Inorganica Chimica Acta, 81, (984) 163–167

Synthesis and Characterization of some Chloride Alkoxides of Chromium(III) and their Addition Complexes

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Received May 11, 1983

Reactions of $CrCl_3 \cdot 3THF$ with sodium alkoxides in 1:1 molar ratio in the corresponding alcohols yield soluble dichloride monoalkoxides with the general formula, $CrCl_2(OR) \cdot 2ROH$, where R = Me, Et, Pr^i or Bu^n. On heating under vacuum these products tend to lose adduct molecules leaving derivatives with the formula, $CrCl_2(OR)$. The latter are insoluble in hydrocarbons but dissolve in alcohols from which bis-adducts can be isolated again. A number of other coordination complexes, $CrCl_2(OR) \cdot 2L$ (where L = pyridine, β-picoline or pyridine N-oxide) have also been synthesized and characterized.

Introduction

In spite of extensive work on alkoxides and chloride alkoxides of earlier transition metals (in their d^0 state), similar derivatives of later transition metals have received scanty attention so far [1–5]. The replacement of alkoxy groups in metal alkoxides by the strongly electron-withdrawing chloride group could be expected to bring about significant changes in the physical and structural characteristics of these derivatives. For example, the enhanced Lewis acid behaviour of the chloro derivatives is expected to increase their adduct formation tendency with donor ligands.

In view of the above and the limited work on the chloride alkoxides of chromium [6], it was considered of interest to synthesize these complexes and to investigate various physico-chemical characteristics.

Results and Discussion

Preliminary investigations showed that the reactions of $CrCl_3 \cdot 3THF$ with sodium alkoxides in 1:1 molar ratio in alcohols yield quantitatively dichloride mono-alkoxide derivatives, which are solube in alcohols:

$$CrCl_3 \cdot 3THF + NaOR \xrightarrow{ROH} Cr(OR)Cl_2 \cdot 2ROH + 2NaCl\downarrow$$

(R = Me, Et, Pr^i and Bu^n)

However, the reactions between the above reagents in 1:2 molar ratio and even the reactions of $Cr(OR)Cl_2 \cdot 2ROH$ with another mole of NaOR under the mildest conditions gave small amounts of insoluble $Cr(OR)_3$ along with a soluble mixture of $Cr(OR)Cl_2 \cdot 2ROH$ and $Cr(OR)_2Cl \cdot ROH$, which could not be separated from each other by any means.

In view of the solubility of chloride alkoxides in parent alcohols, sodium chloride formed in the 1:1 molar reactions was filtered out. The filtrate was then concentrated and allowed to stand overnight, when coloured chloride alkoxides crystallised out from the solution.

All these dichloride monoalkoxides of chromium(III) are coloured hygroscopic solids, soluble in alcohols as well as in benzene (except the methoxide derivative, $Cr(OMe)Cl_2 \cdot 2MeOH$ which is soluble in methanol but insoluble in benzene). Electronic reflectance spectra of these solid chlorides indicate an octahedral geometry for chromium. It is therefore likely that these complexes have a dimeric structure formed probably by their alkoxy groups as bridging ligands. Ebullioscopic measurements of molecular weights of these complexes in parent alcohols showed monomeric behaviour. This appears to indicate that the alkoxy bridges which exist in the solid state, as well as in their solutions in inert solvents, are ruptured when the solid goes into solution in the parent alcohol. The monomeric behaviour coupled with octahedral geometry for chromium in these complexes (as revealed by their solution spectra in the visible region) lead to the conclusion that in these solutions chromium probably attains a hexacoordinated environment by getting another lone pair of electrons from the solvent alcohol molecule. However, repeated attempts to isolate these *tris*-alcoholate complexes were not successful probably due to a

0020-1693/84/$3.00

comparatively looser coordination of the third alcohol molecule, which is lost on trying to remove the excess alcohol even at the room temperature under reduced pressure.

