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THERMAL BEHAVIOR OF MANNICH BASE N,N’-TETRA(4-ANTIPYRYL-METHYL)-1,2 DIAMINOETHANE (TAMEN) AND ITS BINUCLEAR COMPLEXES

Part I. Thermal behavior of $Ni_2(TAMEN)Cl_4$

Viorel Sasca[*], *Elena Maria Mosoarca, Livia Avram, Ramona Tudose and Otilia Costisor*

Institute of Chemistry Timişoara of Romanian Academy, 24 Mihai Viteazu Bd., 300223, Timişoara, Romania

The thermal decomposition of Mannich base N,N’-tetra(4-antipyrylmethyl)-1,2-diaminoethane (TAMEN), and its Ni(II), binuclear complex, $Ni_2(TAMEN)Cl_4$, in air and in nitrogen atmosphere, were investigated. X-ray powder diffractometry, infrared spectroscopy and simultaneous thermogravimetry-differential thermal analysis (TG-DTA), have been used to characterize and to study the thermal behavior of these compounds. The results provided information concerning the stoichiometry, crystallinity, thermal stability and decomposition mechanism of the compound.

Keywords: *antipyrine, binuclear complex, Mannich base, nickel(II), thermal behavior*

Introduction

The property of formaldehyde to bind an amine with a carbon acid via a methylene bridge, discovered in 1912 by Mannich and Krösche, was utilized as an efficient method to obtain pharmaceutical products by implication of acids components which were recognized as substances with therapeutic action [1, 2]. Antipyrine and its derivatives – as carbon acids, have interesting pharmacological properties and are used for different medical purposes. These compounds are reported to exhibit analgesic and anti-inflammatory effects, antiviral, antibacterial, antitumoral and herbicidal activities [3–13].

Our main point of interest refers to the study the Mannich bases complexes of some first row metal ions, in order to explain their biological activity as well as to find new compounds with pharmaceutical effects. Some 3*d* metal complexes with antipyrine derivative ligand N,N’-tetra(4-antipyrylmethyl)-1,2-diaminoethane (TAMEN) [14, 15] and N,N’-bis(4-antipyrylmethyl)-piperazine (BAMP) [16–19], which contains four and two, respectively, antipyrine moieties, have been obtained and studied. The biological activity in vitro for some of them has been demonstrated [20–22].

Thermal behaviour of mixed ligand complexes of cobalt(II) and copper(II) complexes containing BAMP and TAMEN as ligands and 2-aminobenzothiazole, imidazole and 2-mercapto benzothiazole as coligands, has been investigated [23–25]. As a continuous work in this frame, the thermal behaviour for the Mannich base N,N’-tetra(4-antipyrylmethyl)-1,2-diaminoethane (TAMEN) and its binuclear complexes of Ni(II), Cu(II) and Co(II) cations were studied.

In the first part of this work, the TAMEN and Ni(II) complex, $Ni_2(TAMEN)Cl_4$, were investigated by means of X-ray powder diffractometry, infrared spectroscopy and simultaneous TG-DTA. The results of the present study improve the knowledge on these compounds including their thermal stability and reaction mechanism of decomposition process.

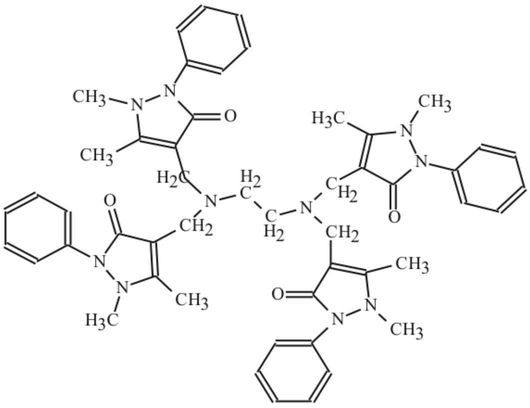

Fig. 1 N,N’-tetra(4-antipyrylmethyl)-1,2-diaminoethane (TAMEN)

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[*] Author for correspondence: viorelsasca@yahoo.co.uk, vsasca@acad-icht.tm.edu.ro

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Experimental

The ligand N,N’-tetra(4-antipyrylmethyl)-1,2-diaminoethane (TAMEN) has been obtained following a Mannich type condensation between antipyrine, 1,2-ethanediamine and formaldehyde, by changing the experimental condition given in literature, in order to obtain an good yield and a pure ligand [1, 2].

