

Action of Some Transition Metal Salts on Methyl Orange

E.A.EL-SAWI *, T.B.MOSTAFA AND I.KH.EL-SAYED
 Chemistry Department
 University College for Women Ain Shams University
 Heliopolis, Cairo Egypt

(Received 20th November, 2002, revised 4th November, 2003)

Summary: Methyl orange reacts with some salts of transition metals such as Ni(II), Cu(II) and Co(II) in non polar solvent to give different metalated products through N=N and C-N bond cleavage. Their structures are confirmed by chemical analysis and some spectroscopic (IR, UV/Vis, MS and X-ray) methods.

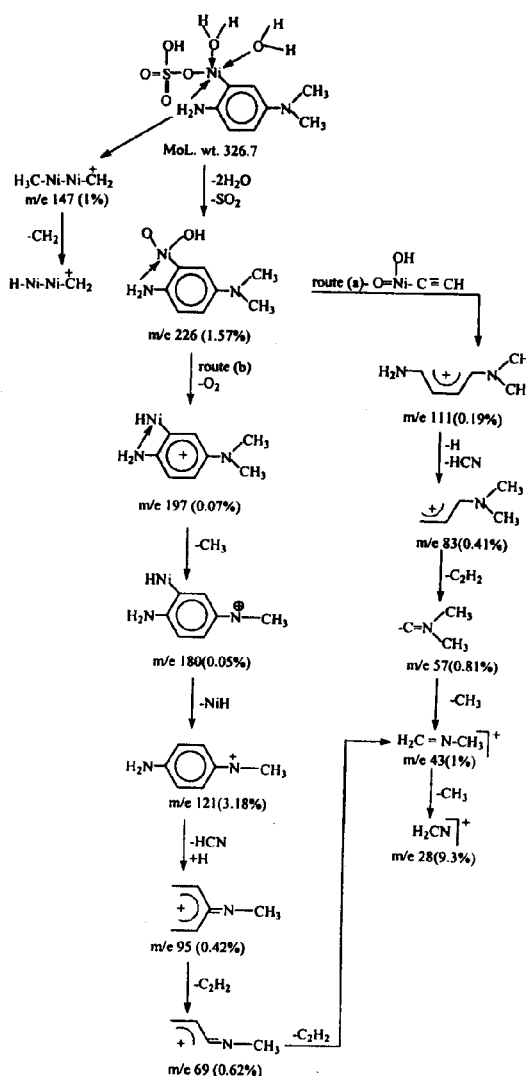
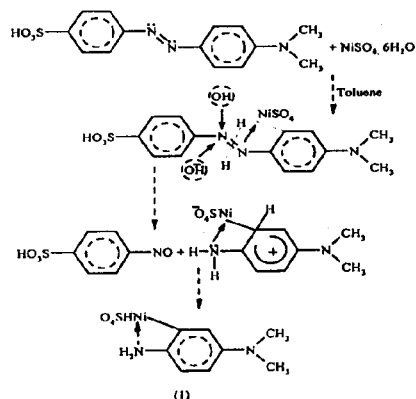
Introduction

Many earlier studies have been reported on the reaction of azobenzene especially azo-dyes with transition metal ions [1-2].

Labile cobalt complexes were suggested as intermediates in carbonylation of azobenzene by cobalt carbonyl [3] stable azobenzene complexes of nickel [4] palladium and platinum [5] were reported and contain the ligand bonded to the metal through nitrogen lone-pair and carbon-metal σ -bond [6-9]. Direct reaction of metal carbonyl with azobenzene gave rise to metallated product involving coordination of nitrogen and formation of five-membered ring with a metal-carbon σ -bond [10].

Results and Discussion

Methyl-orange reacts with nickel sulphate in non polar solvent (toluene) by heating under reflux to give nickelated product (I). Its structure is confirmed by the analytical data, the presence of ionisable sulphur as HSO_4^- and the azo-dye formation. The reaction may take place as follows:



*To whom all correspondence should be addressed.

