Thermochimica Acta, 92 (1985) 705-707
Elsevier Science Publishers B.V., Amsterdam

THERMAL PROPERTIES OF NICKEL(II) COMPLEXES WITH PYRIDINE N-OXIDE AND ITS METHYLDERIVATIVES

E. Jóna and M. Jamnický
Department of Inorganic Chemistry, Slovak Technical University,
Jánska 1, 812 37 Bratislava, Czechoslovakia

ABSTRACT

Thermal properties (the stoichiometry of thermal decomposition and stereochemical changes in thermal decomposition) were studied for the following compounds:

A/ Complexes I of the type $Ni(NCS)_2(q\text{-}MepyNO)_n \cdot x\ H_2O\ (C_2H_5OH)$
(q = 4,3,2, or without substituent; n = 3 or 2; x = 1 or 0; pyNO = pyridine N-oxide)

B/ Complexes II of the type $NiCl_2(q\text{-}MepyNO)_n \cdot x\ H_2O\ (C_2H_5OH)$
(q = 4,3,2, or without substituent; n = 2 or 1; x = 1 or 2)

It was found, that the heating of the complexes I and II led at first to the release of H_2O-molecules (or C_2H_5OH-molecules, respectively). In the further stage already the decomposition of ligands set in. The stereochemical changes in thermal decomposition of this complexes are discussed.

INTRODUCTION

Thermal properties of solid nickel(II) complexes generally depends on various factors: their crystal structure, the experimental conditions in the measurements, as well as, properties of the ligands (electronic and steric) and their mutual interactions [1,2]. The position and nature of substituents in the ligands may play a great role; they influence the stereochemistry of the starting complexes (and also the products formed by decomposition) and moreover the stoichiometry of thermal decomposition [3,4,5]. From the above aspect, our study was oriented to isothiocyanate and chlorocomplexes with pyridine N-oxide and its methylderivatives.

EXPERIMENTAL

Preparations of starting compounds were described in papers [6,7,8]. The thermal properties of the compounds were studied on a Derivatograph (MOM Budapest). In all the thermal

---

Proceedings of ICTA 85, Bratislava

decompositions a sample weight of 100 mg was used and the rate of temperature increase 3 °C min^{-1}. The stereochemistry was stated on the bases of magnetic and spectral data.

RESULTS AND DISCUSSION

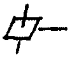
The thermal decomposition reactions of studied complex with pyNO and its methylderivatives may be characterized mostly by two steps: the bonded solvent molecules (H_2O, C_2H_5OH) are released in the first step while in the second one the complexes are completely decomposed as shown by an expressive exothermic peak (above 200 °C) on the DTA curve.

The release of H_2O and C_2H_5OH molecules takes place in well - defined steps, which can be clearly observed by means of the TG and DTG curves. The rate maxima of the water and C_2H_5OH escape (the temperatures of the 1st peak on DTG curves) decrease in the sequence:

pyNO > 2-MepyNO > 3-MepyNO > 4-MepyNO

The data of the composition and thermal properties of studied complexes are listed in Table 1.

Table 1 The composition and thermal properties of NiY_2 (q-MepyNO)$_n$.x H_2O (C_2H_5OH) and NiY_2(pyNO)$_n$.x H_2O complexes

Y	q	n	x	escape of solvent molecules	stereochemical changes
NCS	4	2	1	- H_2O	remain polymeric 
	3	2	1	- C_2H_5OH	
	2	3	0	-	
	-	3	1	- H_2O	remain dimeric 
Cl	4	2	1	- C_2H_5OH	dimeric  — dimeric 
	3	1	2	- 2 H_2O	dimeric  — polymeric 
	2	1	2	- 2 H_2O	polymeric  — mor complicated polymeric 
	-	1	1	- H_2O	

On the bases of composition and thermal properties, the studied complexes can be divided into two groups. The first group includes compounds I (Y = NCS) which have not the coordinated solvent molecules. After the release of H_2O (or C_2H_5OH) molecules the complexes I remain polymeric or dimeric octahedral (Table 1). The second group includes compounds II (Y = Cl) which have coordinated H_2O and C_2H_5OH molecules. After the release of solvent molecules the complexes II showed a stereochemical changes: dimeric octahedral → dimeric pentacoordinated complex, dimeric octahedral → polymeric octahedral complex or polymeric octahedral → mor complicated polymeric octahedral complex.

The study of stereochemistry of prepared complexes indicated that octahedral configuration is preferred (with one exception). For complex with Y = Cl and q = 4 (Table 1) the pentacoordination seems to be more advantageous since the hexacoordination is probably hinderes by steric effects of the voluminous heterocyclic ligands [9].

REFERENCES

1. E. Jóna, T. Šramko, and J. Gažo, J. Thermal. Anal. 16 (1979) 213.
2. M. Jamnický and E. Jóna, Inorg. Chim. Acta 88, (1984) 1.
3. M. Jamnický and E. Jóna, Collect. Chem. Commun. 47, (1982) 2478.
4. M. Jamnický and E. Jóna, Z. anorg. allg. Chem. 487 (1982) 225.
5. E. Jóna and M. Jamnický, J. Thermal. Anal. 27, (1983) 359.
6. D.H. Brown, D. Kenyon, and D.V.A. Sharp, J. Chem. Soc. 1969, 1474.
7. E. Jóna, J. Krchnavá, and M. Žemlička, Z. anorg. allg. Chem. 1985 (in press).
8. A.J. Pappas, F.A. Osterman Jr., and H.B. Powell, Inorg. Chem. 9, (1970) 2695.
9. W.H. Watson, Inorg. Chem. 8, (1969) 1879.