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Low-dimensional compounds containing cyano groups VIII. A spectral and thermal study of dicyanoargentates containing aliphatic diamine ligands

L'ubica Triščíková[a], Ivan Potočňák[b,*], Jozef Chomič[b], Thomas Müller[c]

[a] *Department of Physical Sciences, Faculty of Science, University of Žilina, Hurbanova 15, SK-010 26 Žilina, Slovak Republic*
[b] *Department of Inorganic Chemistry, Institute of Chemistry, P.J. Šafárik University, Moyzesova 11, SK-041 54 Košice, Slovak Republic*
[c] *Institute of Inorganic Chemistry, Martin Luther University, Halle-Wittenberg, Kurt-Mothes-Strasse 2, D-06120 Halle, Germany*

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Abstract

The synthesis, spectral and thermal properties of dicyanoargentates, namely $Cu(tn)_2Ag_2(CN)_4$ (I) (*tn* = 1,3-diaminopropane), $Cu_{8-x}Ag_x(tn)_3(CN)_{10}$ $x = 0.25$ (II), $Cu(pn)_2Ag_2(CN)_4$ (III) (*pn* = 1,2-diaminopropane) and $Cu_2(dabn)_2(NH_3)Ag_4(CN)_8\cdot 2H_2O$ (IV) (*dabn* = 1,4-diaminobutane) are reported. All complexes were isolated from reaction mixtures containing $K[Ag(CN)_2]$, $CuSO_4$ and N-donor ligands (*tn*, *pn* and *dabn*, respectively). Infrared spectra confirm the presence of characteristic functional groups and are consistent with the known structures of complexes (I), (III) and (IV). Thermal decompositions of complexes (I)–(IV) begin by endothermic liberation of ligand molecules followed by strong exothermic redox decomposition of the cyano groups. Comparison of the initial decomposition temperatures of complexes (I)–(IV) yields the following order of the thermal stability (IV) < (I) < (III) < (II).

Keywords: Copper(II) dicyanoargentates; Structure-IR-spectroscopy relationships; Thermal decomposition

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1. Introduction

The chemistry of cyano-bridged coordination polymers is of current interest due to the remarkable diversity of structural types that may be obtained from these systems. The interest of our research group in low-dimensional solids containing cyano bridges has been outlined in the previous papers [1–3] and in a recent review [4]. We are particularly interested in the use of dicyanoargentate anion $[Ag(CN)_2]^-$ as building blocks. The $[Ag(CN)_2]^-$ anion can behave as: (i) a rod ligand building up multi-dimensional structures by bridging between two coordination centres [5,6], (ii) as an unidentate ligand, blocking some coordination sites of the central atom [1,7], or (iii) as a discrete anion playing the role of space filler [8,9], but compounds, in which dicyanoargentate anions exhibit simultaneously two different structural functions, are quite common. Moreover, this anion can also produce polymeric structures via Ag–Ag interactions [2,5,7,10–12]. The varieties of dicyanoargentates with diamagnetic cadmium atom have recently attracted attention of Iwamoto's research group [5,7,11,13], but the thermal stability and stoichiometry associated with thermal decomposition of dicyanoargentates have been studied only to a lesser extent [14–16].

Here we present the results of spectral and thermal study of four dicyanoargentates with aliphatic diamine ligands 1,3-diaminopropane (*tn*), 1,2-diaminopropane (*pn*) and 1,4-diaminobutane (*dabn*) namely, $Cu(tn)_2Ag_2(CN)_4$ (I), $Cu_{8-x}Ag_x(tn)_3(CN)_{10}$ $x = 0.25$ (II), $Cu(pn)_2Ag_2(CN)_4$ (III) and $Cu_2(dabn)_2(NH_3)Ag_4(CN)_8\cdot 2H_2O$ (IV), respectively.

2. Experimental

2.1. Synthesis of the complexes

All chemicals required for syntheses, i.e. copper(II) sulphate pentahydrate ($CuSO_4\cdot 5H_2O$), silver nitrate ($AgNO_3$),

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* Corresponding author. Tel.: +421-55-6228114; fax: +421-55-6222124.
E-mail address: potocnak@kosice.upjs.sk (I. Potočňák).

