

# SYNTHESIS AND CHARACTERISATION OF SOME NEW METAL COMPLEXES OF 3-NITROZO-4-HYDROXY-COUMARIN AND ANTRANILIC ACID

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**abstract:** Some new mononuclear tetracoordinated compounds of Ni(II), Pd(II), Pt(II) and Cu(II) with different donor atoms (OO) and (ON) of the monobasic and bidentate organic ligands: 3-nitrozo-4-hydroxy-coumarin or oxiiimidobenzotetronic acid ( $L^1H$ ) and antranilic acid ( $L^2H$ ) have been synthesized and characterized by elemental analysis, the effective magnetic moment, UV-VIS, IR, spectral data. The elemental analysis and IR spectral data exhibited for all complexes the general formula  $[M(L^1)(L^2)]$ , where  $M = Ni(II), Pd(II), Pt(II)$  and  $Cu(II)$  and  $L^1, L^2$  are the deprotonated ligands above mentioned. The effective magnetic moments and the electronic spectra are in agreement with a square planar geometry for all complexes.

**keywords:** Ni(II), Pd(II), Pt(II) and Cu(II) complexes, 3-nitrozo-4-hydroxy-coumarine, oxiiimidobenzotetronic acid, antranilic acid

## Introduction

Coumarin derivatives have found extensive applications in medicine and biology and they are also known for their tendency to give coordination compounds with different metallic cations [1]. The complexation behaviour of the transition cations in a different environment is always of interest to inorganic chemists [2]. We have focused our attention in synthesising the coordinative compounds with ligands containing condensed aromatic rings.

Such type of ligands are very important in obtaining complexes with an extend  $\pi$  – delocalised electron system where a donor acceptor bond as the metal - ligand bond is, acts as a push-pull molecular device [3÷7].

We have coupled the monobasic and bidentate ligand, 3-nitrozo-4-hydroxy-coumarine or oxiiimidobenzotetronic acid ( $L^1H$ ) with another monobasic and bidentate ligand, antranilic acid ( $L^2H$ ) in order to obtain a giant planar molecule in a hybride inorganic - organic composition as a  $\pi$  delocalised system. The cations Ni(II), Pd(II), Pt(II) and Cu(II) were chosen for these coordinative compounds because they easily give coordinative compounds four coordinated. These results are briefly discussed in an attempt to determine the stereochemistry around the cations and the nature of the bonds.

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## Experimental

*Materials:* NiCl<sub>2</sub>·6H<sub>2</sub>O, PdCl<sub>2</sub>, K<sub>2</sub>[PtCl<sub>4</sub>], CuCl<sub>2</sub>·H<sub>2</sub>O, EtOH, were purchased from MERCK LTD.

### Measurement techniques:

*Elemental analyses* were performed using a Carlo Erba 1108 apparatus. Metallic cations were determined by analytical classical methods.

*Magnetic susceptibility* measurements were performed by the Faraday method, at room temperature, using Hg[Co(SCN)<sub>4</sub>] as standard.

*The IR spectra* were run with a Perkin Elmer FT-IR Spectrophotometer in 4000-200 cm<sup>-1</sup> range, in KBr pellets.

*The UV-VIS spectra* of all compounds were obtained by diffuse reflectance technique, dispersing the sample in MgO, with a M400 Carl Zeiss Jena Spectrophotometer.

### Preparation and isolation of the compounds:

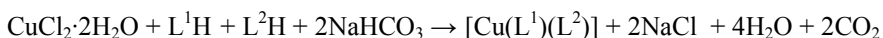
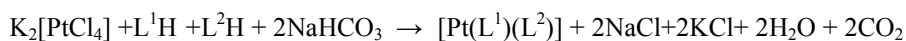
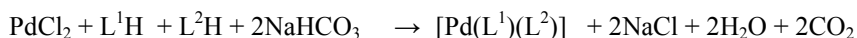
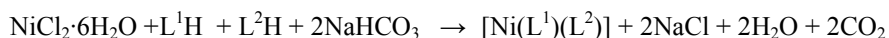
3-nitrozo-4-hydroxy-coumarin or oxiiimidobenzotetronic acid (L<sub>1</sub>H) was prepared by nitrosation of 4-hydroxy - coumarin under acidic conditions [7]. *Chemical analysis: Found:* C 40.81; H 6.12; N 9.52%. *C<sub>5</sub>H<sub>9</sub>O<sub>4</sub>N requires:* C 41.05; H 5.92; N 9.50%.

