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# Spectral properties of some metal complexes derived from uracil-thiouracil and citrazinic acid compounds

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### Abstract

The reaction of FeCl<sub>3</sub> with uracil ( $H_2L^1$ ), citrazinic acid ( $H_2L^6$ ), 5-(phenylazo)citrazinic acid ( $H_2L^7$ ), 5-(*m*-hydroxyphenylazo)citrazinic acid ( $H_2L^8$ ) and 5-(*m*-nitrophenylazo)citrazinic acid ( $H_2L^9$ ) leads to the formation of complexes with the empirical formula Fe( $HL_{)_3} \cdot nH_2O$  (n = 1-3). All of the prepared complexes have octahedral complexation geometry where the azo group is not the reactive site for complexation. Thiouracil ( $H_2L^2$ ) and the 5-(substituted phenylazo)thiouracil ( $H_2L^3 - H_2L^5$ ) ligands are bidentates on complexation with Co(II), Ni(II) and Cu(II). The complexes have been characterized by elemental analyses, IR, electronic spectra, magnetic susceptibility, DTA, electron spin resonance (copper complexes) and Mössbauer spectra (iron complexes). The coordination bond lengths between the metal ion and the active centers for complexation were calculated.

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#### 1. Introduction

Pyrimidine derivatives constitute an important class of compounds because they are components of the biologically important nucleic acid [1,2]. Compounds containing nitrogen and sulphur as donor atoms have an important role to play as anticancer and antiviral agents [3,4]. The Pt–uracil complexes have high antitumor, antibacterial and antiviral activities and have a low level of renal toxicity [5–9].

Citrazinic acid azo dyes were prepared to dye cellulosic and nylon fibers [10]. Citrazinic acid is used in the field of photography [11–13] as an inhibitor-removing wash bath for direct positive colour photographic development [12].

In this paper, an attempt is made to assign the centers of complexation. The structures of complexes are based on various spectroscopic methods (UV, vis, IR, ESR and Mössbauer), magnetic susceptibility and DTA. The coordination bond lengths were calculated. The structures of the ligands are shown in Fig. 1.

#### 2. Experimental

All the azo compounds  $(H_2L^3 \text{ to } H_2L^5 \text{ and } H_2L^7 \text{ to } H_2L^9)$ were prepared in a similar way by the usual diazotization process [14]. An example  $H_2L^3$  is given here: (0.1 mol, 9.3 g) of aniline was dissolved in 5 mL (0.2 mol) HCl and 25 mL distilled water. The hydrochloride compound was diazotized below 5 °C with a solution of NaNO<sub>2</sub> (0.1 mol, 6.9 g) in 20 mL distilled water. The diazonium chloride was coupled with an alkaline solution of  $H_2L^2$  (0.1 mol, 12.8 g) in 30 mL distilled water. The crude dye was filtered and crystallized from 75% ethanol–water (v/v), then dried in a vacuum desiccator over CaCl<sub>2</sub>.

The iron complexes were prepared by dissolving 30 mmol (3.36 g) of the ligand  $(H_2L^1)$  in 150 mL warm ethanol at 70 °C, and mixed with 50 mL of an alcoholic solution containing 15 mmol (4.05 g) of iron(III) chloride for 1 h. The reaction mixture was left to cool at room temperature where the complexes precipitated.

The complexes of cobalt(II), nickel(II) and copper(II) (10 mmol) were prepared in 10 mL of aqueous ammonia solution (25%) and 10 mL ethanol by refluxing 10 mmol of the metal(II) chlorides with 20 mmol of the organic ligand dissolved in 100 mL of ethanol. The reaction mixture was refluxed for 1 h at 70 °C. The precipitated complexes then were separated by filtration and washed with H<sub>2</sub>O followed by drying in a desic-

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Table 1Analytical data of the complexes

