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Computational Structural Assessment on the Stereochemistry of the Transition Metal Complex Formed by a Naphthalene-1,4-dione Based Ligand with Divalent Nickel

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Abstract: *The purpose of this paper is elucidating the stereochemistry of a complex obtained by coordinating to divalent nickel a naphthalene-1,4-dione based chemical compound, namely N-(3-mercapto-naphthalene-1,4-dione-2-yl)nicotinamide. As this particular transition metal ion may lead to different coordination geometries and also tacking into account the fact that the organic ligand contains six heteroatoms, it seem to be worth clarifying denticity of the ligand, the coordination geometry (including stereoisomerism) and, of course, what are the atoms involved into the coordination process. The study has been conducted by computational means, followed by quantum-chemical calculations and comparative interpretation of the UV-Vis spectra of both the ligand and the complex compound, in order to find out in which case the structural assessment is consistent with the electronic transitions exhibited whithin the spectra, i.e. which of the several theoretical coordination posibilities is the actual one. This investigation leads to the conclusion that the organic compound acts as a bidentate ligand and, moreover, the complex compound has a square-planar coordination geometry, the two heteroatoms through which the coordination is realized being the sulfur atom and the nitrogen atom directly bonded to the naphthalene-1,4-dione heterocycle. This is an important achievement, as the properties of the complex compound – including its biologic activity - are obviously related to the coordination manner.*

Keywords*: naphthalene-1,4-dione based ligand, nickel complex, quanto-mechanical study*

1. Introduction

In recent times, various naphthalene-1,4-dione based compounds have been synthesized and thoroughly studied, especially due to their often proved antibacterial potency [1–4].

As this important property of this kind of chemicals seems to enhance by complexation to transitional metal ions, we have lately focused on obtaining and characterizing some coordinative compounds of them.

Consequently, we have newly published the results of a detailed quanto-mechanical study [5] meant to investigate the actual way that such a compound coordinate to divalent nickel and divalent cobalt, mainly by assigning the electronic transitions of both the free ligand and the complex compound and then comparing the assignments in order to draw the conclusion consistent with the UV-Vis spectra.

Moreover, we have also recently reported the results of another comprehensive study involving an analogous ligand [6] that was coordinated to divalent nickel, palladium and platinum ions, but for which the investigation have only been restricted to classical methods of physico-chemical analysis.

This is the reason why we now intend to get back to this ligand, presenting the computational structural study referring to it, which is similar to the first one [5], being also based on quanto-mechanical calculations clarifying the coordination manner of the ligand latter [6] to divalent nickel.

An exhaustive study on the antimicrobial activity exhibited by the ligand and its complex compound with Ni(II) against typical Gram-positive and Gram-negative bacteria was reported elsewhere [17].

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2. Materials and methods

2.1. Reagents

In order to synthesize the organic ligand, we have used the following Sigma-Aldrich reagents: 2,3-dichloronaphthalene-1,4-dione (D67200), nicotinamide (N3376), thiourea (T8656), NaOH pellets (221465), CH_3COOH (W200611) and also ethyl alcohol (493511).

Then, with the aim of synthesizing the complex compound, we have also used Sigma-Aldrich reagents, namely: tetrabutylammonium hydroxide solution, 40 wt. % in H_2O (178780), nickel (II) chloride hexahydrate (654507), diethyl ether (179272) and ethyl alcohol again.

So as to obtain the solutions for the experimental investigation, we have used Sigma-Aldrich DMF (140732) as solvent.

Moreover, for the experimental study we have also needed Sigma-Aldrich tetrabutylammonium perchlorate (86885), potassium bromide (221864) and acetone (179124).

2.2. Synthesis of the ligand

For beginning, N-(3-chloro-naphthalene-1,4-dione-2-yl)nicotinamide has been synthesized, from 5.676 g 2,3-dichloronaphthalene-1,4-dione and 3.053 g nicotinamide.

The solution obtained by dissolving 7.817 g of this product in 3.806 g thiourea whithin ethyl alcohol (80 mL) has been refluxed for three hours and then concentrated to small volume (40 mL), diluted with the same amount of water.

Afterwards, the solution has been alkalized by adding 4 g sodium hydroxide and refluxed for another hour, then warmed in a water bath and acidified with 1N acetic acid (70 mL).

The solid that precipitates is N-(3-mercapto-naphthalene-1,4-dione-2-yl)nicotinamide, which was subsequently purified by dissolving it into a 2N sodium hydroxide solution and finally reprecipitated from a 2N acetic acid solution, with the purpose of using it as ligand (yield: 9.46 g, 82.02%).

2.3. Synthesis of the complex compound

The synthesis of the nickel (II) complex compound has been started by adding 8.515 g of this ligand to 27 mL tetrabutylammonium hydroxide solution (40 wt. % in H_2O).

Then, continuously stirring, this weakly alkaline liquid has been added to a solution that had previously been obtained by dissolving 2.674 g nickel (II) chloride hexahydrate into the minimum necessary volume of ethyl alcohol.

