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THERMAL PROPERTIES OF BIS- AND TRIS-PHENANTHROLINE METAL COMPLEXES WITH DICYANOARGENTATE

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Ten new complex compounds of general formula $[M(Phen)_x][Ag(CN)_2]\cdot nH_2O$ (M = Fe, Mn, Ni, Cu, Zn and Cd; $x=2$ or 3; $n=1$, 2, or 3) were prepared and studied by TG–DTA. A comparison of the thermal stabilities of these compounds showed that the complexes containing three molecules of phenanthroline exhibit lower thermal stability that the corresponding complexes containing two molecules of phenanthroline.

The mild reduction of copper(II) compounds with the cyanides of alkali metals in the presence of neutral ligands containing nitrogen atoms as donor atoms gives rise to copper(I)–copper(II) cyano complexes belonging in the class of compounds with mixed central atoms [1]. If the ligand was ammonia or ethylenediamine, complexes of composition $Cu_3(NH_3)_3(CN)_4$, $Cu_5(NH_3)_4(CN)_6$, $Cu_3(H_2O)(en)_2(CN)_4$, $Cu_4(H_2O)(en)_2(CN)_6$ and $Cu_5(en)_2(CN)_6$ crystallized from the systems [2]. In a further study, we prepared the cyano complexes derived from the first and third of these compounds by replacing Cu(II) by other central atoms in the same oxidation state, i.e. by Co, Ni, Zn and Cd. The results indicated that these complexes contain polymeric anionic formations $[Cu_2(CN)_4]^{-2}$ and cations which may be either isolated, e.g. $[M(H_2O)(en)_2]^{2+}$ and $[M(en)_2]^{2+}$, or built up in polymeric units, as in the compound $Cu_3(NH_3)_3(CN)_4$ [3–5]. The π-electron density of the cyano groups frequently plays an important part in this coordination. From this aspect, it was of interest to prepare cyano complexes by replacing Cu(I) in these complexes by Ag(I) and, in view of its position in the periodic system, to investigate how the exchange of the central atom influences the thermal stability, stoichiometry of thermal decomposition and structure of the complexes.

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Experimental

For preparation of the individual complex compounds, a solution of the sulphate of the corresponding cation (1 mol dm^{-3}) saturated phenanthroline solution and a 0.4 mol dm^{-3} solution of $K[Ag(CN)_2]$ were used. When these solutions were mixed in appropriate molar ratios, the individual complexes separated out from the system. They were filtered off, washed, and dried in air. Some complexes were prepared by the substitution method, using ammine complexes as intermediates.

Measuring methods: The content of silver was determined by precipitation titration, while other metals were determined complexometrically. The contents of C, H and N were estimated microanalytically, by using Hewlett–Packard 185 CHN analyzer.

The infrared spectra were recorded in the region 4000–400 cm^{-1}, by using samples in the solid state (KBr tablets).

The thermal stability and stoichiometry of thermal decomposition were investigated with a MOM OD–102 derivatograph. The thermal measurements were carried out under dynamic conditions. Thus, the TG, DTG and DTA records were obtained in air atmosphere at temperature up to 900°, the rate of heating being 6 or 9 deg min^{-1}. The measurements were made in ceramic crucibles, and Al_2O_3 was used as reference material for DTA.

The gaseous products of thermal decomposition were investigated by gas chromatograph with a CHROM 5 instrument (Laboratory Instruments, ČSSR).

Results and discussion

On the basis of the composition, thermal properties and infrared spectra, the prepared compounds may be divided into two classes:

A)	$[Ni(phen)_3][Ag(CN_2)]_2 \cdot H_2O$	($Ni\text{-}phen_3$)
	$[Zn(phen)_3][Ag(CN)_2]_2 \cdot 3H_2O$	($Zn\text{-}phen_3$)
	$[Fe(phen)_3][Ag(CN)_2]_2 \cdot 2H_2O$	($Fe\text{-}phen_3$)
	$[Mn(phen)_3][Ag(CN)_2]_2 \cdot 3H_2O$	($Mn\text{-}phen_3$)
	$[Cd(phen)_3][Ag(CN)_2]_2 \cdot 3H_2O$	($Cd\text{-}phen_3$)
B)	$[Ni(phen)_2][Ag(CN)_2]_2 \cdot H_2O$	($Ni\text{-}phen_2$)
	$[Zn(phen)_2][Ag(CN)_2]_2 \cdot H_2O$	($Zn\text{-}phen_2$)
	$[Cu(phen)_2][Ag(CN)_2]_2 \cdot H_2O$	($Cu\text{-}phen_2$)
	$Mn(phen)_2][Ag(CN)_2]_2 \cdot 2H_2O$	($Mn\text{-}phen_2$)
	$[Cd(phen)_2][Ag(CN)_2]_2 \cdot H_2O$	($Cd\text{-}phen_2$)

The ligands present in the prepared compounds were identified by infrared spectroscopy.

The presence of the cyano groups gives rise to sharp absorption bands in the region 2170–2120 cm^{-1}, corresponding to the stretching vibration ν_{CN}. As concerns the cyano complexes of class A, only one absorption band was observed, which was consistent with the assumption of their ionic structure. On the other hand, two absorption bands ν_{CN} appeared in the spectra of the cyano complexes of class B. These facts suggest that some cyano groups must form bridges. The absorption bands of phenanthroline were assigned according to literature data [6, 7].

