

2,2,2-Trifluoroethoxy Derivatives of Chromium(III) : Synthesis & Coordination Chemistry

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New trifluoroethoxy derivatives of chromium(III) formulated as $\text{Cr}(\text{OCH}_2\text{CF}_3)_3 \cdot \text{THF}$, $\text{CrCl}(\text{OCH}_2\text{CF}_3)_2 \cdot \text{THF}$ and $\text{CrCl}_2(\text{OCH}_2\text{CF}_3)_2 \cdot 2\text{THF}$, have been synthesised and characterised. With ligands (L), they form adducts of the types $\text{Cr}(\text{OCH}_2\text{CF}_3)_3 \cdot \text{L}$, $\text{CrCl}(\text{OCH}_2\text{CF}_3)_2 \cdot 2\text{L}$ and $\text{CrCl}_2(\text{OCH}_2\text{CF}_3)_2 \cdot 2\text{L}$ for which the magnetic moment data indicate the presence of antiferromagnetic interaction. Their electronic spectra are consistent with octahedral coordination of chromium(III). On the basis of IR and NMR data, it is proposed that the complexes contain bridging trifluoroethoxy groups and the ligands are probably *cis* to each other. Mass spectral data are in favour of a dimeric structure.

Whereas many metal alkoxides have been synthesised¹, the corresponding trifluoroethoxy derivatives are relatively unknown and of these the trifluoroethoxy derivatives of chromium(III) have not been reported so far. The alkoxide group is known to display a great propensity to bridge two or more metal atoms²; therefore, a tendency to form strong polynuclear molecular clusters dominates the structural chemistry of metal alkoxides³. This brings about coordinative saturation which precludes ligation. The alkoxy ligands containing electronegative atoms are expected to not only increase the sensitivity of the central metal atom to nucleophilic attack but also to weaken the alkoxy-bridged polymers and may thus enable coordination by a strong ligand. Here, we report the preparation of 2,2,2-trifluoroethoxy derivatives of chromium(III) and their stable adducts with tetrahydrofuran (THF), dimethyl sulphoxide (DMSO), tetramethylurea (TMU), γ -picoline N-oxide (γ -Pic-N-O), α -, β - and γ -picolines (α -, β -, γ -pic).

Materials and Methods

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.

Preparation of tris(2,2,2-trifluoroethoxy)-chromium(III) tetrahydrofuranone

To a known amount of lithium metal in benzene was added 2,2,2-trifluoroethanol slightly in excess than that required for 1:1 molar ratio and the contents were stirred until the whole of lithium dissolved. To this was added tetrahydrofuran suspension of anhydrous chromium trichloride (molar ratio of CrCl_3 : Li, 1:3) and the contents were stirred

and simultaneously refluxed for 8 hr in order to ensure the completion of the reaction. To this was added dry ether when lithium chloride precipitated which was removed by filtration; the filtrate was concentrated by removing ether *in vacuo* when a solid was obtained. It was washed with petroleum ether (40-60°) to remove any trace of alcohol and dried *in vacuo* to get a green solid which was found on analysis to be $\text{Cr}(\text{OCH}_2\text{CF}_3)_3 \cdot \text{THF}$. All attempts to free it from coordinated tetrahydrofuran failed as it decomposed on heating or distillation under reduced pressure.

Chlorobis(2,2,2-trifluoroethoxy)chromium(III) tetrahydrofuranone, $\text{CrCl}(\text{OCH}_2\text{CF}_3)_2 \cdot \text{THF}$ and dichloro(2,2,2-trifluoroethoxy)chromium(III) bis-tetrahydrofuranone, $\text{CrCl}_2(\text{OCH}_2\text{CF}_3)_2 \cdot 2\text{THF}$ were prepared in a similar manner as mentioned above except that the molar ratio of CrCl_3 :Li was 1:2 and 1:1, respectively, and the products obtained were green hygroscopic solids. The adducts were prepared by dissolving the alkoxides in the liquid ligands and stirring the contents for ~ 4-5 hr followed by precipitation of adducts by addition of ether, petroleum ether (40-60°) and dichloromethane. The adducts with solid ligands (γ -picoline N-oxide) were prepared by adding the alkoxide to the solution of the ligand in chloroform.

