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Polymer complexes. LIII. Supramolecular coordination modes and structural of novel sulphadrug complexes

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ABSTRACT

Novel polymer complexes of copper(II), palladium(II), platinum(II) and cadmium(II) containing homopolymer [4-acrylamido benzene sulphonyl guanidine; (HL)] and various anions (SO_4^{2-}, CH_3COO^-, NO_3^-, Br^- or Cl^-) have been designed and carried out. Their structures were investigated by elemental analyses, spectral (IR, UV–vis, ^1H NMR and ESR) and magnetic moments. The modes of interactions between the ligand and the metals were discussed, where oxygen (of O=S=O group) and nitrogen atom [of imino nitrogen (NH/N) of the guanidine group] are involved in chelation. The homopolymer shows two types of coordination behaviour. In mononuclear polymer complexes **4** and **6**–**10**, it acts as a neutral bidentate ligand chelated through the NH and O atoms, whereas in the polymer complexes **1**–**3**, **5** and **11**, monobasic bidentate ligand is coordinated through the –N and –O atoms. The poly-chelates are of 1:1/1:2 (metal–homopolymer) stoichiometry and exhibit four coordination. On the basis of electronic spectral data and magnetic susceptibility measurement square planar geometry has been proposed. The ESR spectral data provided information about their structure on the basis Hamiltonian parameters and degree of covalency. From the electron paramagnetic resonance and spectral data, the orbital reduction factors were calculated.

1. Introduction

Substantial work has been done by Diab and El-Sonbati and our co-workers [1–8] on poly-chelates derived from hydroxy-ketone, acryloyl chloride and various aliphatic and aromatic amines. However, no attempt seems to have been made to study the synthesis, characterization, coordination chemistry, thermal stability and biological function of some transition metal polymeric complexes for which structural information was obtained by spectrochemical and magneticochemical means. The studies of Cu(II) complexes have been widely explored for the versatility of their coordination geometries, exquisite color, technical application dependent molecular structures, spectroscopic properties and their biochemical significance. Octahedral Cu(II) complexes of ligands containing mixed electron donors have been studied extensively; due to their potential applications as molecular materials [9–13]. The chemistry of sulphadrug derivatives has attention because of their interesting structural properties and applications in diverse areas [14–17].

The field of polymer chemistry is developing very rapidly because of its applications and importance in the area of coordination chemistry [8–17]. The stability of polymeric metals complexes depends upon a number of factors, including the number and types of donor atoms present in the homopolymer and their relative positions with the homopolymer skeleton, as well as the number and the size of the chelate rings formed on complexation [1–15]. Coordination polymers are useful as engineering materials and find an important place in material chemistry [18]. Polymer complexes of lanthanides and or transition metal are currently attracting much attention towards tumor [19] and DNA targeting [20].

As a part of our ongoing work [1–15] in the area of supramolecular assembly of polymer complexes based on aromatic and/or aliphatic amine sulphadrugs, we report herein the synthesis, characterization, structure of HL (Fig. 1) and properties of copper supramolecular polymer complexes of the general formula $[CuHL{\cdot}O_2SO_2]_n$, $[CuL{\cdot}X]_n$ (X = OAc, O_2NO) and $[CuL{\cdot}Cl{\cdot}OH_2]_n$. The most probable coordination, semi-coordination and hydrogen bonds related to inclusion phenomena, guest exchange and molecular based nickel will be discussed more in detail. Recently, El-Sonbati [1,2,6,13,14] published a paper on rare earth/d-block ions with sulphadiazineazo-3-phenyl-2-thioxo-4-thiazolidinone [HL_1], 5-sulphamethazineazo-3-phenyl-2-thioxo-4-thiazolidinone [HL_2], 5-sulphamethoxoleazo-3-phenyl-2-thioxo-4-thiazolidinone

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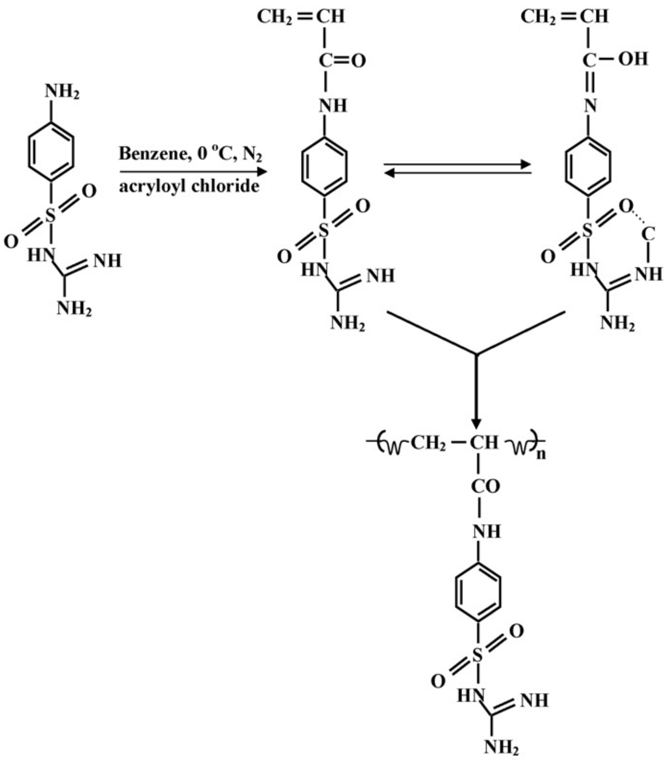


Fig. 1. The preparation and structure of the homopolymer (HL).

