ELSEVIER

Thermochimica Acta 320 (1998) 187–199

thermochimica
acta

Thermal stability of transition-metal complexes

Ahmed M. Donia*

Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt

Received 30 September 1997; accepted 29 June 1998

Abstract

This review aims at justifying the relationship between the room-temperature structures of transition-metal complexes and their thermal stabilities. The different factors affecting the thermal stability were also clarified. The survey of a larger number of transition-metal complexes showed various correlations of thermal stability with metal ion, ligand character or counterion. © 1998 Elsevier Science B.V.

1. Introduction

The measurement of the thermal stability of solid complex compounds is usually carried out by the estimation of the heat of reaction from the metal salts with the ligands. Experimental investigations of the thermal stability of complex compounds, as well known, go back to caloric measurements of Ephraim and Biltz [1] at the beginning of the twentieth century. The reaction enthalpy of hydrates from this measurements allowed a good evaluation of thermal stability. The thermochemistry of complex compounds has been mainly created by Klemm [2], Spacu [3] and Heiber [4]. These studies have been essentially completed by the investigations of Jatzimirski [5] with the publication of a monograph in 1951 summarizing his presentations of the thermal stability of complex compounds.

Nowadays, the thermal analysis techniques (DTA, TGA, DSC,...) play an important role in studying the structure and properties of metal complexes. Liptay [6] reports about the frequency of thermo-analytical investigation during the period 1975–1987. The compounds studied are most often inorganic and coordination compounds. between 15–20% of the contributions in the Journal of Thermal Analysis in the last decade referred to the thermal behaviour of coordination compounds. Numerous transition-metal complexes are of special interest in industry, medicine and biology, e.g. the electrical and thermochromic properties, antioxidation, vulcanization acceleration, protecting paintings, catalyses and antibacterial properties. Up till now a number of solid-state reactions of coordination compounds (such as thermal isomerization, conformational changes, polymorphic transformations, thermal phase transitions, thermochromism) were studied and increasingly enter into the scientific basis of coordination chemistry [7–12]. The above uses and reactions are related to room temperature structures of the compounds as well as their thermal stability. So, a clear picture should be given on the nature of interrelation between structure and thermal stability. The different factors affecting the thermal stability of transition-metal complexes (with homogenous as well as with heterogenous coordination sphere) should also be discussed. These

---

*Corresponding author.

PII S0040-6031(98)00472-9

two points represent the major aim of the present review.

2. Ammino-metal complexes

Wendlandt et al. studied the thermal decomposition of a large number of transition-metal–ammine complexes during the period (1960–1964). Numerous results were extracted form that type of study on complexes with homogenous or heterogenous coordination spheres. They studied complexes of the type $[Co(NH_3)_5Y]X_2$, where X and Y are Cl, Br and I [13]; $[Pd(NH_3)_4]X_2$, where X is Cl, Br, I, NO_3 [14] and $[Cu(NH_3)_6]X_2$, where X is Cl, Br and I [15]. The complexes of cobalt(II and III), platinum(II and IV) and chromium (III) containing ammonia in the coordination sphere and nitrate or chloride ions in the ionization sphere were also investigated [16–19]. The results indicate that the complexes of cobalt(III) and copper(II) decomposed in a single step to give a residue of the type MX_2. The investigation of the thermal stabilities led to the following points

For cobalt(III) and copper(II) complexes, the thermal-stability order is:

(i) chloro- (150°C)>bromo- (100°C) iodo- (50°C)
(ii) The cobalt(III) complexes with two ionizable chloride ions and one halide ion (Cl, Br or I) in the inner sphere follow the thermal stability order: chloride (150°C)>bromide (110°C)>iodide (50°C).
(iii) The cobalt(III) complexes with two ionizable halide ions (Cl, Br, I) and one chloride ion in the inner sphere follow the order: chloride (150°C)>bromide (138°C)>iodide (40°C). It is seen that the complexes containing iodine, either in coordination or ionic spheres, were certainly the least stable. This was perhaps due to the ease of oxidation of iodide ion into free iodine. For palladium(II) and platinum(II) complexes, the decomposition reaction occurs in a two-step (except for nitrate) deamination reaction as indicated from DTA and TGA curves. The peak maxima temperatures for the first deamination reaction increased in the order: iodide (110°C)<bromide (150°C)<chloride (180°C). The nitrate complex decomposed in a single step, giving only one exothermic DTA peak at ca. 245°C. This behaviour was similar to that of cobalt(II) [17,18], chromium(III) [19] and platinum(II) and (IV) [16]; and may be attributable to the oxidation effect of nitrate as a result of its decomposition.

3. Aliphatic diamine metal complexes

The thermal stability of mono-*bis*-and *tris*-(ethylenedioamine (en)) *bis*-(1,2-propanediamine (pn)) and *bis*-(1,3-propanediamine (tm)) of copper(II)sulphate was studied by TGA, DTA, GE and high-temperature reflectance spectroscopy [20]. In general, the relationship between the minimum weight-loss temperature (thermal stability) and the coordinated amine ligand for a number of complexes is given in Fig. 1. It can be seen that the thermal stability of the complexes decreased with change in ligand in the order: en>pn>tm. This relationship appears to be a general one for a number of complexes containing copper(II),

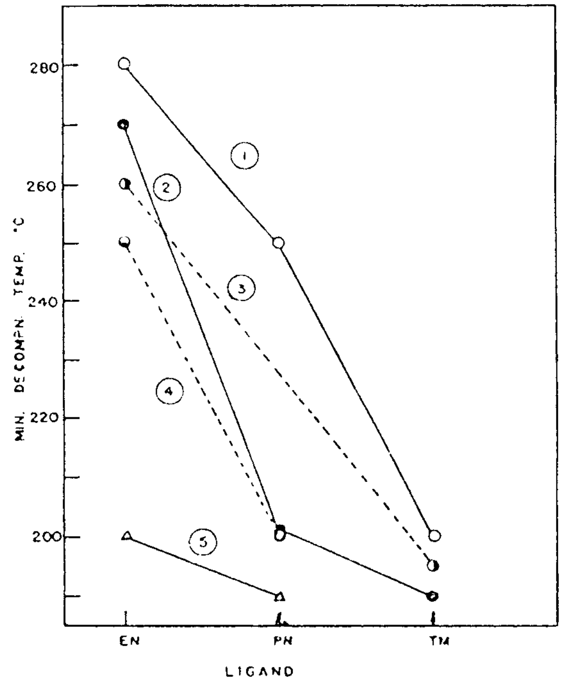


Fig. 1. Relationship between thermal stability and the coordinated amine ligand of some metal complexes: 1, $[Cu(amine)_2]SO_4$; 2, $[Co(amine)_2CO_3]Cl$; 3, $[Co(amine)_3]Cl_3$; 4, $[Pt(amine)_3]Br_4$; and 5, $[Pt(amine)_3]Cl_4$.

cobalt(III) and platinum(IV) as central metal ions. This behaviour of thermal stability can be attributed to the chelate ring size and the steric factor of methyl group (in the case of pn-complexes). For copper-en complexes, the stability follows the order: $[Cu(en)(H_2O)_2]SO_4$ (200°C)<$[Cu(en)_2]SO_4$ (280°C) <$[Cu(en)_3]SO_4$ (>300°C). This order is attributable to the number of chelate rings around the central metal ion. The studies also showed that the counteranions have a pronounced effect on the thermal stability [21,22,16].

