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## Crystal structure, complexation, spectroscopic characterization and antimicrobial evaluation of 3,4-dihydroxybenzylidene isonicotinyl-hydrazone



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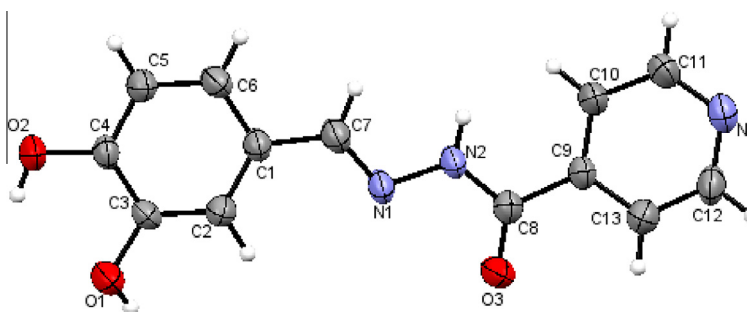
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### HIGHLIGHTS

- XRD structure of 3,4-dihydroxybenzylidene isonicotinylhydrazone.
- $\text{VO}^{2+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pd}^{2+}$  complexes of 3,4-dihydroxybenzylidene isonicotinylhydrazone.
- Binuclear and dimeric complexes.
- Octahedral, tetrahedral and square-planar stereochemistries for the complexes.
- Antimicrobial activity of the ligand and its complexes.

### GRAPHICAL ABSTRACT

The crystal structure of 3,4-dihydroxybenzylidene isonicotinylhydrazone has been solved by X-ray crystallography. The metal complexes have been prepared and characterized. A tetrahedral geometry was proposed for the Co(II), Cu(II), Zn(II) and Cd(II) complexes, square-planar for the Pd(II) complex, square-pyramid for the  $\text{VO}^{2+}$  complex and octahedral for the Ni(II) complex. Some complexes have biological activity.



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### ABSTRACT

A single crystal of 3,4-dihydroxybenzylidene isonicotinylhydrazone, HBINH, has been grown and solved by X-ray crystallography. The  $\text{VO}^{2+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pd}^{2+}$  complexes of HBINH have been prepared and spectroscopically characterized. The data confirmed the formulae  $[\text{Co}(\text{HBINH})(\text{H}_2\text{O})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$ ,  $[\text{Pd}(\text{HBINH})\text{Cl}_2]$ ,  $[\text{Zn}(\text{HBINH})_2\text{Cl}_2]$ ,  $[\text{Cd}(\text{HBINH})(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 1\frac{1}{2}\text{H}_2\text{O}$ ,  $[(\text{VO})_2(\text{HBINH}-3\text{H})(\text{OH})(\text{H}_2\text{O})]$ ,  $[\text{Ni}_2(\text{HBINH})(\text{H}_2\text{O})_6\text{Cl}_2]\text{Cl}_2$ ,  $[\text{Cu}_2(\text{HBINH}-3\text{H})(\text{H}_2\text{O})_2(\text{OAc})]\cdot 3\text{H}_2\text{O}$ ,  $[\text{Zr}_2(\text{HBINH}-3\text{H})\text{Cl}_4]\text{Cl}$ ,  $[\text{Hg}_2(\text{HBINH})\text{Cl}_4]$  and the dimer  $\{[\text{Cu}(\text{HBINH})\text{Cl}]\text{Cl}\}_2$ . Most of the complexes have intense colors and high melting points and some are electrolytes in DMSO solution. The ligand behaves as a neutral bidentate in the Co(II), Cu(II), Pd(II), Zn(II) and Cd(II) complexes; dibasic tetradentate in  $[\text{Ni}_2(\text{HBINH})(\text{H}_2\text{O})_6\text{Cl}_2]\text{Cl}_2$  and tribasic tetradentate in  $[\text{Cu}_2(\text{HBINH}-3\text{H})(\text{OAc})]\cdot 5\text{H}_2\text{O}$ ,  $[(\text{VO})_2(\text{HBINH}-3\text{H})(\text{OH})(\text{H}_2\text{O})]$  and  $[\text{Zr}_2(\text{HBINH}-3\text{H})\text{Cl}_4]\text{Cl}$  by the loss of  $3\text{H}^+$  due to the deprotonation of the two hydroxyl groups and the enolization of the amide ( $\text{O}=\text{CNH}$ ) group. A tetrahedral geometry was proposed for the Co(II), Cu(II), Zn(II) and Hg(II) complexes; square-planar for the Pd(II) complex; square-pyramid for the  $\text{VO}^{2+}$  complex and octahedral for the Ni(II) and Cd(II) complexes. The complexes  $[\text{Cd}(\text{HBINH})(\text{H}_2\text{O})_2\text{Cl}_2]\cdot 1\frac{1}{2}\text{H}_2\text{O}$ ,  $[(\text{VO})_2(\text{HBINH}-3\text{H})(\text{OH})(\text{H}_2\text{O})]$  and  $[\text{Cu}_2(\text{HBINH}-3\text{H})(\text{H}_2\text{O})_2(\text{OAc})]\cdot 3\text{H}_2\text{O}$  have activities against *Bacillus* sp. M3010, *Candida albicans*, *Escherichia coli*, *Staphylococcus aureus* and *Slamonella* sp. PA393.

