Basic Chromium(III) Carboxylates: Reactions of Chromium(III) Chloride with Some Carboxylic Acids

Ramesh Kapoor* and Ramneek Sharma
Department of Chemistry, Panjab University, Chandigarh-160014, India

Z. Naturforsch. 34b, 1369–1372 (1979); received July 10, 1979

Chromium(III) Chloride, Basic Chromium(III) Carboxylates, IR, Magnetic Moment

Anhydrous chromium(III) chloride reacts with pure carboxylic acids (RCOOH where R = CH3, C2H5, n-C3H7, CH2Cl, CHCl3 and CCl4) to give basic trinuclear chromium(III) carboxylates of the general formula [Cr3O(OOCHR)6]Cl4. The reaction of CrCl3 with acetic anhydride, however, gives a partially substituted product, CrCl3(OOCCH3)2. The formation of basic carboxylates has been attributed to the strong affinity of Cr3+ ions for water that they can abstract it even from pure carboxylic acids. Their addition compounds with ammonia have also been prepared. The compounds have been characterized by their elemental analyses, IR, molar conductance and magnetic measurements.

Introduction

Reactions of vanadium(III) and chromium(III) chlorides with boiling glacial acetic acid [1] have been reported to give V3(OH)(OOCCH3)6 and Cr3(OH)(OOCCH3)8, respectively. The formation of V3(OH)(OOCCH3)6 was later confirmed by Bennett and Nicholls [2] who preferred to represent it as H3[V3O(OOCCH3)6] on the basis of its IR studies. Thornton et al. [3], however, suggested a trinuclear formulation, [V3O(OOCCH3)6(OOCCH3)2(H2O)]+ for this compound since it had a low magnetic moment value as compared to a free V3+ ion. So far no attempt has been made to reinvestigate the analogous Cr3+ compound. Our recent studies on the reaction of CrCl3 with formic acid reveal the formation of a basic trinuclear complex [4] and not Cr(OOCH)3 as had been suggested earlier [1]. In this paper, reactions of chromium(III) chloride with some carboxylic acids are reported.

Experimental

Anhydrous chromium(III) chloride was prepared by treating hydrated chromium(III) chloride (AnalaR) with excess of thionyl chloride at room temperature. It was refluxed for about 10–12 h. The reaction ceased when the colour of the product changed from green to violet. It was filtered, washed repeatedly with dry CCl4 and dried in vacuo.

CrCl3

<table>
<thead>
<tr>
<th>Found</th>
<th>Cl 66.9</th>
<th>Cr 32.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcd</td>
<td>Cl 67.2</td>
<td>Cr 32.8</td>
</tr>
</tbody>
</table>

* Reprint requests to Dr. R. Kapoor.

0340–5087/79/1000–1369/$ 01.00/0

The carboxylic acids were purified by distillation as described by standard methods.

Reactions of CrCl3 with carboxylic acids

All reactions were carried out in three-necked flasks. The flasks were fitted with a graduated dropping pipette, a reflux condenser and a gas-inlet tube for the passage of dry N2 gas during the reaction. All efforts were made to exclude moisture. The reflux condenser was connected by glass tubing to a mercury bubbler, which in turn was connected to a bubbler containing silver nitrate solution. In a typical experiment pure acetic acid (300 mmole) diluted with CCl4 (50 cm3) was slowly added to CrCl3 (30 mmole) at —10 °C. The temperature was slowly allowed to rise when a dark violet solution was obtained. At room temperature, there was very slow evolution of HCl gas but on refluxing on a water bath, a steady flow of HCl gas occurred at that temperature. The colour of the solution changed from violet to green in 15–20 min and after about 4 h the evolution of HCl gas had completely ceased. The solvent and excess of acetic acid were removed by vacuum distillation, when a green precipitate (1) was obtained in the flask. It was filtered, washed with CCl4 and petroleum ether (40–60 °C) and dried in vacuo. Similarly, reactions of CrCl3 with propionic, n-butyric, monochloroacetic, dichloroacetic and trichloroacetic acids were carried out to give compounds 2–6.

The partially substituted product, C4H6O2CrCl3 (7) was prepared by refluxing CrCl3 with the solution of acetic anhydride in CCl4 for about 8–10 h. The compound was washed with excess CCl4 and dried in vacuo.

Reactions of these compounds with ammonia were carried out by bubbling dry NH3 gas through the suspension of these compounds in CCl4 for about 2 h.

