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The Preparation and Spectroscopic Studies of Morpholine Complexes with Nickel(II), Copper(II) and Zinc(II) Sulphates

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The preparation of morpholine complexes of nickel(II), copper(II) and zinc(II) sulphates is described. U.v., visible reflectance and i.r. spectra in the rock salt and low frequency region have been recorded for these complexes in the solid state. Possible structures for these complexes in the solid state are discussed. I.r. spectra in the rock salt region indicate coordinated sulphate groups and that the morpholine is coordinated via the nitrogen and not the oxygen atom. It is suggested that (a) Ni(morpholine)$_2$SO$_4$ is a polymeric structure with bridging sulphate groups, (b) Cu(morpholine)$_2$SO$_4$ is square planar with sulphate group acting as a chelate, and (c) Zn(morpholine)$_2$SO$_4$ and Zn(morpholine)SO$_4$ are polymeric structures with the sulphate group functioning probably as chelate and of symmetry lower than C_{2v}. Allocation for the possible metal-oxygen and metal-nitrogen modes have also been made.

Introduction

Studies on the i.r. spectra of morpholine complexes with metal(II) halides have shown that the morpholine is coordinated to the metal via its nitrogen as the N–H stretching frequencies of the free ligand show considerable shifts to lower frequencies in these complexes.[1] The present study of the i.r. spectra of the morpholine complexes with nickel(II), copper(II), and zinc(II) sulphates has been undertaken to elucidate the nature of bonding of the sulphate ion and hence the structure of these complexes.

Experimental Section

Complexes of the formula M(morpholine)$_2$SO$_4$, where $M = Ni^{II}$, Cu^{II} or Zn^{II} were prepared by adding an excess of morpholine to a hot solution of the respective metal(II) sulphate in methanol. The complexes which precipitated were filtered, washed with methanol and dried. Zn(morpholine)SO$_4$ was prepared as a thermal decomposition product of Zn(morpholine)$_2$SO$_4$.

$$Zn(morproline)_2SO_4 \xrightarrow{210°C} Zn(morpholine)SO_4 + morpholine$$

The thermal decomposition of Zn(morpholine)$_2$SO$_4$ was carried out in air on a Stanton Thermal Balance working at a chart speed of 12″ per hour and a temperature rise of 4°C per minute.

The u.v. and visible spectra of nickel(II) and copper(II) sulphate-morpholine complexes were obtained as reflectance spectra using a Hilger Uvispek Spectrophotometer fitted with a reflectance attachement. The samples were diluted with anhydrous potassium chloride by grinding the sample with the diluent in an agate mortar. The machine was checked against zero and 100% reflection using magnesium oxide as standard between each reading.

The i.r. spectra were recorded in the NaCl and KBr region using a Perkin-Elmer 125 Spectrophotometer. Spectra were obtained as Nujol and hexachlorobutadiene mulls in the case of solid complexes and as liquid film in the case of morpholine. The mulls were supported between sodium chloride plates.

The far i.r. spectra (15-45 μ) were recorded as Nujol mulls supported between thin polythene sheets on a Grubb Parson's DM 2 Spectrophotometer fitted with caesium iodide optics.

Results and Discussion

Morpholine was observed to form a 2 : 1 complex with each of the metal(II) sulphate investigated except that the monomorpholinezinc(II) sulphate was obtained as a thermal decomposition product of the bismorpholinezinc(II) sulphate. The stoichiometry of these complexes was established by metal and sulphate analysis. The analytical data are recorded in Table I.

Table I. Analytical Data: Metal(II) Sulphate-Morpholine

Complexes	Experimental Metal %	Experimental Sulphate %	Calculated Metal %	Calculated Sulphate %
Ni(morpholine)$_2$SO$_4$	17.6	28.9	17.9	29.2
Cu(morpholine)$_2$SO$_4$	18.6	28.6	18.9	28.8
Zn(morpholine)$_2$SO$_4$	19.2	29.0	19.3	28.6
Zn(morpholine)SO$_4$	25.9	37.9	26.2	38.6

Contribution due to the cordinated morpholine were selected by comparing the spectra of metal(II) sulphate-morpholine complexes with those for the metal(II) halide-morpholine complexes. The residual

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[1] I. S. Ahuja, *J. Inorg. Nucl. Chem.*, *29*, 2091 (1967).

features were assigned to the coordinated sulphate group and the frequencies are listed in Table II. Strong bands due to the coordinated sulphate group features are believed to superimpose and mask some of the bands due to the organic moiety.

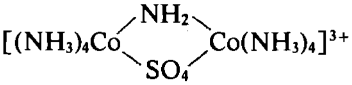
The most outstanding feature of the i.r. spectra in the rock salt region of the metal(II) sulphate-morpholine complexes is immediately apparent in the 3 μ region which shows the morpholine to be coordinated to the metal through its nitrogen as in the metal(II) halide-morpholine complexes.[1] The other characteristc feature of the 2-15 μ spectra is the splitting of the bands in the region for coordinated sulphate group.

