

Thermal Decomposition of Metal Complexes of Type MLX₂ (M = Co(II), Cu(II), Zn(II), and Cd(II); L = DIE; X = NO₃¹⁻) by TG-DTA-DTG Techniques in Air Atmosphere

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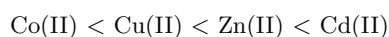
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The nitrate complexes of transition metals with 1,2-diimidazoloethane (DIE) of the general formula M(DIE)(NO₃)₂, where M = Co(II), Cu(II), Zn(II), and Cd(II), were synthesized. The compositions of metal complexes and ligand were investigated by elemental analysis in order to ensure their purity and the structure elucidations were based on conductivity measurements, room temperature magnetic moment studies, proton NMR, and electronic and IR spectra. The thermal behavior of these complexes possessing distorted tetrahedral geometry and their ligand was studied by means of thermoanalytical techniques in static air atmosphere in order to determine their mode of decomposition and thermal stability. All these complexes and ligand show 2-step weight loss upon heating to 740 °C, with simultaneous loss of inorganic and organic fragments exhibiting almost the same mode of decomposition pattern. The residue after heating above 640 °C corresponded to metal oxide. There was no residue in the case of ligand. The composition of intermediates and end products formed during degradation was confirmed by microanalysis and IR spectroscopy. It follows from the results that the thermal stability of the complexes increases in the following sequence:



Introduction

Thermal degradative studies of complexes of transition metals and lanthanides with N-donor ligands and the like have been the subject of a number of communications.¹⁻¹⁸ Metal complexes find many uses in biological

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systems.¹⁹ Metal ions enhance the antimicrobial activity of antibiotics. Metal complexes also play a vital role in antitumor activity.^{20–32} Keeping this importance in mind, it was decided to synthesize and study ligands with biologically active sites. Imidazole was selected because of its significance in biological systems.^{29–30,33} It is also ubiquitous in nature as in macrofungia and in longistrobis.^{34–39} One of its derivatives was prepared, i.e., 1,2-diimidazoloethane (DIE), and complexed.

Our interest in the thermal behavior of 1,2-dipiperidinoethane (DPE), 1,3-dipiperidinopropane (DPP), and derivative of phenomazine with divalent transition and representative metals has resulted in many publications.^{40–46} In continuation of our previous investigation,⁴⁷ the current findings are reported on the thermal pyrolytic studies of complexes of Cd(II), Co(II), Cu(II), and Zn(II) with 1,2-diimidazoloethane using TG-DTA-DTG techniques in static air. Thermal stability and the decomposition pattern were the parameters traced. For the characterization of different degradation products, elemental analysis and IR spectroscopy were used.

Experimental

Chemicals

Salts of metals (hydrated metal nitrates) obtained from standard source suppliers (E. Merck and BDH) were of analytical grade and used without further purification. Solvents were distilled before use. The partial dehydration of metal salts was carried out in a vacuum oven for several hours. For complete removal of water molecules, the partially dehydrated salts were shaken with 2,2-dimethoxy propane.

Preparation of Ligand

The ligand 1,2-diimidazoloethane (DIE) was synthesized by the procedure already reported.⁴⁸ Imidazole (0.25 mol) in absolute ethanol (40 mL) was added drop-wise to dibromoethane (0.1 mol) in methanol (20 mL). A few drops of 5% alcoholic KOH were added to the reaction mixture. The contents were refluxed for 8 h at 80 °C and left overnight. The KBr was filtered; the filtrate was evaporated and recrystallized from ethanol. The yield was 80%.

Preparation of Metal Complexes

The complexes were synthesized by the reported methods.⁴⁸ All the metal complexes were prepared using a similar general procedure. Approximately 10 mmol of partially dehydrated salt was dissolved in the minimum amount of anhydrous solvent. Ethanol was used as solvent for the preparation of metal complexes. The ligand DIE, an excess over 1:2 metal ratio, was also dissolved in the minimum amount of the same solvent and slowly added to the hot metal salt solution with constant stirring. The mixture was stirred and kept at 50 °C for half an hour, and then cooled for about 20 min. The metal complexes precipitated either immediately or upon cooling. The product obtained was filtered through a sintered glass crucible, washed several times with ether, and dried under vacuum at 50 °C. The complexes were re-crystallized from acetone.

Physicochemical Techniques

The microanalyses of C, H, and N were performed with a CHN analyzer, Carlo Erba, Model 1106 at the HEJ Research Institute of Chemistry, University of Karachi. Infrared absorption spectra of the ligand and

complexes were recorded in the range of 4000-600 cm^{-1} on a PYE UNICAM infrared spectrometer as KBr disks. The far IR spectra were examined as KBr disks in the region of 400-200 cm^{-1} (FT-IR SHIMADZU).

