SYNTHESIS AND PHYSICO-CHEMICAL CHARACTERIZATION OF ZINC(II), NICKEL(II) AND COBALT(II) COMPLEXES WITH 2-PHENYL-2-IMIDAZOLINE

Sanja O. Podunavac-Kuzmanović and Ljiljana S. Vojinović

Chlorides and nitrates of zinc(II), nickel(II) and cobalt(II) react with 2-phenyl-2-imidazoline to give complexes of the type \([ML_2X_2]nH_2O\) (M=Zn, Ni or Co; L=2-phenyl-2-imidazoline; \(X=Cl\) or \(NO_3\); \(n=0, 1\) or \(2\)). The complexes were synthesized and characterized by elemental analysis of the metal, molar conductivity, magnetic susceptibility measurements and IR spectra. The molar conductances of the zinc(II) complexes in DMF solutions indicate that the complexes behave as non-electrolytes. The values of magnetic conductivity in the case of nickel(II) complexes indicate that one of the coordinated anions (chloride or nitrate) has been replaced by DMF molecule. The molar conductivity values of cobalt(II) complexes indicate the partial substitution of coordinated anions with solvent molecules. The room temperature effective magnetic moments and IR data of the complexes suggest that all Zn(II), Ni(II) and Co(II) complexes have a tetrahedral configuration, which is realized by participation of the pyridine nitrogen of two organic ligand molecules, and two chloride or nitrate anions, typical for these classes of organic ligands.

KEY WORDS: imidazoline, complexes, zinc(II), nickel(II), cobalt(II), physico-chemical characterization

INTRODUCTION

Considerable attention has been given to the synthesis of transition metal complexes of imidazoles, benzimidazoles and related ligands because of their therapeutic properties and interesting spectral, magnetic and structural aspects. For example, the complexes with cobalt(II), nickel(II), copper(II), zinc(II) have been used as effective antibacterial agents (1-9). Also, zinc(II) and silver(I) complexes were reported to show antifungal activities.

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Many different benzimidazoles exhibit activities as analgetics, anticarcinogens, sedatives, etc. (12).

We have reported earlier the isolation and characterisation of different metal ion complexes with 2-substituted benzimidazoles. As an extension of our previous studies, some new zinc(II), cobalt(II) and nickel(II) complexes with 2-phenyl-2-imidazoline (Fig. 1) were synthesized and characterised.

![Fig. 1. Structural formula of 2-phenyl-2-imidazoline](image)

**EXPERIMENTAL**

**Reagents**

All chemicals used to prepare the complexes were of analytical reagent grade, commercially available from different sources. The ligand was an *Aldrich* product.

**Synthesis of complexes**

All the complexes were prepared following the same procedure. A solution of 2.5 mmol ZnCl₂, NiCl₂·6H₂O or CoCl₂·6H₂O in 10 cm³ of EtOH was added to a solution of 5 mmol of the ligand (2-phenyl-2-imidazoline (L)) in 10 cm³ EtOH. The resulting mixture was boiled under reflux on a water bath for about 2 h and then cooled. The complexes were separated from the reaction mixture by filtration, washed with EtOH and dried *in vacuo* over CaCl₂. The yield of the complexes varied in the range of 45-50%.

**Measurement methods**

Elemental analysis was carried out by standard micromethods. Magnetic susceptibility measurements were made at room temperature using an MSB-MKI magnetic susceptibility balance (Sherwood Scientific Ltd., Cambridge, England). Molar conductivities of freshly prepared 1×10⁻³ mol dm⁻³ solutions (DMF) were measured on a Jenway 4010 conductivity meter. Infrared spectra (KBr pellets) were recorded on an Infrared 457 Perkin-Elmer spectrophotometer.
RESULTS AND DISCUSSION

The elemental analysis of complexes, magnetic moments and molar conductivity data are summarized in Table 1.

**Table 1.** Some physical characteristics and analytical data of the complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>µ&lt;sub&gt;eff&lt;/sub&gt;(µB)</th>
<th>λ&lt;sub&gt;m&lt;/sub&gt;</th>
<th>Metal Found (Calcd.) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn(L)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>white</td>
<td>4.1</td>
<td>15.25 (15.38)</td>
<td></td>
</tr>
<tr>
<td>[Zn(L)&lt;sub&gt;2&lt;/sub&gt;(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;] × 2H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>white</td>
<td>12.4</td>
<td>12.49 (12.64)</td>
<td></td>
</tr>
<tr>
<td>[Ni(L)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>green</td>
<td>3.35</td>
<td>76.8</td>
<td>13.84 (13.91)</td>
</tr>
<tr>
<td>[Ni(L)&lt;sub&gt;2&lt;/sub&gt;(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;] × H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>gray-green</td>
<td>3.37</td>
<td>82.7</td>
<td>12.12 (11.91)</td>
</tr>
<tr>
<td>[Co(L)&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;] × 2H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>blue</td>
<td>4.46</td>
<td>44.8</td>
<td>12.80 (12.87)</td>
</tr>
<tr>
<td>[Co(L)&lt;sub&gt;2&lt;/sub&gt;(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>blue</td>
<td>4.45</td>
<td>57.2</td>
<td>12.01 (12.42)</td>
</tr>
</tbody>
</table>

* In DMF, 1 mmol dm<sup>-3</sup> solution at 25°C; in S cm<sup>2</sup> mol<sup>-1</sup>

The complexes were synthesized in the reaction of warm ethanolic solution of the MX<sub>2</sub>·nH<sub>2</sub>O (M=Zn, Ni or Co; X=Cl or NO<sub>3</sub>; n=0 or 6) with L in a mole ratio 1:2. It should be noticed that the reaction of all metal ions yielded bis(ligand) complexes.

