Polyhedron 41 (2012) 52–60

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Studies on novel Cu(II) complexes of 5-(4-hydroxy-phenyl)-1,3,4-thiadiazole-2-thiol and 5-thiophen-2-yl-3H-1,3,4-oxadiazole-2-thione: Synthesis, spectral and structural characterization

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A R T I C L E I N F O

Article history:
Received 15 March 2012
Accepted 17 April 2012
Available online 3 May 2012

Keywords:
Thiadiazole complex
Oxadiazole complex
Copper(II) complexes
Mixed ligand complexes
Supramolecular architecture

ABSTRACT

Two new mixed ligand complexes, $[Cu(en)_2](4\text{-hpythol})_2\cdot 2H_2O$ (4-hpythol = 5-(4-hydroxy-phenyl)-1,3,4-thiadiazole-2-thiol) (**2**) and $[Cu(en)_2(5\text{-thot})_2]$ (5-thot = 5-thiophen-2-yl-3H-1,3,4-oxadiazole-2-thione (**3**), have been prepared, containing en as the co-ligand. The starting ligands, potassium salts of thiohydrazide carbodithioate (RCSNHNHCSSK)/hydrazine carbodithioate (RCONHNHCSSK), underwent cyclization during the crystallization or complexation in the presence of ethylenediamine (en) and converted to 5-(4-hydroxy-phenyl)-1,3,4-thiadiazole-2-thiol and 5-thiophen-2-yl-3H-1,3,4-oxadiazole-2-thione, respectively. The metal complexes have been characterized with the aid of elemental analyses, IR, magnetic susceptibility and single crystal X-ray studies. The ligand 4-hpythol and complexes **2** and **3** crystallize in the triclinic and monoclinic systems, space group $P\,21/n$, $P\bar{1}$ and $P\,21/c$, respectively. The ligand is present in the deprotonated thiol form in $[Cu(en)_2](4\text{-hpythol})_2\cdot 2H_2O$ (**2**), where it is ionically bonded through the thiol sulfur atom, while potassium *N′*-(thiophene-2-carbonyl) hydrazinecarbodithioate after cyclization is present as the thione form in $[Cu(en)_2(5\text{-thot})_2]$ (**3**) and is covalently bonded through the N atom of the resulting oxadiazole-2-thione. The most noteworthy feature of 4-hpythol (**1**) is its existence in the thiol form in the solid state. Complex **3** show irreversible redox behavior, assignable to a M^{2+}/M^{3+} one electron transfer. ESR signals were registered for complexes **2** and **3**. Both complexes contain extended hydrogen bonding, providing supramolecular frameworks.

1. Introduction

Copper exhibits considerable biochemical action in humans, either as an essential trace metal or as a constituent of various exogenously administered compounds. In its former role it is bound to ceruloplasmin, albumin and other proteins, while in the latter it is bound to ligands of various types forming complexes that interact with biomolecules, mainly proteins and nucleic acids. In particular, the involvement of copper in human diseases has been described from a medicinal-chemical [1] and a biochemical view [2], focusing on the molecular physiology of Cu transport [3]. Current interest in copper complexes is stemming from their potential use as antimicrobial, antiviral, anti-inflammatory, antitumor agents, enzyme inhibitors or chemical nucleases. Markedly, the biochemical action of copper complexes with non-steroidal anti-inflammatory drugs (NSAIDs) has been studied [4], which have reduced side effects, and their mode of action is attributed to their marked superoxide-dismutase (SOD) mimetic activity. Copper-based compounds show potential chemotherapeutic properties [5,6]. The toxic effects of copper complexes lead to cell death either by necrosis or through the activation of the apoptotic process [7]. 1,3,4-Thiadiazole and oxadiazole derivatives, which belong to an important group of heterocyclic compounds, are the subject of extensive study in recent years because of their diverse biological activities, such as anti-tuberculostatic, anti-inflammatory, analgesic, antipyretic, anticonvulsant, antibacterial and antifungal activities [8–13]. These compounds have also been shown to exhibit antimycotic [14] and analgesic action [15]. Some works have reported on the metal complexes of 2,5-bis(2-pyridyl)-1,3,4-thiadiazole [16], 5-phenyl-1,3,4-oxadiazole-2-thione [17,18], 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione [19–20], 5-(3-pyridyl)-1,3,4-oxadiazole-2-thione [21] and 5-(2-pyridyl)-1,3,4-oxadiazole-2-thione [22], but no work seems to have been carried out on the complexes of 1,3,4-thiadiazoles-**2**-thiones/thiols. Therefore it would be of interest to investigate the mixed ligand complexes of thiadiazole-2-thiol and oxadiazoles-2-thiones and to compare the mode of bonding of the ligands and structures of the complexes. In view of this, we have prepared and characterized the Cu(II) complexes

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http://dx.doi.org/10.1016/j.poly.2012.04.025

of 5-(4-hydroxy-phenyl)-1,3,4-thiadiazole-2-thiol and 5-thiophen-2-yl-3H-1,3,4-oxadiazole-2-thione in the presence of ethylenediamine, which acts as a co-ligand.

2. Experimental section

2.1. Chemicals and starting materials

Commercial reagents were used without further purification and all experiments were carried out in the open atmosphere. Ethyl-2-thiophenecarboxylate (Sigma Aldrich), CS_2 (SD Fine Chemicals) and KOH (Qualigens) were used as received. All the synthetic manipulations were carried out in the open atmosphere and at room temperature. The solvents were dried and distilled before use following standard procedures. The complexes were analyzed for their metal content after decomposition with a mixture of conc. HNO_3 and HCl, followed by conc. H_2SO_4 [23].

2.2. Physical measurements

Carbon, hydrogen and nitrogen contents were estimated on a CHN Model CE-440 Analyser and on an Elementar Vario EL III Carlo Erbo 1108. Magnetic susceptibility measurements were performed at room temperature on a Cahn Faraday balance using $Hg[Co(NCS)_4]$ as the calibrant, and electronic spectra were recorded on a SHIMADZU 1700 UV–Vis spectrophotometer. IR spectra were recorded in the 4000–400 cm^{-1} region as KBr pellets on a Varian Excalibur 3100 FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a JEOL AL300 FT NMR spectrometer using TMS as an internal reference. ESR spectra of complexes **2** and **3** were recorded on X-band spectrometer, model Varian E-112, using TCNE as the internal standard. The electrochemical experiments were performed with a CHI-660C (CH Instruments, USA), using three-electrode system with a nickel support as the working electrode, a platinum wire as the counter electrode (area ~8.0 cm^2) and Hg/HgO was used as the reference electrode.

