Synthesis, Reactivity & Structural Studies of Some Titanyl Dithiocarbamates

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Several new titanyl dithiocarbamates, \( \text{O} = \text{Ti(dtch)} \), and their bimetallic derivatives obtained with Hg(II) salts have been prepared and characterised on the basis of various physicochemical studies. In bimetallic derivatives coordination from one of the sulphur atoms of the \( \text{O} = \text{Ti(dtch)} \) to Hg(II) is concluded.

In recent years, there has been great interest in metal dithiocarbamates due to their use as fungicides and pesticides. Many studies have been done on the transition and non-transition metal dithiocarbamates, but only a few reports have appeared on corresponding oxometal derivatives. This paper describes some titanyl dithiocarbamates and their bimetallic derivatives with soft acceptors such as Hg(II) salts. This study, therefore, for the first time reports coordination from the long pair on the sulphur atom, initially loosely bonded to oxotitanium moiety, to Hg(II).

Materials and Methods

Potassium titanium oxalate (Mayfair & Croydon, England) was converted to \( \text{O} = \text{Ti(OH)}_2 \) by interaction with aqueous ammonium hydroxide. Carbon disulphide (B D H), amines (Aldrich), 2,2-dimethoxypropane (Aldrich) and triethyl orthoformate (Aldrich) were distilled/recrystallized before use. The solvents were purified by standard methods.

Preparation of titanyl bis(dithiocarbamates)

The title compounds were prepared by the insertion of CS\(_2\) between titanyl hydroxide and amines using 2,2-dimethoxypropane or triethyl orthoformate (Aldrich) as solvent according to the following equation,

\[ \text{O} = \text{Ti(OH)}_2 + 2\text{CS}_2 + 2\text{R}_2\text{NH} \rightarrow \text{O} = \text{Ti}[\text{S(S)CNR}_2]_2 + 2\text{H}_2\text{O} \]

(for nature of R see Table 1)

In a representative experiment, to a mixture of freshly prepared hydrated titanyl hydroxide (10mmol) and carbon disulphide (20 mmol) suspended in 25 ml of 2,2-dimethoxypropane, was added morpholine (20 mmol) in 10 ml of the same solvents at \( \sim -20^\circ\text{C} \) with constant stirring. The reaction mixture was further stirred for several hours. The precipitated titanyl bis-(morpholine dithiocarbamate) was filtered, washed with diethyl ether and dried under P\(_2\)O\(_5\) in vacuo.

Identical products were obtained by the reaction of titanyl chloride with ammonium morpholine dithiocarbamate in methanol at room temperature.

Reaction of titanyl bis(morpholine dithiocarbamates) with Hg(II) salts

In a representative experiment, to a stirring ethereal solution of titanyl bis-(morpholine dithiocarbamate) (10 mmol), was added \( \text{HgCl}_2 \) (20 mmol) in acetone/diethyl ether mixture. The reaction mixture was stirred for about 10 hr and filtered. The precipitated product was washed several times with acetone/methanol mixture and dried over P\(_2\)O\(_5\) in vacuo. Similar complexes were prepared by using other mercury(II) salts such as \( \text{Hg(SCN)}_2 \), \( \text{Hg(OCCF}_3\text{)}_2 \) and \( \text{Hg(OClO}_3\text{)}_2 \) as acceptors (Table 2).

Ti and Hg were determined gravimetrically by reported methods. Analytical data for C, H, N at the semimicro scale, infrared spectra in the range of 4000-200 cm\(^{-1}\) and UV spectra in absolute methanol were recorded at CDRI, Lucknow. The molar conductance was measured at room temperature by a Phillips magic eye conductivity bridge model PR 9500 using a dip-type conductivity cell. Magnetic susceptibilities were determined at room temperature by Gouy's method. T.G. analysis was carried out at room temperature on a manual balance supplied by the Fertilizer Corporation of india, using a platinum crucible.

