ceptibility of the complex also suggests the presence of a uranium(V) ion. The compound obeys a Curie–Weiss plot at low temperatures with a calculated moment of 1.10 μ_B. With the assumption that there is little or no contribution to the moment from +6, this value is then consistent with moments reported for other uranium(V) complexes.[31,32] The oxidation states may also be calculated from Zachariasen's bond length–bond strength relationships.[33,34] In the present structure the oxidation states of each uranium atom were calculated to be +6.09 and +5.51 for U(1) and U(2), respectively. Abnormally high values for the +5 oxidation state have been obtained in calculations performed in this laboratory on U(V) compounds containing U–O–U bonds. This suggests a better correlation of Zachariasen's formalism to U^{6+} complexes than U^{5+} and may be due in part to more abundant crystallographic data available on bond lengths in U^{6+} compounds as compared to U^{5+} compounds.

In conclusion, the attempted synthesis of uranium(III) phenoxide complexes and subsequent air oxidation has led to the isolation and characterization of a unique mixed-valent alkoxide complex, I. An earlier report of an unusual red uranyl alkoxide, $UO_2(OC_4H_9)_2\cdot 4C_4H_9OH$, isolated from the air oxidation of $U(OC_4H_9)_4$, was characterized only by chemical analysis.[35] In light of the data presented herein, it appears likely that the previously reported red uranyl alkoxide also exists as a mixed-valent complex and not as a pure uranyl alkoxide.

Acknowledgment. The authors wish to thank E. Duesler, University of New Mexico, for the preliminary crystallographic data and J. Smith for the magnetic susceptibility measurements. We also thank R. A. Penneman and P. G. Eller for helpful discussions.

Supplementary Material Available: Listings of structure factors, anisotropic thermal parameters (Table V), and selected carbon distances and angles (Table VI) (19 pages). Ordering information is given on any current masthead page.

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New Triply Hydroxo-Bridged Complexes of Chromium(III), Cobalt(III), and Rhodium(III): Crystal Structure of Tris(μ-hydroxo)bis[(1,4,7-trimethyl-1,4,7-triazacyclononane)chromium(III)] Triiodide Trihydrate

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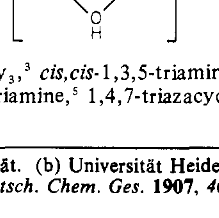
The synthesis of the cyclic amine 1,4,7-trimethyl-1,4,7-triazacyclononane ($Me_3[9]aneN_3$) is reported, and its ligating properties toward chromium(III), cobalt(III), and rhodium(III) are described. Triply OH-bridged binuclear cations have been prepared, $[(Me_3[9]aneN_3)M(OH)_3M(Me_3[9]aneN_3)]^{3+}$ (M = Cr(III), Co(III), Rh(III)). In contrast to their analogues containing the nonmethylated ligand 1,4,7-triazacyclononane the binuclear cations are stable in 2 M perchloric acid—no acid-catalyzed OH-bridge cleavage has been detected. The complex $[(Me_3[9]aneN_3)_2Cr_2(OH)_3]^{3+}$ represents the first genuine tris(μ-hydroxo) complex of chromium(III). The iodide salt, $[(Me_3[9]aneN_3)_2Cr_2(OH)]I_3\cdot 3H_2O$, has been characterized by a three-dimensional X-ray diffraction study. The complex crystallizes in the hexagonal space group C_{6h}^2-$P6_3/m$ with $a = 9.698$ (1) Å, $c = 20.621$ (4) Å, and $V = 1680$ Å^3; $Z = 2$. Diffraction data were collected on a Syntex R3 diffractometer with θ–2θ scan and Mo Kα radiation, and the structure was solved by conventional methods, resulting in a final R factor of 0.046 for 1405 independent reflections. The structure consists of binuclear cations of Cr(III) (face-sharing distorted octahedra), iodide ions, and waters of crystallization, which are bound to the hydroxo bridges via a short hydrogen bond (O···O = 2.787 (4) Å). The Cr–Cr separation is the shortest known to date for binuclear complexes of chromium(III) (2.642 (2) Å).