It is characteristic of both classes of cyano complexes that they are dehydrates in the first stage of thermal decomposition. The pertinent temperatures are given in Table 1.

Table 1 Data concerning decomposition of the prepared compounds

Compound \ Temperature range °C	Dehydratation, °C	Phase trans., °C	1st liber. of $(CN)_2$, °C	Total decomp., °C	ν_{CN}
Ni-$phen_3$	100–140	—	270–320	380–750	2130
Mn-$phen_3$	100–140	280–320	320–360	410–900	2120
Fe-$phen_3$	70–115	—	300–380	380–740	2075
Zn-$phen_3$	60–150	255–280	280–380	380–900	2145
Cd-$phen_3$	70–110	140–180 240–290	290–360	360–900	2156
Ni-$phen_2$	60–110	185–220	290–345	345–560	2150, 2132
Mn-$phen_2$	70–130	250–300	300–360	360–720	2160, 2140
Cu-$phen_2$	70–130	—	150–270	270–580	2175, 2160
Zn-$phen_2$	90–160	250–290	350–425	425–610	2160, 2140
Cd-$phen_2$	80–110	250–300	320–410	450–780	2160, 2145

Further heating produced small exothermic alterations without mass change, which corresponded to phase transformations.

In the subsequent stage of thermal decomposition, the exothermic release of dicyanogen from the dehydrated complex could be observed. The escape of dicyanogen was proved by gas chromatography. It is characteristic of this stage that the exothermic change in the DTA record, corresponding to the first liberation of dicyanogen from the complexes of class A with three molecules of phenanthroline, is shifted and separated from the large exothermic change corresponding to the total thermal decomposition. The relevant temperatures are given in Table 1, and the changes are illustrated for some representatives of these classes in Figs 1 and 2.

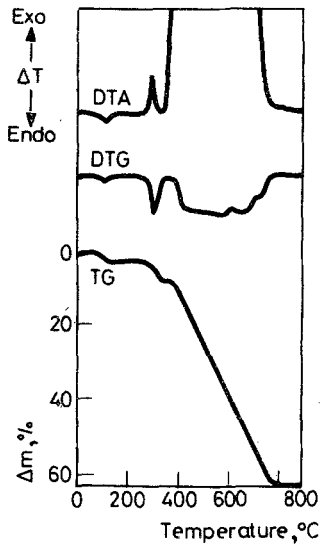

Fig. 1 Thermal curves of $[Ni(phen)_3][Ag(CN)_2]_2 \cdot H_2O$

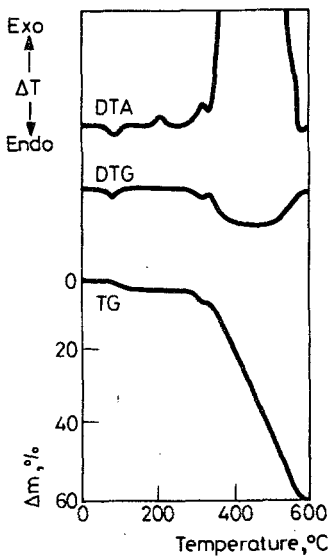

Fig. 2 Thermal curves of $[Ni(phen)_2][Ag(CN)_2]_2 \cdot H_2O$

Conclusion

The thermal stabilities of cyano complexes with different central atoms and different numbers of ligands in the complex cation depend not only on the character of the central atom, but also on the properties of the ligands. A comparison of the thermal stabilities of these compounds demonstrates that the complexes involving three molecules of phenanthroline have lower initial temperature of decomposition than the compounds containing two molecules of phenanthroline. The lowest initial temperature of decomposition was observed for the compound $[Cu(phen)_2][Ag(CN)_2]_2$, which is obviously due to the instability of the corresponding Ag(I) or Cu(II) cyanide at higher temperatures.

The complexes containing phenanthroline as N-donor ligand are more stable than the analogous complexes with ammonia pyridine or ethylenediamine [8].

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Zusammenfassung — Zehn neue Komplexverbindungen der allgemeinen Formel $[M(phen)_x][Ag(CN)_2] \cdot nH_2O$ (M = Fe, Mn, Ni, Cu, Zn, Cd; phen = o-Phenanthrolin; $x = 2$ oder 3; $n = 1$, 2, oder 3) wurden dargestellt und durch TG—DTA untersucht. Ein Vergleich zeigt, dass die Verbindungen mit 3 Phenanthrolin-Molekülen weniger stabil sind als die entsprechenden Komplexe mit 2 Phenanthrolin-Molekülen.

Резюме — Методом ТГ—ДТА были изучены впервые синтезированные комплексы общей формулы M(фенаптролин)$_x[Ag(CN)_2] \cdot nH_2O$, где M — двухвалентные железо, марганец, никель, медь, цинк и кадмий, а $x = 2$ или 3 и $n = 1$, 2 или 3. Сопоставление термоустойчивности исследованных соединений показало, что комплексы с тремя молекулами фенантролина обладают меньшей термоустойчивостью по сравнению с комплексами с двумя молекулами органического лиганда.