

## 一种混合价态钌配合物的合成、晶体结构和电化学性质

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**摘要:**  $[\text{Ru}_6(\mu\text{-O}_2\text{CCH}_3)_{12}(\text{CH}_3\text{OH})_2(\text{HCOO})_2][\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$  ( $\text{Ru}_2(\text{II}, \text{III})$ 混合价)是通过二步反应合成的。首先  $\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}$  在加热条件下与甲醇反应得到红棕色中间物,然后将该中间物在甲醇水(体积比 7:1)溶液中用  $\text{Ag}_2\text{SO}_4$  和  $\text{NH}_4\text{PF}_6$  进行脱氯配位反应得到此化合物。用元素分析、红外光谱、热重分析、循环伏安、X-衍射单晶结构分析等对其进行了表征。晶体结构表明,标题化合物的晶体属单斜晶系,空间群为  $P2_1/n$ ,晶胞参数: $a=0.853\ 62(14)\ \text{nm}$ ,  $b=1.195\ 89(19)\ \text{nm}$ ,  $c=3.664\ 2(6)\ \text{nm}$ ,  $\beta=92.316(3)^\circ$ ,  $Z=2$ , 每个结构单元包含 2 个不同的配离子,其中  $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]^+$  是 1 个双核钌配离子,  $[\text{Ru}_6(\mu\text{-O}_2\text{CCH}_3)_{12}(\text{CH}_3\text{OH})_2(\text{HCOO})_2]^+$  是由另 1 个由甲醇配位、甲酸根桥连的六核钌配离子。2 个独立的结构单元通过氢键形成三维超分子网络结构。采用循环伏安法对其电化学性质进行了表征,结果为一对可逆的氧化还原峰,表明该配合物的中心金属二价钌原子  $\text{Ru}(\text{II})$  与三价钌原子  $\text{Ru}(\text{III})$  之间存在电子转移。

**关键词:**  $\text{Ru}_2(\text{II}, \text{III})$ 混合价; 钌配合物; 晶体结构; 电化学性质

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## Synthesis, Crystal Structure and Electrochemical Properties of a Mixed Valence Ruthenium Complex

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**Abstract:**  $[\text{Ru}_6(\mu\text{-O}_2\text{CCH}_3)_{12}(\text{CH}_3\text{OH})_2(\text{HCOO})_2][\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$  (with mixed valence  $\text{Ru}_2(\text{II}, \text{III})$ ) was synthesized by two-step reactions. Firstly, heat  $\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}$  in methanol under argon to get a brown red intermediate, then treat the intermediate with methanol aqueous solution in the presence of  $\text{Ag}_2\text{SO}_4$  and  $\text{NH}_4\text{PF}_6$  to get the title compound. The compound was characterized by elemental analysis, IR spectra, thermogravimetric analysis, cyclic voltammetry, and X-ray single crystal structure analysis. Its crystal belongs to monoclinic system with  $P2_1/n$  space group, in which  $a=0.853\ 62(14)\ \text{nm}$ ,  $b=1.195\ 89(19)\ \text{nm}$ ,  $c=3.664\ 2(6)\ \text{nm}$ ,  $\beta=92.316(3)^\circ$  and  $Z=2$ . Each structure element of the crystal contains two different match ions,  $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]^+$  and  $[\text{Ru}_6(\mu\text{-O}_2\text{CCH}_3)_{12}(\text{CH}_3\text{OH})_2(\text{HCOO})_2]^+$ . The former is a dinuclear ruthenium match ion. The latter is a six nuclear ruthenium match ion in coordination with methanol and bridge with formic acid. As independent components, the two elements were connected by hydrogen bond to form a three-dimensional supramolecular network. The electrochemical property of ruthenium complex has been studied by means of cyclic voltammetry, the results show that electron transfer between  $\text{Ru}(\text{II})$  and  $\text{Ru}(\text{III})$  in electrolysis is quasi-reversible process. CCDC: 793726.

