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Further Study of Tetracarbonato Diruthenium(II,III) Compounds

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A new synthetic method for the $M_3[Ru_2(CO_3)_4]\cdot nH_2O$ compounds (M = K, Na) has been developed. A previously formulated potassium hexahydrate compound has been determined to have the formula $K_3[Ru_2(CO_3)_4]\cdot 4H_2O$ (**1**), and the structure of $Na_3[Ru_2(CO_3)_4]\cdot 6H_2O$ (**2**) has been redetermined to clarify a disorder ambiguity by X-ray crystallography. Crystal data for these two compounds are as follows. **1**: space group ($C2/c$, a = 17.343 (2) Å, b = 9.183 (2) Å, c = 9.877 (1) Å, β = 96.39 (1)°, V 1563.1 (4) Å^3, Z = 4; Ru–Ru distance = 2.2509 (5) Å. **2**: space group $P\bar{1}$, a = 9.469 (2) Å, b = 9.599 (2) Å, c = 9.879 (2) Å, α = 110.41 (2)°, β = 72.05 (2)°, γ = 92.35 (2)°, V = 798.4 (3) Å^3, Z = 2; average Ru–Ru distance = 2.2506 [3] Å. Cyclic voltammetric studies show a possible quasi-reversible one-electron oxidation for these dimers.

Introduction

The synthesis and study of tetracarboxylates with multiply-bonded diruthenium units formally in the (II,III)[1] or in the (II,II)[2] oxidation state have been reported. However, previously claimed (III,III) analogs[3] have in fact been shown to be also (II,III) derivatives, and there is still no evidence for the existence of any $[Ru_2(O_2CR)_4]^{2+}$ species.[4] In sharp contrast to the carboxylato complexes, the tetrasulfato complex of Ru_2^{6+} along with that of Ru_2^{5+} has been prepared and characterized.[5] Thus far, only one tetracarbonato diruthenium(II,III) compound has been synthesized and characterized.[6] However, from the results of the crystal structure determination, there is some confusion regarding the stoichiometry and, therefore, the oxidation state of the diruthenium unit. The crystallographic results actually correspond to the formula $Na_{3.5}[Ru_2(CO_3)_4]\cdot 6H_2O$. Cyclic voltammetric results have been said to indicate that the compound undergoes a reversible one-electron oxidation. Our long-standing interest in the possibility of preparing tetracarbonato diruthenium(III,III) compounds and in their structure and bonding features led us to reexamine and correct the previous results, to improve the preparative methods, and to elucidate the relationship between diruthenium(II,III) and -(III,III) compounds.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of oxygen-free argon by standard Schlenk techniques. Oxygen-free water was obtained by prolonged boiling under an argon atmosphere.

Infrared spectra in the range 4000–400 cm^{-1} were recorded on a Perkin-Elmer 783 spectrophotometer using liquid paraffin and fluorinated hydrocarbon mulls. Visible spectra were recorded on a Cary 17D spectrophotometer. Microanalyses were performed by Galbraith Laboratory. Cyclic voltammograms were recorded on a BAS-100 electrochemical analyzer in 0.1 mol dm^{-3} NaCl in water at room temperature with platinum working and auxiliary electrodes and a Ag/AgCl reference electrode (against which potassium ferricyanide was reduced at 0.215 V).

$Ru_2(O_2CCH_3)_4Cl$ was prepared according to the literature method.[7]

Preparation of $K_3[Ru_2(CO_3)_4]\cdot 4H_2O$ (1). A 1.5-g sample of $Ru_2(O_2CCH_3)_4Cl$ (3.17 mmol) was suspended in 60 mL of an aqueous solution of 8.85 g (6.40 mmol) of K_2CO_3, and it gradually dissolved. After several hours, an orange precipitate began to form, and the reaction was allowed to continue overnight. The solid was filtered off, washed several times with methanol and ether, and air-dried (yield 1.81 g, 90.5%). Anal. Found (calcd for $C_4H_8K_3O_{16}Ru_2$): C, 7.8 (7.6); K, 17.7 (18.6). An electronic spectrum showed a maximum at 410 nm (ϵ_{max} 850 dm^3 mol^{-1} cm^{-1}). The infrared spectrum registered in the region 1600–1300 cm^{-1} in Fluorolube that was clean in this region showed the following absorptions: 1580 s, 1550 s, 1515 s, 1480 s, 1310 s cm^{-1}. The infrared spectrum in Nujol in the region 1300–400 cm^{-1} showed bands as follows: 1240 s, 1075 m, 1045 s, 825 m, 770 w, 610 m, b, 420 s cm^{-1}. Red-brown crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of acetone into a water solution of the compound.

Preparation of $Na_3[Ru_2(CO_3)_4]\cdot 6H_2O$ (2). This compound was prepared by using a procedure similar to the one described for the potassium analog. A 0.25-g sample of $Ru_2(O_2CCH_3)_4Cl$ (0.52 mmol) was suspended in 10 mL of an aqueous solution of 0.38 g (3.16 mmol) of Na_2CO_3. After 1 day, the product was recovered from the orange-brown solution by adding acetone dropwise until it began to precipitate, and the system was stirred for another 0.5 h. The orange solid was filtered off, washed, and air-dried (yield 0.17 g, 52%).

