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THERMAL PROPERTIES OF THIO- AND SELENOCYANATOCOPPER(II) COMPLEXES WITH BIPYRIDINE AND PHENANTHROLINE

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The paper deals with the thermal properties of complex compounds of the general formula $CuL_2(NCX)_2$ (where L = bipy or phen, X = S or Se). The phenanthroline complexes exhibit a higher thermal stability than those with bipyridine. For the latter complexes thermal decomposition begins with the release of bipyridine molecules, while for the phenanthroline complexes redox reactions of pseudohalogenide ligands with Cu(II) take place. The redox reactions start at a lower temperature for the selenocyanate complexes than for the thiocyanate complexes.

In earlier papers, the thermal properties of thiocyanatocopper(II) complexes with pyridine and all the isomeric forms of picolines and lutidines were studied [1–3]. It was found that the properties of the heterocyclic ligand affect the thermal stability and the stoichiometry of thermal decomposition of these complexes. Thermal decomposition begins with the release of molecules of the heterocyclic base. The release of components stabilizing the oxidation state of Cu(II), together with increased temperature, create conditions for the commencement of redox reactions between the central atom and the thiocyanate ligand. The presence of methyl substituents on the pyridine ligand decreases the thermal stability of he thiocyanate ligands, the redox reactions are shifted to lower temperatures and they are accompanied by the release of heterocyclic ligands.

Likewise, it was also found that a higher number of coordinated monodentate molecules of the heterocyclic base lowers the thermal stability of the thiocyanatocopper(II) complexes [4, 5].

The aim of the present paper was to study the thermal behaviour of those thiocyanatocopper(II) complexes in which an N-donor heterocyclic chelate present as the neutral ligand.

Experimental

Preparation of compounds

Complex compounds $CuL_2(NCX)_2$ (where L = 2,2′-bipyridine or 1,10-phenanthroline, and X = S or Se) were prepared via processes reported in [6–8]. The intermediates of thermal decomposition were obtained by thermal degradation of the initial compounds in nitrogen atmosphere until the respective weight was reached (according to the thermal curves). In the starting complexes and intermediates, the content of Cu was determined electrolytically, that of S as $BaSO_4$, and those of C, N, H using methods of organic analysis.

The calculated and found weight losses for the different steps of thermal decomposition are listed in Tables 1, 3 and 5. The results of analytical evaluation of the decomposition intermediates are given in Tables 2, 4 and 6.

Table 1 Weight losses in different steps of thermal decomposition of $Cu(bipy)_2(NCS)_2$

Step of thermal decomposition	Loss of weight, % calc.	Loss of weight, % found	Intermediate formula
I	31.74	32	$Cu(bipy)(NCS)_2$
II	66.74	68	$CuS_{1.5}(CN)_2$
III	83.83	84	$CuS_{0.5}$

Table 2 Analytical evaluation of thermal decomposition intermediates of $Cu(bipy)_2(NCS)_2$

Intermediate	Analytical composition, %					Ratio of atoms				
	Cu	C	N	H	S	Cu	C	N	H	S
I	18.99	41.85	16.90	2.50	19.76	1	11.65	4.04	8.28	2.06
II	40.40	15.11	16.97	—	27.05	1	1.98	1.90	—	1.33
III	81.09	—	—	—	18.51	1	—	—	—	0.45

Table 3 Weight losses in different steps of thermal decomposition of α- and β-$Cu(bipy)_2(NCSe)_2$

Isomer	Steps of therm. decomposition	Loss of weight, % calc.	Loss of weight, % found	Intermediate formula
α	I	57.76	57	$CuSe_2(CN)$
	II	89.16	89	Cu
β	I	57.76	57	$CuSe_2(CN)$
	II	80.20	81	$Cu(NCSe)_{0.5}$

Table 4 Analytical evaluation of thermal decomposition intermediates of α- and β-Cu(bipy)$_2$(NCSe)$_2$

Isomer	Intermediate	Analytical composition, %					Ratio of atoms				
		Cu	C	N	H	Se	Cu	C	N	H	Se
α	I	27.00	6.59	6.50	—	59.90	1	1.29	1.09	—	1.79
	II	98.50	—	—	—	—					
β	I	26.93	6.74	6.63	—	59.70	1	1.32	1.12	—	1.78
	II	47.15	9.15	7.00	—	36.49	1	1.03	0.67	—	0.62

