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## Spectrophotometric studies of the reaction between 3-(2-hydroxy-4 and 5-substituted-1-phenylazo)-1,2,4-triazoles and manganese(II) and its applications for microdetermination of manganese(II) in real samples

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### ABSTRACT

Manganese(II) reacts with 3-(2-hydroxy-4 and 5-substituted-1-phenylazo)-1,2,4-triazoles to produce a purple violet chelates in aqueous media containing 40 % (v/v) methanol. The article included an extensive study of the optimum conditions that are essential for the spectrophotometric determination of trace amounts of manganese(II) based on its chelates formation with the azodyes under interest. The molecular structures of the formed complexes were found to be 1:1 and 1:2 ( $Mn^{2+}:HL$ ). The colored dye-manganese complexes showed absorption maxima at 510, 535, 460, 480, 520, and 500 nm. Beer's law is valid over manganese(II) concentrations up 27.47, 71.42, 54.94, 54.94, 54.94 and 49.44  $\mu g$  of Mn(II) per 10 ml, with molar absorptivities of  $3.98 \times 10^4$ ,  $1.57 \times 10^4$ ,  $0.20 \times 10^4$ ,  $0.10 \times 10^4$ ,  $0.10 \times 10^4$  and  $0.53 \times 10^4$   $l\ mol^{-1}\ cm^{-1}$  using  $HL^1$ - $HL^6$ , respectively. A notable advantage of the investigated method is that the determination of Mn(II) is possible in the presence of many cations and anions. The method has been applied to the determination of manganese in pharmaceutical formulations with reliable analytical results. Some solid complexes were prepared and subjected to different spectroscopic and analytical techniques as well as thermal analysis in order to investigate the mode of interaction between the azo compounds and Mn(II) ion.

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### KEYWORDS

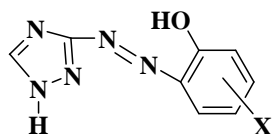
Triazole azodyes;  
Metal complexes;  
Manganese(II) determination.

### INTRODUCTION

However a surplus of manganese in a biological system may damage the nervous system, manganese is a biologically important microelement. Many biological processes, for example photosynthesis, respiration, and transport of substances in plants take place with the participation of manganese. The methods usually used for manganese determination are based on oxidation of Mn(II) to Mn(VII) by heating in presence of oxidizing agents followed by the spectrophotometric detection of

permanganate anion. For spectrophotometric determination of manganese both inorganic<sup>[1]</sup> and organic<sup>[2,3]</sup> reagents have been used. These methods based on the color reaction between manganese and organic complex-forming reagents are more advantageous. But the known existing methods are often complicated and require oxidation and heating<sup>[1]</sup>, involve creating exact reaction conditions, and are frequently characterized by poor sensitivity. Therefore, there is need to develop new analytical procedures for manganese determination which do not have these disadvantages. Recently,

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X = m-OH (L<sup>1</sup>), p-CH<sub>3</sub> (L<sup>2</sup>), p-COC<sub>2</sub>H<sub>5</sub> (L<sup>3</sup>),  
p-COCH<sub>3</sub> (L<sup>4</sup>), p-CHO (L<sup>5</sup>) and p-Br (L<sup>6</sup>)

**SCHEME 1:** The general structure of the investigated azodyes

heterocyclic azodyes have been utilized as indicators for the spectrophotometric and chelatometric determination of metal ions<sup>[4-14]</sup>.

The present study describes and discuss the possibilities of applying some azo derivatives of 3-amino-1,2,4-triazole for the spectrophotometric determination of manganese(II) in different real samples (SCHEME 1). The optimum reaction conditions and other analytical parameters are evaluated. The statistical analysis of the obtained results indicates that the method is precise and accurate.

