

# Synthesis, Properties and Crystal Structure of a Novel Ni(II) Complex Derived from a 4-Heterocyclic Acylpyrazolone

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The new 4-acylpyrazolone 1-(4-chlorophenyl)-3-phenyl-4-thenoyl-1H-pyrazol-5-ol (HCPTP) and its Ni(II) complex  $[\text{Ni}(\text{CPTP})_2(\text{C}_2\text{H}_5\text{OH})_2](\text{C}_2\text{H}_5\text{OH})_2$  were synthesized. The ligand and the complex were characterized by elemental analyses, IR and UV/Vis spectroscopy, thermal analyses, and single-crystal X-ray diffraction. Crystals of HCPTP are monoclinic, space group  $P2_1/c$  with  $Z = 4$  while  $[\text{Ni}(\text{CPTP})_2(\text{C}_2\text{H}_5\text{OH})_2](\text{C}_2\text{H}_5\text{OH})_2$  belongs to the triclinic system, space group  $P\bar{1}$  with  $Z = 2$ . The complex has a six-coordinated Ni(II) center in a distorted octahedral configuration with two ethanol ligands in *cis* position. These octahedral units are connected through hydrogen bonds *via* the coordinated and uncoordinated ethanol molecules.

**Key words:** Acylpyrazolone, Nickel Complex, Crystal Structure, Spectral Characterization

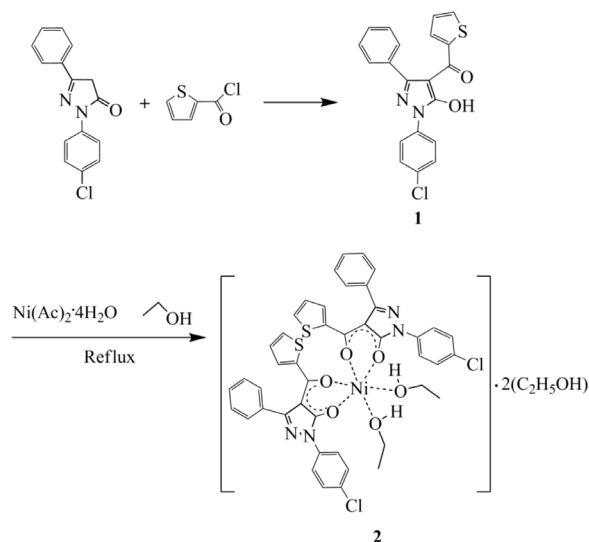
## Introduction

Acylpyrazolones are an interesting class of  $\beta$ -diketone compounds which are widely used in the solvent extractions of metal ions, laser working materials and NMR shift reagents [1–3]. Their metal complexes have been found to display catalytic performance, biological activity and enhanced luminescence [4]. In addition, they are potential antifungal agrochemicals, and show antiviral, antipyretic analgesic, and anti-inflammatory activity in medicine [5, 6].

It is well known that Ni(II) is a good candidate for the construction of magnetic or luminescent metal-organic materials [7, 8], because it can adopt diverse coordination modes with *N*- or *O*-donor ligands. HCPTP (1-(4-chlorophenyl)-3-phenyl-4-thenoyl-1H-pyrazol-5-ol, **1**) is a new 4-heterocyclic acylpyrazolone the formula of which is shown in Scheme 1. In this paper, we present the synthesis of a CPTP<sup>−</sup>-containing Ni(II) complex,  $[\text{Ni}(\text{CPTP})_2(\text{C}_2\text{H}_5\text{OH})_2](\text{C}_2\text{H}_5\text{OH})_2$  (**2**), and report its single-crystal structure, IR- and UV/Vis-spectral properties, and thermal analysis.

## Results and Discussion

HCPTP **1** and the Ni(II) complex **2** were synthesized according to established procedures which are summarized in Scheme 1. Further details are given in the Experimental Section.



Scheme 1. The synthesis of HCPTP (**1**) and  $[\text{Ni}(\text{CPTP})_2(\text{C}_2\text{H}_5\text{OH})_2](\text{C}_2\text{H}_5\text{OH})_2$  (**2**).

