

CRYSTALLOCHEMICAL CAUSES OF THE DIFFERENT THERMAL PROPERTIES OF [Cu(py)₂(NCS)₂] AND [Cu(4-Mepy)₂(NCS)₂] COMPLEXES

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(Received April 29, 1991; in revised form February 10, 1992)

The crystal structures and thermal behaviour of [Cu(py)₂(NCS)₂] (at 293 and [Cu(4-Mepy)₂(NCS)₂] and 180 K) complexes have been compared with their different temperature behaviour. It was found that the thermal stability of coordinated thiocyanate ligands in the course of thermal decomposition depends not only on the properties of the ligand L, but it is related to the arrangement of the thiocyanatocopper chains in the crystal structures.

Keywords: complexes, crystal structures

Introduction

During the study of the properties of thiocyanatocopper(II) complexes of the general formula [CuL₂(NCS)₂] it was found that the coordination mode of the thiocyanate ligand depends on the properties of the ligand L [1]. In accordance with the extent of this influence, the thiocyanate ligand can change either the coordination mode, or its bonding interactions with the central atom. Besides this, the thiocyanate ligand exhibits also its reduction properties in the coordination sphere. That is the way how the ligand L through the bonding mode of the thiocyanate ligand influences the redox stability of thiocyanate Cu(II) complexes [2].

The [Cu(py)₂(NCS)₂] and [Cu(4-Mepy)₂(NCS)₂] complexes exhibit significant differences in their thermal behaviours, which can not be simply explained by conclusions given in [1, 2].

In this article we would like to explain the reason of these differences on the basis of the crystal structures.

Experimental

The complexes $[\text{Cu}(\text{py})_2(\text{NCS})_2]$ and $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$ were prepared by the procedure described in [3].

The position of d-d bands and charge transfer bands in electronic spectra are given in Table 1. The position of d-d bands refers to a pseudooctahedral coordination around the Cu(II) atom in both complexes. The charge-transfer band of $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$ is shifted to higher energies in the UV part of the electronic spectra.

Table 1 Electronic spectrum of $[\text{CuL}_2(\text{NCS})_2]$ compounds

[CuL ₂ (NCS) ₂] for L=	$\nu_{\text{max}} / \text{cm}^{-1}$	
	d-d band	CT band
pyridine	15 600	24 400
4-methylpyridine	13 400sh	24 700

This fact confirms that replacement of pyridine by 4-methylpyridine in the complexes studied has a positive influence on the redox-stability of the central atom.

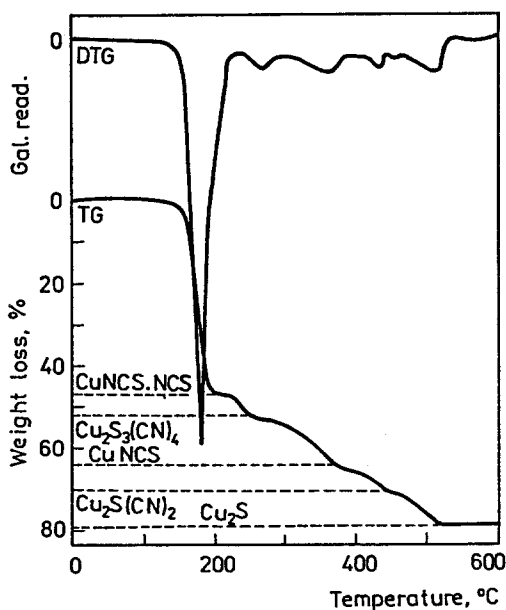
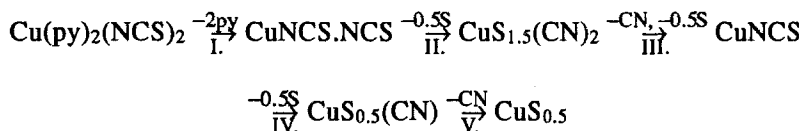


Fig. 1 Thermal decomposition curves of complex (I)

Thermal studies on the mentioned complexes yield the opposite results. The thermal decomposition of the complex $[\text{Cu}(\text{py})_2(\text{NCS})_2]$ starts at 110°C (Fig. 1), then the molecules of pyridine are released up to 300°C and decomposition continues by redox reactions between coordinated thiocyanate ligands and the central atom [4]. It can be expressed by the following scheme:



In the case of the compound $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$ the thermal decomposition starts also at 110°C (Fig. 2) and continues simultaneously by releasing 4-methylpyridine molecules and redox reactions of thiocyanate ligands. The fact that the redox reactions take place at lower temperature (up to 300°C) shows the smaller redox stability of the thiocyanate ligands in this compound. The 2θ values of the diffractions of intermediates (thermal decomposition stopped at 300°C) and CuSCN are given in Table 2. Comparison of the diffraction data shows that the decomposition of $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$ is of greater extent than that of $[\text{Cu}(\text{py})_2(\text{NCS})_2]$ (Table 2).

