SYNTHESIS AND CHARACTERISATION OF SOME NEW
COMPLEXES OF Ni(II), Cu(II), Zn(II), Cd(II) AND Hg(II) WITH
MIXED LIGANDS (NITROGEN, OXIGEN) DONOR GROUPS

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abstract: Some new tetracoordinated Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) complexes with the
Schiff base derived from 5-formyl vanillin and sulphanilamide (AH) and
1-(2’-benzthiazolyl)-3-methyl-pyrazol-5-one (BH) have been synthesized and characterized.
The complexes were formulated as mononuclear species with the general formula [MAB] on the
basis of chemical analyses, molar conductance and IR spectral data. The stereochemistry of the
complexes has been proposed on the basis of electronic data. The magnetic moments at room
temperature agree with the proposed stereochemistry.

keywords: Complexes of Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), 5-formyl vanillin,
sulphanilamide, C_{11}H_{9}N_{3}O 1-(2’-benzthiazolyl)-3-methyl-pyrazol-5-one.

Introduction

Schiff bases have received renewed attention in the recent years due to their proved
antitumoral activities [1-4].

Complexes with mixed ligands, a Schiff base derived from 5-formyl vanillin and
sulphanilamide (AH) and different amines have been reported [5]. However, complexes with
the Schiff base AH and 1-(2’-benzthiazolyl)-3-methyl-pyrazol-5-one (BH) had not been
reported. In the present paper we have focused our attention in synthesizing stable complexes
with these ligands that contain beside donor groups, free functional organic groups (-CHO,
CH_{3}O-, -SO_{2}NH_{2}) available for polymerisation with different organic co-monomers.

Such complexes could be used as monomers that can be linked to a polyurethanic matrix by
these functional groups in order to obtain biomaterials with a controlled released of the
metallic cation in the human body.

Experimental

Materials: NiCl_{2}.6H_{2}O, CuCl_{2}.H_{2}O, ZnCl_{2}, CdCl_{2}, HgCl_{2}, EtOH, were purchased from
MERCK LTD, Schiff base were prepared in our organic laboratory by classical method.
Measurement techniques:

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Chemical analyses were performed using a Carlo Erba 1108 analyser. Metallic cations were determined by analytical classical methods.

Magnetic susceptibility measurements were performed by the Faraday method, at room temperature, using Hg[Co(SCN)$_4$] as standard.

Molar conductances of the complexes were measured in dimethylformamide with a Toshniwal conductivity cell having a cell constant 0.5 cm$^{-1}$.

The IR spectra were run with a Perkin Elmer FT-IR Spectrophotometer in the 4000-200 cm$^{-1}$ 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.

The EPR spectrum was recorded on microcrystalline samples at room temperature with a JES ME-3X spectrometer. The field was calibrated using crystalline diphenylpicrylhydrazyl (g=2.0036).

**Synthesis of complexes:**

An identical procedure was adopted for the synthesis of all metal chelates reported. For the sake of brevity only one reaction has been discussed in detail.

(5-formyl vanillin-sulphanilamide) – nickel (II) chloride: To an ethanolic solution of NiCl$_2$.6H$_2$O (2.376g, 10mmol) was added an ethanolic solution of Schiff base (3.34g, 10mmol) and 1-(2’-benzthiazolyl)-3-methyl-pyrazol-5-one) (1.99g, 10mmol). The reaction mixture (~50ml) was refluxed for 2h and reduced to one third of its volume. On cooling, a brown reddish crystal was obtained and recrystallised from 95% ethanol.

**Results and Discussion**

The reaction of metal chloride with Schiff base (AH: C$_{15}$H$_{14}$N$_2$O$_5$S and 1-(2’-benzthiazolyl)-3-methyl-pyrazol-5-one) (BH: C$_{11}$H$_{9}$N$_3$O) may be depicted as:

\[
\text{MCl}_2 + C_{15}H_{14}N_2O_5S + C_{11}H_9N_3O \rightarrow [M(C_{15}H_{13}N_2O_5S)(C_{11}H_8N_3O)] + 2\text{HCl}
\]  

where M: Ni(II), Cu(II), Zn(II), Cd(II), Hg(II).

