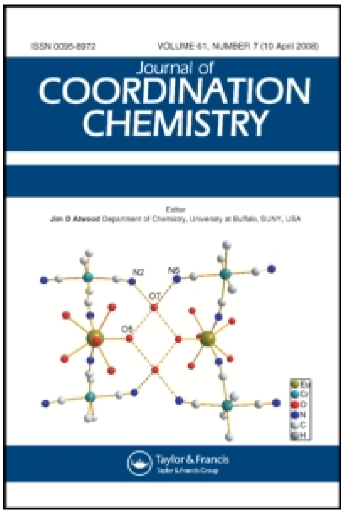

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Nickel(II) and copper(II) complexes of 5-*o*-tolyl-[1,3,4]-oxadiazole-2-thione and ethylenediamine: syntheses, spectral, and structural characterization

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Nickel(II) and copper(II) complexes of 5-*o*-tolyl-[1,3,4]-oxadiazole-2-thione and ethylenediamine: syntheses, spectral, and structural characterization

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The reaction of potassium [N′-(2-methyl-benzoyl)-hydrazinecarbodithioate $[K^+(H_2L)^-]$ with metal acetate yielded $M(H_2L)_2$ $(M = Ni, Cu)$, which on reaction with excess ethylenediamine (en) formed mononuclear mixed ligand complexes $[Ni(en)_2(tot)_2]$ (**1**) and $[Cu(en)_2](tot)_2$ (**2**). The complexes have been characterized by elemental analyses, IR, magnetic susceptibility, and electronic spectral studies. Molecular structures of $[Ni(en)_2(tot)_2]$ (**1**) and $[Cu(en)_2](tot)_2$ (**2**) showed 5-(*o*-tolyl)-[1,3,4]-oxadiazole-2-thione coordinated through oxadiazole nitrogen in **1** and ionically bonded *via* thiol sulfur in **2**.

Keywords: 5-*o*-Tolyl-[1,3,4]-oxadiazole-2-thione; Mixed ligand complexes; X-ray structure; Supramolecular architecture

1. Introduction

1,3,4-Oxadiazoles and their complexes have biological applications such as analgesic [1], muscle relaxant [2], tranquilizing [3], antiproteolytic, anticonvulsive, anti-inflammatory [4, 5], and antifungal activities [6]. Cyclization of N-aroyldithiocarbazates and their esters to 1,3,4-oxadiazoles in the presence of a base is reported [7, 8]. Several other methods are also available for the synthesis of oxadiazoles from acyclic precursors including the oxidative cyclization of acylhydrazones [9], acylthiourea [10–12], and acylthiosemicarbazides [13–16]. 1,3,4-Oxadiazole-2-thiones are important in coordination chemistry because of their exocyclic sulfur or endocyclic nitrogen donor sites. There has been considerable interest in coordination polymers of 1,3,4-oxadiazole-2-thiones due to their interesting role in supramolecular chemistry and crystal engineering [17]. These types of metal–organic framework with intriguing network structures find potential applications in gas storage [18] and photoluminescence [19]. Pyridyl oxadiazoles have been systematically explored for their potential as bridging ligands in coordination polymers [20, 21]. Because of the presence of electronegative elements, namely O, N, and S in 5-aryl-1,3,4-oxadiazole-2-thiones and in

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ethylenediamine, complexes of this system are expected to form extensive intermolecular and intramolecular hydrogen bonds leading to supramolecular architecture [22, 23]. Aromatic or π–π interactions contribute to self-assembly or molecular recognition processes. The π–π interactions range from large biological systems to relatively small molecules and are of fundamental importance for further development of inorganic supramolecular chemistry. Due to the presence of aromatic ring in the ligand under investigation, such π–π stacking is envisaged [24]. Design and assembly of supramolecular architectures with variable cavities or channels are of great interest [21]. A few papers are available on metal complexes of 5-phenyl-1,3,4-oxadiazole-2-thione [22, 25], 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione [17, 18, 20, 21, 26, 27], 5-(3-pyridyl)-1,3,4-oxadiazole-2-thione [23], and 5-(2-pyridyl)-1,3,4-oxadiazole-2-thione [19]. Since the salts of N-aroyl-dithiocarbazates can be converted to 1,3,4-oxadiazole-2-thiol in the presence of a base [7, 8, 22], we wondered whether [N′-(2-methyl-benzoyl)-hydrazinecarbodithioate $[(H_2L)^-]$ bonded to a transition metal can be converted to 1,3,4-oxadiazole-2-thione. Accordingly, Cu(II) and Ni(II) complexes of [N′-(2-methyl-benzoyl)-hydrazinecarbodithioate $[(H_2L)^-]$ were reacted with an excess of ethylenediamine and the results are presented here.