The stable product that has precipitated (yield: 24.75 g, 76.12%) has been left to settle down for an hour, then filtered on a G4 fine porosity glass filter, washed (with ethyl alcohol, as well as with diethyl ether) and finally vacuum dried.

2.4. Instruments used for the elemental and physico-chemical analysis

Elemental analysis has been performed on a Perkin Elmer 2380 (USA) instrument.

The magnetic susceptibility of the coordinative compound has been investigated with a Holmarc Gouy's Method Apparatus, Model HO-ED-EM-08 (India), whereas its electrical conductivity has been measured on a Radelkis OK - 102/1 (Hungary) conductivity meter with a cell constant of 0.9 cm^{-1}, in 10^{-4} M DMF solution, at 23°C.

The polarogram of the complex has been recorded with a Model 7-77-4/b Orion KTS polarograph, measuring the half-wave potentials at room temperature, by means of a calomel reference electrode together with a dropping mercury measuring electrode and a 10^{-1} M solution of tetrabutylammonium perchlorate as supporting electrolyte, the solutions of the complex being 10^{-3} M.

The IR spectra of both the ligand and the complex were recorded by using a Perkin Elmer FT-1600 Hewlett Packard analyzer in anhydous potassium bromide pellets, whereas the UV-Vis spectra were realized on an Ocean Optics (UK) spectrophotometer, in 10^{-3} M acetone solutions.

2.5. Software

The software package that we have used included: Chem3D Ultra 9.0 [7,8], HyperChem 8.0.10 [9,10], MOPAC [11] and ICON-EDiT [12].

2.6. Computational methods

The molecular modeling has been performed by using Chem3D Ultra 9.0.

Then, the structures have been imported from their standard file formats to Hyperchem 8.0.10. However, taking into account the fact that molecular mechanics (MM^+) approach within this computer program (in spite of the fact that it has extensive capabilities) is not suitable for the coordinative compounds, the geometries of both organic ligand and complex with divalent nickel were optimized resorting to the semi-empirical quantum chemistry calculation program named MOPAC, which provided us the Cartesian coordinates for all the atoms of each molecule. Finally, as MOPAC calculation is not perfectly adapted for transitional metal ions, the output data from MOPAC have been used as input data in a semi-empirical Extended Hückel calculation package proposed by Calzaferri [13], namely ICON-EDiT. Therefore, we have obtained, for every molecular orbital (MO), beside its energy and its occupancy, all the mixing coefficients giving the extent in which each atomic orbital (AO) contributes to it and, therefore, a clear information about the main atoms involved, *i.e.* about the exact region of molecule where the MO lies in.

2.7. Quantum-chemical interpretation methods

It is worth stretching out the fact that only few of the molecular orbitals (MOs) are important to such kind of quantum-chemical study, namely the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and a few others close to them. How many of the occupied molecular orbital (OMOs) and, at once, how many of the unoccupied molecular orbitals (UMOs) are truly significant in both these cases was easy to approximate, as we intended to assign the electronical transitions exhibited by two particular chemical substances (the ligand and the complex compound formed by it with divalent nickel).

Having the UV-Vis spectrum already recorded, we had to identify the transition with the highest wavenumber and to take its energy as the maximum energy gap, so there was no need to take into account neither the OMOs separated from LUMO by a larger gap, nor the UMOs separated from HOMO by a larger gap. Further, after restricting the discussion to a small set of important MOs, we did not investigate all the theoretical transitions supposed to occur between every OMO and every UMO from this set, because it is well-known that the assignments have to be made strictly respecting the „zone criteria", *i.e.* keeping in mind that an electronic transition involves two MOs from the same spatial zone.

However, electron-electron, electron-nucleus and electron-electron-nucleus correlation functions could be ignored do to their insignificant contribution to the assignments. This was because the program [12] uses contracted basis sets where each AO is made up of a linear combination of primitive Slater orbitals (STOs) or Gaussian orbitals (GTOs) [14]. The coefficients were those for simple Slater determinants, because this program does not support configuration state functions or other linear combinations of determinants [15].

The last three steps of the study were: concretely assigning all the transitions in the UV-Vis spectra of both the ligand and its studied complex compound formed with divalent nickel, then finding correspondences between the two sets of assignments and, in the end, interpreting the results by observing which heteroatoms are involved into the coordination and which ones, at contrary, play no part in this process.

Consequently, we finally shall be able to decide the actual chemical structure of the investigated complex compound, which is decisive in explaining and even predicting different properties of it, including its biological activity.

3. Results and discussions

3.1. Ligand and complex compound appearance

The ligand appears as a microcrystalline yellowish-orange air-stable powder, being therefore expected to absorb violet and blue radiation, whereas its complex with Ni(II) appears as a microcrystalline orange-red air-stable powder, being thus expected to absorb blue and green (or cyan) radiation.

3.2. Ligand potential denticity

Many chemical structures exhibit conformational mobility due to their various degrees of freedom [16].

The ligand synthesized and used for complexation within this study is a good example in this regard. In order to study its possible conformers with the view of investigating potential denticity, we might neglect the free turnings of the mercapto group around the exocyclic C-S bond.