The thermal behaviour of octahedral $[NiL_2(NCSe)_2]\cdot 2H_2O$ [L=piperazine (pipz) or N-methyl piperazine (N–Me pipz)] complexes was studied [23]. The order of stability with respect to the DTA peak temperature is pipz>N–Me pipz. It is seen that, although N-alkylation increases the basicity of the cyclic ligand, the stability decreases due to the steric effect of methyl group [24,25].

4. Aromatic amine–metal complexes

Bowman and Rogers [26] and House et al., [27,28] have determined the correlation between the stability and ligand basicity of various transition-metal complexes with pyridine and substituted pyridines. The steric factors were also considered. The results showed that the thermal stability increases with the ligand basicity and the steric effect influenced stability in a predictable manner, i.e. when methyl groups blocked the coordination position, the stability decreased. To clarify this point, thermal decompositions of *bis* (dibenzoyl-methanato)oxovanadium(IV) complex with pyridine (PY), 3-methylpyridine (3-MP), 4-methylpyridine (4-MP), 3,5-dimethylpyridine (3,5-DMP), 3-amino-pyridine (3-AP) and 4-aminopyridine (4-AP) were considered [29]. A linear relationship existed between PK_B (basicity constant of ligand towards the proton) values of the bases and the temperature for the decomposition, except for the complexes obtained with (4-AP) and (4-MP). These complexes are less stable than expected from the basicity of the ligands. These observations were discussed in terms of the nature of the metal-ligand bond. The greater the basicity the higher temperature to produce the loss of the ligand. The order of decreasing base strength is 4-AP>3-AP>3,5-DAP>3-MP>PY.

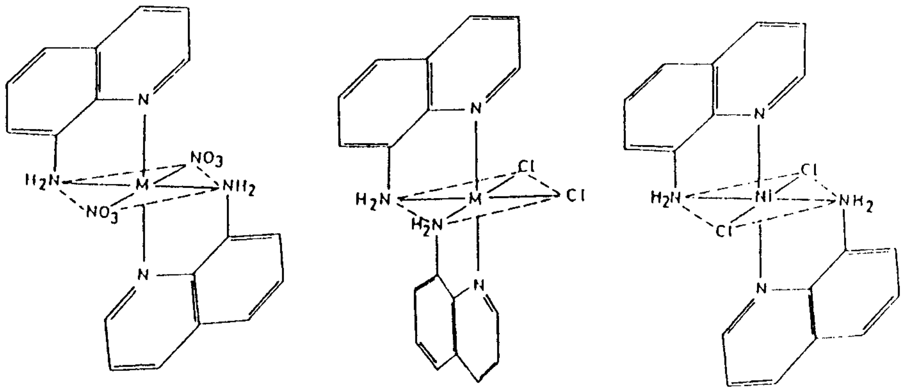
The pronounced effect of methyl and amino-groups in the 4-position on the stability cannot be reflected by the basicity of the ligand, and can be due to the existence of resonating structures which lower the tendency to form metal–ligand π-bonds.

Recently, the effect of bonding mode of water (in inner or outer sphere) on the thermal stability of 2,2′-dipyridyl and 4,4′-dipyridyl complexes with rare-earth elements has been studied [30]. It is seen that the dissociation process proceeds via dehydration followed by deamination. In spite of the different structures of 2-dipy and 4-dipy complexes their decomposition proceeds in a similar way, and the thermal stability of different types of hydrated complexes is similar.

Thermal investigation of different nickel(II) complexes with methylamine (MA), diethanolamine (DEA), 2,2′-dipyridyl (dipy) and 1,10-phenanthroline (phen) was carried out [31]. The decomposition processes proceed via the successive loss of the ligands due to the rupture of M–N bond. The thermal stability follows the order: DEA>MA>dipy>phen. Also, the bromide complexes display a lower stability a lower stability than the corresponding chloride ones. This stability behaviour is attributed to the steric factor contribution in the coordination sphere.

Allan et al. [32–38] have produced a series of papers describing the thermal stability, in air, of different complexes of various metals. The metals include cobalt, nickel, copper and manganese, while the ligands include 7,8-benzoquinoline, anthranilamide, 4-aminobenzylhydrazide, 2,6-diaminopyridine, 4,7-phenanthroline, 1,10-phenanthroline, 2,3-*bis* (2-pyridyl) pyrazine, 2,2-*bis*(acrylamido) acetic acid, *m*-toluidine, nonylamine, poly-(acrylic acid) and 2-butoxy pyridine. Two patterns of behaviour can generally be discerned, one in which the chloro-complex with the metal either exothermically decomposes directly to the oxide or endothermically decomposes to the metal chloride followed by an exothermic conversion to the oxide. In an nitrogen atmosphere, the decomposition reactions gave the powdered metal as the final product. This provides an excellent method of obtaining powdered metals of high reactivity. Allan [39] also provided a review on that topic.

Donia et al. [40,41] reported the thermal behaviour of divalent metal (cobalt, nickel and copper) complexes with some aromatic diamines (2,3-, 1,8- and



Scheme 1.

1,5-diaminonaphthalene). The thermal stabilities were discussed in terms of chelate ring size, counter anions and angle strain.

Donia and El-Boraey [42] also studied the thermal behaviour and decomposition pathways of cobalt(II), nickel(II) and copper(II) with 8-aminoquinoline. The thermal stabilities were discussed in terms of ionic radii, crystal-field splitting energy and steric hindrance. The effective role of the counterions (Cl^- and NO_3^-) on the decomposition temperatures and the final products were also clarified. The results indicate that:

(i) The nitrato complexes gave the metal oxide at a lower temperature than the corresponding chloro ones. This was attributed to the oxidation effect of the nitrate ion.

(ii) The octahedral nitrato complexes have higher thermal stabilities than the corresponding chloro complexes. This may be explained by the distribution of the ligands around the metal (Scheme 1).

(iii) For the isostructural nitrato complexes, the order of the thermal stabilities is: Ni>Cu>Co.

