

Synthesis, crystal structure and magnetic properties of a new dinuclear copper(II) amino acid complex

$$[\text{Cu}_2(\text{L-arg})_2(\mu\text{-HPO}_4\text{-O})(\mu\text{-HPO}_4\text{-O,O}')(\mu\text{-OH})]^- \cdot (\text{H}_3\text{O})^+ \cdot (\text{H}_2\text{O})_6$$

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Abstract

A novel dinuclear copper(II) complex with the amino acid L-arginine (L-arg), with mono and bidentate HPO_4^{2-} oxoanions and an OH^- anion. $[\text{Cu}_2(\text{L-arg})_2(\mu\text{-HPO}_4\text{-O})(\mu\text{-HPO}_4\text{-O,O}')(\mu\text{-OH})]^- \cdot (\text{H}_3\text{O})^+ \cdot 6\text{H}_2\text{O}$ (**1**) was prepared and its structure was determined by X-ray diffraction methods. The two independent copper ions are in a distorted square pyramidal coordination, each bonded to one L-arginine molecule. These two Cu(L-arg) units are bridged by two monoatomic equatorial–apical oxygen ligands belonging to a monodentate hydrogenphosphate group, and to the hydroxyl group. The copper ions in the dinuclear unit at $d = 3.1948(8)$ Å are also connected by two equatorial oxygen belonging to a bidentate hydrogenphosphate. This dinuclear character and bridging scheme, not common for metal–amino acid compounds, is a consequence of the properties of the phosphate anions. The magnetic susceptibility at temperatures between 2 and 300 K and the isothermal magnetization curves at $T = 2.29(1)$ K with applied fields up to 9 T were measured. The magnetic data indicate an antiferromagnetic intradinuclear exchange coupling $J/k_B = -3.7(1)$ K and using a molecular field approximation we estimated a weaker ferromagnetic interaction $J'/k_B \sim 0.3$ K between neighbour dinuclear units.
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1. Introduction

Several derivatives of amino acids and peptides are important for their electrical [1,2] and optical [3–5] properties and important efforts have been done in their synthesis and characterization. As an example, the discovery of non-

linear optical properties of L-arginine phosphate monohydrate (LAP) [3] motivated studies of growth and optical properties of pure and doped LAP crystals [3,5,6].

Metal complexes of amino acids or peptides are also important as model systems in the understanding of biochemical processes in living organisms and for drugs production [7]. Yamauchi and collaborators [8–12] studied a number of ternary Cu(II) complexes containing the cationic core $\text{Cu}[\text{L-arg}]^{2+}$ (arg is the amino acid arginine,

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$C_6H_{14}N_4O_2$) and several counter ions. In the solid state, these compounds show interesting supramolecular structures, self-assembly and self-organization, with infinite single-, double- or triple-stranded helicates. As a consequence of the versatility of the positively charged guanidinium group, a binding site for H-bonds, arginine forms many complexes on reaction with organic and inorganic acids, and also incorporating metal ions [13,14]. The self-assembly is governed by hydrogen bonding, by the coordination of the metal ions, as well as by the nature of the counter ions. The metal compounds studied by Yamauchi and collaborators are essentially three dimensional and we are not aware of any dinuclear or polynuclear metal complex formation either with arginine or with other amino acid. As pointed out by Dey et al. [15] the ligands obtained by forming dinuclear metal complexes are effective devices for the recognition and assembly of external species, and also to mimic sites in which two metal ions cooperate to form a biologically relevant active centre. Thus, as part of our working lines on metal derivatives of amino acids, we found interesting to obtain and characterize dinuclear or polynuclear copper–arginine compounds using appropriate counter ions.

In recent years, Youngme and collaborators [16–18] prepared and characterized structurally and magnetically double and triply bridged dinuclear Cu(II) complexes containing the aromatic ligands 1,10-phenanthroline, 2,2'-bipyridine and di-2-pyridylamine and the $H_xPO_4^{(3-x)-}$ ($x = 1, 2$) oxoanions. In these compounds, the phosphate groups form bridges of different coordination types supporting weak antiferromagnetic interactions between neighbour copper ions. Here we exploited the bridging capabilities of phosphate groups as counter ions and report the synthesis, X-ray crystal structure and magnetic measurements of $[Cu_2(L-arg)_2(\mu-HPO_4-O)(\mu-HPO_4-O, O')(\mu-OH)] \cdot (H_3O)^+ \cdot (H_2O)_6$ (**1**), a new dinuclear copper complex of L-arginine bridged by hydrogenphosphate and hydroxyl groups exhibiting unusual dinuclear interactions with a Cu(II) coordination and bridging mode which has not been observed previously for copper–amino acid complexes.

