



Synthesis of cationic lanthanoid tetraphenylborate crown ether complexes

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ARTICLE INFO

Keywords:

Lanthanoids
Crown ethers
X-ray structures
Synthesis
Non-coordinating anions

ABSTRACT

The efficacy of Me₃NHBPh₄ as a protolytic agent in the generation of reactive lanthanoid cations has been further explored. Reaction of [Nd(BH₄)₃(thf)₄] with Me₃NHBPh₄ in a 1:3 mole ratio, and dibenzo-18-crown-6 (DB18C6) in thf did not yield [Nd(thf)_n][BPh₄]₃, but [Nd(BH₄)₂(DB18C6)][BPh₄]₂·2THF (**1**), a complex primed for further functionalisation, was isolated. The structure has an eight coordinate Nd atom with two *trans* tridentate BH₄⁻ ligands. Redox transmetalation/protolysis (RTP) reactions between Yb metal, PhHgC₆F₅, and Me₃NHBPh₄ in the presence of 18-crown-6 (18C6) or DB18C6 in MeCN or in thf followed by work up with MeCN yields [Yb(CE)(MeCN)₃][BPh₄]₂·nMeCN (CE = 18C6, *n* = 0 (**2**), and DB18C6 *n* = 3 (**3**)), the structures of which have nine coordinate Yb atoms. Two pairs of MeCN ligands are *transoid*, whereas the third pair have a small *cis* N—Yb—N angle. In the absence of a crown ether ligand, the RTP reaction in MeCN yields the known [Yb(MeCN)₈][BPh₄]₂.

1. Introduction

Reactive rare earth cations with labile ligands such as tetrahydrofuran (thf) and 1,2-dimethoxyethane (dme) are of considerable interest for ligand replacement reactions and as targets of nucleophilic substitution. These include lanthanoid cyclopentadienyl tetraphenylborate complexes [Ln(Cp)₂(solv)₂][BPh₄] (Cp = η⁵-methylcyclopentadienyl, η⁵-penta(methyl)cyclopentadienyl, η⁵-1,3-bis(trimethylsilyl)cyclopentadienyl, η⁵-1-(dimethyl(prop-2-enyl)silyl)-2,3,4,5-tetramethylcyclopentadienyl, η⁵-trimethylsilyl-cyclopentadienyl; solv = dme, thf, MeCN, tBuCN, PhCN, py) [1–7], lanthanoid amidinato complexes [Ln(AMD)(CH₂(SiMe₃))(thf)₃][BPh₄] (AMD = *N,N'*-bis(2,6-diisopropylphenyl)-benzamidinate) [8], lanthanoid pyrazolates [Ln(pz)₂][BPh₄] (pz = *tris*(3-(2-pyridyl)pyrazoyl)hydroborate or *tris*((3,5-dimethyl)pyrazoyl)hydroborate) [9] and [Dy(pz)₂(solv)₅][BPh₄] (Hpz = 3-(trifluoromethyl)pyrazole, methylpyrazole, 3-isopropyl-¹H-pyrazole, 3,5-dimethylpyrazole, 3,5-diisopropylpyrazole, pyrazole; solv = thf, py, thiazole) [10], and divalent pentafluorophenyl lanthanoid cations, [Ln(C₆F₅)(THF)₆][BPh₄] [11]. With added reactive functionalities, such as borohydride, they can have further versatility [12–18]. Another useful modification is to block several positions with a polydentate ligand such as a crown ether, so that substitution and reactions with nucleophiles can be directed to a particular part of the molecular surface [19–23]. In these complexes, BPh₄⁻ is a non-coordinating counter ion, though in some cases, it can coordinate where a coordinatively unsaturated rare

earth cation has no other source of electron density [24–26]. In this short paper, we report three new examples of cationic lanthanoid tetraphenylborates, one functionalised by coordinated borohydride, and all with crown ethers, together with their structures.

2. Results and discussion

2.1. Synthesis and characterisation

Reactions between [Nd(BH₄)₃(THF)₄] and Me₃NHBPh₄ in the presence of dibenzo-18-crown-6 (DB18C6) have led to the isolation of a new complex [Nd(BH₄)₂(DB18C6)][BPh₄]₂·2THF (**1**) (Eq. (a)). This product was obtained despite use of enough Me₃NHBPh₄ to remove all BH₄ groups. The synthesis should be applicable to other rare earth elements in the trivalent state, hence providing potential reactants and catalysts, whilst the presence of axial ligands may lead to interesting magnetic properties for the Dy complex. Further, the axial ligands may be replaceable by ones with a stronger ligand field.

