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Spectral and thermal studies of 4-(1H-pyrazolo {3,4-d} pyrimidin-4-ylazo) benzene-1,3-diol complexes of cobalt(II), nickel(II) and copper(II)

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Abstract

4-(1H-Pyrazolo {3,4-d} pyrimidin-4-ylazo) benzene-1,3-diol was synthesized and characterized by various spectral and analytical techniques. Semiempirical quantum calculations using the AM1 method have been performed in order to evaluate the geometry and electronic structure of the title azodye in the ground state. The complex formation between Co(II), Ni(II) and Cu(II) ions and the title azodye was studied conductometrically and spectrophotometrically. The spectrophotometric determination of the title metal ions and titration using EDTA are reported. Co(II), Ni(II) and Cu(II) complexes of the title azodye have been synthesized and characterized by elemental analysis, conductivity, magnetic susceptibility, IR, UV-Vis and thermal analysis (TGA and DTA). The spectral and magnetic data suggested the octahedral geometry for Co(II) and Ni(II) complexes while Cu(II) complexes have square planar geometry. The thermal studies confirmed the chemical formulations of the title complexes. The thermal degradation takes place in two or three steps depending on the type of the metal and the geometry of the complexes. The kinetics of the decomposition was examined by using Coats–Redfern relation. The activation energies and other activation parameters (ΔH , ΔS and ΔG) were computed and related to the bonding and stereochemistry of the complexes.

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Keywords: Azodye metal complexes; Co(II); Ni(II); Cu(II); IR; ESR; UV-Vis spectra; TGA; DTA

1. Introduction

Various studies on the interaction of metal ions with heterocyclic azo-compounds have been reported in recent years [1–4]. The importance of the heterocyclic azodyes may stem from its biological activity and analytical investigations [5–15]. Also, it is well known that the heterocyclic azo compounds have been used to establish the low oxidation states of different metal ions [16]. Hence, structural characteristics of transition metal complexes with bioactive ligands may be a valuable source of information. The metal complexes of pyrimidines play a dominant role in many biochemical systems. Therefore to promote an understanding of these important systems, wide range studies on metal complexes with pyrimidines derivatives have been performed [17–25].

In the present paper, we describe the synthesis and characterization of the title azodye as well as the favourable conditions for complex formation, stoichiometry, and spectrophotometric

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1386-1425/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2007.05.001 determination of Co(II), Ni(II) and Cu(II) ions. Also the interest is focused on study of the chelating properties of the titled azodye based on elemental analysis, magnetic moments, spectral methods (IR, UV-Vis), conductance as well as the thermal behavior.

2. Experimental

All reagents used for the preparation of the complexes were of analytical grade.

2.1. Synthesis of the ligand

The ligand HL (Scheme 1) was prepared and purified according to the method reported in the literature [26]. The purity of the azodye was checked by the melting point constancy, elemental analysis and finally characterized by spectral methods (IR and ¹Hnmr). Found: C 51.2; H 2.92; N 32.4%; C₁₁H₈N₆O₂, cal. C 51.5; H 3.1; N 32.8%; m.p. 214 °C, ¹Hnmr: OH 8.9 and 9.25 ppm, NH 10.15 ppm, aromatic 7.35–7.95 ppm; IR: N=N 1484; OH 3521, 3402; NH 3200 cm⁻¹; yellow colour.



Scheme 1. The structure of azodye (HL).

2.2. Synthesis of the solid complexes

The metal complexes were prepared by mixing a hot ethanolic solution of azodye (0.01 or 0.02 mol) with the appropriate metal acetate (0.01 mol) in ethanol–water (50% (v/v)). The resulting mixture was then refluxed on a waterbath for \sim 12 h and allowed to cool whereby the solid complexes were precipitated. The solid complexes were collected by filtration, washed with 1:1 ethanol–water mixture and dried. The melting points of the solid complexes were higher than 300 °C.

