Journal of Thermal Analysis, Vol. 23 (1982) 123—133

KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA. XX. STUDY OF THE THERMAL DECOMPOSITION OF SOME TETRATHIOCYANATO-DIAMINO-CHROMATE COMPLEXES WITH DERIVATOGRAPH

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(Received May 22, 1981)

The thermal decompositions of 8 complexes of the type A · $H[Cr(NCS)_4(am)_2]$ (A = NH_3, pyridine, α-picoline or aniline, and *am* = NH_3 or aniline) and of 14 complexes of the type $M[Cr(NCS)_4(am)_2]$ (M = K, Ag, Tl, 1/2 Cd, 1/2 Pb or 1/3 Bi, and *am* = NH_3, benzylamine or aniline derivatives) were studied by means of a derivatograph. In the case of the A · H salts the formation of $Cr(NCS)_3$ was observed as a labile intermediate. Characteristic temperatures are discussed in terms of the polarizing effect of the outer sphere cations and of the nucleophilic character of the ligands. The results are compared with those obtained in the thermal decompositions of the analogous salts of the complex acid $H_3[Cr(NCS)_6]$.

The Reinecke salt $NH_3[Cr(NCS)_4(NH_3)_2] \cdot H_2O$ forms a series of well-crystalline, slightly-soluble salts with mono- and bivalent transition metals, with metal (II, III) amines of different types [1, 2], with organic N-bases, and especially with heterocyclic amines and alkaloids in acidic media [3]. These reineckates are of importance from an analytical point of view (gravimetric and volumetric determination of metals and N-bases of biological and pharmaceutical importance) [4].

Substitution of the ammonia in the $[Cr(NCS)_4(NH_3)_2]^-$ ion by aromatic and heterocyclic amines leads to the formation of reinecke salt like compounds. The first compound in this class is the ammonium rhodanylate, $NH_4[Cr(NCS)_4(\text{aniline})_2] \cdot$ $\cdot H_2O$, isolated first by Bergmann [5].

The salt-forming properties of this aniline derivative are analogous with those of the Reinecke salt.

The thermal decomposition of $NH_4[Cr(NCS)_4(NH_3)_2] \cdot H_2O$ was studied first by Aycock [6] (heating on an oil-bath) and by Krausz and Kovács [7]. Some reineckates of the heavy metals were investigated by means of thermogravimetry by Liteanu and Boda [8], and some amine salts by Boda et al. [9]. For the decomposition mechanism Krausz and Kovács propose the formation of the free Reinecke acid, $H[Cr(NCS)_4(NH_3)_2]$, $Cr(NCS)_3$ and CrO_3 as intermediates. During the decomposition of the amine salts (aromatic and heterocyclic amines), Boda et al. [9] did not find CrO_3 as an intermediate in the decomposition.

The simple thermogravimetric study of the reineckates and rhodanylates of some cobalt(III)-amine bases of hexamine, monoacido-pentamine and diacido-tetramine types (e. g. $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(NH_3)_5X]^{2+}$, $[Co(en)_2X(amine)]^{2+}$, $[Co(Diox.H)_2(amine)_2]^+$, $[Co(en)_2X_2]^+$, etc.) shows the thermal decompositions of these complex salts to be very complicated processes; N_2, CO, CO_2, S, SO_2, amines, carbon, free oximes, HX and X_2 (X = Cl, Br, I) are formed in non-stoichiometric ratios during the pyrolyses. The final product at 800° is a stoichiometric amount of $Co_3O_4 + Cr_2O_3$ (1/3 Co_3O_4 + 1 1/2 Cr_2O_3, 1/3 Co_3O_4 + Cr_2O_3, and 1/3 Co_3O_4 + 1/2 Cr_2O_3, respectively). During the thermolyses of these substances, no stoichiometric intermediates are formed [10, 11].

In this paper the thermal degradations of the tetrathiocyanato-diamino-chromates of some monovalent transition metals and of some amine bases were studied by means of a derivatograph. The results are compared with those obtained with the analogous salts of the complex acid $H_3[Cr(NCS)_6]$ [12].

