Asian Journal of Chemistry Vol. 20, No. 1 (2008), 579-585

Synthesis and Characterization of Chromium(III), Manganese(II), Iron(III), Cobalt(II), Nickel(II) and Copper(II) Complexes with N-Phenyl-*p*-nitrobenzohydroxamic Acid

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Transition metal complexes of the reagent N-phenyl-*p*-nitrobenzohydroxamic acid (HPNBHA) with Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II), have been synthesized and their structures were characterized by various physico-chemical methods such as elemental analysis, molar conductance, electronic spectra, FTIR, ^{1}H NMR and magnetic susceptibility measurements. The elemental analysis data reveal the composition of the divalent and trivalent metal ion complexes as $M(PNBHA)_2$ and $M(PNBHA)_3$, respectively. The conductivity measurements data suggests their non electrolytic behaviour, while susceptibility values of all the complexes indicate their paramagnetic nature. The IR spectral studies of the metal complexes show that they are formed by five membered ring structure where the metal atom is bonded to two oxygen atoms.

Key Words: Synthesis, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Complexes, N-Phenyl-*p*-nitro-benzohydroxamic acid.

INTRODUCTION

The coordination compounds formed by transition metal ions with benzohydroxamic acid and it's derivatives have been studied with respect to their kinetics and determination of stability constants. Benzohydroxamic acid and its derivatives are largely employed in the extraction and spectrophotometric determination of various metal ions[1,2] and some of them have been found to be good precipitating agents, useful in gravimetric analysis[3-5]. The work on kinetics and stability constants of transition metal complexes formed by these acids is found to be very common. The chelating ability of benzohydroxamic acid and its derivatives have been studied to suggest their use as chelating agents[6-9]. N-Phenyl-*p*-nitrobenzohydroxamic acid (HPNBHA) is one such derivatives of benzohydroxamic acid which have been reported to be one of the best analytical reagent[10,11]. The stability and structural discussion of its tin complexes have been studied[12]. However, there is no work reported on the synthesis and structural investigation of the solid complexes formed by this ligand with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) metal ions. Hence the present work describes the preparation and structural elucidation of these complexes by various physico-chemical techniques.

EXPERIMENTAL

All the chemicals used were of AR grade. Elemental analysis and ^{1}H NMR spectra were recorded at sophisticated analytical instruments facility center (SAIF), IIT Powai. Electronic spectra were recorded on Jasco UV/Vis. V-530 Spectrophotometer and IR spectra on Jasco FT/IR-410 spectrometer. The magnetic moment values at room temperature were measured on Guoy's balance using $Hg[Co(NCS)_4]$ as calibrant at Institute of Science, Mumbai. Molar conductance measurement were done using an Elico-digital conductivity meter.

The ligand, N-phenyl-*p*-nitrobenzohydroxamic acid was prepared by reduction of nitrobenzene using zinc dust to give N-phenyl hydroxylamine, followed by its condensation with *p*-nitrobenzoyl chloride.The crude product was crystallized twice with methanol. The purity of compound was monitored by TLC using silica gel (Yield-60 %, melting point-167 ºC). The metal complexes were synthesized by mixing aqueous solution of metal ion with methanolic solution of ligand in appropriate ratio. The pH of the mixture was adjusted by solution of sodium acetate and resulting mixture was refluxed for 2 h. The complexes so obtained were filtered, washed repeatedly with hot distilled water and alcohol, dried and analyzed.

RESULTS AND DISCUSSION

All the transition metal complexes are coloured solids and have limited solubility in common organic solvents such as methanol, chloroform, acetone and dimethyl sulphoxide except that of Cu(II) and Fe(III) complex.

The analytical data of the complexes (Table-1) suggest 1:2 metal-ligand stoichiometry for Mn(II), Co(II), Ni(II), Cu(II) complexes and 1:3 metal-ligand stoichiometry for Cr(III) and Fe(III) complexes. Low molar conductance values (Table-1) of these complexes in nitrobenzene indicates their non-electrolytic nature[13].

