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Preparation and X-ray Crystal Structure Analysis of the Hydroxo-Bridged, Dinuclear (π-Arene)ruthenium(II) Cation in $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$

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It was recently reported that reaction of $[\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}_2]$ (**1**) with aqueous sodium carbonate in a 1:2 molar ratio yields the tetrameric cation $[\{Ru(\eta^6\text{-}C_6H_6)(\mu_3\text{-}OH)\}_4]^{4+}$ (**2**), a complex consisting of a cubane-like core arrangement of alternating ruthenium and oxygen atoms.[1] In contrast, treatment of **1** with an excess of sodium carbonate or hydroxide yields a tetranuclear cation, $[Ru_4(\eta^6\text{-}C_6H_6)_4(\mu\text{-}OH)_4(\mu_4\text{-}O)]^{2+}$ (**3**), best described structurally as two binuclear $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_2]^+$ units sharing a tetrahedrally coordinated oxide ion.[2]

Originally, **3** was formulated by Stephenson and co-workers as a trihydroxo-bridged dinuclear ruthenium compound, $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]^+$ (**4**).[3] However, it has recently been suggested that only complexes containing *substituted* arenes, such as $[Ru_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ (**5**),[2] itself prepared from excess hydroxide, form trihydroxo-bridged complexes.

The marked structural differences observed between **2**, **3**, and **5** have been attributed to extreme steric crowding, which would result for tetrameric complexes of this type containing substituted arene rings; that is, triple-hydroxo-bridged and alkoxo-bridged dimeric species[4] are in fact the observed products for the substituted arene systems, while compounds such as **2** and **3** appear to be favored when the less hindered benzene-containing dimer is treated with base.

However, we now wish to report that the trihydroxo-bridged dinuclear ruthenium cation $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]^+$ (**4**), containing unsubstituted rings, has been prepared by a novel high-yield route and characterized by X-ray crystallography.

Results and Discussion

Treatment of the triple-phenoxo-bridged $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OC_6H_5)_3]^+$ (**6**) cation,[3b] prepared from **1** and $TlOC_6H_5$ (1:3 molar ratio), with water at room temperature gives $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]^+$ (**4**) in essentially quantitative yield. Recrystallization from CH_3CN/H_2O using vapor diffusion yielded bright orange crystals of $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ (**7**).

The X-ray analysis of this complex confirms the presence of both π-bonded benzene groups and hydroxo bridges (Figure 1). While crystallographic symmetry is not required for the cation, the dimer closely approximates D_{3h} symmetry in view of the small torsion angle of the benzene rings of 8.8 (4)°. The average bond angle for the bridging hydroxo groups in this cation is 91.5 (1)°, very similar to that found for the binuclear $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_2]^+$ units in tetranuclear **3**[2] but quite different from the 102.6 (2)° angle in the tetrameric cation $[\{Ru(\eta^6\text{-}C_6H_6)(\mu_3\text{-}OH)\}_4]^{4+}$ (**2**).[1] This difference in bridging angles is due to a longer Ru-Ru average distance of 3.292 (8) Å reported for **2** compared to 2.9812 (7) Å found in $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]^+$. The structural features of **7** resemble those obtained for the substituted arene complex $[Ru_2(\eta^6\text{-}1,3,5\text{-}C_6H_3)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ (**5**), where an average Ru-O-Ru angle of 90.9 (4)° and a Ru-Ru distance of 2.989 (3) Å are observed.[2] In the present study, an extensive hydrogen-bonded network links the μ-OH groups to the chloride ions and lattice water molecules. Within the unit cell, the chloride ions and water molecules cohabit planes and alternate with the cation planes.

