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# Hydrogen Activation by Benzene-Ruthenium Complexes in Aqueous Solution: Synthesis, Molecular Structure, and Intercalation of the Cluster Cation $[(C_6H_6)_4Ru_4H_4]^{2+}$

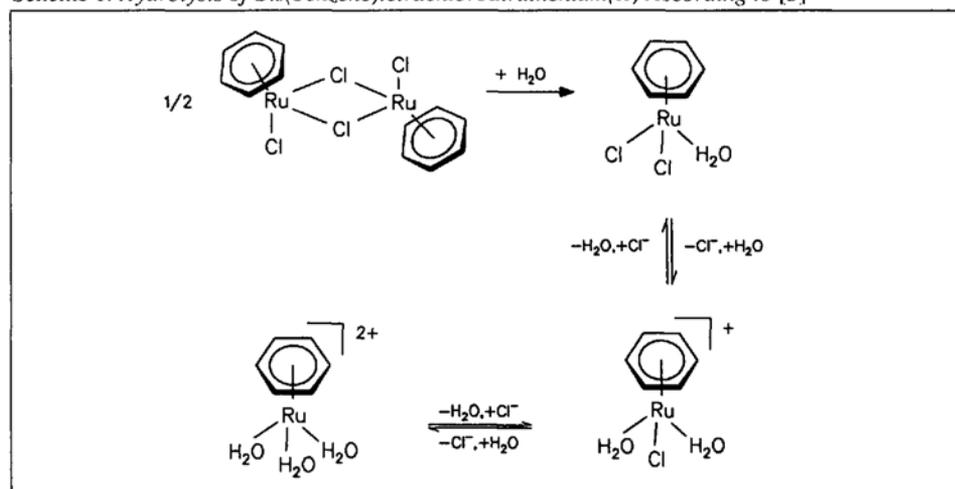
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**Abstract.** The hydrogenation of the aqua complex  $[(C_6H_6)Ru(H_2O)_3]^{2+}$ , prepared *in situ* by hydrolysis of  $(C_6H_6)_2Ru_2Cl_4$  in water, was found to lead to the tetranuclear cluster dication  $[(C_6H_6)_4Ru_4H_4]^{2+}$  (**1**) which crystallizes as the dichloride from the aqueous solution. In the presence of acetate ions, however, the reaction yields the dinuclear cations  $[(C_6H_6)_2Ru_2H(OOCCH_3)X]^+$  ( $X=OH$ : **2**,  $X=Cl$ : **3**) which crystallize as the hexafluorophosphate salts. The X-ray crystal-structure analysis of  $[(C_6H_6)_4Ru_4H_4]Cl_2$  reveals the cluster dication **1** to consist of a tetrahedral ruthenium framework; the four hydrido ligands are presumably coordinated to three faces and to one edge of the  $Ru_4$  tetrahedron. The cationic complexes **1** and **2** have been found to intercalate in sodium hectorite.

At present much interest is focussed on the chemistry of transition-metal complexes containing both organic and water ligands [1]. A well-characterized representative of such a complex is the dication  $[(C_6H_6)Ru(H_2O)_3]^{2+}$ , accessible from bis(benzene)tetrachlorodiruthenium(II) [2]. Little is known about the reactivity of this triaqua(benzene)ruthenium dication

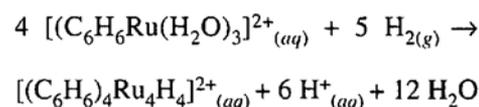
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Scheme 1. Hydrolysis of Bis(benzene)tetrachlorodiruthenium(II) According to [5]



[3][4]. Here we report the reaction of  $[(C_6H_6)Ru(H_2O)_3]^{2+}$  with molecular hydrogen in aqueous solution.