The room temperature magnetic moments of all the complexes are listed in Table-1. The magnetic moment values suggest that they are paramagnetic in nature. The observed magnetic moment of Co(II) and Ni(II) complexes are found to be slightly higher than spin-only values suggesting that they possess high-spin octahedral stereochemistry with a considerable orbital contribution[14,15]. The insoluble nature of these complexes in common organic solvents indicate that they are six-coordinate and polymeric in nature.The octahedral environment in these complexes is probably achieved by metal ion having linkage through oxygen donor atom of neighbouring ligand molecules (Fig. 1).

TABLE-1
ANALYTICAL DATA OF COMPLEXES OF HPNBHA

Complex/colour	Elemental analysis: Found (Calcd.) %				μ_{eff} (BM)	Molar conductance (S cm^2 mol^{-1})
	C	H	N	M		
HPNBHA (Shining yellow)	60.41 (60.46)	3.82 (3.87)	10.79 (10.85)	–	–	–
Cr(PNBHA)$_3$·2H$_2$O (Dark green)	56.52 (56.65)	3.58 (3.63)	10.01 (10.16)	6.69 (6.29)	3.64	0.80
Mn(PNBHA)$_2$ (Yellowish orange)	54.13 (54.65)	3.49 (3.50)	9.79 (9.80)	9.60 (9.61)	5.69	0.70
Fe(PNBHA)$_3$ (Brick red)	56.14 (56.39)	3.58 (3.61)	10.05 (10.12)	6.63 (6.73)	5.72	0.20
Co(PNBHA)$_2$ (Light brown)	53.99 (54.27)	3.40 (3.47)	9.69 (9.74)	10.20 (10.21)	4.81	1.45
Ni(PNBHA)$_2$ (Dark yellow)	54.23 (54.28)	3.42 (3.48)	9.60 (9.74)	10.19 (10.21)	3.34	0.40
Cu(PNBHA)$_2$ (Green)	53.54 (53.83)	3.37 (3.45)	9.61 (9.66)	10.89 (10.95)	1.78	0.60

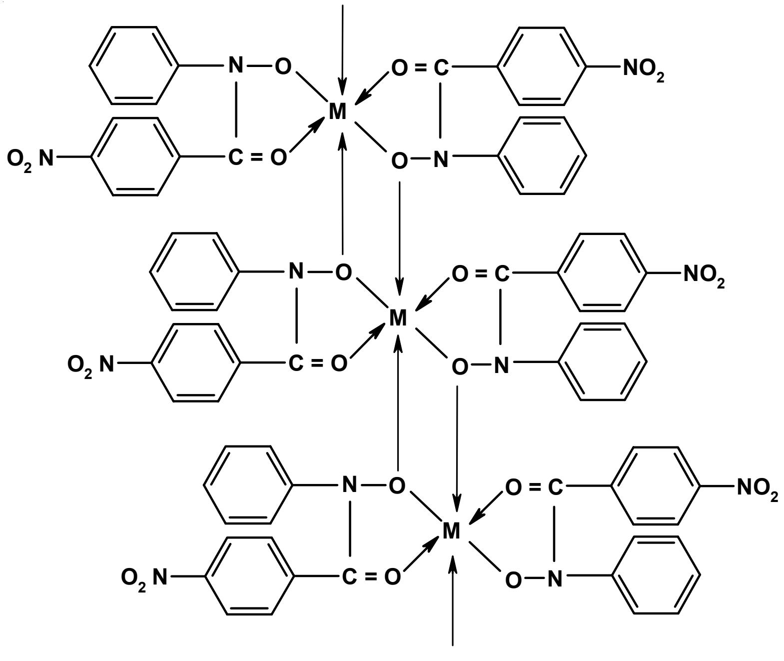

Fig. 1. Tentative structure of Mn(II), Co(II) and Ni(II) complex [M = Mn(II), Co(II) and Ni(II)]

The Mn(II) complex has magnetic moment of 5.69 BM which suggest that it is a high-spin six-coordinate octahedral complex. It's insolubility in common organic solvents may be attributed to its polymeric nature (Fig. 1). The observed magnetic moment of Fe(III) and Cr(III) complexes are close to the spin-only value suggesting a typical octahedral geometry[16,17]. The experimental magnetic moment of Cu(II) complex is found to be 1.79 BM which is close to spin-only value of 1.78 BM thereby suggesting a distorted octahedral structure[18].

