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Cobalt(III) Complexes of [3^5]Adamanzane, 1,5,9,13-Tetraazabicyclo[7.7.3]nonadecane. Report of an Inert, Chelate Hydrogen Carbonate Ion

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Three cobalt(III) complexes of the macrocyclic tetraamine [3^5]adamanzane (1,5,9,13-tetraazabicyclo[7.7.3]-nonadecane) were isolated as salts. The X-ray crystal structures were solved for the compounds [Co([3^5]adz)-(CO_3)]AsF_6 (**1b**), [Co([3^5]adz)(HCO_3)]$ZnBr_4 \cdot H_2O$ (**2a**), and [Co([3^5]adz)(SO_4)]$AsF_6 \cdot H_2O$ (**3a**). The coordination geometry around the cobalt(III) ion is a distorted octahedron with the inorganic ligands at *cis*-positions. Complex **2** is the second example of a cobalt(III) complex for which the X-ray structure shows a chelate binding mode of the hydrogen carbonate entity. The pK_a value of the [Co([3^5]adz)(HCO_3)]$^{2+}$ ion (**2**) was determined spectrophotometrically to be 0.27 (25 °C, $I = 5.0$ M). The protonation appears to occur at the noncoordinated carbonyl oxygen atom of the carbonate group, with hydrogen bonding to the crystal water molecule. Evidence is presented for this oxygen atom as the site of protonation in solution as well. In 5.0 M CF_3SO_3H a slow reaction of the carbonato complex, quantitatively yielding the [Co([3^5]adz)($H_2O)_2$]$^{3+}$ ion, was observed. $k_{obs} = 7.9(1) \times 10^{-6}$ s^{-1} at 25 °C.

Introduction

A new class of macrobicyclic and -tricyclic ligands has recently appeared in the literature.[1−27] The so-called bowl and cage adamanzanes[9−22] are cyclic tetraamines strapped by one or two alkylene chains connecting two nonadjacent nitrogen atoms as illustrated for some bowl adamanzanes in Figure 1.

Large cage molecules were synthesized and studied by Schmidtchen,[8] and related compounds were reported by Takemura et al.[28] and Lehn and co-workers.[29] Recently, Miyahara et al. and we have presented the syntheses and X-ray crystal structures of the small tricyclic tetraamines [2^6]adamanzane,[12] [$2^4.3^2$]adamanzane,[10] [$(2.3)^3$]adamanzane,[11] and [3^6]adamanzane.[7,9] In opposition to the smallest member of the class, the classical compound urotropin (hexamethylenetetraamine, [1^6]-adamanzane), these cage molecules have all of their nitrogen lone pairs pointing into the cavity.[5−7,11,12,28,30] They act as proton sponges,[4−6,9−12] and along with similar molecules they have been the subject of recent studies discussing properties such as basicity and strain energy.[5,6,30−33]

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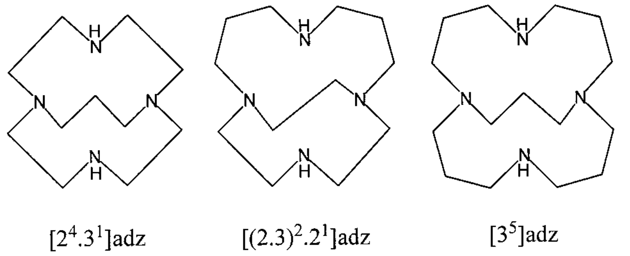

Figure 1. Examples of bowl adamanzanes. Complexes of [3^5]-adamanzane are discussed in the present work.

Bicyclic bowl adamanzanes have also been synthesized,[11−21] and these may act as ligands for transition metal ions.[14,15,23−27]

Macrocyclic compounds in general often display unusual properties and are of current interest due to their application in medicine and as catalysts and because of their importance as model systems within bioinorganic chemistry.[2,4,8,29,30,34−40] The latter may also be said about carbonato complexes. The present paper presents the synthesis and X-ray crystal structure of a chelate carbonatocobalt(III) complex of the macrobicyclic ligand [3^5]adamanzane, [$Co([3^5]adz)(CO_3)]^+$ (**1**). Reaction of this complex with acid is unusually slow. This allows for the isolation of the protonated form, [$Co([3^5]adz)(HCO_3)]^{2+}$ (**2**), for which the X-ray crystal structure shows the retainment of a chelate coordination mode for the hydrogen carbonate ion. The relative inertness of the complex with respect to acid cleavage also allowed for determination of the pK_a value. Alongside these compounds is reported the synthesis and X-ray crystal structure of the corresponding sulfato complex, [$Co([3^5]adz)(SO_4)]^+$ (**3**).

Experimental Section

Abbreviations. See also Figure 1. [$2^4.3^1$]Adamanzane = 1,4,7,10-tetraazabicyclo[5.5.3]pentadecane. [3^5]Adamanzane = 1,5,9,13-tetraazabicyclo[7.7.3]nonadecane. ampy = 2-pyridylamine. tepa = tris(2-(2-pyridyl)ethyl)amine.

