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ORIGINAL ARTICLE

Potentiometric and conductometric studies of malonyl bis(salicyloylhydrazone) and divalent metal complexes

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Abstract A series of complexes of divalent transition metal ions with malonyl bis(salicyloylhydrazone) (H₄MSH) have been prepared and characterized with the help of conductometric, potentiometric methods. The proton–ligand and metal–ligand stability constants were obtained pH-metrically. The electrical conductivity of solid complexes was measured at 289 K. The low molar conductance values observed for these complexes indicate that, they are non-electrolytes. They are soluble to a limited extent in DMF and DMSO. The elemental analyses of the complexes indicate that the complexes have 1:1 and 2:1 (*M:L*) stoichiometry with the existence of water, chloride, acetone molecules inside the coordination sphere as evidence from the IR spectral studies. Further, the complexes have been formulated by comparing C, H, N & metal analysis data, and UV–visible spectra of the complexes have been discussed. The protonation constants of the ligand and the stability constants of their metal complexes will be evaluated potentiometrically. The stoichiometric ratios of the complexes formed in solution will be evaluated applying the molar ratio (spectrophotometric) method and confirmed conductometrically.

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1. Introduction

A number of hydrazone rare earth(III) complexes Guskos et al., 2005 have gained wide interest, because they show a broad spectrum of biological and pharmaceutical activities,

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such as antimicrobial, antitumor, antituberculo-static, and anticancer actions. The values of the protonation constants of 5,5-dimethylcyclo-hexane, 2-(2-hydroxyphenyl)hydrazonol 1,3-dione and the stability constants of its complexes with Ni(II), Sm(III) and Yb(III) were evaluated using pH-metric method (Ramadan et al., 1986) in various mixed aqueous, isopropanol, acetone, ethanol and methanol solvents at 30 °C and ionic strength 0.01 M NaClO₄. The variation of protonation and stability constants with the inverse of dielectric constant or mole-fraction of the solvent was investigated. The metal–ligand stability constants of the Ni(II), Co(II), Zn(II), Mn(II), Cd(II), Fe(III), UO₂(II) and Ln(III) chelates of 3-(α -carboxymethyl aminobenzylidene hydrazino)-5,6-diphenyl-1,2,4-triazine (H₁PHT) were determined in 75% (vol./vol.) dioxane-water medium at 10, 20 and 30 °C and

$\mu = 0.1$ M KNO_3 (Ramadan et al., 1993). The thermodynamic parameters for the proton–ligand and metal–ligand stability constants were obtained by the temperature coefficient method (H_1PHt) behaves as a diprotic bidentate (NNO) donor ligand towards the metal ions as inferred from the IR spectra of its metal complexes. 2,6-Diacetyl pyridine bis (benzoyl hydrazone) (DADBH) and 2,6-diacetyl pyridine bis (2-hydroxybenzoyl hydrazone) (Sasaki, 1986) (DADSH) were prepared, characterized and their analytical applications were studied. Both reagents were compared for the determination of iron and vanadium. A procedure for the determination of V using DADBH was proposed. The reagent reacts with $V(V)$ at pH 2.6–4.0 to produce a yellow complex at $\lambda_{\text{max}} = 335$ nm, $\epsilon = 2.74 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$, in DMF- H_2O (2:8) mixture. DADSH was tested to determine iron. The reagent produces a yellow complex at $\lambda_{\text{max}} = 336$ nm ($\epsilon = 2.77 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) in pH 2–3.5 in DMF- H_2O (1:1) mixture. The sensitivities of the procedures describe are high, but the selectivity is low.

2. Experimental

2.1. Materials and solutions

The chemicals used were of the highest purity available (Aldrich and E. Merck). These were hydrochloric (sp. gr. 1.18), nitric (sp.gr. 1.42) acetic acids, hydrazine hydrate and salicylaldehyde. Copper, nickel, cobalt, iron and chromium chloride, sodium bicarbonate, sodium hydroxide, cetyltrimethylammoniumbromide, potassiumphthalat. Copper and nickel sheets, Ethanol, acetone, diethyl ether, acetonitril, dimethyl formamide and dimethyl sulphoxid. The aqueous solution of metal ion was standardized according to a well known method (Scott and Furman, 1962). Different buffer solution from (pH 2.2–10) were prepared (Vogel, 1978).

2.2. Preparation of ligand (H_4MSH)

To 0.4 M of salicylaldehyde solution, add dropwise 0.2 M of alcoholic solution of malonyldihydrazine with vigorous stirring. The reaction mixture was refluxed on a water bath for one hour and left to cool. The white precipitate which obtained, filtered, washed with ethanol and dried over anhydrous CaCl_2 .

