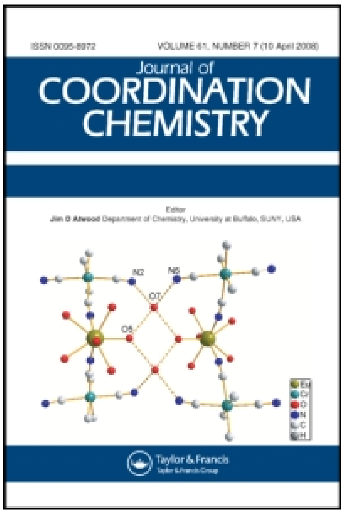

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SYNTHESIS AND PROPERTIES OF TETRAALKOXY-ALUMINATES AND ALLIED DERIVATIVES OF COBALT(II)

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SYNTHESIS AND PROPERTIES OF TETRAALKOXY-ALUMINATES AND ALLIED DERIVATIVES OF COBALT(II)

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Cobalt(II) tetraisopropoxyaluminate reacts with various alcohols to yield derivatives with the formula, $Co[Al(OR)_4]_2$ when ROH = methanol, ethanol, 2,2,2,-trifluoroethanol, 2,2,2-trichloroethanol, *n*-butanol and 1,3-dibromo-2-propanol. The reactions with 1,1'-dimethylethanol (tertiary butyl alcohol) and 1,1'-dimethyl-propanol (tertiary amyl alcohol) yielded derivatives with the formulae, $Co[Al(OPr^i)(OBu^t)_3]_2$ and $Co[Al(OPr^i)_2(OAm^t)_2]_2$ respectively. With acetylacetone (Hacac) in 1:4 molar ratio, $Co[Al(OPr^i)_4]_2$ gave a volatile derivative, $Co[Al(OPr^i)_2(acac)_2]_2$ whereas an excess acetylacetone yielded a mixture of $Co(acac)_2$ and $Al(acac)_3$. These derivatives have been characterized by elemental analyses, infra-red and electronic reflectance spectra, molecular weight determinations and magnetic susceptibility measurements. These studies suggest an octahedral environment (D_{4h}) for cobalt(II).

INTRODUCTION

Even the simple alkoxides of later '3d' transition metals have been studied only in recent years.[1-6] In view of the insoluble polymeric and non-volatile nature of the simple alkoxides[2] of cobalt(II), $Co(OR)_2$, it was considered of interest to synthesise and study the bimetallic alkoxides of cobalt(II). Recently, we have reported[7,8] the synthesis of $Co[Al(OPr^i)_4]_2$ by reacting $CoCl_2$ with potassium tetraisopropoxyaluminate in a isopropanol-benzene medium in the stoichiometric ratio of 1:2. In this paper we report the reactions of $Co[Al(OPr^i)_4]_2$ and synthesis and properties of a number of bimetallic alkoxides of cobalt(II) in detail.

RESULTS AND DISCUSSION

Alcoholysis reactions of the bimetallic isopropoxide of cobalt(II) with aluminium(III), $Co[Al(OPr^i)_4]_2$, have been carried out with lower, higher and halogenated alcohols, such as methanol, ethanol, 2,2,2-trifluoroethanol, 2,2,2-trichloroethanol, *n*-butanol, 1,3-dibromo-2-propanol, tertiary butyl and tertiary amyl alcohols as well as acetylacetone. The reactions of $Co[Al(OPr^i)_4]_2$ with excess methanol, ethanol and 2,2,2-trifluoroethanol in benzene under refluxing conditions yielded finally derivatives corresponding by analysis to $Co[Al(OMe)_4]_2$, $Co[Al(OEt)_4]_2$ and $Co[Al(OCH_2CF_3)_4]_2$ respectively. The methoxide is a purple solid, insoluble in common organic solvents whereas the ethoxide and the 2,2,2-trifluoroethoxide are a violet solid and a purple viscous liquid, respectively. The last two compounds are soluble in the parent alcohols. Of the three, only the last $Co[Al(OCH_2CF_3)_4]_2$, could be distilled under reduced pressure to give a purple liquid.

