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THERMOANALYTICAL INVESTIGATION OF 1,2-DIIMIDAZOLOETHANE COMPLEXES OF COPPER, MERCURY AND CADMIUM BY TG-DTG-DTA TECHNIQUES IN STATIC AIR ATMOSPHERE

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The iodide complexes of transition metals with 1,2-diimidazoloethane (DIE) of the general formula MLI_2, (M=Cu(II), Hg(II), Cd(II); L=1,2-diimidazoloethane) were prepared and studied by means of thermogravimetry (TG/DTG) and differential thermal analysis (DTA) techniques. Their compositions were investigated by elemental analysis in order to ensure their purity and structural elucidations were based on conductivity measurements, room temperature magnetic measurements, proton NMR, XRD and IR spectra. Thermal decomposition of these distorted tetrahedral complexes and the ligand took place in two distinct steps upon heating up to 800°C, with the loss of inorganic and organic fragments. The thermal degradation of all the complexes (except for cadmium complex) in static air atmosphere started at temperatures lower than those observed for the free ligand pyrolysis. The composition of intermediates formed during degradation was confirmed by microanalysis and IR spectroscopy. The residues after heating above 740°C corresponded to metal oxide except for Hg(II) complex, which behaved differently. It was found on the basis of thermal analysis that thermal stability of the complexes increased in the following sequence: Hg(II)<Cu(II)<Cd(II).

Keywords: *1,2-diimidazoloethane (DIE), $M(DIE)I_2$ complexes, tetrahedral complexes, thermoanalytical study*

Introduction

The conditions of thermal decomposition of various complexes of transition metals and lanthanides with various organic N-donor ligands and others have been studied by many workers [1–10]. Metal complexes where coordination can occur between a variety of metal ions and a wide range of ligands, play an important role in many biological systems [11]. It has been observed that metal ions have considerable effect on the antimicrobial activity of antibiotics. Similarly a large number of metal complexes is known for their antitumor activity [12–20]. Realizing the importance of metal chelates in the biological activity, we decided to synthesize and study the coordination of ligands which have biologically active sites. To achieve this linked to the grouping $–N–(CH_2)_n–N–$ replacing piperidine moiety of DPE (1,2-dipiperidinoethane) by imidazole. Imidazole has been proved to be of prime importance in biological systems [17, 18, 21]. 1,2-Diimidazoloethane (DIE) is a derivative of a biologically active molecule:imidazole. The latter is quite important and is widely distributed in nature as in macrofungia and longistrobus [22–27].

In several previous papers [28–34], we studied the thermal behavior of some solid complexes of 1,2-dipiperidinoethane (DPE), 1,3-dipiperidinopropane (DPP) and derivatives of phenhomazine with divalent transition and representative metals. Moreover, we also reported kinetic parameters [32] apart from their decomposition.

Continuing our investigations in this field, we now report our studies on the thermal behavior of solid Cu(II), Hg(II) and Cd(II) complexes of DIE by TG-DTA-DTG techniques with the aim to examine their thermal decomposition and thermal stability during heating in static air atmosphere. Elemental analysis, IR spectroscopy and XRD techniques were applied to characterize the products of thermal decomposition along with the residue.

Experimental

Materials

Salts of transition metals and other chemicals obtained from standard source suppliers, were of analytical grade and used without further purification. Solvents were distilled at least once before use. The partial dehydration of metal salts was carried out in vacuum oven for several hours around 80–100°C.

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Synthesis of ligand

Ligand DIE was synthesized by the procedure already reported [35]; imidazole (0.25 mol) in absolute ethanol (40 mol) was added drop-wise to dibromoethanol (0.1 mol) in methanol (20 mol). Few drops of 5% alcoholic KOH were poured in the reaction mixture. The contents were refluxed for about 8 h at 80°C and left overnight. The KBr was filtered, filtrate was evaporated and recrystallized from proper ethanol. The yield was 80%.

