

## Complexes of Cu(II), Ni(II) and Co(II) with isophthalic dihydrazide

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**Abstract.** Complexes of isophthalic dihydrazide (IPZ) of the type  $MCl_2(IPZ) \cdot H_2O$  [ $M = Cu(II), Ni(II), Co(II)$ ] and  $MSO_4(IPZ) \cdot H_2O$  [ $M = Cu(II), Ni(II)$ ] have been prepared and characterised from elemental analysis, magnetic moment, visible, IR, and ESR spectra. Based on these data a polymeric octahedral structure has been assigned to  $MCl_2(IPZ) \cdot H_2O$  complexes and sulphate bridged four coordinate polymeric structure for  $MSO_4(IPZ) \cdot H_2O$  complexes. Thermogravimetric studies of these complexes show that the thermal stability decreases in the order  $Ni(II) > Co(II) > Cu(II)$ .

**Keywords.** Isophthalic dihydrazide ; metal chloride complexes; metal sulphate complexes.

### 1. Introduction

Benzoyl hydrazide forms complexes with transition (Aggarwal and Narang 1976) and non-transition metals (Aggarwal and Bahadur 1969 ; Aggarwal and Singh 1969) where it is observed that this ligand coordinates through both  $C=O$

$$\begin{array}{c} O \\ || \\ -C-NH-NH_2 \end{array}$$
and  $-NH_2$  of the  $-C-NH-NH_2$  groups keeping the secondary amino group undisturbed. In metal complexes of Co(II), Ni(II) and Cu(II) with oxalic malonic and terephthalic dihydrazides we have noticed (Kumbhar and Sadasivan 1976)

$$\begin{array}{c} O \\ || \\ -C-NH-NH_2 \end{array}$$
that these ligands function as bidentate and different  $-C-NH-NH_2$  groups of the same ligand coordinate to different metal centres resulting in the formation of polymeric complexes. Due to sterically unfavourable positions of hydrazide groups on benzene ring to form chelates when ligand is bifunctional, isophthalic dihydrazide (IPZ) is expected to form polynuclear complexes with metal salts containing both Metal-Nitrogen and Metal-Oxygen bonds simultaneously. In this paper synthesis and characterization of some metal complexes of isophthalic dihydrazide with  $MCl_2$  [ $M = Cu(II), Ni(II)$  and  $Co(II)$ ] and  $MSO_4$  [ $M = Cu(II)$  and  $Ni(II)$ ] are reported. Thermogravimetric studies of these complexes have also been carried out. The preliminary data on the subject have already been published elsewhere (Kumbhar 1980).

## 2. Experimental

Isophthalic acid dihydrazide was synthesised as described in the literature from diethyl isophthalate [M.P. 221° C (Obs), 220° C (Lit)], (Voloviskii and Knorozova 1964). Diethyl isophthalate was prepared after Majumdar and Sharma (1978). Syntheses of metal complexes were carried out by adding hot aqueous solution of ligand to alcoholic solutions of respective metal salts in the molar ratio 1 : 1. The coloured complexes which separated immediately were suction filtered, washed with water, alcohol and ether successively and air-dried.

IR spectra in nujol mull were recorded on Perkin Elmer Spectrophotometer Model 457 using KBr plates. Electronic spectra were obtained in the solid state using nujol mull on Systronics Spectrocolorimeter-103. Magnetic susceptibilities were determined at room temperature by Gouy method using  $\text{HgCo}(\text{CNS})_4$  as calibrant. ESR spectra were recorded on Varian Microwave Spectrometer in the x-band region (9.1 GHz) using DPPH as internal standard. Thermogravimetric study was carried out using MOM-BUDAPEST Model by heating the samples at a rate of 10° C per minute.

