Studies on the Reaction of Alizarin Saphirol B with Ce$^{3+}$, Th$^{4+}$ & UO$_2^{2+}$

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The reaction of alizarin saphirol B with Ce$^{3+}$, Th$^{4+}$ and UO$_2^{2+}$ has been investigated spectrophotometrically and conductometrically. The results indicate the probable formation of 1:1 and 1:2 chelates (metal-ligand). The values of log $\beta$ for the different complexes have been determined. IR spectra of the solid chelates show that the chelate formation takes place through a coordinate bond with one carboxyl group and a covalent bond with an $\alpha$-phenate oxygen.

HYDROXY- and amino-anthraquinones are important from biological and analytical standpoints. Although a few reports are available on the complexes of the hydroxyanthraquinones with Ce$^{3+}$, Th$^{4+}$ and UO$_2^{2+}$, the reaction of alizarin saphirol B (4,8-diamino-1,5-dihydroxyanthraquinone-2,6-disulphonic acid) with these metal ions has not yet been investigated. In this note, preparation and characterization of the solid chelates of alizarin saphirol B with Ce$^{3+}$, Th$^{4+}$ and UO$_2^{2+}$ and their stability constants in solution are reported.

Solutions (10$^{-2}$M) of Th$^{4+}$, UO$_2^{2+}$ and Ce$^{3+}$ were prepared by dissolving the requisite amount of the metal salts (nitrate in the case of Th$^{4+}$ and perchlorate in the case of UO$_2^{2+}$ and Ce$^{3+}$), in redistilled water containing a small quantity of HNO$_3$ or HClO$_4$ to prevent hydrolysis and standardized by recommended methods. UO$_2$(ClO$_4$)$_2$ solution was prepared by dissolving UO$_2$ in a known amount of HClO$_4$ and then diluting it with water. Alizarin saphirol B (AZSB) solution ($10^{-3}$M) was prepared by dissolving an accurately weighed amount of the reagent (BDH) in redistilled water. Buffer solutions consisting of borax, borac acid, succinic acid and sodium sulphate of pH 3-9 were prepared as given by Britton.

The absorption spectra of solutions were measured on a Unicam SP 500 spectrophotometer. The IR spectra of the organic ligand as well as those of the solid chelates were recorded in KBr matrix on a Unicam SP 200 spectrophotometer. Conductometric titrations were carried out using a Pye conductance bridge and a dip-type conductivity cell.

Spectrophotometric measurements — In a previous study it was found that the spectral behaviour of alizarin saphirol B is influenced by the pH of solutions. It seems therefore necessary to look for a medium suitable for the colour development of its complexes with Th$^{4+}$, UO$_2^{2+}$ and Ce$^{3+}$. On using the universal buffer solutions as media, no absorption bands characteristic for complex formation were observed. Thiel buffer solutions are found to be the most suitable media and thorium, uranium and cerium give blue-coloured chelates with AZSB. It was found that the maximum colour development is attained at pH 5-3 for Th$^{4+}$-AZSB, 6-2 for UO$_2^{2+}$-AZSB and 7-6 for Ce$^{3+}$-AZSB chelates. In the visible region the Th$^{4+}$-AZSB complex exhibits $\lambda_{\text{max}} \sim 690$ nm. The band shows an increase in intensity and an apparent red shift, with increasing concentration of either AZSB or the metal ions. UO$_2^{2+}$-AZSB complex exhibits $\lambda_{\text{max}} \sim 420$ and 700 nm. In this case a slight red shift is exhibited at high concentrations of either reactant. The changes in the band intensity and position with concentration of reactants indicate the probable formation of different complexes.

AZSB shows two bands in the visible region at 420 and 570 nm, which undergo a red shift on complexation owing to an enhanced charge transfer from the substituents to the anthraquinone nucleus. The red shift observed on complex formation indicates an enhanced charge transfer which denotes a lower covalent character of the metal-ligand bond.

The composition of the complexes formed in solution was examined by the molar ratio, straight line, continuous variation, slope ratio and the limiting logarithmic methods. The results obtained indicate the probable formation of two types of complexes with stoichiometric ratios 1:1 and 1:2 (metal-ligand) for the three metal ions investigated.

The absorbance-molar ratio plot does not attain a limiting value with Th$^{4+}$ and Ce$^{3+}$ denoting that the 1:2 complexes are strongly dissociated in solution and the equilibrium would thus be in favour of the 1:1 complexes.

The conductance-molar ratio curves are characterized by well-defined breaks denoting the probable formation of 1:1 and 1:2 types of complexes with the metal ions. The plots of the specific conductivity vs the volume of the complexing agent added to the metal ion solutions show gradual increase in conductance, indicating that hydrogen ions are liberated from the ligand through bonding with the metal ion.

The apparent stability constants of the complexes formed were calculated from the measurements and were as follows: Th$^{4+}$ (log $\beta_1 = 4.74$, log $\beta_2 = 8.78$), UO$_2^{2+}$ (log $\beta_1 = 4.37$, log $\beta_2 = 9.32$) and Ce$^{3+}$ (log $\beta_1 = 4.6$, log $\beta_2 = 8.8$). The values indicate that the complexes exhibit moderate stability and can be arranged according to their stability in the following order:

- 1:1 complexes: Th$^{4+}$ > Ce$^{3+}$ > UO$_2^{2+}$
- 1:2 complexes: UO$_2^{2+}$ > Ce$^{3+}$ > Th$^{4+}$