**Key words:** with mixed valence  $\text{Ru}_2(\text{II}, \text{III})$ ; ruthenium compound; crystal structure; electrochemical property

## 0 Introduction

Since the discovery of  $\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}$  in the mid-1960s<sup>[1]</sup>, many mixed-valent  $\text{Ru}_2(\text{O}_2\text{CCH}_3)_4^+$  complexes with a variety of axial and bridging ligands have been reported<sup>[2-15]</sup>. The chloride salts tend to form zigzag chains and can be readily converted to more useful salts, the ruthenium compounds are known to exist as homovalent  $\text{Ru}_2(\text{O}_2\text{CR})_4$  [ $\text{Ru}_2(\text{II}, \text{II})$ ] and as mixed-valent  $\text{Ru}_2(\text{O}_2\text{CCH}_3)_4^+$  [ $\text{Ru}_2(\text{II}, \text{III})$ ] in which the odd electron is delocalized between the metals and the complex can, in effect, be formulated as  $\text{Ru}_2(\text{II}_{1/2}, \text{III}_{1/2})$ <sup>[16]</sup>. Interests in these compounds, particularly on the mixed-valent species, centres around their unique magnetic properties, catalytic properties and unusual stability grew rapidly in recent years. The  $\text{Ru}_2(\text{II}, \text{III})$  species contain three unpaired electrons due to an accidental near-degeneracy of the two highest lying occupied molecular orbitals, the  $\pi^*$  and  $\delta^*$ , to give a  $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$  configuration. Accordingly, we report here the synthesis of a mixed-valent carboxylic acid complex which was characterized by elemental analysis, IR spectra, cyclic voltammetry, and X-ray single crystal structure analysis. Each structure element contains two different metal ions, which are connected by hydrogen bond to form a three-dimensional supramolecular network.

## 1 Experimental

### 1.1 Starting reagents

All reagents and solvents were purchased from commercial sources and used without further purification.  $\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}$  was prepared using the method of Wilkinson and his co-workers<sup>[17]</sup>. All of the synthetic procedures were carried out under an atmosphere of argon.

### 1.2 Physical measurements

The elemental analysis (C, H) was performed on a Perkin-Elmer 2400 Series II element analyzer. FTIR spectra were recorded on a Nicolet 460 spectrophotometer in the form of KBr pellets. Thermogravimetric analysis (TGA) experiments were carried out on a Dupont thermal analyzer from room

temperature to 800 °C under  $\text{N}_2$  atmosphere at a heating rate of 20 °C  $\cdot$  min<sup>-1</sup>. The cyclic voltammogram experiments were carried out on a microcomputer-based electrochemical analyzer (Tianjin LanLiKe Chemical and Electron High Technology Co. Ltd.) in high purity nitrogen atmosphere. A Pt-piece was employed as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire as auxiliary electrode. The supporting electrolyte was 0.1 mol  $\cdot$  L<sup>-1</sup>  $\text{NaClO}_4$ . The half wave potentials  $E_{1/2}$  were obtained from  $E_{pc} + (\Delta E)/2$ .

### 1.3 Preparation of the complex

0.200 g (0.42 mmol) of  $\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}$  was dissolved in 80 mL of methanol. The orange-red solution was heated under reflux temperature with the air of argon for about 10 h until it becomes into a brown-red clear and transparent solution. Enrich it with a rotary evaporator to reduce the volume of the solution to 30 mL. Put it in fridge overnight, filter it to get a brown red solid. Carry out dechlorination by dissolving 0.100 g of the brown red solid in 40 mL of methanol. Add a solution of 0.065 g (0.21 mmol)  $\text{Ag}_2\text{SO}_4$  with 6 mL water into it. Keep the solution in dark with stirring and heat it at 40~50 °C for 2 h. The formed  $\text{AgCl}$  was then filtered off.  $\text{NH}_4\text{PF}_6$  (0.200 g, 1.22 mmol) was added, with stirring, to the brown red solution. Crystals suitable for X-ray analyses formed by slow evaporating from methanol upon cooling at 4 °C for one month. Yield: 50 mg (50%). The compound is soluble in water, methanol, ethanol, acetone, DMF and DMSO. Samples sent for elemental analyses were thoroughly dried in vacuum beforehand to remove hydrated water. Anal. found(%): C, 19.01; H, 2.58. Calcd.(%): C, 19.08; H, 2.74.