Results and discussion

The thermal decompositions of 8 ammonium salts of the general formula A · H[Cr(NCS)$_4$(am)$_2$] and 14 metal salts of the type M[Cr(NCS)$_4$(am)$_2$] have been studied by means of a derivatograph, where A = pyridine, α-picoline, aniline or ammonia, M = K, Ag, Tl, $Cd_{1/2}$, $Pb_{1/2}$ or $Bi_{1/3}$ and *am* = ammonia, benzylamine or various aniline derivatives.

Thermal decomposition of the ammonium salts

Some representative thermal curves are presented in Fig. 1.

The general features of the thermal decomposition are seen to be the same as for the ammonium salts of the complex acid $H_3[Cr(NCS)_6]$ [12], i. e. after the first decomposition stage a not well-defined weight loss stop is observed, corresponding to the formation of $Cr(NCS)_3$ as labile intermediate. The sample weight at this weight loss stop corresponds almost exactly to the composition $Cr(NCS)_3$ in the case of the reineckates, but it is a little higher with the rhodanylates. During this decomposition stage two endothermic peaks are observed in the DTA curves; these are given in Table 1. The decomposition of $Cr(NCS)_3$ is not a single process, but consists of the superposition of several exothermic processes, indicated by two exothermic peaks in the DTA curves, also given in Table 1.

It can be presumed that these exothermic processes are oxidation reactions involving the participation of atmospheric oxygen. The last and largest exothermic peak appears at about 500–525°, as with the hexathiocyanato-chromates. The final product of these reactions is Cr_2O_3 and the mass of the samples attains the corresponding value at about 750°. It is worth mentioning that the final weight at 750° of the product from some rhodanylates slightly exceeds the value corresponding to Cr_2O_3, but it is not consistent with the hypothesis of Krausz and Kovács [7] concerning the formation of CrO_3.

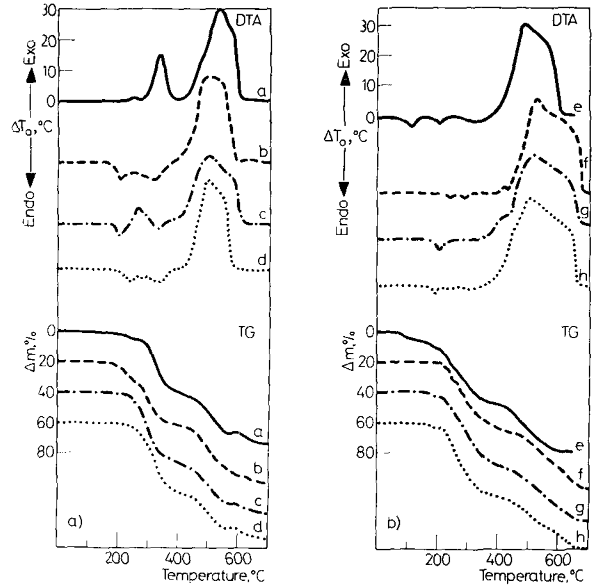

Fig. 1. TG and DTA curves: (a) $NH_4[Cr(SCN)_4(NH_3)_2] \cdot H_2O$, (b) aniline. $H[Cr(NCS)_4(NH_3)_2]$, (c) piridine. $H[Cr(NCS)_4(NH_3)_2]$, (d) α-picoline. $H[Cr(NCS)_4(NH_3)_2]$, (e) $NH_4[Cr(NCS)_4(\text{aniline})_2] \cdot H_2O$, (f) aniline. $H[Cr(NCS)_4(\text{aniline})_2]$, (g) pyridine. $H[Cr(NCS)_4(\text{aniline})_2]$, (h) α-picoline. $H[Cr(SCN)_4(\text{aniline})_2]$

Table 1

DTA peak temperatures (°C) in the thermal decomposition of $A.H[Cr(NCS)_4(am)_2]$ type complexes. Heating rate 10°/min

A	*am*	Endothermic peaks		Exothermic peaks	
pyridine	NH_3	205	327	385	500
α-picoline	NH_3	240	330	380	500
aniline	NH_3	205	315	380	495
NH_3	NH_3	230	290	345	540
pyridine	aniline	198	335	405	520
α-picoline	aniline	190	310	410	500
aniline	aniline	225	390	435	525
NH_3	aniline	200	315	400	490

Since the TG curves of the ammonium salts show two relatively well-defined decomposition stages, an attempt has been made to derive kinetic parameters for these decomposition stages. For this purpose the authors' nomogram method [13] was used.

