

Thermal Properties of Complexes $M(\text{NH}_3)_2[\text{Ag}(\text{CN})_2]_2$ ($M(\text{II}) = \text{Ni}, \text{Cu}, \text{Cd}$)

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Received 25 November 1991

Complexes of composition $M(\text{NH}_3)_2[\text{Ag}(\text{CN})_2]_2$, where $M = \text{Ni}$ (NiA), Cu (CuA), Cd (CdA), have been prepared and identified by infrared and electron spectroscopy and by magnetic susceptibility measurements. Thermal stability and stoichiometry of thermal decomposition were investigated by using a derivatograph. The intermediates of thermal decomposition were identified by IR spectroscopy and X-ray powder diffraction. The results showed that the thermal stability increased in the order CuA, CdA, NiA.

Reduction of copper(II) compounds in aqueous solution with cyanide of alkali metal in the presence of neutral N-donor ligands L(N) results in copper(I)—copper(II) cyano complexes. When L(N) is ammonia or ethylenediamine (en), from the systems $\text{Cu}(\text{II})\text{—L}(\text{N})\text{—CN}^-\text{—H}_2\text{O}$ the following complexes crystallize: $\text{Cu}_3(\text{NH}_3)_3(\text{CN})_4$, $\text{Cu}_5(\text{NH}_3)_x(\text{CN})_6$ ($x = 2$ and 4), $\text{Cu}_4(\text{NH}_3)_2(\text{H}_2\text{O})(\text{CN})_5$, $\text{Cu}_5(\text{en})_2(\text{CN})_6$, $\text{Cu}_4(\text{H}_2\text{O})(\text{en})_2(\text{CN})_6$, and $\text{Cu}_3(\text{H}_2\text{O})(\text{en})_2(\text{CN})_4$. When the ligand is *o*-phenanthroline (phen) or 2,2'-bipyridyl (bipy), only Cu(II) complexes are formed [1—5].

When replacing Cu(II) in $\text{Cu}_3(\text{NH}_3)_3(\text{CN})_4$ and $\text{Cu}_3(\text{H}_2\text{O})(\text{en})_2(\text{CN})_4$ by other M(II) atoms ($M = \text{Co}, \text{Ni}, \text{Zn},$ and Cd), it is possible to prepare compounds of general formulas $M(\text{NH}_3)_n\text{Cu}_2(\text{CN})_4$ and $M(\text{en})_2\text{Cu}_2(\text{CN})_4$ [6]. On the other hand, there is the possibility to replace Cu(I) in these complexes by Ag(I) with regard to its position in the periodic table. Thus, from the systems $M(\text{II})\text{—L}(\text{N})\text{—}[\text{Ag}(\text{CN})_2]^-\text{—H}_2\text{O}$ the complexes with L(N) = en, bipy, and phen were isolated [7—9]. The preparation of complexes with L(N) = ammonia and pyridine has been described in the literature [10], however, their thermal stability, stoichiometry of thermal decomposition, and spectral properties have not been investigated thus far. In the present work we systematically studied the synthesis of complexes from the systems $M(\text{II})\text{—NH}_3\text{—}[\text{Ag}(\text{CN})_2]^-\text{—H}_2\text{O}$, characterized the prepared complexes by IR and electron spectroscopy and by measuring magnetic susceptibility, followed the thermal stability and stoichiometry of thermal decomposition, and compared the obtained results with those published for complexes with other L(N) ligands.

EXPERIMENTAL

All compounds used for syntheses, *i.e.* $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$, AgNO_3 ,

KCN, and ammonia were of anal. grade. The aqueous solutions used in syntheses were of the following concentrations: $c(\text{SO}_4^{2-}) = 1 \text{ mol dm}^{-3}$, $c(\text{K}[\text{Ag}(\text{CN})_2]) = 0.5 \text{ mol dm}^{-3}$; ammonia was non-diluted. The syntheses were performed by addition of solutions of the M(II) salt and ammonia to the solution of $\text{K}[\text{Ag}(\text{CN})_2]$ so that the amount of substance ratio of M(II) and $[\text{Ag}(\text{CN})_2]^-$ was 1 : 2. Ammonia was added in 20 % excess. The precipitated complexes had according to elemental analysis the composition $M(\text{II})(\text{NH}_3)_2[\text{Ag}(\text{CN})_2]_2$, which is in agreement with [10]. We failed to prepare complexes with higher amount of the bound ligand even when using high excess of ammonia. Preparation of an analogous complex with zinc was not reproducible.