2.3. Synthesis

2.3.1. Synthesis of 4-hydroxy-thiobenzoic acid hydrazide

4-Hydroxy-thiobenzoylsulfanyl-acetic acid was prepared by the literature method [24]. 4-Hydroxy-thiobenzoic acid hydrazide was prepared by adding a slightly excess amount of hydrazine hydrate (3.0 mL, 20 mmol) to a solution of 4-hydroxy-thiobenzoylsulfanyl-acetic acid (4.4 g, 20 mmol) prepared in 1 N aq.NaOH, and keeping the reaction mixture for 2 h. This mixture was acidified with dil. acetic acid (20% v/v) whereupon a cream solid of 4-hydroxy-thiobenzoic acid hydrazide was obtained, which was filtered, washed with H_2O, dried and crystallized in ethanol. Yield: 85%; m.p. 170 °C [24].

2.3.2. Synthesis of 5-(4-hydroxy-phenyl)-1,3,4-thiadiazole-2-thiol (4-hpythol) (**1**)

Potassium N′-(4-hydroxy-thiobenzoyl)-hydrazinecarbodithioate was prepared by adding CS_2 (0.9 ml, 10 mmol) dropwise to a suspension of 4-hydroxy-thiobenzoic acid hydrazide (1.68 g, 10 mmol) in methanol (20 ml) in the presence of potassium hydroxide (0.6 g, 10 mmol). The reaction mixture was stirred continuously for 30 min and the separated yellow solid of potassium N′-(4-hydroxy-thiobenzoyl)-hydrazinecarbodithioate was filtered, washed with EtOH and dried. Yield: 60%; m.p. 334–338 °C. This solid was dissolved in a MeOH–H_2O (50% v/v) mixture and after 7 days colorless crystals of 5-(4-hydroxy-phenyl)-1,3,4-thiadiazole-2-thiol, suitable for X-ray analyses, were obtained. Yield: 40%; m.p. 210-215 °C. *Anal.* Found: C, 45.90; H, 2.25; N, 13.50; S, 30.45%. *Anal.* Calc. for $C_8H_5N_2OS_2$ (209.28): C, 45.87; H, 2.38; N, 13.37; S, 30.58 (%). IR (ν cm^{-1}, KBr): ν(OH) 3424, ν(S–H) 2565, ν(C=N) 1588, ν(C–S) 755, ν(N–N) 1070s. ^1H NMR (DMSO-d_6; δ ppm): 8.20–7.54 (m,4H, aromatic protons), 3.60 (s,1H, SH), 3.20 (s, 1H, OH). ^{13}C NMR (DMSO-d_6; δ ppm): 178.10 (C–S), 158.05 (C=N), 128.42 (C3), 127.50 (C4, C8), 129.20 (C6), 125.94 (C5, C7) (Scheme 1).

2.3.3. Synthesis of potassium N′-(thiophene-2-carbonyl) hydrazinecarbodithioate [$K^+(H_2thcd)^-$]

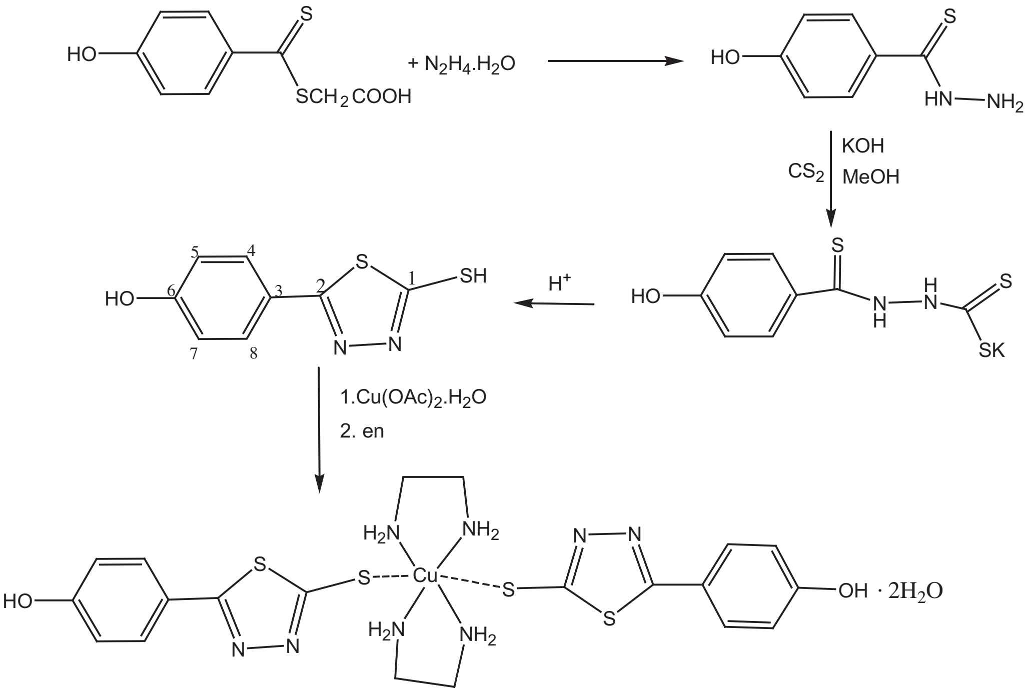
The potassium N′-(thiophene-2-carbonyl) hydrazinecarbodithioate [$K^+(H_2thcd)^-$] was prepared by adding CS_2 (1.5 ml, 20 mmol) dropwise to a suspension of thiophene-2-carbonyl hydrazide (2.28 g, 20 mmol) in methanol (20 ml) in the presence of potassium hydroxide (1.2 g, 20 mmol). The reaction mixture was stirred continuously for 30 min and the white solid [$K^+(H_2thcd)^-$] which separated was filtered, washed with EtOH and dried. Yield: 77%; m.p. 145–150 °C. *Anal.* Found: C, 28.10; H, 2.00; N, 10.85; S, 37.65%. *Anal.* Calc. for $C_6H_5N_2S_3OK$ (256): C, 28.12; H, 1.95; N, 10.93; S, 37.50 (%). IR (ν cm^{-1}, KBr): ν(NH) 3213, 3140, ν(C=O) 1666, ν(N–N) 1062s, ν(C=S) 985. ^1H NMR (DMSO-d_6; δ ppm): 11.74, 10.48 (s,2H) 7.92–7.14 (m, 3H, aromatic protons). ^{13}C NMR (DMSO-d_6; δ ppm): 178.50 (C=S), 160.19 (C=O), 129.18 (C3), 127.68 (C4), 125.97 (C5), 128.40 (C6) (Scheme 2).

