Synthesis, Characterization, and Reactions of Chromyl(VI) Alkoxides

Sunehri L. Chadha,* Vijay Sharma, and Anuradha Sharma
Department of Chemistry, Panjab University, Chandigarh-160 014, India

Alkoxy-bridged chromyl(VI) alkoxides, $[CrO_2(OR)_2]$ and $[CrO_2Cl(OR)]$ (R = CH_2CCl_3, CH_2CF_3, or CH_2CH_2Cl), have been synthesized. They react with oxygen- and nitrogen-donor ligands to form adducts. The alkoxides and their adducts have been characterized by elemental analyses, cryoscopic studies, i.r., ^1H and ^{19}F n.m.r., and mass spectra.

Although the alkoxy derivatives of a large number of metals in their various oxidation states have been prepared and studied, no corresponding chromyl(VI) compounds exist, except for a report[1] of the reaction between CrO_2Cl_2 and ethanol or propanol to yield green compounds of formula $[CrO_2Cl(OR)]\cdot 2ROH$ (R = C_2H_5 or C_3H_7). The reactions of chromyl chloride with some strong acids have been studied,[2,3] which yield yellow or brown chromyl(VI) derivatives, whereas with weak acids green products identified[4] as trinuclear chromium(III) compounds have been obtained. We now report the synthesis and characterization of the hitherto unknown chromyl(VI) alkoxides $[CrO_2(OR)_2]$ and $[CrO_2Cl(OR)]$ (R = CH_2CCl_3, CH_2CF_3, or CH_2CH_2Cl) and their reaction products with the ligands *N,N*-dimethylacetamide (dma), tetramethylurea (tmu), and 2-methylpyridine (mpy).

Experimental

All preparations were carried out in a dry oxygen-free nitrogen atmosphere. Chromyl chloride was prepared using the method described by Brauer.[5]

Synthesis of Chromyl(VI) *Alkoxides*.—Dioxobis(2,2,2-trichloroethoxo)- and dioxobis(2,2,2-trifluoroethoxo)-chromium(VI) were prepared by the reaction of LiOR (R = CH_2CCl_3 or CH_2CF_3) and CrO_2Cl_2 in CCl_4 (molar ratio of CrO_2Cl_2 to Li is 1:2). The solution was stirred for 5—6 h. Diethyl ether (20 cm^3) was added, the solution was filtered to separate the lithium chloride, and the filtrate was dried under vacuum to yield a brown solid. The compounds chlorodioxo(2,2,2-trichloroethoxo)- and chlorodioxo(2,2,2-trifluoroethoxo)-chromium(VI) were prepared similarly except that the molar ratio CrO_2Cl_2: Li was 1:1. Bis(2-chloroethoxo)dioxochromium(VI) was prepared by refluxing a mixture of 2-chloroethanol and CrO_2Cl_2 in a 2:1 molar ratio in CCl_4 (20 cm^3) until the evolution of HCl ceased. The solution was filtered, washed repeatedly with CCl_4, and dried under vacuum.

Preparation of Adducts.—The relevant chromyl(VI) alkoxides and ligands (tmu, dma, or mpy) were mixed in a 1:2 molar ratio and stirred for 2—3 h. The adducts were precipitated by addition of dichloromethane–ether–light petroleum (b.p. 40—60°C).

Chromium and chlorine were estimated gravimetrically.[6] Fluorine was estimated after fusing the compound with sodium metal in a sealed tube and titrating the extract with standard thorium nitrate.[6] Carbon, H, and N analyses were performed on an Elemental Analyzer-MOO 1106 from the Regional Sophisticated Instrument Centre, Panjab University, Chandigarh. Molecular weights were determined cryoscopically. Infrared spectra of the complexes were recorded in Nujol on a Perkin-Elmer 621 spectrophotometer, ^1H and ^{19}F n.m.r. spectra on a Varian EM 390 spectrophotometer at 90 MHz using $SiMe_4$ as a reference, and mass spectra on a Vacuum Generator micromass 70 75 instrument.

Results and Discussion

Reaction of chromyl(VI) chloride with LiOR (R = CH_2CCl_3, CH_2CF_3, or CH_2CH_2Cl) in 1:2 or 1:1 molar ratio yields the hygroscopic, brown solid chromyl(VI) alkoxides, $[CrO_2(OR)_2]$ and $[CrO_2Cl(OR)]$ respectively. Analytical data for various chromyl(VI) alkoxides are given in Table 1.

