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A New Structural Class of Lanthanide Carbonates: Synthesis, Properties, and X-ray Structure of the One-Dimensional Chain Complex $[Co(NH_3)_6]_6[K_2(H_2O)_{10}][Nd_2(CO_3)_8]_2\cdot 20H_2O$

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Introduction

The carbonate ion is a ubiquitous ligand in the chemistry of the f-elements and plays an important role in their separation and purification as well as in the environmental fate and transport of these materials. Research efforts directed toward a deeper understanding of actinide metal carbonate speciation have increased dramatically over the last 20 years, primarily due to the importance of determining how these species may form and behave in natural aquatic environments at near-neutral pH.[2,3] We recently described a series of spectroscopic and structural studies that focused upon the behavior of the light actinides (in particular U(VI), Np(V), and Pu(IV)) in carbonate-rich aqueous media.[4] Owing to the pronounced similarity in charge/size ratio between the lanthanides and actinides in the trivalent oxidation state, the 4f-block elements have been utilized as nonradioactive surrogates for the trivalent actinide elements.[5] We now wish to report the initial results obtained from a study of the lanthanide metal ions in concentrated aqueous carbonate solutions, which is aimed toward modeling the behavior of the actinide cations in their lowest oxidation states.

While a number of lanthanide-containing mineral phases have been recognized, including the normal carbonate phases lanthanite $[La_2(CO_3)_3\cdot 8H_2O]$,[6] calkinsite $[(La, Ce)_2(CO_3)_3\cdot 4H_2O]$,[7] and tengerite $[Y_2(CO_3)_3\cdot nH_2O;\ n = 2-3]$,[8,9] as well as the double carbonates burbankite $[Na_2(Ca_a, Sr_b, Ba_c, Ce_d, La_e)_4(CO_3)_5]$ ($a-e$ variable)[7,10] and sahamalite $[(Ce, La, Nd)_2(Mg, Fe)(CO_3)_4]$,[11] a paucity of detailed structural studies have been reported for these materials. A number of methodologies have been employed in the syntheses of lanthanide carbonates, and literature reports have described materials with a variety of stoichiometries. These include the normal carbonates $Ln_2(CO_3)_3$ and $Ln_2(CO_3)_3\cdot xH_2O$ ($x = 2, 3, 8$),[12−21] the cerium(IV) pentacarbonates $M_6[Ce(CO_3)_5]\cdot xH_2O$ ($M = Na$, $x = 12$; $M = C(NH_2)_3$, $x = 4$)[22] and cerium(IV) tetracarbonates $M_4[Ce(CO_3)_4]\cdot xH_2O$ ($M = Na$, $x = 7$; $M = C(NH_2)_3$, $x = 6$),[23] the dicarbonates $M[Ln(CO_3)_2]$ (M = Li,[24] Na,[25,26] K,[27] Cs,[28] Tl[29]), and the tetracarbonates $M_5[Ln(CO_3)_4]$ (M = Na,[27] Tl[29]). In most cases, however, physical characterization of the materials was limited to a combination of X-ray powder diffraction, infrared spectroscopy and/or thermogravimetric analysis. Single-crystal X-ray diffraction studies of lanthanide complexes containing purely carbonate ligation are limited to only a few examples: (a) the guanidinium salt of the cerium(IV) pentacarbonate $[C(NH_2)_3]_6[Ce(CO_3)_5]\cdot 4H_2O$,[30] (b) the neutral carbonates La_2-

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Table 1. Crystallographic Data for $[Co(NH_3)_6]_6[K_2(H_2O)_{10}][Nd_2(CO_3)_8]_2\cdot 20H_2O$ (**1**)

empirical formula	$C_{16}H_{168}Co_6K_2N_{36}Nd_4O_{78}$
fw	3122.60
temperature	−70(2) °C
wavelength	0.71073 Å
space group	$P2_1/c$ (No. 14)
unit cell dimensions	$a = 13.2320(5)$ Å, $b = 15.5731(7)$ Å, $c = 26.0154(12)$ Å, $\beta = 90.952(1)°$
volume	5360.1(4) Å^3
Z	2
density (calculated)	1.935 Mg/m^3
absorption coefficient	30.0 cm^{-1}
final R indices $[I > 2\sigma(I)]^a$	R1 = 0.0468, wR2 = 0.1107
R indices (all data)	R1 = 0.0751, wR2 = 0.1194

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.031P)^2]$, where $P = [^1/_3 \max(0 \text{ or } F_o^2) + {}^2/_3 F_c^2]$.