2.3. Preparation of the metal complexes by direct interaction

The metal complexes were prepared by slow addition of 20 ml of 2 mM ethanolic solution of the metal salts, (chloride) to 30 ml of 2 mM of aqueous-ethanol solution of the ligand. The mixture was refluxed on a water bath for 3.5 h and concentrated to half of its volume. The isolated solid complex is filtered off, washed with ethanol and finally dried in a vacuum desiccators over anhydrous CaCl_2 , the yield is (~65–70%) Karabocek et al., 2004.

2.4. Preparation of the metal complexes by electrochemical techniques

The direct anodic electrochemical oxidation of metal was performed in a solution of 50 ml acetone containing ~0.3 g of the

ligand plus 0.5 g of cetyltrimethylammonium bromide as electrolyte. The precipitate formed at the anode surface or in solution was collected, washed with diethylether, dried and kept in vacuum desiccators. The yield (~88–98%) was higher than that obtained by the usual chemical procedure.

2.5. Chemical analyses

To access in suggesting the formula of the isolated complexes, elemental analyses of the dried solids were proceeded as follows: Carbon and hydrogen contents were determined in the Microanalytical Unit of the University of Cairo Egypt, Metals were determined by spectrophotometric methods (Vogel, 1978). Infrared spectra of the ligand and their complexes in the region $4000\text{--}400 \text{ cm}^{-1}$ were recorded on a FT-IR 8400S Fourier transform infrared spectrophotometer (Shimadzu) at Girl's College of Education in Jeddah and FT/IR-460 piles (JASCO), Fourier Trans from Infrared Spectrometer at King Abdul Aziz University in Jeddah. Electronic spectra of DMF solution of the solid complexes were carried out on a Spectro UV/vis Auto (UV-2602) Lab Med. Inc. The absorption spectra of solution were measured on the range 300–800 using 1 cm matched quartz cells at Faculty of Applied Science (Girls), Umm-Al Qura University.

2.6. Conductance procedure

- Molar conductivity of 5×10^{-3} M of the solid complexes was measured with a conductivity meter (JENWAY) 4520 (Italy).
- Conductometric titration of the chosen metal with H_4MSH was performed using conductivity meter (JENWAY) 4520 (Italy). The conductivity meter is calibrated by measuring the conductivity of 0.01 M KCl solution from which the cell constant is determined.

2.7. Potentiometric procedure

The procedure for the determination of the protonation constants of the ligand (H_4MSH) and the stability constants of its complexes with different metal ions, involves the preparation of the following:

- 1 ml of 10^{-3} M HCl plus 2.5 ml KCl and 10 ml of acetonitrile plus 2 ml ethyl alcohol (acid mixture).
- 1 ml of 10^{-3} M HCl plus 2.5 ml KCl and 10 ml of 10^{-3} M H_4MSH in plus 2 ml ethyl alcohol (ligand mixture).
- 1 ml of 10^{-3} M HCl plus 2.5 ml KCl, 2 ml of 10^{-3} M of metal and 10 ml of 10^{-3} M H_4MSH (complex mixture).

The volume of every mixture completed to 25 ml with distilled water. The pH-meter used for carrying out potentiometric titrations (Toshniwal inst. CAT NO-CL-54); ($\text{LC} \pm 0.02$ pH unit).

2.8. Calculation

The average number of protons associated with the ligand, \bar{n}_A at different pH values is calculated utilizing the acid and ligand titration curves using Irving and Rossotti equation (Irving and Rossetti, 1953) as follows:

$$\bar{n}_A = y - \frac{(V_2 - V_1)(N^\circ + E^\circ)}{(V^\circ + V_1)T_{CL}^\circ}, \quad (1)$$

where V_1 and V_2 are the volumes of alkali required to reach the same pH in acid and ligand titration curves. T_{CL}° the total ligand concentration, y is the total number of dissociable protons attached to the ligand molecule, N° is the normality of the alkali, E° is the initial concentration of the free acid and V° is the total volume of the titrated solution, where

$$K_a = \frac{\bar{n}_A}{(1 - \bar{n}_A)[H^+]} \quad (2)$$

for monobasic acid

$$\log K_a = \text{pH} + \log \frac{\bar{n}_A}{1 - \bar{n}_A} \quad (3)$$

for dibasic acid

$$\log K_{a1} = \text{pH} + \log \frac{\bar{n}_A - 1}{2 - \bar{n}_A}. \quad (4)$$

The proton–ligand formation constant, K_a was also calculated from the formation curves obtained by plotting \bar{n}_A versus pH where the pH values at $\bar{n}_A = 0.5$ and 1.5 gives $\log K_a$ and $\log K_{a1}$, respectively.

