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Synthesis and Structure of New Lanthanoid Carbonate "Lanthaballs"

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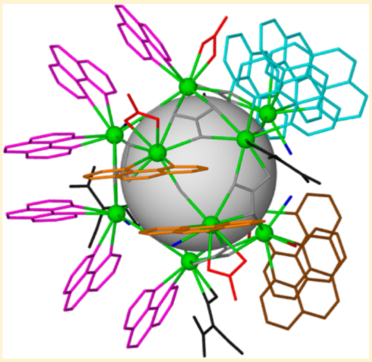
Supporting Information



ABSTRACT: New insights into the synthesis of high-nuclearity polycarbonatolanthanoid complexes have been obtained from a detailed investigation of the preparative methods that initially yielded the so-called "lanthaballs" $[Ln_{13}(ccnm)_6(CO_3)_{14}(H_2O)_6(phen)_{18}]Cl_3(CO_3)\cdot25H_2O$ [**α-1Ln**; Ln = La, Ce, Pr; phen = 1,10-phenanthroline; ccnm = carbamoylcyanonitrosomethanide]. From this investigation, we have isolated a new pseudopolymorph of the cerium analogue of the lanthaball, $[Ce_{13}(ccnm)_6(CO_3)_{14}(H_2O)_6(phen)_{18}]\cdot Cl_3\cdot CO_3$ (**β-1Ce**). This new pseudopolymorph arose from a preparation in which fixation of atmospheric carbon dioxide generated the carbonate, and the ccnm ligand was formed in situ by the nucleophilic addition of water to dicyanonitrosomethanide. From a reaction of cerium(III) nitrate, instead of the previously used chloride salt, with $(Et_4N)(ccnm)$, phen, and $NaHCO_3$ in aqueous methanol, the new complex $Na[Ce_{13}(ccnm)_6(CO_3)_{14}(H_2O)_6(phen)_{18}](NO_3)_6\cdot 20H_2O$ (**2Ce**) crystallized. A variant of this reaction in which sodium carbonate was initially added to $Ce(NO_3)_3$, followed by phen and $(Et_4N)(ccnm)$, also gave **2Ce**. However, an analogous preparation with $(Me_4N)(ccnm)$ gave a mixture of crystals of **2Ce** and the coordination polymer $[CeNa(ccnm)_4(phen)_3]\cdot MeOH$ (**3**), which were manually separated. The use of cerium(III) acetate in place of cerium nitrate in the initial preparation did not give a high-nuclearity complex but a new coordination polymer, $[Ce(ccnm)(OAc)_2(phen)]$ (**4**). The first lanthaball to incorporate neodymium, namely, $[Nd_{13}(ccnm)_4(CO_3)_{14}(NO_3)_4(H_2O)_7(phen)_{15}](NO_3)_3\cdot 10H_2O$ (**5Nd**), was isolated from a preparation similar to that of the second method used for **2Ce**, and its magnetic properties showed an antiferromagnetic interaction. The identity of all products was established by X-ray crystallography.

INTRODUCTION

The highly varied coordination modes of the carbonate anion have facilitated high-nuclearity complex formation,[1] but its tendency to rapidly precipitate metals from solution may act as a deterrent for employing it as a complex building agent.[2] Carbonate anions have therefore generally played a marginal role in high-nuclearity complex formation and have been used mainly in conjunction with other bridging groups,[3] although some recent examples do contain carbonates as the primary complex forming agent.[4] There are three primary routes of introducing carbonate anions into a reaction: (1) the direct addition of Na_2CO_3, $NaHCO_3$, or another carbonate salt;[5] (2) the atmospheric fixation of CO_2, leading to the in situ generation of carbonate;[4a,b,6] and (3) the decomposition of a precursor, giving carbonate as a coproduct.[3c,d]

During our studies of the magnetic properties of polynuclear complexes incorporating nucleophilic addition derivatives of the dicyanonitrosomethanide (dcnm) anion,[7] we reported the one-pot synthesis of tridecanuclear polycarbonatolanthanoid complexes in the compounds $[Ln_{13}(ccnm)_6(CO_3)_{14}(H_2O)_6(phen)_{18}]Cl_3(CO_3)\cdot25H_2O$ (**α-1Ln**; Ln = La, Ce, Pr; phen = 1,10-phenanthroline; ccnm = carbamoylcyanonitrosomethanide).[8] The cationic complexes were termed "lanthaballs" because of their spherical nature (Figure 1a). At the core of the lanthaball complex lies a distinctive $[Ln_{13}(CO_3)_6]$ moiety (Figure 1b), in which a unique central 12-coordinate lanthanoid atom is coordinated by six carbonate ligands. Each of these carbonates, in turn, coordinates to another two lanthanoid atoms to give a

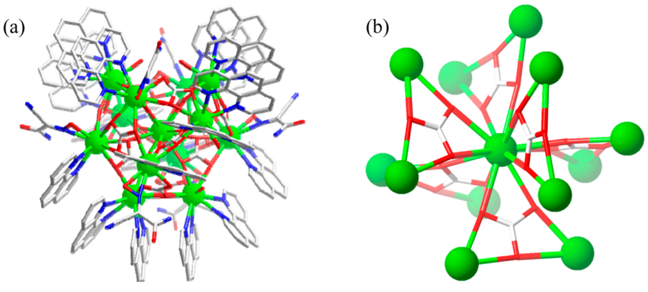


Figure 1. (a) Structure of the cationic "lanthaball" $[Ce_{13}(ccnm)_6(CO_3)_{14}(H_2O)_6(phen)_{18}]^{5+}$ of **α-1Ce**. Hydrogen atoms are omitted for clarity. The compound **α-1Ce** is representative of compounds **α-1Ln** (Ln = La, Ce, Pr). (b) $[Ce_{13}(CO_3)_6]$ moiety at the center of the cationic complex in **α-1Ce**.

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μ-1κ(O,O′):2κ(O′,O″):3κ(O,O″) coordination mode. Additional carbonate ligands bridge between the outer lanthanoid atoms to complete the $[Ln_{13}(CO_3)_{14}]$ core unit. On the surface of the $[Ln_{13}(CO_3)_{14}]$ core are three rows of six π-stacked phen ligands, six η^2(N,O) coordinating ccnm ligands, and six aqua ligands.

To the best of our knowledge, lanthaballs contain the only known examples of lanthanoid atoms chelated by six carbonate ligands in coordination complexes that have been characterized crystallographically. While the existence of a $[Ce^{IV}(CO_3)_6]$ species has been inferred from electrochemical analysis,[9] solid-state examples of high-coordinate homoleptic lanthanoids with carbonate ligands are limited to $[Ce^{IV}(CO_3)_5]^{6-}$ and $[Ln^{III}(CO_3)_4]^{5-}$ (Ln = Y, Dy, Ho, Er, Tm, Yb, Lu).[10,11]

The use of the heavier lanthanoids gadolinium and dysprosium under similar reaction conditions yielded the tetradecanuclear complexes $[Gd_{14}(ccnm)_9(CO_3)_{13}(OH)(NO_3)(H_2O)_6(phen)_{13}](CO_3)_{2.5}\cdot phen$ and $[Dy_{14}(ccnm)_{10}(CO_3)_{13}(OH)(H_2O)_6(phen)_{13}](CO_3)_{2.5}\cdot phen$, respectively.[12] These complexes lack the internal symmetry of the lanthaballs but contain a high degree of structural diversity, with both the carbonate and ccnm ligands displaying four unique coordination modes.