2. Material and methods

The growth solutions were prepared in a two-step process. In the first step, L-arginine phosphate ($C_6H_{14}N_4O_2 \cdot H_3PO_4 \cdot H_2O$) was synthesized by dissolving equimolar quantities of L-arginine (Ajinomoto Co.) and orthophosphoric acid (Merck) in a saturated water solution. The pH value of this solution was adjusted to 4.25. In the second step, Cu(II) ions as copper acetate with mole fractions 0.275 and 0.50, were added to the solution. All reagents were of analytical grade. Slow solvent evaporation at constant temperature was employed in the crystal growth and plate like crystals of **1** with intense blue colour and elongated along one direction, were obtained after few weeks. Atomic Absorption Spectroscopy (Perkin–Elmer Analyst

200) and a CHN analyser (Perkin–Elmer Series II 2400) were used for elemental analyses of C, H, N and Cu contents in **1**. *Anal. Calc.* for $C_{12}H_{46}Cu_2N_8O_{20}P_2$: C, 17.76; H, 5.71; Cu, 15.66; N, 13.81; O, 39.43; P, 7.63. Found: C, 17.98; H, 5.59; Cu, 15.8; N, 13.76%. Oxygen and phosphorus were not measured. The crystal density obtained by the Arquimedes' method is $(1.682 \pm 0.004) \text{ Mg/m}^3$. The experimentally measured composition and density are in good agreement with the values obtained from the X-ray diffraction structural determination.

Diffraction data were collected at 153 K with an Enraf-Nonius Kappa-CCD diffractometer with sealed tube source and graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The unit cell parameters were derived from least squares refinement of 10451 reflections from $\theta = 0.998^\circ$ to $\theta = 27.485^\circ$. The data collection was within $\theta = 27.485^\circ$; however, the final refinement improved when the weakest reflections beyond the usual $\theta = 25.000^\circ$ were removed, and this condition was maintained. Data collection was made using the COLLECT program [19] and the integration and scaling of the reflections were performed with the HKL Denzo-Scalepack system of programs [20]. Absorption correction was carried out using the multi-scan method [21]. The structure of the complex was solved by the Patterson method using SHELXS-97 [22] and refined by full-matrix least-squares method on $(F_{\text{obs}})^2$ using SHELXL-97 [23]. The crystal data and details of the refinement are given in Table 1. Only one H atom of the phosphate groups was found in the difference Fourier maps, and had their coordinates refined. The hydrogen atoms of the water molecules could not be unequivocally assigned from the difference Fourier maps and those of the N atoms were found on Fourier maps, although the free refinement resulted in an unacceptable geometry. Thus, the H-atoms were refined with restraints $N-H = 0.96 \text{ \AA}$ for N1A and N1B, $H \cdots H$ distances of 1.60 \AA compatible with tetrahedral geometry, and $N-H = 0.86 \text{ \AA}$ for other N atoms, with $H \cdots H$ distances of 1.80 \AA , compatible with amino group geometry. The remaining H atoms were placed at calculated positions, assigned a fixed displacement and restrained to ideal geometry with $C-H = 0.99 \text{ \AA}$. The thermal parameters of all hydrogen atoms were related to those of their parent atoms by $U(H) = 1.2U_{\text{eq}}(C, N)$. The absolute configuration of the arginine molecule was determined by the anomalous dispersion method from 3582 Friedel pairs with a Flack parameter of $-0.01(1)$ [24]. The final value of R was 0.0433 for 4995 observed reflections ($F_0 > 4\sigma(F_0)$) and the final value of R_w was 0.1309 for 5174 unique reflections which were not merged before the last refinement cycle. The weighting scheme was $w^{-1} = [\sigma^2(F_o^2) + (0.0894P)^2 + 0.09P]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. The final difference map showed a peak of 1.36 e \AA^{-3} , without exhibiting significant features.

The magnetic susceptibility of a powdered sample of 140 mg of **1** placed in a gelatine capsule sample holder was measured between 2 and 300 K with applied magnetic fields $B_0 = \mu_0 H = 0.2$ and 0.5 T (μ_0 being the vacuum per-

Table 1
Crystal data and structure refinement for **1**

Empirical formula	C ₁₂ H ₄₆ Cu ₂ N ₈ O ₂₀ P ₂
Formula weight	811.59
Temperature (K)	153(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$ (no. 1)
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	7.234(1)
<i>b</i> (Å)	11.395(1)
<i>c</i> (Å)	11.429(1)
α (°)	109.74(1)
β (°)	107.20(1)
γ (°)	100.31(1)
Volume (Å ³)	805.3(2)
<i>Z</i>	1
<i>D</i> _{calc} (Mg/m ³)	1.678
Absorption coefficient (mm ⁻¹)	1.509
<i>F</i> (000)	422
Crystal size (mm)	0.20 × 0.18 × 0.18
Colour	blue
Index ranges	−8 ≤ <i>h</i> ≤ 8, −13 ≤ <i>k</i> ≤ 13, −13 ≤ <i>l</i> ≤ 13
Reflections collected	10451
Independent reflections (<i>R</i> _{int})	5174 (0.0341)
Maximum and minimum transmission	1.045 and 0.960
Refinement method	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	5174/23/443
Goodness-of-fit on <i>F</i> ²	1.195
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0433, <i>wR</i> ₂ = 0.1142
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0493, <i>wR</i> ₂ = 0.1309
Absolute structure parameter	−0.013(12)
Extinction coefficient	0.118(7)
Largest difference in peak and hole (e Å ⁻³)	1.364 and −0.939

meability) with a PPMS magnetometer (Quantum Design, Inc.). Measurements of the magnetization isotherm at a temperature *T* = 2.29(1) K were performed with applied magnetic fields up to 9 T.

