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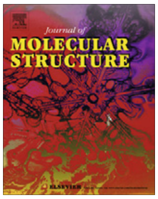

Ion-pair charge transfer complex with near-IR absorption: Synthesis, crystal structure and properties of $[Hb]_2[Cu(mnt)_2]$ (Hb = 1-(4-((1H-imidazol-1-yl) methyl)benzyl)-1H-imidazol-3-ium)

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The compound $[Hb]_2[Cu(mnt)_2]$ (**1**) [Hb = 1-(4-((1H-imidazol-1-yl)methyl)benzyl)-1H-imidazol-3-ium] has been synthesized, starting from 1,4-bis((1H-imidazol-1-yl)methyl)benzene, cupric chloride, and Na_2mnt in methanol. Compound **1** crystallizes in monoclinic system with *C2/c* space group. In the crystal structure, the interactions between cations and anions *via* bifurcated C—H···(NC-mnt)$_2$ hydrogen bonds give rise to a two dimensional supramolecular network. It has also been observed that two cation moieties (Hb) are attached together by a very short C—H···N hydrogen bonding interaction with H···N distance of 1.74 Å, ∠CHN bond angle of 174.9°. Compound **1** is additionally characterized by cyclic voltammetry, UV–Vis, IR, ^{1}H NMR and EPR spectroscopy. The ion-pair compound **1** shows an intense absorption in the near-IR region at ~1214 nm which has been described as a charge transfer band from HOMO of the copper dithiolate anion $[Cu(mnt)_2]^{2-}$, to LUMO of the $[Hb]^+$ cation. The title compound exhibits an oxidative response at +0.46 V vs. Ag/AgCl and a reductive event at −0.67 V vs. Ag/AgCl.

1. Introduction

Interest in metal–dithiolene complexes is due to the unique chemical nature related to their non-classical electronic structure and to their applications in the field of conducting and magnetic materials, dyes, nonlinear optics, and catalysis [1–7]. The near-IR absorption is of special interest in metal-based dithiolene complexes [8], because they are useful in Q-switching lasers applications [9,10]. Ion-pair charge transfer (IPCT) complexes, that contain metal–dithiolene complexes as anions, are important as far as physical properties are concerned [11–14]. IPCT complexes of the type $[NO_2BzPy][M(mnt)_2]$ (M = Ni, Au) have been recently reported with near-IR absorption properties by Ren et al. [15]. We have reported IPCT compounds of the type $[Bu_4N][Ni(XPhdt)_2]$ (X = F, Cl, Br, and NO_2) that are basically asymmetrically substituted bis(1,2-dithiolato)-Nickel(III) complexes exhibiting near-IR absorption and structural diversity [16,17]. In the present study, we have found interesting H-bonding interactions that involve the mnt rings of $[M(mnt)]^{2-}$ complex anion and the aromatic rings of organic receptor cation in the crystal structure of compound **1**. This represents a new type of molecular recognition in the area of supramolecular chemistry. In this complex, protonation occurs *in situ* in one of the imidazole rings of **b** (1,4-bis((1H-imidazol-1-yl)methyl)benzene) in MeOH solution. We wish to report here the synthesis, molecular structure and physical properties of compound $[Hb]_2[Cu(mnt)_2]$ (**1**) [Hb = 1-(4-((1H-imidazol-1-yl)methyl)-benzyl)-1H-imidazol-3-ium]. We have also described the supramolecular features and electrochemical properties of compound **1**. Based on CSD literature search on organic molecules [18–21] and metal-based complexes [22–28], there are very few reports of C—H···N interactions with H···N distance in the range of 1.60–1.80 Å. The relevant ∠CHN bond angle is in the range of 66–179°. So far, the shortest H···N distance of 1.79 Å reported in the literature, is based on metal dithiolene ion-pair complex [29]. Some of these reported C—H···N bond distances and corresponding angles are summarized in the Table 1 that shows the shortest H···N separation in the present study.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents were commercially available and used without further purification. The ligand **b** (1,4-bis((1H-imidazol-1-yl)methyl)benzene) [30] and Na_2mnt [31] were prepared following the procedures reported in literature (see Scheme S1 in Supplementary materials). Elemental analysis (C, H and N) were obtained with a FLASH EA 1112 Series CHNS analyser. FT-IR spectra were recorded in the range 400–4000 cm^{-1} with a JASCO FT/IR-5300

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Table 1
Selected hydrogen bonds from literature (Å, °).[a]