In light of the ongoing interest in the synthesis of polycarbonate complexes, we have continued our study of the lanthaballs and, in particular, ***α*-1Ce**. In the first component of this paper, we report the new pseudopolymorph ***β*-1Ce** resulting from a carbon dioxide (CO_2) fixation reaction and examine how alterations to the reaction conditions that yielded the original series of lanthaballs can give rise to new derivatives while still retaining the $[Ce_{13}(CO_3)_{14}]$ core motif. The following section shows that further variations in the reaction conditions can instead lead to the formation of coordination polymers that do not incorporate the carbonate anion. This latter result highlights the difficulties that may be encountered in attempting to synthesize high-nuclearity, multicomponent complexes without the concurrent formation of coproducts. Furthermore, conditions have been found that generate the first lanthaball complex with neodymium, for which the magnetic data were obtained.

EXPERIMENTAL SECTION

General Procedures. All materials and solvents were purchased from standard commercial sources and used without further purification. $(Et_4N)(ccnm)$ and $(Me_4N)(ccnm)$ were prepared by literature methods.[8,13] $(Et_4N)(dcnm)$ was prepared by a metathesis reaction between Ag(dcnm) and $(Et_4N)Br$ and used as a stock solution. IR data were collected using a PerkinElmer ATR-FTIR spectrometer in the range 4000−500 cm^{-1} with a resolution of 4 cm^{-1}. Elemental analyses were performed by the Campbell Microanalytical Laboratory of the University of Otago, Dunedin, New Zealand.

Synthesis. *Synthesis of $[Ce_{13}(ccnm)_6(CO_3)_{14}(H_2O)_6(phen)_{18}]Cl_3(CO_3)\cdot 25H_2O$ (**β-1Ce**).* $(Et_4N)(dcnm)$ (100 mg, 446 μmol) dissolved in methanol (1 mL) was added to 1,10-phenanthroline monohydrate (44 mg, 222 μmol) in methanol (4 mL). $CeCl_3\cdot 7H_2O$ (41 mg, 110 μmol) dissolved in methanol (1 mL) was then added to the reaction solution, which was allowed to evaporate to dryness over a period of 1 month. A small orange crystal was removed from an amorphous white precipitate and characterized by X-ray crystallography as the pseudopolymorph complex ***β*-1Ce**. Insufficient material was available for further analysis to determine the degree of solvation.

*Synthesis of $Na[Ce_{13}(ccnm)_6(CO_3)_{14}(H_2O)_6(phen)_{18}](NO_3)_6\cdot 20H_2O$ (**2Ce**).* $Ce(NO_3)_3\cdot 6H_2O$ (178 mg, 410 μmol) was dissolved in methanol (3 mL) and added to $(Et_4N)(ccnm)$ (100 mg, 412 μmol) in methanol (2 mL). 1,10-Phenanthroline monohydrate (164 mg, 827 μmol) dissolved in methanol (2 mL) was added to the reaction solution along with $NaHCO_3$ (34 mg, 404 μmol) dissolved in water (1 mL), resulting in the immediate formation of a suspension. After 1 week, orange needle crystals were manually separated from the precipitate and washed with methanol (40 mg, 19%). IR (ATR): ν 3360 (m), 2324 (vw), 2288 (vw), 2218 (vw), 2166 (vw), 2051 (w), 1668 (m), 1624 (vw), 1590 (vw), 1514 (vw), 1460 (sh), 1418 (s), 1342 (w), 1208 (w), 1138 (w), 1101 (w), 1036 (vw), 839 (m), 728 (m) cm^{-1}. Elem anal. Calcd for $C_{248}H_{208}Ce_{13}N_{60}NaO_{98}$ (7441.15): C, 40.03; H, 2.82; N, 11.29. Found: C, 40.07; H, 2.42; N, 11.46. Calcd for a sample dried at 150 °C under high vacuum, resulting in the removal of a lattice solvent, $C_{248}H_{168}Ce_{13}N_{60}NaO_{78}$ (7080.84): C, 42.07; H, 2.39; N, 11.97. Found: C, 41.99; H, 2.30; N, 11.96.

*Alternate Synthesis of **2Ce**.* Na_2CO_3 (22 mg, 208 μmol) dissolved in water (1 mL) was added to $Ce(NO_3)_3\cdot 6H_2O$ (89 mg, 206 μmol) dissolved in methanol (2 mL), resulting in the formation of a white precipitate. 1,10-Phenanthroline monohydrate (81 mg, 407 μmol) dissolved in methanol (2 mL) and $(Et_4N)(ccnm)$ (50 mg, 206 μmol) dissolved in methanol (1 mL) were added to the reaction solution. After 1 month, several orange crystals of the product formed in the reaction solution. The crystals were identified by X-ray crystallography as compound **2Ce**.

*Synthesis of $[CeNa(ccnm)_4(phen)_3]\cdot MeOH$ (**3**).* $Ce(NO_3)_3\cdot 6H_2O$ (116 mg, 267 μmol) was dissolved in methanol (2 mL) and added to Na_2CO_3 (28 mg, 264 μmol) dissolved in water (1 mL), resulting in the immediate formation of a white precipitate. 1,10-Phenathroline monohydrate (106 mg, 535 μmol) dissolved in methanol (2 mL) and $(Me_4N)(ccnm)$ (50 mg, 269 μmol) dissolved in water (1 mL) were added to the reaction solution. Red needles of **3** formed among orange needles, which were identified by X-ray crystallography as **2Ce**, over a period of 5 months. The product **3** was manually isolated, washed with methanol and diethyl ether, and air-dried (5 mg, 6%). Elemental analysis indicates exchange of one molecule of water for one molecule of lattice methanol upon atmospheric exposure. IR (ATR): ν 3471 (w), 3211 (m), 3218 (m), 2214 (w), 1660 (s), 1591 (m), 1515 (w), 1499 (vw), 1417 (s), 1342 (w), 1206 (m), 1123 (m), 1097 (vw), 1020 (w), 862 (vw), 841 (m), 769 (w), 730 (w), 716 (w), 685 (w) cm^{-1}. Elem anal. Calcd for $C_{48}H_{34}CeN_{18}NaO_9$ (1170.01): C, 49.27; H, 2.92; N, 21.55. Found: C, 49.18; H, 3.15; N, 21.18.

*Synthesis of $[Ce(ccnm)(OAc)_2(phen)]$ (**4**).* $Ce(OAc)_3$ (131 mg, 413 μmol) was suspended in methanol (3 mL) and water (1 mL) and added to $(Et_4N)(ccnm)$ (100 mg, 412 μmol) dissolved in methanol (2 mL). 1,10-Phenanthroline monohydrate (164 mg, 827 μmol) dissolved in methanol (2 mL) and $NaHCO_3$ (34 mg, 404 μmol) dissolved in water (1 mL) were added to the reaction solution. Over a period of 3 months, an isolated crystal of **4** formed with no evidence of polycarbonatolanthanoid complexes cocrystallizing from the reaction solution. The single crystal was removed from the reaction solution for X-ray diffraction analysis; insufficient sample was available for further analysis.

