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Synthesis, characterization and quantum chemical *ab initio* calculations of new dimeric aminocyclodiphosph(V)azane and its Co(II), Ni(II) and Cu(II) complexes

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ABSTRACT

The complexes of type $[M_2LCl_2]$ in which M = Co(II), Ni(II) and Cu(II) ions and L are 1,3-o-pyridyl-2,4dioxo-2',4'-bis(3-benzo[d]thiazol-2-yl-2-iminothiophene) cyclodiphosph(V)azane, were prepared and their structures were characterized by different physical techniques (IR, UV–Vis, ¹H NMR, ³¹P NMR, mass, TGA, DTA, XRD, SEM, magnetic moment and electrical conductance measurements). *Ab initio* calculations at the level of DFT B3LYP/6-31G(d) were utilized to find the optimum geometry of the ligand. Spectral characterization of the ligand was simulated using DT-DFT method. Infrared spectra of the complexes indicate deprotonation and coordination of the imine NH. It also confirms that nitrogen atoms of the pyridine group and thiazole group contribute to the complexation. NBO natural charges were computed and discussed in the light of coordination centers. Electronic spectra and magnetic susceptibility measurements as well as quantum chemical calculations reveal square planar geometry for Cu(II) and Ni(II) complexes and tetrahedral geometry for Co(II) complex. The elemental analyses and mass spectral data have justified the M₂LCl₂ composition of complexes.

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SPECTROCHIMICA ACTA

1. Introduction

Phosphazanes, which are the best known and most intensively studied phosphorus-nitrogen compounds, are materials with interesting properties. For example, they exhibit fire-retardant properties, have high refractive indices, and might find application in non-linear optics, as ferroelectric materials, as liquid crystals or as photoactive materials [1–4]. They also possess a number of characteristics such as biomedical properties and applications due to their strong antitumor activity [5–7]. Their antimicrobial and biological activities on bacterial and yeast cells have been studied [8-10]. Some applications include model compounds for polyphosphazenes, starting materials for the preparation of cyclolinear and/or cyclomatrix phosphazane substrates, commercial polymers with carbon backbones containing pendant cyclophosphazane groups, inorganic hydraulic fluids and lubricants, biologically important substrates such as anticancer agents, insect chemosterilants, pesticides and fertilizers, supports for catalysts, dyes, and crown ether phase transfer catalysts for nucleophilic substitution reactions, core substrates for dendrimers, thermal initiators for anionic polymerization reactions and photosensitive materials [11]. The

reaction of hexachlorocyclodiphosph(V)azanes with amino compounds has been investigated in great details [12–14]. Transition metal complexes with amino tetrachlorocyclodiphosph(V)azanes as ligands have been amongst the widely studied coordination compounds in the past few year, since they are found to be important as biochemical, analytical and antimicrobial reagents [15,16]. The present-work aims chiefly to prepare the metal complexes of ligand H₂L. In this work, novel ligand (H₂L) was prepared and its behavior toward some transition metal ions was studied using different techniques such as elemental analyses, IR, ¹H, ³¹P NMR, mass, EPR, TGA, molar conductance, magnetic moment, UV–Vis spectra and DFT quantum mechanical calculations.

2. Experimental

2.1. Physiochemical studies

All reactions were carried out under purified nitrogen by standard Schlenk techniques [17]. All chemicals used in this investigation were of analytical grade, provided by B.D.H. chemicals. Solvents were purified and dried by standard methods and distilled under nitrogen prior to use. The $[(C_5H_5N)NP(O)Cl]_2$ **1** synthesis was carried out according to Ref. [18] and 3-(benzo[d]thiazol-2-yl)-2aminothiophene **2** according to Ref. [19]. The stoichiometric analyses (C, H, N, S, P, Cl and M) of the ligand and its metal complexes were performed by the microanalytical center, Cairo University, Giza, Egypt. The infrared spectra were recorded in Nujol

