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Elaborated studies for the ligitional behavior of thiouracil derivative towards Ni(II), Pd(II), Pt(IV), Cu(II) and UO_2^{+2} ions

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HIGHLIGHTS

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

- A new series of complexes was prepared using different metal ions with a new derivative of thiouracil.
- The complexes were investigated using all valuable spectral and chemical tools.
- ESR spectrum of Cu(II) complex displays axially symmetric g tensor parameters indicating the square– planar geometry.
- The biological effect of all investigated compounds was studied on different microorganisms.

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ABSTRACT

A synthesis of new thiouracil derivative was carried out and deliberately investigated. A new series of complexes was prepared using Ni(II), Pd(II), Pt(IV), Cu(II) and UO_2^{+2} ions. IR spectral data proposed the coordination mod of the ligand towards each metal ion and displays the binegative pentadentate mod as the maximum mod of coordination obtained with Ni(II) and Cu(II) complexes. ¹HNMR spectrum of UO_2^{+2} complex in comparing with the free ligand spectrum supports the binegative appearance of the coordinated ligand through the ionization of C=O and C=S groups. The electronic spectral data as well as the magnetic moment measurements are coincide with each others to propose the square–planar geometry with Ni(II), Pd(II) and Cu(II) complexes and octahedral geometry with the others. ESR spectrum of Cu(II) complex as a ground state with the square–planar geometry. The TG analysis for all isolated complexes were carried out to assert about the presence of water molecules physically or chemically attached with the central atom. The biological study was carried out against different microorganisms as gram negative, gram positive and fungi. The comparable data display the relative priority of Ni(II) complex in comparing with others against all organisms but, the other complexes display activity by the same with the free ligand.

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Introduction

Pyridine derivatives constitute an important class of compounds because they are components of the biologically important nucleic

* Tel.: +966 555761800. *E-mail address:* dr.khlood@hotmail.com acid [1,2] compounds containing nitrogen and sulfur as donor atoms have an important role to play as anticancer and antiviral agents [3,4]. The metal species may have toxicological effects, which involve nucleic acids. The "Platinum blues" contain uracil or thymine as a ligand, behave as antioplatic agents. This may cause breaks in nucleic-acid chains. In spite of, the literature review and papers about the chemistry, but the exact nature of metal bonding

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in complexes is not yet firmly established, and it is too early to conclude whether previous models are correct or even which recent models are corrected. A decision regarding the nature of the binding in such compounds and their complexes require further work. So, the metal binding sites on pyrimidines are less clearly defined and leads to draw logical conclusion. In our laboratory, studies were reported on the structural chemistry of pyrimidine compounds and their transition metal complexes [5–9]. The rich chemistry of the azo compounds is associated with several important biological reactions such as protein synthesis, carcinogenesis, azo reduction monoamine oxidize inhibition mutagenic, immunochemical affinity labeling, nitrogen fixation, important medical and industrial uses [10,11]. Masoud et al. [12-14] published a series of papers to throw light on the chemistry of the biologically active pyrimidines. In this paper i am aiming to the preparation of new derivative of thiouracil compound containing an additive active coordinating center (OH group) has a great ability for the interaction with central atoms in concern beside the other preferable (S and N) towards the coordination. This may facilitate the synthesis of polynuclear complexes which may display a distinguish biological activity through the inhibition role played by the central atoms. This goal was achieved with most isolated complexes.

Experimental

Reagents

All chemicals used for the study were of analytically reagent grade, commercially available from fulka and used without previous purification as $Ni(NO_3)_2$ ·6H₂O, $Cu(NO_3)_2$ ·3H₂O, PdCl₂, H₂PtCl₆ and UO₂(NO₃)₂ compounds. These represents the metal ions in concern for the complexation. All the used solvents were pure or spectroscopic grade.

Synthesis of the ligand

4-Aminophenol (0.1 mol) was mixed with HCl (0.2 mol in 25 ml distilled water) and diazotized below 5 °C with NaNO₂ (0.1 mol) in distilled water (30 ml). The resulting diazonium chloride was coupled with an alkaline solution of 2- thiouracil (0.1 mol) below 5 °C with equal molar ration (0.02 mol). The reaction mixture was stirred under reflux for ≈ 1 h. The volume of the resultant solution was reduced one half by evaporation then the solid product was precipitated, separated and washed with Et₂O and dried in vacuum over calcium chloride (Fig. 1).

Synthesis of metal complexes

All the complexes were prepared by mixing 0.01 mol from each transition metal salt with 0.01 mol of the organic compound

previously dissolved in ammonia solution (1: 1, 25 ml). The reaction mixture was left over night where the resulting solid complexes were removed by filtration. The precipitate then washed several times with EtOH followed by Et₂O and dried under vacuum over anhydrous CaCl₂.

Molecular modeling

An Attempt to obtain an acceptable insight about the molecular modeling structure of the ligand (Fig. 1) and its complexes was done. The geometry optimization representing the lower energy content has been performed by the use of MM⁺ [15] force – field as implemented in hyperchem 5.1 [16].

Antibacterial antifungal screening

In vitro antibacterial screening is performed by the agar disc diffusion method [17]. The species used in the screening are; gram - negative bacteria as: Escherishia coli sp. and Pesudomonas aeruginosa. And gram - positive bacteria as: Bacillus subtilis and Staphylococcus aureas. Fungi as: Aspergillus flavus and Candida albicans. Stock cultures of the tested organisms are maintained on nutrient agar media by sub culturing in Petri dishes. The media are prepared by adding the components as per manufacturer's instructions and sterilized in the autoclave at 121 °C and atmospheric pressure for 15 min. Each medium is cooled to 45-60 °C and 20 cm³ of it, is poured into a Petri dish and allowed to solidify. After solidification, Petri plates with media are spread with 1.0 ml of bacterial or fugal suspension prepared in sterile distilled water. The wells are bored with cork borer and the agar plugs are removed. To each agar well, unique concentration of 100 µg for each compound in DMSO (75 μ l) were applied to the corresponding well (6 mm). All the plates are incubated at 37 °C for 24 h and they are observed for the growth inhibition zones. The presence of clear zones around the wells indicate that the ligand and its complexes are active. The diameter of zone of inhibition is calculated in millimeters. The well diameter is deducted from the zone diameter and the values are tabulated.