Table 2

Characteristic temperatures and kinetic parameters of the two decomposition stages of A.H$[Cr(NCS)_4(am)_2]$ type complexes

Stage	A	*am*	$t_{0.1}$	$t_{0.5}$	$t_{0.9}$	t_m	n	E kJ/mol	log Z
I.	pyridine	NH_3	250	294	337	308	1.61	107.0	7.6
	α-picoline	NH_3	262	312	343	312	0.64	83.6	4.9
	aniline	NH_3	220	287	335	303	0.80	54.3	2.4
	NH_3	NH_3	240	320	355	338	−0.02	42.2	0.8
	pyridine	aniline	225	300	346	305	0.49	46.4	1.4
	α-picoline	aniline	225	278	328	297	1.43	77.7	5.1
	aniline	aniline	235	292	364	293	2.08	84.4	5.5
	NH_3	aniline	195	268	322	295	0.78	44.3	1.6
II.	pyridine	NH_3	417	494	544	495	0.69	91.1	3.5
	α-picoline	NH_3	444	498	537	486	0.95	145.5	7.4
	aniline	NH_3	434	488	535	475	1.36	153.0	8.2
	NH_3	NH_3	436	504	546	520	0.63	108.3	4.6
	pyridine	aniline	450	517	578	520	1.41	129.6	6.1
	α-picoline	aniline	452	508	573	498	2.02	171.8	9.3
	aniline	aniline	470	535	580	520	0.88	129.2	5.8
	NH_3	aniline	427	493	544	482	1.02	114.5	5.2

The results are given in Table 2. This Table contains characteristic temperatures of the TG curves, viz. the temperatures corresponding to the conversion values 0.1, 0.5 and 0.9, and the temperature of the maximum decomposition rate (t_m), as well as the kinetic parameters derived, viz. the apparent reaction order n, the activation energy E and the pre-exponential factor Z (given in s^{-1}) for both stages, presumably corresponding to the reactions:

$$A \cdot H[Cr(NCS)_4(am)_2] \rightarrow Cr(NCS)_3 \qquad (1)$$

$$Cr(NCS)_3 \rightarrow Cr_2O_3 \qquad (2)$$

At first sight no systematic variation can be observed. Accordingly a statistical analysis of the data was performed, including the values obtained for the analogous ammonium salts of the complex acid $H_3[Cr(NCS)_6]$ [12]. For this purpose the mean values of the characteristic temperatures and of the kinetic parameters have been calculated separately for each outer sphere amine (A), irrespective of the nature of *am*, and separately for each inner sphere amine *(am)*, irrespective of A. Since the values obtained for $(NH_4)_3[Cr(NCS)_6]$ show an anomalously high deviation from the mean values obtained, this salt was not included in the present calculations.

General mean values, standard deviations and relative standard deviations have also been calculated. All these values are presented in Table 3.

Table 3

Mean values of the characteristic temperatures and of the kinetic parameters of the two decomposition stages of A.H[Cr(NCS)$_4$(am)$_2$] type complexes. General mean values (Gr. M.), standard deviations (S. D.) and relative standard deviations (R. S. D.)