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mulls on a Shimadzu FT-IR spectrometer using KBr disks. Proton {¹H} and ³¹P {NMR} spectra were obtained on a JEOL JMTC 400 MHz spectrometer using d₆-DMSO solution in 5 mm diameter tubes. ¹H spectra were referenced to TMS and ³¹P referenced to 85% H₃PO₄ as external standards. Electronic spectra were recorded as Nujol mulls and DMF saturated solutions on CARY 5 spectrophotometer. The molar conductance measurements were carried out using a Sybron-Barnstead conductometer. Mass spectra were recorded on GS/MS INCOS XL Finnegan MAT. The magnetic susceptibilities of the complexes in the solid state were recorded on Sherwood Scientific magnetic susceptibility balance. The TGA were recorded on a Shimadzu TGA-50H. TGA was carried out in a dynamic nitrogen atmosphere (20 mLmin^{-1}) with a heating rate of 10 °C min⁻¹. EPR spectra of Cu(II) complex were recorded as polycrystalline sample, at room temperature, on an E4-EPR spectrometer using the DPPH as the g-marker.

2.2. Synthesis of ligand (H₂L)

3-(Benzo[d]thiazol-2-yl)-2-aminothiophene (4.64 g, 0.02 mol) was added in small portions to a well stirred solution of 1,3-(dio-pyridyl)-2,4-(dioxo)-2',4'-dichlorocyclodiphosph(V)azane (3.47 g, 0.01 mol) in 100 ml acetonitrile during half an hour. After the addition was completed, the reaction mixture was heated under reflux for 12 h. After the completion of the reaction (HCl gas ceased to evolve), the reaction mixture was filtered while hot and the solid obtained was washed several times with acetonitrile, diethyl ether and dried in vacuo to give the corresponding aminoacyclodiphazane derivative (H₂L), (yield 86.74%) with mp = 132–134 °C.

2.3. Syntheses of metal complexes

The metal complexes were prepared by adding dropwise a hot aqueous $(60 \,^{\circ}\text{C})$ solution $(100 \,\text{mL})$ of the metal chlorides $(0.1 \,\text{mol})$ to a solution of H₂L $(0.1 \,\text{mol})$ in tetrahydrofuran $(100 \,\text{mL})$ while stirring continuously. After complete addition of the metal salt solution, the reaction mixture was heated under reflux for about 18 h under dry conditions. The complexes obtained were filtered, washed with water, ethanol, and tetrahydrofuran and then dried in vacuo. The products obtained give elemental analyses (Table 1) consistent with the proposed structures.

3. Computational methods

All electronic structural calculations were performed using the Gaussian09 suite of programs [20]. Geometry optimizations for all tautomers have been performed using semi-empirical AM1 method and *ab initio* Density Functional Theory (DFT) at the B3LYP functional [21–23], in conjunction with the 6-31G(d) basis set. For each stationary point, we carried out a vibrational frequency calculation at the same levels to characterize their

nature as minima or transition states and to correct energies for zero-point energy and thermal contribution. The frequencies are scaled by a factor of 0.98. The vibrational modes were animated using the ChemCraft program [24]. Electronic transitions were computed within the time-dependent DFT (TD-DFT) formalism [25] as implemented in Gaussian09 suite of programs [20]. Natural charges were computed within full Natural Bond Orbital analysis, using NBO version 3 implemented in Gaussian09 [20].

4. Results and discussion

4.1. The ligand

The analytically pure ligand H₂L (Fig. 1) was readily synthesized with very good yield (86.74%) by the reaction of 1,3-(di-o-pyridyl)-2,4-(dioxo)-2',4'-dichlorocyclodiphosph(V)azane with two equivalents of 3-(benzo[d]thiazol-2-yl)-2-aminothiophene in acetonitrile. The purity of the ligand 98.68% has been checked by HPLC. Elemental analyses (Table 1) of the ligand reflected that the ligand has the molecular formula that is given above. The EI-mass spectrum (Supplement Fig. S-1a) of the ligand (H₂L) shows a maxima peak at 740 u, corresponding to the aminocyclodiphosph(V)azane dimer moiety ($(C_{32}H_{22}N_8O_2P_2S_4)^+$, calculated atomic mass 740 u) and a number of peaks at 52, 223, 317, 368, 487 and 582 u, attributable to different fragments of the ligand. The mass spectrum of the ligand (H₂L) shows the fragmentation pattern in Supplement Scheme S-1. The ligand H₂L may show keto-enol tautomerism because it contains the phosphenous amide (-NH-P=O) bonds [26,27]. The IR spectrum (Fig. 2a, Table 2) does not show a v(OH) band at 3550 cm⁻¹ but shows the band at 3272 cm⁻¹ corresponding to v(NH) [26], indicating that in solid state, the ligand exists in the keto form for the ligand H₂L. However, the ¹H NMR spectrum (Supplement Fig. S-2a and Table S-1) of ligand exhibits a sharp singlet at 12.62 ppm due to enolic -OH which indicates that the amide groups are transformed into iminol groups in solution [28]. The ³¹P NMR (Supplement Fig. S-3) of the ligand records a signal at δ = 64.63 ppm, which supports the phosphazo (P–N) nitrogen group [5]. The electronic spectrum of H₂L (Supplement Fig. S-4a, Table 3) in ethanol showed absorption bands at 40,818-21,932 cm⁻ regions which is due to intra-ligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions involving molecular orbital of the pyridine ring, a broad shoulder at approximately 22,831 cm⁻¹ was observed. The latter band is attributed to a $n(xygen) \rightarrow \pi^*$ transition of the dipolar zwitter ionic structure or keto-amine tautomer of H₂L [26,29].