Introduction

Binuclear complexes of cobalt(III) with three hydroxo bridges and amine ligands (two face-sharing octahedra) have been described by Werner[2] and since then by many other groups:[3-6]



L = 3 NH_3,[2] 3 py$_3$,[3] *cis,cis*-1,3,5-triaminocyclohexane,[4] diethylenetriamine,[5] 1,4,7-triazacyclononane[6]

The chemistry of these tris(μ-hydroxo) complexes has attracted much interest because in acidic solution one hydroxo bridge is cleaved rapidly and the resulting bis(μ-hydroxo) species (edge-sharing octahedra) are very stable.[2,4,6,7] Thus the kinetics of this OH-bridge cleavage (eq 1) have been studied in detail[5-9] and were mechanistically interpreted in

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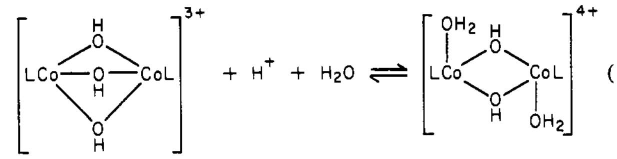
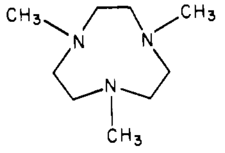

(1)

terms of an OH-bridge cleavage process and a subsequent isomerization step. In two instances it was shown that two coordinated water molecules of the diaquabis(μ-hydroxo) species are in the trans position with respect to each other.[6,10]

Despite earlier claims to the existence of triply hydroxo-bridged complexes of chromium(III),[11] no such complexes have been prepared and fully characterized to date. Attempts to prepare such complexes have so far failed; e.g., the condensation reaction of $[([9]aneN_3)Cr(OH_2)_3]^{3+}$ in alkaline solution affords a trinuclear complex cation $[Cr_3([9]aneN_3)_3(OH)_5]^{5+}$ with intramolecular Cr–Cr separations of 2.97, 3.54, and 3.57 Å.[13] On the other hand, many bis(μ-hydroxo) complexes have been prepared and characterized by X-ray crystallography. The main research interest has been focused on the mechanism of the acid-catalyzed OH-bridge cleavage[11,13-15] (or formation) and on correlations between the structures of magnetically condensed dimers and their magnetic properties.[16] A binuclear chromium(III) complex with two face-sharing octahedra would be of interest in both issues.

Well-characterized binuclear complexes of rhodium(III) have only recently been reported.[17,18] The paucity of known μ-hydroxo-bridged complexes of rhodium(III) is somewhat surprising considering the rich chemistry of binuclear complexes of cobalt(III).

In this paper we report the synthesis and the ligating properties of the cyclic amine 1,4,7-trimethyl-1,4,7-triazacyclononane toward Cr(III), Co(III), and Rh(III). This ligand


$Me_3[9]aneN_3$

is expected to coordinate facially in octahedral complexes. In contrast to the nonmethylated amine 1,4,7-triazacyclononane only *one* ligand per metal center can be bound. Therefore, complexes of the type $[(Me_3[9]aneN_3)M(OH_2)_3]^{3+}$ (M = Cr(III), Co(III), Rh(III)) should be easily prepared and converted to binuclear tris(μ-hydroxo) complexes.

Experimental Section

Preparation of the Ligand 1,4,7-Trimethyl-1,4,7-triazacyclononane. 1,4,7-Triazacyclononane has been prepared by procedures described in the literature.[6,19] The trihydrochloride of the methylated amine has been synthesized according to the procedure reported by Barefield[20] and Kaden[21] by methylation of the triamine with a mixture of formic acid and formaldehyde. The pure amine was obtained by dissolving the hydrochloride in water and treating it under strong cooling and stirring with an excess of an aqueous solution of sodium hydroxide. Water was then eliminated from the amine by adding benzene (2 times the volume of water) to the aqueous solution and refluxing and collecting the azeotrope in a water eliminator. After removal of water, benzene is stripped off on a rotary evaporator and the remaining yellowish liquid is distilled under vacuum. With 27 g of the crude 1,4,7-triazacyclononane as starting material, 18 g of the trimethylated amine was obtained as a colorless liquid at 20 °C (50%).

The ^{1}H NMR spectrum of the trimethylated amine measured in CD_3OD with Me_4Si as internal standard exhibits two resonances at $\delta(CH_2)$ 2.73 (singlet (12 H)) and at $\delta(CH_3)$ 2.34 (singlet (9 H)).

For the preparation of complexes a methanolic solution of 1,4,7-trimethyl-1,4,7-triazacyclononane (1 M) was used, which was stored under a nitrogen atmosphere.

Preparation of Complexes. $[Cr(Me_3[9]aneN_3)Cl_3]$. To a solution of 3 g of chromium trichloride hexahydrate in 10 mL of methanol was added a single piece of granulated zinc. To this mixture was added 10 mL of a 1 M solution of 1,4,7-trimethyl-1,4,7-triazacyclononane in methanol, and it was heated under reflux for 2 h. After cooling, the solid green product was collected, washed with water, acetone, and ether, and air-dried; yield 1.2 g (30%).