In contrast to the facility with which alkoxides of earlier transition metals interchange their alkoxy groups, alkoxides of chromium show a varying tendency of undergoing alcoholysis reactions depending on the nature of alkoxy groups involved [7]. For example, primary alkoxides of chromium do not undergo alcoholysis at all. Chromium isopropoxide undergoes interchange with primary alcohols under refluxing conditions but shows no reactivity towards tertiary or other secondary alcohols.

In the case of chloride alkoxides, $CrCl_2(OR)\cdot 2ROH$, both the adduct alcohol molecules only appear to be interchanged on refluxing them with other alcohols. The alkoxide groups of these chloride alkoxides appear to show an even greater reluctance towards alcoholysis reactions than do chromium trialkoxides, as even the monoisopropoxide dichloride does not interchange its isopropoxide groups with methanol or ethanol. The reaction of $Cr(OMe)Cl_2\cdot 2MeOH$ with isopropanol, however, yields an adduct of the type $Cr(OMe)Cl_2\cdot MeOH\cdot Pr^iOH$, but the second adduct methanol molecule could not be replaced even under forcing conditions. The above behaviour of $Cr(OMe)Cl_2\cdot 2MeOH$ indicates the possibility of one of its two methanol molecules being held more firmly than the other.

The last conclusion appears to receive support from a study of thermal stability of these chloride alkoxides of chromium(III) under reduced pressure. It has been observed that $Cr(OMe)Cl_2\cdot 2MeOH$ is quite stable upto ~100 °C, but when it is heated at this temperature for nearly 8 hours of 0.5 mm pressure, it loses one of its two methanol adduct molecules, while the second one can only be removed on heating for about 15 hours at ~150 °C. The $Cr(OEt)Cl_2\cdot 2EtOH$ and $Cr(OPr^i)Cl_2\cdot 2Pr^iOH$ derivatives are comparatively less stable as both these complexes have been found to lose their first alcohol molecules at ~60 °C on heating for about eight and six hours respectively while both the alcohol molecules are lost on heating at ~80 °C under reduced pressure for about six and four hours respectively. The above studies also show that methanol is more strongly coordinated in the above complexes compared to other alcohols.

While the above chloride alkoxides were treated with t-butanol, the alcoholysis does not proceed in a straightforward manner but hydroxy products are formed in the reaction. Similar observations have been made in the reactions of chloride alkoxides of a number of metals with t-butanol [8, 9].

These chloride alkoxides of chromium(III) have been found to lose the adduct alcohol molecules when they are refluxed in benzene under a fractionating column; the process may be facilitated by the insolubility of the chloride alkoxide $Cr(OR)Cl_2$ formed by de-alcoholation:

$$Cr(OR)Cl_2\cdot 2ROH \xrightarrow[\text{Reflux}]{\text{Benzene}} Cr(OR)Cl_2 + 2ROH$$

$(R = Me, Et, Pr^i)$

Even in these reactions the methanol adduct appears to have a much higher stability. These insoluble chloride alkoxides when treated with an excess of alcohol yield soluble alcoholate complexes again:

$$Cr(OR)Cl_2 + 2R'OH \xrightarrow{\text{Reflux}} Cr(OR)Cl_2\cdot 2R'OH$$

With various nitrogen donor ligands, these chloride alkoxides of chromium(III) undergo substitution reactions to form a number of coordination complexes as shown below:

$$Cr(OR)Cl_2\cdot 2ROH + 2L \xrightarrow[\text{Reflux}]{\text{Benzene}} Cr(OR)Cl_2\cdot 2L + 2ROH$$

(where $R = Et, Pr^i, Bu^n$ and L = Pyridine, β-picoline and pyridine N-oxide)

All these complexes are coloured solids, fairly stable in air and insoluble in common organic solvents.

