

Theoretical study of structural, electronic and vibrational properties of a Ni-salen complex

Alireza Akbari

Department of Chemistry, Payame Noor University (PNU), 19395-4697, Tehran, Iran

E-mail: a_akbari@pnu.ac.ir

Manuscript received online 09 April 2019, accepted 07 May 2019

Density functional theory (DFT) calculations using ADF 2009.01 package was performed for a nickel(II) complex (NiL, H₂L = N,N'-ethylenebis(4-hydroxysalicylideneimine)) and compared with the results of complex characterization (UV-Vis and FTIR techniques). Electronic spectrum of the Ni(II) complex is dominated by charge transfer and intraligand bands at $\lambda < 436$ nm. DFT calculations showed that the HOMO with -4.824 eV energy is metal-dominated, with the $H \rightarrow L_{+1}$ (85%) transfer. The magnitude of bond lengths and angles predicted by DFT calculations are comparable to those determined by X-ray crystallography for similar complex which has the same as bonds as mentioned Ni(II) complex.

The good agreement between experimental and theoretical vibration data allowed the assignment of relevant IR bands to molecular vibration modes.

Ultraviolet-Visible (UV-Vis) spectrum of the mentioned molecule in the gas phase and ground state was evaluated using DFT with the standard PW91 method and compared with experimental.

Keywords: Vibration, electronic, DFT, calculation, PW91, salen, ADF.

Introduction

Density functional theory (DFT) has been proved to be extremely useful in treating the electronic structures of molecules containing transitional metals¹. In the past decade, by increasing development of computational chemistry, electronic structure calculations using DFT have been used extensively to calculate a wide variety of molecular properties such as equilibrium structure, charge distribution, UV-Visible, FTIR and NMR spectra, electronic circular dichroism, and provided reliable results which are in accordance with experimental data².

Computational methods

The calculations were performed in Amsterdam Density Functional (ADF)-molecule package (version 2009-01)³, based on Kohn-Sham density functional approach. Exchange correlation of Generalized Gradient Approximation (GGA) was adopted as a PW91 functional⁴ for computing geometries and vibrational frequencies in gas phase with basis sets as DZ, DZP and TZP⁵. Calculations of electronic spectra at the fully optimized geometries of the ligand and its Ni(II) complex were performed at the PW91 level, for which the used basis set was DZP. The scale factor, 0.72, was used for correction of the calculated singlet-singlet excitations⁶.

Results and discussion

The gas phase optimized structures of mentioned Ni(II) complex with labeling of the atoms is shown in Fig. 1. The tetradentate dianionic Schiff base ligand framework, with N, N, O⁻, O⁻ binding mode, which comes from deprotonation of

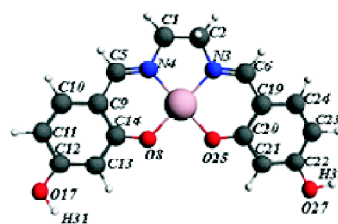


Fig. 1. Optimized structure of NiL at the PW91/DZP level of theory.

H₂L ligand, is bonded to nickel and used for calculation. Results showed that C₅-N₄ (1.324 Å) and C₆-N₃ (1.295 Å) bond lengths are of the approximate value for a C=N, whereas the N₄-C₁ (1.446 Å) and C₂-N₃ (1.448 Å) are a bit shorter than a C-N single bond. The calculated C₁₄-O₈ and C₂₀-O₂₅ bond distances are 1.282 and 1.341 Å, respectively, which are somewhat between the length of a C-O single bond (1.43 Å) and that of a C=O double bond (1.20 Å). These values suggest that electron density may be delocalized throughout the