Of real interest are the free turnings of nicotinamide heterocycle around the exocyclic C-N bond; this can interconvert, on one side, the structures (a) and (c) presented below - belonging to one class of conformers defined from this point of view, and, on the other side, structures (b) and (d) - belonging to another one (of course, there are theoretically an infinity of intermediate structures within each of these classes of conformers).

Regarding in an analogous way, of real interest are also the free turnings of nicotinamide heterocycle around the C-N bond in its amidic part; this can now interconvert the structures (a) and (b) in Figure 1 - belonging to one class of conformers defined from this different point of view, as well as structures (c) and (d) - belonging to another one (of course, again, there are an infinity of intermediate structures within each class - at least theoretically).

Though, we must stretch out that a great part of these conformers are very unlikely because of steric hindrance and electromeric effects.

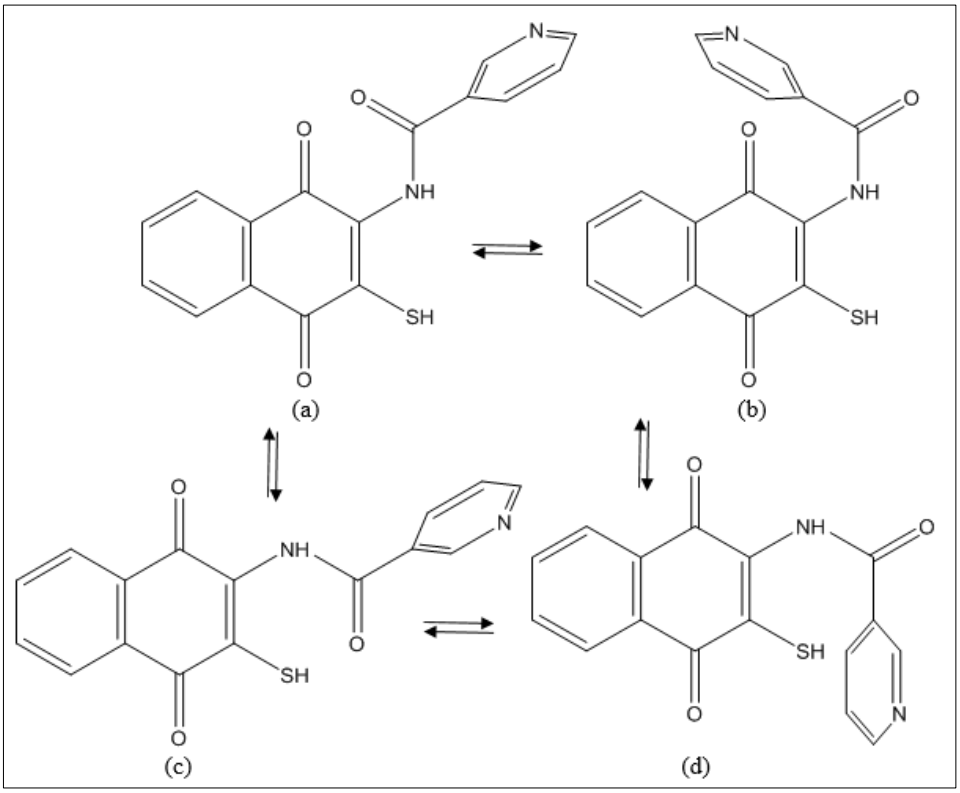

Figure 1. Four of the conformers exhibited by the ligand, N-(3-mercapto-naphthalene-1,4-dione-2-yl)nicotinamide (HL)

As far the denticity is concerned, we can see that there are (again hypothetically speaking) different ways for this heterocyclic molecule to coordinate, acting as bi- or tridentate ligand.

3.3. Results and interpretation of the elemental and physico-chemical analysis

Elemental analysis of the organic substance confirmed its expected molecular formula, hence showing that the ligand synthesis was properly conducted. Anal. Calcd. for $C_{16}H_{10}N_2O_3S$ (M 310.33 g•mol^{-1}): C, 61.93; H, 3.25; N 9.03; S 10.33. Found: C, 62.12; H, 3.42; N 8.88; S 10.20.

Elemental analysis for the complex compound leaded to the molecular formula $C_{32}H_{18}N_4NiO_6S_2$ when written in the Hill system, which might be rewritten as $[Ni(C_{16}H_9N_2O_3S)_2]$, meaning that the organic molecule appears twice within its structure and showing that each of the two identical ligands coordinated to Ni(II) has lost a hydrogen atom during the coordination process, suggesting us to denote the ligand not by L, but by HL, in order to briefly write the formula of the complex as $[NiL_2]$. Anal. Calcd. for $C_{32}H_{18}N_4NiO_6S_2$ (M 677.33 g•mol^{-1}): C, 56.74; H, 2.68; N 8.27; Ni, 8.67; S 9.47. Found: C, 56.89; H, 2.84; N 8.07; Ni, 9.02; S 9.22.