X-ray Crystallography for 1. The crystal for X-ray crystallography was mounted on the end of a quartz fiber with epoxy cement. Routine procedures that were standard in this laboratory[8] were followed to determine the cell parameters and possible space group and to collect the intensity data. Axial photography along the a, b, c and [110] directions showed the cell was C-centered monoclinic. The cell parameters were refined by centering 25 reflections in the 2θ range of 28–31°. Scan width 0.80° + 0.35° tan θ, aperture size 2.4° + 1.05° tan θ, and scan mode ω–2θ were determined from the results of an ω/θ profile analysis (OTPLOT[9]). A learned profile analysis (LEARN[9]) was used to increase the $I/\sigma(I)$ values for intensity data with $I/\sigma(I)$ values less than 30. Variable scan speeds for the ω circle, from 0.915 to 5.493°/min, were determined by the $I/\sigma(I)$ values from prescan measurements. Three intensity standards that were checked after every 2 h of exposure and three orientation standards that were monitored after every 200 reflection scans showed neither crystal decay nor crystal movement.

The intensity data were corrected for Lorentz and polarization effects, and an empirical absorption correction was also applied based on ψ scans of six reflections with their Eulerian χ angles near 90°. Both the direct method and a supersharp Patterson map (SHELXS-86[10]) provided the coordinates for the Ru atom in the centrosymmetric space group $C2/c$, after which an alternating series of least-squares refinements and difference Fourier syntheses revealed most of the non-hydrogen atoms. After these non-hydrogen atoms were refined anisotropically to an R value of 0.040, a difference Fourier map showed two peaks around the fractional coordinates (0.1, 0.1, 0.4). The distance between them was ca. 0.8 Å, and the electron densities were ca. 10 and 3 e Å^{-3}, respectively. Refinements of the former peak as a potassium or an oxygen atom and the latter as an oxygen or a hydrogen atom all failed, resulting in either too high thermal parameters, such as 10 Å^2 for a potassium atom for the former peak and 8 Å^2 for an oxygen atom for the latter peak, or negative ones, which indicated that the existence of either potassium or a water molecule here without statistical distribution was impossible.

In order to clarify the nature of these two peaks, the inversion center symmetry of the cell was removed and both the space groups Cc and $C2$ were tried. In the space group Cc, even the skeleton atoms of the Ru dimer structure could not be refined normally, as several atoms including one of the Ru atoms had negative thermal parameters. However, in the space group $C2$, all the atoms that corresponded to the atoms found in the space group $C2/c$ were found and the refinement proceeded normally.

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Table I. Crystallographic Data for $K_3[Ru_2(CO_3)_4]\cdot 4H_2O$ (**1**) and $Na_3[Ru_2(CO_3)_4]\cdot 6H_2O$ (**2**)

	1	**2**
formula	$Ru_2K_3O_{16}C_4H_8$	$Ru_2Na_3O_{18}C_4H_{12}$
fw	631.54	619.24
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
a, Å	17.343 (2)	9.469 (2)
b, Å	9.183 (2)	9.599 (2)
c, Å	9.877 (1)	9.879 (2)
α, deg	90.0	110.41 (2)
β, deg	96.39 (1)	72.05 (2)
γ, deg	90.0	93.35 (2)
V, Å^3	1563.1 (4)	798.4 (3)
Z	4	2
d_{calcd}, g/cm^3	2.683	2.576
λ(Kα), Å	0.71073 (Mo)	1.54184 (Cu)
μ(Kα), cm^{-1}	27.774 (Mo)	174.834 (Cu)
transm coeff	0.9983–0.7392	1.0000–0.5554
R[a]	0.024	0.022
Rw[b]	0.035	0.025

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Furthermore, one discrete potassium atom and one discrete oxygen atom were located in the positions that together corresponded well to the sites around (0.1, 0.1, 0.4) in the space group *C*2/*c*. In the final refinement in *C*2, the two Ru atoms and the three K atoms were treated anisotropically, while the remaining non-hydrogen atoms were treated only isotropically, which resulted in a decent *R* value of 0.032 for 1124 observable reflections ($I > 3\sigma(I)$) and 125 variables with a goodness-of-fit indicator of 1.458. Refinement of the enantiomeric structure yielded the same results.

Although the structural analysis in the space group *C*2 revealed unambiguously the title formula and gave credible structural parameters, the correlation coefficients in the final least-squares refinement were large. Out of 125 variables, 55 pairs had coefficients greater than 0.5. Especially, all corresponding parameters between the two Ru atoms had coefficients greater than 0.85. Besides, there were unrealistically large differences between the isotropic thermal parameters for several pairs of oxygen atoms and carbon atoms, where each such pair corresponded to a crystallographically unique atom in the *C*2/*c* space group. Examples of this are 0.0 (1) versus 2.0 (2) and 0.2 (2) versus 2.2 (3) Å^2. This kind of situation led us to try a disordered model in the space group *C*2/*c*, in which potassium atoms K(2) were supposed to occupy only four of the eight equivalent sites which had electron densities around 10 e Å^{-3} and oxygen atoms O(9) would occupy four of the eight sites that had electron densities around 3 e Å^{-3} and were close to the four unoccupied K(2) sites. Refinements of this kind of disorder model brought the *R* value down to 0.026, and the ensuing difference Fourier synthesis revealed all the hydrogen atoms. The isotropic thermal parameters for these hydrogen atoms were assigned values 1.3 times the equivalent isotropic thermal parameters of their bonded oxygen atoms. The final refinement, where only their positional parameters were refined, while all non-hydrogen atoms were refined anisotropically, converged to a final *R* value of 0.024 and showed no abnormalities. All the crystallographic data are listed in Table I, the positional and thermal parameters are listed in Table II, and some important bond distances and angles are listed in Table III. Full lists of bond distances and angles including those of hydrogen atoms have been deposited as supplementary material.