Stage	A	*am*	$t_{0.1}$	$t_{0.5}$	$t_{0.9}$	t_m	n	E kJ/mol	log Z
I.	pyridine	—	236	305	354	318	0.89	64.9	3.3
	α-picoline	—	254	302	340	308	1.10	93.1	6.1
	aniline	—	227	277	350	298	1.44	69.3	2.8
	NH_3	—	217	294	338	316	0.38	43.2	1.2
	—	NCS	253	317	363	327	0.89	79.5	4.5
	—	NH_3	243	303	342	315	0.76	71.8	3.9
	—	aniline	220	284	340	297	1.19	63.2	3.4
	Gr.M.		236	299	346	311	0.96	69.9	3.8
	S.D.		22.4	18.0	16.8	16.6	0.62	28.2	2.8
	R.S.D.%		9.5	6.0	4.9	8.3	64.6	40.3	73.7
II.	pyridine	—	444	507	557	505	1.19	140.7	6.9
	α-picoline	—	447	502	550	496	1.31	152.8	7.9
	aniline	—	452	511	557	497	1.12	141.1	7.0
	NH_3	—	431	498	545	501	0.82	111.4	4.9
	—	NCS	454	505	545	502	1.21	171.2	9.1
	—	NH_3	433	496	540	494	0.91	124.5	5.9
	—	aniline	450	513	569	505	1.33	136.3	6.6
	Gr.M.		444	505	553	500	1.14	138.5	6.8
	S.D.		16.3	13.8	17.4	16.3	0.42	32.0	2.3
	R.S.D.%		3.7	2.7	3.1	3.3	36.8	23.1	33.8

The relative standard deviations are seen to be much higher for the first stage of the decomposition, than for the second one. This is in agreement with our presumption that the second stage involves the same chemical reaction [2], but the first stage is different and its characteristic temperatures and kinetic parameters are affected by the nature of both A and *am*. As far as the influence of the outer sphere amine A upon stage 1 is concerned, the general picture is not quite clear. The only thing revealed is that almost all the presented values have their minimum value in the case of A = NH_3. This might be related to the very low boiling point of NH_3 as compared to those of the amines. The influence of the inner sphere *am* is quite clear. All the magnitudes presented in Table 3, except of the apparent reaction order, decrease in the order NCS > NH_3 > aniline. Thus, this order indicates the decreasing thermal stability of the corresponding anions and at the same time the decreasing Cr-ligand bond strength. This order is easily explicable in terms of nucleophilic character and π-bond formation possibilities. If only σ-type metal-ligand bonds are formed, the bond strength increases with increasing nucleophilic character. This is why the reineckate anion is more stable and needs a higher apparent activation energy than rhodanylate anion. Although HNCS is a strong acid,

i. e. its nucleophilic character is extremely reduced, its anions give the most stable complex anion due to the possibility of strong metal-ligand π-bond formation. This is why the characteristic temperatures and the apparent activation energy have their temperatures and the apparent activation energy have their highest values for the salts of the $[Cr/NCS)_6]^{3-}$ anion.

Thermal decompositions of the metal salts

The thermal decompositions of both the metal reineckates and the rhodanylates occur in a very similar way to that of the hexathiocyanato-chromates.

Some representative thermal curves are given in Figs 2 and 3.

The positions of the main DTA peaks are given in Table 4. It may be seen from this Table that no endothermic decomposition stage is observed, except for Cd and Pb rhodanylates, where an endotheric peak appears below 200°. This might be related to the low stability of the complex anion and to the loss of a part of the aniline without its oxidation. As far as the position of the largest exothermic peak is concerned (given in italics in Table 4), it seems to be correlated with the polarizing effect of the outer sphere cation. This peak temperature decreases in the order

$$K > Cd > Ag > Pb > Bi$$

which corresponds to the increasing order of the polarizing effect of the corresponding cation. A surprising exception is observed with the Tl salts, where the largest

Table 4

DTA peak temperatures (°C) in the thermal decomposition of $M[Cr(NCS)_4(am)_2]$ type complexes

