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THERMAL PROPERTIES OF CYANATOCOPPER(II) COMPLEXES WITH PYRIDINE, BIPYRIDINE AND PHENANTHROLINE

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Abstract

The thermal properties of cyanatocopper complexes with pyridine, bipyridine and phenanthroline are described in this paper. It was found that the thermal stabilities of the complexes were found to increase in the order py<<bipy<phen ligands. The significantly higher thermal stability of the complexes with bipyridine and phenanthroline is caused by the presence of dimeric structural units in the crystal structure and intermolecular interactions of the cyanate and heterocyclic ligands.

In our preceding papers we have described the thermal decompositions of thiocyanatocopper complexes $CuL_2(NCS)_2$ (L=pyridine and its methyl derivates) which are composed of the liberation of ligands L and redox reactions of thiocyanate ligands with the central Cu(II) atom [1, 2]. The decomposition temperature of thiocyanate ligands depends on the properties of the ligands L present in the coordination sphere. An analogous course of thermal decomposition was also observed for $[Cu(bipy)_2(NCX)](NCX)$ (X=S or Se) [3]. For the phenanthroline complexes $[Cu(phen)_2(NCX)_2]$ (X=S or Se) the thermal stability was found to increase significantly (by about 140°C) and the decomposition stoichiometry was also changed [3].

The present paper contains the results of thermoanalytical studies on bipyridine and phenanthroline cyanatocopper complexes, and a comparison of the thermal properties of pyridine cyanato and isothiocyanatocopper complexes.

Keywords: complexes, cyanatocopper(II) complexes

Experimental

Preparation of complexes

The complexes $[Cu(bipy)(NCO)_2]_2$ (*bipy*=bipyridine) and $[Cu(phen)(NCO)_2]_2$ (*phen*=phenanthroline) were prepared as described earlier [4, 5].

The intermediates of thermal decomposition were obtained by thermal degradation of the initial compounds until the specific mass determined from the thermoanalytical curves was attained. In the starting complexes and intermedi-

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ates, the content of Cu was determined electrolytically and those of C, N, H and O using methods of organic elemental analysis.

The calculated and found mass losses for the different steps of thermal decomposition are listed in Table 1. The results of analytical evaluation of the decomposition intermediates are given in Table 2.

Table 1 Weight losses in different steps of thermal decomposition of cyanatocopper(II) complexes

Compound	Step of thermal decomposition	Loss of the weight/%		Intermediate formula
		calc.	found	
$[Cu(bipy)(NCO)_2]_2$	I	51.42	51	$Cu(NCO)_2$
$[Cu(phen)(NCO)_2]_2$	I	12.85	12	$Cu_2(phen)_2(NCO)_3$
	II	34.23	35	$Cu_2(phen)(NCO)_3$

Apparatus

The thermal decomposition was carried out with a MOM derivatograph (Budapest, Hungary). A 14 mm diameter Pt crucible and a Pt/Pt-Rh termocouple were used. All samples were pulverized, the grain size not exceeding 0.06 mm. The sample mass was 100 mg and the temperature interval was 20 up to 500°C, with a heating rate of 9°C min^{-1}.

Figures of crystal structures (Figs 1, 2, 4 and 6) were made with the help of the MOLDRAW program [6].

Results and discussion

Thermal properties of $[Cu(py)_2(NCO)_2]$ and $[Cu(py)_2(NCS)_2]$

The course of thermal decomposition of a pyridine cyanato- and thiocyanatocopper complex can be described by the following scheme according to [1, 7]:

$$[Cu(py)_2(NCO)_2 \xrightarrow[110\text{–}170^\circ C]{-py} Cu(py)(NCO)_2 \xrightarrow[170\text{–}220^\circ C]{-py}$$

$$Cu(NCO)_2 \xrightarrow[220\text{–}280^\circ C]{-(CNO)} Cu(NCO)$$

$$Cu(NCO) \xrightarrow[280\text{–}420^\circ C]{-(CN)} CuO$$

$$[Cu(py)_2(NCS)_2] \xrightarrow[110–220°C]{-2py} CuNCS\cdot NCS \xrightarrow[220–280°C]{-0.5S}$$

$$Cu(S)_{1.5}(CN)_2 \xrightarrow[280–400°C]{-0.5S;\ -CN} Cu(NCS)$$

$$Cu(NCS) \xrightarrow[400–450°C]{-0.5S} CuS_{0.5}(CN) \xrightarrow[450–510°C]{-CN} CuS_{0.5}$$

