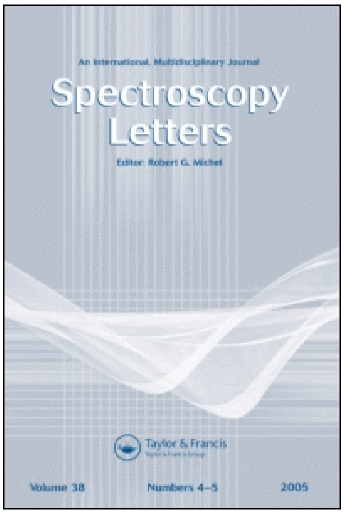

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Synthesis and Analytical Application of the Complexes of 4-Methylesculetin Azo Compounds with Some Transition Metal Ions

M. E. Moustafa[a]; Y. M. Issa[b]; W. F. El-hawary[a]; M. Refaat[a]
[a] Chemistry Department, Faculty of Science, Cairo university, Giza, Egypt [b] Chemistry Department, Faculty of Science, Benha University, Benha, Egypt

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SYNTHESIS AND ANALYTICAL APPLICATION OF THE COMPLEXES OF 4-METHYLESCULETIN AZO COMPOUNDS WITH SOME TRANSITION METAL IONS

Keywords; 8-arylazo-6,7-dihydroxy-4-methylcoumarin, IR, TG, DTA, magnetic moment, spectrophotometric determination of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}.

M.E.Moustafa*, Y.M. Issa, W.F.El-Hawary and M.Refaat
*Chemistry Department, Faculty of Science, Benha University, Benha, Egypt.
Chemistry Department, Faculty of Science, Cairo university, Giza, Egypt

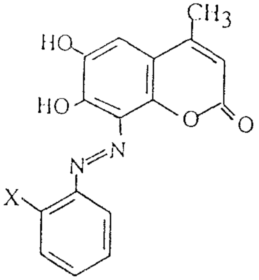
The solid complexes of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} with six azo compounds based on 8-arylazo-6,7-dihydroxy-4-methylcoumarin have been synthesized and characterizd by elemental and thermal analysis, magnetic susceptibility, molar conductance as well as IR spectroscopy, where it is found that metal ions are surrounded by coordinated water molecules and one ligand molecule bonded in a bidentate O and N fashion in the case of ligand 1 and in tridentate ONO fashion in the case of all the remaining ligands forming a coordination number of six in all cases. The potentiality of the prepared azo componds as new chromophoric reagents for the spectrophotometric determination of the metal ions is studied by extensive investigation of the optimum conditions favouring the formation of coloured complexes in solution.

INTRODUCTION

6,7-dihydroxy-4-methylcoumarin was to found to have good ligating properties towards some metal ions (1,2) while the analytical applications of large numbers of azo compounds in the field of analytical chemistry have been reviewed(3-7), so it was thought quite fruitful, in continuity to our previous work(8), to study the complexation behaviour of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} with some azo compounds based on 4-methyl-6,7-dihydroxycoumarin (4-methylesculetin) both in solution and in the solid state. The study in the former case provides a new method for the spectrophotometric determination of these metal ions with high accuracy and reproducibility, while the study in the latter case gives spot light on the mode of chelation and the structure of the solid complexes so formed.

EXPERIMENTAL

The azo compounds under study were prepared by coupling of 6,7-dihydroxy-4-methylcoumarin (in sodium acetate) with the diazonium salt of aniline, o-aminophenol, o-aminobenzoic acid, o-nitroaniline, o-anisidine or o-arsanilic acid. The 6,7-dihydroxy-4-methylcoumarin was prepared as previously mentioned (1). The prepared compounds were crystallized from acetic acid-water (30% v/v), their purity was confirmed by melting point constancy, elemental analysis and different spectral measurements(8), they have the following structural formula:



X= H (1), OH (2), COOH (3), NO_2 (4),OCH_3 (5) and $AsO(OH)_2$ (6)

Solutions of the dyes (10^{-2} M) were prepared by dissolving an accurate weight of the recrystallized product in ethanol. Stock solutions of metal ions (10^{-2} M) were prepared by dissolving accurate weights in bidistilled water then were standardized as previously described (9). Samples for spectral measurements were obtained by accurate dilution. Modified

Britton-Robinson universal buffer solutions were prepared as recommended (10).