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potassium cyanide (KCN), 1,2-diaminopropane ($C_3H_{10}N_2$), 1,3-diaminopropane ($C_3H_{10}N_2$) and 1,4-diaminobutane ($C_4H_{12}N_2$) were purchased in analytical grade and used without further purification. Potassium dicyanoargentate $K[Ag(CN)_2]$ was prepared from silver nitrate and potassium cyanide.

Blue-violet crystals of (I) were prepared according to the literature [1] by successive addition of 2 M aqueous *tn* (2 cm^3, 4 mmol) and 0.2 M aqueous $K[Ag(CN)_2]$ (10 cm^3, 2 mmol) to 0.1 M aqueous solution of $CuSO_4$ (10 cm^3, 1 mmol). The solution thus formed was filtered to avoid any presence of solid impurities and left aside for crystallization. Blue-violet crystals appeared within a week. The crystals were filtered off followed by washing with a small portion of cold water and then dried in air. The compound is air stable and insoluble in water, alcohols and acetone. Elemental analysis of (I): experimentally found: C 23.00; H 3.75; N 20.75; Cu 11.95; Ag 41.25%. Calculated for $C_{10}H_{20}N_8Ag_2Cu$ ($M_r = 531.61$): C 22.59; H 3.79; N 21.08; Cu 11.94; Ag 40.58%.

Crystals of (II) were prepared in a similar way but the amount of *tn* was decreased ($K[Ag(CN)_2]$, $CuSO_4$ and *tn* were in the molar ratio of 1:2:1) and red-violet crystals of (II) appeared within a week days. The crystals were filtered off followed by washing with a small portion of cold water and then dried in air. The compound is air stable and insoluble in water, alcohols and acetone. Elemental analysis of (II): experimentally found: C 22.99; H 2.89; N 21.97; Ag 2.76; Cu 49.18%. Calculated for $C_{19}H_{30}N_{16}Ag_xCu_{8-x}$, $x = 0.25$ ($M_r = 1001.96$): C 22.78; H 3.02; N 22.37; Ag 2.69; Cu 49.15%.

The complex (III) was prepared according to the literature [17] by successive addition of 2 M aqueous *pn* (1 cm^3, 2 mmol) and 0.2 M aqueous $K[Ag(CN)_2]$ (10 cm^3, 2 mmol) to 0.1 M aqueous solution of $CuSO_4$ (10 cm^3, 1 mmol). The dark-violet solution thus formed was filtered to avoid any presence of solid impurities and left aside for crystallization. Dark violet needles appeared within 1 h. The crystals were filtered off followed by washing with a small portion of cold water and then dried in air. The compound is air stable and insoluble in water, alcohols and acetone. Elemental analysis of (III): experimentally found: C 22.68; H 3.64; N 20.91; Cu 11.29; Ag 43.60%. Calculated for $C_{10}H_{20}N_8Ag_2Cu$ ($M_r = 531.61$): C 22.59; H 3.79; N 21.08; Cu 11.95; Ag 40.58%.

The preparation of (IV) was carried out as follows [18]: a blue precipitate containing $[Cu(dabn)_2]^{2+}$ cations, formed by mixing of 0.1 M copper sulphate solution (10 cm^3, 1 mmol) and 2 M aqueous 1,4-diaminobutane (1 cm^3, 2 mmol), was dissolved by addition of concentrated (26%) ammonia solution (1.5 cm^3). The blue solution thus formed was mixed with 0.2 M solution of $K[Ag(CN)_2]$ (10 cm^3, 2 mmol). The resulting blue solution was left to crystallize. Blue crystals of (IV) were obtained after 2 days. The crystals were filtered off followed by washing with a small portion of cold water and then dried in air. Elemental analysis of (IV): experimentally found: C 19.21; H 3.08; N 17.88; Ag 44.78; Cu 13.55%. Calculated for $C_{16}H_{31}N_{13}Ag_4Cu_2O_2$ ($M_r = 996.10$): C 19.29; H 3.14; N 18.28; Ag 43.32; Cu 12.76%.

