A Model for Trivalent Actinides in Media Containing High Carbonate Concentrations − Structural Characterization of the Lanthanide Tetracarbonate $[Co(NH_3)_6][Na(\mu\text{-}H_2O)(H_2O)_4]_2[Ho(CO_3)_4]\cdot 4H_2O$

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Keywords: Actinides / Lanthanides / Carbonate / Coordination chemistry / Structural elucidation

The identity of the limiting Ho^{III} species in aqueous solutions with high carbonate concentrations has been determined to be $Ho(CO_3)_4{}^{5-}$. Single crystals of $[Co(NH_3)_6]$-$[Na(\mu\text{–}H_2O)(H_2O)_4]_2[Ho(CO_3)_4]\cdot 4H_2O$ were obtained by the addition of $[Co(NH_3)_6]^{3+}$ to an aqueous 0.04 M solution of Ho^{III} in 2.1 M Na_2CO_3. The asymmetric unit contains the anion, $[Ho(CO_3)_4]^{5-}$, a $[Co(NH_3)_6]^{3+}$ cation and two Na^+ cations, which are bound to H_2O molecules in an edge-sharing bioctahedral geometry. The $[Ho(CO_3)_4]^{5-}$ anion is eight coordinate with four bidentate carbonate ligands bound to the Ho atom. The molecule has essentially C_{2v} symmetry with two coplanar carbonates making a vane, which is perpendicular to a similar vane produced by the other two carbonate ligands. An alternative way to this view molecule is through the geometry of the C atoms, which are found in a distorted tetrahedron. The average Ho–O distance was determined to be 2.361(5) Å, while the average Ho–C distance was 2.784(6) Å. The IR and Raman spectra were determined in both the solid state and solution in order to confirm the solution speciation. The Raman data show a single $CO_3{}^{2-}$ stretch for the solid at 1062 cm^{-1}. The solution data show multiple peaks with the most prominent being at 1048 cm^{-1}, which is consistent with the literature reports of an equilibrium mixture. The IR data for the solids confirm the X-ray results showing bidentate carbonate ligands by the splitting of the ν_3 band of the $CO_3{}^{2-}$. The crystal data for $[Co(NH_3)_6][Na(\mu\text{-}H_2O)(H_2O)_4]_2[Ho(CO_3)_4]\cdot 4H_2O$ are as follows: monoclinic space group $P2/n$, a = 8.7091(5) Å, b = 10.8744(6) Å, c = 15.7971(9) Å, β = 93.117(1)°, Z = 2, $R1$ = 0.0307, $wR2$ = 0.0756.

Introduction

Carbonate is commonly found in groundwater environments and has a high affinity for metal cations such as lanthanide and actinide ions; thermodynamic formation constants can often be as high as 10^{50}.[1,2] Unlike many metal ions, whose carbonate salts are relatively insoluble, carbonate complexation of the lanthanides and actinides can actually enhance solubility through the formation of highly charged anionic complexes. This enhancement of the solubility of the actinides in carbonic solutions is a serious concern for modeling the transport of these materials through the environment.[1−3] As an example, we note that there are conflicting reports on the nature of the limiting complex in trivalent lanthanide/actinide carbonate system. Recent spectroscopic studies of Cm^{III} in carbonate solution indicate that the tetra-carbonato complex $[Cm(CO_3)_4]^{5-}$ is the limiting species in the An^{III} carbonate system.[4] Other workers who have examined trivalent lanthanide systems have argued that the tris-carbonato complex $[Nd(CO_3)_3]^{3-}$ is the limiting species in the Ln^{III} carbonate system.[5] As a result, it is important to identify the structural models which could have spectroscopic tags for the environmentally relevant complexes formed in the equilibria.

