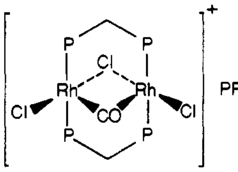
cleanly separated by flash column chromatography.[8] The compounds are eluted in the following order: $Rh_2Cl_6(dppm)_2$, $Rh_2(CO)Cl_4(dppm)_2$, and $Rh_2(CO)_2Cl_4(dppm)_2$.

$Rh_2(CO)Cl_4(dppm)_2$ undergoes a variety of reactions, of which a small number will be discussed. A brown CH_2Cl_2 solution of $Rh_2(CO)Cl_4(dppm)_2$ turns green upon the addition of methanol. A $^{31}P\{^1H\}$ NMR spectrum of the solution (Figure 3b) reveals an AA′A″A‴XX′ pattern, indicating the formation of a symmetrical compound. The AA′A″A‴XX′ pattern and the size of the rhodium-phosphorus coupling constant, 94.6 Hz, are indicative of a Rh-Rh bond. This reaction is reversed when MeOH is removed.

A more permanent transformation to the symmetric species is effected when a CH_2Cl_2 solution of **2** is treated with $AgPF_6$. The green compound, $[Rh_2(CO)Cl_3(dppm)_2][PF_6]$, can be isolated in essentially quantitative yield, and also as a methanol adduct (compound **4**). The $^{31}P\{^1H\}$ NMR spectrum of a CH_2Cl_2 solution of this compound, is essentially the same as that shown in Figure 3b. The solution IR spectrum reveals a band at $\nu = 1790\ cm^{-1}$, consistent with the presence of a bridging CO ligand in the complex, namely



Reactions of **2** with $BF_3 \cdot Et_2O$ and $NaBPh_4$ yield the same cation. The latter two reagents react faster in $MeOH/CH_2Cl_2$ solutions of **2**, presumably because MeOH facilitates initial chloride dissociation, and the larger, noncoordinating anion replaces Cl^-. Crystals of the PF_6 complex, **4**, were grown from $MeOH/CH_2Cl_2$. The solid structure reveals a coordinated methanol solvent molecule. If the solid structure persisted in solution, a complex $^{31}P\{^1H\}$ NMR pattern would have been observed, instead of the simple one discussed above. Crystals of **4**, redissolved in CH_2Cl_2, give the same $^{31}P\{^1H\}$ NMR pattern as shown in Figure 3b. Thus, the MeOH that is coordinated in the crystal of **4** does not remain associated with the complex in solution. The spectrum we observe for our rhodium cation is consistent with that reported by Woods et al.[4]

The carbonyl ligand of **2** may be removed under controlled conditions by the addition of Me_3NO. (Note that a mild decarbonylation reagent, $BF_3 \cdot Et_2O$, yielded only the dirhodium cation.) At room temperature, Me_3NO causes decomposition of **2**; the only product detected by $^{31}P\{^1H\}$ NMR spectroscopy is bis(diphenylphosphino)methane oxide. At -72 °C, the decarbonylation reaction proceeds faster than dimer decomposition, thus affording good yields of $Rh_2Cl_4(dppm)_2$ (**5**). The geometric rearrangement of the phosphine ligands around the rhodium-rhodium vector from transoid in **2** to cisoid in **5** may account for the difficulty in decarbonylating **2**. Compound **5** was previously prepared by the reaction of $Rh_2(O_2CCH_3)_4$ with 2 equiv of dppm and 4 equiv of Me_3SiCl.[6]

Under the forceful reaction condition of 200 psi of CO, $Rh_2Cl_4(dppm)_2$ slowly reacts to form $Rh_2(CO)Cl_4(dppm)_2$ (**2**). $Rh_2(CO)_2Cl_4(dppm)_2$ also forms from this reaction, indicating that carbonylation of **5** is the difficult step. Bubbling CO through a CH_2Cl_2 slurry of $Rh_2Cl_4(dppm)_2$ does not lead to a reaction.

Attempts to find suitable conditions to form $Rh_2Cl_6(dppm)_2$ from $Rh_2Cl_4(dppm)_2$ in Cl_2 (liquid) led only to uncharacterized products. Again, the cisoid to transoid rearrangement of phosphines about the Rh-Rh vector can probably be cited as the principal impediment to the reaction, especially in view of the facile reaction of **2** to form **3** where such a geometrical rearrangement is not necessitated.

Acknowledgment. We thank the National Science Foundation for financial support and Steven K. Silber of this department for helpful discussions regarding $^{31}P\{^1H\}$ NMR spectroscopy. We are also grateful to Dr. R. Poli for useful discussions and assistance at the outset.

