Some Transitional Metal Complexes of 4-dimethylaminobenzilidene-2 mercaptoaniline

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Transitional metal complexes, with the ligand 4-dimethylaminobenzilidene-2-mercaptoaniline, by template synthesis, type: \([M (HL) Cl x \cdot H_2O], M = Cu(II) \text{ and } x = 2; \ [M (L) (H_2O) y \cdot H_2O], M = \text{Ni (II)} \text{ and } x = 1; \ [M (L)_2] x \cdot H_2O, M = \text{Zn (II)} \text{ and } y = 1 \text{ and } M = \text{Cd (II)} \text{ and } x = 0\) were obtained. Complexes were characterized using physico-chemical methods such as: elemental analysis, IR, UV-Vis and 1H-NMR spectroscopy, electric conductivity, magnetic susceptibility and thermogravimetric determinations. The ligand acts as bidentate monoanionic NS ligand, for ions Ni (II), Zn(II) and Cd(II) and as bidentate neutral NS ligand for Cu(II) ions. The Cu(II) and Ni(II) complexes, have octahedral geometry and Zn (II) and Cd (II) tetrahedral geometry.

Keywords: Schiff base, complex, template synthesis, o-aminobenzenethiol, 4-dimethylaminobenzaldehyde.

Aldehydes condensation with o-aminothiofenol (o-aminobenzenethiol or 2-mercaptoaniline), yields the Schiff base and/or benzothiazoline. Benzothiazoline is the unexpected product and appear by a new organic cycle close reaction [1, 2].

In solution Schiff base and benzothiazoline are in equilibrium and adding metallic salts, only the Schiff base complexes are obtained. Metallic ions, induces the rearrangement of the benzothiazolines to Schiff bases complexes [3-5]. The literature specifies a lot of synthesis methods: 1. reactions of metallic ions with Schiff bases [2, 15, 16]; 2. reactions of aldehydes with metallic o-aminobenzothiazol complexes [4]; 3. reactions of metallic ions with benzothiazolines [3, 17]; 4. template synthesis (aldehydes and o-aminobenzothiazol), were adding concomitantly in the metallic salts solutions [12, 15]. In this work we used template synthesis.

Experimental part
Materials and methods

All chemicals used for synthesis were analytical grade. Inorganic and organic reactives, DMF, DMSO, were Merk, S.C.Pam.Corporation and Andra Chem. Bucharest products. Elemental analysis, was determined with a combustion system at Costech instrument ECS-4010 and 1H-NMR spectroscopy. Electronic spectra (1500-200 nm) were performed with Jasco V670 UV-Vis-NIR Spectrophotometer. Magnetic susceptibility was determined using a Faraday’s method. Thermogravimetric analysis of complexes was performed using TGA/SDTA 851- Mettler Toledo Derivatograph, in temperature range 25-1000°C, at heating rate 10°C/min, under synthetic dynamic air.

Synthesis of the ligand
A solution (3 mmol, 60 mL benzene) of 4-dimethylaminobenzaldehyde, was added stirring permanently to a solution (3 mmoli, 30 mL benzene) of o-aminobenzethiol. The mixture, was refluxed 7 h on water bath then, was reduced to 1/2 from initial volume by distillation. After cooling, a yellow solid, was obtained. The compound was filtered, washed several times with benzene and diethyl ether and dried on CaCl2 in a desiccator. Elemental analysis for ligand: \(C_{70.31}H_{6.25}N_{10.93}S\), % calc(exp): C:70.31(69.80): H:6.25(6.15); N:10.93(10.59).

Synthesis of CuC3H30H3O3N4S2Cl2 (1) complex
A solution (2 mmol, 10 mL ethanol 45°C) of o-aminobenzethiol and a solution (2 mmol, 30 mL ethanol 45°C) of 4-dimethylaminobenzaldehyde, were added concomitantly, under stirring, at a solution (1 mmol CuCl2, 2H2O, 40 mL ethanol at 70-75°C) of Cu(II) chloride. After cooling, a brown compound was formed. The compound was filtered, washed several times with ethanol and diethyl ether and dried on CaCl2 in a desiccator.

