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Synthesis, characterization and electrical conductivity properties of homo- and hetero-di and trimetallic complexes of mixed azo dyes

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The synthesis of seven new complexes of mixed ligands and metals are reported. Their stoichiometries (metals:ligands) were found to be 1:3, 2:2 and 3:2 corresponding to FeL_12L_2H, $M_2L_1L_2$ and $M'M_2L_1L_2$, respectively (where $M' = Cu^{2+}$, $M = Cu^{2+}$, Co^{2+} or Ni^{2+}; HL_1 = Methyl Red; H_2L_2 = Alizarin Yellow R). The complexes were characterized by elemental analysis, infrared and Nujol mull electronic spectra and magnetic moment measurements. The results of the electrical conductivity studies for the prepared complexes in the solid state (using compressed tablets) indicated reasonable semiconducting properties. The magnitude of these values, $\log \sigma_{291}$ lay between -5.46 and -8.67, resulting from the structure and nature of the substituent of the two mixed ligands as well as the high metallic content of their complexes.

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1. Introduction

The two azo compounds: Methyl Red, 2[4-(dimethylamino)phenyl azo]benzoic acid (HL_1) and Alizarin Yellow R, sodium *p*-nitrobenzene azo salicylate, or its acidic form (H_2L_2), are widely used as pH indicators [1]. In fact, they have been the subject of interest in many research areas, including the study of their analytical applications [2, 3], acid–base and spectral properties [4], biological activity [5, 6] and dyeing properties as metal free compounds [7].

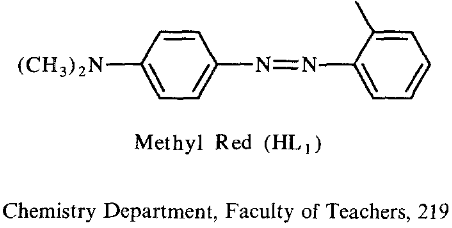
Regarding the industrial importance of the metallized azo dyes relative to their structures, they can be classified into two main types: those in which the azo group participates in the coordination to the metal ion and formation of the chelate ring (medially metallized type) and those in which it is not (terminally metallized type) [8, 9]. Methyl Red represents the former type, being the most important one commercially, while Alizarin Yellow R represents the latter type, and is of less importance, although their metal complexes are generally brighter in hue than those in which the azo group is a ligand [10]. Moreover, Alizarin Yellow R is one of the oldest dyes, used for chromium complex formation on wool [9]. From this standpoint the present paper deals with the synthesis and structural characterization of metal chelates of the two ligands (Methyl Red and Alizarin Yellow R) mixed *in situ*, as well as attempts to isolate their homo- and hetero-dimetallic complexes. Electrical conductivity measurements appeared desirable in order to support characterization.

2. Experimental procedure

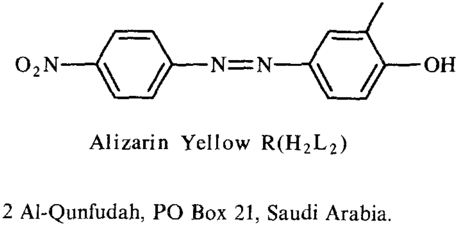
All the reagents used, Methyl Red, Alizarin Yellow R, transition metal chlorides and solvents, were of analytical grade and were used without further purification.

2.1. Preparation of mixed-ligand complexes

A solution of Methyl Red (2.5 mM) in 75 ml hot ethanol was mixed with a solution of Alizarin Yellow R (2.5 mM) in 100 ml hot water-ethanol mixture (75% v/v). To this solution was added a warmed solution of the appropriate metal salt: $FeCl_3$ (2.5 mM in 10 ml water), $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ (2.5 mM in 10 ml water + 2.5 ml of ammonia 25%). The solvent was partially evaporated on a hot plate at 110 °C, whereupon the complexes precipitated. They were filtered off, washed with a little ethanol and dried *in vacuo* over P_4O_{10}.



Methyl Red (HL_1)



Alizarin Yellow R(H_2L_2)

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2.2. Preparation of homo- and heterodimetallic complexes $M'M_2L_1L_2$

Typically, an ammoniacal solution of $CuCl_2 \cdot 2H_2O$ (2.5 mM in 10 ml water + 2.5 ml of ammonia 25%) was added to the solution described above resulting from mixing of the metal salt ($M = Cu^{2+}$, Co^{2+} or Ni^{2+}), Methyl Red and Alizarin Yellow R in the molar ratio of 1:1:1. The complexes, with their bright shades were precipitated during the concentration of the solution mixture gently at 110 °C on a hot plate for about 3 h. They were separated by filtration, washed and dried as described above.

