Synthesis and spectral characterisation of a new metal complex with a bidentate ligand

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Abstract. Literature mentions the important biologic-active, antimalaric, antiviral, antitumoural, tuberculostatic properties of 3-alkyl-and 3-alkenyl-substituted derivatives of 2-hydroxy-1,4-naphthoquinone and arylamino-1,4-naphthoquinones; the same properties are shown by the complexes that these ligands form with metal ions, which act in the biological structures as essential microelement. This paper reports the study of the structure of some new electron-transfer complexes with bidentate ligands of the naphthoquinone series by using IR, visible and UV spectra. A quantum-mechanical interpretation of the electronic transitions for the free and coordinated ligand has been performed in order to get information on the coordination of the heteroatoms to the M(II). The complexes of transitional metals with naphthoquinonic ligand have been prepared by following the procedure described by Jensen and Nielsen. The structural formula of the free and coordinated organic ligand has been modelled on the computer. The electronic spectra of the complexes studied lead to the conclusion that they are square-planar.

1. Introduction
The literature has offered new data related to the complex compounds formed by transition metals and ligands having conjugated double bonds, i.e., a system of delocalized electrons in their molecule. The special interest about these complexes is due, among others to the fact that the complex compounds readily participate in reversible electron-transfer reactions. Literature mentions the important biologic-active, antimalaric, antiviral, antitumoural, tuberculostatic properties of this kind of ligands; the same properties are shown by the complexes that these ligands form with metal ions, which act in the biological structures as essential microelements [1]. The importance of such compounds can be exemplified by the interesting biological activities associated with many 3-alkyl- or 3-alkylamino-substituted derivatives of 2-hydroxy-1,4-naphthoquinone or 2-chloro-1,4-naphthoquinones (figure 1) [2].
Further need for a study of compounds of this type is illustrated by the observation that the ortho-
amino quinoid unit is present in many antitumour antibiotics such as actinomycins, mitomycin C,
porfiromycin and streptonigrin [3]. Because there are few literature [4, 5, 6] regarding the complexes
of the general [M-N2S2] type, we hope that the data provided by this paper will contribute to enrich
the knowledge in this insufficiently studied field.

2. Experimental

2.1. Preparative methods
In this work we have used the new naphthoquinonic ligand containing X=S, Y=N as donor atoms: 2-
mercapto-3- nicotinamido-1,4-naphthoquinone (MNNQ) (figure 2). This ligand was synthesized
according the scheme from (figure 3).

The complex of Ni (II) with naphtoquinonic ligand (MNNQ) has been prepared by the procedure
described by Jensen and Nielsen [7]. The complex is a microcrystalline powder, whose melting point
is higher than that of the pure ligand (table 1). It is air-stable, insoluble in ordinary organic solvents,
sparingly soluble in dichlorethane and dioxane and soluble in dimethylformamide (DMF) and
dimethylsulphoxide (DMSO). The molar electrical conductivity of the complex was measured on a
Model OK-102/1 Radelkis conductivity-meter, in 10^{-4} M DMF solutions, at 22°C.
Table 1. Preparation details, elemental analyses and molar conductance of complex.

| Compound          | Mol wt calcd | mp (°C) | Molar conductance (Ω⁻¹ cm² mol⁻¹) | Appearance                  | Analyses (%) |
|-------------------|--------------|---------|-----------------------------------|-----------------------------|---------------|
| [Ni(MNNQ)_2]     | 676.71       | 122     | 2.98                              | Deep-red microcrystalline   | Ni 8.68 8.97  |
|                   |              |         |                                   |                             | C 56.75 56.89 |
|                   |              |         |                                   |                             | S 9.46 9.22  |
|                   |              |         |                                   |                             | N 8.28 8.07  |
|                   |              |         |                                   |                             | H 2.66 2.84  |

2.2. Spectral determinations

The results of the elemental analyses show that these complex compound is of the type [ML2] where M = Ni(II) and L = MNNQ (figure 4). In order to explain this composition, we must admit that MNNQ act as bidentate ligand.

![Figure 4. Molecular structure of Ni(II) complex.](image)

The assumption has been confirmed by the physical-chemical analyses and quantum-mechanical studies described below. In order to obtain data regarding the nature of the chemical bonds and the type of the atoms involved in the coordination were performed infrared spectra for the free ligand and complex compound. These results are showed in (table 2).

Table 2. Infrared absorption frequencies (cm⁻¹) of ligand and of complex.

| Compound | ν_N-H | ν_C=O | ν_CN coupling C=C | ν_CN coupling NH₂ | ν_SH | ν_C=C | ν_C-H | ν_NH | ν_C=S |
|----------|-------|-------|-------------------|-------------------|------|-------|-------|------|-------|
| L        | 3482 i| 1670 i| 1580 i            | 1356 i            | 680 w| 1150 m| 1005 w| 755 vi| 670 m |
| NiL₂     | 3410 w| 1670 i| 1585 m            | 1355 m            | 650 w| 1145 m| 1005 w| 758 vi| 678 w |

vi=very intense; i=intense, m=medium, w=weak

The absorption bands due to vibrations groups not involved in the coordination appear in the infrared spectra of the free ligand and of the complex in the same spectral regions, with unchanged or at most slightly modified intensities, because of the electromeric effects due to the coordination. The characteristic bands of the N-H and S-H groups, which appear in the IR spectra of the ligand as intense or medium intense bands in the complex spectra the bands are modified in intensity and appear at
slightly modified frequencies, proving the involvement of these groups in the coordination. The metal complex is also characterized by the appearance of some new bands of medium and low intensity at 570 cm\(^{-1}\) and 440 cm\(^{-1}\), which can be assigned to \(\nu(M-S)\) and \(\nu(M-N)\) frequencies. So, IR spectra indicate the participation of both the sulphur and nitrogen atoms in coordination to the metal. The IR spectra were recorded on a Perkin Elmer FT-1600 Hewlett Packard instrument in anhydrous KBr pellets.

