A tetranuclear neodymium cage which tightly binds sodium carbonate molecules

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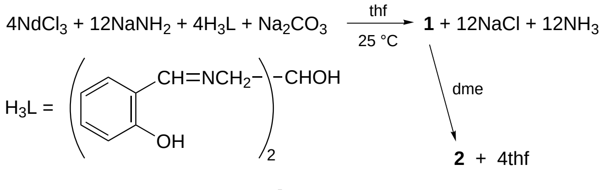
The complexes $[Na_2Nd_4L_4(CO_3)L'_4]$ [H_3L = (*o*-$HOC_6H_4CH{=}NCH_2)_2CHOH$, L′ = tetrahydrofuran or L'_2 = 1,2-dimethoxyethane] have novel cage structures in which $Nd_4O_{12}N_8$ bowl-shaped frameworks of Nd_4L_4 molecules entrap solvated Na_2CO_3 molecules within the cavity of the bowl.

Lanthanoid alkoxide cage complexes are of great interest,[1] but aryloxide analogues are much less common. Some rare examples are based on the 4-methylphenoxide ion and include $[Na_3La_2(\mu_4\text{-OAr})_3(\mu\text{-OAr})_6(thf)_5]$, (thf = tetrahydrofuran, Ar = 4-MeC_6H_4).[2] Cage complexes have the capacity to act as hosts for a variety of guest species,[3] and there is a current focus on incorporation of anionic species, *e.g.* environmentally important contaminants such as phosphate.[4] The Schiff-base ligand (*o*-$HOC_6H_4CH{=}NCH_2)_2CHOH$ (H_3L), which is known to give bimetallics for d-block metals,[5] has the potential, on deprotonation to L^{3-}, to form mixed aryloxo–alkoxo cages with lanthanoid metals. We now report the synthesis and structure of a tetranuclear neodymium cage based on this ligand. This host tightly encapsulates solvated sodium carbonate within the cavity of the cluster, and a novel binding mode of $CO_3{}^{2-}$ is observed.

Reaction of anhydrous $NdCl_3$, H_3L, sodium amide and sodium carbonate in thf at room temperature (Scheme 1) resulted in triple deprotonation of the ligand and gave a blue solution from which was isolated air- and moisture-sensitive pink $[Na_2Nd_4L_4(CO_3)(thf)_4]$ **1**, in good yield.† Recrystallisation of **1** from 1,2-dimethoxyethane (dme) yielded the air- and moisture-sensitive pink complex $[Na_2Nd_4L_4(CO_3)(dme)_2]\cdot 1.5$ dme, **2**·1.5 dme.†

A synthesis in the absence of sodium carbonate gave a product with analytical composition $NdL(thf)_2$ which could not be crystallized in a form suitable for X-ray studies nor were the solubility properties suitable for characterization in solution.

The molecular structures of both **1** and **2** (Fig. 1), established by X-ray crystallography,‡ feature a tetranuclear, bowl-shaped, cage $[Nd_4L_4]$ with quasi-twofold symmetry. Within the cavity of the cage resides a multiply anchored, solvated sodium carbonate molecule, $Na_2CO_3L'_4$ (L′ = thf or L'_2 = dme). One carbonate oxygen bridges two sodium atoms, whilst each of the others bridges one sodium and two neodymium atoms. The carbonate coordination appears unique in combining μ_6-bridging with chelation to two of the bridged atoms (**I**). This contrasts the known simple μ_6-bridging[6] for the unique $CO_3{}^{2-}$ in the centre of $[(VO)_6(\mu_6\text{-}CO_3)(\mu\text{-}CO_3)_3(OH)_9]^{5-}$, and the recently observed μ_9-bridging in a lithium siloxane complex.[7] Each sodium is five-coordinate, being bound not only by the chelating carbonate and thf or dme, but also by a bridging aryloxide oxygen of the cage (see below). Thus, sodium carbonate is securely bonded to the cage.



Scheme 1

The Nd_4L_4 cage contains square-antiprismatic eight-coordinate neodymium atoms with Nd(1) and Nd(1a) of **2** different from Nd(1′) and Nd(1a′) (Fig. 1). The former are coordinated by two imide nitrogens, one η^1- and two μ-aryloxide (NdONd and NdONa) oxygens, one μ_3- and one μ-alkoxide oxygen, and a μ_3-carbonate oxygen (ONd_2Na). By contrast, the latter pair are

