

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Correlation between ionic radii of metals and thermal decomposition of supramolecular structure of azodye complexes



SPECTROCHIMICA ACTA

CrossMark

A.Z. El-Sonbati^{a,*}, M.A. Diab^a, A.A. El-Bindary^a, A.M. Eldesoky^{b,2}, Sh.M. Morgan^{a,1}

^a Chemistry Department, Faculty of Science, Damietta University, Damietta, Egypt
^b Engineering Chemistry Department, High Institute of Engineering & Technology, Damietta, Egypt

HIGHLIGHTS

G R A P H I C A L A B S T R A C T

The structure of the metal complexes.

- Complexes of monobasic tridentate/ neutral bidentate ligand were synthesized and characterized.
- X-ray diffraction pattern show polycrystalline phase for pyrazolone azodye.
- Molecular structures of ligand are optimized theoretically and quantum parameters are calculated.
- The ligand and its Cu(II) complexes (**2** and **4**) have very high antifungal activity against *P. italicum*.
- The inhibition efficiency of the tested ligand increase with increasing of its concentrations.

ARTICLE INFO

Article history: Received 16 May 2014 Received in revised form 4 July 2014 Accepted 17 July 2014 Available online 1 August 2014

Keywords: Pyrazolone azodye Supramolecular structure of complexes ESR study Thermodynamic parameters Corrosion inhibition EIS study $H_{3}C$ N $H_{2}O$ $H_{2}O$ $H_{3}C$ O $H_{2}O$ $H_{3}C$ O $H_{2}O$ $H_{2}O$

M = Cu(II) (4), Co(II) (5), Ni(II) (6)

ABSTRACT

An interesting azodye heterocyclic ligand of copper(II), cobalt(II), nickel(II) and uranyl(II) complexes have been synthesized by the reaction of metal salts with 5-(2.3-dimethyl-1-phenylpyrazol-5-one azo)-2-thioxo-4-thiazolidinone (HL) yields 1:1 and 1:2 (M:L) complexes depending on the reaction conditions. The elemental analysis, magnetic moments, spectral (UV-Vis, IR, ¹H and ¹³C NMR and ESR) and thermal studies were used to characterize the isolated complexes. The molecular structures of the ligand tautomers are optimized theoretically and the quantum chemical parameters are calculated. The IR spectra showed that the ligand (HL) act as monobasic tridentate/neutral bidentate through the (-N=N), enolic $(C-O)^{-}$ and/or oxygen keto moiety groups forming a five/six-membered structures. According to intramolecular hydrogen bond leads to increasing of the complexes stability. The molar conductivities show that all the complexes are non-electrolytes. The ESR spectra indicate that the free electron is in d_{xy} orbital. The calculated bonding parameter indicates that in-plane σ -bonding is more covalent than in-plane π -bonding. The coordination geometry is five/six-coordinated trigonal bipyramidal for complex (1) and octahedral for complexes (**2–6**). The value of covalency factor β_1^2 and orbital reduction factor K accounts for the covalent nature of the complexes. The activation thermodynamic parameters are calculated using Coats-Redfern and Horowitz-Metzger methods. The synthesized ligand (HL) and its Cu(II) complexes (1, 2 and 4) are screened for their biological activity against bacterial and fungal species. The ligand (HL) showed antimicrobial activities against Escherichia coli. The ligand (HL) and its Cu(II) complexes (2 and 4) have very high antifungal activity against Penicillium italicum. The inhibitive action of ligand (HL), against the corrosion of

* Corresponding author. Tel.: +20 1060081581; fax: +20 572403868. *E-mail address:* elsonbatisch@yahoo.com (A.Z. El-Sonbati).

² Present address: Al-Qunfudah Center for Scientific Research (QCSR), Al-Qunfudah, Umm Al-Qura University, Saudi Arabia.

¹ Abstracted from her Ph.D.

C-steel in 2 M HCl solution has been investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

© 2014 Elsevier B.V. All rights reserved.

Introduction

Diab et al. [1–4] reveals an excellent work devoted to synthesis and characterization of azodyes as well as their metal complexes. The variety of coordination modes of rhodanine azo derivatives and/or pyrazolone Schiff base derivatives has been demonstrated in a number of complexes and their biological applications have been of considerable interest.

The field of azodye complexes was fast developing on account of the wide variety of possible structures for the ligands depending upon the amines. Many attempts were done to prepare symmetric/ asymmetric polydentate ligands in order to achieve rare coordination number with divalent metal ions whose importance was mainly due to their ability to form metal chelates. Because of new interesting applications found in the field of pesticides and medicine, the metal complexes with bi/tridentate O, N/O, N, O types of alternative structures had attracted the attention of chemists by El-Sonbati et al. [5,6].

The pyrazolone derivatives and their metal complexes have been played an important role in the development of coordination chemistry and potentiometric studies as they readily form stable complexes with most transition metals by El-Bindary et al. [3,7–9].

Rhodanine azo compounds have been studied the antimicrobial activity and comparing antimicrobial activity results of rhodanine azo compounds with the standard antibacterial and antifungal drugs in addition to studying optical absorption properties [2,10].

Carbon steel is the major structural material in industry, the protection of steel against corrosion has attracted much attention [11]. Inhibitors are used in this process to control metal dissolution. Most of the well-known acid inhibitors are organic compounds containing O, S and/or N atoms [12–17]. Corrosion inhibition occurs *via* adsorption of the organic molecule on the corroding metal surface following some known adsorption isotherms with the polar groups acting as active centers in the molecules.

The objectives of the present work are (i) the synthesis of 5-(2,3dimethyl-1-phenylpyrazol-5-one azo)-2-thioxo-4-thiazolidinone (HL) (Fig. 1); (ii) the synthesis of M(II) complexes derived from this ligand and characterization by elemental analysis, spectral studies, conductance, magnetic measurements as well as thermal analysis studies; (iii) the molecular structures of the ligand tautomers have been discussed; (iv) investigation the stereochemistry of the complexes according to the electronic spectra and other measurements; (v) study the antimicrobial activity of (HL) and Cu(II) complexes (1, 2 and 4) and (vi) study the effect of ligand (HL) as inhibitor for the corrosion of C-steel in 1 M HCl solution and determining the corrosion rate in the absence and presence of different concentrations of HL by the electrochemical techniques (potentiodynamic polarization methods and impedance method) at 25 °C.

Experimental

All the chemicals used were of British Drug House (BDH) quality.

Synthesis of the ligand (HL)

In a typical preparation, 25 ml of distilled water containing 0.01 mol hydrochloric acid were added to 1-phenyl-2,3-dimethyl-4-amino pyrazol-5-one (0.01 mol) as shown in Scheme 1. To the

resulting mixture stirred and cooled to 0 °C, a solution of 0.01 mol sodium nitrite in 20 ml of water was added dropwise. The formed diazonium chloride was consecutively coupled with an alkaline solution of 0.01 mol 2-thioxo-4-thiazolidinone, in 10 ml of pyridine. Immediately, the orange precipitate formed was filtered through sintered glass crucible, washed several times by distilled water. The crude products was purified by recrystallization from hot ethanol, yield ~77% then dried in vacuum desiccator over P_2O_5 . The elemental analysis of the HL is collected in Table 1. The present ligand (HL) was previously prepared under the method described elsewhere [18,19] by coupling an equimolar of 1-phenyl-2,3-dimethyl-4-amino pyrazol-5-one and 2-thioxo-4-thiazolidinone in ethanol (30 ml) (Fig. 1). The structure of formed azodye was established by IR and ¹H NMR spectroscopes.

General method of synthesis of complexes

Complexes of $M(II)/UO_2(II)$ (1, 2 and 4–7) were prepared by refluxing the respective methanolic solutions of the metal salts and the HL in 1:1 except complex (7) (1:2) molar ratio for 4–6 h. The resulting solution, on cooling yielded respective solids, which were filtered, washed with methanol and ether and dried over P_2O_5 in vacuum. Complex (3) was prepared by a methanolic displacement of the acetate anion of the copper acetate by the addition of 1 mmol each of the methanolic solutions of KSCN to the reaction mixture of the ligand and copper acetate in methanol. The resulting solution was refluxed for 3 h and left overnight. The solid separated were filtered, washed with methanol and ether and dried over P_2O_5 in vacuum. The elemental analyses of the HL and its metal complexes are given in Table 1.

Biological activity investigation

For this investigation the agar well diffusion method was applied [2,4]. The antibacterial activities of the investigated compounds were tested against two local Gram positive bacterial species (Bacillus cereus and Staphylococcus aureus) and two local Gram negative bacterial species (Escherichia coli and Klebsiella pneumoniae) on nutrient agar medium. Also, the antifungal activities were tested against four local fungal species (Aspergillus niger, Alternaria alternata, Penicillium italicum and Fusarium oxysporium) on DOX agar medium. The concentrations of each solution were 50 μ g/ml, 100 μ g/ml and 150 μ g/ml. By using a sterile cork borer (10 mm diameter), wells were made in agar medium plates previously seeded with the test microorganism. 200 µl of each compound was applied in each well. The agar plates were kept at 4 °C for at least 30 min. to allow the diffusion of the compound to agar medium. The plates were then incubated at 37 °C or 30 °C for bacteria and fungi, respectively. The diameters of inhibition zone were determined after 24 h and 7 days for bacteria and fungi, respectively. Penicillin and miconazole were used as reference substances against bacteria and fungi, respectively.

Corrosion measurements

Tests were performed on C-steel specimens of the following composition (weight%): 0.200 C, 0.350 Mn, 0.024 P, 0.003 S, and the remainder Fe.



Fig. 1. The structure of pyrazolone azodye (HL).

Solutions

The aggressive solutions 2 M HCl were prepared by dilution of analytical grade (37%) HCl with bi-distilled water. The concentration range of the ligand (HL) used was 1×10^{-6} – 11×10^{-6} M.

