Synthesis, Characterisation, and Biological Activity of Pd(II), Zn(II), Cd(II), and Hg(II) Metal Coordination Compounds of (4-(dimethylamino)benzylidene)hydrazono)butan-2-one oxime

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Abstract:

A metal coordination compounds of of Pd(II), Zn(II), Cd(II) and Hg(II) have been synthesised using a ligand, (4-(dimethylamino)benzylidene)hydrazono)butan-2-one oxime, (HDABHBO), an oximino hydrazone, and characterised by variuos physico-chemical techniques, FT(IR), PMR, Electronic spectra, etc. All complexes synthesised are non-electrolyte in nature and they have high decomposition temperature, indicating strong metal ligand bond. Spectral data suggest that Pd(II) complex is square planar, whereas, Zn(II), Cd(II), Hg(II) coordination compounds are tetrahedral. Prepared coordination compounds were also screened for biological activities.

Keywords: coordination compounds, ligand, biological activity, sensitive.

Introduction

This class of ligands are known for their ambidenticity, good coordination and chelation ability and analytical applications[1-3]. Oximino hydrazone-metal coordination compounds are widely studied for its synthetic flexibility, good coordination ability, structural resemblance with natural biological substances, and their ability to serve as potent biologically active compounds[5-7]. Ligands of this class are known to report metal coordination compounds of varied geometries, stabilities and applications. Scanning of the literature suggests that, present work have not been reported. The present work deals with the synthesis, characterization and biological activities of the metal coordination compounds of Pd(II), Zn(II), Cd(II) and Hg(II) of HDABHBO.

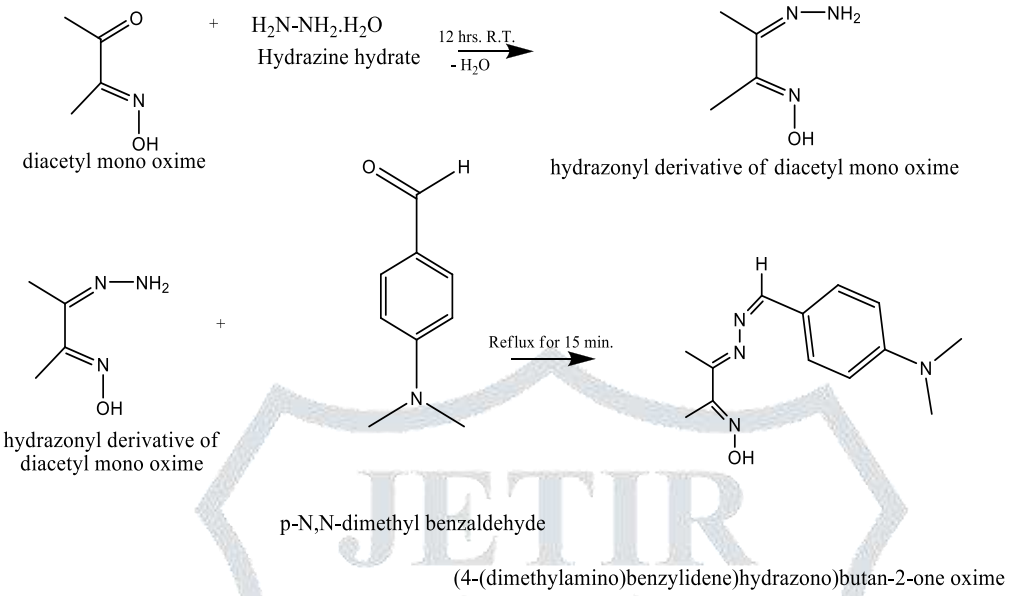
Experimental

Materials and Methods

All chemicals used were of AR grade. Other chemicals if used were purified by standard methods before use. The organic solvents used were purified by standard methods. All metal(II) salts used were as their chloride salts. IR and NMR spectra were recorded at SAIF IIT Bombay, Electronic spectra were obtained on Shimadzu, and magnetic measurements were made on Gouy Balance at Institute of Science. Mumbai.

Synthesis of Ligand

(4-(dimethylamino)benzylidene)hydrazono)butan-2-one oxime, (HDABHBO) have been prepared by reported method[8].



