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## Synthesis, spectral and X-ray structural studies of Ni(II) complexes of N'-acylhydrazine carbodithioic acid esters containing ethylenediamine or *o*-phenanthroline as coligands

### M.K. Bharty<sup>a</sup>, A.K. Srivastava<sup>a</sup>, Ram Dulare<sup>a</sup>, R.J. Butcher<sup>b</sup>, N.K. Singh<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Banaras Hindu University, Varanasi 221 005, India
<sup>b</sup> Department of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA

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#### ABSTRACT

The new complexes [Ni(Hbstbh)<sub>2</sub>(en)] (**1**) and [Ni(Hpchce)(*o*-phen)<sub>2</sub>]Cl-CH<sub>3</sub>OH·H<sub>2</sub>O (**2**) with N'-benzoyl hydrazine carbodithioic acid benzyl ester (H<sub>2</sub>bstbh) and [N'-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid ethyl ester (H<sub>2</sub>pchce) have been synthesized, containing ethylenediamine (en) or *o*-phenanthroline (*o*-phen) as coligands. The ligands and their complexes have been characterized by elemental analyses, IR, magnetic susceptibility and single crystal X-ray data. [Ni(Hbstbh)<sub>2</sub>(en)] (**1**) and [Ni(Hpchce)(*o*-phen)<sub>2</sub>]Cl-CH<sub>3</sub>OH·H<sub>2</sub>O (**2**) crystallized in the monoclinic and triclinic systems, space group *C2/c* and *P* – 1, respectively. The (N, O) donor sites of the bidentate ligands chelate the Ni(II) center and form a five-membered CN<sub>2</sub>ONi ring. The resulting complexes are paramagnetic and have a distorted octahedral geometry.

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#### 1. Introduction

S-Alkyldithiocarbazates behave as versatile ligands, either acting as monodentate (S or N2) donors or bidentate anionic (via N3-S or S, S) chelating ligands [1-3]. They have been widely studied for their biological activities and chemotherapeutic properties [4,5] which may be highly dependent on the nature of the metal ion and binding sites of the ligand. Some Schiff bases of S-alkyl esters of dithiocarbazic acid and their complexes were found to display antifungal and antibacterial properties [6–8]. Several papers are available on the syntheses and spectral characterization of metal complexes of dithiocarbazates [9-15]. Recently, bis chelated complexes of S-benzyl- $\beta$ -N-(benzoyl) dithiocarbazate, a oxygensulfur donor ligand, have been reported [16], but there is no work on the mixed ligand complexes of the dithioester of N-acyl hydrazide, RC(O)NH–NH–C(S)SR which may coordinate via N, O/O, S/N, S. Following our interest in the coordination property of ligands containing the H–N–C=S moiety and with the aim of elucidating the coordination geometry of this class of biologically important ligands, N'-benzoyl hydrazine carbodithioic acid benzyl (H<sub>2</sub>bstbh) and [N'-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid ethyl (H<sub>2</sub>pchce) esters have been synthesized and the present paper

reports the syntheses, spectral characterization and X-ray crystallography of  $[Ni(Hbstbh)_2(en)]$  (1) and  $[Ni(Hpchce)(o-phen)_2]Cl-CH_3OH$  (2) (*o*-phen = *o*-phenanthroline).

#### 2. Experimental

#### 2.1. Materials and methods

Commercial reagents were used without further purification and all experiments were carried out in the open atmosphere. Ethyl benzoate and isonicotinic acid hydrazide (Sigma–Aldrich), CS<sub>2</sub> (SD Fine Chemicals, India) and KOH (Qualigens) were used as received. All the solvents were purchased from Merck Chemicals, India and used after purification. Benzoic acid hydrazide and [Ni(en)<sub>2</sub>(NCS)<sub>2</sub>] were prepared by reported methods [17,18].