Solid complexes — The spectra of AZSB as well as those of the complexed ligand exhibit bands around 1300, 1570 and 3500 cm$^{-1}$, corresponding to νC−N, 8N−H and νN−H. The band at 3200 cm$^{-1}$ in the spectrum of AZSB should, however, correspond to νOH of the bonded OH group. The strong H-bonding reflects itself in the broadening of the band. This band shifts to lower frequency (~3080-3100 cm$^{-1}$) and becomes less intense in the chelates when the ligand is bonded to the respective metal ions. It seems that H-bonding exists in the ligand as may be evident from the position of νOH group and the appearance of νCO at lower
frequency (~1590 cm$^{-1}$). The bands at 1460, 1260 and 1200 cm$^{-1}$ are assigned to \( \delta OH \), \( \delta CH \) and \( \nu C-O \) respectively. The intensity of \( \delta OH \) decreases in the chelates apparently due to the displacement of a proton from one \( OH \) group on complex formation. The band at 1260 cm$^{-1}$ in the ligand appears either as a broad band or a split band specially in the case of uranium and cerium chelates indicating the higher stability of the chelates of uranium and cerium as compared to thorium chelate.

References
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3. ISSA, R. M., under publication.

Chromium(III) Complex with 2-Guanidinobenzimidazole
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Tris-chelated chromium(III) complex with 2-guanidinobenzimidazole has been prepared by complete replacement of thiocyanate groups in \( K_3[Cr(NCS)_6] \) by benzimidazole and its 2-methyl derivative could be effected. In this note we report substitution of all the six thiocyanate groups on refluxing \( K_3[Cr(NCS)_6] \) with 2-guanidinobenzimidazole \( [Cr(GBH^+)_3Cl] \) (GBH$^-$) in ethanol. In the presence of excess of \( Cr(NCS)_6^{3-} \), the complex \( [Cr(GBH^+)_3Cl] \) is formed; Pfeiffer and Werdelmann$^7$ obtained \( [Cr(phen)_3Cl] \) by a similar procedure. However, with excess ligand, followed by treatment with ethanolic KOH, the complex base \( [Cr(GBH^+)_3(OH)] \) is obtained from which different salts, viz. chloride, bromide and sulphate, were prepared by treatment of the base with acids. Iodide and nitrate salts were obtained by suitable metatheses (Table 1).

The conductance value of 386-6 ohm$^{-1}$ cm$^2$ mole$^{-1}$ in aqueous solution at 30° for the complex chloride confirms the tervalency of the cation, and the room temperature magnetic moment values (3.95-4.04 BM) are characteristic of chromium(III). This complex is stable in aqueous solution.

The electronic absorption spectra reveal that 10Dq value of \( [Cr(GBH^+)_3Cl] \) (20200 cm$^{-1}$), as calculated from the transition \( \tau_{2g} \rightarrow \epsilon_{A_{2g}} \) is slightly lower than those of \( [Cr(BigH^+)_3Cl] \) (20747 cm$^{-1}$; BigH$^-$=biguanide) and \( [Cr(en)_3Cl] \) (21930 cm$^{-1}$) containing comparable Cr(III)$N_6$ chromophores$^{10}$. Tris (2-guanidinobenzimidazole) chromium(III) hexathiocyanatochromate(III) — An excess of \( K_3[Cr(NCS)_6] \) on reflux with the ligand in ethanol for 15 min, followed by dilution with a large volume of water, yielded a rose-red solid which was purified by reprecipitation from ethanol and dried in vacuo over CaCl$_2$.

Tris(2-guanidinobenzimidazole)chromium(III) hydroxide — A refluxed mixture of \( K_3[Cr(NCS)_6] \) (2.0 g) and the ligand (2.2 g), when treated with ethanolic KOH (0.5 g/10 ml) followed by dilution with water, gave a voluminous rose-red precipitate. This was purified by reprecipitation from ethanol. On digestion on a steam-bath for about 10 min, a deep red crystalline mass was obtained, which was filtered, washed with water, and dried in vacuo over CaCl$_2$/KOH.

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### Table 1 — Characterization Data of the Various Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Cr (%)</th>
<th>N (%)</th>
<th>Anion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Found</td>
<td>Reqd</td>
<td>Found</td>
<td>Reqd</td>
</tr>
<tr>
<td>( X(OH)_3 )</td>
<td>Red</td>
<td>8.21</td>
<td>8.27</td>
<td>33.78</td>
</tr>
<tr>
<td>( XCl_2 \cdot 3H_2O )</td>
<td>Orange</td>
<td>6.86</td>
<td>6.98</td>
<td>28.22</td>
</tr>
<tr>
<td>( XB_2 \cdot 4H_2O )</td>
<td>do</td>
<td>5.76</td>
<td>5.85</td>
<td>23.87</td>
</tr>
<tr>
<td>( XBr_3 \cdot 6H_2O )</td>
<td>do</td>
<td>5.07</td>
<td>4.89</td>
<td>19.60</td>
</tr>
<tr>
<td>( X(SO_4)_{1.5} \cdot 5H_2O )</td>
<td>Violet pink</td>
<td>6.17</td>
<td>6.34</td>
<td>25.63</td>
</tr>
<tr>
<td>( X(NO_3)_2 \cdot 2H_2O )</td>
<td>Rose-red</td>
<td>6.48</td>
<td>6.50</td>
<td>31.43</td>
</tr>
<tr>
<td>( XCr(NCS)_6 \cdot 5H_2O )</td>
<td>do</td>
<td>9.94</td>
<td>9.74</td>
<td>27.40</td>
</tr>
</tbody>
</table>

\( X = [Cr(C_6H_4N_6)_3Cl] \) $^*$

$^*$Found: C, 34.01% H, 3.50% (Reqd C, 33.73; H, 3.57%).