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Synthesis, characterization and biological activities of Cd(II) complexes with hydrazide ligands

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ABSTRACT

A series of new acid hydrazides have been synthesized by reaction of novel ligands Acetic acid (3- chloro – 4 – hydroxyl benzylidene)-hydrazide (A), Acetic acid (2 – nitro – benzylidene)-hydrazide (B) with cadmium (II) bromide , These new complexes were characterized by elemental analysis, IR spectroscopy and UV spectral techniques. The changes observed between the FT-IR and UV-Vis spectra of the ligands and of the complexes allowed us to establish the coordination mode of the metal in complexes . The results suggest that the Schiff bases coordinate as univalent anions with their two dentate N, O donors derived from the carbonyl and azomethine nitrogen . This newly synthesized compounds have been tested against grampositive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) and gram-negative bacteria (*E.coli* and *Salmonella typhi*) for their antibacterial activity.

Keywords: synthesis, Characterization, Antibacterial Activities, Cadmium complexes; Hydrazide ligands.

INTRODUCTION

Cadmium plays an important role in biological and chemical processes. It also forms useful amalgams with many metals, which find various applications in diverse fields. Due to the numerous applications and the toxic nature of amalgams and cadmium compounds, there is a need for simple and accurate analytical methods that allow for the rapid determination of cadmium content in samples [1]. Cadmium is one of the most toxic heavy metals on earth. The toxicity of cadmium depends on its occurring forms; The coordination chemistry of cadmium (II) differs from most other transition metals due to its large size and d10 configuration. Its interference in biological systems, and its potential as a toxin or as a medicine, has required a better understanding of its coordinative properties[2-3].

The coordination chemistry of transition metals with ligands from the hydrazide family has been of interest due to different bonding modes shown by these ligands with both electron rich and electron poor metals. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions.

Hydrazides possessing an azometine -NHN=CH- Proton constitute an important class of compounds for new drug development. Therefore, many researchers have synthesized these compounds as target structures and evaluated their biological activities. Acidhydrazides have recently been investigated for testing their potentiality as tuberculostats [1-4]. Hydrazides and their condensation products have displayed diverse range of biological properties such as bactericidal [5-7], anti-fungal [8], anti-convulsant [9,10], anti-helminthic [11], anti-tumor [12-15], anti-leprotic [16], anti-malarial [17], anti-cancer [18], anti-depressant [19], anti-HIV [20], analgesic-anti-inflammatory [21], leishmanicidal [22], vasodilator activities [23].

In this paper, we are reporting the synthesis, characterization and biological activities of Schiff base derived from reactions of cadmium (II)bromide with Acetic acid (3 – chloro - 4- hydroxyl - benzylidene) - hydrazide (**A**) and Acetic acid (2 – Nitro - benzylidene) - hydrazide (**B**).

The aim of this work is to synthesize new Schiff bases and their metal complexes and to study their coordination behaviour, spectral and biological activities against various microorganisms.

MATERIALS AND METHODS

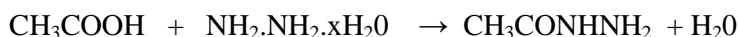
Experimental

All chemicals used were of A.R. grade (either of B.D.H. or Excel-R or Extra pure E. Merck quality). The structures of the compounds were determined by elemental analysis. The UV– Vis spectra in CH₃CN were recorded with a Wpa bio Wave S2 100 spectrophotometer. IR spectra (KBr) are recorded on a Perkin-Elmer 283 spectrophotometer. Melting points of the compounds are determined in open capillary tubes and are uncorrected.

