*-(2,2′-*dipyridylamino*)*phenyl*]benzene). The intermolecular π – π interactions allow for overlap between the cationic moieties thus providing deep voids within the crystal system which hosts $AlCl_4^-$ ions and MeCN molecules.

In the structures of all compounds, the $AlCl_4^-$ anions occupy voids in the lattice created by the cations where the closest H···Cl^- interactions are 2.8 Å and these are considered insignificant, compared with halide interactions with C—H in chloroform where H···Cl^- distances of 2.39 Å are found.[43].

3. Conclusions

Four new structures developing the lanthanoid/18C6 theme have been established. The La (**3**) and Pr (**4**) complexes extend the cationic Ln – Cl crown binding mode that had only been previously observed for Dy [16], but now with the $[AlCl_4]^-$ counter ion. Complexes **1** and **4** show a new structural motif for Pr – Cl crown complexes. The Yb complex **2** is the first structurally characterised encapsulation of Yb^{3+} by 18C6. We have also demonstrated that $[Pr(MeCN)_n][AlCl_4]_3$ undergoes rearrangement in the presence of 18C6 resulting in halide transfer to the lanthanoid with formation of **1**.

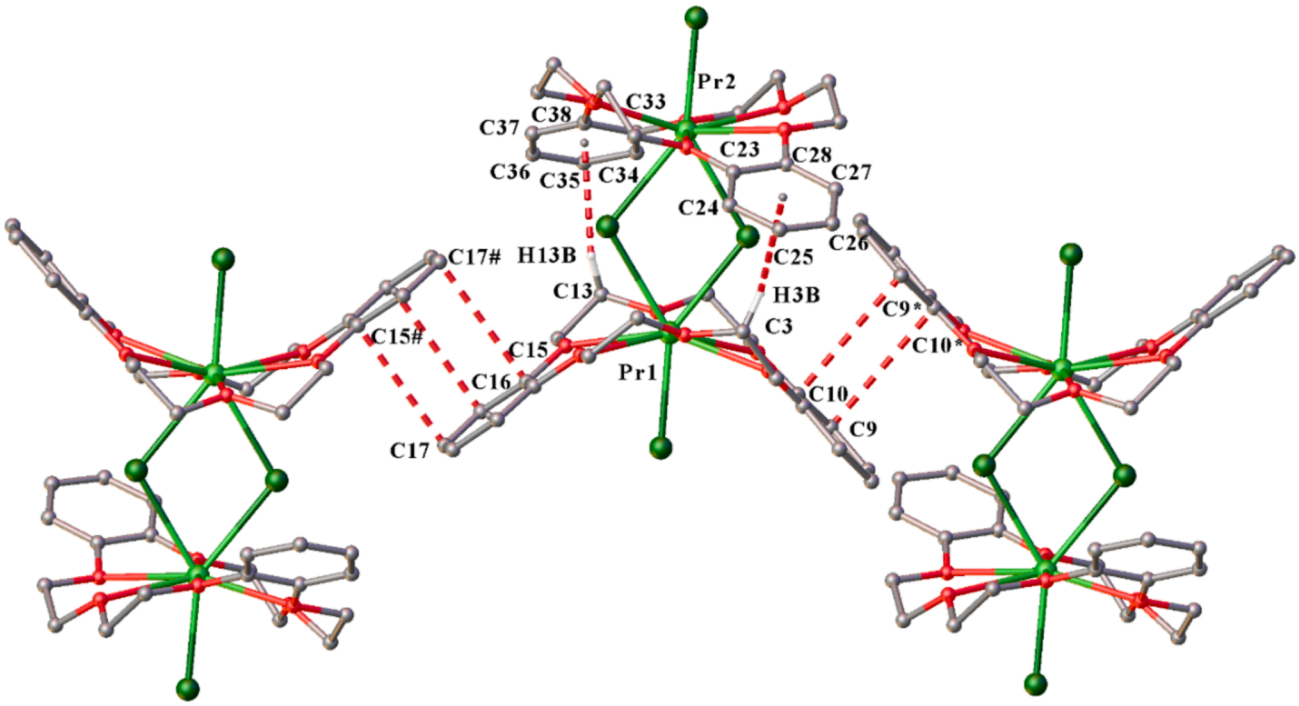


Fig. 4. Intramolecular C — H…Ar (C3 – H3B…Ar(C23-28) and C13 – H13B…Ar(C33-38)) interactions and intermolecular π – π interactions in complexes [PrCl(μ-Cl)(DB18C6)]$_2$[Al-Cl$_4$]$_2$·6.5MeCN (**4**) (representive of La, **3**, Pr, **4**). Symmetry codes: * 1-X,1-Y,2-Z; #2 1-X,2-Y,1-Z.

