

## Synthesis and Crystal Structure of (Di- $\mu$ -dicyanamido-kN1:N5)-bis(benzimidazole)copper(II)

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The complex (di- $\mu$ -dicyanamido-kN1:N5)-bis(benzimidazole)copper(II) with formula  $\text{Cu}(\text{C}_2\text{N}_3)_2(\text{C}_7\text{H}_5\text{N}_2)_2$ , is reported. The crystal structure of this complex is monoclinic, space group  $\text{P2}_1/\text{n}$  with  $a = 8.622(4)$ ,  $b = 11.427(5)$ ,  $c = 9.050(6)$  Å,  $\beta = 107.516(2)^\circ$ ,  $\text{C}_{18}\text{H}_{12}\text{CuN}_{10}$ ,  $\text{Mr} = 431.92$ ,  $V = 850.3(8)$  Å<sup>3</sup>,  $D_c = 1.687$  g/cm<sup>3</sup>,  $F(000) = 438$ ,  $\mu = 1.315$  mm<sup>-1</sup> and  $Z = 2$ , the final  $R = 0.0282$ ,  $\text{WR} = 0.0674$  and  $S = 1.030$  for 1549 observed reflections with  $I > 2\sigma(I)$ . It displays distorted octahedral geometry, with the Cu atom coordinated by four dicyanamide nitrile N atoms [Cu-N = 1.990(2) and 2.018(2) Å] in the basal plane, along with two monodentate benzimidazole N atoms [Cu-N = 2.018(2) Å] in the apical positions, to form a distorted tetragonal bipyramidal geometry. The metal atoms reside on crystallographic inversion centers. Neighbouring metal atoms are connected *via* single dicyanamide bridges to form layers along [101] direction. Adjacent layers are then linked by N-H...H hydrogen bonds and  $\pi$ - $\pi$  stacking interactions of the benzimidazole molecules, resulting in the formation of a three-dimensional structure.

**Key Words:** Coordination polymer, Crystal structure, Dicyanamide.

### INTRODUCTION

Coordination polymers based on dicyanamide (dca) bridging ligands are attracting much attention because of their fascinating structures and interesting magnetic properties<sup>1</sup>. The dicyanamide ligand has shown extreme coordination versatility. It can coordinate either as a monodentate ligand through the nitrile or amide N atom, or as a bi-, tri-, tetra- or even pentadentate bridging ligand with the participation of two or three donor N atoms<sup>2,3</sup>. The varieties of its coordination modes allow for the preparation of complexes with a large variety of architectures. The complexes  $[\text{M}(\text{dca})_2]_n$  ( $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Ag}, \text{etc.}$ ) containing only dicyanamide ligands have been reported<sup>4-6</sup>. The introduction of N-containing conjugated rigid co-ligands, such as 2,2'-bipyridine<sup>7</sup>, 4,4'-bipyridine<sup>8</sup>, pyrimidine<sup>9</sup>, 1,10-phenanthroline<sup>10</sup>, pyrazine<sup>11</sup> and quinoxaline<sup>12</sup>, to binary transition metal dicyanamide systems can not only modify the structures but also adjust the magnetic properties<sup>11</sup>. In order to gain insight into the influence of the nature of co-ligands on the structures and properties of dicyanamide-type complexes, the synthesis and crystal structure of (di- $\mu$ -dicyanamido-kN1:N5)-bis(benzimidazole)copper(II) complex are reported here.

## EXPERIMENTAL

All analytical grade reagents were purchased commercially and used without further purification. Elemental analyses were carried out on an EA1112 CHNS elemental analyzer.

**General procedure:** A solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.2 mmol, 0.034 g) and sodium dicyanamide (Na-dca) (0.4 mmol, 0.036 g) in methanol (5 mL) were mixed thoroughly and an ethanol solution of benzimidazole (0.1 mmol, 0.0119 g) was added dropwise with stirring. The resulting mixture was filtered and the filtrate was left undisturbed at room temperature. After 1 week, A small quantity of transparent blue crystals of  $\text{Cu}(\text{C}_2\text{N}_3)_2(\text{C}_7\text{H}_5\text{N}_2)_2$  was obtained [yield: 45 % based on Na (dca)]. Elemental analysis (%): calcd. for  $\text{Cu}(\text{C}_2\text{N}_3)_2(\text{C}_7\text{H}_5\text{N}_2)_2$ : C 49.88, H 2.77, N 32.33. Found: C 50.03, H 2.93, 32.51.

