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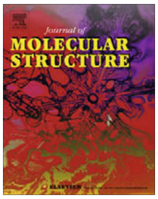

Nickel(II) and copper(II) complexes of 5-(4-methoxy-phenyl) [1,3,4]-oxadiazole-2-thione: Synthesis and X-ray characterization

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ABSTRACT

Two new mixed ligand complexes $[Ni(en)_2(mot)_2]$ (**1**) and $[Cu(en)_2(mot)_2]$ (**2**) derived from potassium N'-(4-methoxy-benzoyl) dithiocarbazate $[K^+(H_2L)^-]$ containing en as the coligand have been synthesized. $[K^+(H_2L)^-]$ undergoes cyclization in the presence of ethylenediamine and is converted to 5-(4-methoxy-phenyl [1,3,4]-oxadiazole-2-thione $(mot)^-$. $[Ni(en)_2(mot)_2]$ and $[Cu(en)_2(mot)_2]$ have been characterized by various physicochemical techniques and single crystal X-ray. In $[Ni(en)_2(mot)_2]$ and $[Cu(en)_2(mot)_2]$ the metal ion has MN_6 core with six coordinate octahedral arrangement from four N atoms of two en and two N atoms from two mot anions.

1. Introduction

N-aroyl dithiocarbazates and their salts can be converted to 1,3,4-oxadiazole-2-thiol/thione which exhibit relevant biological properties and have a wide variety of applications, in both medicine and agriculture [1]. Several methods have been used for the synthesis of these compounds from acyclic precursors. Some of them are oxidative cyclization of acyl hydrazone [2], acylthiourea [3–5] and acylthiosemicarbazide [6–9]. The heterocyclic thiones represent an important type of compounds in the field of coordination chemistry because of their potential multifunctional donor sites, i.e., either exocyclic or endocyclic nitrogen [10]. The cyclization of 3-acyldithiocarbazate esters, *N*-aroyl dithiocarbazates and their salts to the corresponding 1,3,4-oxadiazole in the presence of a base is reported in the literature [11–15]. It is known that the salts of *N*-aroyl dithiocarbazates can be converted to 1,3,4-oxadiazole-2-thiol in the presence of a base [13], it was thought whether the *N*-aroyl dithiocarbazate bonded to a transition metal can be converted to 1,3,4-oxadiazole-2-thione. Accordingly the Cu(II) complex of 4-methoxy-benzoyl dithiocarbazate was reacted with an excess of ethylenediamine and the results of this investigation is presented here.

2. Results and discussion

A methanol solution of $[Ni(en)_2(NCS)_2]$ on reaction with $[K^+(H_2L)^-]$ yields $[Ni(en)_2(mot)_2]$ (**1**). The reaction of $[K^+(H_2L)^-]$ with $CuCl_2 \cdot 2H_2O$ gave a blue precipitate which dissolved in methanolic solution of en on heating at 60 °C to form $[Cu(en)_2(mot)_2]$ (**2**). A simple scheme showing the syntheses of $[K^+(H_2L)^-]$ and the complexes **1** and **2** are given below.

The complexes are air stable, non-hygroscopic shiny crystalline solids, which are insoluble in common organic solvents but soluble in dimethyl formamide (DMF) and dimethylsulfoxide (DMSO). The complexes were fully characterized by magnetic susceptibility measurements, IR, UV–vis and X-ray spectroscopies. Analytical data of the complexes (recorded in Section 4) corroborated well with their respective formulations. ^1H NMR spectrum of $[K^+(H_2L)^-]$ in DMSO-d_6 shows signals at δ 9.65 (2H, NH) and 3.50 (3H, $-OCH_3$) ppm. The benzene ring protons appear as multiplet between 7.0 and 7.7 ppm (m, 4H). The ^{13}C NMR spectrum of $[K^+(H_2L)^-]$ shows signals at δ 178.90, 160.38 and 55.28 ppm which are due to the C=S, C=O and OCH_3 carbons, respectively. The IR spectrum of $[K^+(H_2L)^-]$ in KBr is expected to give rise to characteristic bands due to ν(NH), ν(C=O), ν(N—N) and ν(C=S) which occur at 3246 and 3169; 1637, 1000 and 886 cm^{-1}, respectively. The absorptions appearing in the region 3244–3122 cm^{-1} due to NH stretching vibrations of en are shifted to lower frequency than those encountered in the free en [16]. A negative shift in $\nu(NH_2)$ of en and appearance of a new band due to M—N near 468–471 cm^{-1} suggest formation of a chelate. The IR spectra of the

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complexes are devoid of any peak due to ν(NH) (hydrazinic) (3246 cm^{-1}) which was present in the precursor [Cu(HL)$_2$]. Additionally, ν(C=O) (1637 cm^{-1}) disappeared and new peaks appeared due to the endocyclic C=N and C—O—C at 1608–1585 and 1255–1226 cm^{-1}, respectively, suggesting cyclization of the dithiocarbazate moiety. The IR data are thus consistent with the formation of 1,3,4-oxadiazole moiety during complexation [17]. The magnetic moment and electronic spectral data were used to determine the geometry of the complexes. [Ni(en)$_2$(mot)$_2$] exhibits a magnetic moment of 2.86 B.M. and shows a band at 17,860 cm^{-1} which is considered to arise from the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ transition in an octahedral geometry around Ni(II) [18]. [Cu(en)$_2$(mot)$_2$] shows a magnetic moment of 2.01 B.M. and a broad band at 16400 cm^{-1} assigned to the $^2T_{2g} \rightarrow {}^2E_g$ transition for an octahedral geometry around Cu(II) [18].

