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Polymer complexes. LIV. Structural and spectral studies of supramolecular coordination polymers built from Ni(II), Fe(II) and Pd(II) with sulphadrug

A.Z. El-Sonbati [a,*], A.A.M. Belal [b], M.A. Diab [a], R.H. Mohamed [a]

[a] Chemistry Department, Faculty of Science, (Demiatta), Mansoura University, Egypt
[b] Chemistry Department, Faculty of Science, Port Said University, Egypt

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ABSTRACT

Polymer complexes of *p*-acrylamidyl sulphaguanidine (HL) with Ni(II), Fe(II) and Pd(II) salts have been prepared. The structures of the polymer complexes were elucidated using elemental analysis, ^{1}H NMR, UV–Vis, IR spectroscopies, magnetic moment, molar conductance and thermal analysis. The polymer complexes were isolated in 1:1 and 1:2 (M:L) ratios. The solid monocomplexes (1:1) (M:L) were isolated in the general formula $[Fe(HL)O_2SO_2(OH_2)_2]$. The biscomplexes (1:2) (M:L) solid chelates found to have the general formula $[Ni(HL)_2X_2]_n$ ($X = Cl^-, Br^-, I^-, NO_3^-, NCS^-$), $[Fe(HL)(en)(OSO_3)(OH_2)]_n$ and $[Ni(HL)_2(Py)_2]_nX_2$, while $\{[Pd(L)X]_2\}_n$ (1:1) ($X = Cl^-$ or Br^-). In all the polymer complexes the ligand and anions were found to be coordinated to the Ni(II) and Fe(II) ions. The bidentate nature of the ligand is evident from IR spectra. The magnetic and spectroscopic data indicate a octahedral geometry for complexes. The thermal behaviour of these chelates shows that the hydrated complexes loss water molecules of hydration in the first step followed immediately by decomposition of the anions and ligand molecules in the subsequent steps.

1. Introduction

Sulphadrugs have attracted special attention from their therapeutic importance as they were used against a wide spectrum of bacterial aliments [1]. Some sulphadrugs have been used in the treatment of cancer, malaria, leprosy and tuberculosis [2,3]. Also, the importance of metal ions in biological system is well known [4]. The coordination chemistry of sulphadrug and its derivatives have attracted much attention by virtue of their applicability as potential ligands for a large number of metal ions [5]. Sulphadrug ligands are widespread among coordination compounds and are important components of biological transition metal complexes [6]. The metal chelates thus produced have wide application in the chemistry, as analytical reagents for determination of metals and in biological uses [7]. Sulphadrug complexes are considered to be among the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety [8–13].

As a part of our systematic studies of the coordination chemistry of the early actinides and transition elements, we recently published several papers on the structural chemistry of sulphadrug polymer complexes of Cu (II), Ni (II) and uranium (VI) [14,15]. A number of studies have been undertaken with both ligand system and the formation of chelates with various compositions has been suggested on the basis of spectroscopic data [11–22].

In continuation to our work on sulphadrugs, this article involves the synthesis of polymer complexes of *p*-acrylamidyl sulphaguanidine with Ni(II), Fe(II) and Pb(II) salts. The solid products were characterized by elemental analysis, IR, molar conductance, magnetic moments and reflectance spectra measurements.

2. Experimental

2.1. Materials

Sulphaguanidine and acryloyl chloride (AC) (Aldrich Chemical Co., Inc.) were used without further purification.

2,2′-Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co., Inc.) was purified by dissolving in hot ethanol and filtering [23]. The solution was left to cool. The pure material then being collected by filtration and dried.

$NiX_2 \cdot nH_2O$ ($X = Cl^-, Br^-, I^-$ and NO_3^-, $n = 3–6$) were dried in an oven at 80 °C for 2 h. The left-out products were kept in a vacuum desiccator over fused $CaCl_2$ for 48 h. Anhydrous Ni(II) salts were obtained as microcrystalline solid compounds.

2.2. Preparation of p-acrylamidyl sulphaguanidine (HL) monomer

HL monomer was prepared by the reaction of equimolar amounts of AC and sulphaguanidine in dry benzene until the

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* Corresponding author. Tel.: +20 60081581; fax: +20 502254000.
E-mail address: elsonbatisch@yahoo.com (A.Z. El-Sonbati).

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evolution of hydrogen chloride ceased. The IR spectrum of the monomer showed the presence of an NH absorption band at 3165 cm^{-1}. Microanalysis for $C_{10}H_{12}N_4O_3S$. Found C, 44.8; H, 4.0; N, 15.9; S, 11.5%. Cal. C, 44.6; H, 4.1; N, 15.6; S, 11.9%.