## 2.2. Preparation of N'-benzoyl hydrazine carbodithioic acid benzyl ester $(H_2bstbh)$

 $H_2$ bstbh was prepared by the reaction of  $CS_2$  (1.5 ml, 20 mmol) with a suspension of benzoic acid hydrazide (2.7 g, 20 mmol) in CHCl<sub>3</sub> (20 ml) in the presence of triethylamine (2.0 ml, 14 mmol). Benzyl chloride was added dropwise to the above clear solution and stirred continuously for 4 h at room temperature. The solvent was evaporated at room temperature and the residue was washed with water, which gave a colorless solid. Yield 66%; m.p. 426 K.



<sup>\*</sup> Corresponding author. Tel.: +91 542 6702452.

*E-mail addresses*: mkbharty@bhu.ac.in (M.K. Bharty), singhnk\_bhu@yahoo.com, nksingh@bhu.ac.in (N.K. Singh).

Anal. Calc. for  $C_{15}H_{14}N_2OS_2$  (302): C, 59.60; H, 4.63; N, 9.27; S, 21.19. Found: C, 59.45; H, 4.80; N, 9.36; S, 21.30%. IR ( $\nu$ , cm<sup>-1</sup>, KBr):  $\nu$ (NH) 3205 and 3175,  $\nu$ (C=O) 1685s;  $\nu$ (N–N) 1060;  $\nu$ (C=S) 966. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>;  $\delta$  ppm): 11.80 and 11.60 (s, 2H, NH), 3.7 (s, 2H, CH<sub>2</sub>) 7.0–7.8 (m, 10H aromatic protons). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>;  $\delta$  ppm): 119.25 (C<sup>1</sup>), 129.10 (C<sup>2</sup>, C<sup>6</sup>), 121.10 (C<sup>3</sup>, C<sup>5</sup>), 130.95 (C<sup>4</sup>), 164.69 (C<sup>7</sup>=O), 202.30 (C<sup>8</sup>=S), 38.08 (C<sup>9</sup>H<sub>2</sub>), 134.05 (C<sup>10</sup>), 128.52 (C<sup>11</sup>, C<sup>15</sup>), 130.65 (C<sup>12</sup>, C<sup>14</sup>), 127.30 (C<sup>13</sup>) (Fig. 1).

# 2.3. Preparation of N'-(pyridine-4-carbonyl)-hydrazinecarbodithioic acid ethyl ester

The ligand H<sub>2</sub>pchce was prepared as described earlier [19].

#### 2.4. Preparation of [Ni(Hbstbh)<sub>2</sub>(en)]

[Ni(Hbstbh)<sub>2</sub>(en)] was prepared by adding a MeOH–CHCl<sub>3</sub> solution of freshly prepared N'-benzoyl hydrazine carbodithioic acid benzyl ester (H<sub>2</sub>bstbh) (0.604 g, 2 mmol) to a MeOH solution of [Ni(en)<sub>2</sub>(NCS)<sub>2</sub>] (0.230 g, 1 mmol). The resulting solution was filtered and kept for crystallization. Light pink single crystals of [Ni(Hbstbh)<sub>2</sub>(en)] suitable for X-ray analyses were obtained by slow evaporation of its MeOH-CHCl<sub>3</sub> solution over a period of 15 days. Yield 60%; m.p. > 573 K.  $\mu_{eff}$  = 3.0 BM. *Anal.* Calc. for C<sub>32</sub>H<sub>34</sub>N<sub>6</sub>NiO<sub>2</sub>S<sub>4</sub> (721.60): C, 53.21; H, 4.71; N, 11.64; S, 17.73.



Fig. 1. N'-Benzoyl hydrazinecarbodithioic acid benzyl ester.

Found: C, 53.55; H, 4.90; N, 11.95; S, 17.85%; IR ( $\nu$ , cm<sup>-1</sup>, KBr):  $\nu$ (NH) 3165;  $\nu$ (C=O) 1640s;  $\nu$ (N=N) 1096;  $\nu$ (C=S) 956;  $\nu$ (Ni–N) 450 and 475. The structure was further confirmed by XRD.