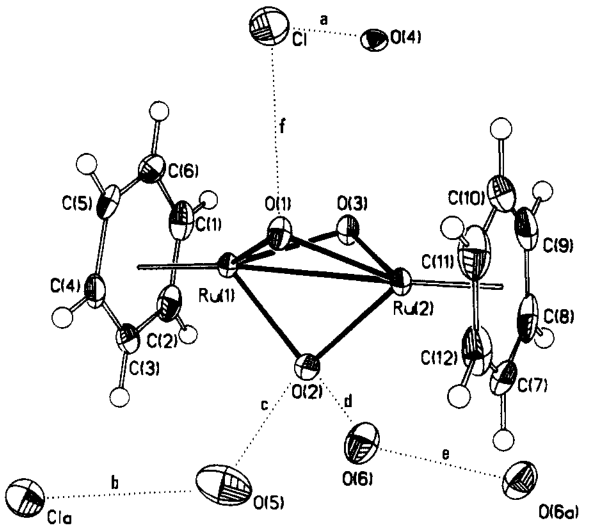

Figure 1. Structure and labeling scheme for $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ (**7**), showing H-bonded interactions between the μ-OH groups, the chloride ion, and the water molecules (O(4), O(5), and O(6)). Some of the shortest interactions are as follows: *a*, 3.09 Å; *b*, 2.97 Å; *c*, 2.80 Å; *d*, 2.79 Å; *e*, 2.75 Å; *f*, 3.09 Å.

The sequence of steps used for the synthesis of the title compound is shown in Scheme I. Although the solubility of the starting material, $[\{\eta^6\text{-}C_6H_6)RuCl_2\}_2]$, is very low in acetonitrile, molecular weight and conductivity measurements have been performed on this chlorobridged dimer and indicate that it is monomeric and a nonelectrolyte.[5] We find that the highest yield of the triple-phenoxo-bridged cation (**6**) occurs when a molar reactant stoichiometry of 1:3 ($[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]:TlOC_6H_5$) is used. Efforts to investigate the reaction chemistry of the $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]^+$ cation have been hampered by its poor solubility in nonaqueous solvents. Metathesis of **7** with $AgPF_6$ produced $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]PF_6$ (**8**); surprisingly, the solubility of the PF_6^- salt is very similar to that of **7**. It is soluble in water but virtually insoluble in common nonaqueous media.

Scheme I. Synthesis of the Dinuclear Ruthenium Cation $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]^{+\,a}$

$$\underset{\mathbf{1}}{[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]} \xrightarrow{\text{i}} \underset{\mathbf{6}}{[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OC_6H_5)_3]^+} \xrightarrow{\text{ii}} \underset{\mathbf{4}}{[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]^+}$$

[a] Key: i, $TlOC_6H_5$ (1:3 molar ratio, in CH_3CN); ii, H_2O (large excess)

As mentioned above, tetrameric complexes containing unsubstituted benzene rings (**2** and **3**) have been prepared in basic medium; quite possibly, the previous inability to isolate $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]^+$ is due to nucleation of the desired dimer resulting in tetramer formation caused by the basic solution conditions employed in its preparation. The method reported herein avoids this possible difficulty and relies on the ready conversion of the phenoxide cation **6** to the bridging hydroxo dimer **4**. While mechanistic studies have not been undertaken, it seems

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Table I. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³)

	x	*y*	*z*	U^a
Ru(1)	2253.2 (2)	5685.8 (2)	5537.4 (2)	20.6 (1)
Ru(2)	2252.3 (2)	6598.5 (3)	7030.4 (2)	21.9 (1)
Cl	4867 (1)	7159 (2)	5860 (1)	54.0 (6)
Cl′	4696 (13)	4993 (18)	6658 (11)	112 (8)
O(1)	2716 (2)	7120 (2)	6029 (2)	28 (1)
O(2)	1220 (2)	6139 (3)	6281 (1)	30 (1)
O(3)	2706 (2)	5156 (3)	6542 (1)	27 (1)
O(4)	4881 (4)	4937 (4)	6679 (3)	25 (1)
O(5)	148 (3)	7874 (3)	5726 (3)	71 (2)
O(6)	157 (3)	4361 (3)	6767 (2)	60 (2)
C(1)	2649 (4)	4185 (4)	4995 (3)	41 (2)
C(2)	1668 (4)	4319 (4)	4930 (2)	40 (2)
C(3)	1318 (4)	5305 (4)	4660 (2)	41 (2)
C(4)	1913 (4)	6180 (4)	4443 (2)	35 (1)
C(5)	2896 (4)	6034 (4)	4510 (2)	34 (1)
C(6)	3267 (4)	5038 (4)	4776 (2)	38 (2)
C(7)	1333 (4)	6991 (6)	7909 (6)	54 (2)
C(8)	1906 (5)	6116 (5)	8121 (2)	49 (2)
C(9)	2882 (4)	6244 (5)	8056 (2)	45 (2)
C(10)	3268 (4)	7205 (5)	7792 (2)	47 (2)
C(11)	2685 (5)	8062 (5)	7579 (3)	55 (2)
C(12)	1703 (5)	7963 (5)	7649 (3)	58 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