5. Oxalato–, succinato–, malonato– and dithiooxalato–metal complexes

The relative thermal stability of $CuC_2O_4 \cdot 1/3H_2O$ and Co $C_2O_4 \cdot 2H_2O$ with polymeric structure was discussed by Donia and Dollimore [43]. The study indicates that the rupture of C–O bond is the first step in the decomposition reaction. The lower thermal stability of copper (220°C) than that of the cobalt complex (290°C) could be attributed to the higher electronegativity of copper, which results in a strong Cu–O bond and a weak C–O bond.

The thermal investigation of transition-metal–oxalato, transition-metal–malonato and transition-metal–succinato complexes having ammonium ion (NH_4^+) or (Li^+) ion outside the coordination sphere has been carried out. The complexes are of the type $(NH_4)_4[ML_3] \cdot nH_2O$ [44] or $Li_4[ML_3] \cdot nH_2O$[45], where M=Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) [46], L=oxalate, malonate and succinate ligands and n=1–7. The results inferred are that the thermal stability decreased approximately with increase of standard potential of the central metal ion. It is also found that, for $(NH_3)_4[FeL_3] \cdot nH_2O$, the decomposition peak temperatures with different ligands follow the order: succinato>oxalato>malonato.

Donia [47] also studied the effect of atmosphere (dynamic air/N_2) on the thermal decomposition of the coprecipitates $Ag_2MC_2O_4)_2 \cdot nH_2O$ (M=Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+}). He found that the atmosphere of decomposition plays a significant role upon the nature of decomposition as well as the type of thermoproducts and their thermal stability.

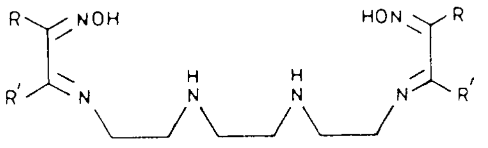
The thermochemistry of 1,2-dithiooxalato–S,S′-complexes has recently been studied by Roman et al. [48–51]. The data indicate that the surrounding atmosphere significantly influences the course of the decomposition as well as the final products. In an oxidative atmosphere, a mixture of nickel(II,III) oxide and sulphide, palladium(II) oxide and metallic platinum were obtained, whereas in an inert atmosphere, nickel(II) and palladium(II) sulphides and platinum

(0) were identified as final products. The thermal stability of the complexes depends on their structures and the atmosphere used.

6. Schiff's base–metal complexes

The thermal investigation of polymeric Schiff's base complexes of 1,4-*bis* (2′-hydroxyphenylazomethine) phenylene (Scheme 2) with metal ions Ti(III), Cr(III), Fe(III), Mn(II), Ni(II) and Cu(II) was reported [52]. The thermograms indicate that the polychelates decompose in two stages and the rate of degradation in the first stage is rapid compared to the second stage. Moreover, the thermal stabilities of polycoordinates are in the order: Ni>Cu>Mn>Cr>Ti>Fe, and the decomposition was completed at ca. 750°C in all chelates.

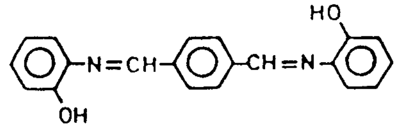
Mohapatra et al. [53]. studied the thermal decomposition of cobalt(III), complexes with hexadentate dioxime Schiff bases (shown below). The studied complexes were of the type $Co(HL)X_2$ [where X=Br, I, NO_3] and $H_2L=H_2L^1$ or H_2L^2.



R = R` = Me (H_2L^1)

R = Me , R` = Ph (H_2L^2)

The complexes were thermally quite stable up to 200°C, beyond which the ligand begins to decompose slowly and lose ligands in discrete steps. The thermal stability follows the relative order: iodide>bromide>nitrate.



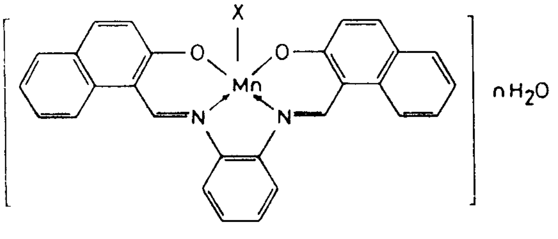
Scheme 2.

On the order hand, the complexes of ligand (H_2L^1) showed a higher thermal stability than those of (H_2L^2). This behaviour can be explained by the steric effect of the phenyl group and the oxidation effect of the nitrate ion [14].

The degradation of Co(II), Ni(II) and Cu(II) complexes with Schiff base derivatives of 1H-indole-3-ethylenesalicyladimine (sal TPA) (Scheme 3) was reported [54].

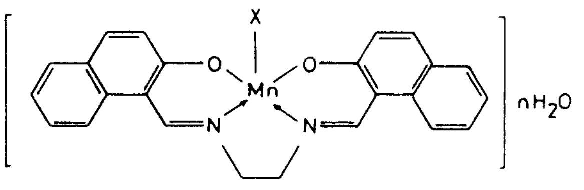
The study established the relationships between thermal stability, metal coordination and position of the functional groups (3-methoxy, 5-methoxy or 5-bromide). Considering the same metal ion, the order of thermal stability is: 3-MeOsal TPA<sal TPA<5-MeO-sal TPA<5-Bromosal TPA. The sequence found may be explained by the larger steric hindrance of $-OCH_3$ in position-3 because of the greater proximity of this group to the chelate ring. For the same ligand, the stability order is: Cu<Co≃Ni. The higher thermal stability of nickel and cobalt is attributed to the type of ligand, which favours planar coordination around the metal. Moreover, in both metals, the trans-planar chromphore MO_2N_2 is less distorted than in the copper complexes.

Donia et al. [55,56] studied the thermal decomposition of two series of square pyramidal manganese(III) complexes with Schiff bases derived from *o*-phenylenediamine (I) and ethylenediamine (II).



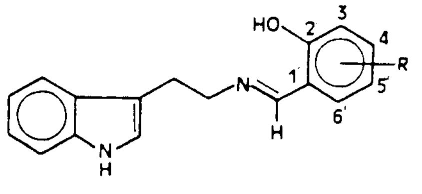
(I)

1: $X = OAc$, $n = 3$; 2: $X = SCN$, $n = 0$;
3: $X = Cl$, $n = 0$; 4: $X = Br$, $n = 0$;
5: $X = I$, $n = 0$



(II)

1: $X = Cl$, $n = 2.5$; 2: $X = Br$, $n = 2.5$;
3: $X = I$, $n = 4$; 4: $x = SCN$, $n = 2$



R = 3 or 5–OCH_3 , 5–Br

Scheme 3.

