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Synthesis and Kinetics of the Decarboxylation of Two Carbonate-Bridged Complexes of Chromium(III) and Rhodium(III). Crystal Structure of μ-Carbonato-di-μ-hydroxo-bis[(1,4,7-triazacyclononane)chromium(III)] Diiodide Hydrate

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The preparation of the dinuclear μ-carbonato-di-μ-hydroxo-bis[(1,4,7-triazacyclononane)chromium(III)] cation and its rhodium(III) analogue is reported. The crystal data for the title compound $[(C_6H_{15}N_3)_2Cr_2(OH)_2CO_3]I_2{\cdot}H_2O$ are as follows: orthorhombic space group *Pbnm* [D_{2h}^{16}-No. 62] with $a = 8.577$ (3) Å, $b = 14.169$ (5) Å, $c = 21.805$ (6) Å, $V = 2650$ Å^3, and ρ(calcd) = 1.806 g cm^{-3} for $Z = 4$. Diffraction data were collected on a AED (Siemens) automated diffractometer by using θ–2θ scan and Mo Kα radiation, and the structure was solved by direct methods, resulting in a conventional final *R* factor of 7.2% for 2545 independent data. Distinct dinuclear cations of $[([9]aneN_3)_2Cr_2(OH)_2CO_3]^{2+}$ have been identified with a symmetric μ-carbonato bridge and two hydroxo bridges. The kinetics of the acid-catalyzed decarboxylation of the two cations have been measured, respectively: rate = $(k_0 + k_1[H^+])$[complex]. The water-assisted decarboxylation has been detected for the Cr_2CO_3 species only ($k_0 = (0.31 \pm 0.05) \times 10^{-4}$ s^{-1} at 30 °C). The values of k_1 at 30 °C and I = 1.0 M for the Rh_2CO_3 and for the Cr_2CO_3 species ($\Delta H^{\ddagger}$ in kcal mol^{-1}; $\Delta S^{\ddagger}$ in cal K^{-1} mol^{-1}) are very similar: $(2.73 \pm 0.05) \times 10^{-4}$ M^{-1} s^{-1} (15.0 ± 0.2, −25.4 ± 0.5); $(0.6 \pm 0.08) \times 10^{-4}$ M^{-1} s^{-1} (15.9 ± 0.5, −25.4 ± 1.8). It has been concluded that acid-catalyzed decarboxylation of a bridged carbonate group and a bidentate carbonato ligand is accomplished by the same mechanism.

Introduction

The acid-catalyzed decarboxylations of various monodentate and bidentate carbonate complexes have been studied in great detail for a wide range of different complex species. No study has been reported for complexes with a bidentate carbonato ligand bridging two metal ions. Well-defined carbonato complexes of chromium(III) have not been described previously.

The decarboxylations of monodentate complexes in general[2-10] follow the mechanism

$$[ML_5OCO_2]^+ + H^+ \rightleftharpoons [ML_5OCO_2H]^{2+} \quad 1/K_1$$

$$[ML_5OCO_2H]^{2+} \rightarrow [ML_5OH]^{2+} + CO_2 \quad k_2$$

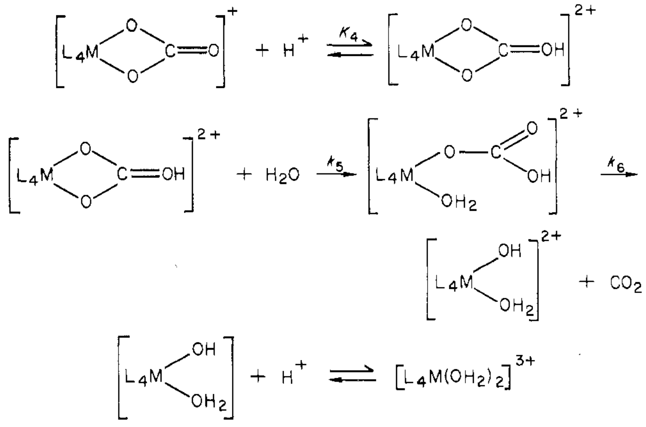
$$[ML_5OH]^{2+} + H^+ \rightleftharpoons [ML_5OH]^{3+} \quad 1/K_3$$

where M = Co(III),[2-7] Rh(III),[8-10] and Ir(III),[8] L_5 = a ligand group consisting of five N donors, K_1 and K_3 are acid-dissociation constants, and k_2 = rate-determining step. The rate law for the given mechanism is

$$k_{obsd} = k_2[H^+]/([H^+] + K_1) \qquad (1)$$

It turns out that $pK_1 \approx pK_3$ and $k_2 \approx 1$ s^{-1} at 25 °C. The magnitude of k_2 clearly illustrates that the process only involves O–C bond breakage, which has also been confirmed with isotopic tracer experiments.[11,12]

