



# Spectral and Thermal Studies on Bivalent Transition Metal Complexes of Oxalic Acid with Morpholine

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## ABSTRACT

Morpholinium transition metal oxalates of the formula  $(\text{Morph})_2[\text{M}^{\text{II}}(\text{ox})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ , where  $\text{M} = \text{Co}, \text{Ni}$  have been prepared by the reaction of respective metal nitrates with an aqueous solution of morpholinium oxalate salts in appropriate mole ratios. These compounds have been characterized by various physico-chemical techniques like elemental analysis, conductance measurements, UV-Vis, IR, TG-DTA, XRD and SEM studies. The elemental analysis confirms the desired composition of the complexes. Conductance measurements show that all the complexes behave as 2:1 electrolytes, augmenting the non-coordination of morpholinium cation. Thermal studies show the presence of two coordinated water molecules and two lattice water molecules. Based on the above results, the geometry of the complexes is assigned as octahedral. The powder X-ray diffraction patterns of these compounds are similar to one another suggesting that they are isomorphous. Scanning electron micrographs are also observed to evaluate the morphology and particle size of the complexes.

**Keywords:** Morpholine; Oxalic acid.

## 1. INTRODUCTION

Oxalic acid (1, 2 - ethanedioic acid) is the simplest dicarboxylic, and it acts as a neutral, monobasic or dibasic chelating ligand and formed a large number of bivalent and trivalent metal complexes (Glietzes *et al.* 1980; Viswamitra *et al.* 1962; Ammeter *et al.* 1979; Antonio *et al.* 2007). In general, the oxalate anion acts as a bidentate ligand through one oxygen atom from each carboxylate group to the same metal, thus forming a five-membered chelate ring. The remaining oxygen atoms are bonded sometimes to adjacent Nano metal atoms to form a polymeric structure with tetradentate coordination of oxalate anion. A number of complexes with bidentate chelating oxalate ligand have been reported (Viswamitra *et al.* 1962). Oxalate complexes of transition metal complexes with polymeric structure contain tetradentate oxalate groups have been reported (Baran *et al.* 2008; Maria *et al.* 2009).

Morpholine has heterocycle features of both amine and ether functional groups. Because of the presence of lone pair of electrons on nitrogen and oxygen atoms, it offers the possibility of different modes of coordination towards metal ions. Many transition metal complexes with morpholine as monodentate ligands (Das *et al.* 1979; Ahuja *et al.* 1967) have been studied. Kumar *et al.* (1979) reported the morpholine complexes of copper alkanoates and chloroacetates. Ahuja *et al.* (1977) published morpholine complexes of nickel thiocyanates. Morpholine complexes of copper aryl carboxylates were reported by Kumar *et al.* (1975).

Morpholine complexes of nickel aryl carboxylates were studied by Kumar *et al.* (1978). Bidentate bridged morpholine complexes with zinc and cadmium cyanides were published by Ahuja *et al.* (1976). In these complexes also morpholine is coordinated to the metal through its nitrogen and not oxygen. Several metal complexes of oxalic acid have been studied; however, there is no report on the transition metal complexes of oxalate with morpholine. Hence, the present work aims at the preparation and characterization of divalent transition metal complexes of oxalates with morpholine and the results are presented in this paper.

## 2. EXPERIMENTAL

The aqueous solution of morpholine was added to the aqueous solution oxalic acid slowly with constant stirring. The respective metal nitrates were added to the above solution with constant stirring (pH 6-7). The coloured precipitates were formed (cobalt- pink, nickel-green) during the addition. The precipitate was filtered and washed with ice-cold water-alcohol (1:1) mixture and air-dried.

## 3. RESULTS & DISCUSSION

The molar conductance studies of the complexes show conductance value in the range 224-232  $\text{cm}^2 \text{mho mol}^{-1}$ , indicating their 2:1 electrolytic nature, for which  $\Lambda_{\text{M}}$  is expected to be in the range 220-260  $\text{cm}^2 \text{mho mol}^{-1}$  (Nathan *et al.* 1989).

The electronic spectral studies of cobalt complexes show a band in the range  $17200 - 18400 \text{ cm}^{-1}$  which usually splits into two bands due to spin-orbit coupling in the  ${}^4T_{1g}(P)$  state and is assigned to the  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  transition of typical six-coordinated Co(II) complexes<sup>37</sup>. The nickel complexes show two bands in the regions  $10700 - 13160$  and  $16550 - 19120 \text{ cm}^{-1}$ , which are ascribable to  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  transitions, respectively, of octahedral Ni(II) complexes (Gerry., 1871).