Table 1. Analytical data for chromyl(VI) alkoxides and their adducts

			Analysis[a]/%				
Compound	Colour	M.p. (°C)	Cr	Cl/F	C	H	N
$[CrO_2(OCH_2CCl_3)_2]$	Brown	122—125	13.0 (13.6)	55.6 (55.9)	11.7 (12.5)	1.1 (1.0)	
$[CrO_2Cl(OCH_2CCl_3)]$	Dark brown	*b*	19.2 (19.4)	52.2 (52.9)	8.9 (8.9)	0.7 (0.75)	
$[CrO_2(OCH_2CF_3)_2]$	Reddish brown	*b*	18.3 (18.4)	39.3 (40.4)[c]	16.4 (17.0)	1.4 (1.4)	
$[CrO_2Cl(OCH_2CF_3)]$	Brown	*b*	22.9 (23.7)	16.0 (16.2)	10.5 (10.9)	0.9 (0.9)	
$[CrO_2(OCH_2CH_2Cl)_2]$	Brown	150	21.2 (21.3)	30.1 (29.2)	19.0 (19.7)	3.2 (3.2)	
$[CrO_2(OCH_2CCl_3)_2]\cdot 2mpy$	Brown	*b*	9.4 (9.1)	37.0 (37.5)	33.5 (33.8)	3.0 (3.1)	4.8 (4.9)
$[CrO_2(OCH_2CCl_3)_2]\cdot 2dma$	Brown	*b*	10.0 (9.3)	38.0 (38.3)	25.1 (25.9)	2.3 (2.3)	4.9 (5.0)
$[CrO_2Cl(OCH_2CCl_3)]\cdot 2mpy$	Brown	*b*	11.0 (11.4)	31.0 (31.2)	35.9 (37.0)	3.5 (3.5)	5.9 (6.1)
$[CrO_2(OCH_2CF_3)_2]\cdot mpy$	Reddish brown	115	13.7 (13.8)	30.4 (30.4)[c]	31.0 (32.0)	2.9 (2.9)	3.7 (3.7)
$[CrO_2(OCH_2CF_3)_2]\cdot dma$	Brown	*b*	14.5 (14.0)		25.0 (25.8)	3.5 (3.5)	3.7 (3.8)
$[CrO_2Cl(OCH_2CF_3)]\cdot mpy$	Brown	116	17.0 (16.6)	10.9 (11.3)			
$[CrO_2Cl(OCH_2CF_3)]\cdot tmu$	Brown	95	15.8 (15.5)	10.2 (10.6)	25.0 (25.1)	4.0 (4.1)	8.0 (8.3)

[a] Calculated values in parentheses. [b] Did not melt up to 260 °C. [c] Value for F.

Table 2. Molecular-weight data for $[CrO_2(OCH_2CF_3)_2]$ and $[CrO_2Cl(OCH_2CF_3)]$ at different concentrations in nitrobenzene

Compound	Concentration/mol dm^{-3}	M
$[CrO_2(OCH_2CF_3)_2]$	0.0056	284.8
	0.0213	410.0
	0.0434	480.5
$[CrO_2Cl(OCH_2CF_3)]$	0.0073	225.0
	0.0869	291.0
	0.1464	365.0

Table 3. Major i.r. bands (cm^{-1}) of chromyl(VI) alkoxides and their adducts

	v(C-O)		v(O=Cr=O)	
Compound	terminal	bridging	asym.	sym.
$[CrO_2(OCH_2CCl_3)_2]$	1 080	1 010	930	900
$[CrO_2Cl(OCH_2CCl_3)]$		1 020	930	920
$[CrO_2(OCH_2CF_3)_2]$	1 080	1 020	980	960
$[CrO_2Cl(OCH_2CF_3)]$		1 030	990	960
$[CrO_2(OCH_2CH_2Cl)_2]$	1 090	1 020	960	950
$[CrO_2(OCH_2CCl_3)_2]$·2mpy	1 090		950	920
$[CrO_2(OCH_2CCl_3)_2]$·2dma	1 050		950	930
$[CrO_2Cl(OCH_2CCl_3)]$·2mpy	1 090		960	940
$[CrO_2(OCH_2CF_3)_2]$·mpy	1 070	1 040		910
$[CrO_2(OCH_2CF_3)_2]$·dma	1 080	1 020	945	920
$[CrO_2Cl(OCH_2CF_3)]$·mpy	1 095	1 035	960	905
$[CrO_2Cl(OCH_2CF_3)]$·tmu	1 060	1 020	940	910