2.3. Instruments

The elemental analyses for C, H and N of the solid compounds were performed by Heraeus instrument. The complexes were analyzed for their metal content by EDTA titration. Molar conductance of 10^{-3} M solutions in DMF was measured at room temperature on a Hanna 8733 conductivity meter. Infrared spectra in the range $4000-200 \text{ cm}^{-1}$ were recorded as KBr discs on a Perkin-Elmer 1430 spectrophotometer. Electronic spectra were recorded on a Shimadzu 240 UV-Vis spectrophotometer. The ¹HNMR spectrum of the ligand was performed using a Varian EM 390-90 NMR spectrometer in d⁶ DMSO as solvent using tetramethylsilane (TMS) as an internal standard. Magnetic susceptibilities were measured by the Gouy method at room temperature using Johnson Matthey magnetic susceptibility balance. The X-band ESR spectra of the complexes were recorded at room temperature on a JOEL-X-band spectrometer equipped with an E101 microwave bridge. Diphenyl picryl hydrazyl free radical (DPPH) was used as standard (g = 2.003). The thermal analysis (TGA and DTA) were carried out in N2 atmosphere with a heating rate 10 °C min⁻¹ using a Shimadzu TGA 50 and DTA 50 thermal analyzer.

2.4. Semiempirical quantum calculations

The geometry of the ground state of HL has been precisely optimized by using quantum chemical calculations at the AM1 level. After geometry optimization, the electronic and geometrical structures as well as dipole moment calculations have been performed. This was achieved with the help of ArgusLab 4.0 software (Mark A. Thompson, Planaria Software LLC, Seattle, WA) [27]. All calculations were performed using the default parameters.

3. Results and discussion

3.1. Study of complexes in solution

The electronic absorption spectra of Co(II), Ni(II) and Cu(II) complexes in media of different pH and different constituents are studied. The results showed that the best media are the borate buffer (pH 9), phosphate buffer (pH 6.8) and acetate buffer (pH 5.5) for Co(II), Ni(II) and Cu(II) complexes, respectively. In the other buffer solutions the colour of the complexes fades with time, probably due to dissociation of the formed complex. The effect of time and temperature were studied and it was found that the complexes were formed instantaneously and remained constant for 48 h. Also, it was found that raising the temperature has no effect on the formation of the complexes.

Experiment on the effect of addition sequence on the efficiency of complex formation showed that the addition sequence ligand-buffer-metal is the best one for Ni(II) and Cu(II) complexes while for Co(II) complex the best sequence is ligand-metal-buffer. The suitable wavelength for the complex formation was determined and found at 440, 380 and 360 nm for Co(II), Ni(II) and Cu(II) complexes, respectively. The stoichiometry of the complexes in solution was firstly established by conductometric titration. The conductometric titration curves indicate that the increase of conductance upon addition of metal ions is mainly due to the release of H⁺ ions via the formation of covalent linkage with the oxygen atom of the OH group. The titration curves show two breaks at molar ratios of 1:1 and 1:2 (M:L). Also, the composition of the complexes was established under the optimum conditions described above applying the mole ratio (MRM) [28] and continuous variation (CVM) [29] methods. The results reveal the formation of 1:1 and 1:2 (M:L) complexes confirming the results of conductometric titration. The conditional stability constants of the complexes formed in solution can be calculated from the data obtained by the different spectrophotometric methods utilized for the determination of their stoichiometry. The results obtained reveal that the stability of the 1:2 complexes is nearly twice as the 1:1 complexes. The free energy (ΔG) of complex formation was also calculated. The -ve values of ΔG indicate that the complexation reaction proceeds spontaneously. The obeyence of the metal complexes to Beer's law was investigated in order to apply these complexes for the spectrophotometric determination of metal ions. Applying the least square method on the absorbance-concentration plots, it was found that these lines have a very small standard deviation and their correlation coefficients are very close to unity. The limits of obedience to Beer's law, Ringbom concentration range, specific absorptivity, Sandell sensitivity, standard deviation and correlation coefficients are listed in Table 1. These values confirm the possible application of the method for the determination of the metal ions. It is clear that the molar absorptivity values follow the order Co–L \sim Ni–L>Cu–L complexes.