Chromium and fluorine were estimated volumetrically^{4,5} while chlorine was estimated gravimetrically⁶. Magnetic susceptibility measurements were carried out by Gouy's method. Infrared spectra of complexes were recorded in nujol on a Perkin Elmer 621 spectrophotometer. The diffuse reflectance spectra of the compounds were recorded on a Hitachi spectrophotometer model 330 in the region 1500-200 nm. NMR spectra of the compounds were recorded on a Varian EM 390 spectrometer at

Table 1—Analytical and IR Spectral Data of 2,2,2-Trifluoroethoxy Derivatives of Chromium(III)

Compound†	Found(Calc.),%					(C-O)t	(C-O)b
	Cr	Cl/F ^a	C	H	N		
Cr(OR _t) ₃ .THF	11.98(12.35)	39.89(40.61) ^a				1060	1010
CrCl(OR _t) ₂ .THF	14.00(14.54)	9.12(9.93)	29.2(30.14)	3.8(3.76)		1080	1045
CrCl ₂ (OR _t) ₂ .2THF	13.97(14.20)	19.27(19.39)	32.95(32.78)	5.00(4.91)			1020
CrCl(OR _t) ₂ .2DMSO	11.54(11.77)	7.98(8.04)				1050	1010
Cr(OR _t) ₃ .TMU	11.08(11.18)	36.34(36.77) ^a				1060	1030
CrCl(OR _t) ₂ .2TMU	9.99(10.04)	6.21(6.85)	35.11(35.10)	5.53(5.85)	10.90(11.70)	1050	1020
CrCl ₂ (OR _t) ₂ .2TMU	11.32(11.45)	15.51(15.63)					1030
Cr(OR _t) ₃ .γ-pic-N-O	11.73(11.35)	37.15(37.33) ^a	31.27(31.44)	2.67(2.83)	3.06(3.05)	1070	1065
CrCl(OR _t) ₂ .2γ-pic-N-O	10.12(10.32)	7.00(7.05)				1075	1025
CrCl ₂ (OR _t) ₂ .2γ-pic-N-O	11.26(11.81)	16.02(16.13)	38.43(38.18)	3.26(3.63)	6.66(6.36)	—	1035
Cr(OR _t) ₃ .α-pic	11.54(11.76)	37.65(38.68) ^a	30.64(32.57)		2.88(3.16)	1080	1020
CrCl(OR _t) ₂ .2α-pic	10.98(11.02)	7.25(7.52)				1085	1030
Cr(OR _t) ₃ .β-pic	11.33(11.76)	37.93(38.68) ¹				1080	1025
CrCl(OR _t) ₂ .2β-pic	11.00(11.02)	7.43(7.52)				1090	1035
CrCl ₂ (OR _t) ₂ .2β-pic	12.26(12.74)	17.22(17.40)					1030
Cr(OR _t) ₃ .γ-pic	10.69(11.76)	37.88(38.68) ^a	31.00(32.57)	2.74(2.94)	3.5(3.16)	1050	1015
CrCl ₂ (OR _t) ₂ .2γ-pic	12.31(12.74)	17.15(17.40)					

†OR_t = OCH₂CF₃. All compounds are green solids which decompose at their melting points; t & b = terminal, bridging respectively; THF = tetrahydrofuran, TMU = tetramethylurea. Pic-N-O = picoline-N-oxide, Pic = picoline.