The infrared spectra both of the prepared complexes and intermediates of thermal decomposition were recorded with a spectrophotometer Specord M-80 (Zeiss, Jena) in the region of $\tilde{\nu} = 200\text{—}4000 \text{ cm}^{-1}$ in KBr pellets and nujol suspension. Electronic spectra of the prepared complexes were measured in solid state on a spectrophotometer Specord M-40 (Zeiss, Jena) in the region of $\tilde{\nu} = 11000\text{—}50000 \text{ cm}^{-1}$ using BaSO_4 as standard. Magnetic susceptibility was measured by the Faraday method at field intensities $H/(10^5 \text{ A m}^{-1})$: 4; 6; 8, using torsion balances with 10^{-6} g sensitivity. The temperature dependences were measured in the range of 77—293 K, using $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ as standard. Thermal measurements were performed with an OD 102 (MOM) Derivatograph in ceramic crucibles under dynamic conditions with the following parameters: sample mass 200 mg, TG 100, DTA and DTG 1/5, rate of heating $5 \text{ }^\circ\text{C min}^{-1}$, atmosphere was air, and the standard was aluminium(III) oxide. The intermediates of thermal decomposition were obtained by heating on the derivatograph and subsequent "freezing" or heating at constant temperature in an electric furnace. X-Ray diffraction measurements of the

products and intermediates of thermal decomposition were performed on a diffractometer Mikrometa 2 with goniometer (Chirana), using Ni-filtered radiation $\text{CuK}\alpha$ ($\lambda = 0.15418$ nm).

RESULTS AND DISCUSSION

The measured infrared spectra of the studied complexes proved the presence of cyano groups and a molecule of ammonia (Table 1). The sharp absorption bands observed in the region of $\tilde{\nu} =$

Table 1. Infrared Spectra of $\text{M}(\text{NH}_3)_2[\text{Ag}(\text{CN})_2]_2$ Complexes ($\tilde{\nu}/\text{cm}^{-1}$)

NiA	CuA	CdA	Assignment
3388	3352	3384	$\nu(\text{NH})$
3296	3276	3288	
3180	3180	3176	
2162	2168	2152	$\nu(\text{C}\equiv\text{N})$
2134	2136		
1604	1612	1604	$\delta_d(\text{NH})$
1192	1228	1164	$\delta_s(\text{NH})$
616	664	580	$\rho(\text{NH})$
380	374	350	$\nu(\text{Ag}-\text{C})$
325	330		$\nu(\text{M}-\text{N})$
260	270	270	$\delta(\text{M}-\text{N})$

2134—2168 cm^{-1} belong to stretching vibration $\nu(\text{C}\equiv\text{N})$. The ionic noncoordinated KCN displays this vibration at $\tilde{\nu} = 2080$ cm^{-1} [11]. AgCN and $\text{K}[\text{Ag}(\text{CN})_2]$ exhibit the same vibration at $\tilde{\nu} = 2164$ and 2140 cm^{-1} , respectively [12]. The value higher than 2080 cm^{-1} points to formation of the coordination bond $\text{Ag}-\text{CN}$, and the values higher than 2150 cm^{-1} indicate the formation of the bridge $\text{Ag}-\text{CN}-\text{M}$ and the polymeric nature of the structure. The existence of the $\text{Ag}-\text{C}$ bond was confirmed also by the bands at $\tilde{\nu} = 350$ — 400 cm^{-1} , belonging to $\nu(\text{Ag}-\text{C})$ vibration [13].