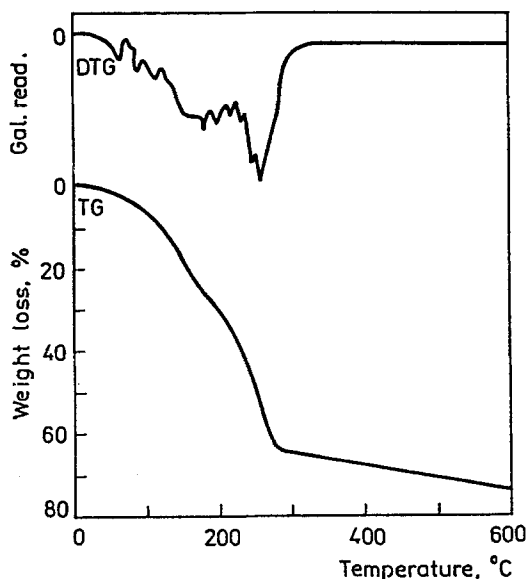


Fig. 2 Thermal decomposition curves of complex (II)

The crystal structures of $[\text{Cu}(\text{py})_2(\text{NCS})_2]$ (I) at 293 K, and of $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$ (II) at 293 K and of $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$ (III) at 180 K are described

in [8, 9, 10]. In the crystal structures of (I), (II) and (III) the central atoms have the tetragonal bipyramidal coordination and CuN_4S_2 chromophores.

Table 2 Diffraction angles 2θ [°] of the intermediates of the thermal decomposition of the compounds $[\text{CuL}_2(\text{NCS})_2]$

Complex $[\text{CuL}_2(\text{NCS})_2]$ for L =		CuNCS [7]
pyridine [5]	4-methylpyridine [6]	
	11–15	
16.1	–	16.1
24.3	–	–
27.2	27.2	27.2
29.1	–	–
30.5	–	–
32.6	32.6	32.6
34.6	–	34.6
37.3	–	37.3
–	46.0	–
47.2	–	47.2

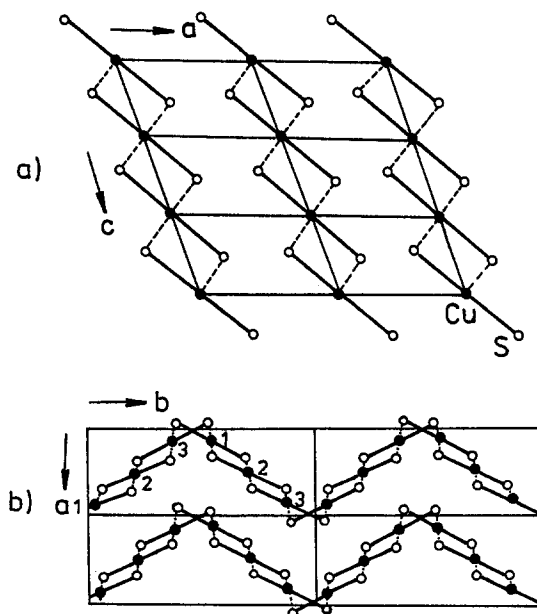


Fig. 3 Orthogonal projection of the orientation of the thiocyanatocopper (II) chains, a) in the complex (I) into xz plane, b) in the complex (II) resp. (III) into yz plane

The thiocyanate and heterocyclic ligands are coordinated to Cu(II) by the nitrogen atoms in the equatorial plane. In the axial positions the central atom is coordinated by sulphur atoms from the bridge-bonded thiocyanate ligands.

Crystal structure (I) consists of one type of symmetrically independent coordination polyhedra connected by thiocyanate ligands.

In the crystal structures (II) and (III) there are, in contrast to (I), three symmetrically independent coordination polyhedra, with different degrees of axial distortion (Fig. 3).

The Cu-N bond lengths in the symmetrically independent coordination polyhedra in complexes (I), (II) and (III) are not significantly different. They fall within the region of 0.189–0.196 nm for Cu-N(NCS) and 0.198–0.205 nm for Cu-N(L). On the other hand, the differences in the Cu-S bond lengths are more pronounced (Table 3). In compound (II) the Cu-S bond lengths in the coordination polyhedron around Cu(2) are comparable to those found in (I), but they are significantly longer in the coordination polyhedron around Cu(1). Considerable asymmetry in the bond lengths is observed in the coordination polyhedron around Cu(3). One of the Cu-S bonds lies within the range given above for the polyhedron around Cu(2), whereas the other is significantly longer.