$N_3-C_6-C_{19}$ fragment, the aromatic ring and the $C_{20}-O_{25}$ bond in the right side of the ligand molecule, i.e. the appearance of the π -electron resonance in this region. Also, in the left side of this molecule π -electrons are delocalized throughout the $N_4-C_5-C_9$ fragment, the aromatic ring and the $C_{14}-O_8$ bond. The hydrogen of hydroxyl in ligand, (O_8-H_{30}), with 1.642 Å bond length is close to N_4 for intermolecular hydrogen bond interaction. This value is larger than $O_{17}-H_{31}$, $O_{27}-H_{32}$ and even $O_{25}-H_{29}$ bond lengths, which are 0.974, 0.973 Å and 1.019 respectively. So, there is just one intermolecular hydrogen bond interaction in whole of ligand. The calculated $N_4 \cdots H_{30}$ distance is 1.069 Å, which confirm existing of the hydrogen bond, whereas $N_3 \cdots H_{29}$ bond is 1.541 Å. This later longer distance is not in favor of the formation of an intermolecular hydrogen bond of the type $O_{25}-H_{29} \cdots N_3$. The engagement in intermolecular hydrogen bond interactions causes the longer O_8-H_{30} bond than $O_{25}-H_{29}$, $O_{17}-H_{31}$ and $O_{27}-H_{32}$. Therefore, the electron density in the O_8-H_{30} bond is lower than in $O_{25}-H_{29}$, $O_{17}-H_{31}$ and $O_{27}-H_{32}$ bonds and the acidic nature of the H_{30} proton of the O_8-H_{30} bond is higher than for $O_{25}-H_{29}$, $O_{17}-H_{31}$ and $O_{27}-H_{32}$. Hence, the O_8 atom has a higher ability for coordination to the metal ion than O_{25} , O_{17} and O_{27} atoms in the first step of complexation. In the coordination region, deprotonating of the hydroxyl group, ($O_{25}-H_{29}$), causes a decrease in the $C_{20}-O_{25}$ bond length from 1.367 Å in ligand to 1.299 Å in complex, while coordination of the N_3 atom to the Ni(II) ion, leads to a bit elongation of the C_6-N_3 bond from 1.311 Å to 1.320 Å. Due to the existing $O_8-H_{30} \cdots N_4$ hydrogen bond, the C_5-N_4 bond length decreases after complex-formation from 1.339 Å to 1.321 Å while the $C_{14}-O_8$ bond length increases from 1.308 Å to 1.298 Å. The average calculated bond length for Ni- O_8 , Ni- O_{25} , Ni- N_4 and Ni- N_3 is 1.892 Å, 1.90 Å, 1.874 Å and 1.872 Å respectively. Related experimental bond lengths in similar complex⁷ are 1.848 Å, 1.853 Å, 1.844 Å and 1.844 Å which confirm the calculations. The average calculated angles around central metal in three mentioned basis sets 177.5° and 176.6° for N_4-Ni-O_{25} angles are close to 176.2° and 177.3° in experimental. The other angles in coordination sphere are also near to the values come from X-ray crystallographic⁷ and confirm my calculations. Comparing bond lengths of Ni(II) complex at PW91/DZP and TZP method leads to geometrical parameters which are much closer to experimental values than DZ method results. The small difference between the computed

values is due to the reason that calculation belongs to gaseous phase and experimental result belongs to solid phase. The equations of graphic correlation between some experimental⁷ and calculated bond angles of Ni(II) complex which are obtained by PW91/DZ, DZP and TZP methods are in following. As a result, the performance of the PW91 method with three mentioned basis sets for prediction of the bond angles is acceptable. The relations between the calculated and experimental bond angles of Ni(II) complex are usually linear and described by the following:

$$\text{DZ: bond angles}_{\text{Cal}}(^{\circ}) = 0.99864 \text{ bond angles}_{\text{Exp}}(^{\circ}) + 0.19533$$

$$\text{DZP: bond angles}_{\text{Cal}}(^{\circ}) = 1.0049 \text{ bond angles}_{\text{Exp}}(^{\circ}) - 0.41716$$

$$\text{TZP: bond angles}_{\text{Cal}}(^{\circ}) = 1.002 \text{ bond angles}_{\text{Exp}}(^{\circ}) - 0.15494$$

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbital take part in chemical stability. The HOMO and LUMO represent the ability of donating and accepting of electron respectively. Their energies which calculated by PW91/DZP method are described here, as an example. The electronic transition absorption corresponds to the transition from the ground state to the first excited state is mainly described by an electron excitation from HOMO to the LUMO. The atomic compositions of the frontier molecular orbital are shown in Fig. 2.

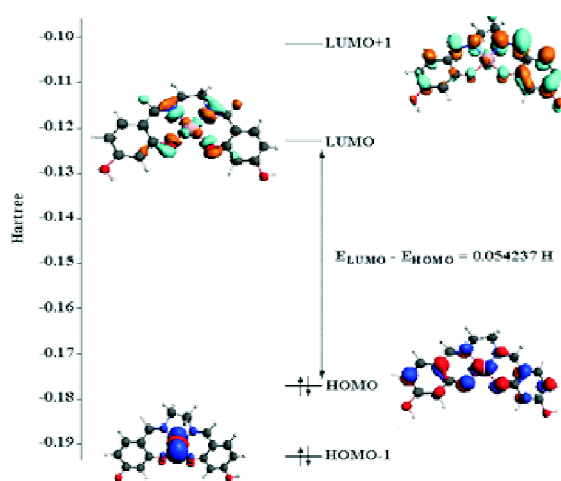


Fig. 2. The atomic orbital compositions of the frontier molecular orbitals for NiL.

