

Ultrasound-Assisted Synthesis of Ruthenium Nitrosyl Cyclen Complex: Crystal Structure, electrochemical and photochemical behavior.

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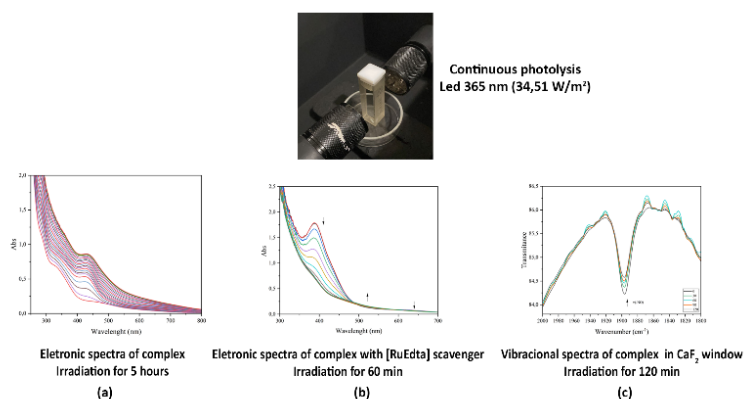
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The complexes that act as controlled nitric oxide (NO) donors is crucial for various biological applications. Nitric oxide serves as a vasodilator, exhibits antibacterial properties, and can inhibit or induce apoptosis in cancer cells depending on its concentration. Moreover, NO enhances the sensitivity of cancer cells to phototherapy and chemotherapy. However, its release must be controlled to avoid damage to healthy cells at high dosages. In this study, we investigated the controlled release of nitric oxide from ruthenium complexes with macrocyclic ligands. The *cis-syn-anti*-[RuNOCl(cyclen)](ClO₄)₂ complex was synthesized using an ultrasonic-mediated methodology. Characterization was performed using FT-IR and UV-Vis Spectroscopy, ¹H NMR, and Differential Pulse Voltammetry (DPV). Also, this is the first instance of isolating the crystal of a ruthenium nitrosyl complex with cyclen, with structural elucidation achieved through X-ray crystallography. The controlled release of NO was examined through electrochemical and photochemical methods. Electrochemical studies indicated that chloride release precedes nitrosyl release forming *cis*-[RuNO(OH₂)(cyclen)]²⁺ followed by NO release to produce the *cis*-[Ru(OH₂)₂(cyclen)]²⁺. Photochemical experiments, conducted using continuous photolysis, involved irradiating a solution of the complex in phosphate buffer (pH 7.4) with a 365 nm LED. An increase in absorbance at 430 nm assigned as a combination of bands as LF and a contribution to a Ligand-Metal Charge Transition (LMCT) $\pi_{H_2O} \rightarrow d\pi_{Ru}$, as shown in scheme 1(a) assigned to the NO release. This was further validated using the NO scavenger [RuHEDTA] scheme 1(b) and IR spectroscopy, which showed a decrease in the ν_{NO} peak at 1890 cm⁻¹ scheme 1(c). The quantum yield of NO release for the complex was determined as 0.208 mol/Einstein, consistent with values for other ruthenium nitrosyl complexes. The photochemical behavior of the complex is an indicative of a potential acting as photosensitive agent under physiological conditions.

Scheme 1: Continuous photolysis experiments in phosphate buffer (pH 7,4) by spectroscopy techniques.



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