Infrared spectra of all the complexes have been recorded with KBr pellets or in Nujol mull in the range 4000–400 cm^{-1}. In the spectra of alcoholate complexes $Cr(OR)Cl_2\cdot 2ROH$, the OH stretching vibrational band was shifted towards the lower frequency side at ~3080 cm^{-1}, indicating the coordinated nature of the alcohol [10]. This band does not appear at all in the spectra of $CrCl_2(OR)$ derivatives, prepared by de-alcoholysis of the adducts. The C–O bands were found to be situated in the characteristic 1200–900 cm^{-1} regions [6]. A strong band appearing in the region 600–500 cm^{-1} may be assigned to ν(Cr–O) vibrations [6]. Strong bands appearing at ~750 cm^{-1} and ~790 cm^{-1} in pyridine and picoline derivatives can be attributed to the νCH deformations [11]. The bands occuring at about 360, 340 and 300 cm^{-1} can be attributed to metal–pyridine and metal–picoline stretching vibrations [12, 13]. Sharp bands observed at ~640 and ~440 cm^{-1} in the pyridine and picoline complexes have been attributed to the ring vibrations of pyridine and picoline respectively.

Electronic spectra of all the compounds have been recorded in the visible range in the solid state using nujol mulls. The spectra of alcoholate complexes in parent alcohols are identical with the diffuse reflectance spectra of the solids. The above observations appear to confirm that in spite of the change from a dimeric alkoxy bridged to form a monomeric product, the geometry of the molecules remains essentially the same and the differences due to the structural changes are too small to be reflected in their spectra.

The spectra of all the compounds exhibit two bands, at around 15,000 cm^{-1} and 21,000 cm^{-1}. The bands are assigned to the $^4A_{2g} \rightarrow {}^4T_{2g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transitions respectively which are typical of octahedral environment of chromium(III) [6]. The ligand field parameter 10 Dq (~15,000 cm^{-1}) lies between the corresponding value for $Cr(H_2O)_6{}^{3+}$ of 17,000 cm^{-1} and that of $CrCl_6{}^{3-}$ of 13,800 cm^{-1} [14]. The interelectronic repulsion parameter (B) in all cases is below the free ion value (1030 cm^{-1}), showing the considerably covalent nature of the metal–ligand bond.

The small changes in the values of 10 Dq and B in the individual compounds $CrCl_2(OR)\cdot 2ROH$ appear to be easily understood on the basis of the slowly increasing inductive effects from methoxide to ethoxide to n-butoxide and a sharper increase in the inductive effect from primary alkoxide to secondary alkoxide (isopropoxide) group. This is reflected in slowly increasing values and decreasing values of 10 Dq and B respectively with increase in the chain length of primary alkoxy, and sharper changes in both their values when the alkoxide group is an isopropoxide.

The magnetic susceptibilities of the alcoholate complexes of all the chloride alkoxides at room temperature in parent alcohols have been found to be slightly below the spin only value of 3.88 B.M. expected for the d^3 ion. Conductivity measurements reveal them to be weak electrolytes in parent alcohols and non-electrolytes in nitrobenzene (Table III).

The spectral and magnetic properties of the methoxy derivative synthesized during the present investigation resemble the properties of the methoxy derivative reported earlier by Winter *et al.* [6].

Experimental

All-glass apparatus with standard Quickfit joints were used throughout. Stringent precautions were taken to exclude moisture. $CrCl_3\cdot 3THF$ adduct was prepared by the thionyl chloride method [15].

TABLE I. Reactions of $CrCl_3\cdot 3THF$ with Sodium Alkoxides and their Alcoholysis Interchange Reactions.