4.2. Quantum chemical calculations

4.2.1. Geometry

Since single crystal X-ray structure for the ligand is not available, quantum chemical calculations were utilized to find the geometry optimized structures for the H_2L at different quantum

Table 1

Elemental analyses, melting points, colours	, yields and composition of	f ligand (H ₂ L) and its	corresponding metal	complexes (1-3
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Compd. No.	M.p. (°C)	.p. (°C) Yield		Elemental analyses Found (Calc.), %					aΛ		
M.F. (M.Wt)		Colour	(%)	М	Cl	С	Н	Ν	Р	S	
H ₂ L	132-134	Yellow	86.74	-	-	51.87 (51.88)	2.94 (2.99)	15.07 (15.13)	8.39 (8.36)	17.30 (17.31)	-
$C_{32}H_{22}N_8O_2P_2S_4$ (740.78) (1) $C_{32}H_{22}Cl_2CO_2N_2O_2P_2S_4$ (927.53)	188-190	Orange	62 68	12 69 (12 71)	7 58 (7 64)	41 41 (41 44)	2 13 (2 17)	12 03 (12 08)	6 64 (6 68)	13 88 (13 83)	5 23
[Co ₂ LCl ₂]	100 150	orunge	02.00	12.03 (12.71)	7.50 (7.01)		2.13 (2.17)	12.03 (12.00)	0.01 (0.00)	15.00 (15.05)	5.25
(2) $C_{32}H_{20}Cl_2N_8Ni_2O_2P_2S_4$ (927.05) [Ni ₂] Cl_2]	192–194	Brown	64.39	12.64 (12.66)	7.62 (7.65)	41.42 (41.46)	2.13 (2.17)	12.04 (12.09)	6.63 (6.68)	13.80 (13.84)	4.64
$\begin{array}{c} \textbf{(3)} C_{32}H_{20}Cl_2Cu_2N_8O_2P_2S_4 \ \textbf{(936.76)} \\ \textbf{[Cu_2LCl_2]} \end{array}$	197–199	Brown	67.26	13.54 (13.57)	7.54 (7.57)	41.07 (41.03)	2.12 (2.15)	11.99 (11.96)	9.64 (6.61)	13.62 (13.69)	7.62

^a Λ (molar conductance Ω^{-1} cm²mol⁻¹).



Fig. 1. Three possible isomeric forms in solution of ligand H₂L.



Fig. 2. (a) IR spectrum of H₂L ligand, (b) IR spectrum of Co(II) complex (1), (c) IR spectrum of Ni(II) complex (2), and (d) IR spectrum of Cu(II) complex (3).

mechanical levels. Fig. 3 shows the optimized structure of the H_2L *cis*-dione at B3LYP/6-31G(d). An inspection of the resulting structure easily shows two close contacts H-bonding interactions between the amine-H and the thiazole-N of length 1.826 Å. This intra-molecular interaction is also shown by H_2L *cis*-ol with a longer H-bond length (1-862 Å). Table 4 presents some selected computed geometrical parameters of H_2L *cis*-dione. Since dispersion energies do not play a considerable role in these types of structures, electron correlations are not so important consequently DFT methods would provide a good quality structures. The P_2N_2 ring is almost planar and P–N bonds in the ring are almost of equal length (1.786 Å). The exocyclic phosphorus-nitrogen groups have exo orientation relative to the phosphazane ring. The phosphoimi-

