



Synthesis, Characterization and Thermal Analysis of a New Acetic Acid (2-Hydroxy-benzylidene)- hydrazide and its Complexes with Hg(II) and Pd(II)

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Abstract: The new complexes have been synthesized by the reaction of Hg(II) and Pd(II) with acetic acid(2-hydroxy-benzylidene)- hydrazide (L). These new complexes were characterized by elemental analysis, IR, H NMR spectroscopy and UV spectral techniques. The changes observed between the FT-IR, H NMR 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. TG- DTA and other analytical methods have been applied to the investigation of the thermal behavior and structure of the compounds $[M(L)_2]Cl_2$ M= Hg, Pd. Thermal decomposition of these compounds is multi-stage processes.

Keywords: Hydrazone ligands, Synthesis, Characterization, 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 species¹⁻⁵.

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 interest⁶⁻¹². A novel cationic complexes have been synthesized with isonicotinic acid (2-hydroxybenzylidene) hydrazide¹³, 2-acetylpyridene-*o*-hydroxybenzoylhydrazone¹⁴, 1,3-diphenyl-4-(salicylidene hydrazide)-acetyl-pyrazolone-5 and 2,2'-bipyridine¹⁵, benzoic acid (2-hydroxy-3-methoxy-benzylidene)-hydrazide, benzoic acid (2,3-dihydroxy-benzylidene)-hydrazide, benzoic acid (2-hydroxy-benzylidene)-hydrazide, benzoic acid (5-bromo-2-hydroxy-benzylidene)-hydrazide, benzoic acid (pyridine-2-yl methylene-hydrazide)¹⁶. In this work, we report the synthesis and structural studies of the ligands and complexes isolated from the reactions of acetic acid (2-hydroxybenzylidene)-hydrazide with mercury(II) halide and palladium(II) halide.

Experimental

All reagents were supplied by Merck and were used without further purification. Melting points were determined in an electrothermal 9200. The FTIR spectra were recorded in the range 400-4000 cm^{-1} by KBr pellets using a Bruker Tensor 27 M 420 FT-IR spectrophotometer. ¹H-NMR spectra in $CDCl_3$ were recorded on Bruker AMX-500 spectrometers. The UV-Vis spectra in CH_3CN were recorded with a Wpa bio Wave S2 100 spectrophotometer.

General synthesis of the Ligand and the Complexes

Synthesis of ligand acetic acid (2-hydroxy-benzylidene)- hydrazide (L)

The ligand was prepared by equimolar mixtures of salicylaldehyde (5.2 mL, 0.05 mol) and acetohydrazide (3.7 g, 0.05 mol) in 20 mL ethanol for 3 h. The isolated compound was filtered off as white crystals, washed with ethylalcohol, recrystallised from absolute ethanol and finally dried. m.p. 203-203 °C. IR: (KBr disc): cm^{-1} , 3075(s), 2952(s), 1681(s), 1621(s), 1407(s), 1328(s), 1032(m), 940(m), 856(w), 764(s), 687(m), 605(w), 547(w), 446(w).

Synthesis of complex $[Hg(L)_2]Cl_2$ (1)

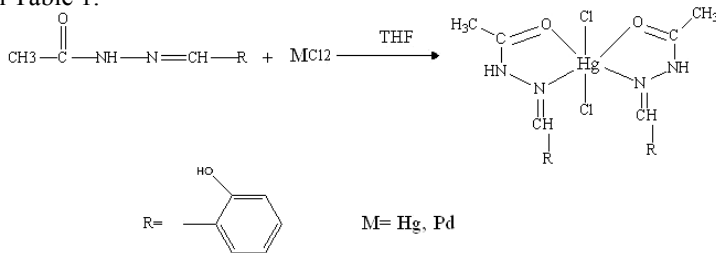
Mercury(II) chloride (1 mmol) was dissolved in acetonitrile (5 mL). To this, (3 mmol) acetic acid (2-hydroxybenzylidene)-hydrazide in THF (5 mL) was added. The mixture was stirred magnetically at room temperature. The precipitated solid was filtered, washed with ether and dried. m.p. 171-172 °C. IR: (KBr disc): cm^{-1} , 3561(s), 3186(m), 3073(m), 2943(m), 2862(m), 1679(s), 1619(s), 1400(s), 1341(m), 1034(m), 944(w), 855(w), 765(m), 696(m), 601(m), 551(m), 483(w); ¹HNMR (500 MHz, $CDCl_3$): 10.91 [1H, O-H], 10.28 [1H, -CH=N-], 9.25 [1H, N-H], 6.98-8.47 [4H, C_6H_4], 2.21 [3H, CH_3]; UV-Vis (CH_3CN): λ_{max} (log ϵ) = 277 (4.26), 286(4.23), 318 (4.94) nm.