2.3. Physical measurements

The chemical analysis for C, H and N, and metals were carried out in the Microanalytical Unit, Chemistry Department, Faculty of Science, Cairo University. Atomic absorption spectrophotometry was used for the determination of metals. Infrared spectra were recorded on a Perkin-Elmer Spectrophotometer model 1430 covering the frequency range of 4000–200 cm^{-1} in KBr discs. Nujol mull electronic spectra [11] of the complexes were measured using a Perkin-Elmer Spectrophotometer Model Lambada 4B in the range 190–900 nm. The magnetic moments were obtained by Gouy measurements on powdered complexes, $Hg[Co(CNS)_4]$ was used as standard; diamagnetic corrections were made employing Pascal's constant. For electrical conductivity measurements, samples were prepared in the form of tablets of 0.1–0.2 cm thickness at a pressure of 5 tons cm^{-2}. All details regarding the instruments and techniques used have been described previously [12]. The conductivity of the samples was obtained using the general equation:

$$\sigma = \frac{Id}{V_c a}$$

where I is the current in A and V_c is the potential drop across the sample of cross-sectional area, a, in cm^2 and thickness d in cm.

3. Results and discussion

The results of microchemical analysis, colours, compositions, Nujol mull electronic spectra and magnetic moments of the isolated complexes are collected in Table I.

3.1. Infrared spectra and mode of bonding

The study of the infrared spectra of the synthesized complexes, the organic mixed ligands, Methyl Red (HL_1) and Alizarin Yellow R (H_2L_2) provided important information about the mode of bonding to the central metal ion. Table II gives the fundamental frequency bands (cm^{-1}) along with their assignments. The following could be deduced:

1. The complexes showed broad strong bands in the 3438–3350 cm^{-1} region, this was in agreement with the results of analysis that water molecules were present [13].
2. The two strong bands assigned to ν(C = O) of the carboxylic group of both HL_1 and H_2L_2 ligands at 1725 and 1672 cm^{-1}, respectively, were replaced by medium–strong bands lying between 1520–1510 and 1439–1419 cm^{-1} due to the asymmetrical and symmetrical stretching modes of the carboxylic groups in the spectra of their chelates [14]. Moreover, the bands due to COO^{-1} scissors and COO^- wagging [15] were slightly shifted to 898–857 and 646–633 cm^{-1}, respectively. Such behaviour was indicative of the participation of carboxylic oxygen in chelation.
3. Careful examination of the -OH phenolic vibrational modes δ(OH), ν(C–OH) and γ(OH) for H_2L_2, located at 1344, 1244 and 857 cm^{-1}, respectively, in comparison with their position in chelates located at 1341–1335, 1263–1254 and at 858–836 cm^{-1}, respectively, clearly indicated binding to the incorporated metal ions [16, 17].
4. The bands which appeared at 1465 and 1482 cm^{-1} in the spectra of the ligands HL_1 and H_2L_2 were assigned to the symmetrical stretching vibration of the azo group [18]. The first band shifted considerably to lie between 1452 and 1447 cm^{-1} in the spectra of their

TABLE I Colours, analysis, Nujol mull electronic spectra and magnetic moments of the complexes