[HL_3], 5-sulphacetamideazo-3-phenyl-2-thioxo-4-thiazolidinone [HL_4], 5-sulphaguanidineazo-3-phenyl-2-thioxo-4-thiazolidinone [HL_5].

Recently in our laboratory, numerous polymer complexes and/or complexes of rhodanine sulphadrug and its derivatives have been reported [1–15]. In this paper, we report the synthesis and spectroscopic characterization of copper(II) polymer complexes with 4-(acrylamido) benzenesulphonyl guanidine (HL).

2. Experimental

Experimental techniques were as described previously [3,7–12]. Homopolymer was prepared by the method described by Diab, El-Sonbati and co-workers [3,7–12].

2.1. Reagents

Sulphaguanidine was bought from Aldrich and used without further purification. Acryloylchloride (Aldrich) was used without purification. 2,2′-Azobisisobutyronitrile (AIBN) was purified by fractional crystallization from EtOH [21].

HL monomer was prepared according to the literature methods [3,7–12]. The IR spectrum of the monomer showed the presence of a NH absorption band at 3165 cm^{-1}. Anal. Found: C, 44.8; H, 4.0; N, 15.9; S, 11.5%. Calcd. For HL($C_{10}H_{11}N_3SO_4$): C, 44.6; H, 4.1; N, 15.6; S, 11.9%. ^1H NMR (300 MHz, DMSO-d_6): δ(ppm) 10.22 (CONH); 5.80, 5.50 ($CH_2{=}C$).

2.2. Polymerization

Monomer HL was polymerized by the method described by Diab, El-Sonbati and co-workers [3,7–12]. The homopolymer has been characterized by IR, ^1H NMR.

2.3. Preparation of the polymer complexes

2.3.1. Method A: copper(II) salts, polymer complexes **1**–**4** and cadmium(II) chloride, polymer complex **5**

All the metal polymer complexes in this work were prepared using 1:1 metal:ligand molar ratio. Polymer complexes were prepared by mixing HL monomer (0.01 mol) in 20 ml dimethylformamide (DMF) and the copper(II) salts and/or Cd(II) chloride (0.01 mol) in 20 ml DMF as a solvent, and 0.1% (w/v) 2,2′-azobisisobutyronitrile (AIBN) as initiator. The mixture was boiled under reflux for 6 h. The hot solution was precipitated by adding to a large excess of distilled water, containing dilute hydrochloric acid, to remove the metal salts that were incorporated into the polymer complexes. The polymer complexes (**1**–**5**, see Table 1) were filtered, washed with water, and dried in a vacuum oven at 40 °C for several days to yield 65–75% of colored crystals.

2.3.2. Method B: palladium(II) salts polymer complexes **6**–**9**

Solution of PdX_2 (X = Cl or Br; 0.01 mol); HL (0.01 or 0.02 mol) and 0.1 (w/v) AIBN (2,2′-azobisisobutyronitrile) as initiator in MeOH–DMF (3:2, v/v) containing a few drops of concentrated HCl were mixed and stirred for 3 h at room temperature, polymer complexes precipitated immediately; then they were reflux for ~2.5 h to complete the reaction; these were poured into a large excess of distilled H_2O containing dilute HCl, to remove the metal salt incorporated into the polymer complexes. The products were filtered, washed with water, methanol and finally, with ether.

2.3.3. Method C: platinum chloride polymer complex **10**

The salt $K_2[PtCl_4]$ was dissolved in water–ethanol (1:1, v/v) and HL in a 0.1N HCl; the pH of both solutions was acidic. The two solutions were mixed and stirred at room temperature for 13 h in the presence of 0.1 (w/v) AIBN (2,2′-azobisisobutyronitrile) as initiator. The obtained precipitate was filtered off and washed with small portions of water, EtOH and Et_2O.

2.3.4. Method D: palladium polymer complex **11**

To a suspension of compounds **7** + **8** in 50 ml of DMF–ethanol (1:1, v/v) was added an aqueous solution (25 ml) of potassium hydroxide (0.4 g). The mixture became clear and yellowish powder was precipitated. The product was washed with water and Et_2O after filtrated.

