

Synthesis, Structural & Antifungal Studies of Manganese(II), Iron(II), Cobalt(II), Nickel(II), Copper(II) & Zinc(II) Complexes of N,N'-Bis(ethoxythiocarbonyl)hydrazine & N-Ethoxycarbonyl-N'-ethoxythiocarbonylhydrazine

N K SINGH, S C SRIVASTAVA & R C AGGARWAL*

Department of Chemistry, Banaras Hindu University, Varanasi 221 005

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N,N'-Bis(ethoxythiocarbonyl)hydrazine [$C_2H_5OC(=S)NHNHC(=S)OC_2H_5$] (H_2 deth) and N-ethoxycarbonyl-N'-ethoxythiocarbonylhydrazine [$C_2H_5OC(=S)NHNHC(=O)OC_2H_5$] (H_2 eceth) form, after deprotonation, 1:1 complexes with Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) which are polymeric in nature. Magnetic and electronic spectral studies suggest square-planar geometry for Ni(deth) and Cu(II) complexes, tetrahedral geometry for Co(II) complexes, octahedral geometry for Fe(II) complexes, and a mixed geometry for Ni(eceth) (tetrahedral + square-planar). IR spectral studies show dinegative bridging tetradentate behaviour of the ligands, the bonding sites being thiole sulphur and enolic oxygen besides hydrazidic nitrogens. Antifungal activities of Co(II), Ni(II) and Cu(II) complexes have been studied against *Alternaria alternata* and *Fusarium oxysporum*. The first two complexes have been found to exhibit greater antifungal activities as compared to the respective ligands.

Transition metal complexes of diacyl hydrazines have been previously reported from our laboratories¹⁻³. Apparently, no work is reported on the complexes of mono- and di-thioacyl hydrazines. The synthesis and structural studies of the title complexes have therefore been undertaken and the results of these investigations are described in the present paper.

Materials and Methods

All the chemicals used were BDH or equivalent reagents. H_2 deth was prepared by the literature method⁴; m.p. 61-63° (lit.⁴ 60-62°). H_2 eceth was, however, prepared by adding slowly a freshly prepared ethanolic solution of ethyl carbazate (0.15 mol) to a solution of (ethoxythiocarbonyl) thioacetic acid (0.15 mol) in ~2N aqueous NaOH. The reaction mixture was left for ~4 hr at room temperature after adjusting its pH at 6.5-7.0. The liberated oil was extracted thrice with ether and the ethereal layer washed with water. The ethereal solution on slow evaporation afforded white crystals of H_2 eceth, which were filtered, washed with petroleum ether and dried *in vacuo*, yield ~60%, m.p. 84-87°. Ethyl carbazate⁵ and (ethoxythiocarbonyl) thioacetic acid⁶ required for the purpose were prepared following the literature procedures. Satisfactory elemental analyses were obtained in each case.

All the complexes except those of Fe(II) were prepared by mixing aqueous solution of the respective metal(II) acetate and the ethanolic solution of the ligands in 1:1 molar ratio followed by the addition of

sodium acetate to the reaction mixture. However, the Mn(II) complexes were precipitated by the addition of a few drops of dil. NH_4OH to the above reaction mixture. Fe(deth). $2H_2O$ and Fe(eceth). $2H_2O$ were prepared by mixing ethanolic solutions of $FeCl_2 \cdot 2H_2O$, ligands and KOH in ~1:1:2 molar ratio and subsequent stirring of the above reaction mixtures in hydrogen atmosphere to prevent their oxidation.

The complexes were analysed for their metal, nitrogen, hydrazine and sulphur contents as reported earlier⁷. The equipment and methods employed for recording magnetic susceptibility, electronic and infrared spectra were the same as described in our previous studies⁷. The values of $10 Dq$ and B' were calculated as described by Lever⁸.

The 1H NMR spectra of H_2 deth and H_2 eceth were recorded on a Varian A-60D spectrometer in $CDCl_3$.

The antifungal activities of H_2 deth, H_2 eceth and their Co(II), Ni(II) and Cu(II) complexes were evaluated against *Alternaria alternata* and *Fusarium oxysporum* by agar plate technique using fine suspension of the compounds at 200, 500 and 1000 ppm⁹. The number of replication in each case was three. The percentage inhibition 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 110 hr and T = diameter of the fungus colony in treated plates after the same period.