2.3.4. Synthesis of [$Cu(en)_2(4\text{-}hpythol)_2$]·$2H_2O$ (**2**)

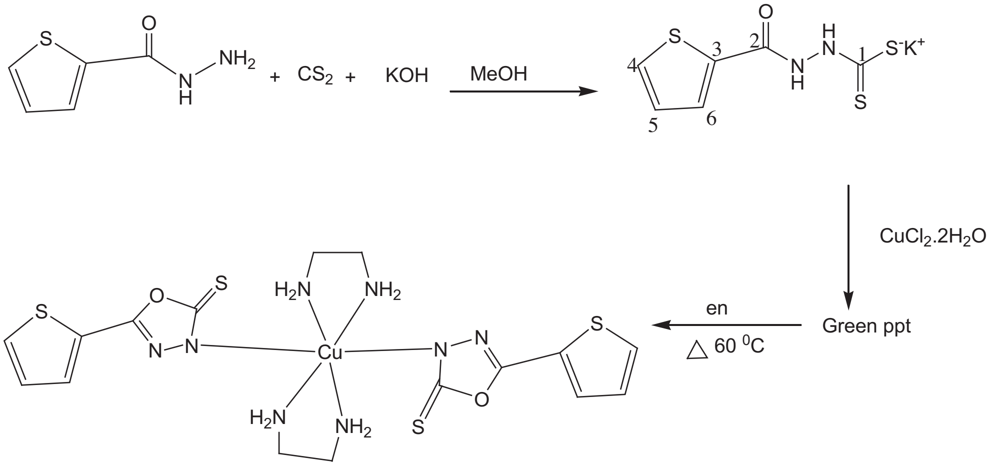
A solution of 4-hpythol (**1**) (0.420 g, 2 mmol) in MeOH (10 ml) was added to a MeOH solution (10 ml) of $Cu(OAc)_2·2H_2O$ (0.200 g, 1 mmol). This mixture was magnetically stirred for 3 h at room temperature. The resulting black precipitate was filtered off, then washed thoroughly with methanol. A methanol solution (10 ml) of ethylenediamine (0.30 ml, 4 mmol) was added to the methanol suspension of the above compound and magnetically stirred for 2 h at room temperature. The resulting clear dark blue solution was filtered off and kept for crystallization. Dark blue single crystals of **2** suitable for X-ray analysis were obtained by slow evaporation of the above solution over a period of 12 days. Yield 58%; m.p. 220 °C. *Anal.* Found: C,37.20; H, 4.55; N, 17.40; S, 20.30; Cu, 10.10%. *Anal.* Calc. for $C_{20}H_{30}CuN_8S_4O_4$ (638.35): C, 37.58; H, 4.69; N, 17.54; S, 20.20; Cu, 9.94 (%). IR (ν cm^{-1}, KBr): ν(OH) 3430, ν(NH) 3210, ν(C=N) 1606, ν(N–N) 1095s, ν(C–S) 745, ν(Cu–N) 524. μ_B = 1.75 BM. UV–Vis [λ_{max}, DMSO, nm]: 580, 361, 339.

2.3.5. Synthesis of [$Cu(en)_2(5\text{-}thot)_2$] (**3**)

$CuCl_2·2H_2O$ (0.170 g, 1 mmol) and freshly prepared potassium N′-(thiophene-2-carbonyl) hydrazinecarbodithioate [$K^+(H_2thcd)^-$] (0.514 g, 2 mmol) were dissolved separately in 15–20 ml methanol, mixed together and stirred for 2 h. The green solid which separated was filtered, washed successively with methanol-water mixture (50:50 v/v) and finally with methanol. A methanol solution (10 ml) of ethylenediamine (0.30 ml, 4 mmol) was added to the methanol suspension of the above compound and stirred for 30 min. A clear dark blue solution was obtained, which was filtered and kept for crystallization. Dark blue crystals of **3** suitable for X-ray analysis were obtained by slow evaporation of the above solution over a period of 15 days. Yield: 50%. m.p. 240 °C. *Anal.* Found: C, 34.75; H, 4.00; N, 20.40; S, 23.35; Cu, 11.45%. *Anal.* Calc. for $C_{16}H_{22}CuN_8S_4O_2$ (550.25): C, 34.89; H, 3.99; N, 20.35; S, 23.26; Cu, 11.54 (%). IR (ν cm^{-1}, KBr): ν(NH) 3231, ν(C–N) 1593, ν(N–N) 1088s, ν(C–S) 755, ν(Cu–N) 518. μ_B = 2.02 BM. UV–Vis [λ_{max}, DMSO, nm]: 606, 350.



Scheme 1. Synthesis of 5-(4-hydroxy-phenyl)-1,3,4-thiadiazole-2-thiol) (4-hpythol) and its Cu(II) complex (**2**).



Scheme 2. Synthesis of potassium *N*′-(thiophene-2-carbonyl) hydrazinecarbodithioate $[K^+(H_2thcd)^-]$ and its Cu(II) complex (**3**).

3. Crystal structure determination

Crystals suitable for X-ray analyses of compounds **1**, **2** and **3** were grown at room temperature. The crystal data were collected on an Oxford Gemini diffractometer equipped with CrysAlis CCD software using a graphite mono-chromated Mo Kα (λ = 0.71073 Å) radiation source at 293 K for **1**, **2** and **3**. Multi-scan absorption correction was applied to the X-ray data collection for all the compounds. The structures were solved by direct methods (SHELXS-08) and refined against all data by full matrix least-squares on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included in the refinement at geometrically ideal positions and refined with a riding model [25]. The MERCURY package and the ORTEP-3 for Windows program were used for generating the structures [26,27].

4. Results and discussion

The ligand 5-(4-hydroxy-phenyl)-1,3,4-thiadiazole-2-thiol reacts with $Cu(OAc)_2·2H_2O$ to form a blue precipitate which is soluble in methanolic solutions of en, yielding $[Cu(en)_2]$ (4-hpythol)$_2$·$2H_2O$ (**2**). A methanol solution of $CuCl_2·2H_2O$ on reaction with potassium *N*′-(thiophene-2-carbonyl) hydrazinecarbodithioate yields $[Cu(en)_2(thot)_2]$ (**3**), suggesting that the potassium *N*-acylhydrazine carbodithioate generates 1,3,4-oxadiazole/thiadiazole-2-thione on cyclization in the presence of en by an internal ring closure reaction *via* desulfurization. A similar cyclization process has been described in the literature [17–20]. The elemental analyses and physical measurements of complex **3** indicate that both hydrazinic hydrogens from the $[–C(O)NHNHC(S)S^-–]$ moiety and one sulfur atom are missing from the resulting complex.

Schemes 1 and 2 depict the formation of the complexes which contain the thione/thiol form of the ligand and ethylenediamine as a co-ligand. Complexes **2** and **3** are insoluble in ethanol and chloroform, but are soluble in DMF and DMSO, and melt at 220 and 240 °C, respectively.

