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PREPARATION AND SOME PROPERTIES OF TETRACYANO COMPLEXES M(en)M'(CN)$_4$ (*M* = Cd(II), Mn(II); *M'* = Ni(II), Cd(II))

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Abstract

Two new tetracyano complexes of the composition MnenNi(CN)$_4$ and MnenCd(CN)$_4$ were prepared and identified. Their structure and properties were investigated by IR and UV-VIS spectroscopy, X-ray powder diffraction and by measuring magnetic moments. The results were confronted with the structure and properties of the compounds CdenNi(CN)$_4$ and CdenCd(CN)$_4$. The results of this study show a considerable similarity between these groups of compounds. The thermal behaviour of all the examined compounds was investigated derivatographically. The following order of thermal stability of the investigated complexes was observed:

$$\text{Cd–Cd}(215^\circ\text{C}) < \text{Mn–Cd}(250^\circ\text{C}) < \text{Cd–Ni}(275^\circ\text{C}) < \text{Mn–Ni}(310^\circ\text{C})$$

Keywords: tetracyano complexes, thermal stability

Introduction

Studies on the crystal structure of the complexes CdenNi(CN)$_4$(Cd–Ni) [1] and CdenCd(CN)$_4$ (Cd–Cd) [2] have shown that all four cyano groups of the square-planar anion [Ni(CN)$_4$]$^{2-}$ form bridges and are bonded through nitrogen atoms to different cadmium atoms. The chelate-bonded molecule of ethyle-

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nediamine (en) completes the coordination of the Cd(II) atom in the complex cation to pseudooctahedral form. Two other complexes containing one molecule of en, namely $ZnenNi(CN)_4$ [3] and $NienNi(CN)_4 \cdot 2H_2O$ [4] have also been described in the literature. The compound $ZnenNi(CN)_4$ exhibits analogous structure as the compound $CdenNi(CN)_4$. The aim of the present work has been to prepare, identify and determine the thermal as well as some other properties of tetracyano complexes with the formula MnenNi(CN)4(Mn–Ni) and $CdenCd(CN)_4$(Cd–Cd). The compounds of this type have not yet been described in the literature. However, the structure of a similar compound $Mn(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$, where en is replaced by ammonia, is known [5].

Experimental

Synthesis

The complexes (Mn–Ni) and (Mn–Cd) were prepared by mixing 10 ml of 1 mol/l solution of $MnCl_2$ with freshly distilled ethylenediamine and with 10 ml of the solution of $K_2[Ni(CN)_4]$ or $K_2[Cd(CN)_4]$. The molar ration of mixing was 1:4:1. The solution of $MnCl_2$ contained 5% of ascorbic acid for hindering the oxidation of manganese. The reaction took place in nitrogen atmosphere. The separated fine-crystalline products were quickly sucked, washed with 5% solution of ascorbic acid, ethanol and ether. The products obtained were stable and did not show any symptoms of decomposition of Mn(II) oxidation in the course of time. The formation of the complexes can be expressed by the following equation:

$$[Mn(en)_3]^{2+} + [M'(CN)_4]^{2-} \xrightarrow{N_2} MnenM'(CN)_4 + 2en$$

where M' = Cd(II) or Ni(II).

The investigated complexes Cd–Ni and Cd–Cd were prepared according to the literature [1, 2].

Elemental analysis

The metals were determined polarographically while carbon, hydrogen and nitrogen were determined on a Hewlett-Packard 185 CHN analyser.

Spectral measurements

The infrared spectra of the investigated complexes were taken on a SPECORD M-80 instrument (KBr technique) in the region 4000–200 cm^{-1}. The UV-VIS reflectance spectra were measured on a SPECORD M-40 spectrophotometer in the region 50000–11000 cm^{-1} using $BaSO_4$ as reference material.

Magnetic measurements

The values of magnetic susceptibilities were obtained by the Faraday method. The experimental values were corrected with respect to diamagnetism according to [6].

Thermal measurements

The thermal measurements were performed with a derivatograph OD-102 in static air atmosphere and in ceramic crucibles under analogous experimental conditions. Sample weight: 100 mg, heating rate: 6 $deg \cdot min^{-1}$.

X-ray powder diffraction

The X-ray diffraction records were taken on MIKROMETA II istrument equipped with GON 3 goniometer using FeK_α radiation.

Results and discussion

It results from Table 1 that the substances prepared were sufficiently pure and suitable for studying. The infrared spectra also confirm the supposed composition of the investigated compounds. The assignment of absorption bands to individual vibrations is consistent with literature data [7, 8]. A list of the observed vibrations is given in Table 2.