In contrast to these findings, the decarboxylation of bidentate carbonate complexes occurs according to a different mechanism[9,13-18] since this process includes a M–O bond breakage as the rate-determining step (k_5).[18]



The rate raw for the mechanism is shown in eq 2 which in

$$k_{obsd} = \frac{k_5K_4[H^+]}{1 + K_4[H^+]} \qquad (2)$$

general simplifies to eq 3[18] since K_4 is usually very small, such

$$k_{obsd} = k_5K_4[H^+] \qquad (3)$$

that $1 + K_4[H^+] \approx 1$ for the experimental conditions concerned. In some systems[10,13-15] eq 3 is in the form of eq 4,

$$k_{obsd} = k' + k''[H^+] \qquad (4)$$

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(1) (a) University of Hannover. (b) Potchefstroom University for Christian Higher Education. (c) University of Heidelberg.

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Table I. Summary of Crystal Data and Intensity Collection for $[([9]aneN_3)_2Cr_2(OH)_2CO_3]I_2 \cdot H_2O$

A. Crystal Parameters at 23 °C

$a = 8.577\ (3)$ Å
$b = 14.169\ (5)$ Å
$c = 21.805\ (6)$ Å
$V = 2650$ Å^3
ρ(calcd) = 1.806 g cm^{-3}

$Z = 4$
cryst system: orthorhombic
space group: $Pbnm[D_{2h}^{16}$-No. 62]
mol wt: 720.2
mol formula: $[C_{13}H_{24}Cr_2N_6O_5]I_2 \cdot H_2O$

B. Measurement of Intensity Data

diffractometer: AED (Siemens)
radiation: Mo Kα ($\lambda = 0.7107$ Å)
data collcn: θ–2θ mode; 2θ range = 4–66°
scan rate: 2.85–11.4°/min
scan width: $[\theta(K\alpha) + 0.20 + 0.228 \tan\theta]^\circ - [\theta(K\alpha) - 0.15 - 0.116 \tan\theta]^\circ$
bkgd estimation: stationary crystal–stationary counter at the extremities of each 2θ scan; each for half the time taken for the 2θ scan
std reflcns: 3 every 100 reflcns; no decay obsd
reflcns collected: 2545 ($I \geq 3.0\sigma(I)$)
abs coeff: $\mu = 31.4$ cm^{-1}; no abs corrections were deemed to be necessary

where $k'' = K_4k_5$ and k' represents the water-assisted decarboxylation path. The behavior of bridged carbonate complexes should be similar to that of bidentate carbonate complexes if such bridged species exist in that form in solution.

We report here the synthesis of two μ-carbonato complexes of chromium(III) and of rhodium(III), the crystal structure of the chromium complex, and the kinetics of their respective decarboxylation in acidic perchlorate media.

Experimental Section

Kinetic Measurements. UV–visible absorption spectra were recorded on a UNICAM SP 1800 spectrophotometer. Kinetic measurements were performed in the thermostated-cell compartment of a Zeiss PMQ II spectrophotometer. $NaClO_4$ was used to maintain the ionic strength at 1.0 M throughout the study. All chemicals were of analytical grade and deionized-distilled water was used in preparing all solutions. The pseudo-first-order rate constants were calculated in the usual way, and first-order plots were linear for at least 2–3 half-lives.

Preparation of Complexes. The preparation of $[([9]aneN_3)_2Rh_2(OH)_2CO_3](ClO_4)_2 \cdot 3H_2O$ has been described elsewhere[19] ($[9]aneN_3$ = 1,4,7-triazacyclononane[20]).

$[([9]aneN_3)_2Cr_2(OH)_2CO_3](ClO_4)_2 \cdot 3H_2O$. A solution of *trans*-diaquo-di-μ-hydroxo-bis[(1,4,7-triazacyclononane)chromium(III)] tetraperchlorate[21] (0.35 g) and sodium carbonate (0.10 g) in 15 mL of water was heated to 70 °C for 30 min. The solution was allowed to stand at 20 °C for 2 days. Red, needle-shaped crystals were collected, washed with ethanol and ether, and air-dried. UV–visible spectrum: λ_{max} 510 nm (ϵ 101 L mol^{-1} cm^{-1}), 373 (84), and a shoulder at 335 (41).

Anal. Calcd: C, 22.01; H, 5.40; Cr, 14.66; Cl, 9.99; N, 11.85. Found: C, 21.8; H, 5.6; Cr, 14.2; Cl, 9.9; N, 12.1.

$[([9]aneN_3)_2Cr_2(OH)_2CO_3]I_2 \cdot 3H_2O$. A solution of the above perchlorate salt (0.6 g) and sodium iodide (3 g) in 30 mL of water was allowed to stand in an open vessel at 20 °C for 2 days. Red crystals were collected, washed with ethanol and ether, and air-dried.

