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Synthesis, molecular modeling, thermal and spectral studies of metal complexes of hydrazone derived from 5-acetyl-4-hydroxy-2*H*-1,3-thiazine-2,6(3*H*)-dione and thiosemicarbazide

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ABSTRACT

Metal complexes with the general formula $[ML(H_2O)(CH_3OH)_x] \cdot nH_2O \cdot (CH_3OH)_y(NO_3)_z$ $[M = Cu(II), Ni(II), Co(II), VO(IV), Cr(III), Cd(II), Zn(II) or UO_2(VI); <math>x = 0-2$; y = 0,1; z = 0,1; n = 0-2, 6 and L = hydrazone (H₂L) derived from condensation of thiosemicarbazide with 5-acetyl-4-hydroxy-2H-1,3-thiazine-2,6(3H)-dione. The synthesized ligand and its metal complexes have been characterized on the basis of elemental analyses, spectral and magnetic studies as well as thermal gravimetric analysis (TGA). The deprotonated ligand acts as a dibasic tridentate (ONS) *via* phenolate oxygen, azomethine (C=N), and thiolate (C-S) groups. Copper(II) complex exhibits square planar geometry. Nickel(II), chromium(III) and dioxouranium(VI) complexes exhibit octahedral geometry. Cobalt(II), cadmium(II) and zinc(II) complexes showed tetrahedral geometry, whereas oxovanadium(IV) reveals square pyramidal geometry. Thermal analysis are investigated and showed either three or four thermal decomposition steps. Kinetic parameters (E_a , ΔH , ΔS and ΔG) of the thermal decomposition stages have been evaluated using Coats-Redfern equations. The molecular parameters of the ligand and its metal complexes have been calculated and correlated with the experimental data such as IR and TGA results.

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1. Introduction

Thiosemicarbazones are well established as an important class of sulfur donor Schiff base ligands particularly for transition metal ions [1,2]. Metal complexes of thiosemicarbazones are a class of important compounds in medicinal and pharmaceutical field, they show various biological activities such as antibacterial [3,4], antifungal [5,6], anticancer [7,8], antitumoral [9], antimalarial [10], antimicrobial [11], antiamebic [12] and pharmacological activities [13]. Also, thiosemicarbazones have been a subject of interest due to their variable applications in industry and analytical chemistry [14,15]. In view of their interesting structural properties and wide ranging uses, studies of the thiosemicarbazone complexes have attracted the attention of many investigators [16-19]. The present work aims to synthesize and characterization of a new thiosemicarbazone ligand (H₂L), derived from the condensation of 5-acetyl-4-hydroxy-2H-1,3-thiazine-2,6(3H)-dione with thiosemicarbazide, and its complexes with the first row transition metals: Cr(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II); and oxy-metals: VO(IV) and UO₂(VI) ions. These compounds have been characterized by elemental analyses, spectral and magnetic studies as well as ther-

1386-1425/\$ - see front matter © 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2011.04.058 mal gravimetric analysis (TGA). Molecular modeling carried out for the free ligand and its complexes and the theoretical results were correlated with the experimental data.

2. Experimental

2.1. Materials

Copper(II), nickel(II), cobalt(II), cadmium(II), zinc(II), chromium(III) and iron(III) were used as nitrate salts and were Merck or BDH. Oxovanadium(IV) sulphate monohydrate and dioxouranium(VI) acetate dihydrate were BDH. Organic solvents (ethanol, absolute ethanol, methanol, diethylether, dimethylformamide (DMF) and dimethylsulfoxide (DMSO)) were reagent grade.

2.2. Synthesis of 2-[1-(4-hydroxy-2,6-dioxo-3,6-dihydro-2H-1,3-thiazin-5-yl)ethylidene] hydrazinecarbothioamide, H₂L, ligand

5-Acetyl-4-hydroxy-2H-1,3-thiazine-2,6(3H)-dione (AHTD) was prepared as described elsewhere [20]. A mixture of AHTD (1.87 g, 10.0 mmol) and thiosemicarbazide (0.91 g, 10.0 mmol) in absolute ethanol (25 mL) was heated under reflux for 1 h. Yellow product was obtained after cooling to room temperature, then

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Scheme 1. Formation of the hydrazone, H₂L, ligand.

filtered and washed with a few portions of ethanol. The fine yellow crystals were recrystallized from ethanol. The yield was 1.53 g (59%) and m.p. 232–233 °C. Scheme 1 illustrates the formation of the H₂L ligand.

2.3. Synthesis of the metal complexes

Methanolic solutions of the deprotonated ligand (0.78 g, 3 mmol, 20 mL) were added gradually to methanolic solutions of the appropriate metal salt (3 mmol, 20 mL) in the molar ratio 1:1. The ligand was firstly deprotonated by lithium hydroxide, LiOH·H₂O (0.246 g, 6 mmol) in the molar ratio 1:2. The reaction mixture of the deprotonated ligand with metal salts was stirred for 3 h at room temperature, except in cases of Cr(III) and UO₂(VI) were heated to reflux for 2 h. The resulting precipitates were filtered and washed with methanol then diethyl ether.

Trials to prepare iron(III) complex of the hydrazone, H_2L , ligand was unsuccessful, it gave oily product and was difficult to isolated in its pure form.

2.4. Molecular modeling

An attempt to gain a better insight on the molecular structure of the ligand and its complexes, geometric optimization and conformation analysis has performed using PM3 forcefield as implemented in hyperchem 7.5 [21].

