# SYNTHESIS AND PROPERTIES OF SOME DIRUTHENIUM ACETATE COMPOUNDS

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Abstract—The compound  $[Ru_2(\mu-O_2CCH_3)_4(THF)_2]BF_4$  (I) containing the  $Ru_2^{5+}$  unit was prepared by reaction of  $Ru_2Cl(\mu-O_2CCH_3)_4$  with AgBF<sub>4</sub> in THF. This compound, in contrast with  $Ru_2Cl(\mu-O_2CCH_3)_4$ , is soluble in several polar organic solvents and reacts in THF with OPPh<sub>3</sub> and PPh<sub>3</sub> giving  $[Ru_2(\mu-O_2CCH_3)_4(OPPh_3)_2]BF_4 \cdot CH_2Cl_2$  (II) and  $[Ru(\mu-O_2CCH_3)(O_2CCH_3)(PPh_3)]_n$  (III), respectively. The complex II has been also obtained as hexafluorophosphate  $[Ru_2(\mu-O_2CCH_3)_4(OPPh_3)_2]PF_6 \cdot CH_2Cl_2$  (IV) by treatment of  $Ru_2Cl(\mu-O_2CCH_3)_4$  with an excess of NOPF<sub>6</sub> and PPh<sub>3</sub> in methanol. In this reaction the triphenylphosphine oxide is generated by oxidation of the triphenylphosphine.

Several diruthenium compounds of the type  $Ru_2ClL_4$  (L = carboxylate, amidate, etc.) have been prepared.<sup>1-6</sup> However, very few examples of complexes containing the  $Ru_2^{4+7-9}$  and  $Ru_2^{6+5,10}$  units are known.

Thus, Wilkinson *et al.*<sup>7</sup> have obtained diruthenium(II,II) tetracarboxylates  $Ru_2(\mu-O_2CR)_4$ (R = H, Me, CH<sub>2</sub>Cl, Et, Ph) by interaction of the reduced "blue solutions" of ruthenium chloride in methanol with alkali-metal carboxylates. The reactivity of these compounds and their adducts towards anionic ligands, donor ligands and oxidizing agents have also been reported. More recently, Drew *et al.*<sup>10</sup> have isolated the complex  $Ru_2(\mu-O_2CCH_3)_4(O_2CCH_3)_2$ ·H<sub>2</sub>O by reaction of  $Ru_2$  $Cl(\mu-O_2CCH_3)_4$  with AgO<sub>2</sub>CCH<sub>3</sub> in HO<sub>2</sub>CCH<sub>3</sub>/ MeOH; this is the first example of a tetra- $\mu$ carboxylate diruthenium(III,III) compound.

However, the low solubility of  $Ru_2Cl(\mu-O_2CCH_3)_4$  is a problem in the study of the reactivity of the  $[Ru_2(\mu-O_2CCH_3)_4]^+$  unit. Here we report the synthesis and characterization of the complex  $[Ru_2(\mu-O_2CCH_3)_4(THF)_2]BF_4$  (I), which is soluble in most common polar organic solvents. We have studied also the reactions of complex I with a  $\sigma$ donor ligand, triphenylphosphine oxide and a  $\sigma$ donor- $\pi$ -acceptor ligand, triphenylphosphine.

On the other hand, we have examined the reac-

tion of  $Ru_2Cl(\mu-O_2CCH_3)_4$  with the oxidizing agent, NOPF<sub>6</sub>, in the presence of PPh<sub>3</sub>.

## **RESULTS AND DISCUSSION**

The reaction of  $Ru_2Cl(\mu-O_2CCH_3)_4$  and  $AgBF_4$ (1:1 mole ratio) in THF, under a dinitrogen atmosphere, leads to the formation of  $[Ru_2(\mu-O_2CCH_3)_4$ (THF)<sub>2</sub>]BF<sub>4</sub> (I) in high yield. The product was obtained as red crystals, is soluble in common polar organic solvents and loses THF in air in short periods of time.