Table I—Characterization Data of H₂deth and H₂eceth Complexes

Compound	Colour	Found (Calc.), %				μ_{eff} (B.M.)
		Metal	N ₂ H ₄	N	S	
[Mn(deth)]	Light yellow	20.80 (21.06)	11.94 (12.27)	10.96 (10.74)	24.30 (25.54)	5.75
[Fe(deth).2H ₂ O]	Dark brown	19.02 (18.75)	—	10.02 (9.40)	21.32 (21.49)	4.85
[Co(deth)]	Green	21.98 (22.25)	11.78 (12.08)	10.12 (10.57)	24.10 (24.16)	4.56
[Ni(deth)]	Brown	21.94 (22.18)	11.88 (12.09)	10.34 (10.58)	24.47 (24.18)	Diamagnetic
[Cu(deth)]	Violet	23.72 (23.58)	11.20 (11.87)	10.78 (10.39)	23.99 (23.74)	1.87
[Zn(deth)]	White	23.78 (24.09)	12.04 (11.80)	10.76 (10.32)	23.20 (23.59)	Diamagnetic
[Mn(eceth)]	Light yellow	22.22 (22.42)	12.88 (13.06)	11.86 (11.44)	13.10 (13.06)	5.88
[Fe(eceth).2H ₂ O]	Dark brown	20.40 (19.83)	—	10.32 (9.94)	11.70 (11.36)	4.90
[Co(eceth)]	Green	23.47 (23.68)	12.72 (12.85)	11.01 (11.25)	12.62 (12.85)	4.32
[Ni(eceth)]	Light-purple	23.42 (23.60)	12.60 (12.87)	10.92 (11.27)	12.68 (12.87)	2.00
[Cu(eceth)]	Violet	24.88 (25.07)	12.40 (12.62)	11.38 (11.05)	13.02 (12.62)	1.89
[Zn(eceth)]	White	25.20 (25.61)	12.24 (12.53)	11.32 (10.97)	12.42 (12.53)	Diamagnetic

Results and Discussion

The analytical data given in Table I show the formation of 1:1 neutral complexes of the type ML.*n*H₂O [*n*=2 for Fe(II) and =0 for others] by the loss of two protons from the ligands. The complexes are insoluble in water and common organic solvents and have high melting or decomposition temperatures suggesting their polymeric nature. The loss of two water molecules at 135-140°C for Fe(II) complexes suggests that they are coordinated¹⁰.

The magnetic moments of Co(deth) and Co(eceth) are indicative of their tetrahedral geometry¹¹. The diamagnetism of Ni(deth) suggests its square-planar geometry while a magnetic moment of 2.0 B.M. for Ni(eceth) indicates that it presumably has a mixed geometry (tetrahedral + square planar)¹². The magnetic moments of Fe(II) and Mn(II) complexes correspond to the presence of four and five unpaired electrons respectively indicating that they are spin-free with octahedral/tetrahedral geometry. Magnetic moment values in the range 1.87-1.89 B.M. for Cu(II) complexes indicate square-planar geometry around Cu(II)¹³.

The visible region spectra of Fe(deth).2H₂O and Fe(eceth).2H₂O yield one broad band at 11765 and 10820 cm⁻¹ respectively which may be assigned to ⁵T_{2g} → ⁵E_g(D) transition in octahedral geometry around Fe(II)¹⁴.

The spectra of Co(deth) and Co(eceth) yield four bands in the regions 8265-8930, 9260-9615, 15385-16525 and 16000-17390 cm⁻¹. The first two bands may be attributed to splitting of ν_2 band [⁴A₂ → ⁴T_{1g}(F)(ν_2)] while the third and fourth bands may be due to the splitting of ν_3 band [⁴A₂ → ⁴T_{1g}(P)(ν_3)], characteristic of tetrahedral geometry around Co(II)¹⁵. The energies of ν_2 and ν_3 transitions have been calculated by the method of Drago¹⁶ from which 10 *Dq* and *B'* have been worked out to be, respectively, 5261 and 692 cm⁻¹ for Co(deth) and 5733 and 523 cm⁻¹ for Co(eceth).

The visible region spectrum of Ni(deth) shows two bands at 14815 and 21050 cm⁻¹ while that of Ni(eceth) yields three bands at 7940, 15625 and 19050 cm⁻¹. The bands occurring in the region 14815-21050 cm⁻¹ in both the complexes may be assigned to the transitions ¹A_{1g} → ¹B_{1g} and ¹A_{1g} → ¹B_{3g}, respectively, on the basis of square-planar geometry¹⁷. The single electron parameter Δ_1 and Δ_2 have been calculated to be 17614 and 7833 cm⁻¹ for Ni(deth) and 18425 and 5025 cm⁻¹ for Ni(eceth) as suggested by Gray *et al.*¹⁸ and assuming after Shupack *et al.*¹⁹ that $F_2 = 10F_4 = 800$ cm⁻¹. The additional band in Ni(eceth) may be attributed to ³T₁ → ³A₂(ν_2) transition in tetrahedral environment of Ni(II).

