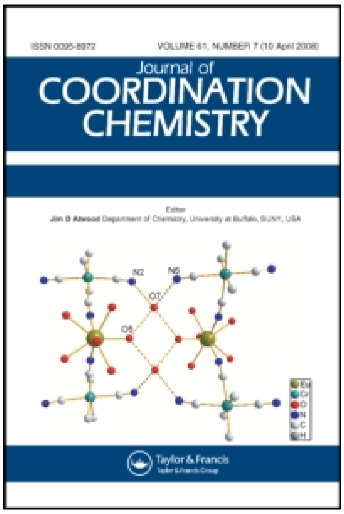

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Hydrothermal synthesis, crystal structure and magnetic properties of a copper(II) phosphonate

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Hydrothermal synthesis, crystal structure and magnetic properties of a copper(II) phosphonate

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The treatment of 3-ammonium-1-hydroxypropylidene-1,1′-bisphosphonate (H_7ahdp) and 4,4′-bipy with $CuCl_2 \cdot 2H_2O$ resulted in a metal phosphonate $[Cu(H_5ahdp) \cdot H_2O]_n$. Its crystal structure has been characterized by single X-ray crystallography. Although there is no 4,4′-bipy in the lattice structure, it plays a very important role in forming the one-dimensional chain of the polymer. Hydrogen bonds link the chains into a 3D network. The dinuclear secondary building units are observed in the compound. The determination of variable-temperature magnetic susceptibilities ($5 \sim 300$ K) shows weak intrachain antiferromagnetic coupling between copper(II) centers. The magnetic data were fitted to the appropriate equations derived from the Hamiltonian $H = -2JS_1S_2$, giving the parameter $J = -25.78\,\mathrm{cm}^{-1}$. Its thermal properties were also investigated.

Keywords: Hydrothermal synthesis; Cu(II) phosphonate; Crystal structure; Magnetic properties

1. Introduction

The design and syntheses of coordination polymers constructed from multifunctional ligands and transition metals have been extensively explored [1–4]. Considerable interest has been devoted to synthesis of various metal phosphonates due to their potential applications in ion-exchange, absorption, catalysis and sensors [5–8]. Consequently, many kinds of metal phosphonates with interesting compositions and topologies have been prepared. For example Mao and co-workers reported the syntheses and crystal structures of two cobalt carboxylate-phosphonates with 4,4′-bipyridine as a secondary metal linker [8a]. Zheng and co-workers described the field-induced magnetic transitions in metal phosphonates with ladderlike chain structures [8b]. Bauer *et al.* have also reported the synthesis and characterization of the open-framework barium bisphosphonate [8c].

In this field, 3-ammonium-1-hydroxypropylidene-1,1′-bisphosphonate (H_7ahdp) has attracted some attention, because of the coexistence of one amino group and two phosphonate groups, H_7ahdp is expected to behave like an amino acid and exhibit

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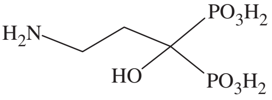
zwitterionic (cationic and anionic) properties in weakly acidic conditions [8d]. However, complexes utilizing H_7ahdp were rare, especially crystal structures [9]. This may be due to the special chemical properties of H_7ahdp moiety, making structural characterization of metal- H_7ahdp polymers difficult to carry out.



H_7ahdp

In this article, we utilized H_7ahdp to react with $CuCl_2$ in the presence of 4,4′-bipy to afford a novel metal phosphonate $[Cu(H_5ahdp) \cdot H_2O]_n$. Although there is no 4,4′-bipy in the lattice structure, it plays a very important role in forming the one-dimensional chain of the polymer. In this compound, the dinuclear secondary building units were connected by H_5ahdp forming an infinite chain. Its one-dimensional chain structure can be compared with the previous three-dimensional Cu(II) phosphonate structure $[Cu_3(H_3ahdp)_2 \cdot H_2O]_n$, which was prepared by H_7ahdp with Cu^{2+} [8d]. The magnetic properties in the temperature range of 5.0–300 K were studied showing intrachain antiferromagnetism between the Cu(II) centers in $[Cu(H_5ahdp) \cdot H_2O]_n$.