Complex no.	Composition	Colour	Found (Calcd.) (%)					μ_{eff} at 298 K (B.M.)	λ_{max} (nm)
			C	H	N	M			
I	$[FeL_1 \cdot 2HL_2]$	Reddish brown	54.4 (54.9)	3.7 (3.3)	14.7 (14.1)	6.3 (6.2)		5.54	400br, 485br, 600sh
II	$[Co_2L_1L_2 \cdot 3NH_3 \cdot 2H_2O(OH)] \cdot 2H_2O$	Pale brown	41.0 (41.4)	4.4 (4.8)	15.0 (15.5)	14.6 (14.5)		5.21	285br, 443br, 585sh
III	$[Ni_2L_1L_2 \cdot 3NH_3(OH)]$	Dark brown	45.8 (45.5)	4.3 (4.2)	17.7 (17.7)	15.2 (15.9)		2.87	485br, 583sh
IV	$[Cu_2L_1L_2 \cdot 3NH_3(OH)] \cdot 4H_2O$	Brownish black	40.8 (41.0)	4.3 (4.7)	15.1 (15.4)	15.4 (15.5)		0.43	216br, 312br, 479br
V	$[Cu_3L_1L_2 \cdot 4NH_3 \cdot 4H_2O(OH)_3] \cdot H_2O$	Pale brown	35.8 (35.3)	4.0 (4.6)	15.3 (14.7)	19.5 (20.0)		1.78	479br
VI	$[CuCo_2L_1L_2 \cdot NH_3 \cdot 4H_2O(OH)_3] \cdot 2H_2O$	Pale brown	36.8 (36.9)	4.4 (4.1)	11.0 (10.8)	13.1 (12.9)	7.2[a] (7.0)	5.18	213br, 316br, 465br
VII	$[CuNi_2L_1L_2 \cdot NH_3 \cdot 4H_2O(OH)_3] \cdot 2H_2O$	Brown	36.6 (36.9)	3.7 (4.1)	11.1 (10.8)	12.0 (12.9)	7.5[a] (7.0)	2.96	486br

HL_1 = Methyl Red; H_2L_2 = Alizarine Yellow R; [a]Copper analysis.

TABLE II Important infrared bands (cm^{-1}) of the ligands and their metal complexes

Ligands		Complexes							
(HL_1)	(H_2L_2)	I	II	III	IV	V	VI	VII	Assignments
3412br	3414br	–	–	–	–	–	–	–	ν (OH)
3067w	3104m	–	–	–	–	–	–	–	ν (H-bonding OH)
–	–	–	3350br	3434br	3373br	3438br	3380br	3381br	ν (H_2O) coupled with ν (NH_3)
–	–	–	–	–	–	3353m	–	–	
1725s	1672s	–	–	–	–	–	–	–	ν (C =O)
1600s	1609m	1601s	1602s	1601s	1605s	1603s	1602s	1602s	
1447m	1571w	–	–	1546m	1551m	–	–	1552w	ω (C =C)
1527m	1531s	–	–	–	–	–	–	–	
–	–	1520m	1517m	1518w	1515m	1511m	1510m	1516m	ν (COO^- asym.)
–	1482s	1482m	1474s	1482s	1483m	1481s	1482s	1481s	ν (N =N sym.)
1465w	–	–	1447vw	1450vw	1452w	1449w	1449w	–	
–	1439s	1439m	1420m	1419m	1421m	1419m	1419m	1420m	ν (COO^- sym.)
–	1344s	1341m	1335s	1337m	1335s	1335s	1335s	1337s	δ (OH)
–	1244s	–	1256m	1263m	1261m	1254m	1254m	1260m	ν (C–O)
890m	896s	898m	–	886w	858m	857s	857m	858s	(COO^- scissors)
–	857s	856s	858s	857m	837m	841w	840w	836m	γ (OH)
637m	629w	635w	–	633w	646w	644w	644w	644w	(COO^- wagging)
–	–	–	509w	–	507w	504w	510w	–	ν (M–N)
–	–	–	434w	433w	443w	429vw	431vw	442w	ν (M–O)

s, strong; m, medium; w, weak; vw, very weak; br, broad.

complexes, while the second band seemed to be unaffected. The band due to the asymmetrical N =N stretching mode, near 1600 cm^{-1} could not be detected, since it merged with the strong ω(C =C) ring vibrations [17].

5. The new weak bands at 510–504 and between 443 and 431 cm^{-1} could be ascribed to M–O and M–N stretching vibrations [19], respectively.

