

Jun Luo,<sup>a,b\*</sup> Bao-Shu Liu,<sup>b</sup>  
Xi-Geng Zhou,<sup>a</sup> Lin-Hong  
Weng,<sup>a</sup> Yan-Rong Li<sup>a</sup> and  
Rui-Fang Cai<sup>a</sup>

<sup>a</sup>Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China, and <sup>b</sup>School of Pharmacy, Second Military Medical University, Shanghai 200433, People's Republic of China

Correspondence e-mail: xgzhou@fudan.edu.cn

#### Key indicators

Single-crystal X-ray study  
T = 293 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$   
R factor = 0.054  
wR factor = 0.109  
Data-to-parameter ratio = 10.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

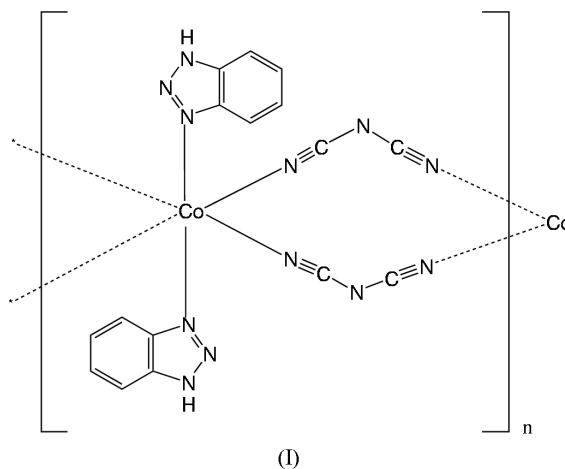
## catena-Poly[[bis(1*H*-1,2,3-benzotriazole- $\kappa\text{N}^3$ )cobalt(II)]-di- $\mu$ -dicyanamido- $\kappa^4\text{N}^1:\text{N}^3$ ]

In the title complex,  $[\text{Co}(\text{C}_2\text{N}_3)_2(\text{bentrz})_2]_n$  (bentrz is 1*H*-1,2,3-benzotriazole,  $\text{C}_6\text{H}_5\text{N}_3$ ), the Co atom occupies a special position with  $2/m$  site symmetry and is coordinated in the equatorial plane by four dicyanamide nitrile N atoms [ $\text{Co}-\text{N} = 2.110(3) \text{ \AA}$ ], and in the apical positions by two monodentate 1,2,3-benzotriazole N atoms [ $\text{Co}-\text{N} = 2.157(4) \text{ \AA}$ ], forming a slightly distorted octahedral geometry. The bentrz ligands lie on a mirror plane. Neighbouring Co atoms are connected *via* double dicyanamide bridges to form a one-dimensional infinite chain; these chains are cross-linked *via* hydrogen-bond interactions between one dicyanamide amide N atom and the H atom on the uncoordinated N atom of a 1,2,3-benzotriazole ligand from an adjacent chain, thus forming a three-dimensional network.

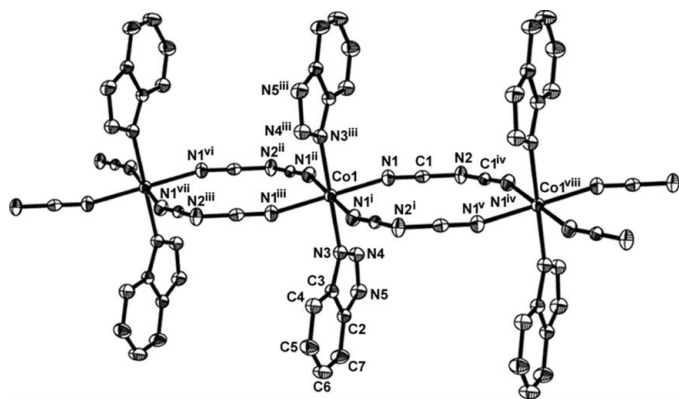
Received 26 August 2004  
Accepted 2 September 2004  
Online 11 September 2004

