

Arsenic (II) complexes of Acetic acid (4-methylbenzylidene)-hydrazide(schiff bases ligands):Synthesis and spectral characterization.

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ABSTRACT: The synthesis and characterization of arsenic(II) complexes with Schiff base ligands, [AsL]Cl₂ (L=Acetic acid (4-methylbenzylidene) – hydrazide) are described. Vibrational study in the solid state of hydrazide derivatives and its new mercury(II) complexes was performed by IR spectroscopy, 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 bidentate N,O donors derived from the carbonyl and azomethine nitrogen.

Keywords: Mercury; complexes; Hydrazide ligands; Synthesis; Characterization.

INTRODUCTION:

Arsenic plays an important role in biological and chemical processes¹. 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 arsenic compounds, there is a need for simple and accurate analytical methods that allow for the rapid determination of arsenic content in samples. Arsenic is one of the most toxic heavy metals on earth. The toxicity of arsenic depends on its occurring forms; organomercurials such as methylmercury are more toxic than elemental arsenic and other inorganic arsenic compounds²⁻³.

The coordination chemistry of arsenic (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 properties⁴⁻⁶. 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. development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes⁷⁻⁹, since it has been recognized that many of these complexes may serve as models for biologically important species. The remarkable biological activity of acid hydrazides R-CO-NH-NH₂, a class of Schiff base, their corresponding aroylhydrazones, R-CO-NH-NCH-R' and the dependence of their mode of chelation with transition metal ions present in the living system have been of significant interest. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications. In this work, we report the synthesis and structural studies of the complexes isolated from the reactions of arsenic (II) halide with Acetic acid (4-methylbenzylidene) – hydrazide(L).

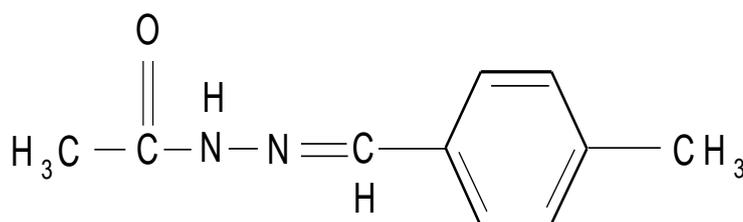


Fig.1 Structure of the ligands

Materials and instruments:

All reagents were supplied by Merck and were used without further purification. Melting points were determined in a Electrothermal 9200. The FT-IR spectra¹⁰⁻¹¹ were recorded in the range 400–4000cm⁻¹ by KBr pellet using a Bruker Tensor 27 M 420 FT-IR spectrophotometer. The UV-Vis spectra in CH₃CN were recorded with a Wpa bio Wave S2 100 spectrophotometer.

General Synthesis of the Ligand :

Schiff base ligands were prepared by the direct reaction of primary aromatic aldehyde derivatives and acetohydrazide in equimolar ratio ethanolic medium. Various ligands have been prepared depends on substituent's and characterized by spectral techniques. The methodology of the synthesis of the ligands prepared is given below .

A hot ethanolic solution of primary aromatic acetohydrazide (5mmol) was added to the 20 ml of ethanolic solution of primary aromatic aldehyde contained (5mmol) in 250 ml of round bottom flask .The reaction mixture was refluxed on a water bath for about 2-3 hours.After refluxing the solution was cooled to room temperature and the product was kept in ice-bath with constant stirring then kept overnight in freezer. Crystals of respective ligand were obtained and were filtered under suction pump and washed

with absolute ethanol and dried. Ligands were recrystallized from methanol before use and subsequently dried over anhydrous CaCl_2 in desiccator¹². All Schiff base ligands are soluble in common organic solvents.

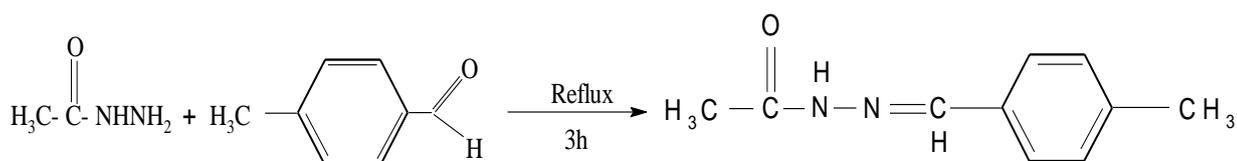
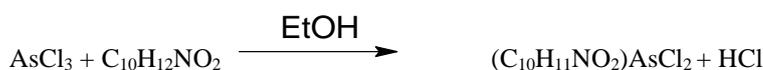


Fig.2 Acetic acid (4-methylbenzylidene)-hydrazide

Synthesis of metal complexes:

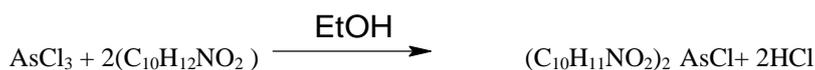
Synthesis of dichloroarsenic(III) acetic acid (4-methylbenzylidene)-hydrazide.

