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# SPECTROSCOPIC CHARACTERIZATION OF SOME CHROMIUM O-ALKYLDITHIOCARBONATES

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***ABSTRACT***. Four chromium O-alkylditiocarbonates, with the general formula $Cr(S_2COR)_3$, where R = methyl, ethyl, i-propyl and metoxiethyl, were prepared and characterized by elemental analysis, IR and UV-VIS spectra. All the compounds show a reduced thermal stability and decomposition was observed on heating. The $CrS_6$ cromophores exhibit a distorted octahedral geometries. The transition $^4T_{1g}(P) \leftarrow\!\!-\!\!-\!\!- {}^4A_{2g}(F)$ was not solved, the calculated value lies in the range 33.600 - 33.930 $cm^{-1}$. The nephelauxetic parameter, with values from 0.428 to 0.445 suggests, as expected, a high degree of covalency. The same conclusion results from EPR spectra. The IR spectra showed strong absorption bands at 1260-1230 $cm^{-1}$ ($\nu$OC), which certified an important contribution of resonance form $^{-2}S_2CO^{+}$-R to the resonance hybrid. On the basis of these values a high degree of covalency was estimated (0,74 - 0,86), also.

## INTRODUCTION

O-alkyldithiocarbonates of transition metals and main group elements was studied in detail and revised [1,2]. The overall structure of these compounds is a resonance hybrid of canonical forms presented in figure 1.

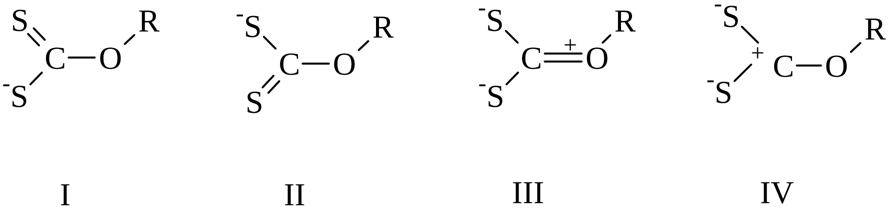

Figure 1. Canonical forms of xanthate moiety.

Chromium O-alkyldithiocarbonates were the subject of synthesis studies [3,4] and they were studied by electronic [5,6] and infrared spectra [7,8]. A number of X-ray structure analyses have become available [9,10]. In an attempt to find more information about chromium xanthates, we prepared four compounds with the general formula $Cr(S_2COR)_3$, where R = $-CH_3$, $-C_2H_5$, $-^iC_3H_7$ and $-CH_2CH_2-OCH_3$ and we investigated them by electronic, infrared and EPR spectra.

## RESULTS AND DISCUSSION

The compounds were prepared by mixing the aqueous solutions of $Cr(NO_3)_3 \cdot 9H_2O$ and the corresponding potassium xanthates. The yield was rather low, because during the precipitation of the compounds, a partial decomposition of the xanthate ligand occurred. The complexes were studied by elemental analysis, electronic, IR and EPR spectra. The yields, melting points and elemental analysis data are listed in Table 1.

The yields of chromium(III) xanthates were lower than in the other cases, the presence of chromium(III) nitrate leading to the decomposition of the desired compounds. During the study of the thermal behavior of chromium(III) xanthates, decomposition was observed on heating. This is suggested by color change of the compounds and by release of gas bubbles. As can be seen in table 1, the melting points decrease with the increase of the number of carbon atoms in the organic radical. On the other hand, the decomposition of chromium complexes is quite different: $Cr(S_2COCH_3)_3$ decompose to the melting point, but the decomposition points of $Cr(S_2COCH_2CH_3)_3$, $Cr(S_2COCH(CH_3)_2)_3$ and $Cr(S_2COCH_2CH_2OCH_3)_3$ are by 10, 40 and 50 degrees higher than the melting point.

## ELECTRONIC SPECTRA

The electronic spectra were recorded in aqueous solution for potassium xanthates and in acetone solution for chromium(III) xanthates. The results of electronic spectra are listed in Table 2. An increase of 10Dq parameter, which fits with the first transition, is observed, along with the increase of the chain of alkyl groups.