## Description of the molecular structures

The molecular structure of **1** is shown in Fig. 1. Table 1 contains selected distances and angles. The chlorophenyl ring is slightly twisted by  $17.79(6)^\circ$  with respect to the pyrazolone ring, and the dihedral angles of the phenyl and thenoyl rings with the pyrazolone are  $43.10(5)$  and  $34.00(8)^\circ$ , respectively. The clear evidence of the hydroxyl H atom in the difference

Table 1. Selected bond lengths (Å) and angles (deg) for HCPTP (**1**) and  $[\text{Ni}(\text{CPTP})_2(\text{C}_2\text{H}_5\text{OH})_2](\text{C}_2\text{H}_5\text{OH})_2$  (**2**) with estimated standard deviations in parentheses.

<b>1</b>		<b>2</b>	
N2–N1	1.3890(15)	Ni1–O1	2.0075(16)
O2–N1	1.2393(17)	Ni1–O2	2.0281(17)
C11–C3	1.7410(13)	Ni1–O3	2.0532(17)
O1–C7	1.3214(16)	Ni1–O4	2.0345(16)
S1–C20	1.6972(18)	Ni1–O5	2.0725(18)
S1–C17	1.7234(13)	Ni1–O6	2.0626(19)
N2–C9	1.3222(17)	O1–C7	1.260(3)
		O3–C29	1.278(3)
C9–N2–N1	105.57(10)	O1–Ni1–O2	89.50(7)
N2–N1–C6	118.71(10)	O1–Ni1–O3	88.92(7)
O2–C16–C17	119.02(12)	O1–Ni1–O6	90.94(7)
C20–S1–C17	91.80(8)	O1–Ni1–O5	90.46(7)
C7–N1–N2	110.83(10)	O4–Ni1–O2	89.82(7)
C7–N1–C6	130.45(11)	O4–Ni1–O3	88.21(7)
O2–C16–C8	117.86(12)	O4–Ni1–O5	90.25(7)
		O4–Ni1–O6	91.95(7)

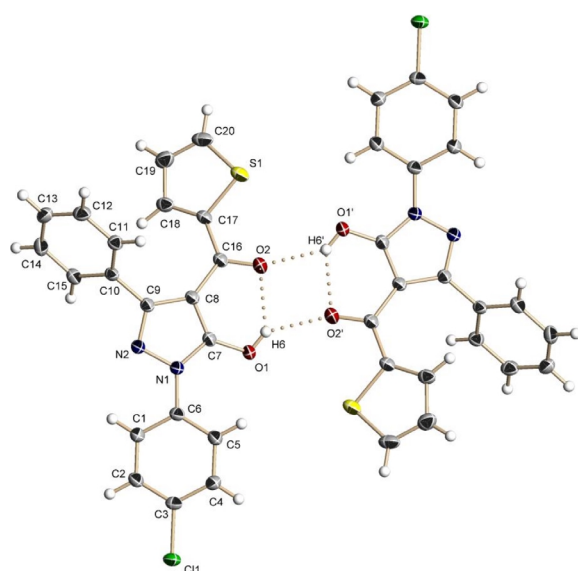


Fig. 1 (color online). The structure of a dimer of HCPTP (**1**) in the solid state with atom numbering scheme adopted. (Hydrogen bonds are shown as dotted lines. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radius. Symmetry code: (')  $-x, 1-y, 2-z$ ).

Fourier synthesis and the absence of any residual electron density in the vicinity of C8 confirm that **1** crystallizes as a pure enol tautomer and that no desmotropism is present [9]. Atom O2 has a partial anionic character, as shown by the lengthening of the C=O bond [1.2393(17) Å] relative to that normally found for carbonyl groups, and this atom acts as hydrogen-bond acceptor (Table 1 and Fig. 1). The intermolecular hydro-

gen bond results in the formation of a dimer with an  $R_2^2(12)$  graph-set motif [10].

The structure of  $[\text{Ni}(\text{CPTP})_2(\text{C}_2\text{H}_5\text{OH})_2](\text{C}_2\text{H}_5\text{OH})_2$  (**2**) together with the atom numbering scheme is illustrated in Fig. 2. Important distances and angles are summarized in Table 1. The structure determination revealed a 6-coordinate mononuclear Ni(II) complex with the metal coordinated by two oxygen atoms of ethanol and four oxygen atoms of two bidentate pyrazolonate ligands  $\text{CPTP}^-$ .

