\textsuperscript{1}M-N is observed in the range 536 to 555. The ligational v NH and vC=N frequencies are observed in the range 3250-3280 and 1500-1550 respectively. In the complexes (1-3) there is slight shift in these peaks as compared to those of the free ligand, indicating that neither the NH\textsubscript{2} group on the ring nor the nitrogen atom of the pyrimidine ring is involved in coordination. 2-Cyanoamino-4,6-dimethylpyrimidine exhibits three peaks at 2150, 2175 and 2260 in its IR spectrum which may be assigned to vC=N. On complexation, the 2260 and 2175 peaks completely disappear and the peak at 2150 shifts to 2160 cm\textsuperscript{-1}. This indicates that the coordination of the cyano group to the metal ion in complexes (1-3) is through the free nitrogen end of the cyano group.

The complexes (4-6) of 2-ureido-4,6-dimethylpyrimidine exhibit in their IR spectra vM-O at 790, 790 and 780 cm\textsuperscript{-1} respectively. In these complexes the ligational frequency due to vC=N shifts by about 10-40 cm\textsuperscript{-1} indicating that the coordination of pyrimidine to the metal ion is through N\textsubscript{3}. This is expected because N\textsubscript{3} of pyrimidine is the more basic site\textsuperscript{11} than N\textsubscript{1}. Complexes (4-6) exhibit vC=O at 1690, 1680 and 1680 respectively. The vC=O of complexes (4-6) are shifted to a large extent indicating the coordination of the metal ion through carboxyl oxygen. The vC=C of the ligand around 1560-1680 cm\textsuperscript{-1} is shifted but only to a slight extent in the complexes (1-3) and to a greater extent in the complexes (4-6) indicating a bidentate coordination of the ligand in the latter complexes.

The magnetic susceptibilities of the complexes measured at 309 K using a Faraday balance are given in Table 1. These values are normal magnetic moments for the high spin 3d\textsuperscript{8}, 3d\textsuperscript{7} or 3d\textsuperscript{6} configuration\textsuperscript{12} for Ni(II), Co(II) and Cu(II) respectively. Complex (3), however, shows a lower magnetic moment of 0.045 B.M. The Ni(II) complexes (I) and (4) have a high spin 3d\textsuperscript{8} configuration as indicated by their magnetic moment\textsuperscript{12} of 3.14 and 3.16 B.M. respectively, corresponding to two unpaired electrons. In complex (3), a 3d\textsuperscript{0} system is expected to show paramagnetism for one unpaired electron in the range 1.75-2.2 B.M. but it shows a subnormal magnetic moment of 0.045 B.M. which can be attributed to its dimeric nature and the consequent coupling of the unpaired spins\textsuperscript{14} on the two Cu(II) ions. The behaviour of complex (3) is similar to cupric acetate monohydrate dimers\textsuperscript{15} which also shows a low magnetic susceptibility. The coupling of spins in dimeric Cu(II) complexes might be through the formation of direct metal-metal bond, most probably a bond by overlap of the dx\textsuperscript{2}-y\textsuperscript{2} orbitals on the copper atoms. Complex (6) has a magnetic moment of 1.56 B.M. corresponding to one unpaired electron as expected.

The electronic spectra of the complexes were measured in ethanol and dimethyl sulfoxide on a Beckman, model DB instrument. All complexes show intense bands in the region 210-276 nm assignable to the ligational peaks and 300-800 nm assignable to d-d-transitions.

\section*{NOTES}

\textbf{Synthesis \& Characterisation of Bis(\gamma'-methylcyclopentadienyl) \& [(\gamma'-Cyclopentadienyl)(\gamma'-methylcyclopentadienyl)] Derivatives of Titanium(II)}

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Bis(\gamma'-methylcyclopentadienyl)tiitanum(II) and (\gamma'-cyclopentadienyl)(\gamma'-methylcyclopentadienyl)-titanium(II) have been synthesised by the reduction of (\gamma'-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4})\textsubscript{2} TiCl\textsubscript{4} and [(\gamma'-CH\textsubscript{3})(\gamma'-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4})] TiCl\textsubscript{4} respectively using potassium naphthalide in THF at low temperature (acetone-liquid air slush). Since the reduction products are highly reactive and pyrophoric in nature, the characterisation of these compounds has been done in solution on the basis of \textit{H} NMR and IR spectra and also from the analytical and spectroscopic data (\textit{H} NMR and IR) obtained on reacting these compounds with excess of iodine.