Table II. Bands (cm^{-1}) in the Infrared Spectra of Metal(II) Sulphate-Morpholine (M) Complexes

Assignment	Ni(M)$_2$SO$_4$	Cu(M)$_2$SO$_4$	Zn(M)$_2$SO$_4$	Zn(M)SO$_4$
N—H	3270	3190	3205	
				3195
stretch	3196	3140	3180	
		1255	1259	1242
	1177	1191	1183	
				1160
		1111	1110	1110
	1094	1085	1086	
				1070-1050
	1042		1040	
		1023	1026	1026
			1000	
S—O		989		990
modes	973		973	
		666		661
				654
		635	640	
	628		625	
	612	610	616	615
	593	596	595	595
	493	488	488	500
Probably		365		
M—N		353		
modes	345		347	
	338			338
Probably			282	
M—O		272		267
modes	254	252		
			247	236

The far i.r. spectra (500-222 cm^{-1}) of these complexes are also expected to give much information concerning ν_2 of the coordinated sulphate group, vibrations possibly due to metal-nitrogen and metal-oxygen modes (arising from the coordinated anion). Morpholine itself gives peaks in the far i.r. near 580, 435, and 258 cm^{-1} and the coordinated morpholine also gives peaks in these regions. These peaks are common to all complexes and have been omitted from Table II (peak at 258 cm^{-1} is merged into the strong metal-oxygen modes in some complexes).

If the evidence of the reflectance and the i.r. spectra of nickel(II) and copper(II) sulphate-morpholine complexes is taken in conjunction with their stoichiometeries, it is clear that the sulphate groups must be coordinated to the metal atoms in these complexes.

The bismorpholinenickel(II) sulphate is pale green in colour and its u.v. and visible reflectance spectrum shows a strong absorption band at 14,500 cm^{-1} with a shoulder at 13,500 cm^{-1}. The nickel(II) ion has a d^8 configuration which gives rise to a $^3A_{2g}$ ground state in a regular octahedral field and a strong absorption band at ~13,500 cm^{-1} corresponding to the transition $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) is considered characteristic of nickel(II) in such an environment.[2] Thus the reflectance spectrum of Ni(morpholine)$_2$SO$_4$ is consistent with an octahedral environment around the nickel atoms. The existence of a unidentate sulphate group in bismorpholinenickel(II) sulphate seems very doubtful since the octahedral arrangement about the metal atom cannot thereby be satisfied. The i.r. spectrum of this compound shows very clearly bands at 1177, 1094, 1042, 973, 628, 612, 593, and 493 cm^{-1} which are very similar to those for  $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}SO_4)Co(NH_3)_4]^{3+}$ (1170, 1105, 1050-1060, 995, 641, 571, and 462 cm^{-1}) known to possess bridged bidentate sulphate group of C_{2v} symmetry and build a polymeric structure linking the two metal atoms.[3] It is thus suggested that the bismorpholinenickel(II) sulphate has a polymeric structure with bridging sulphate groups. Similar structure have also been recently proposed for PdSO$_4$[4] and M^{II}SO$_4$ dmp complexes,[5] where M = Fe, Co, Ni, and dmp = dimethyl-1,10-phenanthroline.

The absorption bands due to the coordinated sulphate group in the i.r. spectrum of the blue complex bismorpholinecopper(II) sulphate are similar to those proposed by earlier workers for bidentate sulphate group.[3] However, a strong band at 1255 cm^{-1} in Cu(morpholine)$_2$SO$_4$ indicates the presence of chelated sulphate group[6-8] and the compound may thus be considered as square planar and a structure similar to that of CuSO$_4$. 5H$_2$O is possible[9] with the two water molecules in the plane being replaced by two molecules of morpholine.

Zinc(II) sulphate forms two complexes with morpholine, namely, Zn(morpholine)$_2$SO$_4$ and Zn(morpholine)SO$_4$. Being a d^{10} ion, zinc(II) shows no d-d transitions and therefore information regarding the stereochemistry of zinc(II) sulphate-morpholine complexes cannot be deduced from their u.v. and visible reflectance spectra. However, from the shifts of the N—H stretching vibration bands to lower frequencies, splitting of the bands due to sulphate group, appearance of bands possibly due to metal-oxygen modes[10-12] in the low frequency region (300-222 cm^{-1}) and the similarity of the i.r. spectra to those of nickel(II) and copper(II) sulphate-morpholine complexes, it can definitely be stated that the morpholine and the sulphate group are coordinated to the metal in both the zinc(II) sulphate-morpholine complexes. Moreover, since these complexes have a strong band at ~1250 cm^{-1} and

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show a greater splitting of bands in the regions for coordinated sulphate it is suggested that the sulphate group is present as a bidentate chelate and the overall symmetry of this anion must be lower than C_{2v} in these complexes.

The low frequency i.r. spectra of all the metal(II) sulphate-morpholine complexes show strong absorption bands, either one or two, at 275 cm^{-1} and 245 cm^{-1} (± 10 cm^{-1}). Since such bands were not observed in the i.r. spectra of metal(II) halide-morpholine complexes[1] it is considered that these bands are most probably metal-oxygen modes, due to the coordinated anion. The frequency of these bands is much lower than that normally associated with metal-oxygen vibrations[13] and is consistent with the presence of oxyanions as bridges[11,12] (cf. lowering of mctal-halogen frequencies on bridging[14]). The M–O–S bending vibration modes would be excepted to occur[10] below 200 cm^{-1}, the lower limit of the far i.r. spectrophotometer used in this work.

In addition to the far i.r. absorption bands which have been allocated and discussed as being derived from essentially metal-oxygen vibration modes, strong absorption bands were also observed at $\sim$350 cm^{-1} in the spectra of practically all the metal(II) sulphate-morpholine complexes. It is suggested that these bands are most probably due to metal-nitrogen modes. Similar bands in this region were also observed and suggested to be possibly due to metal-nitrogen modes in the metal(II) halide-morpholine complexes.[1] Since the position of the bands remain almost constant in all the metal(II) halide-morpholine complexes[1] and also occur in almost the same range in metal(II) sulphate-morpholine complexes, these bands are considered to have most probably been derived from metal-nitrogen modes. However, these bands could also be assigned to a ligand mode which had become lowered in frequency or have become infrared active because of coordination to a heavy metal atom.

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