The dication  $[(C_6H_6)Ru(H_2O)_3]^{2+}$  is formed in an equilibrium mixture with  $[(C_6H_6)Ru(H_2O)_2Cl]^+$  and  $(C_6H_6)Ru(H_2O)Cl_2$ , by hydrolysis of the neutral complex  $(C_6H_6)_2Ru_2Cl_4$  in  $H_2O$  (Scheme 1) [5]. Upon pressurizing of this aqueous hydrolysis mixture with hydrogen (60 atm) at  $55^\circ$ , black-violet crystals of  $[(C_6H_6)_4Ru_4H_4]Cl_2$  (cation **1**) were obtained. In this reaction, molecular hydrogen is heterolytically cleaved without the presence of any auxiliary base. Therefore, the pH of the reaction mixture decreases to values of between 1 and 2 during the hydrogenation. The dication **1** is stable under these conditions, in contrast to the isoelectronic rhodium species  $[(C_5Me_5)_4Rh_4H_4]^{2+}$ , reported by Maitlis and coworkers, which decomposes quickly in an acid solution [6].



In the  $^1H$ -NMR spectrum, **1** gives rise to a signal for the benzene ligand and a resonance for the hydride ligands; the IR spectrum displays only the characteristic absorptions of the benzene ligand (Table).

The X-ray crystal-structure analysis of a single crystal of  $[(C_6H_6)_4Ru_4H_4]Cl_2$

Table. Characteristic IR and  $^1H$ -NMR Data of the Cationic Complexes **1–3**. IR: KBr pellet,  $cm^{-1}$ ;  $^1H$ -NMR:  $(D_4)$ methanol (**1**),  $(D_6)$ acetone (**2, 3**), ppm.

Cation	$\nu(OH)$	$\nu(CH)$	$\nu(CO)$	$\nu(CC_{ar})$	$\delta C_6H_6$	$\delta CH_3$	$\delta RuH$
<b>1</b>		3057s		1435vs	6.12		-14.91
<b>2</b>	3536w	3076vw	1542s, 1438s		6.00	1.67	-7.14
<b>3</b>		3091w	1543s, 1441s	1423s	6.26	1.73	-6.19

