

# Co-ordination Chemistry of Some First Row Transition Metal Complexes with Multi-dentate Ligand ( 1- benzoyl - 3-(4-methylpyridin -2-yl) thiourea), Spectral, Electrochemical and X – ray Single Crystal Studies

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Cd(II) and Cu(II) perchlorate were coordinated with 1- benzoyl - 3-(4-methylpyridin -2-yl) thiourea ligand. All the prepared compounds are deliberately investigated by all possible spectral tools. A comparative study on IR spectra reveals a neutral bidentate coordinating nature of the ligand towards the two metal ions. The Uv/Vis spectra of the complexes display d-d and MLCT transition bands proposed four coordination geometry for the complexes in different forms. MS analysis data are concerned especially with the base peak which is corresponding to  $C_{28}H_{26}N_6O_2S_2Cu$  and  $C_{28}H_{26}N_6O_2S_2CdCl_2O_8$  ions. The fragmentation patterns are relatively matched with each others. Electrochemical study was carried out on Cu(II) complex using platinum wire and Ag/AgNO<sub>3</sub> as counter and reference electrodes, respectively. The data reflect the irreversible nature of the electrode couple and showed two successive one electron transfer process. X-ray single crystal studies are used to verify the four coordination geometry proposed as well as calculating the crystal parameters beside the structural refinements.

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**Keywords:** X-ray single crystal, Cyclic voltametry, spectral, thiourea

## 1. INTRODUCTION

Chelating ligands with conjugated oxygen or nitrogen donor sites represent some of the most important ligands in coordination chemistry and their metal complexes are useful for homogenous catalysis, chemical vapor deposition, supramolecular chemistry, redox sensing, photophysics, magnetic materials, and so on [1]. Organic compounds containing oxygen, nitrogen and sulfur as donors are extensively studied [2]. These complexes cover several areas ranging from general considerations of

the effect of sulfur and electron delocalization in metal complexes behavior which elaborate their applications [3]. A distinguish biological activity was recorded for most investigated complexes especially with the presence of N,S and O heteroatom's [4-14]. This research is considered a continuation of my work, previously, I have contributed in works nearby this research point [15-17]. The aim of the work is based on the significant role played by the metal complexes of pyridine moiety. I have motivated to prepare new complexes derived from pyridine nucleus, which may serve in different fields. The chemistry of the complexes are elaborately investigated by all possible tools. Concerning with the crystal structures of the complexes have been reported by single crystal X-ray diffraction to justify on the geometry isolated. Moreover, I have studied the electrochemical behavior of Cu(II) complex to emphasis on the oxidation state of the central atom after complexation.

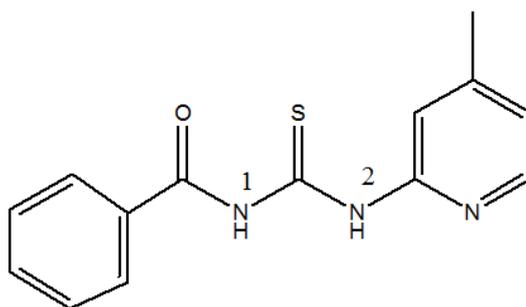
## 2. EXPERIMENTAL

### 2.1. General & Instrumentation

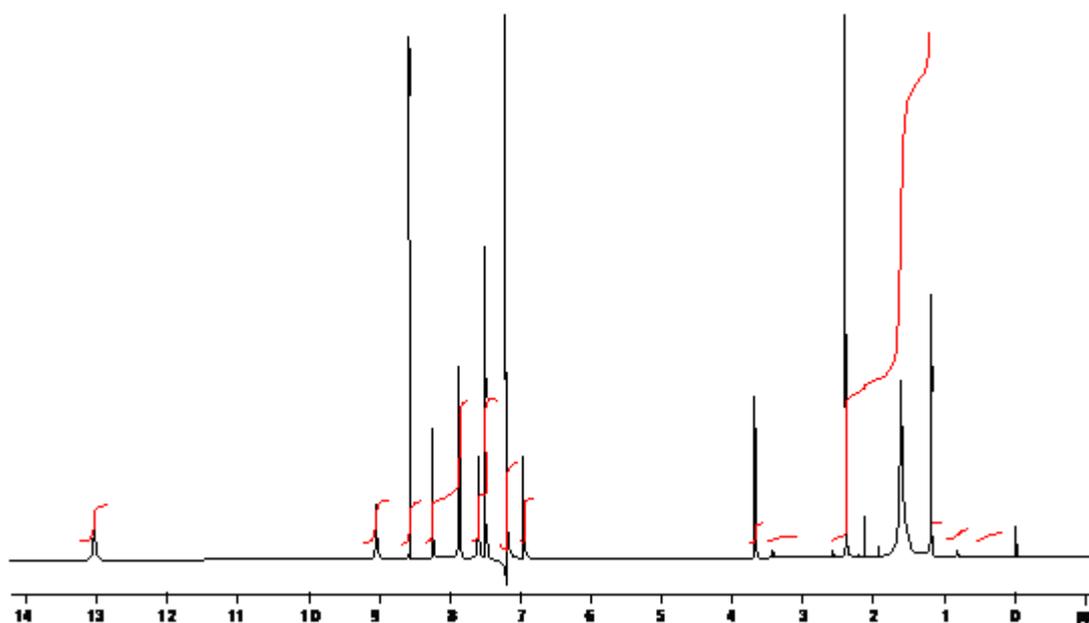
All the compounds used are PDH and purchased from commercial sources and used as it is without previous purification. For infrared spectra, each compound was pressed into a disk with an excess of dried KBr and measured on a Jasco 660 FT-IR spectrophotometer at the range 500 – 4000  $\text{cm}^{-1}$ . Electrospray (ES) and high-resolution (HR) mass spectra were measured on a Waters LCT Premier XE (oa-TOF) mass spectrometer. NMR spectra were measured on a Bruker AM 250-400 or Bruker Av-500 Plus FT-NMR spectrometer. Residual signals of solvent were used for reference for  $^1\text{H}$  and  $^{13}\text{C}$  NMR. UV-VIS absorption spectra were run in HPLC grade acetonitrile (Fisher) and measured on a Jasco V-570 spectrophotometer from 230 to 1,100 nm (optical path length 1.0 cm). Single crystal X-ray data was collected on a Bruker/Nonius Kappa CCD diffractometer using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), equipped with an Oxford Cryostream cooling apparatus. The cyclic voltammetry experiments were carried out with an AUTOLAB PGSTAT12 potentiostat in conjunction with General Purpose Electrochemical System software (GPES version 4.7 for Windows) in a specially designed three-electrode glass cell with a Teflon-coated cell cap. A Bioanalytical platinum working electrode (model no. MF2013) with a 1.6 mm disk was used for all experiments. The counter electrode was a platinum wire and the reference electrode an Ag/AgNO $_3$  electrode. To regain electrochemical sensitivity and reproducibility the working electrode was polished, with 600 grid emery paper, to a mirror surface and then ultrasonicated. Prior to each experiment, the electrode was washed with high performance liquid chromatography (HPLC) grade, CH $_3$ CN and dried in air for about 15 min. A 0.1 M [Bu $_4$ N.BF $_6$ ] (TBATFB) solution in CH $_3$ CN was used as supporting electrolyte. In all cases, ferrocene was used as an internal reference. Solutions were degassed with nitrogen and a nitrogen atmosphere was maintained over the solution during the experiment.