4.1. IR spectra

The IR spectrum of the ligand 5-(4-hydroxy-phenyl)-1,3,4-thiadiazole-2-thiol (4-hpythol) in KBr shows absorptions (cm^{-1}) due to the stretching modes of O–H (3424), S–H (2565), C=N (1588), C–S (755) and N–N (1070). The IR spectrum of potassium *N*′-(thiophene-2-carbonyl) hydrazinecarbodithioate [$K^+(H_2thcd)^-$] in KBr shows absorptions (cm^{-1}) due to the stretching modes of NH (3213 m, 3140 m), C=O (1666), C=S (985) and N–N (1062). The IR spectra of complexes **2** and **3** show bands in the region of 3231–3210 cm^{-1} due to the N–H stretching vibrations of en, which are shifted to lower frequency compared to those encountered in free en [28]. Appearance of a new band near 520 cm^{-1} due to ν(M–N) suggests the formation of a chelate with en in complexes **2** and **3**. The IR data are thus consistent with the presence of 1,3,4-thiadiazole and 1,3,4-oxadiazole moieties in complexes **2** and **3** [29], respectively. This disappearance of ν(S–H) at 2565 cm^{-1} and the presence of ν(C–S) at 745 cm^{-1} in complex **2** indicates that the thiol sulfur is ionically bonded to Cu(II). The slight negative shift in ν(C–S) and ν(C=S) in complexes **2** and **3,** respectively, may be due to the involvement of the thiol or thione sulfur in hydrogen bonding. In complexes **2** and **3**, peaks appearing at 1593–1606 cm^{-1} due to ν(C=N) (endocyclic) and ν(C–S–C) 1285/ν(C–O–C) 1270 cm^{-1} suggest cyclization of the dithiolate moiety to 1,3,4-thiadiazole-2-thiol/1,3,4-oxadiazole-2-thione *via* desulfurization.

4.1.1. ^{1}H and ^{13}C NMR spectra

The ^{1}H NMR spectrum of 4-hpythol exhibits signals at δ 3.60 and 3.20 ppm due to protons of the thiol and phenyl hydroxyl

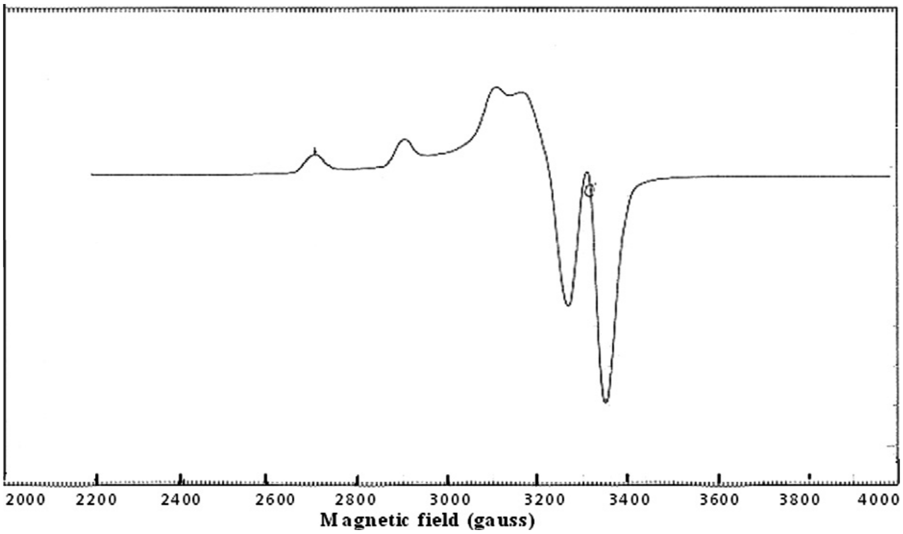


Fig. 1. ESR spectrum of $[Cu(en)_2(4\text{-hpythol})_2]\cdot 2H_2O$ (**2**) in MeOH at LNT.

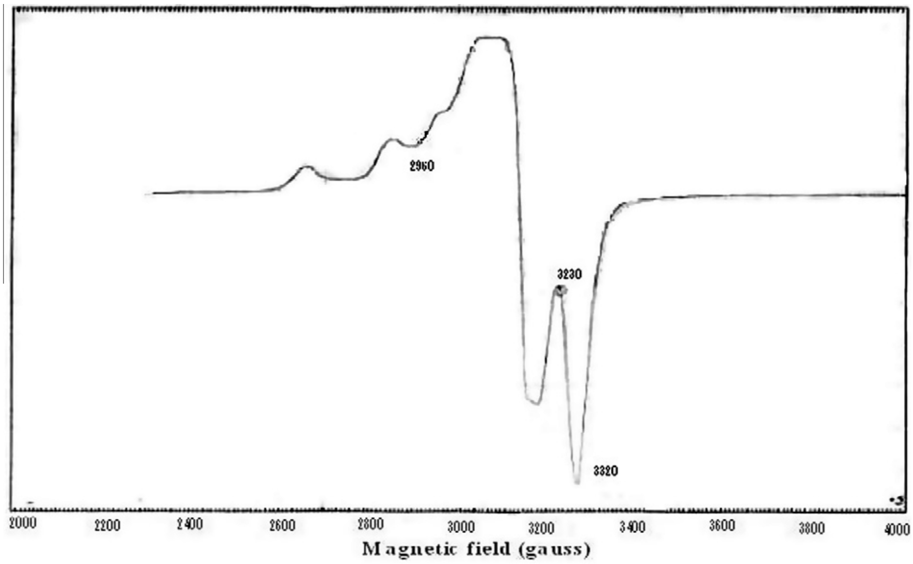


Fig. 2. ESR spectrum of $[Cu(en)_2(5\text{-thot})_2]$ (**3**) at LNT.

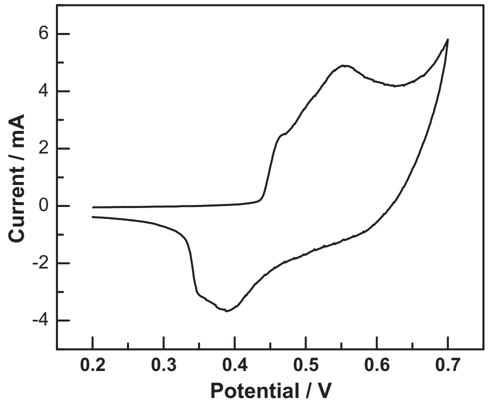


Fig. 3. Cyclic voltammogram of $Cu(en)_2(5\text{-thot})_2$] (**3**).

groups, respectively. Aromatic protons appear between δ 8.20 and 7.54 ppm. The ^{13}C NMR spectrum of 4-hpythol shows signals at δ 178.10 and 158.05 ppm due to C–S and C=N carbons, respectively. The hydroxyl phenyl ring carbons appear at δ 128.42, 129.20 (C3, C6), 127.50, 125.94 (C4, C5) ppm. The NMR data thus indicate that the ligand 5-(4-hydroxy-phenyl)-1,3,4-thiadiazole is present in the thiol–thione tautomeric form in solution. The ^1H NMR spectrum of potassium *N*′-(thiophene-2-carbonyl) hydrazinecarbodithioate [$K^+(H_2thcd)^-$] in DMSO-d_6 shows two signals at δ 11.74 and 10.48 (s, 2H), ppm due to the presence of two NH protons. The phenyl ring protons appear as a multiplet between δ 7.92–7.14 (m, 3H) ppm. The ^{13}C NMR spectrum of $K^+(H_2thcd)^-$ shows signals at δ 178.50 and 161.19 ppm due to >(C=S) and >(C=O) carbons, respectively. The phenyl ring carbons appear at δ 128.40, 129.18 (C3, C6), 127.68 and 125.97 (C4, C5) ppm.

