

TRANSITION METAL COMPLEXES OF 1,2-ETHYLENE MORPHOLINE

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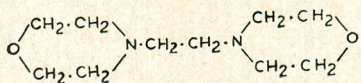
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1,2-Ethylene morpholine forms complexes with copper (II), nickel (II), and cobalt (II) of the type $[M(\text{etmorph})X_2]$, ($X = \text{Cl, Br, I or NO}_3$). Electrical conductivity and magnetic susceptibility measurements indicate that the complexes should have octahedral structure. The diamagnetism of cobalt (II) complexes is apparently unique and they may be regarded as polymerised complexes. The nickel (II) complexes are spin-free.

Introduction

1,2-Ethylene morpholine (etmorph),



is a quadridentate ligand which can only form a planar grouping around a metal ion. It has been used¹ to stabilize gallous ion (Ga^+). It was thought of interest to prepare the transition metal coordination compounds of 1,2-ethylene morpholine and to study the stereochemistry of the complex cations. Twelve complexes of this ligand with the salts of Cu(II) , Ni(II) and Co(II) have been prepared in non-aqueous solvents. Physical properties such as solubility, decomposition point, molar conductance and magnetic susceptibilities of these complexes were studied to determine their structure.

Experimental

PREPARATION OF 1,2-ETHYLENE MORPHOLINE (ETMORPH)

The ligand was prepared by the method reported by S.M. Ali et al.¹

PREPARATION OF COORDINATION COMPOUNDS

1. *Dichloroethylene Morpholine Copper (II)*, $[\text{Cu}(\text{etmorph})\text{Cl}_2]$.—1.23 g. of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 2 g. of the ligand (1:1 molar ratio) were dissolved separately in minimum amount of dry *n*-butanol. On mixing the two alcoholic solutions, orange crystals of the complex were formed. The mixture was allowed to stand overnight in a conical flask when the crystals settled at the bottom of the flask. The crystals were filtered over a suction pump, washed with dry ether and finally dried at 50°C . in a vacuum oven. Yield, 1.8 g.

Copper was determined gravimetrically as cuprous thiocyanate.² Chlorine and other halogens were estimated by Volhard's method.³ The amount of ligand was calculated by difference.

Found: Cu, 19.44; Cl, 21.18; etmorph, 59.38.
Calculated: Cu, 18.99; Cl, 21.52; etmorph, 59.49.

2. *Dibromoethylene Morpholine Copper (II)*, $[\text{Cu}(\text{etmorph})\text{Br}_2]$.—A red coloured crystalline precipitate of the complex was obtained by vigorously shaking 2 g. $\text{CuBr}_2 \cdot 3\text{H}_2\text{O}$ and 3 g. ethylene morpholine in anhydrous *n*-butanol. Yield, 2.8 g. Analysis of the complex was done by the methods described above.^{2,3}

Found: Cu, 15.40; Br, 37.84; etmorph, 46.76.
Calculated: Cu, 15.00; Br, 37.74; etmorph, 47.26.

3. *Sulphatoethylene Morpholine Copper (II)*, $[\text{Cu}(\text{etmorph})\text{SO}_4]$.—Copper sulphate solution in methanol, when mixed with the ligand solution in *n*-butanol, gave green crystalline precipitate of the complex.

The sulphate was determined gravimetrically as BaSO_4 in HCl solution of the complex.³

Found: Cu, 17.25; SO_4 , 27.13; etmorph, 55.62.
Calculated: Cu, 17.67; SO_4 , 26.71; etmorph, 55.62.

4. *Dinitratoethylene Morpholine Copper (II)*, $[\text{Cu}(\text{etmorph})(\text{NO}_3)_2]$.—It was obtained as a blue precipitate by mixing and shaking the methanol solution of copper nitrate with the *n*-butanol solution of the ligand.

Found: Cu, 16.41. Calculated: Cu, 16.39.

5. *Dibromoethylene Morpholine Nickel (II)*, $[\text{Ni}(\text{etmorph})\text{Br}_2]$.—The blue crystals of nickel bromide complex were obtained by mixing the solutions of nickel bromide and the ligand in *n*-butanol. The crystals were washed with ether and vacuum dried at 50°C .

Nickel was determined gravimetrically with dimethyl glyoxime.

Found: Ni, 13.93; Br, 28.15; etmorph, 47.92.
Calculated: Ni, 14.03%; Br, 28.19%; etmorph, 47.78%

6. *Dichloroethylene Morpholine Nickel (II)*, $[Ni(etmorph)Cl_2]$.—This complex was prepared by the method similar to that used for the nickel bromide complex. The crystals were of violet colour.

