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THE RELATIONSHIP BETWEEN THE STRUCTURES OF Cu(II) COMPLEXES AND THEIR CHEMICAL TRANSFORMATIONS: VII.

The influence of acido ligands on the courses of the thermal decompositions of the complexes $Cu(en)_2X_2$ and $Cu(en)_2(NCS)X$

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The thermal decompositions of $Cu(en)_2(NCS)X$, where $X^- = Cl^-, Br^-, NO_3^-, BF_4^-$ and ClO_4^-, have been studied in comparison with the courses of $Cu(en)_2(SCN)_2$ and $Cu(en)_2X_2$ decomposition. It is shown that the presence of the thiocyanate group in the complexes $Cu(en)_2(NCS)X$ is the most important factor in the decomposition course, in agreement with the fact that the anions X^- are not coordinated, or are only semicoordinated. Significant differences were found in the courses of thermal decomposition of two forms of $Cu(en)_2(NCS)(BF_4)$ differing in the structure of their coordination polyhedra.

The influence of the structure on the course of the thermal decomposition of coordination compounds is frequently discussed in the literature. The aim of the present work was to study the course of thermal decomposition of Cu(II) complexes containing ethylenediamine (en) and the thiocyanate group in the heterogeneous coordination sphere. The thiocyanate group exhibits a wide variety of coordination possibilities [1]. In tetragonal-bipyramidal Cu(II) complexes, this group can be coordinated to the central atom via the nitrogen atom (in the equatorial plane and in the axial positions) or via the sulphur atom (in the axial positions only), and it also often forms bridges between Cu(II) atoms. The mode of its coordination to Cu(II) depends both on the properties of the other ligands present in the coordination sphere and on the counter ions. It has been established that the substitution of one—SCN group in $Cu(en)_2(SCN)_2$ for ClO_4^- [2] or Br^- [3] anions leads to N-coordination of the NCS group in $Cu(en)_2(NCS)X$ ($X^- = ClO_4^-, Br^-$), in contrast to its S-coordination in $Cu(en)_2(SCN)_2$ [4]. Analogous differences in the coordination of the thiocyanate group are assumed for other complexes $Cu(en)_2(NCS)X$, where $X^- = Cl^-, NO_3^-$ and BF_4^- [5]. Moreover, the complex with

$X^- = BF_4^-$ has been prepared in two forms differing significantly in the structures of their coordination polyhedra [5]. It was therefore of interest to study manifestations of the structural differences in the course of the thermal decompositions of the complexes $Cu(en)_2(NCS)X$ in comparison with that found for $Cu(en)_2(SCN)_2$.

Experimental

Procedures for the preparation of the complexes under study, as well as the analytical results, are given in [5].

Thermal decompositions of the complexes were performed on an OD–102 derivatograph in dynamic nitrogen atmosphere. All complexes were finely powdered before measurements. The sample weight was 100 mg, the heating rate was 6 or 9 deg min^{-1}, and α-Al_2O_3 was used as reference material for DTA.

Results and discussion

A. Thermal decomposition of the complexes $Cu(en)_2X_2$

The thermal decomposition of $Cu(en)_2(SCN)_2$ (Fig. 1, Table 1) starts at relatively low temperature (150°). Before decomposition, the complex melts at 130°. In the

