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ARTICLE TYPE

Studies of structural diversity due to inter-/intra-molecular hydrogen bonding and photoluminescent properties in thiocarboxylate Cu(I) and Ag(I) complexes

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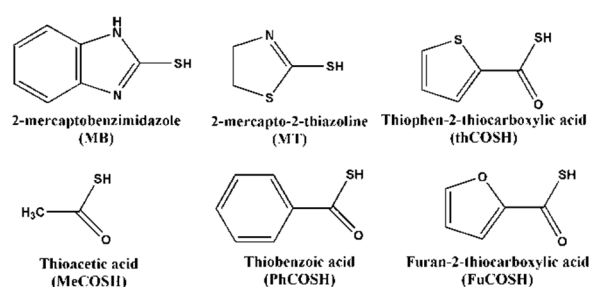
Seven new copper(I) thiocarboxylate and two silver thiocarboxylate complexes, containing 2-mercaptobenzimidazole (MB) and 2-mercapto-2-thiazoline (MT) have been synthesized and characterized by elemental analysis, IR, ¹H NMR, ¹³C NMR and UV-Visible spectroscopic techniques. Molecular structures of all the complexes have been examined by single crystal X-ray diffraction analysis. In case of complexes **1** [(PPh₃)₂Cu(SCOMe)MB] and **3** [(PPh₃)₂Cu(SCOth)MB], direction of hydrogen bonding have been changed from intra-molecular to inter-molecular by increasing the size of R-group of thiocarboxylate ligands. **7** [Cu₂(μ-SCOPh)₂(μ-MT)(MT)]₂ is a tetranuclear complex in which distance between two copper atoms is shorter than the sum of covalent radii of the two atoms without having a formal covalent bond between them, as evinced by NBO (DFT) calculation and bond critical points calculations using the AIM theory. In complex **8** two different molecules, [(PPh₃)₂Ag(SCOPh)MT] and [(PPh₃)₂Ag(SCOPh)] co-crystallized in the same lattice. Unit cell of the complex **9** also possesses two structurally different molecules with same molecular formula. Emission spectra of complexes have been studied in both solution and solid states. Electronic spectral behaviors of the complexes **1** and **7** have been explained by TDDFT calculations.

Introduction

Sulfur containing organic molecules are versatile ligands for a wide range of metals. High polarizability, low electronegativity and the presence of lone pairs of electrons offer a rich sulfur based chemistry of the complexes.^[1] Cu(I) and Ag(I) complexes of sulfur ligands display a wide variety of structural formats ranging from mononuclear discrete molecules to polynuclear clusters.^[2]

The coordination chemistry of heterocyclic thioamides has seen spectacular expansion mainly because of the relevance of these compounds to biological systems.^[3] The key feature of this class of compounds, with respect to their ligating properties along with donor atoms for hydrogen bonding (Scheme 1), is the ability to bind to a metal centre adopting several coordination modes, thus giving rise to a rich variety of complexes with variable nuclearities and often unusual geometries.^[3a,4]

Metal complexes with a d¹⁰ configuration^[5], particularly those containing both phosphine and a sulfur ligand (thiolate, thiocarboxylate, dithiocarbamate and dithioxanthate ligands)^[2f,6] exhibit fascinating photophysical and photochemical properties. Complexes of copper(I) and silver(I) with d¹⁰ configuration have no low-energy ligand-field transitions, however, low-energy charge-transfer excited states are available in these cases, which is an important property of

luminescent materials.^[5a,b,6d]

Scheme 1 Sulfur ligands used

Recently, we have observed that Cu(II) complexes of thiocarboxylate ligands undergo spontaneous desulfurization where as those of Cu(I) are quite stable.^[7] Thiocarboxylate ligand (having both S and O donor sites) form primary bonding with the metal through S atom while the O remains free which can be exploited for hydrogen bonding. In view of these facts we thought it will be worthwhile to study the structural features of copper and silver complexes containing heterocyclic thioamides as well as thiocarboxylates.

Experimental

Reagents and General Procedures

All the solvents were dried according to standard procedures and distilled before use. $[(PPh_3)_2Cu(SCOth)]$ ^[7], Thiophene-2-thiocarboxylic acid, furan-2-thiocarboxylic acid (FuCOSH) ^[8], *bis*(triphenylphosphine)copper(I) nitrate^[9] and *bis*(triphenylphosphine)silver(I) nitrate^[10] were prepared by reported procedures. Thiobenzoic acid, thioacetic acid, 2-mercapto-2-thiazoline (MT) and 2-mercaptobenzimidazole (MB) were purchase from Aldrich and used as received.

Instrumentation

IR spectra were recorded using Varian-3100 FTIR instruments. NMR spectra were obtained using a JEOL AL300 FT NMR spectrometer. Electronic absorption spectral measurements were carried out using a Shimadzu UV-1700 PharmaSpec Spectrometer. Emission spectra were recorded from VARIAN, CARY Eclipse Fluorescence spectrometer. Absorption and emission spectra of the complexes have been recorded in chloroform solution ($\sim 10^{-5}M$). Elemental analyses were performed by the EAT Exeter Analytical Inc. CE-440, elemental analyzer.

Single crystal X-ray analysis

Single crystal X-ray data of all the complexes were collected on a Xcalibur Eos Oxford diffractometer using graphite monochromated $MoK\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). Data collections were carried out at room temperature. Structures were solved by the direct method and then refined on F^2 by the full matrix least square technique with SHELX-97 software ^[11] using the WinGX program package ^[12]. Crystal data of complexes are given in **Table S1** (supporting information). The crystals of a few complexes showed some disorders. The disordered atoms of the thiophene (th) rings were split in two parts and then some geometrical restraints were applied (whenever necessary) for refinement. Similarly, disordered atoms present elsewhere have also been refined. In case of complexes **7** and **9** some a-level could not be removed. These alerts are generated because there is a large amount of disorder in the solvent molecule.

Computational Details

All the calculations were performed using GAUSSIAN 03W software.^[13] Initial atomic co-ordinates were obtained from X-ray crystallographic data which were used as such for NBO and TDDFT ^[14] calculations. The time dependent and NBO calculations were performed using 6-31G** and 6-31+G** respectively for all the atoms at B3LYP level. All the molecular orbital plots were generated by Gauss View 4.5 program.

Syntheses

Synthesis of $[(PPh_3)_2Cu(SCOMe)MB]$ (**1**)

To the stirred methanolic solution (10.0 mL) of sodium thioacetate [prepared *in situ* by mixing thioacetic acid (0.076 g,

1.0 mmol) and sodium methoxide (0.054g, 1.0 mmol)] and 2-mercaptobenzimidazole (MB) (0.150g, 1.0 mmol), a chloroform solution (10 mL) of $(PPh_3)_2Cu(NO_3)$ (0.650g, 1.0 mmol) was added to get a colourless solution. The reaction mixture was stirred for three hours. The solvent was evaporated under reduced pressure and the residue was dissolved in $CHCl_3$ (20 mL) and filtered off to separate out $NaNO_3$. The filtrate was evaporated under reduced pressure. The colorless product was dried under vacuum for 1h. Rectangular crystals were obtained from mixture of chloroform and toluene solution (1:1) at room temperature. Yield: 0.659g (81%). Elemental analysis: Cal. for $C_{45}H_{39}N_2OS_2P_2Cu$: C, 66.44, H, 4.83, N, 3.44. Found: C, 66.27, H, 4.78, N, 3.47. IR spectra (KBr, cm^{-1}): 3054 $\nu(N-H)$, 1582 $\nu(CO)$, 1121, 953 $\nu(C-S)$. NMR ($CDCl_3$, δ ppm): 1H NMR; 2.49 (Me), 7.14-7.37 (Ph and MB ring), 11.42 (NH). ^{13}C NMR; 36.86 (Me), 110.7, 123.2 (MB), 128.2-134.5 (Ph and MB ring), 164.5 (N_2CS), 199.2 (COS).

