

First single-crystal X-ray diffraction study of a lanthanide tricarboxylate complex: $[\text{Co}(\text{NH}_3)_6][\text{Sm}(\text{CO}_3)_3(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$

David L. Clark,^a Robert J. Donohoe,^b John C. Gordon,^{*c} Pamela L. Gordon,^d
D. Webster Keogh,^{*d} Brian L. Scott,^e C. Drew Tait^d and John G. Watkin^{*e}

^a Glenn T. Seaborg Institute for Transactinium Science, Nuclear Materials Technology (NMT-DO, Mail Stop E500) Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

^b Biosciences (B-2, Mail Stop J586) Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

^c Nuclear Materials Technology (NMT-DO, Mail Stop J514) Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

^d Chemical Science and Technology (CST-18, Mail Stop G739) Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

^e Chemical Science and Technology (CST-18, Mail Stop J514) Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

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The first single-crystal X-ray diffraction study of a lanthanide tricarboxylate complex, namely $[\text{Co}(\text{NH}_3)_6][\text{Sm}(\text{CO}_3)_3(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$, is reported and reveals a zigzag chain structure of 9-coordinate samarium metal centers bridged by $\mu\text{-}\eta^2\text{:}\eta^1$ carbonate ligands.

In recent years, studies of the coordination chemistry of actinide metal ions in carbonate-containing aqueous media have assumed increasing importance due to the central role played by carbonate species in the environmental fate and transport of these metals.^{1,2} The primary focus of these investigations has been to establish the identity, spectroscopic properties and solubilities of the principal species which are likely to exist in environmental groundwaters at near-neutral pH. Previously, we have described detailed investigations into the behavior of the principal oxidation states of the light actinides, specifically U(vi), Np(v) and Pu(iv), in carbonate-containing solutions.³ Due to the pronounced similarity in charge/size ratio between the lanthanides and actinides in the +III oxidation state, lanthanides have frequently been employed as non-radioactive surrogates for the trivalent actinides.⁴ Thus we elected to undertake a study of the lanthanide elements in concentrated aqueous carbonate solution, in order to model the speciation of the actinides in their lowest oxidation state.

Explorations of the synthesis and characterization of lanthanide carbonate complexes have a long history.⁵ However, while a number of lanthanide-containing mineral phases have been recognized, including the normal carbonates lanthanite ($\text{La}_2(\text{CO}_3)_3\cdot 8\text{H}_2\text{O}$),⁶ calkinites ($(\text{La,Ce})_2(\text{CO}_3)_3\cdot 4\text{H}_2\text{O}$),^{7a} and tengerite ($\text{Y}_2(\text{CO}_3)_3\cdot n\text{H}_2\text{O}$; $n = 2\text{--}3$),^{7b,8} as well as the double carbonates burbankite ($(\text{Na,Ca})_3(\text{Sr,Ba,Ce,La})_3(\text{CO}_3)_5$)^{7a,9} and sahamalite ($(\text{Ce,La,Nd,Pr})_2(\text{Mg,Fe})(\text{CO}_3)_4$),¹⁰ very few detailed structural studies have been reported for these or any synthetic analogs. Numerous literature reports have described the synthesis of lanthanide carbonates with a range of stoichiometries: the "normal" carbonates $\text{Ln}_2(\text{CO}_3)_3\cdot x\text{H}_2\text{O}$ ($x = 2, 3, 8$),^{11–14} the cerium(IV) pentacarbonates $\text{M}_6[\text{Ce}(\text{CO}_3)_5]\cdot x\text{H}_2\text{O}$ ($\text{M} = \text{Na}$, $x = 12$; $\text{M} = \text{C}(\text{NH}_2)_3$, $x = 4$)¹⁵ and cerium(IV) tetracarbonates $\text{M}_4[\text{Ce}(\text{CO}_3)_4]\cdot x\text{H}_2\text{O}$ ($\text{M} = \text{Na}$, $x = 7$; $\text{M} = \text{C}(\text{NH}_2)_3$, $x = 6$),¹⁶ the dicarbonates $\text{M}[\text{Ln}(\text{CO}_3)_2]$ ($\text{M} = \text{Li}$,¹⁷ Na ,^{18,19} K ,²⁰ Cs ,²¹ Tl)²² and the tetracarbonates $\text{M}_3[\text{Ln}(\text{CO}_3)_4]$ ($\text{M} = \text{Tl}$,²² Na)²⁰. In almost every case, however, characterization has been limited to infrared spectroscopy, thermogravimetric analysis and powder X-ray diffraction. Single-crystal X-ray diffraction studies of lanthanide complexes containing purely carbonate ligation are

