STUDIES OF NEW SCHIFF BASE PYRROLOPYRIMIDINEHYDRAZINE-*o*-FLUOROBENZYLDEHYDE DERIVATIVES

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ABSTRACT

This article describes the HFBHPP ligand and its interactions with metal ions. Elements analysis, electronic, FT(IR), and PMR spectra highlight the complexes' constraints. Electrolytic behavior was assessed by measuring chelates' molar conductance. Magnetic moment measurements showed each chemical was monomeric. S. aureus MCC 2010, B. subtilis MCC 2010, E. coli MCC 2412, and P. aeruginosa MCC 2080, these microorganisms, whose susceptibility to the HFBHPP derivatives has been extensively studied via disc diffusion with DMF. 24 hours at 37°C determined the zone of inhibition. Each compound outperformed the reference compounds and free HFBHPP ligand.

Keywords: Molar conductance data, copper; nickel; palladium complexes; pyrrolopyrimidinehydrazine-*o*-fluorobenzyldehyde.

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INTRODUCTION

Inorganic and bioinorganic chemists are excited by the prospect of designing and analyzing well-arranged metal-containing pyrrolopyrimidines with N-donor atoms[1-11]. Coordination chemistry is driven by in situ one-pot condensation of a template. Electronic delocalization, which causes electric conductivity and oxidizability in pyrrolic compounds like poly- or heteroaryl pyrroles, is widely known. Due to their high reactivity, enaminonitrile-substituted 2-aminopyrrole-3-carbonitrile derivatives are used as intermediates to make new pyrimidine derivatives. Stiff alkaloids3 and antibiotics like tubercidin, toyocamycin, sangivamycin, and cadeguomycin have this heterosystem. In recent years, pyrimidine-derived metal ion complexes have been the subject of intense research because of their many biological activities, such as those against malaria,

bacteria, cancer, and viruses. The development of pharmaceutical–ligand complexes has been supported by numerous researches.

Pyrrolopyrimidinehydrazine-*o*-fluorobenzyldehyde [HFBHPP] and its complexes will form novel heterocyclic Schiff bases. The HFBHPP ligand and its complexes were characterized using a wide range of physical and chemical techniques, as well as elemental, spectral, magnetic, and conductance studies.

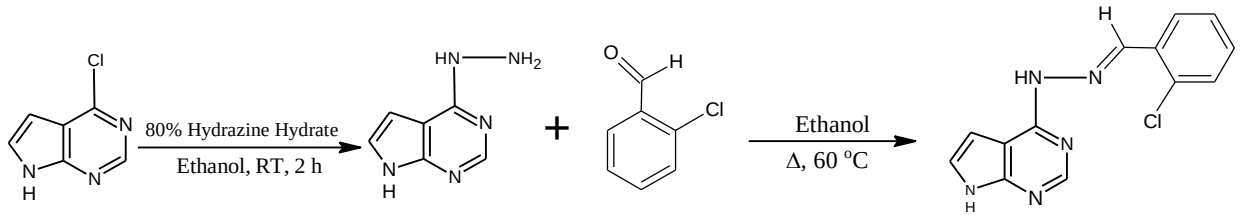
EXPERIMENTAL

Material and Methods

Chemicals and reagents were used as instructed and were of analytical or reagent quality if readily accessible. BRUKER Advance III HD NMR spectra were acquired in DMSO-d_6 at 500 MHz with TMS as the internal standard. BRUKER FT-IR spectrometers collected 4000-500 cm-1 KBr pellet FT-IR spectra. The Carlo-Erba LA-118 microdosimeter was used for the chemical element analysis, which found carbon, hydrogen, nitrogen, and fluorine[12]. Solid compounds were magnetically susceptible using the Gouy method[13].