### 1.4 X-ray crystallography

Single-crystal X-ray diffraction measurement of the title complex was carried out with a Bruker Smart Apex CCD diffractometer at 295 (2) K. Intensities of reflections were measured using graphite-monochromatized  $\text{Mo K}\alpha$  radiation ( $\lambda=0.071\,073\text{ nm}$ ) with the  $\varphi$ - $\omega$  scans mode in the range of  $2.38^\circ \leq \theta \leq 30.10^\circ$ . The structure was solved by direct methods using SHELXS-97 computer program and refined by full-matrix least-

squares methods on  $F^2$  with the SHELXL-97 program. Anisotropic thermal factors were assigned to all the non-hydrogen atoms. Hydrogen atoms were included in calculated position and refined with isotropic thermal

parameters riding on the parent atoms. Crystallographic data parameters for structural analyses are summarized in Table 1.

CCDC: 793726.

**Table 1** Crystal and structure refinement data for the complex

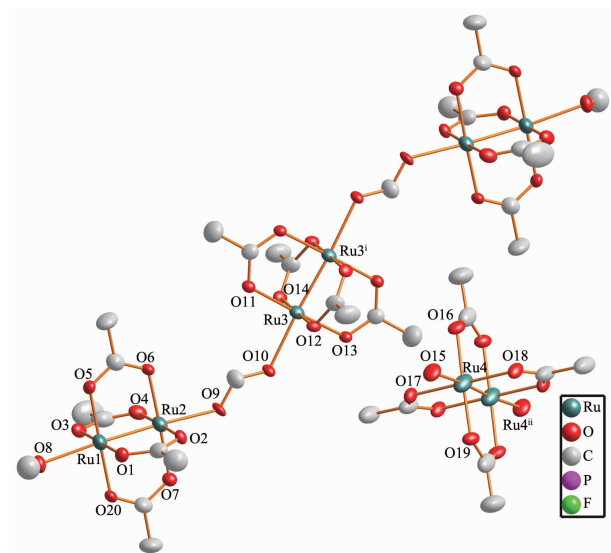
Formula	$\text{Ru}_8\text{O}_{42}\text{C}_{36}\text{H}_{66}\text{P}_2\text{F}_{12}$	Index ranges ( $h, k, l$ )	$-7/10, -12/14, -43/43$
Formula weight	2 269.39	Temperature / K	295(2)
Crystal size / mm	$0.22 \times 0.25 \times 0.30$	$F(000)$	2 216
Crystal system	Monoclinic	$\theta$ range for data collection / ( $^\circ$ )	$2.38 \sim 30.10$
Space group	$P2_1/n$	Reflections collected	19 727
$a$ / nm	$0.853\ 62(14)$	Independent reflections ( $R_{\text{int}}$ )	$6\ 559\ (0.031\ 3)$
$b$ / nm	$1.195\ 89(19)$	Observed reflections ( $I > 2\sigma(I)$ )	5 993
$c$ / nm	$3.664\ 2(6)$	Data / restraints / parameters	$6\ 559 / 21 / 468$
$\beta$ / ( $^\circ$ )	$92.316(3)$	$R_1, wR_2\ (I > 2\sigma(I))$	$0.072\ 4, 0.179\ 8$
Volume / $\text{nm}^3$	$3.737\ 5(10)$	$R_1, wR_2$ (all data)	$0.079\ 7, 0.189\ 3$
$Z$	2	Goodness-of-fit on $F^2$	1.264
$\mu$	1.733	Max. peak / ( $\text{e} \cdot \text{nm}^{-3}$ )	1 196
$D_c$ / ( $\text{g} \cdot \text{cm}^{-3}$ )	2.017	Min. peak / ( $\text{e} \cdot \text{nm}^{-3}$ )	$-2\ 190$

## 2 Results and discussion

### 2.1 X-ray crystal structure description for the compound

The molecular structure is shown in Fig.1. The unit cell packing diagram is given in Fig.2. The selected bond lengths and angles are given in Table 2. The compound crystallizes in monoclinic space group  $P2_1/n$ . As shown in Fig.1, there is no formic acid as the

reactant in all of the synthetic procedures. It is most likely that methanol is oxidized into formic acid. As homovalent diruthenium(II) compounds are sensitive to oxygen, mixed-valent  $[\text{Ru}_2(\text{II}, \text{III})]$  is reduced into homovalent diruthenium(II)  $[\text{Ru}_2(\text{II}, \text{II})]$ , simultaneously methanol is oxidized into formic acid through a self oxidation-reduction procedure, and the central ruthenium atom of the total compound is judged. Usually reducing agents are needed for the oxidation of methanol, which is convinced by Cotton and Sheldricks work on synthesis of some diruthenium(II) complexes from  $\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}$  and the corresponding ligand<sup>[9,18]</sup>. Accordingly, it is better explained the production of formic acid ligand in the compound.