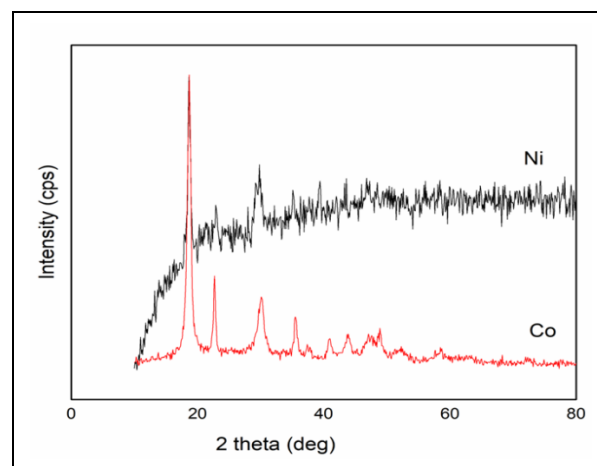
The infrared spectra of both the complexes exhibit strong bands in the region  $3380 - 3400 \text{ cm}^{-1}$  due to O–H stretching, confirm the presence of water molecule in the compound. Both the complexes show moderate bands in the region  $3180 - 3205 \text{ cm}^{-1}$  due to N–H stretching of morpholine in the compounds. The asymmetric and symmetric stretching frequencies of carboxylate ions are seen at  $1620$  and  $1359 \text{ cm}^{-1}$  respectively, with a ( $v_{asy} - v_{sy}$ ) separation of  $269 - 271 \text{ cm}^{-1}$  indicating the monodentate linkage of the carboxylate group in the dianion. The rocking frequencies of NH of morpholine of both compound are seen at  $824 - 826 \text{ cm}^{-1}$ . The C–O–C stretching band of morpholine is seen at  $1110 - 1112 \text{ cm}^{-1}$ . It is thus clear that morpholine does not suffer any significant shift and act as a charge compensating cation.

Thermal studies of the cobalt complex show that it decomposes in four steps. The first weight loss (6.50%) observed endothermically at  $55^\circ\text{C}$  can be attributed to the release of two water molecules (calculated 6.48%). Such low-temperature endothermic dehydration indicates that the water molecules are not coordinated to the metal. In the second step, the remaining water molecule is lost endothermically at  $120^\circ\text{C}$ , suggesting that the water molecule is coordinated to the metal.

The anhydrous compound then loses morpholine exothermically at  $210^\circ\text{C}$  to form cobalt hydrogen oxalate as an intermediate. In the final step, the cobalt hydrogen oxalate intermediate decomposes exothermically at  $400^\circ\text{C}$  to produce the cobalt oxide as the final residue.

Thermal studies of nickel complex also show similar steps of decomposition. The first stage that occurs in the range  $35-100^\circ\text{C}$  is attributed to the loss of two molecules of water. The corresponding DTA peak is observed as an endotherm at  $69^\circ\text{C}$ , suggesting the presence of water molecules as lattice water. The second stage mass loss also takes place endothermically at  $143^\circ\text{C}$ , as shown by DTA. This mass loss corresponds to a loss of the remaining two molecules of water. Such high-temperature dehydration is in support of the presence of coordinated water molecules in the compound. The third stage mass loss also takes place exothermically at  $242^\circ\text{C}$ ,

as shown by DTA. This mass loss is in accordance with the loss of two molecules of morpholine to form nickel-hydrogen oxalate intermediate, which finally undergoes exothermic decomposition to give nickel oxide. In DTA, this is observed as an exotherm at  $550^\circ\text{C}$ . X-ray diffraction pattern of cobalt and nickel compounds was recorded, and the patterns of the complexes were displayed in Fig. 1. The diffraction patterns of complexes are found to be similar. It shows both complexes are isomorphous in nature.



**Fig. 1: X-ray Powder Diffraction of the Complexes**

From the SEM micrographs, it is observed that in both these complexes, the grains are well resolved. The SEM micrographs of cobalt complexes (Fig. 2) show the morphology of needled shaped structure. The length of needles varies from 1 micrometre to 3 micrometers. The SEM micrographs of nickel complexes (Fig. 3) show particle-like morphology. It observed that particles were agglomerated, and the size of particles is in the range of 400 nm to 750 nm.

Based on the evidence drawn from solubility, molar conductance, spectral and thermal properties, it is quite reasonable to propose the structure of the complexes as having  $\text{MorH}^+$  ion, like  $\text{NH}_4^+$ ,  $\text{K}^+$  or  $\text{Na}^+$  as the charge compensating cation outside the anionic complex coordination sphere.

The spectral data show that in both the complexes, oxalate dianion acts as a bidentate ligand by coordinating through two monodentate carboxylate groups. Two water molecules are coordinated to metal in both the complexes, as evidenced from TG and DTA.

The above evidence indicates that the compounds reported herein may have the following structure with octahedral geometry around the metal (Fig.4).

