

# Infrared spectra and thermal degradation pathway of Zn(II), Cd(II) and Hg(II) alloxan diabetes adduct

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**Abstract:** Alloxan diabetes complexes with Zn(II), Cd(II) and Hg(II) metal ions have been separated in solid form and characterized on the basis of elemental analysis, molar conductivity, mid infrared spectra. The thermal decomposition the solid complexes was studied. The ligational behavior of Cd(II) and Hg(II) occurs through the oxygen in position 2 and the nitrogen in position 1. Concerning Zn(II) complex the complexation involving the carbonyl group in position 4 (or 6) can be realized through both pyrimidine nitrogen atom and one of the hydroxyl groups in position 5.

**Keywords:** Alloxan; Infrared spectra; thermal studies; chelation.

## I- INTRODUCTION

Pyrimidine derivatives are known for their varied biological properties. Brugnatelli [1] was the first to isolate "Alloxan", a pyrimidine derivative in 1818 and later this compound was found to possess antineoplastic properties [2]. Alloxan (2,4,5,6 [1H,3H]-pyrimidinetetrone), (H<sub>2</sub>L), is widely used in studies of experimental diabetes, because this agent destroys pancreatic islet  $\beta$ -cells with a specific selectivity [3-5]. A study on the mechanism of action of the typical diabetogenic agent seems to be of great importance for elucidating the cause of insulin-dependent diabetes mellitus. Alloxan has been known to inhibit proinsulin synthesis in pancreatic islets [6]. Uchigata *et al.* proposed that alloxan caused DNA strand breaks to stimulate nuclear poly(ADP-ribose) synthetase, thereby depleting intracellular NAD level and inhibiting proinsulin synthesis [7,8]. Actually, islet DNA strand breaks were observed in vivo by administration of alloxan to rats [9]. Also, alloxan is capable of influencing calcium, zinc, and phosphorus metabolism in organisms of increasing the blood sugar. Therefore, it can be used in experimental studies of diabetes [10]. Moreover, alloxan occurs in living organisms, and is the product of uric acid decomposition [11]. A high biological activity of alloxan determines considerable interest of scientists to its complexation reactions. Thus, Co(II), Ni(II), and Cu(II) complexes with alloxan, ML<sub>2</sub>·5H<sub>2</sub>O, were isolated from aqueous alkaline solutions [12]; manganese(II) alloxanate was obtained by evaporation of an acidified solvent at room temperature [13]. As follows from spectrophotometric data, cerium(III) forms with alloxan a soluble complex ML<sub>2</sub> [14]. Transition-metal salts are known to react with alloxan solutions to give colored complexes: orange-yellow or red for Cd(II), Mg(II), Cu(II), Zn(II), Co(II), Ni(II), dark blue (in the presence of ammonia) for Fe(II) [15]. The compositions and properties of Pb(II), Hg(I), Hg(II), and Ag(I) alloxanates were not studied in detail [15–18]. Previously [19, 20], Kovalchukova *et al.*, was studied the Fe(III) and Co(III) complexes with alloxan; the synthesis of Co(II), Ni(II), and Pd(II) alloxanates was also reported [21]. The study of complexation of a series of *d* and *f* block metals with alloxan was done by Shebaldina *et al* [22]. The present investigation is undertaken to study the course of interaction of alloxan with Zn(II), Cd(II) and Hg(II). The solid products were characterized spectroscopically. The stability of the prepared alloxanate complexes were checked using thermogravimetric.