The absorption spectra of solution of complexes in the range of 200-900 nm using different solvents were obtained on a Jasco DEC-1 spectrophotometer with 1 cm matched quartz-cells. The mass spectrum of ligand was recorded with a MAT 312 mass spectrophotometer.

Molar conductance of the solution of the metal complexes was carried out with a conductivity meter type HI 8333. All measurements were obtained at room temperature from freshly prepared solutions.

Magnetic susceptibilities were measured by the Gouy method at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as standard.⁴⁹ The magnetic moments were calculated. The cations and anions were estimated using analytical procedures.⁵⁰

Proton NMR of ligand was recorded on a ^1H -NMR spectrometer Model EM-390 of magnetic field 21.04 K Gauss.

The thermoanalytical measurements were obtained with a NETZSCH Simultaneous Thermal Analyzer STA 429. Studies were conducted in static atmosphere of air using 35-70 mg samples at a heating rate of 10 deg/min in the range of ambient to 740 °C.

Results and Discussion

The complexes of 1,2-diimidazoloethane (DIE) with transition elements were synthesized and studied. The stoichiometry of the complexes was established on the basis of their elemental analysis. The results of elemental analysis are presented in Table 1. The structural pattern and the geometry of the complexes were assigned on the basis of physico-chemical parameters such as conductance measurements, magnetic susceptibilities, and spectral measurements. The data from conductance measurements, magnetic susceptibilities, and electronic absorption spectra of complexes are summarized in Tables 2 and 3, respectively.

Table 1. Analytical data for 1,2-diimidazoloethane and its metal complexes.

Compound	Composition	Appearance	%C Found	%H Found	%N Found	% Metal	% Anion
–	$(\text{CH}_2\text{N}_2\text{C}_3\text{H}_3)_2$	Colorless	59.21 *(59.25)	6.20 (6.17)	34.60 (34.57)	–	–
I	$\text{Co}(\text{C}_8\text{H}_{10}\text{N}_4)(\text{NO}_3)_2$	Sky blue	27.58 (27.83)	2.76 (2.89)	16.14 (16.23)	17.58 (17.08)	35.90 (35.95)
II	$\text{Cu}(\text{C}_8\text{H}_{10}\text{N}_4)(\text{NO}_3)_2$	Golden	27.62 (27.46)	2.90 (2.86)	16.30 (16.02)	18.20 (18.17)	35.40 (35.47)
III	$\text{Zn}(\text{C}_8\text{H}_{10}\text{N}_4)(\text{NO}_3)_2$	Colorless	27.40 (27.32)	2.76 (2.85)	15.82 (15.94)	18.70 (18.60)	35.10 (35.29)
IV	$\text{Cd}(\text{C}_8\text{H}_{10}\text{N}_4)(\text{NO}_3)_2$	Colorless	24.00 (24.10)	2.52 (2.50)	14.10 (14.05)	28.50 (28.21)	31.00 (31.12)

*Figures in parentheses are the calculated values

Proton NMR of the ligand in D_2O with TMS as an internal standard showed a broad singlet at 7.38 ppm for 2 hydrogens of carbon between 2 nitrogen atoms in the imidazole ring and another broad singlet

at 3.90 ppm for 4 hydrogens of methylene. A sharp multiplet at 6.75 ppm indicated 4 methylene protons in the imidazole ring.

Table 2. Values of molar conductance and magnetic moment for complexes, M(DIE)(NO₃)₂.

Complex	Solvent	Molar Conductance (mS mol ⁻¹)	μ_{eff} (BM)
I	Nitromethane	4.10	4.54
II	DMSO ^a	1.73	1.88
III	Acetone	7.20	Diamagnetic
IV	Acetone	2.90	Diamagnetic

^aDMSO = Dimethyl sulfoxide

Table 3. Maxima of absorption bands in electronic spectra for DIE complexes.

Complex	λ_{max} (nm)	ν (cm ⁻¹)	ϵ_{max} (M ⁻¹ cm ⁻¹)
I	565	17240	230
	660	15380	370
II	450	21740	180
	690	13890	50
III	–	–	–
IV	–	–	–

A mass peak of moderate intensity at m/z 162 corresponding to molecular ion (C₈H₁₀N₄)⁺ was observed in the spectrum of DIE.⁴⁸ The base peak at m/z 81 is probably due to the formation of N-methyl imidazole cation radical, while the signal at m/z 94 could be assigned to N-ethylene imidazole fragment, due to loss of imidazole moiety, which appears at m/z 68. The analytical data shown in Table 1 indicate that only one DIE molecule like DME⁵¹ is found to coordinate with metal ion and form complexes of the general formula [M(DIE)(NO₃)₂], where M = Cu(II), Co(II), Zn(II), Cd(II). The complexes are soluble in DMSO but slightly soluble or insoluble in other solvents.

