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Cover Picture: Synthesis, Crystal Structure, and Characterization of Two Novel One- and Two-Dimensionally Polymeric Copper(II) Phosphonoacetates

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Synthesis, Crystal Structure and Characterization of Two Novel One- and Two-Dimensionally Polymeric Copper(II) Phosphonoacetates

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Abstract: Blue single crystals of $\text{Cu}[\mu_2\text{-OOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ (**1**) and $\text{Cu}_{1.5}[\mu_3\text{-OOC}(\text{CH}_2)\text{PO}_3]\cdot 5\text{H}_2\text{O}$ (**2**) have been prepared in aqueous solution. **1**: Space group C2/c (no. 15) with $a = 1623.3(2)$, $b = 624.0(1)$, $c = 1495.5(2)$ pm, $\beta = 122.45(1)^\circ$. Cu is coordinated by three oxygen atoms stemming from the hydrogenphosphonoacetate dianion and three water molecules to form a distorted octahedron. The Cu–O bonds range from 190.4(3) to 278.5(3) pm. The connection between the Cu^{2+} cations and the hydrogenphosphonoacetate dianions leads to a two-dimensional structure with layers parallel to $(\bar{1}01)$. The layers are linked by hydrogen bonds. **2**: Space group $P\bar{1}$ (no. 2) with $a = 608.2(1)$, $b = 800.1(1)$, $c = 1083.6(1)$ pm, $\alpha = 94.98(1)^\circ$, $\beta = 105.71(1)^\circ$, $\gamma = 109.84(1)^\circ$. There are two crystallographically independent Cu^{2+} cations coordinated in a square pyramidal and an octahedral fashion, respectively. The Cu–O bonds range from 192.9(2) to 237.2(2) pm. The coordination of the phosphonoacetate trianion to Cu(1) results in infinite polyanionic chains parallel to $[100]$ with a composition of $\{\text{Cu}(\text{H}_2\text{O})[\text{OOC}(\text{CH}_2)\text{PO}_3]\}_n^{n-}$. Hydrated Cu(2) cations are accommodated between the chains as counter ions. **1** and **2** show structural features of cation exchangers. Magnetic measurements reveal a paramagnetic Curie-Weiss behaviour. Compound **2** shows antiferromagnetic coupling between Cu^{2+} ions due to a super-superexchange coupling. The UV/Vis spectra of **1** suggests three d–d transition bands at 763 nm ($^2\text{B}_1 \rightarrow ^2\text{E}$), 878 nm ($^2\text{B}_1 \rightarrow ^2\text{B}_2$), and 1061 nm ($^2\text{B}_1 \rightarrow ^2\text{A}_1$). Thermoanalytical investigations in air show that compound **1** is stable up to 165 °C, whereas the decomposition of **2** begins at 63 °C.

Synthesis, Crystal Structure and Characterization of Two Novel One- and Two-Dimensionally Polymeric Copper(II) Phosphonoacetates

Roberto Köferstein^[b], Michael Arnold^[a], and Christian Robl^{*[a]}

Dedicated to Prof. Dr. Wolfgang Beck on the occasion of his 85th birthday.

Abstract: Blue single crystals of $\text{Cu}[\mu_2\text{-OOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ (**1**) and $\text{Cu}_{1.5}[\mu_3\text{-OOC}(\text{CH}_2)\text{PO}_3]\cdot 5\text{H}_2\text{O}$ (**2**) have been prepared in aqueous solution. **1**: Space group C2/c (no. 15) with $a = 1623.3(2)$, $b = 624.0(1)$, $c = 1495.5(2)$ pm, $\beta = 122.45(1)^\circ$. Cu is coordinated by three oxygen atoms stemming from the hydrogenphosphonoacetate dianion and three water molecules to form a distorted octahedron. The Cu–O bonds range from 190.4(3) to 278.5(3) pm. The connection between the Cu^{2+} cations and the hydrogenphosphonoacetate dianions leads to a two-dimensional structure with layers parallel to (101). The layers are linked by hydrogen bonds. **2**: Space group $P\bar{1}$ (no. 2) with $a = 608.2(1)$, $b = 800.1(1)$, $c = 1083.6(1)$ pm, $\alpha = 94.98(1)^\circ$, $\beta = 105.71(1)^\circ$, $\gamma = 109.84(1)^\circ$. There are two crystallographically independent Cu^{2+} cations coordinated in a square pyramidal and an octahedral fashion, respectively. The Cu–O bonds range from 192.9(2) to 237.2(2) pm. The coordination of the phosphonoacetate trianion to Cu(1) results in infinite polyanionic chains parallel to [100] with a composition of $\{\text{Cu}(\text{H}_2\text{O})[\text{OOC}(\text{CH}_2)\text{PO}_3]\}_n^{n-}$. Hydrated $\text{Cu}(2)$ cations are accommodated between the chains as counter ions. **1** and **2** show structural features of cation exchangers. Magnetic measurements reveal a paramagnetic Curie-Weiss behaviour. Compound **2** shows antiferromagnetic coupling between Cu^{2+} ions due to a super-exchange coupling. The UV/Vis spectra of **1** suggests three d–d transition bands at 763 nm ($^2B_1 \rightarrow ^2E$), 878 nm ($^2B_1 \rightarrow ^2B_2$), and 1061 nm ($^2B_1 \rightarrow ^2A_1$). Thermoanalytical investigations in air show that compound **1** is stable up to 165 °C, whereas the decomposition of **2** begins at 63 °C.

