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Dedicated to the memory of
Professor Petru Spacu (1906–1995)

REVIEW

THE INFLUENCE OF THE LIGANDS ON THE THERMAL BEHAVIOUR OF SOLID COORDINATION COMPOUNDS

Oana CARP

Institute of Physical Chemistry "I.Murgulescu" Spl. Independentei no. 202, sect. 6, Bucharest, Roumania, E-mail: carp@capia.ro

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The ligands, due to several properties, such as volatility, basicity, induced inductive and mesomeric effects, number of donor atoms and number of atoms which participate to the coordinative bonds, adopted coordination geometry, induced steric effects, possibility to undergo redox reactions, play an important role in the thermal decomposition of solid coordination compounds. The paper is dedicated to an analysis of the ligands influence on the thermal behaviour of the solid coordination compounds as expressed through the initial temperature of change, decomposition stoichiometry and activation parameters.

GENERAL REMARKS

Generally, the thermal reactions undergone by the coordination compounds can start through:

- **the breaking of the bond between the central metallic ion and the volatile ligand** which is evolved as a whole molecule or as fragments;
- **the breaking of the internal bond of the ligand**, i.e. the decomposition of the ligand itself with formation of a new ligand.

In the **first case the thermal stability** of the coordination compounds which undergo decomposition **depends mainly on the bond strength between the central metallic ion and the ligand.** The thermal decompositions, during which the ligands such as water, ammonia, amine, DMSO a.s.o. are released, belong to the first type of thermal changes.[1-4]

As far as the **second** type of decomposition is concerned, this is represented generally by the decomposition (defragmentation) of chelates, with nonvolatile ligands, such as oximes, ketones, pyrazoles, a.s.o.[5-13] As a general rule, the thermal stability of the coordination compounds which undergo such transformations is influenced by **the bond strength which is broken** during the decomposition. The coordinative bond strength influences in this case the thermal stability, only, if this bond influences the strength of the bond which is broken in the first step.[14]

Ligands can play an important role in the decomposition of the solid coordination compounds due to several properties, such as volatility, basicity (the ability of the donor atoms electrons to interact with metals), induced inductive and mesomeric effects, number of donor atoms and number of atoms which participate to coordinative bonds, adopted coordination geometry, induced steric effects, possibility to undergo redox reactions. An analysis of the influence these properties on the thermal behaviour as expressed through the initial temperature of change, decomposition stoichiometry and activation parameters for the thermal decomposition solid coordination compounds is further carried out.

I. THE CHANGE OF THE INITIAL TEMPERATURE

Usually, due to their coordination, the **thermal stability** of the ligand introduced into complexes is higher with respect to the corresponding free ligands.[15-22] There are also cases, when the complexes exhibited a lower thermal stability than the ligands themselves, which indicates a catalytic effect of the introduced metallic cation(s)[12,23-24] or, the occurrence of some self-propagating reactions.[25-27]

Different **coordination modes** of the ligands represent one of the main reason for sensitive changes in the thermal stability of the solid coordination compounds. As a general rule, **the presence of polydentate bonds and a chelate ring, leads to an increase in the initial decomposition temperature.** A representative example for the first case is the thermal stability of *octahedral nickel coordination compounds*[28-29] in which the coordination is achieved by metallic ion-N (ligand) bonds. In the compounds $[Ni(NH_3)_6]X_2$ (*X*=Cl, Br and J), ammonia is monodentate, and in the series $[Ni(en)_3]X_2$ (*X*=Cl, Br and J and *en*=ethylenediamine) ethylenediamine is a bidentate ligand forming a chelate ring. For both series, the thermal decomposition occurs in three steps (reactions 1 and 2), and the initial temperatures for all decomposition steps are higher for the ethylenediamine compounds:

$$[Ni(NH_3)_6]X_2 \rightarrow [Ni(NH_3)_4X_2] \rightarrow Ni(NH_3)X_2 \rightarrow NiX_2 \quad (1)$$

$$[Ni(en)_3]X_2 \rightarrow [Ni(en)_2X_2] \rightarrow Ni(en)X_2 \rightarrow NiX_2 \quad (2)$$

As far as the influence of ring size upon the stability of chelate complexes is concerned, a decrease with increasing ring size is evidenced,[30-31] explained, to a large extent on the basis of chelate/entropy factor.[30] Oxalates coordination compounds (oxalic acid, usually presented as five membered chelate) present higher decomposition temperature than similar compounds with higher ring size chelate, as example *malates* complexes (malic acid, which may act in distinct condition as a seven-membered chelate).[32-34]

Different coordination modes of the ligands may be achieved due to:

(i) the versatility upon coordination of some ligands:

- coordination compounds with *(hydroxy)polycarboxylates* anions ligands. Lower thermal stability is achieved when the oxalate anions are bonded to the metallic ion as unidentate chelate ligand in comparison with tetradentate bridging one.[35-37]

(ii) the presence of ligands in different isomeric forms:

- coordination compounds with *bipyridine isomers (2,2'-, 2,4'- and 4,4')* ligands. The nitrogen atom position from bipyridine favour different type of coordination. So, 2,2'- bipyridine is a potential bidentate chelating ligand, 4,4'- bipyridine can coordinate as bidentate bridging ligand and 2,4'- bipyridine act as monodendate ligand.[38] Such a coordination leads to more stable complexes when the ligand is 2,2'-bipyridine or 4,4'-bipyridine than those containing 2,4'-bipyridine ligand;[39-40]
- coordination compounds with *dimethoxybenzoates (2,3-,2,4, 3,4-)* anions as ligands. The various positions of methoxy groups ($-OCH_3$) influences the OCO^- group bonding: in 2,4- and 3,4- compounds act as bidentate chelate bridging ligand and in 2,3-ones as bidendate chelate or tridentate chelate ligand.[41-42] The thermal stability of anhydrous compounds increases in order 2,4-<2,3-<3,4-.