Table 5 Weight losses in different steps of thermal decomposition of Cu(phen)$_2$(NCS)$_2$

Step of thermal decomposition	Loss of weight, %		Intermediate formula
	calc.	found	
I	10.75	10	Cu(phen)$_2$(NCS)
II	44.12	45	Cu(phen)(NCS)

Table 6 Analytical evaluation of thermal decomposition intermediates of Cu(phen)$_2$(NCS)$_2$

Intermediate	Analytical composition, %					Ratio of atoms				
	Cu	C	N	H	S	Cu	C	N	H	S
II	20.59	50.95	13.50	2.40	12.49	1	13.09	2.97	7.40	1.20

Apparatus

The thermal decomposition was carried out with a MOM derivatograph Budapest. A 14 mm diameter platinum crucible and a Pt/Pt–Rh thermocouple were used. All samples were pulverized, the grain size not exceeding 0.06 mm. The sample weight was 100 mg and the temperature interval was 20° up to 600°, with a heating rate of 9 deg/min. The measurements were made in nitrogen atmosphere.

X-ray powder patterns were taken with a GON III diffractograph; CuK$_\alpha$ radiation and a Ni filter were used.

Electronic spectra were measured with a SPECORD M–40 apparatus in the range 20,000 to 30,000 cm^{-1}, with the Nujol technique.

Results and discussion

Thermal properties of $Cu(bipy)_2(NCS)_2$

The courses of the TG and DTG curves of the thermal decomposition are shown in Fig. 1. The complex begins to decompose at 130°. In the interval 130° to 230°, one pyridine molecule is released. The compound formed, $Cu(bipy)(NCS)_2$, is stable up to 240°. The release of the second bipyridine molecule in the range 240–330° is overlapped by decomposition of the thiocyanate ligands. The intermediate formed, with composition $CuS_{1.5}(CN)_2$, was also identified in the thermal decomposition of $Cu(py)_2(NCS)_2$ [5]. A further temperature increase up to 600° leads to continued decomposition of the thiocyanate ligands, and Cu_2S is formed (see Tables 1 and 2).

The stoichiometry of the thermal decomposition of $Cu(bipy)_2(NCS)_2$ can be expressed by the scheme:

$$Cu(bipy)_2(NCS)_2 \xrightarrow[\text{I}]{-\text{bipy}} Cu(bipy)(NCS)_2 \xrightarrow[\text{II}]{-0.5S,\ -\text{bipy}}$$

