Low temperature reactions of chromyl chloride with disodium tetracarbonylferrate and sodium cyclopentadienyl-dicarbonylferrate—Synthesis of two new chromium iron cluster complexes

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Chromyl chloride reacts with disodium tetracarbonylferrate and sodium cyclopentadienyl-dicarbonylferrate in THF-CHCl₃ at -40°C to give two new chromium-iron cluster complexes, [CrO₂Fe(CO)₄] (I) and [CrO₂(Fe(η⁵-C₅H₅)(CO)₂)] (II) respectively. The complexes have been characterized on the basis of elemental analysis, IR, NMR and mass spectral data.

Chromyl chloride is a strong oxidizing agent and gives various exothermic reactions with most organic and organometallic reagents. At ordinary temperatures these reactions may be explosive but at low temperatures, controlled reactions can be carried out safely. A few organo-derivatives of Cr(VI) are known, e.g., [CrO₂py]³⁺, [CrO₂(CO)₂] and [CrO₂(dipy)]⁶⁻. The literature survey reveals that Cr⁶⁺-M metal complex has not yet been synthesised. Since Cr-Cl bond is very reactive, it seems interesting whether any Cr⁶⁺-M bonded complex could be prepared at very low temperatures from CrO₂Cl₂. We therefore, attempted two reactions of CrO₂Cl₂ with Na₂[Fe(CO)₄] and Na[Fe(η⁵-C₅H₅)(CO)₂] at -40°C in THF-CHCl₃ mixture.

Experimental
The reactions were carried out under dry nitrogen atmosphere. The solvents were dried and distilled prior to use. The IR spectra were recorded on a PE983 spectrophotometer, PMR spectra in CDCl₃ on a Bruker AM-300 spectrometer and mass spectra on a VG ZAB F-1 instrument. Chromyl chloride was commercially available. The compounds Na₂[Fe(CO)₄] and Na[Fe(η⁵-C₅H₅)(CO)₂] were prepared following published procedures.

![Proposed structure for [CrO₂Fe(CO)₄](I)](image-url)

Reaction of CrO₂Cl₂ with Na₂[Fe(CO)₄]—Formation of the new cluster complex (I)
Na₂[Fe(CO)₄] (1.44 g, 6.7 mmol) dissolved in THF (60 cm³) was cooled to -40°C using a dry ice/acetone bath and a solution of CrO₂Cl₂ (1.04 g, 6.7 mmol) in CHCl₃ (20 cm³) was added dropwise to it with constant stirring. Dense white fumes were observed inside the flask and the solution turned dark brown. Stirring was continued for about 2 h at -40°C, the mixture then slowly warmed to room temperature and solvent was removed under reduced pressure to yield a dark brown mass which was extracted with pet. ether (40-60°C, 60 cm³). The extract was filtered through Kieselguhr and the filtrate on removal of solvent gave a reddish brown solid. The TLC examination (pet. ether/alumina) showed it to be a mixture of two compounds. The solid was then chromatographed on an alumina (70-230 mesh) column and eluted with pet. ether (40-60°C) which gave two distinct bands, one reddish brown and the other green. They were collected separately and removal of solvent gave a reddish brown and a greenish black solid. The latter was identified as Fe₃(CO)₁₂ from its m.p. (140°C) and IR spectrum (νCO 1828, 1858, 1995, 2019 and 2044 cm⁻¹). The reddish brown solid, m.p. 110-112°C (dec.), yield 0.65 g, 38.4%, was characterized to be the new chromium-iron cluster complex (I). A similar reaction between CrO₂Cl₂ and Na[Fe(η⁵-C₅H₅)(CO)₂] in 1:2 molar ratio gave the cluster complex (II) in 52% yield as a purple black crystalline solid, m.p. 152-154°C (dec.).

Results and discussion
The reaction between CrO₂Cl₂ and Na₂[Fe(CO)₄] in THF-CHCl₃ mixture at -40°C gave the cluster complex (I) for which the structure shown (Structure I) is proposed on the basis of its IR and mass spectra.
The IR spectrum of (I) in CH$_2$Cl$_2$ gave three sharp bands at 1913(m), 1983(sh) and 2000(vs) cm$^{-1}$ which are characteristic of terminal CO stretching frequencies. The mass spectrum of (I) clearly showed the molecular ion peak and the expected fragmentation pattern. The prominent peaks are at m/z 504[M$^+$], 476[M-CO$^+$], 448[M-2CO$^+$], 364[M-2CO-CrO$_2$$^+$], 336[M-3CO-CrO$_2$$^+$], 308[M-4CO-CrO$_2$$^+$], 280[M-5CO-CrO$_2$$^+$], 252[M-6CO-CrO$_2$$^+$], 196[M-6CO-CrO$_2$-Fe$^+$], 168[M-7CO-CrO$_2$-Fe$^+$], 140[M-8CO-CrO$_2$-Fe$^+$] and 117[Fe(CO)$_3$. A peak at m/z 399 corresponding to loss of one cyclopentadienyl fragment from the molecular ion was also observed in the spectrum. The formulation (II) is also consistent with the results of C,H analysis [Found: C, 37.82; H, 2.34; Reqd. for C$_{14}$H$_{16}$O$_2$Fe$_2$Cr, C, 38.35; H, 2.28%]. Thus the existing evidences suggest that complex (II) is formed in this reaction according to Eq. (2).

\[
\text{CrO}_2\text{Cl}_2 + 2 \text{Na}_2[\text{Fe} (\eta^5-\text{C}_5\text{H}_5)](\text{CO})_2] \rightarrow \text{CrO}_2[\text{Fe} (\eta^5-\text{C}_5\text{H}_5)](\text{CO})_2]_2 + 2 \text{NaCl}
\]  

The complexes are soluble in most of the common organic solvents including pet. ether and diethyl ether. They are not very stable and slowly decompose even when stored under nitrogen at 0°C and turn black in about a month. We have assigned an oxidation state of VI to chromium in these cluster complexes but this may not be actually so. The bond between iron and chromium atom should in any probability be covalent and in that case chromium should have a formal oxidation of IV, chromium atom in CrO$_2$Cl$_2$ having been subjected to reduction by iron carbonylate ions.

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References