Studies on the Preparation & Properties of Thiol Derivatives of Bis(cyclopentadienyl)- & Bis(indenyl)niobium(IV) Dichlorides

H S MALHOTRA & R K MULTANI*
Department of Chemistry, University of Delhi, Delhi 110007
Received 15 April 1983; revised and accepted 10 January 1984

Bis(cyclopentadienyl)niobium (IV) dichloride (I) and bis(indenyl)niobium (IV) dichloride (II) react with various thiols in THF medium forming complexes of the types (CSH2)2Nb(SR)2 and (CsH9)2Nb(SR)2 where R is = -CH3, = C2H5, = -C9H7, = C4H9, = C6H11(iso). These complexes have been characterised on the basis of analytical, magnetic and spectral data.

Thiol derivatives of Fe, Co, W, Mo, V, W, Co, and Mo have already been reported. We report here the preparation and characterisation of thiol derivatives of bis(cyclopentadienyl)niobium (IV) dichloride (I) and bis(indenyl)niobium (IV) dichloride (II). Compounds (I) and (II) were prepared by the method of Lucas. The various thiol derivatives were prepared by reacting the corresponding thiol with (CsH9)2NbCl2 (I) and (CsH9)2NbCl2 (II) in THF medium. The reactions can be represented as:

(CsH9)2NbCl2 + 2 RSH → (CsH9)2Nb(SR)2 + 2 HCl
(CsH9)2NbCl2 + 2 RSH → (CsH9)2Nb(SR)2 + 2 HCl

Preparation of bis(cyclopentadienyl)niobium (IV) dimethanethiol

Sodium (1.15 g, 0.005 mol) was dissolved in dry methanol (40 ml) and the solution was saturated with hydrogen sulphide. After stirring for 2 hr, bis(cyclopentadienyl)niobium (IV) dichloride (0.735 g, 0.0025 mol) dissolved in 70 ml THF was added. The mixture was stirred and refluxed for 5 hr at 65°C till there was no evolution of HCl gas. The resulting solution was filtered through a G-4 sintered disc. The filtrate on evaporation to dryness under reduced pressure yielded a brown paste which on repeated crystallisations from pet. ether (60-80°C) gave light-brown crystals of (CsH9)2Nb(SCH3)2.

Other cyclopentadienyl and indenyl thiol derivatives of (I) and (II) were prepared in an analogous manner, their analyses are given in Table 1. The compounds are disagreeable in odour and are soluble in common organic solvents like acetone, benzene, tetrahydrofuran, chlorinated methanes and carbon disulphides. The compounds are brown or black solids and are sensitive to moisture, stable under dry and inert atmosphere. These compounds are non-volatile and do not sublime even in vacuum. The compounds when heated with water and dilute acids undergo hydrolysis. Molecular weight measurements show their monomeric nature.

Magnetic measurements have been done by the Gouy method using mercury tetrathiocyanatocobaltate as the calibrating agent (μg = 16.44 x 10-6 c.g.s. units). The magnetic moment values of the compounds are ~1.69 ± 0.02 B.M. corresponding to the one unpaired electron for niobium(IV).

The IR spectra of the complexes have been recorded in the region 4000-600 cm⁻¹. Presence of cyclopentadienyl group in these complexes is indicated by the appearance of the IR bands at ~3070 cm⁻¹ (νC-H), ~810 cm⁻¹ (perpendicular hydrogen wagging mode), ~1020 cm⁻¹ (parallel hydrogen wagging mode) and 1460 and 1100 cm⁻¹ respectively due to νC=C and ring breathing modes of π-bonded cyclopentadienyl ring. The indenyl group, in addition to the usual peaks

<table>
<thead>
<tr>
<th>Compound Found (Calc.)</th>
<th>μnet (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CsH9)2Nb(SCH3)2</td>
<td>45.50 5.040 20.20 29.35 1.67</td>
</tr>
<tr>
<td>(CsH9)2Nb(SC2H5)2</td>
<td>48.82 5.783 18.57 26.95 1.68</td>
</tr>
<tr>
<td>(CsH9)2Nb(SC6H11)2</td>
<td>54.08 7.000 15.96 23.18 1.69</td>
</tr>
<tr>
<td>(CsH9)2Nb(SC4H9)2</td>
<td>54.08 7.000 15.96 23.18 1.69</td>
</tr>
</tbody>
</table>

Table 1—Analytical Data of Thiol Derivatives of (CsH9)2NbCl2 and (CsH9)2NbCl2

C | H | S | Nb
---|---|---|---
(53.88) | (6.984) | (15.96) | (23.19)
of \((\text{C}_5\text{H}_5)\) group, also shows the peaks of phenyl group, the \(\nu\text{C-H}\) vibration at \(\sim 1410 \text{ cm}^{-1}\), \(\text{C-H out-of-plane bending at} \sim 760 \text{ cm}^{-1}\), \(\nu\text{C-C}\) vibration\(^{11}\), \(1620 \text{ cm}^{-1}\) and the methylene rocking vibration at \(710 \text{ cm}^{-1}\). Indene itself shows an absorption band at \(700 \text{ cm}^{-1}\).

The alkyl groups give bands due to \(\nu\text{CH}\) and \(\delta\text{CH}_2\) modes at the usual positions\(^{12,13}\). Isopropyl and isobutyl groups give the characteristic bands in the regions 1170-1140 and 1370-1360 \text{ cm}^{-1}\) respectively. The \(\nu\text{C-S}\) mode generally appears as a weak or moderate intensity band in the range 720-580 \text{ cm}^{-1}\), and some difficulty is experienced in recognizing this band due to the presence of intense \(\text{C-H out-of-plane deformation mode in the same region. The } \nu\text{C-S} \text{ mode appears at } 800 \text{ to } 600 \text{ cm}^{-1} \text{ in compounds with free C-S.}

The IR spectra of these compounds suggest that the coordination of cyclopentadienyl and indenyl rings to the metal atom is through the delocalised \(\pi\)-bonds while the thiol groups coordinate through sulphur after deprotonation.

References