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Synthesis and Characterization of Di(Alkoxy) Tripseudohalido-Tungsten(V)

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Pseudohalide derivatives of the type $(RO)_2W(Ps)_3$ of $(RO)_2WCl_3$ have been synthesized by the interaction of $(RO)_2WCl_3$ with potassium pseudohalides (Ps = thiocyanate, cyanate and azide) in tetrahydrofuran (R = Me, Et, i-Pr, n-Bu, i-Bu and t-Bu). The derivatives have been characterized by their elemental analysis, IR spectra and other physical measurements. It has been observed that the pseudohalide groups are attached to the tungsten atom through the atom with lesser electronegativity in the group.

INTRODUCTION

Alkoxychlorooxo derivatives of tungsten(VI) of the type $[WOCl_3(OR)]^1$ and $[WOCl_2(OR)_2]^{2,3}$ have been reported in the literature. The paramagnetic compounds $WCl_3(OR)_2$ (R = Me, Et) have been characterized[4]. The pseudohalide derivatives of tungsten(VI) of the type $Cp_2WO(Ps)_2$,[5] $WO(Ps)_4$, $WO_2(Ps)_2$,[5] $WO(OR)_2(Ps)_2$ [7] and $WS_2(Ps)_2$ [8] have been synthesized by previous workers. There is no single report of pseudohalide derivatives of W(V) of the type $[W(OR)_2(Ps)_3]$ available in the literature. Hence it was thought desirable to prepare these compounds. WCl_6 on treatment with alcohols is reduced to $WCl_3(OR)_2$ and the three chlorine atoms in it are metathetically replaced by treatment with potassium pseudohalides.

EXPERIMENTAL

All the reactions were carried out in a dry atmosphere using pure and dry solvents. The di(alkoxy) trichlorotungsten(V) compounds were prepared from WCl_6 according to method used in earlier[9] communication.

Preparation of Di(alkoxy) tripseudohalidotungsten(V)

About 1.0 g of the di(alkoxy) trichlorotungsten(V) were taken in about 100 mL of dry THF and potassium pseudohalide in 1 : 3 molar ratio was added to it. The mixture was stirred and refluxed for 17 h at *ca.* 65°C. The deep colour of the solution usually changed to lighter one. The reaction mixture was then filtered and the clear light coloured filtrate was evaporated to dryness under reduced

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pressure. The pasty residues were repeatedly washed with hot petroleum ether when light coloured compounds of the composition $[W(OR)_2(Ps)_3]$ were obtained. They were dried and recrystallized from THF/ether mixture (1 : 5).

All the complexes are white except the thiocyanato derivatives. They are stable in inert and dry atmosphere. They are generally insoluble in common organic solvents. The analytical data of the complexes is given in Table-1.

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF DI(ALKOXY) TRIPSEUDOHALIDOTUNGSTEN(V)

Compound	Colour	Analysis %, Found (Calcd.)		
		W	C	N
$W(OCH_3)_2(SCN)_3$	Grassy green	43.75	14.19	9.88
(methoxy)		(43.80)	(14.28)	(10.00)
$W(OC_2H_5)_2(SCN)_3$	Orangish yellow	41.20	18.62	9.27
(ethoxy)		(41.07)	(18.75)	(9.37)
$W(OC_3H_7)_2(SCN)_3$	Orange	38.59	22.74	8.75
(i-propoxy)		(38.65)	(22.68)	(8.82)
$W(OC_4H_9)_2(SCN)_3$	Light green	36.55	26.08	8.30
(n-butoxy)		(36.50)	(26.19)	(8.33)
$W(OC_4H_9)_2(SCN)_3$	Dark green	36.43	26.23	8.25
(i-butoxy)		(36.50)	(26.19)	(8.33)
$W(OC_4H_9)_2(SCN)_3$	Light orange	36.45	26.11	8.39
(t-butoxy)		(36.50)	(26.19)	(8.33)
$W(OCH_3)_2(CNO)_3$	White	49.53	16.18	11.34
(methoxy)		(49.56)	(16.12)	(11.29)
$W(OC_2H_5)_2(CNO)_3$	White	45.89	21.12	10.45
(ethoxy)		(46.00)	(21.00)	(10.50)
$W(OC_3H_7)_2(CNO)_3$	White	42.88	25.19	9.74
(i-propoxy)		(42.99)	(25.23)	(9.81)
$W(OC_4H_9)_2(CNO)_3$	White	40.39	28.85	9.14
(i-butoxy)		(40.35)	(28.94)	(9.21)
$W(OC_4H_9)_2(CNO)_3$	White	40.44	28.89	9.29
(t-butoxy)		(40.35)	(28.94)	(9.21)
$W(OCH_3)_2(N_3)_3$	White	49.38	6.49	33.76
(methoxy)		(49.46)	(6.45)	(33.87)
$W(OC_2H_5)_2(N_3)_3$	White	45.88	12.10	31.45
(ethoxy)		(46.00)	(12.00)	(31.50)
$W(OC_3H_7)_2(N_3)_3$	White	43.14	16.77	29.38
(i-propoxy)		(42.99)	(16.82)	(29.43)
$W(OC_4H_9)_2(N_3)_3$	White	40.31	20.98	27.59
(n-butoxy)		(40.35)	(21.05)	(27.63)
$W(OC_4H_9)_2(N_3)_3$	White	40.38	20.92	27.68
(i-butoxy)		(40.35)	(21.05)	(27.63)
$W(OC_4H_9)_2(N_3)_3$	White	40.28	21.13	27.56
(t-butoxy)		(40.35)	(21.05)	(27.63)