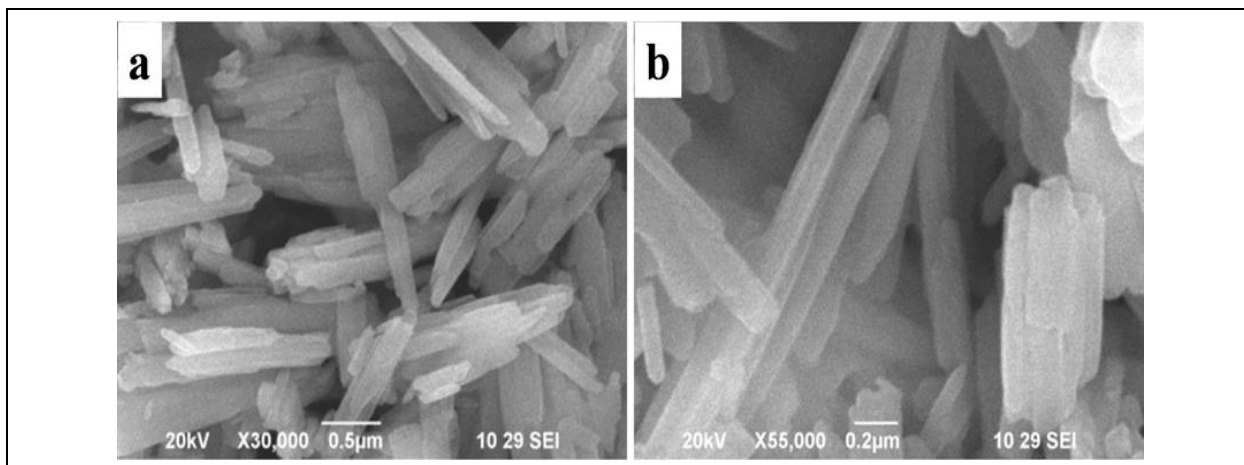


Fig. 2: SEM Micrographs of  $(\text{MorH})_2[\text{Co}(\text{ox})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

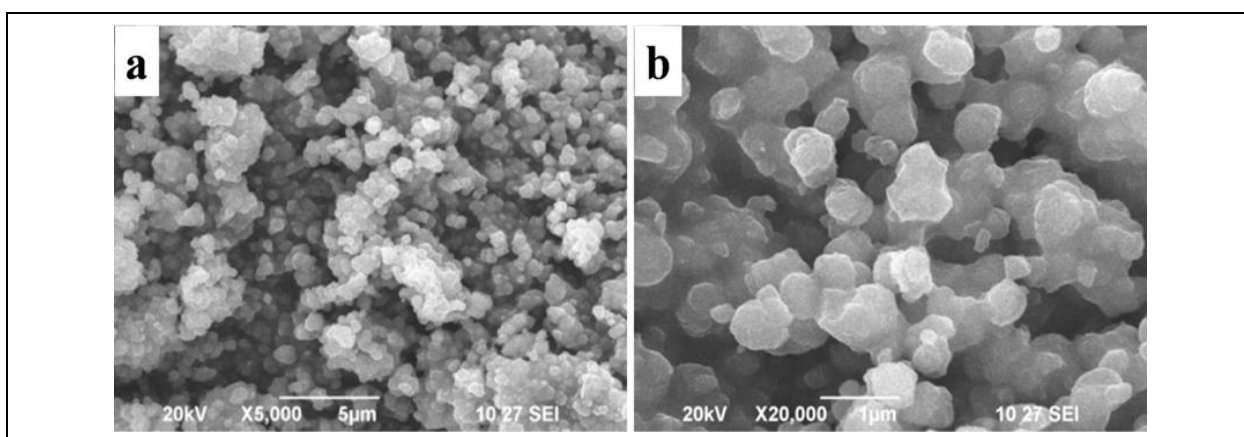


Fig. 3: SEM Micrographs of  $(\text{MorH})_2[\text{Ni}(\text{ox})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

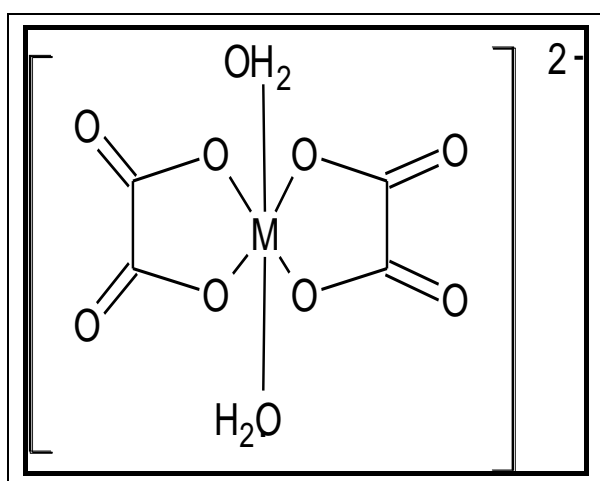


Fig. 4: Proposed Structure of  $[\text{M}(\text{ox})_2(\text{H}_2\text{O})_2]^{2-}$  Anion, Where  $\text{M} = \text{Co}(\text{II})$  or  $\text{Ni}(\text{II})$

#### 4. CONCLUSION

A new divalent transition metal complexes of morpholine with oxalic acid of the formula of  $(\text{MorH})_2[\text{M}(\text{ox})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  where  $\text{M} = \text{Co}, \text{Ni}$  has

been prepared and characterized by physico-chemical techniques. Based on the above studies, six coordination is proposed for both the complexes with octahedral geometry. The powder X-ray diffraction patterns of these compounds are similar to one another suggesting that they are isomorphous. The SEM micrographs of the cobalt complex show the morphology of needed shaped structure, whereas nickel complexes show particle-like morphology.

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