The study revealed that, for series (I), the decomposition reaction begins with the scission of axial anions (M–X bond), and the thermal stability follows the order: OAc<SCN<Cl<Br<I. This order of stability was correlated to the electronegativities (χ) of the axial donor atoms (Fig. 2).

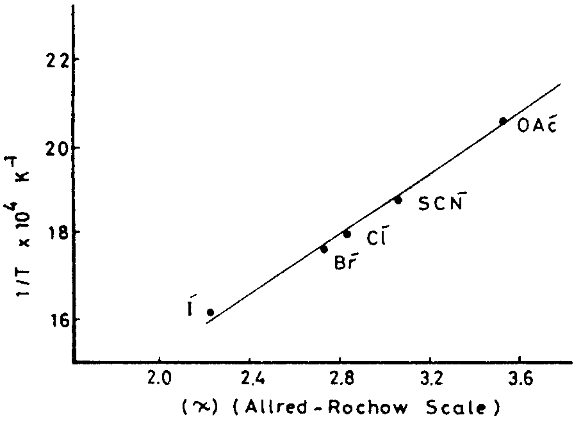
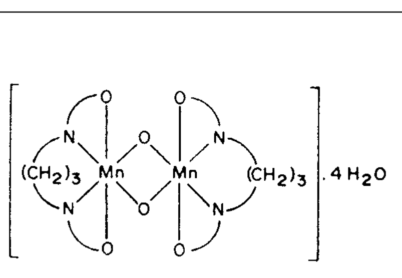


Fig. 2. A plot of the initial decomposition temperatures and electronegativities (χ) of the axial donor atoms.



Complex (1)

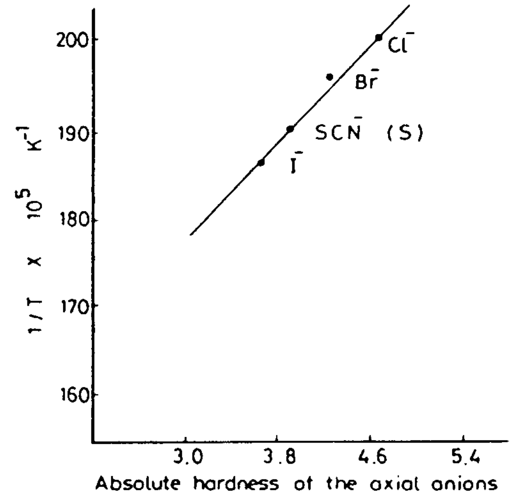
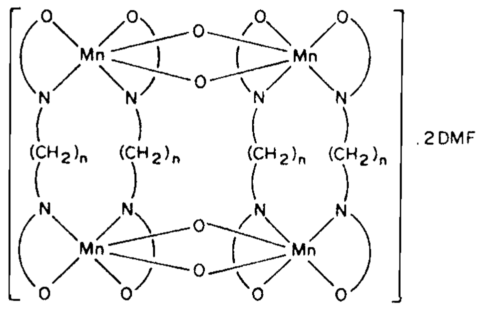


Fig. 3. Correlation between desolvation temperatures and hardness of the axial anions.

This type of correlation was not found in series (II), indicating that the rupture of the axial (M–X) bond is not the first step of the decomposition reaction. Instead, the rupture of the five-membered chelate ring is the first step. Moreover, the complexes of series (II) decompose during the desolvation process, and a correlation was obtained between the initial temperature of desolvation and the hardness of the axial anions (Fig. 3). This indicates that the water of crystallization plays an effective role in the lattice forces through the hydrogen bonding with the axial anions.

The thermal stability of di-μ-oxo-bridged binuclear(1) and tetranuclear (2,3) manganese(IV)–Schiff's base complexes was also investigated by us [57].



n = 3, complex (2)
n = 4, complex (3)

The results indicated that the exothermic scission of di-μ-oxo four-membered ring is the first step in the decomposition reaction. The dimeric complex (1) displays a lower thermal stability (176°C) compared to the tetrameric complexes (2) and (3) (200°C). This difference in the thermal stability could be explained in terms of structural and conformational factors. Thus, the [(di-μ-oxo)Mn_2] core, being a four-membered ring, is subjected to torsional strain; this strain is partially relieved by folding the ring in (2) and (3), but in the case of complex (1) the greater number of six-membered chelate rings around the same core hampers this folding and, therefore, gives a lower stability. The results of thermal stability also throw some light on the ESR inactivity of complex (1).

The thermal behaviour of copper(II), iron(II) and iron(III) with 1-(2′-hydroxybenzyl)-(2′-hydroxyphenyl)-benzimidazole(HBHPB) was reported [58]. The order of thermal stability for copper is: chloride>nitrate>sulphate>acetate, whereas in the case of iron the order is: acetate>nitrate>chloride>sulphate.

The thermal stability of some rare-earth-salicylaldehydre-β-alanine Schiff bases was reported [59]. The complexes are thermally stable up to 128–173°C. The decomposition proceeds via the rupture of C–N single bond to give oxy-or dioxy-metal carbonate [$LuO(CO_3)_2$ or LnO_2CO_3], except with CeL_3 and GdL_3 complexes, which gave CeO_2 and Gd_2O_3, respectively.

7. Mixed ligand–metal complexes

The thermal stability of [$Co(DH)_2Am_2$]X, where DH=dimethylglyoxime, Am=*o* -, *m*- or *p*-halogenato-aniline and X=Cl^-, Br^-, I^- or SCN^- was studied by thermogravimetric analysis (TGA) [60]. The first stage of the thermal decomposition reaction was a substitution reaction with the formation of a nonelectrolytic intermediate [$Co(DH)_2AmX$]. The data revealed that the order of the stability was: $Cl^->Br^->I^->SCN^-$ for the same coordinated amine. The observed decrease in the decomposition temperature was explained in terms of nucleophilic power of the attacking agent (electron-donor constants: $Cl^-=1.24$, $Br^-=1.51$, $SCN^-=1.83$ and $I^-=2.06$). The only apparent exception is the SCN^-, but as it is capable of giving π-bonding with cobalt, which stabilizes the activated intermediate.

The study of thermal stability of mixed ligand lanthanide (Ln^{3+}=Dy, Sm, Ho, Yb) complexes involving cyclopentadienyl (CP) and two different classical chelate ligands (trifluoroacetato and either 8-quinolinolato or *o*-amino-phenolato), with general formula CPLnLL′ was reported [61]. The result of decomposition temperatures and MS data gave the following order of stability: CP Yb LL′>CP Ho LL′>CP DY LL′>CP Sm LL′. This order may be attributable to the lanthanide contraction, which results in strong ligand (anionic)–metal (cationic) interaction. Moreover, according to the concept of correlation of stability with steric saturation [62,63], the above order also may be a consequence of greater saturation around the smaller metal centre. In addition, the 8-quinolinolato complexes have relatively higher decomposition and disproportionation temperatures than the corresponding *o*-aminophenolato complexes. This can be explained by the strong complexing ability of the 8-quinolinolato ligand and its larger steric volume compared with those of *o*-aminophenolate ligand.