The coordinative compounds were prepared by mixing the ethanolic solutions of the metal salts (2.28·10<sup>-3</sup> mols) in 10 ml EtOH with an ethanolic solutions of ligands in a molar ratio M / (L<sup>1</sup>H) / (L<sup>2</sup>H) = 1 / 1 / 1 in 15 ml EtOH and continuous stirring at the room temperature. The solution of the ligands was added step by step to the solution of the metallic salts. After few minutes the pH was adjusted from 4.5 to 7 with a solution of NaHCO<sub>3</sub> 32% and an abundant, intense coloured precipitate arose. The stirring was maintained for 1.5 h, and the precipitate was filtered off and recrystallized from an ethanol / acetone = 1/1 (v/v) solution. All complexes were obtained as microcrystalline powders.

## Results and Discussion

*The chemical analysis* of the metal complexes (Table 1) indicates the same molar ratio of M / (L<sup>1</sup>H) / (L<sup>2</sup>H) = 1 / 1 / 1 used in the synthesis.

The chemical reactions of the synthesis have been formulated on the basis of these data for the following coordinative compounds:



**Table 1.** The chemical analysis, melting points, colour and molecular formulas of the metal complexes

Compounds	C %	H %	N %	M %	Melting points (°C)	Colour
[Ni(L <sup>1</sup> )(L <sup>2</sup> ) <sub>2</sub> ] (1)	(49.92) (48.05)*	(2.60) (3.00)*	(7.28) (7.29)*	(15.23) (15.70)*	315	Brown
[Pd(L <sup>1</sup> )(L <sup>2</sup> ) <sub>2</sub> ] (2)	(44.40) (45.02)*	(2.31) (2.01)*	(6.47) (6.40)*	(24.6) (24.95)*	325	Orange
[Pt(L <sup>1</sup> )(L <sup>2</sup> ) <sub>2</sub> ] (3)	(36.84) (36.22)*	(1.91) (1.82)*	(5.37) (5.92)*	(37.44) (37.05)*	341	Brown greenish
[Cu(L <sup>1</sup> )(L <sup>2</sup> ) <sub>2</sub> ] (4)	(49.29) (49.00)*	(2.56) (2.15)*	(7.18) (7.21)*	(16.30) (16.85)*	297	Greenish brown

( ) theoretical data, ( \* ) experimental data.

### The IR spectral data

The free ligands IR spectra show in 4000 – 2000 cm<sup>-1</sup> region intense, broad absorption bands corresponding to intramolecular hydrogen bonding as it follows: for the (L<sup>1</sup>H) a band at 3400 cm<sup>-1</sup> which belongs to the hydrogen bonding (O-H...O) while for the (L<sup>2</sup>H) a band near 3200 cm<sup>-1</sup> that was assigned to intramolecular hydrogen bonding (N-H...O). In the coordinative compounds these bands disappear.

The IR spectra of all complexes (Table 2) indicate that for the ligand L<sup>1</sup>H the N=O group is involved in bond formation. This fact is supported by the shift of the  $\nu(\text{N}=\text{O})$  frequency from 1565 cm<sup>-1</sup> in the free ligand to 1545 cm<sup>-1</sup> in the complexes [8, 9]. The  $\nu(\text{C}-\text{O})$  frequency of the OH group is also shifted to the lower frequency in the complexes (1320 – 1250 cm<sup>-1</sup>) and the absence of a band at 3400 cm<sup>-1</sup> due to an OH group in the spectra of the complexes suggests the coordination through the oxygen of the hydroxyl group.

**Table 2.** The IR spectral data in the wave number (cm<sup>-1</sup>) of the free ligands and their metal complexes

Compounds	L <sup>2</sup> H	L <sup>1</sup> H	(1)	(2)	(3)	(4)
Assignments						
$\nu(\text{OH}\dots\text{O})$		3400 vs				
$\nu(\text{NH}\dots\text{O})$	3200 s					
$\delta(\text{NH})$ amino acid I	1665 s	–	–	–	–	–
$\nu(\text{N}=\text{O})$	–	1565 s	1545 m	1542 m	1540 m	1545 m
$\delta(\text{NH})$ amino acid II	1552 m	–	–	–	–	–
$\nu(\text{OCO})$	1400 s	–	1325 m	1324 m	1325 m	1328 m
$\nu(\text{C}-\text{OH})$ (coumarin)		1320 s	1300 s	1290 s	1250 s	1300 s
$\nu(\text{M}-\text{N})$	–	–	565 m	590 m	575 m	550 m
$\nu(\text{M}-\text{O})$	–	–	469 m	521 m	492 m	450 m

