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Synthesis, Reactivity, and Structure of $[H_{13}O_6][PtCl_5(H_4O_2)]\cdot 2(18\text{-cr-}6)$: A Crown Ether Complex of a Pentachloroaquaplatinic Acid with an $[H_{13}O_6]^+$ Cation in a Cage of Three Crown Ether Molecules

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An aqueous solution of $H_2[PtCl_6]\cdot 6\ H_2O$ reacts with crown ether 18-crown-6 to give $[H_{13}O_6][PtCl_5(H_4O_2)]\cdot 2(18\text{-cr-}6)$[1] (**1**) and $(H_3O)_2[PtCl_6]\cdot 2(18\text{-cr-}6)$ (**2a**). In the presence of HCl, only **2a** is formed; in an analogous manner, $(H_3O)_2[PtCl_6]\cdot 2(15\text{-cr-}5)\cdot 2\ H_2O$ (**2b**) and $(H_3O)_2[PtCl_6]\cdot 2(\text{DCH-18-cr-}6)$[1] (**2c**) were obtained. **1** is gradually decomposed in water to give $[PtCl_4(H_2O)_2]\cdot(18\text{-cr-}6)\cdot 2H_2O$ (**3**). **1**−**3** were characterized by microanalysis and IR and NMR spectroscopy (^1H, ^{13}C, ^{195}Pt). The X-ray structure analysis of **1** (orange needles; space group $P2_12_12_1$, $a = 7.938(1)$ Å, $b = 15.691(2)$ Å, $c = 34.861(4)$ Å; $Z = 4$) shows an anionic entity $[PtCl_5(H_4O_2)]^-$ and a cationic entity $[H_{13}O_6]^+$ which are separated by a crown ether molecule 18-cr-6. The $[H_{13}O_6]^+$ cations exhibit the structure $[H_3O(H_4O_2)_2(H_2O)]^+$ and are also separated by crown ether molecules in such a way that the crystal is threaded by chains built up of 18-cr-6/$[H_{13}O_6]^+$ units at which the 18-cr-6/$[PtCl_5(H_4O_2)]^-$ moieties are fixed as lateral branches. Thus, the cations $[H_{13}O_6]^+$ are embedded in three crown ether molecules. All terminal hydrogens are involved in hydrogen bridges to oxygen atoms of the crown ether molecules. The $O_w\cdots O_{cr}$ distances are distinctly longer in the mean than the $O_w\cdots O_w$ distances within the $[H_{13}O_6]^+$ moiety.

Introduction

The existence of hydrated proton species in aqueous solution was postulated a very long time ago. The oxonium ion H_3O^+ was considered to be responsible for the role that the proton plays in acid catalysis of esterification, and the formation of this cation was a natural consequence of the Brönsted acid−base theory. Today the state of hydrated protons $[H(H_2O)_n]^+$ is also of wide interest in chemistry, physics, and biological sciences as well. The clustering behavior of protonated water molcecules plays an important role for proton transfer reactions in chemical and biological systems, for charge transfer mechanisms, and for understanding the properties of water. Apart from the "classic" solvation chemistry, this is of relevance to disciplines such as atmospheric chemistry, chemistry in membranes and in biochemistry.[2−4]

IR spectroscopic investigations,[5] X-ray studies,[6] and theoretical calculations[7] provide access to the structure of $[H(H_2O)_n]^+$. Compared to the numerous crystallographic studies of acids and hydrogen salts that revealed the presence of $[H(H_2O)_n]^+$ with $n \leq 4$,[2c,6a,b] there were only two examples of structures containing ions $[H(H_2O)_n]^+$ with $n \geq 5$ known until now, namely, $[Fe(C_5H_5)_2]_4[H_{11}O_5]_2[TcCl_6]_3$ [8] and $[(C_9H_{18})_3(NH)_2Cl][H_{13}O_6]Cl_2$.[9] Here we report the synthesis, reactivity, and structure of a pentachloroaquaplatinate complex with a new isomeric form of an $[H_{13}O_6]^+$ ion in a cage of three crown ether molecules.

Experimental Section

Materials and General Procedures. IR spectra were recorded with a Mattson 5000 spectrophotometer and Raman spectra with a Bruker IR/Raman spectrometer IFS/FRA 106. NMR spectra were obtained on Varian spectrometers Unity 500 and Gemini 200 using solvent signals (^1H, ^{13}C) as internal references and $Na_2[PtCl_6]$ ($\delta(^{195}Pt) = +4520$ ppm) for external reference ($\Xi(^{195}Pt) = 21.4$ MHz), respectively. Microanalyses were performed by the Microanalytical Laboratory of the Pharmaceutical Department of the University. Hexachloroplatinic acid (Degussa, Saxonia, Germany) and the crown ethers (18-cr-6, 15-cr-5, DCH-18-cr-6) (Merck) were commercial products.