*Synthesis of $[Nd_{13}(ccnm)_4(CO_3)_{14}(NO_3)_4(H_2O)_7(phen)_{15}](NO_3)_3\cdot 10H_2O$ (**5Nd**).* Na_2CO_3 (22 mg, 208 μmol) dissolved in water (1 mL) was added to $Nd(NO_3)_3\cdot 6H_2O$ (90 mg, 206 μmol) dissolved in methanol (2 mL), resulting in the formation of a white precipitate. 1,10-Phenanthroline monohydrate (81 mg, 407 μmol) dissolved in methanol (2 mL) and $(Et_4N)(ccnm)$ (50 mg, 206 μmol) dissolved in methanol (1 mL) were added to the reaction solution. After 1 month, puce crystals of the product formed in the reaction solution. The white precipitate was manually removed as a suspension in ethanol, with the remaining product washed with ethanol and left to air dry (17 mg, 17%). IR (ATR): ν 3382 (m, br), 3058 (vw), 2361 (vw), 2216 (w), 1663 (m), 1624 (w), 1590 (w), 1544 (m), 1419 (s), 1342 (w), 1311 (m), 1208 (w), 1138 (w), 1100 (w), 1062 (w), 835 (m), 728 (m) cm^{-1}. Elem anal. Calcd for $C_{206}H_{162}N_{49}Nd_{13}O_{88}$ (6606.89): C, 37.45; H, 2.47; N, 10.39. Found: C, 37.26; H, 2.12; N, 10.51. Calcd for a sample dried at 150 °C under high vacuum, resulting in the removal of a lattice solvent, $C_{206}H_{142}Nd_{13}N_{49}O_{78}$ (6426.74): C, 38.50; H, 2.23; N, 10.68. Found: C, 38.98; H, 2.19; N, 10.97.

Magnetic Susceptibility Measurements. Direct-current (dc) magnetic susceptibility measurements were carried out on a Quantum Design SQUID MPMS-XL 7 magnetometer operating between 2 and 300 K for dc applied fields ranging from 0 to 5 T. Microcrystalline samples were dispersed in Vaseline in order to avoid torquing of the crystallites. The sample mull was contained in a calibrated gelatin capsule held at the center of a drinking straw that was fixed at the end of the sample rod. Alternating-current (ac) susceptibility measurements were carried out on the same instrument utilizing an oscillating ac field of 3.5 Oe and frequencies ranging from 0.1 to 1500 Hz.

X-ray Crystallography. Crystals were mounted on fine glass fibers using viscous hydrocarbon oil. Data were collected on a Bruker X8 Apex II CCD (**2Ce** and **3**) or a Nonius Kappa CCD (**β-1Ce** and **4**) diffractometer, both equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection temperatures were maintained at 123 K using an open-flow N_2 cryostream. For data collected on the Nonius Kappa CCD diffractometer, integration was carried out by the program *DENZO-SMN* and data were corrected for Lorentz−polarization effects and for absorption using the program *SCALEPACK*.[14] For data collected on the Bruker X8 Apex II diffractometer, integration was carried out by the program *SAINT* using the *Apex II* software suite.[15] All data sets were treated for the effects of absorption. Data for **5Nd** were collected at 100 K on the MX1 beamline at the Australian Synchrotron (λ = 0.773430 Å). The data collection and integration were performed within the *Blu-Ice*[16] and *XDS* software programs, respectively.[17] Solutions were obtained by direct methods or Patterson synthesis using *SHELXS-97* followed by successive refinements using the full-matrix least-squares method against F^2 using *SHELXL-97*.[18] The program *X-Seed* was used as a graphical *SHELX* interface.[19]

CCDC 1012371 (for **β-1Ce**), 1012372 (for **2Ce**), 1012373 (for **3**), 1012374 (for **4**), and 1012375 (for **5Nd**) 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.

Crystal data for β-1Ce: $C_{248}H_{168}Ce_{13}Cl_3N_{54}O_{60}$, M = 6792.27, orange block, 0.20 × 0.20 × 0.10 mm^3, orthorhombic, space group *Pbcn* (No. 60), a = 23.163(5) Å, b = 35.460(7) Å, c = 35.715(7) Å, V = 29335(10) Å^3, Z = 4, D_c = 1.538 g cm^{-3}, F_{000} = 13276, $2\theta_{max}$ = 55.0°, 154075 reflections collected, 32407 unique (R_{int} = 0.1280). Final GOF = 0.964, R1 = 0.0678, wR2 = 0.1674, R indices based on 16116 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1691 parameters, 0 restraints. μ = 2.077 mm^{-1}. Large thermal parameters on one phen ligand are most likely due to the fact that it may be delocalized over two positions. Unfortunately, this phen ligand cannot be satisfactorily modeled over two positions, so it remains refined in a single position. Chloride atoms were refined isotropically. The structure contains significant disordered solvent regions of 7664 Å^3 containing highly disordered solvent and anions that could not be satisfactorily assigned. The data were therefore treated with the *SQUEEZE* routine of *PLATON*.[20] The *SQUEEZE* routine accounted for 4751 electrons per unit cell.

Crystal data for 2Ce: $C_{248}H_{208}Ce_{13}N_{60}NaO_{98}$, M = 7441.28, orange shard, 0.40 × 0.30 × 0.20 mm^3, trigonal, space group $P\bar{3}1c$ (No. 163), a = 25.1869(3) Å, c = 30.8325(9) Å, V = 16939.0(6) Å^3, Z = 2, D_c = 1.459 g cm^{-3}, F_{000} = 7330, $2\theta_{max}$ = 55.0°, 56343 reflections collected, 12766 unique (R_{int} = 0.0526). Final GOF = 1.131, R1 = 0.0687, wR2 = 0.1876, R indices based on 8709 reflections with $I > 2\sigma(I)$ (refinement on F^2), 605 parameters, 0 restraints. μ = 1.792 mm^{-1}. The structure contains significant disordered solvent regions of 5823 Å^3 containing highly disordered solvent and anions that could not be satisfactorily assigned. The data were therefore treated with the *SQUEEZE* routine of *PLATON*.[20] The *SQUEEZE* routine accounted for 3504 electrons per unit cell.

Crystal data for 3: $C_{49}H_{36}CeN_{18}NaO_9$, M = 1184.07, dark-orange block, 0.35 × 0.25 × 0.20 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 11.6974(2) Å, b = 18.9426(3) Å, c = 22.8571(5) Å, β = 92.565(1)°, V = 5059.58(16) Å^3, Z = 4, D_c = 1.554 g cm^{-3}, F_{000} = 2388, $2\theta_{max}$ = 55.0°, 24940 reflections collected, 11569 unique (R_{int} = 0.0343). Final GOF = 1.056, R1 = 0.0422, wR2 = 0.0770, R indices based on 8809 reflections with $I > 2\sigma(I)$ (refinement on F^2), 705 parameters, 0 restraints. μ = 0.984 mm^{-1}.

Crystal data for 4: $C_{19}H_{16}CeN_5O_6$, M = 550.49, orange shard, 0.20 × 0.20 × 0.15 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 13.2907(4) Å, b = 18.3890(5) Å, c = 9.0517(2) Å, β = 98.235(2)°, V = 2189.45(10) Å^3, Z = 4, D_c = 1.670 g cm^{-3}, F_{000} = 1084, $2\theta_{max}$ = 55.0°, 16038 reflections collected, 5026 unique (R_{int} = 0.1060). Final GOF = 1.022, R1 = 0.0370, wR2 = 0.0837, R indices based on 4016 reflections with $I > 2\sigma(I)$ (refinement on F^2), 282 parameters, 0 restraints. μ = 2.123 mm^{-1}.

