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Note

Formation of a supramolecular ladder using dinuclear dicyanamide bridged Cu(II) species: Synthesis, crystal structure and magnetic property

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Abstract

The reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with bis(3-aminopropyl)methylamine and sodium dicyanamide in aqueous medium results in the formation of a dimeric dicyanamide complex of Cu(II), $[Cu_2(medpt)_2(dca)_2](ClO_4)_2$. The single crystal X-ray structure reveals that the dinuclear entities are extended to form a supramolecular 1D ladder by H-bonding. Each dinuclear entity is joined to the adjacent unit via the perchlorate anion. Variable temperature magnetic study was performed and the best-fit parameters are $J = -1.20 \pm 0.02\ cm^{-1}$, $g = 2.08 \pm 0.01$ with $R = 2 \times 10^{-5}$. These clearly indicate the antiferromagnetic interaction between the Cu(II) center.

Keywords: Cu(II) complex; Crystal structure; Magnetic measurement; Hydrogen bonding

1. Introduction

Molecular self-assembly has appeared as a potential approach in the synthetic inorganic chemistry for the fabrication and design of new functional compounds, with potentially useful properties for relevant scientific and technological applications [1]. This process involves the spontaneous aggregation of small molecular building blocks organized by covalent or non-covalent interactions that recognize each other to form the extended architectures. One strategy to build a well-spanned framework is to utilize certain features of the potential bridging ligands; such as azide [2], dicyanamide [3], carboxylate [4], enolate [5], various neutral organic spacers [6] and different amines [7] having versatile binding modes, conformational flexibility, and the ability to form hydrogen bonds and other weak interactions [8]. Among the aforementioned bridging ligands, dicyanamide (dca) has been shown to be a versatile ligand and may coordinate to metal ions as a terminal ligand through a nitrile nitrogen [3,9a] or amide nitrogen [3,9b], a μ_2-1,3-bridge through the amide nitrogen and one nitrile nitrogen [3,9c,9d], an end-to-end μ_2-1,5 bridge through two nitrile nitrogen atoms with weak antiferromagnetic coupling [3,9e], a μ_3-1,3,5 bridge through all of the nitrogen atoms showing weak or strong ferromagnetic coupling [3,9f,10] and even the unusual μ-1,1,3,5 mode [3,9g] to construct extended architectures. As a matter of fact, dca can be utilized as a useful connector between metal centers to form higher-dimensional molecular frameworks having exclusive structure and molecular property. To date, a number of higher-dimensional architectures of different transition metals have been reported using dca as bridging ligand, but the number of dinuclear compounds with bridging dca are scarce [11]. Although it is well known that perchlorate anion is capable of forming hydrogen

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bonds in crystals, tripodal directed self-assembly by perchlorate has not been reported.

In this paper, we report the synthesis, crystal structure and magnetic property of a dinuclear Cu(II) complex with molecular formula $[Cu_2(medpt)_2(dca)_2](ClO_4)_2$ which forms a supramolecular ladder like structure by unique tripodal hydrogen bonding generated from perchlorate. To the best of our knowledge, this is the first dinuclear complex of Cu(II) using dca as a bridging ligand.

2. Experimental

2.1. Materials

All chemicals were of AR grade. The IR spectrum was taken on a Nicolet 520 FTIR spectrophotometer as KBr pellets. Experimental analysis (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240 elemental analyzer. Magnetic measurements of complex **1** were performed using a SQUID magnetometer on a crystalline sample (30 mg) in the temperature range 5–300 K in an applied field of 0.5 T. The diamagnetic corrections were evaluated from Pascal's constants.

2.2. Synthesis of $[Cu_2(medpt)_2(dca)_2]\ (ClO_4)_2$

1 mmol of bis(3-aminopropyl)methylamine (medpt) (1 mmol, 0.145 g) was added dropwise to an aqueous solution (10 ml) of 1 mmol of copper (II) perchlorate hexahydrate (1 mmol, 0.370 g) with constant stirring. Then, sodium dicyanamide (1 mmol, 0.89 g) dissolved in water (10 ml) was poured into it. An instantaneous bluish violet precipitation was observed. The reaction mixture was stirred for 30 min and then filtered. After a few days, deep blue single crystals suitable for X-ray diffraction of complex **1** were obtained from the filtrate. Yield 82%. *Anal.* Calc. for $C_{18}H_{38}N_{12}Cu_2$: C, 28.86; H, 5.08; N, 22.45. Found: C, 28.81; H, 5.05; N, 22.42%. An infrared spectrum exhibited the following bands: ν(N–H): 3200–3400; ν(CN): 2150 cm^{-1}.