Anal. Calcd: C, 20.43; H, 5.01; Cr, 13.60; I, 33.20; N, 10.99. Found: C, 20.2; H, 5.2; Cr, 13.3; I, 32.8; N, 11.2.

Description of the X-ray Diffraction Study and Solution of the Structure. The crystal of $[([9]aneN_3)_2Cr_2(OH)_2CO_3]I_2 \cdot H_2O$ selected for the structural analysis was of the approximate dimensions 0.07 × 0.10 × 0.22 mm. The unit cell parameters were obtained at 23 °C by a least-squares refinement of the angular settings of 59 reflections (Table I). Intensity data were collected on an automated diffractometer AED (Siemens) and were corrected for Lorentz and polarization effects. No absorption correction was applied.

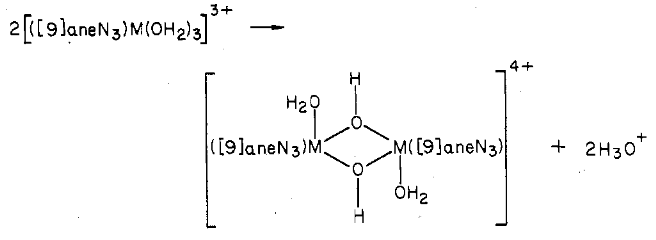
The structure was solved via direct methods, using MULTAN,[22] which revealed the positions of chromium and iodine. Subsequent Fourier syntheses revealed the positions of all nonhydrogen atoms. Several cycles of refinement, using the CRYLSQ program,[23] converged at $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.072$. During the last cycles the temperature factors of all nonhydrogen atoms were treated in the anisotropic form. Due to the low quality of the crystal the positions of the hydrogen atoms could not be located in a difference Fourier synthesis.

Therefore, the hydrogen atoms were omitted in the final refinement. A final difference Fourier synthesis also did not reveal the positions of two additional molecules of water of crystallization per formula unit which are present in freshly prepared crystals. Loss of water of crystallization before the process of intensity data collection leads to the relatively large R value and the anomalously large temperature factors of the oxygen atom of the remaining molecule of water of crystallization. It is noted that no systematic decrease of the intensity of the standard reflections during the measurements has been detected.

The atomic scattering factors for neutral Cr, I, C, N, and O were taken from ref 24. Anomalous dispersion corrections were applied to the I and Cr atoms. The final positional and thermal parameters are given in Table II. A list of observed and calculated structure factors is available as supplementary material.

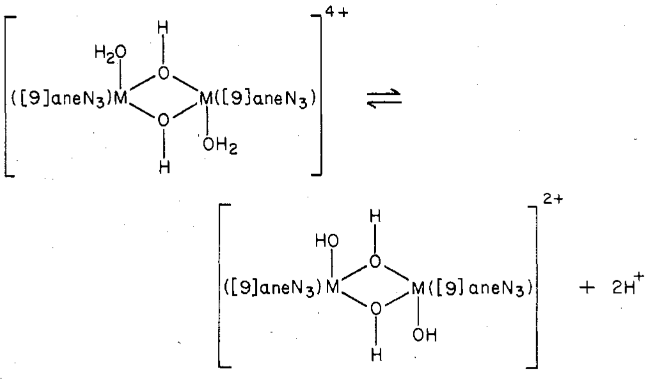
Results and Discussion

Synthesis of Carbonato-Bridged Complexes. In a series of papers the possibility of synthesizing hydroxo-bridged dinuclear complexes of chromium(III),[21] cobalt(III),[20] and rhodium(III)[19] via monomeric triaquo(1,4,7-triazacyclononane)metal(III) complexes in slightly acidic perchlorate media has been investigated:



M = Cr(III), Co(III), Rh(III)

Perchlorate salts of the isostructural *trans*-diaquo-di-μ-hydroxo-bis[(1,4,7-triazacyclononane)metal(III)] cations were isolated and characterized by single-crystal X-ray analyses.[19,21] It was shown that in alkaline solutions (pH 8) the respective Cr(III), and Rh(III), species were deprotonated:



M = Cr(III), Rh(III)

(In case of the cobalt(III) species formation of the tri-μ-

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Table II. Final Positional and Thermal[a] Parameters for $[([9]aneN_3)_2Cr_2(OH)_2CO_3]I_2 \cdot H_2O$ with Standard Deviations