The spectrophotometric titration of Co(II), Ni(II) and Cu(II) ions with EDTA using azodye HL as an indicator in the presence of the suitable buffer of recommended pH values was performed as described previously [24]. The results listed in Table 1 indicate that Co(II), Ni(II) and Cu(II) ions are success-

| Table 1 | |
|---|--|
| Analytical parameters for Cu(II) azo-dye (HL) complex | |

| Parameter | Value/type | | |
|---|----------------------|--|--|
| Wavelength (nm) | 360 | | |
| Buffer | Acetate | | |
| pH | 5.5 | | |
| $\log \beta_n$ | 4.69 | | |
| | (9.59) ^a | | |
| $\Delta G^{ m a}$ | 6.39 | | |
| | (13.0) ^a | | |
| Molar absorptivity ($\varepsilon \times 10^{-3}$) | 14.7 | | |
| Specific absorptivity $(a \times 10^{-2})$ | 23.1 | | |
| Sandell sensitivity (S) | 4.34 | | |
| Standard deviation | 2.6×10^{-3} | | |
| Correlation coefficient | 0.9974 | | |
| Beer's limit (ppm) | 0.0-8.89 | | |
| Ringbom range (ppm) | 1.3-6.03 | | |
| $A \times 10^{-5} \text{ (mol } 1^{-1}\text{)}$ | 5.0 | | |
| $B \times 10^{-5} \; (\text{mol } l^{-1})$ | 5.2 | | |

 ε (L mol⁻¹ cm⁻¹); *a* (cm² g⁻¹); *S* (µg cm²). *A*, concentration of prepared sample; *B*, concentration of sample determined experimentally.

^a 1:2 (M:L) complexes.

fully determined as well as the applied reagent can be used as an indicator for the spectrophotometric titration of the metal ions under investigation.

3.2. Characterisation of the solid complexes

The complexes isolated in the present study are listed in Table 2. The analytical data confirm the proposed empirical formulae. All the complexes are stable in air and insoluble in most organic solvents but soluble in DMF. The low conductance of the metal chelates support the non-electrolytic nature of the metal complexes [30] indicating that the acetate anion is absent or situated inside the coordination sphere.

3.2.1. IR spectra

In order to ascertain the mode of bonding of the azodye to metal ions, the IR spectrum of the free azodye was compared with those of the metal complexes, Table 3.

The IR spectrum of the ligand (HL) shows broad bands at 3521 and 3402 cm^{-1} , assignable to the stretching vibration (v_{OH}) of the free and bonded OH groups [31], respectively. The

Table 3 The IR, electronic spectra and the magnetic moment of metal chelates under investigation

| No. | Infrare | d spectra | (cm^{-1}) | | Electron | $\mu_{	ext{eff}}$ | | |
|-----|--------------|-----------|------------------|------------------|----------|--------------------|-------|-----|
| | $v_{\rm OH}$ | $v_{N=N}$ | υ_{M-N} | υ _{M-0} | СТ | $L\!\rightarrow M$ | d–d | BM |
| 1 | 3418 | 1392 | 448 | 578 | 29412 | 23810 | 18519 | 3.7 |
| 2 | 3420 | 1391 | 446 | 573 | 29412 | 22727 | 18519 | 4.4 |
| 3 | 3424 | 1424 | 424 | 556 | 34482 | 28571 | 17544 | 2.6 |
| 4 | 3424 | 1419 | 419 | 553 | 33333 | 25411 | 17241 | 2.5 |
| 5 | 3437 | 1463 | 429 | 560 | 35714 | 26315 | 20833 | 1.8 |
| 6 | 3445 | 1460 | 430 | 560 | 35714 | 26315 | 16949 | 1.7 |