Elemental analysis, IR, UV/Vis, X-ray and MS spectra are in good agreement with the suggested structure, the IR spectrum of compound 1 shows ν C-Ni at 480 cm^{-1} [8,11], ν SO₄ at $1130\text{-}1080\text{ cm}^{-1}$ and ν OH of SO₃H at $3400\text{-}3180\text{ cm}^{-1}$. The mass spectrum did not show the molecular ion peak (c.f. Fig.1): The compound is fragmented according to the following scheme (scheme 1):

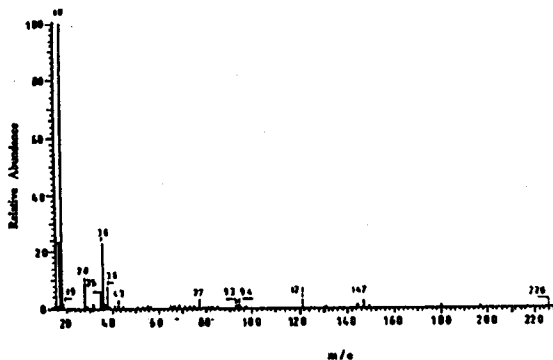


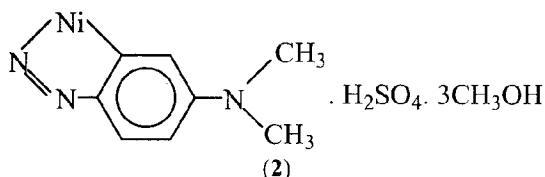
Fig. 1: Mass Spectrum of compound (1)

The x-ray diffraction of product (1) shows the two principle peaks for methyl-orange but with different intensity. Also, the peaks of nickel sulphate disappeared completely and two new peaks have been appeared at $2\theta=32^\circ$ and $2\theta=25.6^\circ$.

Table (1): X-ray Diffraction Pattern of Product (1).

X-ray Line NO.	Methyl-orange		Nickel Sulphate		Methyl orange \pm NiSO ₄	
	2θ	100%	2θ	100%	2θ	100%
1	5.1	51.1	19.3	91.9	13.1	53.2
2	14.4	45.8	97.9	97.6	25.3	32.6
3	20.4	43.2	26.0	96.0	31.6	100
4	31.6	100	30.2	65.0	32.7	33.2
5	45.3	74	42.6	100	45.4	50.0

In boiling methanol, nickel sulphate reacts with methyl- orange to give product (2).



The reaction took place through ArC-N bond cleavage, coordination of Ni to N, subsequent

substitution and five membered ring formation. The structure is confirmed by analytical data, IR and UV spectra. The IR spectrum shows ν C-Ni at 480 cm^{-1} , ν N-Ni at 450 cm^{-1} [8-11], ν N=N at 1575 cm^{-1} , and ν OH at $3800\text{-}3650\text{ cm}^{-1}$. The UV spectrum of compound (2) shows the following bands due to π - π^* , n- π^* and charge transfer transitions with their molar absorptivities.

$$\lambda_{\text{max}} = 200\text{nm. (shoulder)} \quad (\epsilon = 1.23 \times 10^4)$$

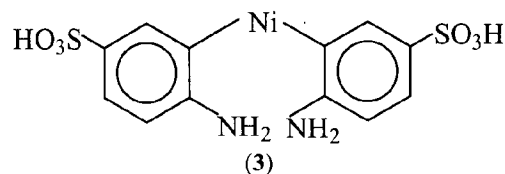
$$\lambda_{\text{max}} = 212\text{ nm.} \quad (\epsilon = 1.3 \times 10^4)$$

$$\lambda_{\text{max}} = 273\text{ nm} \quad (\epsilon = 4.95 \times 10^3)$$

$$\lambda_{\text{max}} = 350\text{ nm. (shoulder)} \quad (\epsilon = 4.7 \times 10^4)$$

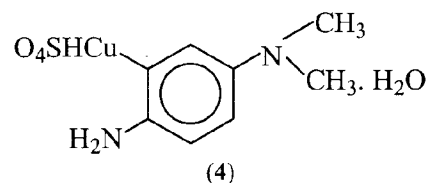
$$\text{and } \lambda_{\text{max}} = 445\text{ nm.} \quad (\epsilon = 1.4 \times 10^4)$$

Methyl orange reacts with nickel acetate in toluene under reflux to give product (3).

