

Synthesis and characterization of Zn(II) and the environmentally important Cd(II) and Pb(II) coordination polymers derived from terephthalic acid and bipyridyl ligands

Maged S.Al-Fakeh*, Aref A.M.Aly, Mahmoud A.Ghandour
Department of Chemistry, Faculty of Science, Assiut University, Assiut, (EGYPT)
E-mail : magedalfakeh@yahoo.com

ABSTRACT

A series of coordination polymers of the general formula $[M(\text{TPA})(\text{BPY})]_x \cdot n\text{H}_2\text{O}$, $M = \text{Zn}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Pb}(\text{II})$ and $x = 1/2$, 1 or 3. Terephthalic acid (TPA) = 1,4-benzenedicarboxylic acid and BPY = 2,2'-bipyridyl has been prepared and characterized. The structure of the complexes has been assigned based on elemental analysis, IR, electronic spectral studies, thermal analysis and Scanning electron microscope. Thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) have been used to study the thermal decomposition of the complexes. The kinetic parameters have been calculated making use of the Coats-Redfern and Horowitz-Metzger equations. The biological screening of the compounds was tested. The bacteria and fungi strains are common contaminants of the environment in Egypt. In this article the studied strains are frequently reported from contaminated soil, water and food.

© 2014 Trade Science Inc. - INDIA

KEYWORDS

Coordination polymers;
Thermal studies;
Biological activity.

INTRODUCTION

Terephthalic (1,4-benzenedicarboxylic acid) and its metal complexes have been a subject of interest in numerous studies because of their chemical and biological activities^[1,2]. They have a wide range of diverse characteristic properties attributed to their chelating ability with metal ions. Really, an important number of terephthalic being bidentate donors. Aromatic polycarboxylates, such as TPA, have been well used to construct coordination frameworks^[3], by direct interaction with metal ions to form discrete polynuclear^[4], 1-, 2- and 3-D coordination networks^[5] in a variety of coordination modes. TPA is involved in a variety of bridging modes and strong

tendency to form large, tightly bound metal cluster aggregates and it has been used as a building block to construct some porous coordination frameworks. In designing 1-, 2-, 3-D extended porous coordination polymers, the selection of appropriate ligands is crucial to determining the structural outcome of target polymers. Carboxylates^[6,7] tend to form relatively rigid frameworks due to the potential bidentate coordination of their carboxylate groups. Recently, mixed-linker systems of both carboxylates and another ligands have proved to be effective in preparation of coordination polymers^[8-13]. In this paper synthesis and characterization of zinc(II), cadmium(II) and lead(II) complexes containing terephthalic acid and 2,2'-bipyridyl ligands are described.

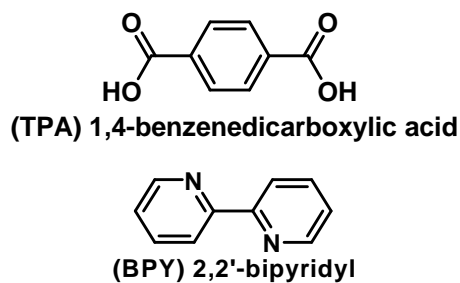


Figure 1 : Structures of the ligands

EXPERIMENTAL

Materials and methods

All chemicals were of analytical grades. (TPA)1,4-benzenedicarboxylic acid and (BPY) 2,2'-bipyridyl were E. Merck grade. Were purchased and used without purification.

