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Studies of synthesis, structural features of Cu(I) thiophene-2-thiocarboxylates and unprecedented desulfurization of Cu(II) thiocarboxylate complexes[†]

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Thiophene-2-thiocarboxylate complexes of Cu(1), $[(Ph_3P)_2Cu(SCOth)]$ (1) and $H[(Ph_3P)_2Cu(SCOth)_2]$ (2) (where th = thiophene) were synthesized and characterized structurally by X-ray crystallography. Electronic absorption and emission spectral properties of the two compounds have been studied. Cu(II) complexes, $[(TMEDA)Cu(SCOth)_2]$ (3b) and $[(Phen)Cu(SCOth)_2]$ (4a) (where TMEDA = tetramethylethylenediamine; Phen = 1,10-phenanthroline) were prepared and characterized by spectroscopic measurements. 3b and 4a underwent desulfurization under ambient conditions readily yielding the corresponding carboxylate complexes $[(TMEDA)Cu(O_2Cth)_2]$ (3a) and $[(Phen)Cu(O_2Cth)_2 \cdot H_2O]$ (4b). 3a and 4b have been characterized crystallographically.

Studies on interaction of copper compounds with sulfur ligands are of current interest because of several reasons. Cu–S interactions are responsible for various enzymatic reactions.¹ Michael reaction using various chiral sulfur ligands is known to proceed *via* Cu(II) catalysis.² Desulfurization reactions have also been carried out by copper compounds by sorption³ as well as catalytic reactions.⁴

Very recently, we have found a catalytic oxidation pathway giving diaryldisulfides by oxidation of the corresponding thiocarboxylate anions using an Ag(I) salt.⁵ Ferretti has reported Cu(I) mediated oxidation of thiobenzoate anion, however, the reaction was non-catalytic in nature and yielded some other products also.⁶ Vittal and co-workers have synthesized a few Cu(I) thiocarboxylate complexes containing triphenylphosphine coligand.⁷ These complexes exhibited different nuclearities varying between one, two and four. In addition, a homoleptic Cu(I) complex $[Cu(SC{O}Me)_2]^-$ has also been reported.⁸ A few heterobimetallic thiocarboxylate complexes containing Cu(I)/In(III),9 Cu(I)/Pb(II),10 Cu(I)/Zn(II) and Cu(I)/Cd(II)11 have also been synthesized and characterized structurally. Notably, in all these complexes, the thiocarboxylate ligand is bound essentially through the sulfur atom (though oxygen atom in some cases is also bound to the metal). Besides limited studies¹² on the Cu(II) complexes of pyridine-2,6-bis(thiocarboxylate) there is no report on any Cu(II) thiocarboxylate compounds and to the best of our knowledge no such complex have yet been structurally characterized.

 $[(Phen)Cu(O_2Cth)_2]$ **Introduction** Studies on interacti are of current intertions are responsible reaction using varie

In light of these facts we thought it was worthwhile to study the reactions of thiocarboxylates with Cu(I) and Cu(II) compounds.

Results and discussion

Syntheses and characterization

Compound 1, $[(PPh_3)_2Cu(SCOth)]$ (where th = thiophene) was obtained by a simple reaction between $(PPh_3)_2Cu(NO_3)$ and sodium thiophene-2-thiocarboxylate. The copper atom in 1 being coordinatively unsaturated can easily bind with another thiocarboxylic acid molecule giving $H[(PPh_3)_2Cu(SCOth)_2]$ (2) (Scheme 1).



