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Notes

Alkylammonium Hexachlorometalates. 5.[1] Bis(1,6-diammoniohexane) Tetraaquahydrogen(1+) Hexachlororhodate(III) Dichloride, $[H_3N(CH_2)_6NH_3]_2[H_9O_4][RhCl_6]Cl_2$: Chain-like $[H_9O_4]^+$ Ions Enclosed in the Cavities of a Complex Organic−Inorganic Framework[†]

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Introduction

Species of the general formula $[H(H_2O)_n]^+$, i.e., hydrated H^+ cations, have always attracted much attention of inorganic, physical, and theoretical chemists.[2] Besides the oxonium cation $[H_3O]^+$ [3] and its monohydrate $[H_5O_2]^+$,[4] the most popular one is a monomeric species $H_9O_4^+$ with three water molecules surrounding one $[H_3O]^+$ cation.[5] Alternative topologies of $[H_9O_4]^+$, especially a chain-like isomer with two water molecules hydrating a central $[H_5O_2]^+$ moiety, have been discussed theoretically,[6] but none of these has been characterized in the solid state as a distinct structural unit not connected by further O···H···O hydrogen bonds as in $[H_{18}O_8]^{2+}$ [7] or in one-dimensional polymeric $[H_9O_4]_n^{n+}$.[8] (See Chart 1.)

In the course of the investigations of α,ω-diammonioalkane cations of different lengths as elements of crystal engineering we recently succeeded in synthesizing and characterizing the structure of bis(1,4-diammoniobutane) diaquahydrogen(1+) hexachlororhodate(III) dichloride, $[H_3N(CH_2)_4NH_3]_2[H_5O_2][RhCl_6]Cl_2$.[1] In view of crystal engineering, the diammoniobutane ions of this compound act as “intelligent” building blocks, because their conformational flexibility enables them to take part in the building of cavities with exactly the right lengths for the inclusion of the guest ions $[H_5O_2]^+$. We now report on the chain-like isomer of $[H_9O_4]^+$ as a first result of our attempts to synthesize frameworks with enlarged cavities by use of longer chain diamines with the aim to enclose larger $[H(H_2O)_n]^+$ ions with a special topology.

Chart 1. Eigen-Type and Chain-like Isomers of $[H_9O_4]^+$.

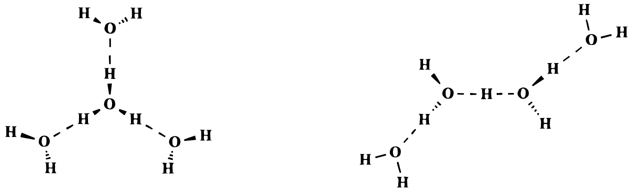

Table 1. Crystallographic Data for **1**

empirical formula $C_{12}H_{45}N_4O_4Cl_8Rh$	formula weight 696.1
$a = 7.6079(6)$ Å	space group $P\bar{1}$ (No. 2)
$b = 9.1720(5)$ Å	$T = 293$ K
$c = 10.8972(7)$ Å	$\lambda = 0.71073$ Å
$\alpha = 97.132(5)°$	$\rho_{\text{calcd}} = 1.597$ g cm^{-3}
$\beta = 104.620(7)°$	$\mu = 1.352$ mm^{-1}
$\gamma = 95.373(6)°$	$R_1 = 0.028^a$
$V = 723.89(9)$ Å^3	w$R_2 = 0.053^a$
$Z = 1$	$w^{-1} = \sigma^2(F^2)$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **1**

atom	x/a	y/b	z/c	U_{eq};^{a} U_{iso}
Rh1	0	0	0	0.02250(4)
Cl1	−0.26807(6)	0.07694(5)	−0.12074(4)	0.03604(9)
Cl2	−0.05712(7)	−0.22403(4)	−0.14096(4)	0.03620(9)
Cl3	−0.17038(6)	−0.10783(5)	0.12578(4)	0.03495(9)
Cl4	−0.15906(7)	0.21964(5)	−0.56189(5)	0.04296(11)
N1	−0.1637(2)	−0.0423(2)	−0.38893(14)	0.0387(3)
N2	−0.4045(2)	−0.8019(2)	−0.8614(2)	0.0445(4)
C1	−0.3319(3)	−0.1478(3)	−0.4465(2)	0.0477(5)
C2	−0.3419(3)	−0.2180(3)	−0.5829(2)	0.0524(6)
C3	−0.5174(3)	−0.3162(3)	−0.6463(2)	0.0521(5)
C4	−0.5140(3)	−0.4090(2)	−0.7719(2)	0.0517(6)
C5	−0.4637(3)	−0.5615(2)	−0.7567(2)	0.0419(4)
C6	−0.4427(3)	−0.6473(2)	−0.8776(2)	0.0394(4)
O1	0.0537(3)	0.4339(2)	−0.0824(2)	0.0636(5)
O2	−0.0391(3)	0.4784(2)	−0.3236(2)	0.0746(6)
H1	−0.057(3)	0.438(5)	−0.059(4)	0.059(14)
H2	−0.0107(4)	0.447(3)	−0.166(2)	0.091(5)
H3	0.052(4)	0.3360(18)	−0.088(3)	0.091(5)
H4	−0.107(4)	0.408(3)	−0.388(3)	0.136(7)
H5	0.006(5)	0.559(3)	−0.348(3)	0.136(7)