Synthesis of $[(PPh_3)_2Cu(SCOth)MT_2]$ (**2**)

To a chloroform (10 mL) solution of $[(PPh_3)_2Cu(SCOth)]$ (0.731g, 1.0 mmol), added a solution of 2-mercapto-2-thiazoline (MT) (0.238g, 2.0 mmol) in 5 mL of methanol with stirring. The reaction mixture was stirred for three hours and evaporated under reduced pressure. The yellow residue was dissolved in mixture of chloroform and methanol (2:1) and kept for crystallization. Yellow block shaped crystals were obtained after few days. Yield: 0.558g (79%) (when $[(PPh_3)_2Cu(SCOth)]$ and MT taken in 1:1 ratio then the same product was obtained in low yield). Elemental analysis: Cal. for $C_{29}H_{28}N_2OS_2PCu$: C, 49.23, H, 3.99, N, 3.96. Found: C, 49.12, H, 3.89, N, 4.03. IR spectra (KBr, cm^{-1}): 3063 $\nu(N-H)$, 1525 $\nu(CO)$, 1042, 936 $\nu(C-S)$. NMR ($CDCl_3$, δ ppm): 1H NMR; 3.46 (CH_2), 3.91 (CH_2), 6.94-7.74 (Ph and th ring), 10.09 (NH). ^{13}C NMR; 33.6 (CH_2), 51.9 (CH_2), 125.2-149.3 (Ph and th ring), 186.3 (COS), 199.2 (NSCS).

Synthesis of $[(PPh_3)_2Cu(SCOth)MB]$ (**3**)

To a chloroform (10 mL) solution of $[(PPh_3)_2Cu(SCOth)]$ (0.731g, 1.0 mmol), added a solution of MB (0.150g, 1.0 mmol), in 5 mL of methanol with stirring. The reaction mixture was stirred for three hours and evaporated under reduced pressure. The yellow coloured residue was dissolved in mixture of chloroform and methanol (2:1) and kept for crystallization. Yellow block shaped crystals were obtained after few days. Yield: 0.731g (83%). Elemental analysis: Cal. for $C_{48}H_{39}N_2OS_3P_2Cu$: C, 65.40, H, 4.46, N, 3.18. Found: C, 65.28, H, 4.42, N, 3.21. IR spectra (KBr, cm^{-1}): 3068 $\nu(N-H)$, 1558 $\nu(CO)$, 1093, 910 $\nu(C-S)$. NMR ($CDCl_3$, δ ppm): 1H NMR; 6.94-7.79 (Ph, th and MB ring), 11.64 (NH). ^{13}C NMR; 110.7, 123.2 (MB), 127.1-150.2 (Ph, th and MB ring), 164.4 (N_2CS), 199.8 (COS).

Synthesis of $H[(PPh_3)_2Cu(SCOth)(SCOFu)]$ (**4**)

The same procedure was followed as mentioned for **3** except the fact that furan-2-thiocarboxylic acid (0.128 g, 1.0 mmol)

was used in place of 2-mercaptobenzimidazole. Red rectangular crystals were obtained from toluene solution. Yield: 0.748 g (87%). Elemental analysis: Cal. for $C_{46}H_{37}O_3S_3P_2Cu$: C, 64.28, H, 4.34. Found: C, 64.09, H, 4.32. IR spectra (KBr, cm^{-1}): 1585, 1558 $\nu(CO)$, 1039, 1017 $\nu(C-S)$. NMR ($CDCl_3$, δ ppm): 1H NMR; 6.44-7.69 (Ph, th and Fu ring), 1.93 (OH). ^{13}C NMR; 127.6-141.3 (Ph, th and Fu ring), 190.4, 197.9 (COS).

Synthesis of $H[(PPh_3)_2Cu(SCOth)(SCOPh)]$ (5)

The same procedure was followed as mentioned for **3** except the fact that thiobenzoic acid (0.138 g, 1.0 mmol) was used in place of 2-mercaptobenzimidazole. Red rectangular crystals were obtained from toluene solution. Yield: 0.809 g (93%). Elemental analysis: Cal. for $C_{48}H_{39}O_2S_3P_2Cu$: C, 66.30, H, 4.52. Found: C, 66.23, H, 4.47. IR spectra (KBr, cm^{-1}): 1584, 1508 $\nu(CO)$, 1094, 999 $\nu(C-S)$. NMR ($CDCl_3$, δ ppm): 1H NMR; 6.89-8.09 (Ph and th ring), 2.11 (OH). ^{13}C NMR; 128.4-140.1 (Ph and th ring), 189.1, 193.9 (COS).

Synthesis of $[(PPh_3)Cu(\mu-SCOPh)_2(\mu-MB)Cu(PPh_3)]$ (6)

The same procedure was followed as mentioned for **1** except the fact that thiobenzoic acid (0.138 g, 1.0 mmol) was used in place of thioacetic acid. Yellow rectangular crystals were obtained from mixture of chloroform and toluene solution (1:1). Yield: 0.828 g (77%). Elemental analysis: Cal. for $C_{57}H_{46}N_2O_2S_3P_2Cu_2$: C, 63.61, H, 4.31, N, 2.60. Found: C, 63.57, H, 4.29, N, 2.63. IR spectra (KBr, cm^{-1}): 3053 $\nu(N-H)$, 1536, 1497 $\nu(CO)$, 1094, 948, 923 $\nu(C-S)$. NMR ($CDCl_3$, δ ppm): 1H NMR; 7.18-7.42 (Ph ring), 11.90 (NH). ^{13}C NMR; 110.9, 123.4 (MB), 127.5-142.4 (Ph and MB ring), 164.1 (N₂CS), 207.8 (COS).

Synthesis of $[Cu_2(\mu-SCOPh)_2(\mu-MT)(MT)]_2$ (7)

To a mixture of sodium thiobenzoate [prepared *in situ* by mixing PhCOSH (0.138 g, 1.0 mmol) and sodium methoxide (0.054g, 1.0 mmol)] and MT (0.119g, 1mmol) in 10 mL of methanol, added solid cuprous chloride (0.099g, 1.0 mmol) with stirring. The reaction mixture was stirred further for five hours. The yellow precipitate formed, was filtered and dried under vacuum. The yellow residue was dissolved in mixture of chloroform and toluene (3:1) and kept for crystallization. Yellow block shaped crystals were obtained after few days. Yield: 0.235g (73%). Elemental analysis: Cal. for $C_{40}H_{40}N_4O_4S_{12}Cu_4$: C, 37.54, H, 3.15, N, 4.38. Found: C, 37.44, H, 3.13, N, 4.40. IR spectra (KBr, cm^{-1}): 2996 $\nu(N-H)$, 1592, 1569 $\nu(CO)$, 1049, 993, 917 $\nu(C-S)$. NMR ($CDCl_3$, δ ppm): 1H NMR; 3.51 (CH_2), 3.92 (CH_2), 7.14-7.97 (Ph ring), 10.09 (NH). ^{13}C NMR; 32.8 (CH_2), 51.4 (CH_2), 125.2-137.3 (Ph ring), 167.2 (COS), 199.9 (NSCS).