Table 1
Crystal data for (**1**) and (**2**).

	1	**2**
Empirical formula	$C_{22}H_{30}N_8NiO_4S_2$	$C_{22}H_{30}CuN_8O_4S_2$
Formula weight	593.37	598.20
T (K)	295(2)	295(2)
λ/Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P21/n$
a (Å)	8.1852	9.6756(4)
b (Å)	13.404	12.2074(4)
c (Å)	13.954	11.5411
α (°)	111.63	90 0
β (°)	106.561	107.672(4)°
γ (°)	92.842	90 0
V (Å^3)	1343.5(5)	1298.83(8)
Z	2	2
D_{calc}/Mg m^{-3}	1.467	1.530
μ (mm^{-1})	0.922	1.047
Crystal size (mm)	0.53 × 0.41 × 0.34	0.57 × 0.39 × 0.35
Reflections collected	40498	24231
Independent reflections	9076 (R_{int} = 0.0423)	4428 (R_{int} = 0.0283)
Data/restrains/parameters	9076/0/337	4428/0/170
Goodness-of-fit	1.062	1.069
R factor [$I > 2\sigma(I)$]	0.0411	0.0291
wR_2 [$I > 2\sigma(I)$]	0.1053	0.0732
R factor (all data)	0.0851	0.0609
wR_2 (all data)	0.1387	0.0929
Largest diff. peak/hole (e Å^{-3})	0.826, −0.465	0.631, −0.241

Molecular structures of **1** and **2** were determined crystallographically. The details of data collection, structure solution and refinement are listed in Table 1. The Ortep diagram of complex **1** and molecular structure of the complex **2** with atom numbering scheme are shown in Figs. 1 and 5, respectively. The selected bond lengths and angles are given in Tables 2 and 3. The single crystal X-ray diffraction studies indicate that the ligand (mot$^-$) adopts the thione form in **1** and **2**. The X-ray structure of complex **1** shows the presence of two independent complexes in the asymmetric unit and in each unit the Ni atom is on a center of inversion. The X-ray crystal structures of both units of **1** show the presence of two mot$^-$ as ligand coordinated to Ni(II) in a distorted octahedral geometry (Fig. 1) having axial bond angles of 90.52(7)° and 87.66(8)° but equatorial bond angles of 82.75(8)° and 82.96(8)°, respectively in units containing Ni(1) and Ni(2). The coordination environment is fulfilled by two axial (mot)$^-$ ions at the trans positions, bonded through oxadiazole nitrogen atoms at the distances

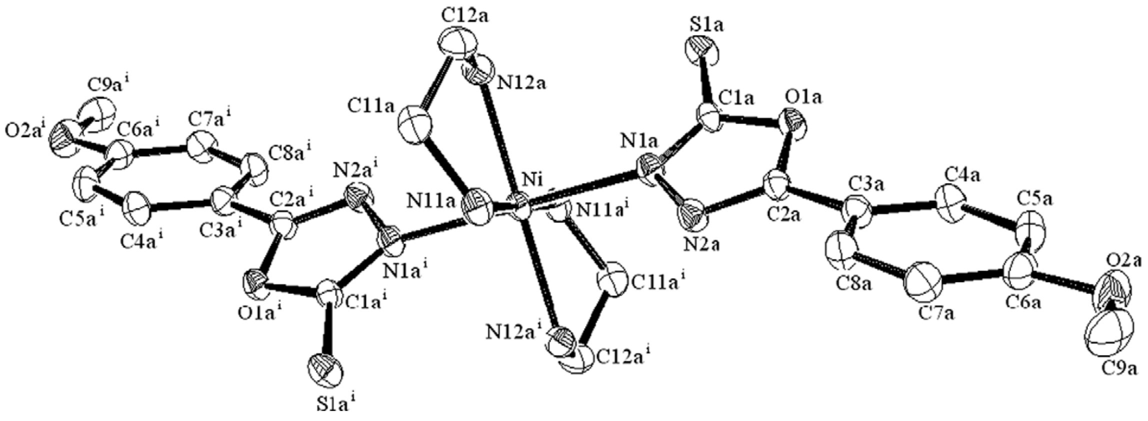


Fig. 1. Ortep plot of [Ni(en)$_2$(mot)$_2$] showing atomic numbering scheme with ellipsoid of 30% probability. Hydrogen atoms are omitted for clarity (symmetry code i = $-x$, $-y+1$, $-z+1$).

Table 2
Selected bond lengths (Å) and bond angles (°) for [Ni(en)$_2$(mot)$_2$].