Polarization measurements

Polarization experiments were carried out in a conventional three-electrode cell with a platinum foil as counter electrode and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as reference electrode. The working electrode was in the form of a square cut from mild steel embedded in epoxy resin of polytetrafluoroethylene (PTFE) so that the flat surface (1 cm^2) was the only surface of the electrode. Tafel polarization curves were obtained by changing the electrode potential automatically from -500 to +500 mV at open circuit potential with a scan rate of 1 mV s⁻¹. Stern–Geary method used for the determination of



Scheme 1. The formation mechanism of pyrazolone azodye (HL).

fable 1	
Elemental analysis (C, H, S, N and M) ^a of the ligand (HL) and its complexes.	

Compound ^b	Found (o				
	С	Н	Ν	S	М
HL	48.21 (48.42)	3.64 (3.75)	19.88 (20.17)	18.22 (18.44)	-
[Cu(L)Cl(OH ₂)] (1)	36.40	3.19	15.32	14.12	13.89
	(36.28)	(3.02)	(15.12)	(13.82)	(13.72)
$[Cu(L)(ONO_2)(OH_2)_2]$ (2)	33.23	3.28	16.87	12.76	12.79
	(33.10)	(3.15)	(16.55)	(12.51)	(12.52)
$[Cu(L)(NCS)(OH_2)_2]$ (3)	35.87	3.33	16.99	19.34	12.77
	(35.75)	(3.18)	(16.68)	(19.07)	(12.62)
$[Cu(L)(OAc)(OH_2)_2] \cdot H_2O$ (4)	36.85	3.86	13.82	12.55	12.45
	(36.74)	(3.64)	(13.40)	(12.25)	(12.25)
$[Co(L)(OAc)(OH_2)_2]$ ·2H ₂ O (5)	35.94	3.73	13.45	12.32	11.36
	(35.83)	(3.55)	(13.06)	(11.94)	(11.00)
[Ni(L)(OAc)(OH ₂) ₂]·2H ₂ O (6)	36.00	3.68	13.44	12.24	11.33
	(35.84)	(3.55)	(13.07)	(11.95)	(10.96)
$[UO_2(L)_2(OH_2)_2]$ (7)	33.74	3.01	14.42	13.21	24.43
	(33.67)	(2.81)	(14.03)	(12.83)	(23.85)

^a The excellent agreement between calculated and experimental data supports the assignment suggested in the present work.

^b L is the anions of the ligand HL as given in Scheme 1, insoluble in water, but partially soluble in ethanol and completely soluble in DMF.

corrosion current is performed by extrapolation of anodic and cathodic Tafel lines to a point which gives $\log i_{corr}$ and the corresponding corrosion potential (E_{corr}) for inhibitor free acid and for each concentration of inhibitor. Then i_{corr} was used for calculation of inhibition efficiency and surface coverage (θ) as in Eq. (1):

$$\% IE = \theta \times 100 = [1 - (i_{\text{corr(inh)}}/i_{\text{corr(free)}})] \times 100, \tag{1}$$

where $i_{\text{corr(free)}}$ and $i_{\text{corr(inh)}}$ are the corrosion current densities in the absence and presence of ligand (HL), respectively.

Impedance measurements

All EIS measurements were performed at open circuit potential E_{ocp} at room temperature over a wide frequency range of (20 kHz to 0.5 Hz). The sinusoidal potential perturbation was 10 mV in amplitude peak to peak.

Analytical and physical measurements

Elemental microanalyses of the separated ligand and solid chelates for C, H, and N were determined on Automatic Analyzer CHNS Vario ELIII, Germany. The analyses were repeated twice to check the accuracy of the analyzed data. The metal content in the complexes was estimated by standard methods [20]. The ¹H NMR spectrum was obtained with a JEOL FX90 Fourier transform spectrometer with DMSO-d₆ as the solvent and TMS as an internal reference. The infrared spectra were recorded as KBr disks using a



Fig. 2. The optimized structures of ligand tautomers within numbering of atoms.

Table 2Net charges on active centers of the ligand tautomers.^a

Atom	Charges			
	(A)	(B)	(C)	(D)
N(15)	-0.171	-0.171	-0.384	-0.427
O(21)	-0.570	-0.527	-0.356	-0.138
N(23)	-0.246	-0.171	-0.417	-0.492
O(6)	-0.570	-0.570	-0.570	-0.570
S(16)	-0.371	-0.242	-0.242	-0.282
S(22)	-0.380	-0.380	-0.380	-0.380

^a Symbols as given in Fig. 2.

Perkin-Elmer 1340 spectrophotometer. X-ray diffraction analysis of the HL and its complexes (4-6) powder forms was recorded on X-ray diffractometer in the range of diffraction angle $2\theta^{\circ}$ = 4–70°. This analysis was carried out using Cu K α radiation $(\lambda = 1.541874 \text{ Å})$. The applied voltage and the tube current are 40 kV and 30 mA, respectively. Ultraviolet-visible (UV-Vis) spectra of the compounds were recorded in nuzol solution using a Unicom SP 8800 spectrophotometer. The magnetic moment of the prepared solid complexes was determined at room temperature using the Gouv's method. Mercurv(II) (tetrathiocyanato)cobalt(II), [Hg{Co(SCN)₄}], was used for the calibration of the Gouv tubes. Diamagnetic corrections were calculated from the values given by Selwood [21] and Pascal's constants. Magnetic moments were calculated using the equation, $\mu_{\rm eff.} = 2.84 [T \chi_{\rm M}^{\rm coor.}]^{1/2}$. Thermal studies were computed on Simultaneous Thermal Analyzer (STA) 6000 system using thermogravimetric analysis (TGA) method. Thermal properties of the samples were analyzed in the temperature range from 50 to 800 °C at the heating rate of 15 °C/min under dynamic nitrogen atmosphere. ESR measurements of powdered samples were recorded at room temperature using an X-band spectrometer utilizing a 100 kHz magnetic field modulation with diphenyl picrylhydrazyle (DPPH) as a reference material. The conductance measurement was achieved using Sargent Welch scientific Co., Skokie, IL, USA.

Computational methods

The calculations of geometry optimization were performed using Perkin Elmer ChemBio 3D software by HF method with 3-21G basis set [22]. Geometry optimization option was employed to obtain the most stable structure.

Results and discussion

Structure of the ligand

Theoretical approaches made by Liang and Lipscomb [23] indicate that the nitrogen atom is more negatively charged than the oxygen atom in the isolated metal ion and consequently it may account for the coordination of the nitrogen atom rather than the oxygen atom, to the metal ion. Moreover, these authors have found that in the presence of the metal, the bidentate binding conformation with both N and O atoms coordinated to the metal ions is favored.

The optimized structures and bond length of the ligand tautomers (**A–D**) are presented in Fig. 2. From Table 2, the computed net charges on active centers for the ligand tautomers (**A–D**), it is found that the most negative charges in ligand tautomers are N(15), O(6) and O(21) for azo-enol form (**C**) and N(15) and O(21) for keto-hydrazo form (**D**) that makes it react stronger with the metal ion. Both the highest occupied molecular orbital (HOMO)

and lowest unoccupied molecular orbital (LUMO) are the main orbital takes part in chemical stability. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The HOMO and LUMO energy for ligand tautomers (A–D) calculated by HF method with 3-21G basis set is presented in Fig. 3. This electronic absorption corresponds to the transition from the ground state to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. Quantum chemical parameters of the ligand tautomers are obtained from calculations such as energies of the highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}) as listed in Table 3. Additional parameters such as HOMO-LUMO energy gap, ΔE^* , absolute electronegativities, χ , chemical potentials, Pi, absolute hardness, η , absolute softness, σ , global electrophilicity, ω , global softness, S, and additional electronic charge, ΔN_{max} , are calculated using the equations mentioned in [18,22,24].

Recently, the energy gap between HOMO and LUMO has been used to prove the activity and stability of the compounds [8,18,22]. The value of ΔE^* for tautomers (**A**), (**C**) and (**D**) was found 0.1011, 0.0637 and 0.0472 a.u., respectively. The calculations indicated that the azo-enol form (**C**) and keto-hydrazo form (**D**) are more stable forms and highly reactive than azo-keto form (**A**).

Our earlier studies on coordination behavior of rhodanine derivatives has shown that this 5-(2,3-dimethyl-1-phenylpyrazol-5-one azo)-2-thioxo-4-thiazolidinone (HL) (Fig. 1) presents a variety of chelating coordination behavior, depending on the nature of the metal ion and the deprotonation of the ligand.

In general, reactions of metal(II) acetate with HL were faster and gave better yields than reactions of metal(II) different anions. Molar conductance data showed that the metal complexes are non-electrolytes in DMSO [25,26].

The data of elemental analysis as given in Table 1 denote that two types of complexes were formed. For the first case the ligand behave as a monobasic and contains one anion (complexes with half equivalent anions) (1 M:1 L molar ration, as shown in Figs. 4 and 5).

$$CuCl_2 \cdot 2H_2O + HL \rightarrow [Cu(L)(Cl)(OH_2)] \quad \textbf{(1)}$$

 $CuX_2 \cdot nH_2O + HL \rightarrow [Cu(L)(X)(OH_2)_2]$ (2,3)

$$M(CH_3COO)_2 \cdot nH_2O + HL \rightarrow [M(L)(CH_3COO)(OH_2)_2] \cdot nH_2O$$
 (4-6)

where L = deprotonated HL, X = NO₃ (**2**) or SCN (**3**) and M = Cu(II) (**4**), Co(II) (**5**), M = Ni(II) (**6**).

For the second case the ligand behave as a monobasic and not contains anion (complex without acetate anions) (1 M:2 L molar ratio, Fig. 6).

 $UO_{2}(CH_{3}COO)_{2} \cdot 2H_{2}O + 2HL \rightarrow [UO_{2}(L)_{2}(H_{2}O)_{2}] \quad (\textbf{7})$

The number of water molecules (n) varies according to the nature of the metals. Thus the results of elemental analysis clarify, that three types of bonding are formed between the M^{2+} ions and the ligand under study, those with covalent, ionic and partially ionic and covalent bonds.