2. Experimental

2.1. *General details*

All chemicals were of reagent grade quality obtained from commercial sources and used without purification. Ligand H_7ahdp was prepared according to the literature method [10].

C, H and N elemental analyses were carried out on a FLASH EA 1112 analyzer. IR data were recorded on a Bruker Tensor 27 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. Thermogravimetric analyses were carried out with a NETZSCH STA 409 unit at a heating rate of 5°C min^{-1} under a nitrogen atmosphere. Variable-temperature magnetic susceptibility data were obtained on a SQUID susceptometer (Quantum Design, MPMS-5) in the temperature range of 5.0–300 K with an applied field of 500 G. All data have been corrected for diamagnetism by using Pascal's constants [11].

2.2. *Preparation of* $[Cu(H_5ahdp) \cdot H_2O]_n$

A mixture of $CuCl_2 \cdot 2H_2O$ (0.0853 g, 0.5 mmol), H_7ahdp (0.1115 g, 0.47 mmol), 4,4′-bipy (0.0483 g, 0.25 mmol) and distilled water (8 mL) was sealed in a 20 mL Teflon-lined stainless-steel autoclave and heated at 140°C for 192 h, followed by slow cooling to room temperature, blue needle-like crystals of $[Cu(H_5ahdp) \cdot H_2O]_n$ were collected. Yield: 48% based on Cu. Anal. Calcd for $C_3H_{11}CuNO_8P_2$: C, 11.61; H, 3.43; N, 4.45%. Found: C, 11.45; H, 3.52; N, 4.46%. IR data (KBr, cm^{-1}): 3569.67(s), 3482.20(m), 3208.89(s), 1651.96(m), 1467.75(m), 1370.82(w), 1165.31(m), 1123.94(s), 1079.33(w), 989.46(m), 921.13(s), 849.52(s), 678.14(s), 565.57(s), 502.31(s).

Table 1. Crystallographic data.

Formula	$C_3H_{11}CuNO_8P_2$
Moleculer weight	314.61
T (K)	291(2)
Wavelength (Å)	0.71073
Color	Blue
Crystal system	Monoclinic
Space group (Å , °)	$P2(1)/c$
a	5.5101(5)
b	14.3923(12)
c	11.6709(10)
α	90
β	103.4820(10)
γ	90
V (Å^3)	900.03(14)
Z	4
D_c (mg m^{-3})	2.322
Absorption coefficient (mm^{-1})	2.809
F(000)	636
Reflections collected/unique	5326/2032 [$R_{(int)} = 0.0130$]
Data/restraints/parameters	2032/4/146
Goodness-for-fit on F^2	1.039
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0204, 0.0573
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e Å^{-3})	0.413 and −0.383

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

2.3. *X-ray crystallography*

Crystal data and experimental details are contained in table 1. A single crystal of dimensions $0.20 \times 0.16 \times 0.13$ mm^3 was used for structural determinations. Data collections were made on a Bruker Smart 1000 diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). All data were collected at 291(2) K using the ω–2θ scan technique. Empirical absorption corrections were applied for the compound.

The structure was solved by direct methods and refined on F^2 by a full-matrix least-squares procedure using the SHELXL 97 crystallographic software package [12]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found by Fourier syntheses or included at calculated positions with isotropic thermal parameters proportional to those of the connected atoms. All hydrogen atoms were refined isotropically. Intensity data were collected in the θ range 2.83–27.50°. The final cycle of full-matrix least-squares refinement was based on 2032 observed reflections and 146 variable parameters. Selected bond lengths and angles, and hydrogen bond parameters are listed in tables 2 and 3, respectively.

3. Results and discussion

3.1. *Preparation*

The hydrothermal reaction of $CuCl_2$ with H_7ahdp in the presence of 4,4′-bipy is an effective route for preparation of the Cu(II) chain phosphonate. Similar reaction of $Cu(NO_3)_2$ or $CuCl_2$ with H_7ahdp without 4,4′-bipy under hydrothermal conditions was performed by Hu *et al.* [8d] who obtained an unusual three-dimensional

Table 2. Selected bond distances (Å) and angles (°).

