Controlled Assembly of Dinuclear Metallacycles into a Three-Dimensional Helical Array**

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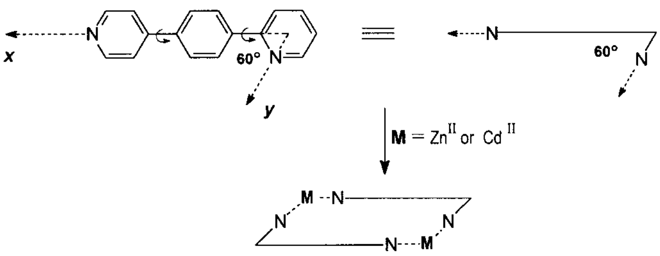
The family of cyclic nanostructures assembled from transition metal junctions and bridging ligands is now a well-established group of coordination compounds.[1] The variety of different metal cation/donor atom interactions that can be used by the coordination chemist provides significant structural flexibility for such "supermolecules".[1b, 2] The diversity of such coordination nanostructures makes them remarkable examples in the growing library of self-assembled entities,[3] which now can be considered for use as construction blocks for larger supramolecular arrays.[4]

It has been demonstrated recently that if discrete metallo-supramolecular species contain additional peripheral binding sites they can assemble into one-dimensional (1D) polymeric structures.[5a] Similarly, the aggregation of metallacycles into 1D polymers can be supported by additional bridging ligands[5b,c] or coordinated counterions.[5d] Understanding the principles of nanostructure formation by polymerization is important not only from the viewpoint of coordination chemistry, but also for the future development of increasingly intricate and functional coordination networks.

We report herein the toposelective self-assembly of a cyclic dinuclear complex using a simple angular ligand, 2,4′-(1,4-phenylene)bispyridine L,[6] and its controlled aggregation into a three-dimensional (3D) infinite framework. The main geometric features of the ligand can be summarized as follows: 1) two heterocycles are linked through a phenylene group, each ring having free rotation around the *x* axis (Scheme 1); 2) the donor atom separation is 9.5 Å; 3) the angle between the N-donor lone pairs is 60°, which cannot be distorted significantly when the ligand coordinates to metal centers because of the rigid nature of the C(sp^2)–C(sp^2) bonds. The rigid bis-monodentate nature of ligand L makes it suitable for the synthesis of cyclic nanostructures, and it can potentially be used to construct a dinuclear metallacycle when combined with a suitable metal center (Scheme 1).



Scheme 1. Geometry of ligand L and its coordination with transition metals.

Treatment of a solution of $Zn(NO_3)_2$ with a solution of ligand L gives the dinuclear complex $[Zn_2(L)_2(NO_3)_4]$ (**1**) in nearly quantitative yield (Figure 1 a). The single-crystal X-ray structure analysis[7] of **1** shows a parallelogram-shaped structural motif with the Zn^{II} cations having a distorted tetrahedral geometry (N1-Zn1-N18^i 127.92(12)°). Two NO_3^- ions are bound to each metal center each by one oxygen donor and function as terminators, preventing further aggregation. The coordinated 2-pyridyl ring is strongly twisted relative to the rest of the ligand molecule (dihedral angle 47.5(2)°) allowing the two other essentially coplanar aromatic rings to be involved in intramolecular π–π stacking with an interplanar separation of 3.394(5) Å. This gives an optimal charge separation which presumably has a beneficial influence on the formation of the metallacyclic entity.[10] The Zn^{II} centers in **1** are coordinatively saturated in their pseudo-tetrahedral