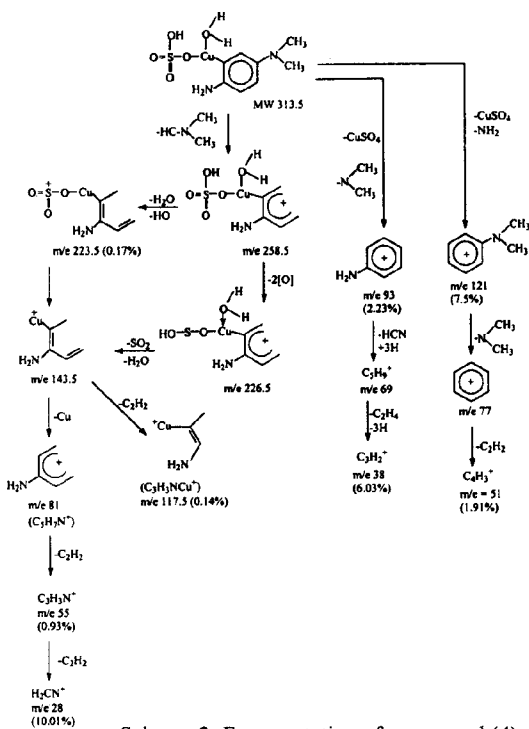


The product (3) is produced through metallation in the ortho position followed by N=N bond cleavage. The proposed structure is confirmed by analytical data, IR, UV spectra and azo-dye formation. The IR spectrum shows new absorption bands for NH₂ and C-Ni vibrations at $3530\text{-}3200\text{ cm}^{-1}$, respectively.

Metallation of methyl-orange with copper sulphate in non-polar solvent (toluene) under reflux gives the metallated product (4)

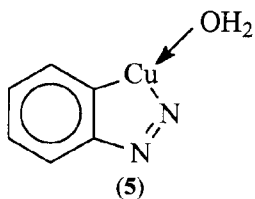


The structure is confirmed by elemental analysis. The IR spectrum shows ν C-Cu [11-12] at 460 cm^{-1} , NH₂ at $3530\text{-}3200\text{ cm}^{-1}$ (two bands), and azo-dye formation. The mass spectrum also confirmed the proposed structure where it does not show the molecular ion peak. The fragmentation takes place as follow:

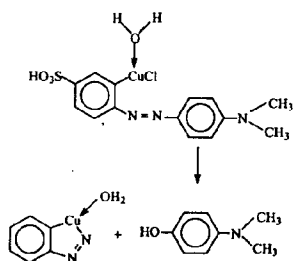


Scheme 2: Fragmentation of compound (4)

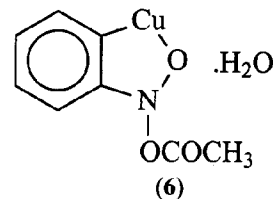
On the other hand, when methyl-orange is metallated by copper chloride in toluene metallated product (5) is produced through coordination, Ar-N bond cleavage followed by electrophilic substitution and accordingly cyclization and finally desulphonation.



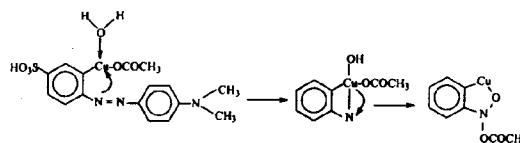
The reaction may proceed as follow:



Carring the reaction of copper acetate with methyl -orange in polar and non-polar solvents gives product (6).

