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PREPARATION AND REACTIONS OF CHROMIUM(III)ALKOXIDES

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ABSTRACT

Reactions of $CrCl_3.3THF$ with lithium alkoxides in 1:3 molar ratio in the respective primary alcohols yield insoluble trialkoxides, $Cr(OR)_3$ (where R = Me, Et, Bu-n). The corresponding reactions with isopropyl and tertiary butyl alcohols, however, yield hydrolysed products only. We have been able to synthesize the isopropoxide and t.butoxide also by alternative routes. All the alkoxides have been characterized by physico-chemical methods and attempts have been made to study their alcoholysis reactions.

INTRODUCTION

In spite of extensive work on alkoxides and chloride alkoxides of earlier transition metals, similar derivatives of later transition metals have received comparatively less attention. This may be due to the insolubility and highly polymeric nature of these compounds.

Although alkoxy derivatives of most of the transition metals can be prepared[1,2] by the reactions of their halides with alcohols in the presence of a proton acceptor(e.g., Na,Li or NH_3), chromium(III)alkoxides could not be synthesized by this simple route, probably due to insolubility of anhydrous $CrCl_3$ in organic solvents. The preparation of amorphous $Cr(OEt)_3$ was first claimed[3] in 1929 by the reaction of $CrCl_3$ in ethanol with sodium ethoxide. This reaction in 1:1 molar ratio of $CrCl_3$ with NaOEt in ethanol was found[4] to yield a soluble adduct, $CrCl_2(OEt)$in EtOH, but the products in higher molar ratios could not be separated from NaCl in view of their insolubility. In 1964,Hornuff and Kappler[5] reported the synthesis of chromium(III)alkoxides by the photolysis

of alcoholic solutions of ammonium chromate. Brown and coworkers[6,7] reported the preparation of chromium(III)alkoxides by photolytic decarbonylation of tricarbonylarenechromium. However, their attempts to prepare higher alkoxides were unsuccessful. In view of the above rather circuitous procedures described for the synthesis of chromium(III) alkoxides, the possibility of extending the generally applicable synthesis involving reactions of anhydrous metal chlorides with alcohol was of considerable interest and has been explored further with success in the present investigations.

The difficulty due to the insolubility of anhydrous $CrCl_3$ in organic solvents could be overcome by starting with a soluble simple adduct, $CrCl_3.3THF$, the reactions of which with n-alkoxides gave $Cr(OR^n)_3$ by simple straightforward methathetic reactions.

RESULTS AND DISCUSSION

Chromium(III) alkoxides, $Cr(OR)_3$ (where R = Me, Et and Bu-n) have been synthesized successfully by the reactions of $CrCl_3.3THF$ with three moles of lithium alkoxides in the respective alcohol and benzene. These reactions can be represented by the following general equation.

$$CrCl_3.3THF + 3Li(OR) \longrightarrow Cr(OR)_3\downarrow + 3\ LiCl$$

(where R = Me, Et, Bu-n)

The insoluble alkoxides (Table 1) formed were separated by filtration and purified by washing with dry alcohols, in which lithium chloride has a fair solubility. The greyish green coloured alkoxides have been found to be insoluble in common organic solvents &non-volatile even under reduced pressure.

In spite of rigorous anhydrous conditions employed during the reactions, the reactions of $CrCl_3.3THF$ with three moles of lithium isopropoxide or t-butoxide, on the other hand, yielded products with much higher chromium and much lower alkoxy contents than those calculated for the tri-alkoxides leading to the conclusion that the products are hydrolysed alkoxides.

Chromium triisopropoxide could, however, be prepared by refluxing chromium triphenoxide in isopropanol.