probable that formation of **4** and **6** involves facile exchange of bridging phenoxo groups with hydroxo ligands caused by protonation of the former by water, with subsequent release of phenol and entry of hydroxide ion into the bridging positions between the ruthenium atoms.

Experimental Section

General Methods. All manipulations involving air-sensitive compounds were performed with Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres inert-atmosphere chamber under prepurified argon. All solvents were distilled under prepurified nitrogen prior to use; acetonitrile was distilled from calcium hydride. ^{1}H NMR spectra were recorded on a Varian XL-400 spectrometer, and NMR data are listed in ppm relative to internal Me_4Si. Thallium phenoxide and ruthenium trichloride trihydrate were purchased from Aldrich Chemical Co. Neutral alumina, Brockman activity I, 80–200 mesh was purchased from Fischer Scientific. $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]$ was synthesized by a published method.[5] Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories.

$[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ (7). To $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]$ (1.50 g, 3.00 mmol) in a 250-mL Schlenk tube with stirbar was added $TlOC_6H_5$ (2.67 g, 9.00 mmol). Approximately 150 mL of CH_3CN was then added to the reaction flask, and the reaction mixture was stirred at room temperature for an 18-h period. During this time an orange solution developed, with formation of solid TlCl. Following filtration of the solution through a medium-porosity frit, the solvent was removed under vacuum affording 1.74 g (86%) of an orange solid, $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OC_6H_5)_3]Cl$; the ^{1}H NMR spectrum of the cation was idential with that of an authentic sample.[3b] This solid was added to 20 mL of water; the solution so formed was stirred for 10 min at room temperature and chromatographed (alumina, water eluent) by using a 1-cm-diameter column with a height of 15 cm. The eluate was collected in a 100-mL round-bottom flask equipped with a stirbar, and an orange crystalline solid, **7**, was obtained by removal of the solvent in vacuo. Yield: 1.26 g (98%). An analytical sample of $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ was prepared by double recrystallization from 50/50 CH_3CN/THF: ^{1}H NMR (D_2O): δ 5.42 (C_6H_6, s).

Anal. Calcd for $C_{12}H_{21}ClO_6Ru_2$: C, 28.89; H, 4.25; Cl, 7.11. Found: C, 29.05, H, 4.16; Cl, 7.25.

$[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]PF_6$ (8). A solution of aqueous $AgPF_6$ (0.63 g, 2.49 mmol) was added dropwise to an aqueous solution of $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ (1.1 g, 2.47 mmol). The reaction mixture was stirred for 5 min at room temperature to insure complete precipitation of AgCl. Following filtration of the mixture through Celite on a medium-porosity frit, the solvent was removed from the filtrate in vacuo. The yellow solid so obtained was dissolved in water and chromatographed (water eluent) with alumina (Brockman Activity I) on a 1-cm-diameter column with a height of 10 cm. The eluate was collected and taken to dryness in vacuo, giving a yellow solid, $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]PF_6$ (yield = 1.2 g, 88%). ^{1}H NMR (D_2O): δ 5.84 (C_6H_6, s).

