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Synthesis, characterization and thermal analysis of Hg(II) complexes with hydrazide ligands

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ABSTRACT

A number of new complexes have been synthesis by reaction of novel ligands Acetic acid (2-Hydroxy-benzyliden)-hydrazide (L^1), Acetic acid (3-phenyl-allylidene)-hydrazide (L^2) with mercury(II) halide. 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. Thermal properties, TG-DTA of these complexes were studied too. TG- DTA and other analytical methods have been applied to the investigation of the thermal behavior and structure of the compounds $[Hg(L)_2]Cl_2$. Thermal decomposition of these compounds is multi-stage processes.

Key words: Mercury complexes; Hydrazide ligands; Synthesis; Thermal properties.

INTRODUCTION

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 [1-5]. Schiff bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years. The remarkable biological activity of acid hydrazides $R-CO-NH-NH_2$, a class of Schiff base, their corresponding aroylhydrazones, $R-CO-NH-N=CH-R'$ and the dependence of their mode of chelation with transition metal ions present in the living system have been of significant interest [6-12]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications [13-14]. They serve as models for biologically important species and find applications in biomimetic catalytic reactions.

In this work, we report the synthesis and structural studies of the complexes isolated from the reactions of mercury(II) halide with (L^1), (L^2).

MATERIALS AND METHODS

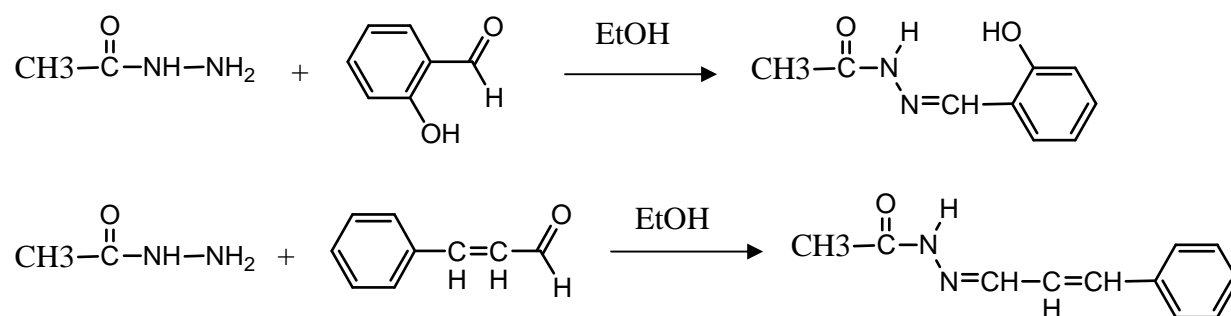
Experimental Section

Materials and instruments

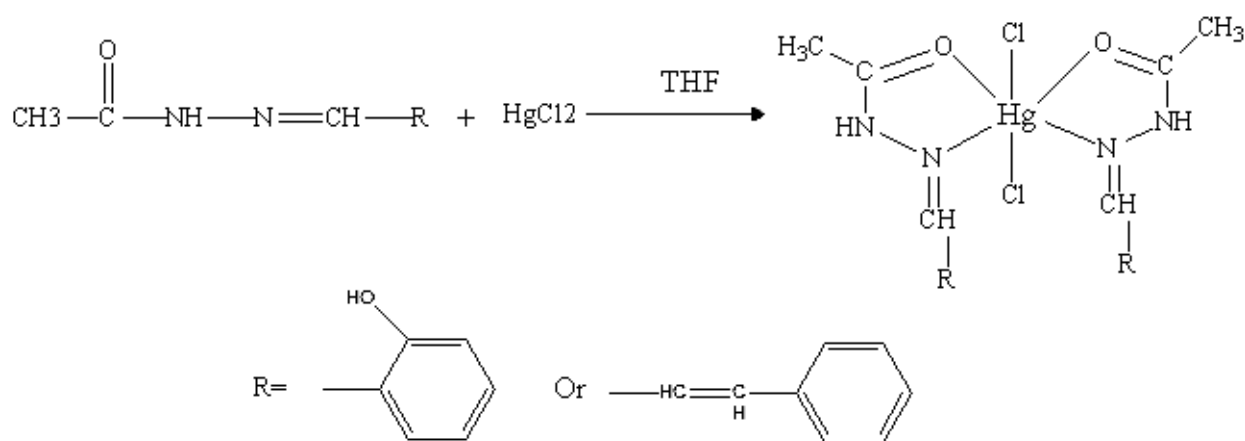
All reagents were supplied by Merck and were used without further purification. Melting points were determined in an Electrothermal 9200. The FT-IR spectra were recorded in the range 400–4000 cm^{-1} by KBr pellet using a Bruker Tensor 27 M 420 FT-IR spectrophotometer. The UV–Vis spectra in CH_3CN were 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.



