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THERMAL DECOMPOSITION OF CYANO COMPLEXES OF THE TYPE $M(NH_3)_3Ni(CN)_4$ (M = Cu, Zn, Cd)

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Three complex compounds with the compositions $Cu(NH_3)_3Ni(CN)_4$ (CuA), $Zn(NH_3)_3Ni(CN)_4$ (ZnA), and $Cd(NH_3)_3Ni(CN)_4$ (CdA) were prepared and identified. Their structures were examined by the methods of infrared spectroscopy and X-ray powder diffraction and compared with one another. The thermal stabilities and stoichiometries of thermal decomposition were investigated with a derivatograph. It follows from the results that the thermal stability increases in the sequence CuA < ZnA < CdA.

During studies relating to the preparation and crystallochemistry of tetracyanonickelates(II), which crystallize from the systems M-ethylenediamine (en)—H_2O—$[Ni(CN)_4]^{2-}$ or NH_3—H_2O—$[Ni(CN)_4]^{2-}$ (M = Ni, Cu, Zn, Cd), we have also investigated their thermal properties. In a previous paper, we described the crystal structures and thermal properties of the complexes with composition $M(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$ (M = Ni, Cd), which crystallized at low molar ratios $M : NH_3$ from the above systems containing NH_4NO_3 [1]. If the molar ratio $M : NH_3$ in these systems is raised, the coordination compounds $M(NH_3)_3Ni(CN)_4$ (M = Cu, Zn, Cd) are formed. The preparation, identification and thermal properties of these coordination compounds are described in this paper.

Experimental

The syntheses were carried out with the use of the following chemicals: $Ni(NO_3)_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, $CdSO_4 \cdot 8/3H_2O$, KCN and NH_3 (25%). All chemicals were analytical grade reagents of Czechoslovak production. All these chemicals were used for the preparation of 1 M stock solutions except KCN. The KCN stock solution was 2 M.

Precipitates of $MNi(CN)_4$ were obtained by mixing solutions of $Ni(NO_3)_2$, KCN

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and MSO_4 (M = Cu, Zn, Cd) in a molar ratio of 1 : 4 : 1. After decantation, each suspension was dissolved in 60 ml of dilute ammonia (1 : 1), and the solution was allowed to stand. Subsequently, crystals or a microcrystalline powder separated out from the solution. These products were filtered off and washed successively with a dilute solution of ammonia, ethanol and ether.

Methods of measurement

Elemental analysis

The metal contents were determined gravimetrically and complexometrically. Carbon, hydrogen and nitrogen were determined with a CHN analyser (Hewlett–Packard).

Infrared spectra

The infrared spectra of the prepared complexes and of the intermediates of their thermal decompositions were recorded with a Specord 75–IR spectrophotometer in the range 4000–400 cm^{-1}, by using the KBr technique.

Thermal measurements

The thermal decompositions were investigated under dynamic conditions with an OD 102 derivatograph (MOM, Budapest). Ceramic crucibles and a Pt/Pt–Rh thermocouple were used. The measurements were performed under the following conditions: weighed amount 100 mg, rate of heating 6 deg/min, air atmosphere.

X-ray powder diffraction

The X-ray powder diffraction patterns were taken with a Mikrometa II instrument equipped with a GON 3 goniometer (Chirana). CuK_α radiation ($\lambda = 1.54178 \times 10^{-10}$ m) was used for these measurements.

Results and discussion

The analytical results presented in Table 1 show that the compositions of the prepared complexes were: $Cu(NH_3)_3Ni(CN)_4$ (CuA), $Zn(NH_3)_3Ni(CN)_4$ (ZnA) and $Cd(NH_3)_3Ni(CN)_4$ (CdA). Our attempts to prepare a complex of analogous composition with Ni failed, but the complex $Ni(NH_3)_2Ni(CN)_4 \cdot 0.5H_2O$ was isolated under identical conditions of synthesis. If concentrated solutions of

Table 1 Results of analyses

Complex	Colour	Ni %		M %		C %		H %		N %	
		calc.	found.	calc.	found.	calc.	found.	calc.	found.	calc.	found.
CuA	blue	21.16	20.86	22.90	23.21	17.32	17.20	3.27	3.49	35.34	34.90
ZnA	yellow	21.02	20.92	23.41	24.13	17.20	17.51	3.25	2.94	35.11	34.32
CdA	yellow	17.99	17.63	34.45	34.18	14.73	13.81	2.78	2.75	30.05	29.86

ammonia were used for the syntheses instead of dilute solutions, the unstable hexammine and tetrammine complexes described in [2] separated out from the systems.