disappearance of the last band in the spectra of the complexes indicates deprotonation of the hydroxyl group upon chelation. Also, the IR spectra of the metal complexes show a new band at 553–578 cm⁻¹ characteristic of v_{M-O} vibration [32]. The IR spectrum of the ligand shows a characteristic $v_{N=N}$ band at 1484 cm^{-1} , which shifts to lower frequency in the spectra of the metal complexes $(1391-1463 \text{ cm}^{-1})$. This indicates the participation of the nitrogen atom of the azo group in complex formation, which is supported by the appearance of a new band in the region 419–448 cm⁻¹ due to v_{M-N} [33]. In the acetate complexes (1, 3, 5) the bands due to v_{as} and v_{s} of the acetate group are displayed within the ranges 1640-1625 and 1380-1365 cm⁻¹, respectively. This frequency separation (Δv) is characteristic of monodentate acetate group [34,35]. The IR spectra of the metal complexes display a band in the range $3400-3370 \,\mathrm{cm}^{-1}$, which can be attributed to the antisymmetric and symmetric OH stretching vibrations of the hydration water molecules present in the complexes.

According to the IR data, the ligand behaves as a monobasic bidentate ligand towards the divalent metal ions via N and O atoms of the azo and hydroxyl groups, respectively.

3.2.2. Electronic, ESR spectra and magnetic measurements

The electronic spectra as well as the magnetic moment values of the complexes are summarized in Table 3 together with the proposed assignments and suggested geometries.

The Nujol mull electronic spectra of the Co(II) complexes 1 and 2 show broad band at 18,519 cm⁻¹ which can be assigned to ${}^{4}T_{1g}$ (F) $\rightarrow {}^{4}T_{1g}$ (P) transition for octahedral environment [36]. The magnetic moments of Co(II) complexes 1 and 2 are 3.7 and

Table 2 Symbol, molecular formula, elemental analysis, and molar conductance of azodye complexes

| No. | Formula | Yield (%) | Percent elemental analysis ^a | | | | Am |
|-----|---|-----------|---|------------|--------------|--------------|------|
| | | | С | Н | Ν | М | |
| 1 | [CoL(AcO)(EtOH) ₃]·3H ₂ O | 75 | 40.4 (39.8) | 6.03 (5.2) | 14.9 (14.62) | 10.28 (9.9) | 0.06 |
| 2 | $[CoL_2(EtOH)_2] \cdot 4H_2O$ | 77 | 42.6 (42.23) | 4.6 (3.9) | 22.9 (22.6) | 8.0 (7.73) | 0.05 |
| 3 | [NiL(AcO) (EtOH) ₃]·4H ₂ O | 80 | 39.2 (38.7) | 6.2 (5.89) | 14.4 (13.85) | 9.97 (9.7) | 0.08 |
| 4 | [NiL ₂ (EtOH) ₂]·4H ₂ O | 74 | 42.6 (42.32) | 4.6 (4.01) | 22.9 (22.54) | 7.9 (7.62) | 0.07 |
| 5 | [CuL(AcO)(EtOH)]·3H ₂ O | 85 | 37.7 (37.4) | 4.6 (3.94) | 17.6 (17.4) | 13.3 (12.81) | 0.07 |
| 6 | [CuL ₂] | 80 | 52.4 (52.01) | 4.0 (3.71) | 20.4 (20.15) | 11.6 (11.3) | 0.08 |

Am (Ω^{-1} cm² mol⁻¹), 10⁻³ M DMF solution.

^a Cal (found)



Fig. 1. X-band ESR spectrum of copper(II) complex 5.

4.4 BM, respectively. These values are comparatively lower than values predicted for tetrahedral or octahedral complexes [37]. These values indicate antiferromagnetic interaction, since the above results as well as the electronic spectral bands of the Co(II) complexes rule out the possibility of mixing Co(III) species with Co(II).