Chromium and chlorine were estimated gravimetrically as Cr2O3 and AgCl, respectively. Carbon, hydrogen and nitrogen were estimated microanalytically. Infrared spectra of the compounds...
were recorded as nujol and hexachlorobutadiene films in NaCl and CsI plates on a double beam grating spectrophotometer 621. Magnetic measurements were made at room temperature by Gouy's method with Hg[Co(NCS)4] as standard. Thermal analysis was carried out on a MOM Budapest Derivatograph. The analytical results along with some of their physical properties are given in Table I. Compounds 1–6 are green in colour, the intensity of the colour increases from acetate to butyrate but decreases regularly with increase in chlorine substitution on the methyl groups. Compound 7 is greyish green in colour.

**Results and Discussion**

Interactions of Lewis acids with carboxylic acids have been investigated mainly in solutions by various physico-chemical techniques [5]. The metal chlorides generally undergo solvolysis and very few stable addition compounds have been isolated.

Interaction of chromium(III) chloride with RCOOH (where R = CH₃, C₆H₅, n-C₃H₇, CH₂Cl₂ and CCl₃) diluted with carbontetrachloride at low temperatures (−10 °C) do not give any stable addition compounds. On refluxing, solvolysed products with empirical formulations from 1–6 are obtained with the loss of HCl gas.

Reaction of CrCl₃ with anhydrous acetic acid yields a green compound, C₁₂H₁₅O₁₃Cr₂Cl₃ (I). However, the product reported in literature corresponds to C₁₅H₂₅O₁₇Cr₃ and has been represented as Cr₃(OH)(OOCCH₃)₆ [1]. Our analytical results (Table I) clearly show that chlorine atoms of CrCl₃ are not completely replaced. Compound I was refluxed with fresh acetic acid for another 4–6 h, but the product still contained chlorine and its analysis again corresponded to I. Funk et al. [1] had used glacial acetic acid, which contained some

Table I. Analytical results and physical properties of basic chromium(III) carboxylates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Analytical results [%]**</th>
<th>Physical properties</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr</td>
<td>Cl</td>
<td>C</td>
</tr>
<tr>
<td>C₁₂H₁₅O₁₃Cr₂Cl₃ (1)</td>
<td>26.1</td>
<td>6.8</td>
<td>23.46</td>
</tr>
<tr>
<td>C₁₅H₂₅O₁₇Cr₃ (2)</td>
<td>25.0</td>
<td>4.9</td>
<td>33.82</td>
</tr>
<tr>
<td>C₂₄H₄₉O₁₅Cr₃Cl</td>
<td>20.6</td>
<td>4.5</td>
<td>38.40</td>
</tr>
<tr>
<td>C₁₂H₁₂O₁₆Cr₃Cl₇ (4)</td>
<td>19.2</td>
<td>3.1</td>
<td>17.69</td>
</tr>
<tr>
<td>C₁₂H₆O₁₄Cr₂Cl₃ (5)</td>
<td>15.9</td>
<td>4.6</td>
<td>15.31</td>
</tr>
<tr>
<td>C₁₂O₁₅CrCl (6)</td>
<td>12.8</td>
<td>5.5</td>
<td>12.36</td>
</tr>
<tr>
<td>C₆H₆O₄CrCl (7)</td>
<td>24.0</td>
<td>15.7</td>
<td>22.84</td>
</tr>
</tbody>
</table>

Adduct                      | Colour         | Analytical results [%]** | Cr  | Cl  | N    |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₂H₂₇O₁₃N₃₅Cr₅Cl (8)</td>
<td>light green</td>
<td>24.2</td>
<td>5.4</td>
<td>6.23</td>
<td></td>
</tr>
<tr>
<td>C₁₅H₂₅O₁₇N₄₅Cr₅Cl (9)</td>
<td>—do—</td>
<td>21.2</td>
<td>4.8</td>
<td>6.18</td>
<td></td>
</tr>
<tr>
<td>C₂₄H₄₉O₁₅N₃₅Cr₃Cl (10)</td>
<td>—do—</td>
<td>18.9</td>
<td>5.0</td>
<td>5.21</td>
<td></td>
</tr>
<tr>
<td>C₁₂H₃₉O₁₃N₅₅Cr₇Cl (11)</td>
<td>greyish green</td>
<td>16.8</td>
<td>26.8</td>
<td>11.80</td>
<td></td>
</tr>
<tr>
<td>C₁₂H₃₉O₁₃N₅₅Cr₇Cl (12)</td>
<td>violet</td>
<td>13.0</td>
<td>41.6</td>
<td>9.04</td>
<td></td>
</tr>
<tr>
<td>C₁₂H₂₄O₁₃N₅₅Cr₇ Cl (13)</td>
<td>violet</td>
<td>10.2</td>
<td>49.3</td>
<td>8.15</td>
<td></td>
</tr>
</tbody>
</table>

