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Synthesis and Structure of [Co(tepa)O_2COH](ClO_4)$_2$·3H_2O, a Chelated Bicarbonate Species Prepared in Aqueous Solution

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The recent work of Buckingham and Clark concerning the mechanism of acid-catalyzed hydrolysis of Co(III)-chelated carbonato complexes has emphasized the importance of preprotonation of the carbonate ligand prior to opening of the chelate ring.[1,2] Their determinations of acidity constants for a number of *bicarbonate* chelates (K_a = 0.42−2.3 M) formed on protonation of the corresponding carbonate species in acidic solution show previous workers have substantially overestimated the acidity of the protonated carbonyl oxygen.[3] As several Co(III) carbonate chelates are known to be remarkably stable toward hydrolysis under acidic conditions,[2,4] the isolation of the chelating bicarbonate species from solutions of moderate acidity should be possible. Structurally characterized monodentate bicarbonate complexes are rare,[5] and are generally prepared by nucleophilic attack of metal-coordinated hydroxide on CO_2 in nonaqueous solvents. To our knowledge, there is only one structurally characterized chelated bicarbonate complex, [Rh(H)$_2$(P(*i*-Pr)$_3$)$_2$$O_2COH$], which was formed from reaction of a rhodium hydride complex with wet CO_2 in hexane as solvent.[6] Herein we report the synthesis and characterization of the chelated bicarbonate complex [Co(tepa)O_2COH](ClO_4)$_2$·3H_2O (**1**) (tepa = tris(2-(2-pyridyl)ethyl)amine[7]) formed by protonation of the parent carbonate complex [Co(tepa)O_2CO]ClO_4 (**2**) in acidic aqueous solution.

1 was prepared as follows: To an aqueous solution of [Co(tepa)O_2CO]ClO_4[8] (0.024 M, 50 mL) were added aqueous $HClO_4$ (5.4 M, 30 mL) and aqueous $NaClO_4$ (5.4 M, 20 mL). Purple crystals of sufficient quality for X-ray structural determination deposited on storage of the solution at 4 °C for 24 h. These were washed with ice-cold water and ethanol and dried in air (0.58 g, 72%).[9] The presence of the bicarbonate ligand in **1** was initially suggested by the observation that dissolution of the purple crystals in water gave an appreciably acidic solution. Titration of this solution with NaOH showed 1 equiv of OH^- was consumed/mol of complex. Further evidence for a bicarbonate ligand came from comparison of IR and ATR spectra of the reactant and product. **2** shows bands due to the carbonate ligand at 1656 and 1241 cm^{-1}. The intensity of the former is considerably reduced in **1** while the latter is absent. The identity of the product was confirmed by X-ray crystallography.[10] Figure 1 shows a diagram of the [Co(tepa)O_2COH]$^{2+}$ cation. The structure consists of a central Co^{3+} ion bound to all four nitrogen atoms of the tepa ligand. Coordination around the metal ion is completed by the two oxygen atoms of the chelating bicarbonate ligand. Two perchlorate ions (disordered; not shown) balance the 2+ charge of the cation. The usual octahedral geometry about the cobalt ion is severely distorted due to the small O2−Co1−O1 angle of 67.64°. The flexibility of the tepa ligand allows other angles in this plane to open to >90°, a feature that has been observed previously in other tripodal amine ligand systems.[11] While the Co−O bond lengths (1.926(4) and 1.932(3) Å) of **1** are essentially the same as those found in other structurally characterized Co(III) carbonate chelates, the C−O_{endo} bonds are significantly shorter (1.292(6) and 1.283(6) Å *vs* 1.31 Å).[4a] Similarly, the C−O_{exo} bond length in **1** is substantially longer than those found in the

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(8) Synthesis of [Co(tepa)O_2CO]ClO_4: To a solution of tepa (6.62 g, 19.9 mmol) in H_2O−MeOH (200 mL, 1:1) was added a solution of Co(ClO_4)$_2$·6H_2O (7.5 g, 20.5 mmol) in H_2O (100 mL). To this were added, with stirring, $NaHCO_3$ (1.73 g, 20.5 mmol) and PbO_2 (7.2 g, 30 mmol). The suspension was stirred overnight at room temperature and then filtered to give a deep purple solution. This was loaded onto a Sephadex SP-C25 cation exchange column, and elution with aqueous $NaClO_4$ (0.1 M) removed a purple band. Concentration of the eluate to low volume (rotavap) and cooling in ice gave the product as magenta microcrystals (6.0 g, 53%). Anal. Calcd for $C_{22}H_{24}N_4ClO_7Co$: C, 47.97; H, 4.39; N, 10.17; Cl, 6.44. Found: C, 47.84; H, 4.28; N, 10.39; Cl, 6.59. [***Caution:*** Although we have experienced no problems with the complexes described herein, perchlorate salts should always be treated as being potentially explosive.]

