



A novel coordination polymer with dicyanamide ligand: multi-dimensional architecture stabilized by hydrogen bonding

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Abstract

A novel dicyanamide (dca) complex, $[\text{Cu}(\text{pn})(\text{dca})_2]_n$ (pn = 1,2-diaminopropane), was synthesized and characterized. X-ray diffraction analysis reveals that the title complex crystallizes in the monoclinic space group $C2/c$ with $a = 12.436(5) \text{ \AA}$, $b = 8.395(3) \text{ \AA}$, $c = 20.747(8) \text{ \AA}$, $\beta = 96.662(6)^\circ$, $Z = 8$, and $R_1 = 0.0476$, $wR_2 = 0.1094$. The complex exhibits one-dimensional zigzag chain structure constructed by $\mu_{1,5}$ -dca bridges. The coordination geometry around the copper atom was a distorted square-pyramid. The spectroscopic and magnetic properties have also been discussed.

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Keywords: Copper(II) complex; Dicyanamide; Crystal structure; Hydrogen bond; Magnetic property

1. Introduction

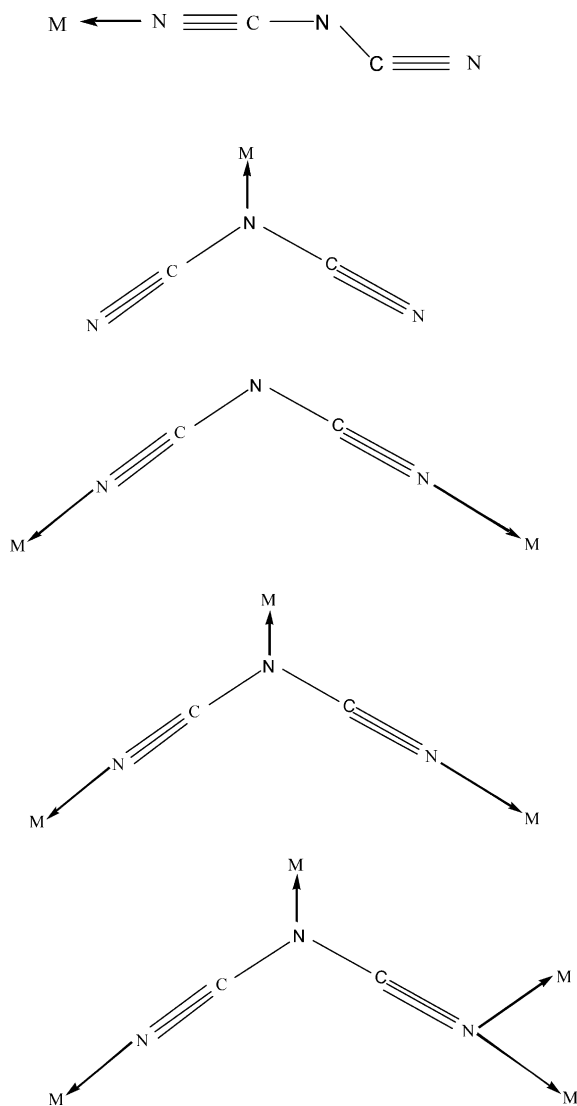
Coordination polymers are a family of materials composed of 1D chains, 2D sheets, and 3D networks of metal-organic building blocks connected via covalent and hydrogen bonds. Recently, they have received considerable attention because of their wide applications in chemical separation technologies and heterogeneous catalysis [1,2]. Transition metal polymers containing dicyanamide (dca) as bridges have been promoted due to their fascinating structural and topological features. Dca may act as monodentate ligand through a nitrile nitrogen atom, or as end-to-end bridging ligand by coordinating to two different metal centers through its two terminal N (nitrile) atoms, or as a tridentate bridging ligand with additional coordi-

nation through the middle N (amide) atom, or as tetradentate bridging ligand as shown in Scheme 1 [3, 4]. A host of complexes $\text{M}^{\text{II}}(\text{dca})_2$ or $\text{M}^{\text{II}}(\text{dca})_2\text{L}$ ($\text{M} = \text{Cu}, \text{Co}, \text{Ni}, \text{Mn}, \text{Zn}$ or Fe , $\text{L} = \text{co-ligand}$) with bidentate bridging mode have been documented so far [5–10], of which magnetic interactions are generally weak. In addition, the evaluation of the weak exchange coupling through the extended dca bridge is quite complicated, due to the lack of theoretical models to analyze the magnetic properties of the high dimensional compounds formed by dca.

