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# THERMAL ANALYSIS IN STRUCTURAL CHARACTERIZATION OF HYDRAZONE LIGANDS AND THEIR COMPLEXES

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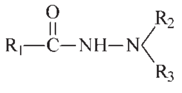
## Abstract

Results of our research on synthesis and characterization of complexes with acylhydrazone derivatives are described in this review paper. Structural characterization of newly synthesized complexes by thermal analysis (TG, DTA, DSC) is particularly emphasized in this paper. Thermal analysis enabled us to study not only structural changes of substances during thermal treatment, but also the mode of coordination and degree of deprotonation of acylhydrazones, as well as geometry of the coordination sphere of complexes, the structure of which had not been determined by X-ray analysis. Topics in this paper are as follows: complexes of dioxomolybdenum(VI) with tridentate hydrazones, usnic acid derivatives and their Cu(II) complexes, as well as transition metal complexes with 2,6-diacetylpyridine bis(hydrazones).

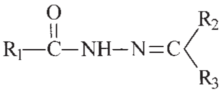
**Keywords:** hydrazone ligands, thermal analysis, transition metal complexes

## Introduction

Our studies have been concentrated on the chemistry of the complexes with hydrazone ligand systems for a long time [1–16]. Hydrazides (Scheme 1), expressing a great coordination capacity with transition metal ions represent a significant group of this type of ligands [17]. The facility of stable complexes formation is the characteristic not only of carboxylic acid hydrazides, but also of the derived corresponding acylhydrazones (Scheme 2).



**Scheme 1**



**Scheme 2**

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Intensified interest in the complexes of transition metals with hydrazides and hydrazones developed as a consequence of their increasing application in medicine, analytical chemistry, syntheses of novel heterogeneous catalysts of oxido-reduction processes, as well as in numerous fields of science and technology [17–18]. Among ligand systems, hydrazones belong to a special place because, quite a number of these compounds express biological activity and complex formation with transition metals sometimes resulting in a several-fold increase of this activity. This enables their application as antitumour, antiviral, bactericide and psychotropic agents [17]. A significant intensification of their pharmacological activity provoked by the introduction of bioelements into their coordination sphere prompted us to focus a part of our studies on the formation of the complexes just with Mo(VI) [1–3], Mo(V) [13], Cu(II) [5, 9–11], Fe(III) [10, 14], Co(II) [4, 6], Mn(II) [15] and Zn(II) [15][*] ions, and, on the other hand, on the examinations of their biological activity [9].

Bioactivity of this class of organic compounds can be increased by a careful choice of metal ion forming a complex. In addition, biological activity can be influenced by linking a hydrazide with pharmacologically active carbonyl compounds during condensation reactions, as well. Thus formed acylhydrazone derivative can also be employed as a chelating agent for the binding of a certain bioelement. In this way, with a choice of a suitable metal and carbonyl functional part, a higher biological activity comparing to the parental hydrazide agent can be achieved. A part of our studies was focused on such investigations. For this purpose we have decided to use usnic acid as a polyfunctional carbonyl component, and varying hydrazide part, different acylhydrazones [4] were produced and subjected to complex formation with Cu(II) ion [9].

In order to understand completely and to explain the biological action of both the ligands themselves and their complexes, it is necessary to determine their structural characteristics and stability in solid state and in solution. With this respect, X-ray structural analysis of monocrystals of these compounds plays an important role, because it represents an absolute method, not only for the detection of molecular structure, but also of the mode of three dimensional packing and total net of intermolecular interactions. Intermolecular forces and especially hydrogen bonds represent one of the key factors in a complex coupling of an active substance and a biological system. However, it is frequently impossible to obtain a substance in monocrystalline form and in such cases the application of other methods for a successful determination of structure is required. During our studies IR, UV-VIS, NMR and EPR spectroscopic methods were employed together with determinations of magnetic moment and molar conductivity. However, it was amazing how suitable thermal analysis was in the case of examination of our systems. It enabled us not only to follow a series of structural changes the compounds were subjected to during thermal treatment, but also to unambiguously determine the mode of coordination and geometry of novel compounds. Even in the case when a compound was characterized

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[*] Let us remember that just complexes of these elements with chelating ligands represent unavoidable constituents of each vitamin–mineral formulation in modern pharmaceutical industry.

by X-ray structural analysis, thermal analysis appeared to be extremely important, because serving as a reference system, it enabled us to comparatively define the structure of a substance which was impossible to obtain in a monocrystalline form.

This discovery prompted us to focus our attention not only on the synthesis of the compounds which could be of applicative significance, but also on some other systems of more fundamental properties, broadening significance of thermal analysis within the scope of our studies. For this purpose, bis(acylhydrazones) of 2,6-diacetylpyridine [4–6, 10, 12–16] were included in our examinations, since these compounds express antibacterial and antifungal properties [19], but also as pentadentates they can form extremely rare pentagonal-bipyramidal complexes of *3d* metals. This exclusive area of coordination chemistry became even more challenging to us due to the varying dentacity of bis(acylhydrazones) and possibility of their single and double protonation. This enabled us to follow the influence of possibility of coordination of polydentates through different donor atoms, as well as the influence of their increasing negative charge on coordination number and geometry of a complex depending also on the central metal ion. In these studies, thermal analysis was of an enormous help.

## Experimental

### *Synthesis*

### Dioxomolybdenum(VI) complexes with hydrazone ligands

Complexes of [$MoO_2$(L)S] type were prepared by heating a mixture of equimolar amounts of ethanolic solutions of $MoO_2(acac)_2$ (*acac*=acetylacetonate anion) and benzoylacetone 1-naphtoylhydrazone ($H_2L^1$), or salicylaldehyde *p*-hydroxybenzoylhydrazone ($H_2L^2$), in presence of monodentate donors S (solvent). Complexes of [$MoO_2$(L)$H_2O$] type were obtained in the reaction of acidic (HCl) aqueous solution of ammonium heptamolybdate and $H_2L$. Using chloroform as a non-coordinating solvent, desolvate complexes of [$MoO_2$(L)] type were obtained. Such complexes could also be obtained by two-hour heating of [$MoO_2$(L)S] at 105°C.

### Hydrazide derivatives of usnic acid and their complexes with Cu(II)

Synthesis of condensation derivatives was performed by refluxing equimolar quantities of usnic acid and α-naphthohydrazide, octanohydrazide, semioxamazide and thiosemicarbazide, respectively in absolute ethanol for two hours.

Complexes of copper(II) and above mentioned derivatives of usnic acid were obtained by refluexing copper(II) hydroxide and usnic acid derivatives (ligands) in absolute ethanol for two hours.

### Complexes of bis(hydrazone) derivatives of 2,6-diacetyl pyridine

Bis(acylhydrazones) complexes of transition metals (Co(II), Cu(II), Ni(II), Fe(III), Mo(V), Mo(VI), U(VI), Mn(II), Zn(II) and La(III) were prepared by template synthesis by refluxing metal salts, 2,6-diacetylpyridine (dap) and semioxamazide (sox) in molar ratio 1:1:2, in a suitable solvent (methanol, ethanol, and/or water). Identical complexes were obtained as products of a direct synthesis.