Synthesis of solid complexes

All the complexes were prepared using similar general procedure [35]. Approximately 10 mol of partially dehydrated salt was dissolved in 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 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 then cooled for about 20 min. The metal complexes precipitated either immediately or upon cooling. The product obtained was filtered through sintered glass crucible, washed several times with ether and dried under vacuum at 50°C. The complexes were recrystallized from acetone.

Physico-chemical methods

Infrared spectra were taken in the range of 4000–600 cm^{-1} on PYE UNICAM Spectrophotometer as KBr disc. The far IR spectra were examined as KBr discs in the region of 400–200 cm^{-1} (FTIR Shimadzu). Metals ions and residues were determined with an XRF-500 Link System, England.

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

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

Magnetic susceptibilities were measured by Guoy method at room temperature using $Hg[Co(SCN)_4]$ as standard [36]. The magnetic moments were calculated. The elemental analysis was carried out at HEJ Research Institute of Chemistry, University of Karachi. The cations and anions were estimated by using analytical procedures.

The thermoanalytical measurements were carried out with NETZSCH simultaneous thermal analyzer STA 429. Samples were contained in an aluminum crucible Al 203 (8 mm dia×10 mm depth) with central base recess. The crucible was then adjusted on palladium/ruthenium crucible support platform, which gave a proportional signal to the recorder and computer interface to plot the mass loss of sample *vs*. temperature.

Results and discussion

The complexes of DIE with the transition elements have been synthesized and studied. The stoichiometry of the complexes was established on the basis of their elemental analysis and the results 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 assignments. The data from conductance measurements and magnetic susceptibilities of complexes are summarized in Table 2.

Proton NMR of the ligand in D_2O with TMS as an internal standard showed a broad singlet at 7.38 ppm for two hydrogens of carbon between two nitrogen atoms in imidazole ring and another broad singlet at 3.90 ppm for four hydrogens of methylene. A sharp multiplet at 6.75 ppm gave the indication for four methylene protons of the imidazole ring.

A mass peak of moderate intensity at *m*/*z* 162 corresponding to molecular ion $(C_8H_{10}N_4)^+$ was observed in the spectrum of DIE [35]. The base peak at *m*/*z* 81 is probably due to the formation of N-methyl imidazole cation, 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.

Analytical data shown in Table 1 indicate that only one DIE molecule like DME [37] is found to coordinate with metal ion and form complexes of the

Table 1 Analytical data for 1,2-diimidazoloethane and investigated complexes

Composition	Appearance	C/% found	H/% found	N/% found	Metal/%	Anion/%
$C_8H_{10}N_4$ (DIE)	colorless	59.5 (59.3)	6.50 (6.2)	35.0 (34.6)	–	–
$Cu(C_8H_{10}N_4)I_2$ (I)	cactus	25.3 (25.2)	2.80 (2.70)	14.8 (14.7)	13.4 (13.3)	52.9 (53.0)
$Hg(C_8H_{10}N_4)I_2$ (II)	colorless	15.7 (15.6)	1.70 (1.65)	9.50 (9.10)	32.6 (32.5)	41.0 (41.2)
$Cd(C_8H_{10}N_4)I_2$ (III)	colorless	18.1 (18.2)	1.90 (1.90)	10.5 (10.6)	21.3 (21.3)	48.0 (48.0)

Values in parentheses are the calculated values

Table 2 Molar conductance, magnetic moment for complexes, $M(C_8H_{10}N_4)I_2$

Complex	Solvent	Molar conductance/ mS mol^{-1}	μ_{eff}/BM
I	DMSO	3.52	1.83
II	acetone	0.70	diamagnetic
III	acetone	2.50	diamagnetic

DMSO=dimethyl sulphoxide

general formula $[M(DIE)I_2]$, where *M*=Cu(II), Hg(II), Cd(II). The molar conductance ranges from 0.70 to 3.52 mS mol^{-1} in various solvents. This shows that complexes of DIE are non-electrolytic. The complex $CuLI_2$ is soluble in DMSO, while $HgLI_2$ and $CdLI_2$ are soluble in acetone (Table 2).

