

## Co(II), Ni(II) and Cu(II) Complexes of Oxalic, Malonic and Terephthalic Dihydrazides

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**Abstract.** Complexes of Co(II), Ni(II) and Cu(II) with Oxalic (OZ), malonic (MZ) and terephthalic (TPZ) dihydrazides have been prepared and characterised from elemental analysis, magnetic moment, visible, IR and ESR Spectra. Based on this data a polymeric octahedral structure has been assigned for the  $MCl_2 \cdot L \cdot H_2O$  complexes and a sulphate bridged four coordinate polymeric structure for the  $CuSO_4 \cdot L \cdot H_2O$  complexes. TGA and DTA results are also reported.

### 1. Introduction

In earlier communication we reported the characterization and thermogravimetric studies of some compounds containing metal-nitrogen and metal-oxygen bonds<sup>1,2</sup>. Here we report some metal complexes of oxalic (OZ), malonic (MZ) and terephthalic (TPZ) dihydrazides where both metal-oxygen and metal-nitrogen bonds are expected to be present. Metal complexes of polyhydrazides<sup>3,4</sup> and malondihydrazides<sup>5</sup> have been reported in literature. In the latter complexes the authors have observed that the ligand coordinates only through the secondary nitrogen atom. In complexes of benzoyl hydrazides<sup>6-8</sup> the ligand coordinates both through  $>C=O$  and  $-NH_2$  of

the  $\begin{array}{c} O \\ || \\ -C- \end{array} NH.NH_2$  group. In the dihydrazides reported in this work if the ligand is

bifunctional it would be expected that different  $\begin{array}{c} O \\ || \\ -C- \end{array} NH.NH_2$  groups would coordinate to different metal centres resulting in the formation of polynuclear complexes. A preliminary communication on the subject has been published elsewhere as a note<sup>9</sup>.

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## 2. Experimental

The metal complexes were prepared by adding hot aqueous solution of dihydrazides to alcoholic solutions of the respective metal salts in the molar ratio 1 : 1. The precipitates, which formed immediately, were suction filtered, washed with water, alcohol and ether, and air dried. The copper sulphate complex of malondihydrazide separated as a thick oily blue layer which on washing with alcohol and standing overnight solidified to a hard mass. The powdered material was used for further studies.

Infra-red 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 a Beckman DK II spectrophotometer. Magnetic susceptibilities were measured at room temperature by the Gouy method using  $HgCo(CNS)_4$  as calibrant. Thermogravimetric study was carried out using *Mom Budapest* model DTA apparatus by heating the samples at a rate of 10°C per minute.

## 3. Results and Discussion

The complexes (Table 1) are quite stable in air and insoluble in water and common organic solvents. They are sparingly soluble in pyridine and *DMF*. Molecular weight measurements could not be carried out owing to the insolubility of these compounds in suitable solvents. Elemental analysis led to the stoichiometry  $MCl_2 \cdot L \cdot H_2O$  ( $M = Co, Ni, Cu$ ) and  $CuSO_4 \cdot L \cdot H_2O$  for the complexes. The association of one water molecule in all complexes was confirmed both from IR spectra and thermogravimetric data.  $NiSO_4$  and  $CoSO_4$  did not complex with *MZ* and *TPZ*, under similar conditions.

Table 1. Analytical data and physical properties for compounds

Sl. No	Compound	Colour	M (%)		Cl/S (%)		$\mu$ (BM)	'g' values
			Found	Cal.	Found	Cal.		
1.	$CuCl_2(OZ) \cdot H_2O$	Dark Green	22.60	23.47	26.20	26.25	2.08	2.09
2.	$CuCl_2(MZ) \cdot H_2O$	Light Green	22.20	22.32	25.10	24.96	2.05	$g_{xx} = 2.17$ $g_{yy} = 2.08$ $g_{zz} = 2.00$
3.	$CuCl_2(TPZ) \cdot H_2O$	Light Blue	17.80	18.30	20.10	20.49	2.08	2.04
4.	$CuSO_4(OZ) \cdot H_2O$	Blue	21.30	21.50	10.60	10.82	1.78	2.08
5.	$CuSO_4(MZ) \cdot H_2O$	Dark Blue	20.90	20.50	10.50	10.34	1.82	2.13
6.	$NiCl_2(OZ) \cdot H_2O$	Pale Blue	22.70	22.10	26.40	26.47	2.82	—
7.	$CoCl_2(OZ) \cdot H_2O$	Pink	21.80	22.17	26.30	26.71	4.37	—

Satisfactory *C* and *H* analysis were obtained for all compounds.

