

The spectra in the region 200-600  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$ . Magnetic susceptibilities of the complexes were determined by Gouy method using  $\text{Hg}[\text{Co}(\text{CNS})_4]$  as the calibrant. The electronic spectra of the complexes in the solid state were recorded using mull 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  $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$  respectively indicating it to be a 1:2 electrolyte<sup>3</sup>. The chloro, bromo and iodo complexes behave as non-electrolytes in nitrobenzene showing  $\Lambda_M$  of 8.29, 13.09 and 12.86  $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$  respectively. However, in methanol the conductance values of the halo complexes are in the range 123.7-152.9  $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ . 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  $\text{cm}^{-1}$  in the free ligand is shifted to 1600  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  in the spectra of the complexes and absent in the ligand spectrum can be attributed tentatively to the metal-oxygen stretching frequency<sup>9</sup>. Similarly, a band observed in the region 310-320  $\text{cm}^{-1}$  for the halo complexes can be assigned to the metal-halogen stretching frequency. In the perchlorate complex  $\nu_3$  and  $\nu_4$  of the perchlorate group appear as strong bands at 625 and 1090  $\text{cm}^{-1}$  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)<sup>10</sup>. 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)<sup>10,11</sup>. However the electronic spectral data supports a distorted octahedral structure for the halo complexes.

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#### Addition Compounds of Uranyl Chloride, Bromide & Nitrate with Diphenyl Sulphoxide, Thianthrene-5-oxide, 2,9-Dimethyl-1,10-phenanthroline & 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-phenanthroline, 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 uranyl chloride, bromide and nitrate with organic ligands have been prepared<sup>1-3</sup> although a large number of the complexes of uranium(IV) halides are reported in the literature<sup>3-8</sup>. 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<sup>9</sup>. Wherever necessary reactions were carried out under  $\text{N}_2$  atmosphere. Uranium chloride and bromine were determined by volumetric method

TABLE 1 — PHYSICAL DATA OF VARIOUS COMPLEXES PREPARED

Complexes	Yield %	m.p. °C	Found (%)*		Mol. formula	Calc. (%)	
			Halogen	U		Halogen	U
UO <sub>2</sub> Cl <sub>2</sub> .2EtAc	92	41	13.8	46.2	C <sub>8</sub> H <sub>16</sub> Cl <sub>2</sub> O <sub>6</sub> U	13.7	46.0
UO <sub>2</sub> Cl <sub>2</sub> .3Ph <sub>2</sub> SO	84	218	7.1	24.8	C <sub>36</sub> H <sub>30</sub> Cl <sub>2</sub> O <sub>6</sub> S <sub>3</sub> U	7.3	25.1
UO <sub>2</sub> Cl <sub>2</sub> .2Ph <sub>2</sub> SO	70	220-22	9.7	31.9	C <sub>24</sub> H <sub>20</sub> Cl <sub>2</sub> O <sub>4</sub> S <sub>2</sub> U	9.5	32.0
UO <sub>2</sub> Cl <sub>2</sub> .2thianox	81	265 (d)	8.9	29.7	C <sub>24</sub> H <sub>12</sub> Cl <sub>2</sub> O <sub>4</sub> S <sub>4</sub> U	8.8	29.54
UO <sub>2</sub> Br <sub>2</sub> .2Ph <sub>2</sub> SO	83	<230	19.0	28.2	C <sub>24</sub> H <sub>16</sub> Br <sub>2</sub> O <sub>4</sub> S <sub>2</sub> U	19.2	28.5
UO <sub>2</sub> Br <sub>2</sub> .2thianox	87	<230	17.3	26.7	C <sub>24</sub> H <sub>16</sub> Br <sub>2</sub> O <sub>4</sub> S <sub>4</sub> U	17.9	26.6
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> .2Ph <sub>2</sub> SO	72	112 (d)	—	29.7	C <sub>24</sub> H <sub>20</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub> U	—	29.9
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> .2thianox	78	153 (d)	—	27.5	C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>10</sub> S <sub>4</sub> U	—	27.7
UO <sub>2</sub> Cl <sub>2</sub> .DM- <i>o</i> -phen	80	<230	12.6	43.5	C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> Cl <sub>2</sub> O <sub>6</sub> U	12.9	43.3
UO <sub>2</sub> Cl <sub>2</sub> .DM-bipy	82	<230	13.3	45.0	C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> Cl <sub>2</sub> O <sub>2</sub> U	13.5	45.3
UO <sub>2</sub> Br <sub>2</sub> .DM- <i>o</i> -phen	71	<230	24.9	37.7	C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> Br <sub>2</sub> O <sub>2</sub> U	25.1	37.3
UO <sub>2</sub> Br <sub>2</sub> .DM-bipy	83	<230	26.3	38.6	C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> Br <sub>2</sub> O <sub>2</sub> U	26.0	38.8
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> .DM- <i>o</i> -phen	73	<230	—	39.3	C <sub>14</sub> H <sub>12</sub> N <sub>4</sub> O <sub>8</sub> U	—	39.5
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> .DM-bipy	75	<230	—	41.0	C <sub>12</sub> H <sub>12</sub> N <sub>4</sub> O <sub>8</sub> U	—	41.2