Results and Discussion

The elemental analyses indicate 1:2 (metal:dithiocarbamate) stoichiometry for the complexes. The compounds are colourless to light grey, inert to atmospheric oxygen and moisture. They are sparingly soluble in methanol, DMSO and DMF, but are insoluble in other common organic solvents. The conductance data (10-20 ohm cm\(^2\) mol\(^{-1}\)) show...
Table 1—Analytical Data of the Titanyl Bis(dithiocarbamates)

<table>
<thead>
<tr>
<th>Complexes</th>
<th>m.p. (°C)</th>
<th>Yield (%)</th>
<th>Found (Calc.) (%)</th>
</tr>
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<tbody>
<tr>
<td>O = Ti[S(S)CN(C₂H₅)₂]₂</td>
<td>&gt;240</td>
<td>85</td>
<td>Ti 13.03 C 33.17 H 5.40 N 7.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(13.33) (33.33) (5.55) (7.77)</td>
</tr>
<tr>
<td>O = Ti[S(S)CNHC₃H₇]₂</td>
<td>&gt;240</td>
<td>88</td>
<td>Ti 13.17 C 32.24 H 5.32 N 7.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(13.33) (33.33) (5.55) (7.77)</td>
</tr>
<tr>
<td>O = Ti[S(S)CN(C₆H₅)₂]₂</td>
<td>&gt;240</td>
<td>94</td>
<td>Ti 10.06 C 45.55 H 7.60 N 5.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(10.16) (45.76) (7.62) (5.93)</td>
</tr>
<tr>
<td>O = Ti[S(S)CN(CH₂C₆H₅)₂]₂</td>
<td>&gt;240</td>
<td>95</td>
<td>Ti 8.50 C 56.30 H 3.40 N 5.00</td>
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<td>(8.69) (56.52) (3.62) (5.07)</td>
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| Table 2—Analytical Data of Titanyl Bis-(morpholine dithiocarbamate).2HgX₂

<table>
<thead>
<tr>
<th>Complexes</th>
<th>m.p. (°C)</th>
<th>Found (Calc.) (%)</th>
</tr>
</thead>
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<tr>
<td>O = Ti[S(S)CN(C₆H₅)₂].2HgCl₂</td>
<td>206(d)</td>
<td>Ti 5.06 C 42.80 H 12.76 N 1.68</td>
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<td></td>
<td></td>
<td>(5.16) (43.01) (12.90) (1.72) (3.01)</td>
</tr>
<tr>
<td>O = Ti[S(S)CN(C₆H₅)₂].2Hg(SCN)₂</td>
<td>168(d)</td>
<td>Ti 4.55 C 39.12 H 16.14 N 1.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(4.70) (39.21) (16.47) (1.36) (8.23)</td>
</tr>
<tr>
<td>O = Ti[S(S)CN(C₆H₅)₂].2Hg(OClO₃)₂</td>
<td>218(d)</td>
<td>Ti 3.86 C 33.60 H 16.44 N 1.44</td>
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<td></td>
<td></td>
<td>(4.04) (33.72) (16.47) (1.36) (8.23)</td>
</tr>
<tr>
<td>O = Ti[S(S)CN(C₆H₅)₂].2Hg(OCCOF₃)₂</td>
<td>143(d)</td>
<td>Ti 3.65 C 32.02 H 16.44 N 1.44</td>
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<tr>
<td></td>
<td></td>
<td>(3.67) (32.25) (16.47) (1.36) (8.23)</td>
</tr>
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their non-electrolytic nature in DMSO. Magnetic measurements showed that the complexes are diamagnetic.

The TG analyses of a few representative samples at a heating rate of 5°C min⁻¹ indicated their slow decomposition at 100°C into CS₂ and organic matter. At 160°C, a mixture of O = Ti−S and TiO₂ was obtained which ultimately changed to TiO₂ at 440°C (ref. 2).