3. Results and analysis

3.1. Crystal structure of **1**

An ORTEP [25] view of the basic structural unit with the corresponding numbering system is depicted in Fig. 1. Selected bond lengths and bond angles are given in Table 2. The crystal structure contains two [Cu(L-arg)]²⁺ cations, two (HPO₄)²⁻ anions, one OH⁻ anion, one H₃O⁺ hydronium and six water molecules in the unit cell. These two Cu(L-arg) units are connected by three bridges: a didentate hydrogenphosphate anion, a monodentate hydrogenphosphate anion and a hydroxyl anion. FT-IR spectrum showed a band at 969 cm⁻¹ and a shoulder around 3452 cm⁻¹ that are assigned to the vibration modes of the OH [26]. In comparison with the other six water molecules, the geometrical analysis of the structure around the isolated oxygen atom O7W shows a tetrahedral environ-

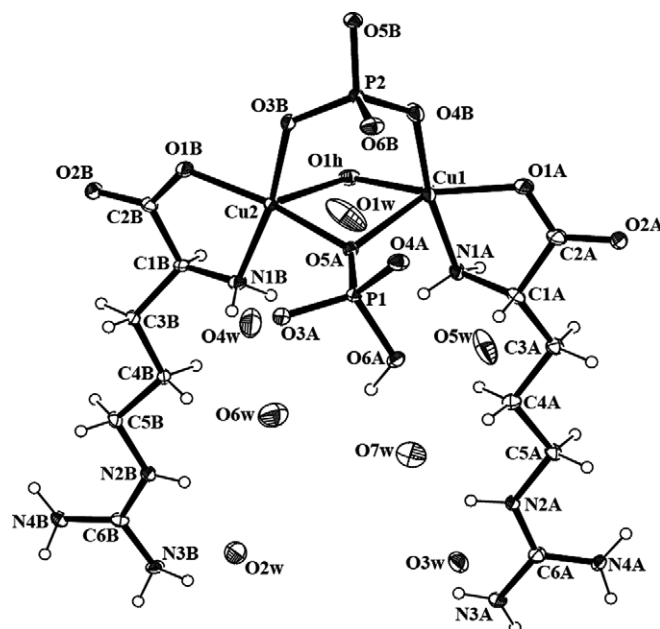


Fig. 1. ORTEP drawing at 30% probability level of **1**. Hydrogen atoms are represented as spheres of arbitrary size, except those of the water molecules which were not found, as explained in the text.

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Cu1–O4B	1.909(4)	O1h–Cu1–O5A	81.14(13)
Cu1–O1A	1.956(4)	O3B–Cu2–O1B	88.18(14)
Cu1–N1A	1.995(4)	O3B–Cu2–O5A	95.73(14)
Cu1–O1h	2.061(4)	O1B–Cu2–O5A	170.25(14)
Cu1–O5A	2.243(3)	O3B–Cu2–N1B	170.25(16)
Cu2–O3B	1.920(3)	O1B–Cu2–N1B	83.16(16)
Cu2–O1B	1.949(4)	O5A–Cu2–N1B	92.15(15)
Cu2–O5A	1.955(3)	O3B–Cu2–O1h	91.06(13)
Cu2–N1B	2.011(4)	O1B–Cu2–O1h	109.34(14)
Cu2–O1h	2.392(4)	O5A–Cu2–O1h	79.58(13)
P1–O3A	1.502(4)	N1B–Cu2–O1h	96.02(15)
P1–O4A	1.516(3)	O3A–P1–O4A	115.7(2)
P1–O5A	1.546(3)	O3A–P1–O5A	110.64(19)
P1–O6A	1.599(3)	O4A–P1–O5A	109.97(18)
P2–O3B	1.516(3)	O3A–P1–O6A	108.54(19)
P2–O4B	1.517(4)	O4A–P1–O6A	105.13(19)
P2–O5B	1.518(3)	O5A–P1–O6A	106.27(19)
P2–O6B	1.605(4)	P1–O5A–Cu2	124.88(19)
O4B–Cu1–O1A	88.08(16)	P1–O5A–Cu1	132.63(18)
O4B–Cu1–N1A	170.87(16)	Cu2–O5A–Cu1	98.89(13)
O1A–Cu1–N1A	82.79(16)	O3B–P2–O4B	112.9(2)
O4B–Cu1–O1h	92.82(16)	O3B–P2–O5B	111.44(19)
O1A–Cu1–O1h	153.65(17)	O4B–P2–O5B	110.7(2)
N1A–Cu1–O1h	95.40(15)	O3B–P2–O6B	108.8(2)
O4B–Cu1–O5A	95.04(14)	O4B–P2–O6B	109.3(2)
O1A–Cu1–O5A	125.04(16)	O5B–P2–O6B	103.26(19)
N1A–Cu1–O5A	90.16(15)	Cu1–O1h–Cu2	91.40(13)