(iii) the existence several donor atoms into ligands which can participate either individual or together at the coordination bonds:

- the series *[Cu(en)$_2$(NCS)]X* with *en*= ethylenediamine and X=Cl^-, Br^-, NO_3^-, BF_4^-, ClO_4^-, NCS.[43] The thiocyanate group is coordinated through the nitrogen atom in the compound $Cu(en)_2(NCS)_2$ and through the sulfur atom in remainder compounds. The higher thermal stability of the coordination compounds with N-coordinated thiocyanate ligands compared with S-coordinated ones has two reasons: stabilization by generation of molecular chains -Cu-N(CS)-Cu-, as well as the absence of the reducing thiocyanate group bonded by the sulfur atom;

Different **molecular symmetries** (the presence of geometric isomers) is an another factor which influences the thermal stability of the coordination compounds. An example represents the decomposition (inert atmosphere, H_2) of the *facial and meridional uns-cis-[Co(III)(eddp)gly]* complexes (*eddp*=ethylenediamine-N,N'-3-propianato, *gly*=glycinato). The meridional isomer underwent a stepwise decomposition with well separated decomposition steps, while the decomposition of the facial one occurs at

lower temperature, in a chain wise manner.[21] These results suggest a higher thermodynamic stability of the meridional isomer, which represents the dominant factor in isomers distribution also (meridional/facial=12/1).

Another important factor in the change of the initial temperature is the **strength of M-X bonds** (*X*=N, S, O, etc.) evidenced for the reaction which occurs with the breaking of such bonds.[44-50] The strength of these bond depend on the:

(i) **basicity** of the ligands: in the absence of steric hindrance the tendency to release the ligands decreases with the increase of their basicity. Linear correlations between the initial temperature of thermal decomposition or the temperature corresponding to the maximum of DTA curve and, the pK_a of the ligand are mentioned in literature.[51-52]

(ii) **changes in the electron cloud density** due to induced inductive and mesomeric effects, due to:

- the size of alkyl group ($-CH_2$) contained by the ligand, a longer chain length decreasing the thermal stability;[53-59]
- the presence of substituents as well as their position[60-63] which influences the electron density of the first bond broken during decomposition:
  - *coordination compounds with dihydroxybenzoates (2,4- and 2,5-)* anions as ligands. The temperature of decomposition of 2,5-dihydroxybenzoates are higher than those for 2,4-dihydroxybenzoates;[64,65]
  - the substitution of one OCH_3 group[66] by CH_3 group in *dimethoxybenzoates (2,3-, 2,4-, 3,4-)* complexes leads to an increase of the thermal stability[41,67];
  - *2-methoxybenzoates* compounds[68] are more stable than 5-chloro-2-methoxybenzoates;[64,69]
  - the thermal stability of *bisazodianils complexes*[50] is dependent on the position of the azo functional group. The complexes formed on terminal azo groups are less stable than complexes formed on internal azo groups. Complexes with two azo groups in *p*-positions have higher thermal stability than complexes with two azo group in *m*-position;
  - different thermal stabilities are obtained for *chloronitrobenzoates* of rare earth metals with various positions of the -Cl and $-NO_2$ substituents on the benzene ring. The 4-chloro-3-nitrobenzoates are more stable in comparison with 5-chloro-2-nitrobenzoates due to the presence of Cl substituent in para position, which stabilizes the aromatic ring;[70,71]
  - complexes of derivates of *N-(2-acetamido) iminodiacetic acid (H_2ADA) and neutral molecules of secondary base ligands imidazoles (B) [$M(ADA)(B)(H_2O)_n$]*[72] (*M*(II)=Co, Cu, Ni) present the following order of thermal stability: M(II)ADA-2-methyl>M(II)ADA>M(II)ADA-1,2-dimethylimidazoles, order which depend upon the strength of the chelation as a result of the effect of the substitution.

(iii) **the conjugation of the ligands donor atom electrons with d-electrons of the metallic ion**. As example we mention two coordination compounds of *palladium (II) with 1-aminopyrene and its derivative*: $Pd(apyr)_2Cl_2$ and $Pd(pmpa)Cl_2$ (*apyr*=1-aminopyrene and *pmpa*=N-(2-pyridylmethylene)-1-pyrenylamine).[73] The nitrogen atom of the first complex is tetrahedral, and there is no conjugation of the pyrenyl π-electron with d-electrons of metal, whereas the amine nitrogen in the second complex is planar and coordinates to metal atom forming a conjugation planar molecule. For this reason, the second complex is more stable than the first.

In some cases, the **steric factor** (and not basicity) plays the decisive role in the thermal stability of the solid coordination compounds:[45,56,75-76]

- linear correlations between the initial decomposition temperature and the deformation degree of coordination polyhedron are mentioned,[43,77] identified for *coordination compounds with molecular chains*;
- the thermal stability of *platinum (II) complexes with esters of 2-quinolylmethylphosphoric acids and halogen anions*, PtL_2X_2 (*L*=diethyl (*2-dqmp*) and monoethyl 2-quinolylmethylphosphonates (*2-Hmqmp*), and *X*=Cl^-, Br^-) depends either on the organophosphorus ligand or halogen anion.[78] The dihalide complexes of the monoethyl ester are more stable compounds with respect to those of the diethyl ester, as well as, chloro complexes compared to their bromo analogues. It may be presumed that this arise from steric effects that increase from monoester to diester and from chloro to bromo derivates. In the ion-pair ionic complexes with protonated phosphonate ligand as cation and the tetrahaloplatinate

or hexahalodiplatinate complex as anion, namely $[LH^+]_2[PtX_4^{2}]$, $[LH^+]_2[Pt_2X_4^{2-}]$ these differences are less pronounced.

