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Polymeric Chain Cleavage Reactions in $Ru_2Cl(O_2CR)_4$: X-ray Crystal Structures of $[Ru^{II}Cl(MeCN)_3(PPh_3)_2]_2[Ru^{II}_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ and $[Ru^{II}Cl(MeCN)_4(PPh_3)][Ru^{II}Ru^{III}Cl_2(O_2CC_6H_4\text{-}p\text{-}OMe)_4]$

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Cationic–anionic complexes $[RuCl(MeCN)_3(PPh_3)_2]_2[Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ (**1**), $[RuCl(MeCN)_4(PPh_3)][Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}OMe)_4]$ (**2**) and $[RuCl(MeCN)_3(PPh_3)_2][Ru_2Cl_2(O_2CR)_4]$ (**3**, R = Me; **4**, R = Ph; **5**, R = C_6H_4-*p*-Me) are prepared by reacting $Ru_2Cl(O_2CR)_4$ with PPh_3 in MeCN. The complexes are characterized from elemental analytical, magnetic and spectral data. The crystal structures of **1** and **2** are determined by X-ray crystallography. Crystal data are as follows: complex **1**, monoclinic, $P2_1/c$, a = 16.051 (2) Å, b = 28.452 (4) Å, c = 15.126 (2) Å, β = 116.43 (1)°, V = 6186 (2) Å^3, Z = 2; complex **2**, monoclinic, $P2_1/c$, a = 12.645 (1) Å, b = 29.327 (3) Å, c = 18.300 (3) Å, β = 93.33 (1)°, V = 6775 (1) Å^3, Z = 4. The Ru–Ru distances in **1** and **2** are 2.291 (2) and 2.299 (1) Å, respectively. Complex **1** is two-electron paramagnetic while complexes **2–5** have three unpaired electrons per dimeric unit. Complex **1** exhibits a visible band at 497 nm. Complexes **2–5** display two electronic spectral absorptions in the ranges 461–470 and 1110–1160 nm. The bands are assigned to $\pi(Ru\text{–}O,Ru_2) \rightarrow \pi^*(Ru_2)$ and $\delta \rightarrow \delta^*$ transitions, respectively. Complexes **2–5** display EPR spectra giving a $g_\perp$ value of ~2.16 ($S = {}^3/_2$) at 77 K in the polycrystalline state or in $CHCl_3$ glass. The ^1H spectra of **1–5** are in agreement with the formulations and the X-ray structures of the complexes. The mechanistic aspects of the Ru–Cl–Ru polymeric chain cleavage reactions of $Ru_2Cl(O_2CR)_4$ are discussed.

Introduction

Among the strongly metal–metal-bonded tetracarboxylates with an $\{M_2(\mu\text{-}O_2CR)_4\}$ core, the diruthenium(II,III) complexes are unique with a spin-quartet ground state.[1-8] Structural studies[5,9] on $Ru_2Cl(O_2CR)_4$ reveal a polymeric nature of the complex, showing the presence of a one-dimensional polymeric chain in which the $Ru_2(O_2CR)_4^+$ units are bridged by axial chloride ions. The reactivity of the tetracarboxylates toward PPh_3 is an interesting aspect of the chemistry of M–M multiple-bonded complexes. While the data are extensive[5] on tetracarboxylates of other metals, a similar data on $Ru_2Cl(O_2CR)_4$ remain relatively unknown. The available reports[10-12] on the reaction between $Ru_2Cl(O_2CMe)_4$ and PPh_3 show the formation of an oxo-bridged complex, $Ru_2O(O_2CMe)_4(PPh_3)_2$.

As part of our systematic investigations on the reactivity of $Ru_2Cl(O_2CR)_4$ with PPh_3, we have shown[13] that reaction in an alcoholic solvent leads to the formation of monomeric ruthenium(II) complexes containing the carbonyl ligand. When the reaction is performed in MeCN, the product is a diruthenium(II,III) complex, $Ru_2(\mu\text{-}OH_2)Cl(MeCN)(\mu\text{-}O_2CR)_2(\eta^1\text{-}O_2CR)_2(PPh_3)_2$,[14] which converts readily to form (μ-oxo)diruthenium(III) complexes.[15] The isolation of the mixed-valence complex with a chloride ligand bonded to one metal center indicates[16] a symmetric cleavage of the polymeric Ru–Cl–Ru chain in $Ru_2Cl(O_2CR)_4$. Such a cleavage is of common occurrence[5,17] in the synthesis of discrete diruthenium(II,III) and diruthenium(II) complexes containing four three-atom bridging ligands and one axial chloride ligand.

We now report the synthesis and characterization of five new cationic–anionic complexes, $[RuCl(MeCN)_3(PPh_3)_2]_2[Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ (**1**), $[RuCl(MeCN)_4(PPh_3)][Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}OMe)_4]$ (**2**), and $[RuCl(MeCN)_3(PPh_3)_2][Ru_2Cl_2(O_2CR)_4]$ (R = Me (**3**), Ph (**4**); C_6H_4-*p*-Me (**5**)). Complexes **1–5** are presumably formed by an asymmetric cleavage of the polymeric chain. Complex **1** exemplifies the first diruthenium(II) complex with two axial chloride ligands bonded to the $\{Ru^{II}_2(\mu\text{-}O_2CR)_4\}$ core.

Experimental Section

Materials and Methods. The precursor complexes, $Ru_2Cl(O_2CR)_4$, were prepared by following reported procedures.[10,18] Chloroform and dichloromethane were purified by conventional techniques. All other reagents were obtained from commercial sources and used without further purification.

Preparation of $[RuCl(MeCN)_3(PPh_3)_2]_2[Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ (1). A mixture of $Ru_2Cl(O_2CC_6H_4\text{-}p\text{-}Me)_4$ (0.40 g) and PPh_3 (0.27 g) was refluxed in MeCN (20 mL) for 30 min. The resulting solution was filtered to remove the unreacted starting material. The filtrate was cooled overnight at −10 °C, and a purple solid, $Ru_2O(O_2CC_6H_4\text{-}p\text{-}Me)_4(PPh_3)_2$,[15] which precipitated on cooling, was removed by filtration. The filtrate obtained was treated with diethyl ether (30 mL) and a trace quantity of a brownish yellow precipitate[19] that formed was rejected. The solution was then evaporated to dryness, the residue obtained was dissolved in dichloromethane, and the reddish brown product **1** was precipitated from the solution by adding petroleum ether (bp 60–80 °C) into it. The product obtained was collected, washed with diethyl ether and finally dried over P_4O_{10} in vacuo. Yield: 0.13 g (~10%). Anal. Calcd for $C_{116}H_{106}N_6O_8P_4Cl_4Ru_4$: C, 58.43; H, 4.45; N, 3.52. Found: C, 59.17; H, 5.27; N, 4.09.

Preparation of $[RuCl(MeCN)_4(PPh_3)][Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}OMe)_4]$ (2). $Ru_2Cl(O_2CC_6H_4\text{-}p\text{-}OMe)_4$ (0.50 g) was reacted with PPh_3 (0.32 g)

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(19) This complex is characterized as $[Ru(O_2CC_6H_4\text{-}p\text{-}Me)(MeCN)_2(PPh_3)_2]Cl$. Anal. Calcd for $C_{48}H_{43}N_2O_2P_2ClRu$: C, 65.58; H, 4.93; N, 3.19. Found: C, 64.23; H, 5.25; N, 3.89.

