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# INFLUENCE OF CARBOXYLIC ACIDS ON THE REACTIONS WITH CHLOROTETRAACETATODIRUTHENIUM(II,III): X-RAY CRYSTAL STRUCTURE OF $[Ru_2(\mu\text{-}O_2CC_4H_3S)_4(OPPh_3)_2]BF_4 \cdot 2H_2O$

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**Abstract**—The reaction of $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$ with indole-2-carboxylic, *N*-methyl-pyrrole-2-carboxylic, furane-2-carboxylic, thiophene-2-carboxylic and benzofurane-2-carboxylic acids, which contain nitrogen, oxygen or sulphur atoms in the $\alpha$ position with respect to the carboxylate group, leads to compounds of the type $Ru_2Cl(\mu\text{-}O_2CR)_4$. In these compounds O,O-coordination of the carboxylate ligands has been found. The analogous reaction with quinoline-2-carboxylic acid (Hquin) gives a disproportionation process with formation of $Ru(quin)_3$ and $Ru_2(quin)_4$; in this case, N,O-coordination of the ligand has been observed. The indole-2-carboxylato derivative has a non-polymeric structure, whereas with the other ligands polymeric structures with chlorine atoms bridging $Ru_2^{5+}$ units are formed. Treatment of $Ru_2Cl(\mu\text{-}O_2CR)_4$ in thf or acetone with $AgBF_4$ gave $[Ru_2(\mu\text{-}O_2CR)_4L_2]BF_4$ (L = thf, acetone; R = *N*-methyl-2-pyrrolyl, 2-furyl, 2-thienyl) or $[Ru_2(\mu\text{-}O_2CR)_4]BF_4$ (R = 2-benzofuryl). The axial positions of these compounds can be occupied by $OPPh_3$ to give the corresponding $[Ru_2(\mu\text{-}O_2CR)_4(OPPh_3)_2]BF_4$. The compounds have been characterized by analytical, spectroscopic and magnetic data. The structure of $[Ru_2(\mu\text{-}O_2CC_4H_3S)_4(OPPh_3)_2]BF_4 \cdot 2H_2O$ has been determined by X-ray crystallography. The dinuclear cation has two ruthenium atoms linked by four bridging thiophene-2-carboxylate ligands and two $OPPh_3$ ligands coordinated to axial positions, with an Ru—Ru distance of 2.2747(11) Å.

In recent years, diruthenium(II,III) chemistry has been actively studied and numerous chlorotetracarboxylatediruthenium(II,III) compounds have been synthesized.[1–10] The determination of the crystal structure of some of these compounds has shown that, in all cases, a polymeric structure is formed, with the $[Ru_2(carboxylate)_4]^+$ units linked by bridging chlorine atoms, giving infinite zig-zag[8] or linear chains.[9] The analogous chlorotetraamidatediruthenium(II,III) are also polymers,[11] whereas, in contrast, the amino- or hydroxypyridinate derivatives are not.[12] We have found recently[10] that the complex $Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf) \cdot thf \cdot H_2O$, similarly to amino- or hydroxypyridinate derivatives, is not polymeric, but its nature cannot be attributed to the steric effect of the ligands (as in the above-mentioned amino- and

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hydroxypyridinate derivatives) and it is probably related to the presence of NH groups in the bridging ligands.

On the other hand, it has been observed previously[13] that the reaction of $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$ with pyridine-2-carboxylic acid, which has a nitrogen atom in the $\alpha$ position with respect to the $CO_2$ group, leads to a disproportionation process; similar behaviour has been observed[14] in the reaction with mandelic acid, which has an OH group in the $\alpha$ position. In this work, we have studied the reactions of $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$ with several carboxylic acids containing nitrogen, oxygen or sulphur atoms in the $\alpha$ position with respect to the carboxylate group, in order to investigate the influence of these atoms on the reactivity of the ligands. Polymeric compounds of the type $[Ru_2Cl(\mu\text{-}O_2CR)_4]_n$ with *N*-methyl-pyrrole-2-carboxylic, furane-2-carboxylic, thiophene-2-carboxylic and benzofurane-2-carboxylic acids have been isolated. A non-polymeric compound has been obtained with indole-2-carboxylic acid and a disproportionation process has been observed in the case of quinoline-2-carboxylic acid. The reactivity of the polymeric $[Ru_2Cl(\mu\text{-}O_2CR)_4]_n$ compounds with $AgBF_4$ has been studied. The synthesis of $OPPh_3$ adducts of the type $[Ru_2(\mu\text{-}O_2CR)_4(OPPh_3)_2]BF_4$ is also described and the crystal structure of $[Ru_2(\mu\text{-}O_2CC_4H_3S)_4(OPPh_3)_2]BF_4 \cdot 2H_2O$ has been determined.

