

## A novel two-dimensional nickel(II) coordination polymer with 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene and azide ligands

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The coordination geometry of the Ni<sup>II</sup> atom in the title complex, poly[diiazidobis[ $\mu$ -1,4-bis(1,2,4-triazol-1-ylmethyl)benzene- $\kappa^2N^4:N^4$ ]nickel(II)], [Ni(N<sub>3</sub>)<sub>2</sub>(C<sub>12</sub>H<sub>12</sub>N<sub>6</sub>)<sub>2</sub>]<sub>n</sub>, is a distorted octahedron, in which the Ni<sup>II</sup> atom lies on an inversion centre and is coordinated by four N atoms from the triazole rings of two symmetry-related pairs of 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (bbtz) ligands and two N atoms from two symmetry-related monodentate azide ligands. The Ni<sup>II</sup> atoms are bridged by four bbtz ligands to form a two-dimensional (4,4)-network.

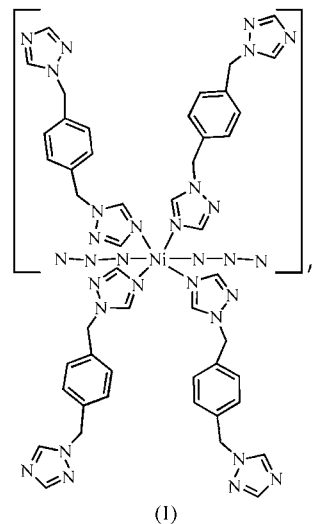
### Comment

Recently, considerable attention has been paid to transition metal coordination polymers, due to their intriguing structures and potential application as functional materials (Batten & Robson, 1998; Blake *et al.*, 1999; Kitagawa *et al.*, 2004). 1,2,4-Triazole and its derivatives are very interesting ligands because they combine the coordination geometry of both pyrazole and imidazole with regard to the arrangement of their three heteroatoms. Some novel coordination polymers with the flexible bis(triazole) ligands have already been synthesized (Haasnoot, 2000; Albada *et al.*, 2000; Zhao *et al.*, 2002; Meng *et al.*, 2004; Li *et al.*, 2005).

In our previous studies, we synthesized several coordination polymers with the flexible ligands 1,2-bis(1,2,4-triazol-1-yl)ethane (bte) (Wang *et al.*, 2005; Zhu *et al.*, 2006) and 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (bbtz; Li *et al.*, 2005). In the present paper, we report the synthesis and crystal structure of the title novel two-dimensional coordination polymer, [Ni(N<sub>3</sub>)<sub>2</sub>(bbtz)<sub>2</sub>]<sub>n</sub>, (I).

As shown in Fig. 1, the Ni<sup>II</sup> atom of (I) occupies an inversion centre. The coordination geometry of the Ni<sup>II</sup> atom is distorted octahedral. It is coordinated equatorially by four N atoms from the triazole rings of two symmetry-related pairs of

bbtz molecules, in which two methylene groups link the benzene ring and two triazole rings [Ni1–N3 = 2.1162 (16) Å



and Ni1–N6<sup>i</sup> = 2.1012 (16) Å; symmetry code: (i)  $x + 1, -y + \frac{3}{2}, z - \frac{1}{2}$ ], and axially by two N atoms from two symmetry-related azide ligands [Ni1–N7 = 2.1112 (17) Å]. This coordination environment is similar to those in [Ni(NCO)<sub>2</sub>(bte)<sub>2</sub>]<sub>n</sub> and [Ni(N<sub>3</sub>)<sub>2</sub>(bte)<sub>2</sub>]<sub>n</sub> (Zhu *et al.*, 2006). The Ni–N(triazole) bond lengths in (I) are in the range 2.1012 (16)–2.1162 (16) Å, corresponding to the values [in the range 2.095 (2)–2.1185 (13) Å] in [Ni(NCO)<sub>2</sub>(bte)<sub>2</sub>]<sub>n</sub> and [Ni(N<sub>3</sub>)<sub>2</sub>(bte)<sub>2</sub>]<sub>n</sub> (Zhu *et al.*, 2006), and in [NiCl<sub>2</sub>(trzppo)<sub>4</sub>·6H<sub>2</sub>O [trzppo is  $\beta$ -(1,2,4-triazol-1-yl)propiofenone; Jian *et al.*, 2003].