**International Journal of Innovative Research in Science,  
Engineering and Technology**

(An ISO 3297: 2007 Certified Organization)

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**II- EXPERIMENTAL**

**II-1- Materials and instrumentation**

All chemicals were reagent grade and were used without further purification. Alloxan was purchased from Fluka Chemical Co., ZnBr<sub>2</sub>, CdCl<sub>2</sub> and HgCl<sub>2</sub> (Merck Co.). Carbon, hydrogen and nitrogen contents were determined using a Perkin-Elmer CHN 2400. The metal content was found gravimetrically by converting the compounds into their corresponding oxides at 800 °C under air condition. IR spectra were recorded on Genesis II FT-IR Spectrometer in the (4000–400 cm<sup>-1</sup>) range with 40 scans in KBr discs. The UV–vis, spectra were determined in the DMSO solvent with concentration (1.00× 10<sup>-3</sup> M) for the alloxan and their complexes using Jenway 6405 Spectrophotometer with 1cm quartz cell, in the range 800–200 nm. Molar conductivities of freshly prepared 1.0×10<sup>-3</sup> mol/dm<sup>3</sup> DMSO solutions were measured using Jenway 4010 conductivity meter. Simultaneous TGA and DTA curves were obtained on a Rigaku 8150 thermoanalyser under dynamic nitrogen atmosphere, at a heating rate of 5 deg min<sup>-1</sup>.

**II.2. Synthesis of metal complexes**

**[ZnL(H<sub>2</sub>O)<sub>2</sub>].4H<sub>2</sub>O complex.**

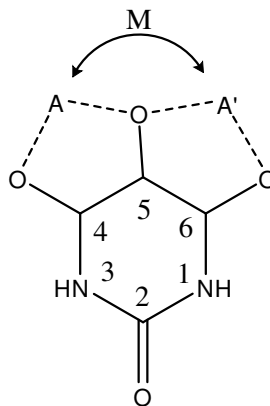
The complex, [ZnL(H<sub>2</sub>O)<sub>2</sub>].4H<sub>2</sub>O, was prepared by mixing equal volumes (30 ml) of alloxan (0.142 gm, 1.0 mmol) with ZnBr<sub>2</sub> (0.224 gm, 1.0 mmol). The mixture was neutralized by titrated with NaOH to adjust pH= 6.5 and then heated on a water bath at 60 °C with constant stirring for about 45 min. A yellow solid complex was precipitated. The obtained precipitate was separated, washed several times with hot methanol and then dried in *vacuo* over anhydrous CaCl<sub>2</sub>.

**[Cd(HL)<sub>2</sub>].5H<sub>2</sub>O and [Hg(HL)<sub>2</sub>].5H<sub>2</sub>O complexes.**

Preparation of these two complexes followed mainly the same procedure as preparation of Zn(II) complex, but the weight of CdCl<sub>2</sub> and HgCl<sub>2</sub> were (0.201 gm, 1.0 mmol) and (0.271 gm, 1.0 mmol), respectively. The pH was adjusted at 7.5.

**III- RESULTS AND DISCUSSION**

Alloxan is one of alterdentate ligand which offers metal ion more than one equivalent coordination site. In an alterdentate ligand there is, principally, always a rearrangement possible in which the metal is transferred from one site to another one. This can be either an inter- or intramolecular process. The rearrangement reaction is kinetically controlled by the activation energy and entropy experienced by the metal on the reaction path. The free energy difference is zero by definition, if the coordination sites are equivalent [23, 24].

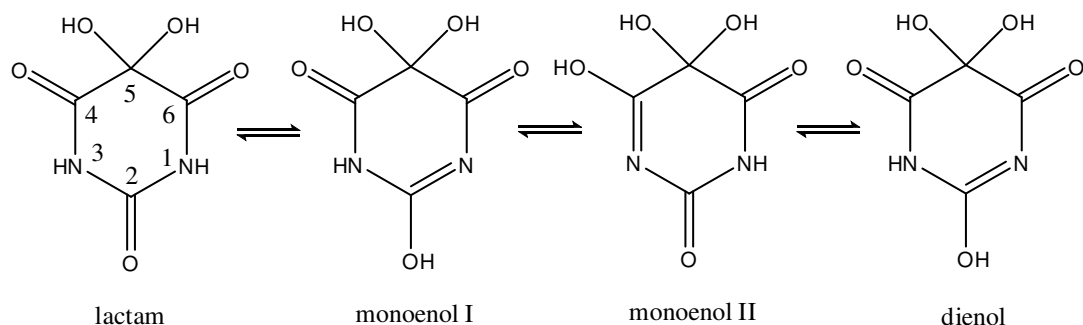


Also, it is known that hydrated alloxan can potentially exist in different tautomeric forms [23, 25]:

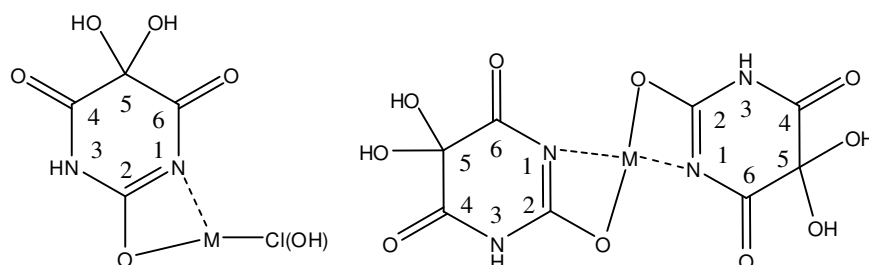
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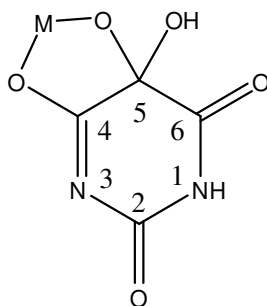
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The calculated atomization heats ( $\Delta H$ ) indicated that of all forms presented, mono-enol II form is most stable in the gas phase ( $\Delta H = 62.71$  eV). Stabilities of mono-enol I, dienol, and lactam forms are somewhat lower ( $\Delta H = 62.44, 62.64,$  and  $62.65$  eV, respectively). According to X-ray diffraction data [26-28], the crystal alloxan molecule exists as the lactam (trioxo) form. However, close intermolecular interaction energies for above tautomers (4.86, 4.27, 4.53, and 5.22 eV) make it possible to suggest that in solutions, several forms exist simultaneously, and can be stabilized during complexation. The literature survey on the alloxanate complexes shows that, alloxan can coordinate by several types of structures: Type 1; the metal chelate ring involving the oxygen in position 2 and the nitrogen in position 1[23].



Type 2: the metal chelate ring involving the oxygen in position 4 and one of the hydroxyl group in position 5[23].

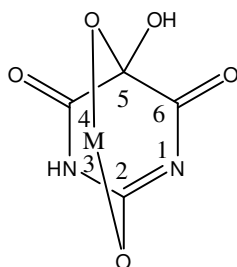


Type 3: the metal chelate ring involving the oxygen in position 2 and one of the hydroxyl group in position 5[23].

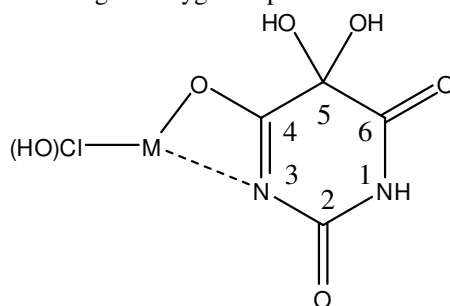
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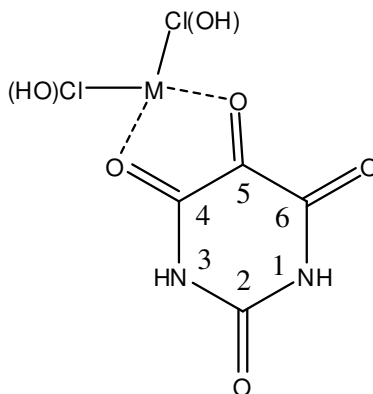
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Type 4: the metal chelate ring involving the oxygen in position 4 and the nitrogen in position 3[19, 29].