### (a) Infra-red Spectra

The important infra-red bands are listed in Table 2. The broad  $\nu(O - H)$  band at 3500  $cm^{-1}$  present in all the complexes disappears from the spectra of the dehydrated

complexes. Weight loss equivalent to one water molecule is also evident in the TGA curve at  $\approx 100^\circ\text{C}$ . The  $\nu(N-H)$  frequencies of the complexes are lower by 70–100  $\text{cm}^{-1}$  as compared to their respective positions in the parent ligands. The  $\nu(C=O)$  is also shifted to lower region in the complexes by 40–50  $\text{cm}^{-1}$ . Thus the amino nitrogen and the carbonyl oxygen are both involved in coordination. The possibility of the enol form of the ligand is not supported by the infra-red spectra. The new strong band appearing in the complexes in the region 1200–1230  $\text{cm}^{-1}$  has been assigned to  $\nu(C-O)$ . The weak band around 600  $\text{cm}^{-1}$  has been assigned to  $\nu(M-O)$  following Adams<sup>10</sup> who has shown that  $\nu(M-O)$  stretching frequency in metal carboxyl complexes occur around 600  $\text{cm}^{-1}$ . The  $\nu(M-N)$  frequencies could not be identified but are expected to occur below 500  $\text{cm}^{-1}$  as shown by Nakamoto<sup>11</sup>. For the OZ complexes,  $\nu(M-O)$  follows the order  $\text{CuCl}_2(\text{OZ})\cdot\text{H}_2\text{O} > \text{CuSO}_4(\text{OZ})\cdot\text{H}_2\text{O} > \text{CoCl}_2(\text{OZ})\cdot\text{H}_2\text{O} > \text{NiCl}_2(\text{OZ})\cdot\text{H}_2\text{O}$ . For the CuCl<sub>2</sub> series  $\nu(M-O)$  are of the order  $\text{CuCl}_2(\text{TPZ})\cdot\text{H}_2\text{O} > \text{CuCl}_2(\text{MZ})\cdot\text{H}_2\text{O} > \text{CuCl}_2(\text{OZ})\cdot\text{H}_2\text{O}$ .

Table 2. Prominent infrared absorption frequencies for the complexes

$\text{CuCl}_2(\text{OZ})\cdot\text{H}_2\text{O}$	$\text{CuCl}_2(\text{MZ})\cdot\text{H}_2\text{O}$	$\text{CuCl}_2(\text{TPZ})\cdot\text{H}_2\text{O}$	$\text{CuSO}_4(\text{OZ})\cdot\text{H}_2\text{O}$	$\text{CuSO}_4(\text{MZ})\cdot\text{H}_2\text{O}$	$\text{NiCl}_2(\text{OZ})\cdot\text{H}_2\text{O}$	$\text{CoCl}_2(\text{OZ})\cdot\text{H}_2\text{O}$	Assignment
3490(s)	3580(s)	3500(s)	3490(b)	3470(b)	3490(b)	3560(b)	$\nu(O-H)$
3195(s)	3140(s)	3210(sb)	3250(sb)	3210(s)	3195(s)	3250(s)	$\nu(N-H)$
1625(s)	1640(s)	1655(s)	1630(s)	1640(s)	1640(s)	1650(s)	$\nu(N-H)$
1565(s)	1530(m)	1570(m)	1580(m)	1580(m)	1560(m)	1570(m)	—
				1530(m)	1510(m)	1510(m)	—
1330(m)	1365(m)	1360(m)	1325(m)q	1300(m)	1320(m)	1300(m)	$\nu(N-N)$
1200(s)	1200(s)	1230(m)	1230(s)	1230(m)	1200(s)	1230(m)	$\nu(C-O)$
—	—	—	1160(m)	1170(m)	—	—	$\nu(SO_4)$
			1120(m)	1110(m)	—	—	—
			1070(m)	1060(m)	—	—	—
950(m)	—	970(m)	—	—	—	—	—
		900(m)	—	—	—	—	—
840(m)	—	—	—	—	840(m)	850(m)	—
—	680(m)	—	—	680(m)	—	—	—
585(m)	595(m)	600(m)	575(m)	570(m)	530(m)	540(m)	$\nu(M-O)$

### (b) Electronic Spectra

The electronic spectra of CuCl<sub>2</sub> complexes of OZ, MZ and TPZ show single broad bands with maxima at 578 nm, 580 nm and 580 nm respectively which are characteristic of Cu(II) in a tetragonally distorted octahedral environment<sup>12,13</sup>. The effective magnetic moment values (Table 1) for these complexes are also in the region expected for octahedral Cu(II). The average 'g' values (Table 1) obtained from EPR spectra of the polycrystalline powder samples<sup>14</sup> show values similar to those reported for Cu(II) complexes with distorted octahedral symmetry<sup>15</sup>. The observed EPR line widths are about 1/2 the theoretically calculated values (exchange narrowing) which can be attributed to the existence of weak exchange interactions between the paramagnetic ions in these complexes.