Synthesis of complex $[Pd(L)_2]Cl_2$ (2)

palladium(II) chloride (1 mmol) was dissolved in water (20 mL) under temperature 60 °C. To this, (3 mmol) Acetic acid (2-hydroxybenzylidene)-hydrazide in THF (5 mL) was added. The mixture was stirred magnetically at room temperature. The precipitated solid was filtered, washed with ether and dried. Decomp. 399 °C. IR: (KBr disc): cm^{-1} , 3437(m), 3188(m), 3067(m), 2936(m), 2861(m), 1678(s), 1610(s), 1402(s), 1362(m), 1036(m), 947(w), 855(w), 755(m), 696(m), 604(m), 553(m), 471(w); ¹HNMR (500 MHz, $CDCl_3$): 11.19 [1H, O-H], 10.73 [1H, -CH=N-], 10.37 [1H, N-H], 6.74-7.96 [4H, C_6H_4], 2.16 [3H, CH_3]; UV-Vis (CH_3CN): λ_{max} (log ϵ) = 279 (2.54), 287(2.53), 317 (2.27) nm.

Results and Discussion

The complexes [acetic acid (2-hydroxy-benzylidene)-hydrazide] Hg(II) and [acetic acid (2-hydroxy-benzylidene)-hydrazide] Pd(II) were prepared in good yield by stirring stoichiometric amounts of HgCl₂ and PdCl₂ with L (Scheme 1). Elemental analysis data are summarized in Table 1.



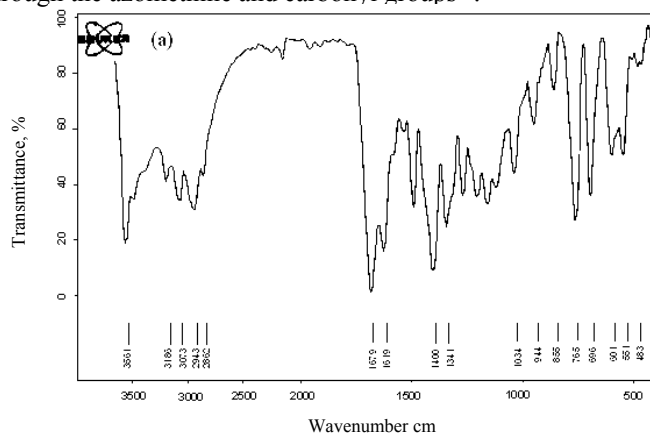
Scheme 1

Table 1. Elemental analysis of the ligands and complexes

Com.	Empirical formula	%C Calc./Foun	%H Calc./Foun	%N Calc./Foun
L	C ₉ H ₁₀ N ₂ O ₂	68.16/68.35	6.86/6.88	15.90/15.86
(1)	C ₁₈ H ₂₀ N ₄ O ₄ HgCl ₂	33.37/33.45	4.04/4.05	14.15/14.21
(2)	C ₁₈ H ₂₀ N ₄ O ₄ PdCl ₂	37.18/37.28	3.81/3.78	13.34/13.29