The free antranilic acid shows a strong band around 1665 cm<sup>-1</sup> and a medium band at 1552 cm<sup>-1</sup> assigned to  $\delta(\text{NH})$  amino acid I and  $\delta(\text{NH})$  amino acid II respectively. These bands disappeared in the complexes, but the band corresponding to  $\nu(\text{COO})$  in the free amino acid at 1410 cm<sup>-1</sup> is shifted in the complexes at 1325 cm<sup>-1</sup> assigned to  $\nu(\text{COO})$

coordinated group. New bands corresponding to  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$  are also present in all the complexes spectra in the  $590\text{-}450\text{ cm}^{-1}$  range.

Thus, the infrared spectra clearly confirm the formation of the complexes and the donor sites in the ligands.

*The electronic absorption spectra and the effective magnetic moments* measurements of the complexes further elucidate the nature and the symmetry of the tetracoordinated complexes (Table 3). The assignments are in agreement with the literature data [10÷12].

**Table 3.** The assignments of the electronic absorption spectra in the wave number ( $\text{cm}^{-1}$ ) and the effective magnetic moments [BM] of the complexes

Complexes	$\mu_{\text{eff}}$ [BM]	$\nu_{\text{max}}$ ( $\text{cm}^{-1}$ )	Assignments
[Ni(L <sup>1</sup> )(L <sup>2</sup> )] (1)	0	21050 24390 27030	<sup>1</sup> A <sub>2</sub> ← <sup>1</sup> A <sub>1</sub> <sup>1</sup> B <sub>1</sub> ← <sup>1</sup> A <sub>1</sub> <sup>1</sup> A <sub>2</sub> ← <sup>1</sup> A <sub>1</sub>
[Pd(L <sup>1</sup> )(L <sup>2</sup> )] (2)	0	18900 24000 28200	<sup>1</sup> A <sub>2</sub> ← <sup>1</sup> A <sub>1</sub> <sup>1</sup> B <sub>1</sub> ← <sup>1</sup> A <sub>1</sub> <sup>1</sup> E ← <sup>1</sup> A <sub>1</sub>
[Pt(L <sup>1</sup> )(L <sup>2</sup> )] (3)	0	20000 26000 29400	<sup>1</sup> A <sub>2</sub> ← <sup>1</sup> A <sub>1</sub> <sup>1</sup> B <sub>1</sub> ← <sup>1</sup> A <sub>1</sub> <sup>1</sup> E ← <sup>1</sup> A <sub>1</sub>
[Cu(L <sup>1</sup> )(L <sup>2</sup> )] (4)	1.88	10900 13100 14300	<sup>2</sup> A <sub>2</sub> ← <sup>2</sup> A <sub>1</sub> <sup>2</sup> B <sub>2</sub> ← <sup>2</sup> A <sub>1</sub> <sup>2</sup> B <sub>1</sub> ← <sup>2</sup> A <sub>1</sub>

The electronic spectra and magnetic data correspond to a square planar geometry for all metallic ions.

We have calculated the ligand field parameters for the platinum complex [Pt(L<sub>1</sub>)(L<sub>2</sub>)] according to the literature data [11]. The bands of the electronic spectrum were labelled with:

$$({}^1\text{A}_2 \leftarrow {}^1\text{A}_1) = \Delta\text{A} (\nu_4); \Delta\text{A} = -35 \text{ F}_4 - 10 \text{ D}_q$$

$$({}^1\text{B}_1 \leftarrow {}^1\text{A}_1) = \Delta\text{B} (\nu_5); \Delta\text{B} = -71 \text{ F}_4 - 4 \text{ D}_s - 5 \text{ D}_t$$

$$({}^1\text{E} \leftarrow {}^1\text{A}_1) = \Delta\text{E} (\nu_6); \Delta\text{E} = 62 \text{ F}_4 - \text{D}_q - 3 \text{ D}_s + 5 \text{ D}_t$$

A  $\text{D}_{4h}$  ligand field is characterized by the following parameters:

$$4 \text{ D}_q + 7 \text{ D}_t = 0; \text{F}_4 = 85 \text{ cm}^{-1};$$

So the relationships become:

$$\Delta\text{A} = -35 \text{ F}_4 - 10 \text{ D}_q;$$

$\Delta\text{A}(\nu_4) \text{ D}_q = -2187.5 \text{ cm}^{-1}$  / comparable with the value  $\text{D}_q = -2848 \text{ cm}^{-1}$  for  $[\text{Pt}\{\text{NH}_3\}_4]^{2+}$  mentioned by the literature data [9] as a square-planar complex.

