The spectra in the region 200-600 cm\(^{-1}\) were obtained on a Beckman spectrophotometer model 12. Conductance measurements were carried out on a Systronics direct reading conductivity meter using a dip type cell having a cell constant of 0.571 cm\(^{-1}\). Magnetic susceptibilities of the complexes were determined by Gouy method using Hg[Co(CNS)\(_4\)] as the calibrant. The electronic spectra of the complexes in the solid state were recorded using null technique on a Unicam SP 700A recording spectrophotometer.

The molar conductance values of the perchlorate complex in nitrobenzene and methanol are 48.97 and 190.1 ohm-cm 2 mole\(^{-1}\) respectively indicating it to be a 1:2 electrolyte. The chloro, bromo and iodo complexes behave as non-electrolytes in nitrobenzene showing \(\Lambda_m\) of 8.29, 13.09 and 12.86 ohm-cm 2 mole\(^{-1}\) respectively. However, in methanol the conductance values of the halo complexes are in the range 123.7-152.9 ohm-cm 2 mole\(^{-1}\). This shows that the halo complexes dissociate considerably in a coordinating solvent like methanol.

A comparison of the IR spectral bands of the free ligand and the complexes shows that the IR frequencies of the amino group do not undergo any appreciable change on complexation. On the other hand the carbonyl stretching frequency observed at 1635 cm\(^{-1}\) in the free ligand is shifted to 1600 cm\(^{-1}\) in the spectra of complexes. This indicates that carbonyl oxygen acts as a donor atom in the complexes and that the amino group is not involved in bonding. A medium to strong intensity band appearing in the range 470-480 cm\(^{-1}\) in the spectra of the complexes and absent in the ligand spectrum can be attributed tentatively to the metal-oxygen stretching frequency. Similarly, a band observed in the region 310-320 cm\(^{-1}\) for the halo complexes can be assigned to the metal-halogen stretching frequency. In the perchlorate complex \(v_4\) and \(v_4\) of the perchlorate group appear as strong bands at 625 and 1090 cm\(^{-1}\) respectively indicating the ionic nature of the perchlorate.

Since the complexes are only sparingly soluble in common solvents, the electronic spectra were recorded in the solid state. The spectra of all the complexes appear to contain an intense band below 400 nm as evidenced by the sharp decrease in the absorption above this wavelength. This may be attributed to a charge-transfer process. Though the solid state electronic spectra do not show any well defined band between 750 and 1400 nm, all the complexes show a comparatively weak absorption maximum in the range 1150-1250 nm. This can be attributed to the weak d-d transition expected around 1000 nm for octahedral complexes of Fe(II).

The effective magnetic moment values show that all the complexes are of the spin-free type. The perchlorate complex shows a magnetic moment of 5.7 BM which is much higher than the spin only value of 4.9 BM. This is not surprising in view of the fact that this complex is likely to have a regular octahedral configuration as suggested by the molecular formula. A large orbital contribution to the magnetic moments is expected for a regular octahedral complex of high spin Fe(II). The magnetic moments of the other complexes (5.17-5.34 BM) are in the ranges expected for tetrahedral or distorted octahedral complexes of Fe(II). However, the electronic spectral data supports a distorted octahedral structure for the halo complexes.

The authors thank the authorities of the Indian Institute of Science, Bangalore, for the electronic spectra and the Indian Institute of Technology, Madras, for the IR spectra.

References

Addition Compounds of Uranyl Chloride, Bromide & Nitrate with Diphenyl Sulphoxide, Thianthrene-5-oxide, 2,9-Dimethyl-1,10-phenanthrolene & 6,6'-Dimethyl-2,2'-bipyridyl

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Addition compounds of uranyl chloride, bromide and nitrate with diphenyl sulphoxide, thianthrene-5-oxide, 2,9-dimethyl-1,10-phenanthrolene and 6,6'-dimethyl-2,2'-bipyridyl have been prepared. IR data of the complexes are discussed and an attempt has been made to explain the type of coordinate bond formed. Diphenyl sulphide, diphenyl sulphone and thianthrene do not form addition compounds.

A FEW complexes of uranium chloride, bromide and nitrate with organic ligands have been prepared although a large number of the complexes of uranium(IV) halides are reported in the literature. The preparation and characterization of addition compounds of the uranyl salts with the title ligands are reported in this note. The addition compounds formed are similar to those reported with uranium tetrahalides.