2.3. Preparation of poly (p-acrylamidyl sulphaguanidine) (PHL) homopolymer

PHL homopolymer was prepared by free radical initiation of HL using 0.1 w/v% AIBN as initiator and DMF as solvent for 6 h. The polymer product was precipitated by pouring in distilled water and dried in a vacuum oven for several days at 40 °C. The PHL homopolymer has been characterized by IR, ^1H NMR. The inherent viscosity ($\eta_{inh} = \ln_{r/c}$, C = 0.5 g/dl), in a Desreux–Bishoff suspended level viscometer at 30 ± 0.01 °C, using chloroform as solvent is $\eta_{inh} = 1.23$.

2.4. Preparation of the polymer complexes

*2.4.1. Ni(II) polymer complexes **1–4***

Method A: The Ni(II) chelates with monomer (HL) was prepared by refluxing anhydrous Ni(II) salt (0.001 mol) with the corresponding ligand (0.002 mol) in 20 ml DMF as a solvent, and 0.1% (w/v) AIBN as initiator. The resulting mixture was heated at reflux for 8 h. The hot solution was precipitated by pouring in a large excesses of distilled water containing dilute hydrochloric acid, to remove the metal salts that were incorporated into the polymer complexes. The polymer complexes (**1**–**4**, see Table 1) were filtered, washed with water, and dried in a vacuum oven at 40 °C for several days.

*2.4.2. Ni(II) polymer complexes **1–4***

Method B: The products **1**–**4** were obtained by another method according to the following procedure: A solution of Ni(II) salts (0.001 mol) in dry alcohol (30 ml); monomer (HL) (0.001 or 0.002 mol) and 0.1% w/v AIBN as initiator were mixed and stirred for 4 h at room temperature. The reaction mixture was heated (80 °C) under reflux for 16–18 h under anhydrous conditions with continuous stirring. The reaction mixture was cooled to room temperature. The product, in each case, was filtered off, then washed several times with dry alcohol and dry diethyl ether and finally dried in a desiccator over fused $CaCl_2$.

*2.4.3. Ni(II) thiocyanate polymer complex **5***

Method C: Ni(II) thiocyanate polymer complex was obtained by method B, refluxing the corresponding chloro complex with potassium thiocyanate in dry ethanol medium for 20 min and filtering off the precipitated potassium chloride. The solution was concentrated on water bath followed by cooling at room temperature. The product, was filtered off, then washed several times with alcohol and dry diethyl ether and finally dried in a desiccator over fused $CaCl_2$.

*2.4.4. Fe(II) polymer complex **6***

Method D: Equimolar amounts of monomer (HL) and $FeSO_4{\cdot}7H_2O$ were dissolved in 50 ml DMF with 0.1% (w/v) AIBN as initiator. The reaction mixture was stirring for 2 h at room temperature, and then heated under reflux for about 8 h under dry condition. The hot solution was precipitated by pouring in a large excesses of distilled water containing dilute hydrochloric acid, to remove the metal salts that were incorporated into the polymer complexes. The polymer complex (**6**, see Table 1) was filtered, washed with water, and dried in a vacuum oven at 40 °C for several days.

*2.4.5. Nickel/Iron mixed ligand polymer complexes **7–9***

Method E: The product (**7**–**9**) were obtained by reacting pyridine (Py) and/or ethylenediamine (en) with the calculated amount of trans-$[Ni(HL)_2Cl_2]$($X = Cl^-$ or Br^-) according to the following procedure: A solution of Py(0.5 ml)/en (2 ml) in 5 ml of DMF was added to a stirred suspension of (**1**, **2** and/or **6**) in 20 ml of the same solvent. After 24 h, Et_2O (5 ml) was added at room temperature

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
$[Ni(HL)_2Cl_2]_n$	A, B	36.3	3.6	17.1	9.4/(9.6)	1:2
1		(36.1)	(3.6)	(16.8)	10.9/(10.7)	
$[Ni(HL)_2Br_2]_n$	A, B	31.7	3.0	14.5	8.1/(8.5)	1:2
2		(31.8)	(3.2)	(14.8)	21.5/(21.2)	
$[Ni(HL)_2I_2]_n$	A, B	28.0	2.8	13.4	7.7/7.5	1:2
3		(28.2)	(2.8)	(13.1)	30.5/(30.3)	
$[Ni(HL)_2(ONO_2)_2]_n$	A, B	33.5	3.2	11.4	8.7/8.9	1:2
4		(33.4)	(3.3)	(11.7)		
$[Ni(HL)_2(SCN)_2]_n$	C, B	37.3	3.3	19.4	13.3	1:2
5		(37.2)	(3.4)	(19.7)	(13.5)	
$[Fe(HL)O_2SO_2(OH_2)_2]_n$	D	28.0	3.6	12.6	14.5	1:1
6		(27.8)	(3.7)	(13.0)	(14.8)	
$\{[Ni(HL)_2(Py)_2]Cl_2\}_n$	E	43.6	4.0	17.2	8.0	1:2:2
7		(43.7)	(4.1)	(17.0)	(7.8)	
$\{[Ni(HL)_2(Py)_2]Br_2\}_n$	E	39.5	3.6	10.5	7.3	1:2:2
8		(39.4)	(3.7)	(15.4)	(7.0)	
$[Fe(HL)(en)OSO_3{\cdot}OH_2]_n$	E	28.6	4.4	16.8	12.9	1:1:1
9		(28.5)	(4.4)	(16.6)	(12.7)	
$\{[Pd(L)Cl]_2\}_n$	F	29.4	2.8	13.9	8.0/(7.8)	1:1
10		(29.4)	(2.8)	(13.7)	8.9/(8.7)	
$\{[Pd(L)Br]_2\}_n$	F	26.6	2.4	12.6	7.3/(7.1)	1:1
11		(26.5)	(2.4)	(12.4)	7.5/(17.7)	

