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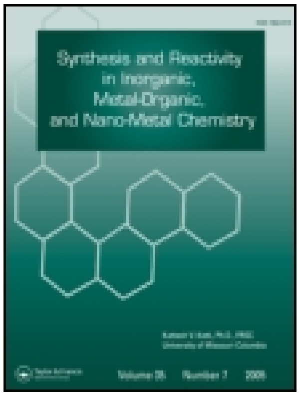

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

A Facile Synthesis, Crystallographic, Spectral, Thermal, and Electrochemical Investigations of Neutral [$Cu_2(Et_2dtc)_4$] Dimer

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Accepted author version posted online: 22 May 2013.Published online: 06 Nov 2013.

To cite this article: Sanjay K. Verma , Rahul Kadu & Vinay K. Singh (2014) A Facile Synthesis, Crystallographic, Spectral, Thermal, and Electrochemical Investigations of Neutral [$Cu_2(Et_2dtc)_4$] Dimer, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 44:3, 441-448, DOI: 10.1080/15533174.2013.776596

To link to this article: http://dx.doi.org/10.1080/15533174.2013.776596

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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 44:441–448, 2014
Copyright © Taylor & Francis Group, LLC
ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2013.776596

A Facile Synthesis, Crystallographic, Spectral, Thermal, and Electrochemical Investigations of Neutral $[Cu_2(Et_2dtc)_4]$ Dimer

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A neutral dimeric complex $[Cu_2(Et_2dtc)_4]$ (dtc = dithiocarbamate) (1) was synthesized in single step under mild conditions. Structure of 1 has been studied using single-crystal XRD to gauge the influence of CH_3 and CH_2 groups of coordinated dithiocarbamate ligands on the association of the molecules in solid state. Evidently 1 features the ability of these groups to form intermolecular $(sp^3)C{-}H\cdots\Pi$(chelate ring) and $(sp^3)C{-}H\cdots S$ stacking interactions leading to fascinating 3D infinite network. Complex has been completely characterized by spectrophotometric methods, optical behavior, and thermal and cyclic voltammetry studies. Cyclic voltammetric study confirmed the binding affinity of 1 toward $H_2PO_4^-$.

Supplemental materials are available for this article. Go to the publisher's online edition of* Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry *to view the supplemental file.

Keywords cyclic voltammetric study, fluorescence, optical band gap, $(sp^3)C{-}H\cdots\Pi$(chelate ring) interaction, $(sp^3)C{-}H\cdots S$ interaction, TGA/DTA, UV-visible

INTRODUCTION

There is a growing interest in identifying the nature of non-conventional intermolecular interactions,[1] because of their increasing demand in the situations where conventional hydrogen bonding does not extend in three dimensions or does not exist due to lack of appropriate donors and acceptors. Interactions of the type $C{-}H\cdots O$,[2] $C{-}H\cdots\Pi$,[3–5] and $\Pi\cdots\Pi$,[6] are well established in the crystal engineering where the hydrogen atoms associated with the aromatic moieties are generally more amenable for $C{-}H\cdots\Pi$ interactions than the hydrogen atoms associated with a sp^3 carbon atoms.[5] However, a recent investigation[4] showed that the directionality and strength of interactions involving $(sp^3)C{-}H$ group are more significant in terms of the access angle and the shorter distance between the hydrogen atom and acceptor. The existence of $C{-}H\cdots S$ interactions is less common[7] than $C{-}H\cdots O$ interactions but may be found in many molecular crystals with fascinating properties such as electrical conductivity or superconductivity.[8] Recently, metal-chelate rings of suitable 1,1-dithiolate metal complexes were reported to act as a C—H acceptors. Thus certain complexes were apparently sustained by $C{-}H\cdots\Pi$(chelate ring) interactions.[9] Since "metalloaromaticity" was discovered in 1945,[10] a large number of transition metal chelate rings feature this metalloaromaticity.[11] However, the existence of $C{-}H\cdots\Pi$(chelate ring) interaction in both coordination and organometallic compounds is very limited and definition of structural parameters for such interactions to occur is still being explored. The hydrogen bond energy for $C{-}H\cdots\Pi$(chelate ring) interactions, 6–11 kJ mol^{-1},[12] was found to be comparable with $C{-}H\cdots\Pi$(organic) interactions, 1–8 kJ mol^{-1}.[13] Thus the reliability on the $C{-}H\cdots\Pi$(chelate ring) synthons certainly provides a new directing tool of molecular assembly for coordination and organo-metallic compounds.

On the other hand, metal complexes with sulfur rich ligands are very interesting due to their involvement in the growth of thin layers of metal sulfides, by metal–organic chemical vapor deposition techniques, electrochemical properties, electrical properties, and biological properties. In particular, the introduction of metal dithiocarbamate complexes bearing a direct metal–sulfur bond, as a single source precursor, has proven to be a very efficient and an alternative route for the synthesis of high-quality semiconductor nanoparticles.[14] Alternatively, the metal dithiocarbamate complexes have been employed as anion binding motifs.[15]

Although the structural investigations on copper(II) bis(*N*,*N*-diethyldithiocarbamate) complex were previously made by Bonamico[16] and Jian's research group,[17] however, we report herein an efficient single-step synthesis of copper(II) bis(*N*,*N*-diethyldithiocarbamate) complex dimer $[Cu_2(Et_2dtc)_4]$ **1**, which

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Received 21 June 2012; accepted 10 February 2013.

