Thermal behaviour of mixed ligand Co(II), Ni(II) and Cu(II) complexes containing terephthalate ligands

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Abstract

Thermal behaviour of a series of ternary Co(II), Ni(II) and Cu(II) complexes with terephthalate ion and some aromatic diamines has been studied by thermogravimetric and differential scanning calorimetric techniques. Dehydration processes of the complexes are very similar—most of them lose water in a single step. Thermal stability of the dehydrated products increases in the order Co < Cu < Ni for 2,2′-dipyridylamine and 2,2′-bipyridine containing complexes, but Cu < Co < Ni for 1,10-phenanthroline containing complexes. The investigated compounds with 2,2′-bipyridine are always the most easily decomposed. The molar dehydration enthalpies are calculated and the possible decomposition mechanisms are assumed. Relations between thermal behaviour of the complexes and their crystal structures, type of central atom and aromatic diamine, as well as the presence of coordinated and/or lattice water molecules are discussed.
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1. Introduction

The dianion of terephthalic (1,4-benzenedicarboxylic) acid, H_2tpht, is a potential bis-bidentate and bridging ligand. Most studies concerning ternary transition metal complexes with tpht ligands are concentrated on Cu(II) complexes and their magnetic properties that are influenced by exchange interaction through the bridging tpht ligands [1]. Although some mononuclear tpht complexes are known [2], binuclear and polymeric complexes with tpht ion acting as a bis-monodentate or bis-bidentate and bridging ligand are much more encountered [3–6].

The review of Donia [7] gives the survey of thermal behaviour of a large number of transition metal complexes and relationships between their structural properties and thermal stability. It follows that factors affecting the thermal stability of transition metal complexes in the solid state are numerous and not well understood. There are some examples in which the following order of the thermal stability was established: Cu < Ni < Co [8–10]. This is just reverse of

the Irving–Williams series [11], i.e. the stability order of the complexes in aqueous solution. However, it seems that the order Cu < Co < Ni predominate [12], but even an inverse trend of thermal stability [13] has been observed.

The thermal behaviour of ternary complexes is much less investigated than the behaviour of binary complexes. Here, we report the thermal behaviour of nine ternary Co(II), Ni(II) and Cu(II) complexes containing tpht ion and some aromatic diamines: 2,2′-dipyridylamine (dipya), 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy).

Four of investigated complexes were obtained as single crystals and their crystal structures have been solved and published elsewhere [2,5,6]. This fact could provide more insight into the factors determining their thermal stability and process of dehydration. In addition, an attempt to calculate energy of $M–OH_2$ and hydrogen bonds, and to compare the obtained values is present.

To the best of our knowledge, only thermal properties of several binary tpht complexes are described so far [14]. However, thermal properties of analogous ternary Co(II), Ni(II) and Cu(II) complexes with the same aromatic diamines and phthalate ion, pht (dianion of 1,2-benzenedicarboxylic acid) are studied [15,16]. This allows the comparison of similar complexes containing 1,2- or 1,4-benzenedicarboxylates.

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2. Experimental

2.1. Preparation and characterisation of the complexes

All complexes were prepared in a similar way using the procedure which was described in the previous paper [2]. Microcrystalline products were obtained from dilute H_2O/EtOH solutions containing M^{2+} ions (M = Co, Ni and Cu), tpht and diamine ligands in a 1:1:1 molar ratio. They are stable in air and insoluble in all common solvents. The complexes were previously characterised by elemental analysis, magnetic measurements, IR and diffuse-reflectance spectroscopy [2].

Thermogravimetry (30–700 °C range) was performed on a Perkin-Elmer model TGS-2 thermobalance. Differential scanning calorimetry (45–300 °C range) was performed on a Perkin-Elmer model DSC-2 calibrated with indium as a standard ($\Delta_{fus}H°$; the accuracy ±1%). The heating rate was 10 °C min^{-1} using less than 10 mg sample mass. The furnace atmosphere consisted of dry nitrogen at a flow rate of 60 cm^3 min^{-1}. The TG, DTG and DSC curves of the samples were used to determine the total content of water of crystallisation, residual metal oxide and dehydration enthalpy.