Anal. Calcd for $[CrC_9H_{21}Cl_3N_3]$: C, 32.79; H, 6.42; N, 12.75; Cr, 15.77. Found: C, 32.6; H, 6.4; N, 12.7; Cr, 15.9.

$[Cr_2(Me_3[9]aneN_3)_2(OH)_3](ClO_4)_3\cdot H_2O$. The pH of a suspension of 0.5 g (1.5 mmol) of $[Cr(Me_3[9]aneN_3)Cl_3]$ in 10 mL of water was adjusted to 10 with 0.5 M NaOH. The suspension was warmed at 60 °C with stirring until a clear deep red solution was obtained. The pH of the solution was maintained between 9 and 10 with dilute sodium hydroxide solution. Solid sodium perchlorate was added at 50 °C to the solution after the pH had been decreased to 7–8 until precipitation started. After cooling, red crystals were filtered off, washed with ethanol and ether, and air-dried; yield 0.6 g (50%).

Anal. Calcd for $[C_{18}H_{45}N_6O_3Cr_2](ClO_4)_3\cdot H_2O$: C, 26.56; H, 5.82; N, 10.33; Cr, 12.78; ClO_4, 36.66. Found: C, 26.4; H, 5.5; N, 10.1; Cr, 13.0; ClO_4, 37.2.

$[Cr_2(Me_3[9]aneN_3)_2(OH)_3]I_3\cdot 3H_2O$. X-ray-quality crystals of the iodide salt were obtained by dissolving the perchlorate salt in dilute sodium iodide solution and keeping it at room temperature in an open vessel for several days.

$[Co_2(Me_3[9]aneN_3)_2(OH)_3](ClO_4)_3$. To 1 g of $CoCl_2\cdot 6H_2O$ dissolved in 15 mL of water was added with stirring 10 mL of a 1 M methanolic solution of the ligand $Me_3[9]aneN_3$. Ten milliliters of H_2O_2 was added to this red-brown solution and stirred for 30 min at room temperature. Upon addition of solid sodium perchlorate and cooling violet cyrstals precipitated from this solution. These were filtered off, washed with ethanol and ether, and air-dried. The product was recrystallized from hot water and $NaClO_4$; yield 2 g.

Anal. Calcd for $[C_{18}H_{45}N_6O_3Co_2](ClO_4)_3$: C, 26.70; H, 5.60; N, 10.38; Co, 14.56; ClO_4, 36.84. Found: C, 26.7; H, 5.6; N, 10.2; Co, 14.8; ClO_4, 36.3.

$[Rh_2(Me_3[9]aneN_3)_2(OH)_3](ClO_4)_3$. To a solution of 1 g of $RhCl_3\cdot 3H_2O$ in 20 mL of ethanol was added with stirring 15 mL of the methanolic solution of the ligand (1 M). The temperature was maintained at 60 °C for 2 h and at room temperature for 12 h during which time a light yellow product precipitated. This was collected on a fritted-glass funnel, washed with ethanol and ether, and air-dried; yield 0.5 g. This yellow solid (presumably $[Rh(Me_3[9]aneN_3)Cl_3]$ was suspended in 15 mL of water, and the pH was adjusted to 11 with sodium hydroxide. It was heated under reflux for 2 h, during which time a clear yellow solution was obtained. The clear solution was treated with solid $NaClO_4$ and warmed on a hot plate until precipitation started. After cooling, the yellow crystals were filtered off, washed with ethanol and ether, and air-dried; yield 0.5 g (43%).

Anal. Calcd for $[C_{18}H_{45}N_6O_3Rh_2](ClO_4)_3$: C, 24.08; H, 5.05; N, 9.36; ClO_4, 33.23. Found: C, 23.8; H, 5.1; N, 9.1; ClO_4, 32.3.

