

Potentiometric and Thermodynamic Studies of Some Azosulfoxine Derivatives and Their Metal Complexes

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Abstract: The proton-ligand dissociation constants of some azosulfoxine derivatives and metal-ligand stability constants of their complexes with the metal ions (Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+}) have been determined potentiometrically in 0.1 M KCl and 50 % (by volume) DMF–water mixture at (298, 308 and 318) K. The stability constants of the formed complexes increases in the order Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} . The effect of temperature was studied and the corresponding thermodynamic parameters (ΔG , ΔH and ΔS) were derived and discussed. The dissociation process is non-spontaneous, endothermic and entropically unfavourable. The formation of the metal complexes has been found to be spontaneous, endothermic and entropically favourable.

Keywords: Azosulfoxines, potentiometry, stability constants and thermodynamics.

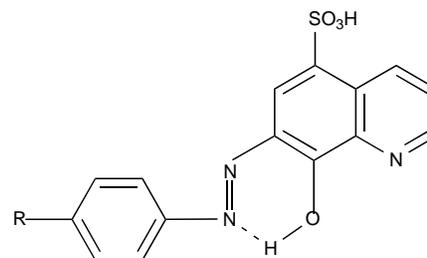
INTRODUCTION

There has been a growing interest in studying azo compounds especially heterocyclic compounds and their transition metal complexes, because of their wide importance in both academic and industrial fields [1-6]. These compounds and their metal complexes are interesting for various reasons. For example the presence of donor atoms such as N, S and O in the compound backbone contributes greatly to their thermal and environmental stability [7]. Other important features include the nature of metal–oxygen bonding interaction and the biological activity of these materials [8]. The presence of $-N=N-$ group can lead to increase the solubility of low valent metal oxidation states due to its π acidity and presence of low lying azo centered π^* molecular orbitals [2, 3]. The azo compounds are used in dyeing processes; some of them are used in analytical separation of many metal ions in a mixture [4], redox active, pH-sensitive and their complexes act as a molecular switch [5]. In continuation of our earlier work [9-13], we report here the dissociation constant of 4-Methoxyphenylazo-5-sulfo-8-hydroxyquinoline (L_1), 4-phenylazo-5-sulfo-8-hydroxyquinoline (L_2) and 4-nitrophenylazo-5-sulfo-8-hydroxyquinoline (L_3) and the stability constants of their complexes with Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} at different temperatures. Furthermore, the corresponding thermodynamic functions of complexation are evaluated and discussed.

EXPERIMENTAL

All compounds and solvents used are pure grade chemicals from BDH Alderich or Sigma.

4-Methoxyphenylazo-5-sulfo-8-hydroxyquinoline (L_1), 4-phenylazo-5-sulfo-8-hydroxyquinoline (L_2) and 4-nitrophenylazo-5-sulfo-8-hydroxyquinoline (L_3) were prepared [14] from aniline or its p-substituted derivatives (10 mmol) which dissolved in hydrochloric acid (20 mmol/25 mL distilled water). The hydrochloric compounds were diazotized below $-5^\circ C$ with a solution of sodium nitrite (0.8 gm, 10 mmol, 30 ml distilled water). The diazonium chloride was coupled with an alkaline solution of sulfoxine (10 mmol) in 20 mL of ethanol containing KOH (10 mmol). The crude dyes were collected by filtration and crystallized from dimethylformamide (DMF), then dried in a vacuum desiccator over anhydrous $CaCl_2$.



R = $-OCH_3$ (L_1), $-H$ (L_2) and $-NO_2$ (L_3)

A ligand solution (0.001 M) was prepared by dissolving an accurately weighed amount of the solid in DMF (Analar). Metal ion solutions (0.0001 M) were prepared from Analar metal chlorides in bidistilled water and standardized with EDTA [15]. Solutions of 0.001 M HCl and 1 M KCl were also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in 50 % (by volume) DMF–water mixture was used as titrant and standardized against oxalic acid (Analar).

The apparatus, general conditions and methods of calculation were the same as in previous work [9-11].

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The following mixtures (i) – (iii) were prepared and titrated potentiometrically at 298 K against standard 0.002 M NaOH in a 50 % (by volume) DMF –water mixture:

- 5 cm³ 0.001 M HCl + 5 cm³ 1 M KCl + 5 cm³ DMF
- 5 cm³ 0.001 M HCl + 5 cm³ 1 M KCl + 5 cm³ 0.001 M ligand.
- 5 cm³ 0.001 M HCl + 5 cm³ 1 M KCl + 5 cm³ 0.001 M ligand + 10 cm³ 0.0001 M metal chloride.