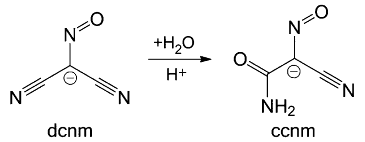
Crystal data for 5Nd: $C_{206}H_{162}N_{49}Nd_{13}O_{88}$, M = 6606.96, purple shard, 0.05 × 0.05 × 0.01 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 22.030(4) Å, b = 46.310(9) Å, c = 26.630(5) Å, β = 90.32(3)°, V = 27168(9) Å^3, Z = 4, D_c = 1.615 g cm^{-3}, F_{000} = 12900, $2\theta_{max}$ = 48.1°, 300450 reflections collected, 41659 unique (R_{int} = 0.0896). Final GOF = 1.058, R1 = 0.0451, wR2 = 0.1231, R indices based on 36652 reflections with $I > 2\sigma(I)$ (refinement on F^2), 2912 parameters, 14 restraints. μ = 2.523 mm^{-1}. Some carbamoyl groups and sections of phen groups refined with DFIX and DANG commands. Two ccnm ligands were refined isotropically with U(iso) values refined using FVAR. The structure contains significant disordered solvent regions of 8645 Å^3 containing highly disordered solvent and anions that could not be satisfactorily assigned. The data were therefore treated with the *SQUEEZE* routine of *PLATON*.[20] The *SQUEEZE* routine accounted for 2136 electrons per unit cell.

■ RESULTS AND DISCUSSION

Synthesis of Cerium Lanthaball Derivatives. Our study on the synthesis of polycarbonatolanthanoid complexes was precipitated by a serendipitous CO_2 fixation reaction in which a single crystal of compound **β-1Ce** formed upon evaporation of a methanolic solution containing $CeCl_3$, (Et_4N)(dcnm) and phen during an attempt to remake the mononuclear complex $(Et_4N)[Ce(dcnm)_4(phen)_2]$.[21] Because only one crystal of the product formed, it was characterized by X-ray crystallography, and the development of an alternate synthetic method that would give a higher yield was necessary. This was achieved through a direct reaction of $LnCl_3 \cdot xH_2O$ (Ln = La, Ce, Pr), (Et_4N)(ccnm), $Na(HCO_3)$, and phen in a methanol/water solution, resulting in the formation of crystals of **α-1Ln**, which were separated from an amorphous precipitate through manual washing.[8]

In the original synthesis of the tridecanuclear complex, two distinct types of in situ ligand formation occurred: the fixation of atmospheric CO_2 to give carbonate anions and the nucleophilic addition of water to the dcnm anion to give the ccnm anion. Because lighter lanthanoids, such as cerium, have yet to demonstrate an ability to promote the nucleophilic reaction with dcnm, it would appear likely that the presence of an acid in the solution catalyzed the reaction.[13] CO_2 dissolved in water exists in equilibrium with carbonic acid,[22] which, in this instance, may act as a suitable proton source to catalyze this reaction (Scheme 1).

Scheme 1. Addition of Water to dcnm to Form ccnm



While the molecular structure of the cerium lanthaball formed by CO_2 fixation is essentially identical with the same complex synthesized by direct reaction with $Na(HCO_3)$,[8] it crystallizes as a different pseudopolymorph in the space group *Pbcn*, with half of the complex in the asymmetric unit. Furthermore, while in the previously reported pseudopolymorph the complex packs in a series of offset columns, in the present pseudopolymorph the complexes form a regular cubic array (Figure 2).

Because the chloride anions in the lattice of compounds **α-1Ln** and **β-1Ce** play an important role in the hydrogen bonding on

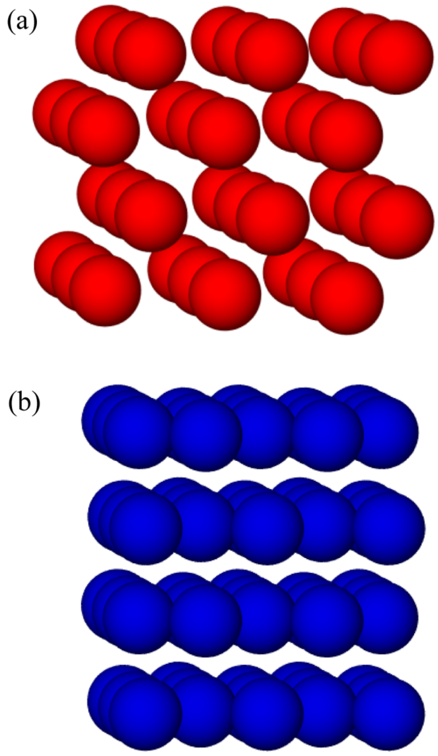


Figure 2. Packing of the cationic complexes in (a) the previously reported pseudopolymorph of **α-1Ce** and (b) the second pseudopolymorph **β-1Ce**, reported here. Both figures are viewed down the crystallographic *b* axis.

the periphery of the complex, the synthesis from cerium nitrate was examined to determine if the change in the counteranion would alter the arrangement of ligands on the surface of the lanthaball. Accordingly, the reaction of $Ce(NO_3)_3 \cdot 6H_2O$ with $(Et_4N)(ccnm)$, $Na(HCO_3)$ and 1,10-phenanthroline hydrate in a methanol/water (4:1, v/v) solution was found to give orange needle crystals of compound **2Ce**, a different stoichiometry from that of **α-1Ln**. As with compounds **α-1Ln**, compound **2Ce** crystallized in the space group $P\bar{3}1c$, with the degree of solvation determined by thermal dehydration studies and elemental analysis.

Because there are six nitrate counteranions per pentacationic lanthaball complex, a countercation is required to charge balance the system. The two most plausible candidates are either a tetraethylammonium or a sodium cation. While neither could be located in the X-ray crystal structure, presumably because of the species being highly disordered throughout the lattice, elemental analysis indicates that a sodium cation is most likely to be present to charge balance the system.

The significant difference between **α-1Ce** and **2Ce** is the presence of six locatable nitrate anions in the crystal structure of **2Ce**, in contrast to the three chloride anions and one carbonate anion in the lattice of **α-1Ce**. While compounds **α-1Ln** have pairs of aqua ligands on the surface of the lanthaball acting as hydrogen-bond donors to a unique chloride anion (Figure 3a), the interatomic distances in the crystal structure of complex **2Ce** suggest that these aqua ligands are now hydrogen-bond donors to a lattice water molecule, which, in turn, acts as a hydrogen-bond donor to two nitrate anions in the lattice (Figure 3b and Table 1).[23] Each nitrate anion also acts as a hydrogen-bond acceptor to the carbamoyl group of an adjacent ccnm ligand.[24] The alteration in hydrogen bonding on the surface of the lanthaball does not cause any significant changes in the $[Ce_{13}(CO_3)_{14}]$ core (Figure 3c), with no statistically significant differences in the bond lengths and angles between **α-1Ce** and **2Ce** (Table 1).