M	*am*	Endothermic peaks	Exothermic peaks				Heating rate °/min
K	NH_3	—	330	445	*540*		5
Ag	NH_3	—	240	*410*	500		10
Ag	aniline	—	180	*370*	430	510	10
Tl	NH_3	—	310	350	470	*560*	10
Tl	aniline	—	300	390	430	*550*	10
$Cd_{1/2}$	NH_3	—	355	430	*495*		5
$Cd_{1/2}$	aniline	160	260	390	*525*		10
$Pb_{1/2}$	NH_3	—	310	*360*	510		10
$Pb_{1/2}$	aniline	180	*330*	420	480	525	10
$Bi_{1/3}$	NH_3	—	*280*				2
$Bi_{1/3}$	aniline	—	240	*260*	360		2
$Bi_{1/3}$	*o*-toluidine	—		*260*	375		2
$Bi_{1/3}$	*p*-toluidine	—	200	*265*	380		2
$Bi_{1/3}$	benzylamine	—	210	*280*	400		2
$Bi_{1/3}$	*p*-anisidine	—	180	*255*	410		2

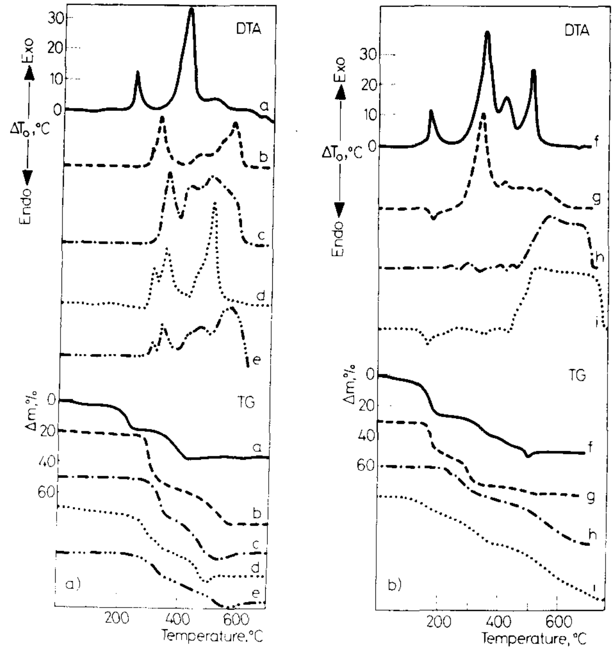

Fig. 2. TG and DTA curves: (a) $Ag[Cr(NCS)_4(NH_3)_2]$, (b) $K[Cr(NCS)_4(NH_3)_2]$, (c) $Cd[Cr(NCS)_4(NH_3)_2]_2$, (d) $Pb[Cr(NCS)_4(NH_3)_2]_2$, (e) $Tl[Cr(NCS)_4(NH_3)_2]$, (f) $Ag[Cr(NCS)_4(aniline)_2]$, (g) $Pb[Cr(NCS)_4(aniline)_2]_2$, (h) $Tl[Cr(NCS)_4(aniline)_2]$, (i) $Cd[Cr(NCS)_4(aniline)_2]_2$

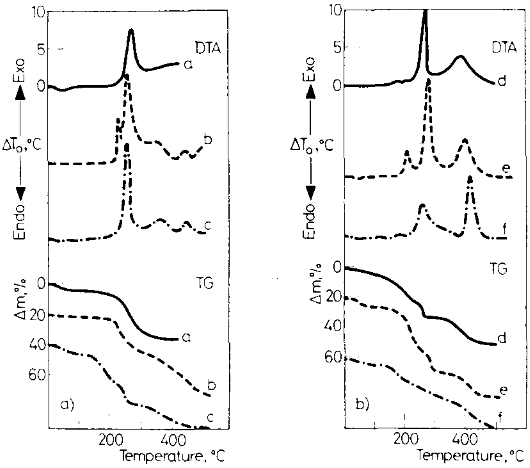

Fig. 3. TG and DTA curves: (a) $Bi[Cr(NCS)_4(NH_3)_2]_3$, (b) $Bi[Cr(NCS)_4(aniline)_2]_3$, (c) $Bi[Cr(NCS)_4(o\text{-toluidine})_2]_3$, (d) $Bi[Cr(NCS)_4(p\text{-toluidine})_2]_3$, (e) $Bi[Cr(NCS)_4(benzylamine)_2]_3$, (f) $Bi[Cr(NCS)_4(p\text{-anisidine})_2]_3$