$[Rh_2(Me_3[9]aneN_3)_2(OH)_3]I_3\cdot 3H_2O$. The iodide salt was obtained by dissolving the perchlorate in dilute sodium iodide solution and keeping it at 20 °C in an open vessel for several days. This iodide salt is isostructural with $[Cr_2(Me_3[9]aneN_3)_2(OH)_3]I_3\cdot 3H_2O$. It crystallizes in the hexagonal space group C_{6h}^2-$P6_3/m$ with a = 9.550 (2) Å and c = 21.264 (3) Å, and the Rh–Rh distance was determined

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Table I. Summary of Crystal Data and Intensity Collection for $[(Me_3[9]aneN_3)_2Cr_2(OH)_3]I_3 \cdot 3H_2O$

A. Crystal Parameters at 22 °C

$a = 9.698\ (1)$ A
$c = 20.621\ (4)$ A
$V = 1680$ A^3
$Z = 2$
space group: $C_{6h}^2 - P6_3/m$
mol wt: 932.3
mol formula: $[C_{18}H_{45}Cr_2N_6O_3]I_3 \cdot 3H_2O$

B. Measurement of Intensity Data

diffractometer: Syntex R3
radiation: Mo Kα ($\lambda = 0.7107$ A)
data collection: θ–2θ mode; 2θ range = 4–65°
scan rate: 2.8–11.4° min^{-1}
bkgd estimation: stationary crystal–stationary counter at the extremities of each 2θ scan; each for half the time taken for the 2θ scan
std reflctns: 3 every 2 h; no decay obsd
reflctns collected: 1405 ($I \geq 2.5\sigma(I)$)
abs coeff: 33.8 cm^{-1}; empirical absorption correction has been carried out

Table II. Final Positional Parameters for $[(Me_3[9]aneN_3)Cr(OH)_3Cr(Me_3[9]aneN_3)]I_3 \cdot 3H_2O$

atom	*x*	*y*	*z*
I1	0.0000	0.0000	0.0000
I2	0.33333	0.66667	0.38410 (3)
Cr	0.33333	0.66667	0.81405 (5)
N1	0.2609 (5)	0.4766 (5)	0.8785 (2)
C1	0.2264 (7)	0.3244 (6)	0.8454 (2)
C2	0.1103 (6)	0.4572 (6)	0.9073 (2)
C3	0.3861 (7)	0.5182 (6)	0.9299 (2)
O1	0.4336 (6)	0.5933 (7)	0.7500
O2	0.403 (1)	0.126 (1)	0.7500
H1A	0.3270 (7)	0.3430 (6)	0.8290 (3)
H1B	0.1516 (7)	0.2933 (6)	0.8103 (3)
H1C	0.1875 (7)	0.2411 (6)	0.8772 (3)
H2A	0.0293 (6)	0.4230 (6)	0.8746 (2)
H2B	0.0753 (6)	0.3789 (6)	0.9411 (2)
H3A	0.3462 (7)	0.5392 (6)	0.9690 (2)
H3B	0.3972 (7)	0.4261 (6)	0.9359 (2)
H1	0.48 (1)	0.61 (1)	0.7500
H2	0.73 (1)	0.59 (1)	0.776 (3)

Table III. Bond Distances (Å) and Angles (Deg)

Cr–N1	2.089 (4)	C2–C3	1.500 (8)
Cr–O1	1.972 (6)	Cr–Cr′	2.642 (2)
N1–C1	1.505 (7)	O1–H1	0.43 (13)
N1–C2	1.499 (8)	O2–H2	0.55 (7)
N1–C3	1.506 (7)	O2–O1[a]	2.787
C1–N1–Cr	112.9 (3)	N1–C2–C3	111.1 (4)
C2–N1–Cr	103.8 (4)	C2–C3–N1	110.2 (4)
Cr–N1–Cr	109.9 (3)	Cr–O1–Cr′	84.1 (3)
C2–N1–C1	109.4 (4)	Cr–O1–H1	125 (9)
C1–N1–C3	109.7 (5)	H2–O2–H2′	154 (10)
C2–N1–C2	103.8 (4)		

[a] Hydrogen bond.

from a preliminary single-crystal X-ray analysis to be 2.96 (1) Å.

Kinetic Measurements. Standard syringe techniques with argon as blanketing gas were used for the reductions of the binuclear complexes of cobalt(III). All kinetic measurements were made on a Unicam SP 1700 spectrophotometer interfaced to a Commodore PET 2001 computer for data acquisition and analysis. All reactions were run under pseudo-frist-order conditions with the reductant $[Cr(OH_2)_6]^{2+}$ in excess over complexes of cobalt(III). Pseudo-first-order rate constants were calculated by using a least-squares program[22] where the absorptions at the beginning ($t = 0$) and at the end of the completed reaction ($t = \infty$) were treated as variables. The observed and calculated values differed only within the uncertainty of the last digit of the readings of the instrument.