As one can see in Fig. 2, the HOMO and specially LUMO are somehow delocalized on the Ni center. My calculation showed that the $d_{x^2-y^2}$, d_{xz} and d_{xy} orbitals of Ni have 45.71% contribution in HOMO while total contribution of Ni orbitals (contain d_{yz} , d_{xz} and d_{xy}) is 54.34% in LUMO. The most contribution in LUMO is for d_{xy} orbital (50.24%) of Ni. The energy of frontier orbitals (HOMO, -4.333 eV, and LUMO, -2.846 eV), the band gap of energy ($E_{\text{HOMO}}-E_{\text{LUMO}}$, -1.487 eV), electronegativity (χ , 3.59), chemical potential (μ , -3.59), global hardness (η , 0.74), global softness (S , 0.67), and global electrophilicity index (ω , 0.71) for Ni(II) complex are calculated using PW91/TZP method as reported in literature⁸. Both the UV-Vis spectra of the free ligand and its Ni(II) complex are recorded in DMSO and comparing with those of calculated. As I reported before⁹, the spectrum of the ligand exhibits three absorption bands at 280, 308 ($\pi-\pi^*$ transition) and 376 nm ($n-\pi^*$ transition) within the Schiff base. Normally, the electronic spectra of the Schiff base ligands in solution consist of a relatively intense band in the 250–390 nm regions, involving $\pi-\pi^*$ and/or $n-\pi^*$ transitions¹⁰. These bands for the mentioned ligand reported as 243, 280, 305, 374 in EtOH for example⁹. The electronic spectrum of the complex showed bands in 303, 396, 436 and 522 nm. The 303 and 396 nm bands are predominantly due to intra ligand charge transfer ($\pi \rightarrow \pi^*$)^{10c}, and 436 nm, which is due to a metal to ligand charge transfer (MLCT). The $d-d$ transition band is observed at 522 nm as weak and broad band. DFT calculations at the PW91/DZP level have been carried out for greater understanding of the transitions happening in NiL complex. Four (of 10 Excitation) selected calculated strong absorptions are $H \rightarrow L$ (95%), $H \rightarrow L+1$ (88%), $H \rightarrow L+2$ (94%) and $H-2 \rightarrow L$ (76%). The DZP basis set results are more near to experimental than the DZ and TZP basis sets. The wavelengths for mentioned excitations calculated as 507, 419, 404 and 308 nm (using 0.72 scaling factor) which are close to experimental (507, 412, 396 and 303 nm) respectively. The assignment of the calculated results to the experimental was based on a general survey of the outline plots and relative energy of the HOMO and LUMO. Calculations showed that the lowest energy absorption of Ni(II) complex is in HOMO to LUMO transition at 507 nm, where HOMO

and LUMO are mainly made of d_{xz} and d_{xy} orbital respectively, and therefore, can be assigned as the metal to metal charge transfer (MMCT). Other absorptions at 412, 396, and 303 nm are referred to the MLCT, LLCT/MLCT and LLCT/MLCT, respectively. The equations of linear correlation diagrams between the experimental and calculated results are as following.

$$\text{DZ: } \lambda_{\text{Calc}} (\text{nm}) = 0.9884 \lambda_{\text{Exp}} (\text{nm}) + 35.598, R = 0.9884$$

$$\text{DZP: } \lambda_{\text{Calc}} (\text{nm}) = 0.9992 \lambda_{\text{Exp}} (\text{nm}) + 0.309, R = 0.9999$$

$$\text{TZP: } \lambda_{\text{Calc}} (\text{nm}) = 0.9652 \lambda_{\text{Exp}} (\text{nm}) + 18.565, R = 0.9991$$

The free Schiff base ligand show a very strong absorption in the 1641 cm^{-1} in its IR spectrum which is characteristic of the azomethine $\nu(\text{C}=\text{N})$ group^{5b}. This absorption shifted to lower wave number (1620 cm^{-1}) indicating the coordination of the Schiff base through the nitrogen atom¹¹. My average calculation for the later has been 1591 cm^{-1} that needs to scale factor for matching with experimental⁶. Vibration of the new Ni-N bond in 424 cm^{-1} is the other evidence which support mentioned coordination. The vibration of phenol hydroxyl substituent $\nu(\text{C}-\text{O})$ in 1365 cm^{-1} is shifted to 1331 cm^{-1} upon complexation, suggesting the coordination via hydroxyl oxygen atom. There is other evidence, $\nu(\text{Ni}-\text{O})$ at 495 cm^{-1} , which confirm this binding. The mean frequencies of Ni-N and Ni-O bonds calculated as 474 and 595 cm^{-1} respectively, and need to 0.83–0.9 coefficient as scaling factor, similar to reported⁶.

Acknowledgements

This work has been supported by the University of Payame Noor (Iran). I would like to thank the Mashhad branch of Payame Noor University and all of my research group members, for any support of this research.

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