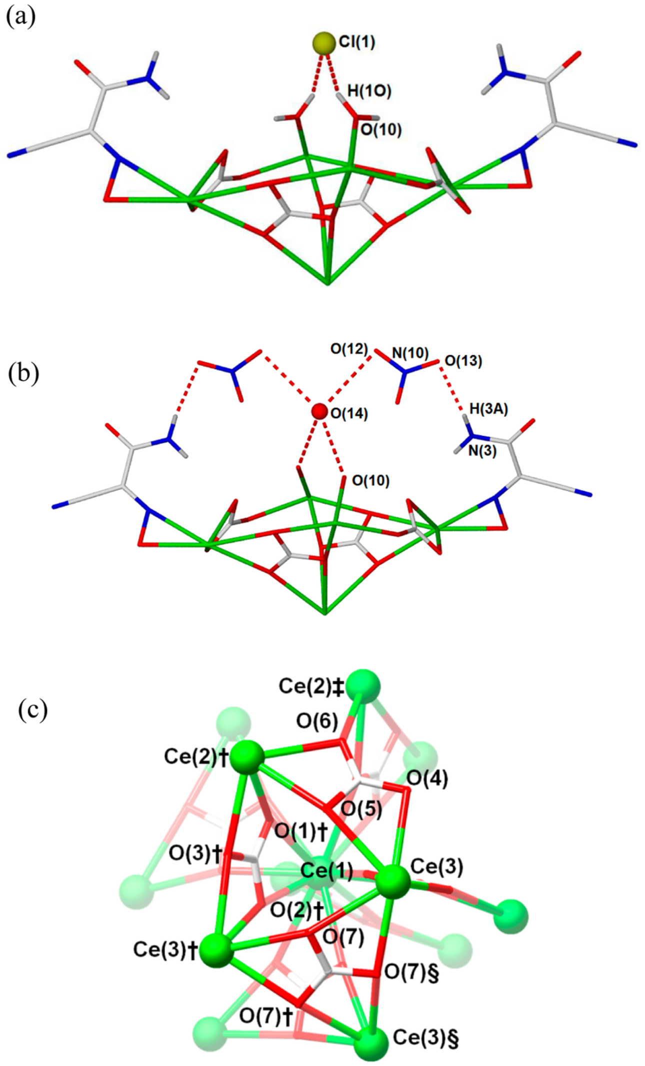


Figure 3. (a) Two coordinated aqua ligands acting as hydrogen-bond donors to a chloride anion in the lattice of **α-1Ce**. Hydrogen bond length (Å) and angle (deg): O(10)···Cl(1), 3.123(9); O(10)−H(10)···Cl(1), 154.7. (b) Hydrogen bonding on the surface of the cationic complex in the structure of **2Ce**.[8] (c) $[Ce_{13}(CO_3)_6]$ moiety and two additional carbonate ligands present in the central core. Symmetry elements used: † = 1 − *y*, *x* − *y*, *z*; ‡ = 1 − *y*, 1 − *x*, $^1/_2$ − *z*; § = 1 − *x* + *y*, 1 − *x*, *z*.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) of 2Ce[a]

Ce(1)−O(1)	2.688(5)	Ce(2)−O(6)‡	2.551(4)
Ce(1)−O(2)	2.638(4)	Ce(3)−O(3)	2.552(5)
Ce(2)−O(1)	2.553(5)	Ce(3)−O(4)	2.533(5)
Ce(2)−O(3)	2.606(5)	Ce(3)−O(5)	2.607(5)
Ce(2)−O(5)†	2.598(5)	Ce(3)−O(7)	2.578(5)
Ce(2)−O(6)†	2.553(5)	Ce(3)−O(7)†	2.607(5)
O(10)···O(14)	2.796(8)	N(3)···O(13)	2.98(2)
O(14)···O(12)	3.06(3)	N(3)−(H3A)···O(13)	151.1

[a] Symmetry elements used: † = 1 − *x* + *y*, 1 − *x*, *z*; ‡ = 1 − *y*, 1 − *x*, $^1/_2$ − *z*.

Coproducts Formed during Cerium Lanthaball Synthesis. Because of the number of components used in the self-assembly of lanthaball derivatives, it is not surprising that specific

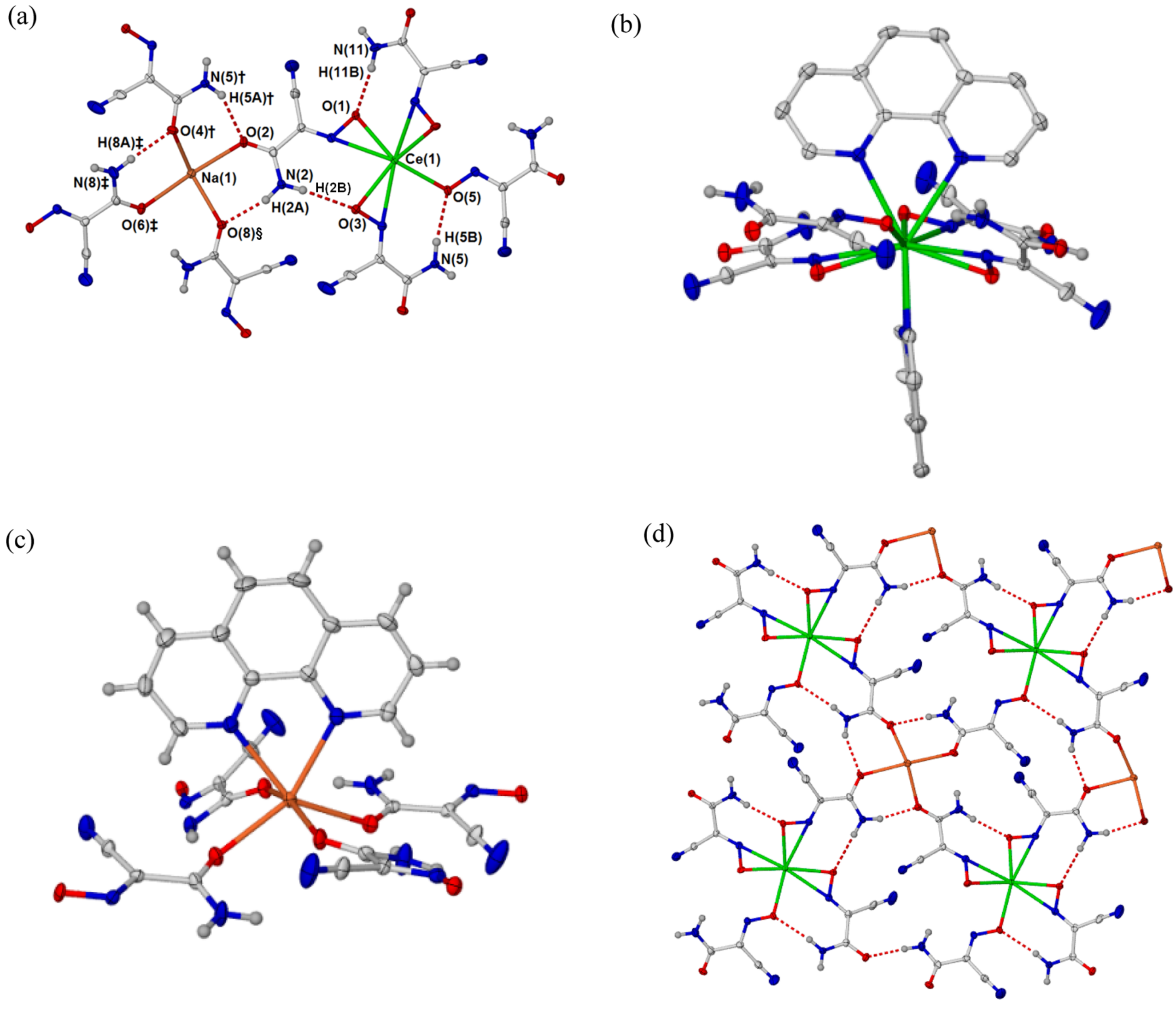


Figure 4. (a) Intramolecular hydrogen bonding around the sodium and cerium metal centers in the crystal structure of **3**. Symmetry elements used: † = $x - 1, y, z$; ‡ = $x - 1, {}^{1}/_{2} - y, {}^{1}/_{2} + z$; § = $x, {}^{1}/_{2} - y, {}^{1}/_{2} + z$. (b) Trans orientation of the phen ligands coordinated to the cerium metal center. (c) Distorted octahedral geometry of the sodium metal center. (d) (4,4) sheets of [CeNa(ccnm)$_4$] in **3**. Ellipsoids are shown at 50% probability, and phen ligands and lattice methanol molecules are omitted for clarity.