2.3. X-ray diffractometry

Suitable single crystals of **1** were mounted on a Siemens SMART diffractometer equipped with a graphite monochromator and Mo Kα ($\lambda = 0.71073$ Å) radiation. The intensity data were corrected for Lorentz and polarization effects. The structure was solved by Patterson method and followed by successive Fourier and difference Fourier syntheses. Full matrix least squares refinements on F^2 were carried out using SHELXL-97 [12b] with anisotropic displacement parameters for all non-hydrogen atoms for the complex. Crystallographic data and structure refinement parameters are given in Table 1. All calculations were carried out using SHELXS 97 [12a], SHELXL 97 [12b], PLATON [13], ORTEP-32 [14] and the WinGX system, Ver 1.64 [15].

Table 1
Crystallographic data and details of structure refinement of the compound

Empirical formula	$C_{18}H_{38}N_{12}Cu_2$
Formula mass (g mol^{-1})	748.58
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	7.6076(7)
b (Å)	16.4412(15)
c (Å)	12.5788(12)
β (°)	99.825(2)
V (Å^3)	1550.3 (2)
Z	2
D_{calc} (g cm^{-3})	1.604
μ (Mo Kα) (mm^{-1})	1.605
F(000)	772
θ Range (°)	2.1–28.3
Number of collected data	9025
Unique data	3443
R_{int}	0.027
Data $I > 2\sigma(I)$	2584
Refined parameters	191
R_1[a] [$I > 2\sigma(I)$]	0.0369
wR_2[a] [$I > 2\sigma(I)$]	0.1091
Goodness-of-fit[b]	1.07
Residuals (e Å^{-3})	0.72 (max) and −0.38 (min)

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$, $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\right]^{1/2}$.

[b] Goodness-of-fit $= \left\{\sum\left[w(F_o^2 - F_c^2)^2\right]/(n-p)\right\}^{1/2}$.

3. Results and discussion

3.1. Description of the structure

The crystal structure of complex **1** is formed by discrete neutral $(medpt)_2Cu_2(dca)_2$ entities connected through hydrogen bonds to form one-dimensional chain. Fig. 1 shows the ORTEP drawing of the dinuclear entity with atom numbering scheme. Here, two copper atoms are bridged by two dca anions in an end-to-end fashion (Fig. 1). Each copper ion exhibits five coordination numbers tilting the geometry towards square pyramidal rather than trigonal bipyramidal geometry with Addison parameter τ value 0.11 [16]. The basal plane of the square pyramid around the Cu(II) center is formed by three N

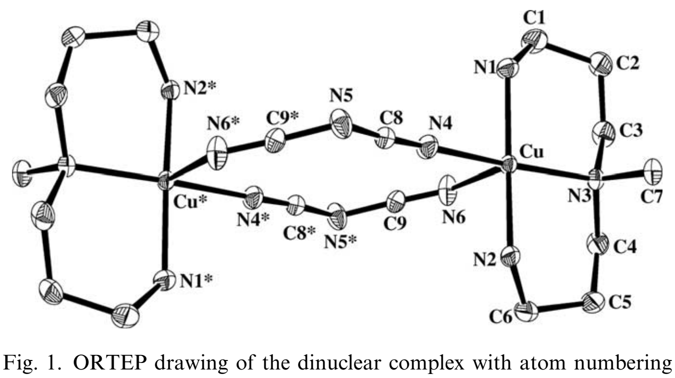

Fig. 1. ORTEP drawing of the dinuclear complex with atom numbering scheme, showing the coordination environment.

atoms (N1, N2 and N3) of amine and one N atom (N4) from the bridging dicyanamide. These four N atoms are nearly co-planar with maximum deviation for N4 atom from the mean plane being 0.036(3) Å. Deviation of the copper atom from the mean plane formed by the four equatorial atoms is 0.1881(3) Å and maximum deviation for the N2 atom from the mean plane is 0.117(3) Å. The basal Cu–N distance range is 1.992(2)–2.078(2) Å (Table 2). The axial site is occupied by another N atom from the bridging dicyanamide, N6 with larger Cu–N distance (2.319 Å). Out of the Cu–N bonds involving the medpt ligand, the central one is a little longer with respect to the other two [Cu–N1 = 2.000(3), Cu–N2 = 1.992(2), Cu–N3 = 2.078(2) Å] (Table 2). The Cu–Cu* distance bridged by two dca ligands is 6.975 Å.

