

**NEW ELECTRON-TRANSFER COMPLEXES OF THE [M-N<sub>2</sub>S<sub>2</sub>] TYPE OF Ni(II), Pd(II) AND Pt(II) WITH BIDENTATE LIGANDS OF THE NAPHTHOQUINONE SERIES.**

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**Abstract**

The paper reports the study of the structure of some new electron-transfer complexes of the [M-N<sub>2</sub>S<sub>2</sub>] type of Ni(II), Pd(II) and Pt(II) with bidentate ligands of the naphthoquinone series by using IR, visible, UV and ESR spectra, conductometric and polarographic data. A quanto-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) using the EHT-MO approach.

**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.<sup>1-9</sup>

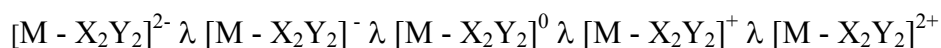
The special interest about these complexes is due, among others to the fact that the complex compounds readily participate in reversible electron-transfer reactions:



These combinations are planar irrespective of the oxidation state of the metal.

Other four coordinated systems, having similar properties to the dithiols, were also investigated.

As a consequence of the electron transfer, the following species can be obtained in this case:



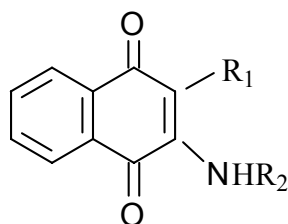
where X = Y = S; X = Y = O; X = Y = N; X = O, Y = S; X = S, Y = N.

These studies revealed that electron-transfer reactions have a reasonably general occurrence and that oxidative stabilities for complexes of the same general composition and charge type have a marked dependence on the nature of the donor atoms.

Because there are few literature regarding the complexes of the general [M-N<sub>2</sub>S<sub>2</sub>]

type, we hope that the data provided by this paper will contribute to enrich the knowledge in this insufficiently studied field.

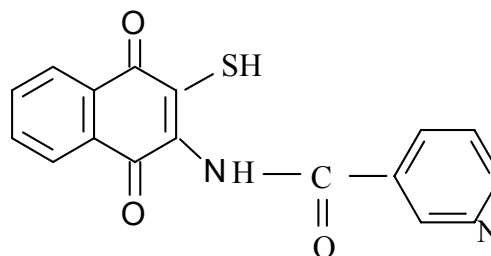
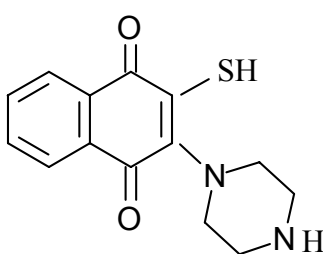
On the other side, literature<sup>10-12</sup> mentions the important biologic-active, antimalaric, antiviral, antitumoural, tuberculostatic properties of this kind of ligands; the same properties are shown by the complexes that these ligands form with metal ions, which act in the biological structures as essential microelements.



The importance of such compounds can be exemplified by the interesting biological activities associated with many 3-alkyl- and 3-alkenyl- substituted derivatives of 2-hydroxy-1,4-naphthoquinone<sup>10</sup> and arylamino-1,4-naphthoquinones.<sup>11</sup>

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.<sup>12</sup>

With the view of extending these investigations to the latter systems, in this work we have used the new naphthoquinonic ligands<sup>14</sup> containing X=S, Y=N as donor atoms: 2-mercapto-3-piperazin-1,4-naphthoquinone (MPPNQ)(II) and 2-mercapto-3-nicotinamido-1,4-naphthoquinone (MNANQ)(III).



### Results and discussion

All the complexes of Ni(II), Pd(II) and Pt(II) with naphthoquinonic ligands (MPPNQ and MNANQ) have been prepared by following the procedure to described by Jensen and Nielsen.<sup>15</sup>

The complexes are microcrystalline variously coloured powders, whose melting points are higher than that of the pure ligand (Table1). They are air-stable, insoluble in ordinary organic solvents, sparingly soluble in dichlorethane and dioxane and soluble in dimethylformamide (DMF) and dimethylsulphoxide (DMSO).