(9) Anal. Calcd for $C_{22}H_{25}N_4Cl_2O_{11}Co{\cdot}H_2O$: C, 39.48; H, 4.07; N, 8.37; Cl, 10.59. Found: C, 39.49; H, 3.92; N, 8.34; Cl, 10.57. Washing with ethanol leads to reproducible partial desolvation.

(10) Crystal data (−142 °C) for $C_{22}H_{25}Cl_2CoN_4O_{11}{\cdot}3H_2O$: triclinic, $P\bar{1}$, a = 7.872(2) Å, b = 10.449(2) Å, c = 18.271(4) Å, α = 74.45(3)°, β = 86.27(3)°, γ = 75.19(3)°, V = 1399.8(5) Å^3, Z = 2, d_{calcd} = 1.659 g cm^{-3}. Refinement of the structure converged with R1 = 0.0679 for 3580 reflections with $F_o > 4\sigma(F_o)$ and wR2 = 0.1742 for all 4861 data.

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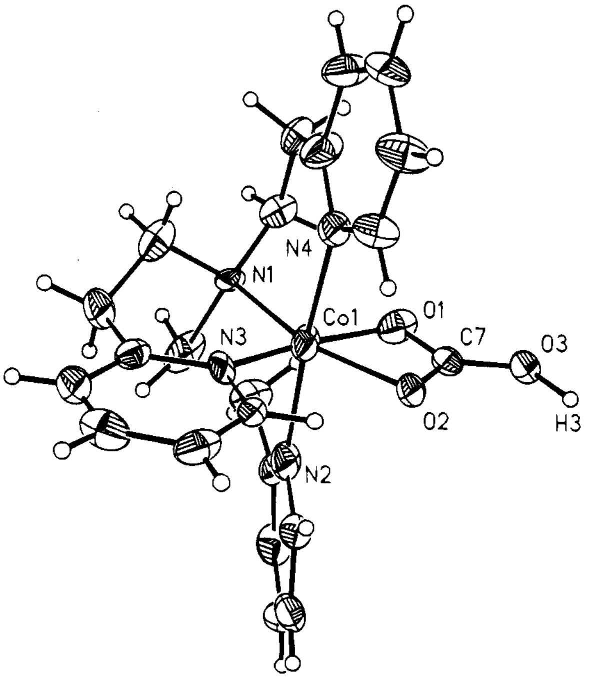

Figure 1. ORTEP diagram of the [Co(tepa)O_2COH]$^{2+}$ cation. Selected bond distances (Å) and angles (deg): Co1−O1 1.926(4), Co1−O2 1.932(3), O1−C7 1.283(6), O2−C7 1.292(6), C7−O3 1.266(6), Co1−N1 2.11(2), Co1−N2 1.98(3), Co1−N3 1.81(2), Co1−N4 2.013(4); O1−Co1−O2 67.64(14), O1−C7−O2 113.1(4), O1−C7−O3 123.3(5), O2−C7−O3 123.7(4), Co1−O1−C7 89.9(3), Co1−O2−C7 89.3(3).

carbonate congeners (1.266(6) Å *vs* 1.23 Å[12]), consistent with protonation at the *exo* oxygen. Similar trends were also observed within the bicarbonate ligand of [Rh(H)$_2$(P(*i*-Pr)$_3$)$_2$O$_2$COH].[6a]

Attempts to measure the pK_a of the bicarbonate complex spectrophotometrically have thus far proven unsuccessful. Acidification of a solution of **2** results in a shift of the absorbance maximum (520 nm) to longer wavelength (525 nm) and is accompanied by a slight decrease in the extinction coefficient. In perchlorate medium (I = 4.69 M) measurements are hampered by rapid crystallization of the bicarbonate complex in the cuvette, while the rate of decomposition (below) appears to be accelerated when HCl is used. In nitric acid a monotonous decrease in absorbance at 520 nm is observed up to [H$^+$] = 2.35 M, but again, the high ionic strength media and the competing decomposition reaction make accurate measurements difficult.

Attempts to isolate the [Co(tepa)(OH$_2$)$_2$]$^{3+}$ species formed on acid hydrolysis of **2** were thwarted by rapid reduction of this complex to Co(II) species. UV/vis spectra of solutions of **2** in concentrated HCl (6 M) showed CoCl$_4^{2-}$ was formed, while in concentrated HClO$_4$, Co(H$_2$O)$_6^{2+}$ was the only cobalt-containing product observed. A similar instability toward reduction has been previously observed on acid hydrolysis of the [Co(py)$_4$O$_2$CO]$^+$ ion.[4b] We are currently investigating the factors responsible for the rapid reduction of [Co(tepa)(OH$_2$)$_2$]$^{3+}$.

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Supplementary Material Available: Text describing the crystallographic work and tables of crystal data and structural refinement details, atomic coordinates, bond lengths and angles, and thermal parameters for **1** (13 pages). Ordering information is given on any current masthead page.

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[12] This value is the average obtained from 10 Co(III) carbonate chelates, having bond lengths in the range 1.21−1.25 Å.