All solvents were dried carefully by conventional methods. Wherever necessary reactions were carried out under \(N_2\) atmosphere. Uranium chloride and bromide were determined by volumetric method.
which is based on the work of Corpel and Regnaud\textsuperscript{10}.

Anhydrous uranyl chloride, prepared from the hydrated sample by heating it in a stream of HCl, raising the temperature to 350° during 4 hr and maintaining at this temperature for another 2 hr, was obtained as a solid which gave satisfactory elemental analysis. Uranyl bromide and nitrate of BDH grade were used as such. Diphenyl sulphoxide (m.p. 143\textsuperscript{\circ}C and thianox (m.p. 161\textsuperscript{\circ}C) before use. 6,6'-Dimethyl-2,2'-bipyridyl and 2,9-dimethyl-1,10-phenanthroline (DM-o-phen) and 6,6'-dimethyl-2,2'-bipiridyld (DM-bipy) gave complexes of the type \( \text{UO}_4\text{X}_5\text{L}_4 \). This may be attributed partly to steric hindrance and partly because these two compounds are chelated ligands.

An interesting feature of the IR spectra (values in cm\textsuperscript{-1}) of uranyl complexes, presently studied, is the broadening of \( \text{UO}_2^{2+} \) stretching band in the region 980-960, and its shift from 925 (ref. 16). The \( \nu(C=O) \) of ethyl acetate appearing at 1740 (ref. 17) is shifted to lower frequency region (1630) in the bis-addition product. The magnitude of shift in \( \nu(C=O) \) in ethyl acetate complexes has been used to estimate the strength of M-O bonds\textsuperscript{18}. The peak in uranium tetrachloride-bis-(ethyl acetate) appears as a doublet at 1620 and 1650 with maxima of equal intensity. These shifts in \( \nu(C=O) \) of ethyl acetate are of the same order as those found by Lappert\textsuperscript{18} for several other bis-(ethyl acetate) complexes with groups III and IV halides. The doublet is a strong indication that the two ethyl acetate ligands are in cis-positions.

The three uranyl salts did not form complexes with ligands containing two bivalent sulphur atoms such as diphenyl sulphide, diphenyl sulphone or thianthrene (C\textsubscript{14}H\textsubscript{12}S\textsubscript{2}) under similar conditions. The bulky organic ligands, 2,9-dimethyl-1,10-phenanthroline(DM-o-phen) and 6,6'-dimethyl-2,2'-bipiridyld (DM-bipy) gave complexes of the type \( \text{UO}_4\text{X}_5\text{L}_4 \).

The two major IR bands of the diphenyl sulphone at \( \sim 730 \) and \( \sim 1250 \) were also shifted to lower frequency region. The shift of the ring vibrations in the region 1700-1400 is due to the presence of the conjugated system in the diphenyl sulphone. The absorption bands of diphenyl sulphone at \( \nu(S=O) = 1075 \) which are shifted to lower frequency region (990-960) on complex formation. These observations indicate coordination of diphenyl sulphone and thianox through oxygen. Similar interpretations are reported for the triphenylphosphine oxide complexes\textsuperscript{5,21}. The IR spectra of U(VI) complexes with DM-o-phen and DM-bipy showed certain differences from those of the free ligands. The most obvious was a general shift of the ring vibrations in the region 1700-1400 to lower frequencies, presumably because of coordination of both the nitrogen atoms of the ligands with the central U(VI) ion. Multiple splittings were

