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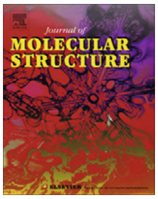

Synthesis and X-ray structural studies of Cd(II) and Ni(II) complexes of 5-(4-methoxy phenyl), 5-(2-pyridyl) and 5-(2-methoxy phenyl)-1,3,4-oxadiazole-2-thione

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ABSTRACT

Three new mixed ligand complexes $[Cd(en)_2(4\text{-mpot})_2]$ (**1**) $[Ni(2\text{-pytone})_2(en)_2]$ (**2**) and $[Ni(2\text{-mpot})_2(en)_2]$ (**3**) {4-mpot = 5-(4-methoxy-phenyl)-1,3,4-oxadiazole-2-thione, 2-pytone = 5-(2-pyridyl)-1,3,4-oxadiazole-2-thione, 2-mpot = 5-(2-methoxy-phenyl)-1,3,4-oxadiazole-2-thione} have been prepared containing en as co-ligand. Potassium N-(4-methoxy benzoyl)-hydrazinecarbodithioate cyclized to 5-(4-methoxy-phenyl)-1,3,4-oxadiazole-2-thiol on addition of tetrabutylammonium bromide which then reacted with $Cd(OAc)_2{\cdot}2H_2O$ and ethylenediamine to form complex **1**, whereas potassium N-(2-methoxy benzoyl/pyridine-2-carbonyl)-hydrazinecarbodithioates (RCONHNHCSSK) underwent cyclization during complexation in the presence of en to give the complexes of the corresponding 5-aryl-1,3,4-oxadiazole-2-thiones. The complexes have been characterized by physicochemical techniques and single crystal X-ray structure determination. In the complexes the metal center has a six coordinate octahedral arrangement coordinated by 4N atoms of two en and two covalently bonded N atoms of the oxadiazole-2-thione anions. All the complexes contain extended hydrogen bonding providing supramolecular framework.

1. Introduction

The coordination chemistry of nitrogen–sulfur chelating ligands is an emerging and rapidly developing area of research [1–3]. The multifaceted chemistry of metal sulfur bonds are apparent in the application of these compounds as catalyst in biological and non-biological processes [4,5]. A class of nitrogen sulfur ligand such as N-aroyl dithiocarbazates and their salts could be converted to 1,3,4-oxadiazole-2-thione, which are biologically important molecules [6–8]. The oxadiazole molecules act as spacer *via* coordination, hydrogen bonding and show intermolecular cooperative interaction [9]. 1,3,4-oxadiazole derivatives, which belong to an important group of heterocyclic compounds is the subject of extensive study in the recent years [7,8]. They show diverse biological activities, such as anti-tuberculostatic, anti-inflammatory, anti-fungal, analgesic, and anti-convulsant [10–12]. Although some work has been reported on the binary complexes of 5-phenyl-1,3,4-oxadiazole-2-thione [13], 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione [14–19] and 5-(2-pyridyl)-1,3,4-oxadiazole-2-thione [20], but scanty of information is available on the mixed ligand complexes of these ligands. Since 1,3,4-oxadiazole-2-thiones may exist in both thione and thiol forms in solution [21,22], it will therefore be of interest to investigate the bonding mode of the ligand in the complexes. In view of this, we have prepared and characterized the Cd(II) complex of 5-(4-methoxy-phenyl)-1,3,4-oxadiazole-2-thione and Ni(II) complexes of 5-(2-pyridyl)-1,3,4-oxadiazole-2-thione and 5-(2-methoxy-phenyl)-1,3,4-oxadiazole-2-thione in the presence of ethylenediamine which act as a co-ligand.

2. Experimental

2.1. Chemical and starting materials

Commercial reagents were used without further purification and all experiments were carried out in open atmosphere. Picolinic acid hydrazide (Sigma–Aldrich), CS_2 (S D Fine Chemicals, India) and KOH (Qualigens) were used as received. 2-Methoxy benzoic acid hydrazide and $[Ni(en)_2(SCN)_2]$ were prepared by reported methods [23,24]. All the solvents were purchased from Merck and used after purification. The yield calculation is based on the weight of the ligand or the initial starting material where intermediate were not isolated.

2.2. Physical measurements

Carbon, hydrogen and nitrogen contents were estimated on a Carlo Erba 1108 model microanalyser. Magnetic susceptibility measurements were performed at room temperature on a Cahn

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Faraday balance using $Hg[Co(NCS)_4]$ as the calibrant. Electronic spectra were recorded on a Shimadzu 1700 UV–Vis spectrophotometer as Nujol mulls. 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 and $CDCl_3$ on a JEOL AL 300 FT NMR spectrometer using TMS as internal reference.

