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Spectral Characterization and DNA Binding Properties of Mononuclear Cobalt (II) Complexes with Pyridine Based Acetoyl and Benzoyl Hydrazones

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ABSTRACT

Mononuclear cobalt (II) complexes of pyridine hydrazones are synthesized by reacting cobalt acetate with respective hydrazones. The complexes are characterized based on analytical and spectral data. Low molar conductivity values suggest that the complexes are non-electrolytes. IR spectral data suggest that the ligands act as mono anionic tridentate NNO donor system. Electronic spectral data suggest octahedral geometry for the complexes. Electrochemical behavior of metal complexes indicated quasi-reversible one electron reduction. DNA binding properties of complexes are investigated using UV-visible spectroscopy. The binding constants suggest that the complexes bind DNA via intercalation.

Keywords: Synthesis, cobalt (II) complexes, pyridine hydrazones, spectral studies, DNA binding properties.

INTRODUCTION

Simple mononuclear cobalt (II) complexes have been investigated to develop models for vitamin B_{12}. Through studying model compounds some insight into the working of natural systems is sought. The most commonly mentioned vitamin B_{12} model system is bis(dimethylgyoximato) cobalt complex [1-2]. It is popularly known as 'cobaloxime'. Metallo-porphyrins are also considered as models for vitamin B_{12}. Recently several macrocyclic cobalt complexes [3-5] have been synthesized, characterized to mimic salient features of vitamin B_{12} in our laboratories.

In recent years there is much interest in the development of artificial nucleases. Artificial metallo-nucleases require ligands which effectively deliver metal ions to the vicinity of DNA. An investigation on metal-DNA interactions has been an area of active research [6]. Studies on chemical modification of nucleic acids with transition metal complexes are of great interest in the design of chemotherapeutic drugs, regulation of gene expression and design of tools for molecular biology [7]. A survey of literature reveals that the most efficient cleavage agents involving hydrolytic mechanism happens to be the "mononuclear" complexes [8-13]. Several mononuclear cobalt (II) complexes of hydrazones have been synthesized and characterized . DNA binding and cleavage properties of only very few mononuclear cobalt(II) complexes of hydrazones are reported in the literature[14].

In the light of the above and in continuation of our ongoing research work [15,16] a series of functionalized hydrazones (Fig 1) and their cobalt(II) complexes have been synthesized and characterized.

MATERIALS AND METHODS

Apparatus: Perkin Elmer UV Lamda 50 double beam spectrophotometer (UV-Visible), Perkin Elmer spectrum 100 Fourier Transform Infrared Spectrometer (FT-IR), CH 660C Electrochemical Analyzer (CV) was used for the present studies.

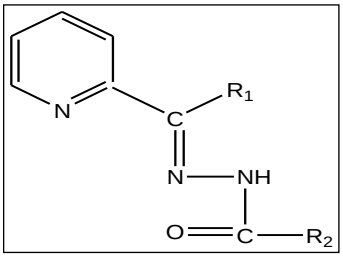
Synthesis of Ligands: Hot aqueous solution of hydrazide (0.5 mmol) was added to a boiling solution of methanolic solution of carbonyl compound (0.5 mmol). The reaction mixture was heated under reflux for 1hr a pale yellow coloured crystalline products were formed in cooling the reaction mixture. The hydrazones collected by filtration, washed several times with hot water and dried in vacuo. The ligands were recrystallized from methanol.

2-Acetylpyridine acetoylhydrazone(APAH): Yield 85%, m.p. 162-164°C, elemental analysis C-61.32(61.00); H- 6.50 (6.25); N- 24.0(23.71); IR spectra,: 3185, 1678, 1620 cm^{-1} are assigned to ν(NH), ν(C=O) and ν(C=N) stretching vibrations respectively. The ^{1}H-NMR spectra in $CDCl_3$ solvent. δ(2.4) (singlet 3H), δ(2.5) (singlet 3H), δ(7.25) (singlet 1H), δ(7.75-7.85) (multiplet 4 H), are respectively assigned to $–CH_3$ (carbonyl), $–CH_3$ (hydrazine), NH- and pyridine protons. LC-MS spectrum of HL shows molecular ion peaks at (*m/z*) 177.