Preparation of the HFBHPP ligand

Pyrrolopyrimidinehydrazide was developed using the literature14. A heated 50 mL solution of 2-fluorobenzaldehyde in ethanol (60°C) was added to a magnetically agitated 0.10 mol solution of pyrrolopyrimidinehydrazide in warm ethanol. (25mL). Refluxing for 3 hours cooled the reaction mixture. Filtering, washing with 60% methanol, and drying the precipitate under pressure crystallized HFBHPP from ethanol.



Scheme 1: Preparation of HFBHPP ligand

Metal Complexes *of* pyrrolopyrimidinehydrazine-*o*-fluorobenzyldehyde (HFBHPP*)*:

0.5 mmol of aqueous ethanolic metal chloride solutions and heated HFBHPP ethanolic sodium hydroxide solutions formed the metal complexes (1.0 mmol). Dilute hydrochloric acid changed the reaction mixture's pH to 7 and digested for 2 hours. To remove any unreacted metal salts or ligands, the solid-colored compounds were filtered and then dried.

Antibacterial assay of synthesized compounds

Disc diffusion assays were performed on four pathogenic bacterial strains to determine the antibacterial activity of the synthesized compounds: S. aureus MCC 2010, B. subtilis MCC 2010, E. coli MCC 2412, and P. aeruginosa MCC 2080. NCMR at Pune, India, provides standard microbial kinds. Comparing synthetics' zone of inhibition to a standard antibiotic disc determined their antibacterial activity (ciprofloxacin). Dissolving test chemicals in dimethylformamide yielded a 1 mg/mL stock solution (DMF). Fresh Luria Bertani broth subcultures were placed on a sterile assay medium (Nutrient Agar) in Petri plates at 40–45 °C and left for 30 minutes. Pipette 30 mL of each drug onto indicated 8-mm sterile paper discs on inoculated agar dishes. The zone of inhibition was determined by incubating Petri plates at 37°C for 24 hours after 1 hour. Triplicate antibacterial activity was tested using DMF as a negative control.

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RESULTS AND DISCUSSION

Analytical and physicochemical data suggest 1:2 (metal: HFBHPP ligand) transition complexes. Table 1. The prepared complexes in nitrobenzene have a low molar conductance of 0.23-1.25 cm2 mol-1, demonstrating that they are not electrolytic[15]. According to magnetic susceptibility tests, Cu(II) and Pd(II) are square-planar in nature and distinguishable from the high-spin octahedral structure of Fe(II), Ni(II), Co(II), and Mn(II) complexes.

Table 1: Analytical and physicochemical properties of the HFBHPP derivatives

Comp	Color	MW	% Yield	MP/DP	Element Content					Cond	MM
					M	C	H	N	F		
HFBHPP	Green	255.25	76.98	195	-	61.17	3.95	27.44	7.44	-	-
Mn(FBHPP)$_2$	Brown	563.438	81.26	245	9.75	55.37	3.19	24.85	6.74	0.78	6.11
Fe(FBHPP)$_2$	Blue	564.34	80.11	239	9.90	55.29	3.19	24.58	6.13	1.25	5.55
Co(FBHPP)$_2$	Brown	569.493	79.39	253	10.40	54.79	3.16	24.58	6.67	0.26	4.48
Ni(FBHPP)$_2$	Green	569.193	83.05	252	10.30	54.81	3.16	24.60	6.68	0.29	3.16
Pd(FBHPP)$_2$	Green	616500	84.52	269	17.19	50.61	2.92	22.71	6.61	0.41	-
Cu(FBHPP)$_2$	Green	563.438	81.66	248	9.75	55.37	3.19	24.85	6.74	0.89	1.93

FT(IR) spectra:

In the KBr medium, the HFBHPP ligand and metal complexes were studied using Fourier transform infrared spectroscopy. The disappearance of stretching vibrations associated with the hydrazide's aldehyde (CHO) and amino (NH2) moiety, as well as the appearance of a significant at 1555 cm^{-1} new band ascribed to the (HC=NN-) group[16], indicate the formation of the HFBHPP ligand. Band shifting to a 1489-1493 cm^{-1} [16, 17] is proof that azomethine-N has been coupled to metal ions by complexation. Because of the pyrrole NH- group, the spectrum of HFBHPP shows a broad band at 3389 cm^{-1}. This wide band vanishes in its prepared M(II) complexes, implying that the pyrrole NH- group participates in coordination via deprotonation. This is also shown by the fact that a band at 517–538 cm^{-1} has been found in metal complexes because of M–N[19, 20]. The presence of the HFBHPP derivatives is suggested by a band in the 3195–3289 cm^{-1} region that has been classified as aliphatic (NH)[21–22]. The (M-N) and (M-N) vibrations contribute to the appearance of new bands of metal complexes at 472-498 and 517-538 cm^{-1}.

Table 2: The HFBHPP derivatives were analyzed using FT(IR) spectroscopy

Comp	NH (Ali)	NH (Aro)	C-H (aldehyde)	>C=N- (aro)	.C=N- (Ali)	C-N (aro amine)	N-N- (Ali)	C-F	o--di sub benzene ring	M-N/M→N
HFBHPP	3195	3389	2833	2070	1555	1312	963	963	739	-
$Mn(FBHPP)_2$	3288	-	2836	2014	1493	1309	1011	903	730	517, 475
$Fe(FBHPP)_2$	3289	-	2839	2013	1489	1389	1013	906	729	533, 472
$Co(FBHPP)_2$	3197	-	2879	1999	1493	1393	1018	915	729	532, 462
$Ni(FBHPP)_2$	3199	-	2877	2000	1490	1315	1017	919	728	538, 498
$Pd(FBHPP)_2$	3268	-	2869	2014	1486	1364	1015	926	728	528, 481
$Cu(FBHPP)_2$	3287	-	2849	2000	1491	1311	1012	899	735	525, 490

Absorption spectra of electrons and magnetic moments:

The iron in the $Fe(FBHPP)_2$ complex is oxidized to +2, and magnetic susceptibility studies taken at room temperature confirmed that the combination was paramagnetic. The Fe(II) complex's absorbance band at 666 nm revealed the $^5T_{2g} \rightarrow {}^5E_g$ transition[23]. 429 and 395 nm bands receive L→M charge transfer. High spin octahedral geometry matched the 5.55 B.M. magnetic moment. $Fe(FBHPP)_2$ complex[24-25].

$Co(FBHPP)_2$ has a 4.48 BM magnetic moment at room temperature. Octahedral Co(II) complexes have similar numbers[26]. Two different absorptions at 889 nm and 508 nm were observed for the Co(II) complex, attributed to $^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$ (ν_1) and $^4T_{1g(F)} \rightarrow {}^4T_{2g(P)}$ (ν_2), respectively. Hence, Co(II)27 may have an octahedral structure. The proper equation can predict this transition, which is analogous to but not immediately observable in the metal-to-ligand charge transfer transition[28].

This $Ni(FBHPP)_2$ complex has a high spin and a magnetic moment of 3.16 BM at room temperature, typical for octahedral complexes[29]. The $Ni(FBHPP)_2$ complex's electronic spectroscopy showed two bands at 968 and 615 nm, corresponding to transitions $^3A_{2g(F)} \rightarrow {}^3T_{2g(F)}$ (ν_1) and $^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$ (ν_2). The octahedral environment's rings encircle the Ni(II) ion. The band-fitting equations31 calculated the third transitions $^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$ (ν_3) and characteristics of the ligand field (*Dq*, *B*, *β*, and *β*%) for complexes of Co(II) and Ni(II). Metal ligand bonds are strongly covalent. Because of orbital overlap and electron delocalization, the metal ion's Racah

parameter (B) is smaller than that of the unbound ion. The nephelauxetic ratio (B) is less than 1 for metal complexes, indicating incomplete metal-ligand bond covalency[32].

