Stabilizing of the Ru_2^{6+} core. Use of highly charged ligands such as sulfate and phosphate

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Abstract

A new, more convenient, and cleaner synthetic route starting from an Ru_2(II,III) carbonate complex to Ru_2(II,III) sulfate complexes has been developed. This route has also provided, for the first time, a new Ru_2(II,III) phosphate complex, $K_4[Ru_2(HPO_4)_3(PO_4)(H_2O)_2]$ (**1**). Electrochemical oxidation has further transformed these sulfate and phosphate complexes to the corresponding Ru_2(III,III) complexes. Magnetic susceptibility measurements on $K_2[Ru_2(SO)_4)_4(H_2O)_2]$ from 10 to 300 K have confirmed the assignment of the ground state as one arising from an unusual $\sigma^2\pi^4\delta\pi^{*2}\delta^*$ configuration. The crystal structure of **1** has been determined to be as follows. Space group $P2_1/n$ (No. 14), $a=9.049(1)$, $b=9.418(1)$, $c=10.235(1)$ Å, $\beta=90.480(9)°$, $V=872.2(2)$ Å^3, $Z=2$, $R=0.023$, Ru–Ru distance $=2.3052(4)$ Å.

Introduction

It has been well documented that most of the chemistry of compounds with Ru_2^{n+} cores has centered around those with Ru_2^{4+} and Ru_2^{5+} cores [1, 2], and the question of whether any Ru_2^{6+} species exist remained, until recently, an open one. While $[Ru_2(O_2CR)_4]^{2+}$ compounds do not exist, the possibility that the Ru_2^{6+} core might be stabilized either by a set of much more basic ligands, or by a set of more negatively charged ligands, or in both ways, posed some interesting synthetic challenges.

The possibility of employing more negatively charged ligands, even though these might be less basic, received encouragement from previous experience with compounds of other M_2^{n+} units that contain SO_4^{2-}, PO_4^{3-} and HPO_4^{2-} ions as bridging ligands. The first example was provided by $[Mo_2(SO_4)_4]^{3-}$, discovered nearly 20 years ago in this laboratory [3]. Whereas the previously well-characterized $Mo_2(O_2CR)_4$ compounds showed no ability to survive even a one-electron oxidation, the $[Mo_2(SO_4)_4]^{3-}$ ion formed spontaneously during the preparation of $[Mo_2(SO_4)_4]^{4-}$ compounds, and is very stable. Even more striking was the discovery [4], several years later, that the HPO_4^{2-} ion was able to stabilize even the Mo_2^{6+} core as $[Mo_2(HPO_4)_4(H_2O)]^{2-}$.

Thus the reports [5] in 1989 that the $[Ru_2(SO_4)_4(H_2O)_2]^{2-}$ ion had been obtained had to be given serious consideration, despite some mildly disquieting aspects of the work. The preparation was not described in full detail and initial efforts to reproduce it were not successful. The crystal structure was not fully described and one could not directly rule out the possibility that there was one undetected additional H^+ (probably involved in a hydrogen bond), thus making the core Ru_2^{5+} rather than Ru_2^{6+}. Finally, the report that the compound has four unpaired electrons, for which a $\sigma^2\pi^4\delta\pi^{*2}\delta^*$ configuration was proposed in explanation, seemed a bit bizarre though certainly not unbelievable.

Because of these uncertainties regarding the authenticity of the $[Ru_2(SO_4)_4(H_2O)_2]^{2-}$ ion we decided to do two things. First to undertake further studies of one of the substances reported to contain this ion, and second, to take a hint from the dimolybdenum compounds discussed above and see if the use of phosphate ligands might lead to Ru_2^{6+} species of equal or (we hoped) even greater accessibility.

Experimental

IR spectra in the range 4000–400 cm^{-1} were recorded on a Perkin-Elmer spectrophotometer, using liquid paraffin and fluorinated hydrocarbon mulls. Visible spectra were recorded on a Cary 17D spectrophotometer. Magnetic susceptibility data over the temperature range 10–300 K were obtained on a SQUID suscep-

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tometer. Elemental microanalyses were performed by Galbraith Laboratory, Inc. $Ru_2(O_2CCH_3)_4Cl$ was made according to the published procedure [6]. $K_3Ru_2(CO_3)_4 \cdot 4H_2O$ was made from $Ru_2(O_2CCH_3)_4Cl$ [7].