Description of the X-ray Diffraction Study and Solution of the Structure. The crystal of $[Cr_2(Me_3[9]aneN_3)_2(OH)_3]I_3 \cdot 3H_2O$ selected for the structural analysis was of the approximate dimensions 0.08 × 0.10 × 0.21 mm. The unit cell parameters were obtained at 22 °C by a least-squares refinement of the angular settings of 26 reflections (Table I). Intensity data were collected on a Syntex R3 diffractometer and were corrected for Lorentz and polarization effects. Three standard reflections were measured every 2 h. An empirical absorption correction was carried out.[23] The scattering factors for neutral nonhydrogen atoms were corrected for both the real and the imaginary components of anomalous dispersion. The function minimized during least-squares refinement was $\sum w_i(|F_o| - |F_c|)^2$ with final convergence to $R_1 = 0.046$ and $R_2 = 0.041$: $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2}$ ($w_i = 1/(\sigma(F)^2)$).

The structure was solved via a three-dimensional Patterson synthesis, which yielded the positions of the chromium and iodine atoms. Subsequent Fourier syntheses revealed the locations of all remaining nonhydrogen atoms. Idealized positions of H atoms bound to carbon atoms were calculated (on the basis of a d(C–H) of 0.97 Å and regular tetrahedral geometry about the C atoms). These were refined as a rigid moiety with isotropic thermal parameters for the H atoms and anisotropic thermal parameters for the C atoms. Refinements were carried out with anisotropic thermal parameters for all other atoms. At this stage a difference Fourier synthesis revealed the positions of the hydrogen atoms bound to O atoms of the hydroxo bridges and of the waters of crystallization. The refinement was continued with these positions (as variables) and a fixed isotropic temperature factor ($U = 0.08$).

The final positional parameters are given in Table II and bond distances and bond angles in Table III. Listings of thermal parameters and of observed and calculated structure factors are available as supplementary material.

Results and Discussion

Preparation and Characterization of Complexes. The tridentate ligands 1,4,7-triazacyclononane ([9]aneN$_3$) and its methylated derivative 1,4,7-trimethyl-1,4,7-triazacyclononane (Me$_3$[9]aneN$_3$) coordinate facially in octahedral complexes. This has been shown for the former by X-ray analysis of complexes of cobalt(III),[6,24] chromium(III),[12,25] rhodium(III),[17] and nickel(II).[26] As can be easily deduced from space-filling models, it is sterically not possible to form octahedral complexes containing two 1,4,7-trimethyl-1,4,7-triazacyclononane ligands in contrast to the case for the nonmethylated ligand.

The reaction of Me$_3$[9]aneN$_3$ with $CoCl_2 \cdot 6H_2O$ and hydrogen peroxide in aqueous solution affords upon addition of solid $NaClO_4$ violet-red crystals of $[(Me_3[9]aneN_3)Co(OH)_3Co(Me_3[9]aneN_3)](ClO_4)_3$ in good yields. The complex is only sparingly soluble in water. The UV–visible spectrum shows a maxima at 547 nm and a shoulder at 310 nm (Table I). The UV–visible spectra of the complex in 2.0 M perchloric acid and in 2 M NaOH are identical with that measured in water. They do not change within 24 h at 25 °C. This indicates that in acidic solution no hydroxo-bridge cleavage is observed. Even from 5 M perchloric acid solution it has not been possible to isolate a diaquabis(μ-hydroxo) species.

This behavior is in marked contrast to all other known tris(μ-hydroxo)bis[(amine)cobalt(III)] cations,[2,4–10] which can readily be converted to the corresponding diaquabis(μ-hydroxo)bis[(amine)cobalt(III)] cation in acidic solutions. The perchlorate salt crystallizes without water of crystallization. Therefore, in the infrared spectrum a single sharp absorption of the ν(O–H) stretching mode is observed at 3570 cm^{-1}.

In methanolic solutions of Me$_3$[9]aneN$_3$ and $CrCl_3 \cdot 6H_2O$ the green monomeric complex [Me$_3$[9]aneCrCl$_3$] is formed, which reacts in water with sodium hydroxide, yielding the red

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Table IV. UV-Visible Absorption Spectra of Tris(μ-hydroxo)-Bridged Dimers in Water at 20 °C

	λ_{max}, nm	ε, L mol^{-1} cm^{-1}
$[Cr_2(Me_3[9]aneN_3)_2(OH)_3]^{3+}$ [a]	505	103
	~378 (sh)	56
	342	90
	322	62
$[Co_2(Me_3[9]aneN_3)_2(OH)_3]^{3+}$ [b]	547	195
	310 (sh)	3.7 × 10^3
$[Rh_2(Me_3[9]aneN_3)_2(OH)_3]^{3+}$	396	230
	332	175

[a] The absorption spectrum in 1.0 M $HClO_4$ does not change even after 48 h and is identical with the spectrum in H_2O. [b] The spectra in 2 M $HClO_4$ *or* in 2 M NaOH do not change (24 h) and are identical with those measured in H_2O.