The general procedure for the preparation of the complexes $Ni_2(TAMEN)Cl_4$, $Cu_2(TAMEN)Cl_4$ and $Co_2(TAMEN)Cl_4$ and their characterization are detailed in [26].

Thermal decomposition was carried out using a TGA/SDTA 851-LF 1100 Mettler apparatus. The samples with mass of about 30 mg were placed in alumina crucible of 150 μL. The experiments were conducted in air or nitrogen flow of 50 mL min^{-1}, in the temperature range of 25–1000°C with a heating rate of 5°C min^{-1}. The air supplied by a compressor (4–5 bar) was passed over granular silica gel. The nitrogen was supplied from Linde gas cilinder (150 bar) of 4.6 purity class.

The X-ray diffraction spectra for the solid residue arised from the thermal decomposition of the before mentioned complexes were obtained with a XD 8 Advanced Bruker diffractometer using the MoK_{α} and CuK_{α} radiation.

IR spectra for ligand N,N’-tetra(4-antipyrylmethyl)-1,2-diaminoethane (TAMEN) and its chloride complexes of Ni(II), Cu(II) and Co(II) were recorded in KBr pellets with a 4200 Jasco FT-IR spectrometer (4000–400 cm^{-1}). Also, the IR spectra of the isothermal heated samples of N,N’-tetra(4-antipyrylmethyl)-1,2-diaminoethane (TAMEN) and its chloride complexes of Ni(II), Cu(II) and Co(II), to 200 and 400°C for 2 hours, were recorded. The temperatures of isothermal treatment were chosen after important processes of decomposition were occurred on the basis of the thermal curves.

Results and discussion

Composition and general description of the complexes

The stereochemistry of the binuclear complexes is described by the bis binucleating ligand TAMEN which acts as a bis-tridentate ligand through two oxygen atoms belonging to the antipyrine fragments and one nitrogen atom of ethylenediamine bridge. A tetrahedral coordination sphere was revealed around the metal ions by UV-Vis spectroscopy and magnetic susceptibility measurements. The far IR spectra denote the presence of metal–nitrogen, metal–oxygen and metal–chloride bonds [26].

Thermoanalytical studies of the ligand and its binuclear Ni(II) complex

The thermal decomposition curves for the TAMEN ligand in air and nitrogen dynamic atmosphere can be seen in Figs 2 and 3.

The thermal decomposition data for the N,N’-tetra(4-antipyrylmethyl)-1,2-diaminoethane (TAMEN) are summarized in Table 1.

The first mass loss of 1.2–1.5%, corresponding to the the water bound physically at the solid surface, accompanied of an endothermal process with peak at about 40°C, was observed between 25–90°C. In the temperature range of 90–180°C, the DTA curves indicate two endothermal processes with maxima at 105–106 and 121–122°C, respectively. The mass loss for these two processes is about 16–19% and corresponds to the loss in two steps of 9–11 molecules of crystallization water. An endothermic process is noticed on DTA curves, in the temperature range of 130–220°C, with maximum at 192.8 in air and at

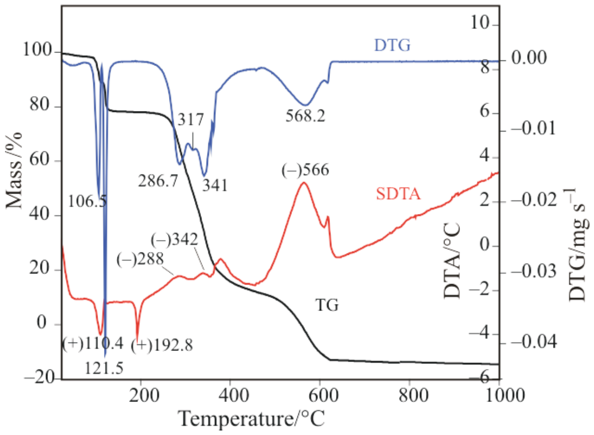

Fig. 2 The thermal decomposition curves for the TAMEN·xH_2O ligand in air; the heating rate of 5°C min^{-1}, the air flow of 50 mL min^{-1}

