Preparation and Spectroscopic Studies of Cobalt ((II), Nickel (II), Copper (II), Zink (II), Complexes with Heterocyclic Azo Pyrazolon Derivite

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Abstract: The preparation and characterization of heterocyclic azopyrazolone ligand (Z)-4-(2-(2-hydroxy-5-nitrophenyl) hydrazono)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (H$_2$L$_1$) have been studied by a set of independent methods: IR, $^1$HNMR, ESR, and UV-VIS spectroscopy. The analytical data showed that all chelate complexes were prepared with (ligand:metal) ratio of (1:1). The quantum-chemical modeling (DFT/B3LYP) of organic ligands and complex compounds was performed, and the structures of the metal complexes were proposed.

Keywords: heterocyclic azopyrazolone, IR absorption spectra, $^1$HNMR spectroscopy, ESR spectroscopy

1. Introduction

Azo compounds derived from pyrazolone 5 are well known and widely spread in the textile industry as dyes and pigments for different types of fabrics. The introduction of metals into their composition increase coloristic characteristics and resistant properties.

In nowadays azo dyes have been studied widely because of their excellent thermal and optical properties and applications such as optical recording medium, toner ,ink-jet printing ,and oil-soluble light fast dyes. Recently, they have also attracted attention due to their interesting electronic features in connection with their application for molecular memory storage, nonlinear optical elements and organic photoconductors [1]

Azo compounds are toxic, highly persistent, and ubiquitously distributed in the environments. The large-scale production and application of azo dyes result in serious environmental pollution of water and sediments. Their transformation into metal complexes of low solubility can help in the process of the removal of wastes from water and soils.

2. Experimental

The metal complexes were synthesized by mixing solutions of metal salts and solutions of ligands, (Z)-4-(2-(2-hydroxy-5-nitrophenyl) hydrazono)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (H$_2$L$_1$). The metal to ligand mole ratio was maintained at 1:1.

At the first the Ligand was dissolved in ethanol then the solution of metal salt (3 ml ) was added of slowly in drops with stirring to (3) ml of solution of Ligand with heating in very low temperature. The solution(L+M) was kept on heating until 20-40 minutes (change of color or formation of precipitation) the precipitated metal complexes were filtered by the Centrifuge Then The complexes precipitated were kept aside to complete drying.

To confirm the classical concepts of tridentate chelate coordination 2 hydroxyarylayzopyrazolon-5 using spectral analysis methods in conjunction with quantum-chemical modeling.

3. Results and Discussion

3.1 IR absorption spectra

IR spectra of (H$_2$L$_1$)1644 cm$^{-1}$, which the authors of numerous work attributed to the stretching vibrations of carbonyl groups of strong intramolecular hydrogen bond (Fig. 3.).
The IR spectra of complex compounds, a shift of the absorption bands of carbonyl groups in the region to ligand 1644 cm\(^{-1}\) for \(H_2L^1\). A large amount of offset points that cycle pyrazolone carbonyl group participates in the coordination of the metal and the M-G have a significant degree of covalence. Classification of some of the absorption bands in the IR spectra of ligands and complexes.

<table>
<thead>
<tr>
<th>compound</th>
<th>H2O</th>
<th>NH_OH</th>
<th>CH_ar</th>
<th>CH3</th>
<th>(\nu)(CO)</th>
<th>(\nu)(CN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_2L^1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1644</td>
<td>1597</td>
</tr>
<tr>
<td>(CuL^1\cdot C_2H_5OH)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1592</td>
<td>1582</td>
</tr>
<tr>
<td>(NiL^1\cdot 2H_2O)</td>
<td>3360</td>
<td></td>
<td></td>
<td></td>
<td>1588</td>
<td>1573</td>
</tr>
<tr>
<td>(CoL^1\cdot H_2O)</td>
<td>3264</td>
<td></td>
<td></td>
<td></td>
<td>1629</td>
<td>1578</td>
</tr>
<tr>
<td>(ZnL^1\cdot C_2H_5OH)</td>
<td></td>
<td>3440*</td>
<td></td>
<td></td>
<td>1591</td>
<td>1576</td>
</tr>
</tbody>
</table>

The frequencies of some absorption bands (cm\(^{-1}\)) \(H_2L^1\), \(H_2L^2\) and their metal in the IR spectra. Quantum-chemical modeling of the vibrational spectra is a difficult task. Firstly, it is due to the nature of the model calculations that make for isolated molecules, whereas the experimental IR spectra tend to remove the solid substances. Secondly, by itself DFT / B3LYP method provides for the oscillation frequency values inflated results that for comparison with experiment has to be multiplied by a reduction factor which depends on the selected basic set of functions. In our case we used a factor of 0.945.