Molar conductance and magnetic moment values for DIE complexes are presented in Table 2. The molar conductance values range from 1.73 to 7.20 mS mol⁻¹ in various solvents. This shows that complexes of DIE are non-electrolytic. Various bands were observed for nitrate complexes with minor variations. These bands could be assigned to transition ⁴A₂(F) – ⁴T₁(P), ν_3 in T_d symmetry. The low energy transition ⁴A₂(F) – ⁴T₁(F), ν_2 was not observed. The intensities and band width are in accordance with the T_d symmetry.⁵² Only 2 bands were observed for the nitrate complex. The Cu(II) complex is non-electrolyte in DMSO and has magnetic moments of 1.88 BM at room temperature. The electronic transitions observed in these complexes are consistent with C_{2v} symmetry. In this symmetry, 4 transitions could be expected.⁵³ The fourth transition is not observed, as was the case in some previous investigations.^{28–29} They resemble Cu(II) complexes having CuN₂X₂ chromophore.⁵⁴

The infrared spectrum of imidazole exhibits a strong absorption band at 3400 cm⁻¹ assigned to N-H stretching vibrations, which is not present in the DIE spectrum. The absorption bands in the regions

1620-1605 cm^{-1} and 1170-1150 cm^{-1} assigned to C=N and C-N stretching vibrations of imidazole were shifted and split, showing substitution on the nitrogen atom of the imidazole ring. The characteristic bands in the infrared spectra (4000-600 cm^{-1}) of DIE and its metal complexes are given in Table 4. In these complexes, the bands at 1620 cm^{-1} and 1605 cm^{-1} assigned to C=N stretching vibrations are split into 4 distinct bands. The strong band at 1620 cm^{-1} moves to the lower frequency side and is observed at 1602 cm^{-1} , whereas the other 2 weak bands shift towards the higher frequency side and are observed at 1640 and 1625 cm^{-1} . Similarly, of the bands due to C-N stretching vibrations, the strong one moves to lower frequency and is observed at 1115 cm^{-1} and the other 2 weak bands shift towards higher frequency and are observed at 1180 and 1170 cm^{-1} . The behavior of the Cd(II) complex is similar to that of the Zn(II) complex. In Co(DIE)(NO₃)₂ the bands attributed to C=N and C-N stretching vibrations are split into 4 distinct bands as compared to the free ligand. In Cu(DIE)(NO₃)₂, the bands ascribed to C=N and C-N suffer changes exactly like those for Co(II) complexes.⁴⁸ The strong absorption peaks move considerably to the lower frequency side and are observed at 1600 and 1120 cm^{-1} .

Table 4. Infrared bands (cm^{-1}) for DIE and its metal complexes.

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N})$	$\nu(\text{M}-\text{X})$	$\nu(\text{M}-\text{N})$
DIE	1620s, 1605w	1165s, 1140w	–	–
I	1635w, 1618m 1610w, 1600vs	1175m, 1150m 1120vs	485-470	288-270
II	1640m, 1628w 1620w, 1600vs	1170m, 1160w 1145sh, 1115s	490-475	280-265
III	1635w, 1625m 1612w, 1600vs	1180m, 1170w 1115vs	475-470	275-265
IV	1640m, 1628m 1612w, 1602vs	1185, 1175w 1118vs	495-475	285-270

m = medium, s = sharp, w = wide, vw = very wide, sh = shoulder, vs = very sharp

Infrared spectra of metal complexes clearly indicate that C-N stretching frequencies are shifted to lower and some to higher frequencies with changes in sharpness and intensities. This is caused by the withdrawal of electron densities from the C-N bond where nitrogen atoms become coordinated to the metal ion. The bands between 1605 and 1635 cm^{-1} assigned to C=N stretching vibrations are split and suffer a small red shift. These changes may have arisen due to solid state effects. 1,2-Diimidazoloethane behaves as a bidentate ligand.

The thermal curves (TG, DTG, and DTA) of 1,2-diimidazoloethane and its metal complexes were recorded in static air atmosphere from ambient to 740 °C and are presented in Figures 1-5. The characteristic data and stages of pyrolysis regarding the thermal behavior of ligand and its complexes (I, II, III, and IV) are given in Table 5. The thermal curves for the complexes permit the following observation: concerning the thermal stability of the compound, the complex I is thermally stable up to 200 °C, complex II to 220 °C, complex III to 260 °C, and complex IV to 300 °C. Thus, from the initiation of the mass loss in TG curves, it can be inferred that the thermal stability⁵⁵⁻⁵⁷ of the complexes M(DIE)(NO₃)₂ increases according to the type of substituents M in the following sequence:



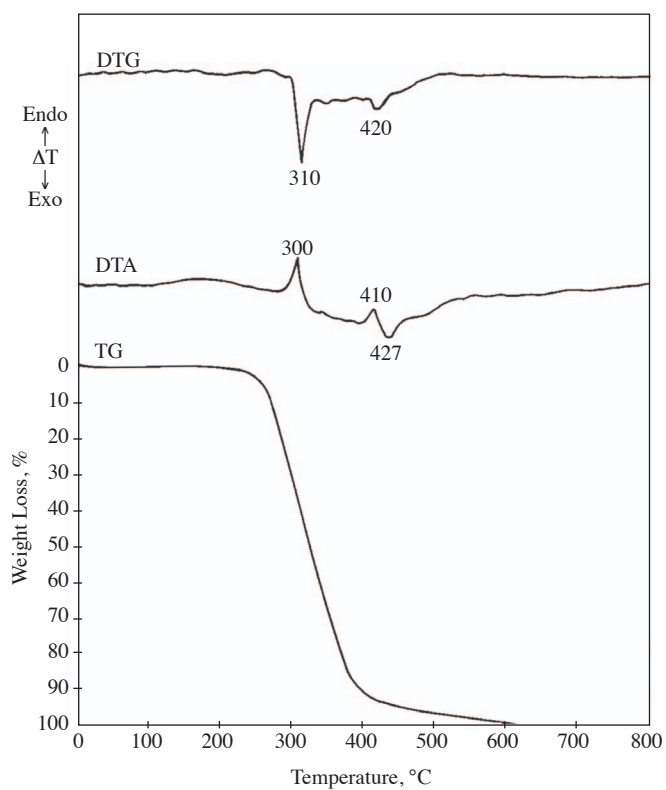


Figure 1. Thermoanalytical curves for $(\text{CH}_2\text{N}_2\text{C}_3\text{H}_3)_2$ in air.

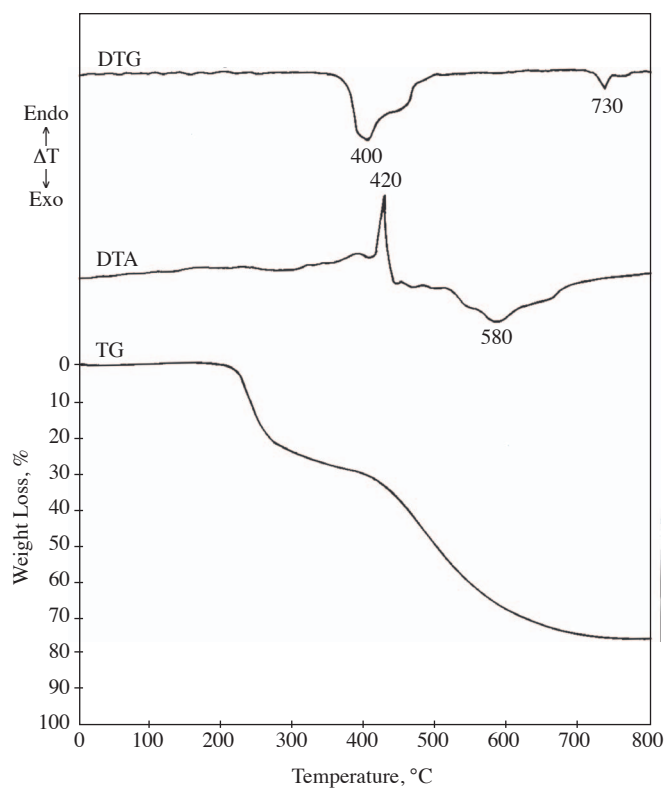


Figure 2. Thermoanalytical curves for $\text{Co}(\text{C}_8\text{H}_{10}\text{N}_4)(\text{NO}_3)_2$ in air.

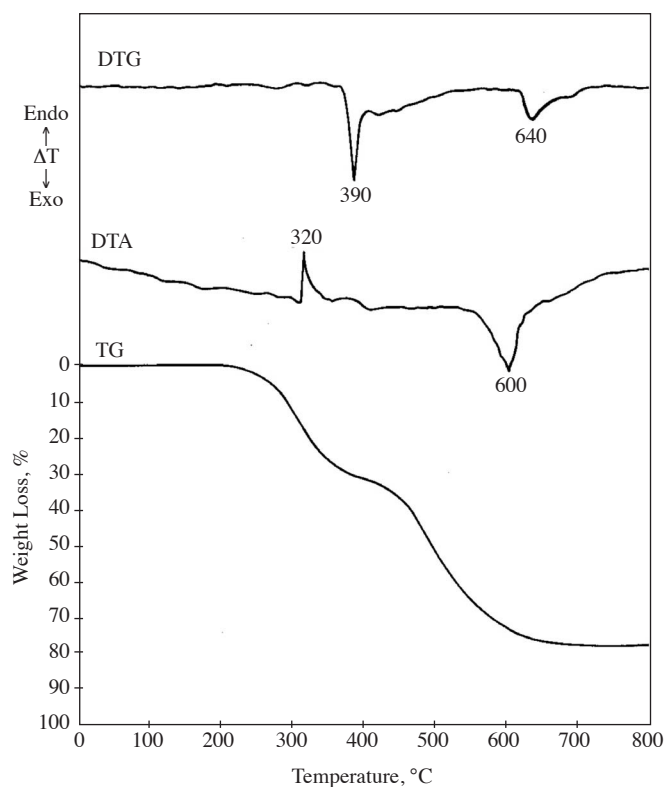


Figure 3. Thermoanalytical curves for $\text{Cu}(\text{C}_8\text{H}_{10}\text{N}_4)(\text{NO}_3)_2$ in air.