Some of the complexes were characterised by X-ray powder diffraction (XRPD) analysis using Philips PW1710 diffractometer with a curved graphite monochromator and Cu Kα radiation ($\lambda = 1.5418$ Å).

3. Results and discussion

The general formula of the investigated complexes is M(tpht)(diamine)·xH$_2$O (M = Co(II), Ni(II) and Cu(II); diamine = dipya, phen and bipy), with $x = 1$–5, while individual empirical formulae are given in Table 1. In the case of known crystal structure, the formulae showing coordination entity are listed, too. In the further text the complexes will be denoted by numbers from Table 1.

In the average, Cu complexes contain less H_2O than the similar Co and Ni complexes. This was already observed in the case of pht complexes [16] and can be attributed to the more regular coordination polyhedra of Co and Ni complexes, with 6 as an usual coordination number. Thus, coordination polyhedra of Co and Ni are often supplementary filled up with H_2O molecules.

The further discussion will start with a short description of the known structures, which will be later related to the thermal properties of obtained microcrystalline products.

The complexes 1 and 2 are isostructural and mononuclear; they consist of discrete complex units with central atoms in a slightly distorted octahedral environment. Surprisingly, tpht is coordinated by only one of its COO groups in a chelate mode [2].

Due to the bridging role of tpht ions, which are asymmetrically coordinated as bis-bidentate and bis-chelate lig-

ands, complex 3 forms zigzag chains. The coordination of the Cu(II) ions is very distorted octahedral and one lattice H_2O molecule per formula unit is present [5].

The crystal structure of [Co(tpht)(phen)(H$_2$O)]$_n$, containing the same ligands as 4, has been solved using room temperature [5] and low temperature data [4]. Apparently, significantly higher H_2O content in our product (Table 1) eliminates the possible isostructurality. The distinction could be attributed to the different synthetic routes.

On the other hand, 6 is very similar to the above-mentioned [Co(tpht)(phen)(H$_2$O)]$_n$ and its formula should be written as [Cu(tpht)(phen)(H$_2$O)]$_n$. The crystal structure determination [6] has shown that 6 consists of zigzag chains with tpht acting as amphimonodentate bridging ligand, whereas Cu(II) ions are in a deformed trigonal-bipyramidal environment. However, the investigated sample showed slightly higher H_2O content (Table 1). The XRPD pattern of microcrystalline product confirmed its identity to the single crystal data, but some broadening of the diffraction maxima was observed. The discrepancy between formulae of microcrystalline and single crystal products can be explained by taking into account that in the structure there is a small void ($V \approx 25$ Å^3) at 0, 0.5, 0 site [6]. The void volume is smaller than the expected volume of H_2O molecule (ca. 40 Å^3). Thus, during the fast precipitation of the very insoluble microcrystalline material such voids very probably capture H_2O molecules causing a slight distortion of the crystal structure and lowering its crystallinity; contrary, the void is empty in the case of slow growing single crystal. According to these facts, excess of 0.3H_2O molecules present in 6 is located statistically in the whole structure, so the true formula should be written as {[Cu(tpht)(phen)(H$_2$O)]·0.3H$_2$O}$_n$. The lattice H_2O molecule form neither classical O–H $\cdots$ O nor N–H $\cdots$ O hydrogen bonds. Only four C–H $\cdots$ O contacts, with C $\cdots$ O distances in the range 3.09–3.17 Å and the corresponding –H $\cdots$ O distances in the range 2.42–2.67 Å are possible [6].

Crystal structures of other investigated complexes are not known. However, XRPD patterns of 4, 5, 7 and 8 showed that the corresponding Co–Ni pairs (i.e. 4 and 5, as well as 7 and 8) are isostructural, just as 1 and 2 [2]. As expected, the complexes with different diamines do not have the same structures because of different bulkiness and planarity/non-planarity of used diamines. Nevertheless, the confirmed isostructurality, together with very similar physical and spectral properties [2], indicate that the coordination mode of tpht ion is very probably identical in all Co and Ni complexes, so they could be presented by the formula [M(tpht)(diamine)(H$_2$O)$_2$]·2H$_2$O similar to the 1 and 2.