The calculation method is the possibility of assigning frequencies to certain fluctuations. Obviously, this is only possible for the characteristic vibrations. Many vibrations are complex and are involved in several atoms. In this regard, we present the results of calculations in the frequency region (3100 – 1550) cm\(^{-1}\), where the characteristic fluctuation and located in the first place, the vibrations of the carbonyl group. The results of calculation of the vibrational spectra of molecules \(H_2L^1\), \(NiL^1\cdot H_2O\), are shown in Table

An interesting fact is a discovery of the calculated spectra and molecular \(H_2L^1\), oscillation frequency \(\nu\) (O-H) and \(\nu\) (N-H) in the region of 3100 cm\(^{-1}\), where the characteristic fluctuation and located in the first place, the vibrations of the carbonyl group. The results of calculation of the vibrational spectra of molecules \(H_2L^1\), \(NiL^1\cdot H_2O\), are shown in Table

3.2 \(^1\)HNMR spectroscopy

Due to the fact that the \(^1\)HNMR method is applicable only to compounds containing unpaired electrons, we synthesized model complex compounds with metals complete d-shell: \(Zn\). As can be seen from Fig. 4, \( ^1\)HNMR spectra of uncoordinated \(H_2L^1\) contain multiple signals in regions 2 - 2.6. In the region of a strong field in the spectra are weak signals, which we attributed to the NH protons hydrazone forms of molecules (\(\delta = 13,41\) ppm for \(H_2L^1\),) and the OH groups in diazo constituent fragment (\(\delta = 12, 28\) ppm).

An interesting fact is a discovery of the calculated spectra and molecular \(H_2L^1\), oscillation frequency \(\nu\) (O-H) and \(\nu\) (N-H) in the region of 3100 cm\(^{-1}\) (Table 1). When this calculated intensity bands \(\nu\) (O-H) is very high and much higher than the intensity of the bands of stretching vibrations \(\nu\) (C-H) aromatic rings. This makes it possible to attribute the observed in 3100 cm\(^{-1}\) frequency vibrations to the O-H or N-H. Obviously, in such complexes spectra have bands.
3.3 ESR spectroscopy

Due to the fact that the EPR method has been most widely used to determine the type of coordination polyhedral and their degree of distortion for complex compounds of copper (II). The ESR spectrum (Fig. 6) was recorded for the complex compound CuL₁ • C₂H₅OH • H₂O.

As can be seen from (Fig. 6), there are bands $g_{\parallel} = 2.30$ and $g_{\perp} = 2.049$, which corresponds to the position of numerous data for slightly elongated octahedral coordination of copper (II) to Cu cation in the ESR spectrum. Due to the fact that organic ligands H₂L₁ tend to form flat square structures, it can be assumed that the molecules of water and ethanol included in the complex compounds will act as a fourth ligand, lying in organic anion plane, and also act an axial bridging ligand, finish building the coordination sphere of the copper cation to 6.

3.4 UV-vis electronic absorption spectra of the ligand and its metal(II)-azo complexes

Similarly, existing data in the literature [19] arylazopyrazolon H₂L₁ is in the electronic absorption spectra of the intensity of the broad band in the red-orange part of the spectrum, which in alkaline solution are shifted to longer wavelengths (bathochromic shift) on 85 and 69 nm, respectively (Fig. 7,8).