2.2. Apparatus

The carbon, hydrogen and nitrogen microanalyses were performed using a CHNS-O Carlo Erba EA 1108 Elemental Analyzer. The silver and copper contents were determined using a SpectrAA-30 Varian spectrometer after mineralization of the samples with diluted HNO_3.

The IR spectra of the compounds were recorded on a MATTSON 5000 FT–IR Spectrometer in the 4000–300 cm^{-1} range using KBr pellets.

The TG, DTA, DTG measurements were carried out using NETZSCH STA 409 C instrument under dynamic conditions in air atmosphere with heating rate 10 °C min^{-1} and sample weights were approximately 20 mg.

The solid thermal decomposition products were identified using powder X-ray diffraction patterns recorded on a Mikrometa 2 diffractomer equipped with Cr K_α radiation ($\lambda = 2.29092$ Å) monochromatized with vanadium foil.

3. Results and discussion

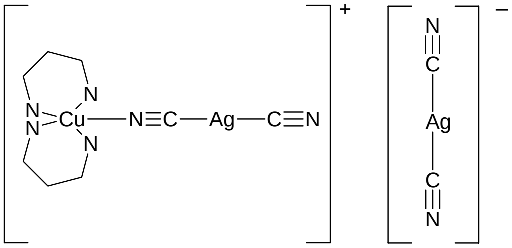
The same general procedure is often used for the preparation of solid cyanocomplexes exhibiting polymeric structures with various degrees of dimensionality. This method is based on a combination of suitable building blocks and is so-called “brick and mortar” method [19]. The building blocks in solution are formed by complex cations with at least two coordination sites occupied by weak ligands (brick) and bridging cyanocomplex anions (mortar), which can replace the weak ligands, and thus inducing polymerization of the structure in solid. Such method was also used in the preparation of our studied compounds. In this way we have prepared following dicyanoargentates by using various “bricks” as $[Cu(tn)_2]^{2+}$, $[Cu(pn)_2]^{2+}$, $[Cu(dabn)_2]^{2+}$ and the same “mortar” $[Ag(CN)_2]^-$: blue-violet crystals of $Cu(tn)_2Ag_2(CN)_4$ (I) [1], red–violet crystals of $Cu_{8\text{-}x}Ag_x(tn)_3(CN)_{10}$ $x = 0.25$ (II), dark-violet crystals of $Cu(pn)_2Ag_2(CN)_4$ (III) [17] and blue crystals of $Cu_2(dabn)_2(NH_3)Ag_4(CN)_8{\cdot}2H_2O$ (IV) [18]. All compounds are air stable and insoluble in water, alcohols and acetone. Other dicyanoargentates with a general formula of $Cu(L)_2Ag_2(CN)_4{\cdot}nH_2O$ (where *L*: N-donor ligand) with $[Cu(4\text{-}Mepy)_2]^{2+}$ (4-*Mepy* = 4-methylpyridine), $n = 0$ [10], $[Cu(NH_3)_2]^{2+}$, $n = 0$ [14], $[Cu(en)_2]^{2+}$ (*en* = 1,2-diaminoethane), $n = 0$ [15], $[Cu(phen)_2]^{2+}$ (*phen* = 1,10-phenanthroline), $n = 1$ [16], $[Cu(bpy)_2]^{2+}$ (*bpy* = 2,2′-bipyridine), $n = 1$ [20], $[Cu(py)_2]^{2+}$ (*py* = pyridine), $n = 0$ [21] “bricks” have been previously prepared in the same way. The formation of the mixed-valence complex (II) is an expression of the Cu(II)/Cu(I) redox equilibrium in the presence of cyano and *tn* ligands in air. Similar processes led to the formation of Cu(II)/Cu(I) cyanoargentates containing ammonia and pyridine, namely $Cu(NH_3)pyAg_{3-x}Cu_x(CN)_5 \cdot py$, $x = 1.243$ and 0.39 [3], or 4-methylpyridine, namely $Cu(4\text{-}Mepy)_3Ag_{2-x}Cu_x(CN)_4$, $x = 0.07$, respectively [22].

