Cu(bapen)M(CN)₄·H₂O exhibiting chain-like structures (bapen = N,N'-bis(3-aminopropyl)-1,2-diaminoethane, M= Ni, Pd): Preparations, crystal structures, spectroscopic and magnetic properties

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Abstract

Single crystals of Cu(bapen)Ni(CN)₄·H₂O and Cu(bapen)Pd(CN)₄·H₂O (bapen = N,N'-bis(3-aminopropyl)-1,2-diaminoethane) were isolated from the aqueous systems copper(II) – bapen – [M(CN)₄]²⁻ (M = Ni, Pd). Crystals of the two compounds are isostructural and are built up of two crystallographically independent quasi-linear chains [-Cu(bapen)-μ₂-NC-Ni(CN)₂-μ₂-CN-]_n and solvate water molecules. The copper(II) centers exhibit the usual distorted octahedral coordination with one tetradentate bapen ligand in the equatorial plane (mean Cu-N are 2.030 Å for Cu(bapen)Ni(CN)₄·H₂O and 2.018 Å for Cu(bapen)Pd(CN)₄·H₂O), while the axial positions are occupied by nitrogen atoms from μ₂-bridging cyanido ligands with longer Cu-N bonds (mean values are 2.544 Å for Cu(bapen)Ni(CN)₄·H₂O and 2.543 Å for Cu(bapen)Pd(CN)₄·H₂O). One of the two independent coordinated bapen ligands is disordered, as are the water molecules of crystallization. The Ni and Pd atoms in (1) and (2) exhibit the usual square coordination with the bridging cyanido ligands trans to each other. Several OH...O, N-H...O and N-H...N hydrogen bonds enhance the stability of the structures. ESR spectra corroborated the presence of Jahn-Teller anisotropy at the copper(II) atoms. Magnetic studies in the temperature range 1.8–300 K

reveal that both $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{bapen})\text{Pd}(\text{CN})_4 \cdot \text{H}_2\text{O}$ follow Curie-Weiss laws with $\theta = -0.51$ K and $\theta = -0.34$ K, respectively, suggesting the presence of weak antiferromagnetic interactions.

Keywords:

Copper(II); tetracyanidocomplexes; X-ray crystal structure; hydrogen bonding; EPR spectrum; magnetic studies.

Introduction

At present it is accepted that magnetic exchange pathways can traverse not only covalent bonds but also weak interactions, e.g. hydrogen bonds. Several examples for such systems can be mentioned: in $[\text{Cu}(\text{5-MeOsAl})_2(\mu\text{-nia})(\text{H}_2\text{O})]_2$ (5-MeOsAl = 5-methoxysalicylato, nia = nicotinamide), $\{\text{Cu}(\text{5-MeOsAl})_2(\text{H}_2\text{O})\}$ dimeric units are held by strong hydrogen bonds and the reported value of the antiferromagnetic coupling constant is $2J = -9.8$ K (6.83 cm^{-1}) [1]. Stronger antiferromagnetic interactions were reported for $\{\text{Cu}_2\}$ dimers held together by O-H $\cdots$ O hydrogen bonds in $[\text{Cu}_2(\text{Hmea})_2(\text{mea})_2\text{ClO}_4]\text{ClO}_4$ (Hmea = 2-aminoethanol, $J = -32.1$ K) [2] and in $[\text{Cu}(\text{poxap})(\text{H}_2\text{O})(\text{NO}_3)]$ (poxap = 2-(o-hydroxyphenyliminomethyl)pyridine N-oxide), $J/k_B = -38.3$ K [3].

We have reported previously that in $\text{Cu}(\text{en})_2\text{Ni}(\text{CN})_4$ (*en* = 1,2-diaminoethane), which exhibits a chain-like structure, hydrogen bonds play an important role in magnetic exchange interactions; moreover, long range ordering was observed at 128 mK as indicated by the λ -like anomaly in the magnetic specific heat [4]. In order to study the correlation between hydrogen bonding and magnetic properties, several new complexes derived from $\text{Cu}(\text{en})_2\text{Ni}(\text{CN})_4$ were synthesized replacing *en* by *N*-methylated ligands [5, 6]. Recently we were successful in preparing and characterizing a set of complexes in which two bidentate *en* ligands were replaced by one tetradentate macrocyclic ligand, cyclam, giving an overall composition $\text{Cu}(\text{cyclam})\text{M}(\text{CN})_4$ (cyclam = 1,4,8,11-tetraazatetracyclodecane; M = Ni, Pd, Pt) [7]. As a continuation of our studies on these systems we have replaced the closed ring cyclam ligand by an acyclic tetradentate ligand *bapen* (*bapen* = *N,N'*-bis(3-aminopropyl)-1,2-diaminoethane) in order to study the influence of this change on the structures of the crystals thus formed, including the hydrogen bonding patterns, as well as to study the magnetic properties of the newly prepared compounds down to 1.8 K. The ligand *bapen* has been used as a blocking ligand in cyanidocomplexes, namely in $\text{Cu}(\text{bapen})\text{Ag}_2(\text{CN})_4$ [8] and $\text{Cu}(\text{bapen})\text{Fe}(\text{CN})_5(\text{NO}) \cdot 1.5\text{H}_2\text{O}$ [9].

