Preparation & Characterization of Bis(cyclopentadienyl)zirconium (IV) Complexes of Sulphur Containing Schiff Bases Derived from S-Methyldithiocarbazate

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The reactions of bis (cyclopentadienyl)zirconium (IV) chloride (Cp2ZrCl2) with bidentate and tridentate sulphur containing Schiff bases derived from S-methyldithiocarbazate have been characterized on the basis of elemental analysis, electronic and IR spectra, electrical conductance and molecular weight data.

**Materials and Methods**

Stringent precautions were taken to exclude moisture throughout the work. THF (Baker) was dried by distilling over LiAlH4. n-Hexane and triethylamine were dried as described by (cyclopentadienyl)zirconium(IV) chloride was prepared by the literature method. Sulphur containing Schiff bases were prepared by the usual methods. Stringent precautions were taken to exclude moisture throughout the work. THF (Baker) was dried by distilling over LiAlH4. n-Hexane and triethylamine were dried as described by (cyclopentadienyl)zirconium(IV) chloride was prepared by the literature method.

Zirconium was estimated gravimetrically as ZrO2, chlorine as AgCl, nitrogen by Kjeldahl's method and sulphur as BaSO4.

The IR spectra (vmax in cm⁻¹) were recorded on a Perkin-Elmer IR 621 instrument in KBr phase in the range 400-200 cm⁻¹. The electronic spectra of the complexes were run on a Perkin-Elmer 1100A instrument in the range of 400-750 nm. Molecular weights of the complexes were determined on a Gallenkamp ebulliometer (W.G. Pye & Co. Ltd, Cambridge). Electrical conductance measurements were carried out in nitrobenzene on an Elico conductivity bridge type CM82T.

Reactions of bis(cyclopentadienyl)zirconium(IV) chloride (1 mol) with bidentate and tridentate sulphur containing Schiff bases derived from S-methyldithiocarbazate (1 mol) — To bis(cyclopentadienyl)zirconium(IV) chloride (0.584 g) and the Schiff base (0.572 g) dissolved in THF (80 g) was added triethylamine (0.203 g) and the mixture stirred for 26 hr. Et3N.HCl which precipitated out was removed by filtration. After distilling the solvent from the filtrate under reduced pressure, the product was recrystallized from n-hexane/THF mixture (yield 90%). The electronic spectra of the complexes were run on a Perkin-Elmer 4000A instrument in the range of 400-750 nm. Molecular weights of the complexes were determined on a Gallenkamp ebulliometer (W.G. Pye & Co. Ltd, Cambridge). Electrical conductance measurements were carried out in nitrobenzene on an Elico conductivity bridge type CM82T.

Reactions of bis(cyclopentadienyl)zirconium(IV) chloride (1 mol) with S-methyl-β-N(diphenylmethylene)dithiocarbazate (2 mol) — A mixture of Cp2ZrCl2 (0.425 g) and the Schiff base (0.832 g) was dissolved in THF (80 g) and to this triethylamine (0.295 g) was added. The mixture was stirred for 24 hr and the Et3N.HCl which precipitated out was removed by filtration. The solvent was removed under reduced pressure and the product (92%) was recrystallized from n-hexane/THF mixture. The electronic spectra of the complexes were run on a Perkin-Elmer 4000A instrument in the range of 400-750 nm. Molecular weights of the complexes were determined on a Gallenkamp ebulliometer (W.G. Pye & Co. Ltd, Cambridge). Electrical conductance measurements were carried out in nitrobenzene on an Elico conductivity bridge type CM82T.