Ni (**1**)		Ni (**2**)	
Ni(1)—N(12A)	2.144(2)	Ni(2)—N(12B)	2.092(18)
Ni(1)—N(1A)	2.107(17)	Ni(2)—N(1B)	2.156(2)
Ni(1)—N(11A)	2.084(18)	Ni(2)—N(11B)	2.102(2)
S(1A)—C(1A)	1.699(2)	S(1B)—C(1B)	1.685(2)
O(1A)—C(2A)	1.363(2)	O(1B)—C(2B)	1.366(3)
O(1A)—C(1A)	1.392(2)	O(1B)—C(1B)	1.399(3)
C(1A)—N(1A)	1.312(3)	C(1B)—N(1B)	1.320(3)
N(11A)#1—Ni(1)—N(1A)#1	89.33(7)	N(11B)#2—Ni(2)—N(1B)#2	90.59(9)
N(11A)—Ni(1)—N(1A)#1	90.67(7)	N(11B)—Ni(2)—N(1B)#2	89.41(9)
N(12A)#1—Ni(1)—N(1A)#1	90.52(7)	N(12B)#2—Ni(2)—N(1B)#2	87.66(8)
N(12A)—Ni(1)—N(1A)#1	89.48(7)	N(12B)—Ni(2)—N(1B)#2	92.34(8)
N(12A)#1—Ni(1)—N(11A)#1	82.75(8)	N(12B)#2—Ni(2)—N(11B)#2	82.96(8)
N(12A)—Ni(1)—N(11A)#1	97.25(8)	N(12B)—Ni(2)—N(11B)#2	97.04(8)

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

Table 3
Selected bond lengths (Å) and bond angles (°) for [Cu(en)$_2$(mot)$_2$].

Cu—N(1)	2.485(12)	N(11)—Cu—N(12)	84.73(5)
Cu—N(11)	2.012(12)	N(11)—Cu—N(12)#1	95.27(5)
Cu—N(12)	2.032(12)	N(11)—Cu—N(1)	88.16(5)
O(1)—C(1)	1.383(17)	N(11)#1—Cu—N(1)	91.84(5)
C(1)—N(1)	1.307(2)	N(12)—Cu—N(1)	93.41(5)
N(1)—N(2)	1.403(19)	N(12)#1—Cu—N(1)	86.59(5)
C(1)—S	1.697(16)		

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

Table 4
Hydrogen bonding parameters for Ni(en)$_2$(mot)$_2$ [Å and °].

D—H...A	d(D—H)	d(H...A)	d(D...A)	∠(DHA)
N(11A)—H(11E)...S(1A)#1	0.90	2.60	3.3561(19)	141.8
N(11A)—H(11F)...N(2A	0.90	2.51	3.107(3)	123.9
N(11A)—H(11F)...S(1B)	0.90	2.87	3.614(2)	140.6
N(12A)—H(12E)...S(1A)	0.90	2.97	3.702(2)	139.3
N(12A)—H(12F)...N(2A)#1	0.90	2.70	3.254(3)	120.9
N(11B)—H(11G)...S(1B)	0.90	3.01	3.711(2)	136.0
N(11B)—H(11H)...S(1A)#3	0.90	2.91	3.535(2)	128.0
N(12B)—H(12G)...S(1B)#2	0.90	2.67	3.457(2)	147.1
N(12B)—H(12H)...N(2B)	0.90	2.45	3.013(3)	120.5

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

of 2.107 Å Ni(1) and 2.156 Å Ni(2), and four equatorial sites are occupied by the two bidentate *N,N*-ethylenediamine. The bond length of Ni(1)—N(1A) (Noxa) is shorter than the corresponding bond length in Ni(2) showing stronger bonds in Ni(1) than Ni(2). The two Ni—N(en) distances in both the units are different. The Ni(1)—N(12A) bond length is larger than Ni(2)—Ni(12B) while Ni(1)—N(11A) is shorter than Ni(2)—N(11B). Due to stronger Ni(1)—N(1A) (Noxa) bonding, the C(1A)—S(1A) bond length is longer in unit 1 as compared to unit 2. The binding of Ni(II) with en involves the formation of a five membered chelate ring with bite angle of 82.75(8)° and represents a major distortion from an octahedral geometry. The geometry and bonding parameters within the en molecule agree with those of related compounds, e.g., Ni [trans (L)$_2$ (en)$_2$] {L = *N*-(5-chlorouracilato)} [19], isothiocyanato [20] and salicylato [21]. Almost planar (mot$^-$) ligands in complex **1** bonded to Ni(II) and designated as Ni(1)—N(1A)#1=Ni(1)—N(1A) 2.107(17) and Ni(2)—N(1B)#1=Ni(2)—N(1B) = 2.156(2) Å are comparable to those of ca. 2.1090–2.1150 Å encountered in the related compound [Ni(en)$_2$(3-pyt)$_2$] (3-pyt)$^-$ = 5-(3-pyridyl)-1,3,4-oxadiazole-2-thione [10]. The two phenyl rings in the Ni(2) complex are almost parallel (∠BCA = 88.48°) having centroid to centroid (Cg···Cg) separation of 3.621 Å but displaced with respect to each other. The displacement as measured by the angle formed between the ring centroids AC and the ring normal BC to the phenyl plane (Fig. 3) is found to be 0.227 Å with a displacement angle of 21.36° which is well within the reported values for π···π interaction [22]. Weak intermolecular N—H···N interaction between oxadiazole nitrogen and NH$_2$ hydrogen atoms of en molecule and N—H···S interactions (Table 4) between thione sulfur and CH$_2$ and NH$_2$ hydrogens of en molecule stabilize the structure of the compound **1** (Fig. 2). The two N···S distances of 3.535(2) and 3.457(2) Å (Table 4) are close to the mean N···S distance for NH···S hydrogen bond reported earlier [23]. The monomeric