**Structure determination:** A blue single crystal with dimensions of 0.21 mm  $\times$  0.09 mm  $\times$  0.07 mm was mounted on a glass fiber and the data were collected on a Bruker SMART-APEXII CCD diffractometer (graphite monochromatized  $\text{Mo K}\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ .) using an  $\omega$  and  $\phi$  scan mode. For the title complex, a total of 8337 reflections were collected at 298(2) K in the range of  $2.73^\circ \leq \theta \leq 27.46^\circ$ , of which 1949 were unique with  $R_{\text{int}} = 0.0315$  and 1549 were observed with  $I > 2\sigma(I)$ . Lorentz-polarization corrections and empirical absorption were applied to the data. The crystal structure of the title complex was solved by direct method using SIR97<sup>13</sup> program and refined anisotropically for all non-hydrogen atoms by full-matrix least squares on all  $F^2$  data using SHELXL97<sup>14</sup>, All H atoms were added according to theoretical models, assigned isotropic displacement parameters and allowed to ride on their respective parent atoms, the  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Final R indices [ $I > 2\sigma(I)$ ]  $R_1 = 0.0282$  and  $wR_2 = 0.0674$ ,  $w = 1/[\sigma^2(F_o^2) + (0.1286P)^2 + 14.3307P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ . The highest and lowest residual peaks in the final difference Fourier map are 0.339 and  $-0.279 \text{ e/\AA}^3$ , respectively,  $(\Delta/\sigma)_{\text{max}} = 0.000$ . The single suite WINGX was used as an integrated system for all the crystallographic programs<sup>15</sup>. Selected bond lengths and bond angles are listed in Tables 1 and 2.

## RESULTS AND DISCUSSION

Each Jahn-Teller distorted Cu(II) ion in the title complex is coordinated to four dicyanamide anions and two benzimidazole ligands to give a distorted octahedral geometry, in which the equatorial plane is formed by four nitrile N atoms (atoms N3, N3<sup>i</sup>, N5<sup>ii</sup> and N5<sup>iii</sup>) of the dicyanamide anions and the apical positions are occupied by two N atoms (N2 and N2<sup>i</sup>) from two monodentate benzimidazole molecules [symmetry codes: (i) 1-x, 1-y, 1-z; (ii) 0.5-x, 0.5 + y, 0.5-z; (iii) 0.5 + x, 0.5-y, 0.5 + z] (Fig. 1). The Cu(II) ion is located in the 0 inversion center and each metal atom is connected to the other four metal centers by means of four single dca bridges, in an end-to-end ( $\mu_{1,5}$ ) coordination mode, leading to layers which grow along the direction of [101]. The single dca bridges are cross-linked by metal centers

and propagate in a zigzag pattern. The monodentate benzimidazole ligands are located on both sides of each layer. The layers are connected through hydrogen bonds (Table-2) and stacking interactions between the aryl rings of the benzimidazole moiety, each one being parallel to an equivalent one in the adjacent layer. The average distance between the average benzimidazole planes is 3.71 Å, which means the stacking interactions are weak (Fig. 2). Symmetry codes: (i) 1-x, 1-y, 1-z.

TABLE-1  
SELECTED BOND LENGTHS (Å)

Bond	Dist.	Bond	Dist.
Cu1-N3	1.990(2)	Cu1-N5 <sup>iii</sup>	2.573(3)
Cu1-N3 <sup>i</sup>	1.990(2)	N3-C8	1.147(3)
Cu1-N2	2.018(1)	C8-N4	1.302(3)
Cu1-N2 <sup>i</sup>	2.018(1)	N5-C9	1.149(3)
Cu1-N5 <sup>ii</sup>	2.573(3)	C9-N4	1.325(3)

Symmetry codes: (i) 1-x, 1-y, 1-z; (ii) 0.5-x, 0.5 + y, 0.5-z; (iii) 0.5 + x, 0.5-y, 0.5 + z.