Table 1. Reactions of $CrCl_3.3THF$ with Lithium Alkoxides and their Alcoholysis Interchange Reactions

S. No.	Reactants	Molar Ratio	Refluxing time and medium	Nature of Product (Yield)	Analyses (%) Found (Calcd.)	
					Chromium	Alkoxy*
1.	$CrCl_3.3THF$ 8.80 g + LiOMe 0.49 g□	1:3	3 hr MeOH	$Cr(OMe)_3$ Greyish blue solid (95%)	35.80 (35.84)	64.31 (64.16)
2.	$CrCl_3.3THF$ 19.25 g + LiOEt 1.10 g□	1:3	3 hr EtOH	$Cr(OEt)_3$ Greyish green solid (97%)	27.58 (27.78)	71.94 (72.22)
3.	$CrCl_3.3THF$ 6.54 g + LiOBu-n 0.36 g□	1:3	3 hr HOBu-n	$Cr(OBu\text{-}n)_3$ Greyish green solid (96%)	19.03 (19.16)	..
4.	$Cr(OEt)_3$ 1.23 g + PhOH 1.86 g□	1:3	20 hr benzene	$Cr(OPh)_3$ Dark green solid (98%)	15.46 (15.70)	..
5.	$CrCl_3$3THF 4.60 g + LiOBu-t 0.26 g□	1:3	10 hr Stirring THF	$Cr(OBu\text{-}t)_4$ Blue solid (20% distilled product)	15.08 (15.26)	..

* Alkoxy group in the samples were determined by methods suggested by Bradley and Mehrotra[15,16]

□ Weight of lithium metal dissolved in the respective alcohol.

$$Cr(OC_6H_5)_3 + \underset{\text{excess}}{3i\text{-PrOH}} \xrightarrow{\text{Reflux}} Cr(OPr\text{-}i)_3 + 3C_6H_5OH \uparrow$$

Chromium phenoxide used above was synthesized by the reaction of chromium triethoxide with phenol under refluxing condition in benzene with continuous azeotropic fractionation of ethanol with benzene.

$$Cr(OEt)_3 + \underset{\text{excess}}{PhOH} \xrightarrow{\text{Reflux}} \underset{\text{Dark green solid, insoluble in organic solvents.}}{Cr(OPh)_3} + EtOH \uparrow$$

Chromium triphenoxide also gave chromium tri-methoxide and ethoxide (Table 2), when it is refluxed with excess of these alcohols.

$$Cr(OPh)_3 + \underset{\text{excess}}{ROH} \xrightarrow{\text{Reflux}} Cr(OR)_3 \downarrow + 3PhOH$$

(where R = Me, Et)

Chromium tri(tertiary-butoxide or -amyloxide), however, could not be prepared even from the triphenoxide route in spite of long refluxing with tertiary alcohols. As mentioned earlier, the reaction of $CrCl_3.3THF$ with three moles of LiOBu-t in t-BuOH yields only hydrolysed products. It was conjectured that this might be due to the reaction of chromium chloride with tertiary butyl alcohol to give $Cr(OH)_xCl_{3-x}$, and t-BuCl [cf., reaction[8] of $SiCl_4$ with t-BuOH giving $Si(OH)_4$ and t-BuCl]. The reaction was, therefore, repeated taking the precaution to exclude free t-BuOH and was found to yield $Cr(OBu\text{-}t)_3$.

Three moles of the lithium tertiary butoxide sample (in the absence of excess t-BuOH), therefore, were treated with one mole of $CrCl_3.3THF$ in tetrahydrofuran. On stirring the reaction mixture in the cold, a blue coloured soluble complex was obtained which could not be separated from the lithium chloride. The blue viscous product sublimed on heating (60-90°C) under reduced pressure. This was characterized to be chromium tetra-tertiary-butoxide, $Cr(OBu\text{-}t)_4$ reported earlier by Bradley et al.[9]

The reaction of the blue $Cr(OBu\text{-}t)_4$ with excess of methanol or ethanol at ambient temperatures yielded insoluble greyish green coloured chromium(III) methoxide and ethoxide, whereas insoluble chromium triisopropoxide was formed only on refluxing $Cr(OBu\text{-}t)_4$ with excess of isopropanol.

