Co(II), Ni(II) and Cu(II) Complexes with 3-Arylazo-1,2,4-triazole Dyes

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The chelates of Co(II), Ni(II) and Cu(II) with some 3-arylazo-1,2,4-triazole dyes were investigated by conductometric titration and by IR, electronic and ESR spectra. The formation of 1:1 and 1:2 (metal:ligand) complexes was established by elemental analysis and conductometric titrations.

Keywords: 3-Arylazo-1,2,4-triazole dyes, Cobalt(II) complex, Copper(II) complex, Nickel(II) complex

1 Introduction

Several metal complexes of azo compounds are receiving special attention during the last few years because of their improved dyeing properties on textiles and fibres in comparison with those of the free dyes. Many azo dyes have been utilized as chromogenic reagents or the colorimetric determination of several metal ions on the basis of their tendency to form chelates with these metal ions. Also, a large number of azo compounds have been used as indicators for complexometric titration of many metal ions.

The object of this investigation was to study the stoichiometry and structure of the complexes formed when Co(II), Ni(II) and Cu(II) salts react with some azo dyes derived from 3-aminoo-1,2,4-triazole. The complexes were characterized by conductometric titration, elemental analysis and by IR, electronic and ESR spectra.

2 Experimental Procedure

All compounds were pure BDH chemicals. The ligands were prepared by the diazotization of the corresponding aromatic amine and coupling of the resulting diazonium salt with the chosen couplers. The azo compounds thus prepared have the general structure:

\[ \text{N}=\text{N}=\text{N}-\text{R} \]

where R =

(a) \( \text{H}_3\text{C}-\text{OH} \)
(b) \( \text{OH} \)
(c) \( \text{CHO} \)
(d) \( \text{COOH} \)

The metal chelates were prepared by mixing an ethanolic solution of the organic ligands (1 or 2 mol) with a solution of the same solvent. The mixture was refluxed for about 30 min; the solid complexes were filtered off, dried at 110°C in an air oven and stored over P₂O₅.

The conductometric titration was carried out by using a dipping cell and a Pye conductance bridge. The IR spectra were obtained with the aid of UNIVAM SP 200 G and SP 1000 spectrophotometers, by using the KBr disc technique. The UV-vis spectra were recorded with a Unicam SP 8000 spectrophotometer. Electron spin resonance (ESR) spectra were recorded on a varian EG1-X-band spectrometer equipped with an E 101 microwave bridge. The magnetic field was calibrated with a 2,2-diphenyl-1-picryl hydrazyl sample.

3 Results and Discussion

The reaction of the divalent metal ions Co²⁺, Ni²⁺ and Cu²⁺ with 3-arylazo-1,2,4-triazole was first studied by a conductometric titration. The titration curves (Fig.1) display two breaks at mole ratios of 1 and 2, indicating the formation of two types of complexes with stoichiometric ratios of 1:1 and 1:2 (M²⁺:L). The titration curves are characterized by a gradual increase in the conductance values, which can be attributed to the displacement of protons from the ligands during complex formation.

The mode of bonding between the ligands and the metal ions investigated was clarified by examining the IR spectra of the complexes in comparison with those of the ligands. The results of the elemental analysis of the solid complexes are given in Table 1. It is not possible to ascertain the proton displacement from the behaviour of the \( \nu_{\text{OH}} \) band since most complexes contain water molecules, whose band masks the
behaviour of the phenolic bands\(^ {11}\). However, the spectra of the metal complexes show a decrease in the intensity of the \(v_{\text{OH}}\) and \(v_{\text{C-OH}}\) bands within the 3100-3140 and 1078-1095 cm\(^{-1}\) range respectively. This supports the proton displacement from the phenolic OH-groups through metal ions. Thus the bonding of the metal ion to the ligand takes place through covalent linkage with the oxygen of the phenolic groups. The IR spectra of complexes show that the bands due to the N=N function in compounds Ia and Ib are shifted to a lower frequency, indicating that the N=N contributes to a coordination bond with the metal ions.

Accordingly, the bonding of the ligands Ia and Ib with the divalent metal ions can be formulated as follows:

\[
\text{Complex with } \text{Ia} \quad \text{Complex with } \text{Ib}
\]

where \(M = \text{Co}^{2+} \) or \(\text{Cu}^{2+} \) in complex with Ia; and \(\text{Co}^{2+} \) in complex with Ib.

The IR spectra of the chelates with the ligands Ic and Id show that the bands due to the C=O vibration are shifted to a higher frequency (10 cm\(^{-1}\)). This shift indicates that the bonding of the ligand to the metal ion takes place through the oxygen of carbonyl and OH-groups. Thus the mode of bonding of the metal ions with ligands Ic and Id can be represented as follows:

\[
\text{Complex with } \text{Ic} \quad \text{Complex with } \text{Id}
\]

**Table 1 — Characterization Data of the Complexes of Co(II), Ni(II) and Cu(II) with Some 3-Arylazo-1,2,4-triazole Dyes**

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Formula(^ {a})</th>
<th>Metal, %</th>
<th>H(_2)O, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Calc. F(_1)</td>
<td>F(_2)</td>
</tr>
<tr>
<td>Cu(^ {2+})</td>
<td>Cu Cl L 3H(_2)O</td>
<td>17.89 17.30</td>
<td>15.72</td>
</tr>
<tr>
<td>Ni(^ {2+})</td>
<td>Ni Cl L 3H(_2)O</td>
<td>20.03 23.50</td>
<td>16.22</td>
</tr>
<tr>
<td>Co(^ {2+})</td>
<td>Co Cl L 3H(_2)O</td>
<td>16.77 16.18</td>
<td>15.72</td>
</tr>
<tr>
<td>Cu(^ {2+})</td>
<td>Cu Cl L 3H(_2)O</td>
<td>15.25 14.70</td>
<td>16.18</td>
</tr>
<tr>
<td>Ni(^ {2+})</td>
<td>Ni Cl L 3H(_2)O</td>
<td>10.98 10.28</td>
<td>10.97</td>
</tr>
<tr>
<td>Co(^ {2+})</td>
<td>Co Cl L 3H(_2)O</td>
<td>15.41 15.00</td>
<td>15.40</td>
</tr>
</tbody>
</table>

\(F_1\) — Found from complexometric titrations

\(F_2\) — Found from TGA measurements

\(^ {a}\) L = Ia, Ib, Ic or Id
where $M = \text{Co}^{2+}$ or $\text{Ni}^{2+}$ or $\text{Cu}^{2+}$ in complex with $\text{Ic}$; and $\text{Co}^{2+}$ or $\text{Cu}^{2+}$ in complex with $\text{Id}$.

From the IR spectra of the complexes of the type 1:2 (metal ion: ligand), it was found that the bands due to the OH and C-OH had disappeared while the bands due to the $N=N$ shifted to a lower frequency. Thus, on the basis of the results of the IR spectra together with the elemental analysis, the structure of the chelates may be formulated as follows:

\[
\begin{align*}
\text{R} & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quarter
coordinated to the metal ion\textsuperscript{12}. According to Fidone, the g values have a negative orbital contribution from the value of the free electron, $g = 2.0023$, which may be due to a decrease in the covalent nature between the ligand and the metal ions.

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