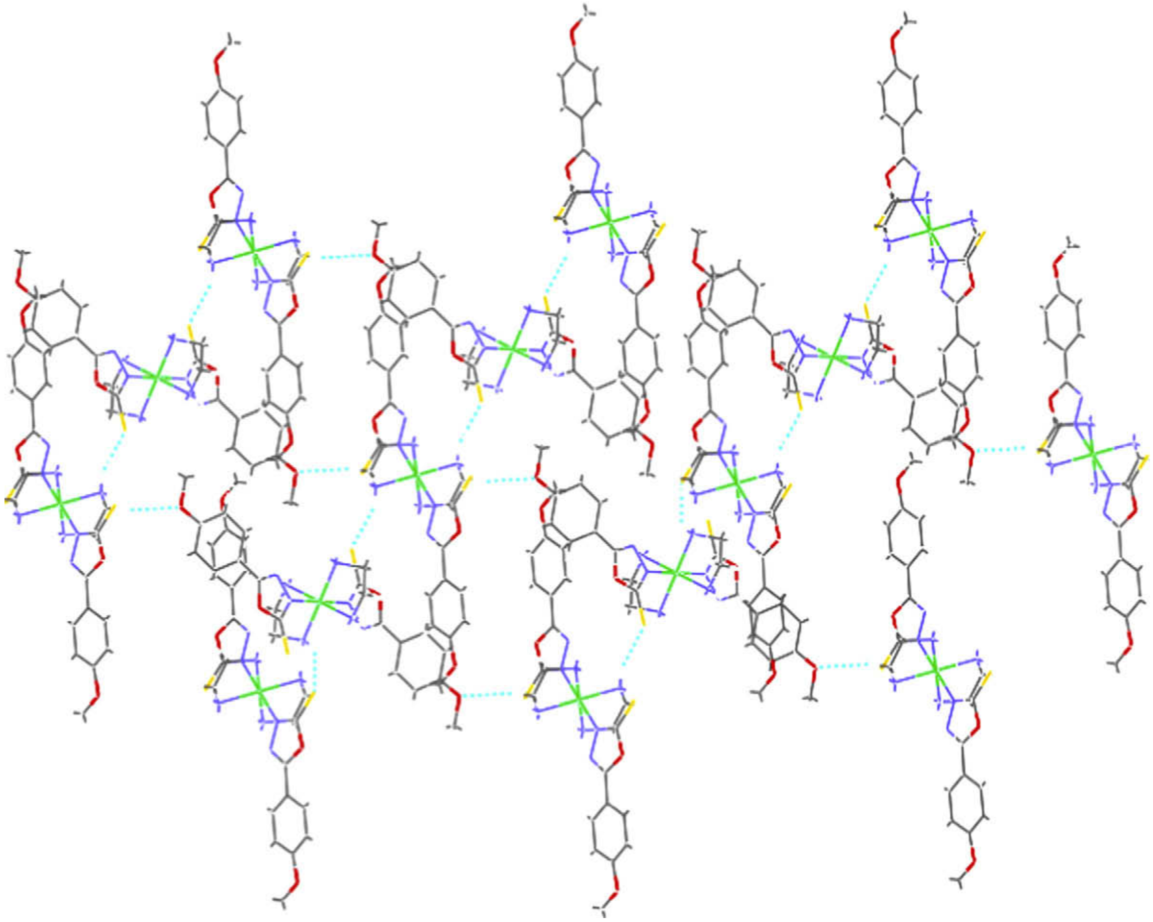


Fig. 2. Perspective view of the crystal packing of [Ni(en)$_2$(mot)$_2$] along the *a* axis showing N—H···S intermolecular hydrogen bonding.

[Ni(en)$_2$(mot)$_2$] units are held together through N—H···S/N intermolecular hydrogen bonding (Table 4). The arrangement of the monomeric units in the three dimensional architecture along *a* axis provides a supramolecular network (Fig. 2). In addition, there are weak C—H···O interactions between oxadiazole oxygen and CH$_2$ hydrogen of en and between methoxy oxygen and phenyl ring hydrogen which lead to the formation of chain like pattern in various layers of the molecular arrangement (Fig. 4).