## 2.2. Synthesis of H<sub>2</sub>L ligand and its characterization

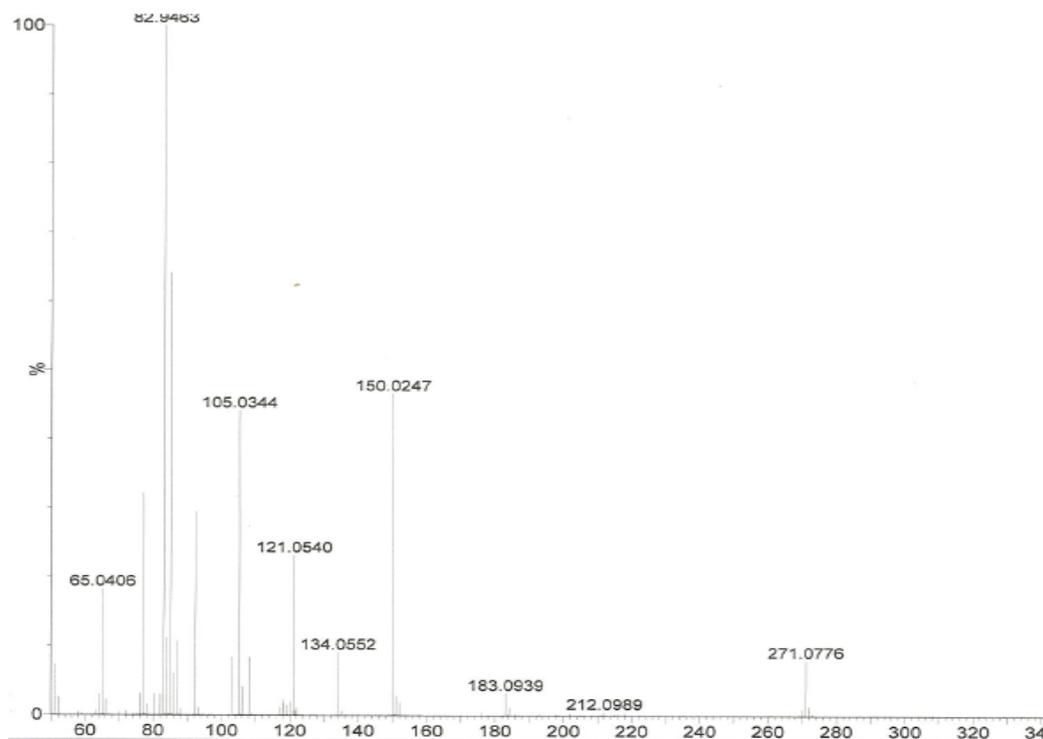
18.49 mmol of 4-methylpyridin -2- amine (2.0 g) dissolved in acetone (50 ml) and benzoyl isothiocyanate (2.48 ml, 18.49 mmol) was added drop- wise. The mixture was heated up to 40 °C for 10 min then allowed to cool at room temperature. The solvent was removed under reduced pressure . Ether was used to precipitate the product as a yellow powder (4.563 g, 91.07%, 16.83 mmol). Recrystallisation from a hot acetonitrile yielded monoclinic crystals (Fig. 1). Significant IR data as follow:  $\nu_{\text{NH}}$  at 3285  $\text{cm}^{-1}$ ;  $\nu_{\text{C=O}}$  at 1677;  $\delta(\text{NH})^1$  at 1606;  $\delta(\text{NH})^2$  at 1556;  $\nu_{\text{C=N}}$  at 1519 and  $\nu^{\text{IV}}\text{C=S}$  at 831  $\text{cm}^{-1}$ .  $^1\text{HNMR}$  (Fig. 2)  $\delta_{\text{H}}$  (400MHz,  $\text{CDCl}_3$ ): 13.0(1H,s, $\text{NH}^2$ ); 9.04(1H,s, $\text{NH}^1$ ); 8.57(2H,d,Py);7.86(2H,d,Py); 6.93-7.49(5H,m,Ar); 3.66(3H,s, $\text{CH}_3$ ); 2.36( $\text{H}_2\text{O}$  of solvent).  $^{13}\text{CNMR}$   $\delta_{\text{C}}$  (250 MHz,  $\text{CDCl}_3$ ): 177.0, 166.6, 151.2 – 148.2, 133- 116, 77.2 and 21.5 for pyridine, benzene and  $\text{CH}_3$  group. Accurate MS (Fig. 3) ( $m/z$ ) =  $\text{M}^+$  271.0776 (calcd. 271.34) of  $\text{C}_{14}\text{H}_{13}\text{N}_3\text{OS}$  and the base peak (100% intensity), 82.95 for an organic part fragment. Uv/ Vis from 230 to 1100 nm in  $\text{CH}_3\text{CN}$ ,  $\lambda_{\text{max}}$ , nm ( $\epsilon\text{M}$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): CT bands are, 308(171433.4) and 267 (292016.5) [17].