For each mixture, the volume was made up to 50 cm³ with bidistilled water before the titration. These titrations were repeated for temperatures of 308 K and 318 K. The temperature was controlled to within ± 0.05 K by circulating thermostated water (Neslab 2 RTE 220) through the outer jacket of the vessel. The pH measurements were carried out using VWR Scientific Instruments Model 8000 pH-meter accurate to ± 0.01 units. The pH-meter readings in the non-aqueous medium were corrected [16]. The electrode system was calibrated according to the method of Irving *et al.* [17]. All titrations have been carried out between pH 4.0 – 11.0 and under nitrogen atmosphere.

RESULTS AND DISCUSSION

The average number of the protons associated with ligands (L₁, L₂ and L₃) at different pH values, \bar{n}_A , was calculated from the titration curves of the acid in the absence and presence of ligands (L₁, L₂ and L₃).

Applying eq. 1:

$$\bar{n}_A = Y + \frac{(V_1 - V_2)(N^\circ + E^\circ)}{(V^\circ + V_1)TC_L^\circ} \quad (1)$$

where Y is the number of available protons in ligands (L₁, L₂ and L₃) (Y=2) and V₁ and V₂ are the volumes of alkali required to reach the same pH on the titration curve of hydrochloric acid and reagent, respectively, V[°] is the initial volume (50 cm³) of the mixture, TC_L[°] is the total concentration of the reagent, N[°] is the normality of sodium hydroxide solution and E[°] is the initial concentration of the free acid. Thus, the formation curves (\bar{n}_A vs. pH) for the proton-ligand systems were constructed and found to extend between 0 and 2 in the \bar{n}_A scale. This means that ligands (L₁, L₂ and L₃) has two ionizable protons (the enolized hydrogen ion of the phenolic OH group, pK₁^H and the enolized hydrogen ion of the –SO₃H, pK₂^H). Different computational methods [18] were applied to evaluate the dissociation constants. Three replicate titrations were performed. The average values obtained are listed in Table 1. The completely protonated form of the ligands (L₁, L₂ and L₃) has two dissociable protons, that dissociates in the measurable pH range. The deprotonation of the phenolic hydroxy group most probably results in the formation of stable intramolecular H-bonding with the nitrogen of the azo group. Such an interaction decreases the dissociation process of ligands (L₁, L₂ and L₃), *i.e.* increases the pK^H value [19, 20].

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ion (\bar{n}_A) vs. the free ligands exponent (pL), according to Irving and

Table 1: Thermodynamic Functions for the Dissociation Constants of Ligands in 50% (by Volume) DMF-Water Mixture and 0.1 M KCl at Different Temperatures

Compound	T/K	Dissociation Constant		Gibbs energy kJ.mol ⁻¹		Enthalpy kJ.mol ⁻¹		Entropy J.mol ⁻¹ .K ⁻¹	
		pK ₁ ^H	pK ₂ ^H	ΔG ₁	ΔG ₂	ΔH ₁	ΔH ₂	-ΔS ₁	-ΔS ₂
L1	298	9.95	5.61	56.77	32.00			66.37	16.07
	308	9.76	5.46	57.55	32.19	36.99	27.21	66.57	16.16
	318	9.56	5.30	58.08	32.32			66.32	16.06
L2	298	9.62	5.48	54.89	31.26			54.53	18.90
	308	9.40	5.31	55.43	31.31	38.64	25.60	54.51	18.53
	318	9.06	5.20	55.16	31.66			51.94	19.05
L3	298	8.56	5.42	48.84	30.92			45.03	23.45
	308	8.34	5.29	49.18	31.19	35.42	23.93	44.67	23.57
	318	8.17	5.18	49.74	31.53			46.49	23.89