All the complexes have high melting point, denoting a strong bonding between the ligand and metal ions. It is interesting to point out that, the data of elemental analysis are in satisfactory agreement with the expected formula which gives support for the suggested composition.

IR spectra and the mode of bonding in the complexes

The IR spectra of the ligand showed the absence of the band at \sim 3405 cm⁻¹ due to amino $v(NH_2)$ stretching vibration and, instead a new band assigned to azodye v(N=N) linkage appeared at 1540 cm⁻¹ [5,18]. This suggested that amino group of the start reagent 1-phenyl-2,3-dimethyl-4-amino pyrazol-5-one (HL) has been converted into their corresponding ligand (Fig. 1).

The ligand may exist in keto-hydrazo and azo-enol tautomeric forms as shown in Fig. 1. It has be shown conclusively from a series of investigations using various techniques, such as IR and ¹H NMR spectra, that hydrazo containing rhodanine groups exist exclusively in the keto-hydrazo form both in solution and in solid state [27]. An intramolecular hydrogen bridge linking one of the carbonyl groups to the NH- moiety of the hydrazo unit was found to be a characteristic feature of this compound class (Fig. 1D and E). The six-membered intramolecular hydrogen bonding ring is possible in the keto-hydrazo tautomer as shown in Fig. 1D. The solid state IR spectra of the ligand shows two intense carbonyl bands ($\nu C=0\cdots H$), ($\nu C=0$) consistent with a keto-hydrazo form with extensive five/six membered intramolecular hydrogen bonding, and this has been confirmed by El-Sonbati et al. [28] and a number of previous published reports of keto-hydrazo analogues [29].

The strong band located at ~1725 cm⁻¹ due to carbonyl stretching vibration mode [18]. The three bands in the 1600–1500 cm⁻¹ region are characteristic for most six-membered aromatic ring system. The frequencies for the N=N stretching lie in the region 1540–1454 cm⁻¹. The region between 1500 and 900 cm⁻¹ is due C–N stretching, N–H in plane or out of plane bending and out-of-plane C–H bending vibrations. The symmetric and antisymmetric (C=C) stretching vibration modes are expected to exist in this region.

The infrared spectrum of HL gives interesting results and conclusions. The ligand give two bands at ~3190–2965 cm⁻¹ due to asymmetric and symmetric stretching vibrations of N—H group and intramolecular hydrogen bonding NH···O systems (Fig. 1D), respectively. It seems that, the OH group (Fig. 1C) is involved in intramolecular hydrogen bond, the O···N and N···O bond distances are the same. But, if such mechanism is occurred in case of intermolecular hydrogen bond, the O···O and O···N bond distances are differ.

The broad absorption band located at \sim 3400 cm⁻¹ is assigned to ν OH. The low frequency bands indicate that the hydroxy hydrogen atom is involved in keto \iff enol (A \iff B) tautomerism through hydrogen bonding (Fig. 1C). Bellamy [30] made detailed studies on some carbonyl compounds containing —NH group. The $\Delta \nu$ NH values were used to study the phenomena of association.

On the other hand, the OH group (Fig. 1B) exhibits more than one absorption band. The two bands located at 1303 and 1346 cm⁻¹ are assigned to in-plane deformation and that at 1170 cm⁻¹ is due ν C—OH.

However, the 870 cm^{-1} band is probably due to the out-of-plane deformation of the —OH group. On the other hand, the two bands located at 670 and 700 cm⁻¹ are identified as $\delta C=O$ and NH.

The infrared spectrum of ligand shows medium broad band located at \sim 3400 cm⁻¹ due the stretching vibration of some sort of hydrogen of hydrogen bonding. El-Sonbati et al. [18,31] made detailed studies for the different types of hydrogen bonding which are favorable to exist in the molecule under investigation:

 Intramolecular hydrogen bond between the nitrogen atom of the -N=N- system and hydrogen atom of the hydroxy hydrogen atom (Fig. 1C). This is evident by the presence of a broad band centered at 3460 cm⁻¹.



Fig. 3. HOMO and LUMO molecular orbital of ligand tautomers.

Table 3					
The calculated	quantum	chemical	parameters	for ligand	tautomers.

Tautomer ^a	E _{HOMO} (a.u.)	E _{LUMO} (a.u.)	ΔE^{*} (a.u.)	χ (a.u.)	η (a.u.)	σ (a.u.) $^{-1}$	Pi (a.u.)	S (a.u.) ⁻¹	ω (a.u.)	$\Delta N_{\rm max}$
(A)	-0.1092	-0.0082	0.1011	0.0587	0.0505	19.7902	-0.0587	9.8951	0.0341	1.1615
(B)	-0.0713	0.0019	0.0733	0.0347	0.0366	27.2933	-0.0347	13.6467	0.0164	0.9468
(C)	-0.0570	0.0067	0.0637	0.0252	0.0319	31.3883	-0.0252	15.6942	0.0099	0.7901
(D)	-0.0399	0.0072	0.0472	0.0163	0.0236	42.3558	-0.0164	21.1779	0.0057	0.6934

^a Symbols as given in Fig. 2.

- (2) Hydrogen bonding of the OH···N type between the hydroxy hydrogen atom and the N—Pyrazole group (Fig. 1C).
- (3) Intermolecular hydrogen bonding is possible forming cyclic dimmer through NH···O=C (H), OH···N=N (G) or OH···OH (F) (Fig. 1).

The presence of broad band located at \sim 3190 cm⁻¹ is strong indication by υ NH (Fig. 1D). In general, the low frequency of such region from its normal position is, again due to hydrogen bond property gathered with keto \iff enol tautomerism.



Fig. 4. The structure of the copper complexes.



M = Cu(II) (4), Co(II) (5), Ni(II) (6)

Fig. 5. The structure of the metal complexes.



Fig. 6. The structure of the uranyl complex.

In general, hydrogen bonding involving both NH and OH groups are proton donors and both -N and -O atoms are proton acceptors. It is of interest since much multiplicity of proton donor and acceptor sites are prevalent in biological systems. Both intra- and intermolecular OH \cdots N and NH \cdots O may form leading to a number of structures in simultaneous equilibrium.

Again the bands located at 1346 and 1303 cm⁻¹ identified as δ OH gathered with the two bands at 1228 cm⁻¹ assigned as ν C–O

are strong indication to keto \iff enol equilibria. The presence of a medium band at ~1604 cm⁻¹ assigned to vC=N illustrates the tracing of keto structure (Fig. 1D). Band at 1620 cm⁻¹ due to v(C=O) stretching frequency of antipyrine moiety.

The following features for some of the prepared complexes are observed:

- 1. The infrared spectrum of the free ligand shows no characteristic absorption assignable to NH_2 function. This confirms the formation of the azo compounds.
- 2. The band located at $\sim 1540 \text{ cm}^{-1}$ assigned to v(N=N) is highly affected by $\sim 20 \text{ cm}^{-1}$ on complexation (1–3), where it is disappeared in complexes (4–7). This focused the attention to that the azo-group takes part on complexes (1–3).
- 3. In solution and in the presence of CuX₂ (Cl, ONO₂, SCN) ions, these compounds exist in a tautomerism equilibrium [25,26] A \iff B \iff C (Fig. 1). The tautomeric form (C) react with metal ions by loss of phenolic proton as mononegative chelating agents producing of CO/OH mode of the free ligand. New bands for v(C–O) (~1106 cm⁻¹) [25,26] in the IR spectra of the complexes indicate the coordination to that metal *via* deprotonation.
- 4. The variation in the spectral bands of the C—C, C=C, C—N and C—H different modes of vibrations of the complexes lead to that, probably, the aromaticity of the complex is differ from one to other.
- 5. A broad band at ${\sim}3400{-}3275~cm^{-1}$ is attributed to $\upsilon(0{-}H)$ aqua of coordinated water.
- 6. The band due to vOH is masked by the intense absorption due to water molecule, and hence no definite conclusion can be drawn for this region. However, δ OH at ~1190 cm⁻¹, vC-OH at ~1106 and γ OH at ~835 cm⁻¹ display a sharp decrease in their intensities to such an extent that they nearby vanish. This can be taken as an indication for the complete removal of OH-group by the Cu²⁺ ions (1-3) reacting with the ligand. Since the ligand react with Cu²⁺ ions, as gathered from the results of elemental analysis, then each Cu²⁺ ion would displace only one proton from the OH group contained in the ligand molecule.
- 7. Band due to C=O stretching frequency of antipyrine moiety, in the free ligand shift toward lower value in the spectra of complexes of the Cu²⁺ (1-3) in accordance with the coordination of oxygen atom of carbonyl a function. This is due to the decrease in electron density around the oxygen atom of the carbonyl group.
- 8. For the nitrato complex (2), three strong bands at 1540, 1385 and 1295 cm⁻¹ are observed corresponding to v_1 , v_2 and v_4 of the nitrato group indicating the presence of a terminal monodentate coordination of the nitrato group [32]. A combination of $(v_1 + v_2)$ which is considered as diagnostic for the monodentate coordination nitrato group has been observed at 1695 cm⁻¹. The bands due to v_3 , v_5 and v_6 could not be assigned due to the richness of the spectrum of the complex. Thiocyanato complex (3) has a very strong band at 2090 cm⁻¹, a medium band at 775 cm⁻¹ and a weak band at 495 cm⁻¹ corresponding to v(CN), v(CS) and $\delta(NCS)$, respectively [33]. The intensity and band position indicate the unidentate coordination of the thiocyanate through nitrogen atom.

The possible structure of the Cu(II) complexes (1-3) could be suggested based on:

(i) the absence of one anion, (ii) the disappearance of C=O, (iii) the coordination of azo-group, and (iv) the shift of CO group of antipyrine moiety.

The HL ligand takes its usual anionic form (L) to chelate Cu(II) through CO of antipyrine moiety, N— of azo group with enol group (Fig. 1C) as the potential binding sites, the aqua ligand and different anions just fit the remaining free coordination position.