2.5. Physical measurements

Elemental analyses of (C, H, N, S) were carried out at the National Research Center, Dokki, Giza, Egypt. Analyses of the metal ions were carried out complexometrically [22,23]. The FT-IR spectra (4000–400 cm⁻¹) of the ligand and its complexes were recorded as KBr discs using FT-IR-4000 (Shimadzu) spectrophotometer. ¹H NMR spectra were recorded using a Gemini spectrometer, 200 MHz. Dimethylsulphoxide, DMSO- d_6 , was used as a solvent and tetramethylsilane (TMS) as an internal reference. The electronic spectra of the ligand and its metal complexes were carried out on a JASCO model V-550 UV–vis spectrophotometer in the range 200–900 nm. ESR spectra were recorded on the Bruker, Model: EMX, X-band spectrometer. Mass spectra were recorded on a Hewlett Packard mass spectrometer model MS 5988. Samples were introduced directly to the probe, and the fragmentations were carried out at 300 °C and 70 eV.

Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using Johnson Matthey, Alfa product, Model No. (MKI), the diamagnetic corrections were calculated from Pascal's constants for all atoms in the compounds [24]. Thermal gravimetric analysis (TGA) data was measured from room temperature up to 800 °C at a heating rate of 10 °C/min. The data were obtained using a Shimadzu TGA-50H instrument. All melting points were recorded on a Stuart SMP3 melting point apparatus.

3. Results and discussion

The analytical and physical data of the free ligand, 2-[1-(4-hydroxy-2,6-dioxo-3,6-dihydro-2*H*-1,3-thiazin-5-yl)ethylidene]hydrazinecarbothioamide (H₂L), and its solid

complexes with Cu(II), Ni(II), Co(II), VO(IV), Cr(III), Cd(II), Zn(II) and UO₂(VI) are presented in Table 1. The ligand (H₂L) might exhibits two tautomeric, thione and thiol, forms. It behaves as a dibasic tridentate with ONS sites as shown in structures of the thione–thiol forms of the free ligand (Fig. 1).

The mass spectrum of the present free ligand (H₂L) showed the molecular ion peak at m/e = 259 (M – 1) corresponding to the molecular formula (C₇H₈N₄O₃S₂, F.W. 260.29 amu). The fragmentation pattern of the mass spectrum is depicted in Scheme 2.

¹H NMR spectrum of the H₂L ligand in DMSO- d_6 showed singlet signal at 2.51 ppm which might attributed to the methyl protons, and broad signals exchangeable with D₂O at 7.26 ppm which assignable to NH protons, in addition to 10.02 and 10.09 ppm attributed to CSNH₂ protons. The absence of the signal at ~4.0 ppm attributable to the S–H proton provides strong evidence of the thione form even in solution. The signal of the –OH for the phenolic proton was not observed in the range of the spectrum as previously reported for the starting material [20].

The main characteristic IR absorption frequencies of the free ligand (H₂L) showed stretching vibrational modes at 3435, 3288, 3162, 1681, 1606 and 1558 cm⁻¹ assigned for OH, NH₂, NH, C=O, C=N and C=C, respectively, in the light of IR data of similar compounds [25,26]. These assignments further supported by the comparison the IR spectrum of the current hydrazone ligand with that of the corresponding 5-acetyl-4-hydroxy-2H-1,3-thiazine-2,6(3H)-dione (AHTD) and thiosemicarbazide. The intense band at 1606 cm^{-1} assigned to the azomethine group (C=N) [25,26]. This assignment confirmed by disappearance of the absorption band that assigned to acetyl C=O of AHTD at 1659 cm⁻¹, emphasizing the condensation between the C=O of the later compound with NH₂ of the thiosemicarbazide as suggested in Scheme 1. The absence of the IR band around 2600 cm⁻¹ due to v(SH) supports the presence of the current ligand (H_2L) in the thione form which agree well with ¹H NMR data.

Electronic spectral data of the H₂L ligand in DMF solution displays two absorption bands at 35,842 and 29,411 cm⁻¹ assigned to the $\pi \rightarrow \pi^*$ (K-band), and $n \rightarrow \pi^*$ transitions (R-band) [27].

3.1. Metal complexes of H₂L ligand

The results of the elemental analyses and physical data of the current solid complexes recorded in Table 1 are in good agreement with the suggested tentative molecular formula; $[ML(H_2O)(CH_3OH)_x] \cdot nH_2O \cdot (CH_3OH)_y(NO_3)_z$; n=0-2, 6; x=0-2; y=0,1; z=0,1.

The thione form of the ligand is the dominant form in either solid state or solution, while the thiolate form is mainly dominant in presence of a base such as LiOH as concluded from IR and ¹H NMR spectral data of the ligand and its metal complexes, respectively.

The deprotonated hydrazone ligand behaves as a dibasic with tridentate ONS sites during the reaction with Cu(II), Ni(II), Co(II), VO(IV), Cr(III), Cd(II), Zn(II) or UO₂(VI) ions yielding the corresponding metal complexes. The isolated complexes were further characterized by FT-IR, mass, UV–vis, ESR spectroscopy and thermal gravimetric analysis (TGA), as well as magnetic susceptibility measurements.

Table 1

Physical and analytical data of the hydrazone, H₂L, ligand and its transition metal complexes.

