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DOI: 10.1002/zaac.200((will be filled in by the editorial staff))

A Novel Three-Dimensional Cu(II) 1,2-Ethylenediphosphonate Framework with Channel-like Voids

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Keywords: 1,2-Ethylenediphosphonic acid; Metal-organic framework, Crystal structure, Voids, Magnetic properties, UV/Vis spectroscopy

Abstract. Turquoise monoclinic single crystals of the novel three-dimensional $\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]\cdot 3.2\text{H}_2\text{O}$ coordination polymer have been prepared using the silica gel method. Space group $C2/m$ (no. 12) with $a = 1483.6(2)$, $b = 668.44(8)$, $c = 436.30(6)$ pm, $\beta = 93.28(2)^\circ$. The Cu^{2+} cation is coordinated by four oxygen atoms stemming from the 1,2-ethylenediphosphonate dianions in a square planar manner and two water molecules in the axial positions. The connection between the Cu^{2+} cations and the $[\text{PO}_3\text{C}]$ units from the 1,2-ethylenediphosphonate dianions leads to layers parallel to (100), which are linked by the ethylene groups to a three-dimensional framework with channel-like voids. The voids

accommodate water molecules not bound to Cu^{2+} and extend parallel along [001] with an opening of about 550×260 pm. Magnetic measurements reveal an antiferromagnetic behaviour due to a superexchange coupling between Cu^{2+} ions through an oxygen bridge. The UV-Vis spectrum reveals three d–d transition bands at 694, 774, and 918 nm. The compound can be fully dehydrated by thermal treatment and rehydrated by storage in ambient air.

coordination polymer [16]. The structures of these coordination polymers can be modified using additional N-donor ligands [19 – 24]. Moreover, transition metal organodiphosphonates have interesting magnetic properties with ferromagnetic and/or antiferromagnetic interactions between the metal atoms [12–15,19,25–30].

Herein, we report on a novel zeolite-like three-dimensional copper 1,2-ethylenediphosphonate with channel-like voids accommodating water molecules.

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Introduction

Metal organophosphonates are of great interest due to their potential application e.g. as gas-phase sensor [1], catalyst [2, 3], and ion exchanger [4]. Using organodiphosphonates as ligands, various porous structures can be synthesized [5–10]. The connection between Cu^{2+} and anions of alkylene- and arylenediphosphonic acids leads to coordination polymers with one-, two and three-dimensional structural features [11–18]. The structure depends on the chain lengths and shape of the organic unit. Cu(II)-alkylenediphosphonates possess mostly three-dimensional frameworks, in which compounds with e.g. butylene and pentylene units have an open three-dimensional framework accommodating water molecules [11]. On the other hand, depending on the synthesis conditions the reaction between Cu^{2+} and 1,4-butylenediphosphonic acid can also result in a layer-like

Results and Discussion

The Cu^{2+} cations in $\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]\cdot 3.2\text{H}_2\text{O}$ occupy a crystallographic inversion centre of space group $C2/m$ (Wyckoff position 4f) and are equatorially surrounded by four oxygen atoms (2x O(1), 2x O(2)) leading to a slightly distorted square planar coordination. The four oxygen atoms stem from four crystallographically equivalent 1,2-ethylenediphosphonate dianions. The Cu–O distances in the equatorial plane are between 193.6(3) and 202.6(3) pm and the O–Cu–O angles do not differ significantly from 90 and 180° (Tab. 1). The best least-square-plane through Cu, O(1), O(2), O(1)^{#1}, and O(2)^{#1} shows only minor deviation from planarity (maximum deviation of 4.3 pm). The water molecules O(w1) coordinate the copper ions in the axial positions with a long distance of

245.3(5) pm. Thus the coordination number is 4+2 resulting in an elongated octahedron with D_{2h} symmetry in good approximation. The O(w1) position is not fully occupied with a site occupancy of 0.85(2). Employing the method of *Breese and O'Keeffe* [31] the bond order is calculated to 2.04. Neighbouring Cu^{2+} octahedra are tilted against each other by $85.9(1)^\circ$ and connected by a common edge [O(1), O(w1)], leading to infinite polyhedra ribbons along [001] (Fig. 1). The shortest $Cu\cdots Cu$ contact is 334.2(1) pm.