The $^2B_{1g} \rightarrow {}^2A_{1g}$ transition causes bands at 630 in the HFBHPP ligand copper compound. A square-planar band[33] surrounds Cu(II). Square planar compounds have a magnetic moment of 1.93 at room temperature[34]. Strong absorption bands at 421 and 516 nm were seen in the electronic spectra of the homo-binuclear [$Mn(FBHPP)_2$]. The metal complexes' octahedral geometry matches these bands' transitions from $^6A_{1g} \rightarrow {}^4E_g(^4D)$, and $^6A_{1g} \rightarrow {}^4T_{1g}(^4P)$. The measured magnetic moment (6.11 BM) supported the [$Mn(FBHPP)_2$] complex's high spin octahedral shape[35].

The PMR spectra:

Aromatic NH proton 12.900[36] in free HFBHPP ligand spectrum. The absence of this signal in Pd(II) metal complex spectra proves that the deprotonated pyrrole group of the HFBHPP coordinates with the central metal ion. The HFBHPP ligand spectrum shows -CH= and aliphatic NH protons at 8.368–8.574 and 8.578–8.625 respectively. HFBHPP ligand and metal complex aromatic protons are 7.561–8.012 ppm[37].

ESR Spectra:

The solid-state electronic spin resonance spectrum of [$Cu(FBHPP)_2$] was recorded at liquid nitrogen temperature to better understand its stereochemistry. The ground state of the [$Cu(FBHPP)_2$] complex is determined by its g-tensor values ($g_{||} = 2.13$, $g_{\perp} = 2.07$, $g_{ave} = 2.09$, $G = 2.43$). In a square planar complex with an unpaired electron in the d_{x2-y2} orbital, the ground state is $^2B_{1g}$, and if it is found in the dz2 orbital, the ground state is $^2A_{1g}$. Because $g_{||} > g_{\perp}$, the unpaired electron in the copper(II) ion is most likely located in the d_{x2-y2} orbital, suggesting a square planar geometry. No spectrum signature at half field ruled out a dimeric form39.

Biological evaluation:

Antimicrobial evaluation

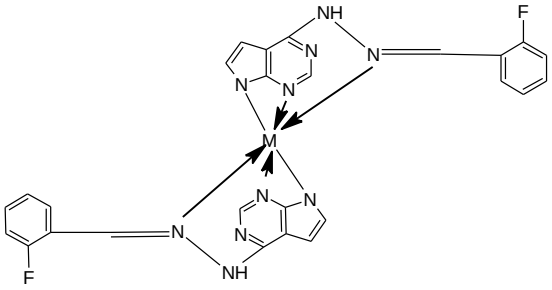
With the disc diffusion method and ciprofloxacin as the gold standard, all synthesized compounds were tested against four bacterial strains: two gram-positive (S. aureus MCC 2010 and B. subtilis MCC 2010) and two gram-negative (E. coli MCC 2412 and P. aeruginosa MCC 2080). Inhibition zones measured activity. Results were tripled. None of the compounds outperformed ciprofloxacin. The most effective of the series was Pd(FBHPP)2, with an E. coli

and S. aureus zone of inhibition of 13.5 mm and 17.5 mm, respectively. All compounds with electron-withdrawing fluoro groups showed weak pathogen inhibition.

CONCLUSION

We synthesized and coordinated mononuclear pyrrolopyrimidine complexes. Agar-well diffusion tested its antibacterial and antifungal properties. Transition metal complexes were synthesized and tested. Pyrrolo, pyrimidine, and hydrazide nitrogen atoms coordinate the metal ion in the azomethine-linked oxime ligand's electronic, IR, and NMR spectra. Results from Scheme II's coordination compound structure.

Possible metabolic inhibition of bacteria by chelated complexes. Possible advantages of the metal complex over the ligand in biological activity include improved solubility, conductivity, and dipole moment.



Scheme-II: Coordination behavior of transition metal complexes

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