reaction conditions may also lead to the concurrent formation of coproducts. While this is typically undesirable, because the crystalline coproducts have to be manually separated from the target product after isolation from the reaction mixture, the coproducts may be of interest in their own right. Complexes and coordination polymers of dcnm[25] and its cyanonitroso-based derivatives[26] are not only of structural interest but also have been shown to display interesting mechanochemical properties.[27] Furthermore, these complexes have been earmarked for application as anticancer and antimicrobial agents,[28] nonelectric gas sensors,[29] and anions in ionic liquids.[30] With this in mind, we have endeavored to characterize any coproducts that crystallize during the synthesis of various lanthaballs.

The reaction of Ce(NO$_3$)$_3$·6H$_2$O, Na$_2$(CO$_3$), 1,10-phenanthroline hydrate, and (Me$_4$N)(ccnm) in a methanol/water (2:1, v/v) solution resulted in the concurrent crystallization of compounds **3** and **2Ce** over a period of 5 months. Although the crystals of both materials have a needle morphology, they can easily be differentiated because of the deep-red color of the crystals of **3** in contrast to the light-orange crystals of **2Ce**. The distinctively colored crystals of **3** had not been observed previously during the synthesis of other cerium lanthaball complexes. Elemental analysis indicated that the methanol molecule within the lattice of the crystal structure is exchanged for one molecule of water upon atmospheric exposure. While formation of the bimetallic complex may be due to the higher concentration of Na$^+$ in solution because of the use of Na$_2$(CO$_3$) instead of Na(HCO$_3$), the Me$_4$N$^+$ countercation must also play a role in the self-assembly of the material because **3** cannot be synthesized in its absence. This is one of the few known examples of the ccnm ligand to be found in a heterobimetallic complex.[31] 3s/4f systems that incorporate cyanonitrosomethanide ligands are rare,[32] and to the best of our knowledge, there are no examples of any that contain the ccnm ligand.

Compound **3** crystallizes in the space group $P2_1/c$ with the formula unit as the asymmetric unit (Figure S1 in the Supporting Information, SI). The crystal structure contains a [Ce(ccnm)$_4$(phen)$_2$]$^-$ moiety, where the ccnm ligands are oriented in an asymmetric propeller configuration around the lanthanoid atom (Figure 4a and Table S1 in the SI). Three ccnm ligands adopt an

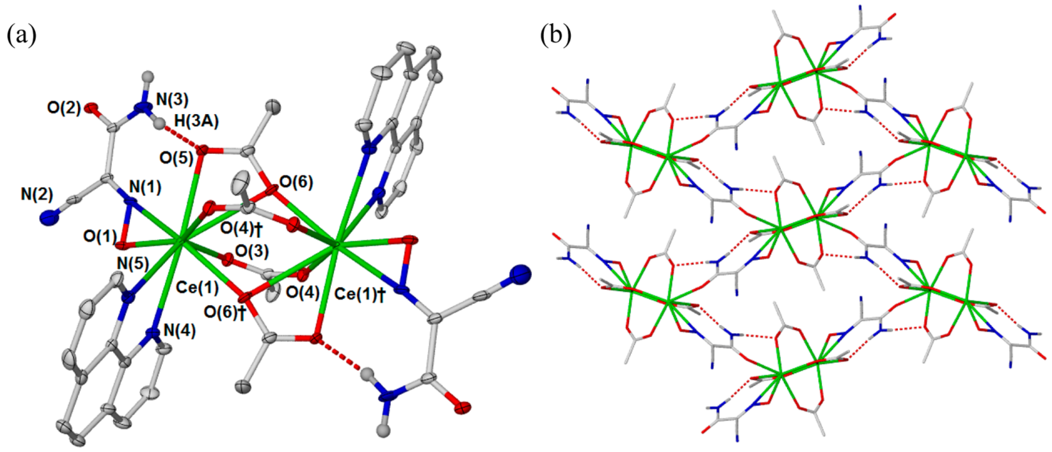


Figure 5. (a) $[Ce_2(ccnm)_2(OAc)_4(phen)_2]$ moiety in the crystal structure of **4**. Ellipsoids shown at 50% probability; hydrogen atoms that do not participate in hydrogen bonding are omitted for clarity. Symmetry element used: † = $1 - x, -y, z - {}^1/_2$. (b) (4,4) topology in the crystal structure of **4** as viewed down the *a* axis. Hydrogen atoms that do not participate in hydrogen bonding and phen ligands are omitted for clarity.

asymmetric η^2-bonding mode through the nitroso group, as observed with the ccnm ligands coordinating to the surface of complexes in **α-1Ln**. Two of these ccnm ligands exhibit intramolecular hydrogen bonding to the nitroso group of an adjacent ccnm ligand via the nitrogen atoms of the carbamoyl group (Table S1 in the SI).

The remaining ccnm ligand is monodentate because the distance between the nitrogen atom of the nitroso group and the cerium metal center is too long to be considered a bond [Ce(1)···N(7), 3.272 Å], and the ligand shows no hydrogen bonding to neighboring nitroso groups. The coordination sphere of the 11-coordinate cerium ion is completed by two trans phen ligands, which are oriented nearly perpendicular to each other (Figure 4b). The sodium atom is 6-coordinate with a distorted octahedral geometry and is coordinated by the oxygen atom of the carbamoyl group of four ccnm ligands and by one phen ligand (Figure 4c).

Formation of a 2D network is facilitated by the oxygen atom of the carbamoyl group of each ccnm ligand bridging to a sodium atom. Furthermore, the NH moieties of three of the carbamoyl groups act as hydrogen-bond donors to the oxygen atoms of adjacent carbamoyl groups that coordinate to the same sodium atom (Figure 4d). The fourth coordinating carbamoyl group, which does not hydrogen bond to another adjacent coordinating carbamoyl group, forms a hydrogen bond with the methanol molecule within the lattice, which, in turn, acts as a hydrogen-bond donor to the nitrile group of a neighboring ccnm ligand (Figure S1 in the SI).

The network has a (4,4) sheet topology, with each metal center acting as a four-connecting node and the ccnm anions acting as simple ditopic bridges (Figure 4d). The sheets stack with interdigitation between π-stacking phen ligands (Figure S2 in the SI). The methanol molecules are located in the lattice between sheets.

