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Self-organized three dimensional architectures based on non-covalent interactions in square planar Cu(II) thiosemicarbazone: Solvent mediated crystallization and EPR based correlation study

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Abstract

A series of copper complexes of 2-acetylpyridine-N⁴-methylthiosemicarbazone (HL4M) were synthesized and characterized by elemental analyses, UV–Vis, FT-IR, conductivity and EPR studies. The molecular structures of [Cu(L4M)Cl] (1), [Cu(L4M)I] (2), [Cu(L4M)OAc]·H₂O (3) and [Cu(μ -S-L4M)(NCS)]₂·DMSO (4) were confirmed by single crystal X-ray crystallography. Complexes 1, 2 and 3 have square planar geometry constituted by NNS donor sites from deprotonated thiosemicarbazone ligand and the fourth site is occupied by anionic group/atom. Complex 4 is a centrosymmetric dimer. The XRD results revealed that the solvents play a decisive role in the crystallization of products. These four complexes exhibit strong hydrogen bonding interactions in the solid state and are self-assembled into infinite 3D supramolecular structure *via* $\pi \cdots \pi$ stacking interactions. The g_{\parallel} and A_{\parallel} of complexes were analyzed by Peisach–Blumberg plot which proves an inverse correlation among NNS and ONS thiosemicarbazone complexes.

Keywords: Copper complexes, X-ray crystal structure, Solvent effect, Hydrogen bonding, Supramolecular structures, A_{\parallel} - g_{\parallel} correlation

1. Introduction

Thiosemicarbazones, an important class of N–S donor ligands, have shown wide range of coordination modes, flexible coordination fashions, structural diversity and outstanding supramolecular binding with most of the transition or rare earth metal ions. Cu(II) thiosemicarbazone chemistry remains an area of unabated attention due to their catalytical, analytical and biological applications. [1-3] Among these, N-heterocyclic thiosemicarbazones have attracted more attention, because many of them displayed promising anticancer activity [4].

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Cu(II) complexes of the type [CuLX], where L is an anionic tridentate thiosemicarbazone and X is a monoanionic donor like Cl, I, OAc etc. and its binuclear complexes are especially attractive due to

their different coordination chemistry. Cu(II) atoms can be bridge through thiolato sulfur atom or by the X atoms giving rise to a centrosymmetric dimer or a non-centrosymmetric box dimer [5-7]. The underlying reasons that govern the nature of the bridging atom (i.e. thiolato bridged versus X-bridged dimers) are not clear to date. The structural motifs of complex molecules are determined by several factors and the changes in the crystallization conditions often leads to structural diversities [8]. In particular, solvents have significant impact on crystallization process and on the coordination trend of the metal centres. They generally affect the crystal structures of coordination complexes in the following ways: (i) solvents participating in coordination highly influence the coordination environment and geometry of the metal ions; (ii) solvents are not coordinated to the metal ions, but they exist in the crystal lattice as guest molecules; and (iii) solvents are not found in the final products, but they have great impact on crystal growth and induce different structural aggregations [9]. However, the exact reasons for these solvent-induced behavior are still under investigation.

In the present work, we have used four different monoanions to prepare copper(II) complexes and except in the case of thiocyanate co-ligand we obtained mono-nuclear complexes. In recent years, self-assembly directed by non-covalent interactions are increasingly used as a powerful tool for the bottom up fabrication of supramolecular architectures. Herein, we report the synthesis, characterization, crystal structures, spectral studies and the role of secondary interactions in the creation of molecular architectures. Interestingly, the use of different solvent systems directly influenced the competitive coordination among components and crystallization of the products. An attempt is made to correlate the hyperfine splitting (A_{II}) and g factor (g_{II}) in copper(II) complexes of ONS and NNS donor ligands.

2. Experimental

2.1. Materials and techniques

The solvents were purchased from Merck and the reactants for syntheses were procured from Aldrich Sigma Ltd. The elemental analysis of carbon, hydrogen, nitrogen and sulfur were carried out using an elementar model Vario EL III elemental analyzer. The IR absorption spectra were performed with a JASCO FT-IR-5300 Spectrometer in the 4000-400 cm⁻¹ region by making their KBr discs. The electronic spectra were taken on a Spectro UV-vis Double beam UVD-3500 spectrometer in the 200-900 nm range. The EPR spectra were recorded on a Varian E-112 X-band spectrometer using TCNE (g = 2.00277) as standard. Systronic model 303 direct reading conductivity bridge was employed for molar conductivity measurements.

2.2. Synthesis

2.2.1. Synthesis of 2-acetylpyridine- N^4 -methylthiosemicarbazone (HL4M)

 N^4 -methylthiosemicarbazide (0.1051 g, 1mmol) dissolved in 10 mL hot 10% acetic acid solution was slowly mixed with 2-acetylpyridine (0.121g, 1 mmol) in the same solution with stirring. The complete mixture was then stirred for additional 30 min. The resulting pale yellow solid was filtered off, washed with hot water, ethanol and dried. Crude product was recrystallized from dichloromethane to yield X-ray quality single crystals by slow evaporation at room temperature. The crystal structure has been already published [10].

The ligand was obtained with 50% yield, M.P.158 °C. *Anal*.Calc. for C₉H₁₂N₄S (208.288): C, 51.90; H, 5.81; N, 26.90; S, 15.39. Found: C, 51.49; H, 5.33; N, 27.35; S, 14.74%. IR (KBr, cm⁻¹): $v(N^{4-}H)$ 3290s; $v(N^{3}-H)$ 3240s; v(C=N) 1534vs; v(N-N) 1116w; v(C=S) 832w; $v(\rho(ip))$ 616. Mass to charge ratio (m/z): 208.2 (M⁺).

2.2.2. Synthesis of [Cu(L4M)Cl] (1)

A suspension of the HL4M (0.104 g, 0.5 mmol,) in 10 mL of EtOH was heated to boiling and 0.5 mmol (0.0852 g) of CuCl₂·H₂O dissolved in minimum amount of water was then added. The mixture on stirring for about 30 minutes afforded green precipitate and single crystals suitable for study was obtained by redissolving the product in DMSO and slowly evaporating the solvent. Yield, 38%. *Anal.* Calc. for C₉H₁₁CuClN₄S (306.27): C, 35.29; H, 3.62; N, 18.29; S, 10.47. Found: C, 35.04; H, 3.91; N, 17.89; S, 10.06%. Λ (ohm⁻¹cm²mol⁻¹, DMF): 4.8. IR (KBr, cm⁻¹): v (N⁴⁻H) 3303s; v(C=N) 1518vs; v(N–N) 1079w; v(C=S) 773w; v(p(ip)) 626m.