[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.

and the resulting mixed polymer complexes (**7**–**9**) were isolated, filtered off and washed with EtOH and dried in a vacuum oven at 40 °C for several days.

*2.4.6. Pd(II) polymer complexes **10**, **11***

Method F: An ethanolic solution of 0.01 mol of PdX_2 ($X = Cl^-$ or Br^-) was mixed with the appropriate weight of the corresponding ligand (HL, monomer) in ethanol (25–40 ml) and 0.1 w/v AIBN as initiator. The reaction mixture was boiled with stirring until the corresponding solid complex separated. On cooling the crystalline product formed was filtered off, washed several times with dry ethanol and dry diethyl ether and finally dried in a desiccator over fused $CaCl_2$.

2.5. 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 [20–22]. 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 Nujol 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 [24] and Pascal's constants. Magnetic moments were calculated using the equation, $\mu_{eff.} = 2.84\ [T\chi_M^{coor}]^{1/2}$. 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 [20,21]. The conductance measurement was achieved using Sargent Welch scientific Co., Skokie, IL, USA.

3. Results and discussion

3.1. General

The reaction of ligand (HL, monomer) with different nickel (II) salts, iron sulphate and the reaction of the isolated polymer complexes with pyridine/en (**7**,**8**/**9**) as described in Section 2 are shown in Table 1. All the polymer complexes are coloured and air stable. They are soluble in solvents like DMF and DMSO but insoluble in common organic solvents. The composition, coordination mode and geometry of the polymer complexes were established on the basis of spectral analyses, thermal analysis, conductivity measurements and magnetic properties and are discussed in detail in the following sections.

3.2. Molar conductance of the polymer complexes

The molar conductance of 10^{-3} M of solutions of the polymer complexes in DMSO was calculated as 25 ± 2 °C. It was concluded from the results that Ni(II) chelates $\{[Ni(HL)_2(Py)_2]X_2\}_n$ [X = Cl (**7**) or Br (**8**)] were found to have molar conductance values of 205 and 190 $\Omega^{-1}\ mol^{-1}\ cm^2$ of HL, respectively, indicating the ionic nature of these polymer complexes. It, also, indicated the non-bonding of chloride and bromide anions to the Ni(II) ions. So, the Ni(II) chelates were considered 1:2 electrolytes with HL ligand [14]. On the other hand, the molar conductivity values of Ni(II)(**1**–**5**), Fe(II)(**6** + **9**) and Pd(II)(**10** + **11**) chelates with HL ligand under investigation were found to have molar conductance values in the range from 3.95 to 12.95 $\Omega^{-1}\ mol^{-1}\ cm^2$ which indicated the non-ionic nature of these polymer complexes and they were considered as non-electrolytes. This is in accordance with the fact that conductivity values for a non-electrolyte are below 50 $\Omega^{-1}\ mol^{-1}\ cm^2$ in DMSO solution [15,16]. Hence the sulphate in iron(II) and chloride/bromide in palladium(II) polymer complexes are coordination sphere. In nickel(II) polymer complexes two (chlorides, bromides, iodides, nitrates, thiocyanates) are in coordination sphere.