Materials. The monohydrate of the macrocycle 1,5,9,13-tetraazabicyclo-[7.7.3]nonadecane ([3^5]adamanzane), [3^5]adz·H_2O, was prepared as previously described,[25] as was the violet $Co(py)_3(CO_3)Cl$.[41] The remaining starting materials were commercially available and of analytical grade. Solvents and deuterated solvents were used as purchased, with no further purification or drying.

Physical Measurements. Elemental analyses (C, H, N) were performed at the Microanalytical Laboratory, H. C. Ørsted Institute, Copenhagen.

Electrospray mass spectra (positive mode) were recorded on a Bruker Esquire LC mass spectrometer using methanol as the matrix.

Optical spectra were recorded on a Cary 3 spectrophotometer in the region 350−800 nm.

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance 400 NMR spectrometer except for the ^{13}C spectrum of the [$Co([3^5]adz)(CO_3)]ClO_4$ salt (**1c**) in 3 M DCl, which was measured on a Bruker AC 250 NMR spectrometer. In D_2O ^{1}H chemical shift values (δ) are reported in ppm and are referenced to internal dioxane (δ(dioxane) = 3.75 ppm), as are the ^{13}C chemical shift values (δ(dioxane) = 67.40 ppm).

Calculations. Ligand field calculations were performed using the PC program LIGFIELD.[42] Calculations for the determinations of equilibrium constants were performed using the program PROC NLIN (DUD method) from the SAS Institute Inc.[43] Calculations involving the kinetic data were performed as previously described.[44]

Caution! *Mechanical handling or heating of perchlorates represents a potential hazard*. In our hands, however, explosions with the present compounds have never occurred.

Preparations.

[$Co([3^5]adz)(CO_3)]Cl$ (1a). [3^5]adz·H_2O (289 mg, 1.1 mmol) was dissolved in absolute ethanol (5 mL). To this solution was added solid $Co(py)_3(CO_3)Cl$ (393 mg, 1.0 mmol) yielding a violet suspension. Vigorous stirring at room temperature overnight followed by filtration yielded a water-soluble violet solid, which was washed thoroughly with diethyl ether. Yield after drying in the air: 392 mg (92%). Anal. Calcd for $CoC_{16}H_{32}N_4O_3Cl$: C, 45.45; H, 7.63; N, 13.25. Found: C, 45.5; H, 7.64; N, 13.0. UV−vis in water [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 570 (174), 388 (213).

[$Co([3^5]adz)(CO_3)]AsF_6$ (1b). [$Co([3^5]adz)(CO_3)]Cl$ (**1a**) (169 mg, 0.40 mmol) was dissolved in water (7 mL), and the violet solution was filtered. Dropwise addition of 1 M $LiAsF_6$ (0.8 mL) gave a violet precipitate, which was separated from the mother liquor by filtration. The solid was washed thoroughly with absolute ethanol and then with diethyl ether. This product was left on the filter and stirred manually with portions of hot water (80 °C), applying the filtration vacuum within 30 s of each addition. The Büchner flask containing the filtrate was partially cooled in ice. The extraction process was continued until the resulting filtrate was distinctly less violet (ca. 45 mL in total), leaving a brown residue on the filter. To the cool filtrate was added 1 M $LiAsF_6$ (2 mL). Swirling and further cooling in ice gave a violet solid, which was filtered off and washed thoroughly with absolute ethanol and then with diethyl ether. Yield after drying in the air: 100 mg (44%).

Crystals of a quality suitable for X-ray crystallographic analysis were grown by dissolving [$Co([3^5]adz)(CO_3)]Cl$ (**1a**) (31 mg, 0.073 mmol) in water (10 mL) after which the violet solution was filtered. Addition of 1 M $LiAsF_6$ (0.1 mL) slowly gave violet crystals. These were filtered off and washed with absolute ethanol. Anal. Calcd for $CoC_{16}H_{32}N_4O_3$-AsF_6: C, 33.35; H, 5.60; N, 9.72. Found: C, 33.4; H, 5.51; N, 9.62. UV−vis in water [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 571 (177), 388 (187).

