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## Synthesis, spectral, thermal, XRD and antibacterial studies on metal EDTA hydrazinate complexes

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### ABSTRACT

Five new complexes of Co(II), Ni(II), Zn(II), Cd(II) and UO<sub>2</sub>(II) with edta hydrazinate ligand have been prepared and characterized by elemental analysis, magnetic measurements, infrared spectra, electronic spectra, X-ray diffraction and thermal analysis. The general formulae M<sub>2</sub>(edta)(N<sub>2</sub>H<sub>4</sub>)<sub>6</sub> where M=Co, Ni or Zn and M<sub>2</sub>(edta)(N<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> where M=Cd or UO<sub>2</sub> been assigned for edta hydrazinate complexes. The magnetic moments and electronic spectra indicate that these complexes are of high-spin octahedral variety. IR spectra of the edta complexes indicate that both carboxylate ions and hydrazine molecules coordinate to the metal ions in the bridging fashion. These complexes undergo exothermic decomposition to give the respective metal oxide as a final residue. X-ray powder diffraction patterns of the metal edta hydrazinate complexes indicate isomorphism among them. Antibacterial activities of these complexes also been studied.

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### KEYWORDS

Synthesis;  
Hydrazine complexes;  
Metal oxides;  
Thermal analysis;  
XRD;  
Antibacterial activity.

### INTRODUCTION

The coordination chemistry of hydrazine is of interest because of its ability to serve as an electron-pair donor. The presence of two, free electron pairs, as in other polybasic ligands, offers the possibility of several different types of coordination behavior towards transition metal ions<sup>[1-3]</sup>.

It can function as a monodentate<sup>[4,5]</sup> and bridging bidentate ligand<sup>[6-10]</sup>. During the two decades there has been considerable interest in the studies of the hydrazine derivatives of metal carboxylates since they serve as precursors of fine particle oxide materials. Most of the studies have been performed on the metal hydrazine mono carboxylic acids<sup>[11-14]</sup> and metal hydrazine

dicarboxylic acids<sup>[15,16]</sup>. Crystal structures of simple metal edta complexes and these with alkali metal or ammonium ions have been well established in the literature. In spite of exhaustive investigations on hydrazine metal edta complexes bis and tris - hydrazine metal edta complexes are scarce in the literature<sup>[17]</sup>. We now report the preparation of metal edta hydrazinate complexes and their characterization by magnetic, spectral, thermal and x-ray studies.

### EXPERIMENTAL

All the chemicals used were of Analar grade: Hydrazine hydrate (99-100%) was used as received. The solvents were distilled prior to use.

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### Preparation of the complexes

#### Preparation of tris-hydrazine metal edta: $M_2(edta)(N_2H_4)_6$ where M=Co, Ni or Zn

An aqueous solution (30 mL) of a mixture of edta (2.929 g, 0.1 mmol) and hydrazine hydrate (3 mL, 0.6 mmol) was slowly added with constant stirring to an aqueous solution (30 mL) of respective metal nitrate hydrates (0.2 mmol). The resulting clear solution was allowed to crystallize at room temperature. The crystalline complexes settled was collected after 24 h, washed with water and then with alcohol and dried in air. These complexes are insoluble in water and most of the organic solvents.

#### Preparation of mono-hydrazine metal edta: $M_2(edta)(N_2H_4)_2(H_2O)_2$ where M=Cd or $UO_2$

An aqueous solution (30 mL) containing a mixture of edta (2.929 g, 0.1 mmol) and hydrazine hydrate (4 mL, 0.8 mmol) was slowly added with constant stirring to an aqueous solution (30 mL) of respective metal nitrate hydrates (0.2 mmol). The resulting clear solution was filtered and allowed to crystallize at room temperature. The crystalline complexes settled was collected after 24 h, washed with water and then with alcohol and dried in air. In case of uranium, the uranyl complex settled immediately was filtered, washed with water then with alcohol and dried in air.

