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Synthesis and Structural Studies on Transition Metal Complexes Derived from 1-(2-Thienyl)-1-ethanole-1H-benzimidazole-2-yl-hydrazone

M. NEELAMMA, B. BHARATH KUMAR and P. VENKATESWAR RAO*
Department of Chemistry, P.G. College of Science, Saifabad, Hyderabad-500 004, India
E-mail: pallapothulav@yahoo.com

Transition metal complexes of Cr(III), Fe(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with 1-(2-thienyl)-1-ethanole-1H-benzimidazole-2-yl-hydrazone (TEBH) have been synthesized. The ligand and its metal complexes were characterized by analytical data, conductance measurements, thermogravimetric and differential thermal analyses, magnetic susceptibility measurements, infrared, ^{1}H NMR, electronic, mass and ESR spectral studies. All the complexes possess the general formulae $[M(II)LCl_2{\cdot}H_2O]$ and $[M(III)LCl_3]$, where L = TEBH. Infrared spectral data suggest that the ligand TEBH behaves as a neutral tridentate ligand with N : N : S donor sequence. On the basis of spectral and analytical data it is proposed that all the complexes possess an octahedral geometry. The ligand and its metal complexes were screened for their physiological activities against *E. coli* and *S. aureus*. The order of activity has been found to be Ni(II) > Cr(III) > Co(II) > Fe(III) > Cu(II) > Zn(II) > ligand against *E. coli* and Cu(II) > Ni(II) > Cr(III) > Zn(II) > Fe(III) > Mn(II) > ligand against *S. aureus*.

Key Words: 1-(2-Thienyl)-1-ethanole-1H-benzimidazole-2-yl-hydrazone, 2-Hydrazino benzimidazole, Transition complexes.

INTRODUCTION

The chemistry and physiological activities of benzimidazole derivatives and their metal complexes are of recent interest[1, 2]. Hydrazones of benzimidazole are biologically active against different bacteria, fungi and microbes. The ligand in the present investigation, 1-(2-thienyl)-1-ethanol-1H-benzimidazole-2-yl-hydrazone (TEBH) (Fig. 1) is a potential chelating agent. Besides its chelating ability, it also has promising antimicrobial activities[3–6]. In view of this, the work on the title compounds was undertaken and the results are reported here.

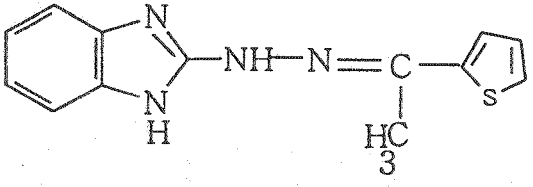


Fig. 1. 1-(2-Thienyl)-1-ethanol-1H-benzimidazole-2-yl-hydrazone

EXPERIMENTAL

All the metal salts and solvents used were E. Merck products. Mercapto benzimidazole, hydrazine hydrate and 2-acetyl thiophene are Fluka reagents. All the other chemicals used were of AR grade.

Elemental analysis (C, H, N and S) was carried out using microanalytical techniques on Heraeus-CHN rapid analyzer. Metal estimations were done on a Perkin-Elmer-2380 atomic absorption spectrophotometer, conductivity measurements were carried out on Elico digital conductivity meter model No. CM-180. The magnetic susceptibility measurements were done on a Faraday balance (CAHN-7600) using $Hg[Co(SCN)_4]$ as calibrant. Thermogravimetric and differential thermal analyses were done on Leeds and Northrup instrument (USA). Infrared spectra were recorded on a Perkin-Elmer-1600 FT-IR spectrophotometer in nujol mull. The electronic spectra were recorded on a Shimadzu UV-160 spectrophotometer. ^1H NMR was obtained on a Varian-XL-200 MHz NMR spectrophotometer using $CDCl_3$ and DMSO-d_6 as solvents. ESR spectra were recorded at room temperature on Jeol-SE-3X ESR spectrophotometer using DPPH as standard.