peak appears at even higher temperature than in the case of the K salt. This is in contradiction with the ionic radius and the electronic structure of the Tl^+ ion and even with our experimental data concerning the behaviour of $Tl_3[Cr(NCS)_6]$, where the largest exothermic peak appeared at lower temperature than for the corresponding Ag salt [12]. It is true that $Tl[Cr(NCS)_4(NH_3)_2]$ and $Tl[Cr(NCS)_4(am)_2]$ also show a strong exothermic peak, at 350 and 300°, respectively, which would be in agreement with the high polarizing effect of Tl^+, but nevertheless the nature of the large exohermic peak at 560 and 550°, respectively, remains quite obscure.

The thermal curves of the Bi salts were recorded at much lower heating rates than in the other cases. Thus, the shift of the exothermic peak temperatures towards lower values is exaggerated. With a heating rate of 10°/min, this shift would be less by about 10–20°. Obviously, this could not modify the order of the peak temperatures.

The data presented in Table 4 show that the maximum exothermic peaks appear at lower temperatures for the rhodanylates than for the corresponding reineckates. This shows the thermal stability to decrease in the order $[Cr(NCS)_4(NH_3)_2]^+ > > [Cr(NCS)_4(am)_2]^+$, corresponding to the order of decreasing nucleophilic character of the inner sphere amine. In the case of the Bi salts the same effect is observed, the peak temperature being higher if *am* $= NH_3$ or benzylamine, while it is lower if *am* is a weak base, such as aniline or an aniline derivative.

As regards the final product of the thermal decomposition, it seems to be a mixture of Cr_2O_3 and M_2SO_4 This conclusion is consistent with the sample weight values at 700–750° and also with the weight gain of the samples at these temperatures, indicating sulphate formation (absorption of atmospheric oxygen). Since the thermal curves of the Bi salts have been recorded only up to 450–500°, the final weights of the samples remain higher than the values corresponding to the abovementioned mixtures.

No kinetic parameters can be derived from the TG curves, due to their irregular shape.

Experimental

$NH_4[Cr(NCS)_4(NH_3)_2] \cdot H_2O$ was obtained in the melted state from $(NH_4)_2Cr_2O_7$ and NH_4NCS. The crude product was dissolved in warm water (60°), filtered and reprecipitated with an excess of NH_4NO_3 [1].

$NH_4[Cr(NCS)_4(am)_2]$ was also formed in the melted state, from $K_3[Cr(NCS)_6]$ and aniline derivatives or benzylamine. The crude product was dissolved in methanol and the ammonium salt was precipitated with an excess of saturated NH_4Cl solution [14].

Metal salts: 5g MNO_3 was dissolved in 200–500 ml water and treated with an excess of 2% $NH_4[Cr(NCS)_4(NH_3)_2]$ in water or 2% $NH_4[Cr(NCS)_4(am)_2]$ in dil. alcohol (1 : 2). The crystalline products formed were filtered off, washed with water and dried in air.

Table 5

Analytical data on the A.H[$Cr(NCS)_4(am)_2$] and M[$Cr(NCS)_4(am)_2$] type complexes

