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RESEARCH ARTICLE

Synthesis, Characterization and Anti-microbial activity of Co(II) and Zn(II) complexes of *o*-nitro benzaldehyde malonoyl hydrazone Schiff's Base (O-NBMH)

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ABSTRACT

Co(II) and Zn(II) metal complexes were derived from o-nitro benzaldehyde and malonic acid hydrazide and characterized by elemental analysis, IR and magnetic studies. The antimicrobial activities were carried out on three non-pathosenic fungi A. flavus, A. japonicoss and penicillium. The metal complexes show enhanced activity as compound to the ligand.

Key words: *Schiff base (NBMH), Transition metal complexes. IR, electronic, magnetic moments, conductance and antimicrobial activity*

INTRODUCTION

Compounds containing an azomethine group (-CH=N) are known as Schiff base. Schiff bases are generally bi, tridentate and chelate ligands, capable of forming very stable complexes with transition metals. Schiff bases and their complexes show analytical (Terzioolu 2003), biological and pharmaceutical activities such as antitumor (Buttger 1961), antitubercular (Todeschini, *et al.,* 1998), antiinflammetry (Kitaev, *et al.,* 1970), pharmacological agents (Schiff 1964). Substituted hydrazones are used for the treatment of Schizophrenia (Buckingham 1987), leprosy (Syamal and Maurya 1987), plant growth regulators (Hafez, *et al.,* 1960), insecticides (Haksar, *et al.,* 1974), rodentisides (Fay and Piper1962; Satpathy and Sahoo 1970; Hafez 1986), antifungal (Rao and Ganorkar 1983), vasodialators (Silva, *et al.,* 2005), antibacterial (Khamankar and Pallapothula 2012), antiviral, antimalarial and analgesic, A detailed survey of literature reveals that biological activity of the ligand can be enhanced on chelation with metal ions.

In view of the importance of Schiff bases both as chelation and biological agents, it has been proposed to prepare ligand (O-NBMH) and its various complexes with metal ions like Co(II), Zn(II).

EXPERIMENT

All the chemicals used were of BDH (Analar) grade. The complexes were analyzed for their metal content employing a standard literature method, after destroying the organic matter with conc. HNO_3 + con. HCl mixture and then evaporating the acid mixture with one drop of conc. H_2SO_4. Carbon, Hydrogen and Nitrogen were estimated at sophisticated instrumentation centre, CDRI, Lucknow. Sulphur was estimated in the form of barium sulphate. The electrical conductivity of the complexes was measured on a WTW conductivity-meter in ethanol (10^{-3}M) while melting points was recorded on Toshniwal m.p. apparatus. IR Spectra of the complexes were recorded on aPerkin Elmer grating spectrophotometer in the range of 4000–600 cm^{-1} at Regional Sophisticated Instrumentation Centre (CDRI) Lucknow.

Electronic spectra of the ligand (O-NBMH) and their metal complexes were recorded on a ELICOSL-159 grating uv-vis spectrophotometer in the range of 200-800nm at Chemistry Department, Agra College, Agra.

The molecular weight of the ligand and their complexes were determined on JEOL-JMD-DA 5000 at Delhi University, Delhi. Magnetic Susceptibility data of the complexes were recorded using Gouy's method at room temperature (31^{0}C), at NPL pusa road, New Delhi.

THE LIGAND (O-NBMH) WAS PREPARED IN THREE STEPS AS FOLLOWS

(i) Preparation of Malonic ester:

6.72 g (0.04M) of Malonic acid was dissolved in 50ml of ethanol. To this homogeneous solution, 1.46ml (0.02M) dimethyl sulphide was added and the whole mixture was refluxed at 80^{0}C for 8 hrs. The solution was cooled to get white crystals. The crystals were filtered, washed with ethanol followed by ether and dried over anhydrous calcium chloride in desiccators (m.p. 115^{0}C).

(ii) Preparation of Malonic acid hydrazide:

6.72 g (0.04M) of Malonic ester was dissolved in 50ml of ethanol. To this clear solution 0.82ml (0.02M) of hydrazine hydrate was added drop wise with constant stirring. The resulting mixture was refluxed for 6 hrs. It was concentrated on water bath and cooled over night to get pale yellow crystals. These crystals were washed with ether and dried over anhydrous calcium chloride in desiccators (m.p. 101^{0}C).

(iii) Preparation of *o*-nitro bezaldehyde malonoyl hydrazone (O-NBMH):

1.36g malonic acid hydrazide was dissolved in 20ml 30% acetic acid and this mixture was heated on water bath to get clear solution. Now 1.51g *o*-nitrobenzaldehyde was added dropwise to above cold solution with stinging. After some time a cream coloured solid was separated out which was filtered, washed with ethanol. It was then dried under reduced pressure in desiccators (m.p. 180^{0}C).