Type 5: the metal chelate ring involving the oxygen in position 4 and the oxygen in position 5[30].



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The results of the elemental analysis and some physical characteristics of the obtained compounds are given in Table 1.

**Table 1:** Elemental analyses and physical data of the alloxanate complexes

compounds	Mwt.	mp/°C	color	Content ((calculated) found)				$\Lambda_m$ ( $\Omega^{-1}\text{cm}^{-1}\text{mol}^{-1}$ )
				% C	% H	% N	%M	
[ZnL(H <sub>2</sub> O) <sub>2</sub> ].4H <sub>2</sub> O	331.5 5	>300	Pale yellow	(14.49 ) 14.45	(4.26) 4.43	(8.45) 8.29	(19.72 ) 19.10	15
[Cd(HL) <sub>2</sub> ].5H <sub>2</sub> O	520.4 0	>300	Pink	(18.46 ) 18.45	(3.10) 4.25	(10.76 ) 9.26	(21.59 ) 21.43	22
[Hg(HL) <sub>2</sub> ].5H <sub>2</sub> O	608.5 9	>300	Pale violet	(15.78 ) 15.65	(2.65) 5.43	(9.20) 8.45	(32.95 ) 32.92	43

The complexes are air-stable, hygroscopic, with higher melting points, all of them over 300 °C, insoluble in H<sub>2</sub>O and most of organic solvents but partly soluble in DMSO. The elemental analysis data (Table 1) of the complexes indicates a 1:1 metal:ligand stoichiometry for [ZnL(H<sub>2</sub>O)<sub>2</sub>].4H<sub>2</sub>O complex but 1:2 for both [Cd(HL)<sub>2</sub>].5H<sub>2</sub>O and [Hg(HL)<sub>2</sub>].5H<sub>2</sub>O. The molar conductivity values for the alloxanate complexes in DMSO solvent (1.00×10<sup>-3</sup> mol) were in the range less than 50  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ , suggesting them to be non-electrolytes nature (Table 1). Conductivity measurements have frequently been used in elucidation of structure of metal chelates (mode of coordination) within the limits of their solubility. They provide a method of testing the degree of ionization of the complexes, the molecular ions that a complex liberates in solution in case of presence of anions outside the coordination sphere), the higher will be its molar conductivity and vice versa [31]. It is clear from the conductivity data that the complexes present seem to be non-electrolytes. In the case of Zn(II), Cd(II) and Hg(II) alloxan complexes, the chloride ions were absent. These results were strongly supported with the chemical analysis (elemental analysis data) where Cl<sup>-</sup> ions are not detected by addition of AgNO<sub>3</sub> solution; this result well matched with CHN data. The main IR data are summarized in Table 2 and IR spectra are shown in Fig. 1. The IR spectrum of crystal alloxan exhibits an intense band due to the carbonyl vibrations: it has poorly defined maxima at 1764, 1737 and 1726 cm<sup>-1</sup>. The band at 1764 cm<sup>-1</sup> was assigned to the vibrations of the carbonyl group in the alloxan amide fragment (-NH-CO-NH-) and the bands at 1737 cm<sup>-1</sup> [19, 20] and 1726 cm<sup>-1</sup> can be attributed to vibrations of the ketone group in position 5 and the two ketone groups in positions 4 and 6, respectively. In the range of 3339–3044 cm<sup>-1</sup>, broad intense bands due to overlapping vibrations of the NH and OH groups were observed. We can divide our alloxanate complexes according to the IR spectra into two groups: Group I: In the spectrum of both the [Cd(HL)<sub>2</sub>].5H<sub>2</sub>O and [Hg(HL)<sub>2</sub>].5H<sub>2</sub>O compounds the band of the carbonyl groups in positions 4 and 6 which appear in the range of 1717 and 1727 cm<sup>-1</sup> remain unchanged, while the bands at 1764 and 1737 cm<sup>-1</sup> disappear due to the formation of hydroxyl group, the metal chelating ring in these compounds involving the oxygen in position 2 and the nitrogen in position 1, as shown in Type 1. Group 2: In the IR spectra of the Zn(II) complex, the three absorption bands of carbonyl groups disappeared, while the absorption intensity in the range of 1650-1450 cm<sup>-1</sup> noticeably increases. The metal-chelate ring involving the carbonyl group in position 4 (or 6) can be realized through both pyrimidine nitrogen atom and one of the hydroxyl groups in position 5, as shown in Type 2. The spectra of the alloxan complexes recorded in DMSO. There are four detected absorption bands at around 215, 220, 240 and 260 nm, the bands 215 and 220 nm are assigned to  $\pi$ - $\pi^*$  and the other two are assigned to n- $\pi^*$  intraligand transitions. These transitions also found in the spectra of the complexes, but they are shifted, confirming the coordination of the ligand to the metallic ions. The second two bands around 240-260 nm are probably due to presence of ketone groups [21]. The complexes Zn(II), Cd(II) and Hg(II) have an absorption bands at ~ 400 nm which may be assigned as charge-transfer [32, 33].