Results of TG and DSC analyses: the total water content, the initial dehydration temperature ($T_{deh,i}$), the final dehydration temperature ($T_{deh,f}$), the temperature of DSC peak maximum (T_{max}), molar dehydration enthalpy ($\Delta_{deh}H_m°$) and the initial decomposition temperature ($T_{dec,i}$) are listed in Table 1. The TG and DSC curves are given in Figs. 1 and 2.

Table 1
Results of TG and DSC analyses

No.	Empirical formula and formula showing coordination entity	H_2O content (wt.%), [found (calculated)]	$T_{deh,i}$ (°C)	$T_{deh,f}$ (°C)	T_{max} (°C)	$\Delta_{deh} H_m^\circ$ (kJ mol^{-1})	$T_{dec,i}$ (°C)	Fragmentation	
								Up to T (°C)	Mass loss (wt.%) [found (calculated)]
1	Co(tpht)(dipya)·5H$_2$O, [Co(tpht)(dipya)(H$_2$O)$_2$]·3H$_2$O	17.90 (18.60)	64	108	115	248	263	392	75.6 (75.6) (5H$_2$O + CO)
2	Ni(tpht)(dipya)·5H$_2$O, [Ni(tpht)(dipya)(H$_2$O)$_2$]·3H$_2$O	18.32 (18.61)	68	121	128	243	300	–	–
3	Cu(tpht)(dipya)·H$_2$O, {[Cu(tpht)(dipya)]·H$_2$O}$_n$	4.22 (4.32)	76	105	110	49	279	344	35.9 (34.0) (H$_2$O + C$_5$H$_5$N + tpht)
4	Co(tpht)(phen)·4H$_2$O	14.86 (15.16)	86	145	139	248	316	381	80.4 (78.9) (4H$_2$O + CO)
5	Ni(tpht)(phen)·4H$_2$O	14.55 (15.17)	94	152	148	218	331	421	41.2 (41.0) (4H$_2$O + CO + phen)
6	Cu(tpht)(phen)·1.3H$_2$O, {[Cu(tpht)(phen)(H$_2$O)]·0.3H$_2$O}$_n$	5.43 (5.43)	90, 144	127, 174	124, 178	16[a], 61[b] (77)[c]	277	323	57.8 (56.5) (1.3H$_2$O + tpht)
7	Co(tpht)(bipy)·4H$_2$O	15.65 (15.97)	100	150	154	252	254	314	73.7 (74.3) (4H$_2$O + CO)
8	Ni(tpht)(bipy)·4H$_2$O	15.98 (15.98)	80	162	177	236	281	–	–
9	Cu(tpht)(bipy)·1.8H$_2$O	7.84 (7.79)	89	265	128	104	265	–	–

[a] The molar dehydration enthalpy after removal of 0.3 mol H$_2$O.
[b] The molar dehydration enthalpy after removal of 1.0 mol H$_2$O.
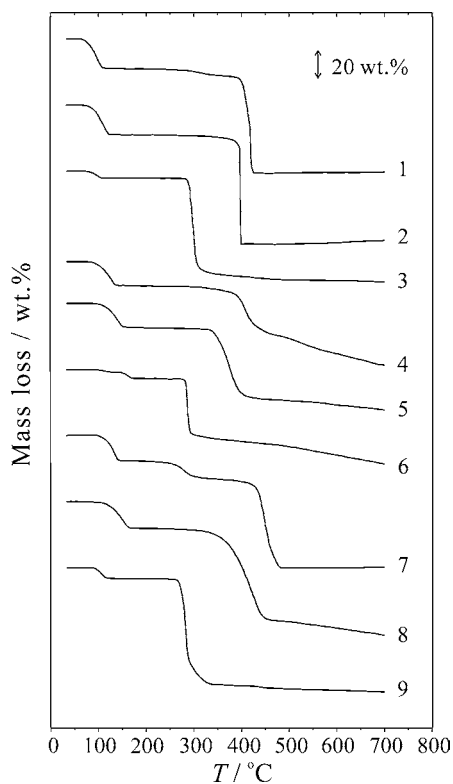[c] The overall molar dehydration enthalpy.