The measured infrared spectra indicate the presence of cyano groups and ammonia molecules in the prepared complexes. The wavenumbers of the absorption bands and the assignments proposed on the basis of [3, 4] are given in Table 2.

There are six absorption bands in the region 2100–2200 cm^{-1} in the infrared spectrum of CuA, which may be explained by the presence of eight different and crystallographically non-equivalent cyano groups in the molecular structure of this compound [5]. The existence of five absorption bands in the infrared spectrum of CdA indicates the similarity between the structures of CdA and CuA. For ZnA, only two strong absorption bands are to be observed in this region, the first of which occurs at 2125 cm^{-1} and may be assigned to the stretching CN vibration of the terminal cyano group, while the second one, at 2158 cm^{-1}, corresponds to the stretching CN vibration of the bridged cyano group.

The coordination of ammonia to the central *M* atom is confirmed by the shifts in the absorption bands of the ν(NH) type towards lower wavenumbers and of the δ_s(NH) type towards higher wavenumbers as compared to those for free ammonia [4].

Thermal decomposition

The thermal decomposition curves (TG, DTG and DTA) of CuA, ZnA and CdA are presented in Figs 1–3. The temperature intervals and the observed and calculated mass loss values are given in Table 3.

As a 3% mass loss was measured in the first step in the thermal decomposition of CuA, and no significant difference between CuA and the first intermediate was observed in either the infrared spectrum or the X-ray powder pattern, the first step in the thermal decomposition may be interpreted as a non-stoichiometric liberation of ammonia from the coordination polyhedra of the copper ions. A similar

Table 2 Assignment of absorption bands in the infrared spectra

Assignment	Complex		
	CuA	ZnA	CdA
ν(NH)	3357m	3330s	3364m
	3268m	3265s	3255m
	3178m	3218m	3164w
		3178m	
ν(CN)	2159m	2158s	2169m
	2141w	2150vw	2153msh
	2132m	2125s	2146s
	2124msh		2137s
	2119s		2126s
	2113s		
δ_d(NH)	1610m	1618m	1595m
δ_s(NH)	1277m	1293m	1257m
	1258s	1248s	1208s
	1247s		1190s
ϱ(NH)	787m	710s	640m
		665m	
ν(Ni—C)	539vw	553vw	567m
ν(M—N)	489vw	476m	
π(Ni—CN)	447w	458m	
δ(Ni—CN)	419m	418m	421m

