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# Two new pseudohalide-bridged Cu(II) complexes with a hydrazone ligand: Syntheses, crystal structures and magnetic studies

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#### Abstract

Two new pseudohalide-bridged copper(II) complexes [{Cu(PBH)( $\mu_{1,1}$ -CNO)}<sub>2</sub>] (1) and {Cu(PBH)( $\mu_{1,5}$ -NCNCN)}<sub>n</sub> (2) (where HPBH = 2-pyridinecarboxaldehyde benzoyl hydrazone) have been synthesised and characterised by elemental analysis, CV, IR and UV–Vis spectral studies. The tridentate hydrazone pro-ligand (HPBH) was obtained by the condensation of benzhydrazide and pyridine-2-carboxaldehyde. Structures of both complexes have been established by X-ray crystallography which shows that 1 is a  $\mu_{1,1}$ -CNO<sup>-</sup>-bridged dimer whereas 2 is a  $\mu_{1,5}$ -dca-bridged (dca = dicyanamide) linear polynuclear structure. Variable temperature magnetic susceptibility studies indicate weak antiferromagnetic interactions with *J* values  $-0.50 \text{ cm}^{-1}$  and  $-0.10 \text{ cm}^{-1}$  for 1 and 2, respectively. © 2008 Elsevier B.V. All rights reserved.

Keywords: Copper(II) complexes; Tridentate hydrazone ligand; Pseudohalide bridged; Crystal structures; Variable temperature magnetic studies

#### 1. Introduction

Aroylhydrazone complexes of transition metal ions are known to provide useful models for the elucidation of the mechanism of enzyme inhibition by hydrazine derivatives [1] and for their possible pharmacological applications [2]. Additionally, hydrazone complexes have been the subject of studies for many years due to their antimicrobial and antitumor activities [3–9]. Copper and cadmium complexes using a tridentate hydrazone ligand, the condensation product of 2-acetylpyridine and benzhydrazide, have been reported by our group [10,11]. In continuation of previous work, we have prepared a similar type of tridentate ligand, HPBH, from the condensation of pyridine-2-carboxaldehyde and benzhydrazide.

Our group is mostly concerned with the magnetic interactions between paramagnetic metal centers bridged by pseudohalides and other spacer ligands. With this in mind we prepared two new Cu(II) complexes with the hydrazone ligand (PBH<sup>-</sup>) and two different pseudohalides, cyanate and dicyanamide [dca,  $N(CN)_2^{-}$ ], to observe the variations in structures and magnetic properties.

Compound 1,  $[{Cu(PBH)(\mu_{1,1}-CNO)}_2]$  is an end-on  $\mu_{1,1}$ -cyanato-bridged dimeric Cu(II) complex, whereas 2 is a dca-bridged polynuclear Cu(II) complex. The larger pseudohalide ligand, dicyanamide, has been extensively used during the last few years to generate a wide variety of polynuclear compounds of different topologies and magnetic properties partly due to the discovery of long range magnetic ordering in the  $\alpha$ -M(dca)<sub>2</sub> compounds [12,13]. A particular feature of the dca ligand is the versatility of its coordination modes [14–18] shown to generate compounds with a large variety of architectures, binding one [19], two [20,21], three [22] or four [23] metal centers. We therefore now wish to prepare high-dimensional metal complexes with dca as bridging ligand and polyamines as coligands. There are few reports of dca-bridged metal com-

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plexes with a Schiff base as the coligand [24–26]. In this paper, we describe the syntheses, X-ray crystal structures, variable temperature magnetic (VTM) susceptibility measurements, spectroscopic results and cyclic voltammetric studies of the two new Cu(II) complexes **1** and **2**.

#### 2. Experimental

#### 2.1. Materials

Benzhydrazide, pyridine-2-carboxaldehyde, copper(II) perchlorate hexahydrate, sodium cyanate and dicyanamide (Fluka) were used as received without further purification. All the solvents were of reagent grade.

