For the complex A.en [Found: Ti, 15·26; Cl, 22·74; S, 10·48; F, 6·28; C, 11·45; H, 3·75; N, 9·53. Reqd.: Ti, 15·53; Cl, 22·97; S, 10·35; F, 6·15; C, 11·55; H, 3·56; N, 9·05%]. For the complex A.DMSO [Found: Ti, 14·89; Cl, 21·32; S, 19·57; F, 5·96; C, 10·60; H, 2·85. Reqd.: Ti, 14·67; Cl, 22·97; S, 11·00; H, 2·75%].

Titanium, sulphur and fluorine were determined gravimetrically as TiO₂, BaSO₄ and (C₆H₆)₅SnF₄ respectively. Chlorine was determined by Volhard’s method. The parent compound and its coordination complexes are yellow, hygrosopic solids, insoluble in common organic solvents. Their melting points are >260°C.

It is now well established that the symmetry of the fluorosulphate group is reduced from C₃₅ to C₂₅ (when it is ionic) to C₃ when it acts as a mono- or bidentate group. However, if it acts as a tridentate ligand its symmetry still remains C₃₅. This lowering of the symmetry (when it acts as a mono- or tridentate ligand) results in an increase of its fundamental vibrations from six to nine, all of which are IR and Raman active. The IR absorption bands for the fluorosulphate group in (A) can be assigned on the basis of C₃₅ symmetry which is maintained not because of the anionic SO₃F⁻ but due to the metal-anion coordination, in which all the three oxygen atoms of the fluorosulphate group are involved in coordination in an equivalent position resulting in hexa-coordination of titanium. That the fluorosulphate group in (A) is tridentate having a hexachlorobutadiene shows bands at 2920 and 1750 in the cesium salt to 1715 in the pure salt. There is consistent, further justifies the suggested mode of coordination.

Stability Constants of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), UO₂²⁺ and VO²⁺ Chelates of o-(N-o-furfuralideneimino)benzoic Acid

D. C. Sengal, P. K. Kanungo & R. K. Mehta

Department of Chemistry, University of Jodhpur, Jodhpur

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Stability constants of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), UO₂²⁺ and VO²⁺ complexes with o-(N-o-furfuralideneimino)benzoic acid have been determined potentiometrically in aqueous media using Calvin-Bjerrum pH titration technique. The measurements have been carried out at three different ionic strengths and temperatures. Thermodynamic stability constants have been obtained by extrapolating the experimental values to zero ionic strength. Values of free energy change have also been calculated.

NOTES

A survey\(^1-3\) of the literature indicated that no work has been done on Co(II), Ni(II), Cu(II), Zn(II), Cd(II), UO\(^{2+}\) and VO\(^{2+}\) chelates of o-(N-n-o-t-furfuralideneimino)benzoic acid (HFB), the Schiff base derived from furfuraldehyde and anthranilic acid. Hence the present work on the potentiometric studies of these chelates was undertaken.

The measurements were carried out using Calvin-Bjerrum pH-titration technique\(^4\) at 25°, 30° and 35° in aqueous media (\([\mu] = 0\cdot1M, 0\cdot05M\) and 0\cdot01M NaClO\(_4\)).

The apparatus and the reagents employed were the same as reported\(^5\) earlier. HFB was synthesized by the general procedure already reported\(^5\).

For the evaluation of the stability constants, experiments were carried out in media of low ionic strengths (0\cdot1M, 0\cdot05M and 0\cdot01M). From the values obtained, an extrapolation to the zero ionic strength was carried out. The following mixtures (total volume 40\cdot0 ml) were titrated against standard carbonate-free sodium hydroxide (0\cdot1M).

The titration curves had the usual shapes. (i) 10\cdot0 ml of 0\cdot01M HFB + 4\cdot0 ml of 1\cdot0M NaClO\(_4\) + 26\cdot0 ml of water, (ii) 10\cdot0 ml of 0\cdot01M HFB + 4\cdot0 ml of 1\cdot0M NaClO\(_4\) + 10\cdot0 ml of 0\cdot01M metal ion solution + 16\cdot0 ml of water, (iii) 20\cdot0 ml of 0\cdot01M HFB + 10\cdot0 ml of 0\cdot01M metal ion solution + 10\cdot0 ml of 0\cdot01M NaClO\(_4\) + 6\cdot0 ml of water.