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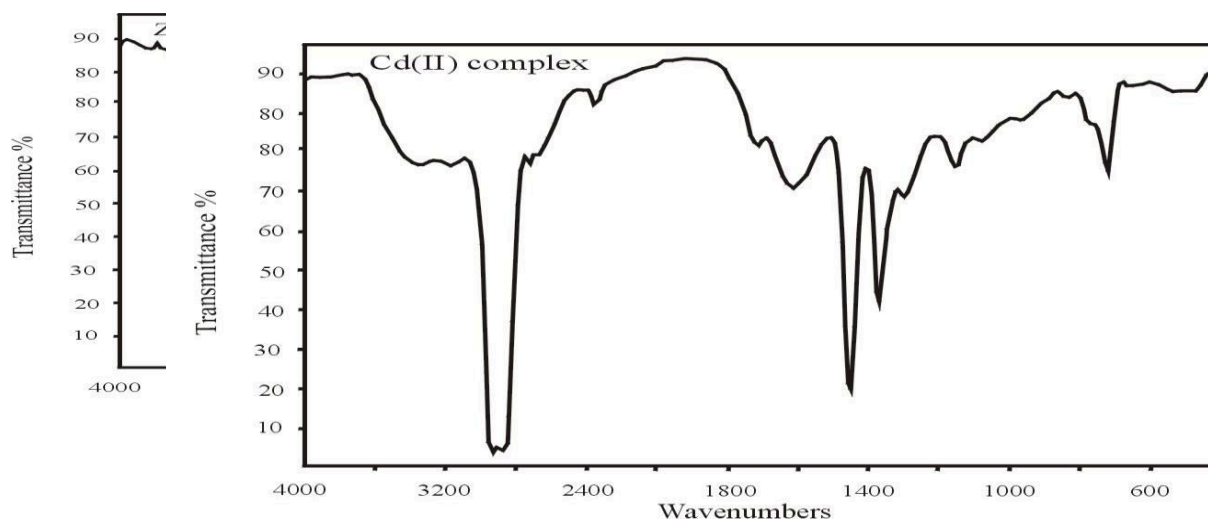
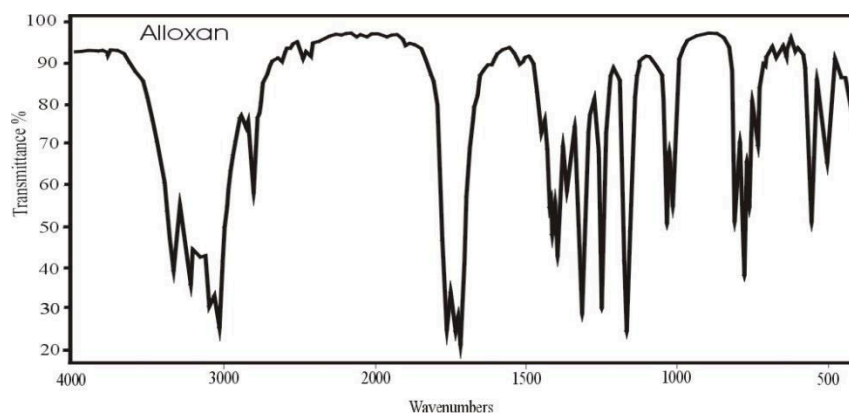
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