2. Experimental

All synthetic manipulations were carried out in open atmosphere at room temperature. The solvents were dried and distilled before use following standard procedures. *o*-Toluic acid, CS_2, and KOH were procured from CDH, SD Fine, and Qualigens Chemicals, India, and used as received. All solvents were purchased from Merck Chemicals, India, and used after purification. *o*-Toluic acid hydrazide was prepared by refluxing 2-methyl-benzoic acid ester with hydrazine hydrate. Carbon, hydrogen, nitrogen, and sulfur were estimated on a CHN Model CE-440 Analyzer and on an Elementar Vario EL III Carlo Erbo 1108. The complexes were analyzed for metal content after decomposition with a mixture of conc. HNO_3 and HCl, followed by conc. H_2SO_4 [28]. 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 from 4000 to 400 cm^{-1} 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.

2.1. *Synthesis of $[K^+(H_2L)^-]$*

$[K^+(H_2L)^-]$ (figure 1) was prepared by the reaction of CS_2 (1.5 mL, 20 mM) with a solution of *o*-toluic acid hydrazide (3.0 g, 20 mM) in EtOH (25 mL) in the presence of KOH (1.12 g, 20 mM). The white precipitate obtained after continuous stirring for 2 h at room temperature was filtered off and washed with a mixture of EtOH : diethyl ether (50 : 50 v/v). Yield: 68%. m.p.: 242°C. Anal. Calcd for $C_9H_9N_2OS_2K$ (%): C, 40.89; H, 3.43; N, 10.60; S, 24.21. Found (%): C, 40.70; H, 3.41; N, 10.54; S, 24.12. IR (KBr ν, cm^{-1}): ν(NH) 3256 m, 3061 m; ν(C=O) 1638s; [β(NH) + ν(CN)] (thioamide I)

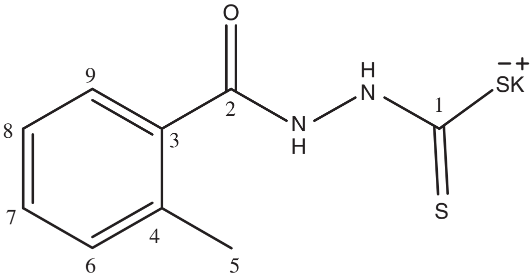


Figure 1. Potassium N′-(2-methyl-benzoyl)-hydrazine-carbodithioate.

1647s; [ν(CN) + β(NH)] (thioamide II) 1565 s; ν(N–N) 1119 m; ν(C=S) 1015s. ^{1}H-NMR (DMSO-d_6; δ ppm): 9.98, 2.00 (m, 2H, NH), 7.20, 7.30, 7.43, and 7.60 (4H, toluene ring), 2.4 (3H, CH_3). ^{13}C-NMR (DMSO-d_6; δ ppm): 204 (C=S), 170.83 (C=O), 134.93 (C3), 136.18 (C4), 129.62(C6), 130.47 (C7), 125.37 (C8), 127.62 (C9).

2.2. *Synthesis of [Ni(en)$_2$(tot)$_2$] (1)*

A solution of [$K^+(H_2L)^-$] (0.264 g, 1 mM) in EtOH (15 mL) was added to a methanolic solution (10 mL) of $Ni(OAc)_2 \cdot 4H_2O$ (0.124 g, 0.5 mM). After stirring the mixture magnetically for 2 h at room temperature, the precipitate was filtered off, washed twice with MeOH and dried. This precipitate was added to an ethanolic solution of ethylenediamine and stirred for 1 h. The resulting clear solution of **1** was filtered and kept for crystallization. After 10 days, pink crystals suitable for X-ray crystallographic study were obtained. Yield: 62%. m.p.: 241°C. Anal. Calcd for $C_{22}H_{30}N_8NiO_2S_2$ (561.37) (%): C, 47.02; H, 5.38; N, 19.95; S, 11.40. Found (%): C, 46.95; H, 5.29; N, 20.05; S, 11.32. $\mu_B = 2.83$ B.M. IR data (ν cm^{-1}, KBr); ν(NH of en) 3330; ν(C=N) 1591; ν_{as}(C–O–C) 1408; ν_s(C–O–C) 1333; ν(N–N) 1126; ν(C=S) 990; ν(Ni–N) 517. UV-Vis [λ_{max}, Nujol, nm]: 769, 514, 402, 326, and 262.