The IR spectrum of I in a KBr disc shows strong absorption bands at 1460 and 1400  $\text{cm}^{-1}$  assigned to the antisymmetric and the symmetric v(COO)stretching vibrations, respectively. The separation between these bands may indicate the symmetrical coordination of the carboxylate groups. A strong absorption band at 1070 cm<sup>-1</sup> is assigned to the vibration of the  $BF_4^-$  group; no absorption bands due to the THF ligand were found in this spectrum. However, if the IR spectrum is registered in Nujol mull, a strong absorption at 870  $\text{cm}^{-1}$ , due to the coordinated THF, is observed. This facile loss of the weakly coordinated axial THF ligand has been also observed by Wilkinson *et al.*<sup>7</sup> in the complex  $Ru_2(\mu-O_2CCH_3)_4(THF)_2$ , but a good analysis could not be obtained.

The reaction of I with  $OPPh_3$  (1:2 mole ratio) in THF or toluene, gives a red solid in high yield. The crystallization of this red solid from di-

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chloromethane-petroleum ether (40-60°C) gives redbrown crystals of  $[Ru_2(\mu-O_2CCH_3)_4(OPPh_3)_2]BF_4$  · CH<sub>2</sub>Cl<sub>2</sub> (II).

The IR spectrum of II exhibits characteristic bands of bridging acetate groups at 1450 and 1400 cm<sup>-1</sup> corresponding to v(COO) stretching frequencies; the v(B—F) stretching of the BF<sub>4</sub> group appears at 1080 cm<sup>-1</sup>; the v(P=O) stretching band of the OPPh<sub>3</sub> ligand is observed at 1140 cm<sup>-1</sup>; this band appears at lower frequencies (*ca* 53 cm<sup>-1</sup>) than that of the free ligand. The presence of CH<sub>2</sub>Cl<sub>2</sub> in this compound shows in the <sup>1</sup>H NMR spectrum ( $\delta = 5.23$  ppm, s); the <sup>1</sup>H NMR spectrum of this paramagnetic compound shows the signals corresponding to the CH<sub>3</sub> protons ( $\delta = -5.29$  ppm, s) and the C<sub>6</sub>H<sub>5</sub> protons ( $\delta = 6.12-5.74$  ppm, m) which are shifted to higher fields, similar to other paramagnetic compounds.<sup>11</sup>

Compounds I and II in acetone solution (~  $10^{-3}$  M) have conductivities corresponding to those for 1:1 electrolytes ( $\Lambda_{\rm M} = 147.94$  and 140.63  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, respectively).

These complexes have the effective magnetic moments per dimer of 4.41 and 4.30 BM, respectively. The magnetic susceptibility measurements at various temperatures (Table 1) indicate that these compounds obey the Curie–Weiss law. These results are similar to those obtained for other carboxylate dimers containing the  $Ru_2^{5+}$  unit.<sup>1,12</sup> This is consistent with a  $\sigma^2 \pi^4 \delta^2 \pi^{*2} \delta^{*1}$  electronic configuration and three electrons unpaired per dimer.<sup>13</sup>

Complex I reacts with triphenylphosphine (1:2 mole ratio) to form a violet compound whose



elemental analysis is consistent with  $[Ru(\mu-O_2 CCH_3)(O_2CCH_3)(PPh_3)]_n$  (III). This compound is soluble in polar and non-polar organic solvents such as dichloromethane, THF, toluene, etc.

Complex III is diamagnetic. The IR spectrum shows four absorption bands in the carboxyl stretching region at 1470, 1415, 1565 and 1355 cm<sup>-1</sup> corresponding to bridging and unidentate acetates; this spectrum also shows the bands corresponding to PPh<sub>3</sub> groups. The <sup>1</sup>H NMR spectrum confirms the presence of two inequivalent acetates, showing two singlets for the methyl resonances at 1.74 and 1.69 ppm; the signal corresponding to the aromatic protons appears at 7.20–7.12 ppm.

The  ${}^{31}P{}^{1}H$  NMR spectrum exhibits only one resonance at 35.30 ppm for the PPh<sub>3</sub> ligands, which is consistent with only one type of phosphine in this compound.

The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum presents four signals due to acetate groups: two signals appearing at 182.53 and 181.82 ppm are assigned to COO, and two signals appearing at 22.92 and 22.07 ppm are assigned to the CH<sub>3</sub> group. These signals are consistent with bridging and terminal acetate groups. Some resonances corresponding to the phenyl groups appear as pseudoquintuplets at 133.94 and 127.64 ppm; this multiplicity may be due to coupling with three phosphorous atoms.

These spectroscopic data corresponding to complex III confirm the stoichiometry  $[Ru(\mu-O_2CCH_3)(O_2CCH_3)(PPh_3)]_n$  and suggest  $n \ge 3$ . Two possible structures, (a) and (b), for this compound are shown above.

