

THE INFLUENCE OF THE CENTRAL METALLIC ION ON THE THERMAL BEHAVIOUR OF SOLID COORDINATION COMPOUNDS

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The paper is dedicated to an analysis of the central metallic ions effect on the solid coordination compounds thermal behaviour expressed by the decomposition temperature, decomposition stoichiometry and activation parameters. The influence of several properties of the central metallic ions such as ionic radius, electronic configuration of the last electronic shell, ionic potential on the thermal decomposition of solid coordination compounds is scrutinized.

GENERAL REMARKS

The interpretation of the data concerning the thermal behaviour of the coordination compounds needs its correlation with some properties of the central metallic ion like **ionic radius, ionic charge, electronic configuration of the last electronic shell, ionic potential**, etc. In the following we will evaluate their influence on the solid coordination compounds decomposition temperature, decomposition stoichiometry and activation parameters.

THE CHANGE OF THE INITIAL TEMPERATURE

The discussions concerning the metallic cation influence on the initial decomposition temperature have to take into account the first broken bond during the decomposition. Generally, the thermal reactions undergone by the coordination compounds can start through the breaking of the bond between the central metallic ion and ligand with the evolving of the volatile ligand or, the breaking of an 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.

As far as the second type of decomposition is concerned, this is represented generally by the decomposition (defragmentation) of chelates, with nonvolatile ligands. The coordinative bond strength (between the central metallic ion and the ligand) influences in this case the thermal stability, only, if this bond influences the strength of the bond which is broken in the first step: a stronger coordination of the free electron pair of the donor atom to the central metal cation may weaken one of the chelate bonds which are first ruptured upon heating.

In the first case, the initial decomposition temperature increases as the ionic radii decrease.¹⁻⁴ The observed regularity can be explained through the decrease of the ion-dipole energy interaction: as the ionic radius decreases, the polarizing power of the ion increases, resulting in an increase in the stability of the bonding between the metal ion and the ligand. Thus, is possible to establish thermal stability series for numerous compounds.⁴⁻²⁰ In the case when the cations suffer during decomposition an oxidation the statement is not any more valid. This is the case of cerium coordination compounds, which are less stable comparative with other lighter trivalent lanthanides with higher ionic radius. The behaviour may be attributed to the simultaneously oxidation of Ce(III) to Ce(IV) together with the oxidation of organic matter.²¹⁻²⁷

For a relatively high number of coordination compounds families, where the central metallic ion

is changed, the thermal stability as expressed by the initial decomposition temperature does not follow the Irving-Williams²⁸ series order concerning the thermal stability of the coordination compounds in solution.²⁹⁻³⁶ These changes which could lead even to inverse series of thermal stabilities, are determinate by various peculiarities introduced by the presence of the solid state. Among them, the strong intermolecular bonds which operate in solid state³⁶⁻³⁸ represent an important factor. On the other hand, when the electrostatic effects prevail, the order is preserved.³⁹⁻⁴⁰

As example, we mention the coordination compounds series containing Co(II), Ni(II) and Cu(II) cations. The stability order of complexes in solution is **Co<Ni<Cu**, identified also in some thermal reactions.⁴¹⁻⁴⁴ But there are not few examples in which others sequences were established. **Co<Cu<Ni** order is obtained in the case of the thermal decomposition of mixed complexes with 4,4'-bipyridine and dichloroacetate anion,⁴⁵ benzylamino-*p*-chlorophenylglyoxime,⁴⁶ 8-aminoquinoline⁴⁷ coordination compounds. **Co<Ni<Cu** order is found during the thermal decomposition of acetylsalicylhydroxamic acid,⁴⁸ 4(5)-hydroxymethyl-5(4)-methylimidazole.⁴⁹