$(CO_3)_3\cdot 8H_2O$[31] and $(La,Ce)_2(CO_3)_3\cdot 8H_2O$,[6c] and (c) the alkali metal salts of dicarbonates $M[Ln(CO_3)_2]$ (M = K, Ln = Nd, Dy; M = Cs, Ln = Pr), synthesized via high-temperature and -pressure routes.[32,33] Notably lacking are literature reports of structural data for tri- or tetracarbonate complexes of the lanthanide elements.[34] Herein, we report the synthesis and a single-crystal X-ray diffraction study of a member of a new structural class of lanthanide *tetra*carbonate complexes.

Results and Discussion

Synthesis and Physicochemical Properties. Following our previous successful use of the cobalt hexaammine cation, $[Co(NH_3)_6]^{3+}$, as a crystallizing agent for highly charged anionic fragments,[35,36] we elected to employ this moiety because of its ability to participate in hydrogen-bonding networks with oxygen-containing ligands such as carbonate. Indeed, it was found that crystalline $[Co(NH_3)_6]_6[K_2(H_2O)_{10}][Nd_2(CO_3)_8]_2\cdot 20H_2O$ (**1**) was slowly deposited following addition of a 0.2 M $[Co(NH_3)_6]Cl_3$ solution to a mixture of $Nd(NO_3)_3$ (0.038 M) and 2.5 M K_2CO_3. The resulting orange rods were isolated and found to be essentially insoluble in all common organic solvents (e.g., hexanes, toluene, tetrahydrofuran, dichloromethane, dimethylformamide, and dimethyl sulfoxide). Elemental analysis results were consistent with the formulation of **1** as shown above, with six cobalt hexaammine cations, one dipotassium decaaquo cation, and two $[Nd_2(CO_3)_8]$ anions.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Co(NH_3)_6]_6[K_2(H_2O)_{10}][Nd_2(CO_3)_8]_2\cdot 20H_2O$

Nd(1)−O(1)	2.514(5)	Nd(1)−O(2)	2.512(4)
Nd(1)−O(6)	2.398(5)	Nd(1)−O(7)	2.501(4)
Nd(1)−O(8)	2.505(4)	Nd(1)−O(10)	2.542(4)
Nd(1)−O(11)	2.489(4)	Nd(1)−O(13)	2.547(5)
Nd(1)−O(14)	2.475(5)	Nd(2)−O(3)	2.438(5)
Nd(2)−O(4)	2.535(4)	Nd(2)−O(5)	2.476(5)
Nd(2)−O(16)	2.546(4)	Nd(2)−O(17)	2.477(5)
Nd(2)−O(19)	2.522(4)	Nd(2)−O(20)	2.519(4)
Nd(2)−O(22)	2.513(4)	Nd(2)−O(23)	2.520(4)
O(1)−Nd(1)−O(2)	51.25(14)	O(4)−Nd(2)−O(5)	51.38(15)
O(7)−Nd(1)−O(8)	52.08(14)	O(7)−Nd(1)−O(10)	70.68(15)
O(7)−Nd(1)−O(14)	158.89(16)	O(8)−Nd(1)−O(11)	159.95(17)
O(8)−Nd(1)−O(13)	73.04(15)	O(10)−Nd(1)−O(11)	52.10(15)
O(10)−Nd(1)−O(13)	161.33(16)	O(11)−Nd(1)−O(14)	70.48(15)
O(13)−Nd(1)−O(14)	51.94(15)	O(16)−Nd(2)−O(17)	52.20(14)
O(16)−Nd(2)−O(20)	166.85(16)	O(16)−Nd(2)−O(22)	69.53(14)
O(17)−Nd(2)−O(19)	69.05(14)	O(17)−Nd(2)−O(23)	154.93(15)
O(19)−Nd(2)−O(20)	51.07(15)	O(19)−Nd(2)−O(22)	171.74(15)
O(20)−Nd(2)−O(23)	69.66(15)	O(22)−Nd(2)−O(23)	51.89(14)

