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Single Crystal and Solution Complex Structure of $Nd(CO_3)_4{}^{5-}$. The First Characterization of a Mononuclear Lanthanide(III) Carbonato Complex

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Carbonate is a strong complexing ligand for f-elements and is expected to play an important role in the environmental fate of lanthanides and actinides.[1,2] Depending on the CO_2 partial pressure, pH, and ionic strength, $MOHCO_3$,[3,4] $M_2(CO_3)_3 \cdot nH_2O$,[3−5] and $NaM(CO_3)_2 \cdot nH_2O$,[6,7] where M = lanthanide or actinide, can be precipitated from carbonate-containing solutions under normal conditions. The few single-crystal structures determined for trivalent lanthanide carbonates consist of extended arrays ($La_2(CO_3)_3 \cdot 8H_2O$[8] and $(La/Ce)_2(CO_3)_3 \cdot 8H_2O$;[9] $CsPr(CO_3)_2$[10]). Most of the solid carbonates have been studied using powder X-ray diffraction;[7,11−13] however, many Ln(III) carbonates are amorphous and have not been characterized structurally. Lanthanide(III) or actinide(III) solution complexes with carbonate of general formula $M(CO_3)_n{}^{3-2n}$ with $n = 1-3$ have been identified spectroscopically.[5,14] While $M(CO_3)_5{}^{6-}$ has been proven to be the limiting complex for tetravalent f-elements,[15,16] the identity of the limiting M(III) carbonate complex remains unclear. Spectroscopic investigations of solution species carried out to delineate the speciation of M(III) in the presence of carbonate have provided overall metal and carbonate stoichiometries and formation constants for individual species. Both $M(CO_3)_3{}^{3-}$ [14] and $M(CO_3)_4{}^{5-}$ [17−19] have been proposed as the limiting carbonate complex, but no definite structural details are available on either. The scarcity of structurally characterized M(III) carbonates has prompted us to obtain single crystals of discrete M(III) carbonate species. Herein, we report the crystallographic characterization of the first mononuclear lanthanide(III) carbonate.

By employing the guanidinium cation, pink crystals of $[C(NH_2)_3]_5[Nd(CO_3)_4(H_2O)] \cdot 2H_2O$ were deposited in a matrix of colorless guanidinium carbonate crystals after slow evaporation of millimolar Nd(III) in a saturated $[C(NH_2)_3](CO_3)$ solution. The same compound was also obtained from a reaction of Nd(III) with guanidinium carbonate in aqueous solution at pH 10. A full single-crystal X-ray structure determination was carried out on one of these crystals.[20] The $Nd(CO_3)_4(H_2O)^{5-}$ anion (Figure 1) contains nine-coordinate Nd in a distorted monocapped antiprism with a twist angle of 23.2°. The central Nd atom is bound to nine O atoms from four bidentate bonded carbonato ligands and one coordinated water molecule. The eight oxygen atoms of the bidentate carbonate ligands define the corners of the square antiprism with the water molecule capping the top. The Nd−O bond distances for the bidentate carbonates range between 2.452(3) and 2.544(3) Å; the longest distance, 2.649(4) Å, is to the coordinated water oxygen (O1W). These Nd carbonate distances compare well with the average of 2.475 Å for bidentate carbonates in $Na_3Eu(CO_3)_3$ which was prepared hydrothermally.[21] Trans-carbonate carbon atoms lie above (0.2270 Å for C(1) and 0.2210 Å for C(2)) and below (0.2204 Å for C(3) and 0.2276 Å for C(4)) a mean plane with the Nd atom residing 0.397 Å above the plane. The angle C1−Nd−C2 is 173°, and C3−Nd−C4 is 155°. The O−C−O angles of the carbonate ligands average 121.4° and 117.3° with the smaller angle lying between oxygen atoms bound to the Nd center.

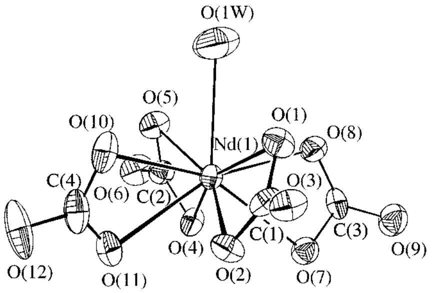

Figure 1. ORTEP diagram (50% probability) of the $Nd(CO_3)_4(H_2O)^{5-}$ anion. Nd−O distances are between 2.452(3) and 2.544(3) Å; the Nd−O1W bond distance is 2.649(4) Å.