Ni<Cu<Co order is achieved for mixed complexes with 4,4'-bipyridine and monochloroacetic anion,⁵⁰ 1,10-phenantroline and orotate anion,⁵¹ hydrazinium double oxalate,⁵² 3-*N*-methylmorpholino-4-amino-5-mercapto-1,2,4-triazole,⁵³ adrenaline (metallic cation/ligand= 1/4 and 1/6),⁵⁴ *N*-(2-acetamido) imidodiacetic and imidazole⁵⁵ ligands. **Ni<Co<Cu** stability order is attained for 3-*N*-methyl-piperidino-4-amino-5-mercapto-1,2,4-triazole,⁵³ adrenaline (metallic cation/ligand= 1/2),⁵⁴ *N,N*-dimethylformamide,⁵⁴ 1,2-diperidinoethane,⁵⁵ 3,3-dimethylglutarates,⁵⁶⁻⁵⁸ 4-methoxybenzoate⁵⁹ compounds. **Cu<Co<Ni** is the order reported for 3,5-dimethoxybenzoates,⁶⁰ 1,4-di-(1-hydroxyimino-2-phenyl-2-oxo-ethylamino)benzene,⁶¹ noradrenaline⁶² (nitrate outer sphere ion), 1,3-dipiperidinopropane,⁶³ 4-methylbenzylidenepyruvate,⁶⁴ ethylenediamine,¹⁸ cyclopropane-1,1 dicarboxylic acid⁶⁵ coordination compounds with citronellal anthranilic, citronellal-5-bromoanthranilic⁶⁶ ligands. **Cu<Co≈Ni** order is obtained for bis(imidazol-2-yl) methane complexes,⁶⁷ noradrenaline⁶² (chloride outer sphere ion), histamine.⁶⁸

For series of chelate coordination compounds with different central metallic ions, whose thermal decomposition begins with the breaking of an internal bond belonging to the chelate ring the

following general behaviour has been evidenced:⁶⁹ the initial decomposition temperature decreases with the increase of the stability constant. Thus, a strong metal-atom donor bond favors the weakening of one bond within the chelate ring which is further broken.

THE CHANGES IN DECOMPOSITION STOICHIOMETRY

Changes in the decomposition stoichiometry as determined by the changes of the central metallic ions may have two causes: specific properties of these metallic ions as well as structural changes which occur during the thermal treatments^{50, 70-85} Additional, catalytically active cations can also decrease the number of decomposition steps.⁸⁶⁻⁸⁷

Several examples of decomposition stoichiometry changes are given below.

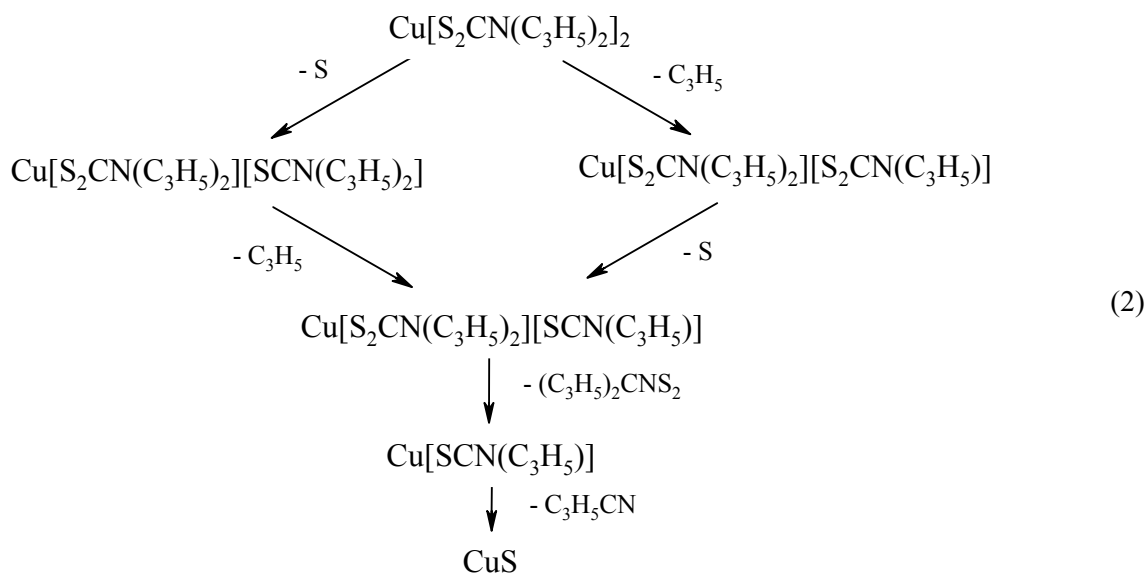
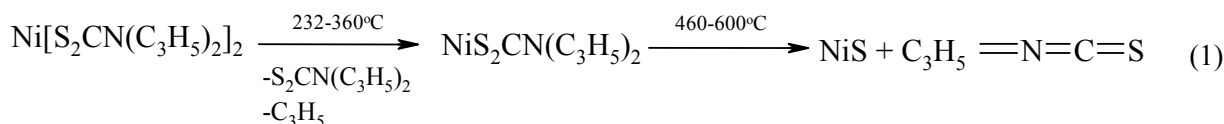
The thermal decomposition of octacyanometallates complexes of Mo(IV) and W(IV) with 8-hydroxyquinoline,⁸⁸ namely $[\text{Mo}(\text{CN})_2(\text{OH})_2(\text{Pz})_2(\text{Hox})]$ and $[\text{W}(\text{CN})_2(\text{OH})_2(\text{Pz})_2(\text{OX}) \cdot 1.5\text{H}_2\text{O}]$ (*Pz*=pyrazine and *Hox*=8-hydroxyquinoline) occurs in the following way: molybdenum complex loses CN^- in the first step (90-180°C) whereas in tungsten compound, CN^- is lost in the final step (460-510°C). Such a behaviour shows that in the second complex cyanide anion is stronger coordinated, determined by the greater ability of the 5d orbitals than 4d orbitals to form strong metal-cyanide bond;