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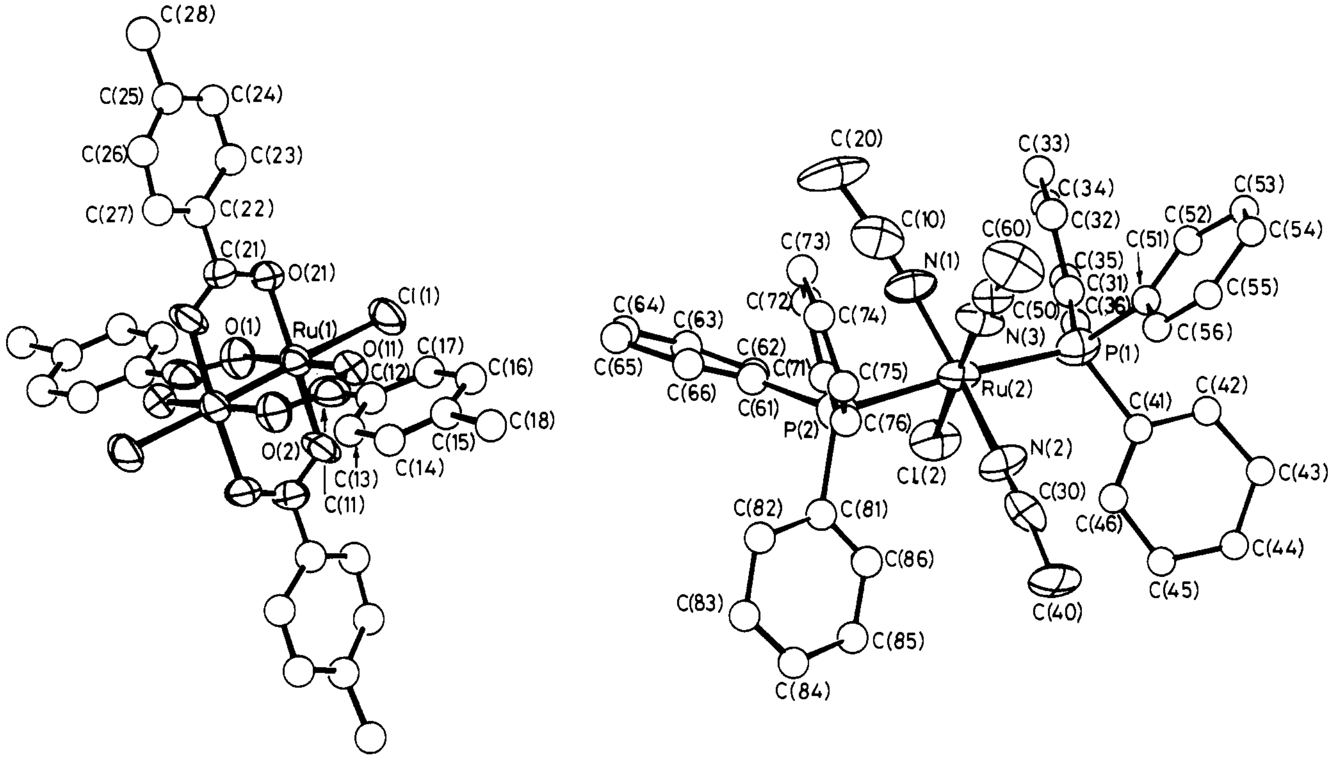

Figure 1. ORTEP view of the cationic and anionic complexes in $[RuCl(MeCN)_3(PPh_3)_2]_2[Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ (**1**) showing the atom-numbering scheme.

in MeCN (30 mL) under refluxing condition for 30 min. The solution obtained was cooled at −10 °C to precipitate a purple solid, $Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_4(PPh_3)_2$,[15] which was removed by filtration. The filtrate was concentrated to a volume of ca. 8 mL, and acetone (20 mL) was added to this solution. The mixture was cooled at −10 °C to obtain the flaky brown product **2**, which was collected, washed with acetone followed by diethyl ether, and then dried in vacuo over P_4O_{10}. Yield: 0.09 g (~10%). Anal. Calcd for $C_{58}H_{55}N_4O_{12}PCl_3Ru_3$: C, 48.31; H, 3.82; N, 3.88. Found: C, 47.81; H, 4.21; N, 3.30.

Preparation of $[RuCl(MeCN)_3(PPh_3)_2][Ru_2Cl_2(O_2CMe)_4]$ (3). The complex $Ru_2Cl(O_2CMe)_4$ (0.20 g) and PPh_3 (0.23 g) were added to MeCN (15 mL). The mixture was stirred for 24 h. The purple solid of $Ru_2O(O_2CMe)_4(PPh_3)_2$,[10] formed in the reaction, was removed by filtration. To the filtrate was added 30 mL of diethyl ether. The orange brown product was separated, washed with diethyl ether, and dried in vacuo over P_4O_{10}. Yield: 0.20 g (~37%). Anal. Calcd for $C_{50}H_{51}N_3O_8P_2Cl_3Ru_3$: C, 46.39; H, 3.94; N, 3.24. Found: C, 46.34; H, 3.85; N, 3.64.

Preparation of $[RuCl(MeCN)_3(PPh_3)_2][Ru_2Cl_2(O_2CPh)_4]$ (4). A 0.50-g sample of $Ru_2Cl(O_2CPh)_4$ was added to 30 mL of MeCN containing 0.37 g of PPh_3. The mixture was refluxed for 30 min followed by cooling overnight at −10 °C. Purple crystals of $Ru_2O(O_2CPh)_4(PPh_3)_2$,[15] formed during cooling, were removed by filtration. The filtrate was allowed to evaporate slowly in air at room temperature. The brown microcrystalline solid obtained this way was thoroughly washed with acetone and finally dried in vacuo over P_4O_{10}. Yield: 0.10 g (~9%). Anal. Calcd for $C_{70}H_{59}N_3O_8P_2Cl_3Ru_3$: C, 54.50; H, 3.83; N, 2.72. Found: C, 55.03; H, 3.75; N, 2.90.

Preparation of $[RuCl(MeCN)_3(PPh_3)_2][Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ (5). A mixture of $Ru_2Cl(O_2CC_6H_4\text{-}p\text{-}Me)_4$ (0.40 g) and PPh_3 (0.27 g) was refluxed in MeCN (30 mL) for 30 min. The resulting solution was filtered to remove the unreacted starting material. The filtrate was cooled at −10 °C to remove $Ru_2O(O_2CC_6H_4\text{-}p\text{-}Me)_4(PPh_3)_2$[15] as a precipitate. The solution thus obtained was kept for slow evaporation at room temperature in air. The resulting solid residue contained few needle-shaped crystals of **1** in addition to the brown product **5** along with some unidentified decomposition product of blackish color. The residue was washed with acetone to remove the decomposed material and recrystallized three times from a mixture of chloroform and diethyl ether to obtain the brown crystalline product **5**. The crystals were washed with diethyl ether prior to drying in vacuo over P_4O_{10}. Yield: 0.06 g (ca. 7%). Anal. Calcd for $C_{74}H_{67}N_3O_8P_2Cl_3Ru_3$: C, 55.57; H, 4.22; N, 2.63. Found: C, 55.37; H, 4.77; N, 2.71.