Supplementary Material Available: For the crystal structures of **2** and **4**, full tables of crystal parameters and details of data collection and refinement, bond distances, bond angles, and anisotropic displacement parameters (34 pages); tables of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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Oxidation States Available to the $Ru_2{}^{n+}$ Core in Tetracarboxylato-Bridged Species

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Prompted by reports of the preparation and properties of two $Ru_2(O_2CR)_4{}^{2+}$ type compounds, we prepared a diruthenium propionate (**1**) by using the method given for the two alleged $Ru_2(O_2CR)_4{}^{2+}$ compounds. The crystal structure study of **1** showed that it was $Ru_2(O_2CCH_2CH_3)_5$, instead of $Ru_2(O_2CCH_2CH_3)_6$. This led us to reinvestigate the two previously described substances. A reanalysis of the structure data for a reported $Ru_2(O_2CCH_3)_6 \cdot 0.7H_2O$ compound, as well as measurements of its spectral, electrochemical and magnetic properties indicated that it was actually $Ru_2(O_2CCH_3)_4 \cdot (CH_3CO_2)_2H \cdot 0.7H_2O$ (**3**). A crystal structure study revealed that another type of compound obtained by the reported method was actually $Ru_2(O_2CCF_3)_5$ (**2**). Our work shows that so far there is no evidence for the existence of $Ru_2(O_2CR)_4{}^{2+}$ type complexes. Crystal data for new compounds are as follows. **1**: space group $P2_12_12_1$; $a = 13.843$ (3) Å, $b = 17.189$ (5) Å, $c = 8.758$ (1) Å, $V = 2084.0$ (8) Å^3, $Z = 4$. **2**: space group $C2/c$; $a = 12.628$ (5) Å, $b = 11.771$ (5) Å, $c = 13.563$ (4) Å, $\beta = 106.98$ (4)°, $V = 1928$ (2) Å^3, $Z = 4$.

Introduction

The existence of Ru-Ru multiple bonding was first recognized in the compound $Ru_2(O_2CC_3H_7)_4Cl$ in 1969[1] although the preparation of this and similar compounds had been reported several years earlier.[2] The first detailed examination of the magnetic and redox properties of this compound was reported only in 1975,[3] and it was not until 1979 that a detailed theoretical study appeared.[4] The voltammetric study of redox properties showed that reduction occurs in the range 0.00 to -0.34 V (vs SCE), with

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[1] Bennett, M. J.; Caulton, K. G.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 1.

[2] Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2285.

[3] Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 388.

[4] Norman, J. G.; Renzoni, G. E.; Case, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5256.

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the exact potential depending upon the concentration of Cl^- ion present. No oxidation process was observed until, at +1.6 V and above, complex, irreversible waves were observed. Thus, it appeared that $Ru_2(O_2CR)_4$ species ought to be obtainable but that $Ru_2(O_2CR)_4^{2+}$ compounds would probably not be.

In spite of the apparently favorable prognosis, in 1975, for the preparation of $Ru_2(O_2CR)_4$ compounds, it was not until 10 years later that the first ones were reported;[5] more recently some of their reactions have been described.[6] In addition to the reported method for making $Ru_2(O_2CR)_4$ compounds, there are others.[7] On the other hand, in view of the distinct counterindication from the electrochemical study, one might have expected not to have seen any report of the preparation and characterization of compounds containing $Ru_2(O_2CR)_4^{2+}$ moieties. However, two such reports have recently appeared, one[8] giving a fairly complete description, including a crystal structure of a substance formulated as $Ru_2(O_2CCH_3)_6 \cdot 0.7H_2O$ and the other[9] describing in less detail (no structure) a compound formulated as $Ru_2(O_2CCH_3)_2(O_2CCF_3)_4(H_2O)_2$.

Because the existence and properties of $Ru_2(O_2CR)_4^{2+}$ type compounds seemed to us to be of exceptional interest and importance (and also to be difficult to reconcile with the earlier electrochemistry), we undertook the preparation of what we hoped would be a homologue of those reported, namely, $Ru_2(O_2CC_2H_5)_6$, employing the preparative method given for the two earlier ones. However, we soon found that our compound was actually $Ru_2(O_2CC_2H_5)_5$. This led us to reinvestigate the two previously described substances with the result that they too are complexes of Ru_2^{5+} and not Ru_2^{6+}.

Experimental Section

Cyclic voltammetry studies were done in MeOH with tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. The reference electrode was Ag/AgCl; working and auxiliary electrodes were Pt. Under the experimental conditions the $E_{1/2}$ for the ferrocene/ferrocenium couple was at +0.40 V. The instrument used was a BAS-100 electrochemical analyzer. UV-vis spectra were recorded on a Cary 17 instrument on MeOH solutions. The magnetic susceptibility of 3 was measured on a Johnson Matthey magnetometer. All the chemicals were of reagent grade and were used as received.

$Ru_2(O_2CCH_3)_4Cl$ was prepared by using a literature method,[10] and from this $Ru_2(O_2CCH_2CH_3)_4Cl$ was prepared by using a carboxylate-exchange procedure. $Ru_2(O_2CCH_3)_4Cl$ (0.764 g) and LiCl (3.27 g) were refluxed in a mixture of $C_2H_5CO_2H$ (7.6 mL) and H_2O (38 mL) under an oxygen-free atmosphere for 3 h. The resulting brown crystalline product was washed with 3 × 10 mL of H_2O and dried under the vacuum. The yield was 97%.

Preparation of $Ru_2(O_2CCH_2CH_3)_5$ (1). $Ru_2(O_2CCH_2CH_3)_4Cl$ (0.0457 g) and AgO_2CCH_3 (0.015 g) were stirred in a mixture of $HO_2CCH_2CH_3$ (1.5 mL) and CH_3OH (5 mL) at ca. 50 °C and in the air for 2 h. After a white precipitate (AgCl) was removed, the reddish brown solution was concentrated slowly in the air. Reddish brown single crystals were formed in a yield of 67% over a period of a week.