Table 2
Interatomic distances (Å) and angles (°) for 4-hpythol (**1**).

Bond lengths (Å)		Bond angles (°)	
S(2)–C(2)	1.734(6)	C(2)–S(2)–C(1)	87.0(3)
S(2)–C(1)	1.747(6)	N(1)–C(2)–S(2)	112.7(4)
S(1)–C(1)	1.731(6)	C(2)–N(1)–N(2)	113.6(5)
C(2)–N(1)	1.300(7)	C(1)–N(2)–N(1)	113.1(5)
N(2)–C(1)	1.276(7)	N(2)–C(1)–S(1)	127.4(5)
O(1)–C(6)	1.323(7)	N(2)–C(1)–S(2)	113.6(4)
N(1)–N(2)	1.425(6)	S(1)–C(1)–S(2)	119.0(3)

4.2. Electronic spectra and magnetic moments

[$Cu(en)_2$](4-hpythol)$_2$·$2H_2O$ (**2**) shows a magnetic moment of 1.75 BM, which indicates the presence of one unpaired electron. The presence of a broad band around 17240 cm^{-1}, assigned to the envelope of the $^2B_1g \rightarrow {}^2A_1g$, ^2B_2g and ^2Eg transitions, suggests a square planar geometry for the complex. Two other high energy bands observed at 27665 and 29420 cm^{-1} may be assigned to intraligand/charge transfer transitions. [$Cu(en)_2(thot)_2$] (**3**) shows a magnetic moment of 2.02 B.M. and a broad band at 16500 cm^{-1}, assignable to the $^2Eg \rightarrow {}^2T_{2g}$ transition for an octahedral geometry around Cu(II) [30].

4.3. ESR spectra

The frozen solution EPR spectra of the copper(II) complexes **2** and **3** (Figs. 1 and 2) were recorded in DMSO and methanol, respectively. EPR spectra of Cu(II) complexes on the high field side are more intense than the low field side, indicating a d_{x2-y2} ground state for the copper(II) ion. Analysis of the spectra give $g_{\parallel} = 2.185$ and 2.216 and $g_{\perp} = 2.009$ and 2.008 for complexes **2** and **3** respectively. The trend $g_{\parallel} > g_{\perp} > g_e$ (2.0023), observed for the complexes

Table 1
Crystallographic data for compounds **1**, **2** and **3**.

Parameters	1	2	3
Empirical formula	$C_8H_5N_2OS_2$	$C_{20}H_{30}CuN_8O_4S_4$	$C_{16}H_{22}CuN_8O_2S_4$
Formula weight	209.28	638.35	550.25
Crystal system	monoclinic	triclinic	monoclinic
Space group	*P* 21/*n*	$P\bar{1}$	*P* 21/*c*
T (K)	103(2)	293(2)	293(2)
λ, Mo Kα (Å)	0.71073	0.71073	0.71073
Unit cell dimensions			
a (Å)	8.0624(3)	6.5080(6)	10.6834(18)
b (Å)	11.3547(3)	7.7549(7)	8.6081(15)
c (Å)	11.2234(3)	15.1301(14)	12.672(2)
α (°)	90	75.869(8)	90
β (°)	91.359(3)	84.854(8)	95.432(16)
γ (°)	90	68.602(9)	90
V, (Å^3)	1027.17(5)	689.45(11)	1160.1(3)
Z	4	1	2
ρ_{calc} (g cm^{-3})	1.353	1.538	1.575
μ (mm^{-1})	0.479	1.138	1.332
F(000)	428	331	566
Crystal size (mm^3)	0.30 × 0.27 × 0.25	0.25 × 0.23 × 0.21	0.31 × 0.27 × 0.24
θ range for data collections (°)	2.55–28.75	2.78–28.86	3.04–29.01
Index ranges	$-10 \leqslant h \leqslant 10$	$-4 \leqslant h \leqslant 8$	$-14 \leqslant h \leqslant 14$
	$-15 \leqslant k \leqslant 14$	$-10 \leqslant k \leqslant 9$	$-11 \leqslant k \leqslant 11$
	$-14 \leqslant l \leqslant 15$	$-18 \leqslant l \leqslant 20$	$-15 \leqslant l \leqslant 17$
No. of reflections collected	7007	3615	3099
No. of independent reflections (R_{int})	2663	1629	1928
No. of data/restrains/parameters	1815/0/428	3615/0/178	3099/0/142
Goodness-of-fit on F^2	1.048	0.942	1.034
R_1[a], wR_2[b] [($I > 2\sigma(I)$]	0.051, 0.1431	0.0342, 0.0503	0.0576, 0.0787
R_1[a], wR_2[b] (all data)	0.1845, 0.1891	0.0836, 00.0879	0.1520, 0.1776
Largest difference peak/hole (e Å^{-3})	0.297, −0.495	0.297, −0.240	0.782, −0.877

[a] $R_1 = \Sigma||F_o| - |F_c||\Sigma|F_o|$.
[b] $R_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

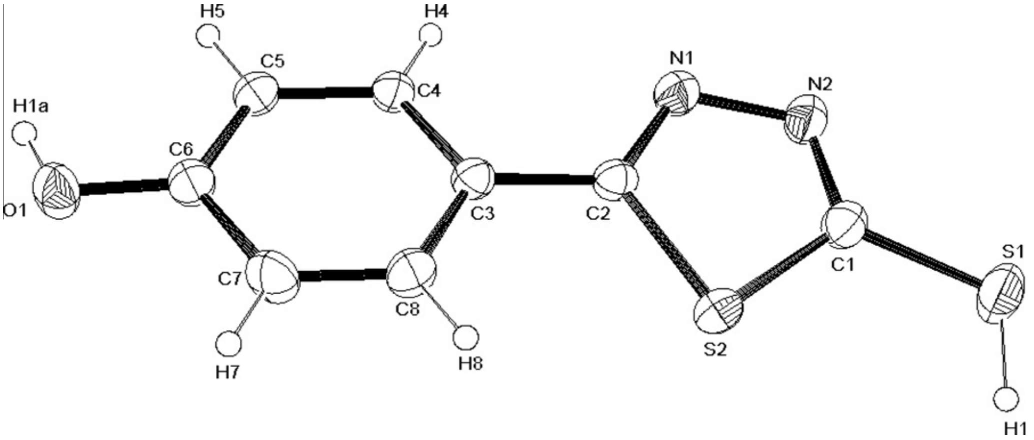


Fig. 4. ORTEP plot of 4-hpythol (**1**) showing the atomic numbering scheme, with ellipsoids of 30% probability.