Cu(1)–O(1)	1.9692(14)	Cu(1)–O(5)#1	2.0209(13)
Cu(1)–O(3)#1	1.9553(13)	Cu(1)–O(5)#2	2.2012(13)
Cu(1)–O(4)	1.9884(13)	Cu(1)–Cu(1)#1	3.0038(5)
P(1)–O(1)	1.5326(14)	P(2)–O(4)	1.5324(13)
P(1)–O(2)	1.5404(14)	P(2)–O(5)	1.5376(13)
P(1)–O(3)	1.5209(14)	P(2)–O(6)	1.5220(13)
O(3)#1–Cu(1)–O(1)	166.72(6)	O(4)–Cu(1)–O(5)#2	112.15(5)
O(3)#1–Cu(1)–O(4)	89.98(6)	O(5)#1–Cu(1)–O(5)#2	80.52(5)
O(1)–Cu(1)–O(4)	90.40(5)	O(3)#1–Cu(1)–Cu(1)#1	84.43(4)
O(3)#1–Cu(1)–O(5)#1	88.91(5)	O(1)–Cu(1)–Cu(1)#1	82.38(4)
O(1)–Cu(1)–O(5)#1	87.80(6)	O(4)–Cu(1)–Cu(1)#1	84.94(4)
O(4)–Cu(1)–O(5)#1	167.25(5)	O(5)#1–Cu(1)–Cu(1)#1	82.31(4)
O(3)#1–Cu(1)–O(5)#2	100.87(5)	O(5)#2–Cu(1)–Cu(1)#1	161.90(4)
O(1)–Cu(1)–O(5)#2	91.27(5)	P(1)–O(1)–Cu(1)	120.68(8)
P(2)–O(4)–Cu(1)	121.04(8)	P(1)–O(3)–Cu(1)#1	120.00(8)
P(2)–O(5)–Cu(1)#1	1222.41(8)	P(2)–O(5)–Cu(1)#3	134.69(8)
Cu(1)#1–O(5)–Cu(1)#3	99.48(5)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $-y+1$, $-z+1$; #2: $x-1$, y, z; #3: $x+1$, y, z.

Table 3. Distances (Å) and angles (°) involving hydrogen bonds.

D–H···A	d(D–H)	d(H···A)	d(D···A)	⟨(DHA)
O(8)–H(8)···O(1)#3	0.82	1.93	2.7294(19)	165.5
O(8)–H(8)···O(5)	0.82	2.67	3.0978(19)	114.6
N(1)–H(1A)···O(7)#2	0.89	2.04	2.794(3)	141.8
N(1)–H(1B)···O(4)#4	0.89	2.04	2.904(2)	165.0
N(1)–H(1C)···O(8)#5	0.89	2.24	3.091(2)	160.1
O(2)–H(2C)···O(6)#6	0.82	1.65	2.4317(19)	158.8
O(7)–H(1W)···O(6)	0.851(10)	2.039(14)	2.872(2)	166(3)
O(7)–H(2W)···O(1)#7	0.846(10)	2.57(3)	3.279(2)	142(3)
O(7)–H(2W)···O(3)#8	0.846(10)	2.35(3)	2.932(2)	126(3)
O(7)–H(2W)···O(5)#4	0.846(10)	2.64(3)	3.233(2)	129(3)

Symmetry transformations used to generate equivalent atoms: #2: $x-1$, y, z; #3: $x+1$, y, z; #4: x, $-y+1/2$, $z-1/2$; #5: $-x+1$, $-y+1$, $-z$; #6: $-x+1$, $y+1/2$, $-z+1/2$; #7: $-x+1$, $y-1/2$, $-z+1/2$; #8: $-x+2$, $y-1/2$, $-z+1/2$.