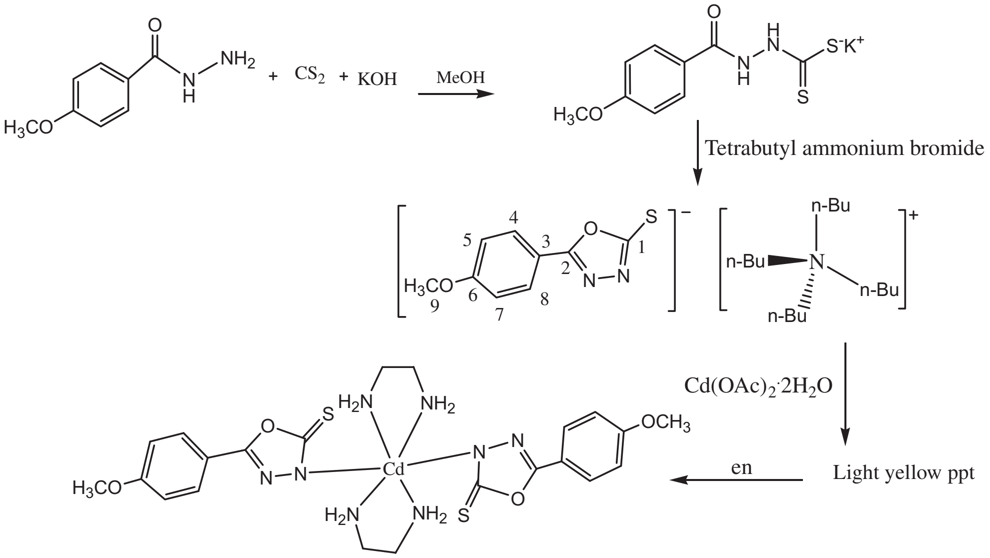
2.3. X-ray crystallography

Crystals suitable for X-ray analyses of the complexes **1**, **2** and **3** were grown at room temperature. Data for complexes **1**, **2** and **3** were recorded at 293(2) and 296(2) on an Oxford Diffraction Gemini [25] and a Bruker three-circle diffractometer, respectively equipped with a CrysAlis Pro./SMART 6000 CCD software using a graphite mono-chromated Mo Kα (λ = 0.71073 Å) radiation source. The structures were solved by direct methods and refined (SHELX-08) 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 [26]. The MERCURY package was used for molecular graphics [27]. Molecular structure diagrams were generated by use of the ORTEP-3 for windows program [28].

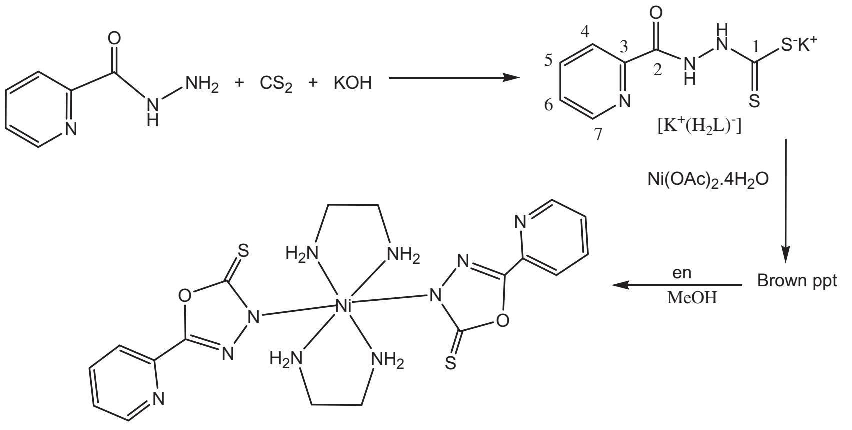
2.4. Synthesis

2.4.1. Synthesis of tetrabutylammonium 5-(4-methoxy phenyl)-1,3,4-oxadiazole-2-thiol

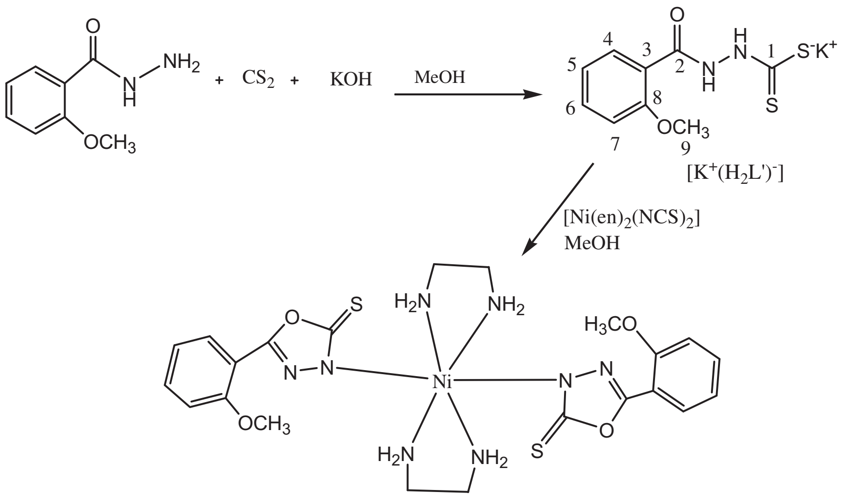
Tetrabutylammonium 5-(4-methoxy-phenyl)-1,3,4-oxadiazole-2-thiol was synthesized by adding CS_2 (1.5 mL, 20 mmol) dropwise to a suspension of 4-methoxy benzoic acid hydrazide (3.32 g, 20 mmol) in methanol (30 mL) in the presence of potassium hydroxide (1.2 g, 20 mmol) and stirring the reaction mixture for 30 min at room temperature. The yellow solid product obtained in the above reaction was dissolved in water and an aq. solution of tetrabutylammonium bromide (3.22 g, 10 mmol) was added. The resulting yellow solid was obtained which was filtered off and dried. Yield (1.625 g, 60 %). Anal. Found: C, 66.72; H, 9.55; N, 9.30; S, 7.05 %. Calc. for $C_{25}H_{43}N_3O_2S$ (449.69): C, 66.77; H, 9.63; N, 9.34; S, 7.13 %. M.p.105 °C; IR (KBr, ν, cm^{-1}): 1602s ν(C=N), 1066s ν(N—N), 988s ν(C=S). ^1H NMR ($CDCl_3$, TMS; δ, ppm): 10.8 (s, 1H, NH), 3.80 (s, 3H, OCH_3), 7.0–7.7 (m, 4H, C_6H_5), 1.0 (t, 3H, CH_3), 1.4 (sext, 2H, CH_2), 1.6 (quint., 2H, CH_2) 3.3 (t, 2H, N—CH_2). ^{13}C NMR ($CDCl_3$; δ, ppm): 197.15 (C—S), 160.38 (C=N), 113.92



Scheme 1. Synthesis of tetrabutylammonium 5-(4-methoxy phenyl)-1,3,4-oxadiazole-2-thiol and Cd(II) complex.



Scheme 2. Preparation of $[Ni(2\text{-pytone})_2(en)_2]$ (**1**).



Scheme 3. Preparation of $[Ni(2\text{-}mpot)_2(en)_2]$ (**2**).