The ^1H NMR spectrum of ligand in $CDCl_3$ exhibit a small peak around 9.1-9.2 ppm and a strong multiplet pattern in the region 7.2-7.7 ppm which has been attributed to proton resonance signal due to N-OH group and phenyl group, respectively[19]. The ^1H NMR spectrum of all the complexes reveal the absence of the proton signal due to N-OH group indicating that the proton of N-OH group is replaced on complexation with the metal ion.

The IR spectrum of the ligand and it's metal complexes have been examined in the region from 4000-400 cm^{-1}. The IR spectrum of the ligand exhibit a strong and broad absorption[20] near 3191 cm^{-1}. However, in it's partially deuterated form, the same absorption is reduced considerably and new band is exhibited[21] around 2400 cm^{-1}. Therefore, the observed band around 3191 cm^{-1} in HPNBHA is attributed to ν-OH absorption. Actually the absorption due to free OH as a strong band is predicted in the region[22,23] 3600-3200 cm^{-1}. Hence the observed absorption frequency of ν-OH band in the IR spectrum of the ligand HPNBHA towards lower side may be due to presence of intramolecular hydrogen bonding[24,25] (Fig. 2).

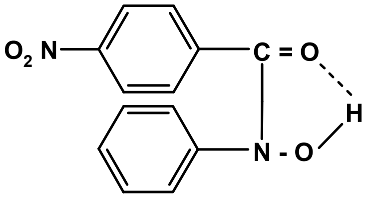

Fig. 2. Intramolecular hydrogen bonding in the ligand HPNBHA

In the IR spectrum of the ligand, another strong absorption is observed at 1620 cm^{-1} which has been assigned to ν(C=O) band. The free ν(C=O) absorption is expected around 1700 cm^{-1}. Therefore, the lowering of ν(C=O) absorption frequency in the ligand HPNBHA, confirms the presence of intramolecular hydrogen bonding[26,27] (Fig .2). The IR spectra of all the metal complexes shows the absence of ν(-OH) band and the shift of ν(N-O) band, observed in ligand at 915 cm^{-1} to a higher side by 20-30 cm^{-1}. This suggest that the proton of N-OH group has been replaced on complexation[6,28]. Another important characteristic of IR spectra of all metal complexes is the reduction and shift of ν(C=O) band towards lower region with simultaneous shift of ν(C-N) band towards higher side suggesting the involvement of carbonyl oxygen atom in complex formation[29]. The new bands observed in IR spectrum of metal complexes in the region 600-450 cm^{-1} may be attributed to metal-oxygen stretching vibrations. All the above facts[6,29,30] indicate that the metal complexes have five-membered ring structure (Fig. 3).

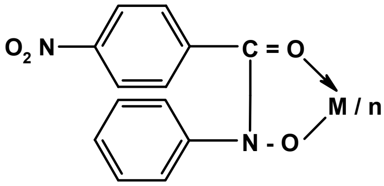

Fig. 3. Tentative structure of metal complexes of the ligand HPNBHA [M = Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and n = valency]

Electronic spectra: The electronic spectral data of ligand and its complexes with their tentative assignments are given in Table-2.