Following successful syntheses of lanthaballs with chloride and nitrate anions, it was investigated whether an analogue with the acetate anion could be prepared. $Ce(OAc)_3$ was reacted with $(Et_4N)(ccnm)$, $Na(HCO_3)$, and phen in a methanol/water (7:2, v/v) solution. No crystals of the target product $[Ce_{13}(ccnm)_6(CO_3)_{14}(H_2O)_6(phen)_{18}](OAc)_5$ formed from the reaction solution, but several small crystals of compound **4** were obtained. The very low yield of the product and difficulty in isolating the crystals of **4** prohibited bulk analysis of the material, but X-ray analysis allowed for unambiguous structure determination.

Compound **4** crystallizes in the space group $P2_1/c$ with the repeating unit of **4** contained within the asymmetric unit. The structure is best viewed as containing $[Ce_2(ccnm)_2(OAc)_4(phen)_2]$ moieties (Figure 5a and Tables 2 and S2 in the SI), which are bridged by the ccnm ligands to form a 2D coordination polymer (Figure 6b). Of the four bridging acetate ligands within the dimer, two exhibit a 3-coordinate bridging coordination mode (μ-1κ(O,O′):2κ(O)), while the other two exhibit a 2-coordinate bridging coordination mode (μ-1κ(O):2κ(O′)). Each 10-coordinate cerium atom has a coordination sphere containing one ccnm ligand chelating through the nitroso group, another ccnm ligand coordinating through the oxygen atom of the carbamoyl group, one bidentate phen ligand, and four acetate ligands, one of which chelates to the cerium atom.

Table 2. Selected Interatomic Distances (Å) of 4[a]

Ce(1)−O(1)	2.487(3)	Ce(1)−N(5)	2.708(3)
Ce(1)−N(1)	2.666(3)	Ce(1)−O(4)†	2.525(3)
Ce(1)−O(3)	2.468(3)	Ce(1)−O(6)†	2.444(2)
Ce(1)−O(5)	2.555(2)	Ce(1)−O(2)‡	2.546(2)
Ce(1)−O(6)	2.844(3)	N(3)···O(5)	2.852(4)
Ce(1)−N(4)	2.747(3)	N(3)···O(4)§	2.872(4)

[a] Symmetry elements used: † = $1 - x, -y, z - {}^1/_2$; ‡ = $x, {}^1/_2 - y, z - {}^1/_2$; § = $1 - x, {}^1/_2 + y, {}^3/_2 - z$.

As observed in the crystal structure of **3**, the coordination polymer forms a 2D sheet with a (4,4) topology, with each $[Ce_2(ccnm)_2(OAc)_4(phen)_2]$ dimer acting as a four-connecting node. The NH_2 of the ccnm ligand acts as a hydrogen-bond donor to the oxygen atoms of both crystallographically unique acetate ligands (Figure 5b). There is π−π stacking between the phen ligands of adjacent 2D sheets (Figure S3 in the SI).

Synthesis of a Neodymium Lanthaball. While the synthesis of lanthaballs proceeded readily using lanthanum, cerium, and praseodymium chloride salts, an analogous reaction with neodymium chloride failed to yield crystals of the desired product, $[Nd_{13}(ccnm)_6(CO_3)_{14}(H_2O)_6(phen)_{18}]\cdot Cl_3\cdot CO_3$, with only a dense precipitate of neodymium carbonate forming from solution. Similarly, the reaction system that yielded **2Ce** failed to yield the neodymium analogue from $Nd(NO_3)_3$. In a new attempt to synthesize a neodymium-containing lanthaball, the reaction conditions were altered by using Na_2CO_3, instead of

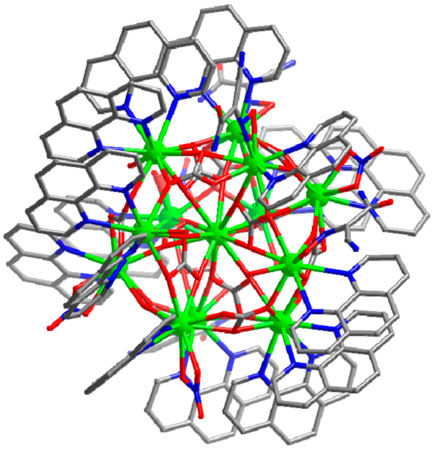


Figure 6. Tricationic complex $[Nd_{13}(ccnm)_4(CO_3)_{14}(NO_3)_4(H_2O)_7(phen)_{15}]^{3+}$ in compound **5Nd**. Hydrogen atoms are omitted for clarity.

Na(HCO_3), and the concentrations of the reactants were halved. This new synthesis proved to be successful, with puce crystals of compound **5Nd** (Figure 6) forming from the reaction solution after 1 month.

Compound **5Nd** crystallizes in the space group $P2_1/n$. The tricationic complex $[Nd_{13}(ccnm)_4(CO_3)_{14}(NO_3)_4(H_2O)_7(phen)_{15}]^{3+}$ contains the same central 12-coordinate $[Ln(CO_3)_6]$ and tridecanuclear $[Ln_{13}(CO_3)_{14}(H_2O)_6]$ moieties that were observed in compounds ***α*-1Ln**, ***β*-1Ce**, and **2Ce**, but the arrangement of ligands on the periphery of the complex is significantly different, with nitrate anions present instead of some ccnm and phen ligands.

The phen ligands are no longer arranged in three equal *π*-stacking rows, as in compounds ***α*-1Ln**, ***β*-1Ce**, and **2Ce**, but are situated on the surface of the core as one row of six, as one row of four, and as two pairs, with a final isolated phen ligand not participating in any intramolecular interactions with adjacent ligands (Figure 7). The four nitrate ligands chelate to the neodymium metal centers on the surface of the ball, while the four ccnm ligands chelate asymmetrically via the oxygen and nitrogen atoms of the nitroso group.[21]

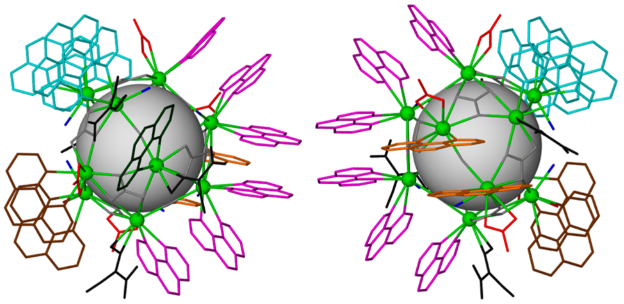


Figure 7. Two perspectives of the irregular surface of the cationic complex in **5Nd**. The ligands coordinating to the metal centers are color coded for clarity: ccnm, black; carbonate, gray; nitrate, red; water, dark blue. The discrete rows of *π*-stacking phen ligands are colored separately for clarity (magenta, cyan, brown, and orange). The isolated phen ligand, which does not participate in *π* stacking, is colored dark green.

All but 1 of the 12 neodymium atoms on the periphery of the $[Nd_{13}(CO_3)_{14}]$ core are 10-coordinate, with the one 9-coordinate neodymium atom [Nd(7)] coordinated by three carbonate ligands (two chelating and one monodentate), two aqua ligands, and one phen ligand (Table S3 in the SI). Of the remaining neodymium atoms, three are coordinated by three bidentate carbonate ligands, one chelating nitrate ligand, and one phen ligand [Nd(6), Nd(10), and Nd(13)], three are coordinated by three chelating carbonate ligands, one η^2 ccnm ligand, and one phen ligand [Nd(2), Nd(4), and Nd(8)], three are coordinated by three carbonate ligands (two chelating and one monodentate), one aqua ligand, and two phen ligands [Nd(3), Nd(9), and Nd(11)], one is coordinated by three carbonate ligands (two chelating and one monodentate), one chelating nitrate ligand, one aqua ligand, and one phen ligand [Nd(12)], and one is coordinated by three carbonate ligands (two chelating and one monodentate), one aqua ligand, one phen ligand, and one η^2 ccnm ligand [Nd(5)].