Synthesis of $\{[(PPh_3)_2Ag(SCOPh)MT][(PPh_3)_2Ag(SCOPh)].Toluene\}$ (8)

The same procedure was followed as mentioned for **1** except the fact that $(PPh_3)_2Ag(NO_3)$ (0.694 g, 1.0 mmol) and MT (0.119g, 1mmol) were used in place of $(PPh_3)_2Cu(NO_3)$ and

MB. Colorless rectangular crystals were obtained from mixture of chloroform and toluene solution (1:1). Yield: 0.596g (69%).

Elemental analysis: Cal. for $C_{97}H_{84}NO_2S_3P_4Ag_2$: C, 67.28, H, 4.89, N, 0.81. Found: C, 67.35, H, 4.82, N, 0.87. IR spectra (KBr, cm^{-1}): 3052 $\nu(N-H)$, 1584, 1542 $\nu(CO)$, 1093, 997, 919 $\nu(C-S)$. NMR ($CDCl_3$, δ ppm): 1H NMR; 2.35 (Me of toluene), 3.51 (CH_2), 3.98 (CH_2), 7.15-8.14 (Ph ring), 9.78 (NH). ^{13}C NMR; 33.9 (CH_2), 51.7 (CH_2), 127.4-133.9 (Ph ring), 207.4, 200.5, (COS), 199.6 (N₂CS).

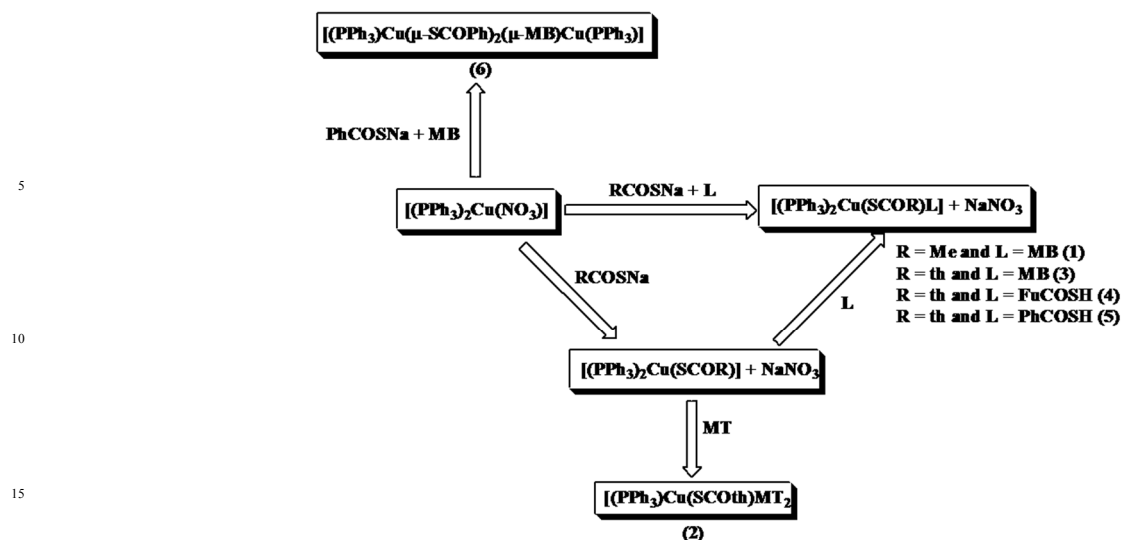
Synthesis of $[(PPh_3)_2Ag(SCOPh)MB].Toluene$ (9)

The same procedure was followed as mentioned for **8** except the fact that MB (0.150g, 1.0 mmol) was used in MT. Colorless rectangular crystals were obtained from mixture of chloroform and toluene solution (1:1). Yield: 0.699g (76%). Elemental analysis: Cal. for $C_{50}H_{41}N_2OS_2P_2Ag$: C, 65.29, H, 4.49, N, 3.05. Found: C, 64.97, H, 4.42, N, 3.13. IR spectra (KBr, cm^{-1}): 3056 $\nu(N-H)$, 1582, 1537 $\nu(CO)$, 1188, 1166, 924 $\nu(C-S)$. NMR ($CDCl_3$, δ ppm): 1H NMR; 2.28 (Me of toluene), 7.00-8.18 (Ph and MB ring), 11.72 (NH). ^{13}C NMR; 110.6, 123.2 (MB), 127.4-144.3 (Ph and MB ring), 166.6 (N₂CS), 207.9 (COS).

Results and Discussions

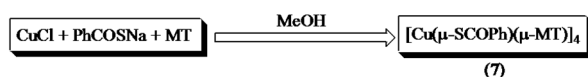
Syntheses and characterizations

The complexes **1-6** have been synthesized either by direct reaction of *bis*(triphenylphosphine)copper(I) nitrate with sodium salt of thiocarboxylate and 2-mercaptobenzimidazole/ 2-mercapto-2-thiazoline/ thiocarboxylic acid or by synthesizing the thiocarboxylate complexes of *bis*(triphenylphosphine)copper(I) and then reacting it with 2-mercaptobenzimidazole/ 2-mercapto-2-thiazoline/ thiocarboxylic acid (**Scheme 2**). The products obtained are of general formula $[(PPh_3)_2Cu(SCOR)L]$ (**1**, **3-5**) except in the case of cases of **2** and **6** where a phosphine ligand is also replaced. In complex **2**, the substitution is by another 2-mercapto-2-thiazoline molecule whereas in case of **6** there is no new substituent molecule, however, the 2-mercaptobenzimidazole bridges between two copper atoms, thus keeping the coordination number of Cu unchanged



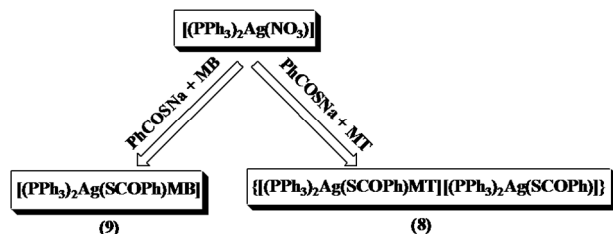
Scheme 2

The complex 7 was synthesized by reaction of cuprous chloride with sodium salt of thiocarboxylate and 2-mercapto-2-thiazoline in equimolar ratio (Scheme 3).



Scheme 3

Complexes 8 and 9 were synthesized by reaction of bis(triphenylphosphine)silver(I) nitrate with sodium thiobenzoate and 2-mercapto-2-thiazoline or 2-mercaptobenzimidazole respectively (Scheme 4).



Scheme 4

All the complexes were isolated in good yields and were found to be quite stable under ambient conditions. The complexes were characterized by elemental analysis, IR, 1H NMR, ^{13}C NMR, and UV-Visible spectroscopic techniques. In the IR spectra of all complexes three distinct absorption bands at 2996-3068, 1592-1597 and 1121-910 cm^{-1} were obtained corresponding to the N-H, C-O and C-S stretchings respectively. 1H NMR spectra of complexes 1-3 and 6-9 showed a broad peak at 9.78-11.64 ppm which can be assigned due to NH protons whereas complexes 4 and 5 showed broad peaks respectively at 1.93 and 2.11 ppm for OH protons.

