

parameters 2602/244. Largest difference Fourier peak and hole 0.74 and $-0.99 \text{ e } \text{\AA}^{-3}$, respectively.^[7b]

- [17] Elemental analysis for $\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_6\text{Cd}$ ($M_r = 468.7$): calcd: C 40.99, H 2.59, N 11.96; found: C 41.17, H 2.73, N 11.87.
- [18] For example, see: a) B. F. Abrahams, P. A. Jackson, R. Robson, *Angew. Chem.* **1998**, *110*, 2801; *Angew. Chem. Int. Ed.* **1998**, *37*, 2656; b) D. M. L. Goodgame, D. A. Grachvogel, D. J. Williams, *Angew. Chem.* **1999**, *111*, 217; *Angew. Chem. Int. Ed.* **1999**, *38*, 153; c) C. J. Kepert, M. J. Rosseinsky, *Chem. Commun.* **1999**, 375; d) O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474.

A Dodecanuclear Copper(II) Cage Containing Phosphonate and Pyrazole Ligands**

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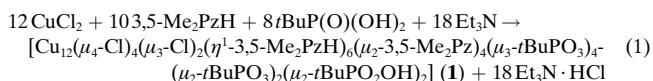
*Dedicated to Professor P. Natarajan
on the occasion of his 60th birthday*

Metal phosphates and phosphonates have received a lot of attention in recent years for several reasons.^[1] For instance, many members of this family function as cation exchangers which could be very useful in the processing of radioactive waste streams.^[2] Other potential applications of these materials include sorption,^[3] catalysis,^[4] catalyst supports,^[4] sensors,^[5] and nonlinear optics.^[6] Many of these potential applications can be attributed to the extensive structural and compositional diversity of these systems. Although many transition metal phosphonates possess layered structures,^[1, 7] other types of formulations such as mononuclear coordination complexes^[1] and one-dimensional linear complexes^[1, 8] are also known in addition to three-dimensional microporous frameworks.^[9] Among the layered compounds further modulation of the structure is possible by varying the transition metal ion and the nature of the alkyl or aryl group attached to the phosphorus, and by post-synthetic changes through addition of appropriate pillaring agents.^[1]

In contrast to the layered phosphonates, molecular systems of multimetal aggregates containing the phosphonate moiety as ligand(s) are relatively rare. Recently molecular phosphonate cages containing Group 13 elements^[10] have been synthesized by the reaction of an alkyl phosphonic acid with alkyl metal compounds. This reaction is driven by the elimination of an alkane and the formation of a M–O bond.

A similar methodology has also been applied to the corresponding arsonates.^[11] Other molecular phosphonates containing zinc^[12] or vanadium^[13] have also been synthesized. In view of the diverse structural types that can result in these systems and also because it is known that the transition metal ions in layered phosphonates can act as Lewis acid sites, we set about preparing molecular phosphonates containing additional chelating ligands such as 3,5-dimethylpyrazolyl in order to gain a better understanding the type of clusters that would result. Apart from the novel structures, polynuclear copper(II) complexes are also of interest because of the growing awareness of the involvement of cluster compounds at the active sites of biological molecules.^[14] Herein we report the synthesis and X-ray crystal structure analysis of a novel dodecanuclear copper phosphonate cluster containing 3,5-dimethylpyrazolyl ligands.

The reaction of $\text{Cu}^{\text{II}}\text{Cl}_2$ with 3,5-dimethylpyrazole (3,5-Me₂PzH) and *tert*-butylphosphonic acid in the presence of triethylamine (used as scavenger for the HCl formed in the reaction) afforded a green solid from which the crystals of the title compound **1** were grown [Eq. (1)].



The X-ray structure analysis of compound **1** shows that it is a dodecanuclear cluster in which the entire copper assembly is encased in a lipophilic sheath composed of alkyl groups emanating from either phosphorus or from the pyrazolyl units^[15] (Figure 1). This structural feature is mainly responsible for the favorable solubility properties of the cluster in