architecture $[Cu_3(H_4ahdp)_2 \cdot 2H_2O]_n$ in which two-dimensional layers with a parquet motif are pillared by $\{CuO_4\}$ square planes. The novelty of our reaction was the presence of 4,4′-bipy, a prominent example for a prototypical bridging ligand and an attractive molecular building block for diverse architectures of coordination polymers [1–4]. A number of coordination polymers constructed by 4,4′-bipy have been reported [13] and a number of phosphonates with 4,4′-bipy as a secondary metal linker have been described [8a, 14]. Researchers find that 4,4′-bipyridine not only functions as a bridge between metal centers but also as a hydrogen-bond acceptor [15]. Furthermore, thermochemical and theoretical properties of 4,4′-bipy have been studied by Silva and coworkers [16]. To our knowledge articles concerning the effect of 4,4′-bipy in the reaction process are lacking. At the same time, the generation of supramolecular frameworks under hydrothermal conditions rests on various parameters, such as the coordination environments of metal centers, position and type of functional groups on the ligands, the ratio between metal salts and ligands, templates, solvent system, counterions, temperature, reaction time, pH value, *etc.* [17]; the factors governing the reaction and formation of the hydrothermal product are complicated. We presume that 4,4′-bipy is first protonated forming 4,4′-bipyH^+ or 4,4′-bipyH^{2+} in the reaction solution, degrading their coordination abilities, then the protonated compounds may show some inductive effects. So the one-dimensional chain polymer without 4,4′-bipy was produced. Most reported metal phosphonates show two or higher-dimensional polymeric structures. The addition of 4,4′-bipy is useful for generation of one-dimensional chain metal phosphonates.

3.2. *Crystal structure*

The molecular structure of $[Cu(H_5ahdp) \cdot H_2O]_n$ was determined by single crystal X-ray diffraction analysis. The molecule crystallizes in the space group $P2(1)/c$. The perspective view together with the atomic numbering scheme is illustrated in figure 1.

As shown in figure 2, two Cu(II) centers were bridged by two $[H_5ahdp]^{2-}$ anions, leading to a dimeric $[Cu_2(H_5ahdp)_2]$ core. The dimeric tetra-bridged cores were connected by oxygen atoms of $[H_5ahdp]^{2-}$ of neighboring dimeric cores leading to a linear $[Cu(H_5ahdp) \cdot H_2O]_n$ chain.

Each Cu(II) is five-coordinate with five bridging oxygen atoms from three $[H_5ahdp]^{2-}$ anions. The Cu–O distances range from 1.9953(13) to 2.2014(13) Å. The Cu1–O5B (2.2014(13) Å) distance is slightly longer than the other four Cu1–O distances (Cu1–O1 = 1.9696(13); Cu1–O5A = 2.0208(13); Cu1–O3A = 1.9553(13); Cu1–O4 = 1.9888(13) Å). The square pyramidal coordination geometry around the copper center was completed. The average Cu–O distance at Cu1 is 2.027 Å. The four-membered ring Cu1–O5A–Cu1C–O5A is perfectly planar. The distance of Cu1–Cu1A is 3.004 Å, comparable to the value 4.389(2) Å for $[Cu_3(H_4ahdp)_2 \cdot 2H_2O]_n$ [8d]. The Cu1–Cu1C distance (3.224 Å) is longer than the Cu1–Cu1A distance.

In the solid-state structure of $[Cu(H_5ahdp) \cdot H_2O]_n$, chains are joined together by hydrogen bonds forming a three-dimensional network. Figure 3 shows the hydrogen bonding systems of the compound. Crystallization water links O and NH_3 of the H_5ahdp forming intermolecular hydrogen bonds at the same time (table 3). Viewed from the *a*-axis, each $[Cu(H_5ahdp) \cdot H_2O]_n$ chain links an adjacent $[Cu(H_5ahdp) \cdot H_2O]_n$ chain leading to a 3-D sheet (figure 3).