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 bifunctional organophosphonates, e.g.

diphosphonate or phosphonocarboxylate units as ligands, various structural motives can be made possible.^[5–14] Zinc 5-phosphonobenzene-1,3-dicarboxylate can be used as catalyst in Friedel-Crafts benzylation reactions and cobalt uranyl phosphonoacetate shows selective CO_2 uptake.^[15–17] One of the simplest phosphonocarboxylic acids is phosphonoacetic acid. The deprotonation of the phosphonoacetic acid can lead to the monoanionic, dianionic, and trianionic form, respectively.^[18] The three forms of the phosphonoacetate anion appear in e.g. $M[\text{HOOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ ($M = \text{Mn}, \text{Co}, \text{Zn}, \text{Cu}$)^[19], $\text{UO}_2[\text{HOOC}(\text{CH}_2)\text{PO}_3]$ ^[20], $\text{Cu}_2[\text{OOC}(\text{CH}_2)\text{PO}_3\text{H}](\text{bpy})_2$ ^[21], and $\text{Mn}_3[\text{OOC}(\text{CH}_2)\text{PO}_3]_2$ ^[22]. The connection between Cu^{2+} and phosphonoacetate anions leads to coordination polymers with one-, two and three-dimensional structural features.^[19,23,24] The obtained structures depend on the reaction temperature, Cu:P ratio, pH value, and the deprotonation stage of the phosphonoacetate anion. The structures of Cu(II) phosphonoacetates can be modified using additional N-donor ligands.^[21]

Herein, we report on a novel two-dimensionally polymeric copper(II) hydrogenphosphonoacetate dihydrate and a one-dimensionally polymeric copper(II) phosphonoacetate pentahydrate.

Results and Discussion

$\text{Cu}[\mu_2\text{-OOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ (**1**)

In $\text{Cu}[\mu_2\text{-OOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ (**1**) the Cu^{2+} cations occupy the general position of space group C2/c. The Cu cations are six-fold coordinated (4+1+1) in a distorted octahedral fashion (Figure 1). The equatorial positions are occupied by the carboxylate oxygen atom O(1), the phosphonate oxygen atom O(3) stemming from the same hydrogenphosphonoacetate dianion, and two water molecules [O(w1), O(w2)]. The Cu–O distances in the equatorial plane range from 190.4(3) to 200.4(4) pm (Table 1). The best least-square-plane through Cu, O(1), O(3), O(w1), and O(w2) shows a significant deviation from planarity (maximum deviation 24.0 pm). The axial positions are occupied by the phosphonate oxygen atom O(4), from a second, but crystallographically equivalent hydrogenphosphonoacetate dianion and the water molecule O(w2)^{#2} with longer bond lengths of 229.5(3) and 278.5(3) pm, respectively. According to Hathaway^[25,26] and Pasquarello et al.^[27] Cu–O distances up to 300 pm (sum of van der Waals radii) should be considered to be bonds. Such long Cu–O bonds were also found in e.g. copper(II)

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malonates^[28], copper(II) oxalatodiethylenetriamine^[29], galactose oxidase^[30], and copper(II) bis(L-amino acid) complexes.^[31,32] The O–Cu–O angles differ considerably in part from the ideal values of 90° and 180°, respectively. The Cu²⁺ coordination polyhedron can be approximately described with a C_{4v} point group symmetry. Employing the method of *Brese and O’Keeffe*^[33] the bond order is calculated to 2.10. Neighbouring Cu²⁺ coordination polyhedra are tilted against each other and linked by a common corner [O(w2)] which leads to infinite ribbons of copper polyhedra along [010] (Figure 2).

Figure 1. The coordination environment of Cu²⁺ in Cu[μ₂-OOC(CH₂)PO₃H]·2H₂O (1). Ellipsoids are given at 50 % probability, arbitrary radii for hydrogen atoms. The index (') indicates the longest Cu–O bond. Symmetry codes as in Table 1.

Figure 2. The connection of the Cu²⁺ polyhedra to infinite ribbons in 1. (a) view to (010), (b) view along [001]. The longest Cu–O(w2) bond is drawn with a light grey bond. Hydrogen atoms are omitted for clarity.

Table 1. The coordination of Cu²⁺ in Cu[μ₂-OOC(CH₂)PO₃H]·2H₂O (1)

Distances (pm)			
Cu–O(1)	198.6(3)	Cu–O(w1)	200.4(4)
Cu–O(3)	190.4(3)	Cu–O(w2)	195.9(3)
Cu–O(4) ^{#1}	229.5(3)	Cu–O(w2') ^{#2}	278.5(3)
Bond angles (°)			
O(3)–Cu–O(w2)	172.71(14)	O(3)–Cu–O(w2') ^{#2}	82.15(11)
O(w2)–Cu–O(1)	86.33(13)	O(w1)–Cu–O(w2') ^{#2}	74.93(13)
O(w2)–Cu–O(w1)	88.32(14)	O(w2)–Cu–O(4) ^{#1}	90.59(13)
O(3)–Cu–O(4) ^{#1}	96.52(12)	O(w1)–Cu–O(4) ^{#1}	96.29(13)
O(1)–Cu–O(4) ^{#1}	95.44(12)	O(w2)–Cu–O(w2') ^{#2}	90.57(11)
O(3)–Cu–O(1)	94.58(13)	O(1)–Cu–O(w2') ^{#2}	93.42(11)
O(3)–Cu–O(w1)	89.29(14)	O(4)–Cu–O(w2') ^{#2}	171.11(11)
O(1)–Cu–O(w1)	167.14(14)	Cu–O(w2) ^{#2} –Cu ^{#2}	119.79(13)

Symmetry codes: The index (') indicates the longest Cu–O bond. #1: -x, -y+1, -z; #2: 0.5-x, 0.5+y, 0.5-z

The carboxylate group in the hydrogenphosphonoacetate dianion is deprotonated. The C–O bond lengths are between

those typical for a double and a single bond. The bond to O(1) is significant longer than to O(2) obviously due to the coordination to Cu^{2+} . The carboxylate group is twisted against the plane through P–C(2)–C(1) by $50.7(4)^\circ$. The phosphorous atom is surrounded by three oxygen atoms and one carbon atom from the ethylene group in a distorted tetrahedral manner (Figure 3). The P–O bonds range from 149.3(3) to 157.7(3) pm, whereas the P–C bond is 180.1(5) pm. The phosphonate oxygen atoms O(3) and O(4), bound to Cu^{2+} form the shortest P–O bonds, whereas the protonated oxygen atom O(5) forms the longest one. The angles within the $[\text{O}_3\text{PC}]$ tetrahedron differ markedly from the ideal values (Table 2). Each hydrogenphosphonoacetate dianion connects two copper ions and adopts a μ_2 coordination mode. Both the phosphonate- and the carboxylate group coordinate in a monodentate manner.

