

Structural Properties of Ruthenium Biimidazole Complexes Determining the Stability of their Supramolecular Aggregates

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Dedicated to Professor Rolf W. Saalfrank on the occasion of his 70th birthday

The results of a detailed investigation of the influence of substituents in a variety of ruthenium biimidazole-type complexes $[\text{Ru}(\text{R-bpy})_2(\text{R}'\text{-bi}(\text{bz})\text{imH}_2)]^{2+}$ ($\text{R} = \text{H}, \text{tBu}$; $\text{R}' = \text{H}, \text{Me}$; $\text{bi}(\text{bz})\text{imH}_2 = 2,2'\text{-bi}(\text{benz})\text{imidazole}$) on selected structural and photophysical properties is reported. The photophysical properties are only marginally influenced by the substituents at the bipyridine and the biimidazole core. All complexes show intense absorptions in the visible range of the spectrum with maxima around 475 nm, and emission from the formed excited state occurs at wavelengths between 650 and 670 nm. The comparison of structural properties determined by X-ray analysis within a series of related complexes shows that the Ru–N bond lengths to the coordinated bipyridines are not significantly influenced by the substituents, but slight differences in the Ru–N bond lengths to the biimidazole-type ligands can be detected. The reactions between ruthenium complexes containing different biimidazole-type ligands with the sulfate dianion, however, show a strong correlation between the substituents at the biimidazole core and the solubility of the product. The bibenzimidazole-containing complexes precipitate from aqueous solution whereas the ruthenium complex containing unsubstituted biimidazole stays in solution. The solid-state structure of one example of the sulfate-containing products (**2b**) shows that strong hydrogen bonds between the secondary amine function of the bibenzimidazole and the oxygen functionalities of the sulfate contribute to this unexpected behavior.

Key words: Ruthenium, Biimidazole, Bibenzimidazole, Supramolecular Chemistry,
Hydrogen Bonds