Synthesis of $K_3[Ru_2(SO_4)_4(H_2O)_2] \cdot 2H_2O$

Method 1. The literature procedure [5a] was used with a modification. After $[Ru_2(O_2CCH_3)_4(H_2O)_2]_2(SO_4)$ was prepared by using a Dowex-50WXI cation-exchange column, from $Ru_2(O_2CCH_3)_4Cl$, eluted with a 6% K_2SO_4 solution, evaporated to dryness, and dissolved in 96% H_2SO_4, it was then important to saturate the solution with K_2SO_4 before it was heated to yield the crystalline product.

Method 2. $K_3Ru_2(CO_3)_4 \cdot 4H_2O$ (0.2 g, 0.32 mmol) was added to a solution of 5 g of K_2SO_4 in 5 ml of 96% H_2SO_4. Evolution of CO_2 was observed and all the ruthenium compound was dissolved. After 1 h a fine yellow–brown precipitate began to form. The reaction mixture was left at 100 °C overnight to digest and then filtered. The product was recrystallized by dissolving it in a minimum quantity of water and adding immediately a saturated solution of K_2SO_4. The crystals were filtered off, washed with a small quantity of water and ethanol, and air dried. Yield 0.15 g, 61%. The IR and visible spectra were the same as those described in the literature [5a].

Preparation of $K_2[Ru_2(SO_4)_4(H_2O)_2]$

$K_3[Ru_2(SO_4)_4(H_2O)_2] \cdot 2H_2O$ (0.10 g, 0.13 mmol) was dissolved in 20% sulfuric acid (15 ml) and the solution was then added to the anodic arm of a U-shaped electrolytic cell. 22% H_2SO_4 (15 ml) was added to the other arm as the cathodic electrolyte. A difference of potential of 5 V was applied to two platinum electrodes, while the system was maintained at 0 °C during the whole process. The solution gradually turned from yellow to dark brown and a dark brown precipitate was formed. The precipitate was filtered, washed with acetonitrile, and air dried. Yield 0.71 g, 80%. *Anal.* Calc.: K, 11.1; Ru, 28.9; S, 18.3. Found: K, 11.7; Ru, 28.5; S, 18.6%. The IR and visible spectra were the same as the literature findings [5a].

Synthesis of $K_4[Ru_2(HPO_4)_3(PO_4)(H_2O)_2]$

Method 1. $K_3Ru_2(CO_3)_4 \cdot 4H_2O$ (0.1 g, 0.16 mmol) was added to a 2 M H_3PO_4 solution (10 ml). The solution turned orange–brown along with the evolution of CO_2 bubbles. After a few hours of stirring acetone was added dropwise until an orange solid began to precipitate. After one more hour of stirring the precipitate was filtered, washed with acetone, and air dried. Yield 0.085 g, *c.* 70%. (Nujol, cm^{-1}): 3400b,m, 1630m, 1300w, 1100b,s, 995b,s, 900sh, 615m, 565s, 525m. The electronic spectrum of a water solution had a peak at 440 nm. Red–brown crystals suitable for X-ray crystallography were grown by slow diffusion of acetone into a water solution.

Method 2. $Ru_2(O_2CCH_3)_4Cl$ (0.1 g, 0.21 mmol) was added to an aqueous saturated solution of K_2HPO_4 (*c.* 16.7 g in 10 ml water) under argon. The starting material gradually dissolved and the solution turned orange–brown. Acetone was added dropwise until an orange precipitate started to form. After one more hour of stirring the precipitate was filtered, washed with acetone, and air dried. Yield 0.095 g, *c.* 58%. The visible spectrum was the same as that obtained by method 1.

Electrochemical oxidation of $K_4[Ru_2(HPO_4)_3(PO_4)(H_2O)_2]$

$K_4[Ru_2(HPO_4)_3(PO_4)(H_2O)_2]$ (0.1 g, 0.13 mmol) was dissolved in a 2 M H_3PO_4 (25 ml) solution and the solution was added to the anodic arm of a U-shaped electrolytic cell. Another 25 ml of the 2 M H_3PO_4 was added to the other arm. Two platinum electrodes were used and a potential difference of 2 V was applied. The orange–brown solution gradually turned purple. Correspondingly, the absorption at 440 nm in the electronic spectrum gradually disappeared and a new characteristic peak at 490 nm grew in. A purple compound was isolated by adding a concentrated CsCl solution in 2 M H_3PO_4 (Cs salt has a smaller solubility). The product isolated by filtration had the following IR absorption bands (Nujol, cm^{-1}): 3400b,m, 1630w, 1300w, 1100b,s, 990b,s, 940m, 565m, 520m. When the compound was dissolved in H_3PO_4 it showed the same electronic spectrum as that of the mother solution. Single crystals of the potassium salt were grown by vapor diffusion of acetone directly into the solution after the electrolysis*