Entry	D—H···A	H···A	∠DHA	Ref.
1	C—H···N	1.61	132	[19]
2	C—H···N	1.74	114	[23]
3	C—H···N	1.71	102	[24]
4	C—H···N	1.71	135	[25]
5	C—H···N	1.77	156	[18]
6	C—H···N	1.79	66	[29]
7	C—H···N	1.74	174.9	Present work

[a] Based on CSD literature.

spectrometer using KBr pellet. UV–Vis spectra were recorded on a Cary 100 Bio UV–Vis spectrophotometer. Diffuse reflectance and near-IR absorption spectra were recorded on a UV-3600 Shimadzu UV–Vis-NIR spectrophotometer. The electron paramagnetic resonance (EPR) spectra were recorded on a (JEOL) JESFA200 EPR spectrometer. ^{1}H NMR spectra were recorded on Bruker DRX-400 spectrometer using $Si(CH_3)_4$ as an internal standard. A Cypress model CS-1090/CS-1087 electroanalytical system was used for cyclic voltammetric experiments. The electrochemical experiments were measured in acetonitrile solvent containing $[Bu_4N][ClO_4]$ as a supporting electrolyte, using a conventional cell consisting of two platinum wires as working and counter electrodes.

2.2. Synthesis of compound $[Hb]_2[Cu(mnt)_2]$ (**1**)

To a 10 mL MeOH solution of Na_2mnt (0.465 g, 2.5 mmol), 5 mL MeOH solution of $CuCl_2{\cdot}2H_2O$ (0.212 g, 1.25 mmol) was added, stirred for 30 min at room temperature and then filtered. To this filtrate solution, 1,4-Bis(imidazol-1-yl-methylene)benzene (0.721 g, 2.5 mmol) in 15 mL MeOH was added, and stirring was continued for another 4 h at room temperature, and again it was filtered. Single crystals, suitable for X-ray structure analysis, were grown by slow evaporation of methanol (filtrate) solution. Yield: 0.273 g (30% based on copper). Anal. Calcd. for ($C_{36}H_{30}N_{12}S_4Cu$): C, 52.57; H, 3.67; N, 20.43. Found: C, 52.35; H, 3.76; N, 20.61. ^{1}H NMR (400 MHz, δ ppm) (DMSO-d_6): 7.27 (s), 5.2 (s), 8.6 (bs). IR (KBR pellet)(υ/cm^{-1}): 3130, 2193 ($\nu_{C\equiv N}$), 1516 (phen), 1454 ($\nu_{C=C}$), 1296, 1149 ($\nu_{C-C\equiv N}$), 1082, 835, 765, 713, 623.

Table 2
Crystallographic data and structure refinement for compound **1**.

Empirical formula	C_{36} H_{30} N_{12} S_4 Cu
Formula weight	822.50
Temperature (K)	298(2)
Crystal size (mm)	0.22 × 0.18 × 0.16
Crystal system	Monoclinic
Space group	*C*2/*c*
Z	4
Wavelength (Å)	0.71073
Unit cell dimensions	
a (Å)	17.939(3)
b (Å)	15.411(3)
c (Å)	13.891(3)
β (°)	100.01(3)
Volume (Å^3)	3781.8(13)
Calculated density (Mg/m^{-3})	1.445
Reflections collected/unique	19,403/3746
R (int)	0.0466
F (000)	1692
Max. and min. transmission	0.8768 and 0.8361
Theta range for data collection (deg.)	1.75–26.10
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3746/0/240
Goodness-of-fit on F^2	1.082
R_1/wR_2 [$I > 2$sigma(I)]	0.0607/0.1393
R_1/wR_2 (all data)	0.0771/0.1481
Largest diff. peak and hole	0.651 and −0.451 e Å^{-3}

2.3. X-ray crystallography

Suitable single crystal of **1** was mounted at 298 K on a Bruker SMART APEX CCD single crystal diffractometer using graphite monochromated Mo-Kα radiation (0.71073 Å), 2400 frames were recorded with ω scan width 0.3°, each for 8 s, crystal-detector distance 60 mm, collimeter 0.5 mm. The SMART software [32] was used for intensity data acquisition and the SAINTPLUS software [32] was used for data extraction. Absorption correction was performed with the help of SADABS program [32]. Programs of SHELX-97 [33] were used for structure solution by direct methods and least-square refinement on F^2. All the non hydrogen atoms were refined anisotropically. The hydrogen atoms on the carbon atoms were included in the structure factor calculation by using a riding model. The hydrogen on the nitrogen atom of the cation has not been located by Fourier electron density map. Detailed information about crystal data and structure determination are summarized in Table 2.