In the hope of throwing more light on this problem, the novel compound $[\text{Cu}(\text{pn})(\text{dca})_2]_n$ was successfully synthesized, which is 1D chain polymer constructed by end-to-end dca bridges. The chain was further assembled into 2D sheet by semi-coordination fashion, and the 3D framework was constructed by various hydrogen bonds. In this contribution, we presented the preparation, structural characterization, spectroscopic and magnetic investigations.

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Scheme 1.

2. Experimental

2.1. General

All chemicals of p.a. grade were purchased from the Aldrich Company and used without further purification.

Elemental analyses for C, H and N were carried out on a Perkin–Elmer analyzer at the Institute of Elemento–Organic Chemistry, Nankai University. IR spectrum was recorded in KBr disks on

a Shimadzu IR-408 infrared spectrophotometer in the 4000–600 cm^{-1} region. Magnetic susceptibilities were measured on a LDJ 9600 Vibrating Sample Magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

2.2. Preparation of $[\text{Cu}(\text{pn})(\text{dca})_2]_n$

1,2-Diaminopropane (1.0 mmol, 74.1 mg) was added to a DMF solution (10 ml) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 185.3 mg), then $\text{Na}(\text{dca})$ (1.0 mmol, 90.0 mg) dissolved in 10 ml of ethanol was added. The resulting mixture was stirred for several hours, then filtered off. After 2 weeks, the bright blue crystals suitable for X-ray structure analysis were obtained by slow evaporation of the filtrate. Yield: 42%. $\text{C}_7\text{H}_{10}\text{N}_8\text{Cu}$ (**1**) (269.77): C 31.92 (calcd 31.17); H 3.24 (3.74); N 41.33 (41.54)%.

3. Structure determination

X-ray diffraction data were collected on a BRUKER SMART 1000 CCD detector with graphite-monochromatized Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct method using the program SHELXS 97 and Fourier difference techniques, and refined by full-matrix least-squares method on F^2 using SHELXL 97 [11,12]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms with common fixed isotropic thermal parameters. Crystal data and structure refinements are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

4. Result and discussion

4.1. Crystal structure of the complex

A uniform chain extending along the a -axis is found (Fig. 1), one of the two dca units serving as an asymmetric end-to-end 1,5-bridging ligand, while another dca is monodentate. The copper atom involves a five-coordinated environment, with a distorted square-pyramid structure. The pn ligand and the two dca anions are coordinated to the copper

Table 1

Data collection and processing parameters for [Cu(pn)(dca)₂]_n

Empirical formula	C ₇ H ₁₀ N ₈ Cu
Formula weight	269.77
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> (Å)	12.436(5)
<i>b</i> (Å)	8.395(3)
<i>c</i> (Å)	20.747(8)
β (degrees)	96.662(6)
Volume (Å ³)	2151.6(14)
<i>Z</i>	8
Density (calculated) (mg/m ³)	1.666
Absorption coefficient (mm ⁻¹)	2.017
<i>F</i> (000)	1096
Crystal size (mm)	0.30 × 0.25 × 0.20
θ range for data collection (degrees)	1.98–25.34
Limiting indices	–14 ≤ <i>h</i> ≤ 11 –10 ≤ <i>k</i> ≤ 8 –17 ≤ <i>l</i> ≤ 24
Reflections collected	4381
Independent reflections	1957 [<i>R</i> (int) = 0.0307]
Max. and Min. Transmission	0.6885 and 0.5829
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1957/0/145
Goodness-of-fit on <i>F</i> ²	1.088
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] _a	0.0476, 0.1066
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0639, 0.1123
Largest diff. peak and hole (e Å ⁻³)	0.921 and –0.473