[a] $U_{eq} = (^1/_3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

Experimental Section

Reagents. Rhodium trichloride was used as a 6 M hydrochloric acid solution of $RhCl_3 \cdot nH_2O$ containing 20% of $RhCl_3$ (Degussa AG). Hydrochloric acid (12 M) (99.9%, Riedel-de Haen) was used as received.

Instrumentation. The infrared spectrum was recorded on a Perkin Elmer IR 883 spectrometer, the UV/vis spectrum on a Carl Zeiss spectralphotometer DMR 10. A Perkin Elmer microanalyzer 240 was used to collect microanalytical data (C, H, N), a Linseis L62 instrument for differential thermal analysis (DTA).

[†] Dedicated to Prof. Dr. Hans Bürger on the occasion of his 60th birthday.

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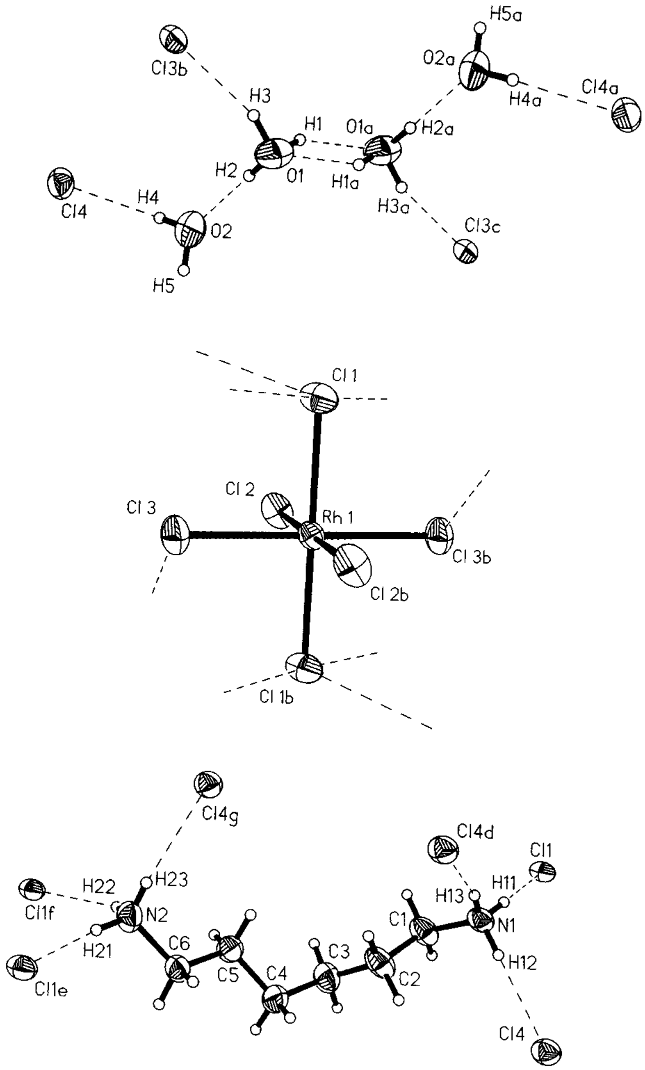

Figure 1. Diagram of the ions of **1** with their environments (displacement ellipsoids at 50% probability level; radii of hydrogen atoms are chosen arbitrarily). Symmetry codes: (a) $-x$, $1 - y$, $-z$; (b) $-x$, $-y$, $-z$; (c) x, $1 + y$, z; (d) $-x$, $-y$, $-1 - z$; (e) x, $-1 + y$, $-1 + z$; (f) $-1 - x$, $-1 - y$, $-1 - z$; (g) x, $-1 + y$, z.

