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THERMAL AND SPECTROSCOPIC INVESTIGATIONS OF SOME CHROMIUM COORDINATION COMPOUNDS WITH THE APPLICATION OF COMPUTER METHODS

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ABSTRACT

Thermal and spectroscopic properties of 6 Cr(III) and 15 Cr(IV) coordination compounds have been presented. The thermal (TG,DTG, DTA) decomposition of all the complexes has been carried out in argon and air atmospheres in the temperature range of 293–1273 K. The activation energies were calculated from the known Kissinger equation and compared with the charge transfer (L–Cr) band energies observed in the diffuse reflectance spectra of all the compounds studied. For the better interpretation of the data a computer resolution was applied yielding some interesting results.

INTRODUCTION

The thermal and spectroscopic investigations of complex compounds may provide useful information on their physicochemical properties. Moreover, the properties of almost any type of substance can be investigated by thermogravimetric analysis. For this type of investigations, among others, numerous groups of metal complexes have been used [1–4].

The physicochemical properties of some Cr(III) and Cr(IV) complexes have been the subject of our investigations for several years [5–9]. Whereas, extensive studies have been devoted to the thermal analysis of Cr(III) and Cr(VI) [e.g.10–12], there are almost no reports concerning the thermal behavior of Cr(IV) compounds [5].

In this paper six $M_3[Cr(NCS)_6]$ solid complexes, where M is K^+ Cs^+, Ag^+, $[Ag(bipy)_2]^+$, $[(CH_3)_4N]^+$ and $[(C_2H_5)_4N]^+$ as well as 15 Cr(IV) compounds as the products of reactions of chromyl chloride and chromyl acetate with alkylaromatics have been investigated by thermal analysis and uv-vis spectroscopy.

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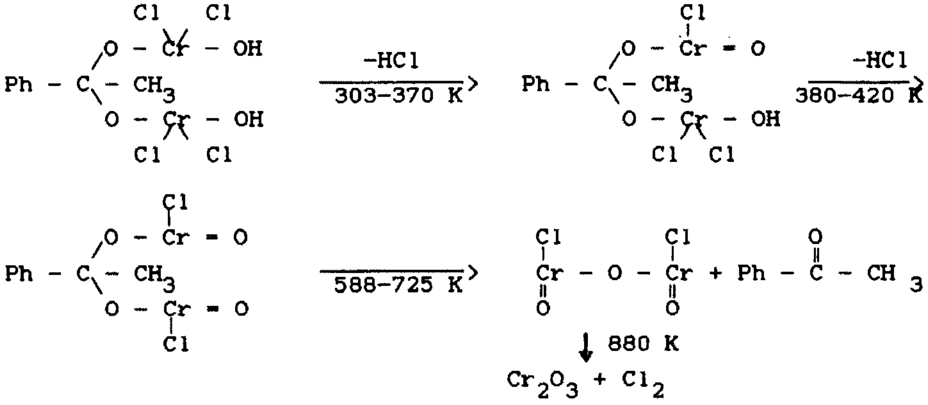
EXPERIMENTAL

The Cr(IV) complexes were synthetized by the method described in [6] as the solid products of chromyl chloride and chromyl acetate reactions with alkylaromatics. The Cr(III) complexes containing $[Cr(NCS)_6]^{3-}$ anion were prepared by using the method in ref. [8]. Simultaneous TG/DTG/DTA curves were obtained with Paulik-Paulik-Erdey OD 102 thermobalance in air and argon atmospheres. The sample weight was maintained as nearly constant (approximately 100 mg). The thermal curves were obtained using the programmed heating of 5 deg/min and were observed in the temperature range of 293-1273 K. The thermal decomposition products corresponding to discrete plateau regions were isolated. The initial compounds and the products were characterized via the methods of elemental analysis as well as by IR and uv-vis spectroscopy. IR spectra were measured with Specord M80 while the diffuse reflectance spectra were performed with Hitachi Model 356 spectrophotometers. The diffuse reflectance spectra as well as DTA curves were resolved into components using computer methods elaborated in our laboratory [13]. The activation energies of the particular steps of decomposition of the complexes studied were calculated from the Kissinger equation [14].

