

Synthesis and characterisation of 2-chloroethoxychromium(III) derivatives and their adducts

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Tris(2-chloroethoxy)-, chlorobis(2-chloroethoxy) and dichloro(2-chloroethoxy)-chromium(III) have been synthesised and characterized. They react with oxygen and nitrogen donor ligands yielding adducts, for which the magnetic susceptibility, IR, reflectance and mass spectral data have been reported. Bridged 2-chloroethoxy structure for the adducts is supported from their IR and mass spectra while the electronic spectra are consistent with octahedral geometry for these compounds.

Although chromium(III) alkoxides are known¹, there has been no report on the corresponding chloroalkoxy derivatives including the 2-chloroethoxides. The strong inter-molecular alkoxy coordination² leading to formation of polymeric metal alkoxides is now well recognised; this leads to coordinative saturation of the metal in these compounds. As a consequence of coordinative saturation in chromium(III) alkoxides¹, there is no reaction of these compounds with bases. However, when an electron-withdrawing atom is substituted in the alkyl group or is replaced by an -OR group, the extent and strength of alkoxy coordination is expected to decrease. Whenever such conditions occur, coordination by another base to the metal atom of the metal alkoxide may take place to yield adducts. We report here the synthesis and characterization of 2-chloroethoxy derivatives of chromium(III) and their coordination chemistry.

Experimental

All the reagents were purified by standard methods before use. All preparations and manipulations were done on a vacuum line, occasionally flushing it with dry oxygen-free nitrogen.

To a known amount of lithium metal in benzene, was added 2-chloroethanol slightly in excess than required for 1 : 1 molar ratio, and contents were stirred until whole of the lithium dissolved. To this was added $\text{CrCl}_3 \cdot 3\text{THF}$ (molar ratio of $\text{CrCl}_3 : \text{Li} : 1 : 3$), and the mixture was stirred and

heated under reflux for about 10-12 hr in order to ensure the completion of reaction. Ether was added to separate lithium chloride. Contents were filtered under anhydrous conditions and the filtrate on concentration *in vacuo* yielded solid product which was washed with carbon tetrachloride to remove any trace of 2-chloroethanol and finally dried *in vacuo*. The chloro and dichloro derivatives, i.e., $\text{CrCl}(\text{OC}_2\text{H}_4\text{Cl})_2 \cdot \text{THF}$ and $\text{CrCl}_2(\text{OC}_2\text{H}_4\text{Cl}) \cdot 2\text{THF}$ were prepared in a similar manner except that the molar ratio of $\text{CrCl}_3 : \text{Li}$ was kept 1 : 2 and 1 : 1 respectively.

The adducts were prepared by adding the liquid ligand to the cold solution of 2-chloroethoxychromium(III) derivatives in ether when solid products separated out. The adducts with solid ligand (γ -pic.N-O) were prepared by mixing the alkoxide with a solution of the ligand in chloroform.

Chromium was estimated volumetrically³ while chlorine was estimated gravimetrically⁴. C, H, N analyses were carried out on an elemental analyzer-MOD 1106. Magnetic measurements were done by Gouy's method. Infrared spectra were reported in nujol on a Perkin Elmer 1430 infrared spectrophotometer. The diffuse reflectance spectra (800-200 cm^{-1}) of the compounds were recorded on a Hitachi spectrophotometer model 330. Mass spectra of the compounds were recorded on 'VG' micromass 7705 instrument.

Results and discussion

Reactions of $\text{CrCl}_3 \cdot 3\text{THF}$ with $\text{LiOCH}_2\text{CH}_2\text{Cl}$ in 1 : 3, 1 : 2 and 1 : 1 molar ratios yield tris(2-chloroethoxy)chromium(III), chlorobis(2-chloroethoxy)chromium(III) monotetrahydrofuran and dichloro(2-chloroethoxy)chromium(III) bistetrahydrofuran respectively as hygroscopic solids. They react with oxygen or nitrogen donors(L) to form adducts having the formulae $\text{Cr}(\text{OR})_3 \cdot \text{L}$, $\text{CrCl}(\text{OR})_2 \cdot 2\text{L}$ and $\text{CrCl}_2(\text{OR}) \cdot 2\text{L}$ ($\text{R} = \text{C}_2\text{H}_4\text{Cl}$) (Table 1). Their insufficient solubilities in benzene or nitrobenzene precluded the determination of molecular weights.