The perchlorate counter anions present in the crystal lattice balance the electronic charge of the complex. Besides this, they play the very important role of carving out supramolecular architecture via hydrogen bonding. Out of four O atoms of the perchlorate anion, only three O atoms (O1, O2 and O3) take part in intermolecular tripodal hydrogen bonding with the N–H hydrogen of the medpt (Table 3). This gives rise to an interesting supramolecular one-dimensional ladder-like architecture (Fig. 2). This 1D motif is further stabilized by the H-bond formed between the N atom of dca (N5) and the N–H hydrogen of the ligated medpt. The H-bonding pattern exhibits ring motif forming $R_3^3(12)$ in Etter's graph notation [17]. These H-bonded 1D ladders are packed parallel to each other to give the overall crystal packing (Fig. 3). The presence of these directed H-bonding is responsible for the stabilization of the pentacoordinated Cu(II) producing unusual dinuclear entity bridged by dca.

Table 2
Selected bond lengths (Å) and bond angles (°) of the complex

Cu–N1	2.000(3)
Cu–N3	2.078(2)
Cu–N6	2.319(3)
N6–C9	1.133(4)
N5–C8	1.302(4)
Cu–N2	1.992(2)
Cu–N4	2.042(3)
N4–C8	1.144(4)
N5–C9*	1.305(4)
N1–Cu–N2	165.04(11)
N1–Cu–N4	84.72(10)
N2–Cu–N3	92.07(10)
N2–Cu–N6	96.43(11)
N3–Cu–N6	94.41(9)
Cu–N4–C8	171.8(3)
C8–N5–C9*	122.7(3)
N1–Cu–N3	94.76(10)
N1–Cu–N6	96.30(12)
N2–Cu–N4	86.54(11)
N3–Cu–N4	171.37(11)
N4–Cu–N6	94.21(11)
Cu–N6–C9	118.8(2)

Symmetry operation for * marked atoms: $-x$, $-y$, $1-z$.

Table 3
Hydrogen bonding interaction (Å, °) of the complex

D–H···A	D–H	H···A	D···A	∠D–H···A
N1–H1A···O2[a]	0.9000	2.3000	3.095(5)	148.00
N1–H1B···O3	0.9000	2.1300	2.998(4)	161.00
N2–H2A···N5[b]	0.9000	2.3600	3.191(4)	153.00
N2–H2B···O1[b]	0.9000	2.5200	3.214(5)	135.00

Symmetry codes: (a) $-1+x, y, z$; (b) $1-x, -y, 1-z$.

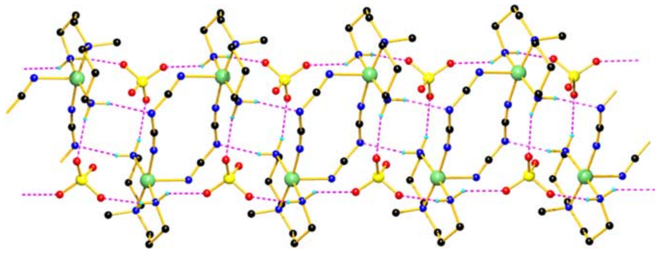

Fig. 2. Supramolecular one-dimensional ladder formed by the intermolecular hydrogen bonding.

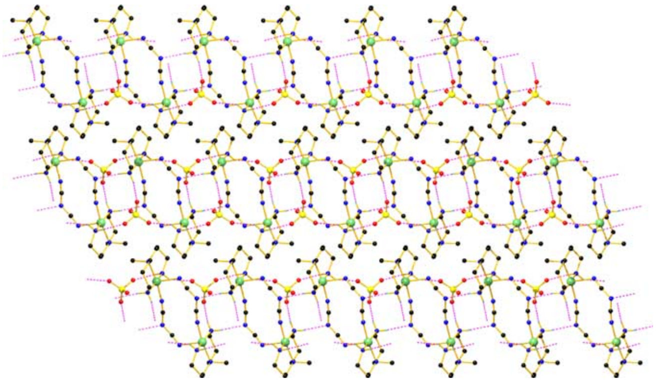

Fig. 3. Crystal packing of successive ladder-like chains.