Preparation of the complexes

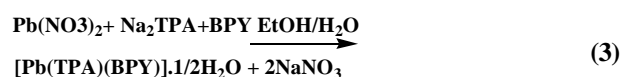
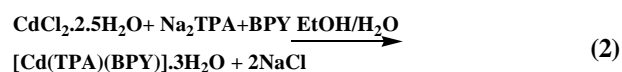
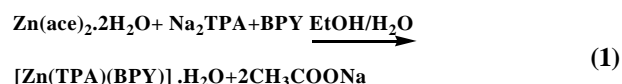
Preparation of the mixed ligand complexes of (TPA)1,4-benzenedicarboxylic acid and (BPY)2,2'-Bipyridyl with Zn(II), Cd(II) and Pb(II) follows essentially the same procedure, $[Zn(TPA)(BPY)].H_2O$ is typical. To an ethanolic solution (15 ml) of zinc(II) acetate (0.526 g, 2.4 mmol) a solution of TPA (0.4 g in 15 ml 0.1 M NaOH, 2.4 mmol) was added dropwise and with stirring, then BPY solution (0.376 g in 15 ml ethanol, 2.4 mmol) was added to the mixture. The mixture was refluxed and then cooled to room temperature. Creamy white precipitate separated, which filtered, washed with distilled water and EtOH and dried in over $CaCl_2$ anhydrous.

Physical measurements

The stoichiometric analyses (C,H,N) were performed using Analyischer Funktionstest Vario El Fab-Nr. 11982027 elemental analyzer. The i.r spectra were recorded on a Shimadzu IR-470 spectrophotometer and the electronic spectra were obtained using a Shimadzu UV-2101 PC spectrophotometer. Thermal studies were carried out in dynamic air on a Shimadzu DTG 60-H thermal analyzer at a heating rate $10^\circ C \text{ min}^{-1}$.

RESULT AND DISCUSSION

The compounds were prepared by the reaction of (TPA)1,4-benzenedicarboxylate with the metal salts and (BPY)2,2'-bipyridyl (dissolved in EtOH). The prepared complexes were found to react in the molar ratio 1: 1: 1 metal : TPA : BPY to yield the corresponding compounds according to the following equations:



The compounds are air stable, insoluble in common organic solvents but partially soluble in dimethylformamide (DMF) and dimethylsulphoxide (DMSO). The compositions of the prepared complexes were established using elemental analysis (C, H and N). The results are listed in (TABLE 1) together with the color and melting point of the complexes.

TABLE 1 : Colors, elemental analysis and melting points of the terephthalic acid complexes

Complex	Color	Found (Calcd.%)			m.p. °C (Decomp)
		C	H	N	
$[Zn(TPA)(BPY)].H_2O$ 1	Creamy white	51.19 (53.55)	3.63 (3.49)	6.64 (6.93)	231
$[Cd(TPA)(BPY)].3H_2O$ 2	Light yellow	43.70 (44.41)	3.23 (3.72)	6.66 (5.75)	210
$[Pb(TPA)(BPY)].1/2H_2O$ 3	White	39.24 (40.29)	2.77 (2.44)	4.35 (5.22)	195

IR spectra

The infrared spectra of these complexes show a number of bands in the ranges $1540-1558 \text{ cm}^{-1}$ and $1362-1370 \text{ cm}^{-1}$ attributed to the asymmetric and symmetric stretching vibration of the carboxylic groups of the TPA coordinated to the metal center (Figure 6).

These together with their difference, $\Delta\nu$, are listed in (TABLE 2). The presence of coordinated and or lattice H_2O molecules causes the appearance of strong and broad $\nu(O-H)$ stretching bands centered at $3452-3267 \text{ cm}^{-1}$. It is evident from TABLE 2 that $\Delta\nu$ values for Zn, Cd and Pb complexes ($\Delta\nu \geq 188 \text{ cm}^{-1}$) indicate a bidentate mode of coordination for the carboxylate

TABLE 2 : Infrared spectral data of mixed ligand complexes

Compound	$\nu(\text{COO})$ asy	$\nu(\text{COO})$ sy	$\nu\Delta$	$\nu(\text{C}=\text{N})$	$\nu(\text{H}_2\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
1	1558	1370	188	1440	3400	410	518
2	1554	1368	186	1445	3380	412	520
3	1540	1362	178	1448	3340	416	500

group^[14]. The stretching vibration of $\nu\text{C}=\text{N}$ for the all complexes appeared it ($1440\text{-}1448\text{ cm}^{-1}$)^[15]. Metal-oxygen and metal-nitrogen bonding are manifested by the appearance of bands in the $500\text{-}520$ and $410\text{-}416\text{ cm}^{-1}$ regions respectively^[16]. This is a further evidence for coordination of the metal ions through nitrogen and oxygen atoms of the ligands.

