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π-CYCLOPENTADIENYLALKOXYOXOCHLOROTUNGSTEN COMPOUNDS

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SUMMARY

The reaction of dicyclopentadienyloxodichlorotungsten with alcohols results in the formation of cyclopentadienylmonoalkoxyoxodichlorotungsten, $C_5H_5WOCl_2(OR)$ and cyclopentadienyldialkoxyoxochlorotungsten $C_5H_5WOCl(OR)_2$, where R is methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and isoamyl radicals. The thermal stabilities and infrared spectra (4000–800 cm^{-1}) of these compounds are reported.

INTRODUCTION

Tetraalkoxyoxotungsten(VI) and dialkoxyoxodichlorotungsten(VI) were reported by Fund, Weiss and Coworkers[1], but there is no reference in the literature to cyclopentadienyl compounds of tungsten(VI) containing alkoxy groups. Studies on alkoxy compounds of di-π-cyclopentadienyldichlorotitanium and -zirconium[2,3] have been published. The present paper deals with the preparation and some of the properties of cyclopentadienylalkoxyoxochlorotungsten(VI) compounds. It has been observed that monoalkoxy derivatives of dicyclopentadienyloxodichlorotungsten[4] can be obtained by refluxing it with excess of methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and isoamyl alcohols, as

$$(C_5H_5)_2WOCl_2 + ROH \rightarrow C_5H_5WOCl_2(OR) + C_5H_6$$

However, on refluxing dicyclopentadienyloxodichlorotungsten in benzene with alcohols in presence of triethylamine, elimination of one chlorine atom and one cyclopentadiene molecule occurs with the formation of dialkoxy derivatives as:

$$(C_5H_5)_2WOCl_2 + 2\,ROH + (C_2H_5)_3N \rightarrow C_5H_5WOCl(OR)_2 + (C_2H_5)_3N\cdot HCl + C_5H_6$$

The resultant alkoxy products of di-π-cyclopentadienyloxodichlorotungsten, are deep green in colour and are very sensitive to air and moisture. The thermal stabilities of these compounds increase as the alkoxy group present in them is changed from CH_3 to C_5H_{11} (Table 1).

The IR spectra of the above compounds were taken in KBr and nujol, on a Perkin–Elmer Infracord Model-137, at 4000–800 cm^{-1}. The data in Table 2 shows evidence of C–C stretching frequency (1790–1510 cm^{-1}), C–H stretching (3100–2900 cm^{-1}), which is analogous to the behaviour of other transitional cyclopentadienyl π-bonded compounds[5,6]. The vibration bands for alkoxy groups are observed for methoxy at 1190, for ethoxy at 1140, 1160, for isopropoxy at 1110, 1170 and for butoxy at 1090, and 1120–1160 cm^{-1} as mentioned in Table 2[7,8]. That the C_5H_5 ring is bound to the tungsten atom by a π-bond is shown by the fact that the C–H stretching region in the IR spectra of the compounds is located at 3050–3100 cm^{-1} and because cyclopentadiene itself shows C–H stretching frequencies at 3100 cm^{-1} and 2900 cm^{-1} (see ref. 5). In addition, the spectra of the compounds also show an absorption at 1600–1650 cm^{-1}, which probably is due to C=C stretching frequency.

TABLE 1

Compound	Decomposition temperature (°C) when R is						
	CH_3	C_2H_5	n-C_3H_7	iso-C_3H_7	n-C_4H_9	iso-C_4H_9	iso-C_5H_{11}
$C_5H_5WOCl_2(OR)$	91	112	116	113	145	131	150.5
$C_5H_5WOCl(OR)_2$	90.5	106	113	110	135–136	126	147

TABLE 2

INFRARED SPECTRA OF $C_5H_5WOCl_2(OR)$ AND $C_5H_5WOCl(OR)_2$

Compound	Medium	C–H-stretching (cm^{-1})	C–C-stretching (cm^{-1})	Alkoxy groups (cm^{-1})
$C_5H_5WOCl_2(OR)$	KBr and Nujol	3010, 3000, 2950, 2910, 2900	1790, 1730, 1710, 1700, 1670, 1650, 1630, 1625, 1580, 1570, 1560, 1550, 1540, 1525, 1520	1190, 1180, 1170, 1160–1120, 1110, 1090
$C_5H_5WOCl(OR)_2$	KBr and chloroform	3100, 3020, 3010, 3000, 2940, 2900	1680, 1620, 1610, 1600, 1520, 1510	1190, 1170, 1160–1120, 1110, 1090

EXPERIMENTAL

All operations were carried out under anhydrous conditions and at reduced pressure. Pure and dry reagents were used. Tetrahydrofuran was first dried by refluxing with potassium hydroxide and then distilled from $LiAlH_4$. Aromatic hydrocarbons were first dried with sodium wire and then distilled, the alcohols were dried by usual methods including azeotropic distillation. Cyclopentadienylsodium was always freshly prepared.

Tungsten oxide tetrachloride, obtained as reddish crystals on refluxing tungsten trioxide with thionyl chloride, after drying under reduced pressure, was finally sublimed (135–140°) under vacuum, and yielded scarlet red crystals of $WOCl_4$.