Magnetic moments of these compounds are given in Table 2. The observed values are lower than the values required for d^3 ion i.e. 3.88 B.M., and this can be explained in terms of the existence of antiferromagnetic interaction⁵ between two or more chromium atoms through the bridging- $\text{OC}_2\text{H}_4\text{Cl}$ groups in a polymeric structure. Their diffuse reflectance spectral data are given in Table 2. The ligand field parameters, Δ , and B have been calculated

Table 1—Analytical and IR data for 2-chloroethoxy derivatives of chromium(III) and their adducts

Compound†	m. Py. (°C)	Found (Calcd.) (%)						(C—O) ^t	(C—O) ^b
		Cr	Cl	C	H	N			
Cr(OR) ₃	120	17.33 (17.90)	36.51 (36.36)	24.44 (24.75)	4.03 (4.13)	—		1050	1000
CrCl(OR) ₂ .THF	125	15.99 (16.32)	33.00 (33.43)	29.20 (30.14)	4.45 (5.02)	—		1060	1020
CrCl ₂ (OR).2THF	120	14.84 (15.00)	30.71 (30.73)	33.50 (34.63)	5.60 (5.77)	—		—	1020
Cr(OR) ₃ .TMU	*	12.89 (12.79)	26.08 (26.19)	32.38 (32.47)	5.28 (5.90)	6.62 (6.88)		1080	1050
CrCl(OR) ₂ .2TMU	120 (d)	10.66 (10.86)	22.00 (22.25)	—	—	—		1050	1035
Cr(OR) ₃ .DMA	90	13.51 (13.77)	27.66 (28.21)	32.20 (31.78)	5.11 (5.56)	3.68 (3.70)		1055	1025
CrCl(OR) ₂ .2DMA	95	12.01 (12.36)	24.95 (25.32)	33.44 (34.24)	5.98 (5.10)	6.55 (6.65)		1050	1030
CrCl ₂ (OR).2NMA	95	14.62 (14.92)	27.34 (30.55)	25.84 (27.45)	5.49 (5.16)	7.91 (8.03)		—	1000
CrCl(OR) ₂ .2DMSO	124	12.36 (12.91)	26.33 (26.45)	21.79 (23.85)	4.49 (4.96)	—		1070	1020
Cr(OR) ₃ . γ -Pic-N-O	160	12.95 (13.01)	26.01 (26.65)	—	—	—		1100	1035
CrCl(OR) ₂ .2 γ -Pic-N-O	170	11.03 (11.19)	21.89 (22.92)	40.60 (41.33)	4.71 (4.73)	5.99 (6.02)		1090	1030
CrCl ₂ (OR).2 γ -Pic-N-O	165	11.71 (12.36)	24.24 (25.32)	38.80 (39.90)	5.30 (5.23)	6.61 (6.65)		—	1020
Cr(OR) ₃ . α -Pic	110	13.49 (13.55)	27.32 (27.77)	—	—	—		1075	1040
CrCl(OR) ₂ .2 α -Pic	—	11.87 (12.02)	24.57 (24.62)	44.40 (44.39)	5.12 (5.08)	6.37 (6.47)		1060	1010
CrCl ₂ (OR).2 α -Pic	115	13.64 (13.88)	27.50 (27.41)	—	—	—		—	1060
Cr(OR) ₃ . β -Pic	105	13.50 (13.55)	27.52 (27.77)	38.43 (37.54)	4.81 (4.95)	3.87 (3.65)		1050	1020
Cr(OR) ₃ . γ -Pic	130	13.52 (13.55)	26.99 (27.77)	36.02 (37.54)	4.15 (4.95)	3.55 (3.65)		1060	1030
CrCl(OR) ₂ .2 γ -Pic	130	12.00 (12.02)	24.39 (24.62)	44.86 (44.39)	5.34 (5.08)	6.64 (6.47)		1060	1030
CrCl ₂ (OR).2 γ -Pic	135	13.16 (13.88)	26.60 (27.41)	—	—	—		—	1025