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad wR_2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum (F_o^2)^2)^{1/2}, \\ w = 1/[\sigma^2(F_o^2) + (0.0442P)^2 + 8.2040P], \quad P = (F_o^2 + 2F_c^2)/3.$$

atom (Cu1–N1 1.997(4), Cu1–N2 1.996(4), Cu1–N3 1.969(4), Cu1–N6 1.977(4) Å) with the angles subtended at the Cu(II) ion varying from 83.97(15) to 91.89(16)° (Table 2) in the slightly distorted plane of square pyramid, while one N atom of dca occupying the fifth coordinated position at a distance of 2.347(4) Å. The equatorial plane has a slight tetrahedral distortion (maximum atomic deviation of 0.009(1) Å) with Cu(II) atom displaced by 0.144(5) Å from this plane in the direction towards the apical ligand atom. The axial Cu–N(dca) bond length (2.347(4) Å) is significantly longer than the corresponding Cu–N bond lengths in Cu–CN complexes, such as 2.175(7) Å in [Cu(dpa)(dca)₂]_n (dpa = 2,2'-dipyridylamine) [13]. This axial elongation may be attributed to a Jahn–Teller distortion and this result is

similar to the published Cu(dca)₂ complex [14]. The Cu···Cu distance spanned by the bridging ligand is 7.502(4) Å, while the closest interchain distance is 7.691(7) Å. As comparison, the Cu···Cu distances across the dca bridge is 7.7011(9) Å in [Cu(pyim)(H₂O)(dca)]_n⁺ (pyim = 2-(2-pyridyl)imidazole) and 7.710 Å in [Cu(μ_{1,5}-dca)₂(phen)]_n (phen = 1,10'-phenanthroline) [13].

In the title complex, adjacent copper atoms are bridged by single end-to-end dicyanamide bridges to form 1D chain (Fig. 1). Interestingly, there exist weak interactions between the Cu atoms and the amide N atoms of non-bridged dca ligands of adjacent chains (Cu···N4 = 3.067(5) Å), which give rise to formation of 2D layer structure (Fig. 2).

The structure parameters of dicyanamide ligands in the title complex correspond well with those in ionic derivatives like Li[N(CN)₂]₂·2CH₃CN [15], and they are hardly influenced by bonding types. For example, the values of C6–N7–C7 and C4–N4–C5 angles are the identical value of 120.4(4)°. The C6–N7 (1.293(6) Å) and C7–N7 (1.316(6) Å) distances are shorter than the standard value for the bond type C(sp)–N(sp²) (1.33 Å); the C6–N6 and C7–N8 bond lengths correspond well with the experience for a triple bond [16].

4.2. Infrared spectrum

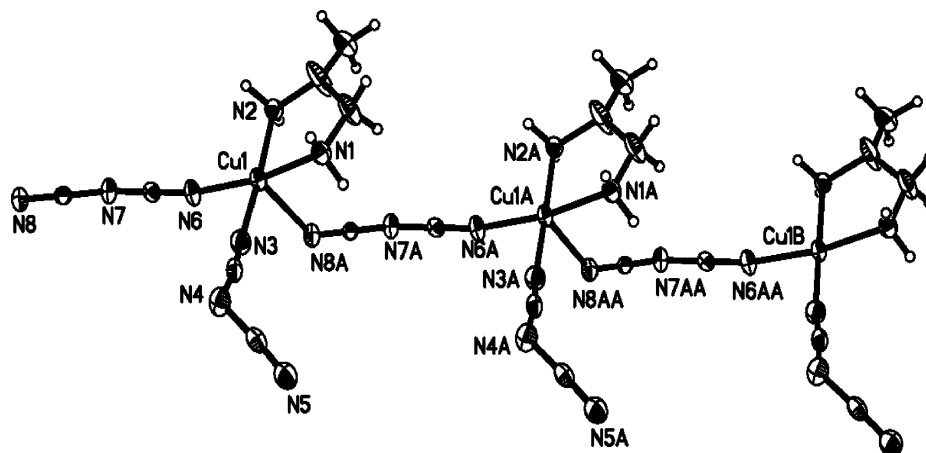
The infrared spectrum of the title compound exhibits strong absorptions in the 2340–2170 cm⁻¹ region corresponding to ν(C≡N) of the dicyanamide ligand [17,18]. The ν_{as}(C≡N) and ν_s(C≡N) of the title complex are 2245 and 2175 cm⁻¹, respectively, which is well consistent with those of the sodium

