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SPECTROSCOPIC STUDIES OF THE THERMAL DECOMPOSITION OF HOMONUCLEAR Fe/II/ LIGAND BRIDGED POLYMERIC COMPLEXES

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ABSTRACT

The thermal decomposition of $Fe/pyz/_2X_2$ /X = Cl, Br/, $Fe/4\text{-}CNpy/_2Cl_2$ polymeric complexes and $Fe/3\text{-}CNpy/_4Cl_2$, where pyz =pyrazine, 3- and 4-CNpy = 3- and 4-cyjanopyridine has been studied in nitrogen. Spectroscopic and magnetochemical methods have been used to investigate the structural changes about the iron during thermal decomposition process.

INTRODUCTION

The FeX_2 compounds /X = Cl, Br, I/ form with such potentially bidentate /two-functional/ ligands as pyrazine /pyz/, 3- and 4-cyanopyridine the compounds of the formulae $Fe/pyz/_2X_2$, $Fe/4\text{-}CNpy/_2X_2$ and $Fe/3\text{-}CNpy/_4X_2$ /2/. Spectroscopic /UV, VIS, IR, Raman, Mössbauer/ and magnetochemical studies indicate that $Fe/pyz/_2X_2$ and $Fe/3\text{-}CNpy/_4X_2$ contain the high-spin Fe/II/ in the FeN_4X_2 chromophore while $Fe/4\text{-}CNpy/_2X_2$ in FeN_2X_4 one. The pyrazine and 4-CNpyridine compounds of the formula FeL_2X_2 have polymeric structures differing in the type of bridges. The pyrazine compounds contain pyrazine bridges whereas the 4-CNpy compounds contain halide bridges. The 3-CNpy complex of the formula FeL_4X_2 is a monomeric compound.

The paper presented deals with the thermal decomposition products of these compounds from the point of view of structural changes around the iron/II/ atom during the thermal decomposition process.

MEASURING METHODS

The thermal decomposition studies were carried out on a Derivatograph Q - 1500 D, MOM Budapest at the heating rate 2 or 3°C/min in a nitrogen atmosphere.

Diffuse reflectance electronic spectra in magnesium oxide were recorded on a Beckman 5240.

The infrared spectra in the region /4000 - 20 cm^{-1}/ were obtained on a Perkin-Elmer 180 spectrometer in both KBr pressed pellets

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The Raman spectra were measured by means of a Jeol IRS-S1 Spectrophotometer using the 488 nm and 514.5 nm exciting line of a Ar-ion laser. The magnetic measurements were made on either a Gouy or a Faraday balance calibrated with $HgCo/NCS/_4$.
Mössbauer spectra were measured by method desribed previoulsy /1/.

RESULTS AND DISCUSSION

Analysis of the TG and DTA curves obtained for the compounds under investigation is indicative of their thermal decomposition according to the following reactions :

$$Fe/pyz/_2X_2 \longrightarrow Fe/pyz/X_2 \longrightarrow FeX_2 \qquad /X = Cl,\ Br/$$

$$Fe/4\text{-}CNpy/_2Cl_2 \longrightarrow Fe/4\text{-}CNpy/Cl_2 \longrightarrow FeCl_2$$

$$Fe/3\text{-}CNpy/_4Cl_2 \longrightarrow Fe/3\text{-}CNpy/_2Cl_2 \longrightarrow Fe/3\text{-}CNpy/Cl_2 \longrightarrow FeCl_2$$

The thermolysis products obtained at various stages were subject to chemical analysis and spectroscopic studies which confirmed their molecular formula determined on the basis of mass decrements.

Thermal decomposition of $Fe/pyz/_2X_2$

The electronic and Mössbauer spectra /Table 1/ of the monopyrazine complex, a dissociation product of one pyrazine molecule in the thermolysis process of $Fe/pyz/_2X_2$ differ significantly from those observed for the initial compound. Nevertheless, the environment of Fe/II/ remains pseudooctahedral. A considerable increase in the splitting parameter $\nu_1 - \nu_2$ for the d - d bands found in the NIR region, decrease in the ν_{av} parameter /or 10Dq in the crystal field approximation/ as well as a considerable decrease in the QS parameter for the Mössbauer spectra reflects changes in the environmet of Fe/II/. The values of these parameters are characteristic of Fe/II/ forming a FeX_4N_2 - type chromophore /3/, i. e. for the polymeric compounds with halide bridges. Such an environment of Fe/II/ in $Fe/pyz/X_2$ may be obtained by forming a space polymer where the $/FeX_2/_n$ chains are bridged by means of the pyrazine molecules. The occurrence of pyrazine bridges is confirmed by the lack of any coincidence between the bands found in the IR and Raman spectra and by the positions of the ν_{Fe-X} and ν_{Fe-N} bands in the Far-IR spectrum.

Table 1

Spectroscopic data for chloride complexes under investigation

Compounds	QS [mms^{-1}]	IS [mms^{-1}]	$\nu_1 - \nu_2$ [cm^{-1}]	ν_{av} [cm^{-1}]
$Fe/pyz/_2Cl_2$	3.24	1.27	-1800	10700
$Fe/pyz/Cl_2$	1.80	1.32	3100	8550
$Fe/4\text{-}CNpy/_2Cl_2$	1.26	1.33	3600	7960
$Fe/4\text{-}CNpy/Cl_2$	1.67	1.35	3240	8970
$Fe/3\text{-}CNpy/_4Cl_2$	2.96	1.32	-2000	8800
$Fe/3\text{-}CNpy/_2Cl_2$	1.67	1.35	3300	8040
$Fe/3\text{-}CNpy/Cl_2$	1.67	1.35	2800	8100

IS relative to sodium nitroprusside

The coordination site set free at the iron atom as a result of one pyrazine molecule being dissociated becomes occupied by the electron pair on a halide coordinated at the adjacent iron atom with simultaneous formation of the $/FeX_2/_n$ bridges with preservation of one pyrazine bridge forming a space polymer.

Thermal decomposition of the compounds with 3- and 4-CNpy

The electronic and Mössbauer spectra of $Fe/3\text{-}CNpy/_2Cl_2$ formed in the first stage of thermolysis indicate explicitly that the environment of Fe/II/ is changed from FeN_4X_2 into FeX_4N_2, i. e. that a polymeric compound with chloride bridges is formed. The structures of both cyanopyridine compounds of the FeL_2Cl_2 formula are the same. The IR spectra of these compounds are indicative of the monodentate bond in 3- and 4-CNpy through the pyridine nitrogen. A loss of the successive 3- and 4-CNpy molecule leads to the formation of the $FeLCl_2$-type compounds whose spectroscopic characteristics /Table 1/ differs slightly with respect to each other and to FeL_2Cl_2. This would allow to assign to these compounds the structure suggested for a corresponding pyridine compound $FepyCl_2$ /4/ in which each iron atom is connected via chloride bridges with the three adjacent iron atoms, forming a double chain.

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