2.4. Measurements

C, H, and N microanalyses were carried out at the Cairo University Analytical Center, Egypt. The metal content in the polymer complexes was estimated by standard methods [7–10]. The ^1H NMR spectrum was obtained with a Jeol FX90 Fourier transform spectrometer with DMSO-d_6 as the solvent and TMS as an internal reference. Infrared spectra were recorded using Perkin-Elmer 1340 spectrophotometer. Ultraviolet–visible (UV–vis) spectra of the polymer were recorded in nuzol solution using a Unicam SP 8800 spectrophotometer. The magnetic moment of the prepared solid complexes was determined at room temperature using the Gouy's method. Mercury(II) (tetrathiocyanato)cobalt(II) $[Hg\{Co(SCN)_4\}]$, was used for the calibration of the Gouy's tubes. Diamagnetic corrections were calculated from the values given by Selwood [22] and Pascal's constants. Magnetic moments were calculated using the equation, $\mu_{\text{eff.}} = 2.84\left[T\chi_M{}^{\text{coor.}}\right]^{1/2}$. EPR measurements of powdered samples were recorded at room temperature (Tanta University, Egypt) using an X-band spectrometer utilizing a 100 kHz magnetic field modulation with diphenylpicrylhydrazyle (DPPH) as a reference material. TG measurements were made using a Du Pont 950 thermobalance. Ten milligram samples were heated at a rate of

Table 1
Analytical data of the polymer complexes[a] (for molecular structure see Fig. 1)[b].

Complex[c]	Method of preparation[d]	Experimental (Calcd.) %				
No.		C	H	N	(S/Cl)[e]	Molar ratio
$[Cu(L)Cl\cdot OH_2]_n$	A	31.5	3.3	14.3	8.5/9.6	1:1
1		(31.3)	(3.4)	(14.6)	(8.3)/9.3	
$[Cu(L)O_2NO]_n$	A	30.7	3.0	18.1	8.0	1:1
2		(30.6)	(2.8)	(17.8)	(8.2)	
$[Cu(L)OAc]_n$	A	37.2	3.6	14.7	8.4	1:1
3		(37.0)	(3.6)	(14.4)	(8.2)	
$[Cu(HL)(O_2SO_2)]_n$	A	28.0	2.8	13.1	15.0	1:1
4		(28.1)	(3.0)	(13.4)	(15.3)	
$[Cd(L)Cl\cdot OH_2]_n$	A	27.5	3.0	13.2	7.7/8.0	1:1
5		(27.7)	(3.0)	(12.9)	(7.4)/8.2	
$[Pd(HL)Cl_2]_n$	B	27.0	2.7	12.6	7.2	1:1
6		(26.8)	(2.7)	(12.9)	(7.4)	
$[Pd(HL)Br_2]_n$	B	22.5	2.3	10.5	6.0	1:1
7		(22.4)	(2.2)	(10.8)	(6.2)	
$\{[Pd(HL)_2]Cl_2\}_n$	B	33.7	3.4	15.7	9.0	1:2
8		(33.6)	(3.3)	(15.5)	(8.8)	
$\{[Pd(HL)_2]Br_2\}_n$	B	29.9	3.0	14.0	8.0	1:2
9		(30.1)	(2.9)	(14.3)	(8.4)	
$[Pt(HL)Cl_2]_n$	C	22.5	2.3	10.5	6.0	1:1
10		(22.2)	(2.1)	(10.8)	(6.2)	
$[Pd(L)_2]_n$	D	37.5	3.5	17.5	10.0	1:2
11		(37.4)	(3.3)	(17.2)	(9.7)	

[a] Microanalytical data as well as metal estimations are in good agreement with the stoichiometry of the proposed complexes.
[b] The excellent agreement between calculated and experimental data supports the assignment suggested in the present work.
[c] HL are the ligand as given in Fig. 1 and L is the anion; air stable; no-hygroscopic; insoluble in water; soluble in coordinating solvents such as DMF and DMSO.
[d] See text.
[e] Estimated gravimetrically.

10 °C/min in a dynamic nitrogen atmosphere (70 ml/min); the sample holder was boat-shaped, 10 mm × 5 mm × 2.5 mm deep; the temperature measuring thermocouple was placed within 1 mm of the holder. The halogen content was determined by combustion of the solid complex (30 mg) in an oxygen flask in the presence of a $KOH–H_2O_2$ mixture. The halide content was then determined by titration with a standard $Hg(NO_3)_2$ solution using diphenyl carbazone as an indicator.

3. Results and discussion

3.1. *Characterization of the uncomplexed*

HL was prepared by the amidation reaction of acryloyl chloride with sulpha guanidine [3,7–12]. The monomer HL was characterized as in Section 2. The monomer was then polymerized as in Section 2. The monomer was then polymerized by radical polymerization initiated by 2,2′-azobisisobutyronitrile (AIBN). The homopolymer has been characterized by various techniques [7–12].

Herein we demonstrate the coordination mode of HL to generate Cu(II) polymer complexes. As expected these complexes are ESR active due to the presence of an unpaired electron. The Cu(II) complexes generally exhibit room temperature magnetic susceptibility as expected for an isolated d^9 transition metal center.

3.1.1. *The ligand*

HL used in this study is elucidated by different tools as, the elemental analysis, which used to propose the HL formula and IR spectrum supported this. ^1H NMR spectrum is the final confirming tool for the ligand structure and displayed a peaks for $C{=}NHNH_2$, SO_2NH and –C=NH. ^1H NMR spectrum of HL [δ(DMSO-d_6)] is the final confirming tool for the ligand structure and displayed a singlet peak at δ = 7.44 ppm by integration assigned to 4H referring to the phenyl group. Also, the three singlet peaks at 11.3, 7.26 and 7.48 ppm each peak by integration assigned to the three hydrogen atoms aggregated from CONH, SO_2NH and –C=NH groups. The relative down field appearance of the third peak (δ = 7.48 ppm) may be due to the intramolecular hydrogen bonding between NH and S=O groups [15]. The broad medium signal centered at δ = 5.45 ppm which could be assigned to the NH_2 protons. These signals disappeared on repeating the measurements in the presence of D_2O. The ^1H NMR spectrum of the ligand showed characteristic protons, which are listed in Table 2.

