Related correlations have been reported by others, involving, e.g., the chronopotentiometric quarter-wave potential $(E_{1/4})$[3].

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Spectroelectrochemistry characterization of the Trinuclear $[Ru_3O(O_2CCH_3)_6(Pyrazine)_3]^{0,+}$ clusters

Henrique E. Toma[*] and Cecilia Cipriano[**]

The chemistry of the trinuclear clusters $[Ru_3O(CH_3CO_2)_6L_3]$ where L = imidazole, pyridine or pyrazine type of ligands, was investigated based on spectroscopic and electrochemical techniques[1],[2]. These complexes are of great interest[3] from the point of view of their electronic and redox properties, providing multisite species for electron transfer processes. They were isolated in solid state, and characterized by means of elementary analyses and infrared spectra.

The electrochemical behavior in acetonitrile solution was typically reversible; the cyclic voltammograms exhibited a series of four or five monoelectronic waves in the range of potentials from -1.8 to 2.0 V (fig. 1) ascribed to the sucessive $Ru^{IV}Ru^{III}Ru^{III}$ / $Ru^{III}Ru^{III}Ru^{III}$ / ... $Ru^{II}Ru^{II}Ru^{II}$ redox couples. The ratios of the anodic and cathodic peak currents are very close to unity. The separation between the anodic and cathodic peak potentials was approximately 60 mV at low potential scan rates (e.g. 20 mV s^{-1}), increasing up to 70 mV at 200 mV s^{-1}. A fifth wave was detected near the limiting potentials (2.4 V) in acetonitrile but the electrochemical response was much less reversible. The differences between the successive redox potentials were about 1 V, indicating strong metal-metal interaction in the trinuclear Ru_3O centre. A difference decreases from 1.0 to 0,45 V in the case of the redox couple involving the $Ru^{II}Ru^{II}Ru^{II}$ complex, which has no empty $d\pi$ orbital contributing to the electron delocalization in the trinuclear cluster. The E° values were strong sensitive to the nature of the N-heterocyclic ligand, increasing with the pi-acceptor properties of the pyridine and pyrazine derivatives, but in a much less pronounced way in the case of the imidazole derivatives. The redox potentials decrease linearly with the pka of the N-heterocyclic ligands. The variation is relatively small at high oxidation states, but increases rapidly as the oxidation states decrease, reflecting the role of π-backbonding in the complexes[4].

In order to characterize the chemical species involved in the electrochemical processes, spectroelectrochemical measurements were carried out for the $[Ru_3O(OOCCH_3)_6(pz)_3]$ cluster in acetonitrile solutions. The electronic spectra exhibited three characteristic

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[*] Instituto de Química, Universidade de São Paulo, Caixa Postal 20780, São Paulo, SP (Brazil)
[**] Instituto de Química, Universidade Federal do Rio de Janeiro, 21910, Rio de Janeiro, RJ (Brazil)

bands, as illustraded in Fig. 2. The low energy band is of composite nature, spanning the range 450-1300 nm as a function of the oxidation states of the trinuclear clusters. The assingnment of the electronic transitions can be discussed based on the qualitative molecular orbital scheme proposed by Cotton and Norman[5] and Baumann et al.[6] for the triangular $\mathrm{Ru_3O}$ centre. According to the molecular orbital scheme, the $[\mathrm{Ru_3O(OOCCH_3)_6(pz)_3}]^+$ complex can be formally described as $\mathrm{Ru^{III}Ru^{III}Ru^{III}}$, exhibiting the electronic configuration $(a_2'')^2(e'_1)^4(a_1')^2(e_2')^4(e'')^4(a_2')$, with an empty a_2'' orbital. Deconvolution of the absorption band at 710 nm leads to two main components at 715 and 630 nm and another weak one at 510 nm, ascribed to the symmetry-allowed $e'' \longrightarrow a_2''$ and $a_1' \longrightarrow a_2''$ transitions, and to the $e_1' \longrightarrow a_2''$ electric dipole forbidden transition, respectively, as in the analogous pyridine complex[6]. The corresponding transitions in the $\mathrm{Ru^{IV}Ru^{III}Ru^{III}}$, $\mathrm{Ru^{III}Ru^{III}Ru^{II}}$ e $\mathrm{R^{III}Ru^{II}Ru^{II}}$ clusters were located a 588, 540, 430; 930, 780, 615 and 1150, 957 and 795 nm, respectively. The optical energies display a linear correlation with the oxidation states, indicating a gradual increase of energy for the occupied metal $d\pi$ levels with the increasing number of electrons. In the case of the totally reduced $\mathrm{Ru^{II}Ru^{II}Ru^{II}}$ cluster, the $d\pi$ orbitals are completely filled and no metal-metal band is observed. In contrast, the $\mathrm{Ru^{IV}Ru^{III}Ru^{III}}$ cluster exhibits two vacant levels and an additional metal-metal band is observed at 785 nm, probably arising from the $e_1' \longrightarrow a_2'$ transition. The pyrazine ligands have π^* orbitals of appropriate symmetry to interact with the ruthenium $d\pi$ molecular orbitals, particularly those of e'' and a_2'' symmetry if one assumes a planar configuration. The absorption band in the ultraviolet region, around 260 nm, is also observed in the free pyrazine ligand and can be ascribed to π-π^* transitions in the aromatic ring. The band of intermediate energy is strongly sensitive to the ocidation states, mocing up from 310 nm in the $\mathrm{Ru^{IV}Ru^{III}Ru^{III}}$ complex to 800 nm in the completely reduced $\mathrm{Ru^{II}Ru^{II}Ru^{II}}$ from, with a dramatic increase in intensity (Fig. 2). There is a linear dependence of the optical energies on the oxidatin states, as can be seen in Fig. 3. This band can be ascribed to a charge-transfer transition from the occupied ruthenium (II) $d\pi$ orbitals, e.g. of e'' symmetry, to the lowest unoccupied π^* orbitals of the pyrazine ligands.