The results of the elemental analyses (Table 1) show that these complex compounds are of the type  $[ML_2]$  where M = Ni(II), Pd(II), Pt(II) and L = MPPNQ and MNANQ.

In order to explain this composition, we must admit that both MPPNQ and MNANQ act as bidentate ligands. The assumption has been confirmed by the physico-chemical analyses and quanto-mechanical studies described bellow.

Data regarding the nature of the chemical bonds and the type of the atoms involved in the coordination were obtained leaning on the infrared spectra performed for the free ligand and complex compounds.<sup>16</sup>

The results of this study are presented in Table 2, where MPPNQ and MNANQ were denoted as L<sub>1</sub> and L<sub>2</sub> respectively.

The data in Table 2 show that the absorption bands due to vibrations groups not involved in the coordination appear in the infrared spectra of the free ligands and of the complexes as well, in the same spectral regions, with unchanged or at most slightly modified intensities, because of the electromeric effects due to the coordination.

By contrast, the characteristic bands of the N-H and S-H groups, which appear in the IR spectra of the ligands as intense or medium intense bands at 3000-3500 cm<sup>-1</sup> and 1210 cm<sup>-1</sup>, 630-680 cm<sup>-1</sup> respectively, in the complexes spectra are modified in intensity and appear at slightly modified frequencies, proving the involvement of these groups in the coordination.

The metal complexes are also characterized by the appearance of some new bands of medium and low intensity at 580-560 cm<sup>-1</sup> and 460-420 cm<sup>-1</sup>, which can be assigned to  $\nu(M-S)$  and  $\nu(M-N)$  stretching frequencies, respectively.<sup>17</sup>

Table 1. Preparation details, elemental analyses and molar conductance of complexes

Compound	Mol wt. calcd.	m.p. (°C)	Molar conductance* ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	Appearance	Analyses (%)		
					Element	Calcd	Found
[Ni(MPPNQ) <sub>2</sub> ]	604.71	142	1.83	red microcryst.	Ni	9.71	9.92
					C	55.56	55.84
					S	10.58	10.46
					N	9.26	9.53
					H	3.97	3.85
[Pd(MPPNQ) <sub>2</sub> ]	652.40	193	1.52	brown microcryst.	Pd	16.31	16.61
					C	51.50	51.72
					S	9.81	9.65
					N	9.58	8.84
					H	3.68	3.92
[Pt(MPPNQ) <sub>2</sub> ]	741.09	198	3.70	brownish red microcryst.	Pt	26.32	26.28
					C	45.34	45.59
					S	8.63	8.34
					N	7.56	7.81
					H	3.24	3.58
[Ni(MNANQ) <sub>2</sub> ]	676.71	122	2.98	deep-red microcryst.	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
[Pd(MNANQ) <sub>2</sub> ]	724.4	158	1.44	orange microcryst.	Pd	14.69	14.75
					C	53.01	53.32
					S	8.83	8.49
					N	7.73	7.27
					H	2.48	2.85
[Pt(MNANQ) <sub>2</sub> ]	813.09	169	2.88	yellowish brown microcryst.	Pt	22.99	22.65
					C	47.22	47.56
					S	7.87	7.67
					N	6.89	6.59
					H	2.21	2.43

\*10<sup>-4</sup> M DMF solution, 22 °C

Table 2. Characteristic infrared absorption frequencies ( $\text{cm}^{-1}$ ) of ligands and complexes