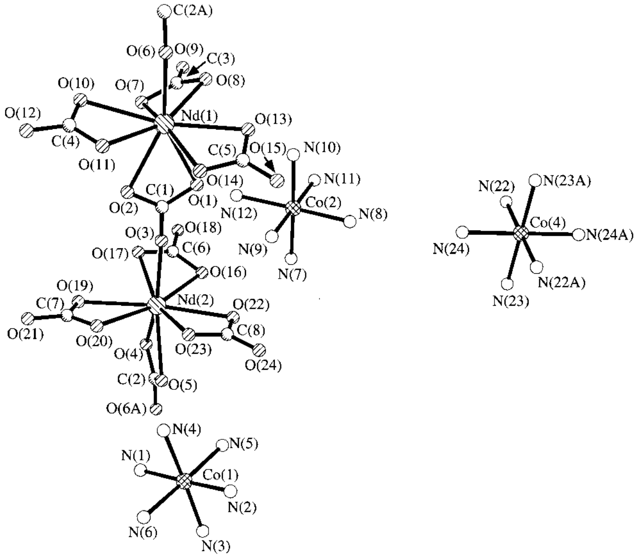

Figure 1. Ball-and-stick view of one $[Nd_2(CO_3)_8]$ repeat unit within the structure of **1**. Three of the $[Co(NH_3)_6]^{3+}$ cation sites are shown, while the $[K_2(H_2O)_{10}]^{2+}$ moiety is omitted for clarity.

Solid-State Molecular Structure. A single-crystal X-ray diffraction study of **1** was undertaken on a crystal taken directly from the reaction mixture described in the Experimental Section. A summary of data collection and crystallographic parameters is given in Table 1, while selected bond distances and angles are listed in Table 2. A ball-and-stick view of the neodymium and cobalt centers in **1** is shown in Figure 1. The overall molecular structure of complex **1** comprises infinite one-dimensional chains of nine-coordinate neodymium cations, with each metal center coordinated by five different carbonate ligands (See Figure 2). Formally, the simplest lanthanide-containing repeat unit in the structure is composed of $[Nd_2(CO_3)_8]^{10-}$ anions. Each of these fragments is charge-balanced by *three* $[Co(NH_3)_6]^{3+}$ cations (in each unit cell, there are four $[Co(NH_3)_6]^{3+}$ moieties per Nd_2 unit, two of which sit on crystallographic inversion centers) and *half* of a dimeric $[K_2(H_2O)_{10}]$ unit (which also occupies an inversion site). An extensive hydrogen-bonding network exists among the hydrogen atoms of the $[Co(NH_3)_6]^{3+}$ cations, the oxygen atoms of the terminal carbonate groups, the coordinated water molecules in the cationic potassium dimer, and the water molecules present in the lattice. Each neodymium metal center is coordinated by three bidentate carbonate ligands in a pseudoequatorial fashion, while a fourth bidentate carbonate ligand occupies an axial coordination site. The distal oxygen atom of this axial ligand participates in a further monodentate interaction with the neighboring metal center and provides the agency whereby neodymium tetracarbonate units are linked together to form a one-dimensional chainlike array. While the three equatorial carbonate ligands of each adjacent neodymium metal are in an essentially eclipsed conformation, the μ_2-η^2,η^1 ligands that link tetracarbonate units together are found to be rotated approximately 90° relative to one another. An examination of the metric parameters in **1** reveals that neither of the standard nine-coordinate geometries