2.2.3. Synthesis of [Cu(L4M)I] (2)

An acetonitrile solution containing cuprous iodide (0.0955 g, 0.5 mmol) was added with constant stirring to HL4M (0.104 g, 0.5 mmol) in EtOH (CH₃CN:EtOH, 1:3) and refluxed. A dark brown shinning residue started to form and refluxing continued for 1 hour. The product was filtered and dried. Dark green crystals were obtained by slow evaporation of its DMSO solution. Yield, 40%. *Anal.* Calc. for C₉H₁₁CuIN₄S (397.74): C, 27.18; H, 2.79; N, 14.09; S, 8.06. Found: C, 27.42; H, 2.91; N, 14.18; S, 7.51%. Λ (ohm⁻¹cm²mol⁻¹, DMF): 30. IR (KBr, cm⁻¹): v(N^{4–}H) 3319s; v(C=N) 1515vs; v(N–N) 1075w; v(C=S) 763w; v(ρ (ip)) 640m.

2.2.4. Synthesis of $[Cu(L4M)OAc] \cdot H_2O(3)$

To a solution of HL4M (0.104 g, 0.5 mmol) in hot ethanol was added a solution of $Cu(OAc)_2 \cdot H_2O$ (0.0995 g, 0.5 mmol) in water. The resultant deep green solution was stirred with refluxing for 1 hour, cooled and the solution was left to stand at room temperature. Few days later, dark green

shining crystals that formed was filtered, washed and dried. Yield, 64%. *Anal.* Calc. for $C_{11}H_{16}CuN_4O_3S$ (347.90): C, 37.98; H, 4.64; N, 16.11; S, 9.22. Found: C, 37.54; H, 4.27; N, 15.85; S, 8.69%. Λ (ohm⁻¹cm²mol⁻¹, DMF): 26. IR (KBr, cm⁻¹): v(N^{4–}H) 3265s; v(C=N) 1534vs; v(N–N) 1022w; v(C=S) 773w; v(\rho(ip)) 617m. v(C–O)_{as} 1587; v(C–O)_{sym} 1338.

2.2.5. Synthesis of $[Cu(\mu$ -S-L4M)(NCS)]₂· DMSO (4)

An ethanolic solution of HL4M (0.104 g, 0.5 mmol) is slowly added to aqueous solution of KSCN (0.0485 g, 0.5 mmol) and stirred for 10 min. The mixture was then refluxed by adding solution of $Cu(OAc)_2 \cdot H_2O$ (0.0995 g, 0.5 mmol) in water. The resultant green precipitate was washed, dried and recrystallized from DMSO. Yield, 32%. *Anal.* Calc. for $[Cu(\mu-S-L4M)(NCS)]_2 \cdot C_2H_6OS$ (655.95): C, 36.52; H, 3.37; N, 21.29; S, 19.50. Found: C, 36.93; H, 3.28; N, 20.85; S, 19.69%. Λ (ohm⁻¹cm²mol⁻¹, DMF): 32. IR (KBr, cm⁻¹): (N^{4–}H) 3325s; v(C=N) 1590vs; v(N–N) 1082w; v(C=S) 783w; v(\rho(ip)) 675m,

2.3. X-ray data collection, structure solution and refinement

Crystallographic data were collected with a Bruker SMART APEX diffractometer with graphite monochromated Mo K α ($\lambda = 0.71073$ Å) X-ray source. Bruker SMART software was used for data acquisition and Bruker SAINT Software for data integration [11]. Absorption corrections were carried out using SADABS based on Laue symmetry using equivalent reflections [12]. The structure was solved by direct methods and refined by full-matrix least-squares calculations with the SHELXL-97 software package [13]. All non-hydrogen atoms were refined with anisotropic displacement parameters and positions of hydrogen atoms were located in the difference Fourier maps and were placed in calculated positions and refined as riding atoms: C-H = 0.93 \Box (heteroaromatic), 0.96 \Box (CH₃) and N-H = 0.86-0.87 \Box with U_{iso} (H) = 1.2 U_{eq} (C,N). Bond lengths and angles were restrained to ensure proper geometry using DFIX and DANG instructions. All the graphical plots were made using ORTEP 3 and MERCURY 3.8 programs [14].

In complex **4** the non-coordinating DMSO molecule is disordered over two conformations with refined occupancies of 0.719(7) and 0.281(7) respectively. For these atoms, SIMU/ISOR/SADI restraints were applied [15].

3. Results and discussion

3.1. Comments on synthesis – An insight into solvent effects on crystallization

Reactions of copper salts with neutral thiosemicarbazone involved deprotonation at ³N position and coordination to Cu(II) center as anion. The structural motifs of the complexes lie on several factors, such as metal-ligand ratio, coordinated anions, pH, experimental conditions, solvent systems etc. Complexes **1**, **2**, and **3** have the same stoichiometry [Cu(L4M)X] (X = Cl, I, OCOCH₃) with four coordinate square planar structure (structure I) and complex **4** has a dimeric structure (structure III).



Figure 1. Coordination modes in NNS donor Cu(II) thiosemicarbazone complexes.

In order to investigate the effect of solvents on crystallization, we used different solvent conditions for the synthesis. The product was isolated as precipitate in all cases except for **3**. No other solvent system (water/EtOH/acetonitrile) yielded good quality single crystals for analysis. Dissolving either the ligand or copper salt in methanol, DMF, dichloromethane and CHCl₃ did not lead to the formation of good quality crystals and no X-ray structure could be established. In order to further investigate the effect of solvents, we made a brief survey on different thiosemicarbazones complexes and its crystallization conditions. The final structures primarily rely on the polarity of the solvent used for recrystallization.

thiosemicarbazone and its copper(II) complexes

Table 1. Color, molar conductivity and partial elemental analyses of 2-acetylpyridine-N⁴-methyl-3-

Compound	Colour	٨	Found (Calc.) %						
Compound	Coloui	/1m -	С	Н	Ν	S			
HL4M	Colourless		51.49 (51.90)	5.33 (5.81)	27.35(26.90)	14.74(15.39)			
[Cu(L4M)Cl] (1)	Dark green	4.8	35.04 (35.29)	3.91 (3.62)	17.89(18.29)	10.06(10.47)			
[Cu(L4M)I] (2)	Dark green	30	27.42 (27.18)	2.91 (2.79)	14.18(14.09)	7.51(8.06)			
$[Cu(L4M)OAc] \cdot H_2O(3)$	Dark green	26	37.54 (37.98)	4.27 (4.64)	15.85(16.11)	8.69(9.22)			
$[Cu(L4M)NCS]_2 \cdot C_2H_6OS (4)$	Dark green	15	36.93 (36.52)	3.28 (3.37)	20.85 (21.29)	19.69 (19.50)			

Reactions of copper halides/acetate with thiosemicarbazones (NNS) either produce mononuclear (structure I and II) or binuclear (structure III and IV, with bridging halogen/sulfur atoms) edifices

(Figure 1). Structural analysis reveal that complexes **1**, **2** and **3** exist as a discrete mononuclear structure (structure I). Correlating the preparation methods and structural features, such a presupposition could be reached: in the Cu(II) thiosemicarbazone systems introduction of different solvent systems can yield complexes with different stoichiometries and structural features.