## EXPERIMENTAL METHODS

### A. Material and solutions

3-Amino-1,2,4-triazole azo derivatives HL<sup>1</sup>-HL<sup>6</sup> (SCHEME 1) were obtained using the diazonium salt of 3-amino-1,2,4-triazole prepared by dissolving it in hydrochloric acid, cooling to 0-5°C, and adding an equivalent amount of ice-cooled sodium nitrite solution with vigorous stirring, then, coupling the formed dizonium salt with the different substituted phenols according to the method given before<sup>[15]</sup>. The formed precipitate were filtered off and recrystallized from the appropriate solvent then the purity of each derivative was checked by different analytical techniques.

All solutions were prepared from high-purity chemicals, solvents and de-ionized water. The 10<sup>-3</sup> M solution of azodyes was prepared by dissolving their appropriate weights in methanol. The 10<sup>-3</sup> M Mn<sup>2+</sup>-solution was prepared by dissolving the calculated amount of manganese acetate in deionized water with subsequent standardization by the recommended method<sup>[16]</sup>. The Britton buffer solutions were prepared as previously described<sup>[17]</sup>.

### B. Equipments

Absorption measurements were made on a Shimadzu

Uv-Vis 240 recording spectrophotometer using 10-mm matched quartz cells with slit width 1 cm. The pH of the solutions was measured using a digital ORION pH-meter model 201 of sensitivity ±0.02 pH unit. The elemental analysis of the prepared solid complexes were determined at the microanalytical unite, Tanta University, Tanta, Egypt. Conductivity measurements were measured at 25°C using a conductance bridge of the type 523 conductometer. A Perkin Elmer 1430 spectrophotometer was used for recording the IR spectra of the solid Mn(II)-complexes with HL<sup>1</sup> and HL<sup>6</sup> over the 4000-200cm<sup>-1</sup> range as KBr discs. The thermogravimetric analysis (TGA) were performed using the TG 50-thermogravimetric analyzer (Shimadzu) in the range 25°C up to 800°C with 10°C/min heating rate using nitrogen as an atmosphere.

### C. Recommended procedures

To an aliquot of the solution containing no more than 71.42µg of Mn(II) in 10 ml calibrated flask, 5 ml of Britton universal buffer of the recommended pH value and 3 ml 1×10<sup>-3</sup> M of ligand solution were added. The contents were shaken, the solution was diluted to the mark with de-ionized water and the absorbance of the chelates was measured at the suitable wavelength against a reagent blank prepared under identical conditions.

### 2.4. Preparation of solid Mn(II)-complexes with azodyes HL<sup>1</sup> and HL<sup>6</sup>

The solid complexes of Mn(II) with HL<sup>1</sup> and HL<sup>6</sup> were prepared by mixing equimolecular ethanolic solutions of azodyes and manganese acetate. The mixture was then refluxed on a water bath for ≈8 Hrs., and allowed to cool whereby the solid complexes separated. The formed precipitate was filtered off, washed with ethanol and dried in vacuum over silica gel then subjected to different analytical techniques.

## RESULTS AND DISCUSSION

The optimum conditions for the spectrophotometric determination of Mn(II) ions resulted from a careful investigation of all factors involved in the procedure as the followings;

### A. Effect of time and temperature

It was found that the color of the complexes are

completely developed spontaneously and remain con-

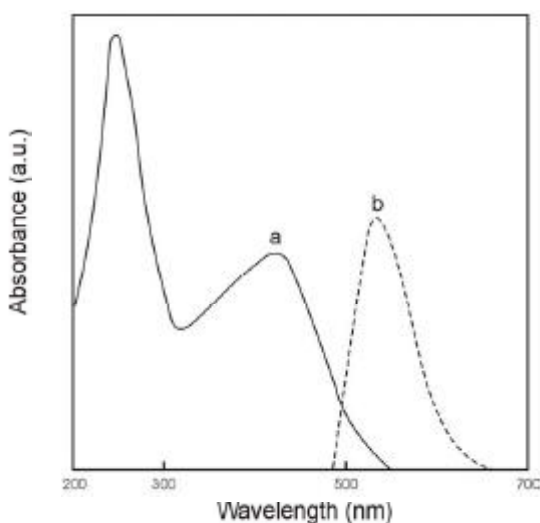


Figure 1: The electronic absorption spectra of HL<sup>2</sup> (a) and its Mn(II) complex (b) in aqueous buffer solution of pH= 11 containing 40% methanol