(C3) 132.77 (C4, C8), 153.10 (C5, C7), 119.36 (C6), 59.04 (OCH_3), 29.12, 24.13, 19.78, 13.68 (*n*-butyl carbons) (Scheme 1).

2.4.2. Synthesis of potassium N-aroylhydrazine carbodithioate

Potassium N-(pyridine-2-carbonyl)-hydrazine carbodithioate $[K^+(H_2L)^-]$ and potassium N′-(2-methoxybenzoyl)]-hydrazine carbodithioate $[K^+(H_2L')^-]$ were prepared by adding CS_2 (1.5 mL, 25 mmol) dropwise to a suspension of picolinic acid hydrazide (2.7 g, 20 mmol) or 2-methoxy benzoic acid hydrazide (3.32 g, 20 mmol) in methanol (30 mL) in the presence of potassium hydroxide (1.2 g, 20 mmol). The reaction mixtures were stirred continuously for 30 min and the solids which separated were filtered off, washed with 10% (v/v) mixture of ethanol ether and dried.

2.4.2.1. Potassium N-(pyridine-2-carbonyl)-hydrazine carbodithioate $[K^+(H_2L)^-]$.

Yield (1.287 g, 85 %). Anal. Found: C, 33.50; H, 2.30; N, 16.75; S, 25.40%. Calc. for $C_7H_6N_3OS_2K$ (251.36): C, 33.41; H, 2.38; N, 16.70; S, 25.46%. M.p. 190 °C; IR (KBr, ν, cm^{-1}): 3211 m, 3073 m ν(NH), 1673s ν(C=O), 1091s ν(N—N), 993s ν(C=S). 1H NMR (DMSO-d_6, δ, ppm): 11.45, 10.07 (s, 2H, NH), 8.64, 8.01, 7.60 (m, 4H, pyridine ring). ^{13}C NMR (DMSO-d_6, δ, ppm): δ 207.65 (>C=S), 162.96 (>C=O), 137.95 (C4), 155.92 (C7), 148.81 (C3), 127.00 (C5), 121.84 (C6) (Scheme 2).

Table 1
Crystallographic data and structure refinement for complexes **1**, **2** and **3**.

Compound	1	2	3
Empirical formula	$C_{22}H_{30}N_8CdO_4S_2$	$C_{18}H_{24}N_{10}NiO_2S_2$	$C_{22}H_{30}N_8NiO_4S_2$
Formula weight	647.09	535.30	593.37
T (K)	293(2)	293(2)	296(2)
Λ (Mo Kα) (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P 21/n	P 21/n	P-1
a (Å)	10.0246(6)	10.941(3)	7.793(5)
b (Å)	12.4246(6)	10.230(2)	13.592(8)
c (Å)	11.6853(6)	11.977(2)	13.937(9)
α (°)	90.00	90.00	70.360(100)
β (°)	110.996(6)	114.06(3)	84.271(10)
γ (°)	90.00	90.00	83.620(10)
V ($Å^3$)	1358.79(13)	1224.1(5)	1378.87(15)
Z	2	2	2
D_{calc}($mg\ m^{-3}$)	1.582	1.452	1.429
μ (mm^{-1})	1.001	0.999	0.898
F (000)	660	556	620
Crystal size (mm^3)	0.30 × 0.27 × 0.25	0.27x0.25x0.23	0.49 × 0.12 × 0.11
θ range (°)	3.28–29.07	3.73–29.00	2.57– 29.58
Index ranges	$-10 \leq h \leq 13$	$-14 \leq h \leq 14$	$-8 \leq h \leq 10$
	$-11 \leq k \leq 16$	$-10 \leq k \leq 13$	$-18 \leq k \leq 19$
	$-14 \leq l \leq 15$	$-16 \leq l \leq 14$	$-19 \leq l \leq 19$
Reflections collected	6178	4739	14,888
Independent reflections	3631	3246	7740
Data/restraints/parameters	3631/0/170	3246/0/152	7740/0/337
Goodness-of-fit on F^2	1.007	1.066	1.064
Final R indices	0.0273	0.0536	0.0363
wR_2 [$I > 2\sigma(I)$](R_{int})	0.0629	0.1543	0.0944
Final R indices (all data)	$R1 = 0.0379$	$R1 = 0.0991$	$R_1 = 0.0511$
	$wR_2 = 0.0684$	$wR_2 = 0.2367$	$wR_2 = 0.0995$
Largest diff. peak/hole (e $Å^{-3}$)	0.317, −0.311	0.863, −1.035	0.785, −0.422

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

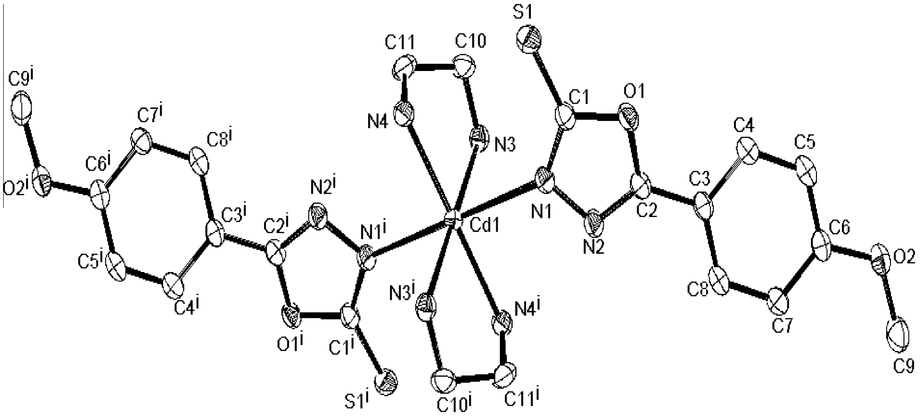


Fig. 1. Ortep diagram of $[Cd(en)_2(4\text{-mpot})_2]$ with the atomic labeling scheme. Hydrogen atoms are omitted for clarity.