3.3. Characterization of the monomer (HL)

3.3.1. HL ligand

HL monomer used in this study is elucidated by different tools as, the elemental analysis, which indicated that the ligand has the molecular formula $C_{10}H_{12}N_4O_3S$ and IR spectrum supported the structure in Fig. 1. ^1H NMR spectrum is the final confirming tool for the ligand structure and displayed peaks for $C{=}NHNH_2$, SO_2NH and —C=NH. ^1H NMR spectrum of HL [δ(DMSO-d_6] 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 [25,26]. 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 HL monomer showed the expected peaks and pattern of the vinyl group ($CH_2{=}CH$), 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 while a triplet at δ 1.86 ppm (t, *J* = 7 Hz) and a doublet at 1.80 ppm (d,

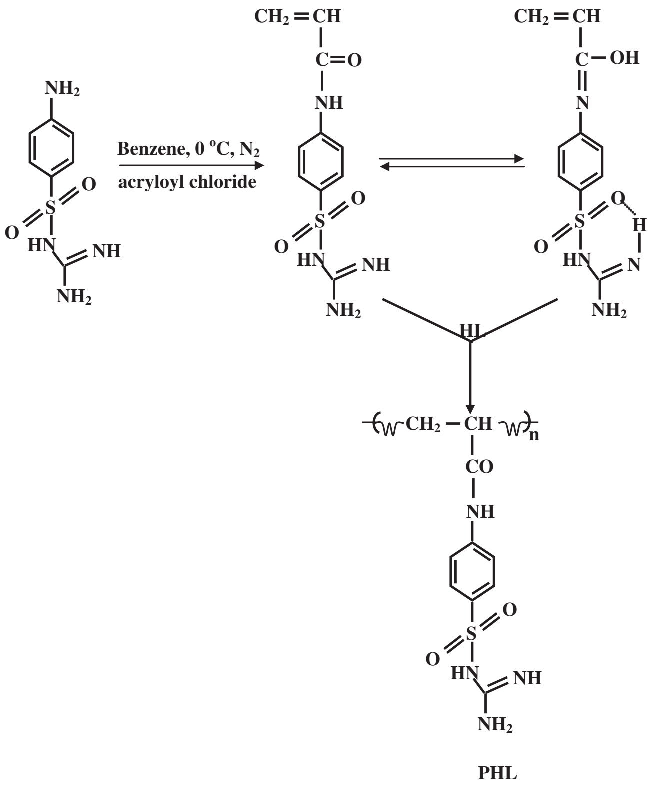


Fig. 1. Structure of the monomer (HL) and homopolymer (PHL).

Table 2
Characteristic ^{1}H NMR spectra for HL, PHL and Pd(II) complex (ppm vs. TMS).[a]

Compound	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, $-C{=}NH$
	6.25	Vinyl CH ($CH_2{=}CH$)
	5.12	Vinyl CH_2 ($CH_2{=}CH$)
PHL	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, $-C{=}NH$
$\{[PdCl\cdot L]_2\}_n$	7.22	d, 4H, ArH's
10	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

[a] The excellent agreement experimental data supports the assignment suggested in the present work.

J = 7 Hz) appeared, indicating that the polymerization of HL monomer occurs on the vinyl group [21,27]. It is worth noting that the rest of the proton spectrum of the monomer and polymer remain almost without change. The ^{1}H NMR spectrum of the ligand (HL, monomer) showed characteristic protons, which are listed in Table 2, and the proposed structure for the ligand is shown in Fig. 1.

In the present work, the synthesis of polymer complexes with homopolymer sulphadrug was investigated. The influence of the position of the O=S=O and —C=NH groups of the side residue of the monomer, on their stereochemistry and chain flexibility was explored. For this purpose, different techniques such as elemental analysis, ^{1}H NMR, UV–Vis, IR spectroscopies, magnetic moment, molar conductance and thermal analysis were adopted.

3.4. Characterization of polymer complexes

3.4.1. Metal polymeric complexes

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 no electrolytes except complexes **7** and **8** [28]. This can be account for by the satisfaction of the bivalency of the metal by the chloride, bromide, iodide, nitrate, thiocyanate, 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 using different physico-chemical methods shows below. The formation of these complexes may proceed according to the following equation

$$NiX_2 + HL \rightarrow [Ni(HL)_2X_2]_n,$$

where X = Cl^- (**1**), Br^- (**2**), I^- (**3**), NO_3^- (**4**), or SCN^- (**5**).

$$FeSO_4 + HL \rightarrow [Fe(HL)(SO_4)(OH_2)_2]_n \quad (\mathbf{6})$$

$$[Ni(HL)_2X_2]_n + Py \rightarrow [Ni(HL)_2(Py)_2]_nX_2,$$

where X = Cl^- (**7**), Br^- (**8**).

$$[Fe(HL)(SO_4)(OH_2)_2]_n + en \rightarrow [Fe(HL)(en)(SO)_4)(OH)_2]_n \quad (\mathbf{9})$$

$$PdX_2 + HL \rightarrow [[Pd(LX)]_2]_n,$$

where X = Cl^- (**10**), Br^- (**11**).