The NMR spectrum of monomer (HL) showed the expected peaks and pattern of the vinyl group ($CH_2{=}CH$), i.e. δ(DMSO-d_6) 6.25 ppm (dd, *J* = 17, 11 Hz) for the vinyl CH proton and proton δ 5.12 ppm (AM part of AMX system dd, *J* = 17, 1 Hz) for the vinyl CH_2 protons, respectively. These peaks disappeared on polymerization

Table 2
Characteristic ^1H NMR spectra for HL, Cd(II) complex (ppm *vs.* TMS)[a].

Compound[b]	Chemical shift δ(ppm)	Assignment
HL	7.44	d, 4H, ArH's
	11.30	d, 1H, CONH
	5.45	br, 2H, $–C{=}NHNH_2$
	7.26	br, 1H, $–SO_2NH$
	7.48	s, 1H, –C=NH
5	7.22	d, 4H, ArH's
	11.15	d, 1H, CONH
	4.48	br, 2H, $–C{=}NHNH_2$
	7.17	br, 1H, $–SO_2NH$
	–	s, 1H, –C=NH
	3.54	br, coordinated H_2O proton
6	7.54	d, 4H, ArH's
	11.18	d, 1H, CONH
	4.82	br, 2H, $–C{=}NHNH_2$
	7.12	br, 1H, $–SO_2NH$
	7.30	s, 1H, –C=NH
8	7.65	d, 4H, ArH's
	11.22	d, 1H, CONH
	4.68	br, 2H, $–C{=}NHNH_2$
	7.07	br, 1H, $–SO_2NH$
	7.25	s, 2H, –C=NH

[a] The excellent agreement experimental data supports the assignment suggested in the present work.
[b] See footnote in Table 1.

while a triplet at δ 1.86 ppm (t, J = 7 Hz) and a doublet at δ 1.80 ppm (d, J = 7 Hz) appeared. This indicates that the polymerization of HL monomer occurs on the vinyl group [7]. It is worth noting that the rest of the proton spectrum of the monomer and polymer remains almost without change.

3.2. Characterization of polymer complexes

3.2.1. Metal polymeric complexes

The HL used in this study is elucidated by different tools as, the elemental analysis, which used to propose the HL formula, IR and ^{1}H NMR supported this. All the isolated polymer complexes are air stable for extended periods and remarkably soluble in DMSO and DMF. The molar conductivities in DMF solution indicate that the polymer complexes are in the range expected for non-electrolytes [23]. This can be account for by the satisfaction of the bi-valency of the metal by the chloride, nitrate, acetate and sulphate. This implies the coordination of the anions to the metal ion centers. The analytical data of the isolated polymer complexes are listed in Table 1. Further, confirmation of the proposed structures of the chelates of HL with metal salts was done by using different physico-chemical methods shown below. The formation of these complexes may proposed according to the following equation:

$$\mathrm{CuSO_4 + HL \rightarrow [Cu(HL)(SO_4)]_{\mathit{n}}} \qquad (1)$$

$$\mathrm{CuX_2 + HL \rightarrow [Cu(L)X]_{\mathit{n}}} \qquad \mathrm{X = OAcorNO_3} \qquad (2)$$

$$\mathrm{MCl_2 + HL \rightarrow [M(L)Cl{\cdot}OH_2]_{\mathit{n}}} \qquad \mathrm{M = Cu(II)\,or\,Cd(II)} \qquad (3)$$

$$\mathrm{MX_2 + HL \rightarrow \{[M(HL)n'X_2]Y_2\}_n}$$

$$M = \mathrm{Pd(II),\ X = Cl\,and/or\,Br;\ Y = nil;}\ n' = 1 \qquad (4)$$

$$\mathrm{MX_2 + HL \rightarrow \{[M(HL)n'X_2]Y_2\}_n}$$

$$M = \mathrm{Pd(II),\ X = nil\,and/or\,Br;\ Y = Cl;}\ n' = 2 \qquad (5)$$

$$\mathrm{MX_2 + HL \rightarrow \{[M(HL)n'X_2]Y_2\}_n}$$

$$M = \mathrm{Pt(II),\ X = Cl;\ Y = nil;}\ n' = 1 \qquad (6)$$

$$\mathrm{PdCl_2 + HL \rightarrow [Pd(L)_2]_{\mathit{n}}} \qquad (7)$$

In order to elucidate the type of homopolymer coordination and related geometry in the polymer complexes, NMR, IR and spectra were recorded.