Physical measurements

Carbon, hydrogen and nitrogen contents were determined using a Perkin–Elmer CHN 2400. The Cl was determined gravimetrically using AgNO₃ and the metal content was determined by the complexometric titration procedure [18] except the UO_2^{+2} complex its metal content was determined as U_3O_8 after its thermal decomposition. 0.1 g of uranyl complex was placed in a clean and dry weight crucible and ignited on bunzen flame for 15 min. After that, the crucible was ignited in a muffle at 1000 °C to constant weight for 2 h. The residue was cooled and weight again as U_3O_8 . IR spectra were recorded on a Mattson 5000 FTIR Spectrophotometer (4000–



Fig. 1. The proposed structure of the (E)-5-((4-hydroxyphenyl) diazenyl-2-thioxo - 2,3 - dihydropyrimidin-4(1H)-one (H₃L) ligand.

Table 1

Analytical and physical data for the H₃L and its metal complexes.

Compound empirical formula (M. Wt.)	Color	Elemental analys	Elemental analysis (%) Calcd. (found)				
		С	Н	Ν	М	Cl	
$(1) [C_{10}H_8N_4SO_2]$	Orange	48.38(48.37)	3.25(3.22)	22.57 (22.55)	-	-	
(2) [Ni ₃ (NO ₃) ₃ H ₂ O(C ₁₀ H ₆ N ₄ SO ₂)]NO ₃ ·3H ₂ O	Yellow	16.25(16.25)	1.91(1.91)	15.16(15.15)	23.83 (23.82)	-	
(3) [Pd ₂ Cl ₂ (C ₁₀ H ₆ N ₄ SO ₂)2H ₂ O]2H ₂ O	Brown	19.95(19.94)	2.34(2.34)	9.31 (9.15)	35.35 (35.34)	11.77 (16.3)	
(4) [Pt Cl ₂ ⁻ H ₂ O(C ₁₀ H ₆ N ₄ SO ₂)]2H ₂ O	Brown	21.21(21.20)	2.14(2.13)	9.89 (9.87)	34.45 (34.44)	6.26(6.26)	
(5) [Cu ₃ (NO ₃) ₃ H ₂ O(C ₁₀ H ₆ N ₄ SO ₂)]NO ₃ 2H ₂ O	Yellowish Brown	16.25(16.24)	1.64(1.64)	15.16(15.15)	25.79(25.78)	-	
(6) [(UO ₂) ₂ (NO ₃) ₂ H ₂ O(C ₁₀ H ₆ N ₄ SO ₂)]3H ₂ O	Yellow	16.57)(16.55)	1.67(1.67)	11.59(11.59)	65.69 (65.68)	-	

Table 2

Assignments of the IR Spectral bands (cm⁻¹) of H₃L and its metal complexes.

Compound	v _{OH}	v _{asNO3}	$v_{C}^{2} = N$	$v_c =_0$	$\delta_{\rm NH}$	$v_N = N$	v _{c-o}	v_{C-S}	v_{M-O}	vM-N
		v _{sNO3}	$v^4 c = N$		δ_{OH}					v_{M-S}
(1) $[C_{10}H_8N_4SO_2]$	3448	-	-	1683	1625	1562	1213	-		
					1340					
(2) $[Ni_3(NO_3)_3(C_{10}H_6N_4SO_2)H_2O]NO_3 \cdot 3H_2O$	3440	1700	1683	-	-	1563	1212	700	550	520
		1563	1627		1330					460
(3) [Pd ₂ Cl ₂ (C ₁₀ H ₆ N ₄ SO ₂)2H ₂ O]2H ₂ O	3478	-	1697	-	-	1544	1218	700	549	500
			1625		1344					480
(4) [PtCl ₂ (C ₁₀ H ₆ N ₄ SO ₂)H ₂ O]2H ₂ O	3475	-	1702	-	-	1546	1232	680	550	510
			1673		1344					470
(5) [Cu ₃ (NO ₃) ₃ H ₂ O(C ₁₀ H ₆ N ₄ SO ₂)]NO ₃ 2H ₂ O	3430	1620	1698	-	-	1540	1221	620	550	510
		1540	1653		1327					470
(6) [(UO ₂) ₂ (NO ₃) ₂ H ₂ O(C ₁₀ H ₆ N ₄ SO ₂)]3H ₂ O	3490	1704	1687	-	-	1538	1213	680	550	520
		1558	1653		1340					455

Table 3

Magnetic moments (BM) and electronic spectra bands (cm⁻¹) of the complexes.