The way in which the thermal stability can be changed **either by ligands basicity or by steric hindrance** is illustrated in the thermal decomposition of *cis* and *trans*-$[Co(en)_2(RCOO)_2]NO_3$ compounds (*R*=H, CH_3, C_2H_5, C_3H_7), which exhibit the following first decomposition step:[79]

$$[Co(en)_2(RCOO)_2]NO_3 \rightarrow [Co(en)(RCOO)_2]NO_3 + en \quad (3)$$

Depending on the group R, for reaction (3) the following series of thermal stability proved are valid:

trans **compounds** > *cis* **compounds**

cis **compounds** $C_3H_7 > C_2H_5 > CH_3 > H$

trans **compounds** $CH_3 > C_2H_5 \sim C_3H_7 > H$

All *trans* compounds (except for the formates) exhibit a higher thermal stability with respect to the corresponding *cis* isomers. This behaviour of the *trans* compounds which cannot be correlated with the ligands basicity, is due to the important cross-liking of the crystalline lattice as a consequence of the generation of intermolecular bonds between opposed carboxylate ions. Successive addition of $-CH_2-$ groups in the hydrocarbon chain reduces the lattice rigidity and, correspondingly the thermal stability. As far as the *cis*-compounds are concerned, the effects due to the cross-linking of the lattice are not important, and the thermal stability decreases with the increase of the $RCOO^-$ ions basicity.

Another cause of thermal stability changes, (very rarely mentioned) is the **coordination compound history**. As an example we mention the decomposition of *4(5)-aminoimidazole-5(4)-carboxamide complexes* (*AIC*) of divalent metals (*M*(II)=Co, Ni and Cu) namely $M(AIC)_2$.[80] The decomposition step for $M(AIC)_2$ compound obtained after water release from $M(AIC)_2 \cdot 2H_2O$ complex, is split into two different processes over a 200°C temperature range, with a final plateau around 500°C. The $M(AIC)_2$ complex obtained from the decomposition $M(AIC)_4Cl_2 \cdot 2H_2O$ compound, after the release of water, two molecules of ligands and two chlorides ions, processes which imply a rearrangement of the coordination environment presents a the final decomposition process shifted to higher decomposition temperatures (almost 100°C), with only one, but sharper decomposition step.[80]

The **presence of an additional ligand** may often decrease the thermal stability of the parent coordination compound, because of its higher volatility. An increase of the thermal stability with addition of a supplementary ligand is very rarely achieved. From the first class of compounds we can mention:

- *copper complexes with 4-methylimidazole* (*4-Meim*) $Cu(4\text{-Meim})_2$ are stable with more than 100°C comparative with mixed complexes containing *salicylic acid* (*Sal*) or *salicylaldoxime* (*Salox*), namely $CuSal(4\text{-Meim})_2$ and $CuSalox(4\text{-Meim})_2$;[81]
- *$[Tb_2(o\text{-}MBA)_6(phen)_2]$* compound (where *o-MBA*= *o*-methylbenzoate and *phen*=1,10-phenanthroline) has a lower decomposition temperature with almost 80°C in comparison with *$[Tb_2(o\text{-}MBA)_6]$* compound,[82] due to the weaker Me-N (with 1,10-phenanthroline) in comparison Me-O ones (with *o*-methylbenzoate);
- in the case of *Zn(II) o-hydroxybenzaldoximates mixed complexes* (*H_2salox*) [83] with 8 hydroxyquinoline (Hox), [Zn(Hsalox)(ox)], *o*-aminophenol (NH_2Ph), [Zn(Hsalox)(NHPh)], and *o*-hydroxybenzoic acid (H_2sal), [Zn(Hsalox)(Hsal)] have a lower decomposition temperature with about 150°C comparative with [Zn(salox)];
- *$Cu_2(RCO_2)_4py_2$* compounds in comparison to *$Cu(RCO_2)_2$* (*R*=$CH_3(CH_2)_{n-2}$, n=14,16, and 18) ones are less stable with approximate 30-40°C.[59] This behaviour is explained by structural features: the weaker inter-dimmer interactions are probably the main reason for significant lowering of pyridine compounds thermal stability.

An example of a higher thermal stability with the addition of a complementary ligand is given below:

- bidentate amine and pseudohalides of complexes of copper *$[Cu(\mu\text{-}X)(Y)(L\text{-}L)]_2$* (*X*=$NNN^-$, NCO^-, *Y*= NNN^-, NCO^-, NCS^- and *L-L*=N-N-diethylethylenediamine, N,N-dimethyl-ethylenediamine and N,N'-dimethylethylenediamine) exhibit higher stability (ranging from ~50 to ~80°C) compared to complexes containing only pseudohalides.[47]

II. THE CHANGES IN DECOMPOSITION STOICHIOMETRY

Changes in decomposition stoichiometry are mainly due to the changes in the basicity of ligands.[84-89] A different electronegativity of a donor atom, may lead to changes of the reaction mechanism, because the first bond which is broken may be changed, and/or stabilization of different intermediates. The main factors which determine such a behaviour are:

(i) different covalent character of the coordination bond:

- the thermal decomposition of the solid coordination compounds described by the formula $\underline{NiL_4Cl_2}$ (*L*= thiourea (*tu*), methyl-thiourea (*mtu*), dimethyl-thiourea (*dmtu*), tetramethyl-thiourea (*tmtu*), di-n-butyl-thiourea (*dbtu*), naphthyl-thiourea (*naftu*), ethylene-thiourea (*etu*) or allyl-thiourea (*altu*)) occurs according to the following two schemes:[90]

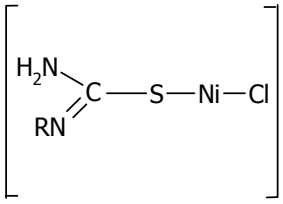
$$[NiL_4Cl_2] \rightarrow [NiLCl_2] \rightarrow NiS \quad (4)$$

where *L*= dmtu, dbtu, etu, tmtu, altu, naptu

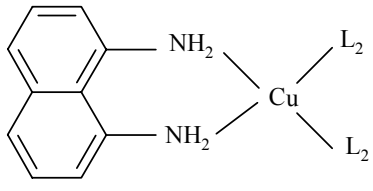
$$[NiL_4Cl_2] \rightarrow [NiLCl] \rightarrow NiS \quad (5)$$