Ligand system Mother liquor Structure Ref [CuL₁Br] NNS DMSO [17] $[CuL_1Cl]$ DMSO DMSO [CuL₁I] [CuL₂C1] DMSO/ether [18] DMSO/CH₃COCH₃ [CuL₃Cl] [19] [CuL₄(OAc)] NNS EtOH [20] [CuL1(OAc)] NNS EtOH/H₂O $[CuL_5 \mu - Cl]_2$ NNS CH₃OH [21] [CuL6 µ-Cl]2 CH₃OH/CH₃Cl [22] [Cu(HL7) µ-Cl2]2 CH₃OH/CCl₄ [23] CH₃OH/CH₃Cl/DCM $[CuL_8(\mu-N_3)]$ [24] DMF/CH₃OH $[Cu_2L_9(\mu\text{-OAc})_2]$ NNO [25] [Cu(µ-SL10)NCS)]2 NNS DMSO [26] $[Cu(\mu-SL_1)NCS)]_2$ NNS DMSO $[Cu(\mu-SL_{11})Cl]_2 \cdot 2 DMF$ NNO DMF/EtOH [27] DMF/EtOH [Cu(µ-SL12)Cl]2·2 DMF NNO [27] * Present work

Table 2. Effect of solvents on structural diversity of Cu(II) complexes

Present work

 $HL_1 = 2$ -Acetylpyridine N4-methyl thiosemicarbazone $HL_2 = 2$ -Benzovlpyridine N4-azepanethiosemicarbazone

 $HL_2 = 2$ -Acetylpyridine N4-tolyl thiosemicarbazone

 $HL_4 = 2$ -Pyridine for mamide N4-dimethyl thiose micarbazone

 $HL_5 = Pyridine-2-carbaldehyde-4-methyl-4-phenyl-3-thiosemicarbazone$

 $HL_{6} = 2$ -Benzoylpyridine N4,N4-(butane-1,4-diyl)thiosemicarbazone

 $HL_7 = 2$ -Pyridineformamide thiosemicarbazone

 $HL_8 = Di-2$ -pyridyl ketoneN4-methyl, N(4)-phenylthiosemicarbazone

 $HL_9 = 2$ -Benzoylpyridine-N(4)-phenylsemicarbazone

HL₁₀ = Pyridine-2-carbaldehyde thiosemicarbazone

 $HL_{11} = 5$ -Methyl-2-oxoindolin-3-ylidene)-N-phenylhydrazinecarbothioamide

 $HL_{12} = 5$ -Fluoro-2-oxoindolin-3-ylidene)-N-phenylhydrazinecarbothioamide

Nucleophilicity of halogens in polar protic solvents follows the order F' < Cl' < Br' < I' and their reactivities are greatly influenced by solvation *via* hydrogen bonding interactions. These solvated species are more stable and less reactive compared to unsolvated "naked" anions. As a result, the electrophilic copper center devoid of electrons forced to form halogen/sulfur bridges to partially balance the electron deficiency. Polar, aprotic solvents such as DMSO and DMF do not solvate anions. This decreased solvation is enough to balance the electrophilic Cu(II) center. Consequently, most of the nucleophiles react more rapidly in solutions prepared from these solvents. Thus, for reaction in DMSO solution, reactivity order of halogens get reversed. Dissolution of dimeric complexes in DMSO can lead to partial dissociation and form different structural aggregates with readily available halogen ions and achieve greater structural stability than in protic solvents. Therefore, we can infer that, in aforementioned systems solvent plays a crucial role in crystallization which sequentially influence the geometry of the complexes. Ligands forming hydrogen bonds are

well solvated by protic solvents and the complex formation with such ligands in protic solvents will therefore be weaker than in aprotic solvents [16]. An exhaustive review of the literature [17-27] shows that, these facts are in agreement with studies on analogous NNO and NNS donor copper(II) complexes, which is shown in Table 2.

Presence of powerful sigma-donor groups (pyridyl and azomethine nitrogen) very effectively stabilizes the higher oxidation state of copper. Accordingly, strong electron donation by the ligand facilitates the ready oxidation of Cu(I). Cu(II) is a borderline acid and anionic ligand coordinates through relatively harder nitrogen ends and soft sulfur end on the basis of HSAB theory.

We employed copper(I) iodide salt for the synthesis of complex 2 due to the reducing nature of the bulky iodide ion. Eventhough, the formation of Cu^{II} -I bond was a challenging task, attempts made to crystallize the complex were finally successful. Shikha *et al* suggested a probable pathway that paved the way for the synthesis of complex 2 (Scheme 1). The neutral ligand reacts with Cu–I to form an adduct (A) by coordination through the S donor atom and undergoes a rearrangement to form an intermediate species B. The formation of complex 2 (C) is achieved by a rapid proton-coupled electron transfer (PCET). PCET occurs only *via* the presence an additional coordinating functionality in the proximity of the donating centers, such as pyridyl group, and no similar reaction occurs if the groups at C2 are Ph, H or Ph, Ph. Thus, the presence of pyridyl group at the C2 atom appears to assist the simultaneous tautomeric transformation and electron transfer from the CuI center. Thus, the thiosemicarbazone ligands with pyridyl rings at the aldehydic/ketonic fragment are capable of forming stable Cu^{II}–I complexes by coordinating in a tridentate manner. The possibility of aerobic oxidation at the copper(I) center is ruled out because the reactions for the formation of the complexes gave identical products under a N₂ atmosphere [28].



Scheme 1. PCET process in the formation of complex 2.

The presence of acidic ³N–H allows ligand to remain either as the thione tautomer or the thiol tautomer or as a mixture of both tautomers. Earlier studies [29, 30] have shown that, in the solid state

as well as in solution, thiosemicarbazones remain in their thione tautomeric form. It can coordinate with metal ions in both the protonated thione and deprotonated thiolato form [31]. Complexes containing the neutral ligand only result from reactions in weakly acidic aqueous media or nonaqueous solvents of low polarity [32]. The molar conductivity values of the complexes show that they are non-electrolytes and the analytical data of the complexes are listed in Table 1.