Results and Discussion

The reaction of bis(cyclopentadienyl)zirconium(IV) chloride (1 mol) with bidentate Schiff bases (1,1 and 2 mol) in THF in the presence of triethylamine yielded complexes of the type Cp2Zr(TSB)Cl and Cp2Zr(TSB)3 in accordance with Eqs (1) and (2) respectively.
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\[ \text{Cp_2ZrCl}_2 + \text{TSBH} + \text{Et}_3\text{N} \rightarrow \text{Cp_2Zr(TSB)Cl} + \text{Et}_3\text{N.HCl} \quad \ldots (1) \]

\[ \text{Cp_2ZrCl}_2 + 2\text{TSBH} + 2\text{Et}_3\text{N} \rightarrow \text{Cp_2Zr(TSB)_2} + 2\text{Et}_3\text{N.HCl} \quad \ldots (2) \]

[TSB] represents the anion of the corresponding Schiff base TSBH.

\[ R = N \rightarrow N = C \]

\[ \begin{array}{c}
\text{SCH}_3 \\
\end{array} \]

These complexes are yellow and soluble in organic solvents. The analytical data and physical properties are given in Table 1.

Reactions of \( \text{Cp}_2\text{ZrCl}_2 \) (1 mol) with tridentate Schiff bases (II–IV) (1 mol), in the presence of triethylamine yielded complexes of the type \( \text{Cp}_2\text{Zr(TS'B)} \) (Eq. 3).

\[ \text{Cp}_2\text{ZrCl}_2 + \text{TS'BH} + 2\text{Et}_3\text{N} \rightarrow \text{Cp}_2\text{Zr(TS'B)} + 2\text{Et}_3\text{N.HCl} \quad \ldots (3) \]

\[ \begin{array}{c}
\text{R} = \text{CH}_3 \text{and C}_6\text{H}_5 \\
\end{array} \]

<table>
<thead>
<tr>
<th>Reactants (molar ratio)</th>
<th>Stirring time (h)</th>
<th>Product, colour and dec. temp.</th>
<th>Found (%) (Calc.)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cp}_2\text{ZrCl}_2 + \text{TSBH} + \text{Et}_3\text{N} ) ( (1 : 1 : 1) )</td>
<td>24</td>
<td>( \text{Cp}_2\text{Zr(TSB)Cl} ), yellow, 98</td>
<td>19.5 (19.6) (6.0) (13.7) (7.6)</td>
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<td>( \text{Cp}_2\text{ZrCl}_2 + \text{TSBH} + 2\text{Et}_3\text{N} ) ( (1 : 2 : 2) )</td>
<td>24</td>
<td>( \text{Cp}_2\text{Zr(TSB)_2} ), yellow, 90</td>
<td>14.02 (14.3) (8.75) (20.0)</td>
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<td>( \text{Cp}_2\text{ZrCl}_2 + \text{TSB}_3\text{H} + 2\text{Et}_3\text{N} ) ( (1 : 1 : 1) )</td>
<td>28</td>
<td>( \text{Cp}_2\text{Zr(TSB)_3} ), yellow, 115</td>
<td>19.1 (19.0) (5.83) (13.3) (7.4)</td>
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<tr>
<td>( \text{Cp}_2\text{ZrCl}_2 + \text{TSB}_4\text{H} + 2\text{Et}_3\text{N} ) ( (1 : 2 : 2) )</td>
<td>30</td>
<td>( \text{Cp}_2\text{Zr(TSB)_4} ), yellow, 130</td>
<td>13.61 (13.65) (8.4) (19.2)</td>
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<td>( \text{Cp}_2\text{ZrCl}_2 + \text{TSB}_3\text{H} + \text{Et}_3\text{N} ) ( (1 : 1 : 1) )</td>
<td>26</td>
<td>( \text{Cp}_2\text{Zr(TSB)} ), yellow, 142</td>
<td>16.7 (16.83) (5.16) (11.8) (6.54)</td>
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<td>( \text{Cp}_2\text{ZrCl}_2 + \text{TSB}_4\text{H} + \text{Et}_3\text{N} ) ( (1 : 2 : 2) )</td>
<td>24</td>
<td>( \text{Cp}_2\text{Zr(TSB)_3} ), yellow, 118</td>
<td>11.45 (11.5) (7.07) (16.17)</td>
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<td>( \text{Cp}_2\text{ZrCl}_2 + \text{TSB}_3\text{H} + \text{Et}_3\text{N} ) ( (1 : 1 : 1) )</td>
<td>24</td>
<td>( \text{Cp}_2\text{Zr(TSB)} ), yellow, 105</td>
<td>20.31 (20.55) (6.3) (14.4) (7.98)</td>
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<td>( \text{Cp}_2\text{ZrCl}_2 + \text{TSB}_4\text{H} + \text{Et}_3\text{N} ) ( (1 : 2 : 2) )</td>
<td>28</td>
<td>( \text{Cp}_2\text{Zr(TSB)_3} ), light brown, 150</td>
<td>15.2 (15.3) (9.4) (21.5)</td>
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<tr>
<td>( \text{Cp}_2\text{ZrCl}_2 + \text{TSB}_3\text{H} + \text{Et}_3\text{N} ) ( (1 : 1 : 1) )</td>
<td>26</td>
<td>( \text{Cp}_2\text{Zr(TSB)} ), light yellow, 222</td>
<td>19.6 (19.9) (6.11) (14.0) (7.74)</td>
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<td>( \text{Cp}_2\text{ZrCl}_2 + \text{TSB}_4\text{H} + \text{Et}_3\text{N} ) ( (1 : 2 : 2) )</td>
<td>30</td>
<td>( \text{Cp}_2\text{Zr(TSB)_3} ), yellow, 201</td>
<td>14.35 (14.6) (9.0) (20.5)</td>
</tr>
</tbody>
</table>