Table 1. The magnetic susceptibilities for compounds I, II and IV at various temperatures

				[Ru <sub>2</sub> (μ-C	$_2$ CCH <sub>3</sub> ) <sub>4</sub>	(THF)2]E	8F4 (I)				
T (K)	294.9	288.8	259.5	229.7	199.9	174.9	150.2	125.2	100.4	90.5	85.1
$\chi_{M} \times 10^{3}$	8.349	8.124	9.226	10.450	11.680	13.730	16.110	19.280	23.070	25.070	26.720
			[Ru <sub>2</sub> (	μ-O <sub>2</sub> CCH		h <sub>3</sub> ) <sub>2</sub> ]BF₄·	$CH_2Cl_2$ (	II)			
T (K)	324.9	289.1	288.3	259.8	250.6	229.2	199.7	175.7	169.9	140.1	110.3
$\chi_{M} \times 10^{3}$	7.128	7.639	7.995	8.632	9.278	9.232	11.360	12.930	13.290	15.830	19.940
			[Ru <sub>2</sub> (	μ-O₂CCH	[₃)₄(OPPł	1 <sub>3</sub> ) <sub>2</sub> ]PF <sub>6</sub> ·	$CH_2Cl_2$	IV)			
T (K)	287.9	258.8	230.0	199.0	168.8	140.1	110.1	99.8	90.2	80.3	
$\chi_M \times 10^3$	7.113	8.070	9.198	10.660	18.690	15.240	19.100	20.840	22.940	26.470	

			Magnetic	Conductivity	IR data $(cm^{-1})$			
Compound	Colour	Analysis (%) Found (Calc.)	(BM)	$(\Omega^{-1} \text{ cm}^{-1})$	v <sub>a</sub> (COO)	v <sub>s</sub> (COO)	(L)	
I	red	C 25.1 (28.7) H 4.2 (4.2)	4.41	147.94	1460	1400	870 (THF)	
П	red-brown	C 47.0 (46.3) H 3.7 (3.8)	4.30	140.63	1445	1400	1140 (O=P)	
III	violet	C 54.0 (54.9) H 4.7 (4.4)			1470 1565	1415 1355	1100 (PPh <sub>3</sub> )	
IV	red-brown	C 44.8 (44.1) H 3.7 (3.6)	4.18	125.74	1445	1400	1140 (O=P)	

Table 2. Physical and IR spectroscopic properties of the compounds I-IV

Table 3. NMR data for the compounds II-IV

	<sup>1</sup> H NMR data (ppm)				<sup>13</sup> C NMR data (ppm)				
Compound	$\delta(O_2CCH_3)$	δ(L)	$\delta(CH_2Cl_2)$	data (ppm)	$\delta(O_2CCH_3)$	$\delta(O_2CCH_3)$	$\delta(L)$		
п	- 5.29(s)	5.93(m)	5.23(s)						
Ш	1.69(s) 1.74(s)	7.16(m)		35.30(s)	22.92(s) 22.07(s)	182.53(s) 181.82(s)	133.94(q) $J = 5.15$ Hz 131.03(d) $J = 44.99$ Hz 129.49(s) 127.67(q) $J = 5.16$ Hz		
IV	-5.28(s)	5.91(m)	5.23(s)						

This compound could be generated in a disproportionation reaction similar to that observed by Wilkinson *et al.*<sup>14</sup>

$$2Ru_{2}^{5+} \rightarrow Ru_{2}^{4+} + Ru_{2}^{6+},$$

followed by a reorganization process in the Ru(II)– Ru(II) complex. The disproportionation reaction would also explain why the yield of complex III is no more than 50%. The nature of the yellow Ru(III)– Ru(III) complex formed or its transformation products is still uncertain and is under study now.

The  $[Ru_2(\mu-O_2CCH_3)_4(OPPh_3)_2]PF_6 \cdot CH_2Cl_2$ complex (IV) has been obtained by reaction of  $Ru_2Cl(\mu-O_2CCH_3)_4$  with NOPF<sub>6</sub> and PPh<sub>3</sub> in excess, in methanol, and posterior crystallization in dichloromethane-petroleum ether (40–60°C). The use of NOPF<sub>6</sub> in this reaction does not produce the oxidation of the  $Ru_2^{5+}$  unit, but the triphenyl-phosphine is transformed into triphenylphosphine oxide.