S. No.	Reactants	Molar ratio and medium	Product	Analyses (%) found (Calcd.)		
				Chromium	Chlorine	Alkoxy
1	2	3	4	5	6	7
1	$CrCl_3\cdot 3THF$ (6.79 g) + Na (0.42 g)	1:1 Methanol	$Cr(OMe)Cl_2\cdot 2MeOH$ Dark green solid	23.40 (23.80)	33.40 (32.50)	43.20 (43.70)
2	$Cr(OMe)Cl_2\cdot 2MeOH$ (1.56 g)	Benzene Excess	$Cr(OMe)Cl_2$ Brown solid	33.46 (33.78)	46.21 (46.48)	19.62 (19.74)
3	$CrCl_3\cdot 3THF$ (3.85 g) + Na (0.23 g)	Ethanol 1:1	$Cr(OEt)Cl_2\cdot 2EtOH$ Light green solid	19.58 (19.99)	26.38 (27.20)	52.37 (52.81)
4	$Cr(OEt)Cl_2\cdot 2EtOH$ (1.92 g)	Benzene Excess	$Cr(OEt)Cl_2$ Brownish violet solid	30.45 (30.97)	41.84 (42.23)	26.40 (26.80)
5	$CrCl_3\cdot 3THF$ (4.10 g) + Na (0.25 g)	Isopropanol 1:1	$Cr(OPr^i)Cl_2\cdot 2Pr^iOH$ Greenish violet solid	17.10 (17.21)	23.38 (23.47)	57.75 (59.32)
6	$Cr(OPr^i)Cl_2\cdot 2Pr^iOH$ (1.38 g)	Benzene Excess	$Cr(OPr^i)Cl_2$ Brownish violet solid	28.42 (28.59)	38.47 (38.97)	32.28 (32.44)
7	$CrCl_3\cdot 3THF$ (3.35 g) + Na (0.20 g).	n-Butanol 1:1	$Cr(OBu^n)Cl_2\cdot 2Bu^nOH$ Greenish violet solid	15.71 (15.16)	21.20 (20.67)	– –
8	$Cr(OBu^n)Cl_2\cdot 2Bu^nOH$ (1.30 g)	Benzene Excess	$Cr(OBu^n)Cl_2$ Brownish red solid	26.18 (26.39)	35.64 (35.99)	– –
9	$Cr(OMe)Cl_2\cdot 2MeOH$ (1.16 g)	n-Butanol Excess	$Cr(OMe)Cl_2\cdot 2Bu^nOH$ Green solid	16.51 (16.67)	22.58 (22.73)	– –
10	$Cr(OMe)Cl_2\cdot 2MeOH$ (0.99 g)	Isopropanol Excess	$Cr(OMe)Cl_2\cdot MeOH\cdot Pr^iOH$ Green solid	21.15 (21.04)	28.52 (28.70)	– –
11	$Cr(OEt)Cl_2\cdot 2EtOH$ (1.17 g)	Isopropanol Excess	$Cr(OEt)Cl_2\cdot 2Pr^iOH$ Greenish violet solid	18.52 (18.97)	25.64 (25.87)	– –
12	$Cr(OPr^i)Cl_2\cdot 2Pr^iOH$ (0.95 g)	Methanol Excess	$Cr(OPr^i)Cl_2\cdot 2MeOH$ Green solid	21.08 (21.13)	28.64 (28.62)	– –

TABLE II. Addition Products of Chloride Alkoxides of Chromium(III).