Fig. 1. TG curves obtained at heating rate of $10\,^{\circ}C\,min^{-1}$ in flowing N_2 (the numbers correspond to the number of complex from Table 1).

Fig. 2. DSC curves obtained at heating rate of $10\,^{\circ}C\,min^{-1}$ in flowing N_2 (the numbers correspond to the number of complex from Table 1).

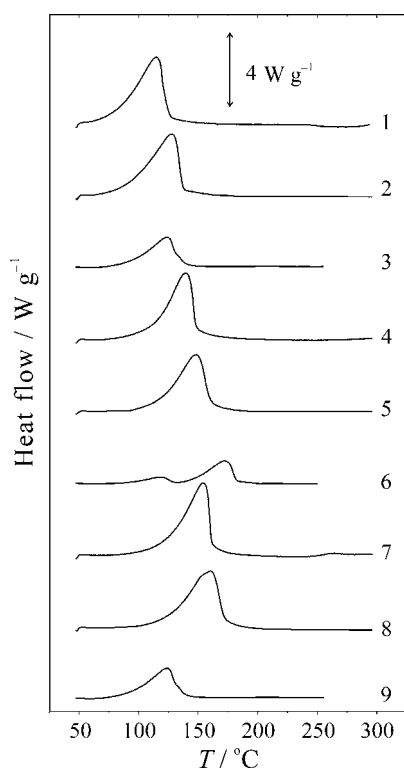### 3.1. Dehydration

The complexes 3, 4, 6, 8 and 9 can be easily obtained as anhydrous compounds, while in 1, 2, 5 and 7 remains 0.1, 0.2, 0.2 and 0.1 mol of the total H_2O content, respectively. These remaining water molecules are eliminated in the subsequent, almost horizontal step and further decomposition usually begins before the compounds are completely dehydrated. Similar behaviour was already noticed during the dehydration of some ternary pht complexes [15,16].

The dehydration processes for the most of complexes are very similar—they lose water in a single step and it is not possible to distinguish between coordinated and lattice H_2O molecules. The only exception is the complex 6, which dehydrates in two well separated steps. Its TG curve (Fig. 1) clearly indicates presence of loosely bound lattice (0.3 mol) and more strongly bound coordinated (1 mol) H_2O molecule. This is in accordance with the previous discussion and the formula given in Table 1.

Sample 3 is monohydrate and the present H_2O is not co-ordinated [5]. Its final dehydration temperature is $105\,^{\circ}C$ and it is evident (Table 1) that this lattice H_2O molecule can be removed up to about $100\,^{\circ}C$. The loss of lattice H_2O molecules which occurs below $120\,^{\circ}C$ is also found for some ternary Ni(II) complexes [17]. In other cases the final dehydration temperatures are higher (Table 1), which is in agreement with approved or assumed (see above) coexistence of coordinated and lattice H_2O molecules.

For dipya and phen complexes the initial dehydration temperatures, $T_{deh,i}$, increase in the order Co < Ni < Cu, and for bipy complexes in the order Ni < Cu < Co. The observed sequence for phen complexes is analogous to the previously described pht complexes [16]. It is also interesting to compare $T_{deh,i}$ for pairs of isostructural Co and Ni complexes: with one exception (for 7 and 8) all characteristic temperatures are higher for Ni complexes.

Although in respect to phen and bipy, dipya is capable to form an additional hydrogen bond, its complexes always have the lowest $T_{deh,i}$, $T_{deh,f}$, and T_{max} (Table 1). This means that they easily and quickly lose H_2O that can be attributed to the nature of dipya, which is the only non-planar ligand, used. According to this, the escape of H_2O should be easier through the channels in the structure when present diamine ligand is not planar.

The observation that we were not able to distinguish between coordinated and lattice H_2O molecules can be explained by the fact that a single hydrogen bond is weaker than coordinative M–OH_2 bond, but every lattice H_2O molecule is usually involved in two, sometimes in three hydrogen bonds. The energy of two and three hydrogen bonds could be higher than the energy of one coordinative bond.