Complex	MW	mp (°C)	% yield	Colour	Empirical formula	Calculated/Found (%)			
						М	С	Н	Ν
$\overline{\text{Fe}(\text{HL}^1)_3 \cdot 3\text{H}_2\text{O}}$	443	320	85	Yellowish brown	C <sub>12</sub> H <sub>15</sub> FeN <sub>6</sub> O <sub>9</sub>	12.6 (12.8)	32.5 (32.6)	3.3 (3.4)	18.9 (19.1)
Fe(HL <sup>6</sup> ) <sub>3</sub> ·3H <sub>2</sub> O	572	325	79	Black	C <sub>18</sub> H <sub>18</sub> FeN <sub>3</sub> O <sub>15</sub>	9.8 (9.6)	37.6 (37.5)	3.1 (3.2)	7.3 (7.0)
Fe(HL <sup>7</sup> ) <sub>3</sub> ·2H <sub>2</sub> O	866	340	77	Brownish yellow	C36H28FeN9O14	6.5 (6.4)	49.9 (49.8)	3.2 (3.1)	14.5 (14.6)
Fe(HL <sup>8</sup> ) <sub>3</sub> ·3H <sub>2</sub> O	932	360	82	Brown	C36H23FeN9O18	6.0 (6.1)	46.4 (46.4)	3.2 (3.2)	13.5 (13.7)
Fe(HL <sup>9</sup> ) <sub>3</sub> ·H <sub>2</sub> O	983	365	80	Brownish yellow	C36H28FeN12O19	5.7 (5.7)	43.9 (43.8)	2.3 (2.2)	17.1 (17.2)
$Co(HL^2)_2 \cdot 3H_2O$	365.9	315	85	Pale brown	C <sub>8</sub> H <sub>12</sub> CoN <sub>4</sub> O <sub>5</sub> S <sub>2</sub>	15.8 (15.5)	26.4 (26.2)	3.3 (3.2)	15.3 (15.0)
Ni(HL <sup>2</sup> ) <sub>2</sub> ·3H <sub>2</sub> O	365.7	319	73	Green	C <sub>8</sub> H <sub>12</sub> NiN <sub>4</sub> O <sub>5</sub> S <sub>2</sub>	15.8 (15.7)	26.2 (26.3)	3.3 (3.2)	15.3 (15.1)
$Cu(HL^2)_2 \cdot H_2O$	335.5	325	76	Pale blue	C <sub>8</sub> H <sub>8</sub> CuN <sub>4</sub> O <sub>3</sub> S <sub>2</sub>	18.9 (18.7)	28.6 (28.5)	2.4 (2.4)	16.7 (16.9)
$Co(HL^3)_2 \cdot 3H_2O$	373.9	318	82	Orange	$C_{20}H_{20}CoN_8O_5S_2$	9.8 (10.0)	41.9 (41.8)	3.5 (3.4)	19.5 (19.3)
$Ni(HL^3)_2 \cdot 3H_2O$	373.7	320	85	Green	C20H20NiN8O5S2	9.7 (9.8)	41.9 (41.8)	3.5 (3.5)	19.5 (19.3)
$Cu(HL^3)_2 \cdot 2H_2O$	561.5	333	82	Green	$C_{20}H_{18}CuN_8O_4S_2$	11.3 (11.2)	42.7 (42.6)	3.2 (3.1)	19.9 (19.8)
Co(HL <sup>4</sup> ) <sub>2</sub> ·3H <sub>2</sub> O	605.9	320	75	Deep brown	$C_{20}H_{20}CoN_8O_7S_2$	9.5 (9.3)	39.7 (39.8)	3.3 (3.3)	18.5 (18.4)
Ni(HL <sup>4</sup> ) <sub>2</sub> ·4H <sub>2</sub> O	623.7	321	76	Light green	C20H22NiN8O8S2	9.3 (9.2)	38.5 (38.5)	3.5 (3.3)	18.0 (17.8)
$Cu(HL^4)_2 \cdot 2H_2O$	593.5	335	80	Blue	$C_{20}H_{18}CuN_8O_6S_2$	10.7 (10.5)	40.4 (40.5)	3.0 (3.1)	18.9 (19.0)
Co(HL <sup>5</sup> ) <sub>2</sub> ·4H <sub>2</sub> O	623.9	322	81	Brown	$C_{20}H_{22}CoN_8O_8S_2$	9.2 (9.1)	38.5 (38.5)	3.5 (3.5)	18.0 (18.0)
$Cu(HL^5)_2 \cdot 3H_2O$	611.5	340	82	Deep green	$C_{20}H_{20}CuN_8O_7S_2$	10.4 (10.3)	39.2 (39.1)	3.3 (3.2)	18.3 (18.1)



Fig. 1. Structures of the ligands.

cator over anhydrous CaCl<sub>2</sub>. The metal content was determined by usual complexometric titration procedures [15]. The analytical data and some of the physical properties are collected in Table 1.

# 3. Results and discussion

#### 3.1. Iron complexes

All of the iron complexes are of 1:3 stoichiometry. A generalized equation is given to represent these reactions:

# $FeCl_3 + 3H_2L \rightarrow Fe(HL)_3 \cdot nH_2O + 3HCl$

L stands for any ligand used  $(L^1, L^6, L^7, L^8, L^9)$  and *n* is 3, 3, 2, 3, 1 in the sequence of these ligands.

# 3.2. Iron–uracil complex

The IR spectra of this complex show the following features:

- (1) The broad bands at 3410 and 3370 cm<sup>-1</sup> in uracil and its iron complex, respectively, are due to  $\nu$ (OH) of water molecules and hydrogen bonds of the type N-H···O [14,16].
- (2) The uracil  $\nu$ (NH) bands at 3111 and 3041 cm<sup>-1</sup> are strongly affected on complexation to iron(III) with the presence of only one band at 3100 cm<sup>-1</sup> due to Fe–N interaction [16].
- (3) Both  $\nu$ (C=O) bands of uracil at 1740 and 1714 cm<sup>-1</sup> are affected on complexation to iron(III) with different degrees. The first band is shifted to 1727 cm<sup>-1</sup>, while the second one disappeared. Such finding typified Fe–O bonding [14].
- (4) The two amide bands of uracil at 1666 and 1643 cm<sup>-1</sup> are affected on complexation. The first band is affected very slightly and appeared at 1663 cm<sup>-1</sup> while the second band is absent. Thus, uracil acts as a bidentate ligand through oxygen and nitrogen atoms on reaction with iron. In the lower-frequency spectral region bands for  $\nu$ (Fe–O) and  $\nu$ (Fe–N) are seen at 548 and 428 cm<sup>-1</sup>, respectively [17].