The coordination around the Ni center is a slightly distorted octahedron (Fig. 2). The two Ni-coordinated ethanol molecules are mutually *cis*, while the two bidentate  $\text{CPTP}^-$  ligands adopt the deprotonated enol form, chelating to the Ni atom *via* their O atoms. The *cis*-configuration may be facilitated by intermolecular hydrogen bonds between the coordinated and uncoordinated ethanol molecules (see below).

The structure of the neutral ligand **1** has changed in the Ni(II) complex **2**. The O(1)–C(7) and O(3)–C(29) bond lengths are 1.260(3) and 1.278(3) Å, respectively, which is shorter than 1.3214(16) Å for the O(1)–C(7) single bond of the free ligand and longer than 1.22 Å

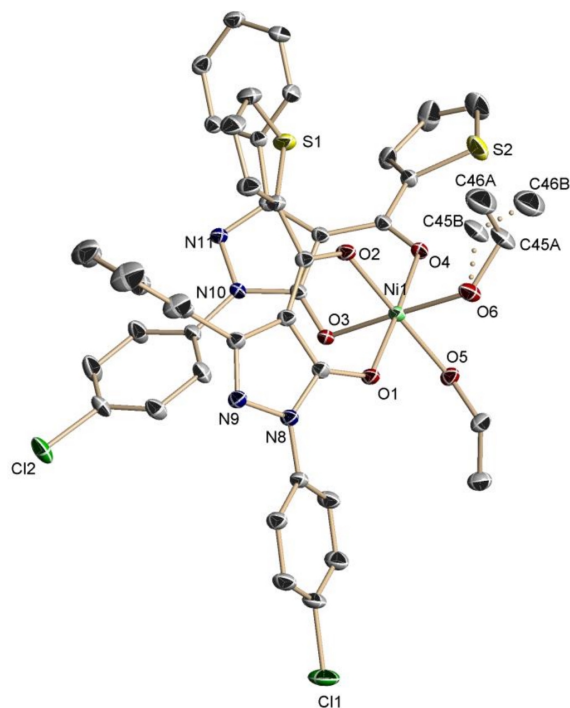


Fig. 2 (color online). The molecular structure of  $[\text{Ni}(\text{CPTP})_2(\text{C}_2\text{H}_5\text{OH})_2](\text{C}_2\text{H}_5\text{OH})_2$  (**2**) in the solid state. (30% probability ellipsoids. The two uncoordinated ethanol molecule are omitted for clarity).

Table 2. Hydrogen bonds for complex **2** (Å and deg)<sup>a</sup>.

D–H...A	D–H	H...A	D...A	D–H...A
O5–H5A...O8(1)	0.80(2)	2.01(2)	2.782(3)	162(3)
O6–H6A...O7(2)	0.80(2)	1.89(2)	2.686(3)	172(4)
O7–H7...N9(3)	0.82	2.16	2.962(3)	167.0
O8–H8...O3(3)	0.82	2.07	2.857(3)	161.7

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: (1)  $x, y-1, z-1$ , (2)  $x, y-1, z$ ; (3)  $1-x, 1-y, 1-z$ .

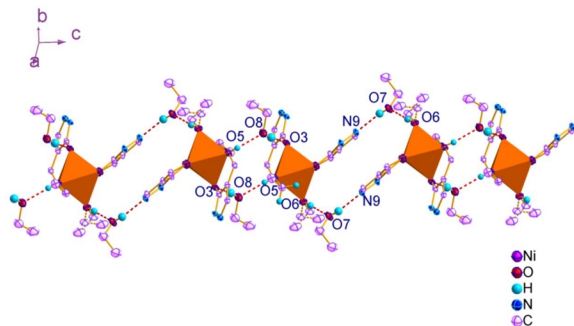


Fig. 3 (color online). View of the crystal structure of  $[\text{Ni}(\text{CPTP})_2(\text{C}_2\text{H}_5\text{OH})_2](\text{C}_2\text{H}_5\text{OH})_2$  (**2**). Some atoms were omitted for clarity.

for a C=O double bond. Moreover, the C(7)–C(8) and C(28)–C(29) bond lengths are close to that of C–C single bonds, confirming that the enol form of the ligand has isomerized to the keto form. These changes indicate a delocalized pyrazolone-ring, averaging the bond lengths.

