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Synthesis, Characterization and Reactions of 2,2,2-Trichloroethoxy Derivatives of Chromium(III)

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Tris(2,2,2-trichloroethoxy)chromium(III) tetrahydrofuran solvate, $Cr(OCH_2CCl_3)_3 \cdot$ *THF*; Chlorobis(2,2,2-trichloroethoxy)chromium(III)tetrahydrofuran solvate, $CrCl(OCH_2CCl_3)_2 \cdot$ *THF* and dichloro(2,2,2-trichloroethoxy) chromium(III) tetrahydrofuran solvate, $CrCl_2(OCH_2CCl_3) \cdot$ *THF* have been prepared. These compounds react with various oxygen and nitrogen donor ligands to form adducts of 1 : 2 composition. 2,2,2-trichloroethoxy bridged structures have been proposed on the basis of their infrared and ^1H nmr spectra. The diffuse reflectance spectral results are consistent with an octahedral geometry for chromium(III) whereas their low magnetic moment values suggest polymeric structures exhibiting antiferromagnetic coupling between chromium(III) atoms. The mass spectral data of $Cr(OCH_2CCl_3)_3 \cdot$ *THF* and $CrCl(OCH_2CCl_3)_2 \cdot$ *THF* support the dimeric structures for these complexes.

(Keywords: 2,2,2-Trichloroethoxy derivatives of chromium(III); Adducts with O- and N-donors)

Synthese, Charakterisierung und Reaktionen von 2,2,2-Trichlorethoxyderivaten von Chrom(III)

Es wurde Tris(2,2,2-trichlorethoxy)chrom(III)-tetrahydrofuransolvat, $Cr(OCH_2CCl_3)_3 \cdot$ *THF*, Chlorbis(2,2,2-trichlorethoxy)chrom(III)tetrahydrofuransolvat, $CrCl(OCH_2CCl_3)_2 \cdot$ *THF*, und Dichlor(2,2,2-trichlorethoxy)-chrom(III)tetrahydrofuransolvat, $CrCl_2(OCH_2CCl_3 \cdot$ *THF*, hergestellt. Diese Verbindungen reagieren mit verschiedenen Sauerstoff- und Stickstoffdonorliganden unter Bildung von Addukten mit der Zusammensetzung 1:2. Basierend auf IR- und ^1H-NMR-Daten wurden 2,2,2-trichlorethoxy-überbrückte Strukturen vorgeschlagen. Die Resultate aus Diffuse-Reflectance-Messungen sind mit einer oktaedrischen Geometrie um Cr(III) in Übereinstimmung, während die niedrigen Werte für die magnetischen Momente polymere Strukturen mit antiferromagnetischer Kopplung zwischen den Chrom(III)-Atomen nahelegen. Die massenspektroskopischen Daten für $Cr(OCH_2CCl_3)_3 \cdot$ *THF* und $CrCl(OCH_2CCl_3)_2 \cdot$ *THF* sprechen für eine dimere Struktur dieser Komplexe.

Introduction

Unlike metal alkoxides [1, 2] the corresponding haloalkoxy derivatives are relatively unknown and of these the trichloroethoxy derivatives of chromium(III) had not so far been reported.

The alkoxide group is known to display a great propensity to bridge [3] two or more metal atoms so that the formation of a strong polynuclear molecular cluster dominates the structural chemistry of metal alkoxides [2] and as a consequence leads to the coordination saturation which in turn precludes ligation. The alkoxy ligands containing electronegative atoms are expected to weaken the alkoxy-bridged polymers and increase the sensitivity of the central metal atom to nucleophilic attack and this may enable the strong ligand coordination. Here we report the preparation of hitherto unknown 2,2,2-trichloroethoxy chromium(III) derivatives and their stable adducts with ligands.

