Thermochimica Acta, 93 (1985) 93-96
Elsevier Science Publishers B.V., Amsterdam

THERMAL PROPERTIES OF SOME BIS- AND TRIS (1,2-DIAMINOETHANE) METAL(II) BIS (DICYANOSILVER) COMPLEXES

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ABSTRACT

The complexes of general formula $M(en)_2Ag_2(CN)_4$ (M = Ni, Cu, Zn, and Cd) as well as complexes $M(en)_3Ag_2(CN)_4$ (M = Ni, Zn, and Cd) were prepared. A comparison the thermal stability of these two groups of compounds has shown that the complexes containing three molecules of ethylenediamine are less stable than the complexes with two molecules of ethylendiamine. It is characteristic of all complexes that the molecules of ethylenediamine are evolved before the decomposition of cyanides except for the complexes of nickel.

INTRODUCTION

A slow reduction of copper(II) compounds with alkaline metal cyanide in the presence of neutral ligands containing nitrogen atoms gives rise to copper(I) - copper(II) cyanocomplexes which may be placed into the group of mixed-valency compounds /1/. If ethylenediamine (en) was the ligand, the complexes of composition $Cu_3(H_2O)(en)_2(CN)_4$, $Cu(H_2O)(en)_2(CN)_6$, and $Cu_5(en)_2(CN)_6$ crystallized from this system /2,3/. In a foregoing study, we prepared the cyano-complexes derived from the first compound where Cu(II) was replaced by other central atom in equal oxidation state, i.e. Co, Ni, Zn, and Cd /4/. The results indicate that the structure of these complexes consists of polymeric anionic network of $[Cu_2(CN)_4]^{2-}$ composition and isolated $[M(H_2O)(en)_2]^{2+}$ or $[M(en)_2]^{2+}$ cations. Provided M = Cu, it has been revealed that an interaction between the cation and the system of π-orbitals of the cyano-groups comes into operation /5/. It appeared to be interesting to investigate the influence of the replacement of Cu(I) by other atom on the structure of anionic skeleton. We tried to prepare such cyano-complexes where Ag(I) was substituted for Cu(I) and, besides other properties, to find out how the exchange of central atom influences the

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Proceedings of ICTA 85, Bratislava

thermal stability and stoichiometry of decomposition of these cyano complexes.

EXPERIMENTAL

All cyano complexes were prepared in crystalline form by mixing aqueous solutions of the sulfates or acetates of Cu, Ni, Zn or Cd with en and $K[Ag(CN)_2]$ in convenient molar ratio. The crystals of complexes crystallized from the systems in the course of a few hours. These crystals were filtered, washed, and dried over $MgClO_4$.

MEASURING METHODS

The content of the metal M was determined complexometrically while silver was determined gravimetrically as AgCl. The content of C, H, and N was found out microanalytically by the use of a CHN analyzer Hewlett Packard 185.

The infrared spectra were taken in the solid state (KBr pellets or nujol suspension) in the region 4000–400 cm^{-1} with a spectrometer Specord 75. The crystal structures of these compounds were compared by the X-ray powder method with an instrument Mikrometa II.

The thermal stability and stoichiometry of thermal decomposition was investigated with an instrument Derivatograph OD - 102 MOM. The thermal measurement were carried out under dynamic conditions. Thus we obtained the TG, DTG and DTA records in air atmosphere up to the temperature of 600°C, the rate of heating being 6°C/min. The measurements were performed in crucibles of ceramic material and Al_2O_3 served as reference material for DTA.

RESULTS AND DISCUSSION

The ligands present in the compounds were indentified by the IR spectroscopy. We are going to describe only the most characteristic absorption bands of these ligands. The cyano groups exhibit a sharp absorption band in the region 2126–2140 cm^{-1} which corresponds to the stretching vibration ν_{CN}. For the coordinately bonded molecules of en the absorption bands in the regions

3120-3350 cm^{-1} (ν_{NH_3}), 2873-2967 cm^{-1} (ν_{CH_2}), 1570-1593 cm^{-1} (δ_{NH_2}), and 470-557^{3}cm^{-1} were observed /6/.^{2}

On the basis of the criteria of thermal stability we may divide the prepared complexes into two classes.

a) The first groups comprises complexes of the type $[M(en)_3][Ag_2(CN)_4]$. They start to decompose at lower temperatures than the corresponding complexes containing two molecules of en. The thermal decomposition begins by liberatien of en in non-stoichiometric amount. This process is diotinctly separate for Ni on the TG and DTG curves, for Cd only on the DTG curve where as it is not unambiguous for Zn. Complexes of the type $[M(en)_2][Ag_2(CN)_4]$ don't arise in the first stage of thermal decomposition of complexes of the type $[M(en)_3][Ag_2(CN)_4]$.

b) The second group comprises the complexes containing two molecules of en. In comparison with the corresponding compounds of the first groups, they are thermally more stable and start to decompose at temperatures higher by 40-50°C. Two weak endothermic peaks without any change in mass are to be observed for the compound with M=Cu. The minima of these peaks on the DTA curves are at 120° and 175°C and correspond to phase transitions. As for the compound with M=Cd, an analogous phase change with a minimum on the DTA curve at 100°C is to be observed. The complexes with M=Zn and Cd of this group melt simultaneously with beginning liberation of en. It manifests itself by a conspicuous endothermic minimum on the DTA curve at 190°C or 215°C which is not proportional to the quantity of liberated ligand. The final products of thermal decomposition in both classes are silver and the corresponding oxides of metals MO.

The temperatures of liberation of individual components are given in Table 1.

The disengagement of en is an endothermic process involving the compounds of both groups whereas the decomposition of cyanides in air is an exothermic process.

CONCLUSIONS

The thermal stability of binary cyanides is significantly affected by the character of central atoms. It results from the comparison between thermal stabilities of the complexes containing Cu(I) and Ag(I). The cyano complexes with Ag(I) are much less stable than the cyano complexes with Cu(I) because AgCN is less stable at higher temperatures than CuCN /4/.

Table 1

Compound	Initial temp. of liberation of en (°C)	Decomposition of AgCN (°C)	Decomposition of $M(CN)_2$ (°C)
$[Nien_2][Ag(CN)_2]_2$	200	230	400
$[Nien_3][Ag(CN)_2]_2$	160	360	420
$[Cuen_2][Ag(CN)_2]_2$	190	260	430
$[Znen_2][Ag(CN)_2]_2$	182	320	415
$[Znen_3][Ag(CN)_2]_2$	140	315	410
$[Cden_2][Ag(CN)_2]_2$	195	320	450
$[Cden_3][Ag(CN)_2]_2$	150	315	445

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