### 2.2. Physical measurements

Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer. The infrared spectra were recorded on a Perkin-Elmer RX 1 FT-IR spectrophotometer with a KBr disc. The electronic spectra were recorded, in acetonitrile, on a Perkin-Elmer Lambda 40 (UV-Vis) spectrophotometer. Electrochemical studies were carried out with a Versastate II cyclic voltammeter using tetrabutylammonium perchlorate as supporting electrolyte. Magnetic susceptibility measurements for 1 and 2 were carried out with a Quantum Design MPMS-5S SQUID magnetometer under an applied magnetic field of 5000 Oe. The temperature dependence of the molar magnetic susceptibility for 1 and 2 was measured on polycrystalline samples in the temperature range 2-300 K. Diamagnetic corrections were estimated from Pascal tables and magnetic data were corrected for diamagnetic contributions of the sample holder.

#### 2.3. Synthesis

#### 2.3.1. Synthesis of the pro-ligand

#### $[C_6H_5C(O)NHN=C(H)C_5H_4N]$ (**HPBH**)

The pro-ligand was synthesised by condensing benzhydrazide with pyridine-2-carboxaldehyde following a method reported elsewhere [27]. The resulting light yellow liquid solution was used without further purification.

*Caution*! Perchlorate salts are potentially explosive and should be prepared in small quantities and handled with much care.

#### 2.3.2. Synthesis of $[{Cu(PBH)(\mu_{1,1}-NCO)}_2]$ (1)

To a methanolic solution (20 ml) of copper perchlorate hexahydrate (0.370 g, 1 mmol), the solution of the hydrazone pro-ligand (**HPBH**) (1 mmol) was added, followed by the addition, with constant stirring, of a solution of sodium cyanate (0.065 g, 1 mmol) in minimum volume of water-methanol mixture. The final solution was kept at refrigerator temperature yielding dark green, square crystals suitable for X-ray diffraction after 1 day. Crystals were isolated by filtration and were air-dried. Yield: 72%. *Anal.* Calc for C<sub>28</sub>H<sub>20</sub>Cu<sub>2</sub>N<sub>8</sub>O<sub>4</sub>: C, 50.99; H, 3.06; N, 16.99. Found: C, 50.87; H, 3.02; N, 16.92%.

#### 2.3.3. Synthesis of $\{Cu(PBH)(\mu_{1,5}\text{-}NCNCN)\}_n$ (2)

Compound 2 was prepared in an analogous way; 1 mmol (0.089 gm) dca in minimum volume of water was used in place of sodium cyanate. Crystals suitable for Xray diffraction were obtained on overnight standing in refrigerator. Yield: 65%.

*Anal.* Calc. for C<sub>15</sub> H<sub>10</sub> Cu N<sub>6</sub> O: C, 50.92; H,2.85; N, 23.75. Found: C, 50.89; H, 2.83; N, 23.71%.

#### 2.4. X-ray crystallography

The determination of the unit cells and the intensity data collection for 1 and 2 were performed on an Oxford Diffraction Xcalibur-3 CCD diffractometer equipped with Mo K $\alpha$  radiation and graphite monochromator. Data were processed using the CRYSALIS-CCD and -RED [28] programs. The structures of both complexes were determined by direct methods procedures in SHELXS [29a], and refined by full-matrix least-squares methods, on  $F^{2}$ 's, in SHELXL [29b]. Carbon-bonded hydrogen atoms were included in idealised positions and set to ride on the parent atoms. The crystallographic data and the refinement results are listed in Table 1.

