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THERMAL DECOMPOSITION OF Cr(III) DITHIOCARBAMATES

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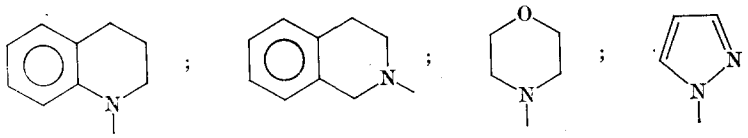
The thermal stability of chromium(III) complexes with dithiocarbamate acid derivatives was studied. The general formula of these complexes is $(RCS_2)_3Cr$ where:

. R = $(CH_3)_2N-$; $(C_2H_5)_2N-$; $(CH_2)_4N-$;

$(CH_2)_6N-$; $C_6H_{11}NH-$; $(C_6H_{11})_2N-$;



The thermal stability of these complexes was found to depend on the kind of R and the decomposition occur in several stages.

The final product of the decomposition of the complexes in the 20–600° temperature range investigated is chromium sulphide, Cr_2S_3 or with incomplete combusted sulfur atoms.

Hitherto only few chromium(III) complexes with dithiocarbamate acid derivatives have been studied compared with complexes of this type with other metals [1]. Since the methods described in the literature for obtaining chromium(III) dithiocarbamates are unsatisfactory because of low yields, we have developed a new method for obtaining these complexes [2].

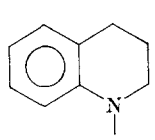
The thermal properties of metal dithiocarbamate complexes have been studied. D'Ascenzo and Wendlandt [3] examined Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I), Hg(II) complexes of diethyl – dithiocarbamic acid. Sceney, Hill and Magee [4] prepared seven copper(II) dithiocarbamate complexes $Cu(R_2Dtc)_2$; $R_2 = Me_2$, Et_2, nPr_2, nBu_2, $cycHex_2$, Et, Ph, pyrrol and pip. and examined their thermal properties. Thermoanalytical data (TG/DTA) have been obtained for bis-monoethanoldithiocarbamato nickel(II) and bis diethanoldithiocarbamato nickel(II) and copper(II) complexes by Bookhari Annuar and coworkers [5].

Of the trivalent metal dithiocarbamate complexes, D'Ascenzo and Wendlandt [6] studied $Fe(Et_2Dtc)_3$ by thermogravimetry.

The present paper reports the thermal properties of a series of the chromium(III) dithiocarbamate $(RCS_2)_3Cr$ where:

R = $(CH_3)_2N-$; $(C_2H_5)_2N-$; $(CH_2)_4N-$;

$(CH_2)_6N-$; $C_6H_{11}NH-$; $(C_6H_{11})_2N-$;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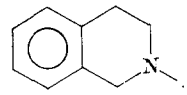
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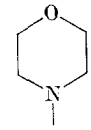
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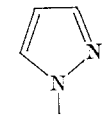
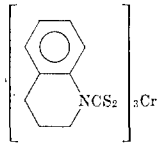
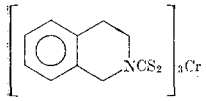
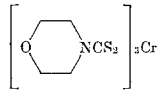
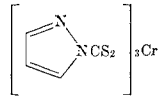


Experimental

The chromium dithiocarbamate complexes were prepared by shaking anhydrous Cr(III) bromide or chloride for 5h with sodium salts of the corresponding dithiocarbamate acids at 1 : 3 molar ratio in isopropanol. The violet precipitate was