The thermal investigation of copper oxalate and its mixed ligand complexes with different amines was also reported [64]. The complexes of composition $CuC_2O_4{\cdot}0.5H_2O$, $CuC_2O_4(NH_3)_2$, $CuC_2O_4(py)$, $CuC_2O_4(An)_2$, $CuC_2O_4(en)_2$, $CuC_2O_4(EtNH_2)_2$ and $CuC_2O_4(MeNH_2)_2$. The results indicate that the amine molecules are lost at lower temperatures than in case of oxalate decomposition, indicating that the Cu–N bond is weaker than the Cu–O bond. This behaviour led to the inference that the decomposition temperature is influenced by the axial base, i.e. amines. The pyridine (py) complex showed different thermal behaviour from the other amine complexes. The amines form complexes through the donation of a nitrogen lone pair of electrons to the metal, whereas in the case of pyridine the nitrogen atom is incorporated into a conjugated ring system, and therefore, acts as a π-acceptor (through a delocalized orbital) as well as a donor ligand, indicating a higher interaction of pyridine moiety, and, thereby, decomposing in different way from the other amine members.

Ludwing et al. [65] studied the thermal behaviour of the mixed ligand complexes of the type CoD_2I_2, where D=acetylacetone or benzoylacetone; I=imidazole or pyrazole. In the case of acetylacetone, the first step is the split of acetylacetone moiety, whereas for benzoylacetone the decomposition starts with the partial elimination of heterocyclic ligands. This indicates the strong interacting nature of benzoylacetone compared to acetylacetone. The data showed that the split of acetylacetone proceeds via proton transfer from the heterocyclic compound to the diketone to give the polymeric *bis*-imidazolato or *bis*-pyrazolato Co(II) complex as a stable intermediates, which decompose completely at higher temperatures. The coordination polymer *bis*-imidazolato-cobalt(II) shows significantly higher thermal stability than the corresponding *bis*-pyrazolato compound.

The thermal stability of transition-metal complexes $[ML'(B)]Cl$, where M=pd(II) or Ni(II), B=pyridine, NH_2Et or $NHEt_2$, L′=methyl-2-(β-amino-ethyl-amino)-cyclopenta-1-enedithiocarboxylate), was investigated by DTA and TGA [66]. The heats of dissociation (ΔH) for the reaction

$$[PdL'(B)]Cl \rightarrow [PdL'Cl] + B$$

have been compared with the analogous nickel(II) complexes. The results indicate that, in all cases, the nickel complexes are more stable. This would mean relatively greater bond strength of Ni–B.

8. Transition-metal-containing polymers

Nowdays, great attention is being paid to the chemical modification of polymers and their bulk properties (thermal stability, electrical conductivity, dielectricity, catalytic action, etc.) by metal-ion loading [67–72]. The collected data indicated that, in general, the bulk properties depend on the nature of 3*d*-metal centre, and, in all cases, the metal-loaded polymers exhibit appreciable improvement in thermal stability.

9. Miscellaneous transition-metal complexes

9.1. Oxime– and pyridine–transition-metal complexes

Lipaty et al.[73] investigated the relationship between the thermal and equilibrium stabilities of some transition-metal complexes. To examine this relationship, they studied two types of Mn(II), Co(II), Ni(II), and Cu(II) complexes.

(i) The mixed pyridine–thiocyanate complexes to study the cleavage of coordinative bond.

(ii) Bidentale oxime complexes to study the cleavage of the chelate ring.

Mn(II), Co(II) and Ni(II) form distorted octahedral mixed-ligand complexes with pyridine and thiocyanate $[MPy_4(SCN)_2]$, whilst copper(II) forms a complex with composition $[CuPy_2(SCN)_2]$, presumably of tetrahedral symmetry. Manganese(II) and nickel(II) complexes liberate on heating the four pyridine ligands in two steps, while the decomposition of cobalt(II) complex presents three distinctly separated processes. Copper(II) complex liberates the two pyridine ligands in a single step. The thermal decomposition of the oxime chelates suddenly starts at a certain temperature. The octahedral complexes liberate their first two pyridine ligands in the order of increasing thermal stabilities of the complexes. According to the stability series given by Irving and Williams [74], the stability of these complexes of increase in the order: Ni>Co≫Mn. The copper complex does not fit into this order, presumably due to its different way of decomposition. The results also showed that the thermal stability of those complexes increases with increasing equilibrium constants. This behaviour is due to the fact that the bond between the central metal ion and the nitrogen donor atom of pyridine is the first to be ruptured upon the action of heating. Thus, the increase in strength of this bond (which corresponds to an increase in the stability constant of the complex) will obviously bring an increase in the thermal stability. For the chelate complexes, it can be seen that the initial temperature of decomposition decreases with an increase of the equilibrium stability constant (Table 1) in the systems of complexes formed by the same ligand with various metals.

The increase of the strength of the coordinative metal-donor atom bond thus results in a decrease of the thermal stability of the complex. This phenomenon may be explained by the fact that thermal decomposition in the system investigated does not begin the coordinative bond, but by the cleavage of another bond in the chelate ring. An increase in the strength of the coordinative bond (a stronger coordination of the free electron pair of the donor atom to the central metal

Table 1
The initial temperatures of thermal decomposition of a few transition-metal-oxime chelates, and their overall stability constants

Complex	Initial decomposition temperature/°C	$\log\beta_2$	Medium of equilibrium measurements/(% dioxane)
Copper(II) salicylaldoxime	170	21.5	75
Iron(II) salicylaldoxime	190	16.7	75
Nickel(II) salicylaldoxime	240	14.3	75
Nickel(II) nitrosalicylaldoxime	185	13.8	75
Iron(II) nitrosalicylaldoxime	260	12.5	75
Copper(II) dimethylglyoxime	160	23.5	50
Nickel(II) dimethylglyoxime	290	21.7	50
Copper(II) nioxime	130	25.7	50
Nickel(II) nioxime	240	22.46	50
Copper(II) furyldioxime	190	18.6	75
Nickel(II) furlydioxime	210	14.1	75

atom) results in a weakening of that of the chelate ring, which is first ruptured upon heating. These observations indicate the role of the nature and structure of the ligand and, consequently, the structure of the complex is considerably greater in the determination of the thermal stability of the chelate complexes than the effect of the strength of the coordinative bond.