Although we believe that more satisfactory results have been obtained from the centrosymmetric space group *C*2/*c*, we do not absolutely reject the space group *C*2, which had a slightly higher *R* value and some large correlation coefficients, but an ordered structure. For the benefit of anyone wishing to make a comparison, corresponding data in the *C*2 space group are all deposited as supplementary material.

X-ray Crystallography for 2. A brown platelike crystal was attached to the tip of a glass fiber by epoxy cement. Unit cell parameters were obtained by centering and indexing eight random reflections in the 2θ range 48–53°, and they were refined by centering 25 reflections in the 2θ range 79–107°. Axial photography confirmed the crystal system and the axial lengths, and no unusual reflections were observed from the photographs. Three standard reflections used to monitor intensity and orientation were checked after each interval of every 250 reflection scans and showed no crystal decay nor change of the crystal orientation during the data collection. The intensity data were corrected for Lorentz and polarization effects, and the intensity data of ψ scans of seven reflections with their χ angles close to 90° were used for an empirical absorption correction.

Table II. Positional and Equivalent Isotropic Thermal Parameters for $K_3[Ru_2(CO_3)_4]\cdot 4H_2O$

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Ru	0.26372 (2)	0.30593 (4)	0.10121 (3)	0.694 (6)
O(1)	0.2490 (2)	0.1139 (4)	0.1973 (3)	1.37 (6)
O(2)	0.2192 (2)	0.0048 (4)	−0.0056 (3)	1.75 (7)
O(3)	0.2029 (2)	−0.1119 (4)	0.1838 (4)	2.03 (7)
O(4)	0.1495 (2)	0.3493 (4)	0.1042 (3)	1.69 (7)
O(5)	0.1222 (2)	0.2369 (4)	−0.0980 (3)	1.51 (6)
O(6)	0.0277 (2)	0.3064 (5)	0.0188 (4)	3.26 (9)
C(1)	0.2236 (3)	0.0011 (5)	0.1259 (5)	1.18 (9)
C(2)	0.0980 (3)	0.2973 (6)	0.0077 (5)	1.55 (9)
K(1)	0.39035 (7)	0.1409 (1)	0.3681 (1)	1.98 (2)
K(2)	0.0491 (2)	0.0277 (3)	0.4106 (3)	3.19 (6)[b]
O(7)	0.1347 (3)	0.2508 (6)	0.3818 (4)	3.9 (1)
O(8)	0.000	0.4682 (7)	0.250	3.1 (1)[b]
O(9)	0.0194 (6)	0.012 (1)	0.350 (1)	4.5 (2)[b]
H(71)	0.136 (6)	0.28 (1)	0.322 (9)	4.7[c]
H(72)	0.162 (5)	0.21 (1)	0.407 (9)	4.7[c]
H(8)	−0.004 (5)	0.413 (9)	0.321 (7)	3.9[c]
H(91)	0.04 (1)	−0.06 (2)	0.33 (2)	5.7[b,c]
H(92)	0.06 (1)	0.09 (2)	0.33 (2)	5.7[b,c]

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Atoms had a half-multiplicity. [c] Hydrogen atoms had fixed isotropic thermal parameters in the final refinement.

Table III. Selected Bond Distances (Å) and Angles (deg) for $K_3[Ru_2(CO_3)_4]\cdot 4H_2O$[a]

Ru–Ru′	2.2509 (5)	O(1)–C(1)	1.302 (6)
Ru–O(1)	2.032 (3)	O(2)–C(1)	1.293 (6)
Ru–O(2)′	2.016 (3)	O(3)–C(1)	1.257 (6)
Ru–O(3)′	2.267 (3)	O(4)–C(2)	1.321 (6)
Ru–O(4)	2.024 (3)	O(5)–C(2)	1.293 (6)
Ru–O(5)′	2.020 (3)	O(6)–C(2)	1.239 (6)
Ru′–Ru–O(3)	172.08 (9)	Ru–O(1)–C(1)	119.3 (3)
O(1)–Ru–O(2)′	178.7 (1)	Ru–O(2)–C(1)	119.8 (3)
O(1)–Ru–O(3)′	83.3 (1)	Ru–O(3)–C(1)	130.2 (3)
O(1)–Ru–O(4)	89.4 (1)	Ru–O(4)–C(2)	120.2 (3)
O(1)–Ru–O(5)′	90.7 (1)	Ru–O(5)–C(2)	120.2 (3)
O(2)′–Ru–O(3)′	96.7 (1)	O(1)–C(1)–O(2)	120.2 (4)
O(2)′–Ru–O(4)	91.8 (1)	O(1)–C(1)–O(3)	120.5 (4)
O(2)′–Ru–O(5)′	88.0 (1)	O(2)–C(1)–O(3)	119.4 (4)
O(3)′–Ru–O(4)	94.0 (1)	O(4)–C(2)–O(5)	118.9 (4)
O(3)′–Ru–O(5)′	86.1 (1)	O(4)–C(2)–O(6)	120.3 (5)
O(4)–Ru–O(5)′	180. (0)	O(5)–C(2)–O(6)	120.8 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