#### Comment

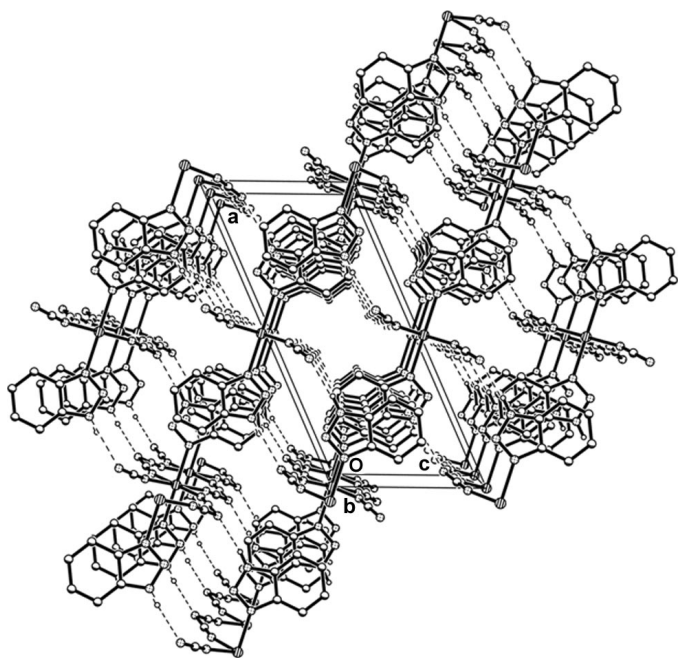
Dicyanamide complexes are the focus of intense research interest since the binary complexes show distinct structural motifs (Manson *et al.*, 1998; Batten *et al.*, 1999) and display fascinating magnetic properties (Manson *et al.*, 1999; Batten *et al.*, 1998). Various workers have shown that modification of the complexes through the use of nitrogen-containing conjugated rigid co-ligands, such as 2,2'-bipyridine (Luo *et al.*, 2002), 4,4'-bipyridine (Jensen *et al.*, 2002), pyrimidine (Manson *et al.*, 2003), 2,2'-bipyrimidine (Triki *et al.*, 2001) and pyrazine (Jensen *et al.*, 2001) can result in new network topologies and interesting magnetic properties.



1,2,3-Benzotriazole (bentrz) is a rigid nitrogen-containing multidentate donor ligand and may be used as a building block to construct high-dimensional complexes. However, until now,



**Figure 1**  
View of a fragment of (I), showing the atom-labelling scheme and the connectivity of adjacent Co atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity (symmetry codes are as in Table 1).



**Figure 2**  
Three-dimensional network structure of (I) formed by hydrogen-bonding interactions (dashed lines).

no structurally characterized dicyanamide complex with bentrz as co-ligand has been reported. Recently, we have synthesized several dicyanamide complexes with polyamine co-ligands, and found that the difference in nature of polyamine co-ligands leads to a significant change of the structures of the complexes from mononuclear to three-dimensional helical network (Luo *et al.*, 2003, 2004). In order to further understand the influence of the co-ligands on the structures and properties of dicyanamide complexes, we report here the synthesis and crystal structure of  $[\text{Co}(\text{C}_2\text{N}_3)_2(\text{bentrz})_2]_n$ , (I).

In (I), the Co atom lies on a special position with symmetry  $2/m$ . The cobalt ion is coordinated by four dicyanamide anions and two *trans*-bentrz molecules to form a slightly distorted octahedral geometry, in which the equatorial plane is formed

by four nitrile N atoms (atoms N1, N1<sup>i</sup>, N1<sup>ii</sup> and N1<sup>iii</sup>; see Table 1 for symmetry codes) of the dicyanamide anions, and the apical positions are occupied by two N atoms (N3 and N3<sup>iii</sup>) from two monodentate bentrz molecules (Fig. 1). The cobalt ions are linked by double dicyanamide anion bridges to form a one-dimensional infinite chain; hydrogen-bond interactions between one amide N atom of a dicyanamide anion and the H atom on the uncoordinated N atom of bentrz from an adjacent chain, listed in Table 2, result in the formation of a three-dimensional network (Fig. 2).

In the complex, the axial Co–N(bentrz) distances [2.157 (4) Å] are slightly longer than the Co–N(dicyanamide) distances [2.110 (3) Å]. These values are comparable to the corresponding distances in other cobalt dicyanamide complexes (Jensen *et al.*, 2001, 2002). The distortion of octahedral geometry for the complex is small, as reflected by the deviation of the *cis*-N–Co–N angles [89.81 (17)–90.19 (17)°] from 90°.

In the complex, the bentrz ligands lie on a mirror plane with  $y = 0$ , and are constrained to be planar. The dicyanamide anions are also close to planar, with typical bond distances and angles (Table 1) (Vangdal *et al.*, 2002; Manson *et al.*, 2003; Carranza *et al.*, 2002).

## Experimental

An aqueous solution (3 ml) of sodium dicyanamide (0.60 mmol, 53.42 mg) was added to an aqueous solution (3 ml) of cobalt nitrate (0.30 mmol, 87.31 mg) and stirred for 2 min. To the mixed solution was added dropwise an aqueous solution (4 ml) of 1,2,3-benzotriazole (0.30 mmol, 35.74 mg). An orange precipitate was immediately formed; the mixture was then warmed slowly until the precipitate dissolved. One week later, orange rod-shaped crystals of (I) were isolated in 45% yield. Analysis calculated for  $\text{C}_{16}\text{H}_{10}\text{CoN}_{12}$ : C 44.77, H 2.35, N 39.16; found C 45.03, H 2.63, N 39.43%.

