Preparation, structure and thermal properties of the complex [(CH₃)₂C₆H₅S][Cu₂(CN)₃] with short Cu(I)...Cu(I) distance (2.655(2) Å)

J. Černák*, K. Györyová, Š. Sabolová

Department of Inorganic Chemistry, P. J. Šafárik University, Moyzesova 11, CS-041 54 Košice (Czechoslovakia)

and M. Dunaj-Jurčo

Department of Inorganic Chemistry, Slovak Technical University, Radlinského 9, CS-815 34 Bratislava (Czechoslovakia)

Abstract

The reaction between K[Cu₂(CN)₃] and [(CH₃)₂(C₆H₅)S]ClO₄ in aqueous solution gives rise to colourless [(CH₃)₂(C₆H₅)S][Cu₂(CN)₃]. This compound crystallizes in the monoclinic space group $P2_1/n$, its lattice parameters being $a = 8.582(5)$, $b = 12.979(5)$, $c = 11.745(6)$ Å, $\beta = 101.10(4)°$ and $Z = 4$. The structure comprises an isolated [(CH₃)₂(C₆H₅)S]⁺ cation and a polymer [Cu₂(CN)₃]⁻ anion. This anion consists of distorted planes which are cross-linked in the third direction through a long Cu(2)–C(1) bond (2.419(2) Å). The planes are composed of distorted hexagons in which two different copper atoms (vertices) are joined with the bridged cyano groups (edges). The Cu(1) atoms exhibit trigonal coordination while the Cu(2) atoms display distorted tetrahedral coordination. The distance between two Cu(2) atoms (in adjacent planes) is very short, i.e. 2.655(2) Å. The pyramidal sulfonium cations are situated between the planes and are disordered in two positions, the occupation factors of which are in the ratio 68:32. The final value of R for 1244 observed diffractions ($F_o \geqslant 4\sigma(F_o)$) is 0.0544. The thermal decomposition was investigated derivatographically in argon atmosphere. The compound starts to decompose at 200 °C and CH₃SC₆H₅ and CH₃CN are liberated. At 470 °C the liberation of (CN)₂ begins.

Introduction

In preceding papers the preparation and thermal properties of different cyano complexes containing tertiary sulfonium cations were described. The tetragonal anions [M(CN)₄]²⁻ (M = Ni, Pd, Pt), the tetrahedral anions [M(CN)₄]²⁻ (M = Zn, Cd, Hg), the octahedral anions [M(CN)₆]³⁻ (M = Co, Mn, Fe) or the linear anion [Au(CN)₂]⁻ were applied as anions in these investigations [1–4]. On the basis of IR spectra and stereochemical considerations we may assume the existence of the ionic structures containing the sulfonium cations in these cyano complexes. It is characteristic of thermal decomposition in inert atmosphere (Ar) of these complexes containing the sulfonium cations (CH₃)₃S⁺-(C₆H₅)₃S⁺ or (CH₃)₂(C₆H₅)S⁺ that various amounts of (CH₃)₂S, CH₃CN/CH₃NC, (C₆H₅)₂S, C₆H₅CN and CH₃SC₆H₅ depending on the kind of cation are liberated at the beginning of decomposition. The final product depending on the kind of central atom and on the type of cation is metal sulfide or elemental metal.

In copper(I) cyano complexes of alkali metals the anions usually exhibit polymer structure, e.g. the anion present in K[Cu(CN)₂] forms an infinite spiral [5] or the anion present in K[Cu₂(CN)₃]·H₂O forms a planar hexagonal network [6]. Up to now, no copper(I) cyano complex containing a sulfonium cation has been described in the literature. On the other hand, the crystal structures of iodomercurates(II) [7–9] and chloromercurates(II) [10] with different sulfonium cations have been solved. In all these complexes isolated sulfonium cations with pyramidal structure are present. Only for the complex compound {(η⁵-CH₃C₅H₄)Mn(CO)₂[(CH₃)₂SCH₂·CH₃]}PF₆ was direct coordination of the sulfonium cation to the central Mn atom observed [11]. The dimethyl-cyclopentadienylidyl cation of tetraiodomercurate(II) is also bonded to the central Hg atom, but through the C(3) atom of cyclopentadienylide [12].

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*Author to whom correspondence should be addressed.