2.9. Metal–ligand stability constants

The step wise formation constants of the metal complexes in a homogenous solution are given by Eq. (5)

$$K_n = \frac{C_{ML_n}}{C_{ML_{n-1}}} \quad (n = 1, 2, 3, \dots, n), \quad (5)$$

where K_n is called the metal stability constant. The formation constants are obtained by plotting a graph between average number of ligand molecules attached to metal ion \bar{n} and the free ligand exponent (pL) where \bar{n} and pL are calculated using Eqs. (6) and (7) (Irving and Rossetti, 1953):

$$\bar{n} = \frac{(V_3 - V_2)(N^\circ + E^\circ)}{(V^\circ + V_2)\bar{n}_A T_{CM}^\circ} \quad (6)$$

and

$$\text{pL} = \frac{1 + \beta_1[H^+] + \beta_2[H^+]^2 + \beta_3[H^+]^3}{T_{CL}^\circ - \bar{n}T_{CM}^\circ} \cdot \frac{V^\circ + V_3}{V^\circ} \quad (7)$$

where T_{CM}° denotes the total concentration of metal present in solution, β_n^H , is the overall proton ligand stability constant, the other terms have their usual meaning as mentioned before. The successive stability constants are computed using the interpolation at half \bar{n} values from \bar{n} vs. pL formation curves. The values of $\log K_1$, $\log K_2$ and $\log K_3$ were obtained by interpolation at 0.5, 1.5 and 2.5, respectively. Alternatively, the least square method was used for calculation of $\log K_1$ or $\log K_2$ by plotting $\log \frac{\bar{n}}{1 - \bar{n}}$ vs. pL or $\log \frac{\bar{n} - 1}{2 - \bar{n}}$ vs. pL respectively.

3. Results and discussion

3.1. Structural characterization of H_4MSH ligand

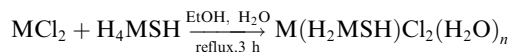
H_4MSH has octa-coordination sites and four labile hydrogen atoms. It may function as mono- and/or di-basic manner through the deprotonation of one or two of the OH groups and tri or tetra-basic through the deprotonation of the car-

bonyl groups. Depending on the data gathered from i.r. spectrum of H_4MSH , the band at 3051 cm^{-1} is due to $\nu(\text{NH})$ of CONH group Husain et al., 1991. The stretching and bending vibrations of the phenolic OH group have appeared at 3205 and 1427 cm^{-1} , respectively (Ibrahim et al., 1985). The sharp bands observed at 1672 and 1651 cm^{-1} are due to the free and bonded carbonyl group (Ibrahim et al., 1985). The $\nu(\text{C}=\text{O})$ phenolic has observed at 1266 cm^{-1} (Husain et al., 1991). The bands at 1571 and 1126 cm^{-1} are attributed to $\nu(\text{C}=\text{N})$ and $\nu(\text{N}=\text{N})$ vibrations, respectively (El-Asmy et al., 1993). The appearance of the $\nu(\text{N}=\text{H})$ band at lower wave number than that reported for similar compounds (Husain et al., 1991; El-Asmy et al., 1993), suggesting an intramolecular hydrogen bonding as shown in Fig. 1a. Strong evidence for the hydrogen bond is the appearance of broad band at 2500 and 1975 cm^{-1} due to $\nu(\text{O}=\text{H} \cdots \text{N})$ vibrations Silverstein et al., 1981.

3.2. Synthesis and structural characterization of $M-H_4MSH$ complexes

New complexes of Cu(II), Ni(II) and Co(II) with H_4MSH , were prepared by chemical and electrochemical methods. The ligand is an example of a novel compound capable of existing multidentate behaviour by virtue of having a greater number of donor atoms and is more flexible in the three dimensions. The reactions of Cu(II), Ni(II), and Co(II) ions with H_4MSH capable of existing the ligand as shown in Fig. 1a – keto, b – keto/enol and c – enol forms under variable experimental conditions.

The major reactions for the complexes prepared by the usual chemical interaction are:



where $M = \text{Cu, Ni or Co}$, $n = 1$ and 2 .

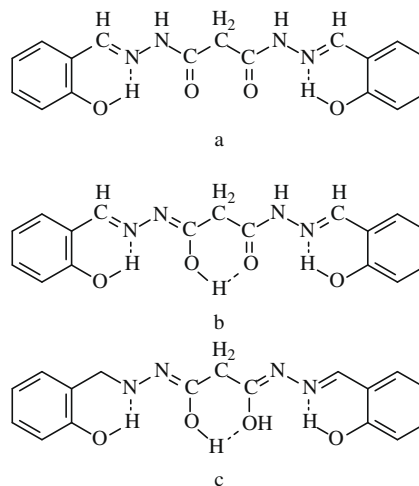
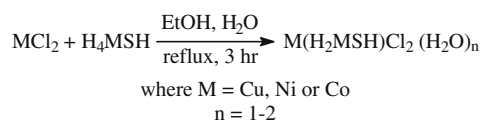
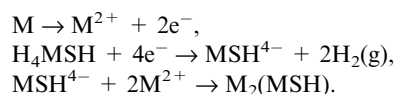


Figure 1 Structural formula of the H_4MSH in the (a) keto (b) keto/enol and (c) enol forms.

