

## Synthesis, X-Ray Structure and Characterization of a Triruthenium Cluster Complex $\text{Ru}^{\text{III}}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})_2\text{Cl}$ with Four Steps One-electron Redox Processes

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**Abstract:** The synthesis and crystal structure of oxo-centered carboxylate-bridge trinuclear ruthenium complex,  $\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2\text{Cl}$  (py = pyridine) (**1**), are reported herein. The complex **1** has been characterized by IR, cyclic voltammetry (CV), UV-Vis and X-ray crystal analysis. The complex **1** in 0.1 mol/L (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NPF<sub>6</sub>-CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature shows four one-electron redox processes at  $E_{1/2} = -1.38, -1.20, -0.17$  and  $1.07$  V vs. Ag/AgCl.

**Keywords:** Crystal structure, ruthenium, carboxylate, electrochemistry.

Great attention is currently paid to the synthesis of polynuclear transition metal complexes as well as their photochemical, photophysical, and electrochemical properties. The design of multicomponent systems capable of performing useful light- and/or redox-induced function is of special interest<sup>1</sup>. The oxo-centered carboxylate-bridge trinuclear ruthenium clusters have been investigated extensively during recent decades because they have remarkable electron-transfer properties, intense visible absorption and intriguing magnetic behavior. In particular, the ligand-bridged trinuclear ruthenium clusters displays a strong electronic coupling<sup>2-4</sup>. Aiming at the design and synthesis of metal cluster-based molecular wires with long-range electron transfer properties, we found the triruthenium cluster complex  $\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2\text{Cl}$  (**1**) is an excellent precursor for the attainment of this purpose. Herein is described the synthesis, X-ray structure and properties of the complex.

### Experimental

A solution of 101 mg (0.1 mmol)  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2(\text{CH}_3\text{OH})]\text{PF}_6^5$  in 20 mL of dichloromethane was allowed to react with 27.8 mg (0.1 mmol) Et<sub>4</sub>NCl for two days at room temperature. The solvent was removed in vacuo and the residue was dissolved in a mixed CH<sub>2</sub>Cl<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (1:1, v/v) to afford well-shaped blue-green crystals suitable for X-ray analysis by layering hexane onto the solution in a few days. Anal. Found: C, 27.83;

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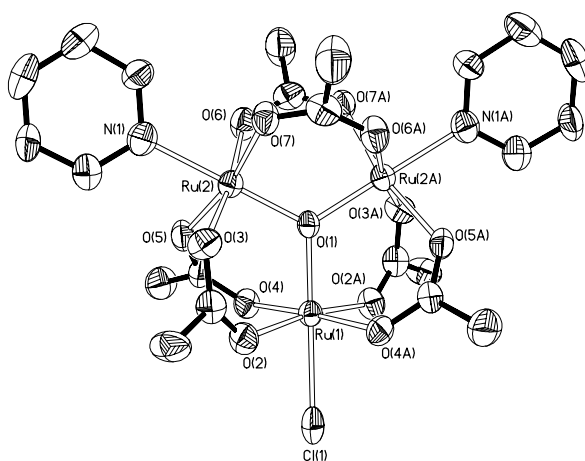
H, 3.65; N, 3.21. Calcd. for  $C_{22}H_{37.33}ClN_2O_{17.67}Ru_3$ : C, 27.78; H, 3.96; N, 2.95. Selected IR (KBr,  $cm^{-1}$ ): 1607, 1481, 1211, 1068, 1035, 941, 844, 760, 689 (-py); 1550 ( $\nu_{asym(OCO)}$ ); 1417 ( $\nu_{sym(OCO)}$ ); 618 ( $\pi_{(OCO)}$ ); 3069, 2921, 1343 (-CH<sub>3</sub>). Absorption spectrum of **1** in CH<sub>2</sub>Cl<sub>2</sub> solution shows a broad peak at 696 nm ( $\epsilon = 5221 M^{-1} cm^{-1}$ ), attributed to transition between MO levels formed by  $d\pi(Ru)-p\pi(\mu_3-O)$  interactions. This transition is also observed for other Ru<sup>III</sup><sub>3</sub> analogs in the similar wavelength region<sup>4</sup>.

### X-ray crystallography

Crystal data were collected using a blue-green crystal of dimensions 0.40×0.30×0.12 mm on a Siemens SMART CCD area detector diffractometer with graphite-monochromatized Mo K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation at 293(2) K. The complex **1** crystallized in the rhombohedral space group *R*-3c with  $a = b = 18.9802(4)$ ,  $c = 54.5586(13) \text{ \AA}$ ,  $\gamma = 120^\circ$ ,  $V = 17021.4(6) \text{ \AA}^3$ ,  $D_c = 1.670 \text{ g/cm}^3$ ,  $Z = 18$ ,  $F(000) = 8526$ ,  $R1 = 0.0667$ , and  $\omega R2 = 0.1874$ . The structure was solved by direct methods using SHELXL-97 program, and all non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in idealized geometries and their contributions were added to the structure factor calculations. Full-matrix least-squares refinement was based on  $F^2$  with the SHELXL-97 program. Molecular graph was drawn with the SHELXL-97 program packages.