$$CuS_{1.5}(CN)_2 \xrightarrow[\text{III}]{-S,\ -2(CN)} CuS_{0.5}$$

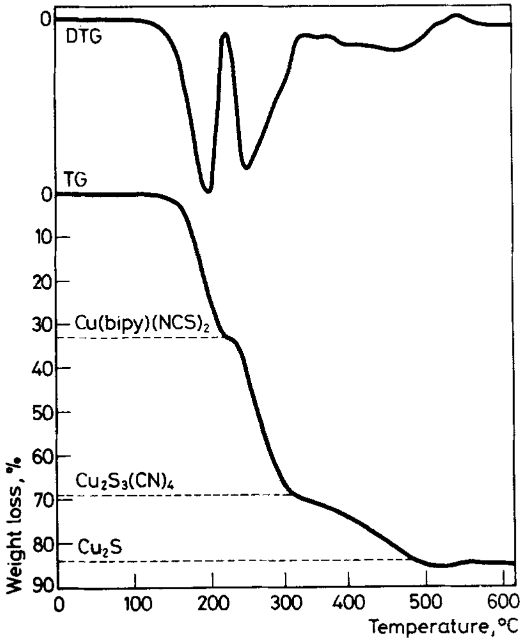

Fig. 1 Thermal curves of compound $Cu(bipy)_2(NCS)_2$

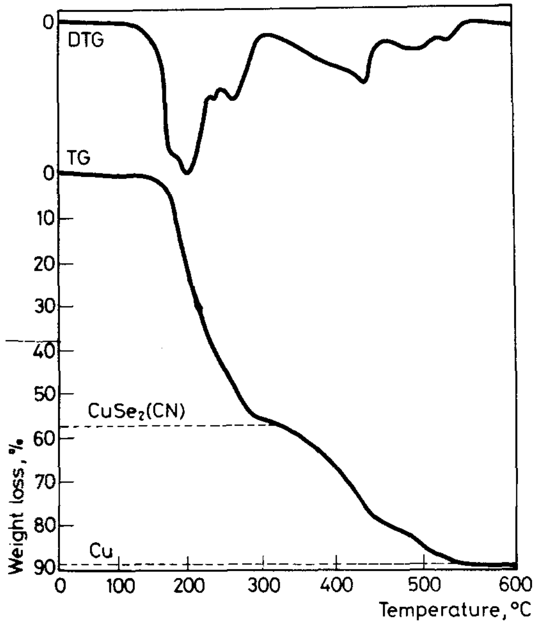

Fig. 2 Thermal curves of compound α-Cu(bipy)$_2$(NCSe)$_2$

Thermal properties of α- *and* β-*Cu(bipy)*$_2$*(NCSe)*$_2$

The selenocyanate complex with bipyridine was prepared in two isomeric forms [7], differing in the degree of distortion of their trigonal-bipyramidal coordination polyhedron around the Cu(II). The courses of the TG and DTG curves are shown in Figs 2 and 3. The two isomeric forms exhibit the same initial decomposition temperature of 130° when the process sets in with the release of bipyridine ligands. In contrast with the thiocyanate complexes, both bipyridine ligands are released in one step, in which decomposition of the selenocyanate ligands also begins. The intermediates prepared from the starting samples by heating to 300° have a composition approximately corresponding to the formula CuSe$_2$(CN). These intermediates exhibit a different diffraction (see Fig. 4) and differ in their decomposition stoichiometry in the temperature interval 300° to 600°. In the thermal decomposition of the α-isomer, the intermediate is decomposed completely and at 600° only elementary copper remains. The thermal decomposition of the β-isomer in the range 300° to 600° (actually at 530°) gives still another intermediate, with the composition Cu(NCSe)$_{0.5}$ (see Tables 3 and 4).

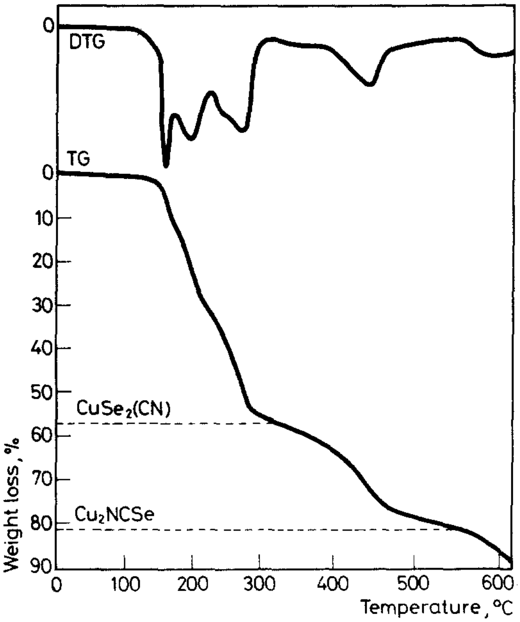

Fig. 3 Thermal curves of compound β-Cu(bipy)$_2$(NCSe)$_2$

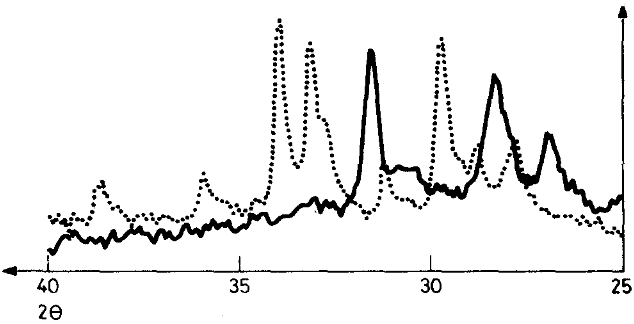

Fig. 4 Diffractograms of thermal decomposition intermediates α- and β-Cu(bipy)$_2$(NCSe)$_2$