Rossotti [21]. The average number of the reagent molecules attached per metal ion, \bar{n} , and free ligands exponent, pL , can be calculated using eqs. 2 and 3:

$$\bar{n} = \frac{(V_3 - V_2)(N^o + E^o)}{(V^o + V_2)\bar{n}_A TC_M^o} \quad (2)$$

and

$$pL = \log_{10} \frac{\sum_{n=0}^{n=j} \beta_n^H \left[\frac{1}{\text{anti log pH}} \right]^n}{TC_L^o - \bar{n} TC_M^o} \cdot \frac{V^o + V^3}{V^o} \quad (3)$$

where TC_M^o is the total concentration of the metal ion present in the solution, β_n^H is the overall proton-reagent stability constant. V_1 , V_2 and V_3 are the volumes of alkali required to reach the same pH on the titration curves of hydrochloric acid, organic ligand and complex, respectively. These curves were analyzed and the successive metal-ligand stability constants were determined using different computational methods [22, 23]. The values of the stability constants ($\log K_1$ and $\log K_2$) are given in Table 2. The following general remarks can be pointed out:

- (i) The maximum value of \bar{n} was ~ 1 indicating the formation of 1:2 (metal : ligand) complexes only [24].
- (ii) The metal ion solution used in the present study was very dilute (2×10^{-5} M), hence there was no

possibility of formation of polynuclear complexes [25, 26].

- (iii) The metal titration curves were displaced to the right-hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand. The large decrease in pH for the metal titration curves relative to ligand titration curves point to the formation of strong metal complexes [27, 28].
- (iv) For the same ligand at constant temperature, the stability of the chelates increases in the order Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} [29, 30]. This order largely reflects that the stability of Cu^{2+} complexes are considerably larger than those of other metals of the 3d series. Under the influence of both the polarizing ability of the metal ion and the ligand field [31] Cu^{2+} will receive some extra stabilization due to tetragonal distortion of octahedral symmetry in its complexes. The greater stability of Cu^{2+} complexes is produced by the well known *Jahn-Teller* effect [32].

The dissociation constant (pK^H) for ligands (L_1 , L_2 and L_3), as well as the stability constants of its complexes with Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} have been evaluated at 298 K, 308 K, and 318 K, and are given in Tables 1 and 2, respectively. The enthalpy (ΔH) for the dissociation and complexation process was calculated from the slope of the plot pK^H or $\log K$ vs.

Table 2: Stepwise Stability Constants for ML Complexes of Ligands in 50% (by Volume) DMF-Water Mixture and 0.1 M KCl at Different Temperatures

Compound	M ⁿ⁺	298K		308K		318K	
		log K ₁	log K ₂	log K ₁	log K ₂	log K ₁	log K ₂
L1	Mn ²⁺	7.41	6.34	7.56	6.48	7.71	6.62
	Co ²⁺	7.59	6.51	7.75	6.65	7.89	6.80
	Ni ²⁺	7.72	6.63	7.88	6.77	8.02	6.91
	Cu ²⁺	7.95	6.87	8.12	7.03	8.25	7.20
L2	Mn ²⁺	7.29	6.22	7.44	6.36	7.60	6.60
	Co ²⁺	7.47	6.39	7.62	6.54	7.76	6.70
	Ni ²⁺	7.60	6.52	7.74	6.66	7.89	6.80
	Cu ²⁺	7.84	6.77	7.98	6.92	8.15	7.08
L3	Mn ²⁺	7.12	6.06	7.25	6.20	7.39	6.34
	Co ²⁺	7.28	6.22	7.42	6.36	7.36	6.60
	Ni ²⁺	7.40	6.34	7.54	6.48	7.70	6.62
	Cu ²⁺	7.66	6.60	7.81	6.75	7.96	6.89

$1/T$ using the graphical representation of *van't Hoff* eqs. 4 and 5:

$$\Delta G = -2.303 RT \log K = \Delta H - T \Delta S \quad (4)$$

or

$$\log K = (-\Delta H / 2.303 R)(1/T) + (\Delta S / 2.303 R) \quad (5)$$

From the ΔG and ΔH values one can deduce the entropy ΔS using the well known relationships 4 and 6:

$$\Delta S = (\Delta H - \Delta G) / T \quad (6)$$

All thermodynamic parameters of the dissociation process of ligands (L_1 , L_2 and L_3) are recorded in Table 1. From these results the following conclusions can be made:

- (i) The pK^H values decrease with increasing temperature, i.e. the acidity of the ligand increases [9].
- (ii) A positive value of ΔH indicates that the process is endothermic.
- (iii) A large positive value of ΔG indicates that the dissociation process is not spontaneous [33].
- (iv) A negative value of ΔS is obtained due to the increased order as a result of the solvation process.