Measurements. Elemental analyses were obtained from a Heraeus CHN-O-RAPID elemental analyzer. Conductivity measurements were made with a Century CC603 digital conductivity meter. ^1H NMR spectra were obtained from Bruker WH-270 and AC(AF)-200 spectrometers. Magnetic susceptibility measurements were carried out on the $CDCl_3$ solutions of the complexes containing 2% CH_2Cl_2 by following the Evans method[20] on the Bruker AC(AF) 200-MHz spectrometer. The mass susceptibility of $CDCl_3$ was approximated by using the measured value for $CHCl_3$ of -0.497×10^{-6} cgsu. The mass susceptibility of CH_2Cl_2 (-0.549×10^{-6} cgsu) was not included in the calculations. EPR spectra were obtained from a Varian E-109 X-band spectrometer (*f*, 9.12 GHz). Electronic spectra were recorded with a Hitachi U-3400 spectrophotometer.

X-ray Crystallographic Procedures. The crystal structures of **1** and **2** were obtained using general procedures reported earlier.[15,16] The intensity data collected on an Enraf-Nonius CAD-4 four-circle diffractometer equipped with Mo Kα radiation, were corrected for Lorentz, polarization, and absorption[21] effects. Both the structures were solved and refined by SHELX programs.[22] The diagrams showing the molecular structures and unit cell packing were obtained by using ORTEP[23] and PLUTO,[24] respectively. The selected crystal data are summarized in Table I. Details of the crystal structure determination and related data are presented as supplementary material. Selected atomic coordinates of **1** and **2** are given in Tables II and III, respectively. Tables IV and V list important bond lengths and angles in **1** and **2**, respectively.

Results

Syntheses, Structures, and Formulations. Complexes **1**–**5** have been prepared by using a common procedure in which $Ru_2Cl(O_2CR)_4$ is reacted with PPh_3 in MeCN. From the reaction, a purple complex[10,15] is isolated as a major product. In the synthesis of **1**, the formation of a trace quantity of a brownish yellow solid

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Table I. Crystallographic Data for $[RuCl(MeCN)_3(PPh_3)_2]_2[Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ (**1**) and $[RuCl(MeCN)_4(PPh_3)][Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}OMe)_4]$ (**2**)

	1	**2**
chem formula	$C_{116}H_{106}N_6O_8P_4Cl_4Ru_4\cdot 4H_2O$	$C_{58}H_{55}N_4O_{12}PCl_3Ru_3\cdot 0.5Et_2O\cdot 0.75H_2O$
fw	2454.04	1490.98
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	16.051 (2)	12.645 (1)
b, Å	24.452 (4)	29.327 (3)
c, Å	15.126 (2)	18.300 (3)
β, deg	116.43 (1)	93.33 (1)
V, Å^3	6186 (2)	6775 (1)
Z	2	4
T, deg	20	20
λ(Mo Kα), Å	0.7107	0.7107
μ(Mo Kα), cm^{-1}	5.53	7.10
transm coeff	0.96–1.00	0.84–1.00
ρ_{calcd}, g cm^{-3}	1.317	1.462
R^a	0.0834	0.0609
$R_w{}^b$	0.0915	0.0642
g	0.001646	0.000188

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

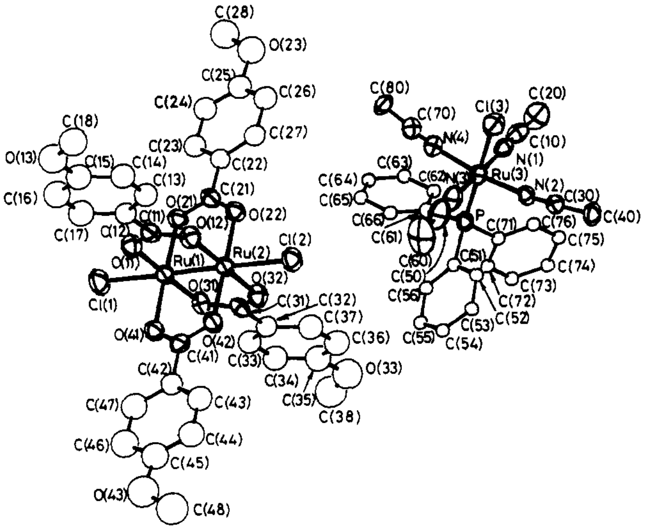

Figure 2. ORTEP view of the constituent ions in $[RuCl(MeCN)_4(PPh_3)][Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}OMe)_4]$ (**2**) along with atom-labeling scheme.

is also observed.[19] The complexes **1–5** are ionic (Table VI). While **1** behaves as a 2:1 electrolyte, **2–5** are 1:1 electrolytic in nature.[25] The unambiguous formulations of **1** and **2** are obtained from single-crystal X-ray studies.

The cationic and anionic complexes of **1**, formulated as $[RuCl(MeCN)_3(PPh_3)_2]_2[Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$, are shown in Figure 1. The cationic complex[26] has a ruthenium(II) center bonded to three MeCN, one chloride, and two trans-orientated PPh_3 ligands. The anionic species is a diruthenium(II) complex with four bridging *p*-methylbenzoato and two axially coordinated chloride ligands. The Ru–Ru distance of 2.291 (2) Å in **1** is longer than the same distance reported in the solvent adducts of the $Ru_2(O_2CR)_4$ core [Ru–Ru, 2.260 (3)–2.276 (3) Å][27-30] and in hydroxypyridinate complexes of diruthenium(II) [Ru–Ru, 2.235

Table II. Full List of Atomic Coordinates and Isotropic Thermal Parameters (×10^3) for $[RuCl(MeCN)_3(PPh_3)_2]_2[Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ (**1**)

