ORIGINAL ARTICLE

Synthesis, spectral and thermal studies of N,N^--pyridine-2,6-diyl bis[N^--phenyl(thiourea)] and its metal complexes

Nasser M. Hosny · Mohsen M. Mostafa

Abstract Four new metal complexes with the general formula, [ML·mH$_2$O]nH$_2$O (where, M = Cu(I), Co(II), Ni(II) or Zn(II); L = N,N^--pyridine–2,6-diyl bis[N^--phenyl (thiourea)] (PDPT); m = 1 or 3 and n = 0.5 or 4.0), have been synthesized and characterized by elemental analyses, spectral analyses (IR, UV–Vis., ^{1}H-NMR and MS), thermal analyses (TGA), conductivity and magnetic measurements. The results showed that the ligand (PDPT) acts in a mononegative tridentate manner towards Cu(I) ion coordinating *via* the two thiol sulfurs and pyridyl nitrogen groups with displacement of only one hydrogen atom from the thiol group, while the ligand behaves in a binegative tridentate manner towards the Co(II), Ni(II) and Zn(II) ions with displacement of two hydrogen atoms from the two thiol groups. The value of magnetic measurements showed a diamagnetic character of the copper complex indicating the reduction of Cu(II) to Cu(I). Semi-empirical calculations of the ligand and its metal complexes have been used to study the molecular geometry using ZINDO/1, PM3 and AM1. Also, the harmonic vibration spectra of the ligand and its metal complexes have been investigated with the purpose to assist the experimental assignment of metal complexes. The results of the optical absorption studies reveal that the optical transition is direct with band gaps energy (E_g) values 2.62, 1.98 and 1.85 eV for Cu, Co and Ni complexes, respectively, indicating that these complexes can behave as semi-conductors.

Introduction

Thiourea derivatives and polyazomethines constitute important classes of chelating agents. Thiourea derivatives have been extensively studied as a potential anti-TB, anti-HIV, anti-tumor and plant growth regulators [1–3]. Poly-azomethines have been widely studied for their high thermal stability, mechanical properties, electrical and magnetic properties, liquid–crystal properties, and non-linear optical properties [4, 5]. Consideration of the high activity of a new thiourea derivative chelating macrocyclic ligand N,N^--pyridine–2,6-diyl-bis[N^--phenyl(thiourea)] (PDPT) has prompted us to undertake systematic studies on the complexation tendency. We report herein the results of investigations on the synthetic, spectral and thermal studies of (PDPT) and its metal complexes with Cu(I), Co(II), Ni(II) and Zn(II) ions. To reveal the conductivity of the isolated metal complexes the band gap energy has been calculated. Also, to facilitate the interpretation of vibration spectra of the ligand and its metal complexes semi-empirical calculations using the ZINDO/1, PM3 and AM1 have been used.

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Experimental

Reagents

All the chemicals used were of analytical grade and used without further purifications.

Technique

The elemental analysis was made using Perkin-Elmer 2408 CHN analyzer. The metal analyses were carried out by the standard methods [6]. Molar conductance measurements of the complexes (10^{-3} M) in DMSO were carried out with a conductivity bridge YSI model 32. Infrared spectra were measured using KBr discs on a Mattson 5000 FTIR Spectrometer. Calibration with the frequency reading was made with polystyrene film. Electronic spectra were recorded on UV2 Unicam UV–vis. Spectrometer using 1 cm stoppered silica cells. Magnetic measurements were carried out on a Sherwood magnetic balance. Thermal analysis measurements (TGA and DTG) were recorded on a Schimadzu model 50 instrument using 20 mg samples. The nitrogen flow rate and heating were 20 cm^3/min and 10 °C/min, respectively. The ^{1}H-NMR spectrum of the ligand was recorded in $CDCl_3$ on a Gemini-200 Spectrometer. Mass spectrum of the ligand was recorded on Shimadzu GC–MS–QP 1000 Ex. at 70 eV mass Spectrometer.

