Effect of Mercuric Salts on Xylenol Orange and Their Halochromic Effect

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Summary: Xylenol orange reacts with mercuric acetate, chloride and iodide in non polar and polar medium to give mercurated products. Their structures are confirmed by analytical data, IR, UV/V and MS spectra. The halochromic effects are studied.

Introduction

Xylenol orange (3,3'-bis N,N-di(carboxymethyl)-aminomethyl o-cresolsulphonphthalein) has been used as metal indicator for complexometric titration with EDTA even in acid solution (pH 3-5). Acidic solutions of xylenol orange are coloured lemon yellow and those of metal complexes intensely red [1].

Many publications have been described for the effect of mercuric salts on organic compounds [2-8], some of these give mercurated compounds or compounds formed by mercuration followed by coordination [3], the other give compounds containing -N-Hg and -N-NH-Hg bonds and aromatic substitution as well as mercuraction accompanied with N=C bond cleavage [6].

The present work deals with the interactions of mercuric acetate, chloride and iodide in different media with xylenol orange followed by studing the spectra in media of different pH.

Results and Discussion

Xylenol orange and mercuric acetate (1:1 molar ratio) in toluene or in polar solvent (e.g. methanol) react to give mono-mercurated product (I) where organometallic compoud is obtained via formation of acetoxymercury salt followed by decarboxylation to form C-Hg bond. This is based on the ability of Hg to replace the carboxylic group in mono and di-carboxylic acids [9]. Elemental analysis, IR, UV and MS spectra are consistant with the proposed structure.

The two broad bands at 1630 and 1585 cm^{-1} due to the $\nu_{C=O}$ of dicarboxylic group for the starting material became one band at 1630 cm^{-1} in (I). This can be attributed to monodecarboxylation. The new band at 530 cm^{-1} can be attributed to Hg-C bond [10]. The spectrum shows also ν_{Hg-O} at 450 cm^{-1} and νSO_2-O at 1400-1430, 1200-1145 cm^{-1}.

The absorption maximum of xylenol orange is affected by change of pH of solution, in acidic medium at 440 nm and in alkaline medium at 572 nm with the formation of isobestic point at 485 nm. At pH 12.5, the absorption

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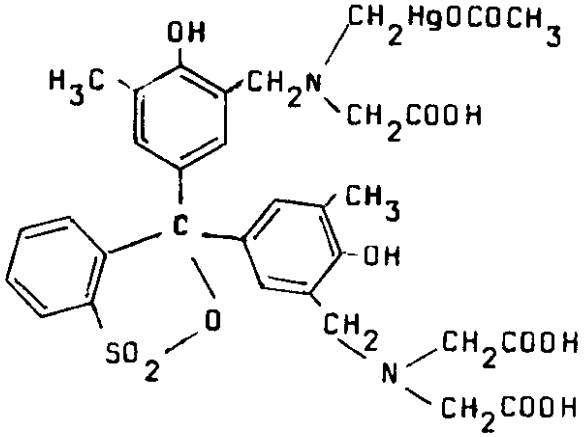
maximum is shifted to longer wave length (580 nm). Intensity increases as pH increases and the reverse is also true.

The absorption spectrum of (I) in alkaline medium shows λ_{max} at 573, 364 and 294 nm. The intensity increases by increasing pH value up to 11.35 then decrease.

In acidic medium ν_{max} = 435 and 270 nm. The isobestic point is at 508 nm.

The acid value is determined using sodium bicarbonate. It shows that the three carboxylic groups are present in compound (I).



(I)

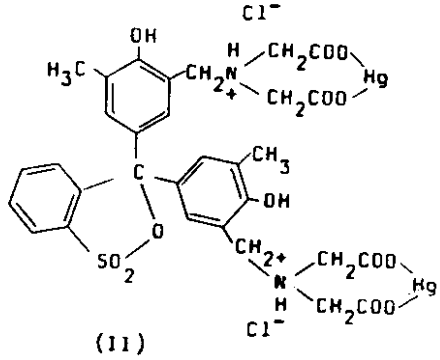
The mass spectra for compound (I) did not show the molecular ion peak at 160, 230 and 250°C.