ment with the shortest distances with respect to neighbouring oxygen atoms, which leads us to attribute this oxygen to the location of a hydronium ion. This hypothesis is corroborated by thermogravimetric measurements that show two stages. The first is associated to the loss of the six water

molecules and the second is consistent with the loss of the H_3O^+ and OH^- groups. The six free water molecules and the hydronium ion which lead to solvent channels parallel to the crystallographic a -axis are involved in a complicated hydrogen bonding network and contribute to stabilize the structure of the complex and the crystal packing. Since the H atoms of the water molecules and the hydronium ion were not located on difference maps, detailed description of the H-bonding network is difficult.

The two phosphate groups show two longer lengths consistent with P–OH bonds. The O6B atom at 2.705(5) Å from the O4A atom, is a good candidate for an H donor because it has the longest distance P2–O6B = 1.609(6) Å.

Both chemically different Cu atoms in the dinuclear unit are in distorted square-pyramidal coordination with different basal planes (see Fig. 1). The Cu1 ion coordinates one carboxylate oxygen (O1A) and one amino nitrogen (N1A) of the associated L-arginine molecule. In its basal plane it also coordinates two oxygen atoms, one from the didentate hydrogenphosphate group (O4B) and the other from the hydroxyl anion (O1h). The apical position of the Cu1 centre is occupied by one oxygen atom from the monodentate hydrogenphosphate group [Cu1–O5A = 2.243(3) Å]. The Cu1 atom is 0.249(2) Å above the basal plane, towards the O5A oxygen atom. The Cu2 ion coordinates one carboxylate oxygen (O1B) atom and one amino nitrogen atom (N1B) of the second L-arginine molecule in a square planar

geometry together with two oxygen atoms from both di-(O3B) and monodentate (O5A) hydrogenphosphate groups. In this case, the apical position is occupied by the OH^- anion [Cu2–O1h = 2.396(4) Å]. The Cu2 atom is 0.118(2) Å above the basal plane, towards the OH^- anion. The two pyramids share the edge made by O1h–O5A = 2.803(5) Å, resulting in two strained angles O1h–Cu1–O5A = 81.1(1)° and O1h–Cu2–O5A = 79.6(1)°. The dihedral angle between the least squares planes defined by the basal atoms O1h–N1A–O1A–O4B and O1B–N1B–O3B–O5A is 13.8(2)°. Both basal planes are close to the planes of the corresponding L-arginine molecule. The quasi-planar conformation of the L-arginine molecules in **1** is markedly different from that observed in L-arginine phosphate monohydrate [27].

Each $[\text{Cu}(\text{L-arg})]^{2+}$ is connected to adjacent ones through two hydrogen bonds with similar lengths. One of these bonds is between one of the guanidinium NH_2 moieties and the oxygen atom of the coordinated carboxylate group. The other is between the second guanidinium NH_2 moiety and the oxygen atom of the uncoordinated carbonyl group. The result is a layered structure (see Fig. 2) with layers nearly parallel to the plane defined by four atoms of four neighbouring molecules of the dinuclear complex: N3B, N3Bⁱ, N4Aⁱⁱ and N4Aⁱⁱⁱ, with translational symmetry operations (i) = $-1 + x, -1 + y, -2 + z$; (ii) = $2 + x, 1 + y, 1 + z$; (iii) = $1 + x, y, -1 + z$, having Miller indices (1–31), and interplanar distance 3.552 Å.