Found: Ni, 17.52; Cl, 22.12; etmorph, 60.36.
Calculated: Ni, 17.80; Cl, 22.03; etmorph, 60.17.

7. *Diiodoethylene Morpholine Nickel (II)*, $[Ni(etmorph)I_2]$.—On mixing the methanol solution of nickel iodide and *n*-butanol solution of the ligand, and distilling the mixture under reduced pressure green crystals of NiI_2 complex were obtained. On washing with ether and drying under vacuum, the colour of the complex changed from green to brown.

Found: Ni, 11.79; I, 49.50; etmorph, 38.7.
Calculated: Ni, 11.46; I, 49.52; etmorph, 39.02.

8. *Dinitratoethylene Morpholine Nickel (II)*, $[Ni(etmorph)(NO_3)_2]$.—The nickel nitrate complex was obtained as a green precipitate from *n*-butanol solution.

Found: Ni, 15.32. Calculated: Ni, 15.34.

9. *Dichloroethylene Morpholine Cobalt (II)*, $[Co(etmorph)Cl_2]$.—A blue crystalline complex was formed by mixing the *n*-butanol solution of cobalt

chloride with the ligand solution in the same solvent. Cobalt was estimated by the cobalt oxinate and potassium bromate method.³

Found: Co, 17.70; Cl, 21.72; etmorph, 60.58.
Calculated: Co, 17.87; Cl, 21.52; etmorph, 60.61.

10. *Dibromoethylene Morpholine Cobalt (II)*, $[Co(etmorph)Br_2]$.—A light blue complex was obtained from *n*-butanol solution.

Found: Co, 13.98; Br, 38.21; etmorph, 47.81.
Calculated: Co, 14.08; Br, 38.16; etmorph, 47.76.

11. *Diiodoethylene Morpholine Cobalt (II)*, $[Co(etmorph)I_2]$.—It was prepared as above. It is of green colour.

Found: Co, 11.47; I, 49.50; etmorph, 39.03.
Calculated: Co, 11.49; I, 49.49 etmorph, 39.02.

12. *Dinitroethylene Morpholine Cobalt (II)*, $[Co(etmorph)(NO_3)_2]$.—Pink crystals of the complex were obtained by mixing the *n*-butanol solutions of the salt and the ligand.

Found: Co, 15.38. Calculated: Co, 15.39.

CONDUCTIVITY AND DECOMPOSITION TEMPERATURES OF THE COMPLEXES

Qualitative experiments showed that these complexes were only slightly soluble in nitrobenzene and cyclohexanone. They were insoluble in dioxane and were decomposed by morpholine and water. Electrical conductivities were measured in nitrobenzene solutions, using a dip type

TABLE I.—COLOUR, DECOMPOSITION POINTS AND CONDUCTIVITIES OF COMPLEXES IN NITROBENZENE.

Complexes	Colour	Decomposition point °C.	Molar conductivity (mhos) at 25 °C.
$[Cu(etmorph)Cl_2]$	Orange	122	21.13
$[Cu(etmorph)Br_2]$	Red	110	22.62
$[Cu(etmorph)(NO_3)_2]$	Blue	185	—
$[Cu(etmorph)SO_4]$	Green	220	—
$[Ni(etmorph)Cl_2]$	Violet	300	—
$[Ni(etmorph)Br_2]$	Blue	290	11.23
$[Ni(etmorph)I_2]$	Brown	130	14.87
$[Ni(etmorph)(NO_3)_2]$	Green	170	13.49
$[Co(etmorph)Cl_2]$	Blue	302	0.12
$[Co(etmorph)Br_2]$	Light blue	294	0.17
$[Co(etmorph)I_2]$	Green	170	0.60
$[Co(etmorph)(NO_3)_2]$	Pink	140	1.22

cell with a Mullard conductivity bridge, in the concentration range of 0.5 to 6×10^{-3} M. The values were corrected for the conductivity of nitrobenzene at the same temperature. The results of electrical conductivity measurements and decomposition points of the complexes are summarized in Table 1.

MAGNETIC SUSCEPTIBILITY MEASUREMENTS

These were carried out on a magnetic interference balance designed by Bhatnagar and Mathur,⁴ using complexes in the solid state. The values of specific susceptibilities (X) were calculated by the following equation:

$$X = \frac{I}{M} X_a M_a + (X_w m_w - X_a m_a) \frac{r - r_1}{r_2 - r_1},$$

where r , r_1 and r_2 are the readings on the interferometer for the tube containing the specimen, empty tube and tube with water respectively; and other letters have the same significance as in Oxley's equation.

Molar susceptibilities, X_m , were calculated from the values of specific susceptibilities. In the case of paramagnetic complexes diamagnetic corrections⁵ for the ligand were applied to X_m . The corrected values of X_m were used to calculate the magnetic moments. Table 2 shows the results of magnetic susceptibility measurements of these complexes.

