Novel Complexes of Copper (II) and Cadmium (II) with S-Functionalised 1,2,4-Triazolic Ligand: Vibrational Study

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Summary

Syntheses of novel metal complexes of Cd²⁺ and Cu²⁺ was carried out in aqueous solution, using CdI₂ and CuCl₂ · 2H₂O as source for metal ions and sodium salt of 4H-4-amino-5-carboxymethylsulfanyl-3-phenyl-1,2,4-triazole as ligand. All the compounds were preliminary characterized by melting point and IR spectroscopy.

Keywords: metal complexes; S-alkylated 1,2,4-triazole; amino-mercaptop-triazole

Introduction

1,2,4-triazole and its derivatives have gained great attention as ligands to transition metals by the fact that they unite the coordination geometry of both pyrazoles and imidazoles, and in addition exhibit a strong and typical property of acting as bridging ligands between two metal centers. In this bridging capacity, the 1,2,4-triazole ligands show a great coordination diversity, especially when the triazole nucleus is substituted with additional donor groups. This property together with their strong σ donor properties and the relative ease of synthesis make them very appealing for the design of new polynuclear metal
complexes with interesting properties [1].

Metal complexes derived from transition metals are known for their antibacterial, insecticidal and pesticidal activities [2]. 1,2,4-Triazole ligands are an important class of compounds, that are used in modern analytical chemistry for the dosage of heavy-metals from waste waters using spectrophotometric methods [3,4]. Also, the triazolic nucleus is widely used in well-known pharmaceuticals (like Fluconazole, Itraconazole, Voriconazole, Terconazole etc.)[5], and in the synthesis of new bio-active agents [6-11].

MATERIALS AND METHODS

The reagents were commercial products (Merck, Fluka, Aldrich) and used without further purification, except compound 1a was prepared by an original method, mentioned in our previous studies [12]. Melting points were determined on a Boethius PHMK (Veb Analytik Dresden) instrument, and thin-layer chromatography was carried out on silica gel-coated plates 60 F254 Merck using benzene: methanol 7:3, benzene: methanol 3:7 or benzene: ethyl acetate 1:1 (v/v) as eluents. IR spectra were recorded in KBr pellet on a Jasco FT/IR-410 spectrophotometer.

Synthesis of ligand (1b) (LNa): sodium salt of 4H-4-amino-5-carboxymethylsulfanyl-3-phenyl-1,2,4-triazole

To a suspension of 4H-4-amino-5-carboxymethylsulfanyl-3-phenyl-1,2,4-triazole (1a) (10.00 g, 40 mmol) in distilled water (50 mL), a NaOH 1M solution is added (40.0 mL). The suspension is heated and maintained at 40°C for 2h, and then the clear, colourless formed solution is purified with active charcoal. After filtration, the solution was cooled at r.t. and the solvent was removed by distillation under reduced pressure (10 mm Hg). The white-crystalline product (1b) (chromatographically pure) was used for the synthesis of the metal complexes.

The syntheses of metal complexes of Cd^{2+} and Cu^{2+} with sodium salt of 4H-4-amino-5-carboxymethylsulfanyl-3-phenyl-1,2,4-triazole (LNa)

The ligand LNa (1b) (0.709g, 26 mmol) was dissolved, under stirring, in distilled water (6 mL), when a colourless solution was formed. Separately, transition metal salts (13 mmol, corresponding to 0.476g CdI\(_2\) and 0.221g CuCl\(_2\)·2H\(_2\)O respectively) were dissolved in distilled water (2.5 mL). The aqueous solution of ligand (1b) was added dropwise under intense stirring to the metal salt solution, and a coloured suspension was obtained instantly. All the suspensions were maintained under stirring for approx. 2h, then filtered off under vacuum and washed with distilled water (20 mL). The products (2,3) were dried in an oven at 80°C for 72h.
RESULTS

The synthesis of ligand (1b) used as starting material 4H-4-amino-5-carboxymethylsulfanyl-3-phenyl-1,2,4-triazole (1a), which by treatment in aqueous medium at 40°C with stoichiometric amount of NaOH forms the corresponding soluble sodium salt (Figure 1). Sodium salt was purified, then isolated by removing water at reduced pressure. The purity of ligand (1b) was confirmed using thin layer chromatography, comparative to compound (1a), using three different elution systems: benzene: ethyl acetate 1:1, benzene: methanol 3:7 and benzene: methanol 7:3, respectively.

![Figure 1. The synthesis of sodium salt of 4H-4-amino-5-carboxymethylsulfanyl-3-phenyl-1,2,4-triazole](image)

The syntheses of Cd²⁺ and Cu²⁺ complexes were carried out in aqueous medium, accordingly to Figure 2:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product Characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(LNa)aq + M²⁺aq → ML₂ + 2Na⁺</td>
<td>Cd²⁺ complex with LNa (2)</td>
</tr>
<tr>
<td></td>
<td>Characterization of product: 0.44g of amorphous white powder; m.p. &gt; 250°C</td>
</tr>
<tr>
<td></td>
<td>IR (KBr, cm⁻¹): 3233, 1555, 1456, 1383, 1228, 769, 693, 592, 463</td>
</tr>
<tr>
<td>Cu²⁺ complex with LNa (3)</td>
<td>Characterization of product: 0.41g amorphous greenish-blue powder; m.p. = 188-189°C (with decomposition, changing colour to brown)</td>
</tr>
<tr>
<td></td>
<td>IR (KBr, cm⁻¹): 3434, 1617, 1460, 1372, 1227, 1134, 1007, 776, 698, 598</td>
</tr>
</tbody>
</table>