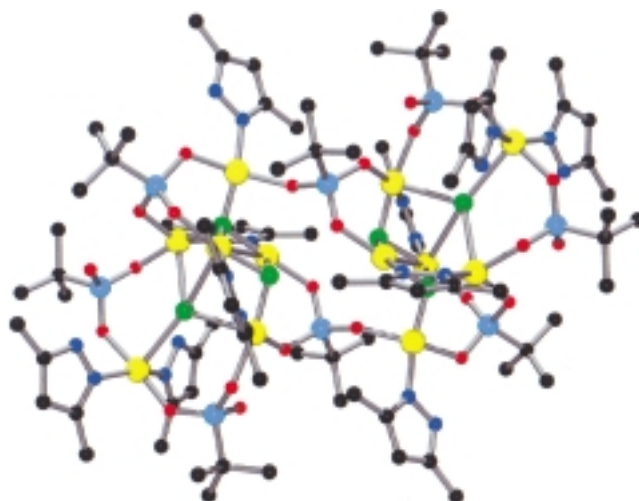


Figure 1. POVray diagram of **1** showing the organic lipophilic envelope surrounding the dodecanuclear Cu^{II} metal framework. Hydrogen atoms omitted for clarity. Color code: carbon: black; chlorine: green; copper: yellow; oxygen: red; phosphorus: cyan; dark blue: nitrogen.

many common organic solvents such as benzene. In addition **1** is stable in air and does not undergo any change upon exposure to ambient atmosphere. Compound **1** consists of two symmetry-related hexameric units that are linked with each other (Figure 2). To the best of our knowledge this kind of structural assembly is unprecedented for copper(II) clusters.

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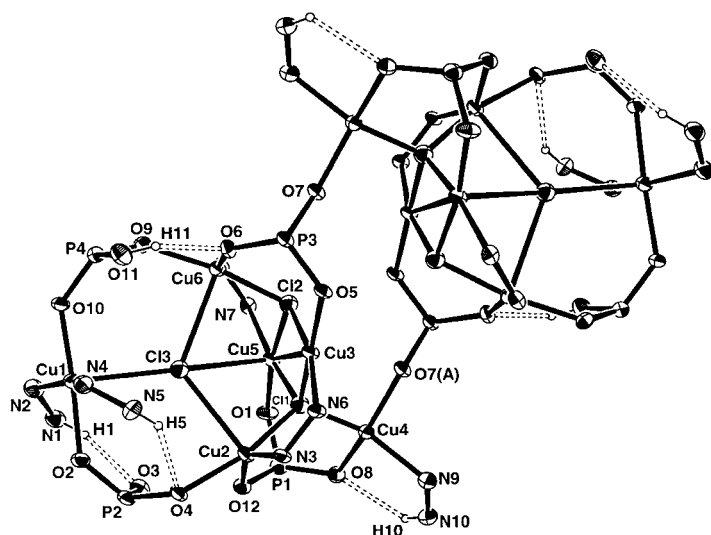


Figure 2. ORTEP diagram of **1** showing the framework of the dodecanuclear copper(II) cluster. All carbon and hydrogen atoms have been omitted. Selected bond lengths [Å]: Cl1–Cu2 1.913(3), Cl1–Cu3 1.935(6), Cl1–Cu4 1.876(12), Cl1–Cu5 1.970(7), Cl2–Cu3 1.988(8), Cl2–Cu5 1.996(4), Cl2–Cu6 1.986(5), Cl3–Cu1 2.670(7), Cl3–Cu2 2.727(1), Cl3–Cu5 2.816(1), Cl3–Cu6 2.721(7), Cu–N (free pyrazoles) range from 1.927–1.966, Cu–N (bridged pyrazoles) range from 1.971–2.012, Cu–O range from 1.919–2.009. This figure also shows the intramolecular hydrogen bonding within **1**: H11...O6 1.800(1), H1...O3 2.098(2), H5...O4 2.349(3), H10...O8 2.122(5).

Furthermore every copper center present in the hexameric assembly is unique by way of coordination environment and/or geometry. Specifically the copper centers present all have distorted geometry and are four- or five-coordinate, and the coordination environment around each copper center contains at least three types of ligating atoms (oxygen, chlorine, and nitrogen). In contrast in layered phosphonates such as $\text{Cu}(\text{O}_3\text{PC}_6\text{H}_5) \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{O}_3\text{PCH}_3) \cdot \text{H}_2\text{O}$, which are prepared by hydrothermal synthesis, the copper centers are all equivalent and display a distorted tetragonal-pyramidal geometry, in which each copper center is coordinated to five oxygen atoms.^[16] Additionally in **1** none of the phosphonate ligands are found in a chelating coordination mode; a feature which is present in several layered phosphonates.^[1]

