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BEHAVIOUR OF TOLUIDINE RED TOWARDS SOME METAL IONS

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ABSTRACT

The reaction of Toluidine Red with some metal salts, e.g. mercuric, copper, cobalt and nickel acetate was studied. The structures of the obtained compounds were confirmed through IR, UV, MS and powder XRD analyses.

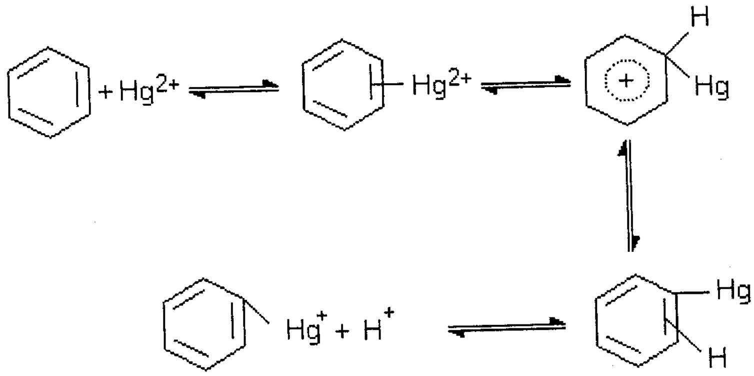
The results revealed that the compounds were of monometallated and dimetallated products. The biological activity of the prepared Toluidine Red metal complexes on Biomphalria Alexandrina snails showed high mortality rate which depends on the type of the metal ion forming the complex.

1. INTRODUCTION

Mercuration reactions are important examples of metal hydrogen exchange and they represent a particularly good way of introducing a metal into an aromatic molecule [1]. The most feasible way for mercuration is the direct method in which a hydrogen atom of benzene, a polynuclear hydrocarbon, or a heterocyclic compound is replaced by a mercury acid group, the most common one being the acetoxymercury group, Hg-O-CO-CH_3. This group is usually introduced by heating the hydrocarbon with mercuric acetate, or with the equivalent molar ratio of mercuric oxide in glacial acetic acid. Thus the reaction of benzene with mercuric acetate in acetic acid at elevated temperature gives phenylmercuric acetate in good yield (Scheme 1).

$$C_6H_6 + Hg(OAc)_2 \rightarrow C_6H_5 - Hg - OAc + HOAc$$

Mechanism :

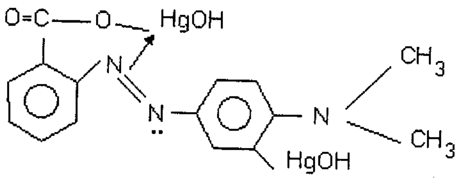


Scheme 1

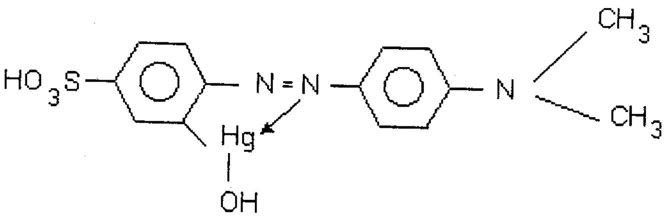
The reaction is known to undergo electrophilic substitutions with considerably more ease than benzene.

A number of direct metallation of azobenzene have been described[2,3] and in all cases metallation occurs in the ortho position presumably by coordination of the metal to an azonitrogen and subsequent substitution of aromatic hydrogen. Mercuration of methyl red and methyl orange with mercuric acetate where the reactants are used in equimolar ratio gave rise to the formation of the corresponding dimercurial complex (A) in case of methyl red. Whereas, in case of using methyl orange, the corresponding mono-and dimercurial complexes (B) and (C) were obtained[4,5,6].

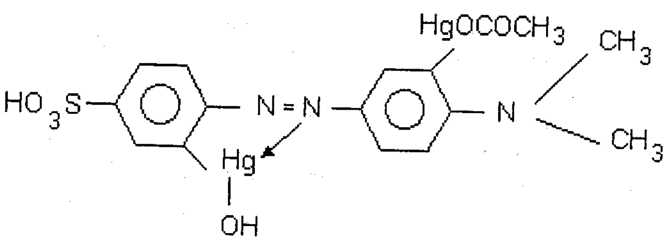
The product of mercuration reaction can be used as an intermediate in the synthesis of the other organometallics. There have been also two indirect ortho metallations of azobenzene reported in literature[3,7]. The mercurials react readily with halogens to produce haloazobenzene easily and in high yields, which in turn can be converted to other derivatives[8,9].