Scheme 1. Schematic representation of Ligands formation of compounds



Scheme 2. Schematic representation of metal complex formation of compounds

Complex Acetic acid (2-Hydroxy-benzyliden)-hydrazide mercury(II) (1)

Mercury chloride (1 mmol) was dissolved in absolute acetonitrile (5 ml). To this, (3mmol) Acetic acid (2-Hydroxy-benzyliden)-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. UV (CH_3CN): λ_{max} ($\log \epsilon$) = 277 (4.26), 286(4.23), 318 (4.94) nm.

Complex Acetic acid (3-phenyl-allylidene)-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). UV-Vis (CH_3CN): λ_{max} ($\log \epsilon$) = 226 (4.55), 312 (5.13) nm.

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

Comp. no.	Molecular formula	M.P. °C	Solubility	Elemental Analysis		
				□ Calculated (found)		
				%C	%H	%N
L^1	$C_9H_{10}O_2N_2$	203	THF	60.67 (60.97)	5.61 (5.63)	15.73 (15.80)
L^2	$C_{11}H_{12}ON_2$	165	THF	70.21 (70.48)	6.38 (6.40)	14.89 (14.96)
(1)	$C_{18}H_{20}O_4N_4HgCl_2$	171	DMSO	34.42 (34.53)	3.18 (3.21)	8.92 (8.89)
(2)	$C_{22}H_{24}O_2N_4HgCl_2$	158	DMSO	40.77 (40.86)	3.70 (3.68)	8.64 (8.59)

RESULTS AND DISCUSSION

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

The complexes were characterized by the usual methods: elemental analysis, FTIR, absorption electronic spectroscopy. The complexes are stable in air and light, and are soluble in organic solvents such as DMSO and insoluble in water and n-hexane.

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 acts as a neutral bidentate through the azomethine and carbonyl groups [15]. 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 $\nu(C=O)$ 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 [16]. The band observed at 1681 and 1669 cm^{-1} in the spectrum of the ligands [17–20], which attributed to $\nu(C=O)$ mode are shifted, in spectra of all the complexes to lower wave number and appears at 1679 and 1664 cm^{-1} region indicating the involvement of O-atom of the carbonyl group in coordination [21]. In the FT-IR spectra the band due to NH stretching in the free ligands occurs in the 3447–3561 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 $\nu(N-N)$ 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 $551\text{-}623\text{cm}^{-1}$ and $483\text{-}493\text{cm}^{-1}$; these bands can be assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ vibrations, respectively [22, 23].

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

Compound	IR in KBr pellets, cm^{-1}					
	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{N-N})$	$\nu(\text{Hg-N})$	$\nu(\text{Hg-O})$
L ¹	3561	1681	1621	1032	—	—
L ²	3447	1669	1618	986	—	—
(1)	3561	1679	1619	1034	483	551
(2)	3447	1664	1617	1009	493	623

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 200–800nm using a quartz cuvette of 1 cm path length. 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 318 and 312 nm is attributed to $n \rightarrow \pi^*$ electronic transition of hydrazone ($-\text{NH}-\text{N}=\text{C}-$) group involving the whole conjugation.

Thermal analysis

The thermal properties of metal (II) complexes were investigated by thermograms (TG, DTG and DTA) and are shown in (Figs. 3, 4) and the corresponding thermal analysis data is presented in Table 2.

In the case of complex (1) (Fig. 3), the decomposition occurs in the $116\text{-}164^\circ\text{C}$ range. There is no mass loss up to 116°C . The first stage of decomposition starts at 116°C and ends at 164°C with a corresponding weight loss 13%, Which is accompanied by endothermic effect in the DTA curve in the range 201°C which is accompanied by weight loss confirming. The second stage of decomposition is observed at $203\text{-}286^\circ\text{C}$ (66% wt loss). Meanwhile the DTA curve exhibits endothermic effect in the range 276°C which is accompanied by weight loss confirming.

