



## Synthesis, spectral, thermal and X-ray diffraction studies on bis-hydrazine metal and mixed metal iminodiacetates

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### ABSTRACT

Bis-hydrazine metal iminodiacetates have been synthesized by the aqueous reaction between respective metal nitrate hydrate and aqueous solution containing a mixture of iminodiacetic acid and hydrazine hydrate in an appropriate ratio. The compositions of the complexes were assigned on the basis of chemical analyses, magnetic moments, electronic absorption spectra, infrared spectra, thermal analyses and X-ray powder diffraction and found to be  $MNH(CH_2COO)_2(N_2H_2)_2$  where  $M = Co, Ni$  or  $Zn$ . Infrared spectra indicate the presence of both bridging bidentate and monodentate hydrazine moieties and monodentate nature of carboxylate ions. The magnetic moments and electronic absorption spectra suggest a high-spin octahedral geometry of cobalt and nickel complexes. The simultaneous TG-DTA analyses reveal that all these complexes undergo two stage decompositions to give respective metal oxide as the final residue. The X-ray powder diffraction patterns are almost super-imposable indicating the isomorphism among these compounds. The hydrazine mixed metal complexes,  $[M_{1/3}Co_{2/3}NH(CH_2COO)_2(N_2H_4)_2]$  where  $M = Ni$  or  $Zn$  have been prepared by the similar method adopted for the simple metal complexes by using a mixture of corresponding metal nitrate hydrate and cobalt nitrate hydrate instead of metal nitrate hydrate. The composition of the complexes were determined by analytical, spectral and XRD data. These complexes on thermal degradation yield respective metal cobaltites, the formation of compounds which were confirmed by IR spectra and XRD data.

**Key words:** bis- hydrazine, iminodiacetic acid, octahedral, bridged bidentate, metal cobaltities.

### INTRODUCTION

Aminocarboxylic acids are well known for their chelating ability and are expected to form stable complexes with transition metals. Depending on the nature, number of carboxylic acid groups and number of amino groups, these aminocarboxylic acids form complexes with stable five or six membered rings during chelation. Due to the less electro negativity, the nitrogen atoms always coordinate to the central metal ions while carboxylate ions may or may not coordinate which depends on the charge and coordination number of the metal ions. An aminocarboxylic acid shows different coordination behavior and thermal properties in the presence of hydrazine as a primary ligand.

Metal aminocarboxylates are very common and several such compounds were reported [1-5]. Among the aminocarboxylates primary, secondary and tertiary amino groups behave differently during complexation. For the past two decades hydrazine complexes of metal aminocarboxylates and metal polyaminopolycarboxylates have been thoroughly investigated and their spectral and thermal properties have been reported [6-10]. However, hydrazine complexes with iminopolycarboxylates such as iminodiacetates, diiminodiacetates are not known to the literature. It is quite interesting to study their coordination behavior and thermal reactivity. Furthermore, the corresponding

mixed metal complexes are expected to show interesting thermal behavior to yield mixed metal oxides, metal cobaltites with high purity and catalytic activity. Hence in this paper, we wish to report the synthesis, characterization, spectral properties and thermal reactivity of hydrazine complexes of metal and mixed metal iminodiacetates.

## EXPERIMENTAL SECTION

### 2.1. Materials

All the chemicals used were of AR grade. Required chemicals were purchased from Sigma Aldrich. The preparation and analyses were carried out using double distilled water and the solvents were distilled before use.

### 2.2. Preparation of bis-hydrazine metal iminodiacetates

An aqueous solution (30 mL) containing a mixture of iminodiacetic acid (0.01 mol, 1.33 g) and hydrazine hydrate (0.04 mol, 2 mL) was added to an aqueous solution (30 mL) of respective metal nitrate hydrate (0.01 mol). The clear solution thus obtained after filtration, on long standing for about 2-5 days resulting in the precipitation of crystalline complexes. The precipitate was filtered, washed with water then with alcohol and dried in air.