2-Acetylpyridine benzoylhydrazone(APBH): Yield 85%, M.P. 145-147°C, elemental analysis C-68.75(70.27); H- 5.50 (5.47); N-17.12 (17.56); IR spectra, 3177, 1654, 1616 cm^{-1} are assigned to ν(NH), ν(C=O) and ν(C=N) stretching vibrations respectively. The ^{1}H-NMR spectra of HL was recorded in $CDCl_3$ solvent. Signals of HL at δ(2.5) (singlet 3H), δ(7.25) (singlet 1H), δ(7.75-7.85) (multiplet 9 H), δ(6.7) are respectively assigned to $–CH_3$, >NH- and aromatic (pyridine + phenyl ring) protons. LC-MS spectrum of HL shows molecular ion peaks at (*m/z*) 239.

2-Benzoyllpyridine acetoylhydrazone (BPAH): Yield 85%, m.p. 145-147°C, elemental analysis C-71.20(70.27); H- 5.70 (5.45); N-17.96 (17.56); IR spectra, 1668, 11615 cm-1 are assigned to ν(C=O) and ν(C=N) stretching vibrations respectively. The ^{1}H-NMR spectra in $CDCl_3$ solvent. δ(1.80) (singlet 3H), δ(7.40) (singlet 1H), δ(7.42- 8.80) (multiplet 9 H), δ(6.7) are respectively assigned to $–CH_3$, >NH- and aromatic (pyridine + phenyl ring) protons. LC-MS spectrum of HL shows molecular ion peaks at (*m/z*) 239.

2-Benzoylpyridine benzoylhydrazone(BPBH): Yield 85%, m.p. 135-137°C, elemental analysis C-75.9(75.72); H-5.23 (5.01); N-14.02 (13.94); IR spectra, 1666 and 1614 cm^{-1} are assigned to ν(C=O) and ν(C=N) stretching vibrations respectively. The ^{1}H-NMR spectra in $CDCl_3$ solvent. δ(7.22) (singlet 1H), δ(7.30- 8.80) (multiplet 13 H), are respectively assigned to imine (>NH-) and aromatic (one pyridine + two phenyl ring) protons. LC-MS spectrum of HL shows molecular ion peaks at (*m/z*) 239.



Ligand	R_1	R_2
APAH	CH_3	CH_3
APBH	CH_3	C_6H_5
BPAH	C_6H_5	CH_3
BPBH	C_6H_5	C_6H_5

Fig 1: Structure of ligands

Preparation of Complexes: The complexes were prepared by mixing hot aqueous solution of $Co(CH_3COO)_2.4H_2O$ and ligand in a molar ratio of 1:2. To the boiling solution of ligand (10mmol) in

methanol (100 ml) was added metal acetate salts (5 mmol) dissolved in minimum quantity of water and the reaction mixture was heated under reflux for 3h. Crystalline complexes which separated out were collected by filtration, washed with hot water, small quantity of methanol and hexane and dried in *vacuo*. Analytical data of complexes are given in table 1.

Table 1: Physico-chemical and analytical data of cobalt (II) complexes

Complex	Colour (Yield, %)	Mol. Wt.	Analyses Found (Calc.) (%)				M. pt† (^oC)	μ_{eff} (BM)	Molar conductivity (Ω cm^2 mol^{-1})
			C	H	N	M			
$[Co(APAH)_2]$	Reddish brown(75)	412 (411.31)	52.95 (52.36)	4.92 (4.89)	20.50 (20.43)	14.86 (14.32)	290-292	1.71	6.5
$[Co(APBH)_2]$	Reddish brown(68)	536 (535.45)	62.94 (62.80)	4.60 (4.51)	15.78 (15.69)	11.55 (11.00)	300-302	1.86	7.8
$[Co(BPAH)_2]$	Brown (89)	536 (535.45)	63.01 (62.80)	4.85 (4.51)	15.91 (15.69)	11.63 (11.00)	294-296	1.75	19.0
$[Co(BPBH)_2]$	Brown (84)	660 (659.59)	69.24 (69.19)	4.40 (4.27)	13.12 (12.74)	9.21 (8.93)	298-300	1.67	13.4