Complexes 2, 7 and 8 showed two peaks at 3.46-3.51 and 3.91-3.98 ppm for the methylene protons of thiazoline. Other than these peaks a bunch of peaks were obtained in the range of 6.44-8.14 ppm due to the protons attached to aromatic rings. The ^{13}C NMR spectra were also consistent with the 1H NMR features (given in experimental section).

Crystal and molecular structures

All the complexes have been characterized by single crystal X-ray diffraction techniques. A summary of crystallographic data and structure solutions are listed in Table S1 (supporting information). Selected bond lengths and bond angles are given in Table S2 (supporting information). The coordination geometry around copper atom in complexes 1-5 can be defined as distorted tetrahedral (Figure 1a-e) and all the bond lengths and bond angles are comparable to reported values for thiocarboxylate and heterocyclic thioamide complexes of copper(I).^[6a,7] In the complexes 1 and 3 copper atom is coordinated by the two phosphorus of triphenylphosphine and sulfur of 2-mercaptobenzimidazole besides the sulfur of thiocarboxylate ligands whereas in 2 (Figure 1b) copper is coordinated by a phosphorus of triphenylphosphine and two sulfur from MT ligand in addition to the thiocarboxylate. Complexes 4 and 5 have similar coordination environments as observed in the case of 1. (Figure 1d and 1e).

In the complexes 1-3, strong hydrogen bonds are present in between NH of heterocycle and O of thiocarboxylate (Table S3, supporting information). In case of 1 and 2 intra-molecular hydrogen bonding are present. On changing the R group of thiocarboxylate (from Me to th) the hydrogen bonding changed from intra-molecular to inter-molecular type (as seen in the case of 3). In case of 1 besides intra-molecular hydrogen bonding, strong inter-molecular $NH\cdots S$ (2.700 Å) and $CH\cdots\pi$

(2.711 Å) interactions are also present. Due to these interactions a helical structure is formed (**Figure 2a**). Presence of inter-molecular hydrogen bonding (NH \cdots O) in **3** results in a linear chain of molecules (**Figure 2b**). In case of complex **4** the hydrogen of thiocarboxylic acid is present in between two oxygens of thiocarboxylate groups but slightly near to the O1 (1.102 Å) and have strong hydrogen bonding with O2 (1.351 Å). The two C-S bonds (1.673 and 1.688 Å) and the two C-O bonds (1.280 and 1.274 Å) of thiocarboxylate groups are

respectively comparable and possibly the H atom oscillates between the two oxygen atoms ^[7] (**Figure 1d**) Complex **5** also has similar hydrogen bonding as in **4** except the fact that the two C-O bonds are of different bond lengths (1.312 and 1.259 Å).