All the thermodynamic parameters of the stepwise stability constants of complexes are recorded in Table 3. It is known that the divalent metal ions exist in solution as octahedrally hydrated species [23] and the obtained values of ΔH and ΔS can then be considered as the sum of two contributions: (a) release of H_2O molecules, and (b) metal-ligand bond formation. Examination of these values shows that:

- (i) The stability constants ($\log K_1$ and $\log K_2$) for ligands (L_1 , L_2 and L_3) complexes increase with increasing temperature, i.e. its stability constants increase with increasing temperature [34].
- (ii) The negative value of ΔG for the complexation process suggests the spontaneous nature of such processes [35].
- (iii) The ΔH values are positive, meaning that these processes are endothermic and favourable at higher temperature.
- (iv) The ΔS values for the ligand complexes are positive, confirming that the complex formation is entropically favourable [11].

An inspection of the results in Table 1 reveals that the pK^H values of (L_2) and its substituted derivatives are influenced by the inductive or mesomeric effect of the substituents. The $p\text{-OCH}_3$ derivatives (L_1) have a lower acidic character (higher pK^H values) than the $p\text{-NO}_2$ (L_3). This is quite reasonable because the

Table 3: Thermodynamic Functions for the Stability Constants of ML Complexes in 50% (by Volume) DMF–Water Mixture and 0.1 M KCl at 298K

Compound	Mn ⁺	Gibbs energy/kJ.mol ⁻¹		Enthalpy/kJ.mol ⁻¹		Entropy/J.mol ⁻¹ .K ⁻¹	
		ΔG_1	ΔG_2	ΔH_1	ΔH_2	ΔS_1	ΔS_2
L1	Mn ²⁺	42.28	36.17	27.21	25.39	233.18	206.57
	Co ²⁺	43.30	37.41	27.23	26.29	236.67	212.85
	Ni ²⁺	49.75	37.82	27.23	25.39	258.32	212.11
	Cu ²⁺	51.06	39.19	27.25	29.92	262.78	231.91
L2	Mn ²⁺	41.59	35.49	28.11	34.37	233.89	234.42
	Co ²⁺	42.62	36.46	26.31	28.11	250.43	216.67
	Ni ²⁺	43.36	37.20	26.29	25.39	233.72	210.03
	Cu ²⁺	44.73	38.60	28.09	28.11	244.36	233.85
L3	Mn ²⁺	40.62	34.57	24.84	25.39	219.66	201.20
	Co ²⁺	41.53	35.49	25.39	34.37	224.56	234.42
	Ni ²⁺	42.22	36.17	27.19	25.39	232.91	206.57
	Cu ²⁺	43.70	37.65	27.21	26.31	237.95	214.63

presence of p -OCH₃ group (i.e. an electron-donating effect) will enhance the electron density by their high positive inductive or mesomeric effect, whereby a stronger O—H bond is formed. The presence of p -NO₂ group (i.e. an electron-withdrawing effect) will lead to the opposite effect. The para substituent in the phenyl moiety have a direct influence on the pK^H values of the investigation compounds, revealing the coplanarity of the molecule and thus affording a maximum resonance via delocalization of its π -system.