Complex	$\Omega^2\mathrm{cm}^{-1}\mathrm{mol}^{-1}$	μ_{eff} (BM)	d-d transition (cm ⁻¹)	Intraligand and charge transfer bands (cm^{-1})
(2)	49	Dia	20,660; 24,907	35,714; 27,933
(3)	14	Dia	25,252; 28,089	35,714
(4)	12	Dia	-	35,461, 31,847, 22,624; 21,367
(5)	45	1.21	19,531	25,000;27,933; 31,847
(6)	10	Dia	20,325; 25,m381	29,412; 32,467

400 cm⁻¹) using KBr pellets. The UV–Vis., spectra were determined in the DMSO solvent with concentration $(1.0 \times 10^{-3} \text{ M})$ for the free ligands and their complexes using Jenway 6405 Spectrophotometer with 1 cm quartz cell, in the range 200-800 nm. Molar conductance were measured using Jenway 4010 conductivity meter for the freshly prepared solutions at 1.0×10^{-3} mole in DMSO solvent. Magnetic measurements were carried out on a Sherwood Scientific magnetic balance using Gouy method. Calibration: two very good solid calibrants are used: Hg[Co(CNS)₄] and [Ni(en)₃](S₂O₃). They are easily prepared in pure state, do not decompose or absorb moisture and pack well. Their susceptibilities at 20 $^{\circ}\text{C}$ are 16.44×10^{-6} and $11.03\times 10^{-6}\,\text{c.g.s.}$ Units, decreasing by 0.05×10^{-6} and 0.04×10^{-6} per degree temperature raise, respectively, near room temperature. The cobalt compound, besides having the higher susceptibility, also packs rather densely and is suitable for calibrating low fields, while the nickel compound with lower susceptibility and density is suitable for higher field. Here we are used Hg[Co(CNS)₄] only as calibrant. ¹H NMR spectrum of the organic compound and its UO₂⁺² complex were recorded on Varian Gemini 200 MHz spectrometer using DMSO-d₆ as solvent. ESR spectrum of solid Cu(II) complex was obtained on a Bruker EMX Spectrometer working in the X-band (9.44 GHz) with 100 kHz modulation frequency. The microwave power was set at 1 mW, and modulation amplitude was set at four Gauss. The low field signal was obtained after four scans with a 10-fold increase in the receiver gain. A powder spectrum was obtained in a 2 mm quartz capillary at room temperature. The X-ray powder diffraction analyses were carried out using Rigku Model ROTAFLEX Ru-200 with copper target. Thermogravimetric and its differential analysis (TGA/DTG) were carried out in dynamic nitrogen atmosphere (30 ml/min) with a heating rate of 10 °C/min using a Shimadzu TGA-50H thermal analyzer.

Results and discussion

The elemental analysis and some physical characteristics are summarized in Table 1. All the isolated complexes are relatively stable in air, they having higher m.p. (\Box 300 °C). They are insoluble in H₂O and most organic solvents except DMSO and DMF, they are completely soluble. The molar conductivity measurements for 1.0×10^{-3} mol (in DMSO) reveals that some of them are conducting and others are non conducting feature as displayed in Table 3. This elucidates the proposal of analysis data for the presence of conjugated anion covalently or ionically attached with the central ions in the investigated complexes.

IR spectra of the complexes

The prominent IR bands elucidating the coordination sites of the ligand are included in Table 2. This ligand may coordinate through different positions till reach to pentadentate coordination mod towards polynuclear complexes. The IR spectrum of ligand (H₃L) exhibits characteristic high intensity bands for vOH at 3448 cm⁻¹ and v for NH groups at 3135 and 3081 cm⁻¹. A lower

intense broad centered at 1830 cm⁻¹ may reflect the presence of intramolecular H - Bonding in between the neighboring function groups [19]. Bands at 1683, 1625 and 1562 cm⁻¹ assigned to υ C=O, δ NH and υ C=N. Bands at 1213, 1166 and 754 cm⁻¹ assigned to other characteristic bands as υ (C–O), υ^{II} (C=S) and υ^{IV} (C=S). A deliberate comparison between the free ligand spectrum and its metal complexes reflects the mod of coordination of the ligand towards each metal ion also characterizing the coordination sites through the shift recorded for bands in concern. The spectrum [Ni₃(NO₃)₃(HL)H₂O]NO₃3H₂O proposed the binegative pentadentate coordination mod for the ligand. The red shift observed for vOH band appeared at 3440 cm⁻¹ may reflects its coordination towards metal ion. The disappearance of characteristic bands assigned for v (C=O) and v (C=S) followed by the appearance of new band assigned for υ^2 (C=N), υ^4 (C=N) and υ (C-S) at 1683, 1627 and 700 cm⁻¹. This proposed the binegative trend observed for the ligand during the covalently attachment of the two concerned sites. The appearance of new bands at 1700 and 1563 cm⁻¹ assigned for v_{as} and v_s (NO₃) in a bidentate attachment towards metal ions. A strong band observed at 1384 cm⁻¹ assigned for ionic NO₃. New bands at 550, 520 and 460 cm⁻¹ assigned for M–L bonds (υ M–O, υ M–N and υ M–S). The spectrum of [Pd₂Cl₂(HL)2H₂O]·2H₂O complex reflects the binegative tetradentate mod of the ligand towards the binuclear atoms. The higher shift observed for υ (OH) band which appeared at 3478 cm⁻¹ may reflect its siding out form the coordination. The disappearance of significant bands assigned for v (C=O) and v (C=S) beside the appearance of new bands at 1697, 1625 and 700 cm⁻¹ assigned for υ (C=N²), υ (C=N⁴) and υ (C-S) bands proposed the ionization of the organic compound during complexation. The appearance of bands at 549, 500 and 480 cm^{-1} assigned for metal – ligand bonds (υ M–O, υ M–N and υ M–S). The spectrum of [PtCl₂(HL)H₂O]2H₂O complex reflects the binegative tridentate ligand coordinates inside the mononuclear complex. The higher shift appearance of υ OH band (3475 cm⁻¹) may reflect also its ruling out during the coordination. The disappearance of significant bands assigned for υ (C=O) and υ (C=S) was observed. This observation is reflecting the mod proposed especially with the appearance of new bands at 1702, 1673 and 680 cm⁻¹ assigned for υ (C=N²), υ (C=N⁴) and υ (C–S) bands. The appearance of new bands at 550, 510 and 470 cm⁻¹ assigned for υ M–O, υ M–N and υ M–S. The spectrum of [Cu₃(NO₃)₃(HL)H₂O]NO₃2H₂O complex reflects the binegative pentadentate mod of the ligand towards multicentre. The lower shift recorded for the vOH broad band centered at 3430 cm⁻¹ may propose its participation in coordination. The disappearance of significant bands assigned for υ (C=O) and υ (C=S) may suppose the same mod proposed previously. The appearance of new bands at 1698, 1653 and 620 cm $^{-1}$ assigned to υ (C=N 2), υ (C=N $^4)$ and υ (C–S) bands. Bands at 1620 and 1540 cm^{-1} assigned for υ_{as} and υ_{s} (NO₃) in a bidentate attachment towards metal ions. A strong band at 1384 cm⁻¹ may be assigned to ionic nitrate. The new bands observed at 550, 510 and 470 cm⁻¹ assigned to ν M–O, ν M–N and vM-S bands are normally appeared with the complex formation with such active sites. The spectrum of [(UO₂)₂(NO₃)₂(HL)]3H₂O complex reflects the binegative tetradentate mod towards the two central atoms. The higher shift observed for υOH and δOH bands may reflect its ruling out from coordination. The disappearance of significant bands assigned to v (C=O) and v (C=S) was also observed. The appearance of new bands coherently attached with their disappearance at 1687, 1653 and 680 cm⁻¹assigned to υ $(C=N^2)$, υ $(C=N^4)$ and υ (C-S) bands proposed the ionization of the organic compound. A strong band at 1704 cm⁻¹ is assigned to v_{as} (NO₃) also the appearance of band at 1558 cm⁻¹ for v_{s} (NO₃) in bidentate attachment. The bands at 1344, 1213, 550, 520 and 455 cm⁻¹ assigned for δ OH, υ (C–O), υ M–O, υ M–N and υ M–S. The bands appeared at 912 and 790 cm⁻¹ assigned for υ_3 and υ_1 of dioxouranium [20]. The value of υ_3 is used to calculate the force constant (F) of O=U=O by the method of McGlynn and smith [21]: $(\upsilon_3)^2 = (1307)^2(F_{U-O})/14.103$. The constant calculated for the complex is found to be 6.87 mdyn/A⁰. This value was then substituted into Jones relation [22]: $R_{U-O} = 1.08 (F_{U-O})^{-1/3} + 1.17$. The values of R_{U-O} are found = 1.738 for the complex. The calculated F_{U-O} value fall in the usual range for the uranyl complexes [20]. The trend observed for the ligand during its coordination with all metal ions is the lonely one. This may refer to that the precipitation process of all complexes is carried out in basic medium (NH₄OH). This devoted the organic compound to ionized during its complexation. This ionization activates the cites towards the covalent attachment with the metal atoms which appeared as heavily coordinates by the organic compound surrounding them.