9.2. Oxine–metal complexes

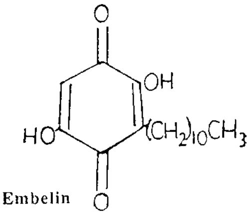
The thermal stability of metal chelates of oxine was investigated by different authors [75–79,73]. The thermal decomposition of 8-hydroxyquinoline metal [Co(II), Ni(II) and Mn(II)] complexes, for example, proceeds in two stages: the first step is dehydration, whereas the second step is the loss of 8-hydroxyquinoline. The initial decomposition temperatures of the complexes as obtained from DTA and TGA analyses indicated the following order of stability: Co>Ni>Mn. The temperatures of the oxide formation increases periodically with increasing the atomic number.

9.3. Mono- and dimethylthiourea–metal complexes

The thermal decomposition of methyl and dimethylthiourea of serval transition metals was studied by thermogravimetric analysis in air and vacuum, and the stability relations established [80]. In vacuum, the Mn, Fe and Co complexes of dimethylthiourea (DMTU) exhibit an order of stability in agreement with the Irving–Williams series. The unusually low decomposition temperature of nickel is associated with a different stoichiometry. Chromium involves a different oxidation state and exhibits a very long decomposition range. The decomposition in air proceeds in two steps rather than the one step observed in vacuum. The decomposition in air also begins at a higher temperature.

9.4. Embelin–metal complexes

Embelin [2,5-dihydroxy-3-undecyl-2,5-cyclohexadiene-1,4-dione) is an orange pigment isolated from the berries of the Indian Shrub *Embelia ribes*, and has a great medicinal importance.



Embelin

The thermal behaviour of some of its transition-metal complexes was studied [81]. The complexes follow the stability sequence Ni>Mn>Cu.

Table 2
Binding energy (BE), energy gap (ΔE), charge density on the metal atom and DTA decomposition temperature for complexes

Compound	BE/(eV)	ΔE of $d_{x-y} \rightarrow \pi^*_{C=N}$/eV calc. (found) [a]	Charge density on the metal ion	DTA T_{decomp}/°C
CoL_2	4.619	0.631 (0.625)	+0.967	250
NiL_2	4.148	0.217 (0.15)	+0.982	240
CuL_2	2.176	1.907 (very low conductivity)	+0.909	210

9.5. Copper(II)-3,5-diisopropylsalicylate hydrate [Cu(DIPS)$_2$]·XH$_2$O

The thermal decomposition of [Cu(DIPS)$_2$]·XH$_2$O [X=3 or 4] was followed up by TGA, DTA and IR-gas phase analyzer [82]. The results showed that the complex melts at 115°C, followed by release of isopropyl alcohol (C_3H_7OH) to yield copper salicylate through two endothermic processes at 130° and 210°C. Subsequently, the copper salicylate released phenol, CO and CO_2 to give CuO as a final product at 250°C. The decomposition reaction is not initiated by the scission of the coordinate bond (M–L), but by cleavage of another bond in the chelate ring, which has been weakened on M–L bond formation. This behaviour is in conformity with the decomposition behaviour of salicylate metal complexes and related compounds [83,84].

9.6. Rare-earth complexes with acidic ligands

The thermal behaviour of rare earths (Y, La–Lu) with different acidic ligands as heptanedioic acid [85], *o*-, *m*- or *p*-chlorobenzoic acids [86–88], 2,4-dichlorobenzoic acid [89] and 2,5-dichlorobenzoic acid [90] was recently investigated. For the heptanedioic acid complexes, with the composition $Lu(C_7H_{10}O_4)_3 \cdot nH_2O$ (n=8, 12 or 16) the thermal stability was discussed in terms of the nature of interaction of water of crystallization. Chiefly, the heavy lanthanide indicates a very wide range thermal stability. Whilst light lanthanide indicate A narrower range of stability. The chlorobenzoate complexes decomposed to give the oxides through intermediate formation of LnOCl, except Ce(III) which directly decomposed to CeO_2. Comparing the temperature of oxide formation (T_k), it is possible to see that they change regularly with the atomic number (Z) with the exception of CeO_2.

9.7. Metformin-metal complexes

The thermal stabilities of Co(II), Ni(II) and Cu(II) metformin complexes were investigated by means of DTA. A correlation has been found between the experimental data and the calculated values (Fig. 4 and Table 2) of bond energy and bond order [obtained form atomic superposition and electron delocalization molecular orbital (ASED-MO)]. The optimization of the structures shows that the order of stability is Co>Ni>Cu, which coincides with that obtained form DTA results (Table 2) [91].

9.8. Alginate–metal complexes

The thermal behaviour of mono-, di-, tetra- and hexavalent metal–alginate complexes was studied by means of TGA, DTA, solid electrical conductivity (EC) and FT-IR [92,93]. The study indicates that the complexes are thermally stable and their thermolysis proceeds via the formation of metal oxalates as intermediates. The temperature range corresponding to the main decomposition stage reveals that the stabilities depend on the ionic size of metal ions.

10. Conclusion

1. The thermal decomposition of metal–ammine complexes is a one- or two-step deamination reaction (according to the type of metal ion). For the same metal, the thermal stability of the complexes depends mainly on the counter ions in both inner and outer spheres. In general, the iodo-containing complexes showed a lower thermal stability due to the ease of oxidation of iodide ion to free iodine.
2. On account of the simplicity of the structure of the aliphatic diamine complexes, they can be