Under such condition the ligand is of tridentate monobasic nature with respect to the evidence above, the structure for the novel complexes are tentatively proposed as follows:

- 9. The absence of any peak attributed to the -N=N- moiety, implies that the ligand exist predominantly in solution as the form shown in Fig. 1D. However, in solution and in the presence of acetate-metals ion, these compounds exist in a tautomeric equilibrium $1C \iff 1D$. The main change is observed in the azo stretching vibration, thus suggesting that the form shown in Fig. 1D prevails. This is rather confirmed from the observation of Karabatoses et al. [34] where the hydrazo formed is more than the azo structure for similar compounds. This tautomeric form losses hydrazo proton when complexed with acetato-metals ion as mononegative chelating agents produces the N=N/NH mode of the free ligand. New band assigned to v(NH) in the free ligand is absent, suggesting the cleavage of intramolecular hydrogen bonding of vNH group and coordination of nitrogen to the metals ion.
- The carbonyl absorption band υ(CO) (of the rhodanine ring) was shifted to frequencies higher by 25–10 cm⁻¹ for all complexes (**4–7**). The change in the carbonyl band position [28] in the IR spectra of the metal complexes (**4–7**) indicates that the carbonyl group is coordinated to the metals ions (Figs. 5 and 6).
- 11. The ligand orbitals of hydrazo are group theoretically, energetically and occupationally suitable for participation in both donor $(M \rightarrow L)$ and acceptor $(L \rightarrow M)$ π -interactions with the metal ions [35]. Convincing evidence [35] has been adduced that $M \rightarrow L \pi$ -bonding makes a significant contribution to the bonding in metal complexes, whereas in Cu(II)-hydrazo rhodanine, Cu $\rightarrow O \pi$ -bonding is generally considered to be relatively weak [36]. This idea is supported by our thermal stability measurements.
- 12. The acetato-metal(II) complexes (**4–6**), display bands at ~1590 and ~1450 cm⁻¹ due to the asymmetric and symmetric modes of vibration characteristic of CH₃COO, respectively, and with $\Delta v = 140$ cm⁻¹ which is consistent with the bidentate nature of the acetate group [37].

According to the structure shown in (Fig. 5) the HL ligand takes its usual anionic (L) to chelate acetate-Cu(II), Ni(II) and Co(II) through N— of hydrazo group and oxygen atom of carbonyl group (Fig. 5) as the potential binding sites, whereas the acetate/aqua anion just fit the remaining free coordination position.

¹H and ¹³C NMR spectra

The ¹H NMR spectrum of the ligand was recorded in DMSO-d₆ at room temperature supports the occurrence of the form depicted in Fig. 1. The =C--CH₃ and -N--CH₃ protons were observed as singlet at δ 2.37-2.55 ppm, respectively, and equivalent to three protons each. In the aromatic region, a few doublets and in few cases some overlapping doublets/multiplets are observed in the range δ 6.78-8.40 ppm. These doublets/multiplets are due to aryl protons of three rings. Another singlet corresponding to one proton for compound is observed in the range $\delta \sim$ 9.2-9.6 ppm. This signal disappeared when a D₂O exchange experiment was carried out. It can be assigned either to OH or NH, in either case it is strongly deshielded because of hydrogen bonding with the other atom (N/O) (Fig. 1). It may be noted that the integration of this signal perfectly matches with one proton and there is no other fragment(s) of this signal, which suggests that only one tautomeric form of the ligand exist in solution under the experimental conditions. Absence of --CH (4.40 ppm) proton signal of the ligand (HL) moiety indicated the existence of the ligand in the azo-enol form. According to El-Sonbati et al. [5,26,31,37], hydrogen bonding leads to a large deshielding of the protons. Comparing with the solid state study, we prefer to assign this signal to NH in complex (7), however, assignment of this peak to NH cannot be ruled out provided solid state structural evidence is not considered [38,39]. The main proton chemical shifts of HL appeared at different values depending upon the metal anions. As reported in a previous study [38], this hydrogen bonding leads to a large deshielding of these protons. The ¹H NMR spectral data are reported along with the possible assignments was found as to be in their expected region [38]. The conclusion drawn from these studies lend further support to the mode of bonding discussed in their IR spectra. In the spectrum of diamagnetic UO₂(II) complex, the resonance arising from NH proton disappears, indicating the chelation of the ligand through the deprotonated hydrazo NH group. The appearance of signals due to HC=N [~8.94 ppm (1H)] protons of the same positions in the ligand and its diamagnetic complex shows the non-involvement of this group in coordination. Also there is a peak found at 4.66 ppm in the $UO_2(II)$ complex indicating that coordinated water molecules are presented in the complex (7).

On the basis of all the above spectral data, an internally hydrogen boned azo-enol structure has been proposed for the ligand (Fig. 1).

The ¹³C NMR spectra of ligand (HL) and diamagnetic complex (**7**) display the signals at ~10.86 and 35.82 ppm are due to carbon atoms of methyl groups attached to the pyrazolone rings (H₃C–C and H₃C–N). The two kinds of C-atoms of the pyrazolone rings (Me–C and N–C) give signals at ~136.24 and 138.64 ppm. The ¹³C NMR spectrum of complex (**7**) shows signals at ~150.18 and 195.86 ppm are due to C-atoms of C=N and C=O group, respectively [26].

Therefore, it is clear from these results that the data obtained from the elemental analyses, IR and ¹H and ¹³C NMR spectral measurements are in agreement with each other.

X-ray diffraction

The X-ray diffraction, XRD, patterns of the as-synthesized powder of HL and complexes (**4–6**) are shown in Fig. 7. The XRD patterns of the ligand (HL) has many sharp diffraction peaks at around $2\theta = 10-15^{\circ}$ and $2\theta = 20-25^{\circ}$ this indicate that HL is a polycrystalline phase (Fig. 7a). For complexes (**5**) and (**6**) the peak



 $\label{eq:Fig. 7. X-ray diffraction patterns for powder forms (a) HL, (b) [Cu(L)(OAc)(OH_2)_2] H_2O, (c) [Co(L)(OAc)(OH_2)_2] H_2O and (d) [Ni(L)(OAc)(OH_2)_2] H_2O.$

appeared at $2\theta = 18^{\circ}$ and $2\theta = 18-26^{\circ}$, respectively, indicates that both of complexes (**5**) and (**6**) are a mixture of crystalline and amorphous phases (Fig. 7c and d). While complex (**4**) there is no significant reflection peaks indicating that the complex (**4**) is completely amorphous phase (Fig. 7b).

Electronic spectra and magnetic moments

HL exhibits bands at ~26,360–26,280 cm⁻¹ (CS) (n $\rightarrow \pi^*$), ~30,560–30,260 cm⁻¹ (CO) (n $\rightarrow \pi^*$), ~32,980–33,180 cm⁻¹ (H-bonding and association), 40,250–39,900 cm⁻¹ (phenyl) (Ph–Ph^{*}), (π – π^*) [5] and ~29,620–29,350 cm⁻¹ transition of phenyl rings overlapped by composite broad π – π^* of azo structure. In the complexes, the (n $\rightarrow \pi^*$) transition shifts to lower energy at ~28,660 cm⁻¹ and the band due to the H-bonding and association is absent as expected. Furthermore, the (CS) (n– π^*) transition shifts slightly to lower energy and remains almost constant. The (CO) (n $\rightarrow \pi^*$) transition disappears with the simultaneous appearance of new bands, being attributed to $\pi \rightarrow \pi^*$ transition moves to lower energy. These shifts or disappearance of the bands are indicative of coordinating of the ligand to metal.

The geometry of the metal complexes has been deduced from electronic spectra and magnetic moment data of the complexes. The values of magnetic moment (1.76–2.06 B.M.) for complexes (1–4) suggest the presence of an unpaired electron.

The magnetic moment of all the Cu(II) complexes at room temperature lie in the range of 1.90–2.06 B.M., corresponding to one unpaired electron. This indicates that these complexes are monomeric in nature and the absence of metal–metal interaction.

Electronic spectra of six-coordinate Cu(II) complexes have either D_{4h} or C_{4v} symmetry, and the e_g and t_{2g} level of the ²D free ion term will split B_{1g}, A_{1g} and E_g level, respectively, (Table 4). Thus the three spin allowed transitions are expected in the visible and near IR region. But only few complexes are known in which such bands are resolved either by Gaussian Analysis or single crystal polarization studies [40]. These bands may be assigned to following transition ²B_{1g} \rightarrow ²A_{1g} (d_{x2-y2} \rightarrow d_{z2}), ²B_{1g} \rightarrow ²B_{2g} (d_{x2-y2} \rightarrow d_{xy}) and ²B_{1g} \rightarrow ²Eg (d_{x2-y2} \rightarrow d_{zx} d_{yz}) in order of increasing energy. The energy level sequency will depend on the amount of distortion due to ligand field and Jahn–Teller effect [41]. Strong bands in the ≈24,000 cm⁻¹ observed in the spectra of all Cu(II) complexes are assigned to 0 \rightarrow Cu and N \rightarrow Cu LMCT transitions. In the chloro complex (1), a shoulder observed at 23,350 cm⁻¹ is assigned as Cl \rightarrow Cu charge-transfer transition [42]. All the complexes gave d–d bands in the 14,500–1600 cm⁻¹ range [43,44]. The reflectance

Table 4

Table 5

Electronic	spectral	assignments	of the	Cu(II)	complexes.

Complex ^a	$\pi - \pi^*$	$n-\pi^*$	LMCT	d-d
2	38,700	32,030	23,900	15,200
3	38,680	32,020	23,910	14,600
4	38,670	32,170	23,910	16,000

^a Numbers as given in Table 1.

The spin	Hamiltonian	narameters	of Cu(II)	complexe

spectrum for complex (1) present a single absorption band at 14,880 cm⁻¹ corresponding to the d–d transition, indicating the low $C_{2\nu}$ symmetry of the Cu²⁺ ion [45].