Experimental

Copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 99 %, Aldrich, N,N'-bis(3-aminopropyl)-1,2-diaminoethane (bapen, $\text{C}_8\text{H}_{22}\text{N}_4$, 98 %, Aldrich), citric acid, ethanolamine, and aqueous ammonia (25 %, in analytical grade) were used as received. Potassium tetracyanonickelate(II) monohydrate ($\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$) was prepared from nickel sulfate heptahydrate and potassium cyanide following the published procedure [10]. Potassium tetracyanopalladate(II) trihydrate ($\text{K}_2[\text{Pd}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$) was prepared from PdCl_2 and potassium cyanide following the published procedure [11].

Preparation of $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ (1)

To an aqueous solution of CuSO_4 (0.1248 g of the pentahydrate, 0.5 mmol, 10 cm^3 of water) successively 0.087 cm^3 of liquid bapen (0.5 mmol) and an aqueous solution of $\text{K}_2[\text{Ni}(\text{CN})_4]$ (0.1205 g as monohydrate, 0.5 mmol, 10 cm^3 of water) were added. Immediately after addition of the solution of $\text{K}_2[\text{Ni}(\text{CN})_4]$ the product $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ appeared in the form of an ink blue-violet precipitate. From the dark violet filtrate dark violet-blue needles of $\text{Cu}(\text{bapen})\text{Pd}(\text{CN})_4 \cdot \text{H}_2\text{O}$ suitable for use in an X-ray study were formed overnight. Both batches of the solid product were separated by filtration and dried in air at laboratory temperature. Yield: 0.137 g (65 %).

Anal. for $\text{C}_{18} \text{H}_{36} \text{Cu}_{1.5} \text{N}_{12} \text{Ni}_{1.5} \text{O}_{1.5}$ ($M = 627.96 \text{ g} \cdot \text{mol}^{-1}$): Found: C, 34.7; H, 5.4; N, 26.8 %. Calc.: C, 34.8; H, 5.7; N, 26.8 %.

IR (in cm^{-1}): 3457(m); 3307(m); 3263(m); 3241(m); 2956(w); 2879(w); 2112(s); 1635(m); 1595(w); 1455(w); 1436(m); 1294(m); 1166(s); 1095(m); 1066(s); 1025(s); 997(m); 923(m); 873(m); 860(m); 634(s); 507(s); 414(s).

Preparation of $\text{Cu}(\text{bapen})\text{Pd}(\text{CN})_4 \cdot \text{H}_2\text{O}$ (2)

The synthesis of (2) was done using essentially the same procedure as for $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$, but instead of the water solution of $\text{K}_2[\text{Ni}(\text{CN})_4]$, a water solution of $\text{K}_2[\text{Pd}(\text{CN})_4]$ (0.1444 g, 0.5 mmol, 10 cm^3) was used. The product (2) in the form of a violet precipitate was formed immediately after mixing. The precipitate was filtered and the filtrate was left aside for crystallization at laboratory temperature. Dark violet-blue crystals of $\text{Cu}(\text{bapen})\text{Pd}(\text{CN})_4 \cdot \text{H}_2\text{O}$ formed overnight. Yield: 0.105 mg (45 %).

Anal. for $\text{C}_{18} \text{H}_{36} \text{Cu}_{1.5} \text{N}_{12} \text{O}_{1.5} \text{Pd}_{1.5}$ ($M = 699.50 \text{ g} \cdot \text{mol}^{-1}$): Found: C, 31.1; H, 5.0; N, 24.4 %. Calc.: C, 31.0; H, 4.7; N, 24.1 %.

IR (cm⁻¹): 3447m; 3307s; 3248s; 2950w; 2124s; 1633m; 1595m; 1451m; 1433m; 1292m; 1250w; 1163s; 1095m; 1064s; 1022s; 996s; 971m; 950m; 922m; 873m; 633s; 505s.

Physical measurements

Elemental analyses were performed on a Perkin Elmer 2400 Series II CHNS/O instrument.