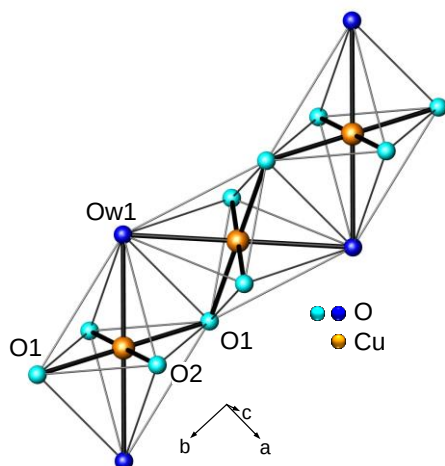


Figure 1. The coordination environment of Cu^{2+} .

Table 1. The Coordination Environment of Cu^{2+}

Distances (pm)			
Cu–O(1)	193.6(3)	Cu–O(1) ^{#1}	193.6(3)
Cu–O(2)	202.6(3)	Cu–O(2) ^{#1}	202.6(3)
Cu–O(w1)	245.3(5)	Cu–O(w1) ^{#1}	245.3(5)
Cu $\cdots$ Cu ^{#4}	334.2(1)		
Bond angles ($^\circ$)			
O(2)–Cu–O(1)	90.6(2)	O(1)–Cu–O(1) ^{#1}	180
O(w1)–Cu–O(2)	88.5(1)	O(2)–Cu–O(2) ^{#1}	180
O(w1)–Cu–O(1)	102.5(1)	O(w1)–Cu–O(w1) ^{#1}	180
Cu–O(w1)–Cu ^{#4}	85.9(1)		

Symmetry code: #1: $-x+0.5, -y+0.5, -z+1$; #4: $-x+0.5, y-0.5, -z+1$

The 1,2-ethylenediphosphonate dianion lies on a mirror plane with a twofold crystallographic axis perpendicular to the C–C bond. The skeleton of the 1,2-ethylenediphosphonate dianion adopts a *trans* (antiperiplanar) conformation with torsions angles of 63.9° (H–C–C–P) and 52.1° (H–C–C–H), respectively. The phosphorous atom is surrounded by three oxygen atoms and one carbon atom from the ethylene group in a distorted tetrahedral fashion. The P–O bonds range from 151.8(3) to 155.7(5) pm, whereas the P–C bond is 179.8(6) pm (Tab. 2). The shorter P–O(2) bond lengths show considerable double bond character, which is also reflected in larger O–P–O angles involving O(2). The bond lengths and angles in the $[PO_3C]$ groups differ only slightly from the values found in the 1,2-ethylenediphosphonic acid molecule [32], whereas the C–C single bond is significantly shorter (151.3(13) pm), and the P $\cdots$ P distance is enlarged by 5.6 pm to 445.1(2) pm. Each phosphonate group is coordinated to four Cu^{2+} cations

in a monodentate manner. The phosphonate oxygen atom O(2) is coordinated to one Cu^{2+} , whereas O(1) connects two Cu^{2+} . Thus each 1,2-ethylenediphosphonate dianion connects eight copper ions and adopts a μ_8 coordination mode in which each $[PO_3]$ group shows a $\mu_4-\eta_1:\eta_1:\eta_1:\eta_1$ connection mode (Fig. 2).

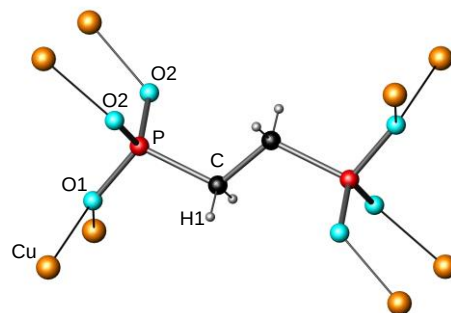


Figure 2. The connection between the 1,2-ethylenediphosphonate dianion and the Cu^{2+} cations.

