

A letter outlining the changes with respect to the referees' comments

Reviewer #1 We would like to show our heartfelt thanks to the reviewer for his kind and helpful comments.

The manuscript "DFT/TDDFT study on spectroscopic properties of zinc(II), nickel(II), and palladium(II) metal complexes with thiourea derivative" is a routine paper, but done with appropriate methodology and results are presented nicely. I would suggest acceptance of the paper after some minor comments:

Comment 1: The author should refer (cite) the works done before on similar systems and same methodology.

Answer: According to the referee's helpful suggestion, we have cited the relevant works in the corresponding position. The sentences are presented on line 6 of page 4: So M06 method is confirmed to perform the following studies, which is reported to be one of the most successful functionals for the metal complexes and has been extensively used in organometallic systems.¹⁸⁻²¹

18. X. H. Yu, N. Wang, H. Q. He, L. Wang, *Spectrochim. Acta A* **122** (2014) 283

19. S. D. Yeole, S. R. Gadre, *J. Chem. Phys.* **132** (2010) 094102-1

20. P. Manna, S. K. Seth, A. Das, J. Hemming, R. Prendergast, M. Helliwell, S. R. Choudhury, A. Frontera, S. Mukhopadhyay, *Inorg. Chem.* **51** (2012) 3557

21. P. Kar, R. Biswas, M. G. B. Drew, A. Frontera, A. Ghosh, *Inorg. Chem.* **51** (2012) 1837

Comment 2: Fig 1. in manuscript should be replaced with Fig S1. There is no point to have Schematic structures of complexes when they have optimized structures. Furthermore, I would suggest authors to put optimized coordinates in Supp. Info.

Answer: We would like to thank the referee for his kind and helpful suggestion. In the revised manuscript, the Fig. 1 has been revised. And the corresponding Cartesian coordination of the ground state structures for complexes $\text{Zn}(\text{C}_{10}\text{H}_{12}\text{N}_3\text{OS})_2$ (**1**), $\text{Ni}(\text{C}_{10}\text{H}_{12}\text{N}_3\text{OS})_2$ (**2**), and $\text{Pd}(\text{C}_{10}\text{H}_{12}\text{N}_3\text{OS})_2$ (**3**) are listed in Table SII.

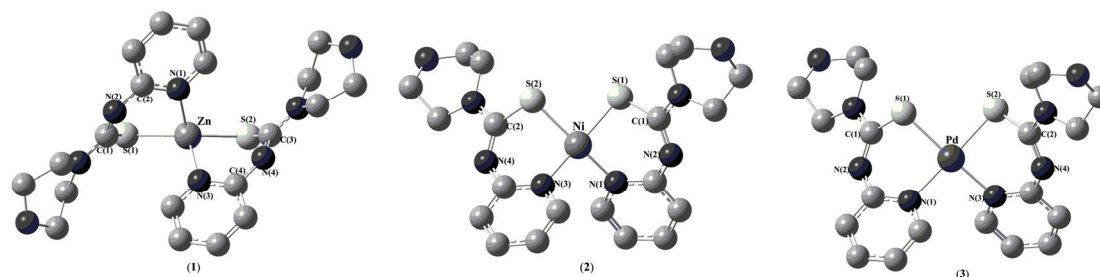


Fig. 1 The optimized ground-state structures for complexes $\text{Zn}(\text{C}_{10}\text{H}_{12}\text{N}_3\text{OS})_2$ (**1**), $\text{Ni}(\text{C}_{10}\text{H}_{12}\text{N}_3\text{OS})_2$ (**2**), and $\text{Pd}(\text{C}_{10}\text{H}_{12}\text{N}_3\text{OS})_2$ (**3**). The hydrogen atoms are omitted for clarity.

Comment 3: Does the authors consider maybe SAOP results for TDDFT, since it is known to give accurate values?

Answer: According to the referee's helpful suggestion, we have investigated the

absorption features simulated at TDDFT/SAOP level. However, the SAOP results do not give accurate evaluation well. The relevant discussions are presented on line 8 of page 3:

To verify the reliability of TDDFT/M06 method, the absorption spectrum of complex **2** is also evaluated by the statistical averaging of (model) orbital potentials (SAOP)^{14,15} in combination with the double- ζ plus polarization (DZP) basis set implemented in the program package ADF.^{16,17} As shown in Fig. S1 of Supporting Information, the absorption features simulated at TDDFT/SAOP level present the inconsistency with the experimental values.⁶ There is no absorption peak in the range of 230-240 nm. In contrast, one moderate absorption bank (239 nm) is reported in experiment. Therefore, TDDFT/M06 functional is more reliable for this system and becomes the final choice to calculate vertical excitation energies.

Comment 4: Conclusion not really gives detail insight and explanation of already studied complexes. I would strongly suggest to the authors to improve it.

Answer: We would like to thank the referee for his kind and helpful suggestion. We have improved the conclusion in the revised manuscript. The sentences are presented on line 1 of page 11:

CONCLUSION

Density functional theory and time-dependent density functional theory were used to investigate the ground-state geometries, electronic structures, and absorption spectra of three thiourea metal complexes **1-3**. Either the geometrical and electronic structures or the absorption properties, complexes **2** and **3** are more similar to each other relative to complex **1**. When the metal center changes from Zn to Ni/Pd, the absorption spectrum presents different features. The number of the absorption peaks increases and the strongest one is blue-shifted. Furthermore, the solvents with different polarities have slight influence on the position and intensity of the absorption peak. However, the absorption spectrum in gas phase shows some distinct diversity.

Reviewer #2 We would like to show our heartfelt thanks to the reviewer for his kind and helpful comments.