The Nujol mull electronic absorption spectra of the yellowish brown–iron complex [Fe(HL<sup>1</sup>)<sub>3</sub>]·3H<sub>2</sub>O (Table 2) gave charge transfer bands at 42,105 and 27,826 cm<sup>-1</sup>. The visible d–d electronic spectral band at 20,121 cm<sup>-1</sup> and the effective room temperature magnetic moment ( $\mu_{eff} = 5.9$  BM) typified the existence of an octahedral high-spin state [18]. The structure in Fig. 2 is proposed for the Fe(III)–uracil complex.

#### 3.3. Iron-citrazinic acid complex

The infrared spectrum of the iron–citrazinic acid complex  $[Fe(HL^6)_3] \cdot 3H_2O$ , shows a band at  $3404 \text{ cm}^{-1}$ , which is due to  $\nu(O-H)$  of the citrazinate moiety or to  $H_2O$  molecules in the structure of the complex. The band at  $3214 \text{ cm}^{-1}$  is due to  $\nu(N-H)$  of the citrazinate moiety. The bands at 1705 and

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Table 2

Nujol mull electronic absorption spectra and room temperature (25  $^{\circ}$ C) magnetic moment values of the metal complexes

Complex	$\lambda (cm^{-1})$	$\mu_{\rm eff}$ (298 K) (BM)
Fe(HL <sup>1</sup> ) <sub>3</sub> ·3H <sub>2</sub> O	42,105; 27,826; 20,121	5.9
Fe(HL <sup>6</sup> ) <sub>3</sub> ·3H <sub>2</sub> O	42,105; 37,175; 21,739	6.1
Fe(HL7)3·2H2O	36,866 23,426; 20,779	5.96
Fe(HL <sup>8</sup> ) <sub>3</sub> ·3H <sub>2</sub> O	36,866; 23,520; 20,000	5.8
Fe(HL <sup>9</sup> ) <sub>3</sub> ·H <sub>2</sub> O	36,866; 31,546; 23,529; 20,000	5.85
$Co(HL^2)_2 \cdot 3H_2O$	45,662; 37,736; 22,727; 17,857	5.1
Ni(HL <sup>2</sup> ) <sub>2</sub> ·3H <sub>2</sub> O	47,170; 35,842; 22,988; 19,685	3.1
Cu(HL <sup>2</sup> ) <sub>2</sub> ·H <sub>2</sub> O	36,900; 27,397; 19,841	1.8
Co(HL <sup>3</sup> ) <sub>2</sub> ·3H <sub>2</sub> O	39,683; 31,746; 23,810; 19,569	5.2
Ni(HL3)2·3H2O	34,483; 29,499; 22,727; 20,000	3.2
$Cu(HL^3)_2 \cdot 2H_2O$	46,512; 37,037; 21,798	1.9
Co(HL <sup>4</sup> ) <sub>2</sub> ·3H <sub>2</sub> O	47,170; 38,462; 22,727; 18,762	5.1
Ni(HL <sup>4</sup> ) <sub>2</sub> ·4H <sub>2</sub> O	38,168; 29,412; 22,890; 19,048	3.1
$Cu(HL^4)_2 \cdot 2H_2O$	37,736; 30,581; 22,222	1.82
Co(HL5)2·4H2O	42,194; 30,769; 23,809; 19,231	5.15
$Cu(HL^5)_2{\cdot}3H_2O$	38,462; 30,770; 20,619	1.83

1685 cm<sup>-1</sup> are due to  $\nu$ (C=O) of the keto group of the citrazinate moiety. The band at 1613 cm<sup>-1</sup> is due to  $\nu$ (C=N). The two bands at 1460 and 1394 cm<sup>-1</sup> are due to  $\nu_{as}$ (COO<sup>-</sup>) and  $\nu_{s}$ (COO<sup>-</sup>), respectively, and confirm that the bonding occurred *via* the bidentate carboxylate group. The presence of the lowfrequency bands at 432 and 365 cm<sup>-1</sup> are due to  $\nu$ (Fe  $\leftarrow$  O) and  $\nu$ (Fe–O) of the carboxylate group [19], respectively.

The Nujol mull electronic absorption spectra of the black iron–citrazinic acid complex [Fe(HL<sup>6</sup>)<sub>3</sub>]·3H<sub>2</sub>O (Table 2) gave charge transfer bands at 42,105 and 37,175 cm<sup>-1</sup>, and a visible band at 21,739 cm<sup>-1</sup> as well as the room temperature magnetic moment value  $\mu = 6.1$  BM, which suggests an octahedral structure of high-spin state [18] as shown in Fig. 3.