Table 1

Analytical date of Cr(III) dithiocarbamates

$(RCS^a)_3Cr$	M. P., °C	Cr, %		N, %	
		Calculated	Found	Calculated	Found
$[(CH_3)_2NCS_2]_3Cr$	340 d	12.60	12.30	10.19	9.99
$[(C_2H_5)_2NCS_2]_3Cr$	250 d	10.48	10.25	8.46	8.32
$[(CH_2)_4NCS_2]_3Cr$	290 d	10.59	10.62	8.56	8.46
$[(CH_2)_6NCS_2]_3Cr$	226	9.04	8.96	7.32	7.45
$[(C_6H_{11})HNCS_2]_3Cr$	205	9.04	8.92	7.32	7.60
$[(C_6H_{11})_2NCS_2]_3Cr$	245 d	6.33	6.08	5.11	4.97
	132 d	7.61	7.24	6.15	5.80
	147 d	7.61	7.28	6.15	6.30
	133—5	9.65	9.51	7.79	7.85
	135	10.79	10.43	17.47	17.20

filtered off or centrifuged, extracted by methylene chloride or chloroform and precipitated by methyl, ethyl or isopropyl alcohol. The complexes were recrystallized from the same solvents. In that way were obtained not only the complexes described in the literature but also new complexes [2]; m.p. and analytic data are given in Table 1.

Thermogravimetric measurements were made with a Paulik F.–Paulik J.–Erdey L. (MOM Budapest) derivatograph under the following conditions: TG about 100 mg, TG sensitivity 100 mg, DTA 1/15, V = 10°/min.

The ranges of characteristic temperatures and mass losses could in most cases not be determined with accuracy because the transitions between the decomposition stages are not clear-cut.

Results and discussion

The thermal curve of chromium(III) dimethyldithiocarbamate (Fig. 1) indicates a two-stage thermal decomposition commencing at about 290°. The mass changes associated with the stages measured from Fig. 2 correspond to the loss of two organic $(CH_2)_3NC$ fragments. The reaction is exothermic and occurs at 345°. The calculated initial mass loss is 27.2%, the measured value is 25.0%. Separation of the third organic fragment and combustion of sulfur occurs around 365° and

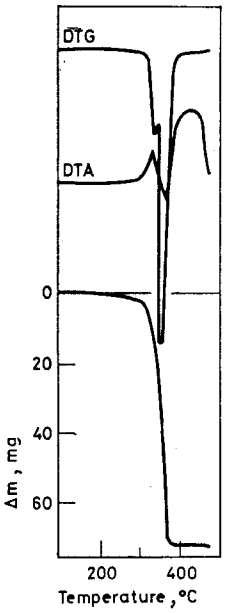


Fig. 1. Thermal curves of Cr(III) dimethyldithiocarbamate

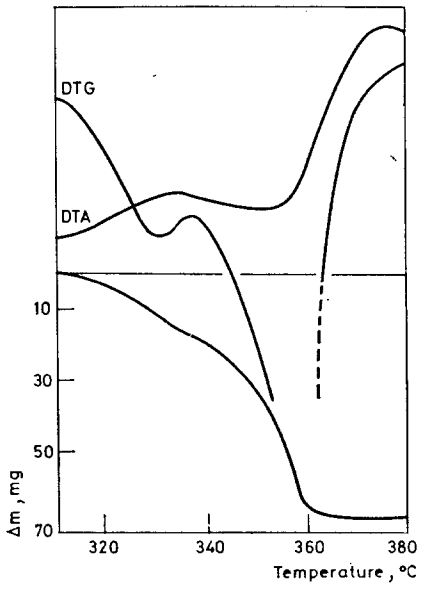


Fig. 2. Thermal curves of Cr(III) dimethyldithiocarbamate

is accompanied by an extended exothermic effect at around 380°. Above 365° the sample mass changes very slowly and the residue mass corresponds approximately to Cr_2S_3; residue 28% of sample mass, theoretical value 24.3% based on Cr_2S_3.

Figure 3 shows the thermal curves of chromium(III) diethyldithiocarbamate. Melting of the sample at 250° is followed by decomposition, the stages of which are not well defined. The first to separate is probably the organic moiety. The initial decomposition is exothermic and followed by an endothermic effect. The final exotherm at around 390° is attributed combustion of sulfur. At the final temperature of the measurement (580°) the mass of the residue is 24% of the sample mass, which corresponds approximately to Cr_2S_3 (20.2%).