ESR spectra

The spin-Hamiltonian parameters of copper complexes are listed in Table 5. The spin-Hamiltonian parameters, electronic absorption spectra and magnetic moment values for the copper complexes (2–4) elongated distorted octahedral Cu(II) complexes, bonding parameters can be obtained from the ESR spectrum of the complex. The g_{\parallel} and g_{\perp} values were computed from the spectra using DPPH free radical as *g* marker. The variation values in g_{\parallel} and g_{\perp} of these complexes indicate that the geometry of the compounds in the solid state is affected by the nature of the coordinating genious. The unpaired electron in this $3d^9$ case assigned to $3d_{x2-y2}$ orbital, and the overlapping of this antibonding orbital with the ligand 2s and 2p σ orbital is often determined by the use of the following equation [46]:

$$\alpha^2 = A_{\parallel}/P_{\rm o} + (g_{\parallel} - 2.0023) + K_{\rm o}(g_{\perp} - 2.0023) + 0.04$$

where α^2 gives an approximate indication of the strength of the interaction between the metal and the ligand. P_0 is the dipolar contribution to the hyperfine splitting value A, which is a negative quantity, and usually assigned the free ion value of 0.036 cm⁻¹ [47]. The constant term of $K_0 = 3/7$ is equated to the Fermi hyperfine contact term of the free ion, which corrects for the Fermi contact contributions from excited state configurations of Cu(II), notably the 3s¹ 3d¹⁰ and 3s² 3d⁸ 4s¹ configurations [48]. This is usually considered to be a constant term for Cu(II) complexes since there is little ligand orbital density at the copper nucleus and the ratio of copper s and d character is assumed to be unchanged in the presence of ligand [46]. The addition of 0.04 to the sum is an approximate correction due to the molecular orbital coefficients of the complex that arise from in plane π bonding (d_{xy}, β_1) and out of plane π bonding (d_{xz}, d_{yz}, β), where the π bonding is negligible $\beta_1 = \beta = 1.0$ and where the in plane σ -bonding $(d_{x^2-y^2}, \sigma)$ coefficient is about 0.9. Thus, α^2 represents the extent to which the unpaired electron residues on the central metal ion in the d_{x2-v2} orbital $(B_{1g} \text{ ground state})$ and reflects the extent of σ -bonding to the ligand. Consequently, a decline in the value of α^2 indicates an increase in the valency of the bond. The in-plane σ -covalency parameter α^2 values account for the fraction of the unpaired electron density to be populated around the Cu(II) ion. In the present case, the in plane σ -covalency parameter α^2 is calculated by using the above equation, and its value found to be $\alpha^2 = 0.92$ which provide a reliable measure of the covalency of Cu(II) ions with ligand.

The observed nearly axial symmetry of the g and A tensors can be explained in terms of the slightly distorted octahedral coordination around the Cu(II) ion. An octahedral complex with a tetragonal elongation would give $g_{||} > g_{\perp} > g_e$ and the tetragonality measure $(g_{||} - g_e)/g_{\perp} - g_e)$ with the ground state is ${}^2B_{1g}$.

The spectra of the complexes (**2–4**) show typical axial behavior with slightly different $g_{||}$ and g_{\perp} values (Table 5). In these Cu(II) complexes tensor values of $g_{||} > g_{\perp} > 2.0023$ are consistent with

Complex ^a	g	g_{\perp}	g _{av.}	G	$A_{\parallel}^{\mathbf{b}}$	α^2	β^2	$K_{ }^2$	K_{\perp}^2	γ^2
2	2.234	2.047	2.109	5.18	71.33	0.489	1.09	0.54	0.45	0.92
3	2.223	2.046	2.105	5.05	62.13	0.452	1.08	0.47	0.42	0.93
4	2.241	2.050	2.114	5.00	86.35	0.539	1.07	0.55	0.49	0.91

^a Numbers as given in Table 1.

^b A values in 10^{-4} cm⁻¹.

 d_{x2-y2} orbital having ${}^{2}B_{1g}$ as a ground state term [49,50]. The geometric parameter *G*, which is a measure of the exchange interaction between the copper centers in the polycrystalline compound, is calculated using the reported equation by others [51,52]. If *G* is higher than 4, exchange interaction is negligible, but if *G* is less than 4, considerable exchange interaction is indicated in the solid complex.

The parameters g_{\parallel} , g_{\perp} and A_{\parallel} of complexes and the energies of the d–d transitions are used to calculated the orbital reduction parameters (K_{\parallel} , K_{\perp}) and the bonding parameter (α^2 and β^2). The factor β^2 which can be evaluated by the expression:

$$\beta^{2} = (g_{\parallel} - 2.0023)E / - 8\alpha^{2}\lambda_{o}$$

$$\gamma^{2} = (g_{\parallel} - 2.0023)E_{xy} / - 2\alpha^{2}\lambda_{o}$$

where $\lambda_o = -828 \text{ cm}^{-1}$ for the free copper ion and *E* is the electronic transition energy. The covalency of the in-plan σ -bonding, $\alpha^2 = 1$ indicates complete ionic character, whereas $\alpha^2 = 0.5$ denotes 100% covalent bonding. The α^2 values for the present copper complexes are 0.489 (**2**), 0.452 (**3**) and 0.539 (**4**), supporting that the covalent nature [18] of the bonding. The β^2 parameter gives an indication of the less covalent. Hathaway [53] pointed out that for pure σ -bonding, $K_{\parallel} \approx K_{\perp} = 0.77$ and for in-plane π -bonding $K_{\parallel} < K_{\perp}$, while for out-of-plane π -bonding $K_{\perp} < K_{\parallel}$. The following simplified expressions are used to calculated K_{\parallel} and K_{\perp} :

 $K_{\parallel} = (g_{\parallel} - 2.0023)E/8\lambda_o$ $K_{\perp} = (g_{\perp} - 2.0023)E/2\lambda_o$

 $\mathbf{R}_{\perp} = (\mathbf{g}_{\perp} = \mathbf{2.0023})\mathbf{L}/\mathbf{2}\mathbf{\lambda}_{0}$

The observed $K_{||}$ (0.47–0.55) > K_{\perp} (0.42–0.49) relation indicates that the absence of significant in-plane π -bonding.

The *g* tensor values for the complex (1) indicate distorted trigonal bipyramidal geometry $(C_{2\nu})$ [54]. The term of fundamental state may be defined with the help of geometric parameter *R* deduced from the relation $R = (g_2 - g_3)/(g_1 - g_2)$ [45,51]. If R > 1, the term of the ground state is defined by the orbital d_z^2 , but if R < 1 it is defined by their orbital d_{xy}^2 . For the complex (1) (R = 2.44), it is clear that the ground state term is d_z^2 . As $g_{\parallel} > g_{\perp}$, the possibility of trigonal bipyramidal geometry has been ruled out and square pyramidal structure is suggested.

$$g_1 = 2.262$$
 $g_2 = 2.2209$ $g_3 = 2.076$

These ESR data showed that:

1. $g_{||}$ Values are dependent on the nature of the second coordinated ligand (other than L) and can be ordered as: OAc > NO₃ > NCS which in agreement with the electronic spectral data. For $A_{||} \times 10^{-4}$ (cm⁻¹), also, this appears to be the order of the strength of metal–anion interactions



Fig. 8. The relation between $g_{\parallel} vs. A_{\parallel} \times 10^{-4} (\text{cm}^{-1})$.

for acetate, nitrate and isothiocyanate. Our results are in agreement with the respective position of the anions as given in the spectrochemical series [18,25,26].

- 2. The value of g_{\parallel} increases with increasing $A_{\parallel} \times 10^{-4} (\text{cm}^{-1})$ (Fig. 8).
- 3. The value of α^2 increases with increasing g_{av} (Fig. 9).
- 4. The value of α^2 increases with increasing $A_{||} \times 10^{-4} (\text{cm}^{-1})$ (Fig. 10).



Fig. 9. The relation between $g_{av.} vs. \alpha^2$.



Fig. 10. The relation between $A_{||} \times 10^{-4} (\text{cm}^{-1}) vs. \alpha^2$.



Fig. 11. The relation between K_{\perp}^2 vs. g_{\perp} .



Fig. 12. The relation between K_{\parallel}^2 vs. g_{\parallel} .

5. $K_{||}^2$ and K_{\perp}^2 increase with increasing $g_{||}$ and g_{\perp} (Figs. 11 and 12), respectively.

Thermogravimetric analysis

The TGA curves for HL and its M(II) complexes (**4–6**) are shown in Fig. 13. The temperature intervals and the percentage of loss of masses are listed in Table 6. TGA curve of HL, the small loss of mass (4.77%) in temperature interval range ~65–178 °C is due to evolution of NH₃ gas. The decomposition of HL starts at about 178 °C *via* evolution of H₂S gas, further decomposition of a part of the ligand (Fig. 13a). In the present study, the TGA of M(II) complexes (**4**–**6**) is taken as a proof for the existing of water molecules as well as the anions to be coordination sphere. The TGA curves of complexes (**4**–**6**) (Fig. 13b–d) show four steps of losing mass. The first step at ~45–125 °C, can be attributed to loss of lattice water molecules. The second step at 125–227 °C, can be attributed to loss of two coordinated water molecules. The third step at ~227–437 °C, is due to loss of one coordinated acetate group for complexes, in addition to decomposition of a part of the ligand for complexes (**5** and **6**). The final weight losses are due to the decomposition of the rest of the ligand molecule leaving metal oxides residue with contaminated carbon atoms.

There are three decomposition stages for $UO_2(II)$ complex (7). The first step corresponds to the removal of coordinated water molecules followed by the subsequent elimination of the ligand and finally it leaves air stable metal oxide (U_3O_8) as residue at high temperatures in the range 659–800 °C. The result is in accord with the composition of metal chelates.