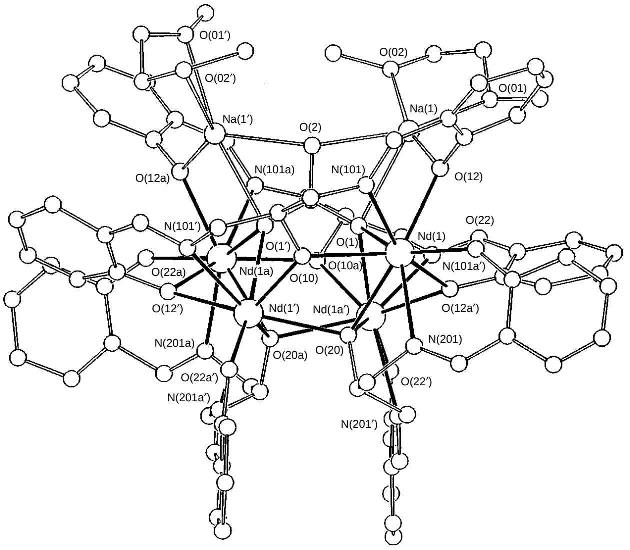
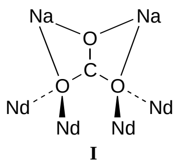


Fig. 1 Molecular projection of $[Na_2Nd_4L_4(CO_3)(dme)_2]$ **2** normal to the quasi-twofold axis; hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Nd–(η^1-OAr), Nd(1)–O(22) 2.24(3), Nd(1a)–O(22a) 2.32(3), Nd(1′)–O(22a′) 2.35(2), Nd(1a′)–O(22′) 2.22(2); M–(μ-OAr), Nd(1)–O(12) 2.26(1), Nd(1)–O(12a′) 2.57(2), Nd(1a)–O(12a) 2.34(1), Nd(1a)–O(12′) 2.61(2), Nd(1′)–O(12′) 2.42(2), Nd(1a′)–O(12a′) 2.39(2), Na(1)–O(12) 2.34(3), Na(1′)–O(12a) 2.25(3); M–(μ-OCH), Nd(1)–O(10) 2.40(1), Nd(1a)–O(10a) 2.34(2), Nd(1′)–O(10) 2.36(2), Nd(1a′)–O(10a) 2.43(2); M–(μ_3-OCH), Nd(1)–O(20) 2.54(2), Nd(1a)–O(20a) 2.57(1), Nd(1′)–O(20) 2.47(1), Nd(1′)–O(20a) 2.46(2), Nd(1a′)–O(20) 2.49(2), Nd(1a′)–O(20a) 2.48(1); Na–(μ-OCO_2), Na(1)–O(2) 2.37(2), Na(1′)–O(2) 2.35(2); M–(μ_3-OCO_2), Nd(1)–O(1) 2.51(2), Nd(1a)–O(1′) 2.48(2), Nd(1′)–O(1′) 2.56(1), Nd(1a′)–O(1) 2.51(1), Na(1)–O(1) 2.56(1), Na(1′)–O(1′) 2.50(1); Nd–N, 2.51(2)–2.63(2); Na–O(dme), 2.48(2)–2.60(2). Selected bond angles (°) O(1)–C(1)–O(1′) 123(1), O(1)–C(1)–O(2) 117(2), O(1′)–C(1)–O(2) 120(2).



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coordinated by two nitrogens, one η^1- and one μ-(NdONd)-aryloxide oxygen, one μ- and two μ_3-alkoxide oxygens and a μ_3-carbonate oxygen.

The deprotonated ligands are bridging pentadentate and bind to each of two Nd atoms with three donor atoms, and to a further Nd by one donor atom. However, two ligands have μ_3-alkoxo donors [O(20) or O(20a)] and two η^1-aryloxide oxygens whereas the other two contain μ-alkoxo donors [O(10) or O(10a)], and two μ-aryloxide oxygens.

The Nd–OAr distances (Fig. 1) feature short bonds to the η^1-bonded oxygens and the μ-oxygens bridging to sodium, whilst the Nd–O(Ar)–Nd bonds are significantly longer for Nd(1,1a) but only marginally longer for Nd(1′,1a′). The Nd–(η^1-O) bond lengths are comparable with those of La–(η^1-OAr) of seven-coordinate lanthanum in the rare aryloxo cluster $NMe_4[Na_2La_2(\mu_4\text{-OAr})(\mu_3\text{-OAr})_2(\mu\text{-OAr})_4(\eta^1\text{-OAr})_2(thf)_5]$, (Ar = 4-$MeC_6H_4$).[2] (The effect of the higher coordination number of **2** offsets that of the smaller lanthanoid radius.) For Nd(1, 1a), Nd–(μ-OCH) distances are markedly shorter than Nd–(μ_3-OCH), whereas these distances differ less for Nd(1′, 1a′) (Fig. 1). However, the range is similar to that for previously reported Nd–(μ or μ_3-OR) bonds (*e.g.* R = CH_2Bu^t, $CHPr^i_2$).[1,8] Average Na–(μ-OAr) distances are somewhat longer than those of four-coordinate $[Na\{OC_6H_2(CF_3)_3\text{-}2,4,6\}(thf)_2]_2$[9] as is reasonable for the coordination number difference. Nd–O–CO_2 distances are comparable with those in the eight-coordinate Nd cage, $[Nd_8(thd)_8(H_2O)_2(\mu\text{-}Bu^tCO_2)_6(\mu_3\text{-OH})_6(\mu_6\text{-}CO_3)_2]$, (thd = 2,2,6,6-tetramethylheptane-3,5-dionate).[10] Although there is considerable variation in the Na–OCO_2 distances (Fig. 1), this can be attributed to the expected difference between bonding to μ- and μ_3-bridged oxygens. Moreover, a similar range has been observed for ‘strongly bonded’ Na–(μ-O) in $[Na_3\{Ru_2(CO_3)_4\}\cdot 6H_2O]_n$.[11] The Nd$\cdots$Nd separations [3.803(3)–3.844(4) Å] are not much larger than the sum (3.63 Å)[12] of the six-coordinate metal radii encouraging our planned investigation of the magnetic properties to explore possible Nd$\cdots$Nd interactions.

