Reactions of Chromyl Chloride with Monocarboxylic Acids

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Chromyl chloride reacts with formic and acetic acids to give products which contain the trinuclear cation $[\text{Cr}_3\text{O}(\text{OOCR})_6(\text{RCOOH})_3]^+$. The compounds have been characterized by elemental analyses, infrared spectral data, magnetic measurements and thermogravimetry.

Introduction

Reactions of chromyl chloride with peroxydisulphuryl difluoride ($\text{S}_2\text{O}_6\text{F}_2$) and fluorosulphuric acid to yield chromyl fluorosulphate $\text{CrO}_2(\text{SO}_3\text{F})_2$ have been reported in literature^{1,2}. In the present communication, the reactions of chromyl chloride with formic and acetic acids have been studied and the compounds characterized.

Experimental

Chromyl chloride was prepared by the literature method³. A solution of formic acid in carbon tetrachloride was added dropwise to chromyl chloride diluted in the same solvent so that the reaction product was always in excess of formic acid. Since the reaction was violently exothermic, the reaction vessel was maintained at 0 °C throughout the addition. After a few minutes, the colour of the solution changed from red to green with brisk evolution of HCl gas. On heating under reflux for several hours, a green solid separated out. Different attempts to prepare the same product always gave

compounds with different composition. However, if the green solid which separated was further refluxed with excess of pure formic acid, more of HCl gas was evolved. The contents were refluxed till the evolution of HCl gas had completely ceased. The final product, compound **1** was washed with dichloromethane and dried *in vacuo*. The compound does not react with strong bases such as pyridine and γ -picoline even on refluxing in carbontetrachloride. However, on passing dry NH_3 gas through a suspension of this compound in carbontetrachloride a new violet compound **2** was obtained.

The reaction of chromyl chloride with an excess of dry acetic acid carried under similar conditions yielded compound **3**. This compound reacted with pyridine in cold to give a light green product **4**. It also reacted with NH_3 to give a light green compound **5**. Their analytical results are given in Table I.

Elemental analysis: Chromium was estimated volumetrically. Chlorine was estimated gravimetrically as AgCl by fusing the compounds with Na_2CO_3 and KOH. Carbon, hydrogen and nitrogen were estimated microanalytically.

Infrared measurements of the compounds were made on Perkin-Elmer 621 grating spectrophotometer using KBr pellets and as nujol mulls. Magnetic measurements were carried out at room temperature on a Gouy balance calibrated with

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Table I. Analytical results.

Compound	Cr [%]		Cl [%]		Analytical data C [%]		H [%]		N [%]	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
$\text{C}_{10}\text{H}_{13}\text{O}_{21}\text{Cr}_3$ (1)	25.34	24.96			18.91	19.20	2.15	2.08		
$\text{C}_7\text{H}_{16}\text{O}_{15}\text{N}_3\text{Cr}_3$ (2)	28.84	29.00			15.42	15.61	3.12	2.97	8.14	7.81
$\text{C}_{18}\text{H}_{30}\text{O}_{19}\text{Cr}_3\text{Cl}$ (3)	20.83	21.04	5.04	4.79	28.71	29.13	3.97	4.05		
$\text{C}_{27}\text{H}_{33}\text{O}_{13}\text{N}_3\text{Cr}_3\text{Cl}$ (4)	19.21	19.54	4.13	4.44	38.92	40.58	4.06	4.13	5.14	5.26
$\text{C}_{12}\text{H}_{27}\text{O}_{13}\text{N}_3\text{Cr}_3\text{Cl}$ (5)	26.12	25.47	5.46	5.80	22.42	23.51	4.32	4.41	7.12	6.87

Hg[Co(NCS)₄]. Thermal analysis was carried out by means of a MOM Budapest Derivatograph (type Páulik, Paulik and Erdey) at a rate of 5 °C/min and covering temperature range between 20–500 °C.