## RESULTS AND DISCUSSION

The reaction of $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$ with indole-2-carboxylic acid in methanol–water and the recrystallization of the solid obtained from thf–petroleum ether gave $Ru_2Cl(\mu\text{-}O_2CC_8H_6N)_4(thf)$ (**1**). Similar reaction with *N*-methyl-pyrrole-2-carboxylic, furane-2-carboxylic, thiophene-2-carboxylic and benzofurane-2-carboxylic acids led to the formation of $Ru_2Cl(\mu\text{-}O_2CR)_4$ [R = *N*-methyl-2-pyrrolyl (**2**), 2-furyl (**3**), 2-thienyl (**4**), 2-benzofuryl (**5**)]. All these compounds are stable to air for several months. Compound **1** is soluble in polar organic solvents such as thf or acetone, whereas compounds **2**–**5** are very insoluble in most polar and non-polar organic solvents. Conductivity measurements in thf or methanol solution show that compound **1** is a non-electrolyte, whereas compounds **2**–**5** are 1 : 1 electrolytes in DMSO solution.

The IR spectra of these compounds show in each case the typical pattern of O,O-coordination of the bridging carboxylate ligand and the absorptions corresponding to the R groups.

The magnetic measurements in the range 295–75 K show that the compounds obey the Curie–Weiss law with magnetic moments corresponding to three unpaired electrons per dimer unit, in accordance with the ground state configuration $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$, analogous to those found in the other carboxylate complexes.[15] There are no appreciable differences in these magnetic properties for compounds **1**–**5**. Table 1 shows the variation of the magnetic susceptibilities for some selected compounds. The magnetic behaviour of the other paramagnetic compounds is very similar.

The properties of compound **1** are similar to those found in the pyrrole-2-carboxylate derivative, which was the first non-polymeric compound of this type described.[10] Thus, although we have not determined the crystal structure of the indole-2-carboxylate derivative, its solubility in thf or acetone, the elemental analysis and the non-electrolyte nature suggests for this compound a similar structure to the pyrrole-2-carboxylate compound, with the $Ru_2^{5+}$ unit bridged by four indole-2-carboxylate ligands and the axial positions occupied by one chlorine ligand and one thf molecule. However, the properties of compounds **2**–**5** suggest a polymeric structure with bridging chlorine atoms between $[Ru_2(\mu\text{-}O_2CR)_4]^+$ units, analogous to the parent $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$ compound. These results indicate that the presence of NH groups in the pyrrole- and indole-2-carboxylate ligands should be responsible for the non-polymeric nature. These NH groups interact by hydrogen bonds with the oxygen atoms of solvents such as thf or acetone, making the compound soluble and with a solvent molecule occupying one axial position. This is also in accord with the fact that when the hydrogen atom of the NH group is substituted by the methyl group in the *N*-methyl-pyrrole-2-carboxylate ligand, the compound is very insoluble, indicating a polymeric structure.

On the other hand, the reaction of $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$ with quinoline-2-carboxylic acid led to disproportionation, with formation of a yellow $Ru^{III}$ complex, $Ru(quin)_3$ (**6**), and the purple dimer $Ru_2(quin)_4$ (**7**). Similar behaviour has been observed in the reaction with pyridine-2-carboxylic acid.[13] Compound **6** is stable to air in the solid state and in solution, whereas **7** decomposes slowly in solution. The IR spectra of these complexes show that the $CO_2$ group is bonded through only one oxygen atom, suggesting an N,O-coordination, which is the most common in quinoline-2-carboxylato compounds.[16] Compound **6** is paramagnetic, with a magnetic moment corresponding to one unpaired electron, in accord with a monomeric compound of $Ru^{III}$. However, compound **7** is diamagnetic and the $^1H$ NMR spectrum is very simple, showing only the presence of a unique type