An interpretation of a supersharp Patterson map (SHELXS-86[10]) showed positions for all non-hydrogen atoms very similar to those in the published results.[6] Therefore, they were assigned accordingly and refined isotropically to convergence. However, the Na(4) atom was found to have an unusually high thermal parameter (ca. 8.5 Å^2), as compared to the other atoms, all of which had values less than 4.5 Å^2. Moreover, the Na(4) atom lay close to an inversion center (0, 0.5, 0) with the Na(4)–Na(4)′ distance being less than 1.20 Å, i.e., entirely unrealistic. In the following difference Fourier map no peaks of chemical significance could be found around it, and no diatomic carbon and/or oxygen species appeared to make any chemical sense; a model was then devised in which the Na(4) atom was located on only one side or the other of the inversion center in each unit cell. In other words, Na(4) was given half-occupancy. The refinement of this model was successful. After all the non-hydrogen atoms has been refined anisotropically to an *R* value of 0.024, a difference Fourier map revealed all the hydrogen atoms, which were then refined isotropically in the final least-squares refinement. A hydrogen-bonding scheme consistent with the adopted assignments of the oxygen and sodium atoms supported the correctness of the entire arrangement.

In order to further confirm the disorder model of Na(4), the space group was changed to *P*1 so that Na(4) and Na(4)′ became independent. Throughout the least-squares refinement, Na(4) and its counterpart Na(4)′, both of which were assigned at half-occupancy, had normal and very similar isotropic and equivalent isotropic thermal parameters (ca. 3.6 vs 3.4 Å^2), which showed that these two positions have indeed equal probability of being occupied. Although the *R* value could be reduced

Table IV. Positional and Equivalent Isotropic Thermal Parameters for $Na_3[Ru_2(CO_3)_4]\cdot 6H_2O$

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Ru(1)	0.03900 (3)	0.11319 (3)	0.05008 (3)	1.037 (6)
Ru(2)	0.44276 (3)	−0.40344 (3)	−0.00694 (3)	0.939 (6)
Na(1)	0.3770 (2)	0.1590 (2)	0.1993 (2)	2.37 (4)
Na(2)	0.500	0.000	0.500	2.81 (6)
Na(3)	−0.0066 (2)	0.6000 (2)	0.3819 (2)	3.61 (5)
Na(4)	−0.0296 (5)	0.4457 (5)	0.0057 (4)	3.8 (1)[b]
O(11)	0.1485 (3)	0.1121 (3)	−0.1609 (3)	2.03 (7)
O(12)	0.2242 (3)	0.0137 (3)	0.0470 (3)	1.80 (6)
O(13)	−0.0691 (3)	0.1130 (3)	0.2623 (3)	1.97 (7)
O(14)	−0.1446 (3)	0.2124 (3)	0.0488 (3)	1.81 (6)
O(15)	0.2098 (4)	0.0022 (4)	−0.4106 (3)	2.65 (7)
O(16)	0.3667 (3)	−0.1866 (3)	−0.0116 (3)	2.10 (6)
O(21)	0.4352 (3)	−0.2845 (3)	0.2076 (3)	1.73 (6)
O(22)	0.4451 (3)	−0.5263 (3)	−0.2205 (3)	1.71 (6)
O(23)	0.6449 (3)	−0.3290 (3)	−0.0832 (3)	1.62 (6)
O(24)	0.2418 (3)	−0.4770 (3)	0.0709 (3)	1.63 (6)
O(25)	0.4993 (4)	−0.2583 (3)	0.4118 (3)	2.75 (7)
O(26)	0.1085 (3)	−0.6467 (3)	0.1429 (3)	1.93 (7)
O(01)	0.5189 (3)	−0.0018 (3)	0.2473 (3)	2.37 (7)
O(02)	−0.4170 (4)	0.6309 (4)	0.5980 (3)	2.87 (7)
O(03)	0.1606 (4)	0.1740 (4)	0.4079 (4)	3.44 (9)
O(04)	−0.1480 (4)	0.6256 (4)	0.2340 (4)	3.60 (9)
O(05)	−0.1190 (4)	0.1875 (5)	−0.3450 (4)	4.3 (1)
O(06)	−0.1592 (4)	0.4341 (4)	0.4878 (4)	4.0 (1)
C(1)	0.1435 (5)	0.0007 (5)	−0.2815 (4)	1.88 (9)
C(2)	0.2458 (4)	−0.1308 (4)	−0.0050 (4)	1.50 (9)
C(3)	0.4961 (5)	−0.3366 (4)	0.2834 (4)	1.68 (9)
C(4)	0.2348 (5)	−0.5999 (4)	0.0988 (4)	1.54 (9)
H(11)	0.493 (5)	−0.095 (5)	0.219 (5)	1 (1)[c]
H(12)	0.607 (7)	−0.022 (7)	0.195 (7)	4 (2)
H(21)	−0.490 (6)	0.586 (6)	0.647 (5)	1 (1)
H(22)	−0.455 (8)	0.654 (8)	0.540 (7)	5 (2)
H(31)	0.084 (8)	0.135 (8)	0.352 (8)	5 (2)
H(32)	0.158 (8)	0.129 (8)	0.461 (8)	6 (2)
H(41)	−0.18 (1)	0.74 (1)	0.22 (1)	13 (4)
H(42)	−0.180 (8)	0.555 (8)	0.237 (7)	5 (2)
H(51)	−0.144 (7)	0.128 (7)	−0.429 (7)	3 (2)
H(52)	−0.20 (1)	0.24 (1)	−0.28 (1)	10 (3)
H(61)	−0.232 (8)	0.477 (8)	0.515 (8)	6 (2)
H(62)	−0.16 (1)	0.35 (1)	0.41 (1)	11 (3)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] The atom was refined with a multiplicity of 0.5. [c] Hydrogen atoms were refined with isotropic thermal parameters.

to 0.025 in *P*1, no more structural details, such as locations of the hydrogen atoms, were obtained. Furthermore, large differences were found between the equivalent isotropic thermal parameters of some pairs of atoms that would be equivalent in $P\bar{1}$, and some atoms could not even be properly refined anisotropically. These results led to the conclusion that the Na(4) atom was indeed disordered around an inversion center in the $P\bar{1}$ space group. The crystallographic details are given in Table I, the positional and thermal parameters are listed in Table IV, and some important bond distances and angles are listed in Table V.