RESULTS AND DISCUSSION

All the compounds studied in this paper are listed in Tables 1-2.
Cr(IV) compounds. The thermal behavior of Cr(IV) complexes was the subject of our investigations in [5]. In this paper we have compared the data obtained from the spectroscopic investigations of these complexes with those resulting from thermal analysis.
We have stated earlier that chromyl chloride products in argon atmosphere decompose as follows:



DTA curve analysis on $Cr(OH)_2(CH_3COO)_2$ in argon atmosphere indicates the existence of an intermediate with the formula $Cr_2O(OH)_2(CH_3COO)_2$. The dichromium(IV) hydroxoacetate showed three step decomposition with the intermediate $Cr_2O_3(CH_3COO)_2$.

In Table 1 we present the activation energies obtained from thermal investigations of these compounds in comparison to those obtained from the diffuse reflectance spectra on the basis of CT band transition. As one can observe the values of activation energies calculated from the CT energies are much higher than those obtained from the thermal decomposition data. The reason of such differences may very probably be due to interaction of other CT bands (e.g. Cl-Cr as well as ligand $\pi - \pi^*$ bands) in the complexes and therefore the shift of the O-Cr CT band to higher energy.

TABLE 1

The activation energies in Cr(IV) complexes from the thermal (air atmosphere) and spectroscopic data

Compound	E_a[kJ/mole] (thermal)	E_{CT}[cm^{-1}]	E_a[kJ/mole] (spectroscopic)
$2CrO_2CL_2 \cdot C_6H_5CH_3$	194	20400	244
$2CrO_2CL_2 \cdot C_6H_5C_2H_5$	192	20400	244
$2CrO_2CL_2 \cdot C_6H_5(n\text{-}C_3H_7)$	214	20620	247
$2CrO_2CL_2 \cdot C_6H_5(iso\text{-}C_3H_7)$	202	21050	252
$2CrO_2CL_2 \cdot (C_6H_5)_2CH_2$	171	20000	239
$Cr(OH)_2(CH_3COO)_2$ $(C_6H_5CH_3)$	196	20830	249
- " - $(C_6H_5C_2H_5)$	194	20830	249
- " - $(C_6H_5(n\text{-}C_3H_7))$	195	20830	249
- " - $(C_6H_5(iso\text{-}C_3H_7))$	195	20830	249
- " - $((C_6H_5)_2CH_2)$	199	20830	249
- " - $((C_6H_5)_3CH)$	193	20830	249
$Cr_2O_2(OH)_4(CH_3COO)_2$ $(C_6H_5CH_3)$	192	19610	234
- " - $(C_6H_5C_2H_5)$	203	19610	234
- " - $(C_6H_5(n\text{-}C_3H_7))$	200	20000	239
- " - ((C H) CH)	196	20000	239

<u>Cr(III) compounds</u> Figs.1 and 2 show the TG and DTA curves for $K_3[Cr(NCS)_6]4H_2O$ and $[(CH_3)_4N]_3[Cr(NCS)_6]$ complexes in argon and air atmospheres as the examples. Table 2 presents the results of thermal decomposition of all the Cr(III) complexes studied.

The DTA curves in Figs 1 and 2 of complexes studied in argon atmosphere are very complicated. Even the DTG curves in all cases of $[Cr(NCS)_6]^{3-}$ compounds are not resolved enough to separate the steps of decomposition of these complexes. Because of this complexity we have applied computer methods for getting more details. The DDTA curves shown in the Figs are the derivative of DTA curves.

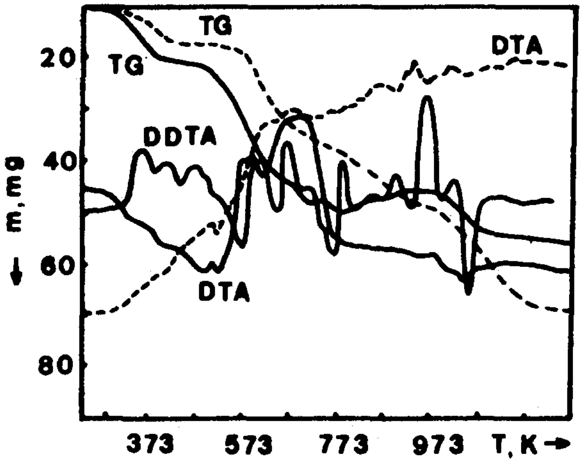


Fig.1. TG, DTA and DDTA curves of $K_3[Cr(NCS)_6]\cdot 4H_2O$ in air (——) and argon (----) atmospheres.