atom	*x*	*y*	*z*	U_{iso}, Å^2
Ru1	0.0181 (1)	0.0174 (1)	0.0747 (1)	51 (0.5)^a
Cl1	0.0611 (3)	0.0533 (1)	0.2422 (3)	76 (2)^a
O1	−0.1201 (6)	0.0202 (3)	0.0396 (7)	54 (4)^a
O2	0.0249 (7)	−0.0472 (3)	0.1313 (7)	61 (4)^a
O71	0.1538 (6)	0.0144 (3)	0.1052 (7)	59 (4)^a
C71	0.1765 (11)	−0.0041 (5)	0.0424 (12)	59 (8)^a
O81	0.0087 (7)	0.0814 (3)	0.0135 (7)	58 (5)^a
C81	−0.0069 (10)	0.0828 (5)	−0.0778 (12)	59 (7)^a
C72	0.2787 (10)	−0.0077 (5)	0.0686 (11)	61 (4)
C73	0.3049 (12)	−0.0326 (6)	0.0046 (13)	80 (5)
C74	0.4001 (13)	−0.0392 (7)	0.0304 (14)	92 (6)
C75	0.4600 (13)	−0.0191 (6)	0.1105 (14)	88 (5)
C76	0.4391 (13)	0.0082 (6)	0.1773 (14)	91 (6)
C77	0.3417 (11)	0.0127 (5)	0.1517 (12)	71 (4)
C78	0.5651 (14)	−0.0267 (7)	0.1410 (16)	113 (7)
C82	−0.0118 (10)	0.1290 (5)	−0.1221 (11)	57 (4)
C83	−0.0020 (10)	0.1700 (5)	−0.0642 (11)	65 (4)
C84	−0.0011 (12)	0.2151 (6)	−0.1091 (13)	82 (5)
C85	−0.0092 (12)	0.2153 (6)	−0.2035 (13)	83 (5)
C86	−0.0083 (12)	0.1749 (6)	−0.2547 (13)	81 (5)
C87	−0.0113 (12)	0.1294 (7)	−0.2179 (14)	89 (5)
C88	−0.0165 (15)	0.2641 (8)	−0.2578 (18)	129 (8)
Ru2	0.4954 (1)	0.2956 (1)	0.3192 (1)	42 (0.5)^a
Cl2	0.5008 (3)	0.2513 (1)	0.1847 (3)	60 (2)^a
P1	0.6608 (3)	0.2974 (1)	0.3819 (3)	47 (1)^a
P2	0.3293 (3)	0.2884 (1)	0.2476 (3)	50 (2)^a
N1	0.4787 (8)	0.3538 (4)	0.2393 (8)	51 (6)^a
C10	0.4639 (11)	0.3854 (6)	0.1916 (11)	62 (8)^a
C20	0.4430 (16)	0.4282 (5)	0.1222 (13)	101 (13)^a
N2	0.5044 (8)	0.2393 (4)	0.4026 (7)	46 (5)^a
C30	0.5061 (9)	0.2089 (5)	0.4487 (10)	51 (6)^a
C40	0.5066 (12)	0.1646 (5)	0.5036 (11)	70 (8)^a
N3	0.4961 (8)	0.3327 (4)	0.4294 (8)	51 (5)^a
C50	0.4935 (10)	0.3488 (5)	0.4962 (12)	58 (7)^a
C60	0.4922 (12)	0.3700 (6)	0.5885 (11)	79 (8)^a
C11	0.6988 (9)	0.3290 (5)	0.3009 (9)	47 (3)
C12	0.6937 (10)	0.3792 (5)	0.2990 (11)	65 (4)
C13	0.7157 (11)	0.4036 (5)	0.2301 (12)	69 (4)
C14	0.7444 (11)	0.3785 (6)	0.1696 (13)	76 (5)
C15	0.7532 (11)	0.3300 (6)	0.1738 (12)	72 (4)
C16	0.7281 (10)	0.3041 (5)	0.2394 (10)	53 (4)
C21	0.7245 (9)	0.2396 (5)	0.4034 (9)	47 (3)
C22	0.8176 (11)	0.2422 (6)	0.4498 (12)	69 (4)
C23	0.8732 (13)	0.1982 (7)	0.4720 (14)	92 (6)
C24	0.8217 (13)	0.1561 (7)	0.4505 (14)	89 (5)
C25	0.7264 (13)	0.1546 (6)	0.4020 (13)	85 (5)
C26	0.6761 (10)	0.1998 (5)	0.3773 (10)	58 (4)
C31	0.7285 (9)	0.3237 (4)	0.5048 (10)	45 (3)
C32	0.7999 (10)	0.3550 (5)	0.5257 (11)	58 (4)
C33	0.8525 (12)	0.3718 (6)	0.6215 (13)	83 (5)
C34	0.8260 (12)	0.3610 (6)	0.6968 (13)	78 (5)
C35	0.7509 (11)	0.3274 (6)	0.6735 (12)	71 (4)
C36	0.7050 (10)	0.3094 (5)	0.5789 (11)	59 (4)
C41	0.2584 (9)	0.3145 (5)	0.1276 (10)	52 (7)
C42	0.2946 (11)	0.3149 (5)	0.0569 (12)	68 (4)
C43	0.2398 (12)	0.3354 (6)	−0.0402 (13)	80 (5)
C44	0.1574 (13)	0.3533 (6)	−0.0605 (14)	84 (5)
C45	0.1125 (15)	0.3537 (8)	0.0032 (17)	115 (7)
C46	0.1733 (13)	0.3320 (6)	0.1029 (14)	86 (5)
C51	0.2840 (9)	0.3162 (5)	0.3271 (10)	51 (3)
C52	0.2774 (11)	0.3657 (5)	0.3234 (12)	66 (4)
C53	0.2498 (12)	0.3893 (6)	0.3894 (14)	85 (5)
C54	0.2344 (11)	0.3627 (6)	0.4596 (12)	76 (5)
C55	0.2488 (12)	0.3154 (6)	0.4647 (13)	85 (5)
C56	0.2735 (10)	0.2909 (5)	0.3980 (12)	64 (4)
C61	0.2845 (10)	0.2268 (5)	0.2298 (10)	54 (4)
C62	0.1905 (11)	0.2205 (6)	0.2104 (12)	72 (5)
C63	0.1545 (12)	0.1736 (6)	0.1949 (13)	77 (5)
C64	0.2157 (12)	0.1376 (6)	0.1998 (12)	75 (5)
C65	0.3056 (12)	0.1449 (6)	0.2182 (12)	74 (5)
C66	0.3417 (10)	0.1910 (5)	0.2325 (11)	57 (4)
OW1	0.4843 (10)	0.0477 (6)	0.4168 (11)	138 (5)
OW2	0.2851 (22)	0.0254 (11)	0.3771 (24)	143 (11)^b
OW3	0.6672 (24)	0.0369 (13)	0.4502 (26)	160 (13)^b

^{a} These atoms, which were refined anisotropically, have been given an equivalent isotropic thermal parameter defined as $U_{iso}(eq) = {}^1/_3[\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*a_i\cdot a_j]$. ^{b} Site occupancy factor: OW2, 0.5; OW3, 0.5.

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Table III. Full List of Atomic Coordinates and Isotropic Thermal Parameters ($\times 10^3$) for $[RuCl(MeCN)_4(PPh_3)][Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}OMe)_4]$ (**2**)