Despite the reported synthesis of a number of materials, there are limited structural data for either the lanthanide or actinide metals with lower carbonate stoichiometries. The proposed lanthanide materials include: $Ln_2(CO_3)_3$, $Ln_2(CO_3)_3\cdot xH_2O$ (x = 2, 3, 8),[6−15] $M_6[Ce(CO_3)_5]\cdot xH_2O$ (M = Na, x = 12; M = $C(NH_2)_3$, x = 4),[16] $M_4[Ce(CO_3)_4]\cdot xH_2O$ (M = Na, x = 7; M = $C(NH_2)_3$, x = 6),[17] $M[Ln(CO_3)_2]$ (M = Li,[18] Na,[19,20] K,[21] Cs,[11] Tl[22]), and $M_5[Ln(CO_3)_4]$ (M = Na,[21] Tl[22]). Typically, the characterization of these materials involved X-ray powder diffraction, vibrational spectroscopy and thermogravimetric analysis. Recently, one of the first examples of a single crystal X-ray determination of a monomeric Ln^{III} tetra-carbonato complex, $[C(NH_2)_3]_5Nd(CO_3)_4(H_2O)$ was re-

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Eur. J. Inorg. Chem. 2001, 2921−2926 1434−1948/01/1111−2921 $ 17.50+.50/0

ported.[23] We have also structurally characterized by single crystal X-ray techniques, $[Co(NH_3)_6][Sm(CO_3)_3(H_2O)]\cdot 4H_2O$[24] and $[Co(NH_3)_6]_6[K_2(H_2O)_{10}][Nd_2(CO_3)_8]_2\cdot 20H_2O$.[25] We sought to extend these studies by structurally characterizing additional carbonato anions, which could be found in the equilibrium systems described above. Studies were initiated with the lanthanides due to the ease of handling, the oxidation state stability and greater resistance to hydrolysis. Since the ionic radii of the lanthanides decrease across the series, we reasoned that the heavier lanthanides would be most likely to produce a mononuclear eight-coordinate tetracarbonate anion. We describe here our efforts in the synthesis and structural characterization of the limiting Ho^{III} tetracarbonate anion $[Ho(CO_3)_4]^{5-}$.

Results and Discussion

Synthesis and Electronic Spectra

The study of the holmium carbonate system is complicated by the precipitation of mineral phase carbonates of the form $Ho_2(CO_3)_3\cdot xH_2O$. The formation of this phase can be avoided by a judicious choice of metal carbonate, for example M_2CO_3 (M = Na, K, Cs, etc.), as well as controlling the total lanthanide and carbonate concentrations. The solutions were prepared by addition of $Ho(NO_3)_3\cdot xH_2O$ to 2.5 M Na_2CO_3, resulting in a yellow 0.1 M Ho^{III} solution. The Ho^{III} solution was analyzed by UV/Vis spectroscopy to identify any shift or change in intensity of the *f-f* transition compared to the Ho^{III} aquo ion. The electronic absorption spectrum was measured from 350 to 800 nm. The five most intense peaks were found at 360, 419, 450, 489, and 539 nm, with optical densities of 8.1, 2.9, 28, 1.9, and 3.5 $M^{-1}cm^{-1}$, respectively. It should be noted that the peaks at 360 and 450 nm are more intense than those of the aquo ion (ε = 1.3 and 3.1 $M^{-1}cm^{-1}$, respectively), indicating a possible lowering of the molecular symmetry.

Single Crystal X-ray Diffraction

Single crystals of $[Co(NH_3)_6][Na(\mu\text{-}H_2O)(H_2O)_4]_2[Ho(CO_3)_4]\cdot 4H_2O$ were obtained by addition of $[Co(NH_3)_6]Cl_3$ to a 0.04 M solution of Ho^{III} in 1.7 M Na_2CO_3, from which yellow orange crystals were obtained after two weeks of slow evaporation at room temperature. The data collection and crystallographic parameters are summarized in Table 1, and the selected bond lengths and angles are given in Table 2. A thermal ellipsoid drawing of $[Co(NH_3)_6][Na(\mu\text{-}H_2O)(H_2O)_4]_2[Ho(CO_3)_4]\cdot 4H_2O$ is shown in Figure 1, which also provides the atom-numbering scheme used in the tables. Figure 2 depicts the crystal matrix down the *b*-axis and shows the extensive hydrogen bonding network within the crystal.