no bonds are much shorter than P–N distances in the P_2N_2 ring (1.741 vs. 1.786 Å) which confirms the multiple PN connection in P=N-thiophen derivative. The lengths of the thiophene-C–N_{imino} bonds are also different from the classical thiophene-C–N_{imino} case. The shortening of thiophene-C–N_{imino} bonds could be due to extension of the π electron conjugation of the thiophene ring. Another possible explanation is that the imino nitrogen atom with sp² hybrid orbitals has more s-character and the maximum of the electron density distribution at sp³ hybridized amino nitrogen, and this leads to shortening of the thiophene-C–N_{imino} bonds. Our structural data given in Supplement Table S-2 agrees well with the available X-ray data on P_2N_2 ring-containing compounds

Table 2		
Important IR bands of H ₂ L ligand and its complexes (1-3) with their assignments

Assignments	Ligand (H ₂ L)	1	2	3
v(NH)	3272	-	-	-
v(C=N)thiazole	1631	1613	1613	1612
v pyridine ring	1510, 595, 475	1525, 614, 525	1523, 612, 524	1522, 610, 523
v(C-S-C)	704s	707	712	710
v(M-N) imine	_	293	296	297
v(M-N)) pyridine	_	348	345	343
v(M–N)thiazole	_	244	246	249
v(M-Cl)	_	328	327	330

Table 3

Molar conductance, magnetic moment and electronic spectral data of the complexes.

Complex	Molar conductance $(\Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1})$	Geometry	Magnetic moments (µB)		Band assignments	$\lambda_{ m max}$ (cm ⁻¹)
			$\mu_{\rm compl.}^{a}$	$\mu_{\mathrm{eff}}{}^{\mathrm{b}}$		
Ligand H ₂ L	_	_		_	INCT $(\pi \rightarrow \pi^*)$ INCT $(\pi \rightarrow \pi^*)$ INCT $(n \rightarrow \pi^*)$ LMCT $(n \rightarrow \pi^*)$ LMCT $(n \rightarrow \pi^*)$ LMCT $(n \rightarrow \pi^*)$	40,818 36,914 34,014 27,025 25,387 21,932
[Co ₂ LCl2]	12.45	Tetrahedral	7.87	4.77	$\label{eq:A2} \begin{array}{l} {}^4A_2 \rightarrow {}^4T_1(P) \\ {}^4A_2 \rightarrow {}^4T_1 \ (F) \\ {}^4A_2 \rightarrow {}^4T_1 \end{array}$	14,948 14,124 4500
[Ni ₂ LCl2]	9.34	Square planar	-	-	$\label{eq:constraint} \begin{array}{c} {}^1A_1 \rightarrow {}^1A_2 \\ {}^1A_1 \rightarrow {}^1B_1 \\ {}^2B_1 \rightarrow {}^2B_2 \end{array}$	15,267 17,890 14,970
[Cu ₂ LCl2]	10.68	Square planar	3.32	1.73	$^2B_1 \rightarrow {}^2E$	19,455

^a $\mu_{\text{compl.}}$ is the magnetic moment of all metal ions present in the complex.

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



Fig. 3. Optimized structure of H₂L cis-dione at the level of B3LYP/6-31G(d).

[30,31]. It is obvious that these ligands with 70 atoms of which 48 heavy atoms are considered large systems for an optimization process using a sophisticated *ab initio* method. They also have flexible structures with large number of degrees of freedom. This would provide a complex potential energy surface which is flat in nature. Supplement Fig. S-5 shows the route of the optimization process for H₂Lwhich exhibit a sharp decrease of energy at point 36. The flatness of the potential energy surface can easily be detected in the Supplement Fig. S-5. The deviation of every optimization step

from the local minimum for the ligand H_2L is presented in Fig. 4. It also reflects the complexity of the potential energy surface as well as its flatness.

4.2.2. Simulated spectra

Simulated IR spectra of different isomers of H_2L were calculated at the level B3LYP/6-31G(d). Fig. 5a and b displays the simulated IR spectra for the *cis*-dione and *cis*-ol tautomers scaled by 0.98 as a scale factor [32]. Inspection of the calculated frequencies shows that they agree with the experimentally measured IR spectra. The vibrational frequencies were animated with ChemCraft to assign frequencies to their normal modes.