The presence of ammonia in the prepared complexes was proved by several absorption bands. The individual bands in the region $\tilde{\nu} = 3176$ — 3388 cm^{-1} were attributed to stretching vibration $\nu(\text{NH})$, those in the region $\tilde{\nu} = 1604$ — 1612 cm^{-1} to deformation vibrations $\delta_d(\text{NH})$, in the region $\tilde{\nu} = 1164$ — 1228 cm^{-1} to symmetrical $\delta_s(\text{NH})$ vibrations, and in the region $\tilde{\nu} = 580$ — 664 cm^{-1} to rocking $\rho(\text{NH})$ vibrations. The vibrations of coordinatively bound ammonia were least shifted against those of free ammonia to lower wavenumbers on account of the $\text{M}-\text{N}$ bond, which is connected with decreasing strength of the $\text{N}-\text{H}$ linkage. The greatest changes were observed in wavenumbers of the symmetrical deformation vibrations $\delta_s(\text{NH})$. They were shifted to higher values by 211 — 278 cm^{-1} and indicated a rather strong $\text{M}-\text{NH}_3$ bond.

The reflectance spectra of CuA and NiA complexes

in the visible region displayed absorption bands belonging to $d \rightarrow d$ transitions (Table 2). With the NiA complex ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$ and ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$ transi-

Table 2. Electronic Spectra of NiA and CuA Complexes

Complex	$\tilde{\nu}/\text{cm}^{-1}$ *	Assignment
NiA	— (10 750)	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$
	13 300 (13 500)	${}^3A_{2g}(\text{F}) \rightarrow {}^1E_g(\text{D})$
	17 440 (17 500)	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$
	28 000 (28 200)	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$
CuA	15 480	${}^2E_g(\text{D}) \rightarrow {}^2T_{2g}(\text{D})$

* The values presented in brackets belong to the $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ion [14].

tions were observed. The appearance of part of an absorption band the maximum of which was out of the range of the instrument might suggest the ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$ transition. The observed spectrum was similar to that of the complex ion $[\text{Ni}(\text{NH}_3)_6]^{2+}$ [14], which pointed to the presence of the NiN_6 chromophore. In the spectrum of the CuA complex only one wide absorption band was observed at $\tilde{\nu} = 15 480$ cm^{-1} , which corresponded to ${}^2E_g(\text{D}) \rightarrow {}^2T_{2g}(\text{D})$ transition. The spectra of both complexes are typical for octahedrally coordinated atoms of Ni and Cu, respectively [15, 16].

The magnetic susceptibilities of NiA and CuA were measured in the temperature range 77 — 293 K. The dependences of the molar magnetic susceptibility χ_m and of its reciprocal value on temperature are illustrated in Fig. 1. In both cases the temperature dependence is governed by the Curie law, according to which the Curie constant C for these complexes is 1.22 and 0.43 $\text{cm}^3 \text{K mol}^{-1}$, respectively.

The value of the magnetic moment of the NiA complex $\mu_{\text{eff}} = 3.12 \mu_B$ is higher than the spin value $\mu_s = 2.83 \mu_B$ for the high-spin electron configuration

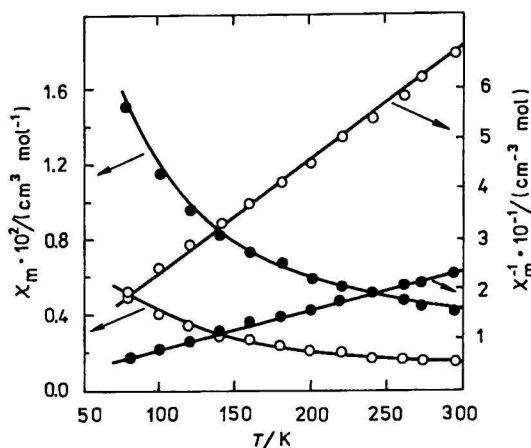


Fig. 1. Temperature dependence of molar magnetic susceptibility χ_m of NiA (●) and CuA (○) and its reciprocal value.

d^8 with the spin $S = 1$. From the μ_{eff} value it follows that the surroundings of the Ni atom are octahedral with the term of the basic state $^3A_{2g}$ [17]. For the CuA complex it follows that the electron configuration of Cu(II) has the spin $S = 1/2$, the value of the magnetic moment $\mu_{\text{eff}} = 1.85 \mu_B$ is close to the spin value $\mu_s = 1.73 \mu_B$, and the term of the basic state is 2E_g [17, 18]. Exchange interactions between paramagnetic atoms were not found. Direct metal—metal interactions between silver and other atoms were not confirmed either. The deviations from the spin value for both CuA and NiA complexes were due to spin-orbital interactions with $\lambda < 0$, and in the case of NiA also due to splitting in zero field at lower symmetry of the Ni atoms [19].