2.3. *Synthesis of [Cu(en)$_2$](tot)$_2$ (2)*

A solution of [$K^+(H_2L)^-$] (0.264 g, 1 mM) in EtOH (10 mL) was added to a methanolic solution (10 mL) of $Cu(OAc)_2 \cdot H_2O$ (0.100 g, 0.5 mM). After stirring for 2 h at room temperature the precipitate was filtered off, washed twice with MeOH, and dried. The above precipitate was added to an ethanolic solution of ethylenediamine and stirred for 1 h. The resulting clear solution of **2** was filtered and kept for crystallization. After 15 days, green crystals suitable for X-ray crystallographic study were obtained. Anal. Calcd for $C_{22}H_{30}N_8CuO_2S_2$ (566.20) (%): C, 46.62; H, 5.34; N, 19.78; S, 11.30. Found (%): C, 46.48; H, 5.25; N, 19.85; S, 11.21. $\mu_B = 1.78$ B.M. m.p.: 241°C. IR (KBr, ν cm^{-1}); ν(NH of en) 3259 m; ν(C=N) 1597s; ν_{as}(C–O–C) 1379s; ν_s(C–O–C) 1276s; ν(N–N) 1114s; ν(C=S) 938 m; ν(Cu–N) 538. UV-Vis [λ_{max}, Nujol, nm]: 540, 253, and 222.

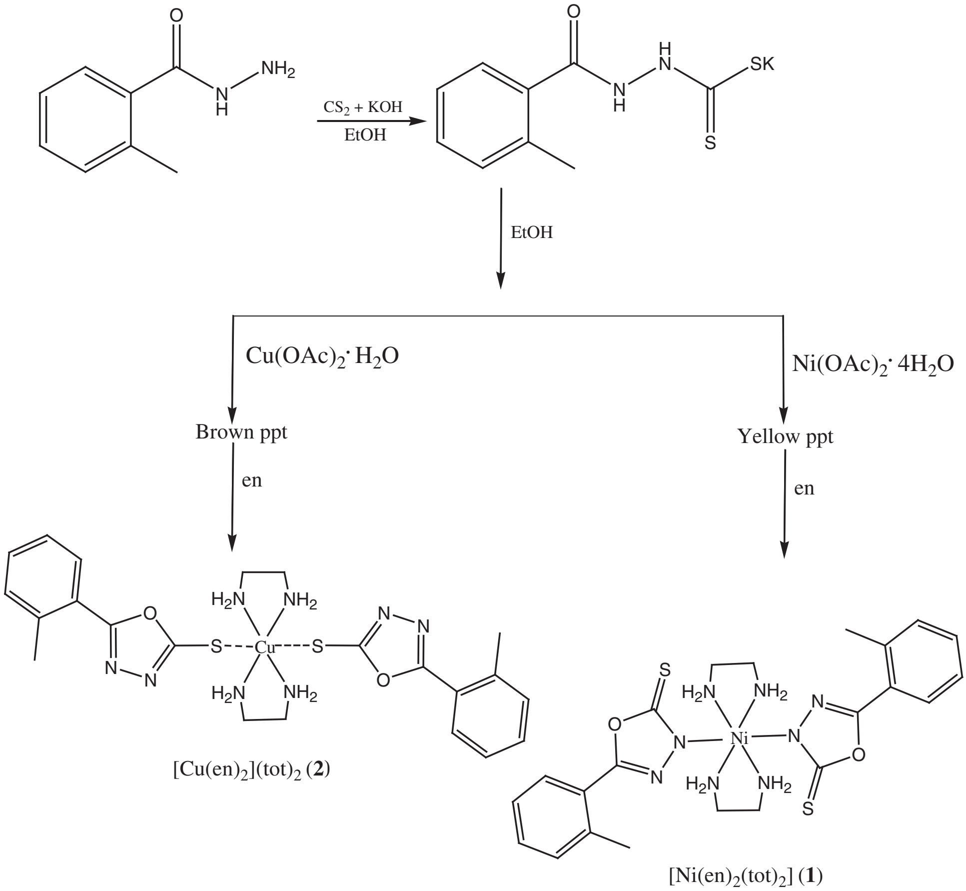
2.4. *Crystallography*

Crystals suitable for X-ray analyses of **1** and **2** were grown at room temperature. Preliminary examination and intensity data were collected on an Oxford Gemini diffractometer equipped with CrysAlis CCD software using graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at 150(2) and 120(2) K for **1** and **2**, respectively [29]. The MERCURY package was used for molecular graphics [30]. The structure was solved by direct methods (SHELXL-97) and refined against all data by full matrix least-square on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogens were included in the refinement at geometrically ideal position and refined with a riding model [31, 32]. Crystal structure diagrams were generated using ORTEP-3 for windows [33].