### Physicochemical techniques

The composition of the complexes was determined by chemical analysis, Hydrazine content was determined by titrating against standard  $KIO_3$  ( $0.025 \text{ mol dm}^{-3}$ ) under Andrews conditions<sup>[18]</sup>, metal content were determined by titrating with EDTA ( $0.01 \text{ mol dm}^{-3}$ ) after decomposing the complexes with concentrated nitric acid<sup>[18]</sup>. IR spectra of the complexes in the region  $4000\text{--}400 \text{ cm}^{-1}$  were recorded on a Perkin-Elmer 597 spectrophotometer using KBr pellets, while the solid state absorption spectra were recorded on a shimadzu 160A/240A UV – vis spectrophotometer by dispersing the sample in nujol mull using  $BaSO_4$  as reference material. The magnetic susceptibility of the complexes was measured using a Gouy balance at room temperature mercury tetrathio cyanato cobaltate  $Hg[Co(NCS)_4]$  was used as the calibrant.

The x-ray powder diffractograms of the complexes

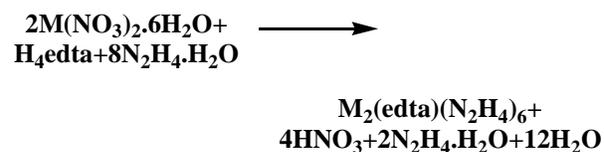
were recorded using a Philips x-ray diffractometer Model PW 1050/70 employing  $Cu\text{-}K_{\alpha}$  radiation and a nickel filter. The simultaneous TG-DTA experiments were carried out using a universal V4.2E TA Instrument version SDT Q600 V8.2 Build 100. Thermal analysis were carried out in air at the heating rate of  $10 \text{ }^{\circ}\text{C min}^{-1}$  using 2 - 3 mg of the samples. Platinum cups were employed as sample holders and alumina as reference.

### Antibacterial activity determination

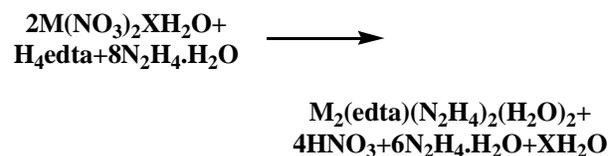
The test of antibacterial activity adopts a method by agar diffusion<sup>[19]</sup> using DMSO as the solvent. The antibacterial activity of the metal edta hydrazinate complexes was studied under two different concentrations. The culture medium (antibiotic medium) consisted of beef extract, albumins and agars. The culture medium, glass plates and filter paper disc of 5 mm diameters were sterilized for 1 hour at  $120 \text{ }^{\circ}\text{C}$ , the culture medium was transferred to glass plates and frozen at about  $37 \text{ }^{\circ}\text{C}$ . After that the bacterial strains were inoculated to the solid culture medium surface, the filter paper disc with  $10 \mu\text{L}$  samples were placed on the surface. They were allowed to incubate at  $37 \text{ }^{\circ}\text{C}$  for 18 hours. The inhibition zone around the disc was calculated as zone diameter in millimeters. Blank tests showed that DMSO solvent does not affect the antibacterial activity of the complexes<sup>[20]</sup>.

## RESULT AND DISCUSSION

The edta metal hydrazinates were prepared in aqueous medium by the reaction of corresponding metal nitrate hydrates, edta and hydrazine hydrate in 2:1:6 ratio or 2:1:8 ratio. The reaction can be represented as follows:



Where M=Co, Ni, or Zn



Where M=Cd or  $UO_2$ .

Our attempts to prepare manganese, copper and iron complexes are not successful. In the case of manganese no precipitate was formed, while in the case of copper,  $\text{Cu}^{2+}$  was reduced to copper metal in the presence of excess of hydrazine. However, in the case of iron, though the brown precipitate was formed, our analyses showed that it was iron hydroxide.

The formulae proposed are in good agreement with the analytical data presented in TABLE 1. All the complexes are stable in air, insoluble in water and common organic solvents. The insoluble nature of these complexes is in accordance with polymeric structure. However the cobalt complex on long standing undergoes air oxidation.