The spectroelectrochemical behavior of the $\mathrm{Ru^{III}Ru^{III}Ru^{III}}$ / $\mathrm{Ru^{III}Ru^{II}Ru^{II}}$ redox couple in aqueous solution is typically reversible, with E° = 0,40 V in agreement with the cyclic voltammograms. The decay of the absorption bands of the $\mathrm{Ru^{III}Ru^{III}Ru^{III}}$ complex at 340 and 705 nm is followed by the rise of strong bands at 420 and 905 nm, with isosbestic points at 274, 385, 545 and 750 nm. At pH > 10, the reduction of the $\mathrm{Ru^{III}Ru^{III}Ru^{II}}$ cluster proceeds reversibly with $E_{1/2} = -0.65$ V, shifting[1] the visible absorption band to 535 nm, with isosbestic points at 455 and 717 nm. The metal-metal band at 885 nm becomes slightly broader and more intense. The spectrum is quite similar to that recorded in acetonitrile solutions for the μ-oxo-bridged $\mathrm{Ru^{III}Ru^{II}Ru^{II}}$ cluster, indicating that the central oxigen bridge remains intact. Below -0.68 V, one observes an increase in intensity for the absorption band at 535 nm. The metal-metal band in the near-infrared region disappears, indicating that the metal $d\pi$ levels are saturated, as expected for the $\mathrm{Ru^{III}Ru^{II}Ru^{II}}$ oxidation state, in agreement with the cyclic voltammograms. The electronic spectrum does not coincide with that of the μ-oxo-bridged $\mathrm{Ru^{II}Ru^{II}Ru^{II}}$ cluster measured in acetonitrile solution (Fig. 2), and the energy for the ruthenium-to-pyrazine charge-transfer transition does not fit the linear correlation (Fig. 3). Therefore, it was ascribed to the completely reduced species with no central oxygen ion. At pH < 5, within the time scale of the spectroelectrochemical measurements, (1 - 5 min.) the μ-oxo-$\mathrm{Ru^{III}Ru^{II}Ru^{II}}$ species does not accumulate, converting rapidly to the $\mathrm{Ru^{II}Ru^{II}Ru^{II}}$ and product after the transfer of the central oxygen ion to the solvent. A closer look at the spectra in Fig. 2E shows that even in acetonitrile solutions there is some loss of the oxygen bridging ion from the trinuclear cluster, as noted by the additional shoulder at 550 nm, coinciding with the absorption band in aqueous solution.

In conclusion, the electrochemical behavior in aqueous and acetonitrile solutions differs by the reactivity of the central oxygen ion at the lowest oxidation states. The central oxygen ion plays an important role in stabilizing ruthenium (III) or (IV) species, by donating π-eletrons to the empty d_{yz} orbitals. However, when the clusters is in Ru (II) form, the d_{yz} orbitals are satured and this type of interaction is no longer possible, facilitating the transfer of the oxygen ion to the proton donor species in the solvents.