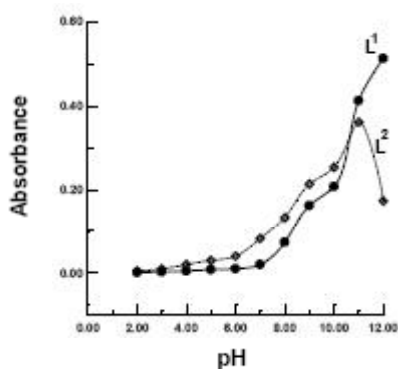


Figure 2: Absorbance-pH curves of Mn(II) complexes with HL<sup>1</sup>[ $\lambda=510$  nm] and HL<sup>2</sup> [ $\lambda=535$  nm]

stant for about 12 h, after which they suffer a slight decrease in absorbance; the original value may be retained by shaking. This was achieved by measuring the absorbance of some samples at different time intervals. It was also found that raising the temperature to 50 has no effect on the absorbance of all complexes, whereas boiling destroys the formed complexes.

## B. Effect of buffer and pH

The Britton universal buffer was the most suitable media for developing the deep violet color of Mn(II)-complexes among those tested borate and acetate buffers. Measurements have shown that the pH at which the maximum complex formation occurs depends on the ligand used. The maximum absorbance ( $\lambda_{\max}$ ) and the optimum pH values are given in TABLE 1. The absorption spectra of the ligands and their Mn(II)-complexes (Figure 1) indicate that the visible absorption bands of the free ligands are bathochromically shifted (i.e shifted to longer wavelengths) in the presence of the Mn(II) ions where the absorption of the azodyes are negligible due to increased delocalization of the electrons on complexation leading to a decrease in the energy gap between the ground and excited states<sup>[18]</sup>. Hence, the absorbance of the complexes was measured at these wavelengths in further experiments.

The complexes formation start at pH 2.0 and increase up to a definite pH values (TABLE 1) as evidenced by increase in absorbance (Figure 2) which may be attributed to decreased acidity of the medium and enhanced ionization of the active protons of the azodye

TABLE 1: The spectrophotometric analytical characteristics of Mn(II)-chelates with HL<sup>1</sup>-HL<sup>6</sup>

Ligand (Substituent)	pH ( $\lambda_{\max}$ )	M/L Ratio	Log $\beta_n$	- $\Delta G^*$	$\epsilon \times 10^{-4}$ (S.S.)	C.C. (S.D.)	Beer's up to (R.R.)	L.O.Q $\times 10^5$ (L.O.D $\times 10^6$ )
HL <sup>1</sup>	12.0	1:1	3.84	22.12	3.9797	0.99997	27.47	0.5
( <i>m</i> .OH)	(510)	1:2	7.71	44.42	(0.0014)	(0.00093)	(2.75-16.48)	(1.5)
HL <sup>2</sup>	11.0	1:1	3.74	21.55	1.6024	0.99996	71.42	1.0
( <i>p</i> .CH <sub>3</sub> )	(535)	1:2	8.09	46.64	(0.0038)	(0.00091)	(5.49-32.96)	(3.0)
HL <sup>3</sup>	9.0	1:1	3.90	22.47	0.2005	0.99992	54.94	1.0
( <i>p</i> .COOEt)	(460)	1:2	8.08	46.58	(0.0273)	(0.00002)	(16.48-54.94)	(3.0)
HL <sup>4</sup>	6.0	1:1	4.19	24.15	0.1024	0.99992	54.94	1.0
( <i>p</i> .COCH <sub>3</sub> )	(480)	1:2	8.71	50.21	(0.0543)	(0.00003)	(16.48-43.95)	(3.0)
HL <sup>5</sup>	10.0	1:1	3.70	21.31	0.1017	0.99998	54.94	1.0
( <i>p</i> .CHO)	(520)	1:2	7.77	44.77	(0.0535)	(0.00002)	(21.98-54.94)	(3.0)
HL <sup>6</sup>	10.0	1:1	2.94	16.93	0.5334	0.99993	49.44	1.0
( <i>p</i> .Br)	(500)	1:2	6.64	38.27	(0.0103)	(0.00012)	(11.00-49.44)	(3.0)