When a reaction of sodium thiophene-2-thiocarboxylate was carried out with hydrated copper(II) nitrate (or sulfate) in the presence of TMEDA (N,N,N'N'-tetramethylethylene-diamine) the complex (TMEDA)Cu(O₂Cth)₂ (**3a**) was obtained whereas the same reaction when carried out with anhydrous copper(II) sulfate resulted in the formation of the compound (TMEDA)Cu(OCSth)₂

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(3b). In an analogous reaction (Phen)Cu(SCOth)₂ (4a) (Phen = 1,10-phenanthroline) was obtained when Phen was used instead of TMEDA. Compound 4a was not very stable in solution and color of the solution changed from red to blue giving (Phen)Cu(O₂Cth)₂ (4b) (Scheme 2) under ambient conditions. Single crystals of 3b and 4a suitable for X-ray analysis could not be grown even by our best efforts under anhydrous atmosphere. Compound 3a and 4b were formed by desulfurization of the thiocarboxylate ligands in the presence of water. Metal thiocarboxylates are known to undergo facile thiocarboxylic anhydride elimination leaving the metal sulfide.^{5,13} Notably, insoluble metal sulfide was not obtained in any of the present cases. Thus the sulfur loss was invariably in the form of H₂S.[‡] On the basis of these experimental evidence a plausible mechanism of the reaction is proposed in Scheme 3.



Scheme 3

All the complexes have been characterized by elemental analyses as well as various spectroscopic techniques. No signal was observed in the ESR spectrum of **2** which evidenced that the Cu atom was in +1 oxidation state. This fact was also supported by the appearance of a broad signal in the ¹H NMR spectrum at 1.87 ppm due to the proton of the coordinated thiocarboxylic acid.

Phosphine adducts of copper thiocarbamates associate/dissociate in solution to give an equilibrium mixture

of different species with various copper-ligand ratios.¹⁴ Due to fast scrambling process solution structures of these compounds have not been studied in details.¹⁵ Notably, a number of studies have been made on Au(I) complexes exhibiting fast/slow scrambling processes.¹⁶ In view of these one would expect ligand association/dissociation in the solutions of **1** and **2**.

Interestingly, the room temperature ³¹P NMR spectrum of **1** showed three sharp peaks at 29.2, 35.9 and 43.3 ppm while a relatively broad peak was observed at -2.6 ppm (Fig. 1). The latter split into three at -30 °C and at least five peaks were visible at -60° C.



Fig. 1 Variable temperature ³¹P NMR spectra of (A) 1 and (B) 2.

The nature of the peaks indicated that the slow exchange limit was not reached. The three peaks at low field were due to cations, $[Cu(PPh_3)]^+$, $[Cu(PPh_3)_2]^+$ and $[Cu(PPh_3)_3]^+$ whereas the peaks observed at high field were due to fast ligand exchange process resulting in the formation of various species such as $[Cu(PPh_3)_2(SCOth)]$, $[Cu(PPh_3)(SCOth)_2]^-$, $[Cu(PPh_3)_2(SCOth)_2]^-$ *etc.* In the ES mass spectrum peaks corresponding to $[Cu(PPh_3)_2]^+$ and $[Cu(PPh_3)_3]^+$ were observed with high relative intensities, however, low intensity peaks due to a number of other species were also noticeable (Fig. S1 and S2 ESI⁺).

In ¹³C NMR spectrum of **2** appearance of a single peak at 197.94 ppm due to the COS carbon indicated the equivalence of both the thiocarboxylate groups in solution at room temperature. At -40° C two carbonyl peaks were observed at 190.97 and 202.40 ppm. The results were consistent with the ³¹P NMR study. There were four ³¹P signals at room temperature, however, the three peaks at low field (43.3, 35.8 and 30.5 ppm) are due to cationic species which do not bear any thiocarboxylate groups. The fast exchange between thiocarboxylate groups resulted in a single averaged peak at -0.9 ppm. This peak split into two at -40° C and further into three (which are still quite broad) at -60° C revealing a very fast scrambling process.

In the IR spectra of **3b** and **4a** the CO stretching band was observed respectively at 1464 and 1418 cm⁻¹ which indicated coordination of the ligand through oxygen atom.¹⁷ Expectedly, the CS stretching showed a blue shift and appeared at 998 and 1022 cm⁻¹ in **3b** and **4a**. The spectrum of **3a**, however, showed CO stretching bands at 1571 and 1524 cm⁻¹ while the same in

 $[\]ddagger$ Evolution of H₂S was confirmed by blackening of a paper strip moistened with lead acetate and acetic acid solutions kept overnight inside a vessel containing a solution of **4a**.

the case of **4b** appeared at 1566 and 1520 cm⁻¹ and CS stretching band was observed in neither of the two spectra. Appearance of two v(CO) bands is indicative of asymmetrical coordination of the carboxylate ligand.