At this point of discussion, we saw that the organic compound either acts as a bidentate ligand (thus the complex being tetracoordinate) or it acts as a tridentate ligand (the complex being hexacoordinate).

Magnetic susceptibility, $[NiL_2]$ (BM): 0. The diamagnetic behavior of the complex showed that there are no unpaired electrons within its electronical structure in the ground state.

Molar electrical conductivity, $[NiL_2]$ (W^{-1}•cm^2•mol^{-1}): 2.98. This magnitude of molar electric conductivity was in good agreement with the data reported in literature for nonelectrolyte square-planar bis-complexes and consistent with the detected loss of two hydrogen atoms during coordination.

Polarography has revealed, through the appearance of three half-wave potentials [6] within the range between + 0.95 V and - 0.95 V (a region in which oxidizing or reducing agents do not break up the complex) the charge-transfer (CT) character of $[NiL_2]$ (electron transfer may occur between the nickel ion and the two identical ligands with conjugated double bonds, *i.e*. this complex compound is able to exhibit CT electronic transitions – assumption which is expected to be hereinafter confirmed by the quantum-chemical interpretation of its UV-Vis spectrum).

IR, HL (cm^{-1}, intensity): (3482, i) ϋ(N–H); (3370, i) ϋ(N–H); (1670, i) ϋ(C=O); (1580, i) ϋ(C–N coupl. C–C); (1356, i) ϋ(C–N coupl. N–H); (1210, i) ϋ(C–S); (1150, m) ϋ(C=C, ske); (1005, w) ϋ(C–H, plane def); (755, vi) ϋ(N–H); (670, m) ϋ(C=S); IR, $[NiL_2]$ (cm^{-1}, intensity): (3410, w) ϋ(N–H); (3310, w) ϋ(N–H); (1670, i) ϋ(C=O); (1585 m) ϋ(C–N coupl. C–C); (1355 m) ϋ(C–N coupl. N–H); (1258 w) ϋ(C–S); (1145 m) ϋ(C=C, ske); (1005 w) ϋ(C–H, plane def); (758 vi) ϋ(N–H); (678 w) ϋ(C=S) - where: vi = very intense; i = intense; m = medium; w = weak. Therefore, IR spectra showed that important changes occur between 3500 and 3000 cm^{-1} – a region including characteristic vibrations of the amino group – ϋ(N–H), as well as that the intense bands within the 1600-1300 cm^{-1} range – ϋ(C–N coupl. C–C) and ϋ(C–N coupl. N–H) appear in the complex compounds at modified wavenumbers and with diminished intensities, both these facts indicating that the two nitrogen atoms from the amino groups are directly involved in the coordination process. Moreover, the vibrational spectra also revealed that the sulfur atoms are strongly adulterated during the coordination, this fact residing in a great wavenumber change and intensity decrement suffered by the band between 1300 and 1200 cm^{-1} and also by the one between 680 and 630 cm^{-1}, leading to the conclusion that the two sulfur atoms, which are parts in systems of delocalized electrons also become bonded to the metal. As a further confirmation stands the fact that the intense band present in the ligand spectrum at about 1670 cm^{-1} is found again in the spectrum of the complex, showing that the oxygen atoms are not involved in any new chemical bonds.

Consequently, IR analysis revealed a tetracoordinate bis-chelated complex with two sulfur atoms and two nitrogen atoms involved into the coordination process, *i.e*. being of $[MN_2S_2]$-type.

Although, it is for the quantum-chemical interpretation of the UV-Vis spectra to finally decide the geometric isomerism of exhibited by it. UV-Vis, HL (cm^{-1}, absorbance): (21729, 0.70); (22973, 0.31); (32723, 0.26); UV-Vis, $[NiL_2]$ (cm^{-1}, absorbance): (13476, 0.08); (20513, 0.75); (29151, 0.34); (32712,

0.25); (37236, 0.57). These absorption bands are to be assigned in what follows by performing the computational study, in order to clarify the structural assessment of the complex compound.

The quantum-chemical calculations were performed for both *cis* and *trans* isomers of square-planar complex [NiL_2] (Figure 2) in order to decide which is compatible with the recorded UV-Vis spectrum.