Copper acetate, copper nitrate, palladium chloride and cadmium chloride under the same condition, give a polymer complexes containing the homopolymer as a monoanion, having lost one proton from C=NH group while copper sulphate, palladium chloride, platinum chloride and palladium bromide form polymer complexes in which the homopolymer is neutral. This occurs in the presence of the sulphate ion as proton acceptor. This indicates that the polymer complexes composition is dependent on the nature and strength of the metal–homopolymer bond.

The ^{1}H NMR spectra of HL and all the diamagnetic polymer complexes showed the same characteristic proton signals for the ligand (HL). The chemical shifts of the different types of protons of HL and diamagnetic **5**, **6** and **8** polymer complex are listed in Table 2. The signal characteristic for –C=(NH) group in polymer complexes **5** and **6** disappeared in the spectra of the isolated polymeric complexes indicating coordination via deprotonated NH atom. Also, the signal characteristic for NH_2 group shifted to lower frequencies due to the complexation. Also, the ^{1}H NMR spectrum of the complex **5** showed a broad signal at 3.54 ppm, which is attributed to the presence of coordinated water molecules. In case of **8**, the signal characteristic for –C=NH(NH_2) group shifted to lower frequency due to the coordination via NH atom.

IR spectra of the polymer complexes suggest that the formation of a stable six-membered ring system with the central Cu(II)/Cd(II) ion having O–NH/O–N donor function taking one of oxygen of O=S=O and nitrogen of the –C=NH(NH_2) and the imino nitrogen (NH/N) of the guanidine residue as bonding sites is the most probable proposition; this substantiated through the present IR spectral studies recorded down to 200 cm^{-1}. The IR spectrum of the homopolymer showed three medium broad bands at 3165, 3280 and 3440 cm^{-1} which consist of overlapping stretching vibration assigned to υ_s(N–H) and υ_{as}(NH and NH_2 groups). The bandwidth further indicates that the NH_2 group is involved in intramolecular hydrogen bonding [24]. Also, the IR spectrum of uncomplexed polymer (HL) shows absorption bands at 3350 and 1630 cm^{-1} due to NH and CO groups, respectively. These bands disappear when the homopolymer is dissolved in DMSO and four absorption bands have been observed at 1600, 1540, 1470 and 1415 cm^{-1} which are attributed to $\upsilon_{asym+sym}$(C=C) and υ(C=N) vibrations. The SO_2 group modes of the HL appear as a bands at 1315 cm^{-1} ($\upsilon_{asym}(SO_2)$) and 1036 cm^{-1} ($\upsilon_{sym}(SO_2)$), respectively.

In the polymer complexes, the asymmetric and symmetric modes are shifted to higher frequencies, at 1330 and 1085 cm^{-1} [25]. Also, the stretching vibration mode characteristic for υ(NH) of –C=(NH) (NH_2) moiety at 3175 cm^{-1} in HL was shifted to higher frequencies (~3195–3215 cm^{-1}) upon coordination to the transition metals [25] via deprotonated NH group, except compound **1**. The υ(C=N) stretching bands of the guanidine part of the ligand appearing around 1645 cm^{-1} [26] has been found to experience a negative shift of ≈8 cm^{-1} pointing to the probable participation of the imino nitrogen/nitrogen of the guanidine moiety of the ligand in complexes. New bands were found in the spectra of the polymer complexes in the regions 450–470 and 495–520 cm^{-1} which were assigned to υ(M–N) and (M–O) stretching vibrations, respectively [1–6,34]. These stretches were not present in the spectra of the ligand. The appearance of band in compounds **1** and **5** at ~800 and ~760 cm^{-1} attributed to coordinated water molecule. The uncoordinated homopolymer exhibits strong and weak bands at 3350, 3372, 1630, 410 and 390 cm^{-1}, respectively. These are assigned to the υ(NH), υ(NH), of the sulphonamide group and C–C out-of-plane vibration [27].

3.2.2. Bands due to anions

Additional, the IR spectra of the polymer complexes show the bands due to coordinated anions. Due to the acetate complex **2** shows the bands at 1430 and 1340 cm^{-1} corresponding to υ_{as}(OAc) and υ_s(OAc) stretching vibrations, respectively. The separation of these two vibrations (90 cm^{-1}) indicates the bidentate coordination of acetate anion [28]. In the spectrum of polymer complex **3**, three additional bands which are not present in the spectrum of free ligand, were observed. Of these, the band around 1028 cm^{-1} is assigned to the υ_2 mode of the nitrate group. The bands in 1463 and 1258 cm^{-1}, are the two split bands of υ_4 and υ_1, respectively, of the coordinated nitrate group. The magnitude of υ_4–υ_1 is about 200 cm^{-1} in the complex **3**, which indicates that the nitrate group is coordinated to the cupper(II) ion in a bidentate fashion [28]. The sulphato complex **4** shows the four bands at 1211, 1131, 1028, and 965 cm^{-1} due to υ_3 and υ_1 stretching vibrations of sulphate anion which indicates that the sulphate anion coordinates in bridging bidentate manner [29]. The chloro complexes **1** and **5** shows the band at ≈332 cm^{-1} due to υ(M–Cl) and also display bands due to coordinated water molecules. The bands in the range of 645–852 and 612–635 cm^{-1} appeared in the spectra of these polymer complexes which may be assigned to pr(H_2O) and ρw(H_2O) [27].