¹HNMR spectra

The proton magnetic resonance spectrum of UO₂⁺² complex was performed in d₆ -DMSO as well as its original ligand was carried out for comparison (Fig. 2). The chemical shifts were recorded as follows: ¹HNMR spectrum of H₃L, δ (ppm): = 2.49 (s, for DMSO), δ = 3.38(s, H₂O in DMSO), δ = 5.77 (s, 1H of CH⁵), δ = 7.61 (m, 4H, benzene), $\delta = 8.02$ (s, 1H, NH²) $\delta = 9.19$ (s,1H, NH¹) and $\delta = 11.17$ (s, 1H, OH). 1HNMR spectrum of UO_2^{+2} complex, δ (ppm): = 2.5 (m, for DMSO and H₂O in it), $\delta = 3.44$ (s, H₂O in complex), δ = 5.75 (s, 1H, CH⁵), δ = 7.48 (m, 4H, benzene) and δ = 9.04 (s, 1H, OH). The ligand spectrum displays signals support the proposed geometry for the isolated compound. The complex spectrum signals are considered a further support for the presence of the ligand molecule as binegative after its ionization through C=O and C=S groups. This is observed by the complete obscure of two NH signals. The presence of intermolecular hydrogen bonding between H₂O molecules surround the complex and the ligand active sites may cause a little downfield shift in the frequency of the signals appeared [23].

Electronic spectra and magnetic properties

The distinguishable absorption bands (Table 3) of Uv-Vis spectra of the ligand and its corresponding complexes are recorded covering the 200-800 nm range in DMSO as well as their reflectance spectra were also recorded. The reflectance spectra recorded for most complexes to emphasis on the absence of solvent (DMSO) interaction during the electronic spectral study which may effect on the complex stereo structure but the spectra are not clear as that in DMSO. So, the data displayed in for the dissolved complexes only. The Uv-Vis. spectra are considered the most essential tool for proposing the stereo structure of the investigated complexes beside their magnetic moments which they must go in a parallel way for the proposal (Fig. 3). Firstly, the H₃L ligand spectrum shows shoulders and bands in the range around 284-318 and 406-484 nm. The strong absorption band at 284-318 nm range can be assigned to $\pi \rightarrow \pi^*$ transition of the ligand. The medium absorption band at 484 nm may be assigned to charge transfer transition inside the ligand for $n \rightarrow \pi^*$ transition[LMCT] [24]. Concerning the [Ni₃(NO₃)₃(HL)H₂O]NO₃3H₂O spectrum in DMSO displays the absorption bands at 35,714 and 27,933 cm⁻¹ attributed to intraligand transition suffering a little shift due to the coordination of concerned function groups. The spectrum shows band at 24,907 and 20,660 assigned to ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}B_{2g}$ transition, respectively corresponding to square planar geometry [25] which also evidenced by the diamagnetic appearance of the complex and the faint color of the complex (yellow) is a further support. Concerning the [Pd₂Cl₂(HL)2H₂O]·2H₂O complex exhibits three spin allowed transitions from lower lying d – levels to the empty $d_{x^2 \ x^2}$ orbital. Although other two electronic transitions