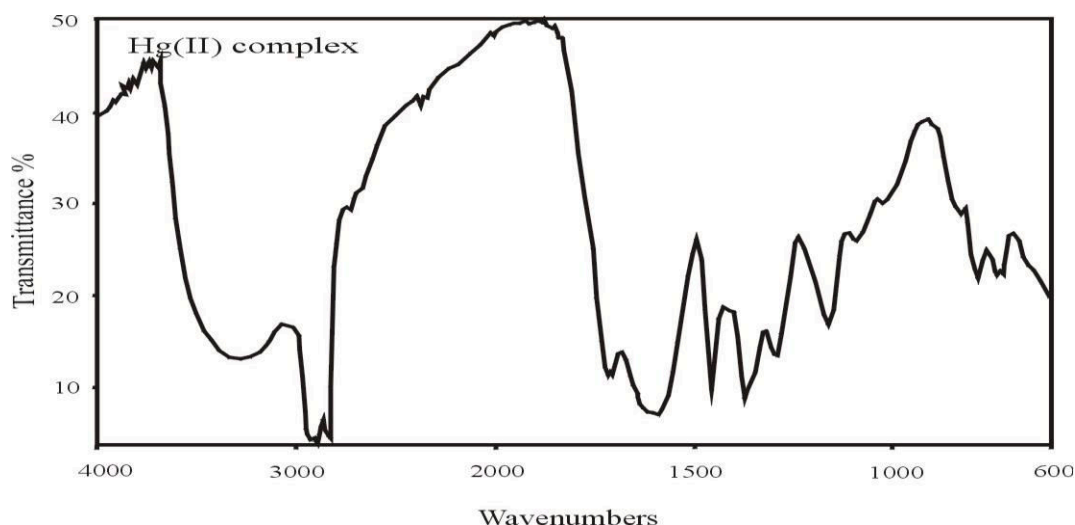
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**Table 2:** IR frequencies ( $\text{cm}^{-1}$ ) of alloxan ( $\text{H}_2\text{L}$ ) and its metal complexes