Table 2—Electronic Spectral and Magnetic Moment Data of 2,2,2-Trifluoroethoxy Derivative of Chromium(III) and Their Adducts

Compound	λ_{\max} (kK)			Δ (kK)	B' (kK)	$\beta = B'/B$ (free ion = 1.03 kK)	μ_{eff} (B.M.)
	A	B	C				
Cr(OR _t) ₃ .THF	16.6	23.5	45.45	16.6	0.70	0.67	3.32 (297K)
CrCl(OR _t) ₂ .THF	16.9	23.8	—	16.9	0.69	0.67	3.53 (300K)
CrCl ₂ (OR _t) ₂ .2THF	16.6	23.3	—	16.9	0.67	0.65	3.63 (300K)
Cr(OR _t) ₃ .TMU	16.8	25.0	37.73	16.8	0.76	0.74	—
CrCl(OR _t) ₂ .2TMU	16.6	23.6	—	16.6	0.71	0.69	3.52 (299K)
CrCl ₂ (OR _t) ₂ .2TMU	16.6	23.5	—	16.6	0.70	0.67	—
Cr(OR _t) ₃ .α-pic	17.1	25.6	36.40	17.1	0.71	0.69	3.38 (297K)
CrCl(OR _t) ₂ .2α-pic	16.6	23.8	—	16.6	0.75	0.72	3.50 (299K)
CrCl(OR _t) ₂ .2β-pic	16.6	23.7	—	16.6	0.72	0.70	—
CrCl ₂ (OR _t) ₂ .2β-pic	16.9	23.8	—	16.9	0.69	0.67	3.64 (300K)
CrCl ₂ (OR _t) ₂ .2γ-pic	16.9	24.0	—	16.9	0.72	0.70	3.65 (300K)
Cr(OR _t) ₃ .γ-pic-N-O	—	—	—	—	—	—	3.40 (299K)

R_t = CH₂CF₃; A = ⁴A_{2g} → ⁴T_{2g}; B = ⁴A_{2g} → ⁴T_{1g}(F); C = ⁴A_{2g} → ⁴T_{1g}(P)

90 MHz; TMS was used as internal reference. Mass spectra of the compounds were recorded on a 'VG micromass 7075 instrument'.

Results and Discussion

The analytical data of the compounds support their proposed formulations (Table 1). They are green hygroscopic solids and are insoluble in common nonpolar solvents, a fact which supports their polymeric nature. They are reasonably soluble in polar/donor solvents. They react with a variety of oxygen and nitrogen donor ligands (L) to form adducts, the analyses of which indicate (Table 1) the stoichiometries Cr(OCH₂CF₃)₃.L, CrCl(OCH₂CF₃)₂.2L and CrCl₂(OCH₂CF₃)₂.2L for them. These

adducts are also insufficiently soluble in non-polar solvents as also in nitromethane and acetonitrile which precludes the determination of their molecular weights.

The observed magnetic moment values (Table 2) at room temperature are slightly lower than the spin-only value for the high spin d³ ion (3.88 B.M.) and this is suggestive of the antiferromagnetic interactions⁷ of two or more chromium atoms through the bridging OCH₂CF₃ groups in these compounds. An increase in the magnetic moment is observed when the alkoxy groups are replaced by chloride ion and this is similar to the results obtained for Cr(OMe)₃ compared to CrCl(OMe)₂ and CrCl₂(OMe)₂⁸. The reflectance spectra of the present

compounds show bands at 16 ± 0.8 and 24 ± 1 kK due to the transitions ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$, respectively and a third spin-allowed transition ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ is observed only in some cases at 37 ± 0.5 kK (Table 2). In addition, the ligand field splitting parameter (Δ), inter-electronic repulsion parameter or Racah parameter (B) and covalency factor (β) have been calculated and are given in Table 2; values of these are consistent with an octahedral geometry for these compounds⁹.