Addition of a crown ether (18-crown-6 (18C6) or dibenzo-18-crown-6 (DB18C6)) to Yb pentafluorophenyl systems in THF resulted in an insoluble precipitate forming. Addition of MeCN to these precipitates gave coloured solutions resulting in [Yb(18-crown-6)(MeCN)₃][BPh₄]₂ (**2**), and [Yb(DB18C6)(MeCN)₃].3MeCN (**3**) (Eq. (b)). Reaction (b) can be considered to involve selective protolysis of the Ph group of an inferred YbPh(C₆F₅) intermediate [11]. In addition **2** was obtained when

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<https://doi.org/10.1016/j.jorgchem.2024.123186>

Received 23 April 2024; Received in revised form 12 May 2024; Accepted 14 May 2024

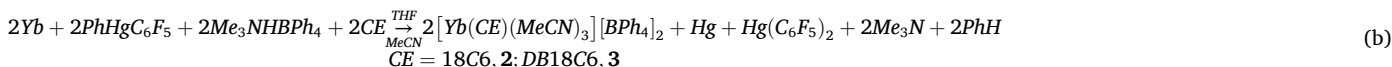
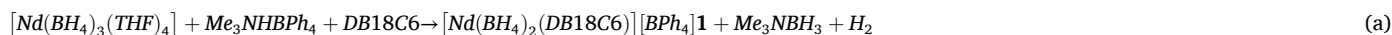
Available online 15 May 2024

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the synthesis **1** was carried out entirely in acetonitrile. **3** was obtained by carrying out the synthesis in acetonitrile in the absence of the crown ether giving $[\text{Yb}(\text{MeCN})_8][\text{BPh}_4]_2$, which was then treated with the crown ether to give **3**. Metal analysis established bulk purity, as problems were experienced obtaining microanalyses for these air/moisture-sensitive compounds.

MeCN at 2254 cm^{-1} [30a].

There are numerous peaks in the infrared spectra that are attributable to various vibrational modes of the BPh_4^- ions in the spectra of all the complexes. All have three weak absorptions around 1942, 1884, and 1820 cm^{-1} attributable to BPh_4^- overtones [29]. Ring C—C stretching is around 1600, 1580 and 1430 cm^{-1} [29,30b]. Bands



The infrared spectrum of $[\text{Nd}(\text{BH}_4)_2(\text{DB18C6})][\text{BPh}_4] \cdot 2\text{THF}$ (**1**) shows features aiding understanding the metal environment. The BH_4^- ions give rise to intense bands at 2475, 2444 and 2225 cm^{-1} in complex **1**, and this observation is consistent with tridentate BH_4^- bonding [12, 27]. In complexes **1-3**, the $\nu_{\text{asym}}(\text{C}-\text{O}-\text{C})$ vibrations of the crown ether are assigned to several absorptions between 1139 and 1020 cm^{-1} and bands between 972 and 951 cm^{-1} are attributed to $\nu_{\text{sym}}(\text{C}-\text{O}-\text{C})$ [28]. The aromatic regions of the infrared spectra for complexes **1** and **3** show overlap between the absorptions for DB18C6 and BPh_4^- making assignment difficult. Even with this overlap it is possible to assign the band at $1506\text{--}1503\text{ cm}^{-1}$ to the skeletal C—C stretching vibration of the dibenzo groups [29]. There is a band at $780\text{--}779\text{ cm}^{-1}$ for complexes **1** and **3**, attributable to C—H out of plane bending of the four adjacent hydrogen atoms of the dibenzo groups [29]. For complexes **2** and **3**, there are bands at 2302–2295 and 2266 cm^{-1} attributable to coordinated MeCN [30a]. Additionally, uncoordinated MeCN is also evident in the infrared spectrum of complex **3** with a band at 2260 close to free

attributable to C—H in plane bending vibrations occur between 1300 and 1000 cm^{-1} , and those to C—H out of plane bending occur between 754 and 704 cm^{-1} as expected for a phenyl group [29,30b].

The $^{171}\text{Yb}\{^1\text{H}\}$ chemical shift value of complex **3** (155 ppm) in C_6D_6 is reasonable for a nine coordinate complex, given that eight coordinate $[\text{Yb}(\text{dme})_4]^{2+}$ and $[\text{YbI}_2(\text{dme})_3]$ have chemical shifts of 380 and 476 ppm respectively [31a], and chemical shifts fall with increasing coordination number in complexes with similar donors [31b-d], and non polar solvents also cause a shift to lower delta [31e].