3. Results and discussion

Ethanolic solutions of $Ni(OAc)_2 \cdot 4H_2O$ and $Cu(OAc)_2 \cdot H_2O$ react with $[K^+(H_2L)^-]$ to give yellow and brown precipitates, respectively, which dissolve in ethanolic solutions of en to form $[Ni(en)_2(tot)_2]$ (**1**) and $[Cu(en)_2](tot)_2$ (**2**) in good yield. Scheme 1 shows the syntheses of Ni(II)(**1**) and Cu(II)(**2**) complexes with $[K^+(H_2L)^-]$.

The complexes are air stable, non-hygroscopic shiny crystalline solids which are insoluble in common organic solvents but soluble in DMF and DMSO. The complexes were fully characterized by magnetic susceptibility measurements, IR, and UV-Vis spectroscopies. Analytical data of the complexes (recorded in section 2) corroborated their respective formulations. The ^{1}H-NMR spectrum of $[K^+(H_2L)^-]$ in DMSO-d_6 shows signals at δ 9.98 and 2.4 for two NH and three CH_3 protons, respectively. The toluene protons are at 7.20, 7.30, 7.43, and 7.60 (4H). ^{13}C-NMR (DMSO-d_6; δ ppm) signals at 204 (C=S), 170.83 (C=O), 134.93 (C3), 136.18 (C4), 19.54 (C5), 129.62 (C6), 130.47 (C7), 125.37 (C8), and 127.62 (C9) ppm suggest the dithiocarbazate in $[K^+(H_2L)^-]$. The IR spectrum of $[K^+(H_2L)^-]$ is expected to have characteristic bands due to ν(NH), ν(C=O), thioamide I, thioamide II, ν(C=S), and ν(N–N), which occur at 3256, 1638, 1472, 943, and 1053 cm^{-1}, respectively. A comparative study of the IR spectra of **1** and **2** with that of $[K^+(H_2L)^-]$ indicates that bands due to the –C(O)NHNHC(S)–, mainly ν(N–H) (hydrazinic) and ν(C=O), are absent; appearance of new bands at 1597–1591 cm^{-1} (endocyclic C=N), 1408–1379 cm^{-1} for ν_{as}(C–O–C), and 1333–1276 cm^{-1} for ν_s(C–O–C) cm^{-1} suggest the cyclization of acyclic dithiocarbazate. The IR data are thus consistent with the presence of a 1,3,4-oxadiazole [34]. A negative shift of 77 cm^{-1} in ν(C=S) in **2** indicates the conversion of C=S to C–S. In **1**, ν(C=S) shows very little negative shift indicating that the exocyclic sulfur is not participating in bonding, but can be involved in hydrogen bonding with NH_2 of ethylenediamine (figure 2). Absorptions at 3330–3135 cm^{-1} due to NH stretching vibrations of en shift to lower frequency due to the presence of N–H $\cdots$ S and N–H $\cdots$ N hydrogen bonding in **1** and **2** [35]. A new band at 538 and 596 cm^{-1} in **1** and **2**, respectively, suggests the formation of metal–nitrogen bonds in both complexes. $[Ni(en)_2(tot)_2]$ has a magnetic moment of 2.83 B.M., indicating two unpaired electrons. Two broad d–d bands at 769 and 514 nm, assigned to $^3A_{2g}$ (F) $\rightarrow$ $^3T_{2g}$ (F), $^3T_{1g}$ (F), respectively, suggest an octahedral complex [35]. Two high-energy bands at 326



Scheme 1. Syntheses of Ni(II)(**1**) and Cu(II)(**2**) complexes with $[K^+(H_2L)^-]$.

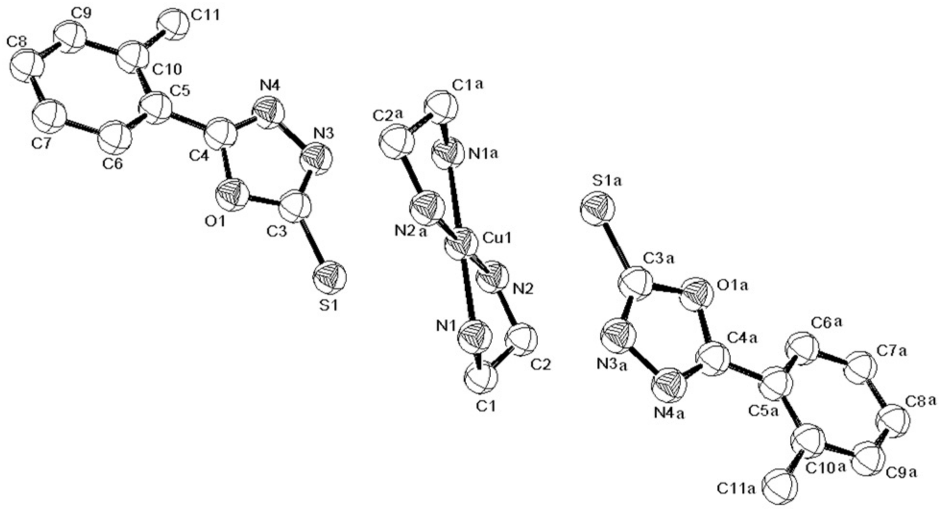


Figure 2. ORTEP diagram of [Cu(en)$_2$](tot)$_2$ with the atomic numbering scheme.