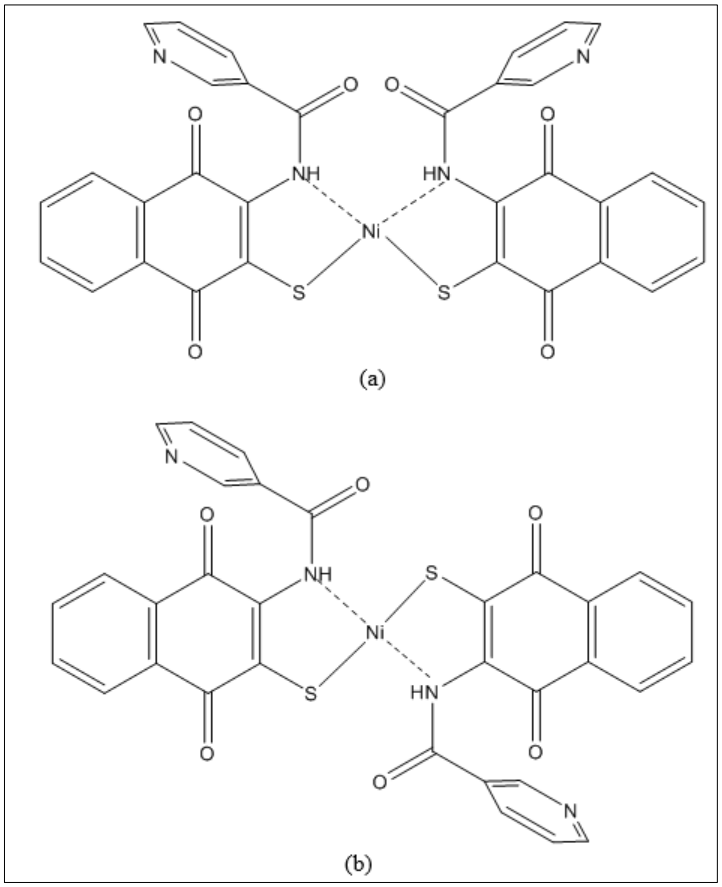

Figure 2. Geometric isomers theoretically possible for the [MN_2S_2]-type complex compound [NiL_2]: (a)– *cis*; (b) – *trans*

Nevertheless, the results will only be reported for the version that proved itself to be the right one, namely the *trans* isomer.

3.4. Molecular orbitals revealed by the quantum-chemical study

The ligand having the chemical formula $C_{16}H_{10}N_2O_3S$, it obviously exhibits 98 MOs (resulted from the interaction of 98 valence-shell AOs brought by the atoms that were combined), from which 54 MOs are OMOs (the total number of the valence-shell electrons being 108) and, clearly, 44 MOs are UMOs. The numbering given by the program starts (despite the usual convention) from the highest energy MO, so that, generically denoting the molecular wave functions by Ψ, the LUMO will be Ψ_{44} and the HOMO will be Ψ_{45}.

Similarly, the divalent nickel complex compound, having the chemical formula [$Ni(C_{16}H_9N_2O_3S)_2$], exhibits 203 MOs, from which 111 MOs are OMOs (the total number of the valence-shell electrons being 222) and, consequently, 92 MOs are UMOs. The numbering starting from the highest energy MO and generically denoting the molecular wave functions by Ψ', it is clear that Ψ'_{92} will be the LUMO and Ψ'_{93} will be the HOMO.

The ICON-EDiT program [12] confirmed the MOs' occupancy, also presenting the total energies of MOs and the mixing coefficients allowing us to estimate the expressions for every molecular wave function and therefore to understand where each MO lies.

However, as mentioned before, only a few MOs are important for the quanto-mechanical study, as there is no need to investigate neither the OMOs separated from LUMO by a larger gap then the energy that corresponds to the electronical transition with the highest wavenumber, nor the UMOs separated from HOMO by a larger gap than it.

Accordingly, for the ligand, we only took into account the MO energies between -11.559 eV and -4.953 eV, because the highest energy photon detected in the electronic spectrum of it was 4.057 eV, whereas HOMO and LUMO were found at -9.010 eV and -7.502 eV, respectively. Similarly, for the complex compound, we neglected the MO energies lower than -12.549 eV, as well as the ones higher than -4.958eV, because the maximum energy photon recorded in its UV-Vis spectrum was 4.681 eV and the energies of HOMO and LUMO were -9.576 eV and -7.931 eV, correspondingly.

We denoted by O(1) the oxygen atom double-bonded to C(1) and by O(2) the oxygen atom double-bonded to C(4). As the denomination of the free organic ligand shows, the N atom is bonded to C(2) in the naphthalene-1,4-dione heterocycle, whereas the S atom is bonded at C(3) in it. Moreover, we simply denoted by S and N the atoms involved in coordination when discussing the ligand's MOs, but we had to use the notation $S_L/S_{L'}$ and $N_L/N_{L'}$ as far as the MOs of the complex are concerned, so as to distinguish the atoms of each moiety. Clearly, similar symbolizations were used for the oxygen atoms.

Furthermore, we denoted by $p_xC(1)$ the p_x orbital of C(1) atom *etc*. The expressions for the MOs in the frontier zone were written bellow taking into consideration only the mixing coefficients exceeding 0.1. One may see that the sum of their squares is very close to the unit, as expected in quantum mechanics.