	Ligand/complex	Molecular formula	M. wt. yield (%)	Color	M.P. (°C)	Elemental analyses found (calcd.) %				
						С	Н	Ν	S	М
	H ₂ L	$C_7H_8N_4O_3S_2$	260.29 (59)	Yellow	232-233	32.28 (32.30)	3.18 (3.10)	21.37 (21.52)	24.60 (24.63)	-
(1)	$[CuL(H_2O)] \cdot H_2O$	$C_7H_{10}N_4O_5 \ S_2Cu$	357.93 (80)	Brown	256	23.60 (23.48)	2.75 (2.81)	15.70 (15.67)	17.90 (17.92)	17.76 (17.75)
(2)	$[NiL(CH_3OH)_2(H_2O)] \cdot 2H_2O$	$C_9H_{20}N_4O_8S_2Ni$	435.19 (60)	Green	>300	25.00 (24.83)	4.34 (4.63)	12.78 (12.89)	14.89 (14.73)	13.26 (13.48)
(3)	$[CoL(H_2O)] \cdot CH_3OH$	$C_8H_{12}N_4O_5S_2Co$	367.31 65	Cumin	>300	26.28 (26.15)	3.54 (3.29)	16.12 (15.27)	17.04 (17.45)	16.23 (16.03)
(4)	$[VOL(H_2O)] \cdot H_2O$	$C_7 H_{10} N_4 O_6 S_2 V \\$	360.99 (49)	Brown	260	24.16 (23.29)	2.98 (2.79)	15.35 (15.54)	17.80 (17.76)	NA (14.01)
(5)	$[CrL(CH_3OH)_2(H_2O)] \cdot (NO_3) 6H_2O$	$C_{9}H_{28}N_{4}O_{15}S_{2}Cr$	548.52 (75)	Grey	256	18.78 (19.70)	5.28 (5.14)	10.95 (10.22)	11.60 (11.69)	9.52 (9.46)
(6)	$[ZnL(H_2O)] \cdot H_2O$	$C_7H_{10}N_4O_5S_2Zn$	359.76 (73)	Yellow	240	23.25 (23.37)	2.74 (2.80)	15.79 (15.59)	17.65 (17.82)	18.32 (18.17)
(7)	$[CdL(H_2O)]\cdot H_2O$	$C_7H_{10}N_4O_5S_2Cd$	406.79 (69)	Yellow	280	20.05	2.74 (2.47)	13.86 (13.79)	15.63 (15.76)	27.58 (27.63)
(8)	$[UO_2L(H_2O)] \cdot H_2O$	$C_7H_{10}N_4O_7S_2U$	564.41 (67)	Orange	>300	14.65 (14.89)	1.74 (1.78)	9.79 (9.94)	11.28 (11.36)	NA (42.17)

NA: not analyzed.







Scheme 2. Mass fragmentation pattern of the hydrazone, H₂L, ligand.

3.1.1. Infrared spectra

The main characteristic IR vibrational frequencies and their assignments for the current free ligand and its complexes are given in Table 2. The sites of coordination are deduced from the comparison of the IR data of the metal complexes with that of the

free ligand. All complexes showed a broad band in the range of $3462-3420 \text{ cm}^{-1}$ assignable to the stretching frequencies of $\nu(OH)$ of water and/or solvated molecules. The band at 1606 cm^{-1} belonging to $\nu(C=N)$ stretching was shifted to a lower frequencies in the range ($1600-1586 \text{ cm}^{-1}$) supporting the participation of C=N in

Characteristic infrared free	mencies (cm ⁻¹) ^a of hydrazone	H _a L ligand	and its transition	metal complexes
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	Ligand/complex	ν(OH)	$\nu(NH_2)$	$\nu(NH)$	ν(C=0)	ν (C=N)	$\nu(C=C)$	$\nu(C-S)$	ν (M–N)	v(M-O)	Other band
	H ₂ L	3435 s	3288 s	3162 s	1681 s	1606 s	1558 w	-	-	-	1340 (C=S)
(1)	$[CuL(H_2O)] \cdot H_2O$	3422 s	3332 w	3210 w	1670 m	1590 s	1517 m	695 w	507 w	485 w	-
(2)	$[NiL(CH_3OH)_2(H_2O)] \cdot 2H_2O$	3420 br, s	3322 w	-	1616 s	1590 s	1517 m	692 w	529 w	444 w	-
(3)	[CoL(H ₂ O)]·CH ₃ OH	3430 br, s	3329 w	-	-	1600 s	1510 m	691 w	507 w	430 w	-
(4)	$[VOL(H_2O)] \cdot H_2O$	3426 s	3329 m	3194 w	1667 s	1593 s	1513 s	693 w	525 w	489 w	1009 w (V=O)
(5)	$[CrL(CH_3OH)_2(H_2O)] \cdot (NO_3) \cdot 6H_2O$	3437 br, s	3329 w	-	1638 m	1587 s	1535 s	691 w	568 w	487 w	1384,832 (NO ₃)
(6)	$[ZnL(H_2O)] \cdot H_2O$	3432 s	3331 w	-	-	1595 s	1518 s	688 w	568 w	479 w	-
(7)	$[CdL(H_2O)] \cdot H_2O$	3435 s	3328 s	3326 s	-	1598 s	1517 s	683 w	525 w	470 w	-
(8)	$[UO_2L(H_2O)] \cdot H_2O$	3462 s	3330 w	3324 s	-	1586 s	1543 m	681 w	508 w	435 w	904 w (U=O)

^a s = strong, m = medium, w = weak, br = broad.

the coordination mode. The disappearance of ν (C=S) band of the free ligand at 1340 cm⁻¹, and appears of new bands in the range (695–681 cm⁻¹) which attributed to ν (C–S) providing strong evidence that the sulfur participates as thiolate [28]. The weak bands in the ranges (489–430) cm⁻¹ and (586–507) cm⁻¹ were assigned to the ν (M–O) and ν (M–N) stretching frequencies for the metal complexes of the H₂L ligand [29]. Hence, the ligand behaves as dibasic tridentate (ONS) *via* the phenolate oxygen, azomethine nitrogen and thiolate sulfur atoms.