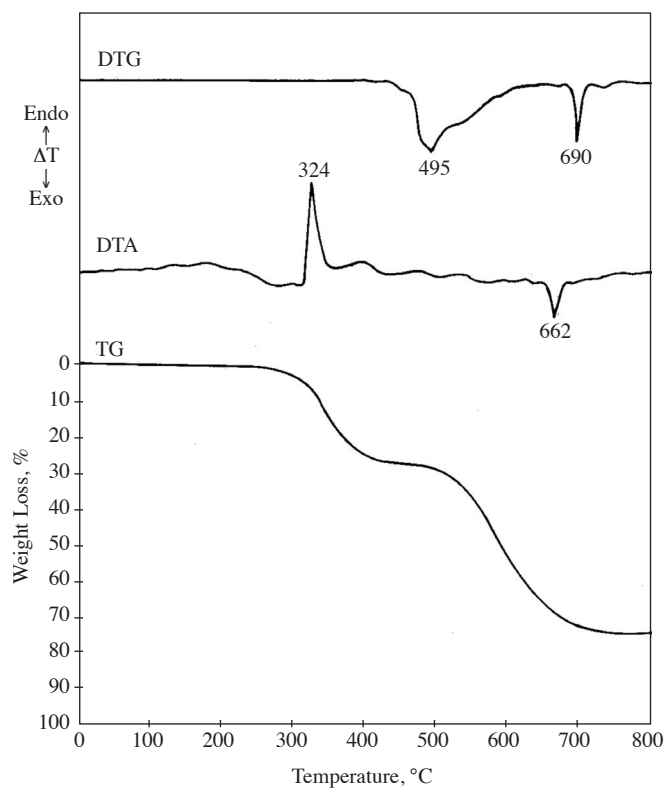


Figure 4. Thermoanalytical curves for $\text{Zn}(\text{C}_8\text{H}_{10}\text{N}_4)(\text{NO}_3)_2$ in air.

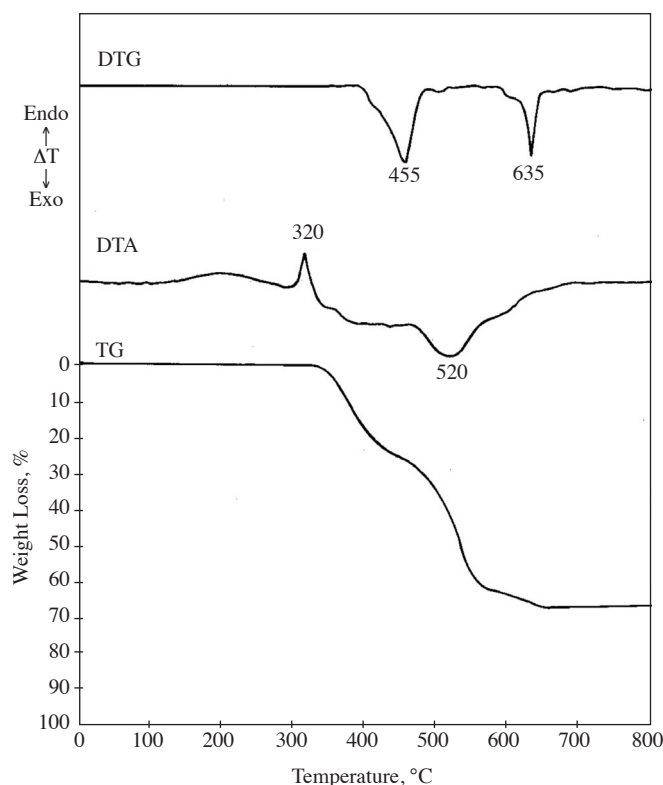


Figure 5. Thermoanalytical curves for $\text{Cd}(\text{C}_8\text{H}_{10}\text{N}_4)(\text{NO}_3)_2$ in air.