The aim of this study has been to prepare a copper(I) cyano complex containing a convenient sulfonium cation, to solve its crystal structure, to compare the results of structural analysis with published data and to estimate the influence of the replacement of the isolated anion by a polymer one on thermal properties of the investigated complex.
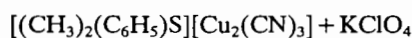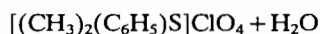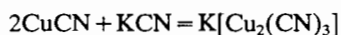
Experimental

Chemicals

$CuSO_4 \cdot 5H_2O$, KCN, methanol (Lachema, Brno), $CH_3SC_6H_5$ (Merck) and $HClO_4$ (Laborchem. Apolda) were used as starting substances. All these chemicals were analytical grade reagents.

Preparation and analysis of $[(CH_3)_2(C_6H_5)S][Cu_2(CN)_3]$

This compound was prepared in conformity with the following equations:

$$CuSO_4 + 2KCN = CuCN + K_2SO_4 + \tfrac{1}{2}(CN)_2$$

$$2CuCN + KCN = K[Cu_2(CN)_3]$$

$$CH_3SC_6H_5 + HClO_4 + CH_3OH =$$

$$[(CH_3)_2(C_6H_5)S]ClO_4 + H_2O$$

$$[(CH_3)_2(C_6H_5)S]ClO_4 + K[Cu_2(CN)_3] =$$

$$[(CH_3)_2(C_6H_5)S][Cu_2(CN)_3] + KClO_4$$

The stoichiometric amount of saturated aqueous solution of $CuSO_4 \cdot 5H_2O$ (4.99 g, 20 mmol) was added to the solution of KCN. The precipitate of CuCN was washed several times with water, then it was dissolved in the course of slow addition of the calculated quantity of KCN under constant stirring. The solution was filtered and after concentration colourless crystals of $K[Cu_2(CN)_3] \cdot H_2O$ were formed. The aqueous solution of $[(CH_3)_2(C_6H_5)S]ClO_4$ (2.38 g, 10 mmol) was added to the saturated solution of $K[Cu_2(CN)_3] \cdot H_2O$ (2.42 g, 10 mmol). After 2 h stirring the white microcrystalline precipitate which formed was filtered off. During standing in a cool place $[(CH_3)_2(C_6H_5)S][Cu_2(CN)_3]$ crystallized from the filtrate. The yield was 45%. The product was poorly soluble in water and insoluble in methanol, ethanol, ether and acetone. The content of C, H and N was determined by means of a Hewlet-Packard analyzer (model 185) and the content of copper was determined complexometrically by using murexide. *Anal.* Found: C, 38.02; H, 2.98; N, 11.97; Cu, 36.01. Calc. for $C_{11}H_{11}N_3SCu_2$: C, 38.39; H, 3.51; N, 12.21; Cu, 36.93%.

The IR spectra were taken on a Specord M80 (Jena) instrument in the range 4000—200 cm^{-1} using the KBr technique. The gaseous reaction products were condensed and their IR spectra in CH_2Cl_2 were measured.

The thermal properties were investigated with a Derivatograph OD 102 (MOM, Budapest) instrument under dynamic conditions. Al_2O_3 was used as the standard substance. Platinum crucibles and an argon atmosphere were used.

Determination of crystal structure

At first, the colourless crystals were investigated by means of a Weissenberg camera. On the basis of the conditions for observed reflexions, the space group $P2_1/n$ was unambiguously determined. The experimental density was estimated by the flotation method using a mixture of bromoform with acetone. The precise lattice parameters were obtained by refining the position angles of 12 diffractions ($10.30 \leqslant 2\theta \leqslant 29.46°$) measured on an automatic diffractometer Syntex P2$_1$. A crystal with dimensions $0.4 \times 0.2 \times 0.1$ mm was used. The crystal data are: $C_{11}H_{11}N_3SCu_2$, $M_r = 344.388$, $a = 8.582(5)$, $b = 12.979(5)$, $c = 11.745(6)$ Å, $\beta = 101.10(4)°$, $V = 1284(1)$ Å^3, $Z = 4$, $F(000) = 692$, $D_c = 1.787$, $D_o = 1.79(1)$ g cm^{-3}, $\mu = 53.69$ cm^{-1} for the Cu Kα radiation monochromatized by graphite. Conditions of intensity data collection: θ–2θ scan technique, $2\theta_{max} = 110°$, index range $h \in \langle 0.9 \rangle$, $k \in \langle 0.13 \rangle$, $l \in \langle -12.12 \rangle$, 1814 diffractions measured of which 1614 were unique, 1244 diffractions observed ($F_o \geqslant 4\sigma(F_o)$), variation of 2 control diffractions 130 and 101 in the range $\pm 5\%$. The measured intensities were corrected for Lp factor as well as for variation of the control intensities by using the XP2$_1$ programme [13].