Figure 4 shows the thermal curves of the Cr(III) pyrollidinedithiocarbamate. The incipient temperature of decomposition is 270°. Mass loss at temperatures up to 360° is approximately 60% and corresponds to the separation of three organic $(CH_2)_4NC$ fragments and two sulfur atoms (theoretical 62.4%). The weak endothermic effect at 335° at the beginning of decomposition is followed by a violent exothermic effect at 450°, attributable to sulfur combustion. In the 360–500° range, the 9.5% mass loss corresponds to 1.5 sulfur atom loss (9.8%). Combustion of the remaining sulfur starts above 540°.

The thermal curves of Cr(III) hexamethylene are shown in Fig. 5. The first decomposition is complete at 195°. The 53% mass loss corresponds approximately to the loss of the three $(CH_2)_6NC$ fragmets, which is exothermic at around 190°.

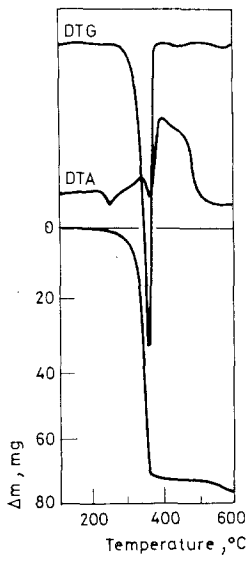


Fig. 3. Thermal curves of Cr(III) diethyldithiocarbamate

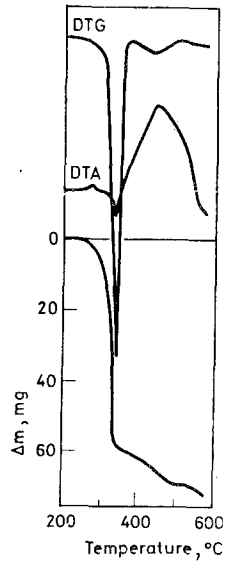


Fig. 4. Thermal curves of Cr(III) pyrollidinedithiocarbamate

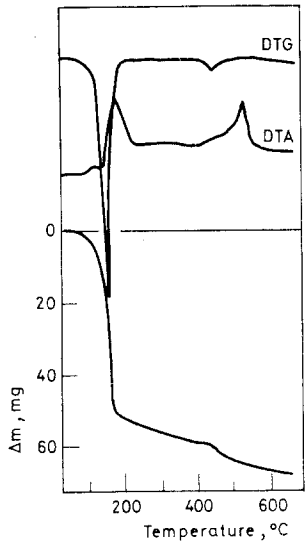


Fig. 5. Thermal curves of Cr(III) hexamethylenedithiocarbamate

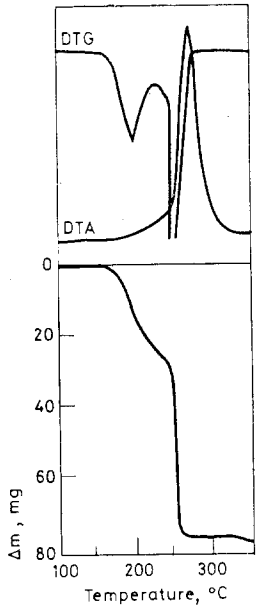


Fig. 6. Thermal curves of Cr(III) cyclohexyldithiocarbamate

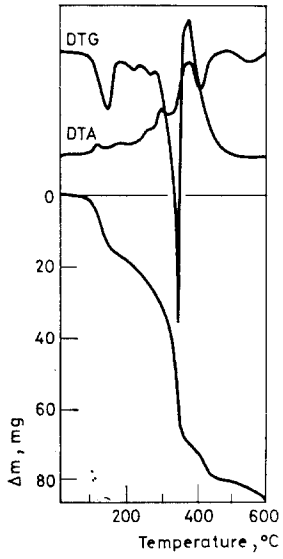


Fig. 7. Thermal curves of Cr(III) dicyclohexyldithiocarbamate

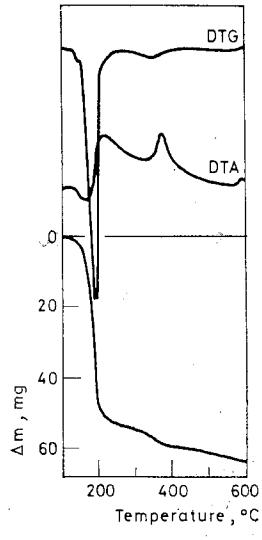


Fig. 8. Thermal curves of Cr(III) tetrahydroquinolinedithiocarbamate

Above 200° the mass changes are slight and correspond to the combustion of sulfur. At the final temperature of measurements, i.e. around 650°, the residue is about 30% of the sample mass and corresponds to Cr_2S_3 plus 2.5 S.

Figure 6 shows the thermal curves of Cr(III) cyclohexyldithiocarbamate. Decomposition begins at 160° and continues up to 210°. The mass loss of around 19% can be attributed to the separation of one organic $(C_6H_{11})HNC$ fragment (calc. 19.2%). Mass loss in the 210–250° range corresponds to the separation of the second fragment, i.e. to about 2/3 of the organic moiety. Up to 273° there is very violent mass decrease accompanied by a pronounced exothermic effect at 270°, corresponding to the separation of the remaining organic moiety and combustion of sulfur. At the endtemperature, the sample mass is 18.1% and corresponds to Cr_2S_3 (17.4%).

