

Spanning Pairs of Rh₂(acetate)₄ Units with Ru(II) Complexes

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A synthetic route to linear pairs of Rh₂ “paddlewheel” dimers bridged by Ru(II) complexes is presented. A bis(4′-(4-carboxyphenyl)-terpyridine)Ru(II) complex spans two Rh₂ dimers and displays a 26 Å separation between the dimers. Increased electronic interaction is found for the dimer of dimers without the phenyl groups using bis(4′-(4-carboxy)-terpyridine)Ru(II) as the bridging complex.

The rational design of supramolecular architectures whose assembly and function stems from dative bonding holds much potential for a wide array of materials.¹ In particular, di-metal paddlewheel complexes have received considerable attention of late due to their propensity to direct the assembly of polynuclear structures.² Rh₂(II,II) tetra- μ -carboxylates are particularly appealing considering that they have found application ranging from catalysis³ to antibacterial⁴ and

anticancer agents.⁵ Since the report of a long-lived, non-emissive photoexcited state of the Rh₂(II,II) tetra- μ -carboxylate motif,⁶ these and other functions are now being explored in the context of photoactivation,⁷ making them an even more intriguing component of supramolecular assemblies.

We have recently demonstrated that the Rh₂(II,II) tetra- μ -carboxylate motif may serve both structural and functional roles in the creation of assemblies composed of the photoactive unit (tpy)₂Ru²⁺, wherein energy transfer to the nonemissive Rh₂(II,II) core may be attenuated by modification of the emissive state of the appended Ru(II) complex.⁸ The photoexcited states of other related dimeric units have also been described recently.⁹

In order to simplify the synthesis of photoactive assemblies, we have prepared a pair of homoleptic, dicarboxylic acid functionalized (tpy)₂Ru²⁺ complexes suitable for binding di-metal units in a linear fashion reminiscent of Mo₂(II,II) and W₂(II,II) dimers.¹⁰ To the best of our knowledge, photoactive Ru(II) polypyridyl complexes have not been used as bridging ligands between metal dimers.

The ligands 4′-(4-carboxyphenyl)tpy¹¹ and 4′-(2-furyl)tpy^{12a} were prepared following established procedures;^{12b} the latter ligand was then oxidized with KMnO₄ to give the desired 4′-(carboxy)tpy in 68% yield. The corresponding

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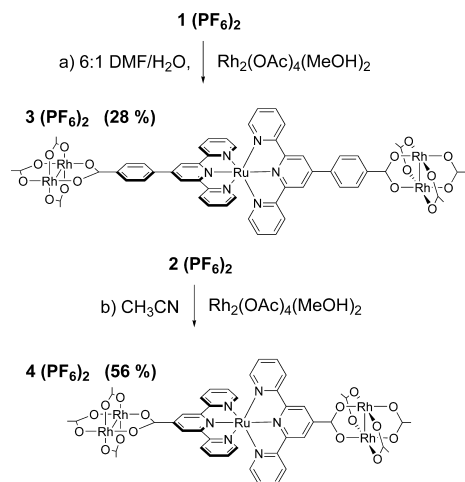
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Scheme 1. Synthesis of Symmetric Rh₂(II,II) Adducts from Diacid Ru(II) Precursor Complexes Using (a) 100°C for 24 hr and 2 equiv of Rh₂(OAc)₄(MeOH)₂ for **3** (PF₆)₂ and (b) 40 h reflux and 8 equiv of Rh₂(OAc)₄(MeOH)₂ for **4** (PF₆)₂.



homoleptic complexes of bis(4'-(4-carboxyphenyl)tpy)Ru(II), **1** (PF₆)₂, and bis(4'-(carboxy)tpy) Ru(II), **2** (PF₆)₂, were prepared in 94 and 98% yields, respectively.^{13a,b}

The charged nature of bridging ligands **1** and **2** makes them inherently unsuited to typical protocols for preparing “dimer–bridge–dimer” systems,¹⁰ considering that they are insoluble in nonpolar solvents and that salt metathesis with suitable cationic dimetal solvate precursors is complicated by the presence of counteranions. However, as we have previously noted,⁸ this charged nature also permits one to control the reaction under conditions that would otherwise lead to uncontrolled oligomerization using charge-neutral dicarboxylic acid.¹³ The poor solubility of the diacids **1** (PF₆)₂ and **2** (PF₆)₂ leads to modest yields for **3** (PF₆)₂ (28%) and **4** (PF₆)₂ (56%), respectively (Scheme 1). The reactions were readily interpreted by thin-layer chromatography, and the resulting complexes were stable to chromatographic purification on silica using a 7:1 CH₃CN/KNO₃ (sat, aq) mix as the eluent.