Palladium chloride under the same condition, give a polymer complex containing the homopolymer as a monoanion, having lost one proton from C=NH group, while nickel(II) salts and iron(II) sulphat form polymer complexes in which the homopolymer is neutral. 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 Pd-diamagnetic complex (**10**) was recorded in dimethylsulphoxide (DMSO-d$_6$) using trimethylsilane (TMS) as internal standard. The chemical shifts of the different types of protons of HL and diamagnetic Pd-complex are listed in Table 2. The signal characteristic for —C= (NH) group disappeared in the spectrum of the isolated polymeric complex indicating coordination *via* deprotonated —C=NH atom. Also, the signal characteristic for —NH$_2$ group shifted to lower frequencies due to the complexation. Construction of molecular models suggest that the formation of a stable six-membered ring system with the central metal 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/or 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}.

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 band width further indicates that the NH$_2$ group is involved in intramolecular hydrogen bonding [29]. Also, the IR spectrum of uncomplexed polymer shows absorption bands at 3350 cm^{-1} and 1630 cm^{-1} due to —NH and CO groups respectively, the absorption singles 3015 cm^{-1} shows —CH of benzene ring stretching frequency, the absorption signals at 2980 and 2935 shows —CH=CH— stretching frequency. The ligand shows C=N and C=C stretching frequency bands. All these results prove that the ligand have been successfully synthesized. The SO$_2$ group modes of the HL appear as a bands at 1315 cm^{-1} (υ_{asym}(SO$_2$)) and 1036 cm^{-1} (υ_{sym}(SO$_2$)), respectively.

In the polymer complexes, the asymmetric and symmetric modes are shifted to higher frequencies, at 1330 cm^{-1} and 1085 cm^{-1} [30]. 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 *via* deprotonated NH group [30]. The υ(C=N) stretching bands of the guanidine part of the ligand appearing around 1645 cm^{-1} 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 [31]. The spectrum of ethylenediamine containing complex [Fe(HL)(en)(SO$_4$)(H$_2$O)] (**9**) display additional splitted broad band at ~3230 cm^{-1} (at lower wavenumber relative to that of free ethylenediamine) characteristic of coordinated —NH$_2$ to the iron(II) ion.

New bands were found in the spectra of the polymer complexes in the regions 450–470 cm^{-1} and 495–520 cm^{-1} which were assigned to υ(M—N) and υ(M—O) stretching vibrations, respectively [9–14,31]. Also, in the **7** and **8** complexes a new band appears in the region 1612–1618 cm^{-1} attributable to coordinated pyridine [18]. Free pyridine shows a strong band at 1585 cm^{-1}. Thus, the nitrogen of the pyridine is coordinated to metal ion. These stretches were not present in the spectrum of the ligand.

The presence of water molecules in the above mentioned complexes [(**6**) and (**9**)] is assigned by the appearance of a broad band within the range 3440–3300 cm^{-1}, which is attributed to ν(OH$_2$) of the water molecules associated with the complex formation. Also, bending vibration of the water molecules; δ(OH$_2$), is found in the range 960–925 cm^{-1}. The other bending vibration of the water molecules; δ(OH$_2$), is usually around 1600 cm^{-1} which always interferes with the skeleton vibration of the benzene ring (C═C vibration).

3.4.2. Bands due to anions

In the IR spectrum of nitrato complex (**4**) three bands are appeared at ~1430, 1325 and 1018 cm^{-1}. The position of these bands suggests that both the nitrate groups are coordinated to the metal ion in a unidentate fashion ($\Delta\upsilon < 150\ cm^{-1}$) [32]. In the IR spectrum of Fe(II) sulphato complex (**6**) absorption bands are appeared at ~1105, ~1062 and ~1040 cm^{-1} suggesting bidentate behaviour of the sulphate ion but in the case of compound (**9**) absorption bands are appeared at ~1182, ~1022 and ~945 cm^{-1} suggesting unidentate behaviour of the sulphate ion [33]. Furthermore, the complex $[Fe(HL)SO_4(H_2O)_2]$ (**6**) and $[Fe(HL)(en)(SO_4)(H_2O)]$ (**9**) display bands, before and after heating at 160 °C for 4 h, confirming the presence of coordinating water molecules rather than water of crystallization [34]. The sulphato complex (**6**) 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 [35].

The IR spectra of $[Pd(L)X]_2$, [X = Cl (**10**), Br (**11**)] exhibit strong bands at 280 and 225 cm^{-1}, characteristic of bridging Cl and/or Br, respectively [18]. According to the electronic and IR spectral of these complexes the following structure could be assumed. This is supported by the presence of υPd—N and υPd—O.

Furthermore, υPd—Br/υPd—Cl lie in the range 0.67–0.70 cm^{-1}, supporting the assumed square-planar symmetry.