3.2. Electronic spectra and magnetic properties

The magnetic moment values, μ_{eff} at room temperature and the electronic absorption bands in Nujol are given in Table I. Charge transfer bands, of moderate intensity, lay in the range 213–400 nm, and were assigned to the n-π* transition arising from transfer of charge from donating centres of the ligands to the vacant π* orbital of the metal ions. The spectrum of the iron complex showed d–d transition bands at 485 and 600 nm, which were assigned to a $^5T_{2g} \rightarrow {}^5E_g$ transition with octahedral geometry [20]. The magnetic moment value of 5.54 B.M. confirmed a high-spin iron(III) complex in octahedral symmetry [20]. The brownish-black homo-dimetallic copper complex was practically diamagnetic ($\mu_{eff} = 0.43$ B.M.), suggesting either a fairly strong anti-ferromagnetic interaction or reduction of copper(II) to copper(I) [21]. Furthermore, its electronic spectrum showed a broad d–d transition band at 479 nm. Such data suggested four co-ordinate square planar geometry [21]. However, a distorted octahedral for the "outside" copper was also possible (Fig. 1b). The pale brown homo-trimetallic copper complex showed only the same broad band at 479 nm with a magnetic moment value of 1.78 B.M., near enough to the spin-only value of 1.73 B.M. to suggest a distorted octahedral environment around the third copper ion outside the core of the organic chelates (Fig. 1c). The pale brown homo-dimetallic cobalt complex II, had a magnetic moment value of 5.21 B.M., denoting a high-spin cobalt complex with octahedral symmetry. This was supported by the band located at 585 nm due to the ν_3-transition $^4T_{1g}$ (F) → $^4T_{1g}$ (P) [21]. The hetero-trimetallic complex VI, had nearly the same magnetic moment value as the dimetallic one (5.18 B.M.). This substantially supported the previous suggestion about the state of copper(II), where no magnetic moment changes were observed. The d–d band at 465 nm was tentatively assigned to the "inside" copper, its broad nature arising for the merging of the ν_3-transition in the OH environment [22]. The same trend was exhibited by the dark brown homo-dimetallic nickel complex III ($\mu_{eff} = 2.87$ B.M.) and the brown hetero-trimetallic complex VII ($\mu_{eff} = 2.96$ B.M.), with no magnetic changes. This behaviour suggested the geometry around the nickel(II) to be of octahedral symmetry with no significant orbital interaction. The band located at 583 nm in the spectrum of the homo complex III, could be ascribed to a ν_3-transition, $^3A_{2g} \rightarrow {}^3T_{1g}$ (P), in an OH environment [23].

From all the above discussions, the proposed structure of the complexes can be illustrated as shown in Fig. 1 where phenolic, carboxylic or hydroxylic oxygen-bridged complexes are involved [24, 25].

3.3. Electrical conductivity of the complexes

The electrical conductivity data are collected in Table III. The conductance was measured over a wide temperature range between 291 and 625 K, reflecting the high thermal stability for these complexes. The dependence of the conductivity of semiconducting materials on temperature is expressed by the equation:

$$\sigma = \sigma_0 \cdot e^{\Delta E/KT}$$

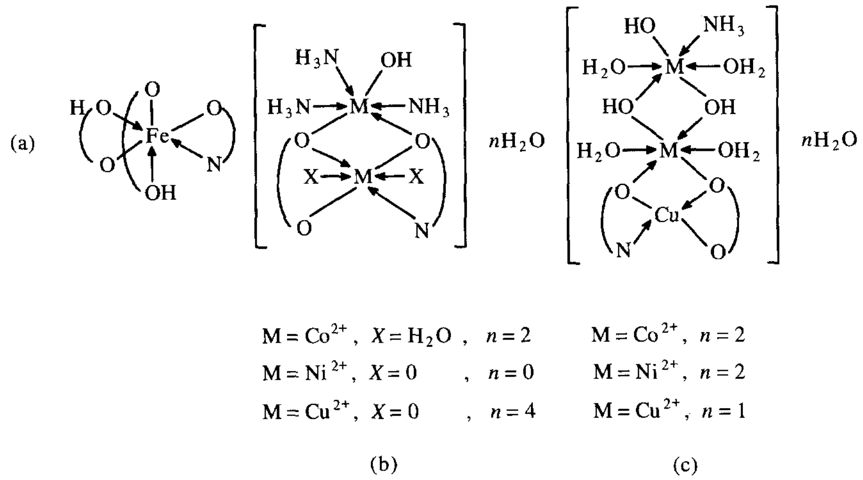

Figure 1 Proposed structure of the complexes.