Preparation of $Ru_2(O_2CCF_3)_5$ (2). The literature method employed for preparation of so-called $Ru_2(O_2CCH_3)_2(O_2CCF_3)_4(H_2O)_2$[9] was used. $Ru_2(O_2CCH_3)_4Cl$ (0.40 g) and AgO_2CCF_3 (0.19 g) were refluxed in HO_2CCF_3 (30 ml) in the air for 0.5 h. AgCl (0.115 g) was filtered off, and the remaining red solution was concentrated in the air. Many brown crystals were formed when the volume of the solution was reduced to about 20 mL.

Preparation and Properties of "$Ru_2(O_2CCH_3)_6 \cdot 0.7H_2O$". We found that the procedure[8] described for the preparation of this substance worked well. We have no reason to doubt that the substance we obtained is the same one reported and assigned the above formula.[8] A typical preparation proceeded as follows.

Table I. Crystallographic Data for **1** and **2**

formula	$Ru_2C_{15}H_{25}O_{10}$	$Ru_2C_{10}F_{15}O_{10}$
fw	567.50	767.22
space group	$P2_12_12_1$	$C2/C$
syst abs	$h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$	hkl, $h + k \neq 2n$; $h0l$, h, $l \neq 2n$
a, Å	13.843 (3)	12.628 (5)
b, Å	17.189 (5)	11.771 (5)
c, Å	8.758 (1)	13.563 (4)
α, deg	90	90
β, deg	90	106.98 (4)
γ, deg	90	90
V, Å^3	2084.0 (8)	1928 (2)
Z	4	4
d_{calc}, g/cm^3	1.809	2.643
cryst size, mm	0.3 × 0.1 × 0.1	0.15 × 0.15 × 0.1
μ(Mo Kα), cm^{-1}	14.67	17.27
data colln instrum	Rigaku AFC5R	Enraf-Nonius CAD-4
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	
orientation reflcns: no; range (2θ), deg	25; 27.9–46.5	25; 20.6–32.0
temp, °C	20 ± 1	−80
scan method	$\omega-2\theta$	ω
data colln range (2θ), deg	$4 < 2\theta < 55$	$4 < 2\theta < 50$
no. of unique data; tot. no. with $F_o^2 > 3\sigma(F_o^2)$	2743; 1530	1966; 1121
no. of params refined	202	186
R^a	0.0574	0.0566
R_w^b	0.0794	0.0704
quality-of-fit indicator^c	1.50	1.91
largest shift/esd, final cycle	0.11	0.02
largest peak, e/Å^3	0.848	0.469

[a] $R = \sum||F_o| - |F_c|| / \sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2 / (N_{observns} - N_{params})]^{1/2}$.

Table II. Positional Parameters and Their Estimated Standard Deviations For $Ru_2(O_2CCH_2CH_3)_5$

atom	x	y	z	B,^{a} Å^2
Ru(1)	0.2982 (1)	0.6863 (1)	0.8570 (1)	2.56 (2)
Ru(2)	0.3053 (1)	0.6884 (1)	0.5977 (1)	2.77 (2)
O(1)	0.2745 (9)	0.8019 (7)	0.856 (1)	3.4 (3)
O(2)	0.1532 (9)	0.6694 (8)	0.842 (1)	3.6 (3)
O(3)	0.325 (1)	0.5723 (7)	0.853 (1)	3.7 (3)
O(4)	0.441 (1)	0.705 (1)	0.866 (1)	4.4 (3)
O(5)	0.283 (1)	0.8049 (9)	0.604 (1)	4.5 (3)
O(6)	0.1627 (9)	0.6677 (8)	0.589 (1)	3.7 (3)
O(7)	0.332 (1)	0.5730 (8)	0.597 (1)	4.2 (3)
O(8)	0.4460 (9)	0.7080 (8)	0.610 (1)	3.3 (3)
O(9)	0.2890 (9)	0.688 (1)	1.103 (1)	4.4 (3)
O(10)	0.303 (1)	0.7001 (8)	0.351 (1)	3.9 (3)
C(1)	0.272 (2)	0.837 (1)	0.725 (2)	4.0 (4)
C(2)	0.254 (2)	0.927 (2)	0.731 (3)	7.5 (7)*
C(3)	0.218 (3)	0.959 (3)	0.883 (5)	5 (1)*
C(3′)	0.189 (7)	0.951 (6)	0.67 (1)	18 (4)*
C(4)	0.113 (1)	0.664 (1)	0.724 (2)	4.0 (4)
C(5)	0.009 (2)	0.655 (1)	0.700 (2)	4.3 (4)*
C(6)	−0.050 (2)	0.642 (2)	0.837 (3)	6.9 (7)*
C(7)	0.337 (1)	0.537 (1)	0.722 (2)	3.7 (4)
C(8)	0.372 (2)	0.454 (1)	0.722 (2)	4.4 (4)*
C(9)	0.474 (2)	0.446 (2)	0.756 (4)	7.4 (7)*
C(10)	0.490 (1)	0.710 (1)	0.736 (3)	4.9 (5)
C(11)	0.597 (2)	0.722 (1)	0.751 (3)	5.7 (5)*
C(12)	0.643 (3)	0.646 (2)	0.700 (5)	4.0 (8)*
C(12′)	0.649 (3)	0.650 (3)	0.805 (5)	5 (1)*
C(13)	0.324 (1)	0.6708 (9)	1.228 (2)	3.1 (4)
C(14)	0.429 (2)	0.628 (2)	0.228 (4)	7.8 (8)*
C(15)	0.412 (3)	0.559 (3)	1.205 (5)	14 (1)*