TABLE 1 : Analytical data

Compound	Empirical formula	Metal salt used (wt in g)	Mol Wt	Colour	Yield (%)	Hydrazine (%)		Metal (%)		Magnetic moment (BM)
						Found	Calcd.	Found	Calcd.	
$\text{Co}_2(\text{edta})(\text{N}_2\text{H}_4)_6$	$\text{Co}_2\text{C}_{10}\text{N}_{14}\text{O}_8\text{H}_{36}$	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.91)	598.35	Pink	75	33.01	32.09	19.00	19.69	5.1
$\text{Ni}_2(\text{edta})(\text{N}_2\text{H}_4)_6$	$\text{Ni}_2\text{C}_{10}\text{H}_{14}\text{O}_8\text{H}_{36}$	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.91)	597.87	Light Blue	80	29.70	32.20	20.00	19.63	3.2
$\text{Zn}_2(\text{edta})(\text{N}_2\text{H}_4)_6$	$\text{Zn}_2\text{C}_{10}\text{N}_{14}\text{O}_8\text{H}_{36}$	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.97)	611.26	Colorless	80	32.21	31.46	20.50	21.40	Diamagnetic
$\text{Cd}_2(\text{edta})(\text{N}_2\text{H}_4)_2(\text{H}_2\text{O})_2$	$\text{Cd}_2\text{C}_{10}\text{N}_6\text{O}_{10}\text{H}_{24}$	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (3.09)	613.15	Colorless	85	9.2	10.45	37.50	36.67	Diamagnetic
$(\text{UO}_2)_2(\text{edta})(\text{N}_2\text{H}_4)_2(\text{H}_2\text{O})_2$	$\text{U}_2\text{C}_{10}\text{N}_6\text{O}_{14}\text{H}_{24}$	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5.12)	931.39	Light yellow	85	10.02	10.15	51.00	51.11	Diamagnetic

### Magnetic properties

The room temperature magnetic moment of 5.2 BM for the Co(II) complexes and 3.1 BM for Ni(II) indicates a high spin octahedral environment for the metal ion<sup>[21,22]</sup>. As expected the zinc, cadmium and uranium complexes are diamagnetic.

### Electronic spectra

The electronic spectrum of Co(II) complex show a band at 20,500  $\text{cm}^{-1}$  which is due to  ${}^4\text{T}_{1g}(\text{F}) \longrightarrow {}^4\text{T}_{1g}(\text{P})$  transition. The nickel complex show two bands at 17,200 and 26,500  $\text{cm}^{-1}$  corresponding to  ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}(\text{P})$  d-d transitions respectively, which are characteristic of octahedral geometry<sup>[23]</sup>.

### Infrared spectra

The infrared spectra of the metal complexes are presented in the TABLE 2. The infrared spectra of all the complexes are similar except Cd and  $\text{UO}_2$  which shows a broad band at 3440 and 3445  $\text{cm}^{-1}$  for the O-H stretching of water molecules. The O-H band at higher frequency region and the absence of band at 850  $\text{cm}^{-1}$  clearly indicates these water molecules are not coordinated to the metal ion<sup>[24]</sup>. Invariably all the complexes show three sharp bands at 3170 to 3310  $\text{cm}^{-1}$  which are assigned for the N-

H stretching of the hydrazine molecules. The asymmetric and symmetric stretching frequencies of the carboxylate ions are seen at 1625 and 1420  $\text{cm}^{-1}$  respectively, with the  $\Delta\nu(\nu_{\text{asym}} - \nu_{\text{sym}})$  separation of 205  $\text{cm}^{-1}$  indicating the monodentate linkage of carboxylate ions in edta<sup>[25]</sup>. The N-N stretching frequency, in these complexes appears in the range 960-980  $\text{cm}^{-1}$  which is observed for the bidentate bridged hydrazine molecules<sup>[26]</sup>.

TABLE 2 : Infrared data

Co	Ni	Zn	Cd	$\text{UO}_2$	Assignments
-	-	-	3440	3445	O-H stretching
-	-	-	3323	3357	
1619	1627	1627	1623	1655	$\text{COO}_{\text{asy}}$
1423	1419	1420	1420	1382	$\text{COO}_{\text{sym}}$
(196)	(208)	(207)	(203)	(273)	$\nu_{\text{asy}}-\nu_{\text{sym}}$
967	971	975	959	960	N-N stretching

### Thermal studies

Thermal data of the complexes are given in TABLE 3. Such data not only corroborate the stoichiometric formulae, number of hydrazine and water molecules, but also reveal different intermediates and confirm metal oxide as the end products except the Zn compound  $\text{ZnCO}_3$ .