Table 2. Bond Lengths and Angles of the 1,2-Ethylenediphosphonic dianion

Bond lengths (pm)			
P–O(1)	155.7(5)	P–C	179.8(6)
P–O(2) ^{#2}	151.8(3)	C–C ^{#6}	151.3(13)
P–O(2) ^{#3}	151.8(3)	C–H	94.9(10)
Bond angles ($^\circ$)			
O(2) ^{#2} –P–O(1)	110.6(2)	O(2) ^{#2} –P–C	107.9(2)
O(2) ^{#2} –P–O(2) ^{#3}	113.4(3)	O(1)–P–C	106.0(3)
C ^{#4} –C–P	114.9(5)	C ^{#6} –C–H(1)	106(4)
		P–C–H(1)	106(4)

Symmetry code: #2: $x, -y, z-1$; #3: $x, y, z-1$; #6: $-x, -y, -z$

The Cu^{2+} polyhedra ribbons and the $[PO_3C]$ tetrahedra are linked by common corners forming infinite layers parallel to (100). The phosphorous atoms are located above and below the Cu^{2+} polyhedra ribbons. These layers are stacked in ...ABAB... sequence along the [100] direction (Fig. 3). The layers are connected by the C–C bonds of the ethylene groups, leading to a three-dimensional framework with small channel-like voids along [001] (Fig. 5 and 4). The largest and narrowest openings of the channel-like voids are approximately 550×260 pm with van der Waals radii [33] of the framework atoms taken into account excluding the weakly bonded water molecule O(w1), which can be easily removed by thermal treatment and is not essential for the stability of the copper 1,2-ethylenediphosphonate framework. Besides the weakly coordinated water molecules O(w1), the channels accommodate water molecules [O(w2), O(w3)] not bound to Cu^{2+} . The site occupancy for O(w2) and O(w3) is 0.41(3) and 0.34(3), respectively.

Poojary et al. [17] and *Riou et al.* [13] reported on blue crystals of a copper 1,2-ethylenediphosphonate dihydrate, in which the Cu^{2+} cations are five coordinated in a square pyramidal fashion. Two square pyramids have a common

edge leading to $[\text{Cu}_2\text{O}_8]$ dimeric units, with a $\text{Cu}\cdots\text{Cu}$ distance of 313 pm, which are linked by tetrahedral $[\text{PO}_3\text{C}]$ groups leading to layers in the (100) plane. These layers are linked by the C_2H_4 groups to a compact three-dimensional framework.

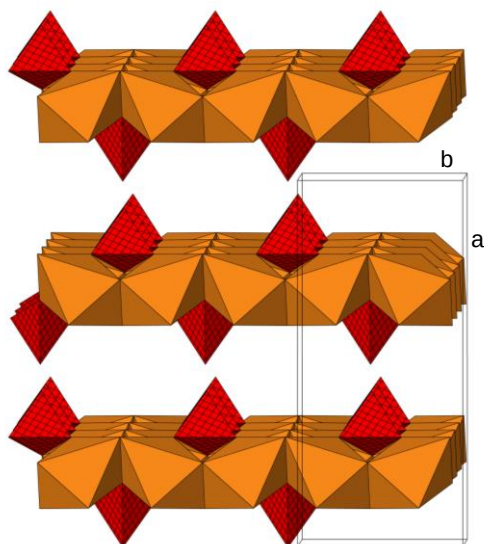


Figure 3. Stacking of the polyhedra layers. (● $[\text{CuO}_6]$ octahedra, ● $[\text{PO}_3\text{C}]$ tetrahedra)

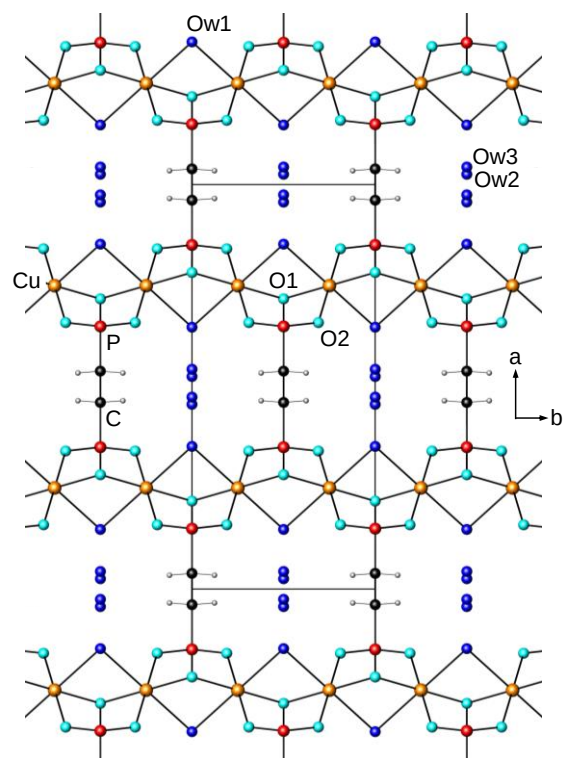


Figure 4. Crystal structure of $\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]\cdot 3.2\text{H}_2\text{O}$ viewed along $[001]$.