The diagnostic band frequencies of the other counter ions (X), ($X = Cl^-/Br^-$) υ(M—Cl) (285–290 cm^{-1}) and υ(M—Br) (260–265 cm^{-1}), indicate the coordinated nature of Cl^- and Br^- ions respectively. In the thiocyanato complex (**5**), the very strong band observed at 2084 cm^{-1} corresponds to υ(C═N). Bands observed at 778, 479 and 459 cm^{-1} are assigned to υ(C═S), δ(NCS) and υ(Ni—N), respectively. These facts indicate that thiocyanate group is N-coordinated to nickel [36].

3.4.3. Magnetic and electronic spectral studies

The room temperature magnetic moment values for all the Ni(II) polymer complexes are magnetically normal 6-coordinate complexes [$\mu_{eff} = 2.74–2.99$ B.M.]. The electronic spectrum of the free HL displays bands due to $\pi \to \pi^*$ and $n \to \pi^*$ transitions, respectively. In all polymer complexes, the first band is replaced by a new intense one assignable to $\sigma_{(N)} \to M^{2+}$ charge transfer transition [37]. The new band (shoulder) in the spectra of all polymer complexes is assigned to $\pi_{(O)} \to M^{2+}$ CT transition [37]. The band due to $n \to \pi^*$ transition is merged into a broad band in all polymer complexes centered that can be assigned as composite of the remaining $n \to \pi^*$ and $\sigma_{(O)} \to M^{2+}$ and other LMCT transitions.

Electronic spectral data indicate that most of the Ni(II) polymer complexes probably belong to O_h or D_{4h} or a group of lower symmetry [38] (Table 3]. The diffuse reflectance spectra of the polymer complexes were characterized by three main bands in the region 8600–10,500 [$^3A_{2g}(F) \to {}^3T_{2g}(F)$], 14,300–15,700 [$^3A_{2g}(F) \to {}^3T_{1g}(F)$] and 21,300–25,000 cm^{-1} [$^3A_{2g} \to {}^3T_{1g}(P)$] transitions in an idealized O_h symmetry. For the polymer complexes $[Ni(HL)_2X_2]_n$ [$X = Br^-, I^-, SCN^-$] and υ_2/υ_1 ratio lying between 1.54 and 1.69 characterize them as essentially pseudo-octahedral in the solid state. However, υ_2/υ_1 values for the rest of the Ni(II) species are found to fall in the range 1.78–1.83 indicating appreciable degree of tetragonal distortion in these octahedral species [39]. Electronic spectral data of the polymer complexes in DMF solutions commensurate that no gross change occurs in the electronic or geometric structures of the complexes on dissolution in the said solvent and show three principal bands, in the range 8880–9500 cm^{-1} (υ_1), 14,050–16,450 cm^{-1} (υ_2) and 22,950–25,000 cm^{-1} (υ_3) [40]. In case of electronic spectra of the DMF solution of $[Ni(HL)_2Cl_2]_n$ and $[Ni(HL)_2(ONO_2)_2]_n$, it is observed that the respective υ_2/υ_1 ratio (Table 3) have come down to the pseudo-octahedral range (1.55–1.58). The data reasonably suggest that there might be an effective change from D_{4h} to O_h symmetry due to solvation effects. The following schematic formulation may be represented to express the extensive solvolysis which might be responsible for the observed conductance data.$[Ni(HL)_2X_2] + DMF \to [Ni(HL)_2(DMF)_2]^{2+} + 2X$, [$X = Cl^-/Br^-/I^-/NCS^-/NO_3^-$]

Table 3
Electronic spectral data cm^{-1} of Ni(II) polymer complexes.

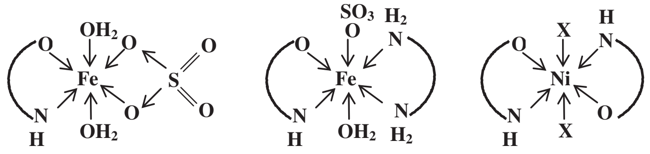
Complexes	υ_2/υ_1	State	Electronic spectral data
1	1.78	Reflectance	8580, 15,320, 25,005
		DMF	8960, 13,960, 23,610
2	1.69	Reflectance	8450, 14,330, 23,900
		DMF	8850, 14,330, 23,600
3	1.48	Reflectance	9850, 14,590, 24,400
		DMF	8850, 14,010, 23,600
4	1.83	Reflectance	8650, 15,800, 21,500
		DMF	8950, 14,150, 23,800
5	1.54	Reflectance	9999, 15,360, 24,100
		DMF	8888, 16,350, 25,100
6	1.64	Reflectance	9100, 14,900, 25,250
		DMF	9260, 16,100, 24,500
7	1.7	Reflectance	9100, 15,500, 21,100
		DMF	8850, 14,050, 23,100