Results and Discussion

Tris(2,2,2-trichloroethoxy)chromium(III)tetrahydrofuran solvate, $Cr(OCH_2CCl_3)_3 \cdot$ *THF*, chlorobis(2,2,2-trichloroethoxy)chromium(III)-tetrahydrofuran solvate, $CrCl(OCH_2CCl_3)_2 \cdot$ *THF* and dichloro(2,2,2-trichloroethoxy)chromium(III)tetrahydrofuran solvate, $CrCl_2(OCH_2CCl_3) \cdot$ *THF* have been prepared from their reaction of anhydrous chromium(III)chloride in tetrahydrofuran and $LiOCH_2CCl_3$ in 1:3, 1:2 and 1:1 molar ratio respectively. An attempted reaction of $Cr(OCH_2CCl_3)_3 \cdot$ *THF* with 2 moles of acetylchloride to obtain the dichloro derivative yields a dark green liquid containing two moles of the corresponding ester molecules and was found on analysis to be $CrCl_2(OCH_2CCl_3) \cdot 2\,CH_3COOCH_2CCl_3$ [$\nu(C=O)$ of coordinated ester 1 605 cm^{-1}]. These 2,2,2-trichloroethoxy derivatives of chromium(III) are insoluble in common organic solvents such as CCl_4, CH_2Cl_2, C_6H_6, $C_6H_5NO_2$, CH_3NO_2, and CH_3CN which indicates that they are polymeric. Their insolubility also precludes conductance and cryoscopic measurements.

The infrared spectrum of $Cr(OCH_2CCl_3)_3 \cdot$ *THF* exhibits C—O stretching modes at 1 090, 1 015 cm^{-1} (Table 2) which may be assigned to the terminal and bridging alkoxy group, respectively [4, 5]. Likewise, $CrCl(OCH_2CCl_3)_2 \cdot$ *THF* exhibits these bands at 1 085 and 1 010 cm^{-1}. In addition, these compounds show bands due to coordinated tetrahydrofuran molecules at 1 030, 900 cm^{-1} and 1 020, 915 cm^{-1} assigned to the symmetric and asymmetric C—O—C stretching vibrations [6]. The spectra of these derivatives also show bands at 510, 460 cm^{-1} and 505, 405 cm^{-1} arising from the vibrations due to the stretching modes for

Cr—O and Cr—O → Cr respectively and the position and assignments compare well with earlier reported results [7]. The infrared spectrum of $\mathrm{CrCl_2(OCH_2CCl_3)} \cdot$ *THF* shows only one band in the C—O region at 1 030 $\mathrm{cm^{-1}}$ and this may be assigned to the bridging C—O vibration only, whereas the band at 460 $\mathrm{cm^{-1}}$ may be assigned to the presence of $\nu(\mathrm{Cr}{\diagup}^{\mathrm{O}}{\searrow}\mathrm{Cr})$. This clearly indicates that all these derivatives contain bridging 2,2,2-trichloroethoxy, and the terminal 2,2,2-trichloroethoxy group, which is present in others, seems to be absent in $\mathrm{CrCl_2(OCH_2CCl_3)} \cdot$ *THF*.

The compounds are paramagnetic and their magnetic moments fall in the range 3.28–3.60 B.M. at room temperature (Table 1). The observed values are significantly below the spin-only value of 3.88 B.M. for chromium(III) [8] suggesting the existence of antiferromagnetic interactions between two or more chromium(III) atoms through the bridging $\mathrm{—OCH_2CCl_3}$ groups. The increase in the magnetic moment on replacement of $\mathrm{—OCH_2CCl_3}$ by Cl atoms may be due to the decrease in the extent of antiferromagnetic interactions; a similar behaviour has earlier been observed for corresponding methoxy derivatives [8].

The diffuse reflectance spectra of these compounds show bands around 16.0 kK, 25.0 kK, and 33.0 kK (Table 3) assigned to $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$, $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)(\nu_2)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ transitions, respectively. These spectra are identical in all respects to the reported spectra of chromium(III) in octahedral environment [9, 10]. The various electronic parameters such as ligand field parameter (10 Dq); *Recah* parameter (B) and the covalency factor (β) (Table 3) have been calculated by the method reported by *Konig* [11]. The values of 'B' and 'β' are indicative of the highly covalent character of the metal ligand bonds in these derivatives [12, 13].