## 3. Results and discussions

### 3.1. Physical properties of complexes

The elemental analysis and physical properties of the complexes are listed in table 1. The complexes are quite stable in air. They are insoluble in common organic solvents and water. However, they decompose in mineral acids and are sparingly soluble in DMF and pyridine. Molecular weights of these complexes could not be measured as they are insoluble in suitable solvents. Elemental analysis leads to the stoichiometry  $\text{MCl}_2(\text{IPZ}) \cdot \text{H}_2\text{O}$  [M = Cu(II), Ni(II) and Co(II)] and  $\text{MSO}_4(\text{IPZ}) \cdot \text{H}_2\text{O}$  [M = Cu(II) and Ni(II)] for the complexes. The association of one water molecule is confirmed both from IR spectra and thermogravimetric data.

Table 1. Analytical data and physical properties of the complexes.

Sl. No.	Compound	Colour	% M		% Cl/S		$\mu_{\text{eff}}$ BM	g values
			Found	Cal.	Found	Cal.		
1.	$\text{CuCl}_2(\text{IPZ}) \cdot \text{H}_2\text{O}$	Green	18.00	18.34	19.90	20.46	2.00	2.19
2.	$\text{NiCl}_2(\text{IPZ}) \cdot \text{H}_2\text{O}$	Light blue	16.90	17.20	21.00	20.76	2.82	2.18
3.	$\text{CoCl}_2(\text{IPZ}) \cdot \text{H}_2\text{O}$	Pink	16.90	17.24	19.90	20.73	4.42	..
4.	$\text{CuSO}_4(\text{IPZ}) \cdot \text{H}_2\text{O}$	Blue	17.00	17.10	8.20	8.61	1.74	2.16
5.	$\text{NiSO}_4(\text{IPZ}) \cdot \text{H}_2\text{O}$	Light blue	15.90	16.01	8.22	8.53	2.98	2.18

Satisfactory carbon and hydrogen analysis was obtained for isophthalic dihydrazide.

### 3.2. Spectral and magnetic moment results

The broad band present in all the complexes around  $3400\text{ cm}^{-1}$  is due to  $\nu(\text{O-H})$ , which disappears from the spectra of dehydrated complexes. Weight loss equivalent to one water molecule is also evident in the TG and DTA curves at  $\approx 110^\circ\text{C}$ . Thus the presence of free water molecule is indicated. Coordinated water would have lost at relatively higher temperatures. The  $\nu\text{-N-H}$  frequencies are lower by  $50\text{-}100\text{ cm}^{-1}$  as compared to their respective positions in the parent ligand. The  $\nu\text{-C=O}$  is also shifted to lower region in the complexes by  $35\text{-}40\text{ cm}^{-1}$ . The shift to lower wave numbers of the amino and carbonyl vibration bands in all the complexes is a clear indication of the involvement of both  $\text{-NH}_2$  and  $\text{>C=O}$  in coordination. The possibility of enol form is not indicated in the IR spectra of the complexes. The new strong band appearing in the region  $1200\text{-}1230\text{ cm}^{-1}$  has been assigned to  $\nu(\text{C-O})$  (Aggarwal *et al* 1976). The medium to weak band in the region  $550\text{-}600\text{ cm}^{-1}$  is assigned to  $\nu\text{-M-O}$  following Adams (1967) who has shown that  $\nu\text{-M-O}$  stretching frequency in the metal carbonyl complexes occurs around  $600\text{ cm}^{-1}$ . It is observed that  $\nu\text{-M-O}$  is higher for  $\text{MSO}_4$  complexes than for  $\text{MCl}_2$  complexes.

Electronic spectra of  $\text{MCl}_2$  complexes give evidence for distorted octahedral symmetry around metal centre. Thus  $\text{CuCl}_2$  complex shows broad bands around  $640\text{ nm}$  and  $560\text{ nm}$  which are characteristic bands for octahedral environment around  $\text{Cu(II)}$  (Billing and Underhill 1968; Mahapatra and Rama Rao 1971).  $\text{Ni(II)}$  complex shows broad bands at  $660\text{ nm}$  and  $580\text{ nm}$  and weak bands at  $520\text{ nm}$  and  $490\text{ nm}$ . Manch and Fernelius (1961) have also observed such bands for octahedral  $\text{Ni(II)}$  in the region  $700\text{-}350\text{ nm}$ .  $\text{CoCl}_2$  complex shows broad bands at  $650\text{ nm}$ ,  $625\text{ nm}$  and  $505\text{ nm}$  which are characteristic bands for octahedral environment around  $\text{Co(II)}$  ion (Aggarwal *et al* 1976). Magnetic moment values (table 1) of the complexes of  $\text{CuCl}_2$  ( $2.00\text{ B.M.}$ ),  $\text{NiCl}_2$  ( $2.82\text{ B.M.}$ ) and  $\text{CoCl}_2$  ( $4.42\text{ B.M.}$ ) show one, two and three unpaired electrons respectively and are well within the range required for octahedral environment around metal centre (Figgis and Lewis 1960).