Fig. 2. ¹HNMR spectra of free H_3L ligand (a) and its UO_2^{+2} complex (b).

are also observed but their intensities are very weak and are neglected. The complex shows the absorption bands at 25,252 and 28,089 corresponding to ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ d-d transition [25]. These bands suggest that the complexes possess symmetry and square planar geometry. Concerning [PtCl₂(HL)H₂O]2H₂O complex spectrum displays absorption bands at 35,461, 31,847, 22,624 and 21,367 cm⁻¹. Bands at 35,461 and 31,847 are attributed to intraligand transitions bands. The absorption bands at 22,624 and 21,367 cm^{-1} are attributed to charge transfer transition probably for $S \rightarrow Pt$ [26]. The octahedral geometry is the preferable for d⁶ system. Concerning the [Cu₃(NO₃)₃(HL)H₂O]NO₃2H₂O complex spectrum displays intraligand transition band at 31,847 cm⁻¹. Charge transfer bands at 25,000 and 27,933 cm⁻¹ for LMCT transition. The d-d transition band at 19,531 cm⁻¹ attributed to ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ transition in square planar geometry [27]. The magnetic of this complex is 1.21 B.M. which is considered lower value than the normally observed for d⁹ systems. This may be referring to the presence of three central atoms in the same complex nucleus are relatively neighboring which may cause metal - metal interaction through the unpaired electron. Also, the antiparallel presence of the atoms through the stereo of the ligand and the distribution of function groups may cause the decrease in magnetic moment value. Concerning the $[(UO_2)_2(NO_3)_2]$ (HL)]3H₂O complex spectrum reveals intraligand transition bands at 29,412 and 32,467 \mbox{cm}^{-1} as well as charge transfer bands at 25,381 and 20,325 cm⁻¹attributed to $\ln g(\alpha) = \frac{-E^*}{RT} + \ln [\frac{AR}{\varphi E^*}]^3 \pi 4$ transition. This bands are similar to the OUO symmetric stretching frequency for the first excited state [28]. While the band at $29,412 \text{ cm}^{-1}$ is assigned to a charge transfer transition probably $0 \rightarrow U$. Some complexes exhibit a band in the range 22,624-25,000 and 25,000–27,933 cm⁻¹. The first region should be assigned to $S \rightarrow M$ transition and the second region assigned to $O \rightarrow M$ charge transfer [29]. The Ni(II), Pd(II), Pt(IV) and UO₂⁺² complexes are represented in a diamagnetic nature as the expected behavior towards strong ligand for d⁶ or d⁸ systems.

Molar conductivity measurements

The molar conductivity values of Ni(II), Pd(II), Pt(IV), Cu(II) and UO_2^{+2} complexes (Table 3) were found to be in the range of 10–49 Ω^2 cm⁻¹mol⁻¹. The values of Pd(II), Pt(IV) and UO_2^{+2} complexes are relatively low which, indicate the non – electrolytic nature of these complexes. The neutrality of the complexes can be accounted by the covalent attaching of the conjugated anion towards metal ions. The values of Ni(II) and Cu(II) complexes are relatively higher values (49 and 45 Ω^2 cm⁻¹ mol⁻¹, respectively) may propose 1: 1 electrolyte in between the coordination sphere and the nitrate anions [30].

Thermogravimetric analysis

The thermogravimetric analysis data were displayed in Table 4. All the investigated complexes are displaying a little thermal stability due to their degradation process was started at lower temperature. This behavior is supporting the presence of hydrated water molecules associated physically with the complex sphere. Such, was proposed previously based on the elemental analysis as well as the IR data. The TG curve of $[Ni_3(NO_3)(HL)H_2O]NO_33H_2O$ complex displays three degradation stages. The first stage at 50– 120 °C is attributed to the removal of three water molecules associated with the complex by 7.3 (Calcd. 7.31%) weight loss. The second degradation stage at 120–320 °C may be attributed to the removal of $H_2O + 4(NO_3)$ molecules surround the central atoms by 36.12 (Calcd. 36.00%) weight loss. The third degradation stage at 320–650 °C may be attributed to the removal of C₆H₅O as organic fragment by 12.55 (Calcd. 12.59%) weight loss. The residual part



Fig. 3. The proposed geometries for all the isolated complexes; where M=Cu(II) or Ni(II) and X = 2 or 3, respectively, with their molecular modeling.

recorded at 650 °C is $[Ni_3(C_4HN_4SO)]$ by 44.02 (Calcd. 44.09) weight percentage. The TG curve of $[Pd_2Cl_2(HL)\cdot 2H_2O]2H_2O$ complex displays three degradation stages. The first stage at the temperature range of 36–190 °C is attributed to the removal of one water molecule attached physically with the complex by 2.77 (Calcd. 2.99%) weight loss. The second stage at the temperature range 190–330 °C may be attributed to the removal of

 $3H_2O + 0.5Cl_2$ molecules by 14.92 (Calcd. 14.87%) weight loss. The third stage at the temperature range 330-650 °C may be attributed to the removal of $0.5Cl_2$ molecule. The residual part recorded at 650 °C is attributed to [Pd₂(HL)] as a major part of the complex by 76.59 (Calcd. 76.25%) weight. The TG curve of [PtCl₂(HL)H₂O]2H₂O complex displays five degradation stages. The first stage at the temperature range 30-239 °C is attributing

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Thermogravimetric data of the investigated complexes.