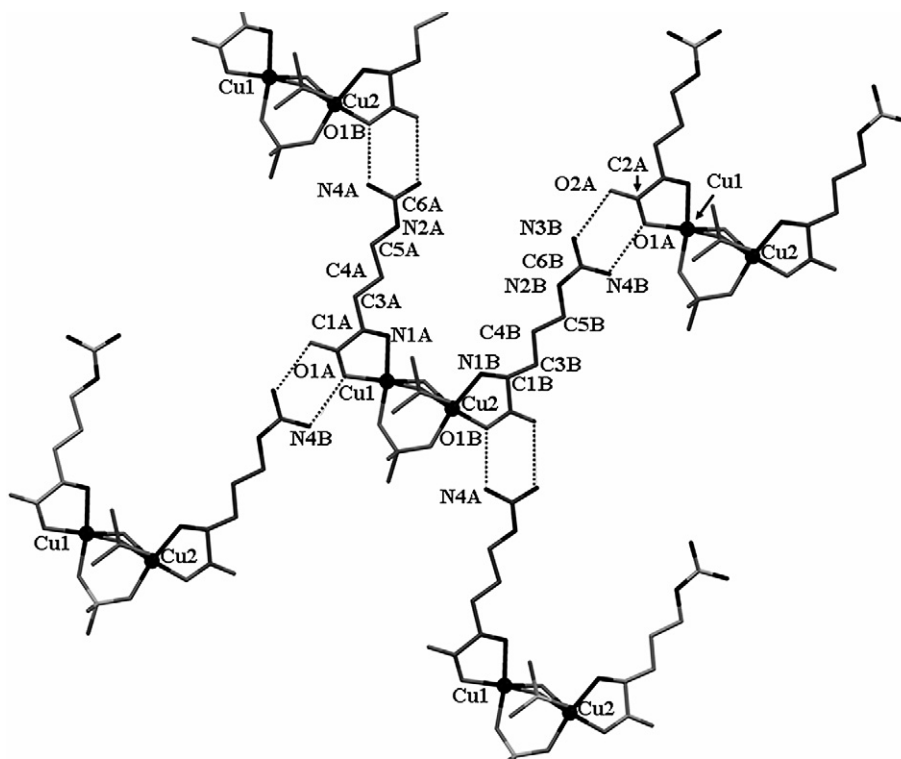


Fig. 2. Crystallographic packing of structure **1**. Cu1 and Cu2 ions of neighbour dinuclear units in a layer are bridged through a pair of H-bonds connecting the tail of the guanidinium group associated to one Cu, to the oxygens of the L-arginine carboxylate group coordinated to the other neighbour copper in the layer. Dashed lines indicate H-bonds. The bridge includes nine diamagnetic atoms plus the proton in the H-bond. The distance between coppers is 13.339 Å and that measured along the bond is 17.006 Å.

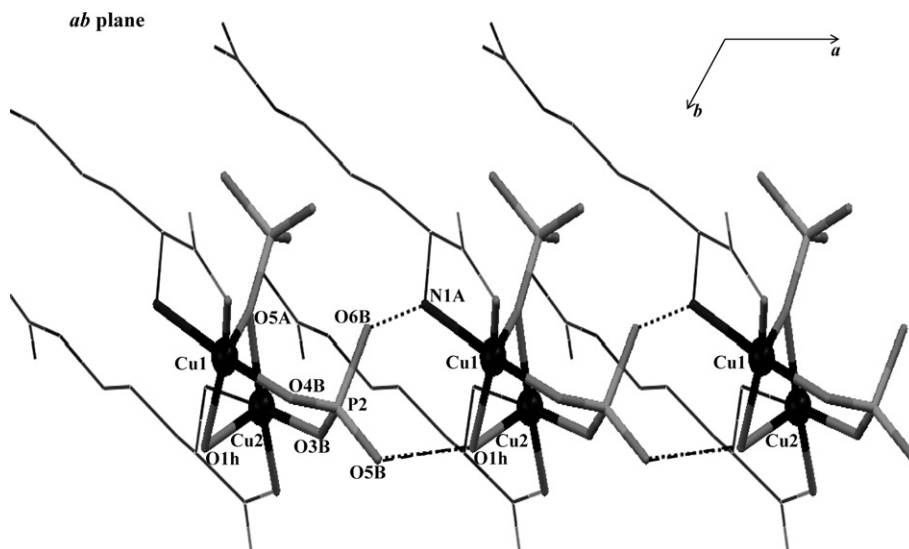


Fig. 3. Chemical bridges connecting dinuclear units in neighbour layers. Oxygens O5B and O6B belonging to the phosphate group providing the O–P–O bridge in dinuclear units are H-bonded to the N1A and O1h ligands to the Cu1 of the neighbour dinuclear unit. This bridge contains 4 diamagnetic atoms plus the H-bond. The distance between Cu1 atoms is 7.234 Å and that measured along the bond is 11.201 Å.

The copper ions are 3.1948(8) Å apart and the chemical paths connecting them are the two equatorial–apical bridges with bond lengths $d[\text{Cu1–O1h–Cu2}] = 4.417$ Å and $d[\text{Cu1–O5A–Cu2}] = 4.194$ Å, and one O–P–O bridge with bond length $d[\text{Cu1–O4B–P2–O3B–Cu2}] = 6.863$ Å, that support the intradinuclear exchange interaction. The bridging angles Cu1–O5A–Cu2 and Cu1–O1h–Cu2 are 98.97° and 91.25°, respectively.