4. Experimental

4.1. General

The lanthanoid 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. Large chunks were filed in the drybox before use. MeCN was dried by distillation from CaH_2. IR and far IR data were obtained as described previously [39]. Metal analyses were carried out by complexometric EDTA titration with the addition of 5 % sulfosalicylic acid to mask Al [44]. Anhydrous $AlCl_3$, $LnCl_3$, 18-crown-6 and dibenzo-18-crown-6 were supplied by Sigma Aldrich. $AlCl_3$ was freshly sublimed prior to use. Conductivity measurements were carried out on a Crison Conductimeter 522 (serial no; 3807), using a locally manufactured cell for inert atmosphere handling. The complex [Pr(MeCN)$_9$][AlCl$_4$]$_3$ was made using previous published methods [24] and conductivity measurements were carried out as mentioned above (368 S cm^2 mol^{-1}, 1.097 × 10^{-3} mol dm^{-3}, MeCN). Crystals were immersed in crystallography oil and were measured on an Enraf-Nonius CCD area detector diffractometer. For compound **1**, the 18-crown-6 supporting ligand was disordered in several of the ethylene links. These were refined with partial occupancy using Parts 1 and 2, and the hydrogen atoms were placed in calculated positions.

4.2. Syntheses of 1-4

4.2.1. [PrCl(μ-Cl)(18C6)]$_2$[AlCl$_4$]$_2$·2MeCN (1)

Method A: [Pr(MeCN)$_9$][AlCl$_4$]$_3$·MeCN (0.20 g, 0.19 mmol) and 18-crown-6 (0.20 g, 0.57 mmol), were dissolved in MeCN (30 ml). The solution was stirred and heated to near boiling to assist dissolution. The resulting green solution was then filtered and reduced in volume. The solution was then cooled at −30 °C yielding small green crystals. (0.21 g (81 %)). m.p. 168 °C(dec), $C_{28}H_{54}Al_2Cl_{12}N_2O_{12}Pr_2$; calcd. Pr 20.54; found Pr 20.76 %. IR (Nujol, υ/cm^{-1}): 2296w, 2255 s, 1641w, 1350 s, 1290 s, 1253 s, 1144 s, 1112 s, 1085 s, 1046 s, 1039 s, 964 s, 947 s, 928w, 854 s, 839 s, 822 s, 803w, 688w, 608w, 496 s.

Method B: A mixture of $PrCl_3$ (0.10 g, 0.40 mmol), $AlCl_3$ (0.16 g, 1.20 mmol), and 18-crown-6 (0.29 g, 0.83 mmol) were dissolved in MeCN (30 ml). The solution was stirred and heated to near boiling to assist dissolution. The resulting green solution was then filtered and reduced in volume. The solution was then cooled at −30 °C yielding small green crystals. (0.44 g (87 %)). m.p. 170 °C(dec), $C_{28}H_{54}Al_2Cl_{12}N_2O_{12}Pr_2$; calcd. Pr 20.54; found Pr 20.84 % IR (Nujol, υ/cm^{-1}): 2291w, 2253 s, 1644w, 1353 s, 1291 s, 1248 s, 1142 s, 1113 s, 1085 s, 1049 s, 1037 s, 966 s, 948 s, 925w, 855 s, 836 s, 819 s, 802w, 687w, 609w, 494 s. ^{27}Al NMR: 104 ppm (AlCl$_4$) Λ_m (C_2H_3N): 225 S cm^2 mol^{-1} (0.95 × 10^{-3} mol dm^{-3}).

