Synthesis and Spectral Studies of Some Novel Organomercury Compounds Containing Azo Group and Their Complexes with Cupper(II)

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Abstract:

A new series of organomercury compounds containing azo group were prepared from 4-acetaminophenol and mercerized aniline derivatives; include 2-(2mercury chloride-4-X-phenyl azo)-4-acetamido phenol {X=sulfonic acid (L_1), acetyl (L_2), carboxy (L_3), nitro (L_4) and sulphamide (L_5)}. All these compounds were characterized by F.T.IR-spectroscopy, ¹H-NMR, Micro-elemental analysis and UV-Vis spectroscopic techniques. The work also involves a study of acid-base properties at different pH values, the ionization and protonation constants were calculated. The complexes of L_1 and L_5 with Cu(II) were prepared . These complexes have been conclude after fixing the optimum conditions (time, pH and sequence of addition effects). It was found that the complexes are 1:2 (M:L) complexes and the overall stability constants were determined by the corresponding solutions method. The spectra of the complexes solutions have been studied for a range of concentrations which Lambert-Beer's law obeyed.

Keywords: Organomercury, 4-Acetamido phenol, Stability constants, Spectral studies

1. Introduction-

Mercury has played a rich role and has made diverse contributions to the field of bio conjugate chemistry, mercury's electronic properties unique have proved useful in designing electrochemical based thiol assay methods (Kolthoff, et al. 1954) Mercury metal microscopy has aided electron characterization of proteins (Prudenté also al. 2010). It forms useful amalgams with many metals, which find various applications in diverse fields. Organomercurials such as methyl mercury are more toxic than elemental mercury and other inorganic mercury compounds (Xiao et al. 2007). Mercury containing ligands e.g., mercuric and mercurous are known to form stable complexes with class b metal ions, such as gold (I) and Se (II) (Eikens, et al. 1994) because mercury is considered to be a soft Lewis base (Anvarhusein, et al. 2006). Azo compounds have been receiving much attention and have been widely used in many practical application such as coloring fiber (Mallakpour, et al., 2007), clothing (Azbar et al. 2004), cosmetics (Rafii et al. 1997), and plastics (.Dong et al. 2007). Sugar indicators (Di Cesar and Lakowicz, 2001). Azo metal chelates have also attracted increase attention due to their interesting electronic and geometrical features in connection with their application for molecular memory storages, nonlinear optical elements printing system (Steter, et al. 2008). Azo dyes of sulfa drugs are well known for their antiseptic activity (Rajinder and, Amandeep, 2012) and some are useful as chemotherapeutic agents (Goodman and Gilman, 1970) and as anticorrosion (Abdul-Nabi & Jasim, 2012). Organomercurials have been used extensively in organic synthesis as well as in mechanism investigation due to their ability to accommodate practically all of the important organic functional groups and their ease in undergoing transmetallation for the synthesis of other organometallic compounds (Kaur et al. 1996). Organomercurials, coupled with

heterocyclic compounds exhibit a wide range of pharmacological activities like fungicidal, bactericidal (Attar *et al.* 1995).

The aim of present study include synthesis five new organomercury compounds containing azo group. The characterization of these compounds by C.H.N, I.R. and ¹HNMR were done. The studies also included, acid- base properties, determination of ionization and protonation constants and their suggested mechanism and determination of the stability constants and optimum conditions for forming complexes of the copper complexes of these compounds

2- Experimental

All the reagents and solvents were of reagent-grad quality. The progress of reaction was monitored by TLC using gel coated plates (0.5mm silica thickness, Merck) and spots were visualized under UV radiation. Infrared spectra (as KBr pellets) were recorded on F.T.IR-8400S Shimadzu. NMR spectra were recorded by Bruker ultra shield 300MHz spectrometer DMSO as solvent and TMS as internal reference. Melting points were determined by Buchi B190 K apparatus. Elemental analysis (C.H.N.), were carried out by Perkin element 2400. UV/Vis. absorption spectra of these compounds in different buffer solutions at room temperature were recorded using Perkin Elmer Lampda EZ 210 UV/Vis. Spectrophotometer.