The stability constants of the bivalent chelates at different ionic strengths and temperatures are given in Table 1. As indicated by the formation curves, the \(\bar{n}\) value is more than 1\cdot5 in the cases of VO\(^{2+}\), UO\(^{2+}\), Cu(II), Ni(II) and Co(II) chelates suggesting the formation of 1:2 complexes. The value of \(\bar{n}\) is less than 1 for Zn(II) and Cd(II) chelates which suggests the formation of 1:1 complexes in these cases. The stabilities of the metal chelates follow the order, VO\(^{2+}\)> UO\(^{2+}\)> Cu(II)> Ni(II)> Co(II)> Zn(II)> Cd(II), which is in accordance with the Irving-Williams rule\(^6\).

The thermodynamic stability constants were obtained by extrapolation of the experimentally obtained stability constants to zero ionic strength in the plots between log of stability constant and \(\sqrt{\mu}\) where \(\mu\) is the ionic strength. The values of thermodynamic stability constants thus obtained for VO\(^{2+}\), UO\(^{2+}\), Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) chelates are, respectively, 8\cdot63, 8\cdot02, 7\cdot70, 7\cdot15, 7\cdot00, 3\cdot49 and 3\cdot31 at 25°; 8\cdot75, 8\cdot20, 7\cdot80, 7\cdot48, 7\cdot10, 3\cdot55 and 3\cdot45 at 30°; and 9\cdot00, 8\cdot28, 7\cdot90, 7\cdot60, 7\cdot25, 3\cdot65 and 3\cdot45 at 35°. The values of \(-\Delta H\) (in kcal/mole) for these chelates at 25°, 30°

### Table 1 — Dissociation Constants of HFB and Stability Constants of Its Bivalent Metal Chelates at Different Ionic Strengths

<table>
<thead>
<tr>
<th>Dissociation/stability constants</th>
<th>25°</th>
<th>30°</th>
<th>35°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0\cdot1M</td>
<td>0\cdot05M</td>
<td>0\cdot01M</td>
</tr>
<tr>
<td>HFB</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\log K_1^H)</td>
<td>6\cdot10</td>
<td>6\cdot25</td>
<td>6\cdot35</td>
</tr>
<tr>
<td>(\log K_1)</td>
<td>4\cdot43</td>
<td>4\cdot56</td>
<td>4\cdot72</td>
</tr>
<tr>
<td>(\log K_2)</td>
<td>3\cdot59</td>
<td>3\cdot85</td>
<td>3\cdot95</td>
</tr>
<tr>
<td>VO(^{2+})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\log K_1)</td>
<td>4\cdot12</td>
<td>4\cdot36</td>
<td>4\cdot40</td>
</tr>
<tr>
<td>(\log K_2)</td>
<td>3\cdot26</td>
<td>3\cdot30</td>
<td>3\cdot38</td>
</tr>
<tr>
<td>Cu(II)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\log K_1)</td>
<td>4\cdot26</td>
<td>4\cdot30</td>
<td>4\cdot35</td>
</tr>
<tr>
<td>(\log K_2)</td>
<td>3\cdot17</td>
<td>3\cdot20</td>
<td>3\cdot25</td>
</tr>
<tr>
<td>Ni(II)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(\log K_1)</td>
<td>3\cdot84</td>
<td>3\cdot87</td>
<td>3\cdot90</td>
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<td>(\log K_2)</td>
<td>3\cdot09</td>
<td>3\cdot10</td>
<td>3\cdot17</td>
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<td>Co(II)</td>
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<td>(\log K_1)</td>
<td>3\cdot68</td>
<td>3\cdot70</td>
<td>3\cdot80</td>
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<td>(\log K_2)</td>
<td>3\cdot03</td>
<td>3\cdot05</td>
<td>3\cdot10</td>
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<tr>
<td>Zn(II)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\log K_1)</td>
<td>3\cdot22</td>
<td>3\cdot30</td>
<td>3\cdot40</td>
</tr>
<tr>
<td>(\log K_2)</td>
<td>3\cdot07</td>
<td>3\cdot15</td>
<td>3\cdot25</td>
</tr>
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</table>
and 35° respectively are, VO$^{2+}$ (11-76, 12-14, 12-69); UO$^{2+}$ (10-92, 11-37, 11-67); Cu(II) (10-50, 10-79, 11-14); Ni(II) (9-75, 10-37, 10-71); Co(II) (9-54, 9-84, 10-22); Zn(II) (4-75, 4-92, 5-14) and Cd(II) (4-51, 4-67, 4-86).

The data were analysed in terms of the Harned’s relation between log $K$ and temperature $[(\rho K_{\text{H}}-ct^{2})=-2\rho t+(\rho K_{\text{m}}-ct^{2})]$. The values of $\theta$ and $\rho K_{\text{H}}$ for HFB were found to be 188° and 4-78 respectively. $\Delta H$ values as calculated from Harned’s equation were found to be 6-624, 6-637 and 6-643 at 298°, 303° and 308°K respectively.