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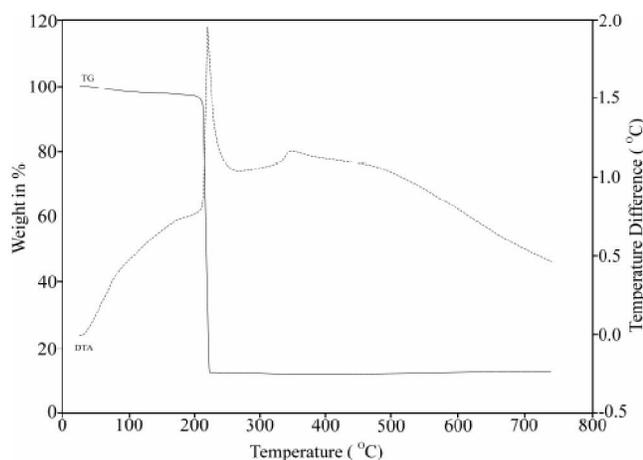
TABLE 3 : Thermal data

Compound	DTA Peak Temp./ °C	Temp. range./ °C	TG weight loss		Residue
			Found	Calcd.	
Co <sub>2</sub> (edta)(N <sub>2</sub> H <sub>4</sub> ) <sub>6</sub>	183(-)	50-210	5.00	5.36	Co <sub>2</sub> (edta)(N <sub>2</sub> H <sub>4</sub> ) <sub>5</sub>
	216(-,s)	210-225	73.00	72.28	Co <sub>2</sub> O <sub>3</sub>
Ni <sub>2</sub> (edta)(N <sub>2</sub> H <sub>4</sub> ) <sub>6</sub>	215(-)	40-220	5.00	5.36	Ni <sub>2</sub> (edta)(N <sub>2</sub> H <sub>4</sub> ) <sub>5</sub>
	237(-,s)	220-225	77.00	75.01	2NiO
Zn <sub>2</sub> (edta)(N <sub>2</sub> H <sub>4</sub> ) <sub>6</sub>	180(-)	160-220	10.00	10.49	Zn <sub>2</sub> (edta)(N <sub>2</sub> H <sub>4</sub> ) <sub>4</sub>
	285(-,s)	220-305	62.00	58.97	2ZnCO <sub>3</sub>
Cd <sub>2</sub> (edta)(N <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	50(+)	40-80	5.00	5.87	Cd <sub>2</sub> (edta)(N <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>
	150(-,b)	80-265	11.00	11.10	Cd <sub>2</sub> (edta)(N <sub>2</sub> H <sub>4</sub> )
	267(-,w)	265-270	25.00	24.82	2Cd(CH <sub>3</sub> COO) <sub>2</sub>
	330(-,w)	270-352	34.00	34.62	2CdC <sub>2</sub> O <sub>4</sub>
	403(-,s)	352-417	57.00	58.12	2CdO
(UO <sub>2</sub> ) <sub>2</sub> (edta)(N <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	80(+,b)	50-200	9.00	10.75	(UO <sub>2</sub> ) <sub>2</sub> (edta)
	150(-,b)				
	237(-,b)	200-374	70.00	70.87	2UO <sub>2</sub> CO <sub>3</sub>
	509(-,s)	374-545	55.00	57.89	2UO <sub>2</sub>

(-), exotherm; (+), endotherm; s-Sharp; b-Broad; w-Weak

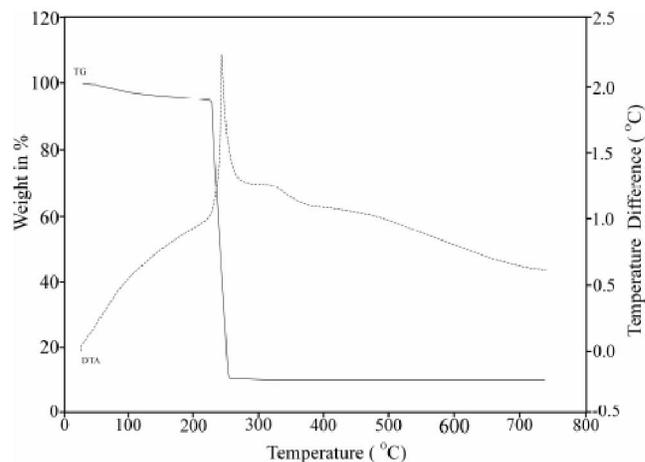
Co<sub>2</sub>(edta)(N<sub>2</sub>H<sub>4</sub>)<sub>6</sub>

The simultaneous TG-DTA curves (Figure 1) of this complexes show two step decomposition. In the first step, a molecule of hydrazine lost exothermically in the temperature range 50-210 °C. The intermediate formed is Co<sub>2</sub>(edta)(N<sub>2</sub>H<sub>4</sub>)<sub>5</sub>, which undergoes exothermic decomposition sharply in the range 210-225 °C to form Co<sub>2</sub>O<sub>3</sub> as the final residue.