### 2.3. Preparation of bis-hydrazine mixed metal iminodiacetate

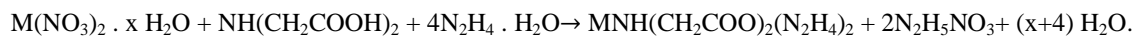
Bis-hydrazine mixed metal iminodiacetate complexes were prepared by adding an aqueous solution (30 mL) containing iminodiacetic acid (0.03 mol, 3.99 g) and hydrazine hydrate (0.12 mol, 6 mL) was added slowly to an aqueous solution (50 mL) containing a mixture of cobalt nitrate hexahydrate (0.02 mol) and respective metal nitrates (0.01 mol) with stirring. The resulting solution was filtered and allowed to crystallize at room temperature. The complexes formed were filtered, washed with water then with alcohol and dried in air.

### 2.4. Physico-Chemical studies

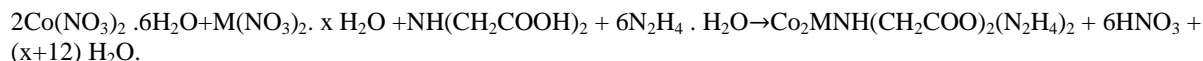
The hydrazine content percent in the complexes were determined by Andrew's method [11]. The metal content in all the complexes were determined by EDTA complexometric titration using Na<sub>2</sub>H<sub>2</sub>EDTA and Eriochrome black-T indicator. The metal content in the mixed metal complexes were determined using  $\alpha$ -nitroso  $\beta$ -naphthol after decomposing a known amount of sample with concentrated nitric acid and evaporating the clear solution to dryness. The filtrate during the separations containing Ni or Zn was treated with chloroform to remove excess  $\alpha$ -nitroso  $\beta$ -naphthol and the metal ions were estimated by titration with standard Na<sub>2</sub>H<sub>2</sub>EDTA solution [12]. The magnetic moments of the complex was measured at room temperature using Gouy balance. The solid state electronic absorption spectra of the complexes in Nujol mull in 200-800 nm range were recorded on a Varian 5000 UV-visible spectrophotometer. The IR spectra of metal complexes were recorded on a Perkin-Elmer 597/1650 spectrophotometer in 4000-400 cm<sup>-1</sup> range using KBr discs. The simultaneous TG-DTA of the complexes in air was carried out using STA 1500 thermal analyzer. The heating rate was 10 °C/min and platinum cups were used as sample holders. X-ray powder diffraction pattern of the complexes and oxides were performed by Bruker D8 Focus diffractometer.

## RESULTS AND DISCUSSION

Bis-hydrazine metal iminodiacetate complexes were obtained by the aqueous reaction between respective metal nitrates and a aqueous mixture of aqueous iminodiacetic acid and hydrazine hydrate. The mixed metal iminodiacetate were obtained by similar procedure using a mixture of metal nitrate and cobalt nitrate. The chemical reaction for the formation of these complexes is represented as follows.



Where M = Co, Ni or Zn.



Where M = Ni or Zn.

The compositions of the complexes were assigned on the basis of hydrazine and metal analyses. The analytical data of the complexes are given in Table 1.

Table 1. Analytical data of the complexes

S.No.	Complex [Empirical formula]	M.W.	Physical appearance	Elemental analysis		% of Co (Found) (Calc.)	Magnetic moment $\mu_{\text{eff}}$ (BM)
				N <sub>2</sub> H <sub>4</sub> % (Found) (Calc.)	M % (Found) (Calc.)		
1	CoNH(CH <sub>2</sub> COO) <sub>2</sub> (N <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> [Co C <sub>4</sub> H <sub>13</sub> N <sub>5</sub> O <sub>4</sub> ]	254.11	Rosy red	24.50 25.18	23.40 23.19	–	5.1
2	NiNH(CH <sub>2</sub> COO) <sub>2</sub> (N <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> [Ni C <sub>4</sub> H <sub>13</sub> N <sub>5</sub> O <sub>4</sub> ]	253.87	Light blue	25.40 25.21	21.90 23.12	–	2.9
3	ZnNH(CH <sub>2</sub> COO) <sub>2</sub> (N <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> [Zn C <sub>4</sub> H <sub>13</sub> N <sub>5</sub> O <sub>4</sub> ]	260.56	Colorless	24.00 24.56	24.80 25.09	–	diamagnetic
4	Co <sub>2/3</sub> Ni <sub>1/3</sub> NH(CH <sub>2</sub> COO) <sub>2</sub> (N <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> [Co <sub>2/3</sub> Ni <sub>1/3</sub> C <sub>4</sub> H <sub>13</sub> N <sub>5</sub> O <sub>4</sub> ]	254.03	Pink amorphous powder	25.04 25.19	7.64 7.70	14.96 15.45	–
5	Co <sub>2/3</sub> Zn <sub>1/3</sub> NH(CH <sub>2</sub> COO) <sub>2</sub> (N <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> [Co <sub>2/3</sub> Zn <sub>1/3</sub> C <sub>4</sub> H <sub>13</sub> N <sub>5</sub> O <sub>4</sub> ]	256.26	Pink amorphous powder	25.08 24.97	8.44 8.50	15.22 15.33	–