2.4.2.2. Potassium N′-(2-methoxybenzoyl)]-hydrazine carbodithioate $[K^+(H_2L')^-]$. Yield (1.013 g, 60 %). Anal. Found: C, 38.60; H, 3.15; N, 10.00; S, 22.90%. Calc. for $C_9H_9O_2N_2S_2K$ (280.40): C, 38.51; H, 3.20; N, 9.98; S, 22.82%. M.p. 245 °C; IR (KBr, ν, cm^{-1}): 3246 m, 3169 m ν(NH), 1637s ν(C=O), 1000 m ν(N—N), 886ν(C=S). ^1H NMR (DMSO-d_6 δ, ppm): 3.80 (s, 3H, OCH_3), 7.0–7.7 (d, 4H, C_6H_5), 9.65 (m, 2H, NH). ^{13}C NMR (DMSO-d_6, δ, ppm): δ 178.90 (C=S), 160.38 (C=O), 117.87 (C1), 113.67 (C2), 126.64 (C3), 128.95 (C4), 55.28 (OCH_3) (Scheme 3).

*2.4.3. Synthesis of $[Cd(en)_2(4\text{-mpot})_2]$ (**1**)*

$Cd(OAc)_2{\cdot}2H_2O$ (0.266 g, 1 mmol) and freshly prepared tetrabutylammonium 5-(4-methoxy-phenyl)-1,3,4-oxadiazole-2-thiol (0.900 g, 2 mmol) were dissolved separately in 15–20 mL methanol, mixed together and stirred for 20 min. The white precipitate was separated by filtration, washed successively with methanol–water mixture (50:50) 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 1 h. A colorless solution was obtained which was filtered and kept for crystallization. White needle shaped crystals of **1** suitable for an X-ray analyses were obtained by slow evaporation of the above solution over a period of 10 days. Yield: (0.323 g, 50 %). Anal. Found: C, 40.72; H, 4.58; N, 17.25; S, 9.80 %. Calc. For $C_{22}H_{30}N_8CdO_4S_2$ (647.09): C, 40.79; H, 4.63; N,17.30; S,9.89 %. M.p. 218 °C; IR (KBr, ν cm^{-1}): 3232s ν(NH) 1609s ν(C=N) 1245s ν(C—O—C) 1066s ν(N—N), 983 ν(C=S), 479s ν(Cd—N).

*2.4.4. Synthesis of $[Ni(2\text{-pytone})_2(en)_2]$ (**2**)*

Freshly prepared potassium N-(pyridine-2-carbonyl)-hydrazine carbodithioate $[(K^+(H_2L)^-]$ (0.500 g, 2 mmol) was dissolved in water (20 mL) and an aqueous solution of $Ni(OAc)_2{\cdot}4H_2O$ (0.250 g, 1 mmol) was added to the above solution and stirred for 15 min. The brown solid which separated was filtered, washed with methanol–water mixture (50:50) and dried. A methanol solution (10 mL) of ethylenediamine (0.30 mL, 4 mmol) was added to the methanol suspension of the above compound and after shaking for a few minutes the resulting clear brown solution was filtered and kept for crystallization. Brown crystals of **2** suitable for an X-ray analysis were obtained by slow evaporation of the solution over a period of 10 days. Yield (0.664 g, 62 %). Anal. Found: C, 44.90; H, 4.90; N, 20.80; S, 12.00. Calc. for $C_{20}H_{26}NiN_8O_2S_2$ (535.30): C, 44.83; H, 4.85; N, 20.92; S, 11.95. M.p. 225 °C; IR (KBr, ν, cm^{-1}): 3231 m ν(NH), 1588 ν(C=N) 1287w ν(C—O—C), 1093 ν(N—N), 999 m ν(C=S), 517 w ν(Ni—N).

*2.4.5. Synthesis of $[Ni(2\text{-mpot})_2(en)_2]$ (**3**)*

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 potassium N′-(4-methoxy-benzoyl)-dithiocarbazate $[K^+(H_2L')^-]$ (0.560 g, 2 mmol) and the reaction mixture was filtered. The filtrate was kept for crystallization; where upon orange crystals of the complex **3** were obtained after 10 days. Yield (0.582 g, 55%). Anal. Found: C, 44.53; H, 5.09; N, 18.80; S, 10.84. Calc for $C_{22}H_{30}N_8O_4S_2Ni$ (593.37): C, 44.69; H, 5.05; N, 18.75; S, 10.95. M.p. 210 °C; IR (KBr, ν cm^{-1}): 3234s ν(NH), 1608s ν(C=N), 1255s ν(C—O—C), 1072s; ν(N—N), 977; ν(C=S), 471s ν(Ni—N).

3. Results and discussion

It has been observed that the potassium salt of N-acylhydrazinecarbodithioates reacted with metal salt and then with ethylenediamine to form the complexes of 1,3,4-oxadiazole-2-thione containing en as the coligand yielding complexes **2** and **3** whereas the potassium N-(4-methoxy benzoyl)-hydrazinecarbodithioate cyclized to 5-(4-methoxy-phenyl)-1,3,4-oxadiazole-2-thiol on addition of tetrabutylammonium bromide which then reacted with $Cd(OAc)_2{\cdot}2H_2O$ and ethylenediamine to form complex **1**. The elemental analyses and physical measurements of complexes **1**, **2** and **3** indicate that both hydrazinic hydrogens from acylhydrazine carbodithioate [—C(O)NHNHC(S)S^-—] moiety and one sulfur atom were missing from the resulting complexes. Thus, complex **2** was obtained by shaking $[Ni(H_2L)_2]$ with a methanol solution of ethylenediamine taken in 1:4 molar ratio whereas complex **3** was obtained by the reaction of potassium N′-(2-methoxybenzoyl)]-hydrazine carbodithioate $[K^+(H_2L')^-]$ with $[Ni(en)_2(NCS)_2]$.

Table 2
Selected bond lengths (Å) and bond angles (°) for $[Cd(en)_2(4\text{-mpot})_2]$.