Computational details

Molecular geometries of all forms of metal complexes were optimized using molecular mechanics and the semi-empirical ZINDO/1, PM3 and AM1 methods using the hyperchem series of programs [7]. Molecular mechanics technique was used to investigate rapidly the geometries of the suggested structures of the metal complexes. The low lying conformers obtained from this search were then optimized at AM1, ZINDO/1 and PM3, (Polak-Ribiere) RMS 0.01 kcal.

Preparation of the ligand

The ligand was prepared by adding phenyl isothocyanate (24 mL; 0.2 mol) dropwise to a solution of 2,6-diamino-pyridine (17 g; 0.1 mol) dissolved in EtOH at room temperature with constant stirring for 2 h. The reaction mixture was refluxed on hot plate for 2 h and then left to cool. The product was filtered off, crystallized from EtOH and then kept to dry in a desiccator over P_4O_{10}.

Preparation of the metal complexes

The metal complexes were prepared by adding stoichiometric quantities of (1 mmol) of the metal (II) acetate in 25 cm^3 absolute EtOH to the ligand (1 mmol) in 25 cm^3 absolute. The mixture was refluxed on a hot plate for 3 h. To ensure the isolation of pure complexes the resulting solid complexes were filtered off immediately, washed several times with hot EtOH and dry Et_2O, respectively, and finally dried in a vacuum desiccator over fused $CaCl_2$.
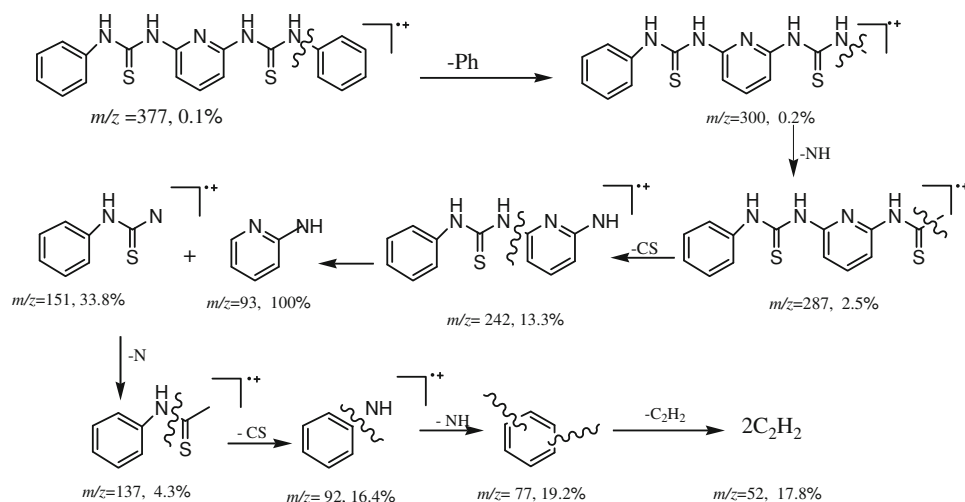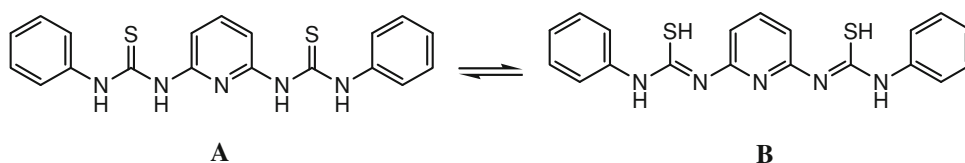
Results and discussion

All complexes are colored and stable on prolonged exposure in air. They are soluble in coordinating solvents such as DMSO and DMF, but insoluble in other common organic solvents. The molar conductivities values in DMF (10^{-3} M) fall in the 1–5 Ω^{-1} cm^2 mol^{-1} range at room temperature suggesting that the complexes are non-electrolytic [8]. Elemental analyses and other physical data are collected in Table 1. Only one type of complexes with the general formula, [ML·mH_2O]nH_2O (where, M = Cu (I), Co (II), Ni (II) or Zn (II); m = 1 or 3 and n = 0.5 or 4.0) are isolated.