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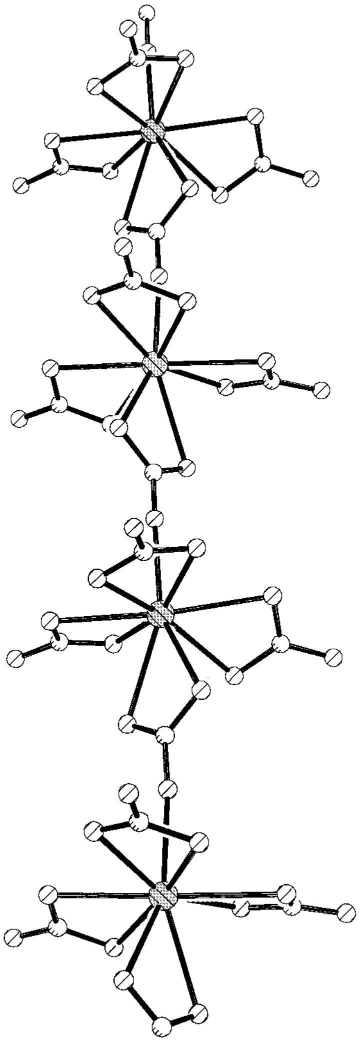

Figure 2. Ball-and-stick view of a portion of the $[Nd_2(CO_3)_8]_\infty$ one-dimensional chain structure of **1**. Neodymium cations are represented by shaded circles.

(i.e., tricapped trigonal prismatic or capped square antiprismatic), in either ideal or distorted forms, can be invoked to describe the coordination environment about each metal center.

Bidentate carbonate ligands in **1** exhibit Nd−O bond distances that fall within the range 2.475(5)−2.547(5) Å, while the Nd−O bonds that form the bridging, monodentate linkages appear to be slightly shorter (2.398(5) and 2.438(5) Å).These distances are similar to those previously reported for the complex $K[Nd(CO_3)_2]$, in which Nd−O(bidentate) distances span the range 2.441(3)−2.574(3) Å, while Nd−O(monodentate) distances lie between 2.315(2) and 2.528(3) Å.[32] Within the equatorial plane, the bite angles within bidentate carbonate ligands span the range 51.1(2)−52.2(1)° in each dimeric unit. Substantial deviation from planarity between adjacent equatorial ligands is evident—thus the sum of all O−Nd−O angles within the equatorial plane is only 336.0(2)°. $[Co(NH_3)_6]^{3+}$ cations display Co−N bond lengths (1.931(5)−1.970(6) Å) and angles similar to those observed previously for this moiety. Because of a disorder problem involving a Co^{3+} cation (see Crystallographic Studies), we were unable to obtain meaningful metric parameters for the dipotassium $[K_2(H_2O)_{10}]^{2+}$ fragment. However, charge-balance considerations strongly suggest that this fragment does exist within the lattice of the molecule, and to the best of our knowledge, this is the first structurally characterized example of a dimeric unit of this type. We also recently observed a similar structural unit containing sodium in a holmium carbonate complex.[37] Bond lengths and angles for this portion of the molecule are presented in the Supporting Information. As a noteworthy point, we have independently determined the structure of two other $Ln_2(CO_3)_8^{10-}$ analogues of complex **1** (Ln = Nd, Eu) from solutions containing Cs_2CO_3. A similar disorder is exhibited by the cationic portion of each molecule (albeit with different relative amounts of Co^{3+} versus Cs^+ in these cases); however, the anionic repeat unit is identical to that in complex **1**.