Mr. Verma and Dr. Singh acknowledge CSIR, New Delhi for financial support (Project No. 01/(2204)/07/EMR-II). Mr. Kadu acknowledges UGC, New Delhi for the fellowship. The authors are thankful to the CSMCRI Bhavnagar for the single crystal and Mr. Shardul Bhatt for Cyclic voltammetric analysis. Professor BVK is greatly acknowledged for providing laboratory facility and his consistent support.

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is characterized by microanalysis, IR, UV-visible, fluorescence, optical, TGA/DTA, cyclic voltammetric, and single-crystal X-ray diffraction techniques. The emphasis has been made on evaluation of weak $CH\cdots\Pi$(chelate ring) and $CH\cdots S$ intermolecular interactions and the role of CH_3 and CH_2 groups of coordinated *N*,*N*-diethyldithiocarbamate ligands on the association of the molecules in solid state.

EXPERIMENTAL

Materials and Measurement

All solvents were purchased from the commercial sources and were freshly distilled prior to use. Reagents such as $Cu(OAc)_2.H_2O$, and CS_2 were purchased from Merck and these were used without further purification. Elemental analyses (C, H, N) were performed on Perkin-Elmer 2400 analyzer. FT-IR (KBr pellets) spectrum was recorded in the 4000–400 cm^{-1} range using a Perkin-Elmer FT-IR spectrometer. UV-visible spectra in DMSO solution were recorded on a Perkin Elmer Lambda 35 UV-vis spectrometer and the optical characterization in solid state was performed by UV-visible transmittance measurements. Florescence was recorded on JASCO make specrofluorometer model FP-6300. Thermal stability analysis was performed on a SII TG/DTA 6300 in flowing N_2 with a heating rate of 10°C min^{-1}. Electrochemical measurements were performed on a CH Instruments 600C potentiostat, using a Pt disk as the working electrode, Ag/AgCl as the reference electrode and a Pt wire as the counter electrode. Cyclic voltammetric study was carried out using 1.0 mM solution of the complex **1** in 0.1 M tetra-n-butylammonium tetrafluoroborate (Bu_4NBF_4) in acetonitrile with a scan rate of 50 mVs^{-1}.

Synthesis of 1

Synthesis of **1** was achieved as per Scheme 1.

The diethyldithiocarbamate ligand required for the preparation of **1** was synthesized *in situ* by reacting Et_2NH (0.154 g, 2.1 mmol) with CS_2 (0.24 g, 3.15 mmol) in 10 mL of Et_3N solvent for 30 min at room temperature. $Cu(OAc)_2.H_2O$ (0.20 g, 1.0 mmol) dissolved in minimum amount of distilled water was added to this reaction mixture followed by continuous stirring for 2 h. A change in color from yellow to brown was observed. The solvent was removed in vacuum and the residue was washed several times by a saturated aqueous solution of $NaHCO_3$, followed by distilled H_2O and hexane respectively. Finally, the residue was dried in vacuum to yield the product **1** quantitatively, Yield: 0.356 g (99%, based on $Cu(OAc)_2.H_2O$); m. p. 200.7°C; Anal. Calcd. (%) for $C_{20}H_{40}Cu_2N_4S_8$: C, 33.32; H, 5.55; N, 7.78, S, 35.55. Found (%): C, 33.43; H, 5.60; N, 7.83, S, 35.65. IR (KBr disc, cm^{-1}): 2981s, 2928s (ν C—H), 1513s (ν C—N), 997s, 913s (ν C—S) stretching frequency, respectively. UV-vis (DMSO): 270 nm ($\pi\rightarrow\pi^*$), 287 nm ($n\rightarrow\pi^*$), 438 nm ($CT\rightarrow M$), 636 nm (d–d) transitions, respectively.

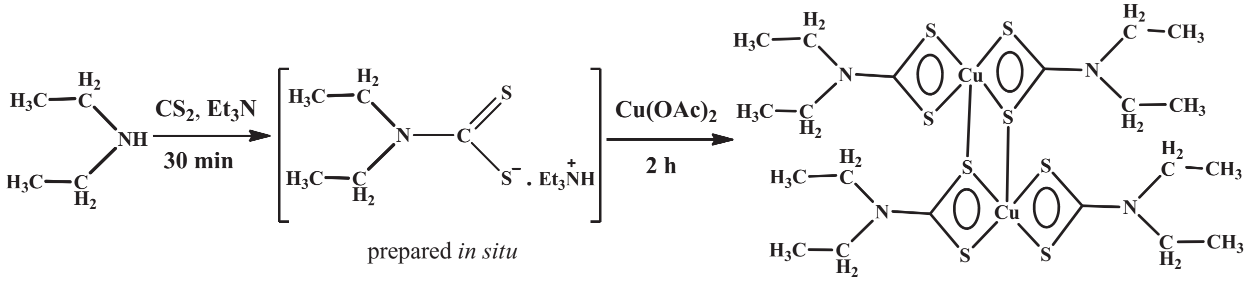
X-Ray Crystallography

Single crystals of **1** suitable for single-crystal X-ray diffraction study were grown by slow evaporation of acetone solution. Intensity data were collected using Mo-K_α X-ray (λ = 0.71073 Å) radiation on Bruker SMART APEX diffractometer equipped with CCD area detector at 110 (2) K. The data integration and reduction were processed with SAINT software.[18] An empirical absorption correction was applied to the collected reflections with SADABS software programs.[19] The structure was solved by direct methods using SHELXTL,[20] and refined on F^2 by the full-matrix least-squares technique using SHELXL-97 program package.[21] All non-hydrogen atoms were refined anisotropically until convergence was reached. Crystallographic data and structure refinement parameters for **1** are given in Table 1.