# 3.4. Iron–5-(phenylazo)citrazinic acid complex

The IR spectra of the iron–5-(phenylazo)citrazinic acid complex gave a well-defined band at 3460 cm<sup>-1</sup> due to  $\nu$ (OH) of the citrazinic ring or to water molecules [14,15]. The bands at 3164, 3097, 1740, 1645, 1525, 1455 and 1410 cm<sup>-1</sup> are due to  $\nu$ (N–H) of the citrazinate nucleus, hydrazo group,  $\nu$ (C=O) of the keto group,  $\nu$ (C=N),  $\nu$ (N=N),  $\nu_{as}$ (COO<sup>-</sup>) and  $\nu_{s}$ (COO<sup>-</sup>), respectively. The appearance of the two bands at 428 and



Fig. 2. Suggested structure of the iron(III)-uracil complex.



Fig. 3. Suggested structure of the iron-citrazinic acid complex.

363 cm<sup>-1</sup> are due to  $\nu$ (Fe  $\leftarrow$  O) and  $\nu$ (Fe–O) of the carboxylate group, respectively [19].The Nujol mull electronic absorption spectra of the brownish yellow [Fe(HL<sup>7</sup>)<sub>3</sub>]·2H<sub>2</sub>O iron–5-(phenylazo)citrazinic acid complex (Table 2) gave three bands at 36,866, 23,426 and 20,779 cm<sup>-1</sup>. Its effective room temperature magnetic moment value ( $\mu = 5.96$  BM) typified the existence of an octahedral spatial structure of high-spin state [18]. Thus, the structure of this complex is suggested as shown in Fig. 4.

# 3.5. Mössbauer spectroscopy of iron complexes

The obtained isomer shift values for the iron–uracil and iron–5-(*m*-nitrophenylazo)citrazinic acid complexes ( $\delta = 0.3616$  and 0.3488 mm/s), respectively, are less than those reported for high-spin Fe(III) complexes ( $\delta = 0.5-0.7$  mm/s) [20], probably due to the increase in the electron density at the nucleus or due to the increase in covalency character of the bond between Fe(III) and the oxygen atoms of the ligand. Such covalency promotes d-electron transfer from the non- $\sigma$ -bonding orbitals of the central atom to  $\pi$ -acceptor orbitals of the ligand with



Fig. 4. Suggested structure of the iron-5-(arylazo)citrazinic acid complexes.

the appropriate symmetry. The symmetry of the charge distribution around the iron nucleus results in a decrease in the electronic field gradient at the position of the nucleus. This leads to a decrease in the quadrupole splitting ( $\Delta E_Q = 0.6624$ , 0.4384 and 0.7008 mm/s, respectively) for the iron–uracil, iron–citrazinic acid and iron–*m*-(nitrophenylazo)citrazinic acid complexes, respectively.

# 3.6. *IR and electronic spectra of cobalt, nickel and copper thiouracil complexes*

The following equation is given to explain the mechanism of complexation for 1:2 complexes:

$$\begin{split} M^{2+} + 2H_2L &\to M(HL)_2 + 2H^+, \\ M &= \text{Co, Ni or Cu, } L = L^2, \ L^3, \ L^4 \text{ or } L^5 \end{split}$$

The IR spectra show the following characteristic features:

- (1) The  $\nu$ (OH) band at 3526 cm<sup>-1</sup> of thiouracil is shifted to 3324, 3370 and 3402 cm<sup>-1</sup> in the corresponding Co(II), Ni(II) and Cu(II) complexes, respectively, probably due to the presence of water molecules in these complexes [21].
- (2) The doublet  $\nu$ (N–H) bands of thiouracil at 3130 and 3042 cm<sup>-1</sup> are absent in the cobalt complex. These are seen at 3080 and 3160 cm<sup>-1</sup> in the Ni(II) and Cu(II) complexes, respectively, to identify M–N interaction [22].
- (3) The  $\nu$ (C=O) and  $\nu$ (C=N) bands of thiouracil at 1696 and 1620 cm<sup>-1</sup>, respectively, are affected on complexation. In the Co(II) complex, the first band is absent and the second band is shifted to 1585 cm<sup>-1</sup>. However, in the Ni(II) complex, both bands appeared at 1645 and 1580 cm<sup>-1</sup>. For the Cu(II) complex, the two bands shift to 1645 and 1595 cm<sup>-1</sup>, respectively. These data verify M–O interaction.
- (4) A new  $\delta$ (OH) band appeared for the Co(II) complex at 1340 cm<sup>-1</sup>. This band is at 1350 and 1335 cm<sup>-1</sup> in Ni(II) and Cu(II) complexes, respectively [23].