2.2. X-ray structures

$[\text{Nd}(\text{BH}_4)_2(\text{DB18C6})][\text{BPh}_4] \cdot 2\text{THF}$ (**1**) (Fig. 1a) crystallises in the monoclinic space group $P2_1/n$. The molecular structure comprises of an eight coordinate Nd atom that is bound to all six oxygen atoms of the DB18C6 ligand, and two tridentate borohydride ligands (each viewed as occupying one coordination site). There is an uncoordinated tetrahedral BPh_4^- anion, as well as two lattice THF molecules. As with the reported complex $[\text{Nd}(\text{BH}_4)_2(\text{THF})_5][\text{BPh}_4]$ [19], the hydrogen atoms of the BH_4^-

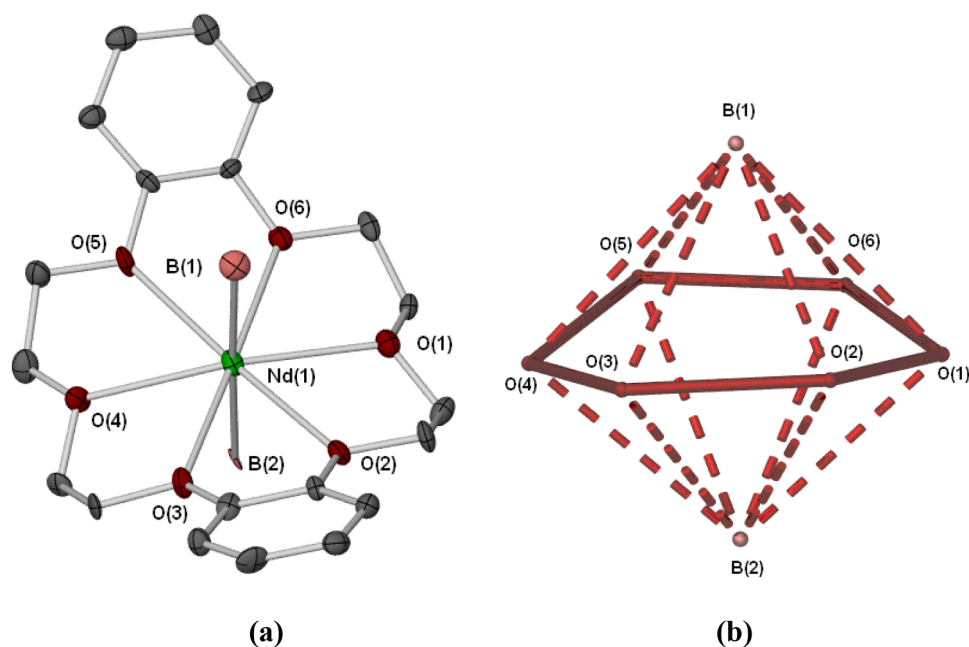


Fig. 1. (a) The X-ray crystal structure of the cation in $[\text{Nd}(\text{BH}_4)_2(\text{DB18C6})][\text{BPh}_4] \cdot 2\text{THF}$ (**1**); (b) The coordination polyhedron, hexagonal bipyramidal observed about Nd(1). Selected bond lengths (Å) and angles ($^\circ$): Nd1—O1 2.635(2), Nd1—O2 2.559(2), Nd1—O3 2.645(2), Nd1—O4 2.676(2), Nd1—O5 2.560(2), Nd1—O6 2.621(2), Nd1—B1 2.610(5), Nd1—B2 2.648(3), B1—Nd1—B2 177.65(13).

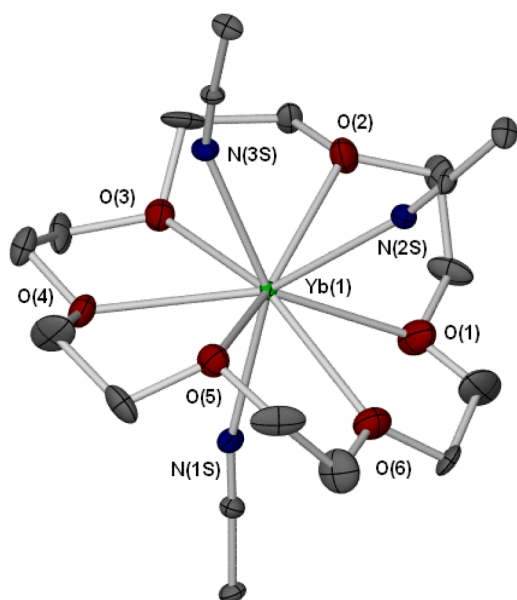


Fig. 2. The X-ray crystal structure of the cation in $[\text{Yb}(\text{18C6})(\text{MeCN})_3][\text{BPh}_4]_2$ (**2**). Selected bond lengths (Å) and angles ($^\circ$): Yb1—O1 2.604(5), Yb1—O2 2.586(4), Yb1—O3 2.563(5), Yb1—O4 2.529(5), Yb1—O5 2.629(5), Yb1—O6 2.582(4), Yb1—N1 2.547(5), Yb1—N2 2.551(5), Yb1—N3 2.620(6), N1—Yb1—N2 148.07(17), N1—Yb1—N3 140.96(15), N2—Yb1—N3 68.71(16).