Compound	$\nu_{\text{NH}}$	$\nu_{\text{CO}}$	$\nu_{\text{C-N}}$ coupling C-C	$\nu_{\text{C-N}}$ coupling $\text{NH}_2$	$\nu_{\text{CS}}$	$\nu^{\text{ske}}$ (C=C)	$\nu_{\text{C-H}}$ plane def.	$\gamma_{\text{NH}}$	$\nu_{\text{C-S}}$
$\text{L}_1$	3360 m 3270 w	1670 i	1588 i	1360 m	1210 m	1100 m	1005 w	730 vi	660 m
$[\text{Ni}(\text{L}_1)_2]$	3370 w 3285 sh	1670 i	1580 w	1358 sh	1230 w	1113 m	1012 w	750 i	665 sh
$[\text{Pd}(\text{L}_1)_2]$	3270 sh 3190 w	1670 i	1577 w	1350 w	1220 w	1110 w	1010 w	750 i	674 w
$[\text{Pt}(\text{L}_1)_2]$	3350 w 3200 sh	1670 i	1578 w	1355 w	1230 w	1115 w	1010 w	740 i	678 sh
$\text{L}_2$	3482 i 3370 i	1670 i	1580 i	1356 i	1210 i	1150 m	1005 w	755 vi	670 m
$[\text{Ni}(\text{L}_2)_2]$	3410 w 3310 w	1670 i	1585 m	1355 m	1258 w	1145 m	1005 w	758 vi	678 w
$[\text{Pd}(\text{L}_2)_2]$	3450 sh 3330 w	1670 i	1590 w	1358 m	1265 sh	1148 m	1005 w	760 vi	675 sh
$[\text{Pt}(\text{L}_2)_2]$	3455 w 3345 sh	1670 i	1585 sh	1360 m	1253 w	1143 m	1005 w	756 i	673 sh

vi = very intense; i = intense; m = medium; sh = shoulder; w = weak

In conclusion, an IR spectral analysis indicates the participation of both the sulphur and nitrogen atoms in coordination to the metal.

In order to establish the coordination geometry of the new complex compounds, a spectral analyses in the visible and UV range was performed. The bands observed in the electronic absorption spectra of the studied complexes were assigned according to Gray and Ballhausen<sup>18</sup> and Vanquickenborne.<sup>19</sup>

The molecular orbital approach was used to explain the structure of square-planar complexes of the  $d^8$  elements. The metal orbitals involved in  $\sigma$ -bonding in square planar complexes are the  $nd_{z^2}$ ,  $nd_{x^2-y^2}$ ,  $(n+1)s$ ,  $(n+1)p_x$  and  $(n+1)p_y$ . Nevertheless, judging from the values of the overlap integrals,  $nd_{x^2-y^2}$ ,  $(n+1)s$ ,  $(n+1)p_x$  and  $(n+1)p_y$  account for most of the  $\sigma$ -bonds, and  $nd_{z^2}$  makes only a minor contributions. The most important  $\pi$ -molecular orbital is formed by the  $(n+1)p_z$  metal orbital and a combination of  $\pi$ -orbitals of the four ligands.

The correlation of the bands observed in the electronic spectra for the studied complexes with those of  $[M(CN)_4]^{2-}$  [ $M = Ni(II), Pd(II), Pt(II)$ ] prompts us to assume the following assignments for the transitions occurring in the electronic spectra: (Table 3):  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  [ $b_{2g}(\pi^*) \rightarrow b_{1g}(\sigma^*)$ ], (d-d);  ${}^1A_{1g} \rightarrow {}^1B_{1g}$  [ $b_{2g}(\pi^*) \rightarrow a_{1g}(\sigma^*)$ ], (d-d);  ${}^1A_{1g} \rightarrow {}^1E_g$  [ $e_g(\pi^*) \rightarrow b_{1g}(\sigma^*)$ ], (d-d);  ${}^1A_{1g} \rightarrow {}^1B_{1u}$  [ $b_{2g}(\pi^*) \rightarrow a_{2u}(\sigma^*)$ ], (C.T.);  ${}^1A_{1g} \rightarrow {}^1E_u$  [ $e_g(\pi^*) \rightarrow a_{2u}(\pi^*)$ ], (C.T.).