The IR, NMR, conductivity and magnetic properties are similar to those of complex II described above (see Tables 2 and 3).

#### EXPERIMENTAL

All reactions were carried out in an inert atmosphere, using standard Schlenk techniques.  $Ru_2$   $Cl(\mu-O_2CCH_3)_4$  was prepared by the literature procedure.<sup>15</sup> RuCl<sub>3</sub>·3H<sub>2</sub>O, NOPF<sub>6</sub> and AgBF<sub>4</sub> were obtained from Johnson Matthey Chemicals Ltd, Ventron and Fluka, respectively. OPPh<sub>3</sub> and PPh<sub>3</sub> were obtained from Probus. Solvents were purified and distilled by standard methods. Methanol was used without previous purification.

Elemental microanalysis for C and H were performed by Elemental Microanalysis Ltd, Devon (U.K.). IR spectra in the region 4000–200 cm<sup>-1</sup> were recorded as KBr discs or Nujol mulls on a Perkin–Elmer 1330 IR spectrophotometer. NMR were recorded on Varian FT-80 or Bruker WM 360 spectrophotometers. Magnetic measurements were made with a magnetometer DSM 5 in the range 85– 295 K. Molar conductivities were measured with a Philips PW 9526 digital conductivity meter, using a Philips PW 9512/60 conductivity measuring cell.

## Synthesis of $[Ru_2(\mu - O_2CCH_3)_4(THF)_2]BF_4$ (I)

Ru<sub>2</sub>Cl( $\mu$ -O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub> (2.00 g, 4.22 mmol) and AgBF<sub>4</sub> (0.82 g, 4.22 mmol) were stirred in THF (80 cm<sup>3</sup>) for 24 h at room temperature, to give a red solution and a white precipitate of AgCl. The solution was filtered and the precipitate was washed with THF until colourless. The red solution and the combined extracts were reduced to 20 cm<sup>3</sup>, and petroleum ether was added to give a crystalline red solid. Yield 2.14 g, 75.7%.

Synthesis of  $[Ru_2(\mu-O_2CCH_3)_4(OPPh_3)_2]BF_4 \cdot CH_2$ Cl<sub>2</sub> (II)

To a solution of I (0.5 g, 0.75 mmol) in THF (30 cm<sup>3</sup>) or to a suspension of I (0.5 g, 0.75 mmol) in toluene (30 cm<sup>3</sup>), was added OPPh<sub>3</sub> (0.42 g, 1.50 mmol). The reaction mixture was stirred at room temperature for 4 h (12 h in toluene). The solvent was removed and the solid was washed with diethyl ether ( $3 \times 15$  cm<sup>3</sup>). The red solid was crystallized from dichloromethane-petroleum ether (40-60°C) as red-brown crystals. Yield 0.59 g, 67%.

Synthesis of  $[Ru(\mu-O_2CCH_3)(O_2CCH_3)(PPh_3)]_n$ (III)

To a solution of I (1 g, 1.49 mmol) in THF (50 cm<sup>3</sup>), was added PPh<sub>3</sub> (0.78 g, 2.99 mmol). The solution was stirred at room temperature for 4 h, and changed from red to violet. The solvent was removed to leave a dry residue, which was extracted with toluene ( $3 \times 20$  cm<sup>3</sup>). The combined extracts were treated with active C and filtered. The solvent was removed to give a microcrystalline solid which was washed with cold diethyl ether. Yield 0.46 g, 32%.

Synthesis of  $[Ru_2(\mu-O_2CCH_3)_4(OPPh_3)_2]PF_6 \cdot CH_2$ Cl<sub>2</sub> (IV)

To  $Ru_2Cl(\mu-O_2CCH_3)_4$  (0.5 g, 1.06 mmol) in methanol (30 cm<sup>3</sup>), was added an excess of NOPF<sub>6</sub> (0.56 g, 3.17 mmol) and PPh<sub>3</sub> (1.39 g, 5.28 mmol). The reaction mixture was stirred at room temperature for 6 h. The solvent was removed to leave a dry residue which was washed with diethyl ether and THF. The orange solid residue was crystallized from dichloromethane-petroleum ether (40- $60^{\circ}$ C) to give red-brown crystals. Yield 0.82 g, 63%.

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