Infrared spectra were recorded on a Perkin Elmer Spectrum 100 CsI DTGS FTIR Spectrometer with UATR 1 bounce-KRS-5 in the range of 4000–300 cm⁻¹ and on a Thermo-Nicolet AVATAR 330 FTIR KBr in the range of 4000 to 400 cm⁻¹.

Electronic absorption spectra were recorded from KBr pellets on a Specord 250 spectrometer (Analytik Jena).

Electron-spin resonance (ESR) data were collected at 2.5 K in an X-band Bruker ELEXSYS E500 spectrometer.

The magnetic susceptibility was taken at 1kG using a commercial SQUID magnetometer in the temperature range from 1.8 to 300 K. The weights of the samples were 44.1 mg and 48 mg for Cu(bapen)Ni(CN)₄·H₂O and Cu(bapen)Pd(CN)₄·H₂O, respectively. The background contribution from the gelatin capsule to the magnetic moment of the sample was subtracted. The data were corrected for diamagnetic contributions using Pascal's constants. The ESR and magnetic measurements were carried out on powdered samples.

X-ray experiment

Diffraction data for both Cu(bapen)Ni(CN)₄·H₂O and Cu(bapen)Pd(CN)₄·H₂O were collected on Oxford Diffraction CCD-based four-circle diffractometers equipped with graphite-monochromated MoK α radiation (λ = 0.71073 Å). No instrument or crystal instabilities were observed during data collection. Data for both Cu(bapen)Ni(CN)₄·H₂O and Cu(bapen)Pd(CN)₄·H₂O were corrected for absorption using the ABSPACK module of CrysAlis Pro [12, 13], which was also used to derive the error models [14]. The two structures, which are isomorphous, were solved by direct methods in SHELXS-97 [15] and refined against the F² data using full-matrix least squares methods with the program SHELXL-97 [16]. Anisotropic displacement parameters were refined for all non-H atoms. During the refinement process it became clear that the atoms C16 and C17 (Figure 1) of the bapen ligand, and consequently the O1W atom are disordered about the centre of symmetry at Cu2, giving half occupancy for the disordered positions.

The hydrogen atoms bonded to carbon and nitrogen atoms were included at idealized positions and refined as riders with isotropic displacement parameters assigned as 1.2 times the U_{eq} values of the corresponding bonding partners. Among the water molecules only the hydrogen atoms linked to O1w in

Cu(bapen)Ni(CN)₄·H₂O could be localized but for the disordered O2w water molecules in both structures the hydrogen atoms were neither located nor modeled geometrically.

Structure graphics were drawn using the program Diamond [17]. Crystal data and final parameters of the structure refinements for Cu(bapen)Ni(CN)₄·H₂O and Cu(bapen)Pd(CN)₄·H₂O are summarized in Table 1, while selected bond lengths and angles are given in Table 2. Possible hydrogen bonds are given in Table 3.

Results and Discussion

Synthesis and spectroscopic characterization

From the aqueous systems copper(II) – bapen – [M(CN)₄]²⁻ (M = Ni, Pd) using analogous synthetic procedures as for the systems with cyclam [7] two cyanidocomplexes Cu(bapen)Ni(CN)₄·H₂O and Cu(bapen)Pd(CN)₄·H₂O exhibiting composition Cu(bapen)M(CN)₄·H₂O were isolated. The products formed immediately after mixing of the initial solutions, but from the filtrates it was possible to isolate X-ray quality single crystals. The results of chemical analyses corroborated the assumed compositions of the crystals, which were later confirmed by single crystal X-ray analyses (see below). In contrast to the previously studied complexes Cu(cyclam)M(CN)₄, both title compounds Cu(bapen)Ni(CN)₄·H₂O and Cu(bapen)Pd(CN)₄·H₂O crystallized as monohydrates. It is interesting to note that from a methanol solution the analogous dicyanidoargentate complex Cu(bapen)Ag₂(CN)₄ was isolated [8].

The measured IR spectra of Cu(bapen)Ni(CN)₄·H₂O and Cu(bapen)Pd(CN)₄·H₂O are very similar (see Experimental). The marked feature of both spectra is the observation of typical sharp absorption bands corresponding to the $\nu(\text{CN})$ stretching vibrations of the cyanido ligand observed at 2112 cm⁻¹ for Cu(bapen)Ni(CN)₄·H₂O and 2124 cm⁻¹ for Cu(bapen)Pd(CN)₄·H₂O, in line with the literature [18]. In the IR spectra of analogous complexes with the cyclam ligand, Cu(cyclam)M(CN)₄, two closely positioned absorption bands were observed at 2119 and 2113 cm⁻¹ for M = Ni and 2133 and 2127 cm⁻¹ for M = Pd [7]. The presence of bapen in both Cu(bapen)Ni(CN)₄·H₂O and Cu(bapen)Pd(CN)₄·H₂O is indicated by several absorption bands, e.g. absorption bands due to $\nu(\text{N-H})$ vibrations are positioned in the region of 3308–3195 cm⁻¹; the values of 3308 and 3198 cm⁻¹ were reported for the analogous Cu(bapen)Ag₂(CN)₄ [8]. Solvent water manifests itself by $\nu(\text{OH})$ absorption bands positioned at 3457 cm⁻¹ in Cu(bapen)Ni(CN)₄·H₂O and at 3447 cm⁻¹ in Cu(bapen)Pd(CN)₄·H₂O.