Electronic spectra

The electronic spectra of the mixed ligand 1-3 complexes are recorded in dimethylsulphoxide (DMSO). The results are shown in TABLE 3. The spectra display two distinct bands in the ranges $38,834\text{-}39,215\text{ cm}^{-1}$ and $34,153\text{-}34,782\text{ cm}^{-1}$ which are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition within TPA and BPY moieties, respectively^[17].

TABLE 3 : Electronic spectral data of the mixed ligand complexes

Complexes	ν_{max} (cm^{-1})	Assignment
1	34.782	$n \rightarrow \pi^*$ transition
	38.834	$\pi \rightarrow \pi^*$ transition
2	34.153	$n \rightarrow \pi^*$ transition
	38.910	$\pi \rightarrow \pi^*$ transition
3	34.722	$n \rightarrow \pi^*$ transition
	39.215	$\pi \rightarrow \pi^*$ transition

Based on the forgoing results the suggested structures for TPA mixed ligand complexes are shown as follows:

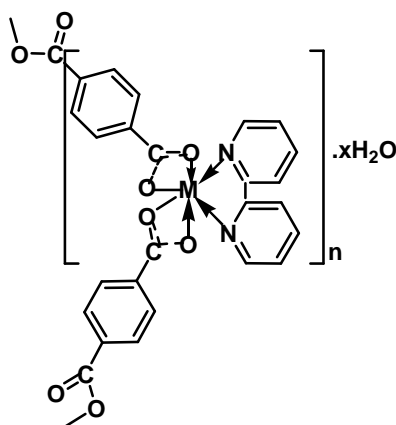
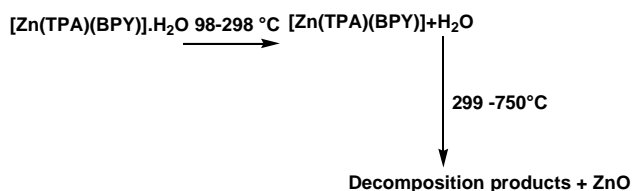


Figure 2 : Suggested structure of the complexes

Thermal studies

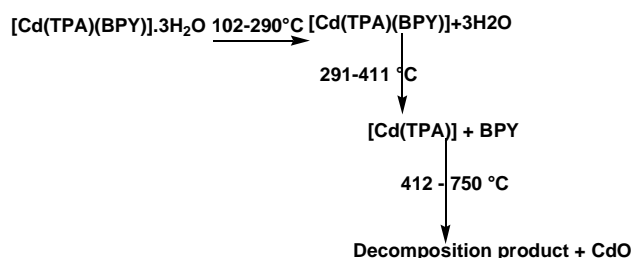
The thermal decomposition of the complexes has been investigated in dynamic air from ambient temperature to 750°C . As a representative example the thermogram of the complex 1 shows decomposition steps in dynamic air. The stepwise course of the thermogravimetric curve of this compound is characterized by four steps namely at $98\text{-}298^\circ\text{C}$, $299\text{-}399^\circ\text{C}$, $400\text{-}436^\circ\text{C}$ and $438\text{-}750^\circ\text{C}$ Figure 3. The first step suggests elimination of one crystalline water molecule (calc. 4.46%, found 4.86%), for which the DTG trace displays a midpoint at 147°C and an endothermic effect at 151°C in the DTA curve. The observed mass loss in the second step agrees with the ligand 2, 2-bipyridyl (calc. 38.69%, found 36.42%) (DTG peak at 369°C). This step is marked on the DTA curve as an endothermic peak at 370°C . The third and fourth steps correspond to the decomposition of ligand TPA (calc. 40.65%, found. 39.16%). The rest of the complex is supposed to be ZnO (calc. 20.16%, found 19.53%). (Scheme 1).