The crystal structure of  $[\text{Ni}(\text{CPTP})_2(\text{C}_2\text{H}_5\text{OH})_2](\text{C}_2\text{H}_5\text{OH})_2$  (**2**) contains two co-crystallized uncoordinated alcohol molecules, which are linked *via* hydrogen bonding to the coordinated ethanol molecules (atoms O8 and O7; see Table 2 and Fig. 3). The latter, in turn, act as hydrogen bond donors to atoms N9 and O3 of neighboring complexes. Thus, the molecules form double-chains of hydrogen bonds along the  $c$  axis, and a one-dimensional supramolecular structure is formed.

#### IR and UV/Vis spectra

The infrared spectrum of **1** was compared with that of the complex **2** (Fig. 4). In **1**, a medium-intensity band at  $3072\text{ cm}^{-1}$  is assigned to  $\nu(\text{OH})$  of the  $\beta$ -diketone. The band is absent in the complex. A band at  $1591\text{ cm}^{-1}$  in the free ligand allocated as  $\nu(\text{C}=\text{O})$  of the pyrazolone ring is shifted to  $1572\text{ cm}^{-1}$  in the complex [11]. The weak band at  $467\text{ cm}^{-1}$  is related to a Ni–O stretching vibration. From these observations it is concluded that the enolic proton of the ligand is absent in the Ni(II) complex.

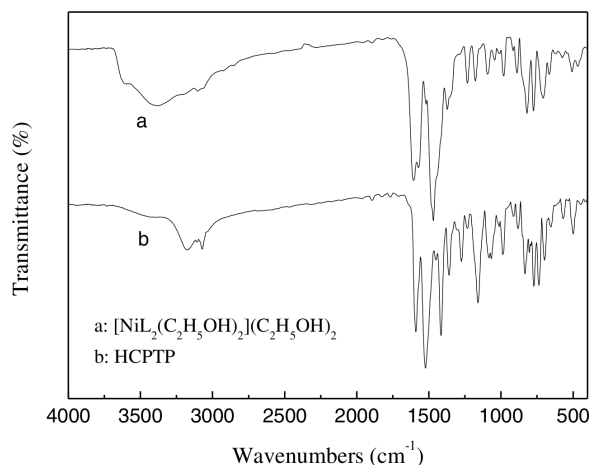


Fig. 4. FT-IR spectra of **1** and **2**.

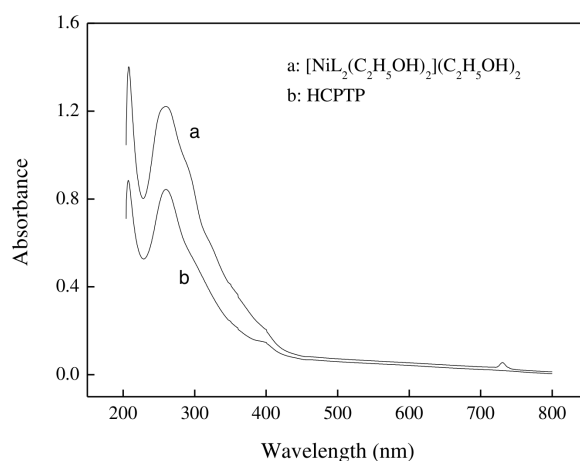


Fig. 5. UV/Vis spectra of **1** and **2**.

UV/Vis absorption spectra (Fig. 5) of **1** and the complex **2** in ethanolic solutions were recorded in the range from 200 to 800 nm. The two absorptions of the complex at 208 and 260 nm are assigned to  $\pi$ – $\pi^*$  transitions of the aryl ring and carbonyl group [12]. Compared with the electronic spectral data of the free ligand, the absorption peaks do not show an obvious shift. In the visible region, very weak absorptions near 730 nm for the Ni(II) complex are assigned to  $d$ – $d$  transitions [13], consistent with nickel in an octahedral environment.