Complex	Steps	Temp. range (°C)	Decomposed assignments	Weight loss found (Calcd. %)
(2)	1st	50-120	-3H ₂ O	7.30 (7.31)
	2nd	120-320	$-H_2O + 4(NO_3)$	36.12 (36.00)
	3rd	320-650	$-C_6H_5O$	12.55 (12.59)
	Residue		$[3Ni + (C_4HN_4SO)]$	44. 03 (44.10)
(3)	1st	36-190	-H ₂ O	2.77 (2.99)
	2nd	190-330	$-3H_2O + 0.5Cl_2$	14.92 (14.87)
	3rd	330-650	$-0.5Cl_{2}$	5.71 (5.89)
	Residue		[Pd ₂ (HL)]	76.59 (76.25)
(4)	1st	30-239	-H ₂ O	3.06 (3.18)
	2nd	239-300	$-2H_{2}O$	6.78 (6.36)
	3rd	300-410	$-0.5Cl_{2}$	6.64 (6.26)
	4th	410-520	$-0.5Cl_{2}$	5.92 (6.26)
	5th	520-630	C ₆ H ₅ O	16.1 (16.44)
	Residue		$[PtO + (C_4HN_4S)]$	61.50 (61.50)
(5)	1st	40-190	$-2.5H_{2}O$	5.67 (6.09)
	2nd	190-220	$-0.5H_2O + 4(NO_3)$	49.29 (49.28)
	3rd	220-400	+C ₆ H ₅ ON	
	4th	400-525	$-C_2N$	5.67 (5.15)
	5th	525-675	$-C_2HN_2S$	11.05 (11.52)
	Residue		2Cu + CuO	28.30 (27.96)
(6)	1st	35-170	$-1.5H_{2}O$	3.61 (3.73)
	2nd	170-350	$-1.5H_2O + 2(NO_3)$	20.52 (20.84)
	3rd	350-620	$-C_6H_5O$	12.85 (12.71)
	Residue		$-[(UO_2)_2(C_4HN_4SO)]$	63.02 (62.72)

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to the removal of water molecule in hydration state by 3.06 (Calcd. 3.18%) weight loss. The second stage at the temperature range 239-300 °C may be attributed to the removal of two water molecules by 6.78 (Calcd. 6.36%) weight loss. The third stage at the temperature range 300-410 °C may be attributed to the removal of 0.5 Cl₂ by 6.64 (Calcd. 6.26%) weight loss. The fourth stage at the temperature range 410–520 °C may be attributed to the removal of 0.5 Cl₂ molecule by 5.92 (Calcd. 6.26%) weight loss. The fifth stage at the temperature range 520-630 °C may be attributed to the removal of C_6H_5O by 16.1 (Calcd. 16.44%) weight loss. The residual part is recorded at 630 °C as [Pt ($C_4H_3N_4SO$)] by 61.5 (Calcd. 61.5%) weight. The TG curve of [Cu₃(NO₃)₃(HL)H₂O]NO₃2H₂O complex displays four degradation stages. The first stage at the temperature range 40–190 °C is attributed to the removal of 2.5H₂O by 5.67 (Calcd. 6.09%) weight loss. The second stage at the temperature range 190-220 °C may be attributed to the removal of 0.5H₂O + 4(NO₃) molecules by 49.29 (Calcd. 49.28%) weight loss. The third stage at the temperature range 220-400 °C may be attributed to the removal of C₂N molecule by 5.67 (Calcd. 5.15%) weight loss. The fourth stage at the temperature range 400-675 °C may be attributed to the removal of C₂N₂SH by 11.05 (Calcd. 11.52%) weight loss. The residual part was recorded at 675 °C as 2Cu + CuO by 28.30 (Calcd. 27.96) weight percentage. The TG curve of [(UO₂)₂(NO₃)₂(HL)]3H₂O complex displays three degradation stages. The first stage at the temperature range 35-170 °C is attributed to the removal of 1.5H₂O molecules by 3.61 (Calcd. 3.73%) weight loss. The second stage at the temperature range 170-350 °C May be attributed to the removal of 1.5H₂O + 2(NO₃) molecules by 20.52 (Calcd. 20.84%) weight loss. The third stage at 350-620 °C may be attributed to the removal of C₆H₅O molecule by 12.85 (Calcd. 12.71%) weight loss. The residue recorded at 620 °C as $[(UO_2)_2(C_4HN_4SO)]$ by 63.02 (Calcd. 62.72%) weight. The high residue percentage is referring to the value recorded at relatively lower temperature (\approx 600) which may be not sufficient for the expel of the rest organic part attached with the central atoms.

Kinetic studies

In order to assess the effect of the metal ion on the thermal behavior of the complexes, the order n, and the heat of activation E of the various decomposition stages were determined from the TG and DTG for all complexes except the Ni(II) which, displays bands in a broad state which prohibit the exact determination of the fraction decompose related to temperature. Several equations [31–38] have been proposed as means of analyzing a TG curves and obtaining values for kinetic parameters. Many authors [31–34] have discussed the advantages of this method over the conventional isothermal method. The rate of the decomposition process can be described as the product of two separate functions of temperature and conversion [2], using:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α is the fraction decomposed at time t, k(T) is the temperature dependant function and $f(\alpha)$ is the conversion function dependent on the mechanism of decomposition. The temperature dependent function k(T) is of Arrhenius type and can be considered as the rate constant k,

$$K = A e^{-E^*/RT} \tag{2}$$

where *R* is the gas constant in (J mol⁻¹ k⁻¹) substituting Eq. (2) into Eq. (1) we get this equation:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\varphi e^{-E'/RT}}\right) f(\alpha) \tag{3}$$

where φ is the linear heating rate dT/dt. From the integration and approximation, this equation can be obtained in the following form:

$$\ln g(\alpha) = \frac{-E^*}{RT} + \ln \left[\frac{AR}{\varphi E^*}\right]$$

where $g(\alpha)$ is a function of α dependant on the mechanism of the reaction. The integral on the right hand side is known as temperature integral and has no closed for solution. So, several techniques have been used for the evaluation of temperature integral. Most commonly used methods for this purpose are the differential method of Freeman and Carroll [31] integral methods of Coat and Redfern [33], the approximation method of Horowitz and Metzger [38]. The kinetic parameters for most investigated complexes are

Table 5	
Kinetic parameters using the Coats - Red fern (CR) and Horowitz - Metzger (HM) operated for the H ₃ L complexes.	