The relatively high intensity of these absorptions is attributed to both metal-centered d–p mixing excepted for non-symmetrical polymer complexes and the covalency effects [41]. The spectral bands given in Table 3 are assigned to [$^3A_{2g}(F) \to {}^3T_{2g}(F)$], [$^3A_{2g}(F) \to {}^3T_{1g}(F)$] and [$^3A_{2g} \to {}^3T_{1g}(P)$] transition denoted as υ_1–υ_3, according to increasing energy, respectively. It is showed that the band positions are in the sequency, $NO_3 > Cl > Br > I$, in case of $[Ni(HL)_2X_2]$. The absorptions of $[Ni(HL)_2(Py)_2]X_2$, $X = Cl^-$ or Br^-, are found to be at the same wavenumbers indicating that the ligand field around the nickel(II) in these complexes is the same and the non-bonding nature of the counter ions. It is noted that the d–d transition energy of these complexes are order as $[Ni(HL)_2(Py)_2]Cl_2 > [Ni(HL)_2(Py)_2]Br_2 > [Ni(HL)_2(ONO)_2] > [Ni(HL)_2(Cl)_2] > [Ni(HL)_2(Br)_2] > [Ni(HL)_2(I)_2]$, depending on the nature of the coordinating atoms X or Py.

The electronic spectrum of the Fe(II) polymer complex (**6**) consisted of a pair of low intensity bands at 13,160, 17,640 cm^{-1} and also for polymer complex (**9**) at 15,340 and 19,010 cm^{-1} which are arising from $^5T_{2g} \to {}^5Eg$ transition [42], similar to those found for distorted octahedral complexes. The band at 25,730 cm^{-1} could be assigned to L → M charge transfer. The doublet is attributed to Jahn–Teller distortion in the excited state [43] and could also be correlated with solution oxidation giving characteristic bands for Fe(III) in the 17,000–19,000 cm^{-1} range. At the room temperature, the magnetic moment [5.2 (**6**) and 5.5 (**9**) BM] corresponding to octahedral symmetry (Fig. 2).

3.4.4. Thermogravimetric analyses

The thermal decomposition studies of the complexes were carried in temperature range 30–700 °C. The complexes (**6**) and (**9**)



X = Cl (**1**), Br (**2**), I (**3**), ONO2 (**4**), NCS (**5**), Py(**7, 8**)

Fig. 2. Structure formulae of HL-metal polymer complexes.

undergo first step decomposition in the temperature range 220–250 °C due to the loss of the coordinated water molecules. All the complexes show the second step decomposition between 380 and 430 °C due to removal of uncoordinated and/or coordinated anions and half part of the ligand. Finally the complexes undergo decomposition between 500 and 650 °C due to loss of remaining part of ligand. The final residue was analyzed by IR spectra and identified as MO.

4. Concluding remarks

Series of Ni(II), Pd(II) and Fe(II) polymer complexes with ligand (HL) have been prepared and fully characterized. 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 affected by number of coordination sites. The ligand (HL) has two coordination sites and formed different geometrical complexes with different anions.

(1) The ligand (HL) 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.
(2) 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.
(3) These results also confirm the non-reactivity of the —CONH— group in coordination (see Fig. 1).
(4) HL 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.
(5) According to the electronic spectra and magnetic data, there is a continuous transition between distorted octahedral and octahedral stereochemistry of the polymer complexes studied. π-electron acceptor mixed ligand (Py) stabilize the polarizable ligand (π-electron donor ligand, e.g. halide ion) and prefers the octahedral structure leads to irregular deformed coordination, suggesting that the bonding effect of the ligand in the axial position cannot be ignored.