A model of the structure was obtained by the heavy atom method using the SHELXS '86 program [14]. Other calculations were performed by means of the SHELX '76 program [15]. In the course of refining the isotropic model it was found that the cation is disordered and the initial orientation of the C(1)—N(1) cyano group is not correct. The correct orientation of this cyano group was verified as follows: after refining of the isotropic model the electron density map without C(1) and N(1) atoms was calculated. The values of the maxima at the places of the C(1) and N(1) atoms were equal to 6.3 and 5.2 e Å^{-3}, respectively. The standard deviation of these values calculated according to Cruickshank [16] was 0.2 e Å^{-3} from which it resulted that the difference between these values is significant. Because of this fact, the atoms C(1) and N(1) were exchanged in the next cycle of the refinement. As a consequence, their temperature factors became normal. After isotropic refinement, the absorption correction following

the method of Walker and Stuart [17] was carried out using the program ABSORB [18]. After absorption correction the occupation factors of the cation were refined in subsequent cycles. The obtained values (0.682(7) and 0.318(7)) were fixed in the course of further refinement. Then all atoms were refined anisotropically except the carbon atoms of the cation with lower occupation factor which were refined isotropically. Owing to the disorder of the cation, the phenyl rings were refined as rigid bodies and the hydrogen atoms were not included in the refinement. In the last cycle of refinement $(\Delta/\sigma) \leqslant 0.29$ for the disordered carbon atoms (slow convergence) and $(\Delta/\sigma) \leqslant 0.032$ for the other atoms. The value of $\Delta\rho$ varied within the range -0.47 to 0.52 e Å^{-3}. The function $\Sigma\omega(F_o - |F_c|)^2$ was minimized. The weighting scheme $\omega = [\sigma^2(F_o) + 0.0001F_o^2]^{-1}$ for which no variation on the value of F_o was observed and the empirical correction for secondary extinction $(g = 1.32(8) \times 10^{-6})$ were used. Final values are: $R = 0.0544$, $R_w = 0.0658$. The atomic factors as well as the corrections for anomalous scattering were taken from the SHELX'76 program [15] (C, H, N, S) or from the International Tables [19] (Cu). The final atomic coordinates as well as their temperature factors are given in Table 1. The bond lengths and the valence angles calculated by means of the PARST program [20] are listed in Table 2.

Results and discussion

The crystal structure of $[(CH_3)_2(C_6H_5)S]$-$[Cu_2(CN)_3]$ consists of an isolated sulfonium cation and a three-dimensional polymer anion (Fig. 1). The basic element of the polymer anion is a hexagon the corners of which are intermittently occupied by the Cu(1) and Cu(2) atoms and the sides consist of the cyano groups. The hexagons form a layer similar to the structure of graphite, the only difference being that they are bent like a molecule of cyclohexane in a chair conformation. The adjoining layers are so shifted with respect to each other that a Cu(1) atom of one layer is directed to the centre of the hexagonal gap of another layer. The cross-linking and formation of a three dimensional skeleton comes into existence by origination of the coordination bonding Cu(2)–C(1) to a carbon atom of the adjoining layer. The molecules of the sulfonium cation are placed in the holes thus formed. In principle, the potassium salt $K[Cu_2(CN)_3] \cdot H_2O$ exhibits the same structure in which the pertinent holes are occupied by the K^+ cations and water molecules [6].

The Cu(1) atoms are trigonally coordinated by three cyano groups of which two are bonded through the carbon atoms and the third one through the nitrogen atom. The copper atom is displaced by $0.060(1)$ Å from the plane formed by the atoms C(2), C(3) and N(1). The bond lengths and the valence angles are normal (Table 2).