3. Results and discussion

3.1. Electronic spectra

The electronic absorption spectra for compound **1** are presented in Fig. 1. The UV–Visible solution absorption spectrum of com-

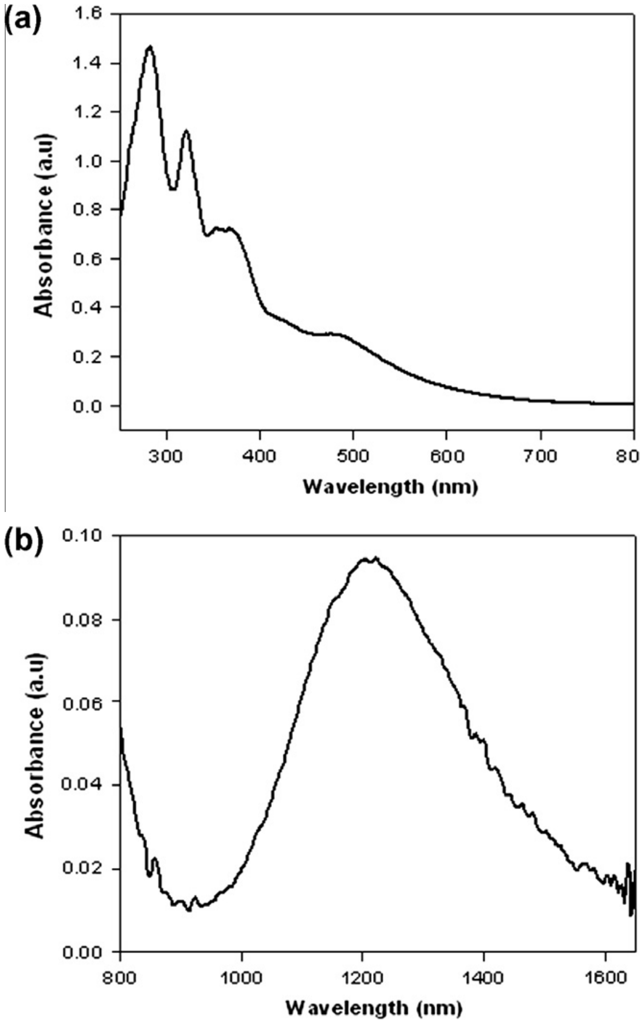


Fig. 1. Electronic absorption spectra for compound **1** in DMF (a) UV–Vis spectrum with 8×10^{-5} M solution and (b) near-IR spectrum with 1×10^{-3} M solution.

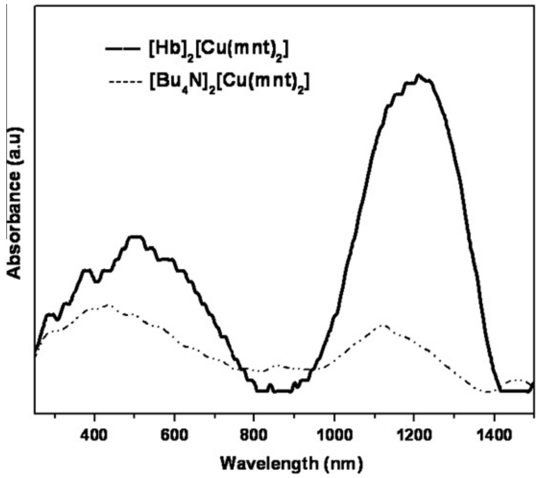
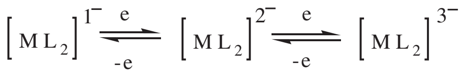


Fig. 2. The diffuse reflectance spectra of [Hb]$_2$[Cu(mnt)$_2$] compound **1**, and [TBA]$_2$[Cu(mnt)$_2$].



$$[ML_2]^{1-} \underset{-e}{\overset{e}{\rightleftharpoons}} [ML_2]^{2-} \underset{-e}{\overset{e}{\rightleftharpoons}} [ML_2]^{3-}$$

Scheme 1.