The connections between rotated copper ions in neighbouring dinuclear units in the same layer are described in Fig. 2. One of them has 10 diamagnetic atoms including one moderate H-bond (Cu1–N1A–C1A–C3A–C4A–C5A–N2A–C6A–N4A–H42A···O1B–Cu2) with total bond length of 17.006 Å, and Cu1–Cu2 distance of 13.339 Å. The other similar connection, Cu1–O1A···H42B–N4B–C6B–N2B–C5B–C4B–C3B–C1B–N1B–Cu2 has a total bond length of 15.633 Å and the distance between copper atoms is 13.263 Å. The chemical bridges connecting Cu dinuclear units in adjacent layers of **1** are shown in Fig. 3; all of them being through the phosphate groups. The distance between two Cu1 atoms or two Cu2 atoms is the same, $d = 7.234$ Å, and the total bond lengths are 11.201 Å and 9.958 Å, respectively. The first path (Cu1–O4B–P2–O6B···H11A–N1A–Cu1) contains four diamagnetic atoms and a weak H-bond defined according to Steiner's criteria [28] (dotted line in the figure) with $d[\text{O6B–N1A}] = 3.039$ Å, while the second path (Cu2–O3B–P2–O5B–O1h–Cu2) is similar to the first one but includes one short contact $d[\text{O5B–O1h}] = 2.068$ Å. The third chemical path connect Cu1 to Cu2 (Cu1–O4B–P2–O5B–O1h–Cu2) separated by a distance of 7.943 Å, with total bond length of 9.949 Å containing four diamagnetic atoms and one short contact O5B–O1h. Finally, the fourth chemical path connect Cu2 to Cu1 (Cu2–O3B–P2–O6B···H11A–N1A–Cu1) separated by a distance of 7.872 Å, with

total bond length of 11.210 Å containing four diamagnetic atoms and one H-bond. Considering the different number of diamagnetic atoms and the lengths of the chemical paths connecting dinuclear units described in Figs. 2 and 3, we conclude that the most relevant paths in supporting exchange interactions are those coupling each dinuclear unit with two dinuclear units in neighbour layers (Fig. 3).

3.2. Magnetic results

The dc magnetic susceptibility data corresponding to one mol of Cu₂ dinuclear units in **1** measured with $B_0 = 0.5$ T at temperatures T between 2 and 300 K are displayed in Fig. 4 as $T\chi(T)$. The values measured with

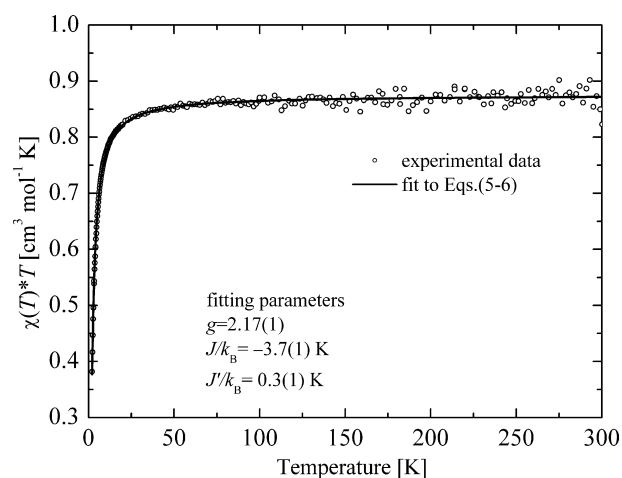


Fig. 4. Values of $T\chi(T)$ obtained with an applied field $B_0 = 0.5$ T at temperatures T between 2 and 300 K in a powder sample of **1** (circles). The solid line displays the best global fit of Eqs. (5) and (6) to the susceptibility, obtained for a dinuclear unit within a molecular field approximation. The values of the parameters obtained in the fit are shown.

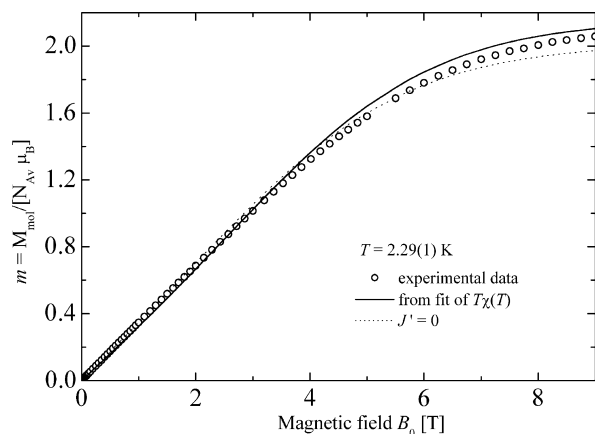


Fig. 5. Values of the molecular magnetization $m(B_0)$ observed with applied fields $0 < B_0 < 9$ T at $T = 2.29(1)$ K in a powder sample of **1** (symbols). The solid line displays the magnetization calculated with a molecular field approximation using Eqs. (2) and (3), considering the intradinuclear and interdinuclear interactions evaluated from the susceptibility data. The dashed line is obtained as the best fitting with a model ignoring the interactions between dinuclear units.