The ^{1}H nmr spectrum of $\mathrm{Cr(OCH_2CCl_3)_3} \cdot$ *THF* in pyridine shows a broad singlet at $\delta = 4.8$ ppm (width at half height = 28 Hz) due to $\mathrm{—CH_2}$ of the $\mathrm{—OCH_2CCl_3}$ group [14] in addition to singlets at $\delta = 2.0$ ppm and $\delta = 3.9$ ppm due to $\mathrm{—CH_2}$ of tetrahydrofuran. The integration ratio of 1.5 : 2 supports the existence of 1 : 1 composition. The ^{1}H nmr spectrum of $\mathrm{CrCl(OCH_2CCl_2)_2} \cdot$ *THF* shows a broad singlet at $\delta = 5.2$ ppm (width at half height = 30 Hz) attributed to $\mathrm{—CH_2}$ of the $\mathrm{—OCH_2CCl_3}$ group and singlets at $\delta = 1.9$ and 3.6 ppm for $\mathrm{CH_2}$ of tetrahydrofuran. The integration ratio of 1 : 2 supports its formulation. The existence of only one $\mathrm{—CH_2}$ signal for both terminal and bridging $\mathrm{—OCH_2CCl_3}$ groups may be explained on the basis of formation of pyridine adducts with these derivatives and these pyridine adducts may be monomeric in pyridine (pyridine signals are observed at $\delta = 7.3$, 7.6 and 8.3 in 2 : 1 : 2 ratio).

The mass spectra of $\mathrm{Cr(OCH_2CCl_3)_3} \cdot$ *THF* and CrCl(O

Table 1. *Analytical data and magnetic moments (B.M.) of 2,2,2-trichloroethoxy derivatives of chromium(III) and their adducts*

Compound	Colour and state	M.P. (°C)	Magnetic moment, $\mu_{eff.}$ (B.M.)	Cr(%) Exp. (calcd.)	Cl(%) Exp. (calcd.)
$Cr(OCH_2CCl_3)_3 \cdot$ *THF*	dark green viscous liquid	—	3.28	9.0 (9.1)	55.7 (56.1)
$Cr(OCH_2CCl_3)_3 \cdot 2$ *TMU*	green solid	[a]	3.51	7.0 (7.1)	43.4 (43.7)
$Cr(OCH_2CCl_3)_3 \cdot 2$ *DMA*	dark green solid	[a]	—	7.4 (7.7) 25.6 (25.0)[b]	47.0 (47.5) 3.6 (3.57)[d] 4.0 (4.1)[c]
$Cr(OCH_2CCl_3)_3 \cdot 2\,\alpha$-*pic*—N—O	light green solid	[a]	—	6.9 (7.2) 30.9 (30.1)[b]	44.0 (44.6) 2.8 (2.79)[d] 3.7 (3.9)[c]
$Cr(OCH_2CCl_3)_3 \cdot 2\,\gamma$-*pic*—N—O	light green solid	[a]	—	7.0 (7.2) 29.6 (30.1)[b]	44.4 (44.6) 3.7 (3.91)