**Figure 1.** 1- benzoyl - 3-(4-methylpyridin -2-yl) thiourea, H<sub>2</sub>L ligand



**Figure 2.**  $^1\text{HNMR}$  spectrum of H<sub>2</sub>L ligand



**Figure 3.** MS spectrum of H<sub>2</sub>L ligand

## 2.2. Procedure for the synthesis of complexes

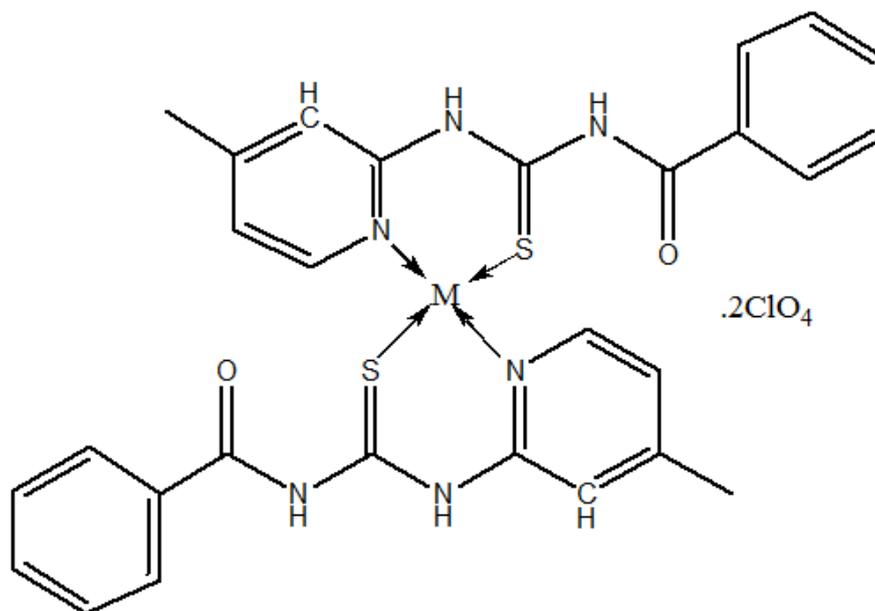
According to this equation;  $2\text{H}_2\text{L} + \text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} \xrightarrow{\text{Solvent}} [\text{M}(\text{H}_2\text{L})_2](\text{ClO}_4)_2$  the equivalent ligand (0mg (0.1845 mmol) was dissolved in a minimum amount of acetonitrile (3ml). The solution was warmed to 60 °C to ensure that the ligand fully dissolved. To this stirring solution, the metal perchlorate, 0.0227g (0.0615 mmol) and 0.0191 g (0.0615mmol) of Cu (II) and Cd(II) salts, respectively dissolved in the same solvent and was added drop wise (*Warning*, perchlorate salts are potentially explosive, care should be taken while handling such complexes). Recrystallization of the complexes was carried out by using diethyl ether and yielded 63.26 % (0.058 mmol) and 52.88 % (0.0322 mmol) for Cu(II) and Cd(II) complexes, respectively.

### 2.2.1 Characterization of $[\text{Cu}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{OS})_2](\text{ClO}_4)_2$ complex

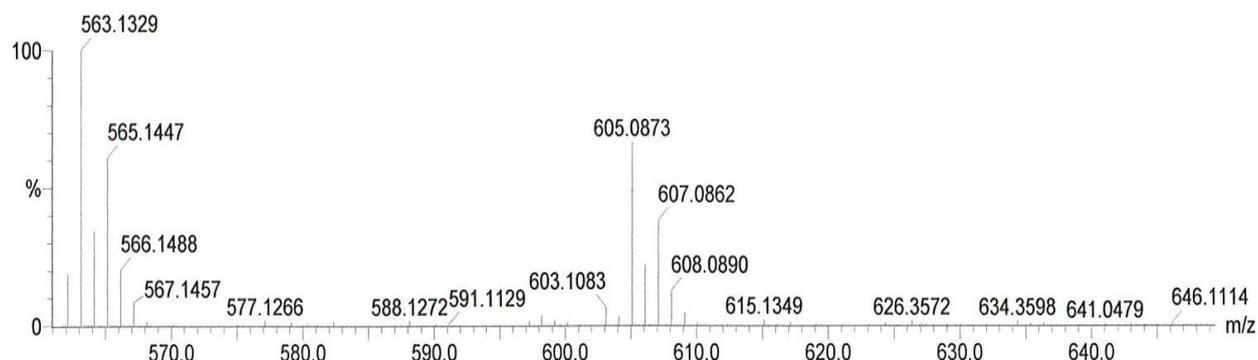
Dark green Monoclinic crystals of the complex (Fig. 4) were investigated: IR data are;  $\nu_{\text{NH}}$  at  $3439 \text{ cm}^{-1}$ ;  $\nu_{\text{C=O}}$  at  $1680$ ;  $\delta(\text{NH})^1$  at  $1615$ ;  $\delta(\text{NH})^2$  at  $1543$ ;  $\nu_{\text{C=N}}$  at  $1518$  and  $\nu^{\text{IV}}_{\text{C=S}}$  at  $802 \text{ cm}^{-1}$ .  $\nu_{\text{Cl-O}}$  at  $1088(\text{m})$  and  $622(\text{s}) \text{ cm}^{-1}$ ;  $\nu_{\text{M-N}}$  and  $\nu_{\text{M-S}}$  at  $540$  and  $510 \text{ cm}^{-1}$ , respectively. Accurate MS (Fig. 5) ( $m/z$ ) =  $646.11(\text{calcd.}805.13)$ , base peak at  $605.09(100\%)$  (calcd.  $605.08$ ) for  $\text{C}_{28}\text{H}_{26}\text{N}_6\text{O}_2\text{S}_2\text{Cu}^{63}$   $\text{Uv/ Vis}$  in  $\text{CH}_3\text{CN}$ ,  $\lambda_{\text{max}}$ , nm ( $\epsilon\text{M}$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ), d-d transitions at ;  $309.5$  ( $21134.65$ ) and  $347.8$  ( $8353.2$ ).

2.2.2 Characterization of  $[Cd(C_{14}H_{13}N_3OS)_2](ClO_4)_2$

Creamy Triclinic needles of the complex (Fig. 4) were investigated: IR data are;  $\nu_{NH}$  at  $3447\text{ cm}^{-1}$ ;  $\nu_{C=O}$  at  $1688$ ;  $\delta(NH)^1$  at  $1622$ ;  $\delta(NH)^2$  at  $1598$ ;  $\nu_{C=N}$  at  $1529$  and  $\nu^{IV}C=S$  at  $796\text{ cm}^{-1}$ .  $\nu_{Cl-O}$  at  $1063(m)$  and  $621(s)\text{ cm}^{-1}$ ;  $\nu_{M-N}$  and  $\nu_{M-S}$  at  $540$  and  $515\text{ cm}^{-1}$ , respectively. Accurate MS (Fig. 6) ( $m/z$ ) =  $985.39(\text{calcd. } 853.99)$ , base peak at  $853.96(100\%)$  for  $C_{28}H_{26}N_6O_2S_2CdCl_2O_8$  ( proposed complex formula).