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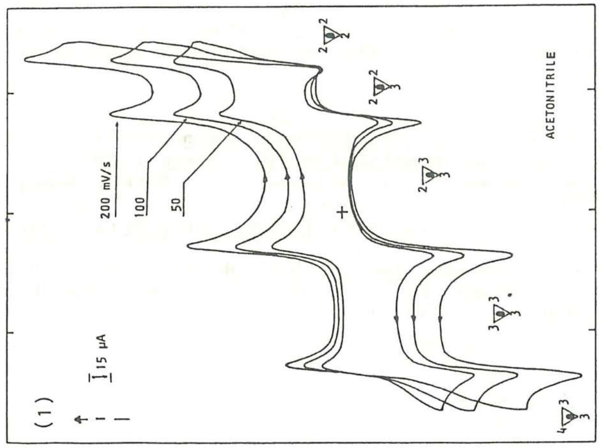

Fig. 1. Cyclic voltammograms of the $[Ru_3O(OOCCH_3)_6(pz)_3]$ cluster (3 mmol dm^{-3}) obtained at several potential scan rates, in acetonitrile ($[NEt_4ClO_4]$ = 0.100 mol dm^{-3}; 298 K), using a platinum working electrode.

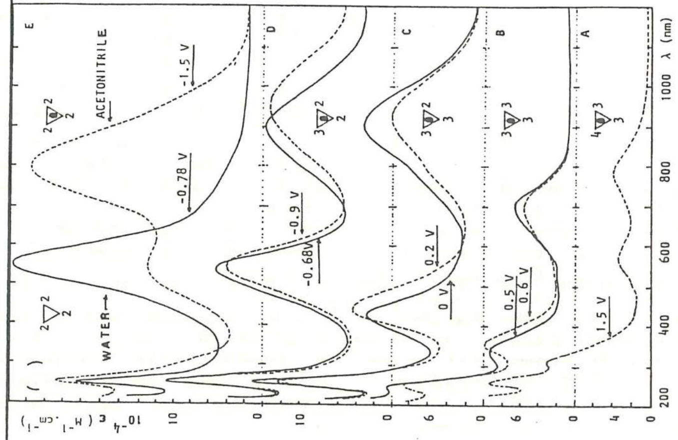

Fig. 2. Spectroelectrochemical behavior of the $[Ru_3O(OOCCH_3)_6(pz)_3]$ cluster in acetonitrile (---) and in aqueous solution (——) at several potentials (in V vs. SHE). [KCl] = 0.100 mol dm^{-3} (water) or $[NEt_4ClO_4]$ = 0.100 mol dm^{-3} (acetonitrile); 298 K.

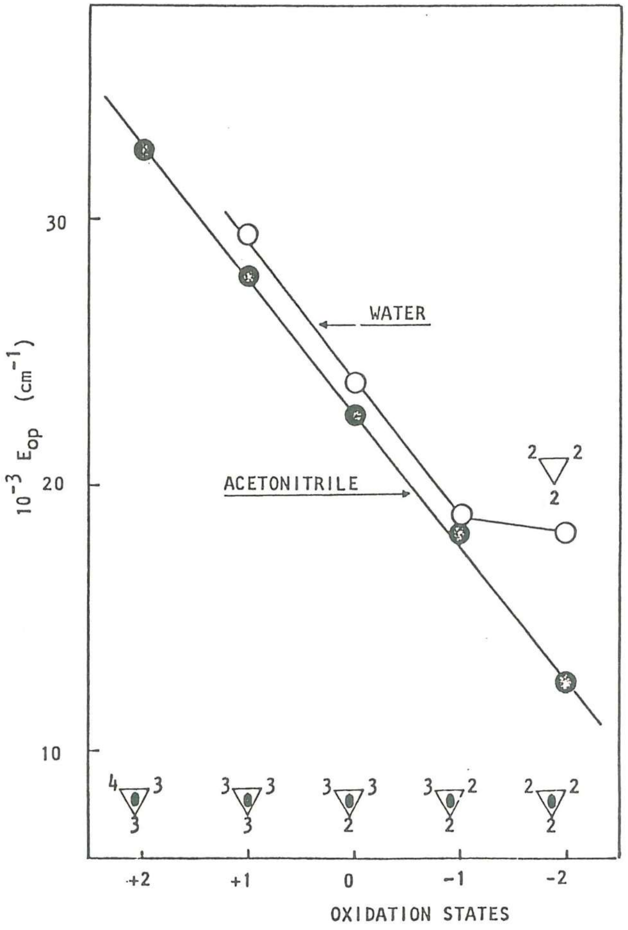

Fig. 3. Correlation of the optical energies for the metal-to-pyrazine charge transfer transitions and the oxidation states of the $[Ru_3O(OOCCH_3)_6(pz)_3]$ cluster in acetonitrile (black circles) and aqueous solutions (empty circles).