Mass spectra

Mass spectrum of the ligand (PDPT) shows molecular ion peak at m/z = 377. This molecular ion peak losses C_6H_5, NH and CS, respectively, to give $C_{13}H_{11}N_4S_2$ radical cation at m/z = 287. This fragment is cleaved at CN bond to give the base peak at m/z = 93 corresponding to PyNH and the radical cation $C_6H_6N_2S$ (Scheme 1). The later is fragmented gradually with loss of N, CS, NH and C_2H_2, respectively.

^{1}H-NMR

The ^{1}H-NMR spectrum of the ligand (PDPT) in $CDCl_3$ shows two singlet signals at 13.32 and 8.83 ppm, downfield with respect to TMS, assignable to the protons of the NH group (attached to pyridyl ring), and the NH group attached to phenyl ring, respectively. The presence of these signals indicates that the ligand exists in the thione form. The

Table 1 Analytical and physical data of the ligand and the isolated metal complexes

Compound	Color	M.P. (°C)	% Found (Calcd)		
			C	H	M
H_2L	Yellow	120	59.6(60.1)	4.8(4.5)	–
[CuL·H_2O]1/2H_2O	Black	180	48.5(48.6)	4.2(3.8)	13.0(13.5)
[NiL·3H_2O]	Green	>300	46.2(46.6)	3.8(4.3)	12.0(11.9)
[ZnL·H_2O]1/2H_2O	Yellow	196	48.2(48.6)	4.0(3.8)	14.2(13.9)
[CoL·3H_2O]4H_2O	Brown	220	40.6(40.8)	4.4(4.1)	17.4(18.0)

Scheme 1 Fragmentation pattern of the ligand (PDPT)

$m/z = 377$, 0.1%

−Ph

$m/z = 300$, 0.2%

−NH

$m/z = 151$, 33.8%

+

$m/z = 93$, 100%

$m/z = 242$, 13.3%

−CS

$m/z = 287$, 2.5%

−N

$m/z = 137$, 4.3%

− CS

$m/z = 92$, 16.4%

− NH

$m/z = 77$, 19.2%

−C$_2$H$_2$

$2C_2H_2$

$m/z = 52$, 17.8%

Fig. 1 Tautomeric forms of the ligand

A   B

multiplet signals in the 4.58–7.75 ppm region is assignable to the protons of pyridyl and phenyl rings.

IR spectra

The infrared spectrum of the free ligand exhibits three bands at 3473, 3343 and 1603 cm^{-1} assignable to υ_{as}(NH), υ_s(NH) and υ(C=N) (azomethine) nitrogen vibrations, respectively. Also, the spectrum shows two bands at 1260 and 722 cm^{-1} assignable to υ(C=S) vibrations [9, 10]. The presence of these bands suggests that the free ligand exists mainly in the thione form (Fig. 1A). In the presence of metal ions, the ligand exists in the thiol form (Fig. 1B). Furthermore, the bands observed at 1628, 1025 and 650 cm^{-1} are assigned to υ(C=C + C=N$_p$), the ring skeletal mode and the in plane-ring deformation mode, respectively, [11, 12]. The positions of these bands play an important role in determining whether this group participates in coordination or not. The ligand (PDPT) behaves as mononegative tridentate coordinating in the thiol form *via* the pyridyl nitrogen and two thiol sulfurs with losing only one proton from the SH group in case of Cu (I) complex, while in case of Co (II), Ni (II) and Zn (II) complexes the ligand behaves as binegative tridentate coordinating through the pyridyl nitrogen and the two thiol groups with losing two protons from the two SH groups (Figs. 2, 3 and 4). The presence of thiol form in all metal complexes is supported by the disappearance of the bands assigned to ν(NH) at 3473 cm^{-1}, ν(C=S) at 1260 and 722 cm^{-1} in the spectrum of the free ligand. The appearance
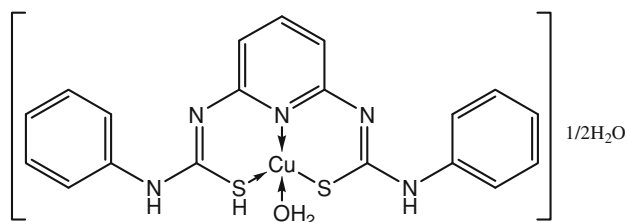
Fig. 2 Suggested structure of Cu (I) complex
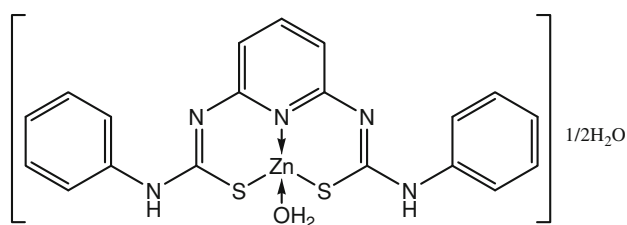
Fig. 3 Suggested structure of Zn (II)
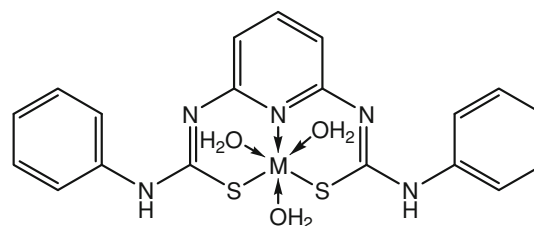
Fig. 4 Suggested structure of Co (II) and Ni (II) complex

