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THERMAL INVESTIGATION OF THE COMPLEX SALTS OF HEXAKIS-DMSO-CHROMIUM(III)

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The thermal behaviours of five new hexakis-DMSO-Cr(III) compounds were investigated by means of the Derivatograph. The composition of these complexes are discussed.

The hexakis-DMSO-chromium(III) cation (designated as M^{3+}) reacts with simple and complex anions. Investigations on the outer-sphere complexes of M^{3+} with simple ligands were described earlier [1]. Only a few literature data are available on the compounds formed with complex anions.

Cotton and Francis prepared compounds of the type $Co(DMSO)_6CoX_4$ from the hexakis-DMSO-cobalt(II) cation ($X = Br^-, I^-, NCS^-$) [2]. Similar compounds were obtained from the hexakis-DMSO-nickel(II) cation with $(NiBr_4)^{2-}$. The method of preparation of the cations was given, and conclusions were drawn from the reflexion spectra. It was stated that the cation has octahedral and the anion tetrahedral structure. In all the compounds prepared the cation and the anion contained the same metal.

The authors of the present paper have made experiments to prepare, in addition to the compound $MCr(NCS)_6$ containing two chromium atoms, compounds of M^{3+} with an anion which is the thiocyanato complex of a transition metal different from chromium. They succeeded in preparing intensely coloured complexes with different metal ions: $MCr(NCS)_6$, $MFe(NCS)_6$, $MRh(SCN)_6$, $MCo(NCS)_5 \cdot H_2O$, and $MNi(NCS)_5 \cdot 2H_2O$. The DMSO and water contents of these compounds were determined by thermal analysis, and from this conclusions were drawn as to the compositions of the compounds.

Experimental

Preparation of the complex salts

The cation of the complex salt was obtained from a solution of $M(NO_3)_3$ prepared [3] and purified [1] as described earlier. For the preparation of solutions of the anions the solid thiocyanato complexes were available in the cases of chromium and rhodium [4, 5]. With the other metals potassium thiocyanate was added to a solution of a water-soluble salt of the metal, to give a metal: thiocyanate molar ratio of 1 : 6.

Thermoanalytical studies

Thermoanalytical studies were carried out with the Derivatograph [6], in an air atmosphere. 100 mg of sample was weighed into a ceramic crucible. The heating rate was 5°/min.

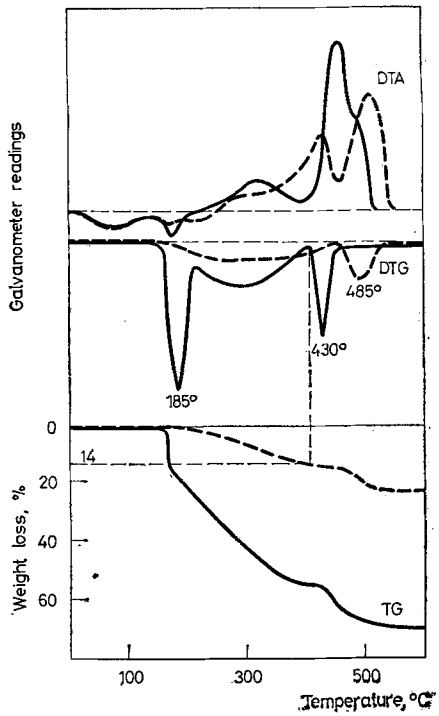

Fig. 1. Thermoanalytical curves of $K_3Rh(SCN)_6$ (- - - - -) and of $Cr(DMSO)_6Rh(SCN)_6$ (— — —)

The aim of the thermal investigations was primarily to determine the amounts of DMSO and water present. According to literature data [7] several reactions may proceed simultaneously during the thermal decomposition of thiocyanate, of which the loss of cyanogen and sulphur involves a weight decrease and the oxidation of sulphide a weight increase. Due to the not well-defined nature of the reactions taking place, we did not succeed in the quantitative determination of thiocyanate by thermal analysis. The decomposition of thiocyanate starts only above 300° with complexes where the bonding is through nitrogen, up to which temperature water and DMSO are completely removed [8]. This means that in this case the thermal curves could be used to determine the amount of DMSO and water without

making any correction. Of the compounds studied, only in the complex $K_4Rh(SCN)_6$ is the thiocyanate bound through sulphur; its decomposition is appreciable, and a correction had to be made for it. Since the solid salt was available, in this case, the decomposition of this served as the basis for the correction.

The thermoanalytical curves of the salts of $Rh(SCN)_6^{3-}$ with simple and complex cations are presented in Fig. 1.

