

Photo-thermal activation study of ruthenium Keppler-type complexes with focus on the release of the nitrosyl ligand using TD-DFT and AIM theories

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INTRODUCTION

New cancer cases arises every day with frightening statistics and one of the greatest challenges in the treatment in recent years, which is the low selectivity of medicines, inefficiency on the metastatic cells, resistance and toxicity thereof. In this context, ruthenium complexes containing nitrosyl group (NO) has gained ground since the release of nitrosyl inside mitochondria can change the functions of the cell and cause its death.¹ Thus, based on the mechanism (Figure 1), the aim of this study is to use the density functional theory (DFT) to evaluate the reduction and release of the nitrosyl group within the cell, and also apply the theory of atoms in molecules (AIM) to gain details of Ru-nitrosyl interaction.

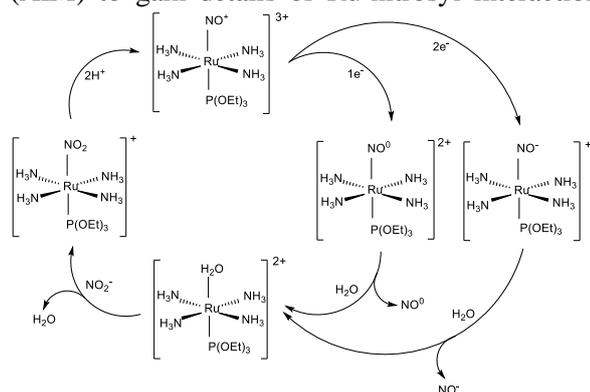


Figure 1: Thermal activation steps of NO in the Ru^{III} complexes, *trans*-[Ru(NO₂)(NH₃)₄P(OEt)₃]²⁺ (Adapted from Tfouni 2012).²

METHODS

All structures were optimized using the B3LYP functional with 6-31G(d) basis set for non-metals and LANL2DZ for the Ru atom. All calculations were carried out in gas and aqueous phase (CPCM). Later, the optimized species were studied using TD-DFT and AIM Bader's theory.

RESULTS AND DISCUSSION

In the reduction step, the loss of an electron ($E^\circ=5.44\text{V}$) is more favorable for its reduction

potential to be greater than the loss of two electrons ($E^\circ=4.56\text{V}$) and the release of the binder NO⁰ energy is lower, compared to NO⁻ release ($\delta\Delta_rG = 85.14 \text{ kcal mol}^{-1}$). From distances of Ru-N bond obtained in DFT, it is observed that the complex [Ru-NO⁰]²⁺ (1.98 Å) the distance is slightly higher compared to [Ru-NO⁻]⁺ (1.95 Å). These data agree with the AIM theory, so that the Laplacian ($\nabla^2\rho$) (Table 1) in the Ru-N bond for complex [Ru-NO⁰]²⁺ is higher than in [Ru-NO⁻]⁺.

Bond	Ru-N	
AIM properties	$\nabla^2\rho$	DI
[Ru-NO ⁻] ⁺	1.094	1.422
[Ru-NO ⁰] ²⁺	0.704	1.032
[Ru-NO ⁻] ⁺	0.523	1.123

Table 1: Laplacian and Delocalization Index for Ru-N bonds in selected complexes.

Coordination to Ru alters properties of N markedly, but affects O rather less. N in NO⁺ bound to Ru contains almost a whole electron more than in the free ligand, despite having an almost identical volume, evidence of substantial donation from metal d-orbitals into the empty, low-lying π^* orbitals on N.

CONCLUSIONS

Through the AIM a good approximation was obtained for Lewis structures. All properties are in good correlation with data obtained from TD-DFT. Also, the thermodynamic study allowed energy assessment involving the metal reduction steps and release of NO group. Transitions states are now being studied.

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- Adeniyi, A. A.; Ajibade, P. A. *J. Molecular Graphics and Modelling*, 38, 60-69, (2012).
- Tfouni, E.; *et al. Nitric Oxide*, 26, 38-53. (2012).