3.1. Spectral study

The measured IR spectra confirm the presence of all characteristic functional groups in the prepared complexes. The vibration wave numbers of the bands confirming the presence of *tn*, *pn* and *dabn* in the spectra of (I)–(IV) are summarized in Table 1, together with some relevant spectral data for comparison. The vibrations observed in the spectrum of free *tn*, *pn* [23] and *dabn* [24] were found in the spectra of (I)–(IV), but the bands were shifted as a consequence of the ligand coordination. The presence of dicyanoargentates in the prepared complexes is proved by strong ν(CN) stretching bands. The position of the stretching ν(CN) vibration is an important tool in distinguishing between terminal and bridging character of the cyano group. This band is observed at 2080 cm^{-1} in ionic KCN [25]. As a consequence of a cyano group coordination, ν(CN) band is shifted towards higher frequencies. In the solid $K[Ag(CN)_2]$ with terminal cyano groups only, the ν(CN) position is at 2140 cm^{-1}, while in AgCN containing bridging cyano groups, this band is shifted to 2164 cm^{-1} [26,27]. The use of different N-donor ligand (*tn*, *pn* and *dabn*) led to a various types of structures and to a different function of the cyano groups (terminal or bridging, respectively), which is reflected by the ν(CN) stretching vibration position in IR spectra of (I)–(IV) (Table 2).

Table 2
The vibration wave numbers (cm^{-1}) of cyanide group for $K[Ag(CN)_2]$ [27], (I), (II), (III) [17] and (IV)

Assignment	$K[Ag(CN)_2]$	(I)	(II)	(III)	(IV)
ν3 ν(CN), $\sum_u^+$					2179w
		2160m			2164vs
	2140vs	2148s			2136s
		2132s	2108vs	2133s	
ν_4 ν(AgC), $\sum_u^+$	390s	412w	362m	390s	388w
		402w			



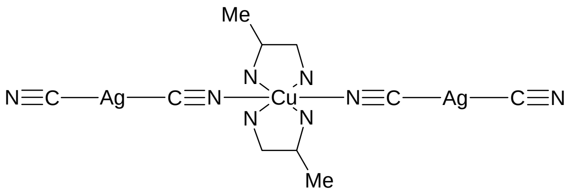
Scheme 1. Structural diagram for (I).

In (I), the strong bands observed at 2132 and 2148 cm^{-1} can be attributed to the stretching vibration of terminal cyano groups, whereas the medium band at 2160 cm^{-1} may arise from the bridging cyano groups. The relative intensities of the absorption bands correspond to the number of the respective types of cyano groups in the structure of (I) (Scheme 1).

According to the known crystal structure of (III) [17] (Scheme 2) we have expected several ν(CN) vibrations for cyano groups. However, the spectrum contains only one ν(CN) absorption band at 2133 cm^{-1} despite the presence of both terminal and bridging cyano groups in the structure of (III). This may be caused by the interplay of two effects: (1) the slight increase of the terminal group absorption band position due to its involvement in hydrogen bonds system,

Table 1
The vibration wave numbers (cm^{-1}) of *tn* [23], *pn* [23], *dabn* [24], (I), (II), (III) [17] and (IV)