Table 2

Selected bond lengths (Å) and angles (degrees) for [Cu(pn)(dca)₂]_n

Cu1–N1	1.997(4)	N3–Cu1–N6	91.66(17)
Cu1–N2	1.996(4)	N3–Cu1–N2	170.58(17)
Cu1–N3	1.969(4)	N6–Cu1–N1	170.65(17)
Cu1–N6	1.977(4)	N6–Cu1–N2	91.89(16)
Cu1–N8#1	2.347(4)	N3–Cu1–N1	91.20(16)
		N2–Cu1–N1	83.97(15)
		N3–Cu1–N8#1	96.40(16)
		N2–Cu1–N8#1	91.79(15)
		N1–Cu1–N8#1	91.10(15)
		N6–Cu1–N8#1	97.42(16)

$$\#1 = x + 1/2, y - 1/2, z$$

Fig. 1. Section of the chain in $[\text{Cu}(\text{pn})(\text{dca})_2]_n$.

dicyanamide salt, 2232 and 2179 cm^{-1} . The smaller shift towards high frequencies, compared with those of the free dca, confirmed that dca coordinated to metal center. The $\nu_{\text{as}}(\text{C}\equiv\text{N})$ ($1400\text{--}1300\text{ cm}^{-1}$ region) and $\nu_{\text{s}}(\text{C}\text{--}\text{N})$ ($950\text{--}900\text{ cm}^{-1}$ region) are also observed. The $\nu_{\text{as}}(\text{N}\text{--}\text{H})$ and $\nu_{\text{s}}(\text{N}\text{--}\text{H})$ of pn ligand appear around 3300 cm^{-1} .

4.3. Magnetic properties

The molar magnetic susceptibility χ_{M} of $[\text{Cu}(\text{pn})(\text{dca})_2]_n$ is measured in the range of 77–300 K in a field of 10 kOe, the plots of χ_{M} versus T and χ_{M}^{-1} versus T are shown in Fig. 3. The value of μ_{eff} at room temperature is 1.746 B.M., which is close to

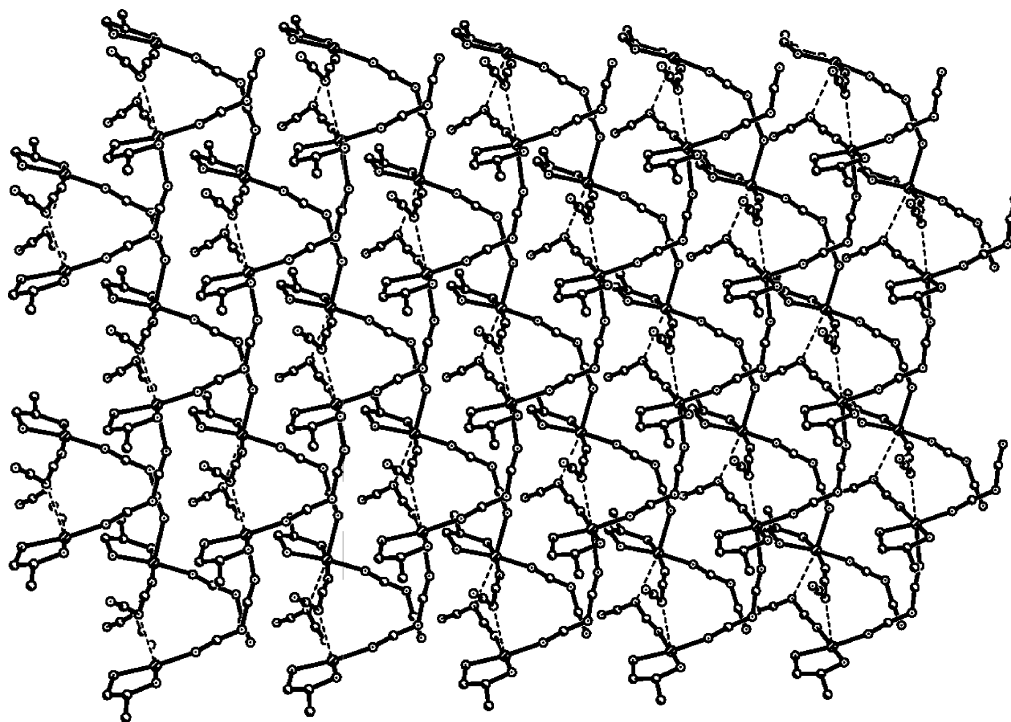


Fig. 2. Interaction between neighboring chains creating a layer structure.