Dicyclopentadienyloxodichlorotungsten was prepared by refluxing freshly distilled cyclopentadiene with tungsten oxide tetrachloride in tetrahydrofuran. It was also prepared by the interaction of cyclopentadienylsodium with tungsten oxide tetrachloride in tetrahydrofuran. To tungsten oxide tetrachloride, 5.20 g (0.15 mole), dissolved in 70 ml THF, was added a thoroughly stirred mixture of 1.5 g of sodium and 5.1 ml of cyclopentadiene in 80 ml of THF. The contents were refluxed for 4–5 h at 80–90°. After cooling, the resultant mixture was filtered and the residue washed with diethyl ether. The filtrate and the washings on drying under reduced pressure yielded a dark brownish mass which when crystallized from petroleum ether (34–45°), gave brown crystals of dicyclopentadienyloxodichlorotungsten

$$WOCl_4 + 2NaC_5H_5 \rightarrow WOCl_2(C_5H_5)_2 + 2NaCl$$

Preparation of cyclopentadienylalkoxyoxodichlorotungsten compounds

An alcoholic soln. (3.10 g) of dicyclopentadienyloxodichlorotungsten in 100 g of ethyl alcohol) was refluxed for 8–10 h at 100–105°. On cooling the products and after evaporation of the excess alcohol under reduced pressure (30–40 mm), the residue was extracted with THF. The extract on drying under reduced pressure, (15–20 mm) yielded greenish coloured crystals of cyclopentadienyl tungsten oxy-dichloro ethoxide. This substance is stable in dry air at room temperature (30–40°). It is sparingly soluble in benzene, toluene, chloroform and carbon tetrachloride. It is hydrolysed by cold alkalies, in which it dissolves on heating. (Found: Cl, 18.6; OC_2H_5, 11.8; W, 48.25. $C_5H_5WOCl_2(OC_2H_5)$ calcd.: Cl, 18.63; OC_2H_5, 11.81; W, 48.29%.)

After decomposition of the compounds with perchloric acid, tungsten was estimated as 8-hydroxyquinolinolate; chloride was estimated as silver chloride and the alkoxy group was determined volumetically by chromic acid methods[9,10]. In some cases the carbon and hydrogen were also estimated by microanalytical methods. The presence of cyclopentadienyl radical was inferred from the IR spectra of the compounds.

TABLE 3

CYCLOPENTADIENYLALKOXYOXODICHLOROTUNGSTEN COMPOUNDS

R in $C_5H_5WOCl_2(OR)$	Colour	Yield (%)	Reaction (h)	Tungsten %	Chloride %	Alkoxy group %
				Found (Calc.)	Found (Calc.)	Found (Calc.)
Methyl	Green	85	7	50.1 (50.13)	19.3 (19.34)	8.38 (8.44)
Ethyl	Green	88	9	48.25 (48.29)	18.6 (18.63)	11.80 (11.81)
n-Propyl	Green	75	11	46.55 (46.57)	17.9 (17.97)	
Isopropyl	Light green	70	10	46.5 (46.57)	17.95 (17.97)	14.9 (14.93)
n-Butyl	Deep green	70	11	44.95 (44.98)	17.3 (17.36)	
Isobutyl	Dirty green	65	10	44.90 (44.98)	17.35 (17.36)	
Isoamyl	Green blue	60	14	43.45 (43.49)	16.75 (16.78)	

Higher alkoxy derivatives were similarly prepared by refluxing dicyclopentadienyloxodichlorotungsten with suitable alcohols at requisite higher temperatures. The analytical data are given in Table 3.

Preparation of cyclopentadienyldialkoxyoxochlorotungsten compounds

A mixture of 3.8 g of dicyclopentadienyloxodichlorotungsten in 80 g of benzene and 50 g of ethyl alcohol, was refluxed for 2–3 h and then treated with 6.51 g of triethylamine, the contents further refluxed for 8–10 h at 120–130°. After cooling the contents, the triethylammonium chloride was removed by filtration under anhydrous conditions. The filtrate after removal of benzene under reduced pressure left a deep green product, which on crystallisation from petroleum ether/benzene (1/2), yielded green crystals and they were identified as cyclopentadienyldiethoxyoxochlorotungsten, m.p. 96–97°. It is very sensitive to moist air and heat. The substance is soluble in benzene, chloroform, methylene chloride and carbon disulphide. Dilute acids and alkalies hydrolyse it to give cyclopentadiene and a resinous product. (Found: Cl, 9.0; OC_2H_5, 23.1; W, 47.1. $C_5H_5WOCl(OC_2H_5)_2$ calcd.: Cl, 9.09; OC_2H_5, 23.04; W, 47.12%.)

The higher dialkoxy derivatives of dicyclopentadienyloxodichlorotungsten were prepared by using suitable alcohols under similar conditions but at higher temperatures. Analytical data are given in Table 4.

IR spectra for all the above compounds are recorded in Table 2.

TABLE 4

CYCLOPENTADIENYLDIALKOXYOXODICHLOROTUNGSTEN COMPOUNDS

R in $C_5H_5WOCl(OR)_2$	Colour	M.p. (°C)	Yield (%)	Reaction time (h)	Amt. of ROH added (g)	Amt. of C_6H_6 added (g)	Amt. of $(C_2H_5)_3N$ added (g)	Tungsten % Found (Calc.)	Chloride % Found (Calc.)	Alkoxy group % Found (Calc.)
Ethyl	Green	96–97	70	6	100	40	6.1	47.1 (47.12)	9.0 (9.09)	23.1 (23.04)
n-Propyl	Green	98–99	60	10	110	60	6.0	43.92 (43.96)	8.41 (8.48)	
Isopropyl	Light green	105–106	55	8	150	70	6.5	43.96 (43.96)	8.45 (8.48)	8.15 (28.19)
n-Butyl	Grey green	135–136	50	10	100	50	7.5	41.15 (41.21)	7.90 (7.95)	
Isoamyl	Deep green	140.5	50	12	80	45	7.2	38.71 (38.73)	7.45 (7.48)	

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