The anion coordinating modes are inferred from the IR data of the complexes. Nitrate complex (**5**) of Cr(III) exhibits two bands at 1384, 832 cm⁻¹ characterized the presence of ionic nitrate (D₃h), $\nu_3(E')$, [$\nu_{ch}(NO)$] mode. This might indicate that the nitrate group in complex **5** is ionic [29]. The IR spectrum of VO(IV) complex (**4**) displayed a band at 1009 cm⁻¹ due to the stretching vibration of the ν (V=O) band in five coordinate structure [30,31]. Similarly, the strong band located at 904 cm⁻¹ for complex (**8**) was assigned to $\nu_{3(asym)}$ of the O=U=O group indicate the six coordinate for the uranyl complex [32,33].

3.1.2. Electronic spectra and magnetic moment measurements

The electronic spectra of the current colored metal complexes in the range 200–900 nm, were carried out as Nujol mulls, since the metal complexes are sparingly soluble in most common solvents. Table 3 shows the electronic spectral bands and their assignments, in addition to the magnetic moments of the current complexes.

The electronic spectrum of the brown Cu(II) complex (**1**) [CuL(H₂O)]·H₂O showed one broad band in the visible region at 17,543 cm⁻¹ might assigned to $d_{xy} \rightarrow d_{x2-y2}$ (²T_{2g}(G) \leftarrow ²E_g) transition, suggesting square planar geometry around the Cu(II) ion [34,35]. The magnetic moment of Cu(II) complex (**1**) was 1.66 B.M. [36].

The electronic spectrum of the green Ni(II) complex (**2**) [NiL(CH₃OH)₂(H₂O)]·2H₂O, showed two absorption bands at 16,393 cm⁻¹ and 23,866 cm⁻¹. Since the spectra of octahedral Ni(II) consist of three bands as a result of the splitting of the free ion in ground state ³F term and the presence of ³P term [37]. These bands were assigned as ${}^{3}T_{2g}(F) \leftarrow {}^{3}A_{2g}(F)$, ${}^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}(F)$ and ${}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}(F)$; the first band is out of the instrument measurements range. The ligand field parameters of Ni(II) complex is calculated and the first transition band in the spectrum can also predicted, at 10,718 cm⁻¹ on the basis Tanab–Sugano diagrams (Table 3). This finding further emphasized by the measured magnetic moment at 3.27 B.M., which lies in the range (2.9–3.3 B.M.) of the Ni(II) octahedral complexes [27].

The electronic spectrum of the cumin Co(II) complex (**3**) showed a single band in the visible region at 16,528 cm⁻¹ indicating tetrahedral geometry [38]. The tetrahedral structure of Co(II) complex (**3**) was further confirmed by the magnetic moment measurements, μ_{eff} =4.4 B.M. which agree well with the tetrahedral structure around Co(II) ion [39]. The ligand field parameter (*B*, β and 10Dq) are calculated (Table 3) according to the equations reported for the tetrahedral Co(II) complexes.

$$\mu_{\text{eff}} = 3.87(1 - 4\lambda/10 \,\text{Dq}), \quad \lambda = -178 \,\text{cm}^{-1}$$

$$B = [4(\nu_3 - 15 \,\text{Dq})^2 - 10 \,\text{Dq}^2]/[60(\nu_3 - 15 \,\text{Dq}) - 18 \,\text{Dg}]$$

$$\nu_1 = 10 \,\text{Dq}$$

The electronic spectrum of the brown oxovanadium(IV) complex (**4**) showed one band at 16,750 cm⁻¹ due to $b_1 \leftarrow b_2$ electronic transition suggesting a penta coordinated structure, which would be square pyrimidal [40]. This conclusion agree well with the data obtained from elemental analysis and IR spectrum of VO(IV) complex (**4**) [41]. Although most oxovanadium(IV) complexes are magnetically simple which having virtually 'spin-only' moments of 1.73 B.M. corresponding to one unpaired electron. In this study, the μ_{eff} = 1.43 B.M., suggesting a vanadyl polymeric complex with a variety of nucleotides such as reported by Katsaros [42] and Dutta [43].