For HL, the expressions of the MOs in the frontier zone are the following:

$\Psi_{41} \simeq 0.616\, p_xS - 0.424\, p_yS - 0.412\, p_zS + 0.224\, p_xC(3) - 0.265\, p_yC(3) + 0.273\, p_xC(4) + 0.174\, p_yC(4) - 0.123\, p_yO(2)$

$\Psi_{42} \simeq -0.818\, p_zO(1) + 0.557\, p_zC(1)$

$\Psi_{43} \simeq 0.906\, p_zO(2) - 0.387\, p_zC(4)$

$\Psi_{44} \simeq 0.557\, p_xN + 0.504\, p_yN - 0.374\, p_xC(2) - 0.309\, p_yC(2) - 0.245\, p_xC(1) + 0.173\, p_yC(1) - 0.223\, p_xO(1) - 0.201\, p_yO(1)$

$\Psi_{45} \simeq 0.648\, p_xS - 0.529\, p_yS + 0.436\, p_xC(3) - 0.316\, p_yC(3)$

$\Psi_{44} \simeq 0.670\, p_xN - 0.583\, p_yN + 0.245\, p_xC(2) - 0.360\, p_yC(2)$

$\Psi_{47} \simeq -0.883\, p_zO(1) - 0.308\, p_zC(1)$

$\Psi_{48} \simeq 0.925\, p_zO(2) + 0.332\, p_zC(4)$

For $[NiL_2]$, the expressions of the most important MOs are as follows:

$\Psi'_{86} \simeq -0.824\, p_zO_L(1) - 0.547\, p_zC_L(1)$

$\Psi'_{87} \simeq -0.812\, p_zO_{L'}(1) - 0.565\, p_zC_{L'}(1)$

$\Psi'_{88} \simeq 0.901\, p_zO_L(2) - 0.399\, p_zC_L(4)$

$\Psi'_{89} \simeq 0.911\, p_zO_{L'}(2) - 0.374\, p_zC_{L'}(4)$

$\Psi'_{90} \simeq 0.219\, p_xS_L - 0.148\, p_yS_L - 0.894\, p_zS_{L'} - 0.212\, p_xC_L(3) + 0.235\, p_yC_L(3)$

$\Psi'_{91} \simeq -0.151\, p_xS_{L'} + 0.164\, p_yS_{L'} - 0.888\, p_zS_{L'} + 0.324\, p_xC_{L'}(3) - 0.158\, p_yC_{L'}(3)$

$\Psi'_{92} \simeq 0.991\, d_{x^2-y^2}$ Ni

$\Psi'_{93} \simeq 0.985\, d_{xy}$ Ni

$\Psi'_{97} \simeq -0.889\, p_zO_L(1) - 0.292\, p_zC_L(1)$

$\Psi'_{98} \simeq -0.878\, p_zO_{L'}(1) - 0.325\, p_zC_{L'}(1)$

$\Psi'_{99} \simeq 0.933\, p_zO_L(2) + 0.316\, p_zC_L(4)$

$\Psi'_{100} \simeq 0.922\, p_zO_{L'}(2) + 0.347\, p_zC_{L'}(4)$

$\Psi'_{101} \simeq 0.519\, p_xS_L - 0.538\, p_yS_L - 0.378\, p_zS_L + 0.339\, p_xC_L(3) - 0.259\, p_yC_L(3) + 0.308\, p_zC_L(3)$

$\Psi'_{102} \simeq -0.534\, p_xS_{L'} + 0.525\, p_yS_{L'} + 0.336\, p_zS_{L'} - 0.312\, p_xC_{L'}(3) + 0.384\, p_yC_{L'}(3) - 0.249\, p_zC_{L'}(3)$

$\Psi'_{103} \simeq 0.192\, p_xN_L - 0.207\, p_yN_L + 0.883\, p_zN_L + 0.203\, p_xC_L(2) - 0.204\, p_yC_L(2) + 0.192\, p_zC_L(2)$

$\Psi'_{104} \simeq -0.247\, p_xN_{L'} + 0.144\, p_yN_{L'} + 0.871\, p_zN_{L'} - 0.167\, p_xC_{L'}(2) + 0.187\, p_yC_{L'}(2) + 0.255\, p_zC_{L'}(2)$

Table 1 and 2 gather the main information about the most important MOs - which was either directly provided by the ICON-EDiT program (referring to occupancy and energy) or consequently obtained by estimating the molecular wave functions, as presented above (regarding the zone with maximum electron density).

Firstly, we have to note that the energies for Ψ_{42} and Ψ_{43}, as well as the ones for Ψ_{47} and Ψ_{48}, are not exactly the same because of the different vicinities of the two oxygen atoms in naphthalene-1,4-dione, but they are so close as to permit us to treat them together, in order to simplify calculations; similar cases were identified for the complex. Then, we have to observe that some MOs of the ligand are found duplicated in its complex formed with divalent nickel, obviously due to the fact that the coordinative compound contains two identical moieties.