limited to the following examples: (i) the cerium(IV) pentacarbonate moiety $[\text{C}(\text{NH}_2)_3]_6[\text{Ce}(\text{CO}_3)_5]\cdot 4\text{H}_2\text{O}$,²³ (ii) the neutral carbonate complexes $\text{La}_2(\text{CO}_3)_3\cdot 8\text{H}_2\text{O}$ ²⁴ and $(\text{La,Ce})_2(\text{CO}_3)_3\cdot 8\text{H}_2\text{O}$,⁶ and (iii) alkali metal salts of the lanthanide dicarbonates $\text{M}[\text{Ln}(\text{CO}_3)_2]$ ($\text{M} = \text{K}$; $\text{Ln} = \text{Nd, Dy}$; $\text{M} = \text{Cs}$; $\text{Ln} = \text{Pr}$), synthesized *via* high temperature and pressure routes.^{21,25} Notably lacking in the literature to date have been structural data for tri- or tetra-carbonato derivatives of the lanthanide elements.²⁶ Here we describe the synthesis and the first single-crystal X-ray diffraction study of a lanthanide tricarboxylate complex.

The cobalt hexamine cation, $[\text{Co}(\text{NH}_3)_6]^{3+}$, has been employed previously as a crystallizing agent for highly-charged anionic moieties, since it can enter into extended hydrogen-bonding networks with oxygen-containing ligands such as carbonate.²⁷ Slow addition of a 0.2 M solution of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ to a mixture of 2.5 M K_2CO_3 and 0.1 M $\text{Sm}(\text{NO}_3)_3$ resulted in the deposition of large, X-ray quality orange crystals of the title complex $[\text{Co}(\text{NH}_3)_6][\text{Sm}(\text{CO}_3)_3(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$ (**1**) over a period of several hours.[†] Once formed, the crystals were found to be essentially insoluble in all common solvents. We note that Saito and Ueno have previously described the isolation of a complex which they formulated as $[\text{Co}(\text{NH}_3)_6][\text{Sm}(\text{CO}_3)_3]\cdot 5\text{H}_2\text{O}$,²⁷ although no structural data were reported.

A single-crystal X-ray diffraction study of **1** was undertaken.[‡] The overall molecular structure of **1** comprises a zigzag chain structure of 9-coordinate samarium metal centers bridged by $\mu\text{-}\eta^2\text{:}\eta^1$ carbonate ligands. Examples of similar $\mu\text{-}\eta^1\text{:}\eta^2$ ligands have been observed previously in lanthanide carbonate²¹ and carboxylate²⁸ chemistry. Each samarium metal center is coordinated by three bidentate carbonate ligands, two monodentate carbonate ligands from the adjacent units in the chain, and a single water ligand (Fig. 1, Fig. 2). The nine oxygen atoms which coordinate the metal center define an irregular geometry which does not conform to any common polyhedral skeleton. An extensive hydrogen-bonding network exists between the hydrogens of the $[\text{Co}(\text{NH}_3)_6]^{3+}$ cations and distal oxygen atoms of the carbonate ligands, resulting in rather low values for the N–H and O–H stretching frequencies in the infrared spectrum of **1** (*vide infra*). An average of four solvent water molecules are dispersed throughout each unit cell of **1**, dispersed over five general positions. The Sm–O bond distances to the bidentate carbonate ligands range from 2.442(9) to 2.516(9) Å, while the distance to the monodentate ligand is slightly