X-ray crystallography

A brown columnar crystal was mounted on the tip of a glass fiber by epoxy cement. Unit cell parameters were obtained by centering and indexing 25 reflections that were found from rotation photography, and refined by centering 25 reflections with high θ angles (22–24°). The crystal system and the axial lengths were confirmed

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*Crystallographic data for the potassium salt were: triclinic unit cell; $a = 8.039(2)$, $b = 8.104(1)$, $c = 7.9430(9)$ Å, $\alpha = 98.63(1)$, $\beta = 114.70(2)$, $\gamma = 114.01(2)°$, $V = 396.2(1)$ Å^3. In the $P\bar{1}$ space group, R and R_w converged to 0.069 and 0.089, respectively, and a Ru_2 center (Ru–Ru: 2.320(3) Å) was found surrounded by four phosphate groups and two axial ligands. However, a serious disorder of the ligands has hampered the completion of the structure determination. An effort is being made to solve the disorder problem and, therefore, to elucidate the stoichiometry.

by axial oscillation photography. Two sets of unique data ($-h$, $\pm k$, $\pm l$) were collected. Three standard reflections were collected following every 97 intensity data. Neither a change of the crystal orientation nor decay was detected.

The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was also applied by the method of Ψ scans of seven reflections with their χ angles near 90°. The agreement factor for averaging equivalent intensity data was 0.012. (Calculations were done on a local Area VAX Cluster (VMS X4.6) with the commercial package SDP/VV3.0.)

The space group was determined unambiguously to be $P2_1/n$ (No. 14) based on the systematic absences. The coordinates of the unique Ru atom were obtained from an interpretation of a supersharp Patterson map (SHELXS-86) [8], and the remaining non-hydrogen atoms were found by a combination of difference Fourier syntheses and least-squares refinements. After all these non-hydrogen atoms were refined anisotropically to an R value of 0.025, the top peaks in a difference Fourier map (1.2–0.7 e/Å^3) showed all the four unique hydrogen atoms. In the final refinement, the three hydrogen atoms that were located in general positions were refined with fixed isotropic thermal parameters that were 1.3 times of those of their bonded oxygen atoms, while the isotropic thermal parameter was independently refined for the fourth one that was located on an inversion center. The crystallographic data are listed in Table 1. Atomic positional parameters and thermal parameters are given in Table 2.

TABLE 1. Crystallographic data for $K_4[Ru_2(HPO_4)_3(PO_4)(H_2O)_2]$

Formula	$Ru_2K_4P_4O_{18}H_7$
Formula weight	777.49
Space group	$P2_1/n$ (No. 14)
Systemic absences	$h0l$, $h+l=2n+1$; $0k0$, $k=2n+1$
a (Å)	9.049(1)
b (Å)	9.418(1)
c (Å)	10.235(1)
α (°)	90.0
β (°)	90.480(9)
γ (°)	90.0
V (Å^3)	872.2(2)
Z	2
D_{calc} (g/cm^3)	2.960
Crystal size (mm)	0.20×0.22×0.38
μ(Mo Kα) (cm^{-1})	31.053
Data collection instrument	P3 equivalent
Radiation (monochromated in incident beam)	Mo Kα ($\lambda\alpha=0.71073$ Å)
orientation reflections: no.; range (2θ) (°)	25; 44–47
Temperature °C	20
Scan method	ω–2θ
Data collection range (2θ) (°)	4–52
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	1537, 1529
No. parameters refined	137
Transmission factors: max., min.	0.9972, 0.8986
R^a	0.023
R_w^b	0.027
Quality-of-fit indicator^c	1.442
Largest shift/e.s.d., final cycle	0.005
Largest peak (e/Å^3)	0.846

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

Magnetic measurements

A SQUID susceptometer was employed and a total of 30 measurements were made at intervals between 10 and 300 K.

