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Synthesis and Physico-chemical Studies of Bimetallic Alkoxy Derivatives of Chromium(III) with Niobium(V) and Tantalum(V)

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Abstract

Reactions of $CrCl_3\cdot 3thf$ with $KM(OPr^i)_6$ in 1:3 molar ratios in benzene yield soluble complexes of the type $Cr[M(OPr^i)_6]_3$ (M = Nb or Ta). On heating under vacuum, these complexes tend to disproportionate into $Cr(OPr^i)_3$ and $M(OPr^i)_5$ (M = Nb or Ta). A number of bimetallic alkoxides have also been synthesized by the alcoholysis of $Cr[M(OPr^i)_6]_3$ with alcohols (methanol, ethanol and t-amyl alcohol). The IR, visible, electron spin resonance and magnetic properties of these newly synthesized complexes throw light on the structural features.

Introduction

Hornuff and Kappler [1] reported the preparation of chromium(III) alkoxide by photolysis of an alcoholic solution of ammonium chromate; this was confirmed by Brown *et al.* [2] by preparing Cr(III) methoxide and ethoxide by a similar method. Alkoxy and phenoxy derivatives of the type $[M(OR)_n]_x$ have also been synthesized in our laboratories recently. These derivatives are insoluble and nonvolatile, presumably due to their polymeric nature [3]. In contrast, the investigations carried out in our laboratories more recently have revealed that the bimetallic alkoxy derivatives of chromium with aluminum are volatile and soluble in common organic solvents [4, 5]. In view of the above, it was considered of interest to synthesize soluble bimetallic alkoxy derivatives of chromium with niobium and tantalum and to investigate their physico-chemical characteristics.

Results and Discussion

Bimetallic alkoxy derivatives of chromium with niobium and tantalum have been synthesized by the reaction:

$$CrCl_3\cdot 3thf + 3KM(OPr^i)_6 \xrightarrow[\text{reflux}]{C_6H_6} Cr[M(OPr^i)_6]_3 + 3KCl\downarrow + 3thf$$

(M = Nb or Ta)

Chromium tris-(hexaisopropoxyniobinate) and tris-(hexaisopropoxytantalate) are green sticky solids, soluble in common organic solvents.

In our earlier studies, chromium tris-(tetraisopropoxyaluminate) could be distilled unchanged under reduced pressure. However, chromium tris-(hexaisopropoxyniobinate) and chromium tris-(hexaisopropoxytantalate) complexes are found to disproportionate on heating under reduced pressure in the following manner:

$$Cr[M(OPr^i)_6]_3 \xrightarrow{\Delta} Cr(OPr^i)_3 + 3M(OPr^i)_5\uparrow$$

The lower stability and disproportionation of these complexes may be ascribed to the bulky nature of the ligands and greater volatility of niobium and tantalum isopropoxides.

Further alcohol interchange reactions of chromium tris-(hexaisopropoxyniobinate) and tris-(hexaisopropoxytantalate) with different alcohols were carried out, yielding products depending upon the nature of the alkoxide group. These complexes react quantitatively with an excess of MeOH and EtOH, yielding the corresponding chromium tris-(hexamethoxy/ethoxyniobinate or tantalate):

$$Cr[M(OPr^i)_6]_3 + 18ROH \xrightarrow[\text{reflux}]{C_6H_6} Cr[M(OR)_6]_3 + 18Pr^iOH$$

(M = Nb or Ta; R = Me or Et)

In contrast, the reaction with a branched alcohol such as t-amyl alcohol is slow and could only be pushed in the forward direction by continuous removal of liberated isopropanol; even under these conditions, only partial replacement of isopropoxy groups could be achieved:

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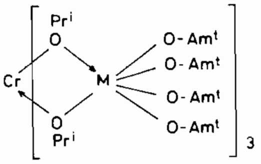
$$\mathrm{Cr[M(OPr^i)_6]_3 + 12Am^tOH \xrightarrow[\text{reflux}]{C_6H_6} Cr[M(OPr^i)_2(OAm^t)_4]_3 + 12Pr^iOH}$$