[$Co([3^5]adz)(CO_3)]ClO_4$ (1c). [$Co([3^5]adz)(CO_3)]Cl$ (**1a**) (626 mg, 1.48 mmol) was dissolved in water (20 mL), and the violet solution was filtered. Dropwise addition of saturated $NaClO_4$ (2.5 mL) gave a violet precipitate, which was separated from the red-violet mother liquor by filtration. The solid was washed thoroughly with absolute ethanol and then with diethyl ether. This product was left on the filter and stirred manually (plastic spatula!) with portions of hot water (80 °C), applying the filtration vacuum within 30 s of each addition. The Büchner flask containing the filtrate was partially cooled in ice. The extraction process was continued until the resulting filtrate was distinctly less violet (ca. 60 mL in total), leaving a brown residue on the filter. To the cool filtrate was added saturated $NaClO_4$ (20 mL). Swirling and further cooling in ice resulted in violet microcrystals, which were filtered off and washed thoroughly with absolute ethanol and then with diethyl ether. Yield after drying in the air: 485 mg (67%). Anal. Calcd for $CoC_{16}H_{32}N_4O_7Cl$: C, 39.47; H, 6.62; N, 11.51. Found: C, 39.7; H, 6.64; N, 11.5. UV−vis [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: in water, 571 (176), 388 (187); in 5.0 M CF_3SO_3H, 584 (112), 382 (183). ES-MS: multiplets centered around m/z 325 ($Co^{III}([3^5]adz - 2H)^+$) and 387 ($Co^{III}([3^5]adz)(CO_3)^+$). ^{13}C NMR ($D_2O$), δ in ppm: 19.1, 21.9, 23.1 (C−CH_2−C), 45.7, 49.8, 55.8, 56.9, 58.1 (N−CH_2), 167.8 (CO_3). ^{1}H NMR (D_2O), δ in ppm (multiplicity, integration): 1.65 (d, 2H), 1.78−2.41 (m, 18H), 2.72 (t, 2H), 3.11 (t of d, 2H), 3.18−3.33 (m, 4H), 3.52 (t, 2H). ^{13}C

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Table 1. Crystallographic Data for Compounds [Co([3^5]adz)(CO_3)]AsF_6 (**1b**), [Co([3^5]adz)(HCO_3)]$ZnBr_4$·H_2O (**2a**), and [Co([3^5]adz)(SO_4)]AsF_6·H_2O (**3a**)

	1b	**2a**	**3a**
formula	$C_{16}H_{32}AsCoF_6N_4O_3$	$C_{16}H_{35}Br_4CoN_4O_8Zn$	$C_{15}H_{34}AsCoF_6N_4O_5S$
fw	576.31	791.42	630.37
temp T/K	120(2)	120(2)	120(2)
cryst system	orthorhombic	monoclinic	orthorhombic
space group	*Pbca*	$P2_1$	*Pnma*
a/Å	12.847(3)	8.919(2)	12.356(3)
b/Å	15.667(3)	15.782(3)	11.251(2)
c/Å	22.024(4)	9.021(2)	15.951(3)
β/deg		103.06(3)	
V/Å^3	4435.9(15)	1237.0(4)	2217.4(8)
Z	8	2	4
D_x/g cm^{-3}	1.726	2.125	1.888
μ(Mo Kα)/mm^{-1}	2.330	8.130	2.436
cryst color	violet	blue-violet	dark-blue
cryst size/mm	0.30 × 0.08 × 0.03	0.25 × 0.13 × 0.01	0.15 × 0.14 × 0.13
θ range/deg	1.85−29.49	2.32−29.61	2.08−29.56
measd reflcns	27 022	8662	14 601
unique reflcns	5721	4501	3031
reflcns with [$I > 2\sigma(I)$]	2193	3435	2580
R(int)	0.2097	0.0677	0.0324
transm factors	1.0000−0.8741	1.000−0.4773	1.0000−0.8703
refined params	280	176	175
R1^a (obsd data)	0.0814	0.0667	0.0426
wR2^b (all data)	0.1827	0.1640	0.1134
goodness-of-fit	1.056	1.003	1.097
min, max $\Delta\rho$/e Å^{-3}	−0.702 and 0.586 (near As)	−2.482 and 1.497 (near Br1 and Br2)	−1.200 and 0.892 (near Ow and F3)

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma w|F_o{}^2 - F_c{}^2|^2/\Sigma wF_o{}^4]^{1/2}$.

NMR (3 M DCl), δ in ppm: 19.2, 22.4, 23.2 (C−CH_2−C), 45.9, 50.5, 55.9, 57.2, 58.8 (N−CH_2), 168.4 (CO_3). ^{1}H NMR (5 M DBr), δ in ppm (multiplicity, integration): 1.43 (d, 2H), 1.61 (d, 2H), 1.80 (d, 2H), 1.84−2.05 (m, 7H), 2.25 (q, 1H), 2.44−2.68 (m, 6H), 2.75−2.89 (m, 2H), 2.99 (t, 2H), 3.18 (q, 2H), 3.40 (t, 2H), 3.74−3.89 (m, 2H), 5.00 (t, 1H), 6.11 (t, 1H).

[Co([3^5]adz)(HCO_3)]$ZnBr_4$·H_2O (2a). [Co([3^5]adz)(CO_3)]ClO_4 (**1c**) (115 mg, 0.24 mmol) was dissolved in 2 M HBr (3 mL) yielding a blue solution, which was filtered. Addition of 2 M Li_2ZnBr_4 (0.25 mL) resulted in instant quantitative precipitation of a dust blue solid, which was isolated by filtration and washed with absolute ethanol and then with diethyl ether. Yield after drying in the air: 159 mg (85%). Anal. Calcd for $CoC_{16}H_{35}N_4O_4ZnBr_4$: C, 24.28; H, 4.46; N, 7.08. Found: C, 24.5; H, 4.30; N, 6.98. UV−vis in water [λ_{max}, nm (ϵ, M^{-1}cm^{-1})]: 571 (176), 388 (188). ES-MS: multiplets centered around m/z 269 (H[3^5]adz$^+$), 325 (Co^{III}([3^5]adz − 2H)$^+$) and 387 (Co^{III}([3^5]adz)(CO_3)$^+$).