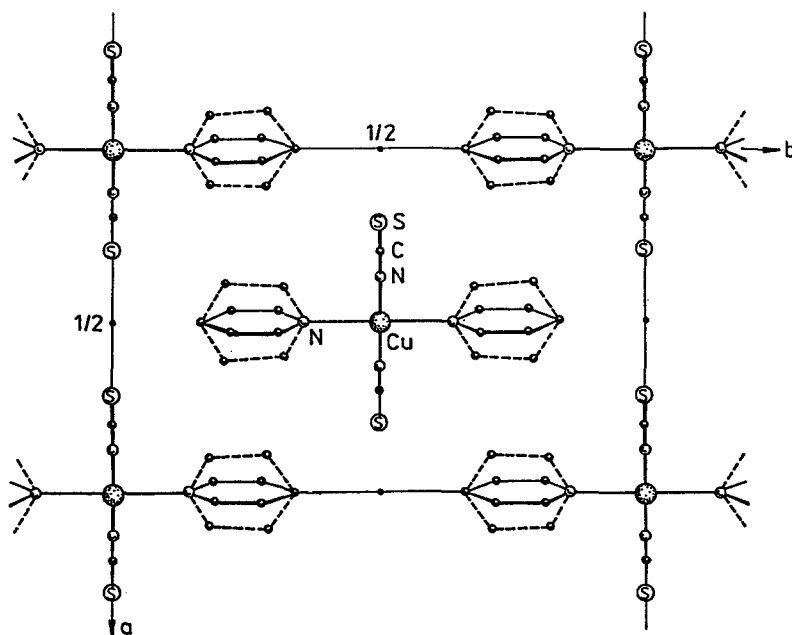


Fig. 4 Schematic representation of symmetrically independent structural units in the crystal structure of complex (II) into *xy* plane

The crystal structures (I), (II) resp. (III) contain thiocyanatocopper(II) chains with different steric orientation. In the pyridine complex (I) the chains are linear and mutually parallel. In the methylpyridine complexes (II), (III) a zig-zag arrangement of chains occurs (Fig. 4). In the coordination polyhedron around Cu(2), placed in the centre of the

linear fragment, the bonds are comparable to those found around copper in (I). In the coordination polyhedra around Cu(1) and Cu(3) longer Cu-S bonds occur, just in the positions where the orientation of the thiocyanatocopper(II) chain is changed. These Cu-S bonds also exhibit significant differences in their length at 180 and 293 K (Table 3).

Table 3 The Cu-S bond lengths in compounds (I), (II) and (III),/ nm

Bond	Complex		
	(I)	(II)	(III)
Cu1-S		0.311(1)	0.311(1)
Cu1-S		0.311(1)	0.311(1)
Cu2-S	0.304(3)	0.298(1)	0.292(1)
Cu2-S	0.304(3)	0.298(1)	0.296(1)
Cu3-S		0.326(1)	0.317(1)
Cu3-S		0.298(1)	0.293(1)

Discussion

Comparing $[\text{Cu}(4\text{-Mepy})_2(\text{NCS})_2]$ with $[\text{Cu}(\text{py})_2(\text{NCS})_2]$ one can observe an unusual behavior in the course of thermal decomposition. In the complex which contains 4-methylpyridine in the coordination sphere we have observed an unexpected reduction in the redox-stability of Cu(II) during the thermal decomposition.

Crystallochemical studies on structures (I), (II), and (III) have proved that the different electronic properties of the 4-methylpyridine ligand really influenced the redox stability of the central atom. Near one half of the Cu-S bonds are longer in crystal(II) than in crystal structure(I). The elongation of Cu-S bonds could affect the linearity of chains and change them to zig-zag form. It is noticeable that breaks of chains occur just at the positions where the elongation of Cu-S bonds were observed. The data obtained from crystal structure(II) at 293 K and (III) at 180 K show that the Cu-S bonds have also different sensitivity to the change of the temperature (Table 3).

According to the mentioned fact, the different changes of interatomic distances with temperature in complex (II) deteriorate the heat transfer in the thiocyanatocopper(II) chains, which can be manifested by their disintegration and a decrease in the thermal and redox stability of coordinated thiocyanate ligands.

Conclusion

The thermal behaviour of Cu(II) thiocyanate compounds are affected not only by the chemical composition of ligands in the coordination sphere, but by the steric arrangement and form of copper thiocyanate chains in the crystal structure, too.

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Zusammenfassung — Es wird die Kristallstruktur und das thermische Verhalten der Komplexe $[\text{Cu}(\text{Py})_2(\text{NCS})_2]$ (bei 293 K) und $[\text{Cu}(4\text{-MePy})_2(\text{NCS})_2]$ (bei 293 und 180 K) untersucht. Man fand, daß die thermische Stabilität der koordinierten Thiocyanatliganden im Verlaufe der thermischen Zersetzung nicht nur von den Eigenschaften des Liganden L abhängt, sondern auch in Beziehung zu Form und Anordnung der Thiocyanatokupferketten innerhalb der Kristallstruktur steht.