$CrCl(OCH_2CCl_3)_2 \cdot$ *THF*	green viscous liquid	—	3.47	11.2 (11.3)	54.3 (54.4)
$CrCl(OCH_2CCl_3)_2 \cdot 2$ *γ-pic*—N—O	green solid	130[e]	3.58	8.4 (8.6) 30.6 (31.6)[b]	40.6 (41.2) 3.2 (2.98)[d] 4.0 (4.64)[c]
$CrCl_2(OCH_2CCl_3) \cdot$ *THF*	violet solid	[a]	3.54	14.5 (15.1) 21.5 (20.9)[b]	51.0 (51.6) 3.0 (2.9)[d]
$CrCl_2(OCH_2CCl_3) \cdot 2\,CH_3COOCH_2CCl_3$	green liquid	—	—	7.8 (7.9)	59.4 (59.6)
$CrCl_2(OCH_2CCl_3) \cdot 2$ *DMA*	green solid	[a]	3.60	11.7 (11.6) 26.0 (26.9)[b]	39.5 (39.8) 5.0 (4.48)[d] 6.8 (6.2)[c]
$CrCl_2(OCH_2CCl_3) \cdot 2$ *NMA*	green solid	[a]	—	12.2 (12.4) 23.2 (22.9)[b]	41.8 (42.2) 4.2 (3.8)[d] 7.0 (6.7)[c]
$CrCl_2(OCH_2CCl_3) \cdot 2$ *γ-pic*—N—O	green solid	140[e]	—	10.8 (10.6) 32.5 (34.3)[b]	35.9 (36.2) 3.1 (3.2)[d] 4.8 (5.7)[c]
$CrCl_2(OCH_2CCl_3) \cdot 2$ *γ-pic*	dark green solid	155[e]	—	11.2 (11.3)	38.5 (38.7)

[a] Did not melt up to 260 °C. [b] Carbon %. [c] Nitrogen %. [d] Hydrogen %. [e] Decomposed

Table 2. *Infrared spectral frequencies of 2,2,2-trichloroethoxy derivatives of chromium(III) and their adducts*

Compound	$\nu(\mathrm{C{-}O{-}C})_{\mathrm{sym}}$[a]; $\nu(\mathrm{C{-}O{-}C})_{\mathrm{asym}}$[a] $\nu(\mathrm{C{=}O})$[b]; $\nu(\mathrm{N{-}O})$[c] $\nu(\mathrm{C{=}C})$ and $\nu(\mathrm{C{=}N})$[d]	$\nu(\mathrm{C{-}O})_{\mathrm{bridging}}$	$\nu(\mathrm{C{-}O})_{\mathrm{terminal}}$	$\nu(\mathrm{Cr{-}O})$	$\nu(\mathrm{Cr}\overset{\mathrm{O}}{\diagup\searrow}\mathrm{Cr})$
$\mathrm{Cr(OCH_2CCl_3)_3}\cdot$ *THF*	1 030, 900 (1 070, 910)[a]	1 015	1 090	510	460
$\mathrm{CrCl(OCH_2CCl_3)_2}\cdot$ *THF*	1 020, 915 (1 070, 910)[a]	1 010	1 085	505	450
$\mathrm{CrCl_2(OCH_2CCl_3)}\cdot$ *THF*	1 020, 900 (1 070, 915)[a]	1 030	—	—	445
$\mathrm{CrCl_2(OCH_2CCl_3)\cdot 2\,CH_3COOCH_2CCl_3}$	1 605	1 030	—	—	—
$\mathrm{Cr(OCH_2CCl_3)_3}\cdot 2$ *DMA*	1 600 (1 653)[b]	1 010	1 080	—	—
$\mathrm{Cr(OCH_2CCl_3)_3}\cdot 2$ *TMU*	1 600 (1 650)[b]	1 030	1 090	—	—
$\mathrm{Cr(OCH_2CCl_3)_3}\cdot 2\,\alpha$-*pic*—N—O	1 210 (1 245)[c]	1 020	1 080	500	440
$\mathrm{Cr(OCH_2CCl_3)_3}\cdot 2\,\gamma$-*pic*—N—O	1 230 (1 255)[c]	1 035	1 090	510	465
$\mathrm{CrCl(OCH_2CCl_3)_2}\cdot 2\,\gamma$-*pic*—N—O	1 230 (1 255)[c]	1 040	1 080	570	520
$\mathrm{CrCl_2(OCH_2CCl_3)}\cdot 2$ *DMA*	1 620 (1 653)[a]	1 025	—	—	470
$\mathrm{CrCl_2(OCH_2CCl_3)}\cdot 2$ *NMA*	1 600 (1 620)[a]	1 040	—	—	465
$\mathrm{CrCl_2(OCH_2CCl_3)}\cdot 2\,\gamma$-*pic*—N—O	1 200 (1 255)[c]	1 040	—	—	460
$\mathrm{CrCl_2(OCH_2CCl_3)}\cdot 2\,\gamma$-*pic*	1 620, 1 580 (1 595, 1 550, 1 490, 1 460)[d]	1 035	—	—	475