Scheme 1

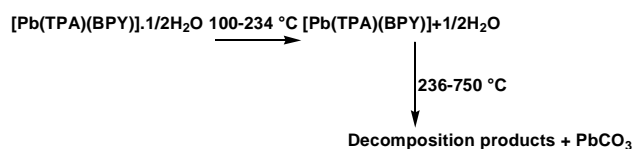
The compound 2 undergoes four decomposition steps recorded in its TG thermogram. The first step corresponds to the elimination of three crystalline water molecules (calc. 11.10%, found 10.72%). A DTG midpoint at 158°C represents this step which is associated with an endothermic peak at 161°C in the DTA curve. The second step is related to the loss of the BPY (calc. 32.09%, found 31.55%). The DTG curve gives correspondingly a peak at 332°C and the DTA curve furnishes an endothermic peak at 335°C . The third and fourth steps correspond to the decomposition of the ligand TPA (calc. 33.71%, found. 32.06%). The

corresponding DTG midpoints occur at 509 and 612 °C, whereas an exothermic DTA peak appears at 512°C and an endothermic peak at 613 °C respectively. Decomposition of the complex leaves a stable residue of CdO (calc. 26.38%, found. 25.66%). (Scheme 2).



Scheme 2

Thermolysis of the compound 3 consists of three decomposition steps namely at 100-234, 236-336, 337-750°C. In the first step a half crystalline water molecule was released (calc. 1.67%, found 1.14%). The DTG midpoint is seen at 210°C with the DTA peak at 215°C. The second and third steps indicate decomposition of the two ligands TPA and BPY. The corresponding DTG midpoints occur at 295 and 475°C, with corresponding DTA endothermic exothermic peaks at 299 and 477 °C, respectively. The residue is PbCO₃ (calc. 49.81%, found 49.30%). (Scheme 3).



Scheme 3

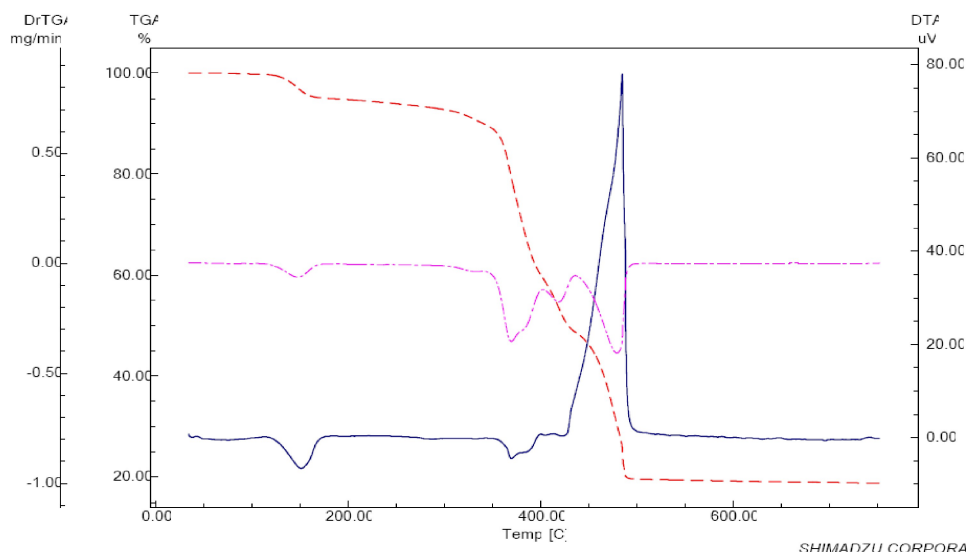
Figure 3 : TG, DTG and DTA thermograms of [Zn(TPA)(BPY)].H₂O (in dynamic air)

TABLE 4 : Thermal decomposition data of the compounds in dynamic air

Compound	Step	TG/DTG			Mass Loss (%)
		Ti	Tm	Tf	
1	1 st	98	147	298	4.86
	2 nd	299	369	399	36.42
	3 rd	400	418	436	11.36
	4 th	438	479	750	27.80
2	1 st	102	158	290	10.72
	2 nd	291	332	411	31.55
	3 rd	412	509	524	18.45
	4 th	525	612	750	13.61
3	1 st	100	210	234	1.14
	2 nd	236	295	336	22.81
	3 rd	337	475	750	26.75

Ti = Initial temperature; Tm = Maximum temperature; Tf = Final temperature

KINETIC ANALYSIS

Non-isothermal kinetic analysis of the complexes was carried out applying two different procedures: the Coats-Redfern^[18] and the Horowitz-Metzger^[19] methods.