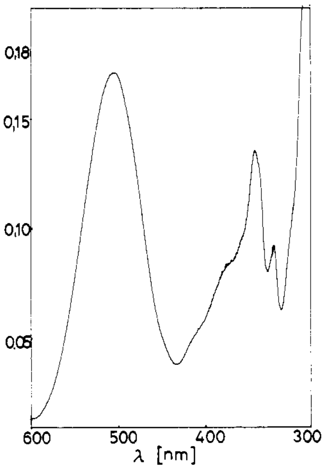

Figure 1. UV–visible absorption spectrum of an aqueous solution of $[(Me_3[9]aneN_3)_2Cr_2(OH)_3](ClO_4)_3 \cdot 3H_2O$ at 25 °C ($[Cr_2] = 5 \times 10^{-4}$ M, 4-cm cell).

cation $[(Me_3[9]ane)Cr(OH)_3Cr(Me_3[9]aneN_3)]^{3+}$, which can be precipitated as the perchlorate or iodide salt. The UV–visible spectrum is shown in Figure 1 (Table IV).

The spectrum of the complex in 1 M perchloric acid also does not change within 48 h at 25 °C and is identical with that measured in water. No acid-catalyzed OH-bridge cleavage is observed. This behavior is also atypical for OH-bridged complexes of chromium(III).[13–15] Since this appears to be the first authentic triply OH-bridged binuclear complex of chromium(III), it was decided to fully characterize its structure by single-crystal X-ray analysis.

Finally, if the above reaction is carried out with $RhCl_3 \cdot 3H_2O$, the yellow binuclear cation $[(Me_3[9]aneN_3)Rh(OH)_3Rh(Me_3[9]aneN_3)]^{3+}$ is formed, which can be precipitated as the perchlorate or iodide salt. The latter is found to be isostructural with the analogous chromium(III) complex. Again no acid-catalyzed OH-bridge cleavage is observed, contrasting with a study by Hancock[18] on $[(en)_2Rh(OH)_2Rh(en)_2]^{4+}$.

Molecular Structure of the Cation $[(Me_3[9]aneN_3)_2Cr_2(OH)_3]^{3+}$. Bond distances and bond angles of the complex cation are listed in Table III. The molecular geometry and the atomic labeling scheme for $[(Me_3[9]aneN_3)Cr_2(OH)_3]^{3+}$ are shown in Figure 2. The structure consists of two distinct dimeric $[(Me_3[9]aneN_3)_2Cr_2(OH)_3]^{3+}$ cations, six iodide anions, and six molecules of water of crystallization per unit cell. The complex cation has crystallographically imposed C_{3h} symmetry. The two chromium(III) centers lie on a threefold axis; they are linked by three hydroxo-bridged face-sharing octahedra. The oxygen atoms and the respective hydrogen atoms lie in a mirror plane at $z = {}^1/_4$. Each of the chromium(III) ions is in a distorted-octahedral environment. A Cr–Cr separation of 2.642 (2) Å represents the shortest distance measured to date in binuclear complexes of chromium(III). For bis(μ-hydroxo) complexes of chromium(III) (edge-sharing octahedra) Cr–Cr distances of 2.9–3.1 Å are reported,[16] and for the binuclear anion $Cr_2Cl_9^{3-}$ (face-sharing octahedra) a Cr–Cr separation of approximately 3.05 Å is observed.[16] The Cr(III) ions are believed to repel each other from the centers of their coordination octahedra. In the binuclear cation $[(NH_3)_3Co(OH)_3Co(NH_3)_3]^{3+}$ a Co–Co distance of 2.565 Å is reported.[3] The difference between the Cr–Cr and Co–Co separations (0.077 Å) of $[(Me_3[9]aneN_3)_2Cr_2(OH)_3]^{3+}$ and of $[(NH_3)_6Co_2(OH)_3]^{3+}$ may simply reflect the difference of ionic radii of the metal centers Co^{3+} (low spin) and Cr^{3+}. Thus no repulsion of the Cr^{3+} centers is detected in the cation $[(Me_3[9]aneN_3)_2Cr_2(OH)_3]^{3+}$.