Table 1. Main characteristics for the most important MOs of HL

Ligand MO	Occupancy	Energy/ medium energy, eV	Atoms in the spatial zone with maximum electron density
Ψ_{41}	UOC	-6.348	S, [C(3), C(4), O(2)]
Ψ_{42}	UOC	-6.964	O(1), [C(1)]
Ψ_{43}	UOC		O(2), [C(4)]
Ψ_{44}	UOC	-7.502	N, [C(2), C(1), O(1)]
Ψ_{45}	DOC	-9.010	S, [C(3)]
Ψ_{46}	DOC	-10.338	N, [C(2)]
Ψ_{47}	DOC	-11.023	O(1), [C(1)]
Ψ_{48}	DOC		O(2), [C(4)]

DOC = doubly occupied; UOC = unoccupied;
[…] – atoms whose AOs bring a minor contribution to the MO expression

Table 2. Main characteristics for the most important MOs of $[NiL_2]$

Complex compound MO	Occupancy	Energy/ medium energy, eV	Atoms in the spatial zone with maximum electron density
Ψ'_{86}	UOC	-6.975	$O_L(1)$, $[C_L(1)]$
Ψ'_{87}	UOC		$O_{L'}(1)$, $[C_{L'}(1)]$
Ψ'_{88}	UOC		$O_L(2)$, $[C_L(4)]$
Ψ'_{89}	UOC		$O_{L'}(2)$, $[C_{L'}(4)]$
Ψ'_{90}	UOC	-7.062	S_L, $[C_L(3)]$
Ψ'_{91}	UOC		$S_{L'}$, $[C_{L'}(3)]$
Ψ'_{92}	UOC	-7.931	M
Ψ'_{93}	DOC	-9.576	M
Ψ'_{97}	DOC	-11.041	$O_L(1)$, $[C_L(1)]$
Ψ'_{98}	DOC		$O_{L'}(1)$, $[C_{L'}(1)]$
Ψ'_{99}	DOC		$O_L(2)$, $[C_L(4)]$
Ψ'_{100}	DOC		$O_{L'}(2)$, $[C_{L'}(4)]$
Ψ'_{101}	DOC	-11.608	S_L, $[C_L(3)]$
Ψ'_{102}	DOC		$S_{L'}$, $[C_{L'}(3)]$
Ψ'_{103}	DOC	-12.513	N_L, $[C_L(2)]$
Ψ'_{104}	DOC		$N_{L'}$, $[C_{L'}(2)]$

DOC = doubly occupied; UOC = unoccupied;
[…] – atoms whose AOs bring a minor contribution to the MO expression

As an example of the previously stated, one may see, by comparing the energies of the MOs, as well as the molecular zones where they are practically localized, that the OMOs Ψ_{47} and Ψ_{48} in the ligand are found again almost identical in the complex compound, where they both get doubled in $\Psi'_{97,98}$ and $\Psi'_{99,100}$ respectively, whereas, similarly, the UMOs Ψ_{42} and Ψ_{43} in the ligand are found again almost identical in the complex compound, being correspondingly duplicated in $\Psi'_{86,87}$ and $\Psi'_{88,89}$.

As all these MOs strongly involve both the oxygen atoms in the naphthalene-1,4-dione heterocycle, one might take this as an *a priori* prove that none of these heteroatoms has anything to do with the coordination.

Nevertheless, in order to be sure of that, and also to make sure that the tetracoordinate bis-chelated complex is indeed of $[MN_2S_2]$-type, all assignments have to be made for the transitions exhibited in the UV-Vis range by both the free organic ligand and its nickel complex compound.

3.5. Assignment and quanto-mechanical interpretation of the electronic transitions

As stated before, after restricting the discussion to these sets of important MOs for both the ligand and its complex compound, we did not investigate all the theoretical transitions between every OMO and every UMO from each set, because all the assignments must be made rigorously respecting the „zone criteria", *i.e*. assuming that every electronic transition occurs between two MOs from the same spatial area.

Table 3 and Table 4 show the main characteristics for the electronic transitions of HL and $[NiL_2]$, respectively, as well as the assignment and quanto-mechanical interpretation for each of them.

One may observe that there is a good accordance between the experimentally found wavelength and the calculated one.

Table 3. Main characteristics for the electronic transitions of HL, assignment and interpretation

Wave-number, cm^{-1} (exp)	Absor-bance	Wave-length, nm (exp)	Assignment	Energy, eV (teor)	Wave-length, nm (teor)	Quanto-mechanical interpretation
21729	0.75	460.2	$\Psi_{45}\rightarrow\Psi_{41}$	2.662	465.8	S-S
22973	0.34	435.3	$\Psi_{46}\rightarrow\Psi_{44}$	2.836	437.2	N-N
32723	0.25	305.6	$\Psi_{47}\rightarrow\Psi_{42}$ $\Psi_{48}\rightarrow\Psi_{43}$	4.059	305.5	O-O

Table 4. Main characteristics for the electronic transitions of $[NiL_2]$, assignment and interpretation

Wave- number, cm^{-1} (exp)	Absorbance	Wave-length, nm (exp)	Assignment	Energy, eV (teor)	Wave-length, nm (teor)	Quanto-mechanical interpretation
13476	0.08	742.1	$\Psi'_{93}\rightarrow\Psi'_{92}$	1.645	753.9	*d-d* *weakly allowed*
20513	0.75	487.5	$\Psi'_{93}\rightarrow\Psi'_{90,91}$	2.514	493.2	*CT (M-L)* M-S_L, M-$S_{L'}$
29151	0.34	343	$\Psi'_{101,102}\rightarrow\Psi'_{92}$	3.677	337.2	*CT (L-M)* S_L-M, $S_{L'}$-M
32712	0.25	305.7	$\Psi'_{97}\rightarrow\Psi'_{86}$ $\Psi'_{98}\rightarrow\Psi'_{87}$ $\Psi'_{99}\rightarrow\Psi'_{88}$ $\Psi'_{100}\rightarrow\Psi'_{89}$	4.066	305	*L-L* $O_{L'}$-$O_{L'}$ $O_{L'}$-$O_{L'}$
37236	0.57	268.5	$\Psi'_{103,104}\rightarrow\Psi'_{92}$	4.582	270.6	*CT (L-M)* N_L-M, $N_{L'}$-M