Complex	Step	Method	Kinetic parameters					
			$E (J mol^{-1})$	A (S ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔH (J mol ⁻¹)	ΔG (J mol ⁻¹)	r
(2)	2nd	CR	9.35E + 04	2.89E + 04	-1.66E + 02	8.79E + 04	2.02E + 05	0.9925
		HM	1.08E + 05	1.30E + 06	-1.35E + 02	1.03E + 05	1.95E + 05	0.99603
(3)	2nd	CR	6.99E + 05	8.64E + 79	1.28E + 03	6.96E + 05	1.22E + 05	0.9932
		HM	6.94E + 05	1.37E + 80	1.29E + 03	6.91E + 05	1.16E + 05	0.99363
(4)	1st	CR	1.99E + 04	3.92E - 01	-2.56E + 02	1.64E + 04	1.24E + 05	0.99345
		HM	2.99E + 04	2.61E + 01	-2.21E + 02	2.64E + 04	1.19E + 05	0.9865
(5)	2nd	CR	4.50E + 04	3.78E + 01	-2.20E + 02	4.02E + 04	1.67E + 05	0.97601
		HM	5.27E + 04	2.79E + 02	-2.04E + 02	4.79E + 04	1.65E + 05	0.97378
(6)	2nd	CR	1.38E + 06	7.73E + 151	2.66E + 03	1.38E + 06	1.23E + 05	0.97385
		HM	1.38E + 06	1.31E + 152	2.66E + 03	1.37E + 06	1.20E + 05	0.97751

Table 6

ESR data of Cu (II) complex at room temperature.

Complex	$g_{ }$	g_{\perp}	$g_{\rm iso}$	$A_{//} imes 10^{-4} ({ m cm}^{-1})$	A_{\perp}	F	G	α^2	β^2
(2)	2.28	2.143	2.19	170	85	134.1	1.97	0.85	0.49





evaluated using the following methods and the results are in good agreement (Table 5) with each other. The used methods are discussed briefly.

Coats-Redfern equation

The equation is a typical integral method, represented as:

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

For convenience of integration the lower limit T₁ is usually taken as zero. This equation on integration gives:

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

A plot of $\ln[\frac{-\ln(1-\alpha)}{T^2}]$ (LHS) against 1/T was drawn. E^{*} is the energy of activation in J mol⁻¹ and calculated from the slop and A is (S⁻¹) from the intercept value. The entropy of activation ΔS^* in (J K⁻¹ mol⁻¹) was calculated by using the equation:

$$\Delta S^* = R \ln \left(\frac{Ah}{K_B T_s}\right) \tag{3}$$

where k_B is the Boltzmann constant, *h* is the Plank's constant and T_s is the DTG peak temperature [37].

Horowitz-Metzger equation

The authors derived the relation:

$$\ln[-\ln(1-\alpha)] = \frac{E}{RT_m}\Theta$$
(4)



Fig. 5. XRD spectra of, (a) Cu(II) complex and (b) Pd(II) complexs.

where α , is the fraction of the sample decomposed at time *t* and $\Theta = T - T_m$. A plot of $\ln[-\ln(1 - \alpha)]$ against Θ , was found to be linear, from the slope of which *E*, was calculated and *Z* can be deduced from the relation:

$$Z = \frac{E\varphi}{RT_m^2} \exp\left(\frac{E}{RT_m}\right)$$
(5)

where ϕ is the linear heating rate, the order of reaction, *n*, can be calculated from the relation:

$$n = 33.64758 - 182.295\alpha_m + 435.9073\alpha_m^2 - 551.157\alpha_m^3 + 357.3703\alpha_m^4 - 93.4828\alpha_m^5$$
(6)

where α_m is the fraction of the substance decomposed at T_m .

The entropy of activation, ΔS^* , was calculated from Eq. (3). The enthalpy of activation ΔH^* , and Gibbs free energy, ΔG^* , were calculated from; $\Delta H^* = E^* - RT$ and $\Delta G^* = \Delta H^* - T\Delta S^*$, respectively. The data tabulated reveals the following observations: (i) the activation energy *E*, increases somewhat through the degradation steps

revealing the high stability of the remaining part suggesting a high stability of complexes characterized by their covalence, (ii) the negative ΔS^* values, indicates the activated fragment has ordered structures (iii) the positive ΔH^* reflects the endothermic decomposition process, (iv) the positive ΔG^* singe reveals that the free energy of the final residue is higher than that of the initial compound, and the decomposition stages are non – spontaneous. This results from increasing $T\Delta S^*$ clearly from one step to another which override the values of ΔH^* reflecting that the rate of removal of the subsequent species will be lower than that of the precedent one [39].