The complex has been synthesized by the reaction of arsenic trichloride (1mmol) with acetic acid (4-methylbenzylidene)-hydrazide (1.5mmol) in 1:1 molar ratio. Arsenic trichloride (1 mmol) is dissolved in absolute acetonitrile (5 ml). To this acetic acid (4-methylbenzylidene)-hydrazide in THF (10 ml) is added. The mixture is stirred magnetically at room temperature. The precipitated complex is filtered, washed with ether. The product is dried in air and stored in a desiccator over anhydrous CaCl_2 under vacuum¹²⁻¹³.



2.5(d) Synthesis of monochloroarsenic(III) acetic acid (4-methylbenzylidene)-hydrazide .

The complex has been synthesized by the reaction of arsenic trichloride (1mmol) with acetic acid (4-methylbenzylidene)-hydrazide (3mmol) in 1:2 molar ratio. Arsenic trichloride (1 mmol) is dissolved in absolute acetonitrile (5 ml). To this acetic acid (4-methylbenzylidene)-hydrazide in THF (10 ml) is added. The mixture is stirred magnetically at room temperature. The precipitated complex is filtered, washed with ether. The product is dried in air and stored in a desiccator over anhydrous CaCl_2 under vacuum¹⁴.



RESULT AND DISCUSSION :

All the new compounds have been characterized by elemental analysis and various physiochemical techniques such as molecular mass measurements, IR and Mass spectrum of complexes¹⁵⁻¹⁷. Attempts were also made to get the crystals of the compounds were unsuccessful. In the present chapter, the main results achieved in the course of the present investigation have been discussed as follows.

3.1 Characterization of dichloroarsenic(III)acetic acid (4- methylbenzylidene)-hydrazide .

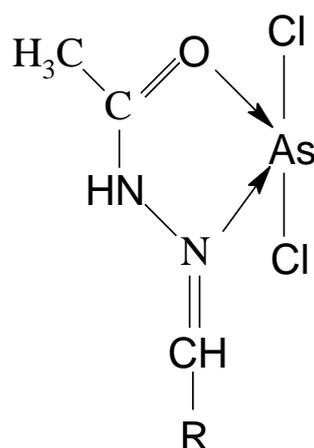
The ligand acetic acid (4-methylbenzylidene)-hydrazide (3) and its metal complex (3a) in 1:1 molar ratio have been characterized and identified with help of following spectral techniques¹⁸⁻¹⁹.

IR spectrum KBr, λ_{max}

The infrared spectra of the complexes taken in the region 400–4000 cm^{-1} were compared with those of the free ligands. Significant differences between the metal(II) complexes and its free ligands were seen. An exhaustive comparison of the IR spectra of the ligands and complexes gave information about the mode of bonding of the ligands in metal complexes²⁰. The IR spectra of (3a) complexes reveals that, the ligand act as a neutral bidentate ligand through the azomethine and the carbonyl groups. characteristic IR bands of As(III) complexes are: 1620 cm^{-1} ($\nu(\text{C}=\text{O})$ carbonyl), 1549 cm^{-1} ($\nu(\text{C}=\text{N})$ azomethine). The spectrum of the ligand have been observed for $\nu(\text{C}=\text{O})$ at 1628 cm^{-1} and $\nu(\text{C}=\text{N})$ at 1559 cm^{-1} . 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 $\text{C}=\text{N}$ band. Moreover, in the spectra of the complexes, a considerable negative shift in $\nu(\text{C}=\text{O})$ is observed indicating a decrease in the stretching force constant of $\text{C}=\text{O}$ as a consequence of coordination through the carbonyl–oxygen atom of the free ligands. In the FT-IR spectra the band due to N-H stretching in the free ligands occurs in the 3181 cm^{-1} region and remains unaffected after complexation. This precludes the possibility of coordination through the nitrogen atom of hydrazine. The small shift to higher frequency of the band due to $\nu(\text{N}-\text{N})$ can be taken as additional evidence of the participation of the azomethine group in bonding²¹⁻²². This result is confirmed by the presence of a new band at 508 cm^{-1} and 421 cm^{-1} , these bands can be assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ vibrations, respectively.

Mass Spectrum

Mass spectra of complex provides a vital clue for elucidating the structure of compounds. The mass spectra of the ligand and its metal complex was used to compare their stoichiometric composition. The ligand [3] showed molecular ion peak $[\text{M}^+]$ at m/z 176, which shows the molecular mass of ligand. The mass spectra of As(III) complex showed a molecular ion peak $[\text{M}^+]$ at m/z = 321 mass of the respective compound. These peaks supported the structure of the complex and confirmed the stoichiometry of metal chelates as ML types.



Where R ,

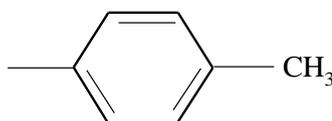


Fig.3 [C₁₀H₁₁N₂O] AsCl₂

Conclusion:-

In this study we have reported the synthesis of new hydrazide derivatives and their complexes. On the basis of spectral techniques, it is suggested that ligand(3) behave as a neutral bidentate ligand and coordinates through the azomethine nitrogen atom and oxygen by carbonyl groups to the As(III)chloride. In the complex (3a) the central metal ion appears to acquire the coordination number four. Exact structure can't be predicted without X-ray diffraction or advanced techniques²³⁻²⁵.

The antimicrobial activity of free ligand and complexes were tested against the bacterial species *E. coli*.

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