(A)



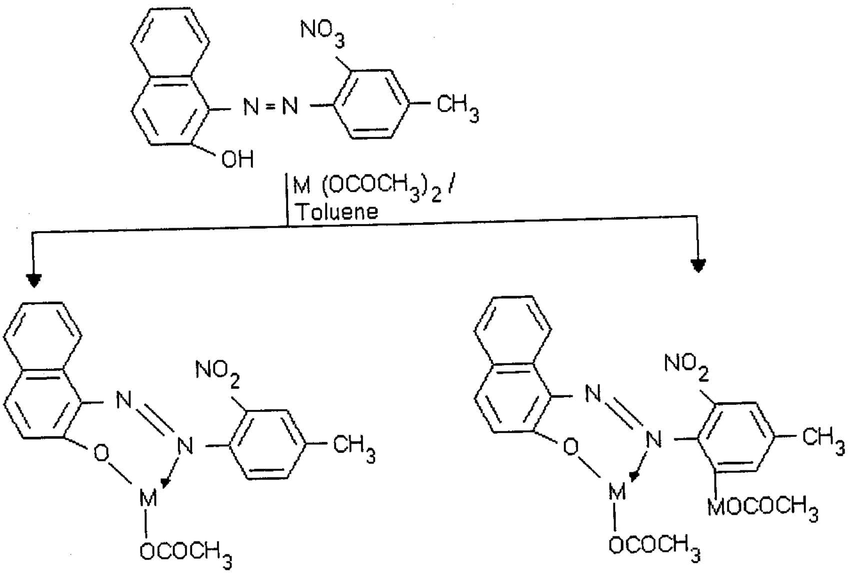
(B)



(C)

2. RESULTS AND DISCUSSION

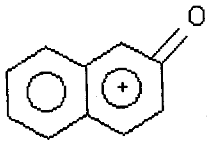
In continuation of our previous work on metallation[10,11] the present work deats with the reaction of Toluidine Red with some metal ions such as : Hg^{+2}, Cu^{+2}, Co^{+2} and Ni^{+2} in presence of toluene and acetic acid to give the following products (Scheme 2.):



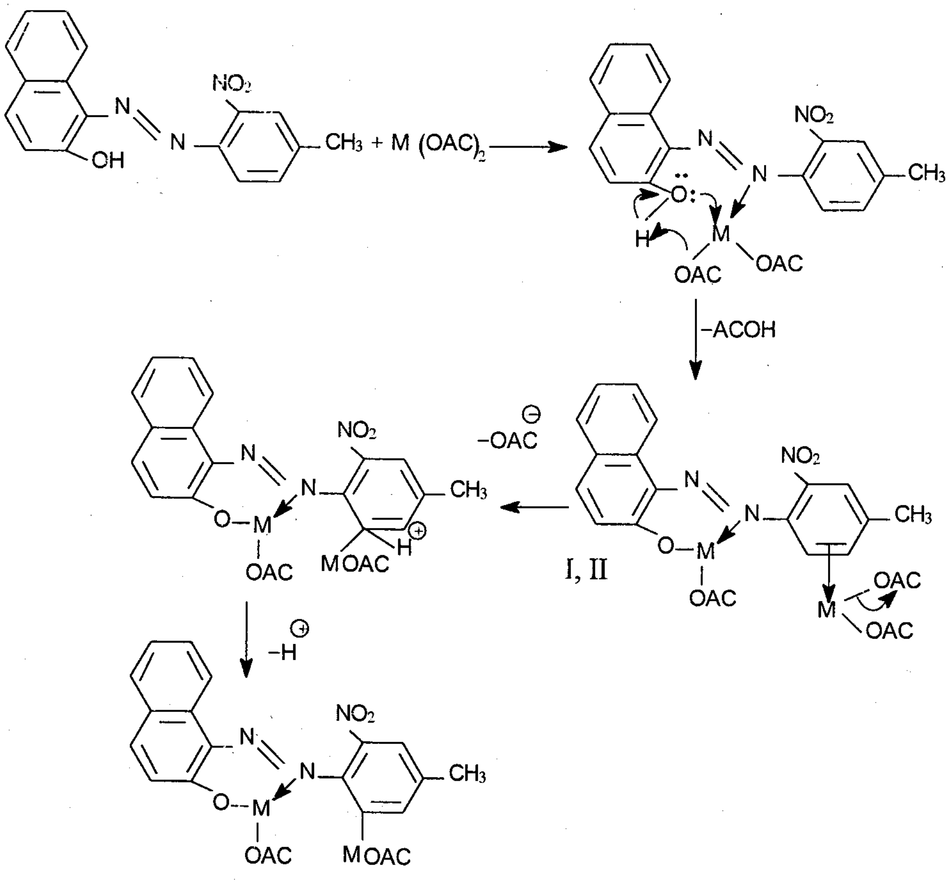
I, M = Hg^{+2} 85%   III, M = CO^{+2} 81%
II, M = Cu^{+2} 88%   IV, M = Ni^{+2} 80.5%