Each of the symmetry-related hexameric copper assemblies in **1** contains a “basket handle” shaped pentameric subunit; the base of the basket is formed by a Cu_2Cl_2 core (Figure 2). Although the two copper atoms involved in this dimeric core (Cu3 and Cu5) are within a distance of 2.967(5) Å, it is unlikely that they are bonded to each other; similar non-bonding distances between copper atoms are found for some tetranuclear copper complexes containing a Cu_4O_4 framework.^[14, 17] The structural integrity of the basket arises from two features. One, a μ_4 -Cl atom (Cl3) holds four of the copper atoms together in a distorted tetrahedral geometry. Other chlorine atoms (μ_4 -Cl1 and μ_3 -Cl2) in the Cu_2Cl_2 core are involved in the propagation of the basket. The sides of the basket are stitched together by μ_2 -phosphonato ligands (O1, O12, O5, and O6) and μ_2 -pyrazolyl ligands (N6, N3, N7, and N8). Additionally μ_3 -phosphonato ligands that are present assist not only in holding two copper centers (Cu2 and Cu6) in the pentameric subunits but also provide linkage (O8 and O7)

to the copper atom(s) (Cu4) that serve as the bridge between the two pentameric subunits. The structure of **1** also shows the varied coordination modes of the ligands, chloride, 3,5-dimethylpyrazole, and phosphonate. Thus the 3,5-dimethylpyrazole groups that are present are either anionic and function as bidentate (μ_2) ligands or remain neutral and function as monodentate ligands (η^1). Similarly of the four phosphonate units present for each half of the cluster three are completely deprotonated. Of these, two units coordinate through all the three oxygen atoms (μ_3), while the other only provides two oxygen atoms (μ_2) for coordination. The fourth ligating moiety of this family is actually a phosphinate $\text{RP}(\text{O})_2(\text{OH})$ and provides coordination through two oxygen atoms (O10 and O9), while the third oxygen atom (O11) remains protonated. Similarly of the three chlorine atoms that are present for each half of the cluster, two function as μ_4 bridges, while one is μ_3 bridging. The presence of hydrogen atoms on the pyrazolyl nitrogen atoms (N1, N5, N10) and on the oxygen atom of $\text{RP}(\text{O})_2(\text{OH})$ (O11) causes intramolecular hydrogen bonding within the cluster. This leads to the preferential orientation of the pyrazolyl rings on Cu1 so as to maximize the hydrogen bonding interaction with the phosphonate oxygen atoms O3 and O4. The hydrogen bonding interaction present in **1** is shown in Figure 2. The extensive and elaborate structural diversity in this molecule appears to be truly remarkable and is brought about by the versatile coordination adaptability of the Cu^{II} ion in the presence of the ligand $[\text{RPO}_3]^{2-}$ and the ancillary 3,5-dimethylpyrazolyl and chloride ligands. In view of these results it would be of interest to study the structural effects brought out by the replacement of the water molecules found in copper phosphonates $\text{Cu}(\text{O}_3\text{PC}_6\text{H}_5) \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{O}_3\text{PCH}_3) \cdot \text{H}_2\text{O}$ by pyrazolyl ligands.

Magnetic susceptibility measurements on the copper cluster **1** were carried out between room temperature and 18 K. The μ_{eff} value decreases with a decrease in temperature. Figure 3 shows the plot of χ_{M} versus T as well as that of μ_{eff} per copper atom versus T . These plots show that **1** displays weakly antiferromagnetically coupled behavior. This is reflected in the interception of the straight line at -30°C in the plot of $1/\chi_{\text{M}}$ versus T (Figure 3).

We have described the synthesis of a novel dodecanuclear copper(II) cluster mediated by *tert*-butylphosphonic acid and 3,5-dimethylpyrazole. The combination of these two ligands leads to the assembly of **1** whose structure is completely different from any structural type known in such copper systems so far. Currently we are adapting this synthetic methodology to other transition and lanthanide metal systems.

Experimental Section

1: Anhydrous copper(II) chloride (0.20 g, 1.50 mmol) was taken up in anhydrous dichloromethane (30 mL). To this was added a solution of 3,5-dimethylpyrazole (0.12 g, 1.25 mmol) in dichloromethane (10 mL) at room temperature. This resulted in a green solution to which a solution of *tert*-butylphosphonic acid (0.14 g, 1.0 mmol) and triethylamine (0.23 g, 2.25 mmol) in dichloromethane (20 mL) was added in one portion. The resulting green solution was stirred at room temperature for 20 h. The solvent was removed in vacuo to afford a green solid, which was treated

