

THERMAL STUDIES OF NEW Cu(I) AND Ag(I) COMPLEXES WITH BIPYRIDINE ISOMERS

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Abstract

The complexes of the general formula MLSCN (M -Cu(I), Ag(I), L =2,2'-bipyridine=2-bipy, 4,4'-bipyridine=4-bipy or 2,4'-bipyridine=2,4'bipy) have been prepared and their IR spectra examined. The nature of metal-ligand coordination is discussed. Thermal decomposition in air of these complexes occurred in several successive endothermic and exothermic processes and the residue was Cu₂O and Ag, respectively.

Keywords: bipyridine isomers, complexes, copper(I), IR spectra, silver(I), thermal decomposition

Introduction

A survey of literature shows that the solid complexes of bipyridine isomers with Cu(I) and Ag(I) ions are not well known. The coloured copper(I) chelates with 2-bipy were first reported by Tartarini [1]. The following compounds were described: Cu(2-bipy)X ($X=I^-$ or SCN^-) and Cu(2-bipy)₂ClO₄ [2]. The compounds of the type CuX(4-bipy) and (CuX)₂(4-bipy), where $X=Cl, Br, I$, were obtained by Guillermo *et al.* [3]. The solid complexes formed between AgNO₃ and 2-bipy and 4-bipy have been prepared (Ag(2-bipy)NO₃, Ag(2-bipy)₂NO₃ and Ag(4-bipy)NO₃) and studies made of their properties [4, 5]. We previously reported the preparation and characterization of 2,4'-bipyridine complexes with silver(I) of the type Ag(2,4'-bipy)₂X (where $X=NO_3^-$ or ClO_4^-) [6].

The present work is a continuation of our studies on the synthesis and thermal decomposition of bipyridine complexes with nd^m metal thiocyanates [7]. The recent our paper [8] discussed the thermal behaviour of 4-bipy and 2,4'-bipy complexes of Co(II), Ni(II) and Cu(II) thiocyanates. The thermal stability of complexes and the decomposition temperature of thiocyanato ligands depends on the properties of other nitrogen donors contained in the coordination sphere [9]. The molecular structure of bipyridine isomers favours mainly following types of coordination: 2-bipy is potential bidentate chelating ligand; 4-bipy acts as bridging ligand; 2,4'-bipy can coordinate via the least-hindered nitrogen N(4') atom. It was interesting to examine the influence of the nitrogen atoms position in the ti-

the ligands on the properties and thermal decomposition of thiocyanato complexes of copper(I) and silver(I) with bipyridine isomers. The solid products of thermal decomposition of these types of compounds have not been studied yet.

Experimental

Physical measurements

The apparatus and measuring conditions were the same as described previously [5, 10]. The IR spectra were obtained using KBr discs (4000–400 cm^{-1}) for copper(I) complexes and in Nujol mull for silver(I) compounds on a Shimadzu spectrophotometer model 200.

Preparation and analysis of the complexes

Copper(I) complexes

The complexes were prepared by dissolving 4.3 mmol CuSCN in a 40 cm^3 aqueous-acetone solution (75% v/v) of 3.6 M KSCN. The gradual residue of CuSCN was removed by filtration. The obtained solution was mixed with 7 cm^3 of an acetone solution containing 12.9 mmol of 2-bipy, 4-bipy or 2,4'-bipy. The reaction mixture was stirred at 50°C for about 15 min. The colour precipitates were formed immediately. The mixture was allowed to cool, and the products were filtered off, washed with a mixture of water and acetone (1:1), then with a solution of acetone: Et₂O (1:1), and dried at room temperature.

Silver(I) complexes

AgLSCN (*L*=2-bipy or 4-bipy) was prepared in following way: AgSCN (6.4 mmol) was dissolved in a mixture containing ca 4.3 g NaSCN in 50 cm^3 75% v/v EtOH and gradual residue of AgSCN was filtered off. The filtrate was collected to dry breaker and ca 2.35 g NaSCN (the NaSCN concentration was chosen so that a double dilution of the solution with 75% v/v EtOH would not cause any turbidity) was added. 12.8 mmol of 2-bipy or 4-bipy solid was added to a warm filtrate with excess NaSCN and intensively stirred for about 20 min at 80°C. Precipitation of the complexes occurred immediately. The final products were removed by filtration, washed with a cold mixture of H₂O and EtOH (1:1), then with a solution of EtOH and Et₂O (1:1) and air dried at room temperature. Ag(2,4'-bipy)SCN complex was prepared similarly, only it was isolated from water solution.

