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Novel mercury(II) complexes of Schiff base ligands: Synthesis and spectral characterization

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ABSTRACT

The synthesis and characterization of mercury(II) complexes with Schiff base ligands, $[Hg(L)_2]Cl_2$ (L^1=Acetic acid (2,4-Dichloro-benzylidene)-hydrazide and L^2=Acetic acid (3-Nitro-benzyliden)-hydrazide) are described. Vibrational study in the solid state of hydrazide derivatives and its new mercury(II) complexes was performed by ^{1}H-NMR, 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 stablish the coordination mode of the metal in complexes. The results suggest that the Schiff bases coordinate as univalent anions with their twodentate N, O donors derived from the carbonyl and azomethine nitrogen.

Key words: Mercury; complexes; Hydrazide ligands; Synthesis; Characterization.

INTRODUCTION

Mercury 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 mercury compounds, there is a need for simple and accurate analytical methods that allow for the rapid determination of mercury content in samples [1]. Mercury is one of the most toxic heavy metals on earth. The toxicity of mercury depends on its occurring forms; organomercurials such as methylmercury are more toxic than elemental mercury and other inorganic mercury compounds [2]. Mercury containing ligands e.g., mercuric and mercurous are known to form stable complexes with class b metal ions, such as gold(I) [3-4] and se(II) [5] because mercury is considered to be a soft Lewis base [6-7].

The coordination chemistry of mercury(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 [8-9]. 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.

The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species [10-14]. 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 [15-22]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications [23-24].

In this work, we report the synthesis and structural studies of the complexes isolated from the reactions of mercury(II) halide with Acetic acid (2,4-Dichloro-benzylidene)-hydrazide (L^1) and Acetic acid (3-Nitro-benzyliden)-hydrazide (L^2) (Chart 1).

Acetic acid (2,4-dichloro-benzylidene) -hydrazide (L^1)

Acetic acid (3-nitro-benzylidene) -hydrazide (L^2)

Chart 1. Structure of the ligands

MATERIALS AND MATERIALS

Materials and instruments

All reagents were supplied by Merck and were used without further purification. Melting points were determined in a Electrothermal 9200. ^{1}H-NMR spectra in CDCl$_3$ and DMSO were recorded on Bruker Avance DRX 500 spectrometers. The FT-IR spectra were recorded in the range 400–4000 cm^{-1} by KBr pellet using a Brucker Tensor 27 M 420 FT-IR spectrophotometer. The UV–Vis spectra in CH$_3$CN were recorded with a Wpa bio Wave S2 100 spectrophotometer.

General Synthesis of the Ligands

The ligands (L^1- L^2) were prepared by equimolar mixtures of derivatives aldehyde (5 mmol) and acetohydrazide (5 mmol) in 20 ml ethanol for 3 h. The isolated compounds were filtered off as white crystals, washed with ethylalcohol, recrystallised from absolute ethanol and finally dried.

Complex Acetic acid (2,4-Dichloro-benzylidene)-hydrazide mercury(II) (1)

Mercury chloride (1 mmol) was dissolved in absolute acetonitrile (5 ml). To this, (3mmol) Acetic acid (2,4-Dichloro-benzylidene)-hydrazide (L^1) in THF (10 mL) was added. The mixture was stirred magnetically at room temperature. The precipitated complexes were filtered, washed with ether and dried. ^{1}H NMR (CDCL$_3$)δppm: 9.6(1H, –HC=N), 8.2(1H, N-H), 8.0-7.3(4H,

C_6H_4), 2.4(3H, CH_3). UV–Vis (CH_3CN): λ max (log ε): 250 (4.06), 285(4.78), 291 (4.77), 316(4.38) nm.

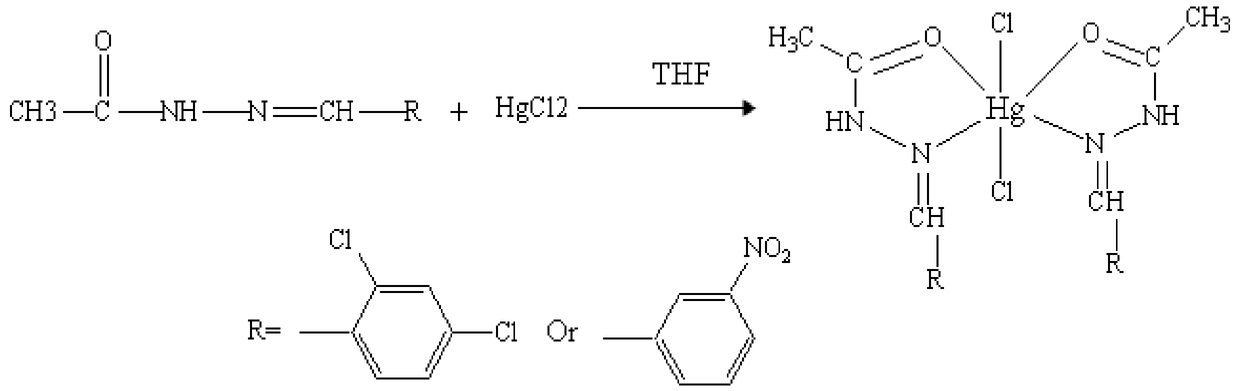
$$CH_3CONHNH+ C_7H_4OCl_2 \xrightarrow{EtoH} CH_3CONHN{=}CH\text{-}C_6H_3Cl2 + H_2O$$
$$2\ C_9H_8N_2OCl_2 + HgCl_2 \longrightarrow C_{18}H_{16}N_4O_2Cl_2HgCl_2$$

