Synthesis and Characterisation of a Novel Copper(II) Azamacrocycle-Phosphonate 3D Polymeric Network

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A new azamacrocycle phosphonate in its hydrocloride form (**1**) has been synthesized and characterised by multinuclear NMR spectroscopy and by a single X-ray analysis. The reaction of **1** with Cu^{II} ions gives a polymeric compound (**2**), which exhibits an unprecedented three-dimensional network containing two-dimensional channels filled with guest molecules. The solid-state structure of **2** and its properties have been characterised by means of various analytical methods which include single-crystal X-ray structure analysis, X-ray powder diffraction, thermogravimetric studies as well as magnetic susceptibility and EPR measurements.

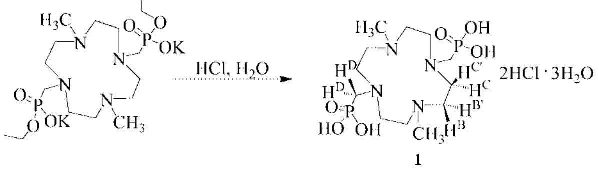
Introduction

Polymeric matrices made up of metal phosphonates and macrocyclic ligands constitute an innovative class of compounds with potential application in catalysis, as sensoring and switching devices, liquid crystals and molecular magnets.[1]

Metal complexes with azacrown ethers, containing phosphonic acids, are often characterised by unusual structures and can also form porous lamellar-structured materials.[2] To the best of our knowledge, no multidimensional network containing channels or cavities assembled by Cu^{II} ions and azamacrocycle phosphonate ligands has been reported in the literature. Indeed, the "macrocyclic effect" exerted by azamacrocycle ligands favours the formation of stable 1:1 adducts, where the nitrogen atoms bind metal ions, such as Co^{II}, Cu^{II} and Ni^{II}. The resulting ML units may be further assembled only in a mono-dimensional chain by hydrogen bonds involving the uncoordinated phosphonate units.[3] In this communication we present the synthesis and characterisation of a new azamacrocycle phosphonate in its HCl-form (**1**), and the synthesis and characterisation of a novel three-dimensional network containing two-dimensional channels assembled by Cu^{II} ions in conjunction with the new macrocycle phosphonate ligand.

Results and Discussion

The new macrocycle 4,10-dimethyl-1,4,7,10-tetraazacyclododecane·-1,7-bis(methanephosphonic acid)·2 HCl·3 H_2O, Me_2DO2P-4H·2 HCl·3 H_2O (**1**) was obtained by acid hydrolysis (HCl) of the known ligand 4,10-dimethyl-1,4,7,10-tetraazacyclododecane·-1,7-bis(methanephosphonic acid monoethyl ester)dipotassium salt, K_2Me_2DO2PME (Scheme 1).[4]



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Scheme 1.

The X-ray structure of **1** consists of two conformations of the new cationic macrocyclic units $[Me_2DO2P\text{-}6H]^{2+}$, chloride anions and solvent water molecules. An ORTEP plot of **1** is presented in Figure 1.

The phosphonate units and the chloride anions are interlinked by water molecules through hydrogen bonding. The two cationic conformations are very similar, as the methyl and the phosphonate groups are oriented on the same side of the planes defined by the four nitrogen atoms N1–N4 and N5–N8. Furthermore, in both macrocyclic cations the phosphonate groups are doubly protonated. As evidenced

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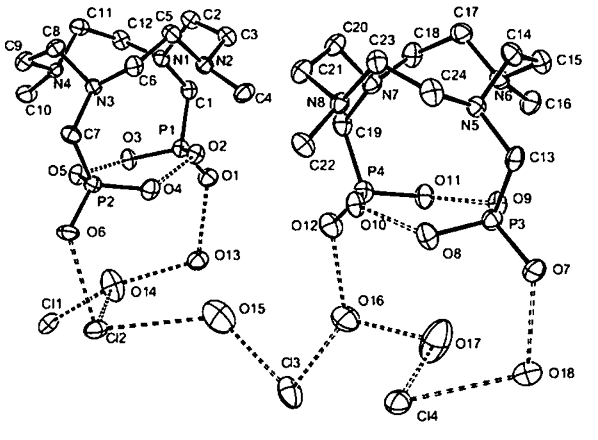