The complexes were characterized by the usual methods: elemental analysis, FT-IR, H-NMR and 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 this of the free ligand. As seen data the IR spectra of two meta(II) complexes are very similar to each other, except some slight shifts and intensity change of a few vibration bands caused by different metal(II) ions, which indicate that the complexes have similar structures (Figure 1). There are some significant changes between the metal(II) complexes and their free ligand for chelation as expected. The main stretching frequencies of the IR spectra of the ligand L and their complexes are tabulated in Table 2. An exhaustive comparison of the IR spectra of the ligand and complexes gave information about the mode of bonding of the ligand in metal complexes. The IR spectra of complexes, the ligand acts as a neutral bidentate through the azomethine and carbonyl groups¹⁴.



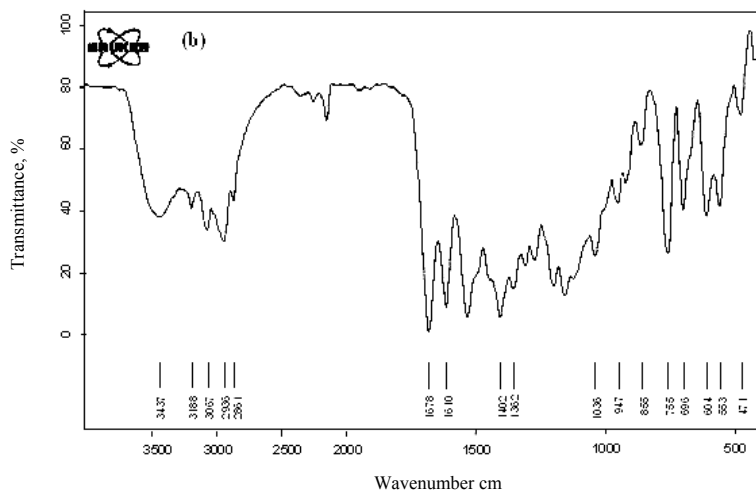


Figure 1. IR spectra of (a) $C_{18}H_{20}O_4N_4HgCl_2$, (b) $C_{18}H_{20}O_4N_4PdCl_2$

Table 2. Selected characteristic IR bands ($400\text{--}4000\text{ cm}^{-1}$) of ligands and their complexes

Compound	$\nu(C=O)$	$\nu(C=N)$	$\nu(N-N)$	$\nu(M-N)$	$\nu(M-O)$
L	1681	1621	1032	-	-
(1)	1679	1619	1034	483	551
(2)	1678	1610	1036	471	553

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 ligands¹³. The band observed at 1681 cm^{-1} in the spectrum of the ligand¹⁷⁻²⁰, which attributed to $\nu(C=O)$ mode are shifted, in spectra of all the complexes to lower wave number and appears at 1679 and 1678 cm^{-1} region indicating the involvement of O -atom of the carbonyl group in coordination²¹. 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 , 553 cm^{-1} and 483 , 471 cm^{-1} ; these bands can be assigned to $\nu(M-O)$ and $\nu(M-N)$ vibrations, respectively²²⁻²⁴.

In NMR spectra of complexes we observed a shift of electron density from the ligand to the metal. 1H -NMR spectra of the complexes (1), (2) show all the expected signals (Figure 2). The 1H -NMR spectrum of the complexes exhibits two signals at 10.28 and 11.19 ppm are assigned to the OH protons, respectively. In all the spectra, a singlet corresponding to a single proton is observed in the range $\delta\ 9.25$, 10.37 ppm , which is attributed to the azomethine proton ($-HC=N$) in (1), (2) complexes, respectively. The 1H -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 $\delta\ 8.47$, 8.18 ppm in (1), (2) complexes, suggesting that the coordination proceeds through the carbonyl oxygen or azomethine nitrogen groups. The downfield shifts of the methyl group signal at 2.21 , 2.16 ppm for the (1), (2) complexes, support the coordination via the azomethine nitrogen.