4.2.2. [YbCl$_2$(18C6)][AlCl$_4$]·MeCN (2)

A mixture of $YbCl_3$ (0.10 g, 0.36 mmol), $AlCl_3$ (0.16 g, 1.20 mmol) and 18-crown-6 (0.13 g, 0.37 mmol), were dissolved in MeCN (30 ml). The solution was stirred and heated to near boiling to assist dissolution. The resulting colourless solution was then filtered and reduced in volume. The solution was then cooled at −30 °C yielding small colourless crystals. (0.48 g (95 %)). m.p. 256 °C(dec), $C_{28}H_{54}Al_2Cl_{12}N_2O_{12}Yb_2$; calcd. Yb 24.10; found Yb 23.64 %. IR (Nujol, υ/cm^{-1}): 2291w, 2250w, 1654w, 1286 s, 1251 s, 1099 s, 959 s, 871w, 835 s 680w, 602w, 491 s. ^{27}Al NMR: 104 ppm (AlCl$_4$) Λ_m (C_2H_3N): 157 S cm^2 mol^{-1} (1.00 × 10^{-3} mol dm^{-3}).

4.2.3. [LaCl(μ-Cl)(DB18C6)]$_2$[AlCl$_4$]$_2$·6.5MeCN (3)

A mixture of $LaCl_3$ (0.10 g, 0.41 mmol), $AlCl_3$ (0.16 g, 1.20 mmol) and dibenzo18-crown-6 (0.15 g, 0.42 mmol), were dissolved in MeCN (30 ml). The solution was stirred and heated to near boiling to assist dissolution. The resulting colourless solution was then filtered and reduced in volume. The solution was then cooled at −30 °C yielding small colourless crystals. (0.64 g (90 %)). m.p. 254 °C(dec), $C_{53}H_{67.50}Al_2Cl_{12}N_{6.50}O_{12}La_2$; calcd. La 15.92; found La 15.81 %. IR (Nujol, υ/cm^{-1}): 2334w, 2305 s, 1612w, 1594w, 1502 s, 1419w, 1324 s, 1285w, 1246 s, 1191 s, 1124 s, 1104 s, 1052 s, 1025 s, 969 s, 948 s, 903w, 853w, 834w, 774 s, 750 s, 682w, 605w, 492 s. ^{27}Al NMR: 104 ppm (AlCl$_4$) Λ_m (C_2H_3N): 229 S cm^2 mol^{-1} (0.99 × 10^{-3} mol dm^{-3}).

4.2.4. [PrCl(μ-Cl)(DB18C6)]$_2$[AlCl$_4$]$_2$·6.5MeCN (4)

A mixture of $PrCl_3$ (0.10 g, 0.40 mmol), $AlCl_3$ (0.16 g, 1.20 mmol) and dibenzo18-crown-6 (0.15 g, 0.42 mmol), were dissolved in MeCN (30 ml). The solution was stirred and heated to near boiling to assist dissolution. The resulting green solution was then filtered and reduced in volume. The solution was then cooled at −30 °C yielding small green crystals. (0.59 g (84 %)). m.p. 265 °C(dec), $C_{53}H_{67.50}Al_2Cl_{12}N_{6.50}O_{12}Pr_2$; calcd. Pr 16.11; found Pr 15.96 %. IR (Nujol, υ/cm^{-1}): 2291w, 2252 s, 1612w, 1594w, 1505 s, 1419w, 1323 s, 1285w, 1246 s, 1194 s, 1171w, 1127 s, 1103 s, 1093 s, 1050 s, 1025 s, 969 s, 949 s, 903 s, 853w, 829w, 774 s, 765 s, 754 s, 604 s, 492 s. ^{27}Al NMR: 104 ppm ($AlCl_4$). Λ_m (C_2H_3N): 216 S cm^2 mol^{-1} (1.06 × 10^{-3} mol dm^{-3}).

CRediT authorship contribution statement

David J. Evans: Writing – original draft, Methodology, Investigation. **Zhifang Guo:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Glen B. Deacon:** Writing – review & editing, Visualization, Supervision, Investigation, Conceptualization. **Peter C. Junk:** Writing – review & editing, Visualization, Supervision, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

CCDC 2380450-2380453 contains the supplementary crystallographic data for compounds **1-4** which are also compiled in Table S2. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, 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. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2024.117270.

Data availability

Data will be made available on request.

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