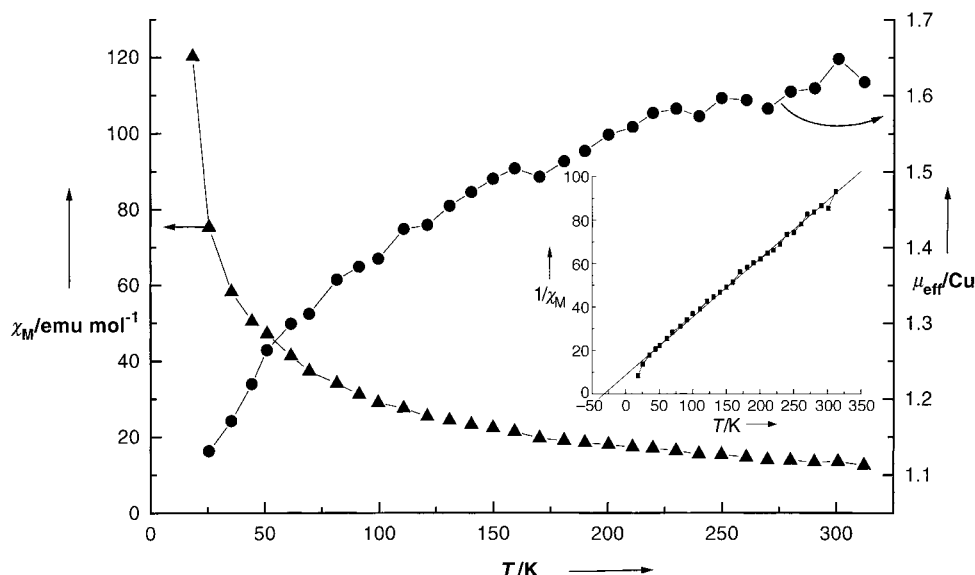


Figure 3. Plots of χ_M versus T/K (▲) and of $\mu_{\text{eff}}/\text{Cu}$ versus T/K (●) for **1**. Inset: Plot of $1/\chi_M$ versus T for **1**.

with benzene (50 mL), filtered, and the solvent was removed from the filtrate affording a crystalline solid (0.31 g) which upon recrystallization from *n*-hexane and dichloromethane (1:1) at room temperature afforded dark green crystals. M.p.: 188 °C. C, H, N analysis: calcd for $\text{C}_{82}\text{H}_{150}\text{Cl}_6\text{Cu}_{12}\text{N}_{20}\text{O}_{24}\text{P}_8$ (3023.29): C 32.57, H 5.00, N 9.26; found: C 32.45, H 5.10, N 9.12; IR (KBr): $\tilde{\nu}$ = 3340(s), 2947(s), 2866(m), 2493(m), 2172(m), 1571(m), 1477(s), 1422(m), 1268(m), 1120(m), 1046(s), 971(m), 917(m), 831(m), 667(s), 524(s), 431(m) cm^{-1} ; UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 730 (860), 246 nm (23140).

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- [15] Crystal data for **1**: Crystal dimensions: $0.40 \times 0.30 \times 0.03$ mm. Molecular formula: $\text{C}_{82}\text{H}_{150}\text{Cl}_6\text{Cu}_{12}\text{N}_{20}\text{O}_{24}\text{P}_8$, M_r = 3023.29, monoclinic, space group $C2/c$, a = 20.721(2), b = 30.323(5), c = 25.07(3) Å, β = 106.90(4)°, V = 15073(16) Å³, Z = 4, T = 293(2) K, ρ_{calcd} = 1.331 g cm⁻³, Enraf Nonius FR590 CAD-4 diffractometer, $\text{MoK}\alpha$ radiation, 9543 reflections collected, 9235 independent reflections (R_{int} = 0.0778), $R1$ = 0.0697, $wR2$ = 0.2042 [$I > 2\sigma(I)$], $R1$ = 0.1658, $wR2$ = 0.2384 (all data), GOF = 1.335. The maximum and minimum residual electron density are 1.058 and -1.526 e Å⁻³, respectively. The structure was solved by using the WINGX1.61 crystallographic collective package (L. J. Farrugia, WINGX ver 1.61, An Integrated Systems of Windows programs for the Solution, Refinement and Analysis of single-crystal X-ray diffraction data, Department of Chemistry, University of Glasgow). The structure was solved initially with SIR92 and refined with the SHELXL-97 package incorporated in WINGX. The structure was refined against F^2 with a full-matrix least-squares algorithm. All hydrogen atoms were included in idealized positions and a riding model was used. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138262. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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