Figure 3. The connection between the hydrogenphosphonoacetate dianion and the Cu^{2+} cations in $\text{Cu}[\mu_2\text{-OOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ (1).

Table 2. Bond lengths and angles of the hydrogenphosphonoacetate dianion in $\text{Cu}[\mu_2\text{-OOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ (1)

Distances (pm)

P–O(3)	151.0(3)	O(1)–C(1)	128.3(5)
P–O(4)	149.3(3)	O(2)–C(1)	125.2(5)
P–O(5)	157.7(3)	C(1)–C(2)	151.1(6)
P–C(2)	180.1(5)	O(5)–H(3)	79(6)

Bond angles ($^\circ$)

O(4)–P–O(3)	115.3(2)	O(1)–C(1)–C(2)	119.7(4)
O(3)–P–O(5)	110.0(2)	O(2)–C(1)–C(2)	119.2(4)
O(4)–P–O(5)	106.6(2)	C(1)–C(2)–P	116.0(3)

O(3)–P–C(2)	108.0(2)	O(5)–P–C(2)	106.3(2)
O(4)–P–C(2)	110.3(2)	O(2)–C(1)–O(1)	121.1(4)

Neighbouring ribbons of copper polyhedra are linked by the $[\text{O}_3\text{PC}]$ tetrahedra through O(3) and O(4) to form infinite layers parallel to (01) (Figure 4). The layers are stacked in a ...ABAB... sequence along the $[101]$ direction (Figure 5). $\text{Cu}[\mu_2\text{-OOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ (1) can be regarded as the protonated form of a cation exchanger with a layer-like structure. The theoretical exchange capacity is 4.2 mval g^{-1} . The surface charge density of the deprotonated layers was calculated as $0.047 \cdot 10^{-4} \text{ e} \cdot \text{pm}^{-2}$ ($21.3 \cdot 10^4 \text{ pm}^2$ per unit charge), which is close to the values found in layered silicates like Muscovite, Zinnwaldite, and Celadonite.^[34]

Figure 4. View on a selected layer in the $(\bar{0}1)$ plane formed through the connection between the Cu^{2+} polyhedra ribbons and the $[\text{O}_3\text{PC}]$ tetrahedra in 1. Hydrogen atoms are omitted for clarity.

Figure 5. Stacking of the layers along (101) in **1**. The red dashed lines show a section of the hydrogen bonds between neighbouring layers. Hydrogen atoms are omitted for clarity.

The layers are linked by hydrogen bonds (Table 3). The hydroxo group O(5)–H(2) from the hydrogenphosphonoacetate dianion and the water molecule O(w2) act as proton donors to form hydrogen bonds to the carboxylate oxygen atom O(2) of the neighbouring layer of rather high and medium strength (Figure 5, Table 3). The water molecules O(w1) and O(w2) are involved in medium strength hydrogen bonds within the same layer to the carboxylate oxygen atom O(1) and to the phosphonate oxygen atoms O(1), O(4), and O(5). The phosphonate oxygen atom O(3) is not involved in any hydrogen bond.

Lodhia et al.^[24] reported on a triclinic copper hydrogenphosphonoacetate monohydrate in which each hydrogenphosphonoacetate dianion is coordinated to three Cu²⁺ cations.

Table 3. Hydrogen bonds in **1**

	O...O Distance (pm)	O–H...O Angle (°)
O(5)–H(3)···O(2) ^[a]	259.5(4)	170(7)
O(w1)–H(12)···O(5)	280.7(5)	171(6)
O(w1)–H(11)···O(1)	280.9(4)	165(6)
O(w2)–H(21)···O(2) ^[a]	270.9(5)	160(5)
O(w2)–H(22)···O(4)	271.4(5)	169(5)

[a] hydrogen bond to neighbouring layers

O(w1)–H(11): 70(5) pm, O(w1)–H(12): 68(5) pm

O(w2)–H(21): 81(5) pm, O(w2)–H(22): 99(5) pm

***Cu*_{1.5}[μ₃-OOC(CH₂)PO₃]*·*5H₂O (**2**)**

There are two crystallographically independent Cu²⁺ cations. Cu(1) occupies the general position, whereas Cu(2) lies on a crystallographic inversion centre (Wyckoff position 1a) of space group *P*₂₁. The Cu(1) cations are five coordinated in a distorted square pyramidal fashion (Figure 6). The equatorial positions are formed by three phosphonoacetate oxygen atoms [O(1), O(3), O(4)] stemming from two, but crystallographically equivalent, phosphonoacetate trianions and one water molecule O(w1). The phosphonoacetate trianion coordinates with both the carboxylate group and the phosphonate group (Figure 7). The Cu(1)–O distances in the equatorial plane range from 192.9(2) to 198.1(2) pm (Table 4). The best least-square-plane through Cu(1), O(1), O(3), O(4), and O(w1) shows only minor deviations from planarity (maximum deviation 3.1 pm). The oxygen atom O(4)^{#1}, from a third phosphonoacetate trianion, coordinates Cu(1) in the axial positions with a longer distance of 229.9(2) pm. Thus the Cu(1) coordination polyhedron can be approximately described with a C_{2v} point group symmetry. Two Cu(1) coordination polyhedra, correlated by an inversion centre, are linked by a common edge [2x O(4)] which leads to dimeric [Cu₂(O)₆(H₂O)₂] units. The shortest Cu(1)···Cu(1) contact is 319.9(1) pm. Cu(2) is surrounded by six water molecules [2x O(w2), 2x O(w3), 2x O(w4)] to form an elongated octahedron (CN: 4+2) (Figure 6). The Cu(2)–O distances in the equatorial plane do not differ significantly from each other (196.8(3)–197.0(2) pm). The axial positions [O(w3)] feature a larger bond length of 237.2(2) pm. Thus the coordination polyhedron of Cu(2) has D_{4h} symmetry in good approximation. According to *Brese and O’Keeffe* [33] the bond order for Cu(1) and Cu(2) is calculated to 1.97 and 2.25, respectively.