$\lambda_{\max}$ : is the suitable wavelength in nm,  $\epsilon$ : Molar extinction coefficient ( $l \text{ mol}^{-1} \text{ cm}^{-1}$ ), Log  $\beta_n$ : Log stability constant, C.C.: Correlation coefficient, Beer's: Beer's law up to ( $\mu\text{g}/10 \text{ ml}$ ), ( $\Delta G^*$ ): Free energy changes ( $\text{Kcal mol}^{-1}$ ), (S.S): Sandell's sensitivity ( $\mu\text{g}/\text{cm}^2$ ), (R.R.): Ringbom range ( $\mu\text{g}/10 \text{ ml}$ ), L.O.D): Detection limits ( $\text{mol l}^{-1}$ ).

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molecule (HL).

This behavior is quite common for complexes formed by proton displacement from reagent through the metal ion<sup>[19]</sup>. Also, a constant absorbance was obtained in addition of up to 5 ml of buffer, hence all experiments were performed in presence of 5 ml Britton buffer of the recommended pH value.

### C. Effect of sequence of addition and ligand concentration

Addition in the sequence azodye-metal-buffer was found to be the most favorable one for color development of all manganese chelates under interest. With the addition of 0.1–4.0 ml of  $1 \times 10^{-3}$  M of ligand solution (HL<sup>1</sup>-HL<sup>6</sup>), the absorbance was unchanged after addition of more than 2.5 ml. So determinations were carried out with 3.0 ml of  $1 \times 10^{-3}$  M of ligand solution.

### D. The composition, conditional stability constants and free energy changes of the formed Mn(II)-complexes

The composition of the Mn(II)-chelates with azodyes HL<sup>1</sup>-HL<sup>6</sup> was investigated in the light of the spectroscopic results obtained from mole ratio and continuous variation methods<sup>[20-22]</sup>. The Mn<sup>2+</sup>:HL ratios were found to be 1:1 and 1:2 in the formed complexes. These results were confirmed by the data obtained from conductometric titration. The conditional stability constants and free energy changes of the formed Mn(II)-complexes are calculated from the results of continuous variation and mole ratio methods and listed in TABLE 1<sup>[23]</sup>. The tabulated results indicate that the stability of the Mn(II) chelates with HL<sup>1</sup>-HL<sup>6</sup> increase with increasing the number of azodye molecules attached to Mn(II) ion and electron donating character of m- and p-substituent groups attached to the phenyl moiety.

### E. Beer's law, sensitivity and statistical Analysis

The chelates adhered to Beer's law (Figure 3) up to 27.47, 71.42, 54.94, 54.94, 54.94 and 49.44  $\mu\text{g}$  of Mn(II) per 10 ml with a molar absorptivities of  $3.98 \times 10^4$ ,  $1.60 \times 10^4$ ,  $0.20 \times 10^4$ ,  $0.10 \times 10^4$ ,  $0.10 \times 10^4$  and  $0.53 \times 10^4$   $\text{l mol}^{-1} \text{cm}^{-1}$ , and a Sandell sensitivities<sup>[24]</sup> of 0.0014, 0.0037, 0.0274, 0.0540, 0.0538 and  $0.0103 \mu\text{g cm}^{-2}$  using HL<sup>1</sup>-HL<sup>6</sup>, respectively.