pound **1** was measured in dimethylformamide, which is similar to those reported in literature for other metal dithiolene [M(mnt)$_2$]$^{n-}$ complexes [34–36]. For the ion-pair compound **1**, we have observed five absorption bands in the region between 200–1300 nm, in which there are four intense bands that are due to allowed transitions. Bands at 220, 370 nm are assigned due to the $L \rightarrow M$ charge transfer transitions in [Cu(mnt)$_2$]$^{2-}$. Bands at 320 nm and 480 nm can be attributed as $L \rightarrow L^*$ and $M \rightarrow L$ transition, respectively. Compound **1** exhibits the fifth band, which is moderate absorbance band in the region of ~1200 nm. Based on literature [17], copper-based dithiolene complex, [TBA]$_2$[Cu(mnt)$_2$] shows an absorption band at ~1200 nm (ε = 70 M^{-1} cm^{-1}). The absorption band of compound **1** is observed at 1214 nm (ε = 94 M^{-1} cm^{-1}), which can be attributed to ion-pair charge transfer (IPCT) transition between the cation and anion and also due to parity forbidden d–d type transition [34,31]. This near-IR absorption band is a characteristic of metal–bis(dithiolene) ion-pair complexes and is generally assigned to $\pi \rightarrow \pi^*$ transition between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The intensity of this $\pi \rightarrow \pi^*$ transition in the NIR region is affected by the presence of counter cation (Hb in the present case) that perturbs the symmetry of the frontier orbitals [37].

In the solid state, compound **1** exhibits a broad band at ~1205 nm with higher intensity in its diffuse reflectance spectrum,

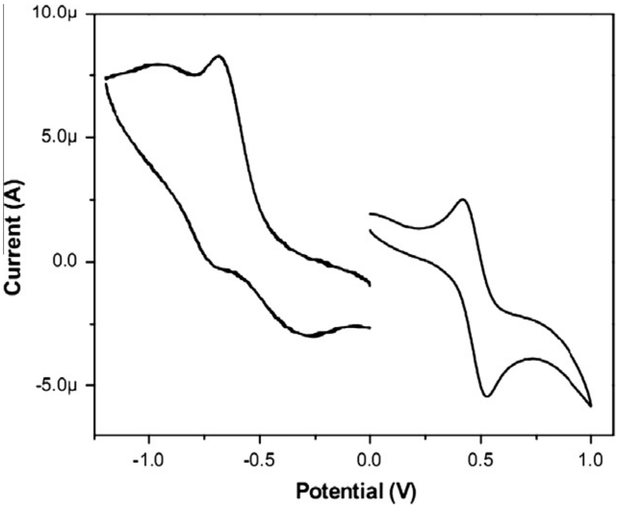


Fig. 3. Cyclic Voltammograms of compound **1** in TBAP/DMF at a scan rate 50 mV s^{-1}.