Figure 1. Perspective view of the asymmetric unit of **1**, showing conformer A (left) and conformer B (right) involved in the most important hydrogen-bonding interactions; hydrogen atoms have been omitted for clarity.

by a difference Fourier map, the protonation involves the oxygen atoms O1, O3, O4, O6 of conformer A and the oxygen atoms O7, O8, O11, O12 of conformer B, which is in agreement with the values of the corresponding P–O lengths ranging from 1.530(3) Å to 1.562(2) Å.[5] As expected, the P–O double bonds show bond lengths ranging from 1.489(3) Å to 1.493(3) Å. Both conformers show strong intramolecular hydrogen bonds between P=O and POH units of different phosphonate groups in order to stabilise eight-membered O–H–O–P–O–H–O–P rings. The protonated oxygen atoms O1, O6, O7, and O12 are strongly bonded to water molecules or to chloride anions in order to build up a complex network of hydrogen bonds. In both conformers, the nitrogen atoms bearing the methyl groups are protonated also (the four protons were detected in difference Fourier maps and successfully refined).

^{1}H NMR studies of **1** in D_2O at pH = 1 and room temperature have revealed that the protons of the ethylenic bridge (B, B′ and C, C′) are diastereotopic. This indicates that the system is locked in a rigid conformation on the NMR timescale.

Bright-blue crystals of the polymeric compound $\{[Cu_2Cl_2(Me_2DO2P\text{-}2H)(H_2O)]\cdot(0.5\,C_3H_6O)\cdot(2.5\,H_2O)\}_n$ (**2**) were isolated from the reaction of an equimolar amount of **1** with $Cu(OAc)_2\cdot H_2O$ or $CuCl_2\cdot 2\,H_2O$ in water/acetone at room temperature in the pH range from 1 to 8 (Scheme 2).

When the reaction was carried out in the pH range 9–14, no formation of **2** was observed, which indicates a strong control of both the pH and chloride ligands on the product formation. Indeed, the reaction of the ligand in its potassium salt form (K_4Me_2DO2P) with $Cu(OAc)_2\cdot H_2O$ or with $CuCl_2\cdot 2\,H_2O$ does not yield **2**, yet an undefined compound is produced. It is worth stressing that **2** was obtained even when the ratio between **1** and $Cu(OAc)_2\cdot 2\,H_2O$ or $CuCl_2\cdot 2\,H_2O$ was much greater than the stoichiometric ratio.

The single-crystal X-ray structure analysis of **2** revealed a structural organization that has never been reported for Cu^{II} diphosphonate compounds.[6a] Indeed, **2** adopts a three-dimensional layered structure containing $\{CuClN_4\}$ units and phosphonate O-bridged $\{Cu_2Cl_2O_6\}$ dimers. An ORTEP plot of compound **2** is presented in Figure 2.

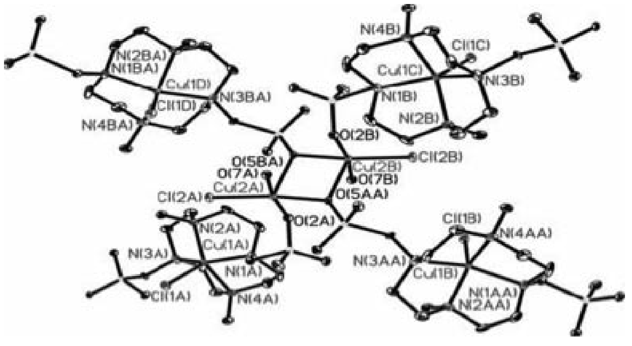
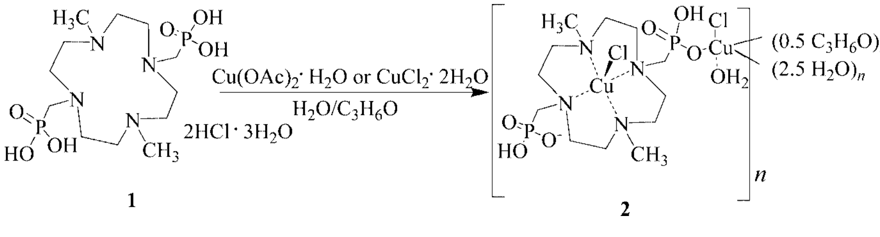