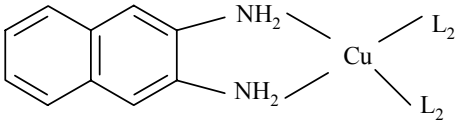
where *L*= tu or mtu

The intermediate detected after the first decomposition step of sequence (5) presents an imine structure. The release of the halide ion simultaneously with the stabilization of the imine-like structure of the intermediate, is determined by the shift of the strong +I effect from the terminal group R of the thiourea ligand forward to the central metallic ion, shift favored by tu and mtu ligands:[90]



- the first bond which is broken during thermal decomposition of the compounds with $[CuL_1(L_2)_2]\cdot nH_2O$ formula[91] where L_1 is an aromatic amine (1,8-diaminonaphthalene and 2,3 diaminonaphthalene) and L_2 is an anionic ligand (Cl^-, OAc^-) with the general formula:



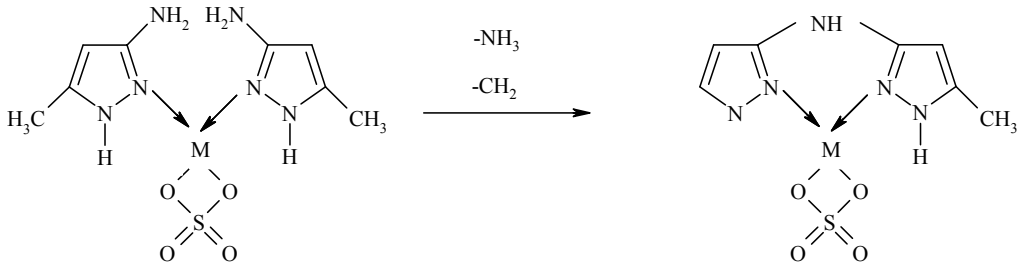


is in the case of $L_2 = Cl^-$, the breaking of the chelate ring while if $L_2 = OAc^-$, the first step is the breaking of the bond metal-acetate;

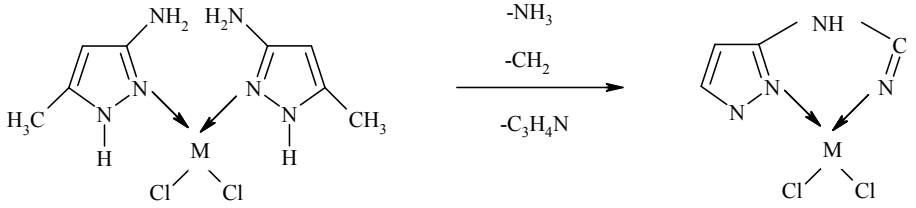
- the decomposition of *Zn(II) o-hydroxybenzaldoximates mixed complexes* (H_2salox)[83] with 8 hydroxyquinoline (Hox), *o*-aminophenol (NH_2Ph) and *o*-hydroxybenzoic acid (H_2sal), occurs as following: for 8-hydroxyquinoline [Zn(Hsalox)(ox)], and *o*-aminophenol complexes [Zn(Hsalox)(NHPh)], it starts by destruction of the two ligands, while

in the case of [Zn(Hsalox)(Hsal)], the weakest bond is the one between the metal ion and the *o*-hydroxybenzaldoximate which cleave the first;

- the course of decomposition is determined by the ligands anions (sulphato and chloro) in *pyrazole-based complexes*. While in the first case, an ammonia molecule and a -CH_2- fragment is eliminated, for the second group, the decomposition takes place at higher temperature with an additional splitting of the pyrazole rings (reactions 6 and 7):[84]



(6)



(7)

(ii) different adopted coordination geometries:

- the thermal decomposition of *Zn(II) complexes with theophylline*[92] *and amines or acetate anion*, namely $[Zn(NH_3)_2(Tph^-)_2]$, $[Zn(mea)_2(Tph^-)_2]$, $[Zn(ipa)_2(Tph^-)_2]$, $[Zn(OH)(CH_3COO)(Tph^-)_2]$ (Tph^-=theophyllinato monoanion, *mea*=ethanolamine and *ipa*=isopropylamine) may be discussed either related to the evolving of amine or theophyllinato monoanion. The evolving of NH_3 and isopropylamine in one step and of mea in two separate steps can be connected with different coordination of the ligands: NH_3 and isopropylamine have only one atom suitable for coordination, so equivalent bonds, and as result, the two ligand molecules are evolved in the same decomposition step. Mea is bidentate bonded, participating to coordination with either oxygen and nitrogen atoms,[93] and as consequence, ethanolamine evolving occurs through two separate steps. On the other hand (except acetate complex), the liberation of the first theophyllinato anion occurs in one step, while the evolving of second occurs through a complex process. The difference is connected with the formation of ZnO as residue. For acetate complex both theophylline anions are liberated in one step, as a consequence of the acetato group, whose oxygen is used for formation of ZnO. Because the exocyclic oxygen of theophylline molecule is not involved in the process of ZnO formation , both theophylline molecules are evolved at the same time

(iii) different reducing/oxidative properties of the ligands:

- *iron and manganese complexes of Schiff bases derived from 6-formylkhellin*,[94] namely *o*- and *p*-penylenediamine derivatives. *o*-phenylenediamine derivative displays reducing properties and as final decomposition products, metals are formed. The *p*-phenylenediamine derivative displays oxidation effect leading to abnormal oxides, namely $MnO_{2.5}$ and FeO_2.