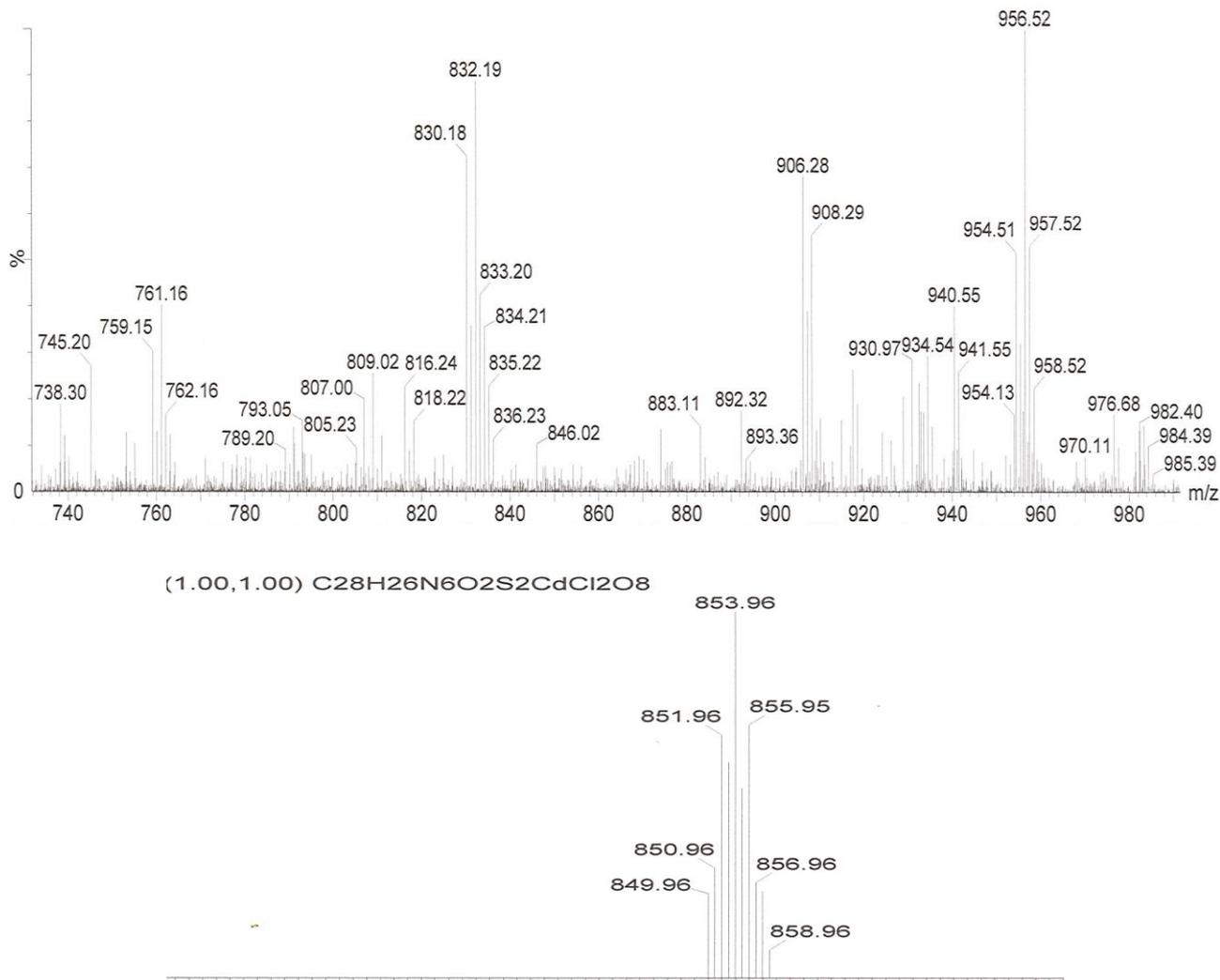


**Figure 4.** The structural formula of the investigated complexes , where M = Cu(II) or Cd(II) ions



Minimum:				-1.5		
Maximum:	200.0	5.0		50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
605.0873	605.0855	1.8	3.0	19.0	1654.4	C28 H26 N6 O2 S2 63Cu

**Figure 5.** MS spectrum of  $[Cu(C_{14}H_{13}N_3OS)_2](ClO_4)_2$  complex



**Figure 6.** MS spectrum of  $[\text{Cd}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{OS})_2](\text{ClO}_4)_2$  complex

### 3. RESULTS AND DISCUSSION

The prepared complexes are highly stable in air, not soluble in water and common organic solvents. They are completely soluble in acetonitrile and producing moderate conducting solutions accompanied with the presence of ionizable perchlorate ions.

#### 3.1. IR and electronic spectra

The ligand  $\nu\text{C}=\text{O}$  and  $\delta\text{NH}^2$  bands appeared at  $1677$  and  $1556\text{ cm}^{-1}$  wave no. (Table 1) this is referring to the presence of intraligand H-bonding but  $\nu\text{C}=\text{N}$  has a normal appearance. Moreover, the band at  $831\text{ cm}^{-1}$  is assigned to another significant contributed group ( $\nu^{\text{IV}}\text{C}=\text{S}$ ). The spectra of the complexes display an observable blue shift with  $\nu\text{C}=\text{N}$  and  $\nu^{\text{IV}}\text{C}=\text{S}$  bands. These bands are attributed to the coordination sites contribute by arms with the central atom in the chelat rings.

**Table 1.** Assignments of the IR Spectral bands ( $\text{cm}^{-1}$ ) of  $\text{H}_2\text{L}$  and its metal complexes

Compound	$\nu_{\text{NH}}^1$	$\nu_{\text{C-N}}$	$\nu_{\text{C=O}}$	$\delta_{\text{NH}}^2$	$\delta_{\text{NH}}^1$	$\nu_{\text{Cl-O}}$	$\nu_{\text{C-S}}^{\text{IV}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-S}}$
1) $[\text{C}_{14}\text{H}_{13}\text{N}_3\text{SO}]$	3285	1516	1677	1556	1606	----	831	.....	.....
2) $[\text{Cu}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{SO})_2](\text{ClO}_4)_2$	3439	1518	1680	1542	1615	1088 622	802	540	510
3) $[\text{Cd}(\text{C}_{14}\text{H}_{13}\text{N}_3\text{SO})_2](\text{ClO}_4)_2$	3447	1529	1688	1598	1622	1063 621	796	540	515

An observable higher shift with  $\nu_{\text{C=O}}$  band is supporting its ruling out from the participation, also the remaining of intraligand H-bonding inside the complex. The complexes spectra reveal characteristic bands at  $\approx 1080$  and  $\approx 620 \text{ cm}^{-1}$  indicative for ionic perchlorate [18,19]. Also, two bands at  $\approx 540$  and  $\approx 510 \text{ cm}^{-1}$  are assigned to  $\nu_{\text{M-N}}$  and  $\nu_{\text{M-S}}$  transitions. The UV/Vis spectra of the ligand and its Cu(II) and Cd(II) complexes were recorded from acetonitrile solution. The ligand shows  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions at 267 and 308 nm, respectively. The spectrum of Cu(II) complex reflects a four-coordinate environment around the central atom in a tetrahedral arrangement. The transitions appeared at 18,690, 28,755 and  $32,314 \text{ cm}^{-1}$  are assigned to the d-d transition band attributed to  ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$  and MLCT bands [20]. The Cd(II) spectrum of square-planar complex reveals charge transfer bands of  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions [21, 22] at 36,132 and  $29,920 \text{ cm}^{-1}$ .