Results and Discussion

Chromyl chloride is a strong oxidant and oxidizes formic and acetic acids and is itself reduced to (+3) oxidation state. This is suggested by the green colour of the compounds and confirmed by their analytical and magnetic measurements. Basic carboxylate complexes of chromium in the oxidation state (+3) generally adopt the oxygen centered trinuclear structure [Cr₃O(OOCR)₆L₃]⁺ 4–7. Each pair of chromium atoms are bridged by two carboxylato groups. The compounds

C₁₀H₁₃O₂₁Cr₃ (1), C₇H₁₆O₁₅N₃Cr₃ (2),
C₁₈H₃₀O₁₉Cr₃Cl (3), C₂₇H₃₃O₁₃N₃Cr₃Cl (4) and
C₁₂H₂₇O₁₃N₃Cr₃Cl (5)

are better represented as

[Cr₃O(OOCH)₆(HCOOH)₃](OOCH),
[Cr₃O(OOCH)₆(NH₃)₃](OOCH),
[Cr₃O(OOCCH₃)₆(CH₃COOH)₃]Cl,
[Cr₃O(OOCCH₃)₆(C₅H₅N)₃]Cl and
[Cr₃O(OOCCH₃)₆(NH₃)₃]Cl,

respectively. Compounds 1 and 3 are insoluble in common organic solvents *viz.* benzene, carbontetrachloride, methylene chloride, nitrobenzene, nitromethane and acetonitrile which indicates that these may be polymeric probably through intercluster hydrogen bonding. Compound 3 is, however, soluble in more basic solvents such as methanol, formamide and dimethylformamide. This may either be explained in terms of the less extensive intercluster bridging or it may be attributed to its dissociation in these media whereby weakly basic acetic acid may have been displaced by the more basic solvent molecules. The molar conductance values at millimolar concentrations are 56 and 35 ohm⁻¹cm²mol⁻¹ in methanol and dimethylformamide respectively. The values are less than those reported for univalent electrolytes⁸, but these are quite significant. This may not be taken to indicate an ionic type of structure but may, however, be explained in terms of formation of ionic species due to the liberation of acetic acid in basic media. Both compounds 1 and 3 are soluble in their parent acids and surprisingly their solutions are conducting. Further observation that compound 1 reacts with ammonia to give compound 2 but fails to react with

bases such as pyridine and γ -picoline may be attributed to steric reasons alone.

Both compounds 1 and 3 are paramagnetic having magnetic moments 2.05 and 2.12 BM, respectively, at room temperature. The low values of their magnetic moments suggest that these are magnetically concentrated. These observations are in accord with the earlier observed magnetic moment values for similar trinuclear compounds^{9,10}.

The infrared spectra of these compounds are quite complex as is expected of their trinuclear formulations. Both compounds 1 and 3 (Table II) show strong bands in the region 3500–3200 cm⁻¹ characteristic of ν O–H $\cdots$ O. We assign bands at 1550 cm⁻¹ (1) and 1545 cm⁻¹ (3) and 1360 cm⁻¹ (1) and 1430 cm⁻¹ (3) to ν (COO⁻)_{asym.} and ν (COO⁻)_{sym.} stretching modes, respectively, of the bridging carboxylate groups. These bands are broad perhaps either because of more than one type of carboxylate groups or other absorptions such as δ OH, δ CH₃, are overlapping in these regions. The $\Delta\nu$ (COO⁻) values are comparable to those observed for many transition metal carboxylates. The presence of bands at 1705 and 1620 cm⁻¹ (1) correspond to lowered ν C=O of the coordinated formic acid which in pure monomeric form is observed at 1770 cm⁻¹ and in dimeric acid at 1754 cm⁻¹ 11. Similarly the bands at 1700 cm⁻¹ and 1625, 1610 cm⁻¹ in compound 3 are also assigned to ν C=O of the coordinated acetic acid which is observed at 1799 and 1752 cm⁻¹ in monomeric and dimeric acetic acid respectively¹². The presence of two distinct bands due to ν C=O suggests that the coordinated acid may be present in different environments. If the three acid molecules were equivalent we may have observed a single ν C=O band. The low frequency bands (below 500 cm⁻¹) which cannot be assigned to interval vibrations of the carboxylate groups have been assigned to the chromium oxygen stretching mode¹³.