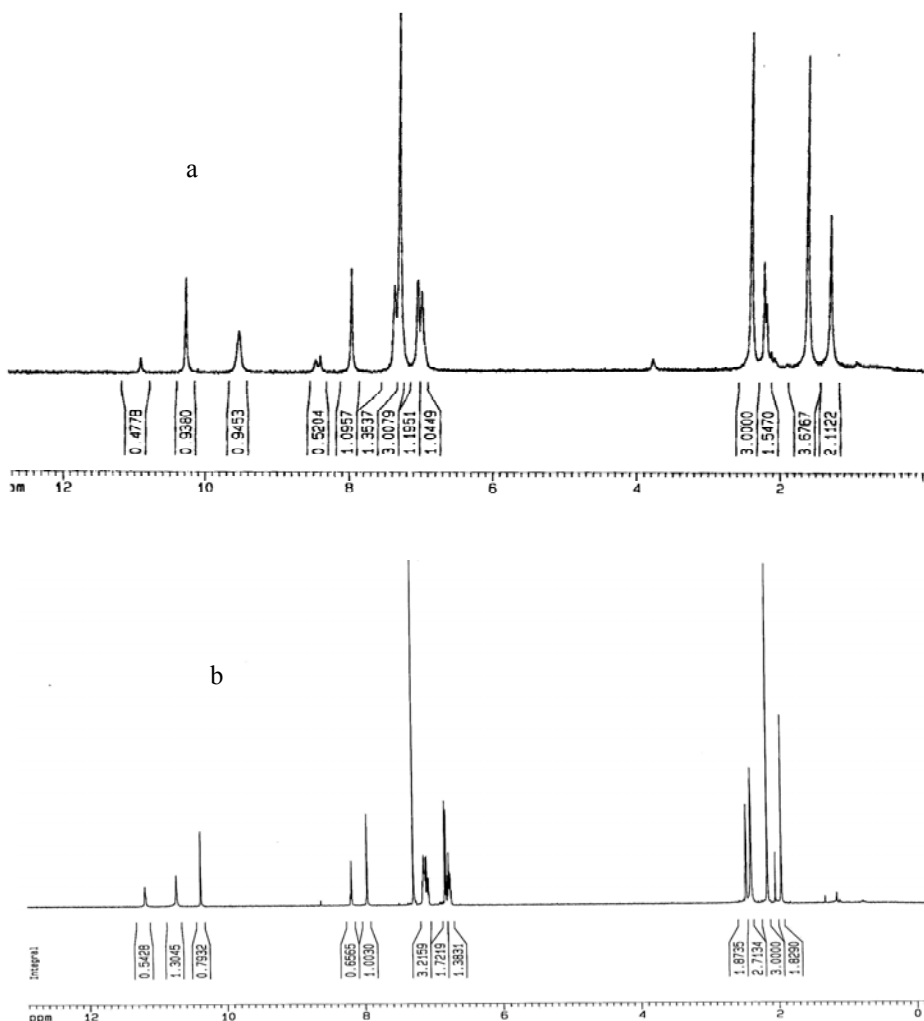


Figure 2. $^1\text{H-NMR}$ spectra of (a) $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_4\text{HgCl}_2$, (b) $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_4\text{PdCl}_2$

Thermal analysis

The thermal properties of metal(II) complexes were investigated by thermograms (TG, DTG and DTA) and are shown in Figure 1, Figure 2. The TG curve of **1** and **2** complexes showed decomposed in two successive stages decomposed. The first stage occurred in the temperature range 116–164 and 175–239 °C with a corresponding weight loss 13 and 39% for **1** and **2** complexes, respectively. Which are accompanied by endothermic effect for complexes **1** and **2** in the DTA curve in the range 201, 202 °C and may be due to the loss of water molecules (one non-coordinated molecule, two coordinated molecules and one non-coordinated molecule, respectively). The second stages of decomposition were observed at 203–286 °C (66% wt loss) and 303–340 °C (36% wt loss) for **1** and **2** complexes, respectively. Meanwhile the DTA curve exhibits endothermic effect for complex **1** and exothermic effect for complex **2** in the range 276, 339 °C which are accompanied by weight loss confirming.