The electronic spectrum of the grey Cr(III) complex (**5**) showed two absorption bands at 17,301 and 23,584 cm⁻¹, suggesting an octahedral geometry for the Cr(III) complex (**5**) attributing to ${}^{4}T_{2g}(F) \leftarrow {}^{4}A_{2g}(F)$ and ${}^{4}T_{1g}(F) \leftarrow {}^{4}A_{2g}(F)$ transitions, respectively. In the Cr(III) octahedral complexes, the splitting of the free ion ground F term along with the presence of the excited P term of the same multiplicity provides the possibility of three spin allowed d–d transitions [44]. The third band expected for Cr(III) octahedral which is due to ${}^{4}T_{1g}(P) \leftarrow {}^{4}A_{2g}(F)$ transition not observed which might lies in the range of the ligand transitions. The ligand field parameters of Cr(III) complex is calculated on the basis Tanab–Sugano diagrams (Table 3) and also predict that the third transition band found to be 37,174 cm⁻¹. The magnetic moment of Cr(III) complex (**5**) μ_{eff} =3.58 B.M. corresponding to the spin-only for three unpaired electrons, due to the absence of any orbital contribution.

The yellow $[CdL(H_2O)] \cdot H_2O$ (**6**) and $[ZnL(H_2O)] \cdot H_2O$ (**7**) complexes, are diamagnetic as expected and are likely to be tetrahedral structure for Cd(II) and Zn(II) complexes. The mass spectra of Zn(II) and Cd(II) complexes showed the molecular ion peak at m/e 359 and 406, respectively. This finding which is consistent with the formula weight, indicated from elemental analysis, and supports the identity of structures.

The electronic spectrum of the orange $UO_2(VI)$ complex (8) arises from the electronic transitions of metal \rightarrow ligand charge transfer and/or appical oxygen \rightarrow F⁰ (U) transition [45]. This is an allowed transition and produces a broad, intense absorption band at 20,000 cm⁻¹ for complex (8) tailing into the visible region, producing the intense yellow color. The magnetic moment measurement suggested that the UO₂(VI) complex is diamagnetic as expected [46].

3.1.3. ESR Spectra

The X-Band ESR spectrum of $[CuL(H_2O)] \cdot H_2O$ (1) complex at room temperature exhibits one broad band with g_{eff} = 1.98. The spectrum is consistent with the square planar geometry around

Table 3	
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Characteristic electronic transition bands and magnetic moments of the transition metal complexes of the hydrazone, H₂L, ligand.

	Complex	π - π^*	n-π*	λ_{max} (cm ⁻¹) Nujol d-d transition assignment		10 Dq	В	β	$\mu_{\mathrm{eff}}{}^{\mathrm{a}}$
	H ₂ L	35,842	29,411	-	_	-	-	-	-
(1)	$[CuL(H_2O)] \cdot H_2O$	33,557	27,700	17,543	${}^{3}T_{2g}(G) \leftarrow E_{g}$	_	-	-	1.66
(2)	[NiL(CH ₃ OH) ₂ (H ₂ O)]·2H ₂ O	33,670	29,069	23,866	${}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}(F)$	1020	447	0.41	3.27
				16,393	${}^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}(F)$				
(3)	[CoL(H ₂ O)]·CH ₃ OH	34,482	28,735	16,528	${}^{4}T_{1}(P) \leftarrow {}^{4}A_{2}(F)$	5199	582	0.60	4.40
(4)	$[VOL(H_2O)] \cdot H_2O$	33,670	26,525	20,000	$b_1 \leftarrow b_2$	-	-	-	1.43
(5)	$[CrL(CH_3OH)_2(H_2O)]\cdot(NO_3)\cdot 6H_2O$	35,971	28,985	17,301	${}^{4}T_{2g}(F) \leftarrow {}^{4}A_{2g}(F)$	1809	605	0.58	3.58
(6)	$[ZnL(H_2O)] \cdot H_2O$	33,898	28,735	-	-	-	-	-	Diam
(7)	$[CdL(H_2O)] \cdot H_2O$	33,670	28,985	-	-	-	-	-	Diam
(8)	$[UO_2L(H_2O)] \cdot H_2O$	35,335	28,818	20,000	Charge transfer	-	-	-	Diam

^a $\mu_{\rm eff}$ is the magnetic moment of one metal ion in the complex.

Cu(II) ion in the complex as concluded from UV/vis spectra [47]. The ESR spectrum of the oxovanadium(IV) complex (4), exhibits one band at $g_{\rm eff}$ =2.06, without hyperfine structure indicating square pyramidal geometry around VO(IV) ion. This finding agrees with that concluded from the IR and UV/vis spectra. The absence of vanadium's hyperfine coupling might attributed to the strong exchange interactions, which average out the interaction with the nuclei or due to simultaneous flipping of neighboring electron spin [48].

3.1.4. Thermal analysis and kinetic studies

The thermal gravimetric analysis (TGA) for the ligand (H_2L) and its metal complexes was carried out within the temperature range from room temperature up to 800 °C.

The main aim of the thermal analysis is to obtain information concerning the thermal stability of the investigated complexes, to decide the number of water or solvent molecules and whether they are inside or outside the coordination sphere. Moreover, the kinetic and thermodynamic parameters using Coats–Redfern method have been also calculated.

Thermograms of the current complexes showed the removal of the lattic water or methanol molecules at 69 °C up to 118 °C. The anhydrous complexes are thermally stable in the range 118–180 °C. The removals of the coordinated water and/or methanol molecules are completed at 180–250 °C. The decomposition of the complexes to CuO, NiO, CoO, VO₂, Cr₂O₃, ZnO, CdO and UO₂ starts within the temperature ranging from 500 to 800 °C.

The stages of decomposition, temperature ranges and decomposition product loss as well the found and calculated weight loss percentages of the ligand and its metal complexes are given in Table 4.