*Did not melt upto 260°C; †All the adducts are green solids, t = terminal, b = bridging, THF = tetrahydrofuran, TMU = tetramethylurea, DMA = dimethylacetamide, NMA = N-methylacetamide, DMSO = dimethyl sulphoxide, Pic-N-O = picoline-N-oxide, Pic = picoline, R = $-\text{C}_2\text{H}_4\text{Cl}$.

ed by spectral fitting procedure⁹. The positions of the bands assignable to the transitions $^4A_{2g} \rightarrow ^4T_{2g}$ (ν_1) $^4A_{2g} \rightarrow ^4T_{1g}$ (F) (ν_2) and $^4A_{2g} \rightarrow ^4T_{1g}$ (P) (ν_3), the values of the parameters Δ , B and β are characteristic of octahedral geometry^{5,7}. The nephelauxetic ratio (β), which is the ratio of Racah interelectronic repulsion parameter (B) for the chromium ion in a complex to its value in the gaseous ion⁸, has been calculated and this comes to 0.737-0.614 indicating a covalent character of Cr—O bond in these derivatives.⁸

The infrared spectra of the complexes do not show any bands in the region 3385-3310 cm^{-1} indicating the absence of free or coordinated alcohol⁹. The compound $\text{Cr}(\text{OC}_2\text{H}_4\text{Cl})_3$ shows two characteristic absorption bands at 1050 and 1000 cm^{-1} due to terminal and bridging $-\text{C}_2\text{H}_4\text{Cl}$ groups^{10,11} (Table 1). Likewise, $\text{CrCl}(\text{OC}_2\text{H}_4\text{Cl})_2\cdot\text{THF}$ shows two $\nu(\text{C}-\text{O})$ bands at 1060 and 1020 cm^{-1} . $\text{CrCl}_2(\text{OC}_2\text{H}_4\text{Cl})\cdot 2\text{THF}$, however, shows only one band at 1020 cm^{-1} , which in turn may be due to the $\nu(\text{C}-\text{O})$ bridging. The peaks due to the asymmetric

Table 2—Electronic spectra and magnetic moment data of 2-chloroethoxy derivatives of chromium(III) and their adducts

