A C T A U N I V E R S I T A T I S L O D Z I E N S I S
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FORMATION OF TRIACETYLTHIOCARBAMIDE CHROMIUM PERCHLORATE*

The method were elaborated for the preparation of $[Cr(CH_3CONHCSNH_2)_3](ClO_4)_3$. In this paper we give conditions for the synthesis, composition, properties and propose the structure of the obtained compound.

C e r v o n e, C a n c e l l i e r i and F u r l a n i [1] prepared a solid compound of Chromium (III) with thiocarbamide (TM) of formula $[Cr(TM)_3]Cl_3$. K h a n [2] used this complex to prepare other six-coordinated mixed complexes of the type: $[Cr(TM)_2L_2Cl_2]Cl$ where L-piridine: $[Cr(TM)_2L'_2]Cl_3$ where L' - O-phenantroline and $[Cr(TM)_2L''_2]Cl$ where L" - phenylarsenic acid. In literature there is a lack of data on Cr(III) complexes containing thiocarbamide derivatives in the internal sphere. During the investigations of the complexing reaction in the system: $Cr(ClO_4)_3$-AcTM-H_2O, where AcTM-N-acetylthiocarbamide $CH_3CO.NH.CS.NH_2$ we determined the formation of a very characteristic crystalline deposit of a new compound. In this paper we give conditions for the synthesis, compósition properties and propose the structure of the obtained compound.

Experimental

Preparation of $[Cr(CH_3CO.NH.CS.NH_2)_3](ClO_4)_3$

To 50 ccm of 0,25 M aqueous solution of $Cr(ClO_4)_3$ kept at room temperature we added 150 ccm of 0,25 M (saturated solu-

* The work has been carried out within the research Problem MR-I-11.

tion) aqueous solution of N-acetylthiocarbamide (Schuchardt-München). After having thoroughly mixed the reagents the solution was heated on a water bath until the moment of sharp colour change from green to darkviolet. After cooling the solution yielded a microcrystalline dark violet deposit. The educed crystals were washed a few times with cold water and dried in the atmosphere of air at room temperature to constant weight. The reaction yield calculated in relation to the initial amount of Cr(III) is almost 100%. It was estabilished that the solution which undergoes crystallization should have an acidic reaction since at higher pH values there takes place the desulphuration of acetylthiocarbamide complexes of Cr(III) with the isolation of H_2S. The presence of chromium, acetylthiocarbamide and perchlorate ions was determined in the obtained precipitate.

The content of C, N, H, S and Cl was determined by elementary analysis methods and the content of Cr(III) by complexometric method.

The analysis results for the assumed formula

$$[Cr(CH_3CO.NH.CS.NH_2)_3](ClO_4)_3$$

are as follows:

calculated: 10.27% Cr, 21.37% C, 16.61% N, 3.59% H, 19.01% S and 21.02% Cl:

found: 10.17% Cr, 20.40% C, 16.71% N, 3.57% H, 19.01% S and 20.02% Cl;

Results

Properties and thermal resistivity of $[Cr(AcTM)_3](ClO_4)_3$

The obtained compound is an anaqueous dark-violet substance, hardly soluble in acetone and in water. Its m.p. temperature is 191°C. During heating with concentrated acids it completely decomposes. It is similarly decomposed by strong alkalis (desulphuration of compound). Investigations made by derivatographis methods in the atmosphere of air showed that the obtained compound is also hardly resistive to the action of high temperatures. The derivatogram of the investigated compound is shown in Fig. 1.

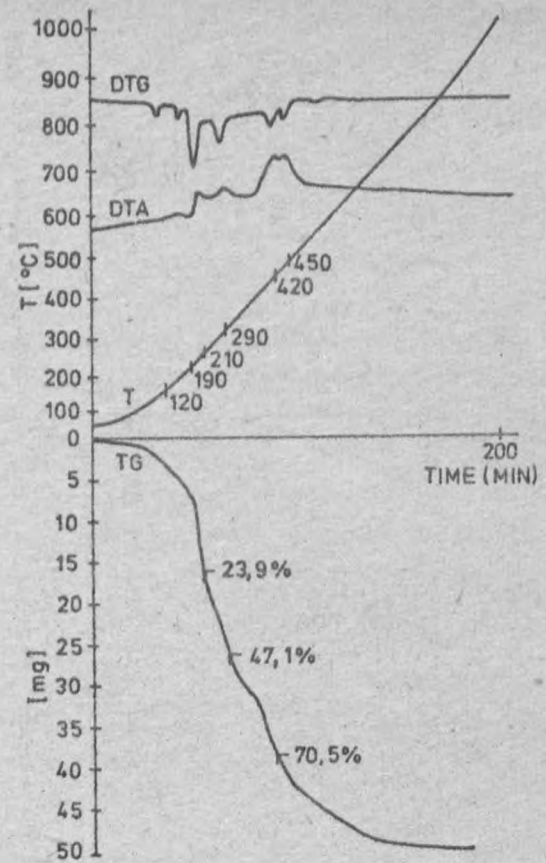

Fig. 1. Thermal analysis curves complex $[Cr(CH_3CO \cdot NH \cdot CS \cdot NH_2)_3](ClO_4)_3$. Derivatograph made in Hungary, heating rate 5°C/min; sample mass 59 mg; sensitivity: DTA - 1/15, DTG - 1/15: TG - - 200. Reference substance α-Al_2O_3