3.2. Structural commentary

3.2. Structural commentary							
Table 3. Crystal and	structure refinement	data for complexes 1-4	l	2			
				6			
Parameters	[Cu(L4M)Cl] (1)	[Cu(L4M)I] (2)	[Cu(L4M)OAc]·H ₂ O (3)	$[Cu(\mu-S-L4M)(NCS)]_2 \cdot C_2H_6OS (4)$			
Empirical formula Formula weight	C ₉ H ₁₁ ClCuN ₄ S 306.27	C ₉ H ₁₁ CuIN ₄ S 397.74	C ₁₁ H ₁₆ CuN ₄ O ₃ S 347.90	$\begin{array}{c} C_{22}H_{28}Cu_2N_{10}OS_5\\ 735.94 \end{array}$			
Temperature	296(2) K	293(2) K	293(2) K	293(2) K			
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å			
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic			
Space group	<i>P</i> 2 ₁ /n	P21/n	<i>P</i> 2 ₁ /c	PI			
Unit cell dimensions a (Å)	0.00004.0						
b (Å)	8.0660(16) 15.994(4)	8.1465(9) 16.3888(19)	7.0284(5 11.1368(9)	9.418(2) 13.556(3)			
c (Å)	9.193(2)	9.5084(12)	19.3407(16)	13.883(3)			
α (°)	90.00	90.00	90.00	61.581(6)			
β(°)	92.356(7)	96.199(3)	99.338(3)	87.597(6)			
γ (°)	90.00	90.00	90.00	80.474(7)			
Volume	1185.0(5) A ³	1262.1(3) A ³	1493.8(2) A ³	1536.0(6) A ³			
Z	4	4	4	2			
Calculated density	1.717 Mg/m ³	2.093 Mg/m ³	1.547 Mg/m ³	1.591Mg/m ³			
Absorption coefficient	2.221 mm ⁻¹	4.320 mm ⁻¹	1.613 mm ⁻¹	1.760 mm ⁻¹			
F(000)	620	764	716	764			
Crystal size	0.50 x 0.30 x 0.30 mm	0.30 x 0.11 x 0.09 mm	0.31 x 0.19 x 0.17	0.30 x 0.11 x 0.09			
θ range for data collection	2.55° to 25.99°	2.49° to 25.50°	mm 2.81° to 27.50°	mm 2.63° to 24.99°			
Limiting indices	$-9 \leq h \leq 9$	$-9 \leq h \leq 9$	$-9 \le h \le 9$	$-11 \leq h \leq 10$			
	$-19 \le k \le 19$	$\text{-}19 \leq k \leq 19$	$-14 \le k \le 13$	$-16 \leq k \leq 15$			
	$-11 \leq l \leq 11$	$-11 \le l \le 11$	$-21 \le l \le 25$	$-13 \leq l \leq 16$			
Reflections collected	6230	7634	10766	6345			
Unique reflections	2306 [R(int) = 0.0694]	2346 [R(int) = 0.0338]	3431 [R(int) = 0.0224]	5402 [R(int) = 0.0220]			
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	0.0324] Full-matrix least-squares on F ²	0.0329] Full-matrix least- squares on F ²			
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0446, wR_2 =$	$R_1 = 0.0307, wR_2 = 0.0694$	$R_1 = 0.0304, wR_2 =$	$R_1 = 0.0547, wR_2 =$			
R indices (all data)	0.1009 R ₁ = 0.0667, wR ₂ = 0.1085	$R_1 = 0.0388, wR_2 = 0.0776$	0.0812 R ₁ = 0.0383, wR ₂ = 0.0865	0.1377 $R_1 = 0.0833$, $wR_2 = 0.1572$			
Largest diff. peak and hole	0.938 and -1.011 e.A ⁻³	0.621 and -0.653 e.A ⁻³	0.368 and -0.402 e.A ⁻³	1.122 and -0.810 e.A ⁻³			

Complexes 1, 2 and 3 crystallizes in non-centrosymmetric polar monoclinic crystal system with space group $P2_1/n$ for complexes 1 and 2 while $P2_1/c$ for complex 3, with four molecules per unit cell. The lattice nature of complex 4 is triclinic with space group symmetry $P\overline{1}$. Figs. 2-5 show the molecular

structures and Table 3 represent the crystallographic details. Selected bond distances and angles for the proligand in the structures are compiled in Table 4 and those involving metal atom in supplementary (Table S1) for the sake of comparison.

In complexes [Cu(L4M)Cl] (1), [Cu(L4M)I] (2) and [Cu(L4M)OAc]·H₂O (3), the central copper(II) cation coordinates in a square planar fashion satisfied by tridentate thiosemicarbazone moiety and the coordination number is made up to four by binding with anionic group or atom (Cl⁻, Γ and CH₃COO⁻). The square plane in each case suffers slight tetrahedral distortion as indicated by the τ_4 values 0.0847, 0.0644 and 0.1018 respectively for complexes 1, 2 and 3 [33], which means the coordination environment is more biased to ideal square planar extreme. Coordination results in structural reorientation of the ligand about C5–C6, N2–C6, N3–C8 bonds and changes its configuration from *E*, *Z*, *E* to *Z*, *E*, *Z*. This suggests that a possible rotation about the azomethine double bond occurs on coordination and pyridyl N and thiocarbonyl S atom are *cis* aligned to coordinate in NNS manner. In the complexes, the central atom deviates negligibly (0.07 Å) from the least squares plane through the

	HL4M	(1)	(2)	(3)	
C(8)–S(1)	1.680(2)	1.744(3)	1.751(5)	1.747(2)	
C(8)–N(3)	1.366(3)	1.325(4)	1.305(5)	1.319(3)	
N(2 –N(3)	1.372(3)	1.369(3)	1.365(5)	1.359(2)	
C(8)–N(4)	1.326(3)	1.349(4)	1.351(6)	1.325(3)	
C(6)–N(2)	1.286(3)	1.281(4)	1.288(5)	1.290(3)	
C(6)-N(2)-N(3)	118.3(2)	119.2(2)	118.7(4)	119.12(16)	
N(3)-C(8)-N(4)	116.3(2)	116.7(3)	117.3(4)	117.7(2)	
N(3)-C(8)-S(1)	119.8(2)	125.9(2)	125.8(3)	125.08(16)	
C(8)-N(3)-N(2)	119.0(2)	111.5(2)	111.8(4)	111.46(16)	

Table 4. Selected bond lengths (Å) and bond angles (°) of HL4M and the complexes 1-3

donor atoms and the *trans* angles, N(1)–Cu(1)–S(1) and N(2)–Cu(1)–X(1) are similar and deviate less from linearity. The coordinated ligand have longer N2–N3 bonds, shorter N3–C8 bond, and longer C8–S1 bonds compared to the parent thiosemicarbazone as reported in the literature [10] and reflects the π delocalization. The Cu–N bond lengths exactly fall in the normal ranges, 1.9476(16) to 2.027(3) Å. The other geometric parameters associated with the complexes are also as expected. The comparison of Cu–pyridine N, N(1) and Cu–azomethine N, N(2) distances in the complexes show that the bond with the azomethine nitrogen atom is stronger, doubtless due to the greater basicity of this nitrogen atom and possibly, the *trans* effect [10].

Table 5. Intermolecular hydrogen bonds in the complexes 1, 2, 3 and 4.