Results and Discussion

The new synthetic method for $K_3[Ru_2(CO_3)_4]\cdot 4H_2O$ and $Na_3[Ru_2(CO_3)_4]\cdot 6H_2O$ by using $Ru^{II}Ru^{III}$ starting material can be formulated as follows:

$$Ru_2(O_2CCH_3)_4Cl + 4M_2CO_3 \xrightarrow{H_2O} M_3[Ru_2(CO_3)_4]\cdot nH_2O + 4MO_2CCH_3 + MCl$$

where M = K, Na and *n* = 4, 6.

In an inert atmosphere, this reaction proceeds smoothly in water under ambient conditions. This method provides several advantages over that reported previously.[6] First, the yield has been increased. The previous preparation adopted a disproportionation from $Ru^{II}Ru^{II}$ to $Ru^{II}Ru^{III}$ and Ru^0:

$$5Ru_2(O_2CMe)_4 + 16M_2CO_3 \xrightarrow{H_2O} 2Ru + 4M_3[Ru_2(CO_3)_4]\cdot xH_2O + 20K(O_2CCH_3)$$

It is obvious that no more than 80% of the starting material can be converted to the $Ru^{II}Ru^{III}$ product. However, since the new method involves only ligand substitution, all of the ruthenium is available. Second, the starting material is easy to prepare, in 80% or higher yield,[7] by simply refluxing $RuCl_3\cdot 3H_2O$ in $Ac_2O/HOAc$, whereas the preparation of $Ru_2(O_2CCH_3)_4$ entails a lengthy process to reduce catalytically a methanol solution of $RuCl_3\cdot 3H_2O$ by hydrogen to a "ruthenium blue solution"[11] and then to reflux this solution with NaOAc resulting in a lower yield of ~60%.[2] Finally, the products from the new reaction can be readily isolated due to their low solubility in water,[12] while in the previous method it is necessary first to filter off the precipitated ruthenium metal at elevated temperature (to keep the product in solution) and then to evaporate the filtrate to collect the product.

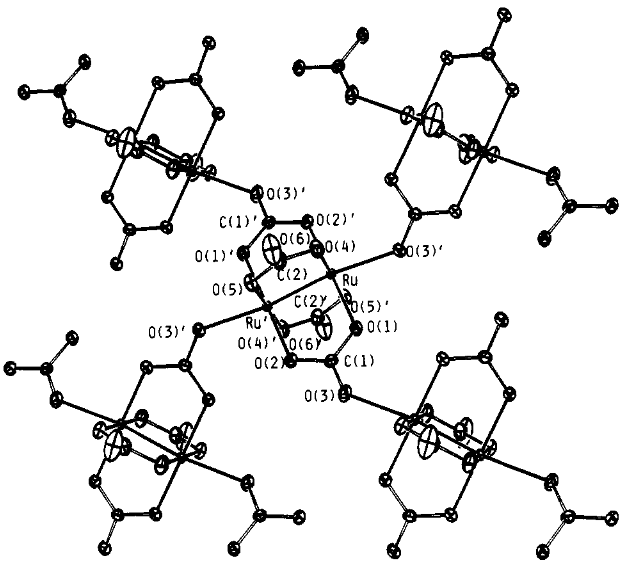

Figure 1. Layer structure of $[Ru_2(CO_3)_4]^{3+}$ in $Na_3[Ru_2(CO_3)_4]\cdot 6H_2O$. Thermal ellipsoids are drawn with 30% probability boundaries.

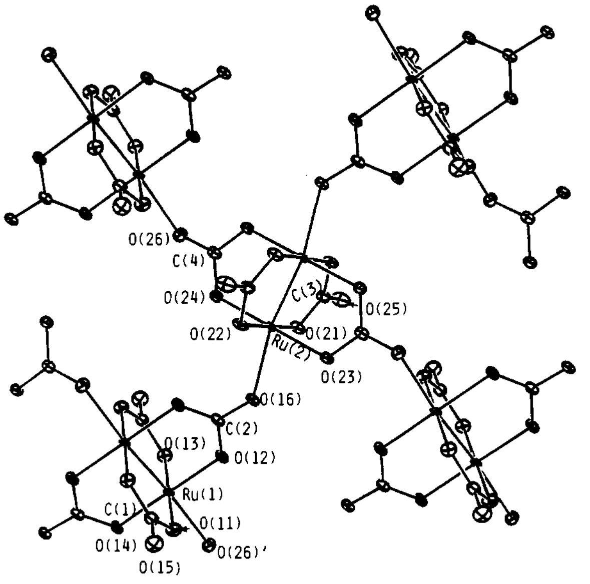

Figure 2. Layer structure of $[Ru_2(CO_3)_4]^{3+}$ in $K_3[Ru_2(CO_3)_4]\cdot 4H_2O$. Thermal ellipsoids are drawn with 30% probability boundaries.