Results and discussion

Ru_2(II,III) and Ru_2(III,III) sulfate complexes

As mentioned above, one of our major goals in this work was to confirm the authenticity and the very unusual magnetic properties of $[Ru_2(SO_4)_4(H_2O)_2]^{2-}$. However, our initial efforts to reproduce the necessary precursor, $K_3[Ru_2(SO_4)_4(H_2O)_2]\cdot 2H_2O$, all failed, until we realized that the product has a very large solubility in 98% H_2SO_4 so that a high concentration of K_2SO_4 in the reaction mixture is crucial for the product to precipitate. Since the reported procedure did not guarantee to provide enough K_2SO_4 in the reaction mixture, the modification of saturating the reaction mixture with K_2SO_4 is necessary.

As shown in our previous work [2], the Ru_2(II,III) carbonate complex $K_3Ru_2(CO_3)_4\cdot 4H_2O$ is a promising starting material for the preparation of other Ru_2(II,III) and Ru_2(II,II) complexes. Procedures can be simplified and product purity can be improved because of the ease of expelling carbon dioxide. This has now been shown in the preparation of Ru_2(II,III) sulfate complexes. Compared with the previously reported method, our method allows us to avoid a tedious ion-exchange process, provides a better yield, and affords a purer product.

As for the preparation of $K_2[Ru_2(SO_4)_4(H_2O)_2]$, the reported procedure [5a] involved an oxidation of the tetrasulfato diruthenium(II,III) by $Ce(SO_4)_2$. However, our electrochemical oxidation has proved to be a better method, which not only has afforded $K_2[Ru_2(SO_4)_4(H_2O)_2]$ in good yield, but avoids any possible contamination of the product by paramagnetic Ce(III) that comprises the major byproduct of the reported chemical oxidation.

From the magnetic susceptibility data measured on $K_2[Ru_2(SO_4)_4(H_2O)_2]$ (Fig. 1) a Curie–Weiss plot (χ^{-1}

TABLE 2. Positional and equivalent isotropic thermal parameters for $K_4[Ru_2(HPO_4)_3(PO_4)(H_2O)_2]$

Atom	x	y	z	B_{eq} (Å^2)[a]
Ru	0.49990(3)	0.46979(3)	0.60913(3)	0.920(5)
O(1)	0.5098(3)	0.4364(4)	0.8322(3)	2.06(6)
O(2)	0.2877(3)	0.3968(3)	0.6029(3)	1.55(5)
O(3)	0.7118(3)	0.5401(4)	0.6336(3)	1.96(6)
O(4)	0.4145(3)	0.6602(3)	0.6614(3)	1.58(5)
O(5)	0.5765(3)	0.2706(3)	0.5716(3)	1.65(5)
P(1)	0.2174(1)	0.3610(1)	0.4688(1)	1.53(2)
P(2)	0.3936(1)	0.7845(1)	0.5677(1)	1.81(2)
O(6)	0.0494(3)	0.3851(4)	0.4727(3)	2.23(6)
O(7)	0.2399(4)	0.2053(4)	0.4348(4)	2.89(7)
O(8)	0.2500(4)	0.8520(4)	0.5770(3)	2.29(6)
O(9)	0.5132(4)	0.8995(4)	0.6082(4)	2.97(7)
K(1)	0.3556(1)	0.1171(1)	0.7196(1)	2.74(2)
K(2)	0.6268(1)	0.7325(1)	0.8450(1)	2.88(2)
H(1)	0.573(7)	0.382(7)	0.866(6)	2.7[b]
H(2)	0.436(7)	0.410(7)	0.869(6)	2.7[b]
H(3)	0.000	0.500	0.500	7(4)[c]
H(4)	0.591(8)	0.956(8)	0.703(7)	3.9[b]