The complexes prepared electrochemically follow the following mechanism:



The data gathered from the elemental analysis are given in Table 2. The structure of H₄MSH and some of its chloro

complexes as shown in Table 1, which show that the ligand reacts in the keto form Fig. 1a in the complexes having the formula of M(H₄MSH)(Cl)_n(H₂O)_m where (M = Cu, Ni and Co; n = 2, m = 0–2). On the light of the following evidence: The small shift (< 10 cm⁻¹) to higher wave number of the carbonyl bands is taking as an evidence for their participation in bonding.

All the amides and NH₂ bands remain more or less at the same position. The appearance of ν(M–O) Abu El-Reash

Table 1 Structural formula of the H₄MSH and its complexes.

	Structure	Mwt
<i>Ligand</i>		
H ₄ MSH		340.33
Malonyl bis(salicylhydrazone) (H ₄ MSH)		
<i>Complex prepared electrochemically</i>		
Cu–H ₄ MSH	[Cu ₂ (MSH)(Me ₂ CO) ₂]	569.5898
Ni–H ₄ MSH	[Ni ₂ (MSH)(Me ₂ CO) ₂ (H ₂ O) ₄]	631.877
<i>Complex prepared from chloride salts</i>		
Cu–H ₄ MSH	[Cu(H ₄ MSH)Cl ₂](H ₂ O) ₂	510.883
Ni–H ₄ MSH	[Ni(H ₄ MSH)Cl ₂ (H ₂ O) ₂]·2H ₂ O	542.0278
Co–H ₄ MSH	[Co(H ₄ MSH)Cl ₂ (H ₂ O) ₂]·H ₂ O	524.2708

Table 2 Elemental analysis data of M–H₄MSH complexes.

Type of complexes	Color	Calculated (%)			Found (%)			Molar conductance (mol ⁻¹) _m (ohm ⁻¹ cm ² A)
		C	H	M	C	H	M	
[Cu ₂ (MSH))(Me ₂ CO) ₂] ^a	Green	35.8	2.81	22.3	35.7	2.91	22.1	
[Cu(H ₄ MSH)Cl ₂](H ₂ O) ₂ ^b	Green	39.9	3.10	12.4	39.8	3.00	12.61	25.9
[Ni ₂ (MSH)(Me ₂ CO) ₂ (H ₂ O) ₄] ^a	Green	32.3	2.50	18.7	32.6	2.48	18.6	
[Ni(H ₄ MSH)Cl ₂ (H ₂ O) ₂]·2H ₂ O ^b	Green	37.6	2.90	10.8	37.1	2.72	10.6	16
[Co(H ₄ MSH)Cl ₂ (H ₂ O) ₂]·Cl·H ₂ O ^b	Pink	36.4	2.80	10.5	39.1	3.10	11.5	46.6

^a Complexes prepared electrochemically.

^b Complexes prepared from chloride salts.

et al., 1992 at $\approx 450\text{ cm}^{-1}$ indicate the bonding through the carbonyl oxygen. The molar conductivity values Table 2 are ($25.9\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$) for $[\text{Cu}(\text{H}_4\text{MSH})\text{Cl}_2] \cdot (\text{H}_2\text{O})_2$, ($16\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$) for $[\text{Ni}(\text{H}_4\text{MSH})\text{Cl}_2(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_2$ lie in the range of non-electrolyte complexes and ($46.6\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$) for $[\text{Co}(\text{H}_4\text{MSH})\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl}$. H_2O commensurate with the value of 1:1 electrolyte. From these observations we can conclude that H_4MSH binds with the metal chloride as neutral bidentate ligand coordinating via its carbonyl groups.

The electrochemical technique which is based on electrochemical oxidation of Cu, and Ni in the presence of non-aqueous solution (acetone) of H_4MSH yields complexes with the formulae $\text{M}_2(\text{MSH})(\text{OH})_2(\text{H}_2\text{O})_n(\text{Me}_2\text{CO})_m$ where ($\text{M} = \text{Cu}, \text{Ni}$ and Co , $n = 0-2$, $m = 2$). The ligand act as a tetrabasic hexa-dentate meaning every metal ion forms three bonds with ligand and replaces the four labile hydrogen atoms and complete its coordination sphere by water or acetone molecules. Most of the products are insoluble in the reaction mixture, the collection procedure involved filtration, after which the solid was washed with diethyl ether. The values of the electrochemical efficiency ($E_f = 0.5 \pm 0.07\text{ mol F}^{-1}$) corroborate with the metal to be divalent in these complex (Vogel, 1978). The electrochemical conditions applied during the preparation of complexes are listed in Table 3. All the complexes are stable in air. They are insoluble in most common organic solvents but are easily soluble in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO).