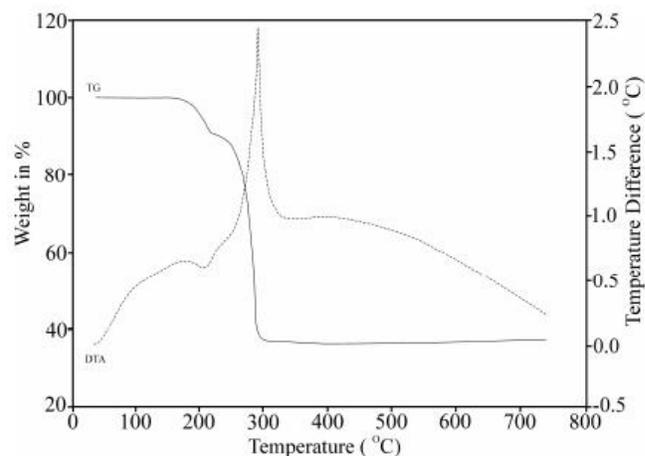
Figure 1 : TG-DTA of Co<sub>2</sub>(edta)(N<sub>2</sub>H<sub>4</sub>)<sub>6</sub>Ni<sub>2</sub>(edta)(N<sub>2</sub>H<sub>4</sub>)<sub>6</sub>

This complex shows two-step decomposition (Figure 2). In the first step one molecule of hydrazine lost

exothermically in the temperature range 40-270 °C to form Ni<sub>2</sub>(edta)(N<sub>2</sub>H<sub>4</sub>)<sub>5</sub> as an intermediate, which decomposes between 280-255 °C to form NiO as the end product.

Figure 2 : TG-DTA of Ni<sub>2</sub>(edta)(N<sub>2</sub>H<sub>4</sub>)<sub>6</sub>Zn<sub>2</sub>(edta)(N<sub>2</sub>H<sub>4</sub>)<sub>6</sub>

Zinc complex decompose initially at higher temperature range 160-220 °C as shown by TG curve (Figure 3) with the loss of two hydrazine molecule to give Zn<sub>2</sub>(edta)(N<sub>2</sub>H<sub>4</sub>)<sub>4</sub> as an intermediate. The DTA show broad exotherm centered at 180 °C. The weight loss observed is 10% which is in accordance with the calculated value the second stage of degradation takes place between 220-303 °C in one stage, continuously which is shown by the sharp exotherm at 285 °C to give ZnCO<sub>3</sub> as the residues.

Figure 3 : TG-DTA of Zn<sub>2</sub>(edta)(N<sub>2</sub>H<sub>4</sub>)<sub>6</sub>Cd<sub>2</sub>(edta)(N<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>

As expected the cadmium complex first undergoes

dehydration at low temperature and DTA shows a moderately sharp endotherm at 47 °C indicating the presence lattice water molecules (Figure 4). The anhydrous complex slowly dehydrates with the loss of one  $N_2H_4$  molecule in the temperature range 80-265 °C with the weight loss of 11%. The residue in the second stage is assigned as  $Cd_2(edta)(N_2H_4)$  on the basis of TG weight loss. Two broad exotherms are observed in DTA at 150 and 200 °C for the second stage. Further decomposition takes place in two stages, both exothermic with the peak temperature 267 and 330 °C to give  $Cd(CH_3COO)_2$  and  $Cd(C_2O_4)$  intermediates successively with the weight loss of 25% and 34%,  $CdO$  as the final product by exothermic and sharp decomposition. The peak temperature of the exotherm is 403 °C and the final degradation temperature is 417 °C.