\textbf{DISCOVERY} of the ability of cyclopentadienyl compounds of low-valent titanium to reduce molecular nitrogen prompted many workers to prepare and characterise (\gamma'-C\textsubscript{6}H\textsubscript{5})\textsubscript{2} Ti(I) derivatives. As a result of these attempts, a number of titanocenes have been obtained\textsuperscript{1}. However, the relationship between various titanocenes is still not clear, and also no definite proof has been presented for the existence...
of a bis (γ-cyclopentadienyl)-titanium(II) unit in many of these species.

Recently Bercaw et al.* obtained decamethyl titanocene and showed the absence of bridging in their compound. We report in this note the results of our studies on the reduction of [5-CH₃C₅H₄]₂TiCl₂ and [(5-CH₃C₅H₄)(5-CH₅C₅H₄)]TiCl₂ and the characterization of the reduction products in solution.

All the operations were carried out in a dry box filled with purified inert gas (either dry purified nitrogen or argon containing no traces of oxygen).

Titanium tetrachloride (obtained from M/s Travancore Titanium Products, India) was freed from iron and vanadium impurities by refluxing it over copper powder; the fraction boiling at 136°C was collected and used.

Samples of THF, freshly obtained by distilling it over sodium benzophenone and used as received, were distilled whenever needed.

Monomeric cyclopentadiene and methylcyclopentadiene were always prepared freshly by depolymerisation of dicyclopentadiene and di(methylcyclopentadiene) whenever needed.

[(5-CH₅C₅H₄)₂]₂TiCl₂ was prepared by the method given by Reynolds and Wilkinson. [(5-CH₃C₅H₄)₂]₂TiCl₂ was prepared by the following method:

To a solution of [(5-CH₅C₅H₄)₂]₂TiCl₂ (2.33 g; 10 m mol), obtained by a method analogous to that used for the preparation of [(5-CH₃C₅H₄)₂]₂TiCl₂ (ref. 7), in about 50 mI of THF, was added [(5-CH₃C₅H₄)₂]₂TI (2.7 g; 10 m mol) and the resulting reaction mixture was refluxed for about 2 hr. The mixture was cooled and filtered through a G-4 sintered glass frit. The residue was washed with 20 ml THF, the filtrate and the washings were combined, the resulting solution was concentrated to about 40 ml and to it was added gradually about 40 ml of pet ether (60-80°) till the precipitation was complete. The supernatant liquid was removed by decantation and the residue thus obtained was washed with pet ether and dried in vacuo to get about 2.2 g of the product, m.p. 210-212°C (d), which on analysis was found to correspond to the formula [(5-CH₅C₅H₄)(5-CH₃C₅H₄)]TiCl₂ (ref. 8).

Synthesis of [(5-CH₅C₅H₄)(5-CH₅C₅H₄)]TiCl₂ (II) and [(5-CH₅C₅H₄)(5-CH₅C₅H₄)]TiCl₂ (III): In a three-necked R.B. flask, after flushing it with dry and purified argon gas, were taken naphthalene (1.4 g; 11 m mol, 10% molar excess), freshly cut small pieces of potassium metal (0.39 g; 10 m mol) and about 20-25 ml of THF which was freshly distilled over sodium benzophenone and degassed with dry, purified argon. The mixture was stirred at room temperature till the formation of the greenish potassium naphthalide was complete as indicated by the complete disappearance of potassium metal. The reaction flask was then placed in a cooling bath (acetone-liquid air slush) and to it was added dropwise a solution of [(5-CH₅C₅H₄)₂]₂TiCl₂ (1.38 g; 5 m mol) or [(5-CH₅C₅H₄)(5-CH₃C₅H₄)]TiCl₂ (1.31 g; 5 m mol in ~25 ml THF) with constant stirring over a period of 1 hr. The dark-green reaction mixtures obtained after stirring for 24 hr at room temperature was filtered through a G-4 sintered glass disc. THF and naphthalene were removed from the filtrate at room temperature using a high vacuum pump. A portion of the residue was tested for the presence of chloride which was found to be absent. The chloride-free, pyrophoric, highly reactive product was kept dissolved in about 20 ml of pure, dry and degassed THF under an atmosphere of pure dry argon, and small portions of this solution were used for further investigation and characterisation. The IR spectra of the reduced species show the following bands:

\[\text{[(5-CH₅C₅H₄)(5-CH₅C₅H₄)]TiCl₂} \text{ (II)}: 3086s, 2983vs, 2950m, 2878s, 2860s, 1500-1490b, 1462s, 1440s, 1370s, 1330v, 1280v, 1235s, 1181s, 1130w, 1076vs, 1640s, 1020m, 911vs, 870m, 820s, 765s.

\[\text{[(5-CH₅C₅H₄)(5-CH₅C₅H₄)]TiCl₂} \text{ (III)}: 3100m, 2981vs, 2970w, 2950w, 2880s, 2868vs, 1495w, 1462w, 1450m, 1375v, 1330m, 1286vs, 1180v, 1069s, 1038s, 1015m, 913v, 820s, 760s.