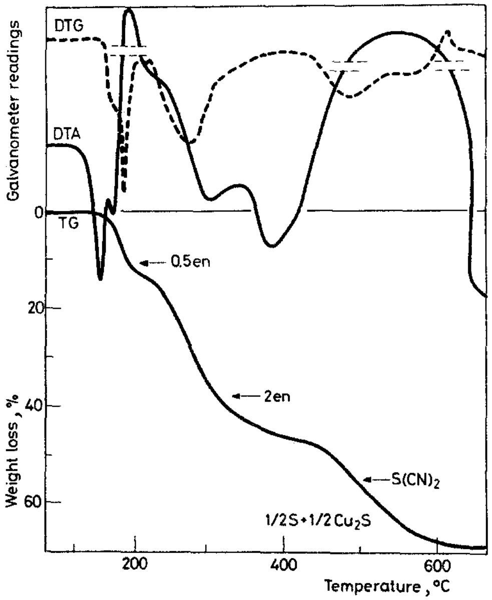

Fig. 1 TG, DTG and DTA curves of $Cu(en)_2(SCN)_2$

Table 1 The course of thermal decomposition of $Cu(en)_2X_2$

X^-	Weight loss	Melting temperature, °C	Temperature of decomposition, °C	Remark
SCN	0.5 en	130	155	endothermic
ClO_4		210	215	explosion
NO_3		195	200	explosion
BF_4	0.5 en		210	exothermic
Br	1 en		230	endothermic
Cl	1 en		215	

first step of decomposition 0.5 mole of ethylenediamine is released, which has also been proved analytically by the content of copper in the intermediate prepared at 150° (Table 3). However, the DTA curve indicates a more complicated course of decomposition, the release of ethylenediamine being accompanied by a small endothermic peak, followed immediately by a strong exothermic peak. This can be caused by recrystallization of the molten sample during the evolution of ethyldiamine, as observed in the decomposition of $Cu(en)SO_4$ [6]. The other complexes $Cu(en)_2X_2$ exhibit higher thermal stabilities (Table 1). The course of their thermal decomposition depends strongly on the anion present. The decompositions of complexes with $X^- = ClO_4^-$ and NO_3^- are accompanied by an explosion. From $Cu(en)_2(BF_4)_2$, a little more than 0.5 mole of ethylenediamine excapes in the first step (Fig. 2). The formation of $Cu(en)X_2$ during the thermal decomposition of bis-ethylenediamine complexes was observed in the TG curve for the complexes with $X^- = Cl^-$ and Br^- only. These reactions proceed with activation energies (calculated according to the Coats–Redfern method [7]) of 153 ± 10 and 221 ± 10 kJ mol^{-1} for Cl^- and Br^-, respectively [8]. However, formation of the monoethylenediamine complex is indicated in the TG curves only by the break in the curve, and no plateau has been observed.

From the above experimental data relating to the decompositions of the complexes $Cu(en)_2X_2$, we can conclude that the chemical properties of the anions present, and their ability to be coordinated or to cause redox reactions, play the most important roles in the course of their thermal decompositions. The lowest thermal stability for $Cu(en)_2(SCN)_2$, as compared with the other complexes $Cu(en)_2X_2$ studied, could be connected with the reducing influence of the thiocyanate group, coordinated to the Cu(II) via the sulphur atom in the direction of unpaired electron localization, as suggested for other Cu(II) complexes [9]. Due to the melting of the complexes before their decomposition, the interpretation of their thermal stabilities on the basis of their room-temperature crystal structures should not be absolutely correct.

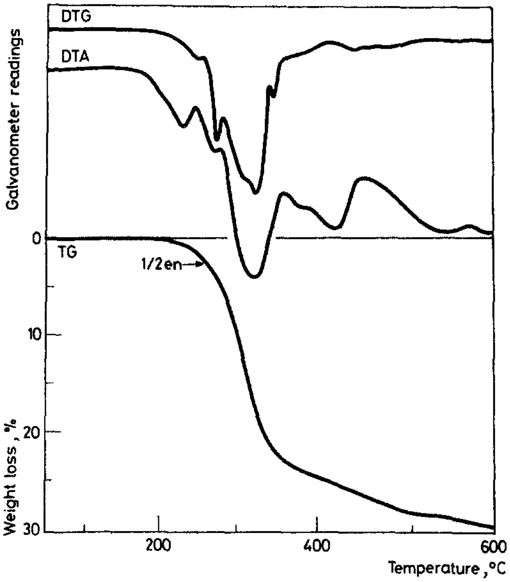

Fig. 2 TG, DTG and DTA curves of $Cu(en)_2(BF_4)_2$

B. Thermal decomposition of the complexes $Cu(en)_2(NCS)X$ *(*$X^- = Cl^-$, Br^-, NO_3^-, ClO_4^- *and* BF_4^-*)*

The melting and decomposition temperatures of the complexes $Cu(en)_2(NCS)X$ (Table 2) are in general higher than those of $Cu(en)_2(SCN)_2$, but lower than those found for $Cu(en)_2X_2$. with the exception of $Cu(en)_2(NCS)ClO_4$. The decomposition of this complex is accompanied by an explosion, although the ClO_4 group is not coordinated to the Cu(II) atom [2]. In this complex the thiocyanate group is