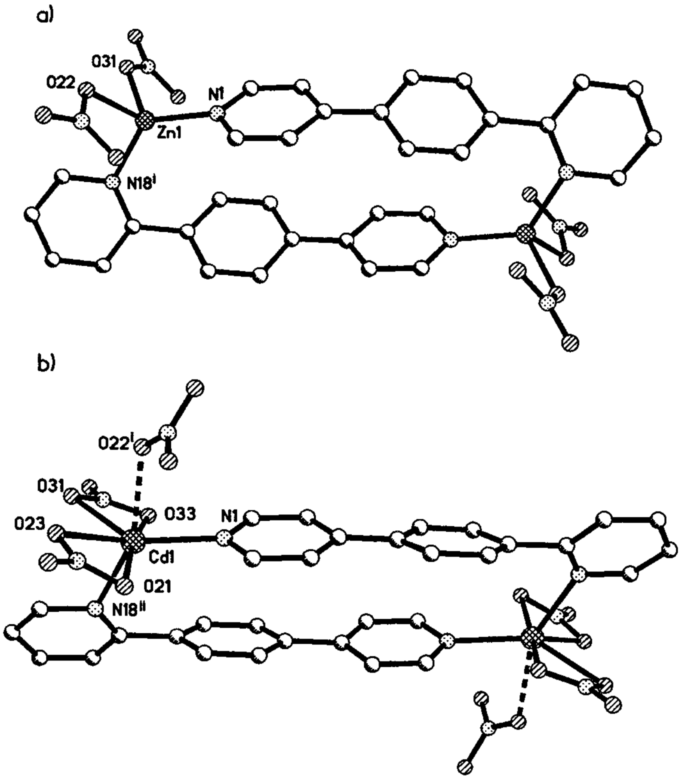


Figure 1. a) Molecular structure of complex **1**. b) Molecular structure of the monomeric unit of **2**; bridging coordination to a NO_3^- ion of a neighboring molecule is shown by a dashed line. Symmetry codes i: $2/3 - x + y$, $1/3 - x$, $1/3 + z$; ii: $1 - x$, $-y$, $1 - z$.

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environment so that the metallacycle is not involved in interactions with neighboring molecules in the solid state, and thus exists as a discrete unit. Complex **1** is very sparingly soluble in common organic solvents but dissolves sufficiently in $MeNO_2$ and MeOH to allow ^1H NMR spectroscopic measurements and electrospray mass spectrometry experiments. The results of these indicate that the metallacyclic structure is maintained in solution. However, in DMSO solution the ^1H NMR spectrum is consistent with disassembly of the complex into its components as would be expected for this more coordinating solvent.

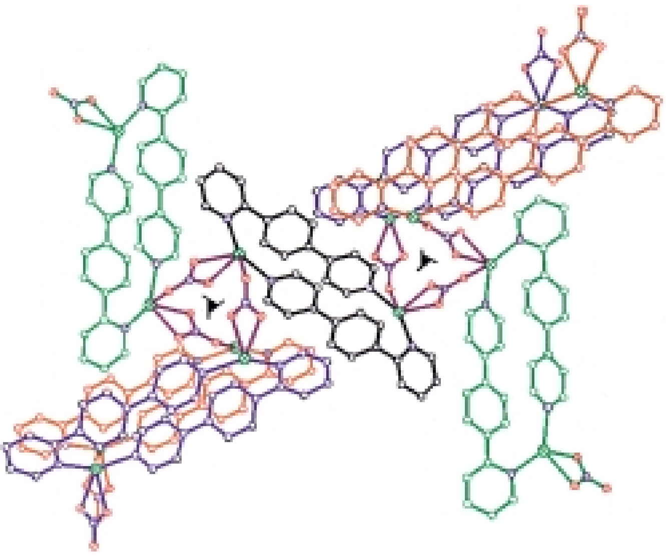

Figure 2. The metallacycle within the structure of **2** (central unit) that forms two helices of opposing hands through NO_3^- bridges; terminating NO_3^- groups are omitted for clarity. Crystallographic symmetry operations are shown to indicate the 3_1 and 3_2 screw axes around which the helices are formed.

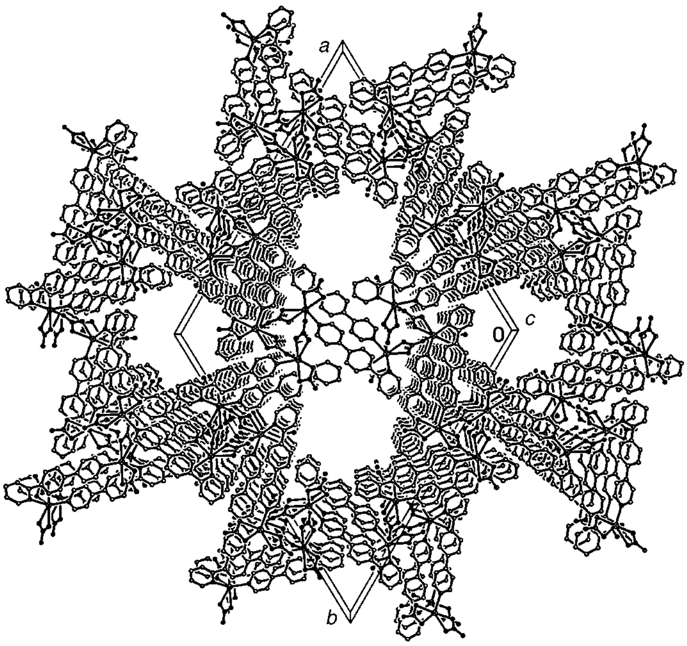

Figure 3. A view of the extended structure of **2**, including the crystallographic unit cell, showing metallacycles aggregated into helices and forming infinite channels with a diameter of about 10 Å.