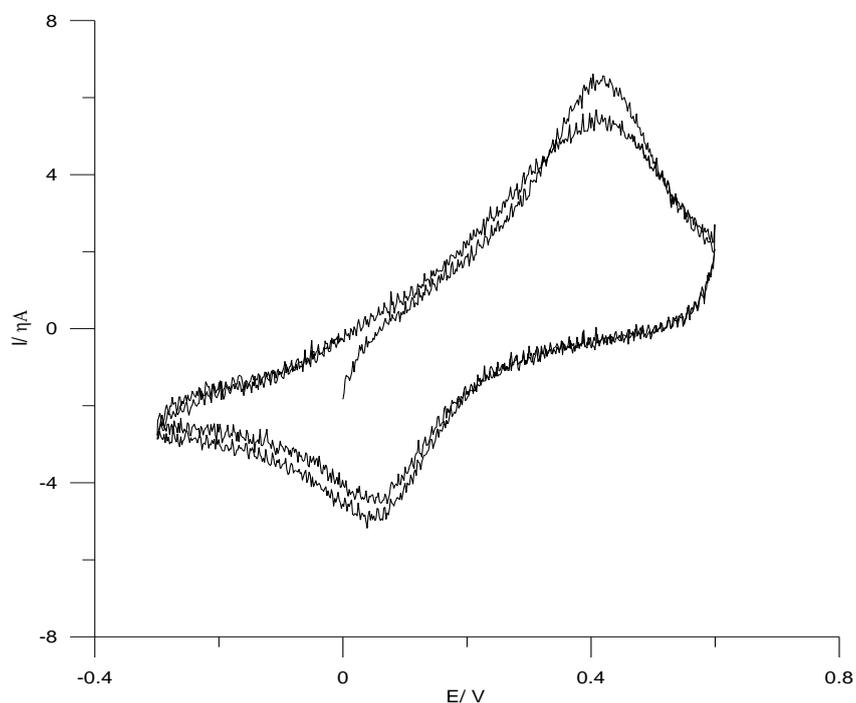
### 3.2. Mass spectral analysis

The mass spectral analysis of the free ligand and its complexes were recorded in  $\text{CH}_3\text{CN}$ . The ligand spectrum displays an accurate molecular ion peak ( $m/z = 271.077$ ) matched with the theoretical proposal. The spectra of the complexes display a notable difference with the molecular ion peak in between the found and the calculated one. This may refer to the probability of a sudden fragmentation may be followed by a definite aggregation for fragments during the evaporation process, which is considered an introductory step in MS analysis. This is an acceptable cause for the positive or negative difference in between the calculated and the found  $m/z$  values. The molecular ion of the Cu(II) complex may lose  $\text{ClO}_4$  groups during the evaporation process although this proposal is not fitted with the results and no possible fragmentation can explain the observed mass spectra. Also, the positive shift in the cadmium complex molecular ion peak may suggest an aggregation of definite fragments. It is sufficient with obtaining the complexes base peaks  $\text{C}_{28}\text{H}_{26}\text{N}_6\text{O}_2\text{S}_2\text{Cu}^{63}$  and  $\text{C}_{28}\text{H}_{26}\text{N}_6\text{O}_2\text{S}_2\text{CdCl}_2\text{O}_8$  formulas. The Cu(II) complex base peak formula is matching with the coordinating area of the complex without perchlorate ions although, the Cd(II) one is matching with all complex formula.

### 3.3 Electrochemical measurements

The electrochemical process is essential with the complexes to assert on the metal ion oxidation state which may be affected during the complexation process due to the ligand basicity. The

effectiveness of CV results from its capability for rapidly observing the redox behavior over a wide potential range. In metal complexes, the redox behavior of a metal centre is also influenced by the nature of the ligand bonded to the metal. The behavior of the Cu(II) complex (Fig. 7) was investigated using the cyclic voltammetric (CV) technique in CH<sub>3</sub>CN solution containing 0.1 M tetra (n-butyl)ammonium perchlorate as the supporting electrolyte. The investigated potential range is -0.3 to +0.6 V, and displayed two well-defined electrode couples. The cyclic voltammogram showed two successive one electron transfer process. The first reduction wave of the complexes is safely assigned to the irreversible couple Cu(II)/Cu(I) with  $E_{pa} = +0.05$  V,  $\Delta E_p (E_{pc} - E_{pa}) = +0.35$  V and represented as follows:  $Cu^{II}L + e^- \leftrightarrow Cu^IL$ . The second couple with  $E_{pc} = +0.40$  V is assigned to irreversible electrode couple Cu<sup>II</sup>/Cu<sup>III</sup> by comparison with analogous Cu(II) complexes [23] the  $E_{1/2} = 0.225$  V. The ratio  $i_{p,c} (6.5) / i_{p,a} (5.0) > 1$  confirms the irreversible nature of the electrode couple [24]. The peak-peak potential separation ( $\Delta E_p$ ) of the electrode couple increased with increasing the scan rate is confirming the occurrence of a slow chemical reaction and a limited mass transfer following the electrode process. Thus, the electron transfer process is irreversible and the species that initially formed in the electrode process may also react further to give products that are not reoxidized at the same potential as in the first formed species [25].