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## Introduction

Hydrazones and their complexes have great interest due to their antimicrobial activities. Oximino-hydrazones have antiparasitic, fungicidal and bactericidal properties [1] while pyridazinyl hydrazones inhibit tyrosine hydroxylase and dopamine hydroxylase (in vivo and in vitro) [2]. The tridentate hydrazones have been evaluated as potential oral iron-chelating drugs for genetic disorders such as thalassemia [3]. Salicylaldehyde benzoylhydrazone appeared to be unusual inhibitor of DNA synthesis and cell growth in human and rodent cell lines [4]. 2-Acetylpyridine acetylhydrazone and 2-benzoylpyridine acetylhydrazone and their Cu(II) complexes were assayed for their cytotoxicity against wild type p53 U87 and mutant p53 T98 glioma cells and against MRC-5 fibroblast cells. The complexes have activity against U87 more than the ligands, but not against T98 cells [5]. The X-ray crystal structure of Fe(III) complex of pyridoxal isonicotinylhydrazone showed that the ligand behaves as tridentate occupied by the chloride ions or water molecules [6]. Compounds containing oxime and amino groups are used as analytical reagents for the microdetermination of some transition metal ions and as ion exchange resins [7]. The  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ce}^{3+}$  and  $\text{UO}_2^{2+}$  complexes of 2-aceto-1-naphthol-N-salicylhydrazone were characterized. The 1:2 (M:L) complexes of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  have an octahedral structure while the 1:1 complexes of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  are square-planar. The ligand was used for the microdetermination of metal ions in solution [8]. Binuclear complexes of  $\text{VO}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  with oxalyl bis(diacetylmonoximehydrazone) were characterized as 2:2 (M:L) molar ratio. An octahedral geometry for  $\text{VO}^{2+}$ , tetrahedral for  $\text{Zn}^{2+}$  and square-planar for the rest complexes were proposed [9]. The  $\text{UO}_2^{2+}$ ,  $\text{VO}^{2+}$  and  $\text{ZrO}^{2+}$  complexes of orotic acid (vitamin B<sub>13</sub>) formulated as  $[\text{M}(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_n$  were tested against some bacteria [10]. 2,5-Dihydroxyacetophenone isonicotinylhydrazone ( $\text{H}_2\text{L}$ ) and its  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{VO}^{2+}$ ,  $\text{Zr}^{4+}$  and  $\text{UO}_2^{2+}$  complexes were investigated [11]. The ligand was found flexidentate and coordinates through the C–O<sub>phenolic</sub> and C=N. The TGA data were analyzed for the kinetic parameters and the thermodynamic functions were calculated. All compounds were screened for their antimicrobial activity against various organisms and the results were discussed. Series of mono and binuclear  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Ru}^{3+}$ ,  $\text{Hf}^{4+}$ ,  $\text{ZrO}^{2+}$  and  $\text{UO}_2^{2+}$  complexes of phenylaminodibenzoylhydrazone were prepared and characterized [12].

Up to date, no work was done on the chelation behavior of 3,4-dihydroxybenzylidene isonicotinylhydrazone, HBINH. On continuation to our earlier work on bis(hydrazone) [13–17], the aim is to depict the structure, ligation and antimicrobial behavior of the ligand and its complexes.

## Experimental

$\text{VO}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ ,  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{ZrCl}_4$ ,  $\text{K}_2\text{PdCl}_4$ , isonicotinic acid hydrazide, 3,4-dihydroxybenzaldehyde, ethanol, diethyl ether and DMSO are the chemicals used in this work and all are obtained pure from Sigma chemicals.