All the complexes are insoluble or sparingly soluble in common organic solvents such as alcohols or acetone, but highly soluble in dimethylformamide and dimethylsulphoxide.

The molar conductivities of the zinc(II) complexes in DMF solutions fall in the range of 4.1-12.4 Scm<sup>2</sup>mol<sup>-1</sup> (Table 1). The values indicate that the complexes behave as non-electrolytes in DMF (9). The molar conductivities of nickel(II) complexes in DMF solutions fall in the range of 65-90 Scm<sup>2</sup>mol<sup>-1</sup>, corresponding to a 1:1 type of electrolyte (9). It indicates that in the case of [Ni(L)<sub>2</sub>Cl<sub>2</sub>] and [Ni(L)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]·H<sub>2</sub>O one of the coordinated anions (chloride or nitrate) has been replaced by DMF molecule. The molar conductivity values of cobalt(II) complexes (Table 1) are higher compared with the values of non-electrolytes. The same values are considerably lower compared with the molar conductivities of the 1:1 type electrolytes (λ<sub>m</sub>=65-90 Scm<sup>2</sup>mol<sup>-1</sup>) (9), which indicates partial substitution of the coordinated anions with solvent molecules.

**Magnetic properties**

An indication of the most probable geometric configuration of the synthesized Co(II) complexes may be their colour and magnetic moments (Table 1). Namely, the blue cobalt(II) complexes usually have a tetrahedral configuration. The magnetic moment values (Table 1) of the cobalt(II) complexes are in the expected range (4.2-4.7 µ<sub>B</sub>) for tetrahedral stereochemistry (13).

The room temperature effective magnetic moments of the both nickel(II) complexes (Table 1) are in the range which also supports their tetrahedral geometry (13).
Infrared spectra

The infrared spectra of the ligand exhibit a band at 3300-3100 cm\(^{-1}\), assigned to \(\nu(\text{NH})\). The lowering of this band frequency is due to association through the intermolecular hydrogen bonding (14). The band appearing at about 1550 cm\(^{-1}\) may be assigned to \(\nu(C=\text{N})\) vibrations (14). Substituted phenyl group shows ring vibrations at 1485 and 740 cm\(^{-1}\). The infrared spectra of the complexes are similar to those of the corresponding ligands. An upward shift (5-15 cm\(^{-1}\)) of the \(\nu(C=\text{N})\) in the IR spectra of the complexes as compared to theirs values in the free ligand, suggests coordination through the pyridine nitrogen of imidazoline. The other bands in the spectrum of each complex are similar to those in the corresponding ligand spectrum except for slight shifts in their positions and changes in their intensities due to coordination.

The presented results (molar conductivity, magnetic moments, electronic and IR spectra) suggest that all Zn(II), Ni(II) and Co(II) complexes have a tetrahedral configuration which is realized by participation of the pyridine nitrogen of two organic ligand molecules, and two chloride or nitrate anions, typical for these classes of organic ligands (6-9).

CONCLUSIONS

With zinc(II), nickel(II) and cobalt(II) 2-phenyl-2-imidazoline formed complexes of the general formula \([M(L)_2A_2]nH_2O\) (M=Zn, Ni or Co; L=2-phenyl-2-imidazoline; A=Cl or NO\(_3\); n=0, 1 or 2). All the complexes have a tetrahedral configuration, which being realized by coordination of the pyridine nitrogen of the two organic ligand molecules and two chloride or nitrate anions.

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REFERENCES

СИНТЕЗА И ФИЗИЧКО-ХЕМИЈСКА КАРАКТЕРИЗАЦИЈА КОМПЛЕКСА ЦИНКА(II), КОБАЛТА(II) И НИКЛА(II) СА 2-ФЕНИЛ-2-ИМИДАЗОЛИНОМ

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Хлориди и нитрати цинка(II), никла(II) кобалта(II) реагују са 2-фенил-2-имидазолином дајући комплексе типа [ML₂X₂](H₂O)ₙ (M=Zn, Ni или Co; L=2-фенил-2-имидазолин; X=Cl или NO₃; n=0, 1 или 2). Комплекси су синтетисани и окарактерисани елементарном анализом метала, магнетним и кондуктометријским мерењима и IR спектрима. Врло ниске вредности моларне проводљивости за комплексе цинка(II) у ДМФ указују на неелектролитне карактеристике ДМФ раствора комплекса. На основу вредности моларне проводљивости за комплекс никла(II) изводи се закључак да је један од координованих аниона (хлоридни или нитратни) замењен молекулом растварача. Увећане вредности моларне проводљивости за комплекс кобалта(II) у односу на комплексе типа неелектролита су знатно мање од моларних проводљивости за комплексе електролита типа 1:1 и указују на парцијалну замену координованих хлоридних или нитратних јона молекулима растварача. На основу вредности магнетних момента и IR спектара изолованих комплекса цинка(II), никла(II) и кобалта(II) може се претпоставити да испитивани комплекси имају тетраедарску структуру која се реализује монодентатном координацијом два молекула лиганда преко пиридинског атома азота и координацијом два хлоридна или нитратна јона.

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