#### 2.5. Preparation of [Ni(Hpchce)(o-phen)<sub>2</sub>]Cl·CH<sub>3</sub>OH·H<sub>2</sub>O (2)

NiCl<sub>2</sub>·6H<sub>2</sub>O (0.237 g, 1 mmol) and H<sub>2</sub>pchce (0.482 g, 2 mmol) were dissolved separately in 20 ml MeOH, mixed together and stirred for 1 h. The brown solid which separated was filtered, washed successively with ethanol and air dried. A methanol solution of *o*-phen (0.400 g, 2 mmol) was added to the methanol suspension of the above compound and stirred for 2 h. The resulting clear brown solution was filtered and kept for crystallization. Brown single crystals of **2** suitable for X-ray analyses were obtained by slow evaporation of its methanol solution over a period of 10 days. Yield 55%; m.p. 483 K.  $\mu_{eff}$  = 2.9 BM. *Anal.* Calc. for C<sub>34</sub>H<sub>29</sub>ClN<sub>7</sub>NiO<sub>3</sub>S<sub>2</sub> (741.92): C, 54.99; H, 3.90; N, 13.20; S, 8.62. Found: C, 55.00; H, 3.95; N, 13.30; S, 8.82%. IR (*v*, cm<sup>-1</sup>, KBr): *v*(OH) 3457 and 3426; *v*(NH) 3179; *v*(C=O) 1630s; *v*(N–N) 1097; *v*(C=S) 985; *v*(Ni–N) 455 and 478.

#### 2.6. 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 Faraday balance using Hg[Co(NCS)<sub>4</sub>] as the calibrant. Electronic spectra were recorded on a Shimadzu 1700 UV–Vis spectrophotometer as Nujol mulls [20]. IR spectra were recorded in the 4000–400 cm<sup>-1</sup> region as KBr pellets on a Varian 3100-FTIR spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in DMSO-d<sub>6</sub> on a JEOL AL 300 FT NMR spectrometer using TMS as an internal reference.

#### 3. Crystal structure determination

Data for the structure of 1 were obtained at 173(2) K on a Bruker three-circle diffractometer equipped with SMART 6000 CCD software, whereas the data for the structure of 2 were obtained



Scheme 1. Preparation of complex 1.

at 293(2) K on an Oxford Diffraction Gemini diffractometer equipped with CrysAlis Pro., using a graphite monochromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation source for both complexes. The structures were 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 positions and refined with a riding model [21]. The MERCURY package and ORTEP-3 for Windows program were used for generating molecular graphics [22,23].

#### 4. Results and discussion

The ligand N'-benzoyl hydrazine carbodithioic acid benzyl (H<sub>2</sub>bstbh) ester reacts with [Ni(en)<sub>2</sub>(NCS)<sub>2</sub>] yielding [Ni(Hbstb-h)<sub>2</sub>(en)] (1), whereas [N'-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid ethyl ester (H<sub>2</sub>pchce) on reaction with NiCl<sub>2</sub>·6H<sub>2</sub>O and then with o-phen yields [Ni(Hpchce)(o-phen)<sub>2</sub>]Cl·CH<sub>3</sub>OH·H<sub>2</sub>O (**2**). The complexes **1** and **2** are stable towards air and moisture, and melt at >573 and 483 K, respectively. Schemes 1 and 2 depict the formation of the complexes, which contain Hbstbh and Hpchce as ligands and en/o-phen as coligands. Both ligands are soluble in

methanol and ethanol, while complexes **1** and **2** dissolve in DMF and DMSO.