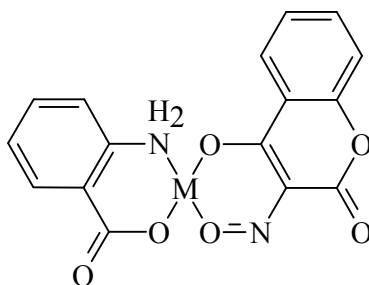
$$\Delta\text{B} = -71 \text{ F}_4 - 20/7 \text{ D}_q - 4 \text{ D}_s; \Delta\text{B}(\nu_5) \text{ D}_s = -5475.75 \text{ cm}^{-1}$$

$$\Delta\text{E} = 62 \text{ F}_4 - 90/7 \text{ D}_q - 3 \text{ D}_s; \Delta\text{E}(\nu_6) \text{ D}_s = 1049 \text{ cm}^{-1}$$

The different values of  $D_s$  computed with these data ( $\nu_5$ ) and ( $\nu_6$ ) of the our spectrum were explained as results of these bands  $24000\text{cm}^{-1}$  and  $29000\text{cm}^{-1}$  that include the forbidden spin transitions  ${}^3B_{1g} \leftarrow {}^1A_{1g}$  and  ${}^3E_g \leftarrow {}^1A_{1g}$ .

A very important conclusion in this case is the fact that the competition between the cation and the organic part of the ligands for the geometry of the complex has been won by the Pt(II) cation. We supposed that it is a result of a more covalent interaction metal-ligand of the Pt(II) cation.

On the basis of these arguments the following structural formula were proposed (Fig. 1).



**Fig. 1.** The proposed formula of the tetracoordinated complexes  
M = Ni(II), Pd(II), Pt(II), Cu(II)

## Conclusions

The tetracoordinated complexes of Ni(II), Pd(II), Pt(II), Cu(II) showed a constant square planar geometry. This geometry is a very stable one for Pd(II) and Pt(II) while Ni(II) and Cu(II) are usually hexacoordinated. We explained this behaviour as a consequence of the presence of five condensed rings with 6 atoms around the metallic cations. On the other hand, the angles of a six membered ring fit probably very well the square planar geometry of the coordinated polyhedra and the  $d_{z^2}$  orbital of Ni(II) and Cu(II) cations are probably involved in the  $\pi$  delocalised system by a  $d\pi - p\pi$  interactions and they are not available for an octahedral symmetry. These structures are very promising to be used in a polymeric matrix in order to produce nanostructured devices.

## REFERENCES

1. Sabbatini, N., Guardigli, M. and Lehn, J.-M. (1993) *Coord. Chem. Rev.* **123**, 201-228.
2. Bath A.N. (1982), **Ph.D. Thesis**, University of Delhip. 109-143.
3. Bardwell, D. A., Jeffery, J. C., Jones, P. L., McCleverty, J. A., Psillakis, E., Reeves, Z. and Ward, M. D. (1997) *J.Chem.Soc., Dalton Trans.* 2079-2086.
4. Berlin, A. and Robinson, R. J. (1962) *Anal.Chim.Acta.* **27**, 50-57.
5. Karyawnis, N. M., Pytewcki, L. L. L. and Mikulski, C. M. (1973) *Coord.Chem.Rev.* **11**, 93-102.
6. Tutt, L. W. and Kost, A. (1992) *Nature* **356**, 225-230.

7. Danilov, O. B. and Sidorov, A. I. (2000) *J. Opt. Techn.* **67**(6), 31-35.
8. Singh, H., Srivasyava and S., Maheshwari, S. (1982) *Termochimica Acta* **57**, 396-401.
9. Saxena, R. C. and Kela, R. K. (1983) *J. Ind. Chem. Soc.* **LX**, 783-788.
10. Binnar, R. and Preti C. (1975) *J. Nuclear Chem.* **37**, 1681-1687.
11. Negoiu, D., Calinescu, M., Emandi, A. and Badau E. (1999) *Russ. J. Coord. Chem.* **25**(1), 36-41.
12. Solomon, E. I. and Lever, A. B. P. (1999) *Inorganic Electronic Structure and Spectroscopy*, vol I, John Wiley and Sons, New York, 32-55.