Table 2. Alcoholysis Reactions of $Cr(OBu\text{-}t)_4$ and $Cr(OPh)_3$

S. No.	Reactants	Reaction conditions	Nature of Product (Yield)	Analysis (%) Found (Calcd.)	
				Chromium	Alkoxy
1.	$Cr(OBu\text{-}t)_4$ + EtOH (excess)	Stirring 1 hr	$Cr(OEt)_3$ Grey green solid (90%)	27.42 (27.78)	71.56 (72.22)
2.	$Cr(OBu\text{-}t)_4$ + i-PrOH (excess)	Refluxing 1 hr	$Cr(OPr\text{-}i)_3$ Green solid (92%)	22.08 (22.70)	77.09 (77.30)
3.	$Cr(OPh)_3$ + MeOH (excess)	Refluxing 5 hr	$Cr(OMe)_3$ Grey blue solid (98%)	35.01 (35.86)	62.59 (64.14)
4.	$Cr(OPh)_3$ + EtOH (excess)	Refluxing 5 hr	$Cr(OEt)_3$ Grey green solid (97%)	27.45 (27.78)	71.82 (72.22)
5.	$Cr(OPh)_3$ + i-PrOH (excess)	Refluxing 5 hr	$Cr(OPr^i)_3$ Green solid (96%)	22.96 (22.70)	77.12 (77.30)

$$Cr(OBu\text{-}t)_4 \xrightarrow[\text{cold or reflux}]{ROH} Cr(OR)_3 + \text{unidentified products}$$

(where R = Me, Et, OPr^i)

Alcohol interchange reactions of chromium trialkoxides have revealed some novel features. In contrast to alkoxides of earlier transition metals which undergo facile alcoholysis reactions, chromium n-alkoxides e.g., ethoxide and methoxide do not appear to undergo alcoholysis reactions. In fact, the interchange reactions of chromium methoxide and ethoxide with n-butanol could not be effected even under refluxing conditions in spite of higher reaction temperature and continuous fractionation of the distillate to remove more volatile ethanol, formed (if any) in the alcoholysis reaction. Transesterification reactions have also been attempted for the interchange of alkoxy groups. Chromium(III) alkoxides do not appear to undergo transesterification also, whereas it has been observed that the alkoxides of a number of other metals undergo very facile alcoholysis and transesterification[10] reactions.

$$Cr(OEt)_3 + CH_3COOBu\text{-}n \longrightarrow \text{no reaction}$$

By contrast, a secondary alkoxide like chromium tri-isopropoxide interchanges its isopropoxy groups when it is refluxed with primary alcohols. However, the isopropoxy group(s) of chromium isopropoxide could not be interchanged with tertiary alkoxy group even under forcing conditions.

Though chromium ethoxide does not appear to undergo alcoholysis reactions with other alcohols, it has been observed that it undergoes slow alcoholysis reaction with a substituted alcohol like monoethanolamine in different stoichiometric ratios in benzene medium. The progress of these reactions could be followed by the determination of the ethanol collected in the azeotrope by fractionation.

$$Cr(OEt)_3 + x\ HOCH_2CH_2NH_2 \longrightarrow Cr(OEt)_{3-x}(OCH_2CH_2NH_2)_x + x\ EtOH\uparrow$$

(where x = 1, 2 & 3)

All these compounds (Table 3) have been found to be insoluble in benzene and to decompose on heating even under reduced pressure.