The Ni(II) complexes exhibit two bands at 28,571 and 17,544 cm⁻¹ for complex 3 and 25,411 and 17,242 cm⁻¹ for complex 4, assigned to the ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(\upsilon_3)$ and ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}(\upsilon_2)$ transitions, respectively, in an octahedral geometry. The room temperature magnetic moments of the Ni(II) complexes 3 and 4 are 2.6 and 2.5 BM, respectively. These values are lower than expected for octahedral Ni(II) complexes. This behavior may be due to some antiferromagnetic properties of the metal ions [38].

The magnetic moment values of the Cu(II) complexes 5 and 6 are 1.8 and 1.7 BM corresponding to one unpaired electron. The former complex shows a band at 20,833 cm⁻¹ due to ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ transition while the latter complex shows a band at 16,949 cm⁻¹

Table 4

Thermal behavior of azodye metal complexes

assigned to the envelope of ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$, ${}^{2}B_{2g}$ and ${}^{2}E_{g}$ transitions suggesting square planar structure of Cu(II) complexes [39]. The ESR spectrum of Cu(II) complex 5, in the solid state, was measured at room temperature, Fig. 1. The calculated data show that $g_{11} = 2.26$ and $g_{\perp} = 2.06$ i.e. $g_{11} > g_{\perp} > 2.0023$. This indicates that the unpaired electron is localized in d_{x2-y2} orbital [40] which is consistent with the proposed planar stereochemistry [41]. Also, the observed value which is <2.3 indicates the covalent nature between the Cu(II) ion and the ligand [42].

All the complexes show an intense bands within the range 29,411–35,714 cm⁻¹, corresponding to the ligand π – π * transitions while the bands within the range 22,727–28,571 cm⁻¹ can be assigned to the ligand to metal charge transfer transitions [43].

3.2.3. Thermal analysis

The TGA curves of the Co(II) complexes 1 and 2 give two-stage decomposition pattern within the ranges 50–95 °C (associated with an endothermic peaks at 80 and 90 °C) and 90–260 °C (with exothermic peak at 180 and 250 °C) for Co(II) complexes 1 and 2, respectively, corresponding to the loss of hydration water molecules and complete decomposition resulting the final product CoO, Table 4.

The decomposition of Ni(II) complexes 3 and 4 proceeds in three steps. The TG curve of complexes show a weight loss in the temperature ranges 50–95 and 50–120 °C, associated with endothermic peaks at 110 and 120 °C, corresponding to loss of hydration water molecules. The next decomposition step in the temperature ranges 190–250 and 120–240 °C, associated with an exothermic peak at 280 and 230 °C, bring weight loss which correlates with elimination of the ligand molecule. The final stage of decomposition above 250 °C with an exothermic peaks at 350 and 400 °C for complexes 3 and 4, respectively, corresponds to the complete decomposition to NiO as the final solid product.

| Complex | Range (°C) | DTA peak (°C) | Decomposition product lost (formula wt) | Mass loss (%) | |
|---|------------|---------------|---|---------------|-------|
| | | | | Found | Cal |
| [CoL(AcO)(EtOH) ₃]·3H ₂ O | 50-90 | 80 | 3H ₂ O | 9.6 | 9.55 |
| | 90-260 | 180 | Residue CoO | 13.00 | 13.25 |
| [CoL ₂ (EtOH) ₂]·4H ₂ O | 50-95 | 90 | 4H ₂ O | 10.0 | 9.82 |
| | 100-250 | 250 | Residue CoO | 10.05 | 10.22 |
| [NiL(AcO) (EtOH)3]·4H2O | 50-95 | 110 | 4H ₂ O | 12.1 | 12.36 |
| | 190-250 | 280 | $C_{11}H_7N_6O_2$ | 43.2 | 43.8 |
| | 250-400 | 350 | Residue NiO | 32.8 | 34.7 |
| [NiL ₂ (EtOH) ₂]·4H ₂ O | 50-120 | 120 | 3H ₂ O | 11.2 | 9.83 |
| | 120-240 | 230 | $C_{22}H_{14}N_{12}O_4$ | 68.8 | 69.6 |
| | 240-390 | 400 | Residue NiO | 10.4 | 10.19 |
| [CuL(AcO) (EtOH)]·3H ₂ O | 50-115 | 110 | 3H ₂ O | 11.0 | 11.3 |
| | 120-400 | 260 | $C_{11}H_7N_6O_2$ | 52.9 | 53.4 |
| | 400-640 | 450 | Residue CuO | 16.40 | 16.65 |
| [CuL ₂] | 170-250 | 270 | $C_{11}H_7N_6O_2$ | 44.0 | 44.5 |
| | 375-640 | 370 | Residue CuO | 13.75 | 13.90 |