Table II. Selected Bond Distances and Bond Angles for $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ (7)[a]

(a) Bond Distances (Å)			
Ru(1)–Ru(2)	2.9812 (7)	Ru(2)–O(1)	2.070 (3)
Ru(1)–CNT(1)	1.651 (5)	Ru(2)–O(2)	2.100 (3)
Ru(2)–CNT(2)	1.638 (5)	Ru(2)–O(3)	2.073 (3)
Ru(1)–O(1)	2.071 (3)	O(1)···O(2)	2.489 (5)
Ru(1)–O(2)	2.092 (3)	O(1)···O(3)	2.563 (5)
Ru(1)–O(3)	2.073 (3)	O(2)···O(3)	2.480 (5)
(b) Bond Angles (deg)			
CNT(1)–Ru(1)–Ru(2)	174 (1)	CNT(2)–Ru(2)–O(2)	137.6 (3)
CNT(1)–Ru(1)–O(1)	137.9 (3)	CNT(2)–Ru(2)–O(3)	134.8 (3)
CNT(1)–Ru(1)–O(2)	129.3 (4)	Ru(1)–O(1)–Ru(2)	92.1 (1)
CNT(1)–Ru(1)–O(3)	139.0 (4)	Ru(1)–O(2)–Ru(2)	90.6 (1)
CNT(2)–Ru(2)–Ru(1)	177.8 (1)	Ru(1)–O(3)–Ru(2)	91.9 (1)
CNT(2)–Ru(2)–O(1)	135.1 (3)		
(c) Torsion Angle (deg)			
CNT(1)–Ru(1)–Ru(2)–CNT(2)	8.8 (4)		

[a] CNT = centroid of benzene ring.

Anal. Calcd for $C_{12}H_{15}F_6O_3PRu_2$: C, 26.00; H, 2.73; F, 20.56. Found: C, 25.76; H, 2.98; F, 20.32. Mol wt.: calcd, 554; found, 548 (H_2O).

X-ray Crystallography

Crystal data for $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ (7): $C_{12}H_{21}ClO_6Ru_2$, orthorhombic, *Pbcn*, $a = 14.273$ (2) Å, $b = 12.125$ (1) Å, $c = 18.541$ (2) Å, $V = 3208.7$ (6) Å³, $Z = 8$, D(calcd) = 2.065 g cm^{-3}, μ(Mo Kα) = 20.37 cm^{-1}, and T(max)/T(min) = 0.493/0.406. An orange crystal (0.21 × 0.31 × 0.33 mm) was used to collect 4121 reflections (one octant, Nicolet R3m/μ diffractometer, graphite monochromator, $4° \le 2\theta \le 55°$, 23 °C) of which 3673 were independent and systematically present, and 2855 were considered observed ($3\sigma(F_0)$). The data were semiempirically corrected for absorption. The structure was solved by heavy-atom methods. The chloride ion is disordered over two positions with the following refined occupancies: Cl, 0.77; and Cl′, 0.23. There is likely an accompanying disorder in the water molecule occupancies, but it was unobserved. At convergence, with all non-hydrogen atoms except Cl′ anisotropic and calculated isotropic hydrogen atom contributions for the benzene rings, $R(F) = 3.38\%$, $R(wF) = 5.05\%$, GOF = 1.235, $\Delta/\sigma = 0.023$, $\Delta(\rho) = 0.71$ e Å^{-3}, and $N_0/N_v = 14.5$. All calculations used the SHELXTL program library (Nicolet Corp., Madison, WI). The atomic cooridnates and isotropical thermal parameters are collected in Table I. Selected bond distances and bond angles are listed in Table II.

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Registry No. 7, 114928-93-7; 8, 114928-94-8; $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl$, 60829-93-8; $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]$, 37366-09-9; $TlOC_6H_5$, 25491-50-3; $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OC_6H_5)_3]Cl$, 114928-92-6.

Supplementary Material Available: A stereoview of the unit-cell packing for $[Ru_2(\eta^6\text{-}C_6H_6)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ and tables of atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (8 pages); a listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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Binuclear Reductive Elimination of Water: New Route to the (Triphenylstannyl)pentacarbonyltungsten Anion, $Ph_3SnW(CO)_5^-$

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Salts of the anions $R_3EM(CO)_5^-$ (E = Si, Ge, Sn; M = Cr, Mo, W) are quite stable and are readily prepared by one of the routes, illustrated for the title anion, shown in eq 1 and 2.[1,2]