The molecular structure of **2** shows that in the centrosymmetric unit of [Cu(en)$_2$(mot)$_2$] the metal ion is six coordinate, bonding through four nitrogens of en and two oxadiazole nitrogens. The separation between two planes formed by the oxadiazole rings in the same complex is 1.525 Å. The dihedral angle between the plane formed by the oxadiazole and phenyl ring is 21.54°. The phenyl ring and oxadiazole ring are almost parallel ($\angle CBA = 86.41$) having a centroid–centroid (Cg...Cg) separation of 3.846 Å but displaced with respect to each other. The displacement as measured by the angle formed between the ring centroids AB and the ring normal BC to the oxadiazole plane (Fig. 6) is found to be 0.092 Å with a displacement angle of 16.89° which is well within the range [22]. In addition, the monomeric units of [Cu(en)$_2$(mot)$_2$] are held together through N—H···S intermolecular and N—H···N intramolecular hydrogen bonding (Table 5), leading to the formation of metal–organic framework along *a* axis (Fig. 7). The shortest intra and inter chain Cu···Cu separations are found to be 11.541 and 8.776 Å, respectively (Fig. 7). In the solid state the complex is stabilized *via* intermolecular N—H···S interaction between thione sulfur and NH$_2$ hydrogen atoms of en and C—H···S interaction between thione sulfur and methoxy hydrogen of a nearby molecule. In addition there are three intramolecular X—H···H (X = N, C) hydrogen bonding formed between oxadiazole nitrogen and hydrogen of NH$_2$, CH$_2$ and phenyl ring. The above observed $\pi\cdots\pi$ interactions, intermolecular and intramolecular hydrogen bonding have stabilized the molecular crystal packing giving a supramolecular

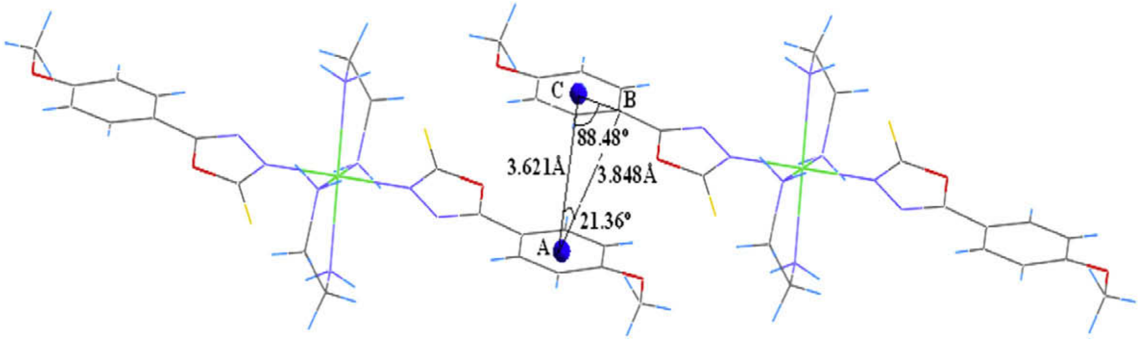


Fig. 3. π–π stacking and relative shift between two phenyl ring centroids in complex **1** containing Ni(2).