The infrared spectra of 2 and 5 are similar in many respects to their parent compounds 1 and 3, respectively. The most important difference is the absence of bands at 1705 and 1620 cm⁻¹ in 2 and at 1700, 1625 and 1610 cm⁻¹ in 5, which suggests the absence of coordinated acid molecules. The bands at 1580–1550 cm⁻¹ and 1355 cm⁻¹ (2) and at 1600–1570 cm⁻¹ and 1420 cm⁻¹ (5) may be assigned to ν (COO⁻)_{asym.} and ν (COO⁻)_{sym.} bands, respectively. The broad nature of the asymmetric bands may be attributed to the overlap of δd (NH₃) absorption

Table II. Infrared spectral bands (cm^{-1}) and their assignments in compounds **1**, **2**, **3** and **5**.

Assignments	1	2	3	5
$\nu\text{O}-\text{H}\cdots\text{O}$	3500–3200 vsb		3500–3200 vsb	
$\nu(\text{NH}_3)$		3200–3080 s		3250–3050 s
$\nu\text{C}=\text{O}$	1705 sh, 1620 sb		1700 sh, 1625 s, 1610 s	
$\nu(\text{COO}^-)_{\text{asym.}}$	1550 sb	1580–1550 sb	1545 sb	1600–1570 sb
$\nu(\text{COO}^-)_{\text{sym.}}$	1360 s	1355 s	1430 m	1420 s
δCH_3			1480 m, 1445 m, 1355 w	
$\delta_s(\text{NH}_3)$		1300 s		1242 m
δOH			1265 w	
$\nu\text{C}-\text{O}$	1180 sh		1280 sh	
ρCH_3			1045 m	1030 m
$\pi(\text{CH})$ or $\pi(\text{COO})$	1045 w	1050 w	620 w	615 m
$\nu(\text{C}-\text{C})$			958 w	950 w
$\delta(\text{OCO})$	760 m	768 m	680 s	670 s
τCC			660 s	660 s
?	630 m, 620 m	630 m, 620 m		
$\nu\text{M}-\text{O}$	450 s, 410 m	460 s, 410 m	440 s, 410 m	425 s, 395 m
$\delta\text{M}-\text{O}$	330 m	340 m	280 m	275 m

vsb = very strong and broad; sb = strong and broad; s = strong; m = medium; sh = shoulder; w = weak.

which is normally observed in the region 1610 to 1580 cm^{-1} ¹⁴. The infrared spectrum of compound **4** also reveals that the acetic acid molecules in **3** have been substituted by pyridine. The band at 1700 cm^{-1} in **3** is now missing. The disappearance of the other two bands at 1625 and 1610 cm^{-1} , due to $\nu\text{C}=\text{O}$ vibrations, could not be ascertained because of the presence of bands near 1600 cm^{-1} in coordinated pyridine. A group of five bands between 990 to 1217 cm^{-1} in pure pyridine are observed with slight changes in coordinated pyridine¹⁵. These have now been observed at 1019, 1032, 1045, 1072 and 1152 cm^{-1} . Another important change is the appearance of the band at 1240 cm^{-1} which is observed between $1235\text{--}1250\text{ cm}^{-1}$ in the spectra of pyridine complexes.

The TG and DTG curves recorded in the presence of air show the thermal decomposition of these compounds as a process consisting of several steps. By projecting the DTG minima (not shown here) on the TG curves, we have shown various inflexion points. By this way we can state without difficulty the extent of the weight changes belonging to each transformation. Compound **1** (Fig. 1, curve A) loses two molecules of formic acid separately in two steps. On heating beyond 250°C the entire volatile component is lost and intermediate corresponding to the formation of $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is formed. Above 375°C water is also lost and the final residue Cr_2O_3 is obtained. The first step in the thermal decomposition of **3** (curve B) corresponds to a loss of one

molecule of acetyl chloride which is complete at 160°C . Above this temperature the entire organic mass volatilizes away leading to the formation of $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ at 450°C . The final residue Cr_2O_3 , is obtained at 500°C . Different modes of thermal decomposition of acid molecules support the earlier hypothesis that all the acid molecules are not in similar environment. Compound **4** (curve C) loses three pyridine molecules in three separate steps between 40 to 230°C . The final residue is again Cr_2O_3 . The last but one level between 230 to 360°C cannot be interpreted in spite of the fact that it is reproducible. It is quite obvious that the intermediate $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is not formed in this compound.

Fig. 1. Thermal decomposition of compounds **1**, **3** and **4**.

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