Reagent grade chemicals used in the preparation of the complexes of 2-bipy (*m.p.* 72°C), 4-bipy (*m.p.* 112°C) and 2,4'-bipy (*m.p.* 61°C) were obtained from Aldrich; other chemicals from POCh-Gliwice.

The complexes were analysed: carbon, hydrogen and nitrogen contents were obtained using a Carlo-Erba elemental analyser; Cu and Ag in mineralized sample were determined by solvent extraction with sodium diethyldithiocarbonate [11] and the Volhard method, respectively.

Results and discussion

In Table 1 the complexes isolated from solution are listed together with their colours and solubilities in water. All complexes have stoichiometry MLSCN; they are a new type of complexes with ligand isomerism. The copper(I) complexes are air stable in room temperature; the silver complexes are photochemically unstable. They were practically insoluble in most organic solvents, but fairly soluble in EtOH and MeOH.

Table 1 Analytical data and solubility (S) of complexes in water at 21°C

	Complex and colour	Analysis: found (calculated)/%				S · 10 ³ / mol l ⁻¹
		M	C	H	N	
I.	Cu(2-bipy)SCN brown	21.80 (22.87)	47.26 (47.56)	2.87 (2.90)	15.11 (15.12)	2.54
II.	Ag(2-bipy)SCN pale-yellow	33.13 (33.49)	40.92 (41.01)	2.44 (2.50)	13.29 (13.04)	8.33
III.	Cu(4-bipy)SCN orange	21.54 (22.87)	47.50 (47.56)	2.93 (2.90)	14.90 (15.12)	2.69
IV.	Ag(4-bipy)SCN white	33.02 (33.49)	41.03 (41.01)	2.46 (2.50)	13.16 (13.04)	29.00
V.	Cu(2,4'-bipy)SCN yellow	22.10 (22.87)	47.62 (47.56)	2.86 (2.90)	15.18 (15.12)	0.91
VI.	Ag(2,4'-bipy)SCN yellow	33.56 (33.49)	40.95 (41.01)	2.43 (2.50)	13.05 (13.04)	7.50

Infrared spectra

In Table 2 the main bands in the infrared of the 2,2'-, 4,4'- and 2,4'-bipy and their complexes are reported. IR spectra of free ligands undergo a certain modification when coordinated with a metal. All these IR data indicated that these ligands are coordinated to a metal ion [12–15]. Moreover, in the case of 2-bipy complexes, the strong band at 753 cm⁻¹ (assignment as the symmetric out-of plane mode of the C–H group) in the uncomplexed ligand is observed at 766 vs cm⁻¹ for Cu(2-bipy)SCN and 760 vs cm⁻¹ for Ag(2-bipy)SCN. The satel-

lite of this band at 734 cm^{-1} gains intensity and is strongly split away from the parent peak. Thus, the obtained compounds are *cis*-2,2'-bipyridine chelate compounds [12, 13, 16]. The comparison of IR bands of free 2,4'-bipy and its Cu(I) and Ag(I) complexes shows that upon coordination the IR spectrum of 2,4'-bipy undergoes a change only in the region of the ring vibration modes of 4-substituted pyridine. These observations allow to assume that 2,4'-bipy coordinates with these metals(I) via least hindered N(4') atom [17]. This coordination of 2,4'-bipy takes place in many complexes [5, 10, 17].

Table 2 Principal IR bands for 2-bipy, 4-bipy, 2,4'-bipy and their complexes [cm^{-1}]

Complex	Assignment for band			
	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	Pyridine 'breathing'	γCH
2-bipy	1579vs	1553s	991s	753vs, 734m
Cu(2-bipy)SCN	1591vs	1570m	1013s	766vs, 735s
Ag(2-bipy)SCN	1604s	1582m	1000s	760vs, 735s
4-bipy	1590vs	1530s	982s	758w, 730s
Cu(4-bipy)SCN	1597vs	1530vs	1003vs	759vs, 731s
Ag(4-bipy)SCN	1599vs	1531vs	1002vs	748w, 729vs
2,4'-bipy ^a	1595vs	1553v	990sh	745sh, 729vs
Cu(2,4'-bipy)SCN	1606vs	1540vs	1011s	740s, 731s
Ag(2,4'-bipy)SCN	1605vs	1558s	1009m	740s, 729s