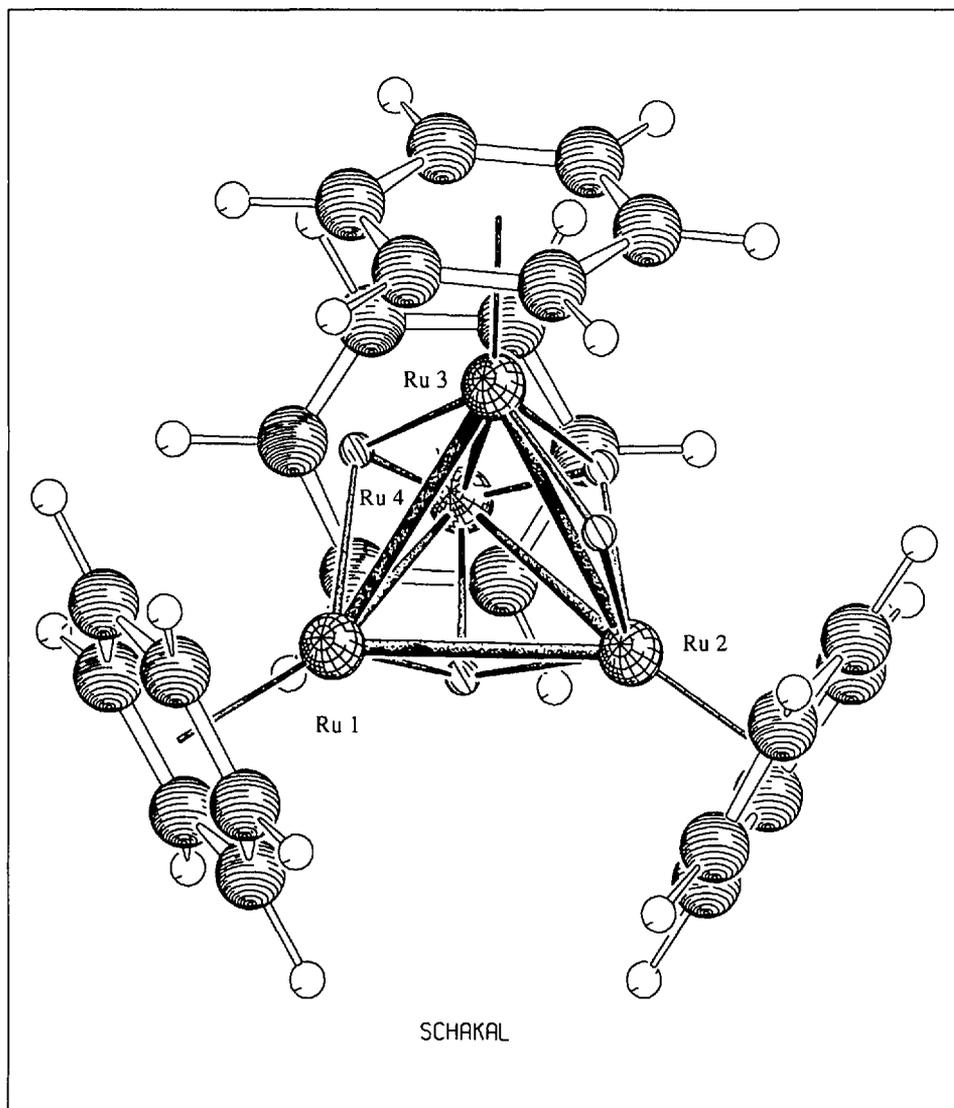
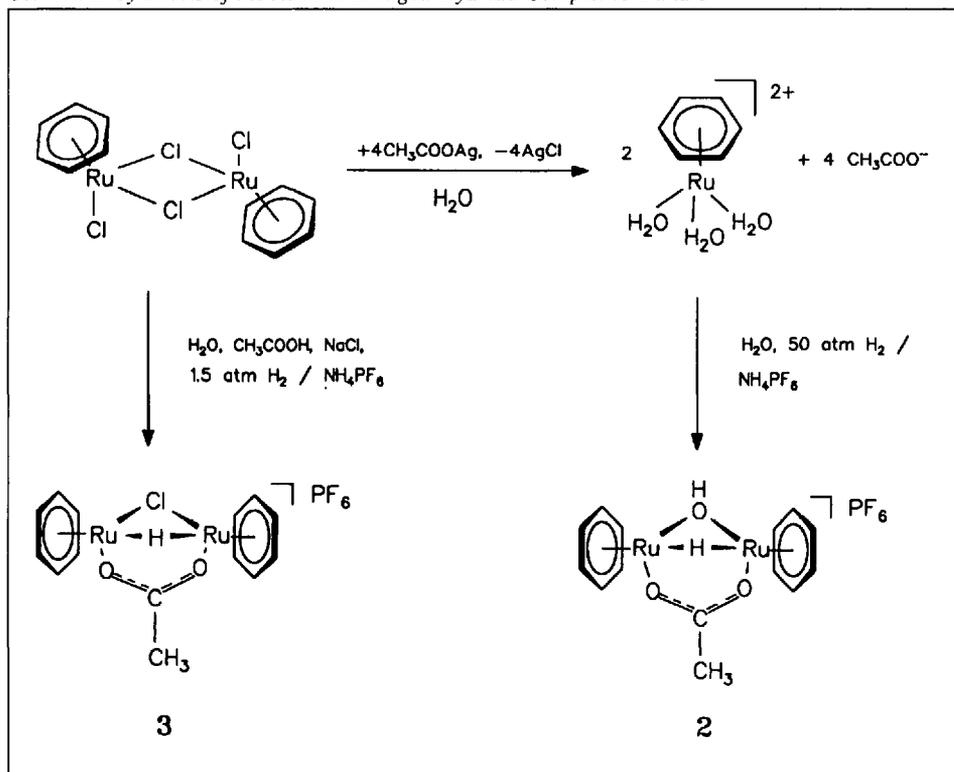


Figure. SCHAKAL plot [8] of the cluster dication  $[(C_6H_4)_4Ru_4H_4]^{2+}$  (**1**). The counterions and crystal water are omitted. Selected bond lengths [Å]: Ru(1)–Ru(2) 2.792(1), Ru(1)–Ru(3) 2.754(1), Ru(1)–Ru(4) 2.813(1), Ru(2)–Ru(3) 2.815(1), Ru(2)–Ru(4) 2.800(1), Ru(3)–Ru(4) 2.747(1).