Bond lengths (Å)		Bond angles (°)	
Cd(1)—N(4)	2.299(18)	N(4)—Cd(1)—N(3)	77.08(7)
Cd(1)—N3)	2.345(19)	N(4)—Cd(1)—N(3)#	102.92(7)
Cd(1)—N(1)	2.445(17)	N(4)—Cd(1)—N(1)	92.76(7)
S(1)—C(1)	1.688(2)	N(4)—Cd(1)—N(1)#	87.24(7)
N(1)—N(2)	1.410(3)	N(3)—Cd(1)—N(1)	85.31(7)

Table 3
Selected molecular dimensions (Å and °) in $[Ni(2\text{-pytone})_2(en)_2]$.

Bond lengths (Å)		Bond angles (°)	
Ni—N(4)	2.101(4)	N(4)—Ni—N(5)	82.61(16)
Ni—N(5)	2.105(4)	N(4)—Ni—N(5)	97.39(16)
Ni—N(3)	2.122(3)	N(4)—Ni—N(3)	89.87(14)
S(1)—C(1)	1.695(5)	N(4)—Ni—N(3)	90.13(14)
O(1)—C(2)	1.353(6)	N(5)—Ni—N(3)	89.79(15)
O(1)—C(1)	1.392(5)	N(5)—Ni—N(3)	90.21(15)
N(3)—N(2)	1.413(5)	N(2)—N(3)—Ni	118.2(3)

Table 4
Selected molecular dimensions (Å and °) in [Ni(2-mpot)$_2$(en)$_2$].

Ni(1)		Ni(2)	
Bond lengths (Å)			
Ni(1)—N(1A)	2.101(18)	Ni(2)—N(1B)	2.088(16)
Ni(1)—N(2A)	2.087(17)	Ni(2)—N(2B)	2.098(17)
Ni(1)—N(3A)	2.111(15)	Ni(2)—N(3B)	2.153(15)
S(1A)—C(3A)	1.687(2)	S(1B)—C(3B)	1.689(2)
O(1A)—C(3A)	1.386(2)	O(1B)—C(3B)	1.384(2)
N(3A)—N(4A)	1.400(2)	N(3B)—N(4B)	1.406(2)
Bond angles (°)			
N(2A)—Ni(1)—N(1A)	82.95(8)	N(2B)—Ni(2)—N(1B)	97.26(7)
N(2A)—Ni(1)—N(1A)	87.05(8)	N(2B)—Ni(2)—N(1B)	82.74(7)
N(2A)—Ni(1)—N(3A)	90.72(6)	N(2B)—Ni(2)—N(3B)	87.08(6)
N(1A)—Ni(1)—N(3A)	90.55(7)	N(1B)—Ni(2)—N(3B)	89.45(6)
N(4A)—N(3A)—Ni(1)	116.87(12)	N(4B)—N(3B)—Ni(2)	118.41(12)

Schemes 1–3 depict the synthesis of ligands and their Cd(II) and Ni(II) complexes. The complexes are stable towards air and moisture for several days. The complexes **1, 2** and **3** are insoluble in ethanol, methanol and chloroform but are soluble in DMF, and melt at 218, 225 and 210 °C, respectively. The complexes were fully characterized by magnetic susceptibility measurements, IR, UV–Vis and single crystal X-ray. The analytical data for the complexes corroborated well with their respective formulations.

3.1. IR spectra

The IR spectrum of tetrabutylammonium 5-(4-methoxyphenyl)-1,3,4-oxadiazole-2-thiol shows no band due to ν(NH) indicating loss of both hydrazinic protons on formation of the salt. Absorption (ν cm^{-1}) due to the stretching modes of C═N (1602), C—S (988) and N—N (1066) indicate the cyclization of dithiolate after loss of H_2S and formation of oxadiazole moiety. A negative shift in ν(NH) of ethylenediamine and appearance of a new band near 520 cm^{-1} due to ν(M—N) suggests formation of a chelate. The IR spectra of complexes **1**, **2** and **3** show bands in the region of 3256–3232 cm^{-1} due to the N—H stretching vibrations of en which are shifted to lower frequencies than those encountered in free en [29]. Absence of ν(NH) band due to hydrazinic moiety of $[K^+(H_2L)^-]$ and $[K^+(H_2L')^-]$ suggests loss of hydrazinic protons in the complexes. Appearance of two new bands near 530 cm^{-1} due to ν(M—N) suggests formation of a chelate with en and bonding of the oxadiazole nitrogen with the metal ion. The IR data are thus consistent with the presence of a 1,3,4-oxadiazole moiety in complexes **1**, **2** and **3** [30]. Complexes **1, 2** and **3** show a very small negative shift in ν(C═S) showing that the exocyclic sulfur is not participating in bonding; rather, this small shift can be attributed to the involvement of sulfur in hydrogen bonding with the NH_2 hydrogens of ethylenediamine.

3.2. Magnetic moment and electronic spectra

[Cd(en)$_2$(4-mpot)$_2$] complex is diamagnetic and show absorption in the high energy region due to intraligand/charge transfer transition. Complexes [Ni(2-pytone)$_2$(en)$_2$] and [Ni(2-mpot)$_2$(en)$_2$] show magnetic moment values of 3.0 and 2.91 BM, respectively and each of these exhibit two d–d bands at 11,430, 20,000, and 12,605, 18,985 cm^{-1} assigned to the $^3A_2g \rightarrow {}^3T_2g(F)$ (ν_1) and $^3T_1g(F)$ (ν_2) transitions, which suggest a distorted octahedral geometry for the complexes **2** and **3** [31].