RESULT AND DISCUSSION

Synthesis

The alkali metal salts of dialkyl dithiocarbamates are known to react with different transition/non-transition metal (II) salts such as $M(ClO_4)_2$ or $M(OAc)_2$ at high temperature to yield the products of the type $[M(R_2dtc)_2]$. Using the same strategy, a polymorph of the titled compound was previously prepared in two steps and studied by Jian and co-workers[17] in 1999. However, we have prepared the complex **1** in a novel single-step procedure under mild conditions. The synthetic strategy used herein is found to be superior as other suffers from disadvantages such as low yields, lengthy sequences, and drastic reaction conditions. The complex has been completely characterized by spectrophotometric methods (UV and fluorescence),



SCH. 1. Synthesis of copper(II) bis(diethyldithiocarbamate) dimer.

TABLE 1
Crystallographic data and structure refinement parameters for **1**

Empirical formula	$C_{20}H_{40}Cu_2N_4S_8$
Formula weight	720.12
Crystal system	monoclinic
Space group	P21/n
a (Å)	9.6805(6)
b (Å)	10.5504(7)
c (Å)	15.5083(10)
α (°)	90
β (°)	101.66
γ (°)	90
V (Å^3), Z	1551.23(17), 4
Calculated density (mg m^{-3})	1.542
Absorption coefficient (mm^{-1})	1.927
F(000)	748
θ range for data collection (°)	2.29 − 28.24
Index ranges	$-9 \leq h \leq 12$, $-14 \leq k \leq 9$, $-17 \leq l \leq 19$
Reflections collected/ unique	8873/ 3608 [$R_{int} = 0.0229$]
Data / restraints / parameters	3608 / 0 / 234
Goodness-of-fit on F^2	1.081
Final R indices [I > 2σ (I)]	R1 = 0.0225, wR2 = 0.0631
R indices (all data)	R1 = 0.0240, wR2 = 0.0637
Largest diff. peak/hole (e A^{-3})	0.409/−0.272

optical behavior, and thermal and cyclic voltammetry studies. In the crystallographic study, the emphasis has been made in the search of weak interactions, which includes a comparative study with the Jian's complex.

Description of the Structure

The copper(II) bis(diethyldithiocarbamate) dimer **1** is built up of centro-symmetric dimeric entity in which both copper(II) atoms are bridged by S(1) atoms of trans chelate rings (CuS_2C). Each copper(II) atom acquires distorted square-pyramid stereochemistry. An ORTEP diagram and selected bond distances (Å) and bond angles (°) of **1** are shown in Figure 1 and Table 2, respectively.

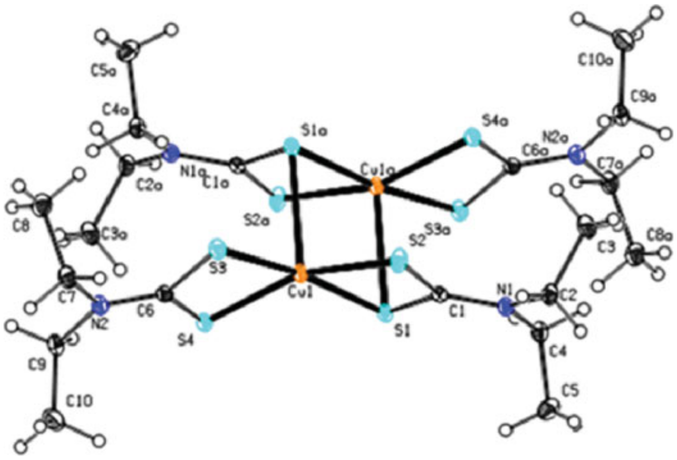


FIG. 1. ORTEP diagram of the complex **1** with atom numbering scheme (40% probability factor for the thermal ellipsoids). (color figure available online).

We have retrieved the crystal data (CCDC no. 111991) of previously reported polymorph[17] of complex **1** and have compared the data as well as crystal packing patterns. In addition to significant differences in the cell parameters, selected bond distances and bond angles, there is a considerable difference in the intermolecular stacking interactions, which is elaborated in our subsequent discussions. The observed differences in selected bond distances and bond angles of **1** with reported structure can be summarized as the axial Cu−S bond distance of 2.7743(4) Å in **1** is significantly shorter than 2.844(1) Å, whereas the equatorial bond distance of Cu−S(1), 2.3369(4) Å, is slightly longer than 2.3270(9) Å; the bond angles of S(1)−Cu(1)−S(2), 76.679(14)°, is slightly shorter than similar bond angle 77.00(3)°, and S(3)−Cu(1)−S(4), 77.124(14)°, is slightly longer than 76.59(3)°; the Cu···Cu separation of 3.500 Å in **1** is significantly shorter than 3.572(1) Å and the Cu(1)−S(1)#−Cu(1)−S(1)#1 plane is comparatively more orthogonal to the S(1)−S(2)−S(3)−S(4) plane with a dihedral angle of 88.77°.