Table 2 Observed and calculated wavenumbers (cm^{-1}) of the ligand (PDPT) and its complexes

Compound	v(NH)	v(C=N*)	v(C=C) + (C=N)	v(C–N)	P$_y$ skeletal
H$_2$L (Exp.)	3473, 3343	–	1628	1340	650
AM1	3425, 3364	–	1613	1344	675
PM3	3344, 3327	–	1588	1325	651
ZINDO/1	5318, 4845	–	1675	1353	645
Cu complex (Exp.)	3328	1670	1600	1380	625
PM3	3342	1661	1612	1394	633
ZINDO/1	4024	1763	1547	1387	625
Ni complex (Exp.)	3397	1635	1572	1347	640
PM3	3354	1622	1560	1338	654
ZINDO/1	5285	1719	1564	1348	633
Zn complex (Exp.)	3330	1613	1557	1334	626
AM1	3400	1614	1580	1322	625
PM3	3343	1636	1515	1421	658
ZINDO/1	5254	1750	1638	1356	662
Co complex (Exp.)	3300	1598	1558	1342	619
PM3	3297	1604	1561	1324	614
ZINDO/1	4399	1641	1568	1309	622

of new band in the region 1670–1598 cm^{-1} assigned to azomethine group v(C=N*) is taken as an additional evidence of the presence of thiol form. The observation of a band at 2550 cm^{-1} attributable to v(SH) vibration in case of the Cu(I) complex indicates the participation of this group in coordination without deprotonation [13]. The negative shifts of the bands in the regions 1557–1600 and 625–640 cm^{-1} attributable to pyridyl ring indicate that this group takes part in coordination [14]. New bands are observed in the regions 480–420 cm^{-1} assigned to v(M–N) and v(M–S), respectively, [12].

It is quite clear from Table 2 that AM1 method agrees well with the characteristic group frequencies in case of the free organic ligand and Zn complex while, PM3 agrees well in case of Cu and Co complexes PM3 and finally ZINDO/1 agree to the same extent in case of Ni complex.

The experimental data are obtained in the solid state, whereas the calculated frequencies are estimated in the gas phase. This may be the cause of the difference between the calculated and experimental values. Also, the difference may be resulted from the hydrogen bonding of water molecules which have not been taken into consideration during the calculations for the optimized molecules.

Electronic spectra and magnetic moments

The electronic spectrum of Cu (I) complex in Nujol shows a band at 23809 cm^{-1} assigned to LMCT. The diamagnetic character and the obscure of any band assigned to d–d transition of suggest the reduction Cu (II) to Cu (I) ion.

The electronic spectrum of Co (II) complex in Nujol shows two bands at 16286 and 19607 cm^{-1}, assigned to

$^4T_{1g} \rightarrow {}^4T_{1g}$(P) and $^4T_{1g} \rightarrow {}^4A_{2g}$ in an octahedral geometry around one Co (II) atom [15]. The ligand field parameters [$B = 873$, $\beta = 0.89$ and 10 Dq = 8730 cm^{-1}, where B = Racah parameters; β is the nephelauxetic parameter; β = B (complex)/B (free ion).], fall in the range suggested for octahedral geometry. The spectrum shows also, a band at 21276 cm^{-1} assigned to LMCT. The magnetic moment value (4.7 B.M.) supports the presence of octahedral geometry around Co ion [16].