(a) Coats-Redfern equation

$$\ln[1-(1-\alpha)^{1-n}/(1-n)T^2] = M/T + B \text{ for } n \neq 1 \quad (4)$$

$$\ln[-\ln(1-\alpha)/T^2] = M/T + B \text{ for } n = 1 \quad (5)$$

where α is the fraction of material decomposed, n is the order of the decomposition reaction and $M = E/R$ and $B = ZR/\Phi E$; E , R , Z and Φ are the activation energy, gas constant, pre-exponential factor and heating rate, respectively.

Full Paper

TABLE 5 : Kinetic parameters of the thermal decomposition of the complexes

Compound	Step	Coats-Redfern equation			Horowitz-Metzger equation		
		r	n	E	r	n	E
1	1 st	0.9809	2.00	62.8	1	2.00	61.5
2	1 st	0.9985	1.00	28.1	1.0000	1.00	42.7
3	1 st	0.9971	0.33	17.3	0.9999	0.33	26.6

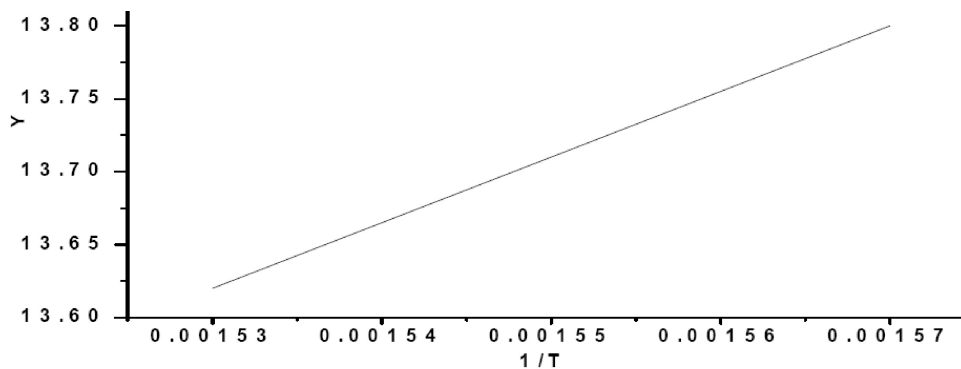
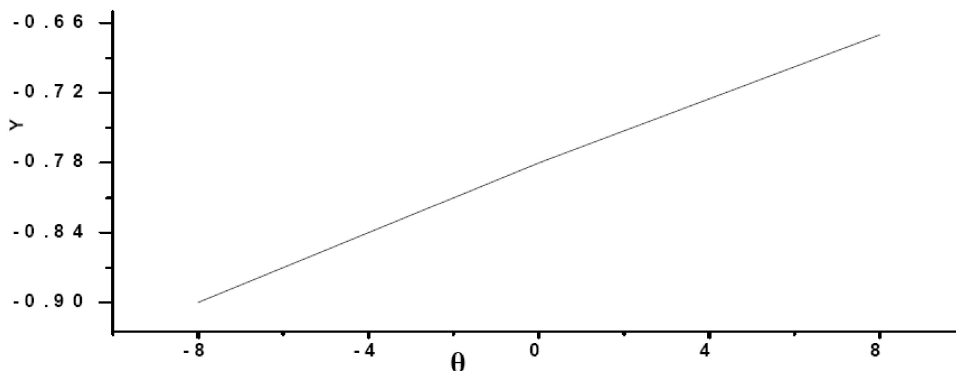
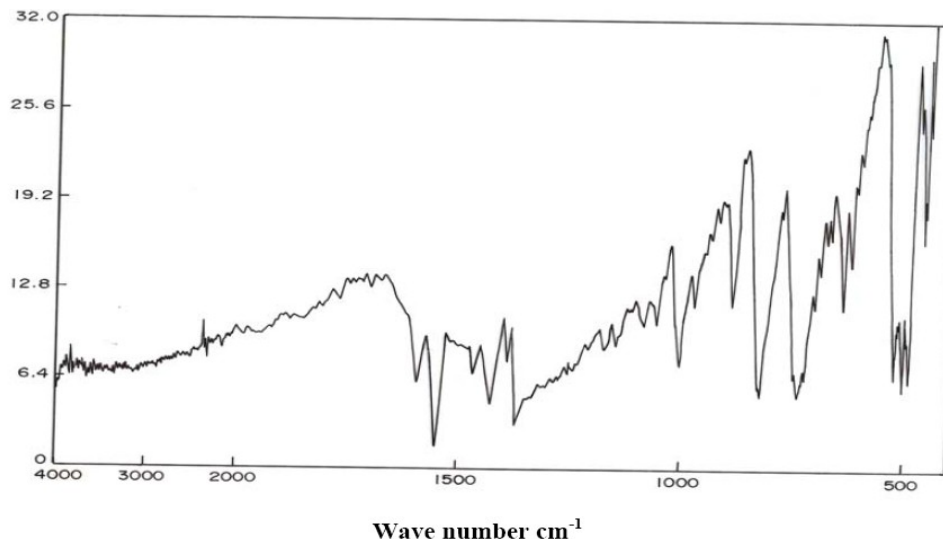
E in kJ mol⁻¹Figure 4 : Coats-Redfern plots for [Zn(TPA)(BPY)].H₂O first step in dynamic air; where $Y = \ln[1 - (1 - \alpha)^{1-n} / (1 - \alpha) T^2]$ for $n \neq 1$ or $Y = \ln[-\ln(1 - \alpha) / T^2]$ for $n = 1$ Figure 5 : Horowitz-Metzger plots for [Zn(TPA)(BPY)].H₂O first step in dynamic air where $Y = \ln[1 - (1 - \alpha)^{1-n} / (1 - n)]$ for $n \neq 1$ or $Y = \ln[-\ln(1 - \alpha)]$ for $n = 1$ Figure 6 : IR spectrum of [Pb(TPA)(BPY)].1/2H₂O