The results of the indirect methods of structural study suggest octahedral coordination of the central atom in the cation complex (chromophores MN_6) and bridge involvement of all cyano groups, the consequence of which is a polymeric nature of the structure. X-Ray powder diffraction patterns of the individual complexes show similarity in the region of lower diffraction angles, suggesting a similarity in structures of the studied complexes.

The curves of thermal decomposition TG, DTA, and DTG of NiA are illustrated in Fig. 2. The curves of CuA and CdA were analogous. The temperature intervals as well as the observed and calculated mass losses are presented in Table 3. In the first step of thermal decomposition of the NiA complex the mass loss Δm 4.5 % corresponded to the release of one ammonia molecule (calc. 4.13 %) and formation of the $Ni(NH_3)[Ag(CN)_2]_2$ intermediate. The diffraction pattern of this intermediate is similar to the original one, except for the peak intensities. In the next step of thermal decomposition the second ammonia molecule was liberated and the mass loss was 4.5 %. According to the diffraction pattern not the binary cyanide $Ni[Ag(CN)_2]_2$ but a mixture of

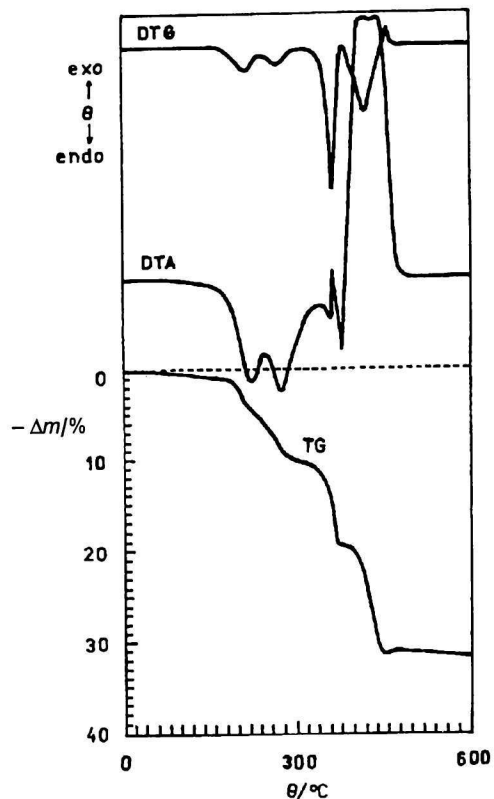


Fig. 2. Thermal decomposition of the $Ni(NH_3)_2[Ag(CN)_2]_2$ complex.

$Ni(CN)_2$ and $AgCN$ was formed. Both processes of liberation of ammonia were endothermic. In the third step of thermal decomposition an exothermic decomposition of cyanides took place under release of 1.5 mol of cyanogen. The mass loss was 9.5 % (calc. 9.46 %). According to the diffraction pattern, the intermediate contained $Ni(CN)_2$, $AgCN$, and Ag . In the fourth step the cyanides were decomposed to NiO and Ag .

The first step of thermal decomposition of CuA was an endothermic process wherein a nonstoichio-