Crystal and molecular structures

Complexes 1, 2, 3a and 4b were characterized by single crystal X-ray diffraction analyses. Complex 1 was crystallized in triclinic system with $P\bar{1}$ space group. Copper is bonded to the sulfur of thiocarboxylate and the two phosphorous atoms of triphenylphosphine ligands. The molecular structure of 1 is depicted in Fig. 2.



Fig. 2 Thermal ellipsoid plot of 1 at 30% probability (hydrogen atoms are omitted for clarity). The thiophene ring is disordered. Selected bond lengths (Å) and angles (°): Cu–S(1) 2.3373(9), Cu–O(1) 2.465, Cu–P(1) 2.2712(8), Cu–P(2) 2.2610(8), S(1)–C(1) 1.700(4), O(1)–C(1) 1.253(4), C(1)–C(2) 1.464(5), S(1)–Cu–(P1) 113.68(3), S(1)–Cu–(P2) 119.01(3), P(1)–Cu–(P2) 126.72(3), S(1)–C(1)–O(1) 121.4(3).

All the bond lengths are within the usual range, however, Cu–O distance (2.465 Å) is longer than the sum of the covalent radii of the two atoms (1.90 Å) but smaller than the sum of the van der Waals radii (2.92 Å) indicating the weak nature of the Cu \cdots O interaction. Cu atom is slightly deviated (0.101 Å) from P1–P2–S1 plane and the bond angles subtended at copper atom are slightly deviated from the ideal trigonal planar angle of 120°. Such deviations are, however, expected because of the large steric bulk of the triphenylphosphine ligands.

The crystals of **2** have (orthorhombic crystal system) space group $P2_12_12_1$. The copper atom is bonded with the sulfur atoms of two thiocarboxylate ligands and two phosphorous atoms of triphenylphosphine ligands. The molecular structure of **2** is depicted in Fig. 3.

The copper atom is at the center of a distorted tetrahedral P_2S_2Cu core. Since the copper atom is in +1 oxidation state, one of the thiocarboxylate ligands should remain protonated even after complexation. A hydrogen atom could indeed be located in between the two oxygen atoms, however, on refinement the same was closer to O1 at a distance of 0.95(6) Å. There is, however, a strong hydrogen bonding between this H atom and O2 as shown by the distance between the two (1.564 Å). To the best of our knowledge this is the first example of a complex where a



Fig. 3 Thermal ellipsoid plot of 2 at 30% probability (hydrogen atoms of rings are omitted for clarity). The thiophene rings are disordered. Selected bond lengths (Å) and angles (°): Cu-S(1) 2.3568(10), Cu-S(2) 2.3241(9), Cu-P(1) 2.2908(10), Cu-P(2) 2.2754(10), S(1)-C(37) 1.683(4), O(1)-C(37) 1.272(5), O(2)-C(42) 1.274(4), C(37)-C(38) 1.461(6), S(1)-Cu-S(2) 119.90(4), S(1)-Cu-P(1) 100.07(4), S(1)-Cu-P(2) 111.36(4), S(2)-Cu-P(1) 105.74(3), S(2)-Cu-P(2) 100.13(4), P(1)-Cu-P(2) 120.80(4), S(1)-C(37)-O(1) 125.0(3).

thiocarboxylic acid without undergoing deprotonation is acting as a ligand. Surprisingly, the bonding patterns of both the protonated and deprotonated thiocarboxylates in **2** are similar. The two Cu– S bond lengths are almost identical and are comparable to that observed in **1**. The two C–O bond lengths are also equal. Possibly, the H atom oscillates between the two oxygen atoms. There are no interactions between oxygen and copper atoms.

In case of **3a** Cu(II) is bonded to two oxygens of the carboxylate ligands and two nitrogen atoms of TMEDA. Molecular structure is depicted in Fig. 4. A chloroform molecule crystallized with complex **3a**. The Cu atom is at the center of a N_2O_4Cu core having a geometry in between those of a trigonal prism and an octahedron. The distortion in structure from regular octahedron is due to the small bite angles of the carboxylate ligands.