atom	x	y	z	U_{iso}, Å^2	atom	x	y	z	U_{iso}, Å^2
Ru1	0.1162 (1)	0.2107 (1)	0.3943 (1)	38 (0.3)^a	C46	0.5443 (11)	0.1642 (4)	0.2606 (7)	82 (4)
Ru2	0.1895 (1)	0.2753 (1)	0.4471 (1)	37 (0.3)^a	C47	0.4453 (10)	0.1751 (4)	0.2876 (7)	71 (3)
Cl1	0.0361 (2)	0.1400 (1)	0.3396 (2)	62 (1)^a	O43	0.7244 (8)	0.1827 (3)	0.2520 (5)	104 (3)
Cl2	0.2667 (2)	0.3477 (1)	0.5002 (1)	54 (1)^a	C48	0.8168 (13)	0.2137 (5)	0.2635 (8)	107 (5)
O11	0.1676 (5)	0.1754 (2)	0.4845 (4)	49 (2)^a	Ru3	−0.1001 (1)	0.5304 (1)	0.3508 (1)	46 (0.3)^a
O12	0.2381 (5)	0.2384 (2)	0.5362 (3)	46 (2)^a	C13	0.0755 (2)	0.5577 (1)	0.3992 (2)	70 (1)^a
C11	0.2178 (5)	0.1957 (2)	0.5373 (4)	47 (4)^a	P1	−0.2609 (2)	0.5055 (1)	0.3030 (2)	48 (1)^a
C12	0.2585 (8)	0.1697 (3)	0.6010 (6)	48 (2)	N1	−0.1560 (7)	0.5343 (3)	0.4517 (5)	48 (3)^a
C13	0.3027 (9)	0.1917 (4)	0.6623 (6)	56 (3)	C10	−0.1877 (9)	0.5353 (4)	0.5064 (7)	56 (4)^a
C14	0.3433 (9)	0.1675 (4)	0.7245 (6)	64 (3)	C20	−0.2350 (10)	0.5387 (4)	0.5781 (7)	82 (5)^a
C15	0.3348 (9)	0.1196 (4)	0.7190 (7)	67 (3)	N2	−0.1357 (6)	0.5964 (3)	0.3351 (4)	47 (3)^a
C16	0.2912 (10)	0.0959 (4)	0.6604 (7)	74 (4)	C30	−0.1486 (8)	0.6347 (4)	0.3325 (6)	53 (4)^a
C17	0.2529 (9)	0.1216 (4)	0.5994 (7)	69 (3)	C40	−0.1646 (10)	0.6846 (3)	0.3284 (6)	64 (4)^a
O13	0.3718 (7)	0.0926 (3)	0.7782 (5)	89 (3)	N3	−0.0380 (8)	0.5253 (3)	0.2524 (6)	63 (4)^a
C18	0.4240 (11)	0.1149 (4)	0.8400 (7)	84 (4)	C50	−0.0104 (12)	0.5244 (4)	0.1946 (9)	92 (7)^a
O21	−0.0210 (5)	0.2254 (2)	0.4408 (3)	44 (2)^a	C60	0.0279 (17)	0.5227 (5)	0.1169 (8)	143 (10)^a
O22	0.0508 (5)	0.2878 (2)	0.4924 (3)	40 (2)^a	N4	−0.0527 (7)	0.4669 (3)	0.3797 (5)	50 (3)^a
C21	−0.0266 (5)	0.2609 (2)	0.4799 (3)	43 (4)^a	C70	−0.0312 (8)	0.4329 (4)	0.4039 (6)	51 (4)^a
C22	−0.1292 (7)	0.2727 (3)	0.5095 (5)	41 (2)	C80	−0.0076 (9)	0.3879 (3)	0.4395 (6)	59 (4)^a
C23	−0.2172 (8)	0.2456 (3)	0.4913 (6)	52 (3)	C51	−0.2828 (9)	0.5131 (4)	0.2032 (6)	61 (3)
C24	−0.3165 (8)	0.2567 (4)	0.5176 (6)	55 (3)	C52	−0.2516 (10)	0.5541 (4)	0.1749 (7)	73 (3)
C25	−0.3214 (9)	0.2946 (4)	0.5621 (6)	58 (3)	C53	−0.2713 (12)	0.5631 (5)	0.0995 (9)	98 (5)
C26	−0.2344 (9)	0.3217 (4)	0.5822 (6)	57 (3)	C54	−0.3167 (15)	0.5301 (6)	0.0550 (10)	128 (6)
C27	−0.1378 (8)	0.3102 (3)	0.5543 (5)	46 (2)	C55	−0.3565 (15)	0.4896 (6)	0.0817 (11)	130 (6)
O23	−0.4163 (7)	0.3081 (3)	0.5904 (5)	80 (2)	C56	−0.3362 (11)	0.4804 (5)	0.1599 (8)	88 (4)
C28	−0.5123 (11)	0.2800 (4)	0.5742 (7)	86 (4)	C61	−0.2775 (8)	0.4457 (3)	0.3240 (6)	52 (3)
O31	0.0668 (5)	0.2485 (2)	0.3058 (3)	42 (2)^a	C62	−0.3188 (9)	0.4356 (4)	0.3910 (7)	68 (3)
O32	0.1388 (5)	0.3106 (2)	0.3584 (3)	45 (2)^a	C63	−0.3169 (10)	0.3875 (4)	0.4143 (7)	79 (4)
C31	0.0858 (8)	0.2910 (3)	0.3065 (6)	43 (4)^a	C64	−0.2770 (11)	0.3543 (4)	0.3740 (7)	81 (4)
C32	0.0445 (8)	0.3190 (3)	0.2430 (5)	45 (2)	C65	−0.2358 (11)	0.3641 (5)	0.3106 (7)	83 (4)
C33	−0.0096 (8)	0.3001 (4)	0.1827 (6)	56 (3)	C66	−0.2319 (10)	0.4123 (4)	0.2807 (7)	75 (4)
C34	−0.0506 (6)	0.3275 (4)	0.1253 (6)	64 (3)	C71	−0.3837 (8)	0.5306 (3)	0.3337 (6)	53 (3)
C35	−0.0353 (10)	0.3740 (4)	0.1309 (7)	69 (3)	C72	−0.4808 (9)	0.5126 (4)	0.3061 (6)	63 (3)
C36	0.0169 (9)	0.3945 (4)	0.1905 (7)	67 (3)	C73	−0.5748 (10)	0.5298 (4)	0.3271 (7)	73 (3)
C37	0.0624 (9)	0.3667 (4)	0.2489 (6)	65 (3)	C74	−0.5774 (10)	0.5664 (4)	0.3750 (7)	75 (4)
O33	−0.0721 (7)	0.4051 (3)	0.0775 (5)	93 (3)	C75	−0.4783 (10)	0.5856 (4)	0.4045 (7)	72 (3)
C38	−0.1276 (12)	0.3869 (5)	0.0115 (8)	104 (5)	C76	−0.3808 (8)	0.5673 (4)	0.3820 (6)	55 (5)
O41	0.2552 (5)	0.1980 (2)	0.3486 (3)	44 (2)^a	O1	0.5852 (29)	0.1244 (13)	0.4955 (22)	195 (14)^b
O42	0.3268 (5)	0.2611 (2)	0.4005 (4)	47 (2)^a	C1	0.5613 (34)	0.1025 (15)	0.4489 (26)	146 (15)^b
C41	0.3322 (8)	0.2251 (3)	0.3603 (5)	45 (3)^a	C2	0.5400 (28)	0.1387 (12)	0.5452 (22)	110 (11)^b
C42	0.4345 (8)	0.2153 (3)	0.3279 (6)	48 (3)	C3	0.6138 (37)	0.0781 (16)	0.3969(25)	176 (17)^b
C43	0.5201 (9)	0.2453 (4)	0.3406 (6)	64 (3)	C4	0.5744 (32)	0.1474 (13)	0.6029 (24)	141 (14)^b
C44	0.6174 (10)	0.2363 (4)	0.3161 (7)	71 (3)	OW1	0.6752 (33)	0.0327 (14)	0.3699 (22)	111 (13)^b
C45	0.6269 (11)	0.1965 (4)	0.2767 (7)	77 (4)	OW2	0.8119 (13)	0.0819 (5)	0.2522 (9)	80 (5)

[a] These atoms, which were refined anisotropically, have been given an equivalent isotropic thermal parameter defined as $U_{iso}(eq) = {}^1/_3[\sum_i\sum_j U_{ij}a_i^*a_j^*a_i{\cdot}a_j]$. [b] Site occupancy factors for atoms: O1, C1, C2, C3, C4, and OW1, 0.50; OW2, 0.25.