shows the dication **1** to consist of a tetranuclear ruthenium framework which coordinates four benzene and four hydrido ligands (Fig.). The four Ru-atoms of the metal skeleton define a slightly distorted tetrahedron; two of the six Ru–Ru distances (mean 2.75 Å) are significantly shorter than the other four (mean 2.80 Å). The distortion of the  $Ru_4$  tetrahedron finds its counterpart in the arrangement of the four hydride ligands: The positions of the four H-atoms suggest that three of them act as  $\mu_3$ -capping ligands, while the fourth seems to represent a  $\mu_2$ -bridging ligand. All four hydride ligands become equivalent in solution as reflected in a single hydride resonance in the  $^1H$ -NMR spectrum. Contrary to the hydride ligands, the four benzene ligands are equivalent also in the solid state: They are all  $\eta^6$ -bound, the average Ru–C distance being 2.19(2) Å, slightly longer than in  $[(C_6H_6)Ru(H_2O)_3]SO_4$  (2.14(1) Å) [2]. A similar structure, containing a slightly distorted  $Rh_4$  tetrahedron, has been observed for the cluster cation already mentioned,  $[(C_5Me_5)_4Rh_4H_4]^{2+}$  crystallized as the tetrafluoroborate [6]; the structure of the analogous ruthenium complex  $[(p\text{-Me}_2\text{CH-C}_6\text{H}_4\text{-Me})_4Ru_4H_4]^{2+}$  [7] is unknown.

In order to eliminate the chloro species  $[(C_6H_6)Ru(H_2O)_2Cl]^+$  and  $(C_6H_6)Ru(H_2O)Cl_2$  from the hydrolysis mixture of  $(C_6H_6)_2Ru_2Cl_4$ , the hydrolysis can be carried out in the presence of silver acetate which causes the precipitation of silver chloride, giving exclusively the triaqua cation  $[(C_6H_6)Ru(H_2O)_3]^{2+}$  (Scheme 2). Hydrogenation of this solution, however, does not lead to the tetranuclear cluster dication **1**, with the acetate ions present the acetato-bridged dinuclear cation  $[(C_6H_6)_2Ru_2H(OOCCH_3)OH]^+$  (**2**) is formed. Without precipitation of the chloride by silver acetate, but in the presence of acetic acid, the chloro analogue  $[(C_6H_6)_2Ru_2H(OOCCH_3)Cl]^+$  (**3**) is obtained. Both cations are precipitated from the aqueous solution as the hexafluorophosphate salts.

Scheme 2. Synthesis of the Acetato-Bridged Hydrido Complexes **2** and **3**



The solvent  $H_2O$  plays a crucial role in the hydrogenation of  $(C_6H_6)_2Ru_2Cl_4$ : The formation of **2** and **3** (just as of **1**) obviously involves the intermediacy of aqua complexes. Accordingly, the reaction of  $(C_6H_6)_2Ru_2Cl_4$  with  $H_2$  in  $CH_2Cl_2$  solution is reported to give the neutral dinuclear complex  $(C_6H_6)_2Ru_2Cl_3H$  [9].

Both cationic complexes **2** and **3** are composed of two  $(C_6H_6)Ru$  moieties held together by two three-electron donor bridges ( $CH_3COO$  and  $OH$ ) and a one-electron bridge ( $H$ ). The structure should be similar to the one reported for the *p*-cymene osmium analogue  $[(p\text{-Me}_2\text{CH-C}_6\text{H}_4\text{-Me})_2Os_2H(OOCH)OH]^+$  [10].

Analogous ruthenium derivatives containing *p*-cymene, mesitylene, durene, and hexamethylbenzene as aromatic ligands are known for the chloro-bridged cation; the benzene representative **3**, however, was not accessible by the synthetic route reported [9].

The cations **1** and **2** react with sodium hectorite in H<sub>2</sub>O or in acetone, respectively, to give the supported materials **1a** and **2a** (Scheme 3). The ion-exchange reaction is visualized by the decolourization of the aqueous or acetonic solutions of **1** or **2**, respectively. The clay minerals **1a** and **2a** thus obtained display in the IR spectrum the characteristic absorptions of **1** and **2**, slightly shifted to higher wavenumbers. The enlargement of the interlayer spacing by the bulky cations **1** and **2** is reflected in the *d*<sub>001</sub> peaks of the XRD spectra: For **1a**, *d*<sub>001</sub> was observed at 18.5 Å, for **2a** at 15.5 Å, as compared to unmodified sodium hectorite (12.8 Å). Work to test these supported materials as heterogeneous catalysts is in progress.