The elemental analyses were performed at RSIC, CDRI Lucknow. Molecular weights of the complexes were determined by using Rast's method. Magnetic measurements of complexes were carried out at 298 K in Faraday's magnetic susceptibility balance (Sherwood Scientific, Cambridge, UK). High purity pentahydrated copper sulphate was used as a standard. The conductivity measurements were recorded using ELICO CM model 162 conductivity cell at 298±2 in dry and purified DMF. The electronic spectra of metal complexes were recorded in DMF with UV lamda50 (PerkinElmer) spectrophotometer. The infrared spectra were recorded in the range 4000-400cm^{-1} with Perkin Elmer spectrum 100spectrometer in KBr discs. The cyclicvoltammetry was performed with a CH Instruments 660C electrochemical analyzer and a conventional three electrode configuration with glassy carbon working electrode, silver/silver chloride reference electrode and platinum counter electrode. Nitrogen was used as a purge gas and all solutions were 0.1M concentration in tetrabutylammonium hexafloro phosphate ($TBAPF_6$) supporting electrolyte.

DNA Binding Experiments: Interaction of complexes with calf thymus DNA was studied by electronic absorption spectroscopy. All the experiments involving interaction of the complexes with CT-DNA were carried out in a water buffer containing 5mM tris (hydroxyl methyl) ammonia methane (Tris) and 50mM NaCl and adjusted to pH 7.0 with HCl. The solution of CT-DNA in 5mMTris HCl/50mM NaCl gave a ratio of UV absorbance at 260 and 280 nm (A_{260}/A_{270}) of 1.8–1.9, indicating that the DNA is sufficiently free from proteins [17]. A concentrated stock solution of DNA was prepared in 5 mM Tris-HCl/50 mM NaCl in water at pH 7.0 and the concentration of CT–DNA was determined per nucleotide by taking the absorption coefficient (6,600 dm^3 mol^{-1} cm^{-1}) at 260 nm [18]. Stock solutions are stored at 4^oC and were used after no more than 4 days. Doubly distilled water was used to prepare buffer solutions. Absorption Titrations were performed by maintaining the metal complex concentration 2×10^{-5} M and varying the nucleic acid concentration ($0\text{-}26.4\times10^{-6}$ M). Absorption titration experiments were performed by maintaining the metal complex concentration constant while gradually increasing the concentration of CT-DNA within 0-100 μM.

RESULTS AND DISCUSSION

The complexes are stable at room temperature, non-hygroscopic, sparingly soluble in water, partially soluble in methanol, ethanol and readily soluble in acetonitrile (CH_3CN), DMF and DMSO. The analytical data (Table 1) are consistent with the proposed molecular formulae of complexes. The molar conductivity data suggest that the complexes are non-electrolytes. The magnetic moment values of the complexes correspond to their respective spin-only values.

IR spectra of hydrazone ligands are compared with those of metal complexes to determine donor atoms of ligand. Important IR spectral bands and their tentative assignments are given in table 2. Typical IR spectrum of $[Co(BPAH)_2]$ is shown in fig 2.