#### Thermal analysis

The thermal stability of a crystal is an important factor for crystal growth and potential applications. Therefore, DSC and TG analyses were carried out over

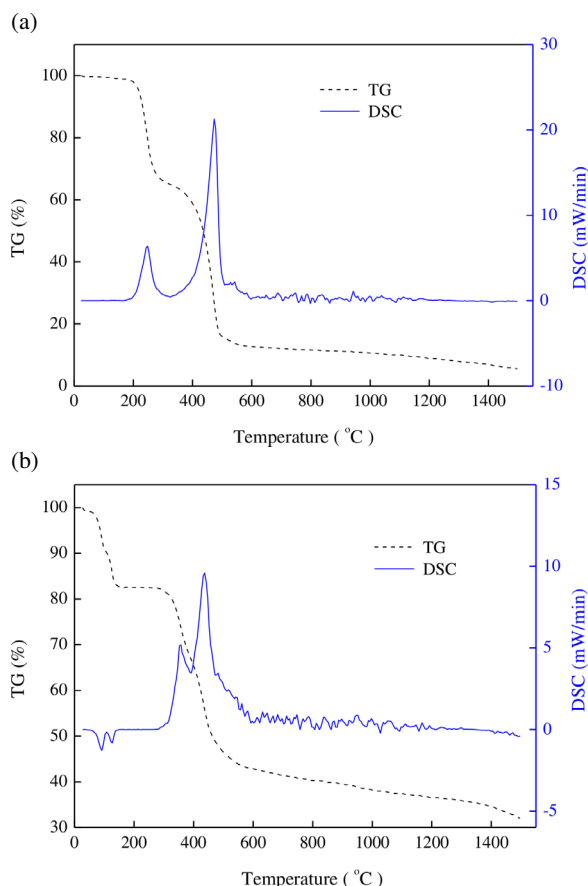


Fig. 6 (color online). TG-DSC curves of **1** (a) and **2** (b).

the temperature range from 25 to 1500 °C under a nitrogen atmosphere.

The TG-DSC curves of **1** and **2** are shown in Fig. 6. The HCPTP molecule (**1**) began to decompose at 168 °C. The TG-DSC curves of [Ni(CPTP)<sub>2</sub>-(C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub>](C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub> (**2**) shows decomposition of the complex in three steps. The first step at about 52–102 °C with a mass loss of 9.1 % (calcd. 9.2 %) is due to the evolution of two solvate ethanol molecules, for which the DSC curve shows an endothermic peak. The second decomposition at 102–167 °C with a mass loss of 8.6 % is close to the theoretical mass loss of two ethanol molecules coordinated to Ni. The last step occurs at 267–592 °C, accompanied by two exothermic peaks in the DSC curve due to the decomposition of the organic residues.

In summary, a new 4-heterocyclic acylpyrazolone nickel(II) complex [Ni(CPTP)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub>](C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub> has been synthesized. The coordination around the Ni is a slightly distorted octahedron. In-

Table 3. Crystallographic data for HCPTP (**1**) and [NiL<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub>](C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub> (**2**).

	<b>1</b>	<b>2</b>
Formula	C <sub>20</sub> H <sub>13</sub> ClN <sub>2</sub> O <sub>2</sub> S	C <sub>48</sub> H <sub>48</sub> C <sub>12</sub> N <sub>4</sub> NiO <sub>8</sub> S <sub>2</sub>
<i>M<sub>r</sub></i>	380.84	1002.63
Crystal size, mm <sup>3</sup>	0.25 × 0.20 × 0.20	0.37 × 0.30 × 0.30
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	6.0686(2)	11.8800(6)
<i>b</i> , Å	18.6887(5)	14.1744(7)
<i>c</i> , Å	14.9734(4)	14.5643(7)
$\alpha$ , deg	90	91.598(1)
$\beta$ , deg	91.559(1)	104.050(1)
$\gamma$ , deg	90	91.335(1)
<i>V</i> , Å <sup>3</sup>	1697.57(9)	2377.1(2)
<i>Z</i>	4	2
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.49	1.40
$\mu$ (MoK $\alpha$ ), cm <sup>-1</sup>	0.4	0.7
<i>F</i> (000), e	784.0	1044
<i>hkl</i> range	-7 → +8, $\pm$ 24,	-14 → +13, $\pm$ 17,
	$\pm$ 19	-16 → +17
$((\sin \theta)/\lambda)_{\max}$ , Å <sup>-1</sup>	0.667	0.606
Refl. measured /	22656	28134
unique /	4206	8847
<i>R</i> <sub>int</sub>	0.0239	0.0250
Param. refined	236	606
<i>R</i> ( <i>F</i> ) / <i>wR</i> ( <i>F</i> <sup>2</sup> ) <sup>a</sup> (all refl.)	0.0337 / 0.0913	0.0390 / 0.1036
GoF ( <i>F</i> <sup>2</sup> ) <sup>b</sup>	1.061	1.042
$\Delta\rho_{\text{fin}}$ (max / min), e Å <sup>-3</sup>	0.36 / -0.30	0.90 / -0.37