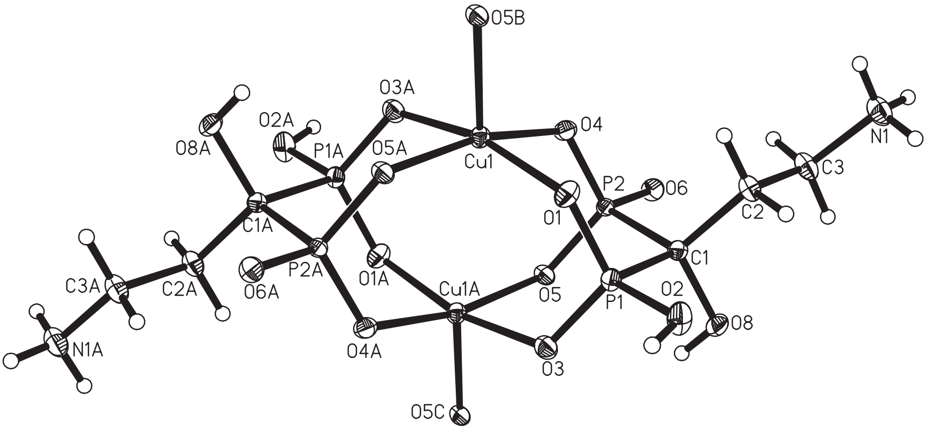


Figure 1. Perspective view of $[Cu(H_5ahdp) \cdot H_2O]_n$ with atom labeling scheme.

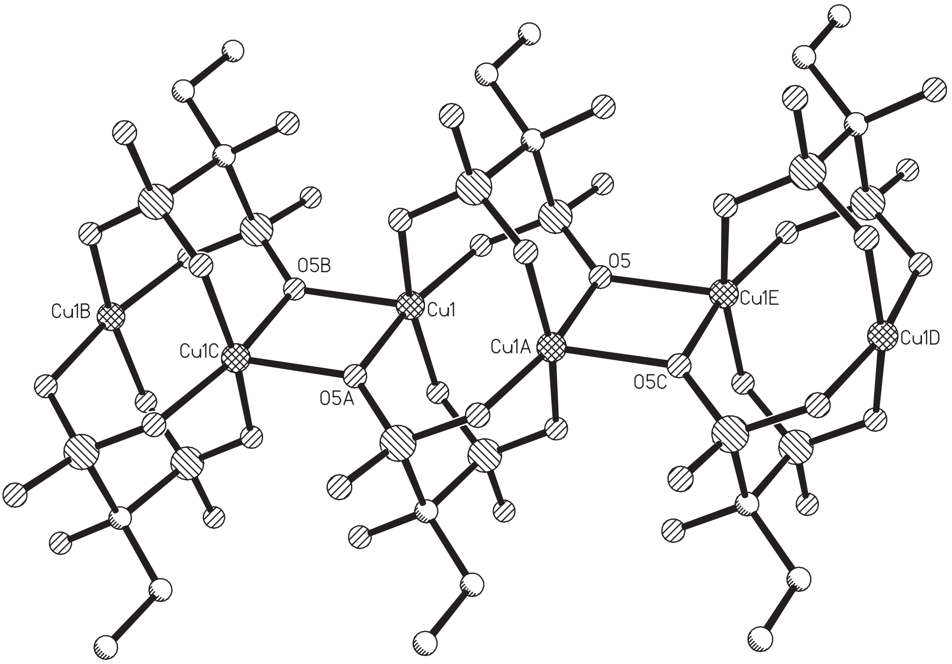


Figure 2. The one-dimensional infinite chain structure of $[Cu(H_5ahdp) \cdot H_2O]_n$. (The nitrogen and hydrogen atoms are omitted for clarity).