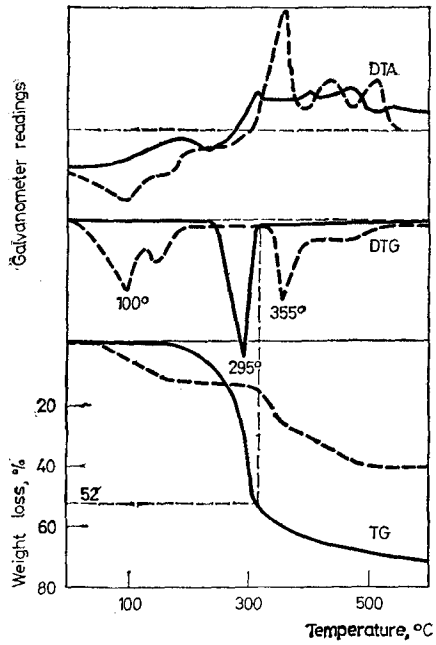

Fig. 2. Thermoanalytical curves of $K_3Cr(NCS)f \cdot 4H_2O$ (- - - - -) and of $Cr(DMSO)_6Cr(NCS)_6$ (— — —)

As reflected by the thermal curves of $K_3Rh(SCN)_6$, the decomposition begins at about 200°; considering what was said earlier, no particular chemical reaction can be assigned to the weight loss of about 14% observed up to 400°. In the evaluation of the decomposition of $MRh(SCN)_6$, the weight loss due to the decomposition of thiocyanate also has been taken into consideration. According to the TG curve the decomposition starts at 170°, which means that the compound does not contain any water. The weight loss occurring between 180 and 200°, which has maximum rate at 185°, corresponds to the departure of exactly 2 moles of DMSO. By correction of the weight loss in the temperature interval 200–400° for the weight loss of thiocyanate in the same interval, a weight loss corresponding to 4 moles of DMSO is obtained. Accordingly, the composition of the light-brown rhodium complex is $MRh(SCN)_6$. DMSO leaves in two steps.

The decompositions of the two complexes of $Cr(NCS)_6^{3-}$ were studied similarly. The results obtained are given in Fig. 2.

In the case of $K_3Cr(NCS)_6 \cdot 4H_2O$ the TG curve indicates that the crystal water leaves in two steps and corresponds to 4 moles of water. The decomposition of the thiocyanate starts above 300°, reaches its maximum rate at 355° and is complete at about 500°. The complexity of the decomposition is shown by the three well-

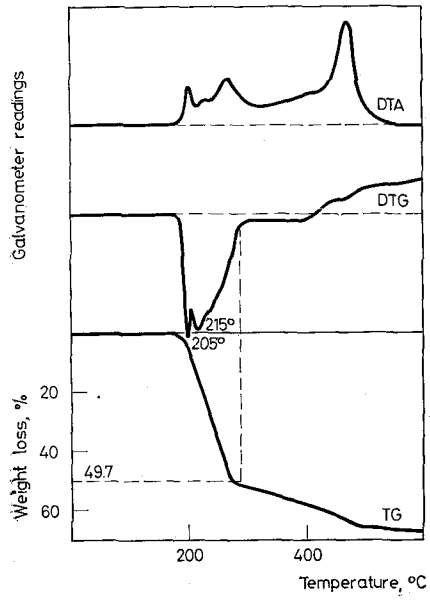

Fig. 3. Thermoanalytical curves of $Cr(DMSO)_6Fe(NCS)_6$

separated exothermic peaks on the DTA curve. As shown by the curves of $MCr(NCS)_6$, this compound is stable up to 200°, i.e. it does not contain crystal water. DMSO is completely removed in a single step in the range 220–320°; the DTG maximum lies at 295°, before the decomposition of thiocyanate. The weight loss is 52%. It became clear from the fact that the salt studied did not contain any water, and from the results which will be given later in this paper, that the ratio of the metal contents of the complex cation and complex anion is 1 : 1. The compound was assumed to have the composition $Cr(DMSO)_6Cr(NCS)_6$, the theoretical DMSO content being 51%, which was in good agreement with the experimental value of 52%. From the TG curve the composition of the light-violet complex salt is $MCr(NCS)_6$.

The thermal behaviour of $MFe(NCS)_6$ is similar to that of $MCr(NCS)_6$, as shown by Fig. 3. 6 moles of DMSO leave in the temperature range between 190 and 270°, with DTG peaks at 205 and 215°. The composition of the purple complex is $MFe(NCS)_6$.

Figure 4 presents thermoanalytical curves of the compound of M^{3+} with cobalt thiocyanate.

The composition of the light-blue complex proved to be $MCo(NCS)_5 \cdot H_2O$. The compound is stable up to 130°. The water leaves above 130°, showing that it is bound by co-ordination forces. This does not result in a separate TG step, however, due to the relatively small weight loss and to the beginning of the departure of DMSO. The total weight loss, including that due to the removal of DMSO, with maximum rate at 295°, corresponds to 5DMSO + $1H_2O$.