Figure 2. X-ray crystal structure of **2**, showing the connectivity of the centrosymmetric moieties $\{Cu_2Cl_2O_6\}$, projected perpendicular to the *a* axis. Hydrogen atoms and noncoordinating solvent molecules are omitted for clarity.

A three-dimensional porous structure with continuous channels (Figure 3) is apparently formed with no need for a templating agent.[6]

The 12-membered azamacrocycles are tilted towards each other by 35.3°. The methyl and phosphonate groups bound to the nitrogen atoms are all oriented on the same side of the N_4 plane.[7] The Cu^{II} centres of **2** exhibit two different distorted square-pyramidal coordination geometries, which represents an unprecedented structural feature for layered Cu^{II} diphosphonates. The Cu(1A) atom lies 0.546 Å above the N_4 ring, while Cu(2A) deviates by 0.105 Å from the basal plane defined by Cl(2A), O(2A), O(5AA), and O(7A). Typically, the apical Cu(2A)–O(5BA) bond length of 2.241(3) Å is significantly longer than the Cu(2A)–O(5AA) bond length of 1.989(3) Å.[6a,8] The oxygen bridged $\{Cu_2(\mu\text{-}O)_2\}$ dimeric units show a Cu(2A)···Cu(2B) distance of 3.140(1) Å, which is in line with comparable structures.[8a,9] The next larger Cu···Cu distances within the layers are 6.403(1) Å for Cu(1B)···Cu(2B) and



Scheme 2.

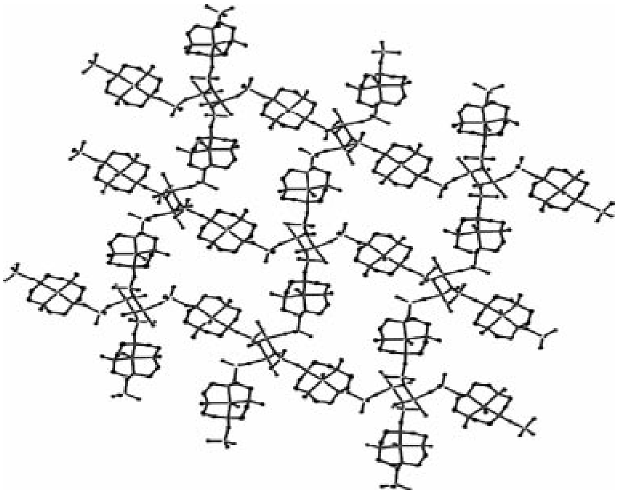


Figure 3. ORTEP plot, showing the propagation of the asymmetric unit in two dimensions, with the projection direction perpendicular to the *a* axis; hydrogen atoms and solvent molecules are omitted for clarity.

6.545(1) Å for Cu(1A)···Cu(2A). The shortest Cu···Cu distance between the layers is 8.277(1) Å. Considering the packing in $\{[Cu_2Cl_2(Me_2DO2P\text{-}2H)(H_2O)]\cdot(0.5\,C_3H_6O)\cdot(2.5\,H_2O)\}_n$ for $n = 2$, four water molecules hold together two adjacent layers by strong hydrogen bonding to two different phosphonate anions. Four O···O contacts in the range 2.54–2.91 Å have been detected. The central disordered water molecule also makes a short contact of 2.83 Å to this chain of hydrogen bonds. Disordered acetone molecules fill up the continuous channels (Figure 4).