Table 3. Reactions of $Cr(OEt)_3$ with Monoethanolamine in Different Molar Ratios

S. No.	Reactants	Molar Ratio	Refluxing time in benzene	Nature of Product (Yield)	Analyses: Found (Calcd.)		
					Cr %	N %	EtOH in azeotrope(g)
1.	$Cr(OEt)_3$ 1.71 g + $NH_2CH_2CH_2OH$ 0.56 g	1:1	2 hr	$(OEt)_2Cr(OCH_2CH_2NH_2)$ Bluish green solid (95%)	25.50 (25.69)	6.71 (6.91)	0.41 (0.42)
2.	$Cr(OEt)_3$ 1.43 g + $NH_2CH_2CH_2OH$ 0.93 g	1:2	3 hr	$(OEt)Cr(OCH_2CH_2NH_2)_2$ Bluish green solid (94%)	24.18 (23.94)	12.60 (12.81)	0.68 (0.71)
3.	$Cr(OEt)_3$ 1.06 g + $NH_2CH_2CH_2OH$ 1.04 g	1:3	3 hr	$Cr(OCH_2CH_2NH_2)_3$ Bluish green solid (95%)	22.92 (22.38)	17.69 (18.08)	0.67 (0.70)

The higher reactivity of ethanolamine compared to ethanol with $Cr(OEt)_3$ may be due to stronger initial coordination due to chelation, such as in $NH_2(CH_2CH_2)\overset{H}{O} \longrightarrow Cr(OR)_3$, which serves as an intermediate. However, the analysis of the final product shows that amine groups do not bring about replacement of alkoxy groups of $Cr(OEt)_3$. This indicates that in the reactions with ethanolamine, chromium alkoxides show a resemblance to alkoxides of Ti, Zr and Ni[11] and are in contrast to the alkoxides of tin and niobium, etc.[1] in which case the amine group of monoethanolamine also takes part in the replacement reactions.

Infrared spectra of all the derivatives have been recorded in the range 4000-200 cm^{-1} with KBr pellets or in Nujol mulls. Sharp bands at 1040-1060 cm^{-1} have been assigned to the C-O stretching[12] frequency of the alkoxy group. Following the publication of Barraclough et al.[13] on isopropoxides of earlier transition metals, the bands at $\sim$1150, 1120 and 950 cm^{-1} in the spectra of the isopropoxy derivative have been assigned to vibration modes of the isopropoxy group. A band at $\sim$ 1210 cm^{-1} in the spectra of phenoxide has been assigned to the C-O stretching vibration[12]. A sharp band observed at $\sim$ 3300 cm^{-1} has been assigned to the νN-H stretching vibration in the spectra of aminoalkoxide derivatives[11]. Characteristic Cr-O stretching vibrations have been observed in the range 450-550 cm^{-1} in all the spectra.

Electronic spectra of all the alkoxides have been measured in the visible range in Nujol mulls. The spectra are very similar and may be interpreted on the basis of an octahedral environment of chromium(III); the bands around 17,000 cm^{-1} (ν_1) and 24,000 cm^{-1} (ν_2) are assigned to the $^4A_{2g} \longrightarrow {}^4T_{2g}$ and $^4A_{2g} \longrightarrow {}^4T_{1g}$ (F) transitions, respectively.

The parameter B was obtained from the Tanabe-Sugano diagram for a d^3 configuration by fitting the observed spectra. The interelectronic repulsion parameters are in all cases much lower than those observed for the free ion showing the considerable covalent nature of the metal-ligand bond in these alkoxides. The positions of the observed maxima, the proposed assignments, the ligand field parameter (10 Dq) and the Racah parameter(B) are summarized in Table 4.

Table 4. Electronic Visible Spectra of Chromium(III) Alkoxides

S.No.	Product	$^4A_{2g} \longrightarrow {}^4T_{2g}$ (10 Dq) (cm^{-1})	$^4A_{2g} \longrightarrow {}^4t_{1g}$ (cm^{-1})	B (cm^{-1})
1.	$Cr(OMe)_3$[a]	17,610	24,150	612
2.	$Cr(OEt)_3$[a]	17,000	23,470	600
3.	$Cr(OBu\text{-}n)_3$[a]	17,060	23,700	610
4.	$Cr(OPh)_3$	16,900	23,920	615
5.	$Cr(OMe)_3$[b]	17,240	23,800	609
6.	$Cr(OEt)_3$[b]	16,370	23,470	654
7.	$Cr(OPr\text{-}i)_3$[b]	15,880	22,940	720
8.	$Cr(OMe)_3$[c]	17,180	24,150	613
9.	$Cr(OPr\text{-}i)_3$[c]	16,180	23,280	728

a) Prepared from LiCl method
b) Prepared from $Cr(OPh)_3$
c) Prepared from $Cr(OBu\text{-}t)_4$

