

## Hydrogen bonds mediated magnetism in $\text{Cu}(\text{bmen})_2\text{Pd}(\text{CN})_4$

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### Abstract

Results of synthesis, X-ray structure analysis, electron spin resonance, susceptibility, magnetization and specific heat measurements of powdered  $\text{Cu}(\text{bmen})_2\text{Pd}(\text{CN})_4$  (*bmen* = *N,N'*-dimethyl-1,2-diaminoethane) are reported. Its structure is formed of quasi-linear chains of the  $[-\text{Cu}(\text{bmen})_2-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-]_n$  composition; these are interlinked by hydrogen bonds (HBs) leading to two-dimensional patterns. Upon magnetic, spectral and thermodynamic measurements the compound was identified as an  $S = 1/2$  Heisenberg antiferromagnet on a square lattice with  $J/k = -0.48$  K due to the dominant role of HBs in creating a square network. The long-range ordering observed at 0.24 K is proposed to be of a Néel type. The possibility of tuning the exchange interactions in various directions is considered.

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### 1. Introduction

One of the fundamental problems of quantum magnetism is connected with understanding the interplay between geometrical frustration and quantum fluctuations which can lead to novel ground states and excitations. In this context, properties of two-dimensional  $S = 1/2$  spatially anisotropic Heisenberg antiferromagnets on triangular lattices (SAH) are of interest [1,2]. In particular, the deviations from linear spin wave theory in these systems were found to be more pronounced than those reported for  $S = 1/2$  spatially anisotropic Heisenberg antiferromagnets on a square lattice [3,4]. Ground state properties of SAH strongly depend on the ratio of exchange coupling in different directions. Specifically, two distinct spin liquid phases for the different ratio of exchange interactions were theoretically predicted [2]. Experimentally,  $\text{Cs}_2[\text{CuCl}_4]$  and organic compounds such as  $\kappa$ -(BEDT-TTF) $_2[\text{Cu}_2(\text{CN})_3]$  (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene) were proposed as representatives of SAH [5,6].

Systematic studies of SAH require a class of materials in which the ratio of exchange interactions can be tuned. For example, the spatial anisotropy can be obtained by considering

a chain material, where the exchange interaction along the chain is mediated by covalent bonds, while hydrogen bonds (HBs) among the chains support the formation of exchange paths in the other direction. It should be stressed that the ability of HBs to mediate exchange interactions has been already well established [7–10].

In the present work, magnetostructural correlations in a new material,  $\text{Cu}(\text{bmen})_2\text{Pd}(\text{CN})_4$  (*bmen* = *N,N'*-dimethyl-1,2-diaminoethane), are discussed. The structural features of the title compound suggest the presence of spatial anisotropy of the exchange interaction on the triangular lattice. Consequently, the estimation of the ratio of the exchange coupling in different directions and studying subsequent physical properties resulting from the value of this ratio represents the main motivation of this work. Moreover, this investigation falls within a broader program dealing with the study of the tetracyanocomplexes of Cu(II) coordinated by *N*-donor ligands in which different structural and magnetic dimensionality was observed due to the influence of HBs present in the structure [11–14].

### 2. Experimental procedure

#### 2.1. Preparation of $\text{Cu}(\text{bmen})_2\text{Pd}(\text{CN})_4$

The preparation was made using a general procedure already published for  $\text{Cu}(\text{dmen})_2\text{Pd}(\text{CN})_4$  (*dmen* = *N,N*-dimethyl-1,