III. THE CHANGE OF THE VALUES OF THE ACTIVATION PARAMETERS

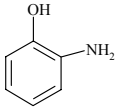
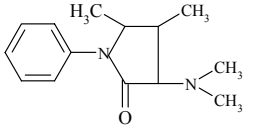
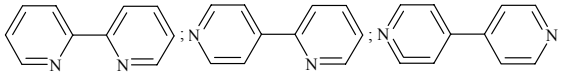
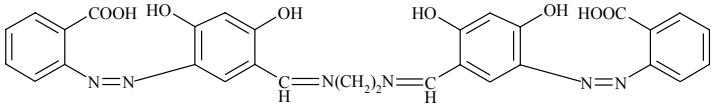
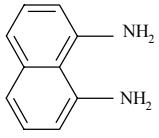
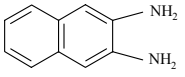
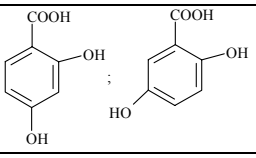
The values of the activation parameters corresponding to the thermal decomposition steps undergo changes when changing the ligands.[87,95-100] For some series of coordination compounds the literature mentions **correlations between the decomposition activation energy and the strength of the bond which is broken.**

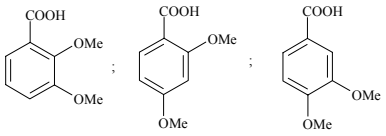
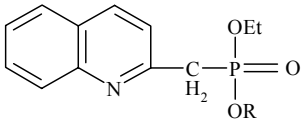
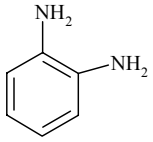
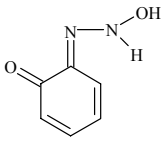
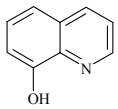
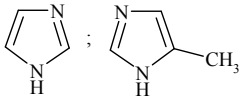
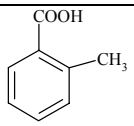
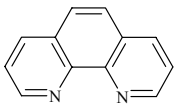
- [*Co(amine)$_2$(NCS)$_2$*] (*amine* = *p*-toluidine, *m*-toluidine, aniline) compounds.[101,102] The activation energy of the first deamination step of the compounds decreases in the order *o*-toluidine > *m*-toluidine > aniline, in the same order as the amine nucleophilic character;
- *mercury (II) bis(dialkyldithiocarbamate) complexes* $Hg(S_2CN\text{-}R_2)_2$, (*R*=ethyl, *n*-propyl, *n*-butyl and *iso*-butyl). The activation energy of the first decomposition step ascribed to the partial decomposition of the ligand and mercury sulfide,[103] decreases in the order *i*Bu>*n*Pr>*n*Bu>Et, which can be attributed to the inductive effect of alkyl substituents.

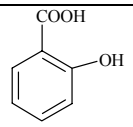
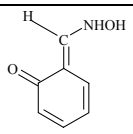
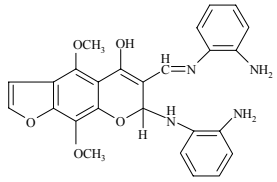
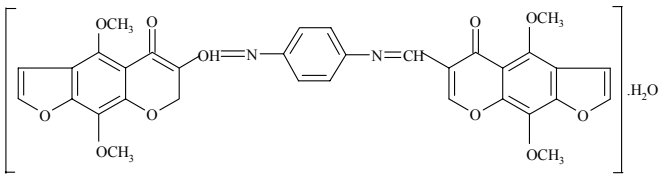
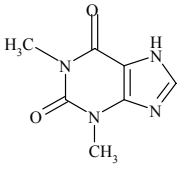
The change of the chelate ring (number of atoms in the ring, the existence of some substituents as well as their position in the ring) could determine changes in the values of nonisothermal kinetic parameters. For the decomposition of the coordination compounds with the general formula *CuL_2NO_3*,[104] (*L* = ethylenediamine (*en*); tetramethylenediamine (*tmn*); *o*-phenylenediamine (*opd*); 2,2-bipyridine (*bpy*)) the activation energy values of the first deamination step change in the order bpy > opd > en > tmn. These results can be explained considering that:

– the coordination compounds with cyclic ligands (*bpy* and *opd*) are more stable as compared with the coordination compounds which contain open chain ligands;
– the higher stability of the coordination compounds with *bpy* as compared to that with *opd* is due to the higher coordinating capacity of the nitrogen from the first compound;
– the reduced stability exhibited by the coordination compound with *tmn*, is due to a steric crowding at the coordinated nitrogen atom, determined by the two methyl groups.

Molecular formula of the mentioned ligands (alphabetical order)

Ligand	Molecular formula
acetic acid=	CH_3COOH
o-aminophenol (NH_2Ph)=	
1-aminopyrene (apyr)=	
bipyridine isomers (2,2'-, 2,4'- and 4,4')=	
bisazodianils=	
1,8-diaminonaphthalene=	
2,3 diaminonaphthalene=	
dihydroxybenzoic acid (2,4- and 2,5-)=	

dimethoxybenzic acid (2,3-,2,4, 3,4-)=	
monoethyl and diethyl 2-quinolylmethylphosphonates= (2-Hmqmp, 2-dqmp)	 R=H, Et
ethanolamine (mea)=	$HO\text{-}CH_2\text{-}CH_2\text{-}NH_2$
ethylenediamine (en); tetramethylenediamine (tmn); *o*-phenylenediamine (opd);	$NH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$; $NH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$; 
ethylenediamine-N,N'-3-propionic acid (eddp)=	$COOH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}COOH$
glycine (gly)=	$COOH\text{-}CH_2\text{-}NH_2$
o-hydroxybenzaldoxime (H_2salox)=	
8-hydroxyquinoline (Hox)=	
isopropylamine (ipa)=	$(CH_3)_2CHNH_2$
imidazole (im); 4-methylimidazole (4-Meim)=	
malic acid=	$HOOC\text{-}CHOH\text{-}CH_2\text{-}COOH$
o-methylbenzoic acid (*o*-MBA) =	
iminodiacetic acid (H_2ADA)=	$HOOC\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}COOH$
N-N-diethylethylenediamine; N,N-dimethylethylenediamine; N,N'-dimethylethylenediamine=	$NH_2\text{-}CH_2\text{-}CH_2\text{-}N(C_2H_5)_2$ $CH_3\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_3$ $C_2H_5\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}N(CH_3)_2$
oxalic acid=	$HOOC\text{-}COOH$
pyrazole=	
1,10-phenanthroline (phen) =	

