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A Study of Reactions of WCl_6, $WOCl_4$ and WO_2Cl_2 with Alcohols—Synthesis of Dialkoxy Derivatives of Tungsten

P. DABAS†, R. SAXENA and M.K. RASTOGI*
Departiment of Chemistry
Hindu College, Delhi-110 007, India

Dialkoxy derivatives of the type $(RO)_2WOCl_2$, $(RO)_2WO_2$ and $(RO)_2WCl_3$ have been prepared and characterized. The starting materials are tungsten(VI) oxychlorides $WOCl_4$, WO_2Cl_2 and tungsten hexachloride WCl_6. It has been observed that WCl_6 undergoes reduction to yield tungsten(V) dialkoxy derivatives. These alkoxides have been characterized by elemental analysis, IR and electronic spectra; while magnetic and conductivity measurements have been carried out in some cases.

INTRODUCTION

Metal alkoxides find catalytic applications in a variety of chemical reactions due to their chemical reactivity coupled with their volatility and solubility in common organic solvents. WCl_6 can be converted to haloalkoxy derivatives $WCl_{6-n}(OR)_n$ by reaction with Me_3SiOR[1, 2] and NaOMe[3]. Partial substitution with reduction has been observed by dissolution of WCl_6 in alcohols[4].

Chloroalkoxo complexes of tungsten(V) of the type $M[WCl_4(OR)_2]$, $M[WCl_5(OR)]$, $M_2[WCl_6(OEt)]$ (m = tetraalkylammonium, R = Me, Et, n-Pr) have been isolated[5–7]. Partial substitution of chlorine by alkoxy groups in $WOCl_4$ to yield $WOCl_3(OR)$ has been reported[8]. There is no report on substitution of alkoxy groups for chlorine in WO_2Cl_2. In the light of the above facts it was thought desirable to pursue a systematic investigation of such alkoxy derivatives of tungsten. Attention has been focussed on the dialkoxy derivatives.

EXPERIMENTAL

Since the alkoxy derivatives are extremely moisture sensitive, every precaution was taken to exclude moisture from all the apparatus and chemicals. A good grade of WCl_6 was used; $WOCl_4$ and WO_2Cl_2 were prepared from tungstic acid as described in the literature[9].

Preparation of di(alkoxy)dichlorooxotungsten(VI)

To 1.1 g of $WOCl_4$ in 40 mL of dry benzene about 20 mL of dry alcohol was added. The reaction mixture was refluxed for about 5 h and cooled. The resultant

†Department of Chemistry, Gargi College, New Delhi-110 049, India.

solution was evaporated under reduced pressure. The semisolid left was repeatedly washed with petroleum ether when different coloured solids were obtained. The alcohols used were MeOH, EtOH, n-PrOH, i-Pr(OH), n-Bu(OH), i-Bu(OH), t-Bu(OH) and n-amyl alcohol.

These compounds are slightly stable in dry and inert atmosphere. They decompose on heating without melting. They are partially soluble in solvents like THF, alcohol, acetone and are readily soluble in benzene and the parent alcohol. Their physical data is given in Table-1.

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF
DI(AlKOXY) DICHLOROOXOTUNGSTEN(VI)

Compound	Colour	Analysis % Found (Calcd.)			
		W	Cl	C	Alkoxy
$WOCl_2(OCH_3)_2$ (methoxy)	Deep grey	54.98 (55.23)	20.60 (21.33)	7.28 (7.21)	17.42 (18.62)
$WOCl_2(OC_2H_5)_2$ (ethoxy)	Creamish yellow	50.65 (50.96)	19.42 (19.67)	13.22 (13.30)	24.36 (24.94)
$WOCl_2(OC_3H_7)_2$ (n-propoxy)	Greenish grey	46.92 (47.28)	18.03 (18.26)	18.45 (18.51)	29.72 (30.34)
$WOCl_2(OC_3H_7)_2$ (i-propoxy)	Light brown	46.50 (47.28)	17.87 (18.26)	18.58 (18.51)	29.51 (30.34)
$WOCl_2(OC_4H_9)_2$ (n-butoxy)	Light green	43.98 (44.12)	16.87 (17.03)	22.95 (23.02)	—
$WOCl_2(OC_4H_9)_2$ (i-butoxy)	Grey	44.03 (44.12)	16.75 (17.03)	22.89 (23.02)	—
$WOCl_2(OC_4H_9)_2$ (t-butoxy)	Greyish	43.90 (44.12)	16.93 (17.03)	22.97 (23.02)	—
$WOCl_2(OC_5H_{11})_2$ (n-amyloxy)	Dirty green	40.85 (41.32)	15.76 (15.96)	26.90 (26.97)	—