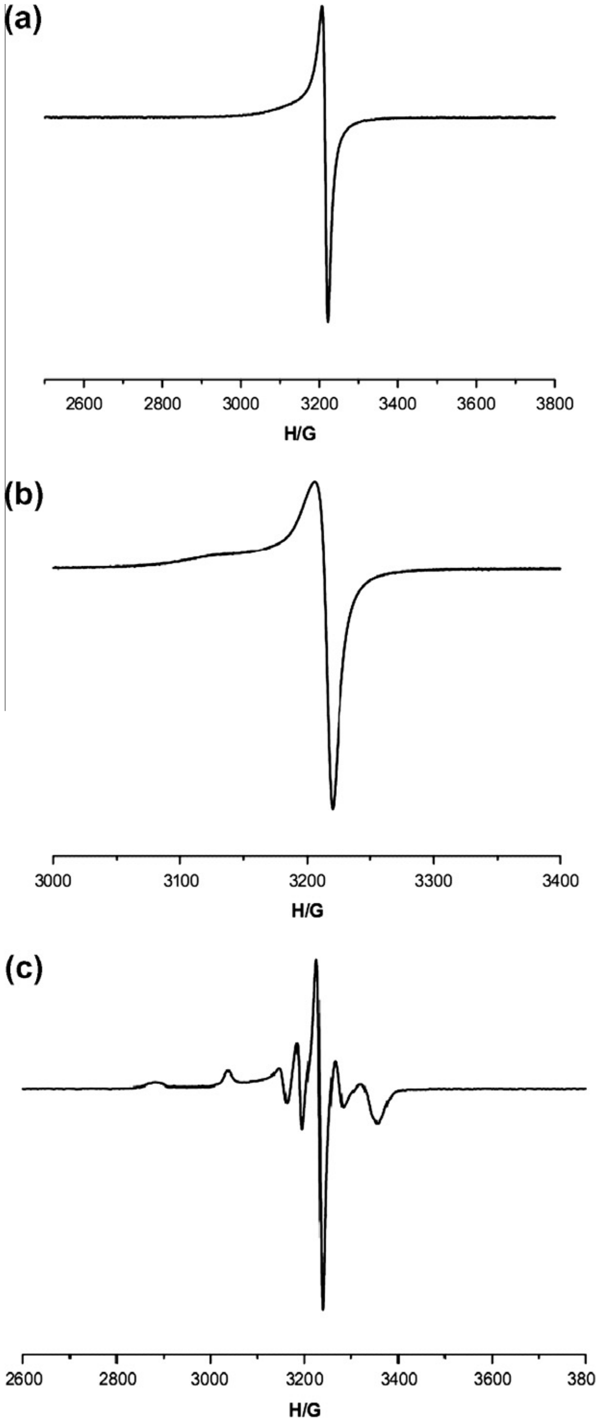


Fig. 4. The EPR spectra of compound [Hb]$_2$[Cu(mnt)$_2$] (**1**): at room temperature (a) solid state, at liquid nitrogen temperature (b) solid state at room temperature, and (c) in DMF (frozen state).

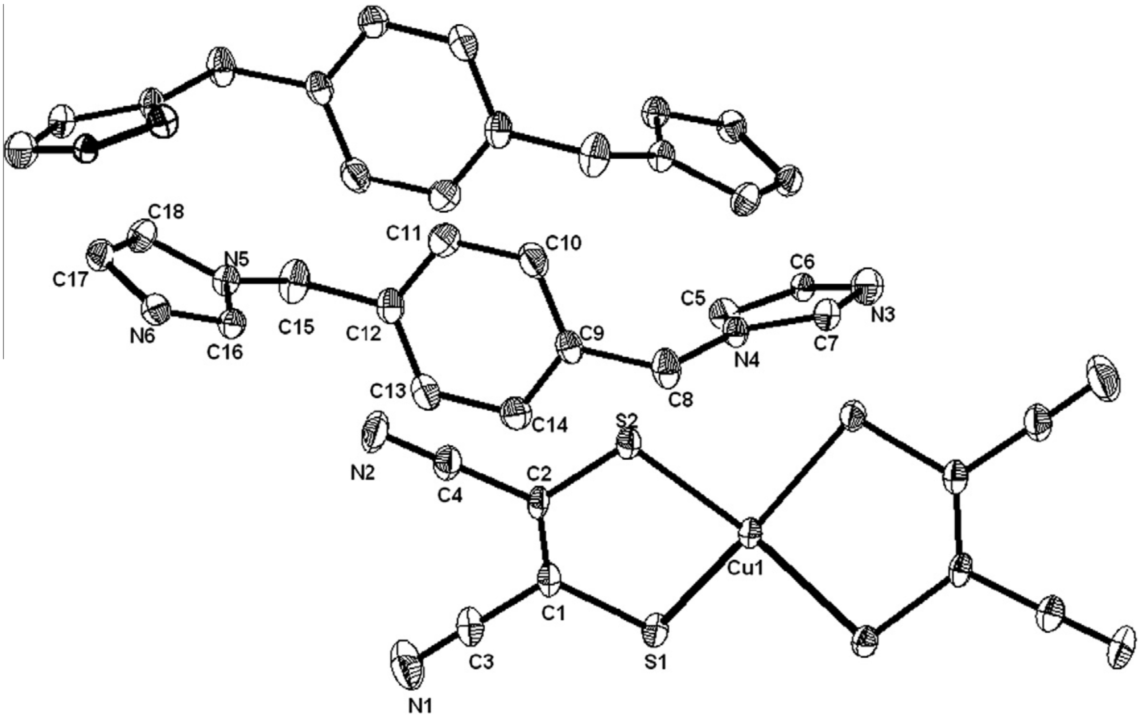


Fig. 5. Thermal ellipsoidal plot of the asymmetric unit of compound $[Hb]_2[Cu(mnt)_2]$ (**1**), hydrogen atoms are not shown for clarity (30% probability).

Table 3
Selected list of bond lengths (Å) and angles (°) for $[Hb]_2[Cu(mnt)_2]$ (**1**).

Cu(1)–S(1)	2.2563(11)	N(3)–C(16)	1.327(5)
Cu(1)–S(2)	2.2811(10)	N(3)–C(18)	1.372(5)
S(1)–C(1)	1.737(4)	N(3)–C(15)	1.477(5)
S(2)–C(2)	1.736(4)	N(5)–C(5)	1.334(5)
N(2)–C(4)	1.138(5)	N(5)–C(7)	1.370(5)
S(1)–Cu(1)–S(1)#1	155.83(6)	C(1)–C(2)–C(4)	119.1(4)
S(1)–Cu(1)–S(2)#1	92.79(4)	C(1)–C(2)–S(2)	123.5(3)
S(1)#1–Cu(1)–S(2)#1	91.89(4)	C(18)–N(3)–C(15)	124.2(3)
S(2)#1–Cu(1)–S(2)	157.51(6)	C(5)–N(5)–C(7)	107.5(3)
C(1)–S(1)–Cu(1)	100.89(14)	C(17)–C(16)–N(3)	110.2(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, y, -z+1/2$.

where as the complex $[Bu_4N]_2[Cu(mnt)_2]$ does not show any intense band in the near-IR region. Fig. 2 compares this situation. We, therefore, timidly assign this 1205 nm band (in the solid state electronic spectrum of complex **1**) to a d–d absorption that is overlapped by an IPCT-band [17]. These solid state bands are generally explained by anion–cation type intermolecular interactions in their ion-pair complexes.