Table 3. Data of Thermal Decomposition of Complexes

Complex	$\theta/^\circ C$	Effect	$-\Delta m(\text{found})$ %	$-\Delta m(\text{calc.})$ %	Composition of the product
NiA	165–238	endo	4.5	4.13	$Ni(NH_3)[Ag(CN)_2]_2$
	238–304	endo	4.5	4.13	$Ni(CN)_2 + 2 AgCN$
	310–370	exo	9.5	9.46	$Ni(CN)_2 + 0.5 AgCN + 1.5 Ag$
	380–448	exo	12.5	11.89	$NiO + 2 Ag$
			31.0	29.61	
CuA	102–115	endo	2.0	2.04	$Cu(NH_3)_{1.5}[Ag(CN)_2]_2$
	115–202	endo	6.25	6.12	$Cu[Ag(CN)_2]_2$
	202–280	exo	3.35	3.12	$(0.5 Cu[Cu(CN)_2] + 2 AgCN)$
	280–375	exo	6.0	6.23	$CuCN + 0.5 AgCN + 1.5 Ag$
	375–465	exo	13.5	13.18	$CuO + 2 Ag$
			31.10	30.69	
CdA	95–185	endo	7.5	7.31	$Cd[Ag(CN)_2]_2$
	185–370	exo	5.5	5.58	$Cd(CN)_2 + AgCN + Ag$
	370–460	exo	14.5	13.32	$CdO + 2 Ag$
			27.5	26.21	

metric amount of ammonia, corresponding to 0.5 mol of NH_3 , was released. This process was followed by an immediate liberation of another ammonia molecule. We failed to isolate the intermediate corresponding to 0.5 mol of NH_3 even by slow heating to lower temperature (80—90 °C). The intermediate was probably metastable, wherein the individual positions of the NH_3 ligand were occupied statistically in the coordination polyhedron of the Cu atom. Such a phenomenon was observed with the $\text{Cu}(\text{NH}_3)_3\text{Cu}_2(\text{CN})_4$ complex, where the ammonia molecules statistically occupy four positions. In the case of full occupation its composition would correspond to the formula $\text{Cu}(\text{NH}_3)_4\text{Cu}_2(\text{CN})_4$ [20]. After liberation of ammonia the decomposition proceeded by nonstoichiometric release of cyanogen at simultaneous reduction of Cu(II) to Cu(I). In further exothermic process the cyanides were decomposed under temporary formation of CuCN and AgCN. The final product of thermal decomposition was a mixture of CuO and Ag.

In the first step of thermal decomposition of the CdA complex both molecules of ammonia were liberated and the intermediate $\text{Cd}[\text{Ag}(\text{CN})_2]_2$ was isolated. According to the diffraction pattern this compound was identical with independently prepared binary cyanide. In further processes the exothermic decomposition of cyanides took place. The final product of thermal decomposition was a mixture of CdO and Ag.

On the basis of comparison of the initial temperatures of thermal decomposition and rate of release of ammonia it may be concluded that the thermal stability of the investigated complexes increases in the order CuA, CdA, and NiA. For the complexes of composition $\text{M}(\text{NH}_3)_3\text{Cu}_2(\text{CN})_4$ (M = Ni, Cu, Zn, Cd) the following increase of stability was published [6]: Zn (30 °C), Cd (50 °C), Ni (110 °C), Cu (120 °C). When considering the fact that the $\text{Cu}(\text{NH}_3)_3\text{Cu}_2(\text{CN})_4$ complex contains by one NH_3 molecule less and corresponds to the $\text{Cu}(\text{NH}_3)_4\text{Cu}_2(\text{CN})_4$ complex at full occupation of four coordination positions by ammonia molecules, we obtain the same order, because at room temperature the tetraamino complex is not stable [1].

Recently a light-violet compound of composition $[\text{Ag}(\text{NH}_3)]_2\text{Ni}(\text{CN})_4 \cdot 0.1\text{C}_6\text{H}_6$ has been described [21]. Its formula is, except for the content of $0.1\text{C}_6\text{H}_6$, the same as that of the NiA complex and so is its ther-

mal decomposition. On the other hand, it is known that the presence of the $[\text{Ni}(\text{CN})_4]^{2-}$ anion generates a yellow to orange colour, not a light-violet one (the $[\text{Ag}(\text{NH}_3)]^+$ ion does not absorb in the visible region of the spectrum). We assume an exchange of the positions of Ni and Ag atoms due to higher affinity of silver to cyano groups bound *via* carbon atom, giving rise to the compound $\text{Ni}(\text{NH}_3)_2[\text{Ag}(\text{CN})_2]_2 \cdot 0.1\text{C}_6\text{H}_6$. Similar conclusions resulted also from the work [10].

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Translated by A. Kardošová