[a] Starred values denote isotropically refined atoms. Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2 b_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac)\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

$Ru_2(O_2CCH_3)_4Cl$ (0.94 g, 2 mmol), CH_3COOAg (0.33 g, 2 mmol), 20 mL of CH_3COOH, and 8 mL of MeOH were refluxed in air for 8 h. The reaction mixture was cooled and filtered through a short Celite column. The column was washed with MeOH to remove the remaining compound. The solution was evaporated to dryness under vacuum to give 0.90 g (80%) of the red-brown product. The UV-vis spectrum is presented in Figure 5 and agrees well with that reported by McCann.[8] The

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(5) Lindsay, A. J.; Motevalli, M.; Hursthouse, M. B.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1985**, 2321.

(6) Lindsay, A. J.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 2723.

(7) Zhong, B., unpublished work.

(8) Drew, M. G. B.; Higgins, P.; McCann, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1385.

(9) Higgins, P.; McCann, G. M. *J. Chem. Soc., Dalton Trans.* **1988**, 661.

(10) Mitchell, R. W.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 846.

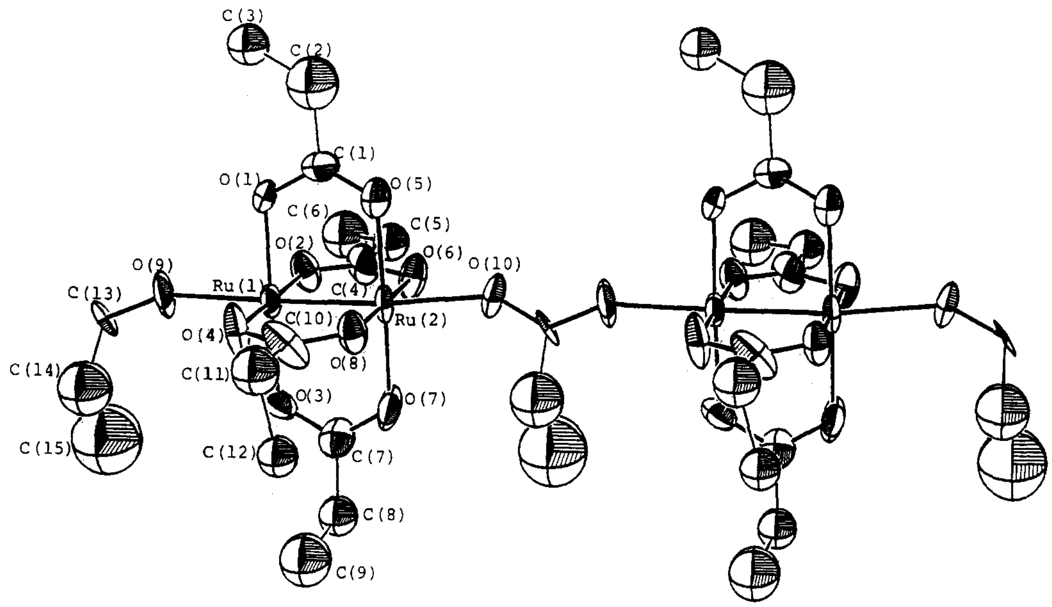

Figure 1. ORTEP drawing of two $Ru_2(O_2CCH_2CH_3)_5$ molecules in an infinite chain. There are two disordered positions for C(3) and for C(12), and only one set of positions are shown in the drawing.