Absorption bands of the type ν(C–C) and ν(C–N) appear in the region 1100–950 cm^{-1}. The chelate bonding of ethylenediamine is confirmed by the presence of the band δ(NCCN) in the region 480–450 cm^{-1}. This chelate bonding has been evidenced by elucidating the structure of the Cd–Ni and Cd–Cd complexes. The strong absorption bands ν(C≡N) in the region 2170–2150 cm^{-1} are characteristic of the investigated complexes. Their shift to

Table 1 Results of analyses

Compound	% C		% H		% N		% Mn		% M'	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
Mn enNi(CN)$_4$	25.19	25.94	3.31	2.90	30.21	30.25	18.70	19.77	21.20	21.12
Mnen Cd(CN)$_4$	21.69	21.73	2.35	2.43	26.34	25.35	16.58	15.60	34.10	33.94

Table 2 Infrared spectra

Vibrations	Complex			
	Cd–Ni	Mn–Ni	Cd–Cd	Mn–Cd
ν (NH)	3372 s	3364 s	3372 s	3368 s
	3312 s	3304 s	3312 s	3308 s
ν (CH_2)	2976 m	2980 m	2052 m	2956 m
	2920 m	2924 m	2892 m	2896 m
	2876 m	2880 m	2962 m	2965 m
			2972 m	2975 m
ν (CN)	2152 vs	2148 vs	2168 s	2168 s
	2144 vs	2140 vs		
δ (NH_2)	1592 s	1588 s	1598 s	1598 s
			1586 s	1580 s
			1576 s	
δ (CH_2)	1452 m	1456 m	1460 m	1464 m
ρ(NH_2)	558 s	584 s	572 s	574 s
δ (NCCN)	466 s	468 s	444 s	468 s
			458 sh-m	456 sh-m
δ (Ni–CN)	428 s	430 vs		
ν (Cd–C)			345 s	370 s
			360 s	

v–very; s–strong; m–medium; sh–shoulder

higher values with respect to the values measured for the free anion indicates a bridging. The simultaneous fine splitting of the ν(C≡N) band observed in the case of the Mn–Ni and Cd–Ni complexes may be due to a reduced site symmetry of the $[Ni(CN)_4]^{2-}$ anion in the solid state.

The values of magnetic moments of Mn–Ni and Mn–Cd complexes approach the spin value observed for the high-spin MnN_6 complexes and are in agreement with the assumed pseudooctahedral coordination of the atoms of manganese.

The values given in Table 3 indicate that the cyanide groups are bound through nitrogen atoms to manganese atoms. The fundamental state of a manganese atom in this configuration is the state $^6A_{1g}$. All electron transitions are spin-forbidden (Table 3) and thus the corresponding intensities of transitions are low. The electron reflectance spectra also indicate the coordination of the Mn(II) like in the chromophore MnN_6. The lower number of bands as well as the energy values indicate that the coordination of the Cd(II) atom is tetrahedral while the coordination of the Ni(II) atom is square-planar owing to which the corresponding chromophores CdC_4 and NiC_4 arise.

Table 3 UV–VIS reflectance spectra and magnetic moments

	Complex	
	Mn – Ni	Mn – Cd
$^6A_{1g} \rightarrow {}^4T_{1g}$	16280	16040
$^6A_{1g} \rightarrow {}^4T_{2g}$	21000	21000
$^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g$ (G)	23800	24040
$^6A_{1g} \rightarrow {}^4T_{2g}$ (D)	28800 sh	
$^1A_1 \rightarrow {}^1A_{2u}, {}^3E_u$ (π)CT	34300	34000
$^1A_1 \rightarrow {}^1E_u, {}^3E_u$ (π)CT	35080	
$^1A_1 \rightarrow {}^1A_{2u}d \rightarrow \pi^*$	36400	37300
$^1A_1 \rightarrow {}^1A_{2u}\ \pi \rightarrow \pi^*$ C≡N	38300	45040
μ_{eff} [B. M.]	5.61	5.71