The TG and DTA curves reveal that ligand 1,2-diimidazoloethane decomposes in 2 steps in the temperature range 240-600 °C (Figure 1). In the first step, which is rapid, ligand loses imidazolo and N-methylene imidazolo by breakage of C-N and C-C bonds around 240-390 °C with accompanying endothermic effects and the intermediate then decomposes exothermally in the temperature range 390-600 °C (second step), liberating the methylene group. The first endothermic peak at about 300 °C may be attributed to the phase changes during the melting (300 °C) of ligand, and the second sharp endothermic peak at 410 °C corresponds to the loss of the above-mentioned 2 species. The second step is slower and is ascribed to the oxidation and vaporization of methylene, indicating that pyrolysis is exothermic in nature.⁴⁵ Ligand is thermally stable up to 300 °C and heating it above 600 °C leaves no residue. The sequence of loss is comparable with the mass spectrum.^{48,58} The TG and DTA curves show that complexes decompose in 2 stages. The TG curves indicate that the first stage involves the loss of 2 nitrate radicals in the form of N_2O_5 ^{41,46,55,59-61} for all the complexes. The second decomposition stage appears as an exothermic peak 427 °C) in the DTA curves. The residue left in the crucible consists of corresponding metal oxide.^{41,62-64}

Characteristic features of the thermal decomposition of the complexes



The thermal decomposition of this complex takes place in the temperature range of 200-740 °C (Figure 2). The first step involves decomposition (200-400 °C) in which the complex loses 2 nitrate radicals

in the form of N_2O_5 . In the second stage, the intermediate pyrolyzes further with the evolution of 1,2-diimidazoloethane and leaves CoO as residue.



The nitrate radicals begin to evolve in the temperature range 220-400 °C (first step). Further decomposition of the complex occurs in the second step in the range 400-660 °C (Figure 3). The residue of the foregoing decomposition is CuO . The DTA curve shows endothermic and exothermic peaks at 320 and 600 °C, respectively, corresponding to the first and the second step of the TG curve.



This complex loses 2 nitrate radicals in the temperature range 260-500 °C (Figure 4) and for this step of decomposition the DTA curve shows a strong endothermic peak (324 °C). In the second stage of pyrolysis (500-700 °C), another peak at 662 °C in the DTA curve indicates that this degradation stage is exothermic in nature. The end product is ZnO .



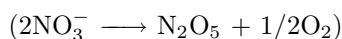
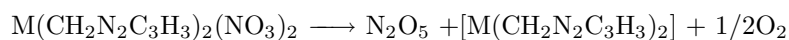
This complex is stable up to 300 °C and begins to decompose in 2 steps in the temperature range 300-640 °C (Figure 5). Endothermic and exothermic peaks accompany the decomposition processes at 320 and 520 °C, respectively. Heating the sample above 640 °C leaves the respective metal oxide as residue.

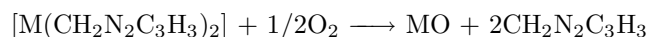
Table 5. Thermoanalytical results for the complexes, $M(DIE)(NO_3)_2$.

Compound	DTA Peak Temp. °C	TG	Weight Loss, %		Phenomena
		Temperature range, °C	Calc.	Found	
DIE	300(-)	240-390	91.35	91.64	$C_3H_3N_2$, $C_4H_5N_2$ -CH ₂ -
	410(-), 427(+)	390-600	8.64	8.34	
I	420(-)	200-400	31.31	31.00	N_2O_5 $C_8H_{10}N_4$ CoO
	580(+)	400-740	46.96	47.11	
	--	>740	21.72	21.85	
II	320(-)	220-400	30.89	31.13	N_2O_5 $C_8H_{10}N_4$ CuO
	600(+)	400-660	46.34	46.00	
	--	>660	22.75	22.85	
III	324(-)	260-500	30.73	30.24	N_2O_5 $C_8H_{10}N_4$ ZnO
	662(+)	500-700	46.10	46.36	
	--	>580	23.16	23.30	
IV	320(-)	300-460	27.10	27.46	N_2O_5 $C_8H_{10}N_4$ CdO
	520(+)	460-640	40.66	40.00	
	--	>640	32.23	32.53	

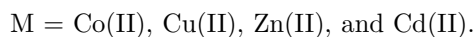
Temp. = Temperature, Calc. = Calculated
(-) = Endothermic (+) = Exothermic

On the basis of the observed thermal decomposition studies, it can be inferred that all the complexes undergo thermal decomposition in 2 steps according to the following general equations:





where



The highest thermal stability is displayed by complex IV. The solid residues were 17%-29% of the initial mass and elemental analysis indicated that these were pure metal oxides.