METHOD

3.8g (0.02 mole) malonic acid hydrazide was dissolved in 50ml ethanol and heated on water bath till it dissolved. To the above hot solution 0.01 mole metal nitrate solution and 3.02g (0.02 mole) *o*-nitrobenzaldehyde were added with stirring and then whole mixture was refluxed for 12 hrs. On cooling the resulting precipitate was collected by filteration. It was washed with ethanol and dried over anhydrous calcium chloride. This method is known as template synthesis.

BIOLOGICAL STUDIES

The complexes and ligand (O-NBMH) were screened by the filter paper disc method using potato dextorose agar (PDA) and nutrient agar (NA). The percentage of inhibition was, calculated by the equation as shown below

$$\text{Inhibition} = \frac{C\ x\ T}{C} \text{ x } 100$$

C = diameter of organism colony in control plate

T = diameter of the organism colony in test plate.

The various pathogens (fungi and bacteria) selected for this study were as follows.

Aspergillus niger, Aspergillus flavus, Perinillium chrysogenum, Alternaria cladosporium herbasium, pseudomonas aureoginosa, proteus vulgarius, acrobactor aerogenes.

RESULTS AND DISCUSSION

The analytical data of the ligand (O-NBMH) and their metal complexes, given in table 1 indicating 1: 2 metal-ligand ratio and the complexes can be represented by the general formula $M(O\text{-}NBMH)_2.2H_2O$. Whese M = Co(II) and Zn(II).

Elemental analysis data, colour. Molecular weights are given in table 1. The complexes are soluble in organic solvents like methanol, acetone and chloroform. The molar conductance of the complexes (10^{-3} M solution) is negligible suggesting their non-electrolytic nature. All the complexes decomposes above 300^{0}C.

ELECTRONIC SPECTRA

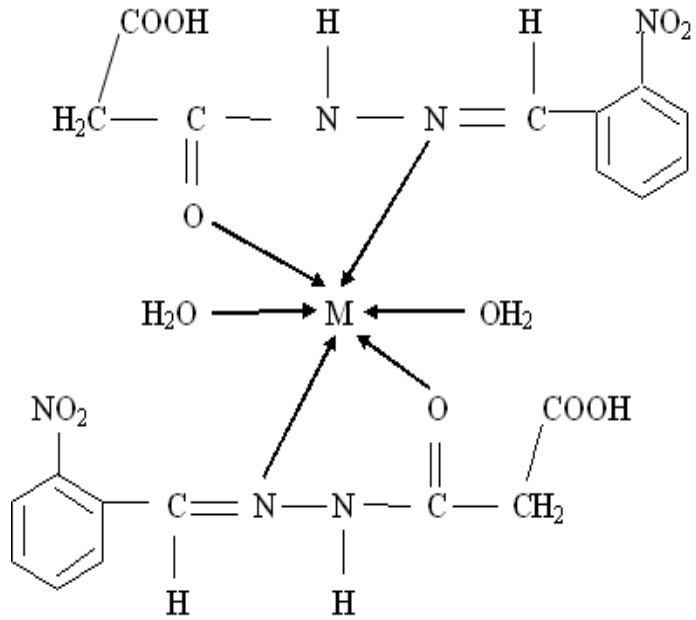
Co(II) complex is blue due to presence of an absorption bant at ~16000 cm^{-1} region of the spectrum due to $^2E_g \rightarrow {}^2T_2g$ transition indicating six-coordinate octahedral field around Co(II). Zn(II) complex is also blue while Zni(II) square planer complexes are commonly brown in colour. In the present study Zn $(O\text{-}NBMH)_2$ shows three absorption bands at 12200 cm^{-1}, 19300 cm^{-1} and 26400 cm^{-1} due to $^3A_2g \rightarrow {}^3T_2g$ (F), ^3A_2g (F) $\rightarrow {}^3T_1g$ (F) and ^3A_2g (F) $\rightarrow {}^3T_1g$ (P) transitions.

INFRARED SPECTRA

IR spectra of the ligand and its complexes are very complex, therefore some important bands have been chosen for the study. A band at ~ 2770 cm^{-1} suggest intramolecular H-bonding. The bands at 1670-1600 cm^{-1}, 1250 cm^{-1} and 650 cm^{-1} have been assigned to amide I υ (C=O), amide II υ (C-N + δN-H) and amide III δN-H respectively. The strong bands observed between 3050 – 3000 cm^{-1} and 1620 – 1615 cm^{-1} have been assigned to υ (N-H) and υ (C=N) of the azomethine group. In the complexes the υ (C=N) bands appear at a lower frequency (~10 cm^{-1}), indicating the coordination of the N-atom of azomethine group to metal atom. The spectra of the ligand shows bands around 1520 cm^{-1} and 1280 cm^{-1} assigned to υ (NCO) and υ (C-O) respectively. In the complexes these bands appear at higher frequency around 1550 – 1540 cm^{-1} and 1310-1290 cm^{-1} suggesting bonding of the ligand to the metal through O atom of the C-O group. The bands between 440-420 cm^{-1}assigned to M – N bonding.