#### 4.1. IR spectra

The IR spectrum of the ligand N'-benzoyl hydrazine carbodithioic acid benzyl ester (H<sub>2</sub>bstbh) shows absorptions due to the stretching modes of NH at 3205 and 3175. C=O at 1685. C=S at 966 and N–N at 1060 cm<sup>-1</sup>. The IR spectrum of complex **1** shows a band at 3165 cm<sup>-1</sup>, indicating the presence of one NH group upon complexation. The appearance of two new bands for v(Ni-N) at 450 and 475  $cm^{-1}$  suggests bonding of Ni(II) with en and one hydrazinic nitrogen after loss of a proton. The v(C=0) and v(N-N) bands suffer negative and positive shifts of 45 and 36 cm<sup>-1</sup>, respectively, indicating that H<sub>2</sub>bstbh is acting as a uninegative bidentate ligand, bonding through the carbonyl oxygen and hydrazinic nitrogen in complex 1. The IR spectrum of [Ni(Hpchce)(o-phen)<sub>2</sub>]Cl·CH<sub>3</sub>OH·H<sub>2</sub>O (2) shows two bands at 3457 and 3426 cm<sup>-1</sup> for v(OH) of H<sub>2</sub>O and CH<sub>3</sub>OH, and a band at 3185 cm<sup>-1</sup> for v(NH) of the ligand. The absence of one v(NH) band, together with the appearance of two new bands for v(Ni-N) at 455 and 478 cm<sup>-1</sup>, suggest bonding of Ni(II) with one hydrazinic nitrogen after loss of a proton and *o*-phen nitrogen. The v(C=0) and



Scheme 2. Preparation of complex 2.



Fig. 2. ORTEP diagram of [Ni(Hbstbh)<sub>2</sub>(en)] (1) at the 30% ellipsoids probability level. Hydrogen atoms are omitted for clarity.

Table 1				
Crystallographic data for	Ni(Hbstbh) <sub>2</sub> (en)	and [Ni(Hpcho	e)(o-phen)2]Cl	·CH <sub>3</sub> OH·H <sub>2</sub> O

Compound	1	2
Empirical formula	$C_{32}H_{34}N_6NiO_2S_4$	$C_{34}H_{29}ClN_7NiO_3S_2$
Formula weight	721.62	741.92
T (K)	173(2)	293(2)
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	C2/c	P-1
Unit cell dimensions		
a (Å)	22.430(7)	10.813(8)
b (Å)	9.073(3)	12.633(11)
<i>c</i> (Å)	18.385(6)	12.823(13)
α (°)	90.0	104.066(8)
β(°)	117.486(4)	96.496(7)
γ (°)	90.0	96.042(7)
$V(Å^3)$	3319.1(18)	1672.3(3)
Ζ	4	2
$\rho_{\rm calc}  ({\rm g/cm^3})$	1.444	1.473
$\mu ({ m mm^{-1}})$	0.876	0.832
F(0 0 0)	1504	766
Crystal size (mm)	0.50 x 0.40 x	0.27 x 0.25 x 0.23
	0.23	
$\theta$ Range for data collection (°)	2.50 - 30.52	2.03 - 28.93
Index ranges	$-31 \leq h \leq 32$	$-14 \leqslant h \leqslant 14$
	$-12 \leqslant k \leqslant 12$	$-15 \leqslant k \leqslant 17$
	$-25 \leqslant l \leqslant 23$	$-16 \leqslant l \leqslant 17$
No. of reflections collected	18 356	12 249
No. of independent reflections $(R_{int})$	5073 (0.0228)	8835 (0.0493)
Number of data/restraints/parameters	5073/0/204	8835/0/425
Goodness-of-fit on $F^2$	1.057	1.089
$R_1, w R_2^{a,b} [(I > 2\sigma(I))]$	0.0274, 0.0702	0.0608, 0.1932
$R_1$ , $wR_2^{a,b}$ (all data)	0.0319, 0.0721	0.0807, 0.2008
Largest difference in peak and hole (e	0.321 and	1.014 and -0.988
Å <sup>-3</sup> )	-0.365	
<sup>a</sup> $R_1 = \Sigma   F_0  -  F_0  \Sigma  F_0 $ .		
<sup>b</sup> $R_2 = \left[\sum w( F_0^2  -  F_c^2 )^2 / \sum w F_2^0 ^2\right]^{1/2}.$		

v(N-N) bands suffer negative and positive shifts, indicating bonding through the carbonyl oxygen and one hydrazinic nitrogen.