Complexes **3** and **4** were identified by both electrospray ionization mass spectrometry (ESI-MS) and ¹H NMR, the latter of which bears strong resemblance to that of the respective Ru(II) precursor complexes (see ESI). Evidence for coordination is provided by relative integration of the proton resonances of the acetates, located between 1.8 and 1.9 ppm (in CD₃CN), with those of the pyridyl rings located between 7.0 and 9.0 ppm. In addition, there is a marked electronic effect on the phenyl doublets for **1**, which merge into a singlet and shift upfield by 0.15 ppm upon coordination to the Rh₂(II,II) unit. This effect suggests a slight electron-releasing effect of the metal dimer.

Single crystals of **3** suitable for X-ray diffraction could be grown upon vapor diffusion of isopropyl ether into an acetonitrile/toluene solution containing the complex. The structure is depicted in Figure 1 as the tetra-acetonitrile

adduct and lies on a crystallographic 2-fold symmetry axis passing through Ru1, N2, N4, C8, C9, C21, and C22. The central points of the pairs of Rh dimers form a linear arrangement with the Ru(II) ion (180° angle from the central points of the Rh–Rh bonds through the Ru(II) ion).

Bond lengths and angles related to the (tpy)₂Ru²⁺ fragment are typical of related compounds.¹⁴ There exist two unique Rh₂(II,II) fragments, the structural parameters of which are typical of other Rh₂(O₂CR)₄ complexes,¹⁵ and these are related to the (tpy)₂Ru²⁺ core by torsion angles defined by C₇–C₈–C₉–C₁₀ (28.3(4)°) and C₂₀–C₂₁–C₂₂–C₂₃ (33.5(3)°). The dirhodium bond lengths (Rh₁–Rh₁ = 2.3933(9) Å and Rh₂–Rh₂ = 2.3913(9) Å) and Rh–N_(axial) bond lengths (Rh₁–N₂₁₀ = 2.231(6) Å and Rh₂–N₂₀₀ = 2.233(7) Å) are consistent with those of Rh₂(OAc)₄(CH₃CN)₂.¹⁶ We have noted previously that the appendage of more than one carboxy-functionalized Ru(II) complex about the Rh₂(II,II) core results in a change in the Rh–O_(carboxy) bond lengths.⁸ In particular, it was noted that the Rh–O_(acetate) bond length (1.936 Å) is unusually short (~0.1 Å) with respect to that of the Ru(II) complex for a 4+ assembly bearing the Ru(II) fragments in a trans disposition. We have ascribed this occurrence to electrostatic effects, whereby the acetates are drawn closer to buffer electrostatic repulsions between the cationic centers. Here, however, owing presumably to the lower 2+ charge, the Rh–O bond lengths are relatively uniform (Rh₁–O₁ = 2.036(3) Å, Rh₁–O₂ = 2.039(4) Å, and Rh₁–O₃ = 2.042(3) Å and Rh₂–O₅, Rh₂–O₆ = 2.023(3) Å, and Rh₂–O₇ = 2.027(5) Å). The tip-to-tip distance for this complex is ~35 Å, while the Rh₂–Rh₂ separation is ~26 Å, making this the largest separation between di-metal units reported to date for this class of compound.¹⁰

The electrochemistry of adducts **3** and **4** was investigated by both cyclic and square-wave voltammetry and is characterized by metal-based oxidations, corresponding to the Ru^{3+/2+} and Rh₂^{5+/4+} couples at a positively applied potential and irreversible ligand-based reductions at negatively applied potentials. For adduct **3**, these metal-based processes are essentially coincident in the cyclic voltammogram (*E*_{1/2} = 1.22 V vs SCE) and are barely discernible in the square-wave voltammogram. However, elimination of the phenyl spacer leads to enhanced resolution of these processes. Two reversible couples are defined at *E*_{1/2} = 1.42 and 1.28 V from the cyclic voltammogram of complex **4**, the relative integration of which leads to a 1:2 current ratio according to the square-wave voltammogram and permits their unambiguous assignment to the Ru^{3+/2+} and Rh₂^{5+/4+} redox processes, respectively (see ESI). The origin of this enhanced resolution is attributed solely to the anodic displacement of the Rh₂^{5+/4+} couple ($\Delta E_{1/2}$ = 260 mV) relative to that for Rh₂(OAc)₄,¹⁷ as the Ru^{3+/2+} couple does not deviate significantly from that