Compound	N(NH)+ $\nu(\text{OH})$	$\nu(\text{C}(4)=\text{O}), \nu(\text{C}(6)=\text{O})$	$\nu(\text{N}=\text{C}-\text{O})$
$\text{H}_2\text{L}^*$	3339-3044	1726	-
Zn(II)	3391-2817	-	1643
Cd(II)	3360-2835	1717	1617
Hg(II)	3350-2850	1727	1614

\*  $\text{H}_2\text{L}$  has  $\nu(\text{C}(2)=\text{O})$  at  $1764 \text{ cm}^{-1}$  and  $\nu(\text{C}(5)=\text{O})$  at  $1737 \text{ cm}^{-1}$





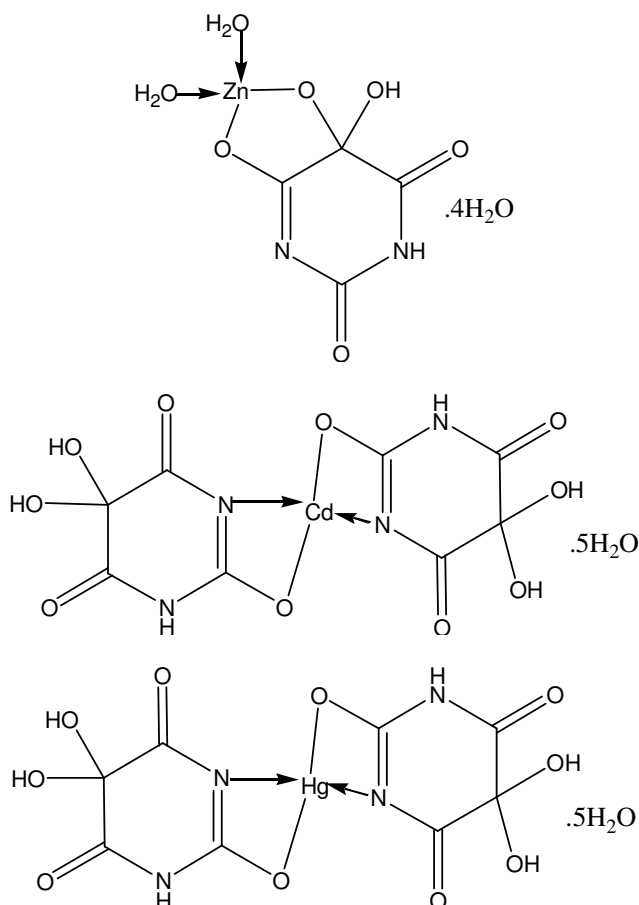
**Fig. 1:** The FT-IR spectra of alloxan and their complexes

The thermal analyses data are summarized and refereeing in Table 3 as follows. The final residue at the end of the degradation processes in Zn(II), Cd(II) and Hg(II) complexes was assigned to the association of metal oxides.

**Table 3:** Thermal analyses data of alloxan and its metal complexes

Compound	Steps	Temperature range (°C)	DTG peak (°C)		TG Weight loss (%)		Assignments
			Endo	Exo	Calc.	Found	
[ZnL(H <sub>2</sub> O) <sub>2</sub> ].4H <sub>2</sub> O	1 <sup>st</sup>	50-225	120	-	21.72	21.48	4H <sub>2</sub> O
	2 <sup>nd</sup>	225-300	225	-	10.86	10.59	2H <sub>2</sub> O
	3 <sup>rd</sup>	300-440	-	410	14.49	14.05	NO <sub>2</sub> + H <sub>2</sub>
	4 <sup>th</sup>	440-600	-	525	13.88	12.00	NO <sub>2</sub>
					39.05	41.88	ZnO + 4C (residue)
[Cd(HL) <sub>2</sub> ].5H <sub>2</sub> O	1 <sup>st</sup>	50-275	175	-	17.20	17.27	5H <sub>2</sub> O
	2 <sup>nd</sup>	275-600	-	340	39.58	39.95	4NO <sub>2</sub> + H <sub>2</sub> O + 2H <sub>2</sub>
					43.22	42.78	CdO + 8C (residue)
[Hg(HL) <sub>2</sub> ].5H <sub>2</sub> O	1 <sup>st</sup>	50-125	100	-	14.78	14.46	5H <sub>2</sub> O
	2 <sup>nd</sup>	125-380	-	300	35.17	35.95	C <sub>6</sub> H <sub>6</sub> N <sub>4</sub> O <sub>5</sub> (organic moiety)
	3 <sup>rd</sup>	380-500	-	450	14.46	15.30	2CO <sub>2</sub>
					35.59	34.29	HgO (residue)

Accordingly, the above mentioned discussions using elemental analysis, molar conductance, (infrared and <sup>1</sup>H-NMR) spectra as well as thermogravimetric analysis; the suggested structures of the alloxanate complexes can be represented in Scheme 1.



**Scheme 1:** Suggested structures of Zn(II), Cd(II) and Hg(II) alloxan complexes

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