Table 3. Electronic spectra in the UV and visible range of complex compounds

Compound	$\nu_{\max}$ (cm <sup>-1</sup> )	$\lambda_{\max}$	Assignment
[Ni(MPPNQ) <sub>2</sub> ]	23,634	140	${}^1A_{1g} \rightarrow {}^1A_{2g}$ [ $b_{2g}(\pi^*) \rightarrow b_{1g}(\sigma^*)$ ]
	30,250	270	${}^1A_{1g} \rightarrow {}^1B_{1g}$ [ $b_{2g}(\pi^*) \rightarrow a_{1g}(\sigma^*)$ ]
	32,467	750	${}^1A_{1g} \rightarrow {}^1B_{1u}$ [ $b_{2g}(\pi^*) \rightarrow a_{2u}(\sigma^*)$ ]
	37,714	10,500	${}^1A_{1g} \rightarrow {}^1E_u$ [ $e_g(\pi^*) \rightarrow a_{2u}(\pi^*)$ ]
Pd(MPPNQ) <sub>2</sub> ]	16,800	350	${}^1A_{1g} \rightarrow {}^1A_{2g}$ [ $b_{2g}(\pi^*) \rightarrow b_{1g}(\sigma^*)$ ]
	21,250	9,000	${}^1A_{1g} \rightarrow {}^1B_{1g}$ [ $b_{2g}(\pi^*) \rightarrow a_{1g}(\sigma^*)$ ]
	30,724	12,000	${}^1A_{1g} \rightarrow {}^1E_g$ [ $e_g(\pi^*) \rightarrow b_{1g}(\sigma^*)$ ]
[Pt(MPPNQ) <sub>2</sub> ]	21,675	125	${}^1A_{1g} \rightarrow {}^1A_{2g}$ [ $b_{2g}(\pi^*) \rightarrow b_{1g}(\sigma^*)$ ]
	26,320	254	${}^1A_{1g} \rightarrow {}^1B_{1g}$ [ $b_{2g}(\pi^*) \rightarrow a_{1g}(\sigma^*)$ ]
	30,333	8,500	${}^1A_{1g} \rightarrow {}^1E_g$ [ $e_g(\pi^*) \rightarrow b_{1g}(\sigma^*)$ ]
[Ni(MNANQ) <sub>2</sub> ]	20,517	185	${}^1A_{1g} \rightarrow {}^1A_{2g}$ [ $b_{2g}(\pi^*) \rightarrow b_{1g}(\sigma^*)$ ]
	29,150	293	${}^1A_{1g} \rightarrow {}^1B_{1g}$ [ $b_{2g}(\pi^*) \rightarrow a_{1g}(\sigma^*)$ ]
	32,714	880	${}^1A_{1g} \rightarrow {}^1B_{1u}$ [ $b_{2g}(\pi^*) \rightarrow a_{2u}(\sigma^*)$ ]
	37,233	11,200	${}^1A_{1g} \rightarrow {}^1E_u$ [ $e_g(\pi^*) \rightarrow a_{2u}(\pi^*)$ ]
[Pd(MNANQ) <sub>2</sub> ]	16,813	480	${}^1A_{1g} \rightarrow {}^1A_{2g}$ [ $b_{2g}(\pi^*) \rightarrow b_{1g}(\sigma^*)$ ]
	21,340	10,400	${}^1A_{1g} \rightarrow {}^1B_{1g}$ [ $b_{2g}(\pi^*) \rightarrow a_{1g}(\sigma^*)$ ]
	30,620	13,700	${}^1A_{1g} \rightarrow {}^1E_g$ [ $e_g(\pi^*) \rightarrow b_{1g}(\sigma^*)$ ]
[Pt(MNANQ) <sub>2</sub> ]	21,680	115	${}^1A_{1g} \rightarrow {}^1A_{2g}$ [ $b_{2g}(\pi^*) \rightarrow b_{1g}(\sigma^*)$ ]
	26,320	304	${}^1A_{1g} \rightarrow {}^1B_{1g}$ [ $b_{2g}(\pi^*) \rightarrow a_{1g}(\sigma^*)$ ]
	30,340	7,000	${}^1A_{1g} \rightarrow {}^1E_g$ [ $e_g(\pi^*) \rightarrow b_{1g}(\sigma^*)$ ]