Table 3
Magnetic moment and electronic spectral data of the Cu(II) polymer complexes (for molecular structures see Fig. 2).

Species[a]	μ_{eff}. (B.M.)[b]	Band position (cm^{-1})	Assignments	Geometry	Ref.
1	1.90	10,150, 18,620, 27,368, 38,595	$d_{x2-y2} \rightarrow d_{z2}$ (υ_1) $\rightarrow d_{xy}$ (υ_2) $\rightarrow d_{xy}$, d_{yz}(υ_3) CT	Square planar	[32,42]
2	1.85	10,530, 18,620, 26,170, 38,015	-do-		[32,42]
3	1.92	10,330, 18,618, 26,310, 37,585	-do-		[32,42]
4	1.82	10,512, 18,618, 27,240, 36,300	-do-		[32,42]

[a] See footnote in Table 1.
[b] The order of $\mu_{eff.}$ is 3 > 1 > 2 > 4. Per metal. Measured at room temperature.

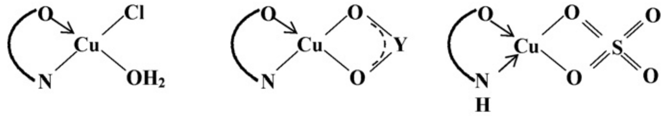
The far IR data of the polymer complexes give an insight into the structure and bonding in the solid state. The υ(M–Cl)$_L$ (M = Pd, Pt) modes are assigned to strong intensity bands in the region 350–340 cm^{-1} for **6** and **10**. They shift to the 240–225 cm^{-1} region in **7**. The appearance of these bands is consistent with the formulation [M(HL)X$_2$]. The presence of two υ(M–X)$_L$ vibrations in each far IR spectrum confirms the cis-structures of the square planar complexes **6**, **7** and **10** [30]. In polymer complexes of stoichiometry [Pd(HL)X$_2$], the monomer coordinates to the metal ion via the nitrogen atom [of imino nitrogen (NH) of guanidine group] and the oxygen [of O=S=O group]. This is further supported by the appearance of IR active bands at 280–285 [υ(Pd–O)] and 475–485 cm^{-1} [υ(Pd–N)] vibrational modes [30].

3.3. *Magnetochemical and ligand field spectral studies of Cu^{2+} polymer complexes*

The electronic spectra of the polymer complexes (Table 3) are in good agreement with other spectra and the literatures [4,5,10]. The room temperature magnetic moments of copper(II) polymer complexes fail in range 1.82–1.92 B.M. which are typical for square planar (D$_{4h}$) and tetrahedrally distorted (D$_{2h}$) mononuclear copper(II) complexes and did not indicate any anti-ferromagnetic coupling of spines at this temperature. The relatively higher 1.92 B.M. value observed for **3**, seem to suggest the relatively high tetrahedral distortion from square planar geometry for these complexes than others in polycrystalline state. On the other hand, the B.M. data for **1**, **2**, and **4** fall in the 1.82–1.90 B.M. range and are well consistent with a square planar geometry (D$_{4h}$) around the copper centers (Table 3). The electronic spectra of the polymer complexes show the absorption bands corresponding to and [$^2B_{1g} \rightarrow {}^2Eg$]($\Delta_1$), [$^2B_{1g} \rightarrow {}^2B_{2g}$]($\Delta_2$) and [$^2B_{1g} \rightarrow {}^2A_{1g}$], transitions, respectively [31]. The polymer complexes also display the high-energy charge transfer. These transition commensurate the square planar geometry and D$_{4h}$ symmetry for the complexes [32] (Table 3).

3.4. *Electron spin resonance*

To obtain further information about the stereochemistry and the site of the ligand bonding and to determine the magnetic interaction in the metal polymer complexes, ESR spectra of the complexes were recorded in the solid state. The spin Hamiltonian parameters of the complexes were calculated and summarized in Table 4.



(1) Y= NO (2), CCH$_3$ (3) (4)

Fig. 2. Structure of polymer complexes. (1) [Cu(L)Cl·OH$_2$], (2) [Cu(L)O$_2$NO], (3) [Cu(L)OAc] and (4) [Cu(HL)O$_2$SO$_2$].

The ESR spectra of the copper polymer complexes have been recorded at room temperature (Table 4) which exhibit an axially symmetric *g*-tensor parameters with $g_{||} > g_{\perp} > g_e(2.0023)$, was observed for all the complexes, corresponding to the presence of unpaired electron most likely reside in the d_{x2-y2} (or less likely a d_{xy}) ground state [33] which is consistent with the proposed planar stereochemistry [34]. The *g* values are given in Table 4. The deviation of *g* value from the free electron value (2.0023) may be due to angular momentum contribution in the polymer complexes. In all the polymer complexes, the $g_{||}$ values are less than 2.3, which shows that the complexes are largely covalent. Further, the values are consistent with Cu–N and Cu–O bonded copper complexes. The $g_{||}$ values are found in the order **4** > **1** ≈ **3** > **2**. On the basis of these values, it is clear that compound **2** is a strong ligand and create strong ligand field. Our results are in agreement with the respective positions of the anions as given in the spectrochemical series [32]. The average *g* values (g_{iso}) are calculated, and give values in the range 2.086–2.112. The ESR data are reported in Table 4. The g_{iso} values for the polymer complexes studied follow the order **4** > **1** > **3** > **2**.