In order to establish the coordination geometry of the new complex, a spectral analyses in the visible and UV range was performed. The bands observed in the electronic absorption spectra of the studied complex were assigned according to Gray and Ballhausen [8] and Vanquickenborne [9]. An Unicam UV-visible 2-300 spectrophotometer was used to perform the electronic spectra, which were obtained with 10\(^{-3}\) M acetone solutions. The structure of the complex was explained using the molecular orbital approach. The metal orbitals involved in \(\sigma\)-bonding in square planar complexes are: \(nd_z^1\), \(nd_{x^2-y^2}^2\), \((n+1)s\), \((n+1)p_x\) and \((n+1)p_y\). Judging from the values of the overlap integrals, \(nd_{x^2-y^2}^1\), \((n+1)s\), \((n+1)p_x\) and \((n+1)p_y\) account for most of the \(\sigma\)-bonds, and \(nd_z\) makes only a minor contributions. The most important \(\pi\)-molecular orbital is formed by the metal orbital and a combination of \(\pi\)-orbitals. In table 3 there are the assignments for the transitions occurring in the electronic spectra.

| Compound          | \(\lambda_{\text{max}}\) (cm\(^{-1}\)) | \(\nu_{\text{max}}\) (cm\(^{-1}\)) | Assignment                        |
|-------------------|----------------------------------------|----------------------------------|-----------------------------------|
| [Ni(MNNQ)\(_2\)] | 20517                                  | 185                              | \(^1\)A\(_{1g}\) \rightarrow \(^1\)A\(_{2g}\) [b\(_{2g}\)(\(\pi^*\)) \rightarrow b\(_{1g}\)(\(\sigma^*\))] |
|                   | 29150                                  | 293                              | \(^1\)A\(_{1g}\) \rightarrow \(^1\)B\(_{1g}\) [b\(_{2g}\)(\(\pi^*\)) \rightarrow a\(_{1g}\)(\(\sigma^*\))] |
|                   | 35714                                  | 880                              | \(^1\)A\(_{1g}\) \rightarrow \(^1\)B\(_{1u}\) [b\(_{2g}\)(\(\pi^*\)) \rightarrow a\(_{2u}\)(\(\sigma^*\))] |
|                   | 37233                                  | 11200                            | \(^1\)A\(_{1g}\) \rightarrow \(^1\)E\(_u\) [e\(_g\)(\(\pi^*\)) \rightarrow a\(_{2u}\)(\(\pi^*\))] |

2.3. Computer modeling

The structural formula of the free and coordinated organic ligand has been modelled on the computer. The molecular geometry has been optimized using the Molecular Mechanics approach (MM+) [10].

\[ h\nu_{\text{calc}} = 4.41 eV \]
\[ \sigma_{\text{calc}} = 35571 cm^{-1} \]
\[ \sigma_{\text{calc}} = 35714 cm^{-1} \]

\[ \text{Figure 5. Transition 100-103.} \]

In the complexes of Ni(II) the first absorption band is assigned to an electron transfer from an electron lone pair localized on the sulphur atom and the second one to an electron transfer from an electron lone pair localized on the nitrogen atom. These transitions are shifted toward higher wave numbers for the coordinated ligand just as a consequence of the coordination. These shifts are caused by the mixing of the antibonding states with d-metal orbitals as well as to the lowering the electron
lone pairs energy that occurs after coordination. By comparing the spectra of the complex with the one of the free ligand, we observed that the first two bands are shifted, while the last two ones are unshifted, meaning that the oxygen atoms are not involved in the coordination, this one being made by the sulphur and nitrogen atoms of the ligand. The absorption maximum from 35714 cm$^{-1}$ is attributed to 100→103 transition, the absorbed photon energy being 4.41 eV, that corresponds to $\bar{\nu} = 35711$ cm$^{-1}$. This is a ligand-metal transition, the 100 orbital being practically an orbital with unparticipating electrons from sulphur and 103 being a molecular orbital from a d orbital of Ni(II) ion (figure 5). The absorption maximum from 20517 cm$^{-1}$ is attributed to a d-d transition between 102→103 orbitals, both being molecular orbitals from d orbitals of the central metallic ion (figure 6).

![Figure 6. Transition 102-103.](image)

3. Conclusions
Correlation between elementary analysis and physical-chemical determinations suggests that Ni complex is [ML2] type. Electronic spectra proved that it is a square-planar structure complex. So, on one hand, using computer analysis of animated vibrations, we proved that the molecule is square-planar and appears as trans isomer, and, on the other hand, using computer analysis for molecular orbitals, we proved that the coordination is assured by the two sulphur atoms from the “mercapto” group and the two nitrogen atoms from amidic group of the nicotinamide, situated in ortho-position toward the sulphur atoms.

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