

Lei Zheng, Jia Zhang, Ming-Ming Yu, Zhong-Hai Ni and Hui-Zhong Kou*

Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

Correspondence e-mail: kouhz@mail.tsinghua.edu.cn

Key indicators

Single-crystal X-ray study
 T = 298 K
 Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
 R factor = 0.037
 wR factor = 0.104
 Data-to-parameter ratio = 11.8

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

Bis(2-guanidinobenzimidazole- κ^2N,N')copper(II) bis(dicyanamide)

In the title compound, $[\text{Cu}(\text{C}_8\text{H}_9\text{N}_5)_2](\text{C}_2\text{N}_3)_2$, the Cu complex cation and dicyanamide anions lie on a twofold axis. Discounting the weak coordination of a dicyanamide anion, the Cu^{II} atom is coordinated by four N atoms from two 2-guanidinobenzimidazole ligands in a tetrahedrally distorted square-planar geometry. The cations and anions are linked *via* $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds, forming a two-dimensional network parallel to (010).

Received 22 August 2006
 Accepted 31 August 2006

Comment

Benzazoles are common components in organisms and are active in many biological processes (Castillo-Blum & Barba-Behrens, 2000). The coordinating behaviour of benzimidazole chelating ligands has been studied to mimic biological activities (Aminabhavi *et al.*, 1987). After functionalization, they have many applications, such as in fertilizers, antimicrobics, antibiotics, pesticides and neuroprotectors (Tanabe *et al.*, 1997; Katsura *et al.*, 1999; Schnur *et al.*, 1991; Jimonet, 1999; Barba-Behrens *et al.*, 1991). 2-Guanidinobenzimidazole (abbreviated as gb), a derivative of benzazole, has attracted much interest in recent years. Coordination compounds with guanidines or benzazoles as ligands have been studied (Barba-Behrens *et al.*, 1996; Andrade-López *et al.*, 1997; Cenicerós-Gómez, Barba-Behrens, Bernès *et al.*, 2000; Cenicerós-Gómez, Barba-Behrens, Quiroz-Castro *et al.*, 2000; Bishop *et al.*, 2001, 2002, 2003; Arablo *et al.*, 2003; van Albada *et al.*, 2002, 2006). As part of our continuing interest in dicyanamide-bridged Cu^{II} complexes, compound (I) was prepared by the reaction between $[\text{Cu}(\text{gb})_2]^{2+}$ and dicyanamide (dca^-) ions. In this paper, we report the crystal structure analysis of (I).

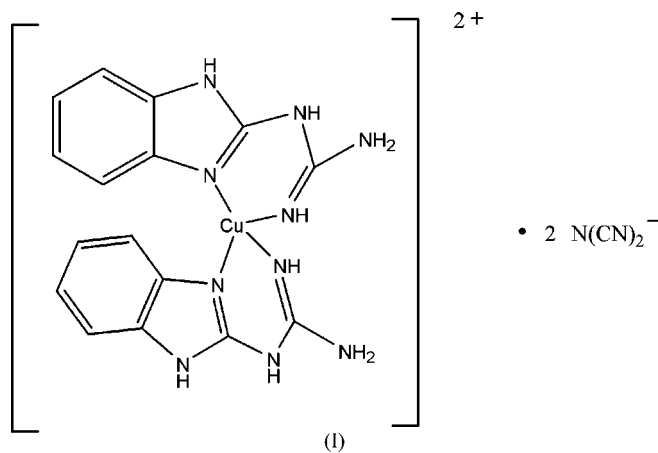


Fig. 1 shows the molecular structure of (I). The Cu atom is situated on a twofold axis, and is coordinated by four N atoms

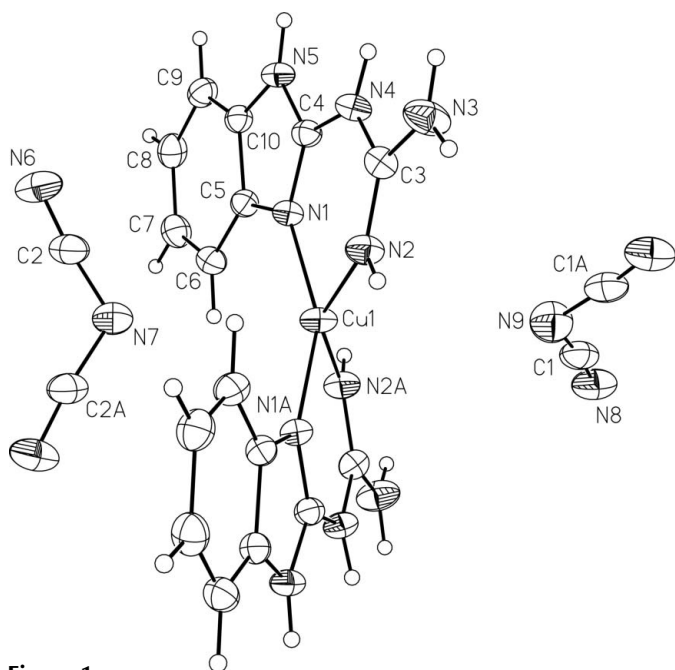


Figure 1

The formula unit of (I) (twice the asymmetric unit), showing 30% probability displacement ellipsoids and the atom-numbering scheme. Atoms N1A/N2A/C1A/C2A and unlabeled atoms are related to N1/N2/C1/C2 and other labeled atoms by the symmetry code $(1 - x, y, \frac{1}{2} - z)$.