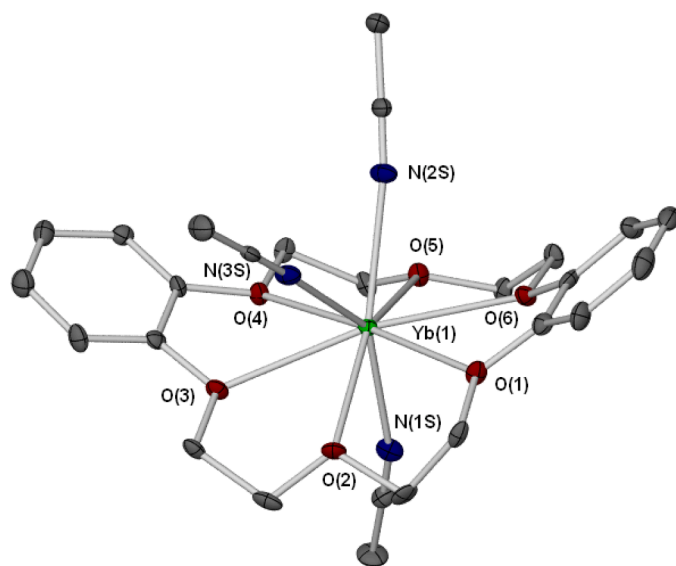


Fig. 3. The X-ray crystal structure of the cation in $[\text{Yb}(\text{DB18C6})(\text{MeCN})_3][\text{BPh}_4]_2 \cdot 3\text{MeCN}$ (**3**). Selected bond lengths (Å) and angles ($^\circ$): Yb1—O1 2.582(3), Yb1—O2 2.655(2), Yb1—O3 2.674(3), Yb1—O4 2.630(3), Yb1—O5 2.589(2), Yb1—O6 2.643(3), Yb1—N1 2.506(4), Yb1—N2 2.580(3), Yb1—N3 2.514(4), N1—Yb1—N2 145.01(11), N1—Yb1—N3 142.88(11), N2—Yb1—N3 70.87(10).

ions were not able to be located on a difference map, but the infrared spectral data are consistent with tridentate borohydride, attached through three hydrogen atoms. The polyhedron about the Nd^{3+} ion can be best described as hexagonal bipyramidal, with the ether oxygen atoms forming the hexagon and the *trans* boron atoms of the BH_4^- ions creating the pyramid (Fig. 1b) [32].

The Nd—O distances range from 2.559(2) to 2.676(2) Å following the trends for eight coordinate Nd—O distances observed in $[\{\text{NdCl}_2(\mu\text{-Cl})(\text{DME})\}_2]$ (2.575–2.637 Å) [33]. The Nd—B internuclear distances of

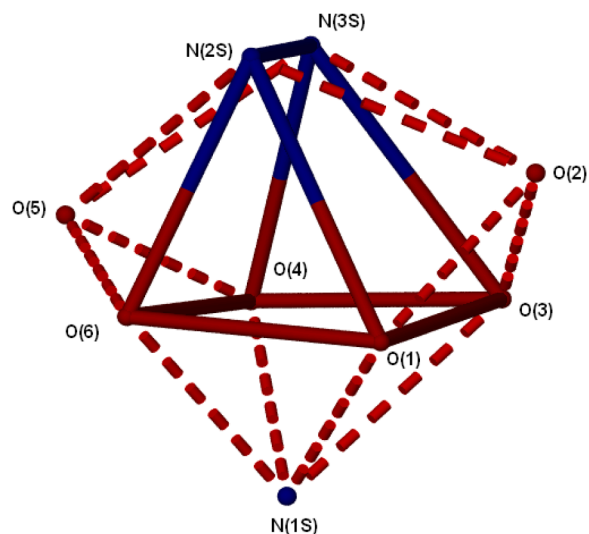


Fig. 4. The tricapped trigonal prismatic geometry about Yb observed in complexes **2** and **3**.

2.610(5) and 2.648(3) Å are shorter than those observed in seven coordinate $[\text{Nd}(\text{BH}_4)_2(\text{THF})_5][\text{BPh}_4]$ (2.727(3) and 2.740(4) Å) [19], but these are not bonds.