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(1) Abbreviations: cr = crown; DCH-18-cr-6 = dicyclohexano-18-crown-6; O_{cr} = crown ether oxygen; O_w = water oxygen.

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Synthesis of $[H_{13}O_6][PtCl_5(H_4O_2)]\cdot 2(18\text{-cr-}6)$ (1). From the mixed solutions of $H_2[PtCl_6]\cdot 6\,H_2O$ (2.59 g, 5.0 mmol) in water (10 mL) and 18-cr-6 (5.55 g, 21.0 mmol) in water (10 mL), **1** started to crystallize as orange needles after few hours. After standing for two to three days, the crystals were filtered off, washed with few drops of water, and dried. After that, the crystallization of **1** was still going on. After five to six days, **2a** started to crystallize as red-orange cube-shaped crystals. At that time, an amount of water was added that just dissolved the crystals of **2a**, and a further portion of **1** was isolated as described above. After that, hydrochloric acid (concentrated; ~3 mL) was added. After standing overnight, the precipitated **2a** (0.63 g, 13%) was filtered off, washed with acetone, and dried. Yield: 1.94 g (37%); mp 140 °C. Found: C, 27.89; H, 6.25; Cl, 16.84. $C_{24}H_{65}O_{20}Cl_5Pt$ requires: C, 27.56; H, 6.26; Cl, 16.94. IR (CsBr, cm^{-1}): 3392 m, 2906 s, 1637 w, 1477 m, 1350 s, 1284 m, 1251 m, 1101 vs, 957 s, 835 s, 358 w, 333 s, 313 sh. Ra (cm^{-1}): 364 m, 356 w, 339 s, 323 s. ^1H NMR (D_2O, ppm): δ 3.94 (s; CH_2). ^{13}C NMR (D_2O, ppm): δ 69.9 (s; CH_2). ^{195}Pt NMR (D_2O; ppm): 5023. ^{195}Pt NMR (CH_2Cl_2 with D_2O capillary as lock; ppm): δ 5152.

Synthesis of $(H_3O)_2[PtCl_6]\cdot 2(18\text{-cr-}6)$ (2a). To a solution of $H_2[PtCl_6]\cdot 6\,H_2O$ (0.78 g, 1.51 mmol) in hydrochloric acid (10%, 0.6 mL) was added a solution of 18-cr-6 (1.76 g, 6.68 mmol) in water (2.5 mL). After standing overnight, **2a** crystallized as red-orange crystals which were filtered off, washed with acetone, and dried. Yield: 0.62 g (42%); mp 164 °C. Found: C, 29.62; H, 5.47; Cl, 21.76. $C_{24}H_{54}O_{14}Cl_6Pt$ requires: C, 29.58; H, 5.59; Cl, 21.83. IR (CsBr, cm^{-1}): 2916 w, 1476 m, 1352 s, 1290 w, 1250 m, 1100 s, 957 s, 835 m, 321 vs. Ra (cm^{-1}): 335 s, 310 s. ^1H NMR (D_2O, ppm): δ 3.95 (s, CH_2). ^{13}C NMR (D_2O, ppm): δ 69.9 (s; CH_2). ^{195}Pt NMR (D_2O, ppm): δ 4530.

Synthesis of $(H_3O)_2[PtCl_6]\cdot 2(15\text{-cr-}5)\cdot 2\,H_2O$ (2b). From the mixed solutions of $H_2[PtCl_6]\cdot 6\,H_2O$ (0.30 g, 0.58 mmol) in water (0.5 mL) and 15-cr-5 (0.57 g, 2.59 mmol) in water (0.5 mL), **2b** crystallized within few days as well-shaped orange crystals, which were filtered off and dried. Yield: 0.38 g (71%); mp 121 °C. Found: C, 26.37; H, 5.46; Cl, 21.90. $C_{20}H_{50}O_{14}Cl_6Pt$ requires: C, 26.04; H, 5.46; Cl, 23.06. IR (CsBr, cm^{-1}): 2872 s, 1460 m, 1356 s, 1302 m, 1250 s, 1118 s, 944 s, 844 m, 330 s. Ra (cm^{-1}): 338 s, 314 s. ^1H NMR (D_2O, ppm): δ 3.61 (s, CH_2). ^{13}C NMR (D_2O, ppm): δ 69.9 (s, CH_2).