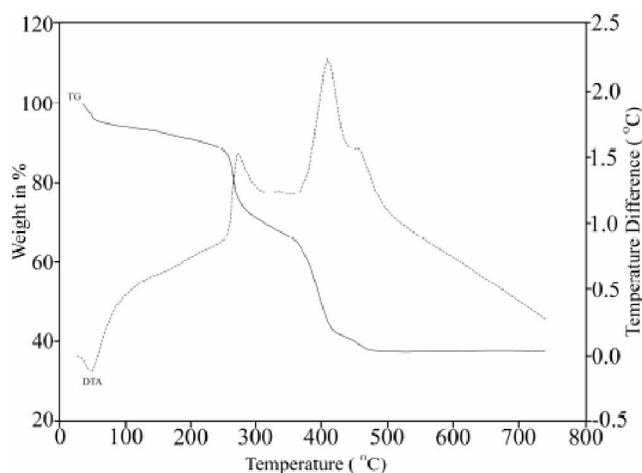


Figure 4 : TG-DTA of  $Cd_2(edta)(N_2H_4)_2(H_2O)_2$

#### $(UO_2)_2(edta)(N_2H_4)_2(H_2O)_2$

This complex, in the temperature range 50-200 °C, shows an endotherm and a broad exotherm for the loss of two water and two hydrazine molecules to give  $(UO_2)_2(edta)$  as an intermediate. This decomposes slowly in the wide temperature range, between 200 to 374 °C to give uranyl carbonate which at higher temperature gives  $UO_2$  as the final residue. The DTA shows a strong and sharp exotherm at 509 °C corresponding to the last stage (Figure 5).

Due to the continuous composition it is not possible to isolate the intermediates. However, the final products formed by the thermal degradation of the above complexes were confirmed by heating a known amount of the respective complexes in silica crucible at

the suitable temperature and the weight losses were determined. There are also in agreement with the expected values.

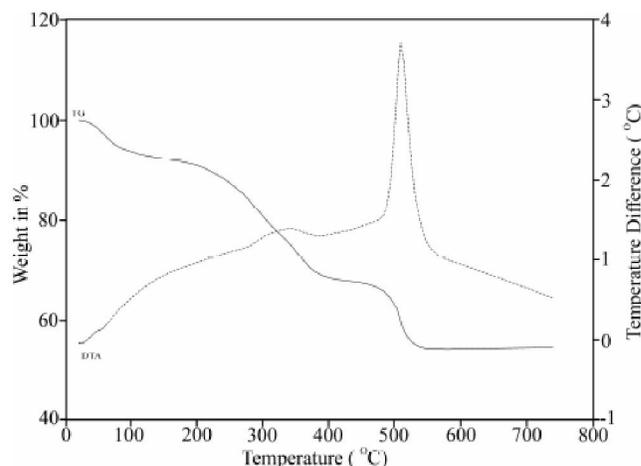


Figure 5 : TG-DTA of  $(UO_2)_2(edta)(N_2H_4)_2(H_2O)_2$

#### X-ray powder diffraction

X-ray diffraction data for the synthesized complexes are given in TABLE 4. The values of d-spacings and intensity are compared to ascertain isomorphism among the complexes. The tris-hydrazine complexes of Co and Ni show isomorphism. The zinc complexes also exhibit

TABLE 4 : X-ray powder data of  $M_2(edta)(N_2H_4)_6$  d-spacing in Å and relative intensity (in parenthesis)

COBALT	NICKLE	ZINC
6.91(75)	7.08(53)	7.03(100)
5.57(28)	5.87(74)	-
4.08(100)	4.08(100)	4.08(62)
3.99(41)	3.99(45)	3.95(45)
3.52(20)	3.53(16)	3.53(12)
3.49(24)	3.44(18)	3.44(20)
3.35(20)	3.36(36)	3.35(45)
2.86(64)	2.88(26)	2.84(54)
2.80(24)	2.82(67)	2.80(46)
2.67(40)	2.66(31)	2.64(10)
2.57(15)	2.59(39)	2.59(30)
2.36(12)	2.36(9)	2.36(12)
2.22(18)	2.23(10)	2.22(18)
2.20 (12)	2.20(32)	2.19(38)
1.97(26)	2.01(16)	1.97(29)
1.80(9)	1.80(9)	1.80(5)
1.77(7)	1.78(11)	1.77(5)
1.64(9)	1.63(5)	1.63(5)
1.56(8)	1.56(9)	1.56(9)

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isomorphism. The X-ray patterns of Co, Ni and Zn complexes are shown in Figures 6-8.

