

Syntheses and characterization of oxo-centered triruthenium clusters with ortho-metallated ligands

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The oxo-centered triruthenium clusters ($[\text{Ru}_3\text{O}(\text{OAc})_6(\text{L})_3]^n$ where L = ligands), consists an important class of transition metal compounds and they exhibit several applications¹. The abundant chemistry of these clusters is intensified by the possibility of substitution of the bridging acetate and the axial ligands¹. In this last case, the coordinated of solvent molecules can be easily substituted by different terminal ligands¹. In the last decade some studies demonstrate that chelating ligands can substitute the bridging acetate and clusters with $[\text{Ru}_3\text{O}(\text{OAc})_5(\text{py})_2(\text{L})]^n$ (where L = ortho-metallated ligands) structure can be obtained². Therefore, in this study two clusters were synthesized with ortho-metallated ligands which belong to the class of extended phenazines. It is important to emphasize that these ligands (dppz = dipyrido[3,2-a:2',3'-c]phenazine and phen = 1,10 phenantroline) were chosen because combine interesting properties (a rigid and planar highly conjugated aromatic structure as well as its bidentate coordination capacity) and many studies reported that these ligands are efficiently in DNA intercalation or as potential agents to cell death³. Therefore, this work presents the preparation, electrochemical and spectroscopic properties of two clusters. By using the precursor (**1**) $[\text{Ru}_3\text{O}(\text{OAc})_6(\text{py})_2(\text{CH}_3\text{OH})](\text{PF}_6)$ (py = pyridine), two compounds were successfully synthesized (**2**) $[\text{Ru}_3\text{O}(\text{OAc})_5(\text{py})_2(\text{phen})](\text{PF}_6)$ and (**3**) $[\text{Ru}_3\text{O}(\text{OAc})_5(\text{py})_2(\text{dppz})](\text{PF}_6)$ where (**3**) is a new complex². The formation of the clusters (**2**) and (**3**) involved substitution of the axial methanol and one of bridging acetates in the precursor compound (**1**) and the subsequently cleavage of the *ortho* C-H bonds in the ligands². These complexes show characteristic absorption low-energy bands in the visible to near-infrared region (around 690 nm) that are characteristic of an intracluster charge transfer (IC) transition in the $[\text{Ru}_3\text{O}]^n$ unit and cluster-to-ligand charge transfer (CLCT) transitions at 340-380 nm (Table 1). In the infrared spectra the asymmetric stretching mode $\nu_{\text{as}}(\text{OCO})$ of the acetate bridges and symmetric stretching mode $\nu_{\text{s}}(\text{OCO})$ were observed². The sharp absorption band of the counter anion $\nu(\text{PF}_6)$ is located around 850 cm^{-1} (Table 1). The redox chemistry of compounds has been investigated by cyclic voltammetry and three redox processes were observed at -1.47, -0.19 and 0.95 V for (**2**) and -1.45, -0.28, and 0.86 V for (**3**). The mass spectra (ES-MS) show the peak of the molecular ion corresponding to the complexes without the counter ion PF_6 ((**2**) $m/z = 952.9$ and (**3**) $m/z = 1024.9$). According to results obtained it is demonstrated that a bridging acetate substitution by a chelating ligands affects significantly the electronic and redox characteristics of the oxo-centered triruthenium cluster compounds. At the moment further study is being pursued and new complexes have been synthesized and biological studies will be conducted.

Table 1: Absorption Spectral Data in acetonitrile and infrared stretching in KBr pellets for complexes (**2**) and (**3**)

Complexes	CLCT $\lambda_{\text{max}}/\epsilon$ $\epsilon \text{ mol}^{-1} \text{ L cm}^{-1}$	IC $\lambda_{\text{max}}/\epsilon$ $\epsilon \text{ mol}^{-1} \text{ L cm}^{-1}$	$\nu_{\text{as}}(\text{OCO})$	$\nu_{\text{s}}(\text{OCO})$	$\nu(\text{PF}_6)$
Complex (2)	384 nm /9507	693 nm/6203	1547 cm^{-1}	1415 cm^{-1}	852 cm^{-1}
Complex (3)	347 nm /21019	696 nm/6497	1554 cm^{-1}	1420 cm^{-1}	850 cm^{-1}

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