

## Synthesis and Spectral Studies on Transition Metal Complexes Derived from a Physiologically Active Macrocyclic Ligand

P. VENKATESWAR RAO\*, K. ASHWINI and KANEEZ FATIMA

Department of Chemistry, Post Graduate College of Science

Saifabad, Hyderabad-500 004, India

E-mail: pallapothulav@yahoo.com

Complexes of VO(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) with a new ligand *N'*-1-[(*Z*)-1-(2-hydroxy-6-methyl-4-oxo-4H-3-pyran-2-yl) ethylidene]-2-[(*E*)-1-(2-hydroxy-6-methyl-4-oxo-4H-3-pyran-2-yl)ethylidene]-1-hydrazene carbothiohydrazide (HEHCTH) of composition [ML<sub>2</sub>·xH<sub>2</sub>O], where L = HEHCTH, x = 0 or 2, have been synthesized. The Cu(II) and Ni(II) complexes have been assigned square planar geometry, the Mn(II), Fe(II) and Co(II) complexes octahedral geometry and VO(II) complex is assigned a square pyramidal geometry. The ligand and the metal chelates have been screened for antibacterial activity.

**Key Words:** Synthesis, Transition metal complexes.

### INTRODUCTION

The chemistry of carbohydrazide and thiocarbohydrazide derivatives has been reviewed by Kurzer and Wilkinson<sup>1</sup>. Both the hydrazine groups are reactive towards carbonyl compounds and can yield mono- and di-hydrazones. The derivatives of thiocarbohydrazides possess various biological activities<sup>2,3</sup> and are also potent chelating agents<sup>4,5</sup>. Dehydroacetic acid [3-acetyl 6-methyl-2H-pyran-(2,4)-3H-dione] also possesses potential chelating ability besides its strong antifungal activities<sup>6</sup>. Hence, the transition metal complexes derived from *N'*-1-[(*Z*)-1-(2-hydroxy-6-methyl-4-oxo-4H-3-pyran-2-yl) ethylidene]-2-[(*E*)-1-(2-hydroxy-6-methyl-4-oxo-4H-3-pyran-2-yl)ethylidene]-1-hydrazene carbothiohydrazide (HEHCTH) are synthesized and characterized [Fig. 1].

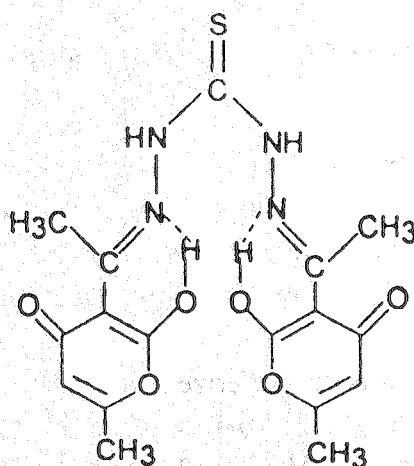


Fig. 1. Structure of the ligand [DHATCDH]

## EXPERIMENTAL

**Synthesis of the ligand:** To dehydroacetic acid (0.02 mol, 0.336 g) dissolved in hot ethanol (10 mL), thiocarbohydrazide (0.01 mol, 0.106 g) in hot ethanol (10 mL) was added and the mixture refluxed for 2–3 h. The pH of the solution was adjusted to 8 and was refluxed further for 3 h. The solution was then cooled overnight and the resulting yellow crystals were recrystallized in (1 : 1) ethanoldimethyl formamide solution and dried *in vacuo* (yield 73%, purity, 99%, m.p. 190°C).

**Synthesis of metal complexes:** A mixture of hot ethanolic solution of the metal chloride (0.01 mol) (except in the case of Fe(II) and VO(II) complexes where aqueous ethanolic solutions were used) and ligand (0.01 mol, 0.406 g) was refluxed for 3 h on a water bath. The pH was adjusted to 7–8 using methanolic sodium acetate solution. The solution was further refluxed for three more hours. Upon cooling the solution overnight the respective metal chelates separated out. The complexes were washed with ethanol, petroleum ether (60–80°) and dried *in vacuo* (yield 32–58%).

IR spectra (KBr) were recorded on a Perkin-Elmer 1380 spectrophotometer,  $^1\text{H}$  NMR spectra ( $\text{CF}_3\text{COOD}$  or  $\text{DMSO-d}_6$ ) on a Varian EM-390 (90 MHz) spectrometer using TMS as internal standard, mass spectra on a Finnigan MAT 8230 spectrometer at 70 eV, electronic spectra (nujol) were recorded on a DMR-21 spectrophotometer in the range 300–1500 nm and ESR spectra (powder) on a Varian EPR-E<sub>4</sub> spectrometer at liquid nitrogen temperature. Conductivity was measured in DMF at 25°C using a Systronics 304 conductivity meter. C, H, N were analyzed at CDRI, Lucknow. Magnetic susceptibility was measured on a Faraday (CAHN 7550-03) balance using  $\text{HgCo}(\text{SCN})_4$  as calibrant.