Crystals used for X-ray crystallography were grown over a period of 2 h at room temperature by the addition of a small volume of an aqueous solution of Li_2ZnBr_4 (2 M) to a dilute, pale blue solution of [Co([3^5]adz)(CO_3)]ClO_4 (**1c**) in 25% HBr. The blue-violet needle-shaped crystals were dichromic, alternating between turquoise and pink under a polarization microscope.

[Co([3^5]adz)(SO_4)]AsF_6·H_2O (3a). [Co([3^5]adz)(CO_3)]AsF_6 (**1b**) (100 mg, 0.17 mmol) was dissolved by heating to 60 °C in 3 M sulfuric acid (8.8 mL). Stirring of the reaction mixture at 60 °C for a total of 2 h and 10 min yielded a turquoise solution containing a turquoise precipitate. The reaction mixture was cooled in ice after which 1 M $LiAsF_6$ (1 mL) was added dropwise. The solid was isolated by filtration and washed three times with 0.1 M $LiAsF_6$ until neutral pH of the filtrate was reached. This was followed by thorough washing with absolute ethanol and then with diethyl ether. Yield after drying in the air: 93 mg (85%). Anal. Calcd for $CoC_{15}H_{34}N_4SO_5AsF_6$: C, 28.58; H, 5.44; N, 8.89. Found: C, 29.1; H, 5.41; N, 8.91. UV−vis in water [λ_{max}, nm (ϵ, M^{-1}cm^{-1})]: 593 (139), 388 (165). ES-MS: multiplets centered around m/z 326 (Co^{II}([3^5]adz − H)$^+$) and 423 (Co^{III}([3^5]adz)(SO_4)$^+$). ^{13}C NMR (D_2O/CD_3CN 50/50), δ in ppm: 19.2, 21.5, 22.9 (C−CH_2−C), 45.5, 49.7, 56.0, 57.0, 59.0 (N−CH_2). ^{1}H NMR (D_2O/CD_3CN 50/50), δ in ppm (multiplicity, integration): 1.25 (d, 2H), 1.50 (d of d, 2H), 1.66 (d of d, 2H), 1.77−2.40 (m, 15.4H (residual CH_3CN)), 3.05 (t of d, 2H), 3.12−3.27 (m, 4H), 3.40−3.58 (m, 4H).

Dark turquoise crystals used for X-ray crystallographic measurements were grown over a period of one month at 10 °C from a solution of [Co([3^5]adz)(CO_3)]AsF_6 (**1b**) (20 mg, 0.035 mmol) in 3 M sulfuric acid (1 mL).

X-ray Crystallography. Crystal data for the compounds are listed in Table 1. The crystals of the compounds are cooled to 120 K using a Cryostream nitrogen gas cooler system. The data were collected on a Siemens SMART Platform diffractometer with a CCD area sensitive detector. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 of all data. In the structure of **3a** the atoms Co, S, O(2), O(3), N(1), N(3), C(8), As, F(1), F(2), and Ow and the hydrogen atoms attached to these atoms are positioned on a mirror plane. Two of the fluorine atoms, F(3) and F(4), are disordered with the population factors 0.604(6) and 0.396(6), respectively. In the structures of **1b** and **3a** the non-hydrogen atoms were refined anisotropically, whereas, in **2a**, due to the rather poor quality of the crystals, the atoms of the [3^5]adamanzane ligand were refined isotropically. The hydrogen atoms in all three structures were at calculated positions using a riding model with C−H = 0.99 Å, N−H = 0.93 Å, and fixed thermal parameters [U(H) = 1.2U for attached atom]. In **2a** the hydrogen atoms attached to Ow could not be located. In **3a** the hydrogen atoms attached to Ow were refined with fixed distance of 0.9 Å and fixed thermal parameters. The Flack x-parameter is −0.02(2) for **2a**, indicating that this is the correct absolute structure.[45,46] Programs used for data collection, data reduction, and absorption were SMART, SAINT, and SADABS.[47,48] The program SHELXTL 95[49] was used to solve the structures, and for molecular graphics. PLATON[50] was used for molecular geometry calculations.

Electronic Spectroscopy. Ligand field calculations were performed using the angular overlap model[51] assuming a perfect octahedral ligand field. The choice of this simple model was dictated by the fact that no

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splitting of the absorption bands was observed. The obtained ligand field splitting parameters, e_σ ($=1/3\Delta_{O_h}$), describe the average ligand field per ligator exerted by the four nitrogen and the two oxygen ligator atoms. Since no spin-forbidden transitions were observed the electron repulsion Racah parameters were restricted to the conventional choice of $C = 4B$.