TABLE-2
ELECTRONIC SPECTRAL DATA

Name	Absorbance (cm^{-1})	Tentative assignments
HPNBHA	39,370	$\pi \rightarrow \pi^*$
	33,333	$n \rightarrow \pi^*$
$Cr(PNBHA)_3 \cdot 2H_2O$	39,680	$\pi \rightarrow \pi^*$
	33,220	Charge transfer
	26,950	$^4A_{2g} \rightarrow {}^4T_{1g}(P)$
	15,873	$^4A_{2g} \rightarrow {}^4T_{1g}$
$Mn(PNBHA)_2$	39,680	$\pi \rightarrow \pi^*$
	26,310	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$
$Fe(PNBHA)_3$	38,460	$\pi \rightarrow \pi^*$
	28,730	Charge transfer
	21,970	$^6A_{1g} \rightarrow {}^4T_{1g}$
$Co(PNBHA)_2$	35,710	$\pi \rightarrow \pi^*$
	27,320	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
$Ni(PNBHA)_2$	35,710	$\pi \rightarrow \pi^*$
	27,320	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
$Cu(PNBHA)_2$	38,310	$\pi \rightarrow \pi^*$
	28,490	Charge transfer
	15,940	Typical octahedral transition
	13,000	Typical octahedral transition

The ligand HPNBHA shows two absorption maxima at 39,370 and 33,333 cm^{-1} corresponding to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions, respectively. The electronic spectra of the dark green coloured $Cr(PNBHA)_3\cdot 2H_2O$ complex in chloroform exhibits an intense absorption at 39,680 cm^{-1} which may be attributed to $\pi\rightarrow\pi^*$ transition. In addition to this, three absorption bands are observed around 33,220, 26,950 and 15,873 cm^{-1} which may be attributed to charge transfer, $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ transitions, respectively. These are in consistent with most of octahedral chromium(III) complexes[31]. The yellowish orange coloured $Mn(PNBHA)_2$ complex in chloroform show absorption band at 39,680 cm^{-1} suggesting $\pi\rightarrow\pi^*$ transition. Besides, it also exhibits a weak absorption around 26,310 cm^{-1} which may be attributed to $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ transition. The observed magnetic moment of $Mn(PNBHA)_2$ (5.69 BM) and the two absorptions suggest a high-spin octahedral stereochemistry for this complex[32-34]. The brick red coloured $Fe(PNBHA)_3$ complex shows a highly intense absoption band at 38,460 cm^{-1} which has been assigned to $\pi\rightarrow\pi^*$ transition. It also exhibits a broad absorption at 21,970 cm^{-1} corresponding to $^6A_{1g} \rightarrow {}^4T_{1g}$ transition, consistent with octahedral iron(III) complexes[35]. A strong band is also observed at 28,730 cm^{-1} which may be due to charge-transfer transition. The light brown coloured $Co(PNBHA)_2$ complex and dark yellow coloured $Ni(PNBHA)_2$ complex show a strong absorption at 35,710 cm^{-1} which may be attributed to $\pi\rightarrow\pi^*$ transition.The bands observed at 27,320 cm^{-1} in these complexes may be attributed to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively. This suggest an octahedral environment around Co(II) and Ni(II) in their complexes, respectively which is confirmed by the observed higher magnetic moment values over calculated ones[36-38].

The green coloured $Cu(PNBHA)_2$ complex reveal a sharp absorption at 38,310 cm^{-1} and a broad band at 28,490 cm^{-1} which may be attributed to $\pi\rightarrow\pi^*$ and charge transfer transitions, respectively. Besides this, the spectra also show two weak absorption bands around 13,000 and 15,940 cm^{-1}. The observed magnetic moment of complex (1.78 BM) and the above transitions suggest a distorted octahedral stereochemistry for the complex[6,39].

Antimicrobial activity: The antibacterial activity of all the complexes were investigated against two bacterial strains using the disc diffusion method. The complexes showed significant positive response against bacteria like *Escherichia coli* and *Staphylococcus aureus*.

ACKNOWLEDGEMENTS

The authors are thankful to Sophisticated Analytical Instruments Facility center (SAIF), IIT Powai, Mumbai, Institute of Science, Mumbai, Department of Chemistry, IIT Powai, Mumbai & Kores (India) Limited, Thane for instrumental analysis. Thanks are also due to Mumbai University for financial support and V.G. Vaze College, Mumbai for providing the research facilities.

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(*Received*: 15 December 2006; *Accepted*: 14 September 2007) AJC-5863