The stoichiometry of this decomposition can be expressed by the schemes:

$$\alpha\text{-Cu(bipy)}_2\text{(NCSe)}_2 \xrightarrow[\text{I}]{-2\text{bipy},\ -(\text{CN})} \text{CuSe}_2\text{(CN)} \xrightarrow[\text{II}]{-2\text{Se},\ -(\text{CN})} \text{Cu}$$

$$\beta\text{-Cu(bipy)}_2\text{(NCSe)}_2 \xrightarrow[\text{I}]{-2\text{bipy},\ -(\text{CN})} \text{CuSe}_2\text{(CN)} \xrightarrow[\text{II}]{-1.5\text{Se},\ -0.5(\text{CN})}$$

$$\text{Cu(NCSe)}_{0.5}$$

Thermal properties of $Cu(phen)_2(NCS)_2$

The courses of the TG and DTG curves are shown in Fig. 5. As compared with the analogous complex with bipyridine, the phenanthroline complex exhibits a considerably higher thermal stability. Its thermal decomposition begins at 260°. In contrast with the bipyridine complex, this begins with the release of thiocyanate ligands. Since the reaction of release of the pseudohalogenide ligand takes place in the temperature range 260° to 290°, this process is also connected with redox reactions of the central atom. In the temperature interval 290° to 400°, the first step is followed by the liberation of one phenanthroline molecule (see Tables 5 and 6). On further heating up to 600°, a continuous loss of weight takes place, which is evidence of the complete destruction of the compound under study.

Thermal properties of $Cu(phen)_2(NCSe)_2$

The courses of the TG and DTG curves are presented in Fig. 6. In comparison with the analogous complex with thiocyanate ligand, this complex shows a lower initial decomposition temperature, at 190°. In the case of this complex too, thermal decomposition begins with a redox reaction of the pseudohalogenide ligand. The redox process for the selenocyanide anion has another mechanism. In the temperature range 190° to 250°, the CN group is released from the selenocyanate ligand. On increase of the temperature to the interval 250° to 370°, one

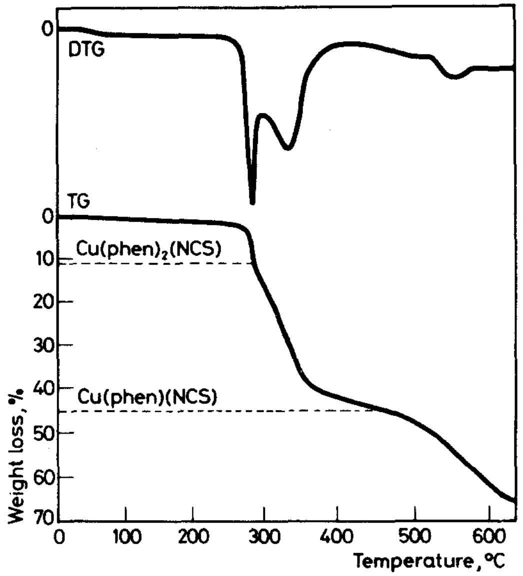

Fig. 5 Thermal curves of compound $Cu(phen)_2(NCS)_2$

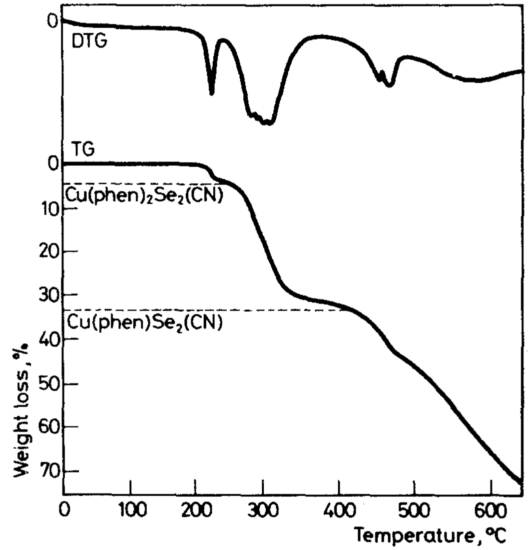

Fig. 6 Thermal curves of compound Cu(phen)$_2$(NCSe)$_2$

phenanthroline molecule is released (see Tables 7 and 8). On further temperature increase up to 600°, a continuous loss of weight occurs.

The study of the thermal behaviour of the complexes discussed here showed that the complexes with chelate ligands have significantly higher thermal stabilities than those of the monodentate ligands (see Table 9). Of the two ligands studied, the phenanthroline complexes exhibit higher thermal stability. This may be ascribed to the chelate effect.