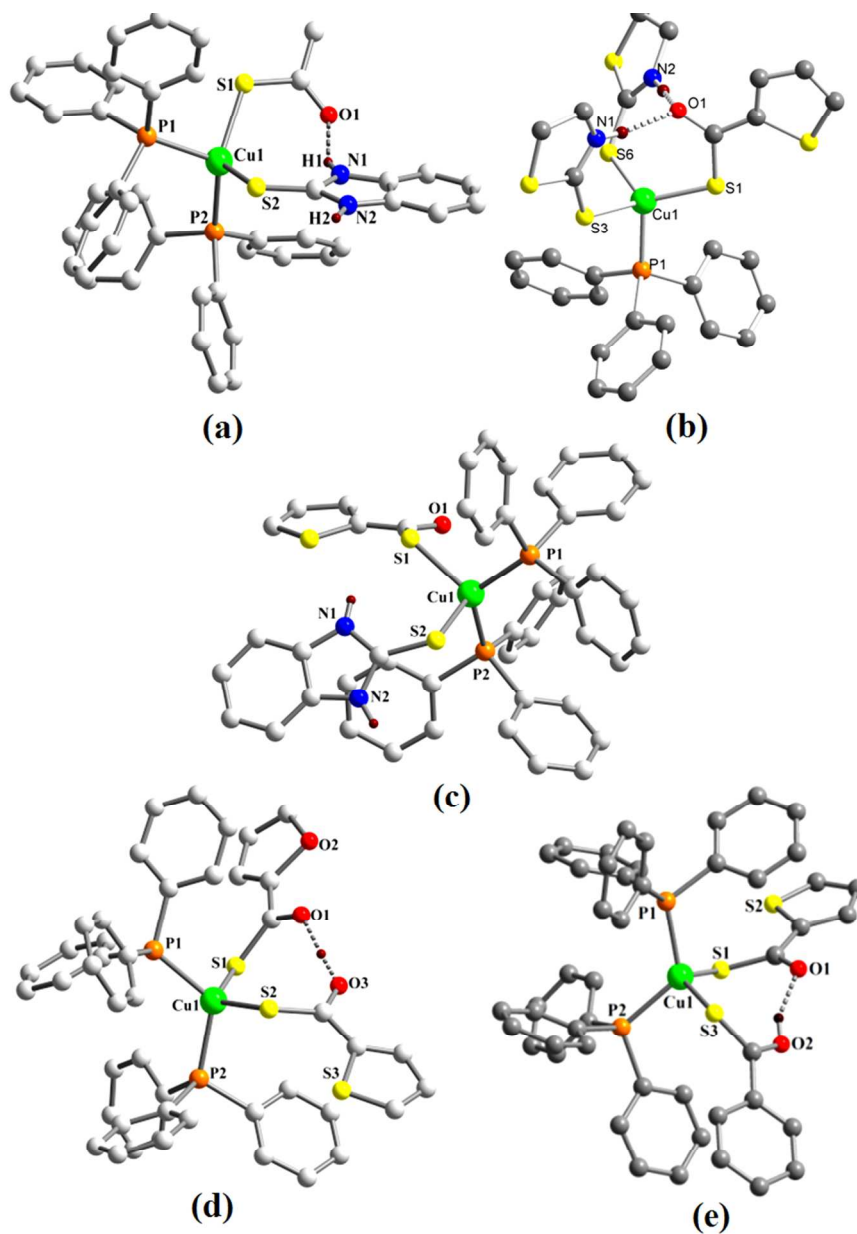


Figure 1 Molecular structure of complexes 1-5

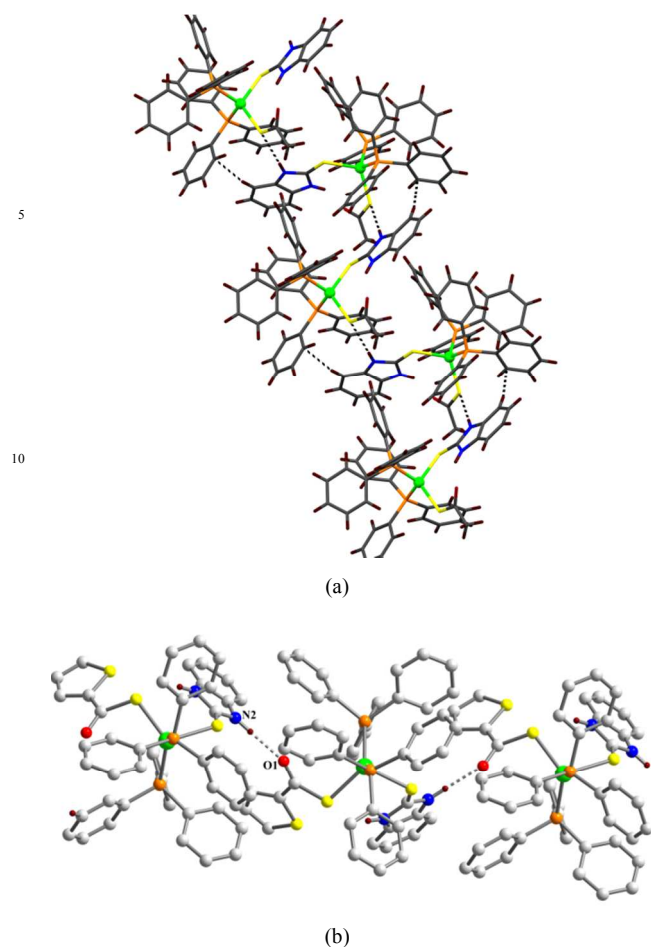


Figure 2 Arrangement of **1** (a) and **3** (b) due to intermolecular H-bonding

Complex **6** is bimetallic molecule in which two copper centres are bridged by two thiocarboxylate and one sulfur of 2-mercaptobenzimidazole. Molecular structure of **6** is depicted in **Figure 3**. In this complex two different types of binding modes of thiobenzoate ligands are observed; O, S (bidentate) bridging which represents the classical binding mode of the ligands and S bridging. Besides these bridging ligands a strong Cu–Cu interaction is also responsible for holding the two metals together. The Cu–Cu distance [2.7180(18) Å] is slightly longer than the sum of the covalent radii of the two atoms (2.64 Å). Both the copper atoms have tetrahedral geometries with different degrees of distortions.

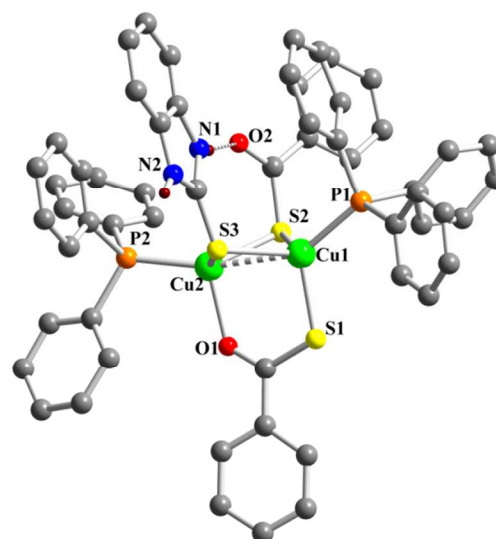


Figure 3 Molecular structure of **6**

Besides the intra-molecular hydrogen bonding between N1H and O2 inter-molecular hydrogen bonding is also present in between N2H and S3 (**Table S3**, supporting information). Pairing of molecules occurred due to presence of these inter-molecular hydrogen bondings (**Fig. 4**).

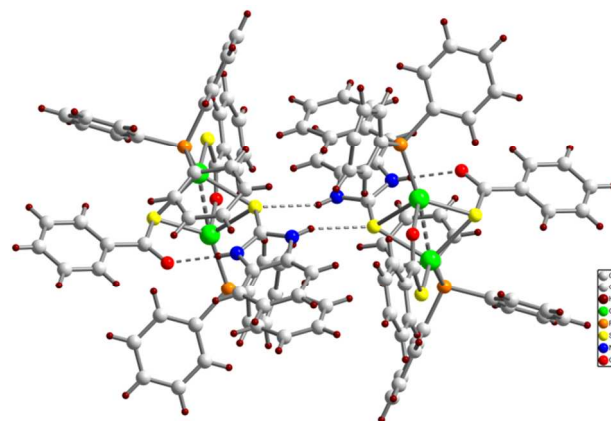


Figure 4 A pair of **6** due to intermolecular H-bonding

Complex **7** is crystallized in triclinic system with *P*-1 space group. A solvent (disordered) molecule co-crystallized with **7** which could not be identified. The molecular structure of complex depicted in **Figure 5a**. Complex **7** is a tetra-nuclear (Cu_4) compound, with a planar six membered ring constituted by two copper atoms and one sulfur atom alternatively (**Figure 5b**). Distance between the two adjacent copper atoms (2.598 Å) are very short even shorter than sum of covalent radii (2.64 Å) but bond angles around metal centres do not suggest the

existence of a covalent bond between the two. As revealed by the bond angles around Cu1 (which are very close to 120°), it possesses a trigonal planar geometry with slight deviation (0.018 \AA) from the plane constituted by S1, S2 and S3 atoms. Notably, the geometry around Cu2 is highly deviated from trigonal planar it is situated above the plane constituted by S1, S2' and S5 atoms by 0.417 \AA . This deviation may be because of the strong interaction between of Cu2 and S3 atoms (2.812 \AA) which is shorter than the sum of van der Waals radii of two atoms (3.20 \AA). Complex 7 also have two intra-molecular $\text{NH}\cdots\text{O}$ hydrogen bonding with distances 1.991 and 2.053 \AA respectively.

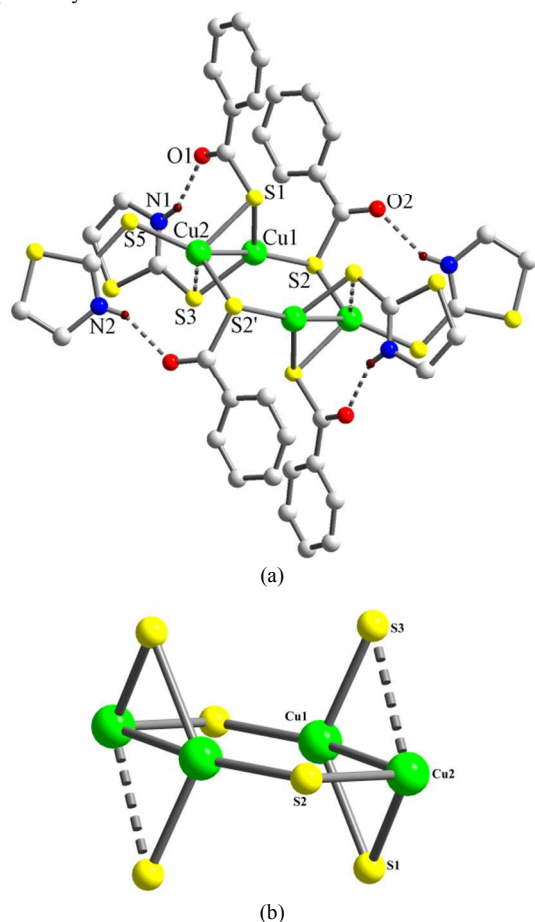


Figure 5 (a) Molecular structure of 7 and (b) its core structure

In the complex 8 two different types of molecules co-crystallized together along with a toluene molecule (**Figure 6**). Both the molecules are connected with toluene by $\text{CH}\cdots\pi$ interactions with distances of 3.445 and 2.686 \AA respectively. In the first molecule, silver having distorted tetrahedral geometry is bonded with two phosphorus of triphenylphosphine and sulfur of 2-mercapto-2-thiazoline besides the sulfur of thiobenzoate. All the bond lengths and bond angles are comparable to reported values for thiobenzoate

and heterocyclic thioamide complexes of silver(I).^[15,2e] An intra-molecular hydrogen bonding also present in between NH of heterocycle and oxygen of thiocarboxylate (**Table S3**, supporting information).