Figure 7 : Microbiological screening of compound 2 against *Candida albicans*

tions (3) and (4) against $1/T$ and against θ for equations (5) and (6) (Figure 4 and 5). The kinetic parameters calculated according to the above two methods are cited in (TABLE 5).

Microbiological screening

Terephthalic and some ternary complexes were tested against some bacteria and fungi. The antimicrobial activity of the synthesized chemical compounds was tested against six fungal and five bacterial species (TABLE 6). Figure 7 shows the antimicrobial effect for compound 2.

Scanning electron micrographs (S.E.M)

The scanning electron micrographs of the complex

TABLE 6 : Antimicrobial activity of the coordination polymers

Compound	<i>B. Cereus</i> (G+ve)	<i>S. aureus</i> (G+ve)	<i>S. Marcescens</i> (G-ve)	<i>E. coli</i> (G-ve)	<i>P. aeruginosa</i> (G-ve)	<i>T. rubrum</i>	<i>A. flavus</i>	<i>C. albicans</i>	<i>F. oxysporm</i>	<i>G. candidum</i>	<i>S. brevicaulis</i>
1	8	8	14	9	0	0	0	0	0	8	0
2	9	8	12	0	0	16	15	20	0	10	16
3	8	12	14	11	10	0	10	12	0	16	20