Fig. 2. Coats–Redfern plots for the decomposition steps of complexes (1–6); (a) first step, (b) second step and (c) Third step. $Y = \ln\{[1-(1-\alpha)^{1-n}]/[T^2(1-n)]\}$ for $n \neq 1$ and $Y = \ln\{[-\ln(1-\alpha)]/T^2\}$ for n = 1.

The TGA curve of the Cu(II) complex 5 consists of three stages of mass loss within the temperature ranges 50–115, 120–400 and 400–640 °C associated with endothermic peak at 110 °C and exothermic peaks at 260 and 450 °C which can be attributed to a loss of hydration water molecules, release of the ligand molecule and complete decomposition with the formation of CuO. Cu(II) complex 6 decomposes in two steps within the temperature ranges 170–250 and 375–640 °C associated with exothermic peaks at 270 and 370 °C, corresponding to the decomposition of the complex with the formation of CuO as a final product.

The order (n) and the activation energies (E) of the different stages of the thermal decomposition reactions have been evaluated from TGA curves by using the Coats–Redfern method [44]. The equations used are in the form:

$$\ln\left\{\frac{[1-(1-\alpha)^{1-n}]}{[T^2(1-n)]}\right\} = \left[\frac{M}{T}\right] + B \quad \text{for } n \neq 1$$
(1)

$$\ln\left\{\frac{\left[-\ln(1-\alpha)\right]}{T^2}\right\} = \left[\frac{M}{T}\right] + B \quad \text{for } n = 1 \tag{2}$$

where α is the fraction decomposed at a given temperature T(K), A is the frequency factor, R is the gas constant, Q is the heating rate, M = -E/R and $B = \ln (AR/QE)$ Since $1-(2RT/E) \sim 1$, a plot of L.H.S of the above equation versus (1/T) gives straight line (Fig. 2) whose slope and intercept are used for calculate the values of E and A, respectively. Linear curves were drawn for different values of n. The value of n, which gave the best fit i.e. high correlation coefficient, was chosen as the order parameter for the decomposition stage of interest. The activation entropy ΔS , the activation enthalpy (ΔH^*) and the free energy of activation (ΔG^*) can be calculated using equations:

$$A = \left(\frac{KT_{\rm s}}{h}\right) e^{\Delta S/R}$$
$$\Delta H = E - RT$$
$$\Delta G = \Delta H - T\Delta S$$

where K is the Boltzman constant, h is the Plank's constant and T_s is the peak temperature. The various kinetic parameters calculated are given in Table 5. M. Gaber et al. / Spectrochimica Acta Part A 69 (2008) 534-541

