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Effects of a monoelectronic oxidation on trinuclear ruthenium complexes

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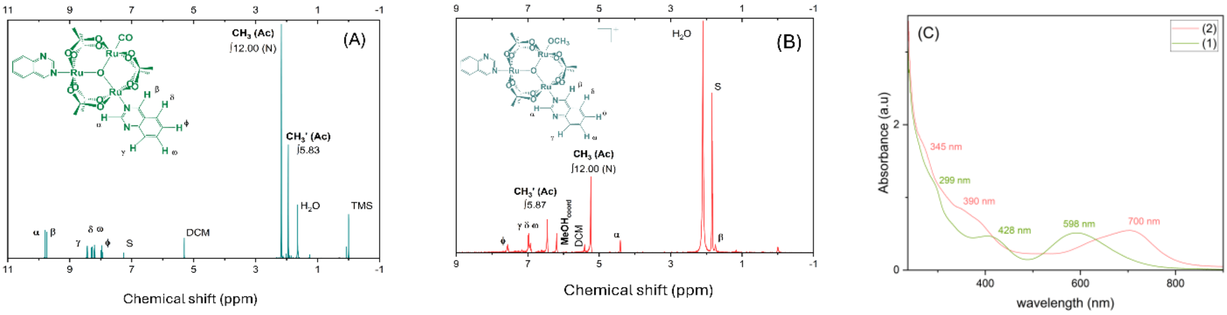
Studies of trinuclear ruthenium carboxylates date back to the 30s, with one of the earliest syntheses described by Mond.[1] Trinuclear ruthenium complexes with the formula $[Ru_3O(CH_3COO)_6(L)_3]^n$ (where L = N-heterocyclic ligand, CO, NO etc., n = 0/+1) are studied for several applications,[2,3] and the main interest of our research group is to develop new candidates to metallo-drugs.[2] Symmetrical compounds with three identical ligands exhibit planar triangular structure with angles close to 120°. In contrast, asymmetric clusters, such as those with a CO ligand, have a geometry resembling an isosceles triangle, with angles deviating from 120°.[4] These compounds are characterized by the interaction between the d_{xz} orbitals of the ruthenium ions and the p_z orbital of the central oxide ion, forming a delocalized orbital involving the four atoms of the $[Ru_3O]$ unit. To better understand their chemistry, a comparative study of $[Ru_3O(CH_3COO)_6(qui)_2CO]$ **(1)** and $[Ru_3O(CH_3COO)_6(qui)_2(CH_3OH)]PF_6$ **(2)** (qui = quinazoline) were performed. These compounds are related since **2** is obtained through a monoelectronic oxidation of **1,** followed by CO substitution by a solvent molecule. In the reduced complex **1**, the coordination of the carbonyl ligand localizes the valence of one ruthenium ion ($Ru_2^{III}ORu^{II}$). Cyclic voltammetry reveals that CO's higher affinity for Ru^{II} shifts the $E_{1/2}$ value of the $[Ru_3O]^{0/+1}$ reduction to more positive values compared to complex **2**. Additionally, compound **1** is diamagnetic, while complex **2** have one unpaired electron, which causes paramagnetic anisotropic shifts, significantly altering hydrogen chemical shifts compared to **1** and free quinazoline in their ^1H NMR spectra (Figure 1A and 1B). The strong π-acceptor character of the carbonyl ligand causes a large hypsochromic shift in the intracluster (IC) transition band in the electronic spectrum (λ_{IC2}= 700 nm and λ_{IC1} = 598 nm, Figure 1C). Furthermore, a bathochromic shift in the C≡O bond's stretching frequency occurs due to π-backbonding with the Ru^{II} ion ($\nu_{free\ CO}$ = 2143 cm^{-1} and $\nu_{coordinated\ CO}$ = 1936 cm^{-1}).

Figure 1. ^1H-NMR spectra of the complex (1) (A) and (2) (B) in $CDCl_3$ (2 x 10^{-2} M) and electronic absorption spectra (C) of the complex (1) and (2)



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