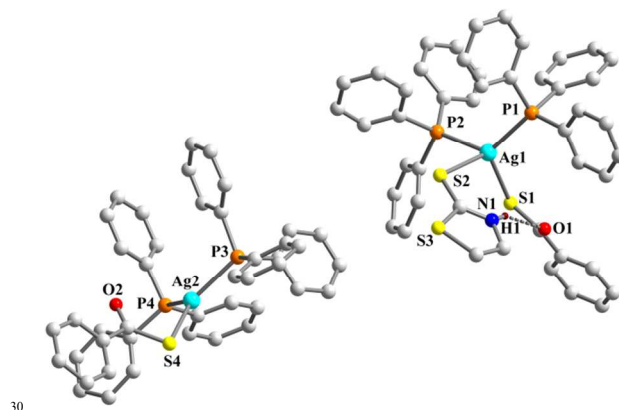


Figure 6 Molecular structure of 8

In the second molecule, silver is surrounded by two phosphorus of triphenylphosphine and sulfur of thiobenzoate group. In this case also all the bond lengths and bond angles are comparable to the analogous bond lengths and angles reported for silver thiobenzoate.^[2e] The geometry around Ag2 atom is trigonal planar and the Ag atom is slightly tipped above (0.011 \AA) the plane constituted by S4, P3 and P4 atoms.

Complex 9 also has two types of molecules both of which have distorted tetrahedral geometry. Each Ag(I) is surrounded by two phosphorus of triphenylphosphine and one sulfur of 2-mercaptobenzimidazole besides sulfur of thiobenzoate. Notably, the orientation of thiocarboxylate groups are not identical. In one rotamer oxygen of thiobenzoate is facing towards the benzimidazole ring whereas in the other it is facing away from benzimidazole ring (**Figure 7**).

The two molecules are interconnected by intra and inter-molecular hydrogen bonding between NH of heterocycle and O of thiocarboxylate as well as $\text{NH}\cdots\text{S}$ hydrogen bonds (**Table S3**, supporting informations). A linear chain of molecules are formed due to the presence of $\text{NH}\cdots\text{O}$ and pair of $\text{NH}\cdots\text{S}$ hydrogen bonds (**Figure 8**).

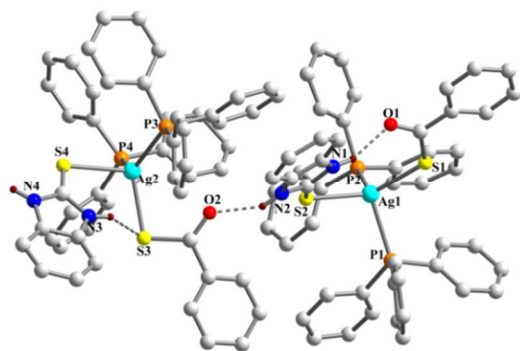


Figure 7 Molecular structure of 9

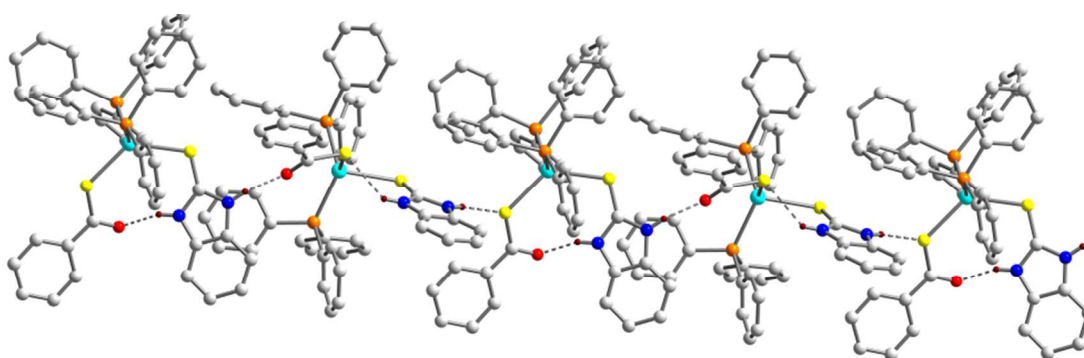


Figure 8 A linear chain of 9 due to intra and intermolecular H-bonding

Theoretical calculations

To get further insight into the nature of Cu-Cu interaction in 6 and 7, we have carried out density functional calculations. The results of second order perturbation analysis of Fock matrix (NBO) reveal that there are significant intra-molecular interactions. In case of 6 electron transfer from Lp^* orbitals of Cu1 to Lp^* of Cu2 amounts to 227 kcal/mol of energy lowering. It may therefore, be concluded that the short Cu-Cu distance is not merely a consequence of steric constraints imposed by the ligands but is a result of strong bonding interactions between the two atoms.

In case of 7 two Cu-Cu distances (2.598 and 2.987 Å) are observed. In the first case distance between two copper atoms (2.598 Å) is even shorter than the sum of covalent radii of the two atoms indicating the existence of a covalent bond between the two atoms. Surprisingly, a look into the maximum stabilisation energy associated with electron transfers between a pair of Cu atoms revealed that the pair with a longer Cu-Cu distance has a stronger interaction ($Lp^*Cu48 \rightarrow Lp^*Cu62 = -43$ kcal/mol) as compared to that between the other two (Cu53 to Cu48 = -36.9 kcal/mol).

To get further insight about the Cu-Cu interaction in 7, bond critical points (bcp) were calculated using the Atoms in

Molecules (AIM) theory.^[16] The bond critical points were not observed between the pairs copper atoms (Cu56-Cu62 and Cu48-Cu53) with shorter Cu-Cu distances, thus confirming the absence of any bond between these pairs of Cu atoms (Figure 9). However, the presence of bond critical point in between Cu48 and Cu62, shows the presence of weak interaction between these two copper atoms. However, the distance between these two atoms is slightly longer than the sum of their van der Waals radii. The value of electron density (ρ_{bcp}); Laplacian electron density ($\nabla^2\rho_{bcp}$); bond ellipticity (ϵ) and total energy density (H) at the bond critical point for Cu-Cu interactions in 7 are +0.012891, +0.035751, +0.258915 and 0.000176 au respectively. It is evident that the electron density at bond critical point (ρ_{bcp}) for Cu48-Cu62 being less than +0.10 au, is indicative of weak closed shell Cu-Cu interactions. Additionally, the Laplacian of the electron density $\nabla^2\rho_{bcp}$ in this case being positive indicates the depletion of electron density in the region of contact between the Cu-Cu atoms which is characteristic of closed shell interactions. The bond ellipticity (ϵ) measures the extent to which the density is preferentially accumulated in a given plane containing the bond path. The ϵ values for 7 indicate that Cu-Cu interactions are cylindrically non-symmetrical in nature.