The reactions of $Co[Al(OPr^i))_4]_2$, with 2,2,2-trichloroethanol and 1,3-dibromo-2-propanol have been carried out in 1:8 molar ratios in benzene medium, giving the products $Co[Al(OCH_2CCl_3)_4]_2$ and $Co[Al\{OCH(CH_2Br)_2\}_4]_2$, respectively.

Alcoholyses of $Co[Al(OPr^i)_4]_2$ have been carried out with an excess of *n*-butyl, tertiary butyl and tertiary amyl alcohols also in benzene medium. With *n*-butanol the reaction was facile and all the isopropoxy groups could be replaced with *n*-butoxy groups, giving the product $Co[Al(OBu^n)_4]_2$. With tertiary butyl and tertiary amyl alcohols, the reactions were not so facile; only six and four out of eight isopropoxy groups per mole of $Co[Al(OPr^i)_4]_2$could be replaced by the tertiary butoxy and amyloxy groups, respectively. The analysis of the products obtained from these reactions corresponded to the $Co[Al(OPr^i)(OBu^t)_3]_2$ and $Co[Al(OPr^i)_2(OAm^t)_2]_2$, respectively.

The mixed isopropoxy-tertiary-butoxy and isopropoxy-tertiary-amyloxy derivatives also could be sublimed/distilled under reduced pressure without change in composition. The formation of mixed rather than tetraalkoxy products with highly ramified alcohols can be understood on the basis of steric factors.[9]

Reactions of $Co[Al(OPr^i)_4]_2$ with acetylacetone have also been carried out in benzene medium in 1:4 and 1:8 molar ratios.

Progress of the reaction was followed by estimating the amount of isopropanol liberated in the azeotrope. The product isolated in the first reaction is a purple viscous liquid, the analysis of which corresponded to $Co[Al(OPr^i)_2(acac)_2]_2$. This liquid could be distilled under reduced pressure and its molecular weight measured ebullioscopically in benzene corresponded to the formula weight. The purple powder obtained in the latter reaction was found to be a mixture of $Co(acac)_2$ and $Al(acac)_3$ in a 1:2 molar ratio. When this powder was subjected to heat under reduced pressure, $Al(acac)_3$ was obtained as a sublimate. A few common properties of these derivatives are given in Table I.

The infrared spectra of the cobalt(II) bimetallic derivatives have been recorded in the range 4000–400 cm^{-1} in nujol mull or film. These exhibit all the characteristic frequencies (Table II) for alkoxy groups, aluminium-oxygen and cobalt-oxygen bonds.

Electronic spectra of cobalt(II) derivatives are to be interpreted with caution. A choice between the two main stereochemistries, tetrahedral and octahedral becomes difficult because environments give rise to spectra in the visible region in approximately the same range but generally the tetrahedral derivatives exhibit[10] the band $\nu_3[{}^4A_2 \rightarrow {}^4T_1(P)]$ nearly at 15,000 cm^{-1} and octahedral derivatives gave the band $\nu_3[{}^4T_{1g} \rightarrow {}^4T_{1g}(Po)]$ around 19,000 cm^{-1}. The spectra of tetrahedral cobalt(II) derivatives are, however, generally more intense than those of octahedral cobalt(II) derivatives, but complications due to strong contributions from a UV charge transfer tail are often involved. For cobalt(II) derivatives, a value of ν_2/ν_1 lying in the range 2.1 to 2.2 appears to be rather a reliable criterion for octahedral geometry. The electronic spectra of all the bimetallic derivatives of cobalt(II) have been recorded in film, nujol or an organic solvent. Like $Co[Al(OPr^i)_4]_2$, the spectra of other bimetallic derivatives of cobalt(II), $Co[Al(OEt)_4]_2$, $Co[Al(OBu^n)_4]_2$, $Co[Al(OPr^i)(OBu^t)_3]_2$, $CO[Al(OPr^i)_2(OAm^t)_2]_2$ and $Co[Al(OCH_2CF_3)_4]_2$ show a very intense band in the visible region with a maximum at 18,000 cm^{-1} and a shoulder on the higher frequency side. This spectral transition can be assigned as $\nu_3[{}^4T_{1g} \rightarrow {}^4T_{1g}(P)]$ which is characteristic of octahedral geometry for Co^{2+} ions. The following type of distorted octahedral structure may, therefore be proposed in which the $[Al(OR)_4]$ unit acts as a terdentate ligand.