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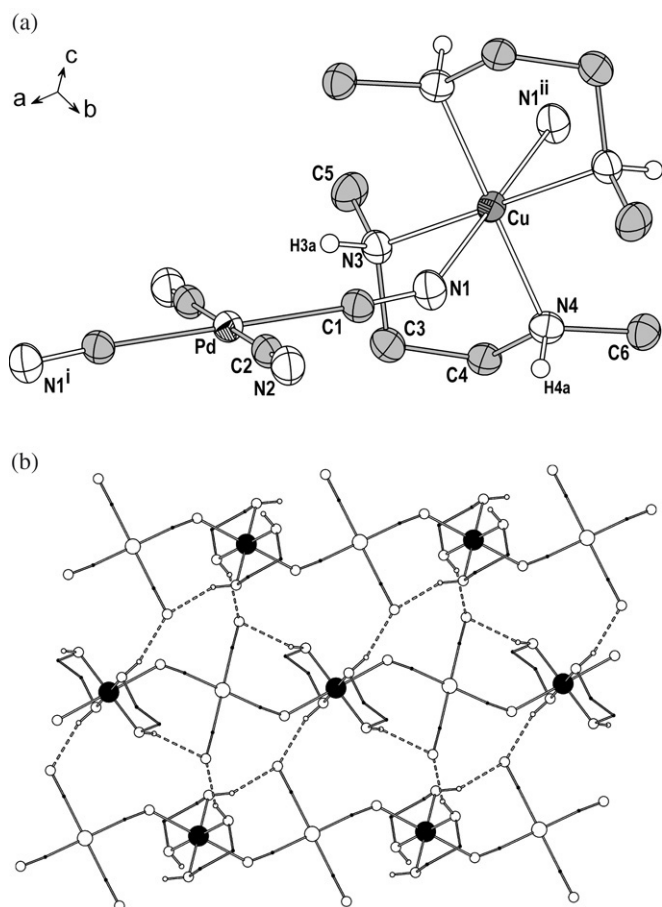


Fig. 1. (a) ORTEP plot of the crystal structure of  $\text{Cu}(\text{bmen})_2\text{Pd}(\text{CN})_4$  (i:  $-x, -y, -z$ ; ii:  $-1-x, -y, -z$ ). (b) Packing of the chains displaying hydrogen bonds. Cu(II) atoms are denoted by large black balls, medium white balls represent Pd atoms. Small white balls denote N atoms, whereas hydrogen bonds are denoted by dashed lines.

2-diaminoethane) but instead of *dmen* as ligand *bmen* was used [15]. Within a few days blue needles were separated. IR (KBr, Bruker IFS 113V, in  $\text{cm}^{-1}$ ),  $\nu$  (NH): 3299 (s), 3208 (vs),  $\nu$  (CH): 2968 (w), 2939 (m), 2877 (w),  $\nu$  (CN): 2135 (vs), 2124 (vs),  $\delta$  (Pd-CN): 377 (s). Analysis found: C: 31.71, H: 5.12, N 24.82%; calculated: C: 32.01, H: 5.37, N: 24.88%.

## 2.2. X-ray diffraction analysis

A single crystal of  $\text{Cu}(\text{bmen})_2\text{Pd}(\text{CN})_4$  with size of  $0.17 \times 0.05 \times 0.02 \text{ mm}^3$  was used for data collection (KUMA KM4 diffractometer, Mo  $K_\alpha$  radiation,  $\lambda = 0.71069 \text{ \AA}$  at  $-80 \text{ }^\circ\text{C}$ ,  $\theta$  range  $2.98^\circ$ – $28.51^\circ$ ). Crystal data: orthorhombic, *Pbca*,  $a = 10.243(2) \text{ \AA}$ ,  $b = 12.4957(2) \text{ \AA}$ ,  $c = 13.502(2) \text{ \AA}$ ,  $Z = 4$ ,  $D_c = 1.731 \text{ d cm}^{-3}$ . The crystal structure was solved by the heavy atom method with the SHELXS-97 program [16]. Full matrix least-squares refinements were performed on  $F^2$  against all reflections with the SHELXL-97 program [17]. All atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and treated as riding on their parent atoms, with C–H distances of  $0.98$ – $0.99 \text{ \AA}$  and N–H distances of  $0.92 \text{ \AA}$ . The  $U_{\text{iso}}(\text{H})$  values were set at  $1.2U_{\text{eq}}$  of the parent atom. The final parameters were  $R1 = 0.0464$ ,  $wR2 = 0.1084$ ,  $\text{GooF} = 1.156$ , residual electron density