Kinetic studies

The kinetic parameters such as activation energy (E_a), enthalpy (ΔH^*), entropy (ΔS^*), and Gibbs free energy change of the decomposition (ΔG^*) are evaluated graphically by employing the Coast–Redfern [55] and Horowitz–Metzger [56] methods.

Coast-Redfern equation

The Coast–Redfern equation, which is a typical integral method, can represent as:



Fig. 13. TGA curves for (a) HL, (b) $[Cu(L)(OAc)(OH_2)_2] \cdot H_2O$, (c) $[Co(L)(OAc)(OH_2)_2] \cdot 2H_2O$ and (d) $[Ni(L)(OAc)(OH_2)_2] \cdot 2H_2O$.

Table 6			
The thermal analyses	data of the	HL and its	s complexes.

Compound ^a	Temp. range (°C)	Found mass loss (calc.) %	Assignment
HL	65–178	4.53 (4.89)	Evolution of NH_3 gas
	178–238	10.43 (9.79)	Evolution of H_2S gas
	238–357	28.36 (28.82)	Decomposition of a part of the ligand (C_3H_2SNO)
	357–607	40.70 (42.65)	Decomposition of a part of the ligand ($C_2H_2N_2O$)
4	45–114 114–202 202–335 335–665	3.13 (3.44) 8.19 (6.89) 26.40 (25.46) 39.88 (42.01)	Loss of one coordinated water molecules Loss of two coordinated water molecules Loss of one coordinated acetate group, further evolution of H_2S gas and decomposition of a part of the ligand (C_2H_2N) Decomposition of a part of the ligand ($C_9H_8SN_4O$) leaving CuO residue with contaminated carbon atoms
5	45–125	7.68 (6.72)	Loss of two water molecules in outside of the coordination sphere
	125–227	8.06 (6.72)	Loss of two coordinated water molecules
	227–437	33.31 (33.01)	Loss of one coordinated acetate group, further decomposition of a part of the ligand ($C_2H_2S_2N_2$)
	437–785	25.12 (26.12)	Decomposition of a part of the ligand ($C_6H_{10}N_3O$) leaving CoO residue with contaminated carbon atoms
6	45–124	7.18 (6.72)	Loss of two water molecules in outside of the coordination sphere
	124–222	7.20 (6.72)	Loss of two coordinated water molecules
	222–421	33.91 (33.04)	Loss of one coordinated acetate group, further decomposition of a part of the ligand ($C_2H_2S_2N_2$)
	421–795	32.52 (32.85)	Decomposition of a part of the ligand ($C_0H_{10}N_3O$) leaving NiO residue with contaminated carbon atoms

^a Numbers as given in Table 1.



Fig. 14. Coats-Redfern (CR) of the ligand (HL) and its complexes (4-6).

(2)

 $\int_0^a \frac{dx}{(1-\alpha)^n} = \frac{A}{\varphi} \int_{T_1}^{T_2} \exp\left(-\frac{E_a}{RT}\right) dt$

For convenience of integration, the lower limit T_1 usually taken as zero. This equation on integration gives:



Fig. 15. Horowitz-Metzger (HM) of the ligand (HL) and its complexes (4-6).

Table 7Kinetic parameters of the HL and its complexes.

Compound ^a	Decomposition temperature	Method	Parameter					Correlation coefficient
	(°C)		E _a (kJ mol ⁻¹)	$A(s^{-1})$	ΔS^{*} (J mol ⁻¹ K ⁻¹)	ΔH^{*} (kJ mol ⁻¹)	ΔG^{*} (kJ mol ⁻¹)	(r)
HL	170–359	CR HM	52.2 56.1	$\begin{array}{c} 3.19\times10^2\\ 1.63\times10^3\end{array}$	$\begin{array}{c} -2.02 \times 10^2 \\ -1.88 \times 10^2 \end{array}$	47.9 51.6	156 153	0.9979 0.9977
4	142-375	CR HM	35.4 43.3	$\begin{array}{c} 7.32\times10^{0}\\ 8.12\times10^{1} \end{array}$	$\begin{array}{c} -2.33 \times 10^2 \\ -2.13 \times 10^2 \end{array}$	31.0 38.8	155 152	0.9848 0.9756
5	141–441	CR HM	27.6 37.5	$\begin{array}{c} 4.37 \times 10^{-1} \\ 1.06 \times 10^{1} \end{array}$	$\begin{array}{c} -2.57 \times 10^2 \\ -2.31 \times 10^2 \end{array}$	22.9 32.8	168 163	0.9939 0.9918
6	150-425	CR HM	46.3 45.0	$\begin{array}{c} 1.76\times10^{0}\\ 4.43\times10^{1}\end{array}$	$\begin{array}{c} -2.45 \times 10^2 \\ -2.19 \times 10^2 \end{array}$	41.6 40.3	179 163	0.9873 0.9969

^a Numbers as given in Table 1.

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = -\frac{E_a}{RT} + \ln\left[\frac{AR}{\varphi E_a}\right]$$
(3)

where $k_{\rm B}$ is the Boltzmann constant, *h* is the Plank's constant and $T_{\rm s}$ is the TG peak temperature.

A plot of left-hand side (LHS) against 1/T was drawn (Fig. 14). E_a is the energy of activation and calculated from the slop and A in (s⁻¹) from the intercept value. The entropy of activation calculated by using the equation:

$$\Delta S^* = 2.303 \left[\log \left(\frac{Ah}{k_B T_s} \right) \right] R \tag{4}$$

Horowitz-Metzger equation

The Horowitz-Metzger equation is an illustrative of the approximation methods. These authors derived the relation:

$$\log\left[\frac{1 - (1 - \alpha)^{1 - n}}{1 - n}\right] = \frac{E_{a}\theta}{2.303RT_{s}^{2}}, \quad \text{for } n \neq 1$$
(5)



Fig. 16. The relation between E_a and ionic radii of metal complexes (**4**–**6**).

when n = 1, the LHS of Eq. (5) would be $\log[-\log(1 - \alpha)]$ (Fig. 15). For a first order kinetic process, the Horowitz–Metzger equation may write in the form:

$$\log\left[\log\left(\frac{W_{\alpha}}{W_{\gamma}}\right)\right] = \frac{E_{a}\theta}{2.303RT_{s}^{2}} - \log 2.303$$
(6)

where $\theta = T - T_s$, $w_\gamma = w_\alpha - w$, w_α = mass loss at the completion reaction; w = mass loss up to time *t*. The plot of log [log (w_α/w_γ)] *vs*. θ was drawn and found to be linear from the slope of which E_a was calculated. The pre-exponential factor, *A*, calculated from equation:

$$\frac{E_a}{RT_s^2} = \frac{A}{\left[\varphi \exp\left(-\frac{E_a}{RT_s}\right)\right]}$$
(7)

The entropy of activation, ΔS^* , is calculated from Eq. (4). The enthalpy activation, ΔH^* , and Gibbs free energy, ΔG^* , calculated from:

$$\Delta H^* = E_{\rm a} - RT \tag{8}$$

$$\Delta G^* = \Delta H^* - T \Delta S^* \tag{9}$$

The calculated values of E_a , A, ΔS^* , ΔH^* and ΔG^* for the decomposition steps for ligand (HL) and its complexes (**4–6**) are summarized in Table 7. The kinetic data obtained from the two methods are comparable and can be considered in good agreement with each other.

As shown in Fig. 16 the activation energy (E_a) of the complexes is expected to increase with the increasing thermal stability of complexes. Therefore, the E_a value for the complex (**6**) is higher

Antibacterial activity data of	ligand (HL)	and its Cu(II) com	plexes. The results w	ere recorded as the di	iameter of inhibition zone ((mm)
					,	

Compound ^a	Concentration (µg/ml)	Gram positive bacte	ria	Gram negative bacte	ria
		Bacillus cereus	Staphylococcus aureus	Escherichia coli	Klebsiella pneumoniae
HL	50	-ve	-ve	2	-ve
	100	-ve	-ve	2	-ve
	150	-ve	-ve	-ve	-ve
1	50	-ve	-ve	-ve	-ve
	100	-ve	-ve	-ve	-ve
	150	-ve	-ve	-ve	-ve
2	50	-ve	-ve	-ve	-ve
	100	-ve	-ve	-ve	-ve
	150	-ve	-ve	-ve	-ve
4	50	1	-ve	-ve	1
	100	1	-ve	-ve	1
	150	1	-ve	-ve	1
Penicillin	50	1	2	1	-ve
	100	3	2	3	-ve
	150	3	2	3	-ve

^a Numbers as given in Table 1.

Table 9

Table 8

Antifungal activity data of ligand (HL) and its Cu(II) complexes. The results were recorded as the diameter of inhibition zone (mm).

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Compound ^a	Concentration (µg/ml)	Aspergillus niger	Fusarium oxysporum	Alternaria alternata	Penicillium italicum
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	HL	50	-ve	1	1	6
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		100	-ve	-ve	1	5
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		150	-ve	-ve	2	7
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1	50	-ve	-ve	-ve	-ve
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		100	-ve	-ve	1	-ve
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		150	-ve	-ve	3	1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	50	-ve	-ve	-ve	-ve
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		100	-ve	-ve	-ve	5
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		150	-ve	-ve	-ve	5
100 2 -ve -ve 4 150 2 -ve -ve 5 Miconazole 50 1 2 5 1 100 3 3 6 1	4	50	2	-ve	-ve	9
150 2 -ve -ve 5 Miconazole 50 1 2 5 1 100 3 3 6 1		100	2	-ve	-ve	4
Miconazole 50 1 2 5 1 100 3 3 6 1		150	2	-ve	-ve	5
100 3 3 6 1	Miconazole	50	1	2	5	1
		100	3	3	6	1
150 4 3 6 2		150	4	3	6	2

^a Numbers as given in Table 1.



Fig. 17. Potentiodynamic polarization curves for the corrosion of C-steel in 2 M HCl in the absence and presence of various concentrations of HL at 25 $^{\circ}$ C.