s = strong, m = medium, w = weak, vw = very weak, sh = shoulder

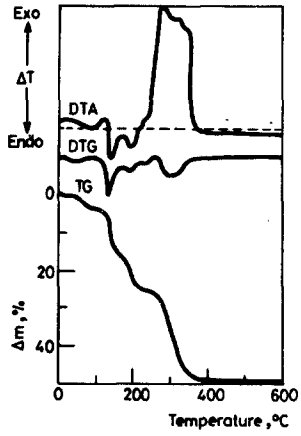

Fig. 1 Thermal curves of $Cu(NH_3)_3Ni(CN)_4$

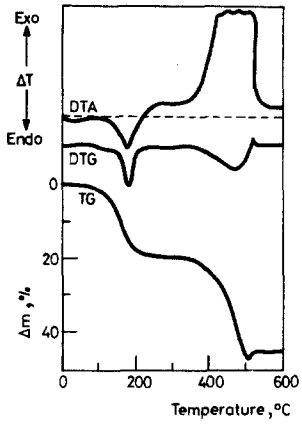

Fig. 2 Thermal curves of $Zn(NH_3)_3Ni(CN)_4$

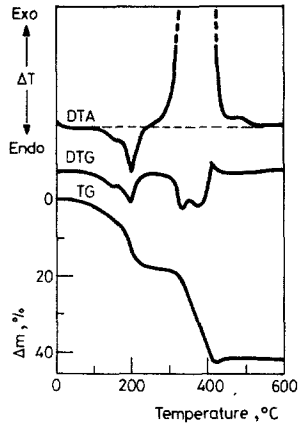

Fig. 3 Thermal curves of $Cd(NH_3)_3Ni(CN)_4$

Table 3 Data concerning thermal decomposition of the prepared complexes

Complex	Range of TG, °C	Weight loss %		Composition of the product
		obs.	calc.	
CuA	25–110 (endo)	3.0	3.1	$Cu(NH_3)_{2.5}Ni(CN)_4$
	125–240 (endo)	12.0	24.7	$Ni(CN)_2 + CuCN$
	(endo)	11.0		
	240–345 (exo)	23.5	22.4	$NiO + CuO$
		49.5	50.2	
ZnA	45–190 (endo)	19.0	18.3	$ZnNi(CN)_4$
	340–520 (exo)	26.0	25.9	$ZnO + NiO$
		45.0	44.2	
CdA	60–205 (endo)	17.0	15.6	$CdNi(CN)_4$
	275–410 (exo)	26.0	27.0	$(Ni + Cd)O$
		43.0	42.6	

statistical occupation of individual coordination positions around the Cu(II) ions was found for the complex $Cu_3(NH_3)_3(CN)_4$, the composition of which would correspond to $Cu_3(NH_3)_4(CN)_4$ [6] if all the coordination positions were occupied by molecules of ammonia. The second and third steps in the thermal decomposition are associated with each other and it is not possible to isolate an intermediate after the second step in the thermal decomposition. Simultaneously, Cu(II) is reduced to Cu(I) and dicyanogen is released. The final products were identified as a mixture of CuO and NiO.

The thermal decompositions of ZnA and CdA are analogous. The total ammonia content is liberated during the first step in the thermal decomposition. The only difference consists in the fact that the DTA and DTG curves suggest a two-step process for CdA. In both cases, we may isolate the intermediates $MNi(CN)_4$. The second step in the thermal decomposition involves the decomposition of cyanides and oxidation of the metal by atmospheric oxygen.

If we compare the thermal stabilities of CuA, ZnA and CdA on the basis of the initial temperatures of decomposition, we obtain the following sequence of increasing thermal stability: CuA < ZnA < CdA. For the complexes $M(NH_3)_3Cu_2(CN)_4$ (M = Cu, Zn, Cd), the following stability sequence was reported [7]: Zn (30°), Cd (50°) and Cu (120°). However, if we take into account that the complex $Cu(NH_3)_3Cu_2(CN)_4$ is short of one molecule of NH_3 and corresponds to $Cu(NH_3)_4Cu_2(CN)_4$ at full occupation of all the coordination positions, we obtain an equal sequence, because the tetramine complex is not stable at laboratory temperature [8].

The results obtained by means of X-ray powder diffraction have shown that the complexes are not isomorphous and exhibit low symmetry.

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Zusammenfassung — Drei Komplexverbindungen der Zusammensetzung $Cu(NH_3)_3Ni(CN)_4$ (CuA), $Zn(NH_3)_3Ni(CN)_4$ (ZnA) und $Cd(NH_3)_3Ni(CN)_4$ (CdA) wurden dargestellt und identifiziert. Die Strukturen der Verbindungen wurde infrarotspektroskopisch und röntgendiffraktometrisch untersucht und miteinander verglichen. Die thermische Stabilität und die Stöchiometrie der thermischen Zersetzung wurden mittels eines Derivatographen untersucht. Die thermische Stabilität nimmt in der Reihenfolge CuA < ZnA < CdA zu.

Резюме — Получены и идентифицированы три комплекса состава $Cu(NH_3)_3Ni(CN)_4$ (CuA), $Zn(NH_3)_3Ni(CN)_4$ (ZnA) и $Cd(NH_3)_3Ni(CN)_4$ (CdA). Структура комплексов была изучена методом ИК спектроскопии и порошковой рентгенографии, а полученные при этом данные сопоставлены друг с другом. С помощью дериватографа исследована термоустойчивость и стехиометрия термического разложения всех трех соединений. Установлено, что термоустойчивость увеличивается в ряду CuA < ZnA < CdA.