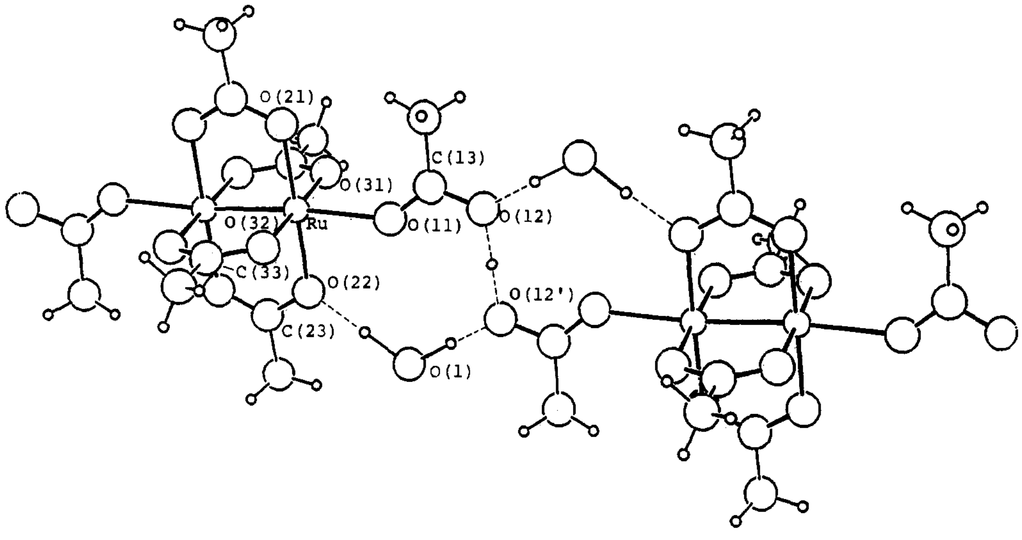

Figure 2. ORTEP drawing of two $Ru_2(O_2CCH_3)_4{\cdot}(CH_3CO_2)_2H{\cdot}0.7H_2O$ molecules. Arbitrary radii are used for all atoms. The positions of the two hydrogen atoms on O(1) are arbitrary. Selected distances and angles: Ru–O(11) = 2.243, O(11)–C(13) = 1.222, O(12)–C(13) = 1.298, O(12)–O(12′) = 2.469, O(12′)–O(1) = 2.669, O(1)–O(22) = 2.829 Å; O(12′)–O(12)–C(13) = 117.7, O(12)–O(12′)–O(1) = 110.5, O(12′)–O(1)–O(22) = 118.3, Ru–O(22)–O(1) = 123.8, O(1)–O(22)–C(23) = 116.6°.

reaction was repeated several times, both in air and under anaerobic conditions, with the same results; i.e., AgCl was formed, and a simple ligand exchange took place. The cyclic voltammogram of "$Ru_2(O_2CCH_3)_6$"$\cdot 0.7H_2O$ is given in Figure 6. Within the solvent limits we observed only one reduction with $E_{1/2} = -0.01$ V ($I_c/I_a \approx 1$) versus Ag/AgCl, which is indicative of the presence of the Ru_2^{5+} core. We could not reproduce the cyclic voltammetry results reported by McCann.[8]

X-ray Crystallography. The crystal structures of **1** and **2** were obtained by using the general procedures described elsewhere.[11] The crystal parameters and the information concerning the data collection and structure refinement are summarized in Table I. Complete tables of anisotropic thermal parameters, bond distances, bond angles, and structure factor data are available as supplementary material.

Results and Discussion

Table II records the atomic positional and thermal parameters for compound **1**. Selected bond distances and angles are presented in Table III, and Figure 1 shows the ORTEP drawing of **1**. Two atoms, C(3) and C(12), are disordered. The drawing shows only one of the two sets of disordered positions. Each dimer has four carboxylate groups as bridging ligands and shares two axial propionates with two other dimers to form an infinite chain. It is obvious that the compound has a Ru_2^{5+} core rather than a Ru_2^{6+} core as claimed for a diruthenium acetate[8] prepared under the same conditions. Naturally, this raised a question as to the true identity of the reported $Ru_2(O_2CCH_3)_6$.

Reexamination of the structure of the acetate employing the original atomic coordinates obtained by Drew et al.[12] leads unambiguously to the conclusion that the compound is actually $Ru_2(O_2CCH_3)_4(CH_3CO_2)_2H{\cdot}0.7H_2O$. As shown in the ORTEP drawing of this structure (Figure 2), there must be a proton sitting at the crystal inversion center between O(12) and O(12′) because the distance between these oxygen atoms is only 2.469 Å, which is too short for a nonbonded intermolecular distance, but perfect for a symmetric hydrogen bond. Furthermore, the C(13)–O(12) bond is longer than the C(13)–O(11) bond, which indicates also that O(12) is involved in a hydrogen bond. We also found that

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[11] Bino, A.; Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1979**, *18*, 2599.

[12] The atomic positional parameters were obtained from the Cambridge Crystallographic Data Center.

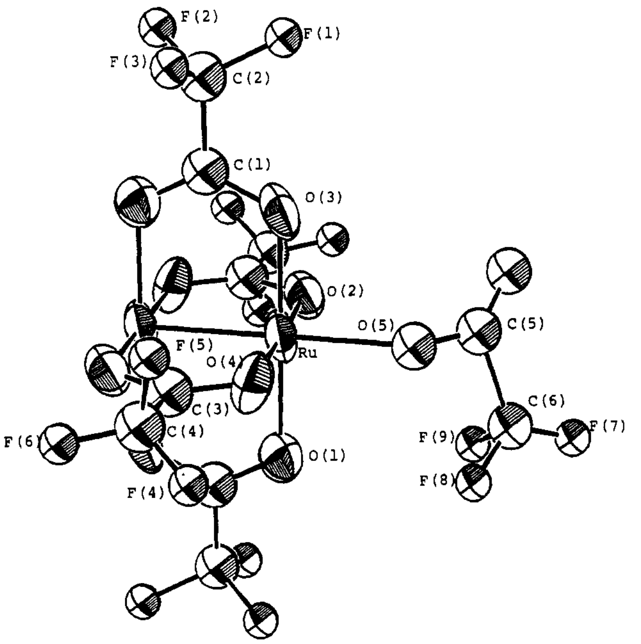

Figure 3. ORTEP drawing of $Ru_2(O_2CCF_3)_5$. Ru, O(1), O(2), O(3), and O(4) are represented by their thermal parameters. The other atoms have arbitrary atomic radii. The unlabeled atoms are generated by the inversion center between the two Ru atoms. C(5) sits on a 2-fold axis, and C(6), F(7), F(8), and F(9) are disordered. Only one of the two sets of positions of those atoms are shown.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $Ru_2(O_2CCH_2CH_3)_5$[a]