D-H···A (Å)	d (D-H) (Å)	d (H···A) (Å)	$d (D \cdots A) (Å)$	∠DHA (°)
Complex (1)				
$N(4)$ - $H(4A)$ ···· Cl^a	0.86	2.57	3.431(3)	177.9
Complex (2)				
N(4)- $H(4A)$ ···I(1) ^b	0.875(10)	2.894(12)	3.766(4)	174(5)
Complex (3)				
$N(4)-H(4')\cdots O(1W)^{c}$	0.872(10)	2.106(13)	2.936(3)	159(2)
O(1W)-H(1A)····O(1) ^d	0.845(10)	2.029(10)	2.869(2)	173(2)
O(1W)-H(1B)····O(2) ^e	0.846(10)	1.975(14)	2.779(2)	158(3)
Complex (4)				
N(4)-H(4')O(1) ^f	0.873(10)	2.23(5)	2.938(10)	138(6)

Symmetry transformations used to generate equivalent atoms:

a = x - 1/2, -y + 1/2, z - 1/2; b = x + 1/2, -y + 5/2, z + 1/2; c = x, y - 1, z; d = -x + 1, y + 1/2, -z + 3/2; e = -x + 2, y + 1/2, -z + 3/2; f = x + 1, y, z + 1/2, -z + 3/2; d = -x + 1, y + 1/2; d = -x + 1, y



Figure 2. ORTEP diagram of complex 1. Displacement ellipsoids are drawn with 30% probability.



Figure 3. ORTEP diagram of complex 2. Displacement ellipsoids are drawn with 30% probability.

Quasi-planar [Cu(L4M)NCS] entity forms the crystal structure of complex **4** [Cu₂(μ -S-L4M)₂(NCS)₂]·DMSO (**4**) stacked through thiolate atom, which leads to dinuclear centrosymmetric species. The unequal Cu–S distances of its central Cu(μ -S)₂Cu core, forms a parallelogram. Each copper atom is further coordinated to a terminal N of thiocyanate, imine nitrogen and pyridine nitrogen making the Cu1 and Cu2 coordination environments square pyramidal ($\tau = 0.08$ and 0.04 respectively) and the DMSO molecule present in the lattice completes the asymmetric unit. The square pyramids are oriented in such a manner that basal-apical edges are shared with parallel basal planes [5]. The fragments are related to each other by a C₂ axis passing through the thiolate bridged corners of the Cu₂S₂ core. Copper(II) dimers with same core and similar arrangement of square pyramids are rare among thiosemicarbazone complexes, the related dimeric complexes [34-37] being other examples. A perspective view of the dimer is shown in Fig. 5 and bond parameters and core angles are given in supplementary table S2. The intradimeric and the minimum interdimeric Cu···Cu distances are 3.499(1) and 4.7145(14) Å respectively.



Figure 4. ORTEP diagram of complex 3. Displacement ellipsoids are drawn with 30% probability. (H₂O molecule has been omitted for clarity).



Figure 5. ORTEP diagram of complex $[Cu_2(\mu$ -S-L4M)₂(NCS)₂] ·C₂H₆OS (4). Displacement ellipsoids are drawn with 30% probability. (DMSO molecule has been omitted for clarity).

Supramolecular features. The molecular structures of complexes [Cu(L4M)Cl] (1) and [Cu(L4M)I] (2) reveal their nearly planarity and only methyl groups are out of the plane. On probing into the crystal packing, it was deduced that complexes 1 and 2 are associated into 1D supramolecular network sustained by N–H \cdots X hydrogen bonding interactions. Hydrogen bonding parameters are presented in Table 5. Each unit cell comprises four chains of this type. The halogen atom and uncoordinated nitrogen have significant impact on packing and adopts an edge to face 'herringbone' arrangement with an interplanar distance of 4.7607(8) and 4.5314(10) Å respectively for complexes 1 and 2. Crystal packing is also augmented by weakly attractive chelate ring-chelate ring interactions and chelate ring-pyridine ring interactions. The unique propagation of the supramolecular chains is an important structural feature of these complexes and these propagation modes have been unknown in the literature so far. Viewed along the 'c' axis, the zipper-like chains in complex 1 propagates by intercepting the 'c' axis and complex 2 is characterized by propagation perpendicular to the 'b' axis. Usually supramolecular chains are aligned along/parallel to any of the three crystallographic axes. The 1D motif interact in turn through further $\pi \cdots \pi$ interactions which expand the supramolecular aggregation to three-dimensional framework. Pairs of such chains related to one another by inversion symmetry and hence running antiparallel, are linked by $\pi \cdots \pi$ stacking interactions. Thus the formation of framework can be most simply analyzed in terms of two substructures, one of them one-dimensional and involving N-H \cdots X hydrogen bond, while the other is two dimensional and involves five stacking interactions [38]. Combination of two interactions generates parallel sheets and the successive layers are interconnected by utilizing the other three interactions. Owing to the

isostructural behavior of complexes 1 and 2, we only restrict our discussion to the supramolecular aggregation of complex 2.

Figure 6. Formation of 1D 'zipper like' chain in complex 1 intercepting 'c' axis



Figure 8. 3D network drawing for complex 2 (H atoms have been omitted for clarity).

In the first substructure, the nitrogen atom at (x, y, z) acts as a hydrogen bond donor to Γ at (x+1/2, -y+5/2, z+1/2) forming a $C_1^1(5)$ chain. In the second substructure, parallel layers are formed by the stacking interactions between rings Cu1, S1, C8, N3, N2 at (x, y, z) with Cu1, S1, C8, N3, N2 at their closest approach with centroid-to-centroid distance of 3.584(2) and the ring-centroid separation 3.245(13) and corresponding to a ring offset of 1.520 and Cu1, N1, C5, C6, N2 at (2-x, 2-y, -z) (centroid-to-centroid distance is 3.431(2) and ring-centroid separation is 3.3231(15)). The propagating chains interact each other through five membered chelate rings and pyridine ring. The rings Cu1, S1, C8, N3, N2 and Cu1, N1, C5, C6, N2 at (x, y, z) act as donors respectively to N1, C1-C5; Cu1, S1, C8, N3, N2 (symmetry code: 1-x, 2-y, z) and Cu1, N1, C5, C6, N2 act as donor to N1, C1-C5 (symmetry code: 1-x, 2-y, z). Thus the combination of moderately strong ring interactions links the sheet aggregates to three dimensional framework. The fragments of supramolecular architecture are depicted in Figs. 7 and 8.



Figure 9. Water molecules (shown in space filling model) sandwiched between two symmetry-related layers of complex 3.