The chemical analyses (Table 1) indicate a 1:1:1 (M : AH : BH) stoichiometry for all complexes. The complexes are stable in DMSO, dimethylformamide, and acetone. The molar conductance values of 0.001M solutions of the complexes in DMF indicate non-electrolyte behaviour in this solvent [6, 7].

**The IR spectral data**

The infrared spectra (Table 2) of the free ligands are mainly modified after complexation in the ranges corresponding to the vibration modes characteristically to the azomethinic and phenolic group as is depicted in the Fig. 1. The Schiff base derived from 5-formyl vanillin and sulphanilamide exhibits two strong bands at 1600 cm$^{-1}$ ($\nu$(C= N)) and 1269 cm$^{-1}$ ($\nu$(C-OH)) and a broad absorption band near 3400 cm$^{-1}$ that is assigned to the intramolecular hydrogen bonding (O-H…N) that disappear after complexation [8]. The first
two bands are found to be shifted to lower frequencies in the spectra of the corresponding metal complexes indicating the involvement of C=N and OH groups in complexation [9-10].

**Table 1.** Analytical and Physical Data of Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>m. p. [°C]</th>
<th>Analysis %: calc./found</th>
<th>ΛM [Ω⁻¹ cm² mole⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(C₁₅H₁₃N₂O₇S)(C₁₁H₈N₂O)] (1)</td>
<td>205</td>
<td>9.94 (9.90)</td>
<td>52.97 (52.01)</td>
</tr>
<tr>
<td>[Cu(C₁₅H₁₃N₂O₇S)(C₁₁H₈N₂O)] (2)</td>
<td>216</td>
<td>10.69 (10.52)</td>
<td>52.52 (52.10)</td>
</tr>
<tr>
<td>[Zn(C₁₅H₁₃N₂O₇S)(C₁₁H₈N₂O)] (3)</td>
<td>232</td>
<td>10.95 (10.88)</td>
<td>52.32 (52.30)</td>
</tr>
<tr>
<td>[Cd(C₁₅H₁₃N₂O₇S)(C₁₁H₈N₂O)] (4)</td>
<td>240</td>
<td>17.46 (17.40)</td>
<td>48.49 (42.30)</td>
</tr>
<tr>
<td>[Hg(C₁₅H₁₃N₂O₇S)(C₁₁H₈N₂O)] (5)</td>
<td>252</td>
<td>28.06 (28.00)</td>
<td>42.26 (42.15)</td>
</tr>
</tbody>
</table>

**Table 2.** Important IR bands (cm⁻¹) of 5-formylvanillic-sulfanylamide and 1-(2'-benzthiazolyl)-3-methyl-pyrazol-5-one and their metal complexes

<table>
<thead>
<tr>
<th>AH</th>
<th>BH</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400m</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>v OH-N</td>
</tr>
<tr>
<td>1678s</td>
<td>1650s</td>
<td>1650s</td>
<td>1655m</td>
<td>1660m</td>
<td>1660m</td>
<td>v C=O</td>
<td></td>
</tr>
<tr>
<td>1600s</td>
<td>1590m</td>
<td>1590m</td>
<td>1570m</td>
<td>1510</td>
<td>1520m</td>
<td>v C=N</td>
<td></td>
</tr>
<tr>
<td>1269s</td>
<td>1210m</td>
<td>1205m</td>
<td>1210m</td>
<td>1230m</td>
<td>1240m</td>
<td>v C-OH</td>
<td></td>
</tr>
<tr>
<td>1141-1156 s</td>
<td>1096w</td>
<td>1098w</td>
<td>1096w</td>
<td>1096w</td>
<td>1098w</td>
<td>v benzothiazolic ring</td>
<td></td>
</tr>
<tr>
<td>580w</td>
<td>580w</td>
<td>590w</td>
<td>590w</td>
<td>620wy</td>
<td>v M-N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>420w</td>
<td>420w</td>
<td>440w</td>
<td>440w</td>
<td>450w</td>
<td>v M-O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 1.** The frequencies of the organic groups of the free ligands before complexation

The bands corresponding to the pyrazolone derivative 1-(2'-benzthiazolyl)-3-methyl-pyrazol-5-one undergoes two main shifts to lower wavenumbers in complexes. One of them is the band assigned to v(C=O) and the other strong band is the benzothiazolic ring, which suggests that the carbonylic oxygen and the benzothiazolic nitrogen are involved in