	Distances		
Ru(1)–Ru(2)	2.273 (1)	O(1)–C(1)	1.30 (2)
Ru(1)–O(1)	2.013 (12)	O(2)–C(4)	1.17 (2)
Ru(1)–O(2)	2.032 (12)	O(3)–C(7)	1.31 (2)
Ru(1)–O(3)	1.995 (12)	O(4)–C(10)	1.32 (3)
Ru(1)–O(4)	2.010 (13)	O(5)–C(1)	1.21 (2)
Ru(1)–O(9)	2.157 (10)	O(6)–C(4)	1.37 (2)
Ru(2)–O(5)	2.026 (15)	O(7)–C(7)	1.25 (2)
Ru(2)–O(6)	2.008 (13)	O(8)–C(10)	1.26 (3)
Ru(2)–O(7)	2.017 (15)	O(9)–C(13)	1.24 (2)
Ru(2)–O(8)	1.979 (13)	O(10)–C(13)	1.22 (2)
Ru(2)–O(10)	2.172 (10)		
	Angles		
Ru(2)–Ru(1)–O(1)	89.3 (3)	O(5)–Ru(2)–O(10)	86.1 (5)
Ru(2)–Ru(1)–O(2)	88.8 (3)	O(6)–Ru(2)–O(7)	90.3 (6)
Ru(2)–Ru(1)–O(3)	89.4 (4)	O(6)–Ru(2)–O(8)	179.1 (5)
Ru(2)–Ru(1)–O(4)	89.6 (3)	O(6)–Ru(2)–O(10)	88.0 (5)
Ru(2)–Ru(1)–O(9)	178.2 (4)	O(7)–Ru(2)–O(8)	89.4 (6)
O(1)–Ru(1)–O(2)	88.9 (6)	O(7)–Ru(2)–O(10)	95.3 (5)
O(1)–Ru(1)–O(3)	178.2 (5)	O(8)–Ru(2)–O(10)	92.8 (5)
O(1)–Ru(1)–O(4)	90.0 (6)	Ru(1)–O(1)–C(1)	118 (1)
O(1)–Ru(1)–O(9)	89.0 (5)	Ru(1)–O(2)–C(4)	122 (1)
O(2)–Ru(1)–O(3)	92.3 (6)	Ru(1)–O(3)–C(7)	120 (1)
O(2)–Ru(1)–O(4)	178.0 (5)	Ru(1)–O(4)–C(10)	119 (1)
O(2)–Ru(1)–O(9)	90.6 (5)	Ru(2)–O(5)–C(1)	119 (1)
O(3)–Ru(1)–O(4)	88.8 (6)	Ru(2)–O(6)–C(4)	118 (1)
O(3)–Ru(1)–O(9)	92.3 (6)	Ru(2)–O(7)–C(7)	120 (1)
O(4)–Ru(1)–O(9)	91.0 (5)	Ru(2)–O(8)–C(10)	122 (1)
Ru(1)–Ru(2)–O(5)	89.1 (3)	Ru(1)–O(9)–C(13)	150 (1)
Ru(1)–Ru(2)–O(6)	89.7 (3)	Ru(2)–O(10)–C(13)	147 (1)
Ru(1)–Ru(2)–O(7)	89.6 (3)	O(1)–C(1)–O(5)	125 (2)
Ru(1)–Ru(2)–O(8)	89.5 (3)	O(2)–C(4)–O(6)	121 (2)
Ru(1)–Ru(2)–O(10)	174.6 (4)	O(3)–C(7)–O(7)	121 (2)
O(5)–Ru(2)–O(6)	91.6 (6)	O(4)–C(10)–O(8)	120 (2)
O(5)–Ru(2)–O(7)	177.7 (6)	O(9)–C(13)–O(10)	126 (2)
O(5)–Ru(2)–O(8)	88.7 (6)		

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

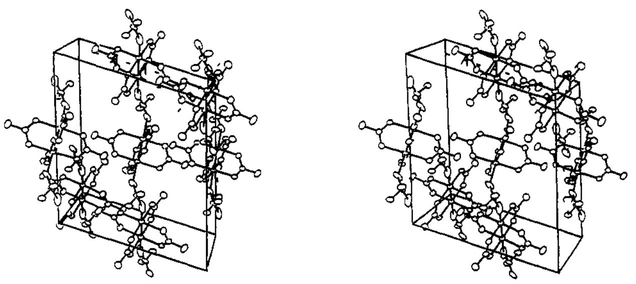

Figure 4. Stereo ORTEP drawing of the unit cell of $Ru_2(O_2CCF_3)_5$. The F atoms are omitted for clarity. Both of the two sets of positions of disordered C(6) are shown.