The kinetic and thermodynamic parameters of the thermal degradation of the complexes namely, activation energy (E_a), enthalpy (ΔH), entropy (ΔS) and free energy changes (ΔG) were calculated using Coats–Redfern method [49]. The Coats–Redfern equations are in the following form:

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

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

where α represents the fraction of sample decomposed at time t, defined by: $\alpha = (w_o - w_t)/(w_o - w_\infty)$, w_o , w_t and w_∞ are the weight of the sample before the degradation, at temperature t °C and after total conversion, respectively. *T* is the derivative peak temperature. $M = -E_a/R$ and $B = \ln AR/\Phi E_a$; E_a , R, A and Φ are the heat of the activation, the universal gas constant, pre-exponential factor and heating rate, respectively.

The correlation coefficient, *r*, was computed using the least square method for different values of *n* (n=0.33, 0.5, 0.66 and 1), by plotting the left-hand side of Eqs. (1) or (2) versus 1000/*T*



Fig. 2. Coats–Redfern plots for $[CuL(H_2O)] \cdot H_2O(1)$, where $Y = \ln[-\ln(1-\alpha)/T^2]$.

(Figs. 2 and 3). The *n* value which gave the best fit ($r \approx 1$) was chosen as the order parameter for the decomposition stage of interest. From the intercept and linear slope of such stage, the A and E_a values were determined. The other kinetic parameters, ΔH , ΔS and ΔG were also computed using the relationships; $\Delta H = E_a - RT$, $\Delta S = R[\ln(Ah/kT) - 1]$ and $\Delta G = \Delta H - T\Delta S$, where *k* is the Boltzmann's constant and *h* is the Plank's constant. The following remarks can be pointed out on the kinetic parameters listed in Table 5. (1) All complexes decomposition stages show a best fit for (n = 1) indicating a first order decomposition in all cases. (2) Non-spontaneously (endergonic reactions) and the endothermicity of the desolvation process. (3) The negative values of activation entropies ΔS indicate a more order activated complex

Table 4

Thermal gravimetric results of H₂L and its metal complexes.

Compound (molecular weight)	DTG peak (°C)	Temperature range (°C)	Decomposition product lost (formula weight)	Weight loss (%) found (calculated)
H ₂ L	237	77–253	-NH ₄ SCN	32.14 (29.19)
	279	253-328	-C4HOS	48.53 (48.84)
	535	328-800	$-(CH_3CN+OH)$	20.00 (22.28)
$[CuL(H_2O)] \cdot H_2O$	91	49-155	$-H_{2}O$	5.0 (5.02)
	236	154–278	$-(H_2O + NH_2SCN)$	25.40 (25.70)
	521	278-800	$-C_5H_6N_2O$	38.00 (38.09)
		Residue	-(CuO+S)	31.60 (31.20)
$[NiL(CH_3OH)_2(H_2O)]\cdot 2H_2O$	85	35–137	-2H ₂ O	8.80 (8.27)
	384	138-470	$-(2CH_3OH + H_2O + C_3H_5N_3S + 2CO + NH)$	45.54 (45.26)
	536	470-637	$-(NiO + C_2S)$	15.27 (16.31)
		Residue		30.00 (30.00)
[CoL(H ₂ O)]·CH ₃ OH	68	34–116	−CH ₃ OH	8.14 (8.71)
	308	118-357	$-(H_2O + NH_2SCN)$	25.45 (26.20)
	508	357-750	$-C_6H_3NO_2S$	41.92 (41.93)
		Residue	-(NH + CoO)	25.00 (24.48)
$[VOL(H_2O)] \cdot H_2O$	85	24–104	$-H_2O$	5.00 (4.98)
	289	105-322	$-(H_2O + C_3H_5N_3S)$	36.40 (36.84)
	618	322-800	$-C_4O_2NHS$	35.00 (35.18)
		Residue	$-VO_2$	23.70 (22.88)
$[CrL(CH_{3}OH)_{2}(H_{2}O)] \cdot (NO_{3}) 6H_{2}O$	82	32–92	$-6H_2O$	19.70 (19.68)
	290	93–325	$-(2CH_3OH + H_2O + NH_3)$	18.75 (18.04)
	491	325-679	$-(C_3H_3N_2S + NO_2)$	25.62(26.43)
		Residue	$-(C_4O_3NHSCr)$	35.29 (35.96)
$[ZnL(H_2O)]\cdot H_2O$	85	24–143	$-H_2O$	5.00 (5.00)
	290	144–345	$-(H_2O + NH_2SCN)$	25.00 (25.57)
	622	345-712	$-(CH_3CN+C_4O_2NHS)$	45.54 (46.69)
		Residue	-ZnO	22.96 (22.61)
$[CdL(H_2O)] \cdot H_2O$	86	25-162	$-H_{2}O$	4.32 (4.42)
	296	162-340	$-(H_2O + NH_2SCN)$	23.33 (22.61)
	500	340-800	$-C_6H_4O_2N_2$	33.65 (33.49)
		Residue	-(CdO + S)	40.00(39.33)
$[UO_2L(H_2O)] \cdot H_2O$	118	31-148	$-H_{2}O$	3.07 (3.18)
	180	148-239	$-(H_2O + NH_3)$	6.66 (6.20)
	297	239–495	$-(CH_3CN + SCN + HNCO)$	25.42 (25.15)
	555	497-684	-(CO+2C)	9.66 (9.21)
		Residue	$-(UO_2 + O + S)$	56.00 (56.34)

Table 5

Temperatures of decomposition and the kinetic parameters of H₂L ligand and its metal complexes.