In an analogous way complexes of Co(II) and Cu(II) with ethyl-hydrazinoacetate (etha) instead of semioxamazide (sox) were obtained.

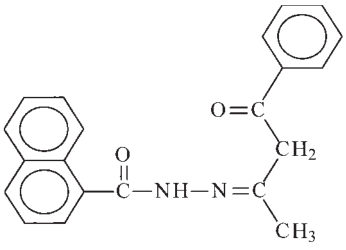
### *Measurements*

Elemental C, H, N analyses were carried out by standard micromethods at the Centre for Instrumental Analysis of the Faculty of Chemistry in Belgrade. Infrared spectra were recorded on a Perkin Elmer FTIR 1726x spectrometer as KBr discs, NMR spectra on a Gemini 2000 spectrometer at 200 MHz (DEPT technique) and electronic spectra on a GBC UV-VIS 911A spectrometer. Molar conductances were measured on a Jenway 4009 digital conductivity meter. The thermogravimetric analyses were carried out on a DuPont 9900 instrument with the 910 differential scanning calorimeter and the 951-thermogravimeter analyzer module. Heating rate: 10°C $\text{min}^{-1}$ in nitrogen atmosphere. Magnetic susceptibilities were measured at room temperature using a MSB-MKI balance (Sherwood Scientific Ltd., Cambridge, England) and $HgCo(SCN)_4$ for calibration. The diamagnetic corrections were performed employing the Pascal constants. The polycrystalline powder EPR spectra were recorded at 293, 195 and 77 K on a Varian E-104-A spectrometer, which operates in the X-band and uses DPPH as a standard. X-ray analyses of monocrystals were performed.

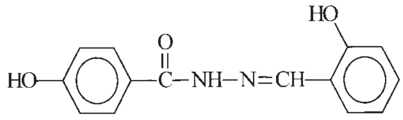
## Results and discussion

### *Dioxomolybdenum(VI) complexes with hydrazone ligands*

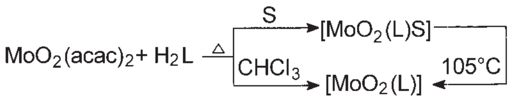
In addition to chemistry of technecium, renium and ruthenium, chemistry of molybdenum represents an area of fundamental chemistry of transition metals that has been the most rapidly developing during the last decade [20]. It has been widely applied within the scope of industrial catalysis and metallurgy [21–23]. Development of molybdenum chemistry was also supported by the role it plays in biological systems [24]. Within the second series of transition metals, only molybdenum represents a biometal, important for microorganisms, plants and animals. In oxomolybdenum complexes, which are the components of quite a number of redox systems that also take part in biological nitrogen fixation, higher oxidation states [25–27] are dominant. The interest in the synthesis of dioxomolybdenum(VI) complexes has intensified greatly upon identification of $MoO_2^{2+}$-group in the last oxidation step of numerous redox enzymes [28, 29]. Cofactors of these enzymes are most probably coordinatively unsaturated, which enables an efficient substrate binding. Introduction of dianionic tridentate ligand into coordination sphere of $MoO_2^{2+}$-group leaves an open active site on molybdenum. For that reason, dioxomolybdenum(VI) complexes with bibasic tridentate ligands occupy a significant place within the scope of fundamental chemistry of this metal. Our studies were devoted to relatively simple mixed complexes of dioxomolybdenum(VI) with tridentate acylhydrazones $H_2L^1$ (1-naphthoyl-hydrazone of benzoylacetone) (Scheme 3) and $H_2L^2$ (*p*-hydroxybenzoylhydrazone of salicylaldhehyde) (Scheme 4), and with different monodentate donors (S) weakly bound to molybdenum, which are in *trans*-position in relation to oxo-oxygen. The atom of oxo-oxygen is responsible for the elongation and weakening of the bond in its *trans*-position and because of that, the corresponding ligands can be easily substituted by different substrates. Functioning of molybdenum enzymes is beased on this easy substitution of *trans*-ligand with the molecule of a substrate [30]. The complexes synthesized throughout our studies (Scheme 5)[**] contain tridentate ONO dianion planar ligands ($L^{1-}$, i.e. $L^{2-}$) and *cis*-$MoO_2^{2+}$ cation. They can be divided into three groups.



**Scheme 3**



**Scheme 4**



(S= MeOH, EtOH, $H_2O$, DMSO, DMF, py, $PPh_3$)

**Scheme 5**

The first group includes solvated $[MoO_2(L)S]$ octhadral complexes (Fig. 1a) with monodentate S situated at sixth coordination site in *trans*-position in relation to oxo-oxygen. This makes these complexes labile with regard to substitution reaction of the following type: $[MoO_2(L)S]+S' \rightarrow [MoO_2(L)S']+S$. Based on reactions of this type qualitative order of Mo–S bond could be assumed to be: EtOH<MeOH<$H_2O$< DMF<py<DMSO<$PPh_3$. Desolvated $[MoO_2(L)]$ complexes obtained from chloroform as a non-coordinating solvent represent the second type of the complexes. They

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[**] acac – acetyl acetonate anion

were suggested to have a monomeric pentacoordinated structure (Fig. 1b), otherwise rare for oxo-molybdenum compounds. Complexes of the same stoichiometric composition were also produced by isothermal heating of [$MoO_2$(L)S] complex but they have polymeric octahedral structure (Fig. 1c).

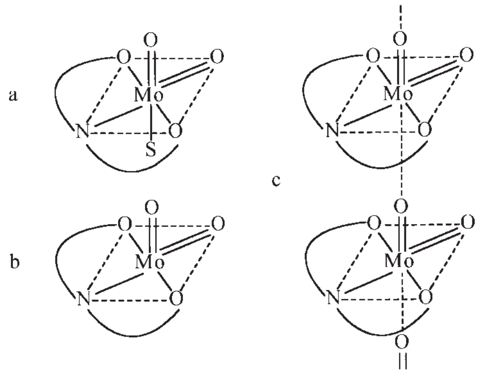


**Fig. 1** Schematic presentation and structure of [$MoO_2$(L)S] and [$MoO_2$(L)] complexes

All these complexes were characterized by elemental analysis, electron and IR spectra, thermal analysis (TG, DTA and DSC), as well as by determination of molar conductivity and magnetic susceptibility. In order to confirm structural assumptions of [$MoO_2$($L^1$)MeOH] complex, X-ray structural analysis [3] was employed and the results confirmed the monomeric octahedral structure. It should be emphasized that thermal analysis and its correlation with IR spectroscopy played a key role in detection of structural characteristics of the novel complexes [1, 2]. In this way it was established that the processes of structural transformations and thermal decomposition of the complexes can be presented by Scheme 6. This scheme is valid for the complexes with $H_2L^1$ and $H_2L^2$ ligand, as well. However, the fact that polymerization process of the complex with $H_2L^1$ ligand was recorded as an exothermic change, while in the complex with $H_2L^2$ ligand this process was detected by an endothermic peak on DSC curve, represents a key difference. This difference originates from the difference in structure and the mode of packing of the complexes with $H_2L^1$ and $H_2L^2$. Namely, different from 1-naphthoyl-hydrazone of benzoylacetone ($H_2L^1$), *p*-hydroxybenzoylhydrazone of salicylaldehyde ($H_2L^2$) has an extra oxygen atom (phenolic –OH group) that enables the formation of additional intermolecular hydrogen bonds and dictates different packing and more stable crystalline structure of the complex. More precisely, the decomposition of coordinated tridentate ligand $H_2L^2$ starts at 300°C and that of $H_2L^1$ at approximately 240°C. Based on these data it can be concluded that for structural transformations in the complex with $H_2L^2$ ligand which is