Assignment	*tn*	(I)	(II)	*pn*	(III)	*dabn*	(IV)
$\nu(NH_2)$	3360s	3332s	3301s	3369s	3329s	3346s	3327w
$\nu(NH_2)$	3282s	3256s	3245s	3284s	3264s	3280s	3269w
$\nu(CH_2)$		2968m	2941m		2983w		2978m
$\nu(CH_2)$	2925vs	2944s		2958vs	2954m	2926vs	2945m
$\nu(CH_2)$	2855s	2892m	2890m	2922s	2923m		2887m
$\nu(CH_2)$	2835vs	2840w		2861s	2879w	2853vs	2868w
$\delta(NH_2)$	1601s	1612vs	1585s	1603s	1599s	1606s	1582s
$\delta(NH_2)$	1471m	1472m	1470w	1455m	1455m	1497s	1469m
$\rho_w(CH_2)$	1434m	1406m	1401m	1375m	1384w	1390w	1380m
$\rho_w(CH_2)$	1369m			1349m	1375m	1353vw	1364m
$\rho_t(CH_2)$	1319w		1313m	1299m	1301w	1309vw	1250m
$\delta_t(NH_2)$	1096m	1096w	1095w	1186w	1195w	1145vw	1149s
ν(CN)	1069m	1060w	1056w	1061m	1070m	1070m	1043m
ν(CN)			1027s		1052s		
$\rho_w(NH_2)$		1009s			1019m	954w	970s
$\rho_w(NH_2)$							
$\rho_r(CH_2)$ + $\rho_w(NH_2)$		904s	901s		931w	878m, br	
$\rho_r(CH_2)$	864m, br	888m	884m	861m, br		863m, br	
$\rho_r(CH_2)$						738w	



Scheme 2. Structural diagram for (III).

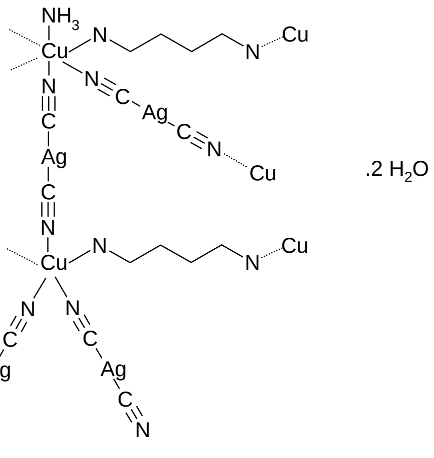
and (2) the slight decrease of the bridging group absorption band position due to the weaker coordination of the bridging cyano group to the copper atom, resulting in overlapping of both ν(CN) absorption bands. Similar situation was found in the Cu(*en*)$_2$Ag$_2$(CN)$_4$ (*en* = ethylendiamine) compound for which the single ν(CN) absorption band was observed at 2136 cm^{-1} [2].

The spectrum of (II) contains one ν(CN) absorption band at rather low value of 2108 cm^{-1}. As the position of ν(CN) stretching vibration in KCu(CN)$_2$ is at lower wave number than in KAg(CN)$_2$ [26,27] we suppose that the lower ν(CN) wave number in (II) could be caused by partial substitution of silver cation by cupric ion. Because there is only one ν(CN) absorption band in (II), we can expect either polymeric structure with only bridging cyano groups, or the structure may contain both terminal and bridging cyano groups involved in hydrogen bonds and in a weak coordination to the copper atom respectively, as observed in (III) and Cu(*en*)$_2$Ag$_2$(CN)$_4$ [2].

Taking into consideration the known structure of (IV) [18] (Scheme 3), the strong band at 2136 cm^{-1} can be attributed to the stretching vibration of terminal cyano group, while those at 2179 and 2164 cm^{-1} can arise from the bridging cyano groups.

3.2. Thermal study

The usual way of thermal decomposition of cyano complexes is characterized by liberation of N-donor ligands followed by separated decomposition of all cyano groups in one step. Thermal decompositions of the compounds (I)–(IV) are multi-stage processes.



Scheme 3. Structural diagram for (IV).

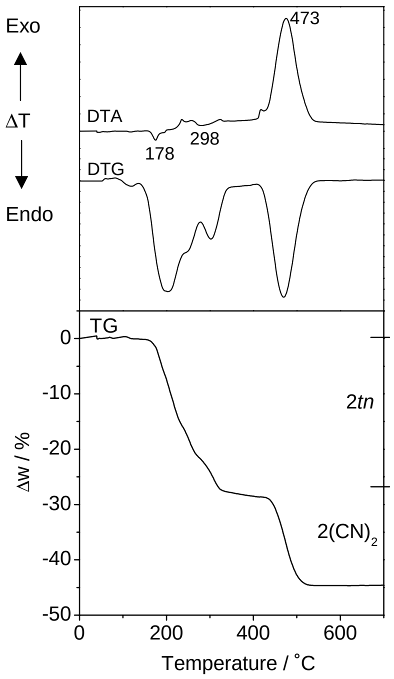


Fig. 1. Thermal curves for (I).