Scheme 2.

The reaction of Toluidine Red with mercuric acetate in toluene afforded compound I. The reaction pathway may be proceed via coordination of mercury with azonitrogen followed by removal of acetic acid molecule through nucleophilic attack by naphthyl – OH at the nitrogen – coordinated metal to afford mono – mercurated compound I. Its structure was confirmed by elemental analysis, IR, UV and MS spectra. The IR spectrum showed new absorpation bands at 1750 cm^{-1} and 480 cm^{-1} due to $\nu_{C=O}$ and ν_{O-Hg}, respectively. Its UV spectrum showed λ_{max} at 221 nm ($\in = 2\times10^{4}$), 229 nm ($\in = 2.2\times10^{4}$) and 500 nm ($\in = 4\times10^{4}$). The MS spectrum does not show the molecular ion peak at m/z =565. The base peak is at m/z=143 (100%) which can be attributed to :



The suggested mechanism may be as depicted in the following Scheme 3 :



I, II

III, IV

Scheme 3

The reaction of Toluidine Red with copper acetate gave also a monometallated product II via the same mechanism as suggested for compound I. The data obtained from elemental analysis, IR, UV, X-ray and MS spectra are consistent with the proposed structure. Thus, the IR spectrum shows new absorption bands at 1710 cm^{-1} , and 460 cm^{-1} which attributed to $\nu_{C=O}$ and ν_{O-Cu}, respectively. In addition, the [dA°] values and relative intensities [I/I°] of X-ray pattern for the Toluidine Red with copper acetate illustrated in Table 1.

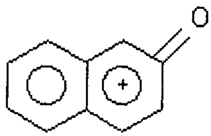
Table 1. X-Ray diffraction data of Toluidine Red with copper acetate

Toluidine Red		**Copper Acetate**		**Product**	
dA°	**I / I°**	**dA°**	**I / I°**	**dA°**	**I / I°**
10.0	30	6.9	100	10.5	35
7.97	100	6.33	35	8.19	100
6.5	25	5.87	25	6.91	45
5.8	12	5.75	16	6.70	25
5.3	5	4.3	2	5.40	14
4.7	7	4.05	2	5.09	12
4.2	3	3.58	12	4.48	6
3.83	9	3.45	4	4.19	3
3.67	5	3.35	4	3.86	8
3.40	40	3.29	4	3.70	11
3.17	3	2.96	2	3.45	30
2.3	<1	2.87	2	3.14	5
2.05	5	2.68	2	2.44	<1
1.6	<1	2.54	4	2.28	2
		2.51	2	2.19	<1
		2.39	4	2.4	4
		2.33	8	2.014	3
		2.22	4	1.77	2
		2.03	2	1.67	<1
		1.97	<1	1.63	<1
		1.92	2	1.45	2
		1.87	2	1.38	<1
		1.83	2	1.23	2
		1.75	<1		
		1.69	2		
		1.66	<1		
		1.63	<1		
		1.45	<1		

Thus, the x-ray diffraction (XRD) data for Toluidine Red and copper acetate indicate that the new peaks for toluidine red appear at d=7.97, 6.5, 3.67 and 3.4 A°, while for copper acetate the main peaks appear at d=6.9, 6.33, 5.75, 3.58, 3.45, 3.35, 2.4, 1.92, 1.83 and 1.75 A°. For Toluidine Red with copper acetate (1:1 molar ratio), XRD shows new peaks at d= 10.5, 8.19, 5.40, 5.09, 4.48, 3.86, 3.70, 3.14, 2.44, 2.28, 2.19, 2.014, 1.77, 1.63, 1.45, 1.38 and 1.24 A°.