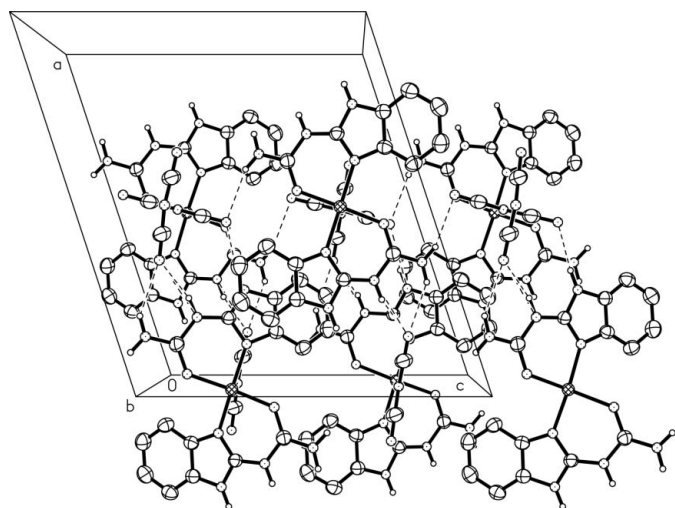


Figure 2

The two-dimensional network of (I) formed by hydrogen bonds (dashed lines) and π - π stacking interactions. H atoms have been omitted unless they are involved in hydrogen bonds.

from two gb ligands. The dicyanamide anions also have twofold rotational symmetry. Atom N7 of one of the dca⁻ anions weakly coordinates to the Cu^{II} atom at a distance of 3.123 (4) Å (Table 1). The primary coordination geometry is tetrahedrally distorted square-planar, the dihedral angle between the chelate rings (Cu1/N1/C4/N4/C3/N2 and its symmetry-related partner) being 43.8 (4)°. Compared to $[M(\text{gb})_2]^{2+}$ ($M = \text{Ni}, \text{Zn}$), despite having similar stoichiometries and coordination numbers, the coordination geometries are very different because of the distinctive electronic structures. The Ni^{II} complex displays a square-planar coordination

(Barba-Behrens *et al.*, 1996; Andrade-López *et al.*, 1997; Bishop *et al.*, 2001, 2002, 2003), while the Zn^{II} complex adopts a close to ideal tetrahedral geometry (Andrade-López *et al.*, 1997).

Each terminal N of the dicyanamide ions forms two N—H···N hydrogen bonds (Table 2). The $[\text{Cu}(\text{gb})_2]^{2+}$ cations and dicyanamide anions are linked by N—H···N hydrogen bonds, forming one-dimensional chains along the *a* axis (Fig. 2). The conjugated benzimidazole rings of the gb ligands of adjacent chains are parallel and stacked with a perpendicular interplanar distance of 3.25 Å. The chains are further connected by N—H···N hydrogen bonds, forming a two-dimensional network parallel to (010).

Experimental

The ligand and the copper salt were purchased commercially. Compound (I) was prepared by the following procedure: 5 ml aqueous solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (17 mg, 0.1 mmol) was slowly diffused into a methanol solution (5 ml) of sodium dicyanamide (18 mg, 0.2 mmol) and gb (35 mg, 0.2 mmol) through a single glass tube. After 3 d, dark-blue crystals of (I) appeared at the interface (yield 20%).

Crystal data

$[\text{Cu}(\text{C}_8\text{H}_9\text{N}_5)_2](\text{C}_2\text{N}_3)_2$
 $M_r = 546.05$
 Monoclinic, $C2/c$
 $a = 15.587$ (2) Å
 $b = 11.1008$ (13) Å
 $c = 13.7083$ (18) Å
 $\beta = 108.174$ (10)°
 $V = 2253.6$ (5) Å³

$Z = 4$
 $D_x = 1.609$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 1.02$ mm⁻¹
 $T = 298$ (2) K
 Block, dark blue
 $0.3 \times 0.3 \times 0.3$ mm

Data collection

Bruker P4 diffractometer
 ω scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.737$, $T_{\max} = 0.744$
 2486 measured reflections
 1992 independent reflections