Equilibrium Studies. The pK_a value of the [Co([3^5]adz)(HCO_3)]$^{2+}$ complex (**2**) was determined at 10.0 and 25.0 °C by absorption spectroscopy (350−800 nm) on solutions of the [Co([3^5]adz)(CO_3)]-ClO_4 salt (**1c**). The solutions contained triflouromethanesulfonic acid of varying concentrations ranging from 0 to 5.0 M. Sodium triflouromethanesulfonate was used to keep the ionic strength at 5.0 M. The spectra were measured immediately after dissolution, and all remained unchanged within 15 min of recording of the first spectrum. Three isosbestic points were observed (Figure S1, Supporting Information).

Kinetic Measurements. Absorption spectra (350−800 nm) of a solution of [Co([3^5]adz)(CO_3)]ClO_4 (**1c**) in 5.0 M triflouromethanesulfonic acid were followed with time at 25 °C. Four isosbestic points were observed, and the measurements were continued until the product spectrum remained constant for several half-lives. The data were unambiguously interpreted in terms of a first-order reaction. The absorption maxima of the product spectrum are the following [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 599 (142), 389 (163).

Results and Discussion

X-ray Crystal Structures of [Co([3^5]adz)(CO_3)]AsF_6 (1b), [Co([3^5]adz)(HCO_3)]$ZnBr_4\cdot H_2O$ (2a), and [Co([3^5]adz)(SO_4)]-$AsF_6\cdot H_2O$ (3a).

Compound **1b** consists of [Co([3^5]adz)(CO_3)]$^+$ and AsF_6^- ions, and **2a** of [Co([3^5]adz)(HCO_3)]$^{2+}$ and $ZnBr_4^{2-}$ ions and one water molecule. Compound **2a** is the second example of a cobalt(III) complex for which the X-ray structure shows a chelate binding mode to the HCO_3^- entity.[52]

Bond lengths and angles of the coordination sphere around the cobalt ion are given in Table 2. The labeling of the atoms of the cations is shown in Figure 2, Figure 3, and Figure S2, Supporting Information. The CO_3^{2-} and HCO_3^- ligands are coordinated as bidentates giving a *cis* configuration as found in the nickel complexes with the ligand [$2^4.3^1$]adamanzane[26] and with [3^5]adamanzane.[25] In the present structures, the angles around the cobalt ion show substantial distortions with respect to those of a regular octahedron. This is mainly due to the very small angle O(1)−Co−O(2) of 68.5(2) and of 67.6(4)° in [Co([3^5]adz)(CO_3)]AsF_6 (**1b**) and [Co([3^5]adz)(HCO_3)]$ZnBr_4\cdot H_2O$ (**2a**), respectively. As a consequence, the CO_3^{2-} ligand in **1b** and the HCO_3^- ligand in **2a** show distortion from regular trigonal symmetry, the O(1)−C(16)−O(2) angle being 109.5(7)° in the carbonato (**1b**) and 115(1)° in the hydrogen carbonato (**2a**) compounds, respectively. These values are similar to those found in [Co(tren)(CO_3)]$Cl\cdot 2H_2O$.[53]

In [Co([3^5]adz)(CO_3)]AsF_6 (**1b**) the C(16)−O(3) bond of 1.234(9) Å is shorter than the C(16)−O(1) and the C(16)−O(2) bonds of 1.323(8) and 1.312(9) Å, respectively. This is in agreement with what was found in [Co(tren)(CO_3)]$Cl\cdot 2H_2O$.[53] In [Co([3^5]adz)(HCO_3)]$ZnBr_4\cdot H_2O$ (**2a**) the C(16)−O bonds of 1.268(14), 1.302(15), and 1.271(15) Å are of the same length as the bonds found in [Co(tepa)(HCO_3)]$(ClO_4)_2\cdot 3H_2O$.[52] The distance between O(3) and Ow (x, y, $1 + z$) is short enough [2.551(12) Å] for a hydrogen bond to be present. Also, Ow may be involved in hydrogen bonds with Br(1) and Br(2), the Ow···Br(1) distance and Ow···Br(2) ($1 - x$, $-1/2 + y$, $1 - z$) distance being 3.246(10) and 3.314(10) Å, respectively. This may indicate that a hydrogen atom is attached to O(3) [the H(calcd position)···Ow (x, y, $1 + z$) is 2.538(13) Å] even though the quality of the crystals are rather poor.