The single-crystal X-ray structure analysis[7b, 11] of the Cd^{II} analogue shows that it forms a similar parallelogram-shaped unit (Figure 1b) which has a more "ideal" structure (N1-Cd1-N18^{ii} 121.5(2)°, when the ligand nondistorted geometry requires an angle of 120° (Scheme 1)) than complex **1**. Cd^{II} is known to have a more flexible coordination sphere than Zn^{II} and it can adopt coordination numbers between four and eight, particularly in the presence of the NO_3^- ion.[12] Despite both NO_3^- ions in complex **2** binding to the Cd^{II} center in a bidentate fashion, not all of the coordination sites of the cation are occupied. As a result, each Cd^{II} cation interacts with a NO_3^- ion of a neighboring molecule.[13] The resulting interaction through the bridging NO_3^- ion allows aggregation to give an infinite $[Cd(NO_3)]_\infty$ helix arranged around a crystallographic $\bar{3}$ axis (Figure 2). The supramolecular arrangement of the metallacycles has the effect of bridging two different helices, of opposite hands, to give a structure with no overall chirality. However, the ligands positioned between adjacent helices form fascinating hydrophobic hexagonal channels with a diameter of about 10 Å which comprise 17% of the volume of the structure[14] (Figure 3). As the network is uncharged, these channels are anion-free and available for the inclusion of guest species, potentially as large as adamantane-sized molecules. Significantly, the crystallographic analysis showed residual electron density inside the channels, but the nature of the included species could not be established because of extreme disorder around a threefold inversion axis. However, elemental analysis and NMR spectroscopic studies of complex **2** dissolved, and disassembled, in DMSO revealed no other organic molecule in its structure except ligand L. The elemental analysis gave a metal:ligand ratio of 1:1.25 indicating that the 1:1 Cd:L complex was supplemented by 0.25 equivalents of uncoordinated L within the channels. The metal:ligand ratio observed by elemental analysis of 1:1.25 corresponds with 4.5 extra molecules of L per unit cell which is consistent with the channel volume.[14] Powder X-ray diffraction studies of bulk samples, with elemental analysis consistent with the formula $\{[Cd_2(L)_2(NO_3)_4]0.5\,L\}_n$, confirmed that the structure observed in the single-crystal X-ray studies was maintained (see Supporting Information). What appears to be preferred inclusion of free ligand guest molecules over other small guests was further supported by the inclusion of *p*-terphenyl (PhC_6H_4Ph) into **2**, when **2** is prepared in the presence of this guest molecule. The inclusion of *p*-terphenyl was confirmed by ^1H NMR spectroscopy of the compound subsequently disassembled in DMSO solution. The elongated π-electronic system (10 Å in length) may even be acting as a template for the formation of the 3D structure observed for **2** through edge–face π interactions.[15] Attempts to include other guest molecules (e.g. C_6H_6, PhOMe, PhCN, MeOH, MeCN, CH_2Cl_2) by using these species as solvents gave crystals of **2** that contained only $Cd(NO_3)_2$ and the ligand in the same 1:1.25 M:L ratio, as confirmed by elemental analysis and by ^1H NMR spectroscopy of crystals dissolved in $[D_6]$DMSO.

We were interested to see whether the guest ligand molecules could be removed from the channels of compound **2** and to this end single crystals of **2** were refluxed in toluene (a solvent in which the free ligand is soluble) for 12 h and then dried in vacuo for 5 h at 70 °C. Under these conditions sufficient crystallinity was maintained in the resulting samples **3**, which showed only a slight colorization due to surface decomposition, to allow a redetermination of the single-crystal X-ray structure.[7b],[16] The 3D framework structure was maintained and interestingly *no* residual electron density was observed in the hexagonal channels.[14] The total residual electron density in the channels was assessed by using the SQUEEZE routine[14] giving a value for the residual net electron density of 0.0(17) e^- per unit cell and a total solvent accessible volume of 1597.6 Å^3. Elemental analysis of **3** was also consistent with removal of guest molecules from the channels.[17] This represents a rare example of a coordination framework acting as an analogue of porous zeolite-like frameworks.[18]

In summary, rigid bis-monodentate angular ligand L forms a dinuclear cyclic complex with exclusive "head-to-tail" ligand placement using its self-complementarity. The parallelogram can exist either as a discrete unit when the metal centers are completely coordinatively saturated (Zn^{II}) or assembles into a highly unusual 3D polymeric array when the metal centers have a high coordination number (Cd^{II}). The polymeric complex **2** is an unprecedented supramolecular aggregate of dinuclear cyclic molecules which has a multi-helical structure in which the organic molecules form large hydrophobic channels with a cross-section of about 10 Å. We have also demonstrated removal of the guests from the channels in **2** generating an open "host" framework.