<sup>a</sup>  $R1 = \frac{\sum |F_o| - \sum |F_c|}{\sum |F_o|}$ ,  $wR2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]}{1/2}$ ,  $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ , where *P* = (Max(*F<sub>o</sub><sup>2</sup>*), 0) + 2*F<sub>c</sub><sup>2</sup>* / 3 and *A* and *B* are constants adjusted by the program; <sup>b</sup> GoF =  $[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$ , where *n*<sub>obs</sub> is the number of data and *n*<sub>param</sub> the number of refined parameters.

termolecular hydrogen bonds O–H...O and O–H...N provide further stability.

## Experimental Section

### General methods and materials

All reagents were obtained from commercial sources and used without purification. C, H and N analyses were carried out with an Elementar vario EL III elemental analyzer. Infrared spectra were recorded using a Nicolet 5700 spectrophotometer (4000–400 cm<sup>-1</sup>) with a crystalline sample in KBr pellets. Thermal analysis was performed on a Netzsch STA449F3 TG-DSC thermal analyzer in an atmosphere of N<sub>2</sub> with a heating rate of 5 K min<sup>-1</sup>. UV/Vis spectra were recorded on a Perkin-Elmer Lambda35 spectrophotometer.

### Synthesis of HCPTP (**1**, Scheme 1)

Compound **1** was synthesized from 1-(4-chlorophenyl)-3-phenyl-1H-pyrazol-5(4H)-one and 2-thenoyl chloride (thiophene-2-carbonyl chloride) and purified according to the method proposed by Jensen [14]. Starting materials: 1-(4-chlorophenyl)-3-phenyl-1H-pyrazol-5(4H)-one, 6.77 g,

25 mmol; 2-thenoyl chloride, 2.68 mL, 25 mmol. The overall yield was 73%. – Analysis for  $C_{20}H_{13}ClN_2O_2S$ : calcd. C 63.07, H 3.18, N 7.36; found C 63.02, H 3.12, N 7.41. Block-shaped golden single crystals suitable for single-crystal X-ray diffraction were grown from toluene by slow evaporation of the solvent over a period of several days.

*Synthesis of [Ni(CPTP)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub>](C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub> (2; Scheme 1)*

A mixture of a 10 mL of a solution of HCPTP (2 mmol, 0.5365 g) in anhydrous ethanol and 10 mL of an ethanolic solution of Ni(Ac)<sub>2</sub>·4H<sub>2</sub>O (1 mmol, 0.2488 g) was refluxed for 4 h at 75–80 °C. Green single crystals were obtained by slow evaporation of the solvent from the reaction mixture at r. t. after several days; yield: 87%. – Analysis for  $C_{34}H_{34}N_4O_8Ni$  (%): calcd. C 59.59, H 5.00, N 8.18; found C 59.75, H 4.92, N 8.05.

*Crystal structure determinations*

Crystallographic measurements were made on a Bruker Smart CCD single-crystal diffractometer with MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) by using  $\phi$  and  $\omega$  scan techniques at r. t. Accurate unit cell parameters and the orientation ma-

trix were obtained from least-squares refinements using the programs SMART and SAINT [15], and the data were integrated using SAINT. The structures were solved by Direct Methods (SHELXS-97 [16]) and refined by full-matrix least-squares techniques on  $F^2$  using SHELXL-97 [16]. The hydrogen atoms were observed in the difference Fourier syntheses or placed geometrically and treated as riding on their parent atoms except H atoms of OH. The C atoms (C45A, C45B and C46A, C46B) of one of the two ethanol molecules coordinated to the Ni atom were found to be disordered over two sites in a ratio of 0.593(5):0.407(5). Table 3 contains the crystal data and numbers pertinent to the data collection and structure refinement of **1** and **2**.

CCDC 846953 and 846813 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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