Table 1

C / 11	1 .	1	C /	1 .	c	1 4	1	•
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Complex	1	2
Chemical formula	C28H20N8O4Cu2	C <sub>15</sub> H <sub>10</sub> N <sub>6</sub> OCu
Formula weight	659.6	353.8
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$ (equiv. to	<i>P</i> 1 (no. 2)
	no. 14)	
Z	2	2
<i>a</i> (Å)	7.2133(9)	7.5489(8)
b (Å)	11.2710(6)	9.4986(16)
<i>c</i> (Å)	16.896(2)	10.1997(13)
α (°)	90	86.824(12)
β (°)	103.799(11)	76.482(11)
γ (°)	90	85.064(11)
$V(Å^3)$	1334.0(3)	707.99(17)
Temperature (K)	140(1)	140(1)
Density (Mg/m <sup>3</sup> )	1.642	1.660
Absorption coefficient $(mm^{-1})$	1.646	1.556
<i>F</i> (000)	668	358
Crystal size (mm)	$0.51 \times 0.08 \times 0.02$	$0.7\times0.08\times0.02$
$\theta$ Range for data collection (°)	3.8-30.0	3.6-30.0
Reflections collected	23883	10962
Independent reflections $(R_{int})$	3879 (0.062)	4027(0.058)
Number of 'observed'	2746	2974
reflections		
Goodness-of-fit, $F^2$	0.944	0.961
R indices (all data)	$R_1 = 0.065;$	$R_1 = 0.066;$
	$wR_2 = 0.069$	$wR_2 = 0.076$
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.033;$	$R_1 = 0.040;$
	$wR_2 = 0.063$	$wR_2 = 0.071$
Largest difference in peak and hole $(e \text{ Å}^{-3})$	0.50 and -0.41	0.66 and -0.63

#### 3. Results and discussion

#### 3.1. Description of the crystal structures

3.1.1. Description of the structure of the pro-ligand (HPBH) An X-ray analysis of the hydrazone molecule by Paschalidis et al. [30] shows that **HPBH**, in the free state, exists in the keto tautomeric form and the structural conformation of the molecule is E with respect to the imine double bond. It is during complexation the molecule switches to its enol form and is then deprotonated to act as a potentially tridentate NNO donor with subsequent change of conformation from E to Z.

## 3.1.2. Description of the structure of $[{Cu(PBH)(\mu_{I,I}-NCO)}_2](1)$

An ORTEP diagram of 1 with atom numbering scheme is given in Fig. 1. Bond dimensions about the copper atom are listed in Table 2. The structural study reveals that 1 is a centrosymmetric dimer in which the copper centers are fivecoordinate, bonded to three coordinating atoms [N<sub>2</sub>O] from the PBH<sup>-</sup> ligand and the nitrogen atoms from two bridging cyanato anions. Each cyanato anion bridges in end-on fashion and this leads to a relatively small Cu-Cu (3.0874(6) Å) separation. A similar structure with acetato and chloro bridging has been reported earlier [31]. The cyanato ion bridges in an asymmetric (basal-apical) fashion so that the Cu-N bond lengths are significantly different (Ad = 0.411 Å). The cyanate ions are nearly linear with N–C–O angle of 177.7(2)°. The geometry of the Cu(II) centers is close to square pyramidal with  $\tau = 0.192$ ,  $[\tau = |\beta - \alpha|/60^\circ$ , where  $\beta$  and  $\alpha$  are the two largest angles around the central atom;  $\tau = 0$  and 1 for the perfect square pyramidal and trigonal bipyramidal geometries, respectively] [32]. The square base is formed by pyridyl and imine nitrogen atoms, a benzovl oxygen atom and one bridging cyanato nitrogen atom and the Cu(II) atom is shifted from this base by 0.1320(8) Å. The nitrogen atom from the other

Fig. 1. View of a dimer molecule of complex 1 indicating the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table 2

Molecular	dimensions	(bond	lengths	in	Å	and	angles	in	°)	about	the
copper ato	ms in compl	exes 1	and 2								