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	0.744 84 (18)	0.221 63 (9)	0.316 46 (5)	2.64 (6)	2.23 (6)	1.66 (5)	0.02 (7)	−0.003 (66)	−0.072 (47)
I	0.762 98 (9)	0.943 80 (7)	0.572 09 (4)	4.70 (4)	6.23 (5)	6.27 (5)	0.53 (4)	−0.46 (4)	−0.26 (4)
O1	0.610 71 (105)	0.263 69 (77)	0.250 00 (0)	2.72 (44)	4.26 (63)	1.65 (40)	0.54 (42)	−0.0	−0.0
O2	0.901 95 (104)	0.228 47 (68)	0.250 00 (0)	2.97 (44)	2.04 (46)	2.58 (45)	−0.14 (38)	−0.0	−0.0
O3	0.703 72 (81)	0.086 33 (47)	0.301 70 (28)	4.59 (40)	2.36 (33)	2.55 (30)	−0.13 (28)	−0.07 (28)	−0.10 (25)
O4	0.615 52 (126)	0.966 24 (74)	0.250 00 (0)	4.81 (58)	2.78 (56)	2.96 (48)	−0.46 (46)	−0.0	−0.0
N1	0.580 47 (101)	0.219 47 (68)	0.386 61 (42)	3.77 (44)	3.14 (46)	2.98 (46)	−0.25 (39)	0.91 (36)	−0.36 (37)
N2	0.900 71 (109)	0.194 15 (63)	0.387 53 (40)	4.21 (48)	3.02 (45)	2.39 (41)	−0.18 (36)	−0.74 (36)	−0.04 (33)
N3	0.774 21 (94)	0.359 55 (55)	0.346 59 (35)	3.50 (41)	2.51 (37)	3.01 (35)	0.03 (33)	−0.03 (34)	−0.23 (29)
C1	0.672 16 (148)	0.047 09 (88)	0.250 00 (0)	3.37 (59)	1.35 (58)	2.49 (55)	0.31 (47)	−0.0	−0.0
C2	0.620 20 (145)	0.391 30 (85)	0.369 58 (54)	5.43 (66)	3.53 (61)	3.85 (60)	1.04 (51)	0.94 (53)	0.01 (50)
C3	0.548 38 (140)	0.314 97 (94)	0.410 70 (56)	4.41 (62)	5.15 (75)	4.56 (66)	0.11 (53)	1.35 (52)	−1.58 (60)
C4	0.646 44 (148)	0.149 71 (100)	0.432 77 (52)	6.22 (72)	5.90 (80)	2.86 (53)	−1.93 (62)	0.13 (54)	1.11 (56)
C5	0.001 29 (138)	0.280 87 (102)	0.391 54 (54)	4.13 (59)	6.311 (83)	3.62 (56)	−1.05 (60)	−0.53 (48)	−1.26 (57)
C6	0.898 58 (143)	0.369 73 (91)	0.393 97 (54)	4.99 (65)	4.79 (74)	3.61 (60)	−1.52 (56)	−0.86 (51)	−0.19 (51)
C7	0.813 42 (153)	0.173 66 (92)	0.446 41 (51)	6.54 (74)	4.59 (71)	2.79 (51)	−0.007 (59)	−0.31 (50)	0.67 (48)
O_w	0.307 01 (178)	0.262 43 (200)	0.250 00 (0)	2.79 (75)	18.9 (25)	23.9 (29)	2.08 (116)	−0.0	−0.0

[a] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$.

Table III. Bond Distances (Å)

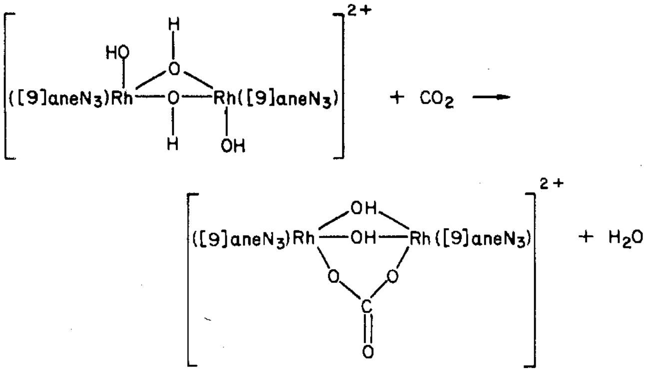
Cr-Cr′	2.898 (2)	N1-C3	1.477 (16)
Cr-O1	1.944 (6)	N1-C4	1.520 (16)
Cr-O2	1.981 (6)	N2-C5	1.504 (16)
Cr-O3	1.976 (7)	N2-C7	1.514 (15)
Cr-N1	2.081 (9)	N3-C2	1.483 (15)
Cr-N2	2.083 (9)	N3-C6	1.492 (14)
Cr-N3	2.077 (8)	C2-C3	1.534 (18)
O3-C1	1.286 (9)	C4-C7	1.502 (18)
O4-C1	1.244 (16)	C5-C6	1.538 (19)

Table IV. Bond Angles (Deg)