Dehydroacetic acid and thiocarbohydrazide were Fluka samples and were used as such. All the metal salts were AR samples. Solvents were purified before use.

## RESULTS AND DISCUSSION

All the metal complexes are coloured and they are stable towards air and moisture. They are insoluble in common organic solvents but are sparingly soluble in dimethyl formamide, dimethyl sulphoxide and dioxane. The analytical data (Table-1) show that the metal to ligand ratio in all the chelates has been found to be 1 : 1. The conductance data (Table-1) show that all the metal chelates are non-electrolytes.

The ligand (HEHCTH) was characterized by analytical, IR,  $^1\text{H}$  NMR and mass spectral data:  $\delta$  ( $\text{CF}_3\text{COOD}$ ), 2.15 (6H, s, pyran C<sub>6</sub>-CH<sub>3</sub>), 2.6 (6H, s, C<sub>7</sub> and C<sub>13</sub>-CH<sub>3</sub>), 5.65 (2H, s, pyran C<sub>5</sub>-H), 7.9 (2H, s, NH), 11.3 (2H, s, OH);  $m/z$  406 ( $\text{M}^+$ ).

TABLE-I  
PHYSICAL DATA OF THE LIGAND AND METAL COMPLEXES

Compound	Colour	$\Lambda_M$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	m.p. ( $^{\circ}\text{C}$ )
HEHCTH(L)	Yellow	—	190
VO(II)L	Green	12.6	>245
Mn(II)L·2H <sub>2</sub> O	Yellow	16.8	>250
Fe(II)L·2H <sub>2</sub> O	Brown	21.3	>260
Co(II)L·2H <sub>2</sub> O	Red	20.1	>270
Ni(II)L	Red	18.4	>230
Cu(II)L	Black	17.8	>245

\*All compounds gave satisfactory elemental analyses.

IR spectrum of the ligand showed bands at  $3400 \text{ cm}^{-1}$  which is (intramolecular H bonded OH) vibration. The medium intensity bands observed at  $1700 \nu(\text{C}=\text{O})$  (lactone),  $1680 \nu(\text{C}=\text{O})$  (azide),  $1640 \nu(\text{C}=\text{N})$  (azomethine) and  $1510 \nu(\text{C}-\text{O})$  (phenolic)<sup>7</sup>. In the spectra of all the complexes the band at  $3400 \text{ cm}^{-1}$  disappeared. In the spectra of Mn(II), Fe(II) and Co(II) a broad band characteristic of  $\nu(\text{OH})$  of coordinated water was observed<sup>8</sup> in the range  $3500-3200 \text{ cm}^{-1}$ . The presence of coordinated water is further confirmed by the appearance of a non-ligand band at  $840-830 \text{ cm}^{-1}$ , assignable to rocking mode of water<sup>9</sup>. Besides, it is also established by TG and DT analyses. The absence of the ligand band at  $3400 \text{ cm}^{-1}$  ( $\nu(\text{OH})$  phenolic) of the ligand in the spectra of all the complexes suggests the cleavage of intramolecular hydrogen bonded  $\nu(\text{OH})$  and subsequent deprotonation of the phenolic group and coordination of phenolic oxygen to the metal ion. This is further confirmed<sup>10</sup> by an upward shift in  $\nu(\text{C}-\text{O})$  (phenolic) band at ( $1510 \text{ cm}^{-1}$ ) by  $20-30 \text{ cm}^{-1}$ . The chelation of  $\nu(\text{C}-\text{O})$  has been found to be mono-dentate in nature. This is further substantiated by the disappearance of <sup>1</sup>H NMR signal of OH at  $\delta$  11.3 of the free ligand in the spectra of the complexes. The ligand band at  $1640 \text{ cm}^{-1}$  in the free ligand underwent a downward shift by  $20-30 \text{ cm}^{-1}$  in the spectra of all the complexes, suggesting the participation of azomethine nitrogen in complexation<sup>11</sup>. A sharp band at  $960 \text{ cm}^{-1}$  in the case of VO(II) complex<sup>12</sup> is due to  $\nu(\text{V}=\text{O})$ . New bands have been observed in the region  $600-400 \text{ cm}^{-1}$ , which are attributed to  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{O})$ <sup>13</sup>. From the IR spectral data, it has been concluded that HEHCTH behaves as a dibasic tetradentate ligand coordinating through deprotonated phenolic oxygens and azomethine nitrogens in O : N : N : O donor sequence.