The compared complexes have equal thermal stabilities and their decomposition begins by the liberation of pyridine molecules. In both complexes all cyanate or thiocyanate ligands are bifunctionally bridged; however, they differ in their decomposition temperatures. The smaller thermal stability of cyanate ligands in comparison with thiocyanate ligands may be explained similarly as in [8] in terms of the different arrangement of thiocyanato- or cyanato copper chains in the individual crystal structures (Figs 1 and 2). In the thiocyanatocopper complex copper atoms are always joined mutually with two bridging thiocyanate ligands. In this arrangement they are part of compact, linear, mutually parallel chains [9]. In the cyanatocopper complex, copper atoms are mutually connected only by a single bridging cyanate ligand and in the crystal structure they form a three-dimensional skeleton [10]. A greater value of the minimal interatomic distance Cu...Cu=6.06Å in a cyanatocopper complex, points to a freer arrangement of structural units in the crystal structure of $[Cu(py)_2(NCO)_2]$.

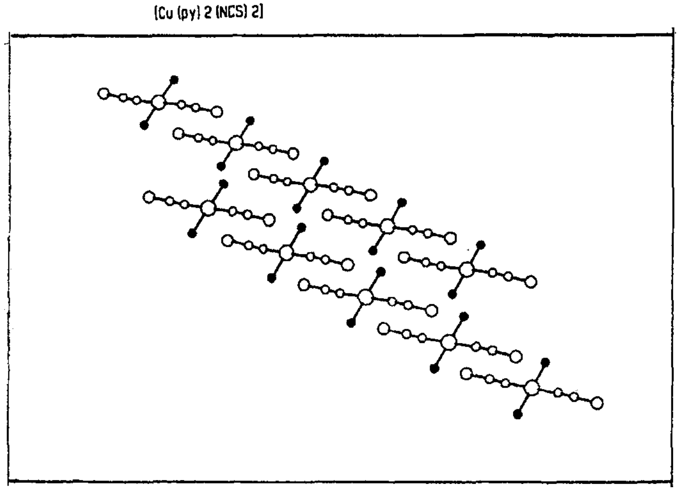

Fig. 1 Thiocyanatocopper chains in $[Cu(py)_2(NCS)_2]$. For clearness only nitrogen atoms from pyridine ligands are marked (with full circles). Minimal distance: Cu–SCN–=3.04Å; Cu–Cu=5.62Å

Table 2 Analytical evaluation of thermal decomposition intermediate of [Cu(bipy)(NCO)$_2$]$_2$ (A) and [Cu(phen)(NCO)$_2$]$_2$ (B) complexes

Compound	Intermediate	Analytical composition/%					Ratio of atom				
		Cu	C	N	H	O	Cu	C	N	H	O
(A)	I	42.8	16.5	19.0	–	21.2	1	2.04	2.01	–	1.97
(B)	II	29.1	42.5	16.0	0.5	10.8	1	7.73	2.49	0.92	1.47

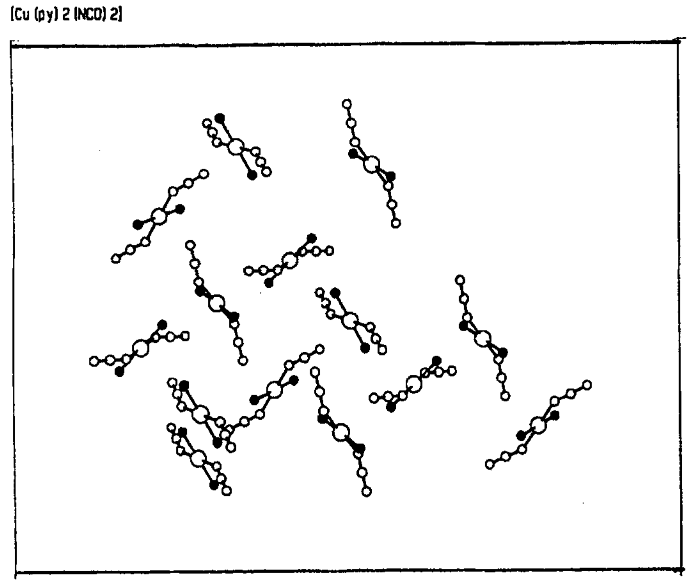

Fig. 2 Cyanatocopper chains in $[Cu(py)_2(NCO)_2]$. For clearness only nitrogen atoms from pyridine ligands are marked (with full circles). Minimal distance: Cu–OCN–=2.61Å; Cu–Cu=6.06Å

Thermal properties of $[Cu(bipy)(NCO)_2]_2$

The TG and DTG curve of the thermal decomposition are presented in Fig. 3. The complex begins to decompose at 250°C and before attaining 500°C liberates molecules of bipyridine while and $Cu(NCO)_2$ is formed.