The two bands in the visible region were used in the calculation of the nephelauxetic parameter ($\beta$). The small value of this parameter covers a small range (0.425 -0.445) like in the other cases for $CrS_6$ cromophores [11-13]. This value certifies a high degree of covalency of the metal-sulfur bonds. On the basis of literature data [14], we have also approximated the position of the $\nu 3$ band corresponding to the $^4T_{1g}(P) \leftarrow\!\!-\!\!-\!\!- {}^4A_{2g}(F)$ transition (table 2) with values situated between 33660 and 33930 $cm^{-1}$. A rigorous assignment is not possible, because of the presence in the near environment of a strong band due to $\pi$-$\pi^*$ transition, characteristic of the xanthate moiety. On the other hand, the shoulder at 28700 -29400 $cm^{-1}$ region can be associated with $\nu 3$ band. The high value of the molar extinction coefficient, $\varepsilon$, is explained by the intensity transfer from the nearby $\pi$-$\pi^*$.

**Table 1.**

**Elemental Analysis and Some Properties of Compounds (*)**

| Compound | η (%) | Color | % Cr | | % S | | Thermal behavior (°C) |
|---|---|---|---|---|---|---|---|
| | | | calc. | found | calc. | found | |
| KMexn (147) | 85 | bright yellow | - | - | 43.53 | 41.75 | 205-210 melting with gas release 225-brown-redish; |
| Cr(Mexn)$_3$ (373) | 36.1 | indigo | 13.94 | 14.15 | 51.47 | 50.25 | 147-150 melting with gas release; |
| KEtxn (161) | 82 | white | - | - | 39.75 | 38.12 | 209 melting with gas release; 250-oil; |
| Cr(Etxn)$_3$ (415) | 21.68 | dark blue | 12.53 | 12.05 | 46.26 | 45.02 | 130-132 melt, the color becomes green; 145 gas release; |
| K$^i$Prxn (175) | 70.5 | white yellowish | - | - | 36.57 | 35.50 | 219 beige; 260 brown oil; |
| Cr($^i$Prxn)$_3$ (457) | 23.75 | blue-indigo | 11.37 | 11.82 | 42.01 | 40.85 | 121-122 melt, the color becomes green; 165 gas release; |
| KMeOEtxn (191) | 68.48 | white yellowish | - | - | 33.50 | 32.35 | 200-202 orange; 260 waxy oil; |
| Cr(MeOEtxn)$_3$ (505) | 19.8 | blue | 10.29 | 9.85 | 38.01 | 36.85 | 68-69 melt; 129-130 gas release; |

*)Mexn = O-methyldithiocarbonate; Etxn = O-ethyldithiocarbonate; $^i$Prxn = O-izo-propyldithiocarbonate; MeOEtxn = O-methoxyethyldithiocarbonate

We can also see (table 2) that the positions of π-π* and n-σ* bands decrease by coordination with values from 550 to 700 $cm^{-1}$ and from 7400 to 8540 $cm^{-1}$ respectively, printing out the electronic structure modifications in the ligand along with the formation of complex combinations as can be seen in table 3.

The distorted Oh geometry of the $CrS_6$ chromophore is suggested by the large ν1 and ν2 bands in the visible region. The values of the bands half widths are quite large (table 3). However, the bands are not split, so we can assume that the distortion is not so pronounced.

**Table 2.**

**Electronic spectra of Cr(III) O-alkyldithiocarbonates ***

| Compound | $^4T_{2g}(F)\leftarrow{}^4A_{2g}(F)$ $\nu_1$ (ε) | $^4T_{1g}(F)\leftarrow{}^4A_{2g}(F)$ $\nu_2$ (ε) | $^4T_{1g}(P)\leftarrow{}^4A_{2g}(F)$ $\nu_3$(calc) | B ($cm^{-1}$) (β) | $\pi\rightarrow\pi^*$ (ε) | $n\rightarrow\sigma^*$ (ε) |
|---|---|---|---|---|---|---|
| $Cr(Mexn)_3$ | 15974<br>$(1.77 \cdot 10^2)$ | 20449<br>$(1.82 \cdot 10^2)$ | 33661 | 410<br>(0.445) | 29428 u<br>$(3.6 \cdot 10^3)$<br>32573<br>$(1.57 \cdot 10^3)$ | 35842<br>$(1.138 \cdot 10^4)$ |
| $Cr(Etxn)_3$ | 16025<br>$(1.76 \cdot 10^2)$ | 20325<br>$(1.8 \cdot 10^2)$ | 33660 | 391<br>(0.425) | 28818 u<br>$(3.6 \cdot 10^3)$<br>32258<br>$(1.56 \cdot 10^4)$ | 35460<br>$(1.136 \cdot 10^4)$ |
| $Cr(^iPrxn)_3$ | 16080<br>$(1.75 \cdot 10^2)$ | 20480<br>$(1.78 \cdot 10^2)$ | 38825 | 402<br>(0.437) | 32240<br>$(1.50 \cdot 10^4)$ | 35652<br>$(1.31 \cdot 10^4)$ |
| $Cr(MeOEtxn)_3$ | 16160<br>$(1.71 \cdot 10^2)$ | 20480<br>$(1.77 \cdot 10^2)$ | 33932 | 394<br>(0.428) | 28735 u<br>$(3.8 \cdot 10^3)$<br>32258<br>$(0.919 \cdot 10^4)$ | 35974<br>$(1.30 \cdot 10^4)$ |