$B_0 = 0.2$ T (not shown) agree within the experimental uncertainty with those in Fig. 4. The molecular magnetization measured at 2.29(1) K as a function of B_0 is shown in Fig. 5. The contributions of the sample holder, the diamagnetism and temperature independent paramagnetism of the sample have been already subtracted from the data displayed in Figs. 4 and 5. At room temperature $T\chi(T) = 0.871$ cm³ K/mol. This value is reduced to $T\chi(T) = 0.38$ cm³ K/mol at 2 K, indicating a predominant antiferromagnetic coupling between copper ions (Fig. 4). The magnetic moment per dinuclear unit at 2.29 K and at the highest field (9 T), where still is not fully saturated, amounts $2.06 \mu_B$ (Fig. 5).

The susceptibility data were fitted assuming a Hamiltonian involving equal values for the angular average of the g -factor of the two copper ions, and isotropic intra- and interdinuclear exchange interactions J and J' , respectively. The interdinuclear interactions J' with the relevant $z = 2$ neighbouring dinuclear units are identical (see the structural description and Fig. 3), so in the molecular field approximation the Hamiltonian of a dinuclear unit can be written as:

$$\mathcal{H} = \mu_B g(S_{1z} + S_{2z})B_0 - JS_1 \cdot S_2 - zJ'(S_{1z} + S_{2z})\langle S_z \rangle \quad (1)$$

In the last term, $\langle S_z \rangle$ is the thermal average of the component along B_0 of the spin of a neighbour dinuclear unit. Thus, in units of μ_B , the molecular magnetization m of a dinuclear unit under an effective field B acting on each copper ion pair at temperature T is:

$$m = (M_m/N_{Av}) = 2g \exp(J/k_B T) \sinh(g\mu_B B/k_B T)/Z \quad (2)$$

where Z is the partition function:

$$Z = 1 + \exp(J/k_B T)[1 + 2 \cos h(g\mu_B B/k_B T)] \quad (3)$$

In the molecular field model used in Eq. (1), the effective field B is the sum of the applied field B_0 plus a contribution due to the interaction with the neighbour dinuclear units:

$$B = B_0 - \frac{zJ'}{g\mu_B} \langle S_z \rangle = B_0 - \frac{zJ'}{g^2 \mu_B^2} m \quad (4)$$

As shown by O'Connor [29] and Kahn [30] the Bleaney–Bowers equation [31] for the magnetic susceptibility of this dinuclear unit is:¹

$$T\chi(T) = \frac{2N_{Av}g^2\mu_B^2}{3k_B} \frac{T}{(T - \theta)[1 + \frac{1}{3} \exp(-J/k_B T)]} \quad (5)$$

with:

$$\theta = \frac{-2zJ'/k_B}{3 + \exp(-J/k_B T)} \quad (6)$$

A least squares fit of Eqs. (5) and (6) to the susceptibility data in Fig. 4 gives $g = 2.17(1)$, $J/k_B = -3.7(1)$ K and $zJ'/k_B = 0.6(1)$ K, indicating antiferromagnetic intradinuclear exchange interaction, as indicated by the low temperature behaviour of $T\chi(T)$ in Fig. 4, and an effective ferromagnetic coupling $J'/k_B = 0.3$ K (considering $z = 2$) between neighbour dinuclear units. The solid line in Fig. 4 is calculated with these parameters. They were also used to evaluate the molecular magnetization m considering Eqs. (2) and (4) and the results are shown as a solid line in Fig. 5. The prediction for the molecular magnetization m is not as good as that for $T\chi(T)$. The two types of data correspond to well separate regions in the phase diagram of the generalized susceptibility through the quantity $T \frac{1}{N_{Av}} \left(\frac{\partial M_m}{\partial B_0} \right)$ versus T and B_0 . Consequently, it is not surprising to find small discrepancies between the predictions in the values of M_m versus B_0 using the parameters obtained from the $T\chi(T)$ data. To emphasize the role of the interdinuclear interactions, we also display in Fig. 5 results obtained by fitting these data with a model that neglects the interdinuclear coupling J' .

The antiferromagnetic intra-dinuclear interaction $J/k_B = -3.7$ K is associated with the Cu–O–Cu and Cu–O–P–O–Cu bridges shown in Fig. 1. We propose that the smaller ferromagnetic coupling $J'/k_B = 0.3$ K between dinuclear units in neighbour layers is supported by the paths described in Fig. 3.

