The IR spectra of the ligands in solution exhibit νN-H mode at 3300 cm⁻¹ which shifts to the lower frequency region in the spectra of their complexes suggesting the involvement of NH group(s) in coordination. Amid-I band occurring in the region 1720-1705 cm⁻¹ in the spectra of all the ligands except PTSC shows negative shift in SnX₄ -PTSC (X = Cl, Br or I) and remains practically unchanged in SnCl₄-PTSC and SnCl₄ IPTSC suggesting the coordination of the keto group in the former and its non-involvement in the latter complexes. The νC=S band occurring in the region 1350-1285 cm⁻¹ suggests the involvement of 3NH group(s) in the complexes SnCl₄ (APTSC-H) and SnCl₄ IPTSC suggesting the coordination of the ligand through the sulfur of the thioketo group in the first category of complexes, non-participation in bonding in the second category of complexes and removal of νC=S group presumably via enolization in the third category of complexes.

The νSn-Cl is reported at 403 cm⁻¹ (ref. 4, 5) in SnCl₄ which shifts to the lower frequency side in the octahedral complexes. The presently investigated tin(IV) chloride complexes show a broad band in the region 325-280 cm⁻¹ which may be due to a cis-octahedral geometry of the complexes. SnCl₄ (PTSC-H) shows two widely separated bands at 358 and 280 cm⁻¹ which may be explained by assuming a chlorine bridged dimeric structure for the above complex. The higher frequency band may be due to the terminal νSn-Cl while the lower frequency band may be due to the bridging νSn-Cl mode. The tin-bromine and tin-iodine vibrations could not be observed because they lie beyond the range of the infrared spectrophotometer used in the present studies. The non-ligand bands occurring in the regions 490-480, 480-465, 416-400 and 270-250 cm⁻¹ may be tentatively assigned to νSn-O (ref. 8), νSn-O (ref. 8), νSn-O (ref. 6) and νSn-N (ref. 9) modes respectively.

The authors are thankful to the Head, Chemistry Department, Banaras Hindu University, Varanasi, for laboratory facilities and one of the authors (R.B.S.Y.) is thankful to CSIR, New Delhi, for financial assistance.

References


Stepwise Formation Constants of the Chelates of Substituted Azobenzene with Cu(II), Ni(II), Co(II), Zn(II) & Cd(II)

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CSIR Trivandrum Complex, Trivandrum 19

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Stepwise formation constants of the chelates of 3-formyl-4-hydroxy-2'-nitroazobenzene (HF2NB), 3-formyl-4-hydroxy-3'-nitroazobenzene (HF3NB) and 3-formyl-4-hydroxy-4'-nitroazobenzene (HF4NB) with Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) have been determined using the Calvin-Bjerrum titration technique. The order of the formation constants considering log K, is found to be Zn(II) < Cu(II) > Ni(II) > Co(II) > Cd(II). Stability constants are in fair agreement with Irving-William's order.

In continuation of our earlier work³,² on the chelates of substituted azobenzenes, we report in this note the synthesis of 3-formyl-4-hydroxy-3'-nitroazobenzene (HF3NB) and 3-formyl-4-hydroxy-2'-nitroazobenzene (HF2NB) and the stabilities of the complexes of these ligands along with those of 3-formyl-4-hydroxy-4'-nitroazobenzene (HF4NB) with Cu(II), Ni(II), Co(II) Zn(II) and Cd(II) employing Calvin-Bjerrum pH titration technique³,². The experiments were done in 60% (v/v) ethanol-water at 28±0.1° and μ = 0.2 M (KNO₃).

The ligands HF3NB and HF2NB were prepared using Analar grade chemicals by a method similar to the one reported earlier¹. The nitrilines employed were recrystallized from ethanol. HF2NB is a redish brown solid, m.p. 149° (Found: C, 57.56; H, 3.31; N, 15.48%). HF3NB is a yellowish red solid, m.p. 159° (Found: C, 57.53; H, 3.30; N, 15.51%). Both require C, 57.55; H, 3.32; N, 15.50%. The IR spectra of the ligands were compatible with their structures.

All solutions were prepared in doubly distilled, CO₂-free water. Nitrogen gas pressurized with the solvent was kept bubbling through the experimental solution so as to keep an inert atmosphere. The metal solutions were prepared from the respective nitrates. The corrections in pH were done according to Bates⁵. The following solutions (total volume 50 ml) were taken and titrated against 0.2N standard sodium hydroxide: (A) 1 ml of 4×10⁻² M HClO₄ + 10 ml of 1.0M KNO₃; (B) A + 25 ml of 5×10⁻³ M ligand solution; and (C) B + 5 ml of 5×10⁻² M metal solution. Cu(II) precipitated at 4.0, 4.2, 4.3 pH in the case of HF3NB, HF2NB and HF4NB respectively. The other metals precipitated between pH 5.0 and 6.5 with the above ligands. In the case of solution (C), fall in pH was observed which clearly showed the formation of complexes.