Symmetry codes: <sup>i</sup>  $-x+1, -y+1, -z$ ; <sup>ii</sup>  $-x+2, -y, -z$ ;  $\text{PF}_6^-$  ions are omitted for clarity

Fig.1 Molecular structure for the compound with 30% probability ellipsoids

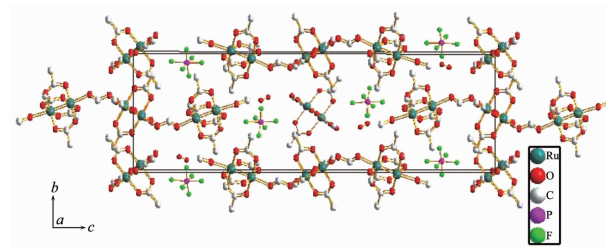


Fig.2 Molecular crystal cell packing for the compound

The  $\text{Ru}(4)\text{-Ru}(4)^{\text{ii}}$  bond distance ( $0.226\ 4(2)\ \text{nm}$ ) is slightly longer than the  $\text{Ru} \cdots \text{Ru}$  distance of  $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2](\text{PF}_6) \cdot 3\text{H}_2\text{O}^{\text{[1]}}$  ( $0.225\ 95(7)\ \text{nm}$ ), while  $\text{Ru}(1)\text{-Ru}(2)$  bond distance is found to be similar to that