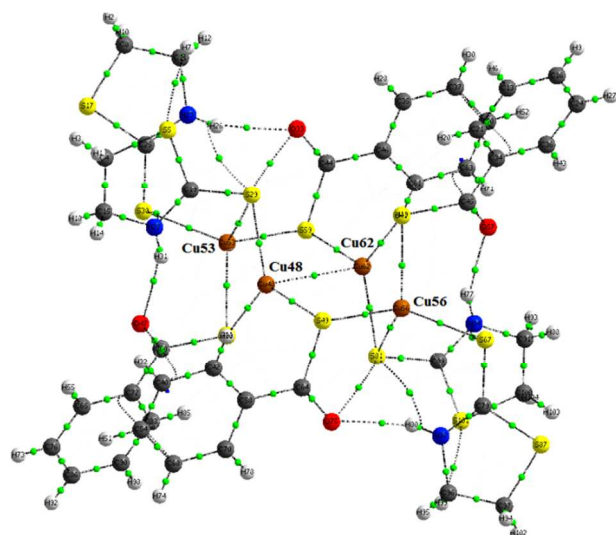


Figure 9 Molecular graphs for the **7** by AIM calculations using B3LYP/6-31G** level of theory. (Bond critical points are shown by green spots)

Electronic Absorption and Photoluminescent Spectra

Absorption spectra of **1**, **3**, **6** and **9** have similar absorption bands in which 2-mercaptobenzimidazole coordinated to the metal (**Figure S1** and **S2**, supporting information). Complex **1** shows bands at 244, 254, 280 and 309 nm. The spectra of **2**, **4**, **5** and **8** have similar absorptions bands listed in **Table 1**. The spectrum of complex **7** shows bands at 249, 279 and 366 nm. In general, lower energy peaks appear because of the metal to ligand (or ligand to metal) charge transfers while peak below 300 nm are due to inter- or intra-ligand charge transfers.

Table 1 Absorption bands of complexes

Complex	Absorption bands (nm)
1	309, 280(broad), 254, 244
2	345(broad), 279, 253
3	310, 255, 244
4	335(broad), 261, 242
5	333(broad), 257, 244
6	309, 302, 245
7	366 (broad from 310-404), 279, 249
8	317(broad), 276(shoulder), 245
9	309, 300(shoulder), 247

For unambiguous assignment of the absorption bands time dependent density functional theory (TDDFT) calculations have been performed for the complexes **1** and **7** at B3LYP level. The orbital transition plots of **1** are shown in **Figure 10**. The calculated absorptions at 299 and 311 nm are due to electron transfers from lone pair of sulfur, phosphorous, oxygen and copper atoms to the phenyl rings of triphenylphosphine and benzimidazole ring ($n \rightarrow \pi^*$). Other absorption peaks at 280, 254 and 244 nm are due to intra- and

inter-ligand charge transfers.

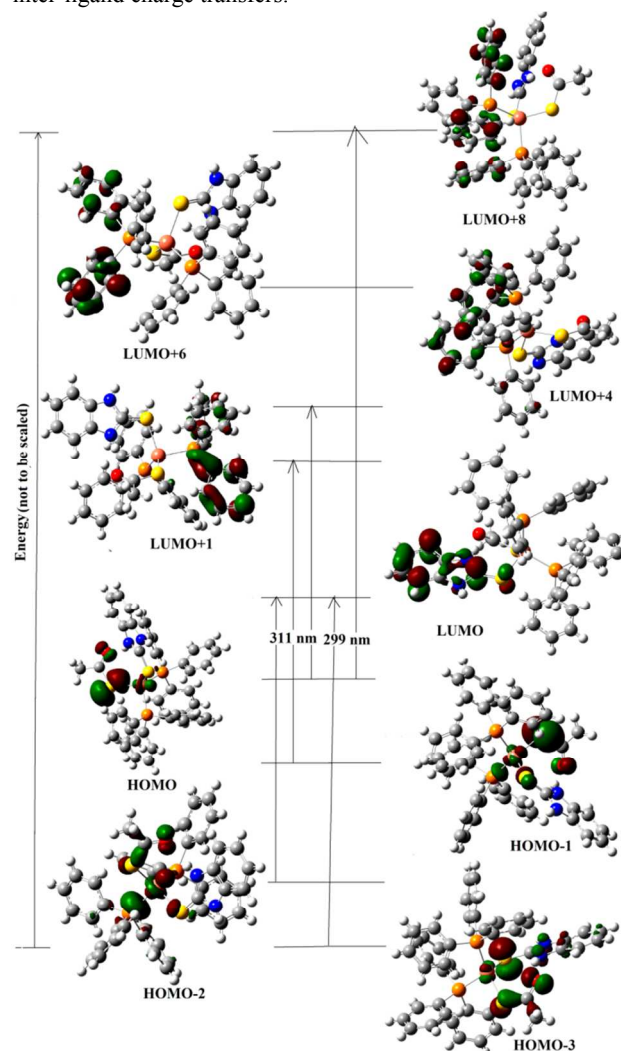


Figure 10 Selected orbital transitions in **1** (orbital contour value 0.05)

In case of complex **7** calculated band at 372 nm is due to charge transfers from the lone pair of sulfur of thiobenzoate and copper atoms to phenyl rings of thiobenzoate ligands ($n \rightarrow \pi^*$) as shown in **Figure 11**.

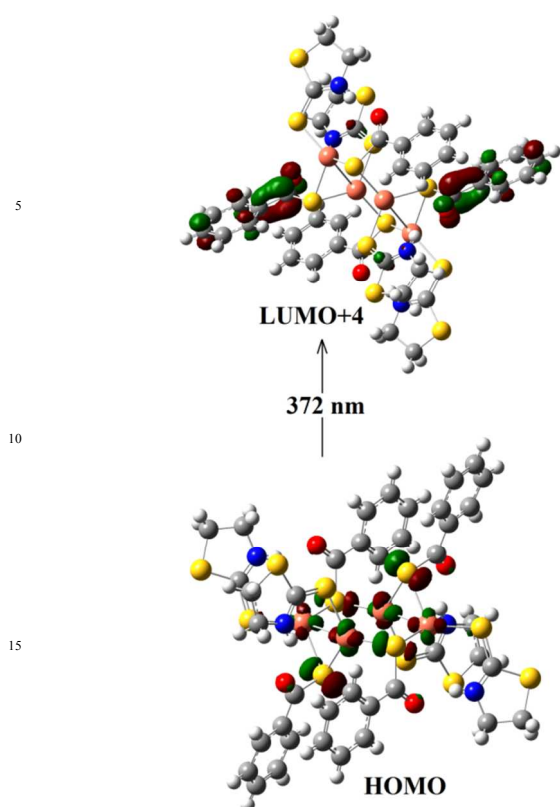


Figure 11 Selected orbital transitions in **7** (orbital contour value 0.05)

Emission spectra of all the complexes recorded in solution (**Figure S3** and **S4**, supporting information) as well as in solid state (**Figure S5** and **S6**, supporting information). The emission and excitation data of complexes are summarized in **Table 2**. Upon excitation at 375 nm (calculated excitation wavelength) in chloroform solution at room temperature, complexes **1** give rise to an intense emission band at 435 nm other than a shoulder emission band at 412 nm, while in solid state emission band obtained at 406 nm and 491 nm (shoulder) (**Figure 12**).