3.3. Crystal structure description of complexes *1, 2* and *3*

The molecular structures of complexes **1**, **2** and **3** were determined by single crystal X-ray diffraction. The details of data

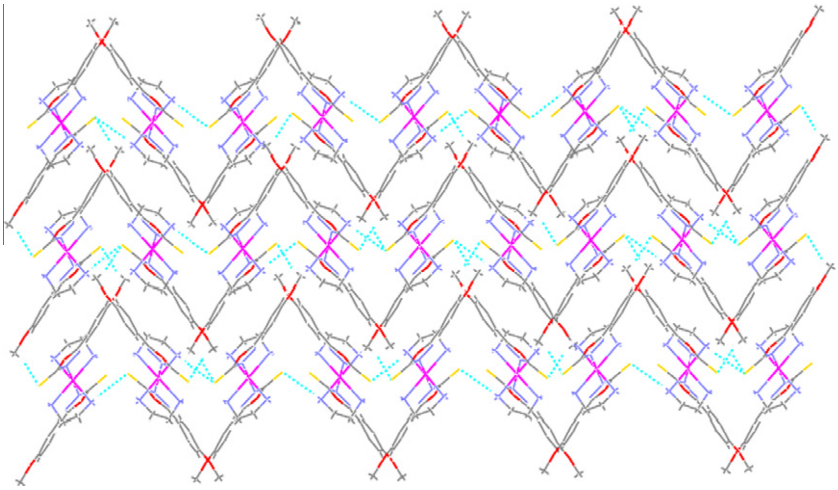


Fig. 2. Regular arrangement of molecules of Cd(II) complex forming a supramolecular architecture by N—H···S and C—H···S hydrogen bonding.

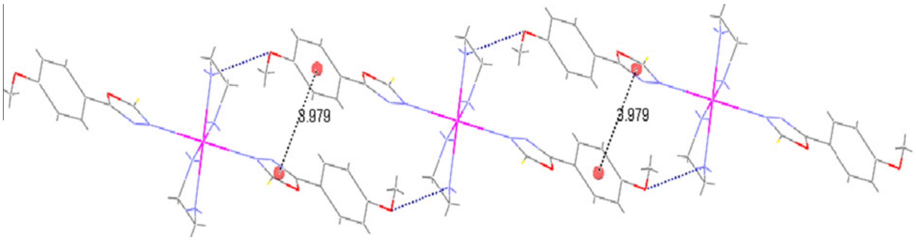


Fig. 3. π–π Stacking and N—H···O hydrogen bonding in complex **1**.

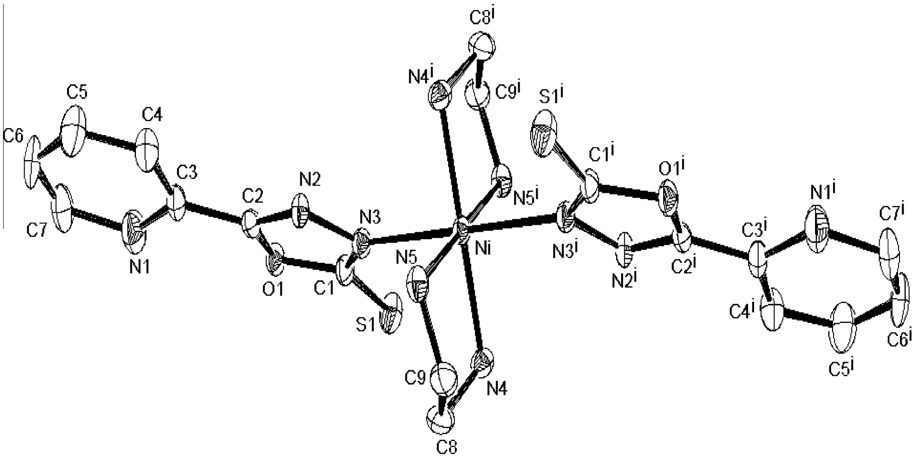


Fig. 4. ORTEP diagram of $[Ni(2\text{-pytone})_2(en)_2]$ showing atomic numbering scheme with ellipsoids of 30% probability. H atoms are omitted for clarity.

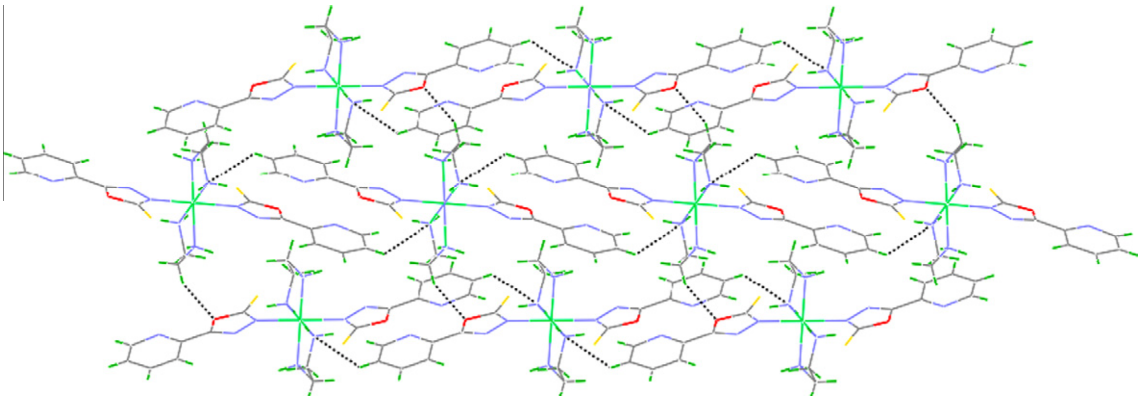


Fig. 5. C—H···O and C—H···N hydrogen bonding in complex **1**.

collection, structure solution and refinement are listed in Table 1. Ortep diagrams of complexes **1, 2** and **3** with atom numbering schemes are shown in Figs. 1, 4 and 6 respectively. Selected bond lengths and angles are given in Tables 2–4. The single crystal X-ray diffraction studies indicate that the ligands adopt the thione form in complexes **1, 2** and **3**.