Preparation of the Ligands

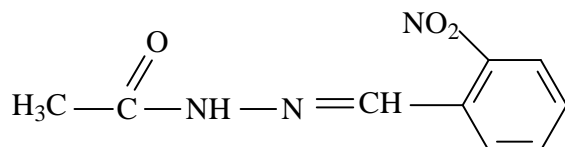
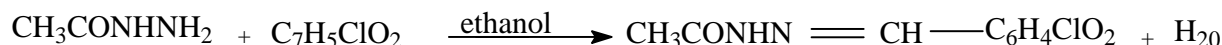
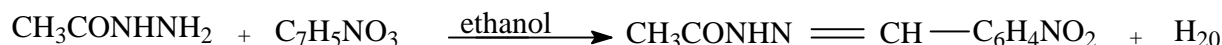
Synthesis of Acetohydrazide

Acetic acid (5mmol) was refluxed with hydrazine hydrate (5mmol) in 50 ml ethanol for 4 hrs. The solid obtained was filtered off, washed with cold water. The white crystals obtained was recrystallized from ethanol and dried to give the product. Scheme 1.

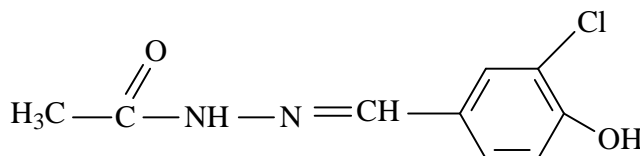


Scheme 1. Schematic representation of formation of Acetohydrazide compound

Equimolar mixture of the the corresponding product (acetohydrazide) (6mmol) were refluxed with the derivative aldehyde i.e 2 – nitro benzaldehyde and 3- chloro – 4- hydroxyl benzaldehyde (6mmol) in 50 ml ethanol for 4 hrs. The products obtained were filtered, washed with ethanol, and dried. Color (white), yield (76%) for (**A**), and Color (white), yield (66%) for (**B**). Scheme 2.



Acetic acid (2 - Nitro - benzylidene) - hydrazide (B) .



Acetic acid (3 - chloro - 4- hydroxyl - benzylidene) - hydrazide (A)

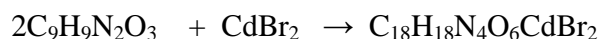
Scheme 2. Schematic representation of Ligands formation of compounds

Formation of the Complexes

Acetic acid (3 - chloro - 4- hydroxyl - benzylidene) – hydrazide Cadmium (II) (C)

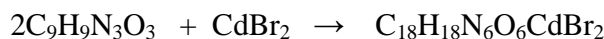
Cadmium bromide (4 mmol) was dissolved in absolute acetonitrile (10 ml) , the mixture was then introduced into (4mmol) of Acetic acid (3 – chloro - 4- hydroxyl - benzylidene)-hydrazide (A) in 10 ml of ethanol . The mixture

was stirred magnetically at room temperature. The precipitated complexes were filtered, washed with ether and dried in a desiccator for few days. Color (milky) , yield (68%) .



Acetic acid (2 – Nitro - benzylidene)-hydrazide cadmium (II) (D)

Complex (D) was synthesized in a similar manner to that used for complex (C), reacting a mixture of (B) (4 mmol) and cadmium bromide (4 mmol) in THF (10 mL). Color (milky) , yield (56%) .



RESULTS AND DISCUSSION

The complexes [Acetic acid (3 – chloro - 4- hydroxyl - benzylidene)-hydrazide] Cd(II) (C) and [Acetic acid (2 – Nitro - benzylidene)-hydrazide] Cd(II) (D) were prepared in good yield by stirring stoichiometric amounts of CdBr₂ and (A) and (B) . (Fig 1 .) . The complexes were characterized by the usual methods: elemental analysis, IR and UV– Vis spectra . The complexes are stable in air and are soluble in inorganic solvents such as HCl₃ and DMSO, less soluble in methanol, ethanol and insoluble in water and n-hexane. The physical and analytical data are summarized in Table 1.