Metal chelates were prepared by refluxing an ethanolic mixture of metal chloride (1 mmol) and the ligand (1 mmol) for about 6 hours. On cooling the solution mixture to room temperature, the crystalline solid obtained was filtered, washed with etanol and dried in vacuum over P_2O_5. Analysis for carbon, hydrogen and nitrogen were carried out in the Micro Analytical Center, Cairo University, Cairo, Egypt. Metal contents were determined by EDTA titration after decomposition of chelates (11). All instruments used in the present study have been described elsewhere (12).

RESULTS AND DISCUSSION

(A) Studies on the Solid Chelates

Data of elemental analysis of the isolated solid chelates Table (1) show a satisfactory agreement with the proposed formula. All the solid complexes are soluble in DMF but insoluble in common organic solvents and do not possess sharp melting points but decompose on heating above 350°C. The insolubility in common organic solvents and non-melting nature suggest that they are polymeric or ionic. The molar conductivities of the complexes (10^{-3} M) in DMF as a solvent at 25°C indicated the ionic nature of all complexes formed with ligand **1**,**4** and **5** (molar conductance values lie within the range 11.77-90.88 ohm^{-1} cm^2 $mole^{-1}$) while those of ligands **2**,**3** and **6** (except for Fe^{3+} complexes) are non-electrolytes. In case of being ionic, the electrolytic complexes are neutralized by Cl^- outside the coordination sphere which is detected by the precipitation of AgCl on addition of $AgNO_3$ to solubilized chelates in DMF.

The stiochiometry of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} complexes with the ligands under study was investigated by conductometric titrations, which indicate the probable formation of 1:1 complexes. The steady increase in equivalent conductance-molar ratio curves is due to the liberation of the easily mobile H^+ ion through the formation of covalent bonding between oxygen and metal ion in a six membered ring fashion.

The results of thermal analysis of some selected chelates show that they degrade in three stages. The first step in the decomposition sequence (at

Table (1): Elemental analysis, molar conductance, magnetic moments and IR spectral frequencies (cm^{-1}) of some metal complexes with ligands (I - 6).