**Table 2** Selected bond lengths (nm) and angles (°) for the complex

Ru(1)-Ru(2)	0.226 94(13)	Ru(2)-O(4)	0.201 9(9)	Ru(3)-O(13)	0.202 6(7)
Ru(1)-O(1)	0.203 7(9)	Ru(2)-O(6)	0.201 7(8)	Ru(3)-O(14)	0.2015(7)
Ru(1)-O(2)	0.200 9(8)	Ru(2)-O(7)	0.202 9(8)	Ru(4)-Ru(4) <sup>ii</sup>	0.226 4(2)
Ru(1)-O(3)	0.203 5(9)	Ru(2)-O(9)	0.221 0(7)	Ru(4)-O(15)	0.2252(10)
Ru(1)-O(5)	0.203 3(8)	Ru(3)-Ru(3) <sup>i</sup>	0.227 09(15)	Ru(4)-O(16)	0.2024(9)
Ru(1)-O(8)	0.229 9(9)	Ru(3)-O(10)	0.224 4(7)	Ru(4)-O(17)	0.2034(8)
Ru(1)-O(20)	0.200 7(8)	Ru(3)-O(11)	0.202 8(8)	Ru(4)-O(18)	0.202 5(8)
Ru(2)-O(2)	0.200 9(8)	Ru(3)-O(12)	0.200 6(7)	Ru(4)-O(19)	0.202 5(9)
O(1)-Ru(1)-O(8)	92.1(3)	O(6)-Ru(2)-O(9)	92.9(3)	O(16)-Ru(4)-O(17)	89.3(4)
O(2)-Ru(2)-O(4)	178.6(3)	O(6)-Ru(2)-Ru(1)	89.3(2)	O(16)-Ru(4)-O(18)	90.4(4)
O(2)-Ru(2)-O(6)	91.4(3)	O(7)-Ru(2)-O(9)	88.7(3)	O(16)-Ru(4)-O(19)	178.6(4)
O(2)-Ru(2)-O(7)	89.6(3)	O(7)-Ru(2)-Ru(1)	89.0(2)	O(16)-Ru(4)-Ru(4)	89.6(3)
O(2)-Ru(2)-O(9)	88.5(3)	O(9)-Ru(2)-Ru(1)	177.1(2)	O(17)-Ru(4)-O(15)	87.5(4)
O(2)-Ru(2)-Ru(1)	89.6(2)	O(10)-Ru(3)-Ru(3) <sup>i</sup>	176.4(2)	O(17)-Ru(4)-Ru(4)	88.7(3)
O(3)-Ru(1)-O(1)	178.5(4)	O(11)-Ru(3)-O(10)	94.1(3)	O(18)-Ru(4)-O(15)	93.0(4)
O(3)-Ru(1)-O(8)	88.8(4)	O(11)-Ru(3)-Ru(3) <sup>i</sup>	89.2(2)	O(18)-Ru(4)-O(17)	179.4(4)
O(3)-Ru(1)-Ru(2)	89.3(3)	O(12)-Ru(3)-O(10)	89.3(3)	O(18)-Ru(4)-O(19)	88.6(4)
O(4)-Ru(2)-O(7)	89.4(4)	O(12)-Ru(3)-O(11)	90.5(3)	O(18)-Ru(4)-Ru(4) <sup>ii</sup>	90.8(3)
O(4)-Ru(2)-O(6)	89.8(4)	O(12)-Ru(3)-O(13)	89.5(3)	O(19)-Ru(4)-O(15)	88.9(4)
O(4)-Ru(2)-O(9)	92.4(4)	O(12)-Ru(3)-O(14)	178.9(3)	O(19)-Ru(4)-O(17)	91.7(4)
O(4)-Ru(2)-Ru(1)	89.4(3)	O(13)-Ru(3)-O(10)	87.3(3)	O(19)-Ru(4)-Ru(4)	89.4(3)
O(5)-Ru(1)-O(1)	89.6(4)	O(13)-Ru(3)-O(11)	178.6(3)	O(20)-Ru(1)-O(1)	89.5(4)
O(5)-Ru(1)-O(3)	91.6(4)	O(13)-Ru(3)-Ru(3)	89.4(2)	O(20)-Ru(1)-O(3)	89.4(4)
O(5)-Ru(1)-O(8)	94.0(3)	O(14)-Ru(3)-Ru(3)	89.7(2)	O(20)-Ru(1)-O(5)	178.9(3)
O(5)-Ru(1)-Ru(2)	89.9(2)	O(14)-Ru(3)-O(10)	91.7(3)	O(20)-Ru(1)-O(8)	86.5(3)
O(12)-Ru(3)-Ru(3) <sup>i</sup>	89.3(2)	O(14)-Ru(3)-O(11)	89.0(3)	O(20)-Ru(1)-Ru(2)	89.6(2)
O(12)-Ru(3)-O(10)	89.3(3)	O(14)-Ru(3)-O(13)	90.9(3)	Ru(2)-Ru(1)-O(8)	175.7(2)
O(6)-Ru(2)-O(4)	89.6(4)	O(15)-Ru(4)-Ru(4)	175.8(3)		
O(6)-Ru(2)-O(7)	178.1(3)	O(16)-Ru(4)-O(15)	92.1(4)		

Symmetry codes: <sup>i</sup>  $-x+1, -y+1, -z$ ; <sup>ii</sup>  $-x+2, -y, -z$ .

of Ru(4)-Ru(4)<sup>ii</sup> (0.226 4(2) nm) and another homovalent tetraacetate adduct for which structure is available:

$\text{Ru}_2(\text{O}_2\text{CCH}_3)_4(\text{CH}_3\text{OH})_2[\text{Ru}_2(\text{II}, \text{II})]$  (the Ru $\cdots$ Ru distance, 0.226 53(4) nm)<sup>[10]</sup>. Ru(3)-Ru(3)<sup>i</sup> bond distance of 0.22 09(15) nm is the longest because of the existence of formic acid. It is corresponding to the above interpretation for the production of formic acid.

## 2.2 Hydrogen bonding of the compound

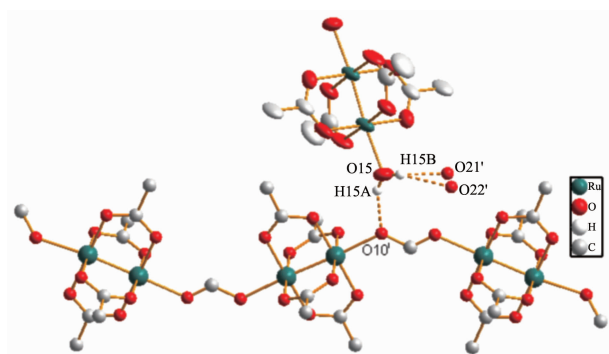
As shown in Table 3 and Fig.3, hydrogen bond between O15-H15A and formic acid molecular links  $[\text{Ru}_6(\mu\text{-O}_2\text{CCH}_3)_{12}(\text{CH}_3\text{OH})_2(\text{HCOO})_2]^+ [\text{Ru}_2(\text{II}, \text{III})]$  and  $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]^+ [\text{Ru}_2(\text{II}, \text{III})]$  cations together with an O-O distance at 0.282 5(12) nm. The hydrogen bond between O15-H15A and O21 as well as that

