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THERMAL STABILITY AND STOICHIOMETRY OF THERMAL DECOMPOSITION OF DIPYRIDINE-METAL(II) TETRACYANONICKELATES(II)

Jozef Chomič, Ján Skoršepa, Juraj Černák, P.J.Šafarik's
University
Košice, Czechoslovakia

ABSTRACT

The influence of different central atoms on thermal stability and stoichiometry of thermal decomposition of tetracyanonickelates(II) of the type /M(C_5H_5N)$_2$/ /Ni(CN)$_4$/ (M = Mn, Fe, Co, Ni, Zn and Cd) has been investigated. Both molecules of pyridine are liberated in one step at different temperatures depending on the character of central atom in the first stage of thermal decomposition of all prepared compounds except the complex with M = Co. After liberation of pyridine the decomposition of cyano complexes starts.

INTRODUCTION

The first compounds including benzene of the general formula $M(NH_3)_2Ni(CN)_4.2C_6H_6$ were described by Hofmann /1,2/. Further compounds derived from them by replacing benzene with other aromatic molecules (aniline, phenol, pyrol, furan, pyridine) were called clathrates of the Hofmann type. In our laboratory we studied the properties of the clathrate compounds and paid special attention to the stoichiometry of thermal decomposition /3,4,5/. The results of some studies have shown that clathrates of the Hofmann type have also separating ability and separate e.g. the substituted derivatives of pyridine /6/. We may assume that the interaction between clathrates of the Hofmann type and pyridine or its derivative gives rise to cyano complexes containing pyridine or its derivatives. For this reason, we resolved to investigate the thermal properties of cyano complexes containing pyridine.

The preparation of cyano-complexes of the type /M(C_5H_5N)$_2$/ /Ni(CN)$_4$/ (M = Mn, Fe, Co, Ni, Cu, Zn, and Cd) was already described and the crystal structure was solved for the compound containing cadmium /7,8/. The structure of this compound

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is analogous with the structure of the host component of clathrates of the Hofmann type. The crystal structure of $/Cd(C_5H_5N)_2/$ $/Ni(CN)_4/$ consists of infinite layers of $/Cd(NC)_4Ni/_{\infty}$. The atom of cadmium completes its coordination number to six by two molecules of pyridine in axial positions. As for other complexes, the lattice parameters were determined and it is assumed that they are isomorphous with the compound $/Cd(C_5H_5N)_2/$ $/Ni(CN)_4/$/7/.

EXPERIMENTAL

The complexes were synthetized by the method modified with regard to the method described in paper /7/. Aqueous suspensions of binary cyanides $MNi(CN)_4$ were prepared and vapour of pyridine was distilled through them over during two hours at laboratory temperature. The complexes obtained in the form of powder were filtered, washed, and dried over silica gel.

MEASURING METHODS

The content of carbon, hydrogen and nitrogen was determined microanalytically with a CHN analyzer Hewlett Packard 185. The metals M were determined complexometrically and nickel was estimated gravimetrically with dimethylglyoxime.

The infrared spectra of samples in solid state (KBr pellets) were recorded with a spectrophotometer Specord 75 IR in the region 4000-400 cm^{-1}. The individual phases were determined by the X-ray powder diffraction 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 measurements were carried out under dynamic conditions. Thus the TG, DTG, and DTA records were obtained for air atmosphere up to the temperature of 600°C, the heating rate being 3° and 6°C/min. The crucibles used for investigating thermal stability were of ceramic material and Al_2O_3 served as reference material for DTA.

RESULTS AND DISCUSSION

The ligands present in the prepared compounds were identified by infrared spectroscopy. For simplicity, we are going to mention only the basic characteristic bands of individual ligands.

The cyano-groups exhibit a sharp absorption band in the region 2145 - 2158 cm^{-1} which corresponds to the stretching vibration $\nu_{\bar{C}N}(E_u)$. Only the compound with M = Cu exhibited two absorption bands at 2132 and 2172 cm^{-1} which was evidently due to distorsion of the coordination polyhedron CuN_6. The absorption band at 1598 cm^{-1}/9/ is characteristic of the coordinately bonded molecule of pyridine. For the prepared complexes this absorption band was observed in the region 1589 - 1599 cm^{-1}. Two absorption bands corresponding to the stretching vibrations ν_{CH} (A_1, B_1) appeared in the regions 3045 - 3092 cm^{-1} for each complex. As for the compound with cobalt, two additional weak absorption bands corresponding to the stretching vibrations of water molecules $\nu_{OH}(A_1, B_1)$ were observed in the region 3450 - 3600 cm^{-1} while one absorption band corresponding to the bending vibration of water molecules $\delta_{HOH}(A_1)$ appeared at 1620 cm^{-1}.

On the basis of the result of thermal analysis, we may divide the prepared complexes into three classes.

a) The complexes with M = Zn, Cd may be put into the first class. In the first stage, they evolve two molecules of pyridine in single step and the intermediate after liberation of pyridine can be isolated. The stoichiometry of thermal decomposition may be expressed by the equations:

$$/M(C_5H_5N)_2//Ni(CN)_4/\ (s) \longrightarrow M/Ni(CN)_4/\ (s) + 2\ C_5H_5N\ (g)$$

$$M/Ni(CN)_4/\ (s) \longrightarrow MO\ (s) + NiO\ (s) + \text{gaseous products}$$

b) The second class comprises the complexes with M = Fe, Mn, Ni and Cu. There are two molecules of pyridine liberated in the first stage which is immediately succeeded by the decomposition of cyanides. The end of liberation is indicated only by a break on the TG curve.

c) The third class contains the compound $/Co(H_2O)_2(C_5H_5N)_2//Ni(CN)_4/$. The water molecules are liberated in the first stage in one step according to the equation

$$/Co(H_2O)_2(C_5H_5N)_2//Ni(CN)_4\ (s) \longrightarrow /Co(C_5H_5N)_2//Ni(CN)_4\ (s) + 2\ H_2O\ (s)$$

Further course of thermal decomposition is like decomposition in class b.

CONCLUSIONS

It ensues from the results of thermal analysis that the course and temperatures of thermal decomposition are dependent on the central atom M to which the molecules of pyridine are coordinated. The most stable is the complex with M = Cd and the least stable is complex with M = Zn. It will be interesting in further research to investigate the thermal properties of such complexes in which derivatives of pyridine are coordinated in the place of pyridine for the sake of comparision.

REFERENCES

1 K.A. Hofmann, F. Küspert, Z.Anorg. Chemie 15 (1897) 204
2 K.A. Hofmann, F. Höchtlen, Ber. Deutsch. Chem. Gesellschaft 36 (1903) 1149
3 J. Chomič, J. Skoršepa, TERMANAL '73, Vysoké Tatry 1973, A 67
4 J. Skoršepa, J. Chomič, TERMANAL '73, Vysoké Tatry 1973, A 63
5 A. Sopková, TERMANAL '73, Vysoké Tatry 1973, A 72.
6 A. Sopková, M. Šingliar, P. Králik, J. of Incl. Phenom., 1 (1984) 263
7 R.L. Morehouse, K. Aytac, D. Ülku, Z. f. Kristallographie 145 (1977) 157
8 D. Ulku, Z. f. Kristallographie 142 (1975) 271
9 M. Horák, D. Papoušek, Infračervená spektra a struktura sloučenin, Academia, Praha 1976