Vibrational Spectroscopy. Infrared and Raman spectroscopic studies were reported previously for a number of lanthanide complexes proposed to contain di-, tri-, and tetracarbonato ligation.[36,38,39] Here, we report a solid-state spectroscopic characterization of **1** and correlate spectroscopic features with the single-crystal X-ray structure (it should be emphasized that the solid-state X-ray and spectroscopic data for complex **1** may not necessarily reflect the nature of the lanthanide metal−carbonate ligand interactions present in aqueous solution). Infrared spectra of **1** exhibit broad absorptions at 3503, 3282, and 3081 cm^{-1} due to N−H and O−H stretching modes of cobalt-bound ammonia ligands and water molecules within the $[K_2(H_2O)_{10}]^{2+}$ unit and also in the lattice. A medium-intensity feature at 1632 cm^{-1} is assigned to the δ(N−H) and δ(O−H) modes of the same species, while two intense bands at 1479 and 1397 cm^{-1} can be ascribed to carbonate-based asymmetric stretching modes (ν_3). The existence of two features in this region is indicative of carbonate groups complexed in a bidentate fashion and/or two different types of carbonate ligands (equatorial vs axial bridging groups).[40] Two weak bands (ν_1 symmetric stretching modes) are also observed at 1055 and 1072 cm^{-1}, which correlate closely with the two bands observed in the solid-state Raman spectrum 1060 and 1070 cm^{-1}. Additional infrared carbonate features are present at 866 (ν_2), 712, and 693 cm^{-1} (free carbonate bending modes (ν_4) that are split upon metal complexation). IR data previously reported by Taravel and co-workers for a series of aquated lanthanide carbonate solids (formulated as tetracarbonate complexes)[38] are qualitatively similar to the data obtained here. However, the slightly more complex IR spectrum of **1** may be accounted for by the fact that this complex contains two distinct types of bidentate ligands, rather than the single bidentate coordination mode expected for a discrete monometallic tetracarbonate complex.

In conclusion, we have isolated and structurally characterized a novel example of a one-dimensional chainlike tetracarbonate complex of a lanthanide element. In an attempt to understand the role that factors such as ionic radius play in determining the generality of the structure seen in complex **1**, further studies of the carbonate coordination chemistry of the 4f-elements across the series are currently underway.

Experimental Section

General Considerations. All operations were carried out in the open atmosphere and at room temperature. Aqueous solutions were prepared using deionized water from a Millipore purification system. $[Co(NH_3)_6]Cl_3$, K_2CO_3, and $Nd(NO)_3 \cdot 6H_2O$ were purchased from Aldrich and used

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as received. Raman vibrational spectra were obtained using near-infrared excitation from a Ti−sapphire CW laser (752 nm, Spectra Physics model 3900s) with detection accomplished through a CCD detector (Princeton Instruments). The Raman scattering was dispersed with a single-stage monochromator (diffraction gratings blazed at 1150 nm; 4 cm^{-1} resolution) after being prefiltered through an interference filter designed to remove Rayleigh scattered laser light. The Raman samples were recorded in sealed 5 mm glass NMR tubes or mounted on a glass plate with silicone grease.

Preparation of $[Co(NH_3)_6]_6[K_2(H_2O)_{10}][Nd_2(CO_3)_8]_2 \cdot 20H_2O$ (1). To 2 mL of a 0.038 M solution of $Nd(NO_3)_3$ in 2.5 M K_2CO_3 was added 0.7 mL of aqueous 0.2 M $[Co(NH_3)_6]Cl_3$. After 3 days, crystals of **1** deposited as orange rods, which were washed with water and methanol and air-dried. Yield: 0.023 g (39%, relative to the limiting reagent, which in this case was $Nd(NO_3)_3$). IR (cm^{-1}): 3503 (m, sh), 3282 (s), 3081 (s, sh), 1632 (m), 1479 (s), 1397 (s), 1338 (s, sh), 1072 (w), 1055 (w), 908 (m), 900 (m), 866 (m), 712 (w), 693 (w). Raman (cm^{-1}): 1340 (s), 1318 (s), 1246 (s), 1033 (s), 1023 (s, sh), 867 (s), 807 (s), 764 (m), 514 (w), 494 (w), 458 (w, sh), 448 (w), 320 (w). Anal. Calcd for $C_{16}H_{168}Co_6K_2N_{36}Nd_4O_{78}$: C, 6.15; H, 5.42; N, 16.15. Found: C, 6.14; H, 5.61; N, 16.15.