In order to obtain more insight into dehydration processes, DSC analysis of the complexes was performed up to $300\,^{\circ}C$. The expected endothermic effect for dehydration is observed in the DSC curve of all complexes, and from this effect the molar dehydration enthalpies ($\Delta_{deh}H_m^{\circ}$) are calculated

and together with DSC peak maxima (T_{max}) summarised in Table 1.

DSC curves for the most complexes compose of a unique endothermic peak (Fig. 2). Only DSC curve for 6 has two maxima (at 124 and 178 °C), because this complex, as shown by TGA, is dehydrated in two steps.

DSC curves for all Co and Ni complexes (Fig. 2) are very similar and their maxima are shifted to the higher temperatures in the following order: dipya < phen < bipy (Table 1). $\Delta_{deh}H_m^\circ$ for Co and Ni complexes are close to each other (217.5–251.9 kJ mol^{-1}), and dipya complexes do not clearly show the presence of an extra H_2O molecule. The values for Ni complexes are always lower than for Co complexes with the same ligand. If different number of present H_2O molecules is taken into account, similar $\Delta_{deh}H_m^\circ$ values are already found for some ternary Co and Ni complexes [18,19].

The maxima of DSC curves for Cu complexes are shifted to the higher temperatures (Fig. 2) in the following order: dipya < phen < bipy, but $\Delta_{deh}H_m^\circ$ values are substantially smaller than those for Co and Ni complexes (Table 1). This is in agreement with smaller number of H_2O molecules in their formulae. Published $\Delta_{deh}H_m^\circ$ values for some other ternary Cu complexes [18] are similar to the values observed for 3, 6 and 9 in this study.

The ratio of $\Delta_{deh}H_m^\circ$ values for 3, 6 and 9 (49:77:104 ≈ 1:1.6:2.1) only approximates the ratio (1:1.3:1.8) of H_2O molecules found (Table 1). From $\Delta_{deh}H_m^\circ$ the bond energies of lattice H_2O are 49 for 3 and 53 (=16/0.3) kJ mol^{-1} for 6, while the bond energy of coordinated H_2O for 6 is 61 kJ mol^{-1}. According to these values, it seems that 9 contains 1 mol of coordinated and 0.8 mol of lattice H_2O. Because of the polymeric nature of 3 [5] and 6 [6], the probable structural formula for 9 is $\{[Cu(tpht)(bipy)(H_2O)]\cdot 0.8H_2O\}_n$.

3.2. Energies of coordinative M–OH$_2$ and hydrogen bonds

Determined enthalpies of dehydration and known crystal structures of some investigated complexes enable to calculate the mean energy (enthalpy) of hydrogen and M–OH$_2$ bonds. Apparently, the first three complexes (Table 1) can be used as a suitable starting set for this calculation. In 1 and 2 there are 11 hydrogen bonds per molecule [2], which means that, besides the H_2O molecule which is also bonded to the amine N from dipya, every H_2O molecule participates in 2 hydrogen bonds; in addition two M–OH$_2$ bonds exist. The complex 3 also contains dipya and three hydrogen bonds, but H_2O molecule is not coordinated [5].

$\Delta_{deh}H_m^\circ$ value of 3 is 49 kJ mol^{-1}. Since only three hydrogen bonds exist therein, the mean energy of hydrogen bond (per 1 mol of H_2O) is about 16 kJ. Because in 1 and 2, as stated above, there are 11 hydrogen bonds, their overall energy is approximately 180 kJ mol^{-1}. By subtracting this result from the experimental $\Delta_{deh}H_m^\circ$ values it is possible

to calculate the energy of M–OH$_2$ bonds. Thus, about 68 and 63 kJ mol^{-1} is obtained for 1 and 2, respectively. Since in both cases there are two coordinated H_2O molecules, the calculated values should be divided by 2, so the final mean M–OH$_2$ bond energies for 1 and 2 are 34 and 32 kJ mol^{-1}, respectively.

Similar calculations for complexes 4, 5, 7 and 8 with eight hydrogen and two M–OH$_2$ bonds assumed resulted in mean M–OH$_2$ bond energies: 60 (for 4), 45 (for 5), 62 (for 7) and 54 kJ mol^{-1} (for 8).