The mode of chelation is confirmed on the light of the following observation: The disappearance of $\nu(\text{C}=\text{O})$ and $\nu(\text{N}_1\text{H})$, $\nu(\text{N}_2\text{H})$ indicating the eno-lization of the amide groups with the appearance of new bands at ≈ 1530 , 1080 and $\approx 990\text{ cm}^{-1}$ due to $\nu(\text{C}=\text{N})$ Abu El-Reash et al., 1992, $\nu_{\text{as}}(\text{C}-\text{O})$ and $\nu_{\text{s}}(\text{C}-\text{O})$ Silverstein et al., 1981 vibrations, respectively. The stretching and bending vibrations of the OH group are completely absent indicating its deprotonation during the complex formation. The band at 1517 cm^{-1} assigned to $\nu(\text{C}=\text{N})$ in the ligand shifts to 1515 cm^{-1} proving that the azo-

methine group is taking part in coordination. The bands observed at the low frequency region at ≈ 450 and $\approx 460\text{ cm}^{-1}$ are assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ vibration respectively (Specia et al., 1974; Ibrahim et al., 1991) The appearance of new bands at $\approx 570\text{ cm}^{-1}$ is a strong evidence of the coordinated water molecules. All these observation suggest the structure as shown in Table 1.

The electronic spectra of Cu(II) complexes. $[\text{Cu}(\text{H}_4\text{MSH})\text{Cl}_2] \cdot (\text{H}_2\text{O})_2$ show two bands at $23,360\text{ cm}^{-1}$ and $29,069\text{ cm}^{-1}$, which is safely assigned to the ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ transition in an tetrahedral symmetry. The magnetic moments value 1.87 BM is below the expected values ($1.7-2.2\text{ BM}$) for a tetrahedral geometry (Said and Tuck, 1981). On the other hand the electronic spectrum of $[\text{Cu}(\text{H}_2\text{MSH})] \cdot (\text{H}_2\text{O})_2$, shows one band at $25,348\text{ cm}^{-1}$ indicating a square-planar geometry (Preti and Tosi, 1976). For square-planar complexes, three spin-allowed transition are possible, assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ but the band could not resolved into three bands. This geometry is further supported by the value of its magnetic moment 1.55 BM . The electronic spectra of other H_4MSH complexes are shown in Fig. 2 and listed in Table 4.

3.3. Absorption spectra of M-H₄MSH complexes

The absorption spectra of the ligand H_4MSH in definite buffer solution at specific pH were scanned over the range $300-800\text{ nm}$. The maxima were obtained for the ligand H_4MSH at 325 nm . On comparing the absorption spectra of $\text{M}^{n+}-\text{L}$ (where $\text{M} = \text{Cu}, \text{Ni}$ and Co) with that of the L alone as shown in Fig. 3 for Cu- H_4MSH .

The red shift of the maximum absorbance of the complexes from the maximum absorption of ligand reveals the formation of compound between the metal species and the ligand. Results listed in Table 5 indicate the maximum absorption of each mixture and their shift from that assigned to the H_4MSH .

The data indicate the presence of shifts account of $\approx 49-204\text{ nm}$ such conspicuous shift is attributed to the increase of

Table 3 The electrochemical data of the M- H_4MSH complexes.

Amount of ligand (mg)	Metal	Initial volt (V)	Time of electrolysis (h)	Metal used (mg)	Yield (mg)	Percent (%)	E_f (mol F^{-1})
300	Cu	25	3	48	370	94	0.47
300	Ni	35	3	22	365	88.3	0.49

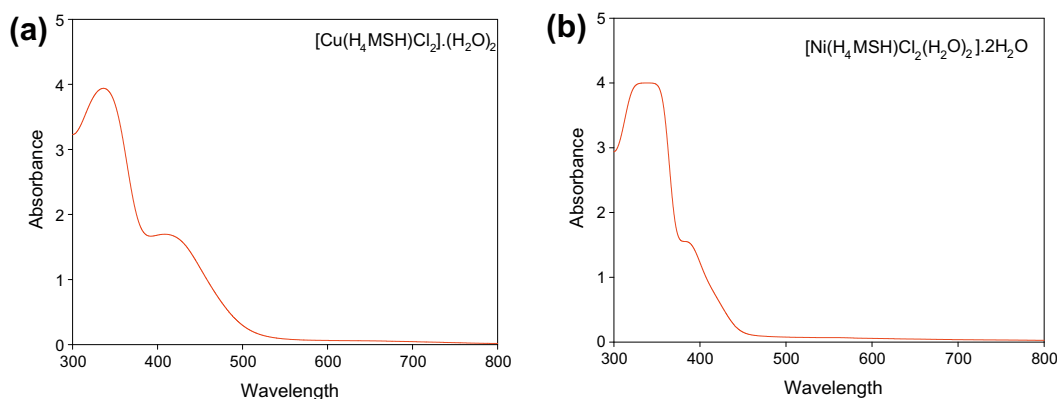


Figure 2 Electronic spectra of (a) Cu- H_4MSH and (b) Ni- H_4MSH complexes prepared from chloride salts.

