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Synthesis and Physicochemical Studies of Some Novel Chromium(III) Tetraalkoxyaluminates and Allied Derivatives

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A variety of novel bimetallic alkoxides have been synthesized by the alcoholysis of chromium(III) tetraisopropoxyaluminate with alcohols (methanol, ethanol, *n*-butyl alcohol, 2,2,2-trifluoroethanol, and *tert*-butyl and -amyl alcohols) and acetylacetone. Various physicochemical and spectroscopic studies (viz., infrared, visible reflectance, electron spin resonance, and magnetic susceptibility as well as molecular weight determinations) have been carried out to throw light on the structural features of the new compounds.

Introduction

Compared to the alkoxide chemistry of earlier transition elements[1] (particularly in their d^0 state) and lanthanons[2,3] the chemistry of alkoxides of later transition metals has received very little attention; this may possibly be due to the insoluble and nonvolatile nature of the alkoxides of later 3d metals and instability of the alkoxy derivatives of platinum metals in general. We have recently reported[4,5] the synthesis of volatile tetraisopropoxyaluminates of a few later 3d transition metals with the general formula, $M[Al(O\text{-}i\text{-}Pr)_4]_n$ ($n = 3$ for M = Cr; $n = 2$ for M = Mn, Co, Ni, and Cu), which are volatile and monomeric soluble products compared to the insoluble, nonvolatile, polymeric simple alkoxides, $[M(OR)_n]_x$, of these metals.

A characteristic feature of simple bimetallic alkoxides of non transition metals (e.g., B, Al, Ga, Ge, Sn, As, and Sb) and earlier transition metals (e.g., lanthanons, Ti, Zr, Nb, and Ta) is their facile reactivity with alcohols[1] and enolic compounds[6] . By contrast, the investigations carried out in our laboratories more recently have revealed that insoluble simple alkoxides of some later transition metals (viz., Cr,[7] Co,[8] and Ni[9]) are in some cases much less reactive toward other alcohols and show a novel type of specificity in such reactions. For example, while $[Cr(O\text{-}i\text{-}Pr)_3]_n$ undergoes facile alcoholysis with primary alcohols, no interchange could be detected on refluxing it with tertiary and other secondary alcohols.[7] In view of the above, it was considered of interest to make a detailed study of the reactions of $Cr[Al(O\text{-}i\text{-}C_3H_7)_4]_3$ with alcohols and acetylacetone. Efforts have also been made to characterize the new derivatives by spectroscopic and magnetic measurements.

Results and Discussion

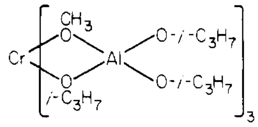
Synthetic Studies. A number of bimetallic alkoxy derivatives of chromium(III) with aluminum have been synthesized by the reactions

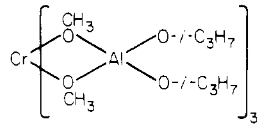
$$Cr[Al(O\text{-}i\text{-}C_3H_7)_4]_3 + 3nROH \xrightarrow{\text{benzene}} Cr[Al(O\text{-}i\text{-}C_3H_7)_{4-n}(OR)_n]_3 + 3n\,i\text{-}C_3H_7OH$$

where R = CH_3, C_2H_5, $n\text{-}C_4H_9$, F_3CCH_2, $(H_3C)_3C$, and $(CH_3)_2(C_2H_5)C$.

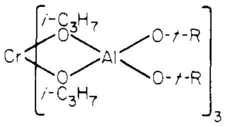
All the above alcohol-interchange reactions have been carried out in refluxing benzene, and the isopropyl alcohol liberated has been continuously fractionated out in cases of higher boiling alcohols.

The bimetallic isoproproxide reacts quantitatively with an excess of CH_3OH, C_2H_5OH, $n\text{-}C_4H_9OH$, and CF_3CH_2OH, giving the corresponding tetraalkoxyaluminates. Except for $Cr[Al(OCH_3)_4]_3$, which is a nonvolatile insoluble green solid, all other products are volatile green solids or viscous liquids (Table I). In view of the insolubility of $Cr[Al(OCH_3)_4]_3$, the reactions with methanol were also carried out in 1:3 and 1:6 molar ratios, giving solid green products, $Cr[Al(OCH_3)(O\text{-}i\text{-}C_3H_7)_3]_3$ and $Cr[Al(OCH_3)_2(O\text{-}i\text{-}C_3H_7)_2]_3$. Of these, the former is volatile and readily soluble in benzene (in which it depicts monomeric behavior), whereas the latter sublimes in rather poor yields at a higher temperature and is soluble only in hot benzene. The insolubility of $Cr[Al(OCH_3)_4]_3$ could be ascribed to the smallness of the methyl groups permitting extensive polymerization. In view of their souble nature, the mixed methoxide isopropoxides may be respresented by the following formulas with isopropoxy groups occupying terminal positions and hindering further association:





Although terminal isopropoxy groups in $Cr[Al(O\text{-}i\text{-}C_3H_7)_4]_3$ should be more amenable to attack by methoxy groups, the resulting terminal methoxy groups may afterward prefer to exchange their positions with bridging isopropoxy groups to release strain in the molecule (cf. soluble $[Zr(OCH_3)(O\text{-}t\text{-}C_4H_9)_3]_2$ and $[Al(OCH_3)(O\text{-}i\text{-}C_3H_7)_2]_2$[1,10]). The difference in the behavior of bridging and terminal isopropoxy groups is further brought out by the reactions of $Cr[Al(O\text{-}i\text{-}C_3H_7)_4]_3$ with excess *tert*-butyl and -amyl alcohols (*t*-ROH). The replaceability of only six out of 12 groups indicates that the alcoholysis reaction, occurring probably (in view of the nonreactivity of chromium isopropoxide with *tert*-butyl alcohol) on the aluminum atom, is effectively hindered when the same is surrounded with two isopropoxy and two *tert*-alkoxy groups in a product with the formula



(cf. $[Al(O\text{-}i\text{-}C_3H_7)(O\text{-}t\text{-}R)_2]_2$[1,10]). Reactions of $Cr[Al(O\text{-}i\text{-}C_3H_7)_4]_3$ with acetylacetone in 1:3, 1:6 and 1:12 molar ratios gave products corresponding in analysis to $Cr[Al(O\text{-}i\text{-}C_3H_7)_3(acac)]_3$, $Cr[Al(O\text{-}i\text{-}C_3H_7)_2(acac)_2]_3$, and $Cr[Al(acac)_4]_3$. The first two products can be distilled unchanged

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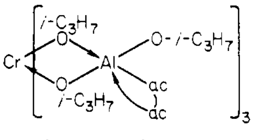
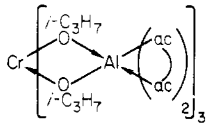
Table I. Reactions of Chromium Aluminum Isopropoxide with Various Alcohols and Acetylacetone

amt of $Cr[Al(O\text{-}i\text{-}Pr)_4]_3$, g	reagent (g/mol)	liberated *i*-PrOH, g/mol	product (% yield/nature)	volatility, °C (mmHg)	% found (% calcd)			mol wt found (calcd)
					Cr	Al	OR	
1.45	methanol (0.16/3)		$Cr[(Al(O\text{-}i\text{-}Pr)_3(OMe)]_3$ (41/lt green solid sol in benzene)	215 (0.8)	6.59 (6.86)	10.80 (10.86)		
1.34	methanol (0.30/6)		$Cr[Al(O\text{-}i\text{-}Pr)_2(OMe)_2]_3$ (20/green powder sol in hot benzene)	225–235[a] (0.8)	7.46 (7.72)	11.71 (12.02)		
1.07	methanol (25/excess)		$Cr[Al(OMe)_4]_3$ (98/green powder insol in benzene and methanol)		10.38 (10.29)	15.96 (16.03)	72.10 (73.68)	
1.36	ethanol (30/excess)		$Cr[Al(OEt)_4]_3$ (20/green solid sol in benzene–ethanol mixture)	235–240[a] (0.8)	7.57 (7.73)	11.96 (12.03)	79.71 (80.24)	
2.42	2,2,2-trifluoroethanol (5/excess)		$Cr[Al(OCH_2CF_3)_4]_3$ (32/dk green viscous compd sol in benzene)	120 (0.8)	3.90 (3.93)	6.30 (6.13)		1353 (1321)
2.52	*n*-butyl alcohol (20/excess)	1.99/11	$Cr[Al(O\text{-}n\text{-}Bu)_4]_3$ (69/green viscous liq sol in benzene)	225 (0.8)	4.96 (5.14)	7.70 (8.01)		1040 (1010)
2.76	*tert*-butyl alcohol (25/excess)	1.17/6	$Cr[Al(O\text{-}i\text{-}Pr)_2(O\text{-}t\text{-}Bu)_2]_3$ (48/lt green solid sol in benzene)	230–240[a] (0.8)	5.78 (5.61)	8.77 (8.74)	37.14 (38.27)	973 (926)
2.16	*tert*-amyl alcohol (20/excess)	0.92/6	$Cr[Al(O\text{-}i\text{-}Pr)_2(O\text{-}t\text{-}Am)_2]_3$ (59/lt green viscous liq sol in benzene)	220 (0.8)	3.90 (3.93)	6.30 (6.13)		1353 (1321)
2.77	acetylacetone (0.98/3)	0.58/3	$Cr[Al(O\text{-}i\text{-}Pr)_3(acac)]_3$ (54/green pasty solid sol in benzene)	240 (0.8)	5.29 (5.40)	7.48 (8.41)		967 (962)
1.69	acetylacetone (1.2/6)	0.70/6	$Cr[Al(O\text{-}i\text{-}Pr)_2(acac)_2]_3$ (30/green solid sol in benzene)	180–90[b] (0.8)	4.75 (4.80)	7.39 (7.48)		1233 (1082)
2.46	acetylacetone (3.53/12)	2.04/12	$Cr[Al(acac)_4]_3$ (disproportionates/brownish powder sol in benzene)		3.84[c] (3.93)	6.01[c] (6.12)		