The TG, DTA and DTG curves for (I) are shown in Fig. 1. The thermal decomposition of (I) consists of two distinguished stages corresponding to the separated release of *tn* molecules and cyano groups decomposing. Complex (I) is stable up to 150 °C. In the 150–368 °C temperature range, a weight loss of 26.8% corresponding to the release of two *tn* molecules (calc 27.8%) is observed during endothermic multi-stage process (these stages are overlapped). The second step in the 368–514 °C temperature range, with observed weight loss of 16.6%, involves the decomposition of cyanides (calc 16.6%). Their decomposition includes oxidation of four CN$^-$ groups to form two cyanogen molecules during reduction of two silver cations and one half of oxygen molecule from the air ambient. This process is accompanied by a strong exothermic effect as a consequence of the cyanogen molecules pyrolysis. The final thermal decomposition product is a mixture of CuO (tenorite, 45-0937) and metallic Ag (4-0783) detected by X-ray powder diffractometry (solid residue 56.6%; calc 55.6%). The most probable thermal decomposition scheme for (I) is:

$$\mathrm{Cu}(tn)_2\mathrm{Ag}_2(\mathrm{CN})_4 \xrightarrow[2tn]{150\text{–}368\,^\circ\mathrm{C}} \mathrm{CuAg}_2(\mathrm{CN})_4 \xrightarrow[2(\mathrm{CN})_2]{368\text{–}514\,^\circ\mathrm{C}} \mathrm{CuO} + 2\mathrm{Ag}$$

The TG, DTA and DTG curves for (II) are shown in Fig. 2 The thermal decomposition of this complex consists of the three *tn* molecules release in two steps followed by decomposing of all cyano groups in one step. Complex (II) is stable up to 225 °C. In the 225–282 °C temperature range a

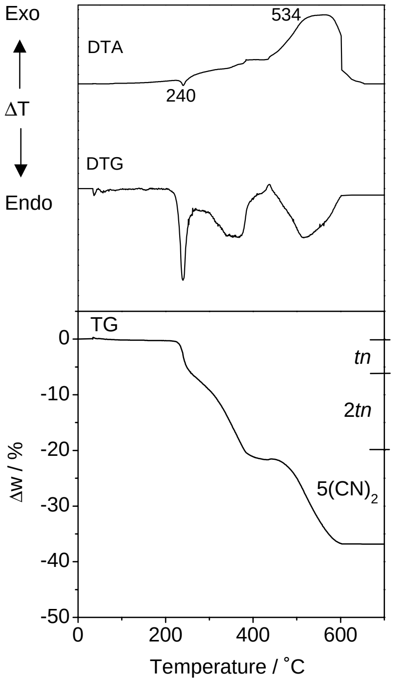


Fig. 2. Thermal curves for (II).

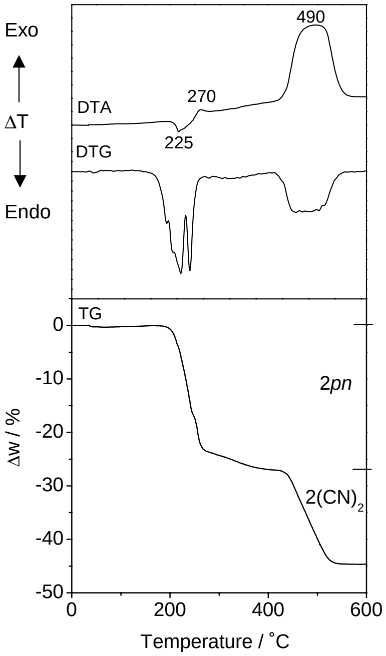


Fig. 3. Thermal curves for (III).