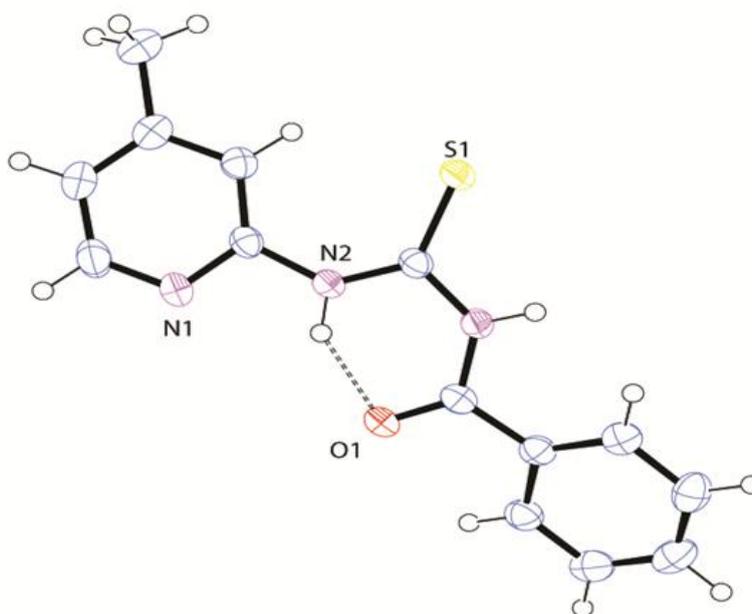


**Figure 7 .** Cyclic voltammogram of Cu(II) complex

### 3.4. Crystallographic studies

Crystal parameters, details of the data collection and structural refinements are presented in Table 2. The data was corrected for Lorentz and polarization effects and for absorption using SORTAV [26]. Structure solution was achieved by direct methods (Sir-92 program system) [27], and

refined by full-matrix least-squares on  $F^2$  (SHELXL-97) [28]. Molecular structures were drawn with ORTEP-3.0 for Windows (version 2.02) [29]. Relevant crystal data are given for all structures in Table 3 along with relevant bond lengths and angles. Yellow monoclinic crystals of the ligand displays bond lengths of C=N and C=S groups are 1.334(3) and 1.667(2) Å, respectively. A similar structures show C=S bond lengths ranging inbetween 1.655 and 1.679 Å. There are one intramolecular hydrogen bond (Fig.8) which help establishing the molecular conformation of H<sub>2</sub>L. Specifically, this interaction occurs between the carbonyl oxygen atom and the thiourea hydrogen atom immediately adjacent to pyridyl group in the 2-position. Hydrogen bond length are 2.0 Å, which found in a normal region. The hydrogen bond interactions in these examples ranges from 1.85 to 2.0 Å [30].

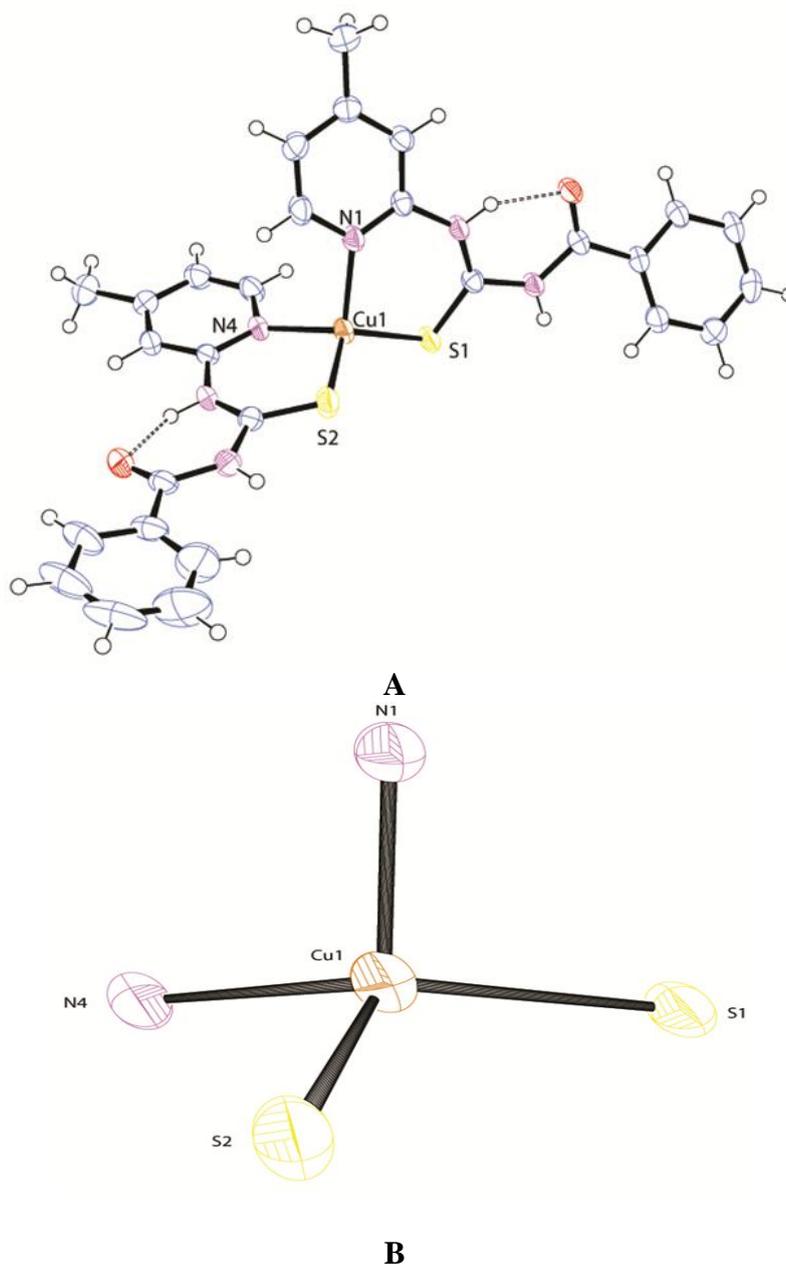


**Figure 8.** ORTEP diagram of H<sub>2</sub>L ligand showing some atomic numbering scheme

#### 3.4.1. X-ray single crystal of [Cu(H<sub>2</sub>L)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> complex

The crystallographic data and structural refinement details are given in Table 2. Selected bond distances and bond angles are given in Table 3. Fig. 9,a shows the ORTEP diagram of the complex with atomic numbering scheme for the coordinating sites. The metal center in the complex is coordinated in an N<sub>2</sub>S<sub>2</sub> core (Fig. 9,b) through bidentate ligand nucleus. The pyridyl nitrogen and thione sulfur atoms are the sites contribute N<sub>2</sub>S<sub>2</sub>. A relatively unsymmetric tetrahedral environment is drawn based on bond distances and bond angles. All the angles surround the central atom are deviated from the classical region (120°) and supporting the distorted structure which is normal with d<sup>9</sup> systems. N(1) – Cu(1) – S(1) 98.40(6)°, N(1) – Cu(1) – S(2) 118.21(7)°, N(4) – Cu(1) – N(1) 100.04(9)°, N(4) – Cu(1) – S(1) 124.91(7)° and N(4) – Cu(1) – S(2) 99.50(7)° [31]. The bond lengths of C=S and C=N groups within two ligands are 1.669(3)°, 1.662(3)° and 1.352(4)°, 1.355(4)° Å, which are longer than those of the corresponding distances in the free ligand. This suggests a considerable delocalization of a charge on the chelate ring [32] which elongated the length of the contributed donor group. The bond distances for Cu-N1, Cu-N4, Cu-S2 and Cu-S1 are 2.077(2)°, 2.049(2)°, 2.2214(8)° and 2.2202(7)° Å,