The most important features of the mass spectra at the three temperatures are given in table-1.

When the reaction is carried out with mercuric chloride in toluene (non -polar medium) it gives rise to product (II).

The IR spectrum shows no change in the aromatic substitution region which indicates that no substitution reaction occurs on the aromatic nucleus. It shows νSO_2-O at 1440-1340, 1200-1145 cm^{-1}, ν_{OH} at 3680-3100 cm^{-1}, ν_{Hg-O} at 480 cm^{-1}.

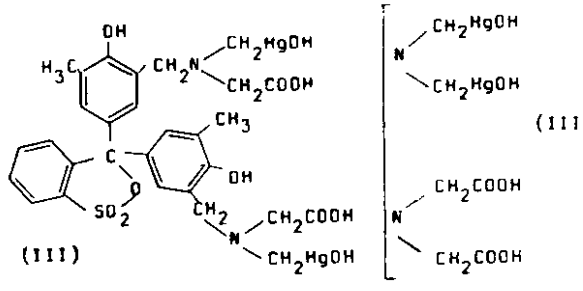
The acid values shows the absence of carboxylic groups.



(II)

The qualitative analysis indicates the presence of ionizable halogen.

In polar medium (methanol) the reaction proceeds with the decarboxylation of two carboxylic groups to give dihydroxy-mercury compound (III).



(III)

The structure (III) is the more probable than the other (II) due to steric hindrance.

All the data obtained from analysis, IR, UV, MS spectra and acid value shows the presence of two carboxylic groups.

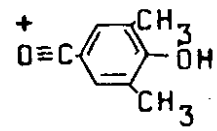
The IR spectrum for compound (III) shows the presence of ν_{Hg-O} at 450 cm^{-1} and ν_{Hg-C} at 535 cm^{-1}.

Table-1: Mass Spectra of Compound (I) at Different Tempt.

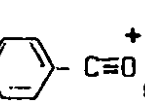
m/z	Fragment	at 160°C	at 230°C	at 250°C
15	CH_3^+	67.30%	40%	84.1%
28	H_2CN^+	61.53%	25%	64.77%
39	$C_3H_3^+$	65.38%	35%	56.81%
43	$CH_3C{=}O^+$	44.23%	27.5%	100%
59	$OCOCH_3^+$	100%	65%	14.77%
64		-	12.5%	3%
77		-	1.25%	1%
91		-	3.75%	2%
105		5.22%	25%	9.09%
155		1%	1%	1%
200	200_{Hg}^+	24.34%	100%	28.4%
202	202_{Hg}^+	5.22%	100%	36.36%

The electronic spectrum for (III) shows λ_{max} in acidic medium at 440,270 nm (= 1.2 x 10^4 and 32x10^3 respectively) and 574, 360 and 295 nm in alkaline medium. At pH 11.6 the maximum intensity at 547 nm (= 3.8 x 10^4).

The MS spectrum for compound (II) did not show the molecular ion peak. The base peak is at m/e 149 (100%) due to



The intense peaks at m/z 39 (63.63%), m/z 45 (73.86%), m/z 51 (67.04%), m/z 77 (63.63%), 105 (23.86%), m/z 200 (29.54%) and 202 (36.36%) are attributed to $C_3H_3^+$, HCO_2^+, $CHCH_3^+$, $C_6H_5^+$, $C_6H_5^+$



200 Hg + and 202 H+.

The small peaks at 65 (10.22%), 90 (11.36%), 91 (13.63%) and 204 (5.68%) can be attributed to $C_5H_5^+$, $C_7H_6^+$,