Table 4 The electronic spectra of M–H₄MSH complexes.

Metals	Type of metal	Empirical formula	Number of bands	λ_{\max} (cm ⁻¹)	Transition	Structure	Magnetic susceptibility (BM)
Cu	Cu ^a	[Cu ₂ (MSH))(Me ₂ CO) ₂]	2	24,038 28,730	² T _{2g} → ² E _g	Tetrahedral	1.92
	Cu ^b	[Cu(H ₄ MSH)Cl ₂](H ₂ O) ₂	2	23,360 29,069	² T _{2g} → ² E _g	Tetrahedral	1.87
Ni	Ni ^a	[Ni ₂ (MSH))(Me ₂ CO) ₂ (H ₂ O) ₄]	2	25,720 31,308	³ A _{2g} → ³ T _{1g} (F) ³ A _{2g} → ³ T _{1g} (P)	Octahedral	3.54
	Ni ^b	[Ni(H ₄ MSH)Cl ₂ (H ₂ O) ₂].2H ₂ O	2	25,531 28,738	³ A _{2g} → ³ T _{1g} (F) ³ A _{2g} → ³ T _{1g} (P)	Octahedral	3.56
Co	Co ^b	[Co(H ₄ MSH)Cl ₂ (H ₂ O) ₂].Cl.H ₂ O	2	24,331 28,571	⁴ T _{1g} → ⁴ A _{2g} ⁴ T _{1g} → ⁴ T _{1g} (P)	Octahedral	4.5

^a Complexes prepared electrochemically.

^b Complexes prepared directly from chloride salt.

delocalization of the π electrons during the reaction with the metal ions leading to the decrease in the energy gap between the excited and ground state (Babko and Plipenko, 1971).

3.4. Molar ratio (spectrophotometric) method

The molar ratio method has been utilized to investigate the type of the compound formed in solution. A series of solutions was prepared by keeping the metal concentration constant and the ligand concentration varied between (1×10^{-5} – 2.3×10^{-4} M).

For H₄MSH, the absorbance of the resulting solutions was measured at their λ_{\max} against the ligand solution as blank. The plots of the absorbance versus the mole fraction of the metal species are presented graphically in Fig. 4 and the distinct stoichiometric ratios of the compounds formed in solution are summarized in Table 6. The data indicate that the forma-

tion of compounds with different ratios, the highly stable complex is formed with 1:2 and 1:1 ratio for Cu²⁺, Ni²⁺ and Co²⁺ with H₄MSH.

Conductometric titrations were performed for in sight to the nature of bonding and stoichiometry of the formed species in solution. In the procedure, the variation of conductance of 50 ml of 10^{-4} M solutions of MSH was followed during the course of titration with 5×10^{-3} M solution of Cu²⁺, Ni²⁺ or Co²⁺. The molar ratio (M/L) was calculated for each increment of metal species and plotted against the conductance values as shown in Fig. 5. The titration graphs obtained are more or less smooth-straight with breaks at definite molecular ratios corresponding to the composition of the formed species in solution. A general behavior of the formed species is the continuous increase in conductance of their solutions. This may be due to the liberation of the highly conducting species

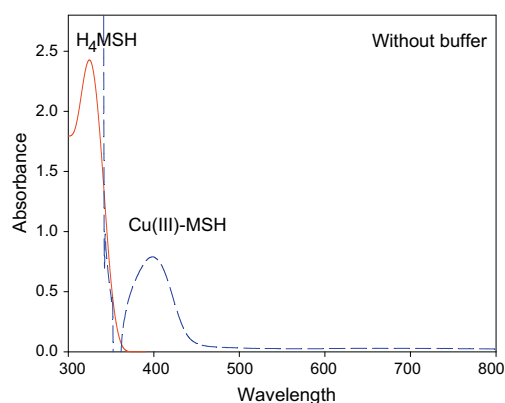


Figure 3 Absorption spectra for H₄MSH and Cu–H₄MSH mixture at pH 6.