## Experimental

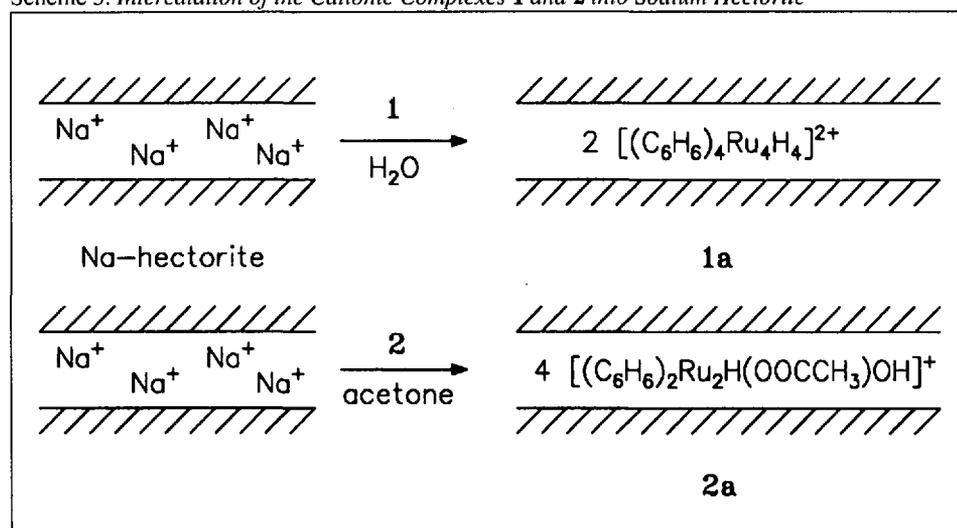
All syntheses were carried out in N<sub>2</sub>-saturated, bidistilled H<sub>2</sub>O. The starting complex (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Ru<sub>2</sub>Cl<sub>4</sub> was prepared according to [11]. CH<sub>3</sub>COOAg was commercially available (*Fluka*). The NMR spectra were recorded on a *Varian Gemini 200 BB*, IR spectra were run on a *Perkin Elmer FT-IR 1720X* spectrometer.

**Synthesis of 1.** A suspension of 150 mg (0.3 mmol) of (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Ru<sub>2</sub>Cl<sub>4</sub> in 20 ml of H<sub>2</sub>O was hydrogenated in a stainless-steel autoclave at 55° and at a pressure of 60 atm. After 14 h the autoclave was cooled, the pressure released, and the violet soln. filtered under N<sub>2</sub>. Evaporation of most of the H<sub>2</sub>O at reduced pressure, followed by crystallization at 2° for 1 d, gave **1** as dark-violet crystals. [(C<sub>6</sub>H<sub>6</sub>)<sub>4</sub>Ru<sub>4</sub>H<sub>4</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O, yield: 81 mg (65%). Anal. calc. for C<sub>24</sub>H<sub>32</sub>Cl<sub>2</sub>O<sub>2</sub>Ru<sub>4</sub>: C 34.83, H 3.90; found: C 34.76, H 3.94.

**Synthesis of 2.** A suspension of 150 mg (0.3 mmol) of (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Ru<sub>2</sub>Cl<sub>4</sub> and 201 mg (1.2 mmol) of silver acetate in 18 ml of H<sub>2</sub>O was stirred for 2 h. After filtration of the precipitated AgCl, the soln. was transferred into a stainless-steel autoclave and hydrogenated at r.t. at 50 atm. After 9 h the pressure was released and the soln. filtrated under N<sub>2</sub>. Precipitation with 150 mg NH<sub>4</sub>PF<sub>6</sub> in 2 ml of H<sub>2</sub>O gave **2** in anal. purity. [(C<sub>6</sub>H<sub>6</sub>)Ru(μ-H)(μ-OH)(μ-OOCCH<sub>3</sub>)Ru(C<sub>6</sub>H<sub>6</sub>)]PF<sub>6</sub>, orange crystals, yield: 110 mg (65%). Anal. calc. for C<sub>14</sub>H<sub>17</sub>F<sub>6</sub>O<sub>3</sub>PRu<sub>2</sub>: C 28.97, H 2.95; found: C 28.96, H 2.83.