The bands between 875 – 670 cm^{-1} indicating presence of coordinated water. The band positions of the ligand and their metal complexes have been summarized in Table III.

Fig. 1: Structure of the complexes $M(O\text{-}NBMH)_2.2H_2O$



(Where M = Cu, Zn & Co)

CONCLUSION

The antimicrobial activity at the Co(II) and Zn(II) complexes were found to be more active than their hydrazones. Complexes containing nitro group increases the antimicrobial activity. It has been further seen that the addition at hydroxyl group to the above complexes decreases the activity both in case of fungi and Bacteria. Therefore the first fens complexes compound at Co(II) and Zn(II) containing nitro group can be considered as promising antimicrobial agents.

Table 1: Analytical Data of Cobalt Complexes Hydrazones of *o*-Nitro Benzaldehyde and Malonic acid

S.N.	Molecular Formula	Molecular weight Calculated (Found)	Colour	Analytical Data Calculated (found) %			
				C	H	N	Co
1.	$[Co\ (C_{17}H_{14}O_6N_6)(H_2O)_2](NO_3)_2$ Cobalt complex of o-NBMH	658.54	Brown	32.82	2.89	18.01	10.22
2.	$[Co\ (C_{17}H_{14}O_6N_6)(H_2O)_2](NO_3)_2$ Cobalt complex of m-NBMH	658.52	Brown	32.77	2.83	18.00	10.19
3.	$[Co\ (C_{17}H_{14}O_6N_6)(H_2O)_2](NO_3)_2$ Cobalt complex of p-NBMH	658.51	Brown	32.78	2.81	17.99	10.18
4.	$[Co\ (C_{17}H_{12}O_8N_6)]$ Cobalt complex of 3-NHBMH	658.54	Brown	41.50	2.44	22.78	12.92
5.	$[Co\ (C_{17}H_{12}O_8N_6)]$ Cobalt complex of 4-NHBMH	658.50	Brown	41.47	2.41	22.76	12.91
6.	$[Co\ (C_{17}H_{12}O_8N_6)]$ Cobalt complex of 5-NHBMH	658.49	Brown	41.49	2.43	22.75	12.89

Table 2: Analytical Data of Zinc Complexes Hydrazones of *o*-Nitro Benzaldehyde and Malonic acid

S.N.	Molecular Formula	Molecular weight Calculated (Found)	Colour	Analytical Data Calculated (found) %			
				C	H	N	Zn
1.	$[Zn\ (C_{17}H_{14}O_6N_6)(H_2O)_2](NO_3)_2$ Zinc complex of o-NBMH	665.71 (665.68)	White	33.07 (33.04)	2.91 (2.88)	18.16 (18.13)	9.51 (9.50)
2.	$[Zn\ (C_{17}H_{14}O_6N_6)(H_2O)_2](NO_3)_2$ Zinc complex of m-NBMH	665.71 (665.66)	White	33.07 (33.02)	2.91 (2.89)	18.16 (18.14)	9.51 (9.48)
3.	$[Zn\ (C_{17}H_{14}O_6N_6)(H_2O)_2](NO_3)_2$ Zinc complex of p-NBMH	665.71 (665.67)	White	33.07 (33.03)	2.91 (2.87)	18.16 (18.13)	9.51 (9.49)
4.	$[Zn\ (C_{17}H_{12}O_8N_6)]$ Zinc complex of 3-NHBMH	665.71 (665.67)	White	41.91 (41.88)	2.46 (2.42)	23.01 (22.97)	12.06 (12.03)
5.	$[Zn\ (C_{17}H_{12}O_8N_6)]$ Zinc complex of 4-NHBMH	665.71 (665.68)	White	41.91 (41.87)	2.46 (2.42)	23.01 (22.98)	12.06 (12.04)
6.	$[Zn\ (C_{17}H_{12}O_8N_6)]$ Zinc complex of 5-NHBMH	665.71 (665.69)	White	41.91 (41.89)	2.46 (2.42)	23.01 (22.99)	12.06 (12.05)

M = Methanol A = Acetone C = Chloroform E = Ethanol

Table 3: IR spectral data of the complexes (cm^{-1}) and Ligand (O-NBMH)

S.N.	Functional Groups	Co (O-NBMH)$_2$.2 H_2O	Co (O-NBMH)$_2$.H_2O	Zn (O-NBMH)$_2$.2H_2O	Zn (O-NBMH)$_2$.H_2O
1.	- (N – H)	3150	3150	3150	3150
2.	- (C = O)	1660	1670	1665	1675
3.	- (N – N)	1070	1070	1070	1070
4.	- (C = N)	1580	1585	1580	1580
5.	M – O	-	450	460	450
6.	M - N	-	380	375	380
7.	(-OH)	1380	-	1400	-

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