The fact that both the transitions $\Psi_{47}\rightarrow\Psi_{42}$ and $\Psi_{48}\rightarrow\Psi_{43}$ from the ligand's spectrum were found again duplicated in the complex compound's spectrum, as $\Psi'_{97}\rightarrow\Psi'_{86}$, $\Psi'_{98}\rightarrow\Psi'_{87}$ and $\Psi'_{99}\rightarrow\Psi'_{88}$, $\Psi'_{100}\rightarrow\Psi'_{89}$ respectively confirmed our previous assumption that neither of the oxygen atoms in naphthalene-1,4-dione plays no part in the coordination of the ligand to the central metal ion.

On the other side, based on the fact that $\Psi_{45}\rightarrow\Psi_{41}$ (involving the sulfur atom) and $\Psi_{46}\rightarrow\Psi_{44}$ (involving the nitrogen atom in nicotinamide) were not found in the other spectrum, we already supposed that these two heteroatoms are the ones through which the coordination is realized. This supposition was confirmed by the assignments of the three CT transitions in the spectrum of the complex: $\Psi'_{93}\rightarrow\Psi'_{90,91}$, $\Psi'_{101,102}\rightarrow\Psi'_{92}$ (proving that the sulfur atom is directly bounded to nickel) and $\Psi'_{103,104}\rightarrow\Psi'_{92}$ (proving the coordinate bond between the nitrogen atom in nicotinamide and the transitional ion).

As far as the transition with maximum wavelength is concerned, it provides no information with respect to the atoms which the coordination is realized through, as it a weakly allowed *d-d* transition, meaning that it would be parity-forbidden by the Laporte selection rule for the centrosymmetric molecules, but, taking into account that a vibration can destroy the inversion symmetry and consequently

the „gerade"/„ungerade" classification no longer applies, it becomes vibronically allowed. However, the very poor absorbency of this *d-d* transition represents an argument in support of the assertion that the complex compound is structured as a *trans* isomer.

Anyway, a similar study has been performed for the *cis* isomer of the complex, but there was no good accordance between the computational data and the recorded UV-Vis spectrum, so that the attempt to assign the electronic transitions has failed for the hypothetical case that the coordinative compound could be found in this latter form.

4. Conclusions

Within this paper, which is a continuation of our previous works on this topic [5, 6], a new quanto-mechanical study was presented, regarding the actual coordination manner of a naphthalene-1,4-dione based ligand to divalent nickel.

It was established that the organic compound that was in question, namely N-(3-mercapto-naphthalene-1,4-dione-2-yl)nicotinamide, loses the hydrogen atom from the mercapto group while coordinating to the central metal ion, this being the reason why we denoted it by HL, whereas for the complex formed by it with Ni(II) the chemical formula $[NiL_2]$ was revealed.

Based on the results gathered from physico-chemical analysis, we concluded that the naphthalene-1,4-dione based compound, whose denticity is not obvious from the start, as it contains several heteroatoms, and, furthermore, may exhibit free turnings around different covalent bonds' axes, does not act as a tridentate ligand, but as a bidentate one, so $[NiL_2]$ is not a hexacoordinate complex, but a tetracoordinate one.

Moreover, the complex proved itself to present a square-planar geometry, belonging to the $[MN_2S_2]$-type, *i.e.* involving into the coordination process the sulfur atom from the mercapto group and the nitrogen atom from nicotinamide.

However, there was still a doubt regarding the geometric isomerism of this coordinative compound, which is essential in determining its behaviour, including the biological activity, given the fact that similar complexes were already found to act as antibacterial and antifungal agents, so this particular compound, among others that we have synthesized, is at this time thoroughly tested from this point of view and the results are to be subsequently reported.

The quanto-mechanical study presented through this paper leaded to the ultimate conclusion that the complex formed by N-(3-mercapto-naphthalene-1,4-dione-2-yl)nicotinamide with divalent nickel, coordinated by the sulfur atom from the mercapto group and the nitrogen atom from nicotinamide, is in the form of its *trans* isomer, that being the one for which the quantum-chemical calculations were found in very good agreement with the experimentally recorded data (this statement being also supported by the very weak absorbency of the *d-d* transition identified in the UV-Vis spectrum of the coordination compound).

Thus, the paper provided a useful quantum-chemical tool to establish the stereochemistry of the transition metal complex formed by the investigated naphthalene-1,4-dione based ligand with divalent nickel.

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