The manuscript by Wang et al deals with analysis of optimized structures and electronic spectra of three thiourea derivative metal complexes using density functional theory and its time dependent variant. The paper contains interesting results and I suggest major revision before it is accepted.

Comment 1: page 2: Sentence concerning basis sets used for metal atoms should be corrected (I assume pseudo potentials are used for core electrons, and LANL2DZ basis set for valence electrons).

Answer: According to the referee's helpful suggestion, the sentences are presented on line 2 from the bottom of page 2:

The 6-31+G(d) basis set was employed for non-metal atoms. The "double- ζ " quality basis set LANL2DZ associated with quasi-relativistic pseudo-potentials proposed by Hay and Wadt^{11,12} were served for the metal atoms, in which the LANL2DZ basis set was adopted for valence electrons and the pseudo potentials were used for core electrons.

Comment 2: page 6, lines 123, 124 and 129: Statements "the composition of C atoms and Mor groups can be negligible for all selected FMOs", "the LUMOs mainly distribute over the π^* orbital of Py group; (3) the N atoms" and "the composition of S atom in FMOs of complexes 2 and 3 is higher than that of 129 complex 1" should be reformulated.

Answer: According to the referee's helpful suggestion, we have refined the relevant statements as follows:

1. On line 7 of page 7:

The similar points are: (1) the contribution of C atoms (C(1), C(2), and C(3)) can be negligible for all selected FMOs; (2) the electron density distributions of L+1 and L+2 are mainly distributed over the π^* orbital of Py groups (Py(A) and Py(B)); (3) the Mor groups (Mor(A) and Mor(B)) and N atoms (N(2) and N(4)) have little contribution to the LUMOs.

2. On line 15 of page 7:

The other one is that the electrons extended over the S atoms (S(1) and S(2)) in FMOs of complexes 2 and 3 is more than that of complex 1.

Comment 3: pages 7-8: I do not think it is necessary to present both wavelengths and wavenumbers associated with certain transitions. Additionally, it is common to present assignments in terms of orbital types (for example $\pi \rightarrow \pi^*$) instead of corresponding atoms (for example N(2) $\rightarrow$ Py(A)).

Answer: We would like to thank the referee for his kind and helpful suggestion. In the revised manuscript, the wavenumbers associated with certain transitions have been deleted. And we have present assignments in terms of orbital types in the corresponding positions.

Comment 4: page 9: Could the authors elaborate the statement "It is one of distinguishable advantages for theoretical study to separate peaks that is hard to be completed by experimental measurement. The calculated ""?

Answer: According to the referee's helpful suggestion, we have elaborated the relevant statements as follows:

On line 2 from the bottom of page 9:

It is one of the distinguishable advantages for theoretical study to separate peaks that is hard to be completed by experimental measurement. For example, complex **2** presents seven absorption peaks in the theoretically simulated wavelength range. However, two moderate absorption bands located at 281 nm and 251 nm are not observed in the experiment.⁶

Comment 5: page 9: Assignment $p \rightarrow \pi^*$ sounds strange. Is it $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$?

Answer: According to the referee's helpful suggestion, we have revised the term of $p \rightarrow \pi^*$.

Comment 6: Since the focus of the paper are UV/VIS spectra of the three complexes, the results section and the discussion section should be extended. The authors might, for example, compare PCM results with gas phase calculations, as well as calculations in other selected solvents, and address influence of the solvent on peak position and intensity.

Answer: We would like to thank the referee for his kind and helpful suggestion. In the revised manuscript, the influence of different solvents on the absorption spectral properties is evaluated. The relevant discussions are presented on line 4 of page 10:

Additionally, the absorption spectra for complex **2** in gas phase and in solvents (tetrahydrofuran (THF, $\epsilon=7.426$), dichloroethane (DCE, $\epsilon=10.125$), and dimethylformamide (DMF, $\epsilon=37.219$)) with different polarities are investigated at the same level to explore the solvent effect on the absorption features. It is clear from Fig. 4 that absorption bands do not show significant solvent sensitive to the variation of polarity. Although the intensities of the absorption peaks are strengthened with increasing solvent polarity, the positions in different solvents remain almost constant. However, the absorption curve simulated in gas phase presents distinct differences. The number of the absorption peaks is reduced and their oscillator strengths are decreased obviously. Besides, their wavelengths show slight red-shift as compared with the absorption spectra in different solvents.

Comment 7: I am not a native speaker myself, but I have noticed numerous grammar mistakes and strange sentence constructions which should be corrected.

Answer: We would like to thank the referee for his kind and helpful suggestion. The manuscript is carefully revised.

Comment 8: Also, references concerning theoretical analysis of similar systems are missing.

Answer: According to the referee's helpful suggestion, we have cited the relevant

works in the corresponding positions. The sentences are presented on line 6 of page 4: So M06 method is confirmed to perform the following studies, which is reported to be one of the most successful functionals for the metal complexes and has been extensively used in organometallic systems.¹⁸⁻²¹

18. X. H. Yu, N. Wang, H. Q. He, L. Wang, *Spectrochim. Acta A* **122** (2014) 283
19. S. D. Yeole, S. R. Gadre, *J. Chem. Phys.* **132** (2010) 094102-1
20. P. Manna, S. K. Seth, A. Das, J. Hemming, R. Prendergast, M. Helliwell, S. R. Choudhury, A. Frontera, S. Mukhopadhyay, *Inorg. Chem.* **51** (2012) 3557
21. P. Kar, R. Biswas, M. G. B. Drew, A. Frontera, A. Ghosh, *Inorg. Chem.* **51** (2012) 1837