(1)–2.259 (1) Å].[31,32] In **1**, the axial chlorides are expected[3] to increase the Ru–Ru distance due to $\sigma(Cl) \rightarrow \sigma^*(Ru_2)$ donation and $\pi(Cl) \rightarrow \pi^*(Ru_2)$ charge transfer. However, a much longer Ru–Ru distance of 2.417 (2) Å is reported[33] for a diamagnetic complex, $[Ru_2\{(tol)NNN(tol)\}_4]$. An analysis of the Ru–Ru distances with the magnetic properties of diruthenium(II) complexes made by Cotton et al.[31] suggests the following order of bond lengthening: $\pi^{*4} > \pi^{*3}\delta^{*1} > \delta^{*2}\pi^{*2}$.

Complex **2**, shown in Figure 2, is a cationic–anionic complex of formulation $[RuCl(MeCN)_4(PPh_3)][Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}OMe)_4]$. The cationic complex of **2** is different from that of **1**. The anionic complex has a diruthenium(II,III) core with four bridging *p*-methoxybenzoato and two axial chloride ligands. The Ru–Ru distance of 2.299 (1) Å is consistent with those reported for discrete dimeric and polymeric diruthenium(II,III) complexes [Ru–Ru, 2.267 (1)–2.290 (1) Å].[5,8,9,17a–e]

On the basis of the crystal structures of **1** and **2**, the complexes **3**–**5** are formulated as $[RuCl(MeCN)_3(PPh_3)_2][Ru_2Cl_2(O_2CR)_4]$ (R = Me, **3**; Ph, **4**; C_6H_4-*p*-Me, **5**). Elemental analytical and conductivity data on **3**–**5** are in agreement with this formulation.

Magnetism and EPR Spectra. Complexes **1**–**5** are paramagnetic (Table VI). The μ_{eff} value of 3.07 μ_B in **1** corresponds to two unpaired electrons per dimeric unit. This indicates[4] a $\pi^{*3}\delta^{*1}$ or $\delta^{*2}\pi^{*2}$ ground state with a Ru–Ru bond order of 2.0. The μ_{eff} values of the other complexes are in accordance[4] with a $(\delta^*\pi^*)^3$ ground state. The Ru–Ru bond order in **2**–**5** is 2.5. The diruthenium(II,III) complexes, **2**–**5**, exhibit EPR spectra at 77 K giving a $g_\perp$ value of ~2.16 ($S = {}^3/_2$). Complex **1** displays no detectable EPR spectrum at 77 K. This could presumably be due to the presence of large positive zero-field splitting resulting from strong magnetic dipole–dipole interactions in the triplet ground state.[28,30,34] The EPR spectral features of **2**–**5** are similar to those reported[2,4] for $Ru_2Cl(O_2CC_3H_7)_4$, showing a $g_\perp$ value of 2.18 in methanol glass. Considerable broadening of the EPR signal is known[4] to occur in diruthenium(II,III) carboxylates due to magnetic exchange interactions resulting in fast electron spin relaxation.

^{1}H NMR and Solution Electronic Spectra. The presence of both a diamagnetic ruthenium(II) center and a paramagnetic diruthenium core in **1**–**5** causes considerable shifts of the proton resonances over a range of $\delta = -45$ ppm to $\delta = +34$ ppm. Two

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Table IV. Selected Bond Distances (Å) and Angles (deg) for $[RuCl(MeCN)_3(PPh_3)_2]_2[Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ (**1**)

	Distances		
Ru1–Ru1′	2.291 (2)	Ru1–Cl1	2.528 (4)
Ru1–O1	2.041 (10)	Ru1–O2	2.010 (9)
Ru1–O71	2.017 (10)	Ru1–O81	2.017 (9)
Ru2–C12	2.427 (4)	Ru2–P1	2.389 (4)
Ru2–P2	2.399 (4)	Ru2–N1	1.998 (11)
Ru2–N2	2.005 (11)	Ru2–N3	1.969 (13)
N1–C10	1.110 (20)	C10–C20	1.544 (23)
N2–C30	1.104 (19)	C30–C40	1.507 (22)
N3–C50	1.127 (23)	C50–C60	1.529 (26)
	Angles		
Ru1′–Ru1–Cl1	178.1 (1)	Ru1′–Ru1–O1	89.5 (3)
Ru1′–Ru1–O2	88.1 (3)	Ru1′–Ru1–O71	88.9 (3)
Ru1′–Ru1–O81	90.2 (3)	O71–Ru1–O81	89.8 (4)
O2–Ru1–O81	178.2 (3)	O2–Ru1–O71	90.9 (4)
O1–Ru1–O81	89.7 (4)	O1–Ru1–O71	178.3 (4)
O1–Ru1–O2	89.6 (4)	Cl1–Ru1–O81	91.5 (3)
Cl1–Ru1–O71	90.1 (3)	Cl1–Ru1–O2	90.2 (3)
Cl1–Ru1–O1	91.4 (3)	N2–Ru2–N3	85.6 (4)
N1–Ru2–N3	90.9 (5)	N1–Ru2–N2	175.3 (5)
P2–Ru2–N3	90.8 (4)	P2–Ru2–N2	88.3 (4)
P2–Ru2–N1	88.5 (3)	P1–Ru2–N3	93.8 (3)
P1–Ru2–N2	90.6 (3)	P1–Ru2–N1	92.8 (4)
P1–Ru2–P2	175.2 (1)	C12–Ru2–N3	177.6 (4)
C12–Ru2–N2	95.3 (3)	C12–Ru2–N1	88.2 (3)
C12–Ru2–P2	91.4 (2)	C12–Ru2–P1	84.0 (2)

Table V. Selected Bond Distances (Å) and Angles (deg) for $[RuCl(MeCN)_4(PPh_3)][Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}OMe)_4]$ (**2**)

