New homoleptic anionic aryloxolanthanide(III) complexes with unusual coordination trapping of the alkali-metal counter ions

David L. Clark,*†[a] Glen B. Deacon,*[b] Tiecheng Feng,[b] Rebecca V. Hollis,[a] Brian L. Scott,[a] Brian W. Skelton,[c] John G. Watkin*†[a] and Allan H. White[c]

[a] *Chemical Sciences and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
[b] *Chemistry Department, Monash University, Clayton, Victoria 3168, Australia*
[c] *Chemistry Department, University of Western Australia, Nedlands, Western Australia 6907, Australia*

The complex $\{Cs_2[La(OAr)_5]\}$ ($Ar = C_6H_3Pr^i_2$-2,6), from $LaCl_3$ or $La_2(OAr)_6$ and CsOAr in tetrahydrofuran, has an unprecedented polymeric structure in which five-coordinate $[La(OAr)_5]^{2-}$ anions are bonded to caesium in a three- dimensional network solely by Ar–Cs π bonds, whilst $\{Na[Nd(Odpp)_4]\}$ (dpp = $C_6H_3Ph_2$-2,6), from $NdCl_3$ and NaOdpp in 1,3,5-tri-*tert*-butylbenzene at 300 °C, has an unexpected monomeric structure with sodium bonded to three oxygens and encapsulated by three phenyl groups of $[Nd(Odpp)_4]^-$.

Metathesis reactions between alkali-metal reagents and lanthanide halide derivatives dominate synthetic routes to a wide range of inorganic and organometallic lanthanide complexes.[1] However, there are many cases in which the alkali-metal reagent is retained within the lanthanide coordination sphere giving salt or 'ate' complexes.[2] Thus, in the sole reported examples of anionic homoleptic aryloxolanthanide(III) complexes $\{M[Ln(O\text{-}C_6H_3Pr^i_2\text{-}2,6)_4]\}_n$ (M = K, Cs), $Ln(OAr)_4^-$ units are linked to the alkali metal by multihapto π-arene interactions and also in some cases oxygen bridging to give a one-dimensional chain or two-dimensional sheets.[3] We now report that further exploration of homoleptic anionic aryloxolanthanide(III) complexes has revealed two unique new ways of incorporating alkali metals into lanthanide complexes. First, use of the large caesium ion and the largest lanthanide has given the first five-coordinate anionic aryloxolanthanide complex $\{Cs_2[La(OAr)_5]\}$, which has a *three*-dimensional extended structure held together exclusively by caesium–π-arene interactions. Secondly, use of the bulkier 2,6-diphenylphenolate ligand has given the molecular bimetallic $\{Na[Nd(Odpp)_4]\}$, which unexpectedly is monomeric owing to encapsulation of sodium by phenyl groups.

Reaction of anhydrous lanthanum trichloride with caesium 2,6-diisopropylphenoxide (mol ratio 1 : 5) in tetrahydrofuran (thf), followed by removal of solvent and crystallization of the reddish purple residue from toluene, leads to the isolation of the dicaesium complex $\{Cs_2[La(OAr)_5]\}$ **1** [eqn. (1)]. **1** may also be prepared in higher yield from the reaction of $La_2(OAr)_6$[4] with caesium 2,6-diisopropylphenoxide (mol ratio 1 : 4) in thf at room temperature for 72 h [eqn. (2)], followed by crystallization from hot toluene.

$$LaCl_3 + 5\,CsOAr \xrightarrow{\text{thf}} \underset{\mathbf{1}}{\{Cs_2[La(OAr)_5]\}} + 3\,CsCl \qquad (1)$$

$$La_2(OAr)_6 + 4\,CsOAr \xrightarrow{\text{thf}} 2\underset{\mathbf{1}}{\{Cs_2[La(OAr)_5]\}} \qquad (2)$$

Reaction of neodymium trichloride with NaOdpp·0.5thf in 1,3,5-tri(*tert*-butyl)benzene (tbb) at 240–300 °C followed by annealing at 120 °C to induce crystallization gave $\{Na[Nd(Odpp)_4]\}$ **2** [eqn. (3)] in high yield.

$$NdCl_3 + 4NaOdpp \xrightarrow[\text{tbb}]{240\text{–}300\ {}^\circ C} \underset{\mathbf{2}}{\{Na[Nd(Odpp)_4]\}} + 3NaCl \qquad (3)$$