**Table 3** Selected hydrogen bonding parameters for the complex

D-H $\cdots$ A	$d(\text{D-H})$ / nm	$d(\text{H}\cdots\text{A})$ / nm	$d(\text{D}\cdots\text{A})$ / nm	$\angle \text{D-H}\cdots\text{A}$ / (°)
O15-H15A $\cdots$ O10 <sup>i</sup>	0.082	0.205	0.282 5(12)	157
O15-H15B $\cdots$ O21 <sup>i</sup>	0.082	0.155	0.231(5)	153
O15-H15B $\cdots$ O22 <sup>i</sup>	0.082	0.227	0.306(5)	163

Symmetry code: <sup>i</sup>  $x+1, y, z$ .

between O15-H15C and O22 belongs to intermolecular interactions between bond water and unbond water. These interactions are relatively symmetrical (O15-H15B $\cdots$ O21 0.231(5) nm and O15-H15B $\cdots$ O22 0.306(5) nm). Additionally, the bond angle of Ru(2)-Ru(1)-O(8) for the compound is 175.7(2) $^\circ$ , which is slightly less than 179.2(2) $^\circ$  found in the BF<sub>4</sub> salt of Ru complexes<sup>[19-20]</sup>. This is most likely due to hydrogen bonds interactions.



Symmetry code:  $\frac{1}{2}x+1, y, z$ ; Dash lines indicate the intermolecular interactions hydrogen bonds, some have been omitted for clarity, only hydrogen atoms involved in the hydrogen bonds are shown

Fig.3 Hydrogen bonds of the title compound

### 2.3 Infrared spectrum

The infrared spectrum of the compound shows typical symmetric ( $\nu_{\text{sym}}$ ) and asymmetric ( $\nu_{\text{asym}}$ ) carboxylate stretching frequencies in the range of 1 396~1 448  $\text{cm}^{-1}$  with  $\Delta\nu$  range from 30~50  $\text{cm}^{-1}$ , indicating a  $\eta^2$  binding mode<sup>[21]</sup>. Oxygen atoms on carboxylic ligands are bridged with two central ruthenium atoms with the  $\nu(\text{PF}_6^-)$  at 840  $\text{cm}^{-1}$ <sup>[13]</sup>. The compound has strong bands at 1 581 (HCOOH), 3 415 (O-H) and 2 850~3 019  $\text{cm}^{-1}$  (C-H).

### 2.4 Thermal stability

TG analysis shows that weight loss begins at 70  $^\circ\text{C}$ , and 2 mol of bonded methanol molecules release from 70 to 161  $^\circ\text{C}$  (calcd., 5.653%; found, 5.448%). Then 2 mol of bonded formic acid molecules and 3 mol of water molecules lose from 161 to 246  $^\circ\text{C}$  (calcd., 12.72%; found, 12.03%). Another 8 mol of acetic anhydride molecules lose from 246 to 318  $^\circ\text{C}$  (calcd., 41.70%; found, 47.36%). The last remaining amount of the compound loses from 318 to 800  $^\circ\text{C}$  (calcd., 39.93%; found, 35.16%).

### 2.5 Electrochemical property

Cyclic voltammetry measurements in aqueous solution show a quasi-reversible wave (peak-to-peak separations ranging from 3~113 mV at a rate of 100  $\text{mV}^{-1}$ ). Cyclic voltammogram for the complex scanning from -0.500 to 0.500 V is shown in Fig.4. The oxidation-reduction peak corresponds to Ru(II)/Ru(III) redox process,  $E_{\text{pa}}=0.113$  V,  $E_{\text{pc}}=-0.003$  V,  $\Delta E=0.116$  V,  $E_{1/2}=0.061$  V,  $i_{\text{pa}}/i_{\text{pc}}=0.93$ . The results show that electron transfer between Ru(II) and Ru(III) in electrolysis is quasi-reversible process.