Discussion

1,2-Ethylene morpholine forms complexes of empirical formulae $[M(\text{etmorph})X_2]$ with copper (II), nickel (II) and cobalt (II), where $X =$

Cl, Br, I and NO_3 . With copper sulphate the empirical formula of the complex is $[\text{Cu}(\text{etmorph})\text{SO}_4]$. The molecular solubilities of these complexes are too low to allow the molecular weight determinations. The complex of cobalt are non-electrolytes in nitrobenzene which suggests that cobalt has coordination number six with an octahedral structure. The cobalt complexes were found to be diamagnetic, an unusual result which call for comment. Even in a spin paired octahedral complex, Co^{+2} ion (d^7) should have one unpaired electron with magnetic moment of 1.8. The unexpected diamagnetism of cobalt-etmorph complexes may be due to their very distorted octahedral structure,⁶ (Fig.1.)

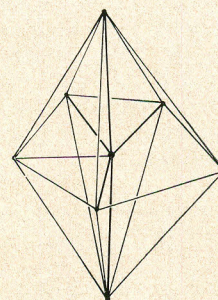


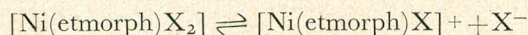
Fig. 1.

The unpaired electron resides at the apex outside the octahedron where it gets paired with the similar electron of the other molecule. The sharing of two irregular octahedra results in a weak Co-Co bond making the complex diamagnetic in the solid state. We, therefore, conclude that cobalt (II) ethylene morpholine complexes are spin-paired polymers in the solid state with a very irregular octahedral structure.

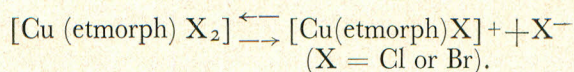
TABLE 2.—SPECIFIC SUSCEPTIBILITIES, MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF TRANSITION METAL COMPLEXES OF 1, 2—ETMORPH.

Complex	$X \times 10^{-6}$	$X_m \times 10^{-6}$	μ_{eff} (B.M.)
$[\text{Cu}(\text{etmorph})\text{Cl}_2]$	3.313	1108.1	1.77
$[\text{Cu}(\text{etmorph})\text{Br}_2]$	2.406	1018.6	1.69
$[\text{Ni}(\text{etmorph})\text{Cl}_2]$	4.184	1379.5	1.86
$[\text{Ni}(\text{etmorph})\text{Br}_2]$	4.554	1732.7	3.73
$[\text{Ni}(\text{etmorph})\text{I}_2]$	3.435	1073.4	3.44
$[\text{Ni}(\text{etmorph})(\text{NO}_3)_2]$	4.432	1696.1	2.13
$[\text{Co}(\text{etmorph})\text{Cl}_2]$	-1.947	-642.4	Diamagnetic
$[\text{Co}(\text{etmorph})\text{Br}_2]$	-1.650	-690.9	„
$[\text{Co}(\text{etmorph})(\text{NO}_3)_2]$	-1.221	-467.6	„

The nickel-ethylene morpholine complexes are paramagnetic with magnetic moments in the range 1.86-3.73 B.M., corresponding to two unpaired electrons. Thus Ni^{+2} ethylene morpholine complexes are spin-free with octahedral structure in the solid state, because the crystal field stabilization energy is greater for this symmetry than for tetrahedral symmetry.⁷ These complexes dissociate in a polar solvent like nitrobenzene and their molar conductivities in nitrobenzene are comparable with the molar conductivities of other 1:1 electrolytes in the same solvent.^{8,9} The dissociation could be attributed to the following equilibrium:—



The magnetic measurements are of no help in determining the structure of copper (II) complexes, as Cu^{+2} ion with d9 electrons in these complexes will always have one unpaired electron in tetrahedral, octahedral as well as in square planar symmetry. The experimental values of magnetic moments of the two copper-ethylene morpholine complexes are 1.77 and 1.69 B.M., corresponding to one unpaired electron. The copper sulphate complex and copper-nitrate complex are non-conducting in nitrobenzene, suggesting coordination number six for the copper atom in an octahedral structure. As the SO_4^{--} ion usually coordinates only at one position, the copper sulphate complex may be regarded a polymer with a SO_4^{--} ion being shared between the two octahedra resulting in a chain-like structure. ($\text{Cu}(\text{etmorph})\text{Cl}_2$) and $\text{Cu}(\text{etmorph})\text{Br}_2$ behave as 1:1 electrolyte in nitrobenzene. This may be due to their dissociation in the polar solvent.



In the solid state these complexes may have octahedral structure.

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