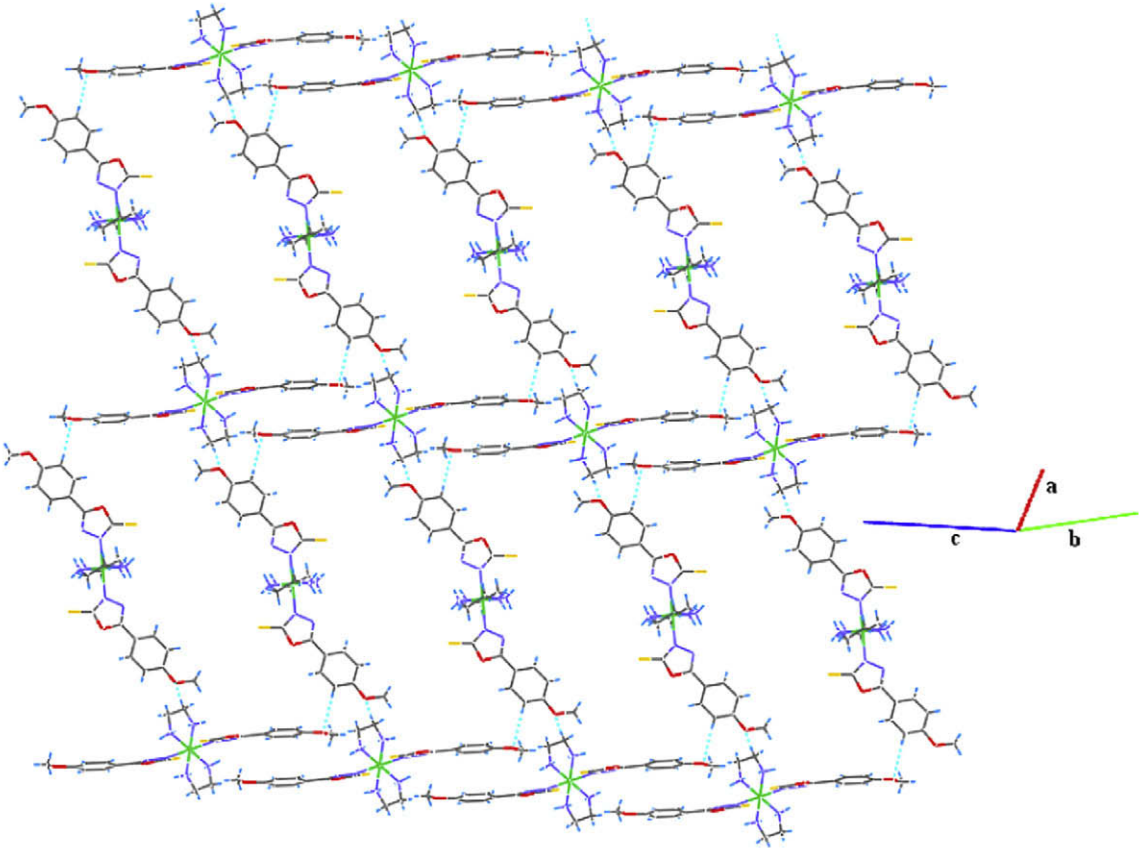


Fig. 4. Network structure of [Ni(en)$_2$(mot)$_2$] down the a axis forming layers of chain *via* C—H···O interactions.

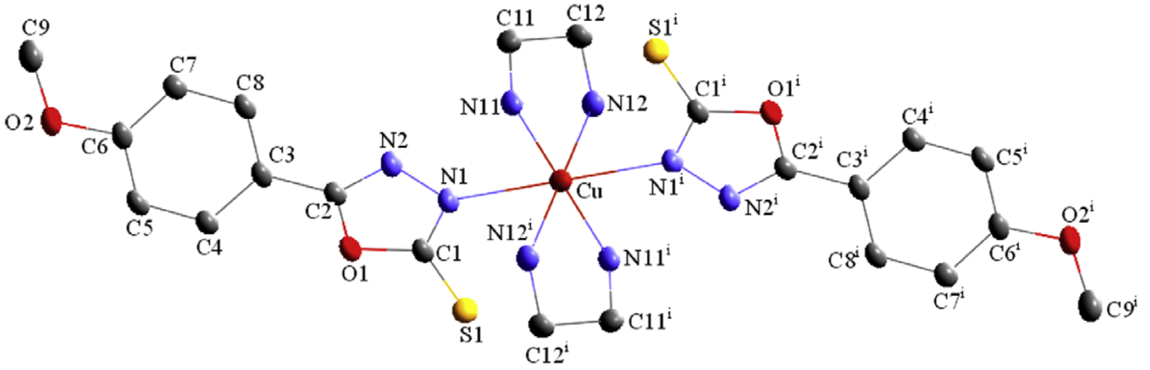


Fig. 5. Molecular structure of $[Cu(en)_2(mot)_2]$ with the atomic labeling scheme. Hydrogen atoms are omitted for clarity. (Symmetry code i = $-x + 1$, $-y$, $-z$).

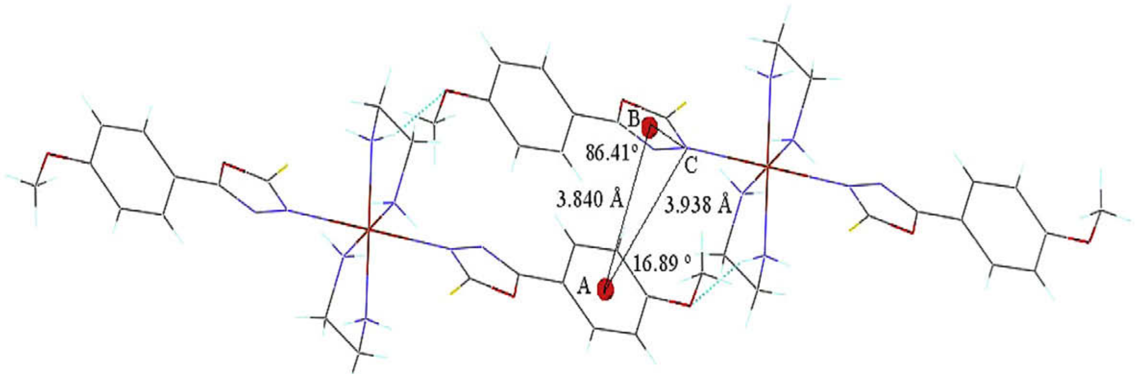


Fig. 6. π–π stacking and relative shift between phenyl ring and oxadiazole ring centroids in complex **2**.

Table 5
Hydrogen bonding parameters for $Cu(en)_2(mot)_2$ [Å and °].