Figure 6. The coordination spheres of Cu(1) and Cu(2) in *Cu*_{1.5}[μ₃-OOC(CH₂)PO₃]*·*5H₂O (**2**). Ellipsoids are given at 50 % probability, arbitrary radii for hydrogen atoms. The index (#) indicates the longest Cu–O(4) bond which is drawn with a light-grey bond. Symmetry codes as in Table 4.

Table 4. The coordination of Cu²⁺ in Cu_{1.5}[μ₃-OOC(CH₂)PO₃]-5H₂O (**2**)

Distances (pm)

Cu(1)–O(1)	192.9(2)	Cu(2)–O(w2)	196.8(3)
Cu(1)–O(3)	196.0(2)	Cu(2)–O(w2) ^{#2}	196.8(3)
Cu(1)–O(w1)	194.6(2)	Cu(2)–O(w3)	237.2(2)
Cu(1)–O(4)	198.1(2)	Cu(2)–O(w3) ^{#2}	237.2(2)
Cu(1)–O(4') ^{#1}	229.9(3)	Cu(2)–O(w4)	197.0(2)
		Cu(2)–O(w4) ^{#2}	197.0(2)
Cu(1)···Cu(1) ^{#1}	319.9(1)		

Bond angles (°)

O(1)–Cu(1)–O(w1)	163.07(11)	O(w2)–Cu(2)–O(w2) ^{#2}	180
O(w1)–Cu(1)–O(3)	87.65(10)	O(w2)–Cu(2)–O(w3)	93.39(9)
O(w1)–Cu(1)–O(4)	86.60(9)	O(w4)–Cu(2)–O(w3)	89.84(9)
O(1)–Cu(1)–O(4') ^{#1}	99.79(8)	O(w2)–Cu(2)–O(w4)	90.46(10)
O(3)–Cu(1)–O(4') ^{#1}	101.23(8)	O(w4)–Cu(2)–O(w4) ^{#2}	180
O(1)–Cu(1)–O(3)	93.68(9)	O(w3)–Cu(2)–O(w3) ^{#2}	180
O(1)–Cu(1)–O(4)	90.63(9)	Cu(1)–O(4)–Cu(1) ^{#1}	96.47(8)
O(3)–Cu(1)–O(4)	172.92(8)		
O(w1)–Cu(1)–O(4') ^{#1}	96.49(10)		
O(4)–Cu(1)–O(4') ^{#1}	83.53(8)		

Symmetry codes: The index (') indicates the longest Cu–O bond. #1: -x, -y-1, -z-1; #2: -x, -y, -z

The phosphonoacetate anion is completely deprotonated. The phosphorous atom of this trianion in Cu_{1.5}[μ₃-OOC(CH₂)PO₃]-5H₂O (**2**) is bound to three oxygen atoms and one carbon atom from the ethylene group in a distorted tetrahedral fashion. The P–O bonds range from 152.1(2) to 154.0(2) pm, whereas the P–C bond is 181.4(3) pm. The angles within the [O₃PC] tetrahedron differ slightly from the ideal value (Table 5). The C–O bond lengths in the carboxylate group do not differ significantly from each other, although only O(1) is coordinated to Cu(1). The torsion angle between the carboxylate group and a plane through O(4)–P–C(2)–C(1) is 68.0(2)°. The phosphonate group is coordinated to three Cu(1) cations and the carboxylate group to one Cu(1) in a monodentate manner. Thus each phosphonoacetate trianion connects three copper ions and adopts a μ₃ coordination mode in which the [PO₃] group shows a μ₃-η₁:η₁:η₁ and the carboxylate group a μ₁-η₁ connection mode (Figure 7). Both the carboxylate oxygen atom O(2) and the phosphonate atom O(5) are not coordinated to Cu²⁺. The coordination of O(3) and O(1) to Cu(1) connects the phosphonate group with the carboxylate group and leads to the formation of six-membered ring [O(1)–C(1)–C(2)–P–O(3)–Cu(1)] similar to the one of compound **1**.