Complex **2** crystallises in the monoclinic space group $P2_1/c$ and complex **3** crystallises in the orthorhombic space group $Pbca$. The divalent Yb complexes $[\text{Yb}(\text{18C6})(\text{MeCN})_3][\text{BPh}_4]_2$ (**2**) and $[\text{Yb}(\text{DB18C6})(\text{MeCN})_3][\text{BPh}_4]_2 \cdot 3\text{MeCN}$ (**3**), both have a Yb^{2+} ion that is bound by six ether oxygen atoms and three MeCN molecules, giving an overall coordination number of nine about Yb (Figs. 2 and 3). Both of these divalent cations are charge balanced by tetrahedral BPh_4^- ions and complex **3** also has lattice MeCN molecules. The best fit polyhedron for these complexes can be described as a tricapped trigonal prism, with the atoms O(2), O(5) and N(1S) capping the prism (Fig. 4) [32]. The Yb—O distances range from 2.529(5) to 2.674(3) Å for both complexes following the trends observed in $[\text{Yb}(\text{DIME})_3][\text{Co}(\text{CO})_4]_2$ (2.49–2.69 Å) (DIME = diethylene glycol dimethyl ether) [34]. The Yb— N_{MeCN} bond lengths range from 2.506(4)–2.620(6) Å giving an average of 2.55 Å. This is similar to the average Yb—N length of 2.56 Å observed in $[\text{Yb}(\text{MeCN})_8][\text{BPh}_4]_2$ [1c], despite the coordination number difference. In both **2** and **3**, two pairs of MeCN ligands have a *transoid* disposition, whereas the other pair has a narrow *cis* relationship (Figs. 2 and 3).

In complexes **1–3**, the extent of crown ether distortion differs possibly due to the steric repulsions caused by the other coordinated ligands. For complex **1** the difference between the planes drawn by the atoms O(1, 2, 3, 4) and O(1, 4, 5, 6) is 162.86°. In complex **1**, the Nd resides almost in the same plane at O(2, 3, 5, 6) (0.093 Å out of plane) and 0.261 Å above the vector drawn between O1 and O4. In complex **2**, the crown ether distorts so that the angle between the planes O(1, 2, 5, 6) and O(2, 3, 4, 5) is 116.78°. The angle between the O(1, 2, 5, 6) and O(2, 3, 4, 5) for complex **3** is 155.66°. Interestingly, the angles between the planes for complexes **1** and **3** are close to each other. The dibenzo groups must provide greater rigidity to the crown ether therefore making distortion more difficult, due to aromatic-to-aromatic repulsions.

The BPh_4^- ions add an interesting factor to the way that these complexes pack in the solid state. The aromatic rings of the BPh_4^- ion act as an acceptor in C—H... π interactions between the cation and the anions. In complexes **1–3**, C—H... π interactions occur between the backbone of the crown ether and the aromatic rings of the BPh_4^- ions (Fig. 5). The distances of the intermolecular C—H... π interactions are comparable to those of $[\{\text{ZnCl}_2\}_3(\text{tdapb})]$ (C— π distance 3.60–3.85 Å) [35] (tdapb = 1, 3,5-*tris*[*p*-2,2'-dipyridylamino]phenyl]benzene), as well as those observed in $[\text{Ca}(\text{THF})_6][\text{Me}_3\text{Si}(\text{fluorenyl})_2\text{-C}_6\text{H}_6]$ and $[\text{Ca}(\text{THF})_6][\text{ACp}]_2\text{-C}_6\text{H}_6$ (ACp = 7,9-diphenylcyclopenta[*a*]acenaphadienyl) [36].