salicylic acid (Sal)=	
salicylaldoxime (Salox)=	
Schiff bases derived from 6-formylkhellin: *o*- and *p*-penylenediamine derivatives=	 
theophylline (tph) =	
thiourea (tu) methyl-thiourea (mtu); dimethyl-thiourea (dmtu); tetramethyl-thiourea (tmtu); di-n-butyl-thiourea (dbtu); ethylene-thiourea (etu); allyl-thiourea (altu); naphthyl-thiourea (naftu)=	$NR_1R_2CSNHR_3R_4$ $R_1=R_2=R_3=R_4=H$; $R_1=R_3=CH_3$, $R_2=R_4=H$; $R_1=R_2=R_3=R_4=CH_3$; $R_1=R_3=CH_3$ $R_2=R_4=H$; $R_1=R_3=CH_3(CH_2)_2$-, $R_2=R_4=H$; $R_1=CH_3CH_2$, $R_2=R_3=R_4=H$; $R_1=CH_2CH$, $R_2=R_3=R_4=H$; $R_1=C_{10}H_8$,$R_2=R_3=R_4=H$,

REFERENCES

1. W.W. Wendland and P.J. Smith, "Thermal Properties of Transition Metal Amine Complexes", Elsevier, Amsterdam, London, NY, 1967.
2. J.J. Zhang, R.F. Wang, J.B. Li, H.M. Liu and H. F. Yang, *J.Therm.Anal.Cal.,* **2000**, *62* 747.
3. O. Geras'ko, V. Fedorov, V. Logvinenko, K. Hegetsweiler, M.R. J. Elsegood and U. Hyon Paek, *J.Therm.Anal.Cal*., **1998**, *53*, 411.
4. D. Czakis-Sulikowska and J. Kałuźna-Czaplińska, *J.Therm.Anal.Cal.***, 2000**, *62*, 821.
5. H. Langfelderova, *J.Therm.Anal.Cal.*, **1994**, *41*, 955.
6. D.Z. Obadov, D.M. Petrovic, V.M. Leovac and S. Caric, *J.Therm.Anal.Cal.*, **1990**, *36*, 99.
7. K. Mézáros Szécsény, E.Z. Ivegeš, V.M. Leovac, A. Kovács, G. Pokol and Ž.K. Jaćimović, *J.Therm.Anal.Cal.*, **1999**, *56*, 49.
8. K. Mézáros Szécsény, V.M. Leovac, Ž.K. Jaćimović, V.I. Češljevič, A. Kovács and G. Pokol, *J.Therm.Anal.Cal.*, **2001**, *63*, 723.
9. K. Mézáros Szécsény, Ž.K. Jaćimović, V.I. Češljevič, A. Kovácsand G. Pokol, *J.Therm.Anal.Cal.*, **2001**, *66*, 573.
10. A.S. Zidan, A. I. El-Said and A.A. Aly, *Synth.React.Inorg.Met-Org.Chem*., **1992**, *22*, 1355.
11. A.S. Zidan, *Synth.React.Inorg.Met-Org.Chem.*, **1994**, *24*, 227.
12. A.S. Zidan, A. I. El-Said, M. S. El-Meligy, A. A. M.Aly and O. F. Mohammed, *J.Thermal.Anal.Cal.*, **2000**, *62*, 665.
13. A.S. Zidan, *J.Therm.Anal.Cal.*, **2002**, *68*, 1045.
14. N. Rajić, D. Stojakovic and R. Gabrovšek, *J.Therm.Anal.Cal.*, **2001**, *63*, 191.
15. R. Mrozek, Z. Rzączyńska and M. Sikorska-Iwan, *J.Therm.Anal.Cal.*, **2001**, *63*, 839.
16. M. Sikorska-Iwan, R. Mrozek and Z. Rzączyńska, *J.Therm.Anal.Cal.*, **2000**, *60*, 139.