Synthesis of $(H_3O)_2[PtCl_6]\cdot 2(\text{DCH-18-cr-}6)$ (2c). Analogously to **2b** starting from $H_2[PtCl_6]\cdot 6\,H_2O$ (0.30 g, 0.58 mmol) and DCH-18-cr-6 (0.23g, 0.61 mmol) in water (25 mL), **2c** was obtained. Yield: 0.29 g (42%); mp 145 °C. Found: C, 40.02; H, 6.34; Cl, 17.70. $C_{40}H_{78}O_{14}Cl_6Pt$ requires: C, 40.34; H, 6.60; Cl, 17.86. IR (CsBr, cm^{-1}): 2936 vs, 2862 s, 1697 w, 1448 s, 1356 m, 1277 w, 1244 m, 1211 m, 1071 vs, 994 s, 932 m, 881 w, 836 m, 325 vs. Ra (cm^{-1}): 338 s, 313 s. ^1H NMR (CD_3CN, ppm): δ 1.31 (m, 4H, CH_2, cyclohexane), 1.54 (m, 8H, CH_2, cyclohexane), 1.81 (m, 4H, CH_2, cyclohexane), 3.68 (m, 20H, CH_2O, CHO). ^{13}C NMR (CD_3CN, ppm):[10] δ 22.1/22.3 (C11, C12, C24, C25), 26.8/27.0 (C10, C13, C23, C26), 68.1/68.3 (C3, C7, C16, C20), 71.2/71.5 (C4, C6, C17, C19), 79.1/79.0 (C1, C9, C14, C22).

Synthesis of $[PtCl_4(H_2O)_2]\cdot(18\text{-cr-}6)\cdot 2H_2O$ (3). After stirring a solution of **1** (0.20 g; 0.19 mmol) in water (1.5 mL) for 1 h, a yellow precipitate of **3** was formed which was filtered off, washed with few drops of water, and dried. Yield: 0.021 g (17%); mp 115 °C. Found: C, 21.85; H, 4.78; Cl, 20.55. $C_{12}H_{32}O_{10}Cl_4Pt$ requires: C, 21.41; H, 4.79; Cl, 21.06. IR (CsBr, cm^{-1}): 3456 m, 2915 s, 1583 w, 1472 w, 1351 m, 1290 w, 1255 w, 1102 vs, 957 s, 837 m, 375 w, 342 m, 329 sh, 312 w. Ra (cm^{-1}): 379 m, 369 w, 335 s. ^1H NMR (D_2O, ppm): δ 3.53 (s; CH_2). ^{13}C NMR (D_2O, ppm): δ 69.9 (s, CH_2). ^{195}Pt NMR (D_2O, ppm): δ 5017.

X-ray Crystal Structure Determination of 1. Crystal data are summarized in Table 1. A needle-shaped, orange crystal of the size $0.57 \times 0.11 \times 0.10$ mm^3 was mounted on a Stoe STADI4 diffractometer with an Oxford Cryosystems Cryostream low-temperature equipment. All measurements were performed at 200 K using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Lattice constants were derived from a least-squares treatment of the setting angles for 76 reflections in the θ range 12.4−15.0°. Intensity data were collected in the $2\theta/\theta$ scanning mode for a total of 6289 reflections ($1.2 \le \theta \le 27.0°$, h,k,l from −1,−20,−44 to 10,20,44) yielding 5582 unique reflections ($R_{int} = 0.060$), 3389 of them with $I > 2\sigma(I)$ were considered observed. All reflections were corrected for Lorentz and polarization as well as for absorption effects. The latter were corrected by an empirical method based on Ψ scans of 10 reflections ($3.7 \le \theta \le 19.0°$) with minimum and maximum transmission coefficients of 0.4347 and 0.5537, respectively. No extinction correction was applied. The intensity of three hourly measured check reflections varied ~6.1%.

Table 1. Crystallographic Data for **1**

chemical formula	$[H_{13}O_6][PtCl_5(H_4O_2)]\cdot 2(C_{12}H_{24}O_6)$
formula weight	1046.10
T	200(2) K
λ	0.71073 Å
space group	$P2_12_12_1$ (No. 19)
a	7.938(1) Å
b	15.691(2) Å
c	34.861(4) Å
V	4342.1(9) Å^3
Z	4
ρ_{calcd}	1.600 g cm^{-3}
μ	36.07 cm^{-1}
$R(F_o)^a$	0.0475
$Rw(F_o^2)^b$	0.1137

^{a} $I > 2\sigma(I)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} All data, $Rw = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

The structure was solved by Patterson methods in SHELXS-86[11] and refined by full-matrix least-squares techniques on F^2 for 5017 non-negative F^2 values in SHELXL-93.[12] The default values of scattering factors of SHELXL-93 were used. Non-H atomic positions have been assigned anisotropic displacement parameters. One of the crystal water molecules is strongly disordered; a splitting of its location into two sites with equal occupancy has been found to be a good approximation within the structural model. Hydrogen atoms were located on the basis of geometrical considerations and treated according to the riding model during refinement with isotropic displacement parameters corresponding to the heavy atoms they are linked to. The choice of the correct absolute structure has been approved by a Flack absolute structure parameter of $x = -0.01(1)$. The maximum shift/error value of a parameter in the last refinement cycle amounted to 0.01, minimum and maximum electron density in a final difference Fourier map were −1.633 and 0.833 e Å^{-3}, respectively. Final atomic parameters for the non-hydrogen atoms are listed in Table 2.

All drawings were done using the Siemens XP/PC program package.[13] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-406030, the names of the authors, and the journal citation.