Figure 7. The connection between the phosphonoacetate trianion and the Cu(1) cations in **2**.**Table 5.** Bond length and angles of the phosphonoacetate trianion in **2**

Distances (pm)

P–O(3) ^{#3}	154.0(2)	O(1)–C(1)	127.0(4)
P–O(4)	152.9(2)	O(2)–C(1)	126.0(3)
P–O(5)	152.1(2)	C(1)–C(2)	150.2(4)
P–C(2) ^{#3}	181.4(3)		

Bond angles (°)

O(5)–P–O(4)	112.40(12)	O(3) ^{#3} –P–C(2) ^{#3}	106.05(12)
O(5)–P–O(3) ^{#3}	111.46(11)	O(2)–C(1)–O(1)	120.1(3)
O(4)–P–O(3) ^{#3}	110.68(11)	O(1)–C(1)–C(2)	119.0(2)
O(5)–P–C(2) ^{#3}	109.12(12)	O(2)–C(1)–C(2)	120.9(3)
O(4)–P–C(2) ^{#3}	106.82(12)	C(1)–C(2)–P ^{#4}	111.8(2)

Symmetry codes: #3: x+1, y, z; #4: x-1, y, z

In **2**, the coordination of the phosphonoacetate trianions to the Cu(1) cations leads to infinite chain-like polyanions with {Cu(H₂O)[OOC(CH₂)PO₃]}_nⁿ⁻ composition (Figure 8). The centrosymmetric polyanionic double chains extend along [100] and are stacked in ...AAA... sequence in both the [010] and [001] direction. The negative excess charge of the chains is compensated for by hydrated Cu(2) cations ([Cu(H₂O)₆]²⁺) which are intercalated between neighbouring chains (Figure 9). Therefore, Cu_{1.5}[μ₃-OOC(CH₂)PO₃]-5H₂O can be regarded as a chain-like cation exchanger loaded with [Cu(H₂O)₆]²⁺. The theoretical exchange capacity of the {Cu(H₂O)[μ₃-OOC(CH₂)PO₃]}_nⁿ⁻ polyanionic chains is calculated to 4.6 mval g⁻¹ with a linear charge density of 0.164·10⁻² e·pm⁻¹ (608 pm per unit charge). The water molecule O(w1), bound to Cu(1), forms a medium strength hydrogen bond to O(2) from a neighbouring

chain (Table 6, Figure 10). Furthermore, the polyanionic chains are linked by hydrogen bonds via the hydrated Cu(2) cation and the non-coordinating water molecule O(w5). The coordinating water molecules O(w2), O(w3), and O(w4) of the Cu(2) cation form strong and medium strength hydrogen bonds to the carboxylate oxygen atom O(2) and to the phosphonate oxygen atoms O(3) and O(5) from the phosphonoacetate anion as well as to the coordinated water molecule O(w1). A rather weak hydrogen bond is formed between the water molecule O(w3) and O(1). The non-coordinating water molecule O(w5) acts as proton donor to O(5). O(w1), O(w2), and O(w4) act as proton donors in medium strength hydrogen bonds to O(w3) and O(w5). The phosphonate oxygen atom O(4) is not involved in any hydrogen bonds.

Similar structures with polyanionic chains and cation exchanger features were found in e.g. dicobalt-1,2,4,5-benzenetetracarboxylate octadecahydrate and hexa-aquacadmium(II)-*catena*-[bis(4-amino-1,2,4-triazole)tetraaquabis-(benzene-1,3,5-tricarboxylato)-dicadmium(II)] dihydrate.^[35,36]

Figure 8. Coordination between Cu(1) cations and $[\text{OOC}(\text{CH}_2)\text{PO}_3]^{3-}$ anions to infinite polyanionic double chains along [100] in **2**. The longest Cu–O(4) bond is drawn with a light-grey bond.

Figure 9. Crystal structure of $\text{Cu}_{1.5}[\mu_3\text{-OOC}(\text{CH}_2)\text{PO}_3] \cdot 5\text{H}_2\text{O}$ (**2**) viewed from [010].

Figure 10. Structure of **2** with hydrogen bonds (thin red lines) viewed from [100]. The rather weak hydrogen bond between O(w3) and O(1) as well as hydrogen bonds between water molecules are omitted for clarity.

Table 6. Hydrogen bonds in **2**

	O...O Distance (pm)	O-H...O Angle (°)
O(w1)–H(11)···O(2) ^[a]	268.9(4)	151(4)
O(w1)–H(12)···O(w3)	268.3(4)	172(5)
O(w2)–H(22)···O(2)	280.5(3)	168(5)
O(w2)–H(21)···O(w5)	271.3(3)	176(5)
O(w3)–H(31)···O(5)	275.7(3)	175(5)
O(w3)–H(32)···O(2)	286.2(4)	167(5)
O(w3)–H(32)···O(1)	294.5(4)	130(4)
O(w4)–H(42)···O(3)	276.9(3)	160(4)
O(w4)–H(41)···O(w5)	272.1(4)	174(5)
O(w5)–H(51)···O(5)	275.0(3)	175(4)
O(w5)–H(52)···O(5)	276.7(4)	164(5)

[a] hydrogen bond to neighbouring chains

O(w1)–H(11): 90(5) pm, O(w1)–H(12): 73(5) pm

O(w2)–H(21): 69(4) pm, O(w2)–H(22): 68(5) pm

O(w3)–H(31): 70(4) pm, O(w3)–H(32): 90(5) pm

O(w4)–H(41): 96(6) pm, O(w4)–H(42): 73(4) pm

O(w5)–H(51): 93(4) pm, O(w5)–H(52): 61(5) pm

Figure 11. X-ray powder diffraction patterns of Cu[μ₂-OOC(CH₂)PO₃H]·2H₂O (**1**). (a) calculated pattern, (b) experimental pattern. **Figure 12.** X-ray powder diffraction patterns of Cu_{1.5}[μ₃-OOC(CH₂)PO₃]·5H₂O (**2**). (a) calculated pattern, (b) experimental pattern.

Figure 11 and 12 show the XRD patterns of powdered Cu[μ₂-OOC(CH₂)PO₃H]·2H₂O (**1**) and Cu_{1.5}[μ₃-OOC(CH₂)PO₃]·5H₂O (**2**) crystals together with the calculated patterns obtained from the single crystal data. The experimental patterns match with the calculated patterns. No reflections from secondary phases are visible indicating the syntheses routes lead to single phase products.