Complex Acetic acid (3-Nitro-benzyliden)-hydrazide mercury(II) (2)
Complex (2) was synthesized in a similar manner to that used for complex (1), reacting a mixture of (L^2) (3 mmol) and $HgCl_2$(1 mmol) in THF (10 mL). 1H NMR (DMSO) δppm: 11.5(1H, –HC=N), 11.3(1H, N-H), 8.4-7.6(4H, C_6H_4), 2.2(3H, CH_3). UV–Vis (CH_3CN): λ max (log ε) : 252 (4.52), 279(4.77) nm.

$$CH_3CONHNH+ C_7H_5NO_3 \xrightarrow{EtoH} CH_3CONHN{=}CH\text{-}C_6H_4NO_2 + H_2O$$
$$2\ C_9H_9N_3O_3 + HgCl_2 \longrightarrow C_{18}H_{18}N_6O_6HgCl_2$$

RESULTS AND DISCUSSION

The complexes [Acetic acid (2,4-Dichloro-benzylidene)-hydrazide] Hg(Π) and [Acetic acid (3-Nitro-benzyliden)-hydrazide] Hg(Π) were prepared in good yield by stirring stoichiometric amounts of $HgCl_2$ and L^1 and L^2 (Scheme 1). The physical and analytical data are summarized in Table 1.



Scheme 1. Schematic representation of metal complex formation of compounds

The complexes were characterized by the usual methods: elemental analysis, FTIR, ^{1}H-NMR, absorption electronic spectroscopy. The complexes are stable in air and light, and are soluble in organic solvents such as $HCCl_3$ and DMSO, less soluble in methanol, and insoluble in and water and n-hexane.

^{1}H-NMR spectra

In NMR spectra of complexes we observed a shift of electron density from the ligand to the metal. ^{1}H-NMR spectra of the complexes (1), (2) show all the expected signals. In all the spectra, a singlet corresponding to a single proton is observed in the range δ 9.6, 11.5 ppm, which is attributed to the azomethine proton (–HC=N) in (1), (2) complexes, respectively. The ^{1}H-NMR spectra of the $[HgL_2]Cl_2$ complexes show a negative shift of the signal due to the NH group. This signal is observed at δ 8.2, 11.3 ppm in (1), (2) complexes, suggesting that the coordination

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proceeds through the carbonyl oxygen or azomethine nitrogen groups. The downfield shifts of the methyl group signal at 2.4, 2.2 ppm for the (1), (2) complexes, support the coordination via the azomethine nitrogen. The multi signals within the range δ 8-7.3, 8.4-7.6 ppm are assigned to the aromatic protons of ring in (1), (2) complexes, respectively.

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

Comp. no.	Molecular formula	M. Wt.	M.P. °C	Solubility	Elemental Analysis Found (Calc.)		
					%C	%H	%N
L^1	$C_9H_8N_2OCl_2$	231	188	THF	46.78 (46.86)	3.49 (3.51)	12.12 (12.08)
L^2	$C_9H_9N_3O_3$	207	230	THF	52.17 (52.26)	4.38 (4.41)	20.28 (20.33)
(1)	$C_{18}H_{16}N_4O_2Cl_2Hg\ Cl_2$	663	192	DMSO, CHCl3	29.44 (29.52)	2.1 (2.09)	7.63 (7.59)
(2)	$C_{18}H_{18}N_6O_6HgCl_2$	686	242	DMSO, CHCl3	31.49 (31.58)	2.62 2.61)	12.24 (12.19)

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 metal(II) complexes and their free ligands for chelation as expected. The main stretching frequencies of the IR spectra of the ligands (L^1–L^2) 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 $[HgL_2]Cl_2$ complexes, the ligands act as a neutral bidentate through the azomethine and carbonyl groups [25]. The characteristic IR bands of Hg(II) complexes are: 1673, 1679 cm^{-1} (ν(C=O) carbonyl), 1584, 1628 cm^{-1} (ν(C=N) azomethine), (1) and (2) complexes respectively. The spectrum of the ligands have been observed for ν(C=O) at 1686, 1687 cm^{-1} and ν(C=N) at 1591, 1635 cm^{-1}, respectively (L^1) and (2) [26-29].

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 [30]. In the FT-IR spectra the band due to N-H stretching in the free ligands occurs in the 3185, 3094 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 υ(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 556, 527 cm^{-1} and 479, 433 cm^{-1}; these bands can be assigned to υ(M–O) and υ(M–N) vibrations, respectively [31].

Table 2. IR Spectral Bands of Ligands and Its Metal Complexes

Compound	ν(N-H)	ν(C=O)	ν(C=N)	ν(N-N)	ν(M–N)	ν(M–O)
L^1	3185	1686	1591	1006	—	—
L^2	3094	1687	1635	1027	—	—
(1)	3185	1673	1585	1011	479	556
(2)	3094	1679	1628	1029	433	527

Electronic spectra

The formation of the metal(II) complexes was also confirmed by UV–Vis spectra. The absorption spectra of the diamagnetic Hg(II) complexes were recorded as 10^{-4} M CH_3CN 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 d^{10} Hg(II) complexes [32] . When compared complexes with the free ligands values have shifts frequency. The data of The spectra of the metal(II) complexes in CH_3CN solutions are shown that absorption band observed at 279 and 316 nm is attributed to $n \rightarrow \pi^*$ electronic transition of hydrazone (–NH–N=C–) group involving the whole conjugation.

CONCLUSION

In this study we have reported the synthesis of new hydrazide derivatives and their Hg(II) complexes. The structural characterizations of synthesized compounds were made by using the elemental analysis, ^{1}H-NMR, IR and UV spectral techniques. From the spectroscopic characterization, it is concluded that ligands acts as a neutral bidentate through the azomethine nitrogen atom and carbonyl groups.

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