Table 2 The course of thermal decomposition of $Cu(en)_2(NCS)X$

X^-	Weight loss	Melting temperature, °C	Decomposition temperature, °C	Remark	ν_{max} of *dd* transition, cm^{-1}
ClO_4		230	235	explosion	18.500
NO_3	0.5 en	140	140	endotherm	18.100
Br	0.5 en	160	170	endotherm	18.080
Vl	0.5 en	130	165	endotherm	17.760
v-BF_4[a]	0.5 en	150	170	endotherm	18.000
b-BF_4[b]	2 en		120	?	14.700

[a] violet form

[b] blue form

coordinated via the nitrogen atom to two copper atoms, thereby forming —Cu—N(CS)—Cu-chains; together with the absence of a reducing thiocyanate group bonded via the sulphur atom, this could be the reason for the somewhat higher thermal stabilities of the complexes $Cu(en)_2(NCS)X$ as compared with that of $Cu(en)_2(SCN)_2$. The decomposition temperatures of the tetragonal-bipyramidal complexes $Cu(en)_2(NCS)X$ increase with the increasing degree of their coordination polyhedra deformation (evaluated from *d-d* absorption band maxima—Table 2), analogously to other series of tetragonal-bipyramidal Cu(II) complexes [10]. The overall course of thermal decomposition of all the tetragonal-bipyramidal complexes $Cu(en)_2(NCS)X$ ($X^- = Cl^-$, Br^-, No_3^- and BF_4^-, violet form) is dominated by the presence of the NCS group, while the X^- ions exert a relatively small influence (Table 2, Figs 3 and 4). This is understandable when it is considered that the anions X^- are not coordinated in these complexes.

The differences between the structures of the two isomers of $Cu(en)_2(NCS)(BF_4)$ (violet and blue forms) are reflected very expressively in the courses of their thermal decompositions. The violet form, which is presumed to have a tetragonal-bipyramidal structure of the coordination polyhedron with a semicoordinated BF_4 group [5], is decomposed (Fig. 5) in a similar way as the other tetragonal-bipyramidal complexes under discussion. For the blue $Cu(en)_2(NCS)(BF_4)$, a