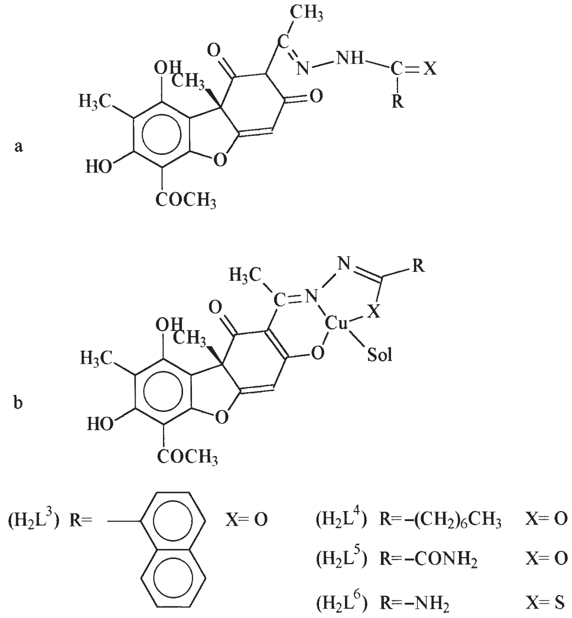
$$[MoO_2(L)S] \xrightarrow{-S} [MoO_2(L)] \xrightarrow{\approx 120°C} [MoO_2L]_n \xrightarrow{-L} MoO_3$$

**Scheme 6**

more stable, a larger energy consumption is necessary because of breaking of a higher number of intermolecular bonds. It is worth mentioning that the appearance of exothermic (for a series with $H_2L^1$), i.e. endothermic (for a series with $H_2L^2$) peak on TG curve which is not accompanied by the corresponding mass loss points to the polymerization proceeds immediately before tridentate starts to decompose. This transition of monomeric pentacoordinated structure into polymeric octahedral structure was recorded in $[MoO_2(L)S]$, but also in $[MoO_2(L)]$ complexes obtained from $CHCl_3$ solution. Complexes $[MoO_2(L)]$ obtained by thermic treatment of solvate complexes do not produce the above peaks pointing to already established polymeric structure of the complex. These studies confirmed without any doubt structural characteristics of novel complexes presented in Fig. 1.

*Hydrazide derivatives of usnic acid and their complexes with Cu(II)*

Usnic acid represents a natural antibiotic isolated from lichens, also known to possess a certain cytostatic activity [31]. It is characterized by a number of functional groups (phenol groups, as well as exo- and endocyclic keto-groups), which enables the synthesis of various derivatives. Only several of its acylhydrazide derivatives have been known till 1996 [32] and a part of our studies [7] was directed towards the synthesis of usnic acid derivatives with acylhydrazides of α-naphthoic ($H_2L^3$), caprylic ($H_2L^4$) and oxamic acid ($H_2L^5$), as well as with thiosemicarbazide ($H_2L^6$) shown in Scheme 7a. Derivatives of usnic acid have not been exactly characterized as judged by data from the available literature. This prompted us to perform a precise NMR



**Scheme 7**

characterization of all derivatives and, besides, to determine the structure of $H_2L^3$ derivatives employing X-ray structural analysis [7]. In this way, the structure of novel compounds was established and their biological activity was evaluated during further examinations [7]. Although biological activity of the derivatives did not exceed that of usnic acid itself, different from usnic acid, its derivatives behave as donors, which enabled the formation of the complexes. Somewhat later, our studies were focused on the synthesis and characterization of the complexes with Cu(II) ion and the following compounds were produced [$CuL^3$(EtOH)], [$CuL^4$(EMK)], [$CuL^5$(THF)] and [$CuL^6$(EMK)][***] presented in Scheme 7b. These complexes expressed a significantly higher antibacterial activity in comparison with usnic acid itself, as well as with its derivatives and Cu(II) ion [9]. They had a square-planar geometry with tridentately linked derivatives as dianions. This makes the complexes neutral and lipophilic and these properties play a role in their biological activity. Usnic acid, its derivatives and their complexes were further subjected to thermal analysis (TG, DSC) in nitrogen atmosphere within a temperature range from 20–600°C [8]. These examinations demonstrated that neither usnic acid derivatives, nor their complexes were more stable than usnic acid itself. Namely, hydrazide side chain introduced by condensation breaks and decomposes more easily at higher temperatures than much more stable polycyclic aromatic nucleus of usnic acid. On the other hand, one could expect an increased thermal stability of the ligands introduced into the complexes due to coordination. However, continuation and exothermic nature of Cu(II) complexes performed in an inert atmosphere that starts at lower temperatures comparing to free ligands, suggest autooxidation processes to occur. These processes are by all means catalyzed Cu(II) ion, and because of that the complexes expressed a lower thermal stability than the ligands themselves.

### *Complexes of bis(hydrazone) derivatives of 2,6-diacetyl pyridine*

With an aim of understanding better the influence of $d^n$ configuration of a transition metal and negative charge of polydentate ligand on the geometry of complex compounds, we have synthesized and characterized in detail sixteen complexes with 2’,2’’’-(2,6-pyridindiyl-diethylidene)dioxamohydrazide ($H_2$dapsox) [4–6, 10, 12–16], two complexes with dioxo-2,6-pyridindiylbis(ethylidine-1-hydrazinyl-2-ylidene)diacetic acid ($H_2$dapoamh) [14, 16] and two complexes with 2,6-bis-[1-(methoxycarbonyl-methyl-hydrazono)ethyl]pyridine ($H_2$dapetha) [11] (Table 1). A special attention has been paid to the effects of aforementioned factors on the possibility of rare pentagonal-bipyramidal (PBP) complex formation of *3d* metals. The formation of different geometries around *3d* metal ions can be explained by observing the distribution of *d* orbitals by the energy in PBP geometry (*dxy*, *dyz*; *dxy*; $dx^2$–$y^2$; $dz^2$), their occupation with electrons and direction towards donor atom orbitals, i.e. this explains different modes of polydentate coordination (Fig. 2).