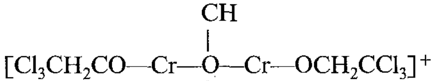
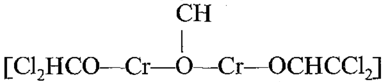
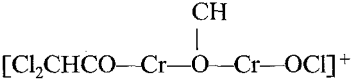
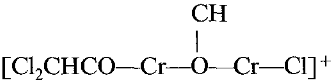
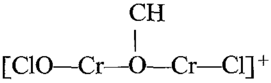
The values given in the parenthesis are the corresponding free ligand vibrations ($\mathrm{cm^{-1}}$)

[a] Did not melt up to 260 °C. [b] Carbon %. [c] Nitrogen %. [d] Hydrogen %

Table 3. *Electronic spectral data of chromium(III) alkoxides and their adducts with some oxygen and nitrogen donor ligands*

Compound	$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$ (kK)	$^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)(\nu_2)$ (kK)	$^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ (kK)	10 Dq (kK)	B (kK)	β
$Cr(OCH_2CCl_3)_3 \cdot$ *THF*	16.6	25.0	33.0	16.6	0.546	0.59
$CrCl(OCH_2CCl_3)_2 \cdot$ *THF*	16.0	25.2	33.2	16.0	0.693	0.75
$CrCl_2(OCH_2CCl_3) \cdot$ *THF*	16.4	25.0	34.0	16.4	0.653	0.71
$Cr(OCH_2CCl_3)_3 \cdot 2$ *TMU*	16.5	24.8	33.6	16.5	0.593	0.65
$Cr(OCH_2CCl_3)_3 \cdot 2$ *DMA*	15.6	25.2	32.0	15.6	0.653	0.71
$Cr(OCH_2CCl_3)_3 \cdot 2$ *α-pic*—N—O	16.0	24.8	32.0	16.0	0.586	0.63
$CrCl(OCH_2CCl_3)_2 \cdot 2$ *γ-pic*—N—O	15.6	24.3	32.6	15.6	0.686	0.74
$CrCl_2(OCH_2CCl_3) \cdot 2$ *DMA*	15.3	23.8	31.0	15.3	0.593	0.64
$CrCl_2(OCH_2CCl_3) \cdot 2$ *NMA*	14.9	23.5	30.5	14.9	0.620	0.67
$CrCl_2(OCH_2CCl_3) \cdot 2$ *γ-pic*	15.6	23.2	32.0	15.6	0.56	0.61

Table 4. *m/e Peak positions in* $Cr(OCH_2CCl_3)_3 \cdot$ *THF and* $CrCl(OCH_2CCl_3)_2 \cdot$ *THF*

m/e (Peak position)[a]	Possible assignment
430 w	 $[Cl_3CH_2CO{-}Cr{-}\overset{\overset{CH}{\vert}}{O}{-}Cr{-}OCH_2CCl_3]^+$
	$\downarrow -2\,HCl$
357 w	 $[Cl_2HCO{-}Cr{-}\overset{\overset{CH}{\vert}}{O}{-}Cr{-}OCHCCl_2]^+$
	$\downarrow -C_2HCl$
297 m	 $[Cl_2CHCO{-}Cr{-}\overset{\overset{CH}{\vert}}{O}{-}Cr{-}OCl]^+$
281 s	 $[Cl_2CHCO{-}Cr{-}\overset{\overset{CH}{\vert}}{O}{-}Cr{-}Cl]^+$
	$\downarrow -C_2HCl$
220 m	 $[ClO{-}Cr{-}\overset{\overset{CH}{\vert}}{O}{-}Cr{-}Cl]^+$
	$\downarrow -CH$
207 vvs	$[ClO{-}Cr{-}O{-}Cr{-}Cl]^+$
191 s	$[Cl{-}Cr{-}O{-}Cr{-}Cl]^+$
168	
148.5 s	$-OCH_2CCl_3$
133 s	$-CH_2CCl_3$
119 m	$-CCl_3$
72 vs	*THF*

