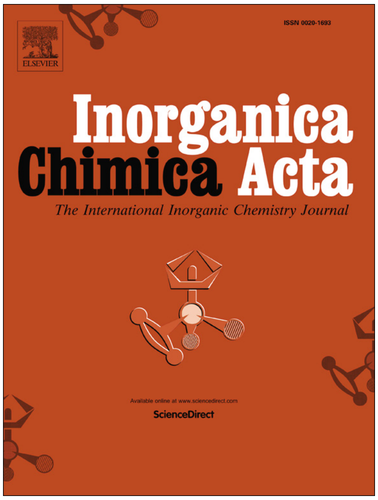

Research paper

Mechanism and oxidation state involved in the nitric oxide (NO) photorelease in a terpyridine-bipyridine-based ruthenium nitrosyl complex

Valerii Bukhanko, Pascal G. Lacroix, Isabelle Sasaki, Marine Tassé, Sonia Mallet-Ladeira, Zoia Voitenko, Isabelle Malfant

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Mechanism and oxidation state involved in the nitric oxide (NO) photorelease in a terpyridine-bipyridine-based ruthenium nitrosyl complex

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ABSTRACT

A new nitric oxide ($NO^{\cdot}$) donor of formula $[Ru^{II}(MeO\text{-}Phtpy)(bpy)(NO)](PF_6)_3$, where MeO-Phtpy is the 4'-(4-methoxyphenyl)-2,2':6',2''-terpyridine and bpy the 2,2'-bipyridine, has been synthesized and fully characterized. The X-ray crystal structure of the complex is provided together with that of its photoproduct of formula $[Ru^{II}(MeO\text{-}Phtpy)(bpy)(MeCN)](NO_3)_2$. The electronic properties have been investigated theoretically using the time dependent density functional theory (TD-DFT) approach. They reveal that the low-lying electronic transitions exhibit a strong charge transfer character towards the withdrawing nitrosyl unit, which suggest good $NO^{\cdot}$ donating capabilities under irradiation performed on a large frequency range. The photorelease of $NO^{\cdot}$ has been investigated in acetonitrile at two different wavelengths, $\lambda = 365$ and 436 nm, leading to related quantum yields equal to 0.08 and 0.03, respectively. The evolution of the oxidation states of the species involved within the release process is tracked by EPR and ^{1}H-NMR spectroscopy. It is confirmed that nitrosyl is released as $NO^{\cdot}$ radicals while the related ruthenium(III) photoproduct is readily reduced to ruthenium(II). The mechanism involved in the release is discussed on the basis of the present experimental data and the TD-DFT analysis.

Keywords: Ruthenium complexes, Nitric oxide, NO release, DFT computations.

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