O1-Cr-O2	80.9 (3)	Cr-N1-C3	112.0 (7)
O1-Cr-O3	94.0 (4)	Cr-N1-C4	104.1 (7)
O1-Cr-N1	98.7 (3)	Cr3-N1-C4	115.4 (9)
O1-Cr-N2	172.6 (4)	Cr-N2-C5	105.0 (7)
O1-Cr-N3	91.1 (4)	Cr-N2-C7	110.4 (7)
O2-Cr-O3	92.9 (3)	C5-N2-C7	113.0 (9)
O2-Cr-N1	178.0 (3)	Cr-N3-C2	106.5 (6)
O2-Cr-N2	96.7 (3)	Cr-N3-C6	113.4 (7)
O2-Cr-N3	95.9 (4)	C2-N3-C6	111.9 (8)
O3-Cr-N1	89.1 (3)	O3-C1-O4	118.7 (6)
O3-Cr-N2	93.1 (3)	O3-C1-O3	122.5 (11)
O3-Cr-N3	170.4 (3)	N3-C2-C3	110.0 (10)
N1-Cr-N2	83.4 (4)	N1-C3-C2	111.3 (10)
N1-Cr-N3	82.1 (3)	N1-C4-C7	109.8 (10)
N2-Cr-N3	82.1 (3)	N2-C5-C6	110.0 (9)
Cr-O1-Cr	96.4 (4)	N3-C6-C5	107.9 (9)
Cr-O2-Cr	94.0 (4)	N2-C7-C4	110.3 (9)
Cr-O3-C1	126.9 (7)		

hydroxo-bis[(1,4,7-triazacyclononane)cobalt(III)] cation was observed.[20])

Exposure of alkaline solutions of the rhodium(III) species to air led to the slow formation (within 2 days) of a μ-carbonato complex.[19]



The same reaction occurs when alkaline solutions of *trans*-diaquo-di-μ-hydroxo-bis[(1,4,7-triazacyclononane)chromium(III)] perchlorate are reacted with CO_2. A pink-red perchlorate and an iodide salt were isolated: $[([9]aneN_3)_2Cr_2(OH)_2CO_3](ClO_4)_2 \cdot 3H_2O$ and $[([9]aneN_3)_2Cr_2(OH)_2CO_3]I_2 \cdot 3H_2O$. Aqueous solutions of the respective *trans*-diaquo-di-μ-hydroxo-bis[(1,4,7-triazacyclononane)metal] cations react also with sodium carbonate at 70 °C rapidly to give the above μ-carbonato complexes.

The Molecular Structure of the Cation $[([9]aneN_3)_2Cr_2(OH)_2CO_3]^{2+}$. Bond distances and bond angles of the complex cation are listed in Tables III and IV, respectively. The molecular geometry and the atomic-labeling scheme for $[([9]aneN_3)_2Cr_2(OH)_2CO_3]^{2+}$ are shown in Figure 1. The structure consists of four distinct dimeric $[([9]aneN_3)_2Cr_2(OH)_2CO_3]^{2+}$ cations, eight iodide anions, and four molecules of water of crystallization per unit cell. The complex cation has crystallographically imposed C_s (m) symmetry. Atoms O1, O2, O4, and C1 lie in a mirror plane at $z = {}^1/_4$. The two chromium ions are linked by two hydroxo bridges and a bridging carbonate ion; each of the chromium(III) ions is in a distorted octahedral environment. Only two oxygen atoms of the carbonate ligand (O3 and O3′) are attached to a chromium(III) center (A), respectively, in contrast with an interesting structure (B) with a bridging carbonate between two copper(II) ions involving all three oxygen atoms of the carbonate.[25] The bridging role of O3 and O3′ leads to an increase in the C1–O3 distance (1.286 (9) Å) relative to the C1–O4 distance (1.244 (16) Å) which very closely resembles

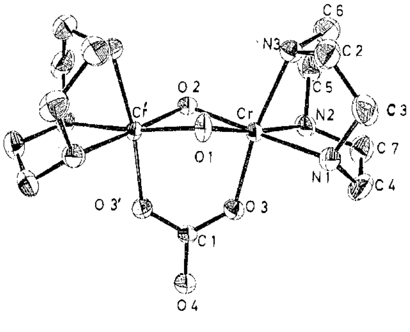


Figure 1. Structure of the $[([9]aneN_3)_2Cr_2(OH)_2CO_3]^{2+}$ cation showing 50% ellipsoids for all nonhydrogen atoms and the atom-labeling scheme.