The average 'g' value for  $\text{CuCl}_2$  complex ( $g = 2.19$ ) calculated from ESR spectra of polycrystalline powder samples is comparable to those reported for  $\text{Cu(II)}$  complexes with octahedral symmetry (Sadasivan and Arora 1976). Similarly 'g' value for  $\text{NiCl}_2$  complex ( $g = 2.18$ ) is also consistent with those observed for  $\text{Ni(II)}$  complexes having octahedral symmetry (Arora and Kumbhar 1977).

Thus in the  $\text{MCl}_2 \cdot \text{L} \cdot \text{H}_2\text{O}$  complexes the stoichiometry and bidentate nature of ligand suggest a polymeric structure as shown in figure 1a. The stoichiometry and insolubility of the compounds in common organic solvents support this contention.

Although electronic spectra for  $\text{CuSO}_4(\text{IPZ}) \cdot \text{H}_2\text{O}$  complex exhibit broad band at  $550\text{ nm}$  consistent with tetragonally distorted octahedral structure, the effective magnetic moment ( $1.74\text{ B.M.}$ ) value is comparable to the values reported for square planar and tetrahedral copper sulphate complexes (Saconi and Ciapolini 1964; Beadle *et al* 1969). The tetrahedral  $\text{Cu(II)}$  complexes have the magnetic moment values within the range  $1.89\text{-}1.92\text{ B.M.}$  and square planar  $\text{Cu(II)}$  in the range  $1.83\text{-}1.86$  (Saconi 1966). The observed magnetic moment value for  $\text{CuSO}_4(\text{IPZ}) \cdot \text{H}_2\text{O}$  is more close to square planar symmetry. The splitting of the strong

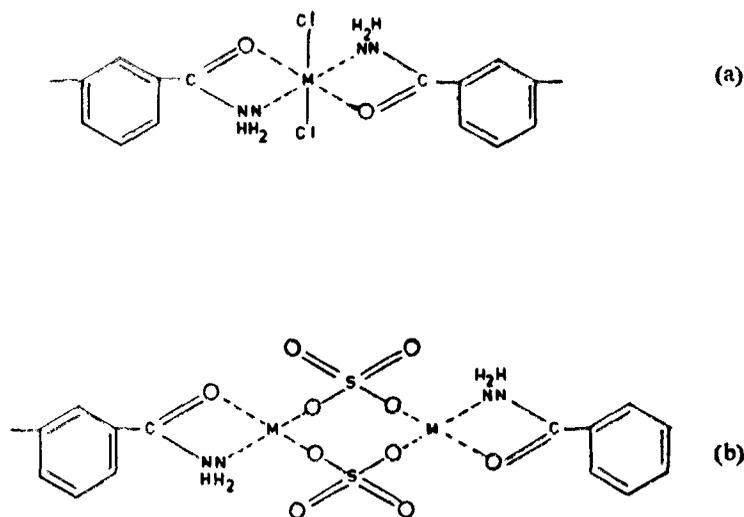


Figure 1. (a) Proposed structure for  $MCl_2$  complexes [ $M = Cu(II), Ni(II), Co(II)$ ]; (b) Proposed structure for  $[MSO_4]$  complexes  $M = Cu(II), Ni(II)$ .

sulphate bands in the infrared spectrum (bands at  $1175\text{ cm}^{-1}$ ,  $1130\text{ cm}^{-1}$ ,  $1050\text{ cm}^{-1}$ ) is consistent with bidentate bridged  $SO_4^{2-}$  ion (Nakamoto *et al* 1957). Hence a square planar polymeric structure is suggested for  $CuSO_4(IPZ)\cdot H_2O$  consisting of bidentate ligand and bridging sulphate ion as shown in figure 1b.