DT-DFT calculations were done for the free ligand in the molecular gas state. The computed UV–Vis spectra of H₂L diketo *cis* gives three absorption bands at 218.8 (f = 0.0015), 273.3 (f = 0.5893) and 280.6 (f = 0.1185) nm. It is clear that the computed UV data could be compared with the measured spectra.

4.2.3. Natural charges

Natural charges were computed within full Natural Bond Orbital analysis, using NBO version 3 implemented in Gaussian09 [19]. Computed natural charges of H_2L *cis*-dione at b3lyp/6-31G(d) are shown in Table 4. Charges are distributed homogenously on the molecular structure with a charge separation detected. The most negative centers are ring-N (-1.16), amino-N (-1.06), the exo-cyclic O (-1.04), thiazole-N (-0.59) and pyridine-N (-0.55). These places of accumulated negative charges are the most likely coordinated centers. On the other hand the positive charges are populated on the P (2.45), the amino-H (0.52) and C5,17 in the pyridine rings (0.46) is between two more electronegative N atoms. Sulfur atoms are also positively charged where the thiophene-S is more positive (0.4) than the thiazole-S (0.29). This is possibly because of two reasons, the presence of more electroneg-

Table 4

Computed natural charges of H₂L cis-dione at b3lyp/6-31G(d).

Atomic center	Natural charge	Atomic center	Natural charge
C1	-0.15	C36	0.14
C2	-0.33	C37	-0.23
C3	0.07	C38	-0.22
N4	-0.55	C39	-0.23
C5	0.46	C40	-0.24
C6	-0.33	N41	-0.59
N7	-1.16	S42	0.29
P8	2.45	C43	-0.2
Р9	2.45	C44	0.14
N10	-1.16	C45	-0.23
N11	-1.06	C46	-0.24
C12	0.16	C47	-0.23
C13	-0.27	C48	-0.22
C14	-0.22	H49	0.25
C15	-0.42	H50	0.25
S16	0.4	H51	0.24
C17	0.46	H52	0.26
C18	-0.33	H53	0.52
C19	-0.15	H54	0.26
C20	-0.33	H55	0.27
C21	0.07	H56	0.26
N22	-0.55	H57	0.25
023	-1.04	H58	0.25
N24	-1.06	H59	0.24
C25	0.16	H60	0.52
C26	-0.27	H61	0.26
C27	-0.22	H62	0.27
C28	-0.42	H63	0.25
S29	0.4	H64	0.26
C30	0.2	H65	0.25
C31	0.2	H66	0.24
032	-1.04	H67	0.25
N33	-0.59	H68	0.24
S34	0.29	H69	0.25
C35	-0.2	H70	0.26

ative N atom and the engagement of the mobile electron cloud in the delocalization of the extended benzothiazole system.

4.3 Complexes

On the basis of elemental analyses, the complexes were assigned to possess the composition shown in Table 1. Nitrobenzene solutions of the complexes show negligible conductance. Hence, it is concluded that the anions are present in the coordination sphere of the molecules [26]. Thus, these complexes may be formulated as $[[M_2LCl_2]]$, where M = Co(II), Ni(II) and Cu; L = 1,3-(di-o-pyridyl)-2,4-(dioxo)-2',4'-bis(3-(benzo[d]thiazol-2-yl)-2-iminothiophene) cyclodiphosph(V)azane.

4.3.1. IR spectra and mode of bonding

The assignments of the main IR absorption bands of the free ligand and its metal complexes are given in Fig. 2, Table 2. The IR spectrum of the ligand shows a broad band at 3272 cm⁻¹, which can be attributed to v(NH) group [33]. This band disappears in all complexes, which can be attributed to the involvement NH in coordination. In the IR spectra of the complexes (Fig. 2b and c) the most useful vibrational bands of the complexes for establishing the mode of coordination are reported in Table 2. All IR spectra of the complexes exhibit medium to strong bands at about 1576-1592 and 1465–1482 cm^{-1} as expected for the highest pyridine and thiazole ring vibrations [34]. In addition, the peak at 704 cm⁻¹ attributed to the absorption of v_{C-S-C} of the benzothiaz-olyl ring [35] appears in the range 707–712 cm⁻¹ in the M(II) complexes, indicating that the S atom is not coordinated with the metal ion too. The C=N stretching vibration observed at 1631 cm⁻¹ for H_2L is shifted to ca.1613 cm⁻¹ in the M(II) complexes, and the shift extent is similar to the M(II)-imidazole complex [36,37]. These facts indicated that H₂L is coordinated with M(II) via nitrogen atom on the thiazole ring, which is similar to the binding of benzothiazole derivatives to a number of other metals reported previously [38–42]. The pyridine-ring-stretching, in-plane-ring-bending and out of-plane-ring-bending vibrations are found at 1510, 595 and 475 cm⁻¹, respectively. These absorptions are highly affected when nitrogen atom of pyridine ring takes part in coordination. In the complexes the position of these absorption bands is shifted to