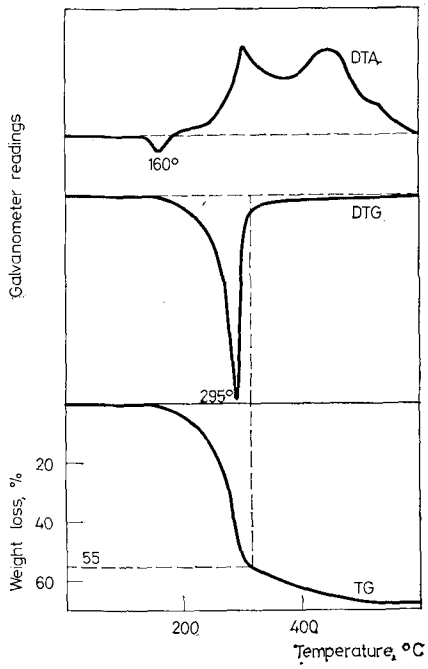

Fig. 4. Thermoanalytical curves of $Cr(DMSO)_6Co(NCS)_5 \cdot H_2O$

Figure 5 shows the thermal curves of the light-green complex, which proved to have the composition $MNi(NCS)_5 \cdot 2H_2O$.

Of the four TG steps, the first corresponds to $1H_2O$. The DTG peak at 110° indicates that the water is not co-ordinatively bound. The weight loss having a DTG maximum at 205° corresponds to 3DMSO + $1H_2O$. The weight loss in the third step exceeds that corresponding to 3DMSO, which can be ascribed to the fact that in the case of nickel the decomposition of thiocyanate might start below 300°. We have assumed that 1 mole of water is present within the co-ordination sphere. This assumption is supported by the infrared spectra of the compounds. The spectra of the complexes of hexakis-DMSO with the thiocyanates of iron,

Table 1

Solubilities [mole × dm^{-3}]

$Cr(DMSO)_6Rh(SCN)_6$	$Cr(DMSO)_6Cr(SCN)_6$	$Cr(DMSO)_6Fe(SCN)_6$
1.16×10^{-6}	5.23×10^{-5}	5.97×10^{-4}

$Cr(DMSO)_6Co(SCN)_5\cdot H_2O$	$Cr(DMSO)_6Ni(SCN)_5\cdot 2H_2O$
5.20×10^{-3}	2.57×10^{-2}

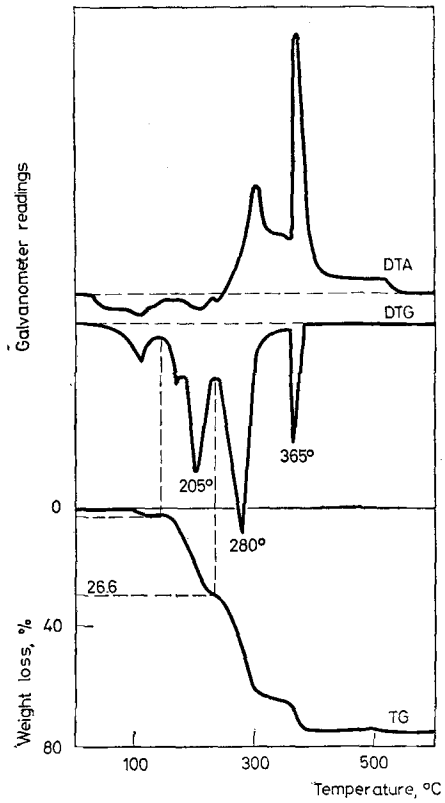

Fig. 5. Thermoanalytical curves of $Cr(DMSO)_6Ni(NCS)_5 \cdot 2H_2O$

cobalt, nickel and chromium have similar structure, which is indicative of the similar symmetries of the molecules. It seems probable that the anion, similarly to the cation, has octahedral symmetry.

The compounds studied are only slightly soluble in water, but readily soluble in DMSO. The solubilities in water (Table 1) were determined at 25°. 200 – 300 mg of the complex salt was weighed into a flask fitted with a ground-glass stopper, 25 ml of water was added, and the flask was shaken for 1 hour. After filtration the metal content of the solution was determined by atomic absorption spectroscopy and spectrophotometry. These results also proved the 1 : 1 Cr : M ratio, which, after comparison with the thermoanalytical results, was taken into account in determining the compositions of the complexes.

Further investigation of the structures of the compounds by Fourier spectroscopy is in progress.

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RÉSUMÉ — On a étudié le comportement thermique de cinq nouveaux composés Hexakis-DMSO-Cr(III) à l'aide du "Derivatograph". On discute la stabilité thermique et la composition de ces complexes.

ZUSAMMENFASSUNG — Das thermische Verhalten von fünf neuen Hexakis-DMSO-Cr(III)-Verbindungen wurde mit dem Derivatograph untersucht. Die Hitzebeständigkeit und Zusammensetzung dieser Komplexe wurden erörtert.

Резюме — С помощью дериватографа было изучено термическое поведение пяти новых гексакис-диметилсульфоксидных комплексов Cr(III). Обсуждены состав этих комплексов и их термическая стабильность.