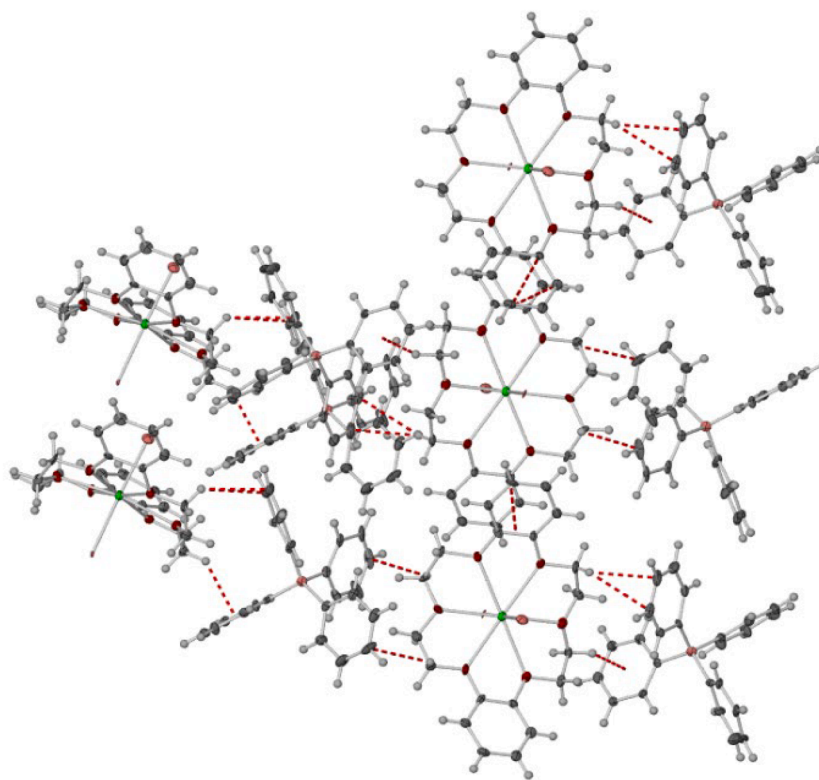


Fig. 5. The X-ray crystal structure of complex 2 illustrating C—H \cdots O interactions producing a linked network of cations and anions.

The C—H \cdots O interaction is comparable to that observed in $[\text{Cu}_2(\text{bpy})_2(\text{H}_2\text{O})(\text{OH})_2(\text{SO}_4)] \cdot 4\text{H}_2\text{O}$ (C—O distance = 3.278 Å) [37] (bpy = 2, 2'-bipyridine). Table S1 summarises the intermolecular interactions observed in complexes 1 and $[\text{Nd}(\text{BH}_4)_2(\text{THF})_5][\text{BPh}_4]$ [19].

In complexes 2 and 3, numerous C—H \cdots O interactions bind the cation into a box-like framework [36]. The BPh_4^- ions interact with the C—H groups of the crown ethers and with the methyl groups of the MeCN molecules, resulting in complete enclosure of the cation (Fig. 6). The lengths and angles of these interactions are shown in Table S2. There are several interactions where the H-acceptor distance is well below the sum of van der Waals radii for C and H (2.90 Å) [36]. These are comparable with the H-acceptor distances observed in the cations isolated by Harder in $[\text{Ca}(\text{THF})_6][\text{Me}_3\text{Si}(\text{fluorenyl})]_2 \cdot \text{C}_6\text{H}_6$ and $[\text{Ca}(\text{THF})_6][\text{ACp}]_2 \cdot \text{C}_6\text{H}_6$ (ACp = 7.9-diphenylcyclopenta[*a*]acenaphadienyl) [36].

3. Conclusions

A new lanthanoid borohydride crown ether complex $[\text{Nd}(\text{BH}_4)_2(\text{DB18C6})][\text{BPh}_4] \cdot 2\text{THF}$ 1 has been prepared by protolysis of $[\text{Nd}(\text{BH}_4)_3(\text{thf})_4]$, but complete displacement of all BH_4 groups was not achieved. Additionally, we have synthesized two new divalent cationic complexes $[\text{Yb}(\text{18C6})(\text{MeCN})_3][\text{BPh}_4]_2$ 2 and $[\text{Yb}(\text{DB18C6})(\text{MeCN})_3][\text{BPh}_4]_2 \cdot 3\text{MeCN}$ 3 by redox protolysis from Yb metal, PhHgC_6F_5 and $\text{Me}_3\text{NHBPh}_4$. In the structure of 1, neodymium is eight coordinate with *trans* tridentate BH_4 ligands, whilst in 2 and 3 ytterbium has a coordination number of nine. Examples of Yb^{2+} encapsulation by 18C6 are known where the coordination numbers are eight and nine [38]. The preparative method for isolation of $[\text{Yb}(\text{C}_6\text{F}_5)]^+$ cationic complexes by selective redox protolysis of PhHgC_6F_5 [11] does not extend from thf to MeCN as solvent. Instead reorganisation into $[\text{Yb}(\text{MeCN})_8][\text{BPh}_4]_2$ is observed.