17. S.B. Jagtap, R.C. Chikate, O.S. Yemul, R. S. Ghadage and B. A. Kulkarni, *J.Therm.Anal.Cal.*, **2004**, *78*, 251.
18. R.R. Mahajan, P.S. Makashir and J.P. Agrawal, *J.Therm.Anal.Cal.*, **2001**, *65*, 935.
19. I.M.M. Kenawy, M. A. Hafez and R.R. Lashein, *J.Therm.Anal.Cal.*, **2001,***65*, 723.
20. K. Mészáros Szécsény, V. M.Leovac, Ž.K. Jaćimović and G. Pokol, *J.Therm.Anal.Cal.*, **2003**, *74*, 943.
21. N. Petranovič, D. Minič, J.T. Sabo and D. Dokovič, *J.Therm.Anal.Cal.*, **2000**, *59*, 807.
22. C. Bâtiu, I. Panea, L. Ghizdavu, L. David and S. Ghizdavu Pellascio, *J.Therm.Anal.Cal.*, **2005**, *79*, 129.
23. K. Andjelković, M. Šumar and I. Ivanović-Burmazović, *J.Therm.Anal.Cal.*, **2001**, *66*, 759.
24. M. Badea, R. Olar, E. Cristurean, D. Marinescu, A. Emandi, P. Budrugeac and E. Segal, *J.Therm.Anal.Cal.*, **2004**, *77*, 815.
25. I. Mindru, L. Patron and M. Brezeanu, *Roum.Chem.Quartely Rev.*, **1996**, *4*, 167.
26. O. Carp, L. Patron and A. Reller, *Rev.Roum.Chem.*, **2003**, *48*, 513
27. O. Carp, L. Patron and M. Brezeanu, *J.Therm.Anal.Cal.*, **1999**, *56*, 561.
28. E. Segal, "Festkörperchemie", Boldyrev-Meyer Eds., VEB Deutscher Verlag fur Grundstoffchemie, (1973), p. 404-432.
29. A. K. Majundar and A. K. Mukjerjee, *J. Inorg. Nucl. Chem.*, **1964**, *26*, 2177.
30. H. Irving, R.J.P. Williams, D.J. Ferrett and A.E. Williams, *J.Chem.Soc.*, **1954**, 3494.
31. E. Princz, K. Mogyorósi and I. Labadi, *J.Therm.Anal.Cal.*, **2004**, 77, 767.
32. B.S .Randhawa and K.J. Sweety, *J.Therm.Anal.Cal.*, **2001**, *65*, 829.
33. B.S. Randhawa and K.J. Sweety, *J.Therm.Anal.Cal.*, **2000**, *62*, 295.
34. A.S. Brar, S. Brar and S. S. Sdandhu, *J.Therm.Anal.Cal.*, **1986**, *31*, 1083.
35. O. Carp, *Rev.Roum.Chem.*, **2001**, *46*, 1189.
36. G. Marinescu, L. Patron, O. Carp, L. Diamandescu, M. Brezeanu, A. Meghea, N. Stanica, J.C. Grenier and J. Etourneau, *J.Mater.Chem.*, **2002**,*12*, 3458.
37. O. Carp, L. Patron, G. Marinescu, G. Pascu, P. Budrugeac and M. Brezeanu, *J.Therm.Anal.Cal.*, **2003**, *72*, 263.
38. A. S. Ahuja, R. Singh and C. L. Yadava, *J.Mol.Struct.* **1991**,*74*, 43.
39. D. Czakis-Sulikowska, J. Kałuźna and J. Radwańska-Doczekalska, *J.Therm.Anal.Cal.*, **1998**, *54*, 103.
40. D. Czakis-Sulikowska, J. Radwańska-Doczekalska and M. Markiewicz, *J.Therm.Anal.Cal.*, **2000**, *60*, 145.
41. W. Ferenc and A. Walków-Dziewulska, *J.Therm.Anal.Cal.*, **2002**, *70*, 949.
42. W. Ferenc and A. Walków-Dziewulska, *J.Therm.Anal.Cal.*, **2003**, *74*, 511.
43. H. Langfelderova, L. Macaskova, K. Otrubova and J. Gazo, J. Thermal Anal., **1986**, *31*, 1143
44. B. Ptaszyński and A. Zwilińska, *J.Therm..Anal.Cal.*, **2003**, *74*, 237.
45. J. Pérez, G. Sánchez, J. Garcia, J.L. Serrano and G. López, *J.Therm.Anal.Cal.*, **2001**, *66*, 361.
46. R. F. Fabrias, L. Martínez and C. Airoldi, *Thermochim.Acta*, **2001**, *376*, 91.
47. V. Sargentelli, A.E. Mauro, A.V. de Godoy Netto, M.P.D. Mattioli, V.M. Nogueira and V.A. De Lucca Neto, *J. Therm. Anal. Cal.*, **2002**, *69*, 445.
48. D. Czakis-Sulikowska, A. Czylkowska and J. Radwańska-Doczekalska, *J.Therm.Anal.Cal.*, **2001**, *63*, 387
49. D. Czakis-Sulikowska, A. Czylkowska and A. Malinowska, *J.Therm.Anal.Cal.*, **2001**, *65*, 505.
50. N.A. El-Wakiel, *J.Therm.Anal.Cal.*, **2004**, *77*, 839.
51. M. Szpakowska, I. Uruska and R. Teszner, *J.Therm.Anal.Cal.*, **1987**, *32*, 717.
52. H.E Toma and L.A Marino, *J.Therm.Anal.Cal.*, **1990**, *36*, 7.
53. T. K. Maji, D. Das, S. Sain and N. Ray Chaudhuri, *J.Therm.Anal.Cal.*, **2002**, *68*, 319.
54. A. Mondal, D. Das and N. Ray Chaudhuri, *J.Therm.Anal.Cal.*, **1999**, *55*, 165.
55. C. Pariya, A. Ghosh and N. Ray Chaudhuri, *Thermochim.Acta*, **1995**, *249*, 199.
56. S. Petriček and M. Petrič, *Thermochim.Acta*, **1997**, *302*, 35.
57. M. Merdivan, R. S. Aygun and N. Kulcu, *J.Therm.Anal.Cal.*, **1997**, *48*, 1423.
58. M. Merdivan, F. Karipcin, N. Kulcu and R. S. Aygun, *J.Therm.Anal.Cal.*, **1999**, *58*, 551.
59. M. Pajtášová, E. Jóna and P. Šimon, *J.Therm.Anal.Cal.*, **2002**, *67*, 129.
60. S. C. Mojumdar, E. Jóna and M. Melnik, *J.Therm.Anal.Cal.*, **2000**, *60*, 571.
61. K. Györyová, J. Kovářova, M. Melník and E. Andogová, *J.Therm.Anal.Cal.*, **1999**, *56*, 503.
62. R. Kurpiel-Gorgol and W. Bryzka, *J.Therm.Anal.Cal.*, **2005**, *82*, 389.
63. R. Kurpiel-Gorgol and W. Bryzka, *J.Therm.Anal.Cal.*, **2001**, *66*, 77.
64. W. Bryska and K. Kula, *Thermochim.Acta*, **1992**, *211*, 199.
65. W. Bryska and K. Kula, *J.Therm.Anal.Cal.*, **1998**, *53*, 161.
66. W. Bryzka and W. Ozga, *J.Therm.Anal.Cal.*, **2002**, *70*, 467.
67. W. Bryska, *J.Therm.Anal.Cal.*, **2000**, *59*, 799.
68. S.B. Pirkes, G.N. Makuszeva and A.V. Lapitskaya, *Zh.Neorg.Khim.*, **1976**, *21*, 1214.
69. W. Ferenc and B. Bocian, *J.Therm.Anal.Cal.*, **2000**, *62*, 831.
70. J. Shorter, "Correlation analysis in organic Chemistry. An Introduction to linear free-energy relationships", Clarendon Press, Oxford, 1973.
71. W. Ferenc and B. Bocian, *J.Therm.Anal.Cal.*, **1999**, *55*, 671.
72. E.M. Abdalla and A.A. Said, *Thermochim.Acta*, **2003**, *405*, 269.
73. J. Sun, Z. Lu, Y. Li and J. Dai, *J.Therm.Anal.Cal.*, **1999**, *58*, 383.
74. L. Nagy, J. Zsakó, Cs. Novák, Cs. Várhely, Gy. Vankó and G. Liptay, *J.Therm.Anal.Cal.*, **1999**, *57*, 433.
75. D. Fatu and V. Popescu, *J.Therm.Anal.Cal.*, **2003**, *71*, 521.
76. M.K. Nair and P.K. Radhakrishnan, *J.Therm.Anal.Cal.*, **1998**, *52*, 475.
77. M.N. Akhtar, A.A. Isab and A. Hassan, *J.Thermal.Anal.Cal.*, **2000**, *61*, 119.