Synthesis of Metal Coordination compounds of ligand

i. Synthesis of Pd(II) coordination compound of HDABHBO: Hot ethanolic solution of ligand (0.04 mol) was added drop-wise to the hot aqueous, acidic (HCl) solution of Pd(II) chloride salt (0.02 mol), with constant and vigorous stirring, the coordination compound precipitated out without adding ethanolic ammonia solution. The precipitated coordination compound was then refluxed for 30 min for reaction completion. The precipitated coordination compound was filtered at suction pump, through sintered glass crucible, washed with water, followed by cold ethanol, and then dried at 110°C.

ii. Synthesis of Zn(II) coordination compound of HDABHBO: Hot ethanolic solution of ligand (0.04 mol) was added drop-wise to the hot ethanolic solution of Zn(II) chloride salt (0.02 mol), with constant and vigorous stirring, after complete addition of ligand solution, ethanolic solution of ammonia was added drop-wise till coordination compound precipitated (precipitation occurred at pH = 8.2). The precipitated coordination compound was then digested on the water bath for 20 min, filtered at suction pump, through whatman paper no. 1, washed with water, followed by cold ethanol, and then dried at 110°C.

iii. Synthesis of Cd(II) coordination compound of HDABHBO: Hot ethanolic solution of ligand (0.04 mol) was added drop-wise to the hot ethanolic solution of Cd(II) chloride salt (0.02 mol), with constant and vigorous stirring, after complete addition of ligand solution, ethanolic solution of ammonia was added drop-wise till coordination compound precipitated (precipitation occurred at pH = 8.2). The precipitated coordination compound was then digested on the water bath for 20 min, filtered at suction pump, through whatman paper no. 1, washed with water, followed by cold ethanol, and then dried at 110°C.

iv. Synthesis of Hg(II) coordination compound of HDABHBO: Hot ethanolic solution of ligand (0.04 mol) was added drop-wise to the hot ethanolic solution of Hg(II) chloride salt (0.02 mol), with

constant and vigorous stirring, after complete addition of ligand solution, ethanolic solution of ammonia was added drop-wise till coordination compound precipitated (precipitation occurred at pH = 8.2). The precipitated coordination compound was then digested on the water bath for 20 min, filtered at suction pump, through whatman paper no. 1, washed with water, followed by cold ethanol, and then dried at 110°C.

Results and Discussion

Characterisation of Ligand

Ligand, HDABHBO have been synthesised and characterised as enumerated in our previous research paper[8].

Characterisation of Coordination Complexes:

Pd(II), Zn(II), Cd(II), Hg(II) complexes of HDABHBO represented by the general formula $[ML_2]$. These observations are in conformity with molecular weights determined by Rast's method[9].

All metal coordination compounds are insoluble in wate, soluble in organic solvents, such as hot-ethanol, hot-methanol, chloroform, nitrobenzene, DMF, DMSO, etc. Those are insoluble in dilute alkali solution, suggesting the absence of oximino proton, in these complexes. All the coordination compounds are stable at up to 193 °C, suggesting high thermal stability and strong metal—ligand bond. Conductance measurement in nitrobenzene suggests that they are non-electrolytic in nature.

A common feature of the electronic absorption spectrum of the synthesised coordination compounds in chloroformic solution shows absence of any appreciable absorption band beyond 14.00kK. This is typical of square planar Pd(II) and tetrahedral Zn(II), Cd(II), and Hg(II) complexes.

IR spectral studies:

The band appearing at 1610 cm^{-1} due to the azomethine group has shifted to lower frequency by about 10-15 cm^{-1} indicating involvement of azomethine nitrogen[10] in the complexation. Further evidence of coordination of ligand to metal is evident by the appearance of weak low frequency new bands at 565-640 cm^{-1} and 435-522 cm^{-1} which may be assigned[11,12] to metal-nitrogen (M—N) and metal-oxygen (M—O) bonds respectively. These bands are observed in the spectrum of coordination compounds but not in the spectra of ligand, confirming the participation of nitrogen and oxygen in coordination.