REFERENCES

- [1] Butler MS. The Role of Natural Product Chemistry in Drug Discovery. *J Nat Prod* 2004; 67: 2141-53. <http://dx.doi.org/10.1021/np040106y>
- [2] Kurihara M, Hirooka A, Kume S, Sugimoto M, Nishihara H. Redox-conjugated reversible isomerization of ferrocenylazobenzene with a single green light. *J Am Chem Soc* 2002; 124: 8800-10. <http://dx.doi.org/10.1021/ja026625+>
- [3] Yamaguchi K, Kume S, Namiki K, Murata M, Tamia N, Nishihara H. UV-Vis, NMR, and time-Resolved spectroscopy analysis of photoisomerization behavior of three- and six-azobenzene-bound tris(bipyridine) cobalt complexes. *Inorg Chem* 2005; 44: 9056-67. <http://dx.doi.org/10.1021/ic0513538>
- [4] Mubarak AT, El-Assiery SA. Supramolecular structures and properties models of macrocyclic polymer complexes. *Appl Organomet Chem* 2004; 18: 343-52. <http://dx.doi.org/10.1002/aoc.645>
- [5] Otsuki J, Omokawa N, Yoshiba K, Yoshiba I, Akasaka T, Suenobu T, *et al.* Synthesis and structural, electrochemical, and optical properties of Ru(II) complexes with azobis(2,2'-bipyridine)s. *Inorg Chem* 2003; 42: 3057-66. <http://dx.doi.org/10.1021/ic026040g>
- [6] Aziz MS, El-Sonbati AZ, Hilali AS. D.C. conduction phenomenon of some rhodanine azo complexes. *Chem Pap* 2002; 56: 305-308.
- [7] Li X, Jiao Y, Li S. The syntheses, properties and application of new conducting polymers. *Eur Polym J* 1991; 27: 1345-51. [http://dx.doi.org/10.1016/0014-3057\(91\)90233-E](http://dx.doi.org/10.1016/0014-3057(91)90233-E)
- [8] Misra TK, Das D, Sinha C. Chemistry of azoimidazoles: synthesis, spectral characterization and redox properties of bis(N(1)-alkyl-2-(aryloxy)imidazole) copper(I) and silver(I) complexes. *Polyhedron* 1997; 16: 4163-70. [http://dx.doi.org/10.1016/S0277-5387\(97\)00127-7](http://dx.doi.org/10.1016/S0277-5387(97)00127-7)
- [9] El-Bindary AA, El-Sonbati AZ, Diab MA, Abd El-Kader MK. Potentiometric and Thermodynamic Studies of Some Schiff-base Derivatives of 4-Aminoantipyrine and Their Metal Complexes. *J Chem* 2013; ID 682186.
- [10] Mubarak AT, Al-Shihri AS, Nassef HM, El-Bindary AA. Potentiometric and thermodynamic studies of vanillin and its metal complexes. *J Chem Eng Data* 2010; 55: 5539-42. <http://dx.doi.org/10.1021/je100266u>
- [11] Mubarak AT, El-Bindary AA. Potentiometric and thermodynamic studies of 4-(1H-indol-3-yl)butanoic acid and its metal complexes. *J Chem Eng Data* 2010; 55: 5543-46. <http://dx.doi.org/10.1021/je100267s>
- [12] Al-Sarawy AA, El-Bindary AA, El-Sonbati AZ, Mokpel MM. Potentiometric and thermodynamic studies of azosulfonamide drugs. *Polish J Chem* 2006; 80: 289-95.
- [13] El-Ghamaz NA, El-Mallah HM, El-Sonbati AZ, Diab MA, El-Bindary AA, Barakat AM. Optical properties studies on metal-ligand bonding of novel quinoline azodyes thin films. *Solid State Sci* 2013; 22: 56-64. <http://dx.doi.org/10.1016/j.solidstatesciences.2013.05.005>
- [14] Diab MA, El-Sonbati AZ, El-Bindary AA, Barakat AM. Supramolecular spectral studies on metal-ligand bonding of novel quinoline azodyes. *Spectrochim Acta Part A* 2013; 116: 428-39. <http://dx.doi.org/10.1016/j.saa.2013.07.053>
- [15] Jeffery GH, Bassett J, Mendham J, Deney RC, Vogel's textbook of quantitative chemical analysis. 5th ed. Longman: London 1989.
- [16] Bates RG, Paabo M, Robinson RA. Interpretation of pH measurements in alcohol-water solvents. *J Phys Chem* 1963; 67: 1833-38. <http://dx.doi.org/10.1021/j100803a022>
- [17] Irving HM, Miles MG, Pettit LD. A Study of some problems in determining the stoichiometric proton dissociation constants of complexes by potentiometric titrations using a glass electrode. *Anal Chim Acta* 1967; 38: 475-88. [http://dx.doi.org/10.1016/S0003-2670\(01\)80616-4](http://dx.doi.org/10.1016/S0003-2670(01)80616-4)
- [18] Irving H, Rossotti HS. The Calculation of formation curves of metal complexes from pH titration curves in mixed solvents. *J Chem Soc* 1954; 2904-10. <http://dx.doi.org/10.1039/jr9540002904>
- [19] Farkas E, Csoka H. Solution equilibrium studies on metal complexes of 2,3-dihydroxy-phenylalanine-hydroxamic acid (Dopaha) and models: Catecholate versus hydroxamate coordination in iron(III)-, aluminium(III)- and molybdenum(VI)-Dopaha complexes. *J Inorg Biochem* 2002; 89: 219-26. [http://dx.doi.org/10.1016/S0162-0134\(02\)00379-3](http://dx.doi.org/10.1016/S0162-0134(02)00379-3)
- [20] Omar MM, Mohamed GG. Potentiometric, spectroscopic and thermal studies on the metal chelates of 1-(2-thiazolylazo)-2-naphthalenol. *Spectrochim Acta Part A* 2005; 61: 929-36. <http://dx.doi.org/10.1016/j.saa.2004.05.040>
- [21] Irving H, Rossotti HS. Methods for computing successive stability constants from experimental formation curves. *J Chem Soc* 1953; 3397-405. <http://dx.doi.org/10.1039/jr9530003397>
- [22] Rossotti FJC, Rossotti HS. Graphical methods for determining equilibrium constants. I. Systems of mononuclear complexes. *Acta Chem Scand* 1955; 9: 1166-76. <http://dx.doi.org/10.3891/acta.chem.scand.09-1166>
- [23] Beck MT, Nagybal I. Chemistry of complex equilibrium. Wiley: New York 1990.
- [24] Khalil MM, Radalla AM, Mohamed AG. Potentiometric investigation on complexation of divalent transition metal ions with some zwitterionic buffers and triazoles. *J Chem Eng Data* 2009; 54: 3261-72. <http://dx.doi.org/10.1021/je9002459>
- [25] Sanyal P, Sengupta GP. Potentiometric studies of complex-formation of some trivalent rare-earths with p,p' -bromosulphonosalicylidene anil. *J Ind Chem Soc* 1990; 67: 342-46.
- [26] Sridhar S, Kulanthaipandi P, Thillaiarasu P, Thanikachalam V, Manikandan G. Protonating and chelating efficiencies of some biologically important thiocarbonohydrazides in 60 % (v/v) ethanol-water systems by potentiometric and spectrophotometric methods. *World J Chem* 2009; 4: 133-40.
- [27] Athawale VD, Lele V. Stability constants and thermodynamic parameters of complexes of lanthanide ions and (\pm)-norvaline. *Chem Eng Data* 1996; 41: 1015-19. <http://dx.doi.org/10.1021/je950306z>
- [28] Athawale VD, Nerkar SS. Stability constants of complexes of divalent and rare earth metals with substituted salicynals. *Monatsh Chem* 2000; 131: 267-76. <http://dx.doi.org/10.1007/s007060070102>