**Synthesis of 3.** A mixture of 150 mg (0.3 mmol) of (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Ru<sub>2</sub>Cl<sub>4</sub>, 1.5 ml of AcOH and 350 mg of NaCl in 20 ml of H<sub>2</sub>O was placed in a pressure *Schlenk* tube and stirred at a H<sub>2</sub> pressure of 1.5 atm at r.t. After 48 h the soln. was filtered and **3** precipitated with 150 mg of NH<sub>4</sub>PF<sub>6</sub> in 2 ml of H<sub>2</sub>O. Washing with 4 ml of ice-cold H<sub>2</sub>O gave complex **3** in anal. purity. [(C<sub>6</sub>H<sub>6</sub>)Ru(μ-H)(μ-Cl)(μ-OOCCH<sub>3</sub>)Ru(C<sub>6</sub>H<sub>6</sub>)]PF<sub>6</sub>, red crystals,

Scheme 3. Intercalation of the Cationic Complexes **1** and **2** into Sodium Hectorite



yield: 80 mg (45%). Anal. calc. for C<sub>14</sub>H<sub>16</sub>F<sub>6</sub>ClO<sub>2</sub>PRu<sub>2</sub>: C 28.08, H 2.69; found: C 28.21, H 2.82.

**Intercalation of 1 and 2 in Hectorite.** 0.3 g of Na hectorite were treated with 1.8 · 10<sup>-4</sup> mol of the complexes in H<sub>2</sub>O (**1**) or acetone (**2**) for 48 h at r.t. The modified hectorites were filtered off under N<sub>2</sub> and dried under vacuum.

**X-Ray Crystal Analysis of 1.** C<sub>24</sub>H<sub>28</sub>Ru<sub>4</sub>·Cl<sub>2</sub>·5H<sub>2</sub>O, *M*<sub>r</sub> = 881.8, crystal dimensions 0.76 × 0.76 × 0.65 mm, monoclinic, P2<sub>1</sub>/n, *a* = 9.463(2), *b* = 17.675(3), *c* = 17.501(2) Å, *V* = 2906.2 Å<sup>3</sup>, *Z* = 4, *D*<sub>x</sub> = 2.015 g·cm<sup>-3</sup>, λ = 0.71073 Å, μ = 2.20 mm<sup>-1</sup>, *F*(000) = 5122 unique reflections, 4355 observed [*I* > 3σ(*I*)], *R* = 0.042, unit weights, *S* = 0.53. Maximum shift/sigma 0.014, residual density (e/Å<sup>3</sup>) max. 1.31 near atom Cl(2), min -1.19.

Intensity data were collected at r.t. on a *Stoe AED2* 4-circle diffractometer using MoK<sub>α</sub> graphite monochromated radiation using the ω/θ scan mode. It was difficult to find a suitable crystal for X-ray analysis. The crystal used was rather large because it was found that on cutting the crystals they tended to disintegrate. The crystal used was covered with a thin layer of epoxy resin to protect it from the atmosphere. Three standards were measured every h; a 3% intensity variation was corrected for. No correction for absorption was made. The structure was solved by direct methods using the programme SHELXS-86 [12]. All further calculations were carried out using the NRCVAX [13] system. Neutral complex-atom scattering factors in NRCVAX are from [14]. The hydrides are located from difference maps. They were initially refined and then held fixed (*U*<sub>iso</sub> = 0.075 Å<sup>2</sup>). H-atoms for waters O(W)1-3 were located from difference maps but held fixed (*U*<sub>iso</sub> = 0.12 Å<sup>2</sup>). The remaining H atoms were included in calculated positions and their positions renewed after every third cycle of refinement (*U*<sub>iso</sub> = *U*<sub>eq</sub>(C) + 0.01 Å<sup>2</sup>). Anion Cl(2) undergoes considerable thermal motion. A region of electron density ca. 2.8 Å from atom Cl(2), with three discrete peaks, was attributed to three disordered H<sub>2</sub>O molecules, O(W)4-6. Their H-atoms could not be located. The non-H-atoms were refined anisotropically using full-matrix least-squares and unit weights. Atomic parameters and complete tables of bond distances and angles have been deposited with the *Cambridge*

*Crystallographic Data Centre*, Union Road, Cambridge CB2 1EZ, U.K.

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