A quantum-mechanical interpretation of the absorption bands proper to the free and coordinated organic ligands gives informations about the coordination of the heteroatoms to the transition metal ion Ni(II).

The structural formula of the free and coordinated organic ligands have been modeled on the computer. Their molecular geometry has been optimized using the Molecular Mechanics approach (MM<sup>+</sup>), the cartesian coordinates of the atoms being used to perform EHT calculation.<sup>20</sup> The computation were performed without iteration upon change and configuration, the EHT practice showing that the results thus obtained are more reliable if the electronic transitions between MO levels are compared with the spectral ones.

In the complexes of Ni(II) the first absorption band is assigned to an electron transfer from n 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 shift toward higher wavenumbers for the coordinated ligands just as a consequence of the coordination.

The shifts are caused by the mixing of the antibonding states with d-metal orbitals as well as to the lowering an the electron lone pairs energy that occurs after coordination.

The last two bands are due to transitions between molecular orbitals practically localised on the oxygen atoms of naphthoquinone.

By comparing the spectra of the complex compounds with the ones of the free organic ligands, it shows that the first two bands are shifted, while the last two ones are unshifted, meaning that the oxigen atoms have nothing to do with the coordination, which is realised by means of the sulphur and nitrogen atoms of the ligands.

Strong ESR spectra were obtained for the nickel compounds. A [Ni-N<sub>2</sub>S<sub>2</sub>] type compound has a spectrum consisting of three components (Figure 1).

The first two components originate in the splitting of the unpaired electron in the axial symmetry field of the complex ( $g_{\parallel}=2.0618$ ,  $g_{\perp}=2.0175$ ), while the third one is the result of the donor-acceptor-type strong interaction between ligands and the central ion ( $g_i=2.0022$ , which is alike the value for the free electron).

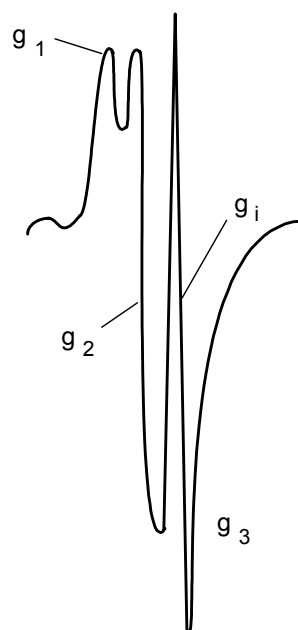
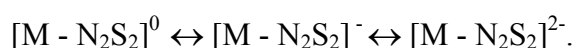


Fig. 1. ESR spectrum of  $[\text{Ni}(\text{MPPNQ})_2]$

The conductivity measurements (Table 1) show that the compounds of  $[\text{ML}_2]$  type, where  $\text{M} = \text{Ni}(\text{II}), \text{Pd}(\text{II}), \text{Pt}(\text{II})$ , while  $\text{L} = \text{MPPNQ}, \text{MNANQ}$ , are non-electrolytes, which have  $1.44\text{--}3.70 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in  $10^{-4} \text{ M}$  DMF solution, at  $22^\circ \text{C}$ , confirming the proposed structures.