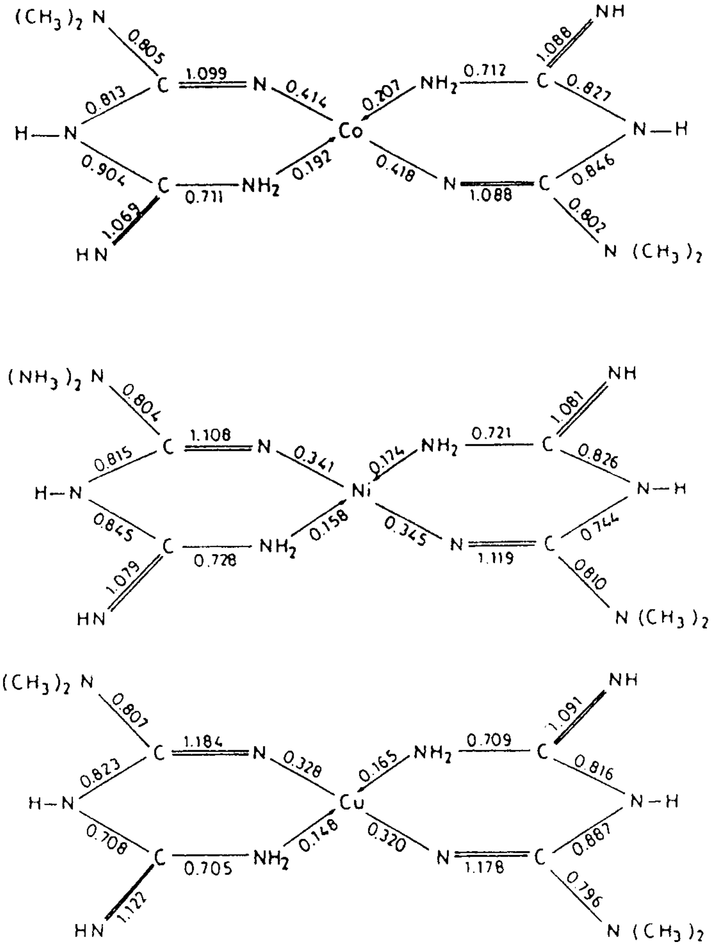


Fig. 4. Structures for complexes with calculated bond orders.

considered as a model for studing the relation between thermal stability and chelate ring size, number of chelate rings and steric hindrance for the same metal: en>Pn>tm; and for the same ligand $[Cu(en)(H_2O)_2]SO_4 < [Cu(en)_2]SO_4 < [Cu(en)_3]SO_4$.

3. The decomposition reaction of aromatic amine–metal complexes begins with the scission of the M–N bond. A correlation was found between the thermal stability and the basicity of the ligand. The steric effect of the substituent on the aromatic amine moiety was also considered.
4. The decomposition of oxalate complexes starts with the rupture of the C–O bond, which affect by the strength of the M–O bond. Thus, the thermal stability depends on the nature of the M–O bond.
5. For Schiff's base complexes, the thermal stability shows no steady behaviour, but it depends, to a great extent, on the room-temperature structures. However, some correlations were found between the thermal stability and the counterions or the substituents for the isostructural complexes.
6. The thermal stability of mixed ligand complexes depends mainly on the nature of weakly bonded ligand as well as the decomposition reaction. For the same mixed ligands, the stability is influenced by the nature of metal ions; for example, the

stability of a series of lanthanide complexes was correlated with the lanthanide contraction.

7. The thermal stability of transition-metal-containing polymer depends on the type of the 3*d* metal ion.
8. A correlation was found between the thermal stability and the equilibrium stability of some pyridine-metal complexes.
9. The nature of interaction of the water of crystallization plays a significant role on the thermal stability of metal complexes.

References

[1] W. Biltz, C. Manu, Z. Allg. Anorg. Chem. 148 (1925) 177.
[2] W. Klemm, Z. Allg. Anorg. Chem. 163 (1927) 240.
[3] P. Spacu, Z. Allg. Anorg. Chem. 214 (1933) 113.
[4] W. Hieber, H. Appel, Z. Allg. Anorg. Chem. 196 (1931) 193.
[5] K. Jatzimiski, Thermochemie Von Komplexverbindungen, 156 akademie-Verlag, Berlin.
[6] G. Liptay, Thermochim. Acta 150 (1989) 93.
[7] H.R. Beer, H.R. Oswald, Thermal Analysis-Proceedings of the VIICTA Conf., Bir Khauser 2 (1980) 121.
[8] A.M. Donia, E.M. Ebeid, Thermochim. Acta 131 (1988) 1.
[9] A.M. Donia, Thermochim. Acta 162 (1989) 335.
[10] A.M. Donia, E. El-Shereafy, M.A. El-Ries, Reactivity of Solids 8 (1990) 1.
[11] A.M. Donia, H.A. El-Boraey, Transition Met.Chem. 18 (1992) 303.
[12] A.M. Donia, H.A. El-Boraey, Transition Met. Chem. 18 (1993) 315.
[13] W.W. Wendlandt, J.P. Smith, J. Inorg. Nucl. Chem. 25 (1963) 843.
[14] W.W. Wendlandt, L.A. Funes, J. Inorg. Nucl. Chem. 26 (1964) 1879.
[15] J.P. Smith, W.W. Wendlant, J. Inorg. Nucl. Chem. 26 (1964) 1157.
[16] W.W. Wendlandt, Tex. J. Sci. 14 (1962) 264.
[17] W.W. Wendlandt, J. Inorg. Nucl. Chem. 25 (1963) 545.
[18] W.W. Wndlandt, J.P. Smith, Inorg. J. Nucl. Chem. 25 (1963) 985.
[19] W.W. Wendlandt, C.Y. Chou, J. Inorg. Nucl. Chem. 26 (1964) 943.
[20] W.W. Wendlandt, J. Inorg. Nucl. Chem. 25 (1963) 833.
[21] T.D. O'Brien, J.C. Bailar, J. Am. Chem. Soc. 67 (1945) 856.
[22] J.L. Bear, W.W. Wendlandt, J. Inorg. Nucl. Chem. 17 (1961) 286.
[23] L.K. Singh, S. Mitra, Inorg. Chem. Acta 133 (1987) 141.
[24] W.K. Musker, M.S. Hussain, Inorg. Chem. 5 (1966) 1416.
[25] J.E. Huheey, Inorganic Chemistry, 3rd edn., Harper, New York, 1983, pp. 298, 299.
[26] P.W. Bowman, L.B. Rogres, J. Inorg. Nucl. Chem. 28 (1966) 2215.
[27] A. Akhavein, J.E. House, J. Inorg. Nucl. Chem. 32 (1970) 1479.
[28] R. Farran, J.E. House, J. Inorg. Nucl. Chem. 34 (1972) 2219.
[29] R. Lozano, J. Martinez, A. Martinez, A. Doadrio Lòpez, Polyhedron 2 (1983) 293.
[30] D. Czakis-Sulikowska, J. Radwanska-Doczekalska, J. Therm. Anal. 43 (1995) 33.
[31] S. Mitra, L.N. Singh, Thermochim. Acta 239 (1994) 87.
[32] J.R. Allan, B. MeCloy, A.D. Paton, W.F. Smith, D.L. Gerrard, Thermochim. Acta. 198 (1992) 127; 205; 219; 229.
[33] J.R. Allan, A.R. Gardner, B. McCloy, W.E. Smith, Thermochim. Acta, 208 (1992) 107; 115; 125.
[34] J.R. Allan, B. McCloy, Thermochim. Acta, 211 (1992) 85; 214 (1993) 219.
[35] J.R. Allan, P.C. Beaumont, G.H.W. Milburn, I. Wood, Thermochim. Acta, 214 (1993) 241; 219 (1993) 159.
[36] J.R. Allan, B. McCloy, A. D Paton, Thermochim. Acta 214 (1993) 211.
[37] J.R. Allan, A.D. Paton, Thermochim. Acta, 214 (1993) 227; 235.
[38] J.R. Allan, B. McCloy, A.R. Gradner, Thermochim. Acta 214 (1993) 249.
[39] J.R. Allan, Thermochim. Acta 200 (1992) 355.
[40] A.M. Donia, M.M. Gouda, M.I. Ayad, H.A. El-Boraey, Thermochim. Acta 194 (1992) 155.
[41] A.M. Donia, J. Therm. Anal. 39 (1993) 323.
[42] A.M. Donia, H.A. El-Boraey, J. Thermal Anal., 48 (1997), proof.
[43] A.M. Donia, D. Dallimore, Thermochim. Acta 290 (1996) 139.
[44] H.L. Saha, S. Mitra, Thermochim. Acta 112 (1987) 275.
[45] H.L. Saha, S. Mitra, Thermochim. acta 116 (1987) 53.
[46] G.A.M. Hussein, H.M. Ismail, K.M.E. Attyta, J. Anal. Appl. Pyrolysis 31 (1995) 157.
[47] A.M. Donia, Polyhedron, (1997), in press.
[48] P. Román, J.I. Beitia, A. Luque, A. Aranzabel, Polyhedron 12 (1993) 1345.
[49] P. Román, A. Luque, J.I. Beitia, C. Guzmán-Miralles, Thermochim. Acta 231 (1994) 231.
[50] P. Román, J.I. Beitia, A. Luque, Thermochim. Acta 233 (1994) 223.
[51] P. Román, J.I. Beitia, A. Luque, Thermochim-Acta 241 (1994) 113.
[52] M.K. Hassan, M.A. Abd-Alla, R.M. Hassan, J. Macromol. Sci. Chem. A 27 (1990) 1501.
[53] M. Mohapatra, V. Chakravortty, K.D. Dash, Thermochim. Acta 154 (1989) 299.
[54] C. Valenzuela, A. Bernalte, Thermochim. Acta 156 (1989) 231.
[55] A.M. Donia, M.I. Ayad, R.M. Issa, Transition Met. Chem. 16 (1991) 518.
[56] A.M. Donia, M.I. Ayad, Monatshefte Für Chemie 124 (1993) 981.
[57] A.M. Donia, S.A. Amer, R.M. Issa, M. Gaber, Transition Met. Chem. 15 (1990) 465.
[58] K.M.M.S. Prakash, L.D. Prabhakar, M.C. Chowdary, Thermochim. Acta 119 (1987) 377.