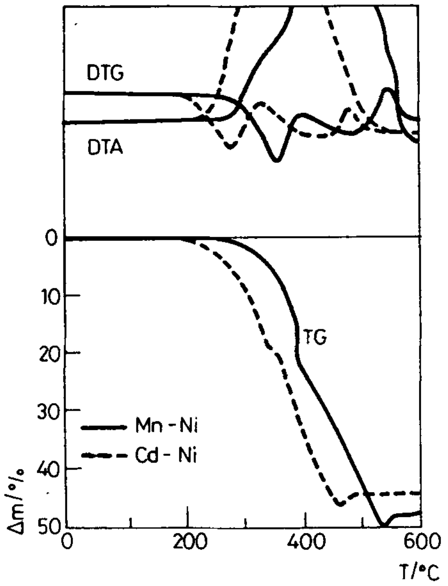

Fig. 1 Thermal curves of the complexes Mn–Ni and Cd–Ni

The courses of thermal decomposition of the investigated compounds are represented in Figs 1 and 2. It results from these figures that the thermal de-

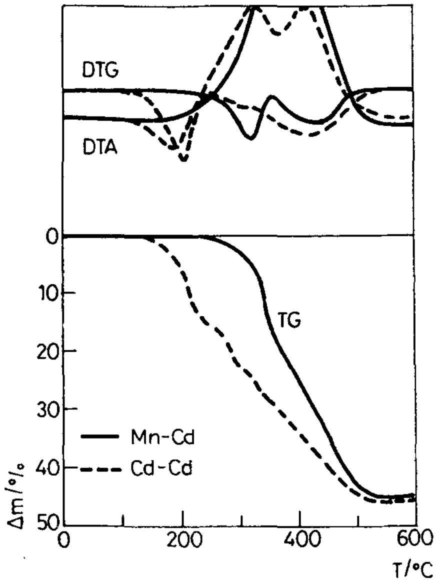

Fig. 2 Thermal curves of the complexes Mn–Cd and Cd–Cd

compositions of these compounds exhibit a two-step character and are poorly distiguishable except the one of the Cd–Cd compound. The first step of decomposition may be interpreted as the exothermal liberation of ethylenediamine, except for the Cd–Cd compound because the liberation of en from this compound is an endothermal process. The liberation is followed by a complicated exothermal decomposition of cyanides. On the basis of the observed mass loss, infrared spectra and X-ray records of the intermediates arising after liberation of en we can assume the formation of cyanide $Cd(CN)_2$ or binary cyanides $CdNi(CN)_4$, $MnCd(CN)_4$ and $MnNi(CN)_4$. The final products of decomposition were identified by X-ray powder diffraction as oxides of the corresponding metals. We can observe the formation of CdO (calc.66%, found 65.5%) from the compound Cd–Cd, CdO + Mn_3O_4-hausmanit (calc.60.5%, found 61.7%) from Mn–Cd, CdO+NiO (calc.60.6%, found 60.5%) from Cd–Ni, and NiO+$NiMn_2O_4$ (calc.58.2%, found 56.0%) from Mn–Ni.

If we compare the initial temperatures of decomposition of the individual compounds with each other, we obtain the following order of thermal stability of the investigated complexes

Cd–Cd(215°C) < Mn–Cd(250°C) < Cd–Ni(275°C) < Mn–Ni(310°C)

This order shows a higher thermal stability of tetracyanonickelates when compared with tetracyanocadmates. At the same time, these temperatures show the higher thermal stability of the complexes containing manganese with respect to the complexes containing cadmium in the complex cation. This fact is consistent with the values of the formation constants of cadmium(II) and manganese(II) complexes [7]. The relatively high thermal stability of the investigated complexes may be due to their three-dimensional cross-linked crystal structure.

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Zusammenfassung — Zwei neue Tetracyanokomplexe der Zusammensetzung $MnenNi(CN)_4$ und $MnenCd(CN)_4$ wurden hergestellt und identifiziert. Ihre Struktur und Eigenschaften wurden mittels IR und UV-VIS-Spektroskopie, der Debye-Scherrer -Methode und durch Messung des magnetischen Moments untersucht. Die Ergebnisse wurden der Struktur und den Eigenschaften der Verbindungen $CdenNi(CN)_4$ und $CdenCd(CN)_4$ gegenübergestellt. Die Resultate dieser Untersuchung zeigen eine erhebliche Ähnlichkeit zwischen diesen Ver- bindungsgruppen. Das thermische Verhalten aller untersuchten Verbindungen erfolgte derivatografisch. Für die untersuchten Komplexe wurde folgende Stabilitätsreihenfolge ermittelt:

$$\text{Cd-Cd}(215^\circ\text{C}) < \text{Mn-Cd}(250^\circ\text{C}) < \text{Cd-Ni}(275^\circ\text{C}) < \text{Mn-Ni}(310^\circ\text{C})$$