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Note

Syntheses, characterization and properties of oxo-centered triruthenium cluster with tetrathiafulvalene-fused ligands

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ABSTRACT

A series of oxo-centered triruthenium–acetate complexes with tetrathiafulvalene-fused ligands, $[Ru_3O(OAc)_6(py)_2(dtpy)](PF_6)$ (**2**, py = pyridine, dtpy = 4′,5′-dimethyldithiotetrathiafulvenyl-4-pyridine), $[Ru_3O(OAc)_5\{\mu\text{-}\eta^1(C), \eta^2(N,N)\text{-}L\}(py)_2](PF_6)$ (L = dtpn, **3**, L = btpn, **4**; dtpn = 4′,5′-dimethyldithiotetrathiafulvenyl[4,5-f][1,10]phenanthroline, btpn = 4′,5′-bis(methyloxycarbonyl)dithiotetrathiafulvenyl [4,5-f][1,10]phenanthroline), have been prepared. These new compounds are characterized by UV–vis, IR, ^{1}H NMR, ESI-MS spectroscopic methods and elemental analysis. Cyclic and differential-pulse voltammetry reveal that all the compounds show interesting stepwise redox processes in solution.

1. Introduction

Oxo-centered triruthenium acetate clusters with general formula $[Ru_3(\mu_3\text{-}O)(\mu\text{-}RCOO)_6L_3]^{n+}$, where R = alkyl or aryl, L = axial ligands, constitute an important class of transition metal cluster compounds [1–8]. Owing to their reversible multi-step redox behavior and intriguing mixed-valence chemistry, they are regarded as excellent precursors for the design of molecular assemblies such as molecular wires, switches and molecular nanomaterials [9–12].

The richness of the triruthenium chemistry is enhanced by the diverse substitution of the axial ligands or the bridging acetate. Previous studies demonstrate that the substitution reactivity of axial ligands in the solvent-coordinated oxo-centered triruthenium acetate clusters, such as $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6L_2(CH_3OH)]^+$, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CO)L(H_2O)]$ and $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CH_3OH)_3]$, is high owing to their lability [4,7,12]. The coordinated solvent molecules can be easily substituted by terminal ligands with nitrogen or phosphorus donors [13–19]. If chelating ligands are employed, such as 2,2′-bipyridine derivatives, the axial methanol as well as one of the bridging acetates in the precursor cluster can be substituted. In this case, the bipyridine ligand takes an unusal $\mu\text{-}\eta^1(C), \eta^2(N,N)$ coordination mode, chelating one of the Ru centers via its two N donors and bonding to another Ru center via the C donor adjacent to the N donor [20–22].

Since the pioneering works of Wudl and Ferraris [23,24], tetrathiafulvalene (TTF) and its derivatives remain the most intensively investigated redox-active organic systems. They are considered as the gateway to the emerging fields of molecule-scale electronics and devices [25–31]. By covalent incorporation of the oxo-centered triruthenium cluster with redox-active TTF unit, it is possible to build new series of mixed-valence system. Meanwhile this system would provide an ideal template upon which mechanistic details of the factors controlling electron transfer, and the external stimuli-response between two or more oxidation levels can be extracted [32,33]. In this study, the TTF-fused terminal ligand with mono pyridine (4′,5′-dimethyldithiotetrathiafulvenyl-4-pyridine, **dtpy**) and the chelating ligands (4′,5′-dimethyldithiotetrathiafulvenyl [4,5-f][1,10]phenanthroline, **dtpn**;4′,5′-bis(methyloxycarbonyl)dithiotetrathiafulvenyl[4,5-f][1,10]phenanthroline, **btpn**) are specially chosen to annulate the triruthenium cluster to TTF skeleton (Scheme 1). By using the triruthenium precursor $[Ru_3O(OAc)_6(py)_2(CH_3OH)](PF_6)$ (py = pyridine) (**1**), a series of triruthenium derivatives, $[Ru_3O(OAc)_6(py)_2(dtpy)](PF_6)$ (**2**), $[Ru_3O(OAc)_5\{\mu\text{-}\eta^1(C), \eta^2(N,N)\text{-}L\}(py)_2](PF_6)$ (L = dtpn, **3**, L = btpn, **4**), are successfully synthesized (Scheme 2). Herein, the preparation, electrochemical and spectroscopic properties of these complexes are described.

2. Results and discussion

The synthetic routes to complexes **2**–**4** are outlined in Scheme 2. Reactions between the triruthenium precursor