Owing to always smaller $\Delta_{deh}H_m^\circ$ values for Ni complexes in comparison to Co complexes with the same diamine ligand, the Ni–OH$_2$ bonds are weaker than the Co–OH$_2$ bonds. This is just opposite to the trend of hydration energies of gaseous Co(II) and Ni(II) ions, lattice energies of corresponding compounds [20] and to the M–OH$_2$ bond distances, where for isostructural complexes Ni–OH$_2$ distances are shorter than Co–OH$_2$ [2].

The mean Cu–OH$_2$ bond energy in 6 and 9 can be calculated, too. If 0.3 mol of lattice H_2O molecule and the well-separated thermal effect of its elimination in 6 are neglected, this compound has explicitly one coordinated H_2O, which builds two additional hydrogen bonds. Based on the above-calculated mean energy of hydrogen bond ($\approx$16 kJ mol^{-1}) Cu–OH$_2$ bond energy is ca. 29 kJ mol^{-1}.

With assumption that in 9 there are 0.8 lattice and 1 coordinated H_2O molecule and that both of them participate in two hydrogen bonds, the calculated energy of Cu–OH$_2$ bond is about 46 kJ mol^{-1}. Thus, within series of Co, Ni and Cu complexes containing the same diamine ligands, Cu–OH$_2$ bonds are always the weakest.

From the previous considerations and calculated values, it can be concluded that the energy of two hydrogen bonds is approximately equal to or slightly lower than the energy of one coordinative bond. This observation explains the impossibility to distinguish coordinated and lattice water molecules in described complexes.

Some limitations of the above approach must be emphasised. First, bond energies depend on bonds geometry, which are different within one complex and from complex to complex, too; these fine details are not known for all samples. This could be a reason for dispersion (from 29 to 62 kJ mol^{-1}) of calculated M–OH$_2$ bond energies, which also present mean values only. Second, three hydrogen bonds in 3 are in the range 2.743–2.920 Å [5], i.e. they could be described as "normal" to long. It is, therefore, possible that the calculated mean energy of hydrogen bonds (16 kJ mol^{-1}) is slightly underestimated causing that the mean energy of M–OH$_2$ bonds is overestimated. Finally, we expect that there is something like "resistance of crystal lattice" to the water escaping. This is previously shown by disordering and partial or total amorphisation of investigated samples after dehydration [16]. During this process some bonds are broken, some other bonds could appear, but, generally speaking, the energy of such system must be higher than the energy of well-ordered crystal lattice. Thus, the calculated bond

energies should be described as "effective values" and they take into account this and probably some other phenomena.

3.3. Thermal decomposition of anhydrous compounds

Thermal properties of the complexes were observed from room temperature to 700 °C and only complexes 2, 7 and 8 are totally decomposed in this range (Fig. 1). However, while 2 and 7 are already decomposed up to 399 and 481 °C, respectively, the residual mass of 8 slowly decreases above 451 °C and reaches the theoretical value about 700 °C. The oxides of MO type were confirmed as residues (2: found 15.5%, calculated 15.4%; 7: found 17.8%, calculated 16.6%; 8: found 16.8%, calculated 16.6%). In other cases, the residue does not reach constant mass up to 700 °C perhaps forming mixtures of different oxides and/or carbides, which are also found in the study of some ternary pht complexes [15]. Under N_2 atmosphere, the constant mass in some pht complexes is not always reached even up to 850 °C [16].

After dehydration, all Co complexes (1, 4 and 7) decompose via several steps (Fig. 1 and Table 1), also confirmed by the presence of several DTG maxima. In all cases decomposition process starts by decarboxylation and lost of CO. Similar fragmentation is found during the thermal decomposition of mixed Cu(II) complexes with pht ligands [15] and zinc phthalate [21]. Further steps are more or less irresolvable. Still, up to 479 °C, removal of $4H_2O$ + tpht could be assumed for complex 4, but agreement between found (53.8%) and calculated (50.3%) value is not so good.

The decomposition of Ni and Cu complexes is practically a single step process, but only 2 is fully decomposed in this step, while the other samples show a predominant step and slow weight loss after that (Fig. 1).

