

A novel two-dimensional cobalt(II) coordination polymer with 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene

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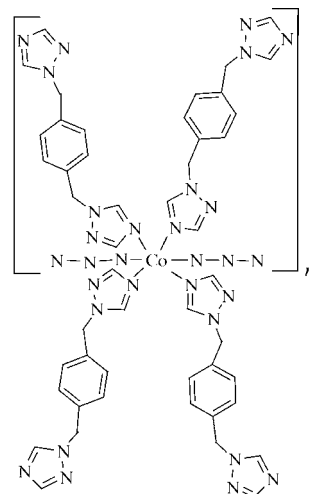
In the crystal structure of the title complex, poly[[diazidocobalt(II)]-di- μ -1,4-bis(1,2,4-triazol-1-ylmethyl)benzene- $\kappa^4 N^4:N^4$], $[\text{Co}(\text{N}_3)_2(\text{bbtz})_2]_n$, where bbtz is 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene ($\text{C}_{12}\text{H}_{12}\text{N}_6$), the Co^{II} atom, which lies on an inversion centre, is six-coordinated by four N atoms from four bbtz ligands and by two N atoms from two azide ligands, in a distorted octahedral coordination environment. The Co^{II} atoms are bridged by four bbtz ligands to form a two-dimensional [4,4]-network.

Comment

The construction of coordination polymeric architectures is a rapidly developing area of research, because of their fascinating structural motifs and potential applications as functional materials (Batten & Robson, 1998; Moulton & Zaworotko, 2001). Rigid rod-like N-donor ligands have been intensively employed and a variety of topological architectures have been synthesized (Fujita *et al.*, 1994; Li *et al.*, 2001). However, flexible ligands containing triazole or imidazole have not been well studied to date (Effendy *et al.*, 2004; Van Albada *et al.*, 2000; Shen *et al.*, 1999). In our previous studies, we have synthesized several coordination polymers with the flexible ligand 1,2-bis(1,2,4-triazol-1-yl)ethane (bte; Li *et al.*, 2003; Zhu *et al.*, 2004). We report here the preparation and crystal structure of the title compound, (I), a novel two-dimensional coordination polymer incorporating the 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (bbtz) ligand.

As shown in Fig. 1, the Co^{II} atom of (I) occupies an inversion centre. The coordination geometry of the Co^{II} atom is distorted octahedral, coordinated equatorially by four N atoms from the triazole rings of four symmetry-related bbtz ligands, and axially by two N atoms from two symmetry-related azide ligands. This coordination environment is similar to those observed in the structures of $[\text{Co}(4\text{-benzoyl-}$

pyridine) $_4(\text{N}_3)_2]$ (Goher & Mautner, 1999a), $\{[\text{Co}(\text{bpm})_2(\text{N}_3)_2][\text{Co}(\text{bpm})_2(\text{H}_2\text{O})_2]\}(\text{ClO}_4)_2$ [bpm is bis(pyrazol-1-yl)methane; Tang *et al.*, 2000] and $[\text{Co}(4\text{-methylpyridine})_4(\text{N}_3)]\text{-PF}_6$ (Goher & Mautner, 1999b).



(I)

The azide anion normally coordinates to cobalt(II) and other metal atoms in the μ -1,1- or μ -1,3-mode (De Munno *et al.*, 1996; Viau *et al.*, 1997; Goher & Mautner, 1999b; Wang *et al.*, 2003; Ribas *et al.*, 1999). Few studies of cobalt(II) complexes with monodentate azide have been reported to date (Randaccio *et al.*, 1998; Goher & Mautner, 1999a; Tang *et al.*, 2000). The $\text{Co}-\text{N}(\text{N}_3)$ bond length in (I) is 2.1381 (18) Å, longer than the corresponding values reported for azidecobalamin [1.985 (3) Å; Randaccio *et al.*, 1998], $[\text{Co}(4\text{-benzoylpyridine})_4(\text{N}_3)_2]$ [2.091 (2) Å; Goher & Mautner, 1999a] and $\{[\text{Co}(\text{bpm})_2(\text{N}_3)_2][\text{Co}(\text{bpm})_2(\text{H}_2\text{O})_2]\}(\text{ClO}_4)_2$ [2.107 (3) Å; Tang *et al.*, 2000], and a little shorter than those found in the structure of $[\text{Co}(4\text{-methylpyridine})_4(\text{N}_3)]\text{PF}_6$, containing μ -1,3-bridging azide ligands (2.153–2.159 Å; Goher & Mautner, 1999b). The $\text{Co}-\text{N}-\text{N}(\text{N}_3)$ bond angle is 130.23 (15)°, which is close to the corresponding values of 116.0 (3), 128.2 (2), 129.3 (3) and 135.4 (2)°, respectively, in these same four cited compounds. The azide ligand is almost linear in (I) [$\text{N}-\text{N}-\text{N} = 176.2 (3)^\circ$], in good agreement with data usually obtained for monodentate azide complexes.