$NiSO_4\cdot L\cdot H_2O$  shows broad band at 580 nm which is characteristic for tetrahedral nickel complexes (Saconi 1966). Literature survey reveals (Yamada 1966) that square planar nickel complexes are diamagnetic and red in solid state. Magnetic moment value for  $NiSO_4$  complex (2.98 B.M.) is within the range for tetrahedral environment. The possibility of pseudo-tetrahedral environment is rather less because such complexes possess magnetic moment in the range  $3.2\text{--}3.3$  B.M. (Saconi 1966). Hence we are tempted to suggest a tetrahedral polymeric structure for  $NiSO_4(IPZ)\cdot H_2O$  (figure 1b).

### 3.3. Thermogravimetric analysis

Thermogravimetric study of all the complexes show almost similar decomposition pattern. The DTA peaks are given in table 2. The endothermic peaks at  $105\text{--}110^\circ\text{C}$  in all the complexes on DTA curve is accompanied by weight loss equivalent to one water molecule on TG curve.

In the case of  $MCl_2$  complexes loss of chlorine occurs in the temperature range  $105\text{--}320^\circ\text{C}$  which is followed by elimination of amine groups in the temperature range  $300\text{--}450^\circ\text{C}$ , with subsequent decomposition of the ligand and carbonization of the aromatic ring residue which spreads over the temperature range  $450\text{--}600^\circ\text{C}$ . The formation of respective metal oxides occurs at  $600\text{--}700^\circ\text{C}$ . The thermal stability of these complexes decreases in the order  $NiCl_2(IPZ)\cdot H_2O > CuCl_2(IPZ)\cdot H_2O > CoCl_2(IPZ)\cdot H_2O$ , similar to the results obtained by Marvel and Tarkoy (1957).

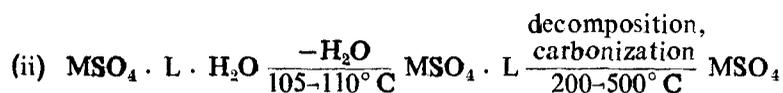
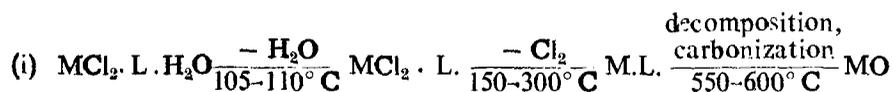
Table 2. Thermal decomposition data.  $MCl_4$  and  $MSO_4$  complexes.

Compound	DTA peak temp. (°C)				
$CuCl_2(IPZ) \cdot H_2O$	110 (-)	215 (+)	360 (+)		
$NiCl_2(IPZ) \cdot H_2O$	105 (-)	330 (+)	425 (+)		
$CoCl_2(IPZ) \cdot H_2O$	100 (-)	250 (+)	450 (+)	600 (+)	640 (+)
$CuSO_4(IPZ) \cdot H_2O$	110 (-)	240 (+)	420 (+)	720 (-)	
$NiSO_4(IPZ) \cdot H_2O$	105 (-)	280 (+)	340(+)	440 (+)	530 (+)
		750 (-)			

(-) and (+) signs after temperatures represent endotherm and exotherm respectively.

For  $MSO_4$  complexes, after the elimination of one water molecule and decomposition of amino groups, formation of anhydrous  $MSO_4$  takes place at temperature around  $500^\circ C$ . Anhydrous  $MSO_4$  finally decomposes to respective metal oxide via intermediate oxide formation as represented below. Formation of MO to  $MO_2$  is evidenced by peaks at 720 and  $750^\circ C$  on DTA curves for Cu(II) and Ni(II) complexes, which are also supported by the corresponding peaks on DTA curves at the same temperature. Percentage residue observed on TG curve also agrees well with calculated values for each intermediate stage of decomposition.

The decomposition pattern for  $MCl_2$  and  $MSO_4$  complexes can be represented as



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