

Reactions of Chromyl Chloride with Carboxylic Acids and Carboxylic Acid Anhydrides

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Chromyl Chloride, Trinuclear Basic Chromium(III) Carboxylate, Dinuclear Oxochromium(III) Carboxylate, Magnetic Susceptibility, IR Spectra, UV-Vis Spectra

Chromyl Chloride reacts with carboxylic acids $[RCOOH]$ where $R = C_2H_5$, $n-C_3H_7$, CH_2Cl , $CHCl_2$ and CCl_3 to give reduced chromium(III) carboxylates, $[Cr_3O(OOCR)_6(H_2O)_3]Cl$. Magnetic susceptibility, UV-visible and IR measurements are all consistent with their trinuclear basic structures. Reactions of chromyl chloride with carboxylic acid anhydrides $[(RCO)_2O]$ where $R = CH_3$, C_2H_5 and $n-C_3H_7$ give dinuclear oxo-bridged complexes of the type, $[Cr_2O(OOCR)_3]Cl$. These compounds behave as non-electrolytes in polar organic solvents. IR spectra suggest the presence of bridging carboxylato groups containing $Cr-O-Cr$ chains. Their low magnetic moment values suggest polymeric structures exhibiting antiferromagnetic coupling between Cr atoms.

Introduction

Reactions of chromyl chloride with strongly acidic solvents, HSO_3F and HSO_3Cl yield $CrO_2(SO_3F)_2$ [1] and $CrO_2(SO_3Cl)_2$ [2], respectively. However, its reactions with formic and acetic acids yield reduced trinuclear chromium(III) compounds containing $[Cr_3O(OOCR)_6]^+$ species [3]. A few other chromyl compounds like $CrO_2(SO_3CF_3)_2$ and $CrO_2(NO_3)(SO_3CF_3)$ [4] have been prepared by anion-interchange using $CrO_2(OOCCF_3)_2$ [5] as the starting material. Reactions of chromyl chloride with carboxylic acid anhydrides have not been investigated so far. In this communication, we now report the results of our studies on reactions between chromyl chloride and a few carboxylic acids and carboxylic acid anhydrides.

Experimental

Chromyl chloride was prepared by the literature method [6]. Reactions of chromyl chloride with excess of carboxylic acids and carboxylic acid anhydrides were followed by a method as outlined in our earlier paper [3].

Reaction of $Cr_2O(OOCC_3H_7)_3Cl$ with silver trifluoroacetate

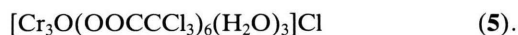
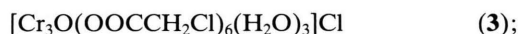
Both compounds were dissolved in nitromethane and an equimolar mixture of the two was stirred for few hours when $AgCl$ was removed by filtration. The filtrate on evacuation, repeated washings with petro-

leum ether yielded green a product which gave analysis corresponding to $[Cr_2O(OOCC_3H_7)_3](OOCCF_3)$ (9).

Other experimental details are the same as outlined in [3].

Results and Discussion

Chromyl chloride reacts with carboxylic acids $[RCOOH]$, where $R = C_2H_5$, $n-C_3H_7$, CH_2Cl , $CHCl_2$ and CCl_3 exothermally to give reduced chromium(III) compounds (1) to (5) (Table I). These compounds contain chromium in (+3) oxidation state which is suggested by their green colour and also by their inability to oxidize acidic KI to I_2 . Reaction of chromyl chloride with pure trifluoroacetic acid in CCl_4 medium at reflux temperature, however, yields a yellow-brown crystalline solid whose elemental analysis and IR spectrum correspond to an earlier reported chromyl compound, $CrO_2(OOCCF_3)_2$ [5]. The analytical results along with pertinent vibrational bands are given in Tables I and II, respectively. Compounds 1 to 5 may be represented as:



The compounds are insoluble in common organic solvents such as CCl_4 , CH_2Cl_2 , C_6H_6 , $C_6H_5NO_2$ and CH_3NO_2 , except (4) which is soluble in $C_6H_5NO_2$, a

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Table I. Analytical results and some physical properties.