The unprecedented feature of **1** revealed by single-crystal X-ray diffraction study is the intermolecular stacking of **1** into a fascinating 3D motif directed by novel (sp^3)C—H···Π(chelate ring) and (sp^3)C—H···S interactions (Figure 2). Overall, the structural parameters for these interactions are in general accord with the literature,[9] although at higher level of precision to support inter molecular stacking of **1** as depicted by black dotted lines in Figures 3 and 4.

In fact, in the centro-symmetric unit, there is one independent molecule which provides two acceptor {Π(chelate ring)} and two donor {(sp^3)C—H} sites to form (sp^3)C—H···Π(chelate ring) interactions with four neighboring molecules. Based on C8–H8C···Π(chelate ring) interactions, the crystal packing of **1** appears similar to the crystal packing of earlier structure,

TABLE 2
Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths (Å)		Bond angles (°)	
Cu(1)-S(2)	2.3080 (4)	S(2)-Cu(1)-S(4)	160.385 (18)
Cu(1)-S(4)	2.3109 (4)	S(2)-Cu(1)-S(3)	101.715 (15)
Cu(1)-S(3)	2.3233 (4)	S(4)-Cu(1)-S(3)	77.124 (14)
Cu(1)-S(1)	2.3369 (4)	S(2)-Cu(1)-S(1)	76.679 (14)
Cu(1)-S(1)#1	2.7743 (4)	S(4)-Cu(1)-S(1)	101.592 (15)
S(1)-C(1)	1.7301 (15)	S(3)-Cu(1)-S(1)	171.704 (16)
S(2)-C(1)	1.7178 (15)	S(1)-Cu(1)-S(1)#1	94.023 (13)
S(3)-C(6)	1.7232 (15)	S(3)-Cu(1)-S(1)#1	94.273 (14)
S(4)-C(6)	1.7227 (16)	S(4)-Cu(1)-S(1)#1	98.618 (14)

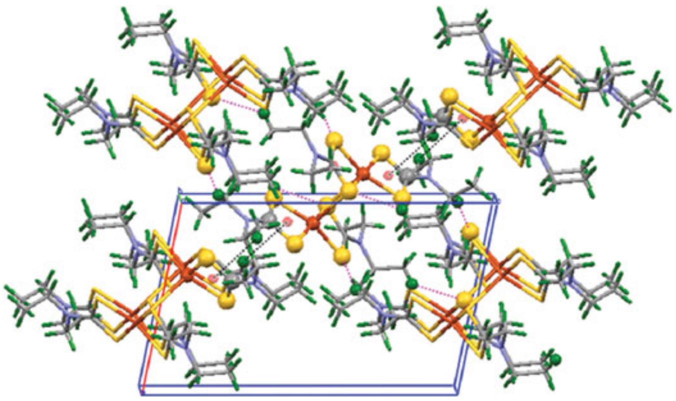


FIG. 2. 3D view of supramolecular unit of **1** showing nine molecule aggregate *via* (sp^3)C—H··· Π(chelate ring) and (sp^3)C—H···S interactions. (color figure available online).

however, a significant differences in the structural parameters are observed, which can be summarized as both C8—H8C···Cg and C8···Cg distances of 2.74 Å and 3.672 Å in **1** are shorter than the similar distances of 3.098 Å and 3.715 Å, respectively (Cg represents the centroid of chelate ring C6S3S4Cu1 and H8C atoms being from methyl groups of different diethyldithiocarbamate ligands). The favorable α angle (angle between the line connecting the H8C atom and Cg and the normal to the chelate ring plane; Figure 5) of 8.42° (= 90.00–81.58°) and the beta angle C8—H8C···Cg of 127.27° (Figure 6) in **1** are significantly larger than the similar angles of 6.89° and 125.84°.

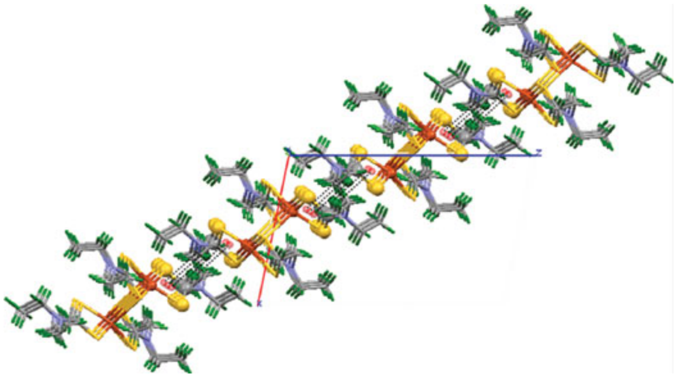


FIG. 4. View of **1** along *b*-axis involving (sp^3)C—H··· Π(chelate ring) interactions showing a part of the 3D structure. (color figure available online).

Unlike Jian's structure where molecule present in the centro-symmetric unit is connected through four (sp^3)C—H···S interactions, involving CH$_2$ groups only, our structure clearly demonstrates the existence of eight (sp^3)C—H···S interactions involving both CH$_3$ and CH$_2$ groups of coordinated diethyldithiocarbamate ligands (Figure 2). Thus, the presence of more number of (sp^3)C—H···S contacts certainly provides additional stability to the structure of **1**. Further, C—H···S interactions in our case seems to be stronger (2.836 Å) than the similar distances (2.909 Å) appear in the earlier structure.

