



## Case study presenting the use of quantum-mechanical "zone criterion" as a clue in assigning the electronic transitions exhibited by a complex compound

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### Abstract:

As quantum-mechanical criteria are extremely useful in investigating the molecular structure of a newly synthesized chemical compound (in particular, in assigning its electronic transitions), this paper aims to present the results obtained by using "zone criterion" as a clue in interpreting the UV-Vis spectrum of a complex compound that we dealt with, which was formed by the coordination to Ni(II) of a 1,4-naphthalenedione derivate (namely, 2-mercapto-3-niacinamido-1,4-naphthalenedione). So, by taking into account the fact that an electronic transition extremely unlikely occurs between two quantum-mechanical states involving spatially separated parts of a certain molecule (which we simply called "zone criterion"), we used a specialized software package in order to perform a molecular modeling that was able to lead us (through specific semi-empirical calculation) to the assignment of all the recorded electronic transitions. The results thus obtained proved themselves to be in a very good accordance with the classical interpretation of the UV-Vis spectrum (which we already had reported), showing, once again, that quantum-mechanical analysis can serve as an useful clue and represents a powerful tool in characterizing the structure of a new complex compound.

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**Keywords:** complex compounds, electronic transitions, quantum-mechanical study

## 1. INTRODUCTION

Various 1,4-naphthalenedione-based compounds have lately been synthesized and investigated [1-6], mostly due to their frequently proved antibacterial properties, which seem to get enhanced by coordination. Within this context, we aimed to obtain and characterize some complex compounds of this class. One of our newly published papers refer to the complex formed by the coordination to divalent nickel of the bidentate ligand 2-mercapto-3-niacinamido-1,4-naphthalenedione, for which we have reported results regarding the synthesis and the characterization – obviously including the interpretation of its UV-Vis spectrum [7] – and, later, also some results referring to its antibacterial activity [8]. However, afterwards, in addition, a quantum-mechanical study was performed, in order to verify, by semi-empirical calculation, the assignment of all the electronic transitions. The results of it will be presented in what follows.

## 2. MATERIALS AND METHODS

### *2.1. Synthesis of the ligand and complex; elemental and physico-chemical analysis*

All details have already been reported, as well as the structures [7].

### *2.2. Software and computational tools*

Within the specialized software package that we have used are included: ChemBio3D Ultra 12.0; HyperChem Professional 8.0; MOPAC.

The molecular modeling has been performed, then a semi-empirical Extended Hückel calculation has been carried out, so as to obtain, for the molecular orbitals (MOs), not only their energy and occupancy, but also the mixing coefficients showing the contribution of all atomic orbitals [9] (AOs) to each of them, in order to identify the spatial part of the molecule in which each MO is localised. Lastly, we have done assignments of the UV-Vis transitions, based on the "zone criterion", stating that an electronic transition extremely unlikely occurs between two quantum-mechanical states involving spatially separated parts of a molecule [9]. Based on the comparison between the two sets of data (for the ligand and for the complex), we were able to decide which atoms are involved in chelation.

### 3. RESULTS AND DISCUSSION

#### 3.1. Atoms involved in the coordination process

As only few of the MOs are important to the quantum-chemical study, namely the occupied molecular orbitals (OMOs) close to the highest occupied molecular orbital (HOMO) and also the unoccupied molecular orbitals (UMOs) close to the lowest unoccupied molecular orbital (LUMO), all assignments of the transitions exhibited in the UV-Vis range have to be made within them (for both the free organic ligand and its complex [9]).

The chemical formula of the ligand being  $C_{16}H_{10}N_2O_3S$ , it plainly has 98 MOs, out of which 54 are OMOs; the chemical formula of the complex being  $C_{32}H_{18}N_4NiO_6S_2$ , it clearly has 203 MOs, out of which 111 are OMOs.

Thus, denoting the MOs by  $\Psi$  for the ligand and  $\Psi'$  for the complex and starting the numbering from the lowest energy MOs, the HOMOs are  $\Psi_{54}$  and  $\Psi'_{111}$ , whereas the LUMOs are  $\Psi_{55}$  and  $\Psi'_{112}$ . By analyzing all the energies of the main OMOs and UMOs, but also the zones where they are almost localized, we saw that  $\Psi_{51}$  and  $\Psi_{52}$  can be found again nearly identical after the complexation, doubled as  $(\Psi'_{104/105}; \Psi'_{106/107})$  respectively, as  $\Psi_{56}$  and  $\Psi_{57}$  are re-found nearly identical, doubled as  $(\Psi'_{115/116}; \Psi'_{117/118})$ , indicating that the oxygen atoms, on which they are practically localized in 1,4-naphthalenedione, are not involved in the complexation. Following a similar way [9], we found that chelation is made by nitrogen and sulfur.