Of the complexes studied only $K_3[Cr(NCS)_6]$ $4H_2O$ derivative contains crystallization water. The water molecules must be linked to the cation through hydrogen bridges. For this complex the first decomposition stage is endothermic with release of the crystallization water, this occurs in temperature range 318–413 K. On the DDTA curve we observe four peaks corresponding to dehydration of four water molecules. The activation energy for dehydration of $K_3[Cr(NCS)_6]$ $4H_2O$ calculated from the slope of Arrhenius plot was 42 kJ/mole and 47 kJ/mole in air and argon atmospheres, respectively. In air atmosphere all the compounds show the exothermic DTA complex bands in the range of about 500–800 K. They are probably connected with further decomposition of the complexes to thiocyanate compounds of the type M-NCS and $Cr(NCS)_3$ and then with their oxidation to metal oxides(the increase of weight of the samples on TG curves). In the case of complexes with organic cations (see Fig.2) one observes the great weight loss of about 60% which corresponds to decomposition to $[(CH_3)_4N]NCS\uparrow$ and $Cr(NCS)_3$. The weight loss occurring between about 513–823 K presumably begins with an endothermic decomposition reaction but this is transformed into a more complicated exothermic process with the participation of atmospheric oxygen. In argon atmosphere the decomposition is probably connected with the Cr_2S_3 or Cr_2N_3 or CrC_2 formation and then their decomposition at about 1000 K. The diffuse reflectance spectra as well as IR spectra of black residue show no appropriate bands.

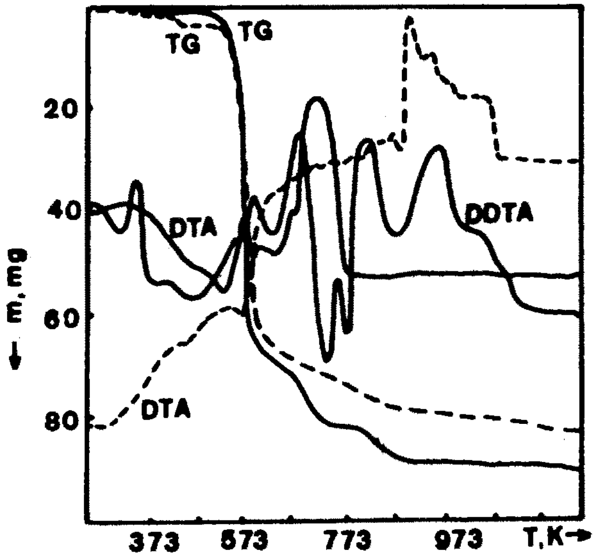


Fig. 2. TG, DTA and DDTA curves of $[(CH_3)_4N]_3$ $[Cr(NCS)_6]$ in air (——) and argon (---) atmospheres.

Table 2

The comparison of energies of CT transitions with the activation energies of Cr(III) complexes

Compound	E_a [kJ/mole] (thermal)	E_{CT} [cm^{-1}]	E_a [kJ/mole] (spectroscopic)
$K_3[Cr(NCS)_6]\cdot 4H_2O$	358	33400 27000 29200	400 323 349
$Cs_3[Cr(NCS)_6]$	346	33200 28000 29800	397 335 357
$[(CH_3)_4N]_3[Cr(NCS)_6]$	362	33000 28000 29400	395 335 352
$[(C_2H_5)_4N]_3[Cr(NCS)_6]$	371	33000 28000 29400	395 335 352
$Ag_3[Cr(NCS)_6]$	376	33600 27000 29200	402 323 349
$[Ag(bipy)_2]_3[Cr(NCS)_6]$	372	34000 27000 29200	407 323 349

Cesium complex is more stable. The decomposition of this compound in argon atmosphere occurs mainly in the formation of thiocyanates of Cs(I) and Cr(III) and next to the decomposition of these into sulphides and dicyane $(CN)_2$. The residue after decomposition shows no characteristic bands. Only in the case of compounds studied in air atmospheres both the diffuse reflectance and IR spectra showed the bands characteristic for Cr_2O_3 compound. In Table 2 we show the activation energies of the compounds studied together with the calculated from CT band energies. In the Table there are 3 CT bands observed in the diffuse reflectance spectra of these compounds but only the I-st one is the CT SCN-Cr band. In this case the activation energy calculated from the Kissinger equation is smaller than predicted from CT bands. The lowering of this value is connected probably with the interaction of neighbouring CT bands.

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