The thermal decomposition of $[\text{Mg}(\text{NH}_3)_2](\text{NO}_3)_2$ in inert atmosphere is different than from of $[\text{Ni}(\text{NH}_3)_2](\text{NO}_3)_2$ compound.⁸⁹ In both cases the decomposition is connected with the redox processes, but in the case of magnesium compound, contrary to the nickel one, in the second stage, besides the liberation of nitrogen, nitrogen oxides and H_2O , undergoes the liberation of NH_3 and the formation of $\text{Mg}(\text{NO}_3)_2$, which in turn decomposes next, in the third stage to the oxygen, nitrogen oxides and MgO . This third stage is not present in the case of nickel compound, which decomposition undergoes directly to the final oxides (NiO_{1+x}) without the formation of $\text{Ni}(\text{NO}_3)_2$, because the autocatalytic effect of the formed NiO .

Neutral *trans*-octahedral malonamide compounds, $[\text{M}(\text{LH}_2)_2\text{Cl}_2]$ (*M*(II)= Co, Ni or Zn) decompose forming free ligand and MCl_2 by an exothermic reaction, while in the case of $\text{Cu}(\text{LH}_2)_2\text{Cl}_2$ a polymeric compound with bridging chlorines $[\text{Cu}(\text{LH}_2)\text{Cl}_2]_n$ is formed.⁹⁰

An interesting example is represented by the thermal decomposition of dialkyldithiocarbamate Ni(II) and Co(II) complexes, $M[S_2CN(C_3H_5)_2]_2$.⁹¹ In the case of Ni compound, the thermal decomposition to NiS occurs by initial elimination of $S_2CN(C_3H_5)_2$, C_3H_5 and subsequent loss of

$C_3H_5-N=C=S$ (reaction 1). On the other hand, the pyrolysis to CuS occurs via $[CuS_2CN(C_3H_5)_2][SCN-C_3H_5]$ and by sequential elimination of $S_2CN(C_3H_5)_2$ followed by elimination of RCN (reaction 2):



The thermal decomposition of metal complexes with 3,5-pyrazoledicarboxylate ligand, $[Mpz(COO)_2(H_2O)_2]$ ($M(II)=Mn, Co, Ni, Cu$ or Zn , $pz(COO)_2=3,5$ -pyrazoledicarboxylate) lead to metal oxides as final decomposition products, except manganese compound from which manganese carbonate is obtained.⁹² The partial ionic character of manganese compound may be responsible for this behaviour.⁹³

Depending on the present metallic cation, the thermal decomposition of some bivalent transition coordination compounds containing bromide and pyridine: $[MBr_2(py)_2]$,⁹⁴ $[MBr_2(an)_2]$,⁹⁵ $[MBr_2(p-caln)_2]$ ⁹⁶ and $[MBr_m(tp)_n]$,⁹⁷ where $M(II)=Mn, Co, Ni, Cu$ or Zn , py =pyridine, an =aniline $p-caln$ =4-chloraniline and tp =triphenylphosphine, $m=1$ or 2 , $n=1.5, 2$ or 3 , is characterized by different number of decomposition steps and different decomposition stoichiometries. As example we detailed the thermal degradation of $[MBr_2(py)_2]$ compounds, which decomposes in two stages (Co, Cu and Zn compounds) and, three (Mn and Ni ones). The ligand is evolved in the first step (Co, Ni and Zn compounds) or in the first two steps

(Mn compound) or all the ligand and part of the bromide in the first step (Cu compound). The compounds containing Co, Ni, Cu and Zn lost part of the metal in the last step (up to $950^\circ C$).