weight loss of 7.4% corresponding to the release of one *tn* molecule (calc 7.4%) is observed during endothermic process. It is overlapped by another endothermic process in the 282–436 °C temperature range, with observed weight loss of 12.2%, corresponding to the release of two *tn* molecules (calc 14.8%). The third step in the 436–577 °C temperature range, with observed weight loss of 16.7%, involves the decomposition of cyanides. This process is accompanied by a strong exothermic effect as a consequence of pyrolysis of cyanogen molecules. These are formed by oxidation of CN^- groups during reduction of silver cations and oxygen molecules from the present air, and simultaneously, the copper(I) is oxidized by atmospheric oxygen (calc 13.6%). The final thermal decomposition product is a mixture of CuO (tenorite, 45-0937) and metallic Ag (4-0783) detected by X-ray powder diffractometry (solid residue 63.7%; calc 64.2%). The most probable thermal decomposition scheme for (II) is:

$$\mathrm{Cu_{7.75}Ag_{0.25}}(tn)_3(\mathrm{CN})_{10} \xrightarrow[1tn]{225\text{–}282\,^\circ\mathrm{C}} \mathrm{Cu_{7.75}Ag_{0.25}}(tn)_2 \times (\mathrm{CN})_{10} \xrightarrow[2tn]{282\text{–}436\,^\circ\mathrm{C}} \mathrm{Cu_{7.75}Ag_{0.25}} \times (\mathrm{CN})_{10} \xrightarrow[5(\mathrm{CN})_2]{436\text{–}577\,^\circ\mathrm{C}} 7.75\mathrm{CuO} + 0.25\mathrm{Ag}$$

The TG, DTA and DTG curves for (III) are shown in Fig. 3. Complex (III) is stable up to 215 °C. In the 215–420 °C temperature range a weight loss of 27.0% corresponding to the release of two *pn* molecules (calc 27.8%) is observed during endothermic process (maximum at 225 °C in DTA) followed by small exothermic effect (maximum at 270 °C in DTA). In the 420–540 °C temperature range an observed weight loss of 17.5% involves the decomposition of cyanides (calc 16.6%). The decomposition includes oxidation of four CN^- groups to form two cyanogen molecules during reduction of two silver cations and one half of oxygen molecule from the air ambient. This process is accompanied by a strong exothermic effect (maximum at 490 °C in DTA) as a consequence of the pyrolysis of cyanogen molecules. The final thermal decomposition product is a mixture of CuO (tenorite, 45-0937) and metallic Ag (4-0783) detected by X-ray powder diffractometry (solid residue 55.5%; calc 55.6%). The most probable thermal decomposition scheme for (III) is:

$$\mathrm{Cu}(pn)_2\mathrm{Ag_2(CN)_4} \xrightarrow[2pn]{215\text{–}420\,^\circ\mathrm{C}} \mathrm{CuAg_2(CN)_4} \xrightarrow[2(\mathrm{CN})_2]{420\text{–}540\,^\circ\mathrm{C}} \mathrm{CuO} + 2\mathrm{Ag}$$

The thermal decomposition of (IV) consists of the H_2O, NH_3 and *tn* molecules release, followed by cyano groups decomposing. The TG, DTA and DTG curves for (IV) are shown in Fig. 4. Complex (IV) is stable up to 80 °C. In the 80–110 °C temperature range a weight loss of 5.5% corresponding to the release of two H_2O and one NH_3 molecules (calc 5.3%) is observed during endothermic process. In the 110–310 °C temperature range, observed weight loss of 17.9% involves the endothermic release of two *dabn* molecules (calc 17.7%). The decomposition of cyanides with a weight loss of 18.2% is observed in the 310–370 °C temperature range (calc 17.7%). This process is accompanied by a strong exothermic effect as a consequence of the pyrolysis of four cyanogen molecules, which are formed by oxidation of eight CN^- groups during reduction of four