2.1 Preparation of 2-mercurychloride -4-X-aniline derivatives:

Mercury chloride 4-X aniline derivatives [where X = sulphonic acid, acetyl, carboxyl, nitro and sulphamide] were prepared by mixed (0.05 mole) aniline derivatives and (0.05 mole 15.93g) mercury (II) acetate in 50 ml of ethanol and reflux with string for 2 hr, then (0.04 mole, 2.5g) of LiCl

was dissolved in 10 ml ethanol and added to the product, reflux the mixture for 1 h. the hot solution was

2.2 Synthesis of Organomercury

containing azo group (L_1-L_5) :

The Organomercury, 2-(2-mercury chloride-4-sulfonic acid phenyl azo)-4acetamido phenol (L_1), 2-(2-mercury chloride-4-acetyl phenyl azo)-4acetamido phenol (L_2), 2-(2-mercury chloride-4-carboxy phenyl azo)-4acetamido phenol (L_3), 2-(2-mercury chloride-4-nitro phenyl azo)-4acetamido phenol (L_4) and 2-(2mercury chloride-4-sulfamide phenyl azo)-4-acetamido phenol (L_5) , were prepared by dissolving 0.004 mole of 2-mercurychloride-4-X-aniline derivatives with 1.4 ml concentrated HCl and 20 ml distilled water then drop by drop with stirring adding

filtered with suction, The solid was washed with 50 ml of hot ethanol (Al-Rubaie *et al.* 2011)

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solution of (0.304 g sodium nitrite in 20 ml distilled water) to form diazonium salt at -5° C temperature. The alkaline solution of 0.004 mole of 4-acetaminophenol in (1.2%)v/wNaOH) was added to the above diazonium salt. Then converting the prepared compound from sodium salt into hydrogen form by adding of dilute HCl. The dyes were purified by recrystallization from methanol and dried at 50°C in an oven to give azo dyes. By the aid of CHN, NMR and IR, the suggested molecular structures of organomercury compounds were shown in Scheme-1.



$X = SO_{3}H(L_{1}), COCH_{3}(L_{2}), COOH(L_{3}), NO_{2}(L_{4}), SO_{2}NH_{2}(L_{5})$

Scheme (1): Suggested molecular structure of dyes

To calculate the ionization and protonation constants for hydroxyl and nitrogen groups, a series of acetate and universal buffer solutions were prepared with different pH values [0.5-12] for each organomercury compounds (Beck.1970).

3-Results and Discussion

The compounds were prepared in good yield. The compounds are stable in air and light. Elemental analysis data and physical properties of compounds are summarized in table (1)

Table 1: The physical and analytical data of organomercury compounds and their complexes

Comp	Molecular	M.Wt.	Color	M.P	Elemental Analysis		
	Formula			°C	Found (Calc.)		
					%C	%H	%N
L ₁	C ₁₄ H ₁₂ N ₃ O ₅ SHgCl	570	Orange	331	28.99(29.47),	2.07(2.11),	7.48(7.37)
L ₂	$C_{16}H_{14}N_3O_3HgCl$	532	Red	183	36.71(36.09),	2.22(2.63),	8.01(7.89)
L ₃	$C_{15}H_{12}N_3O_4HgCl$	534	Orange	175	33.99(33.71),	2.31(2.25),	7.97(7.87)
L ₄	$C_{14}H_{11}N_4O_4HgCl$	535	Orange	159	31.91(31.40),2	2.10(2.06), 1	0.56(10.47)
L ₅	$C_{14}H_{13}N_4O_4SHgCl$	569	Orange	231	30.01(29.53),	2.32(2.28),	9.93(9.84)
C ₁	$Cu(C_{14}H_{11}N_3O_5SHgCl)_2$	1201.5	Red	>360	27.42 (27.97),	1.65(1.83),	7.04(6.99)
C ₂	$Cu(C_{14}H_{12}N_4O_4SHgCl)_2$	1199.5	Red	>360	28.54(28.01),	1.88(2.00),	9.64(9.34)