\*Satisfactory C and H analyses were also obtained.

which is based on the work of Corpel and Regnaud<sup>10</sup>. This method was found to be rapid and precise<sup>10</sup>.

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. 71°)<sup>11</sup> and thianox (m.p. 143°) were prepared by oxidation of the sulphides with N<sub>2</sub>O<sub>4</sub> in carbon tetrachloride<sup>12</sup> Ph<sub>2</sub>SO<sub>2</sub> (Eastman grade) recrystallized from ethanol m.p. 128° (ref. 13) before use. 6,6'-Dimethyl-2,2'-bipyridyl and 2,9-dimethyl-*o*-phenanthroline (m.p. 161°) recrystallized from ethyl acetate before use.

Reactions between the metal salts and the appropriate quantity of ligand were carried out in anhydrous ethyl acetate; yields, m.ps. and analytical data for the products are recorded in the Table 1.

Uranyl chloride dissolves readily in ethyl acetate, and on evaporating this solution at room temperature under reduced pressure yellow crystalline product of uranyl chloride-bis-(ethyl acetate), m.p. 42° (d), was obtained. Uranium tetrachloride-bis-(ethyl acetate), m.p. 41° (d), has been prepared in a similar manner<sup>14</sup> and reported here for comparison purposes.

Uranyl chloride and bromide dissolve in ethyl acetate and when solutions of diphenyl sulphoxide in ethyl acetate were added to the uranyl salt solutions in a molar ratio of 2:1, yellow crystalline complexes of the type UO<sub>2</sub>X<sub>2</sub>.2Ph<sub>2</sub>SO, (where Ph<sub>2</sub>SO = diphenyl sulphoxide, and X = Cl, Br or NO<sub>3</sub>), were obtained.

However, the above reaction of diphenyl sulphoxide in 4:1 (ligand-metal) molar ratio gave the complex UO<sub>2</sub>Cl<sub>2</sub>.3Ph<sub>2</sub>SO. This complex was previously prepared by the atmospheric oxidation of the green crystalline addition compound UCl<sub>4</sub>.4Ph<sub>2</sub>SO in ethanol<sup>15</sup>. Though the complex crystallized unchanged from warm ethyl acetate, it decomposed on boiling to give yellow crystals of UO<sub>2</sub>Cl<sub>2</sub>.2Ph<sub>2</sub>SO, and diphenyl sulphoxide was recovered from the filtrate.

Uranyl chloride, bromide, and nitrate formed addition compounds with thianthrene-5-oxide (thianox) of the type UO<sub>2</sub>X<sub>2</sub>.2-thianox.

The three uranyl salts did not form complexes with ligands containing two bivalent sulphur atoms such as diphenyl sulphide, diphenyl sulphone or thianthrene (C<sub>6</sub>H<sub>4</sub>S)<sub>2</sub> under similar conditions. The bulky organic ligands, 2,9-dimethyl-1,10-phenanthroline (DM-*o*-phen) and 6,6'-dimethyl-2,2'-bipyridyl (DM-bipy) gave complexes of the type UO<sub>2</sub>X<sub>2</sub>.L. 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<sup>-1</sup>) of uranyl complexes, presently studied, is the broadening of UO<sub>2</sub><sup>2+</sup> stretching band in the region 980-960, and its shift from 925 (ref. 16). The ν(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 ν(C=O) in ethyl acetate complexes has been used to estimate the strength of M—O bonds<sup>18</sup>. The peak in uranium tetrachloride-bis-(ethyl acetate) appears as a doublet at 1620 and 1650 with maxima of equal intensity. These shifts in ν(C=O) are of the same order as those found by Lappert<sup>18</sup> 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 IR spectrum<sup>19</sup> of diphenyl sulphoxide shows a band at 1040 corresponding to ν(S=O) which shifts to lower frequency region (990-960) on complex formation. The complex, UO<sub>2</sub>Cl<sub>2</sub>.3Ph<sub>2</sub>SO exhibited a doublet<sup>20</sup> with well-defined maxima at 990 and 965. The ν(S=O) in thianox appearing at 1075 which changes into a doublet in the region 980-960 on complex formation. These observations indicate coordination of diphenyl sulphoxide and thianox through oxygen. Similar interpretations are reported for the triphenylphosphine oxide complexes<sup>3,21</sup>. 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

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<sup>22</sup>.