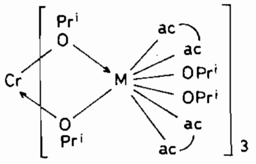
The replaceability of only twelve out of eighteen isopropoxy groups from $\mathrm{Cr[M(OPr^i)_6]_3}$ can be explained on steric grounds. The niobium and tantalum atoms are effectively hindered when they are surrounded with two bridging isopropoxy and four t-amyloxy groups in the complexes chromium tris-(diisopropoxytetra-t-amyloxyniobinate or tantalate):



The reaction of $\mathrm{[CrM(OPr^i)_6]_3}$ with a bidentate ligand such as 2,4-pentanedione(acacH) has also been carried out in 1:6 molar ratio in refluxing benzene medium:

$$\mathrm{Cr[M(OPr^i)_6]_3 + 6acacH \longrightarrow Cr[M(OPr^i)_4(acac)_2]_3 + 6Pr^iOH}$$

The above can, therefore, be represented by the following formula in which chromium is six-coordinate, but niobium and tantalum achieve eight coordination:



IR Spectra

IR spectra of all these complexes were recorded in Nujol mull in the range 4000–200 $\mathrm{cm^{-1}}$. The characteristic observed bands for these derivatives in the regions 1000–1100, 550–600 and 450–525 $\mathrm{cm^{-1}}$ can be assigned to ν(C–O), ν(Nb–O)/ν(Ta–O) and ν(Cr–O) vibrations, respectively [2, 6, 7].

Visible Spectra

Electronic spectra of these complexes have been recorded in the range of 50 000–12 500 $\mathrm{cm^{-1}}$ in the benzene solution (Table III). The observed bands in the regions 15 500–17 600, 21 350–26 600 and 35 700 $\mathrm{cm^{-1}}$ can be attributed to the three allowed transitions

$$\mathrm{{}^4A_{2g} \longrightarrow {}^4T_{2g}\,(10\,Dq),\quad {}^4A_{2g} \longrightarrow {}^4T_{1g}\,(F)}\text{ and}$$
$$\mathrm{{}^4A_{2g} \longrightarrow {}^4T_{1g}\,(P)}$$

respectively, indicating an octahedral environment for Cr(III) in these complexes [8]. The values for LFSE (Ligand Field Stabilization Energy) (kJ/mol) are found to be in the range of 200 ± 15. However, these values are lower compared to the values (235 ± 15) for the bimetallic derivatives chromium tris-(tetralkoxyaluminate) [5].

The nephelauxetic ratio (β_{35}), which is the ratio of a given Racah interelectronic repulsion parameter (B) for the chromium ion in a complex to its value in the gaseous ion, has also been calculated for these complexes [3]. The value for B and β_{35} are found in the range of 660 ± 50 $\mathrm{cm^{-1}}$ (1030 $\mathrm{cm^{-1}}$ for the free $\mathrm{Cr^{3+}}$ ion) and 0.65 ± 0.05, respectively, indicating the highly covalent character of the metal–ligand bonds in these derivatives [9, 10].

ESR Spectra

In the ESR spectra the chromium tris-(hexaisopropoxyniobinate) and chromium tris-(hexaisopropoxytantalate) complexes show only one $g_\perp$ absorption at approx. 2, indicating that the zero field splitting value is higher ($D > h\nu$) in these cases [11].

Magnetic Susceptibility Measurements

Magnetic susceptibilities of these complexes have been determined. The magnetic data also support an octahedral configuration for Cr(III) in these complexes. The μ_{eff} values of Cr(III) complexes at ambient temperatures are found to be in the range of 3.85 ± 0.1. For a high spin $\mathrm{Cr^{3+}}$ ion ($\mathrm{d^3}$) in an 'octahedral' environment, the magnetic moment is expected to be close to the spin-only value and to remain practically independent of temperature ($\mu_{\mathrm{so}} = 3.87$ BM for $S = 3/2$) [12].

Experimental

An all-glass apparatus with standard Quickfit joints was used throughout. Stringent precautions were taken to exclude moisture. Benzene and alcohols were dried according to literature procedures. Acetylacetone was purified by distillation (boiling point 135–137 °C). $\mathrm{CrCl_3{\cdot}3thf}$ adduct was prepared by the thionyl chloride method described by Zeiss and co-workers [13]. Niobium and tantalum isopropoxides were prepared from their anhydrous chlorides and distilled and analysed before use [6]. Niobium or tantalum and chromium were estimated as mixed oxide. Chromium was estimated as lead chromate.