Conclusions

The available experimental data suggest that the prepared complexes of different metals as well as ligand decompose in a 2-step process. All the complexes possessing distorted tetrahedral geometry have a similar mode of degradation pattern with the evolution of inorganic and organic fragments when heated up to 740 °C. Above this temperature corresponding metal oxides as residue are left except for ligand, which behaves differently. Ligand appears to be more stable than the complexes as it exhibits a higher initial decomposition temperature. The coordination of metal ion to ligand is not responsible for weakening of the system to a greater extent. The intermediate products are not stable over a long range of temperature and decompose soon after their formation. The source of oxygen in the formation of residue (metal oxide) appears to have been the decomposition products and not the atmosphere^{41,43,59} as there is no gain in weight observed in TG curves at the end. Zinc and cadmium complexes show greater thermal stability, probably owing to less distortion of the tetrahedral structure and the smaller size of zinc and cadmium ions.⁶⁵

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References

1. M.A.V.R daSilva, M.D.M.C.R. daSilva, L.C.M. daSilva, F. Dietze and E. Hoyer, **Thermochim. Acta**, **378**, 45-50 (2001).
2. D. Czakis-Sulikowski and J. Katuzna, **J. Thermal Anal.** **47**, 1763-76 (1996).
3. J. Bubanec and A. Sopkova, **J. Thermal Anal.** **50**, 831-41 (1997).
4. E. Ingier-Stocka, **J. Thermal Anal.** **50**, 603-10 (1997).
5. R. Kurpiel Gorgol, W. Brzyska, **J. Thermal Anal. Calorim.** **71**, 539-48 (2003).
6. D. Czakis Sulikowska, A. Czylkowska, **J. Thermal Anal. Calorim.** **71**, 395-406 (2003).
7. C.B. Melios and M. Ionashiro, **Thermochim. Acta** **400**, 187-98 (2003).
8. T.V. Albu, L. Patron and E. Segal, **J. Thermal Anal.** **48**, 359-66 (1997).
9. N.R. Sperandeo, C.V. Mattia and M.M. de Berterello, **J. Thermal Anal.** **48**, 267-76 (1997).

10. L. Abate and C. Gandolfo, **J. Thermal Anal.** **46**, 5-14 (1996).
11. S. Materazzi, G. Dascenzo, S. Aquili, K.M. Kadish and J.L. Bear, **Thermochim. Acta** **397**, 129-34 (2003).
12. W. Brzyska and W. Ferenc, **J. Thermal Anal.** **22**, 53-59 (1981).
13. W. Brzyska and E. Swita, **J. Thermal Anal.** **32**, 1005-13 (1987).
14. W. Brzyska and M. Hakim, **J. Thermal Anal.** **34**, 47-53 (1988).
15. W. Ferenc and A. Walkow Dziewulska, **J. Thermal Anal. Calorim.** **70**, 949-58 (2002).
16. H. Kanno and Y. Suzuki, **J. Thermal Anal. Calorim.** **71**, 501-8 (2003).
17. C.B. Melios and M. Ionashiro, **Thermochim. Acta** **393**, 145-50 (2003).
18. A.S.M. AlShihri, H.M. Abdel Fattah, **J. Thermal Anal. Calorim.** **71**, 643-50 (2003).
19. S. Sener and A. Mete, **Synthetic Communications**, **27 (2)**, ISS2, 307-313 (1997).
20. E.C. Newman and C.W. Frank, **J. Pharm. Sci.** **657**, 729-734 (1976).
21. T. Sakaguchi and K. Taguchi, **Pharm. Bull.** **3**, 166-170 (1955) and references therein.
22. L.H. Conover, **Special publication No. 5**, The Chemical Society London, 1958.
23. T. Sakaguchi, K. Taguchi and N. Obi, **Yakugaku Zasshi**, **79**, 1381-1385 (1959).
24. J.T. Doluisio and A.N. Martin, **J. Med. Chem.** **6**, 16-20 (1963).
25. L.Z. Benet and J.E. Goyan, **J. Pharm. Sci.** **54**, 983-987 (1965).
26. W.A. Baker Jr. and P.M. Brown, **J. Am. Chem. Soc.** **88**, 131- (1966).
27. L.A. Mitschar, A.C. Bonacci, B. Slater-Eng, A.K. Hacker and T.D. Sokoloski, **Antimicro. Agents Chemother.** 111-115 (1969).
28. R.P. Gupta, B.N. Yadav, O.P. Tiwari and A.K. Sri Vastara, **Inorg. Chim. Acta** **32**, 195-196 (1979).
29. T.L. Blundell, G.G. Drelson, D.C. Hodgkin and M. Vigayan, **Recent Advan. Horm. Res.** **27**, 19-23 (1971).
30. W.J. Eilbeck, F. Holmes and A.E. Underhill, **J. Chem. Soc. (A)**757-761 (1967).
31. A. Albert, **Nature (London)** **172**, 201-201 (1953).
32. A. Albert, **Nature (London)** **177**, 483-484 (1958).
33. W.J. Eilbeck, F. Holmes, C.E. Taylor and A.E. Underhil, **J. Chem. Soc. Dalton**, 1968 (1972).
34. R.M.W.C. Gilvery, **"Biochemistry, A Functional Approach"**, pp. 14, W.B.Saunders Co., Philadelphia, Pa., 1970.
35. R.M. Silverstein, G.C. Basler and T.C. Morrill, **"Spectroscopic Identification of Organic Compounds"**, 4th ed, pp.95. John Wiley and Sons, New York, 1981.
36. The Sadtler Standard Spectra Published by Sadtler Res. Labs., Vol. 5, pp. 5991. Philadelphia 2, PA. 1874.
37. M.S. Hussain, T. Ali and S.M. Ali, **Pak. J. Sci. Ind. Res.** **16(3-4)**, 96-99 (1973).
38. M.S. Hussain, T. Ali and S.M. Ali, **Pro. Pak. Acad. Sci.** **13(1)**, 17-27 (1976).
39. D.L. Wood and J.P. Pemeika, **J. Chem. Phys.** **46**, 3595-3601 (1967).
40. S. Rehman, M. Arshad, S.A. Khan, K. Masud, N. Arshad, A.H. Qureshi and S.A. Ghauri, **Thermochim. Acta** **345**, 81-91 (2000).
41. M. Arshad, S. Rehman, S.A. Khan, K. Masud, N. Arshad and A. Ghani, **Thermochim. Acta** **364**, 143-53 (2000).