Fig. 4. The deviation from local minimum geometry at every optimization step of H₂L cis-dione at the level of B3LYP/6-31G(d).



Fig. 5a. Simulated IR spectrum of cis-dione H₂L at b3lyp/6-31G(d).

higher region. This indicates that the nitrogen of pyridine ring is involved in coordination [43]. The low frequency pyridine $v(M-N_{Pyr-idine})$ and thiazole $v(M-N_{Thiazole})$ modes lie in the ranges 348–343 and 244–249 cm⁻¹, respectively. This suggests the involvement of pyridine [44] and thiazole [44] rings in coordination. The bands at 327–330 cm⁻¹ are present in chloro complexes which are attributed to the v(M-Cl) [45]. The bands at 293–297 cm⁻¹ may comprise the two $v(M-N_{imino})$ vibrations [26]. These IR spectral data reveal to suggest that the ligand is hexadentate coordinating through nitrogen only [N₆].

4.3.2. Mass spectra

The FAB mass spectra of Co(II) (Supplement Fig. S-1b), Ni(II) (Supplement Fig. S-1c) and Cu(II) (Supplement Fig. S-1d) com-



Fig. 5b. Simulated IR spectrum of cis-ol H2L at b3lyp/6-31g(d)

plexes have been recorded. The mass spectra give $[M]^+$ 927 for $[Co_2LCl_2]$ (1), $[M+1]^+$ 929 for $[Ni_2LCl_2]$ (2) and $[M]^+$ 936 $[Cu_2LCl_2]$ (3). These data in good agreement with the proposed molecular formula for these complexes. In addition to the peaks due to the molecular ion, the spectra exhibit peaks assignable to various fragments arising from the thermal cleavage of the complexes. The peal intensity gives an idea of the stability of the fragments. The pathway fragmentation pattern of the mass spectrum of the Co(II) complex is described in Supplement Scheme S-2.

4.3.3. Magnetic moment

The magnetic moments for the complexes are shown in Table 1. The magnetic moments of the copper(II) and cobalt(II) complexes are 1.73 and 4.77 BM, respectively, which suggest square planar geometry for copper(II) complex and tetrahedral geometry for cobalt(II) complex [46,47]. For tetrahedral cobalt(II) complex, the state acquires orbital angular momentum only indirectly through the mixing of the ${}^{4}T_{2}$ state by a spin–orbit coupling perturbation. The nickel(II) complex is diamagnetic at room temperature revealing the square planar geometry for nickel(II) complex around the metal (II) ion [46].

4.3.4. Electronic spectra

The electronic spectra of the complexes are presented in Table 3. Two very strong bands in the region 34,014-21,932 and 40,818–36,914 cm⁻¹ in the spectra of the complexes, are attributed to $n \to \pi^*$ and $\pi \to \pi^*$ transitions in aromatic ring and C=N chromophore [48]. Cobalt(II) complex (Supplement Fig. S-4b) shows absorption bands at 14,948 cm⁻¹ assigned to ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$ transition. The existence of spin-orbit coupling also allows some quartet \rightarrow doublet spin transition to occur. Another band at 14,124 cm⁻¹ is assigned to ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$ (F). The expected ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$ transition appearing at a 4500 cm⁻¹ is overlapped by ligand vibration transitions (i.e., the infrared bands) suggests tetrahedral geometry of the complex [49,50] which is also corroborated by magnetic moment value of the complex. Spectra of the nickel complex (Supplement Fig. S-4c) show an absorption band at 15,263 cm⁻¹, assignable to a ${}^{1}A_{1} \rightarrow {}^{1}A_{2}$ transition and a shoulder at 17,892 cm⁻¹ corresponding to a ${}^{1}A_{1} \rightarrow {}^{1}B_{1}$ transition which are consistent with square planar stereochemistry about the nickel(II) ion [40]. The visible spectrum of copper complex (Supplement Fig. S-4d), shows two absorption bands at 14,970 and 19,455 cm⁻¹ assignable to ${}^2B_1 \rightarrow {}^2B_2$ and ${}^2B_1 \rightarrow {}^2E$ transitions respectively, which indicates the possibility of square planar geometry of the metal complex [51].