Synthesis of the NiC3H30H3O3N4S2Cl2 (2) complex
A solution (2 mmol, 30 mL ethanol) of 4-dimethylaminobenzaldehyde, was added under stirring at a solution (2 mmol, 20 mL ethanol) of o-aminobenzethiol. The mixture was refluxed 30 min on a water bath. A solution (1 mmol NiCl2, 6H2O, 35 mL ethanol) of Ni(II) chloride was added to refluxed mixture. After cooling, the pH was adjusted to 6 – 6.5 with some drops of saturated lithium hydroxide solution. The mixture was refluxed 1h on the water bath. After cooling the complex was filtered, washed several times with ethanol and diethyl ether and dried on CaCl2 in a desiccator.
Synthesis of the ZnC$_{30}$H$_{32}$ON$_4$S$_2$ (3) complex

A solution (2 mmol, 30 mL ethanol) of 4-dimethylaminobenzaldehyde, was added under stirring to a solution (2 mmol, 20 mL ethanol) of o-aminobenzenethiol. The mixture was refluxed 30 min on the water bath. A solution (1 mmol, 25 mL ethanol) of ZnCl$_2$ was added. The new mixture was refluxed 1 h on the water bath, and reduced to 1/3 by distillation. The product was filtered and dried in air. By recrystallization from ethanol, an orange-red complex was obtained.

Synthesis of CdC$_{30}$H$_{30}$N$_4$S$_2$ (4) complex

A solution (2 mmol, 30 mL ethanol) of 4-dimethylaminobenzaldehyde, was added under stirring, to a solution (2 mmol, 20 mL ethanol) of o-aminobenzenethiol. The mixture, was refluxed 30 min on the water bath. A solution (1 mmol, 25 mL ethanol) of CdCl$_2$ . 2 . 1/2H$_2$O, was added. The new mixture was refluxed 1 h on the water bath, and reduced to 1/3 by distillation. The product was filtered and dried in air. By recrystallization from ethanol, an orange-red complex was obtained.

Results and discussions

Structural formula and $^1$H-NMR spectrum of ligand, are presented in figure 1. In the $^1$H-NMR spectrum of ligand, the signal assigned to hydrogen of azomethinic group, appear at 8.345 ppm, confirming that the ligand is a Schiff base. Aromatic protons signals, appear as multiplet in 6.8-8.2 ppm range and the CH$_3$ groups protons signals, appear near 3.00 ppm value [13].

Elemental analysis data and some physical properties of ligand and complexes, are presented in table 1. Elemental analysis suggests M(II):L of 1:2 stoechiometry for all complexes.

Complexes are insoluble in common organic solvents but soluble in DMF and DMSO. They are colored solids and decompose at higher 250-300°C temperatures. Molar conductance values (10$^{-3}$ M, in DMF at 20°C), suggests that complexes are nonelectrolytes [7, 8, 21].

IR spectra

The IR data (4000-400 cm$^{-1}$) of the ligand and the complexes, are presented in table 2. In order to determinate the coordination mode of ligand, the IR spectra of the complexes were compared with the corresponding spectra of the ligand [16]. The stretching vibration band
νC=N, appears in IR spectrum of ligand, at 1600 cm⁻¹. This band was shifted to lower wave numbers, in the IR spectra of complexes 1-2. The same band was shifted to higher wave numbers, in IR spectra of complexes 3 and 4. This shifting suggests the participation of the azomethinic nitrogen in coordination [18,19]. New bands, in the spectra of complexes in the region 506-539 cm⁻¹, assigned to νM-N mode of vibration confirm the coordination of the azomethinic nitrogen [25, 26].