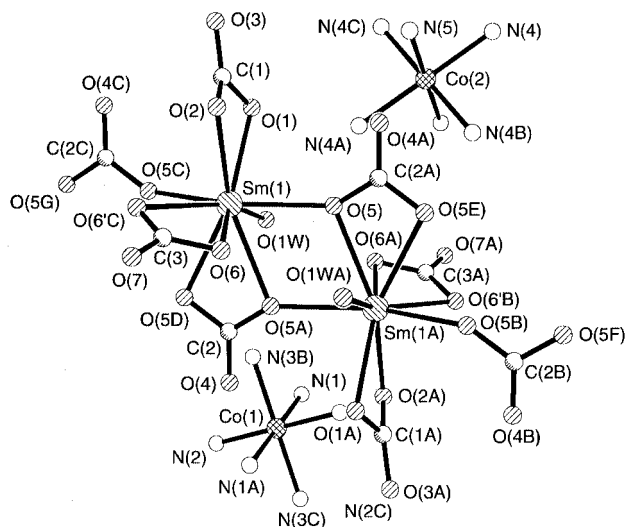


Fig. 1 Ball-and-stick view of two $[\text{Sm}(\text{CO}_3)_3(\text{H}_2\text{O})]^{3-}$ moieties also showing the location of the $[\text{Co}(\text{NH}_3)_6]^{3+}$ cations within the lattice. Selected bond lengths and angles: Sm(1)–O(1) 2.444(7), Sm(1)–O(2) 2.442(9), Sm(1)–O(5) 2.391(5), Sm(1)–O(5)#2 2.516(5), Sm(1)–O(6) 2.457(14), Sm(1)–O(6')#1 2.516(9), Sm(1)–O(1W) 2.568(6); O(1)–Sm(1)–O(2) 53.5(3), O(1)–Sm(1)–O(5) 80.98(13), O(1)–Sm(1)–O(6) 135.2(4), O(1)–Sm(1)–O(1W) 74.1(2), O(2)–Sm(1)–O(5) 94.42(14), O(6)–Sm(1)–O(6')#1 52.3(5), O(5)#2–Sm(1)–O(1W) 75.2(2), O(5)#3–Sm(1)–O(6) 69.0(4), O(5)#3–Sm(1)–O(6')#1 105.6(3), O(5)#3–Sm(1)–O(1W) 75.2(2), O(2)–Sm(1)–O(6) 84.6(4), O(2)–Sm(1)–O(6')#1 69.5(3), O(5)–Sm(1)–O(6) 88.1(4), O(5)–Sm(1)–O(5)#3 66.84(19), O(5)–Sm(1)–O(1W) 75.72(15), O(5)#1–Sm(1)–O(6')#1 73.0(3), O(5)#2–Sm(1)–O(5)#3 50.5(2), O(5)#2–Sm(1)–O(6) 83.7(4), O(5)#2–Sm(1)–O(6')#1 79.3(3), Sm(1)–O(5)–Sm(1)#3 113.16(19). Symmetry transformations used to generate equivalent atoms: #1 $x, -y + 1, z$; #2 $-x + 1/2, y + 1/2, -z + 1$; #3 $-x + 1/2, -y + 1/2, -z + 1$.

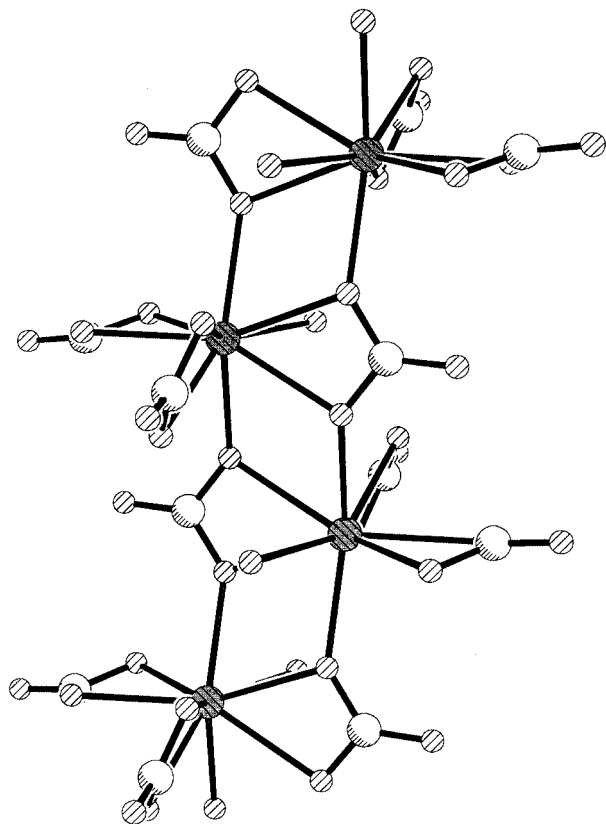


Fig. 2 Ball-and-stick view of a portion of the zigzag chain structure of **1** (cations omitted for clarity).

shorter (Sm(1)–O(5) = 2.391(5) Å). These samarium–oxygen distances may be compared to those of 2.441(3) and 2.600(2) in the samarium fluorocarbonate complex $\text{Ba}[\text{Sm}(\text{CO}_3)_2\text{F}]$,²⁹

which represents the only other example of a structurally characterized samarium complex containing carbonate ligands. Comparison may also be made with the $\mu\text{-}\eta^1\text{:}\eta^2$ carboxylate ligands in the structurally-characterized complex $[\text{Sm}(\text{CH}_3\text{CO}_2)_3(\text{H}_2\text{O})_2]\cdot\text{CH}_3\text{CO}_2\text{H}$, which show Sm–O bond lengths to the bidentate ligand of 2.565(6) and 2.523(5) Å, and a monodentate distance of 2.408(3) Å.³⁰ The Sm–O bond length to the water ligand in **1** is 2.568(6) Å, while O–Sm–O “bite” angles within the bidentate carbonate ligands are 53.5(3), 50.5(2) and 52.3(5)° for the three crystallographically independent ligands. The geometry about the bridging oxygen atom (O(5)) is almost trigonal planar, with the angles about O(5) summing to 353.8°. The Co–N distances (1.888(19)–2.014(9) Å) and N–Co–N angles within the cobalt hexamine cations are typical of those observed previously for this moiety.