3.1 FTIR Spectra

The IR spectral analysis of compounds are in good arrangement with the synthesis compounds. The sharp medium band at 3503 -3300 cm⁻¹ indicating the presence of free phenolic OH group, The band at 1406-1432 cm⁻¹ (-N=N-) of the compounds undergoes negative shift in the compounds indicating nitrogen coordination of the diazo moiety. the low frequency and the broadening of these bonded suggest that these compounds having a (Hg N) bonding in the solid state (Bellú, et al The presence of a sharp band 2003). at 1586-1575 cm⁻¹ due to to the (C-C)ring vibrations) (S=O str. Assym. appear at 1264-1274 cm⁻¹, The bands around 1472 cm⁻¹ and 1346 cm⁻¹ observed due to -NO₂ group for the L4. The bands at 755 cm^{-1} for (N-H wag.).The peak appearing in the region 1325-1344 cm⁻¹ are attributed to (C-N) stretching vibration The band belonging to (N-H) stretching vibration is not observed probably due to overlapping with the broad hydroxyl peak .The other characteristic peaks of compounds are given in Table (2) and Fig (1). These data are in agreement with those previously reported for similar compound (Jarallah and Hudi 2012; Mossalamy 2005).

Comp.	_{NH &OH} str. cm ⁻¹	C-N str. cm ⁻¹	c=o str. cm ⁻¹	N=N str. cm ⁻¹	o=s=o Asy.Sym cm ⁻¹
L ₁	3500-3350 b	1325 w	1670 s	1429 w	1365 w & 1195 s
L ₂	3300-3200 b	1355 w	1658 s	1415 (w)	
L ₃	3450-3250 m	1332 w	1652 s	1406 s	
L ₄	3350-3300 b	1323 w	1610 s	1432 w	
L ₅	3500-3300 b	1375 w	1656 s	1433 w	1300 w & 1137 w

Table 2: The I.R spectral data of the Organomercury compounds	(KBr disc)
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b = board s= strong m= medium w=weak



Fig. 1: FT-IR Spectra of organomercury compounds L_1 and L_2

3.2 ¹HNMR spectra

¹H-NMR spectra of the prepared organomercury compounds were deuterated performed in dimethyl sulfo-xide with solutions tetramethylsaline as an internal standard. All these spectra showed a peak at 2.5 ppm which was due to

DMSO solvent and some spectra showed a sharp peak at 3.33 ppm due to dissolved water in DMSO. Figures 2-6 represent the¹H-NMR spectra of the compounds and Table (3) shows the data of ¹H NMR these compounds (Silverstein and Webster 1996). Table 3: ¹H-NMR- Spectra of organomercury compounds.

Comp.	(ppm)
L ₁	2.02 (S,3H,CH ₃),6.9-7.9(m, 6H, Ar-H), 7(S, 1H, SO ₃ H), 9.8 (S, 1H,
	NH),10.7 (S, 1H, OH)
L_2	2.02(S, 3H, NH-CO-CH ₃), 6.5-8.2(m, 6H, Ar-H), 2.4(S, 3H, COCH ₃), 9.65
	(S, 1H, NH), 9.9(S, 1H, OH)
L ₃	2.03 (S, 3H,CH3), 6.6-8(m, 6H, Ar-H),9.8(S,1H,NH),10.1(S, 1H, OH)
L ₄	2.02 (S,3H, CH ₃), 6.6-8.5(m, 6H, Ar-H), 6.7(S, 1H, NH), 9.9(S, 1H, OH)
L_5	2.02 (S, 3H, CH ₃), 6.6-7.9(m, 6H, Ar-H), 7.31(S, 2H, SO ₂ NH ₂), 9.67 (S, 1H,
	NH), 9.9(S, 1H, OH)



Fig. 2: HNMR spectrum of L₁



Fig. 3: HNMR spectrum of L₂



Fig. 4: HNMR spectrum of L₃



Fig.-5: HNMR spectrum of L₄



Fig. 6: HNMR spectrum of L₅

3.3 Electronic absorption spectra:

Table 4 shows the summary ($_{max}$, medium and isobestic points) of the electronic absorption spectra of organomercury compounds (L_1 - L_5 of each concentration of 2.4x10⁻⁴ M) at different pH values (0.7-12) using acetate and universal buffer solutions. Figs 7-11 show the absorption bands due various electronic transitions liable to occur within the molecules due to * electronic and * transitions n of N=Ngroup and the whole electronic system of the organomercury compounds influenced inter-molcular by charge transfer character (Fahad al., 2011). et