Table 1. Magnetic data at various temperatures for selected compounds

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Ru_2Cl(\mu\text{-}O_2CC_8H_6N)_4(thf)$ ($C_8H_6N$ = 2-indolyl) (**1**) | | | | | | | | | | | | | | |
| $T$ (K) | 288.07 | 268.71 | 248.98 | 228.78 | 208.81 | 188.97 | 166.82 | 149.28 | 129.80 | 109.23 | 98.58 | 89.38 | 79.70 | 76.44 |
| $\chi_M (\times 10^3)$ | 7.758 | 8.195 | 8.711 | 9.414 | 10.35 | 11.50 | 12.80 | 14.12 | 16.18 | 18.52 | 20.19 | 21.78 | 23.89 | 24.46 |
| $\mu$ (B.M.) | 4.25 | 4.21 | 4.18 | 4.17 | 4.18 | 4.19 | 4.15 | 4.12 | 4.12 | 4.04 | 4.01 | 3.96 | 3.92 | 3.88 |
| $Ru_2Cl(\mu\text{-}O_2CC_5H_6N)_4$ ($C_5H_6N$ = *N*-methyl-2-pyrrolyl) (**2**$\cdot 2H_2O$) | | | | | | | | | | | | | | |
| $T$ (K) | 289.50 | 288.88 | 248.86 | 226.30 | 209.08 | 189.06 | 169.29 | 149.88 | 127.68 | 109.00 | 100.15 | 89.23 | 78.92 | 75.89 |
| $\chi_M (\times 10^3)$ | 8.180 | 8.863 | 9.504 | 10.17 | 11.08 | 12.19 | 13.25 | 15.13 | 17.42 | 19.50 | 20.68 | 22.92 | 25.29 | 25.48 |
| $\mu$ (B.M.) | 4.37 | 4.38 | 4.37 | 4.31 | 4.32 | 4.31 | 4.25 | 4.28 | 4.24 | 4.14 | 4.09 | 4.06 | 4.01 | 3.95 |
| $[Ru_2(\mu\text{-}O_2CC_5H_6N)_4(thf)_2]BF_4$ ($C_5H_6N$ = N-methyl-2-pyrrolyl) (**8**) | | | | | | | | | | | | | | |
| $T$ (K) | 286.61 | 265.80 | 245.23 | 228.78 | 209.29 | 189.09 | 169.36 | 149.64 | 129.31 | 108.99 | 87.93 | 78.49 | 75.71 | |
| $\chi_M (\times 10^3)$ | 7.762 | 8.432 | 8.924 | 9.870 | 10.85 | 11.86 | 12.85 | 15.00 | 17.08 | 19.57 | 23.51 | 25.59 | 25.98 | |
| $\mu$ (B.M.) | 4.24 | 4.25 | 4.20 | 4.27 | 4.35 | 4.25 | 4.19 | 4.26 | 4.22 | 4.15 | 4.08 | 4.03 | 3.98 | |
| $[Ru_2(\mu\text{-}O_2CC_5H_6N)_4(OPPh_3)_2]BF_4\cdot$acetone ($C_5H_6N$ = *N*-methyl-2-pyrrolyl) (**12**$\cdot$acetone) | | | | | | | | | | | | | | |
| $T$ (K) | 288.28 | 269.12 | 245.59 | 228.73 | 208.83 | 189.30 | 168.80 | 149.76 | 129.99 | 109.00 | 100.51 | 89.23 | 78.92 | 74.92 |
| $\chi_M (\times 10^3)$ | 5.631 | 6.219 | 6.720 | 7.310 | 8.102 | 8.932 | 9.945 | 11.17 | 12.86 | 15.06 | 16.21 | 18.39 | 20.24 | 20.80 |
| $\mu$ (B.M.) | 3.62 | 3.67 | 3.65 | 3.67 | 3.69 | 3.69 | 3.68 | 3.67 | 3.67 | 3.64 | 3.62 | 3.64 | 3.59 | 3.54 |

of quinoline-2-carboxylate ligand. The elemental analysis and the spectroscopic properties are in accordance with a dimeric structure. Thus, although all *O*,*O*-carboxylatediruthenium(II) complexes are paramagnetic, in some $Ru^{II}$ dimers with N,N-coordination of the ligands diamagnetic behaviour has been observed.[17] The N,O-coordination of the quinoline-2-carboxylato ligands in **7** locates this complex in a central position. Thus, small differences in the nature of the ligand could explain the formation of diamagnetic or paramagnetic compounds with $\sigma^2\pi^4\delta^2\pi^{*4}$ or $\sigma^2\pi^4\delta^2\pi^{*3}\delta^{*1}$ configurations. Unfortunately, we have not obtained single crystals of **7** for X-ray determination, and the possibility of other structures such as dimeric diruthenium(II) compounds without a metal–metal bond cannot be discounted.

The different behaviour of the pyrrole-2-carboxylate and indole-2-carboxylate ligands relative to pyridine-2-carboxylate and quinoline-2-carboxylate ligands may be due to the presence of one hydrogen on the nitrogen atom and to the different electronic density of the nitrogen atom in five- and six-membered rings.

Finally, the presence of oxygen or sulphur atoms in the ligands does not have any influence on their reactivity towards $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$, leading to substitution reactions with formation of polymeric compounds.

The polymeric structures of **2**–**4** can be broken with $AgBF_4$ in thf or acetone, giving solvated $[Ru_2(\mu\text{-}O_2CR)_4L_2]BF_4$ [L = thf, R = *N*-methyl-2-pyrrolyl (**8**), 2-furyl (**9**), 2-thienyl (**10**)] compounds. These derivatives lose thf or acetone very easily, giving the unsolvated species $[Ru_2(\mu\text{-}O_2CR)_4]BF_4$. The unsolvated $[Ru_2(\mu\text{-}O_2CR)_4]BF_4$ [R = 2-benzofuryl (**11**)] compound has been obtained in acetone. All these compounds are soluble in polar organic solvents, such as acetone or methanol; compounds **8**–**10** are partially soluble in thf but compound **11** is almost insoluble in this solvent. The IR spectra of these compounds are similar to the starting complexes, but in addition show a very strong and broad band at *ca* 1070 $cm^{-1}$, corresponding to the $BF_4^-$ group. Similarly to other thf adducts,[7,18] due to the lability of thf or acetone coordinated axially, the IR spectra in KBr discs do not show bands assigned to these ligands. The magnetic susceptibility measurements are similar to the starting materials, with magnetic moments corresponding to three unpaired electrons per dimer.