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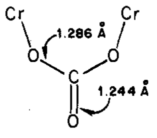
Table V. Rate Data for the Acid-Catalyzed Decarboxylation of Rh_2CO_3[c]

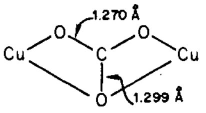
temp, °C	$[H^+]$, M	10^4k_A,[a] s^{-1}	k_{A0}, s^{-1}	10^4k_{A1}, M^{-1} s^{-1}	10^4k_B,[a] s^{-1}	10^5k_{B0}, s^{-1}	10^4k_{B1}, M^{-1} s^{-1}
30.0	1.0	2.76 ± 0.12	(−0.2 ± 3.3) × 10^{-6}	2.73 ± 0.05	0.57 ± 0.02	0.17 ± 0.08	0.56 ± 0.01
	0.8	2.14 ± 0.18			0.46 ± 0.02		
	0.6	1.63 ± 0.23			0.36 ± 0.01		
	0.4	1.10 ± 0.06			0.23 ± 0.01		
	0.2	0.55 ± 0.11			0.13 ± 0.01		
40.2	1.0	6.42 ± 0.13	(−1.6 ± 1.4) × 10^{-5} [b]	6.71 ± 0.23[b]	1.43 ± 0.06	0.93 ± 0.46	1.31 ± 0.07
	0.8	5.44 ± 0.27			1.12 ± 0.06		
	0.6	3.93 ± 0.21			0.86 ± 0.08		
	0.4	2.40 ± 0.12			0.57 ± 0.07		
	0.2	0.99 ± 0.04			0.40 ± 0.03		
50.3	1.0	14.4 ± 0.2	(0.9 ± 2.0) × 10^{-5}	14.2 ± 0.3	3.43 ± 0.04	2.42 ± 0.86	3.10 ± 0.13
	0.8	11.4 ± 0.4			2.64 ± 0.06		
	0.6	8.38 ± 0.05			2.06 ± 0.09		
	0.4	5.98 ± 0.08			1.46 ± 0.06		
	0.2	2.90 ± 0.35			0.92 ± 0.12		
60.3	1.0	29.9 ± 1.5	(0.9 ± 3.6) × 10^{-5}	29.8 ± 0.6	8.00 ± 0.40	3.49 ± 2.65	7.40 ± 0.40
	0.8	23.8 ± 1.2			5.96 ± 0.30		
	0.6	17.8 ± 0.9			4.78 ± 0.30		
	0.4	12.5 ± 0.6			3.21 ± 0.16		
	0.2	5.77 ± 0.29			1.98 ± 0.10		
$\Delta H^{\ddagger}$, kcal mol^{-1}				15.0 ± 0.2		19.3 ± 3.6	16.3 ± 0.5
$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}				−25.4 ± 0.5		−20.6 ± 11.4	−24.3 ± 1.7

[a] Mean value of between two and four kinetic runs. [b] Calculated by including one zero point in the data. [c] [Complex] = 2.5 × 10^{-4} M; ionic strength = 1.0 M; wavelength = 252 nm.

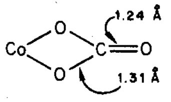
the bonding situation of a carbonate ligand coordinated to merely one metal center via two oxygen atoms (C).[26]



A



B

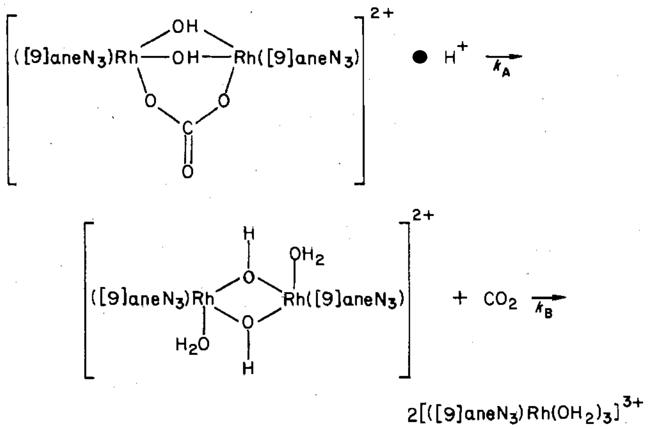


C

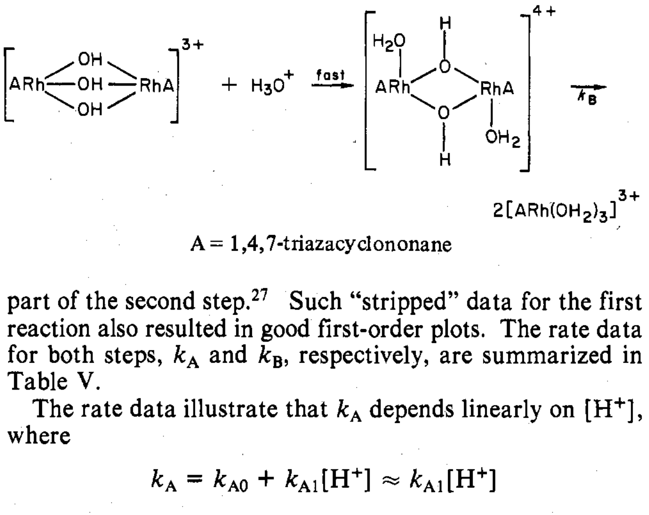
The 1,4,7-triazacyclononane framework of the ligands takes up a (λλλ) and (δδδ) conformation, respectively. The distances and angles of the coordinated amine are very similar to those observed in $[([9]aneN_3)_3Cr_3(OH)_5]I_4{\cdot}5H_2O$,[21] $[([9]aneN_3)_2Co_2(OH)_2(OH_2)_2](ClO_4)_4{\cdot}4H_2O$,[20] and $[([9]aneN_3)_2Rh_2(OH)_2(OH_2)_2](ClO_4)_4{\cdot}4H_2O$.[19]