The study of these new complex compounds has been completed with polarographic determinations. In the polarograms of the studied compounds there are three polarographic half-wave potentials. This fact proved the existence, in solution, of several reduced species. It also proves that at the dropping mercury electrode takes place the reduction of the neutral and monoanionic species, according to the general reaction:



The other observed waves are due to the reduction of the ligands. The data collected in connection with these complexes show that, aside from participating in electron-transfer reactions, the evidenced species can also be obtained chemically, because the half-wave potentials range  $+0.95 \text{ V}$  and  $-0.95 \text{ V}$ , a region in which oxidizing or reducing agents do not break up the complex.



### Conclusion

The correlation of the elemental chemical analyses with the results of the physico-chemical determinations suggest that the complexes described in this paper are of the type  $[M-N_2S_2]$ , where  $M=Ni(II)$ ,  $Pd(II)$ ,  $Pt(II)$ . This formulation is supported by the IR spectral analyses, which confirm that MPPNQ and MNANQ act as bidentate ligands having both nitrogen and sulfur as donor atoms. The electronic spectra of the complexes studied lead to the conclusion that they are square-planar. Polarography data prove their involvement in the electron-transfer processes.

### Experimental

Reagents:  $NiCl_2 \cdot 6H_2O$  (Merck, p.a.), aqueous solution (0.02M);  $PdCl_2$  (BDH, p.a.), aqueous solution (0,02M);  $K_2[PtCl_4]$  (BDH, p.a.); MPPNQ (double recrystallized), dimethylformamidic solution (0.02M); MNANQ (double recrystallized), dimethylformamidic solution (0.02 M).

Instruments: The IR spectra ( $400-4000\text{ cm}^{-1}$ ) were recorded on a Perkin Elmer FT-1600 Hewlett Packard instrument in anhydrous KBr pellets. An Unicam UV-visible 2-300 spectrophotometer was used to perform the electronic spectra ( $13000-45000\text{ cm}^{-1}$ ), which were obtained in  $10^{-3}$  M acetone solutions. The polarograms were recorded with a Model 7-77-4/b Orion KTS polarograph. The half-wave potentials were measured at room temperature, using a calomel reference electrode and a dropping mercury measuring electrode; the solutions of these complexes were  $10^{-3}$  M. As supporting electrolyte, a 0.1 M solution of tetra-*n*-butylammonium perchlorate was used. The molar electrical conductivity of the complexes was measured on a Model OK-102/1 Radelkis conductivity-meter, in  $10^{-4}$  M DMF solutions, at 22 °C. The ESR spectra were recorded with an IFA Bucharest AR7-5 spectrometer, working in the X band (9060 MHz) and having a 100 kHz modulation of the magnetic field. The spectra were obtained at room temperature with a  $Mn^{2+}$  standard ( $g_3=2.03584$ ,  $g_4=1.98040$ ,  $H_3=3179.5$ ,  $H_4=3268.5$ ).

General procedure: The  $[Ni(MPPNQ)_2]$  compound has been obtained by adding dimethylformamidic solution of ligand (MPPNQ) 0.02 M to aqueous solution of nickel dichloride 0.02 M in a 2:1 molar ratio. After settling for an hour, the formed precipitate has been filtered on a  $G_4$  porosity glass filter, washed with 96% ethyl alcohol,

diethylether and finally dried under vacuum. The complex is a microcrystalline stable red powder, which exhibits a low solubility in organic and inorganic solvents.

The other complexes have been prepared using analogous methods.

### References and Notes

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### Povzetek

Delo obravnava raziskave strukture nekaterih novih kompleksov s prenosom elektrona vrste [M-N<sub>2</sub>S<sub>2</sub>] z Ni(II), Pd(II) in Pt(II) ter bidentatnimi ligandi naftokinonske vrste z IR, vidno, UV in ESR spektroskopijo, meritvami prevodnosti ter polarografskimi podatki. Prehodi elektronov so bili opredeljeni na podlagi kvantno mehanske teorije in EHT-MO pristopa.