respectively, which are comparable to the bond lengths reported for similar Cu(II) complexes in the literature [33]. The NS donor sites from bidentate ligands coordinates the Cu(II) center to form two six membered  $C_2N_2SCu$  rings. The complex is stable in the solid state due to delocalization of  $\pi$  – electrons and the presence of  $N2 - H2 \cdots O1(1.853)$ ,  $N5 - H5 \cdots O2(2.222)$  and  $N3 - H3 \cdots O3(1.837)$  hydrogen bond interactions inbetween amine hydrogen towards carbonyl oxygen or perchlorate oxygen. The perchlorate counter ion accept H – bond from one NH group by 2.222 Å length. The two counter ions are absent from the diagram although the presence of their data and I couldn't find a suitable discussion. Although, there is no doubt for its necessitates presence especially with the appearance of all ligand hydrogen atoms neighboring to C=S and C=O groups which exclude the elimination of perchloric acid molecules.



**Figure 9. a)** ORTEP diagram of Cu(II) complex showing some atomic numbering scheme, **b)** the geometrical core of the complex

**Table 2.** Crystallographic data for H<sub>2</sub>L, [Cu(H<sub>2</sub>L)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> and [Cd(H<sub>2</sub>L)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> complexes

The parameter	ligand	Cu(II) complex	Cd(II) complex
Empirical formula	C <sub>28</sub> H <sub>26</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	C <sub>30</sub> H <sub>29</sub> Cl Cu N <sub>7</sub> O <sub>6</sub> S <sub>2</sub>	C <sub>28</sub> H <sub>26</sub> Cd Cl <sub>2</sub> N <sub>6</sub> O <sub>10</sub> S <sub>2</sub>
Formula weight	542.67	746.71	853.97
T(K)	150(2)	150(2)	150(2)
$\lambda$ (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P21/c	P21/c	P-1
a(Å)	11.9590(4)	11.0690(2)	7.3260(3)
b(Å)	5.2260(2)	29.7550(5)	10.0240(4)
c(Å)	21.6520(9)	10.3530(2)	11.7150(7)
$\beta$ (°)	96.9930(10)°	109.6680(10)	71.980(2)
$v$ (Å <sup>3</sup> )	1343.13(9)	3210.91(10)	804.84(6)
z	2	4	1
$\rho_{\text{calc}}$ (Mg cm <sup>-3</sup> )	1.342	1.545	1.762
$\mu$ (mm <sup>-1</sup> )	0.236	0.949	1.041
F(000)	568	1536	430
Crystal size (mm)	0.40 x 0.10 x 0.10	0.35 x 0.35 x 0.30	0.30 x 0.20 x 0.10
$\Theta$ rang for data collections (°)	2.40 to 27.51	2.83 to 27.51	2.93 to 27.50
Index ranges	-15<=h<=15, -6<=k<=6, -28<=l<=27	-14<=h<=14, -38<=k<=35, -13<=l<=13	-9<=h<=9, -12<=k<=13, -15<=l<=12
No. of reflections collected	5410	12213	5468
N0. Of independent reflections ( $R_{int}$ )	3045(0.0470)	7147(0.0321)	3642(0.0335)
No. of data /restraints/parameters	3045/0/173	7147/0/427	3642/0/224
Goodness-of-fit(GOF) on F <sup>2</sup>	1.045	1.023	1.078
$R_1, wR_2^{ab}$ [I>2 $\sigma$ (I)]	0.0527, 0.1204	0.0470, 0.1048	0.0406, 0.0888
$R_1, wR_2^{ab}$ [all data]	0.0837, 0.1338	0.0681, 0.1157	0.0513, 0.0940
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.292 and -0.358	0.629 and -0.534	0.413 and -0.905

**Table 3.** Selected bond lengths (Å) and angles (°) for the Cu(II) complex

<b>Bond lengths</b>		S(1)-Cu(1)	2.2202(7)
C(5)-N(1)	1.354(4)	S(2)-Cu(1)	2.2214(8)
C(7)-S(1)	1.669(3)		
N(1)-Cu(1)	2.077(2)		
N(4)-Cu(1)	2.049(2)		
<b>Bond angles</b>			
C(5)-N(1)-Cu(1)			
C(1)-N(1)-Cu(1)	126.94(18)	N(4)-Cu(1)-N(1)	100.04(9)
C(19)-N(4)-Cu(1)	115.96(19)	N(4)-Cu(1)-S(1)	124.91(7)
C(15)-N(4)-Cu(1)	126.10(19)	N(1)-Cu(1)-S(1)	98.40(6)
C(7)-S(1)-Cu(1)	116.72(18)	N(4)-Cu(1)-S(2)	99.50(7)
C(7)-S(1)-Cu(1)	105.56(9)	N(1)-Cu(1)-S(2)	118.21(7)
	106.53(11)	S(1)-Cu(1)-S(2)	115.98(3)