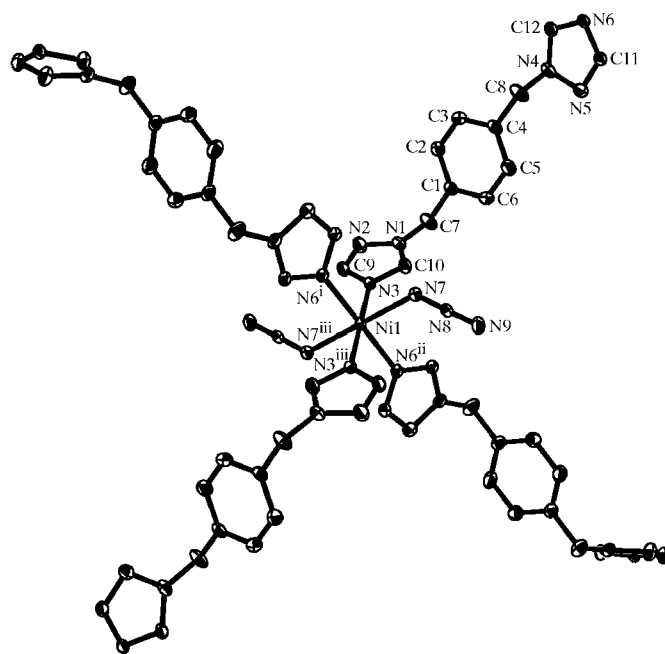


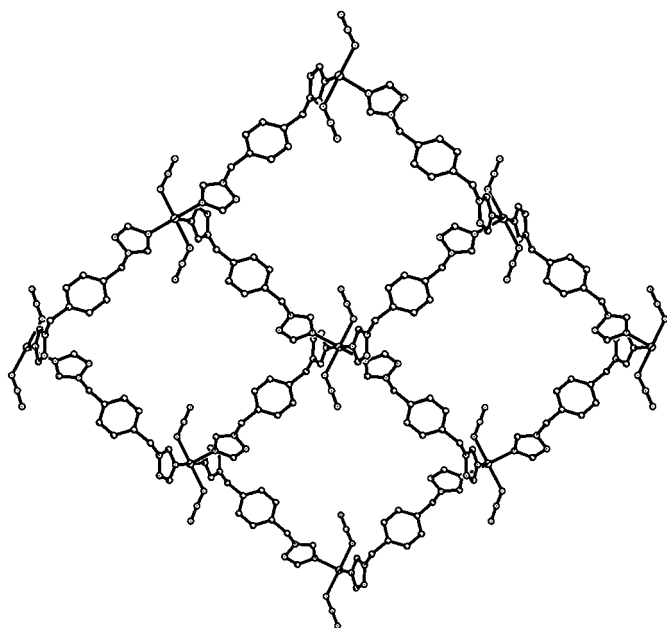
Figure 1

The coordination environment of the Ni<sup>II</sup> atom of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i)  $x + 1, -y + \frac{3}{2}, z - \frac{1}{2}$ ; (ii)  $-x, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $-x + 1, -y + 1, -z$ .]

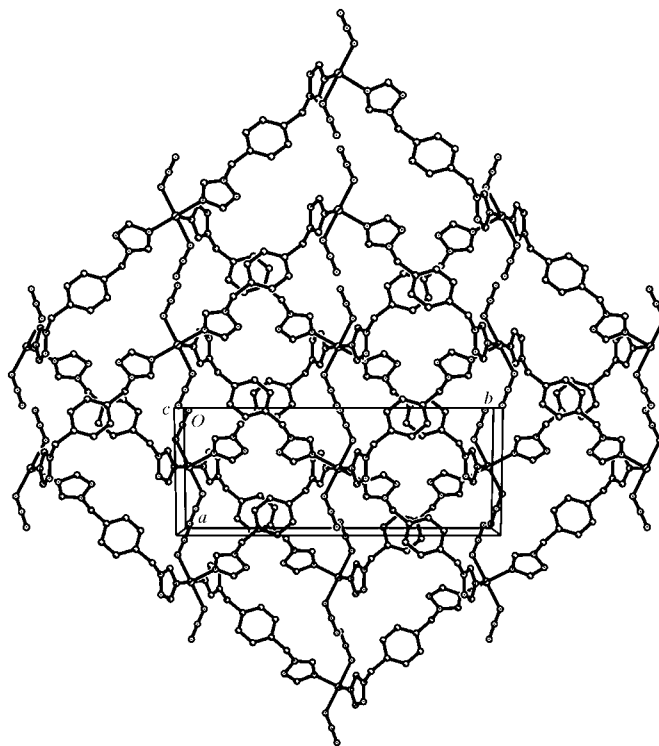
The N–Ni–N bond angles are in the range 86.11 (6)–93.89 (6)°, close to 90°. The Ni–N(azide) bond lengths are 2.1112 (17) Å, similar to the Ni–N(triazole) bond lengths, compared with the Ni–N(azide) bond lengths of 2.100 (3) and 2.108 (3) Å in the monodentate coordination azide complex  $[\text{Ni}(\text{N}_3)_2(\text{bte})_2]_n$  (Zhu *et al.*, 2006). The azide ligand is almost linear [bond angle N7–N8–N9 = 177.2 (3)°], in good agreement with the results usually obtained for monodentate azide complexes. The Ni1–N7–N8 bond angle is 129.58 (14)°.