Decarboxylation of Rh_2CO_3. Repetitive scan spectra of solutions of Rh_2CO_3 in 1 M $HClO_4$ at 40 °C in the range 230–400 nm indicated two mechanistic steps. During the first (faster) reaction the absorbance at 343 nm (ε 430 L mol^{-1} cm^{-1}) increases to an extinction value of approximately 600 L mol^{-1} cm^{-1}, whereas the strong absorbance in the region <300 nm decreases significantly from ε ~3100 to ε ~2400 at 250 nm. During the second (slower) reaction both the absorbances at 343 nm (~600 L mol^{-1} cm^{-1}) and in the region <300 nm decrease such that the extinction at 250 nm changes from ca. 2400 to ca. 80 L mol^{-1} cm^{-1}. The spectrum of the final product coincides with that reported for the decomposition product of the *trans*-diaquo-di-μ-hydroxo species, viz., the monomer species,[19] for which λ_{max} = 340 nm (ε 250) and 280 (90). Both steps do not exhibit any characteristic isosbestic points.

Scheme I



Scheme II



A = 1,4,7-triazacyclononane

The observed spectral changes can be interpreted in terms of Scheme I. Kinetic measurements were performed at 252 nm (decrease in absorbance). First-order plots show an initial fast step followed by a slower step for which good first-order behavior is observed. Back-extrapolation of the second part of the curve allows the calculation of the contribution of the first (faster) reaction on the basis of the difference between the exerimental first-order curve and the back-extrapolated part of the second step.[27] Such "stripped" data for the first reaction also resulted in good first-order plots. The rate data for both steps, k_A and k_B, respectively, are summarized in Table V.

The rate data illustrate that k_A depends linearly on $[H^+]$, where

$$k_A = k_{A0} + k_{A1}[H^+] \approx k_{A1}[H^+]$$

This equation is of the general form of eq 3 and describes the

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Table VI. Rate Data for the Acid Decomposition of *trans*-$Rh_2(\mu\text{-}OH)_2(OH_2)_2$ [b]

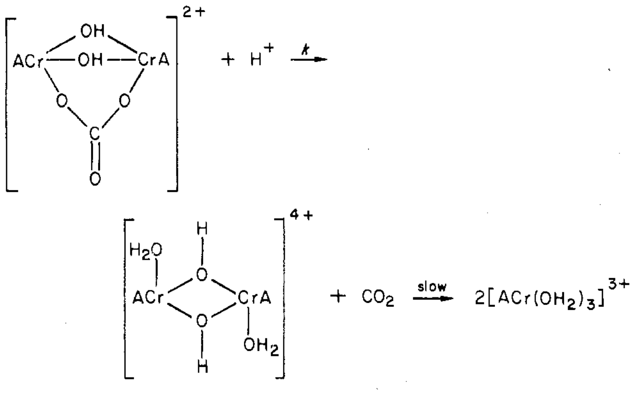
$[H^+]$, M	10^4k_{obsd},[a] s^{-1}	$[H^+]$, M	10^4k_{obsd},[a] s^{-1}
0.2	0.75 ± 0.03	0.8	2.53 ± 0.03
0.4	1.35 ± 0.03	1.0	3.11 ± 0.05
0.6	1.92 ± 0.14		

$10^5k_{B_0} = 1.61 \pm 0.11\ s^{-1}$

$10^4k_{B_1} = 2.95 \pm 0.16\ M^{-1}\ s^{-1}$

[a] Mean value of at least two kinetic runs. [b] [Complex] = 2.5 × 10^{-4} M; ionic strength = 1.0 M; wavelength = 252 nm; temperature = 50.3 °C.