We have also recently prepared and crystallographically characterized other complexes which incorporate the Nd_4L_4 stoichiometry. These include $[Na_5Nd_4L_4(OH)(OMe)_4(HOMe)(dme)_3]$, which contains the Nd_4L_4 cage in a different arrangement and encapsulates NaOH and NaOMe molecules.[13] This indicates the cage can be prepared independently of Na_2CO_3 and will accommodate other species.

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Footnotes

† All operations were carried out under an atmosphere of purified N_2 or Ar because of the extreme sensitivity of the compounds to air and moisture. **1**: a mixture of $NdCl_3$ (0.50 g, 2.0 mmol), H_3L (0.59 g, 2.0 mmol), $NaNH_2$ (0.40 g, 8.0 mmol) and Na_2CO_3 (0.20 g, 1.7 mmol) in thf (50 ml), was rapidly stirred at ambient temperature for 48 h, whereupon a light blue solution and a white precipitate was produced. After filtration, concentration and addition of a small amount of pentane (*ca.* 5 ml), dichroic light pink crystals of **1** deposited on prolonged standing (yield 66%) (Found: C, 47.4, H, 4.5, N, 5.5, Nd, 28.2, Na, 1.9%. $C_{85}H_{92}N_8Na_2Nd_4O_{19}$ requires C, 47.4, H, 4.3, N, 5.2, Nd, 26.8, Na, 2.1%). IR (Nujol): 1629vs, 1596s, 1550m, 1538s, 1347s, 1323s, 1302s, 1245w, 1218m, 1193m, 1145s, 1124m, 1107w, 1063m, 1040s, 1026s, 965w, 896m, 865m, 848w, 791w, 756s, 738s, 702m, 646w, 592m cm^{-1}. λ_{max} (thf)/nm (ε/$dm^3\ mol^{-1}\ cm^{-1}$): 575 (213), 582 (209), 737 (130).

2: complex **1** was recrystallised from dme, and dichroic light pink crystals of **2** were obtained on prolonged standing (Found: C, 46.4, H, 4.8, N, 5.4%. $C_{83}H_{95}N_8Na_2Nd_4O_{22}$ requires C, 45.7, H, 4.4, N, 5.1%). IR (Nujol): 1627vs, 1596s, 1540m, 1341m, 1322m, 1290m, 1193w, 1146w, 1125w, 1057w, 1028m, 974w, 896w, 865w, 851w, 789w, 758s, 738m, 728m, 694w, 624w, 588w cm^{-1}. λ_{max} (thf)/nm (ε/$dm^3\ mol^{-1}\ cm^{-1}$): 528 (78), 577 (100), 583 (115), 737 (93), 756 (89).

‡ *Crystallographic data*: **2**: air-sensitive pink crystals, $C_{83}H_{95}N_8Na_2Nd_4O_{22}$, M = 2179.8, monoclinic, space group $P2_1/c$, a = 25.90(1), b = 22.88(2), c = 15.331(6) Å, β = 90.89(4)°; $2\theta_{max}$ = 45°. N (unique) = 10733; N_0 [$I > 3\sigma(I)$; absorption corrected] = 4197. R, R_w = 0.066, 0.052. Anisotropic thermal parameter refinement for Nd, Na, O, N; $(x, y, z, U_{iso})_H$ included at constrained estimates. Abnormal features: high thermal motion on the ether ligands.

1 (a less satisfactory result): $C_{85}H_{92}N_8Na_2Nd_4O_{19}$, M = 2152.7, modelled as orthorhombic; space group *Pnca*, a = 25.30(3), b = 23.67(1), c = 15.077(5) Å; $2\theta_{max}$ = 40°. N, N_o = 4868, 2773. R, R_w = 0.092, 0.097. (Nd, Na anisotropic) with similar connectivity to **2** which it predates. The result of **2** raises the possibility that **1** is actually isomorphous, pseudo-orthorhombic, with monoclinic β = 90°; no further adequately crystalline material has been forthcoming to pursue the point further.

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 182/345.

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