TGA/DTA studies were carried out in air from room temperature to 1000 °C at a heating rate of 10 K min⁻¹. Cu[μ₂-OOC(CH₂)PO₃H]·2H₂O (**1**) is stable up to 165 °C (Figure 13). A following endothermic process with an onset temperature of 167 °C causes a weight loss of 14.3 % up to 233 °C. This weight loss corresponds to the loss of two water molecules per formula unit (calcd. 15.2 %). Strong exothermic reactions with onset temperatures of about 250, 340, and 490 °C lead to the complete decomposition up to 640 °C. X-ray powder diffraction of the colourless residue showed reflections of Cu₂P₂O₇ and small traces of Cu₃(PO₄)₂. The total weight loss of 37.6 % is close to the calculated one of 36.6 % for pure Cu₂P₂O₇ as the final product. As seen in Figure 14 the decomposition of Cu_{1.5}[μ₃-OOC(CH₂)PO₃]·5H₂O (**2**) starts at 63 °C. The endothermic reaction with an onset temperature of 65 °C leads up to 138 °C to a weight loss of 21.4 %. A following smaller second weight loss caused by a weak endothermic process (onset at 180 °C) results up to 300 °C in a total weight loss of 27.2 %. This weight loss corresponds well to the loss of five water molecules per formula unit (calcd. 27.9 %). Further heating leads to several very strong and fast decomposition steps accompanied by exothermic processes with onset temperatures of 304, 328, and 576 °C. The decomposition is finished at 590 °C. The blue residue was identified as triclinic Cu₃(PO₄)₂ by X-ray powder diffraction. The total weight loss of 41.3 % matches very well with the calculated one of 41.0 %.

Figure 13. Thermal analysis of $\text{Cu}[\mu_2\text{-OOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ (**1**).

Figure 14. Thermal analysis of $\text{Cu}_{1.5}[\mu_3\text{-OOC}(\text{CH}_2)\text{PO}_3]\cdot 5\text{H}_2\text{O}$ (**2**).

Figure 15 shows the IR spectra (ATR technique) of $\text{Cu}[\mu_2\text{-OOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ (**1**) and $\text{Cu}_{1.5}[\mu_3\text{-OOC}(\text{CH}_2)\text{PO}_3]\cdot 5\text{H}_2\text{O}$ (**2**). The O–H stretching vibrations appear in **1** at 3329, 3327, and 3119 cm^{-1} , whereas **2** has a broad band between 3500 and 3000 cm^{-1} . The weak band at 2921 cm^{-1} in **1** and 2937 cm^{-1} in **2** is due the CH_2 stretching mode. A comparison with copper 1,2-ethylenediphosphonate^[7] shows that the band at 1413 cm^{-1} (**1**) and 1426 cm^{-1} (**2**) is caused by the CH_2 bending mode, whereas the bands at 1543 and 1392 cm^{-1} (**1**) and at 1558 and 1393 cm^{-1} (**2**) represent the asymmetric (ν_{as}) and symmetric (ν_{s}) vibrations of the carboxylate group, respectively. The carboxylate group coordinates Cu^{2+} in a monodentate manner (Figure 3 and 7) and therefore a difference between ν_{as} and ν_{s} of $\geq 200 \text{ cm}^{-1}$ should be expected.^[37] However, the observed difference of 151 cm^{-1} (**1**) and 165 cm^{-1} (**2**) suggests a bidentate coordination mode. As

shown in Table 3 and 6, the uncoordinated carboxylate oxygen atom O(2) is involved in several hydrogen bonds, leading to a “pseudo-bidentate” vibration behaviour.^[37, 38] P–O stretching modes appear at 1272, 1239, 1151, and 1062 cm^{-1} (**1**), and at 1205, 1126, 1070, and 1034 cm^{-1} (**2**), respectively.^[39–41]

Figure 15. IR spectra of (a) $\text{Cu}[\mu_2\text{-OOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ (**1**) and (b) $\text{Cu}_{1.5}[\mu_3\text{-OOC}(\text{CH}_2)\text{PO}_3]\cdot 5\text{H}_2\text{O}$ (**2**).

The magnetic measurements were carried out between 3 and 300 K. $\text{Cu}[\mu_2\text{-OOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ (**1**) shows a paramagnetic behaviour with a Curie constant of $5.73 \cdot 10^{-6} \text{ m}^3 \text{ K mol}^{-1}$. The magnetic moment was calculated as $\mu_{\text{eff}} = 1.91 \mu_{\text{B}}$ per formula unit.

The development of the susceptibility of $\text{Cu}_{1.5}[\mu_3\text{-OOC}(\text{CH}_2)\text{PO}_3]\cdot 5\text{H}_2\text{O}$ (**2**) (Figure 16) can be fitted by a Curie-Weiss law with a Curie constant of $5.93 \cdot 10^{-6} \text{ m}^3 \text{ K mol}^{-1}$ and a Weiss temperature of $\Theta = -1.39 \text{ K}$. The magnetic moment was calculated as $\mu_{\text{eff}} = 1.94 \mu_{\text{B}}$ per Cu^{2+} . The slightly larger value than the theoretical spin only one of $1.73 \mu_{\text{B}}$ per Cu^{2+} is due to a weak spin-orbital interaction as often found in Cu^{2+} complexes.^[42–44] The temperature dependence of the magnetic moment per Cu^{2+} in **2** is shown in Figure 17. The magnetic moment was calculated considering the Weiss temperature as $\mu_{\text{eff}}/\mu_{\text{B}} = 797.73[\chi_{\text{mol}}(T-\Theta)]^{0.5}$.^[45] Between 300 and 20 K the value of the magnetic moment does not change significantly. However, below 20 K the magnetic moment decreases slightly indicating a possible weak antiferromagnetic interaction between the Cu(1) cations. An interaction involving Cu(2) cations can be ruled out. The shortest distance between two Cu(1) ions is 319.9(1) pm, thus a direct exchange coupling can be excluded. A possible superexchange path between two neighbouring Cu(1) cations involves the phosphonate oxygen atom O(4) with a small Cu(1)–O(4)–Cu(1)[#] angle of 96.47(8)° (Figure 6). According to Crawford et al.^[46] and Merz and Haase^[47] the Cu–O–Cu angle for a antiferromagnetic interaction in hydroxo- and alkoxide-