Tentative formula **	Calcd. (found) %				Λ^*_M	μ_{eff} (B.M)	IR spectral bands				
	C	H	N	M			ν_{OH}	$\nu_{N=N}$	δ_{OH} in-plane	ν_{M-N}	ν_{M-O}
$C_{16}H_{12}O_4N_2$ (1)	64.85(64.17)	4.09(4.03)	9.46(9.55)	--	-	--	3355	1443	1353	---	---
[Mn 1. $4H_2O]^+ Cl^-$	41.99(42.05)	4.18(4.10)	6.12(6.20)	12.00(12.11)	40.08	4.72	3350	1433	1350	465	415
[Fe 1. $4H_2O]^{2+} 2Cl^-$	38.90(38,80)	3.88(3.70)	5.67(5.55)	11.30(11.20)	53.77	4.90	3325	1428	1340	465	395
[Cu 1. $4H_2O]^+ 2Cl^-$	41.21(41.15)	4.11(4.08)	6.01(5.97)	13.63(13.70)	29.15	0.88	3340	1435	1348	460	405
$C_{16}H_{12}O_5N_2$ (2)	60.53(60.57)	3.88(4.01)	8.97(9.02)	---	--	--	3420_{br}	1465	1353	---	---
[Fe 2. $3H_2O]^+ Cl^-$	42.18(42.22)	3.54(3.40)	6.15(6.20)	12.26(12.30)	33.17	4.88	3410	1428	1350	470	420
[Co 2. $3H_2O$]	45.41(45.31)	3.81(3.70)	6.62(6.70)	13.92(14.00)	6.05	4.80	3395	1451	1345	490	380
[Cu 2. $3H_2O$]	44.92(44.81)	3.77(3.65)	6.55(6.60)	14.85(14.77)	7.10	1.20	3385	1450	1345	480	403
$C_{16}H_{12}O_6N_2$ (3)	60.00(60.54)	3.56(3.78)	8.23(8.50)	---	---	---	3330	1446	1350	---	---
[Co 3. $3H_2O$]	45.24(45.60)	3.57(3.50)	6.21(6.32)	13.06(13.00)	10.00	3.92	3325	1428	1350	455	400
[Ni 3. $3H_2O$]	45.27(45.46)	3.58(3.42)	6.21(6.30)	13.02(12.95)	8.91	2.35	3340	1435	1335	456	395
[Cu 3. $3H_2O$]	44.79(44.90)	3.54(3.70)	6.15(6.25)	13.94(14.05)	6.58	1.22	3315	1428	1340	480	415
$C_{16}H_{11}O_6N_3$ (4)	56.30(57.00)	3.26(3.51)	12.31(12.03)	---	---	---	$3355_{v.br}$	1445	1343	---	---
[Mn 4. $3H_2O]^+ Cl^-$	39.57(39.46)	3.53(3.42)	8.65(8.50)	11.31(11.15)	37.08	4.86	3340	1435	1340	470	415
[Co 4. $3H_2O]^+ Cl^-$	39.24(39.08)	3.50(3.34)	8.58(8.32)	12.03(12.10)	40.34	4.23	3350	1425	1340	460	395
[Ni 4. $3H_2O]^+ Cl^-$	39.26(39.15)	3.50(3.41)	8.59(8.35)	11.90(11.99)	11.77	2.67	3328	1430	1335	465	415
$C_{17}H_{14}O_5N_2$ (5)	62.57(61.88)	4.33(4.12)	8.59(8.79)	--	--	--	3300_{br}	1445	1350	---	---
[Mn 5. $3H_2O]^+ Cl^-$	43.38(43.40)	4.28(4.18)	5.95(5.75)	11.67(11.50)	42.51	4.78	3350	1430	1330	460	435
[Ni 5. $3H_2O]^+ Cl^-$	43.03(42.90)	4.25(4.10)	5.90(5.58)	12.37(12.10)	51.43	2.34	3385	1428	1345	485	445
[Cu 5. $3H_2O]^+ Cl^-$	42.60(42.42)	4.21(4.09)	5.84(5.75)	13.26(13.10)	39.72	1.52	3375	1435	1335	475	450
$C_{16}H_{13}O_7N_2As$ (6)	45.71(45.03)	3.12(3.17)	6.67(6.02)	---	---	---	3340_{br}	1441	1350	---	---
[Fe 6. $3H_2O]^+ Cl^-$	33.98(33.80)	3.03(3.08)	4.95(4.85)	9.88(9.75)	44.18	5.20	3320	1420	1345	468	425
[Ni 6. $3H_2O$]	36.05(35.78)	3.22(3.71)	5.26(5.10)	11.02(11.09	10.13	1.70	3325	1435	1345	455	435
[Cu 6. $3H_2O$]	35.73(35.70)	3.19(3.00)	5.21(5.32)	11.82(11.75)	15.32	1.32	3330	1430	1340	475	440

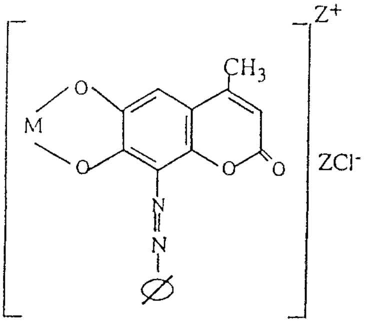
* Molar conductance(ohm^{-1} cm^2 mol^{-1})

** *Coordination sphere derived from molar conductance* and elemental analysis

70-90°C) corresponds to the loss of physically combined water molecules from outer surface or interstice of the crystal lattice, while the second step within the temperature range 125-160°C represents the removal of coordinated water molecules leading to the formation of anhydrous complexes. The latter decomposed, in the third step, forming the metal oxide as a final product. The number of coordinated water molecules and the percent of M^{n+} are calculated from the corresponding inflections on the TG curves whose values are in good agreement with those obtained from elemental analysis.

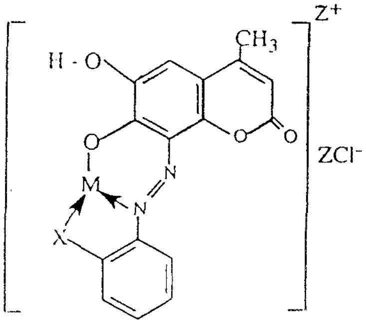
The $\mu_{eff.}$ values of the majority of complexes show lower values than the respective spin-only values Table (1). In a large number of ONO donor metal complexes, lower magnetic moments have been reported (13-15) and attributed to antiferromagnetic interactions as a consequence of dimeric or polymeric structural arrangements.