Table 2. Bond Lengths (in Å) and Bond Angles (in deg) of the Coordination Sphere around the Metal Ions in [Co([3^5]adz)(CO_3)]-AsF_6 (**1b**), [Co([3^5]adz)(HCO_3)]$ZnBr_4\cdot H_2O$ (**2a**), and [Co([3^5]adz)(SO_4)]$AsF_6\cdot H_2O$ (**3a**)

	1b	2a	3a[a]
Co−O(1)	1.907(5)	1.955(9)	1.946(2)
Co−O(2)	1.917(5)	1.944(8)	1.946(2)
Co−N(1)	1.981(6)	1.977(10)	2.022(4)
Co−N(2)	2.032(6)	2.034(10)	2.042(3)
Co−N(3)	2.016(6)	2.026(10)	2.003(4)
Co−N(4)	2.054(6)	2.028(11)	2.042(3)
O(1)−Co−O(2)	68.5(2)	67.6(4)	72.56(13)
O(1)−Co−N(1)	90.6(2)	91.0(4)	92.60(10)
O(2)−Co−N(1)	91.4(2)	89.4(4)	92.60(10)
O(1)−Co−N(3)	92.4(2)	90.3(4)	90.61(11)
O(2)−Co−N(3)	90.8(2)	92.8(4)	90.61(11)
N(1)−Co−N(3)	176.8(3)	177.7(4)	176.02(15)
O(1)−Co−N(2)	93.3(2)	95.0(4)	91.88(10)
O(2)−Co−N(2)	161.8(2)	162.5(4)	164.43(10)
N(1)−Co−N(2)	90.3(2)	89.2(4)	88.01(9)
N(3)−Co−N(2)	88.4(3)	88.8(4)	89.53(10)
O(1)−Co−N(4)	163.6(2)	161.6(4)	164.43(10)
O(2)−Co−N(4)	95.1(2)	94.0(4)	91.88(10)
N(1)−Co−N(4)	90.3(3)	90.5(4)	88.01(9)
N(3)−Co−N(4)	87.2(3)	88.7(4)	89.53(10)
N(2)−Co−N(4)	103.0(2)	103.4(4)	103.69(15)

[a] In **3a** the [3^5]adamanzane ligand is situated on a mirror plane. Therefore, O(1)^i and N(2)^i (i: x, $^1/_2 - y$, z) in **3a** correspond to O(2) and N(4) in **1b** and **2a**.

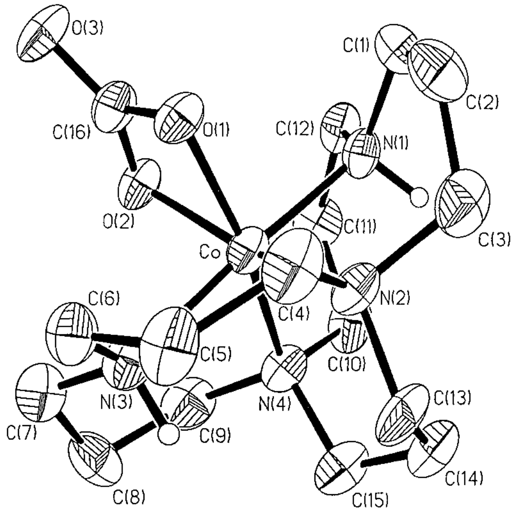

Figure 2. View of the cation in [Co([3^5]adz)(CO_3)]AsF_6 (**1b**). In this and the following figure the thermal ellipsoids are drawn at a 50% probability level. With exception of H(1) and H(3) bound to N(1) and N(3), respectively, the hydrogen atoms have been omitted for clarity.

In the present three structures the Co−N bonds are similar and so are the Co−O bond lengths.

In the carbonato (**1b**) and hydrogen carbonato (**2a**) compounds the two six-membered rings containing N(1) are in a twist-boat conformation, whereas the other three rings are in a chair form. The [3^5]adamanzane ligand has the same conformation here as found in the Ni([3^5]adz)X$^+$ complexes (X = NO_3^-, ClO_4^-).[25]

The N(2)···N(4) distance between the bridgehead nitrogen atoms is 3.198(8) Å in [Co([3^5]adz)(CO_3)]AsF_6 (**1b**) and 3.187-

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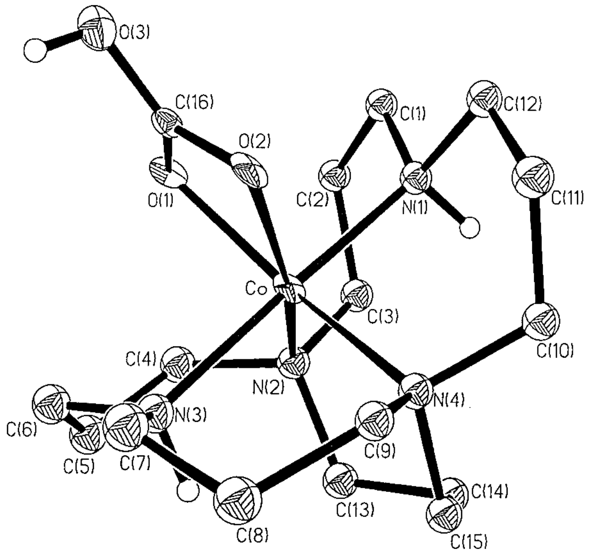

Figure 3. View of the cation in $[Co([3^5]adz)(HCO_3)]ZnBr_4{\cdot}H_2O$ (**2a**).