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

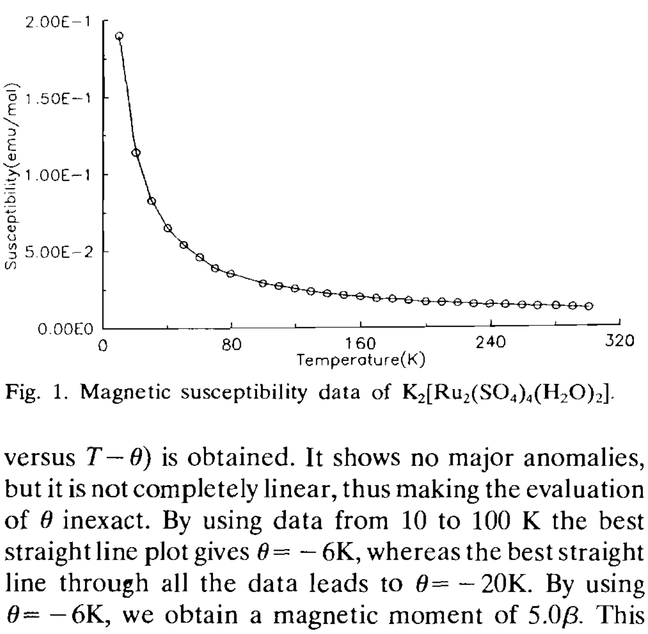

Fig. 1. Magnetic susceptibility data of $K_2[Ru_2(SO_4)_4(H_2O)_2]$.

versus $T-\theta$) is obtained. It shows no major anomalies, but it is not completely linear, thus making the evaluation of θ inexact. By using data from 10 to 100 K the best straight line plot gives $\theta = -6$K, whereas the best straight line through all the data leads to $\theta = -20$K. By using $\theta = -6$K, we obtain a magnetic moment of 5.0β. This result essentially confirms the values reported by the Russian workers and we concur with their assignment of the ground state of the $[Ru_2(SO_4)_4(H_2O)_2]^{2-}$ ion as one arising from the $\sigma^2\pi^4\delta\pi^{*2}\delta^*$ configuration. This electron configuration is also consistent with the Ru–Ru distance. The loss of one δ electron from the Ru_2^{5+} species would tend to lengthen the bond by a small amount as would the increase in total charge on the Ru_2^{n+} core from $n=5$ to $n=6$. Together, these two factors can account for the small change, 2.303 to 2.343 Å, on going from $Ru_2^{5+}(\sigma^2\pi^4\delta^2\pi^{*2}\delta^*)$ to $Ru_2^{6+}(\sigma^2\pi^4\delta\pi^{*2}\delta^*)$ [5b].

Crystal structure of $K_4[Ru_2(HPO_4)_3(PO_4)(H_2O)_2]$

The results of the X-ray crystallographic study of this compound reveal a crystal structure consisting of potassium ions and the anionic diruthenium phosphate complex. The configuration of the complex is shown in Fig. 2. This is a typical paddle wheel structure. Some pertinent bond distances and angles are listed in Table 3. The two metal atoms are bridged by four phosphate groups in a way very similar to that observed in its sulfate analogue [5b]. Apart from four basal oxygen atoms from the four phosphate groups, each Ru atom is further coordinated by a water oxygen atom and the other Ru atom in the axial positions.

Since the anion is required by the crystallographic symmetry to have inversion symmetry, only half of the anion is unique. There are four crystallographically independent hydrogen atoms. Two hydrogen atoms, H(1) and H(2) are bonded to the water oxygen atom, O(1), and each forms a hydrogen bond to a terminal phosphate oxygen atom from a neighboring dimer unit. On the whole, each dimer unit forms four such hydrogen bonds to its neighboring dimer units, and is in turn bonded by four hydrogen bonds from its neighbors so that an infinite structure is formed. Moreover, this infinite skein is further reinforced by a strong intermolecular, effectively symmetric hydrogen bond with an O...O distance of 2.410(5) Å from a phosphate hydrogen atom, H(3), which is located on an inversion center. The fourth hydrogen atom, H(4), is attached to another phosphate group. Its bond to the oxygen atom O(9) (1.31(7) Å) seems weaker than the others (0.84(7), 0.81(6) and 1.205(3) Å for H(1), H(2) and H(3), respectively). Besides, it forms only a very weak, if any, hydrogen bond to a neighboring oxygen atom, O(3), with a H...O distance of 2.56(7) Å and an O(3)–H(4)–O(9) angle of 168(5)°, and no other H...O contact shorter than this value has been found. In view of the large e.s.d. for this (and two of the other O–H distances) further discussion would not be justified. From the location of all the four hydrogen atoms and their multiplicities the title formula is confirmed, and we conclude that no disproportionation, which is not uncommon in the Ru_2(II,III) chemistry [2], has occurred during the preparative substitution reactions.