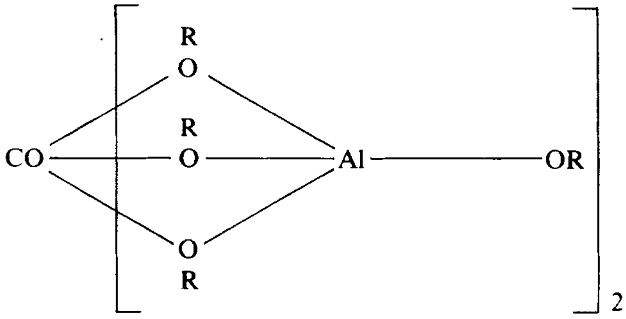

TABLE I

Reactions of Cobalt Tetraisopropoxyaluminate with Various Alcohols and Acetylacetone.

$Co[Al(OPr^i)_4]_2$ (g)	Reagent used	Isopropanol liberated Found	Nature of the distilled product (Yield %)	Volatility °C/mm	Mixed Metals	Al	OR	Mol. wt. Found (Calcd)
3.59	Methanol 25 ml (Excess)		$Co[Al(OCH_2CF_3]_2$ (98) Purple powdered solid		31.54 (31.25)	15.27 (14.95)	69.09 (68.72)	
4.48	Ethanol 30 cm^3 (Excess)		$Co[(OEt)_4]_2$ (99) Violet Solid	Decomposed at 190/0.6	24.35 (23.87)	11.92 (11.41)	75.90 (76.13)	
2.86	2,2,2-Trifluoro ethanol (7 g) (Excess)		$Co[Al(OCH_2CF_3)_4]_2$ (55) Purple viscous compound	105/0.6	12.92 (12.47)	6.48 (5.96)		
2.43	2,2,2-Trichloro ethanol 4.96 g (8 mol)	1.95 (1.99)	$Co[Al(OCH_2CCl_3)_4]_2$ (99) Blackish violet solid insoluble in benzene		8.90 (8.68)	4.40 (4.15)		
4.83	*n*-Butanol 40 cm^3 (Excess)	3.88 (3.97)	$Co[Al(OBu^n)_4]_2$ (98) Purple sticky solid	Decomposed 240/0.6	16.70 (16.17)	8.02 (7.73)		
2.37	1,3-Dibromo-2- propanol 7.20 g (8 mol)	1.92 (1.95)	$Co[Al\{OCH(CH_2Br)_2\}_4]_2$ (99) Green solid insoluble in benzene		6.38 (6.11)	3.14 (2.92)		
3.70	*t*-Butanol 35 cm^3 (Excess)	2.15 (2.28)	$Co[Al(OPr^i)(OBu^t)_3]_2$ (51) Purple powder	*160–170/0.6	16.98 (16.86)	8.11 (8.06)	16.37 (17.64)	776 (670)
3.67	*t*-Amyl alcohol 40 cm^3 (Excess)	1.48 (1.51)	$Co[Al(OPr^i)_2(OAm^t)_2]_2$ (73) Purple viscous liquid	185/0.6	16.30 (16.17)	7.91 (7.73)		746 (698)
4.29	Acetylacetone 2.95 g (4 mol.)	1.73 (1.75)	$Co[Al(OPr^i)_2(acac)_2]_2$ (70) Purple viscous liquid	160/0.6	15.02 (15.14)	6.99 (7.24)		641 (746)
3.14	Acetylacetone 4.32 g (8 mol.)	2.55 (2.58)	$Co(acac)_2 + 2\ Al(acac)_3$ (86) Light purple powder[12]	*180/0.6	12.57 (12.47)	6.35 (5.96)		305 (906)

*$Al(acac)_3$ sublimed

TABLE II
Characteristic IR Absorption Bands of Bimetallic Alkoxides and Allied Derivatives.