* In methanol (the values required for 1:1 electrolytes fall in the range 80–115 cm²·ohm⁻¹·mole⁻¹ [8]). ** Required values are given in the parentheses.
water and this probably led to the formation of a completely solvolyzed product. Compound 1 can be represented as [Cr₃O(OOCC₂H₅)₆]⁺Cl⁻ by analogy to the known basic trinuclear Cr³⁺ acetate [6]. In spite of perfectly anhydrous reagents and dry conditions, we always obtained the basic salts and not pure Cr³⁺ carboxylates. This would suggest that Cr³⁺ ions are abstracting water from carboxylic acids. In a separate experiment, chromium(III) chloride was refluxed with acetic acid, the volatile products were trapped and traces of acetyl chloride were isolated. Similarly, traces of acid chlorides were also recovered on distillation of reaction mixtures of other reactions. It is difficult to understand the exact mode of production of water in the system, but by analogy to the reported reaction of iron(III) chloride in acetic acid [7], the following equilibrium may be assumed,

\[ 2 \text{CH}_3\text{COOH} \rightleftharpoons \text{H}_2\text{O} + \text{CH}_3\text{CO}^+ + \text{CH}_3\text{COO}^- \]

which in the presence of Cr³⁺ ions due to their strong affinity for water becomes significant. Anhydride formation

\[ 2 \text{CH}_3\text{COOH} \rightleftharpoons (\text{CH}_3\text{CO})_2\text{O} + \text{H}_2\text{O} \]

is unlikely since in our investigations no traces of free acetic anhydride could be observed. In order to further understand this system, the reaction of CrCl₃ with acetic anhydride was studied. A simple partially substituted product, CrCl(OOCC₂H₅)₂ (7) was obtained. It is, therefore, obvious that water is being abstracted from the carboxylic acids by Cr³⁺ ions. 2–6 may similarly be represented as,

\[
\begin{align*}
\text{[Cr}_3\text{O(OOCC}_2\text{H}_5)_6]^{+}\text{Cl}^- \quad (2), \\
\text{[Cr}_3\text{O(OOCC}_2\text{H}_7)_6]^{+}\text{Cl}^- \quad (3), \\
\text{[Cr}_3\text{O(OOCC}_2\text{H}_5\text{Cl)}_6]^{+}\text{Cl}^- \quad (4), \\
\text{[Cr}_3\text{O(OOCC}_2\text{Cl)}_6]^{+}\text{Cl}^- \quad (5), \\
\text{[Cr}_3\text{O(OOCC}_2\text{Cl)}_6]^{+}\text{Cl}^- \quad (6),
\end{align*}
\]

Compounds 1–6 are only slightly hygroscopic. They are insoluble in common organic solvents such as CC₄, C₆H₆, C₆H₅NO₂, CH₃NO₂, CH₅CN and except 6 they all dissolve in methanol. They are also soluble in their respective parent acids. At molar concentrations, their molar conductance values in methanol are fairly close to those expected for 1:1 electrolytes [8]. Compound 7 is insoluble in all the solvents mentioned above.

The compounds are paramagnetic having magnetic moments between 2.45 to 2.75 BM at room temperature. These values are significantly lower from the value expected for a high spin Cr³⁺ ion. They are in the same range as observed for similar trinuclear Cr³⁺ carboxylates [6]. Compound 7 has a room temperature magnetic moment of 3.10 BM which is also lower than the value expected for a free Cr³⁺ ion. Probably 7 is a polymeric compound with significant Cr–Cr interaction through bridging acetato groups. This is also suggested by its insoluble nature.