- [29] Ibañez GA, Escandar GM. Complexation of cobalt(II), nickel(II) and zinc(II) ions with mono and binucleating azo compounds: A potentiometric and spectroscopic study in aqueous solution. *Polyhedron* 1998; 17: 4433-41. [http://dx.doi.org/10.1016/S0277-5387\(98\)00249-6](http://dx.doi.org/10.1016/S0277-5387(98)00249-6)
- [30] Malik WU, Tuli GD, Madan RD. Selected topics in inorganic chemistry. 3rd ed: Chand S & Company LTD, New Delhi 1984.
- [31] Harlly FR, Burgess RM, Alcock RM. Solution equilibria. Ellis Harwood: Chichester 1980; p. 257.
- [32] Orgel LE. An introduction to transition metal chemistry ligand field theory. Methuen; London 1966; p. 255.
- [33] Bebot-Bringaud A, Dange C, Fauconnier N, Gerard C. ³¹P NMR, potentiometric and spectrophotometric studies of phytic acid ionization and complexation properties toward Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Cd²⁺. *J Inorg Biochem* 1999; 75: 71-78. [http://dx.doi.org/10.1016/S0162-0134\(99\)00041-0](http://dx.doi.org/10.1016/S0162-0134(99)00041-0)
- [34] Gaber M, Al-Shihry SS, El-Bindary AA. Potentiometric and thermodynamic studies of 2-mercapto-5-(1-hydroxynaphthylidene amino)-1,3,4-thiadiazole and its metal complexes. *J Therm Anal Calorim* 2005; 82: 63-68. <http://dx.doi.org/10.1007/s10973-005-0842-z>
- [35] Mubarak AT, El-Sonbati AZ, El-Bindary AA. Potentiometric and conductometric studies on the complexes of some transition metals with rhodanine azosulfonamide derivatives. *XI. Chem Pap* 2004; 58: 320-23.

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