The Cu(2) atom is deformed tetrahedrally coordinated (Fig. 2). Two coordination positions are occupied by nitrogen atoms of the bridged cyano groups. The third coordination position at a distance of 1.959 Å is occupied by a carbon atom of another bridged cyano group an at a greater distance (2.419 Å) a carbon atom of the bridged cyano group belonging to the adjoining layer is bonded in the fourth coordination position. Thus a cross-linking of the structure in the direction perpendicular to the layers is obtained. The observed distance is unusually long, nevertheless it may be regarded as a bond. It is also confirmed by the significant distortion of the N(1)–C(1)–Cu(2) angle to the value of 162.0(7)° when compared with the value of 173.7° observed for the angles Cu(1)–C(2)–N(2) and Cu(1)–C(3)–N(3). The formation of this bond means that the C(1)–N(1) cyano group becomes three-functional. The carbon atom bridges two copper atoms like in carbonyl complexes. This kind of coordination of the cyano group to our knowledge has been hitherto described only for the complexes $CuCN \cdot NH_3$ in which the Cu–C distances are, however, significantly shorter (2.13 and 2.09 Å) [21] and for the complex $Cu_5(CN)_6(dmf)_4$ (dmf = dimethylformamide) in which these Cu–C distances are equal to 1.972(7) and 2.326(8) Å [22].

It is worth noting that the Cu–N distance in cyano copper(I) complexes is usually greater by about 0.1 Å than the Cu–C distance [6]. As to this structure, that observation is fully valid for the C(2)–N(2) and C(3)–N(3) cyano groups. However, the opposite was observed for the C(1)–N(1) cyano group as the Cu(2)–C(1) bond is longer by 0.021 Å than the Cu(1)–N(1) bond. Notwithstanding, that is only an apparent inconsistence because we must take into consideration that the coordination numbers of the Cu(1) and Cu(2) atoms are different. On the basis of the data from ten cyano copper(I) complexes [5, 6, 23–28], it was found that the mean Cu–C and Cu–N bond lengths are: Cu–C, 1.82(2) (coordination number = 2), 1.92(2) (c.n. = 3), 1.97(5) (c.n. = 4) Å; Cu–N, 1.97(4) (c.n. = 3) and 2.00(6) (c.n. 4) Å. So, if we judge the observed values of bond lengths from the viewpoint of the coordination number of the copper atoms, we can see that they are normal.

The observed short value of the Cu...Cu interaction (2.655 Å) is strange. It is a distance that is only longer by 0.1 Å than the distance in metallic copper. The quantum chemical calculations concerning the

TABLE 1. Fractional coordinates of atoms ($\times 10^4$) with equivalent ($K=0.682(7)$) or isotropic ($K=0.318(7)$) temperature factors U_{eq}/U ($\times 10^2$ Å^2)

Atom	x	y	z	U_{eq}/U[a]	K[b]
Cu(1)	441.1(13)	1986.9(8)	3537.9(9)	4.20(5)	
Cu(2)	5519.3(13)	102.7(8)	4011.9(10)	4.41(5)	
S(1)	4935(4)	2972(2)	2559(3)	4.9(1)	0.682(7)
S(11)	5697(9)	3780(5)	2024(5)	5.4(3)	0.318(7)
N(1)	2488(8)	1330(5)	4030(5)	4.5(3)	
N(2)	-72(8)	3922(5)	2070(6)	4.7(3)	
N(3)	-2510(10)	846(5)	3920(6)	6.1(3)	
C(1)	3616(10)	859(5)	4215(7)	3.7(3)	
C(2)	185(9)	3230(6)	2660(7)	3.8(3)	
C(3)	-1338(10)	1263(6)	2836(7)	4.0(3)	
C(4)	6252(16)	2763(10)	1551(11)	5.7(6)	0.682(7)
C(5)	3825(14)	4060(9)	1851(12)	5.6(5)	0.682(7)
C(6)	5920(10)	3192(5)	4857(6)	5.5(6)	0.682(7)
C(7)	6770(10)	3659(5)	5855(6)	6.7(6)	0.682(7)
C(8)	7751(10)	4500(5)	5763(6)	6.0(6)	0.682(7)
C(9)	7882(10)	4873(5)	4672(6)	7.2(7)	0.682(7)
C(10)	7032(10)	4406(5)	3673(6)	6.1(6)	0.682(7)
C(11)	6051(10)	3566(5)	3765(6)	3.8(5)	0.682(7)
C(41)	3544(31)	3721(20)	1950(23)	5.3(7)	0.318(7)
C(51)	6099(26)	2439(17)	1806(19)	3.5(6)	0.318(7)
C(61)	5874(17)	3253(10)	4306(12)	4.2(6)	0.318(7)
C(71)	6429(17)	3389(10)	5493(12)	4.0(6)	0.318(7)
C(81)	7451(17)	4204(10)	5888(12)	4.9(7)	0.318(7)
C(91)	7918(17)	4883(10)	5097(12)	5.8(8)	0.318(7)
C(101)	7364(17)	4747(10)	3909(12)	5.9(8)	0.318(7)
C(111)	6342(17)	3932(10)	3514(12)	3.9(6)	0.318(7)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*\vec{a}_i\vec{a}_j$.   [b] K is occupation factor.