[a] Sublimes. [b] Disproportionates into $Cr(acac)_3$ and $Al(acac)_3$. [c] Analysis of the undistilled product.

and show monomeric behavior in refluxing benzene; these can, therefore, be respresented by the following formula, in both of which chromium is six-coordinate, but aluminum is five-[11] and six-coordinate, respectively:





The last product was found to be a mixture of $Cr(acac)_3$ and $Al(acac)_3$, as revealed by thee identity of its spectrum with $Cr(acac)_3$; it could also be separated into its components by fractional crystallization or vaporization.

Infrared Spectra. The infrared spectra of these bimetallic derivatives have been recored as Nujol mulls or KBr pellets in the range 4000–200 cm^{-1}. These exhibit characteristic frequencies[12,13] for Cr–O, Al–O, and C–O bands.

Visible Spectra. Electronic spectra of all the bimetallic derivatives have been recorded in the range 28000–4000 cm^{-1} in solution (benzene and parent alcohol) as well as Nujol mulls. These spectra (Table II) are quite similar to one another and may be interpreted on the basis of an octahedral environment for chromium(III) in these derivatives.[14] The observed bands in the regions ~15000 and 22000 cm^{-1} (Table II) for all these derivatives can be assigned to the first two spin-allowed transitions ν_1 (10*Dq*) ($^4A_{2g} \rightarrow {}^4T_{2g}(F)$) and ν_2 ($^4A_{2g} \rightarrow {}^4T_{1g}(F)$) respectively. No spin-forbidden bands have been observed. The position of the third spin-allowed transition ν_3 ($^4T_{2g} \rightarrow {}^4T_{1g}(P)$), which could not be detected under the experimental conditions used, can be calculated along with Racah parameter, *B*, by the equations of Underhill and Billing:[15] $340Dq^2 - 18(\nu_2 + \nu_3)Dq + \nu_2\nu_3 = 0$ and $B = (\nu_3 + \nu_2 - 30Dq)/15$. The values of ν_1 (10*Dq*), ν_2, and ν_3 (calculated) transitions are given in Table II. It is interesting to note from the data listed in Table II for simple chromium(III) alkoxides that these latter show stronger ligand fields (10*Dq*)[5,7] in comparison to those of the corresponding bimetallic alkoxides.

Comparison of the value (620 ± 100 cm^{-1}) for the Racah interelectronic repulsion parameter (*B*) against the value[7] (1030 cm^{-1}) for the free Cr^{3+} ion indicates considerable covalent character of the metal–ligand bands in these derivatives with the covalency factor (β_{35} for spin-allowed transitions) varying in the range 0.6 ± 0.1.

On the basis of the above and other reported[16,17] values for *Dq* and β_{35}, the placements are indicated in the following spectrochemical and nephelometric series, respectively: $Cl^- < Br^- < F^- < CF_3CH_2O^- < i\text{-}C_3H_7O^- < C_2H_5O^- < n\text{-}C_4H_9O^- < CH_3O^- < H_2O < NH_3 < CN^-$; $S^{2-} < CH_3O^- < CN^- < n\text{-}C_4H_9O^- \simeq Cl^- < C_2H_5O^- \simeq CF_3CH_2O^- < i\text{-}C_3H_7O^- < NH_3 < H_2O < F$.