Compound	Colour	Λ_m (ohm ⁻¹ cm ² mole ⁻¹)	m. p. (°C)	μ_{eff} (BM)	Cr	Analytical results** (%)			
						Cl	C	H	F
C ₁₈ H ₃₆ O ₁₆ Cr ₃ Cl (1)	green	50.4 ^a	—	3.40	23.1 (22.3)	5.1 (5.1)	31.02 (30.88)	5.26 (5.15)	—
C ₂₄ H ₄₈ O ₁₆ Cr ₃ Cl (2)	-do-	34.7 ^a	—	3.32	19.5 (19.9)	4.3 (4.5)	36.80 (36.76)	6.18 (6.12)	—
C ₁₂ H ₁₈ O ₁₆ Cr ₃ Cl ₇ (3)	-do-	32.3 ^a	—	3.02	19.2 (19.0)	30.4 (30.2)	17.34 (17.51)	2.20 (2.19)	—
C ₁₂ H ₁₂ O ₁₆ Cr ₃ Cl ₁₃ (4)	-do-	18.1 ^a , 2.8 ^b	—	3.21	15.4 (15.2)	44.8 (44.8)	13.97 (13.99)	1.54 (1.16)	—
C ₁₂ H ₆ O ₁₆ Cr ₃ Cl ₁₉ (5)	-do-	13.6 ^a	—	3.07	12.5 (12.1)	54.7 (54.5)	11.67 (11.65)	0.52 (0.48)	—
C ₆ H ₉ O ₇ Cr ₂ Cl (6)	-do-	—	> 250	2.80	30.8 (31.3)	10.7 (10.7)	21.64 (21.65)	2.98 (2.71)	—
C ₉ H ₁₅ O ₇ Cr ₂ Cl (7)	-do-	16.5 ^a	117–118	3.01	26.9 (27.8)	9.4 (9.5)	28.90 (28.83)	4.20 (4.00)	—
C ₁₂ H ₂₁ O ₇ Cr ₂ Cl (8)	-do-	9.0 ^a , 12.4 ^c	80–81	3.21	25.0 (25.0)	8.7 (8.5)	34.61 (34.57)	5.22 (5.04)	—
C ₁₄ H ₂₁ O ₉ Cr ₂ F ₃ (9)	-do-	—	89–90	—	21.4 (21.0)	—	34.00 (34.01)	4.43 (4.25)	11.6 (11.5)

* Required values for 1:1 electrolytes fall in the range: a, 120–160; b, 20–30 and c, 75–95 ohm⁻¹ cm² mole⁻¹, respectively;

** required values are given in the parentheses.

fact which indicates that they are polymers. These compounds are, however, soluble in more basic solvents like CH₃OH and CH₃CN and also dissolve in their parent acids. Molar conductances of their millimolar solutions in CH₃CN suggest their non-ionic nature [7]. These compounds are paramagnetic and their magnetic moments fall in the range 3.0 to 3.4 BM at room temperature. The values are significantly below the spin only value of 3.87 BM [8] for Cr^{III} but are well in the range expected for magnetically concentrated trinuclear complexes [9]. The UV-visible spectra of **2** and **3** in methanol in the region 200–800 nm exhibit strong bands at 435 and 580 nm with shoulders at 660 and 705 nm. These spectra are identical in all respects to the reported spectra of trinuclear chromium complexes [10].

IR spectra of these compounds (Table II) exhibit a broad medium intensity band in the region 3300–3100 cm⁻¹ characteristic of a $\nu(\text{OH})$ band. Bands at *ca.* 1660, 1600 and at *ca.* 1400 cm⁻¹ are assigned to $\nu_a(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ stretching vibrations, respectively, of the bridging carboxylate groups [11, 12]. The broad nature of the $\nu_a(\text{COO}^-)$ bands in these compounds may be attributed to the

overlap of $\delta(\text{HOH})$ which is also expected in this region. The large $\Delta\nu(\text{COO}^-)$ value of the order of 200 cm⁻¹ is what is normally observed for bridging carboxylates. Few other bands have been assigned by analogy to the spectra of sodium salts of these carboxylic acids [13, 14]. A weak to medium intensity band at *ca.* 540 cm⁻¹ is assigned to the Cr₃O group [15].

Reactions of chromyl chloride with carboxylic acid anhydrides [(RCO)₂O, where R=CH₃, C₂H₅ and *n*-C₃H₇] give dinuclear oxo-bridged complexes of the type, [Cr₂O(OOCR)₃]Cl, (**6**) to (**8**) (Table I). They are green amorphous solids, and intensity of their colour increases from acetate to butyrate. The compounds do not liberate I₂ from acidified KI solution thereby suggesting that chromium is in a lower (+3) oxidation state. However, reaction of chromyl chloride with trifluoroacetic anhydride did not yield any compound. Compound **6** is non-hygroscopic whereas **7** and **8** are quite sensitive to moisture. The acetate (**6**) is insoluble in most of the common organic solvents such as CCl₄, CH₂Cl₂, C₆H₆, CH₃NO₂, C₆H₅NO₂, CH₃CN and CH₃OH; the propionate (**7**) is soluble in CH₃OH and CH₃CN, and the butyrate (**8**)