Table 4: The $_{max}$, medium and isobestic points of the absorption spectra of organomercury compounds (L₁-L₅)

Azo	max nm. and Medium	Isopiestic point
dyes		
L ₁	400 (acidic), 500 (Alkaline)	440
L ₂	280 (acidic), 330 (Alkaline)	270,280,290
L ₃	330 (all media), 430 (all media)	380
L_4	380 (all media)	410
L ₅	420 (acidic), 500 (Alkaline)	430



Fig.7-:Electronic spectra for L_1 at different pH values



Fig. 8: Electronic spectra for L_2 at different pH values



Fig.9- Electronic spectra for L_3 at different pH values



Fig.10 Electronic spectra for L₄ at different pH values



Fig. 11: Electronic spectra for L_5 at different pH values

in schemes (2 and 3) for L_1 and L_5 The suggested mechanism of respectively. The protonation and ionization was shown



Scheme 2: The suggested mechanism of L_1



Scheme 3: The suggested mechanism of L₅

3.4 Ionization and protonation constants of compounds

Fig. 12 shows the relation between absorbance and pH values of L_1 - L_5 at max of each organomercury compounds. The protonation and ionization constants (pK_p and pK_a) of organomercury compounds were determined from their spectral behavior in buffer solution of varying pH. From the absorbance-pH curves. The pK_a and pK_p values were determined by using of half height method (Beck, 1970). pK = pH (at $A_{1/2}$) $A_{1/2} = (A_l + A_{min}) / 2$

Where A_1 and A_{min} are limiting and minimum absorbencies respectively





Fig. 12: Absorbance-pH curves for L₁-L₅

pK _a)	constants	were	calculated	(table
5).				

From above relations and Figs (12) so the protonation (pK_p) and ionization (

Table 5: The ionization and protonation constants of organomercury compounds

Dye	max	pk _{p1}	pk _{p2}	pk _{p3}	pk _{a1}	pk _{a2}
	(nm)					
L ₁	515	1.4	3.5		6.2	9.3
L_2	330	3.5			7.8	10.5
L ₃	480	4.5			6.5	9.8
L_4	390	3.2	5.6		7.7	
L_5	500	1.4	3.5	6	9.2	

 $\overline{K_a}$ = ionization constant of –OH group pkp= protonation constants

3.5 Complex formation studies:

Interaction of the cupper ions with L_1 and L_5 ($_{max}$ of L_1 is 400 nm & L_5 is 420 nm) has been studied in solution. An aqueous-ethanolic solutions were always performed complexes of L_1 and L_5 with copper(II) ($C_1\&C_2$) respectively, these complexes were identified optimum conditions for the composition of these complexes (time, pH and sequence of addition effects). The interaction of the copper ion with the ligand manifest itself in the absorption spectra by the appearance of a peak in the range (530 and 520 nm) for ($C_1 \& C_2$) respectively . A great bathochromic shift in the visible

region was detected in the complex solutions spectra with respect to that of the free ligand. The high shift in the (_{max}) gave a good indication for complex formation. (Fig-13).



Fig. -13: The electronic spectra of $L_1 and \, L_5$ and their complexes ([Cu^{2+}=[L]=2.4 x $$10^{-4}\ M$)

3.3 The optimum conditions for complexes formation:

3.6.1 Time effect:

It was found the two complexes C_1 & C_2 are of high stability by the aid of the stable absorbance measurements at max. The more intense color was for in the region of (1-40 min) and (1-120 min) with respect of $C_1 \& C_2$. The color is stable over night for both two complexes.

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3.6.2 pH effect:

The influence of pH values on the absorbance of complexes $C_1 \& C_2$ was studied at different pH values (Fig. 14) by using of acetate and universal buffer solutions (pH 0.7-13). It was

found that the highest absorbance at pH 8 for two complexes. This is because of the anionic formation of reagent, which can easily react with cupper ion to form complexes.