Figure 7 shows the thermal curves of Cr(III) dicyclohexyldithiocarbamate. The TG and DTG curves shows the exothermic decomposition of that complex to occur in a multistage process. Mass loss at temperatures up to about 375° is around 71%, which corresponds to the loss of the three organic $(C_6H_{11})_2NC$ fragments (70.3%). Mass loss in the 375–430° range is about 8.5% and corresponds to the combustion of two sulfur atoms (7.9%) and is accompanied by an extended exothermic effect at around 425°. At the endtemperature of measurements, i.e. around 570°, the residue is about 15% of the sample mass and corresponds to Cr_2S_3 (12.3%).

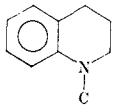
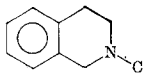
Figure 8 shows the thermal curves of Cr(III) tetrahydroquinolinedithiocarbamate. Decomposition begins at 120°. Mass loss at temperatures up to 270° is 64% and corresponds to the separation of the three organic  fragments (63.4%). On raising the temperature above 270° there is gradual combustion of sulfur; the exothermic effect is at 380° and 590°. At about 600° the endtemperature of the measurement the residue is about 25% of the original sample mass.

Figure 9 shows the thermal curves of Cr(III) tetrahydroisoquinolin-dithiocarbamate. Mass loss in the 180–390° range is around 63% corresponding to the calculated loss of the three organic  fragments (63.4%). Decomposition in this range is at first endothermic (325°), then exothermic (355°). Above 390° there is multistage combustion of sulfur accompanied by an extended exothermic effect at 490°. At the endtemperature of the measurements (700°) the residue is about 23%. The calculated mass based on Cr_2S_3 is 14.9%.

In the two last described cases (Figs 8 and 9) the mass of the residue after completion of the measurements is about 10% higher than that calculated for Cr_2S_3 and corresponds to the mass of the two sulfur atoms (9.4%).