The IR absorption spectra of the solid chelates were compared to those of the free ligands, the most important frequencies of the spectral bands are cited in Table (1). The complexes are studied to show whether the free ligands interact with metal ions through their adjacent hydroxyl groups retaining the azo center unaffected thus,



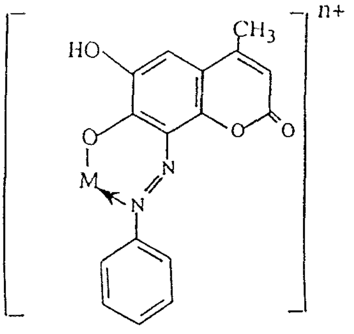
z = 0 for M^{2+} and 1 for Fe^{3+}

or through the azo center with only one hydroxyl group and substituent X in o-position.



Comparison between the IR spectra of the free ligands and those of their metal chelates showed the absence of the weak broad band at 2930 cm^{-1} due to intramolecular hydrogen bonded OH group (16) with the appearance of a new band within the range 420-380 cm^{-1} due to the stretching vibration of the M-O bond (17). In the same time, the stretching vibration of the N=N of the free ligands, found at 1466-1401 cm^{-1}, is shifted to lower frequency by 10-25 cm^{-1} on complex formation suggesting that one nitrogen atom of the azo group participates in a coordination bond with the metal ion in addition to the simple covalent one formed through the oxygen atom of the O-OH group, this is supported by the new band observed at 490-455 cm^{-1} due to the stretching vibration of metal-nitrogen bond (ν_{M-N}). It is worthy to mention that, the frequency of the stretching vibration of the second OH group is obscured by those of coordinated water molecules giving rise to a broad band centered around 3340 cm^{-1}. For compounds **2**,**3** and **6** [X=OH, COOH and $AsO(OH)_2$], the stretching vibrations of COOH and $AsO(OH)_2$ groups found at 1673 and 803 cm^{-1} respectively are shifted to lower frequencies (*cf.* Table 1) as a result of deprotonation indicating their contribution in the complexation process and the dibasic nature of such ligands, the fact which is supported by molar conductance measurements whose values amount to 6.05-15.32 ohm^{-1} cm^2 $mole^{-1}$ for divalent metal ions indicating their non-electrolytic nature, while those of Fe^{3+} are 33.17-44.18 ohm^{-1} cm^2 $mole^{-1}$ indicating univalent cationic complex.

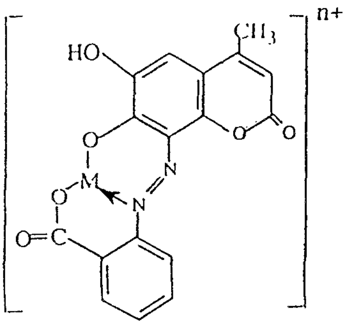
These assumptions lead to the fact that metal ions are bonded to ligand molecules in a bidentate O and N fashion in the case of ligand **1** and in tridentate O, N and O fashion in the case of all the remaining ligands. Water molecules surround the metal ions so as to complete the coordination number six in all cases.



Ligand 1

n = +1 for Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}

= +2 for Fe^{3+}



Ligand 3

n = 0 for Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}

= 1 for Fe^{3+}

(B) Analytical Studies

Optimization: The optimum conditions favouring the method of determination of Mn^{2+}, Fe^{3+}, Co^{2+},Ni^{2+} and Cu^{2+} are carefully investigated. Universal buffer solutions containing 30% (v/v) ethanol were the most suitable media for the formation of coloured complexes. The absorption spectra of the complexes in buffer solutions of various pH values are characterized by one broad band which is bathochromatically shifted from that of the free ligand (*cf.*Fig.1). The optimum pH values for complex development and the maximum wavelengths (λ_{max}) are listed in Table (2). The effect of time and temperature showed that complexes are spontaneously developed and remain stable for about 2 h. It is found also that raising the temperature up to 50°C has no effect on the absorbance of the coloured complexes while boiling destroys them.

*Molecular stoichiometry:*The molecular stoichiometry of the complexes was investigated in the light of molar ratio, continuous variation and straight line methods which revealed the formation of 1:1 complexes. The logarithmic stability constants of the formed complexes, calculated from the spectroscopic data, are listed in Table (2).