Reaction of [(5-CH₅C₅H₄)(5-CH₅C₅H₄)]TiCl₂ (II) and [(5-CH₅C₅H₄)(5-CH₅C₅H₄)]TI (III) with iodine — To a solution of [(5-CH₅C₅H₄)(5-CH₅C₅H₄)]TI (II) or [(5-CH₅C₅H₄)(5-CH₅C₅H₄)]TI (III) in about 50 ml of THF was added gradually with constant stirring, iodine (3.81 g; 15 m mol) in about 100 ml of degassed THF under an atmosphere of argon. After about 30-40 min of stirring, the reaction mixture was cooled to room temperature and transferred quantitatively to a 250 ml graduated flask, and the volume was made up to 250 ml with THF.

To an aliquot (10 ml) of the above solution, 25 ml of 10% aqueous KI solution was added and the mixture, after vigorous shaking, was titrated against 0.01N Na₂S₂O₃ solution using freshly prepared starch solution as the indicator. The amount of unreacted iodine in the above reaction mixture was determined which showed that I₂ reacted in 1:1 molar ratio with both the Ti compounds. The rest of the reaction mixture was concentrated to about 50 ml by evaporating the excess THF in vacuo and the black crystalline product deposited was collected and recrystallised from THF. IR and IH NMR spectra of products obtained in the two cases were also recorded. The analytical and IR data are presented below:

Reaction product obtained from [(5-CH₅C₅H₄)(5-CH₅C₅H₄)]TI (II) and iodine, m.p. 236°C (d) (lit., 235°C (d) for further investigation and characterisation. The IR char
carried out using sodium naphthalide as well as potassium naphthalide in THF at low temperature. Potassium naphthalide was found to be a better reducing agent than sodium naphthalide and reduction at lower temperature gave better yields. The reactions taking place may be visualised as (Eqs 1 and 2).

\[
\begin{array}{c}
\text{THF} \\
(\eta^5\text{-C}_5\text{H}_{12})\text{TiCl}_2 + 2\text{K}/\text{C}_{10}\text{H}_8 \\
\rightarrow -80^\circ C \\
(\eta^5\text{-C}_5\text{H}_{12})_2\text{Ti}(\text{II}) + 2\text{KCl} + 2\text{C}_{10}\text{H}_8 \\
\ldots(1)
\end{array}
\]

\[
\begin{array}{c}
\text{THF} \\
[(\eta^5\text{-C}_5\text{H}_{12})(\eta^5\text{-C}_5\text{H}_{12})\text{TiCl}_2 + 2\text{K}/\text{C}_{10}\text{H}_8 \\
\rightarrow -80^\circ C \\
[(\eta^5\text{-C}_5\text{H}_{12})(\eta^5\text{-C}_5\text{H}_{12})\text{Ti}(\text{II}) + 2\text{KCl} + 2\text{C}_{10}\text{H}_8 \\
\ldots(2)
\end{array}
\]

The presence of cyclopentadienyl and methylcyclcopentadienyl groups in the complexes is indicated by the appearance of bands at 3100, ~1440 and ~820 cm\(^{-1}\) in the infrared spectra and by the presence of signals at 3.4 \(\tau\), 2.7\(\tau\) and 7.29 \(\tau\) in the \(^1\text{H}\) NMR spectra of these compounds (Table 1).

Since the pyrophoric reduction products on analysis were found to be chlorine-free and also diamagnetic in nature, the formation of bivalent metallic species is indicated\(^{10,11}\). The possibility of the formation of Ti(I) and Ti(III) species is ruled out as these would be paramagnetic in nature. Absence of chlorine in the complexes rules out the possibility of Ti(IV) species also.

Further, \(^1\text{H}\) NMR spectra of these compounds show neither any broadening nor any splitting of the signals; hence, the compounds under investigation may safely be concluded to be bivalent titanium species. The monovalent and trivalent titanium species would give broad \(^1\text{H}\) NMR signals and the absence of splitting rules out the possibility of any bridging as suggested by Pez\(^{13}\) in the case of reduction of (\(\eta^5\text{-C}_5\text{H}_{12})\text{TiCl}_2\) with various reducing agents.