Molecular Weight Determination.—The compounds $[CrO_2(OCH_2CF_3)_2]$ and $[CrO_2Cl(OCH_2CF_3)]$ have good solubility in nitrobenzene and their molecular weights were determined at different concentrations (Table 2). Increasing the concentration of these compounds increases the molecular weight, which indicates that they are monomers at low concentration but their degree of association increases at higher concentration. Similar observations have been made on some titanium(IV) alkoxides.[7]

Infrared Spectra.—Infrared spectra of the compounds $[CrO_2(OR)_2]$ show two bands at 1 090—1 080 and 1 020—1 010 cm^{-1} assigned to terminal and bridging v(C-O) respectively.[8–11] The compounds $[CrO_2Cl(OR)]$ show only one band at 1 030—1 020 cm^{-1} due to the presence of a bridging -OR group only. The alkoxides also show bands in the range 990—900 cm^{-1} arising from the symmetric and asymmetric Cr=O stretching vibrations (Table 3).[12]

Proton and ^{19}F N.M.R. Spectra.—The ^1H n.m.r. spectrum of $[CrO_2(OCH_2CCl_3)_2]$ shows singlets at δ 4.7 and 4.1 p.p.m. which may be assigned to the bridging and terminal alkoxy groups respectively, similar to the spectrum observed for dimeric tris(2,2,2-trichloroethoxo)aluminium(III).[13] The spectrum of $[CrO_2Cl(OCH_2CCl_3)]$ shows a singlet at 4.0 p.p.m. assigned to a bridging OCH_2CCl_3 group. The ^1H n.m.r. spectrum of $[CrO_2(OCH_2CF_3)_2]$ in acetonitrile shows a singlet at 3.95 p.p.m. in addition to the signals due to acetonitrile. The existence of one signal for both alkoxy groups, *i.e.* bridging and terminal, may be attributed to an exchange between them at room temperature. The ^1H n.m.r. spectrum of $[CrO_2Cl(OCH_2CF_3)]$ in acetonitrile shows a singlet at 3.8 p.p.m. assigned to the presence of a bridging alkoxy group. That of $[CrO_2(OCH_2CH_2Cl)_2]$ shows a singlet at 4.2 p.p.m. which may be due to the presence of the alkoxy group.

Fluorine-19 n.m.r. spectra of $[CrO_2(OCH_2CF_3)_2]$ and $[CrO_2Cl(OCH_2CF_3)]$ show singlets at 78.6 and 80.0 p.p.m. respectively, which can be assigned to the presence of the symmetrical fluorine atoms of the CF_3 group.[3]

Table 4. Mass spectral data

m/z	Identity
357w	$M_2^+ - OCH_2CF_2$
	$\downarrow -CrO_2ClF$
219.5	M^+
218.5	
	$\downarrow -CF_3$
149.5	$M^+ - CF_3$

Mass Spectral Data for $[CrO_2Cl(OCH_2CF_3)]$.—No parent molecular ion peak for the dimer (M_2^+) has been observed (Table 4) but the weak peak at m/z 357 arises due to the loss of the OCH_2CF_3 group from the dimer. A strong peak at m/z 218.5 corresponds to monomeric (M^+) species. The compound $[CrO_2Cl(OCH_2CF_3)]$ gives a strong peak at m/z 149.5 corresponding to the loss of CF_3 from M^+; similar behaviour was observed earlier for some metal hexafluoroisopropoxides.[14]

Reactions with Ligands.—These alkoxides react with oxygen- and nitrogen-donor ligands such as *N,N*-dimethylacetamide (dma), tetramethylurea (tmu), and 2-methylpyridine (mpy) to form adducts of 1:1 or 1:2 stoicheiometry (Table 1). The i.r. spectra of the adducts show that the number and position of C-O bands for the pure alkoxides is retained (Table 3), whereas the characteristic ligand vibration shows changes, the trend of which confirms the co-ordination of the ligands.[15,16] The adducts also show two bands in the range 960—905 cm^{-1} assigned to asymmetric and symmetric Cr=O modes.[2,12]

The ^1H n.m.r. spectrum of $[CrO_2(OCH_2CCl_3)_2]$·2mpy shows a singlet at δ 4.2 p.p.m. in addition to signals due to co-ordinated mpy. The integration ratio suggests the existence of a 1:2 stoicheiometry. The ^1H n.m.r. spectrum of $[CrO_2(OCH_2CF_3)_2]$·mpy shows a singlet at 3.7 p.p.m. which may be attributed to the presence of the alkoxy group and the integration ratio confirms the 1:1 stoicheiometry. Its ^{19}F n.m.r. spectrum shows a singlet at 76 p.p.m. assigned to symmetrical fluorine atoms.

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