Results and Discussion

From a concentrated aqueous solution of hexachloroplatinic acid and crown ether 18-crown-6, a substance with the composition $[H_{13}O_6][PtCl_5(H_4O_2)]\cdot 2(18\text{-cr-}6)$ (**1**) crystallizes as orange needles within few days. When the solution is left untouched for a longer time, hexachloroplatinic acid complexed by crown ether, $(H_3O)_2[PtCl_6]\cdot 2(18\text{-cr-}6)$ (**2a**), is gradually precipitated as red-orange crystals. Obviously, the hydrolysis of the hexachloroplatinic acid is reduced due to the increasing content of HCl in the solution. In accordance with it, **2a** is

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[10] The first figure refers to the *cis−anti−cis* and the second one to the *cis−syn−cis* isomer of DCH-18-cr-6 (2,5,8,15,18,21-hexaoxotricyclo-[20.4.0.0^{9,14}]hexacosane); cf. Buchanan, G. W.; Bourque, K.; Bovenkamp, J. W.; Rodrigue, A.; Bannard, R. A. B. *Tetrahedron Lett.* **1984**, *25*, 3963.

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[12] Sheldrick, G. M. *SHELXL-93, Program for the refinement of crystal structures*; University of Göttingen, Germany, 1993.

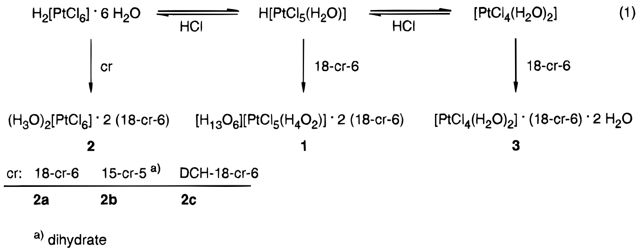
[13] *XP/PC, Molecular graphics program package for display and analysis of sterochemical data*; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for Non-Hydrogen Atoms[a]

atom	x	y	z	U_{eq}
Pt1	0.0689(1)	−0.0367(1)	0.9188(1)	0.024(1)
Cl1	0.0609(7)	0.1103(2)	0.9195(1)	0.058(1)
Cl2	−0.2220(4)	−0.0375(3)	0.9140(1)	0.047(1)
Cl3	0.1024(4)	−0.0394(2)	0.8541(1)	0.037(1)
Cl4	0.0623(6)	−0.1841(2)	0.9215(1)	0.050(1)
Cl5	0.3572(4)	−0.0359(3)	0.9256(1)	0.058(1)
O1	0.798(1)	0.5390(6)	0.9128(2)	0.040(2)
O2	0.510(1)	0.6420(6)	0.9385(3)	0.042(3)
O3	0.268(1)	0.5638(5)	0.9849(2)	0.039(2)
O4	0.238(1)	0.3863(6)	0.9678(2)	0.047(3)
O5	0.530(1)	0.2867(6)	0.9407(2)	0.041(3)
O6	0.775(1)	0.3637(6)	0.8913(2)	0.045(2)
O7	−0.523(1)	0.1543(6)	0.8179(2)	0.045(3)
O8	−0.798(1)	0.2465(6)	0.7796(2)	0.040(2)
O9	−0.756(1)	0.3307(6)	0.7073(3)	0.046(2)
O10	−0.499(1)	0.2439(6)	0.6658(2)	0.041(2)
O11	−0.217(1)	0.1551(6)	0.7040(3)	0.046(2)
O12	−0.275(1)	0.0652(6)	0.7732(3)	0.051(3)
O1w	0.052(1)	−0.0370(5)	0.9778(2)	0.038(2)
O2w	0.690(1)	0.4289(6)	0.9749(2)	0.043(2)
O3w	0.342(1)	0.4966(5)	0.9070(2)	0.042(2)
O4w	−0.500(1)	−0.0800(6)	0.6506(2)	0.051(3)
O5w	−0.666(1)	0.1429(5)	0.7191(2)	0.043(3)
O6w	−0.340(1)	0.2544(6)	0.7655(3)	0.047(3)
O7w	−0.461(1)	0.3924(5)	0.7356(2)	0.047(2)
O8wa	−0.630(3)	−0.014(2)	0.7127(6)	0.051(7)
O8wb	−0.515(3)	−0.005(2)	0.7131(8)	0.059(7)
C1	0.771(2)	0.6258(8)	0.9050(4)	0.047(4)
C2	0.682(2)	0.6664(9)	0.9385(4)	0.047(4)
C3	0.413(2)	0.6880(8)	0.9663(4)	0.051(4)
C4	0.248(2)	0.6483(9)	0.9719(4)	0.048(4)
C5	0.111(2)	0.5178(9)	0.9885(4)	0.052(4)
C6	0.151(2)	0.427(1)	0.9989(4)	0.051(4)
C7	0.279(2)	0.299(1)	0.9773(4)	0.061(5)
C8	0.368(2)	0.257(1)	0.9432(5)	0.063(5)
C9	0.622(2)	0.2438(9)	0.9100(4)	0.062(5)
C10	0.792(3)	0.2806(9)	0.9057(4)	0.061(5)
C11	0.936(2)	0.4109(9)	0.8922(4)	0.054(4)
C12	0.893(2)	0.5004(9)	0.8832(4)	0.046(4)
C13	−0.697(2)	0.1543(9)	0.8296(4)	0.046(4)
C14	−0.774(2)	0.2405(9)	0.8193(4)	0.046(4)
C15	−0.887(2)	0.3207(8)	0.7688(4)	0.047(4)
C16	−0.913(2)	0.3221(9)	0.7265(4)	0.051(4)
C17	−0.763(2)	0.3135(9)	0.6681(4)	0.051(4)
C18	−0.588(3)	0.3135(8)	0.6511(3)	0.055(4)
C19	−0.330(2)	0.245(1)	0.6534(5)	0.064(5)
C20	−0.243(2)	0.1645(9)	0.6640(4)	0.052(4)
C21	−0.129(2)	0.081(1)	0.7145(5)	0.066(5)
C22	−0.112(2)	0.076(1)	0.7567(5)	0.065(5)
C23	−0.270(2)	0.072(1)	0.8129(4)	0.060(5)
C24	−0.450(2)	0.0739(8)	0.8272(4)	0.055(4)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Scheme 1