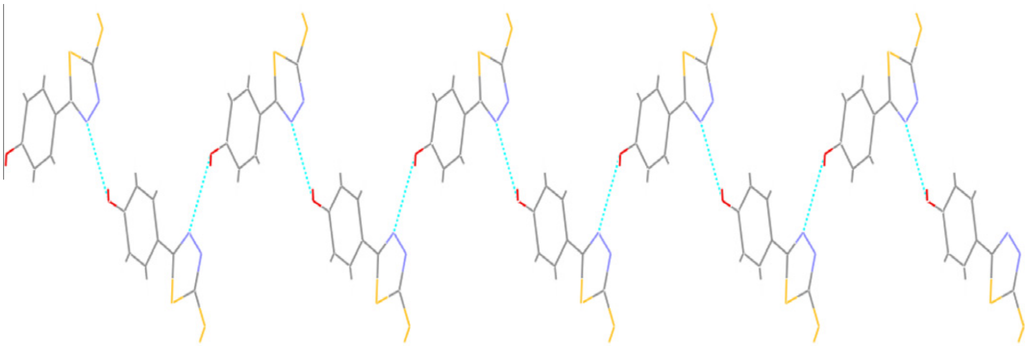


Fig. 5. Showing N–H···O hydrogen bonding forming a linear structure for **1**.

under investigation, also suggests a d_{x2-y2} ground state for the Cu(II) ion [31–33]. Also, the observed $g_{\|}$ values of less than 2.30 provide evidence for the appreciable covalent character of bonding between the Cu(II) ion and the attached ligand in the complexes [34].

4.4. Electrochemical studies

The cyclic voltammogram of complex **3** (Fig. 3) obtained at a platinum electrode in the potential range +0.2 V to +0.7 V, with a scan rate of 50 mVs^{-1}, exhibits a cathodic peak at $E_{pc} = 0.392$ V and the associated anodic peak at $E_{pa} = 0.550$ V with respect to the Ag/AgCl reference. The separation between the cathodic and anodic peak potentials ($\Delta E_p = E_{pa} - E_{pc}$) of 0.158 V indicates an irreversible process assignable to the Cu(II)/Cu(III) couple with a redox potential of 0.471 V (Fig. 3) [35]. However, it is to be noted that the peak separation ($\Delta E_p = E_{pa} - E_{pc}$) is quite large as compared to that expected for a one electron process.

4.5. Crystal structure description of 4-hpythol (**1**)

The crystallographic data and structural refinement details for 4-hpythol (**1**) are given in Table 1 and selected bond distances and bond angles in Table 2. Fig 4 shows the ORTEP diagram of the

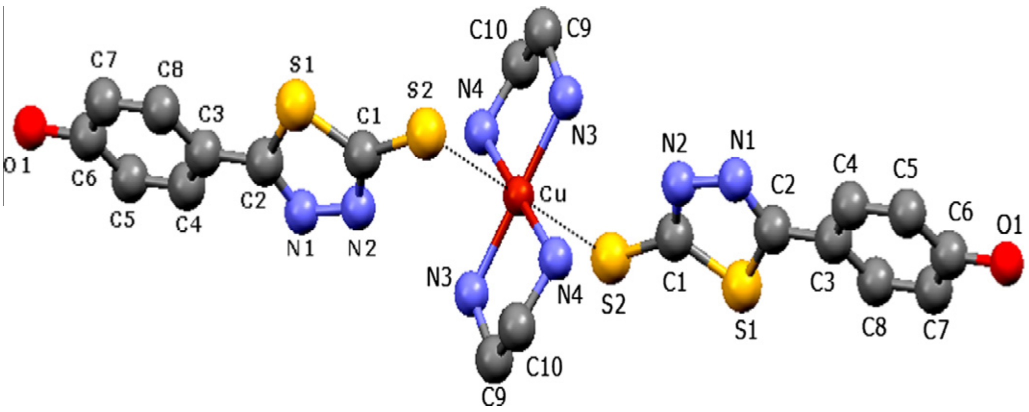


Fig. 6. Molecular structure of $[Cu(en)_2](4\text{-hpythol})_2 \cdot 2H_2O$ (**2**).

Table 3
Interatomic distances (Å) and angles (°) for $[Cu(en)_2](4\text{-hpythol})_2{\cdot}2H_2O$ (**2**).

Bond lengths (Å)		Bond angles (°)	
Cu(1)–N(3)	1.993(2)	N(3)–Cu(1)–N(3)	180.0
Cu(1)–N(4)	2.004(2)	N(3)–Cu(1)–N(4)	85.17(9)
N(1)–C(2)	1.295(3)	N(3)–Cu(1)–N(4)#1	94.83(9)
N(3)–C(9)	1.469(4)	C(9)–N(3)–Cu(1)	107.93(19)
C(10)–C(9)	1.487(4)	C(1)–N(2)–N(1)	113.5(2)
S(2)–C(1)	1.716(3)	N(4)–C(10)–C(9)	109.3(2)
S(1)–C(2)	1.725(3)	N(1)–C(2)–C(3)	123.2(2)
S(1)–C(1)	1.746(3)	C(3)–C(2)–S(1)	123.94(19)
N(4)–C(10)	1.472(4)	S(2)–C(1)–S(1)	122.99(16)
N(1)–N(2)	1.391(3)	N(2)–C(1)–S(2)	125.3(2)
N(9)–C(9)	1.236(7)	C(2)–N(1)–N(2)	113.4(2)
N(8)–C(8)	1.286(7)	C(2)–S(1)–C(1)	88.60(13)

ligand with the atomic numbering scheme. The most noteworthy feature of the ligand 4-hpythol (**1**) is its stabilization in the thiol form, in contrary to other 1,3,4-thiadiazoles which exist in the thione form. The dihedral angle between the thiadiazole and the attached hydroxyl phenyl rings is 9.6(6)°, indicating that both rings are almost coplanar. The bond lengths and angles in the phenyl ring and thiadiazole ring are generally normal. The exocyclic S(1)–C(1) [1.731(6) Å] and endocyclic S(2)–C(2) [1.734(6) Å] bond lengths are comparable, and they are longer than typical carbon sulfur double-bonds [S═C (1.56 Å)] [36], which indicate that the exocyclic sulfur has single bond character and the ligand is present in the thiol form. This is further supported by the N(2)–C(1) bond length of [1.276(7) Å], which comes in the range of N═C double bonds [1.27 Å] [37]. The structure is stabilized by intermolecular O–H···N hydrogen bonding occurring between the thiadiazole N and OH of a nearby molecule, producing a linear chain structure (Fig. 5). The values found for O–H, N···H and ∠O–H···N are close to the bond distances and bond angles reported earlier [38,39].

