

Synthesis, structure and spectral and electrochemical properties of new mixed ligand monomeric Ru(II) complexes of *bis*(pyrid-2-yl)- and *bis*(benzimidazol-2-yl)-dithioether ligands

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Two novel binuclear Ru(II) complexes [Ru(pdto)(mCl)]₂(ClO₄)₂ **1** [pdto = 1,8-*bis*(pyrid-2-yl)-3,6-dithiooctane] and [Ru(bbdo)(mCl)]₂(ClO₄)₂ **2** [bbdo = 1,8-*bis*(benzimidazol-2-yl)-3,6-dithiooctane] have been prepared to elucidate the effect of Ru–S bond on the electronic properties of Ru(II) centres. The complex **1** has been shown to be a binuclear species in which two Ru(II) octahedra are bridged by two chloride ions constituting a common edge between the octahedra. The facile symmetrical bridge cleavage reaction of **1** and **2** with the diimine ligand 2,2'-bipyridine or 1,10-phenanthroline has been employed to obtain the mononuclear Ru(II) complexes [Ru(pdto)(bipy)](ClO₄)₂ **3**, [Ru(bbdo)(bipy)](ClO₄)₂ **4**, [Ru(pdto)(phen)](ClO₄)₂ **5** and [Ru(bbdo)(phen)](ClO₄)₂ **6**. The crystal structures of **3**, **4**, **5** and **6** contain a distorted Ru(II) octahedra composed of two nitrogen atoms of 2,2'-bipyridine (**3** and **4**) or 1,10-phenanthroline (**5** and **6**) and two thioether sulphurs and two pyridine or benzimidazole nitrogen atoms of the pdto or bbdo ligand. The ¹H NMR spectra of the complexes are helpful in assessing their solution geometry. Electronic spectra of all the complexes in MeCN solution exhibit two MLCT bands. Electrochemical measurements on the complexes in MeCN solution reveal that the lower redox potential of Ru(II)/Ru(III) couple in **4** and **6**, compared to **3** and **5** respectively, is due to the enhanced σ-donor capacity of benzimidazole nitrogen atoms in **4** and **6**, which leads to an increase in negative charge on ruthenium; this is reflected in the energies of the MLCT bands. The mononuclear dicationic species are more difficult to oxidise than the corresponding binuclear dicationic species, which is in line with the observation of the dP[®] P^{*2} MLCT band at lower energies. The redox properties of the complexes are illustrated with the help of the Lever parameters. The coordinated thioethers raise the Ru(II)/Ru(III) redox potentials by stabilising Ru(II) oxidation state.