Tables 1 and 2 gather the main results for the ligand and its complex.

Table 1. Wavelengths ( $\lambda$ ) of the electronic transitions, assignment and type

$\lambda_{exp.}$ (nm)	Assignment	$\lambda_{calcd.}$ (nm)	Atoms involved
460	$\Psi_{54} \rightarrow \Psi_{58}$	466	S-S
435	$\Psi_{53} \rightarrow \Psi_{55}$	437	N-N
306	$\Psi_{52} \rightarrow \Psi_{57}$	306	O-O
	$\Psi_{51} \rightarrow \Psi_{56}$		

Table 2. Wavelengths ( $\lambda$ ) of the electronic transitions, assignment and type

$\lambda_{exp.}$ (nm)	Assignment	$\lambda_{calcd.}$ (nm)	Transition type / atoms involved
742	$\Psi'_{111} \rightarrow \Psi'_{112}$	754	<i>d-d (weakly allowed)</i>
488	$\Psi'_{111} \rightarrow \Psi'_{113/114}$	493	CT (M-L): M-S <sub>L</sub> , M-S <sub>L'</sub>
343	$\Psi'_{102/103} \rightarrow \Psi'_{112}$	337	CT (L-M): S <sub>L</sub> -M, S <sub>L'</sub> -M
306	$\Psi'_{106/107} \rightarrow \Psi'_{117/118}$	305	L-L: O <sub>L</sub> -O <sub>L</sub> ; O <sub>L'</sub> -O <sub>L'</sub>
	$\Psi'_{104/105} \rightarrow \Psi'_{115/116}$		
269	$\Psi'_{100/101} \rightarrow \Psi'_{112}$	271	CT (L-M): N <sub>L</sub> -M, N <sub>L'</sub> -M

### 3.2 Stereoisomerism of the complex compound

The *d-d* transition is a weakly allowed one, meaning that it would be parity-forbidden by Laporte's selection rule for the centrosymmetric molecules, but, knowing that vibration can destroy the inversion centrum and subsequently the „gerade/ungerade“ classification applies no more, this transition becomes vibronically allowed; nevertheless, its quite poor absorbency leads us to the statement that this complex is a *trans* isomer.

## 4. CONCLUSION

After assigning all the transitions in the UV-Vis spectra of both the ligand and its complex compound with divalent nickel, we have found correspondences between these sets of assignments and, lastly, we have interpreted the findings, perceiving which atoms are involved into the process of coordination and which ones, on the contrary, play no part in it.

Hence, we have concluded that the ligand, namely 2-mercapto-3-niacinamido-1,4-naphthalenedione, loses the hydrogen from the mercapto group through chelation process, in order to involve the sulfur atom into coordination and also that the other atom through which it coordinates to divalent nickel is the nitrogen from the amidic part of niacinamido group, so as to form a *trans* isomer of the investigated complex compound, thus confirming our former published assumptions related to its structure.

## REFERENCES

- [1] N. S. Mone, S. Harihar, S. Salunke-Gawali, S. Satpute, A. Patil, V. Mokashi, M. Jadhav and R. J. Butcher, *Inorg. Chim. Acta*, 546 (2023) 121290.
- [2] G. Navarro-Tovar, S. Vega-Rodríguez, E. Leyva, S. Loredó-Carrillo, D. de Loera and L. I. López-López, *Pharmaceuticals (Basel)*, 16/4 (2023) 496.
- [3] Z. Liu, Z. Shen, S. Xiang, Y. Sun, J. Cui and J. Jia, *Front. Environ. Sci. Eng.*, 17/3 (2023) 31.
- [4] M. B. Alshammari, A. A. Aly, S. Bräse, M. Nieger, M. A. A. Ibrahim and L. E. Abd El-Haleem, *ACS Omega*, 7/38 (2022) 34463.
- [5] D. Aminin and S. Polonik, *Chem. Pharm. Bull.*, 68/1 (2020) 46.
- [6] F. Hassan, M. Fayed and N. Abdalla, *Open J. Inorg. Non met. Mater.*, 10 (2020) 15.
- [7] L.-S. Sbîrnă and C. S. Moldovan, *An. Univ. Craiova, Ser. Chim.*, XLVII/1 (2021) 59.
- [8] L.-S. Sbîrnă, C. S. Moldovan and F. R. Ciolan, *An. Univ. Craiova, Ser. Chim.*, XLVII/2 (2021) 12.
- [9] L.-S. Sbîrnă and C. S. Moldovan, *An. Univ. Craiova, Ser. Chim.*, XLV/1 (2018) 18.