The νC-S sim. and νC-S asym. stretching vibrations bands, appear in ligand spectrum at 756 cm⁻¹ and 729 cm⁻¹ respectively. These bands were shifted to lower wavenumbers in the IR spectra of complexes 2-4. The same bands were shifted to higher wavenumbers in the IR spectra of the complex 1. Theses shifting mode of vibration confirm the coordination of the azomethinic nitrogen [25, 26].

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Electronic spectra

Absorption bands in region UV-Vis of ligand and complexes are presented in table 3. The electronic spectrum of ligand presents two intense absorption bands, at 32258 cm⁻¹ (310 nm) and 25641 cm⁻¹ (390 nm), assigned to transitions π → π* and n → π*. The ligand spectrum presents a weak intensity band at 18181 cm⁻¹ (550 nm), assigned to a CT transition. These bands appear shifted in the complexes spectra confirming the coordination of ligand to metallic ions. Complexes bands superpose on the CT band of ligand [16] (table 3).

The electronic spectrum of complex 1, presents a broad week intensity band, in region 16600-10526 cm⁻¹ (600-950 nm), centered to 12903 cm⁻¹ (775 nm), assigned to a LMCT transition [11, 24, 33].

Table 2

<table>
<thead>
<tr>
<th>Nr. Comp.</th>
<th>Compound</th>
<th>$ν_{OH}$</th>
<th>$ν_{C=N}$</th>
<th>$γ_{OH}$</th>
<th>$ν_{C-S}$ sim</th>
<th>$ν_{C-S}$ asym</th>
<th>$ν_{M-N}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$C_3H_6N_2S$</td>
<td>-</td>
<td>1600</td>
<td>-</td>
<td>756</td>
<td>729</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>$C_3H_6O_2N_4S_2Cl_2$</td>
<td>3356</td>
<td>1588</td>
<td>-</td>
<td>759</td>
<td>-</td>
<td>517</td>
</tr>
<tr>
<td>3.</td>
<td>$C_3H_6O_2N_4S_2$</td>
<td>3444</td>
<td>1592</td>
<td>865</td>
<td>747</td>
<td>720</td>
<td>506</td>
</tr>
<tr>
<td>4.</td>
<td>$C_3H_6O_2N_4S_2$</td>
<td>3434</td>
<td>1607</td>
<td>-</td>
<td>753</td>
<td>722</td>
<td>510</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Nr. Comp.</th>
<th>Compound</th>
<th>Absorption maxime $nm 	imes cm^{-1}$</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_3H_6N_2S$</td>
<td>32258(310)</td>
<td>π → π*</td>
</tr>
<tr>
<td></td>
<td>$C_3H_6O_2N_4S_2Cl_2$</td>
<td>24691(405) sh</td>
<td>n → π*</td>
</tr>
<tr>
<td></td>
<td>$C_3H_6O_2N_4S_2$</td>
<td>21050(465) sh</td>
<td>M-C-T</td>
</tr>
<tr>
<td></td>
<td>$C_3H_6N_2S$</td>
<td>30769(325) sh</td>
<td>π → π*</td>
</tr>
<tr>
<td></td>
<td>$C_3H_6O_2N_4S_2Cl_2$</td>
<td>25000(400)</td>
<td>n → π*</td>
</tr>
<tr>
<td></td>
<td>$C_3H_6O_2N_4S_2$</td>
<td>18691(355)</td>
<td>LMCT</td>
</tr>
<tr>
<td></td>
<td>$C_3H_6O_2N_4S_2$</td>
<td>12269(815)</td>
<td>π → π*</td>
</tr>
<tr>
<td></td>
<td>$C_3H_6O_2N_4S_2$</td>
<td>9090(1100)</td>
<td>n → π*</td>
</tr>
<tr>
<td></td>
<td>$C_3H_6O_2N_4S_2$</td>
<td>32786(305)</td>
<td>π → π*</td>
</tr>
<tr>
<td></td>
<td>$C_3H_6O_2N_4S_2$</td>
<td>27397(365)</td>
<td>n → π*</td>
</tr>
<tr>
<td></td>
<td>$C_3H_6O_2N_4S_2$</td>
<td>23656(430)</td>
<td>π → π*</td>
</tr>
</tbody>
</table>