Preparation of di(alkoxy)dioxotungsten(VI)

0.15 g of sodium metal was made to react with about 20 mL of dry alcohol till whole of it reacts. About 1.0 g of WO_2Cl_2 was added to this sodium alkoxide solution in parent alcohol, 20 mL of more alcohol was added and the reaction mixture was refluxed for 10 h and cooled. It was filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was washed several times with petroleum ether and dried. The alcohols used were MeOH, n-PrOH, i-PrOH, n-BuOH, i-BuOH and t-BuOH. The methoxy, i-propoxy and t-butoxy compounds are white while others are coloured. These are stable in inert and dry atmosphere. They are non-volatile and decompose on heating before melting. They are partialiy soluble in THF, acetone etc. but completely soluble in chloroform and parent alcohol. Their physical data is summarized in Table-2.

TABLE-2
PHYSICAL AND ANALYTICAL DATA OF DI(ALKOXY) DIOXOTUNGSTEN(VI)

Compound	Colour	Analysis % Found (Calcd.)		
		W	C	Alkoxy
$WO_2(OCH_3)_2$ (methoxy)	White	65.98 (66.16)	8.52 (8.63)	22.12 (22.31)
$WO_2(OC_3H_7)_2$ (n-propoxy)	Yellowish	54.74 (55.06)	21.44 (21.55)	35.16 (35.34)
$WO_2(OC_3H_7)_2$ (i-propoxy)	Creamish white	54.88 (55.06)	21.49 (21.55)	35.30 (35.34)
$WO_2(OC_4H_9)_2$ (n-butoxy)	Light brown	50.96 (50.82)	26.32 (26.51)	—
$WO_2(OC_4H_9)_2$ (i-butoxy)	Light brown	51.02 (50.82)	26.47 (26.51)	—
$WO_2(OC_4H_9)_2$ (t-butoxy)	White	50.48 (50.82)	26.38 (26.51)	—

Preparation of di(alkoxy)trichlorotungsten(V)

About 1.0 g of WCl_6 was dissolved in 30 mL of dry benzene and 30 mL of dry alcohol was added to the solution. The mixture was refluxed for *ca.* 12 h. The resulting dark coloured solution was evaporated to dryness under reduced pressure. The dark coloured solid was washed well with petroleum ether and dried. The alcohols used were MeOH, EtOH, i-PrOH, n-BuOH, i-BuOH and t-BuOH.

The compounds vary in colour from green to dark blue. They are stable in inert and dry atmosphere but are readily attacked by miosture. These are partially soluble in benzene and soluble completely in MeCN and dichloromethane but are insoluble in THF, $CHCl_3$, acetone etc. Their physical data is given in Table-3.

TABLE-3
PHYSICAL AND ANALYTICAL DATA OF
DI(ALKOXY) TRICHLOROTUNGSTEN(V)

Compound	Colour	Analysis % Found (Calcd.)			
		W	C	Cl	Alkoxy
$WCl_3(OCH_3)_2$ (methoxy)	Dark blue	51.88 (52.19)	6.65 (6.80)	30.02 (30.21)	17.45 (17.58)
$WCl_3(OC_2H_5)_2$ (ethoxy)	Dark blue	48.26 (48.35)	12.48 (12.61)	27.75 (27.98)	23.45 (23.65)
$WCl_3(OC_3H_7)_2$ (i-propoxy)	Dark blue	44.85 (45.04)	17.55 (17.62)	25.90 (26.07)	28.72 (28.88)
$WCl_3(OC_4H_9)_2$ (n-butoxy)	Green	41.89 (42.15)	21.75 (21.99)	24.12 (24.39)	—
$WCl_3(OC_4H_9)_2$ (i-butoxy)	Yellowish green	41.75 (42.15)	21.85 (21.99)	24.08 (24.39)	—
$WCl_3(OC_4H_9)_2$ (t-butoxy)	Dirty green	41.83 (42.15)	21.80 (21.99)	24.05 (24.39)	—

RESULTS AND DISCUSSION

Di(alkoxy)dichlorooxotungsten(VI)

The compounds show poor conductivity in acetonitrile indicating their non-electrolytic nature. Very low values of magnetic susceptibilities indicated that they are diamagnetic. The electronic spectra of the complexes showed sharp bands at *ca.* 26300 cm^{-1} and 28200 cm^{-1} which may be assigned to charge transfer (Cl→W) and at 37100 cm^{-1} due to charge transfer (O→W)[13].