Moreover, our data clearly revealed that C3—H3B and C9—H9B groups of each molecules are directed toward S1 and S2 of neighboring molecules, approaching them from the same

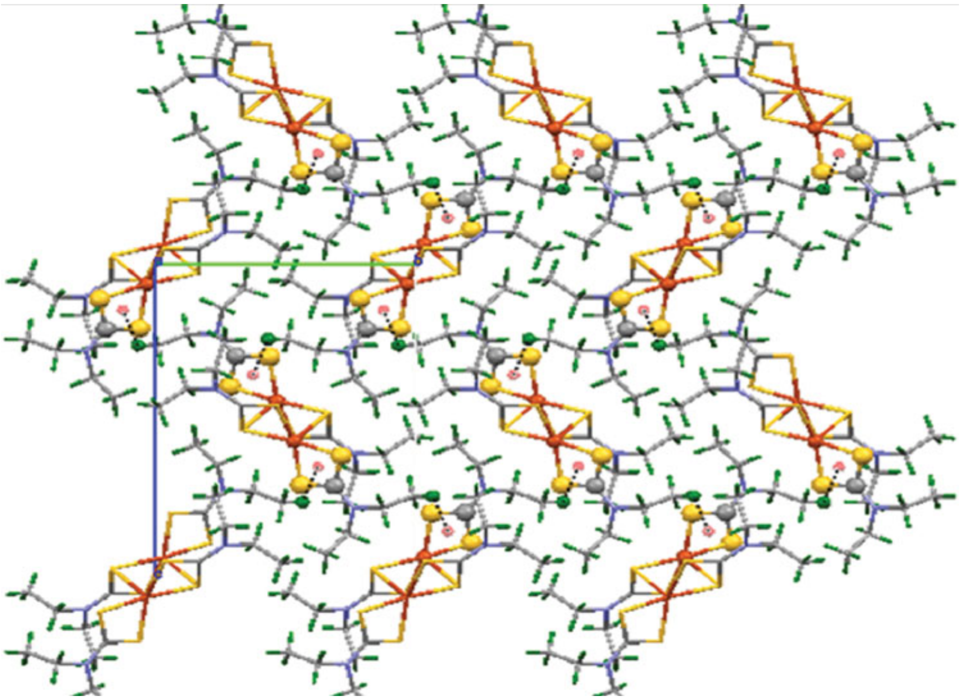


FIG. 3. View of **1** along *a*-axis involving (sp^3)C—H··· Π(chelate ring) interactions, which built up by symmetry operations for donors x, y, z, –1/2 + x, 1/2 – y, 1/2 + z, 1/2 – x, 1/2 + y, 1/2 – z, –x,1 – y, 1 –z. Key geometrical parameters: C8—H8C 0.97(2) Å, H8C···Cg 2.74 Å, C8···Cg 3.672 Å, C8—H8C···Cg 127.27°. (color figure available online).

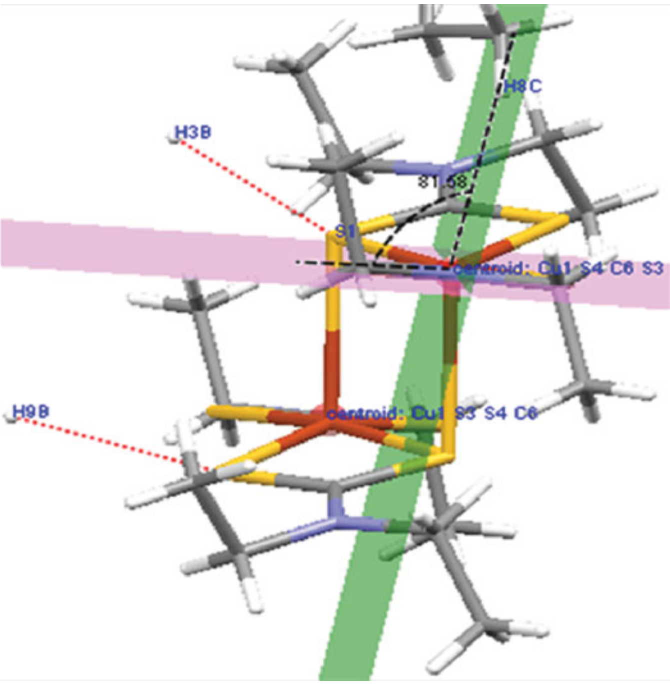


FIG. 5. Angle between the line connecting the H8C and Cg and the chelate ring plane. (color figure available online).

sides and forming four C3—H3B···S1 contacts with H3B···S1 contacts with distances of 2.928 Å and C3···S1 distances of 3.602 Å and four C9—H9B···S2 contacts with H9B···S2 distances of 2.836 Å and C9···S2 distances of 3.749 Å, respectively, as shown in Figure 6. The H3B and H9B atoms belong to methyl and methylene groups, respectively, whereas S1 and S2 belong to the *trans* chelate rings, not participated in C—H···Π(chelate ring) interactions. The angles C3—H3B···S1 and C9—H9B···S2 of 130.11° and 162.04° (Figure 6) are large enough to facilitate these (sp^3)C—H···S interactions with a concomitant linking of molecules of **1** into a 3D architecture (Figure 7). The strength of C9—H9B···S2 interactions involving methylene H9B atoms appears to be of higher significance in terms of the shorter distance between the hydrogen atom and acceptor.