The derivatogram of acetylthiocarbamide is shown in paper 3. It follows from derivatographic data that the thermal decomposition of the obtained compound is of a complex nature. The run of phenomena connected with effects shown on DTG, DTA and TG curves can be described by the following scheme:

$$[Cr(AcTM)_3](ClO_4)_3 \xrightarrow[-AcTM]{210^\circ C} [Cr(AcTM)_2](ClO_4)_3 \xrightarrow[-AcTM]{290^\circ C}$$

$$[Cr(AcTM)](ClO_4)_3 \xrightarrow[-AcTM]{420^oC} Cr(ClO_4)_3 \xrightarrow{450^oC}$$

$$CrO_{(1,5+x)} + ClO_2 + Cl_2 + \frac{1}{2}(8,5-x)\,O_2 \xrightarrow{450^oC}$$

$$Cr_2O_3$$

The decomposition end product is Cr_2O_3. Stages of the thermal decomposition proposed by us in Table 1 were confirmed by additional analytic studies of obtained thermolysis products of the investigated compound. A Cr(III) cation attributed probably to Cr_2O_3 was identified in an agglomerate prepared at 800°C. Conclusions drawn from our studies are in accordance with Buzas' data [4].

Table 1

Stages of thermal decomposition of $[Cr(AcTM)_3](ClO_4)_3$

Stage	Temperature range (°C)	Loss of mass (%)		Maximum of endoeffect on DTA curve	Maximum of exoeffect on DTA curve	Process
		found	calculated	°C		
1	20-120	8	-	120	-	demoisturization
2	180-210	-	-	191	-	melting of sample
3	200-230	23.9	23.4	-	210	elimination of the first molecule AcTM
4	270-320	47.1	46.7	-	290	elimination of the second molecule AcTM
5	370-440	70.5	70.0	-	420	elimination of the third molecule AcTM
6	440-460	-	-	-	450	decomposition of $Cr(ClO_4)_3$

IR spectrum of $[Cr(CH_3CONHCSNH_2)_3](ClO_4)_3$

Table 2 gives characteristic bands observed in IR spectra for acetylthiocarbamide and for the obtained compound. Analysis of these data made on the basis of papers [2, 3, 5-7] shows that the Cr(III) ion coordinates with N-acetylthiocarbamide through

Table 2

Characteristic absorption bands in IR spectra recorded within the range 4600-700 cm^{-1}. Specord 71 IR, KBr pellets

Entry	Characteristic bands, cm^{-1}		Types of vibration
	$CH_3CO.NH.CS.NH_2$	$[Cr(CH_3CO.NH.CS.NH_2)_3](ClO_4)_3$	
1	3420 vw	3420	$\nu NH(B_1)$
2	3260 vw	3250	
3	3220 m	3200	
4	3170 m	3170	
5	1590 s	1600 vs	δNH_2 (B_1)
6	1400 s	1420 m	νNCN (A_1) δNH_2 (A_1) νCS (A_1)
7	1360 m	1370 m	δCH_3
8	1035 vs	1040 vw	$\delta r\ NH_2$ (A_1) $\nu(NCN)$ (A_1) $\delta r\ NH_2$ (B_1) νCS (A_1)
9	715 s	700 s	νCS (A_1) πCH

the sulphur atom (Cr ⟵ S). It is indicated by a small change of the bands (ν_{N-H}, δ_{NH_2}) in the complex. A band at 715 cm^{-1}, characteristic for AcTM is shifted in the complex to lower frequencies suggesting the formation of a metal-sulphur band [5]. Such a conclusion is also backed by a 20 cm^{-1} shift of a

complex band (ν_{NCN}, $\delta_r NH_2$, ν_{CS}, δ_{CH_3}) to higher frequencies in the complex (1420 cm^{-1}) in comparison to AcTM (1400 cm^{-1}). Such a direction of changes was observed by Khan [2] in IR spectre of related compounds.

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POWSTAWANIE NADCHLORANU TRÓJACETYLOTIOKARBAMIDOCHROMOWEGO

Badając reakcje kompleksowania w układzie: $Cr(ClO_4)_3$-AcTM-H_2O stwierdziliśmy powstawanie bardzo charakterystycznego, krystalicznego osadu nowego związku, dla którego w oparciu o wyniki analizy chemicznej proponujemy wzór $[Cr(CH_3CONHCSNH_2)_3](ClO_4)_3$.

Wykonane widma w podczerwieni wskazują, że jon Cr(III) koordynuje z N-acetylotiokarbamidem przez atom S (Cr←S). Otrzymany związek jest mało odporny na działanie wysokich temperatur. Z danych derywatograficznych wynika, że badany związek rozpada się w kilku etapach w zakresie temperatury 200-460°C, a końcowym produktem stałym jest Cr_2O_3.

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ОБРАЗОВАНИЕ $[Cr(CH_3CONHCSNH_2)_3](ClO_4)_3$

В реакции комплексования в системе: $Cr(ClO_4)_3$-АсТМ-H_2O (АсТМ = $CH_3CONHCSNH_2$) получается новое соединение $[Cr(AcTM)_3](ClO_4)_3$. Проведенный анализ инфракрасных спектров указывает на связь типа Cr←S. Это соединение разлагается при температуре 200-460°С.