The overall solid-state structure of **1**‡ features a network of alternating $[La(OAr)_5]^{2-}$ anions and Cs^+ cations held in an extended three-dimensional structure by means of multiple caesium–η-arene interactions. Each unit cell contains two crystallographically independent five-coordinate lanthanum metal centres, which are each ligated by five 2,6-diisopropylphenoxide ligands in a pseudo-trigonal bipyramidal geometry. One of the unique $[La(OAr)_5]^{2-}$ anions [containing La(1)] coordinates two unique caesium cations [Cs(2) and Cs(3)] by means of Cs–η-arene interactions as shown in Fig. 1. The second $[La(OAr)_5]^{2-}$ anion [containing La(2)] lies on a twofold axis such that the two caesium cations coordinated to its aryloxide ligands are symmetry-related. The overall three-dimensional structure of **1** may be considered to be built up from layers of two-dimensional sheets containing Cs^+ cations and $[La(OAr)_5]^{2-}$ anions. Each two-dimensional sheet is comprised of one-dimensional chains of alternating $[La(OAr)_5]^{2-}$ anions and Cs(2) cations cross-linked by interactions of Cs(3) with both La(1)- and La(2)-containing $[La(OAr)_5]^{2-}$ moieties. The two-dimensional sheets are further held together in a stacked three-dimensional array through the interactions of Cs(1) with both La(1)- and La(2)-containing $[La(OAr)_5]^{2-}$ moieties from adjacent sheets. The three-dimensional structure features channels which contain four toluene solvent molecules for every three $Cs_2[La(OAr)_5]$ units.

1 appears to be the first structurally characterized example of a lanthanide metal centre coordinated by five aryloxide ligands, and possesses a geometry similar to that observed in the uranium(IV) complex $[Li(thf)_4][U(OC_6H_3Pr^i_2\text{-}2,6)_5]$.[5] The average La–O distance of 2.32 Å [*cf.* U–O of the uranium(IV) complex: 2.15(1)–2.19(2) Å][5] is larger than <La–Odpp> (2.24 Å) of five-coordinate $[La(Odpp)_3(thf)_2]$[6a,b] and longer than

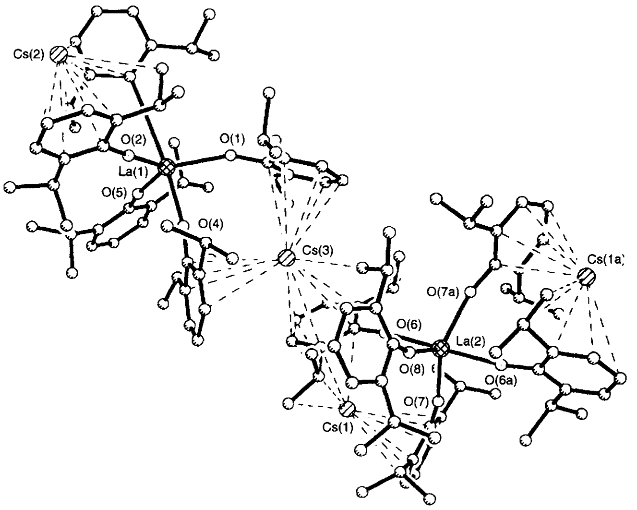

Fig. 1 Ball-and-stick view of a portion of **1**

terminal La–O bond lengths in complexes with coordination number 6-8,[2b,6c,d] indicative of marked steric crowding at the metal centre.

The three unique caesium cation environments all consist exclusively of multihapto Cs–C interactions, with no Cs–O contacts of < 4.6 Å being present within the structure. Cs(1) is found to make Cs–C contacts of < 4.0 Å with a total of 19 carbon atoms. The principal interactions are two η^6-arene interactions [Cs–C ranges 3.32(2)–3.82(2), 3.44(3)–3.57(3) Å] and an η^4-interaction with a third arene moiety. Cs(1) also makes significant interactions with two methyl groups [Cs–C 3.81(2), 3.42(3) Å] in addition to a methine carbon atom. These Cs–C distances lie within the range of 3.35(4)–4.12(1) Å found in other structurally characterized complexes containing Cs–arene interactions.[7] The coordination environment of Cs(2) is similar to that described for Cs(1), in that it also contacts 19 carbon atoms at separations of < 4.0 Å. Once again, two η^6-arene interactions are the primary contacts with Cs–C distances in the range 3.40(2)–3.75(2) Å. Cs(3) makes 18 carbon contacts of < 4.0 Å. Two η^6-arene interactions with Cs–C distances ranging from 3.41(3) to 3.79(3) Å make up the majority of the coordination environment of this caesium cation, with an η^4-arene interaction and two methyl group contacts completing the bonding sphere.