v, m, s, sh – very, medium, strong, shoulder; a – for 4-substituted pyridine

Beside the organic ligand vibrations, the IR spectra of the investigated complexes exhibit additional bands which are identified as $\nu(\text{CN})$, $\nu(\text{CS})$ and $\delta(\text{NCS})$ of thiocyanato group [18–20] (Table 3). IR spectra of all these complexes indicate clearly the presence of coordination thiocyanato groups. The absorption bands in the $\nu(\text{CN})$ region appear above $2070\text{--}2124\text{ cm}^{-1}$, what suggests the presence of weak bridged SCN groups [18, 20, 21] in the complexes I, II, IV–VI. The polymeric structures with bridged SCN groups are characteristic for complexes of group Ib metals [18, 22, 23]. However, the presence of bands $\nu(\text{CN})$ at $2106, 2052\text{ vs, pd } [\text{cm}^{-1}]$ and $\delta(\text{NCS})$ at $486\text{ s } [\text{cm}^{-1}]$ for Cu(4-bipy)SCN can show on existing probably of only terminal N-bonded SCN group in this complex [18, 19]. Terminal N-thiocyanates have been reported for several copper(I) complexes [24].

Thermal investigations

Thermal decomposition data obtained from TG, DTG and DTA curves, supported by chemical analysis and the X-ray diffraction pattern investigations are

Table 3 IR bands of thiocyanato groups [cm^{-1}]

Complex	IR spectra		
	$\nu(\text{CN})$	$\nu(\text{CS})$	$\delta(\text{NCS})$
Cu(2-bipy)SCN	2117, 2070vs, pd	Δ	451m
Cu(4-bipy)SCN ^a	2106, 2052vs	Δ	486s
Cu(2,4'-bipy)SCN	2122vs	740s	488s
Ag(2-bipy)SCN	2115vs	Δ	450s
Ag(4-bipy)SCN	2108, 2096vs, pd	700m	451s
Ag(2,4'-bipy)SCN	2124vs, 2071sh	738m	449w

Δ – overlaid by bipy absorption; pd – poorly resolved doublet; a – probably as Cu(4-bipy)NCS

summarized in Table 4. Copper(I) complexes display very similar behaviours during their thermal decomposition. All complexes decompose progressively. The thermal curves for these compounds are given in Figs 1a, b, c. The complexes(I) and (III) are stable up to 160°C. The deamination of complex(I) is one stage process. At 360°C CuSCN with ca. 6% of solid organic fragments occurred. 4-Bipyridine was split off in two stages for Cu(4-bipy)SCN. At first 0.5 mol of 4-bipy was eliminated to form $(\text{CuSCN})_2 \cdot 4\text{-bipy}$ (160–260°C). In the temperature interval 260–380°C, further decomposition steps take place and CuSCN (with ca 2% organic fragments) is formed. DTA curve minima occur at 260 for(I), 250 and 340°C for(III). The exothermic peak at 220°C for the complex(I) corresponds to the phase transformation. Cu(2,4'-bipy)SCN loses 2,4'-bipy above 180 and 350°C CuSCN is formed with an endothermic peak at 300°C. The observed mass loss for this process is comparable with the theoretical values. In all cases, after removal of bipyridine, the decomposition of copper(I) thiocyanate begins. At ca 465°C, $\text{Cu}_2\text{S}(\text{CN})_2$ is probably formed temporarily. The suggested stoichiometry of thermal decomposition of Cu(SCN) in this step is in agreement with the data published by Kabešová *et al.* [25]. On increasing the temperature this intermediate product decomposes via mixture of CuSO_4 , Cu_2OSO_4 and CuO to pure CuO, as described earlier for the complexes of 4-bipy and 2,4'-bipy with copper(II) thiocyanate [8]. Formation of Cu_2O begins above 850°C. The combustion of remaining organic fragments and the decomposition of CuSCN relate to the exothermic effects. The corresponding exothermic peak on the DTA curve for complexes(I) and (V) is high and broad with maximum ca 420°C and is probably composed of two overlapping exothermic effects. The DTA curve of compound(III) show exothermic peaks at 380 and 430°C.