The supramolecular array in complex **3** shows that the solvent molecule in the lattice has a key role in the self-assembly of molecules into a two dimensional structure. The water molecules are sandwiched by two symmetry-related layers of complex molecules as shown in Fig. 9. The solvent molecules are held in place by interaction with three complex molecules through three hydrogen bonds. The O1 and O2 acceptor positions of acetate moiety establish strong O–H…O hydrogen bonds [symmetry codes: - x+1,y+1/2,-z+3/2; -x+2,y+1/2,-z+3/2,] and these chains are further cross-linked by means of N(4)– (H4')…O(1W) hydrogen bonds [symmetry code: x,y-1,z], resulting in an extended bidimensional assembly parallel to the crystallographic *ab* (110) plane. The most attractive aspect is that, the two dimensional sheets resembles a seamless tribal pattern with men holding hands (Fig. 10). The layers are further linked *via* combination of $\pi \dots \pi$ and C–H… π interactions along 'c' axis to generate a three dimensional framework. The molecules are π stacked in two nonequivalent layers which are nearly

vertical to each other due to the occurrence of C–H··· π intermolecular contacts. The ring centroid separation between metallocycle Cu1 N1, C5, C6, N2 and the pyridyl ring [at (x, y, z) and (1-x, -y, 1-z), respectively] is 3.7488(12) \Box with dihedral angle 1.89(9)°. Moreover the supramolecular aggregation is reinforced by π ··· π stacking interaction between metallocycles Cu1 N1, C5, C6, N2 at (x, y, z) and (1-x, -y, 1-z): the ring centroid separation is 3.5391(11) \Box , corresponding to a ring offset of 1.077 \Box . The three dimensional packing of the layers in the crystal building of the compound is shown in Fig. 11.



Figure 10. A view of the 2D supramolecular architecture in the crystal structure of complex 3 extending in the ab plane (resembles a seamless tribal pattern with men holding hands).



Figure 11. 3D Supramolecular array in **3** showing π - π interaction.

In complex 4, the supramolecular structure is comparatively less complex than that in the case of other three complexes. The structure contains two intermolecular N(4)–H(4')…O(1) and C(14)–H(14)…S(2) hydrogen bonds running parallel to the 'a' axis. But these interactions cannot be regarded as structurally important, because the N–H…O and C–H…S angles are very close to 140° [39]. Nevertheless, the combination of graphitic $\pi \dots \pi$ stacking and ring-metal interactions, rendering low dimensional supramolecular aggregation running parallel to 'b' axis has great impact on the overall stability of the complex (Fig.12).



Figure 12. Graphitic $\pi \cdots \pi$ stacking interactions in complex 4.

3.3. Spectral investigation

3.3.1. Infrared spectra and coordination mode

Absorptions between 3200 and 3350 cm⁻¹ correspond to the stretching modes of N–H groups. The band at 3240 cm⁻¹ in the spectrum of free ligand due to N³–H vibration disappears in the spectra of all complexes, thus proving the ligand coordination around Cu(II) ion in the deprotonated thiolate form. The occurrence of the v(N–N) band at higher frequencies in the IR spectra of the complexes, compared to that observed for the ligand, confirms coordination through the azomethine nitrogen atom. The thioamido band, which contains considerable v(CS) character, is less intense in complexes and is found at lower wavenumbers [40]. Two absorption bands in the imine region are consistent with the formation of a new imine bond upon coordination of copper to sulfur in the thiolato form. The acetate complex **3** has an additional broad band at 3453 cm⁻¹ corresponds to the O–H stretching of water. In addition to this, a strong peak is observed near 1300 cm⁻¹, characteristic of C–O vibration. The antisymmetric (v_{asym}) and symmetric (v_{sym}) O–C–O vibrations, together with the difference $\Delta v_{asym-sym}$, is indicative of the strength of coordination, and the mode of binding, which can be monodentate or bidentate. The v_{asym} at 1587 cm⁻¹ and v_{sym} at 1338 cm⁻¹ with a difference of 249 cm⁻¹ confirms the monodentate coordination of acetate [41-43]. Complex **4** exhibits a strong band at 2058 cm⁻¹, a

medium band at 735 cm⁻¹ and a weak band at 479 cm⁻¹, attributable to v(CN), v(CS) and v(NCS) respectively of a typical N-bonded thiocyanate complex [44].

3.3.2. Electronic spectra

The data obtained for the complexes in DMF solutions are indicative of square planar geometry and are dominated by intense intraligand and charge transfer bands. However, possible *d-d* bands $[{}^{2}B_{1g}\rightarrow{}^{2}A_{1g}, {}^{2}B_{1g}\rightarrow{}^{2}B_{2g} \text{ and } {}^{2}B_{1g}\rightarrow{}^{2}E_{g}]$ corresponding to the energy levels $d_{x}{}^{2} \cdot {}^{2} \gg d_{xy} > d_{z}{}^{2} > d_{xz}$, d_{yz} have been hidden within a single broad band with maxima in the range 589-598 nm, as expected. The intense bands in the range 408-412 nm are assignable to a combination of $S\rightarrow$ Cu(II) and $N\rightarrow$ Cu(II) charge transfer transitions. The ligand showed absorption band around 310 nm and this transition are shifted in the spectra of all the complexes by appropriate amounts. The relative intensity and frequency of absorption varies with π donor properties of ligand. The d-d transitions of π acceptor ligands to be of a higher frequency than the π donor.

3.3.3. EPR studies

In order to obtain further information concerning the electronic structure of the metal and its immediate surroundings, EPR spectra were recorded in the polycrystalline state and in frozen DMSO solution. The magnetically non-diluted solid state spectra are not self-explanatory with regard to the hyperfine structure, which indicate the existence of anisotropy caused by *g* factors and strong dipolar interaction between the Cu centres. Transmission of hydrophobic interactions through weak non-negligible exchange interaction also contribute to the lack of hyperfine structure in the solid epr spectra [45]. In order to exclude unwanted effects, spectra were recorded in DMSO solution at 77 K. The spectra were paired with simulation using Easyspin 4.0.0 package [46]. The effort to get virtuous fit failed due to the asymmetric nature of superhyperfine structure. In frozen solution the complexes show hyperfine splitting into four lines, characteristic of monomeric Cu(II) complexes corresponding to -3/2, -1/2, 1/2 and 3/2 transitions ($\Delta Ms = \pm 1$). The EPR spectral parameters of the title complexes in the polycrystalline state at 298 and in DMSO solution at 77 K are presented in Table 6 and 7.

It is seen that complexes 2 and 3 display isotropic spectra and 1, 4 show typical axial behavior in the polycrystalline state (Figure S3 and S4). All the solution spectra are axial in nature with tensor values $g_{\parallel} > g_{\perp} > 2.002$, which are consistent with a d_{x-y}^{2-2} ($^{2}B_{1g}$) ground state indicating the presence of the unpaired electron. The existence of exchange coupling between copper centers in a polycrystalline state is quantified by geometric parameter G = $(g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$, G < 4 [47]. The exchange interactions are ensued *via* the N(4)–H(4)…X (Cl / O) hydrogen bonding which relates the nearest Cu(II) ions at distances 4.7607(8) and 3.499(3) \Box for 1 and 4 respectively. Larger Cu…Cu

interatomic distances in complex **2**, $5.4752(11) \square$ and **3**, $5.3468(4) \square$ may result in weak exchange coupling between Cu(II) paramagnetic centres [48].