adducts of CuI with tantalocenes have shown that this short distance corresponds to the Cu(I)–Cu(I) bond [29]. An even shorter distance between copper atoms (2.42 Å) was observed in the complex CuCN·NH$_3$ [21]. In K[Cu$_2$(CN)$_3$]·H$_2$O this distance is equal to 2.95 Å.

In accordance with expectation the sulfonium cation is in a pyramidal form (C_{2v}). The cation is disordered in two positions which are bound by internal axis C_2 (Fig. 3). The phenyl rings in both positions are almost coplanar. The value of the angle formed by them is equal to 3.3(3)°. If both positions are equivalent from the potential energy point of view, then they should be occupied in the ratio 1:1. The observed ratio of about 2:1 indicates deficient equivalence of both occupied positions. An explanation of different occupation may be presented on the basis of stereochemical repulsion. The atoms belonging to a statistically less probable position have four contacts with atoms of the anion skeleton up to 3.3 Å. There are only two such contacts for the cation placed in a statistically more probable position. Moreover, the sulfur atom S(11) with a much larger atomic radius has two contacts up to 3.45 Å. The S(1) atom has no contact shorter than 3.65 Å.

The observed values of bond lengths and valence angles are consistent with the values found for [(CH$_3$)$_2$(C$_6$H$_5$)S]ClO$_4$ [30] except the S–C(C$_6$H$_5$) bond which is shorter by approximately 0.1 Å in our case. There is a question as to whether or to what extent the value of this bond length in perchlorate is correct if the obtained value of the R factor was 0.14 (for photographic data). Such a shortening of the S–C(C$_6$H$_5$) bond with respect to the S–C(CH$_3$) bond may be explained by the partially double character of this bond.

The measured IR spectrum of the studied complex is in line with the solved crystal structure and confirms the presence of the individual functional groups. The assignment of the relevant observed absorption bands given in Table 3 was made on the basis of refs. 31–33. For the sake of comparison the corresponding absorption bands observed in the spectra of [(CH$_3$)$_2$(C$_6$H$_5$)S]ClO$_4$ and K[Cu$_2$(CN)$_3$]·H$_2$O are also given in this Table. It can be seen that the corresponding parts of the spectra are very similar and only small shifts in the position of individual bands are observed. This observation is in accordance with the known crystal structures of these compounds.

The thermal decomposition of [(CH$_3$)$_2$(C$_6$H$_5$)S]-[Cu$_2$(CN)$_3$] is represented in Fig. 4. In the first stage

TABLE 2. Bond lengths (Å) and valence angles (°)

Anion

Cu(1)–N(1)	1.938(7)	C(2)–Cu(1)–C(3)	120.7(4)
Cu(1)–C(2)	1.905(8)	N(1)–Cu(1)–C(3)	116.5(3)
Cu(1)–C(3)	1.882(9)	N(1)–Cu(1)–C(2)	122.5(3)
Cu(2)–C(1)	1.959(9)	C(1)–Cu(2)–N(2)^i	113.7(3)
Cu(2)–N(2)^i	1.981(7)	C(1)–Cu(2)–N(3)^{ii}	120.4(3)
Cu(2)–N(3)^{ii}	1.968(8)	C(1)–Cu(2)–C(1)^{iii}	106.2(3)
Cu(2)–C(1)^{iii}	2.419(8)	N(2)^i–Cu(2)–N(3)^{ii}	114.0(3)
		N(2)^i–Cu(2)–C(1)^{iii}	98.2(3)
		N(3)^{ii}–Cu(2)–C(1)^{iii}	100.1(3)
Cu(2)–Cu(2)^{iii}	2.655(2)	Cu(2)–C(1)^{iii}–Cu(2)^{iii}	73.8(3)
C(1)–N(1)	1.130(10)	Cu(1)–N(1)–C(1)	171.5(6)
C(2)–N(2)	1.130(10)	Cu(2)–C(1)–N(1)	162.0(7)
C(3)–N(3)	1.163(12)	N(1)–C(1)–Cu(2)^{iii}	123.7(6)
		Cu(1)–C(2)–N(2)	173.7(7)
		Cu(1)–C(3)–N(3)	173.7(7)
		Cu(2)–N(2)^i–C(2)^i	178.0(7)
		Cu(2)–N(3)^{ii}–C(3)^{ii}	177.7(7)

