

Synthesis, Characterisation, and Biological Activity of Metal Coordination Compounds of Oximino Hydrazone

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Abstract:

A novel ligand (4-(dimethylamino)benzylidene)hydrazono)butan-2-one oxime, (HDABHBO) and its metal complexes of Co(II), Ni(II) and Cu(II) have synthesised and characterised by elemental analysis, physico-chemical techniques, FT(IR), Electronic spectra, ESR etc. Ambidenticity, good coordination and chelation ability, analytical applications¹⁻³. Prepared compounds also screened by biological activities against human pathogenic bacteria. Ligands of this class are also known for their antimicrobial activity⁴.

Introduction

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 compounds⁵⁻⁷. Ligands of this class are known to report metal coordination compounds of varied geometries, stabilities and applications. Scanning of the literature reveals that present ligand and its metal complexes including its biological activities have not been studied. The ligand is expected to exhibit interesting structures for its metal complexes. As such the present work deals with the synthesis, characterization and biological activities of the present ligand and its Co(II), Ni(II), Cu(II) metal complexes.

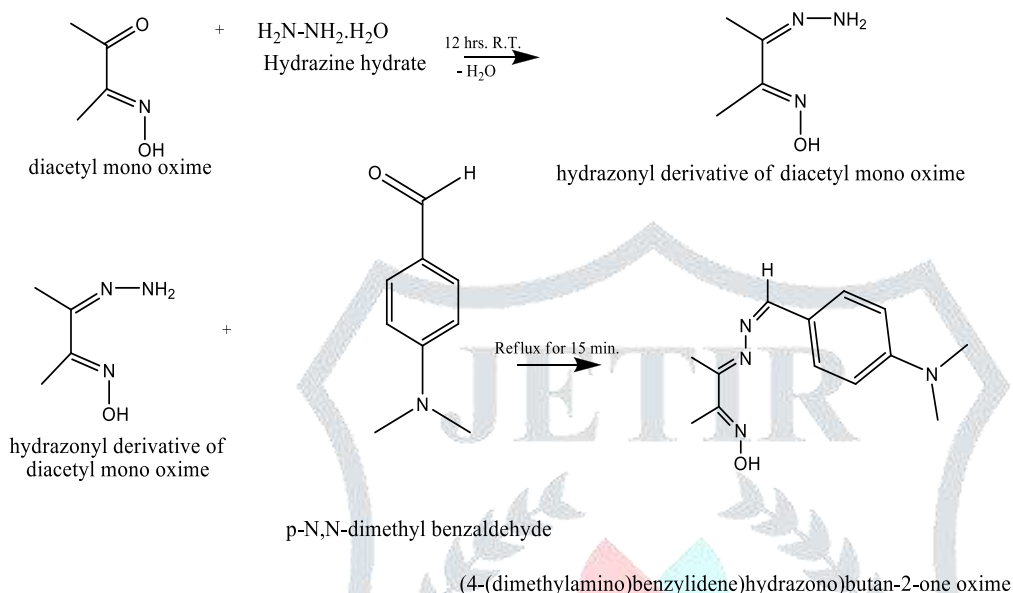
Experimental

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

Hydrazone derivative of diacetyl monoxime have been prepared by reported method⁸. 50 mmol of hydrazone derivative of diacetyl monoxime and 50 mmol of p-(N,N-dimethyl amino) benzaldehyde in 50.0 mL of ethanol was refluxed for 30 min. reaction was monitored for its progress and completion by TLC. A bright yellow coloured product separated out was filtered, washed thoroughly with water, recrystallized from ethanol, dried in the oven at 110°C.