The regression analysis of the calibration graphs and other quantitative data like detection limits and the lim-

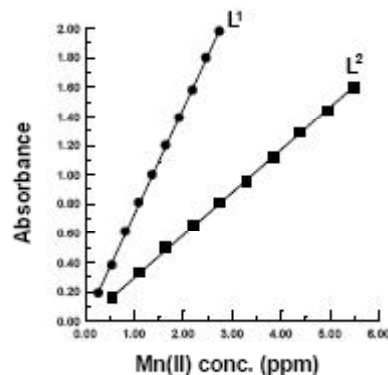


Figure 3: Absorbance-concentration plots of Mn(II)-HL<sup>1</sup> [pH=12 and  $\lambda=510$  nm] and Mn(II)-HL<sup>2</sup> [pH=11 and  $\lambda=535$  nm] systems

its of quantification as defined by IUPAC<sup>[25]</sup> for the obtained calibration graphs is presented in TABLE 1. The results obtained donate that HL<sup>1</sup> is the most sensitive chromogenic reagent for the spectrophotometric determination of Mn(II) ion.

The precession of the suggested method using HL<sup>1</sup> as the best chromogenic has been evaluated by seven replicate determinations of standard solution containing 27.47  $\mu\text{g}$  of Mn(II) in 10 ml. Satisfactory results were obtained with a variation coefficient and relative error equal 0.15% and 0.55%, respectively.

### F. Effect of foreign ions

Solutions containing 2.75 mg/l and various foreign ions were prepared and the recommended procedure using HL<sup>1</sup> as the best chromogenic reagent for the determination of manganese was carried out. With a relative error of  $\pm 5\%$ , the tolerance limits (mg) for various foreign ions are as follows: of Li<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Ag<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, CH<sub>3</sub>COO, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, (12); Pb<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, La<sup>3+</sup>, Bi<sup>3+</sup>, Sb<sup>2+</sup>, As<sup>3+</sup>, and Mo<sup>6+</sup> (6); Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> (3). The selectivity of the present methods stems from the fact that acetic, boric, and phosphoric acids, as constituents of the buffer used, act as masking agents for many cations.

### G. Analysis of manganese content in pharmaceutical formulations

One capsule of the analyzed pharmaceutical formulation was taken in a 25 ml crucible and treated with few drops of 8 M hydrochloric acid then digested at 500°C. The residue was dissolved in 5 ml concentrated

**TABLE 2: Spectrophotometric determination of manganese in pharmaceutical formulations**

Pharm. formu.	Manganese content (mg)		R.S.D.	R.E.
	Certified value	Using HL <sup>1</sup>	%	%
Royal VIT G. <sup>A</sup>	1.000	1.005	0.561	0.500
Supradyn-R <sup>B</sup>	0.500	0.497	0.600	0.660

R.S.D.%: Relative standard deviation. R.E.%: Relative error, <sup>A</sup>: produced by SEDICO pharmaceutical CO. 6 October city – Egypt. <sup>B</sup>: Produced by rocche consumer health (Worldwide) S.A., isvicre ile roche mustahzarlari Sanayi, Anonim Sirketi, Levent, Istanbul - Turkey.

HCl and heated in a water bath for 2 min, then it was diluted with 5-10 ml of doubly distilled water and filtered when necessary. The acid concentration in the filtrate was decreased by repeatable dilution and evaporation. The solution was transferred into a 100 ml calibrated flask, diluted to the mark with distilled water and mixed well. Into 0.1 ml of this solution, 3 ml ( $1 \times 10^{-3}$  M) of HL<sup>1</sup> (the best chromogenic reagent) and 5 ml buffer solution of pH=12.0 were added, then the volume was completed to the mark of 10 ml calibrated flask. The absorbance was measured at 510 nm against a reagent blank solution prepared in the same manner for seven times and the results are listed in TABLE 2. The very small values of the relative standard deviations and relative errors of the obtained results compared with the certified values are good indication for the high precession and good accuracy of the investigated method.