Cation

S(1)–C(4)	1.808(15)	C(4)–S(1)–C(5)	99.0(6)
S(1)–C(5)	1.813(12)	C(4)–S(1)–C(11)	106.6(5)
S(1)–C(11)	1.731(7)	C(5)–S(1)–C(11)	100.8(5)
		S(1)–C(11)–C(6)	117.9(6)
		S(1)–C(11)–C(10)	122.2(5)
S(11)–C(41)	1.83(3)	C(41)–S(11)–C(51)	100(1)
S(11)–C(51)	1.80(2)	C(41)–S(11)–C(111)	100(1)
S(11)–C(111)	1.74(1)	C(51)–S(11)–C(111)	102.7(9)
		S(11)–C(111)–C(61)	121(1)
		S(11)–C(111)–C(101)	119(1)

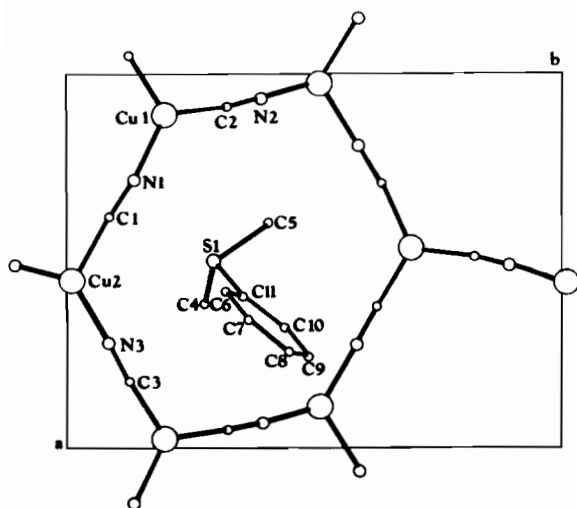Symmetry codes: i: $0.5-x, y-0.5, 0.5-z$; ii: $1+x, y, z$; iii: $1-x, -y, 1-z$.

Fig. 1. Projection of the structure into the xy plane along with the atom numbering scheme. For the sake of clarity the position of the cation with the lowest occupation factor is omitted.
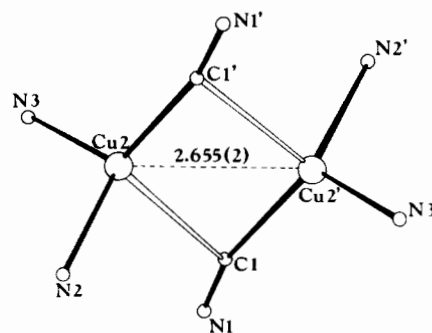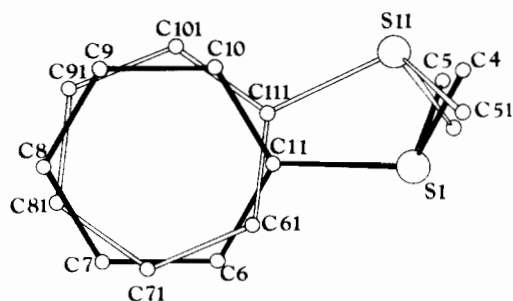

Fig. 2. The coordination of the Cu(2) atom.

Fig. 3. Two disordered positions of the $[(CH_3)_2(C_6H_5)S]^+$ cation along with the atom numbering scheme. Projection into the plane formed by C_6–C_{11} atoms.