	ν(C=O)	ν(C-O)	ν(M-O)
$Co[Al(OMe)_4]_2$		1070(b, vs) 945(w)	600(b, s) 530(b,s)
$Co[Al(OEt)_4]_2$		1090(vs) 960(w)	590(b, s) 540(b, s)
$Co[Al(OBu^n)_4]_2$		1010(b, vs) 970(m)	Broad spectrum
$Co[Al(OPr^i)_4]_2$		1035(vs) 965(vs)	690(s) 438(m) 468(sh) 528(s)
$Co[Al(OPr^i)(OBu^t)_3]_2$		1080(b, m) 940(s)	665(m) 520(w)
$Co[Al(OPr^i)_2(OAm^t)_2]_2$		1075(vs) 1045(s) 950(vs) 900(s)	660(vs) 615(m) 560(m) 530(m) 470(m)
$Co[Al(OCH_2CF_3]_2$		1040(m) 970(m)	640(m) 600(b, m)
$Co[Al(OPr^i)_2(acac)_2]_2$	1600(vs) 1530(vs)	1070(m) 1015(vs) 970(vs) 935(s)	680(s) 660(s) 625(vs) 580(s) 490(vs)
$Co[Al(OCH_2CCl_3)_4]_2$		1090(s) 1060(m) 1020(w)	640(b) 570(m)

Abbreviations: v = very; s = strong, b = broad, m = medium, w = weak.

The positions of spectral bands are given in Table III. It is worth noting that the ν_3 transition value 17670 cm^{-1} for $Co[Al(OEt)_4]_2$ is in fairly good agreement with the reported[11] value of 17,700 cm^{-1} for this derivative.

The μ_{eff} values of all the bimetallic alkoxide derivatives of cobalt(II) at room temperature are shown in Table IV and they lie almost in the range of 4.39–4.78 B.M.; this is lower than that (4.7–5.2 B.M.) expected for octahedral cobalt(II) in the high spin state[13] ($S = 3/2$). Such lowering of the observed magnetic moments has also been reported for magnetically concentrated as well as dilute[13] systems such as $Co(C_2O_4)$ (4.55 B.M.)., $KCOF_3$ (4.03 B.M.) and $Co(N_2H_4)_2$ $(acetate)_2$ (4.40 B.M.) for Co^{2+} in an octahedral environment. It has also been observed in these bimetallic derivatives that magnetic moments are somewhat lower when measured in the solid form than in solution.

For one compound, $Co[Al(OPr^i)_2$ $(acac)_2]_2$, the temperature dependence of the magnetic susceptibility has been examined in the range 88 to 300K. In this case, the Curie-Weiss law is obeyed with a Weiss constant of + 20K (Table V). The magnetic moment values remain practically constant (4.5 + 0.12 B.M.) and a positive value of θ suggests the presence of a weak cooperative phenomenon.

Thus the magnetic studies also support the previous spectral interpretation for a distorted octahedral (D_{4h}) configuration of these bimetallic alkoxy derivatives of cobalt(II).

TABLE III
Electronic Spectra of Cobalt Aluminium Isoproxide and its Allied Derivatives.

	Medium	Transition
		$^4T \rightarrow {}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ (ν_3) (cm^{-1})
$Co[Al(OMe)_4]_2$	Nujol	18180
$Co[Al(OEt)_4]_2$	Nujol	17670
$Co[Al(OPr^i)_4]_2$	Benzene	18115
	Pr^iOH	18350
$Co[Al(OBu^n)_4]_2$	Benzene	18315; 19610
$Co[Al(OPr^i)(OBu^t)_3]_2$	Benzene	18380; 19800
$Co[Al(OPr^i)_2(OAm^t)_2]_2$	Benzene	18250; 19610
$Co[Al(OCH_2CF_3)_4]_2$	Benzene	18215; 19685
$Co[Al(OPr^i)_2(acac)_2]_2$	Benzene	18280; 19800

TABLE IV
Room Temperature Magnetic Susceptibilities of Bimetallic Alkoxides of Cobalt(II).

	μ_{eff}(B.M.)
$Co[Al(OMe)_4]_2$	4.67
$Co[Al(OEt)_4]_2$	4.70
$Co[Al(OBu^n)_4]_2$	4.78
$Co[Al(OCH_2CF_3)_4]_2$	4.72
$Co[Al(OPr^i)(OBu^t)_3]_2$	4.76
$Co[Al(OPr^i)_2(OAm^t)_2]_2$	4.68

TABLE V
Temperature Dependant Magnetic Susceptibility of $Co[Al(OPr^i)_2(acac)_2]_2$.