TSBH = S-Methyl-β-N-(phenyl)methylenedithiocarbazate; TSBH = S-Methyl-β-N(phenyl)ethylenedithiocarbazate; TSBH = S-Methyl-β-N-(diphenyl)methylenedithiocarbazate; TSBH = S-Methyl-β-N-(cyclopentyl)dithiocarbazate; and TSBH = S-Methyl-β-N-(cyclohexyl) dithiocarbazate.

*Satisfactory carbon and hydrogen, analyses were obtained for all the compound.
[TS'B]$^{2-}$ represents the anion of the corresponding Schiff base TS'BH$_2$.

These complexes are yellow to orange and soluble in organic solvents. The analytical data and physical properties are given in Table 2.

All these complexes are susceptible to hydrolysis and decompose on heating in the range of 90–245°C. Magnetic susceptibilities measured at room temperature by Gouy's method using copper sulphate as calibrant show that all the complexes are diamagnetic. Electrical conductances measured in nitrobenzene show them to be essentially non-electrolytes. Molecular weights of the complexes in boiling benzene indicate that the complexes are monomeric in nature.

On the basis of elemental analysis, molecular weight determination, IR and electronic spectra, the complexes of the type Cp$_2$Zr(TS'B)Cl, Cp$_2$Zr(TS'B)$_2$, and Cp$_2$Zr(TS'B)$_3$ have been assigned the structures (V), (VI) and (VII) respectively.

Similar structures have been reported for Schiff base complexes of bis(cyclopentadienyl)zirconium(IV) and bis(cyclopentadienyl)titanium(IV) 11,12. In the complexes having the structures (V) and (VII) the coordination number of zirconium appears to be five, which is well known for zirconium complexes 11,15,16. For complexes with structure (V) the appearance of a band ~350 in the IR spectra due to v(Zr-Cl) confirms the presence of coordinated chlorine. In structure (VI) zirconium attains the well known coordination number six 11,13.

The complexes show bands ~3000 (~C-O), ~1435 (~C-H), ~1300 (~C-C), ~1020, 820 (~C=N, in-plane and out-of-plane respectively) characteristic of cyclopentadienyl ring. Similar bands have been observed in bis(cyclopentadienyl)zirconium(IV) chloride 15. The persistence of the bands of the cyclopentadienyl rings in the sulphur containing Schiff base complexes indicates that these groups remain delocalized and p-bonded (π) to the metal and retain their aromatic character.