formed exclusively when a little amount of HCl is added at the beginning. Aqueous solutions of **1** are not stable for a longer time: after few minutes a yellow precipitate—sometimes as fine yellow needles—of $[PtCl_4(H_2O)_2]\cdot(18\text{-cr-}6)\cdot 2H_2O$ (**3**) starts to separate. The reactions giving **1**−**3** are summarized in Scheme 1.

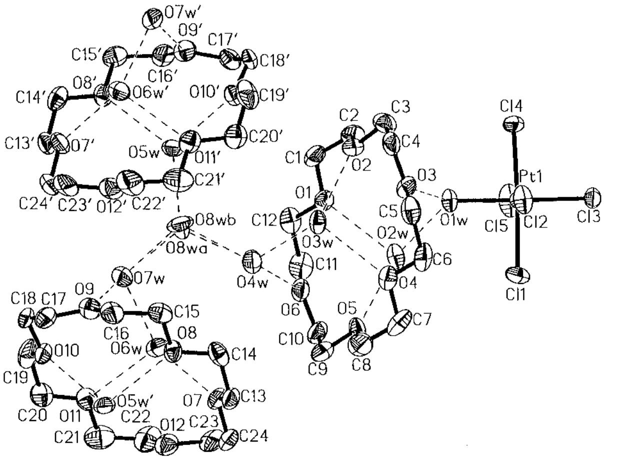


Figure 1. ORTEP plot and atom labeling scheme for $[H_{13}O_6][PtCl_5(H_4O_2)]\cdot 2(18\text{-cr-}6)$ (**1**). Displacement ellipsoids are drawn at the 50% probability level; H atoms are omitted. Broken lines represent hydrogen bonds. Primed atoms (′) are generated by a 2-fold screw axis from the corresponding nonprimed atoms.

Crown ether complexes of hexachloroplatinic acid of the general composition $(H_3O)_2[PtCl_6]\cdot 2cr$ (**2**), with cr = 15-cr-5 (**2b**), DCH-18-cr-6 (**2c**), can be obtained in the same way as described for the 18-cr-6 complex **2a**. Complexes **2** form orange, air-stable crystals; **2b** crystallizes as dihydrate.

The complexes **1**−**3** were characterized by microanalysis as well as by IR, Raman, and NMR spectroscopy. In accordance with the O_h point symmetry of $[PtCl_6]^{2-}$, the vibrational spectra of **2** are characterized by one very strong (IR) Pt−Cl stretching vibration (F_{1u}) at 321−330 cm^{-1} and two strong Raman active ν(Pt−Cl) at 310−314 (E_g) and 335−338 cm^{-1} (A_{1g}). The vibrational spectra of **3** point to a *cis* configuration. There are no characteristic differences between the chemical shifts $\delta(^1H)$ and $\delta(^{13}C)$ of the crown ethers in complexes **1**−**3** compared with the noncomplexed crown ethers. The platinum chemical shifts $\delta(^{195}Pt)$ of the hexachloroplatinate complex **2a** (4530 ppm) and of the pentachloroaquaplatinate complex **1** (5023 ppm) are in good agreement with the values of the corresponding platinum complexes in the absence of crown ethers (4529 and 5033 ppm, respectively).[14] The chemical shift $\delta(^{195}Pt)$ of **3** (5017 ppm) is at higher field compared with values given for acid aqueous solutions (pH = 1−3) of *cis*-$[PtCl_4(H_2O)_2]$ (5534 ppm) and *trans*-$[PtCl_4(H_2O)_2]$ (5655 ppm).[14]

The molecular structure and crystal packing of complex **1** are shown in Figures 1 and 2. Relevant bond lengths and angles are listed in Table 3. The O···O distances of hydrogen bonds are summarized in Table 4.