bridged copper centres should be greater than 97.5° and 95.7° , respectively. Cu(1) is coordinated in a square pyramidal fashion, thus the magnetic orbital is $d_{x^2-y^2}$ pointing to the equatorial oxygen atoms O(w1), O(1), O(2), and O(4).^[26] In this case, the magnetic Cu–O–Cu superexchange path should involve only equatorial oxygen atoms between adjacent copper cations. As shown in Figure 6 the two Cu(1) polyhedra are linked by the oxygen atom O(4), which occupies the equatorial position (short contact of 198.1(2) pm) of one Cu(1) polyhedron and simultaneously caps the axial position of the other Cu(1) polyhedron with a longer distance of 229.9(3) pm. Thus, an antiferromagnetic superexchange via the Cu(1)–O(4)–Cu(1)^{#1} path is unlikely, because of the Cu–O–Cu angle close to 90° and the exchange path involves both axial and equatorial Cu–O bonds. Analogous arrangements were also found in e.g. BaCuP₂O₇ and KCuMoO₄(OH).^[48,49]

Consequently, a Cu–O···O–Cu super-superexchange via the Cu(1)–O(4)–P–O(3)^{#3}–Cu(1)^{#3} path, in which the oxygen atoms occupy the equatorial positions, is obviously responsible for the weak antiferromagnetic interaction (Figure 8). The strength of such spin exchange increases with decreasing O···O distances and rising Cu–O···O angles.^[50] The O(4)···O(3)^{#3} distance is 252.5(3) pm (smaller than the sum of the van der Waals radii) and the Cu(1)–O(4)···O(3)^{#3} and Cu(1)^{#3}–O(3)···O(4) angles are $142.92(14)^\circ$ and $136.34(14)^\circ$, respectively. The Cu(1)···Cu(1)^{#3} distance is 608.2(1) pm and the torsion angle of Cu(1)–O(4)···O(3)^{#3}–Cu(1)^{#3} accounts to $4.0(2)^\circ$. Such super-superexchange paths are also found in e.g. copper phosphates^[48,51], sodium copper methylenediphosphonate monohydrate^[52], copper hydrogen-3-phosphonopropionate^[53], and other copper phosphonates^[54,55].

Figure 16. Susceptibility vs. temperature of Cu_{1.5}[μ₃-OOC(CH₂)PO₃]·5H₂O (2).

Figure 17. Change of the magnetic moment vs. temperature of Cu_{1.5}[μ₃-OOC(CH₂)PO₃]·5H₂O (2). The magnetic moment was calculated considering the Weiss temperature.

The diffuse reflectance UV/Vis spectrum was recorded for powdered crystals of Cu[μ₂-OOC(CH₂)PO₃H]·2H₂O (1) and is shown in Figure 18. A broad asymmetric band appears between 500 and 1400 nm caused by d–d transitions. The measured curve can be well fitted by three bands with maxima at 763, 878, and 1061 nm (13106, 11390, and 9425 cm⁻¹). The Cu²⁺ polyhedron can be approximately described by C_{4v} symmetry. Thus, in contrast to an ideal octahedral ligand field (O_h symmetry), the ground state ²E_g splits into ²B₁ and ²A₁, whereas the ²T_{2g} splits into ²B₂ and ²E energy levels. According to Tomlinson and Hathaway^[56] and Sreeramulu et al.^[57] the ground state is ²B₁ and the energy level sequence is ²B₁ < ²A₁ < ²B₂ < ²E and therefore three transitions bands are expected. The fitted absorption band at 763 nm can be assigned as the ²B₁ → ²E transition, that at 878 nm as the ²B₁ → ²B₂, and that at 1061 nm as the ²B₁ → ²A₁ transition.^[56] The octahedral and tetragonal crystal field parameters are Dq = 1139 cm⁻¹, Ds = 1592 cm⁻¹, and Dt = 611 cm⁻¹. The crystal field parameters were calculated from the observed band positions as 4Ds + 5Dt = 8335 cm⁻¹, 10Dq + 3Ds – 5Dt = 13106 cm⁻¹, and 10Dq = 11390 cm⁻¹ as described elsewhere.^[58]

Figure 18. Diffuse reflectance UV/Vis spectrum of powdered $\text{Cu}[\mu_2\text{-OOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ (**1**). Three Gaussian curves (red dashed lines) were used to fit the spectrum and their sum is presented by the thick red curve. The inset shows the whole spectrum from 250 to 1400 nm [$F(R)$ = Kubelka-Munk-Function]

Conclusions

The synthesis and crystal structure of $\text{Cu}[\mu_2\text{-OOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ (**1**) and $\text{Cu}_{1.5}[\mu_3\text{-OOC}(\text{CH}_2)\text{PO}_3]\cdot 5\text{H}_2\text{O}$ (**2**) is reported herein. In **1** the connection between the Cu^{2+} cations and the hydrogenphosphonoacetate dianion leads to infinite layers features of cation exchangers. The layers are only connected by hydrogen bonds. Compound **1** is thermally stable up to 165 °C. The UV/Vis spectra show three d–d transition bands at 763, 878, and 1061 nm and the magnetic measurement reveal a paramagnetic Curie-Weiss behaviour. The crystal structure of **2** shows infinite centrosymmetric polyanionic chains. The negative excess charge is compensated by hydrated copper cations intercalated between the chains. Thus compound **2** can be regarded as a copper loaded cation exchanger. The thermal decomposition starts at 63 °C and is finished at 590 °C. Magnetic measurements show a paramagnetic behaviour with an obviously weak antiferromagnetic interaction at low temperatures due to a super-superexchange coupling.