Synthesis of Metal Coordination compounds of ligand

- i. Synthesis of Co(II) coordination compounds of Ligand: Hot ethanolic solution of ligand (0.04 mol) was added drop-wise to the hot ethanolic solution of Co(II) chloride salt (0.02 mol) solution, 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 nearly and neutral pH), resultant content was then refluxed for 30 min for reaction completion. The precipitated coordination compound was filtered at suction pump, through whatman paper no.1, washed with water, followed by cold ethanol and then dried at 110°C.
- ii. Synthesis of Ni(II) coordination compound of Ligand: Hot ethanolic solution of ligand (0.04 mol) was added drop-wise to a hot ethanolic solution of Ni(II) chloride salt (0.02 mol) solution, 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 = 7.2), resultant solution was then refluxed for 30 min for reaction completion. The precipitated coordination compound was 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 Cu(II) coordination compound of Ligand: Hot ethanolic solution of ligand (0.04 mol) was added drop-wise to the hot ethanolic solution of Cu(II) chloride salt (0.02 mol) solution, 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 nearly neutral pH), resultant solution was then refluxed for 30 min for reaction completion. The precipitated coordination compound was filtered at suction pump, through whatman paper no.1, washed with water, followed by cold ethanol and then dried at 110°C.

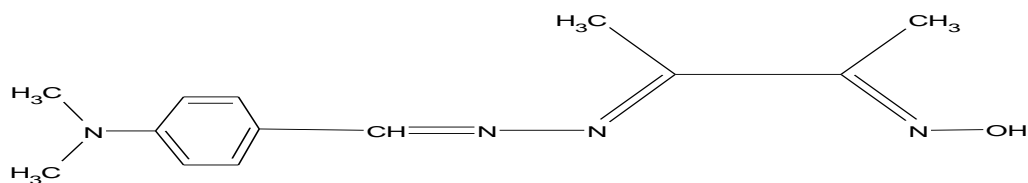
Results and Discussion

Ligand Characterisation: Characterisation of ligand is done by interpretation of analytical data obtained from FTIR, PMR, UV Visible spectroscopy, elemental analysis, etc. Melting point of the compound is 181°C. It is bright yellow crystalline solid, soluble in chloroform, acetone, DMF, DMSO, dioxane, dilute alkali, etc., and soluble in hot ethanol and methanol.

UV Visible spectral studies: The electronic absorption spectrum of the methanolic solution of the ligand HBMHDAB in the ultra-violet region shows three high intensity band at 45.87kK ($\epsilon = 13460 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 40.98kK ($\epsilon = 9853 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and at 27.02kK ($\epsilon = 13933 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). This may be due to intra ligand, $\pi^* \leftarrow \pi$ (allowed) transitions of azomethine environment in the molecule. The ultra-violet spectrum of the ligand HHBHDAB in dilute alkali solution (0.1N NaOH) solution reveals that the band observed at 27.02kK ($\epsilon = 13933 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in the methanol solution spectrum somewhat suppressed and shifted to the higher wavelength i.e. at 23.89kK ($\epsilon = 6199 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The bathochromic shift in the band at 24.94kK and the lowering of intensity suggests formation of anion BHDAB⁻ in the alkaline solution due to the deprotonation of the oximino group.

IR spectral studies: IR spectra of the ligand showed the absence of bands at 1725 and 3300 cm^{-1} those are ascribed for carbonyl ($>\text{C}=\text{O}$) and ($-\text{NH}_2$) stretching vibrations and, instead, appearance of strong new band at $\sim 1610 \text{ cm}^{-1}$ is assigned to the azomethine⁹ ($>\text{C}=\text{N}-$). It suggests that amino and carbonyl moieties of the starting reagents are absent and have been converted into azomethine.

PMR studies: The pmr spectrum of HBMHDAB in (d₆) DMSO solvent reveals a broad singlet at $\delta 11.80$, suggesting the highly acidic nature of this proton. A multiplet observed around $\delta 6.80 - 7.67$ due to phenyl rings in the ligand structure. The singlet observed at $\delta 8.30$ is suggested to be due to $-\text{CH}=\text{}$ group in the ligand. The methyl protons observed at around $\delta 2.00-2.25$, region in the ligand. On the basis of spectral studies, ligand structure can be assigned as;



i. Characterisation of Coordination Complexes:

UV Visible spectral studies:

The electronic spectral data of metal (II) complexes were recorded in Chloroform. The electronic spectrum of the Co(II) complex displayed bands at 10.58kK ($\epsilon=12\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) and 22.57kK ($\epsilon=383\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$). These two bands are assignable to ${}^4\text{T}_{2g}\rightarrow{}^4\text{T}_{1g}(\text{F})$ (ν_1) and ${}^4\text{A}_{2g}\rightarrow{}^4\text{T}_{1g}(\text{F})$ (ν_2) transitions respectively. The value of $\nu_2/\nu_1=2.13$ lies in the range 2.1–2.2, reported for most of the octahedral Co(II) compounds¹². [Ni(BMHDAB)₂] shows two bands at 10.28kK ($\epsilon=9\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) and 16.051kK ($\epsilon=870\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) due to ${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{2g}(\nu_1)$ and ${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{2g}(\text{F})$ (ν_2) transitions respectively on the basis of idealized octahedral geometry¹⁵. The ratio ν_2/ν_1 is found to be 1.56, which falls in the range reported for the other octahedral complexes of Ni(II) supporting the assignment¹⁶. From the observed position of ν_1 and ν_2 transitions, the frequency of the third transition ${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{1g}(\text{P})$ (ν_3) and B values has been calculated¹⁷. The third band ν_3 is expected to occur at 19.17kK. However, this band is not observed in the solution spectrum of the complex probably because, it is masked by the tail-end of the strong charge transfer band around 25.97kK. The value of the Racah interelectronic repulsion parameter B is 7060cm^{-1} , the covalency factor is found to be 8216cm^{-1} and is in close agreement octahedral Ni(II) complexes¹⁸.

A band at 16.31kK is attributed to ${}^2\text{E}_g\rightarrow{}^2\text{T}_{2g}(\text{D})$ transition suggesting a distorted octahedral geometry for Cu(II) complex.

IR spectral studies:

The band appearing at 1610cm^{-1} due to the azomethine group has shifted to lower frequency by about 10-15 cm^{-1} indicating involvement of azomethine nitrogen¹⁰ in the complexation. A band appearing at 3414-3449 cm^{-1} in coordination compounds have significantly different characteristics of ν_{OH} stretching vibration is due to stretching modes in coordinated water molecules. 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.

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				
[Co(DABHBO) ₂ (OH ₂) ₂]	Triclinic ¹²	12.9830	14.0920	14.6710	115.70°	100.03°	102.11°	1.366
[Ni(DABHBO) ₂ (OH ₂) ₂]	Triclinic ¹³	17.2620	17.9425	18.4478	70.61°	82.36°	63.12°	1.612
[Cu(DABHBO) ₂ (OH ₂) ₂]	Monoclinic ¹⁴	15.4850	9.5620	30.2340	_____	104.05	_____	1.487

ii. 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 (*Staphylococcus 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 method¹⁵: 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			
	<i>Escherichia coli</i>	<i>Staphylococcus aureus</i>	<i>Corynebacterium diptheriae</i>	<i>Pseudomonas spp</i>
HDABHBO	Inactive	Inactive	Inactive	Inactive
[Co(DABHBO) ₂ (OH ₂) ₂]	Sensitive	Sensitive	Sensitive	Sensitive
[Ni(DABHBO) ₂ (OH ₂) ₂]	Inactive	Inactive	Inactive	Inactive

[Cu(DABHBO) ₂ (OH ₂) ₂]	Inactive	Sensitive	Sensitive	Inactive
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b. Plug diffusion method¹⁶: 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
[Co(DABHBO) ₂ (OH ₂) ₂]	Sensitive	Sensitive	Sensitive	Sensitive
[Cu(DABHBO) ₂ (OH ₂) ₂]	_____	Sensitive	Sensitive	_____

Conclusion:

A novel ligand (4-(dimethylamino)benzylidene)hydrazono)butan-2-one (an oximino-hydrazone) was obtained by the condensation reaction of hydrazone derivative of diacetyl mono oxime and p-N,N-dimethyl benzaldehyde and its novel transition metal complexes with Co(II), Ni(II) and Cu(II) were prepared, characterised and were screened for their biological activity.

[Co(DABHBO)₂(OH₂)₂] coordination compound showed biological activity towards Escherichia coli, Staphylococcus aureus, Corynebacterium diptheriae and Pseudomonas spp, [Ni(DABHBO)₂(OH₂)₂] was biologically inactive, whereas, [Cu(DABHBO)₂(OH₂)₂] was biologically active towards Staphylococcus aureus and Corynebacterium diptheriae.

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