The Nujol mull electronic absorption spectral bands of the cobalt–thiouracil complex  $[Co(HL)_2]$ ·3H<sub>2</sub>O (Table 2), gave charge transfer bands at 45,662 and 37,736 cm<sup>-1</sup>, and visible d–d electronic spectral bands at 22,727 and 17,857 cm<sup>-1</sup>, and a magnetic moment value of 5.1 BM, typical of an octahedral spatial configuration of high-spin state [23,24].

The Nujol mull electronic absorption spectra of the green Ni(II)–thiouracil complex  $[Ni(HL^2)_2]\cdot 3H_2O$  (Table 2), gave four bands at 47,170, 35,842, 22,988 and 19,685 cm<sup>-1</sup>, probably due to octahedral spatial configuration. The  $[Ni(HL^2)_2]\cdot 3H_2O$  complex has an effective room temperature magnetic moment value of 3.1 BM, reflecting spin–orbit coupling in an octahedral configuration.

The electronic absorption spectrum for the pale blue 1:2 copper(II)-thiouracil complex  $[Cu(HL^2)_2] \cdot H_2O$ , gave three bands at 36,900, 27,397 and 19,763 cm<sup>-1</sup>, which may be assigned to square-planar  $D_{2h}$  symmetry of the Cu(II) complex [25]. The effective room temperature magnetic moment value



Fig. 5. Suggested structure of metal– $H_2L^2$  complexes.

equals 1.8 BM. All of the data suggest a square-planar geometry for such complexes.

Thus, the bidentate nature of thiouracil is suggested and its complexation to the metal is given through oxygen and nitrogen atoms as shown in Fig. 5.

# 3.7. *IR and electronic spectra of 5-(phenylazo)thiouracil and its metal complexes*

The IR spectra show the following characteristic features:

- (1) The broad  $\nu$ (OH) band at 3470 cm<sup>-1</sup> of the free ligand is shifted to 3440, 3425 and 3420 cm<sup>-1</sup> in the corresponding Co(II), Ni(II) and Cu(II) complexes, respectively, probably due to the presence of water molecules in these complexes [21].
- (2) The doublet  $\nu$ (N–H) bands of the free ligand at 3110 and 3070 cm<sup>-1</sup> shift to 3165 and 3050 cm<sup>-1</sup> for the Co(II) complex. However, both shift to 3155 and 3065 cm<sup>-1</sup> for the Ni(II) complex and for the Cu(II) complex to 3140 and 3050 cm<sup>-1</sup>. Thus, the imino nitrogen acts as a chelation site [26,27].
- (3) The  $\nu$ (C=O) band of the free ligand at 1700 cm<sup>-1</sup> is redshifted to 1660, 1675, and 1675 cm<sup>-1</sup> in the corresponding Co(II), Ni(II) and Cu(II) complexes, respectively, due to complexation with the metal ion [27].
- (4) The  $\nu$ (N=N) band of the ligand at 1510 cm<sup>-1</sup> is shifted slightly on complexation to 1520, 1530 and 1530 cm<sup>-1</sup> in the Co(II), Ni(II) and Cu(II) complexes, respectively, i.e. no M-azo bonding exists [26,27].
- (5) The δ(OH), γ(OH), δ(NH) and ν(C–N) modes of vibrations of the free ligand are affected on coordination with the metal ions to suggest that the oxygen and nitrogen N(3) atoms are considered as centers for complexation [27].

The Nujol mull electronic absorption spectral bands of the orange cobalt–5-(phenylazo)thiouracil complex  $[Co(HL^3)_2(H_2O)_3]$  (Table 2), gave charge transfer bands at 39,683 and 31,746 cm<sup>-1</sup>. The visible d–d electronic spectral



Fig. 6. Suggested structure of metal complexes 5-(arylazo)thiouracil.

bands observed at 23,810 and  $19,569 \text{ cm}^{-1}$  and the room temperature magnetic moment value of 5.2 BM prove that this complex exists in an octahedral complexation. The ligand is bonded to Co(II) via the N(3) nitrogen adjacent to the carbonyl group and via the oxygen atom. The electronic spectral data of the Ni(II) complex [Ni(HL<sup>3</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>] (Table 2), gave electronic spectral bands at 34,483 and  $29,499 \text{ cm}^{-1}$  due to charge transfer electronic transitions of the free ligand. The bands at 22,727 and  $20,000 \,\mathrm{cm}^{-1}$  and the effective room temperature magnetic moment value of 3.2 BM support the octahedral complexation for this complex [28]. The ligand is bonded to Ni(II) ion through the oxygen and nitrogen N(3) atoms of the pyrimidine ring. The 5-(phenylazo)thiouracil-copper complex [Cu(HL<sup>3</sup>)<sub>2</sub>]·2H<sub>2</sub>O gave bands at 46,512, 37,037 and  $21,798 \text{ cm}^{-1}$ . The room temperature magnetic moment for the copper complex is 1.9 BM. All of these data identified square-planar geometry [27].

So, the bidentate nature of 5-(arylazo)thiouracil is suggested and its complexation to the metal occurs through oxygen and nitrogen atoms as shown in Fig. 6.