and 262 nm may be due to charge transfer/intraligand transitions. The magnetic moment of 1.78 B.M. for $[Cu(en)_2](tot)_2$ shows one unpaired electron. A broad band around 540 nm assigned to the envelope of $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{2g}$,^2E_g suggests the square planar structure of **2** [36]. Bands at 253 and 222 nm may be due to charge transfer/intraligand transitions.

3.1. *Crystal structures*

Molecular structures of **1** and **2** were determined crystallographically with the details of data collection, structure solution, and refinement listed in table 1. The ORTEP diagrams of **1** and **2** with atom numbering scheme are shown in figures 2 and 3, respectively. Important geometrical parameters are presented in table 2. Complex **1** crystallizes in monoclinic space group *P2₁/c* and **2** crystallizes in the triclinic space group $P\bar{1}$. The crystal structure of **1** shows a distorted octahedral geometry with the coordination of two $(tot)^-$ ligands and two bidentate ethylenediamine. The monomeric unit of $[Ni(en)_2(tot)_2]$ is centrosymmetric around nickel situated on the inversion center. In **1**, the coordination environment is fulfilled by two axial $(tot)^-$ anions at *trans* positions bonded through the nitrogen of oxadiazole and four equatorial sites occupied by two bidentate N,N′-ethylenediamine ligands. The en ligands Ni–N(3) and Ni–N(4) are 2.093(3) and 2.079(3) Å, respectively. The formation of two five-membered C_2N_2Ni chelate rings with a bite angle of 83.41(11)° indicates a slight deviation from octahedral. Geometry and bonding within the en agrees with those of the related compounds, e.g. Ni[*trans*(L)$_2$(en)$_2$] {L = N-(5-chlorouracilato)} [37], isothiocyanato [38], and salicylato [39]. Almost planar (tot^-) ligands in **1** bonded to Ni(II) and designated as Ni–N(1)#1 = Ni–N(1), 2.091(3) Å, are significantly lengthened in comparison to Ni–N bond lengths of 1.907(3) and 1.895(4) Å reported for [Ni{η^5-(2-dimethylaminoethyl)cyclopentadienyl}(pti)]0.5(C_7H_8) [40], [Ni{η^5-1-methylindene)(pti)(PPh_3)] [41] {pti = phthalimidate}, respectively, but comparable to those of *ca* 2.1090 and 2.1150 Å encountered in $[Ni(en)_2(3\text{-}pyt)_2]$ {(3-pyt) = 5-(3-pyridyl)-1,3,4-oxadiazole-2-thione} [27]. Hydrogen bonding parameters are given in table 3. Weak intermolecular N–H···S interaction (figure 4) between thione sulfur and NH_2 of en and weak intramolecular N–H···N interactions between oxadiazole nitrogen and NH_2 stabilize the structure of **1**. The arrangement of monomeric $[Ni(en)_2(tot)_2]$ units in 3-D architecture along the *a*-axis provide a supramolecular network (figure 4). Monomeric $[Ni(en)_2(tot)_2]$ units are held together through N–H···S intermolecular hydrogen bonding, leading to wave-like metal–organic chains along the *c*-axis (figure 5).

The molecular structure of **2** shows that in the centrosymmetric unit of $[Cu(en)_2](tot)_2$, copper is square planar, bonded with two en molecules and ionically linked *via* thiolato sulfur of two $(tot)^-$ anions. Thus, the complex consists of two ethylenediamine molecules which chelate Cu(II) and two 1,3,4-oxadiazole-2-thiolato anions. The Cu–N distances of 2.014(4) and 2.031(4) Å (table 4) are normal for the Cu–N amine coordination [42, 43]. The bite angle for the CuC_2N_4 five-membered ring is 84.49(15)°, indicating distortion from a regular square-planar geometry. Similar geometrical parameters have been reported for diaquabis(ethylenediamine)Cu(II) salts [42, 43]. Each $[Cu(en)_2]^{2+}$ forms a pair of intermolecular Cu···S interactions with a distance of 2.961 Å, which is within 3.2 Å for the sum of van der Waals' radii of Cu and