The X-ray structure of {Na[Nd(Odpp)$_4$]} **2**‡ reveals two independent but very similar monomeric molecules (**2a**, **2b**); **2a** is shown in Fig. 2. In **2**, each neodymium is coordinated by the oxygen of one terminal and three bridging (Nd–O–Na) Odpp ligands in a highly distorted tetrahedral array, whilst sodium is surrounded by three bridging oxygen and three phenyl groups, one from each of the bridging Odpp ligands. The three phenyl groups encapsulating sodium not only block association through intermolecular interactions (*cf.* **1**) but also form intramolecular π-Ph–Na interactions. With the limit of *ca.* 3.0–3.1 Å for Na–C(Ph) π bonding established for the unsolvated (only π-Ph bonded) sodium of {Na[(C$_2$Ph$_4$)-Na(OEt$_2$)$_2$]}$_n$[8], rings 12, 26 and 36 of **2a** are η^1-, η^2-, and η^2-bonded respectively to sodium (all Na–C < 3.00 Å; all other Na···C > 3.20 Å). For **2b**, similar bonding can be proposed, although three of the five Na–C distances are in the range 3.00–3.05 Å and there is an additional Na···C contact at 3.113(10) Å. Oxygen bridging between Nd and Na in **2a** leads to small < O$_{br}$–Nd–O$_{br}$ > (85.9°) and large < O$_{br}$–Nd–O$_{ter}$ > (127.7°) angles, but only a marginally longer < Nd–O$_{br}$ > distance (2.239 Å) than Nd–O$_{ter}$ [2.208 Å(4)]. < Nd–O > is similar to that of [Nd(Odpp)$_3$(thf)] (2.193 Å),[6b] which has additional intramolecular η^3-Ph–Nd bonding, and to Nd–O [2.211(8) Å] of the μ-(O,η^6-Ph)-OAr ligand of [Nd$_2$(OAr)$_6$], but significantly longer than < Nd–O$_{ter}$ > (2.122 Å) of the last complex.[4a] Neodymium contacts to C(462) and C(222) are within or close to the range [2.898(12)–3.183(10) Å] for established intra- or inter-molecular π-Ph–Nd bonding in {K[Nd(OAr)$_4$]},[3a] [Nd(Odpp)$_3$(thf)][6b] and [Nd$_2$(OAr)$_6$],[4a] and are considered significant interactions. Interaction of **2** with bis(2-methoxyethyl) ether (diglyme) gives [Na(diglyme)$_2$]-[Nd(Odpp)$_4$] containing the first discrete homoleptic aryloxolanthanide complex anion.[9]

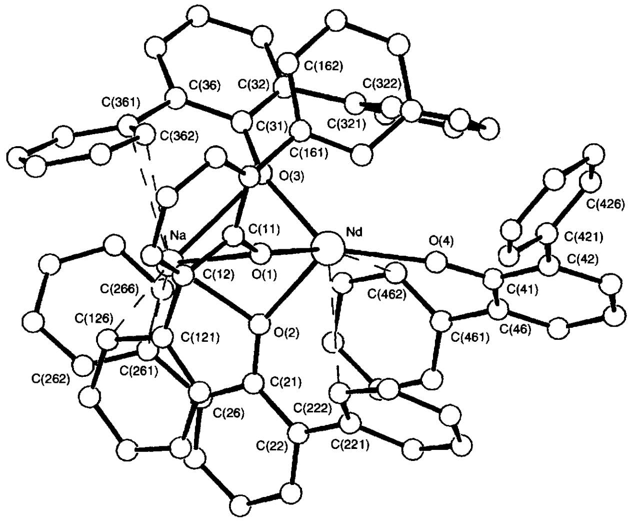

Fig. 2 One of the molecules **2a** of the bimetallic **2**

We are grateful to LANL's Laboratory Directed Research and Development Program (D. L. C., J. G. W.) and the Australian Research Council (G. B. D., A. H. W.) for support.

