INTRODUCTION

This work concerns the luminescence lifetimes of Ru(II) polypyridine complexes such as the much studied tris(2,2'-bipyridine) ruthenium(II) ion. The present work is part of the continuation of previous work aimed at clarifying factors responsible for long luminescence lifetimes which has already resulted in two publications [1, 2]. These two publications sought to find ligand field theory (LFT) like luminescence indices which correlated with experimental high luminescence lifetimes. A more direct evaluation of the luminescence indices involves calculating the height of the transition state barrier (or barriers) on the lowest triplet state potential energy surface of these complexes. It is the goal of the present study to calculate these barriers for at least several of these complexes to compare against the previously developed luminescence indices.

The difference between the $^3$MLCT and $^3$MC states is whether the excited electron is in a ligand $\pi^*$ orbital or in a metal $e_g^*$ orbital. Relative positions of the metal $t_{2g}$ and $e_g^*$ energies and the ligand $\pi^*$ energies can predict the $^3$MLCT $\rightarrow$ $^3$MC barrier height.

OBJECTIVES

$Ll3 = \left(\frac{\epsilon_{e_g^*} + \epsilon_{\pi^*}}{2}\right)^2$

Direct calculation of the $^3$MLCT $\rightarrow$ $^3$MC barriers ($E_t$) at the same level as Ll3 (gas-phase calculations, B3LYP/6-31G, 6-31G(d)).

SPECIAL TOOLS

SPECTRUM.PY: Converts the spectral function to the molar extinction coefficient for comparison against experiment.

PDOS.PY: PDOS analysis based upon Mulliken charges technique to extract ligand field theory (LFT) like information from DFT calculations.

COMPUTATIONAL DETAILS

- GAUSSIAN 09, B3LYP/6-31G and 6-31G(d) LANL2DD EC for Ru. Ultrafine grid and Very Tight SCF, DFT, TD-DFT, IRC.
- ORCA, NORTI, B3LYP/G, NEB.
- Trans-dissociation of two bonds (2D-scan) with a step size of 0.005 is done from 1.90 to 2.50 Å to find a possible 3TS.

EXTRACTION OF $t_{2g}$ $e_g^*$ AND $\pi^*$ ENERGIES FROM PDOS-LFT

B3LYP PDOS calculated for $[\text{Ru(bpy)}_3]^2+$ for 6-31G basis set

REFERENCES


PERFORMANCE OF LI3

Performance of LI3 for complexes of formula [Ru(N)]^2+ Li3 is in (ev)

2D SCAN CONTOUR PLOT

Trans-dissociation of Ru-N3, Ru-N4 dissociation plotted with in house python program SimpleContourPlot.py

BOND LENGTH VARIATION WITH IRC SCAN

- There is overall large symmetry of the IRC and associated Ru-N distance plot.
- “Pseudorotation” 3TS point between $^3$MC Jahn-Teller distorted structures detected which is close to expected TS.
- Use an alternative algorithm for finding the IRC is by using the nudged elastic band (NEB) method.

CONCLUSION

- New difficulties were encountered in the project due, apparently, to near-laying transition states or to transition states shared by more than one reaction pathway.
- We have developed many techniques, and overcome many difficulties, for finding and proving TSs in ruthenium polypyridine complexes.
- New Nudged Elastic Band (NEB) calculations started with the ORCA program with NORTI, B3LYP/G to get a better/more accurate guess for the 3TS.

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Test of the Orbital-Based LI3 Index as a Predictor of the Height of the $^3$MLCT $\rightarrow$ $^3$MC Transition-State Barrier for Gas-Phase [Ru(N\&N)^2+] Polypyridine Complexes

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