### 3.1. Magnetic Moments and Electronic spectra

The room temperature magnetic moment of the cobalt complex is found to be 5.1 BM and that of nickel complex is 2.9 BM. These values clearly suggest the high-spin nature of the metal ions. As expected zinc complex is diamagnetic. The electronic spectrum of the cobalt complex show a band at 20,900 cm<sup>-1</sup> which is assigned to <sup>4</sup>T<sub>1g(F)</sub> → <sup>4</sup>T<sub>1g(P)</sub> transition. The nickel complex shows two bands at 27,100 and 17,600 cm<sup>-1</sup> which are attributed to <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g(F)</sub> and <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g(P)</sub> transitions respectively. These transitions suggest an octahedral geometry around the cobalt and nickel ions [13].

### 3.2. Infrared Spectra

The bis-hydrazine metal and mixed metal complexes shows similar and almost super-imposable infrared spectra. All the complexes show three bands in the region 3100–3350 cm<sup>-1</sup> which are ascribable for the N – H stretching of hydrazine and iminodiacetate ion. The  $\nu_{\text{asy}}$  and  $\nu_{\text{sym}}$  stretching of the carboxylate ions are observed in the region 1600–1630 cm<sup>-1</sup> and 1400–1420 cm<sup>-1</sup> respectively with the  $\Delta\nu$  separation of 200–210 cm<sup>-1</sup> which indicates the monodentate coordination behavior of carboxylate ions [14]. The N – N stretching of hydrazine molecule is observed at 960–970 cm<sup>-1</sup> and 920 cm<sup>-1</sup> which clearly indicates the presence of bridged both bidentate and monodentate hydrazine molecules [15]. The IR spectra of nickel complex and cobalt–zinc mixed metal complex are shown in Fig. 1 and 2 respectively.

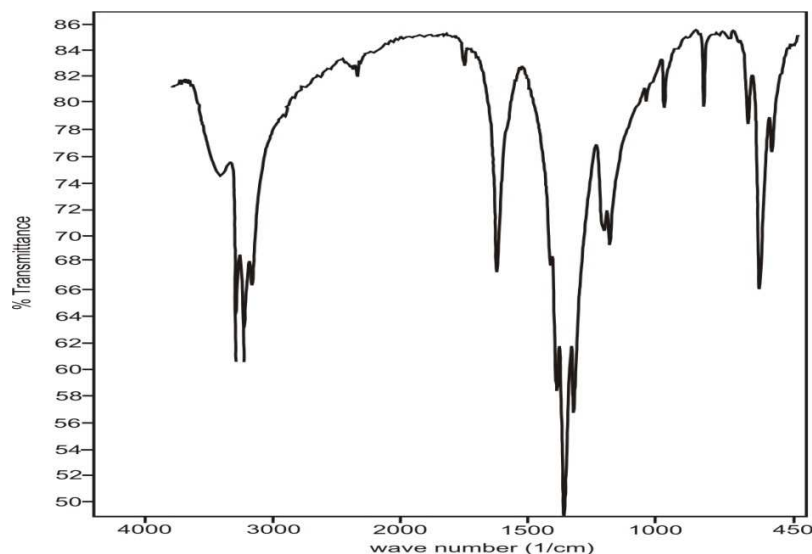


Fig. 1. IR Spectrum of NiNH(CH<sub>2</sub>COO)<sub>2</sub>(N<sub>2</sub>H<sub>4</sub>)<sub>2</sub>