Magnetic Susceptibility Measurements. Magnetic susceptibility data also support an octahedral configuation[18] for these

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Table II. Electronic Spectra of Bimetallic Alkoxides and Allied Derivatives of Chromium in Benzene Solution

	transitions, cm^{-1}						
compd	$^4A_{2g} \rightarrow {}^4T_{2g}$ (1)	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$ (2)	$^4A_{2g} \rightarrow {}^4T_{1g}(P)$ (3)	*Dq*,[a] cm^{-1}	LFSE, kJ/mol	*B*, cm^{-1}	β_{35}
$Cr[Al(OMe)_4]_3$	16 800	22 500	36 000	1680 (1760)	241	550	0.53
$Cr[Al(O\text{-}i\text{-}Pr)_2(OMe)_2]_3$	15 800	22 500	35 200	1580	228	690	0.66
$Cr[Cl(O\text{-}i\text{-}Pr)_3(OMe)]_3$	15 700	22 300	34 900	1570	226	670	0.65
$Cr[Al(OEt)_4]_3$	15 800	22 200	34 900	1580 (1700)	227	655	0.64
$Cr[Al(O\text{-}i\text{-}Pr)_4]_3$	15 300	22 000	34 300	1530 (1590)	220	700	0.68
$Cr[Al(O\text{-}n\text{-}Bu)_4]_3$	16 000	22 400	35 150	1600 (1705)	230	635	0.62
$Cr[Al(O\text{-}i\text{-}Pr)_2(O\text{-}t\text{-}Bu)_2]_3$	15 500	22 200	34 700	1550	223	695	0.67
$Cr[Al(O\text{-}i\text{-}Pr)_2(O\text{-}t\text{-}Am)_2]_3$	15 500	22 200	34 600	1550	222	690	0.67
$Cr[Al(OCH_2CF_3)_4]_3$	15 200	21 650	33 800	1520	218	660	0.64
$Cr[Al(O\text{-}i\text{-}Pr)_3(acac)]_3$	16 750	23 800	37 190	1675	241	720	0.69
$Cr[Al(O\text{-}i\text{-}Pr)_2(acac)_2]_3$	16 900	23 800	37 330	1690	243	690	0.67
$Cr[Al(acac)_4]_3$	17 900	23 500	38 035	1790	256	530	0.52
$Cr(acac)_3$	17 800	24 000	38 375	1780	256	590	0.57

[a] *Dq* values for the corresponding simple alkoxides, $[Cr(OR)_3]_n$, are given in parentheses after the values for $Cr[Al(OR)_4]_3$.

derivatives. The measured μ_{eff} values for the new derivatives at ambient temperatures lie in the range 3.87 ± 0.05 μ_B. For one product, $Cr[Al(O\text{-}i\text{-}C_3H_7)_4]_3$, the magnetic susceptibility has been determined in the temperature range T = 100–300 K; the plot of T vs. $1/\chi_M$ (cor) was found to be (in accordance with Curie Law) a straight line with $\Theta = 0$ K.

ESR Spectra. When the zero field splitting is small ($D < h\nu$), three strong transitions are expected in the ESR spectrum. However, when $D > h\nu$, only one allowed transition has been detected under the experimental conditions employed, having "g" values[19] between 2 ($g_\parallel$) and 4 ($g_\perp$). Out of the seven chromium bimetallic derivatives, four (viz., ethoxy, trifluoroethoxy, mixed butoxy, and acetylacetonate) show ESR spectra characteristic of $D > h\nu$; $g_\parallel$ and $g_\perp$ both are observed with varying relative intensities. Normally, $g_\perp$ absorption is much stronger compared to the $g_\parallel$ absorption. The methoxy, mixed amyloxy, and isopropoxy derivatives show only one ESR signal with a g value of ~2, which is quite similar to the $g_\parallel$ signals observed in the first four cases. It is difficult to account for the lowering in the intensity of $g_\perp$ signal in these latter cases. The spectrum of $Cr[Al(O\text{-}i\text{-}Pr)_4]_3$ was, therefore, recorded at liquid-nitrogen temperature also, and as expected, it becomes much better resolved and exhibits both $g_\perp$ and $g_\parallel$ features, with values of 3.86 and 1.93, respectively.

Experimental Section

All-glass apparatus with interchangeable joints were used throughout, and exterme precautions were taken to exclude moisture. Benzene and alcohols were dried by the literature procedures.[4] Acetylacetone (BDH) was used after careful fractionation (bp 135–137 °C). 2,2,2-Trifluoroethanol (Aldrich) was used after distillation. $CrCl_3 \cdot 3THF$ adduct was prepared by the action of thionyl chloride on a THF solution of $CrCl_3 \cdot 6H_2O$ (J. T. Baker) according to the method described by Zeiss and co-workers.[20] Aluminum isopropoxide was prepared from aluminum foil and distilled (bp 95 °C (0.5 mm)) before use. Aluminum was estimated as aluminum oxinate after removing chromium as lead chromate. Alcohols were estimated by an oxidimetric[10] method.