In these compounds the thf or acetone ligand can easily be substituted by other ligands. Thus, the reaction of $[Ru_2(\mu\text{-}O_2CR)_4L_2]BF_4$ (L = thf, acetone) or $[Ru_2(\mu\text{-}O_2CR)_4]BF_4$ with $OPPh_3$ in acetone or dichloromethane gave $[Ru_2(\mu\text{-}O_2CR)_4(OP\text{-}$

$Ph_3)_2]BF_4$ [R = *N*-methyl-2-pyrrolyl (**12**), 2-furyl (**13**), 2-thienyl (**14**), 2-benzofuryl (**15**)]. These compounds are more soluble in polar organic solvents than the parent thf adducts, and in general the crystals do not lose crystallinity by exposure to air. The IR spectra of **12**–**15** showed the absorption bands of the corresponding starting compounds and the characteristic vibrations due to the coordinated $OPPh_3$ ligands. The magnetic measurements were also similar to the parent compounds with magnetic moments corresponding to three unpaired electrons per dimer unit.

### *X-ray crystal structure of* **14**·$2H_2O$

Figure 1 shows one view of the X-ray structure of the cation $[Ru_2(\mu\text{-}O_2CC_4H_3S)_4(OPPh_3)_2]^+$. Table 2 gives selected bond distances and angles of the compound. Crystals of **14**·$2H_2O$ consist of dinuclear $[Ru_2(\mu\text{-}O_2CC_4H_3S)_4(OPPh_3)_2]^+$ cations, $BF_4^-$ anions and water molecules of solvation. The dinuclear cation has two ruthenium atoms linked by four bridging thiophene-2-carboxylate ligands and two $OPPh_3$ ligands coordinated in axial positions. Both ruthenium atoms have a distorted octahedral coordination geometry with four oxygen atoms in the equatorial positions and one $OPPh_3$ ligand and the other ruthenium atom in the apical positions. The distortion of the octahedral structure arises essentially from the longer Ru—$O_{axial}$ and Ru—Ru distances with respect to the Ru—$O_{equatorial}$ distances. In this structure a notable feature is the positional disorder observed in the thiophene rings in which the sulphur atoms are statistically distributed among the possible positions. This could be a consequence of the free rotation of the thiophene rings in solution and because these are no interactions of the sulphur atom in hydrogen bonding. This is a very important difference with respect to the crystal structure of $Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4$(thf)·thf·$H_2O$, in which all nitrogen atoms of the pyrrole rings are involved in hydrogen bonding.

The Ru—Ru distance of 2.2747(11) Å and the distances and angles of the $[Ru_2(O_2C)_4]^+$ unit are similar to those found in other diruthenium(II,III) carboxylate compounds.[8,9] The Ru—$O_{axial}$ distance is analogous to those found in two other $OPPh_3$ adducts of diruthenium[19] and also to those found in the phenylphosphinate and phenylphosphonate derivatives of tetraacetatodiruthenium(II,III).[20]

## EXPERIMENTAL

All reactions were carried out in an inert atmosphere, using standard Schlenk techniques. Ruthenium trichloride, carboxylic acids, $AgBF_4$ and $OPPh_3$ were purchased from commercial sources. Solvents were used without previous puri-

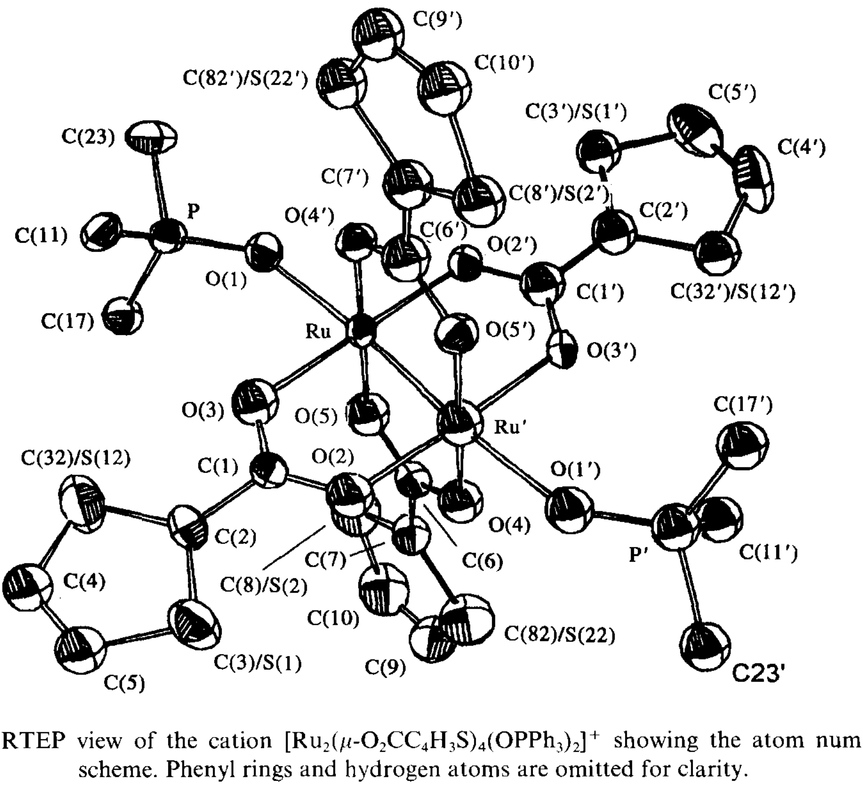

Fig. 1. ORTEP view of the cation $[Ru_2(\mu\text{-}O_2CC_4H_3S)_4(OPPh_3)_2]^+$ showing the atom numbering scheme. Phenyl rings and hydrogen atoms are omitted for clarity.