3.2. Electrochemistry

The electrochemical behavior of the complex **1** was performed in dimethylformamide solution, which contains $[Bu_4N][ClO_4]$ (TBAP) as supporting electrolyte at a platinum working electrode. A representative cyclic voltammogram is shown in Fig. 3, which exhibit an quasi-reversible oxidative response at $E_{1/2} = +0.46$ V ($\Delta E = 99$ mV) vs. Ag/AgCl. The present electrochemical data can be explained on the basis of Scheme 1, proposed by Hoyer [38] and others [39]. According to this scheme, the oxidative response for compound **1** is ascribed to the $[Cu^{III}(mnt)_2]^{1-}/[Cu^{II}(mnt)_2]^{2-}$ redox couple, indicating that Cu(III) is fairly stable in the electrochemical scale. An irreversible reductive response at $E_{1/2} = -0.67$ V for compound **1** is assigned to the $[Cu^{II}(mnt)_2]^{2-}/[Cu^{I}(mnt)_2]^{3-}$ redox couple.

3.3. EPR spectroscopy

Fig. 4 illustrates the EPR spectra of compound **1** in the solid state at both room temperature (Freq = 9155.007 MHz, Power = 0.998 mW, Amplitude CH1 = 10.0, CH2 = 2.0) and liquid nitrogen temperature (Freq = 9156.949 MHz, Power = 0.998 mW, Amplitude CH1 = 10.0, CH2 = 2.0), and solution state only at liquid nitrogen temperature (Freq = 9139.291 MHz, Power = 0.998 mW, Amplitude CH1 = 40.0, CH2 = 2.0). The EPR features are almost identical both at room temperature and liquid nitrogen temperature at solid state as far as g values are concerned ($g_{||} = 2.035$, $g_{\perp} = 2.027$ at room temperature and $g_{||} = 2.037$, $g_{\perp} = 2.027$ liquid nitrogen temperature). The relevant plots are shown in Fig. 4a and b respectively. The g values are comparable to those of non-planar Cu(II)-dithiolene complexes ($g_{||} = 2.090$, $g_{\perp} = 2.024$ for $[mb]_2[Cu(mnt)_2]\cdot Me_2CO$ (mb = methylene blue [40] and $g_{||} = 2.08$, $g_{\perp} = 2.03$ $[4,4'\text{-}H_2bpy][Cu(mnt)_2]$ [17]). These g values are also comparable to those of planar Cu(II)-dithiolene complexes (for example, $g_{||} = 2.08$, $g_{\perp} = 2.02$) for $[Bu_4N]_2[Cu(mnt)_2]$ [41]). The solution state (frozen) EPR spectrum of compound **1** at liquid nitrogen temperature exhibits hyperfine structure due to $^{63,65}Cu$ nuclei as shown in Fig. 4c.

3.4. Crystal structure description and discussion

Compound **1** crystallizes in monoclinic system with a space group *C2/c*. The thermal ellipsoidal plot of the full molecule is shown in Fig. 5, in which relevant asymmetric unit contains half of the molecule of compound $[Hb]_2[Cu(mnt)_2]$ (represented as labeled atoms). The basic crystallographic data and the relevant bond lengths and angles for compound **1** are described in Table 2 and Table 3 respectively. The overall charge of this Cu(II) complex anion $[Cu(mnt)_2]^{2-}$ in compound **1** as expected is -2, and this