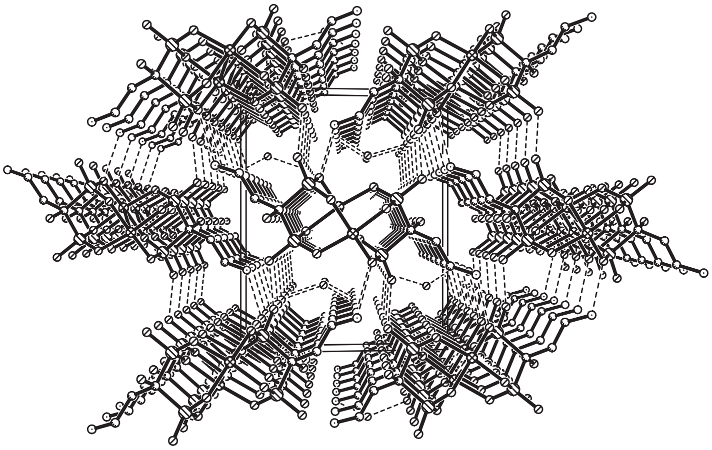


Figure 3. The three-dimensional network supported by hydrogen bonds of $[Cu(H_5ahdp) \cdot H_2O]_n$ along the [100] direction.

In $[Cu(H_5ahdp) \cdot H_2O]_n$, the hydroxyl groups of the H_5ahdp ligands are uncoordinated, and all the amino groups are protonated and uncoordinated, only oxygen atoms of phosphonate groups take part in the coordination. On contrast, in the related three-dimensional polymer $[Cu_3(H_4ahdp)_2 \cdot 2H_2O]_n$ [8d], all the oxygens of H_5ahdp ligands including those from hydroxyl groups and two phosphonate groups are coordinated to the Cu(II) centers. Similarly, the amino groups in $[Cu_3(H_4ahdp)_2 \cdot 2H_2O]_n$ are protonated and uncoordinated, but can form intramolecular H-bonds with phosphonate groups. We believe that the different coordination modes of the H_5ahdp ligands led to the different Cu(II) products.

3.3. *IR spectroscopy*

The characteristic P–O bands are in the region 900–1200 cm^{-1}, the C–H bending and stretching bands are at ca. 1370 and 2950 cm^{-1}, respectively [8d]. The bands attributable to H_2O occur at 3209 and 1651 cm^{-1}. In conclusion, the IR data are consistent with the crystal data of the compound.

3.4. *Thermogravimetric analysis (TGA)*

TG data shows that the polymer is stable up to 243.4°C. There are three main stages of weight loss. The first stage begins at 243.4°C and is completed at 483.3°C corresponding to loss of one water molecule and the NH_3–CH_2–CH_2 unit of the ligand (observed 19.54%, calculated 20.02%). The second stage, occurring between 483.3°C and 657.1°C, corresponds to further decomposition of the ligand (losing one O_3H unit; observed 15.04%, calculated 15.57%). The third stage is between 657.1 and 896.8°C corresponding to further decomposition of the compound. Assuming the final product is a mixture of $Cu_2P_2O_7$ and $Cu(PO_3)_2$ in a molar ratio of 1 : 1, the total weight loss should be 40.43%. The observed weight loss (37.89%) is slightly smaller than the theoretical value. That indicates that the polymer has decomposed incompletely at 896.8°C. There are three exothermic peaks at 269.8, 382.8 and 525.1°C on the DTA curve of the polymer.

3.5. *Magnetic properties*

Variable-temperature magnetic study on the compound was carried out over the temperature range 5.0–300 K. A plot of $\chi_M T$ *versus* T is shown in figure 4. The magnetic moment at 300 K ($\mu_{eff} = 1.750\mu_B$) per copper(II) center is near to that expected for an isolated paramagnetic system with $S = 1/2$ ($\mu_{eff} = 1.73\ \mu_B$). As can be seen from figure 4, $\chi_M T$ value decreases from 0.387 $cm^3\,mol^{-1}\,K$ at 300 K to 0.004 $cm^3\,mol^{-1}\,K$ at 5.0 K. Such behavior can be attributed to the presence of a weak antiferromagnetic coupling between the Cu(II) ions [18].