Preparation of $[H_3N(CH_2)_6NH_3]_2[H_9O_4][RhCl_6]Cl_2$ (1). Hydrochloric acid (12 M, 4 mL) containing 0.15 g (0.072 mmol) of $RhCl_3$ was carefully added to a hydrochloric acid solution of 0.11 g (0.95 mmol) of 1,6-diaminohexane. From this dark red solution can be harvested small single crystals (diameter: 0.1−0.03 mm) after a few days. For characterization by physical measurements and elemental analysis a sufficient number of crystals with a small amount of adhesive mother liquor were isolated and transferred as fast as possible to the measuring devices.

Analytical Data. Found: C, 20.7; H, 6.4; N, 8.0. Calcd for $C_{12}H_{45}N_4O_4Cl_8Rh$ (696.1): C, 20.70; H, 6.53; N, 8.05. IR data (KBr disk): ν (cm^{-1}) 3567 (m), 3506 (m), 3170 (s), 3001 (m), 2926 (m), 2859 (m), 1626 (w), 1574 (m), 1494 (m), 1395 (w), 1311 (w), 1241 (w), 1116 (w), 1104 (w), 1057 (w), 1034 (w), 1002 (w), 926 (w), 783 (w), 732 (w), 471 (w), 358 (w), 313 (s), 228 (s). DTA: 20 mg of the dark red crystals of **1**, grown as described above, was taken from the crystallization medium and sealed in a glass ampule without drying. For calibration of the apparatus the melting points of potassium (63.3 °C) and indium (156.6 °C) were used, and the heating rate was 2 °C/min; one endothermic effect in the range of 20−160 °C; T_{onset}, 42.1 °C; T_{react}, 43.8 °C; T_{max}, 45.7 °C; T_{offset}, 49.5 °C; with dry material continuous decomposition occurred already at room temperature, and DTA curves strongly depend on the heating rate and on the history of the material. UV/vis spectrum (12 M hydrochloric acid): λ_{max} (nm) (log ϵ) 249 (4.509), 413 (1.908), 518 (2.003).

Description of the X-ray Study of 1. Dried crystals decompose within some seconds by loss of HCl and H_2O. For mounting on the diffractometer a crystal with adhesive mother liquor was dropped in RS2000 oil (Hoechst AG) and additionally put in a thin-walled glass capillary (0.82 × 0.55 × 0.50 mm^3); 9171 reflection data (5272 unique, $R_{int} = 0.0186$) were collected at rt on a Siemens P4 diffractometer. The structure was solved by the heavy atom method and successive difference Fourier syntheses (SHELXTL-Plus[13]). All H atoms were readily located. The H atoms of the diammonio cation were then treated as riding on the N and C atoms, respectively. Common U_{iso} values were used for H atoms of each NH_3 and CH_2 group. The positions of the H atoms in the $[H_9O_4]^+$ cation were refined with O−H distances restrained to 0.95 Å with a standard deviation of 0.02 Å; the site occupation factor of the disordered H1 atom was set to 0.5 and not refined; H1 has an individual U_{iso} value; H2 and H3 as well as H4 and H5 have a common U_{iso} value. A full matrix least squares refinement of 182 parameters including anisotropic displacement parameters for all "non-H atoms" using all but 47 reflections with negative F^2 values (SHELXL-93[14]) converged at the R values given in Table 1.

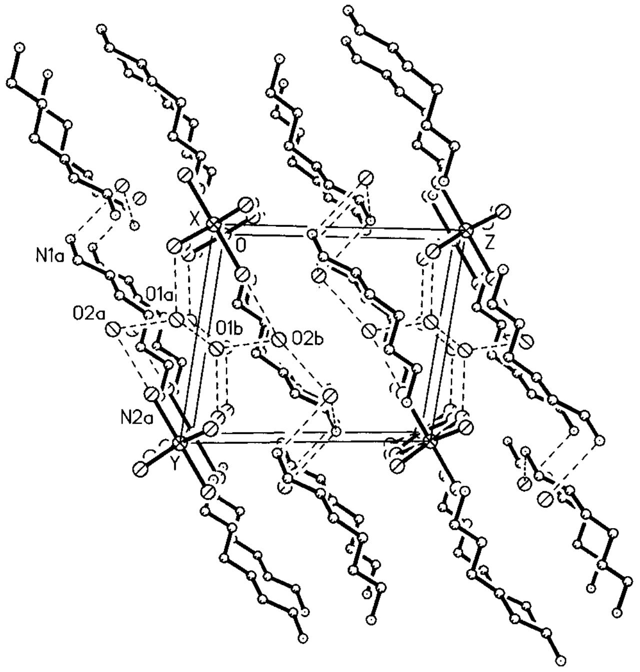

Figure 2. Packing diagram of **1**, view direction [−1 0 0]; hydrogen atoms are omitted for clarity, dashes between O and O and between O and Cl atoms, respectively, indicate O−H−O and O−H−Cl hydrogen bonds in and at the $[H_9O_4]^+$ ions.