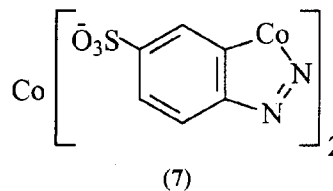


The structure is confirmed by elemental analysis, IR and UV spectra. The product is formed through coordination of copper to azo- nitrogen, N=N bond cleavage, ortho-substitution and desulphonation.



The IR spectrum shows new absorption band for C-Cu bond and absence of N=N bond.

Cobalt sulphate reacts with methyl orange (1: 1 molar ratio) in toluene at boiling point to give product (7) where ortho-metallation, cleavage, cyclization and salt formation through sulphonate group takes place.



All the data are in good agreement with the proposed structure. The IR spectrum shows new absorption band for C-Co at 470 cm⁻¹ and N=N absorption band at 1575 cm⁻¹.

UV/Vis spectrum shows :

$$\lambda_{\text{max}} \text{ at } 217 \text{ nm} \quad (\epsilon = 3.5 \times 10^3)$$

$$\lambda_{\text{max}} \text{ at } 250 \text{ nm (shoulder)} \quad (\epsilon = 1.3 \times 10^3)$$

$$\lambda_{\text{max}} \text{ at } 300 \text{ nm} \quad (\epsilon = 7.1 \times 10^2)$$

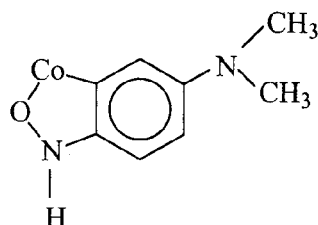
Table (2): Elemental Analysis and Some Physical Properties of Metallated Products.

Compound No	Empirical formula	Colour	Yield (%)	M.P.C	Elemental analysis				%Calculated.			
					%Found				%Calculated.			
					C	H	N	M	C	H	N	M
(1)	C ₁₂ H ₁₂ O ₁₄ N ₂ S Ni	Dark-brown	69.00	260(d)	33.30	4.17	9.72	19.60	33.20	4.15	9.68	20.20
(2)	C ₁₂ H ₈ N ₂ Ni. H ₂ SO ₄ . 3CH ₃ OH	Reddish-brown	87.50	164-166	32.30	6.00	10.50	14.26	33.02	5.75	10.50	14.70
(3)	C ₁₂ H ₁₂ O ₁₄ N ₂ S ₂ . Ni. 5H ₂ O	Reddish-brown	91.30	180(d)	28.50	4.00	5.40	11.80	29.22	4.50	5.68	11.90
(4)	C ₁₂ H ₁₂ O ₁₄ N ₂ SCu.H ₂ O	Pale-brown	95.00	314-315	30.45	4.35	8.78	20.05	30.60	4.46	8.93	20.25
(5)	C ₁₂ H ₁₂ N ₂ Cu.H ₂ O.2HCl	Dark-brown	97.27	173-174	29.50	3.15	11.50	25.35	29.00	3.22	11.29	25.40
(6)	C ₁₂ H ₁₂ O ₁₄ N ₂ Cu.H ₂ O	Deep-brown	95.33	185-186	39.50	3.70	5.60	25.34	38.95	3.65	5.68	25.72
(7)	C ₁₂ H ₁₂ O ₁₄ N ₂ S ₂ Co ₂ .12H ₂ O	Reddish-brown	61.65	230(d)	18.40	4.10	6.90	22.00	18.12	4.20	7.04	22.23
(8)	C ₁₂ H ₁₀ ON ₂ Co.2HCl.5H ₂ O	Dark-brown	94.00	197-198	25.58	5.32	7.20	15.70	25.81	5.90	7.52	15.85
(9)	C ₁₂ H ₁₀ N ₂ SCo.CH ₃ COOH.3H ₂ O	Reddish-brown	78.39	160-162	26.70	4.00	8.10	16.45	26.89	3.90	8.80	16.52

λ_{\max} at 390 nm ($\epsilon = 8.6 \times 10^2$)

λ_{\max} at 480 nm ($\epsilon = 2.2 \times 10^3$)

Due to $\pi-\pi^*$, $n-\pi^*$ and charge transfer transitions.