| | • | | | | | | | |
|-----------|------|------|---------|-------------------------------|---|----------------------|--------------------------------|---|
| Compounds | Step | п | r | E^* (kJ mol ⁻¹) | $\Delta H^* (\mathrm{kJ}\mathrm{mol}^{-1})$ | $A(S^{-1})$ | $\Delta S^* (JK^{-1}mol^{-1})$ | $\Delta G^* (\mathrm{kJ}\mathrm{mol}^{-1})$ |
| 1 | 1st | 1 | 0.9950 | 39.29 | 36.64 | 2.24×10^{5} | -143.10 | 82.27 |
| | 2nd | 0 | 0.9840 | 46.89 | 42.93 | 1.40×10^3 | -188.52 | 132.67 |
| 2 | 1st | 1 | 0.9920 | 43.84 | 40.92 | 2.6×10^5 | -142.63 | 91.12 |
| | 2nd | 0 | 0.9998 | 52.41 | 48.37 | 4.6×10^3 | -178.86 | 135.29 |
| 3 | 1st | 1 | 0.9926 | 37.67 | 34.65 | 1.65×10^{3} | -184.94 | 101.79 |
| | 2nd | 0 | 0.9880 | 86.85 | 82.51 | 3.8×10^4 | -161.88 | 167.01 |
| | 3rd | 1 | 0.9910 | 78.16 | 72.91 | 1.76×10^5 | -150.73 | 168.17 |
| 4 | 1st | 1 | 0.9987 | 49.03 | 52.19 | 6.4×10^{5} | -135.80 | 103.79 |
| | 2nd | 0.66 | 0.9833 | 79.56 | 75.47 | 4.1×10^{6} | -122.42 | 135.70 |
| | 3rd | 0 | 0.9937 | 23.27 | 18.17 | 5.192 | -237.21 | 165.58 |
| 5 | 1st | 1 | 0.9965 | 36.23 | 33.33 | 1.52×10^4 | -166.18 | 91.12 |
| | 2nd | 0.66 | 0.9906 | 20.68 | 15.9 | 1.93 | -244.93 | 156.85 |
| | 3rd | 1 | 0.9968 | 54.72 | 47.61 | 69.99 | -218.36 | 234.41 |
| 6 | 1st | 1 | -0.9982 | 87.15 | 81.97 | 3.7×10^{6} | -133.56 | 165.23 |
| | 2nd | 0 | -0.9924 | 89.51 | 82.74 | 3.4×10^3 | -174.74 | 224.96 |

Table 5 The kinetic and thermodynamic data of the thermal decomposition of the metal complexes

The following remarks can be pointed out:

- (i) The reaction orders of the decomposition stages of the complexes are 1, 0.66, 0.33 and zero. The reaction order of a solid stage decomposition has no intrinsic meaning, but is rather a mathematical smoothing device [45].
- (ii) The activation energy of the first step for 1:1 complexes indicates that the Co(II) complex is more stable than the Ni(II) and Cu(II) complexes.
- (iii) The values of ΔG increase for the subsequent decomposition steps of a given complex. This reflects that the rate of removal of the subsequent ligand will be lower than that of the precedent ligand [46,47].
- (iv) The -ve values of ΔS indicate that the reactions are slow in nature and/or a more ordered activated complex than the reactants [48].

3.3. Theoretical calculations

Semiempirical quantum calculations using the AM1 method have been performed in order to evaluate the geometry and electronic structure of the azodye HL in the ground state.



Fig. 3. Optimized geometry of ground state using AM1 calculations.

The calculations indicated a stable non-planar structure with a minimum energy, as shown in Fig. 3. According to this structure, the phenyl-azo group is out of plane with respect to the pyrimidine ring. The distortion from planarity is due to rotation around the C₄–N₁₀ and C₁₂–N₁₁ bonds by 54.1° and 8.6°, respectively. Also, intramolecular hydrogen bond formation between N₁₀–H₂₇ increases the stability of the molecule (ΔH_f = 99.3 kcal/mol compared to 100.6 kcal/mol for the non-hydrogen bonded conformer). The calculations reveal a long distance between N₁₀–H₂₇ with a length equals to 2.17A° which is consistent with the length of the H-bond. The calculated charge densities, bond orders and bond lengths of the molecular skele-

| able 6 |
|--|
| he calculated net charge on the molecular skeleton of HL using AM1 |