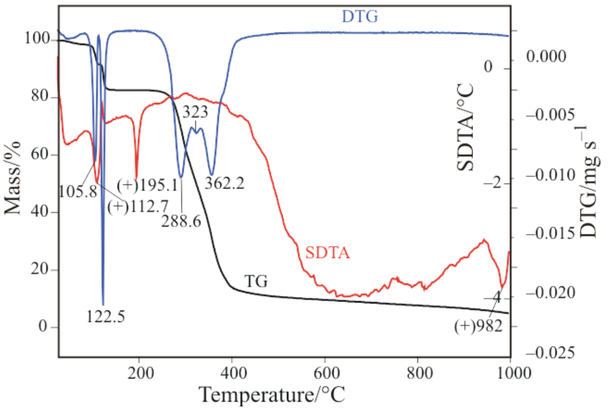

Fig. 3 The thermal decomposition curves for the TAMEN·xH_2O ligand in nitrogen; the heating rate of 5°C min^{-1}, the air flow of 50 mL min^{-1}

Table 1 The thermal decomposition data for the TAMEN·xH$_2$O in air and nitrogen atmosphere

Air, x=11			Nitrogen, x=9			Mass losses assignements
Temp. range/ °C	Mass loss/%		Temp. range/ °C	Mass loss/%		
	Calc.	Found		Calc.	Found	
25–180	1.0	1.2[1]	25–180	1.0	1.5[1]	moisture
	18.5	18.6		15.7	16.0	crystallization water
220–310	29.1	23.2[2]	220–310	30.1	29.7	phenyl groups
310–335	10.4	10.2	310–340	10.8	10.4	bridge –CH$_2$–, >N–(CH$_2$)$_2$–N<
335–475	41.0	28.0[3]	–	–	–	2,3-dimethyl-5-pyrazolone
475–1000		18.7[3]	340–1000	42.5	37.5[4]	
Total loss	100.0	99.9	Total loss	100.1	95.1[4]	–
Solid residue	–	–	Solid residue	–	4.9	–

[1] moisture content; [2] the difference with reference to calc. mass loss corresponds to 4O (~6 mass%) that was inserted by the ligand as partial oxidation process result and that causes the decrease of the found mass to 23.2%; [3] the difference with reference to calc. mass loss corresponds to the 4O content of partial oxidation compounds (found mass=41+6≈28+18.7≈47); [4] the difference with reference to calc. mass loss corresponds to 4.9% of the ligand rest

195.1°C in nitrogen. As no mass loss appear, the process is attributed to a melting one.

All the IR characteristic bands of the ligand were put in evidence after an isothermal treatment to 200°C for two hours, this means that ligand structure was preserved within the range temperature of 25–200°C. The assignement is also supported by IR measurements as well as by our previous results [26].

Over the 200°C, the thermal decomposition of TAMEN begins and it occurs in three steps. The first step, between the temperature range of 220–310°C in air and nitrogen, reflected by small thermal effects on DTA curves, correspond to a mass loss of 23.2% in air and 29.7% in nitrogen. In the FTIR spectra of ligand heated isothermally to 400°C for 2 hours, no specific bands of phenyl group were observed, so it can be supposed that four phenyl groups were released. In air, the loss is smaller with about 6% than in nitrogen. This is tentatively assigned to an oxidation process which takes place simultaneously with the phenyl groups release.

The second step occurs in the temperature range of 310–340°C with a mass decrease of 10.1–10.4%, in both air and nitrogen atmosphere, corresponds to the loss of the (–CH$_2$)$_2$N–CH$_2$–CH$_2$–N(CH$_2$–)$_2$ central moiety group. Thus, the FTIR spectra, of the ligand heated isothermally to the 400°C for 2 h, do not show anymore the bands at 1046 cm^{-1} attributed to $-\nu_{C-C}/\nu_{C-N}$ mode of the ethylenediamine group [27].