Infrared spectra were recorded on a Perkin-Elmer 735-B spectrophotometer using Nujol mulls. Electronic reflectance spectra were recored on a Bechman Model 26 spectrophotometer. Electron spin resonance spectra were recored on a Varian V-4502-12 spectrophotometer. Magnetic susceptibility measurements were carried out by the standard Gouy method. Molecular weights of the compounds were determined by a Gallankamp ebulliometer using a thermistor sensing device.

Reaction of Chromium Aluminum Isopropoxide, $Cr[Al(O\text{-}i\text{-}Pr)_4]_3$, with Methanol. Addition of methanol (3:1 molar ratio) to $Cr[Al(O\text{-}i\text{-}Pr)_4]_3$ dissolved in benzene caused an exothermic reaction. The reaction mixture was refluxed for 0.5 h. Excess solvents were removed, and the compound was finally dried and distilled under reduced pressure. Details of these reactions are given in Table I.

Reactions of $Cr[Al(O\text{-}i\text{-}Pr)_4]_3$ with Ethanol and 2,2,2-Trifluoroethanol. An exothermic reaction occurred on adding an excess of ethanol, *n*-butyl alcohol, or 2,2,2-trifluoroethanol to a solution of $Cr[Al(O\text{-}i\text{-}Pr)_4]_3$ in benzene. After the reaction mixture was refluxed for 0.5 h, the excess solvent was removed under reduced pressure. The products thus obtained were purified by vacuum distillation. The synthetic and analytical data of the reactions are given in Table I.

Reactions of $Cr[Al(O\text{-}i\text{-}Pr)_4]_3$ with Excess *tert*-Butyl and -Amyl Alcohols. $Cr[Al(O\text{-}i\text{-}Pr)_4]_3$ was dissolved in benzene, and an excess of *tert*-butyl or -amyl alcohol was added to it. The reaction mixture was refluxed for about 2 days with continuous fractionation of the isopropyl alchol (liberated in the reaction) azeotropically with benzene, until even traces of isopropyl alcohol could be detected in the azeotrope. Excess solvent was removed, and the compound obtained was finally dried and distilled under reduced pressure. It was found that only six isopropoxy groups are replaced by *tert*-butoxy or -amyloxy groups in these alcoholysis reactions, even after refluxing and fractionating the isopropyl alcohol liberated for ~50 h (Table I).

Reaction of $Cr[Al(O\text{-}i\text{-}Pr)_4]_3$ with Acetylacetone in 1:3, 1:6, and 1:12 Molar Ratios. To a benzene solution of $Cr[Al(O\text{-}i\text{-}Pr)_4]_3$ was added acetylacetone (in 1:3, 1:6, or 1:12 molar ratios). The reaction mixtures were refluxed over a column for 1, 4, and 6 hours, respectively, and the liberated isopropyl alcohol was collected azeotropically along with benzene between the temperatures 73–80 °C. The progress of the reaction was checked by estimating the quantity of the isopropyl alcohol collected in the azeotrope. Excess solvent was stripped off from the reaction mixture and the product finally subjected to distillation under reduced pressure. Detailed data of these reactions are given in Table I.

Registry No. $Cr[Al(OMe)_4]_3$, 88904-99-8; $Cr[Al(O\text{-}i\text{-}Pr)_2(OMe)_2]_3$, 88904-96-5; $Cr[Al(O\text{-}i\text{-}Pr)_3(OMe)]_3$, 88904-95-4; $Cr[Al(OEt)_4]_3$, 78798-88-6; $Cr[Al(O\text{-}i\text{-}Pr)_4]_3$, 70504-53-9; $Cr[Al(O\text{-}n\text{-}Bu)_4]_3$, 88905-00-4; $Cr[Al(O\text{-}i\text{-}Pr)_2(O\text{-}t\text{-}Bu)_2]_3$, 88904-97-6; $Cr[Al(O\text{-}i\text{-}Pr)_2(O\text{-}t\text{-}Am)_2]_3$, 88904-98-7; $Cr[Al(OCH_2CF_3)_4]_3$, 78798-87-5; $Cr[Al(O\text{-}i\text{-}Pr)_3(acac)]_3$, 78821-02-0; $Cr[Al(O\text{-}i\text{-}Pr)_2(acac)_2]_3$, 78820-99-2.

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