

A Novel Octanuclear Molecular Loop Formed by Linkage of Oxo-centered Triruthenium Cluster Units

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Abstract: A novel dimeric complex $[\text{Ru}_3^{\text{III,III,II}}(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})(\text{CO})_2(\mu\text{-dppf})(\mu\text{-odppf})]$ (dppf = 1, 1'-bis(diphenylphosphio)ferrocene, odppf = 1, 1'-bis(oxodiphenylphosphoranyl)ferrocene) (**1**) of oxo-centered triruthenium-aetate cluster units was synthesized and characterized by X-ray crystallography. Compound **1** exhibits a cyclic structure formed by linkages of two triruthenium cluster units $\text{Ru}_3^{\text{III,III,II}}(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{CO})$ through dppf and odppf ligands, respectively. The diameter of the molecular loop is *ca.* 1.0 nm.

Keywords: Carboxylate, crystal structure, diphosphine, ruthenium, cluster complex.

The synthesis and structural characterization of large and discrete molecules with specific geometric shapes is becoming an attractive research topic¹⁻⁴. It has been shown that with proper choice of metal components, a great variety of polygons and polyhedra is attainable¹⁻³. Current synthetic strategy is mainly focused on the use of mono- or dinuclear metal units as the metal components¹⁻⁴, utilizing multinuclear metal cluster units as the building blocks, however, is neglected comparatively^{4,5}. Oxo-triruthenium cluster complex $\text{Ru}_3^{\text{III,III,II}}\text{O}(\text{CH}_3\text{COO})_6(\text{CO})(\text{CH}_3\text{OH})_2$ that affords multistep redox properties, versatile catalysis and intriguing magnetic behavior is an excellent metal cluster building block to design various shaped molecular materials⁶⁻⁸. We described herein the synthesis and X-ray crystal structure of a novel molecular loop complex $[\text{Ru}_3^{\text{III,III,II}}(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})(\text{CO})_2(\mu\text{-dppf})(\mu\text{-odppf})]$ **1** utilizing $\text{Ru}_3^{\text{III,III,II}}\text{O}(\text{CH}_3\text{COO})_6(\text{CO})$ and dppf as the components.

Compound **1** was prepared by the reaction of the methanol (15 mL) solution of $\text{Ru}_3^{\text{III,III,II}}\text{O}(\text{CH}_3\text{COO})_6(\text{CO})(\text{CH}_3\text{OH})_2$ ⁹ (76.6 mg, 0.1 mmol) with a dichloromethane solution (10 mL) of bis(diphenylphosphio)ferrocene (55.4 mg, 0.1 mmol) with stirring at room temperature for 2 days. The solvent was removed in vacuo and the residue was dissolved in $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_4\text{Cl}_2$ (1:1, v/v) to afford well-shaped blue crystals suitable for X-ray analysis by layering hexane onto the solution in a few days. IR (KBr pellet, cm^{-1}): 3435(vw), 3128(w), 2924(m), 2853(w), 1941(vs)(CO), 1614(s), 1581(m)(COO), 1402(vs)

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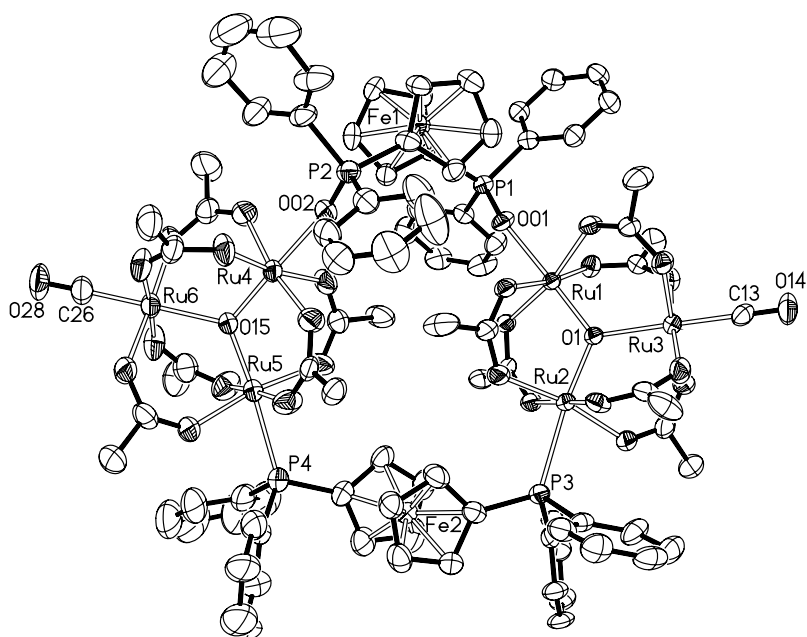
(COO), 1346(w), 1188(s)(P=O), 1165(s), 1119(s), 1101(m), 1033(w), 854(w), 749(w), 724(s), 702(s), 694(s) (COO), 620(w), 565(s), 530(w), 500(m), 448(w). UV/Vis (CH₂Cl₂): λ_{\max}/nm (ϵ , dm³ mol⁻¹ cm⁻¹) = 420 (9892), 564 (9830).