It could be assumed that the residue mass in decomposition of complex 3 corresponds to the removal of $H_2O + C_5H_5N$ + tpht, while the residue mass for complex 6 corresponds to the removal of $1.3H_2O$ + tpht. Both possibilities were found previously during the study of the analogous mixed Cu complexes with dicarboxylate ions and heterocyclic polyamines [15], as well as in the investigation of thermal stability of some ternary pht complexes [16]. The differences were explained by the different π-acceptor abilities of the aromatic polyamine ligands [15]. In the complexes containing strong π-acceptors (such as phen), the Cu–N bond should be stronger than the Cu–O bond and the dicarboxylato ligand is removed first. If diamine ligands are weak π-acceptors (like dipya), the order of elimination is reversed. According to this, it can be assumed that 3 probably decomposes in two running steps that were not separable. The first step corresponds to the removal of C_5H_5N segment of dipya and subsequent to the removal of tpht. However, complex 5 does not fit in this scheme (Table 1).

For complexes 8 and 9 removal of total H_2O content + C_5H_4N + tpht in the predominant step could be expected by analogy. However, the calculated residual masses are 3–5% higher than the observed values. This indicates that the frag-

mentation very probably is not so simple or that decomposition steps are strongly overlapped.

3.4. Thermal stability

The initial decomposition temperatures ($T_{dec,i}$) for dipya and bipy complexes increase as Co < Cu < Ni, and for phen complexes as Cu < Co < Ni (Table 1, Fig. 3). This means that anhydrous Ni complexes are the most stable, no matter what diamine ligand is present. It should also be emphasised that Ni complexes are always more stable
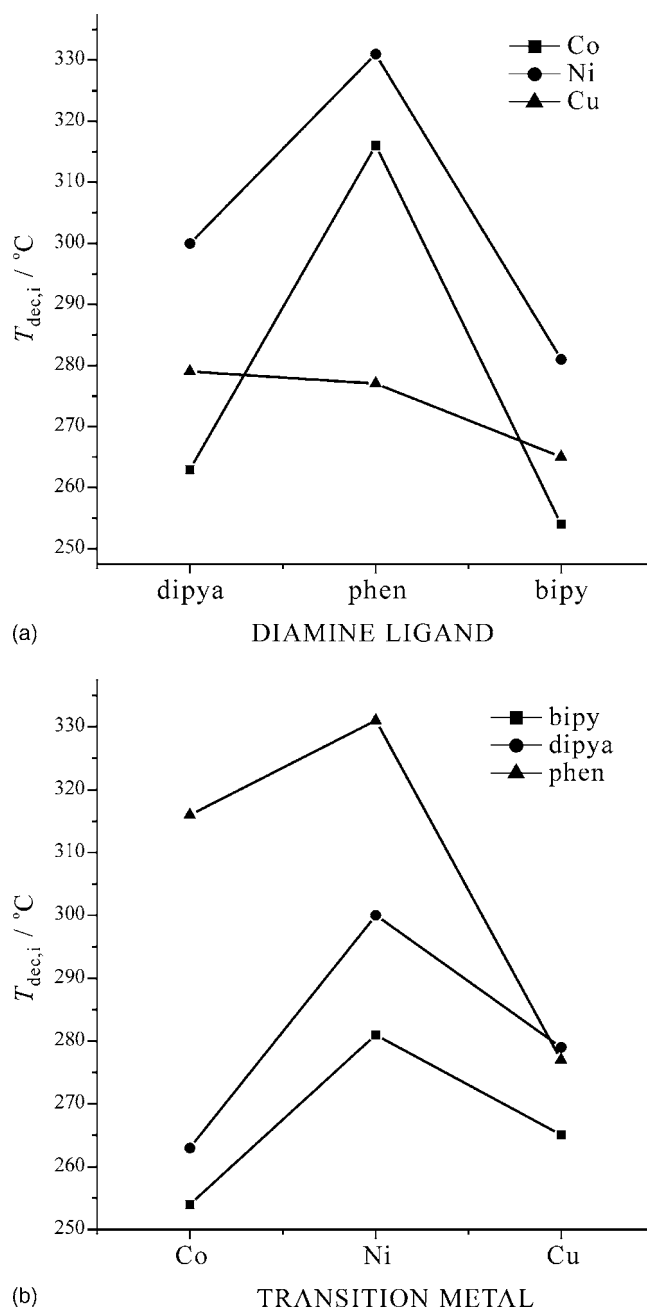

Fig. 3. Relationships between the initial decomposition temperature and (a) diamine ligand, (b) transition metal.