The infrared spectra of the Schiff bases show a strong band in the region of 1590-1620 which can be assigned to the absorption band of the azomethine group (~C=N) 16. In the spectra of the complexes ~v(C=N) shifts to lower range by 20–25 cm$^{-1}$, indicating the coordination of the nitrogen to metal. Four bands around 1540, 1200, 1075 and 780, assignable to thiocarbonyl band 21 in the Schiff bases are not pure bands but have contributions from ~v(N-H), ~v(C=S), ~v(C=N) and ~v(C=S) respectively. All the four bands register a downward shift of 15 cm$^{-1}$ in the spectra of complexes 16,20, these shifts are consistent with the coordination of the metal through sulphur of thiocarbonyl group 21,22. The possibility of thione, thiol tautomerism (NH-C=S~N =C-SH) is ruled out, since no band characteristic of thiol group (2500-2650) is found in the spectra of ligands and the complexes. Thus the infrared spectra reveal that the ligands are bidentate and tridentate and chelate through thioketo sulphur and unsaturated nitrogen of the N=N=C group.

### Table 2 — Reactions of Bis(cyclopentadienyl) zirconium (IV) chloride with Tridentate Sulphur Containing Schiff Bases (II–IV)

<table>
<thead>
<tr>
<th>Reactants (molar ratio)</th>
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</tr>
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<tbody>
<tr>
<td>Cp$_2$ZrCl$_4$ + TS'BH$_2$ + Et$_2$N</td>
<td>26</td>
<td>Cp$_2$Zr(TS'B)$_3$, yellow, 115</td>
<td>20.32</td>
<td>6.32</td>
</tr>
<tr>
<td>Cp$_2$ZrCl$_4$ + TS'B$_2$H$_2$ + Et$_2$N</td>
<td>30</td>
<td>Cp$_2$Zr(TS'B)$_4$, yellow brown, 165</td>
<td>18.2</td>
<td>5.60</td>
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<tr>
<td>Cp$_2$ZrCl$_4$ + TS'B$_3$H$_2$ + Et$_2$N</td>
<td>28</td>
<td>Cp$_2$Zr(TS'B)$_5$, pale yellow, 245</td>
<td>19.0</td>
<td>5.84</td>
</tr>
<tr>
<td>Cp$_2$ZrCl$_4$ + TS'B$_4$H$_2$ + Et$_2$N</td>
<td>24</td>
<td>Cp$_2$Zr(TS'B)$_6$, light yellow, 183</td>
<td>21.2</td>
<td>6.59</td>
</tr>
<tr>
<td>Cp$_2$ZrCl$_4$ + TS'B$_5$H$_2$ + Et$_2$N</td>
<td>26</td>
<td>Cp$_2$Zr(TS'B)$_7$, orange, 156</td>
<td>18.6</td>
<td>6.61</td>
</tr>
</tbody>
</table>

TS'BH$_2$ = S-methyl-β-N-(2-hydroxyphenyl) methylenedithiocarbazate (II, R' = H); TS'B$_2$H$_2$ = S-methyl-β-N-(2-hydroxy-2-naphthyl) methylenedithiocarbazate (III); TS'B$_3$H$_2$ = S-methyl-β-N-(2-hydroxy-5-methylphenyl) methylenedithiocarbazate (II, R' = CH); TS'B$_4$H$_2$ = 2-hydroxy-5-methyl-5,6-diaza-7-thione-8-thianono-2, 4-diene and TS'B$_5$H$_2$ = 2-hydroxy-4-phenyl-5, 6-diaza-7-thione-8-thianona-2, 4-diene.

*Satisfactory analyses were obtained for carbon and hydrogen.
The IR spectra of tridentate Schiff bases exhibit bands at 3300 and 1282 cm\(^{-1}\) assigned to \(\nu(\text{OH})\) and \(\nu(\text{C-O})\) respectively. The first band vanishes in the complexes while other shifts towards lower frequency, suggesting bonding between zirconium and oxygen. Bands in the regions 570-530, 520-450 and 370-350 cm\(^{-1}\) are attributed to \(\nu(\text{Zr-N})\), \(\nu(\text{Zr-O})\) and \(\nu(\text{Zr-S})\) respectively as reported earlier. The electronic spectra of all complexes recorded in acetone show a single band in the region of 23580 to 22930 which can be assigned to the charge-transfer band. This is in accord with their \((n-1)d^2, ns^0\) electronic configurations.

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References