78. Lj. Tušek-Božic and R. Trojko, *J.Therm.Anal.Cal.*, **2005**, *81*, 153.
79. U. Biader Ceipidon, R. Bucci, V. Carunchio, A.M. Girelli and A.D. Magri, *J.Therm.Anal.Cal.*, **1989**, *35*, 1513.
80. S. Materazzi, G. D'Ascenzo, S. Aquili, K.M. Kadish and J.L.Bear, *Thermochim.Acta*, **2003**, *397*, 129.
81. A. Turek and M. Olczak-Kobza, *J.Therm.Anal.Cal.*, **1998**, *54*, 133.
82. J.J. Zhang, R.F. Wang and H. M. Liu, *J.Therm.Anal.Cal.*, **2001**, *66*, 431.
83. M. Olczak-Kobza and M. Cichecka, *J.Therm.Anal.Cal.*, **2001**, *66*, 379.
84. K. Mészáros-Szécsényi, E. Z. Ivegeš, V. M. Leovac, A. Kovács, G. Pokol and Ž. Jaćimović, *J.Therm.Anal.Cal.*, **1999**, *56*, 493.
85. C.A. Ribeiro, M.S. Crespi, C.T.R.Guerreiro and L.S. Guinesi, *J.Therm.Anal.Cal.*, **2001**, *64*, 637.
86. C.T. Guerreiro, C.A. Ribeiro, M.S. Crespi and C. Torres, *J.Therm.Anal.Cal.*, **1999**, *56*, 519.
87. V. Logvinenko, A. Minina, Yu. Mikhaylov, Yu. Yukhin and B. Bokhonov, *J.Therm.Anal.Cal.*, **2003**, *74*, 407.
88. S. C. Mojumdar, L. Martiška, D. Valigura and M. Melník, *J.Therm.Anal.Cal.*, **2005**, *81*, 243.
89. D. Czakis-Sulikowska and J. Kałuźna, *J.Therm.Anal.Cal.*, **1999**, *58*, 51.
90. E. Jona, *J.Therm.Anal.Cal.*, **1988**, *34*, 1053.
91. A. M. Donia, *J.Therm.Anal.Cal.*, **1993**,*39*, 323.
92. V. Zelenák, K. Györová and E. Andogová, *Thermochim.Acta*, **2000**, *354*, 81.
93. Ch. Chaudhuri, C. Stockheim, K. Wieghardt, W. Deck, R. Gregorzik, H. Vahrenkamp, B. Nuber and J.Weiss, *Inorg.Chem.*, **1992**, *31*, 1451.
94. A.M. Donia, H.A. El-Boraey and M.F. El-Samalehy, *J.Therm.Anal.Cal.*, **2003**, *73*, 987.
95. J. Zsako and H.E. Arz, *J.Therm.Anal.Cal.*, **1974**, *6*, 651.
96. E. Ingier-Stocka, *J.Therm.Anal.Cal.*, **1988**, *33*, 487.
97. M. Lalia-Kantouri, G.A. Katsoulos, C.C. Hadji-Kostas and P. Kokorotsikos, *J.Therm.Anal.Cal.*, **1989**, *35*, 2411.
98. W. Brzyka and S. Karasinski *J.Therm.Anal.Cal.*, **1987**, *32*, 55.
99. B.S. Garg, R. Dixit and A.S. Singh, *J.Therm.Anal.Cal.*, **1990**, *32*, 2567.
100. J. Zsako and J. Zsako Jr., *J.Therm.Anal.Cal.*, **1980**, *19*, 46.
101. J. Zsako, Cs. Varhely, B. Csegedi and J. Zsako Jr., *Thermochim.Acta*, **1981**, *45*, 11.
102. L.S. Prabhumirashi, G. N. Nata and J. K. Khoje, *J.Therm.Anal.Cal.*, **1989**, *35*, 1027.
103. A.M. Ramalho, M.M. Conceição, V.J. Fernandes Jr., J.C. Machado, L.E.B. Soledade and A.G. Souza, *J.Therm.Anal.Cal.*, **2005**, *79*, 319.
104. M.P.B. Attard, J.O. Hill, R.J. Magee, S. Prakash and N.N. Sastri, *J.Therm.Anal.Cal.*, **1986**, *35*, 1027.