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Yield</th>
<th>m.p. °C</th>
<th>Halogen</th>
<th>MoI. formula</th>
<th>Calc. (%)</th>
</tr>
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<tr>
<td>( \text{UO}_4\text{Cl}_2\text{2EtAc} )</td>
<td>92</td>
<td>41</td>
<td>Cl</td>
<td>( \text{C}_4\text{H}_6\text{Cl}_4\text{O}_4\text{U} )</td>
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<tr>
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<td>84</td>
<td>218</td>
<td>Cl</td>
<td>( \text{C}_4\text{H}_6\text{Cl}_4\text{O}_4\text{U} )</td>
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<tr>
<td>( \text{UO}_4\text{Cl}_2\text{2PhH}_2\text{SO} )</td>
<td>70</td>
<td>220-22</td>
<td>Cl</td>
<td>( \text{C}_4\text{H}_6\text{Cl}_4\text{O}_4\text{U} )</td>
<td>9-5 32-0</td>
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<td>( \text{UO}_4\text{Br}_2\text{2thianox} )</td>
<td>81</td>
<td>265 (d)</td>
<td>Br</td>
<td>( \text{C}_4\text{H}_6\text{Br}_4\text{O}_4\text{U} )</td>
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<tr>
<td>( \text{UO}_4\text{Br}_2\text{2thianox} )</td>
<td>83</td>
<td>&lt;230</td>
<td>Br</td>
<td>( \text{C}_4\text{H}_6\text{Br}_4\text{O}_4\text{U} )</td>
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<tr>
<td>( \text{UO}_4\text{Br}_2\text{2thianox} )</td>
<td>87</td>
<td>&lt;230</td>
<td>Br</td>
<td>( \text{C}_4\text{H}_6\text{Br}_4\text{O}_4\text{U} )</td>
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<tr>
<td>( \text{UO}_4\text{Cl}_2\text{3PhH}_2\text{SO} )</td>
<td>72</td>
<td>112 (d)</td>
<td>Cl</td>
<td>( \text{C}_4\text{H}_6\text{Cl}_4\text{O}_4\text{U} )</td>
<td>29-9</td>
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<tr>
<td>( \text{UO}_4\text{NO}_3\text{2thianox} )</td>
<td>78</td>
<td>153 (d)</td>
<td>NO</td>
<td>( \text{C}_4\text{H}_6\text{NO}_3\text{O}_4\text{U} )</td>
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<tr>
<td>( \text{UO}_4\text{Cl}_2\text{DM-o-phen} )</td>
<td>74</td>
<td>240</td>
<td>Cl</td>
<td>( \text{C}_4\text{H}_6\text{Cl}_4\text{O}_4\text{U} )</td>
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<tr>
<td>( \text{UO}_4\text{Cl}_2\text{DM-bipy} )</td>
<td>72</td>
<td>&lt;230</td>
<td>Cl</td>
<td>( \text{C}_4\text{H}_6\text{Cl}_4\text{O}_4\text{U} )</td>
<td>39-5</td>
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</table>

*Satisfactory C and H analyses were also obtained.
also observed in both the complexes in the region 900-725. Similar behaviour of the other metal complexes with o-phenanthroline was observed by Schilt and Taylor\textsuperscript{21}.

References

Tris(trimethyl-stannyl,-germyl,-silyl)borates
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Tris(trimethylstannyl)borate has been synthesized by the reaction of bis(trimethylstannyloxide) with boronic acid. Tris(trimethyl-silyl and -germyl)borate was prepared by the reaction of tris(trimethylstannyl)borate with trimethylchloro-silane and -germane. The compounds have been characterized on the basis of IR and PMR spectra.

The reactions of B=O-C linkage, e.g. in alkyl borates, have been extensively studied. In recent years, attention has been directed to derivatives having B-O-M linkage\textsuperscript{23}. Only a few such derivatives having B-O-Si\textsuperscript{4} linkage have previously been known. The present paper deals with the synthesis as well as spectral studies of tris(trimethyl-silyl, -germyl and -stannyl)borates.

The preparation of tris(trimethylsilyl)borate by the reaction of boronic acid with trimethylchlorosilane was reported by Abel and Singh\textsuperscript{5}. The corresponding germanium and tin derivatives, B(OOMe)\textsubscript{3}, (M = Ge and Sn) could not be obtained by the above route\textsuperscript{6}. Recently, we synthesized tris(trimethyl-stannyl)borate by an alternative route\textsuperscript{6} involving the reaction

\[ \text{C}_3\text{H}_8 \text{B(OH)}_3 + \text{M} \mathrm{Cl}_2 \rightarrow \text{B(OOMe)}_3 + \text{MCl}_2 \text{Me}_3 \]

Tris(tributyl-germyl)borate could also be synthesized easily by the above method. The corresponding reaction between bis(trimethyl-germanium) oxide and boronic acid appears to be quite slow. Thus, tris(trimethyl-germyl)borate, B(OGeMe)\textsubscript{3}, could be easily obtained by the interaction between (Me\textsubscript{3}Ge)\textsubscript{2}O and boronic acid. This reaction did not appear to proceed at all in case of silicon even after 24 hr of refluxing.

