

Note

Comment on “Theoretical studies on the ground states in $[M(\text{terpyridine})_2]^{2+}$ and $[M(4-(4-(t\text{-butyl})\text{phenyl})\text{terpyridine})_2]^{2+}$ ($M = \text{Fe, Ru, Os}$) and excited states in $[\text{Ru}(\text{terpyridine})_2]^{2+}$ using density functional theory” [1]

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ARTICLE INFO

Article history:

Received 18 February 2008

Received in revised form 24 June 2008

Accepted 29 June 2008

Available online 4 July 2008

Keywords:

Terpyridine

Iron

Density functional theory

ABSTRACT

The nature of the first excited state of $[\text{Fe}(\text{terpyridine})_2]^{2+}$ has been reinvestigated. In contrast to previous findings, it is metal-to-ligand charge transfer in nature, thus fitting in the series of the Ru and Os complexes.

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Recently, a report has been published concerning theoretical calculations on the lowest excited states of $[M(\text{terpyridine})_2]^{2+}$ and $[M(4-(4-(t\text{-butyl})\text{phenyl})\text{terpyridine})_2]^{2+}$ ($M = \text{Fe, Ru, and Os}$) complexes calculated using the TD-DFT approach [1]. A difference was claimed between the character of the lowest transition of $[\text{Fe}(\text{terpyridine})_2]^{2+}$ and that of the other five considered compounds: whereas the iron complex had intraligand (IL) $\pi-\pi^*$ character, the lowest transitions of the Ru and Os complexes were predominantly metal-to-ligand charge-transfer (MLCT) excitations. In order to gain insight into this remarkable difference [2–3], we have undertaken a computational study at the same level of theory (B3LYP/LANL2-DZ) as the original authors and found that our results for $[\text{Fe}(\text{terpyridine})_2]^{2+}$ differ from those previously reported.

Optimisation of the geometry at the B3LYP/LANL2-DZ level [4] resulted in an identical geometry as reported in [1], identified as a local minimum by normal mode analysis. The orbital energies agreed with the reported values within 0.02 eV. Our TD-DFT [5] results also agreed well with those of Zhou et al. (Table 1 and Tables

S1–S3), aside from one low-energy transition with zero oscillator strength (f). In line with the previous study, the first electronic transition with non-zero oscillator strength ($f = 0.0122$) can be assigned to a degenerate $\text{HOMO} \rightarrow \text{LUMO}/\text{HOMO} \rightarrow \text{LUMO}+1$ pair transition. The energy of this transition (2.59 eV) agrees with the experimental value of 2.25 eV in aqueous solution [3].

The difference between our results and the reported study is the nature of the orbitals involved in this transition, on which the assignment of the character of this transition is based. In contrast to the original findings that the HOMO of $[\text{Fe}(\text{terpyridine})_2]^{2+}$ is ligand-based [1], we find that the HOMO is predominantly metal-based (Fig. 1, Fig. S1 and Table S2). Hence, the current calculations demonstrate that this lowest-energy absorption in $[\text{Fe}(\text{terpyridine})_2]^{2+}$ has MLCT character, instead of IL character. These results thus eliminate the reported difference between the Fe complex and its Ru and Os congeners and lead to overall consistency in the set $[M(\text{terpyridine})_2]^{2+}$ ($M = \text{Fe, Ru and Os}$).

The assignment of this transition to a MLCT transition is independent of basis set: enlargement of the basis to the Ahlrichs-pVDZ basis set [6] or to the non-relativistic cc-pVTZ basis for Fe and to the cc-pVDZ basis set [7] for the other atoms gives similar results. The first non-vanishing transition originates from the metal-based HOMO, Table 1, Tables S4–S7 and Figs. S2–S3; the first visible transition still corresponds to a $\text{HOMO} \rightarrow \text{LUMO}/\text{HOMO} \rightarrow \text{LUMO}+1$ excitation and the HOMO consists mainly of an Fe d-orbital (Fig. S3). The energy of the MLCT transition decreases upon

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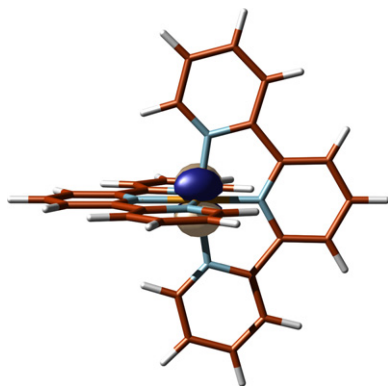
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² Though Zhou et al. consequently refer to $[M(4-(4-(n\text{-butyl})\text{phenyl})\text{terpyridine})_2]^{2+}$ [1] in the main document text, $[M(4-(4-(t\text{-butyl})\text{phenyl})\text{terpyridine})_2]^{2+}$ is displayed in figures.