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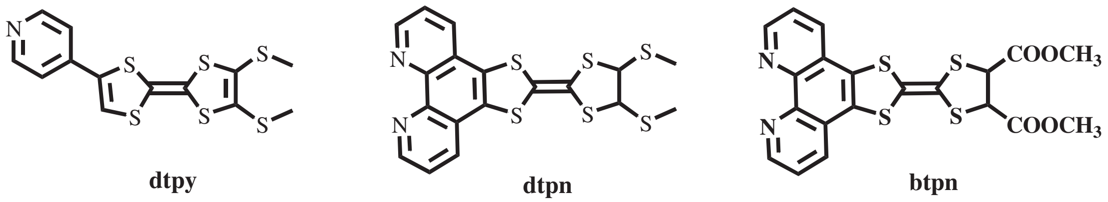
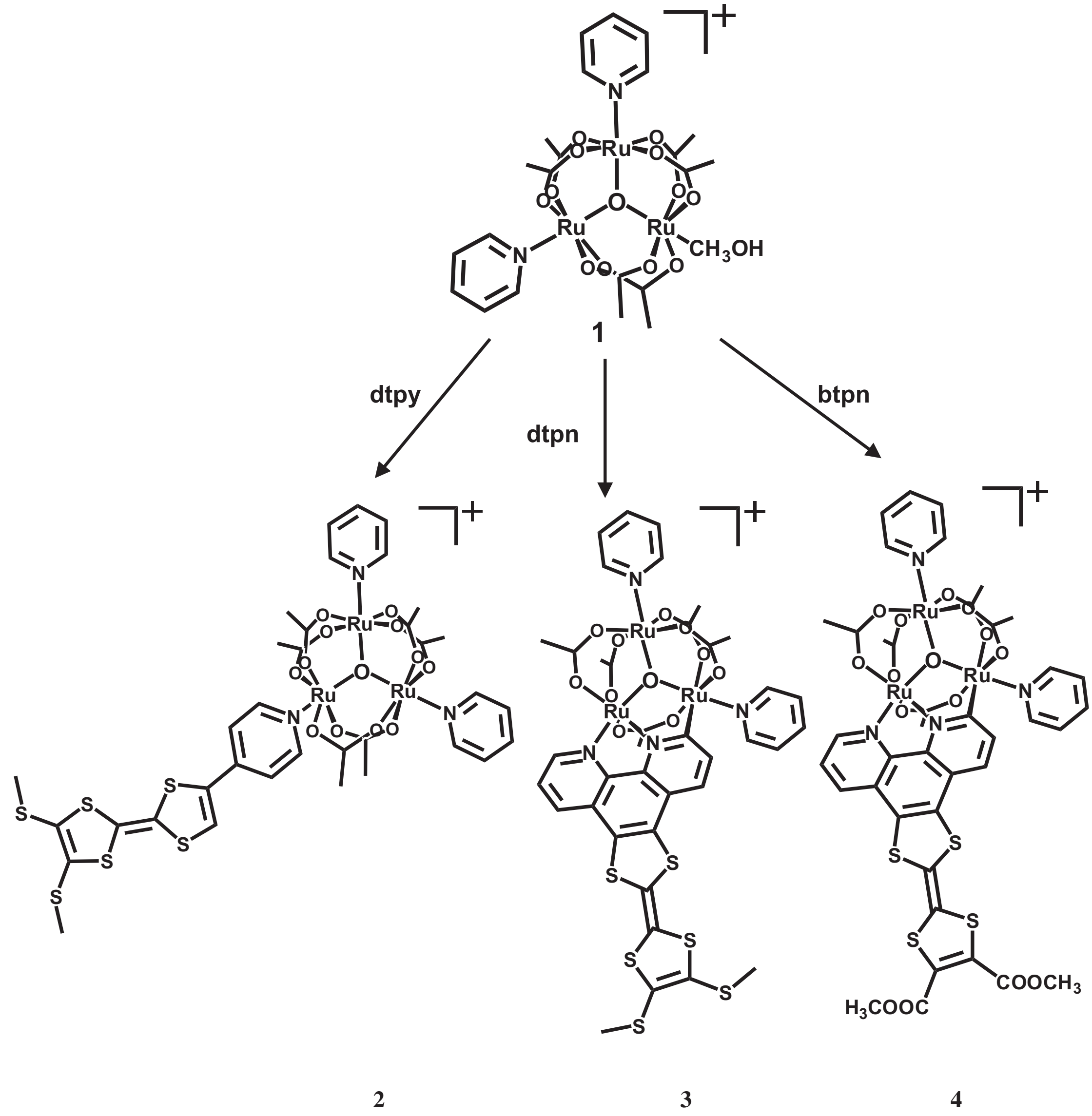


Scheme 1. Structures of TTF-fused ligands.

$[Ru_3O(OAc)_6(py)_2(CH_3OH)](PF_6)$ (**1**) and TTF-fused terminal ligand (**dtpy**) or chelating ligands (**dtpn** and **btpn**) in 1:1 M ratio afforded corresponding TTF-fused triruthenium derivatives **2**–**4**, respectively. The pure product is accessible readily by silica column chromatography. All new complexes are soluble in common polar organic solvents. However, recrystallization of **2**–**4** failed to give crystals good enough for X-ray crystal structure determinations. Compounds **2**–**4** were characterized by elemental analysis, IR, ^{1}H NMR, ESI-MS, UV–vis spectroscopies, cyclic and differential-pulse voltammetry.

In the infrared spectra of **2**–**4**, the asymmetric stretching mode ν_{as}(OCO) of the acetate bridges shows two broad absorption peaks around 1609 cm^{-1} and 1544 cm^{-1}, and the symmetric stretching mode ν_s(OCO) give one sharp peak around 1420 cm^{-1}, indicating that they are homovalent triruthenium complexes [5,20–22,34]. The sharp absorption band of the counter anion (PF_6^-) is located at 842 cm^{-1}. Whereas for complex **4**, the stretching band ν(C=O) of methoxycarbonyl groups occurs at 1731 cm^{-1}.

The +1 triruthenium compounds **3**–**4** show paramagnetic shifts because of the influence of unpaired electron (the spectral data



Scheme 2. Synthetic routes to complexes **2**–**4**.