S. No.	Reactants	Molar ratio	Refluxing time and medium	Product	Analyses (%) Found (Calcd.)	
					Chromium	Chlorine
1	$Cr(OEt)Cl_2\cdot 2EtOH$ (1.60 g) + pyridine (0.98 g)	1:2	2 hrs benzene	$Cr(OEt)Cl_2\cdot 2$pyridine Dark green solid	15.82 (15.89)	21.08 (21.74)
2	$Cr(OPr^i)Cl_2\cdot 2Pr^iOH$ (1.31 g) + pyridine (0.63 g)	1:2	2 hrs benzene	$Cr(OPr^i)Cl_2\cdot 2$pyridine Dark green solid	14.86 (15.20)	20.46 (20.86)
3	$Cr(OBu^n)Cl_2\cdot 2Bu^nOH$ (1.60 g) + pyridine	1:2	2 hrs benzene	$Cr(OBu^n)Cl_2\cdot 2$pyridine Green solid	14.59 (14.69)	19.44 (20.01)
4	$Cr(OEt)Cl_2\cdot 2EtOH$ (1.81 g) + β-picoline (1.31 g)	1:2	2 hrs benzene	$Cr(OEt)Cl_2\cdot 2$picoline Green solid	15.19 (15.03)	20.04 (20.01)
5	$Cr(OPr^i)Cl_2\cdot 2Pr^iOH$ (1.23 g) + β-picoline (0.77 g)	1:2	2 hrs benzene	$Cr(OPr^i)Cl_2\cdot 2$picoline Green solid	13.96 (14.13)	18.89 (19.23)
6	$Cr(OBu^n)Cl_2\cdot 2Bu^nOH$ (1.21 g) + β-picoline (0.66 g)	1:2	2 hrs benzene	$Cr(OBu^n)Cl_2\cdot 2$picoline Green solid	13.46 (13.60)	18.18 (18.55)
7	$Cr(OEt)Cl_2\cdot 2EtOH$ (1.14 g) + C_5H_5NO (0.85 g)	1:2	2 hrs benzene	$Cr(OEt)Cl_2\cdot 2C_5H_5NO$ Brown solid	14.46 (14.59)	19.68 (19.90)
8	$Cr(OPr^i)Cl_2\cdot 2Pr^iOH$ (1.17 g) + C_5H_5NO (0.74 g)	1:2	2 hrs benzene	$Cr(OPr^i)Cl_2\cdot 2C_5H_5NO$ Brown solid	13.36 (14.04)	18.86 (19.15)
9	$Cr(OBu^n)Cl_2\cdot 2Bu^nOH$ (1.13 g) + C_5H_5NO (0.63 g)	1:2	2 hrs benzene	$Cr(OBu^n)Cl_2\cdot 2C_5H_5NO$ Brown solid	13.46 (13.53)	18.12 (18.45)

TABLE III. Electronic Visible Spectra of Chloride Alkoxides of Chromium(III) and their Addition Complexes.

S. No.	Compound	$^4A_{2g}\rightarrow{}^4T_{2g}$ (10 Dq)	$^4A_{2g}\rightarrow{}^4T_{1g}$	B	μ_{eff}*	Conductivity in ohm^{-1} cm^{-2} mol^{-1} M/1000	
						in parent alcohol	in nitro benzene
1	$Cr(OMe)Cl_2\cdot 2MeOH$	15,035 cm^{-1}	20,600 cm^{-1}	522 cm^{-1}	3.66	135.0	0.465
2	$Cr(OEt)Cl_2\cdot 2EtOH$	14,577 cm^{-1}	20,162 cm^{-1}	503 cm^{-1}	3.72	28.5	0.386
3	$Cr(OPr^i)Cl_2\cdot 2Pr^iOH$	15,290 cm^{-1}	20,325 cm^{-1}	437 cm^{-1}	3.75	4.0	0.320
4	$Cr(OBu^n)Cl_2\cdot 2Bu^nOH$	14,577 cm^{-1}	19,841 cm^{-1}	486 cm^{-1}	–	3.2	0.300
5	$Cr(OEt)Cl_2\cdot 2EtOH$ (in EtOH)	14,810 cm^{-1}	21,650 cm^{-1}	641 cm^{-1}	–	–	–
6	$Cr(OPr^i)Cl_2\cdot 2Pr^iOH$ (in Pr^iOH)	15,500 cm^{-1}	20,840 cm^{-1}	617 cm^{-1}	–	–	–
7	$Cr(OBu^n)Cl_2\cdot 2Bu^nOH$ (in Bu^nOH)	14,810 cm^{-1}	21,730 cm^{-1}	640 cm^{-1}	–	–	–
8	$Cr(OMe)Cl_2$	14,200 cm^{-1}	20,620 cm^{-1}	554 cm^{-1}	–	–	–
9	$Cr(OEt)Cl_2$	14,320 cm^{-1}	19,610 cm^{-1}	478 cm^{-1}	–	–	–
10	$Cr(OPr^i)Cl_2$	14,390 cm^{-1}	19,850 cm^{-1}	499 cm^{-1}	–	–	–
11	$Cr(OEt)Cl_2\cdot 2C_5H_5N$	16,077 cm^{-1}	22,026 cm^{-1}	559 cm^{-1}	–	–	–
12	$Cr(OPr^i)Cl_2\cdot 2C_5H_5N$	15,432 cm^{-1}	21,008 cm^{-1}	514 cm^{-1}	–	–	–
13	$Cr(OBu^n)Cl_2\cdot 2C_5H_5N$	16,077 cm^{-1}	21,929 cm^{-1}	536 cm^{-1}	–	–	–
14	$Cr(OEt)Cl_2\cdot 2CH_3C_5H_4N$	15,773 cm^{-1}	22,026 cm^{-1}	563 cm^{-1}	–	–	–
15	$Cr(OBu^n)Cl_2\cdot 2CH_3C_5H_4N$	15,822 cm^{-1}	21,551 cm^{-1}	528 cm^{-1}	–	–	–
16	$Cr(OEt)Cl_2\cdot 2C_5H_5NO$	14,840 cm^{-1}	20,410 cm^{-1}	516 cm^{-1}	–	–	–
17	$Cr(OPr^i)Cl_2\cdot 2C_5H_5NO$	15,020 cm^{-1}	20,920 cm^{-1}	536 cm^{-1}	–	–	–
18	$Cr(OBu^n)Cl_2\cdot 2C_5H_5NO$	14,790 cm^{-1}	20,750 cm^{-1}	528 cm^{-1}	–	–	–