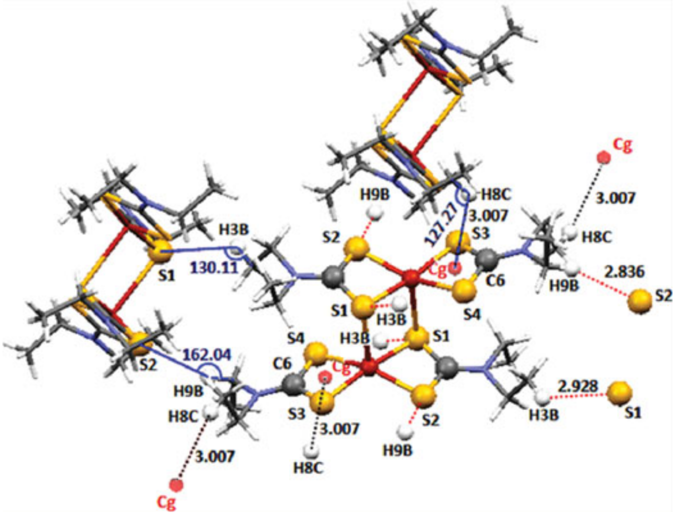


FIG. 6. Key geometrical parameters are shown for all the contacts *viz*. H8C···Cg, H3B···S1, and H9B···S2. (color figure available online).

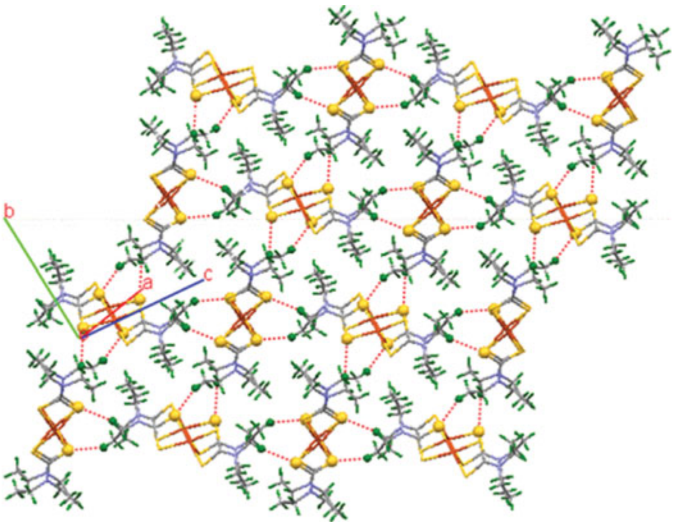


FIG. 7. View of **1** along a-axis involving C3-H3B···S1 and C9—H9B···S2 interactions and showing a part of the 3D structure which built up by symmetry operations for acceptors x, y, z; 1/2 + x, 1.5 – y, 1/2 + z; –1/2 – x, –1/2 + y, 1/2 – z, –x, 1 – y, 1 – z, and x, y, z; 1/2 – x, 1/2 + y, 1.5 – z, –1/2 + x, 1/2 – y, –1/2 + z, –x, 1 – y, 1 – z, respectively. Key geometrical parameters: C3-H3B 0.93(3) Å, H3B···S1 2.928 Å, C3···S1 3.602 Å, C3-H3B···S1 130.11°, C9—H9B 0.95(2) Å, H9B···S2 2.836 Å, C9···S2 3.749 Å, C9—H9B···S2 162.04°. (color figure available online).

Fluorescence Spectral Study

The fluorescence properties of the free ligand and its complex **1** studied at room temperature (298 K) in the DMSO solution. Although the free ligand did not give any emissions upon irradiation by ultraviolet light, its complex **1** gave a maximum emission at 339 and 520 nm upon excitation at 270 and 438 nm, respectively. Such red-shifting of intramolecular charge-transfer emissions by coordination of ligands to copper(II) were previously observed in dialkoxo-bridged dinuclear copper(II)[22] and Salen-type bisoxime copper(II)[23] complexes. The fluorescence spectrum of complex **1** is shown in Figure 8. These fluorescent emissions may be attributed to the intraligand and CT→M fluorescence. The enhancement of fluorescence of **1** may be attributed to the increased conformational rigidity and decreased nonradiative energy loss. The emission spectrum of the complex **1** suggests that it can be applied in the material science in making light-emitting devices (LED).

Optical Band Gap Measurement

Since complex **1** absorbs in the visible range of the solar spectrum, which is primary requisite for a compound to act as a photosensitizer for wide band-gap semiconductors, we have

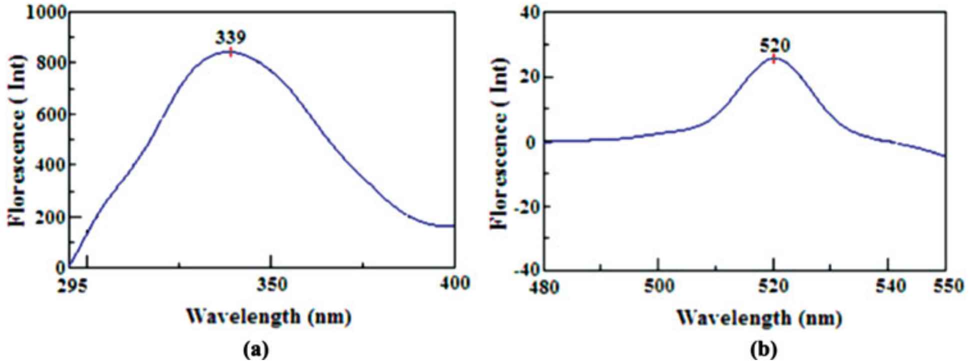


FIG. 8. Florescence spectra of complex **1** at room temperature in DMSO solution under UV excitation at (a) 370 and (b) 438 nm. (color figure available online).