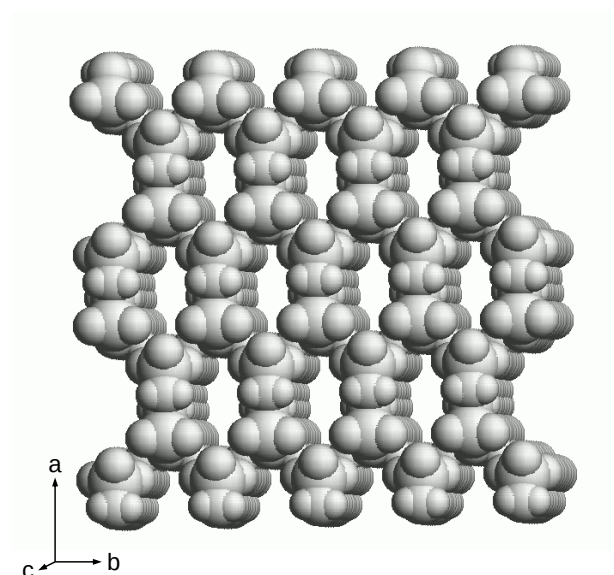


Figure 5. Space-filling model of the framework of $\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]\cdot 3.2\text{H}_2\text{O}$. The water molecules $\text{O}(\text{w}1)$, $\text{O}(\text{w}2)$ and $\text{O}(\text{w}3)$ are omitted.

Fig. 6 shows both the XRD pattern of powdered $[\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]\cdot 3.2\text{H}_2\text{O}]$ microcrystals from synthesis in aqueous solution and the calculated pattern obtained from

the single crystal data. The experimental pattern matches the calculated pattern, showing that the synthesis in aqueous solution leads to a single phase product with the same crystal structure as the samples obtained by crystallization in silica gel.

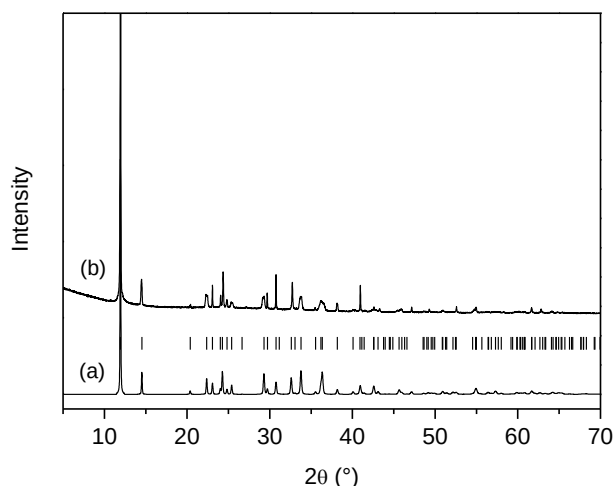


Figure 6. X-ray powder diffraction patterns of $[\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]] \cdot 3.2\text{H}_2\text{O}$. (a) calculated pattern, (b) experimental pattern.

TGA/DTA studies (Fig. 7) were carried out in air from room temperature to 1000 °C at a heating rate of 10 K min⁻¹. The loss of water molecules occurs stepwise in two endothermal processes. The first step is finished at approximately 138 °C and the second one at 240 °C. The weight loss of 14.8 % corresponds to the release of all water molecules (calc. 15.5 %). The dehydrated compound is stable up to 320 °C. This is obviously due to the small contribution of the weakly bound water molecule (O(w1)) to the bond valence sum of Cu²⁺. Thus making it unnecessary to reconstruct the coordination sphere during dehydration, which causes crystal structures of many coordination polymers often to collapse on heating. A small increase of weight between 320 and 360 °C is followed by a steep weight loss during a highly endothermic process. This can be associated to the decomposition of the 1,2-ethylenediphosphonate anion, which was similarly observed in other organodiphosphonate complexes [11,18]. Between 370 °C and 450 °C an increase in weight occurred. XRD patterns of samples annealed between 380 and 450 °C showed an amorphous fraction and only reflections of CuO. The following weight loss leads to the formation of Cu₂P₂O₇ and is finished at about 660 °C. The colourless residue was identified as phase pure Cu₂P₂O₇ by X-ray powder diffraction. The entire weight loss up to 1000 °C of 19.2 % is in good agreement with the calculated one of 18.8 % with Cu₂P₂O₇ as the final product.