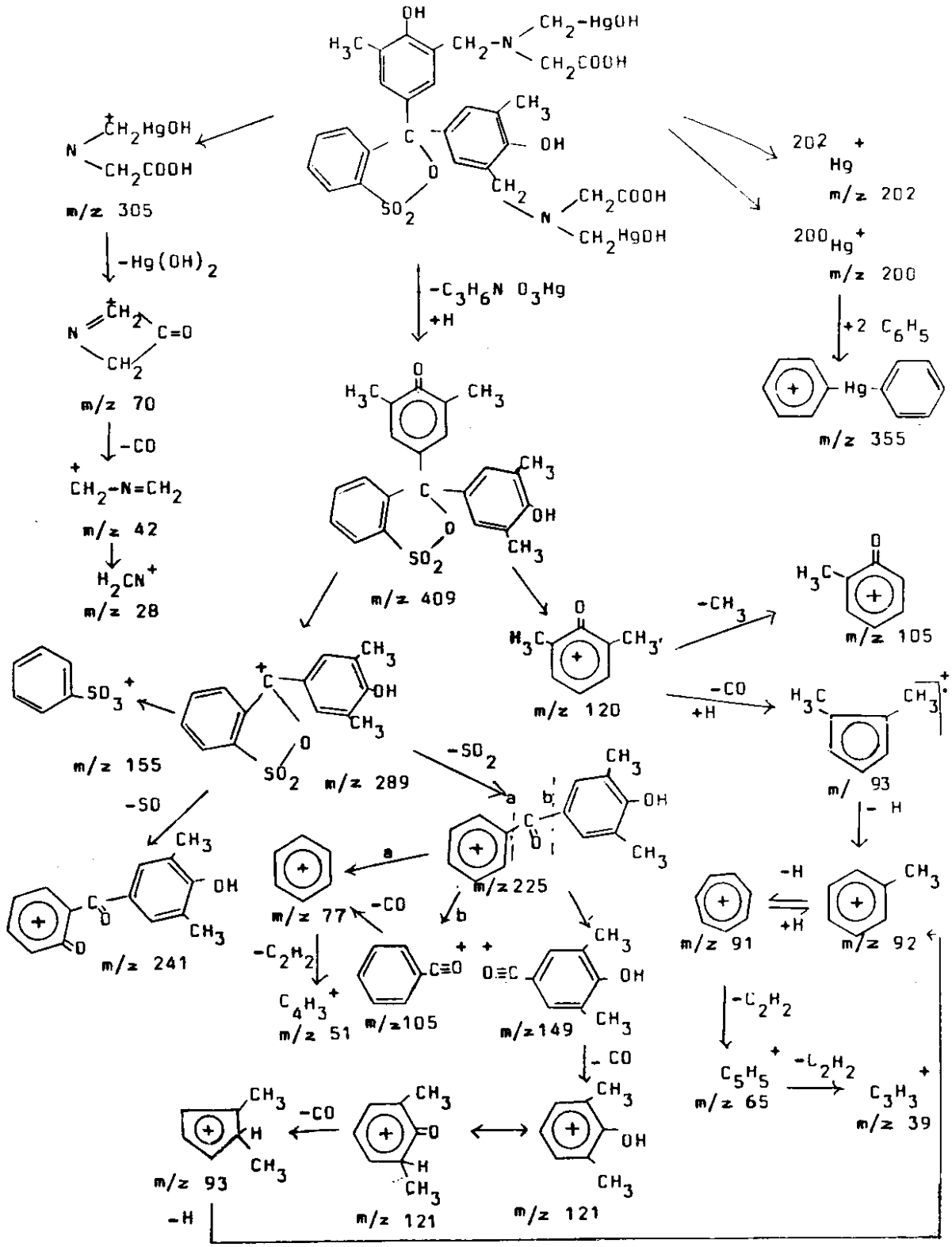
and $C_{15}H_{13}O_2$.

Table-2: Mass Spectra for Compound (III) at Different Tempr.