The coordination polyhedron around the platinum atom $[PtCl_5O]$ has C_{4v} symmetry in good approximation. The four equatorial Pt−Cl bonds vary only from 2.301(3) to 2.316(3) Å and have an average value of 2.310(7) Å (here, as well as in the following, the standard deviations given for mean values represent a scatter of the individual values from the mean). The $PtCl_4$ unit is planar within 0.039(2) Å (shift of the Pt atom toward Cl3). All angles at Pt between the *cis* standing ligands are in the small range of 87.4(3)−92.5(3)°. The distance between Pt and the axial Cl3 amounts to 2.273(3) Å and is significantly shorter than the bond lengths $Pt-Cl_{eq}$ due to the *trans* influence $H_2O < Cl^-$.[15]

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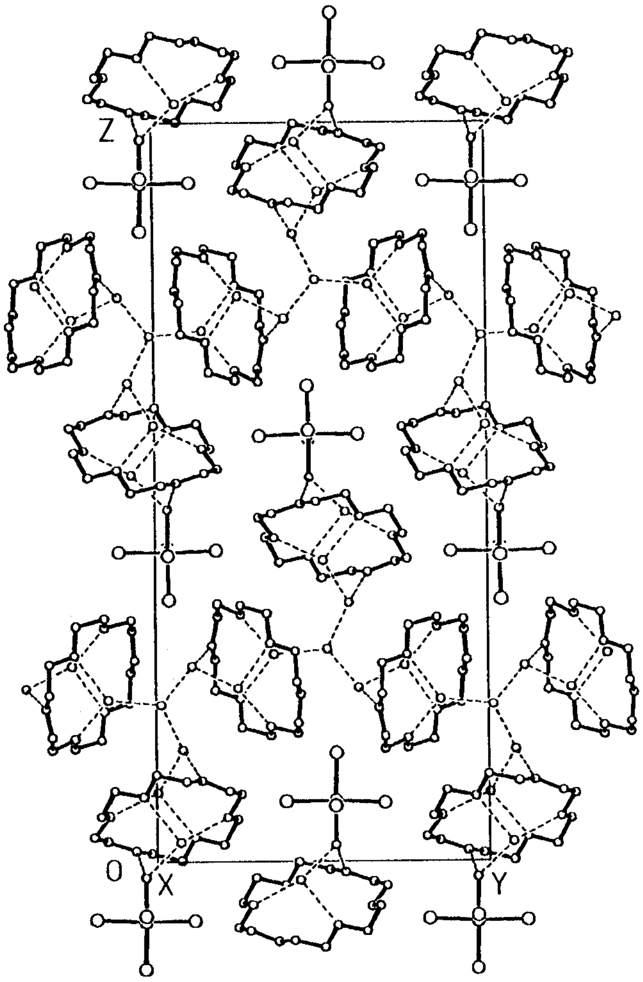

Figure 2. Crystal packing of $[H_{13}O_6][PtCl_5(H_4O_2)]\cdot 2(18\text{-cr-}6)$ (**1**). The projection is along the crystallographic *x* axis. H atoms are omitted. Broken lines represent hydrogen bonds.

Table 3. Selected Bond Lengths and Angles for the $[PtCl_5(H_4O_2)]^-$ Anion in **1**

	Bond Lengths (Å)		
Pt1−Cl1	2.306(3)	Pt1−Cl4	2.316(3)
Pt1−Cl2	2.315(3)	Pt1−Cl5	2.301(3)
Pt1−Cl3	2.273(2)	Pt1−O1w	2.060(6)
	Bond Angles (deg)		
Cl1−Pt1−Cl2	88.8(2)	Cl2−Pt1−O1w	90.5(3)
Cl1−Pt1−Cl3	91.9(1)	Cl3−Pt1−Cl4	91.4(1)
Cl1−Pt1−Cl4	175.9(1)	Cl3−Pt1−Cl5	89.2(1)
Cl1−Pt1−Cl5	91.2(2)	Cl3−Pt1−O1w	176.8(2)
Cl1−Pt1−O1w	89.5(3)	Cl4−Pt1−Cl5	91.3(2)
Cl2−Pt1−Cl3	92.5(1)	Cl4−Pt1−O1w	87.4(3)
Cl2−Pt1−Cl4	88.5(2)	Cl5−Pt1−O1w	87.8(3)
Cl2−Pt1−Cl5	178.3(1)		

Table 4. O···O Distances of ≤2.90 Å and $O_w\cdots O_w\cdots O_w$ Angles of Hydrogen Bridges in **1**[a]