3.2. Magnetic study

Plots of χ_M and $\chi_M T$ versus T are shown in Fig. 4. Taking into consideration the structural aspect, the magnetic data for **1** are given for two copper (II) ions, as it is a dinuclear system. Here, $\chi_M T$/Cu is close to 0.40–0.41 $cm^3 mol^{-1}$ K, which is the typical value for isolated Cu(II) ions ($g > 2.00$). This value is almost constant up to 50 K, decreasing rapidly from 50 to 2 K. This feature is indicative of weak antiferromagnetic coupling for the complex. The experimental data of complex **1** has been fitted to a Bleaney–Bowers equation for a dinuclear copper (II) system [18]. The best-fit parameters are $J = -1.20 \pm 0.02$ cm^{-1}, $g = 2.08 \pm 0.01$ with $R = 2 \times 10^{-5}$. The small J coupling parameter agrees with the structure of the dinuclear complex, in which the two copper (II) ions are linked by two dicyanamide ligands in axial-equatorial positions. This reduces the possible magnetic coupling. The long dicyanamide bridging ligand generally gives small coupling. The Addison parameter τ is 0.11 for the copper (II) ions,

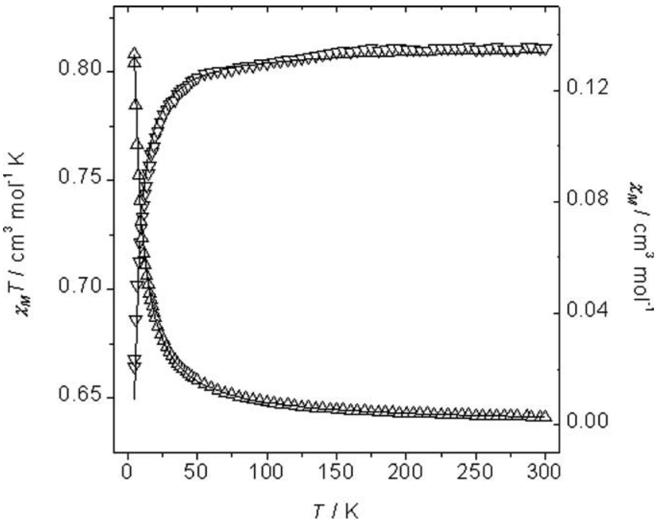

Fig. 4. Plots of χ_M and $\chi_M T$ vs. T for complex **1** (open triangles are the experimental data and solid lines represent the best-fit parameter obtained).

giving the possibility of a small overlap between the magnetic orbitals ($d_{x^2-y^2}$ and d_{z^2}, respectively).

Summarizing the magnetic data, it can be stated that the $\mu_{1,5}$-dicyanamide ligand is a poor magnetic bridging ligand. Even in some cases, it is observed that there is no detectable magnetic coupling in some Cu^{II} complexes through $\mu_{1,5}$-dca bridges [19,20]. When J values are measurable, with one or two bridges, these values are very small, from −0.1 to −0.4 cm^{-1} [21]. Only in one case, it is clearly demonstrated that this $\mu_{1,5}$-dca mediator can create weak ferromagnetic coupling [20]. In two other cases, this unusual ferromagnetic coupling has been attributed to π–π interactions of the terminal planar aromatic ligands [22].

4. Conclusion

We have synthesized a dicyanamido-bridged dinuclear copper (II) complex. This dinuclear complex by intermolecular hydrogen bonding forms a novel 1D straight ladder like supramolecular chain, where perchlorate anion plays a very important role. To the best of our knowledge, this is the first example of dicyanamido-bridged dinuclear copper (II) system. In fact, dca has a strong tendency to form polymeric complexes and that is why dinuclear dicyanamido-bridged complexes are scarce in the literature. The directed H-bond, which gives this complex an overall 1D structure, may be responsible for the stabilization of the coordinated dinuclear form. The work described here is a unique case of perchlorate forming a component of supramolecular 1D network.

5. Supplementary material

Crystallographic data reported in this paper have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication CCDC No. 272760. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or on the web www: http://www.cam.ac.uk).

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