The complexes 2 and 3 recorded in 77 K show quartet hyperfine structure in the low field range, characteristic of square planar or square pyramidal coordination environment around copper centers. The high field g_{\perp} component is well resolved with superhyperfine lines due to interaction of two nitrogens with Cu(II) xy plane. Complex 4 displays an axial spectrum with four hyperfine lines. There is no half field signal corresponding to the forbidden magnetic dipolar transition for complex 4 (Figure S2), confirming the absence of dimeric structure. It proves that dimeric structure existing in solid state was destroyed by DMSO. Low temperature spectra of complex 2 and 3 are depicted in Fig 13. Low temperature spectrum of Complex 1 shown in Figure S1.

Table 6. EPR spectral parameters of the complexes in the polycrystalline state.

	Polycrystalline sta	te (273 K)		
Compound	g⊫	g⊥	g _{iso}	G
Complex 1	2.236	2.06		4.05
Complex 2	-	-	2.11	-
Complex 3	-	-	2.09	-
Complex 4	2.24	2.07		3.51

Table 7. EPR spectral parameters of the complexes in DMSO solution.

Compound		DMSO solution (77 K)												
	g⊫	g_{\perp}	g_{av}	^{Cu} A _{ll} ^a	${}^{Cu}\!A_{\!\perp}{}^a$	^{Cu} A ₀ ^a	$^{N1}A_0^{a}$	$^{N2}A_0^{a}$	α^2	β^2	γ^2	K	K_{\perp}	f ^b
Complex 1	2.16	2.09	2.113	186	0	62			0.752	0.838	1.249	0.630	0.941	115
Complex 2	2.188	2.043	2.091	203	24	83	5.95	4.73	0.808	0.848	0.794	0.686	0.642	107
Complex 3	2.191	2.044	2.09	206	27	87	10.17	7.19	0.819	0.836	0.786	0.686	0.645	106
Complex 4	2.16	2.046	2.084	186	0	62			0.734	0.865	0.911	0.635	0.669	115

^a Expressed in units of cm⁻¹ multiplied by a factor of 10⁻⁴

^b expressed in units of cm

In a tetragonal (D_{4h}) crystal field the effective spin-Hamiltonian [49] of the EPR spectra of copper(II) complexes can be described as,

$$H = \beta[g_{\parallel}HzSz + g_{\perp}(HxSx + HyS_y)] + {^{Cu}A_{\parallel}SzIz(Cu)} + {^{Cu}A_{\perp}[SxIx(Cu) + Sy Iy(Cu)]} + [{^{N}A_{\parallel}SzI_z(N)} + {^{N}A_{\perp}[SxIx(N) + SyIy(N)]}]$$

The degree of distortion, f factor $(g_{\parallel}/A_{\parallel})$ is regarded as an empirical index of deviation from idealized geometry [50]. For square planar complexes, f = 105-135 and increases with increasing tetrahedral distortion. Values from 106 to 115 cm for the present series of complexes suggest structures close to planarity. Since the superhyperfine structure is well resolved, the ligating system (NNS) appears to be coplanar with the two chelate rings, thus corroborating the nearly planar geometry $(g_{\parallel}>g_{\perp})$ [51].



Figure 13. Low-temperature (77 K) EPR spectrum of complexes **2** (a) and **3** (b) in DMSO solution paired with its simulation (blue line).

Table 8. Comparison of epr pa	arameters A_{\parallel} and g_{\parallel} for	or complexes 1-	4 with other reported	ONS and NNS donor
Cu(II) thiosemicarbazone com	plexes			

NN	S donor thiosemicarbazone comp	lexes			ONS donor thiosemicarbazone complexes						
	Complex	g _{ll}	A	Ref.	Cor	nplex	g _{ll}	A	Ref.		
Α	[Cu(L4M)Cl]	2.16	186	*	F	[(CuL ₄) ₂]	2.177	182.3	[57]		
	[Cu(L4M)I]	2.191	206	*		[CuL ₄ dmbipy]	2.167	190.5	[57]		
	[Cu(L4M)OAc]·H ₂ O	2.16	186	*	G	[Cu(L ₅)(bpy)]	2.17	175	[58]		
	$[Cu(\mu-S-L4M)(NCS)]_2$ ·			*							
	C ₂ H ₆ OS	2.188	203			$[Cu(L_5)(phen)]$	2.17	175	[58]		
В	[Cu(L)NCS]_H ₂ O	2.192	208	[56]		$[Cu(L_5)(dmp)]$	2.17	175	[58]		
	[Cu(L)I]	2.204	205	[56]	Н	$[Cu(HL_6)Br_2]$	2.21	181	[59]		
С	[CuL ₁ Cl]	2.1607	186.6	[21]		$[Cu(L_6)_2]$	2.22	188	[59]		
	$[CuL_1NO_3]_2$	2.1787	195	[21]		$[Cu(L_6)(OAc)(H_2O)]$	2.195	188	[59]		
	$[CuL_1N_3]2 \cdot 2/3H_2O$	2,1544	187.75	[21]		[Cu(L ₆)(ClO4)(H ₂ O)]	2.205	185	[59]		
	$[CuL_1]2(ClO4)2 \cdot 2H_2O$	2.1787	194.9	[21]		$[Cu(L_6)(NO_3)(H_2O)_2]$	2.4	116	[59]		
D	[CuL ₂ Cl] ₂	2.1625	188.5	[21]	Ι	$[Cu_2(L_7)_2(Et_3N)_2(H_2O)_4](NO_3)_2$	2.228	176	[60]		
	[CuL ₂ N ₃]	2.1563	187.92	[21]		$[Cu(L_7)_2(H_2O)_2]$	2.236	177.3	[60]		
	$[Cu(HL_2)_2](ClO_4)_2 \cdot 1/2EtOH$	2.1697	192.5	[21]		$[Cu(L_7)(OAc)(H_2O)_2]$	2.370	160	[60]		
Е	$[Cu(HL_3)(SO_4)] \cdot H_2O$	2.175	192	[6]	J	[Cu(L ₈)(2,20-bipy)]	2.193	170	[61]		
	$[CuL_3Br]_1/2H_2O$	2.16	193	[6]		[Cu(L ₈)(1,10-phen)]	2.19	172	[61]		
	[CuL ₃ (NCS)]	2.178	209	[6]	Κ	[Cu(L ₉)(2,20-bipy)]	2.194	170	[61]		
	$[Cu_2L_3(OAc)_2] \cdot H_2O$	2.184	193	[6]		[Cu(L ₉)(1,10-phen)]	2.19	170	[61]		
	$[Cu_2L_3I_2]$	2.194	204	[6]	L	[Cu(L ₁₀)(2,20-bipy)]	2.19	166.7	[61]		
						[Cu(L ₁₀)(1,10-phen)]	2.174	173.3	[61]		

* Present work

в =

C =

E =

H =

К=

F =

L =

I =



Kivelson and Neiman [52] reported that, g_{\parallel} values less than 2.3 is an indication of significant covalent character. From the spectral data we can infer that the g_{\parallel} values are nearly same for all the four complexes (< 2.3) and show appreciable covalent character. The EPR parameters and *d*–*d* transition energies were used in the evaluation of other spectral parameters.