# 3.8. Electron spin resonance of copper complexes

The room temperature polycrystalline X-band ESR spectra of Cu(II)  $(HL^2)_2 \cdot H_2O$ , Cu(II)  $(HL^3)_2 \cdot 2H_2O$  and Cu(II)  $(HL^3)_2 \cdot 2H_2O$  gave similar spectral patterns. All complexes are of broad signals due to polymeric property. The data are of isotropic nature with  $g_s$  values at 2.14, 2.13 and 2.16 and A values at 225, 250 and 200, respectively. [29]

### 3.9. Calculation of the coordination bond length

The calculations are based on recording the change in the frequency of the band positions of the free ligand with respect to its complexes. If it is suggests that the C=N or C=O groups obtained by tautomerism are bonded to the metal ion, the coordination bond length (r) can be determined from the relation [30] of (1).

$$\Delta \nu = \left(\frac{32\pi\alpha}{a^2}\right) \left(\frac{\nu_{x=y} - \nu_{x-y}}{\ell}\right) \exp\left(-z\pi\sqrt{\frac{2r}{a}}\right) \tag{1}$$

Ligand	$\mathcal{V}_{X=Y}$	Cobalt compl	lex			Nickel compl	ex			Copper compl	ex		
		$v_{x=y}$	Δν	$v_{x=y}$	<i>r</i> (Å)	$v_{x=y}$	Δν	$v_{x=y}$	<i>r</i> (Å)	$v_{x=y}$	Δν	$v_{x=y}$	<i>r</i> (Å)
H <sub>2</sub> L <sup>2</sup>	1620 (1696)	1585(-)	35 (-)	1275(-)	1.96 <sup>a</sup> (–)	1580 (1645)	40(51)	1275 (1380)	1.94 <sup>a</sup> (1.91 <sup>b</sup> )	1595 (1645)	25 (51)	1270(1389)	2.04 <sup>a</sup> (1.93 <sup>b</sup> )
$H_2L^3$	1615(1700)	1595(1660)	20(40)	1267(1450)	$2.30^{a}$ (1.90 <sup>b</sup> )	1580 (1675)	35(25)	1235 (1453)	$1.98^{a}$ $(1.97^{b})$	1590 (1675)	25 (25)	1235 (1454)	$2.06^{a}$ (2.01 <sup>b</sup> )
$H_2L^4$	1610	1590	20	1280	$2.03^{a}$	1595	15	1280	2.07 <sup>a</sup>	1590	20	1270	2.07 <sup>a</sup>
$H_2L^5$	1600	1590	10	1260	2.11	I	I	I	1	1590	10	1270	2.16 <sup>a</sup>

Table 3

This is due to M–N bond length. This is due to M–O bond length. M.S. Masoud et al. / Spectrochimica Acta Part A 67 (2007) 662-668

Table 4
Thermal properties of iron-uracil, iron-citrazinic acid and cobalt-thiouracil complexes

Complex	$T_{\rm m}$ (°C)	п	$\Delta E (\mathrm{kJ}\mathrm{mol}^{-1})$	$\alpha_{ m m}$	$Z(s^{-1})$	$\Delta S^*  (\mathrm{kJ}  \mathrm{K}^{-1}  \mathrm{mol}^{-1})$	$\Delta H^*$ (kJ mol <sup>-1</sup> )	Weight of the product (mg)
Fe(HL <sup>1</sup> ) <sub>3</sub> ·3H <sub>2</sub> O	105	1.03	43.28	0.627	4.76	0.253	95.66	
	340	0.83	90.18	0.659	6.07	0.250	156.35	18.1
	410	1.18	128.62	0.600	7.81	0.254	173.48	
	90	1.02	35.93	0.626	4.10	0.254	92.19	
Fe(HL <sup>6</sup> ) <sub>3</sub> ·3H <sub>2</sub> O	220	0.93	33.896	0.735	2.80	0.260	128.02	12.0
	365	0.82	98.73	0.664	6.39	0.225	162.67	13.9
	440	1.18	295.0	0.602	17.79	0.247	176.32	
	175	0.98	218.74	0.636	22.32	0.242	108.24	
$Co(HL^2)_2 \cdot 3H_2O$	265	0.92	97.69	0.650	7.58	0.252	135.64	10.2
	410	1.11	133.56	0.614	9.20	0.252	152.93	10.3
	423	0.996	209.75	0.630	12.79	0.250	173.17	

The  $T_{\rm m}$ , n,  $\Delta E$ ,  $\alpha_{\rm m}$ , Z,  $\Delta S^*$  and  $\Delta H^*$  values are assigned to sample temperature at which the peak DTA deflection occurs, reaction order, activation energy, value decomposed substance fraction, collision factor, entropies of activation and enthalpy of activation, respectively.