Experimental Section

Single crystals of $\text{Cu}[\mu_2\text{-OOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ (**1**) can be synthesized in aqueous solution in two ways. 0.002 mol phosphonoacetic acid, 0.001 mol $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ and 0.001 mol tetraethylammonium chloride were dissolved in 7.5 ml deionized water. 1 M NaOH solution was added until a pH value of 3 was reached. The clear solution was kept at room temperature. After four days blue crystals appeared.^[59] A second way to obtain $\text{Cu}[\mu_2\text{-OOC}(\text{CH}_2)\text{PO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ is given by the following convenient procedure. 0.001 mol phosphonoacetic acid, 0.002 mol $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, and 50 mg urea were dissolved in 5 ml water in a round bottom flask and kept at 80 °C in a drying oven. After two days blue crystals were formed.

Crystals of $\text{Cu}_{1.5}[\mu_3\text{-OOC}(\text{CH}_2)\text{PO}_3]\cdot 5\text{H}_2\text{O}$ (**2**) can be obtained from aqueous solution. 0.002 mol phosphonoacetic acid and 0.001 mol $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ were dissolved in 10 ml deionized water. A 1 M NaOH solution was dropwise added until a pH value of 3 was reached. The appropriate pH value of the reaction solution is essential for the formation of compound **2**. The following procedure helps to find the required reaction parameters. After the phosphonoacetic acid and the copper salt were dissolved in water a 1 M NaOH solution was added until a permanent precipitate is formed. Afterwards the precipitate was dissolved by adding 0.05 M HNO_3 dropwise. By adding of 95 mg urea blue crystals appeared after several days at room temperature.

IR (ATR): **1:** 3329 (m), 3327 (m), 3119 (w), 1543 (m), 1413 (m), 1392 (m), 1272 (m), 1239 (m), 1151 (s), 1062 (s), 932 (m), 850 (m), 732 (w), 655 (w,sh), 620 (s), 542 (s), 480 (m), 421 (s), 397 (m,sh), 332 (m) cm^{-1} .
2: 3500–3000 (s,broad), 2937 (w), 1558 (s), 1426 (s), 1393 (s), 1205 (s), 1126 (s), 1070 (m), 1034 (s), 979 (m), 957 (m), 816 (m), 758 (m), 642 (m), 530 (m), 497 (w), 446 (m), 349 (m) cm^{-1} .

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^{-1} were performed in flowing air using a Netzsch STA 449 device. Temperature dependent magnetizations were measured at $\mu_0 H = 0.3$ T in the temperature range of 3 to 300 K using a Quantum Design PPMS 9. The magnetic data were corrected against the diamagnetic moment of the sample holder. The X-ray powder diffraction pattern was recorded at room temperature on a Bruker D8-Advance diffractometer, equipped with a one-dimensional silicon strip detector (LynxEye™) and operated 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 24.00° and 28.00°, respectively. Face-indexed 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.^[60] The C bound hydrogen atoms were positioned geometrically. The further hydrogen atom positions were located in Difference Fourier maps and refined with isotropic displacement parameters. An empirical extinction coefficient was used with (**2**). Crystallographic data are compiled in Table 7. Further crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1518841 (**1**) and 1518854 (**2**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

Table 7. Crystallographic Data

Compound	1	2
Empirical formula	$\text{C}_2\text{H}_7\text{PCuO}_7$	$\text{C}_2\text{H}_{12}\text{PCu}_{1.5}\text{O}_{10}$
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)
Lattice constants	$a = 1623.3(2)$ pm $b = 624.0(1)$ pm $c = 1495.5(2)$ pm $\beta = 122.45(1)^\circ$	$a = 608.2(1)$ pm $b = 800.1(1)$ pm $c = 1083.6(1)$ pm $\alpha = 94.98(1)^\circ$ $\beta = 105.71(1)^\circ$ $\gamma = 109.84(1)^\circ$

Cell volume	1.2783(3) nm ³	0.46808(3) nm ³
Formulas in unit cell	8	2
Formula weight	237.59 g mol ⁻¹	322.40 g mol ⁻¹
Density (calc.)	2.469 g cm ⁻³	2.287 g cm ⁻³
Wavelength	71.073 pm	
Absorption coefficient	3.658 mm ⁻¹	3.647 mm ⁻¹
Numerical absorption correction	min./max. transmittance 0.6486/0.9306	min./max. transmittance 0.7160/0.8455
Temperature	293(2) K	
Crystal size (mm)	0.22 x 0.08 x 0.02	0.04 x 0.12 x 0.10
F (000)	952	325
Θ-range	2.97° – 24.00°	2.76° – 28.00°
Limiting indices	h: -18/+18; k: -7/+7; l: -17/+17	h: -1/+8; k: -10/+10; l: -14/+14
Reflections collected	2070	3486
Independent reflections	1004 (R _{int} = 0.0349)	2249 (R _{int} = 0.0327)
Structure solution	Direct methods	
Structure refinement	Full-matrix least-squares on F ²	
Refined parameters	118	166
Extinction coefficient		0.0040(5)
Final max. shift/esd	-0.059 (H(22))	0.008 (H(42))
Final mean shift/esd	0.006	0.001
Goodness-of-fit on F ²	1.412	1.143
Residuals (all data)	R ₁ = 0.0377, wR ₂ = 0.0763	R ₁ = 0.0451, wR ₂ = 0.0565
Max. features in last Difference Fourier synthesis	575 and -639 e-nm ⁻³	440 and -396 e-nm ⁻³

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Keywords: Phosphonoacetic acid • UV-Vis spectroscopy • coordination polymer • Crystal structure • Magnetic properties

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