The bonding parameter α^2 is considered as measure of the covalency of the in-plane σ -bonding between the 3d-metal orbital and the ligand orbital. β^2 and γ^2 are in-plane π bonds and out-of-plane π bonds respectively. $K_{\parallel}^2 = \alpha^2 \beta^2$ and $K_{\perp}^2 = \alpha^2 \gamma^2$ are the orbital reduction factors.

Hathaway [53] has pointed out that for pure sigma bonding $K_{\parallel} \approx K_{\perp} \approx 0.77$, for in plane π -bonding $K_{\parallel} < K_{\perp}$ and for out-of plane π -bonding, $K_{\perp} < K_{\parallel}$. For complexes 1 and 4, it is observed that $K_{\parallel} < K_{\perp}$ indicates significant in plane π -bonding. For other complexes out of plane π -bonding is important.

The stronger covalency should result in smaller hyperfine interaction. In the case of 100% ionic character, α^2 values are expected to be 1.0 and becomes smaller with increasing covalent bonding. It is inferred that the in-plane-bonding of investigated Cu(II) complexes have partial ionic and partial covalent character with the α^2 values 0.75, 0.80, 0.81 and 0.73 respectively. These values indicate that approximately 70-80% of the spin population is in the copper $d_x^2 g^2$ orbital of all the Cu(II) species concerned [54].

 A_{\parallel} - g_{\parallel} correlation analysis: The A_{\parallel} - g_{\parallel} ratios reflect the degree of tetrahedral distortion. Nevertheless the Peisach – Blumberg correlation diagram [55] suggest the nature of the coordinated atoms to the Cu(II). Presently, we are analyzing trends in A_{\parallel} - g_{\parallel} relations of ONS donor Cu(II) complexes with NNS donor Cu(II) complexes from collected experimental data (Table 8) [56-61].

According to molecular orbital theory [62] Cu(II) complexes having d_{x-y}^{2-2} ground state, hyperfine splitting($A_{||}$) and g-factor($g_{||}$) is related as

 $A_{||} = P[(-\kappa - \frac{4}{7})\alpha^2 + \Delta g_{||} + \frac{3}{7}\Delta g_{\perp}]$

where P characterizes average radius r_d of the ground state *d*-orbital and is equal to 0.036 cm⁻¹ for free Cu²⁺ ion, κ is the Fermi contact hyperfine interaction parameter which is equal to 0.43 for free Cu²⁺ ion, $\Delta g = g_i - 2.0023$ and α^2 is unpaired electron density in Cu²⁺ ground state reflecting the degree of coordination bond covalency. Plot of A_{ll} vs. g_{ll} is a straight line and the slope of the line is determined by the P-value and line is shifted to the left when covalency grows (α^2 decreases) [63].



Figure 14. Peisach - Blumberg correlation diagram for NNS donor thiosemicarbazone Cu(II) complexes



Figure 15. Peisach - Blumberg correlation diagram for ONS donor thiosemicarbazone Cu(II) complexes.

For ONS donor complexes it has been observed that g_{\parallel} increases with concomitant decrease in A_{\parallel} component, which means the parameters have a negative linear correlation. Versatility and more flexibility in coordination can be introduced by varying the heterocyclic group. Nonetheless, the additional donor site impart a surprising inverse relation between these parameters. The correlation line gives a negative slope with smaller range of g_{\parallel} factors and A_{\parallel} splitting. The g_{\parallel} value decreases and hyperfine splitting A_{\parallel} grows as nitrogen replaces oxygen of thiosemicarbazones (NNS donor). Peisach – Blumberg plot of selected complexes are depicted in Figs. 14 and Fig. 15.

A correlationship of A_{\parallel} and f (Fig. 16) is investigated and suggests that A_{\parallel} linearly decreases with f as a consequence of the deformation of the square planar geometry. Moreover, it results in

unsymmetrical electron delocalization which in turn influences the copper hyperfine structure. From the results we can infer that the magnetic and physicochemical properties of the complexes differ as chromophoric group varies.



Figure. 16. Correlationship of A_{\parallel} and *f* for ONS and NNS donor thiosemicarbazone Cu(II) complexes from Table 7.

4. Concluding remarks

In summary, we have solvent-dependently synthesized four Cu-based thiosemicarbazone complexes where Cu(II) is in a (3+1) coordination environment for complexes 1-3. For complex 4, Cu(II) formed thiolate bridged dinuclear complex. The physico-chemical analyses confirmed the structures of all the new products. Structural analysis indicates the importance of solvent for different geometry and coordination mode enables an understanding of the crucial role of solvents in the assembly, crystallization and stability of the supramolecular architectures. Substitution of different anions alter the hydrogen bonding patterns and hence the intermolecular interactions, as well as supramolecular patterns. The evaluated values of α^2 , β^2 and γ^2 of the complexes are consistent with strong in-plane π bonding and out-of-plane π bonding. Ligands, capable of forming extended networks through hydrogen bonding can act as a channel for transferring magnetic exchange interactions. The correlation between g-factor and hyperfine splitting factor for ONS and NNS donor thiosemicarbazone complexes is depicted using Peisach-Blumberg diagram and we found that the A_{ii} *vs* g_{ii} correlation is a straight line and are inversely related as it is suggested by a collection of experimental data.

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Appendix A. Supplementary data

CCDC 1527237 – 38 and 1527240 - 41 contains the supplementary crystallographic data for compounds **1**, **2** and **3**, **4** respectively. Copies of this information may be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Director, CCDC, 12 Union Road, Cambridge, CB2, IEZ, UK (fax: +44-1223-336-033; e-mail: <u>deposit@ccdc.cam.ac.uk</u>).

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Self-organized three dimensional architectures based on non-covalent interactions in square planar Cu(II) thiosemicarbazone: Solvent mediated crystallization and EPR based correlation study

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Highlights

- Four copper (II) complexes of 2-acetylpyridine-N⁴-methyl thiosemicarbazone were prepared.
- Stability of complexes in polar protic and aprotic solvents were investigated and the effects of solvents were studied.
- EPR parameters g_{\parallel} and A_{\parallel} of complexes were analyzed by Peisach–Blumberg plot and established an inverse correlation among NNS and ONS thiosemicarbazone complexes.
- The detailed crystal structures and supramolecular interactions of all the prepared complexes showed the role of secondary interactions in the creation of molecular architectures.

Self-organized Three Dimensional Architectures based on Non-covalent Interactions in Square planar Cu(II) Thiosemicarbazone: Solvent mediated crystallization and EPR based Correlation Study

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Peisach – Blumberg correlation diagrams for NNS and ONS donor thiosemicarbazone Cu(II) complexes