Table 7 Weight losses in different steps of thermal decomposition of Cu(phen)$_2$(NCSe)$_2$

Step of thermal decomposition	Loss of weight, %		Intermediate formula
	calc.	found	
I	3.95	4	Cu(phen)$_2$Se$_2$(CN)
II	32.53	33	Cu(phen)Se$_2$(CN)

Table 8 Analytical evaluation of thermal decomposition intermediates of Cu(phen)$_2$(NCSe)$_2$

Intermediate	Analytical composition, %					Ratio of atoms				
	Cu	C	N	H	Se	Cu	C	N	H	Se
I	10.48	49.22	11.85	2.54	25.91	1	24.85	5.13	15.25	1.99
II	15.05	38.00	10.50	2.70	33.75	1	13.36	3.16	11.28	1.81

Table 9 Initial decomposition temperatures of some thio- and selenocyanatocopper(II) complexes

Complex	Temperature, °C
$Cu(py)_4(NCS)_2$	20
$Cu(bipy)_2(NCS)_2$	130
$Cu(phen)_2(NCS)_2$	260
$Cu(bipy)_2(NCSe)_2$	130
$Cu(phen)_2(NCSe)_2$	190
$Cu(py)_2(NCS)_2$	110
$Cu(bipy)(NCS)_2$	230

In the course of the thermal decomposition, however, besides the release of molecules of the heterocyclic base, the redox reaction of pseudohalogenide ligands with Cu(II) also takes place. The temperatures at which redox reactions occur depend on the properties of the neutral ligand, viz. its stabilizing contribution to the oxidation state of the central atom [9], the type of the pseudohalogenide ligand and the strength of its reducing properties [10]. It follows from the experimental results that the starting temperatures for the redox reactions are lower in the selenocyanate complexes. This is in good agreement with the conception of the more expressed reducing properties of the selenocyanate ligand. This finding may be correlated with the positions of the maxima of the charge-transfer bands from the pseudohalogenide ligand to the central atom (see Table 10).

Table 10 Positions of maxima of CT-bands and decomposition temperatures of pseudohalogenide ligands in thio- and selenocyanatocopper(II) complexes

Complex	$X = S$		$X = Se$	
	CT-band, cm^{-1}	temperature, °C	CT-band, cm^{-1}	temperature, °C
$Cu(bipy)_2(NCX)_2$	24,680	240	22,280	130
$Cu(phen)_2(NCX)_2$	25,880	260	23,420	190

The stabilizing effects of the bipyridine and phenanthroline ligands in the studied complexes are supported by the bonding properties of these ligands in the coordination sphere of Cu(II). From the crystal structure data [6–8], it follows that phenanthroline and bipyridine ligands in the Cu(II) coordination sphere each occupy one equatorial and one axial position. Such a coordination prevents the possibility of the pseudohalogenide ligand bonding via the sulphur or selenium atom, respectively, in the axial position, which is the determining factor for the start of the redox reaction in the copper(II) complexes [10].

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Zusammenfassung — Vorliegende Arbeit behandelt die thermischen Eigenschaften von Komplexverbindungen der allgemeinen Formel $CuL_2(NCX)_2$ (mit L = Bipyridin oder Phenanthrolin und X = S oder Se). Die Phenanthrolinkomplexe zeigen eine grössere thermische Stabilität als die Bipyridinkomplexe. Die thermiscne Zersetzung letzterer beginnt mit der Abgabe von Bipyridinmolekülen, während bei den Phenanthrolinkomplexen Redoxreaktionen von Pseudohalogenidliganden mit Cu(II) stattfinden. Diese Redoxreaktionen beginnen bei den Selenozyanatkomplexen bei niedrigeren Temperaturen als bei den Thiozyanatkomplexen.

Резюме — Описаны термические свойства комплексных соединений общей формулы $CuL_2(NCX)_2$, где L = дипиридин или фенантролин, а X = сера или селен. Комплексы с фенантролином обладают большей термоустойчивостью по сравнению с дипиридином. Термическое разложение комплексов с дипиридином начинается с выделения молекул дипиридина, тогда как в случае комплексов с фенантролином — имеет место окислительно-восстановительная реакция псевдогалоидных лигандов с двухвалентной медью. Такие окислительно-восстановительные реакции для селеноцианатных комплексов начинаются при более низкой температуре, чем для тиоцианатных комплексов.