1		2	
Bond lengths			
Cu–O(1)	1.9785(13)	Cu-O(1)	1.9746(16)
Cu-N(3)	1.9326(16)	Cu-N(3)	1.9660(18)
Cu-N(42)	2.0232(16)	Cu–N(2)	1.9414(18)
Cu-N(51)	1.9458(16)	Cu-N(22)	2.0148(19)
Cu-N(51')	2.3571(17)	Cu-N(34')	2.2031(19)
Bond angles			
N(3)–Cu–O(1)	79.07(6)	N(2)–Cu–O(1)	78.87(7)
O(1)-Cu-N(42)	159.13(6)	O(1)-Cu-N(22)	158.42(7)
N(51)-Cu-O(1)	99.36(6)	N(3)-Cu-O(1)	98.21(7)
O(1)-Cu-N(51')	93.81(6)	O(1)-Cu-N(34')	94.30(7)
N(3)-Cu-N(42)	80.55(6)	N(2)-Cu-N(22)	80.32(7)
N(3)-Cu-N(51)	170.66(7)	N(2)-Cu-N(3)	154.52(7)
N(3)-Cu-N(51')	100.46(6)	N(2)-Cu-N(34')	106.23(7)
N(51)-Cu-N(42)	100.02(7)	N(22)-Cu-N(34')	96.94(7)
N(42)-Cu-N(51')	94.27(6)	N(3)-Cu-N(34')	99.22(7)
N(51)-Cu-N(51')	88.81(6)	N(3)-Cu-N(22)	98.09(7)
Cu-N(51)-Cu'	91.19(6)		

bridging cyanato group (with the longer Cu–N distance) is at the apex.

The dimensions in the hydrazone ligand confirm that this is in the enolate form. The whole ligand is approximately planar, with the normals to the two six-membered rings differing by  $4.00(13)^\circ$ . Each ligand is overlapped by a neighbouring ligand, related by an inversion center; the planes are *ca.* 3.38 Å apart. The dimer molecules are thus linked, through the  $\pi$ - $\pi$  interactions, to form staggered chains through the crystal, Fig. 2.

### 3.1.3. Description of the structure of $\{Cu(PBH)(\mu_{1,5}-NCNCN)\}_n$ (2)

An ORTEP diagram of the  $Cu(PBH)^+$  fragment of 2 and the NCNCN ligands which are bonded to it, with atom numbering scheme, is shown in Fig. 3. Bond dimensions about the copper atom are listed in Table 2. The copper atoms are five-coordinate, with a square pyramidal bonding pattern,  $\tau = 0.065$ . The tridentate hydrazone ligand (PBH<sup>-</sup>) is, again, in the enolate form and close to planar; the normals to the two six-membered rings are 6.84(9)° apart. It coordinates through its O1, N2, N22 donor atoms in the basal plane, and the remaining basal position is occupied by a nitrogen (N3) of a bridging dca ion. The apical position is occupied by the nitrogen atom of a second dca ion with slightly longer Cu-N34' bond length. The trans-base angles  $[N2-Cu1-N3 = 154.52(3)^{\circ}$  and O1- $Cu1-N22 = 158.42(7)^{\circ}$  correspond to the displacement of the Cu atom by 0.3052(9) Å from the mean basal plane. The bridging Cu-N-C-N-Cu' unit adopts a "V" shaped conformation resulting from the sp<sup>2</sup> hybridisation of the central N atom of the dca, where the C31-N32-C33 angle is 122.3(3)°. The  $[N(CN)_2]$  ligand has pseudo  $C_{2v}$  symmetry with average C–N and C=N bond lengths of 1.303(3) and 1.151(3) Å, respectively, as commonly observed [33]. The sp hybridised C atoms of the dca ligand



Fig. 2. A series of dimer molecules of complex 1, connected in chains through overlapping  $\pi$ - $\pi$  interactions. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.



Fig. 3. View of the Cu(PBH)<sup>+</sup> unit and its coordinated  $\mu_{1,5}$  bridging dca ligands in complex 2, indicating the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

show near linearity whereas the C–N–Cu angles of  $152.0(2)^{\circ}$  and  $136.4(2)^{\circ}$  show different degrees of bending.