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

References

[1] E.C. Okafor, P.U. Adiukwu, B.A. Uzoukwn, Synth. React. Inorg. Met. – Org. Chem. 23 (1993) 97.
[2] A. Tantawy, F. Goda, A.M. Abdelal, Chin. Pharm. J. 47 (1995) 37.
[3] A.C. Ojha, R. Jain, Pol. J. Chem. 56 (1982) 1553.
[4] P. Nagpal, R.V. Singh, Appl. Organomet. Chem. 18 (2004) 221.
[5] C.Y. Wu, L.H. Chen, W.S. Hwang, H.S. Chen, C.H. Hung, J. Organomet. Chem. 689 (2004) 2192.
[6] (a) T. Semba, Y. Funahashi, N. Ono, Y. Yamamoto, N.H. Sugi, M. Asada, K. Yoshimatsu, T. Wakabayashi, Clin. Cancer Res. 10 (2004) 1430;
(b) D.B. Clyson, J.A.S. Pringle, G.M. Ranses, Biochem. Pharmacol. 16 (1967) 614.
[7] Q. Clen, P.N.P. Rao, E.E. Knaus, Bioorg. Med. Chem. 13 (2005) 2459.
[8] A.K. Gadad, M.N. Noolyi, R.V. Karpoomath, Bioorg. Med. Chem. 12 (2004) 5651.
[9] A.Z. El-Sonbati, M.A. Diab, M.S. El-Shehawy, M.M. Makpel, Spectrochim. Acta A 75 (2010) 394.
[10] A.Z. El-Sonbati, A.A. Al-Sarawy, M. Moqbel, Spectrochim. Acta A 74 (2009) 463.
[11] A.T. Mubarak, A.Z. El-Sonbati, Polym. Bull. 57 (2006) 683.
[12] A.Z. El-Sonbati, R.M. Issa, A.M. AbdEl-Gawad, Spectrochim. Acta A 68 (2007) 134.
[13] J.A. Dean, Lange's Hand Book of Chemistry, 14th ed., MEGRAW-Hill, New York, 1992. p. 35.
[14] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
[15] L.K. Thompson, F.L. Lee, E.J. Gabe, Inorg. Chem. 27 (1988) 39.
[16] A.Z. El-Sonbati, A.A. El-Bindary, R.M. Issa, H.M. Kera, Desig. Mon. Polym. 7 (2004) 445.
[17] R.M. Issa, A.A. El-Bindary, A.Z. El-Sonbati, H.M. Kera, Bull. Polym. 51 (2004) 293.
[18] A.Z. El-Sonbati, A.A. El-Bindary, M.A. Diab, Spectrochim. Acta A 59 (2003) 443.
[19] A.Z. EL-Sonbati, A.A. EL-Bindary, R.M. Issa, H.M. Kera, Desig. Mon. Polym. 7 (2004) 445.
[20] A.Z. EL-Sonbati, M.A. Diab, M.M. El-Halawany, N.E. Salam, Spectrochim. Acta A 77 (2010) 755.
[21] A.Z. El-Sonbati, A.A. El-Bindary, M.A. Diab, S.A. Mazrouh, Mon. Chem 124 (1993) 793.
[22] A.Z. El-Sonbati, M.A. Diab, M.M. El-Halawany, N.E. Salam, Mater. Chem. Phys. 123 (2010) 439.
[23] D.M. Grant, N. Grassie, Polym. Sci. 42 (1960) 587.
[24] P.W. Selwood, Magneto Chemistry, Interscience Pub. Inc., New York, 1956.
[25] A.Z. El-Sonbati, A.A. El-Bindary, R.M. Ahmed, Spectrochim. Acta A 57 (2003) 333.
[26] A.Z. El-Sonbati, M.A. Diab, R.H. Mohamed, Spectrochim. Acta A 77 (2010) 795.
[27] A.Z. El-Sonbati, A.A. El-Bindary, M.A. Diab, M.A. El-Ela, S.A. Mazrouh, Polym. Deg. & Stab. 4 (1993) 1.
[28] C.M. Sharaby, Spectrochim. Acta A 62 (2005) 326.
[29] A.G. Raso, J.J. Fiol, S. Rigo, A.L. Lopez, E. Molins, E. Espinosa, E. Borras, G. Alzuet, J. Borras, A. Castineiras, Polyhedron 19 (2000) 991.
[30] C.M. Sharaby, G.G. Mohamed, M.M. Omar, Spectrochim. Acta A 66 (2007) 935.
[31] J.R. Ferraro, Low Frequency Vibrations of Inorganic and Coordination Compounds, first ed., Plenum Press, New York, 1971. pp. 168–196.
[32] M. Shakir, O.S.M. Nasem, A.K. Mohamed, S.P. Varkey, Ind. J. Chem. 32 (2007) 240.
[33] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley Interscience, New York, 1970.
[34] A.Z. El-Sonbati, M.A. Diab, M.F. Kotb, H.M. Killa, Bull. Soc. Chim. Fr. 128 (1991) 623.
[35] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, third ed., Wiley Interscience, New York, 1978.
[36] D.X. West, G. Ertem, R.M. Makeever, Trans. Met. Chem. 10 (1986) 41.
[37] A.K. Shehata, G.Y. Ali, A. Soyed, A. El-Dissouky, Trans. Met. Chem. 21 (1996) 117.
[38] A.B.P. Lever, J. Lewis, R.S. Nyholm, J. Chem. Soc. (1964) 4761.
[39] A.B.P. Lever, Coord. Chem. Rev. 3 (1968) 119.
[40] K.C. Patel, D.E. Goldberg, J. Inorg. Nucl. Chem. 34 (1972) 637.
[41] A.B.P. Lever, Inorganic Electronic Spectroscopy, second ed., Elsevier, New York, 1984.
[42] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, sixth ed., Wiley, New York, 1999.
[43] A.B.P. Lever, Inorganic Electronic Spectroscopy, second ed., Elsevier, Amsterdam, 1984.