Experimental Section

General: All reagents (Aldrich) were used as received. Ligand L was prepared by the literature method.[6] Elemental analyses (C,H,N) were carried out at the University of Nottingham. Infrared spectra were obtained as KBr pressed pellets using a Perkin-Elmer 1600 series FTIR spectrometer. NMR spectra were recorded at 300 MHz on a Bruker DPX300 spectrometer.

1: A solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.064 g, 2.2×10^{-4} mol) in CH_3CN (12 mL) was layered over a solution of L (0.051 g, 2.2×10^{-4} mol) in CH_2Cl_2 (12 mL). After two weeks yellow crystals suitable for X-ray diffraction were formed (yield 0.182 g, 98 %). Elemental analysis for $C_{32}H_{24}N_8O_{12}Zn_2$ ($M_r = 843.33$): calcd: C 45.54, H 2.85, N 13.28; found: C 45.25, H 2.79, N 13.32; ^{1}H NMR ([D$_6$]DMSO, 300 MHz, 25 °C): $\delta = 7.40$ (dd, $^1J = 9$ Hz, $^2J = 5$ Hz, 1 H), 7.77 (d, $^1J = 6$ Hz, 2 H), 7.88–7.91 (m, 1 H), 7.94 (d, $J = 8$ Hz, 2 H), 8.04 (d, $J = 9$ Hz, 1 H), 8.23 (d, $J = 8$ Hz, 2 H), 8.70 (d, $J = 6$ Hz, 2 H), 8.75 (d, $J = 5$ Hz, 1 H); ^{1}H NMR (CD_3NO_2, 300 MHz, 25 °C): $\delta = 7.48$–7.54 (m, 1 H), 8.00–8.06 (m br., 4 H), 8.07–8.13 (m br., 2 H), 8.25–8.34 (m br., 2 H), 8.73–8.81 (m br., 3 H); MS (electrospray in MeOH): *m*/*z*: 817 [$M - NO_3^- + 2H_2O$].

2: A solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.011 g, 3.6×10^{-5} mol) in CH_3CN (2 mL) was layered over a solution of L (0.008 g, 3.6×10^{-5} mol) in CH_2Cl_2 (2 mL). After one week a solid precipitate was filtered off. Diffusion of Et_2O vapor into the filtrate yielded crystals suitable for X-ray diffraction (yield: 0.006 g, 40 %). Elemental analysis for $C_{20}H_{15}N_{4.5}O_6Cd$ ($M_r = 526.9$): calcd: C 45.59, H 2.85, N 11.97; found: C 46.01, H 3.15, N 11.59.

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[7] a) Single-crystal X-ray experiments were performed on a Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems open-flow cryostat (graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). All structures were solved by direct methods[8] and all non-hydrogen atoms were located by using difference Fourier methods.[9] Crystal structure data for **1** $C_{32}H_{24}N_8O_{12}Zn_2$, $M_r = 843.33$, triclinic, space group $P\bar{1}$, $a = 7.300(2)$, $b = 9.911(3)$, $c = 12.203(5)$ Å, $\alpha = 74.669(17)$, $\beta = 82.37(2)$, $\gamma = 72.943(19)°$, $V = 812.6(5)$ Å^3, $T = 220(2)$ K, $Z = 1$, $\rho_{calcd} = 1.723$ Mg m^{-3}, $F(000) = 428$, $\mu(Mo_{K\alpha}) = 1.557$ mm^{-1}. Crystal morphology: colorless blocks. Crystal dimensions: $0.23 \times 0.16 \times 0.12$ mm. A total of 3674 reflections was collected, 2873 unique ($R_{int} = 0.0501$), $\theta_{max} = 25.03°$. Absorption correction by ψ scans. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0397P)]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$. Goodness-of-fit on F^2 was 0.992, $R1$ (for 2219 reflections with $I > 2\sigma(I)) = 0.0392$, $wR2 = 0.0755$. Data/parameters 2873/244. Largest difference Fourier peak and hole 0.32 and -0.36 e Å^{-3}, respectively. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137731 (**1**), CCDC-137732 (**2**), and CCDC-137733 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[11] Crystal structure data for **2** $C_{20}H_{15}N_{4.5}O_6Cd$, $M_r = 526.9$, trigonal, space group $R\bar{3}$, $a = 36.475(9)$, $c = 7.570(3)$ Å, $V = 8722(5)$ Å^3, $T = 150(2)$ K, $Z = 18$, $\rho_{calcd} = 1.606$ Mg m^{-3}, $F(000) = 4176$, $\mu(Mo_{K\alpha}) = 1.165$ mm^{-1}. Crystal morphology: colorless columns. Crystal dimensions: $0.47 \times 0.15 \times 0.13$ mm. A total of 12 854 reflections was collected, 3808 unique ($R_{int} = 0.0727$), $\theta_{max} = 26.00°$. Absorption correction by ψ scans. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.1089P)^2 + 142.9P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$. Goodness-of-fit on F^2 was 1.133, $R1$ (for 2974 reflections with $I > 2\sigma(I)) = 0.0601$, $wR2 = 0.1740$. Data/parameters 3808/244. Largest difference Fourier peak and hole 2.4 and -0.94 e Å^{-3}, respectively.[7b].