Table II. Some characteristic vibrational bands (cm^{-1}) of compounds **1–9***

Assignments	1	2	3	4	5	6	7	8	9
(OH) mode	3300– 3100 mb	3300– 3100 mb	3300– 3100 mb	3300– 3100 mb	3300– 3100 mb	–	–	–	–
COO asym. str.	1665 sh, 1600 sb	1650 sh, 1600 sb	1660 sh, 1600 sb	1655 sh, 1590 sb	1660 s, 1600 mb, 1555 m	1605 s, 1500 mb	1605 s	1600 s	1650 m, 1605 s, 1565 w
COO sym. str.	1399 s	1420 s	1395 s	1410 s	1400 s	1400 sb	1415 m	1420 s	1440 s
CH ₂ sym. bend. def.	1460 sh	1460 sh	–	–	–	–	1465 m	1455 sh	1450 sh
–CH ₂ COO (adj. to COO)	1440 sh	1440 s	1440 s	–	–	–	1440 s	–	1440 sh
CH ₃ bend. def.	1375 sh	1345 w	–	–	–	1430 sh	1370 s	1360 sh	1370 w
–CH ₂ wagging	1245 w	1310 w, 1255 w	1265 w, 1245 m	–	–	–	1300 m	1315 s	1310 w, 1255 w
CH bend	–	–	–	1225 s	–	–	–	–	–
CF ₃ asym. str.	–	–	–	–	–	–	–	–	1200 s, 1155 s
CH ₃ rock	1070 m, 1005 s	1090 m, 1050 w, 960 w	–	–	–	1070 sh, 1030 m,	1070 s, 1010 w,	1090 mb, 1040 sh, 965 sh	1100 w, 1045 w, 960 w
+ C–C skeltel	890 w	945 w, 890 w	950 m, 925 m	970 s	980 m, 945 w	955 m, 890 w, 840 w	890 w	945 m, 900 m, 870 w	895 w, 860 w, 840 w
CH ₂ rock	–	800 m	–	–	–	–	810 m	750 sh	–
(Cr–O–Cr) modes	–	–	–	–	–	790 m	–	790 m	–
+ CF ₃ sym. str.	–	–	–	–	–	–	–	–	790 m
CCl _n asym. str.	–	–	–	825 s	865 s, 835 s, 760 s	–	–	–	–
			790 s						
CCl _n sym. str.	–	–	–	790 s	695 s	–	–	–	–
CCOO in plane bend	710 w	720 m	705 sb	720 s	710 w	725 m	720 m	725 m	730 m
COO def.	648 s	645 s	645 sb	685 m, 640 m	640 w	660 s	645 m	640 mb	640 m
CH or COO out of plane	–	615 m	575 m	620 w	625 w	610 m	620 w	620 m	620 w
(Cr ₃ O) modes	–	545 s	540 w	540 m	530 m, 510 m	–	–	–	–
(Cr–O–Cr) modes	–	–	–	–	–	560 m	565 sh	565 sh	560 sh
ν & δ (Cr–O) modes	415 m, 350 w, 290 wb	385 m, 330 w, 290 w	425 m, 330 w, 290 w	335 w, 300 w, 240 w	410 m, 400 m, 265 m, 240 m	430 s, 230 sh	430 s, 280 sh	465 s, 380 w, 280 sh	500 w, 440 s, 375 m, 300 w

* s = strong; m = medium; sh = shoulder; w = weak and b = broad.

is soluble in all polar solvents *viz.* C₆H₅NO₂, CH₃NO₂, CH₃CN and CH₃OH. Molar conductances of their millimolar solutions suggest that these compounds are nonionic [7]. These compounds are paramagnetic but their μ_{eff} values at room temperature (Table I) are below the 3.87 BM expected for free

Cr³⁺ ion [9], thereby suggesting some antiferromagnetic interaction between Cr atoms.

IR spectra of these compounds show strong bands at *ca.* 1600 and 1400 cm^{-1} which have been assigned to $\nu_{\text{a}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ stretching modes, respectively (Table II). A large $\Delta\nu$ value suggests the

presence of bridging carboxylato groups. Bands at 790 and at *ca.* 560 cm^{-1} have been assigned to Cr—O—Cr modes [16].

The reaction of **8** with silver trifluoroacetate in CH_3NO_2 , yields $[\text{Cr}_2\text{O}(\text{OOCCH}_3)_3] (\text{OOCCH}_3)$ (**9**) (Table I). Compound **9** behaves as a non-electrolyte

in CH_3NO_2 and that the trifluoroacetate ligand is covalently bonded. Its IR spectrum suggests that the trifluoroacetate ion behaves as a bidentate ligand [17]. The compound exhibits bands which are also characteristic of bridging butyrate groups.

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