The electronic spectra of $\text{Cu(bapen)Ni(CN)}_4 \cdot \text{H}_2\text{O}$ and $\text{Cu(bapen)Pd(CN)}_4 \cdot \text{H}_2\text{O}$ display a broad absorption band with maximum absorption at 559 nm for both compounds. The shape of the absorption bands (the presence of shoulders at higher wave lengths) indicates that the observed absorption band represents an envelope incorporating *d-d* transitions formed of at least three components [19]. The corresponding maxima in the electronic spectra of the analogous Cu(cyclam)M(CN)_4 compounds exhibited values of 516 (M = Ni) and 510 nm (M = Pd) indicating stronger coordination of the cyclam ligand.

Crystal structure

The isostructural complexes $\text{Cu(bapen)M(CN)}_4 \cdot \text{H}_2\text{O}$ (M = Ni, Pd) exhibit chain-like structures with water molecules of crystallization located between the chains (Fig. 1, Fig. 2). The chains are built up of $[\text{Cu(bapen)}]^{2+}$ cations and tetracyanonickellate anions which are linked by bridging μ_2 -cyanido ligands, which are situated *trans* to each other in both cations and anions; thus the chain is of the 2,2-TT type according to the previously described nomenclature [20]. The structures are thus similar to the previously described anhydrous Cu(cyclam)M(CN)_4 (M = Ni, Pd, Pt), containing the macrocyclic cyclam ligand [7] and to $\text{Cu(en)}_2\text{Ni(CN)}_4$ with two bidentate ligands [21]. In both $\text{Cu(bapen)M(CN)}_4 \cdot \text{H}_2\text{O}$ (M = Ni, Pd) there are two crystallographically independent $[-\text{Cu(bapen)-NC-Ni(CN)}_2\text{-CN-}]_n$ chains designated C(Cu1) (this chain contains Cu1 atoms) and C(Cu2). While in the $[\text{Cu1(bapen)}]^{2+}$ cation the tetradentate bapen ligand is ordered, in the second chain the bapen ligand is disordered over two positions related by a centre of symmetry (-1) located at the Cu2 atom with C16 and C17 atoms placed alternatively on both sides of the Cu center within the equatorial plane (Fig. 1).

Both copper atoms Cu1 and Cu2 are coordinated in the form of an elongated tetragonal bipyramid. The equatorial sites are occupied by four nitrogen atoms from the bapen ligand giving a CuN_4 donor set with mean Cu—N bonds of 2.030 Å (M = Ni) and 2.018 Å (M = Pd) (Table 2); these values are in agreement with those found in $\text{Cu(bapen)Fe(CN)}_5(\text{NO}) \cdot 1.5\text{H}_2\text{O}$ (2.056 Å) [9]. The axial Cu—N(C) bonds are elongated with mean values of 2.544 Å for $\text{Cu(bapen)Ni(CN)}_4 \cdot \text{H}_2\text{O}$ and 2.543 Å for $\text{Cu(bapen)Pd(CN)}_4 \cdot \text{H}_2\text{O}$, due to the Jahn-Teller effect indicating weaker coordination of the bridging cyanido ligands. The corresponding angles Cu—N $\equiv$ C with mean values of 130.0° for $\text{Cu(bapen)Ni(CN)}_4 \cdot \text{H}_2\text{O}$ and 129.4° for $\text{Cu(bapen)Pd(CN)}_4 \cdot \text{H}_2\text{O}$ (Table 2) are rather bent, but a similar value of 131.0° was found in the analogous $\text{Cu(eten)}_2\text{Pd(CN)}_4$ (eten = N-ethyl-1,2-diaminoethane) [22].

The two independent nickel atoms in $\text{Cu(bapen)Ni(CN)}_4 \cdot \text{H}_2\text{O}$ are coordinated by four cyanido ligands in the usual square coordination. The geometric parameters associated with both anions (Table 2) are as expected

[21]. The same type of square coordination is seen for the Pd atoms in (2) and the geometric parameters associated with the $[\text{Pd}(\text{CN})_4]^{2-}$ anions are very similar to those observed in $\text{Cu}(\text{dmen})_2\text{Pd}(\text{CN})_4$ (dmen = N,N-dimethylethylenediamine) [23].