Kivelson and Neiman [35] have shown that $g_{||}$ is a parameter sensitive function for indicate covalence. The $g_{||}$ values for all the Cu(II) polymer complexes are less than 2.3 is an indication of significant covalent bonding in these polymer complexes (Cu–L). In axial symmetry the *g* values are related to the *G*-factor by the expression, $G = g_{||} - 2.0023/g_{\perp} - 2.0023 = 4$, which measures the exchange interaction between copper centers in the solid. According to Hathaway [36], 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 calculated *G* values for copper complexes are greater than 4, suggesting the absence of exchange coupling between copper(II) centers in the solid state [37]. The *G* values follow the order **3** > **2** > **4** > **1**. This is consistent with the order of the strength of metal–anion interactions. Our results are also in agreement with the respective positions of these anions as given in the spectrochemical series [38].

3.4.1. *Bonding parameters and orbital reduction parameters*

The ESR parameters $g_{||}$, $g_{\perp}$, g_{iso}, $A_{||}$ and $A_{\perp}$ and the energies of the d–d transition are used to calculate the bonding parameters α^2 and β^2, which are the measure of covalency of the in-plan σ-bonding and covalency of the in-plane π-bonding and out-of-plane

Table 4
ESR parameters of complexes.

Complex[a]	$g_{\|\|}$	$g_{\perp}$	g_{iso}	G	$A_{\|\|}$[a]	$A_{\perp}$[b]	A_{iso}[b]	α^2
1	2.219	2.054	2.11	4.17	117.8	66.18	83.39	0.61
2	2.180	2.039	2.09	4.84	113.6	57.26	76.04	0.55
3	2.218	2.043	2.10	5.30	99.3	62.03	74.45	0.61
4	2.225	2.056	2.11	4.24	114.9	65.71	82.11	0.61

[a] See footnote in Table 1.
[b] A value is presented in 10^{-4} cm^{-1}.

Table 5
Bonding parameters and orbital reduction of complexes.

Complex[a]	$K_{\|}^2$	$K_{\perp}^2$	K^2	$\beta_1{}^2$	β^2
1	0.60	0.85	0.77	0.98	1.39
2	0.49	0.58	0.55	0.89	1.05
3	0.60	0.65	0.63	0.96	1.03
4	0.59	0.88	0.78	0.96	1.27

[a] See footnote in Table 1.

π-bonding, respectively and orbital reduction factor K^2 (Table 5). The value of α^2 and β^2 was estimated from the following expression [39] where $\alpha^2 = 1.0$ indicates complete ionic character, where $\alpha^2 = 0.5$ denotes 100% covalent bonding, with the assumption of negligibly small values of the overlap integral. The in-plane covalency parameter $\alpha^2_{(\mathrm{Cu})}$ was calculated by following the relation:

$$\alpha^2_{(\mathrm{Cu})} = (A_{\|} - 0.036) + (g_{\|} - 2.0023) + \left(\frac{3}{7}\right)(g_{\perp} - 2.0023) + 0.04 \tag{8}$$

The calculated value (Table 5) accounts for the fraction of the unpaired electron density on copper(II) ion and hence the covalent character of these polymer complexes. The in-plane and out-of-plane π-bonding parameters β_1 and β are obtained from the expression [40]:

$$\alpha^2\beta_1^2 = (g_{\|} - 2.0023)\Delta_2/8\lambda_o \tag{9}$$

$$\alpha^2\beta^2 = (g_{\perp} - 2.0023)\Delta_1/2\lambda_o. \tag{10}$$

The orbital reduction factors $k_{\|}$ and $k_{\perp}$, which are the measure of the spin–orbit coupling constant ($\lambda_o = -823\ \mathrm{cm}^{-1}$) for free copper(II) ion in these complexes are obtained by using the following expression [13,41] and are shown in Table 5.