4.3.5. ¹H NMR and ³¹P NMR spectral study

The proton NMR spectra of the ligand H₂L and its diamagnetic Ni(II) complex (Supplement Fig. S-2a and b) were recorded in DMSO-*d*₆ solution using tetramethylsilane (TMS) as internal standard. The chemical shifts of the different types of protons of the ligand H₂L and its diamagnetic Ni(II) complex are listed in Supplement Table S-1. The NH signal found at 3.03 ppm in the spectrum of the ligand H₂L is completely disappeared in the spectra of the Ni(II) complex. This indicates the involvement of the NH group in chelation with Ni(II) through displacement of the NH proton. The phosphorus thirty one NMR spectra of the ligand H₂L and its diamagnetic Ni(II) complex (Supplement Fig. S-3a and b) were recorded in DMSO- d_6 solution using H₃PO₄ as internal standard. The ³¹P NMR study also supports the proposed structure of the compounds. As reported earlier the position of the ³¹P chemical shifts is not influenced by the paramagnetic nature of the metal ions. The ³¹P spectra of H₂L showed signal at 64.63 ppm. In the case of complex the ³¹P spectrum of Ni(II) complexes showed signal at 59.23 ppm [26], respectively. This signal is actually shifted downfield due to the drifting of environmental electrons toward the nickel ion.

4.3.6. EPR spectra

The EPR spectrum of Co(II) complex was recorded as polycrystalline sample. No EPR signal was observed at room temperature because the rapid spin lattice relaxation of Co(II) broadens the lines at higher temperature. It shows a very broad signal at liquid nitrogen temperature. The deviation of 'g' values from the free electron value (2.0023) may be due to angular momentum contribution in the complexes [52,53]. The EPR spectrum of the copper(II) complex (Supplement Fig. S-6) shows two lines having $g_{||}$ value at 2.11 and g_{\perp} at 2.04. $g_{||}$ value being less than 2.3, witnesses more covalency in metal–ligand interaction [52]. Further it is noteworthy that the relation $g_{||} > g_{\perp}g_e$ (2.0029) is typical of axially symmetric d^9 Cu^{II} ion having one unpaired electron in $d_{x^2-y^2}$ orbital [53].

4.3.7. Cyclic voltammetry studies

The cyclic voltammogram of the copper complex (Supplement Fig. S-7) recorded at room temperature shows a quasi-reversible peak for the Cu(II) \rightarrow Cu(III) couple at 0.72 V with a direct cathodic peak for Cu(III) \rightarrow Cu(II) at 0.61 V. It also exhibits two irreversible peaks in cathodic region characteristics for Cu(II) \rightarrow Cu(I) at -0.74 V and Cu(I) \rightarrow Cu(0) at -0.92 V. These two peaks show their reduction behavior of copper in complex. In anodic region it exhibits two peaks which correspond to oxidative behavior of Cu(0) \rightarrow Cu(I) and Cu(I) \rightarrow Cu(II) is observed.

4.3.8. X-ray diffraction and SEM analysis

No peaks have been observed in X-Ray diffraction (Fig. 6) patterns of the powdered ligand (H₂L) and its metal complexes (**1**-**3**) and this confirmed their amorphous nature. The morphology and particle size of the ligand H₂L and Ni(II) metal complex have been illustrated by the scanning electron micrography (SEM). Supplement Fig. S-8 depicts the SEM photographs of the synthesized ligand H₂L and Ni(II) metal complex. It was noted that there is a uniform matrix of the synthesized complexes in the pictograph which leads to a belief that it is a homogeneous phase material. An ice rock like shape is observed in the ligand H₂L with the particle size of 10 µm. However Ni(II) complex is an ice sponge shaped morphology with 10 µm particle size.