The molecular structure of **1** shows that in the monomeric unit $[Cd(en)_2(4\text{-mpot})_2]$ possesses a centrosymmetry cadmium at the inversion center. The elements of the structure are joint to each other in the crystal packing by means of an extended system of H-bonds where hydrogen belonging to the en are participating in the structure. Its coordination environment is fulfilled by two axial (4-mpot) anions at trans position to each other, each bonded through oxadiazole nitrogen atom and the four equatorial sites are occupied by the two bidentate N,N′-ethylenediamine. The bonding of two en designated as, Cd—N(4) has a distance of 2.299(9)° and that of Cd—N(3) at a distance of 2.345(2) Å, (Table 2) the complex involves two five membered chelate rings C_2N_2Cd with bite angle of 77.08(7)°, and represent a major deviation from the octahedral geometry. The geometry and bonding parameters

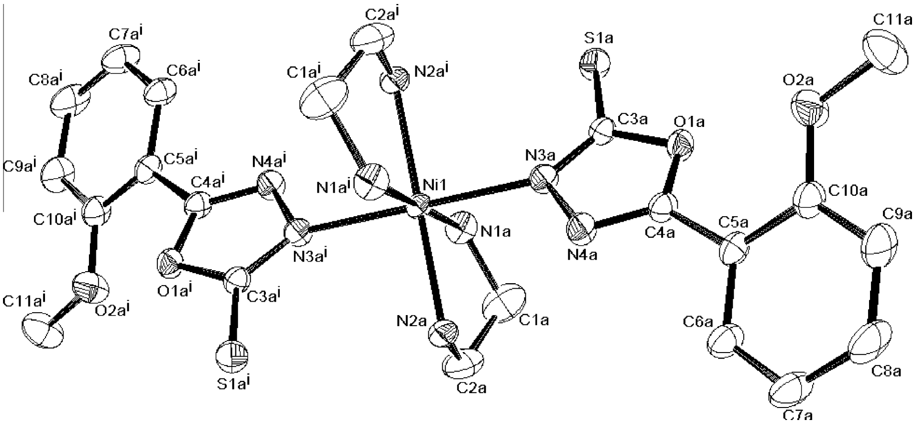


Fig. 6. ORTEP diagram of $[Ni(2\text{-mpot})_2(en)_2]$ showing atomic numbering scheme with ellipsoids of 30% probability. H atoms are omitted for clarity.

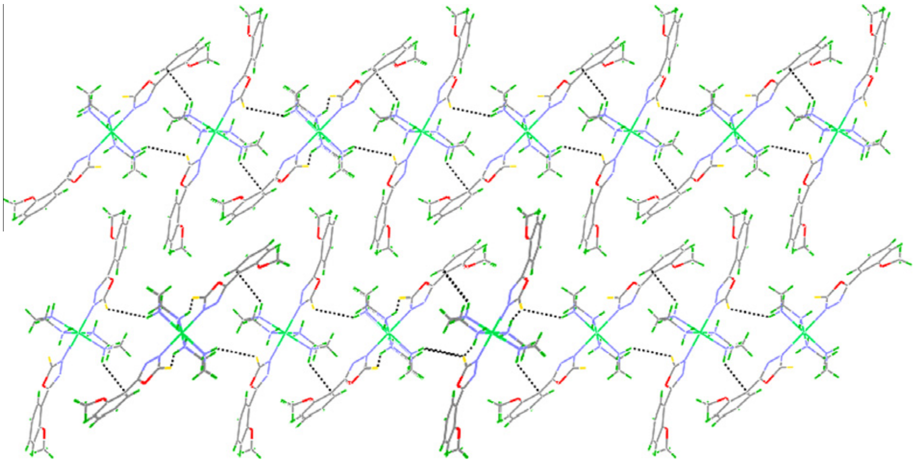


Fig. 7. Perspective view of the crystal packing of [Ni(2-mpot)$_2$(en)$_2$] along the *a* axis.

Table 5
Hydrogen bond parameters in [Ni(2-mpot)$_2$(en)$_2$] (Å and °).

D—H···A	*d*(D—H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(1A)—H(1AD)···S(1A)	0.90	2.86	3.596(2)	139.8
N(2A)—H(2AC)···S(1A)#3	0.90	2.83	3.3879(17)	121.1
N(2A)—H(2AD)···S(1A)#1	0.90	2.62	3.4113(18)	147.2
N(1B)—H(1BC)···S(1B)#4	0.90	2.86	3.3564(17)	116.1
N(1B)—H(1BD)···S(1B)#2	0.90	2.64	3.4278(18)	146.9
N(2B)—H(2BC)···S(1A)#3	0.90	2.72	3.4618(18)	140.0
N(2B)—H(2BD)···S(1B)	0.90	2.68	3.4430(19)	142.9

#1 $-x+1, -y+2, -z$.
#2 $-x, -y+1, -z$.
#3 $x-1, y, z$.
#4 $x+1, y, z$.

within the en molecule agree with [Cd(en)$_3$](ClO$_4$)$_2$ [32]. Weak intermolecular N—H···S interaction between thione sulfur and NH$_2$ hydrogen atoms and C—H···S interaction between thione sulfur and CH$_3$ hydrogen atoms provide a supramolecular network which stabilize the structure of Cd(II) complex (Fig. 2). In addition, the complex **1** is stabilized by weak π···π interactions occurring between phenyl (Cg$_{ph}$) and 1,3,4-oxadiazole (Cg$_{oxa}$) rings from a nearby molecule with a distance of 3.979 Å (Fig. 3).

The molecular structure of **2** shows that in the centrosymmetric unit of [Ni(2-pytone)$_2$(en)$_2$] the metal ion is six coordinate, bonding through four nitrogens of en and two oxadiazole nitrogens. The complex consists of two ethylenediamine ligands which chelate nickel in the equatorial positions and two 1,3,4-oxadiazole-2-thione ligands in the apical positions, in a *trans* manner. The Ni—N distances are in the range of 2.101–2.105 Å (Table 3) which is normal for Ni—N amine coordination. The bite angle for the NiC$_2$N$_4$ five membered rings is 82.61°(16) indicating a minor distortion from an octahedral geometry in the molecule. The geometry and bonding parameters within the en molecule agree with those of other en complexes [33–35]. The nickel in D$_{4h}$ symmetry is bonded to four nitrogen atoms of two en ligands which offer interesting hydrogen bonding. The elements of the structure are linked together in the crystal packing *via* intramolecular C—H···N interactions between the pyridine carbon atoms and NH$_2$ hydrogen atoms of the en. The C—H···O intramolecular interactions occur between the oxadiazole oxygen and NH$_2$ hydrogen atoms of en molecule leading to the formation a supramolecular network (Fig. 5).