The IR spectrum of the complex **1** displays the characteristic bands of COO group at 1581 and 1402 cm⁻¹, the characteristic band of CO group at 1941 cm⁻¹, and the characteristic band of P=O double bond at 1188 cm⁻¹. The characteristic band of CO group in the compounds Ru₃^{III,III,II}O(CH₃COO)₆(CO)(CH₃OH)₂ and Ru₃^{III,III,II}O(CH₃COO)₆(CO)(py)₂ are at 1963 and 1950 cm⁻¹, respectively. The complex **1** is insoluble in all common organic solvents but slightly soluble in CH₂Cl₂. In the UV-Vis spectrum of the complex **1**, the band at 420 nm (ϵ = 9892 dm³ mol⁻¹ cm⁻¹) is ascribable to the cluster to ligand charge transition (CLCT), and the other band at 564 nm (ϵ = 9830 dm³ mol⁻¹ cm⁻¹) is the characteristic band of the oxo-bridged triruthenium center.

Crystal data were collected using a blue crystal of dimensions 0.52×0.46×0.28 mm on a Siemens SMART CCD area detector diffractometer with graphite-monochromatized Mo K α (λ = 0.71073 Å) radiation at 293(2) K. The complex **1** crystallized in the triclinic space group $P\bar{1}$ with a = 16.1468(2) Å, b = 16.45690(10) Å, c = 27.9701(4) Å, α = 102.9990 (10)°, β = 95.8240 (10)°, γ = 107.4880 (10)°, V = 6791.94 (13) Å³, D_c = 1.268 g/cm⁻³, Z = 2, $F(000)$ = 2594, $R1$ = 0.0813, and $wR2$ = 0.2183. The structure was solved by direct methods and the remaining non-hydrogen atoms were located from the successive difference of Fourier synthesis. Full-matrix least-squares refinement was based on F^2 with the SHELXL-97 program. The 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.

As shown in **Figure 1**, the dimeric complex [Ru₃^{III,III,II}(μ_3 -O)(μ -CH₃COO)(CO)]₂(μ -dppf)(μ -odppf) is a molecular loop formed by the linkages of two triruthenium units [Ru₃^{III,III,II}(μ_3 -O)(μ -CH₃COO)(CO)] with dppf and odppf ligands, respectively. The distance between the μ_3 -O_{oxo} atoms (O1 and O15) of two triruthenium units [Ru₃^{III,III,II}(μ_3 -O)(μ -CH₃COO)(CO)] and that between the Fe atoms (Fe1 and Fe2) of two of the diphosphine ligands (dppf and odppf) is 9.575 and 10.114 Å, respectively. In other word, the diameter of the molecular loop is *ca.* 1.0 nm. Three Ru atoms of each triruthenium unit [Ru₃^{III,III,II}(μ_3 -O)(μ -CH₃COO)(CO)] forms an inequilateral triangle (Ru1⋯Ru2 = 3.314, Ru1⋯Ru3 = 3.410, Ru2⋯Ru3 = 3.442 Å; Ru4⋯Ru5 = 3.32, Ru4⋯Ru6 = 3.415, Ru5⋯Ru6 = 3.457 Å). The inequilateral triangle is caused by the difference of the Ru-O_{oxo} bond lengths (Ru1-O1 = 1.882(6), Ru2-O1 = 1.918(6), Ru3-O1 = 2.071(6) Å; Ru4-O15 = 1.888(7), Ru5-O15 = 1.916(7), Ru6-O15 = 2.082(7) Å) because of the different trans effects of the CO, O and P donors bound to the Ru atoms. The angle between the triangular planes Ru1Ru2Ru3 and Ru4Ru5Ru6 is 31.6°. The P-O bond lengths (1.486(8) and 1.488(9) Å) indicate the double-bond character, similar to those (1.497(7) and 1.501(7) Å) found in the complex [Cu(dppf)(odppf)]BF₄¹⁰.

Figure 1 The structure of $[\text{Ru}_3^{\text{III,III,II}}(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})(\text{CO})_2(\mu\text{-dppf})(\mu\text{-odppf})\cdot 0.5\text{C}_2\text{H}_4\text{Cl}_2]$



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