The ultraviolet spectra of a few representative compounds were screened in absolute methanol in the range 400-200 nm. The strong absorptions observed at 260 nm and 290 nm are tentatively assigned to intraligand π−π* transitions. The absence of splitting supports the chelating behaviour of the dithiocarbamate group.

In the IR spectra of oxotitanium bis(dithiocarbamates) in KBr, a consistent strong single band occurring in the region 1020 ± 5 cm⁻¹ has been assigned to νC = S; it suggests chelating behaviour of the dithiocarbamate group. An absorption around 1430 ± 5 cm⁻¹, assigned to νC=S=N, is characteristic of the thioureide bond having a partial double bond character. Absorptions located at 1040 ± 5 and 380 ± 2 cm⁻¹ are tentatively assigned to ν(Ti=O) and ν(Ti−S) modes of vibration, respectively. Titanyl bis(dithiocarbamates) may be assigned structure (I) in the solid state.

Spectra of a few titanyl bis(dithiocarbamates) were screened in methanol solution also which showed distinct splitting of ν(C=S) and ν(C= S) absorptions. The two absorptions appeared at 1510 ± 5, 1470 ± 10 and 1008 ± 5 and 995 ± 5 cm⁻¹, respectively indicating a change from bidentate to unidentate mode of bonding by the dithiocarbamate group in solution.

In the IR spectra of the complexes, O = Ti(dtcur2).2HgX₂, (X = SCN, Cl, OClO₃, OCOCF₃), appearance of a single strong band due to ν(C=S)
around 1005 cm\(^{-1}\) and of \(v(C\rightarrow N)\) at 1470±5 indicates coordination from both the sulphur atoms, one of which is bonded to titanium and the other forms a bridge with the soft Hg(II) atom. Due to the formation of a new coordinate bond, an electron drift from the alkyl group (R) takes place resulting in an increase in the double bond character of (C\rightarrow N) and decrease in that of (C = S) bond. The former, therefore, shows a distinct positive shift while the latter undergoes a negative shift. The titanium associated absorptions, however, remain unaltered. The Hg –S absorption lies beyond the recording range of the spectrophotometer.

The characteristic absorption associated with group X have been identified. In Hg(SCN)\(_2\), \(vC=N\), \(vC=S\), and \(\delta NCS\) appear at 2050, 730 and 465 cm\(^{-1}\) respectively indicating Hg –S bonding\(^{17}\). In Hg(OCCF\(_3\))\(_2\), two diagnostic absorptions due to \(v_s\)OCO and \(v_{sym}\)OCO appear at 1690 and 1420 cm\(^{-1}\) respectively indicating unidentate bonding of the trifluoroacetate group to Hg\(^{18}\). In Hg(ClO\(_4\))\(_2\), \(v_{as}\)Cl\(-O\), \(v_{sym}\)Cl\(-O\), \(\delta_{as}\)Cl\(-O\), \(\delta_{sym}\)Cl\(-O\), \(\delta_{as}\)ClO\(_3\), \(\delta_{as}\)ClO\(_3\) are located at 910, 1040, 1130, 690 and 615 cm\(^{-1}\) respectively showing covalent character\(^{19,20}\) of the perchlorate group. The Hg atom in the molecule is thus tri-coordinated as described by several other workers\(^{21}\).

One of the sulphur atoms of the dithiocarbamate group in O = Ti(dtch)\(_2\) in presence of mercury salts coordinates to soft Hg atom, thus giving rise to bimetallic dithiocarbamates which are a new group of compounds and are liable to possess significant biological importance. Structure (II) is proposed for the bimetallic dithiocarbamates.

Efforts were made to react titanyl bis-(morpholine dithiocarbamate) with lewis bases having strong O, N donor sites and also with tetraalkyl ammonium halides. The absence of an interaction indicated the metal to be coordinatively saturated. Titanyl bis-(morpholine dithiocarbamate) also failed to react with hard Lewis acids such as Ni(II) and Cu(II).

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References