ESR spectrum

The spin Hamiltonian parameters and the *G* value of solid state Cu(II) complex are calculated (Table 6). Its ESR spectrum (Fig. 4) displayed axially symmetric g tensor parameters with $g_{11} > g_{1} > 2.0023$ indicating that the orbital as a ground state. In axial symmetry the g-values are related to the G-factor by the expression, $G = (g_{11} - 2)/(g_{\perp} - 2) = 4$, which measures the exchange interaction between copper centers in the solid. According to Hathaway [40], if the value of G is greater than 4, the exchange interaction between copper(II) centers in the solid state is negligible, whereas when it is less than 4, a considerable exchange interaction exists in the solid complex. The *G* value is less than 4 (1.97), this supports the little presence of exchange coupling between copper(II) centers in the solid state [41]. This hyperfine interaction observed for the complex is attributed to the interaction with nitrogen and oxygen nuclei adjacent to copper ion. Kivelson and Neiman, [42] have reported the g₁₁ value <2.3 for covalent character of the metal - ligand bond and >2.3 for ionic character. Applying this criterion the covalent character of the metal - ligand bond in the complex under study can be predicated. The trigonal bipyramidal and square - pyramidal have a ground state configuration ${}^{2}B_{1}$ (unpaired electron in $d_{\chi^{2}-\gamma^{2}}$ orbital) and ${}^{2}A_{1}$ (unpaired electron in d_{z^2} orbital), respectively. Molecular orbital coefficients, α^2 (A measure of the covalence of the in-plane σ -bonding between a copper 3d orbital and the ligand orbital) and β^2 (covalent in-plane π -bonding), were calculated by using the following equations [42– 46], where $\alpha^2 = 1$ indicates complete ionic character, whereas α^2 = 0.5 denotes 100% covalent bonding, with the assumption of negligibly small values of the overlap integral.

$$\alpha^{2} = ((A_{//}/0.036) + (g_{//} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04)$$

$$\beta^{2} = (g_{1/} - 2.0023)E / - 8\lambda\alpha^{2}.$$

where $\lambda = -828 \text{ cm}^{-1}$ for the free copper ion and *E* is the electronic transition energy. From Table 6, the α^2 and β^2 values indicate that the in-plane σ - bonding and the in-plane π -bonding are highly covalent. The lower value of β^2 compared to α^2 indicates that the in-plane σ -bonding is more covalent than the in-plane π -bonding. The β^2 value for copper (II) complex indicates a strong covalency in the bonding between the Cu (II) ion and the ligand.

X-ray powder diffraction of some complexes

X – ray powder diffraction pattern in the $10^{\circ} < 20 < 70^{\circ}$ of the Pd(II) and Cu(II) complexes were carried out as example in order to give an insight about the lattice dynamics of the compounds. The X-ray powder diffraction obtained reflects a shadow on the fact that each solid represents a definite compound by a definite structure which is not contaminated with starting materials. This identification of the complexes was done by the known method [47]. Such facts suggest that the two complexes are nanocrystalline in nature (Fig. 5).

Table 7

The values of zone inhibition of bacteria for the ligand and its metal complexes.

Compound	Zone of inhibition (mm)							
	Bacillus subtilis- Staphylococcus aureas Gram (+) bacteria	Escherishia coli sp - Pesudomonas aeruginosa Gram (–) bacteria	Aspergillus flavus-Candida albicans Fungi					
(1) H ₃ L	12-15	12-13	0-0					
(2)	15-16	12–15	15-17					
(3)	11-12	11-12	0.0-0.0					
(4)	14-15	13-13	0.0-0.0					
(5)	12-14	12-13	0.0-0.0					
(6)	13–15	11–13	0.0-13					

Molecular modeling

An attempt to gain a better insight on the molecular structure of the ligand and its complexes geometry optimization has been performed by the use of MM⁺ [15] force field as implemented in hyperchem 7.5 [16]. The drown modeling structures of the free ligand displays the stable stereo structure includes the lowest energy level (total energy 9.679 kcal/mol) for the stereo proposed. This arrangement of sites welling to coordination may support the mode of coordination proposed in the investigated complexes. The optimized geometry for the investigated complexes was supported by the calculation of their lowest energies as follow: Ni(II) is 169.252, Pd(II) is 47.79, Pt(IV) is 98.97, Cu(II) is 216.167 kcal/ mol. The data reflect the relative stability for the proposed geometry. The energy content of the UO_2^{+2} complex cannot calculated due to the program cannot detect the central atom.

Antibacterial antifungal activity

The biological activity of H₃L ligand and its complexes are tested against different organisms as gram - negative, gram positive and fungi using only one concentration from them in DMSO and used as a control. The zone of inhibition against the growth of microorganisms for the compounds is given in Table 7. It has been suggested that the ligand with the N, O and S donor system might have inhibited enzyme production, since enzymes which require free hydroxyl groups for their activity appearance to the especial susceptibility to deactivation by the ions of the complexes. The complexes facilitate their diffusion through the lipid layer of spore membranes to the site of action ultimately killing them by combining with -OH groups of certain cell enzymes. The variation in the effectiveness of different biocidal agents against different organisms depends on the impermeability of the cell. On chelation, the polarity of the metal ion is reduced to a greater extent [48] due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of p-electrons over the whole chelate ring and enhances the lipophilicity of the complex. The increased lipophilicity enhances the penetration of the complexes into lipid membranes and blocking the metal binding sites on the enzymes of the microorganism. Also, however the metal salts alone exhibit a higher activity than the investigated complexes but cannot use as antibacterial agents because of their toxicity and the probability of binding to the free ligands presented in the biological systems such as the nitrogen bases of nucleic acid and proteins. The normal cell process may be affected by the formation of hydrogen bond, through the donor atoms with the active centers of cell constituents [49]. Also, the absence of bulkiness observed around the metal ions which may permit their interaction easily with the cell enzymes is considered the main cause for the activity. From the results, it is clear that all investigated complexes displays an inhibition towards most investigated organisms. Ni(II) complex exhibits a strong inhibition towards all the studied microorganisms in comparing with the free ligand but the other complexes display the activity closer to the free ligand. From structure point of view of the prepared compounds with their effects on microbial test. It is clear that the formation of the chelate derived 3: 1 or 2: 1 M ratio (M: L) sometimes increase the biological activities of the complex compared to the free ligand. This is may be attributed to the presence of N, O and S groups around the three central atoms arising the inhibition activity of the central atoms which is not the only responsible for the biological activity of its complex. Some metal complexes can enhance the activity and others can reduce this activity with respect to the parent ligand.

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