Table 1. Crystal data and structure refinement for $[Ho(CO_3)_4][Co(NH_3)_6][Na(\mu\text{-}H_2O)(H_2O)_4]_2\cdot 4H_2O$

Empirical formula	$C_4H_{44}CoHoN_6Na_2O_{26}$
Molecular weight	862.29
Temperature	203(2) K
Wavelength λ (Mo-K_α)	0.71073 Å
Crystal system	monoclinic
Space group	*P*2/*n*
Unit cell dimensions	a = 8.7091(5) Å b = 10.8744(6) Å; β = 93.117(1)° c = 15.7971(9) Å
Volume	1493.87(15) $Å^3$
Z	2
Density (calculated)	1.917 Mg/m^3
Absorption coefficient	3.317 mm^{-1}
*T*min./*T*max.	0.85/0.95
F(000)	868
Crystal size	0.06 × 0.06 × 0.12 mm^3
Theta range for data collection	1.9 to 26.4°.
Index ranges	$-10 \le h \le 10$, $0 \le k \le 13$, $0 \le l \le 19$
Reflections collected	6986
Independent reflections	2945 [R(int) = 0.0232]
Data/restraints/parameters	2945/0/187
Goodness-of-fit on F^2	1.281
Final *R* indices [$I > 2\sigma(I)$]	$R1$ = 0.0267,[a] $wR2$ = 0.0741[b]
R indices (all data)	$R1$ = 0.0307, $wR2$ = 0.0756
Largest diff. peak and hole	0.772 and −0.504e.$Å^{-3}$

[a] $R1 = \sigma||F_o| - |F_c||/\sigma|F_o|$. – [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0397*P)^2 + 5.0273*P]$

Table 2. Selected bond lengths [Å] and angles [°] for $[Co(NH_3)_6][Na_2(H_2O)_{10}][Ho(CO_3)_4]\cdot 4H_2O$

Ho(1)−O(2)	2.386(3)	Ho(1)−C(1)	2.793(4)
Ho(1)−O(3)	2.352(3)	Ho(1)−C(2)	2.775(4)
Ho(1)−O(5)	2.357(3)	Ho(1)−O(1)	4.057(5)
Ho(1)−O(6)	2.348(3)	Ho(1)−O(2)	4.041(1)
Na(1)−O(7)	2.503(3)	Na(1)−O(10)	2.388(3)
Na(1)−O(8)	2.414(3)	Na(1)−O(11)	2.425(4)
Na(1)−O(9)	2.417(3)	Na(1)−O(9A)	2.423(3)
Na(1)−Na(1A)	3.555(3)		
O(3)−Ho(1)−O(5A)	76.99(9)	O(5)−Ho(1)−O(2)	90.86(10)
O(6)−Ho(1)−O(5)	55.73(9)	C(2A)−Ho(1)−C(2)	100.77(15)
O(6A)−Ho(1)−O(2)	169.77(9)	C(2A)−Ho(1)−C(1)	132.26(10)
O(6)−Ho(1)−O(2)	90.39(11)	C(2)−Ho(1)−C(1)	99.73(11)
O(3)−Ho(1)−O(2)	55.27(9)	C(1)−Ho(1)−C(1A)	97.42(15)
O(10)−Na(1)−O(8)	86.04(11)	O(10)−Na(1)−O(11)	176.96(14)
O(10)−Na(1)−O(9)	97.49(12)	O(8)−Na(1)−O(11)	90.95(12)
O(8)−Na(1)−O(9)	91.83(11)	O(9)−Na(1)−O(11)	83.00(13)
O(10)−Na(1)−O(9A)	93.43(12)	O(9A) −Na(1)−O(11)	89.60(12)
O(8)−Na(1)−O(9A)	177.15(13)	O(10)−Na(1)−O(7)	76.92(11)
O(9)−Na(1)−O(9A)	85.46(11)	O(8)−Na(1)−O(7)	97.06(11)
O(9)−Na(1)−O(7)	169.09(12)	O(11)−Na(1)−O(7)	103.09(13)
O(9)a−Na(1)−O(7)	85.54(11)		