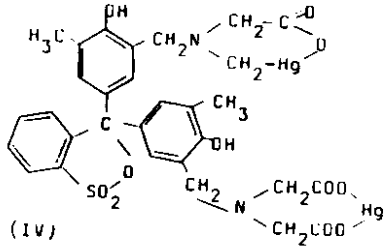
Fragment	m/z	% Relative Abundance at 200°C	m/z	at 250°C
CH_3^+	15	(71.6%)	15	(12.29%0
H_2CN^+	28	(50.74%)	28	(43.44%)
$C_3H_3^+$	39	(100%)	39	(41.80%0
$C_4H_3^+$	51	(68.65%)	51	(9.83%)
$C_4H_6^+$	54	(27.94%)	54	(100%)
$C_5H_5^+$	65	(38.8%)	65	(58.19%)
$C_6H_5^+$	77	(5.97%)	77	(87.01%)
	82	(28.35%)	82	(18.18%)
	91	(62.86%)	91	(22.07%)
	105	(29.85%)	105	(29.87%)
	121	(4.5%)	121	(28.75%)
	149	(4.47%)	149	(25.97%)
200_{Hg}^+	200	(29.85%)	200 (7%)	
202_{Hg}^+	202	(89.85%)	202	(7%)
CH_3Hg^+	215	(1.49%)	215	(5.19%)
$C_{15}H_{13}O_2^+$	225	(1.49%)	225	(3.89%)
$C_3H_3Hg^+$	239	(1.49%)	239	(4.54%)
$C_4H_3Hg^+$	265	(2.98%)	265	(1.94%)

The mass spectra for compound (III) are carried out at 200 and 250°C. It did not show the molecular ion peak. Table-2 shows the base peaks at each temperatures and the relative abundance of the fragments.

Fragmentation may be schematically summarized as follows:



The reaction of xylenol orange with mercuric iodide in toluene (non-polar medium) gives the product (IV). The results of acid value determination show the absence of carboxylic groups.

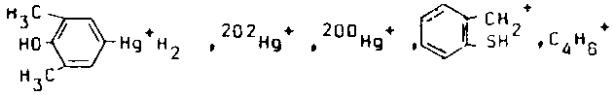


(IV)

The data obtained from elemental analysis, IR, UV, MS spectra also the acid value confirm the proposed structure. IR spectrum shows ν_{OH} at 3650-3000, $\nu_{C=O}$ at 1625, ν_{C-Hg} at 510, ν_{Hg-O} at 450 and ν_{SO_2-O} at 1410-1330 cm^{-1}.

The electronic spectra shows that at acid medium, two bands are given at 270 and 433 nm with small difference in absorbance. In basic medium, three bands are obtained at 292, 364 and 572 nm with maximum intensity at pH 11.66 and 3 times more than in acidic medium.

The mass spectrum for compound (IV) at 150°C is carried out and did not show its molecular ion peak. The base peak is at m/z 452 (100%) due to $C_{25}H_{27}NSO_5^+$. The intense peaks are at m/z 325 (15.45%), 202 (33.63%), 200 (26.36%), 123 (22.72%), 56 (12.27%), 39 (14.09%), 32 (27.27%), 28 (30.45%), 19 (22.72%), and 15 (29.09%) are for



$^{202}Hg^+$, $^{200}Hg^+$,

$C_4H_6^+$, $C_3H_3^+$, $NHOH^+$, H_2CN^+, H_3O^+ and CH_3^+

The small peaks at 255 (9.54%), 227 (11.82%), 101 (4.54%), 91 (2.27%) 65 (2.27%), 58 (12.27%), 54 (7.27%) and 43 (9.54%) are for $C_{17}H_{21}NO^+$.