 $\Delta v$  is the shift in the oscillator frequency ( $v_{\text{ligand}} - v_{\text{complex}}$ ), and  $\alpha$  is the bond polarizability. The  $\alpha$  values were computed based on published data for complexes with a similar pyrimidine compound to our complexes [31]. These are 48.61, 46.59 and 42.50 for cobalt, nickel and copper, respectively; *a* is the lattice constant of the metal salt [*a*=3.5, 3.524 and 3.614 for cobalt, nickel and copper, respectively] [32];  $v_{x=y}$  the frequency of the oscillator with a double bond [v(C=N) and v(C=O), respectively];  $v_{x-y}$  the frequency of the oscillator with a single bond [v(C-N) and v(C-O), respectively];  $\ell$  is the length of the oscillator coordination to the metal ion. A literature survey for uracil and pyrimidine complexes shows that the most prominent feature is that the N(3)–C(4) distance is 1.364 Å and the O–C(4) distance is 1.257 Å [33].

In the present work, one can use these values as the  $\ell$  parameter in the calculation [33]. From such data, the *r*-values for the bond between the metal and the nitrogen atom of the C=N group and the oxygen atom of the C–O group are computed [34].

Table 3 collects the values of the frequency shift,  $\Delta v (v_{\text{ligand}} - v_{\text{complex}}), v_{x-y}$  and r(Å). For the thiouracil complexes, the values of the calculated coordination bond length of the transition metal complexes decrease in the sequence either to the oxygen or the nitrogen atom:

Ni < Co < Cu

For the octahedral Co(II) and Ni(II) complexes, the coordination bond lengths are smaller than that of the square-planar Cu(II) complex. In general, the M–N bond length is longer than that of M–O. This is attributed to the electronegativity difference between the oxygen and nitrogen atoms. Also, square-planar complexes (e.g., copper) have longer bond lengths than octahedral ones (e.g., cobalt and nickel). Thus, the geometry of the complex compound plays a major factor for controlling such trends. In turn, the flexibility factors assist such behaviour.

### 3.10. Differential thermal analysis (DTA)

The DTA curves of the octahedral iron complexes obtained from  $H_2L^1$  and  $H_2L^6$  of the stoichiometry [Fe(HL)<sub>3</sub>]·3H<sub>2</sub>O

showed well-defined strong endothermic peaks. These peaks are at 105, 340 and 410 °C for the  $[Fe(HL^1)_3] \cdot 3H_2O$  complex, while the  $[Fe(HL^6)_3] \cdot 3H_2O$  complex gave four peaks at 90, 220, 365 and 440 °C. The peaks at 90 and 105 °C are due to dehydration of water molecules in the outer sphere of the two complexes. However, the second peak at 220 °C in the thermogram of the iron–citrazinic acid complex may be due to the formation of some decomposition products. On the other hand, the last two peaks of both complexes represent their decomposition to Fe<sub>2</sub>O<sub>3</sub> as a final decomposition product [17]. Calculation of the thermal analysis data, ln  $\Delta t$  against 1000/*TK* plots, gives best-fit straight lines for all peaks. The thermal parameters were calculated and both complexes decompose via first order reactions.

The octahedral cobalt–thiouracil complex  $[Co(HL^2)_2 \cdot 2H_2O]$ H<sub>2</sub>O gave an endothermic peak at 175 °C probably due to dehydration of water molecules in the inner sphere of the complex. The second peak at 265 °C may be due to the formation of some decomposition products, while the last two peaks at 410 and 423 °C indicate the formation of CoO as the final product [22]. The ln  $\Delta t$  against 1000/*T* plots give straight lines for all peaks. All the thermodynamic parameters were evaluated as shown in Table 4.

### References

- [1] E.R. Tucci, N.C. Li, J. Inorg. Nucl. Chem. 25 (1963) 17.
- [2] H.R. Lindsay, J.C. Ramine, M.Y. Wong, Arch. Biochem. Biophys. 126 (1968) 812;
  - H.R. Lindsay, J.C. Ramine, M.Y. Wong, Chem. Abstr. 69 (1968) 94735t.
- [3] A. Ali, S.E. Livingstone, Coord. Chem. Rev. 13 (1974) 102.
- [4] J. Bauerova, K. Sebesta, F. Sorm, Z. Sormova, Collec. Czech. Chem. Commun. 25 (1960) 2906;
- J. Bauerova, K. Sebesta, F. Sorm, Z. Sormova, Chem. Abstr. 55 (1961) 4672a.
- [5] T. Shimura, T. Tomohiro, H. Okuno, Inorg. Chim. Acta 155 (1989) 21.
- S. Sakamoto, M. Matsubara, H. Kudo, S. Suzuki, L. Liu, T. Nakayama, T. Mitamura, H. Nagasawa, Anticancer Res. 14 (1994) 2515;
   S. Sakamoto, M. Matsubara, H. Kudo, S. Suzuki, L. Liu, T. Nakayama, T. Mitamura, H. Nagasawa, Chem. Abstr. 122 (1995) 281582r.
- [7] L. Novotny, A. Vachalkova, Neoplasma 38 (1991) 223;
   L. Novotny, A. Vachalkova, Chem. Abstr. 115 (1991) 105588u.