[a] The peaks in both of them appear at the same position

$CH_2CCl_3)_2 \cdot$ *THF* do not exhibit *m*/e peaks for the ions corresponding to the theoretical value for the dimer or monomeric species. However, the strong *m*/e peaks each corresponding to possible mass distribution of dichromium ion has been observed in both of them (Table 4). The strong peak at 191 mass units corresponds to Cl—Cr—O—Cr—Cl. On this basis the strong peaks at *m*/e 207, 220, 281, 297, 357 and 430 may be assigned to other dichromium species. In view of these observations, the dimeric structures for these derivatives may be proposed in vapour phase.

These 2,2,2-trichloroethoxy derivatives react with some oxygen and nitrogen donor ligands such as tetramethylurea (*TMU*), dimethylacetamide (*DMA*), *n*-methylacetamide (*NMA*), α-, γ-picoline-N-oxide (α-, γ-*pic*—N—O) and γ-picoline (γ-*pic*) to yield adducts having 1 : 2 stoichiometry (Table 1) and the variation in the composition of reacting species did not alter the stoichiometry of the adducts. These adducts show similar spectral and magnetic susceptibility features as have been observed in the corresponding 2,2,2-trichloroethoxy derivatives. The ligand vibrations, however, undergo changes on complexation and such changes are similar to those reported for the complexes of these ligands with metal halides [15–18]. This confirms the coordination of the ligands to the 2,2,2-trichloroethoxy derivatives of chromium(III).

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Experimental

All the reactions have been done on vacuum line or under dry oxygen free nitrogen. $LiOCH_2CCl_3$ was prepared by a method outlined in our earlier paper [5].

$Cr(OCH_2CCl_3)_3 \cdot THF$

Anhydrous chromium(III) chloride (22.1 mmol, 3.5 g) in 50 ml of tetrahydrofuran was added dropwise to $LiOCH_2CCl_3$ (66.3 mmol, 10.3 g). The contents were stirred and refluxed on a waterbath for 3–4 h. Dry diethylether (100 ml) was added to separate solid LiCl from soluble $Cr(OCH_2CCl_3)_3$. The reaction mixture was filtered under anhydrous conditions and the filtrate on vacuum drying yielded the dark green viscous compound.

$CrCl(OCH_2CCl_3)_2 \cdot THF$

This was prepared under similar conditions as above except that the amount of $LiOCH_2CCl_3$ was 44.2 mmol, 6.86 g. The contents were refluxed on a waterbath for 8–9 h and processed as described above to yield the green viscous liquid product.

$CrCl_2(OCH_2CCl_3) \cdot THF$

Reaction of anhydrous chromium(III) chloride (28.4 mmol, 4.5 g) in 20 ml tetrahydrofuran was reacted with 28.4 mmol, 4.4 g of $LiOCH_2CCl_3$ under the conditions as above but refluxing the contents on a waterbath for a prolonged period (~ 15 h), yielding the violet solid compound.

Preparation of Adducts with Ligands

The above alkoxides were dissolved in various ligands in 1 : 2 molar ratio and the contents were stirred for 3–4 h. Green coloured adducts were precipitated by addition of ether/petroleum ether/methylene chloride.

Chromium was estimated volumetrically [19] and chlorine was estimated gravimetrically [20]. Other experimental details for spectral recordings are the same as described earlier [5].

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