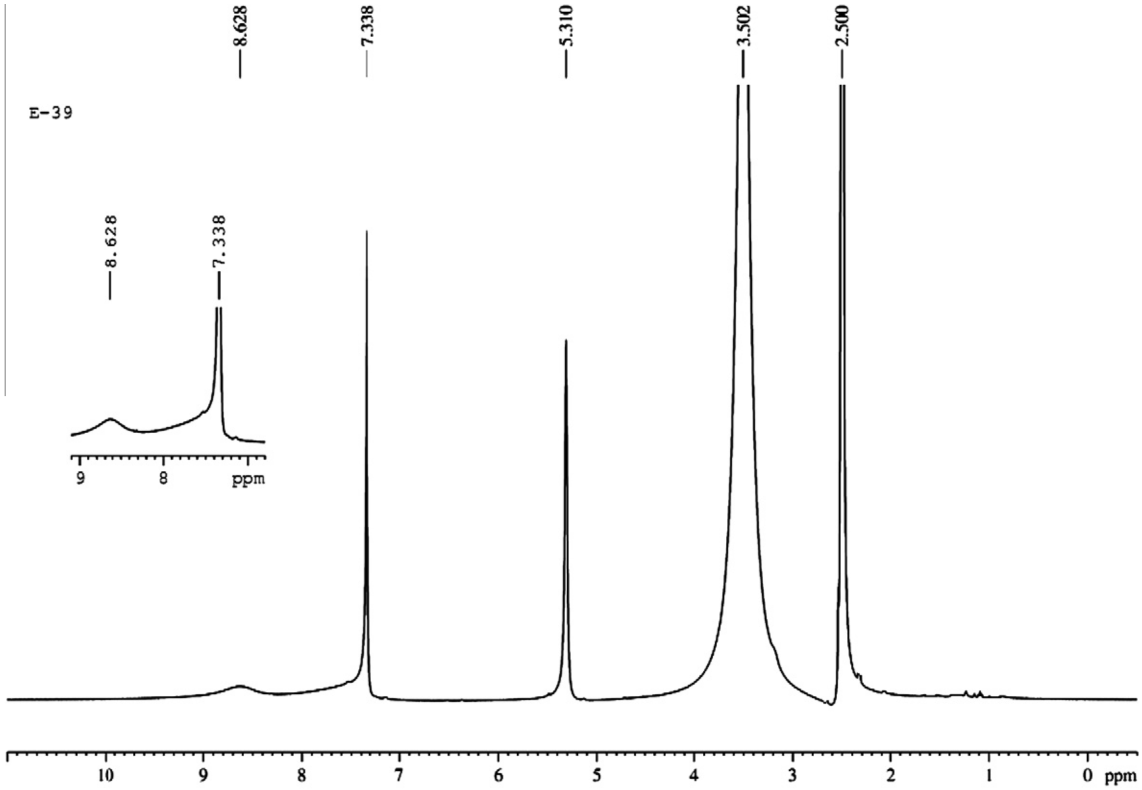


Fig. 6. ^{1}H NMR (DMSO-d_6) spectrum of the compound $[Hb]_2[Cu(mnt)_2]$ **(1)**.

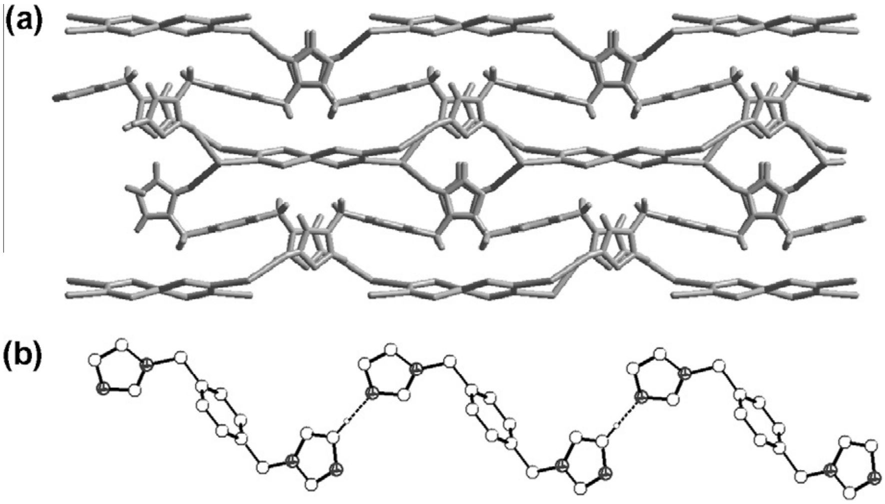


Fig. 7. (a) The molecular packing diagram of $[Hb]_2[Cu(mnt)_2]$ characterized by C—H···N weak interactions (2-D network through supramolecular interactions). (b) One dimensional supramolecular chain characterized by C—H···N hydrogen bonding interactions among cations.