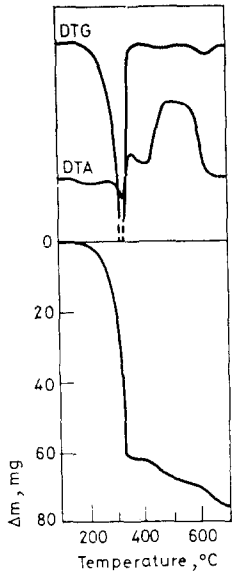


Fig. 9. Thermal curves of Cr(III) tetrahydroisoquinolinedithiocarbamate

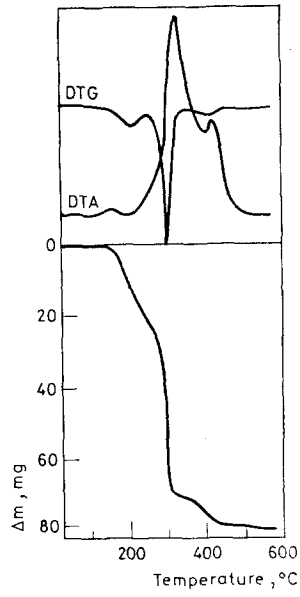


Fig. 10. Thermal curves of Cr(III) morpholinedithiocarbamate

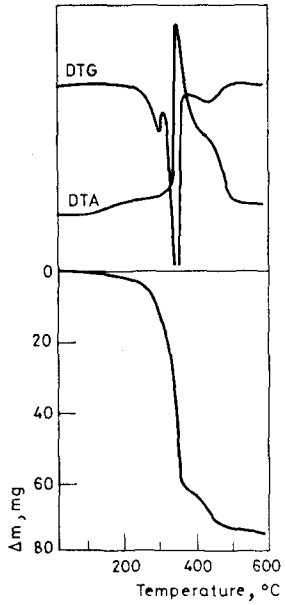


Fig. 11. Thermal curves of Cr(III) pyrazoledithiocarbamate

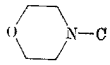
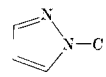
Figure 10 shows the thermal curves of Cr(III) morpholinedithiocarbamate. The first decomposition occurs around 150°; the mass loss of around 17% at temperatures up to 220° is attributable to the separation of the organic  fragment (18.2%). The second similar fragment separates at temperatures up to 270°; the mass loss at around 360° is approximately 75% and corresponds to the loss of the third organic fragment plus 3.5 S (75.5%). There is a pronounced exothermic effect at 335°. In the 390–460° range there is exothermic combustion of one sulfur atom (435°), causing mass loss of around 6% (theoretical 5.9%). At the endtemperature of the measurement, the residue is 17.5% and corresponds to the formation of Cr_2S_3 (18.5%).

Figure 11 shows the thermal curves of Cr(III) pyrazoledithiocarbamate. Mass loss within the 120–300° temperature range is 15% and corresponds to the separation of the organic  fragment (theoretical 16.4%). The main exothermic decomposition at 360° involving a mass loss of about 63.5%, corresponds to the separation of two organic fragments similar to the one mentioned above (theoretical 62.5%). Up to 500° there is further decomposition with an exothermic effect around 440°. The mass loss of around 12.5% is attributable to combustion of two sulfur atoms (theoretical 13.3%). At the endtemperature the sample mass is insignificantly greater than that calculated for Cr_2S_3.

Conclusions

Investigation on the thermal decomposition of Cr(III) dithiocarbamates in the temperature range of 20–600° permitted the determination of the stages of thermal decomposition of these complexes.

The thermal stability of the complexes was found to depend on the nature of the N-substituents of the dithiocarbamate ligand.

Separation of the organic fragment (containing no sulfur) is a multi-stage process, but in the case of pyrollidyne-, hexametylene-, dicyclohexyl-, tetrahydroquinoline-, and tetrahydroisoquinoline-dithiocarbamate of Cr(III), the whole of the organic moiety separates at one stage.

In each case the final decomposition product is chromium sulphide (Cr_2S_3) or Cr_2S_3 plus sulfur.