(Fig. 3) than analogous and isostructural Co complexes. The same order of the thermal stabilities is found for isostructural nitrato Co, Ni and Cu complexes with dipya and bipy [7].

On the other hand, thermal stability for Cu complexes increases in the order bipy < phen < dipya, while for Co and Ni complexes the order is bipy < dipya < phen. In the view of these results, bipy complexes are most unstable (Table 1, Fig. 3), no matter what transition metal is present. The inverse trend in thermal stability (phen < bipy) has been found for some Ni(II) complexes [22].

The comparison of obtained results with data for similar ternary complexes does not reveal analogous behaviour. For example, thermal behaviour of isostructural [23] pht complexes $[M(pht)(phen)(H_2O)_3]\cdot H_2O$, M = Co, Ni showed that Co complex is more stable than Ni complex [16]. Here described tpht complexes (4 and 5) with identical empirical formulae are generally more stable than pht complexes, but 4 has lower $T_{dec,i}$ than 5. Also, dipya containing pht complexes: $[M(pht)(dipya)]$ (M = Co or Cu) were found to be significantly more stable than complexes with phen [16], which is not the case for here investigated complexes. However, previously described dipya complexes do not contain water of crystallisation and are very probably of polymeric nature.

4. Conclusions

Some factors influencing the thermal stability of transition metal complexes in the solid state and mechanism of their decomposition are summarised in the review article of Donia [7]. Here described results and comparison with some previous studies on similar compounds [9,10,16] showed that there are some other factors, which should be added to the list as probably very important. They are: (a) a decrease of the intermolecular forces in the solid state with increasing strength of the intramolecular metal–ligand bonds, (b) π-bonding ability of ligands (and possibly π-stacking interactions between them), (c) bulkiness and planarity/non-planarity of ligands, and (d) discrete or polymeric nature of the complexes.

However, the factors are numerous and apparently competitive, so they can be used as a predictive tool solely within a series of similar complexes. Strongly speaking, only the thermal behaviour of isostructural complexes could be compared and the knowledge of crystal structure is very desirable. If examined complexes contain water of crystallisation, redistribution of bonds and changes of their geometry are expected after dehydration. Since it is very hard to characterise such, at least partially disordered intermediary products, changes induced by dehydration are more or less unpredictable. This introduces an additional uncertainty in the prediction and explanation of the thermal stability of complexes.

In the structure of H_2tpht the dihedral angles between plane of benzene ring and planes of COOH groups are iden-

tical and very small (5.2°) [24]. Consequently, the whole molecule is close to the coplanar conformation, which should be the most stable, at least in gas phase [25]. On the other hand, these angles in tpht and similar aromatic polycarboxylate complexes vary in very wide range [1–6,23]. According to Kaduk and Golab [25], the energy barrier for rotation around $C_{aromatic} - C_{carboxyl}$ bond does not exceed $50\,kJ\,mol^{-1}$, and for the rotation (torsion) angle of 20° it has the value of only about $9\,kJ\,mol^{-1}$ for two twisted groups. The observed deviations from planarity could be ascribed to the significant improvement of crystal packing [25]. However, our calculations show that the formation of only one hydrogen bond should be more than enough to stabilise high rotation angles of COO groups.

Finally, it is worth noticing that in all cases dehydration enthalpies per mole of H_2O are similar to or slightly higher than the sum of enthalpy of fusion and enthalpy of evaporation for H_2O ($46.7\,kJ\,mol^{-1}$). Thus, energy required to remove water of crystallisation is close to the energy of its sublimation. In other words, in the investigated complexes, state of energy of coordinated and/or lattice H_2O molecules is similar to the energy of the pure H_2O in solid state.

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