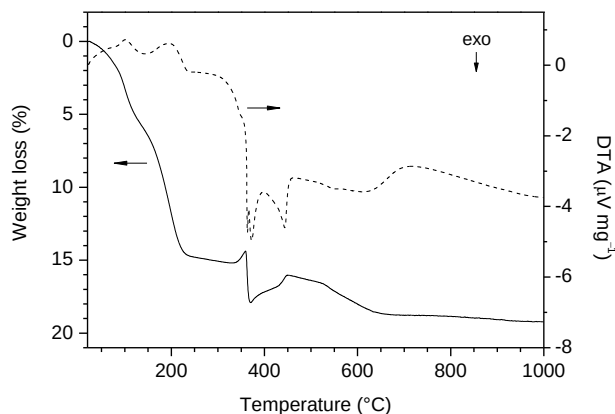


Figure 7. Thermal analysis of $\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3] \cdot 3.2\text{H}_2\text{O}$.

The water of crystallization in $\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3] \cdot 3.2\text{H}_2\text{O}$ can be removed reversibly. Heating in a furnace at 260 °C for 10 min led to the completely dehydrated compound and the colour turned from turquoise to blue. The observed weight loss of 15.7 % corresponded very well with the loss of all water molecules (15.5 %). The dehydrated sample was split into two fractions. One fraction was stored in water at room temperature for 24 h and the other one was stored at ambient air for 7 days leading to a nearly complete rehydration and the colour turned back to turquoise in both cases. Thermogravimetric analysis of the rehydrated samples up to 1000 °C showed a total weight loss of 16.9 % and 17.0 %, respectively, indicating that the rehydrated samples contained 2.7 H₂O rather than 3.2 H₂O per formula unit. Fig. 8 shows the XRD patterns of the dehydrated and rehydrated samples compared with the as-prepared material $\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3] \cdot 3.2\text{H}_2\text{O}$. There is no significant change in the patterns indicating that the crystal structure of the host has not been changed during the dehydration and rehydration process. Furthermore, the compound can be partially dehydrated by storage in a desiccator over sulfuric acid. After 7 days the colour had turned to blue and a weight loss of 9.6 % was observed corresponding to the loss of 2 H₂O per formula unit. A longer storing time in the desiccator did not lead to further weight losses.

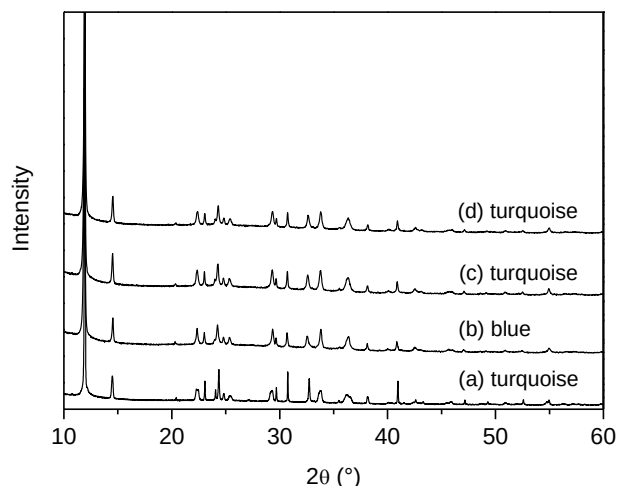


Figure 8. XRD patterns of dehydrated and rehydrated samples. (a) $\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]\cdot 3.2\text{H}_2\text{O}$, (b) dehydrated sample after heating at 260 °C, (c) rehydrated sample stored in water for 24 h, (d) rehydrated sample stored in ambient air for 7 d.

The IR spectrum (ATR technique) of $\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]\cdot 3.2\text{H}_2\text{O}$ is shown in Fig. 9. The O–H stretching vibrations of the water molecules appear at 3478 and 3262 cm^{-1} , whereas the band 1649 cm^{-1} probably reflects the H–O–H bending mode. The band at 1412 cm^{-1} is caused by the CH_2 bending mode. Absorption bands at 1196 and 1124 cm^{-1} are due to the asymmetrical and symmetrical P–O stretching vibrations. P–C stretching and CH_2 rocking vibrations result in bands at 767, 730, and 690 cm^{-1} , respectively [34,35].