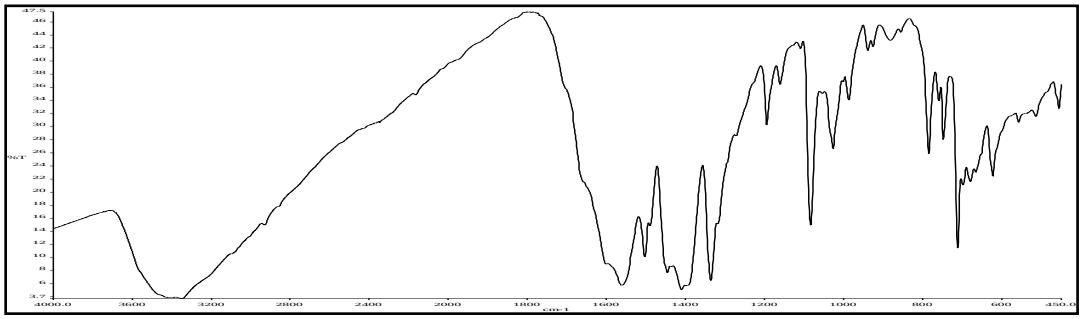


Fig 2: FT-IR spectrum of $[Co(BPAH)_2]$

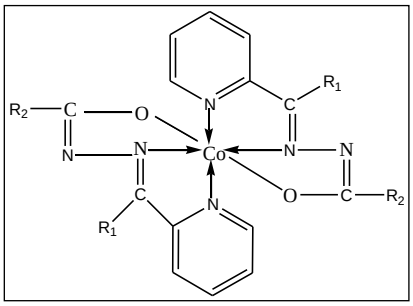
The IR spectra of ligands have several prominent bands due to $\nu_{N-H,}$ $\nu_{C=O}$ and $\nu_{C=N}$ stretching modes. The $\nu_{N-H,}$ and $\nu_{C=O}$ bands disappeared in spectra of complexes. A new band is observed in the spectra of complexes in the range 1050-1058 cm^{-1} due to enolization of ligand followed by its complexation with metal ion and with concomitant formation of C-O bond. The $\nu_{C=N}$ (imine) observed in the spectrum of free hydrazone is shifted to lower frequency in the spectra of all complexes suggesting the involvement of azomethine nitrogen in chelation. IR data suggest that the hydrazones act as monobasic tridentate ligand in mononuclear cobalt(II) complexes. In the spectra of metal complexes the non-ligand absorption bands in 523 - 597 and 445 - 465 cm^{-1} regions are tentatively assigned to $\nu_{(M-O),}$ and $\nu_{(M-N)}$ stretching vibrations respectively.

Table 2: Important IR Spectral bands (cm^{-1}) and their assignment*

$[Co(APAH)_2]$	$[Co(APBH)_2]$	$[Co(BPAH)_2]$	$[Co(BPBH)_2]$	Assignment
--- (3185)	--- (3177)	--- (3454)	--- (3453)	ν_{N-H}
--- (1678)	--- (1654)	--- (1666)	--- (1685)	$\nu_{C=O}$
1587(1620)	1561(1616)	1560 (1586)	1562 (1598)	$\nu_{C=N}$
523	597	548	535	ν_{M-O}
465	---	455	445	ν_{M-N}

*Prominent peaks due to $\nu_{N-H,}$ $\nu_{C=O}$ and $\nu_{C=N}$ stretching modes of ligands are given in parenthesis.

Based on molar conductance, magnetic susceptibility measurements, electronic and IR spectral data, a tentative and general structure for mononuclear cobalt (II) complexes is given in fig 3.



R_1 = CH_3 ; R_2 = CH_3 **APAH**

R_1 = CH_3 ; R_2 = C_6H_5 **APBH**

R_1 = C_6H_5 ; R_2 = CH_3 **BPAH**

R_1 = C_6H_5 ; R_2 = C_6H_5 **BPBH**

Fig 3: Structure for cobalt (II) complexes

Electronic Absorption Titrations: Electronic absorption spectroscopy is an effective method for examining the interaction of DNA with metal complexes. The interaction of present cobalt (II) complexes with calf-thymus DNA was monitored by UV-visible spectroscopy. Hyperchromic and hypochromic effects are the spectral changes when a complex interacts with DNA and forms a new complex. The absorption spectra of complexes may be recorded in the absence and in the presence of CT-DNA. In the presence of increasing amounts of DNA, the spectra of complexes may show strong decrease (hypochromicity) or increase (hyperchromicity) intensity with shift in absorption maxima towards lower (blue-shift) or higher (red-shift) wavelengths. The change in absorbance values with increasing amount of CT-DNA have been used to evaluate the intrinsic binding constant K_b for the complex. In general, a complex binding with DNA through intercalation usually results in hypochromism and bathochromism of the absorption band due to the intercalative mode involving a strong π- stacking interaction between the aromatic chromophore and base pairs of DNA [19].

Absorption spectra were recorded in the range of 250-600 nm. All the complexes exhibit an intense absorption band in 276-401 nm region attributed to $\pi \rightarrow \pi^*$ transition. Absorption spectra of $[Co(APBH)_2]$ complex in the absence and in the presence of CT-DNA are shown in fig 4.