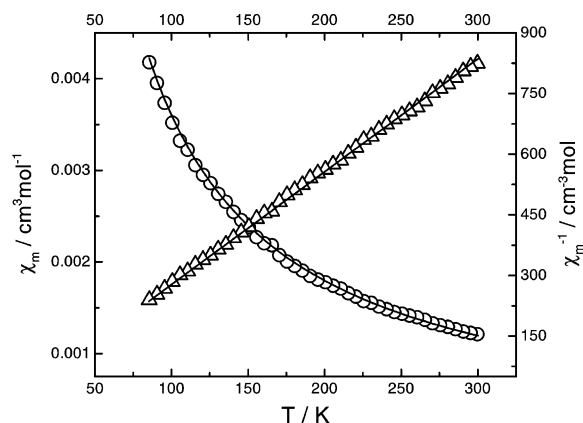


Fig. 3. Plots of χ_M versus T (○) and χ_M^{-1} versus T (▽) for $[\text{Cu}(\text{pn})(\text{dca})_2]_n$. The solid line is the best fit.

the expected value for an isolated spin doublet. Upon cooling, the μ_{eff} value steadily decreases to 1.625 B. M. at 77 K. The Curie–Weiss constants in the range 77–300 K are $\theta = -0.47$ K and $C = 0.36$ cm³ K mol⁻¹. The negative θ value indicates the antiferromagnetic coupling between adjacent metal ions. Given that the structure consists of uniformly spaced chains of copper(II) ions, its magnetic data were fit with the theoretical expression (the Hamiltonian being $-J \sum \hat{S}_i \hat{S}_{i+1}$) proposed by Hall [19] for a uniform chain of localized spins $S = 1/2$, Eq. (1)

$$\chi_M = (N\beta^2 g^2 / k_z T) (0.25 + 0.14955x + 0.30094x^2) / (1 + 1.9862x + 0.68854x^2 + 6.0626x^3) \quad (1)$$

where N , β and g have their usual meanings, $x = |J|/k_z T$ and J is the exchange coupling constant describing the magnetic interaction between two nearest-neighbouring spin doublets. This expression, which is derived from the numerical results from Bonner and Fisher [20], has been widely used for the treatment of the magnetic data of uniform copper(II) chains. Least-squares fit of the magnetic data of the title complex through Eq. (1) leads to the following parameters: $J = -0.76$ cm⁻¹, $g = 2.12$ and $R = 3.2 \times 10^{-5}$ (R is the agreement factor defined as $\sum_i [(\chi_M T)_{\text{obs}(i)} - (\chi_M T)_{\text{calc}(i)}]^2 / \sum_i [(\chi_M T)_{\text{obs}(i)}]^2$).

The present result shows that the antiferromagnetic coupling between copper(II) ions through

the end-to-end dca bridge in the title complex is weak. The weak coupling may be understood as follows: magnetic orbital describing the unpaired electron on a copper(II) ion in square pyramid is the $d_{x^2-y^2}$ type (the x and y axes being roughly defined by the short equatorial bonds), and the overlap between two of these orbitals through the polyatomic $\mu_{1,5}$ -dca bridge is expected very small. Consequently, the antiferromagnetic coupling which is proportional to the square of this overlap [21,22] is predicted to be a weak one, as mentioned above.

5. Conclusions

In this study a novel chain-like copper polymer constructed by dca bridges was obtained, and the magnetic study shows weak antiferromagnetic coupling between copper(II) ions. The weak interactions between the amide N atoms of non-coordinated dca ligands and Cu(II) atoms expand the 1D chain into 2D layer. From the crystal structure we can find that dca cannot only act as bridging ligand but also form multi-dimensional networks assembled by hydrogen-bonds, which often exhibit novel properties, and are important in the crystal engineering of nonlinear optical, magnetic and conducting materials. At this point more attention should be paid in this area.

6. Supplementary materials

Crystallographic data (excluding structure factors) for the structure in this paper has been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC 195754 for $[\text{Cu}(\text{pn})(\text{dca})_2]_n$. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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