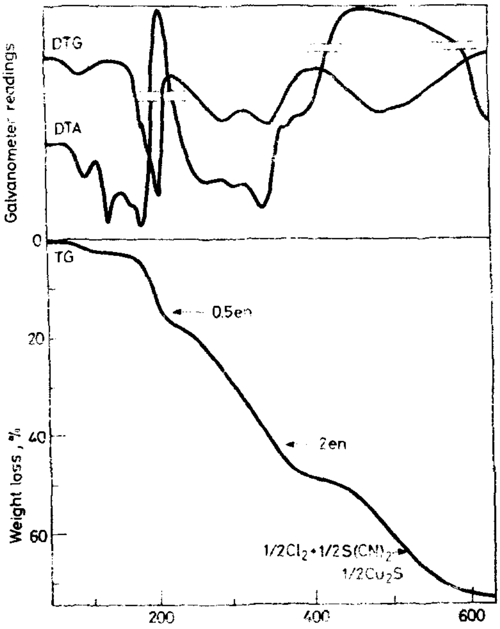

Fig. 3 TG. DTG and DTA curves of $Cu(en)_2(NCS)Cl$

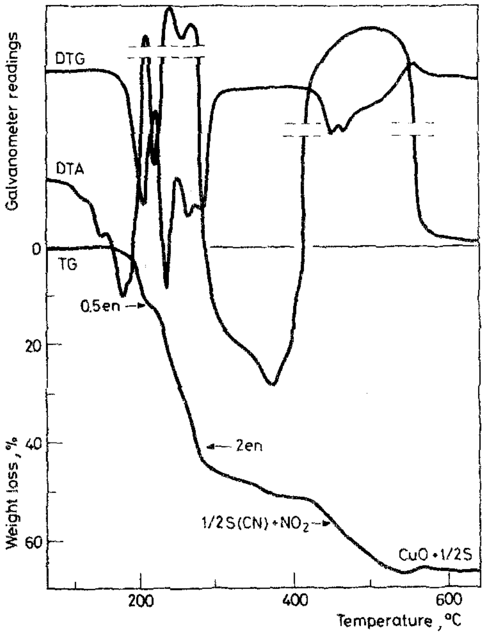

Fig. 4 TG, DTG and DTA curves of $Cu(en)_2(NCS)(NO_3)$

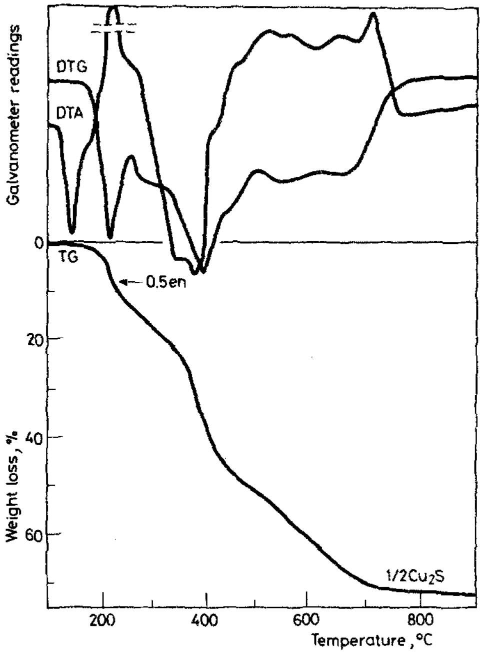

Fig. 5 TG, DTG and DTA curves of the violet form of $Cu(en)_2(NCS)(BF_4)$

tetragonal-pyramidal structure with an N-coordinated thiocyanate group and a non-coordinated BF_4^- group is presumed [5]. This means that in this complex the stabilizing effect of chain formation is absent. Indeed, the decomposition temperature is lower than those observed for other complexes of the same composition (Table 3). Moreover, a quite different decomposition stoichiometry was found for this complex. In the first step, according to the TG curve (Fig. 6), both molecules of ethylenediamine are released. Nevertheless, the DTA curve suggests a more complicated decomposition course, and further we found the formation of $Cu(BF_4)_2$ to be not very probable. Unfortunately, the difficulties involved in the synthesis of a greater amount of this complex prevented us from studying the decomposition stoichiometry in detail.

Table 3 Analytical composition of thermal decomposition intermediates

Complex	Presumed intermediate	Content of Cu, %		Temperature of the intermediate preparation, °C
		calcd.	found	
$Cu(en)_2(SCN)_2$	$Cu(en)_{1.5}(SCN)_2$	23.57	23.74	150
$Cu(en)_2(NO_3)_2$	(release of NO_2)		14.54	194
$Cu(en)_2(BF_4)_2$	$Cu(en)(BF_4)_2$	21.37	21.90	214
$Cu(en)_2(NCS)(NO_3)$	$Cu(en)_{1.5}(NCS)(NO_3)$	23.13	22.64	180
$Cu(en)_2(NCS)Cl$	$Cu(en)_{1.5}(NCS)Cl$	25.70	26.75	180