TABLE 3. Infrared Spectroscopic data (cm^{-1})

Compound			Assignment
[Me$_2$PhS]-ClO$_4$	K[Cu$_2$(CN)$_3$]·H$_2$O	[Me$_2$PhS]-[Cu$_2$(CN)$_3$]	
3030w		3020w	$\nu(C_{ar}$–H)
2940w		2940w	$\nu(C$–H)
	2115s	2108s	$\nu(C\equiv N)$
	2090s	2084s	
1480s			
1475s		1475m	$\nu(C=C)$
1445s		1448s	
1430s		1418s	$\delta(C_{ar}$–H)
1345s			$\delta_s(C$–H)
1325s			
		1042s	$\delta(C$–H)
990m		990s	$\gamma(C_{ar}$–H)
750s		756s	$\gamma(C$–H)
680s		688s	$\delta(C_{ar}$–H)

s = strong; m = medium; w = weak.

of decomposition CH$_3$SC$_6$H$_5$ and CH$_3$CN (exp. 164.8/theoret. 165 g mol^{-1}) are liberated which manifests itself on the DTA curve as an endothermic process at 200 °C. This decomposition goes on and in an exothermic process cyanogen is liberated at 470 °C
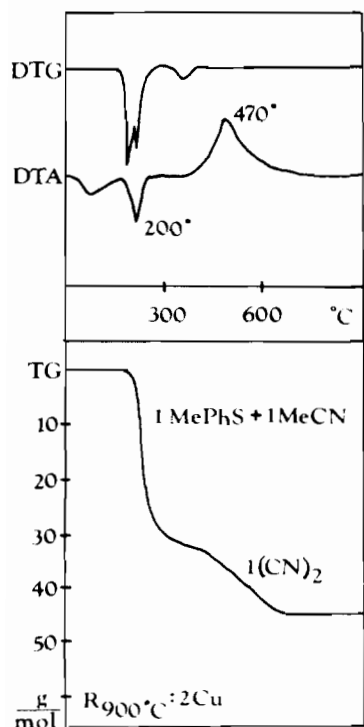
Fig. 4. Thermal decomposition of $[(CH_3)_2(C_6H_5)S]$-$[Cu_2(CN)_3]$.
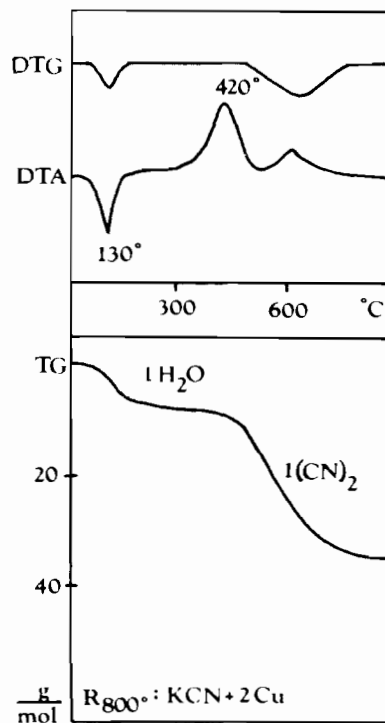
Fig. 5. Thermal decomposition of $K[Cu_2(CN)_3]\cdot H_2O$.

(exp. 50.48/theoret. 52.0 g mol^{-1}). The final product of decomposition of this cyano complex is copper.

The thermal decomposition of $K[Cu_2(CN)_3]\cdot H_2O$ was also studied (Fig. 5). The first step of the thermal decomposition consists of endothermic dehydration at 120 °C. After loss of water the total exothermic decomposition of the cyano complex is observed at 420 °C and $(CN)_2$ is released. These results show that the thermal decomposition processes for the potassium and sulfonium complexes are different.

The thermal decomposition of the studied sulfonium complex could be compared with the thermal decompositions of some other analogous complexes. Thus, the complex $[(CH_3)_2(C_6H_5)S][Ag_2(CN)_3]$ is thermally less stable than the copper complex because it decomposes at 120 °C and in contrast to the copper complex only $(CH_3)_2S$ and $(CN)_2$ are liberated [34]. The higher thermal stability of the copper complex could be explained on the basis of the higher stability of CuCN when compared to AgCN. On the other hand, the complex $[(CH_3)_3S][Cu_2(CN)_3]$ decomposes in an endothermic process at 300 °C and $(CH_3)_2S$ and CH_3CN are liberated [35]. The higher thermal stability of this complex is probably the consequence of better enclosure of the trimethylsulfonium cation into the polymeric anion.