Effect of interfering ions: A systematic study on the influence of foreign ions led to the conclusion that the presence of the following ions up to 20 times that of metal ion at the recommended pH do not interfere: Na^+, K^+,

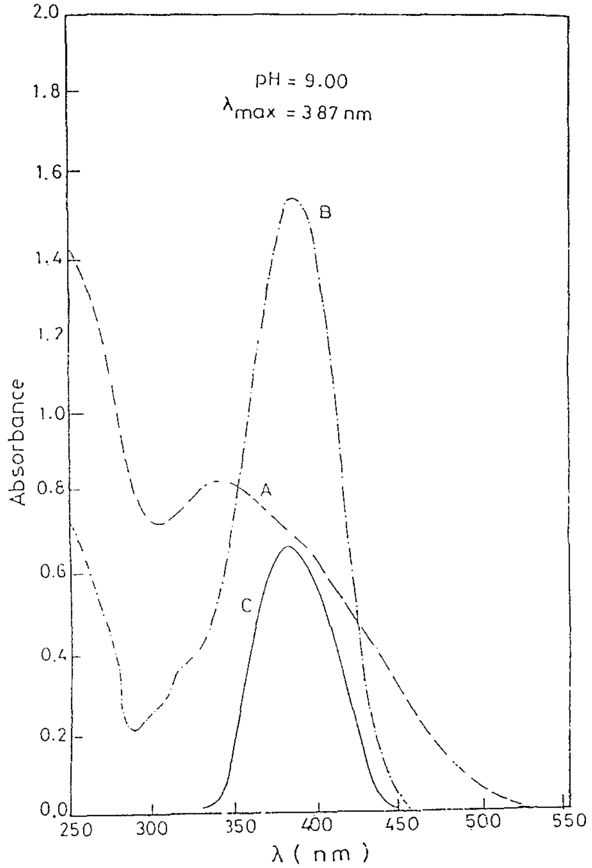


Fig.(1): The absorption spectra of Cu^{2+} - ligand (1) complex.

A-2 X 10^{-4} M ligand I using buffer as blank

B- 1 X 10^{-4} M Cu^{2+} - ligand I complex using buffer as blank

C- B using A as blank

Table (2) commulative data of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+} complexes with-8-arylazo 6,7-dihydroxy-4-methylcoumarin. (1-6).

M^{n+}	Ligand	pH	λ (nm)	μg/10 ml (EDTA)	(Ringbom) μg/ml	(Beer's) μg/ml	ε°	a x10^{-2}	S.S	S.D	error %	log β^*_n	- Δ G**
Mn^{2+}	1	8.20	360	60.43	0.56-6.11	6.30	2.28	1.25	0.0241	0.73	1.10	12.41	16.93
	2	5.00	372	54.90	0.55-5.22	5.50	2.84	1.56	0.0193	0.66	1.00	12.67	17.28
	3	7.11	385	49.45	0.54-4.80	4.90	2.04	1.12	0.0269	0.95	1.40	12.85	17.53
	4	9.00	420	54.90	0.55-5.40	5.50	2.37	1.30	0.0232	1.22	2.00	12.72	17.35
Fe^{3+}	1	7.11	365	61.44	0.60-6.00	6.00	1.53	0.86	0.0365	0.49	0.90	11.69	15.94
	2	8.20	384	61.44	0.60-6.10	6.20	2.72	1.52	0.0205	0.63	1.20	11.73	16.00
	5	9.00	370	61.44	0.62-6.05	6.10	1.96	1.09	0.0285	0.91	1.80	11.56	15.77
	6	4.00	392	50.27	0.62-5.00	5.10	2.73	1.52	0.0205	1.12	2.00	11.07	15.10
Co^{2+}	3	8.20	390	53.50	0.80-5.25	5.30	2.36	1.39	0.0250	0.56	0.80	11.18	15.25
	4	10.22	375	58.94	0.81-5.82	5.90	2.50	1.50	0.0236	0.97	1.40	10.59	14.44
	5	9.00	408	58.94	0.80-5.79	5.90	1.69	1.00	0.0349	0.81	1.20	10.88	14.84
	6	7.11	385	58.94	0.79-5.84	5.90	3.65	2.15	0.0162	1.14	1.80	12.15	16.57
Ni^{2+}	1	5.50	377	64.58	0.62-6.31	6.40	1.64	0.96	0.0353	0.41	0.50	11.53	15.73
	2	7.11	365	64.58	0.63-6.45	6.50	2.09	1.23	0.0281	0.72	0.80	11.26	15.36
	4	8.20	370	58.71	0.60-5.70	5.80	3.54	2.07	0.0162	0.96	1.30	11.42	15.58
	5	11.10	397	64.58	0.62-6.10	6.20	2.85	1.60	0.0206	0.69	0.80	11.30	15.41
Cu^{2+}	1	8.20	390	69.89	0.79-7.14	7.20	1.50	0.96	0.0424	0.83	1.10	13.18	17.98
	3	9.00	400	76.25	0.83-7.49	7.60	2.03	1.29	0.0313	0.69	1.00	10.81	14.74
	4	2.97	390	63.54	0.85-6.45	6.50	2.93	1.86	0.0217	0.98	1.40	11.79	16.08
	6	7.11	403	63.54	0.87-6.40	6.50	3.25	2.06	0.0196	0.62	0.80	12.50	17.05