The absorption bands in the regions 1620–1605 and 1165–1140 cm^{-1} [38, 39] assigned to C=N and C–N stretching vibrations of imidazole have been shifted. The characteristic bands in the infrared spectra (4000–600 cm^{-1}) of DIE and its metal complexes are given in Table 3. In these complexes the bands assigned to C=N stretching vibrations of the ligand is being splitted into four distinct bands. Whereas the other two weak bands shift towards higher frequency and are found at 1635 and 1612 cm^{-1}. Similarly for bands due to C–N stretching vibrations, the strong one moves to lower frequency and appears at 1115 cm^{-1} and the other two weak bands shift towards higher frequency and are observed at 1180 and 1170 cm^{-1}.

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 density from the C–N bond where nitrogen atoms become coordinated to the metal ion.

The thermal curves (TG, DTG and DTA) of 1,2-diimidazoloethane and its complexes were recorded in static air atmosphere from ambient to 800°C (Figs 1–4). The characteristic data and stages of pyrolysis regarding the thermal behavior of ligand (DIE) and its complexes (I, II and III) are given in Table 4. The TG and DTA curves reveal that ligand decomposes in two steps in the temperature range 240–600°C (Fig. 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 accompanying endothermic effects and the intermediate then decomposes exothermally (2nd step) in the

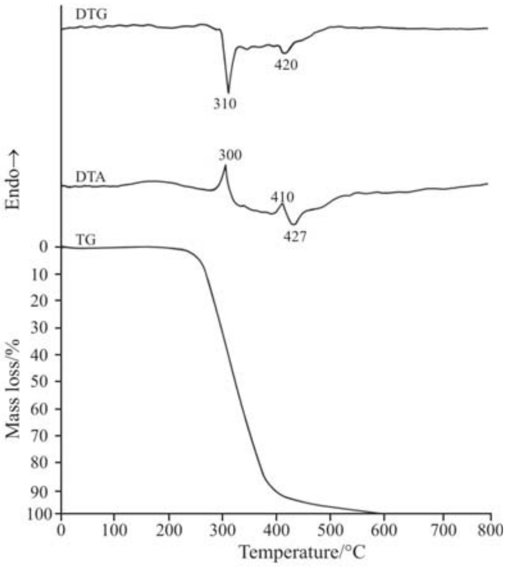

Fig. 1 Thermoanalytical curves for $(CH_2N_2C_3H_3)_2$ in air

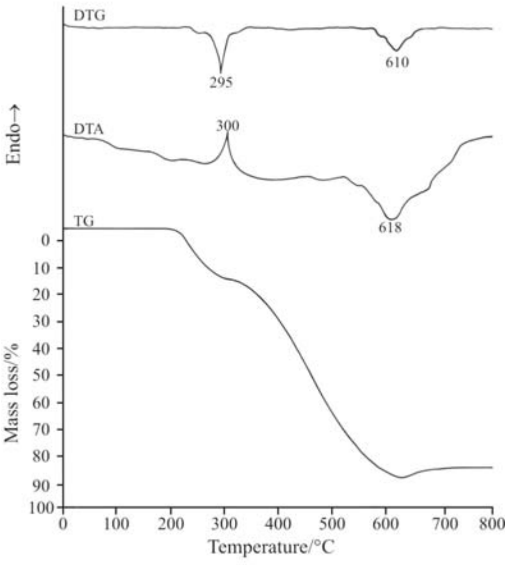

Fig. 2 Thermoanalytical curves for $Cu(C_8H_{10}N_4)I_2$ in air

Table 3 IR spectra for DIE and its metal complexes

Compound	IR spectra/cm^{-1}			
	$\nu_{C=N}$	$\nu_{C–N}$	$\nu_{M–X}$	$\nu_{M–N}$
DIE	1620s, 1605w	1165s, 1140w	–	–
I	1645w, 1632m, 1622w, 1600vs	1175m, 1165m, 1140sh, 1118s	–	–
II	1645m, 1635w, 1612w, 1600vs	1185m, 1170w, 1148sh, 1115vs	490	290–270
III	1640m, 1618w, 1612w, 1600vs	1182w, 1170w,1115vs	85–470	290–280