The structures of the potassium and sodium salts are shown in Figures 1 and 2, respectively. The basic structural unit is $Ru_2(CO_3)_4$, which provides two other dimer units with two remote oxygen atoms as axial ligands and in turn receives two oxygen atoms as axial ligands from two other dimer units. In this manner, these units are linked in a two-dimensional layer structure. These

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(11) (a) Rose, D.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 1791. (b) Gilbert, J. D.; Rose, D.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 2765.

(12) The sodium derivative is easily recovered by adding acetone dropwise.

Table V. Selected Bond Distances (Å) and Angles (deg) for $Na_3[Ru_2(CO_3)_4]\cdot 6H_2O$[a]

Ru(1)–Ru(1)′	2.2508 (4)	O(12)–C(2)	1.300 (5)
Ru(1)–O(11)	2.018 (3)	O(13)–C(1)′	1.313 (5)
Ru(1)–O(12)	2.018 (3)	O(14)–C(2)′	1.294 (5)
Ru(1)–O(13)	2.030 (3)	O(15)–C(1)	1.240 (5)
Ru(1)–O(14)	2.022 (3)	O(16)–C(2)	1.258 (5)
Ru(1)–O(26)′	2.315 (3)	O(21)–C(3)	1.301 (6)
Ru(2)–Ru(2)′	2.2503 (5)	O(22)–C(3)′	1.305 (5)
Ru(2)–O(16)	2.251 (3)	O(23)–C(4)′	1.293 (5)
Ru(2)–O(21)	2.007 (3)	O(24)–C(4)	1.297 (5)
Ru(2)–O(22)	2.020 (3)	O(25)–C(3)	1.238 (5)
Ru(2)–O(23)	2.029 (3)	O(26)–C(4)	1.261 (5)
Ru(2)–O(24)	2.019 (3)	H(11)–O(21)	1.85 (5)
Na(1)–O(12)	2.453 (3)	H(11)–O(01)	0.89 (5)
Na(1)–O(16)′	2.630 (3)	H(12)–O(01)	0.82 (6)
Na(1)–O(23)′	2.345 (4)	H(21)–O(22)′	1.91 (6)
Na(1)–O(01)	2.342 (4)	H(21)–O(02)	0.91 (5)
Na(1)–O(02)′	2.411 (3)	H(22)–O(25)′	1.90 (9)
Na(1)–O(03)	2.383 (3)	H(22)–O(02)	0.85 (9)
Na(2)–O(15)	2.613 (3)	H(31)–O(13)	1.89 (9)
Na(2)–O(25)	2.325 (3)	H(31)–O(03)	1.02 (8)
Na(2)–O(01)	2.441 (3)	H(32)–O(15)′	2.2 (1)
Na(3)–O(26)′	2.664 (3)	H(32)–O(03)	0.8 (1)
Na(3)–O(03)′	2.529 (3)	H(41)–O(11)′	1.6 (1)
Na(3)–O(04)	2.339 (5)	H(41)–O(04)	1.3 (1)
Na(3)–O(05)′	2.400 (5)	H(42)–O(04)	0.73 (7)
Na(3)–O(06)	2.399 (5)	H(51)–O(15)′	1.90 (6)
Na(3)–O(06)′	2.411 (5)	H(51)–O(05)	0.93 (6)
Na(4)–O(14)	2.562 (5)	H(52)–O(21)′	2.2 (1)
Na(4)–O(24)′	2.418 (6)	H(52)–O(05)	0.85 (9)
Na(4)–O(26)′	2.522 (6)	H(61)–O(02)	2.10 (8)
Na(4)–O(04)	2.282 (4)	H(61)–O(06)	0.74 (8)
Na(4)–O(04)′	2.327 (5)	H(62)–O(13)	2.24 (9)
O(11)–C(1)	1.307 (5)	H(62)–O(06)	0.93 (9)
Ru(1)′–Ru(1)–O(26)′	175.24 (9)	Ru(1)–O(11)–C(1)	121.0 (3)
O(11)–Ru(1)–O(12)	88.6 (1)	Ru(1)–O(12)–C(2)	120.8 (3)
O(11)–Ru(1)–O(13)	179.3 (1)	Ru(1)–O(13)–C(1)′	120.6 (2)
O(11)–Ru(1)–O(14)	90.3 (1)	Ru(1)–O(14)–C(2)′	119.4 (3)
O(11)–Ru(1)–O(26)′	87.6 (1)	Ru(2)–O(16)–C(2)	135.3 (3)
O(12)–Ru(1)–O(13)	90.8 (1)	Ru(2)–O(21)–C(3)	121.8 (2)
O(12)–Ru(1)–O(14)	178.9 (1)	Ru(2)–O(22)–C(3)′	119.9 (3)
O(12)–Ru(1)–O(26)′	94.9 (1)	Ru(2)–O(23)–C(4)′	120.6 (3)
O(13)–Ru(1)–O(14)	90.3 (1)	Ru(2)–O(24)–C(4)	119.4 (3)
O(13)–Ru(1)–O(26)′	92.5 (1)	Ru(1)′–O(26)–C(4)	126.9 (2)
O(14)–Ru(1)–O(26)′	85.2 (1)	O(11)–C(1)–O(13)′	118.3 (4)
Ru(2)′–Ru(2)–O(16)	168.83 (8)	O(11)–C(1)–O(15)	120.4 (4)
O(16)–Ru(2)–O(21)	85.2 (1)	O(13)′–C(1)–O(15)	121.2 (3)
O(16)–Ru(2)–O(22)	95.4 (1)	O(12)–C(2)–O(14)′	119.9 (4)
O(16)–Ru(2)–O(23)	81.2 (1)	O(12)–C(2)–O(16)	118.0 (4)
O(16)–Ru(2)–O(24)	98.9 (1)	O(14)′–C(2)–O(16)	122.1 (3)
O(21)–Ru(2)–O(22)	178.3 (1)	O(21)–C(3)–O(22)′	118.5 (3)
O(21)–Ru(2)–O(23)	89.5 (1)	O(21)–C(3)–O(25)	121.1 (4)
O(21)–Ru(2)–O(24)	90.0 (1)	O(22)′–C(3)–O(25)	120.4 (5)
O(22)–Ru(2)–O(23)	92.1 (1)	O(23)′–C(4)–O(24)	120.2 (4)
O(22)–Ru(2)–O(24)	88.4 (1)	O(23)′–C(4)–O(26)	121.3 (4)
O(23)–Ru(2)–O(24)	179.5 (1)	O(24)–C(4)–O(26)	118.6 (4)
O(14)–Na(4)–O(24)′	86.5 (2)	O(21)–H(11)–O(01)	167. (5)
O(14)–Na(4)–O(26)′	70.8 (2)	O(22)′–H(21)–O(02)	149. (6)
O(14)–Na(4)–O(04)	101.0 (2)	O(25)′–H(22)–O(02)	165. (7)
O(14)–Na(4)–O(04)′	108.7 (2)	O(13)–H(31)–O(03)	166. (7)
O(24)–Na(4)–O(26)	155.1 (2)	O(15)′–H(32)–O(03)	166. (7)
O(24)′–Na(4)–O(04)′	86.8 (2)	O(11)′–H(41)–O(04)	158. (9)
O(24)′–Na(4)–O(04)′	97.4 (2)	O(15)′–H(51)–O(05)	174. (6)
O(26)′–Na(4)–O(04)	87.5 (2)	O(21)′–H(52)–O(05)	158 (1)
O(26)′–Na(4)–O(04)′	99.5 (2)	O(02)–H(61)–O(06)	170. (8)
O(04)–Na(4)–O(04)′	150.2 (2)	O(13)–H(62)–O(06)	148. (11)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

