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Synthesis, FT-IR and DTA Studies of Mercury Complexes of Hydrazones

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N-Benzylidene-N-(2,4-dinitrophenyl)hydrazine (L[1]) and dimetheyl-{4-[(4-nitro-2-nitrosophenyl)hydrazonomethyl]phenyl}amine (L[2]) were used as ligands for the synthesis of mercury(II) complexes. Vibrational study in the solid state of 2,4-dinitrophenyl hydrazine derivatives and its new mercury(II) complexes was performed by elemental analysis, IR, UV-vis, ^{13}C and ^{1}H NMR techniques. The changes observed between the spectra of the ligands and their mercury(II) complexes allowed to establish the coordination mode of the metal in complexes and the mechanism of C-H activation is discussed. Thermal properties, TG-DTA of these complexes were also studied.

Key Words: Mercury complexes, Hydrazine ligands, Synthesis, Thermal properties.

INTRODUCTION

The coordination chemistry of mercury(II) differs from most other transition metals due to its large size and d^{10} 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. Mercury plays an important role in biological and chemical processes. 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[1]. The coordination chemistry of transition metals with ligands from the hydrazine family has been of interest due to different bonding modes shown by these ligands with both electron rich and electron poor metals[2-4].

The carbon-hydrogen bond is commonly regarded as an unfunctional and unreactive group. Functionalization of C-H bonds remains a problem of great current interest, but many important advances have been made in recent years[5,6]. This has opened up its broad synthetic potential and C-H functionalization has become an important topic in organometallic chemistry[7,8]. The C-H activation obviously depends on both the electron density on the metal and that on the C-H bond that is to be activated and may be promoted by steric hindrance[9,10]. The C-H bond is much stronger than the M-C bond and the thermodynamic barrier for homolytic cleavage of a C-H bond is high[11].

We now report the synthesis of mercury(II) chloride complexes of N-benzylidene-N-(2,4-dinitrophenyl)hydrazine (L[1]) and dimetheyl-{4-[(4-nitro-2-nitrosophenyl)hydrazonomethyl]-phenyl}amine (L[2]) and study the role of nitro groups towards metal assisted C-H activation of 2,4-dinitrophenyl hydrazine derivatives[12].

EXPERIMENTAL

All reagents were supplied by Merck and were used without further purification. Melting points were determined in a Electrothermal 9200. The FT-IR spectra were recorded in the range 4000-400 cm^{-1} by KBr pellet using a Brucker Tensor 27 M 420 FT-IR spectrophotometer. The UV/vis spectra in CH_3CN were recorded with a Wpa bio Wave S2 100 spectrophotometer. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ were recorded on a Bruker Avance DRX 500 spectrometer.

General synthesis of the ligands: The ligands L[1]-L[2] were synthesized by dissolving 2,4-dinitrophenyl hydrazine (0.39 g, 2 mmol) in 10 mL absolute acetonitrile under tempture 60 ºC and addition of this solution derivatives aldehyde (2 mmol dissolved in 5 mL absolute ethanol) was added. The reaction mixture was refluxed for 2 h. After cooling, the precipitate solid was collected, filtered off and finally washed with 5-10 mL cold absolute ethanol and re-crystallized from ethanol. UV/Visible, IR, ^{1}H and ^{13}C NMR were all consistent with the ligands structure.

Synthesis of complex [N-benzylidene-N-(2,4-dinitrophenyl)hydrazine]Hg(II), [Hg(L^1)$_2$]: Mercury chloride

(1 mmol) was dissolved in absolute acetonitrile (5 mL). To this, (3 mmol) N-benzylidene-N-(2,4-dinitrophenyl)hydrazine (L^1) in DMSO (10 mL) was added. The mixture was stirred magnetically at room temperature. The precipitated solid was filtered, washed with H_2O and hexane and allowed to stand for 3 days at room temperature, where upon the red solid precipitate was deposited. UV/Visible, IR, ^1H and ^{13}C NMR were all consistent with the $[Hg(L^1)_2]$ structure. m.p. 246 ºC. Anal. calcd. (%) for $C_{26}H_{18}N_8O_8HgCl$: C, 40.51; H, 2.33; N, 14.54. Found. (%): C, 40.48; H, 2.34; N, 14.57.

Synthesis of complex [dimetheyl-{4-[(4-nitro-2-nitrosophenyl)hydrazonomethyl]phenyl}amine]Hg(II), $[Hg(L^2)_2]$: 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 DMF (10 mL). UV/Visible, IR, ^1H and ^{13}C NMR were all consistent with the $[Hg(L^2)_2]$ structure. m.p. 235 ºC. Anal. calcd. (%) for $C_{30}H_{28}N_{10}O_8Hg$: C, 42.05; H, 3.27; N, 14.95. Found. (%): C, 41.93; H, 3.24; N, 15.04.