Conclusion

In this study we have reported the synthesis of new hydrazide complexes with mercury(II) halide and palladium(II) halide. The structural characterizations of synthesized compounds were made by using the elemental analysis, IR, H-NMR 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. Thermal properties, TG-DTA of these complexes were studied too.

References

1. Chohan Z H and Sheazi S K A, *Synth React Inorg Met-Org Chem.*, 1999, **29**, 105-118.
2. Jayabalakrishnan C and Natarajan K, *Synth React Inorg Met-Org Chem.*, 2001, **31**, 983-395.
3. Jeeworth T, Wah H L K, Bhowon M G, Ghoorhoo D and Babooram K, *Synth React Inorg Met-Org Chem.*, 2000, **30**, 1023-1038.
4. Dharmaraj N, Viswanalhamurthi P and Natarajan K, *Trans Met Chem.*, 2001, **26**, 105-109.
5. Colins C H and Lyne P M, *Microhiul Methods*, University Park Press, Baltimore, 1970, 422.
6. Savanini L, Chiasserini L, Gaeta A and Pellerano C, *Bioorg Med Chem.*, 2002, **10**, 2193-2198.
7. Ochiai E, *Bioinorganic Chemistry*, Allyn and Bacon, Boston, 1977.
8. Anten J A, Nicholis D, Markpoulos J M and Markopoulou O, *Polyhedron*, 1987, **6**, 1074.
9. Tossadis I A, Bolos C A, Aslanidis P N and Katsoulos G A, *Inorg Chim Acta.*, 1987, **133**, 275-278.
10. Maiti A and Ghosh S, *Indian J Chem.*, 1989, **28A**, 980-983.
11. Aggarwal R C, Singh N K and Singh R P, *Inorg Chim Acta.*, 1981, **29**, 2794.
12. Craliz J C, Rub J C, Willis D and Edger J, *Nature*, 1955, **34**, 176.
13. Abou-Melha Khlood S, *Spectrochim Acta Part A*, 2008, **70**, 162.
14. Nawar Nagwa and Mohamed Hosny Nasser, *Chem Pharm Bull.*, 1999, **47(7)**, 944-949.
15. Hu Xin, Zhang Li, Liu Lang, Liu Guang-Fei, Jia Dian-Zeng and Xu Guan-Cheng, *Polyhedron*, 2008, **27**, 12-24.
16. Pouralimardan Omid, Chamayou Anne-Christine, Janiak Christoph and Hosseini-Monfared Hassan, *Inorg Chim Acta.*, 2007, **360**, 1599-1608.
17. El-Rached G M Abu, Ibrahim K M and Bekheit M M, *Bull Soc Chim Fr.*, 1991, **128**, 149.
18. Shrivastav Anuraag, Tripathi Pratibha, Srivastava Ajay K, Singh Nand K and Sharma Rajendra K, *Eur J Med Chem.*, 2008, **43(3)**, 577-583.
19. Chandra Sulekh and Pundir Meenakshi, *Spectrochim Acta Part A*, 2008, **69(1)**, 1-7.
20. Andelkovic K, Sladic D, Bacchi A, Pelizzi G, Filipovic N and Rajkovic M, *Trans Met Chem.*, 2005, **30**, 243-250.
21. Silverstein R M, Bassler G C and Morrill T C, *Spectrometric Identification of Organic Compounds*, Fourth Ed., Wiley, New York, 1981.
22. Specca A N, Karayani N M and Pytlewski L L, *Inorg Chim Acta.*, 1974, **9**, 87.
23. Beecroft B, Compbell M J M and Grzeskowiak R, *J Inorg Nucl Chem.*, 1974, **36**, 55-59.
24. Drożdżewski Piotr, Brożyna Anna, Kubiak Maria and Lis Tadeusz, *Vib Spectros* 2006, **40(1)**, 118-126.



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