PMR spectral studies:

The 1H NMR spectra of HDABHBO complexes show a multiplet in the aromatic region δ6.80 – 7.67 due to the phenyl ring, this is slightly changeable region, these described that the phenyl does not contribute the coordination in metal complexes. The singlet peak due to the N – OH proton at δ11.80 in HBMHDAB is absent in its Pd(II), Zn(II), Cd(II) and Hg(II) complexes, suggesting the deprotonation of the hydroxyl group of the oxime in the ligand.

Powder XRD studies: Following are the results of powder XRD studies of coordination compounds.

Coordination Compound	Crystal Type	Cell Parameters (Å)			α	β	γ	Density g/cm^3
		a	b	c				
[Zn(DABHBO)$_2$]	Monoclinic	11.3000	13.6540	10.7290	_____	94.02°	_____	1.956
[Cd(DABHBO)$_2$]	Monoclinic	7.6514	20.2928	16.6137	_____	97.18	_____	1.999
[Hg(DABHBO)$_2$]	Monoclinic	9.7601	25.7230	14.0525	_____	114.21°	_____	1.784
[Pd(DABHBO)$_2$]	Monoclinic	7.6640	17.9545	21.5137	_____	92.96°	_____	1.839

i. Biological studies: Sterile apparatus were used for the investigation of antibacterial activity of the test samples. The biological activity of synthesised ligand and their metal coordination compounds have been studied against the bacteria (Stapylococcus aureus, Corynebacterium diptheriae, Escherichia coli and Pseudomonas Spp). In the present study, three methods viz. ditch plate method, plug diffusion method and cup diffusion method were used to assay the antimicrobial activity of the test compounds. Considering the feeble solubility of the synthesised coordination compounds in water, ditch plate method was first employed to screen compounds' antimicrobial activity and the compounds that exhibited positive antimicrobial activity in the ditch plate method were further studied for reaffirmation of their antimicrobial activity by plug diffusion and cup diffusion methods. In vitro antimicrobial activity of the ligand and its metal(II) coordination compounds evaluated as follows:

Microorganisms are termed as sensitive, or susceptible, or resistant depending on the growth observed around or over or beneath compound being tested.

a. Ditch plate method[13]: Taking into considerations the feeble solubility of the coordination compounds (test compounds) a ditch plate method was first employed to investigate the microbial activity of the test compounds. See Table.1

Table.1

Test Compounds	**Test Organisms**			
	Escherichia coli	**Staphylococcus aureus**	**Corynebacterium diptheriae**	**Pseudomonas spp**
Ligand	Inactive	Inactive	Inactive	Inactive
[Zn(DABHBO)$_2$]	Inactive	Inactive	Inactive	Inactive
[Cd(DABHBO)$_2$]	Sensitive	Sensitive	Sensitive	Sensitive
[Hg(DABHBO)$_2$]	Sensitive	Sensitive	Sensitive	Sensitive
[Pd(DABHBO)$_2$]	Inactive	Sensitive	Sensitive	Inactive

b. Plug diffusion method[14]: In this method a nutrient agar plug impregnated with the test compound is/are placed on a fresh sterile nutrient agar plate surface seeded with bacteria. The activity of the test compound was then investigated for zone of inhibition. See Table.2

Table.2

Test Compounds	Test Organisms			
	Escherichia coli	**Staphylococcus aureus**	**Corynebacterium diptheriae**	**Pseudomonas spp**
$[Cd(DABHBO)_2]$	Sensitive	Sensitive	Sensitive	Sensitive
$[Hg(DABHBO)_2]$	Sensitive	Sensitive	Sensitive	Sensitive
$[Pd(DABHBO)_2]$	_____	Sensitive	Sensitive	_____

Conclusion:

A novel d-block metal (Zn(II), Cd(II), Hg(II) and Pd(II)) coordination compounds of HDABHBO have been synthesised, characterised and were studied further for their biological activity.

$[Cd(DABHBO)_2]$ and $[Hg(DABHBO)_2]$ coordination compound showed biological activity towards Escherichia coli, Staphylococcus aureus, Corynebacterium diptheriae and Pseudomonas spp, $[Pd(DABHBO)_2]$ was biologically active towards Staphylococcus aureus, and Corynebacterium diptheriae.

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