The third step of thermal decomposition, within the temperature range of 335–1000°C, occurs in different way in air and nitrogen. In air, the remained ligand fragment (the 2,3-dimethyl-5-pyrazolone group with inserted oxygen), decomposes in two stages. The first stage (330–475°C) is accompanied of a slight exothermal effect, whereas the second one (in the temperature range of 475–630°C) exhibits a strong exothermal effect. The total mass loss for both stages is of 46.7% and this corresponds to the equivalent mass loss of the 2,3-dimethyl-5-pyrazolone group (41 mass%) and 4O (~6 mass%). Over 630°C a slight mass decrease without thermal effects was observed on TG and DTA curves.

The TG curve in nitrogen atmosphere shows that within the temperature range of 340–1000°C the mass loss represents 37.5%. The result of the ligand heating is an organic deposit of 4.9%. The sum of the both percentages (42.5%) corresponds to the equivalent mass loss of the 2,3-dimethyl-5-pyrazolone group.

In brief, the following scheme of thermal decomposition of N,N'-tetra(4-antipyrylmethyl)-1,2-diaminoethane (TAMEN)·9–11H$_2$O is proposed:

- In air flow:

$$\mathrm{C_{50}H_{56}N_{10}O_4\cdot 11H_2O} \xrightarrow{25\text{–}120^{\circ}\mathrm{C},\ -5\mathrm{H_2O}}$$

$$\mathrm{C_{50}H_{56}N_{10}O_4\cdot 6H_2O} \xrightarrow{120\text{–}180^{\circ}\mathrm{C},\ -6\mathrm{H_2O}} \mathrm{C_{50}H_{56}N_{10}O_4}$$

$$\xrightarrow{192.8^{\circ}\mathrm{C}} \mathrm{C_{50}H_{56}N_{10}O_{4\ (l)}} \xrightarrow{180\text{–}310^{\circ}\mathrm{C},\ -4\mathrm{C_6H_5},\ +2\mathrm{O_2}}$$

$$\mathrm{C_{26}H_{36}N_{10}O_8} \xrightarrow{310\text{–}335^{\circ}\mathrm{C},\ -6\mathrm{CH_2},\ -\mathrm{N_2}} \mathrm{C_{20}H_{24}N_8O_8}$$

$$\xrightarrow{335\text{–}475^{\circ}\mathrm{C},\ -0.55(\mathrm{C_{20}H_{24}N_8O_8})} 0.45(\mathrm{C_{20}H_{28}N_8O_8})$$

$$\xrightarrow{475\text{–}1000^{\circ}\mathrm{C},\ -0.45(\mathrm{C_{20}H_{24}N_8O_8})+n\mathrm{O_2}} \text{Volatile compounds}$$

- In nitrogen flow:

$$\mathrm{C_{50}H_{56}N_{10}O_4\cdot 9H_2O} \xrightarrow{25\text{–}120^{\circ}\mathrm{C},\ -4\mathrm{H_2O}}$$

$$\mathrm{C_{50}H_{56}N_{10}O_4\cdot 5H_2O} \xrightarrow{120\text{–}180^{\circ}\mathrm{C},\ -5\mathrm{H_2O}} \mathrm{C_{50}H_{56}N_{10}O_4}$$

$$\xrightarrow{195^{\circ}\mathrm{C}} \mathrm{C_{50}H_{56}N_{10}O_{4\ (l)}} \xrightarrow{210\text{–}310^{\circ}\mathrm{C},\ -4\mathrm{C_6H_5}} \mathrm{C_{26}H_{36}N_{10}O_4}$$

$$\xrightarrow{310\text{–}340^{\circ}\mathrm{C},\ -6\mathrm{CH_2},\ -\mathrm{N_2}} \mathrm{C_{20}H_{24}N_8O_4}$$

$$\xrightarrow{340\text{–}1000^{\circ}\mathrm{C},\ -0.89(\mathrm{C_{20}H_{24}N_8O_4})} \text{Solid residue}$$

(4.9% organic deposit)

The thermal decomposition curves for the complex $Ni_2(TAMEN)Cl_4 \cdot xH_2O$ in air and nitrogen dynamic atmosphere are presented in Figs 4 and 5.

The thermal decomposition data for the $Ni_2(TAMEN)Cl_4 \cdot xH_2O$ are given in Table 2.