* Average values of molar ratio, continuous variation and straight line methods

** ΔG = K. Cal mol^{-1}

$\varepsilon° = \varepsilon \times 10^{-3}$ (L.mol^{-1} cm^{-1})

S.S = Sandell sensitivity (μg / cm^2)

a = specific absorptivity (L g^{-1} cm^{-1})

S.D = Standard deviation

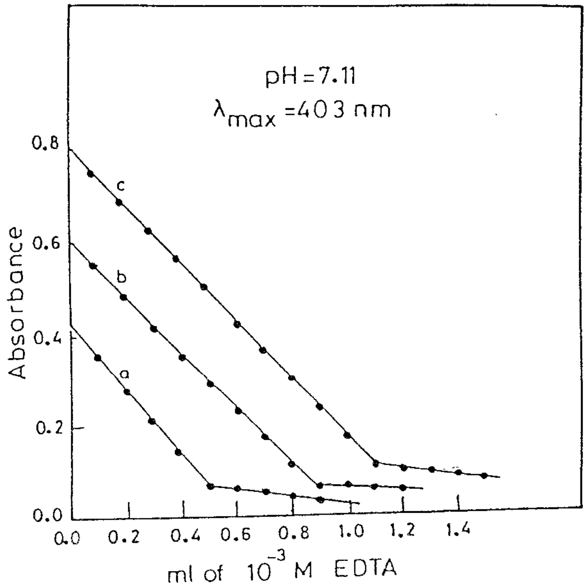


Fig.(2): Spectrophotometric titration of Ni^{2+} with EDTA using ligand (III) as indicator.

a) = 0.5 ml 10^{-3} M Ni^{2+} + X ml 10^{-3} M EDTA
b) = 0.9 ml 10^{-3} M Ni^{2+} + X ml 10^{-3} M EDTA
c) = 1.1 ml 10^{-3} M Ni^{2+} + X ml 10^{-3} M EDTA

Al^{3+}, Pd^{2+}, Mg^{2+}, Ca^{2+}, Sr^{3+}, Ba^{2+}, SO_4^{2-}, WO_4^{2-}, VO^{2+} and tartrate while La^{3+}, Ce^{4+}, Th^{4+}, Pt^{4+}, EDTA and oxalate interfere.

Quantification, accuracy and precision: The colour formed through the reaction of ligands **1-6** with metal ions under study can be applied to the determination of their microquantities. This is gathered from the high molar absorptivities and Sandell sensitivities that reflect the stability of the complexes and accuracy of the method. Table (2) lists the limits of conformance to Beer's law, the values of molar absorptivity (ε, l mol^{-1} cm^{-1}), specific absorptivity (a, ml g^{-1} cm^{-1}), Sandell sensitivity (S.S, μg cm^2), Ringbom and standard deviation (S.D). The results indicate the high sensitivity and applicability of using these new ligands in the microdetermination of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} ions.

Spectrophotometric titration with EDTA: Each of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} can be determined by direct spectrophotometric titration with EDTA using the ligands as indicators. All titration curves show a sharp end point intersection; Fig. (2). The results indicate that such method is reliable for the determination of the metal ions up to the recorded concentration.

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