Scheme III



A = 1,4,7-triazacyclononane

acid-catalyzed decarboxylation process of the bridged carbonate species. The acid dependence of k_B follows a similar relation

$$k_B = k_{B0} + k_{B1}[H^+]$$

and describes the decomposition of the *trans*-diaquo-di-μ-hydroxo species to produce the monomer species. k_{B0} can be interpreted as the rate constant for the water-assisted path. An identical rate law has been reported for the decomposition of *trans*-diaquo-di-μ-hydroxo-bis[triamminecobalt(III)] to form monomeric species.[28] In order to clarify this point, we performed some kinetic experiments, on the acid-catalyzed decomposition of the tri-μ-hydroxo-bis[(1,4,7-triazacyclononane)rhodium(III)] cation.[19] This complex decomposes rapidly under the present experimental conditions in a number of steps[29] to the *trans*-diaquo-di-μ-hydroxo-bis[(1,4,7-triazacyclononane)rhodium(III)] species, which slowly decomposes to the monomer species (Scheme II). First-order plots for absorbance measurements at 252 nm do not exhibit any deviations, and the observed rate constants (Table VI) are in good agreement with k_B, k_{BO}, and k_{B1} data reported in Table V. This futher underlines the validity of the proposed reaction mechanism.

Table VII. Rate Data for the Acid-Catalyzed Decarboxylation of Cr_2CO_3 [b]

temp, °C	$[H^+]$, M	10^4k_{obsd},[a] s^{-1}	$10^4k'$, s^{-1}	$10^4k''$, M^{-1} s^{-1}
30.0	1.0	0.96 ± 0.08	0.31 ± 0.05	0.61 ± 0.08
	0.8	0.74 ± 0.02		
	0.6	0.65 ± 0.03		
	0.4	0.53 ± 0.01		
	0.2	0.46 ± 0.01		
40.1	1.0	2.87 ± 0.03	1.20 ± 0.12	1.55 ± 0.18
	0.8	2.30 ± 0.11		
	0.6	2.10 ± 0.19		
	0.4	1.82 ± 0.23		
	0.2	1.56 ± 0.16		
50.0	1.0	6.12 ± 0.66	2.70 ± 0.13	3.33 ± 0.19
	0.8	5.31 ± 0.42		
	0.6	4.66 ± 0.10		
	0.4	3.91 ± 0.08		
	0.2	3.49 ± 0.05		
$\Delta H^\ddagger$, kcal mol^{-1}			20.5 ± 2.5	15.9 ± 0.5
$\Delta S^\ddagger$, cal K^{-1} mol^{-1}			−11.5 ± 8.1	−25.4 ± 1.8

[a] Mean value of between two and four kinetic runs. [b] [Complex] = 2.35 × 10^{-3} M; ionic strength = 1.0 M; wavelength = 530 nm.

Decarboxylation of Cr_2CO_3. During the acidification of the μ-carbonato-di-μ-hydroxo-bis[(1,4,7-triazacyclononane)chromium(III)] species the spectrum in the visible region slowly changes to that for the *trans*-diaquo-di-μ-hydroxo-bis[(1,4,7-triazacyclononane)chromium(III)] species and isosbestic points are observed at 388 and 455 nm. After several half-lives, a secondary reaction becomes observable which exhibits isosbestic points at 366, 434, and 535 nm. These spectral changes are ascribed to the same type of mechanism as suggested in the previous section for the Rh_2CO_3 complex (Scheme III). Further proof for this reaction sequence was obtained from repetitive scan spectra for the acid decomposition of the *trans*-diaquo-di-μ-hydroxo species under similar experimental conditions. These spectra showed isosbestic points at 364, 435, and 535 nm, which are in excellent agreement with those reported above for the secondary process observed in the decomposition of the μ-carbonato complex. The effect of the secondary process can be bypassed if the decarboxylation reaction is measured at an isosbestic point of the secondary process. Kinetic measurements of the decarboxylation process at 535 nm (Table VI) resulted in linear first-order plots without an indication of any secondary deviations.

Summary

Two binuclear complexes of chromium(III) and rhodium(III) containing a symmetrical carbonato bridge have been prepared. The crystal structure of the complex of chromium(III) shows that two metal ions are coordinated to two different oxygen atoms of the carbonate ligand in the solid state. The kinetic data for the respective acid-catalyzed decarboxylation clearly indicate that these species exist in this form in solution. The rate data and activation parameters for k_{A1} (Table V) and k'' (Table VII) are in good agreement with those reported for the decarboxylation of bidentate carbonato complexes elsewhere.[9,17] Thus the bridging carbonate group exhibits kinetically the typical behavior of a coordinated carbonato ligand.

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Registry No. $[([9]aneN_3)_2Cr_2(OH)_2CO_3]I_2{\cdot}H_2O$, 74175-93-2; $[([9]aneN_3)_2Cr_2(OH)_2CO_3](ClO_4)_2$, 74144-11-9; $[([9]aneN_3)_2Rh_2(OH)_2CO_3](ClO_4)_2$, 73203-33-5; *trans*-diaquodi-μ-hydroxo-bis[(1,4,7-triazacyclononane)chromium(III)] tetraperchlorate, 71480-26-7.

Supplementary Material Available: A list of observed and calculated structure factors for $[([9]aneN_3)_2Cr_2(OH)_2CO_3]I_2{\cdot}H_2O$ (11 pages). Ordering information is given on any current masthead page.

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