### Crystal data

$[\text{Co}(\text{C}_2\text{N}_3)_2(\text{C}_6\text{H}_5\text{N}_3)_2]$   
 $M_r = 429.29$   
 Monoclinic,  $C2/m$   
 $a = 17.259$  (6) Å  
 $b = 7.249$  (3) Å  
 $c = 8.030$  (3) Å  
 $\beta = 114.002$  (5)°  
 $V = 917.8$  (6) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.553$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 701 reflections  
 $\theta = 2.6$ – $22.9$ °  
 $\mu = 0.97$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Rod, orange  
 $0.15 \times 0.05 \times 0.02$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.869$ ,  $T_{\max} = 0.981$   
 1920 measured reflections

878 independent reflections  
 678 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.059$   
 $\theta_{\max} = 25.0$ °  
 $h = -14 \rightarrow 20$   
 $k = -8 \rightarrow 8$   
 $l = -9 \rightarrow 7$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.109$   
 $S = 1.10$   
 878 reflections  
 83 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0489P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.42$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.27$  e Å<sup>-3</sup>

This project was supported by the National Natural Science Foundation of China.

**Table 1**  
Selected geometric parameters (Å, °).

Co1—N1	2.110 (3)	N1—C1	1.150 (5)
Co1—N3	2.157 (4)	N2—C1	1.324 (5)
N1 <sup>i</sup> —Co1—N1	89.81 (17)	N1—Co1—N3 <sup>iii</sup>	89.83 (12)
N1 <sup>i</sup> —Co1—N1 <sup>iii</sup>	90.19 (17)	N3—Co1—N3 <sup>iii</sup>	180
N1 <sup>i</sup> —Co1—N3	89.83 (12)	C1—N1—Co1	160.8 (3)
N1 <sup>ii</sup> —Co1—N3	90.17 (12)	C1 <sup>iv</sup> —N2—C1	115.5 (4)
N1—Co1—N3	90.17 (12)	N1—C1—N2	176.3 (4)
N1—Co1—N1 <sup>iii</sup>	180		

Symmetry codes: (i)  $-x, y, -z$ ; (ii)  $x, -y, z$ ; (iii)  $-x, -y, -z$ ; (iv)  $x, 1 - y, z$ .

**Table 2**  
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N5—H5A $\cdots$ N2 <sup>v</sup>	0.86	2.10	2.951 (6)	173

Symmetry codes: (v)  $\frac{1}{2} - x, \frac{1}{2} - y, -z$ .

All the H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with N—H distances of 0.86 Å and C—H distances of 0.93 Å. The constraint  $U_{iso}(H) = 1.2U_{eq}(\text{carrier atom})$  was applied in all cases.

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

## References

- Batten, S. R., Jensen, P., Kepert, C. J., Kurmoo, M., Moubaraki, B., Murray, K. S. & Price, D. J. (1999). *J. Chem. Soc. Dalton Trans.* pp. 2987–2997.
- Batten, S. R., Jensen, P., Moubaraki, B., Murray, K. S. & Robson, R. (1998). *Chem. Commun.* pp. 439–440.
- Bruker (2000). *SMART* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Carranza, J., Brennan, C., Sletten, J., Lloret, F. & Julve, M. (2002). *J. Chem. Soc. Dalton Trans.* pp. 3164–3170.
- Jensen, P., Batten, S. R., Moubaraki, B. & Murray, K. S. (2001). *J. Solid State Chem.* **159**, 352–361.
- Jensen, P., Batten, S. R., Moubaraki, B. & Murray, K. S. (2002). *J. Chem. Soc. Dalton Trans.* pp. 3712–3722.
- Luo, J., Zhou, X.-G., Gao, S., Weng, L.-H., Shao, Z.-H., Zhang, C.-M., Li, Y.-R., Zhang, J. & Cai, R.-F. (2004). *Inorg. Chem. Commun.* **7**, 669–672.
- Luo, J., Zhou, X.-G., Weng, L.-H. & Hou, X.-F. (2003). *Acta Cryst. C* **59**, m392–m395.
- Luo, J.-H., Hong, M.-C., Cao, R., Liang, Y.-C., Zhao, Y.-J., Wang, R.-H. & Weng, J.-B. (2002). *Polyhedron*, **21**, 893–898.
- Manson, J. L., Gu, J., Schlueter, J. A. & Wang, H.-H. (2003). *Inorg. Chem.* **42**, 3950–3955.
- Manson, J. L., Kmety, C. R., Epstein, A. J. & Miller, J. S. (1999). *Inorg. Chem.* **38**, 2552–2553.
- Manson, J. L., Lee, D. W., Rheingold, A. L. & Miller, J. S. (1998). *Inorg. Chem.* **37**, 5966–5967.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (2000). *SHELXTL*. Version 6.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Triki, S., Thétiot, F., Galán-Mascarós, J.-R., Pala Sala, J. & Dunbar, K. R. (2001). *New J. Chem.* **25**, 954–958.
- Vangdal, B., Carranza, J., Lloret, F., Julve, M. & Sletten, J. (2002). *J. Chem. Soc. Dalton Trans.* pp. 566–574.