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[***] EtOH – ethanol; EMK – ethyl-methyl ketone; THF – tetrahydro furane

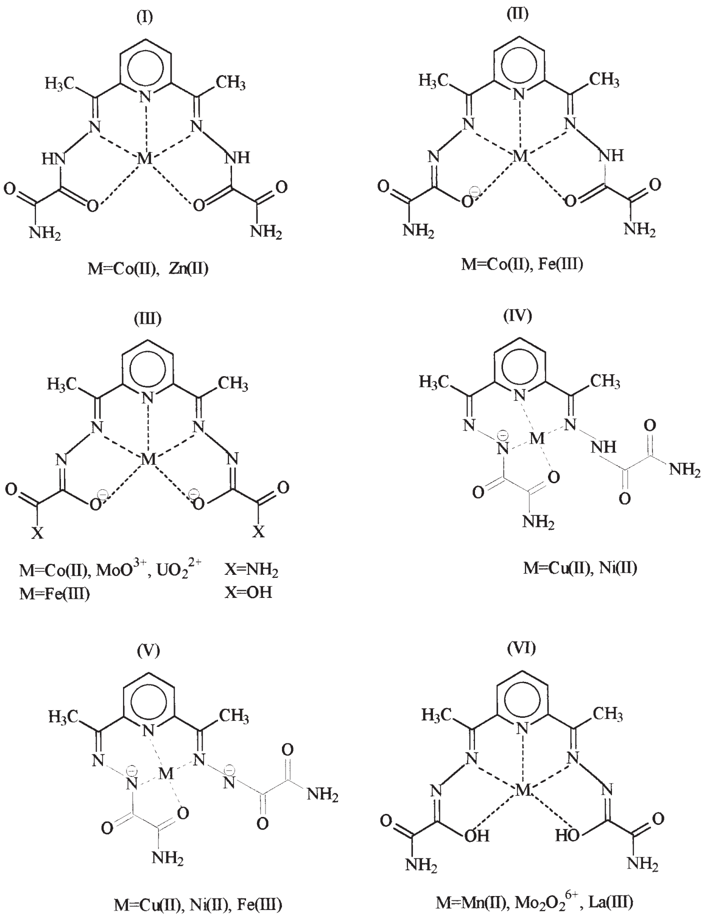


**Fig. 2** The mode of $H_2$dapsox and $H_2$dapoamh coordination

Thermal analysis was found to be suitable for the detection of the above mentioned modes of coordination of $H_2$dapsox, $H_2$dapoamh and $H_2$dapetha ligands and their mono- and dianions. The details on the processes of thermal decomposition of the complexes, 7, 11, 13, 14, 15 and 16, listed in Table 1 were described previously [12, 13, 15, 16] and here we will discuss the details on thermal analysis of the complexes 3, 5, 8, 9, 17 and 18 (Table 1). The structures with perchlorate anion were not subjected to thermal analyses because they can easily explode and decompose in a single step, which results in the appearance of a strong exothermic peak on DSC curve. Because of that, it is impossible to draw conclusions related to structural characteristics of these complexes.

The presence of crystalline and coordinated water in the structure of Co(II) complex (Table 1, compound 3) was confirmed by thermal analysis in nitrogen stream (Fig. 3) when it was observed that the process of endothermic crystalline water loss

**Table 1** Bis(hydrazone) complexes and the methods for their characterization

| No. | Complex | Geometry | Mode of binding | Methods for characterization |
|---|---|---|---|---|
| 1 | $[Co(H_2dapsox)(H_2O)(MeOH)](ClO_4)_2$ [4] | PBP | I | X-ray, IR, EA, $\Lambda_M$, $\mu_{eff}$ |
| 2 | $[Co(Hdapsox)(H_2O)_2]ClO_4$ [6] | PBP | II | IR, EA, $\Lambda_M$, $\mu_{eff}$ |
| 3 | $[Co(dapsox)(H_2O)_2]\cdot 6H_2O$ [6] | PBP | III | X-ray, TG/DSC, IR, EA, $\Lambda_M$, $\mu_{eff}$ |
| 4 | $[Cu(Hdapsox)(H_2O)]ClO_4$ [10] | SP | IV | X-ray, IR, EA, $\Lambda_M$, $\mu_{eff}$ |
| 5 | $[Cu(dapsox)(H_2O)]\cdot H_2O$ [5] | SP | V | X-ray, TG/DSC, IR EA, $\Lambda_M$, $\mu_{eff}$ |
| 6 | $[Ni(Hdapsox)(MeOH)_2]ClO_4$ [10] | Oh | IV | IR, EA, $\Lambda_M$, $\mu_{eff}$ |
| 7 | $[Ni(dapsox)]$ [16] | SPl | V | TG/DSC, IR, $\mu_{eff}$ |
| 8 | $[Fe(Hdapsox)Cl_2]\cdot H_2O$ [10] | PBP | II | TG/DSC, IR, EA, $\Lambda_M$, $\mu_{eff}$ |
| 9 | $[Fe(dapsox)Cl]\cdot H_2O$ [14] | SP | V | EPR, TG/DSC, IR, EA, $\mu_{eff}$ |
| 10 | $[Fe_2O(dapoamh)_2(H_2O)_2]\cdot 3H_2O$ [14] | PBP | III | X-ray, IR, EA, $\mu_{eff}$ |
| 11 | $[Mo_2O_2(H_2dapsox)_2]Cl_6\cdot 4H_2O$ [13] | PBP/PP | VI | EPR, TG/DSC, IR, $\Lambda_M$, $\mu_{eff}$ |
| 12 | $[MoO(dapsox)]^+$ [13] | PBP | III | EPR, EA, $\mu_{eff}$ |
| 13 | $[UO_2(dapsox)]\cdot 3H_2O$ [12] | PBP | III | TG/DSC, NMR, IR, EA |
| 14 | $[Mn(H_2dapsox)Cl(H_2O)]Cl\cdot H_2O$ [15] | PBP | VI | TG/DSC, IR, EA, $\Lambda_M$, $\mu_{eff}$ |
| 15 | $[Zn(H_2dapsox)(H_2O)_2]Cl_2\cdot H_2O$ [15] | PBP | I | TG/DSC, NMR, IR, $\Lambda_M$, |
| 16 | $[La(H_2dapsox)(NO_3)_2]NO_3$ [13] | PBP | VI | TG/DSC, IR, $\Lambda_M$ |
| 17 | $[Co(H_2dapetha)Cl_2]$ | TBP | – | TG/DSC, IR |
| 18 | $[Cu(H_2dapetha)Cl_2]$ [11] | TBP | – | X-ray, TG/DSC, IR, EA |
| 19 | $[Ni(H_2dapoamh)_2](ClO_4)_2$ [16] | Oh | – | X-ray |

PBP – pentagonal-bipyramidal; SP – square-pyramidal; Oh – octahedral; SPl – square-planar; PP – pentagonal-pyramidal; TBP – trigonal-bipyramidal
TG/DSC – thermal analysis; IR – infrared spectroscopy; EA – electron absorption spectroscopy; $\Lambda_M$ – molar conductivity; $\mu_{eff}$ – magnetic susceptibility

begins already at room temperature and ends at 71°C ($\Delta m_{\text{found}}$=4.32%; $\Delta m_{\text{calc}}$=4.05%) accompanied by the process of coordinated water removal which is completed at 165°C ($\Delta m_{\text{found}}$=8.25%; $\Delta m_{\text{calc}}$=8.11%). (Thermal analysis was performed using $[\text{Co(dapsox)(H}_2\text{O)}_2]\cdot\text{H}_2\text{O}$, formed upon long-term exposure of the complex 3 shown in Table 1 to the air.) Decomposition of the organic ligand started at 363°C to be followed by two exothermic steps up to the temperature of 525°C. In the first step of the coordinated ligand decomposition N–N bond of both side chains gets broken when $\text{NH}_2$–COCON– fragments are removed, but one coordinated hydrazide oxygen atom remains bound to Co ($\Delta m_{\text{found}}$=35.70%; $\Delta m_{\text{calc}}$=35.11%). The fact that N–N bond and not N=C bond is broken confirmed the presence of α-oxyazine form of dianionic pentadentate, coordinated via negatively charged oxygen atom (Fig. 2-III). In the second step, decomposition of dapsox$^{2-}$ residue ($\Delta_{\text{(total)found}}$=82.64%; $\Delta_{\text{(total)calc}}$=83.11%) affords CoO as the end-product.