	Distances		
Ru1–Ru2	2.299 (1)	Ru1–Cl1	2.493 (3)
Ru1–O11	2.024 (6)	Ru1–O21	2.022 (6)
Ru1–O31	2.031 (6)	Ru1–O41	2.025 (6)
Ru2–C12	2.508 (3)	Ru2–O12	2.023 (6)
Ru2–O22	2.016 (6)	Ru2–O32	1.999 (6)
Ru2–O42	2.022 (7)	Ru3–P1	2.286 (3)
Ru3–N1	2.018 (9)	Ru3–N2	2.004 (8)
Ru3–N3	2.012 (11)	Ru3–N4	2.017 (8)
N1–C10	1.100 (15)	C10–C20	1.477 (18)
N2–C30	1.137 (14)	C30–C40	1.479 (15)
N3–C50	1.133 (20)	C50–C60	1.529 (23)
N4–C70	1.119 (13)	C70–C80	1.494 (15)
	Angles		
N3–Ru3–N4	92.3 (4)	N2–Ru3–N4	171.8 (3)
N2–Ru3–N3	92.3 (4)	N1–Ru3–N4	85.8 (4)
N1–Ru3–N3	177.3 (4)	N1–Ru3–N2	89.3 (3)
P1–Ru3–N4	92.8 (3)	P1–Ru3–N3	91.1 (3)
P1–Ru3–N2	93.8 (2)	P1–Ru3–N1	91.0 (3)
C13–Ru3–N4	87.6 (3)	C13–Ru3–N3	87.5 (3)
C13–Ru3–N2	85.9 (2)	C13–Ru3–N1	90.5 (3)
C13–Ru3–P1	178.5 (1)	Ru3–N1–C10	178.1 (9)
Ru1–Ru2–Cl2	177.6 (1)	Ru3–N2–C30	172.6 (8)
Ru2–Ru1–Cl1	178.8 (1)	Ru3–N3–C50	174.1 (11)
Cl1–Ru1–O_{eq}	91.0 (2)	Ru3–N4–C70	171.4 (9)
Cl2–Ru2–O_{eq}	90.8 (2)		

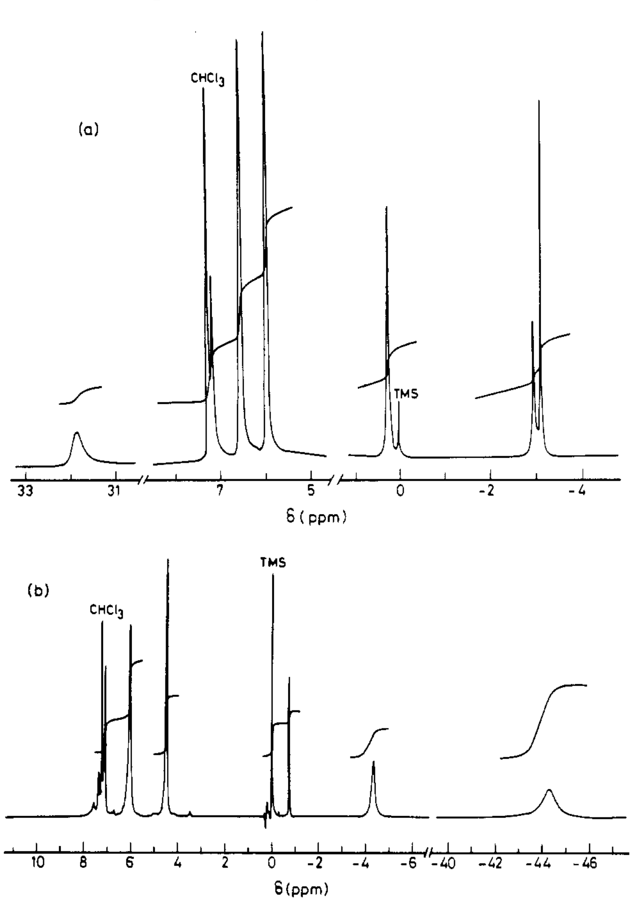


Figure 3. ^1H NMR spectra of cationic–anionic complexes: (a) $[RuCl(MeCN)_3(PPh_3)_2]_2[Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ (**1**); (b) $[RuCl(MeCN)_3(PPh_3)_2][Ru_2Cl_2(O_2CMe)_4]$ (**4**).

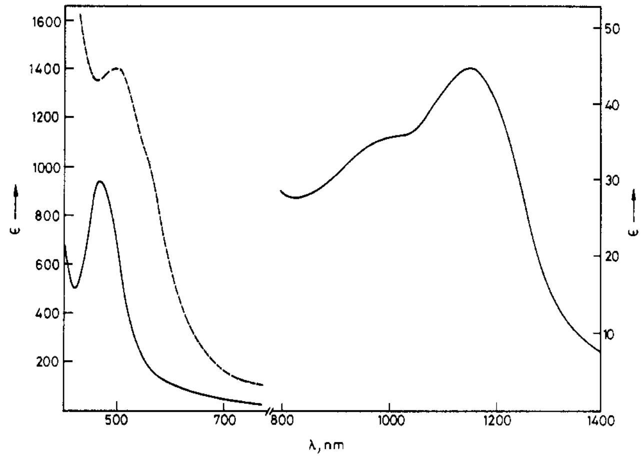


Figure 4. Visible and near-infrared spectra of $[RuCl(MeCN)_3(PPh_3)_2]_2[Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ (**1**) (---) and $[RuCl(MeCN)_4(PPh_3)][Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}OMe)_4]$ (**2**) (—) in $CHCl_3$.

representative ^1H NMR spectra are shown in Figure 3 and the data are presented in Table VII. A singlet observed near δ 32 in **1**, **2**, and **5** is assignable to the ortho protons of the bridging carboxylato ligands. In **4**, these protons appear at δ 33.24 and 19.52. In **1** and **3–5**, the trans and cis MeCN ligands of the cationic species appear as two singlets with a 1:2 intensity ratio. Four equivalent MeCN ligands in the cationic complex of **2** show a singlet at δ = −1.30. The singlets at δ 0.22, 5.64, and −3.12 are tentatively assigned to the methyl protons of O_2CR in **1**, **2**, and **5**, respectively. The acetate protons in **3** are observed as a singlet at δ −44.26. The three peaks in the range of δ 7.10–4.49

Table VI. Conductivity,[a] Magnetic, EPR, and Electronic Spectral Data for **1–5**