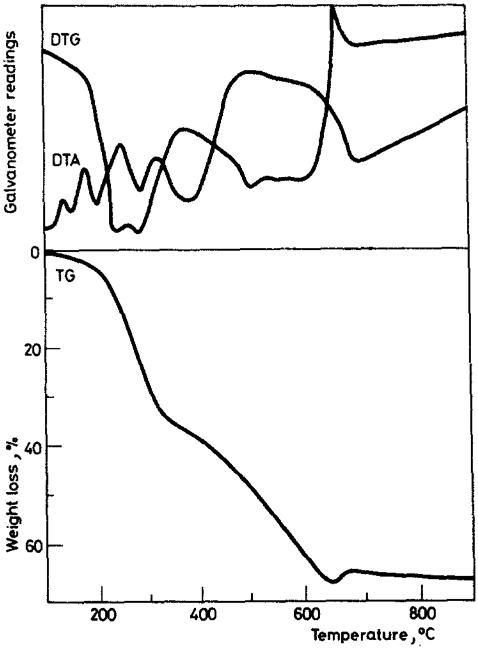

Fig. 6 TG, DTG and DTA curves of the blue form of $Cu(en)_2(NCS)(BF_4)$

The decomposition stoichiometries of all the complexes under study are quite complicated. The products of the first step of decomposition are black, sintered materials. As it has already been mentioned, this could be connected with recrystallization of the melted sample after release of the first ethylenediamine portions. Analytical evaluation of the Cu(II) contents in these intermediates (Table 3) showed that, with the exception of $Cu(en)_2(NCS)(NO_3)$, the contents of Cu(II) are in agreement with their assumed compositions. Isothermal study of the decompositions of the complexes showed that the melting of the crystals and the release of the ethylenediamine molecules are practically simultaneous. After the weight loss corresponding to the first step in the TG curve is reached, the samples are solidified again and the decomposition proceeds in a quite complicated manner. As it can be seen from the respective TG curves, neither the monoethylenediamine complexes nor the compounds Cu(NCS)X were recorded as decomposition intermediates. The decomposition of the respective anions starts in the presence of ethylenediamine. The decomposition of the thiocyanate group is analogous to its decomposition in complexes which contain pyridine or substituted pyridines as neutral ligands in their coordination spheres [11], and it is accompanied by redox changes of the central atom.

In conclusion, we can say that the courses of thermal decomposition of the ethylenediamine complexes are strongly influenced by the chemical properties of the anions present. The mode of thiocyanate group coordination is reflected in the thermal stabilities of the complexes, the complexes with S-coordination being less stable than those with an N-coordinated thiocyanate group. However, the higher thermal stabilities of the N-coordinated complexes can be caused by chain formation as well. The increase in thermal stability owing to chain formation is mostly demonstrated in the differences in the thermal stabilities of the blue and violet forms of $Cu(en)_2(NCS)(BF_4)$. The differences in the courses of thermal decomposition of the two complexes also demonstrate the importance of the structures of the coordination polyhedra for their chemical reactivity.

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Zusammenfassung — Die thermische Zersetzung von $Cu(en)_2(NCS)X$ (X = Cl, Br, NO_3, BF_4 und ClO_4) wurde untersucht und mit der von $Cu(en)_2(SCN)_2$ und $Cu(en)_2X_2$ verglichen. Der den Verlauf der Zersetzung entscheidend bestimmende Faktor ist die Anwesenheit der Thiocyanat-Gruppe in den $Cu(en)_2(NCS)X$-Komplexen, was in Übereinstimmung damit steht, daß die Anionen X nicht oder nur teilweise koordiniert sind. Es wurden signifikante Unterschiede im Verlauf der thermischen Zersetzung von zwei sich in der Struktur ihrer Koordinationspolyeder unterscheidenden Formen von $Cu(en)_2(NCS)(BF_4)$ gefunden.

Резюме — Термическое разложение комплексов $Cu(en)_2(NCS)X$, где X = Cl, Br, NO_3, BF_4 и ClO_4, было исследовано в сопоставлении с разложением комплексов $Cu(en)_2(SCN)_2$ и $Cu(en)_2X_2$. Показано, что наличие тиоцианатной группы в комплексах $Cu(en)_2(NCS)X$ является определяющим фактором процесса разложения и согласуется с фактом, что анионы X в комплексах не координированы или только полукоординированы. Установлены значительные различия процессов термического разложения двух форм $Cu(en)_2(NCS)BF_4$, отличающихся строением координационного многогранника.