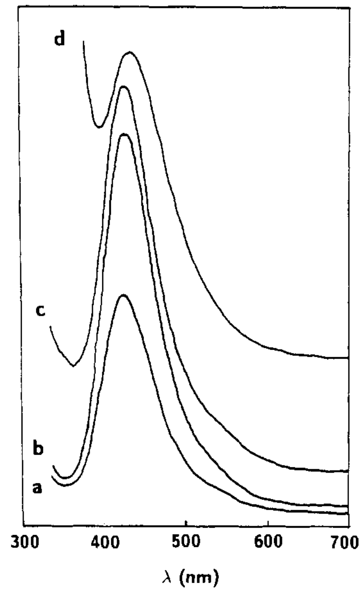

Figure 5. Electronic spectra of diruthenium carboxylates in methanol (λ_{max} in nm): (a) $Ru_2(O_2CCH_3)_4{\cdot}(CH_3CO_2)_2H{\cdot}0.7H_2O$ (424); (b) $Ru_2(O_2CCH_3)_4Cl$(427); (c) $Ru_2(O_2CCH_2CH_3)_5$ (426); (d) $Ru_2(O_2CCF_3)_5$ (438).

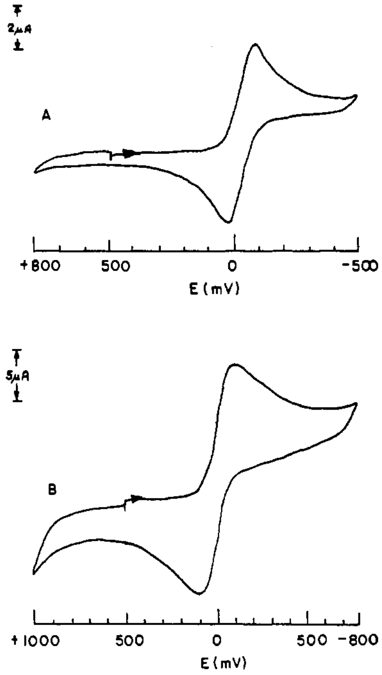

Figure 6. Cyclic voltammograms for **1** (upper) and **3** (lower).

the water molecule is bonded to O(22) and O(12′) via hydrogen bonding. There are five hydrogen bonds between each pair of the dimers, and those hydrogen bonds connected all dimers to form infinite chains.

In our preparative work on both **1** and **3**, we have carried out equally successful preparations, giving about the same yields, regardless of (a) whether the reactions were done in air or in an

Table IV. Positional Parameters and Their Estimated Standard Deviations for $Ru_2(O_2CCF_3)_5$

atom	*x*	*y*	*z*	*B*,[a] Å^2
Ru	0.98751 (7)	0.06413 (8)	0.43470 (6)	4.07 (2)
F(1)	1.1313 (9)	0.2232 (8)	0.8030 (6)	10.8 (3)
F(2)	1.082 (1)	0.3429 (8)	0.6848 (8)	11.9 (4)
F(3)	1.2331 (8)	0.266 (1)	0.7111 (9)	14.7 (4)
F(4)	1.3378 (9)	−0.154 (1)	0.495 (1)	19.6 (5)
F(5)	1.376 (2)	−0.011 (2)	0.555 (2)	36 (1)
F(6)	1.3303 (9)	−0.020 (1)	0.411 (1)	24.4 (4)
F(7)	1.075 (2)	0.414 (1)	0.255 (1)	11.2 (6)
F(8)	0.995 (1)	0.375 (1)	0.359 (1)	10.0 (4)
F(9)	1.140 (2)	0.339 (2)	0.371 (2)	15.7 (8)
O(1)	1.0516 (5)	0.1873 (6)	0.5399 (5)	4.8 (2)
O(2)	1.1419 (6)	0.0308 (6)	0.4292 (5)	4.5 (2)
O(3)	0.9237 (6)	−0.0593 (7)	0.3314 (5)	5.0 (2)
O(4)	0.8329 (6)	0.0969 (6)	0.4436 (6)	4.9 (2)
O(5)	0.9671 (8)	0.1865 (9)	0.3122 (7)	13.2 (3)
C(1)	1.0824 (9)	0.160 (1)	0.6322 (8)	5.6 (3)
C(2)	1.137 (1)	0.248 (1)	0.708 (1)	6.7 (4)
C(3)	1.1984 (9)	−0.043 (1)	0.4885 (8)	5.0 (3)
C(4)	1.310 (1)	−0.062 (1)	0.481 (1)	6.8 (3)
C(5)	1.000	0.224 (1)	0.250	5.0 (4)
C(6)	1.040 (2)	0.349 (2)	0.297 (2)	5.8 (6)

[a] All atoms were refined anisotropically. Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table V. Selected Bond Distances (Å) and Angles (deg) for $Ru_2(O_2CCF_3)_5$[a]