Table 2. Principal bond lengths (Å) and bond angles (°) for $[Ru_2(\mu\text{-}O_2CC_4H_3S)_4(OPPh_3)_2]BF_4 \cdot 2H_2O$

| | | | |
|---|---|---|---|
| Ru—Ru′ | 2.275(1) | O(4)—C(6) | 1.28 (1) |
| Ru—O(1) | 2.216(7) | O(5)—C(6) | 1.27 (1) |
| Ru—O(2′) | 2.031(6) | C(1)—C(2) | 1.46 (1) |
| Ru—O(3) | 2.020(6) | C(6)—C(7) | 1.48 (2) |
| Ru—O(4′) | 2.014(8) | C(2)—C(32)/S(12) | 1.59 (1) |
| Ru—O(5) | 2.024(8) | C(2)—C(3)/S(1) | 1.598(9) |
| O(1)—P | 1.497(8) | C(7)—C(82)/S(22) | 1.65 (1) |
| O(2)—C(1) | 1.26 (1) | C(7)—C(8)/S(2) | 1.66 (1) |
| O(3)—C(1) | 1.27 (1) | | |

| | | | |
|---|---|---|---|
| O(5)—Ru—O(4′) | 179.3(3) | O(1)—Ru—O(3) | 87.4(2) |
| O(3)—Ru—O(4′) | 91.6(3) | O(1)—Ru—O(4′) | 91.0(3) |
| O(3)—Ru—O(5) | 88.6(3) | O(1)—Ru—O(5) | 89.6(3) |
| O(2′)—Ru—O(4′) | 88.8(3) | C(3)/S(1)—C(2)—C(32)/S(12) | 113.4(5) |
| O(2′)—Ru—O(5) | 91.0(3) | C(2)—C(3)/S(1)—C(5) | 96.8(6) |
| O(2′)—Ru—O(3) | 178.6(3) | C(2)—C(32)/S(12)—C(4) | 98.0(7) |
| Ru′—Ru—O(2′) | 89.7(2) | C(3)/S(1)—C(5)—C(4) | 116 (1) |
| Ru′—Ru—O(3) | 89.0(2) | C(32)/S(12)—C(4)—C(5) | 116 (1) |
| Ru′—Ru—O(4′) | 89.9(2) | C(8)/S(2)—C(7)—C(82)/S(22) | 119.6(7) |
| Ru′—Ru—O(5) | 89.4(2) | C(7)—C(8)/S(2)—C(10) | 91.1(7) |
| Ru′—Ru—O(1) | 176.3(2) | C(7)—C(82)/S(22)—C(9) | 92.0(7) |
| Ru—O(1)—P | 142.2(4) | C(8)/S(2)—C(10)—C(9) | 119 (1) |
| O(1)—Ru—O(2′) | 94.0(2) | C(82)/S(22)—C(9)—C(10) | 119 (1) |

fication. $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$ was prepared by the literature procedure.[2b] IR spectra were recorded as KBr discs on a Perkin–Elmer 1330 IR spectrophotometer. Magnetic susceptibility measurements were made using a fully automatic DSM 8 magneto-susceptometer, based on the Faraday methods. $^1H$ NMR spectra were recorded on a Varian 300S spectrophotometer using $D_2O$ as solvent and TMS as external reference. Elemental analyses for carbon, hydrogen and nitrogen were performed at the Microanalytical Service of the Complutense University of Madrid.

### *Synthesis of* $Ru_2Cl(\mu\text{-}O_2CC_8H_6N)_4(thf)$ $(C_8H_6N =$ *2-indolyl*$)$ (**1**)

To a solution of $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$ (0.3 g, 0.63 mmol) in methanol–water (1 : 1, 80 $cm^3$), an excess of indole-2-carboxylic acid (0.61 g, 3.79 mmol) was added. The reaction mixture was heated under reflux for 4 h, giving a brown solid. The solution was filtered and the solid was treated again with the ligand (0.41 g, 2.52 mmol) in methanol–water under reflux for 4 h, to ensure the complete substitution of the acetate ligands. The solution was filtered and the solid was washed twice with 10 $cm^3$ of water and dried *in vacuo*. The resulting solid was extracted with thf and layered with petroleum ether to give $Ru_2Cl(\mu\text{-}O_2CC_8H_3N)_4(thf)$. Found: C, 50.5; H, 3.4; N, 5.9. Calc. for $C_{40}H_{32}O_9N_4ClRu_2$: C, 50.6; H, 3.4; N, 5.9%. $\nu_{max}$ (KBr disc), $cm^{-1}$: 3420m(br) (NH), 1580m and 1550vs (C=C), 1450s(sh) and 1410vs(br) ($CO_2$). $\mu_{eff} = 4.25$ B.M.