Formula	Mol. weight calcd.	Analysis		
		calcd. %		found %
$NH_4[Cr(NCS)_4(NH_3)_2] \cdot H_2O$	354.4	Cr	14.67	14.45
		S	36.19	36.05
$K[Cr(NCS)_4(NH_3)_2] \cdot H_2O$	375.5	Cr	13.85	13.76
		S	34.15	34.27
$NH_4[Cr(NCS)_4(\text{aniline})_2] \cdot H_2O$	506.6	Cr	10.26	10.34
		S	25.32	25.55
$Ag[Cr(NCS)_4(NH_3)_2]$	426.3	Cr	12.20	12.43
		S	30.00	29.87
$Ag[Cr(NCS)_4(\text{aniline})_2]$	578.5	Cr	8.99	8.85
		S	22.17	22.40
$Tl[Cr(NCS)_4(NH_3)_2]$	522.8	Cr	9.95	10.13
		S	24.53	24.39
$Tl[Cr(NCS)_4(\text{aniline})_2]$	674.9	Cr	7.70	7.66
		S	19.00	18.76
$Pb[Cr(NCS)_4(NH_3)_2]_2$	844.0	Cr	12.32	12.45
		Pb	24.55	24.80
$Pb[Cr(NCS)_4(\text{aniline})_2]_2$	1148.4	Cr	9.05	8.88
		Pb	18.04	18.30
$Cd[Cr(NCS)_4(NH_3)_2]_2$	749.2	Cr	13.88	13.65
		S	34.25	34.37
$Cd[Cr(NCS)_4(\text{aniline})_2]_2$	1053.5	Cr	9.87	9.74
		S	24.36	24.52
pyridine $\cdot H[Cr(NCS)_4(NH_3)_2]$	398.5	Cr	13.05	12.89
		S	32.18	32.34
pyridine $\cdot H[Cr(NCS)_4(\text{aniline})_2]$	550.7	Cr	9.44	9.32
		S	23.29	23.11
α-picoline $\cdot H[Cr(NCS)_4(NH_3)_2]$	412.5	Cr	12.61	12.56
		S	31.10	30.90
α-picoline $\cdot H[Cr(NCS)_4(\text{aniline})_2]$	564.7	Cr	9.21	9.34
		S	22.71	22.63
aniline $\cdot H[Cr(NCS)_4(NH_3)_2]$	412.5	Cr	12.61	12.44
		S	31.10	31.25
aniline $\cdot H[Cr(NCS)_4(\text{aniline})_2]$	564.7	Cr	9.21	9.09
		S	22.71	22.89

Ammonium salts: 10 mmole of the corresponding amine (aniline, pyridine or picoline) was treated with 10 ml conc. HCl and then dissolved in 50 – 100 ml water. The solutions obtained were treated with an excess of 2% $NH_4[Cr(NCS)_4(NH_3)_2]$

Table 6

New bismuth salts of the type $Bi[Cr(NCS)_4(am)_2]_3$

Formula	Mol. weight calcd.	Appearance	Analysis		
			calcd. %		found %
$Bi[Cr(NCS)_4(NH_3)_2]_3$	1164.2	red-violet microcryst., soluble in acetone, DMF (1 : 2)	Bi	17.95	18.20
			Cr	13.40	13.32
			S	33.07	33.20
$Bi[Cr(NCS)_4(aniline)_2]_3$	1620.7	red-violet microcryst. soluble in acetone, DMF	Bi	12.90	13.20
			Cr	9.62	9.50
			S	23.75	23.83
$Bi[Cr(NCS)_4(o\text{-}toluidine)_2]_3$	1704.9	red-violet microcryst.	Bi	12.26	12.12
			Cr	9.15	9.08
			S	22.58	22.72
$Bi[Cr(NCS)_4(p\text{-}toluidine)_2]_3$	1704.9	red-violet microcryst.	Bi	12.26	12.33
			Cr	9.15	9.26
			S	22.58	22.32
$Bi[Cr(NCS)_4(benzylamine)_2]_3$	1704.9	red-violet microcryst.	Bi	12.26	12.19
			Cr	9.15	9.17
			S	22.58	22.55
$Bi[Cr(NCS)_4(p\text{-}anisidine)_2]_3$	1802.9	red-violet microcryst.	Bi	11.59	11.47
			Cr	8.65	8.57
			S	21.35	21.22

Bi determined gravimetrically as Bi_2O_3

or with 2% $NH_4[Cr(NCS)_4(am)_2]$. The slightly-soluble complex salts were filtered off, washed with water and dried in air.

The purities of the products were checked by chemical analysis (Tables 5, 6). Chromium contents were determined iodometrically after oxidation to chromate, NH_3 contents acidimetrically after distillation, the nitrogen by the Dumas method, and the thiocyanate gravimetrically as $BaSO_4$.

The thermal measurement were carried out with a MOM derivatograph [15]. Sample weight: 100 mg; atmosphere: static air; reference material: α-Al_2O_3; platinum crucible.