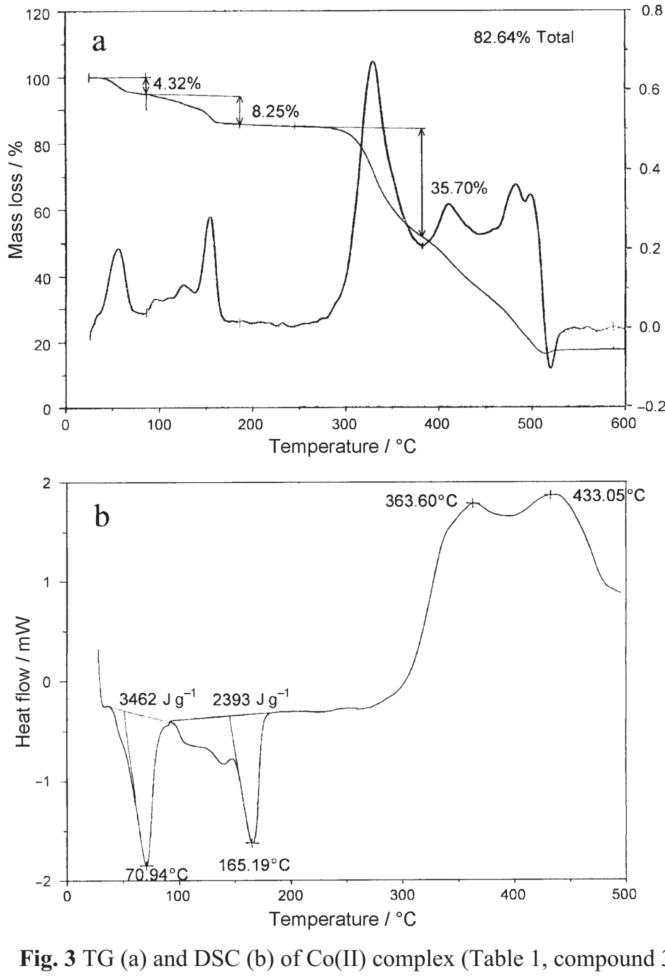


**Fig. 3** TG (a) and DSC (b) of Co(II) complex (Table 1, compound 3)

Data on thermal analysis of the Cu(II) complex (Table 1, compound 5) (Fig. 4) are in accordance with its structural characteristics [5]. In a single endothermic step that ends at 137.6°C, both crystalline and coordinated water get removed ($\Delta m_{\text{found}}$=8.69%; $\Delta m_{\text{calc}}$=8.36%), which could be explained by the participation of crystalline water in the formation of a higher number of hydrogen bonds. Removal of water molecules also means the disappearance of a number of hydrogen bonds which were taking part in the fixation of 'hanging' chain the conformation of which becomes more free and its higher mobility results in the break of the remained hydrogen bonds. This was recorded on DSC curve by an endothermic change that immediately proceeds the change resulting from water molecule removal during which this step is not followed by the mass loss on TG curve. Coordinated dapsox$^{2-}$ decomposes in two exothermic steps. The first step begins at 261°C when N–N bond of the 'hanging' chain breaks and $NH_2$–CO–CO–N fragment gets removed.

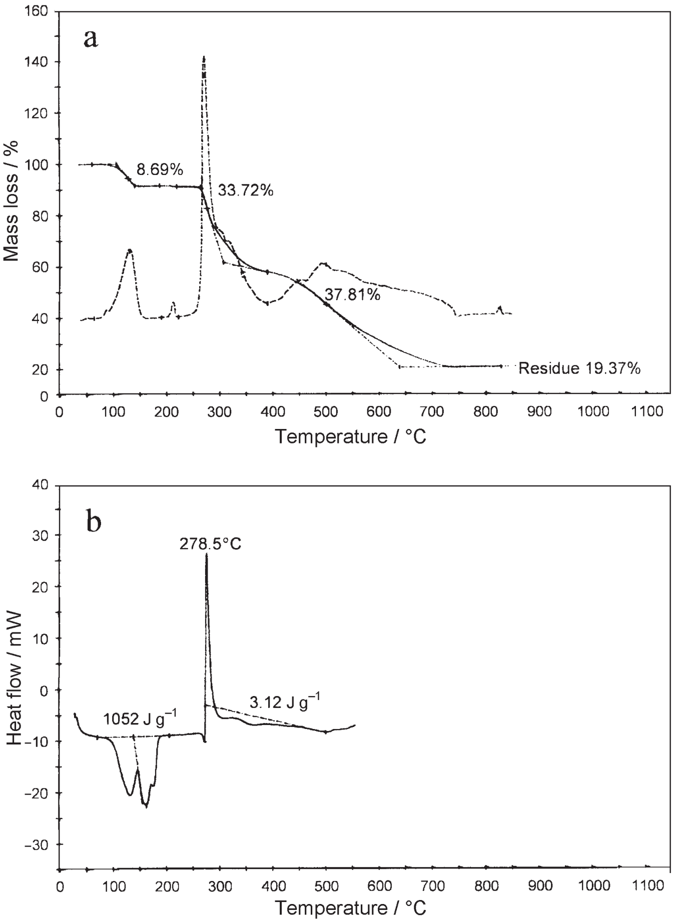


**Fig. 4** TG (a) and DSC (b) of Cu(II) complex (Table 1, compound 5)

At the same time N–C and C–O bonds of the five-membered chelate ring get broken and $NH_2$–C–CO– fragment gets removed (Fig. 2-V) ($\Delta m_{\text{found}}$=33.72%; $\Delta m_{\text{calc}}$=32.98%). Oxygen molecule of the terminal carbonyl group of five-membered chelate ring remains bound to Cu, producing after the second step of the organic ligand decomposition CuO as the end-product ($\Delta m_{\text{found}}$=19.37%; $\Delta m_{\text{calc}}$=18.47%). Breaking of the mentioned N–C and C–O bonds, but not of N–N bond demonstrates a significant participation of hydrazide >C=N–$N^-$–C–(=O)– form in coordination, what fits well the elongation of the first two and shortening of the third bond in comparison with the corresponding bonds in the 'hanging' chain.