TABLE-2  
SELECTED BOND ANGLES (°)

Angle	(°)	Angle	(°)
N3-Cu1-N3 <sup>i</sup>	180.0	C8-N3-Cu1	164.1(1)
N3-Cu1-N2	89.8 (1)	N3-C8-N4	173.0(2)
N3 <sup>i</sup> -Cu1-N2	90.2(1)	N5-C9-N4	175.6(2)
N3-Cu1-N2 <sup>i</sup>	90.2(1)	C8-N4-C9	119.6(1)
N3 <sup>i</sup> -Cu1-N2 <sup>i</sup>	89.8 (1)	N2-Cu1-N2 <sup>i</sup>	180.0

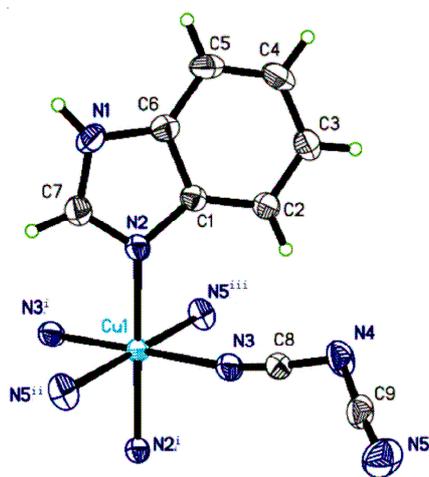


Fig. 1. View of the asymmetric unit of (I) and Cu N6 octahedron showing the atom-labelling

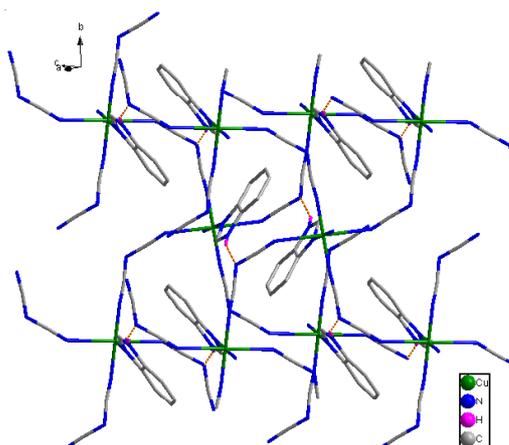


Fig. 2. Perspective view of the 2D layers of (I) showing the stacking interactions between benzimidazole ligands

In the title complex, the CuN<sub>6</sub> chromophore consists of two Cu-N2, Cu-N3 and Cu-N5 bond distances of 2.018(1), 1.990(2) and 2.573(3) Å, respectively. This situation is quite different from the similar structure previously reported<sup>12</sup>. The *cis* N-Cu-N', bond angles deviate slightly from Oh symmetry and range from 87.6(1)°-92.4(1)°. Each dca moiety is almost planar. Two different bond angles are found: C-N-C angle [119.6°] and N-C-N angles [173.0-175.6°]. Nitrile and amide carbon-nitrogen distances in the dca groups are 1.146 and 1.325 Å, respectively. These values are consistent with the triple and single carbon nitrogen bond character and they are in agreement with those observed in other complexes where dca features the end-to-end coordination mode<sup>9,12,16</sup>. As expected, the dca anions do not coordinate linearly to the metal center, exhibiting C-N-Cu angle of 164.1(3)°. In the title complex, the benzimidazole moiety is also planar and the bond distances and angles of it [1.316-1.402 Å and 105.0-122.6°, respectively] are in the normal ranges observed in benzimidazole-containing complex<sup>17</sup> (Table-3).

TABLE-3  
HYDROGEN BOND LENGTHS (Å) AND BOND ANGLES (°)

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠DHA
N1—H1...N4 <sup>i</sup>	0.86	2.38	3.206(3)	160

Symmetry codes : (i) -x + 1/2, y + 1/2, -z + 3/2.

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