The infrared absorption spectrum of **1** shows broad absorption for water and ammonia ligands at 3430, 3257 and 3194 cm^{-1} . A shoulder at 1633 cm^{-1} is assigned to the $\delta(\text{N-H})$ and $\delta(\text{O-H})$ modes of ammonia and water ligands, while bands at 1529, 1478, 1373 and 1326 cm^{-1} are due to split carbonate ν_3 modes. These modes represent the asymmetric stretching modes of carbonate ligands in different bonding environments. For the totally symmetric stretching region, labeled as ν_1 for free carbonate, three peaks are observed in the IR at 1080, 1057 and 1018 cm^{-1} . In the corresponding Raman spectrum, there are also three peaks observed in this region at 1092, 1056 and 1020 cm^{-1} . Lower frequency IR peaks include modes at 858 cm^{-1} (π mode) and at 743, 719, 687 and 624 cm^{-1} from the splitting of the ν_4 $\delta(\text{O-C-O})$ peaks of the different carbonate ligands. IR data previously reported by Fromage *et al.* for the guanidinium salt of a samarium tricarboxylate anion, namely $[\text{C}(\text{NH}_2)_3][\text{Sm}(\text{CO}_3)_3]\cdot 4\text{H}_2\text{O}$,³¹ and also for the lanthanide tricarboxylates $\text{Na}_3[\text{Er}(\text{CO}_3)_3]\cdot 6\text{H}_2\text{O}$ and $\text{Na}_3[\text{Gd}(\text{CO}_3)_3]\cdot 6\text{H}_2\text{O}$,³² are qualitatively similar to the data obtained here.

In summary we have isolated, characterized and reported structural data for a lanthanide tricarboxylate complex. Further studies of lanthanide speciation in carbonate-containing aqueous media are currently in progress.

Acknowledgements

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Notes and references

† Into a 20 mL scintillation vial was placed 800 μL of 2.5 M K_2CO_3 followed by 600 μL of 0.1 M $\text{Sm}(\text{NO}_3)_3$. To this mixture, 300 μL of 0.2 M $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ was added dropwise. After gentle shaking, the mixture was left undisturbed and open to air. Orange crystals began to deposit within 20 minutes of addition. The mother liquor was decanted away, the crystals washed with water and methanol, and air dried. IR (cm^{-1}): 3430 (sh), 3257 (s), 3194 (sh), 1633 (sh), 1529 (sh), 1478 (s), 1373 (s), 1326 (s), 1080 (w), 1057 (w), 1018 (w), 858 (m), 829 (w), 743 (w), 719 (w), 687 (w), 624 (w). Raman (cm^{-1}): 1346 (s), 1316 (s), 1092 (m), 1056 (s), 1020 (br, m), 738 (w), 521 (sh), 506 (s), 455 (m), 326 (br, w). Calcd. for $\text{C}_3\text{H}_{28}\text{CoN}_6\text{O}_{14}\text{Sm}$: C, 6.20; H, 4.85; N, 14.45. Found: C, 6.38; H, 4.99; N, 14.38%.

‡ Crystal data for complex **1**: $\text{C}_3\text{H}_{28}\text{CoN}_6\text{O}_{14}\text{Sm}$, $M = 581.59$, monoclinic, $C2/m$, $a = 21.895(2)$, $b = 6.7568(6)$, $c = 14.5776(14)$ Å, $\beta = 125.668(2)^\circ$, $U = 1752.1(3)$ Å³, $Z = 4$, $\mu = 4.346 \text{ mm}^{-1}$, $T = 203 \text{ K}$. $R1 = 0.0372$ [$I > 2\sigma(I)$] for 1336 unique reflections. An orange, irregularly-shaped crystal was attached to a glass fiber and was placed onto a Bruker P4/CCD/PC diffractometer cooled to 203 K using a Bruker LT-2 low-temperature device. A hemisphere of data were collected using a combination of φ and ω scans, with 20 second frame exposures and 0.3° frame widths. The structure was solved in space group $C2/m$ using direct methods and difference Fourier techniques. Most of the lattice water molecules were refined at partial occupancies. The carbonate ligands were all disordered across mirror planes, and one of the $\text{Co}(\text{NH}_3)_6$ anions was disordered on a $2/m$ site. Due to the disorder, hydrogen atom positions were not considered in the structural model. The final refinement included anisotropic temperature factors

on all atoms, and converged with final residuals of $R1 = 0.0372$ [$I > 2\sigma(I)$] and $R2_w = 0.1052$. CCDC reference number 186/1955. See <http://www.rsc.org/suppdata/dt/b0/b000778/> for crystallographic files in .cif format.

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