The asymmetric unit contains the anion $[Ho(CO_3)_4]^{5-}$, a $[Co(NH_3)_6]^{3+}$ cation, two Na^+ cations, and 14 H_2O molecules, which are either bound to the Na^+ cations or found in the lattice. The metrical parameters for the $[Co(NH_3)_6]^{3+}$ ion are all within normal ranges. The $[Ho(CO_3)_4]^{5-}$ anion is eight coordinate, with four bidentate carbonate ligands bound to the Ho atom. The molecule has essentially C_{2v} symmetry with two coplanar carbonates making a vane, which is perpendicular to a similar vane produced by the other two carbonate ligands. Another view of this molecule is obtained through the geometry of the C atoms, which are found in a severely distorted tetrahedral geometry. The

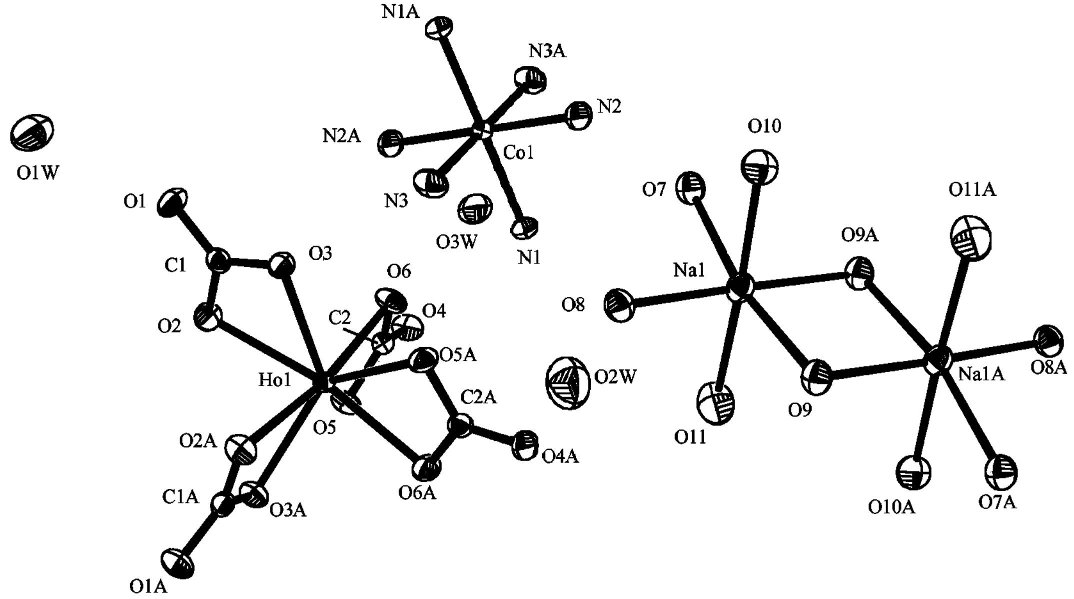

Figure 1. Thermal ellipsoid plot (50% probability) of $[Co(NH_3)_6][Na_2(H_2O)_{10}][Ho(CO_3)_4]\cdot 4H_2O$, giving the atom numbering scheme used in the tables

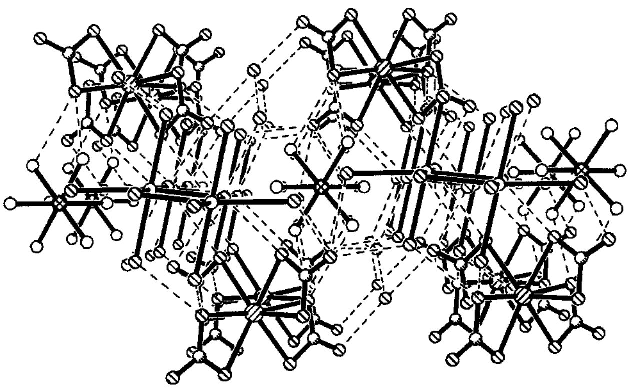

Figure 2. Ball and stick drawing depicting the crystal matrix of $[Co(NH_3)_6][Na_2(H_2O)_{10}][Ho(CO_3)_4]\cdot 4H_2O$ down the *b*-axis; the hydrogen bonding within the complex is shown by the dashed lines