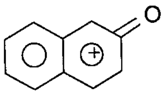
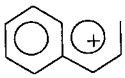
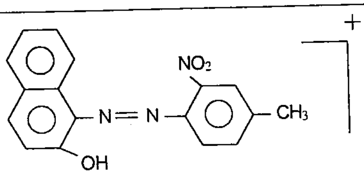
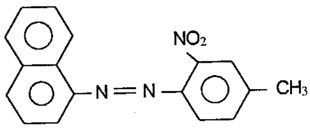
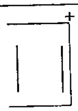
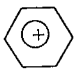
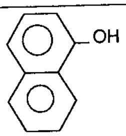
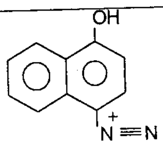
These results prove the formation of a complex between these two reactants.

The reactions of Toluidine Red with cobalt acetate and nickel acetate under the same conditions gave a dimetallated compounds III and IV, respectively. Elemental analyses were in good agrement with the proposed structures. IR spectrum for compound III showed new absorption bands for $\nu_{C\text{-}Co}$, $\nu_{O\text{-}Co}$ and $\nu_{C=O}$ at 470 cm^{-1}, 455 cm^{-1} and 1756 cm^{-1}, respectively. Its UV spectrum showed λ_{max} at 501 nm ($\in = 1.5\times10^4$), λ_{max} at 299 nm ($\in = 9.2\times10^3$) and λ_{max} at 217 nm ($\in = 6.7\times10^3$). However, for compound IV its IR spectrum showed $\nu_{O\text{-}Ni}$, $\nu_{C\text{-}Ni}$ and two $\nu_{C=O}$ at 450 cm^{-1}, 480 cm^{-1}, 1710 cm^{-1} and 1720 cm^{-1}, respectively. The MS spectrum of compound III does not show the molecular ion peak at m/z 565.6 the base peak is at m/z 143 (100%) which can be attributed to:



The UV spectrum of structure IV indicates, λ_{max} at 501 nm ($\in = 3.7\times10^4$) λ_{max} 299 nm ($\in = 2.2\times10^4$) and λ_{max} at 214 nm ($\in = 1.5\times10^4$). The results of the fragmentation pattern of the MS spectra of the newly synthesied metallated compounds are summarized in Table 2.

Table 2. Fragmentation features of the mass spectra for metallated Toluidine Red compounds.

m/z	Fragment	M^{+2} %		
		Hg^{+2}	Cu^{+2}	Co^{+2}, Ni^{+2}
143		100	100	100
115		55.2	47.0	50.0
307		39.2	40.8	40.7
290		28.4	27.1	27.2
51		13.8	16.0	13.2
77		13.5	13.1	11.5
144		84.0	11.1	11.4
171		21.0	21.4	21.4

3. EXPERIMENTAL

Analysis were carried out in the Microanalytical Lab., National Research Centre, Dokki, Giza, and Microanalytical Lab., Cairo University, Giza. The infrared spectra were measured on perkin Elemer 1430 Infrared spectrometer using KBr wafer technique. The UV/vis spectra were measured on a perkin Elmer $\lambda_{4\beta}$ and $\lambda_{3\beta}$ UV spectrophotometer. The mass spectra were measured on Mass spectrometer MAT 112 Electron Impact Ionization 70 ev under vacuum 10^{-6} Torr, Karlsruhe University, Germany. X-Ray diffraction was measured on (philips type PW 1390) diffractometer using Ni-filtered $Cu-K_{\alpha}$ radiation with the type operated at 40 kv and 25 mA, and the patterns were scanned between 5° and 90° 2θ at 1° 2θ /min.

4. GENERAL PROCEDURE

A mixture of metal acetate (1 mol), Toluidine Red (1 mol) in toluene and few drops of acetic acid was refluxed while stirring for 3 hours. The reaction mixture was left overnight at room temperature and the precipitate that formed was filtered off, dried and recrystallized from ethanol-ether mixture (Table 3);
Table 4. Shows IR data for all the new products.