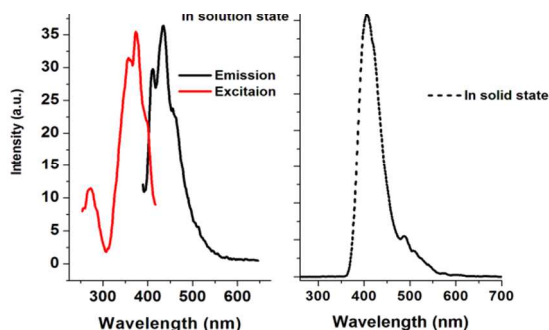


Figure 12 Emission spectra of **1** in solution and solid state

Table 2 Emission bands of complexes in solution and solid state

Complex	Excitation band (nm)	Emission band (nm)	
		Solution state	Solid state
1	375	412 (shoulder), 435	406, 491 (shoulder)
2	379	436, 463 (shoulder)	396 (intense band), 308, 509, 604 (weak band)
3	375	410 (shoulder), 434	398 (intense band), 307, 488, 602 (weak band)
4	371	408, 431	393 (intense band), 306, 604 (weak band)
5	375	409, 433	390 (intense band), 307, 605 (weak band)
6	374	436, 460 (shoulder)	396, (intense band), 306, 510, 602 (weak band)
7	371	424	396 (intense band), 305, 491, 602 (weak band)
8	358	436	393 (intense band), 305, 603 (weak band)
9	337	407	410 (intense band), 306, 601 (weak band)

Similar emission bands are also observed in case of complexes **2–6** given in table 5 (**Figure S3** and **S5**, supporting information). In solution state, complex **7** showed weak and broad emission band (**Figure S3**, supporting information) at 424 nm when it was excited at 371 nm where as in solid state an intense emission band observed at 396 nm along with weak emission bands at 305, 491 and 602 nm. Complexes **8** and **9** showed emission bands (**Figure S4** and **S6**, supporting information) at 436 and 407 nm respectively in solution state and intense emission bands at 393 and 410 nm respectively in solid state along with three weak emission bands (**Table 2**). Though the assignments of the emissive excited states in the Cu(I) complexes is a difficult task, yet a few inferences could be drawn. The strong emission peaks around 400 nm are similar to that observed in a large number of Cu(PPh₃) complexes, which indicates that the origin of these emissions involves emissive state derived from ligand-centered [$\pi-\pi^*$] transition.^[17] All the complexes (except **1**) in solid state exhibit a low-energy emission with k_{em} at ~600 nm, which is due to M-S (thiocarboxylate) charge transfer. Interestingly, another emission (centered between 488–510 nm) is observable in the spectra of the Cu(I) complexes except **4** and **5** originated due to Cu(I)-S (heterocyclic thioamides) charge transfer. Since the

Cu(I) ion express strong tendency for charge transfer of this type, the emissions cannot be considered purely to be intra-ligand origin.^[17]

Conclusions

Seven new copper(I) thiocarboxylate complexes, [(PPh₃)₂Cu(SCOR)L] [when L = MB and R = Me (**1**), th (**3**), R = th and L = FuCOSH (**4**) and PhCOSH (**5**)], [(PPh₃)Cu(SCOth)MT₂], (**2**) [(PPh₃)Cu(μ-SCOPh)₂(μ-MB)] (**6**), [Cu₂(μ-SCOPh)₂(μ-MT)(MT)]₂ (**7**) and two silver thiocarboxylate complexes, {[(PPh₃)₂Ag(SCOPh)MT][(PPh₃)₂Ag(SCOPh)].C₇H₈} (**8**), [(PPh₃)₂Ag(SCOPh)MB].C₇H₈ (**9**) containing 2-mercaptobenzimidazole and 2-mercapto-2-thiazoline have been synthesized and structurally characterized. All the complexes have either intra or inter-molecular hydrogen bonding between oxygen/sulfur of thiocarboxylate and hydrogen of heterocyclic thioamides. From single crystal structures of complexes it is clear that direction of hydrogen bonding can be customized by modifying the size of terminal R-groups of thiocarboxylate and heterocyclic ring. **7** is a tetranuclear copper(I) complex in which two copper atoms are forced to sit very close (but without any direct Cu-Cu bonding interaction) within their covalent radii by bridging of sulfur donor ligand and intra-molecular hydrogen bonding. In case of complex **8** two different types of molecules co-crystallized in same lattice and they are connected by weak interactions (CH...π) through a toluene molecule. In case of complex **9** also two different molecules are present in lattice having same molecular formula but are different rotamers. All the complexes showed photoluminescent property in both solution and solid states, these may find applications as fluorescent sensors.

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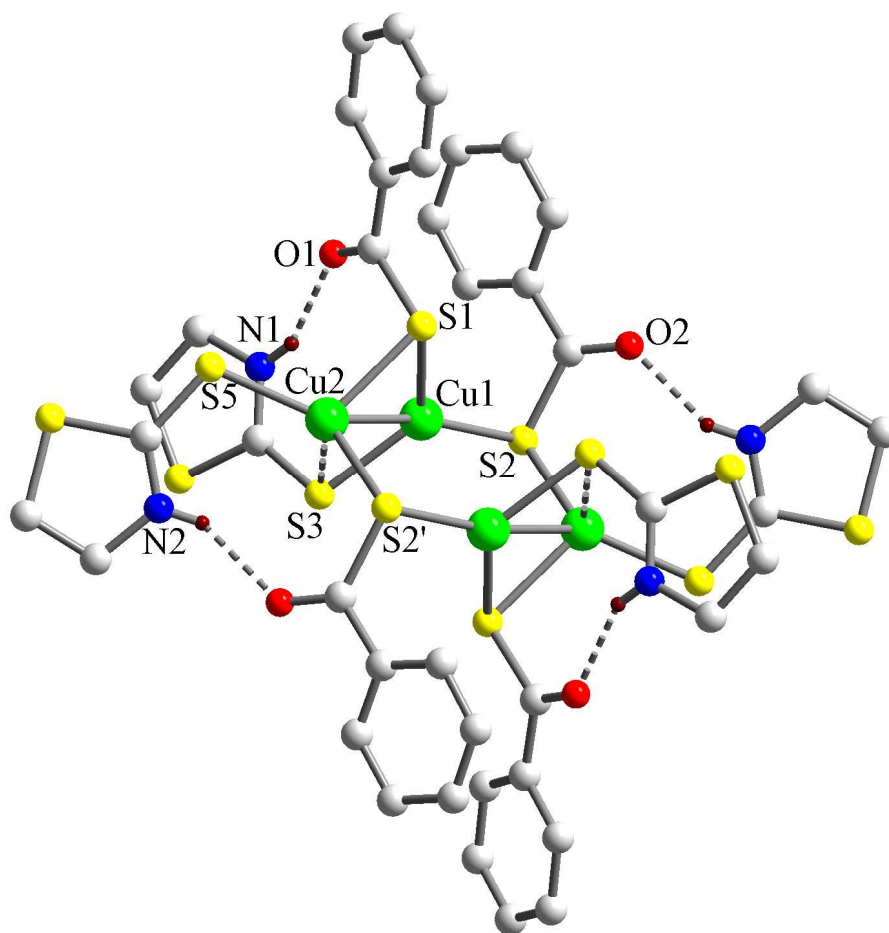
Notes and References

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† Electronic Supplementary Information (ESI) available: **Table S1-S3** and **Fig. S1-S6** and the crystallographic data in CIF format. CCDC 935064-935072 contain the crystallographic data for complexes **1-9** respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>. See DOI: 10.1039/b000000x/

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Seven new copper(I) thiocarboxylate and two silver thiocarboxylate complexes containing 2-mercaptobenzimidazole and 2-mercapto-2-thiazoline have been synthesized and structurally characterized. Direction of hydrogen bonding have been changed from intra-molecular to inter-molecular by increasing the size of R-group of thiocarboxylate ligands. Absence of real bond between two copper atoms in **7** has been confirmed by NBO calculation and bond critical points calculations using the AIM theory. In complex **8** two different molecules, $[(PPh_3)_2Ag(SCOPh)MT]$ and $[(PPh_3)_2Ag(SCOPh)]$ are co-crystallized in the same lattice. Complex **9** also possesses two structurally different molecules present of the same molecular formula. Electronic spectral behaviors of the complexes **1** and **7** have been explained by TDDFT calculations. Emission spectra of complexes have been studied in both solution and solid states.