The anions are linked together in the unit cell via hydrogen bonding with the guanidinium cations (N_{guan}) and lattice waters (O2W and O3W) (Figure 2). The hydrogen bonding is quite strong, as indicated by the following short distances: 2.954 Å between carbonate oxygen O12 and O2W, a range of 2.794−

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(20) Single-crystal X-ray analysis on the title compound was performed on a Bruker P4/CCD/PC system. A hemisphere of data was collected using a combination of ϕ and ω scans, with 0.3° frame widths. The data were corrected for absorption using an analytical technique. Crystal data: orthorhombic, space group $Pna2_1$, $a = 21.472(1)$ Å, $b = 6.8615(3)$ Å, $c = 18.8797(9)$ Å, Z = 4, V = 2781.5(2) Å^3, $T = 203$ K, ρ(calc) = 1.764 g/cm^3, $\mu = 19.57$ cm^{-1}, $\lambda = 0.71073$ Å, $2\theta_{max} = 52.8°$, total data 12266, unique data 2907 ($R_{int} = 0.0274$), R/R_w $[I > 2\sigma(I)] = 0.0192/0.0498$. All non-hydrogen atoms refined anisotropically. Hydrogen atom positions on water molecules were not considered in the structural model. The amine hydrogen atom positions were idealized and refined using a riding model. SHELXTL version 5.1 was used for structure solution, refinement based on F^2, graphics, and publication materials.
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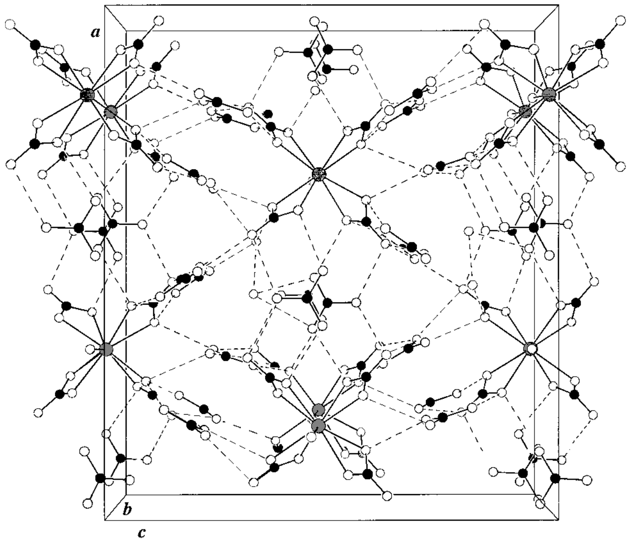

Figure 2. Ball-and-stick drawing of $[C(NH_2)_3]_5[Nd(CO_3)_4(H_2O)]\cdot 2H_2O$ illustrating the packing and hydrogen bonding of ions and lattice waters.

3.267 Å between N_{guan} and carbonate oxygen atoms, and 2.470 Å between O2W and O3W. One water molecule (O3W) does not interact with the central Nd(III) carbonate anion, but hydrogen bonds to N_{guan} with distances ranging between 2.854 and 3.605 Å. The anions are linked via hydrogen bonding of O1W and one carbonate oxygen (2.997 Å for O1W−O11).

This single-crystal X-ray diffraction study verifies that the $Nd(CO_3)_4(H_2O)^{5-}$ ion exists in the solid state. We used conventional UV−vis−near-IR absorbance spectroscopy for identification of the limiting complex in saturated K_2CO_3 and $[C(NH_2)_3]_2CO_3$ solutions. The electronic absorption spectrum of Nd^{3+} shows a manifold of Laporte-forbidden f−f transition bands in the visible region 400−800 nm.[22] The dominant absorbance of the Nd^{3+} aquo ion at 574.1 nm is shifted with complexation to 583.6 nm in saturated carbonate solution. The diffuse reflectance spectra of $[C(NH_2)_3]_5[Nd(CO_3)_4(H_2O)]\cdot 2H_2O$ crystals ground into a powder showed the most intense peak at 582.3 nm. The peak-to-peak correlation of peak maxima in the diffuse reflectance spectrum of the solid and the absorbance spectra of the Nd(III) solution suggests similar mononuclear chromophores in both states. However, the spectra are not identical and the solution clearly contains other lower carbonate to metal species in addition to $Nd(CO_3)_4^{5-}$.

The nature of the limiting M(III) (M = Ln, An) complex in solution at high carbonate concentrations has been debated for years. This work is the first elucidation of the molecular structure of a mononuclear M(III) carbonate compound. The coordination environment around the Nd atom is consistent with the coordination number of 9 in $NdOHCO_3$[12] and $Na_3Eu(CO_3)_3$.[21] However, in the few Ln(III) carbonate structures reported, carbonates are both monodentate and bidentate and are bridging to form extended chains, sheets, or three-dimensional arrays. The information presented on the mononuclear Nd(III) tetracarbonate provides a better understanding of carbonate interaction with trivalent f-elements in aqueous solution and may enable more accurate modeling of interfacial processes on mineral surfaces. Comparing with $M(CO_3)_5^{6-}$ (known for An(IV)), where all coordination sites are occupied by five bidentately bonded carbonates, opens speculation about the potential replacement of the bonded water molecular with a monodentately bonded carbonate ligand.

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Supporting Information Available: Figures of UV−vis−near-IR solution absorption spectra, diffuse reflectance spectra of the powdered single crystal, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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