Table 1. Crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{22}H_{30}N_8NiO_2S_2$	$C_{22}H_{30}N_8CuO_2S_2$
Formula weight	561.37	566.20
Temperature (K)	150(2)	120(2)
Wavelength (Mo-Kα) (Å)	0.71073	0.71073
Color and habit	Pink block	Green needle
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	11.157(3)	6.9792(17)
b	10.3194(18)	7.221(2)
c	12.127(3)	13.356(3)
α	90	92.21(2)
β	115.74(3)	93.223(18)
γ	90	112.48(3)
Volume (Å^3), Z	1257.7(5), 2	619.7(3), 1
Calculated density (g cm^{-3})	1.482	1.517
Absorption coefficient (mm^{-1})	0.974	1.087
Crystal size (mm^3)	$0.23 \times 0.18 \times 0.15$	$0.23 \times 0.18 \times 0.15$
Reflections collected	9280	5207
Unique reflections	2207	2187
Goodness-of-fit on F^2	1.039	1.124
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0431$, $wR_2 = 0.0882$	$R_1 = 0.0564$, $wR_2 = 0.1548$
R indices (all data)	$R_1 = 0.0642$, $wR_2 = 0.0941$	$R_1 = 0.0796$, $wR_2 = 0.1733$

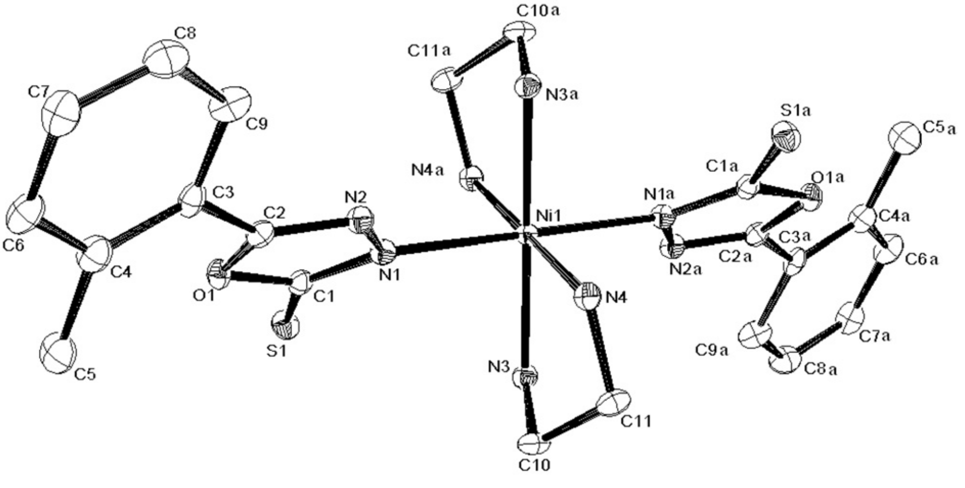


Figure 3. ORTEP plot of $[Ni(en)_2(tot)_2]$ showing atomic numbering scheme with 30% ellipsoid probability. Hydrogens are omitted for clarity.

S [44], but greater than Cu–S covalent bonds [45]. The different bonding behavior of nickel(II) and copper(II) may be related to the Jahn–Teller distortion in $[Cu(en)_2](tot)_2$. The Cu(II) in D_{2h} symmetry is bonded to four nitrogens of two en molecules. The hydrogens of en are involved in hydrogen bonding with oxadiazole nitrogens (figure 6).

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

Ni(1)–N(4)#1	2.079(3)	N(4)–Ni(1)–N(1)	88.82(12)
Ni(1)–N(1)#1	2.091(3)	N(4)#1–Ni(1)–N(1)	91.18(12)
Ni(1)–N(3)#1	2.093(3)	N(4)–Ni(1)–N(3)	96.59(11)
N(3)–C(10)	1.464(4)	N(4)–Ni(1)–N(3)#1	83.41(11)
S(1)–C(1)	1.679(3)	N(1)–Ni(1)–N(3)	90.23(10)
O(1)–C(1)	1.388(4)	C(1)–N(1)–Ni(1)	133.8(2)
N(1)–N(2)	1.400(3)	O(1)–C(1)–S(1)	121.5(2)
		N(1)–C(1)–S(1)	129.7(2)

#1 = $-x+1$, $-y$, and $-z+1$.

Table 3. Hydrogen bond parameters for **1** (Å and °).

D···H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(D–H ···A)
N(3A)–H(3A)···S(1)	0.92	2.77	3.5199	140
N(3)–H(3B)···N(2)#1	0.92	2.62	3.1878	121
N(4)–H(4A)···S(1)#1	0.92	2.61	3.4081	145
N(4)–H(4B)···N(2)	0.92	2.50	3.1040	123
C(5)–H(5C)···O(1)	0.98	2.46	2.9226	109

#1 = $1-x$, $1-y$, $-z$.