On both TG curves (air and nitrogen) of $Ni_2(TAMEN)Cl_4 \cdot xH_2O$ decomposition, in the range 25–180°C the DTA curves indicate an endothermal process with maxima at 77.6 and 79°C, respectively. The mass loss for this process is about 13.4% in air, respectively 11.8% in nitrogen and these corresponds to the loss of 9.5 and 8 molecules of crystallization water, respectively. The melting process occurred in course of ligand heating has not observed.

A complex decomposition process occurred in air within the temperature range of 180–475°C. The corresponding mass loss was of 34.5% in air, equivalent to the difference between $4Cl+4C_6H_5+{>}N{-}CH_2{-}\ CH_2{-}N{<}$ loss and the acquisition of 4O inserted in the left ligand. The decomposition process is accompanied by two thermal effects on DTA curves, a small one and medium the other. The two exothermal peaks, one with maximum at 252°C on DTA curves, in air and also in nitrogen flow, can be assigned to a change in crystallization state as no mass modification was observed and the other with maximum at 317.2°C on DTA curve, only in air, can be assigned to the oxidation process by 4O acquisition.

In the FTIR spectra of ligand heated isothermally to the 400°C for 2 h, only specific bands of pyrazolone moieties were observed, so it can be supposed that 4Cl, $4C_6H_5$, $2CH_2$ fragments and one N_2 molecule were released.

The next step of thermal decomposition in air occurred in the temperature range of 475–590°C with a mass loss of 40.9% corresponding to the equivalent

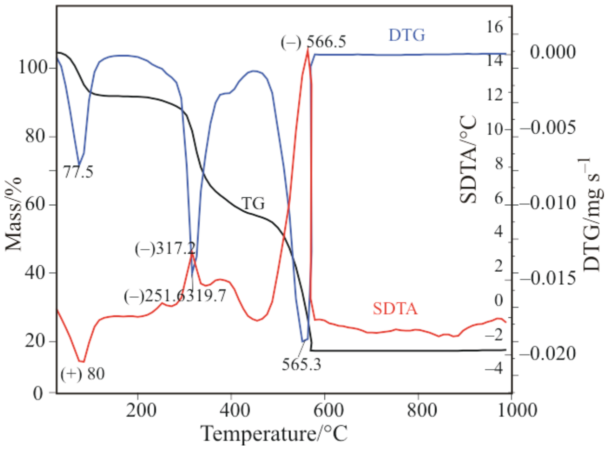

Fig. 4 The thermal decomposition curves of $Ni_2(TAMEN)Cl_4 \cdot 9.5H_2O$ in air; the heating rate of 5°C min^{-1}, the air flow of 50 mL min^{-1}

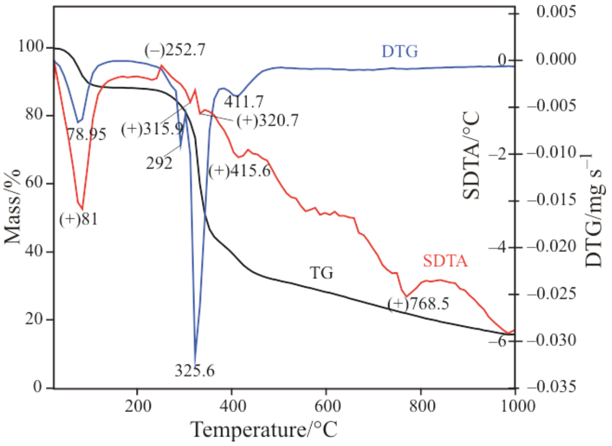

Fig. 5 The thermal decomposition curves of $Ni_2(TAMEN)Cl_4 \cdot 8H_2O$, in nitrogen; the heating rate of 5°C min^{-1}, the air flow of 50 mL min^{-1}

Table 2 The thermal decomposition data for the $Ni_2(TAMEN)Cl_4 \cdot xH_2O$ in air and nitrogen atmosphere