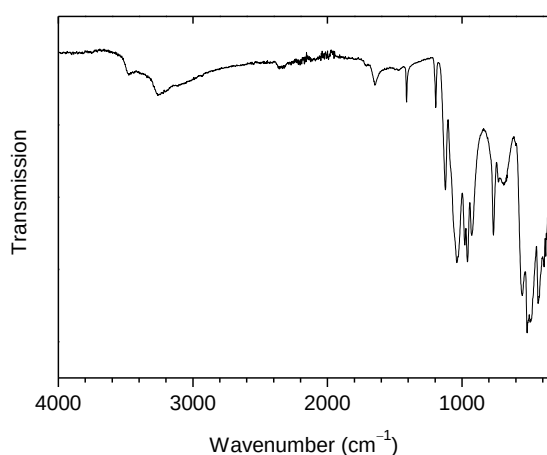


Figure 9. IR spectrum of $\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]\cdot 3.2\text{H}_2\text{O}$.

Fig. 10 shows the diffuse reflectance UV-Vis spectrum of $\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]\cdot 3.2\text{H}_2\text{O}$. Between 500 and 1200 nm a broad asymmetric band with two visible maxima (I, II)

caused by d–d transitions can be seen. The experimental spectrum can be fitted well by three bands with maxima at 694, 774 and 918 nm. Since the Cu^{2+} coordination polyhedron has D_{2h} symmetry four d–d transition bands are expected according to selection rules [36]. A precise inspection shows that the polyhedron deviates only slightly from D_{4h} symmetry (three transition bands), therefore the energy levels of the d_{xz} and d_{yz} orbitals are very close to each other, resulting in almost identical transition bands [37,38]. According to Billing and Hathaway [36] the order of the energy levels is $d_{x^2-y^2}^2 > d_z^2 > d_{xy} > d_{xz} \approx d_{yz}$. The fitted absorption band at 694 nm is assigned to the $d_{yz}(d_{xz}) \rightarrow d_{x^2-y^2}^2$, at 774 nm to the $d_{xy} \rightarrow d_{x^2-y^2}^2$, and at 918 nm to the $d_z^2 \rightarrow d_{x^2-y^2}^2$ transition.

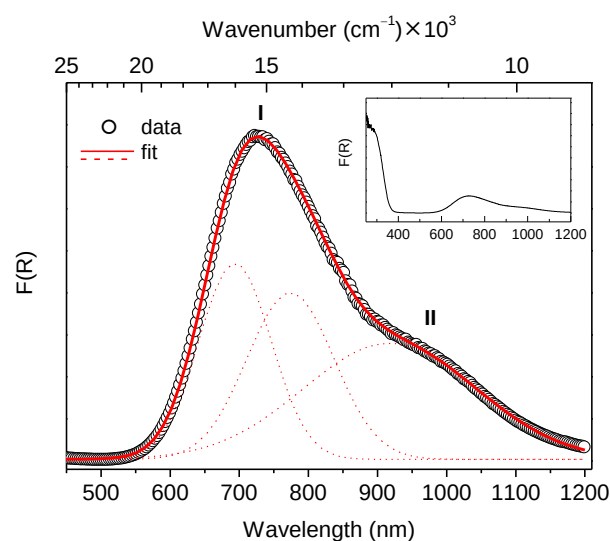


Figure 10. UV-Vis spectrum (diffuse reflectance) of powdered $[\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]]\cdot 3.2\text{H}_2\text{O}$. The inset shows the whole spectrum from 250 to 1200 nm. Three individual Gaussian profiles (red dashed curves) were used to fit the spectrum and their sum is presented by the thick red curve. ($F(R)$ = Kubelka-Munk-function)

The magnetic susceptibility of $\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]\cdot 3.2\text{H}_2\text{O}$ was measured between 3 and 300 K (Fig. 11). The compound shows a paramagnetic behaviour. The change of the susceptibility in the range 35–300 K followed the Curie-Weiss law with a Curie constant of $C = 11.77 \cdot 10^{-6} \text{ m}^3 \text{ K mol}^{-1}$. The observed Weiss temperature of $\Theta = -19.45 \text{ K}$ suggests an antiferromagnetic interaction. From the Curie constant the magnetic moment is calculated as $\mu_{\text{mag}} = 2.74 \mu_B$ per formula unit, which is close to the calculated spin-only value for two isolated Cu^{2+} ions (two unpaired electrons) of $2.83 \mu_B$. Figure 12 shows the magnetic moment depending on temperature. It can be seen that the magnetic moment decreases drastically below approximately 100 K indicating an antiferromagnetic coupling between Cu^{2+} ions. A direct exchange (δ bond) between neighbouring Cu^{2+} can be certainly excluded because of the long $\text{Cu}\cdots\text{Cu}$ distance of 334.2(1) pm. The antiferromagnetic behaviour can be explained by superexchange coupling between Cu^{2+} through the