Thus, H<sub>2</sub>pchce acts as a uninegative bidentate ligand in complex

Table	2
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Selected bond lengths (Å) and angles (°) for [Ni(Hbstbh)<sub>2</sub>(en)] (1).

Bond length		Bond angle	
S(1)-C(8)	1.770(14)	O(1)-C(7)-N(2)	120.51(10)
S(1)-C(9)	1.809(13)	O(1)-C(7)-C(1)	121.60(11)
S(2)-C(8)	1.700(13)	N(1)-C(8)-S(2)	125.64(9)
O(1)-C(7)	1.251(15)	N(1)-C(8)-S(1)	111.47(9)
N(1)-C(8)	1.321(16)	(S2)-C(8)-S(1)	122.83(7)
N(2)-C(7)	1.336(16)	C(10)-C(9)-S(1)	107.97(9)
N(1)-N(2)	1.395(13)	O(1)-Ni(1)-O(1)	174.42(5)
N(3)-C(16)	1.480(2)	O(1)-Ni(1)-N(3)	89.68(5)
C(1) - C(6)	1.387(18)	N(3)-Ni(1)-N(3)	83.08(7)
C(1) - C(2)	1.394(19)	O(1)-Ni(1)-N(1)	78.43(4)
Ni(1)-O(1)	2.081(10)	O(1)-Ni(1)-N(1)	105.57(4)
Ni(1)-N(3)	2.097(12)	N(3)-Ni(1)-N(1)	94.52(5)
Ni(1)-N(1)	2.111(11)	N(3)-Ni(1)-N(1)	164.41(4)
		N(1)-Ni(1)-N(1)	91.77(6)
		C(16)-Ni(1)-N(3)	107.68(9)

Table 3	
Hydrogen bonding parameters for $[Ni(Hbstbh)_2(en)]$ (1).	

$D{-}H{\cdot}{\cdot}{\cdot}A$	D–H (Å)	H…A (Å)	$D{\cdots}A~({\mathring{A}})$	$\angle D - H \cdots A$ (°)
N2−H2B···S2	0.88	2.42	2.854(13)	110.6

**2** [24]. On the basis of IR data alone, How et al. have concluded that the bonding in bis chelated complexes of S-benzyl- $\beta$ -N-(benzoyl) dithiocarbazate takes place through oxygen and sulfur, which is in contrast to the present finding. The bonding through oxygen and nitrogen in our mixed ligand complexes is supported by X-ray data.

#### 4.2. <sup>1</sup>H and <sup>13</sup>C NMR spectra

The <sup>1</sup>H NMR spectrum of H<sub>2</sub>bstbh in DMSO-d<sub>6</sub> shows two signals at  $\delta$  11.80 and 11.60 ppm for the amide and thioamide



Fig. 3. Crystal packing of complex 1 along the *c* axis.



Fig. 4. Showing N-H···S hydrogen bonding, leading linear chain structure.

protons, respectively. Phenyl ring protons appear as a multiplet between  $\delta$  7.0 and 7.8 ppm. The <sup>13</sup>C NMR spectrum of H<sub>2</sub>bstbh shows signals at  $\delta$  202.30 (C8) and 164.69 (C7) ppm due to the >C=S and >C=O carbons, respectively. The phenyl ring carbons appear in the region  $\delta$  119.25–134.05 ppm.