TABLE III Conductivity data

Complex no.	ΔE_1	ΔE_2	ΔE_3	$\log\sigma_0$	$\log\sigma$ at 291 K
I	0.88	0.36	–	– 4.45	– 6.75
II	0.20	0.76	0.12	– 3.58	– 5.46
III	0.89	1.27	0.23	– 4.63	– 6.75
IV	1.04	0.21	–	– 4.83	– 6.98
V	1.66	0.64	–	– 5.20	– 7.75
VI	0.97	1.66	0.39	– 3.88	– 6.12
VII	0.20	–	–	– 5.93	– 8.67

σ and σ_0 expressed in $\Omega^{-1}\,\text{cm}^{-1}$ units.

where E is the activation energy for conductance, σ_0 is the specific conductivity as defined by $\sigma_0 = \sigma(T \rightarrow \infty)$ and K is the Boltzman constant. Fig. 2 shows the plots of $\log\sigma$ versus $1/T$. The relationship showed the following three categories: 1. straight line with no segments and obviously one activation energy, as given by complex VII; 2. straight line with one segment and two different activation energy values, as given by complexes I, IV and V; 3. a discontinuity in the conductivity curve with two segments and three activation energies as introduced by complexes II, III and VI, Table III. The phenomenon of discontinuation in the conductivity curves was argued to a molecular rearrangement or phase transition, where the ΔE values were temperature dependent [12].

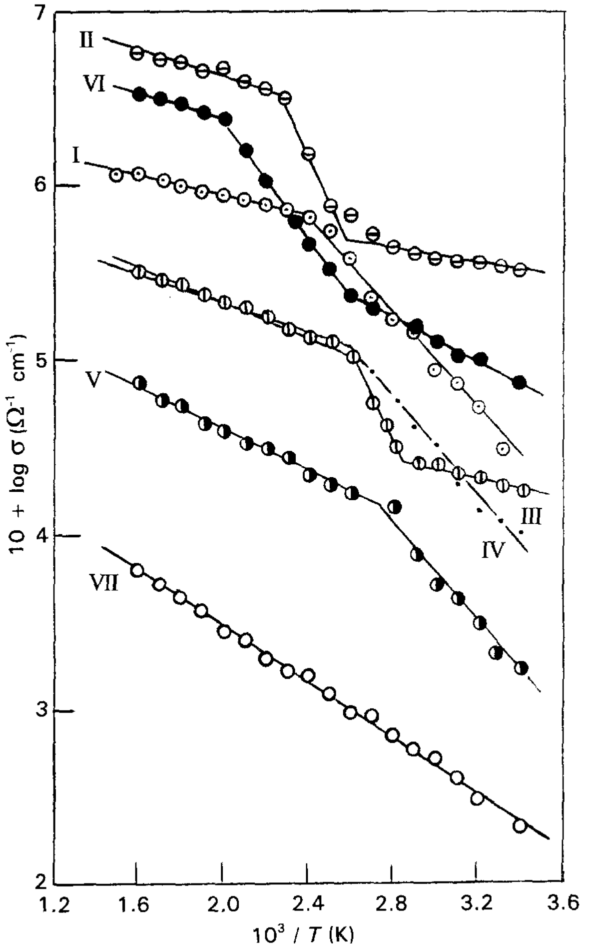

Figure 2 $\log\sigma$ versus $1/T$ relationship from the complexes.

The conductivity data presented in Table III show that the metal complexes under investigation had significantly higher conductivity values ($\log\sigma_{291}$ lay between – 5.46 and – 8.67; $\log\sigma_0$ lay between – 3.58 and – 5.93) than other metal complexes [26, 27]. These values reflected reasonable semiconducting behaviour. However, this may be understood based on two factors. Firstly, related to the structure and nature of the substituent for both of the mixed ligands. The first ligand (HL_1) contained two methyl groups of an electron donating nature, while the other ligand (H_2L_2) had a nitro group of strong electron attracting character, two such groups, with their different electronic potentialities in para-position to azo groups, facilitated electronic conduction via the metal ion, acting in this case as a bridge between the two ligands. Such conditions enhanced the transfer of current carriers leading to an increase in electrical conductivity with a decrease in activation energy [12]. The second factor is related to the metallic content of such a system, this is observed satisfactorily for the dimetallic complexes II–IV, where the $\log\sigma_{291}$ values were – 5.46, – 6.75 and – 6.98, respectively; this trend was extended to $\log\sigma_0$, with values of – 3.58, – 4.63 and – 4.83, respectively. However, for the trimetallic complexes V–VII, resulting from the incorporation of a third copper(II) ion, the conductivity values decreased to become −7.75, −6.12 and −8.67, respectively. This may have been due to distortions in the conduction pathway [28].

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