Molecular weights were determined in a semimicro ebulliometer (Gallenkamp) with a thermistor sensing device. Infrared spectra were recorded on a Infrared Grating 621 spectrophotometer. Electronic spectra were recorded on a Beckman spectrophotometer.

Reaction of $CrCl_3 \cdot 3THF$ with NaOEt in (1:1) Molar Ratio in Ethanol

Sodium (0.23 g) in ethanol was added dropwise to a solution of $CrCl_3 \cdot 3THF$ (3.85 g) in ethanol (40 ml). The color of the solution changed from violet to green with the separation of white solid. The reaction mixture was reflexed for ~2 hrs. The soluble green solution was separated by filtration and dried under reduced pressure (40 °C/0.5 mm). A light green solid soluble in benzene was obtained (yield, 90%). Found: Cr, 19.58; OEt, 52.37; Cl, 26.38%. Calcd. for $Cr(OEt)Cl_2 \cdot 2EtOH$: Cr, 19.99; OEt, 52.81; Cl, 27.20%.

The above product (1.92 g), $CrCl_2(OEt) \cdot 2EtOH$, was refluxed with benzene and the benzene-ethanol azeotrope was fractionated slowly (~12 hrs). A brownish violet insoluble product was obtained and dried under reduced pressure. Found: EtOH (in the azeotrope), 0.66 g; Cr, 30.45; OEt, 26.40; Cl, 41.81%. Calcd. for $Cr(OEt)Cl_2$: EtOH, 0.68 g (for 2 moles); Cr, 30.97; OEt, 26.80; Cl, 42.23%.

The reactions of $CrCl_3 \cdot 3THF$ with other sodium alkoxides and their alcoholysis interchange reactions are given in Table I.

Reaction of $Cr(OEt)Cl_2 \cdot 2EtOH$ with Pyridine (molar ratio 1:2) in Benzene

To $Cr(OEt)Cl_2 \cdot 2EtOH$ (1.60 g) in benzene (20 ml) was added pyridine (0.98 g) in benzene dropwise with shaking. A dark green solid started separating. The reaction mixture was refluxed for 2 hrs. The dark green insoluble portion was separated by decantation, washed several times with n-hexane, and dried under reduced pressure. A dark green product was obtained (yield, 95%). Found: Cr, 15.82; Cl, 21.08%. Calcd. for $Cr(OEt)Cl_2 \cdot 2C_5H_5N$: Cr, 15.89; Cl, 21.74%.

All other reactions are given in Table II.

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