#### 4.3. Electronic spectra and magnetic moments

A magnetic moment of 3.0 BM for [Ni(Hbstbh)<sub>2</sub>(en)] and the presence of two bands at 15 040 and 22 320 cm<sup>-1</sup> assigned to the  ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(F)$  ( $\nu_{2}$ ) and  ${}^{3}T_{1}g(P)$  ( $\nu_{3}$ ) transitions, respectively, suggest a distorted octahedral geometry for the complex [25]. A magnetic moment of 2.9 BM for [Ni(Hpchce)(*o*-phen)<sub>2</sub>]Cl·CH<sub>3</sub>OH·H<sub>2</sub>O (**2**) and the presence of a band at 17 275 cm<sup>-1</sup> assigned to the  ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(F)$  transition, suggests a distorted octahedral geometry for the complex [25].

#### 4.4. Crystal structure description of [Ni(Hbstbh)<sub>2</sub>(en)] (1)

Fig. 2 shows an ORTEP diagram of the complex [Ni(Hbstb $h_{2}(en)$ ] (1) together with the atom numbering scheme, which contains a pair of monodeprotonated ligands and one en coordinated to Ni(II) ion via a carbonyl oxygen, β-nitrogen (N2) and both nitrogens of en, forming three five membered chelate rings. The crystallographic data and structural refinement details are given in Table 1 and the selected bond distances and bond angles are presented in Table 2. The elements of the structure are joined to each other in the crystal packing (Fig. 3) by means of an extended system of H-bonds where hydrogen atoms belonging to the en ligand are participating in the structure. The hydrogen bonding parameters of complex 1 are given in Table 3. The deprotonation of the hydrazinic nitrogens adjacent to carbonyl group, viz. N2/N2', in complex 1 results in a narrowing of the endocyclic angles C(7)–N(2)–N(1) by 9° (Table 2). The environment around the metal atoms may be described as a distorted octahedral with bite angles of 78.43(4) [N(1)-Ni-O(1)] and 83.08(7) [N(3)-Ni-N(3)]. The formation of a five membered chelate ring, C<sub>2</sub>N<sub>2</sub>Ni, with a bite angle of 82.71(9)° represents a major deviation from an octahedral geometry. The geometry and bonding parameters within the en molecule agree with those of the related compound  $[Ni(trans(L)_2(en)_2]]$  $\{L = N-(5-chlorouracilato)\}$  [26]. The distances within the chelate rings are intermediate between single and double bond lengths. The average bond lengths, N2–N1 = 1.395(13), N2–C7 = 1.336(16), N1-C8 = 1.321(16), C7-O1 = 1.251(15) Å, suggest considerable delocalization of charge [27]. In complex 1 the chelate rings and the phenyl ring lie nearly in the same plane. The phenyl ring thus makes an extended coplanar system with the two chelate rings. The values of the dihedral angles suggest that the extended coplanar ring system of the two ligands approach each other orthogonally and shows an unsymmetrical coordination of the two ligands. In the solid state the complex is stabilized *via* intermolecular N-H···S interactions between dithio sulfur atoms and NH<sub>2</sub> hydrogen atoms of the en molecule, leading to the formation of a symmetrical linear chain structure (Fig. 4).

#### 4.5. Crystal structure description of [Ni(Hpchce)(o-phen)<sub>2</sub>] Cl·CH<sub>3</sub>OH·H<sub>2</sub>O (**2**)

Fig. 5 shows an ORTEP diagram of complex **2** together with the atom numbering scheme. The structural refinement data related to complex **2** are listed in Table 1 and the selected bond distances and bond angles are listed in Table 4. The (N, O) donor sites of the uninegative bidentate ligand chelate the Ni(II) center to form a five- membered CN<sub>2</sub>ONi ring. The resulting complex has a distorted octahedral geometry. The average bond lengths in complex **2** are: O1–C6 = 1.295(5), N3–C7 = 1.326(5), N2–N3 = 1.397(5), N2–C6 = 1.311(5) Å which suggest considerable delocalization of



Fig. 5. ORTEP diagram of  $[Ni(Hpchce)(o-phen)_2]Cl·CH_3OH·H_2O$  (2) at the 30% ellipsoids probability level. Hydrogen atoms and solvent molecules are omitted for clarity.