### Synthesis of HBINH

3,4-Dihydroxybenzylidene isonicotinylhydrazone, Fig. 1, was prepared by mixing solution of 6.5 g (0.05 mol) of isonicotinic acid hydrazide in 30 mL absolute EtOH with the solution of 6.8 g (0.05 mol) of 3,4-dihydroxybenzaldehyde in 20 mL absolute EtOH and heating the mixture under reflux for 3 h. The precipitate was filtered, crystallized from absolute ethanol and dried. The crystals

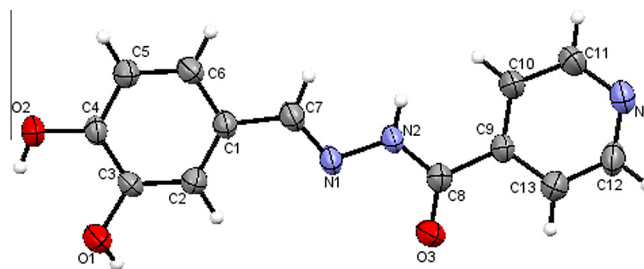


Fig. 1. Crystal structure of 3,4-dihydroxybenzylidene isonicotinylhydrazone.

formed in the filtrate solution, after evaporation, were solved by X-ray crystallography. The ligand was characterized by spectral studies and elemental analysis. Its  $^1\text{H}$  NMR spectrum gave signals at  $\delta = 11.846$ , 9.412, 8.783–8.276, 7.926–6.786 and 6.815 ppm corresponding to the protons of NH, OH, pyridine CH, aromatic CH and aliphatic CH, respectively. Its  $^{13}\text{C}$  NMR spectrum showed peaks at 161.29, 150.33, 148.36, 145.83, 140.76, 121.48, 121.56, 115.65 and 112.78 due to C=O, C=N and all of CH's.

### Synthesis of the metal complexes

The solid metal complexes were prepared by reacting the calculated amounts for the 1:1 ratio [M:L] of the metal salt and the ligand, each dissolved in 30 mL EtOH. The solution was heated under reflux on a heating mantle for 6–8 h. In the preparation of  $\text{VO}^{2+}$  and copper acetate complexes, the reaction was carried out in  $\text{H}_2\text{O}$ –EtOH (1:1 by volume) solution. The precipitates thus formed were filtered off, washed with hot water, hot ethanol, diethyl ether and finally dried in a vacuum desiccator over silica gel. Trials to grow single crystals for the complexes in different solvents were unsuccessful.

### Analysis and instruments

C, H and N content of HBINH and its complexes was determined at the Microanalytical Unit, Varian Micro V1.5.8, CHNS Mode, 15073036, Kuwait University. The FTIR spectra were recorded on a FT/IR-6300 type A (200–4000  $\text{cm}^{-1}$ ) as KBr discs. The electronic spectra (UV–Vis) of the compounds were recorded on a Cary 5 UV–Vis Spectrophotometer, Varian (200–900 nm). The NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ) spectra of the ligand and its diamagnetic complexes were recorded in  $\text{DMSO}-d_6$ , on a Bruker WP 200 SY Spectrometer (400 MHz) at room temperature using tetramethylsilane (TMS) as external standard. The mass spectra of the ligand and some of its complexes were recorded in Thermo (GC–MS–FAB) Spectrometer. The magnetic measurements were carried out on a Johnson–Matthey magnetic balance, UK. The TGA thermograms were measured (10–800  $^\circ\text{C}$ ) on a Shimadzu TGA-60; the nitrogen flow and heating rate were 50 ml/min and 10  $^\circ\text{C min}^{-1}$ , respectively. The X-ray single crystal diffraction data of HBINH were collected on a Rigaku R-Axis Rapid diffractometer using filtered  $\text{Mo-K}\alpha$  radiation. The structure was solved by the direct methods and expanded using Fourier techniques at Kuwait University.

### Antimicrobial studies

The *in vitro* antimicrobial activity of HBINH and its complexes was tested against *Bacillus* sp. M3010, *Candida albicans*, *Escherichia coli*, *Staphylococcus aureus* PA128 and *Slamonella* sp. PA393. The hole plate diffusion method [16] was adopted for the activity measurements. The bacterial strains were grown in nutrient agar slants. A suspension of the studied compounds (0.2 ml of each (10  $\mu\text{g/ml}$ ) was incubated at 36  $^\circ\text{C}$  for 36 h for the bacterial culture. After

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