further investigated its optical behavior toward wide band-gap semiconductors using UV-vis transmittance measurements. The optical absorption coefficient, α, can be obtained from the transmittance spectrum of **1** using the formula $\alpha = \frac{1}{d}\ln[\frac{1}{T}]$, where d is thickness of the sample and T is the transmittance. The relation between the absorption coefficients α and the incident photon energy (hν) can be determined using the well known Davis and Mott equation,[24] which is $\alpha h\nu = [D(h\nu - Eg)]^{\gamma}$, where constant D is the edge width parameter. In order to determine optical band gap of the complex **1**, we applied the models for both direct and indirect transitions. For this, the $(\alpha h\nu)^2$ (direct transition) and $(\alpha h\nu)^{1/2}$ (indirect transitions) versus hν were plotted. From these results, it was concluded that the absorption in the sample corresponds to direct energy gap. The band gap energy ($Eg = 1.42$ eV) was obtained by extrapolating the linear part of the Tauc plot[25] (a plot between $(\alpha h\nu)^{1/\gamma}$ and $h\nu$) (Figure 9). The result indicates that complex **1** exhibits the feature of a direct band gap semiconductor.

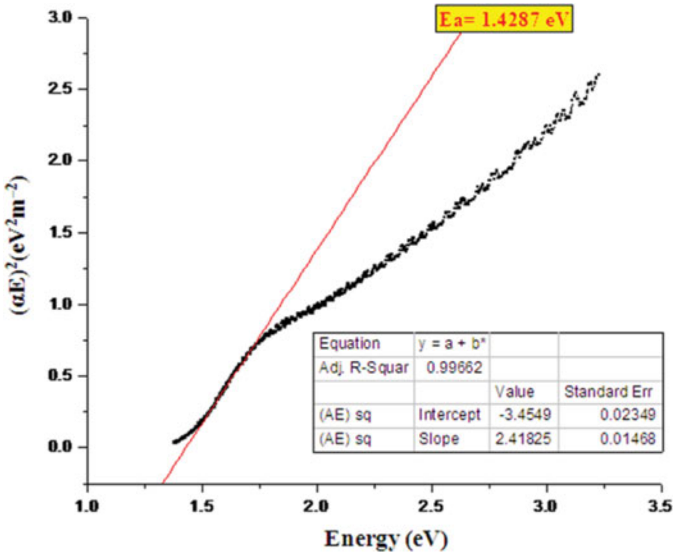


FIG. 9. A plot of $(\alpha E)^2(eV^2m^{-2})$ versus energy (eV) for **1**. (color figure available online).

Thermogravimetric Study

Thermogravimetric study of **1**, performed under N_2 atmosphere suggests that the complex is stable up to 200.0°C (Figure 10). An insignificant mass loss ($<1\%$) was observed on the TG curve at 200.2°C (probably due to loss of solvent impurities). The appearance of a sharp endothermic peak at 200.7°C on DTA curve suggests the occurrence of phase change due to its melting. After this process, a continuous mass loss of 76.6% was observed on TG curve between 205–305°C. The appearance of a broad endothermic peak at 303.0°C on DTA curve indicates the total destruction of **1**, essentially taking place in one stage. The remaining mass of 23.4% is stable after 305°C and is in good agreement with the CuS being a final product (theoretical 26.5%). These results are consistent with the DTG curve which shows two peaks at 200.2 and 304.9°C confirming two stages of mass loss, first due to loss of solvent impurities and the second is due to total destruction of complex **1**. However, the thermal data is in contrast to the literature report where a thermal decomposition of similar dialkyldithiocarbamate transition metal (II) complexes[26] proceeds in several stages involving many exothermic processes.

Cyclic Voltammetric Study

Cyclic voltammetric study of **1** displayed a broad quasireversible Cu(II)/Cu(III) redox couple, (Figure 11) which appear at more anodic potentials than the copper(II) bis(diethyldithiocarbamate) monomer. This anodic displacement of the Cu(II)/Cu(III) redox couple is however consistence with some acyclic and macrocyclic copper(II) bis-(diethyldithiocarbamate) complexes bearing imidazolium moieties.[15] This suggests that a higher potential is required to oxidize the Cu(II) center to Cu(III) in **1** as compared to the monomeric copper(II) bis(diethyldithiocarbamate) complex. The separation between the anodic and cathodic peaks, DE = Epa – Epc, is 90 mV at 50 mV/s scan rate, which is larger