Fig. 6. C-H...Cl, N-H...O and C-H...O hydrogen bonding forming a six membered C, Cl, O arrangement (shown as a Ball and Stick model).

Table 4
Selected bond lengths (Å) and angles (°) for $[Ni(Hpchce)(o-phen)_2]Cl\cdot CH_3OH \cdot H_2O$ (2).

Bond lengths		Bond angles	
Ni-O1	2.033(3)	01-Ni-N3	78.60(12)
Ni-N3	2.079(3)	O1-Ni-N4	91.20(12)
Ni-N4	2.099(3)	N3-Ni-N4	95.89(13)
Ni-N5	2.109(3)	O1-Ni-N5	169.15(12)
Ni-N6	2.109(3)	N3-Ni-N5	107.05(13)
Ni-N7	2.139(3)	N4-Ni-N5	79.11(13)
S2-C7	1.677(4)	O1-Ni-N6	95.03(12)
S1-C8	1.804(6)	N3-Ni-N6	95.15(13)
S1-C7	1.810(4)	N4-Ni-N6	168.21(12)
01-C6	1.295(5)	N5-Ni-N6	93.69(12)
N3-C7	1.326(5)	O1-Ni-N7	87.72(12)
N3-N2	1.397(5)	N3-Ni-N7	164.32(13)
N2-C6	1.311(5)	N4-Ni-N7	91.98(13)
C5-C6	1.475(5)	N5-Ni-N7	87.73(13)
C8-C9	1.464(9)	N6-Ni-N7	78.31(13)
03-C34	1.339(10)	N2-N3-Ni	112.4(2)
N7-C29	1.303(6)	S2-C7-S1	121.7(2)
N7-C30	1.352(5)	01-C6-N2	126.2(4)

charge [27]. Complex **2** is stabilized in the solid state by weak intermolecular C–H···Cl interactions between the phenyl ring hydrogens and chlorine atoms, and N–H···O interaction between the hydrazinic hydrogen and oxygen of water molecule, as well as C–H···O interactions between the hydrogens of methanol and the oxygen of the water molecule (Fig. 6). Masui suggested that if active electron delocalization within a metal–N–heterocyclic chelate ring is present, it would exhibit some degree of metalloaromaticity [28,29]. In the complex the chelate rings and the pyridine rings lie nearly in the same plane, forming a dihedral angle of 7.88°. The Ni–O, Ni–N and Ni–N(phen) bond distances of 2.033(3), 2.079(3) and 2.099(3) Å, respectively are comparable to the bond lengths reported earlier [19].

#### 5. Conclusions

The new ligand N'-benzoyl hydrazine carbodithioic acid benzyl (H<sub>2</sub>bstbh) ester and two new complexes [Ni(Hbstbh)<sub>2</sub>(en)] (**1**) and [Ni(Hpchce)(*o*-phen)<sub>2</sub>]Cl·CH<sub>3</sub>OH·H<sub>2</sub>O (**2**) have been synthesized. The crystal structure of complex **1** is stabilized through a weak intermolecular N-H···S interaction between the dithio sulfur

atoms and NH<sub>2</sub> hydrogen atoms of the en molecule. The crystal structure of complex **2** is stabilized in the solid state by weak intermolecular C-H···Cl interactions between the phenyl ring hydrogens and chlorine atoms and N-H···O interaction between the hydrazinic hydrogen and oxygen of water molecule, as well as C-H···O interactions between the hydrogens of methanol and the oxygen of the water molecule.

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#### Appendix A. Supplementary material

CCDC 792156 and 795157 contain the supplementary crystallographic data for  $[Ni(Hbstbh)_2(en)]$  (1) and  $[Ni(Hpchce)(o-phen)_2]Cl-CH_3OH H_2O$  (2). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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