As with compounds ***α*-1Ln**, ***β*-1Ce**, and **2Ce**, the solvent molecules and counterions in the lattice are highly disordered and could not be located by crystallographic methods, but elemental analysis suggests that the tricationic complex is charge-balanced by the presence of three nitrate anions. Elemental analysis also suggests that there are 10 molecules of water in the lattice per complex. This is a lower degree of solvation than was observed for compounds ***α*-1Ln** and **2Ce**, but the lanthaballs in **5Nd** pack in a more efficient fashion than the other lanthaballs and there are cavities of only 2161 Å^3 per complex in the crystal lattice (compared with 3832 and 2912 Å^3 for ***β*-1Ce** and **2Ce**, respectively), consistent with a lower degree of solvation.

Because an analogous synthesis with cerium performed at the same concentration yielded crystals of **2Ce**, it would appear that the change in the complex composition is induced largely by a change of the metal ion. This is most remarkable given the fact that the ionic radii of Ce^{III} and Nd^{III} differ by only 0.03 and 0.07 Å for 9- and 12-coordinate species, respectively,[33] although abrupt structural changes between lanthanoids adjacent on the periodic table are known.[34] However, when the arrangement of ligands on the surface of the complex is compared with that of ***α*-1Ln**, ***β*-1Ce**, and **2Ce**, it is apparent that the nitrate anions also cause a considerable change in the formation of the complex. Furthermore, unlike all other reported examples of lanthaball complexes, compound **5Nd** has no internal crystallographic symmetry, with the entire complex contained within the asymmetric unit.

Magnetic Susceptibility Measurements. dc magnetic susceptibility studies were carried out on a polycrystalline sample of **5Nd** in the temperature range 2−300 K at 1 T (Figure 8a). Nd^{III} ions possess large unquenched orbital angular momentum associated with the internal nature of the valence f orbitals. The orbitally degenerate ground state is therefore easily split by spin−orbit coupling and by crystal-field effects. The magnetic properties of Nd^{III} ions are strongly influenced by this. At room temperature, the value of the product $\chi_M T$ (where χ_M is the molar magnetic susceptibility) is 16.38 cm^3 K mol^{-1}. This value is lower, but in reasonable agreement, with that calculated for 13 noninteracting Nd^{III} ions of $\chi_M T = 21.32$ cm^3 K mol^{-1} ($^4I_{9/2}$, $g = {}^8/_{11}$), taking into account electron−electron interactions, spin−orbit coupling, and antiferromagnetic interactions (below). The $\chi_M T$ product decreases immediately from room temperature to around 50 K and then decreases more rapidly, reaching a value of 6.53 cm^3 K mol^{-1} at 2 K. The decrease of $\chi_M T$ upon reduction of the temperature can be ascribed to a combination of the exchange interactions between the Nd^{III} ions and the progressive depopulation of excited Stark sublevels, derived

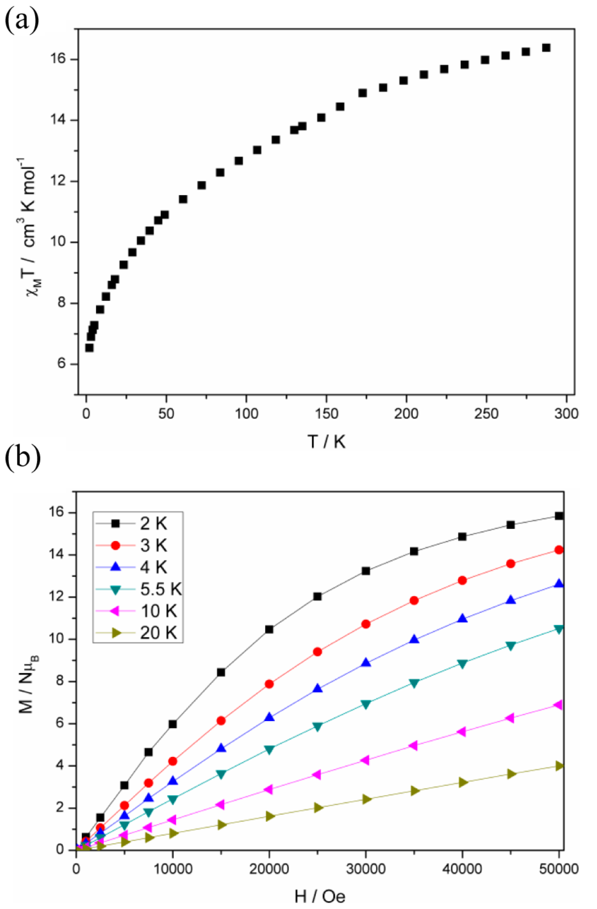


Figure 8. (a) Plot of $\chi_M T$ versus T for **5Nd**, measured under a 1 T magnetic field. (b) Isothermal M versus H plot for **5Nd**.

from the splitting of the free ion ground state by the crystal field. A quantitative analysis of the exchange is precluded because of the complexity of the structure. It is likely, however, from both the profile of the plot and the lower than expected room temperature $\chi_M T$ value, compared to that of the expected uncoupled value, that the exchange is dominated by antiferromagnetic interactions. The isothermal M versus H (Figure 8b) data at 2 K shows a rapid increase of the magnetization at low field, which eventually reaches the value of 15.85 μ_B at 5 T without any sign of saturation. This value is lower than the expected saturation value of 42.51 μ_B (uncoupled ions). This difference is due to the antiferromagnetic interaction between the metal ions and/or anisotropy resulting from the crystal field eliminating the 10-fold degeneracy of the $^4I_{9/2}$ ground state. Because of the implied presence of magnetic anisotropy, ac susceptibility measurements were performed on **5Nd** to probe for any slow magnetic relaxation. No out-of-phase susceptibility (χ'') signals were observed, and therefore no single-molecule magnet behavior is found above 1.8 K (Figure S4 in the SI).

■ CONCLUSIONS

The series of tridecanuclear polycarbonate lanthanoid complexes known as lanthaballs has been expanded to include a new cerium pseudopolymorph (***β*-1Ce**) and a nitrate analogue (**2Ce**). We have demonstrated that two of the ligands in the complexes, ccnm and carbonate, may form through an in situ path during the one-pot synthesis of ***β*-1Ce**. The serendipitous formation of two coordination polymers, **3** and **4**, illustrates the difficulty that can be encountered in attempting to synthesize structurally complicated compounds that contain a large number of components in a one-pot reaction. A neodymium member of the lanthaball class (**5Nd**) has been synthesized for the first time and has a stoichiometry and a periphery different from those of the ***α*-1Ln**, ***β*-1Ce**, and **2Ce** classes. It displays intracluster antiferromagnetic coupling but does not exhibit single molecule magnetism.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures of complexes **3** and **4**, tables containing selected interatomic distances and angles for complexes **3** and **4**, a list of the ligands coordinating to metal centers in **5Nd**, and χ_M'' versus T for **5Nd**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to the memory of Prof. John D. Corbett, a leader in solid-state rare-earth chemistry and an inspiration to many.

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