average Ho−O distance was determined to be 2.361(5) Å, while the average Ho−C distance was 2.784(6) Å. As was previously stated, this is the first structural characterization of a mononuclear homoleptic carbonato complex of a trivalent lanthanide. In fact, the only structurally well characterized homoleptic lanthanide carbonate molecules are $[C(NH_2)_3]_6[Ce(CO_3)_5]\cdot 4H_2O$,[26] $La_2(CO_3)_3\cdot 8H_2O$,[27] $(La,Ce)_2(CO_3)_3\cdot 8H_2O$,[28] and $M[Ln(CO_3)_2]$ (M = K, Ln = Nd, Dy; M = Cs, Ln = Pr).[11,29,30] A comparison of the bond lengths may be made with $[Ho(oxam)_3(H_2O)_3]_4\cdot 2.75H_2O$ (**I**),[31] Ho(2,6-dihydroxybenzoato-*O*)$_2$(2,6-dihydroxybenzoato-*O,O*)$(H_2O)_4\cdot 2H_2O$ (**II**),[32] and $Ho(HCO_3)_3(H_2O)_4\cdot 2H_2O$ (**III**).[33] These complexes all contain terminal aquo ligands and carbonate or carboxylate groups with the Ho−O bond lengths being slightly different for $Ho-O_{(aquo)}$ and $Ho-O_{(O\text{-}R)}$. For **I** the average $Ho-O_{(aquo)}$ bond length is 2.37(1) Å, while the average for $Ho-O_{(O\text{-}R)}$ is 2.42(1) Å with values ranging from 2.362(8)−2.535(8) Å.[31] For **II** the average $Ho-OH_2$ distance is 2.37(1) Å, with a range for all Ho−O distances of 2.297(3)−2.486(3) Å.[32] Lastly, the average $Ho-OH_2$ distance in **III** is 2.36(1) Å, while the bond lengths of the bicarbonate ligands range from 2.442(9)−2.557(9) Å.[33] Clearly the bond lengths for the $Ho(CO_3)_4{}^{5-}$ ion are reasonable relative to other known Ho complexes. There are three main O−Ho−O angles of interest. The first type is the "bite" angle of the carbonate ligands, for example O(3)−Ho(1)−O(2), whose average is 55.5 (1)°. The other two angles are based on those between the carbonate ligands: O(3)−Ho(1)−O(5A) at 76.99(9)° and O(2)−Ho(1)−O(6A) at 169.77(9)°. An indication of the planarity between the two sets of carbonate ligands can be obtained by addition of the angles, which gives 358(1)°, quite close to the theoretical 360°. The C−Ho−C angles come in pairs and range from 132.26(11) to 97.42(15)° with the average being 107.5(2)°. The large range in the angles indicates the severe distortion from a tetrahedral geometry. The average distal C−O distance, 1.265(4) Å, is significantly shorter than the average metal-bound C−O distance, 1.301(5) Å. The O−C−O angles of the carbonate ligand deviate from the ideal value of 120°. The O−C−O angle between O atoms bound to Ho (the bite angle) averages 115.4(3)° while the remaining two O−C−O angles have opened up somewhat to 122.3(6)°. These distortions are typically found within carbonate ligands that are complexed to metal centers. The carbonate ligands are also involved with an extended hydrogen-bonding network. There are close contacts between the O atoms of the Ho carbonate ligands to the N atoms of the $[Co(NH_3)_6]^{3+}$ [average O···N is 3.09(1) Å]. The carbonate O atoms also have close contacts with the H_2O molecules in the lattice and those bound to the Na atoms [average O···O is 2.81(1) Å]. These distances are all well within the range expected for weak H-bonding interactions.[34]

Another interesting structural feature is the sodium aquo ion dimer $[Na_2(H_2O)_{10}]^{2+}$. Each of the Na atoms is six-coordinate, with four terminal and two bridging H_2O molecules; the overall geometry is best described as an edge-shared bioctahedron. The two Na atoms are separated by a reasonable 3.555(3) Å. The average Na−O distance is 2.43(1) Å with values ranging from 2.388(3) Å to 2.503(3) Å. The octahedra are distorted by an approximate 5° tilt of the axial ligands towards the center of the molecule. This distortion is further indicated by the average $O(11)-Na-O_{(cis)}$ angle of 91.7(1)°, while the average $O(10)-Na-O_{(cis)}$ angle is 88.5(1)°.