Changes in the electronic absorption spectra when titrated H₂L₁ NaOH solution in the pH range from 6.36 to 9.36. According to the results of the spectrophotometric titration of the first dissociation constant H₂L₁ was calculated, which are shown in Table. 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Neutral</th>
<th>Alkaline</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂L₁</td>
<td>413,0</td>
<td>498,0</td>
<td>7,43±0,11</td>
</tr>
</tbody>
</table>

Provision of electronic bands in the absorption spectra of H₂L₁ and values of their acid dissociation constants. Adding a different nature to the solutions of metal salts of organic ligands H₂L₁ leads to a significant bathochromic shift of the long-wavelength absorption bands ($\Delta\lambda =$ 55-60 nm) (Figure 10, Table 3.).

<table>
<thead>
<tr>
<th>№</th>
<th>M²⁺</th>
<th>Ligand H₂L₁</th>
<th>$\lambda_{\max, nm}$</th>
<th>$\Delta\lambda_{\max, nm}$</th>
<th>lgε</th>
<th>n (MLn)</th>
<th>lgβ</th>
<th>lgβ/n</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co²⁺</td>
<td>H₂L₁</td>
<td>468,0</td>
<td>55,0</td>
<td>4,68</td>
<td>2</td>
<td>0,32</td>
<td>1,31</td>
</tr>
<tr>
<td>2</td>
<td>Cu²⁺</td>
<td>H₂L₁</td>
<td>470,0</td>
<td>57,0</td>
<td>4,76</td>
<td>2</td>
<td>0,41</td>
<td>1,42</td>
</tr>
<tr>
<td>3</td>
<td>Ni²⁺</td>
<td>H₂L₁</td>
<td>470,0</td>
<td>57,0</td>
<td>4,84</td>
<td>2</td>
<td>0,42</td>
<td>1,46</td>
</tr>
<tr>
<td>4</td>
<td>Zn²⁺</td>
<td>H₂L₁</td>
<td>473,0</td>
<td>60,0</td>
<td>4,62</td>
<td>2</td>
<td>0,31</td>
<td>1,57</td>
</tr>
</tbody>
</table>

Position of long-wavelength absorption bands of ligands H₂L₁ in the titration with metal salt solutions, the composition and size of the complexes formation constants.

Have a bathochromic shift of the long-wavelength band upon complexation may be due to two reasons. Firstly,
ionization of the OH and NH groups, and secondly, the flattening of the molecule.

4. Conclusions

Based on the analysis of gross formula of the synthesized complex compounds $\text{H}_2\text{L}^1$, its spectral characteristics

1) According to the chemical analysis, the organic molecules are part of the complexes in the form of double-ionized.

2) The $^1\text{HNMR}$ spectra of complex compounds proton signals disappear NH and OH groups, confirms that ionization of molecules in the coordination ligand.

3) The IR spectra of the complex compounds are characterized by a considerable (54 - 80 cm$^{-1}$) shift of the absorption bands of the carbonyl groups of a molecule fragment pyrazolone, indicating that they participate in coordination.

4) ESR spectra indicate octahedral environment of the central ion.

5) The bathochromic shift of the long-wavelength absorption bands of the ligands in coordination can be explained by the flattening of organic molecules in the coordination, which indirectly confirms the hydroxyl group oxygen atom involved in metal coordination.

6) Quantum-chemical modeling (DFT / B3LYP) shows the possibility of the participation of organic molecules $\text{H}_2\text{L}^1$ to coordinate as tridentate chelate ligand, forming coordination bonds heavily covalence.

7) X-ray analysis shows that for $\text{H}_2\text{L}^1$ possible coordination with the participation of two chelating center, which leads to the formation of polymeric structures. Based on the above, we propose the following scheme of the structure of complex compounds (Fig. 10).

![Diagram of the structure of complex compounds](image)

**Figure 10:** Diagram of the structure of complex compounds $\text{H}_2\text{L}^1$

References


[7] Chen ZM, Wu YQ, Gu DH, Gan FX. Nickel(II) and copper(II) complexes containing 2-(2-(5-substitued isoxazol-3-yl)hydrazono)-5,5-dimethyclohexane-1,3-dione ligands: synthesis, spectral and thermal characterizations. Dyes and Pigments 2008;76:624-31


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