	Compound	Step	<i>T</i> (K)	$A(S^{-1})$	$\Delta E (\mathrm{kJ}\mathrm{mol}^{-1})$	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	$\Delta G (kJ mol^{-1})$
	H ₂ L	First	510	2.74×10^{27}	270.25	266.00	270	128.3
		Second	552	4.41×10^{10}	114.11	109.52	-54	137.12
(1)	$[CuL(H_2O)] \cdot H_2O$	First	364	$4.98 imes 10^5$	29.49	26.46	-145	79.24
		Second	507	5.84×10^{13}	22.04	17.82	5.90	14.82
		Third	794	$6.99 imes 10^6$	31.79	25.18	-130	128.4
(2)	$[NiL(CH_3OH)_2(H_2O)]\cdot 2H_2O$	First	358	$5.94 imes10^5$	35.33	32.35	-144	83.87
		Second	657	$1.99 imes 10^8$	41.10	35.63	-100	101.31
		Third	809	$6.63 imes 10^7$	35.90	28.77	-103	112.04
(3)	[CoL(H ₂ O)]·CH ₃ OH	First	345	$4.79 imes 10^5$	41.23	38.36	-145	88.32
		Second	581	$5.38 imes 10^6$	37.74	32.91	-130	108.05
		Third	781	$2.11 imes 10^8$	24.19	17.69	-101	96.57
(4)	$[VOL(H_2O)] \cdot H_2O$	First	342	$3.82 imes 10^7$	52.87	50.02	-109	87.27
		Second	562	1.09×10^{15}	164.79	160.11	29	143.81
		Third	891	$2.74 imes10^{8}$	32.08	24.67	-100	113.77
(5)	$[CrL(CH_3OH)_2(H_2O)]\cdot(NO_3)\cdot 6H_2O$	First	355	1.56×10^{17}	114.90	111.94	74	138.21
		Second	563	$7.80 imes10^{6}$	31.93	27.24	-131	101.09
		Third	764	$5.63 imes 10^8$	12.30	5.94	-93	76.99
(6)	$[ZnL(H_2O)]\cdot H_2O$	First	349	9.64×10^4	23.86	20.95	-159	76.48
		Second	563	$2.13 imes10^5$	54.12	49.43	-159	138.94
		Third	895	$1.08 imes 10^7$	62.60	55.15	-127	168.82
(7)	$[CdL(H_2O)]H_2O$	First	359	$1.05 imes 10^5$	34.32	31.33	-158	88.02
		Second	569	$6.58 imes 10^6$	80.98	76.24	-128	149.07
		Third	773	$8.62 imes 10^6$	12.88	6.45	-128	106.32
(8)	$[UO_2L(H_2O)]\cdot H_2O$	First	391	1.36×10^{14}	32.17	28.92	15	23.06
		Second	453	$8.66 imes 10^4$	47.93	44.16	-162	117.54
		Third	570	$6.69 imes 10^7$	24.61	19.87	-108	26.026
		Fourth	828	$6.16 imes 10^8$	17.00	10.11	-93	87.55

than reactant and/or the reaction are slow. (4) The positive values of ΔH means that the decomposition processes are endothermic [50].

The linear relationship between ΔH values of the second stages against to the ν_{M-O} vibrational frequencies of the cur-

rent complexes: $\Delta H_2 = 492.56 \pm 2.61 - 0.46\nu_{M-O} \pm 0.05$, r = 0.99, except Ni(II) and Co(II) complexes. This finding suggests that the breaking of it becomes difficult with the increase of the M–O bond strength (the source of oxygen is water or methanol).

Table 6

Molecular parameters of the ligand and its complexes.

Property	H ₂ L thione (thiol)	Cu(II)	Ni(II)	Co(II)	Cr(III)	Zn(II)	Cd(II)
Total energy (kcal/mol) Binding energy (kcal/mol) Electronic energy (kcal/mol) Heat of formation (kcal/mol) Dipole moment (D) HOMO (eV)	-65,784 (-65,799) -2399 (-2414) -382,145 (-38,002) -22.75 (-37.44) 7.22 (5.58) -8.88 (-9.00) 1 10 (-1.26)	-96,184 -2388 -489,922 -199 3.208 -9.43 1.57	-139,311 -5561 -115,754 -494 6.58 -8.79 1.01	-90,882 -2892 -536,951 -354 6.56 -4.14	-120,864 -5276 -11,120,262 -216 12,31 -7,36 0.62	-73,232 -2542 -436,195 -75 6.12 -8.98 1.24	-73,094 -2519 -421,075 -56 7.84 -8.39

Table 7

Calculated bond lengths (Å) of the free ligand and its complexes.

Compound	C=N	NH ₂	NH	N–N	C=N ^a	C–S	OH	OH _{solv.}	M–S	M-O _L	M-N	M-O _{solv.}	C=S
H ₂ L	1.32	0.994	1.005	1.403	-	1.78 ring	1.324	-	-	-	-	-	1.64
Cu(II)	1.33	0.991	1.004	1.444	1.34	1.80	-	0.956	2.13	1.85	1.88	1.82	-
Ni(II)	1.31	0.99	1.009	1.37	1.36	1.74	-	0.96	2.50	1.84	1.81	1.93	-
Co(II)	1.33	0.990	0.996	1.378	1.357	1.81	-	0.964	2.17	1.85	1.86	1.99	-
Cr(III)	1.34	0.99	1.00	1.45	1.32	1.80	-	0.968	2.28	1.84	1.92	2.05	-
Zn(II)	1.33	0.993	1.005	1.40	1.335	1.80	-	0.95	2.29	1.96	2.00	2.30	-
Cd(II)	1.34	0.995	1.004	1.41	1.32	1.79	-	0.95	2.40	2.16	2.37	4.49	-

^aBond length of HN-C.