Crystallographic Study of $[Co(NH_3)_6]_6[K_2(H_2O)_{10}][Nd_2(CO_3)_8]_2 \cdot 20H_2O$. An orange rod-shaped crystal was attached to a glass fiber using silicone grease, placed on a Bruker P4/CCD/PC diffractometer, and cooled to −70 °C using a Bruker LT-2 low-temperature device. The data were collected using a sealed, graphite-monochromated Mo Kα X-ray source ($\lambda = 0.71073$ Å). A hemisphere of data were collected using a combination of φ and ω scans, with 20 s frame exposures and 0.3° frame widths. Data collection, initial indexing, and cell refinement were handled using SMART[41] software, and frame integration and final cell parameter calculations were carried out with SAINT[42] software. The final cell parameters were determined from a least-squares fit to 4402 reflections. The data were corrected for absorption using the DIFABS[43] program. Decay of reflection intensity was not observed.

The structure was solved in space group $P2_1/c$ (No. 14) using Direct Methods and difference Fourier techniques. The initial solution revealed the neodymium, cobalt, potassium, and the majority of all non-hydrogen atom positions. Several lattice water molecules were discovered during subsequent Fourier synthesis [atoms labeled O(7W) to O(17W)]. Two of these lattice water molecules had large temperature factors when refined at full occupancy and were subsequently refined at half-occupancy (atoms labeled O(16W) and O(17W); these water sites are believed to be only partially occupied). Hydrogen atoms were fixed (N−H = 0.89 Å) on the ammonia ligands, which were allowed to rotate to maximize electron density at the hydrogen atom positions, and were refined with isotropic temperature factors set to 1.5 times the equivalent isotropic U values of the atoms to which they were bound. At this point, a large residual of 6 e $Å^{-3}$ was noted on the inversion center occupied by the $[K_2(H_2O)_{10}]^{2+}$ cation. Our best explanation for this residual electron density, based on charge balance and chemistry, is that the $[K_2(H_2O)_{10}]^{2+}$ cation site is occupied by a pseudooctahedral $[Co(NH_3)_5(OH)]^{2+}$ cation approximately 12.5% of the time. The degree of partial occupancy was determined from a joint site-occupancy refinement on the potassium and cobalt atoms and fixed for the final refinement. Four of the ligand sites corresponding to the $[Co(NH_3)_5(OH)]^{2+}$ cation were coincident with the $[K_2(H_2O)_{10}]^{2+}$ cation ligands, and the fifth and sixth sites correspond to the ligand O(6W) and its inversion pair. The O(6W) atom was refined at an occupancy of 0.125 to correspond to the partial occupancy of the Co site. The final refinement[44] included anisotropic temperature factors for all non-hydrogen atoms except O(6W). Because of disorder, NH_3 and OH^- ligands within the $[Co(NH_3)_5(OH)]^{2+}$ fragments were refined using oxygen scattering factors. The structure solution and graphics were obtainedusing SHELXTL PC.[45] SHELX-93 was used for structure refinement and creation of publication tables.[46] Additional details of data collection and structure refinement are listed in Table 1.

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Supporting Information Available: A thermal ellipsoid view of the disordered $[K_2(H_2O)_{10}]$ cationic unit and X-ray crystallographic files, in CIF format, for the structure determination of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(41) *SMART*, Version 4.210; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1996.

(42) *SAINT*, Version 4.05; **1996**, Bruker Analytical X-ray Systems, Inc.: Madison, WI 1996.

(43) Spek, J. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.

(44) $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.031P)^2]$, where $P = [{}^1/_3\max(0 \text{ or } F_o^2) + {}^2/_3F_c^2]$.

(45) *SHELXTL PC*, Version 4.2/360; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 1994.

(46) Sheldrick, G. *SHELX-93*; University of Göttingen: Göttingen, Germany, 1993.