References

1 K. Györyová and B. Mohai, Z. Anorg. Allg. Chem., 492 (1982) 175–187.
2 K. Györyová and J. Skoršepa, Monatsh. Chem., 114 (1983) 1137–1139.
3 K. Györyová and J. Skoršepa, Workbook 4th European Symp. Thermal Analysis and Calorimetry, Jena, 1987, p.C20.
4 K. Györyová and J. Skoršepa, Thermochim. Acta, 128 (1988) 1–7.
5 D. T. Cromer, J. Phys. Chem., 61 (1957) 1388–1392.
6 D. T. Cromer and A. C. Larson, Acta Crystallogr., 15 (1962) 397–403.
7 R. H. Fenn, Acta Crystallogr., 20 (1966) 20–23.
8 R. H. Fenn, Acta Crystallogr., 20 (1966) 24–27.
9 D. A. Pears, J. F. Stoddart, J. Crosby, B. L. Allwood and D. J. Williams, Acta Crystallogr., Sect. C, 42 (1986) 804–806.
10 P. Biscarini, L. Fusina, G. Nivellini and G. Pelizzi, J. Chem. Soc., Dalton Trans., (1977) 664–668.
11 R. D. Adams and D. F. Chodosh, J. Am. Chem. Soc., 100 (1978) 812–817.
12 N. C. Baenziger, R. M. Flynn and N. L. Holy, Acta Crystallogr., Sect. B, 36 (1980) 1642–1644.
13 F. Pavelčik, Program XP21, Comenius University, Pharmaceutical Faculty, Bratislava, Czechoslovakia, 1986.
14 G. M. Sheldrick, SHELXS '86, program for solution of crystal structures, University of Gottingen, F.R.G., 1986.
15 G. M. Sheldrick, SHELX '76, program for crystal structure determination, University of Cambridge, U.K., 1976.

16 D. W. H. Cruickshank, *Acta Crystallogr., 2* (1949) 65–82; *3* (1950) 72–73.

17 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158–166.

18 F. Ugozzoli, *Comput. Chem., 11* (1987) 109–120.

19 *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, U.K., 1974.

20 M. Nardelli, *Comput. Chem., 7* (1983) 95–98.

21 D. T. Cromer, A. C. Larson and R. B. Roof, Jr., *Acta Crystallogr., 19* (1965) 192–197.

22 S.-H. Peng and D-S. Liaw, *Inorg. Chim. Acta, 113* (1986) L11–12.

23 C. Kappenstein and R. Hugel, *Inorg. Chem., 16* (1977) 250–254.

24 C. Kappenstein and R. Hugel, *Inorg. Chem., 17* (1977) 1945–1949.

25 R. B. Roof, Jr., A. C. Larson and D. T. Cromer, *Acta Crystallogr., Sect. B, 24* (1968) 269–273.

26 C. Kappenstein and U. Schubert, *J. Chem. Soc., Chem. Commun.*, (1980) 1116–1118.

27 R. J. Williams, A. C. Larson and D. T. Cromer, *Acta Crystallogr., Sect. B, 28* (1972) 858–864.

28 D. T. Cromer and A. C. Larson, *Acta Crystallogr., Sect. B, 28* (1972) 1052–1058.

29 T. M. Arkhireeva, B. M. Bulychev, A. I. Sizov, T. A. Sokolova, V. K. Belsky and G. L. Soloveichik, *Inorg. Chim. Acta, 169* (1990) 109–118.

30 A. Lopez-Castro and M. R. Truter, *Acta Crystallogr., 17* (1964) 465–471.

31 *IRSCOT*, Infrared structural correlation tables and data cards, Heyden, London, 1969.

32 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds* (Russian translation), Mir, Moscow, 1966.

33 A. G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals*, Academic Press, London, 1976.

34 K. Györyová and J. Skoršepa, *Proc. Meet. Czechoslovak Chemical Society, Ústi nad Labem, Czechoslovakia, 1987*, p. 107.

35 K. Györyová and J. Skoršepa, *Proc. XIth Czechoslovak Conf. Thermal Analysis, TERMANAL '88, High Tatras, Czechoslovakia, Sept. 20–23, 1988*, p. 143.