The electronic spectrum of Ni (II) complex shows two bands at 14705 and 24038 cm^{-1} assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}$(P) in an octahedral geometry around Ni (II) atom. Two other forbidden transition bands are observed at 21008 and 18518 cm^{-1} [16]. Also, the ligand field parameters ($B = 758$, $\beta = 0.72$ and Dq = 910 cm^{-1}) fall in the range suggested for octahedral geometry of Ni (II). The magnetic moment value (2.90 B.M.) gives an additional evidence of the existence of an octahedral geometry.

Thermal analyses

The thermal analyses (TGA and DTG) curves of the complexes were carried out within a temperature range from room temperature up to 800 °C. The estimated mass losses were computed based on the TGA results and the calculated mass losses are computed using the results of microanalyses (Table 3). The results show good agreement with the theoretical formula as suggested from the analytical data (Table 1). The determined temperature range and percent losses in mass are given in Table 3.

The thermograms of [CuL·H$_2$O] 1/2H$_2$O complex show the losses of half molecule of lattice water followed by the

Table 3 Thermo analytical results (TG) of Cu (I), Co (II), Ni (II) and Zn (II) metal complexes

Complex	T range (°C)	Mass loss estim (calcd%)	E*	ΔH*	ΔG*	ΔS*	Assignment
[CuL·H$_2$O]1/2H$_2$O	50–110	1.4 (1.9)	50	105	111	-200	Loss of 1/2 H$_2$O (crystal water)
	110–431	59.9(58.6)	35	146	191	-202	Loss of H$_2$O (coordinated), 2Ph, 2HSCN
	432–750	16.7(17.8)	81	212	191	-25	Loss of N$_2$ and Py
[ZnL·H$_2$O]1/2H$_2$O	70–110	1.6(1.9)	42	42	135	-272	Loss of 1/2 H$_2$O (crystal water)
	111–396	60.4(61.5)	105	149	146	-226	Loss of coordinated H$_2$O, 2Ph and 2HSCN
	397–720	23.2(22.5)	212	188	122	-191	Loss of N$_2$ and Py
[NiL·3H$_2$O]	150–296	26.1(26.6)	156	122	235	-185	Loss of 3H$_2$O (coordinated), Ph
	296–615	41.0(39.4)	129	155	94	-102	Loss of 2HSCN and Ph
	615–650	16.2(15.2)	167	283	99	-224	Loss of Py
[Co$_2$L·3H$_2$O] 4H$_2$O	42–170	11.5(12.8)	88	42	88	-178	Loss of 4H$_2$O(crystal water)
	172–282	24.2(23.3)	146	139	53	-100	Loss of 3H$_2$O(coordinated) and Ph
	283–750	52.1(52.2)	218	86	38	-58	Loss of Ph, N$_2$, Py and 2HSCN

E, ΔH*, ΔG*, are in KJ mol^{-1} and ΔS* in KJ mol^{-1} deg^{-1}
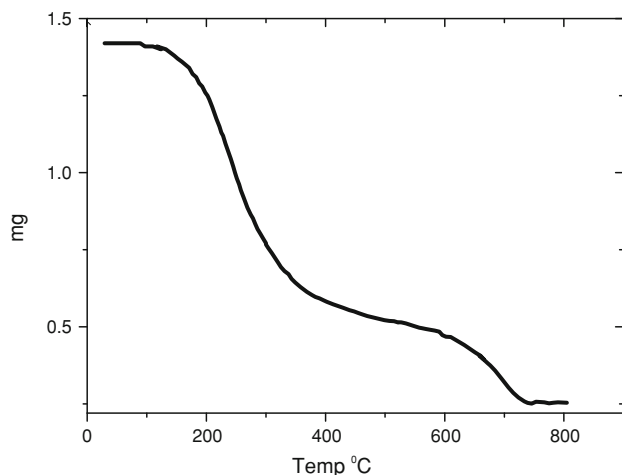
Fig. 5 TGA of Zn complex

loss of two phenyl, two HSCN and coordinated H$_2$O. The last step corresponds to the elimination of N$_2$ and Py. The residue of 21.8% (Calcd. 21.0) is Cu$_2$O.