Table 1The first three excited states of $[\text{Fe}(\text{terpyridine})_2]^{2+}$, calculated at the B3LYP/LANL2-DZ, B3LYP/Ahlrichs-pVDZ and B3LYP/cc-pVTZ-NR(Fe)+cc-pVDZ level of theory

#	LANL2-DZ			Ahlrichs-pVDZ			cc-pVTZ-NR(Fe) + cc-pVDZ		
	<i>E</i> (eV)	<i>f</i> ^a	Character (<i>c</i> ^{2 b})	<i>E</i> (eV)	<i>f</i> ^a	Character (<i>c</i> ^{2 b})	<i>E</i> (eV)	<i>f</i> ^a	Character (<i>c</i> ^{2 b})
1	2.291	0.0000	H → L + 10 (.49)	2.107	0.0000	H → L + 10 (.46)	2.144	0.0000	H → L + 10 (.46)
2/3	2.589	0.0122	H-2 → L + 10 (.09) H → L (.36) H-1 → L + 10 (.09) H → L + 1 (.36)	2.430	0.0120	H-2 → L + 10 (.10) H → L (.33) H-1 → L + 10 (.10) H → L + 1 (.33)	2.469	0.0100	H-2 → L + 10 (.13) H → L (.21) H-1 → L + 10 (.13) H → L + 1 (.21)

^a Oscillator strength.^b Weight of the orbital transition component in the electronic excitation.**Fig. 1.** Plot of the B3LYP/LANL2-DZ HOMO of $[\text{Fe}(\text{terpyridine})_2]^{2+}$.

expansion of the basis to Ahlrichs-pVDZ. Further expansion to the non-relativistic cc-pVTZ basis for Fe and to the cc-pVDZ basis set slightly increases the transition energy. However, the character of the transition is consistent between the different DFT calculations.

As DFT is known to present problems with the prediction of excitations possessing significant charge-transfer character, we attempted to justify the use of the B3LYP approach for this particular case by performing CC2 [8] calculations. Unfortunately, we were only able to perform the CC2 calculation with the smallest basis set used in our DFT study (LANL2-DZ) [9]. The RHF orbitals differ significantly from the B3LYP orbitals. Unlike the situation in our DFT study, the RHF//LANL2-DZ HOMO possesses tpy based character while the metal-based levels are found at lower energy, Table S8 and Fig. S4. On the other hand, the RHF/LANL2-DZ low-lying empty orbitals are ligand-based, identical to the results of our DFT study.

At the CC2 level, the first (doubly degenerate) excitation with non-zero oscillator strength is predicted at 2.39 eV and is assigned to excitation from the HOMO-15/HOMO-5 to the ligand-based LUMO+1 (Table 2). The energy of this excitation is significantly lower than that obtained by TDDFT using the same basis set (2.59 eV, Table 1). The nature of this transition is determined using a Mulliken population analysis [10] of the orbitals involved: the HOMO-15 and HOMO-5 consist of 71% and 17% of Fe d-orbitals, respectively, Table S8. Thus, at this level of theory, the first excited state also possesses considerable metal-to-ligand charge-transfer character, thereby confirming the results obtained using the B3LYP method, demonstrating that DFT methodology is applicable for the current system. For a more accurate comparison between the predictions made by the CC2 method and the TDDFT method, the use of larger basis sets is required.

In summary, in contrast to the previous assignment [1], the first excited state of $[\text{Fe}(\text{terpyridine})_2]^{2+}$ can be described as a metal-to-ligand charge-transfer excitation, thus fitting in the series of the Ru and Os complexes.

Table 2The first six excited states of $[\text{Fe}(\text{terpyridine})_2]^{2+}$, calculated at the CC2/LANL2-DZ level of theory

#	<i>E</i> (eV)	<i>f</i> ^a	Character (<i>c</i> ^{2 b})
1	1.946	0.000	H-15 → L + 47 (.24) H-15 → L + 39 (.18) H-5 → L + 47 (.11) H-5 → L + 39 (.8)
2	2.212	0.000	H-13 → L (.11) H-12 → L + 1 (.11) H-17 → L (.9) H-16 → L + 1 (.9)
3/4	2.388	0.022	H-15 → L + 1 (.38) H-5 → L + 1 (.22)
5/6	2.525	0.022	H-15 → L + 1 (.31) H-5 → L + 1 (.18)

^a Oscillator strength.^b Weight of the orbital transition component in the electronic excitation.

Acknowledgements

This work is part of the research programme of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). We acknowledge the National Research School Combination-Catalysis (NRSC-C) and the project FULLSPECTRUM within the Sixth Framework Program under number SES6-CT-2003-502620. We acknowledge NWO/NCF for supercomputer time on ASTER, SARA (The Netherlands, Project Number SG-032).

Appendix A. Supplementary material

Optimised geometry of $[\text{Fe}(\text{terpyridine})_2]^{2+}$, orbital energies, Mulliken population on Fe, plots of frontier orbitals and complete listing of electronic transitions from TD-DFT. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.06.033.

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