Thermal analysis of Fe(III) complex (Table 1, compound 8) (Fig. 5) pointed to the presence of crystalline water, removal of which starts at 50°C and ends somewhat above 100°C ($\Delta m_{\text{found}}$=2.20%; $\Delta m_{\text{calc}}$=1.90%). At about 260°C the complex begins to decompose and this process proceeds in three exothermic steps. In the first step the

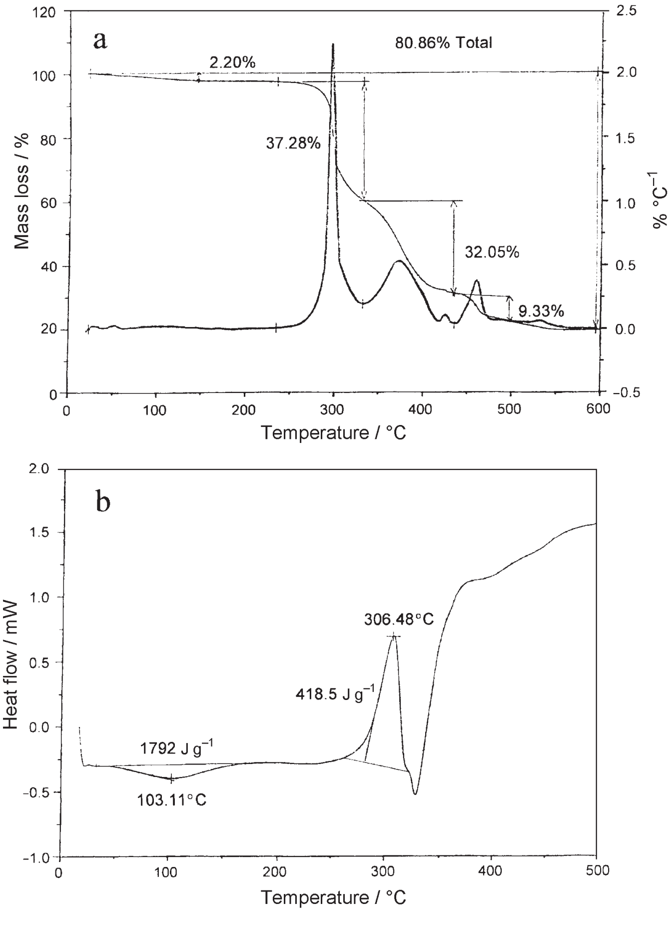


**Fig. 5** TG (a) and DSC (b) of Fe(III) complex (Table 1, compound 8)

entire neutral chain $CH_3$–C=N–NH–C(=O)–C(=O)–$NH_2$ and uncoordinated part of negatively charged chain $NH_2$–C(=O)– are removed and this is followed by a relatively mild exothermic change ($\Delta m_{found}$=37.28%; $\Delta m_{calc}$=36.75%). Both the second and third step are accompanied by a stronger exothermic change. In the second step, ethylenylpyridine fragment ($CH_3$–C(=)–$C_5H_3N$–) and a part of chlorine are removed ($\Delta m_{found}$=32.05%; $\Delta m_{calc}$=32.33%), while in the third step negatively charged segment of pentadentate (=N–N=C–$O^-$) and a part of oxygen get out ($\Delta m_{found}$= 9.33%; $\Delta m_{calc}$= 9.67%) and FeO·1/2$FeCl_2$ mixture remains as a solid residue. Exothermic nature of decomposition process of the coordinated ligand results from its oxidation with Fe(III) ion. A single ligand deprotonation led to the strengthening of Fe(III) ion bond with negatively charged chain and as a result, in decomposition process of the

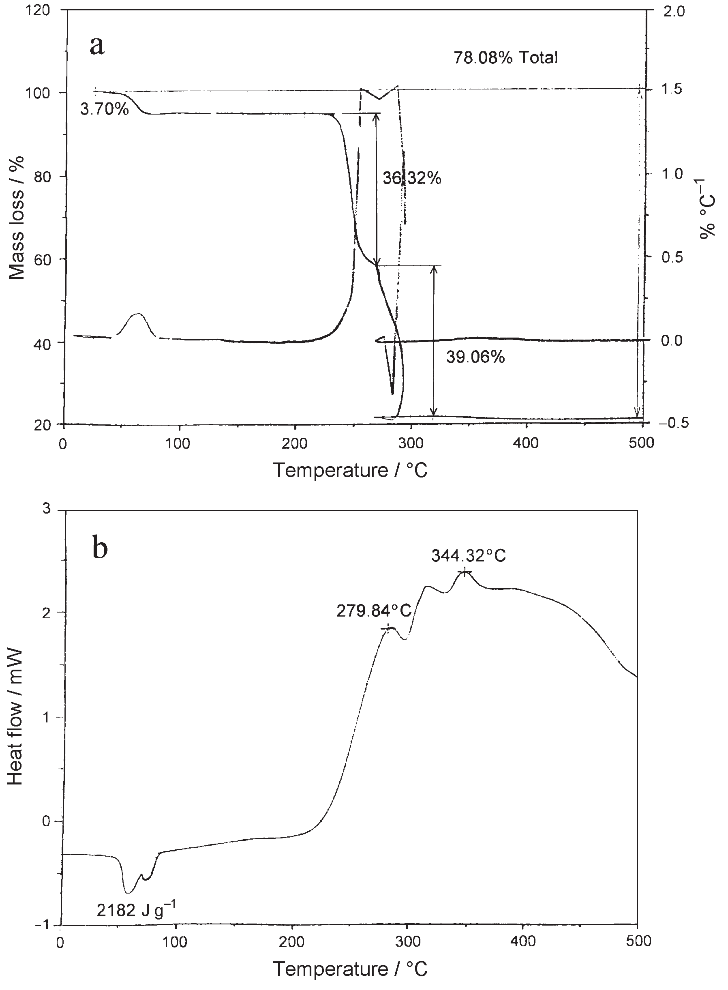


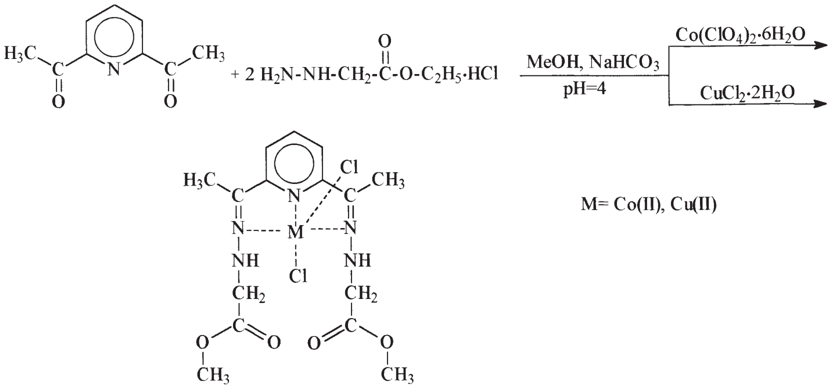
**Fig. 6** TG (a) and DSC (b) of Fe(III) complex (Table 1, compound 9)

Fe(III) complex (Table 1, compound 8), the processes of degradation of each of the two chains are clearly separated.