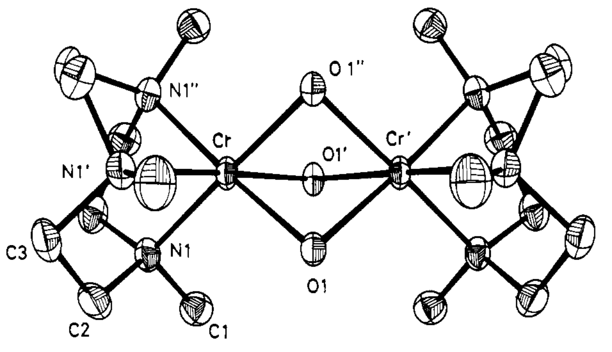

Figure 2. Structure of the $[(Me_3[9]aneN_3)_2Cr_2(OH)_3]^{3+}$ cation showing 50% ellipsoids for all nonhydrogen atoms and the atom-labeling scheme.

Table V. Kinetic Data for the Reduction of $[(Me_3[9]aneN_3)_2Co_2(OH)_3]^{3+}$ with Cr(II) at 25 °C (I = 1.0 M (LiCl))

[H$^+$], M	[Cr(II)], M	$10^4 k_{obsd}$, s^{-1} [a]	[H$^+$], M	[Cr(II)], M	$10^4 k_{obsd}$, s^{-1} [a]
0.9	0.021	2.68	0.5	0.042	5.5
0.9	0.021	2.90	0.1	0.021	3.10
0.5	0.021	2.79	0.1	0.021	3.0

[a] $[Cl^-]_t = 0.94$ M and $[Co_2]_t = 5 \times 10^{-4}$ in each run.

Three molecules of water of crystallization are bound via short hydrogen bonds to the binuclear cation—one to each hydroxo bridge.

Kinetics of Cr(II) Reductions of $[(Me_3[9]aneN_3)_2Co_2(OH)_3]^{3+}$ and of $[([9]aneN_3)_2Co_2(OH)_3]^{3+}$. The reductant $[Cr(OH_2)_6]^{2+}$ has in the past been used to scavenge for aqua complexes of cobalt(III) formed by bridge-cleavage processes,[27–29] which may occur catalyzed by acid or independent of [H$^+$] in aqueous solution. In some cases the resultant Cr(II)-independent rate term in these studies has been taken as a measure of the rate of bridge cleavage.[27,28] Reduction of these aqua complexes by Cr(II) is believed to occur rapidly via inner-sphere electron-transfer reactions, whereas the uncleaved hydroxo complexes are slowly reduced via an outer-sphere mechanism. The latter mechanism has been proposed for the [H$^+$]-independent reduction of the tetramer $[((NH_3)_4Co(OH)_2)_3Co]^{6+}$.[27] Only one example for the reduction of a triply bridged (μ-OH,OH,NH_2) binuclear complex of cobalt(III) has been reported previously.[29] The reported rate law did not have a [Cr^{2+}]-independent term.

Because of low solubility of the perchlorate salt of $[(Me_3[9]aneN_3)_2Co_2(OH)_3](ClO_4)_3$ the kinetics of its reduction by Cr(II) were studied in chloride-containing media by using

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pseudo-first-order conditions with excess reductant ($[Cl^-] = 0.94$ M). The perchlorate salt ($[Co_2]_t = 5 \times 10^{-4}$ M) was dissolved in water and was mixed with solutions containing hydrogen ions ($[H^+] = 0.1$–0.9 M), chromous ions ($[Cr(II)] = 0.02$–0.04 M), and chloride ions. The reaction products were $[(H_2O)_5CrCl]^{2+}$, $[Co(OH_2)_6]^{2+}$, and the free ligand $Me_3[9]aneN_3$ in its protonated form. Kinetic data are given in Table V. The rate law (eq 2) is independent of $[H^+]$ and first order

$$k_{obsd} = k_{Cr}[Cr^{2+}] \qquad (2)$$

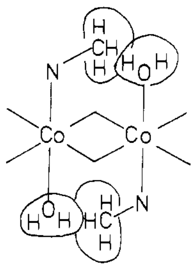
in $[Cr^{2+}]$ at constant $[Cl^-]$. This is taken as further evidence that no bridge-cleavage processes occur in acidic solution. The cation $[(Me_3[9]aneN_3)_2Co_2(OH)_3]^{3+}$ is reduced by the strong reductant $[(H_2O)_5CrCl]^+$ via an outer-sphere process. It is noted that there is no experimental evidence for the reduction of a protonated species as has been proposed in ref 28.