### *Preparation of complexes of the type* $Ru_2Cl(\mu\text{-}O_2CR)_4$[R = *N-methyl-2-pyrrolyl* (**2**), *2-furyl* (**3**), *2-thienyl* (**4**), *2-benzofuryl* (**5**)]

These compounds were obtained following a general method of preparation. To a solution of $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$ (0.3 g, 0.63 mmol) in methanol–water (1 : 1, 60 $cm^3$), an excess of carboxylic acid (3.79 mmol) was added. The reaction mixture was heated under reflux for 4 h, giving a brown solid. The solution was filtered and the solid was washed and dried *in vacuo*.

Compound **2** was washed twice with 10 $cm^3$ of acetone and characterized as $\mathbf{2} \cdot 2H_2O$. Found: C, 37.8; H, 3.3; N, 6.9. Calc. for $C_{24}H_{24}N_4O_8ClRu_2$: C, 37.4; H, 3.7; N, 7.3%. $\nu_{max}$ (KBr disc), $cm^{-1}$: 3420m(br) (OH), 1545s (C=C), 1430s and 1400s ($CO_2$). $\mu_{eff} = 4.37$ B.M.

Compound **3** was washed twice with 10 $cm^3$ of water. Found: C, 35.0; H, 2.2. Calc. for $C_{20}H_{12}O_{12}ClRu_2$: C, 35.2; H, 1.8%. $\nu_{max}$ (KBr disc), $cm^{-1}$: 1580vs (C=C), 1470vs(br) and 1415vs ($CO_2$). $\mu_{eff} = 4.02$ B.M.

Compound **4** was washed twice with 10 $cm^3$ of diethyl ether. Found: C, 32.2; H, 1.9. Calc. for $C_{20}H_{12}O_8S_4ClRu_2$: C, 32.2; H, 1.6%. $\nu_{max}$ (KBr disc) $cm^{-1}$: 1520vs (C=C), 1425vs(br) and 1395vs ($CO_2$). $\mu_{eff} = 4.16$ B.M.

Compound **5** was washed twice with 10 $cm^3$ of methanol and characterized as $\mathbf{5}\cdot 2H_2O$. Found: C, 47.4; H, 2.6. Calc. for $C_{36}H_{20}O_{12}ClRu_2$: C, 47.8; H, 2.9%. $\nu_{max}$ (KBr disc), $cm^{-1}$: 3400m(br) (OH), 1600m and 1555vs (C=C), 1430s(sh) and 1400vs(br) ($CO_2$). $\mu_{eff} = 4.43$ B.M.

### *Reaction of* $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$ *with quinoline-*2*-carboxylic acid*

To a solution of $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$ (0.3 g, 0.63 mmol) in methanol (45 $cm^3$) was added quinoline-2-carboxylic acid (0.63 g, 3.80 mmol). The colour of the solution changed to purple and after 4 h under reflux a purple solution with some purple solid was obtained. The reaction mixture was pumped to dryness and the residue was extracted with acetone, giving a red–violet solution and a purple solid. The acetone solution was evaporated in air giving red crystals of $Ru(quin)_3\cdot$acetone, which were washed quickly with acetone; the unsolvated yellow $Ru(quin)_3$ (**6**) was obtained when $Ru(quin)_3\cdot$acetone was dried *in vacuo*. The purple solid was dried *in vacuo* to give $Ru_2(quin)_4$ (**7**).

Compound **6**·acetone. Found: C, 58.5; H, 3.5; N, 6.2. Calc. for $C_{33}H_{24}N_3O_7Ru$: C, 58.7; H, 3.6; N, 6.2%. $\nu_{max}$ (KBr disc), $cm^{-1}$: 1660vs(br) ($CO_2$, asymm.) 1585m (C=C), 1310vs ($CO_2$, symm.). $\mu_{eff} = 1.80$ B.M.

Compound **7**. Found: C, 53.9; H, 2.7; N, 6.3. Calc. for $C_{40}H_{24}N_4O_8Ru_2$: C, 54.7; H, 3.1; N, 6.1%. $\nu_{max}$ (KBr disc), $cm^{-1}$: 1670vs(br) ($CO_2$, asymm.), 1590m (C=C), 1320vs(br). $\delta_H$ ($D_2O$): 7.98 (1H, dd), 8.19 (1H, dd), 8.32 (1H, d), 8.37 (1H, d), 8.39 (1H, d), 9.18 (1H, d).