**The electronic absorption spectra**

The electronic spectra of Ni(II) complex (Table 3), show multiple visible bands. Since the effective magnetic moment, $\mu_{\text{eff}}$, is around 2.91 BM we assigned the band at 16 755 cm$^{-1}$ to $^{3}T_{1}(^{3}P)\rightarrow^{3}T_{1}(^{3}F)$ ($v_{3}$) transition and the band 24 300 cm$^{-1}$ to a charge transfer band in a tetrahedral geometry around Ni(II) cation [13].

The Cu(II) complex (Table 3) shows in the range 10000–15000 cm$^{-1}$ three bands (10900 cm$^{-1}$, 13100 cm$^{-1}$, 14300 cm$^{-1}$) and this range is in good agreement with a square planar field. The assignments were presented in the (Table 3). The effective magnetic moment, $\mu_{\text{eff}}$, is around 1.85 BM and it corresponds to an unpaired electron [14].

The Zn(II), Cd(II), Hg(II) complexes are presumable tetrahedral and show bands in the visible region that lie in the range of 24 000 – 14 500 cm$^{-1}$ and were assigned as CT charge transfer bands [15].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption maxima (cm$^{-1}$)</th>
<th>Assignement</th>
<th>$\mu_{\text{eff}}$ (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>16 755</td>
<td>$^{3}T_{1}(^{3}P)\leftrightarrow^{3}T_{1}$</td>
<td>2.91</td>
</tr>
<tr>
<td></td>
<td>24 300</td>
<td>CT</td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td>10 900</td>
<td>$^{2}A_{2g}\leftrightarrow^{2}A_{1g}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13 100</td>
<td>$^{2}B_{1g}\leftrightarrow^{2}A_{1g}$</td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td>14 300</td>
<td>$^{2}B_{1g}\leftrightarrow^{2}A_{1g}$</td>
<td>1.85</td>
</tr>
</tbody>
</table>

The RPE spectrum of the Cu(II) complex gave the experimental values $g_{\parallel} = 2.335$ and $g_{\perp} = 2.062$ that are in good agreement with the theoretical g values accounted from the electronic data:

$$g_{\parallel} = 2.0023 - \frac{8\lambda}{\Delta E(B1g - B2g)} = 2.502 \quad \text{and}$$

$$g_{\perp} = 2.0023 - \frac{2\lambda}{\Delta E(Eg - B1g)} = 2.112$$

The literature data underline that the value $g_{\parallel} < 2.3$ corresponds to a covalent bond Cu – ligand and $g_{\parallel} > 2.3$ corresponds to an ionic interaction Cu – ligand. If we compared the experimental and the theoretical data of $g_{\parallel}$ we conclude that the Cu(II) is in the border between the covalent and ionic interaction. We have also calculated the $G$ value using the experimental values $g_{\parallel}$ and the relationship of $G$ factor according to the literature data [16-18].

$$G = \frac{g_{\parallel} - 2.002}{g_{\perp} - 2.002}$$

The literature [11] data have mentioned a more ionic interaction metal-ligand and a weak field for the $G \geq 4$. It was obtained $G = 4.5$, which also corresponds to the limit situation between the covalent and ionic interaction. We proposed the general formula (Fig. 2):
Conclusions

The tetracoordinated Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) complexes of the Schiff base derived from 5-formyl vanillin and sulphanilamide and 1-(2-benzthiazolyl)-3-methylpyrazol-5-one have been synthesised and characterised in order to establish the synthesis method and the symmetry of the ligand field. The complexes are very stable in time at the room temperature and the normal pressure and the electronic spectra and the magnetic susceptibilities agree with a tetrahedral stereochemistry for Ni(II), Zn(II), Cd(II), Hg(II) and a square planar one for Cu(II).

The presence of uncoordinated carboxylic and sulphonamidic groups in the structures of complexes confers them the ability of implication in co-polymerisation reaction with different polyuretanic units in order to obtain different metal complex biomaterials. The works for obtaining this type of species are in progress in our laboratory.

REFERENCES