anionic charge is compensated by a two $[Hb]^+$ cations. The cation is formed *in situ* in methanol solution by protonation of one of the imidazole rings, and further it was confirmed by the broad peak at δ 8.62 ppm in its ^{1}H NMR spectrum (generally making integration is difficult for the paramagnetic complexes) [16,42,43], as shown in Fig. 6. In the crystal structure, the geometry around copper ion (Cu^{2+}) is distorted square planar, in which the copper ion is surrounded by four sulfur atoms of two mnt^{2-} ligand with a dihedral angle of 32.43° between two chelated rings in compound **1**, which is not uncommon to the metal-based dithiolene complexes. The non-planarity around the metal ion is caused by dimerization *via* M···S interactions as observed in similar other complexes, $[RBzPy]_2[Fe_2(mnt)_4]$ [44], $[Et_4N]_2[Mn_2(edt)_4]$ [45,46], $Co_2[S_2C_2(CF_3)_2]_4$ [47]. Deviation from planarity were also found in copper-based dithiolene complexes $[ClBzPy]_2[Cu(mnt)_2]$ [48], $[DABCOH]_2[Cu(mnt)_2]$ (DABCOH = monoprotonated 1,4-diazabicyclo-[2,2,2]octane) [48], $[(Ph)_4As]_2[Cu(mnt)_2]$ [49], $[NMe_4]_2[Cu(mnt)_2]$ [50] and $[TBA][Cu(dcmdtcroc)_2]$ (dcmdtcroc = dithiodicyanomethanecroconato) [51] with dihedral angles of 27°, 34° (one is mentioned among three), 30°, 41° and 36°, respectively. These deviations are generally explained by the weak supramolecular interactions between anion and cations through S···H, N···H interactions [48,52,53]. In this paper, we present a distorted square-planar geometry around the Cu^{2+} ion, caused by the supramolecular interactions between cation and anions through all possible hydrogen bonding sites in the ion-pair complex **1**. In the five member chelated ring, the average Cu—S, C—S, C=C bond lengths and S—Cu—S bond angles are 2.268 (11), 1.736 (4), 1.348 (6) Å and 91.89°, respectively. The molecular packing of ion-pair complex **1**, has been characterized by C—H···N hydrogen bonding interactions between cation of the aromatic ring and anion of the $[Cu(mnt)_2]^{2-}$ complex anion, as shown in Fig. S1 (Supplementary materials); this interaction results in a 2-D supramolecular network (the hydrogen atom on the nitrogen of the cation has not been located) as shown in Fig. 7a. Based on literature [54], the C—H···N contacts with H···N distances and C—H···N angles are in the range of 1.8–3.0 Å and 110–180° respectively. Interestingly in compound **1**, there are very strong hydrogen bonding interactions between two cations, in which the C(17)···N(6) distance is 2.66 (5) Å (C—H···N, H···N bond distance is 1.74 Å), which is clearly shorter than the sum of van der Waals radii of the involved nuclei (1.70 Å for carbon, 1.55 Å for nitrogen) [55], and the C—H···N angle is 174.9° (which corresponds to a almost linear feature). This shortest hydrogen bonding supramolecular interaction leads to a 1-D chain of the cations as shown in Fig. 7b. In the crystal structure of compound **1**, there is a centroid–centroid (cg–cg) interaction between two five membered rings ($C_{18}N_4C_{17}C_{16}N_3$ and its symmetry equivalents) of the aromatic cations, with 3.52 Å, as shown in Fig. S2 (Supplementary materials). The relevant hydrogen bonding geometrical parameters for compound **1** are listed in Table S1 (Supplementary materials).

4. Conclusion

In conclusion, we have synthesized an ion-pair dithiolene-based compound with copper metal and it was fully characterized by single crystal X-ray structure analysis and spectroscopic methods. In compound **1**, the cation is prepared *in situ* from MeOH solution, in which only one imidazole ring of **b** (1,4-bis((1H-imidazol-1-yl)methyl)benzene) was protonated. We have demonstrated the shortest C—H···N hydrogen bonding contact among the cations in the crystal structure of compound **1** as far as the relevant literature is concerned. Compound **1** exhibits a broad absorption in the near-IR region at 1205 nm in its diffuse reflectance spectrum. The EPR spectroscopy reveals a typical tetragonal feature for a Cu(II) ion in its solid state and hyperfine interactions in solution state. The electrochemical studies show both oxidative and reductive responses corresponding to Cu^{III}/Cu^{II} and Cu^{II}/Cu^{I} couples.

Acknowledgements

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Appendix A. Supplementary material

CCDC 790171 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing deposit@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax:+44 1223 336033. Experimental procedure (schematic presentation) and spectroscopic data for the compounds **b** and **1**. Figures related to the crystal structure of compound **1**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.12.053.

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