The IR spectrum of each of the complexes has been measured and the bands are presented in Table II. The band assignments have been made by comparison with the spectrum of sodium salt of the parent acid [9]. The difference (\(\Delta \nu\)) between \(\nu_a(\text{COO}^-)\)

<table>
<thead>
<tr>
<th>Assignments</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_a(\text{COO}^-))</td>
<td>1605 s, 1600 s, 1605–1595 sb, 1640–1620 sb, 1660 s, 1700 m, 1740 m, 1745 sh, 1705 sb, 1580 w, 1575 m, 1560 s, 1550 s, 1540 s</td>
<td>1540 s, 1530 m, 1530 m, 1555 s, 1620 s, 1670 m, 1650 w, 1605 s, 1600 s, 1605–1595 sb, 1640–1620 sb, 1660 s, 1740 m, 1745 sh, 1705 sb, 1580 w, 1575 m, 1560 s, 1550 s, 1540 s</td>
<td>800 m</td>
<td>800 m</td>
<td>800 m</td>
<td>800 m</td>
<td>800 m</td>
</tr>
<tr>
<td>(\nu_b(\text{COO}^-))</td>
<td>1450 s, 1440 s, 1425 mb, 1440 s, 1410 s, 1400 s, 1410 s</td>
<td>960 m, 965 m, 980 m, 980 s, 930 m</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
</tr>
<tr>
<td>(\nu(\text{CC}))</td>
<td>952 m</td>
<td>960 m, 965 m, 980 m, 980 s, 930 m</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
</tr>
<tr>
<td>(\nu_a(\text{CCX}))</td>
<td>1075 m, 1100 m, 805 m, 800 m</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
</tr>
<tr>
<td>(\nu_a(\text{CCl}))</td>
<td>805 m, 800 m</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
<td>820 s, 860 s, 830 s, 760 s, 750 s</td>
</tr>
</tbody>
</table>

Table II. Some characteristic vibrational bands (cm⁻¹) of compounds 1–7.
and \( \nu(CO_2^-) \) frequencies has been extensively used in the structure elucidation of metal carboxylates since \( COO^- \) stretching frequencies have been observed to be sensitive to coordination to a metal. The bands around 1600 cm\(^{-1}\) or at higher wave numbers are assigned to \( \nu(CO_2^-) \) mode of bidentate carboxylate groups. These bands are observed at a higher region than expected for a free carboxylate ion and may also suggest the presence of coordinated carboxylic acid. But this is ruled out as no band is observed above 3000 cm\(^{-1}\) which may be attributed to \( \nu(0H) \) of the carboxylic acid. The \( \Delta \nu(CO_2^-) \) values are suggestive of the presence of bridging carboxylato groups. The symmetrical nature of the spectra are also in accord with the proposed tri-nuclear representations. The bands below 450 cm\(^{-1}\) may be assigned to \( \nu(Cr-O) \) modes arising due to the bonding of carboxylate groups to Cr atom. The appearance of weak to medium intensity bands around 1745, 1706, 1650 and 1605 cm\(^{-1}\) which may be assigned to coordinated acetic anhydride [11]. These bands persisted even when 7 was repeatedly washed with carbon tetrachloride and kept under a vacuum of 10\(^{-4}\) Torr for 24 h. Our analytical results are also suggestive of the presence of a small fraction of \( Ac_2O \) per chromium atom. The results are in better agreement if 1/6 \( Ac_2O \) is attached to 7. The required values are: Cr 23.4, Cl 15.9 and C 25.17%.

The TG–DTG curves of these compounds show that their decomposition takes place in a single step. They begin to lose weight on heating above 50 °C; the loss is slow at the beginning but becomes rapid around 250 °C and the formation of the final residue \( Cr_2O_3 \) is complete near 550 °C. The total weight loss value in each case is in agreement with the value calculated on the basis of their proposed formulations.

Compounds 1, 2 and 3 react with \( NH_3 \) to give 8, 9 and 10, respectively. These compounds may be represented as,

\[
[Cr_2O(OOCCH_3)_{6}(NH_3)_3]Cl \quad (8), \\
[Cr_2O(OOCCH_2)_{6}(NH_3)_3]Cl \quad (9), \quad \text{and} \\
[Cr_2O(OOCCH_2H_2)_{6}(NH_3)_3]Cl \quad (10).
\]

The chloroacetates 4, 5 and 6 give products 11, 12 and 13 which may be formulated as,

\[
[Cr_3O(OOCCH_2Cl)_{6}(NH_3)_3]Cl, 5 NH_3 \quad (11), \\
[Cr_3O(OOCCHCl_2)_{6}(NH_3)_3]Cl, 5 NH_3 \quad (12), \quad \text{and} \\
[Cr_3O(OOCCHCl_3)_{6}(NH_3)_3]Cl, 5 NH_3 \quad (13),
\]

respectively. The IR spectra of these compounds retained all those bands which were observed in their parent compounds and in addition some new bands at around 3250 and 3130–20 cm\(^{-1}\) which may be assigned to coordinated \( NH_3 \) have also been observed.