RESULTS AND DISCUSSION

The compounds are essentially non-electrolytes as is indicated by their poor conductivities. Their magnetic susceptibilities are *ca.* 1.9 BM indicating the paramagnetism corresponding to one unpaired electron. Their electronic spectra showed bands in the range 37500–35000 cm^{-1} which could be assigned to charge transfer $(N \rightarrow W)^{10}$ and $(O \rightarrow W)$.

The IR spectra of the thiocyanato compounds showed a strong band at *ca.* 2050 cm^{-1} due to $\nu(CN)$, a strong band at *ca.* 800 cm^{-1} due to $\nu(CS)$, and a medium band at *ca.* 480 cm^{-1} due to $\delta(NCS)$[11, 12]. These observations point out that the thiocyanate group is linked through nitrogen atom to the tungsten. A band at *ca.* 370 cm^{-1} may be assigned to $\nu(W—N)$ supporting the above indication[13].

The cyanate group is indicated in the IR spectra of the cyanato complexes by the appearance of bands *ca.* 2160 cm^{-1} due to $\nu(CN)$, two weak to medium bands at *ca.* 1250 and 1030 cm^{-1} due to $\nu(CO)$ and Fermi resonance effects between the actual $\nu(CO)$ and the first overtone of $\delta(OCN)$[14]. In addition, two $\delta(OCN)$ bands were observed[15] at *ca.* 650 and 590 cm^{-1}. This indicates that the cyanato group is linked to tungsten atom through oxygen which is supported by the appearance of a band at *ca.* 410 cm^{-1} which could be assigned to $\nu(W—O)$.

The azide group is ascertained by the presence of two bands in the IR spectra of azido compounds in the range 2200–2050 cm^{-1} due to $\nu_{asym}(NNN)$; the bands at *ca.* 1340 and 1255 cm^{-1} may be assigned to $\nu_{sym}(N—N—N)$; a band at *ca.* 660 cm^{-1} is due to $\delta(NNN)$[16–18]. The splitting in all the N—N—N group frequencies indicates the inequality of the two N—N bonds which points to the covalent bonding between the metal and the azido group. A band at *ca.* 390 cm^{-1} may be assigned to $\nu(W—N)$.

The $\nu(CO)$ of the various alkoxy groups appeared in the IR spectra of the respective complexes at *ca.* 1160 cm^{-1} for methoxy, *ca.* 1170 and 1110 cm^{-1} for ethoxy, *ca.* 1170 and 1080 cm^{-1} for i-propoxy, *ca.* 1170 and *ca.* 1070 cm^{-1} for n-butoxy, *ca.* 1170, 1150 and 1060 cm^{-1} for i-butoxy, and at *ca.* 1170, 1150, 1080, 920 and 740 cm^{-1} for t-butoxy groups. The $\nu(CH)$ appeared at *ca.* 2950 cm^{-1}, $\delta_{asym}(CH)$ in the range 1460–1410 cm^{-1} and $\delta_s(C—H)$ in the range 1640–1580 cm^{-1}.[4] Appearance of bands in the range 450–400 cm^{-1} may be assigned to $\nu(WO)$ in all these alkoxy compounds[19]. The $\nu(CH)$ of the CH_3 group appeared at *ca.* 2970 cm^{-1}, $\delta_{asym}(CH)$ at *ca.* 1460 cm^{-1}, $\delta_{sym}(CH)$ at *ca.* 1370 cm^{-1} and $\pi(CH)$ at *ca.* 1630 cm^{-1}.

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