layers are connected further to form three-dimensional infinite structures by cations and hydrogen bonds between interstitial water molecules and carbonate groups. Although the numbers of unique structural units in the two structures are different, bonding parameters in the two structures are very similar, with the average Ru–Ru, Ru–O_{eq}, and Ru–O_{ax} bond distances being 2.2509 (5), 2.023 [6],[13] and 2.267 (3) Å for the potassium salt and 2.2506 [3], 2.020 [7], and 2.28 [3] Å for the sodium salt. Essentially the same results were obtained for the published structure of the sodium salt: 2.254 [1], 2.022 [5], and 2.28 [4] Å. The metal–metal distances are shorter than those in their sulfate analog, 2.303 (1) Å,[5] and fall in the low end of the range for the diruthenium(II,III) carboxylate compounds, 2.248 (1)–2.292 (7) Å.[3a,4,14]

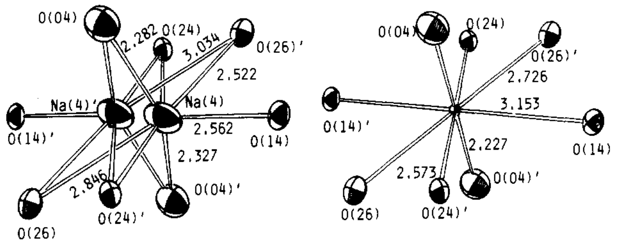

Figure 3. (a) Left: Coordination of the disordered Na(4) cation. (b) Right: Supposed coordination of the Na(4) cation at the inversion center.

Table VI. Cyclic Voltammetric Data for $Na_3[Ru_2(CO_3)_4]\cdot 6H_2O$

rate, mV/s	$(\text{rate})^{1/2}$, $(\text{mV/s})^{1/2}$	$10^6 i_a$, A	$10^6 i_c$, A	i_a/i_c	$E_a - E_c$, mV	$(E_a + E_c)/2$, mV
10	3.16	4.386	2.965	1.479	90	644
50	7.07	9.656	5.426	1.780	114	642
100	10.00	13.486	7.027	1.919	119	644
200	14.14	18.720	8.067	2.321	140	647
250	15.81	20.523	7.762	2.644	157	644
350	18.71	23.167	9.263	2.501	181	653
450	21.21	25.973	8.619	3.013	192	647

In both structures some of the alkali metal cations are disordered. The coordination of the Na(4) atom in **2** is shown in Figure 3 along with a proposed one surrounding the inversion center. It is obvious that by being displaced from the inversion center the Na(4) atom gains bonding interaction with the O(14) atom (from 3.153 to 2.562 Å) and avoids a too short contact with O(04) (from 2.227 and 2.227 to 2.282 and 2.327 Å), so that its electrostatic interaction in all directions can become more even. Since the separation of these two sites is too small (1.20 Å), only one of the two sites in a given unit cell is allowed to be occupied by Na, which means the site occupancy is 0.5 and the formula indeed is $Na_3[Ru_2(CO_3)_4]\cdot 6H_2O$.