Fig. 1 Two crystallographically independent parts of the structure of $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ (a) and $\text{Cu}(\text{bapen})\text{Pd}(\text{CN})_4 \cdot \text{H}_2\text{O}$ (b). The bapen ligands coordinated to Cu2 atoms (namely C16 and C17 atoms with the corresponding hydrogen atoms) and the corresponding O1 atoms in both $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{bapen})\text{Pd}(\text{CN})_4 \cdot \text{H}_2\text{O}$ are disordered but for the sake of clarity only one position is shown. Both disordered positions of O2 atoms in both $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{bapen})\text{Pd}(\text{CN})_4 \cdot \text{H}_2\text{O}$ are shown. Hydrogen atoms bound to the carbon atoms are omitted for clarity. The thermal ellipsoids are drawn at the 30 % probability level.

Fig. 2 View of the crystal structure of $\text{Cu(bapen)Ni(CN)}_4\cdot\text{H}_2\text{O}$ along $[001]$ displaying the positions of water molecules of crystallization between the chains running along the viewing direction. Both disordered positions of the bapen ligand in the C(Cu2) chains are shown. The hydrogen atoms are omitted for clarity.

The disordered water molecules of crystallization occupy free channel-like space between two C(Cu1) and two C(Cu2) chains (Fig. 2). Both C(Cu1) and C(Cu2) chains are surrounded by four other chains; the chain C(Cu1) is surrounded by two C(Cu1) and two C(Cu2) chains while there are four C(Cu1) chains around the C(Cu2) chain. The closest distances between the paramagnetic copper(II) atoms within the chains in $\text{Cu(bapen)Ni(CN)}_4\cdot\text{H}_2\text{O}$ is $10.0615(3)$ Å for $\text{Cu2}\cdots\text{Cu2}^i$ (symmetry code: $x, y, -1 + z$) ($10.1944(2)$ in $\text{Cu(bapen)Pd(CN)}_4\cdot\text{H}_2\text{O}$) and between the chains is $7.2272(4)$ Å in $\text{Cu(bapen)Ni(CN)}_4\cdot\text{H}_2\text{O}$ for $\text{Cu2}\cdots\text{Cu1}^i$ (symmetry code: $0.5 + x, 0.5 - y, -0.5 + z$) ($7.2147(4)$ Å in $\text{Cu(bapen)Pd(CN)}_4\cdot\text{H}_2\text{O}$). The $\text{CuN}(\text{eq})_4$ planes bearing the magnetic orbitals in neighboring cations of $\text{Cu1N}_4 - \text{Cu2N}_4$ form an angle of $19.00(9)^\circ$ in $\text{Cu(bapen)Ni(CN)}_4\cdot\text{H}_2\text{O}$ ($19.17(10)^\circ$ in $\text{Cu(bapen)Pd(CN)}_4\cdot\text{H}_2\text{O}$).

Figures 3 and 4 display the hydrogen bonds and other close non-covalent contacts in $\text{Cu(bapen)Ni(CN)}_4\cdot\text{H}_2\text{O}$ and $\text{Cu(bapen)Pd(CN)}_4\cdot\text{H}_2\text{O}$ (Table 4). The topology of this hydrogen bonding differs substantially from that observed in the analogous compounds Cu(cyclam)M(CN)_4 ($\text{M} = \text{Ni, Pd, Pt}$) [7] or

$\text{Cu}(\text{bmen})_2\text{M}(\text{CN})_4$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$; $\text{bmen} = \text{N,N}'\text{-dimethyl-1,2-diaminoethane}$) [5, 24, 25]. The complexity in this case reflects the higher number of NH donors available, as compared to one cyclam or two bmen ligands, as well as the presence of disorder and water molecules of crystallization. It is interesting to note that neighboring (Cu1) chains interact via one $\text{N-H}\cdots\text{N}(\text{C})$ hydrogen bond, $\text{N2-H2}\cdots\text{N8}(\text{C})$; but we observe no hydrogen bond that directly links the C(Cu1) chain with its C(Cu2) neighbors or which links adjacent C(Cu2) chains. On the other hand, there are several hydrogen bonds between water molecules of crystallization and the two chains, so water serves both as a filler and as a binder between the chains.

a)

b)

Fig. 3 Hydrogen bonding scheme in $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ with participation of a) $[-\text{Cu1}(\text{bapen})-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-]_n$ chains; and of b) $[-\text{Cu2}(\text{bapen})-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-]_n$ chains. The carbon atoms and their hydrogen atoms are omitted for clarity.

Fig. 4 Overall view of possible hydrogen bonding scheme in $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$.

