

Studies on Manganese(II), Iron(II), Cobalt(II & III), Nickel(II), Copper(II) & Zinc(II) Complexes of Ethoxythiocarbonyl Hydrazide

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Ethoxythiocarbonyl hydrazide (Heth) forms complexes of the types $[\text{Ni}(\text{Heth})_3]\text{Cl}_2$, $[\text{Co}(\text{Heth})_3]\text{Cl}_3$, $\text{M}(\text{Heth})\text{Cl}_2$ [$\text{M} = \text{Cu}(\text{II})$, $\text{Zn}(\text{II})$] and $\text{M}(\text{eth})_2 \cdot x\text{H}_2\text{O}$ [$\text{M} = \text{Mn}(\text{II})$, $\text{Fe}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$; $x = 2$ for $\text{Fe}(\text{II})$ & 0 for others]. Magnetic and electronic spectral studies suggest tetrahedral geometry for $\text{Co}(\text{eth})_2$; octahedral geometry for $\text{Fe}(\text{eth})_2 \cdot 2\text{H}_2\text{O}$, $\text{Ni}(\text{Heth})_3\text{Cl}_2$ and $\text{Co}(\text{Heth})_3\text{Cl}_3$; and square-planar geometry for $\text{Ni}(\text{eth})_2$ and $\text{Cu}(\text{eth})_2$. Infrared spectral studies show neutral/uninegative bidentate behaviour of the ligand; the bonding sites are terminal nitrogen and sulphur. $\text{Co}(\text{III})$, $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ chloride complexes have been found to exhibit pronounced antifungal activity against *A-flavus* and *H-sporium*.

Although a few papers are available on the transition metal complexes of thiohydrazides^{1,2}, dithiocarbazic acid ($\text{N}_2\text{NNHCS}_2\text{H}$) and its alkyl and aryl derivatives³, no work seems to have been done on the complexes of ethoxythiocarbonyl hydrazide [$\text{H}_2\text{NNHC}(\text{S})\text{OEt}$, (Heth)]. The preparation of $\text{Mn}(\text{II})$, $\text{Fe}(\text{II})$, $\text{Co}(\text{II}, \text{III})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ complexes and their characterization by various physicochemical methods have, therefore, been undertaken and the results of these investigations are described here.

All the chemicals used were BDH reagents or of equivalent quality. Heth and its hydrochloride (Heth.HCl) were prepared as described in literature⁴; m.p. 142° ($142\text{--}143^\circ$).

$[\text{Ni}(\text{Heth})_3]\text{Cl}_2$, $[\text{Co}(\text{Heth})_3]\text{Cl}_3$ and $[\text{M}(\text{Heth})\text{Cl}_2]$ ($\text{M} = \text{Cu}^{\text{II}}$, Zn^{II}) were prepared by mixing the ethanolic solutions of the respective metal(II) chlorides and Heth.HCl in $\sim 1:3$ molar ratio; $\text{Co}(\text{Heth})_3\text{Cl}_3$ was, however, obtained by the addition of a few drops of hydrochloric acid to the reaction mixture. The complexes obtained on slow evaporation of the solvent were filtered, washed with ethanol and dried *in vacuo*.

The complexes with deprotonated ligand, $\text{M}(\text{eth})_2 \cdot x\text{H}_2\text{O}$, were prepared by mixing ethanolic solutions of the respective metal(II) chlorides and Heth.HCl in $\sim 1:2$ molar ratio and adding two equivalents of ethanolic KOH in the case of $\text{Fe}(\text{II})$ and

$\text{Ni}(\text{II})$ and raising the pH to 5-6 with dilute ammonia for others. The complexes which separated immediately were digested on a water-bath for a few minutes, filtered, washed with water and ethanol and dried *in vacuo*. $\text{Fe}(\text{eth})_2 \cdot 2\text{H}_2\text{O}$ was prepared in hydrogen atmosphere to prevent its oxidation.

The complexes were analysed for their metal contents by standard procedures after destroying the organic matter with a mixture of nitric and hydrochloric acids and then with conc. sulphuric acid. Sulphur and chloride were estimated as BaSO_4 and AgCl , respectively. Nitrogen was determined by microanalysis. Hydrazine was estimated volumetrically⁵ using KIO_3 after refluxing the complexes in $\sim 7\text{ N HCl}$ for $\sim 2\text{--}3$ hr. The analytical data are given in Table 1.