IR spectra were recorded on a Perkin-Elmer 557 spectrophotometer using Nujol mulls. Electronic spectra were recorded on a Pye Unicam model SP8-100 spectrophotometer. Magnetic susceptibility measurements were carried out by the standard Gouy method on a Bruker model B-E70B8 magnetic balance.

TABLE I. Reactions of $CrCl_3 \cdot 3thf$ with $KNb(OPr^i)_6$ and their Alcoholysis Interchange Reactions

Reactants	Molar ratio and medium	Liberated isopropanol (g/mol)	Product/nature	Analyses (found (calc.)) (%)		
				Total metal	Chromium	Alkoxy
$CrCl_3 \cdot 3thf$ (1.75 g) + $KNb(OPr^i)_6$ (6.83 g)	1:3 Benzene		$Cr[Nb(OPr^i)_6]_3$ green sticky solid, soluble in benzene	24.44 (23.71)	3.68 (3.72)	75.48 (76.28)
$Cr[Nb(OPr^i)_6]_3$ (2.12 g) + MeOH (excess)	1:18 Benzene		$Cr[Nb(OMe)_6]_3$ green solid, soluble in benzene	31.98 (32.22)	5.59 (5.83)	
$Cr[Nb(OPr^i)_6]_3$ (3.22 g) + EtOH (excess)	1:18 Benzene		$Cr[Nb(OEt)_6]_3$ green sticky solid, soluble in benzene	24.83 (24.40)	4.49 (4.55)	70.73 (71.05)
$Cr[Nb(OPr^i)_6]_3$ (2.14 g) + Am^tOH (excess)	1:12 Benzene	1.10/12	$Cr[Nb(OPr^i)_2(OAm^t)_4]_3$ dark green sticky solid, soluble in benzene	16.31 (16.11)	2.85 (3.00)	
$Cr[Nb(OPr^i)_6]_3$ (3.23 g) + acacH (1.39 g)	1:6 Benzene	0.82/6	$Cr[Nb(OPr^i)_4(acac)_2]_3$ dark green sticky solid, soluble in benzene	17.40 (17.05)	3.09 (3.14)	

TABLE II. Reactions of $CrCl_3 \cdot 3thf$ with $KTa(OPr^i)_6$ and their Alcoholysis Interchange Reactions

Reactants	Molar ratio and medium	Liberated isopropanol (g/mol)	Product/nature	Analyses (found (calc.)) (%)		
				Total metal	Chromium	Alkoxy
$CrCl_3 \cdot 3thf$ (1.38 g) + $KTa(OPr^i)_6$ (6.37 g)	1:3 Benzene		$Cr[Ta(OPr^i)_6]_3$ green sticky solid, soluble in benzene	36.89 (35.86)	3.02 (3.13)	63.89 (64.13)
$Cr[Ta(OPr^i)_6]_3$ (2.12 g) + MeOH (excess)	1:18 Benzene		$Cr[Ta(OMe)_6]_3$ green solid, soluble in benzene	48.13 (47.02)	4.24 (4.50)	
$Cr[Ta(OPr^i)_6]_3$ (2.67 g) + EtOH (excess)	1:18 Benzene		$Cr[Ta(OEt)_6]_3$ green sticky solid, soluble in benzene	39.01 (38.59)	3.48 (3.70)	57.48 (57.71)
$Cr[Ta(OPr^i)_6]_3$ (2.50 g) + Am^tOH (excess)	1:12 Benzene	1.09/12	$Cr[Ta(OPr^i)_2(OAm^t)_4]_3$ dark green sticky solid, soluble in benzene	27.87 (27.21)	2.47 (2.60)	
$Cr[Ta(OPr^i)_6]_3$ (2.84 g) + acacH (1.03 g)	1:6 Benzene	0.66/6	$Cr[Ta(OPr^i)_4(acac)_2]_3$ dark green sticky solid, soluble in benzene	29.21 (28.59)	2.63 (2.74)	