Synthesis of ligand

2-Acetyl thiophene (0.01 mol, 1.26 g) was added to a solution of 2-hydrazino benzimidazole (0.01 mol, 1.48 g) in methanol (100 mL) and the mixture was refluxed for about 3 h. Later on the mixture was poured into ice-cold water, when a brown crystalline compound separated out. It was filtered and rectrystallized from methanol.

Syntheses of metal complexes

The metal chelates were prepared by refluxing the methanolic solutions of the respective metal chlorides (0.01 mol) and the ligand 1-(2-thienyl)-1-ethanol-1H-benzimidazole-2-yl-hydrazone (0.01 mol, 2.44 g) on a water bath for about 3–4 h. The pH of the solution was adjusted to 7 by dropwise addition of 10% methanolic ammonia solution. The metal chelates were separated out after cooling overnight and washed with methanol followed by petroleum ether (60–80°C) and dried in vacuum.

RESULTS AND DISCUSSION

All the metal chelates except Zn(II) complex are coloured. They are stable towards air and moisture, decompose at high temperatures (500–600°C). They are insoluble in common organic solvents, but are soluble in DMF and DMSO. The analytical data (Table-1) of the metal complexes show that all the metal chelates have 1 : 1 metal to ligand stoichiometry. Molar conductance values of the complexes in 1×10^{-3} M DMF solution at room temperature suggest their non-electrolytic nature. All the complexes possess the general compositions $[M(II)LCl_2 \cdot H_2O]$ (M = Mn, Co, Ni, Cu or Zn) and $[M(III)LCl_3]$ (M = Cr or Fe) where L = TEBH.

^1H NMR spectrum of the ligand in DMSO-d^6 exhibits the following signals (δ, ppm): 8.0 (s, NH-proton), 6.9, 7.1 and 7.5 (m, thiophene ring protons), 2.1 (s, CH_3, protons) and two sharp multiplets at 7.28 and 7.45 due to aromatic benzimidazole protons.

The infrared spectrum of the ligand shows a sharp peak at 3500 cm^{-1} which is assigned to ν(NH) (free). The ν(NH) (ring) is observed at 3059 cm^{-1}. Two sharp bands observed at 1624 and 1558 cm^{-1} are ascribed to ν(C═N) (free), ν(C═N) (ring), respectively. A band observed at 864 cm^{-1} is due to ν(C═S) stretching vibration[7]. The ν(N—N) stretching frequency is observed at 1025 cm^{-1}. A broad trough due to NH protons in the spectrum of the ligand is changed to two sharp peaks in the spectra of complexes indicating the restriction of mobility of NH protons in complexes. These would have a free mobility in free ligand[8]. The stretching frequency due to ν(C═N) (free), which was at 1624 cm^{-1}, underwent a downward shift of 20 cm^{-1} upon complexation, confirming the participation of azomethine nitrogen in complexation[9]. The ν(C═N) (ring) which was at 1558 cm^{-1} in the ligand undergoes a negative shift of 25 cm^{-1} in complexes, thereby substantiating the involvement of ν(C═N) (ring) in chelation[10]. The positive shift of ν(N—N) at 1025 cm^{-1} by 20–28 cm^{-1} in the complexes further supports the participation of azomethine nitrogen (free) in complexation. The ν(NH) out-of-plane deformation vibration of free ligand remains unaltered, ruling out the possibility of involvement of imine nitrogen in coordination[9]. The ν(C═S) vibration undergoes a negative shift of 20 cm^{-1}, supporting its involvement in complex formation. The presence of non-ligand bands in the regions 920–840 and 685–625 cm^{-1} indicates the rocking and wagging modes, which support the presence of coordinated water. The presence of coordinated water is further established by TG and DT analyses. The far infrared spectra of metal complexes exhibit non-ligand bands in the range 400–200 cm^{-1} which indicate the ν(M—Cl) bonds and the bands in the region 600–400 cm^{-1} are assigned to ν(M—N) and ν(M—S) bonds. On the basis of infrared spectral data the ligand TEBH behaves as a neutral tridentate N : N : S donor ligand.