In contrast to the simple rate law eq 2 a considerably more complex expression is found for the reduction of the $[([9]aneN_3)_2Co_2(OH)_3]^{3+}$ cation by $[Cr(OH_2)_6]^{2+}$ in the $[H^+]$ range 0.05–0.3 M (eq 3). The details of this work will be

$$k_{obsd} = a + b[H^+] + c[H^+][Cr(II)] \qquad (3)$$

described elsewhere.[30] It is not obvious why the equilibrium eq 1 is shifted completely to the left-hand side when 1,4,7-trimethyl-1,4,7-triazacyclononane is the ligand L and why a value of $K = 11 \pm 2$ M^{-1} (20 °C, $\mu = 1.0$ M) is found for the analogous complex with the nonmethylated ligand 1,4,7-triazacyclononane.[6]

From space-filling models (structure A) it can be shown that



A

with $Me_3[9]aneN_3$ being the ligand the product, a diaqua-bis(μ-hydroxo) species cannot be formed because a sterically demanding CH_3 group of each ligand will interfere with the steric demands of the respective aqua ligand. The same explanation may account for the unreactivity of the corresponding complexes of chromium(III) and of rhodium(III) toward acid-catalyzed OH-bridge cleavage.

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Registry No. $[Cr_2(Me_3[9]aneN_3)_2(OH)_3]I_3\cdot 3H_2O$, 81898-05-7; $Cr(Me_3[9]aneN_3)Cl_3$, 81915-50-6; $[Cr_2(Me_3[9]aneN_3)_2(OH)_3](ClO_4)_3$, 81915-52-8; $[Co_2(Me_3[9]aneN_3)_2(OH)_3](ClO_4)_3$, 81898-07-9; $[Rh_2(Me_3[9]aneN_3)_2(OH)_3](ClO_4)_3$, 81898-09-1; $[Rh_2(Me_3[9]aneN_3)_2(OH)_3]I_3$, 81898-10-4.

Supplementary Material Available: Listings of observed and calculated structure factors and anisotropic thermal parameters for $[(Me_3[9]aneN_3)_2Cr_2(OH)_3]I_3\cdot 3H_2O$ (10 pages). Ordering information is given on any current masthead page.

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Structure and Properties of a Palladium Methoxide Derivative, $Pd_2(\mu\text{-}CH_3O)_2(F_6acac)_2$. Reactions of Palladium Bis(hexafluoroacetylacetonate) with Aliphatic Alcohols

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Palladium bis(hexafluoroacetylacetonate), $Pd(F_6acac)_2$, reacts with methanol at room temperature to produce $Pd_2(\mu\text{-}CH_3O)_2(F_6acac)_2$. Crystal data: $P2_1/c$; $a = 8.945$ (4), $b = 7.149$ (6), $c = 29.36$ (1) Å; $\beta = 93.89$ (3)°; $V = 1873$ Å^3; $Z = 4$. The molecule is a dimer with two methoxy groups bridging two nearly planar palladium atoms which are also attached to two η^2-F_6acac ligands. The Pd_2O_2 ring is folded along the vector passing through the bridging oxygen atoms so that the dihedral angle between the PdO_2 planes is 26°. In the ring, $d(Pd\text{–}O)_{av}$ is 1.996 (7) Å and $d(Pd\text{–}Pd)$ is 2.984 (1) Å. At ca. 100 °C, the palladium methoxide decomposes to palladium metal, $Pd(F_6acac)_2$, methanol, methyl formate, and dimethoxymethane. $Pd(F_6acac)_2$ and 1-propanol react in the presence of oxygen to form propyl propionate, propionaldehyde, and propyl trifluoroacetate. The complex $[(C_5O_5)_2Pd]^{2-}$ was prepared from croconate(2−) and $Pd(F_6acac)_2$.

Introduction

The electron-withdrawing effect of the four trifluoromethyl groups in palladium bis(hexafluoroacetylacetonate), $Pd(F_6acac)_2$, leads to strong metal-centered acceptor behavior in this fluorinated organometallic compound. Facile displacement of chelating and oxygen- and carbon-bonded F_6acac groups is the source of an extensive acid–base chemistry as illustrated by our previous characterization of 1:1, 2:1, 3:1, and 4:1 adducts of $Pd(F_6acac)_2$ with molecular Lewis basis[1-4] and 2:1 adducts with solid donors such as silica and alumina.[5,6] Since the hexafluoroacetylacetonate anion is a good leaving group, $Pd(F_6acac)_2$ is a useful reagent in cyclometallation[7] and β-diketonate exchange reactions[8] and in the synthesis of highly colored (η^2-formazanyl)palladium compounds.[9] The present paper extends the synthetic chemistry of $Pd(F_6acac)_2$ and

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