TABLE III. Electronic Spectra of Bimetallic Alkoxides and Allied Derivatives of Chromium(III)

Compound	Transitions (cm^{-1})			Dq (cm^{-1})	LFSE (kJ/mol)	B (cm^{-1})	β_{35}
	$^4A_{2g} \to {}^4T_{2g}$ (ν_1)	$^4A_{2g} \to {}^4T_{1g}(F)$ (ν_2)	$^4A_{2g} \to {}^4T_{1g}(P)$ (ν_3)				
$Cr[Nb(OMe)_6]_3$	16700	23600	35700	1670	199	621	0.60
$Cr[Nb(OEt)_6]_3$	16400	23300	35700	1640	196	647	0.63
$Cr[Nb(OPr^i)_6]_3$	16300	23150	35700	1630	195	656	0.64
$Cr[Nb(OPr^i)_2(OAm^t)_4]_3$	16500	21400	35700	1650	185	699	0.68
$Cr[Nb(OPr^i)_4(acac)_2]_3$	17500	26500	35700	1750	209	651	0.63
$Cr[Ta(OMe)_6]_3$	16700	23800	35700	1670	199	636	0.62
$Cr[Ta(OEt)_6]_3$	16400	23400	35700	1640	195	670	0.65
$Cr[Ta(OPr^i)_6]_3$	16200	23400	35700	1620	194	696	0.67
$Cr[Ta(OPr^i)_2(OAm^t)_4]_3$	16000	23000	35700	1600	191	715	0.69
$Cr[Ta(OPr^i)_4(acac)_2]_3$	17600	26600	35700	1760	210	634	0.62

Reactions of $CrCl_3 \cdot 3thf$ with Potassium Hexaisopropoxyniobinate or Tantalate, $KM(OPr^i)_6$

$KM(OPr^i)_6$ (M = Nb or Ta) in isoproponol–benzene was added slowly to a solution of $CrCl_3 \cdot 3thf$ in benzene. The colour of the solution changed from violet to green with a separation of white solid. The reaction mixture was refluxed for two hours. The resulting soluble green solution was filtered to remove KCl formed during the reaction. A green sticky solid soluble in benzene was obtained. The details of the syntheses are reported in Tables I and II.

Reactions of Chromium tris-(Hexaisopropoxyniobinate or Tantalate) with Methanol

Dry methanol was added to a clear green solution of $Cr[M(OPr^i)_6]_3$ in benzene. An exothermic reaction occurred. The colour of the solution changed to light green. The reaction mixture was refluxed for two hours. Excess solvent was removed and dried under reduced pressure. Details of these reactions are given in Tables I and II.

Reactions of Chromium tris-(Hexaisopropoxyniobinate or Tantalate) with Ethanol

Addition of ethanol to a clear green solution of $Cr[M(OPr^i)_6]_3$ in benzene caused an exothermic reaction to occur. The reaction mixture was refluxed for about 2 h. Excess solvent was removed and dried under vacuum. The synthetic and analytical data are given in Tables I and II.

Reactions of Chromium tris-(Hexaisopropoxyniobinate or Tantalate) with t-Amyl Alcohol

$Cr[M(OPr^i)_6]_3$ was refluxed in dry benzene and t-amyl alcohol. The isopropanol liberated was continuously fractionated out azeotropically with benzene, until only traces of isopropanol could be detected in the azeotrope. The product was dried under vacuum. It was observed that only twelve isopropoxy groups were replaced by t-amyloxy groups in these reactions, even after refluxing and fractionating the isopropanol liberated for approx. 48 h. Details of these reactions are given in Tables I and II.

Reaction of $Cr[M(OPr^i)_6]_3$ with Acetylacetone in 1:6 Molar Ratio

Acetylacetone was added to a clear green solution of $Cr[M(OPr^i)_6]_3$ in benzene. The contents were refluxed with continuous fractionation of the isopropanol azeotropically with benzene. The progress of the reaction was assured by estimating of the liberated isopropanol during the reaction. Excess solvent was removed and dried under reduced pressure. Details of the syntheses are presented in Tables I and II.

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