The spectrum of $Cr(OBu\text{-}t)_4$ shows bands at $\sim$ 15,700 cm^{-1}, 13,870 cm^{-1} and a shoulder at 25,300 cm^{-1} which can be assigned on the basis of an earlier report[9] to the tetrahedral environment for chromium in this compound.

EXPERIMENTAL

All-glass apparatus with standard Quickfit joints were used throughout. Stringent precautions were taken to exclude moisture. $CrCl_3.3THF$ adduct was prepared by the thionyl chloride method[14]. infrared spectra were recorded on a Infrared grating Perkin-Elmer 621 Spectrophotometer. Electronic Spectra were recorded on a Beckman Spectrophotometer.

Chromium was estimated as lead chromate. Methanol, ethanol and isopropanol in the benzene-azeotrope or in the chromium alkoxides were estimated [15] volumetrically, as these undergo oxidation to carbon dioxide (under refluxing conditions), acetic acid and acetone (under ambient conditions) respectively with a N $K_2Cr_2O_7$ solution in 12.5% H_2SO_4.

Reaction of $CrCl_3$.3THF with lithium methoxide in (1:3)molar ratio in methanol

To $CrCl_3$.3THF (8.80 g, 23.5 mmol) in methanol(~ 70mL) was added a solution of lithium methoxide prepared by dissolving lithium (0.49 g, 71.01 mmol)in methanol(~ 20mL) and benzene(~25mL). A greyish green insoluble precipitate was separated. The reaction mixture was refluxed for about 3 hrs. The insoluble portion was separated by filtration and washed with dry methanol till the washings gave negative test for chloride ion. It was finally dried under reduced pressure (80°C/0.5 mm) for 2 hrs. A greyish blue solid was obtained.

Found:: Cr, 35.80 ; OMe, 64.30%

Calculated for $Cr(OMe)_3$; Cr, 35.84 ; OMe, 64.16%

Reaction of $Cr(OEt)_3$ with phenol (molar ratio 1:3) in benzene

To a weighed amount of $Cr(OEt)_3$, (1.23 g, 6.58 mmol) in benzene (~ 50 mL) was added phenol (1.86 g, 19.78 mmol). No apparent change was observed. The reaction mixture was refluxed under a fractionating column followed by the distillation of the ethanol-benzene azeotrope over a period of 20 hrs. The colour of the product gradually changed to dark-green. The insoluble dark green solid obtained was washed several times with boiling benzene to remove any excess phenol present and finally, dried under reduced pressure (80°C/0.5 mm) for two hours. A dark green product was obtained. Results are summarised in Table 1.

Reaction of $Cr(OEt)_3$ with monoethanolamine (molar ratio 1:1) in benzene

To $Cr(OEt)_3$, (1.71 g, 9.18 mmol) in benzene(~ 50 mL) was added monoethanolamine (0.56 g, 9.18 mmol). The reaction mixture was refluxed for about 3 hrs. and the alcohol formed was removed azeotropically (20 hrs).

Removal of the remaining solvent at 40°C/0.5 mm gave a bluish green coloured insoluble product (Yield, 1.76 g, 95%).

Found: EtOH (in the azeotrope), 0.41 g ; Cr, 25.59 ; N, 6.71%

Calculated for $(OEt)_2Cr(OCH_2CH_2NH_2)$: EtOH, 0.42 g (for one mole);
Cr, 25.69 ; N, 6.91%.

For brevity, experimental procedure has been described above for only one typical case each and the details of other products, synthesized during these investigations, have been summarized in Tables 1 to 3.

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