$$K_{\|}^2 = (g_{\|} - 2.0023)\Delta_2/8\lambda_o \tag{11}$$

$$K_{\perp}^2 = (g_{\perp} - 2.0023)\Delta_1/2\lambda_o \tag{12}$$

$$K^2 = \frac{1}{3}\left[K_{\|}^2 + K_{\perp}^2\right] \tag{13}$$

The $K_{\|}$ and $K_{\perp}$ parameters have been related by variously as purely orbital coefficient and are related by $K_{\|} = \mathrm{ca.}\ \alpha, \beta_1$, and $K_{\perp} = \mathrm{ca.}\ \alpha, \beta$, where α, β_1, and β are the coefficients of $d_{x_2-y_2} \rightarrow d_{xy}$ and d_{xz}, d_{yz} orbitals in MO's to which they contribute; thus α measure σ-bonding, β_1 and β are in-plane π-bonding and out-of-plane π-bonding coefficient, respectively. By assuming $\beta_1 = 1$ (since the ligand has no lone pairs available on N atom for bonding with (d_{xy}). The values of α and β are calculated for copper(II) polymer complexes and are reported in Tables 4 and 5. The estimated α-coefficient for all complexes indicates fairly covalent σ-bonding, whereas β coefficient suggests very little bonding of d_{xz}, d_{yz} with orbital of axial anion in these polymer complexes. According to Hathaway [36], $K_{\|} \approx K_{\perp} \approx 0.77$ for pure in-plane σ-bonding and $K_{\|} < K_{\perp}$ for in-plane π-bonding, while for out-of-plane π-bonding $K_{\|} > K_{\perp}$. In all the Cu(II) polymer complexes, it is observed that $K_{\|} < K_{\perp}$ which is a good evidence for the assumed $^2B_1$ ground state for the polymer complexes and also, indicates the presence of significant in-plane π-bonding. The values of bonding parameters α and $\beta_1 < 1.0$ indicate significant in-plane σ-bonding and in-plane π-bonding.

3.5. Geometry of the Pd^{2+}–Pt^{2+} polymer complexes

Table 6
Electronic spectral data and ligand field parameters of the complexes.

Complex[a,b]	Spectral bands (obs.) (cm^{-1})	υ_2/υ_1	Δ_1	Δ_2	Δ_3
6	18,620 27,400, 30,675 34,250, 36,760	1.47	20,720	6680	6950
7	18,640 27,430, 30,700 34,260, 36,750	1.47	20,740	6690	6920
8	19,150 27,520, 30,700 34,260, 36,850	1.44	21,250	6270	6855
9	20,230 27,600, 30,700 34,260, 37,050	1.36	22,330	5270	6775
10	19,550 27,400, 29,120 34,360, 36,360	1.40	21,650	5750	6975
11	19,900 27,800, 30,700 34,800, 37,100	1.40	22,000	5800	6575

[a] See footnote in Table 1.
[b] Diamagnetic.

The magnetic moment studies that all the polymer complexes of Pd(II)/Pt(II) are diamagnetic with spin-paired d^8 system. The electronic spectra of palladium(II) and platinum(II) polymer complexes (Table 6) three spin-allowed d–d transition from three lower lying d-levels to the empty d_{x2-y2} orbital corresponding to $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_g$ d–d transitions [30] are observed, respectively. Moreover in the polymer complexes, the high intensity charge transfer absorption bands are also corresponding to $^1A_{1g} \rightarrow {}^1A_{2u}$ and $^1A_{1g} \rightarrow {}^1E_u$ transitions, respectively. The three orbital parameters Δ_1, Δ_2 and Δ_3, were calculated using a value of $F_2 = 10$ and $F_4 = 600\ \mathrm{cm}^{-1}$ for a Slater Condon interelectronic repulsion [30]. The υ_2/υ_1 were also calculated and are in close agreement with data reported earlier for square planar complexes.

4. Concluding remarks

A series of Cu(II)/Pd(II)/Pt(II) polymer complexes with ligand (HL) have been prepared and fully characterized. The characteristics of the prepared polymer complexes are discussed. The coordination behaviour of the anions is also discussed on the basis of IR and molar conductance measurements. It was observed that coordination of anions with metal was effected by number of coordination sites, which was further confirmed by molar conductance.

The geometries of the polymer complexes are also effected by number of coordination sites and ligand (HL) has two coordination sites and formed different geometrical complexes with different anions. Polymer complexes of ligand are compared and it observes that these complexes are two coordinated in metal(II) anions complexes. It proved direct effect of coordination sites on complexation (Table 1).

(1) The purpose for the synthesizing polymeric complexes was as a model for the active site of the enjume and also a good model for the physical properties of the protein active sites.
(2) It is also clear has a high affinity for chelation with metal ions under study accordance to the increasing charge density of the metal ion and hence to the increasing of their coordination affinities.
(3) The formulae $[Cu(HL)O_2SO_2]_n$, $[Cu(L)X]_n$ (X = OAc, O_2NO), $[M(L)Cl{\cdot}OH_2]_n$ (M = Cu or Cd), $[Pd(HL)X_2]$, $[Pd(HL)_2](X_2)$ (X = Cl or Br), $[Pt(HL)Cl_2]$ and $[Pd(L)_2]$ has been proposed on the basis of analytical and various physico-chemical data. The HL is bonded to the metal ion in bidentate fashion through oxygen (of O=S=O group) and nitrogen atom [of imino nitrogen (NH/N) of the guanidine group] as inferred from IR and ^{1}H NMR spectra.

(4) These results also confirm the non-reactivity of the –CONH– group in coordination (see Fig. 1).

(5) The calculations show that HL studied exist in a molecular form with the intramolecular O–HN form.

(6) The present study demonstrates perfectly an application of IR spectra and molecular modeling in revealing not only the multiple inter/intramolecular of π–π stacking among the aromatic groups as well as the hydrophobic interactions among hydrogen bonding species between NH moieties involving in a series of novel salpha drug derivatives.

(7) It is also clear has a high affinity for chelation with metal ions under study accordance to the increasing charge density of the metal ion and hence to the increasing of their coordination affinities.

Further studies with the title ligand, using different metal ions, are in progress and will be published in course.

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