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. Complexes $\text{Me}_3\text{NHBPh}_4$ [30b], $[\text{Nd}(\text{BH}_4)_3(\text{THF})_4]$ [12b] and $[\text{PhHg}(\text{C}_6\text{F}_5)]$ [39] were prepared by the literature methods. Lanthanoid metals were from Santoku. Large chunks were filed in the drybox before use. THF was dried by distillation over sodium or sodium benzophenone ketyl before being stored under an atmosphere of nitrogen, and acetonitrile was dried by distillation over calcium hydride. IR spectra were recorded as Nujol mulls between NaCl plates using a Perkin Elmer FTIR-106 and a Bruker IFS48 within the range 4000–700 cm^{-1} . Multi-nuclear NMR spectra were recorded with a Bruker BZH 300/52 NMR spectrometer with a Varian console. ^{11}B NMR spectra were referenced to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in CDCl_3 , and the $^{171}\text{Yb}\{^1\text{H}\}$ NMR spectrum (solvent C_6D_6) was referenced to external $\text{Yb}(\text{C}_5\text{Me}_3)_2$ in THF/10 % C_6D_6 [40]. Metal analyses were conducted through complexometric EDTA titration [41]. Crystals were immersed in crystallography oil and were measured on an Enraf–Nonius CCD area detector diffractometer. Crystal data and refinement details are given in Table S3. CCDC 2347708–2347710 for compounds 1–3, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.2. Syntheses

4.2.1. $[\text{Nd}(\text{BH}_4)_2(\text{DB18C6})][\text{BPh}_4] \cdot 2\text{THF}$ (1)

A mixture of $[\text{Nd}(\text{BH}_4)_3(\text{THF})_4]$ (0.10 g 0.25 mmol), $\text{Me}_3\text{NHBPh}_4$ (0.29 g 0.77 mmol) and dibenzo18-crown-6 (0.09 g, 0.25 mmol) was dissolved in THF (100 ml). The reaction mixture was stirred for 3 h and then allowed to settle. The resulting purple solution was filtered and the

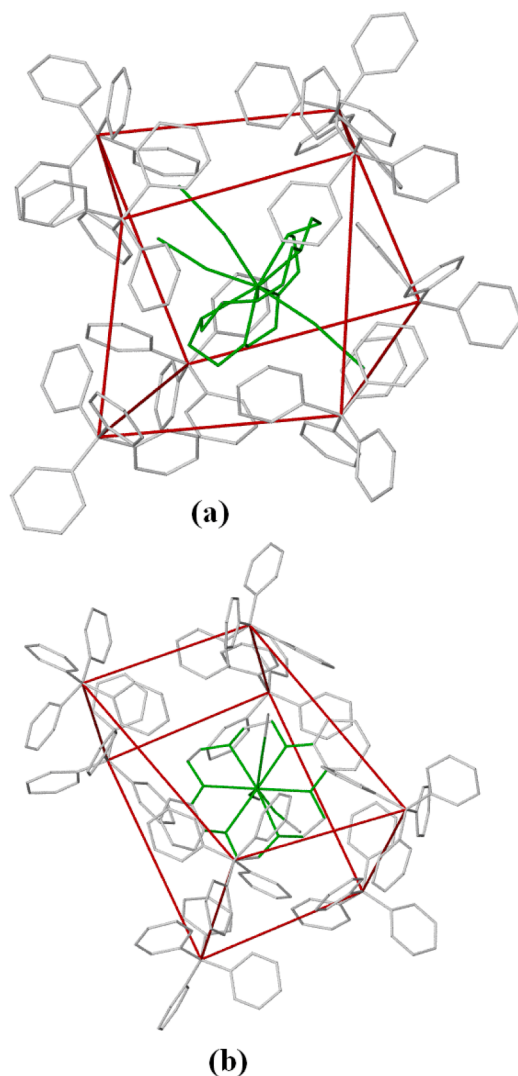


Fig. 6. The packing observed in complexes 2 and 3 showing BPh_4^- ions providing the corners of a cube (cation shown in green). This creates a molecule in a box effect [36].

volume reduced. Storage at -30°C afforded purple crystals (0.23 g, (93 %), $\text{C}_{52}\text{H}_{68}\text{B}_3\text{NdO}_8$; calcd. Nd 14.46; found 14.65 %. IR (Nujol, ν/cm^{-1}): 2475 and 2444s, 2225s, 1944w, 1889w, 1822w, 1617s, 1594s, 1587s, 1506s, 1422s, 1323s, 1283s, 1246s, 1192s, 1127s, 1084s, 1050s, 1022s, 972s, 951s, 899s, 849s, 778s, 709s.