The thermal curves for silver(I) complexes are shown in Figs 2a, b, c. When heated, the silver(I) complexes in the first stages decompose in various ways. The Ag(2-bipy)SCN and Ag(2,4'-bipy)SCN are stable up to 100–105°C. The Ag(4-bipy)SCN is more stable and begin to decompose at 140°C. Within the

Table 4 Decomposition process of complexes in air

Complex	Ranges of decomposition/ °C	DTA peaks	Mass loss		Intermediate and products
			found/ %	calc./ %	
Cu(2-bipy)SCN	160–360	220exo	50.0	56.22	CuSCN with ca 6% of organic fragments
	360–462	260endo			Cu ₂ S(CN) ₂
	>462	360sh, 418exo 650, 740 endo	10.0	5.77	mixture of CuSO ₄ + Cu ₂ OSO ₄ +CuO pure CuO
Cu(4-bipy)SCN	770		10.5	9.38	Cu ₂ O*
	>850				CuSCN(4-bipy) _{0.5}
	160–260	250endo	28.0	28.11	CuSCN with ca 2% of organic fragments
	260–380	340endo	27.0	28.11	Cu ₂ S(CN) ₂
Cu(2,4'-bipy)SCN	380–465	380, 430exc	7.8	5.77	
	180–350	Further, as in the case of Cu(2-bipy)SCN 300endo	56.0	56.22	CuSCN
	350–465	380sh, 420exo Further, as in the case of Cu(2-bipy)SCN	6.8	5.77	Cu ₂ S(CN) ₂

Table 4 Continued

Complex	Ranges of decomposition/ °C	DTA peaks	Mass loss		Intermediate and products
			found/ %	calc./ %	
Ag(2-bipy)SCN	100-295	105, 245endo, br	53.5	53.46	AgSCN·AgCN
	295-495	385, 480exo	9.0	8.08	Ag ₂ S
	495-620	600exo			mixture of Ag ₂ S+ Ag ₂ SO ₄ +Ag
Ag(4-bipy)SCN	>620				mixture of Ag ₂ SO ₄ +Ag
	>920	960endo	4.0	4.97	pure Ag
	140-218	218endo	12.0	12.12	Ag(4-bipy) _{0.75} SCN**
	218-260		24.0	24.24	Ag(4-bipy) _{0.25} SCN**
	260-290	270endo	13.0	12.12	Ag ₂ SCN
Ag(2,4'-bipy)SCN	290-495	400, 480exo	13.0	13.06	Ag ₂ S***
		Further, as in the case of Ag(2-bipy)SCN			
	105-218	178endo	24.0	24.24	Ag(2,4'-bipy) _{0.5} SCN**
	218-280	250endo	25.0	24.24	Ag ₂ SCN
	280-500	370, 480exo	12.0	13.06	Ag ₂ S***
		Further, as in the case of Ag(2-bipy)SCN			

* - very slowly, ** - by projecting minimum of the DTG curve on TG curve, *** - via xAgSCN·yAgCN, br - broad

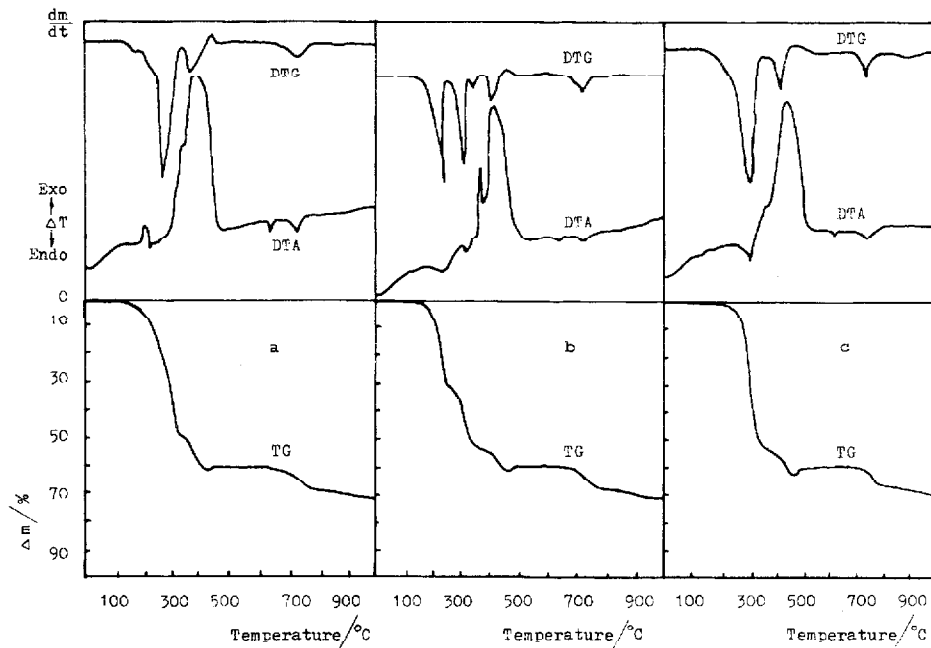


Fig. 1 Thermoanalytical curves of Cu(2-bipy)SCN (a), Cu(4-bipy)SCN (b), Cu(2,4'-bipy)SCN (c)