*) transitions ($cm^{-1}$) and ε ($l \cdot mol^{-1} \cdot cm^{-1}$)

**Table 3.**

**Some characteristic features of the bands from the electronic spectra**

| R | π-π* ($cm^{-1}$) | | Δ | n-σ* | | Δ | Δ ν1/2 | |
|---|---|---|---|---|---|---|---|---|
| | xanthate ion | complex | | xanthate ion | complex | | ν1 | ν2 |
| $-CH_3$ | 33200 | 32573 | 627 | 44320 | 35842 | 8478 | 5140 | 3575 |
| $-C_2H_5$ | 32800 | 32528 | 542 | 44000 | 35400 | 8600 | 4576 | 3000 |
| $-^iC_3H_7$ | 33040 | 32240 | 800 | 43400 | 34900 | 8500 | 4720 | 3200 |
| $-C_2H_4OCH_3$ | 32960 | 32258 | 702 | 44240 | 35971 | 8269 | 4862 | 2860 |

## INFRARED SPECTRA

IR spectra were recorded for both chromium(III) xanthates and the corresponding potassium xanthates. For $KS_2COCH_3$, $KS_2COCH_2CH_3$, $Cr(S_2COCH_3)_3$ and $Cr(S_2COCH_2CH_3)_3$ our IR spectra are similar to the literature spectra [7,8,15,16]. For the other compounds $KS_2CH(CH_3)_2$, $KS_2COCH_2CH_2OCH_3$, $Cr(S_2CH(CH_3)_3)_3$ and $Cr(S_2COCH_2CH_2OCH_3)_3$ there are no detailed studies of their IR spectra.

The IR spectra were interpreted by comparison with the results obtained by normal coordinate analysis on free and coordinated ion $^{-}S_2COCH_3$ [16,17]. The vibrational assignments for the absorption bands ($cm^{-1}$) of the infrared spectra are listed in table 4.

For $KS_2COCH_3$ and $Pt(S_2COCH_3)_2$ the potential energy distribution of the vibrational states is listed, considering only the components with a contribution higher than 10 %. It was found that almost all vibration are strongly coupled, so an interpretation of the IR spectra is very difficult to make.

When the IR spectra of chromium(III) xanthates are compared with those of potassium xanthates we can see a major change in the 1300 - 1200 $cm^{-1}$ region, where the νOC stretching is located (νOC is the stretching vibration of carbon-oxygen bond in the O-$CS_2$ group and νCO is the stretching vibration of carbon-oxygen bond in the R-O group).