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

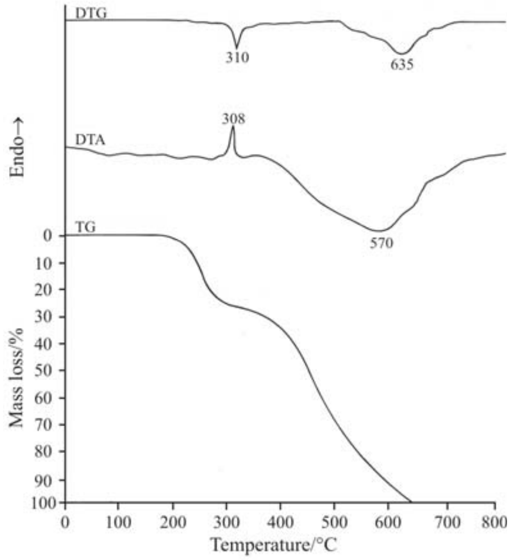

Fig. 3 Thermoanalytical curves for Hg($C_8H_{10}N_4$)I_2 in air

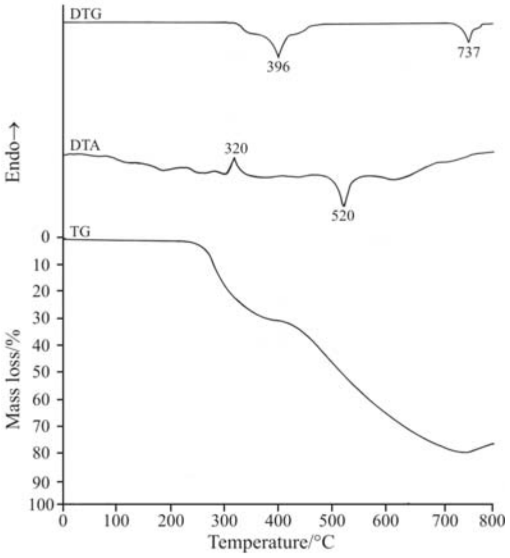

Fig. 4 Thermoanalytical curves for Cd($C_8H_{10}N_4$)I_2 in air

temperature range 390–600°C liberating 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 second sharp endothermic peak at 410°C corresponds to the loss of two species. The second step is slower one and ascribed to the oxidation and vaporization of methylene indicating this process as exothermic in nature [33]. Ligand is thermally stable up to 240°C and heating it above 600°C leaves no residue. The sequence of loss is comparable with the mass spectrum [35, 40].

The thermal decomposition of Cu(DIE)I_2 (I) takes places in the temperature range of 200–620°C (Fig. 2). The first step involves decomposition (200–300°C) in which the complex loses N-methylene imidazole moiety. In the second stage (300–620°C), the intermediate decomposes further with the evolution of N-methylene-imidazole fragment of the ligand followed by the decomposition and evolution of I_2 leaving CuO as final residue. One endothermic peak (300°C) and one exothermic peak (618°C) correspond to the first and second step of decomposition.

The DIE portion begins to degrade in the temperature range 190–320°C (first step) for the complex, Hg($C_8H_{10}N_4$)I_2 (II). Further decomposition of the complex occurs in second step in the range 320–640°C (Fig. 3) which shows no end product. The DTA curve shows endothermic and exothermic peaks at 308 and 570°C, respectively, corresponding to the first and the second step of the TG curve.