Identical mode of dapsox$^{2-}$ anion coordination (Fig. 2-V) found in template-produced Cu(II) and Fe(III) complexes (Table 1, compounds 5 and 9) was confirmed by thermal analysis of the complex 9 (Fig. 6). After removal of water at about 230°C, an abrupt two-step decomposition of tetradentately coordinated dianion begins, accompanied by an intensive exothermic change. Just as in the case of Cu(II) complex with dianionic ligand and of Fe(III) complex, in the first step non-coordinated part of singly-bound chain ($NH_2$–C(=O)–C(=O)$N^-$–) and a part of double-bonded chain ($NH_2$–C(=O)–C(=O)–, as well as a part of chlorine are removed, but a fraction of coordinated oxygen remains bound to the iron atom ($\Delta m_{found}$=36.32%; $\Delta m_{calc}$=36.14%). Mass loss ends at about 280°C and after that exothermic structural transformations within solid residue consisting of $FeO\cdot 1/2FeCl_2$ mixture ($\Delta m_{found}$=20.92%; $\Delta m_{calc}$=20.50%) occur. The intensive exothermic property of the decomposition process is due to the oxidation of the organic ligand with Fe(III) ion, just as in the case of the complex 8 (Table 1). Break of N–C and not of N–N bond of the doubly deprotonated chain demonstrates identical resonance forms of dapsox$^{2-}$ ligand present in the structures 5 and 9 (Table 1).

Based on experimental results, as well as on theoretical considerations reported in our previous papers [10, 15] we concluded that symmetrical electron distribution in $dxy$, $dx^2$–$y^2$ and $dz^2$ orbitals adds to the stability of PBP structure and as a consequence Co(II) and Mn(II) complexes of this geometry are the most stable among all *3d* metal complexes. Our investigations of thermal stability of novel PBP complexes (Table 1) just confirmed such a statement, since decomposition of bis(acylhydrazones) pentadentately coordinated with Co(II) and Mn(II) (Table 1, compounds 1 and 14, respectively) begins at the temperature above 300°C, while in the case of other *3d* PBP complexes at the temperatures up to 260°C, even at lower ones. So, since Zn(II) complexes are generally labile, taking into account complete occupation of the *3d* orbitals with electrons and repulsive interactions with donor atom orbitals, Zn(II) PBP complex was thermally the most unstable in the series of our complexes (Table 1, compound 15) and decomposition of $H_2$dapsox in this complex begins already at 200°C. In addition to the thermal stability of the complexes which was an important result, the mechanism of thermal decomposition was of key value for the detection of the coordination mode in neutral, mono- and dianionic forms of bis(acylhydrazones). More precisely, we have established almost a direct interrelationship between the thermal decomposition of the complex and mode of the polydentate coordination. So, whenever 2-acylhydrazone chains of pentacoordinated $H_2$dapsox, i.e. dapsox$^{2-}$ were symmetrically bound to the metal and symmetrically charged (Fig. 2-I, III, VI), decomposition of the complexes proceeded in two steps with symmetrical decomposition of the side chain bonds. It is interesting to mention that in all cases (Table 1, compounds 3, 11, 14 and 16) with the exception of the $Zn^{2+}$ complex (Table 1, compound 15), during the first step N–N bonds of both side chains get broken simultaneously. The break of N–N instead of N–C bonds demonstrates the double character of N–C bond in the presence of prevailing α-oxyazine form of the hydrazide in coordination. In the case of Zn(II) complex (Table 1, compound 15), at first the breaking of C–C bond occurs in both side chains. Only decomposition of $UO_2^{2+}$ complex (Table 1, compound 13) was found to be a single-step process, in spite of the presence of symmetrical pentacoordination of dianion such as in the Co(II) complex (Table 1, compound 3) (Fig. 2-III). The reason for this was found in a high degree of electron delocalisation and already established complete conjugation along the entire dapsox$^{2-}$ what led to the uniformity in the strength of bonds. In asymmetrically tetracoordinated dapsox $^{2-}$ in Cu(II) (Table 1, compound 5), Ni(II) (Table 1, compound 7) and Fe(III) (Table 1, compound 9) (Fig. 2-V) complexes, asymmetrical breaks of the side chain bonds occur, as a consequence of their ununiform coordination. Decomposition of bis(acylhydrazones) was also a two-step process and in the first step N–N bond of singly-bound chain and N–C bond of doubly-bound chain are broken. The break of N–C bonds demonstrates a single character of this bond and localization of negative charge on hydrazine nitrogen in all three above complexes. Three-step decomposition of polydentates with clearly distinguished decomposition processes of the first and then of the second chain was recorded only in the case of Fe(III) complex (Table 1, compound 8) with singly deprotonated Hdapsox$^-$. Although we have symmetrical pentacoordination here (Fig. 2-II), asymmetry of the side chains charge affects the asymmetry in their thermal decomposition. In the first step, the entire neutral chain gets removed, in the second one the ethylpyridine fragment and in the end the negatively charged polydentate segment go out.

Based on the electron absorption spectra, as well as magnetic characteristics of the complexes described in the present review article, the conclusions related to the effects of ligand deprotonation degree on the ligand field strength can be drawn. Namely, doubly deprotonated dapsox$^{2-}$ (Table 1, compounds 3, 5, 7, 9, 12, 13) and its derivative dapoamh$^{2-}$ (Table 1, compound 10) represent ligands of much stronger field than their monoanionic and neutral forms. Changes in the symmetry of electron density provoked by an increased strength of the ligand field due to deprotonation, also influences the difference in the geometry of the produced complexes. It has been established that the degree of polydentate deprotonation affects not only magnetic



**Scheme 8**

properties and spectral parameters of the central metal ion, but also the characteristics of the bond between a metal and donor atoms. A high degree of planarity together with delocalization of pentadentate acted increasing covalent property of metal-ligand bonds in *xy* plane. In dinuclear Fe(III) and Mo(V) complexes (Table 1, complexes 10 and 11, respectively), the above mentioned delocalisation includes also unpaired electrons of *dxy* orbitals of metal ions. This plays a key role in the increased intensity of magnetic coupling between metal ions in dimeric systems (such as Fe(III) ion in the complex 10 and Mo(V) ion in the complex 11, (Table 1) and this represents an original conclusion never reported before in relevant literature.