RESULTS AND DISCUSSION

The complexes [N-(2,4-dinitrophenyl)-N-(3-phenylallylidene)hydrazine] Hg(II) (**1**) and [N-(2,4-dinitrophenyl)-N(4-methyl-benzylidene)hydrazine] Hg(II) (**2**) were prepared in good yield by stirring stoichiometric amounts of $HgCl_2$ and L^1 and L^2.

$$HgCl_2 + 2C_{13}H_{10}N_4O_4 \rightarrow [Hg(C_{26}H_{18}N_8O_8)] \quad (1)$$

$$HgCl_2 + 2C_{15}H_{15}N_5O_4 \rightarrow [Hg(C_{30}H_{28}N_{10}O_8)] \quad (2)$$

The infrared spectra of the complexes and ligands taken in the region 4000-400 cm^{-1}. There are some significant changes between the metal(II) complexes and their free ligands for chelation as expected. 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 presence of electron withdrawing substituents such as a NO_2 group on the aryl ring was regarded to inhibit cyclometallation by rendering the aryl ring as an electrophile, which in turn would have made it unavailable for the attack of an electron deficient metal center[13].

The IR spectra of $[Hg(L)_2]$ complexes, the ligands acts as a bidentate through the azomethine nitrogen atom and carbon atom, which is *meta* to both the NO_2 groups. In the IR spectra of the complexes a sharp medium band at 1619 and 1606 cm^{-1} owing to the ν(C=N) (azomethine) vibration is shifted to lower frequencies in complexes (**1**) and (**2**), respectively which indicates the use of the azomethine group as one of the coordinating sites of the ligand. 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. In the FT-IR spectra the band due to NH stretching in the free ligands occurs in the 3286 and 3276 cm^{-1} region and remains unaffected after complexation. In the FT-IR spectra the N-H in-plane bending vibrations assigned in the region 1220, 1209 cm^{-1} for the complexes (**1**) and (**2**) respectively. Also, 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 precludes the possibility of coordination through the hydrazine nitrogen atom also supports the above coordination[14-16]. The bands at 1446, 1416 and 1330 cm^{-1} could represent the respective ν_{as}(N=O), ν(C-NO_2), ν_s(N=O) modes for complex **1** and these bonds for complex **2** can be assigned to 1447 cm^{-1} ν_{as}(N=O), 1413 cm^{-1} ν(C-NO_2), 1325 ν_s(N=O) modes, respectively.

The formation of the metal(II) complexes was also confirmed by UV/vis spectra. The following are the main points emerged out of the electronic spectrum of $[Hg(L)_2]$. The transitions in $[Hg(L)_2]$ are charge transfer, because of the Hg^{2+} state d^{10} electronic configuration. The UV/vis solution spectra of the ligands and complexes the main data are included in (Table-1).

TABLE-1
TRANSITIONS SPECIFICATIONS OF THE COMPOUNDS

Comp.	λ_{CT}(LMCT) (log ε)	λ_{CT}(LMCT) (log ε)	λ_{CT}(LMCT) (log ε)	λ_{CT}(LMCT) (log ε)
L^1	262 (4.31)	298 (4.07)	378 (4.68)	–
L^2	246 (4.60)	320 (4.62)	425 (4.84)	–
(**1**)	247 (4.44)	281 (4.28)	380 (4.84)	–
(**2**)	243 (4.69)	273 (4.30)	321 (4.48)	421 (4.80)

When compared complexes with the free ligands values have shifts frequency. Thus, we have obtained direct evidence from the spectra of $[Hg(L)_2]$ complex, that ligand molecules coordinate to mercury. The two absorption bands appearing in the range 243-247 and 273-281 nm may be assigned to a $\pi \rightarrow \pi^*$ transition of the aromatic ring and a $n \rightarrow \pi^*$ transition of the -C=N group, respectively. In addition, the low energy absorption peaks in the wavelength range 380-421 nm is associated with a charge transfer transition. The spectra of the complexes do not show any *d-d* transitions.

Thermal analysis: The thermal properties of Hg(II) complexes were investigated by thermograms (TG, DTG and DTA). The thermal analysis data are listed in (Table-2). The first stage occurred in the temperature range 222-324 °C for (**1**) and (**2**) complexes, respectively. The second stages of decomposition were observed at 392-576 °C for (**1**) and (**2**) complexes, respectively, which are accompanied by exothermic effect for complexes (**1**) and (**2**) in the DTA and DTG curves. The corresponding TG curves show a series of weight loss.

TABLE-2
THERMAL ANALYSIS OF THE COMPLEXES

Compounds	Decomp. (ºC)	DTA (ºC)	DTG (ºC)
$C_{26}H_{18}N_8O_8Hg$	222	293 Exothermic peak	298 Exothermic peak
	392	477 Exothermic peak	532 Exothermic peak
$C_{30}H_{28}N_{10}O_8Hg$	243	250 Exothermic peak	250 Exothermic peak
	494	470 Exothermic peak	575 Exothermic peak

Under 222 °C there are no exothermic peaks and no weight loss on corresponding TG curves, indicating that there are no crystal or coordinate solvent molecules. TG curves shows that decomposition with weight loss occurs above 243 °C for complexes (**2**), which is higher than for complexes (**1**) at 222 °C. Clearly, complex (**2**) has excellent thermal stability.

Conclusion

In this study we have reported the synthesis of new hydrazone derivatives and their Hg(II) complexes. The structural characterizations of synthesized compounds were made by using the elemental analysis, by IR, UV-visible, ^{13}C and ^{1}H NMR spectra techniques. From the spectroscopic characterization, it is concluded that C-H activation process is believed to proceed *via* an electrophilic substitution mechanism.

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