Magnetic properties

The ESR spectra of the complexes $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{bapen})\text{Pd}(\text{CN})_4 \cdot \text{H}_2\text{O}$ obtained at 2.5 K on powdered samples have been analyzed using the ESR spectra simulation package EasySpin (Fig. 5) [26]. Since the structural data in both complexes corroborate the presence of two chains with different distortion directions of the coordination octahedron, two copper(II) centres (referred to as A and B) with independent g -tensors were included in the fit. The best fit to the experimental data using a least-squares method has been obtained for the g -factors and linewidths (the full width at half-height) presented in Table 4. It was not possible to describe the experimental spectra using a single linewidth, therefore anisotropic broadening of the resonance line was included. Such anisotropic linewidth broadening can reflect the low-dimensional character of the magnetic subsystem in both complexes. The hyperfine structure expected for copper(II) atoms could not be resolved in the spectrum, suggesting the existence of exchange couplings between magnetic centers [27]. The g -factors ($g_{\perp} < g_{\parallel}$) are consistent with the axial type of anisotropy due to the Jahn-Teller effect typical for copper(II) atoms and confirmed by the crystal structures of $\text{Cu}(\text{bapen})\text{M}(\text{CN})_4 \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Ni}, \text{Pd}$). An unpaired electron of the copper(II) atom for such coordination resides in the $d_{x^2-y^2}$ orbital [28] and the major exchange paths will propagate along the directions determined by the lobes of the $d_{x^2-y^2}$ orbital located in the planes of bapen ligands.

Fig. 5 Comparison of the experimental ESR spectra of $\text{Cu(bapen)Ni(CN)}_4\cdot\text{H}_2\text{O}$ (complex 1) and $\text{Cu(bapen)Pd(CN)}_4\cdot\text{H}_2\text{O}$ (complex 2) measured at 9.4 GHz and the EasySpin [26] fit for parameters summarized in Table 4.

The magnetic behaviour of the complexes $\text{Cu(bapen)Ni(CN)}_4\cdot\text{H}_2\text{O}$ and $\text{Cu(bapen)Pd(CN)}_4\cdot\text{H}_2\text{O}$ in the temperature range of 1.8-300 K can be characterized by Curie-Weiss law. A slight decrease of μ_{eff} below 10 K (Fig. 6), suggests the presence of a weak antiferromagnetic (AF) exchange coupling. The analysis of the inverse susceptibility between 1.8 and 150 K, yielded $g = 2.15$ and $\theta = -0.51$ K for $\text{Cu(bapen)Ni(CN)}_4\cdot\text{H}_2\text{O}$ and $g = 2.02$ and $\theta = -0.34$ K for $\text{Cu(bapen)Pd(CN)}_4\cdot\text{H}_2\text{O}$. Similar weak AF interactions were also observed in the analogous compounds $\text{Cu(en)}_2\text{Ni(CN)}_4$ [5] and $\text{Cu(bmen)}_2\text{Pt(CN)}_4$ [25] and specific heat studies revealed magnetic ordering, indicated by a λ -like anomaly, at 0.128 K and 0.22 K, respectively. The short-range correlations were described by an $S = 1/2$ quadratic Heisenberg AF model, where the exchange interactions between the covalent chains are mediated by hydrogen bonds.

Fig. 6 Temperature dependence of the ZFC static inverse susceptibility and temperature dependence of the effective magnetic moment of Cu(bapen)Ni(CN)₄·H₂O (inset).

Conclusions

The present study on the two complexes Cu(bapen)M(CN)₄·H₂O (M = Ni, Pd) has shown that the use of an acyclic tetradentate ligand bapen instead of the tetradentate cyclic ligand cyclam or two bidentate ligands en led invariably to the formation 2,2-TT type chain-like structures of the $[-\text{Cu}(\text{L}_\text{N})_x\text{-NC-M}(\text{CN})_2\text{-CN-}]_n$ type (L_N = bapen ($x = 1$), cyclam ($x = 1$), en ($x = 2$)). The N-donor amine ligand(s) occupy the equatorial plane in the tetragonally distorted octahedron $\{\text{CuN}_6\}$, while the N-bonded bridging cyanido ligands are placed in the axial positions; these N-bonded bridging cyanido ligands are bound more weakly due to the Jahn-Teller effect. On the other hand, the use of various N-donor ligands bound to the copper(II) atoms led to the formation of different hydrogen bonding patterns in the structures studied. EPR and magnetic studies confirmed the presence of weak AF exchange coupling between copper(II) atoms. The results indicate that the exchange coupling mediated largely by hydrogen bonds follows the directions of the lobes of $d_{x^2-y^2}$ orbital in which the highest spin density is located.