The metal–metal distance in **1**, 2.3052(4) Å, is well within the range for Ru_2(II,III) compounds with four three-atom-bridging ligands. It is the same as that of the sulfate analogue $K_2H[Ru_2(SO_4)_4(H_2O)]\cdot 6H_2O$, 2.303(1) Å [5b], a little longer than those of carbonate [2, 7, 9], carboxylate [1, 9, 10], and hydroxopyridine [10b, 10d, 11] analogues, 2.25–2.30 Å, and a little shorter than those in some $PhNPy^-$ analogues, 2.275(3)–2.319(3) Å [10b, 11a, 12]. The strong metal–

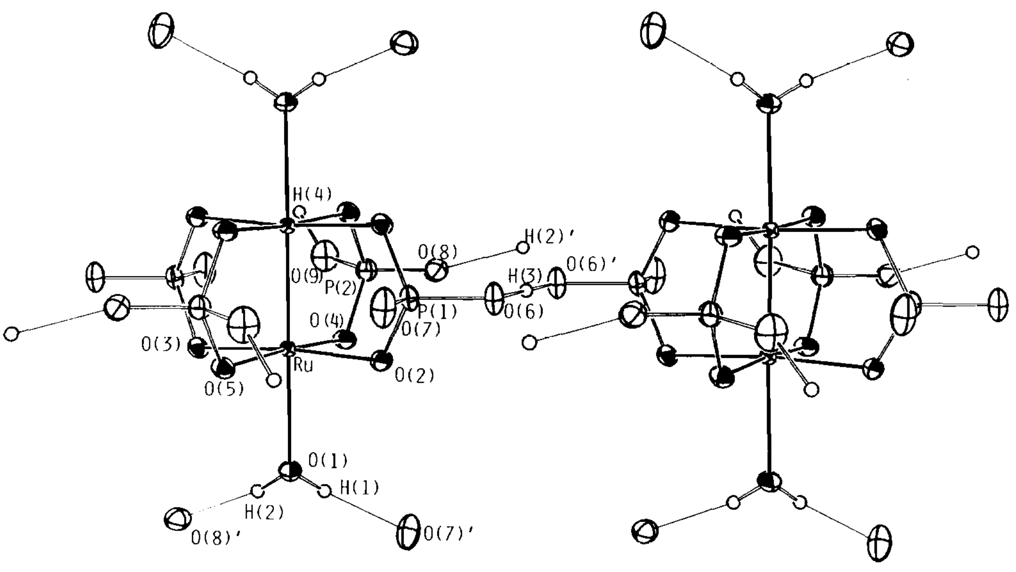

Fig. 2. Configuration of $[Ru_2(HPO_4)_3(PO_4)(H_2O)_2]$ showing the atom-labeling scheme. Thermal ellipsoids are presented at the 30% probability level, and the hydrogen atoms are drawn with arbitrary radii for clarity.

TABLE 3. Selected bond distances (Å) and angles (°) for $K_4[Ru_2(HPO_4)_3(PO_4)(H_2O)_2]$

Bond distances					
Ru–Ru′	2.3052(4)	Ru–O(5)	2.038(3)	P(1)–O(6)	1.538(3)
Ru–O(1)	2.306(3)	O(2)–P(1)	1.546(3)	P(1)–O(7)	1.521(4)
Ru–O(2)	2.040(3)	O(3)–P(1)′	1.545(3)	P(2)–O(8)	1.450(3)
Ru–O(3)	2.042(3)	O(4)–P(2)	1.525(3)	P(2)–O(9)	1.584(4)
Ru–O(4)	2.026(3)	O(5)–P(2)′	1.543(3)	O(6)–H(3)	1.205(3)
Bond angles					
Ru′–Ru–O(1)	173.17(8)	O(2)–Ru–O(4)	86.9(1)	Ru–O(3)–P(1)′	120.5(2)
O(1)–Ru–O(2)	90.8(1)	O(2)–Ru–O(5)	90.3(1)	Ru–O(4)–P(2)	124.0(2)
O(1)–Ru–O(3)	83.9(1)	O(3)–Ru–O(4)	92.3(1)	Ru–O(5)–P(2)′	123.2(2)
O(1)–Ru–O(4)	82.6(1)	O(3)–Ru–O(5)	90.1(1)	O(2)–P(1)–O(3)′	107.5(2)
O(1)–Ru–O(5)	92.9(1)	O(4)–Ru–O(5)	174.7(1)	O(4)–P(2)–O(5)′	107.5(2)
O(2)–Ru–O(3)	174.7(1)	Ru–O(2)–P(1)	118.8(2)		

Numbers in parentheses are e.s.d.s in the least significant digits.

metal interaction is also evidenced by a 0.088 Å deviation of each metal atom from its basal least-squares plane of four oxygen atoms towards its neighbor.