4.2.2. $[\text{Yb}(\text{MeCN})_3(18\text{C}6)][\text{BPh}_4]_2$ (2)

Method 1: A mixture of Yb metal (1.00 g, 5.78 mmol), $[\text{PhHg}(\text{C}_6\text{F}_5)]$ (2.60 g, 5.85 mmol), $\text{Me}_3\text{NHBPh}_4$ (2.20 g, 5.81 mmol), and 18-crown-6 (1.00 g, 5.78 mmol) was dissolved in THF (150 ml) over a 6 h period and a grey precipitate of Hg was seen to be deposited. The colourless solution was evaporated to dryness then the complex was extracted into MeCN giving a yellow solution. The yellow solution was then filtered and reduced in volume. The solution was then cooled at -8°C yielding yellow crystals. (3.20 g (81 %)). m.p. 120–122 $^\circ\text{C}$. $\text{C}_{66}\text{H}_{73}\text{B}_2\text{N}_3\text{O}_6\text{Yb}$: calcd. Yb 14.43; found Yb 14.50 %. IR (Nujol, ν/cm^{-1}): 2297s, 2266s, 1941w, 1887w, 1821w, 1601s, 1579s, 1427s, 1389s, 1293s, 1181s, 1139s, 1085s, 1032s, 965s, 924s, 882s, 840s, 795s, 753s, 706s. ^{11}B NMR: 3.5 ppm.

Method 2: A mixture of Yb metal (1.00 g, 5.78 mmol), $[\text{PhHg}(\text{C}_6\text{F}_5)]$ (2.60 g, 5.85 mmol), and $\text{Me}_3\text{NHBPh}_4$ (2.20 g, 5.81 mmol), was dissolved in MeCN (150 ml) at 60°C over a 6 h period where Hg was seen to

be deposited. The orange solution was filtered into a Schlenk flask containing 18-crown-6 (1.00 g, 5.78 mmol). The resulting yellow solution was then filtered and reduced in volume, The solution was then cooled at -8°C yielding yellow crystals of $[\text{Yb}(\text{MeCN})_3(18\text{-crown-6})][\text{BPh}_4]_2$ (confirmed by unit cell determination).

4.2.3. $[\text{Yb}(\text{MeCN})_3(\text{DB}18\text{C}6)][\text{BPh}_4]_2 \cdot 3\text{MeCN}$ (3)

Method 1: A mixture of Yb metal (1.00 g, 5.78 mmol), $[\text{PhHg}(\text{C}_6\text{F}_5)]$ (2.60 g, 5.85 mmol), and $\text{Me}_3\text{NHBPh}_4$ (2.20 g, 5.81 mmol), was dissolved in MeCN (150 ml) at 60°C over a 6 h period where Hg was seen to be deposited. The orange solution was filtered and reduced in volume, precipitating red crystals of $[\text{Yb}(\text{MeCN})_8][\text{BPh}_4]_2$ (confirmed by unit cell determination) [1c]. The complex was dissolved with gentle heating and then filtered into a Schlenk flask containing dibenzo-18-crown-6 (1.0 g, 5.0 mmol). The yellow solution was filtered and reduced in volume, The solution was then cooled at -8°C yielding yellow crystals. (3.20 g (81 %)). m.p. 120–122 $^\circ\text{C}$. $\text{C}_{80}\text{H}_{82}\text{B}_2\text{N}_6\text{O}_6\text{Yb}$: calcd. Yb 12.20; found Yb 12.33 %. IR (Nujol, ν/cm^{-1}): 3055s, 2301s, 2267s, 2250s, 1944w, 1884w, 1823w, 1598s, 1579s, 1503s, 1427s, 1390s, 1327s, 1250s, 1204s, 1119s, 1062s, 1033s, 967s, 954s, 919s, 856s, 843s, 780s, 748s, 704s. $^{171}\text{Yb}\{^1\text{H}\}$ NMR (C_6D_6): 155.1 ppm. ^{11}B NMR: -6.9 ppm.

Method 2: A mixture of Yb metal (1.00 g, 5.78 mmol), $[\text{PhHg}(\text{C}_6\text{F}_5)]$ (2.60 g, 5.85 mmol), $\text{Me}_3\text{NHBPh}_4$ (2.20 g, 5.81 mmol), and dibenzo-18-crown-6 (1.0 g, 5.0 mmol) was dissolved in THF (150 ml) over a 6 h period where a grey precipitate of Hg was seen to be deposited. The colourless solution was evaporated to dryness then the complex was extracted into MeCN giving a yellow solution. The yellow solution was then filtered and reduced in volume. The solution was then cooled at -8°C yielding yellow crystals of $[\text{Yb}(\text{MeCN})_3(\text{dibenzo-18-crown-6})][\text{BPh}_4]_2 \cdot 3\text{MeCN}$ (confirmed by unit cell determination).

CRedit authorship contribution statement

David J. Evans: Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Zhifang Guo:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **Glen B. Deacon:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition, Formal analysis, Conceptualization. **Peter C. Junk:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no conflict of interest.

Data availability

Data will be made available on request.

Acknowledgements

PCJ and GBD gratefully acknowledge the ARC for funding (DP230100112).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2024.123186](https://doi.org/10.1016/j.jorganchem.2024.123186).

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