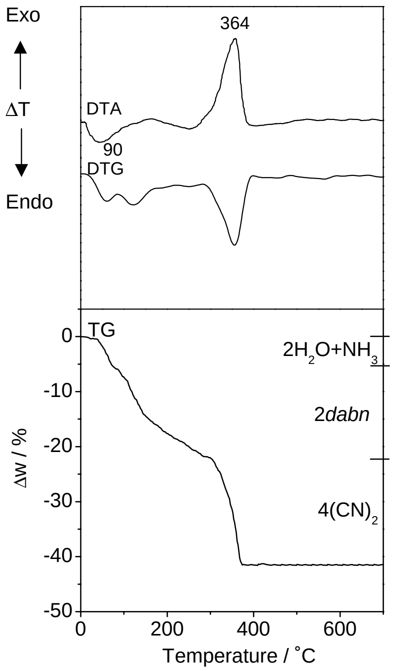


Fig. 4. Thermal curves for (IV).

silver cations and one oxygen molecule from the air ambient. The final thermal decomposition product is a mixture of CuO (tenorite, 45-0937) and metallic Ag (4-0783) detected by X-ray powder diffractometry (solid residue 58.4%; calc 59.3%). The most probable thermal decomposition scheme of (IV) is:

$$\mathrm{Cu_2}(dabn)_2\mathrm{(NH_3)Ag_4(CN)_8}\ \cdot 2\mathrm{H_2O} \xrightarrow[2\mathrm{H_2O},\ 1\mathrm{NH_3}]{80\text{–}110\,^\circ\mathrm{C}}$$

$$\mathrm{Cu_2Ag_4}(dabn)_2\mathrm{(CN)_8} \xrightarrow[2dabn]{110\text{–}310\,^\circ\mathrm{C}}$$

$$\mathrm{Cu_2Ag_4(CN)_8} \xrightarrow[4\mathrm{(CN)_2}]{310\text{–}370\,^\circ\mathrm{C}} 2\mathrm{CuO} + 4\mathrm{Ag}$$

Comparison of the thermal stability of the studied complexes with analogous dicyanoargentates with a general formula of $\mathrm{Cu}(L)_2\mathrm{Ag_2(CN)_4}\cdot n\mathrm{H_2O}$ ($n = 0, 1$) containing N-donor ligands like ammonia [14], 1,2-diaminoethane [15], 1,10-phenanthroline [16], 2,2′-bipyridine [20], pyridine [21], 4-methylpyridine [22], yields the next order of stability with the respect to the liberation temperature of these ligands (there are given the N-donor ligand liberation temperatures in the parentheses): *py* (95 °C), $\mathrm{NH_3}$ (102 °C), 4-*Mepy* (117 °C), *bpy* (140 °C), *phen* (148 °C), (I) (*tn*, 150 °C), *en* (190 °C), (III) (*pn*, 215 °C). It can be seen from this series that the complexes containing chelate N-donor ligands are more thermally stable than the complexes with monodentate ligands.

4. Conclusion

The IR spectra of the prepared copper(II) dicyanoargentates with aliphatic diamine ligands have been measured. The spectra confirm the presence of all function groups. Moreover, the number and intensity of ν(CN) stretching vibrations observed in the spectra of the complexes (I), (III) and (IV), respectively, are in consistence with the presence of bridging and terminal cyano groups in the structures of corresponding complexes. We assume, on the base of the IR-spectrum of complex (II) that this complex is either of polymeric structure with only bridging cyano groups, or the structure may contain both terminal and bridging cyano groups involved in hydrogen bonds and in a weak coordination to the copper atom, respectively.

Thermal decompositions of the complexes (I)–(IV) are multi-stage processes, which begin by diamine or water molecules liberation followed by decomposition of all cyano groups. Comparison of the initial decomposition temperatures yields the following order of thermal stability (IV) < (I) < (III) < (II). Similar thermal decompositions of dicyanoargentates with separated decomposition of organic ligands and cyano groups were previously observed in other dicyanoargentates with N-donor ligands and are usual for this type of compounds [14–16,20–22]. Complexes containing chelate ligands are more thermally stable than the complexes with monodentate ligands.

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