Table 2

SIGNIFICANT IR BANDS (4000 – 400 cm⁻¹) OF LIGAND (HL) AND COMPLEXES

Table 3

ABSORPTION BANDS IN REGION UV – Vis OF LIGAND AND COMPLEXES
The electronic spectrum of complex 2 presents the absorption bands: 18691 cm⁻¹ (535 nm); 12261 (815 nm); 9090 cm⁻¹ (1100 nm) assigned to transitions: \(^3\text{A}_2 \rightarrow ^3\text{T}_1\text{(P)}\); \(^3\text{A}_2 \rightarrow ^3\text{T}_1\text{(F)}\) and \(^3\text{A}_2 \rightarrow ^3\text{T}_2\), suggesting an octahedral geometry for Ni (II) ions. The magnetic moment value of complex is in agreement with this geometry [28, 31, 34].

The electronic spectra of complexes 3 and 4 present absorption bands in range: 28571-22988cm⁻¹ (350-435nm) and 27397-23655cm⁻¹ (365-430nm) respectively. Tetrahedral geometry was proposed for this complexes, according to elemental analysis, thermal analysis, IR spectroscopy, molar conductance and special literature [7, 12, 15].

**Thermal analysis**

The thermogravimetric curves TG, DTG and DTA of complexes are presented in figure 2 and decomposition steps in table 4. The thermogravimetric curves, indicates the presence of crystallisation and coordination water in complexes.

Complex 1 decomposes in three exotherm steps. The first mass loss of 5.27% in temperature range 50-120°C, was assigned to removal of two crystallisation water molecules. The followed mass loss estimated at 20.0%, with a molar mass 140.0, in temperature range 120-420°C, is assigned to partial decomposition of complex, releasing two molecules of hydrochloric acid and two molecules of sulfhidric acid. The last step in range 420-610°C with mass los 59.43%, may be regarded as a final decomposition of ligand, leaving CuO residue. Total mass loss of complex 1 at thermal decomposition was 84.70% [14, 16].

Complex 2 decomposes in three stages. The first mass loss of 2.88% in temperature range 50-120°C is assigned to the removal of one crystallisation water molecule. The second mass loss of 5.77% in range 110-250°C is
assigned to removal of two coordination water molecules. The third mass loss, in the temperature range 250-760°C, is of 49.10%, and is assigned to decomposition of ligand, leaving NiO as residue [16].

The dehydration of complex 3 occurs in the range 50-150°C corresponding to loss of one water molecules. The ligand decomposes in two stages. The first stage, in temperature range 150-320°C is assigned to ligand decomposition. The second step in temperature range 320-644°C is assigned to the final decomposition of ligand, leaving ZnO as residue.

The dehydration of complex 3 occurs in two steps. The TG curve shows that, the complex does not include water. The first step in temperature range 50-317°C presenting 32.00% mass loss, is attributed to the decomposition of ligand. The second step in range 317-644°C presenting 52.77% mass loss is attributed to final decomposition of the ligand, leaving CdO as residue.

Proposed formulae of complexes, are in good agreement, with the thermal analysis results. We proposed the complexes formulae from scheme 1.

Conclusions

Four new complexes of transitional metals Cu (II), Ni (II), Zn (II) and Cd (II) with 4-dimethylaminobenzilidene-2-mercaptoaniline, by template synthesis, at molar ratio M(II):SB of 1:2 were obtained. The ligand behaves as bidentate NS ligand, coordinating by azomethinic nitrogen and thiofenolic sulphur. The ligand acts as neutral ligand for Cu (II) ion and as monoanionic ligand for Ni (II), Zn (II) and Cd (II) ions. Analyses results suggesting octahedral geometry for Cu (II), and Ni (II) complexes and tetrahedral for Zn (II) and Cd (II) complexes.

References

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