| Atom | Charge | Bond | Bond length | Bond order |
|------|---------|---------|-------------|------------|
| N1 | -0.2131 | N1-C2 | 1.351 | 1.474 |
| C2 | 0.0158 | C2-N3 | 1.370 | 1.316 |
| N3 | -0.2378 | N3-C4 | 1.359 | 1.444 |
| C4 | 0.1909 | C4–C5 | 1.417 | 1.247 |
| C5 | -0.2328 | C5–C6 | 1.403 | 1.233 |
| C6 | 0.1018 | C6-N1 | 1.367 | 1.274 |
| N7 | -0.3048 | C6–N7 | 1.403 | 1.165 |
| N8 | -0.0536 | N7–N8 | 1.347 | 1.118 |
| C9 | -0.1459 | N8-C9 | 1.148 | 1.676 |
| N10 | -0.1534 | C9–C5 | 1.449 | 1.145 |
| N11 | -0.0059 | C4-N10 | 1.448 | 0.989 |
| C12 | -0.1811 | N10-N11 | 1.332 | 1.845 |
| C13 | -0.0544 | C12-C13 | 1.3793 | 1.284 |
| C14 | -0.2630 | N11-C12 | 1.424 | 1.051 |
| C15 | 0.1456 | C12-C13 | 1.423 | 1.3214 |
| C16 | -0.3289 | C13-C14 | 1.380 | 1.508 |
| C17 | 0.1816 | C14-C15 | 1.412 | 1.278 |
| O18 | -0.2945 | C15-C16 | 1.394 | 1.389 |
| 019 | -0.3061 | C16-C17 | 1.410 | 1.327 |
| | | C17-C12 | 1.420 | 1.288 |
| | | C17-O19 | 1.364 | 1.103 |
| | | C15–O18 | 1.388 | 1.085 |



Fig. 4. HOMO-LUMO representation (bottom and top, respectively).

ton of the HL are collected in Table 6. The values of bond order, calculated after ground state geometry optimization, are consistent with the expected ones and indicate the existence of a weak H-bond between N_{10} and H_{27} (bond order is 0.0077). The ground state dipole moment (μ_g) is calculated. The calculated value is 1.3 D indicating some charge transfer interaction between the phenolic group as an electron donor and the pyrimidine one as an acceptor, via the azo-bridge. Further confirmation for this fact comes from charge density calculations, Table 6, where it was found that the charge density on the azo-pyrimidine and phenolic moieties are -0.1477 and +0.1478 e, respectively. In addition, the calculations indicate different electronic transitions from which the $\pi - \pi^*$ transition at 336 nm (oscillator strength = 0.65) which corresponds to the HOMO-LUMO transition, is in agreement with the experimental results (the absorption maximum in *n*-heptane is 340 nm). This transition is well represented by plot of the HOMO (at -0.3423 eV) and LUMO (at -0.0459 eV) molecular orbitals as illustrated in Fig. 4.

4. Conclusions

A new hydroxy azopyrimidine ligand and its Co(II), Ni(II) and Cu(II) complexes have been synthesised and characterized by combination of elemental analyses, spectral, magnetic, conductance measurements, thermal and theoretical methods. From the analytical and spectral data, it is concluded that the title azodye acts as monobasic bidentate ligand with azo-nitrogen and phenolic oxygen atoms. The spectral and magnetic data reveal octahedral structure for Co(II) and Ni(II) complexes and square planar for Cu(II) complexes. The thermal decomposition of the metal complexes is discussed in relation to structure and different thermodynamic parameters of the decomposition stages are evaluated. The spectrophotometric titration of Co(II), Ni(II) and Cu(II) ions with EDTA using azodye HL as an indicator indicates that Co(II), Ni(II) and Cu(II) ions are successfully determined as well as the applied reagent can be used as an indicator for the spectrophotometric titration of the metal ions under investigation.

Based on the above results, the structures of the complexes are represented as given in Scheme 2.



Complex 1, M = Co, X=Y= EtOH, n=3Complex 3, M = Ni, X=Y= EtOH, n=4Complex 5, M = Cu, X= EtOH, Y= 0, n=0



Complex 4, M = Ni, X = EtOH, n=4Complex 6, M = Cu, X = n=0

Scheme 2. Suggested structures of Co(II), Ni(II) and Cu(II) complexes.

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