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[13] The overall geometry around the Cd^{II} center is a distorted pentagonal bipyramid. Two chelating NO_3^- groups are in the equatorial plane. The axially coordinated 2-pyridyl nitrogen atom and the bridging NO_3^- group form a N18^{ii}-Cd1-O22^{i} angle of 152.2(2)°.

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[16] Crystal structure data for **3** $C_{16}H_{12}N_4O_6Cd$, $M_r = 468.7$, trigonal, space group $R\bar{3}$, $a = 36.42(8)$, $c = 7.799(15)$ Å, $V = 8959(33)$ Å^3, $T = 298(2)$ K, $Z = 18$, $\rho_{calcd} = 1.564$ Mg m^{-3}, $F(000) = 4176$, $\mu(Mo_{K\alpha}) = 1.134$ mm^{-1}. Crystal morphology: pale brown needle. Crystal dimensions: $0.50 \times 0.06 \times 0.04$ mm. A total of 3563 reflections was collected, 2602 unique ($R_{int} = 0.1089$), $\theta_{max} = 22.49°$. Numerical absorption correction. Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0002P)^2 + 813P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$. Goodness-of-fit on F^2 was 1.198, $R1$ (for 1381 reflections with $I > 2\sigma(I)) = 0.111$, $wR2 = 0.2681$. Data/

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

[17] Elemental analysis for $C_{16}H_{12}N_4O_6Cd$ ($M_r = 468.7$): calcd: C 40.99, H 2.59, N 11.96; found: C 41.17, H 2.73, N 11.87.

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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 $Cu^{II}Cl_2$ with 3,5-dimethylpyrazole (3,5-Me_2PzH) 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)].

$$\begin{aligned}&12\,CuCl_2 + 10\,3,5\text{-}Me_2PzH + 8\,t BuP(O)(OH)_2 + 18\,Et_3N \rightarrow \\ &\quad [Cu_{12}(\mu_4\text{-}Cl)_4(\mu_3\text{-}Cl)_2(\eta^1\text{-}3,5\text{-}Me_2PzH)_6(\mu_2\text{-}3,5\text{-}Me_2Pz)_4(\mu_3\text{-}t BuPO_3)_4\text{-} \\ &\qquad (\mu_2\text{-}t BuPO_3)_2(\mu_2\text{-}t BuPO_2OH)_2]\ (\mathbf{1}) + 18\,Et_3N\cdot HCl\end{aligned} \qquad (1)$$

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 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.

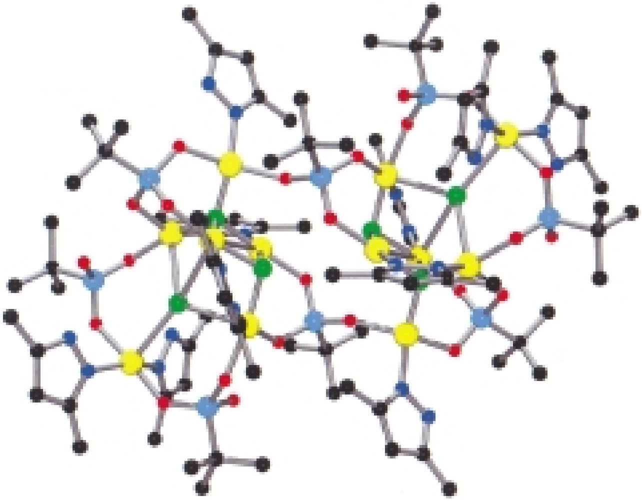

Figure 1. POVRAY diagram of **1** showing the organic lipophilic envelope surrounding the dodecanuclear Cu^{II} metal framework. Hydrogen atoms omitted for clarity. Color code: carbon: black; chlorine: green; copper: yellow; oxygen: red; phosphorus: cyan; dark blue: nitrogen.

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