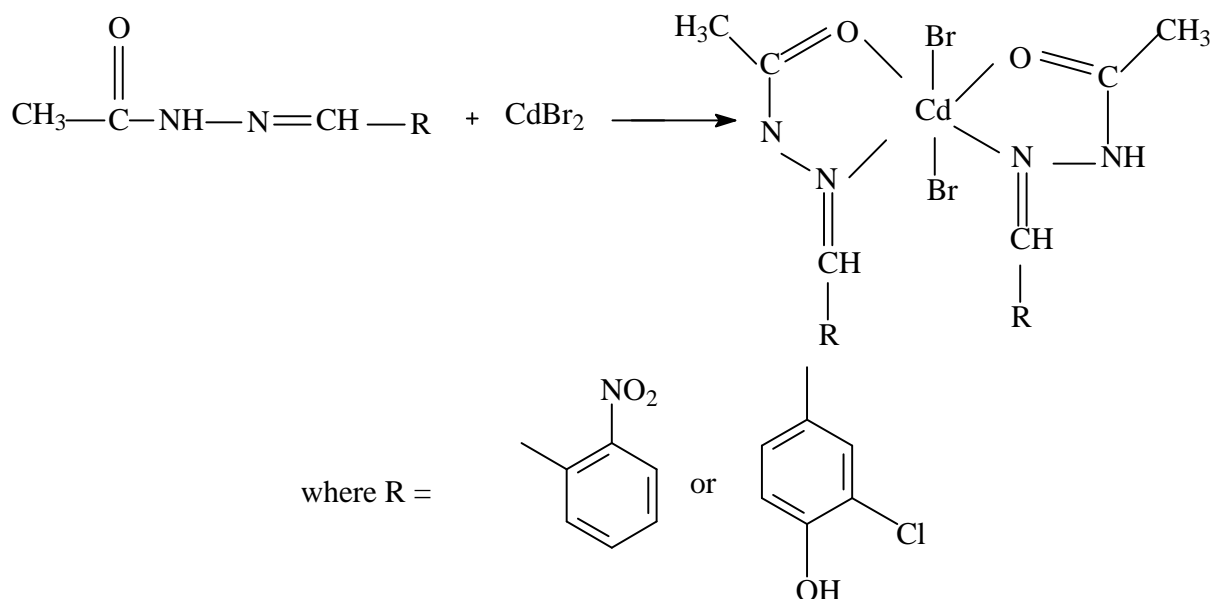


Fig . 1. Schematic representation of metal complex formation of compounds

Table 1. The physical and analytical data of the ligands and complexes

S/n	Compound no.	Molecular formulae	Molecular weight	m. p. °c	Solubility	Elemental analysis Found (calc .)				
						H%	M%	N%	C%	O%
1 .	A	C ₉ H ₉ N ₂ O ₃ Cl	228.5	166	THF	3.97 (3.94)	-	12.20 (12.25)	47.28 (47.26)	21.04 (21.01)
2 .	B	C ₉ H ₉ N ₃ O ₃	207	215	THF	4.30 (4.35)	-	20.34 (20.29)	52.19 (52.17)	23.20 (23.19)
3 .	C	C ₁₈ H ₁₈ N ₄ O ₆ Cl ₂ CdBr ₂	729	176	THF	2.57 (2.47)	15.39 (15.36)	7.69 (7.68)	29.67 (29.63)	13.20 (13.17)
4 .	D	C ₁₈ H ₁₈ N ₆ O ₆ CdBr ₂	686	234	THF	2.61 (2.62)	16.31 (16.32)	12.23 (12.24)	31.50 (31.49)	14.01 (13.99)

Table 2. IR Spectral Bands of Ligands and Its Complexes

S/n	Compound no.	IR in KBr pellets , cm ⁻¹					
		v(C=N)	v(N-H)	v(N-N)	v(C=O)	v(Cd- O)	v(Cd-N)
1 .	A	1593	3175	1003	1676	-	-
2 .	B	1625	3084	1024	1677	-	-
3 .	C	1588	3175	1055	1663	473	541
4 .	D	1615	3084	1033	1669	483	533