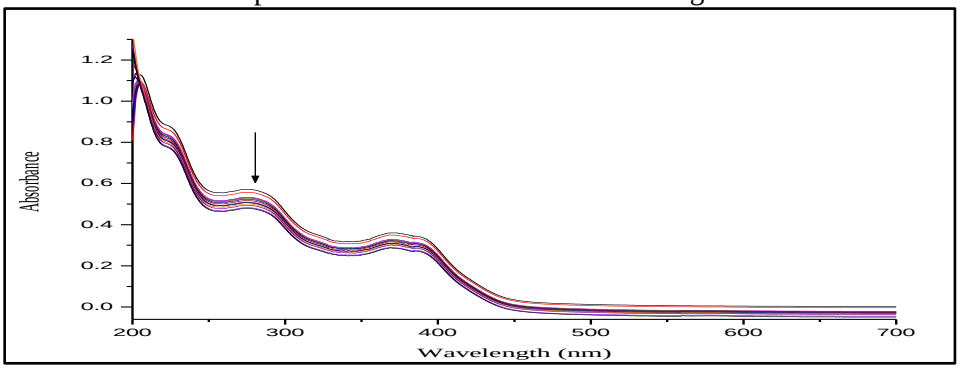


Fig 4: Absorption spectra of $[Co(APBH)_2]$ complex in the absence and in the presence of increasing amounts of CT-DNA

The metal-free hydrazone ligands did not show any DNA binding activity. The intrinsic binding constants (K_b), was determined by using the equation,

$$[DNA] / (\varepsilon_a-\varepsilon_f) = [DNA] / (\varepsilon_b-\varepsilon_f) + 1/ K_b(\varepsilon_b-\varepsilon_f) \text{ ---------- } (1)$$

Where [DNA] is the concentration of DNA in base pairs, ε_a, ε_b and ε_f are apparent extinction coefficient ($A_{obs}/[M]$), the extinction coefficient for the metal (M) complex in the fully bound form and the extinction coefficient for free metal (M) respectively. A plot of $[DNA] / (\varepsilon_a-\varepsilon_f)$ versus [DNA] gave a slope of $1/(\varepsilon_b-\varepsilon_f)$, and vertical intercept equal to $1/ K_b(\varepsilon_b-\varepsilon_f)$; K_b was calculated from these values. Electronic absorption spectral data (upon addition of CT-DNA) and binding constants of these complexes are given in the table 3.

Table 3: Electronic absorption data upon addition of CT-DNA to the complexes

Complex	λ_{max} (nm)		Δλ	H (%)	K_b (M^{-1})
	Free	Bound			
$[Co(APAH)_2]$	354	355	1	+13.44	$1.68x10^5$
$[Co(APBH)_2]$	276	274	2	+12.46	$3.59x10^5$
$[Co(BPAH)_2]$	385	386	1	+3.23	$1.09x10^5$
$[Co(BPBH)_2]$	401	401	0	+1.83	$2.13x10^5$

The data suggest that the [Co(APBH)$_2$]complex bind DNA strongly. On addition of DNA, the absorbance of all the complexes decreases (hypochromism) and absorption maximum is shifted slightly to higher wavelength (bathochromism). These observations suggest that the complexes bind DNA through intercalation involving a strong π - stacking interaction of the aromatic chromophore (pyridine moiety) between base pairs of DNA.

In the presence of increasing amounts of CT-DNA, the UV-Visible absorption spectra of cobalt complexes show a slight redshift (1nm) in absorption maximum (λ_{max}). From the table 3 it is also evident that cobalt(II) complexes show hypochromism. It is also evident that all the complexes bind with DNA with high affinities and, the calculated binding constants are of the order of 10^5 M^{-1}. The high binding constants of complexes may be attributed to the π- stacking interaction of the aromatic chromophore between base pairs of DNA.

As given in table 3, the complex Co (APBH)$_2$ show hypochromism with slight blueshift (2nm). This kind of binding may cause a slight change in conformation of DNA due to the cleavage of secondary structure [20]. This results indicates a non-intercalative binding mode of the Co (APBH)$_2$ complex.