Preparative chemistry of Ru_2(II,III) and Ru_2(III,III) phosphate complexes

A conventional ligand substitution reaction of $Ru_2(O_2CCH_3)_4Cl$ in a K_2HPO_4 saturated solution has allowed the synthesis of an Ru_2(II,III) phosphate complex as shown by X-ray crystallography. More important, a new convenient, fast, and clean synthetic method has been developed starting from $K_3Ru_2(CO_3)_4 \cdot 4H_2O$ in 2 M H_3PO_4.

Although X-ray crystallography failed to give conclusive details for the structure of an Ru_2(III,III) phosphate complex, the determined Ru–Ru distance 2.320(3) Å compares with the above well determined Ru–Ru bond distance 2.3052(4) Å in the crystal structure of $K_4[Ru_2(HPO_4)_3(PO_4)(H_2O)_2]$, in the same way as the distances in their sulfate analogues (2.303(1) Å for Ru_2(II,III) complex and 2.343(1) Å for the Ru_2(III,III) one). Moreover, the electronic spectra of the phosphate complexes also display the same trend as their sulfate analogues. Electrochemical oxidation of $K_4[Ru_2(HPO_4)_3(PO_4)(H_2O)_2]$ shifts the absorption band from 440 to 490 nm, as shown in Fig. 3, while the oxidation of $K_3[Ru_2(SO_4)_4(H_2O)_2]$ to $K_2[Ru_2(SO_4)_4(H_2O)_2]$ shifts the band from 325 to 355 nm.

Conclusions

We believe it is now completely certain that the Ru_2^{6+} core can be stabilized by the use of four relatively 'hard' but highly charged bridging ligands, namely,

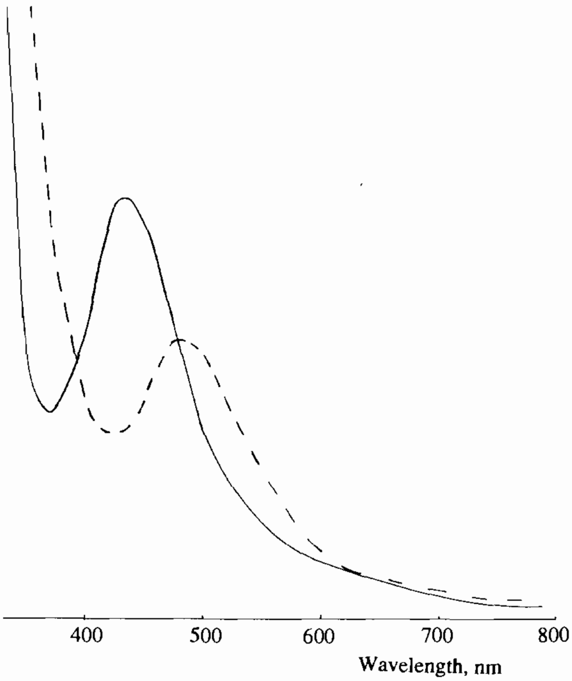

Fig. 3. Electronic spectra of $K_4[Ru_2(HPO_4)_3(PO_4)(H_2O)_2]$ (solid line) and its oxidized species (dashed line).

SO_4^{2-} or $H_nPO_4^{-3+n}$. Moreover, in these environments the Ru_2^{6+} core has a ground state derived from the electron configuration $\sigma^2\pi^4\delta\pi^{*2}\delta^*$, as originally proposed by Zhilyaev, Fomina, Kuzmenko and Baranovskii. Finally, the preparation of the compounds is best achieved by employing $K_3Ru_2(CO_3)_4 \cdot 4H_2O$ as the starting material to produce the Ru_2^{5+} compounds and then oxidizing these electrochemically rather than with Ce(IV) to obtain the Ru_2^{6+} species.

Supplementary material

For the crystal structure of **1** full tables of bond distances and angles including hydrogen bonds, anisotropic thermal parameters (4 pages); tables of observed and calculated structure factors (8 pages); tables of least-squares planes (3 pages); ORTEP drawings of unit cell contents (2 pages); a table of magnetic susceptibility measurements on $K_2[Ru_2(SO_4)_4(H_2O)_2]$ from 10 to 300 K (1 page). All are available on request from author F.A.C.

Acknowledgement

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