TG and DT analyses of the complexes show the presence of two moles of coordinated water in case of Mn(II), Fe(II) and Co(II). Two endothermic peaks are observed in the DT analyses. The loss of water occurs at  $165$  and  $175^{\circ}\text{C}$ ,  $156$  and  $164^{\circ}\text{C}$  and  $160$  and  $163^{\circ}\text{C}$  for Mn(II), Fe(II) and Co(II) complexes, respectively.

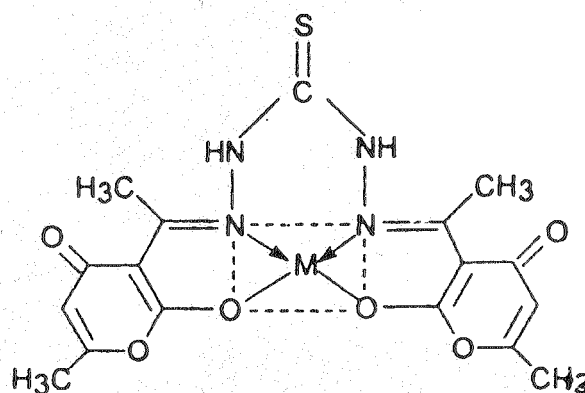
The magnetic moment values of all the complexes have been determined at room temperature ( $27^{\circ}\text{C}$ ). All the complexes are paramagnetic except Ni(II) complex which is diamagnetic. The  $\mu_{\text{eff}}$  values of VO(II), Mn(II), Fe(II), Co(II)

and Cu(II) complexes are 1.85, 5.90, 4.87, 4.1 and 1.81 B.M., respectively. They are in accordance with the geometry of the complexes.

The electronic spectrum of VO(II) complex exhibited three transitions at 13699, 17483 and 22321  $\text{cm}^{-1}$  which were assigned to  ${}^2E \leftarrow {}^2B_2(\nu_1)$ ;  ${}^2B_1 \leftarrow {}^2B_2(\nu_2)$  and  ${}^2A_1 \leftarrow {}^2B_2(\nu_3)$  transitions in a square pyramidal geometry<sup>14</sup>. The UV-Vis spectrum of the Mn(II) complex exhibited three absorption peaks at 8390, 17250, 19240  $\text{cm}^{-1}$ . The spectrum of Fe(II) complex showed two transitions at 12346 and 18657  $\text{cm}^{-1}$  which were assigned  ${}^5E_g \leftarrow {}^5T_{2g}$  and to a charge transition respectively in an octahedral geometry<sup>15</sup>. The Co(II) complex showed two main absorption bands at 8772 and 17606  $\text{cm}^{-1}$  which were attributed to  ${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)(\nu_1)$  and  ${}^4T_{2g}(P) \leftarrow {}^4T_{1g}(F)(\nu_2)$  transitions in an octahedral configuration around the metal<sup>14</sup>. The electronic spectral bands of the Ni(II) complex at 15267 and 22989  $\text{cm}^{-1}$  were assigned to  ${}^1A_{2g} \leftarrow {}^1A_{1g}(\nu_1)$  and  ${}^1B_{1g} \leftarrow {}^1A_{1g}(\nu_2)$  transitions in a square planar geometry<sup>15</sup>. The red colour of the complex and the absence of a transition band below 10,000  $\text{cm}^{-1}$  indicate the absence of octahedral and tetrahedral geometries. The Cu(II) complex showed two absorption bands at 15140 and 19607  $\text{cm}^{-1}$  which were assigned to  ${}^2A_{1g} \leftarrow {}^2B_{1g}(\nu_1)$  and  ${}^2E_g \leftarrow {}^2B_{1g}(\nu_2)$  transitions in a square planar geometry and in a  $D_{4h}$  symmetry<sup>16</sup>.

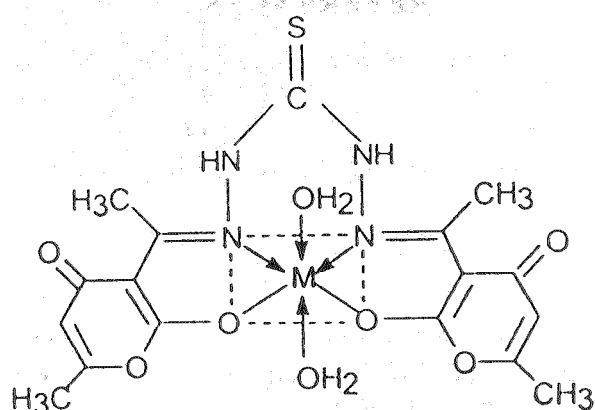
The ESR spectrum of Cu(II) complex was recorded in powder form at room temperature. The spectrum shows  $g_{\parallel}$ ,  $g_{\perp}$  and  $g_{av}$  values of 2.195, 2.047 and 2.096, respectively. The  $g_{av}$  was calculated from the equation  $g_{av} = 1/3 (g_{\parallel} + 2g_{\perp})$ . These values indicate that the overall symmetry around Cu(II) is  $D_{4h}$ . The  $g_{\parallel}$  value (2.195) is less than 2.3 and hence the metal ligand bonding in this complex is regarded as covalent.