- [8] A. Vachalkova, L. Novotony, Neoplasma 37 (1990) 555;
   A. Vachalkova, L. Novotony, Chem. Abstr. 114 (1991) 223757a.
- [9] A. Tsunoda, M. Shibusawa, N. Yasuda, K. Nakao, M. Kusamo, Anticancer Res. 14 (1994) 2637;
   A. Tsunoda, M. Shibusawa, N. Yasuda, K. Nakao, M. Kusamo, Chem.
- Abstr. 122 (1995) 281259r. [10] A. Lee, J. Dvovak, V. Chmatal, P. Kuthan, J. Vencl, Ger. Offen. 755 (1978) 683:

A. Lee, J. Dvovak, V. Chmatal, P. Kuthan, J. Vencl, Chem. Abstr. 89 (1978) 112366t.

- [11] K. Satorus, K. Shigeharu, K. Masayuki, H. Mooko, Japanese Patent, Konishiroku Photo Industry Co., Ltd., 28 January, 1988;
  K. Satorus, K. Shigeharu, K. Masayuki, H. Mooko, Chem. Abstr. 111 (1989) 184060i.
- [12] Y. Kazuyoshim I. Yoshio, Japanese Patent, Fuji Photo Film Co. Ltd., Jpn. Kokai Tokkyo Koho, 30 June, 1992;
- Y. Kazuyoshi, I. Yoshio, Appl. Chem. Abstr. 118 (1993) 4979j.
- [13] K. Hiroaki, N. Shinsaku, K. Tsugio, K. Shigeharu, Japanese Patent, Konica Co., Jpn., Kokai Tokkyo Koho, 13 October, 1988; K. Hiroaki, N. Shinsaku, K. Tsugio, K. Shigeharu, Chem. Abstr. 114 (1991)
- 111793c.
- [14] M.S. Masoud, Z.M. Zaki, Trans. Met. Chem. 13 (1988) 321.
- [15] G. Schwarzenbach, in: H. Irving (Ed.), Complexometric Titration, Methnen Co., London, 1957.
- [16] M.S. Masoud, E.A. Khalil, A.M. Hindawy, A.M. Ramadan, Can. J. Anal. Sci. Spectrosc. 50 (4) (2005) 175.
- [17] M.S. Masoud, S.S. Haggag, E.A. Khalil, Nucleosides, Nucleosides Nucleotides Nucleic Acids 25 (2006) 73.
- [18] D.W. Barnum, J. Inorg. Nucl. Chem. 22 (1961) 183.
- [19] M.S. Masoud, A.M. Ibrahim, E.A. Khalil, A. El-Marghany, Bull. Fac. Sci. Assist. Univ. 25 (3-B) (1996) 7.

- [20] S.J. Lippard, J.M. Berg, Principles of Bioinorganic Chemistry, University Science Books, Mill Valley, CA, 1994, p. 91.
- [21] G.S. Pandemy, P.C. Nigum, V. Agrwala, Inorg. Chem. 39 (1977) 1877.
- [22] M.S. Masoud, S.A. Abou El Enein, H.M. Kamel, Ind. J. Chem. A 40 (2002) 297.
- [23] K. Jorgensen, Absorption Spectra and Chemical Bonding in Complexes, Pergamon Press, 1962.
- [24] F. Albert Cotton, Advanced Inorganic Chemistry, 3rd ed., Wiley Eastern Limited, London, 1979.
- [25] L. Dubick, R.L. Martin, Inorg. Chem. 5 (1966) 2203.
- [26] M.S. Masoud, O.H. Abdel-Hamid, Z.M. Zaki, Trans. Met. Chem. 19 (1994) 21.
- [27] M.S. Masoud, S.S. Haggag, Z.M. Zaki, M. El-Shabasy, Spectrosc. Lett. 27 (1994) 775.
- [28] M.S. Masoud, A.K. Ghonaim, S.A. Abou El Enein, A.A. Mahmoud, J. Coord. Chem. 55 (2002) 79.
- [29] M.S. Masoud, E.A. Khalil, A.M. Hafez, A.F. El-Husseiny, Spectrochim. Acta A 61 (2004) 989.
- [30] G. Karagonins, O. Peter, Z. Electrochem. Ber. Bunsenges. Phys. Chem. 63 (1959) 1170;

G. Karagonins, O. Peter, Chem. Abstr. 54 (1960) 5241F.

- [31] C.H. Macgillavry, G.D. Riech, in: K. Lansdale (Ed.), Physical and Chemical Tables, vol. 3, 1962.
- [32] R.K. Parashar, R.C. Sharma, A. Kuma, A. Kumor, G. Mohan, Inorg. Chim. Acta 151 (1988) 201.
- [33] H. Rauter, E. Hillgeris, E. Andren, B. Lippert, J. Am. Chem. Soc. 116 (1994) 616.
- [34] M.M. Abou Sekkina, S.M. El-Hebawy, Proc. Indian Natl. Sci. A 51 (1985) 559;
  - M.M. Abou Sekkina, S.M. El-Hebawy, Chem. Abstr. 102 (1985) 124377n.