Air, x=9.5			Nitrogen, x=8			
Temp. range/ °C	Mass loss, %		Temp. range/ °C	Mass loss/%		Mass losses assignements
	Calc.	Found		Calc.	Found	
25–180	13.9	13.3	25–180	11.3	11.8	crystallization water
180–475	39.4	34.4[1]	180–310	11.2	10.9	chlor
			310–370	33.5	33.6	phenyl groups,bridge $-CH_2-$, $>N-(CH_2)_2-N<$
475–590	38.4	40.9[2]	370–1000	34.8	28.4[4]	2,3-dimethyl-5-pyrazolone
Total	91.0	88.6[3]	Total	90.8	84.7[4]	–
Solid residue	9.1Ni/ 11.6NiO	11.6NiO	Solid residue	9.3Ni	15.5 (9.3Ni+6.2 l.r.)	–

[1]the difference with reference to calc. mass loss corresponds to 4O (~5 mass%) that was inserted by the ligand as a partial oxidation process result which causes the decrease of the found mass to 34.4 %; [2]the difference with reference to calc. mass loss corresponds to the ~5 mass% content of 4O from partial oxidation compounds and to the 2.5% O of NiO (found mass=38.4+5–2.5=40.9); [3]the difference with reference to calc. mass loss corresponds to the 2.5% O of NiO and that causes the decrease of the found mass (91.1–2.5=88.6); [4]the difference with reference to calc. mass loss corresponds to 6.2% of the ligand rest

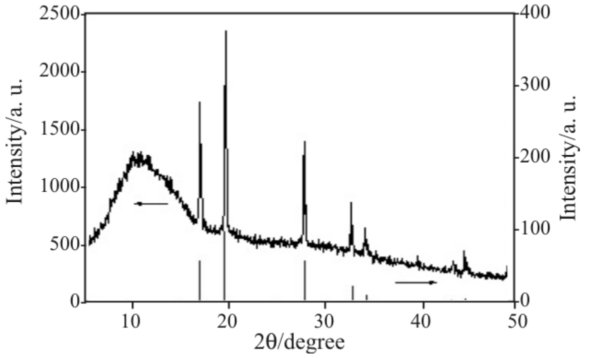

Fig. 6 The X-ray diffractogram of solid residue resulted from the thermal decomposition of the $Ni_2(TAMEN)Cl_4\cdot xH_2O$ in the temperature range of 25–1000°C with a heating rate of 5°C min^{-1}, in air flow of 50 mL min^{-1} (above), ASTM sheet: 01-1239 (below)

mass loss of the 2,3-dimethyl-5-pyrazolone-methylene group with inserted oxygen, and it was accompanied of a strong exothermal effect produced of fast oxidation processes. Finally, a solid residue of 11.6% mass consisting of NiO (see X-ray diffraction spectrum of the Fig. 6) was obtained. All bands from X-ray diffractogram showed in Fig. 6 belongs to NiO cubic crystallization system.

In nitrogen flow, the thermal decomposition, after the crystallization water loss, has occurred in three steps:

- the first step within the temperature range of 180–310°C with 10.9% mass loss corresponding to the 4Cl release;
- the second step within the temperature range of 310–370°C with 33.6% mass loss that corresponds to $4C_6H_5+4(–CH_2–)+(>N–CH_2–CH_2–N<)$ mass;
- the third step within the temperature range of 370–1000°C accompanied of about 28.4% mass loss and as final decomposition result a solid residue of 15.5% was obtained (it consists of 9.3% of Ni and 6.2% for an organic deposit). The sum of 28% mass loss and 6.2% for organic deposit corresponds to 2,3-dimethyl-5-pyrazolone group mass. The decomposition processes occurred in same way as for TAMEN, but the rate of oxidation processes over 400°C was increased.

On the whole, the $Ni_2(C_{50}H_{56}N_{10}O_4)Cl_4\cdot xH_2O$ thermal decomposition is similar with the TAMEN thermal decomposition in air and nitrogen.