Fig.-14: Effect of pH on complexes (C_1 and C_2) spectra. ([Cu^{2+}]=[L]=2.4 x10⁻⁴ M)

3.6.3 Effect of kind of buffer solution:

Buffer solutions of pH=8 including, universal (U), Hexamin (H), Phosphate and Sodium bicarbonate (B) were used. The results are summarized in table (6), Hexamin buffer solution is best medium

Type of Buffer	Absorbance of C ₁ at	Absorbance of C ₅ at	
	max	max	
Р	0.158	0.110	
U	0.247	0.156	
Н	1.063	0.407	
В	0.467	0.099	

Table 6: Effect of buffer kind solution of pH=8. ($[Cu^{2+}]=[L]=3 \times 10^{-4} M$)

3.7 The composition of the complexes

(stoichiometry)

The composition of the complexes formed in solution has been established by mole ratio and job

methods. In both cases the results reveals (1:2) metal to ligand ratio. (Fig.15).



Fig. 15: Mole ratio (A) and Job (B) methods for C₁ and C₅ respectively

3.8 Beer's law and sensitivity

The calibration curve shows that Beers law is obeyed in the concentration range of (0-15.25 μ g ml⁻¹) and (0-11.43 μ g ml⁻¹) for complex C₁ and C₂

respectively. Table (7) shows the data obtained, that represented by $_{max}$, the molar absorbitivity coefficient (, L.mol⁻¹.cm⁻¹ and sensitive index (S, µg.cm⁻²), with higher precision that represented by the results of standard deviation (S.D), and high linearity of Beer's law which represent by the correlation coefficient (r) which is nearly to unity. And the detection limit (DL μ g.ml) of the complexes C₁ and C₂ 0.76 and 0.56 respectively (Fahad *et al.* 2011).

Comp.	max nm.	L.mol ⁻¹ .cm	S.D	S µg.ml ⁻¹	DL µg.ml ⁻¹	r	Beers law limt. ppm
C ₁	520	7302.3	0.021	0.0087	0.76	0.9946	15.25
C ₂	530	6097.3		0.0104	0. 56	0.9929	11.43

Table 7: Some results obtained from Beers law

3.9 The stability of the complexes:

The stability constants of complexes C_1 and C_2 were calculated using Corresponding Solutions method (by aid of half-value method) (Beck 1970). This method required two series of solutions of total metal ion concentration C_{1M} (concentrated series =2.4 x 10⁻⁴ M) and C_{2M} (diluted series =1.2 x 10⁻⁴ M) and varying ligand concentrations C_{1L} (0.6-4.8 x 10⁻⁴) and C_{2L} (0.387-1.646 x 10⁻⁴ M), then the diluted series was multiplied by the factor (C_{1M} / C_{2M}). The corresponding solutions are those which have the same absorbance at different ligand (dye) concentration. From the absorbance- C_L plots (Fig. 16), many pairs of C_{1L} and C_{2L} consequently, \tilde{n} (complex formation function) and [L] free ligand concentration can be determined where:

$$\tilde{n} = (C_{1L} - C_{2L}) / (C_{1M} - C_{2M})$$

and

 $[L] = (C_{1M}C_{2L} - C_{2M}C_{1L}) / (C_{1M} - C_{2M})$



Fig. 16: Absorbance-CL plot of complexes C_1 (A) and C_2 (B)

By using the half value method, the log $_1$ and log $_2$ are obtained from a plot of \tilde{n} against pL (Fig. 17), when $\tilde{n} = 0.5$ gives log $_1$ (log K₁) and $\tilde{n} = 1.5$ gives log $_2$ (log K₁+ log K₂). It was

found that \log_{-1} values of $C_1 \& C_2$ are 5.55 & 3.79 respectively, and \log_{-2} values of $C_1 \& C_2$ are 9.4 & 6.81 respectively (where K and are step stability and overall stability constants.