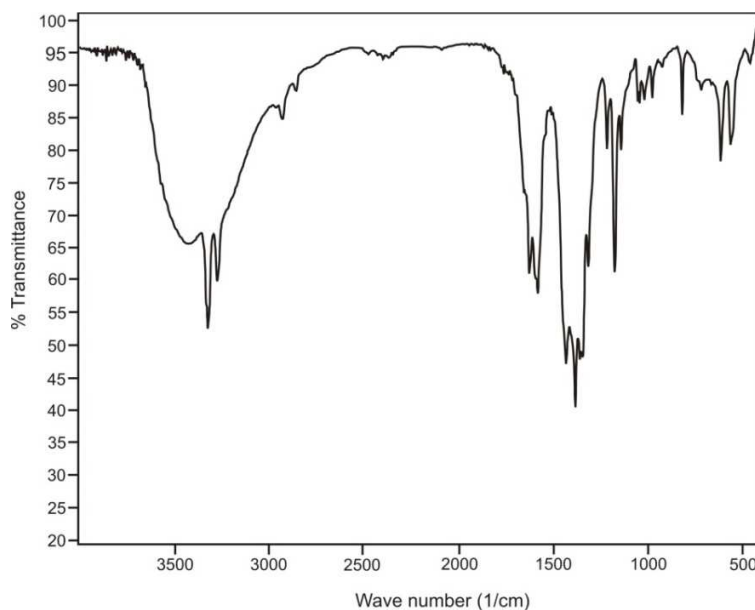


Fig. 2. IR Spectrum of  $\text{Co}_{2/3}\text{Zn}_{1/3}\text{NH}(\text{CH}_2\text{COO})_2(\text{N}_2\text{H}_4)_2$

### 3.3. Thermal Degradation

#### 3.3.1. Thermal degradation of bis-hydrazine cobalt iminodiacetate

This complex shows two steps decomposition. In the first stage one hydrazine molecule is removed at the temperature range 222-300 °C and the intermediate mono hydrazine cobalt iminodiacetate,  $\text{CoNH}(\text{CH}_2\text{COO})_2(\text{N}_2\text{H}_4)$  undergoes continuous degradation in the temperature range 300-400 °C with both dehydrazination and ligand pyrolysis to give  $\text{Co}_2\text{O}_3$  as the residue. The DTA shows two sharp exotherm for the two stages at 280 and 345 °C respectively. The simultaneous TG-DTA of the cobalt complex is shown in Fig. 3 as representative model.

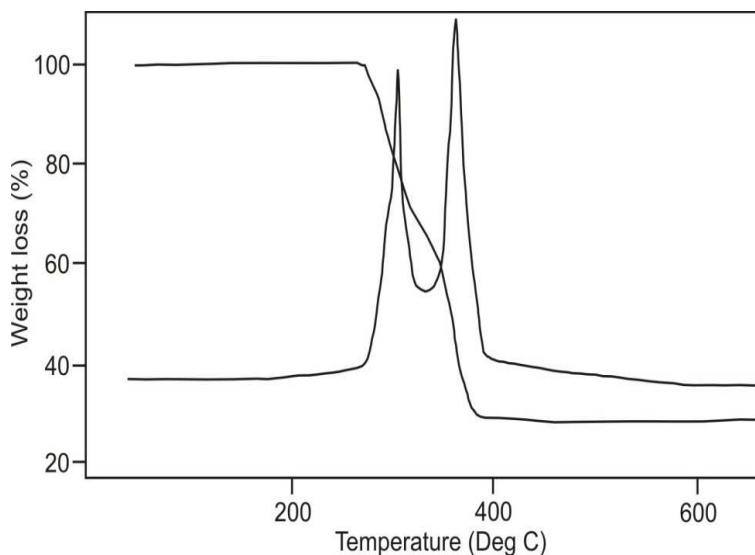


Fig. 3. Simultaneous TG-DTA of  $\text{CoNH}(\text{CH}_2\text{COO})_2(\text{N}_2\text{H}_4)_2$

#### 3.3.2. Thermal degradation of bis-hydrazine nickel iminodiacetate

The nickel complex also shows two step decompositions. However, the temperature ranges are 280-320 °C and 320-400 °C and NiO is formed similar to the cobalt complex. The DTA of nickel complex also shows two sharp exotherm at 300 and 360 °C .