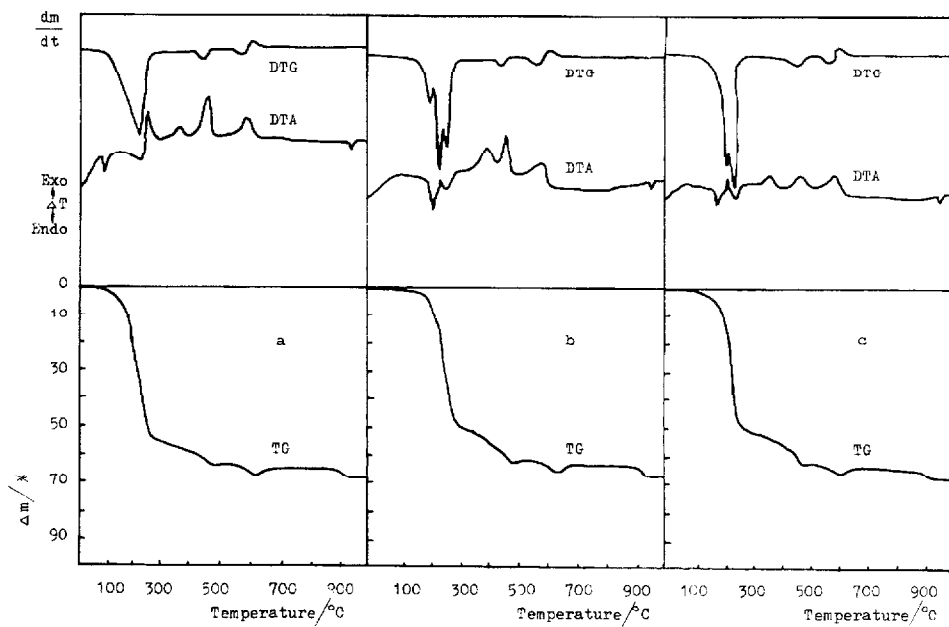


Fig. 2 Thermoanalytical curves of Ag(2-bipy)SCN (a), Ag(4-bipy)SCN (b), Ag(2,4'-bipy)SCN (c)

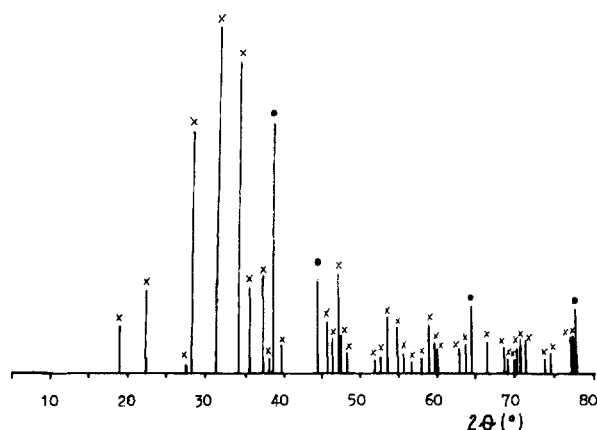


Fig. 3 X-ray diffraction patterns of decomposition products of Ag(4-bipy)SCN heated up to 700°C; x - Ag₂SO₄, • - Ag