Structure **2** is a chain polymer of Cu(PBH)<sup>+</sup> units bridged by dca anions in  $\mu_{1,5}$  fashion. Pairs of these chains form a double-stranded chain, running parallel to the *a* axis, by the overlap of PBH ligands arranged alternately from the two chains, Fig. 4. Within each double-stranded chain, each hydrazone is overlapped on both sides by symmetry-related molecules. On one side, the overlap extends over the whole ligand, and the ligand mean-planes are *ca*. 3.46 Å apart; on the other side, only the edges of the rings are involved in the overlap, *ca*. 3.37 Å apart.

#### 3.2. Infrared spectra

The IR spectra of the complexes in the region 4000– $250 \text{ cm}^{-1}$  were analysed in comparison with that of the pro-ligand. The data give evidence for the coordination of the ligand PBH to the metal ion via two nitrogen atoms and one oxygen atom. The infrared spectra of complexes **1** and **2** display IR absorption bands at 1608 and 1605 cm<sup>-1</sup>, respectively, which can be assigned to the C=N stretching frequency of the coordinated ligand **PBH**<sup>-</sup> whereas for the free ligand the same band is observed at 1663 cm<sup>-1</sup>. The shift of this band on complexation towards lower wave



Fig. 4. Portion of a double strand of a  $\{Cu(PBH)(dca)\}_{\infty}$  chain in complex 2.

number indicates coordination of the azomethine nitrogen to the metal center [34]. The low energy pyridine ring inplane and out-of-plane vibrations observed in the spectrum of the pro-ligand at 625 and 406 cm<sup>-1</sup>, respectively, compared with the corresponding bands for the complexes which are shifted to higher frequencies at 638-640 and  $419-422 \text{ cm}^{-1}$ , respectively, are good indications of the coordination of the heterocyclic nitrogen atom[35]. In the spectra of 1 a strong bifurcated band at 2172 and  $2224 \text{ cm}^{-1}$  indicates the presence of bridging cyanato groups [36]. The dicyanamide anion in NaN(CN)<sub>2</sub> shows three sharp and strong characteristic bands in the frequency region 2290–2170 cm<sup>-1</sup> attributed to  $v_s$  (C=N) combination modes (2286 cm<sup>-1</sup>),  $v_{s(C=N)}$  (2232 cm<sup>-1</sup>) and  $v_{s(C=N)}$  (2179 cm<sup>-1</sup>), respectively [37]. The infrared spectra of 2 shows strong absorption bands in the region 2372-2174 cm<sup>-1</sup>. The splitting of the maxima is found at 2372, 2294 cm<sup>-1</sup> ( $v_{as} + v_{s(C=N)}$ ), 2257, 2228 cm<sup>-1</sup> ( $v_{as(C=N)}$ ) and 2174 cm<sup>-1</sup> ( $v_{s(C=N)}$ ). The shift towards higher frequencies of these peaks in 2 as compared to the free dca anion is due to the bridging coordination modes of dca in the complex. The ligand coordination to the metal center is substantiated by two bands appearing for each complex, at 410, 379 and 479, 360 cm<sup>-1</sup> attributable to  $v_{Cu-N}$ ,  $v_{Cu-Q}$ , respectively, for complexes 1 and 2.

#### 3.3. Electronic spectra

The electronic spectra of 1 and 2 in acetonitrile solution show two strong absorption bands in the region 267 and 299 nm. These bands are clearly charge-transfer in origin [38]. The band around 382 nm is assigned to the  $n-\pi^*$  transition of the azomethine group. In the spectrum of the complex, the bands of the azomethine chromophore  $n-\pi^*$ transition are shifted to lower frequencies indicating that the imine nitrogen atom is involved in coordination to the metal ion [38]. The visible spectra of **1** and **2** display a single broad band at 673 and 663 nm, respectively. These spectral features are consistent with the five-coordinate geometry of the Cu(II) complex. In general typical five coordinated Cu(II) complexes of SP or distorted SP geometries exhibit a band in the range 550–660 nm, whereas the corresponding TBP complexes usually show a maximum at  $\lambda > 800$  nm with a higher energy shoulder [39]. This indicates that the solution spectrum of the complex ion is adequately explained by a d–d transition for the Cu(II) ion in a distorted SP geometry where the absorption maximum band observed in the visible region results from a  $^{2}E \rightarrow ^{2}B_{1}$  transition.