Compound	$\lambda_{\max}$ (kK)			Δ (kK)	B (free ion = 1.03)	β	μ_{eff} (B.M.) (at K)
	ν_1	ν_2	ν_3				
$\text{Cr}(\text{OC}_2\text{H}_4\text{Cl})_3$	14.28	22.7	32.25	14.28	0.640	0.621	3.30 (297)
$\text{CrCl}(\text{OC}_2\text{H}_4\text{Cl})_2 \cdot \text{THF}$	14.28	21.0	32.25	14.28	0.721	0.700	3.48 (300)
$\text{CrCl}_2(\text{OC}_2\text{H}_4\text{Cl})_2 \cdot 2\text{THF}$	14.28	21.27	32.25	14.28	0.721	0.691	3.58 (300)
$\text{Cr}(\text{OC}_2\text{H}_4\text{Cl})_3 \cdot \text{DMA}$	14.28	21.27	—	14.28	0.691	0.670	—
$\text{CrCl}(\text{OC}_2\text{H}_4\text{Cl})_2 \cdot 2\text{DMA}$	14.92	21.27	—	14.92	0.649	0.630	—
$\text{CrCl}(\text{OC}_2\text{H}_4\text{Cl})_2 \cdot 2\text{DMSO}$	14.92	21.27	—	14.92	0.649	0.623	—
$\text{CrCl}(\text{OC}_2\text{H}_4\text{Cl})_2 \cdot 2\text{TMU}$	15.01	22.10	—	15.01	0.760	0.737	—
$\text{Cr}(\text{OC}_2\text{H}_4\text{Cl})_3 \cdot \nu\text{-Pic-N-O}$	15.31	22.22	—	15.31	0.736	0.714	—
$\text{CrCl}(\text{OC}_2\text{H}_4\text{Cl})_2 \cdot 2\gamma\text{-Pic-N-O}$	15.31	22.42	—	15.31	0.757	0.734	—
$\text{CrCl}_2(\text{OC}_2\text{H}_4\text{Cl})_2 \cdot 2\gamma\text{-Pic-N-O}$	15.15	22.31	—	15.25	0.750	0.728	3.62 (300)
$\text{Cr}(\text{OC}_2\text{H}_4\text{Cl})_3 \cdot \alpha\text{-Pic}$	15.38	22.22	—	15.38	0.750	0.728	3.50 (300)
$\text{Cr}(\text{OC}_2\text{H}_4\text{Cl})_3 \cdot 2\gamma\text{-Pic}$	16.66	23.25	37.03	16.66	—	—	3.40 (297)
$\text{CrCl}(\text{OC}_2\text{H}_4\text{Cl})_2 \cdot 2\gamma\text{-Pic}$	15.87	22.22	—	15.87	0.633	0.614	3.50 (300)

and symmetric C—O—C stretching vibrations of the coordinated THF molecule ($1040, 850\text{ cm}^{-1}$) are reduced in frequency as compared to those of the free ligand ($\text{C}_4\text{H}_8\text{O}$; 1070 and 920 cm^{-1})¹². The IR spectra of the adducts also show bands in the (C—O) region, i.e., $\nu(\text{C—O})$ terminal at $1100\text{--}1050\text{ cm}^{-1}$ and $\nu(\text{C—O})$ bridging at $1040\text{--}1000\text{ cm}^{-1}$ (Table 1). For $\text{CrCl}_2(\text{OC}_2\text{H}_4\text{Cl})_2 \cdot 2\text{L}$, only one band appears in C—O region due to $\nu(\text{C—O})$ bridging. The data are characteristic of 2-chloroethoxy bridged structure for these compounds. The IR spectra of adducts with TMU, DMA, NMA, DMSO, Pic-N-oxides and α -, β -, γ -picolines suggest the coordination of these ligands to metal through oxygen or nitrogen as is evident from the changes in the ligand vibrations; the band positions compare well with those reported for their complexes with usual acceptors^{13,14}. An interesting feature is the splitting of $\nu(\text{N—O})$ (1210 and 1190 cm^{-1} in adducts; free ligand 1250 cm^{-1}) for the 2:1 complexes of γ -picoline N-oxide with $\text{CrCl}(\text{OC}_2\text{H}_4\text{Cl})_2$ and $\text{CrCl}_2(\text{OC}_2\text{H}_4\text{Cl})$, which suggests the ligands to have the *cis* relationship¹⁵. $\nu(\text{Cr—O})$ and $\nu(\text{Cr—Cl})$ vibrations in the compounds are present at $500\text{--}445$ and $360\text{--}325\text{ cm}^{-1}$ respectively⁵. Mass spectra of $\text{Cr}(\text{OC}_2\text{H}_4\text{Cl})_3$ and $\text{CrCl}(\text{OC}_2\text{H}_4\text{Cl})_2 \cdot \text{THF}$ show strong *m/e* peaks at 280, 218 and 148 mass numbers which may be assigned to $[\text{Cr}_2(\text{OR})_2\text{OH}]^+$, $[\text{Cr}_2(\text{OR})(\text{OH})_2]^+$ and $[\text{Cr}(\text{OR})(\text{OH})]^+$ species, respectively. In view of this, 2-chloroethoxy-bridged structure may be proposed for these compounds.

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