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All the ligands were monoprotic in nature and hence gave one buffer region in their titration curves, as a result of neutralizing one equivalent of base. The protonation constants \( \log K_H \) were found out by the method of Irving and Rossotti. The protonation constants \( \log K_H \) were also calculated at 28° (Table 1). The values of stability constants were also calculated from Eq. (1) using the direct calculation method.

\[
\log K_H = \log \frac{\bar{n}^H}{\bar{n}^H - 1} + \rho A \quad \ldots (1)
\]

The values of \( \bar{n} \) and \( \rho A \), where \( \bar{n} \) is the formation function, were calculated using the method devised by Bjerrum and Calvin and formation curves for different metal systems were plotted with \( \bar{n} \) against \( \rho A \). The stepwise stability constants \( \log K_1 \) and \( \log K_2 \) were taken directly from formation curves at points corresponding to \( \bar{n} = 0.5 \) and \( \bar{n} = 1.5 \) respectively. These values along with the overall value of stability constants are given in Table 1. The values of stability constants were refined using computational methods devised by Rossotti and Rossoetti. Overall changes in free energy \( \Delta F = -RT \ln K \) were also calculated at 28° (Table 1).

In all the cases, Cu(II) formed only 1:1 complexes. The stabilities of the chelates taking \( \log K_1 \) into consideration were in the order: Zn(II) > Cu(II) > Ni(II) > Co(II) > Cd(II), in accord with Irving-Williams order for bivalent metal ion of 3d-series. Even though Zn(II) and Cd(II) have got the same \( \bar{n}^H \) configuration, Cd(II) has greater ionic radius than Zn(II) and hence it forms a less stable complex.

As is seen from the \( \log K \) values, out of the three nitro substituted azobenzenes, HF3NB with \( \log K \) value 7-30 forms the most stable set of complexes and HF4NB with \( \log K \) value 7-10 forms the least stable ones. HF2NB with \( \log K \) value 7-20 forms complexes of intermediate stability.

Considering the reported values of stability constants of the methyl substituted azobenzenes, it is observed that the nitro substituted series have, in general, a diminished complex forming capacity.

The authors are grateful to Dr. C. P. Prabhakaran, University of Kerala, for his valuable suggestions.

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**Formation Constants of UO₂⁺ & Th(IV) Complexes of 2,5-Dimercapto, 1,3,4-thiadiazole (Bismuthiol I)**

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Stability constants of the chelates of Bismuthiol I with UO₂⁺ and Th⁺⁺ have been determined inaq. ethanol at 25° ± 0.1° and \( \mu = 0.05, 0.1 \) and 0.15M using Calvin-Bjerrum titration technique. While UO₂⁺ forms only a 1:1 complex, Th⁺⁺ forms 1:1, 1:2 and 1:3 complexes.

**The analytical utility of 2,5-dimercapto, 1,3,4-thiadiazole (Bismuthiol I) is now well known. Recently we have reported the nature of its Cu(I) and Cu(II) complexes. The stability constants of its chelates with UO₂⁺ and Th⁺⁺ ions, have now been determined inaq. ethanol \( \rho H \)-metrically using Calvin-Bjerrum titration technique at 25° ± 0.1° and \( \mu = 0.0, 0.1 \) and 0.15M maintained by adding 1.0M NaClO₄.**

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**Table 1 — Stepwise Stability Constants of the Different Complexes**

<table>
<thead>
<tr>
<th>Metal</th>
<th>HF3NB</th>
<th>HF2NB</th>
<th>HF4NB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \log K_1 )</td>
<td>( \log K_2 )</td>
<td>( \log K_3 )</td>
</tr>
<tr>
<td></td>
<td>kcal/mole</td>
<td>kcal/mole</td>
<td>kcal/mole</td>
</tr>
<tr>
<td>Cu(II)</td>
<td></td>
<td>6·20</td>
<td>6·20</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ni(II)</td>
<td>5·95</td>
<td>5·95</td>
<td>8·19</td>
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<tr>
<td>Co(II)</td>
<td>4·26</td>
<td>4·18</td>
<td>9·83</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn(II)</td>
<td>3·95</td>
<td>9·35</td>
<td>9·10</td>
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<tr>
<td>Cd(II)</td>
<td>5·20</td>
<td>5·20</td>
<td>7·16</td>
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(a) Bjerrum values and (b) midpoint slope.