D—H...A	d(D—H)	d(H...A)	d(D...A)	∠(DHA)
N(11)—H(11C)...S#1	0.90	2.70	3.5058(14)	149.5
N(11)—H(11D)...N(2)	0.90	2.56	3.0661(18)	116.0
N(12)—H(12C)...O(2)#2	0.90	2.18	3.0483(18)	163.2
N(12)—H(12D)...S#3	0.90	2.75	3.6171(13)	161.6

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

network. The axial and equatorial Cu—N distances for the complex are 2.4858(12) and 2.03225(12) Å, respectively, whereas the respective distances for the nickel complex are 2.0847(18) and 2.1072(17) Å. This suggests an axially distorted octahedral geometry for the copper complex due to Jahn–Teller distortion whereas an almost regular octahedral geometry is found in the case of the nickel complex. The soft donor site of the ligand mot^- shows no tendency for coordination with Ni(II) and Cu(II) as they are hard metal ions and prefer to bind with comparatively hard nitrogen site of the ligand.

3. Conclusion

Two new mixed ligand complexes $[Ni(en)_2(mot)_2]$ (**1**) and $[Cu(en)_2(mot)_2]$ (**2**) with 5-(4-methoxy-phenyl) [1,3,4]-oxadiazole-2-thione have been prepared and their structures investigated. During the formation of these complexes the metal-bound *N*-(4-methoxy benzoyl dithiocarbazate is cyclized to 5-(4-methoxy-phenyl) [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.

4. Experimental

4.1. General methods

All reagents were of AR grade and used without further purification. Methyl 4-methoxy benzoate (Sigma–Aldrich), CS_2 (SD Fine Chemicals) and KOH (Qualigens) were used as received. 4-Methoxy benzoic acid hydrazide and $[Ni(en)_2(SCN)_2]$ were prepared by reported methods [24]. All the synthetic manipulations were carried out in open atmosphere and at room temperature. The solvents were dried and distilled before use following the standard procedure. 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 [25]. 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.

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

This compound was prepared by adding carbon disulfide (1.2 mL, 20 mmol) drop wise to a mixed solution of 4-methoxy benzoic acid hydrazide (3.32 g, 20 mmol) and potassium hydroxide

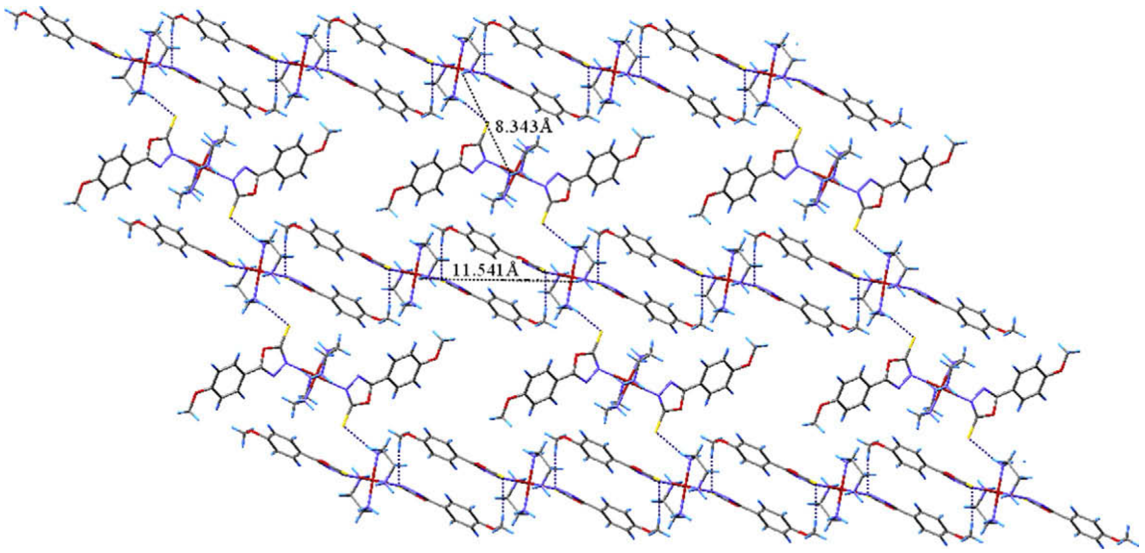


Fig. 7. N—H···S hydrogen bonding and Cu···Cu separation in the metal organic framework of [Cu(en)$_2$(mot)$_2$] along *a* axis.

(1.12 g, 20 mmol) in methanol (30 mL) and stirring the reaction mixture for 2 h. The solid separated was filtered off, washed with a mixture of ethanol–ether (10% v/v) and dried in *vacuo*. Yield 1.44 g, 55%. m.p.: 245 °C. Anal. Calc. for $C_9H_9O_2N_2S_2K$ (280.40): C, 38.60; H, 3.15; N, 10.11; S, 22.60. Found: C, 38.57; H, 3.10; N, 10.00; S, 22.85%. IR data (ν cm^{-1}, KBr): ν(NH) 3246 m, 3169 m; ν(C=O) 1637 s; ν(N—N) 1000 m; ν(C=S) 886. ^{1}H NMR (DMSO-d_6; δ ppm): 3.80 (s, 3H, OCH$_3$), 7.0–7.7 (d, 4H, C$_6$H$_5$), 9.65 (m, 2H, NH). ^{13}C NMR (DMSO-d_6: δ ppm) 178.90 (C=S), 160.38 (C=O), 117.87 (C1), 113.67 (C2), 126.64 (C3), 128.95 (C4), 55.28 (OCH$_3$). Based on the above physicochemical studies the tentative structure of the ligand is depicted in Scheme 1.