Because the methyl C atom of bbtz can rotate freely to adjust itself to the coordination environment, bbtz can exhibit the *trans-gauche* and *gauche-gauche* conformations, similar to the ligand 1,4-bis(imidazol-1-ylmethyl)benzene (bix), as shown in the polyrotaxane $[\text{Ag}_2(\text{bix})_3](\text{NO}_3)_2$ (Hoskins *et al.*, 1997a). The bbtz ligands exhibit the *trans-gauche* conformation in (I), similar to bix in $[\text{Mn}(\text{bix})_3(\text{NO}_2)_2]\cdot 4\text{H}_2\text{O}$, (II) (Shen *et al.*, 1999). 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 61.94 (19)°, compared with 39.1° in the terminal bix in (II). The dihedral angles between the benzene plane and the N1- and N4-triazole planes are 67.26 (9) and 66.96 (7)°, respectively, similar to the corresponding values in the terminal bix in (II) of 88.9 and

77.4°. In the bridging bix in ligand (II), the dihedral angles between the imidazole and benzene planes are 106.0 and 91.4°, respectively. Comparison with the free-ligand structures *p*-(*N,N*-dimethylamino)phenyl 1,2,4-triazol-1-yl ketone *p*-nitrophenylhydrazone, (III) (Stanković *et al.*, 1991), and (*RS,SR*)-4-[3-(4-fluorophenyl)-2-hydroxy-1-(1,2,4-triazol-1-yl)propyl]benzotrile, (IV) (Sodervall & Mutikainen, 2002), containing three rings (one triazole ring and two benzene rings), shows a much wider variation in these interplanar angles. For example, the dihedral angles between the two benzene planes are 9.0 and 62.7° (mean) for (III) and (IV), respectively.

As illustrated in Fig. 2, each bbtz ligand in (I) coordinates to Co^{II} atoms through its two triazole N atoms, thus acting as a bridging bidentate ligand to form a two-dimensional neutral [4,4]-network. The networks contain square grids (52-membered rings), with a Co^{II} atom at each corner and a bbtz ligand at each edge connecting two Co^{II} atoms. The square-grid sheets are stacked in an offset fashion parallel to the *c* direction. The offset half-cell superposition of each pair of adjacent networks divides the voids into smaller rectangles. The azide anions of one sheet project into the holes of the next sheet. In the superposition structure, the sheets are arranged in the sequence ...*A*-*B*-*A*-*B*... As a consequence of the symmetry of the crystal structure, the edge lengths are equal, with a value of 14.4156 (18) Å, similar to the corresponding metal-metal separations in the related bix complexes [Zn(bix)₂(NO₃)₂]·4.5H₂O [15.037 (2) Å; Hoskins *et al.*, 1997*b*], [Ag₂(bix)₃(NO₃)₂] [14.626 (2) Å; Hoskins *et al.*, 1997*a*] and [Mn(bix)₃(NO₂)₂]·4H₂O [12.659 Å; Shen *et al.*, 1999].

The structures of [Cu(btp)₂(CH₃CN)(H₂O)](CF₃SO₃)₂, (V), and [Cu(btp)₂(CH₃CN)₂](ClO₄)₂, (VI), with the related triazole ligand 1,3-bis(1,2,4-triazol-1-yl)propane (btp; Van

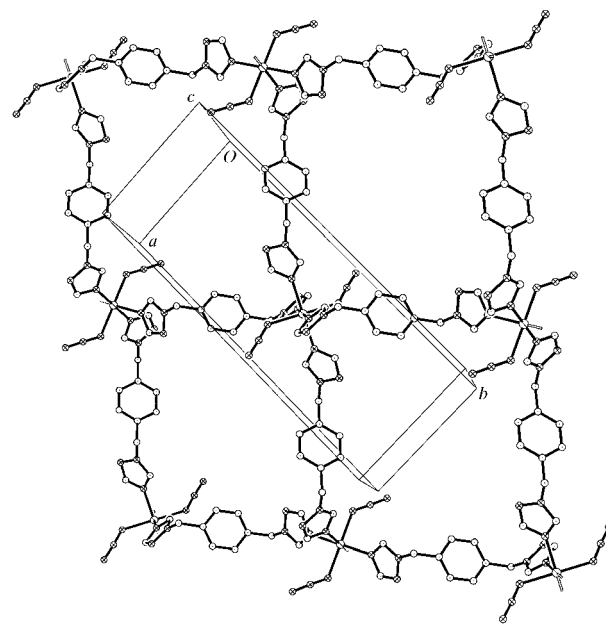


Figure 2

Part of the two-dimensional sheet of the [4,4]-network in (I). H atoms and the next offset sheet (see text) have been omitted for clarity.