References

1. O. T. Christensen, J. prakt. Chem., (2), 45 (1892) 213, 356.
2. O. Nordenskjöld, Z. anorg. allg. Chem., 1 (1892) 126.
3. P. Duquennois and M. Faller, Bull. Soc. chim. France, (5), 1 (1939) 998.
4. R. Coupechoux, J. Pharm. Chim., 30, 118 (1939) 118.
5. M. Bergmann, J. biol. Chem., 110 (1935) 476.
6. B. F. Aykock, J. Amer. Chem. Soc., 73 (1951) 1351.
7. P. J. Krausz and J. Kovács, Ann. Univ. Sci. Budapestiensis de R. Eötvös nom. Sect. Chim., 4 (1962) 37.
8. C. Liteanu and G. Boda, Studia Univ. Babeş-Bolyai, Cluj, Chemia, 7 (1962) 41.
9. G. Boda, Cs. Várhelyi and Á. Mostis, Studia Univ. Babeş-Bolyai, Chemia, 10 (2) (1965) 63.
10. Cs. Várhelyi, G. Boda and L. Bradu, Anal. Univ. Bucureşti, sect. Stiinţ. nat., 14 (1) (1965) 69.
11. I. Gănescu, Cs. Várhelyi and D. Oprescu, Rev. Roumaine Chim., 13 (1968) 1321.
12. G. Liptay, Cs. Várhelyi, E. Brandt-Petrik and J. Zsakó, J. Thermal Anal., 22 (1981) 205
13. J. Zsakó, J. Thermal Anal., 15 (1979) 369; J. Zsakó, M. Várhelyi, and Cs. Várhelyi, J. Thermal Anal., 17 (1979) 123.
14. J. Zsakó, Cs. Várhelyi and I. Gănescu, Rev. Roumaine Chim., 13 (1968) 581.
15. F. Paulik and J. Paulik, Z. analyt. Chem., 160 (1958) 241.

Zusammenfassung — Die thermische Zersetzung von 8 Komplexverbindungen des Typs $A \cdot H[Cr(NCS)_4(am)_2]$ (A = NH_3, Pyridin, α-Picolin, Anilin und "am" = NH_3 und Anilin) und von 14 Komplexen des Typs $M[Cr(NCS)_4(am)_2]$ (M = K, Ag, Tl, 1/2 Cd, 1/2 Pb, 1/3 Bi und "am" = NH_3, Anilin und Anilinderivate) wurde mit dem Derivatographen untersucht. Im Falle der A. H Salze wird die Bildung von $Cr(NCS)_3$ als labiles Zwischenprodukt beobachtet. Die charakteristischen Temperaturen und kinetischen Parameter werden abgeleitet und auf der Basis der molekularen Struktur erörtert. Im Falle der M Salze werden die DTA-Peaks aufgrund des Polarisationseffektes der Kationen der äußeren Sphäre und des nukleophilen Charakters der Liganden diskutiert. Die Ergebnisse werden mit jenen der thermischen Zersetzung der analogen Salze des $H_3[Cr(NCS)_6]$ Komplexes verglichen.

Резюме — С помощью дериватографа изучено термическое разложение восьми комплексов типа A. $H[Cr(NCS)_4(ам)_2]$, где A — аммиак, пиридин, α-пиколин и анилин, а «ам»-аммиак и анилин. Наряду с этим изучено разложение четырнадцати комплексов типа $M[Cr(NCS)_4(ам)_2]$, где M—K, Ag, Tl, 1/2 Cd, 1/2Pb и 1/3 Bi, а «ам» — аммиак, анилин и производные анилина. В случае солей типа A. H наблюдалось образование $Cr(NCS)_3$, как нестойкого промежуточного продукта. Установлены характерные температуры и кинетические параметры, обсуждение которых проведено на основе молекулярной структуры. В случае солей типа M, ДТА температурные пики обсуждены на основе поляризационного влияния внешне-сферных катионов и нуклеофильного характера лигандов. Результаты исследования сопоставлены с данными по термическому разложению аналогичных солей кислоты $H_3[Cr(NCS)_6]$.