## H. Structure elucidation

In order to investigate the molecular structure of the formed Mn(II) complexes with azodyes HL<sup>1</sup>-HL<sup>6</sup>, the solid (1:1) Mn(II)-complexes with HL<sup>1</sup> and HL<sup>6</sup> were prepared and subjected to different analytical methods. The prepared complexes were found to have the following molecular compositions; [MnL<sup>1</sup>AcO(H<sub>2</sub>O)].4H<sub>2</sub>O(1) and [MnL<sup>6</sup>AcO(H<sub>2</sub>O)].4H<sub>2</sub>O(2). The data of elemental analysis are in satisfactory agreement with those calculated from the suggested formula. The complexes are stable to the atmosphere and insoluble in most organic solvents but soluble in DMF.

The low molar conductance values for  $10^{-3}$  M solution of Mn(II)-complexes in DMF which were found to be 5.69 for (1) and 5.76 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> for (2) indicated the non-ionic character of the complexes and also that the acetate ion is inside the coordination sphere of the metal ion<sup>[26]</sup>.

The bonding of the azodyes HL<sup>1</sup> and HL<sup>6</sup> to Mn(II) ions was investigated by comparing the IR spectra of the complexes with those of the free azodyes which reveals the following points:

1. The IR spectra of the solid Mn(II)-complexes (1) and (2) exhibit very broad bands at 3420 and 3351 cm<sup>-1</sup>, respectively, can be assigned to  $\nu(\text{OH})$  of the water molecules associated with the complexes. The presence of lattice water molecules in the complexes makes it is difficult to consider the behavior of the  $\nu(\text{OH})$  band of the phenolic OH groups.
2. The  $\nu(\text{N}=\text{N})$  bands of HL<sup>1</sup> and HL<sup>6</sup> at 1395 and 1405 appeared at 1400 and 1399 cm<sup>-1</sup> in the spectra of the complexes (1) and (2), respectively. These shifts revealed the coordination of the azo nitrogens to the Mn(II) ions.
3. The bonding of the Mn(II) ions to the oxygen of the hydroxy groups and the azo nitrogens is supported by the appearance of two new bands at 535, 425 for complex (1) and 581, 430 cm<sup>-1</sup> for complex (2) which can be assigned to the  $\nu(\text{Mn}-\text{O})$  and  $\nu(\text{Mn}-\text{N})$ , respectively<sup>[27]</sup>.
4. The complexes contain two bands near 1575 and 1535 cm<sup>-1</sup> corresponding to a monodentate acetate anion<sup>[28]</sup>.

The observed magnetic moment for the Mn(II)-complexes amounted to be 5.92 for complex (1) and 5.82 BM for complex (2) at room temperature, are indicative of five unpaired electrons.

The electronic spectra of the Mn(II) complexes were studied as nujol mull and in DMF solution within the range 200-700 nm. The shifts of the band positions together with the change in color of the complexes compared with the free ligands indicate complex formation. The electronic absorption spectra of Mn(II)-complexes compared with those of the free ligands exhibit two new bands at 482 and 558 nm for complex (1) and 487 and 545 nm for complex(2). These two bands can be assigned to  ${}^6\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$  (G) and  ${}^6\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}$  (G) for  $d^5$  systems, respectively. The position of  $\lambda_{\text{max}}$  and the shape of the bands indicate a tetrahedral geometry<sup>[29,30]</sup> of the Mn(II) complexes.

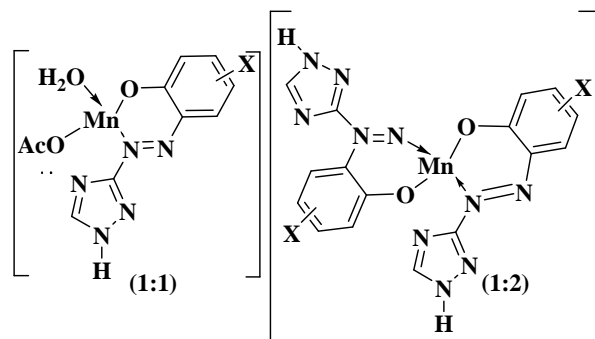
The TGA curves of the investigated Mn(II)-complexes show four essential steps. The first step within temperature range (95-125 °C) is attributed to loss of lattice water molecule (% cal.: 13.75 and 15.11; found

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TABLE 3: Kinetic parameters of the thermal decomposition stages of Mn(II)-complexes (1) and (2).