Vibrational Spectroscopy

Metal-carbonate complexation results in the splitting of the doubly degenerate e' and e'' modes of the free carbonate (D_{3h} symmetry). The extent of this splitting can be used to indicate whether the complexation is mono- or bidentate in nature.[35−37] This is especially true of the e' ν_3 carbonate band composed of the asymmetric stretch of the free ligand. For bidentate complexation to a trivalent metal, the higher frequency stretch is pushed to over 1500 cm^{-1}, and the splitting between this band and the lower stretch is greater than 100 cm^{-1}. Conversely, monodentate complexation shifts the higher stretch to less than 1500 cm^{-1} and results in a splitting of less than 100 cm^{-1}. Another vibrational mode of interest, the metal−oxygen stretch, gives information on the strength of the bonding. For carbonate complexes with trivalent metals, this peak is typically in the 300−400 cm^{-1} region.[36]

Both Raman and infrared absorption (IR) measurements were performed to aid the characterization of the mode of carbonate complexation to Ho^{III}. The Raman spectrum from a single crystal of Ho^{III} carbonate is dominated by bands due to the $Co(NH_3)_6{}^{3+}$ moiety, with the only clear carbonate mode due to the symmetric stretch at 1062 cm^{-1}(Figure 3). The spectrum of the crystal differs from that of the parent solution, in which peaks at 1048 and 1066 cm^{-1} are observed. The latter feature is due in large part to free carbonate and obscures any measure of the tetracarbonato species, while the former demonstrates that a significant amount of the Ho in solution is a lower carbonato complex. This is consistent with earlier work that indicated an equilibrium mixture of complexes even up to 2.0 M $CO_3{}^{2-}$.[38] No Raman feature due to the Ho−O stretch could be observed, perhaps due to it being obscured by the cobalt hexaammine peak at 295 cm^{-1}, but also possibly due to the lack of covalent character of the holmium-carbonate bonding.

More carbonate bands for the $Ho(CO_3)_4{}^{5-}$ solid are found in the IR spectrum obtained from a ground sample prepared as a KBr pellet (Figure 4). In contrast to the Raman spectrum, the cobalt hexaammine peaks do not mask large areas of the spectral region: peaks are observed at 826, 1328 (shoulder), and 1653 cm^{-1},[36] with the latter also receiving any contribution from H_2O absorption. The remaining IR peaks are similar to those found for a holmium carbonate complex previously postulated to be the tetracarbonato species.[39] The coincidence of the IR peaks shown in the earlier work and the peaks reported here confirm that the holmium carbonato species is the same in both reports. While the nature of the species was postulated in the earlier work, water molecules directly bonded to the holmium had been postulated to sterically force the carbonates to bond in a monodentate fashion.[39] The crystal structure here shows that these water molecules are not bonded to holmium but rather to sodium, and that the carbonate bonds are indeed bidentate. The IR peaks support this bidentate bonding scheme.[35−37] Specifically, there is clearly a high frequency carbonate peak at 1519 cm^{-1}, consistent