TABLE-1
ANALYTICAL DATA OF TEBH METAL COMPLEXES

Complex (m.f.)	Anal. (%), Calcd. (Found)						Λ_M (mho cm^2 mol^{-1})
	C	H	N	Cl	S	M	
Ligand $C_{13}H_{12}N_4S$	60.93 (60.90)	4.68 (4.66)	21.87 (21.82)	—	12.5 (12.47)	—	—
Cr(III) complex $CrC_{13}H_{12}N_4SCl_3$	37.60 (37.57)	2.89 (2.84)	13.51 (13.48)	25.65 (25.62)	7.70 (7.67)	12.52 (12.50)	35
Mn(II) complex $MnC_{13}H_{14}N_4OSCl_2$	39.00 (38.94)	3.50 (3.57)	14.00 (13.94)	17.75 (17.71)	8.00 (7.96)	13.72 (13.68)	11
Fe(III) complex $FeC_{13}H_{12}N_4SCl_3$	37.29 (37.24)	2.86 (3.82)	13.38 (13.34)	25.46 (25.42)	7.65 (7.63)	13.33 (13.28)	37
Co(II) complex $CoC_{13}H_{14}N_4OSCl_2$	38.62 (38.59)	3.46 (3.42)	13.86 (13.82)	17.57 (17.52)	7.92 (7.89)	14.58 (14.54)	15
Ni(II) complex $NiC_{13}H_{14}N_4OSCl_2$	38.64 (38.60)	3.46 (3.43)	13.87 (13.84)	17.58 (17.53)	7.92 (7.90)	14.54 (14.49)	36
Cu(II) complex $CuC_{13}H_{14}N_4OSCl_2$	38.18 (38.14)	3.42 (3.39)	13.70 (13.66)	17.38 (17.35)	7.38 (7.36)	15.54 (15.49)	34
Zn(II) complex $ZnC_{13}H_{14}N_4OSCl_2$	3.02 (38.00)	3.41 (3.38)	13.64 (13.62)	17.30 (17.27)	7.79 (7.75)	15.91 (15.87)	14

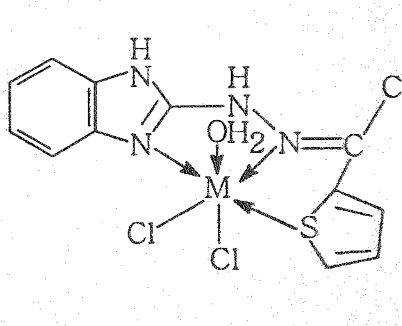
TG and DT analyses of the complexes exhibit endothermic and exothermic peaks. The loss of coordinated water is observed in the range 160–190°C. The loss of water is a one-step process. In all the chelates of divalent metals, one mole of coordinated water is lost per mole of the complex. The loss of coordinated water occurs at 160°C for Cu(II), at 180°C for Co(II), at 190°C for Ni(II), at 170°C for Mn(II) and Zn(II) complexes. The exothermic peaks around 300–400°C region in all the complexes may be due to phase transfer of the complexes and the endothermic peaks around 500–600°C are due to melting of complexes.

The magnetic moment value for Cr(III) complex is 4.0 BM, which is well within the range for octahedral stereochemistry. The magnetic moment of Fe(III) complex is 5.95 BM, which is consistent with octahedral geometry. The Mn(II) complex possesses a magnetic moment value of 6.0 B.M. and is in the range of octahedral complexes. The Co(II) complex has a value of 4.68 B.M., which coincides well with the octahedral geometry. The Ni(II) complex exhibits a value of 2.9 B.M. which is well within the range of octahedral metal chelates. The Cu(II) complex shows a magnetic moment value of 2.1 B.M., which is well within the range of octahedral geometry[11].