(15) Å in $[Co([3^5]adz)(HCO_3)]ZnBr_4{\cdot}H_2O$ (**2a**). The N(1)···N(3) distance is 3.995(9) and 4.003(14) Å in the carbonato (**1b**) and the hydrogen carbonato (**2a**), respectively. The hydrogen atoms attached to N(1) and N(3) are in both structures oriented away from the inorganic ligand. The same was found in the five- and six-coordinated Co(II), Ni(II), and Cu(II) complexes of the ligand.[25] In $[Co([3^5]adz)(CO_3)]AsF_6$ (**1b**) the hydrogen atom at N(1) is involved in a hydrogen bond of 3.078(8) Å (D···A) with O(3) ($-{}^1/_2 + x$, ${}^1/_2 - y$, $1 - z$), and between the hydrogen atom at N(3) and F(5) there is a hydrogen bond of 2.963(10) Å (D···A). In $[Co([3^5]adz)(HCO_3)]ZnBr_4{\cdot}H_2O$ (**2a**) there is a weak hydrogen bond between the hydrogen atom at N(1) and Br(1) ($2 - x$, ${}^1/_2 + y$, $2 - z$) of the $ZnBr_4^{2-}$ anion of 3.545(10) Å (D···A). The X-ray crystal structure of $[Co([3^5]adz)(SO_4)]AsF_6{\cdot}H_2O$ (**3a**) is discussed in Appendix S1 (Supporting Information).

Synthesis and Reactivity. The complex cation $[Co([3^5]adz)(CO_3)]^+$ (**1**) was synthesized as the chloride salt (**1a**) by simple ligand exchange from the precursor $Co(py)_3(CO_3)Cl$. As observed from comparison of the UV−vis spectra the product (**1a**) contained an impurity, which was removed upon reprecipitation as the hexafluoroarsenate (**1b**) or the perchlorate (**1c**) salt.

The $[Co([3^5]adz)(CO_3)]^+$ complex (**1**) is stable in neutral aqueous solution showing a constant optical spectrum over 24 h at 40 °C. In acidic solution, however, the initial protonation to give the blue $[Co([3^5]adz)(HCO_3)]^{2+}$ species (**2**) is followed by an unusually slow decarboxylation process, quantitatively yielding the diaqua complex (see below).

In sulfuric acid (3 M), however, the result of the reaction is exchange of the carbonate ion for a chelate sulfate ion. This yields the turquoise $[Co([3^5]adz)(SO_4)]^+$ cation (**3**), which was isolated as the hexafluoroarsenate salt (**3a**).

In the presence of other anionic ligands such as fluoride, chloride or bromide ions, the decarboxylation reaction is greatly complicated by the presence of several additional reactions of comparable or larger rates. Autoreduction is also observed, and the previously reported[25] pink, tetrahedral $[Co([3^5]adz)]^{2+}$ complex is among the products and can be isolated.

Acidity Constant for the Hydrogen Carbonato Complex (2). The pK_a value of the blue $[Co([3^5]adz)(HCO_3)]^{2+}$ complex (**2**) was determined spectrophotometrical (Figure S1, Supporting Information). The acid dissociation constants were determined at 10 °C ($K_a = 0.60(3)$) and at 25 °C ($K_a = 0.54(2)$) which gave $\Delta H_0 = -5(2)$ kJ mol^{-1} and $\Delta S_0 = -21(10)$ J mol^{-1} K^{-1}. The absorption maxima for the calculated spectrum of the protonated species (**2**) are the following [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 593 (107), 382 (183).

The value of p$K_a = 0.27$ is similar to that determined by Springborg and Schäffer[41] for the complex $[Co(py)_4(HCO_3)]^{2+}$ (p$K_a = 0.15$, 4 M $NaClO_4$) and close to those recently reported by Buckingham and Clark[54,55] for a series of $[Co(L)_4(HCO_3)]^{z+}$ species which all have pK_a in the range 0.5−2 ($(L)_4$ = aliphatic amines, nitrilotriacetate, and glycine).

NMR. The ^{13}C NMR spectrum of the $[Co([3^5]adz)(CO_3)]^+$ complex (**1**) is consistent with the presence of a single symmetry element, a mirror plane through the carbonate carbon atom, the central cobalt ion, and the middle of the macrocycle bridge. Apparently the coordinated adamanzane ligand displays restricted flexibility in aqueous solution at room temperature; a fast up−down flip of the macrocycle bridge would give rise to a coalescence of the eight observed macrocyclic ^{13}C signals to five.

The mirror plane is preserved upon the addition of strong acid. In 3 M DCl ^{13}C NMR of the cobalt−carbonato complex yields eight signals in the aliphatic region. This equilibrium mixture spectrum (80% of the protonated species) does not allow for distinction between protonation occurring on the carbonyl group or on one of the coordinated oxygen atoms. The proton exchange between the two oxygen atoms required for the latter interpretation to be valid is expected to be fast on the ^{13}C NMR time scale.