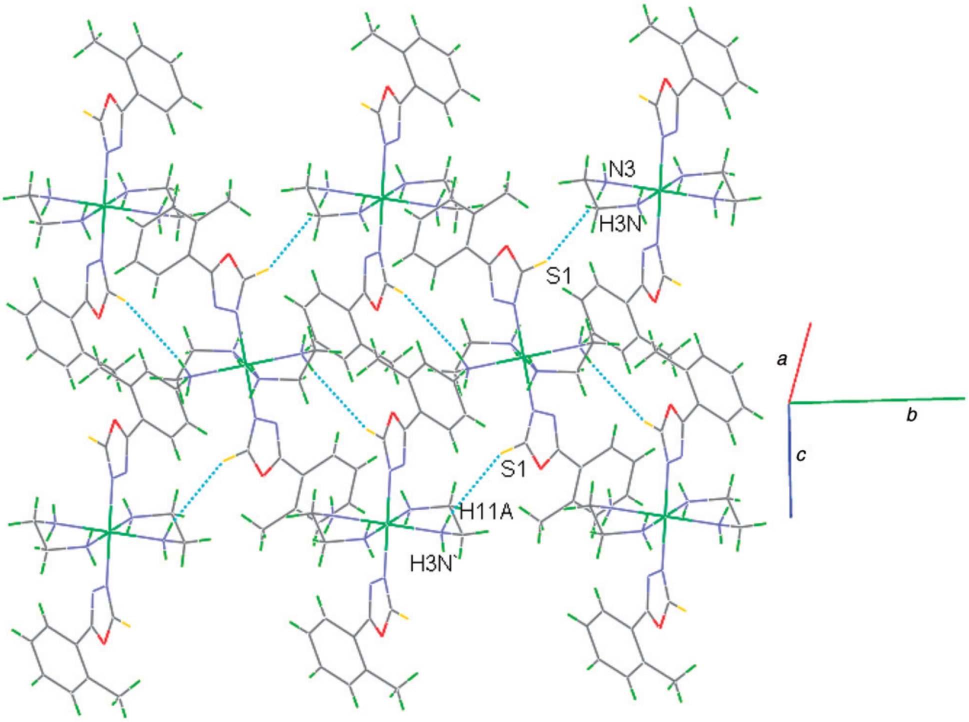


Figure 4. Perspective view of the crystal packing of [Ni(en)$_2$(tot)$_2$] showing N–H···S intermolecular hydrogen bonding.

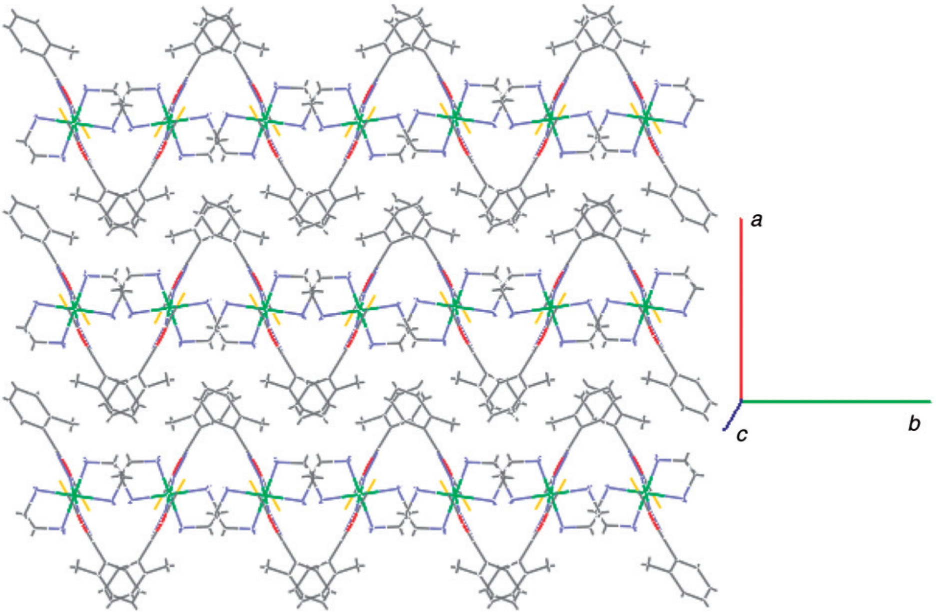


Figure 5. The framework of [Ni(en)$_2$(tot)$_2$] along the *c*-axis leading to the wave-like supramolecular architecture.