Fig. 18. Equivalent circuit model used to fit the impedance spectra.

compared to the other complexes, due to the lower ionic radius which indicate that the complex (**6**) is more stable than other complexes [57].

From the values of the energy of activation (E_a) of the ligand (HL) and its complexes (**4–6**), it is observed that the complexes (**4–6**) are less stable than the ligand (HL) and may be attributed to the loss of water molecules from complexes. These results are inconsistent with our previous results [18].

The entropy of activation energies reflects the thermal stability of the compounds. The entropy of activation is found to be of negative values in the HL and its complexes (**4–6**) which indicate that the decomposition reactions proceed spontaneously [18]. The values of ΔG^* is positive considered as favorable or spontaneous reaction.

Microbiological investigation

Table 10

The antimicrobial activity of ligand and its complexes (**1**, **2** and **4**) was tested against some bacterial and fungal species. More than

one test organism used tested to increase the chance of detection of their antimicrobial activities.

The results of the antibacterial activities of the synthesized compounds were recorded in Table 8. The ligand (HL) has low antibacterial activity only against *E. coli* (inhibition zone = 2 mm at concentrations = 50 and 100 μ g/ml) while no antibacterial activities for other types of bacteria. Cu(II) complexes of HL have no antibacterial activities for all antibacterial activities except complex (**4**) has low antibacterial activity only against *B. cereus* and *K. pneumoniae* (inhibition zone = 1 mm for all concentrations).

From Table 8 it is observed that the complex (4) was more potent antibacterial than the ligand (HL) and the other complexes against *K. pneumoniae*. This may support the argument that some type of biomolecular binding to the metal ions or interchelation or electrostatic interactions causes the inhibition of biological synthesis. So it can be concluded that the some complexes exhibits higher antimicrobial activity than the free ligand [58].

The results of the antifungal activities of the synthesized compounds were recorded in Table 9. It found that the ligand (HL) has no antifungal activities against A. niger. The ligand (HL) was found to has low antifungal activity against F. oxysporium and A. alternata (inhibition zone = 1, 1 and 2 mm at concentrations = 50, 100 and 150 μ g/ml, respectively), but high effect was observed against P. italicum (inhibition zone = 6, 5 and 7 mm at concentrations = 50, 100 and 150 μ g/ml, respectively). Cu(II) complexes (1, 2 and 4) of HL have no antifungal activities for A. alternata and F. oxysporium activities except complex (1) has low antifungal activity against A. alternata (inhibition zone of complex (1) = 1 and 3 mm at concentrations = 100 and 150 μ g/ml, respectively). It found that complexes (4) has low antifungal activity against A. *niger* (inhibition zone of complex (4) = 2 mm for all concentrations) and high effect against P. italicum (inhibition zone of complex (4) = 9, 4 and 5 mm at concentrations = 50, 100 and $150 \,\mu\text{g/ml}$, respectively), and inhibition zone of complex (2) = 5 and 5 mm at concentrations = 100 and 150 μ g/ml, respectively.

It is observed that the complex (**4**) is more potent antifungal than the ligand (HL) and the other complexes against *P. italicum* at concentration = $50 \mu g/ml$.

Potentiodynamic polarization

Anodic and cathodic polarizations were carried out potentiodynamic in unstirred 2 M HCl solution in the absence and presence of various concentrations of the HL at 25 °C over potential range 300 mV \pm OCP. The results are represented in Fig. 17. The obtained potentiodynamic polarization parameters are given in Table 10. These results indicate that the cathodic and anodic curves obtained exhibit Tafel-type behavior. Additionally, the form of these curves is very similar either in the cathodic or in the anodic side, which indicates that the mechanisms of C-steel dissolution and hydrogen reduction apparently remain unaltered in the presence of this additive. Addition of HL decreased both the cathodic and anodic current densities and caused mainly parallel displacement to the more negative and a positive value, respectively, i.e. the presence

Data from potentiodynamic polarization of C-steel in 2 M HCl containing various concentrations of HL at 25 °C.

Concentration (molar)	$-E_{\rm corr}$ (mV vs. SCE)	$i_{\rm corr}~({ m mA~cm^{-2}})$	$\beta_{\rm c} ({\rm mV}{\rm decade}^{-1})$	β_{a} (mV decade ⁻¹)	θ	%IE
0.0	535	21.420	550	521	-	-
$1 imes 10^{-6}$	516	10.820	451	385	0.495	49.5
$3 imes 10^{-6}$	520	8.779	435	370	0.590	59.0
$5 imes 10^{-6}$	502	8.029	450	363	0.625	62.5
$7 imes 10^{-6}$	515	5.878	399.9	325.4	0.726	72.6
$9 imes 10^{-6}$	503	4.872	377	300	0.773	77.3
11×10^{-6}	504	4.502	379	303	0.790	79.0

Concentration (molar)	$R_{\rm S} (\Omega {\rm cm}^2)$	$Y_{\rm o} (\mu \Omega^{-1} { m s}^n { m cm}^{-2})$	n	$R_{\rm ct}$ (Ω cm ²)	$C_{\rm dl}~(\mu {\rm F~cm^{-2}})$	θ	%IE
0.0	2.529	192.70	0.853	31.77	80.13	-	-
$1 imes 10^{-6}$	2.419	105.50	0.856	87.01	48.08	0.635	63.5
$3 imes 10^{-6}$	2.483	87.16	0.863	99.27	46.68	0.680	68.0
$5 imes 10^{-6}$	3.182	74.24	0.866	145.80	41.36	0.782	78.2
$7 imes 10^{-6}$	4.721	60.60	0.855	187.00	37.58	0.830	83.0
$9 imes 10^{-6}$	5.203	51.58	0.884	226.90	31.84	0.860	86.0
$11 imes 10^{-6}$	6.187	31.89	0.872	279.20	19.50	0.886	88.6

 Table 11

 EIS data of C-steel in 2 M HCl in the absence and presence of different concentrations of HL at 25 °C.

of HL in solution inhibits both the hydrogen evolution and the anodic dissolution processes with overall shift of E_{corr} to more negative values with respect to the OCP.

The results also show that the slopes of the anodic and the cathodic Tafel slopes (β_a and β_c were slightly changed on increasing the concentration of the tested HL. This indicates that there is no change of the mechanism of inhibition in presence and absence of HL. The fact that the values of β_c are slightly higher than the values of β_a suggesting a cathodic action of the inhibitor. This could be interpreted as an action of mixed inhibitor control over the electrochemical semi-reactions. This means that the HL is mixed type inhibitor, but the cathode is more preferentially polarized than the anode. The higher values of Tafel slope can be attributed to surface kinetic process rather the diffusion-controlled process [59]. The constancy and the parallel of cathodic slope obtained from the electrochemical measurements indicate that the hydrogen evolution reaction was activation controlled [60] and the addition of Pyrazolone azodye did not modify the mechanism of this process. This result suggests that the inhibition mode of the Pyrazolone azodye did was by simple blockage of the surface by adsorption.

Electrochemical impedance spectroscopy

Impedance diagram (Nyquist) at frequencies ranging from 1 Hz to 1 kHz with 10 mV amplitude signal at OCP for C-steel in 2 M HCl in the absence and presence of different concentrations of HL. The equivalent circuit that describes our metal/electrolyte interface is shown in Fig. 18 where $R_{\rm s}$, $R_{\rm ct}$ and CPE refer to solution resistance,



Fig. 19. Electrochemical Impedance Spectroscopy (EIS) Nyquist plots for C-steel in 2 M HCl in the absence and presence of different concentrations of HL at 25 °C.



Fig. 20. Comparative analysis of ligand (HL) for potentiodynamic polarization measurements and electrochemical impedance spectroscopy (EIS).

charge transfer resistance and constant phase element, respectively. EIS parameters and % IE were calculated and tabulated in Table 11. In order to correlate impedance and polarization methods, $i_{\rm corr}$ values were obtained from polarization curves and Nyquist plots in the absence and presence of different concentrations of HL using the Stern–Geary equation:

$$i_{\rm corr} = \frac{\beta_{\rm a}\beta_{\rm c}}{2.303(\beta_{\rm a} + \beta_{\rm c})R_{\rm ct}} \tag{10}$$

The obtained Nyquist plot for HL is shown in Fig. 19. Each spectrum is characterized by a single full semicircle. The fact that impedance diagrams have an approximately semicircular appearance shows that the corrosion of C-steel is controlled by a charge transfer process. Small distortion was observed in some diagrams, this distortion has been attributed to frequency dispersion [61]. The diameters of the capacitive loop obtained increases in the presence of HL, and were indicative of the degree of inhibition of the corrosion process [62].

It was observed from the obtained EIS data that R_{ct} increases and C_{dl} decreases with the increasing of inhibitor concentrations. The increase in R_{ct} values, and consequently of inhibition efficiency, may be due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface to form an adherent film on the metal surface. And this suggests that the coverage of the metal surface by the film decreases the double layer thickness. Also, this decrease of C_{dl} at the metal/solution interface with increasing the inhibitor concentration can result from a decrease in local dielectric constant which indicates that the inhibitor was adsorbed on the surface at both anodic and cathodic sites [63].

Comparative analysis for inhibition efficiency (%IE) study of ligand (HL) is shown in Fig. 20. It is observed that the %IE obtained from EIS measurements are close to those deduced from polarization measurements.

Conclusion

The results obtained can be summarized as follows:

- (1) This study has suggested that HL behave as a chelating monobasic tridentate/neutral bidentate ligand, bonding deprotonated (C–O)[–], nitrogen of (–N=N–) and carbonyl oxygen atoms. The IR data reveal that the anions are banded to the metal ions.
- (2) The study indicates the possibilities of significant variations of the structure and, therefore, properties of metal chelate complexes caused by diverse structural modifications of the azodye ligand.
- (3) The antimicrobial activity of the ligand (HL) and its Cu(II) complexes (1, 2 and 4) were studied.
- (4) It found that Cu(II) complexes (4) high effect was observed against P. italicum.
- (5) It was found that the ligand exists in the azo-enol form (**B**) and keto-hydrazo form (**D**) more stable and highly reactive than azo-keto form (A).
- (6) The thermal analysis of the ligand (HL) and its complexes was studied by TGA technique to give more information on the structure of the investigated complexes. The thermodynamic parameters of the decomposition reaction were evaluated and discussed.
- (7) Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) of the C-steel surface revealed that this azodye ligand prevented C-steel from corrosion by adsorption on its surface to form a protective film and acts as a barrier to corrosive media.
- (8) The inhibition efficiency of the tested ligand (HL) increase with increasing of its concentrations.