When heated in a static air atmosphere, the Cd($CH_2N_2C_3H_3$)$_2$$I_2$ (III) is stable up to 240°C and begins to decompose in two steps in the temperature range 240–740°C (Fig. 4). The first step (240–400°C) involves decomposition in which the complex loses N-methylene imidazole moiety. In the second stage, 400–740°C, evolution of I_2 takes place accompanied by oxidation of residue. Endothermic and exothermic peaks coincide the decomposition processes at 320 and 520°C, respectively. Heating the sample

Table 4 Thermoanalytical results for the complexes, M($C_8H_{10}N_4$)I_2

Compound	DTA peak temperature/°C	TG Temperature range/°C	Mass loss/% calc.	 found	Phenomena
DIE	300(–), 410(–)	240–390	91.35	91.64	$C_3H_3N_2$, $C_4H_5N_2$
	427(+)	390–600	8.64	8.34	$-CH_2-$
I	300(–)	200–300	16.89	17.01	$CH_2N_2C_3H_3$
	618(+)	300–620	69.84	70.14	$CH_2N_2C_3H_3$, I_2
	–	>620	16.59	16.40	CuO
II	308(–)	190–320	26.28	27.22	$2CH_2N_2C_3H_3$
	570(+)	320–640	73.71	72.76	I_2, Hg
III	320(–)	240–400	30.66	30.28	$2CH_2N_2C_3H_3$
	520(+)	400–740	48.04	48.53	I_2
	–	>740	24.31	24.58	CdO

calc.=calculated, (–)=endothermic, (+)=exothermic above 740°C leaves the respective metal oxide as residue [41–43].

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

$$M(C_8H_{10}N_4)I_2 \rightarrow M(CH_2N_2C_3H_3)I_2 + CH_2N_2C_3H_3\uparrow$$
$$M(CH_2N_2C_3H_3)I_2 + 1/2O_2 \rightarrow MO + I_2\uparrow + CH_2N_2C_3H_3\uparrow$$
$$\text{where } M=\text{Cu(II)} \qquad \text{(i)}$$

$$M(C_8H_{10}N_4)I_2 \rightarrow MI_2 + 2CH_2N_2C_3H_3\uparrow$$
$$MI_2 + \text{air} \rightarrow M\uparrow + I_2\uparrow$$
$$\text{where } M=\text{Hg(II)} \qquad \text{(ii)}$$

$$M(C_8H_{10}N_4)I_2 \rightarrow MI_2 + 2CH_2N_2C_3H_3\uparrow$$
$$MI_2 + 1/2O_2 \rightarrow MO + I_2\uparrow$$
$$\text{where } M=\text{Cd(II)} \qquad \text{(iii)}$$

while comparing the thermal stabilities of complexes on the basis of initial temperature of decomposition [44, 45], the following sequence of increasing thermal stability was observed:

$$II<I<III$$

The highest thermal stability is displayed by the complex III. The solid residues comprised 13–24% of the initial mass (except for Hg(II) complex) and elemental analysis indicated that these were pure metal oxides.

Conclusions

The available experimental data allow to suggest that the prepared complexes of different metals as well as ligand decompose in a two-step process. All the complexes possessing distorted tetrahedral geometry show almost a similar decomposition pattern (except for ligand and Hg(II) complex, which behave differently) with the evolution of inorganic and organic fragments leaving corresponding metal oxides as residue when heated above 740°C. Ligand appears to be more stable than the complexes as it exhibits higher initial decomposition temperature (cadmium complex also shows similar behavior). The coordination of metal ion to ligand is responsible for weakening of the system, that's why complexes start losing mass at lower temperatures and at a faster rate, and consequently, decomposition of complexes is completed earlier than that of pure ligand. The intermediate products are not stable over a long range of temperature and decompose soon after their formation. Cadmium complex shows greater thermal stability, probably owing to the lower distortion of the tetrahedral structure and the smaller size of cadmium ions [46].

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