Electrical conductances were measured on a WTW conductivity meter in MeOH. The magnetic susceptibilities of the complexes were determined by the Faraday method using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as the calibrant. The electronic and IR spectra of the ligand and the complexes were recorded on a Cary-14 and Perkin Elmer 621 spectrophotometers respectively in nujol.

The antifungal activities of $\text{Co}(\text{III})$, $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ chloride complexes were evaluated against *Helminthosporium* and *Aspergillus flavus* by agar plate technique^{6,7} at three different concentrations, viz., 1:100, 1:1000 and 1:10000. The number of replication in each case was three. The percent inhibition given in Table 2 was calculated using the formula:

$$\% \text{ inhibition} = \frac{(C - T) \times 100}{C}$$

where C = diameter of the fungus colony in the control plate after 72 hr and T = diameter of the fungus colony in treated plates after the same period.

The values of the molar conductance ($\text{mhos cm}^2 \text{ mol}^{-1}$) at 10^{-3} M concentration in MeOH for $\text{Ni}(\text{Heth})_3\text{Cl}_2$ (163) and $\text{Co}(\text{Heth})_3\text{Cl}_3$ (295) show their 1:2 and 1:3 electrolytic behaviour respectively while those of $\text{Cu}(\text{Heth})\text{Cl}_2$ (38) and $\text{Zn}(\text{Heth})\text{Cl}_2$ (33) indicate them to be non-electrolytes⁸.

The magnetic moments of $\text{Cu}(\text{II})$ complexes are normal and are indicative of square-planar geometry⁹. The diamagnetic nature of $\text{Co}(\text{Heth})_3\text{Cl}_3$ and $\text{Ni}(\text{eth})_2$ (greenish-gray) indicates the former complex to be low-spin octahedral and the latter to be square-planar. The magnetic moments of $\text{Co}(\text{eth})_2$ and $[\text{Ni}(\text{Heth})_3]\text{Cl}_2$ are consistent with tetrahedral and

Table 1—Analytical Data and General Behaviour of the Heth Complexes

Compound	Colour	Found (Calc.), %					μ_{eff} (B.M.)	m.p. (°C)
		Metal	N ₂ H ₄	N	Cl	S		
[Co(Heth) ₃]Cl ₃	Violet	10.96 (11.21)	18.49 (18.28)	15.40 (15.99)	19.80 (20.23)	18.50 (18.28)	dia.	255 ^d
[Ni(Heth) ₂]Cl ₂	Blue	12.22 (11.99)	18.82 (19.61)	16.90 (17.16)	14.70 (14.48)	19.70 (19.61)	3.15	> 300
[Cu(Heth)Cl ₂]	Green	24.61 (24.98)	12.28 (12.58)	11.20 (11.01)	27.13 (27.87)	12.65 (12.58)	1.78	150
[Zn(Heth)Cl ₂]	White	25.90 (25.51)	12.84 (12.49)	10.42 (10.92)	27.10 (27.67)	12.62 (12.49)	dia.	185
Mn(eth) ₂	Dirty-yellow	19.17 (18.75)	21.20 (21.86)	18.83 (19.12)	—	21.75 (21.86)	5.90	> 300
Fe(eth) ₂ ·2H ₂ O†	Brown	17.22 (16.92)	—	16.54 (16.97)	—	19.82 (19.40)	4.90	> 300
Co(eth) ₂	Brown	19.66 (19.85)	21.12 (21.56)	19.21 (18.87)	—	21.67 (21.56)	4.31	> 300
Ni(eth) ₂ ‡	Greenish-grey	18.99 (19.79)	21.52 (21.57)	19.00 (18.88)	—	21.85 (21.57)	dia.	250 ^d
Ni(eth) ₂ ‡	Light yellow	20.22 (19.79)	21.17 (21.57)	18.25 (18.88)	—	21.90 (21.57)	1.53	> 300
Cu(eth) ₂	Blue-violet	21.68 (21.08)	20.97 (21.22)	17.95 (18.56)	—	21.40 (21.22)	1.75	210 ^d
Zn(eth) ₂	White	22.12 (21.56)	19.88 (21.11)	17.80 (18.47)	—	21.28 (21.11)	dia.	> 300

†Weight loss = 10.56% at 120°C, Fe(eth)₂·2H₂O requires 10.91% for the loss of 2H₂O (d) decomposes; ‡These were prepared by the addition of dil. ammonia and alcoholic KOH, respectively.