#### 3.4. Redox potential

The electrochemical studies of 1 and 2 were performed in acetonitrile using tetrabutylammonium perchlorate as supporting electrolyte at a scan rate of 50 mV/s. 1 shows two metal centered irreversible reduction peaks. The first reductive response for 1 is observed at -0.6 V (w.r.t. SCE) and the second is at -0.828 V. Compound 2 shows only one reversible reductive response, at -0.177/-0.122 V. The two metal centers in 1 can communicate electrically through the shorter pseudohalide cyanate but for 2, with the larger dca, this was not possible and only one peak was observed.

#### 3.5. Magnetic properties

The curve of  $\chi_M T = f(T)$  for **1** is almost constant above 40 K with a value near 0.78 cm<sup>3</sup> K mol<sup>-1</sup>, in good agreement with the expected value for two Cu(II) ions. Below 40 K,  $\chi_M T$  decreases to reach a value of 0.73 cm<sup>3</sup> K mol<sup>-1</sup> at 4 K, thus the dinuclear complex exhibits a very small antiferromagnetic interaction. According to the dimeric structure of the compound, the  $\chi_M T$  curve has been fitted using a classical Bleaney and Bowers law, using the phenomenological Hamiltonian  $H = -JS_A \cdot S_B$ . The resulting law used for fitting has the following form:

$$\chi_{\rm M}T = \frac{2Ng^2\beta^2}{k[3 + \exp(-J/kT)]}$$

Best fit was obtained for Lande factor g = 2.03, isotropic interaction parameter  $J = -0.50 \text{ cm}^{-1}$ . The temperature dependence of  $\chi_{\rm M}T$  for **1** is depicted in Fig. 5.

The temperature dependence of  $\chi_M T$  for **2** is shown in Fig. 6. Due to the chain structure of the complexes, the model of equally spaced copper(II) ions has been used. The spin Hamiltonian in zero-field is  $H = -J\sum_{i=1}^{n-1} S_{A_i} \cdot S_{A_{i+1}}$  where the summation runs over the n sites of the chain. When n tends to infinity, there is no analytical method to determine the magnetic susceptibility. However, the results can be fitted using the numerical expression for J < 0 [40]



Fig. 5. Experimental ( $\blacksquare$ ) and calculated (—) temperature dependence of  $\chi_M T$  for 1.



Fig. 6. Experimental ( $\Box$ ) and calculated (—) temperature dependence  $\chi_M T$  for **2**.

$$\chi_{\rm M}T = \frac{Ng^2\beta^2}{k} \\ \times \frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3} \quad \text{with } x \\ = -J/kT.$$

For complex **2**, the best fit was obtained with a Lande factor g of 2.11, and isotropic interaction parameter  $J = -0.10 \text{ cm}^{-1}$ . This small value is in line with those for similar reported structures [25,33,41].

The weak coupling inside the chain is due to the longer distance between the copper(II) ions as dicyanamide acts as  $\mu_{1,5}$ -bridging ligand. The weak interaction can also be explained by the fact that one end of the dca bridge is in the apical position of the square pyramidal copper. Since the magnetic orbital ( $d_{x^2-y^2}$ , again) is perpendicular to that direction, no overlap between magnetic orbitals is expected. This explains the low absolute value of *J* for **2**.