1784 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$
 $\theta_{\text{max}} = 25.0^\circ$
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.104$
 $S = 1.06$
 1992 reflections
 169 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 2.3317P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.61$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—N2	1.952 (2)	C1—N9	1.309 (4)
Cu1—N1	1.9615 (19)	C2—N6	1.143 (4)
Cu1—N7	3.123 (4)	C2—N7	1.310 (4)
C1—N8	1.150 (4)		
N2 ⁱ —Cu1—N2	148.87 (15)	N1—Cu1—N1 ⁱ	156.10 (12)
N2—Cu1—N1	90.06 (9)	C2 ⁱ —N7—C2	119.1 (4)
N2—Cu1—N1 ⁱ	96.32 (9)	C1—N9—C1 ⁱ	121.3 (4)

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

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N5-H5A\cdots N8^{ii}$	0.86	2.09	2.916 (3)	162 (1)
$N4-H4A\cdots N6^{iii}$	0.86	2.00	2.836 (4)	165 (1)
$N3-H3A\cdots N8^{iv}$	0.86	2.34	3.151 (3)	158 (1)
$N3-H3B\cdots N6^{iii}$	0.86	2.35	3.103 (4)	146 (1)

Symmetry codes: (ii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x, -y + 1, z + \frac{1}{2}$.

All H atoms were positioned geometrically and treated as riding, with $N-H = 0.86$ Å, $C-H = 0.93$ Å and $U_{iso}(H) = 1.2U_{eq}(C,N)$.

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

This work was supported by the Natural Science Foundation of China (No. 20201008).

References

Albada, G. A. van, Mutikainen, I., Riggio, I., Turpeinen, U. & Reedijk, J. (2002). *Polyhedron*, **21**, 141–146.
Albada, G. A. van, Mutikainen, I., Turpeinen, U. & Reedijk, J. (2006). *J. Mol. Struct.* **789**, 182–186.

Aminabhavi, T. M., Biradar, N. S., Patil, S. B., Hoffman, D. E. & Biradar, V. N. (1987). *Inorg. Chim. Acta*, **135**, 139–143.
Andrade-López, N., Ariza-Castolo, A., Contreras, R., Vázquez-Olmos, A., Barba-Behrens, N. & Tlahuext, H. (1997). *Heteroat. Chem.* **8**, 397–410.
Arablo, N., Torabi, S. A. A., Morsali, A., Skelton, B. W. & White, A. H. (2003). *Aust. J. Chem.* **56**, 945–947.
Barba-Behrens, N., Mutio-Rico, A. M., Joseph-Nathan, P. & Contreras, R. (1991). *Polyhedron*, **10**, 1333–1341.
Barba-Behrens, N., Vázquez-Olmos, A., Castillo-Blum, S. E., Höjer, G., Meza-Höjer, S., Hernández, R. M., Rosales-Hoz, M. J., Vicente, R. & Escuer, A. (1996). *Transition Met. Chem.* **21**, 31–37.
Bishop, M. M., Lee, A. H. W., Lindoy, L. F. & Turner, P. (2003). *Polyhedron*, **22**, 735–743.
Bishop, M. M., Lindoy, L. F., Skelton, B. W. & White, A. (2001). *Supramol. Chem.* **13**, 293–301.
Bishop, M. M., Lindoy, L. F. & Turner, P. (2002). *Supramol. Chem.* **14**, 179–188.
Bruker (1998). *SMART* (Version 5.0) and *SAINT* (Version 4.0) for Windows NT. Bruker AXS Inc., Madison, Wisconsin, USA.
Castillo-Blum, S. E. & Barba-Behrens, N. (2000). *Coord. Chem. Rev.* **196**, 3–30.
Ceniceros-Gómez, A. E., Barba-Behrens, N., Bernès, S., Nöth, H. & Castillo-Blum, S. E. (2000). *Inorg. Chim. Acta*, **304**, 230–236.
Ceniceros-Gomez, A. E., Barba-Behrens, N., Quiroz-Castro, M. E., Bernès, S., Nöth, H. & Castillo-Blum, S. E. (2000). *Polyhedron*, **19**, 1821–1827.
Jimonet, P. (1999). *J. Med. Chem.* **42**, 2828–2843.
Katsura, Y., Nishino, S., Ohno, M., Sakane, K., Matsumoto, Y., Morinaga, C., Ishikawa, H. & Tagasugi, H. (1999). *J. Med. Chem.* **42**, 2920–2926.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst. A* **24**, 351–359.
Schnur, R. C., Fliri, A. F. J., Kajiji, S. & Pollack, V. A. (1991). *J. Med. Chem.* **34**, 914–918.
Sheldrick, G. M. (1997). *SHELXL97* and *SHEXS97*. University of Göttingen, Germany.
Sheldrick, G. M. (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Tanabe, Y., Kawai, A., Yoshida, Y., Ogura, M. & Okamura, H. (1997). *Heterocycles*, **45**, 1579–1588.