Table 2—Antifungal Activity of the Complexes [Medium: Czapek's; Time 72 hr; Temp. 25 ± 1°C]

Compound	Average percentage inhibition					
	<i>H. sporium</i>			<i>A. flavus</i>		
	Conc. used (p.p.m.)			Conc. used (p.p.m.)		
	1:100	1:1000	1:10000	1:100	1:1000	1:10000
[Co(Heth) ₃]Cl ₂	80.0	73.0	60.0	98.6	85.70	71.4
[Ni(Heth) ₃]Cl ₂	73.0	70.6	60.0	97.0	76.5	64.3
[Cu(Heth)Cl ₂]	73.3	66.7	60.0	85.7	71.4	57.1

octahedral (high-spin) geometries around Co(II) and Ni(II) in these complexes. The deprotonated complexes of Mn(II) and Fe(II) are spin-free with five and four unpaired electrons respectively. The magnetic moment of Ni(eth)₂ (light yellow) may be explained by assuming a mixed stereochemistry (square-planar and tetrahedral) around Ni(II)¹⁰.

The visible region spectrum of Fe(eth)₂·2H₂O shows one broad band at 11100 cm⁻¹ assignable to ⁵T_{2g} → ⁵E_g(D) transition in octahedral environment of the metal ion¹¹.

The spectrum of Co(eth)₂ yields three bands at 8130, 14815 and 16665 cm⁻¹; the first band may be assigned to ⁴A₂ → ⁴T₁(F) (ν₂) transition while the second and third bands may be attributed to split components of ⁴A₂ → ⁴T₁(P) (ν₃) transition in tetrahedral geometry.

The energy of ν₃ band has been calculated as 15740 cm⁻¹ by taking the average of the second and third transitions as suggested by Drago¹². From the above values of ν₂ and ν₃, the values of 10Dq, B and β work out to be 4826 cm⁻¹, 617 cm⁻¹ and 0.635, respectively as described by Lever¹³.

Co(Heth)₃Cl₃ shows two bands at 11630 and 16950 cm⁻¹ assignable to ¹A_{1g} → ³T_{1g} and ¹T_{1g} transitions respectively in octahedral geometry of Co(III). The values of 10Dq and Racah parameter, C, have been calculated to be 19610 and 2660 cm⁻¹, respectively¹⁴.

Ni(Heth)₃Cl₂ shows bands at 10530, 16665 and 26000 cm⁻¹ assignable to ³A_{2g}(F) → ³T_{2g}(F) (ν₁), ³T_{1g}(F)(ν₂) and ³T_{1g}(P)(ν₃) transitions respectively in octahedral geometry¹⁰.

The spectrum of diamagnetic Ni(eth)₂ (greenish-

grey) shows two bands at 16950 and 23530 cm^{-1} in the visible region which may be assigned to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and $\rightarrow {}^1B_{3g}$ transitions respectively in D_{2h} symmetry¹⁵. The single electron parameters Δ_1 and Δ_2 have been calculated from the observed $d-d$ transitions as suggested by Gray *et al.*¹⁶ assuming after Shupack *et al.*¹⁷ that $F_2 = 10$, $F_4 = 800 \text{ cm}^{-1}$; the calculated values are 19750 and 8180 cm^{-1} , respectively.

Of the three bands observed at 9520, 17700 and 22730 cm^{-1} in the visible spectrum of paramagnetic $\text{Ni}(\text{eth})_2$ the first one may be assigned to ${}^3T_1 \rightarrow {}^3A_2$ (ν_2) transition in the tetrahedral geometry¹⁴ while the other two may be attributed to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and $\rightarrow {}^1B_{3g}$ transitions in the square-planar geometry. Thus the mixed geometry (tetrahedral + square-planar) of the complex as indicated by its magnetic moment value is supported by the electronic spectral studies.

$\text{Cu}(\text{Heth})\text{Cl}_2$ and $\text{Cu}(\text{eth})_2$ yield three and two bands respectively in the region 13160-23250 cm^{-1} indicating their square-planar geometries¹⁸.