The situation in the potassium salt is a little different. One of the potassium cations, K(2), is disordered with a water oxygen atom, O(9), around a general position and its seven equivalent positions. To avoid a very short contact between them (ca. 0.8 Å), each one has to evacuate four of its eight sites to make room for the other, which means a half-occupancy for each of the two. On the basis of this disorder model, the potassium salt can be correctly formulated as a tetrahydrate. Thus, the former assignment as a hexahydrate,[6] which may have been based on analogy to the sodium salt, cannot be justified, and all corresponding molar properties, such as conductivity and magnetic susceptibility, need minor corrections.

The infrared spectrum of **1** is composed of many bands in the region 1600–700 cm^{-1}. From the structure determination of the two crystals, we can identify a kind of carbonate group whose terminal oxygen atom acts as an axial ligand and another that simply bridges two ruthenium centers. In each carbonate group we can see that two oxygen atoms are involved in equatorial coordination to the Ru atoms, while the third may become axially coordinated to a Ru atom or involved only in the interaction with cations or hydrogen atoms. Therefore, it is understandable that the infrared spectrum displays many different C–O stretching bands.[15]

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(13) Parentheses denote esd of an individual value; square brackets denote mean deviation from the unweighted arithmetic mean.

(14) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(15) In the previous report, the IR spectrum was not shown and only four bands at 1551, 1490, 1246, and 1045 cm^{-1} were cited. We obtained more bands for **1** as shown in a figure deposited as supplementary material and also for a sample prepared by repeating the reported method using $Ru_2(O_2CCH_3)_4$.

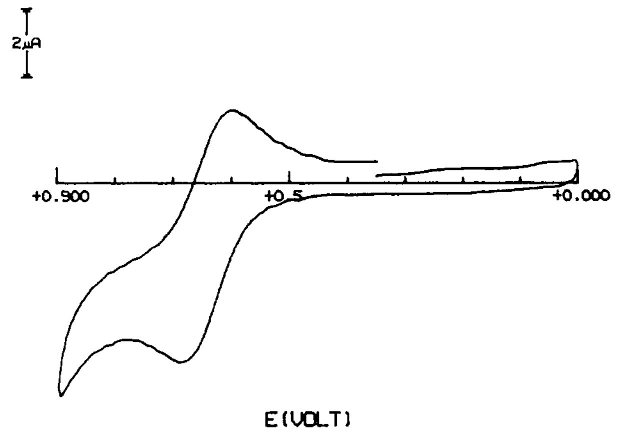

Figure 4. Typical voltammogram of $Na_3[Ru_2(CO_3)_4]\cdot 6H_2O$ at the scan rate 10 mV/s in 0.1 M NaCl solution.

Table VII. Cyclic Voltammetric Data for $K_3Fe(CN)_6$

rate, mV/s	$(\text{rate})^{1/2}$, $(\text{mV/s})^{1/2}$	$10^6 i_a$, A	$10^6 i_c$, A	i_a/i_c	$E_a - E_c$, mV	$(E_a + E_c)/2$, mV
15	3.87	1.032	1.006	1.02	66	214
25	5.00	1.554	1.511	1.03	72	212
50	7.07	2.125	2.086	1.02	81	215
100	10.00	2.947	2.905	1.01	80	215
200	14.14	4.080	3.994	1.02	89	217
250	15.81	4.574	4.518	1.01	93	216
350	18.71	5.419	5.255	1.03	100	216
450	21.21	6.095	5.905	1.03	106	216

A set of cyclic voltammograms was recorded at different scan rates between 10 and 450 mV/s for **2** in 0.1 M NaCl solution. The results are shown in Table VI, and Figure 4 shows a typical voltammogram of this compound at the scan speed of 10 mV/s. The compound exhibits an oxidation at 644 mV, which is in fact the same as observed previously, 0.59 V (vs SCE).[6] However, the separations between the peaks of the cathodic and anodic waves are larger than 90 mV for all the scan speeds, and the ratios between the cathodic and anodic currents are considerably different from unity. Moreover, there is no linear relation between the cathodic currents and the square roots of the scan rates. To test the equipment and reaction system, a set of cyclic voltammograms was also registered for 2.5×10^{-3} M $K_3Fe(CN)_6$ in 0.1 M NaCl solution, and the results are shown in Table VII. It is obvious that a truly reversible reduction displays its proper characteristics with the equipment we used. Therefore, it may not be appropriate to regard the oxidation of $[Ru_2(CO_3)_4]^{3+}$ as reversible. At most, it is a possible quasi-reversible oxidation, which may imply that the CO_3^{2-} group, though "harder" than carboxylate groups which tend to stabilize $Ru_2^{4+/5+}$ cores, is not "hard" enough to stabilize well the Ru_2^{6+} core in water solution.

Concluding Remarks

The structure determinations of **1** and **2** have unequivocally delineated the oxidation states and the stoichiometries of the previously reported diruthenium tetracarbonate compounds. The new and high-yield synthetic method makes compounds of this type very good starting materials for other diruthenium(II,III) derivatives. The cyclic voltammetric study shows a one-electron oxidation that is at best quasi-reversible. This probably indicates low stability of the oxidized species in water, thus explaining the failure to isolate any tetracarbonato diruthenium(III,III) compound.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: An infrared spectrum of **1** and, for the crystal structures of **1** and **2**, full tables of crystallographic data, bond distances and angles, and anisotropic thermal parameters, ORTEP drawings of unit cell contents, and corresponding tables and drawings for **1** in the space group *C*2 (27 pages); tables of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.