Table 1  
Selected geometric parameters of  $\text{Cu}(\text{bmen})_2\text{Pd}(\text{CN})_4$  [ $\text{\AA}$ ,  $^\circ$ ]

Cu–N1	2.474(2)	C2–N2	1.146(4)	Cu–N1–C1	136.31(2)
Cu–N3	2.040(2)	N3–C5	1.497(4)	N3–Cu–N4	85.4(2)
Cu–N4	2.077(2)	N3–C3	1.485(4)	C2–Pd–C1 <sup>a</sup>	90.7(3)
Pd–C2	1.991(4)	C3–C4	1.560(5)	C2–Pd–C1	89.3(3)
Pd–C1	1.987(3)	C4–N4	1.487(4)	N1–C1–Pd	175.8(3)
C1–N1	1.150(4)	N4–C6	1.510(4)	N2–C2–Pd	178.3(3)

<sup>a</sup>  $-x + 2, -y, -z + 2$ .

was  $1.374$  and  $-0.916 \text{ e \AA}^{-3}$ . Geometric parameters were calculated using PARST [18] and figures were drawn using the DIAMOND program [19].

## 2.3. Electron spin resonance, magnetic and thermodynamic properties

An electron spin resonance (ESR) experiment was performed in a homemade X band spectrometer at temperature  $4.2 \text{ K}$ , frequency  $10.05 \text{ GHz}$  and magnetic field up to nominally  $0.4 \text{ T}$ . For this measurement, a spherical sample of diameter about  $1 \text{ mm}$  was formed using GE 7031 varnish.

Static susceptibility and magnetization were studied in a commercial SQUID magnetometer. Susceptibility was measured from  $2 \text{ K}$  to  $300 \text{ K}$  in  $0.1 \text{ T}$  magnetic field, whereas field dependence of the magnetization was studied at  $4.2 \text{ K}$  and  $12 \text{ K}$  in magnetic fields up to  $6 \text{ T}$ . The diamagnetic contribution of the sample container was measured in an independent run and subtracted from the total signal. The contribution of core diamagnetism has been subtracted using a standard method of Pascal constants.

Temperature dependence of the specific heat in zero magnetic field was investigated from  $0.1$  to  $2 \text{ K}$  in a commercial dilution refrigerator using relaxation techniques. The specific heat study was conducted using a  $65 \text{ mg}$  powdered sample pressed in the form of a pellet and the inaccuracy of this measurements was  $3\%$ .

## 3. Results and discussion

The structure consists of electroneutral chains  $[-\text{Cu}(\text{bmen})_2-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-]_n$  running along the  $c$  axis (see Fig. 1). The copper atom coordination sphere displays the usual axial deformation due to the Jahn–Teller effect, with longer axial bonds ( $\text{Cu}-\text{N}_{\text{eq}} = 2.0585(2) \text{ \AA}$  and  $\text{Cu}-\text{N}_{\text{ax}} = 2.474(2) \text{ \AA}$ ) (Table 1). The corresponding values in the analogous compound  $\text{Cu}(\text{dmen})_2\text{Pd}(\text{CN})_4$  were  $2.0538(1) \text{ \AA}$  and  $2.5528(1) \text{ \AA}$  [15]. The equatorial positions of the Cu(II) atoms are occupied by two chelate bonded *bmen* ligands. The paramagnetic Cu(II) ions are linked by covalent bonds via non-magnetic  $[\text{Pd}(\text{CN})_4]^{2-}$  units in the chain direction. The Pd(II) atom in the anion lies on a symmetry center, so the  $\text{PdC}_4$  chromophore is exactly planar. Among the four cyano groups, the two in *trans* positions exhibit bridging character. Closer look at the structure reveals the presence of HBs linking adjacent chains and, together with the covalent bonds, form a potential triangular network of exchange paths (Table 2). The different nature of chemical interactions in the different directions

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