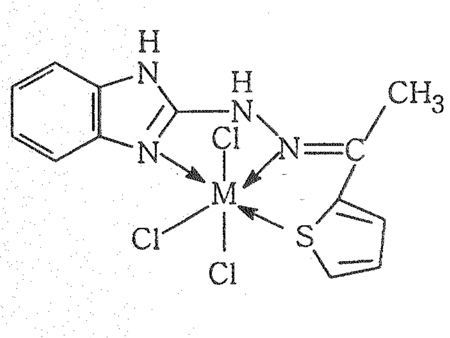
The electronic spectrum of Cr(III) complex shows two medium intensity bands at 26666 and 18346 cm^{-1}. These are assignable to $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{2g}(F)$. These transitions are in accordance with octahedral geometry. The electronic spectrum of Mn(II) complex shows two weak absorption bands at 15174 and 26315 cm^{-1} which are not of any help in deciding the geometry. The Fe(III) complex shows absorptions at 13793 and 27777 cm^{-1} which cannot be assigned to any transitions. However, other data suggest that they are octahedral in geometry. The Co(II) complex shows three absorption bands centred at 13297, 18018 and 22177 cm^{-1} which are interpreted to be $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively[12]. These are in accordance with octahedral geometry. The Ni(II) complex shows three absorption bands at 13700, 15150 and 23250 cm^{-1} which are ascribed to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, respectively in an octahedral disposition[13]. The Cu(II) complex exhibits absorption bands at 13986, 14925 and 22123 cm^{-1} which are assigned to $^2B_1 \rightarrow {}^2A_2$, $^2B_1 \rightarrow {}^2B_2$ and $^2B_1 \rightarrow {}^2E$ transitions in a distorted octahedral stereochemistry[14].

The ESR spectrum of Cu(II) complex at room temperature shows a peak at 2.052, which is assigned to g_{av} value and it is consistent with the octahedral geometry of the complex.

On the basis of analytical, conductivity, magnetic susceptibility measurements, TGA and DTA, IR, electronic and ESR spectral data, octahedral stereochemistry may be proposed for all the complexes as follows:



M(II) complexes (M = Mn, Co, Ni, Cu or Zn)



M(III) complexes (M = Cr or Fe)

Physiological activity

The culture medium was prepared by the addition of 1.5 g of beef extract, 1.5 g of yeast extract, 5.0 g of peptone, 1.0 g of dextrose, 3.5 g of NaCl, 3.68 g of dipotassium hydrogen phosphate, 1.32 g of monopotassium dihydrogen phosphate and 15 g of agar agar in one litre of water. The pH of the medium was adjusted to 7. The medium was sterilized at 121°C in an autoclave at 15 lbs pressure for 15–20 min. The medium was cooled to 45–50°C. 20 mL of medium was poured in each of the petridishes. All the apparatus used were sterilized before use. *E. coli* and *S. aureus* were introduced into the petri plates and were grown.

Bacteriological testing

Bacteriological testing was done using paper disc method. Paper discs were soaked in the solutions of ligand and complexes in DMF. Solutions were prepared in two different concentrations, *i.e.*, 100 µg/mL and 1000 µg/mL. Paper discs were sterilized and soaked in these solutions. They were dried. The dried paper discs were introduced into the fully grown culture plates of *E. coli* and *S. aureus*. The percentage inhibition of bacteria was calculated by the following equation:

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

where C = diameter (mm) in the controlled plates after 72 h and T = diameter of bacteria in treated plates after 72 h. From the data it is observed that the ligand shows 8.9 and 44.5% inhibition at 100 µg/mL and 1000 µg/mL. The complexes also show a minimum percentage inhibition of 9.29% at 100 µg/mL and 44.5–100% inhibition at 1000 µg/mL. The order of inhibition against *E. coli* is Ni(II) > Cr(III) > Co(II) > Fe(III) > Cu(II) > Zn(II) > ligand. The order of inhibition against *S. aureus* is Cu(II) > Ni(II) > Cr(III) > Zn(II) > Fe(III) > Mn(II) > ligand.

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