Table 3.

Cempound No.	Mol.Formula/ Mol.Wt	m.p.°c	Yield %	Analysis calcd./Found			
				%C	%H	%N	%Metal
I	$C_{19}H_{15}O_5N_3Hg$ (565.6)	260	85	40.3 40.7	2.7 3.0	7.4 7.0	35.5 35.9
II	$C_{19}H_{15}O_5N_3Cu$ 428.54	250	88	53.2 52.8	3.5 3.9	9.8 9.2	14.7 15
III	$C_{21}H_{18}O_7N_3Co_2$ 541.88	110	81	46.5 46.8	3.3 3.3	7.7 7	21.8 22.1
IV	$C_{21}H_{18}O_7N_3Ni_2$ 541.50	190	80.5	46.5 46.2	3.3 3.5	7.8 7.2	21 20.6

IR data of metal salts

Table 4.

Metal Salt	IR	
	$\nu_{C=O}$	ν_{O-M^*}
Mercuric acetate	1750 cm^{-1}	480 cm^{-1}
Cupper acetate	1710 cm^{-1}	460 cm^{-1}
Cobalt acetate	1756 cm^{-1}	455 cm^{-1}
Nickel acetate	1710, 1720 cm^{-1}	450 cm^{-1}

M^* : Hg^{+2}, Cu^{+2}, Co^{+2} and Ni^{+2} respectively

5. THE BIOLOGLOGICAL ACTIVITY

Ayad et al, and El-Gindy reported that copper sulphate as a molluscicide against different embryonic stages of snial vectors of bilharziasis in Egypt. The aim of this work is to synthesis a new metallated compounds of expected activity on snail vectors of schistosomiasis. The effect of Toluidine Red metallated compounds as Killing agents for snail vectors of Schistosomiasis without affecting the surrounding environment was investigated. It has been found that the results of Toluidine Red against B. alexandrina as a principal material had no mortality rate even when used in 2000 ppm concentrations. Whereas when the metallated Toluidine Red compounds I-IV were subjected for testing on snails showed noticeable mortality rate (L_{C50}, L_{C90}) ascited in table (4). The most toxic effect of metals are the copper repesented by (L_{C50}=18 ppm), when compared by Nickel (L_{C90}=360 ppm).

Table 5. L_{C50} and L_{C90} values for adult B alexandrina after 24 hours exposure.

Compound	Mortality rate	
	L_{C50} (ppm)	L_{C90} (ppm)
I	40	120
II	18	65
III	80	110
IV	360	510

* L_{C50} : leathal concentration that killed 50% of the total snails
* L_{C90} : leathal concentration that killed 90% of the total snails

REFERENCES

[1] Kitching, W., Organometal. Chem. Rev. 1968, **3**,35.
[2] Parshall, G.W., Acc. Chem. Res. 1970, **3**,139.
[3] Cross, R.J., Tennent, N.H., Organometal. Chem. Rev. 1973, **61**,33.
[4] El-Sawi, E.A., Hassan, H.A., El-Deak, M., J. Ind. Chem. Soc. 1981, **58**,831.
[5] Ramadan, A.T., Abdel-Rahman, R.M., Seada, M.H., Asian J. Chem. 1992, **4**,569.
[6] Awad, A.I., Abdel Monem, M.A., J. Chem. Technol. Biotechnol. 1992, **55**,333.
[7] Astyn Yuk, Y.A., Barinov, V., Sirotkina, E.I., Akad. Nauk. SSSR, 1969, **187**, C.A., **71**, 70721, 1969.
[8] Roling, P.V., J. Org. Chem., 1975, **40**, 2421.
[9] Al-Rubaie, A.Z., Al-Salim, N.I., Al-Jadaan, A.N., J. Org. Chem., 1993, **443(2)**,67.
[10] El-Sawi, E.A., Mostafa, T.B., El-Sayed, I.Kh., Ahmed, S.M., Commun. Fac. Sci. Univ. Ankara Ser. B, 1997, Vol.**43**, 33.
[11] El-Sawi, E.A., Mostafa, T.B., Mostafa, B.B., J. Egypt. Soc. Parasitol., 1998, **28(2)**, 481.