The carboxylate ligands are asymmetrically coordinated to the Cu(II) center. The shorter Cu1–O1 and Cu1–O3 bonds are comparable to the sum of their covalent radii while the other two though longer, are much shorter as compared to the sum of the van der Waals radii of the two atoms. Expectedly, the longer Cu– O bond lengths correspond to shorter CO bonds, however, the variation in CO bond lengths is quite small.

As mentioned earlier, our attempts to crystallize 4a were not successful. Its structure was therefore optimized by DFT calculations. We selected two different possible structures as initial geometries for the calculations. In one case the sulfur atoms were considered to be the bonding sites while in the other case oxygen atoms were the donor atoms. Bonding of the phen ligand was considered identical (N,N' bidentate) in both the cases. When we considered the sulfur atoms as donors the optimized structure became five-coordinated with a distorted trigonal bipyramidal geometry around copper (Fig. 5a). On the other hand, when oxygen atoms were considered as donors the optimization process led to a structure with distorted square planar geometry around the copper atom (Fig. 5b). The latter was found to be more



Fig. 4 Thermal ellipsoid plot of 3a at 30% probability (hydrogen atoms are omitted for clarity). The thiophene rings are disordered. Selected bond lengths (Å) and angles (°): Cu-O(1) 2.010(5), Cu-O(2) 2.386(6), Cu-O(3) 1.975(5), Cu-O(4) 2.564, Cu-N(1) 2.018(7), Cu-N(2) 2.044(7), O(1)-C(7) 1.270(9), O(2)-C(7) 1.238(9), C(7)-C(8) 1.474(12), O(3)-C(12) 1.254(10), O(4)-C(12) 1.226(10), C(12)-C(13) 1.523(12), O(1)-Cu-O(2) 59.0(2), O(1)-Cu-O(3) 93.2(3), O(1)-Cu-O(4) 93.28, O(1)-Cu-N(1) 92.4(3), O(1)-Cu-N(2) 161.6(3), O(2)-Cu-O(3) 94.6(2), O(2)-Cu-O(4) 140.31, O(2)-Cu-N(1) 104.6(3), O(2)-Cu-N(2) 103.0(3), O(3)-Cu-O(4) 56.22, O(3)-Cu-N(1) 160.1(3), O(3)-Cu-N(2) 92.2(3), O(4)-Cu-N(1) 104.45, O(4)-Cu-N(2) 104.26, N(1)-Cu-N(2) 88.3(3).

favored thermodynamically (by 2.993 kcal mol⁻¹ than the trigonal bipyramidal one). As mentioned in the succeeding section, the spectral data also suggested a square planar geometry of 4a.

Crystal data of 4b are given in Table 2. Since the molecular structure (Fig. 6) has already been reported¹⁸ earlier we refrain from giving any further details of it.

Electronic absorption spectra

Electronic absorption spectra of 1 and 2 recorded in 10^{-4} M chloroform solution as well as in solid state (Table 1). Notably, 2 showed a broad charge transfer band in the visible region which is responsible for its red color (Fig. S3 ESI[†]).

Time-dependent absorption spectra of 4a were recorded in 10^{-4} M DMSO solution (Fig. 7). Initially it showed sharp absorption bands at 217, 243 and 272 nm in the UV region. In addition it exhibited two broad absorption bands in the lower energy region centered at 372 and 455 nm. After 24 h the intensity of the two higher energy bands (217 and 243 nm) increased considerably and a new peak arose at 263 nm while the peak at 272 remained almost unaltered. The lower energy bands (372 and 455 nm) disappeared and a new peak centered at 687 nm appeared resulting in the change in solution color from red to blue.