Supplementary materials

Crystallographic data for the compounds Cu(bapen)M(CN)₄·H₂O (M = Ni, Pd) have been deposited with the Cambridge Crystallographic Data Centre, CCDC 858998 and 858999, respectively. Copies of the information

may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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Table 1 Crystal data and structure refinement for Cu(bapen)Ni(CN)₄·H₂O and Cu(bapen)Pd(CN)₄·H₂O

Empirical formula	C ₃₆ H ₇₂ Cu ₃ N ₂₄ Ni ₃ O ₃	C ₃₆ H ₇₂ Cu ₃ N ₂₄ O ₃ Pd ₃
M _r	1255.92	1399.00
Crystal dimensions (mm)	0.16 x 0.09 x 0.045	0.26 x 0.14 x 0.04
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ /n
Unit cell dimensions:		
<i>a</i> (Å)	9.9709(4)	10.0135(3)
<i>b</i> (Å)	27.1117(10)	26.9852(5)
<i>c</i> (Å)	10.0615(3)	10.1944(2)
β (°)	93.707(4)	93.133(2)
<i>V</i> (Å ³)	2714.2(2)	2750.6(2)
<i>Z</i>	2	2
<i>D</i> _{calc} (g·cm ⁻³)	1.537	1.689
<i>T</i> (K)	100 (1)	150 (2)
μ (mm ⁻¹)	2.231	2.156
Index ranges	-12 ≤ <i>h</i> ≤ 12	-10 ≤ <i>h</i> ≤ 12
	-34 ≤ <i>k</i> ≤ 33	-35 ≤ <i>k</i> ≤ 34
	-13 ≤ <i>l</i> ≤ 12	-8 ≤ <i>l</i> ≤ 13
θ ranges (°)	3.73 – 27.50	2.78 – 27.50
Reflections collected	6077	6046
Independent reflections	3818 [<i>R</i> _{int} = 0.0498]	3870 [<i>R</i> _{int} = 0.0397]
Absorption corr., <i>T</i> _{min}	0.8905	0.7564
<i>T</i> _{max}	1.0000	1.0000
Goodness-of-fit on <i>F</i> ²	0.967	0.988
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0355, <i>wR</i> ₂ = 0.0575	<i>R</i> ₁ = 0.0304, <i>wR</i> ₂ = 0.0412
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0709, <i>wR</i> ₂ = 0.0610	<i>R</i> ₁ = 0.0634, <i>wR</i> ₂ = 0.0435
Max. and min. residual	0.629, -0.559	0.535 -0.458
electron density (e·Å ⁻³)		

Table 2 Selected geometric parameters [$\text{\AA}$, $^\circ$] for $\text{Cu}(\text{bapen})\text{M}(\text{CN})_4 \cdot \text{H}_2\text{O}$ (M = Ni, Pd).

	Ni	Pd		Ni	Pd
Cu1-N1	2.028 (2)	2.024 (2)	M2-C18	1.869 (3)	1.984 (4)
Cu1-N2	2.015 (2)	2.007 (2)	M2-C19	1.875 (3)	1.996 (3)
Cu1-N3	2.055 (2)	2.041 (2)	N9-Cu2-N10	91.79(9)	91.41(10)
Cu1-N4	2.016 (2)	2.005 (2)	N10 ^v -Cu2-N9	88.21 (9)	88.59 (10)
Cu2-N9	2.041 (2)	2.030 (3)	N2-Cu1-N1	93.37 (10)	93.07 (10)
Cu2-N10	2.021 (2)	2.003 (3)	C18-M2-C19	91.66 (11)	91.60 (12)
Cu1-N5	2.508 (2)	2.532 (3)	C11-M1-C9	175.64 (12)	175.78 (13)
Cu1-N7 ⁱ	2.484 (3)	2.479 (3)	Cu2-N12-C19	128.3 (2)	127.3 (2)
Cu2-N12	2.591 (3)	2.580 (3)	Cu1-N5-C9	131.7 (2)	129.0 (2)
M1-C9	1.871 (3)	1.991 (3)	Cu1 ^{iv} -N7-C11	134.2 (2)	133.9 (2)
M1-C10	1.874 (3)	1.999 (4)			