4.6. Crystal structure description of $[Cu(en)_2](4\text{-hpythol})_2{\cdot}2H_2O$ (**2**)

The crystal structure of complex **2** consists of a complex cation $[Cu(en)_2]^{2+}$ and the 1,3,4-thiadiazole thiolate (4-hpythol) anion and two lattice held water molecules. The ethylenediamine molecules chelate Cu(II), and two 1,3,4-thiadiazole-2-thiolate anions are ionically bonded in every unit of structure **2**. This is shown as the molecular structure of complex **2** in Fig 6, with the atom labeling scheme and a weak Cu···S interaction. Crystallographic data and structural refinement details related to complex **2** are given in Table

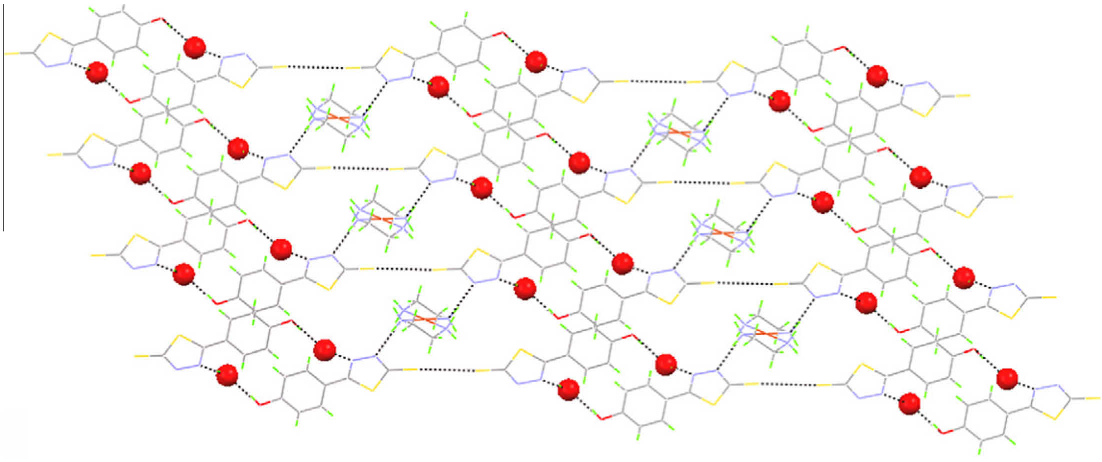


Fig. 7. O–H···O and N–H···O and O–H···S interactions in $[Cu(en)_2(4\text{-hpythol})_2]{\cdot}2H_2O$ (**2**) (oxygen atoms are shown as a ball and stick model).

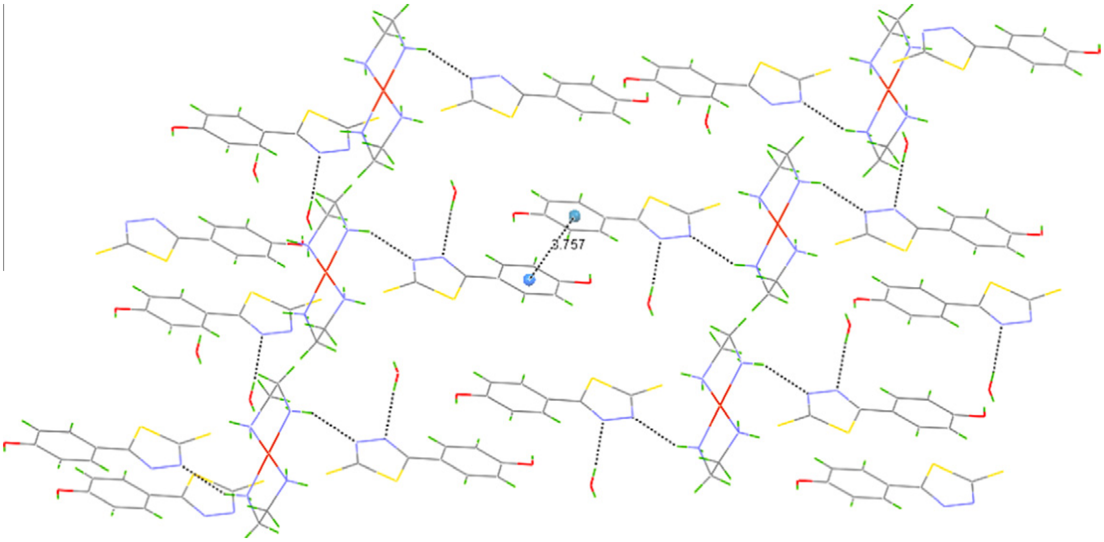


Fig. 8. π···π interactions in $[Cu(en)_2(4\text{-hpythol})_2]{\cdot}2H_2O$ (**2**).

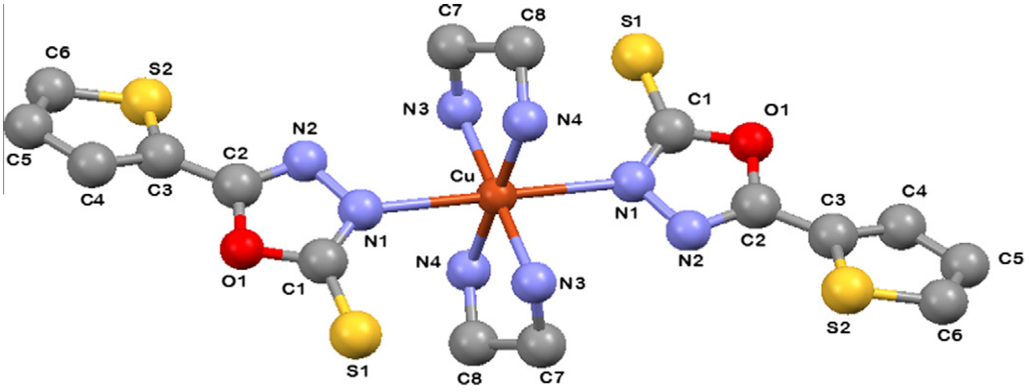


Fig. 9. Molecular structure of [Cu(en)$_2$(5-thot)$_2$] (**3**).