[59] Wu. Shurong, Li. Zhiyong, Thermochim. Acta 133 (1988) 377.

[60] J. Zsakó, Cs. Várhelyi, E. Kékedy, J. Inorg. Nucl. Chem. 28 (1966) 2637.

[61] Z. Wu, F. Zhao, Z. Zhou, Polyhedron 9 (1990) 2143.

[62] W.J. Evans, Polyhedron 6 (1987) 803.

[63] R.D. Fischer, L. Xing-Fu, J. Less Common Met. 112 (1985) 404.

[64] P.C. Srivastava, B.N. Singh, S.D. Adhya, K.C. Banerji, J. Therm. Anal. 27 (1983) 263.

[65] W. Ludwing, M. Döring, R. Fisher, A. Friedrich, W. Seidel, E. Uhlig, D. Walther, J. Therm. Anal. 38 (1992) 239.

[66] R. Roy, S.K. Mondal, K. Nag, J. Chim. Soc., Dalton Trans. (1983) 1935.

[67] A. Mukherjee, M. Biswas, J. Appl. Polym. Sci. 50 (1993) 1485.

[68] M.G. Mikhael, Polymer Degradation and Stability 36 (1992) 43.

[69] J.R. Allan, B.R. Carson, B. McCloy, W.E. Smith, Eur. Polym. J., 29 (1993) 523; 805.

[70] J.R. Allan, P.C. Beaumont, B.R. Carson, G.H.W. Milburn, I.J. Wood, Eur. Polym. J. 30 (1994) 145.

[71] J.R. Allan, B.R. Carson, D.L. Gerrard, J. Birnie, Eur. Polym. J. 26 (1990) 241.

[72] J.R. Allan. G.H.W. Milburn, F. Richmond, D.L. Gerrard, J. Birnie, A.S. Wilson, Eur. Polym. J., 27 (1991) 419; 669.

[73] G. Liptay, E. Papp-Molnár, K. Burger, J. Inorg. Nucl. Chem. 31 (1969) 247.

[74] H. Irving, R.J.P. Williams, Nature 162 (1948) 746.

[75] V. Seshagiri, S. Rao, S. Brahmaji, Z. Anal. Chem. 262 (1972) 275.

[76] R.S. Naidu, R. Naidu, Indian J. Chem. 15 (1977) 652.

[77] R.S. Bottei, D.L. Greene, J. Inorg. Nucl. Chem. 30 (1968) 1469.

[78] R.S. Bottei, C.P. Mceachern, J. Inorg. Nucl. Chem. 32 (1970) 2653.

[79] P. Kokkonen, L. Palmu, L.H.J. Lajunen, Thermochim. Acta 14 (1987) 329.

[80] R.A. Bailey, W.J. Tangred, J. Inorg. Nucl. Chem. 38 (1976) 2221.

[81] K.K. Abdul Rasheed, J. Chacko, P.N.K. Nambisan, Polyhedron 3 (1983) 293.

[82] G.A.M. Hussein, H.M. Ismail, S.A.A. Mansour, J. Anal. Appl. Pyrolysis 36 (1996) 17.

[83] V. Sheshagiri, S. Brahmaji, Z. Anal. Chem. 262 (1972) 275.

[84] P. Lumme, M.C. Korvala, Thermochim. Acta 13 (1975) 419.

[85] M. Dabkowska, J. Therm. anal. 36 (1990) 1319.

[86] W. Brzyska, E. Swita, Pol. J. Chem. 66 (1992) 603.

[87] W. Brzyska, E. Swita, Pol. J. Chem. 63 (1989) 59.

[88] W. Brzyska, E. Swita, Pol. J. Chem. 65 (1991) 867.

[89] W. Brzyska, E. Swita, Pol. J. Chem. 67 (1993) 1.

[90] W. Brzyska, E. Swita, Thermochim. Acta 231 (1994) 135.

[91] A.M. Donia, M.K. Awad, J. Therm. Anal. 44 (1995) 1493.

[92] A.A. Said, R.M. Hassan, Polymer Degradation Stability 39 (1993) 393.

[93] A.A. Said, M.M.M. Abd El-Wahab, R.M. Hassan, Thermochim. Acta 233 (1994) 13.