**Table 4.**

**Vibration frequencies of $Cr(S_2COR)_3$ ($cm^{-1}$)**

| Assignments | (1) | (2) | (3) | (4) | (5) | (6) |
|---|---|---|---|---|---|---|
| $\nu_aCH_3$ | 2995 | 3020 | 3025 | 2995<br>(2953) | 2979 | 2987 |
| $\nu_sCH_3$ | 2937 | 2980 | 2939 | 2928 | 2930 | 2931 |
| $\delta_aCH_3$ | 1447 | 1455 | 1453 u | 1455 | 1459 | 1467 |
| $\delta_sCH_3$ | 1429 | 1442 | 1438 | 1446<br>1434 | - | 1440 |
| $\rho CH_3+\nu_aCS_2$ | 1189 | 1183 $\rho CH_3(61)$ +$\delta COC$ (17) | 1171 | 1143 | 1183 | 1187 |
| $\rho CH_3+\nu_a CS_2$ | 1114 | - | 1123 | 1119 | - | 1115 |
| $\nu CO(78)+$<br>$\nu OC(25)+$<br>$\nu_sCS_2(15)$ | 1055 | 1024 $\nu CO(36)+\nu_aCS_2(30)$<br>949 $\nu CO(71)+\nu_aCS_2(24)$ | 1037<br>942 | 1029 | 1034<br>934 | 1053<br>987<br>973 |
| $\nu OC(80)+$<br>$\nu CO(25)+$<br>$\nu_sCS_2(15)$ | 945 | 1290 $\nu OC(89)+\nu_sCS_2(17)$ | 1243 | 1274<br>1246 | 1268<br>1242 | 1247<br>1220 |
| $\nu_sCS_2(41)+$<br>$\delta COC(26)$ | 664<br>618 | 610 $\nu_sCS_2(45)+\nu_aCS_2(15)$ | - | 650 | 654 | 513 |
| $\gamma CS_2$ | 580 | 455 $\delta COC(30)+$<br>$\nu_aCS_2(25)+\nu_sCS_2(22)$ | 458 | 441 | 463 | |
| $\delta COC(28)+$<br>$\nu_sCS_2(28)+$<br>$\nu_aCS_2(12)$ | 472 | 364 $\nu_aPtS_2(89)$ | 376 | 397<br>359 | 391 | |
| $\delta CS_2(87)$ | 333 | 332 $\delta CS_2(97)+\nu_sPtS_2(45)$<br>291 $\nu_sPtS_2(77)$ | 324<br>- | 321<br>- | 321<br>- | |

1= $S_2COCH_3^{-}$; 2= $Pt(CH_3OCS_2)_2$; 3= $Cr(S_2COCH_3)_3$; 4= $Cr(S_2COC_2H_5)_3$;
5= $Cr(S_2CO^{i}C_3H_7)_3$; 6= $Cr(S_2COEtOCH_3)_3$

In the 1300-1200 $cm^{-1}$ region there are no bands for $KS_2COCH_3$ and $KS_2CH(CH_3)_2$ while for $KS_2COCH_2CH_3$ and $KS_2COCH_2CH_2OCH_3$ there are one and two bands respectively of low intensity. For the corresponding chromium(III) complexes this region is dominated by large and strong bands. The presence of these bands is correlated with the increase of double character of the O-C bond. This fact is confirmed by X-ray diffraction studies, which reveal in most of the cases of metallic xanthates, smaller values for O-C bonds length as compared to the length of C-O bonds. For $KS_2COCH_2CH_3$ the length of O-C and C-O bonds are 1.35 Å and 1.48 Å respectively and for $Cr(S_2COCH_2CH_3)_3$ the corresponding values are 1.297 Å and 1.471 Å respectively [9]. The increase of the O-C bond length as compared to the C-O bond length is correlated with a greater participation of the canonical form III (fig.1) to the overall structure. For $Cr(S_2COCH_2CH_3)_3$ the contribution of canonical form III was calculated to be 36 % [9]. The smaller the length of this band, the greater the participation of the limit structure III.

The positions of bands in the 1300-1200 $cm^{-1}$ region for chromium(III) complexes, as compared to the corresponding positions for potassium xanthates are the following:

| **R** | **$-CH_3$** | **$-CH_3CH_2$** | **$-CH(CH_3)_2$** | **$-CH_2CH_2OCH_3$** |
|---|---|---|---|---|
| $K^+$ | 945w | 1008w | - | 1270w |
| | | 1286vw | - | 1230w |
| Cr(III) | 1243vw | 1274vs1268vs1277vs | | |
| | | 1246vs1242vs1230vs | | |

where vw = very weak, w = weak, vs = very strong.

Assuming the idea that the greater covalent bond character appears in $Pt(S_2COCH_3)_2$ for the series of transition metals due to the great affinity of platinum ion for sulfur, on the basis of a simple formula we can approximate the covalency degree:

$$\gamma = \frac{\nu OC[complex] - \nu OC[free\ anion]}{\nu OC[Pt(S_2COCH_3)_2 - \nu OC[free\ anion]} = \frac{\Delta\nu'}{\Delta\nu''}$$

The results are listed in table 5.

The values of gamma parameter, from 0.74 to 0.95 indicates a high covalecy degree in chromium(III) xanthates.