On the basis of the results octahedral geometry has been proposed for the Mn(II), Fe(II) and Co(II) complexes, square planar geometries to Ni(II) complex and Cu(II) complexes and square pyramidal geometry to VO(II) complex (Figs. 2–4).



where M = Cu(II), Ni(II)

Fig. 2. Proposed structure of Ni(II) and Cu(II) complexes



where M = Mn(II), Fe(II) and Co(II)

Fig. 3. Proposed structure of Mn(II), Fe(II) and Co(II) complexes

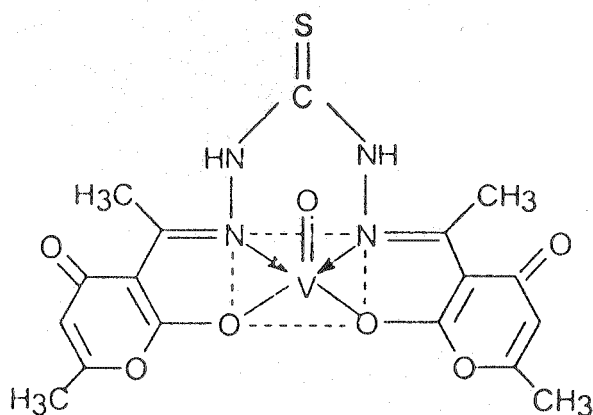


Fig. 4. Proposed structure of VO(II) complex

### Bacteriological testing

Bacteriological testing was done using paper disc method at concentrations 500 and 1000  $\mu\text{g/mL}$  in DMF against *E. coli* and *S. aureus*. It is observed that the ligand showed 8.2 and 42.5% inhibition at 500 and 1000  $\mu\text{g/mL}$  against *E. coli* and 6.8 and 41.5% against *S. aureus* at the same concentration. The complexes also show a minimum percentage inhibition of 9.5% at 500  $\mu\text{g/mL}$  and 40.5–100% inhibition at 1000  $\mu\text{g/mL}$  against *E. coli* and a minimum of 9.8% at 500  $\mu\text{g/mL}$  and 42–100% inhibition at 1000  $\mu\text{g/mL}$  against *S. aureus*.  $\text{LD}_{50}$  for physiological activity is 250  $\mu\text{g/mL}$ .

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## REFERENCES

1. B. Moubaralli, K.S. Murray, D.J. Ranford, J.J. Vittal and X.W. Xiaobai, *J. Chem. Soc., Dalton Trans.*, **20**, 3573 (1999).
2. K. Rachana and P. Singh, *Asian J. Chem.*, **12**, 23 (2000).
3. M.T.S. Cordero, A.G. Torres and J.M. Canopavon, *Talanta*, **40**, 691 (1993).
4. N.K. Singh and S.K. Kushawaha, *Synth. React. Inorg. Met.-Org. Chem.*, **34**, 1769 (2004).
5. D.S. Rao, C.S. Reddy, M.C. Ganorkar and V.T. John, *Curr. Sci.*, **49**, 511 (1980).
6. N.K. Singh and S.K. Kushawaha, *Indian J. Chem.*, **39A**, 1070 (2000).
7. N.S. Biridar, V.B. Mahale and B.R. Havinale, *Curr. Sci., Sect. A.*, **45**, 6 (1976).
8. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, pp. 159, 167, 214 (1970).
9. P.S. Mane, S.G. Shirodkar and T.K. Chondhekar, *J. Indian Chem. Soc.*, **79**, 376 (2002).
10. D.C. Dash, A. Mahapatra, P. Jena and S.B. Patjoshi, *J. Indian Chem. Soc.*, **79**, 339 (2002).
11. D.U. Warad, C.D. Satish, V.H. Kulkarni and S.B. Chandrasekhar, *Indian J. Chem.*, **39A**, 415 (2002).
12. N.K. Gaur, R. Sharma and R.S. Sindhu, *J. Indian Chem. Soc.*, **78**, 26 (2001).
13. K.L. Reddy and S. Upendar, *Indian J. Chem., Sect. A.*, **39**, 1202 (2000).
14. M.B.H. Howalder, M.S. Islam and M.R. Karim, *Indian J. Chem.*, **39A**, 407 (2000).
15. K.R. Chowdhary, B.N. Keshari and L.K. Mishra, *J. Indian Chem. Soc.*, **77**, 29 (2000).
16. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, New York, pp. 272, 324, 334 (1968).

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