Molecular Engineering of Redox Rich Diruthenium Compounds: Further Investigation of Ru₂(Yap)₄X Type Compounds

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Three new diruthenium compounds, Ru₂(L₁)₄Cl (1), Ru₂(L₂)₄Cl (2) and Ru₂(ap)₄F (3) were synthesized and characterized, where L₁, L₂, and ap are 2-(3-methoxyanilino)pyridinate, 2-(3-propoxyanilino)pyridinate, and 2-anilinopyridinate, respectively. Structural study revealed the Ru–Ru bond lengths of 2.2816(7) Å (1) and 2.2785(6) Å (3). All three compounds are S = 3/2 molecules. Each of three diruthenium compounds displays two reversible one electron couples, an oxidation and a reduction, and the potential data appear to indicate that the axial fluoro ligand is a much stronger donor than the chloro ligand.

KEY WORDS: Diruthenium; modified ap ligands; Ru–F bond; molecular wires.

INTRODUCTION

Diruthenium paddlewheel species constitute an important segment of compounds containing multiple bonds between metal atoms [1]. Detailed magnetic and spectroscopic studies of Ru₂(II,II) and Ru₂(II,III) species in late 80s by Cotton and others provided key insights to the understanding of complex electronic structures due to the pseudo-degeneracy of π*(Ru–Ru) and δ*(Ru–Ru) orbitals [2, 3]. Recent years have seen a surge in the synthesis of novel diruthenium compounds, especially those with potential material applications. Extensive studies by the Kadish/Bear group

1 Dedicated to Dick Walton, friend, statesman, and the maestro who has shown us the intricacy and beauty of dirhenium chemistry, on the occasion of his 65th birthday.
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uncovered several stable Ru$_2$(III,III) compounds, including Ru$_2$(DPhF)$_4$(C$_2$Ph)$_2$ (DPhF is diphenylformamidinate) and Ru$_2$(hpp)$_4$Cl$_2$ (hpp is 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-$a$]pyrimidinate) [4]. Linear free energy relationships in diruthenium compounds were explored based on electrochemical and spectroscopic data by the Ren [5] and Kadish/Bear groups [6]. Taking advantage of the propensity of axial ligation in Ru$_2$(II,III) species, Cotton et al. obtained dimer and linear polymers linked through ditopic ligands [7], while Chen et al. realized heterometallic assemblies involving diruthenium units [8]. Using non-linear multidentate linkers such as TCNQ and Co(CN)$_6^{3-}$, diruthenium tetracarboxylate units self-assemble into two- and three-dimensional networks that exhibit unusual magnetisms [9]. The recent successes in the high yield synthesis of Ru$_2$(DArF)$_4$(OAc)$_4$Cl type compounds (DArF is diarylformamidinate) [10] provide additional venues to supramolecular chemistry based on diruthenium compounds [11].

Our current endeavor in diruthenium chemistry focuses on achieving molecular electronic wires based on oligomers of diruthenium compounds bearing axial alkynyl ligands [12]. Facile electron transfer between two Ru$_2$ units across a polyyn–diyl linker, as reflected by a very small $\beta$-value (0.064 Å$^{-1}$), was established based on electrochemical and spectroelectrochemical studies of [Ru$_2$(ap)$_4$]$_2$(μ-C$_2$m) (ap is 2-anilinopyridinate) [13]. Similar study of the electronic coupling between two ferrocenyl units in trans-(FcC≡C)Ru$_2$(DMBA)$_4$(C≡CFc) (DMBA is N,N’-dimethylbenzamidinate) indicated that the diruthenium unit also efficiently mediates electron transfer over distance [14]. During the course of the above-mentioned work and other Ru$_2$(ap)$_4$-based chemistry [15], we have experienced difficulties in purification associated with the low solubility of Ru$_2$(ap)$_4$-compounds. Seeking to increase solubility through ligand modification, we have prepared $ap$-derivatives 2-(3-methoxyanilino)pyridine (HL1) and 2-(3-propoxyanilino)pyridine (HL2) and the corresponding diruthenium compounds Ru$_2$(L1)$_4$Cl (1) and Ru$_2$(L2)$_4$Cl (2). Reported herein are the synthesis and structural characterization of ligands HL1 and HL2, diruthenium compounds 1 and 2, and Ru$_2$(ap)$_4$F (3) (Scheme 1).

Scheme 1. Diruthenium $Y_{ap}$ compounds. 1: $Y$ = OCH$_3$, $X$ = Cl; 2: $Y$ = O$i$Pr, $X$ = Cl; 3: $Y$ = H, $X$ = F