It has been reported earlier [42] that dinuclear distorted square pyramidal structures of Cu(II) can show magnetic interactions whereas the perfect square pyramids are not

Table 3	
Structural and magnetic properties of bis(cyanato) copper(II) dimers	

Formula of the complex	$\theta/R$	$J (\mathrm{cm}^{-1})$
$[Cu_2(\mu_{1,1}\text{-}NCO)_2(NCO)_2(dpyam)_2]$	37.57	6.03
$[Cu_2(\mu_{1,1}\text{-}NCO)_2(NCO)_2(phen)]$	37.405	13.75
$[Cu_2(\mu_{1,1}-NCO)_2(Medien)_2](ClO_4)_2$	40.626	-4.6
$[{Cu(PBH)(\mu_{1,1}-CNO)}_2]$	37.678	-0.5

reported to show any such interactions. This is due to the fact that in the latter geometry the magnetically active  $[d_{x^2-y^2}$  orbital in case of Cu(II)] orbitals on each monomeric unit are orthogonal to each other and there is no suitable orbital on the part of ligand, which participates in the bridging, through which magnetic interaction can take place. As a consequence greater distortion from the perfect square pyramidal geometry will give rise to greater magnetic interaction between the paramagnetic metal centers.

Of the structures, where cyanate acts as a bridging ligand [43], as far as our search goes, very few had variable temperature magnetic studies. Due to lack of magnetic data no definite conclusion could be drawn about the magneto structural correlation in penta-coordinated cyanate bridged Cu(II) dinuclear structures. Of the three data available with VTM studies two showed ferromagnetic interactions [44] and the other one showed antiferromagnetism [45]. We take the  $\theta/R$  ratio [where  $\theta$  is the Cu–N–Cu bridge angle and R is the longer Cu-N separation in the axial bond length in Cu and bridging NCO<sup>-</sup>] as an authentic parameter for magneto structural correlation as done by Marsh et al. [46]. For the complex  $[Cu_2(\mu_{1,1}-NCO)_2(NCO)_2(dpyam)_2]$  (dpyam = di-2-pyridylamine),  $\theta/R$  is 37.57 and  $J = 6.03 \text{ cm}^{-1}$  where as for  $[Cu_2(\mu_{1,1}-NCO)_2(NCO)_2(phen)]$  the same ratio is 37.405 and the J is 13.75 cm<sup>-1</sup>. The only previous report that we found where antiferromagnetism is operative is  $[Cu_2(\mu_{1,1} NCO_{2}$  (Medien)<sub>2</sub> (ClO<sub>4</sub>)<sub>2</sub> (Medien = 4-Methyldiethylenetriamine). But there are two independent types of dimmers with different bond parameters, one symmetric and the other asymmetric. Considering the  $\theta/R$  for the symmetric unit it comes out to be 40.626 where as the J is  $-4.6 \text{ cm}^{-1}$ . For complex 1 that we are reporting here the  $\theta/R$  is 37.678 and J is -0.5 cm<sup>-1</sup>. All the above data are summarized in Table 3. So it could be stated that with increase in  $\theta/R$  ratio the interaction changes from ferromagnetic to antiferromagnetic gradually.

#### 4. Conclusions

Two new Cu(II) complexes with a tridentate hydrazone ligand, PBH<sup>-</sup> and with CNO<sup>-</sup> and dca as counter ions, have been prepared. Complex **1** is dimeric with the isocyanate ligands bridging in  $\mu_{1,1}$  mode; the dimer units are linked through  $\pi$ - $\pi$  interactions to form chains through the crystal. Complex **2**, however, is a doublestranded coordination polymer in which each strand comprises Cu(PBH)<sup>+</sup> units linked through  $\mu_{1,5}$  bridging dca ligands; the PBH<sup>-</sup> ligands from the two strands alternate in  $\pi$ -stacks parallel to the *a* axis. Both the complexes show the copper atoms with distorted square pyramidal geometry which can be verified from the UV–Vis spectra and X-ray crystallography. Magnetic studies of the complexes show that both are antiferromagnetically coupled.

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#### Appendix A. Supplementary material

CCDC 638165 and 643521 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.01.020.

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