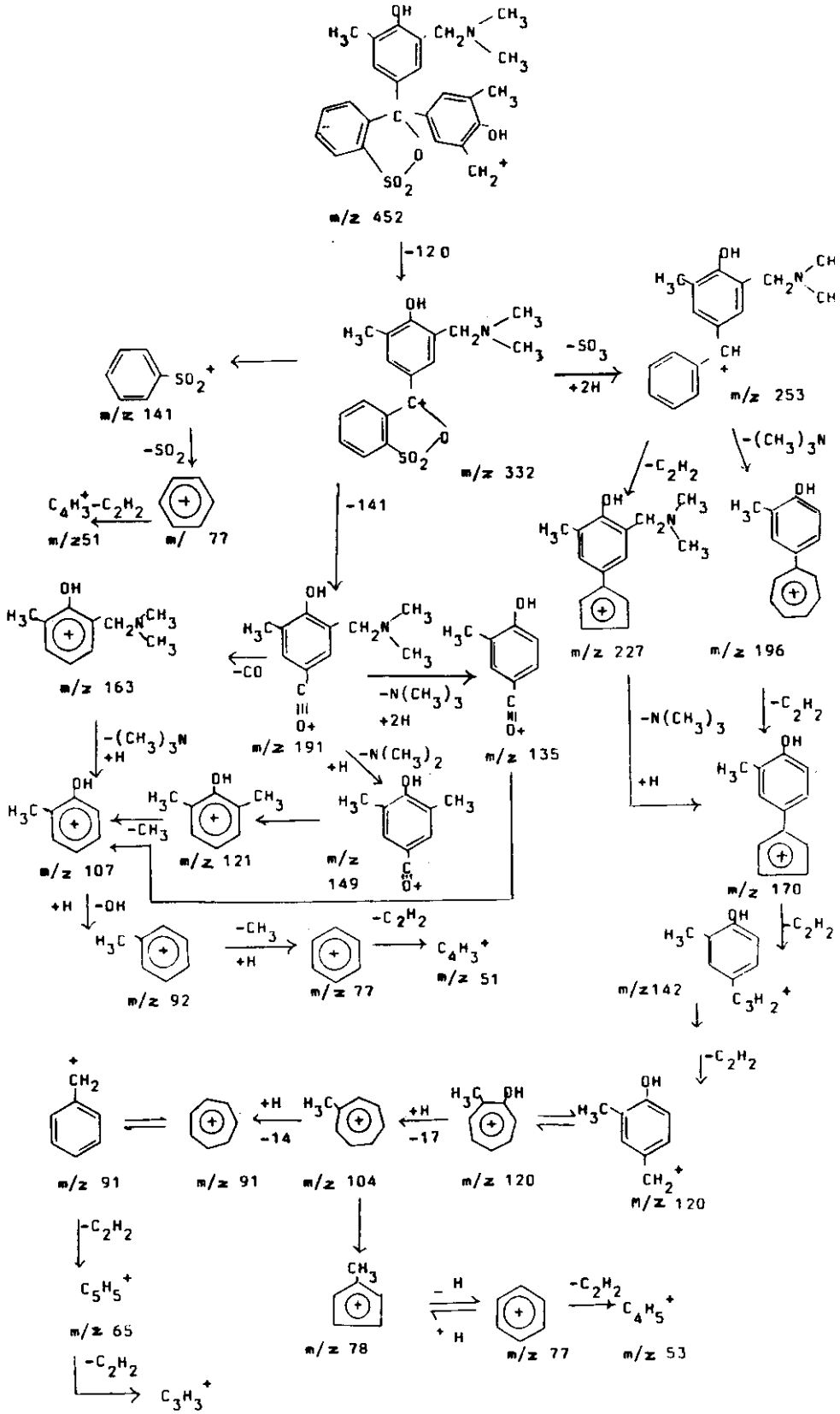
$C_{15}H_{17}NO^+$, $HC\equiv C-$

$C_7H_7^+$, $C_5H_5^+$, $C_3H_8N^+$, $C_4H_6^+$ and $C_2H_3O^+$.