	Distances		
Ru–Ru	2.278 (1)	O(1)–C(1)	1.240 (12)
Ru–O(1)	2.029 (7)	O(2)–C(3)	1.258 (12)
Ru–O(2)	2.012 (7)	O(3)–C(1)	1.297 (15)
Ru–O(3)	2.015 (7)	O(4)–C(3)	1.271 (14)
Ru–O(4)	2.028 (8)	O(5)–C(5)	1.134 (12)
Ru–O(5)	2.157 (10)		
	Angles		
Ru–Ru–O(1)	89.5 (2)	O(3)–Ru–O(4)	89.0 (3)
Ru–Ru–O(2)	89.1 (2)	O(3)–Ru–O(5)	90.7 (3)
Ru–Ru–O(3)	90.0 (2)	O(4)–Ru–O(5)	91.0 (4)
Ru–Ru–O(4)	89.8 (2)	Ru–O(1)–C(1)	117.9 (8)
Ru–Ru–O(5)	178.9 (3)	Ru–O(2)–C(3)	119.1 (8)
O(1)–Ru–O(2)	88.5 (3)	Ru–O(3)–C(1)	116.8 (6)
O(1)–Ru–O(3)	179.4 (3)	Ru–O(4)–C(3)	117.2 (6)
O(1)–Ru–O(4)	90.9 (3)	Ru–O(5)–C(5)	147.9 (9)
O(1)–Ru–O(5)	89.9 (3)	O(1)–C(1)–O(3)	126 (1)
O(2)–Ru–O(3)	91.6 (3)	O(2)–C(3)–O(4)	125 (1)
O(2)–Ru–O(4)	178.8 (3)	O(5)–C(5)–O(5)	134 (2)
O(2)–Ru–O(5)	90.0 (4)		

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

inert atmosphere and (b) whether we used 1 equiv of $Ag(O_2CCH_3)$ or 2 equiv. These results clearly show that no oxidation is occurring, either by action of O_2 or by action of Ag^+. The silver acetate is used simply to remove a chloride ion according to

$$Ru_2(O_2CR)_4Cl + Ag^+ + R'CO_2^- \rightarrow AgCl + Ru_2(O_2CR)_4(O_2CR')$$

We also reinvestigated the reported $Ru_2(O_2CCH_3)_2(O_2CCF_3)_4(H_2O)_2$, another alleged Ru_2^{6+} compound.[9] The reported preparative procedure[9] was used for the synthesis of compound **2** except that we stopped evaporating the red solution when we observed the formation of reddish brown crystals. We solved the structure for this compound, since its structure had not been done. Again, it is a Ru_2^{5+} complex instead of a Ru_2^{6+} complex. The atomic positional and thermal parameters and selected bond distances and angles are presented in Tables IV and V. Like **1**, $Ru_2(O_2CCF_3)_5$ dimers form infinite chains by sharing axial trifluoroacetate groups. The ORTEP drawing (Figure 3) only shows one unit in a chain. There is an inversion center in the midpoint of the Ru–Ru bond and a 2-fold axis containing C(5). The CF_3 group on C(5) is disordered. Figure 4 shows the chains in a unit cell. The Ru–O(5) bond distance (2.157 Å) is significantly longer than that between Ru and bridging O's (ca. 2.02 Å), so it may be easier to replace an axial ligand than a bridging one. When the red solution is evaporated to a very small volume as in ref 9, the concentration of HO_2CCH_3 will become larger due to the higher boiling point of HO_2CCH_3; therefore, the axial O_2CCF_3 might be replaced by O_2CCH_3 to form $Ru_2(O_2CCF_3)_4O_2CCH_3$ or $Ru_2(O_2CCF_3)_4{\cdot}2(CH_3CO_2)_2H$, both of which are consistent with the mass spectrometric results reported in ref 9.

Even before we had obtained the crystallographic data for **3**, which prove, conclusively, by themselves that this compound contains a Ru_2^{5+} core, we had obtained strong evidence of this from its spectroscopic, electrochemical and magnetic properties. Its UV–vis spectrum in MeOH solution is essentially identical with that of **1**, and both of them closely resemble previously reported spectra[4] for Ru_2^{5+} compounds. Figure 5 shows four such spectra, including those of **1**–**3**. Our spectrum for **3** is the same as that reported in ref 8. Second, the magnetic susceptibility given in ref 8, which does differ appreciably from that expected for the three unpaired electrons typically found in $Ru_2(O_2CR)_4X$ species, was not found in this laboratory. Instead, we measured a susceptibility at ca. 25 °C from which a magnetic moment of 3.86 μ_B is obtained, in excellent accord with the expectation[3] for a $Ru_2(O_2CR)_4X$ compound.

Finally, the cyclic voltammograms (CVs) of **1**–**3** are all very similar (see Figure 6 for those of **1** and **3**) and in accord with expectation. The CV we obtain for **3** is not in agreement with that in ref 8.

We conclude that removing Cl^- from $Ru_2(O_2CR)_4Cl$ by adding Ag^+ in HO_2CR' results in a simple axial ligand exchange to form $Ru_2(O_2CR)_4O_2CR'$ or $Ru_2(O_2CR)_4(R'CO_2)_2H$ rather than in oxidation of Ru_2^{5+} to Ru^{6+}. The early contraindication of the accessibility of $Ru_2(O_2CR)_4^{2+}$ compounds, mentioned in the Introduction, appears to have been entirely reliable.

Acknowledgment. We thank the National Science Foundation for support and J. Czuchajowska for measuring the magnetic susceptibility.

Supplementary Material Available: Tables of anisotropic displacement parameters and bond distances and bond angles for **1** and **2** and a stereo packing diagram for **1** (10 pages); tables of observed and calculated structure factors for **1** and **2** (14 pages). Ordering information is given on any current masthead page.