The single crystal X-ray diffraction studies of complex **3** indicate that the ligand (2-mpot$^-$) adopts the thione form with two independent complexes in the asymmetric unit; in each unit Ni atom is on a center of inversion. The arrangement of the monomeric units of [Ni(2-mpot)$_2$(en)$_2$] (**3**) in two dimensional arrangement along

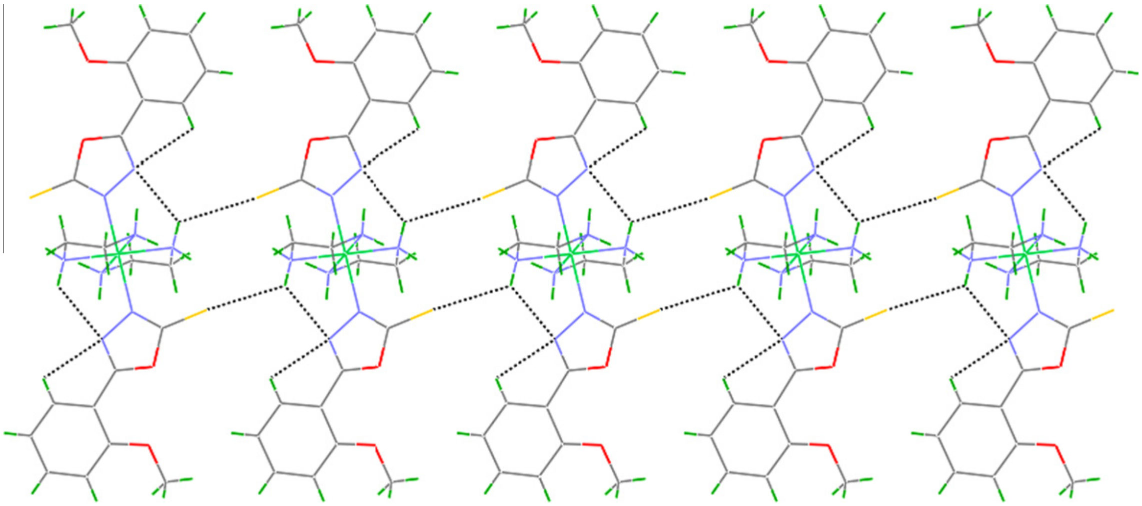


Fig. 8. Intermolecular N—H···S and intramolecular C—H···N hydrogen bonding in complex **2**.

the *a* axis provides a supramolecular network by means of various types of H-bonds (Fig. 7). The two 2-mpot$^-$ ligands are covalently bonded to nickel in a distorted octahedral geometry with axial bond angles of 90.73(6) and 92.92(6)° but equatorial bond angles of 82.95(8) and 82.74(7)°, respectively in units containing Ni(1) and Ni(2). The two 2-mpot anions occupy the *trans* positions, bonded through oxadiazole nitrogens at the distances of 2.111 Å Ni(1) and 2.153 Å Ni(2). The four equatorial sites in complex **3** are occupied by the two bidentate N,N′-ethylenediamine co-ligands. The bond length for Ni(1)—N(3A) (Noxa) is shorter than the corresponding bond length in Ni(2), showing stronger bonds in Ni(1) as compared to Ni(2). The two Ni—N(en) distances in both the units are different. The Ni(1)—N(1A) bond length is longer than Ni(2)—N(1B) while Ni(1)—N(2A) is shorter than Ni(2)—N(2B). The binding of nickel with en involves the formation of two five membered chelate rings with bite angles of 82.95(8)° and 82.74(7)° in Ni(1) and Ni(2), respectively, again showing a slight distortion from an ideal octahedral geometry. Weak intermolecular N—H···S interactions (Table 5) between thione sulfur of oxadiazole and CH_2 and NH_2 hydrogens of en stabilize the crystal structure of **3** (Fig. 8). In addition, there are intramolecular C—H···N interactions between hydrogen of phenyl ring and nitrogen atoms of oxadiazole ring which lead to the formation of a supramolecular architecture (Fig. 8).

4. Conclusion

This paper reports on the syntheses and crystal structures of three new Cd(II) and Ni(II) complexes of 5-(4-methoxy-phenyl)-1,3,4-oxadiazole-2-thione, 5-(2-pyridyl)-1,3,4-oxadiazole-2-thione and 5-(2-methoxy-phenyl)-1,3,4-oxadiazole-2-thione containing ethylenediamine as the coligand. In $[Cd(4\text{-mpot})_2(en)_2]$ (**1**), $[Ni(2\text{-pytone})_2(en)_2]$ (**2**) and $[Ni(2\text{-mpot})_2(en)_2]$ (**3**) the metal ion has a six coordinate octahedral arrangement involving 4N atoms of two en ligands and two covalently bonded N atoms of oxadiazole-2-thione anions. There are two independent complexes in the asymmetric unit of complex **3** and in each unit the nickel atom is on the center of inversion. The crystal structures of the complexes are stabilized by intermolecular and intramolecular hydrogen bonding. Complex **1** is also stabilized by weak π···π interactions occurring between phenyl (Cg_{ph}) and 1,3,4-oxadiazole (Cg_{oxa}) rings.

Appendix A. Supplementary material

CCDC 840588, 813076 and 813077 contain the supplementary crystallographic data for $[Cd(4\text{-mpot})_2(en)_2]$ (**1**), $[Ni(2\text{-pytone})_2(en)_2]$ (**2**) and $[Ni(2\text{-mpot})_2(en)_2]$ (**3**), respectively. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data center, 12 Union Road, Cambridge CB2 IEZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.12.015.

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