**Table 5.**

**Empirical evaluation of covalency coefficients of xanthate compounds**

| Compound | νOC | νOC free anion | Δν’ | γ |
|---|---|---|---|---|
| $Cr(S_2COCH_3)_3$ | 1243 | 945 | 298 | 0.86 |
| $Cr(S_2COC_2H_5)_3$ | 1260 | 1008 | 257 | 0.73 |
| $Cr(S_2CO^iC_3H_7)_3$ | 1265 | 927 | 328 | 0.95 |
| $Cr(S_2COC_2H_5OCH_3)_3$ | 1233 | 975 | 258 | 0.74 |

The calculations carried out so far [16,17] have shown that the frequencies of carbon-sulfur vibrations are distributed in several domains of the IR spectrum, both for the free anion and for the coordinated one (table 4). With a certain prudence concerning the assignments made in table 4, we can admit that the $\nu CS_2$ frequencies decrease from the free anion to complexes, or new bands appear as related to non-coordinated anions. Frequencies of the νNiS vibrations, located between 376 and 397 $cm^{-1}$, could also be identified in the IR spectra of the complexes.

## EPR SPECTRA

The shapes of the EPR spectra (Fig. 2 a-c) depends on length of the alkyl radicals and are typical for the isolated $Cr^{3+}$ ions in a pseudo-octahedral geometry (mononuclear species) [18]. At $g_{eff}$ 2, a broad band characteristic for strongly exchange coupled Cr(III) ions prevails (dimeric or polynuclear species) [19,20]. The number of clustered ions decreases with the dimension of alkyl radicals. The shape of the spectra is also dependent by the radical nature, the spectra being simple for methyl and $^i$propyl, but more complex for ethyl.

EPR spectra were interpreted in term of the following spin Hamiltonian [21]:

$$H = g\,\mu_B\, B\cdot S + D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + E\left(S_x^2 - S_y^2\right)$$

where $\mu_B$ is the Bohr magneton, $S_x$, $S_y$ and $S_z$ are the components of the electron spin S, D and E are the axial and rhombic zero field splitting parameters, respectively.

The perturbation theory in the second-order approximation leaded to the following three resonance fields [22]:

$$B_1 = B_0 - D(3\cos^2\theta - 1)$$

$$B_2 = B_0 + \frac{3\sin^2\theta}{B_0} D \cdot E, \quad with\ B_0 = \frac{h\nu}{g\mu_B}$$

$$B_3 = B_0 + D(3\cos^2\theta - 1)$$

For the complex $Cr(S_2COC_2H_5)_3$ (Fig. 2.a) the zero field splitting parameters D and E were estimated by considering $\theta = 0^o$ in the $B_1$ and $B_3$ expressions (and which correspond to $B_1$ and $B_5$ values in the spectrum) (table 6). The relative great value of the E parameter is due to the important rhombic distorsion of the local symmetry around the metallic ions.

The broad line at g ≈ 2, assigned to coupled $Cr^{3+}$ ions, can be described by the following spin Hamiltonian, in which only the isotropic exchange and Zeeman interactions were taken into account, all other interactions being negligible:

$$H = J\,S_1 \cdot S_2 + g\mu_B(S_1 + S_2)$$

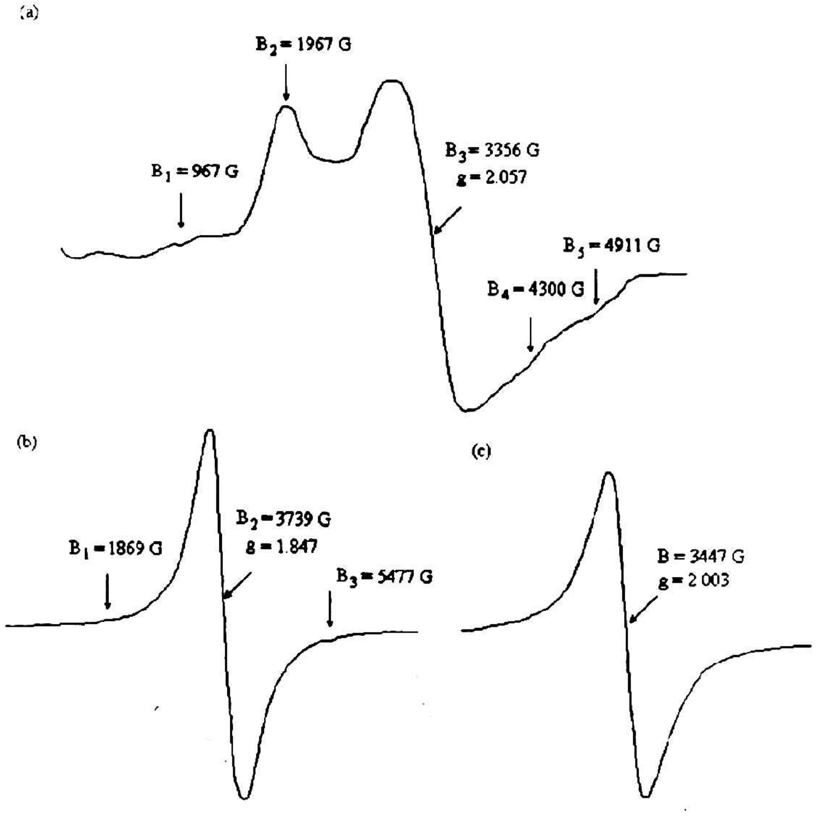

Figure 2. Powder EPR spectra of Cr(III)-tris-O-alkyldithiocarbonates at room temperature.

The exchange term is dominant and the large value of the spin-spin coupling parameter J not allows any transition between the S (=1,2,3) states. The allowed ($\Delta M_s = \pm 1$) transitions between the multiplets of the same spin state occur at $g_{eff} = 2$ [19]. The appearance of the coupled species is also confirmed by the mean of the value of 3.63 MB obtained for the effective magnetic moment of the studied compounds (table 6) which is smaller than the spin only value ($\mu_S = 5.92$ MB). The values of the magnetic moments (table 6) increase with the length of the organic radicals due to the presence of weaker metal-metal interaction.

**Table 6.**

**EPR parameters of the investigated Cr(III) compounds**

| Compound | g | D[G] | E[G] | $B_1$[G] | $B_2$[G] | $B_3$[G] | $B_4$[G] | $B_5$[G] | $\mu_{eff}$ [MB] |
|---|---|---|---|---|---|---|---|---|---|
| $Cr(S_2COC_2H_5)_3$ | 2.057 | 986 | 414 | 967 | 1967 | 3356 | 4300 | 4911 | 3.70 |
| $Cr(S_2COCH_3)_3$ | 1.847 | - | - | - | 1869 | 3739 | - | 5477 | 3.60 |
| $Cr(S_2CO^iC_3H_7)_3$ | 2.003 | - | - | - | - | 3447 | - | - | 3.63 |

## EXPERIMENTAL

### Reagents and Procedure.

The starting materials and all solvents were commercial products of analytical grade purity and were used as supplied.

Electronic spectra were recorded on an ATI UNICAM-UV/VIS apparatus and IR spectra were recorded as follows: the spectra of $KS_2COCH_3$, $KS_2COCH_2CH_3$, $KS_2COCH(CH_3)_2$, $Cr(S_2COCH_3)_3$, $Cr(S_2COCH_2CH_3)_3$ and $Cr(S_2COCH(CH_3)_2)_3$ on a Perkin Elmer 1330 spectrometer and the spectra of $KS_2COCH_2CH_2OCH_3$ and $Cr(S_2COCH_2CH_2OCH_3)_3$ on a SPECORD apparatus (KBr pellets).

EPR spectra were recorded at 9.4 GHz (X band) using a standard JEOL-JES-3B equipment with a magnetic field modulation of 100 KHz. Magnetic moments studies were carried out on a Faraday balance.

### Synthesis of potassium xanthates.

The synthesis of potassium xanthates were prepared from the appropriate alcohol, potassium hydroxide and carbon disulfide, with excess alcohol acting as solvent. All chromium xanthates were prepared by a similar procedure given for $Cr(S_2COCH_3)_3$.

### *Synthesis of $Cr(S_2COCH_3)_3$.*

To a solution of $Cr(NO_3)_3 \cdot 9H_2O$ (0.4 g, 0.001 moles in 25 ml $H_2O$) was added, under stirring, a solution of $KS_2COCH_3$ (0.438 g, 0.003 moles in 50 ml $H_2O$). After standing 5 hours at room temperature, the precipitate was filtered off, washed with 50 ml $H_2O$ and dried over $P_4O_{10}$.

The chromium content was determined by titration with EDTA and the sulfur content by oxidation to S(VI) followed by precipitation as barium sulfate.

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