Electrochemical Studies: Redox behaviour of the cobalt(II) complexes has been investigated by cyclic voltammetry in DMF having 0.1M tetrabutylammonium hexaflourophosphate (TBAHEP) as supporting electrolyte. The cyclic voltammetric profile of [Co (APBH)$_2$] complex is given in fig 5. The electrochemical data of cobalt(II) complexes are presented in table 4.

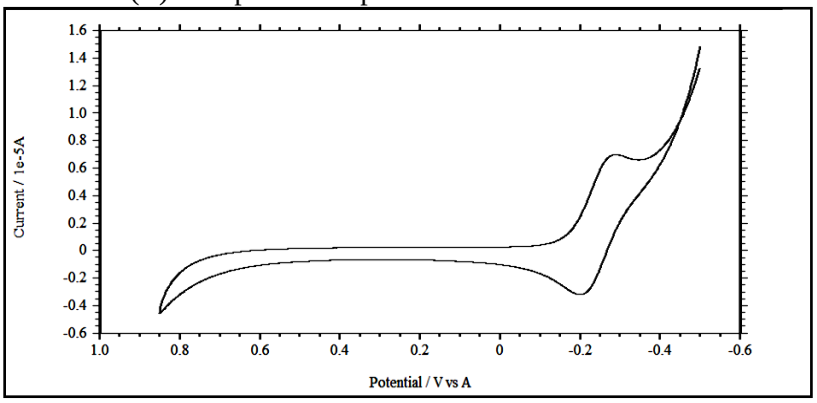


Fig 5: Cyclic voltammetric profile of [Co(APBH)$_2$] complex scan rate at 50 mVs^{-1}

Table 4: Cyclicvoltammetric data of cobalt (II) complexes

Complex	Redox couple	E_{pc}	E_{pa}	ΔE_p(mV)	$E_{1/2}$(V)	$-i_c/i_a$	$LogK_c^b$	ΔG^0
[Co(APAH)$_2$]	II/I	-0.342	-0.235	107	-0.288	1.08	0.314	1803
[Co(APBH)$_2$]	II/I	-0.290	-0.200	90	-0.254	3.48	0.373	2141
[Co(BPAH)$_2$]	II/I	-0.201	-0.111	90	-0.156	1.31	0.373	2141
[Co(BPBH)$_2$]	II/I	-0.227	-0.151	76	-0.189	1.38	0.442	2537

The cyclic voltammograms of cobalt complexes show an active responses in the range of -0.156 to -0.288 V vs Ag/AgCl region, assigned to the Co (II)/Co (I) couple (Table 4). The non-equivalent current in cathodic and anodic peaks for complexes indicates quasi-reversible behavior. The complexes have large separation (90-107 mV) between anodic and cathodic peaks indicating quasi-reversible character. The potential difference ΔEp = Epc - Epa in all the complexes exceeds the Nerstian requirement of 59/n mV

(n= number of electrons involved in oxidation reduction) which suggests quasi-reversible character of the electron transfer reaction.

APPLICATIONS

Cobalt complexes of azomethine ligands have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications [21-24]. They serve as models for biologically important species and find applications in biomimetic catalytic reactions. It is known that the existence of metal ions bonded to biologically active compounds (like hydrazones) may enhance their activities. There has been a growing interest in the chemistry and biochemistry of cobalt because of its implication in many biological redox processes [25,26]. There is also much interest in the development of artificial nucleases. Artificial metallo-nucleases require ligands which effectively deliver metal ions to the vicinity of DNA. An investigation on metal-DNA interactions has been an area of active research [27]. Studies on chemical modification of nucleic acids with transition metal complexes are of great interest in the design of chemotherapeutic drugs, regulation of gene expression and design of tools for molecular biology [28].

CONCLUSIONS

Mononuclear cobalt (II) complexes of pyridine hydrazones are synthesized by reacting cobalt acetate with respective hydrazones. The complexes are characterized based on analytical and spectral data. Low molar conductivity values suggest that the complexes are non-electrolytes. IR spectral data suggest that the ligands act as mono anionic tridentate NNO donor system. Electronic spectral data suggest octahedral geometry for the complexes. Electrochemical behavior of metal complexes indicated quasi-reversible one electron reduction. DNA binding properties of complexes are investigated using UV-visible spectroscopy. The binding constants suggest that the complexes bind DNA via intercalation.

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