Acknowledgement

The authors would like to thank Dr. M.I. Abou-Dobara, Botany Department, Faculty of Science, Damietta University, Egypt for her help during testing antimicrobial activity.

References

- [1] M.A. Diab, A.Z. El-Sonbati, A.A. El-Bindary, M.Z. Balboula, J. Mol. Struct. 1040 (2013) 171–179.
- [2] M.I. Ábou-Dobara, A.Z. El-Sonbati, Sh.M. Morgan, World J. Microbiol. Biotechnol. 29 (2013) 119-126.
- [3] A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, M.K. Abd El-Kader, Spectrochim. Acta A 99 (2012) 211-217.
- [4] A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, M.I. Abou-Dobara, H.A. Seyam, Spectrochim. Acta A 104 (2013) 213-221.
- [5] A.Z. El-Sonbati, M.A. Diab, A.A.M. Belal, Sh.M. Morgan, Spectrochim. Acta A 99 (2012) 353-360.
- [6] A.Z. El-Sonbati, A.A.M. Belal, S.A. Abd El-Meksoud, R.A. El-Boz, J. Mol. Struct. 1027 (2012) 200-206.
- [7] A.A. El-Bindary, A.Z. El-Sonbati, M.A. Diab, M.K. Abd El-Kader, J. Chem. 2013 (2013) 1 - 6
- [8] A.A. El-Bindary, A.Z. El-Sonbati, M.A. Diab, E.E. El-Katori, H.A. Seyam, Int. J. Adv. Res. 2 (2014) 493-502.
- [9] N.A. El-Ghamaz, A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, H.A. Seyam, Solid State Sci. 19 (2013) 19-26.
- [10] N.A. El-Ghamaz, A.Z. El-Sonbati, Sh.M. Morgan, J. Mol. Struct. 1027 (2012) 92-98
- [11]R.H. Perry, D.W. Green, J.O. Maloney, Perry's Chemical Engineer's Handbook, seventh ed., McGraw-Hill Publishing, 1997.
- [12] A. Chetouani, B. Hammouti, A. Aouniti, N. Benchat, T. Benhadda, Prog. Org. Coat. 45 (2002) 373-378.

- [13] K. Bekkouch, A. Aouniti, B. Hammouti, S. Kertit, J. Chim. Phys. 96 (1999) 838-850
- [14] S. Kertit, B. Hammouti, M. Taleb, M. Brighli, Bull. Electrochem. 13 (1997) 241-244.
- [15] S.A. Abd El-Meksoud, A.M. El-Desoky, A.Z. El-Sonbati, A.A.M. Belal, R.A. El-Boz, Int. J. Sci. Eng. Res. 4 (2013) 1986-1994.
- [16] A.A. Al-Sarawy, M.A. Diab, A.M. El-Desoky, R.A. El-Bindary, Int. J. Sci. Eng. Res. 4 (2013) 1510-1521
- [17] A.S. Fouda, A.M. Eldesoky, A.Z. El-Sonbati, S.F. Salam, Int. J. Electrochem. Sci. 9 (2014) 1867-1891.
- [18] A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, Sh.M. Morgan, Spectrochim. Acta A 127 (2014) 310-328.
- [19] N.A. El-Ghamaz, A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, M.K. Awad, Sh.M. Morgan, Mater. Sci. Semicond. Process. 19 (2014) 150-162
- [20] B.S. Furniss, A.S. Hannaford, V. Rogers, P.W.G. Smith, A.R. Tatchell (Eds.), Vogels's Text Book of Practical Organic Chemistry, fourth ed., EIBS Logman Group Ltd., London, 1978.
- [21] P.W. Selwood, Magnetic Chemistry, Interscience Pub. Inc., New York, 1956.
- [22] N.A. El-Ghamaz, M.M. Ghoneim, A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, M.K. Abd El-Kader, J. Saudi Chem. Soc. http://dx.doi.org/10.1016/ j.jscs.2014.03.010.
- [23] J. Liang, W. Lipscomb, Biochemistry 28 (1989) 9724-9733.
- [24] P. Geerlings, F.D. Proft, W. Langenaeker, Chem. Rev. 103 (2003) 1793–1873.
- [25] M.A. Diab, A.Z. El-Sonbati, A.A. El-Bindary, A.M. Barakat, Spectrochim. Acta A 116 (2013) 428-439.
- [26] A.Z. El-Sonbati, A.A. El-Bindary, M.A. Diab, S.G. Nozha, Spectrochim. Acta A 83 (2011) 490-498.
- [27] M. Szymczyk, A. El-Shafei, H.S. Freednan, Dyes Pigm. 72 (2007) 6-15.
- [28] A.Z. El-Sonbati, A.A. El-Bindary, A. El-Dissouky, T.M. El-Gogary, A.S. Hilali, Spectrochim. Acta A 58 (2002) 1623-1629.
- [29] B. Kirkan, R. Gup, Turk. J. Chem. 32 (2008) 9-17.
- [30] L.J. Bellamy, The Infrared Spectra of complex Molecules, Wiley, New York, 1958.
- [31] M.A. Diab, A.A. El-Bindary, A.Z. El-Sonbati, O.L. Salem, Mol. Struct. 1007 (2012) 11-19
- [32] R.N. Patel, V.L.N. Gundla, D.K. Patel, Polyhedron 27 (2008) 1054-1252.
- [33] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fifth ed., Wiley, New York, 1997.
- [34] G.J. Karabatoses, B.I. Shapiro, E.M. Vane, J.S. Fleining, J. Ratka, J. Am. Chem. Soc. 85 (1931) 2784.
- [35] D.W. Barnum, J. Inorg. Nucl. Chem. 22 (1961) 221-237.
- [36] J.P. Fackler, F.A. Cotton, Inorg. Nucl. Chem. 22 (1963) 102-106.
- [37] A.Z. El-Sonbati, M.A. Diab, M.M. El-Halawany, N.E. Salam, Spectrochim. Acta A 77 (2010) 755-766.
- [38] A.Z. El-Sonbati, A.A. Al-Sarawy, M. Mogbel, Spectrochim. Acta A 74 (2009) 463-468
- [39] M.A. Diab, A.Z. El-Sonbati, R.H. Mohamed, Spectrochim. Acta A 77 (2010) 795-801
- [40] S. Chandra, Sangeetika, A. Rathi, J. Saudi Chem. Soc. 5 (2001) 175–182.
- [41] A.B.P. Lever, Inorganic Electronic Spectroscopic, second ed., Elsevier,
- Amsterdam, 1984.
- [42] M.J.M. Campbell, Coord. Chem. Rev. 15 (1975) 279-312.
- [43] R.P. John, A. Sreekanth, V. Rajakannan, T.A. Ajith, M.R.P. Kurup, Polyhedron 25 (2004) 2549-2559.
- [44] M. Joseph, M. Kuriakose, M.R.P. Kurup, E. Suresh, A. Kishore, G. Bhat, Polyhedron 25 (2006) 61-70.
- [45] S. Tyagi, B.J. Hathaway, J. Chem. Soc. Dalton Trans. (1983) 199-203.
- [46] D. Kivelson, R. Neiman, J. Chem. Phys. 35 (1961) 149-155.
- [47] A. Abragam, M.H.L. Pryce, Proc. Roy. Soc. (Lond.) A 205 (1951) 1355–1357.
- [48] A. Abragam, M.H.L. Pryce, Proc. Roy. Soc. (Lond.) A 206 (1951) 164-172.
 [49] B.J. Hathaway, A.A.G. Tomlinson, Coord. Chem. Rev. 5 (1970) 1–43.
- [50] A. Sreekanth, M.R.P. Kurup, Polyhedron 22 (2003) 3321-3332.
- [51] B.J. Hathaway, D.E. Billing, Coord. Chem. Rev. 5 (1970) 143-207.
- [52] A.Z. El-Sonbati, A.S. Al-Shihri, A.A. El-Bindary, Spectrochim. Acta A 60 (2004) 1763-1768.
- [53] B.J. Hathaway, Struct. Bond. 14 (1973) 49-67.
- [54] J.U.R. Wasson, D.M. Klassen, H.W. Richardson, W.E. Hatfield, Inorg. Chim. Acta 16 (1977) 1906–1914.
- [55] A.W. Coats, J.P. Redfern, Nature 20 (1964) 68-79.
- [56] H.W. Horowitz, G. Metzger, Anal. Chem. 35 (1963) 1464-1468.
- [57] S.T. Breviglieri, É.T.G. Cavalheiro, G.O. Chierice, Thermochim. Acta 356 (2000) 79-84
- [58] M. Hanif, Z.H. Chohan, Appl. Organomet. Chem. 27 (2013) 36-44.
- [59] H.M. Hassan, A.M. Eldesoky, R.M. Younis, W.A. Zordok, Int. J. Adv. Res. 2 (2014) 550 - 568
- [60] A.S. Fouda, A.M. El-desoky, D.M. Ead, Int. J. Electrochem. Sci. 8 (2013) 8823-8847
- [61] F. Mansfeld, M.W. Kendig, S. Tsai, Corros, 38 (1982) 570-580.
- [62] A.S. Fouda, A.M. El-desoky, M.M. Muhtar, J. Adv. Chem. 4 (2013) 323-350.
- [63] E. McCafferty, N. Hackerman, J. Electrochem. Soc. 119 (1972) 146–154.