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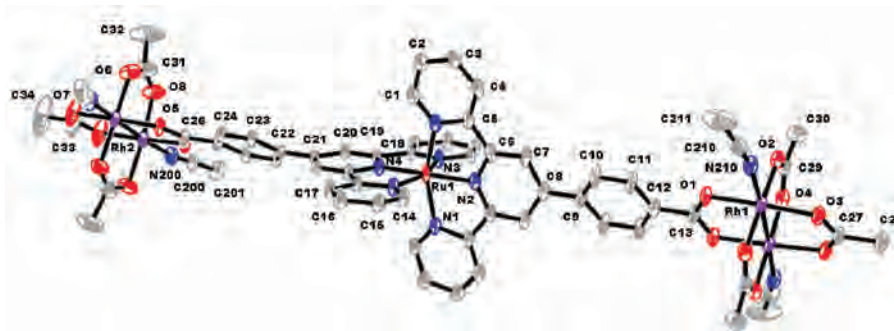


Figure 1. X-Ray crystal structure of complex **3** (PF₆)₂ with thermal ellipsoids at 50% probability. Counteranions and solvent have been omitted for clarity.

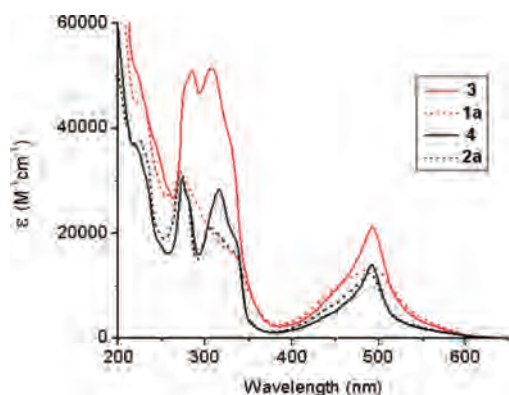


Figure 2. UV-vis spectra in acetonitrile (5×10^{-5} M) of **3** (red trace, solid) and **4** (black trace, solid) with the methyl esters of their respective parent complexes **1** (**1a**, red trace, dashed) and **2** (**2a**, black trace, dashed).

of the parent complex **2**, for which $\Delta E_{1/2} = 1.40$ V. This may be understood considering that the Rh₂(II,II) units exist here in the context of a 2+ cation.

The electronic absorption spectra for adducts **3** and **4** are shown in Figure 2 along with the methyl esters of their respective parent complexes. In the case of **3**, comparison to the methyl ester of **1**, complex **1a**, is made due to the insolubility of the precursor diacid complex **1**. For both adducts, the absorption profiles are very similar to their respective precursors with no significant change in band maxima for the characteristic ¹MLCT and ligand-centered transitions located at ~480 nm and 250–350 nm, respectively.¹⁸ However, incorporation of the Rh₂(II,II) units does seem to have some effect on the intensity of these transitions. This is particularly the case for adduct **3**, which displays intensities well beyond that arrived at from simple summation of the contributions of the individual components.¹⁹ Occurrences of this nature have been interpreted by others to be due, at least in part, to alteration of the electronic coupling between the components of such supramolecular assemblies.²⁰

The capacity for the Rh₂(II,II) tetracarboxylate fragment to serve as an energy reservoir upon photoexcitation of the appended (tpy)₂Ru²⁺ complex was previously noted.⁸ This

Table 1. Room Temperature Luminescence of Compounds **1–4** in Deaerated Acetonitrile

compound	luminescence, 298 K		
	λ , nm	Φ	τ , ns
1	646	1.0×10^{-4}	3.6
2	652	6.3×10^{-4}	25.6
3			
4	656	$<10^{-5}$	0.7

energy-transfer process was found to be efficient owing to a large thermodynamic driving force that effectively quenches the emissive ³MLCT state of (tpy)₂Ru²⁺. Preliminary luminescence measurements reveal analogous quenching of the weakly emissive state for complex **1** upon formation of the corresponding adduct **3** (Table 1). Complex **4**, however, remains slightly emissive (656 nm), which may be due to the somewhat smaller driving force for energy transfer in **4** compared to that of **3**.

In conclusion, we have described herein the first examples of linear (bis)-Rh₂(II,II) adducts spanned by cationic and photoactive dicarboxylate derivatives of (tpy)₂Ru²⁺. Although the bridging components do not appear to mediate electronic coupling between di-metal termini, the di-metal units do act as energy reservoirs in the photoactive assemblies. To this end, analogues based upon other di-metal units are currently under investigation, in addition to those comprised of mixed-di-metal units based upon mono-Rh₂ adducts of complexes **1** and **2**.

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Supporting Information Available: Crystallographic data in CIF format for **3**. The preparation, ¹H NMR, and electrochemistry of **3** and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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