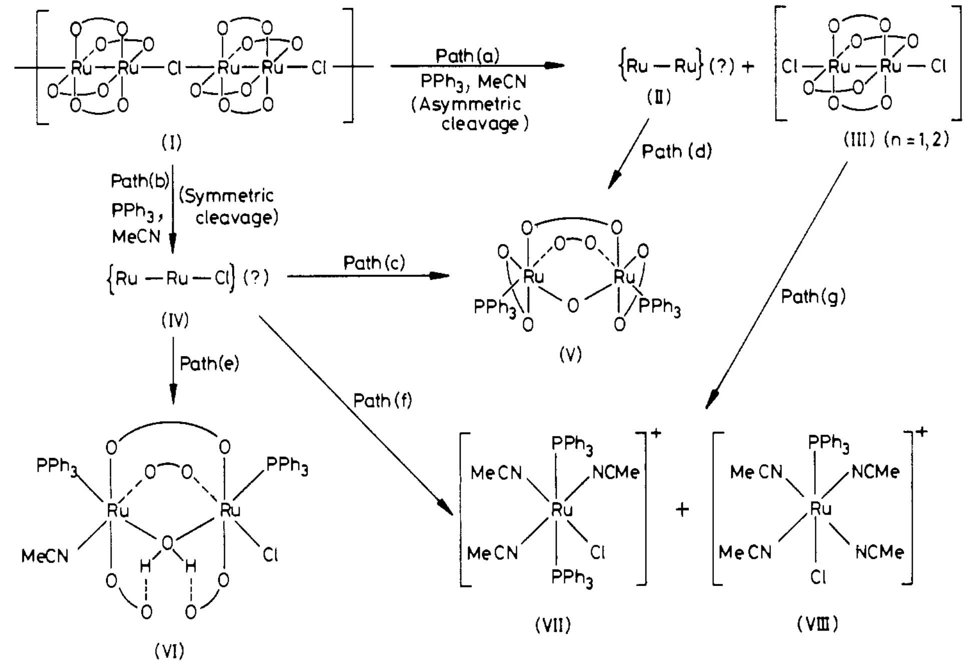
complex	Λ_M, mho $cm^2\ M^{-1}$	μ_{eff},[b] μ_B	EPR g ($S = {}^3/_2$)	λ_{max},[c] nm (ε, $M^{-1}\ cm^{-1}$)
$[RuCl(MeCN)_3(PPh_3)_2]_2[Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ (**1**)	260	3.07		497 (1400)
$[RuCl(MeCN)_4(PPh_3)][Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}OMe)_4]$ (**2**)	140	3.99	2.15[d]	470 (940), 1160 (45)
$[RuCl(MeCN)_3(PPh_3)_2][Ru_2Cl_2(O_2CMe)_4]$ (**3**)	145	3.67	2.17[d]	461 (1200), 1110 (42)
$[RuCl(MeCN)_3(PPh_3)_2][Ru_2Cl_2(O_2CPh)_4]$ (**4**)	138	3.64	2.15[e]	461 (640), 1147 (30)
$[RuCl(MeCN)_3(PPh_3)_2][Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ (**5**)	140	3.70	2.16[d]	470 (670), 1150 (54)

[a] In MeCN. [b] For diruthenium unit. [c] In $CHCl_3$. [d] $CHCl_3$ glass at 77 K. [e] Polycrystalline state at 77 K.

Table VII. ^{1}H NMR Data for **1–5** in $CDCl_3$

complex	δ, ppm [*n* H] *o*-H(O_2CR)	MeCN	Me(O_2CR)	aryl groups
$[RuCl(MeCN)_3(PPh_3)_2]_2[Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ (**1**)	31.85 [8]	−2.99 [6], 3.15 [12]	0.22 [12]	7.21 [10], 7.12 [12], 6.49 [24], 5.90 [22]
$[RuCl(MeCN)_4(PPh_3)][Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}OMe)_4]$ (**2**)	31.64 [8]	−1.30 [12]	5.64 [12]	7.37 [5], 7.09 [4], 5.04 [7], 3.60 [7]
$[RuCl(MeCN)_3(PPh_3)_2][Ru_2Cl_2(O_2CMe)_4]$ (**3**)		−4.33 [6], −0.75 [3]	−44.26 [12]	7.10 [6], 6.05 [12], 4.49 [12]
$[RuCl(MeCN)_3(PPh_3)_2][Ru_2Cl_2(O_2CPh)_4]$ (**4**)	32.24 [3], 19.52 [2]	−2.48 [3], 0.25 [6]		7.22–7.31 [11], 6.57 [12], 6.11 [12]
$[RuCl(MeCN)_3(PPh_3)_2][Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ (**5**)	31.77 [8]	−7.44 [3], −0.98 [6]	−3.12 [12]	7.14 [14], 5.71 [12], 4.18 [12]

Scheme I. Symmetric and Asymmetric Cleavage Pathways of the Ru–Cl–Ru Polymeric Chains in $Ru_2Cl(O_2CR)_4$



with an intensity ratio of 1:2:2 could be due to para, ortho, and meta protons of the phenyl rings in PPh_3 of **3**. Extensive broadening of the phenyl ring protons has been observed in **4**, giving a lower value of the H(aryl):H(methyl) ratio than the calculated one.

The visible and near-infrared spectra of **1** and **2** are shown in Figure 4. While **1** exhibits[28] a band at 497 nm, complexes **2–5** display two absorptions in the spectral ranges 461–470 and 1110–1160 nm (Table VI). The visible band in these complexes is assignable[3,6,7] to a $\pi(\text{Ru–O,Ru–Ru}) \rightarrow \pi^*(\text{Ru–Ru})$ transition. The low-energy band is a characteristic spectral feature of the diruthenium(II,III) tetracarboxylates. A band near 1000 nm ($\epsilon \sim 25$–50) reported earlier by Wilson and Taube[35] for $Ru_2(O_2CR)_4^+$ has later been assigned to a $\delta \rightarrow \delta^*$ transition by Norman et al.[3] and Gray et al.[6,7] The observed splitting of the band (Figure 4) is related[6] to the vibronic component of this transition. The absence of a $\delta \rightarrow \delta^*$ transition in the two-electron paramagnetic complex **1** suggests a $\delta^{*2}\pi^{*2}$ ground electronic configuration for the diruthenium(II) core.

Discussion

The mechanistic aspects of the reactions leading to the formation of cationic–anionic (**1–5**) as well as (μ-aquo/oxo)bis(μ-carboxylato)diruthenium complexes are of interest[13,14] to us. The probable pathways showing the cleavage of the polymeric chain in $Ru_2Cl(O_2CR)_4$ are given in Scheme I. Isolation of **1–5**, in absence of any externally added chloride ion, suggests an asymmetric cleavage of the Ru–Cl–Ru chain (path a). The polymeric chain can also undergo a symmetric cleavage to form a discrete dimeric core containing an axial chloride ligand (path b). This mode of cleavage is observed[17] in the synthesis of VI and several discrete dimeric complexes with an axial chloride ligand.

A purple complex of formulation $Ru_2O(O_2CR)_4(PPh_3)_2$[10,15] (V) is isolated as a major product in the syntheses of **1–5**. The formation of the $\{Ru_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2^{2+}\}$ core is likely to proceed[11,16] through the proposed intermediate species (II) and (IV) (pathways c and d) as well as from the μ-aquo complex (VI).[16] Similarly, a cleavage of the {RuRuCl} and {ClRuRuCl} cores, shown in pathways f and g, may lead[11] to the formation of monomeric cationic complexes.

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Registry No. **1**, 139490-51-0; **2**, 139347-42-5; **3**, 139405-68-8; **4**, 139490-52-1; **5**, 139405-69-9; $Ru_2Cl(O_2CC_6H_4\text{-}p\text{-}Me)_4$, 139347-44-7; $Ru_2Cl(O_2CMe)_4$, 38833-34-0; Ru, 7440-18-8; $Ru_2Cl(O_2CPh)_4$, 38832-60-9.

Supplementary Material Available: For $[RuCl(MeCN)_3(PPh_3)_2]_2[Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}Me)_4]$ (**1**) and $[RuCl(MeCN)_4(PPh_3)][Ru_2Cl_2(O_2CC_6H_4\text{-}p\text{-}OMe)_4]_2$ (**2**), text giving the details of the crystal structure determination, unit cell packing diagrams, and tables of crystal data, anisotropic thermal parameters, bond lengths, and bond angles (15 pages); tables of observed and calculated structure factors (70 pages). Ordering information is given on any current masthead page.

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[35] Wilson, C. R.; Taube, H. *Inorg. Chem.* **1975**, *14*, 2276.