### 3.3.3. Thermal degradation of bis-hydrazine zinc iminodiacetate

The zinc complex undergoes decomposition in the wide temperature range between 200-600 °C, the DTA shows two broad exotherm at 320 and 500 °C and ZnO is formed as the final residue. The TG-DTA data of the complexes are summarized in Table 2.

Table 2. Simultaneous TG-DTA analysis data

S.No.	compound	stage	DTA peak Temp. (°C)	TG Temp. range (°C)	Weight loss (Found) (Calc.)	Residue
1	CoNH(CH <sub>2</sub> COO) <sub>2</sub> (N <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	I	280 (exo)	222-300	13.00 12.50	CoNH(CH <sub>2</sub> COO) <sub>2</sub> (N <sub>2</sub> H <sub>4</sub> )
		II	345 (exo)	300-400	70.00 70.74	Co <sub>2</sub> O <sub>3</sub>
2	NiNH(CH <sub>2</sub> COO) <sub>2</sub> (N <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	I	300 (exo)	280-320	25.00 25.03	Ni NH(CH <sub>2</sub> COO) <sub>2</sub>
		II	360 (exo)	320-400	68.00 70.80	NiO
3	ZnNH(CH <sub>2</sub> COO) <sub>2</sub> (N <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	I	320 (exo)	200-300	22.00 24.40	Zn NH(CH <sub>2</sub> COO) <sub>2</sub>
		II	500 (exo)	200-600	68.00 69.00	ZnO

exo - exotherm

### 3.4. X-ray powder diffraction

The X-ray powder diffraction patterns of the metal complexes and mixed metal complexes were recorded to understand the isomorphism among the complexes. The pattern for the complexes is found to be super-imposable indicating the isomorphism among the three complexes. The X-ray powder diffraction pattern of the nickel complex is shown in Fig. 4. The X-ray powder diffraction data for the complexes are given in Table 3.

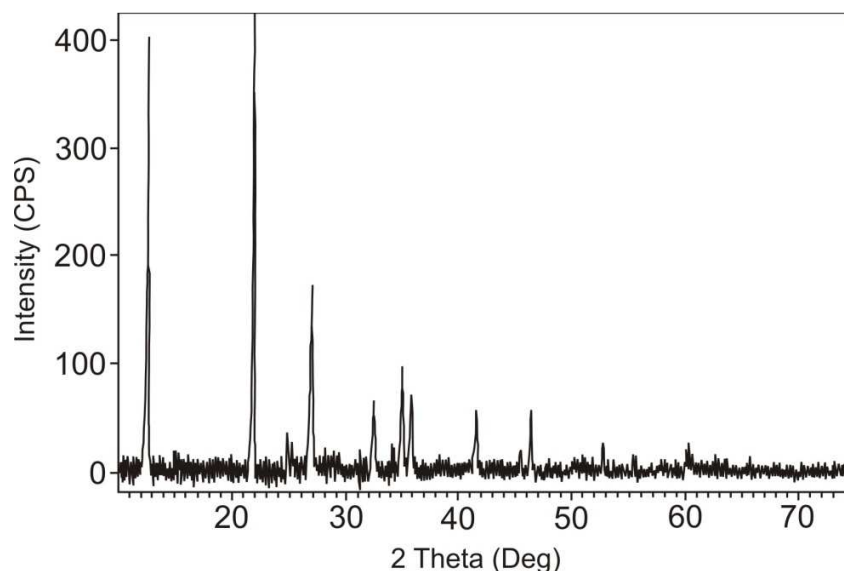


Fig. 4. X-ray powder diffraction pattern of Ni NH(CH<sub>2</sub>COO)<sub>2</sub> (N<sub>2</sub>H<sub>4</sub>)<sub>2</sub>

### 3.5. Metal cobaltites

The metal cobaltites were prepared by heating the respective mixed metal complexes in a pre heated silica crucible at 400 °C for about 10 minutes. The infrared spectra and X-ray powder patterns were recorded to confirm the formation of metal cobaltites. The powder patterns are found to be identical with the standards which clearly reveal the formation of desired cobaltites [16]. The patterns are however very weak and broad indicates the amorphous nature of the cobaltites. The X-ray powder diffraction pattern of the NiCo<sub>2</sub>O<sub>4</sub> is given in Fig. 5.