O1w···O2w#2	2.61(1)		O1···O2w	2.90(1)
O3w···O4w#5	2.65(1)		O2···O3w	2.86(1)
O4w···O8w	2.61(3)	[2.48(3)]	O3···O1w#3	2.64(1)
O5w···O8w	2.49(3)	[2.62(3)]	O4···O3w	2.86(1)
O6w···O7w	2.59(1)		O5···O2w	2.83(1)
O7w···O8w#4	2.43(2)	[2.42(3)]	O6···O4w#1	2.78(1)
			O7···O6w	2.82(1)
O4w···O8w···O5w	120.8(10)	[120.9(10)]	O8···O5w	2.86(1)
O4w···O8w···O7w#6	105.0(10)	[109.8(10)]	O9···O7w	2.72(1)
O5w···O8w···O7w#6	124.3(10)	[119.6(11)]	O10···O5w	2.78(1)
O3w#5···O4w···O8w	129.4(7)	[118.3(7)]	O11···O6w	2.82(1)
O6w···O7w···O8w#4	95.5(7)	[106.7(7)]		

[a] Operators for generating equivalent atoms: (#1) $-x, y + {}^1/_2, -z + {}^3/_2$; (#2) $x - {}^1/_2, -y + {}^1/_2, -z + 2$; (#3) $x + {}^1/_2, -y + {}^1/_2, -z + 2$; (#4) $-x$ -1, $y + {}^1/_2, -z + {}^3/_2$; (#5) $-x, y + {}^1/_2, -z + {}^3/_2$; (#6) $-x$-1, $y - {}^1/_2, -z + {}^3/_2$.

The water molecule with the oxygen atom O1w is directly coordinated to the Pt atom. Besides, it is connected with another water molecule by a relatively short hydrogen bond [O1w···O2w = 2.61(1) Å]. Thus, the complex anion of **1** should be formulated pentachloro(diaqua)platinate(VI) $[PtCl_5(H_4O_2)]^-$. Its counterion is a hydrated proton $[H_{13}O_6]^+$. Because of the heavy platinum and the less than high quality of the crystal used in X-ray analysis, the positions of the H atoms in the structure of **1** could not be experimentally located. Therefore, the following discussion concerning the hydrogen bonds is based on the O···O distances. But their inspection (cf. Table 4) gives a plausible structural model of the hydrogen-bonding network in **1**. As a further complication, the structure shows disorder of the position of atom O8w (and the corresponding water molecule, of course). This oxygen atom can occupy two alternative positions which are referred to as a and b with a site occupation of 0.5 to 0.5. Data concerning position b are given in brackets in the following.

The geometric arrangement of the $[H_{13}O_6]^+$ ion is that of a five-membered chain of water molecules and the sixth water molecule laterally bonded to O8w. The water molecules are connected by $O_w{-}H\cdots O_w$ hydrogen bonds. The $O_w\cdots O_w$ distances are in the range of 2.43(2) to 2.65(1) Å [2.42(3) to 2.65(1) Å] with an average of 2.55(9) Å [2.55(10) Å]. As mentioned above, the excess proton of the $[H_{13}O_6]^+$ ion could not be located. But starting from the fact that the water molecules must donate the H bonds to the crown ether O atoms (see below), the successive assignment of the available hydrogens to the water molecules with regard to their function as donors or acceptors, respectively, leads to the compound $[H_3O(H_4O_2)_2(H_2O)]^+$ and to the model of a dihydrated triaquaoxonium ion with O8 as the formal fixing point for the excess proton and a primary (three water molecules with O4w, O5w, O7w) and a secondary hydration shell (two water molecules with O3w and O6w). This model is supported by the observed $O_w\cdots O_w$ distances: The average value of the distances of the water molecules of the secondary shell to those of the primary shell (2.62(4) Å) are a little bit longer than the mean value of the distances between O8w and the three water molecules of the primary shell being 2.51(9) Å [2.51(10) Å]. This interpretation agrees with the model proposed by Eigen[16] for the hydration of the proton in aqueous solution and ice as well as with the results of theoretical studies of the system $[H(H_2O)_n]^+$ for $n = 2{-}10$[7a] and especially $n = 6$.[7c]

The average of the strongly differing O···O···O angles within the $H_9O_4^+$ subunit (cf. Table 4) is 117(10)° [118(6)°]), indicating some flattening of the pyramidal Eigen-type structure. In comparison with two crystal structures with discrete $H_9O_4^+$ ions, in $[H_9O_4][Te_3Br_{13}]$,[6f] the very similar value of 117.1(2)° was found, but in $[H_9O_4][CB_{11}H_6Br_6]$[17] is was 108(9)°. The wide range of ∼15° in the individual O···O···O angles in **1** can be explained by environmental effects such as H-bonding to the secondary shell and packing forces.