Electronic spectra of both  $NiCl_2(OZ) \cdot H_2O$  and  $CoCl_2(OZ) \cdot H_2O$  show single broad bands with maxima at 574 nm and 498 nm respectively.  $Ni(II)$  and  $Co(II)$  octahedral complexes generally show two bands in the region 700-300 nm<sup>16,17</sup>. In fact the absorptions in these complexes are very broad and may well consist of two overlapping semi-degenerate transitions which might be resolved only at temperatures below 20°K. The occurrence of a single broad unresolved band would suggest a distorted octahedral symmetry for the complexes. Thus in the  $MCl_2(L) \cdot H_2O$  complexes the stoichiometry and bidentate nature of the ligands would suggest a polymeric structure as shown in Fig. 1(a). The stoichiometry and insolubility of the compounds in common inorganic and organic solvents support this contention.

$CuSO_4(OZ) \cdot H_2O$  and  $CuSO_4(MZ) \cdot H_2O$  although exhibit broad shoulderless absorptions at 595 nm and 600 nm respectively, consistent with tetragonally distorted octahedral geometries, the effective magnetic moments (1.78 and 1.82 BM) are comparable to the value reported for square planar<sup>18</sup> and tetrahedral<sup>19</sup>  $Cu(II)$  complexes. The splitting of the strong sulphate bands in the infrared spectrum are consistent with a bidentate bridged  $SO_4^{2-}$  ion<sup>20</sup>. Thus a four coordinate polymeric structure is suggested for the sulphate complexes, consisting of bidentate  $OZ$  or  $MZ$  ligands and bridging sulphate ions as shown in (Fig. 1b). The observed 'g' values are in accord with this structure. The good agreement between the experimental and calculated values of EPR line widths for the  $CuSO_4 \cdot L \cdot H_2O$  complexes suggest the existence of dipolar interaction between like spins and absence of exchange interaction between neighbouring ions.

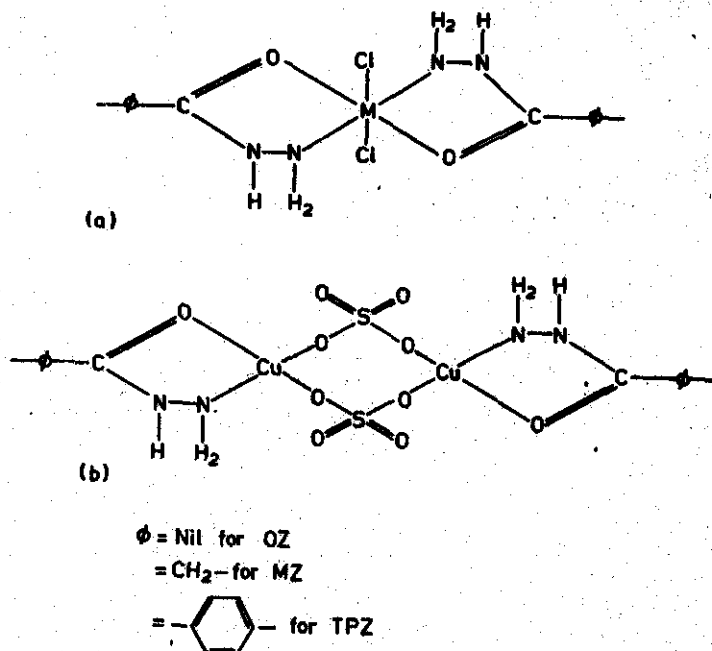


Figure 1(a)-1(b).

### (c) Thermogravimetric Studies

Thermogravimetric Studies of  $CuCl_2$  complexes of  $OZ$ ,  $MZ$ , and  $TPZ$  show almost similar decomposition mechanism. The DTA peaks are given in Table 3. The

endothermic peak at 100–110°C in all three complexes is accompanied by a weight loss equivalent to one water molecule. The TG data suggests that loss of chlorine occurs

Table 3. Thermal decomposition data for Cu(II) compounds

Compounds	DTA peak temp. (°C)
$CuCl_2(OZ)H_2O$	105(-), 180(+), 260(+), 320(+), 420(+), 500(+)
$CuCl_2(MZ)H_2O$	110(-), 180(+), 260(+), 440(+), 540(+)
$CuCl_2(TPZ)H_2O$	100(-), 180(+), 260(+), 340(+), 400(+), 480(+)

(-) and (+) signs after temperatures represent endotherms and exotherms respectively.

in the temperature range 160 to 180°C in all three complexes, which is followed by elimination of amine groups in the temperature range 200–320°C with subsequent decomposition of the ligands and carbonization of the organic ring residues which spread over the temperature range 320–450°C. Final formation of CuO occurs in the temperature range 500 to 550°C. The thermal stabilities of these compounds follow the order  $CuCl_2(MZ) > CuCl_2(TPZ) > CuCl_2(OZ)$ .

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