The IR spectra of $\text{Cr}(\text{OCH}_2\text{CF}_3)_3 \cdot \text{THF}$ and $\text{CrCl}(\text{OCH}_2\text{CF}_3)_2 \cdot \text{THF}$ and their adducts show bands at 1090-1050 and 1040-1010 cm^{-1} which have been assigned to the $\nu\text{C-O}$ modes of the terminal and bridging $-\text{OCH}_2\text{CF}_3$ groups^{1,10,11} respectively (Table 1). The symmetric and asymmetric $\nu(\text{C-O-C})$ vibrations of the coordinated THF¹² molecules appear at 870, 910 and 1025 cm^{-1} . The compound $\text{CrCl}_2(\text{OCH}_2\text{CF}_3)_2 \cdot 2\text{THF}$ and its adducts, however, show only one band (1035-1020 cm^{-1}) and its position compares well with that of the bridging alkoxy groups which suggests that the terminal $-\text{OCH}_2\text{CF}_3$ groups are absent in these compounds. The spectra also show shifting of ligand vibrations in these complexes when compared to those of the pure ligands which indicates coordination of the ligands to chromium^{13,14}. For example, the displacement of the characteristic bands of picolines to higher spectral region on complex formation was comparable to that of their reported adducts with other acceptors; the lowering of $\nu\text{S}=\text{O}$, $\nu\text{N-O}$ and $\nu\text{C}=\text{O}$ modes of DMSO, amine-oxides and amides respectively in the complexes of these ligands is in accord with the earlier results on the adducts of these ligands. In the bis-(picoline-N-oxide) (ligand, 1255 cm^{-1} ; adducts 1215, 1200 cm^{-1}) complexes $\nu(\text{N-O})$ appears as a doublet which suggests that the ligands are in *cis* positions.¹⁵ The bands around 560-450 cm^{-1} in these compounds are assigned to Cr-O stretching vibrations confirming the existence of covalent bonds between Cr and $-\text{OCH}_2\text{CF}_3$ ligand while the bands around 360-325 cm^{-1} have been assigned to $\nu(\text{Cr-Cl})$ vibrations.⁹

¹H NMR spectrum of $\text{Cr}(\text{OCH}_2\text{CF}_3)_3 \cdot \text{THF}$ in D_2O solution at room temperature shows two signals; a quartet at δ 4.2 ppm and a singlet at δ 2.2 ppm. The signal at 4.2 ppm (10H) is due to the overlapping of $-\text{CH}_2$ protons of $-\text{OCH}_2\text{CF}_3$ group (δ for CH_2 protons of $\text{CF}_3\text{CH}_2\text{OH} = 3.9$ ppm) and ethereal protons of THF and the signal at 2.2 ppm (4H) is due to other CH_2 protons of THF (δ for CH_2 protons of free THF = 3.75 and 1.85 ppm). The observation of a single peak for $-\text{OCH}_2\text{CF}_3$ group may be attributed to an exchange of terminal and bridging $-\text{OCH}_2\text{CF}_3$ groups. The ¹⁹F NMR spec-

trum of $\text{Cr}(\text{OCH}_2\text{CF}_3)_3 \cdot \text{THF}$ gives a single fluorine resonance^{16,17} at δ 78 ppm.

The mass spectra of $\text{Cr}(\text{OCH}_2\text{CF}_3)_3 \cdot \text{THF}$ (1), $\text{CrCl}(\text{OCH}_2\text{CF}_3)_2 \cdot \text{THF}$ (2) and $\text{Cr}(\text{OCH}_2\text{CF}_3)_3 \cdot \alpha$ -picoline (3) do not show any peak corresponding to the dimeric or the monomeric species. However, the spectra of the compounds give rise to strong *z/e* peaks corresponding to dichromium species. The peaks at *z/e* 220 and 148 in (1) may be assigned to the species $[\text{F}_2\text{C-Cr-O-Cr-CF}_2]^+$ and $[\text{CH}_2\text{-Cr-O-Cr-CH}_2]^+$, respectively. Peak at *z/e* 148 in (2) may be assigned to $[\text{CH}_2\text{-Cr-O-Cr-CH}_2]^+$ and at *z/e* 205 and 148 in (3) may be assigned to the species $[\text{F}_2\text{H}_2\text{C-Cr-O-Cr-CH}_2\text{F}]^+$ and $[\text{H}_2\text{C-Cr-O-Cr-CH}_2]^+$, respectively. These observations, therefore, tentatively suggest a 2,2,2-trifluoroethoxybridged dimeric structure for these compounds.

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