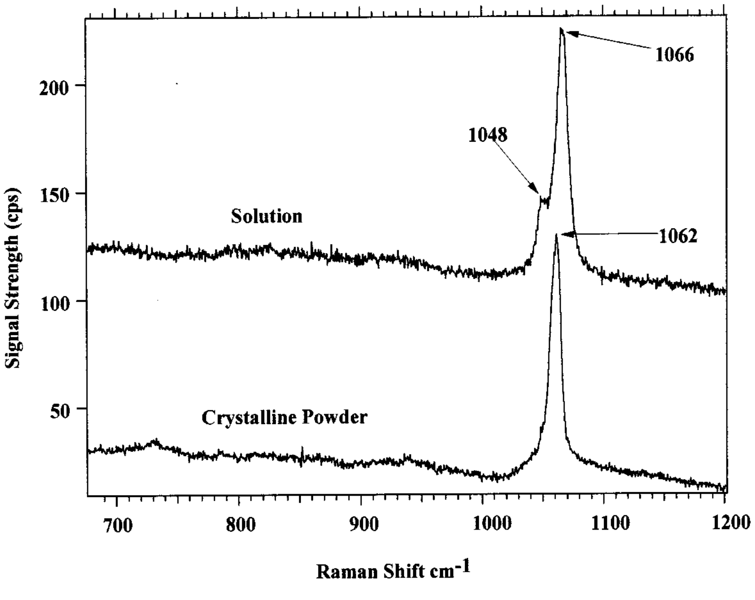

Figure 3. Raman spectra of 0.01 M Ho^{III} in 2.5 M Na_2CO_3 (upper) and solid $[Co(NH_3)_6][Na_2(H_2O)_{10}][Ho(CO_3)_4]\cdot 4H_2O$ (lower)

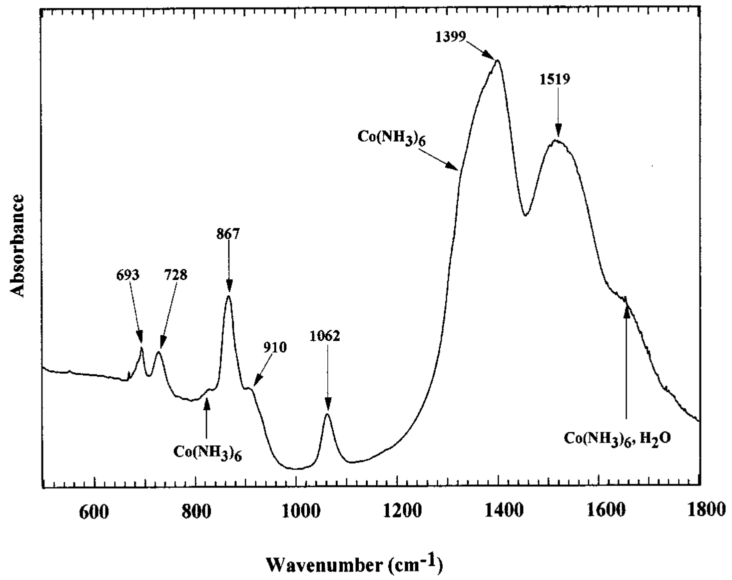

Figure 4. Infra-red spectrum of solid $[Co(NH_3)_6][Na_2(H_2O)_{10}][Ho(CO_3)_4]\cdot4H_2O$ in a KBr matrix

with the higher asymmetric stretch from bidentate carbonate complexation. The other partner to this split e′ mode is observed at 1399 cm^{-1}, yielding a 120 cm^{-1} splitting of these peaks, consistent with bidentate complexation. To complete the vibrational description, the two peaks at 694 and 729 cm^{-1} are the result of splitting the ν_4 e′′ free carbonate bending mode upon complexation, the 867 cm^{-1} peak is the trampoline π mode, and the symmetric stretching mode can be seen at 1062 cm^{-1}, consistent with the Raman spectrum, and very close to the value observed in solution for the free carbonate ion. Therefore, the Raman and IR spectra are consistent with bidentate carbonate complexation with little covalent character.

Conclusion

The identification of the limiting complex in the Ho^{III} carbonate system under high carbonate concentration has been determined using a combination of single-crystal X-ray diffraction, electronic absorption and vibrational spectroscopy. It has been shown that the limiting complex is the mononuclear $[Ho(CO_3)_4]^{5-}$ ion. The solution from which the solid tetracarbonate was isolated was confirmed to contain an equilibrium mixture of complexes. This molecule can now be used as a structural and spectroscopic model for tetracarbonates of other Ln^{III} as well as $An^{III/IV}$ ions. However, it should be noted that this is only one structure type, and other expanded coordination environments could be observed in the larger lanthanide and actinide ions. Similar studies to determine the identity of the other species in the Ln^{III}, An^{III} and Pu^{IV} carbonate systems of importance to nuclear waste isolation and disposal programs are currently in progress.