The course of thermal decomposition of the bipyridine copper complex can be illustrated by the Scheme.

$$[Cu(bipy)(NCO)_2]_2 \xrightarrow[250\text{–}500^{\circ}C]{-2(bipy)} Cu(NCO)_2$$

A cyanatocopper complex with bipyridine has, in comparison with $[Cu(py)_2(NCO)_2]$, a significantly higher thermal stability (by about 140°C). Its crystal structure contains chained dimeric units $[Cu(bipy)_2(NCO)_2]_2$ in which only half of the cyanate ligands have a bifunctional bridge coordination. The other half of cyanate ligands are coordinated to Cu(II) only by nitrogen atoms, and by oxygen atoms they take part in intermolecular interactions with heterocyclic moieties of bipyridine ligands from neighbouring structural units (Fig. 4).

In connection with the crystal structure with bipyridine, it is worth mentioning that several types of interactions may exist which are not seen in $[Cu(py)_2(NCO)_2]$ and which may influence the thermal stability of a bipyridine complex [4].

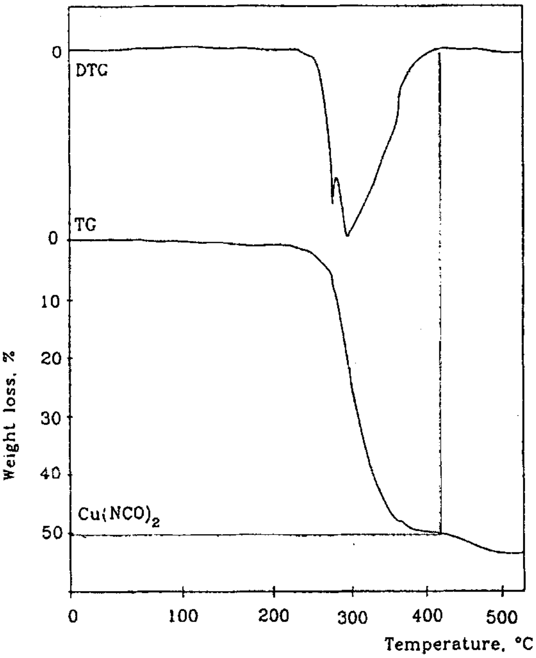

Fig. 3 TG and DTG curves of $[Cu(bipy)(NCO)_2]_2$

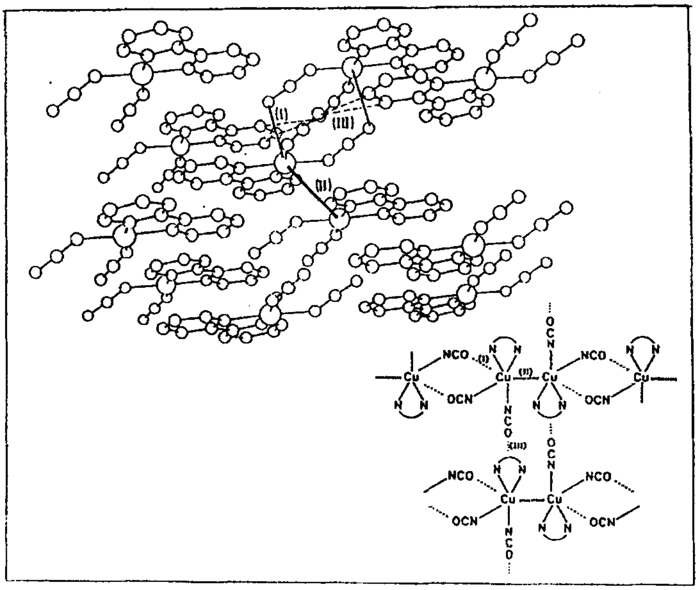

Fig. 4 Crystal structure of $[Cu(bipy)(NCO)_2]_2$. Minimal distance: Cu–OCN–2.87Å(marked I) Cu–Cu=3.38Å(marked II) –NCO–C) from bipy ligand)=3.14Å(marked III)

As an example:

- chelate effect of a heterocyclic ligand;
- Cu–Cu (3.38Å) interactions which occur in dimeric units $[Cu(bipy)(NCO)_2]_2$;
- intramolecular interactions of monodentate cyanate ligands which support cohesion of linear chains in the crystal structure (Fig. 4).