4.2. Synthesis of [Ni(en)$_2$(mot)$_2$] (**1**)

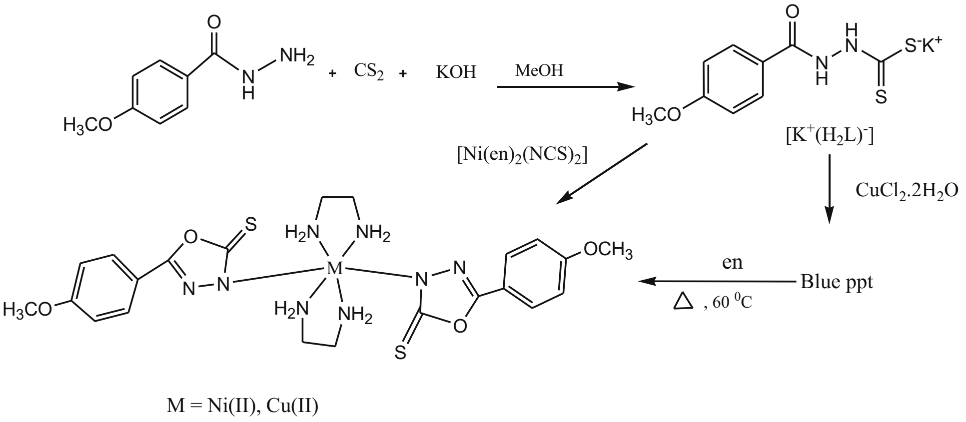
A methanolic solution (10 mL) of [Ni(en)$_2$(NCS)$_2$] (0.23 g, 1 mmol) was mixed with an aqueous methanolic solution (50:50 v/v) (10 mL) of [K$^+$(H$_2$L)$^-$] (0.56 g, 2 mmol) and the reaction mixture was filtered. The filtrate was kept for crystallization; where upon orange crystals of the complex **1** were obtained after 10 days. Anal. Calc. for $C_{22}H_{30}N_8O_4S_2Ni$ (593.37): C, 44.69; H, 5.05; N, 18.75; S, 10.95; Ni, 9.82. Found: C, 44.53; H, 5.09; N, 18.80; S, 10.84; Ni, 9.82% (9.90). μ_B = 2.86 B.M., m.p.: 218 °C. IR data (ν cm^{-1}, KBr): ν(NH) 3234 s; ν(C=N) 1608 s; ν(C—O—C) 1255 s; ν(N—N) 1072 s; ν(C=S) 977; ν(Ni—N) 471 s. UV–vis [λ_{max}, cm^{-1} (DMF)]: 17,850.

4.3. Synthesis of [Cu(en)$_2$(mot)$_2$] (**2**)

A methanolic solution (10 ml) of CuCl$_2$·2H$_2$O (0.17 g, 1 mmol) was stirred with an aqueous methanolic solution (50:50 v/v) (10 mL) of [K$^+$(H$_2$L)$^-$] (0.56 g, 2 mmol) in a 1:2 M ratio, the precipitate obtained was filtered and washed with a mixture of H$_2$O—MeOH (50:50 v/v). This precipitate was suspended in MeOH—H$_2$O to which an excess (0.30 mL, 4 mmol) of ethylenediamine (en) was added and the mixture was heated at 60 °C until total dissolution of the complex was observed. The resulting solution was filtered off and kept for 15 days where upon dark brown crystals suitable for XRD were obtained. Anal. Calc. for $C_{22}H_{30}N_8O_4S_2Cu$ (598.20): C, 44.25; H, 5.02; N, 10.55; S, 10.80; Cu, 10.48. Found: C, 44.17; H, 5.05; N, 10.71; Cu, 10.62%. μ_B = 2.01 B.M., m.p.: 145 °C. IR data (ν cm^{-1}, KBr): ν(NH) 3244 m; 3122 m; ν(C=N) 1585 m; ν(C—O—C) 1226 m; ν(N—N) 1039 s; ν(C=S) 901; ν(Cu—N) 468. UV–vis [λ_{max}, cm^{-1} (acetonitrile)]: 16,400.

4.4. X-ray crystallography

Crystals suitable for X-ray analyses of the complexes [Ni(en)$_2$(mot)$_2$] (**1**) and [Cu(en)$_2$(mot)$_2$] (**2**) were grown at room temperature. Preliminary examination and intensity data were collected using Bruker three circle diffractometer equipped with a SMART 6000 CCD software using a graphite monochromatized Mo Kα



Scheme 1. Syntheses of the ligand and complexes.

radiation at 295(2) [26]. The MERCURY package was used for molecular graphics [27]. 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 hydrogen atoms were included in the refinement at geometrically ideal position and refined with a riding model [28,29]. Crystal structure diagrams were generated by use of the ORTEP-3 for windows program [30].

5. Supplementary material

CCDC 679050 and 679051 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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