Selected bond lengths (Å) and angles (°) for Cd(II) complex

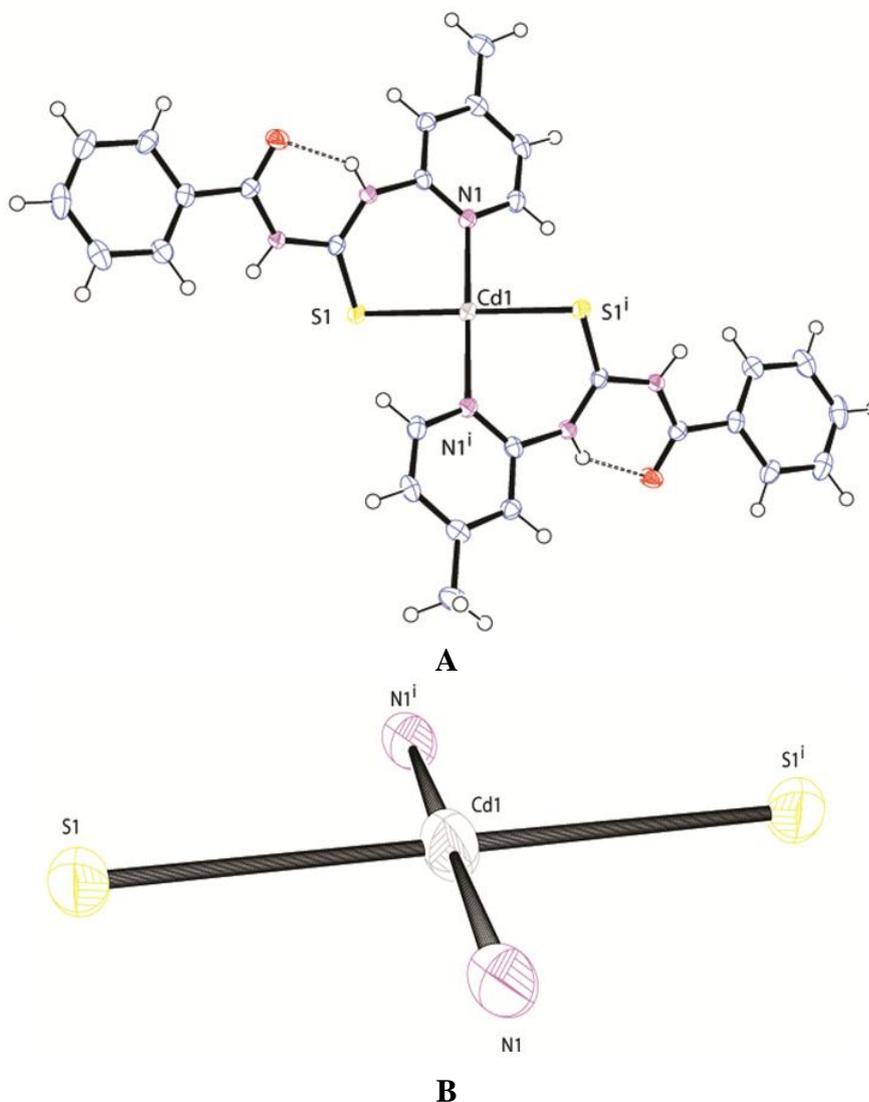
<b>Bond lengths</b>		S(1)-Cd(1)	2.5746(8)
C(5)-N(1)	1.336(4)	Cd(1)-N(1)#1	2.293(3)
C(6)-S(1)	1.689(3)	Cd(1)-O(2)#1	2.474(2)
N(1)-Cd(1)	2.293(3)	Cd(1)-S(1)#1	2.5746(8)
<b>Bond angles</b>			
C(5)-N(1)-Cd(1)		O(2)-Cd(1)-O(2)	180.00(7)
C(1)-N(1)-Cd(1)	123.9(2)	N(1)-Cd(1)-S(1)#1	95.95(7)
C(6)-S(1)-Cd(1)	119.6(2)	N(1)#1-Cd(1)-S(1)#1	84.05(7)
Cl(1)-O(2)-Cd(1)	97.21(10)	O(2)#1-Cd(1)-S(1)#1	85.65(6)
N(1)#1-Cd(1)-N(1)	135.77(14)	O(2)-Cd(1)-S(1)#1	94.35(6)
N(1)-Cd(1)-O(2)#1	180.00(8)	N(1)-Cd(1)-S(1)	84.05(7)
N(1)#1-Cd(1)-O(2)#1	86.48(8)	N(1)#1-Cd(1)-S(1)	95.95(7)
N(1)-Cd(1)-O(2)	93.52(8)	S(1)#1-Cd(1)-S(1)	180.00(4)
N(1)#1-Cd(1)-O(2)	93.52(8)		
	86.48(8)		

### 3.4.2. X-ray single crystal of $[Cd(H_2L)_2](ClO_4)_2$ complex

Figure 10,a, shows the ORTEP diagram of the complex together with the atomic numbering scheme for the coordinating sites. Pair of bidentate ligands taking place in a relatively regular square-planar geometry (Fig. 10,b). The binucleus ligands coordinate through pyridyl nitrogen and thione sulphur atoms.

The crystallographic data and structural refinement details are given in Table 2. Selected bond distances and bond angles are presented in Table 3. The Cd-N(1) and Cd-S(1) bonding have distances of 2.293(3)° and 2.5746(8)° Å, respectively, which are comparable to the bond lengths reported elsewhere [34,35]. Two six membered  $C_2N_2S$  chelate rings are forming by the two ligands. Most of angles surround the central atom are deviated from the classical region (90°). A small deviation is observed with, N(1)-Cd(1)-S(1)# 95.95(7)°, N(1)-Cd(1)-S(1) 84.05(7)° and N(1) #-Cd(1)-S(1) 95.95(7)° angles but a standard appearance with N(1)-Cd(1)-N(1)# 180.00(8)° and S(1)#-Cd(1)-S(1)180.00(8)° angles. Such appearance represents a slight distortion from an ideal geometry. The

bond lengths of C=S and C=N groups in the complex are 1.689(3)<sup>o</sup> (L) and 1.354(4)<sup>o</sup> Å(L) (L= longer). Which are longer than those of the corresponding distances in the free ligand due to the bonding towards the Cd(II) center.



**Figure 10. a.** ORTEP diagram of Cd(II) complex showing some atomic numbering scheme, **b)** the geometrical core of the complex

The bond C(7) –O(1) distance, 1.220(4)<sup>o</sup>, shows partial double bond character due to the delocalization of  $\pi$  – electrons throughout the aromatic ring [36]. Also, the Cd(II) complex is stable in the solid state due to  $\pi$  – electron delocalization and the presence of N2 – H2 $\cdots$ O1(1.831), N2 – H2 $\cdots$ O1(2.524) and N2 – H2 $\cdots$ O3(2.101) H- bond interaction inbetween amine hydrogen, carbonyl oxygen and perchlorate anion. The two counter ions are absent from the diagram, although their presence in MS base peak formula. A strong interaction may be proposed in between the central atom and the perchlorate oxygen based on the presence of the bond length and bond angles data includes a non coordinating anion (ClO<sub>4</sub>)<sup>-</sup>.

#### 4. CONCLUSION

Two metal ion complexes are prepared using 1- benzoyl - 3-(4-methylpyridin -2-yl) thiourea ligand. The isolated complexes are investigated elaborately based on spectral tools. The ligand behaves as bidentate nucleus towards the metal ions through C=S and C=N ( pyridine). The four coordination arrangements are appeared with the metal ions through two ligand nucleus. The tetrahedral geometry is clearly appeared with Cu(II) complex in X-ray single crystal diagram, moreover a square – planar are observed with Cd(II) complex. Electrochemical study was carried out on Cu(II) complex to support the ion oxidation state which is not affected during the complexation. A notable difference was observed the complexes molecular formulas and the molecular ion peak appeared. Such observation was discussed briefly.

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