Experimental Section

General: All operations were carried out in an open atmosphere and at room temperature. $Co(NH_3)_6Cl_3$, Na_2CO_3, and $Ho(NO_3)_3\cdot5H_2O$ (Aldrich) were all used as received. The solution electronic absorption measurements were obtained in 1.0 cm matched quartz cells on a Perkin−Elmer Lambda 19 or Cary Model 5 spectrophotometer. Complete spectra in the range from 400 to 1000 nm as well as absorbance values at selected wavelengths were obtained. Measurements were made at 23 ± 1 °C. Raman vibrational spectra were obtained using near-infrared excitation obtained 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 silicon grease. Elemental analyses were performed with a Perkin−Elmer Series II CHNS/O Analyzer.

Preparation of Ho^{III} Carbonate Solutions: A solution of Ho^{III} (1.0 mL, 0.08 M) was prepared by dissolving $Ho(NO_3)_3\cdot5H_2O$ (0.707 g, 1.60 mmol) in 20 mL of H_2O. The carbonate solution was then prepared by the addition of 1.0 mL of the Ho^{III} stock solution to 1.0 mL of a 4.1 M Na_2CO_3 solution. The resulting solution concentrations were 0.04 M Ho^{III} and 2.1 M Na_2CO_3.

Preparation of $[Co(NH_3)_6][Na_2(H_2O)_{10}][Ho(CO_3)_4]\cdot4H_2O$: $Co(NH_3)_6Cl_3$ (0.4 mL, 0.2 M) was added to a solution of Ho^{III} (2.0 mL, 0.04 M) in 2.1 M Na_2CO_3. The mixture was allowed to sit open to the atmosphere for two weeks, during which time yellow-orange blocks formed. Raman: $\tilde{\nu}$ = 1064 cm^{-1}. − IR: $\tilde{\nu}$ = 694, 727, 827, 867, 907 1062, 1399 (CO_3^{2-}), 1520 (CO_3^{2-}), 1646 cm^{-1}. − $C_4H_{46}CoHoN_6Na_2O_{26}$ (864.3): calcd. C 5.56, H 5.36, N 9.12; found C 5.83, H 5.07, N 10.16.

X-ray Crystallography: A yellow-orange, irregular shaped crystal was attached to a glass fiber with a spot of silicone grease. The crystal was mounted from a matrix of mineral oil. The crystal was immediately placed on a Bruker P4/CCD/PC diffractometer, and cooled to 203 K using a Bruker LT-2 temperature device. The data were collected using a sealed, graphite monochromatized Mo-K_α X-ray source. A hemisphere of data were collected using a combination of and ω scans, with 20 second frame exposures and 0.3° frame widths. Data collection, initial indexing and cell refinement was handled using SMART[40] software. Frame integration and final cell parameter calculation were carried out using SAINT[41] software. The data were corrected for absorption using the DIFABS[42] program. Decay of reflection intensity was not observed.

The structure was solved in the space group $P2/n$ using Direct methods and difference Fourier techniques. The initial solution revealed the holmium, cobalt, and the majority of all non-hydrogen atom positions. Several lattice water molecules were discovered during subsequent Fourier synthesis [atoms labeled O(1W) to O(3W)]. The hydrogen atoms were fixed (N−H= 0.89 Å) on the amine groups, which were allowed to rotate in order 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 of the atoms to which they are bound. The hydrogen atom positions associated with the water molecules were not considered in the structural model. The final refinement included anisotropic temperature factors on all non-hydrogen atoms, and converged to $R1 = 0.0267$ and $wR2 = 0.0741$. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL/NT.[43] Additional details of the data collection and structure refinement are listed in Table 1.

Further details of the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-411045.

Acknowledgments

We thank Dr. T. W. Newton and Dr. Th. Fanghänel for helpful discussions. This research was supported by the US DOE Office of Basic Energy Sciences and US DOE Office of Defense Programs, under Contract W-7405-ENG-36 with the University of California.

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Received November 10, 2000
[I00428]