Fig. 6. (a) XRD diagram of H₂L ligand, (b) XRD diagram of Co(II) complex (1), (c) XRD diagram of Ni(II) complex (2), and (d XRD diagram of Cu(II) complex (3).

4.3.9. Thermal analyses

Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were carried out for Co(II). Ni(II) and Cu(II) complexes in ambient conditions. The correlations between the different decomposition steps of the complexes with the corresponding weight losses are discussed in terms of the proposed formula of the complexes. The thermal decomposition of [Co₂LCl₂] complex (Supplement Fig. S-9a) with the molecular formula [C₃₂H₂₀Cl₂N₈O₂P₂S₄₋ Co₂] proceeds with two main degradation steps. The first step occurs within the temperature range 480–585 K with an estimated mass loss 49.62% (calculated mass loss = 49.66%) which is reasonably accounted for the loss of two molecules of C22H12N4S4 fragment. The DTG curve gives an exothermic peak at 640 K (the maximum peak temperature). The second step occurs within the temperature range 590–790 Kwith an estimated mass loss 34.13% (calculated mass loss = 34.18%), which is reasonably accounted for the loss of rest of the ligand molecule, leaving CoO as residue. The DTG curve gives an exothermic peak at 700 K (the maximum peak temperature). Total estimated mass loss is 83.75% (calculated mass loss = 83.84%). The thermal decomposition of $[Ni_2LCl_2]$ complex (Supplement Fig. S-9b) with the molecular formula [C₃₂H₂₀Cl₂N₈O₂P₂S₄Ni₂] also proceeds with two main degradation steps. The first estimated mass loss of 24.44% (calculated mass loss = 24.84%) within the temperature range 590-620 K could be attributed to the liberation of C₁₁H₆N₂S₂ fragment. The DTG curve gives an exothermic peak at 590 K (the maximum peak temperature). The second step occurs within the temperature range 650-820 K with an estimated mass loss 59.00% (calculated mass loss = 59.04%), which is reasonably accounted for the decomposition of remaining part of the ligand molecule $(C_{21}H_{14}Cl_2N_6P_2S_2)$ leaving NiO as residue. The DTG curve gives an exothermic peak at 760 K (the maximum peak temperature). Total estimated mass loss is 83.84% (calculated mass loss = 83.88). The complex $[Cu_2LCl_2]$ with the molecular formula $[C_{32}H_{20}Cl_2N_8O_2P_2S_4Cu_2]$ is thermally decomposed in two successive decomposition steps (Supplement Fig. S-9c). The first estimated mass loss of 34.38% (calculated mass loss = 34.41%) within the temperature range 540–590 K may be attributed to the loss of $(C_{16}H_{10}N_4S_2)$ fragment. The DTG curve gives an exothermic peak at 553 K (the maximum peak temperature). The second step occurs within the temperature range 661-853 K with the estimated mass loss 48.54% (calculated mass loss = 48.59%) which corresponds to the loss of C₁₆H₁₀N₄S₂Cl₂P₂ fragment leaving CuO as residue. The DTG curve gives an exothermic peak at 770 K (the maximum peak temperature). Total estimated mass loss is 83.00% (calculated mass loss = 82.95%).

The final product of decomposition at 875 K corresponds to the formation of metal oxide as the end product, which was confirmed by comparing the observed/estimated and the calculated mass of the pyrolysis product. From the above thermogravimetric analyses, the overall weight losses for the Co(II), Ni(II) and Cu(II) complexes agree well with the proposed formulae obtained by elemental analyses, IR, UV–Vis, ¹H NMR, ³¹P NMR, Cyclic voltammetry, Mass, and magnetic susceptibility measurements. Finally, the previous findings indicated that the coordination occurs through the nitrogen of the pyridine ring and thiazole ring and the imine NH group to give the structures shown in Supplement Fig. S-10.

4.3.10. Quantum chemical calculations on complexes

Geometry of Cu, Co and Ni complexes was investigated by semiempirical molecular orbital calculations using the PM3 Hamiltonian. The resulting structures prove square planar geometry for Ni complex, distorted square planar geometry for Cu complex and a tetrahedral geometry for the Co complex. These can be detected in their optimized geometry present in Supplement Figs. S-11–S- 13. These quantum chemical calculations agree well with the experimental findings of the spectral and magnetic observations.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.04.005.

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