Table 4
Interatomic distances (Å) and angles (°) for [Cu(en)$_2$(5-thot)$_2$] (**3**).

Bond lengths (Å)		Bond angles (°)	
Cu(1)–N(3)	2.041(3)	N(4)–Cu(1)–N(4)	180.0(18)
Cu (1)–N(4)	2.010(3)	N(3)–Cu(1)–N(4)	84.16(14)
N(3)–C(7)	1.476(5)	N(3)–Cu(1)–N(4)#1	95.84(14)
C(4)–C(5)	1.423(6)	C(7)–N(3)–Cu(1)	108.3(2)
S(2)–C(6)	1.682(5)	C(8)–N(4)–Cu(1)	109.6(3)
C(7)–C(8)	1.499(6)	N(3)–C(7)–C(8)	109.2(3)
N(1)–N(2)	1.407(5)	N(4)–C(8)–C(7)	108.0(3)

1 and selected bond lengths and angles are in Table 3. The Cu–N distances are in the range 1.993–2.004 Å (Table 3), which is normal for Cu–N amine coordination. The bite angles for the CuC$_2$N$_4$ five membered rings are 85.17(9)° and 94.83(9)°, indicating a substantial distortion in the molecule. Similar geometrical parameters for the coordination sphere have been reported for other diaquabis (ethylenediamine) Cu(II) salts [40,41]. Each [Cu(en)$_2$]$^{2+}$ forms a pair of intermolecular Cu···S interactions with a distance of 3.032 Å, which is well under the distance of 3.2 Å for the sum of the van der Waals' radii of Cu and S [42] and greater than a Cu–S covalent bond [43]. The Cu(II) center, in D$_{2h}$ symmetry, is bonded to four nitrogen atoms of en groups which offer interesting hydrogen bonding packing. The elements of the structure are joined to each other in the crystal packing by means of an extended system of H-bonds, where hydrogen atoms belonging to en participate in the structure. In the solid state, the complex is stabilized *via* an intermolecular N–H···N interaction between the thiadiazole nitrogen atoms and the NH$_2$ hydrogen atoms of en. An N–H···O interaction is present between the thiol nitrogen and hydrogen atoms of the water molecule, as well as a weak O–H···O interaction between the phenolic OH and hydrogen of the water molecule (Fig. 7). In addition there is a π···π interaction between the thiadiazole and phenyl rings in complex **2**. The distance between the thiadiazole and phenyl ring centroids contacts (Cg···Cg) is 3.757 Å (Fig. 8).

*4.7. Crystal structure description of [Cu(en)$_2$(5-thot)$_2$] (**3**)*

Fig. 9 shows the molecular structure of complex **3** with the atom labeling scheme. Crystallographic data and structural refinement details related to complex **3** are given in Table 1 and selected bond lengths and angles are in Table 4. The molecular structure of **3** shows that in the centro symmetric unit of [Cu(thot)$_2$(en)$_2$], the metal ion is six coordinate, bonded with four nitrogens of two en ligands and two nitrogens of two oxadiazole anions. The dihedral angle between the plane formed by the oxadiazole and phenyl ring is 25.78°. The bond angles N(4)–Cu–N(3) 84.16(14) and N(4)–Cu–N(3) 95.84(14)° indicate a minor deviations from an ideal octahedral geometry. The bond lengths Cu–N(4) and Cu–N(3) are 2.010(3) and 2.041(3) Å, respectively, which is normal for Cu–N amine coordination. In the solid state the complex is stabilized *via* an intermolecular N–H···S interaction between the thione sulfur and NH$_2$ hydrogen atoms of en, and a C–H···S interaction between the thione sulfur and CH$_2$ hydrogen atoms of an en molecule, leading to the formation of a wave-like metal-organic framework (Fig. 10). The above observed intermolecular and intramolecular hydrogen bondings have stabilized the molecular crystal packing, giving a supramolecular network. The axial and equatorial Cu–N distances for the complex are 2.010(3) and 2.041(3) Å respectively, suggesting an axially distorted octahedral geometry for the copper complex due to Jahn–Teller distortion. The hard acceptor, *viz.* Cu(II), shows no tendency for coordination with the soft donor sulfur, but prefers to bind with the comparatively hard nitrogen site of the ligand.

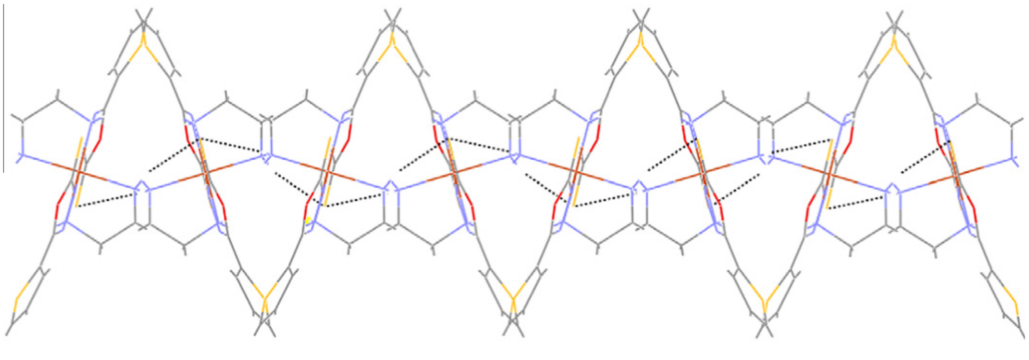


Fig. 10. N–H···S and C–H···S hydrogen bonding in complex (**3**) leading to a wave-like structure.

5. Conclusion

This paper reports the syntheses, spectral and crystal structure investigations of two new complexes, $[Cu(en)_2](4\text{-hpythol})_2\cdot 2H_2O$ (**2**) (4-pythol = 5-(4-hydroxy-phenyl)-1,3,4-thiadiazole-2-thiol) and $[Cu(en)_2(5\text{-thot})_2]$ (**3**) (thot = 5-thiophen-2-yl-3H-1,3,4-oxadiazole-2-thione), containing en as the co-ligand. It was found that potassium thiohydrazide carbodithioate cyclized to 1,3,4-thiadiazole-2-thiol during crystallization in $MeOH–H_2O$. In complex **3**, the metal-bound *N′*-(thiophene-2-carbonyl) hydrazine carbodithioate is cyclized to 5-thiophen-2-yl-3H-1,3,4-oxadiazole-2-thione in the presence of ethylenediamine *via* desulfurisation. This strategy has been found to be an easy and facile route to synthesize mixed ligand complexes of 1,3,4 oxadiazole-2-thione. The structures of the complexes are stabilized through weak intermolecular/intramolecular C–H···S, N–H···S, O–H···S and N–H···N hydrogen bonding. In addition, complex **2** contains a $\pi\cdots\pi$ interaction between the phenyl rings of two units of the complex.

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