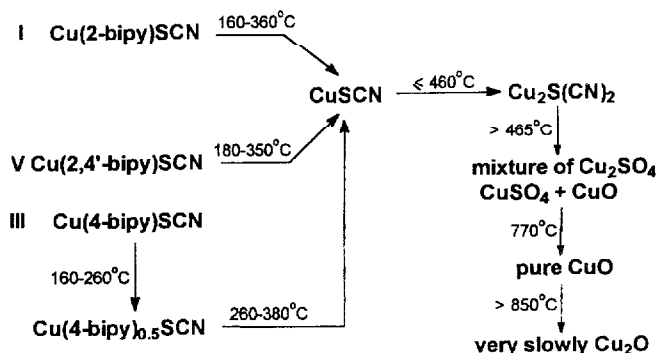
100–295°C range, decomposition of Ag(2-bipy)SCN took place and intermediate product AgSCN·AgCN was formed. According to Duval [26] this compound is formed during thermal decomposition of AgSCN at 224°C. The endothermic effects are seen in the DTA curves at 105 and 245°C. The second transformation corresponds to the formation of silver sulphide at 495°C (found 37.5%, calc. 38.46%). The corresponding exothermic peaks on the DTA curve appear at 385 and 480°C. The complexes Ag(4-bipy)SCN and Ag(2,4'-bipy)SCN deaminate progressively. For these complexes gradual liberation of organic ligand is shown only by DTG curves. For the compound (IV) and (VI) the stepwise elimination of bipy processes overlap, but by projecting minimum of the DTG curve on TG curve [27] it can be established that 0.25 and 0.5 moles of 4-bipy are lost for (IV) and 0.5 moles of 2,4'-bipy for (VI). The intermediate compound of the general formula $x\text{AgSCN}\cdot y(\text{bipy})$ is formed. The transient products decompose with the formation of AgSCN at 290°C for (IV) and at 280°C for (VI). Organic ligands are split off with endothermic effects. After removal of these ligands, the decomposition of AgSCN begins, and its conversion to Ag₂S, probably via $x\text{AgSCN}\cdot y\text{AgCN}$ [26, 28] takes place. Next, in all cases, the process of Ag₂S gradual decomposition takes place and non-stoichiometric mixture of Ag₂SO₄ and Ag is formed (Fig. 3). As an example, at 700°C in the sinter of Ag(2-bipy)SCN were obtained 29.4% Ag and 6.2% Ag₂SO₄. Pure metallic silver is obtained above 920°C. The peak occurring on the DTA curve at 960°C corresponds to the melting-point of silver.

Conclusions

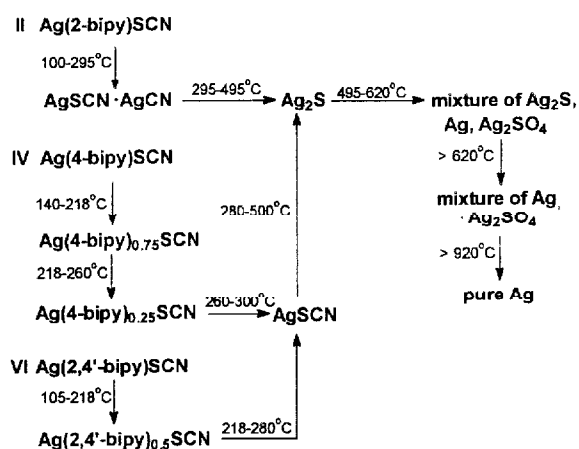
Copper(I) and silver(I) thiocyanates form with 2-bipy, 4-bipy and 2,4'-bipy (L) complexes of general formulae MLSCN. IR studies indicate clearly that or-

ganic ligands and SCN-groups are coordinated in these complexes. The complexes form probably polymeric structures in solid state. However, X-ray studies can lend more conclusive support for the structures of investigated complexes.

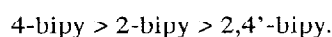
The thermal decomposition of discussed compounds, and their inter-relation are shown in the Scheme 1 for CuLSCN



and Scheme 2 for AgLSCN

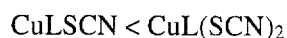


The change of the position of nitrogen atoms in the bipyridine molecule occur on the steps of deamination of MLSCN complexes and the temperature range of elimination of all bipyridine. The number of moles bipy liberated during the thermal decomposition partially depends on species of metal and bipyridine isomers. The temperature range of elimination of all bipyridine decrease in order:



The initial decomposition temperature of thiocyanato ligands generally increases in the complex in comparison with free MSCN [26]. Nature of the transition products formed during decomposition of MSCN (after removal of bipyri-

dine) and the temperature of final products (Cu_2O and Ag, respectively) formation are not depending on the bipyridine isomers present. The study of thermal behaviour of the complexes MLSCN discussed here showed that the complexes of Cu(I) have higher thermal stabilities than Ag(I) complexes. Increase in valency of the copper appears to increase of the thermal stability in the order [8, 29]:



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