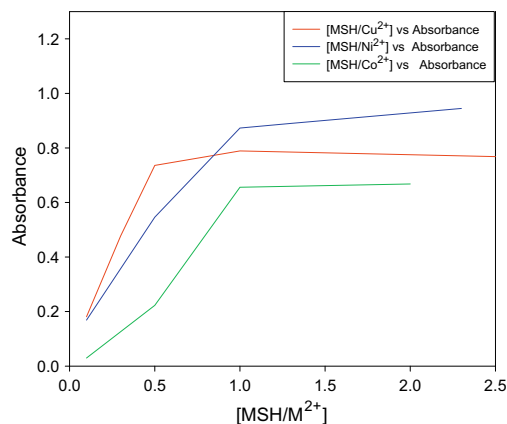


Figure 4 The relation between absorbance vs. [H₄MSH/M²⁺] of M–H₄MSH complexes.

Table 5 Maximum absorbance of the different M–L mixtures and their shift from λ_{\max} of the ligand.

Ligand	Metal species	λ_{\max} M–L (nm)	λ_{\max} L (nm)	Shift from the maxima of absorbance of the ligand (nm)
H ₄ MSH	Cu ²⁺	400	325	75
	Ni ²⁺	379	325	54
	Co ²⁺	390	325	65

Table 6 Stoichiometric ratios of the formed compounds applying from the conductometric titration and molar ratio methods.

Metal ion [M ⁿ⁺]	H ₄ MSH	
	M.R.	Cond.
Cu ²⁺	1:1, 2:1	1:1, 2:1
Ni ²⁺	1:1, 2:1	1:1, 2:1
Co ²⁺	1:1, 2:1	1:1, 2:1

during complexation like hydrogen ions. Since the slopes of portions of the graphs are governed by the change in ionic conductance of the ion present. The slopes of the portions of the graphs vary widely with the ratio of the compound formed. Further the increases of conductance during titration indicate that chelation takes place after deprotonated of ligand at high pH values.

A comparison between the stoichiometric ratios obtained by applying the molar ratio and conductometric titration methods is given in Table 6. Inspection of the data indicates the agreement of results of the stoichiometric ratio of the compounds formed in solution either from the spectrophotometric molar ratio method or from the conductometric titration technique. The titration graphs obtained by applying the preceding

steps are less smooth straight with breaks corresponding to the formation of 1:1 and 2:1 ratio. The 2:1 metal to ligand complexes is highly dissociated and less stable than 1:1 complexes.

3.5. Determination of protonation constants of malonyl bis (salicyloylhydrazone) H₄MSH

Potentiometric method is widely applicable technique currently available for the study of ionic equilibria in solution (Ibrahim et al., 2007). The method depends upon titration of three mixtures (acid mixture, ligand mixture and complex mixture) respectively. The titration curves of H₄MSH Fig. 5 are characterized by the presence of two neutralization steps. So the average number of protons associated with the ligand molecule \bar{n}_A at different pH values was calculated from the acid and ligand titration curves where the first and second protonation constants $\log k_nH$ ($n = 1, 2$) are evaluated from the protonation ligand formation curves Fig. 6 corresponding to 0.5 and 1.5 on the \bar{n}_A scale. In some cases the first protonation constant, $\log k_1H$ cannot be evaluated from the protonation curves as the curves fall at more than 0.5 on the \bar{n}_A scale. Therefore, the values of $\log k_1H$ are calculated using Eq. (8) (Sadhu et al., 1976)

$$\log k_1 = 2pH_{(\bar{n}=1)} - pH_{(\bar{n}=1.5)} \tag{8}$$

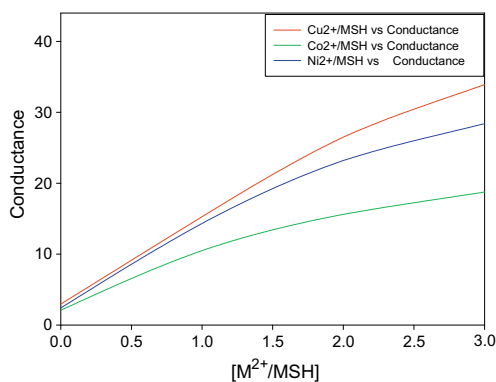


Figure 5 The relation between Conductance vs. [M²⁺/H₄MSH] for (M–H₄MSH) complexes.

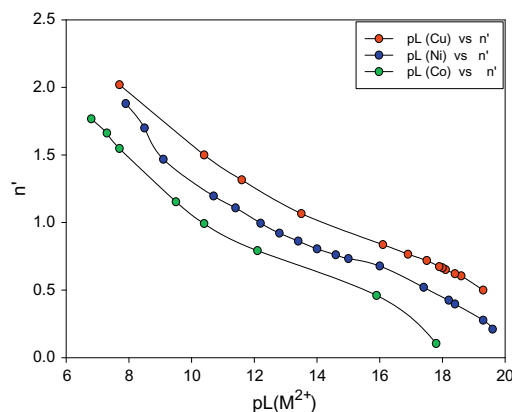


Figure 7 Relation between \bar{n} vs. pL using half method for (M–H₄MSH) complexes.