Electronic absorption spectral assignments were supported by time-dependent density functional theory.¹⁹ TD-DFT calculations on 4a (Fig. 8) and 4b (Fig. 9) have been carried out. In case of 4a absorption at 473 nm^{20} was responsible for the *d*-*d* transition $(d_{xy} \rightarrow d_{x^2-y^2}; b_{2g} \rightarrow b^*_{1g})$, in addition to the ligand to metal and interligand charge transfers (Fig. S6 ESI[†]). Due to the overlapping nature of these peaks the experimental absorption spectrum (in



Fig. 5 Optimized geometries of 4a.



Fig. 6 Thermal ellipsoid plot of 4b at 30% probability (hydrogen atoms are omitted for clarity). The thiophene rings are disordered.

solid state) showed a broad and intense peak at 492 nm. Whereas in the case of 4b a peak appeared at 734 nm due to the d-d transition $(d_{z^2} \rightarrow d_{x^2-y^2})^{21}$ (Fig. 9).

Emission spectra

Emission spectra of complexes 1 and 2 have been recorded in solid state. When excited at $\lambda_{max} = 400$ nm both the complexes showed a strong emission at 422 nm possibly due to inter-ligand transitions involving the phosphine ligands The weak intensity emissions at 485 and 546 nm (Fig. 10) are possibly due to ligand centered (involving thiocarboxylate ligands) charge transfer. One can clearly observe the effect of thiocarboxylate ligand on the band intensities; the intensity ratio of the peaks at 422 nm and 546 nm

Table 1 Electronic absorption bands

Compound	Electronic transitions bands (nm) in solution (bands observed in solid state are given in parentheses) (Fig. S4, S5 ESI†)			
	LLCT	MLCT/LMCT ¹⁰	<i>d-d</i> transition	
1	258, 302	330, 347		
2	252, 304	326, 348, 520 (480)		
3a	249, 293		678–728	
	,		(657)	
3b	(270, 286)	(351)	(420, 444)	
4a	217, 243, 272	372	455 (492)	
4b	217, 243, 263, 272		687 (696)	

Table 2 Crystal data and structure refinement of 1, 2, 3a and 4b

	1	2	3a	4b
Empirical formula	C ₄₁ H ₃₃ CuOP ₂ S ₂	$C_{46}H_{37}CuO_2P_2S_4$	$C_{17}H_{23}Cl_3CuN_2O_4Cl_3S_2$	$C_{22}H_{16}CuN_2O_5S_2$
Formula weight	731.27	875.53	553.41	514.04
T/K	293	293	100	293
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P\overline{1}$	$P2_{1}2_{1}2_{1}$	$Pbc2_1$	$P2_1$
a/Å	10.2597(15)	13.1000(3)	17.575(4)	10.5195(10)
b/Å	12.9616(6)	17.9804(4)	17.691(3)	13.8376(12)
c/Å	14.459(2)	18.1855(3)	15.398(3)	14.5830(12)
β (°)	75.151(14)	90	90	92.567(8)
$V/Å^3$	1792.8(4)	4283.47(15)	4787.5(16)	2120.6(3)
Ζ	2	4	8	4
μ (Mo–K α)/mm ⁻¹	0.847	0.817	1.447	1.265
Flack parameter		0.003(13)		
Reflections Collected/unique	12577/7722	16813/9378	30700/11587	10879/8141
R (int)	0.0461	0.0313	0.0598	0.0372
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 0.0502$	$R_1 0.0436$	$R_1 0.0756$	$R_1 0.1081$
	$wR_2 0.1278$	$wR_2 0.0913$	wR ₂ 0.1955	$wR_2 0.2794$
R indices (all data)	$R_1 0.0745$	$R_1 0.0727$	$R_1 0.1282$	$R_1 0.1432$
· · /	$wR_2 0.1367$	$wR_2 0.0978$	$wR_2 0.2470$	$wR_2 0.2986$
GOF on F ²	0.933	0.916	1.056	1.035

changed from 11:1 (in 1) to 6:1 (in 2). Following the addition of another thiocarboxylate the ligand inter- and intra-ligand charge transfers increase resulting in an increase in the intensity of the signal²² at 546 nm in the case of 2. As the peak positions remain the same in both 1 and 2, it may be tentatively inferred that metal centered transitions do not influence the luminescent properties of these compounds.