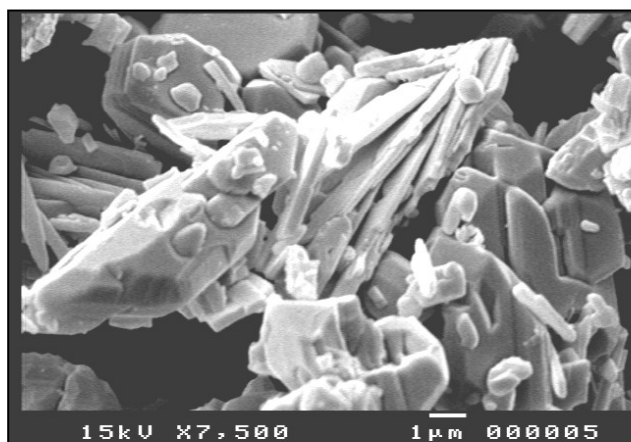


Figure 8 : S.E.M of $[Pb(TPA)(BPY)]. 1/2H_2O$

(b) Horowitz-Metzger equation

$$\ln[1-(1-\alpha)^{1-n}/1-n] = \ln ZRT_s^2/\Phi E - E/RT_s + E\theta/RT_s^2 \text{ for } n \neq 1 \quad (6)$$

$$\ln[-\ln(1-\alpha)] = E\theta/RT_s^2 \text{ for } n = 1 \quad (7)$$

where $\theta = T - T_s$, T_s is the temperature at the DTG peak.

The correlation coefficient r is computed using the least squares method for equations (4), (5), (6) and (7). Linear curves were drawn for different values of n ranging from 0 to 2. The value of n , which gave the best fit, was chosen as the order parameter for the decomposition stage of interest. The kinetic parameters were calculated from the plots of the left hand side of equa-

tion (3) is give in Figure 8. This compound is crystalline and the size of the particles is indicated under each figure in μm .

REFERENCES

- [1] D.B.Clayson, L.Fishbein, S.M.Cohen, Food.Chem. Toxic, **33**, 771 (1995).
- [2] S.H.Swan; Environmental Research, **108**, 177 (2008).
- [3] T.Steiner; Angew.Chem.Ed.Engl., **41**, 48 (2002).
- [4] A.Nangia; Cryst.Eng.Comm., **4**, 93 (2002).
- [5] G.Aullon, D.Bellamy, A.G.Orpen, L.Brammer, E.A.Bruton; Chem.Comm., 653 (1998).
- [6] G.R.Desiraju; Acc.Chem.Res., **29**, 441 (1996).
- [7] C.Janiak; J.Chem.Soc.Dalton Trans., 3885 (2000).
- [8] P.Pyykko; Chem.Rev., **97**, 597 (1997).
- [9] W.Clegg; Compreh.J.Coord.Chem., **1**, 579 (2004).
- [10] L.Carlucci, G.Ciani, D.M.Proserpio; Coord.Chem. Rev., **246**, 247 (2003).
- [11] K.T.Holman, H.H.Hammud, S.Isber, M.Tabbal; Polyhedron, **24**, 221 (2005).
- [12] H.J.Choi, M.P.Suh; Inorg.Chem., **38**, 6309 (1999).
- [13] A.Y.Robin, K.M.Fromm, H.Goesmann, G.Bernardinelli; Cryst.Eng.Comm., **5**, 405 (2003).
- [14] J.Rogan, D.Poleti, L.Karanovic, G.Bogdanovic,

Full Paper

- A.Spasojevic-de Bire, D.M.Petrovic; Polyhedron, **19**, 1415 (2000).
- [15] M.A.Ali, D.A.Chowdhury, M.N.Vddin; Polyhedron, **3**, 595 (1984).
- [16] T.H.Rakha; Synth.React.Inorg.Met.Org.Chem., **30**, 205 (2000).
- [17] S.L.Zheng, J.H.Yang, X.L.Yu, X.M.Chen, W.T.Wong; Inorg.Chem., **43**, 830 (2004).
- [18] A.W.Coats, J.P.Redfern; Nature, **20**, 68 (1964).
- [19] H.H.Horowitz, G.Metzger; Anal.Chem., **35**, 1464 (1963).