Atoms in Molecules (AIM) comparative study of Ru–NO complexes. Gaining an important insight related to photo-thermal activation.

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Introduction

Metal complexes have been considered very important in many diseases treatments including cancer and Alzheimer's. Through the last decades the focus have been directed towards a description of the interaction between metal and nuclear DNA. However, new insights have been reported which includes "clamps" in the DNA phosphate backbone and the induction to apoptosis via nitrosyl (NO^-, NO, NO^+) releasing.[1] Regarding the latest, Ru–NO complexes occupies a very relevant position in several biological processes, for instance, in the inhibition synaptic transmission and immune responses.[2]

Depending the target, the understanding on the selectivity of NO release or capture by Ru complexes through its photochemical and thermal activation have been investigate in this work by theoretical methodologies. Atoms in Molecules theory (AIM) has been applied in order to understand the behavior of metal-ligand bond in complexes such as *trans*-$[Ru^{II}(NO^+)(NH_3)_4P(OEt)_3]^{3+}$ (**1**).

Results and Discussion

Here, all species involved in the activation cycle of complex **1**, as described by Tfouni,[1] were optimized by density functional theory (DFT), using water solution in polarizable continuum method, at the B3LYP/6-31+G(d,p)/LANL2DZ level of theory. Afterwards, AIM was applied in order to get relevant properties from the bond critical points (BCP).

The appropriated comparison between all species is now in written process for future publication. However, in this abstract, a brief discussion is presented as follow. All data, including electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), ellipticity and the electron delocalization index (DI), which states for the average number of shared electrons between atoms A and B were evaluated. Figure 1 show ρ values and BCPs for complex **2**, the one with the neutral (doublet) NO.

Table 1 shows some of these electronic properties provided by AIM results.

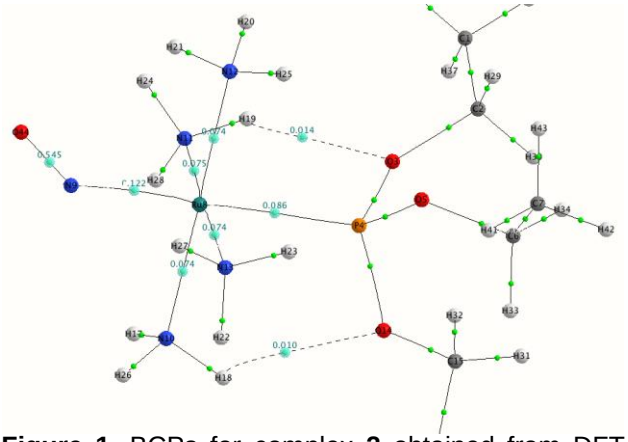

Figure 1. BCPs for complex **2** obtained from DFT optimized geometry.

Table 1. BCPs $\nabla^2\rho$ and DI values for the main bonds for NO species involved in the activation cycle.

Complexes/Bonds	Ru–N	Ru–P	N–O
$[Ru^{II}(NO^+)(NH_3)_4P(OEt)_3]^{3+}$ (**1**)	1.094/ 1.422	0.111/ 0.653	-2.096/ 2.104
$[Ru^{II}(NO^0)(NH_3)_4(P(OEt_3))]^{2+}$ (**2**)	0.704/ 1.032	0.208/ 0.729	-1.617/ 2.088
$[Ru^{II}(NO^-)(NH_3)_4(P(OEt_3))]^{+}$ (**3**)	0.523/ 1.123	0.218/ 0.692	-1.209/ 1.888

All values are presented in hartrees.

By the DI data one can be seen that the bond order decrease from NO^+ to NO^-. Also, the Laplacian indicates that the electronic charge is in fact concentrate in the N–O bond as can be seen by the trending observed at Ru–N bond.

Conclusions

AIM results provided a good insight about Lewis structure of Ru–NO complexes. Besides the AIM data discussed here and other data from parameters not shown, the thermodynamics involved in the electron transfer reactions is also under study.

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