**References**


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Spectrophotometric Determination of Uranium(VI) with Thiobenzoyltrifluoroacetone

G. N. Rao & V. S. Chouhan

Chemistry Department, Indian Institute of Technology
New Delhi 110029

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Thiobenzoyltrifluoroacetone (SBTA) has been used for the extraction and spectrophotometric determination of uranium(VI). Quantitative extraction of the yellow uranium(VI) complex has been carried out in the pH range 6-8-7-0. Absorbance of the complex was measured at 375 nm. Interference due to a number of cations and anions has also been studied.

Thiobenzoyltrifluoroacetone (STTA) has been used for spectrophotometric determination of several metals$^{1-3}$. Compared to thenoyltrifluoroacetone its thio-derivative forms more intensely coloured chelates with several transition metal ions$^{4}$. Benzoyltrifluoroacetone (BTA) has been used for the extraction and spectrophotometric determination of Cu(II), Ni(II), Co(II)$^{5,6}$ and U(VI)$^{7}$. In this paper extraction and spectrophotometric determination of uranium(VI) with thiobenzoyltrifluoroacetone is described.

Spectrophotometric measurements were performed on Bausch Lomb spectronic-20 spectrophotometer and Unicam SP-500 spectrophotometer. For pH measurements Elico pH-meter was used. Thiobenzoyltrifluoroacetone was prepared starting from benzoyltrifluoroacetone (Fluka reagent grade), following the method of Berg and Reed$^{4}$ with some modifications. Its purity was established by micro-analysis and molecular weight determination (freezing point method). Visible and infrared spectra provided further checks on its purity. Stock solution of uranium(VI) was prepared from reagent grade uranyl acetate and estimated by standard methods. Solutions of required concentrations for the extraction experiments were obtained by suitable dilution. Buffer solutions of the required pH range were prepared from mixtures of acetic acid and sodium acetate and ammonia and ammonium chloride.

**General procedure** — An aliquot (5 ml) of uranium(VI) solution was mixed with the buffer solution (5 ml) of desired pH value in a pyrex glass-stoppered bottle. Thiobenzoyltrifluoroacetone solution (10 ml, 1 mM) in chloroform was added to this solution and the contents were shaken on a wrist-action flask shaker for different intervals of time. After allowing the two layers to settle the organic layer was carefully separated employing a separating funnel and the absorbance of the yellow coloured complex was measured against the reagent blank at 375 nm.

Both the ligand and the metal complex absorb in the region 300-420 nm. Since the maximum difference between the absorbance of the metal complex and the ligand occurs at 375 nm, this wave length was adopted for further detailed work. From experiments carried out with buffers in the pH range 1-9 [uranium(VI) = 160 µg/10 ml, 10 ml of 1 mM SBTA in CHCl$_3$] it was found that quantitative extraction of uranium(VI) occurs in the pH range 6-8-7-0. This was confirmed by checking for uranium(VI) in the aqueous phase. Different amounts of uranium(VI) in the concentration range 3 µg/ml were extracted with 1 mM SBTA in CHCl$_3$. The plot of absorbance versus concentration of uranium(VI) is linear passing through the origin, indicating that Beer’s law is applicable under these conditions. Molar absorptivity of the complex was 9900 $\pm$ 200 and standard deviation was found to be 1-6% in a set of ten measurements with 160 µg of uranium(VI). Experiments conducted with different concentrations of the ligand indicated that 10 ml of 1 mM SBTA was sufficient for quantitative extraction of uranium up to 250 µg. As the ligand also absorbs at 375 nm, there is no advantage in using a higher concentration of the ligand. Effect of diverse ions on the extraction of 160 µg of uranium (VI) with 10 ml of 1 mM SBTA in chloroform was studied by adding the aqueous solutions of the required salts. In presence of 2000 µg of citrate and oxalate the extraction was completely suppressed. Similar amounts of borate and fluoride interfere in the estimation. However, there is no interference from up to 2000 µg of Cl$^-$, Br$^-$, NO$_3^-$, SO$_4^{2-}$, Cd$^{2+}$, Mn$^{2+}$, Th$^{4+}$, Mo(VI), W(VI), Ba$^{2+}$, Ca$^{2+}$, Na$^+$, K$^+$ or Mg$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Pd$^{2+}$, Fe$^{3+}$, Ag$^+$, Cu$^{2+}$, Pb$^{2+}$ and Hg$^{2+}$ are tolerated up to 200 µg. Thus, this method is accurate, sensitive and useful for the determination of uranium(VI) in microgram amounts.

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**References**