The particular stability of the Eigen-type cation $H_9O_4^+$ is demonstrated by its presence in a series of crystal structures.[6] But structurally characterized higher hydrates $[H(H_2O)_n]^+$ with $n \geq 5$ are very rare. In the crystal structure of $[Fe(C_5H_5)_2]_4[H_{11}O_5]_2[TcCl_6]_3$ [8] the proton was not located; the $O_w\cdots O_w$ distances are in the range 2.48(1)−2.58(1) Å. In $[(C_9H_{18})_3(NH)_2Cl][H_{13}O_6]Cl_2$ [9] the $[H_{13}O_6]^+$ unit has another

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structure than in the platinate complex **1**. It shows crystallographic C_{2h} symmetry and each of the four equivalent terminal H atoms of the central $[H_5O_2]^+$ entity donates an H bond to a water molecule. The central $O_w\cdots O_w$ distance is rather short (2.39(2) Å) whereas the other ones are normal in length (2.52(1) Å).

The just described $[H_5O_2(H_2O)_4]^+$ ion is an isomer of the $[H_3O(H_4O_2)_2(H_2O)]^+$ ion in **1**. Density functional calculations[7c] have shown (for the gas phase) that these two isomers are more stable than other ones and very similar in energy. The difference was calculated to only 1.14 kcal/mol in favor on **1**, and the $O_w\cdots O_w$ distances should be in the range of 2.57−2.77 Å. Until now, each of the two isomers is represented by only one example. In both cases, all terminal H atoms of the $[H_{13}O_6]^+$ cation are involved in hydrogen bonds to acceptor atoms of the other components of the crystalline compounds (O_{cr} atoms in **1** and Cl in the other case). Thus, the structure of $[H_{13}O_6]^+$ seems to be enforced by its packing and environment within the crystal. In **1**, the $[H_{13}O_6]^+$ cation is surrounded by three crown ether molecules. Its eight terminal H atoms are involved in hydrogen bonds to oxygen atoms of the crown ethers. On the other hand, except for O12, all oxygen atoms of the macrocycles are involved in the coordination of water molecules via $O_w-H\cdots O_{cr}$ bridges. The $O_w\cdots O_{cr}$ distances are in the range 2.72(1)−2.90(1) Å and on average distinctly longer than the $O_w\cdots O_w$ distances within the $[H_{13}O_6]^+$ cluster and the H_4O_2 unit (2.81(7) vs 2.56(8) Å).

There are two crystallographically independent, but in relation to their conformation, very similar 18-crown-6 molecules in the crystal structure of **1**. Both have D_{3d} symmetry in rough approximation. The torsion angles (absolute values) are in the ranges 166−180° for C−O−C−C and 60−75° for O−C−C−O; the conformation of the macrocycles is characterized by an alternating sequence of the partial conformation of the OCCO subunits *ap*, −*sc*, *ap* and *ap*, *sc*, *ap*. This whole conformation is quite different from that found for the unhydrated solid 18-crown-6.[18] But it is in good agreement with that observed for the hydrated crown ether in general and for the binary hydrates 18-crown-6·nH$_2$O (n = 4, 6, 8, 12)[19] in particular. In the macrocycles of **1**, the intramolecular distances $O_{cr}\cdots O_{cr}$ bridged by a water molecule (O1···O5, O2···O4, O7···O11, O8···O10) are distinctly shorter than those between the other second-nearest oxygen atoms around the ring (range 4.60(1)−4.67(1) Å and a mean value of 4.64(3) vs 5.04(1)−5.12(1) and 5.05(6) Å, respectively). Almost exactly, the same values were observed in the binary hydrate 18-crown-6·6H$_2$O.[19a]

The $[PtCl_5(H_4O_2)]^-$ anion is connected with the crown ether C1··· via three hydrogen bonds donated by the H_4O_2 unit (acceptors O1, O3, O5). There are one shorter (2.64(1) Å) and two longer $O_w\cdots O_{cr}$ distances (2.83(1) and 2.90(1) Å); the former is from O1w, which is coordinated directly to the platinum atom. The same crown ether molecule is connected on its opposite side with the $[H_{13}O_6]^+$ moiety via three hydrogen bonds (acceptors O2, O4, O6). Moreover, the cation for its part is attached to two further crown ether molecules, namely, C13··· (via O6w and O7w) and C13′··· (via O5w). Thus, the crystal is threaded by chains built up of 18-cr-6/$[H_{13}O_6]^+$ units, which are related by the space group 2-fold screw axes parallel *b* and at which the 18-cr-6/$[PtCl_5(H_4O_2)]^-$ moieties are fixed as lateral branches (see Figure 2). It can be seen from Figure 2 that there are in the crystal of **1** cations $[H_{13}O_6]^+$ and anions $[PtCl_5(H_4O_2)]^-$ separated by crown ether molecules.

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Supporting Information Available: Complete lists of bond lengths and bond angles (Table S1), anisotropic displacement parameters (Table S2), coordinates and isotropic displacement parameters of H atoms (Table S3), and crystal data and structure refinement parameters (Table S4) (4 pages). Ordering information is given on any current masthead page.

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