

## Study of nitric oxide photorelease from a trinuclear ruthenium cluster.

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**Introduction:** Trinuclear ruthenium clusters have a variety of oxidation states, which leads to an extensive mixed valence chemistry. Besides the interesting redox properties, electrochromic and catalytic clusters containing labile ligands and / or bridging ligands can act as building blocks of supramolecular structures. The NO molecule has versatile and important functions, particularly in biological systems. Due to systematic changes in electronic properties for the successive oxidation states, triangular clusters of ruthenium acetate provide unique species to interact with NO molecules. **Objective:** This study aims to synthesize and to characterize the cluster  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(3\text{-pic})_2(\text{NO})]^+$ , and also to study the release of nitric oxide in the aqueous solution at physiological pH. **Methods:** The cluster  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(3\text{-pic})_2(\text{NO})]^+$  was obtained by bubbling nitric oxide into the precursor solution of  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(3\text{-pic})_2(\text{H}_2\text{O})]^+$  for about one hour in dichloromethane. The complex were precipitated with petroleum ether and dried under vacuum. **Results:** The characterization of the cluster was performed using various spectroscopic techniques. The vibrational spectroscopy is very important in characterizing nitrosyl, since the NO ligand has a characteristic strong stretching band. In the case of cluster  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(3\text{-pic})_2(\text{NO})]^+$  it was observed at  $1883\text{ cm}^{-1}$ . The electronic spectrum of the  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(3\text{-pic})_2(\text{NO})]\text{PF}_6$  consists of four bands at 730 nm ( $\epsilon=597.21\text{ cm}^{-1}\text{mol}^{-1}\text{L}$ ), 542 nm ( $\epsilon=1394\text{ 67 cm}^{-1}\text{mol}^{-1}\text{L}$ ), 456 nm ( $\epsilon=1610.53\text{ cm}^{-1}\text{mol}^{-1}\text{L}$ ) and 372 nm ( $\epsilon=2057.92\text{ cm}^{-1}\text{mol}^{-1}\text{L}$ ). Three quasi-reversible waves were observed at -0.77, -0.061, and +1.38 V, which were tentatively assigned to the  $\text{Ru}^{\text{III}}\text{Ru}^{\text{II}}\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}/\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}\text{Ru}^{\text{IV}}$  redox couples, characteristic of the cluster; however the wave at -0.061 V may involve the process  $\text{NO}^+/\text{NO}^0$ . Ruthenium has seven isotopes, 104Ru (18.7%), 102Ru (31.6%), 101Ru (17.0%), 100Ru (12.6%), 99Ru (12.7%), 98Ru (a, 88%) and 96Ru (5.52%). The mass spectrum of the cluster shows the molecular ion peak (890 m/z) and occurs the loss of one molecule of 3-picoline, leading to a fragment with methanol (peak m/z826). The cluster  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(3\text{-pic})_2(\text{NO})]^+$  has the formal oxidation state  $\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}$ , characterizing an oxidized cluster. These clusters are paramagnetic and the  $^1\text{H}$  NMR signals of their ligands are not only sensitive to the inductive effects of the metal center, but also at the center  $\text{Ru}_3\text{O}$  paramagnetism. Reduced clusters in formal oxidation state  $\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}\text{Ru}^{\text{II}}$  are diamagnetic and the signals of the coordinated ligands are close to the free ligands. The  $^1\text{H}$  NMR signals of ligands of  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(3\text{-pic})_2(\text{NO})]\text{PF}_6$  behave as the ligands coordinated to a reduced cluster, because the  $\text{NO}^0$  ligand (which also has an unpaired electron) has a strong electronic coupling with the center  $\text{Ru}_3\text{O}$ , which leads to an increase in electron density of the metal center, thus reducing the paramagnetic effect. The photolysis of the complex  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(3\text{-pic})_2(\text{NO})]^+$  were made in phosphate buffer, pH 7.4 and monitored by spectral changes as a function of time. There was a gradual reduction of the band at 456nm and the formation of a band at 682nm, accompanied by two isosbestic points, one at 565nm and the other at 386nm. The yield of NO release was  $2.35\text{ 10}^{-6}\text{ mol/L}$  at 377nm,  $2.18\text{ 10}^{-6}\text{ mol/L}$  at 447nm,  $1.15\text{ 10}^{-6}\text{ mol/L}$  at 532 nm and 0 mol/L in 660 nm. **Conclusion:** So far, the data obtained for the cluster  $[\text{Ru}_3\text{O}(\text{CH}_3\text{COO})_6(3\text{-pic})_2(\text{NO})]^+$  confirm its structure. The cluster obtained has advantages over the others, because despite of not releasing NO within the therapeutic window, it releases NO in the visible region in aqueous medium, at physiological pH. **Keywords:** Trinuclear ruthenium cluster, spectroscopy, electrochemistry, flash photolysis. **Financial support:** CAPES, CNPq, FAPESP.