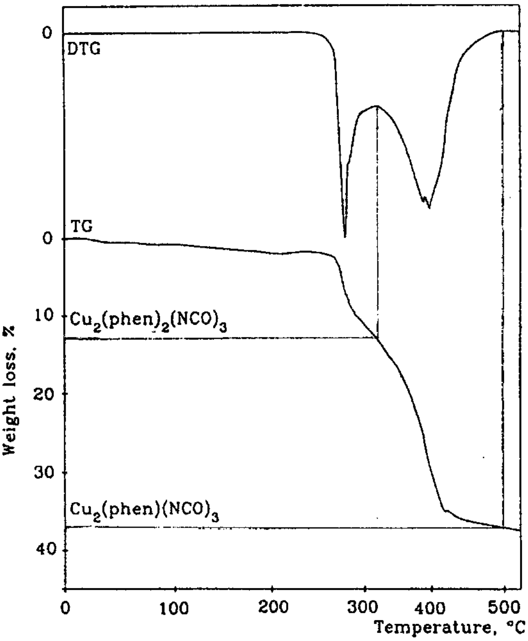

Fig. 5 TG and DTG curves of $[Cu(phen)(NCO)_2]_2$

Thermal properties of $[Cu(phen)(NCO)_2]_2$

The TG and DTG curves of the thermal decomposition of the complex are shown in Fig. 5. The decomposition starts at 270°C, and one cyanate group and one phenanthroline molecule are liberated up to 500°C.

The thermal decomposition of the phenanthroline complex can be described by the following Scheme:

$$[Cu(phen)(NCO)_2]_2 \xrightarrow[270\text{–}320\text{–}450^\circ C]{-NCO;\ -phen} Cu_2(phen)(NCO)_3$$

The cyanatocopper complex with phenanthroline exhibits slightly higher thermal stability than $[Cu(bipy)(NCO)_2]_2$. In the crystal structure there are also dimeric units of $[Cu(phen)(NCO)_2]_2$ in which all cyanate ligands are coordinated to Cu(II) only by a nitrogen atom [5]. All cyanate ligands take part with their oxygen atoms in intramolecular interactions with the heterocyclic moieties of phenanthroline ligands (Fig. 6).

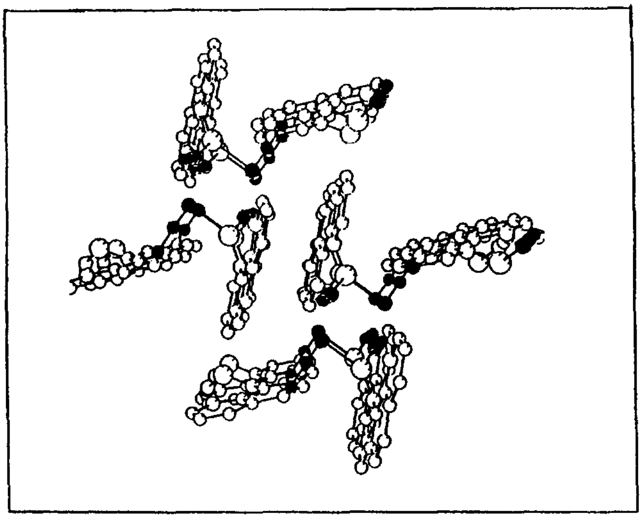

Fig. 6 Fragment of the crystal structure of $[Cu(phen)(NCO)_2]_2$ representing mutual intermolecular interaction of cyanate ligands with phenanthroline. (Atoms from cyanate ligands are marked by full circles)

The thermal stability of this complex, similarly as in the foregoing case, can be influenced by:

- the chelate effect of the heterocyclic ligand;
- the Cu–Cu interactions (3.20Å) which occur in dimeric units of $[Cu(phen)(NCO)_2]_2$;
- a greater number of intermolecular interactions of cyanate ligands with phenanthroline ligands in the three-dimensional skeleton of the crystal structure.

Conclusion

It was found that the thermal stabilities of complexes $[Cu(py)_2(NCO)_2]$, $[Cu(bipy)(NCO)_2]_2$ and $[Cu(phen)(NCO)_2]_2$ increase in the order of ligands, pyridine<<bipyridine<phenanthroline. A significant increase of thermal stability of complexes with bipyridine and phenanthroline is due to

- mutual intermolecular interactions of cyanate and heterocyclic ligands; and
- the presence of dimeric structural units in the crystal structure.

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