### *Synthesis of complexes of the type* $[Ru_2(\mu\text{-}O_2CR)_4(thf)_2]BF_4$ [R = N-*methyl-*2*-pyrrolyl* (**8**), 2-*furyl* (**9**), 2-*thienyl* (**10**)]

These complexes were obtained by a general procedure. A suspension of $Ru_2Cl(\mu\text{-}O_2CR)_4$ (0.20 mmol) in thf (60 $cm^3$) was treated with $AgBF_4$ (0.04 g, 0.20 mmol) and the mixture was stirred for 24 h. The precipitate, containing AgCl, was filtered over celite and extracted (3 × 25 $cm^3$) with thf. The solution and the extract were concentrated under reduced pressure to 20 $cm^3$ and petroleum ether (40–60°C) was added to give brown–red solids characterized as $[Ru_2(\mu\text{-}O_2CR)_4(thf)_2]BF_4$.

Compound **8**. Found: C, 40.9; H, 4.45; N, 5.8. Calc. for $C_{32}H_{40}N_4O_{10}BF_4Ru_2$: C, 41.3; H, 4.3; N, 6.0%. $\nu_{max}$ (KBr disc), $cm^{-1}$: 1545vs (C=C), 1490m and 1425vs(br) ($CO_2$), 1080–1050s(br) ($BF_4^-$). $\mu_{eff} = 4.24$ B.M.

Compound **9**. Found: C, 37.8; H, 2.8. Calc. for $C_{28}H_{28}O_{14}BF_4Ru_2$: C, 38.3; H, 3.2%. $\nu_{max}$ (KBr disc), $cm^{-1}$: 1580vs (C=C), 1480vs and 1420 vs(br) ($CO_2$), 1080s(br) ($BF_4^-$). $\mu_{eff} = 3.64$ B. M.

Compound **10**. Found: C, 35.4; H, 3.3. Calc. for $C_{28}H_{28}O_{10}S_4BF_4Ru_2$: C, 35.7; H, 3.0%. $\nu_{max}$ (KBr disc), $cm^{-1}$: 1530vs (C=C), 1420vs(br) and 1400vs ($CO_2$), 1090–1050s(br) ($BF_4^-$). $\mu_{eff} = 3.88$ B.M.

These reactions can also be carried out in acetone, giving the corresponding acetone adducts.

### *Synthesis of* $[Ru_2(\mu-O_2CC_8H_5O)_4]BF_4$ ($C_8H_5O$ = 2-*benzofuryl*) (**11**)

A suspension of **5** (0.2 g, 0.22 mmol) in acetone (20 $cm^3$) was treated with $AgBF_4$ (0.04 g, 0.22 mmol) and the mixture was stirred for 24 h. The precipitate of AgCl was removed by filtration over celite and extracted with acetone (3 × 15 $cm^3$). The resulting solution was concentrated *in vacuo* and layered with petroleum ether (40–60°C), giving a brown–red solid. The solid was filtered and dried *in vacuo* to give $[Ru_2(\mu\text{-}O_2CC_8H_5O)_4]BF_4$. Found: C, 46.5; H, 2.5. Calc. for $C_{36}H_{20}O_{12}BF_4Ru_2$: C, 46.3; H, 2.2%. $\nu_{max}$ (KBr disc), $cm^{-1}$: 1580s (C=C), 1450m and 1420vs(br) ($CO_2$), 1080s(br) ($BF_4^-$). $\mu_{eff} = 3.79$ B.M.

### *Synthesis of compounds of the type* $[Ru_2(\mu\text{-}O_2CR)_4(OPPh_3)_2]BF_4$ [R = N-*methyl-*2*-pyrrolyl* (**12**), 2-*furyl* (**13**), 2-*thienyl* (**14**), 2-*benzofuryl* (**15**)]

These complexes were obtained by a general procedure. A solution (40 $cm^3$) of $[Ru_2(\mu\text{-}O_2CR)_4(thf)_2]BF_4$ or **11** (0.21 mmol) was treated with $OPPh_3$ (0.12 g, 0.42 mmol). The mixture was stirred for 24 h at room temperature. The red solution was pumped to dryness and the residue washed twice with diethyl ether.

Compound **12** was obtained using acetone as solvent. An acetone solution was layered with petroleum ether (40–60°C) to give crystals characterized as **12**·acetone. Found: C, 54.6; H, 4.6; N, 3.8. Calc. for $C_{63}H_{60}N_4O_{11}P_2BF_4Ru_2$: C, 54.05; H, 4.3; N, 4.00%. $\nu_{max}$ (KBr disc), $cm^{-1}$: 1540vs (C=C), 1430vs(br) and 1400s ($CO_2$), 1150vs (O=P), 1080–1055 vs ($BF_4^-$). $\mu_{eff} = 3.62$ B.M.

Compound **13** was prepared using $CH_2Cl_2$ as solvent and recrystallized from dichloromethane–petroleum ether (40–60°C). Found: C, 52.0; H, 3.2. Calc. for $C_{56}H_{42}O_{14}P_2BF_4Ru_2$: C, 52.15; H, 3.3%. $\nu_{max}$ (KBr disc), $cm^{-1}$: 1580vs (C=C), 1140s

(O=P), 1440vs and 1420vs(br) ($CO_2$), 1070vs(br) ($BF_4^-$). $\mu_{eff} = 3.10$ B.M.