Fig. 17 : \tilde{n} - pL curves for determination of log K₁ & log K₂ for complexes

The solid complexes

The solid complexes have been prepared by direct reaction of alcoholic solution of the ligands L_1 and L_5 with the aqueous solution of the cupper ion at the optimum pH and in a (M: L) ratio of (1: 2). The C. H. N and metal contents of these complexes were in a good agreements with the calculated values (Table 1). The molar conductance of the complexes as in ethanol indicating their non- electrolytic nature (Geary, 1971; Ray et al. 2004). The UV-Vis spectra of the prepared complexes dissolved in ethanol $(1x10^{-3})$ M of each Cu & L) have been measured. Again the large bathochromic shift of the (max) to 520 (19230.7cm⁻¹) and 530 nm (18867.9 cm-1) assigned to (${}^{2}B_{2}g$

 $^{2}B_{1}g$) of d-d transition of copper (Dawood *et al.* 2009).

In order to study the binding mode of the ligand (organomercury compounds) with the Cu^{2+} ions, a comparison have been made for the F.T. IR spectra the prepared complexes and were tabulated in (Table-8).

Table 8: Infrared spectral data (wave number) cm^{-1} of the copper complexes C_1 and

1	٦
C	-2

Dye	(N – H)	(N=N)	(M– O)	(M- N)	Additional bands
C ₁	3448	1380	568	474	2923w (C–H) alpha. 2854 w (C– H).alpha
C ₂	3419	1365	567	480	3150w (С–Н) arom.2950vw (С–Н) alpha.

The IR spectrum of the C_1 and C_2 (Figs. 18 &19) exhibited broad bands at 3448 and 3419 cm⁻¹ was assigned to the stretching vibration of (NH) group (Yildiz and Boztepe 2002). Since no change in this band was noticed, great change to lower observed frequency was on complexation with metal ion. Coordination of the ligand to the metal through the azo nitrogen atom are expected to reduce the electron density in the azo 1 links and lower the N=N

absorptions frequency. In the spectra of all the new azo complexes, the bands due to N=N were shifted to lower frequencies (from 1429 to 1380) cm^{-1} and (from 1433 to 1365 cm^{-1}) for C_1 and C_2 respectively. The appearance of the two new bands in the regions 568-567 and 474-480 cm^{-1} in the metal chelates suggests the formation of M—O and M—N bonds, for C_1 and C_2 respectively (Saleen *et* al. 2003).



Fig. 18: FT.IR spectrum of copper complex C_1



Fig. 19: FT.IR spectrum of copper complex C₂

The conductivity measurements values are 9.45-14.65 S. cm² mol⁻¹, in DMSO (1x10⁻³M) at room temperature for C₁ and C₂ respectively the values indicating that non-ionic character (Drago ,1965).

According to the results obtained from the ratios of metal to ligand as confirmed by their elemental analysis and IR analysis. The complexes are non-electrolytes as confirmed by their conductivity measurements. The electronic spectral data suggest tetrahedral possible a structure geometry around the metal ions as shown in the proposed structure (Jarad, 2012) (Scheme 4)



 $M^{+2}=Cu$

Scheme 4: The proposed structural formula of Cu(II) complex

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Synthesis of Novel Acidic Mono Azo Dyes and an Investigation of Their Use in the Textile Industry. Turk. J. Chem; 26, 897-903, حضير ودراسه طيفيه لبعض مركبات الزئبق العضويه الحاويه على مجموعه الايزو

ومعقداتها مع النحاس الثنائي

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الخلاصه

تم تحضير سلسله جديدة من مركبات الزئبق العضويه التي تحتوي على مجموعه الازو من مفاعله 4-اسيتئمايد فينول ومشتقات الانلين الزئبقيه وشملت -4-(2-mercury chloride-4-X- phenyl azo)-2 acetamido phenol

{X=sulfonic acid (L₁), acetyl (L₂), carboxy (L₃), nitro (L₄) and sulphamide (L₅)}.

وشخصت جميع هذه المركبات بوسطه التحليل العنصري الدقيق ومطيافيه الاشعه تحت الحمراء والرنين النووي المغناطيسي و الاشعه المرئية البنفسجية ودرست الخصائص الحامضيه والقاعديه و لهذه التأين والبرتنه لها _وحضرت معقدات النحاس لبعض هذه المركبات ودرست في