Experimental

All the reactions were carried out under nitrogen atmosphere. Solvents were purified using standard methods. Sodium thiophene-2-thiocarboxylate²³ and bis-triphenylphosphine copper(1) nitrate²⁴ were synthesized using reported methods.

IR spectra were recorded using Perkin-Elmer RX-1, FT-IR and Varian-3100 FTIR instruments. ¹H and ¹³C NMR spectra were obtained using a JEOL AL300 FT NMR spectrometer, however, variable temperature ³¹P NMR spectra were recorded using a 400 MHz Bruker spectrometer using orthophosphoric acid as an external standard ($\delta = 0.0$ ppm). Elemental analyses were performed using an Exeter model E-440 CHN analyser and Electronic absorption spectra were recorded using a Shimazdu UV-1700 PhermaSpec Spectrophotometer. Solid state emission spectra were recorded from VARIAN, CARY Eclipse Fluorescence spectrometer. Single crystal X-ray data of 1, 2 and 4b were collected on Xcalibur Oxford Diffractometer while those of 3a were collected on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.7107$ Å). Data collections for 3a were carried out at 100 K while those for 1, 2 and 4b were carried out at 293 K. Crystal data of compounds are given in Table 2. The structures were solved and refined by SHELX²⁵ set of software using WinGX (ver 1.80.05)²⁶ platform. The disordered atoms of the thiophene rings were refined by splitting them into two parts without fixing any site occupancy factor (sof). The occupancies of the split atoms were refined by means of a free variable. For the C2 atom of the thiophene rings dummy atom constraint (EXYZ) was used. Restraints such as DFIX and FLAT were also applied in some cases.

Syntheses

Synthesis of (PPh₃)₂Cu(SCOth), (1). To a suspension of (PPh₃)₂Cu(NO₃) (0.650 g, 1.00 mmol) in 10 ml of methanol was added a methanolic solution (5 mL) of sodium thiophene-2-thiocarboxylate (0.166 g, 1.00 mmol) while stirring. The reaction mixture was stirred for three hours and the yellow precipitate formed was filtered out. The precipitate was re-dissolved in chloroform and kept for crystallization after layering with diethyl ether. After two days yellow rod shaped crystals were obtained. Yield: 0.665 g, (91%). M. P. 160–162 °C. Anal. Cal. for C₄₁H₃₃OS₂P₂Cu:



Fig. 7 Variable time absorption spectra of 4a (10⁻⁴ M DMSO solution).



Fig. 8 Metal centered transition (from d_{xy} to $d_{x^2-y^2}$ orbital) in **4a** (orbital contour value = 0.05).

C, 67.34, H, 4.55. Found: C, 67.64, H, 4.49. IR spectra (KBr, cm⁻¹): 1582 v(CO), 923 v(CS).: ¹H NMR (CDCl₃, ppm) 6.87–7.55 (Ph, th rings).¹³C NMR (CDCl₃, ppm) 127.00–149.37 (Ph, th rings), 195.64 (COS).

Synthesis of H[(PPh₃)₂Cu(SCOth)₂], (2). To a solution of thiophene-2-thiocarboxylic acid (0.332 g, 2.0 mmol) in 5.0 ml



Fig. 9 Metal centered transition (from d_{z^2} to $d_{x^2-y^2}$ orbital) in **4b** (orbital contour value = 0.05).

of methanol, added a (5.0 ml) methanolic solution of sodium methoxide (0.054 g, 1.0 mmol) (prepared *in situ* by a reaction of Na metal and methanol) drop wise with stirring in ice bath. After five minutes of stirring solid (PPh₃)₂Cu(NO₃) (0.650 g, 1.0 mmol) was added resulting in a orange-red colored precipitate which was filtered and dried under reduced pressure. Recrystallized from chloroform/petroleum ether (60–80 °C). Yield: 0.690 g (79%). M. P. 150–152 °C. Anal. Cal. for C₄₆H₃₇O₂S₄P₂Cu: C, 63.10, H, 4.26. Found: C, 63.74, H, 4.19. IR spectra (KBr, cm⁻¹): 1582 v(CO), 908 v(CS). ¹H NMR (CDCl₃, ppm) 1.87 (CSOH), 6.99–7.68 (Ph, th rings).¹³C NMR (CDCl₃, ppm) 127.05–148.77 (Ph, th rings), 197.94 (COS).