Compound **14** was prepared using $CH_2Cl_2$ as solvent. Recrystallization from commercial $CH_2Cl_2$ gave crystals of **14**·$2H_2O$ suitable for X-ray determination. Found: C, 49.3; H, 3.3. Calc. for $C_{56}H_{42}O_{10}P_2S_4BF_4Ru_2$: C, 49.7; H, 3.1%. $\nu_{max}$ (KBr disc), $cm^{-1}$: 3400m(br) (OH), 1530vs (C=C), 1420vs(br) and 1400s ($CO_2$), 1150s (O=P) 1070s(br) ($BF_4^-$). $\mu_{eff} = 3.63$ B.M.

Compound **15** was prepared using acetone as solvent to give $[Ru_2(\mu\text{-}O_2CC_8H_5O)_4(OPPh_3)_2]BF_4 \cdot 2H_2O$. Found: C, 56.3; H, 3.7. Calc. for $C_{72}H_{54}O_{16}P_2BF_4Ru_2 \cdot 2H_2O$: C, 56.7; H, 3.6%. $\nu_{max}$ (KBr disc), $cm^{-1}$: 3400m(br) (OH), 1580vs (C=C), 1450s and 1420vs(br) ($CO_2$), 1150s (O=P), 1080s(br) ($BF_4^-$). $\mu_{eff} = 4.18$ B.M.

### *X-ray structure determination*

A summary of the fundamental crystal data are given in Table 3. A reddish crystal showing well defined faces was epoxy resin-coated and mounted in a kappa diffractometer. Cell dimensions were refined by least-squares fitting the $\theta$ values of 25 reflections with a $2\theta$ range of 16–25°. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for ruthenium, phosphorus and sulphur were taken from the *International Tables for X-ray Crystallography*.[21] The position of the heavy atom was obtained from the Patterson function. The rest of the structure was solved by means of Fourier synthesis. It is worth noting that some degree of positional disorder was found for

Table 3. Crystallographic data for $[Ru_2(\mu\text{-}O_2CC_4H_3S)_4(OPPh_3)_2]BF_4 \cdot 2H_2O$

| | |
|---|---|
| Formula | $Ru_2C_{56}S_4O_{12}P_2BF_4H_{46}$ |
| Mol. wt | 1390.1 |
| Crystal system | Monoclinic |
| Space group | $C2/c$ (No. 15) |
| Cell dimensions | |
| $a$ (Å) | 26.517(5) |
| $b$ (Å) | 18.236(3) |
| $c$ (Å) | 14.324(7) |
| $\alpha$ (°) | 90.00 |
| $\beta$ (°) | 112.94(2) |
| $\gamma$ (°) | 90.00 |
| $Z$ | 4 |
| $V$ (Å$^3$) | 6379(4) |
| $D_{calc}$ (g $cm^{-3}$) | 1.45 |
| $F(000)$ | 2804 |
| Temp. (K) | 295 |
| Diffractometer | Enraf–Nonius |
| Radiation | graphite-monochromated<br>Mo-$K_\alpha$ ($\lambda = 0.71069$ Å) |
| $\mu$(Mo-$K_\alpha$) ($cm^{-1}$) | 7.04 |
| Crystal dimensions (mm) | 0.25 × 0.25 × 0.2 |
| $2\theta$ range (°) | 2–60 |
| Scan technique | $\omega$–$2\theta$ |
| Data collected | (−37,0,0) to (37,25,20) |
| Unique data | 10134 |
| Observed reflections | 5593 |
| $R_{int}$ (%) | 1.6 |
| Decay | — |
| Standard reflections | 3/111 |
| Weighting scheme | unit |
| $R = \Sigma \lvert\Delta F\rvert / \Sigma \lvert F_0\rvert$ | 0.071 |
| $R_w = (\Sigma w\Delta^2 F / \Sigma w \lvert F_0\rvert^2)^{1/2}$ | 0.079 |
| Maximum shift/error | 0.002 |
| Absorption correction range | 0.97–1.01 |

the thiophene rings. Since they are not involved in hydrogen bonding, the sulphur atoms are statistically distributed among all the possible positions. This means that the thiophene rings show different relative orientations for different molecules along the crystal. This situation is described in our structural model using population factors of 50% for the carbon and sulphur atoms sharing the same crystallographic position. An empirical absorption correction[22] was applied at the end of the isotropic refinements.

A final refinement was undertaken with unit weights and anisotropic thermal motion for the non-hydrogen atoms. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions determined by molecular geometry. No trend in $\Delta F$ vs $F_0$ or sin $\theta/\lambda$ was observed. The only significant electron densities found by the difference synthesis, performed at the final step of the structure determination, were located around the oxygen atoms corresponding to water of crystallization. Since there is no hydrogen bonding in the crystal, these water molecules show free rotation at room temperature, and it is impossible to locate their hydrogen atoms. Most of the calculations were carried out with the X-ray 80 system.[23]

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