Footnotes

† *Present address*: LANL, Mail Stop G739, D. L. C.; LANL, Mail Stop C346, J. G. W.

‡ *Crystallographic data*: for **1**; $C_{208}H_{287}Cs_6La_3O_{15}$, $M = 4241.8$, orthorhombic, space group $P2_12_12$, $a = 18.472(2)$, $b = 40.259(6)$, $c = 14.750(2)$ Å, $U = 10969$ Å^3, $D_c = 1.284$ g cm^{-3}, $Z = 2$, $T = 173$ K. Final $R_1 = 0.067$ and $wR_2 = 0.17$ for 8274 observations with $F > 4\sigma(F)$. For **2**: $C_{72}H_{52}NaNdO_4$, $M = 1148.4$, triclinic, space group $P\bar{1}$, $a = 21.232(6)$, $b = 21.250(8)$, $c = 13.912(4)$ Å, $\alpha = 81.32(3)$, $\beta = 80.82(2)$, $\gamma = 63.85(3)°$, $U = 5539$ Å^3, $D_c (Z = 4) = 1.38$ g cm^{-3}. Conventional R on $|F| = 0.048$, R_w (statistical weights) = 0.044. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/135.

References

1 H. Schumann, J. A. Messe-Marktscheffel and L. Esser, *Chem. Rev.*, 1995, **95**, 865; R. C. Mehrotra, A. Singh and U. M. Tripathi, *Chem. Rev.*, 1991, **91**, 1287; F. T. Edelmann, *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 4, ch. 2, pp. 11–212.

2 Most recent examples: (*a*) R. Taube, H. Windisch, F. H. Gorlitz and H. Schumann, *J. Organomet. Chem.*, 1993, **445**, 85; (*b*) W. J. Evans, R. E. Golden and J. W. Ziller, *Inorg. Chem.*, 1993, **32**, 3041; (*c*) S. Song, Q. Shen and S. Jin, *Polyhedron*, 1992, **11**, 2868; (*d*) H. C. Aspinall, S. R. Moore and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1993, 993.

3 (*a*) D. L. Clark, J. C. Huffman and J. G. Watkin, *Inorg. Chem.*, 1992, **31**, 1554; (*b*) D. L. Clark, J. C. Gordon, J. C. Huffman, R. L. Vincent-Hollis, J. G. Watkin and B. D. Zwick, *Inorg. Chem.*, 1994, **33**, 5903; (*c*) D. L. Clark, R. V. Hollis, B. L. Scott and J. G. Watkin, *Inorg. Chem.*, 1996, **35**, 667.

4 (*a*) D. M. Barnhart, D. L. Clark, J. C. Gordon, J. C. Huffman, R. L. Vincent, J. G. Watkin and B. D. Zwick, *Inorg. Chem.*, 1994, **33**, 3487; (*b*) R. J. Butcher, D. L. Clark, S. K. Grumbine, R. L. Vincent-Hollis and J. G. Watkin, *Inorg. Chem.*, 1995, **34**, 5468.

5 P. C. Blake, M. F. Lappert, R. G. Taylor, J. L. Atwood and H. Zhang, *Inorg. Chim. Acta*, 1987, **139**, 13.

6 (*a*) G. B. Deacon, B. M. Gatehouse, Q. Shen, G. Ward and E. R. T. Tiekink, *Polyhedron*, 1993, **12**, 1289; (*b*) G. B. Deacon, T. Feng, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1995, **48**, 741; (*c*) C. J. Schaverien, N. Metjboom and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1992, 124; (*d*) P. Blech, C. Floriani, A. Chiesi-Villa and C. Gustini, *J. Chem. Soc., Dalton Trans.*, 1990, 3557.

7 (*a*) J. M. Harrowfield, M. I. Ogden, W. R. Richmond and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1991, 1159; (*b*) R. Ungaro, A. Casnati, A. P. Ugozzoli, J. F. Dozol, C. Hill and H. Rouquette, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1506; (*c*) A. Steiner and D. Stalke, *Inorg. Chem.*, 1993, **32**, 1977; (*d*) H. Bock, T. Hauck and C. Näther, *Organometallics*, 1996, **15**, 1527.

8 H. Bock, K. Ruppert and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1685.

9 G. B. Deacon, T. Feng, B. W. Skelton and A. H. White, unpublished work.

Received, 1st April 1996; Com. 6/02246D