Comp no.	Step no.	n	r	E (kJ mol <sup>-1</sup> )	ΔH*(kJ mol <sup>-1</sup> )	A(S <sup>-1</sup> )	-ΔS*(kJ K <sup>-1</sup> mol <sup>-1</sup> )	ΔG*(kJ mol <sup>-1</sup> )
1	1	1	0.9749	41.86	39.21	4.9×10 <sup>8</sup>	0.0875	68.04
	2	1	0.9598	26.00	23.36	3.0×10 <sup>8</sup>	0.0915	59.75
	3	0.66	0.8339	22.46	19.81	5.5×10 <sup>7</sup>	0.1056	70.68
	4	1	0.8983	36.36	33.70	4.2×10 <sup>8</sup>	0.0887	89.70
2	1	1	0.9957	28.91	26.26	3.4×10 <sup>8</sup>	0.0906	57.19
	2	1	0.9913	46.85	43.18	4.8×10 <sup>8</sup>	0.0903	83.10
	3	0	0.9955	50.82	48.18	5.9×10 <sup>8</sup>	0.1222	111.61
	4	0	0.9798	27.39	24.74	3.2×10 <sup>8</sup>	0.0910	88.27

E\*: Activation energy, ΔH\*: Enthalpy, A: Frequency factor, ΔS\*: Entropy, ΔG\*: Free energy, r: Correlation coefficient



SCHEME 2: Representative structures of the mode of bonding formed between Mn(II) ion and the azodyes under interest. In which X = m-OH (HL<sup>1</sup>), p-CH<sub>3</sub> (HL<sup>2</sup>), p-COC<sub>2</sub>H<sub>5</sub> (HL<sup>3</sup>), p-COCH<sub>3</sub> (HL<sup>4</sup>), p-CHO (HL<sup>5</sup>) and p-Br (HL<sup>6</sup>)

13.21 and 15.00). The second decomposition step within temperature range 125-180°C is due to loss of the coordinated water molecules (% cal.: 3.44 and 3.78; found: 3.05 and 3.67). The third step involves evolution of the coordinated acetate groups as acetic acid molecules in temperature range 240-280°C (% cal.: 11.26 and 12.38; found: 11.43 and 12.00) for complexes (1) and (2), respectively. The last step involves complete decomposition of the organic part in two unseparated stages, evolution of CO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>O as bi-products and formation of manganese oxide as a final product on temperature range 325-500°C. The results of thermal analysis are a good confirmation for the molecular formula suggested based on the data of elemental analysis.

The kinetic parameters such activation energy (E\*), enthalpy (ΔH\*), entropy (ΔS\*), and free energy (ΔG\*) of the decomposition were evaluated graphically from the Coatsa-Redfern equation<sup>[31]</sup>. The calculated values of E\*, ΔH\*, ΔS\*, and ΔG\* for the different decomposition steps are listed in TABLE 3. The negative values of ΔS indicate that the activated complexes have more ordered systems than reactants.

## CONCLUSION

The results obtained above indicated that the proposed method is high sensitive and selective for the spectrophotometric determination of microgram amounts of manganese(II). It offers advantages like reliability and reproducibility in addition to its simplicity, instant color development and suffers from less interference. It has been successfully applied to the determination of manganese at trace level in pharmaceutical formulations. Based on the data obtained from the solid complexes studies, the Mn(II) ions would be bonded to each ligand molecule (HL<sup>1</sup>-HL<sup>6</sup>) by one covalent bond with the phenolic oxygen in the *ortho*-position to the azo group by proton displacement and one coordination bond with the azo nitrogens which means that the ligands under study behaves as mono basic bidentate ligands toward Mn(II) ion (SCHEME 2).

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