Exact results in the investigation of the mechanisms of thermal decomposition can be obtained by the use of mass spectrometry.

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The autors would like to thank Doc. dr h. J. F. Biernat for valuable discussions.

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2. B. BATOR-SAWICKA, G. BŁOTNY and J. DOBROWOLSKI, Konferencje — Prace Naukowe Instytutu Chemii Nieorganicznej i Metalurgii Pierwiastków Rzadkich Politechniki Wrocławskiej, 28 (5) (1976) 161; C. A. 85, 115932e (1976).
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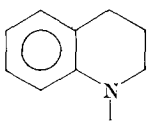
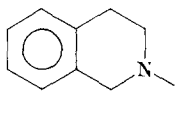
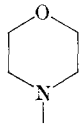
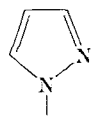
6. G. D'ASCENZO and W. W. WENDLANDT, J. Inorg. Nucl. Chem., 32 (1970) 2431.

RÉSUMÉ — On a étudié la stabilité thermique des complexes du chrome(III) avec les dérivés de l'acide dithiocarbamique. La formule générale de ces complexes est $(RCS_2)_3Cr$ où:

R = $(CH_3)_2N-$; $(C_2H_5)_2N-$; $(CH_2)_4N-$;

$(CH_2)_6N-$; $C_6H_{11}NH-$; $(C_6H_{11})_2N-$;

 ;  ;  ; 

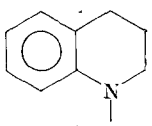
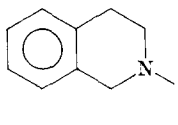
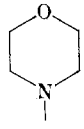
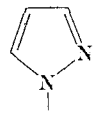
On a trouvé que la stabilité thermique de ces complexes dépendait de la nature du radical et que la décomposition se déroulait en plusieurs étapes.

Dans l'intervalle de température étudié, de 20 à 600°, le produit final de la décomposition des complexes est le sulfure de chrome, Cr_2S_3, éventuellement accompagné de soufre résultant d'une combustion incomplète.

ZUSAMMENFASSUNG — Die Thermostabilität von Chrom(III)-Komplexen mit sauren Derivaten von Dithiocarbamat wurde untersucht. Die allgemeine Formel dieser Komplexe ist

R = $(CH_3)_2N-$; $(C_2H_5)_2N-$; $(CH_2)_4N-$;

$(CH_2)_6N-$; $C_6H_{11}NH-$; $(C_6H_{11})_2N-$;

 ;  ;  ; 

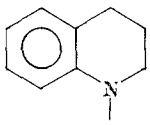
$(RCS_2)_3Cr$. Es wurde festgestellt, daß die Thermostabilität dieser Komplexe von der Art von R abhängt und die Zersetzung in mehreren Stufen verläuft.

Das Endprodukt der Zersetzung der Komplexe im untersuchten Temperaturbereich von 20 bis 600° ist Chromsulfid, Cr_2S_3, oder solches mit überschüssigem Schwefel.

Резюме — Изучена термическая стабильность комплексов хрома (III) с поизводными тионтиловой кислоты. Общая формула этих комплексов — $(RCS_2)_3$ Cr, где

R = $(CH_3)_2N-$; $(C_2H_5)_2N-$; $(CH_2)_4N-$;

$(CH_2)_6N-$; $C_6H_{11}NH-$; $(C_6H_{11})_2N-$;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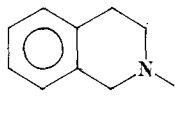
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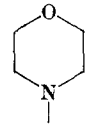
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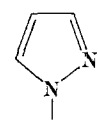

Найдено, что термическая стабильность этих комплексов зависит от типа радикала R и разложение протекает в несколько стадий. В исследованной области температур 20—600° конечным продуктом разложен комплексов является сульфид хрома или Cr_2S_3 с непольностью сгоревшими атомами серы.