The FT-IR spectra of metal complexes 2,3 (Figures 3,4) were recorded in the 4000 – 400 cm⁻¹ spectral range. Preliminary vibrational studies regarding IR spectroscopy of title compounds are discussed accordingly to literature data [13, 14].
DISCUSSION

The FT-IR spectra of metal complexes 2,3 (Figures 3, 4) were recorded in the 4000 – 400 cm\(^{-1}\) spectral range. Preliminary vibrational studies regarding IR spectroscopy of title compounds are discussed accordingly to literature data [13].

The 4000 – 2000 cm\(^{-1}\) spectral range is relevant for the characterization of the OH and CH groups. The presence of crystallization water in the metal complexes (2,3) generates complex, broad bands for \(\nu(H_2O)\) in the 2500-3500 cm\(^{-1}\) region of the IR spectra, for chelated compounds. On the other hand, the characteristic band for the carboxylic OH group (IR of 1a: 3620 cm\(^{-1}\)) disappears in the IR spectra of 2,3, sustaining the formation of a coordination compound with carboxylate anion.

![IR spectrum for Cd\(^{2+}\) complex](image)

<table>
<thead>
<tr>
<th>Result of Peak Picking</th>
<th>No.</th>
<th>Position</th>
<th>Intensity</th>
<th>No.</th>
<th>Position</th>
<th>Intensity</th>
<th>No.</th>
<th>Position</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 3233.07</td>
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<td>6: 1353.68</td>
<td>15.2500</td>
<td>7: 1222.43</td>
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<tr>
<td>2: 2952.46</td>
<td>93.2777</td>
<td>3: 1003.31</td>
<td>2.7396</td>
<td>4: 1425.99</td>
<td>28.1795</td>
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<tr>
<td>3: 1116.58</td>
<td>83.7008</td>
<td>10: 1074.16</td>
<td>76.0707</td>
<td>11: 1007.62</td>
<td>65.1848</td>
<td>12: 956.20</td>
<td>69.7320</td>
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<tr>
<td>4: 905.42</td>
<td>67.5705</td>
<td>14: 769.46</td>
<td>41.6810</td>
<td>15: 693.28</td>
<td>18.7685</td>
<td>16: 593.06</td>
<td>57.5864</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3.** IR spectrum for Cd\(^{2+}\) complex

The 2000 – 1000 cm\(^{-1}\) spectral range is relevant for both heterocyclic and alkyl-carboxylic units of the ligand. The most important bands characteristic for the heterocyclic fragment fall in the 1560 – 1400 and 1200 – 1075 cm\(^{-1}\) spectral ranges, and are assigned to the \(\nu(C=O)\) and \(\nu(N-N)\) vibrating modes, respectively. As it concerns the alkyl-carboxylic substituent, the title spectral range offers information about both CH\(_2\) and COOH groups: the presence of the CH\(_2\) unit is sustained by the assignment of the \(\delta(CH_2)\) at 1474 – 1430 cm\(^{-1}\) in both spectra.

90
NOVEL COMPLEXES OF COPPER (II) AND CADMIUM (II)

The most interesting behaviour is revealed by the COOH/COO\(^{-}\) group: according to literature [13, 14], the COOH group is characterized by two major vibrational modes: \(\nu(C=O)\) and \(\nu(C-OH)\), the latter being represented by two bands. With the deprotonation of COOH group in alkaline medium, the COO\(^{-}\) group is expected to adopt a C\(_{2v}\) symmetry and to reveal in IR spectra both \(\nu(COO)\) and \(\nu'(COO)\) vibrations. For the synthesized complexes, the band corresponding to \(\nu(C=O)\) vibrational mode falls at 1555 cm\(^{-1}\) for Cd\(^{2+}\) complex and at 1617 cm\(^{-1}\) for Cu\(^{2+}\) complex respectively, comparative to the one for protonated form of ligand (1a), where \(\nu(C=O)\) appears at 1714 cm\(^{-1}\).

In conclusion, we may suggest the deprotonation of the carboxylic group in both metal derivatives and the coordination of the resulting carboxylato unit to the metal centers. However, the coordination behaviour of the ligand can be elucidated only by more spectral and structural investigations.

**CONCLUSION**

One ligand, namely the sodium salt (1b) of 4H-4-amino-5-carboxymethylsulfanyl-3-phenyl-1,2,4-triazole and two new metal complexes (2,3) were synthesized and preliminary-characterized by vibrational spectroscopy.
By the analysis of IR spectra of title compounds (2,3), it is suggested the presence of crystallization water in the structure of the metal derivatives. On the other hand, the characteristic band for the carboxylic OH group (IR of 1a: 3620 cm\(^{-1}\)) disappears in the IR spectra of 2,3, sustaining the formation of a coordination compound with carboxylate anion. Also, the deprotonation of the carboxylic group in all metal derivatives is sustained by the \(\nu(C=O)\) vibrational mode, that falls at lower values in complexes, comparative to protonated ligand (1a).

**References**