Thermal analyses curves of [ZnL·H$_2$O]1/2H$_2$O complex (Fig. 5) show that, it losses half molecule of water of crystallization then, removal of two Ph and two HSCN and finally, losses of N$_2$ and Py. The ZnO is the remaining part, 18.4% (Calcd. 17.3).

The thermograms of [NiL·3H$_2$O] show three decomposition stages. The first corresponds to the loss of three coordinated water molecules and Ph. The second corresponds to the loss of Ph, and two HSCN and the last corresponds to elimination of Py leaving NiO as residue, 16.3% (Calcd. 15.2%).

Thermal analyses curves (TGA and DTG) of [CoL·3H$_2$O]4H$_2$O show that, the complex decomposes by elimination of water of crystallization, coordinated water and Ph. Then, the second Ph, N$_2$, Py and two molecules of HSCN leaving CoO as residue, 12.2% (Calcd. 13.3%).

The thermodynamic parameters (E*, ΔH*, ΔG* and ΔS*) were calculated by the Coats-Redfern equations [17] (Table 3). The negative ΔS* values indicate that the activated complex has more ordered structure that the reactants. The positive values of ΔG* indicate the non-spontaneous character of the decomposition steps. The positive values of ΔH* shows endothermic decomposition.

Optical band gap (E$_g$)

The use of solid state materials for conversion of solar energy into electricity is a topic of much interest to scientists. Photosensitization of TiO$_2$ with transition metal complexes has been reported [18]. The most successful sensitizers used are based on polypyridine transition metal complexes.

Herein, the optical band gaps (E$_g$) of Cu, Co and Ni complexes were calculated from absorption spectra. It was recorded using DMSO at 25 °C. The measured absorbance (A) was used to calculate approximately the absorption coefficient (α) by using the relation [19, 20]: $\alpha = 1/d \ln A$ (1) where, d is the width of the cell. The relation between the absorption coefficient and optical band gap (E$_g$) is expressed to calculate the band gap of the compound by the following relation [20, 21]: $\alpha h\nu = A(h\nu - E_g)^m$ (2), where m is equal to 1/2 and 2 for direct and indirect transitions, respectively, A is an energy independent constant. The values of α calculated from relation 1 were used to plot $(\alpha h\nu)^2$ vs. $h\nu$ a direct band gap was found (Fig. 6), by extrapolating the linear portion of the curves to $(\alpha h\nu)^2 = 0$.

From the curves it is clear that the values of the direct band gaps (E$_g$) equal 2.6, 1.98 and 1.85 eV for Cu, Co and Ni complexes, respectively. It is observed that E$_g$ values do not show any certain trend according to atomic number of the metal ion but, depend significantly on the metal coordination [21]. These values suggest that the present compounds are
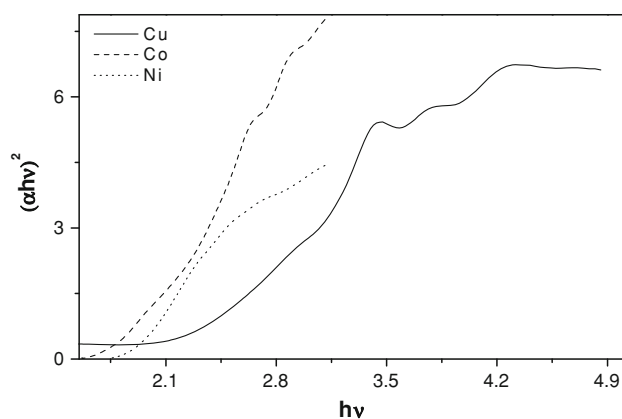
Fig. 6 The plots of $(\alpha h\nu)^2$ versus $h\nu$ of Cu(I), Co(II) and Ni(II) complexes

semiconductors since the values of energy band gaps are in the same range of highly efficient photovoltaic materials. These compounds could be considered potential materials for absorption of solar radiation in solar cell application [22].

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