Synthesis of TMEDACu(O_2 Cth)₂, (3a). To a magnetically stirred solution of Cu(NO_3)₂·3H₂O (0.241 g, 1.00 mmol) in 5 ml of methanol was added a methanolic solution of TMEDA (0.116 g, 1.00 mmol) followed by a solution of sodium thiophene-2-thiocarboxylate (0.332 g, 2.00 mmol) in 5 ml methanol. A greenishblue colored precipitation occurred. Continued stirring for half an hour and then filtered the precipitate, washed with diethyl ether and dried it under reduced pressure. Recrystallized from a mixture of chloroform and acetonitrile (2:1). Yield: 0.382 g (82%). Anal. Cal. for C₁₆H₂₂N₂O₄S₂Cu·CHCl₃: C, 36.90, H, 4.19, N, 5.06. Found: C, 36.78, H, 4.22, N, 4.98. IR spectra (KBr, cm⁻¹): 1571, 1524 v(CO).

Synthesis of TMEDACu(SCOth)₂ (3b). Same procedure was adopted as described above for the synthesis of **3a** except the fact that anhydrous CuSO₄ (0.159 g, 1.00 mmol) was used instead of Cu(NO₃)₂·3H₂O. All the manipulations were carried out under dry dinitrogen atmosphere. A brown colored precipitate was obtained which is insoluble in common solvents. Yield: 0.363 g (78%). Anal. Cal. for C₁₆H₂₂N₂O₂S₄Cu: C, 41.22, H, 4.76, N, 6.01. Found: C, 41.10, H, 4.78, N, 5.99. IR spectra (KBr, cm⁻¹): 1464 v(CO), 998 v(CS).

Synthesis of (Phen)Cu(SCOth)₂, (4a). To a stirred solution of $Cu(NO_3)_2 3H_2O(0.241 \text{ g}, 1.0 \text{ mmol})$ in 5.0 ml of methanol added a solution of phen (0.180 g, 1.0 mmol) in 5.0 ml of methanol followed



Fig. 10 Emission spectra of compounds 1 and 2 in solid state.

by a solution of sodium thiophene-2-thiocarboxylate (0.332 g, 2.0 mmol). The reaction mixture was stirred for ten minutes and then filtered the red colored precipitate, washed with diethyl ether and dried under *vacuo* and stored under nitrogen atmosphere. Yield: 0.439 (83%). Anal. Cal. for $C_{22}H_{14}N_2O_2S_4Cu$: C, 49.84, H, 2.66, N, 5.28. Found: C, 49.79, H, 2.69, N, 5.25. IR spectra (KBr, cm⁻¹): 1418 v(CO), 1022 v(CS).

Synthesis of (Phen)Cu(O₂Cth)₂, (4b). 4a was dissolved in chloroform and kept for crystallization. After an hour color of solution become greenish blue and some precipitation was observed. Then reaction mixture was dried and dissolved in methanol kept for crystallization. After a day blue colored rectangular crystals were obtained. Yield: 0.360 g (70%). Anal. Cal. for $C_{22}H_{14}N_2O_4S_2Cu\cdotH_2O$: C, 51.20, H, 3.13, N, 5.43. Found: C, 51.25, H, 3.05, N, 5.22. IR spectra (KBr, cm⁻¹): 1566, 1520 v(CO).

Computational details

The energy optimized geometry of **4a** was calculated using the B3LYP²⁷ correlation functional. The effective core potential (ECP) standard basis set $6-31G^{**28}$ was utilized for all atoms. The energies and intensities of 50 lowest-energy spin allowed electronic excitations were calculated using the TD-DFT at the same level of theory. In case of **4b** X-ray coordinates were used for calculation of electronic excitation. All the theoretical calculations were performed using the GAUSSIAN 03 W²⁹ set of programs. Molecular orbital plots were generated using the program MOLDEN.³⁰

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