The two NH protons of the nonbridged amine groups are clearly observed in the ^1H NMR spectrum of the carbonato complex in 5 M DBr, consistent with the known inertness in acidic solution of NH-protons of coordinated amines. They are inequivalent and are separated from each other by more than 1 ppm, indicating that in this medium the above-mentioned up−down flip of the macrocycle bridge is slow on the ^1H NMR time scale as well.

Electronic Spectroscopy. For low-spin octahedral cobalt(III) complexes two absorptions are observed. These are ascribed to $\nu_1 = {}^1T_{1g} \leftarrow {}^1A_{1g}$ and $\nu_2 = {}^1T_{2g} \leftarrow {}^1A_{1g}$ transitions. From the absorption maxima given above the ligand field parameter for the carbonato species (**1**) were calculated to $e_\sigma = 6380$ cm^{-1} and $B = 639$ cm^{-1} and for the hydrogen carbonato species (**2**) the values are $e_\sigma = 6233$ cm^{-1} and $B = 764$ cm^{-1}.

Site of Protonation for the Hydrogen Carbonato Complex (2). One of the few known X-ray crystal structures which have been reported for transition metal complexes with a chelate hydrogen carbonate ion is the *cis*-$(ampy)_2Co(acac)(HCO_3)$ in which protonation on one of the coordinated oxo groups is observed.[56] A rhodium(III) hydrogen carbonate complex is known for which the hydrogen atom has been located on the carbonyl group.[57] Likewise the only known hydrogen carbonate Co(III) complex is $[Co(tepa)(HCO_3)](ClO_4)_2{\cdot}3H_2O$, which also has protonation on the carbonyl group.[52]

For the present hydrogen carbonato complex (**2**) the carbonyl oxygen atom is protonated in the solid (see above) as well as in solution. Strongly acidic solutions of salts of the carbonato (**1**) and hydrogen carbonato (**2**) complexes have the same blue-violet color as the solid $[Co([3^5]adz)(HCO_3)]ZnBr_4{\cdot}H_2O$ salt

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(**2a**). The ligand field splitting parameter, e_σ, hardly changes from one species to the other, the changes in the optical spectrum being almost solely due to a change in the electron repulsion parameters. This is indicative of the increased overall charge as being responsible for the spectral changes with only slight accompanying modification of the coordination sphere; i.e., the protonation interaction is unlikely to be occurring on one of the coordinated oxygen atoms.

Acid Cleavage of the Carbonato Complex. The spectral data for the reaction in 5.0 M triflouromethanesulfonic acid followed first-order kinetics and was interpreted in terms of the overall reaction seen in eq 1, yielding a value for k_{obs} at 25 °C of 7.9(1) $\times$ 10^{-6} s^{-1} (equivalent to a half-life of 24.3 h).

$$\mathrm{Co([3^5]adz)(CO_3)^+ + 2H^+ + H_2O \xrightarrow{k_{obs}} Co([3^5]adz)(H_2O)_2{}^{3+} + CO_2} \quad (1)$$

Electronic as well as steric factors have been invoked to explain unusual slowness in the decarboxylation process of cobalt(III)−carbonato complexes.[54,55,58,59] In the present case steric factors probably play an important role. The hydrogen atoms of the nonbridged amine groups point away from the anionic oxo ligand. This configuration of the [3^5]adamanzane ligand leaves the metal ion deeply embedded in the organic framework of the macrocycle,[25] and a certain degree of sterical shielding of the carbonate moiety may be present. It is generally accepted that the rate-determining step is dechelation via the protonated carbonato species. This leads initially to a five-coordinate transition state which may either take up water to give a monodentate hydrogen carbonate intermediate or re-form the chelate hydrogen carbonate. In the present case the former process seems to be sterically hindered by the macrocycle. Buckingham and Clark[54,55] have suggested that the reactive intermediate is protonated not on the carbonyl oxygen (like **2** in the present study) but on the carbonyl to the ring oxygen and again steric shielding by the macrocycle may prohibit the transfer of a proton from the nonligating to the ligating oxygen.

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Supporting Information Available: Three X-ray crystallographic files in CIF format, Figure S1, showing variation at 25 °C with acid concentration of the optical spectra of solutions of the [Co([3^5]adz)-(CO_3)]ClO_4 salt (**1c**) and a calculated spectrum for the [Co([3^5]adz)-(HCO_3)]$^{2+}$ ion (**2**), Figure S2, showing a view of the cation in [Co([3^5]adz)(SO_4)]AsF_6·H_2O (**3a**), and Appendix S1, presenting a discussion of the X-ray crystal structures of [Co([3^5]adz)(SO_4)]AsF_6·H_2O (**3a**). This material is available free of charge via the Internet at http://pubs.acs.org.

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