Symmetry codes:

i: x, y, 1+z; ii: x, y, z-1; iii: -x, -y, -z; iv: x, y, z-1; v: 1-x, 1-y, 1-z

Table 3 Possible hydrogen bonds in Cu(bapen)Ni(CN)₄·H₂O (a) and Cu(bapen)Pd(CN)₄·H₂O (b) (in Å and °)

a)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1A...O2A ⁱ	1.04	2.09	3.046 (4)	151
N1-H1A...O2B ⁱ	1.04	2.13	3.132 (2)	160
N2-H2...N8 ⁱ	0.92	2.20	2.974 (3)	141
N4-H4A...N11 ⁱⁱ	0.90	2.30	3.136 (3)	154
N9-H9A...N6 ⁱⁱ	0.92	2.54	3.218 (3)	131
N9-H9B...O1	0.92	2.30	3.165 (5)	156
N10-H10A...N11 ⁱⁱⁱ	0.92	2.40	3.201 (3)	145
O1-H1E...O2B	0.85	1.84	2.686 (2)	177
O1-H1E...O2A	0.85	2.02	2.789 (5)	150
O1-H1F...O1 ^{iv}	0.85	1.90	2.652 (8)	147

Symmetry codes:

i: x+1/2, 1/2-y, z+1/2; ii: x-1/2, 1/2-y, z+1/2; iii: x, y, z+1; iv: -x, 1-y, 1-z

b)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1A...O2A ⁱ	0.92	2.22	3.036 (4)	148
N1-H1A...O2B ⁱ	0.92	2.23	3.04 (2)	146
N2-H2...N8 ⁱ	0.93	2.16	2.973 (3)	145
N4-H4A...N11 ⁱⁱ	0.92	2.27	3.158 (4)	164
N9-H9A...N6 ⁱⁱ	0.92	2.48	3.195 (4)	135
N9-H9B...O1	0.92	2.39	3.249 (6)	155
N10-H10A...N11 ⁱⁱⁱ	0.92	2.48	3.246 (4)	142

Symmetry codes: i: x+1/2, -y+1/2, z+1/2; ii: x-1/2, -y+1/2, z+1/2; iii: x, y, z+1

Table 4 Values of the g-factor and linewidth obtained from the analysis of X-band EPR.

complex	$g_{A\perp}$	$g_{A\parallel}$	$H_{A\perp}$ (G)	$H_{A\parallel}$ (G)	$g_{B\perp}$	$g_{B\parallel}$	$H_{B\perp}$ (G)	$H_{B\parallel}$ (G)
Cu(bapen)Ni(CN) ₄ ·H ₂ O	2.089	2.169	93	295	2.063	2.226	75	410
Cu(bapen)Pd(CN) ₄ ·H ₂ O	2.089	2.176	89	264	2.060	2.238	69	392

Maximum error in the estimation of the g-factor is ± 0.003 and linewidth ± 5 G.

Captions to the figures

Fig. 1 Two crystallographically independent parts of the structure of $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4\cdot\text{H}_2\text{O}$ (a) and $\text{Cu}(\text{bapen})\text{Pd}(\text{CN})_4\cdot\text{H}_2\text{O}$ (b). The bapen ligands coordinated to Cu2 atoms (namely C16 and C17 atoms with the corresponding hydrogen atoms) and the corresponding O1 atoms in both $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4\cdot\text{H}_2\text{O}$ and $\text{Cu}(\text{bapen})\text{Pd}(\text{CN})_4\cdot\text{H}_2\text{O}$ are disordered but for the sake of clarity only one position is shown. Both disordered positions of O2 atoms in both $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4\cdot\text{H}_2\text{O}$ and $\text{Cu}(\text{bapen})\text{Pd}(\text{CN})_4\cdot\text{H}_2\text{O}$ are shown. Hydrogen atoms bound to the carbon atoms are omitted for clarity. The thermal ellipsoids are drawn at the 30 % probability level.

Fig. 2 View of the crystal structure of (1) along [001] displaying the positions of water molecules of crystallization between the chains running along the viewing direction. Both disordered positions of the bapen ligand in the $\text{C}(\text{Cu}2)$ chains are shown. The hydrogen atoms are omitted for clarity.

Fig. 3 Hydrogen bonding scheme in (1) with participation of a) $[-\text{Cu}1(\text{bapen})-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-]_n$ chains; and of b) $[-\text{Cu}2(\text{bapen})-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-]_n$ chains. The carbon atoms and their hydrogen atoms are omitted for clarity.

Fig. 4 Overall view of possible hydrogen bonding scheme in $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4\cdot\text{H}_2\text{O}$.

Fig. 5 Comparison of the experimental ESR spectra of $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4\cdot\text{H}_2\text{O}$ (complex 1) and $\text{Cu}(\text{bapen})\text{Pd}(\text{CN})_4\cdot\text{H}_2\text{O}$ (complex 2) measured at 9.4 GHz and the EasySpin [26] fits for parameters summarized in Table 4.

Fig. 6 Temperature dependence of the ZFC static inverse susceptibility and temperature dependence of the effective magnetic moment of $\text{Cu}(\text{bapen})\text{Ni}(\text{CN})_4\cdot\text{H}_2\text{O}$ (inset).