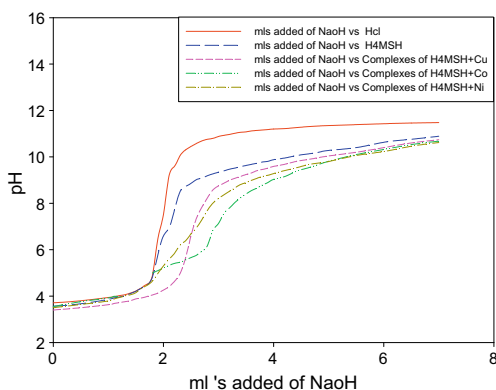


Figure 6 Potentiometric titration curves for (M–H₄MSH) complexes.

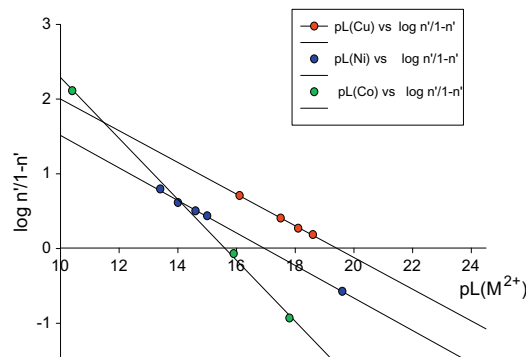


Figure 8 The relation between $\log \frac{\bar{n}}{1-\bar{n}}$ vs. pL for M²⁺.

Table 7 Stability constants for M–H₄MSH complexes.

System M–L	Haff method			Least-squares method		
	Log K_1	Log K_2	Log β	Log K_1	Log K_2	Log β
Cu(II)–MSH	19.2	10.4	29.6	19.4	10.9	30.3
Ni(II)–MSH	17.6	9	26.6	16.9	9.25	26.15
Co(II)–MSH	15.4	8	23.4	15.6	7.65	23.2

The pK_a values are also calculated applying the point wise method by plotting $\log \frac{\bar{n}_A}{1-\bar{n}_A}$ for the first ionization step and $\log \frac{\bar{n}_A-1}{2-\bar{n}_A}$ for the second ionization step versus pL; straight lines are obtained intersecting the x -axis at the pK_a -values Fig. 8.

The high basicity of the hydrazones may be attributed to the presence of strong intramolecular H-bonding especially in less polar medium (95% acetonitrile + 5% DMF). The values of pK_H in acetonitrile and DMF (H₄MSH) are close those reported in literature (Seleem et al., 2003; Seleem, 2003; Moez et al., 1989) for similar hydrazones under the same experimental conditions. Inspection of the data reveals the following: $K_1/K_2 > 1.0$ for most complexes, indicating that the vacant sites of the metal ions are more freely available for binding (Seleem et al., 2006).

3.6. Determination of stability constants for (M–H₄MSH) complexes

The stability constants of Cu²⁺, Ni²⁺ and Co²⁺ complexes with (H₄MSH) are calculated from the complexes and ligand titration curves Fig. 6. The stability constants were calculated by plotting the average number of ligand attached per metal ion \bar{n} against free exponent (pL) as shown in Fig. 7. The \bar{n} and pL values were calculated using the equation indicated in experimental section. The pK values are also calculated applying point wise method by plotting $\log \frac{\bar{n}}{1-\bar{n}}$ against pL for pK_1 as see in Fig. 8.

The calculation of the stability constants ($\log k_1$ and $\log k_2$) of the investigated metal complexes is based on the fact that the pH-measurements during the titration of a ligand solution in presence and in the absence of a metal ion could be used to calculate the free base exponent (pL) and the number of ligand molecules attached per metal ion \bar{n} . The Irving–Rossetti relations $\log \frac{\bar{n}}{1-\bar{n}} = \log k_1 - pL$ and $\log \frac{\bar{n}-1}{2-\bar{n}} = \log k_2 - pL$, have been constructed and analyzed to determine $\log k_1$ and $\log k_2$, respectively. The stability constants are summarized in Table 7.

4. Conclusion

The interaction of Malonyl bis (salicyloylhydrazone) (H₄MSH) with bivalent metal ions has been investigated using different method. The stoichiometry of the formed complexes in solution was ascertained using the spectrophotometric molar ratio method and was confirmed by the conductometric titration technique, the results obtained indicate the formation of 1:1 and 2:1 (M:L), the arrangement of the stability constant in the order Cu²⁺ > Ni²⁺ > Co²⁺ agree with the trend previ-

ously reported (Shukla and Sharma, 1994). The higher of the stability constant of Cu²⁺ complexes is due to Jahn–Teller distortion and to its nature as 3d⁹ element which is different from 3dⁿ elements.

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