3.1.5. Molecular orbital calculations

The experimental results were compared with theoretical data which were obtained from molecular mechanical calculations on the basis of the semi-empirical PM3 level provided by HyperChem 7.5 software. The calculated heat of formation, dipole moment, HOMO and LUMO energies as well as bond lengths after geometri-



Fig. 3. Coats–Redfern plots for $[NiL(CH_3OH)_2(H_2O)]\cdot 2H_2O$ (**2**), where $Y = ln[-ln(1-\alpha)/T^2]$.

cal optimization of the structures of free ligand and its complexes are given in Table 6. A comparison between the bond lengths of the ligand and its metal complexes demonstrated in Table 7. The theoretical data were compared with the experimental data, molecular orbital calculations for vanadyl and uranyl-complexes are failed.

The calculated bond lengths of M-O, M-N and M-S coordinated bonds of the current complexes are lincorrelated with their measured IR frequencies: early lengths = $11.25 \pm 0.72 - 0.0194 V_{M-0} \pm 0.0015$, M-O bond r = 0.99 except Ni(II) and Co(II)-complexes and M–S bond lengths = $17.68 \pm 3.48 - 0.022 \nu_{C-S} \pm 0.005$, r = 0.99, except Ni(II) complex. The deviation of Ni(II) complex bond lengths could be explained as a result of presence it as an octahedral structure. The negative slopes reveal increase of the bond strength, as indicated from their vibrational frequencies, with the shortness of the calculated coordinated bond lengths of M-O and M-S. This finding supports the assignment of the IR vibrational modes of M-O and M-S.

The calculated energies of the high occupied molecular orbital (HOMO) and low unoccupied molecular orbital (LUMO) are linearly correlated with the IR data of the corresponding complexes:



Fig. 4. Molecular modeling of [NiL(CH₃OH)₂(H₂O)]·2H₂O (2).



Fig. 5. Molecular modeling of [CoL(H₂O)]·CH₃OH (3).



Fig. 6. Molecular modeling of [CrL(CH₃OH)₂(H₂O)]·(NO₃)·6H₂O (5).



Fig. 7. Molecular modeling of $[ZnL(H_2O)] \cdot H_2O(\mathbf{6})$.

 $E_{\text{LUMO}} = -8.27 \pm 1.67 \pm 0.0136 \nu_{\text{M-N}} \pm 0.0031$, r = 0.96 (except Zn(II) complex). However, $E_{\text{LUMO}} = 32.80 \pm 1.18 - 0.05 \nu_{\text{C-S}} \pm 0.0017$, r = 0.99, (except Ni(II) and Cr(III) complexes) and $E_{\text{HOMO}} = 37.91 \pm 2.45 - 0.098 \nu_{\text{M-O}} \pm 0.005 r = 0.99$ (except Ni(II) and Cr(II) complexes). The positive slopes indicate increase of M–N bond strength (vibrational frequencies increases) as LUMO and HOMO energies increases, respectively. This might attributed to the weakness (longer) of the bonds neighbor to the coordinated centers with strengthen the metal ligand bonds in parallel



Fig. 8. Molecular modeling of $[CdL(H_2O)] \cdot H_2O(7)$.

with the increase of E_{LUMO} . However, the increase of E_{HOMO} is accompanied by weakness (elongation) of metal-ligand bonds which leading to strengthen (shortness) of the sites adjacent to the metal ligand centers. This interpretation agrees well with the Gutmann's variation rules "the bond strength increases as the adjacent bonds becomes weaker" such as found by Linert et al. [51].

On the other hand, the calculated dipole moment values (μ) are related along the activation parameters values obtained from thermal gravimetric analysis $(\Delta H_1$: hydration water) given the following relation: $\mu = -4.28 \pm 0.35 \pm 0.071 \pm 0.005 \Delta H_1$, r = 0.97 except Zn(II) and Cd(II) complexes. The positive slope indicates increasing the possibility of hydration/solvation (outer sphere) with the increase of the dipole moment of the complex, which support the proposed structures for these complexes and their tentative TGA assignments.

4. Conclusion

The condensation reaction of thiosemicarbazide with 5acetyl-4-hydroxy-2*H*-1,3-thiazine-2,6(3*H*)-dione afforded the corresponding thiosemicarbazone, H₂L, ligand. Reaction of the newly synthesized ligand with Cu(II), Ni(II), Co(II), VO(IV), Cr(III), Cd(II), Zn(II) and UO₂(VI) in the molar ratio (1:1) gave the corresponding mononuclear metal complexes with the general formula $[ML(H_2O)(CH_3OH)_x] \cdot nH_2O \cdot (CH_3OH)_y(NO_3)_z$. In the absence of Xray single crystal data of the current complexes and based on the physicochemical studies and geometrical optimization discussed above, a tentative mononuclear structure could be proposed as shown in Figs. 4–8.

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