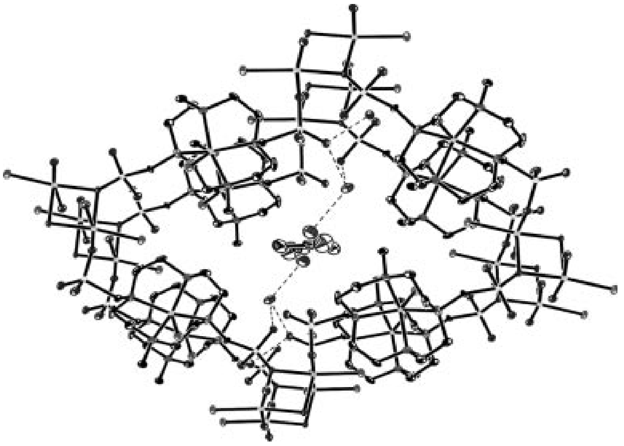


Figure 4. Packing diagram of **2** revealing the continuous channel in the projection plane perpendicular to the *a* axis, occupied by solvent molecules and formed through stacking of macrocyclic moieties. The chain of solvent molecules is indicated with a broken line.

The polymeric compound **2** is soluble in water but insoluble in all common organic solvents. When a sample of **2** is heated in air at 125 °C, its colour becomes bright green, due to the loss of the coordinated water. The crystal morphology does not change even at 160 °C. When the green solid is allowed to cool to room temperature, it again turns dark blue indicating that the coordination of water to the metal centre is restored. The removal of the guest molecules (water, acetone) and its reversible process, which is very important for designing new architectures of porous materials or chemical sensors, was studied by means of a thermogravimetric analysis (TGA) and X-ray powder diffraction (XRPD).

The thermogravimetric analysis of **2**, in the temperature range 36–160 °C, showed a 7% loss of weight, which corresponds to the release of half a molecule of acetone and one molecule of coordinated water per asymmetric unit. Between 160 and 190 °C, a further weight loss of 1.2% was detected, due to the release of the water molecule (half a molecule per formula unit) located in the channel and that shows a short contact of 2.83 Å to the water molecule hydrogen-bonded to two phosphonate units (Figure 4). No chemical decomposition was observed up to 200 °C, yet the bright-green solid lost the original crystal morphology. The X-ray powder diffraction (XRPD) pattern of **2** did not show any change after a dehydration/rehydration cycle conducted by heating of **2** at 160 °C for 10 min and rehydrating at room temperature in a water/acetone (1:10) (v/v) mixture. The sample changed its colour from dark blue to bright green during the heating step, while it turned back to deep blue during cooling and exposure to the water/acetone mixture.

Apparently, the three-dimensional network is sufficiently robust to show reversible coordination of water molecules as well as inclusion of acetone as the guest molecule.

Magnetic susceptibility measurements of **2** showed a Curie–Weiss behaviour down to 5 K. The calculated value of the Curie constant per asymmetric unit, $C = 0.413\ \text{cm}^3\,\text{K}\,\text{mol}^{-1}$ (corresponding to a μ_{eff} value of 1.82 μ_B), indicates that only one Cu^{II} centre, namely that pertaining to the $(CuClN_4)$ unit, contributes to the magnetic moment of the system. Consistently, the Cu^{II} centres in the $(Cu_2Cl_2O_6)$ units did not display any EPR signal, due to the very intense Cu^{II}–Cu^{II} antiferromagnetic coupling. The observed *g* values [$g_{\parallel} = 2.15(3)$, $g_{\perp} = 2.07(1)$], which did not change on cooling, suggest that the signal can be assigned to the $Cu^{II}N_4$ moiety.[10,11]

Conclusions

We synthesized a very rare organic–inorganic Cu^{II} polymer, which represents the first example of a polymeric coordination network obtained by combining an azamacrocycle phosphonate ligand with Cu^{II} ions. Given the hemilability of **1**, the formation of **2** may be seen as a weak-link approach to supramolecular coordination complexes.[12] TGA and XRPD experiments clearly indicate that guest molecules, like water and acetone, can be removed from the three-dimensional network without affecting the solid-state morphology. Intercalation reactions of amines and other organic solvents with the dehydrated compound **2** are being investigated in our laboratories.