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## Tris(trimethyl-stannyl-, -germyl-, -silyl)borates

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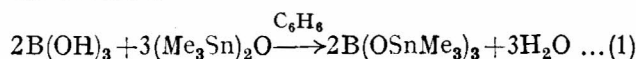
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Tris(trimethylstannyl)borate has been synthesized by the reaction of bis(trimethyltin)oxide with boric acid. Tris(trimethyl-silyl and -germyl)borates have been prepared by the reactions of tris(tributylstannyl)-borate with trimethylchloro-silane and -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<sup>1</sup>. In recent years, attention has been directed to derivatives having B-O-M linkage<sup>2,3</sup>. Only a few such derivatives having B-O-Si<sup>4</sup> 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 boric acid with trimethylchlorosilane

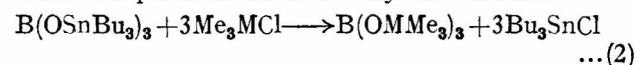
was reported by Abel and Singh<sup>2</sup>. The corresponding germanium and tin derivatives, B(OMMe<sub>3</sub>)<sub>3</sub>, (M = Ge and Sn) could not be obtained by the above route<sup>5</sup>. Recently, we synthesized tris(trimethylstannyl)borate by an alternative route<sup>6</sup> involving the reaction



Tris(tributyl-germyl)borate could also be synthesized easily by the above method. The corresponding reaction between bis(trimethyl-germanium) oxide and boric acid appears to be quite slow. However, tris(trimethyl-germyl)borate, B(OGeMe<sub>3</sub>)<sub>3</sub>, could be easily obtained by the interaction between (Me<sub>3</sub>Ge)<sub>2</sub>O and boric oxide. 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 boric 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:



(M = Si and Ge)

IR spectral absorptions of tris(trimethyl-silyl, -germyl and -stannyl)borates in the range 3600-400 cm<sup>-1</sup> with tentative assignments have been tabulated in Table 1.

The ν<sub>as</sub> (B-O-M) frequencies showed a gradual decrease in going from silicon (1325 cm<sup>-1</sup>) via germanium (1315 cm<sup>-1</sup>) to tin (1300-1285 cm<sup>-1</sup>). The tentative assignment of ν<sub>as</sub> (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<sup>-1</sup> due to ν<sub>as</sub> (Sn-O-Sn) disappears completely and a strong peak appears at 1300-1285

TABLE 1 — INFRARED DATA OF TRIS(TRIMETHYL-SILYL, -GERMYL, -STANNYL)BORATES

B(OSiMe <sub>3</sub> ) <sub>3</sub>	B(OGeMe <sub>3</sub> ) <sub>3</sub>	B(OSnMe <sub>3</sub> ) <sub>3</sub>	Tentative assignments
2970 s	2975 m	2975 m	ν <sub>as</sub> CH <sub>3</sub>
2900 w	2920 m	2920 m	ν <sub>s</sub> CH <sub>3</sub>
1410 s	1400 m	1400 w(sh)	δ <sub>as</sub> CH <sub>3</sub>
1370 vs	1345 vs	1345 vs(sh)	ν <sub>as</sub> (BO <sub>3</sub> )
1325 vs	1315 vs	1300-1285 vs(br)	ν <sub>as</sub> (B-O-M)
1257 vs	1240 vs	1188 s	δ <sub>s</sub> (CH <sub>3</sub> )
883 vs			ν <sub>as</sub> (Si-O)
842 vs	821 vs, 725 s	775-65 vs(br)	ρ <sub>as</sub> (CH <sub>3</sub> ) <sub>3</sub> M
755 vs	755, 685 w	685 s	ρ <sub>s</sub> (CH <sub>3</sub> ) <sub>3</sub> M
677 w	609 vs	532 vs	ν <sub>as</sub> C <sub>2</sub> M
618 w	568 w	507 w	ν <sub>s</sub> C <sub>2</sub> M

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