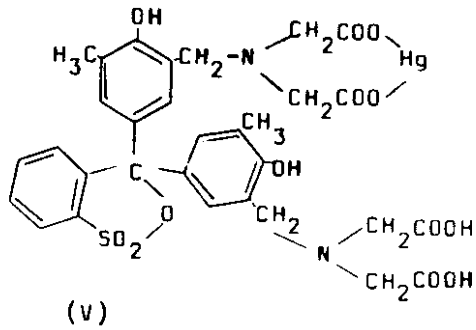
Table-3

Compound	m.p.°C	Yield %	Analysis	%C	%H	%N	%S	%Hg
$C_{32}H_{34}N_2O_{13}HgS$(I)	203-204	94	Found	43.0	3.60	3.33	3.4	22.4
			Calcd.	43.31	3.83	3.16	3.6	22.6
$C_{31}H_{28}N_2O_{13}Hg_2S.2HCl$	150-151	45	Found	33.72	2.62	2.77	2.67	35.91
(II)			Calcd.	33.51	2.70	2.52	2.88	36.14
$C_{29}H_{32}N_2O_{11}Hg_2S$(III)	d.230	43	Found	33.98	2.97	2.50	2.90	39.02
			Calcd.	34.21	3.145	2.75	3.15	39.44
$C_{30}H_{28}N_2O_{13}Hg_2S$(IV)	120-121	45	Found	36.38	2.76	2.62	3.32	41.12
			Calcd.	36.69	2.85	2.85	3.26	40.89
$C_{31}H_{30}N_2O_{13}HgS$ (V)	142-143	92	Found	42.35	3.36	2.0	3.50	22.9
			Calcd.	42.73	3.45	2.22	3.67	23.04

Fragmentation of m/e 452 can take place as follows:



The reaction of xylenol orange with mercuric iodide in methanol gives rise to the product (V) Acid value determination indicates the presence of two carboxylic groups.

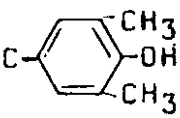


(V)

The data obtained from chemical analysis, IR, electronic spectra and MS agree with the proposed structure.

The IR spectra shows ν_{OH} at 3650-3000, $\nu_{C=O}$ at 1630, ν_{SO_2}-O at 1340 and ν_{Hg-O} at 450 cm^{-1}.

The electronic spectra show two bands at λ_{max} 268 and 435 nm in acidic medium with maximum intensity at pH 3. At pH 7.55 two bands appear at λ_{max} 444 and 572 and by increasing pH value the intensity decreases and shifted to 572 nm.

The MS spectra are carried out at two temperatures 100°C and 200°C. They did not show the molecular ion peak. The base peak at 100°C is at m/z 149 (100%) due to  , whereas the base peak at 200°C is at m/e 200 due to $^{200}Hg^{+}$.

Experimental

The analysis were carried out in the Microanalytical lab., National Research Centre (Cairo). Infra red spectra were measured on Perkin-Elmer 398 Infra red Spectrophotometer using KBr wafer technique. The Mass spectra were recorded at 70 ev on Varian MAT-711 Spectrophotometer. UV spectra were recorded on Perkin Elmer 555 UV. Vis. Spectrophotometer. Mercury is determined after wetdigestion by thiocyanate method using ferric alum as indicator.

General Procedure

The reaction of xylenol orange with mercuric salts in methanol

Xylenol orange (0.001 mole) in 25 ml methanol was added drop by drop to (0.001 mole) mercuric salt in 25 ml methanol. The reaction mixture was stirred for 5 hours, then left to stand over-night, concentrated and ether was added to give crystalline mercurated product. The product was filtered, dried and recrystallized from methanol -ether mixture. The filtrate was then evaporated under reduced pressure to obtain the recovered unreacted material if present.

The reaction of xylenol orange with mercuric salts in toluene

A mixture of 1:1 molar ratios of the reactants in 50 ml toluene was refluxed for 3 hours. The reaction mixture was left to stand overnight. The precipitated product was filtered, dried and recrystallized from ether-petroleum ether 40-60°. The filterate was evaporated under reduced pressure to obtain the recovered unreacted materials if present.

Yields, melting points and analysis are given in table-3.

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