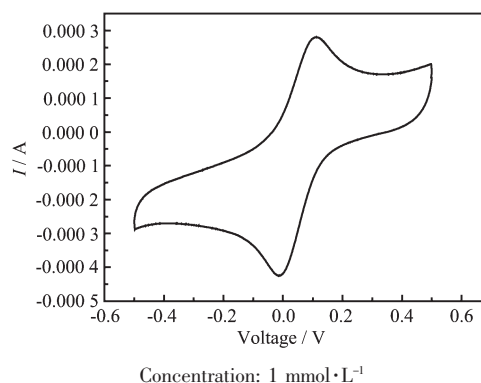


Fig.4 Cyclic voltammetry for the compound in aqueous solution

## 3 Conclusions

A new mixed-valent ruthenium compound is prepared and fully characterized. This diruthenium tetraacetate complex is relatively stable with a remarkable solubility in a big range of polar and/ or non-polar solvents. It appears a similar physico-chemical properties to other ruthenium compound. The hydrogen bonds within the complex influence its structure greatly. Electrochemical property of the complex shows that electron transfer between Ru(II) and Ru(III) in electrolysis is quasi-reversible process.

### References:

- [1] Drysdale K D, Beck E J, Cameron T S, et al. *Inorg. Chim. Acta*, **1997**, *256*:243-252
- [2] Chifotides H T, Dunbar K R. *Acc. Chem. Rvs.*, **2005**, *38*:146-156
- [3] Handa M, Sayama Y, Mikuriya M, et al. *Bull. Chem. Soc. Jpn.*, **1995**, *68*:1647-1675

- [4] Barral M C, Jimenez-Aparicio R, Royer E C, et al. *Inorg. Chem.*, **1994**,**33**(12):2692-2694
- [5] Cogne A, Belorizky E, Laugier J. et al. *Inorg. Chem.*, **1994**,**33**(15):3364-3369
- [6] Cukiernik F D, Giroud-Godquin A M, Maldivi P, et al. *Inorg. Chim. Acta*, **1994**,**215**(1/2):203-207
- [7] Cotton F A, Kim Y, Ren T. *Polyhedron.*, **1993**,**12**(6):607-611
- [8] Aquino M A S. *Coord. Chem. Rev.*, **2004**,**248**:1025-1045
- [9] Cotton F A, Kim Y, Yokochi A S. *Inorg. Chim. Acta*, **1995**, **236**:55-61
- [10] Barral M C, Gonzalez-Prieto R, Jimenez-Aparicio R. et al. *Inorg. Chim. Acta*, **2005**,**358**(1):217-221
- [11] Vamvounis G, Caplan J F, Cameron T S, et al. *Inorg. Chim. Acta*, **2000**,**304**(1):87-98
- [12] Brigand G G, Cooke M W, Cameron T S, et al. *Inorg. Chem.*, **2001**,**40**:3267-3268
- [13] WANG Wen-Zhen (王文珍), LIAO Dai-Zheng (廖代正), WANG Geng-Lin (王耕霖). *J. Fudan Univ. (Fudan Daxue Xuebao)*, **2003**,**42**(6):897-902
- [14] LI Min-Na (李敏娜), ZHAO Chang-Zhi (赵常志), LIU Jian-Hui (刘建辉). *J. Dalian Univ. Technology (Dalian Ligong Daxue Xuebao)*, **2007**,**47**(2):165-169
- [15] LI Hong (李红), CAO Hui (巢晖), JIANG Xiong (将雄), et al. *Acta Phy.-Chim. Sinica (Wuli Huaxue Xuebao)*, **2001**,**17**(8): 728-732
- [16] Aquino M A S. *Coord. Chem. Rev.*, **1998**,**170**:141-202
- [17] Mitchell R W, Spencer A, Wilkinson G. *J. Chem. Soc., Dalton. Trans.*, **1973**:846-854
- [18] Sheldrick W S, Mintert M. *Inorg. Chim. Acta*, **1994**,**219**:23-26
- [19] Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, 5th Ed.* New York: John Wiley and Sons, **1997**.
- [20] Bino A, Cotton F A, Feltthonse T R. *Inorg. Chem.*, **1979**,**18**: 2599-
- [21] Marsh R E, Schomaker V. *Inorg. Chem.*, **1981**,**20**:299-303