Albada *et al.*, 2000), have a similar distorted octahedral structure, coordinated equatorially by four N atoms from the triazole rings of four symmetry-related btp ligands, and axially by one N atom from one acetonitrile molecule and one O atom from one water molecule for (V), and axially by two N atoms from two acetonitrile molecules for (VI). In both these structures, the Cu^{II} atoms are linked by the bridging btp ligands, resulting in two-dimensional networks with shortest Cu···Cu distances 8.753 (3) Å in (V) and 8.946 (4) Å in (VI). The metal-metal distances in structures containing triazole and imidazole ligands confirm the important ability of this family of ligands to adjust that distance.

Experimental

A H₂O-CH₃CN solution (1:1 v/v, 20 ml) of 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (bbtz; 0.060 g, 0.25 mmol) was added to one leg of a H-shaped tube, and a H₂O-CH₃CN solution (1:1 v/v, 20 ml) of NaN₃ (0.078 g, 1.2 mmol) and Co(NO₃)₂·6H₂O (0.146 g, 0.5 mmol) was added to the other leg. Well shaped pink crystals of (I) suitable for X-ray analysis were obtained after about three months. The product is stable under ambient conditions and is insoluble in most common inorganic and organic solvents. Analysis found: C 46.17, H 3.91, N 40.38%; calculated for C₂₄H₂₄CoN₁₈: C 46.23, H 3.88, N 40.44%.

Crystal data

[Co(N₃)₂(C₁₂H₁₂N₆)₂]
M_r = 623.54
 Monoclinic, *P*2₁/*c*
a = 8.2682 (17) Å
b = 20.593 (4) Å
c = 8.3738 (17) Å
 β = 103.273 (4)°
V = 1387.7 (5) Å³
Z = 2

D_x = 1.492 Mg m⁻³
 Mo K α radiation
 Cell parameters from 5765 reflections
 θ = 3.1–27.5°
 μ = 0.67 mm⁻¹
T = 193.2 K
 Block, pink
 0.60 × 0.25 × 0.22 mm

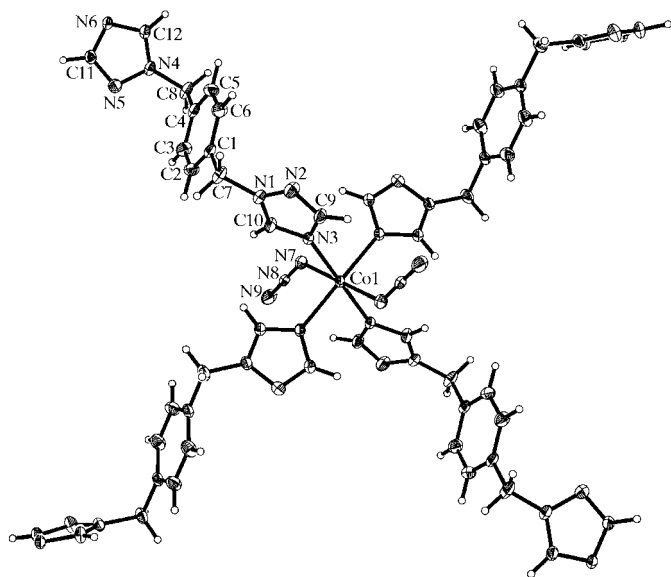


Figure 1

A view of the coordination of the Co^{II} atom in (I), with displacement ellipsoids drawn at the 50% probability level. The symmetry code is as given in Table 1.

Data collection

Rigaku Mercury CCD area-detector diffractometer	2772 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.032$
Absorption correction: multi-scan (North <i>et al.</i> , 1968)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.786$, $T_{\text{max}} = 0.867$	$h = -10 \rightarrow 10$
15 397 measured reflections	$k = -26 \rightarrow 22$
3172 independent reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.6596P]$
$R(F) = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.106$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.36 \text{ e } \text{Å}^{-3}$
3172 reflections	$\Delta\rho_{\text{min}} = -0.32 \text{ e } \text{Å}^{-3}$
197 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Co1—N7	2.1381 (18)	N7—N8	1.163 (2)
Co1—N6 ⁱ	2.1529 (17)	N8—N9	1.172 (3)
Co1—N3	2.1628 (17)		
N7—Co1—N6 ⁱ	88.95 (7)	N8—N7—Co1	130.23 (15)
N7—Co1—N3	85.51 (7)	N7—N8—N9	176.2 (3)
N6 ⁱ —Co1—N3	87.11 (6)		

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

H atoms were placed in idealized positions and refined as riding, with C—H distances of 0.95 (triazole and benzene) and 0.99 Å (methane), 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: GA1074). Services for accessing these data are described at the back of the journal.

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