4. Discussion and conclusions

Our single crystal X-ray diffraction measurements indicate that the synthesized ternary copper compound **1** is triclinic with two chemically different copper ions in dinuclear units. Each copper ion is in a square pyramidal geometry coordinated to a nitrogen from the α -amino group and to an oxygen from the carboxylate group of the L-arginine molecules. They are bridged by two HPO₄²⁻ and one OH⁻ anions, showing a dinuclear copper structure that is not common in metal derivatives of amino acids. This structure appears as a consequence of the bonding possibilities offered by the phosphate groups bridging these units,

¹ See Eq. (6.5.12) in Ref. [30].

combined with the ample possibilities of bonding of the guanidinium group of arginine. The magnetic measurements indicate a weak antiferromagnetic intradinuclear coupling ($J/k_B = -3.7$ K) between copper ions supported by Cu–O–Cu and phosphate bridges, and a smaller ferromagnetic coupling ($J/k_B = 0.3$ K) between dinuclear units in neighbour layers, supported by bridges containing four diamagnetic atoms plus the H-bond (Fig. 3). As discussed earlier, the distance between the connected Cu1 atoms in neighbour dinuclear units 7.234 Å and that measured along the path is 11.201 Å.

Our structural results for the dinuclear units in **1** show two equatorial–apical paths, one involving a phosphate oxygen (O5A) and the other through an O1h. Because of the distortion of the pyramidal units one may guess that the ground orbital states of the individual Cu ions in dimeric units are not a pure $d_{x^2-y^2}$ orbital (supported by a $g = 2.17$). Thus, one expects some small contributions to the antiferromagnetic coupling caused by this distortion. The basal planes around each Cu are not parallel producing a lack of orthogonality between apical and equatorial electronic densities. A third connection between the Cu ions is produced by an equatorial–equatorial path –O4B–P2–O3B– that will also contribute to the coupling, in spite that this occurs through three diamagnetic atoms.

A search in the Cambridge Crystallographic Database [32–34] was performed without much success to locate other compounds with similar intradinuclear chemical bridges. Dinuclear copper compounds with hydrogenphosphate bridges were reported recently by Youngme and collaborators [16–18] for dinuclear compounds with the aromatic ligands di-2-pyridylamine, 1,10-phenanthroline and 2,2'-bipyridine bipyridine ($[\text{Cu}(\text{dpyam})(\mu\text{-H}_2\text{PO}_4)(\text{H}_2\text{PO}_4)]_2$, $[\text{Cu}_2(\text{phen})_2(\mu\text{-H}_2\text{PO}_4\text{-O},\text{O}')_2(\text{H}_2\text{PO}_4)]$, $[\text{Cu}_2(\text{phen})_2(\mu\text{-H}_2\text{PO}_4\text{-O},\text{O}')(\mu\text{-H}_2\text{PO}_4\text{-O})(\mu\text{-HPO}_4\text{-O})_2(\text{H}_2\text{O})_9]$, and $[\text{Cu}_2(\text{bpy})_2(\mu,\eta^2\text{-HPO}_4)-(\mu,\eta^1\text{-H}_2\text{PO}_4)(\mu,\eta^2\text{-H}_2\text{PO}_4)]_n$). In order to make comparisons or find similarities, it is worth to remark that in the compound studied here the Cu1–Cu2 coupling in the dinuclear unit is supported by three bonds (see Fig. 3).

In Ref. [16], two compounds with di-2-pyridylamine are reported. In the first one, there are two equatorial–equatorial didentate dihydrogenphosphate bridging ligands connecting copper ions at 5.14 Å. The reported exchange interaction $J/k_B \sim -4$ K is similar to that observed for **1**, but the two equatorial–equatorial bridges supporting the interaction and the distance between coppers are too different to allow comparisons. The second compound is polymeric, and the magnitude J of the interaction, supported by an equatorial–equatorial tridentate hydrogenphosphate bridge is much larger than that in compound **1**. Reference [17] reports a compound containing phenanthroline having two chemically different dinuclear units in the unit cell. One of them (unit B) is similar to compound **1**, with a distance $d = 3.074(3)$ Å between coppers and similar bridges and they attribute to this unit a *ferromagnetic* coupling $J/k_B \sim 1.4$ K. However, the experimental uncertainty of

this value introduced by the coexistence of two different dinuclear units may be large, and a comparison with our result for **1** is hard to make. Our situation seems to be closer to that reported by Phuengphai et al. [18] for their compound named **1**, except for the non-existence of the equatorial–apical bond formed through O1h. They estimate $J/k_B = -7.4$ K for that compound. Even if, the structure of the phosphate bridge is different from ours as to establish a clear cut comparison of the magnetic interaction observed in **1**, one is tempted to speculate that the lack of the equatorial–apical bond formed through O1h, tend to enhance the antiferromagnetic behaviour, as observed in Ref. [18].

Regarding the observed interactions between dinuclear units, Chattopadhyay et al. [35] claimed that bridges containing H-bonds propagate antiferromagnetic interactions between metal centres. However, for the title compound and for the compounds reported in Refs. [16,17], the coupling J' is ferromagnetic. Clarifying this point would require more experimental information in other similar situations and detailed calculations.

5. Supplementary material

CCDC 292513 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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