Temp. (K)	$\chi_{M'} \times 10^6$*	μ_{eff} (B.M.)
88.0	29379	4.54
91.0	27902	4.51
96.5	26292	4.50
101.0	24467	4.45
115.5	22411	4.55
133.0	19672	4.57
157.5	16121	4.57
223.5	11687	4.58
297.0	8976	4.62

*$\chi_{M'}$ is the corrected molar susceptibility in the usual cgs units.

EXPERIMENTAL

All glass apparatus fitted with interchangeable standard joints were used throughout the course of present synthetic work. Stringent precautions were taken to exclude moisture. The apparatus was carefully cleaned and rinsed with rectified spirit before placing it for about two hours in an oven maintained at 110°C–120°. The apparatus was then cooled either in a desiccator or protected with guard tubes, filled with fused anhydrous calcium chloride. Special weighing tubes and pipettes with standard joints for solids and liquids were used for sampling the compounds for analytical purposes. All fractionations were carried out in a column packed with Rasching rings and fitted to a total condensation variable take-off stillhead.

Anhydrous $CoCl_2$ was prepared by heating hydrated $CoCl_2$ (B.D.H.) in a current of dry HCl gas. Aluminium isopropoxide, $Al(OPr^i)_3$, was prepared from aluminium foil and distilled (B.P. 95°/0.5 mm) before use. Benzene and alcohols were dried according to literature procedures. 2,2,2-Trifluoro-ethanol, 2,2,2-trichloro-ethanol and 1,3-dibromo-2-propanol (Aldrich) were used after distillation.

A semi-microebulliometer (Gallenkamp) with thermistor sensing was used for molecular weight determinations. The infrared spectra were recorded on a Perkin-Elmer-621 spectrophotometer using nujol mulls or direct films. The electronic reflectance spectra of the compounds were recorded on Perkin-Elmer 4000A and Beckman Model-26 spectrophotometers. The magnetic susceptibility measurements were carried out using the Guoy method.

Reactions of Cobalt Tetraisopropoxyaluminate with Methanol, Ethanol and 2,2,2-trifluoroethanol

A weighed amount of $Co[Al(OPr^i)_4]_2$ (3.59 g), methanol(25 cm^3) and benzene(50 cm^3) were mixed together and refluxed for some time at a bath temperature of 120–130°. The reaction mixture was cooled and benzene and methanol were stripped off under reduced pressure. The product was finally dried at 30°/1 mm, and analysed. A similar procedure was adopted to synthesize the corresponding derivatives of ethanol and 2,2,2-trifluoroethanol. For the sake of brevity, the details of these reactions are given in Table I.

Reactions of $Co[Al(OPr^i)_4]_2$ with n-butyl, tertiary butyl and amyl alcohols, 2,2,2-Trichloroethanol and 1,3-dibromo-2-propanol

All these reactions were carried out using a similar alcohol interchange technique. In general, $Co[Al(OPr^i)_4]_2$ was dissolved in benzene and an excess of *n*-butyl, tertiary butyl or amyl alcohol was added to it separately in 100 cm^3 round bottom flasks. The reaction mixture was refluxed on an oil bath (120–130°) with continuous fractionation of the isopropanol-benzene azeotrope between 72.5–80° at a high reflux ratio. In the case of the reaction with tertiary butyl alcohol, this alcohol gets slowly removed as an azeotrope (b.p. 73°) with benzene along with the azeotrope of isopropanol-benzene. Fresh quantities of tertiary butyl alcohol and benzene were, therefore, added as required. When the temperature did not fall below 80° for a long time, refluxing was stopped and the collected azeotrope was analysed for its isopropanol content which indicated the progress of the reaction. Excess benzene was distilled from the reaction flask and the product was isolated by stripping off the volatile fraction under reduced pressure. Similarly alcoholyses of $Co[Al(OPr^i)_4]_2$ with 2,2,2-trichloroethanol and 1,3-dibromo-2-propanol were carried out in 1:8 molar ratios. All these reactions are summarized in Table I. The reactions with *n*-butyl alcohol, 2,2,2-trichloroethanol and 1,3-dibromopropan-2-ol were complete in a much shorter time whereas only six and four isopropoxy groups were interchanged in reactions of $Co[Al(OPr^i)_4]_2$ with tertiarybutyl and amyl alcohols, respectively, even after refluxing and fractionation for 50–60 hours.

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