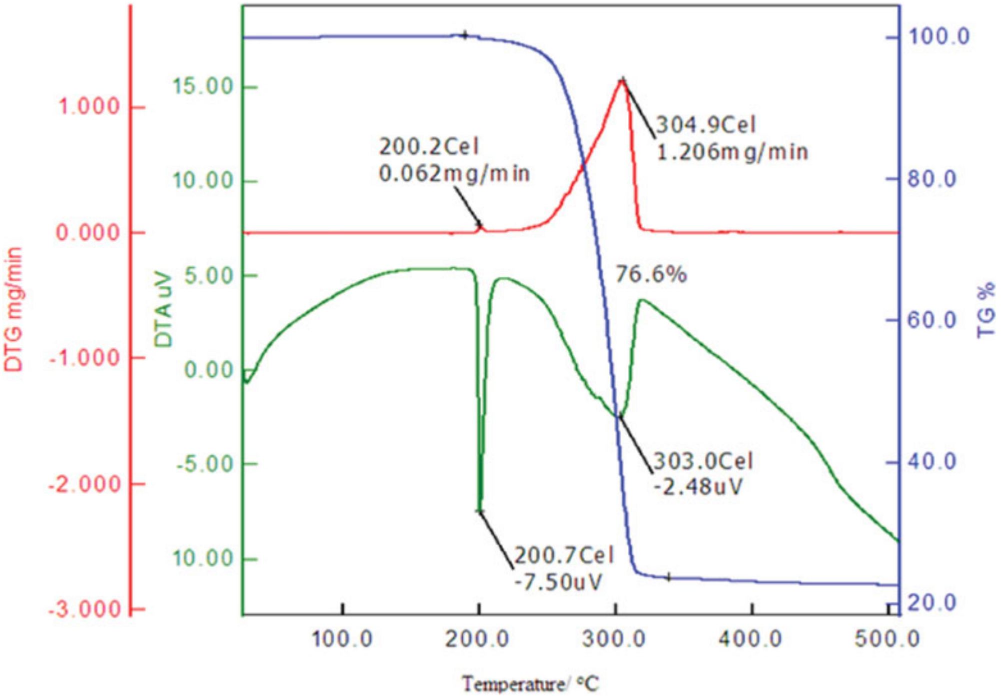


FIG. 10. TG/DTG/DTA curves for [$Cu_2(Et_2dtc)_4$] **1**. (color figure available online).

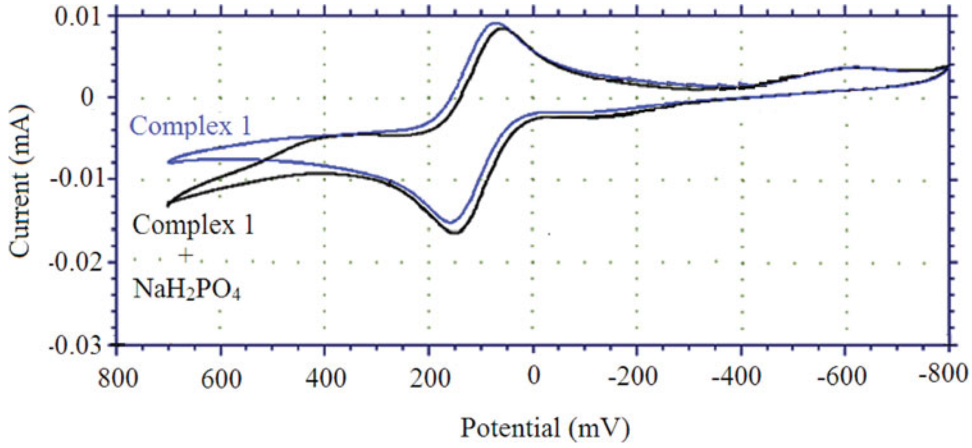


FIG. 11. Cyclic voltammogram of the Cu(II)/Cu(III) redox couple of 1 (0.1 M TBABF4/MeCN, 50 mV/s, vs. Ag/Ag+). (color figure available online).

than DE = 59/n mV and the ratio of the current intensity of the cathodic and anodic peaks is 1.56, which is different from unity. This clearly suggests a quasireversible process,[27] probably occurring due to rearrangement of the coordination sphere on going from the Cu(II) to the Cu(III) oxidation state.[28] On addition of five equivalents of $H_2PO_4^-$ anion to electrochemical solution of **1**, the cathodic peak potential for **1** significantly shifted to a more negative value by 20 mV, which suggests that the complexed anion stabilizes the Cu(III) redox state and hence lower potential is required for the oxidation of Cu(II) to Cu(III).[29]

CONCLUSION

The study allow us to conclude that the methyl and methylene groups of coordinated diethyldithiocarbamate ligands and metalloaromaticity of the four membered chelate rings (MS_2C) of **1**, generate intermolecular $(sp^3)C{-}H\cdots\Pi$(chelate ring) and $(sp^3)C{-}H\cdots S$ interactions which lead to the formation of a supramolecular unit consisting of a nine molecule aggregate (Figure 2). Such supramolecular units can be used for the generation of a fascinating 3D array. Our comments about metalloaromaticity through $(sp^3)C{-}H\cdots\Pi$(chelate ring) interactions can be of potential interest to the researcher working in the area of molecular assembly of coordination compounds. The electronic absorption and emission spectrum suggest that **1** can finds its application in the material science in making LED. Further, complex **1** exhibits the feature of a direct band gap ($Eg =$ 1.42 eV) semiconductor. Thermal decomposition of **1** suggests the formation of CuS as a final product and hence it can provide a single source material for the synthesis of CuS nanoparticles. A significant cathodic shift on addition of $H_2PO_4^-$ anion to the electrochemical solution of **1** clearly demonstrated that **1** can sense the binding of $H_2PO_4^-$ electrochemically.

SUPPLEMENTARY MATERIALS

CCDC 863877 for **1** contains supplementary crystallographic data for this article. This data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: t44-1223/336-033; Email: deposit@ccdc.cam.ac.uk).

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