Table 4. Selected bond lengths (Å) and angles (°) for **2**.

Cu(1)–N(1)#1	2.014(4)	N(1)#1–Cu(1)–N(2)	95.51(15)
Cu(1)–N(2)#1	2.031(4)	N(1)–Cu(1)–N(2)	84.49(15)
N(1)–C(1)	1.488(6)	O(1)–C(3)–S(1)	119.4(3)
N(2)–C(2)	1.473(6)	O(1)–C(4)–C(5)	116.2(4)
S(1)–C(3)	1.699(5)	C(1)–N(1)–Cu(1)	108.3(3)
O(1)–C(3)	1.383(5)	C(2)–N(2)–Cu(1)	108.2(3)

#1 = −*x*, −*y*, −*z*.

The elements of the structure are joined to each other in the crystal packing by an extended system of H-bonding and weak π–π interactions (between toluene rings (Cg_{tol}) of adjacent layers with a distance of 3.678 Å) (figure 6). In the solid state, the complex is stabilized *via* intermolecular N–H $\cdots$ N and N–H $\cdots$ S interactions between oxadiazole nitrogens, thiol sulfur, and NH_2 hydrogens of en. The hydrogen bonding parameters for **2** are listed in table 5. The π–π interactions, intermolecular, and intramolecular hydrogen bonds stabilize the crystal packing.

4. Conclusion

This article reports the [Ni(en)$_2$(tot)$_2$] and [Cu(en)$_2$](tot)$_2$ complexes of 5-*o*-tolyl-[1,3,4]-oxadiazole-2-thione/thiol (tot)$^-$ containing en. Desulphurization of {–C(O)–NHNH–C(S)–} moiety of [N′-(2-methyl-benzoyl)-hydrazinecarbodithioate was observed during

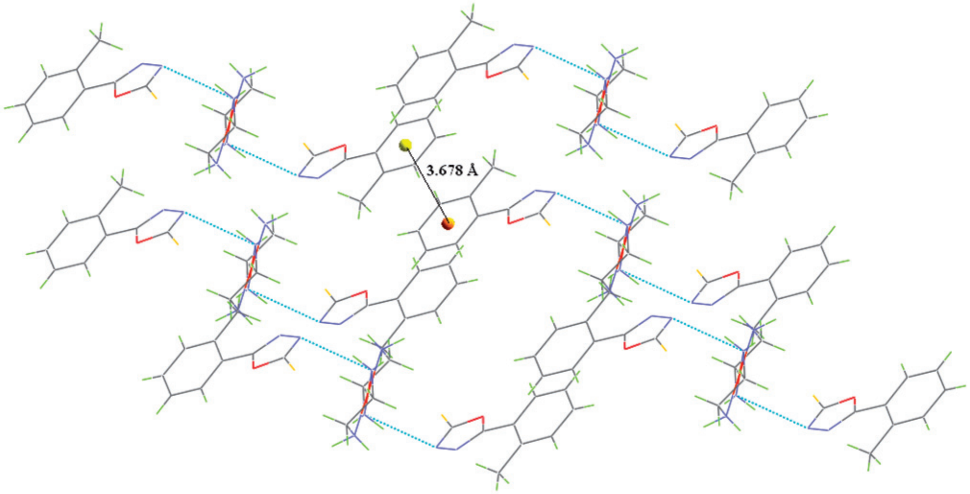


Figure 6. Molecular packing, $\pi \cdots \pi$ stacking between two toluene ring centroids and weak N–H$\cdots$N interactions in **2**.

Table 5. Hydrogen bond parameters for **2** (Å and °).

D$\cdots$H$\cdots$A	*d*(D–H)	*d*(H$\cdots$A)	*d*(D$\cdots$A)	∠(D–H$\cdots$A)
N(1)–H(1AI)$\cdots$N(3)#1	0.92	2.19	3.0757	161
N(1)–H(1BI)$\cdots$N(3)#2	0.92	2.32	3.1116	145
N(2)–H(2AI)$\cdots$S(1)	0.92	2.83	3.6038	143
N(2)–H(2BI)$\cdots$N(4)#3	0.92	2.31	3.1911	162
C(6)–H(6)$\cdots$O(1)	0.95	2.41	2.7557	101

#1 = x, $1+y$, z; #2 = $1-x$, $1-y$, $-z$; and #3 = $1+x$, $1+y$, z.

complexation. Both complexes are stabilized by extended weak intermolecular and intramolecular hydrogen bonding providing supramolecular frameworks. In addition, $[Cu(en)_2](tot)_2$ shows π–π interactions between toluene rings of the adjacent layers.

Supplementary material

CCDC Nos 717645 and 717646 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

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