The crystal structure of the complex **1** is shown in **Figure 1** with atomic numbering scheme. The crystal structure of **1** consists of  $Ru_3O(CH_3COO)_6(py)_2Cl$  and 14/3H<sub>2</sub>O. There is a crystallographic 2-fold axis passing through Ru(1)-O(1).

**Figure 1** The structure of  $Ru_3^III(\mu_3-O)(\mu-CH_3CO_2)_6(py)_2Cl \cdot 14/3H_2O$



The triangle formed by three Ru atoms is isosceles rather than equilateral. The distances of Ru(1)⋯Ru(2) and Ru(1)⋯Ru(2A) (3.370 Å) are significantly longer than that

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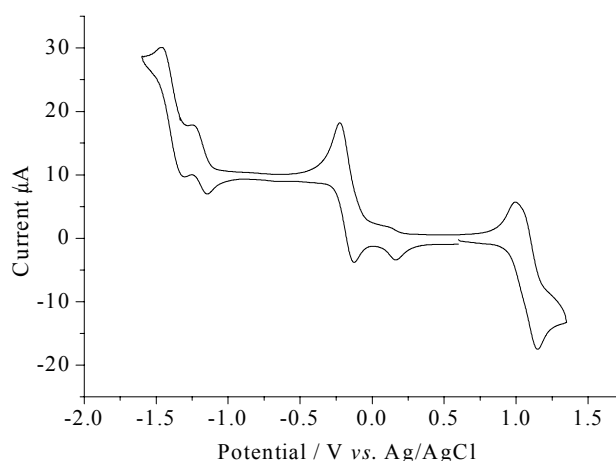
of Ru(2)···Ru(2A) (3.322 Å). This is caused by the lengthening of the Ru(1)-O(1) bond (1.981(10) Å) because of trans effect of Cl ligand, as compared with the Ru(2)-O(1) bond (1.914(7) Å). Similar phenomena was also observed in the CO-containing complex  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{mbpy}^+)_2(\text{CO})](\text{ClO}_4)_2 \cdot 2\text{DMF}$ <sup>6</sup>, and the CNXy-containing complex  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2(\text{CNXy})] \cdot 2\text{CHCl}_3$ <sup>7</sup>, in which the Ru-O<sub>oxo</sub> distances at the CO and CNXy site are longer than the two others.

The trans effect of the chloride also exerts an obvious influence on the Ru-O<sub>acetate</sub> distances. The bond distances of Ru(1)-O<sub>acetate</sub> (2.073(7) Å and 2.045(7) Å) at the Cl site are significantly longer than those of the Ru(2)-O<sub>acetate</sub> (2.026(7), 2.038(7), 2.043(7), and 2.062(7) Å) at the pyridine site, as those observed in the CO and CNXy-containing complexes<sup>6,7</sup>.

### Cyclic voltammogram (CV)

The cyclic voltammogram (CV) of the complex **1** in 0.1 mol/L (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NPF<sub>6</sub>-CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature is shown in **Figure 2**. It exhibits four “Ru<sub>3</sub>O”-cluster-based quasi-reversible one-electron redox processes ( $E_{1/2} = -1.38, -1.20, -0.17$  and  $1.07$  V vs. Ag/AgCl at a scan rate of  $100 \text{ mV s}^{-1}$ ), ascribed to the redox couples, Ru(II)Ru(II)Ru(II)/Ru(III)Ru(II)Ru(II), Ru(III)Ru(II)Ru(II)/Ru(III)Ru(III)Ru(II), Ru(III)Ru(III)Ru(II)/Ru(III)Ru(III)Ru(III) and Ru(III)Ru(III)Ru(III)/Ru(IV)Ru(III)Ru(III), respectively, as reported for the complex  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(\text{py})_2(4,4'\text{-bpy})\text{Ru}(\text{bpy})_2\text{Cl}](\text{PF}_6)_2$ <sup>8</sup>.

**Figure 2** Cyclic voltammogram of the complex **1**



Further studies on the design and synthesis of molecular wire having electronic coupling with triruthenium building block are currently pursued.

### Acknowledgments

This work was financially supported by the National Natural Science Foundations of China (No. 20171044 and 20273074) and Chinese Academy of Sciences for “hundred talents”.

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Received 4 July, 2002