$[Cu(H_5ahdp) \cdot H_2O]_n$ exhibits two types of magnetic exchange interactions between Cu(II) ions: one is through tetra-bridges *via* the $[H_5ahdp]^{2-}$ ligands and the other is through the two oxygen bridges O5 and O5C. Considering the compound has a dinuclear structure in which the Cu(II) ions are bridged by four O–P–O bridges, the susceptibility data were fitted by Bleaney–Bowers expression based on a Heisenberg Hamiltonian $H = -2JS_1S_2$ [18].

$$\chi'_M = \frac{Ng^2\beta^2}{KT}\left[\frac{1}{3+\exp(-2J/KT)}\right](1-\rho) + \frac{Ng^2\beta^2}{4KT}\rho$$

$$\chi_M = \frac{\chi'_M}{1 - zJ'\chi'_M}$$

where g is the Lande g-value, N is Avogadro's number, β is the Bohr magneton, K is Boltzmann's constant, J is the exchange coupling parameter describing the magnetic

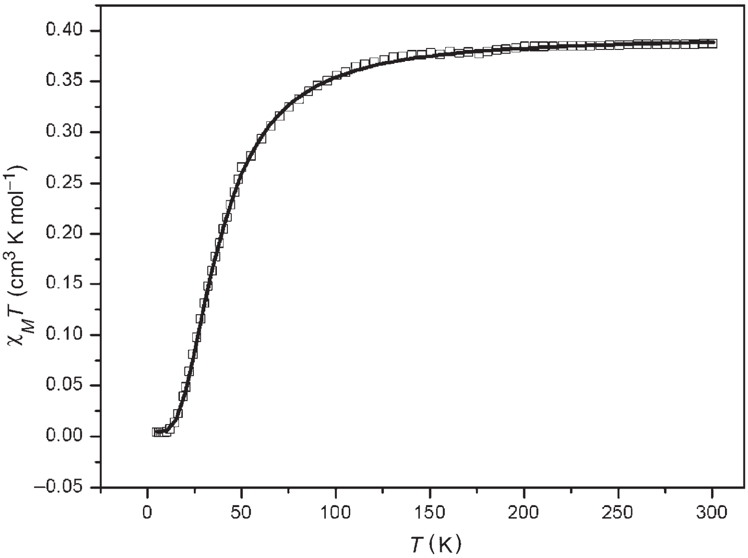


Figure 4. Plot of $\chi_M T$ *vs*. T for $[Cu(H_5ahdp) \cdot H_2O]_n$.

interaction between the two nearest-neighbor $S = 1/2$ spins, zJ' accounts for the interdimer exchange, and ρ is a variable fraction of paramagnetic impurities. A good fit resulted in the solid line in figure 4, with the parameters $g = 2.15$, $J = -25.78\,\mathrm{cm}^{-1}$, $\rho = 0.012$, $zJ' = 13.46\,\mathrm{cm}^{-1}$ and $R = 1.3 \times 10^{-4}$ (R is the agreement factor defined as $R = [\Sigma(\chi_{obs} - \chi_{Calcd})]^2/\Sigma(\chi_{obs})^{1/2}$).

In the polymer, the unpaired electron of each copper(II) in a square pyramid is $d_{x^2-y^2}$ with a very small admixture of d_{z^2}. So the overlap between the magnetic orbitals is small under these conditions, and, since the magnetic coupling is proportional to the square of the overlap integral [19], the resulting magnetic exchange is weak, as observed. The magnetic behavior of our Cu(II) phosphonate can be compared to the reported Cu(II) phosphonate, $Cu(C_6H_{10}(OH)PO_3)(H_2O)_2$ ($g = 2.21$, $J = 8.47\,\mathrm{cm}^{-1}$, $zJ' = -1.31\,\mathrm{cm}^{-1}$) [8e], in which the O–P–O bridged dimeric cores are connected through intermolecular hydrogen bonds.

4. Conclusion

By addition of 4,4′-bipy we prepared a crystalline product from the hydrothermal reaction of H_7ahdp with $CuCl_2$ in water and clearly characterized its crystal structures. The elemental analyses and IR data are consistent with the X-ray analysis results. On the basis of the magnetic studies, antiferromagnetic coupling between copper(II) ions can be observed.

Supplementary data

Crystallographic data for the structure reported in this article in the form of CIF file has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-606915. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk).

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