The thermal decomposition of complex malates ($Fe(III), M(II)=Zn$ or Ni) occurs also through a different number of decomposition steps and via different decomposition intermediates.⁹⁸ While for $Fe(III)$ and $Ni(II)$ coordination compounds form during decomposition an oxoacetate intermediate, for $Zn(II)$ an hydroxycarbonate one is evidenced.

THE CHANGE OF THE VALUES OF THE ACTIVATION PARAMETERS

The change of the activation parameters, corresponding to some thermal decompositions when the central metallic ions is changed, was investigated for a limited number of solid coordination compounds.⁹⁹⁻¹⁰⁷

The metallic ion-volatile ligand bond length could represent the main factor which determines the value of the decomposition activation energy.

An inverse dependence between radius and activation energy is valid only in the case of the coordination compounds with rigid coordination polyhedron and, only for the decomposition which occurs through similar mechanisms and begin with the breaking of metallic ion-ligand bond.¹⁰⁸⁻¹²⁰

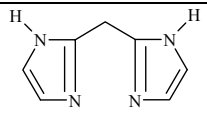
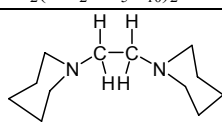
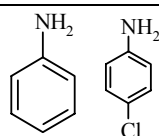
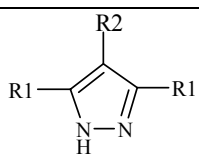
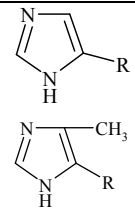
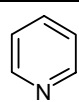
The possibility of oxidation/reduction of the metallic cation represents another cause of activation parameter changes. So during the decomposition in inert atmosphere of some rare earth (Ln(III)= La, Nd, Dy or Eu) picrates and 2,2'-dithiobis (pyridine-N-oxide) compounds, the obtained results are similar for La(III), Nd(III) and Dy(III), but different in the case of Eu(III).¹²¹ Such a difference arises due to the +2 oxidation number, which may have been caused by the nitrogen atmosphere with an eventual oxygen removal.


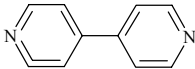
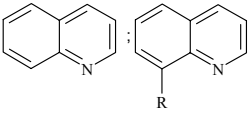
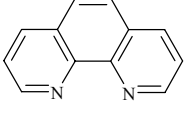
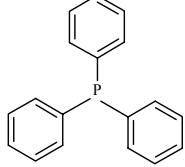
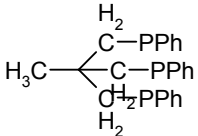
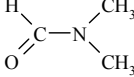
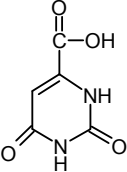
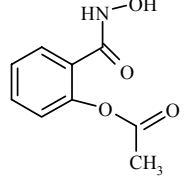
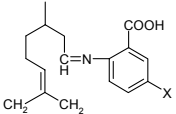
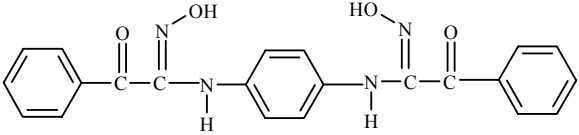
The value of the decomposition activation energy depends strongly on the covalent/ionic