phosphonate oxygen atom O(1), which connects two copper ions (see Fig. 1 and 4). The coupling through the bridging water molecule O(w1) can be excluded because of its considerably longer distance to the Cu^{2+} ions. Between 100 K and 300 K the magnetic moment changes only slightly and is close to the theoretical value indicating that there is no antiferromagnetic coupling.

storage in ambient air. Magnetic measurements show an antiferromagnetic interaction between the copper ions by a superexchange through the phosphonate oxygen atoms.

Experimental Section

Single crystals of $\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]\cdot 3.2\text{H}_2\text{O}$ were grown in a silica gel matrix [39]. To a mixture of 6 ml 2M HNO_3 , 3 ml water, and 6 ml of 0.1M 1,2-ethylenediphosphonic acid solution an aqueous Na_2SiO_3 solution (2M) was added until a pH value of 6 was reached. The mixture was placed in a test tube and within 24 h it turned to a high viscous gel. A 0.1M $\text{Cu}(\text{NO}_3)_2$ solution was placed on the top of the gel. The sealed test tube was kept at 45 °C in a drying oven and after seven days turquoise crystals appeared. Larger amounts of fine crystalline material of $\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]\cdot 3.2\text{H}_2\text{O}$ can be obtained by the following procedure in aqueous solution. 1 g urea was added to 5 ml of a 0.1M 1,2-ethylenediphosphonic acid solution in a round bottom flask and was kept at 80 °C in a drying oven. After 24 h 5 ml of a 0.2 M $\text{Cu}(\text{NO}_3)_2$ solution was added whereupon a pale blue precipitate appeared immediately. The whole solution was kept at 80 °C again and within four days a turquoise fine crystalline precipitate appeared (yield 92 %).

Results of elemental analysis: (molecular weight 370.72) C 6.41 (calcd. 6.48); H 2.57 (2.83)%.

IR-ATR (cm^{-1}): 3478(m), 3262(m), 1649(m), 1412(m), 1196(m), 1124(s), 1038(s), 980(m), 959(m), 927(s), 767(s), 730(w), 690(w), 553(m), 517(s), (m), 495(m), 435(s), 391(w).

ATR Fourier transformed infrared (IR-ATR) measurements were carried out at room temperature with a resolution of 2 cm^{-1} using a Bruker Alpha FT-IR spectrometer equipped with diamond ATR unit. Thermoanalytic measurements with a heating rate of 10 K/min were performed in flowing air using a Netzsch STA 449 device. Temperature dependent magnetizations were measured at $\mu_0 H = 0.3\text{ T}$ in the temperature range of 3 to 300 K using a Quantum Design PPMS 9. The X-ray powder diffraction patterns were recorded at room temperature on a Bruker D8-Advance diffractometer, equipped with a one-dimensional silicon strip detector (LynxEyeTM) and operating with Cu-K α radiation. The diffuse reflectance UV-Vis spectrum was obtained using a Perkin Elmer UV-Vis spectrometer Lambda 19. BaSO_4 was used as a white standard. X-ray single crystal structure determination was performed on a Siemens P4 four-circle diffractometer (MoK α , graphite monochromator) in a theta range up to 27.98° . Numerical absorption corrections have been applied. The phase problem was solved by direct methods. Full matrix least squares refinement employing $|F|^2$ made use of the SHELXTL program suite [40].

Hydrogen atom positions of water molecules have not been taken into account. The C bound hydrogen atom was located in a Difference Fourier map and has been refined with an isotropic displacement parameter. Crystallographic data are given in Table 3. Further details concerning the crystal structure analysis have been deposited with Cambridge Crystallographic Data Centre, The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK, Fax +(1223)336-033, e-mail data_request@ccdc.cam.ac.uk, www.ccdc.cam.ac.uk/data_request.cif under CCDC 1490380.