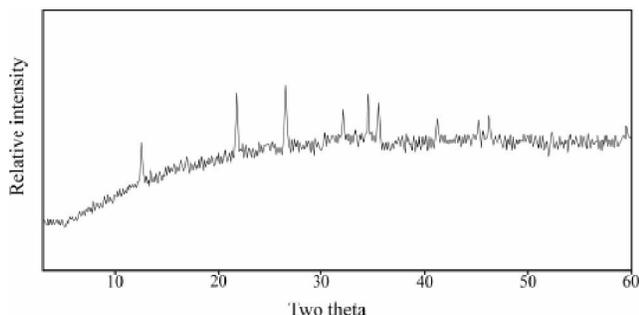


Figure 6: X-ray powder diffraction pattern of  $\text{Co}_2(\text{edta})(\text{N}_2\text{H}_4)_6$

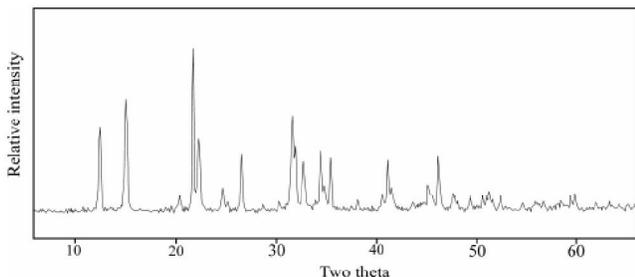


Figure 7: X-ray powder diffraction pattern of  $\text{Ni}_2(\text{edta})(\text{N}_2\text{H}_4)_6$

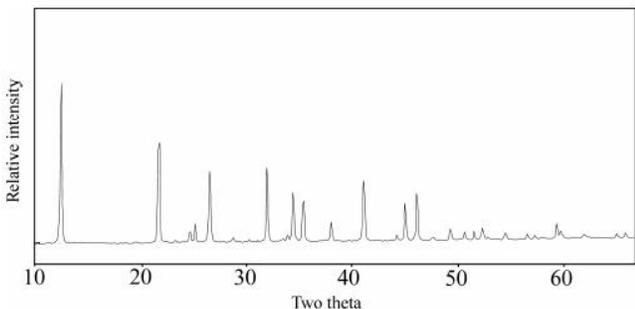


Figure 8: X-ray powder diffraction pattern of  $\text{Zn}_2(\text{edta})(\text{N}_2\text{H}_4)_6$

### Antibacterial studies

The bacterial cultures used for screening antibacterial activity of the complexes are *Staphylococcus Aureus*, *Bacillus*, *Klebsiella Pneumoniae* and *Pseudomonas Aeruginosa*. From the data in the TABLE 5 it is observed that all the complexes exhibited antibacterial activity against tested bacterial culture. The antibacterial activities of all the complexes increase with concentration. The increase in antibacterial activity is due to faster diffusion of metal complexes as a whole through the cell membrane or due to the combined activity effect of the metal and ligand. The test indicates that the antibacterial activity lies not only in the composition and its concentration of the compound but also the type of bacteria.

TABLE 5 : Antibacterial activities of the complexes (Diameter zone of inhibition in mm)

Complex Formula	BACTERIAL CULTURES							
	Staphylococcus Aureus		Bacillus		Klebsiella Pneumoniae		Pseudomonas Aeruginosa	
	C <sub>1</sub>	C <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>
$\text{Co}_2(\text{edta})(\text{N}_2\text{H}_4)_6$	8	11	6	8	6	9	-	-
$\text{Ni}_2(\text{edta})(\text{N}_2\text{H}_4)_6$	9	11	10	12	6	7	7	8
$\text{Zn}_2(\text{edta})(\text{N}_2\text{H}_4)_6$	8	10	9	11	8	9	7	8
$\text{Cd}_2(\text{edta})(\text{N}_2\text{H}_4)_2(\text{H}_2\text{O})_2$	9	10	8	11	8	10	6	7
$(\text{UO}_2)_2(\text{edta})(\text{N}_2\text{H}_4)_2(\text{H}_2\text{O})_2$	9	11	9	11	8	9	6	7

Here, C<sub>1</sub>: 500ppm; C<sub>2</sub>: 800ppm

### CONCLUSION

All the complexes form the corresponding metal oxides at low temperatures around 300-500 °C. The edta complexes undergo multi-step decomposition to give respective metal oxide as the final residue except Co and Ni which undergo two step decomposition to give the metal oxide. All the complexes are stable except  $\text{Co}_2(\text{edta})(\text{N}_2\text{H}_4)_6$  which on long standing undergoes slow decomposition under atmospheric condition. All the metal complexes were prepared by the aqueous reaction of the respective metal nitrate hydrate, edta, hydrazine and characterized by spectral and analytical data. These data indicated that the complexes are of high-spin octahedral variety. IR spectra of the edta complexes indicated that both carboxylate ions and hydrazine molecules coordinated to the metal ions in the bridging fashion.

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