During further studies on coordination characteristics of bis(acylhydrazones), complexes of Co(II) and Cu(II) (Table 1, compounds 17 and 18, respectively) with $H_2$dapetha ligand produced by condensation of 2,6-diacetylpyridine (dap) with ethylhydrazino acetate (etha) were synthesized (Scheme 8). Namely, our intention was to examine a possibility of MNNCCO chelate rings formation by removing hydrazide oxygen from both side chains. However, as confirmed by X-ray structural analysis of Cu(II) complex (Table 1, compound 18) [11], a potential pentadentate coordinates only via three nitrogen atoms thus forming trigonal-bipyramidal geometry with two $Cl^-$ and pyridine nitrogen in equatorial plane. Analogous structure of the Co(II) complex (Table 1, compound 17) was postulated on the basis of elemental analysis, IR spectra and thermal analysis (TG, DSC), as shown in Fig. 7a and 8. The DSC curve indicates that the Co(II) complex is stable up to 250°C. At this temperature, a two-step exothermal decomposition begins. In the first step, the decomposition of non-coordinated side chain takes place and the second step proceeding slightly above 300°C, corresponds to the decomposition of tridentately coordinated part of the ligand and in the end $CoCl_2$ remains as a final residue. The DSC curve of the Cu(II) complex (Table 1, compound 18) is much more complicated (Fig. 9), as the structure consists of two crystallographically independent molecules and a single molecule of crystalline water. Therefore, the first endothermal peak in the DSC curve

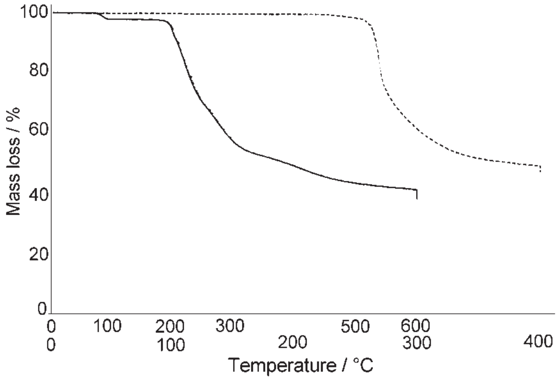


**Fig. 7** TG of Co(II) complex (- -) and Cu(II) complex (—) (Table 1, compounds 17, 18). The upper temperature scale refers to the Co(II) complex and the lower scale to the Cu(II) complex

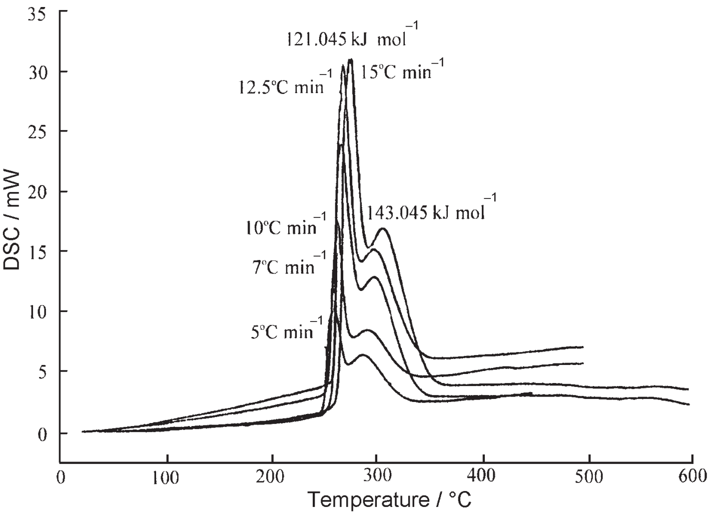


**Fig. 8** DSC of Co(II) complex (Table 1, compound 17)

of the Cu(II) complex corresponds to the loss of the crystalline water molecule. As the measurements were performed in an inert atmosphere (nitrogen), exothermal behaviour of decomposition of both complexes indicates the autooxidation processes, probably catalysed by copper(II) or cobalt(II) ions.

Tridentate property of bis(imine) derivatives of dap is rare and expressed only by condensation products of dap with hydrazines, such as $H_2$dapetha [11], or with amines [33]. On the other hand, it is not known whether hydrazide derivatives of dap (acylhydrazones) including our $H_2$dapsox, also express tridentate properties, taking

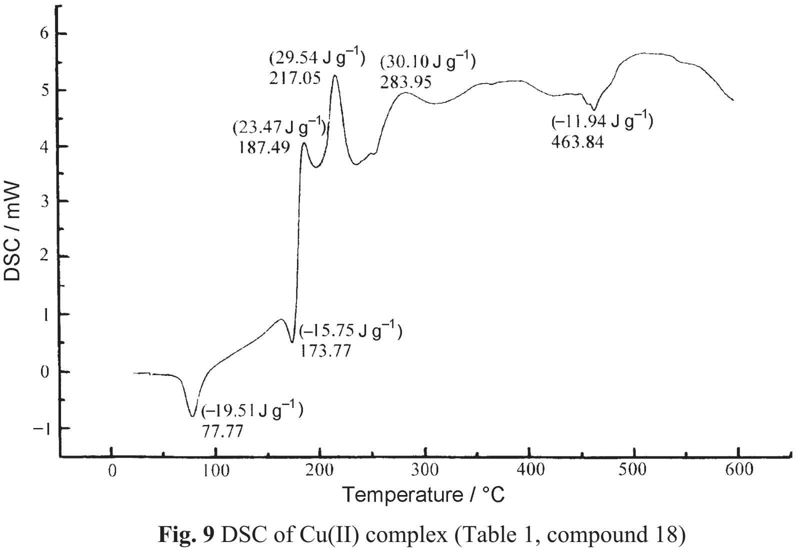


**Fig. 9** DSC of Cu(II) complex (Table 1, compound 18)

into account the formation of stable five-membered MNNCO rings. However, only in Ni(II) complex (Table 1, compound 19) with $H_2$dapoamh [16] ligand produced by hydrolysis of parental $H_2$dapsox, tridentate binding of two bis(acylhydrazones) and the formation of octahedral structure occurred. The geometry of the complex was confirmed by X-ray structural analysis [16]. This suggests that a great tendency of Ni(II) to formation of the structures with orthogonal metal-ligand bonds [34] involving octahedral geometry is crucial for unusual three-dentate coordination of acylhydrazones. Connected to that, our further studies will be concentrated on the syntheses of analogous systems with bis-coordinated bis(acylhydrazones) of 2,6-diacetylpyridines. Upon their characterization novel products will be checked for their biological and pharmacological activity with the hope that some of them might represent potential pharmaceuticals.

## Conclusions

In this paper application of thermal analysis for characterization of complexes has been shown, giving it a broader scope.

With molybdenum(VI) complexes, transformation of monomeric pentacoordinated structure into polymeric octahedral structure which could be easily detected by DSC curves was found to be particularly interesting. With the biologically active derivatives of usnic acid and their copper(II) complexes, it was shown that the stability of ligands in complexes was not higher than in non-coordinated form. Continual and exothermic nature of copper(II) complexes degradation starts at even lower temperatures compared to free ligands, indicated autooxidation processes promoted by copper(II) ion. Finally, transition metal complexes with 2,6-diacetylpyridine bis(acylhydrazones) were analysed. Thermal analyses were found rather suitable to define the structure, i.e. the manner of polydentate coordination in the novel systems. Comparison of thermal data of complex compounds, the structure of which was determined by X-ray structural analysis, with the corresponding data of the novel complexes of unknown structure, enabled to precisely define the geometry of these compounds. In addition, we had the possibility to follow a series of structural transformations during thermal decomposition of the novel complexes, as well as of some previously synthesized compounds. Comparative analyses of these results enabled to draw important conclusions related to coordination properties of *bis*(hydrazone) ligands.

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