The ν(CO) bands in the methoxy complex appeared at 1175 cm^{-1}, in ethoxy complex at 1170 and 1150 cm^{-1}, in n-propoxy compound at 1100 cm^{-1}, in i-propoxy derivative at 1150 and 1110 cm^{-1}. In the n-butoxy compound the alkoxy group showed ν(CO) bands at 1150, 1110 and 1080 cm^{-1}, at 1170, 1150, 1130, and 1070 cm^{-1} in the i-butoxy derivative, at 1170, 1150, 1130, 1050, 910 and 730 cm^{-1} in the t-butoxy compound[14] and at 1260, 1080 cm^{-1} in the amyloxy derivative. Appearance of bands in the range 450–400 cm^{-1} may be assigned to ν(W—O) in all these alkoxy derivatives[15–17]. The sharp bands in the range 970–950 cm^{-1} indicated the presence of a terminal W=O group in all these compounds[18]. The ν(C—H) of the CH_3 group appeared at 2970 cm^{-1}, δ_{asym}(CH) at *ca.* 1460 cm^{-1}, δ_{sym}(CH) at 1370 cm^{-1}, π(CH) at 1630 cm^{-1} and the —CH_2 scissoring mode is observed at *ca.* 1470 cm^{-1} in these compounds.

Di(alkoxy)dioxotungsten(VI)

The poor conductivity of these compounds suggests their non-electrolytic nature; magnetic measurements indicate them to be diamagnetic. The electronic spectra of complexes showed the charge transfer band at *ca.* 47500 cm^{-1} (O→W)[19].

The respective alkoxy groups showed their ν(CO) bands at 1150 cm^{-1} in methoxy compound, at 1080 cm^{-1} in n-propoxy compound, at 1150 cm^{-1} in i-propoxy compound, at 1140 and 1090 cm^{-1} in n-butoxy compound, at 1150 and 1080 cm^{-1} in the i-butoxy compound and at 1140 and 1090 cm^{-1} in the t-butoxy compound. The ν(W—O) appeared at *ca.* 510 cm^{-1} in all these complexes. The sharp medium band at *ca.* 770 cm^{-1} indicated the presence of a bridging W—O—W group in these compounds suggesting a polymeric nature[18]. However in the methoxy and propoxy compounds there is a band at *ca.* 950 cm^{-1} also, which is absent in all the butoxy compounds. This indicates the existence of a terminal W=O group in the former compounds and absence of such a group in the butoxy derivatives.

Di(alkoxy)trichlorotungsten(V)

These compounds are essentially non-electrolytes as they show very poor conductivity. Their magnetic susceptibilities are *ca.* 1.81 BM pointing out their paramagnetic nature for one unpaired electron. Their electronic spectra showed bands in the range 34482–37735 cm^{-1} which could be assigned to charge transfer (Cl→W).

The alkoxy groups in the respective compounds are identified by their ν(CO) (in their IR spectra) which were observed at 1180 cm^{-1} in methoxy compound,

at 1175 and 1110 cm^{-1} in the ethoxy compounds, at 1160 and 1090 cm^{-1} in the i-propoxy derivative, at 1145, 1100 and 1080 cm^{-1} in n-butoxy derivative, at 1175, 1140 and 1080 cm^{-1} in i-butoxy compound and at 1170, 1145, 1050, 900 and 720 cm^{-1} in the t-butoxy compound. The ν(CH) of the CH_3 group in all these complexes appeared at *ca.* 2900 cm^{-1}, δ_{asym}(CH) and δ_{sym}(CH) appeared at *ca.* 1450 and 1370 cm^{-1} respectively, the π(CH) is assigned at *ca.* 1650 cm^{-1}, and the —CH_2 scissoring mode is observed at *ca.* 1470 cm^{-1}. The ν(W—O) is assigned at *ca.* 500 cm^{-1}. A broad band is observed below 500 cm^{-1} which may be assigned to ν(W—Cl) terminal and bridged both.

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