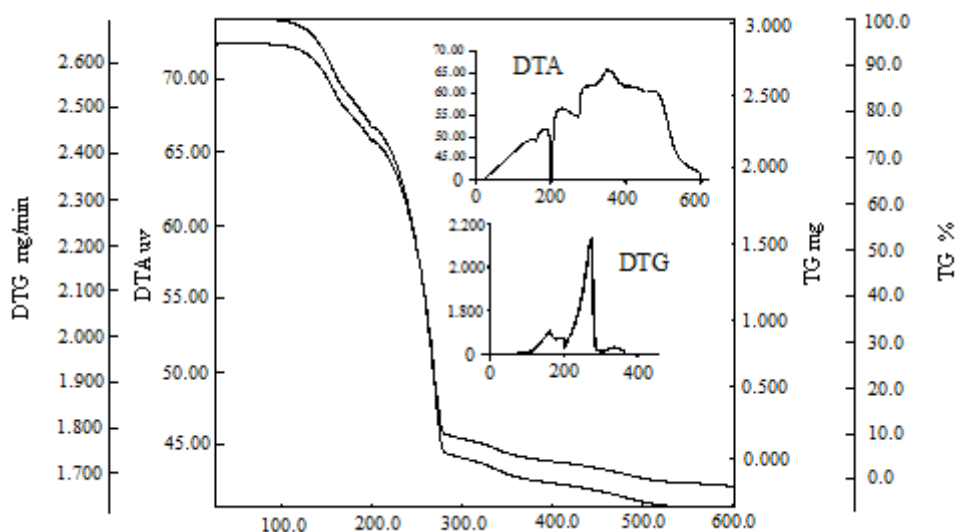


Fig. 3. The TG-DTA curves of complex (1)

In the case of complex (2) (Fig. 4), there is no mass loss up to 194 °C. The first stage of decomposition starts at 194 °C and ends at 342 °C with a corresponding weight loss 77%, Which is accompanied by exothermic effect in the DTA curve in the range 210°C which is accompanied by weight loss confirming. The second stages of decomposition were observed at 526-592 °C (19 % wt loss). Meanwhile the DTA curve exhibits exothermic effect in the range 582 °C which are accompanied by weight loss confirming.

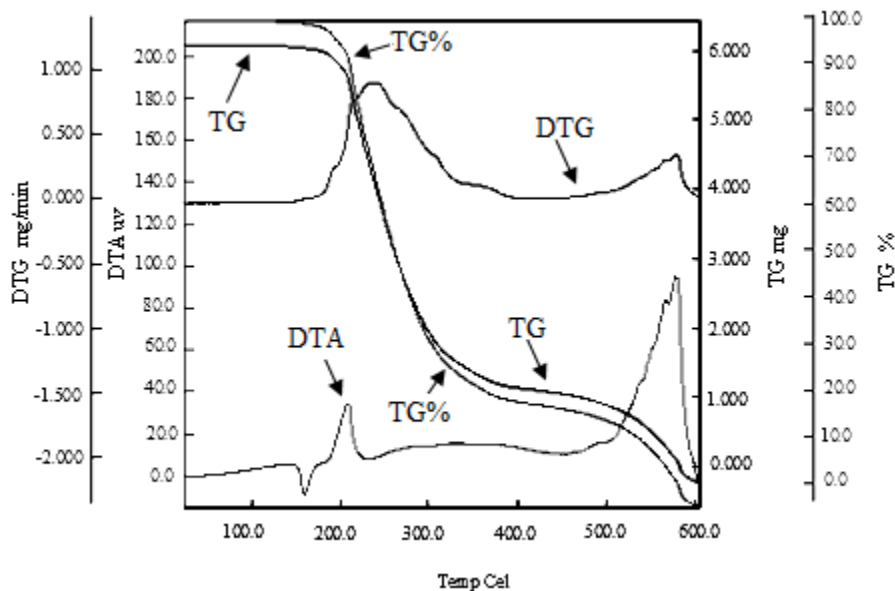


Fig. 4. The TG-DTA curves of complex (2)

TGA in air (Figs. 3, 4) shows that decomposition with weight loss occurs above 194 °C for complexes (2), which is higher than for complexes (1) at 116 °C. Clearly, complex (2) has excellent thermal stability.

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, 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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