Electronic spectra

The formation of the cadmium(II) complexes was also confirmed by UV-Vis spectra. The absorption spectra of the diamagnetic Cd(II) complexes were recorded as 10⁻⁴ M CH₃CN solutions in the range 200–800 nm using a quartz cuvette of 1 cm path length. The complexes show only the charge transfer transitions which can be assigned to charge transfer from the ligand to the metal and vice versa, no d-d transition are expected for d₁₀ Cd(II) complexes [24] . When compared complexes with the free ligands values have shifts frequency. The data of The spectra of the cadmium(II) complexes in CH₃CN solutions are shown that absorption band

observed at 269 and 326 nm is attributed to $n \rightarrow \pi^*$ electronic transition of the hydrazide ($-\text{NH}-\text{N}=\text{C}-$) group involving the whole conjugation.

Infrared spectra

The infrared spectra of the complexes taken in the region 400–4000 cm^{-1} were compared with those of the free ligands. There are some significant changes between the cadmium(II) complexes and their free ligands for chelation as expected. The main stretching frequencies of the IR spectra of the ligands (**A** and **B**) and their complexes are tabulated in Table 2. An exhaustive comparison of the IR spectra of the ligands and complexes gave information about the mode of bonding of the ligands in metal complexes. The IR spectra of $[\text{CdA}]\text{Br}_2$ complexes, the ligands act as a neutral bidentate through the azomethine and carbonyl groups [24]. The characteristic IR bands of Cd(II) complexes are: 1663, 1669 cm^{-1} (ν (C=O) carbonyl), 1588, 1615 cm^{-1} (ν (C=N) (azomethine), (**C**) and (**D**) complexes respectively. The spectrum of the ligands have been observed for ν (C=O) at 1676, 1677 cm^{-1} and ν (C=N) at 1593, 1625 cm^{-1} , respectively (A and B) [25]. The azomethine band is shifted to lower frequency in all metal complexes, suggesting that this group takes part in coordination. The coordination of nitrogen to the metal atom would be expected to reduce the electron density on the azomethine link and thus cause a shift in the C=N band. Moreover, in the spectra of the complexes, a considerable negative shift in ν (C–O) are observed indicating a decrease in the stretching force constant of C–O as a consequence of coordination through the carbonyl–oxygen atom of the free ligands [26]. In the FT-IR spectra the band due to N-H stretching in the free ligands occurs in the 3175, 3084 cm^{-1} region and remains unaffected after complexation. This precludes the possibility of coordination through the hydrazine nitrogen atom. The small shift to higher frequency of the band due to ν (N–N) can be taken as additional evidence of the participation of the azomethine group in bonding. This result is confirmed by the presence of a new band at 541, 533 cm^{-1} and 473, 483 cm^{-1} ; these bands can be assigned to ν (M–O) and ν (M–N) vibrations, respectively [27].

Antibacterial Activities

Antibacterial activity of A and B ligands and its metal (II) complexes were studied against grampositive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) and gram-negative bacteria (*E.coli* and *Salmonella typhi*) at a concentration of 50 μ g/ml by agar cup plate method. Methanol system was used as control in this method. The area of inhibition of zone measured in mm.[28].

Table 3 : Antibacterial activities of the ligands and complexes

S/n	Comp. No.	Zone of inhibition mm			
		Gram +ve		Gram -ve	
		<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i>	<i>Salmonella typhi</i>	<i>E. coli</i>
1.	A	55	67	65	54
2.	B	44	65	77	63
3.	C	59	74	75	71
4.	D	68	58	72	59

The antimicrobial activity of the ligands and its metal(II) complexes are presented in Table 3 . The data suggest that all the samples are toxic to bacteria . The data also suggest that the percentage of bacteria is inhibited in the range of 44 to 75% . All the compounds have good microbicidal activity.

CONCLUSION

This study reports the successful synthesis of the title compounds in good yields and from the elemental analysis, UV-Visible, and IR spectral data it was possible to determine the type of coordination of the ligands in their metal complexes. In the complexes, it is concluded that the ligands acts as a neutral bidentate through the azomethine nitrogen atom and carbonyl groups and all the compounds have good microbicidal activity .

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