Results and Discussion

From the red solution, obtained on mixing hydrochloric acid solutions of rhodium trichloride and 1,6-diammoniohexane dichloride, after some days dark red crystals could be harvested. The material was characterized by elemental analysis, DTA, IR and UV/vis spectroscopy as well as a crystal structure investigation, and all findings were consistent with the formula $[H_3N(CH_2)_6NH_3]_2[H_9O_4][RhCl_6]Cl_2$ (**1**). According to the DTA measurements the substance is stable up to 42 °C in a hydrochloric acid atmosphere.

1 crystallizes in the triclinic space group $P\bar{1}$. Figure 1 shows the ionic components with their direct environments, Figure 2 a packing diagram. Bond lengths and angles of the $[RhCl_6]^{3-}$ anion[9] and of the 1,6-diammoniohexane cation[10] are as expected (Table 3). Starting from the energy-favored, zigzag chain-like all-trans conformation, the bow-shaped conformer of the diam-

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Table 3. Selected Bond Lengths (Å) and Angles and Torsion Angles (deg) for **1**

Rh1−Cl1	2.3524(6)	C1−C2	1.525(3)
Rh1−Cl2	2.3415(6)	C2−C3	1.492(3)
Rh1−Cl3	2.3516(8)	C3−C4	1.528(3)
N1−C1	1.476(2)	C4−C5	1.502(3)
N2−C6	1.496(2)	C5−C6	1.501(3)
Cl1−Rh1−Cl2	90.44(3)	C3−C4−C5	113.6(2)
Cl2−Rh1−Cl3	89.90(3)	C4−C5−C6	113.5(2)
Cl1−Rh1−Cl3	89.66(3)	N1−C1−C2−C3	−175.6(2)
N1−C1−C2	112.1(2)	C1−C2−C3−C4	−169.1(2)
N2−C6−C5	112.2(2)	C2−C3−C4−C5	94.9(3)
C1−C2−C3	112.9(2)	C3−C4−C5−C6	−174.4(2)
C2−C3−C4	113.0(2)	C4−C5−C6−N2	−176.3(2)

monio cation present in **1** is achieved mainly by rotating half the cation 94.9(3)° around the C3−C4 axis. According to force field calculations[11] this conformation is 0.88 kJ/mol higher in energy than the all-trans conformation. The conformation is an important feature of the solid state structure, because it determines the distance of the hydrophilic centers of this building block (N···N 7.90 Å) and therefore the dimension and shape of the cavities in the organic−inorganic matrix.

The $[H_9O_4]^+$ cation enclosed in the cavity system lies on a crystallographic inversion center, and the central H1 atom shows the typical dynamic 1:1 disorder for a symmetrical double-potential-well hydrogen bond.[12] As to be expected from theoretical work,[6] it is best described as a $[H_5O_2]^+$ cation with a very strong O1···H1···O1a hydrogen bond with an additional molecule of water at each side acting as a hydrogen bond acceptor, i.e., via an oxygen lone pair. In contrast to the theoretical predictions there is less distance (= bond strength) equilibration between the central (O1···O1a 2.398(4) Å) and the terminal O−H···O bond (O1···O2 2.637(3) Å), probably caused by the weak but significiant O−H···Cl interactions with the Cl^- (Cl4···H4−O2 (Cl4···O2 3.175(2) Å)) and the $[RhCl_6]^{3-}$ anions (Cl3b···H3−O1 (Cl3b···O1 3.211(2) Å)).

To verify our ideas concerning crystal engineering with flexible cationic building blocks and to explore the structure-directing role of the hydronium cations, we have started attempts to synthesize and crystallize compounds with longer chain α,ω-diammonioalkane cations and also the acid free compound $[H_3N(CH_2)_6NH_3]_2[RhCl_6]Cl$ for direct comparison with the title compound.

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Supporting Information Available: Three X-ray crystallographic files, in CIF format, are available. Access information is given on any current masthead page.

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