In brief, the next scheme of thermal decomposition for $Ni_2(C_{50}H_{56}N_{10}O_4)Cl_4\cdot xH_2O$ was proposed:

- In flow of air

$$Ni_2(C_{50}H_{56}N_{10}O_4)Cl_4\cdot 9.5H_2O \xrightarrow{25–180℃,\ -9.5H_2O}$$

$$Ni_2(C_{50}H_{56}N_{10}O_4)Cl_4$$

$$\xrightarrow{180–475℃,\ -4Cl,\ -4C_6H_5,\ -2CH_2,\ -N_2,\ +2O_2} Ni_2(C_{24}H_{32}N_8O_8)$$

$$\xrightarrow{475–1000℃,\ -(C_{24}H_{32}N_8O_8),\ +nO_2} \text{Solid residue (11.6\%, NiO)}$$

- In flow of nitrogen

$$Ni_2(C_{50}H_{56}N_{10}O_4)Cl_4\cdot 8H_2O \xrightarrow{25–180℃,\ -8H_2O}$$

$$Ni_2(C_{50}H_{56}N_{10}O_4)Cl_4 \xrightarrow{180–310℃,\ -4Cl} Ni_2(C_{50}H_{56}N_{10}O_4)$$

$$\xrightarrow{310–370℃,\ -4C_6H_5,\ -6CH_2,\ -N_2} Ni_2(C_{20}H_{24}N_8O_4)$$

$$\xrightarrow{370–1000℃,\ -0.82(C_{20}H_{24}N_8O_4)} \text{Solid residue (15.5\% containing Ni=9.3\% and } 0.18(C_{20}H_{24}N_8O_4)\text{=6.2\%)}$$

The partial superposition of the mentioned stages of decomposition makes the assigning of a mass loss to a certain process probable one, especially for high degree of superposition as in the case of strong cation influence on ligand, that can be observed by comparison the curves of the Figs 2 and 4, Figs 3 and 5, respectively.

Conclusions

The $Ni_2(C_{50}H_{56}N_{10}O_4)Cl_4\cdot xH_2O$ contains $9.5H_2O$ in air, respectively $8H_2O$ in nitrogen as crystallization water, less as $TAMEN\cdot xH_2O$ that contains $11H_2O$ in air, $9H_2O$ in nitrogen, respectively. The TAMEN and its Ni(II) complex compound as $Ni_2(C_{50}H_{56}N_{10}O_4)Cl_4$ loose their crystallization water under 180°C.

On the whole, the $Ni_2(C_{50}H_{56}N_{10}O_4)Cl_4\cdot xH_2O$ thermal decomposition, is similar with the $TAMEN\cdot xH_2O$ thermal decomposition in air and nitrogen, after the Cl release:

- the first step is the loss of phenyl group followed of the loss of the $>N–CH_2–CH_2–N<$ group and the CH_2 fragments;
- the last, the degradation of 2,3-dimethyl- 5-pyrazolone group and its partially release in nitrogen, respectively its burning in air.

The main differences for thermal decomposition in air are:

- the higher temperature for decomposition beginning of the 2,3-dimethyl-5-pyrazolone group of Ni complex compound, about 475°C, in comparison with about 340°C for TAMEN as result of cation stabilizing effect on ligand by the bonds with two oxygen atoms belonging to antipyrine;
- the higher rate of oxidation process in the last stage of ligand degradation for $Ni_2(C_{50}H_{56}N_{10}O_4)Cl_4\cdot xH_2O$ in the temperature range of 475–590°C that can be assigned to the Ni catalytic action in oxidation reactions.

The main differences in nitrogen are:

- the higher temperature for the decomposition beginning of the 2,3-dimethyl-5-pyrazolone group of $Ni_2(C_{50}H_{56}N_{10}O_4)Cl_4\cdot xH_2O$, about 370°C, in comparison with about 340°C for the same ligand fragment of TAMEN;

- the lower rate in the last stage of ligand degradation for $Ni_2(C_{50}H_{56}N_{10}O_4)Cl_4{\cdot}xH_2O$, in the temperature range of 370–1000°C in comparison with TAMEN degradation. Both the differences can be assigned to a stabilizer Ni cation effect on the 2,3-dimethyl-5-pyrazolone group.

In air, the TAMEN was completely burned to volatile compounds whereas, $Ni_2(C_{50}H_{56}N_{10}O_4)Cl_4{\cdot}xH_2O$ gives solid NiO residue as result of thermal decomposition. In nitrogen flow, some solid organic deposit was arised from TAMEN decomposition, respectively metallic Ni and an undecomposed fragment of TAMEN were arised from $Ni_2(C_{50}H_{56}N_{10}O_4)Cl_4$.

The assigning of a mass loss to a certain process is a probable one, because the partial superposition of the stages of decomposition.

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