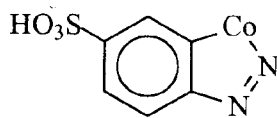


(8)

The reaction of methyl orange with cobalt chloride in toluene under reflux gives compound (8).

All the data obtained confirmed the proposed structure. The IR spectrum shows new absorption band for C-Co at 470 cm^{-1} and the disappearance of N=N bond.

On metallation of methyl orange with cobalt acetate in toluene gives rise to metallated product (9).



(9)

The proposed structure is confirmed by analytical data, IR, the UV Nis spectra show $\lambda_{\max} = 215 \text{ nm}$ ($\epsilon = 1.5 \times 10^5$) and $\lambda_{\max} = 200 \text{ nm}$ ($\epsilon = 1.1 \times 10^4$).

Experimental

Analysis were carried out in the micro-analytical lab., national research center. Dokki, Cairo and Microanalytical Lab., Cairo University, Giza.

The infrared spectra were measured on Perkin-Elmer 1430 infrared spectrometer using KBr wafer technique.

The NMR spectra were measured on EM 390 on varian. MAT711 spectrophotometer. The UV/Vis spectra were measured on a Perkin Elmer λ 4B and λ 3B UV/Vis spectrophotometer.

The mass spectra were measured on mass spectrometer MAT112 Electron Impact Ionization 70 ev under vacuum 10^{-6} Torr. Karlsruhe University Germany.

X-ray diffraction method (Philips Type Pw 1730.) diffractometer was used with Ni-filtered Cu-K α radiation with the type operated at 36 KV and 16mA and the patterns were scanned between 5° and $90^\circ 2\theta$ at $1^\circ 20/\text{min}$.

General Procedure

A mixture of methyl orange (1 mole), metal salt in toluene or methanol and few drops of acetic acid were refluxed with stirring for five hours. The reaction mixture was left to stand overnight and the precipitate formed was filtered off, dried and recrystallized from methanol-ether mixture (table 2).

References

1. E.A. El-Sawi, H.A. Hassan and M. El-Deek, *J. Ind. Chem. Soc.*, **58**, 831 (1981).
2. P.V. Rolling, D.D. Kirt, J.T. Dill, S. Hall and C. Homstrom, *J. Org. Met. Chem.*, **116**, 39 (1976).
3. S. Murahashi and S. Horiie, *J. Am. Chem. Soc.*, **77**, 6403 (1955); **78**, 4816 (1956).
4. J.P. Kleiman and M. Dubeck, *J. Am. Chem. Soc.*, **85**, 1544 (1963).
5. A.C. Cope and R.W. Sickman, *J. Am. Chem. Soc.*, **87**, 3272 (1965).
6. K.K. Yang and R.G. Bergmo, *Org. Met.*, **4**, 129 (1985).

7. L. Carollo, and B. Floris, *J.Org. Met. Chem.*, **583**, 80 (1999).
8. M.Tschinke, R.E. Bachman, F.P. Gabbai, *J. Org. Met. Chem.*, **582**, 40 (1999).
9. W.A. Chupka and E. Lindholen, *Arkiv Fysik*, **25**, 349 (1963); *Chem. Abs.*, **62**, 3562 (1965).
10. R.F. Heck, *J. Am. Chem. Soc.*, **90**, 313 (1968).
11. F. Brezina, Z. Sinddar and K. Pastonk, *Fac. Rerum Nat.*, **88**, 9, 1987; *Chem. Abst.*, **109**, 103523 w (1988).
12. M.I. Defrulos, M.D. Alonos, M.P. Gomez, A. Molinero and A. Doadriolopez, *An. Quim. Ser. B*, **83**, 281 (1987); *Chem. Abst.* **108**, 179010b (1988).