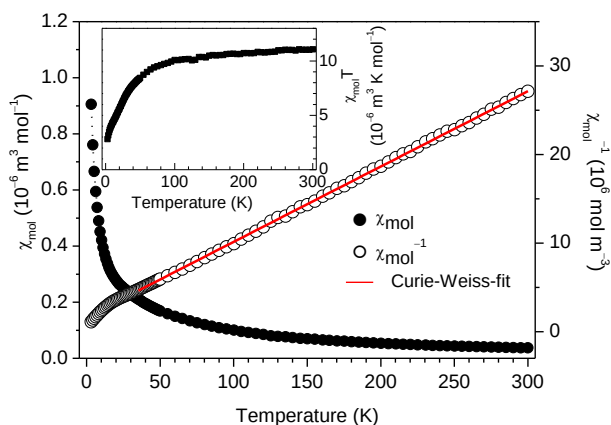


Figure 11. Susceptibility depending on temperature of $[\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]]\cdot 3.2\text{H}_2\text{O}$. The inset shows χT versus temperature. ($\mu_0 H = 0.3\text{ T}$)

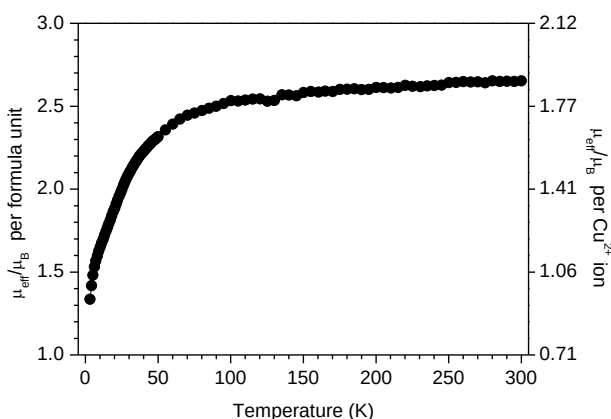


Figure 12. Change of the magnetic moment versus temperature of $[\text{Cu}_2[\mu_8\text{-O}_3\text{P}(\text{CH}_2)_2\text{PO}_3]]\cdot 3.2\text{H}_2\text{O}$.

Conclusions

In summary, we reported on the synthesis and crystal structure of a novel three-dimensional Cu(II)-1,2-ethylenediphosphonate coordination polymer with channels accommodating water molecules. Thermal investigations reveal that the dehydrated compound is stable between 240 and 320 °C. The dehydrated sample can be rehydrated upon

Table 3. Crystallographic Data

Empirical formula	C ₂ H _{10.4} P ₂ Cu ₂ O _{9.2}
Crystal system	Monoclinic
Space group	C2/m (no.12)
Lattice constants	<i>a</i> = 1483.6(2) pm <i>b</i> = 668.44(8) pm <i>c</i> = 436.30(6) pm β = 93.28(2)°
Cell volume	0.43196(10) nm ³
Formulas in unit cell	2
Formula weight	370.72 g/mol
Density (calc.)	2.850 g/cm ³
Wavelength	71.073 pm
Absorption coefficient	5.329 mm ⁻¹
Numerical absorption correction	min./max. transmittance
Temperature	293(2) K
Crystal size (mm)	0.06 x 0.08 x 0.20
F (000)	368
Θ -range	2.75° – 27.98°
Limiting indices	h: -1/+19; k: -1/+8; l: -5/+5
Reflections collected	727
Independent reflections	570 (<i>R</i> _{int} = 0.0400)
Structure solution	Direct methods
Structure refinement	Full-matrix least-squares on $ F ^2$
Refined parameters	557
Extinction coefficient	0.001(2)
Final mean shift/esd	0.000
Goodness-of-fit on $ F ^2$	1.368
Residuals (all data)	<i>R</i> ₁ = 0.0509, <i>wR</i> ₂ = 0.1156
Max. features in last difference Fourier synthesis	1076 and -1397 e-nm ⁻³

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R. Köferstein, M. Arnold, C. Robl, *A Novel Three-Dimensional Cu(II) 1,2-Ethylenediphosphonate framework with Channel-like Voids*, *Z. Anorg. Allg. Chem.* **642** (2016) 1126–1132. (DOI: 10.1002/zaac.201600248)

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Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

R. Köferstein, M. Arnold, C. Robl, *A Novel Three-Dimensional Cu(II) 1,2-Ethylenediphosphonate framework with Channel-like Voids*, Z. Anorg. Allg. Chem. 642 (2016) 1126–1132. (DOI: 10.1002/zaac.201600248)