Because the methyl C atom of bbtz can rotate freely to adjust itself to the coordination environment, bbtz can exhibit *trans-gauche* and *gauche-gauche* conformations (Li *et al.*, 2005). The bbtz ligands of (I) exhibit the *trans-gauche* conformation, similar to the free bbtz molecule (Peng *et al.*, 2004). The three rings (two triazole rings and one benzene ring) of one bbtz ligand are not coplanar. The dihedral angle between the two triazole planes is 63.70 (9)° in (I), but 0° in free bbtz due to symmetry. The dihedral angles between the benzene ring plane and the N1–N3/C9/C10 and N4–N6/C11/C12 triazole planes in (I) are 66.46 (9) and 66.10 (7)°, respectively, compared with 77.81 (9)° in free bbtz (Peng *et al.*, 2004).

As illustrated in Fig. 2, each bbtz ligand in (I) coordinates to  $\text{Ni}^{\text{II}}$  atoms through its two 4-position triazole N atoms, thus acting as a bridging bidentate ligand to form a two-dimensional neutral (4,4)-network. The networks contain nearly square grids (52-membered rings), with an  $\text{Ni}^{\text{II}}$  atom at each corner and a bbtz ligand at each edge connecting two  $\text{Ni}^{\text{II}}$  atoms. As a consequence of the crystal structure symmetry, the edge lengths are equal, with a value of 14.3646 (15) Å. The diagonal lengths of the nearly square grid are 20.542 (2) and 20.084 (2) Å, and the angles of the square are 88.7 (1) and 91.3 (1)°.



**Figure 2**  
A view of the two-dimensional (4,4)-network of (I) along the *c* direction.



**Figure 3**  
The cell packing of (I).

The nearly square grid sheets are stacked in an offset fashion parallel to the *c* direction. The offset half-cell superpositions of each pair of adjacent networks divide the voids into smaller rectangles whereby the azide anions of one sheet project into the holes of the next sheet. In the superposition structure, the sheets are arranged in an ...*A-B-A-B*... sequence (Fig. 3).

Complex (I) has a two-dimensional (4,4)-network, while  $[\text{Ni}(\text{NCO})_2(\text{bte})_2]_n$  and  $[\text{Ni}(\text{N}_3)_2(\text{bte})_2]_n$  (Zhu *et al.*, 2006) form one-dimensional double chains. The reason may be that bte is more flexible than bbtz.

### Experimental

A H<sub>2</sub>O–MeOH solution (20 ml, 1:1 *v/v*) of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.145 g, 0.50 mmol) was added to one leg of a H-shaped tube, and a H<sub>2</sub>O–MeOH solution (20 ml, 1:1 *v/v*) of bbtz (0.240 g, 1.00 mmol) and  $\text{NaN}_3$  (0.065 g, 1.00 mmol) was added to the other leg of the tube. After several weeks, well shaped blue single crystals of (I) were obtained. Analysis found: C 46.21, H 3.83, N 40.38%; calculated for  $\text{C}_{24}\text{H}_{24}\text{N}_{18}\text{Ni}$ : C 46.25, H 3.88, N 40.46%.

#### Crystal data

$[\text{Ni}(\text{N}_3)_2(\text{C}_{12}\text{H}_{12}\text{N}_6)_2]$	$V = 1378.3 (4) \text{ \AA}^3$
$M_r = 623.32$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 8.2566 (14) \text{ \AA}$	$\mu = 0.76 \text{ mm}^{-1}$
$b = 20.542 (3) \text{ \AA}$	$T = 193 (2) \text{ K}$
$c = 8.3351 (14) \text{ \AA}$	$0.40 \times 0.30 \times 0.18 \text{ mm}$
$\beta = 102.850 (4)^\circ$	

## Data collection

Rigaku Mercury CCD area-detector diffractometer  
Absorption correction: multi-scan (Jacobson, 1998)  
 $T_{\min} = 0.752$ ,  $T_{\max} = 0.876$

15202 measured reflections  
3157 independent reflections  
2850 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.028$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.102$   
 $S = 1.08$   
3157 reflections

196 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.29 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.44 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Ni1—N6 <sup>i</sup>	2.1012 (16)	Ni1—N3	2.1162 (16)
Ni1—N7	2.1112 (17)		
N6 <sup>i</sup> —Ni1—N7	88.23 (6)	N8—N7—Ni1	129.58 (14)
N6 <sup>i</sup> —Ni1—N3	88.09 (6)	N9—N8—N7	177.2 (3)
N7—Ni1—N3	86.11 (6)		

Symmetry code: (i)  $x + 1, -y + \frac{3}{2}, z - \frac{1}{2}$ .

H atoms were placed in idealized positions and refined as riding, with C—H distances of 0.95 (triazole and benzene) and 0.99  $\text{\AA}$  (methyl), and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3092). Services for accessing these data are described at the back of the journal.

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