Experimental Section

Elemental analyses were performed with a Carlo–Erba model 1106 elemental analyser. The IR spectroscopic measurements were performed with a FT-IR Spectrum GX instrument. TGA measurements were performed with a TA SDT Q600 apparatus at a heating rate of 2 °C min^{-1} in the range of 30–200 °C. XRPD measurements were performed with a Philips PW 3830 diffractometer (Co, λ = 1.7889 Å) with a voltage of 40 kV and a current of 40 mA. The magnetic susceptibility measurements were carried out in a temperature range from 2 to 300 K at a magnetic field of 1 T with a Cryogenic S600 SQUID magnetometer. The EPR powder spectra were recorded with a Varian E9 spectrometer equipped with a ^{4}He continuous flow cryostat for variable temperature measurements. ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR spectra were recorded at 200.13, 50.32, and 81.01 MHz, respectively, with a Bruker ACP-200 spectrometer or at 400.13, 100.62, and 161.97 MHz, respectively, with a Bruker Avance DRX-400 spectrometer. Chemical shifts are relative to tetramethylsilane as external reference or were calibrated against solvent resonances. The assignments of the signals resulted from 2D-^{1}H COSY and proton detected ^{1}H-^{13}C correlations using degassed nonspinning samples. 2D-NMR spectra were recorded with a Bruker Avance DRX-400 spectrometer.

1. Synthesis of 4,10-Dimethyl-1,4,7,10-tetraazacyclododecane·-1,7-bis(methanephosphonic acid)·2 HCl·3 H_2O [(Me_2DO2P-4H)·2 HCl·3 H_2O, 1]

A solution of 4,10-dimethyl-1,4,7,10-tetraazacyclododecane-1,7-bis(methanephosphonic acid monoethyl ester) dipotassium salt, (K_2Me_2DO2PME) (2.4 g, 4.23 mmol) in HCl (35 mL of a 6 M solution) was stirred at reflux for 3 days in a sealed Schlenk tube. Afterwards, the solvent was concentrated to a small volume (10 mL), and then the slow addition of acetone (5 mL) led to the precipitation of a white crystalline product. The solution was was decanted, and the solid dried under vacuum. The hygroscopic compound was used without further purification and stored under N_2 at room temperature. Yield: 2.1 g (88 %). $C_{12}H_{38}Cl_2N_4O_9P_2$ (515.30): calcd. C 27.97, H 7.43; N 10.87; found: C 27.69, H 7.40, N 10.61. ^{1}H NMR (400.13 MHz, D_2O, pH = 1, 25 °C): δ = 3.37 (ddd, $^2J_{B,B'}$ = 14.1, $^3J_{C,B}$ = 3.5, $^3J_{B,\ C'}$ = 7.1 Hz, 4 H, H_B), 3.18 (ddd, $^3J_{B',C}$ = 7.5, $^3J_{B',C'}$ = 2.9 Hz, 4 H, $H_{B'}$), 3.07 (ddd, $^2J_{CC'}$ 14.9 Hz, 4 H, H_C), 2.93 (s, 6 H, CH_3), 2.86 (ddd, 4 H, $H_{C'}$), 2.79 (d, H_D, $^2J_{H,P}$ = 11.07 Hz, 4 H) ppm. ^{13}C{^{1}H} NMR (100.62 MHz, D_2O, pH = 1.0, 25 °C): δ = 54.18(s,C_B), 51.73 (d, ^3J(P,C) = 4.53 Hz, C_c), 52.03 (d, $^1J_{C,P}$ = 108.69 Hz, C_D), 44.12 (s, CH_3) ppm. ^{31}P{^{1}H} NMR (161.97 MHz, D_2O, pH = 1.0, 25 °C): δ = 22.48 ppm. IR features (KBr disk): $\tilde{\nu}$ = 3276 s, 3136 s, 1734 s, 1469 s, 1216 m, 1200–900 s cm^{-1}.