The fact that the complexes obtained in the present investigation contain Ti(II) species has also been established by the reactions of these complexes in solution with excess of iodine. Determination of the amount of iodine used, in the oxidative additive reaction, shows that one mole of iodine is used up for each mole of (\(\eta^5\text{-C}_5\text{H}_{12})\text{H}_2\text{Ti}(\text{II})\) and [(\(\eta^5\text{-C}_5\text{H}_{12})\text{H}_2\text{Ti}(\text{II})\) [(\(\eta^5\text{-C}_5\text{H}_{12})\text{H}_2\text{Ti}(\text{II})\) [(\(\eta^5\text{-C}_5\text{H}_{12})\text{H}_2\text{Ti}(\text{II})\) [(\(\eta^5\text{-C}_5\text{H}_{12})\text{H}_2\text{Ti}(\text{II})\) [(\(\eta^5\text{-C}_5\text{H}_{12})\text{H}_2\text{Ti}(\text{II})\) [(\(\eta^5\text{-C}_5\text{H}_{12})\text{H}_2\text{Ti}(\text{II})\)

**Table 1** — Proton Chemical Shifts (in ppm) at 30°C in THF and CDCl\(_3\) Solution Relative to TMS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Peak assignments</th>
<th>(\eta^5\text{-C}<em>5\text{H}</em>{12}) of (\eta^5\text{-C}<em>5\text{H}</em>{12}\text{H}_2\text{Ti}(\text{II}))</th>
<th>(\eta^5\text{-C}<em>5\text{H}</em>{12}\text{H}_2\text{Ti}(\text{II})) of (\eta^5\text{-C}<em>5\text{H}</em>{12}\text{H}_2\text{Ti}(\text{II}))</th>
<th>CH(_3) of ring</th>
<th>CH(_3) of ring</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\eta^5\text{-C}<em>5\text{H}</em>{12})\text{H}_2\text{Ti}(\text{II}))</td>
<td>3.4</td>
<td>7.29</td>
<td>2.7</td>
<td>5.28</td>
<td>7.27</td>
</tr>
<tr>
<td>((\eta^5\text{-C}<em>5\text{H}</em>{12})\text{H}_2\text{Ti}(\text{II}))</td>
<td>3.17</td>
<td>5.38</td>
<td>7.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\eta^5\text{-C}<em>5\text{H}</em>{12})\text{H}_2\text{Ti}(\text{II}))</td>
<td>3.2</td>
<td>5.33</td>
<td>7.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Studies made in THF solution; extra signals due to THF protons occur at 6.6 (\(\alpha\text{-CH}_2\)) and 8.4 (\(\beta\text{-CH}_2\)).

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Dioxouranium(VI) Complexes with Sulphur Donor Schiff Bases Derived from Salicylaldehyde, Substituted Salicylaldehydes & 3-Aminothiophenol

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General method of synthesis of Schiff bases — An ethanolic solution of 3-aminothiophenol (0.63 g., 0.005 mol in 10 ml) was added to an ethanolic solution of the appropriate aldehyde (0.002 mol in 10 ml). The mixture was stirred magnetically for 30 min. The separated compound was suction filtered, washed with ethanol and dried in vacuo at room temperature, yield = 90%.

Syntheses of dioxouranium (VI) complexes : Complexes of the type [UO₂L.CH₃OH]₂ — A methanolic solution of the appropriate aldehyde (0.001 mol in 15 ml) was added to 1 ml of a methanolic solution of 3-aminothiophenol (0.13 g., 0.001 mol in 10 ml). The mixture was refluxed on a water-bath for 30 min when a clear yellow solution was obtained. It was added to a methanolic solution of dioxouranium(VI) acetate dihydrate (0.43 g., 0.001 mol in 20 ml) and the contents refluxed on a water-bath for 2 hr. A methanolic solution of sodium methoxide (0.11 g., 0.002 mol in 15 ml) was added and the mixture refluxed for 1 hr. The separated compound was filtered, washed with methanol and dried in vacuo, yield = 70%.

Complexes of the type UO₂(LH)₂ — A methanolic solution of the appropriate aldehyde (0.002 mol in 20 ml) was added to a methanolic solution of 3-aminothiophenol (0.25 g., 0.002 mol in 15 ml). The mixture was refluxed on a water-bath for 30 min. The freshly prepared methanolic solution of dioxouranium(VI) acetate dihydrate (0.43 g., 0.001 mol in 20 ml) was added to this solution. The mixture was refluxed on a water-bath for 4 hr. The partial evaporation of the solvent under a fan produced the compound which was filtered, washed with methanol and recrystallized from methanol. The compound was dried in vacuo, yield = 60%.

Complexes of the type UO₂(LH)₂(NO₃)₂ — A methanolic solution of the appropriate aldehyde (0.002 mol in 20 ml) was added to a methanolic solution of 3-aminothiophenol (0.25 g., 0.002 mol in 15 ml). The mixture was refluxed on a water-bath for 30 min. A freshly prepared methanolic solution of dioxouranium(VI) nitrate hexahydrate


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