Thus, the reactivity of bis(trimethyl-metal)oxide with boronic acid (or oxide) decreases in the following order: Sn>Ge>Si.

B-O-Sn linkage is readily cleaved by chloro-silanes and chloro-germanes and, therefore, the reaction offers a convenient route for synthesis of tris(trimethyl-silyl and -germyl)borates (Eq. 2). The reactions of tris(tributyl-stannyl)borate with trimethylchloro-silane or -germane are exothermic and the products are obtained in quantitative yields. Fractional distillation gave pure products (PMR) as tris(trimethyl-silyl or -germyl)borate distils at a lower temperature than tributyl-tin chloride:

\[ \text{B(OOSnBu)}_3 + \text{Me}_3\text{MCl} \rightarrow \text{B(OOMe)}_3 + \text{Bu}_3\text{SnCl} \]

(\text{M} = \text{Si or Ge})

IR spectral absorptions of tris(trimethyl-silyl, -germyl and -stannyl)borates in the range 3600-400 cm\textsuperscript{-1} with tentative assignments have been tabulated in Table 1.

The \( \nu_{as} \) (B-O-M) frequencies showed a gradual decrease in going from silicon (1325 cm\textsuperscript{-1}) via germanium (1315 cm\textsuperscript{-1}) to tin (1300-1285 cm\textsuperscript{-1}). The tentative assignment of \( \nu_{as} \) (B-O-M) in the range 1305-20 finds support from the following two observations:

(i) During the preparation of tris(trimethylstannyl)borate from bis(trimethyltin)oxide, the strong absorption at 740 cm\textsuperscript{-1} due to \( \nu_{as} \) (Sn-O-Sn) disappears completely and a strong peak appears at 1300-1285 cm\textsuperscript{-1}.

Table 1 - Infrared Data of Tris(trimethyl-silyl, -germyl, -stannyl)borates

<table>
<thead>
<tr>
<th>B(OOMe)\textsubscript{3}</th>
<th>B(OGeMe)\textsubscript{3}</th>
<th>B(OSnMe)\textsubscript{3}</th>
<th>Tentative assignments</th>
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</thead>
<tbody>
<tr>
<td>2970 s</td>
<td>2975 m</td>
<td>2975 m</td>
<td>( \nu_{as} ) ( \text{CH}_3 )</td>
</tr>
<tr>
<td>2900 w</td>
<td>2920 m</td>
<td>2920 m</td>
<td>( \nu_{as} ) ( \text{CH}_3 )</td>
</tr>
<tr>
<td>1410 s</td>
<td>1400 m</td>
<td>1400 w(ah)</td>
<td>( \nu_{as} ) ( \text{BO}_3 )</td>
</tr>
<tr>
<td>1370 vs</td>
<td>1345 vs</td>
<td>1345 vs(ah)</td>
<td>( \nu_{as} ) (B-O-M)</td>
</tr>
<tr>
<td>1325 vs</td>
<td>1315 vs</td>
<td>1300-1285 vs(br)</td>
<td>( \nu_{as} ) (B-O-M)</td>
</tr>
<tr>
<td>1257 vs</td>
<td>1240 vs</td>
<td>1188 s</td>
<td>( \delta_{\text{CH}_3} )</td>
</tr>
<tr>
<td>833 vs</td>
<td></td>
<td></td>
<td>( \nu_{as} ) (Si-O)</td>
</tr>
<tr>
<td>842 vs</td>
<td>821 vs, 725 s</td>
<td>775-65 vs(br)</td>
<td>( \nu_{as} ) (Si-O)</td>
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<tr>
<td>755 vs</td>
<td>755, 685 w</td>
<td>685 s</td>
<td>( \delta_{\text{Si-Ge}} )</td>
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<tr>
<td>677 w</td>
<td>609 vs</td>
<td>532 vs</td>
<td>( \nu_{as} ) (Si-O)</td>
</tr>
<tr>
<td>618 w</td>
<td>568 w</td>
<td>507 w</td>
<td>( \nu_{as} ) (Si-O)</td>
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</table>