42. S. Rehman, M. Arshad, M. Ahmad, K. Masud, A. Ghani, N. Arshad, A.H. Qureshi and S.A. Gahuri, **J. Chin. Chem. Soc.** **47**, 501-508 (2000).
43. S.A. Khan, S. Rehman, M. Arshad and K. Masud, **The Nucleus**, **35**, 173-78 (1998).
44. M. Arif, S. Rehman, M. Arshad, K. Masud and N. Arshad, **Turk. J. Chem.** **25**, 73-79 (2001).
45. S. Rehman, M. Arshad, K. Masud, S.A. Khan, N. Arshad, A.H. Qureshi, C.A. Gafoor, M. Nawaz, M.Z. Haq and A. Ghani, **The Nucleus** **39(1-2)**, 33-40 (2002).
46. S. Rehman, M. Ahmad, M. Arshad, K. Masud and N. Arshad, **The Nucleus** **35 (3-4)**, 187-95 (1998).
47. M. Arshad, A.H. Qureshi, S. Rehman and K. Masud, **J. Therm. Anal. Cal.** **89** (2) 561-566 (2007).
48. A. Gero, **J. Am. Chem. Soc.** **76**, 5158- (1954).
49. S. Rehman, S. Pervez, S.A. Khan, J. Shah, S. Khattak, N. Ali and M. Arshad, **J. Chem. Soc. Pak.** **25**, 147-52 (2003).
50. B.N. Figgis, J. Lewis and R.G. Wilkins, "**Modern Coordination Chemistry**", pp. 412, Interscience Publishers, Inc. New York, 1960.
51. L.H. Keith (Editor), "**Compilation of EPA'S Sampling and Analysis Methods**", 2nd edn. Lewis Publishers, London, 1996.
52. M.S. Hussain, T. Ali and S.M. Ali, **J. Sci. Ind. Res.** **13**, 174-177 (1976).
53. G. Basee, R. Belford and R. Dickerson, **Inorg. Chem.** **1**, 438-439 (1962).
54. C. Sung-Nack, R.D. Bereman and J.R. Wasson, **J. Inorg. Nucl. Chem.** **37**, 2087-2090 (1975).
55. E.M. Baschmann, L.M. Weinstock and M. Germack, **Inorg. Chem.** **13**, 1297-1300 (1974).
56. S.A. Khan, S. Rehman, M. Arshad and K. Masud, **The Nucleus** **35** (3-4), 173-78 (1998).
57. V.A. Logvinenko, "**Thermal Analysis of Coordination Compounds and Clathrates**", Nauka, Novosibirsk, 1982.
58. E. Jona, M. Jammicky and I. Ostelny, **J. Thermal Anal.** **32**, 513-520 (1987).
59. J. Wilken, M. Kossenjans, W. Saak, D. Haase, S. Ohl and J. Martens, **Liebigs Annalen-Recueil, ISS** **3**, 573-579 (1997).
60. S. Rehman, **J. Chem. Soc. Pak.** **9**, 503-14 (1987).
61. M.S. Hussain and S. Rehman, **Z. Naturforsch.** **33B**, 67-74 (1978).
62. M.S. Hussain and S. Rehman, **Inorg. Chem. Acta** **60**, 231-238 (1982).
63. J. Maslowska and A. Baranowska, **J. Thermal Anal.** **29**, 309-515 (1984).
64. J. Cernak and J. Chonic, **J. Thermal Anal.** **32**, 527-532 (1987).
65. B.N. Sivasankar and S. Govindarajan, **J. Thermal Anal.** **46**, 117-128 (1996).
66. I. Tossidis and A.S. Kourakou, **J. Thermal Anal.** **32**, 491-503 (1987).