2. Synthesis of {[Cu_2Cl_2(Me_2DO2P-2 H)(H_2O)]·(0.5 C_3H_6O)·(2·5 H_2O)}$_n$ (2)

Method A: Me_2DO2P-4H·2 HCl·3 H_2O (0.3 g, 0.580 mmol) was dissolved in water (10 mL). The reaction mixture was then treated with a solution of Cu(OAc)$_2$·H_2O (0.115 g, 0.58 mmol) in water (5 mL) at room temperature. The resulting blue solution was layered with acetone (15 mL), and on standing, blue crystals separated, which were filtered off and recrystallised from a water/acetone solution (1:1, v/v). Yield: 0.35 g, (44 %). $C_{13.5}H_{38}Cl_2Cu_2N_4O_{10}P_2$ (676.40): calcd. C 23.97, H 5.66, N 8.28; found: C 24.02, H 5.80, N 8.59. IR features (KBr disk): $\tilde{\nu}$ = 3412 s (hydrogen bonded water), 3200 s (coordinated water), 2370 m, 2210 w, 2920 s, 2850 s, 1712 s, 1160 s, 1050–915 s cm^{-1}.

Method B: Me_2DO2P-4H·2 HCl·3 H_2O (0.3 g, 0.58 mmol) was dissolved in water (10 mL) and the pH was adjusted to 8 by addition of 1 M KOH. The reaction mixture was then treated with a solution of $CuCl_2$·2 H_2O (0.1 g, 0.58 mmol) in water (5 mL) at room temperature. The resulting blue solution was layered with acetone (15 mL), and on standing, blue crystals separated, which were filtered off and washed with a water/acetone solution (1:1, v/v). Yield: 0.30 g, (38 %).

X-ray Crystallographic Studies

X-ray quality crystals of **1** and **2** were obtained from a mixture of water/acetone solution (1:10, v/v) of the respective compounds.

Compound 1: $C_{12}H_{38}Cl_2N_4O_9P_2$, M_r = 515.30, dimensions 0.450 × 0.275 × 0.075 mm, triclinic, space group *P*-1, a = 14.244(3) Å, b = 15.374(7) Å, c = 11.109(1) Å, α = 97.72(2)°, β = 95.89(1)°, γ = 86.62(3)°, V = 2395.4(12) Å^3, Z = 4, D_c = 1.429 g cm^{-3}, μ(Mo-K_α) = 0.452 mm^{-1}. X-ray data were collected with an Enraf–Nonius CAD4 automatic diffractometer at 293(2) K in the range of $2.01 < \Theta < 23.47°$. Unit cell parameters were determined by least-squares refinement of the setting angles of 25 carefully centred reflections. The structure was solved by direct methods and refined by full-matrix on F^2, with the WINGX package,[13a] converging at R = 0.0488 [$I > 2\sigma(I)$] with a goodness-of-fit on F^2 of 0.885 for 579 parameters and 7550 reflections, 7046 unique reflections.

Compound 2: $C_{13.5}H_{38}Cl_2Cu_2N_4O_{10}P_2$, M_r = 676.40, dimensions 0.100 × 0.08 × 0.03 mm, monoclinic, space group *P*21/*n*, a = 8.2771(3) Å, b = 20.8384(8) Å, c = 14.9980(4) Å, β = 98.548(2)°, V = 2558.12(2) Å^3, Z = 4, D_c = 1.756 g cm^{-3}, μ(Mo-K_α) = 2.051 mm^{-1}. X-ray data were collected with a Nonius–Kappa CCD diffractometer at 243(2) K in the range of $2.39 < \Theta < 26.02°$. Cell refinement, data reduction, and the empirical absorption correction were done by Denzo and Scalepack programs.[13b] Unique reflections were used to solve the structure by direct methods with SHELXS-97.[13c] Structure refinement on F^2 by full-matrix least-square methods were carried out with SHELXL-97,[13d] converging at R = 0.030 [$I > 2\sigma(I)$] with a goodness-of-fit on F^2 of 1.014 for 342 parameter and 9687 reflections, 4932 unique reflections.

CCDC-262040 (for **1**) and -242225 (for **2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information: See also footnote on the first page of this article. A thermogravimetric study of compound **2**, a comparison of the XRPD patterns before and after the dehydration/hydration cycle, and magnetic susceptibility as well as EPR measurements of **2** are included.

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