The bands observed at 18180 and 20000 cm⁻¹ in Cu(deth) and Cu(eceth), respectively, may be assigned to the envelopes of ²B_{1g} → ²A_{1g}; → ²B_{2g} and → ²E_g

transitions in square-planar geometry²⁰. The findings from the electronic spectral studies of the various complexes are in accord with the magnetic moment data already discussed.

The ¹H NMR spectrum of CH₃CH₂OC(=S)-NHNHC(=S)OCH₂CH₃ displays signals at δ 1.40 [t, *J* = 7 Hz, 6H, CH₃CH₂-], 4.60 [q, *J* = 7 Hz, 4H, CH₃CH₂OC(=S)-] and 8.25-9.38 [br, 2H, -NH-NH-] while that of CH₃CH₂OC(=S)NHNHC(=O)OCH₂CH₃ exhibits signals at δ 1.30 [t, *J* = 7 Hz, 3H, CH₃CH₂OC(=O)-], 1.36 [t, *J* = 7 Hz, 3H, CH₃CH₂(=S)-], 4.23 [q, *J* = 7 Hz, 2H, CH₃CH₂OC(=O)-], 4.51 [q, *J* = 7 Hz, 2H, CH₃CH₂OC(=S)-], 6.91-7.23 [br, 1H, =OC(=O)-NH-] and 8.46-9.16 [br, 1H, -OC(=S)-NH-]. The additional signals appearing at δ 1.30 and 4.23 for -CH₃ and -CH₂ protons, respectively, in the spectrum of the latter compound as compared to the former may be due to the presence of these groups in two different environments in the molecule. The poor solubility of the complexes in suitable solvents precluded their ¹H NMR study.

The ν (NH), ν (C=O) and thioamide-IV [(mainly due to ν (C=S)] bands found in the ligands at 3400, 1730 and ~810 cm⁻¹, respectively, disappear in the spectra of their complexes indicating destruction of these groups through deprotonation, thioenolisation and enolisation. The appearance of a new band in the region 710-720 cm⁻¹ due to ν (C-S) in the spectra of all the complexes and ν (NCO) in the region 1560-1600 cm⁻¹ in the spectra of only H₂(eceth) complexes are in accord with the above findings. The bands occurring in the regions 1440-1460, 1300 and 1050-1090 cm⁻¹ in the ligands due to thioamide-I (β NH + ν CN), -II (ν CN + β NH) bands²¹⁻²³ and ν (N-N)²⁴, respectively, show positive shifts of 40-80, 30-70 and 50-85 cm⁻¹ respectively in complexes, supporting bonding through thio sulphur and both the hydrazidic nitrogens.

The bands observed around 3300 cm⁻¹ and 720-740 cm⁻¹ in the hydrated Fe(II) complexes but absent in the anhydrous complexes may be assigned to ν (OH) and ρ (H₂O) modes of coordinated water molecules²⁵. The non-ligands bands occurring in the regions 350-390, 280-310 and 330-350 cm⁻¹ may be tentatively assigned to ν (M-N), ν (M-S) and ν (M-O) modes respectively^{22,26,27}.

The IR spectral studies thus indicate the dinegative bridging tetradentate behaviour of the ligands which coordinate through the two hydrazide nitrogens and thio sulphur atoms in the case of H₂deth and two hydrazidic nitrogens, enolic oxygen and thio sulphur in the case of H₂eceth.

The results of antifungal activity given in Table 2 show that the ligands and their complexes are

Table 2—Antifungal Activity of H₂deth and H₂eceth and their Complexes

[Medium: Czapek's; time 110 hr; temp. 25 ± 1°C]

Compound	Average percentage inhibition					
	<i>Alternaria alternata</i>			<i>Fusarium oxysporum</i>		
	(ppm)			(ppm)		
	200	500	1000	200	500	1000
H ₂ deth	56.00	65.00	68.80	62.50	71.00	72.00
[Co(deth)]	63.50	73.20	80.50	66.00	77.00	78.50
[Ni(deth)]	60.80	68.90	75.60	64.00	75.00	76.70
[Cu(deth)]	55.10	61.00	66.50	57.50	66.00	70.80
H ₂ eceth	38.00	56.00	78.00	37.80	50.70	68.60
[Co(eceth)]	52.00	60.50	84.00	44.70	58.20	76.10
[Ni(eceth)]	42.00	59.00	80.00	42.30	55.30	73.10
[Cu(eceth)]	36.00	42.00	50.00	37.30	41.80	49.20

fungitoxic and their activities increase with increasing concentrations. Further, the antifungal activities of Co(II) and Ni(II) complexes are greater than those of the free ligands. The antifungal activities of the ligands and their complexes are believed to be due to the presence of thioamide, amide and hydrazine groups²⁸.

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