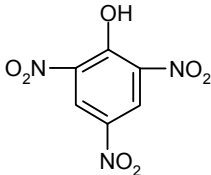
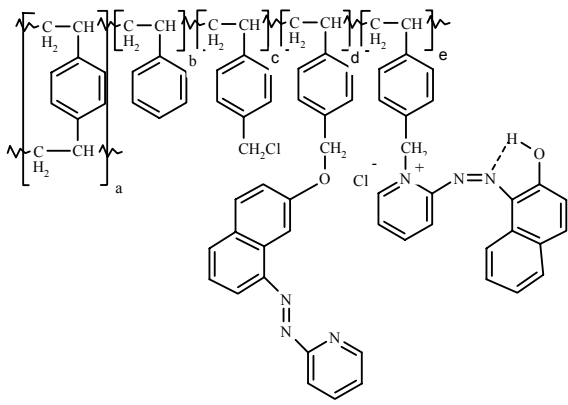
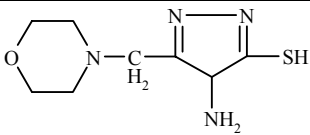
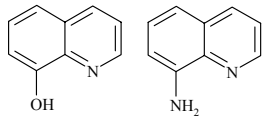
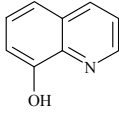
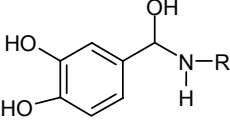
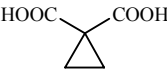
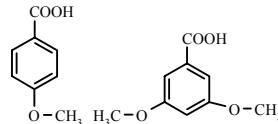
character of the M-X bond.^{58,122} Higher activation energy is obtained at a higher covalent character of metallic ion-ligand bond. So, for the coordination compounds of chlorometylated poly(styrene)-PAN resin (PAN= α -pyridylazo- β -naphthol) with some transition metal ions, the calculated thermodynamic parameters and activation energy confirm a stability order $\text{Cu} < \text{Mn} < \text{Fe} < \text{Cr} < \text{Au} < \text{Pt}$.¹²³ Such a behaviour is determined by the different nature of the chelation and transition metal ions. In the case of Au(III) and Pt(IV) ions a covalent bond is formed,¹²⁴ while during the chelation of the other metallic ions proton are liberated and the bond presents some ionic character.

For few investigated series, correlations between the decomposition activation energies and the stability constants have been revealed.¹²⁵⁻¹²⁷

Ligands molecular formula

Compound	Formula
Nitrogen containing compounds	
ethylenediamine (en)	$\text{NH}_2-(\text{CH}_2)_2-\text{CH}_2-\text{NH}_2$
hydrazine	N_2H_4
bis(imidazol-2-yl) methane	
1,3-diperidinopropane	$\text{CH}_2(\text{CH}_2\text{NC}_5\text{H}_{10})_2$
1,2-diperidinoethane	
aniline <i>p</i> -Cl-aniline	
pyrazole pyrazole (R1=R2=H) 3,5-dimethylpyrazole (R1=-CH3; R2=H) 3,5-pyrazole dicarboxylic acid (R1=COOH; R2=H)	
imidazole (im) (R=H); 4-methylimidazole (4-Meim) (R=-CH3); histamine (R=CH2-CH2-NH2) 4(5)-hydroxymethyl-5(4)-methylimidazole (R=CH2OH)	
pyridine	

pyrazine	
4,4'-bipyridine	
quinoline 8-hydroxyquinoline (R=OH, Hox) 8-aminoquinoline (R=-NH ₂)	
<i>o</i> -phenanthroline (phen) (1,10)	
Sulfur containing compounds	
Dialkylthiocarbamate R ₁ =R ₂ =-C ₃ H ₅	(R ₁ R ₂)NSSH
Phosphorous containing compound	
triphenylphosphine	
tripodal phosphine (Htripos)	
Nitrogen-oxygen containing compounds	
dimethylformamide	
orotic acid	
acetylsalicylhydroxamic acid	
citronellal anthranilic (X=-H) citronellal-5-bromoanthranilic (X=-Br)	
1,4-di-(1-hydroxyimino-2-phenyl-2-oxoethylamino)benzene	

picric acid	
chloromethylated polystyrene- α -pyridylazo- β -naphthol	
Sulfur-nitrogen and sulfur-nitrogen-oxygen containing compounds	
3-N-methyl-morpholino-4-amino-5-mercapto-1,2,4-triazole	
Aminohydroxylated compounds	
8-hydroxyquinoline (Hox)= 8-aminoquinoline	
8-hydroxyquinoline (Hox)	
noradrenaline (R=H) drenaline (R=-CH ₃)	
Carbonylic compounds	
malonamide	$\text{CH}_2(\text{CONH}_2)_2$
Aliphatic acids	
monochloroacetic acid	ClCH_2COOH
dichloroacetic acid	Cl_2CHCOOH
cyclopropane-1,1 dicarboxylic acid	
4-methylbenzylidenepyruvate	$4\text{-CH}_3\text{-C}_6\text{H}_4\text{-CH=CH-CO}_2\text{COOH}$
oxalic acid	HOOC-COOH
malic acid	$\text{HOOC-CHOH-CH}_2\text{-COOH}$
3 methylglutaric acid	$\text{HOOCCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{COOH}$
Aromatic acids	
4-methoxybenzoic acid dimethoxybenzoic acid (3,5-)	

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