The bands at 3400 and 3260 cm^{-1} in the IR spectrum of the ligand are due to $\nu(\text{NH})$ modes of secondary and primary amine groups respectively. The first band remains unchanged (except in complexes with deprotonated ligand where it disappears) in the complexes, while the second band shows a negative shift of 40-140 cm^{-1} indicating coordination through amino nitrogen. The disappearance of 3400 cm^{-1} band in complexes of the type $\text{M}(\text{eth})_2 \cdot x\text{H}_2\text{O}$ indicates probably the removal of the proton of secondary amine nitrogen through thioenolisation. $\beta(\text{NH})_2$ and $\nu(\text{N-N})$ bands observed in the ligand at 1630 and 975 cm^{-1} respectively show a negative shift of 10-30 cm^{-1} and a positive shift of 20-60 cm^{-1} , respectively in all the complexes suggesting that the primary amine nitrogen is involved in bonding¹⁹.

The bands occurring at 1480 and 1310 cm^{-1} in the ligand are assignable to $\beta\text{NH} + \nu\text{CN}$ [mainly $\beta(\text{NH})$] and $\nu\text{CN} + \beta\text{NH}$ [high $\nu(\text{CN})$] respectively²⁰ which show positive shifts of 20-60 cm^{-1} in the complexes indicating the involvement of sulphur atom in bonding²¹⁻²³. $\nu(\text{C}=\text{S})$ mode, observed at 890 cm^{-1} in the ligand, shows negative shift of 20-25 cm^{-1} in the cationic-anionic and dichloro complexes and disappears in the complexes with deprotonated ligand, and a new band due to $\nu(\text{C-S})$ is observed²⁴ at $\sim 710 \text{ cm}^{-1}$. These observations suggest bonding through thiono sulphur in the former type of complexes and through thiolate sulphur in the latter.

Bands observed at 3350 and 740 cm^{-1} in the spectrum of $\text{Fe}(\text{eth})_2\text{H}_2\text{O}$ may be assigned to $\nu(\text{OH})$ and $\rho_f(\text{H}_2\text{O})$ modes of coordinated water molecule²⁵. The non-ligand bands occurring in 280-340 and 280-320 cm^{-1} regions may be tentatively assigned to $\nu(\text{M-N})$ and $\nu(\text{M-S})$, respectively^{2,24,26}. Thus IR results

show that Heth behaves as a neutral/uninegative bidentate ligand in the complexes, bonding sites being primary amine nitrogen and sulphur.

The X-ray diffraction patterns of $\text{Ni}(\text{Heth})_3\text{Cl}_2$ and $\text{Cu}(\text{Heth})\text{Cl}_2$ obtained on a Phillips-1010 X-ray generator using CuK_α radiation have been satisfactorily indexed for orthorhombic symmetry by Hesse-Lipson's method²⁷. The lattice parameters calculated for the above symmetry are given below:

$\text{Ni}(\text{Heth})_3\text{Cl}_2$:

$$a = 7.593 \text{ \AA}, b = 9.168 \text{ \AA}, c = 15.100 \text{ \AA}, V = 1051 \text{ \AA}^3, \\ \rho = 1.52 \text{ g cm}^{-3}, Z = 2.$$

$\text{Cu}(\text{Heth})\text{Cl}_2$:

$$a = 7.244 \text{ \AA}, b = 10.390 \text{ \AA}, c = 15.750 \text{ \AA}, V = 1185 \text{ \AA}^3, \\ \rho = 1.42 \text{ g cm}^{-3}, Z = 4.$$

The results shown in Table 2 indicate that these complexes are fungitoxic and their activity increases with increasing concentration. The antifungal activity of these complexes is believed to be due to the presence of thiocarbonyl and hydrazine groups²⁸. $[\text{Co}(\text{Heth})_3]\text{Cl}_3$ is more fungitoxic than $[\text{Ni}(\text{Heth})_3]\text{Cl}_2$ and $[\text{Cu}(\text{Heth})\text{Cl}_2]$ as expected due to smaller²⁹ size of Co^{3+} as compared to those of Ni^{2+} and Cu^{2+} . Further, the higher toxicity of $\text{Ni}(\text{II})$ complex as compared to that of $\text{Cu}(\text{II})$ may be due to the higher coordination number of $\text{Ni}(\text{II})$.

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