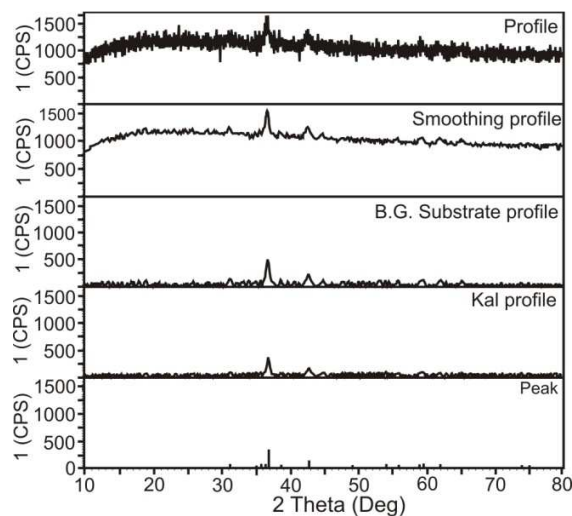
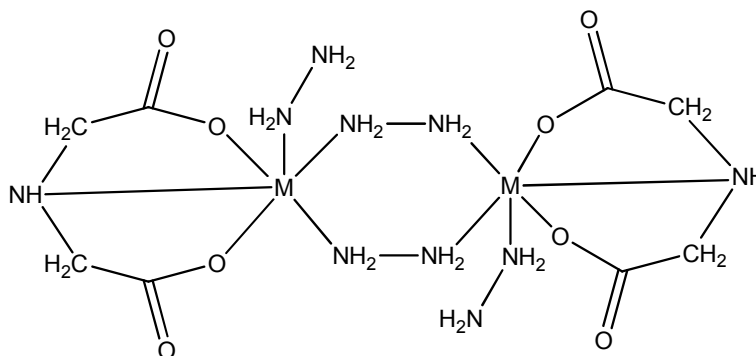
Fig. 5. X-ray powder diffraction pattern of  $\text{NiCo}_2\text{O}_4$ 

Table 3. X-ray powder diffraction data - d spacing in Å and relative intensity in percentage

$\text{CoNH}(\text{CH}_2\text{COO})_2(\text{N}_2\text{H}_4)_2$		$\text{NiNH}(\text{CH}_2\text{COO})_2(\text{N}_2\text{H}_4)_2$		$\text{ZnNH}(\text{CH}_2\text{COO})_2(\text{N}_2\text{H}_4)_2$	
d value (Å)	Relative intensity (%)	d value (Å)	Relative intensity (%)	d value (Å)	Relative intensity (%)
7.16	70	7.05	90	6.99	85
3.98	100	4.07	100	3.99	100
3.62	10	3.58	5	3.56	15
3.34	42	3.31	36	3.33	48
2.77	20	2.76	14	2.75	25
2.62	18	2.57	20	2.56	20
2.49	16	2.51	15	2.50	18
2.15	10	2.17	9	2.18	12
1.98	5	1.99	3	1.98	8
1.96	12	1.96	11	1.97	10
1.74	7	1.73	4	1.73	8
1.53	4	1.54	3	1.54	3

### CONCLUSION

Bis-hydrazine metal iminodiacetate complexes  $\text{MNH}(\text{CH}_2\text{COO})_2(\text{N}_2\text{H}_4)_2$  where  $\text{M} = \text{Co}, \text{Ni}$  or  $\text{Zn}$  and mixed metal complexes have been successfully prepared. The infrared spectrum of bis-hydrazine metal and mixed metals indicate the hydrazine acts as a bridged bidentate ligand and acid coordinate through monodentate carboxylate ions. The magnetic moment and the electronic spectra of the complex show that these are of high-spin octahedral geometry. Based on the analytical and spectral studies it is possible to suggest octahedral structure around metal ion with bridged bidentate iminodiacetate ions and bridged bidentate hydrazine molecules. However, the strong chelating nature of iminodiacetate ions which is expected to act as tridentates chelating ligand and hence the more probable structure is given as follows.



This structure is further supported by thermal studies which suggest the presence of two types of hydrazine molecules. The IR spectrum is also in favor of this structure with two bands for N – N stretching at 920 and 970 cm<sup>-1</sup> for the monodentate as well as bridged bidentate hydrazine molecules.

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