

A Nanoscopic Molecular Cadmium Phosphonate Wrapped in a Hydrocarbon Sheath**

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*Dedicated to Dr. Manfred Flad
on the occasion of his 90th birthday*

Preparing a material that has particles of uniform dimension has been one of the biggest challenges for chemists as well as material scientists. The traditional ways of imparting order at the nanoscopic level have changed since the synthesis of fullerene clusters.^[1] The use of techniques such as epitaxy and metal-organic chemical vapor deposition (MOCVD) have been used extensively in this regard. The synthesis of giant inorganic molecules, such as polyoxoanions,^[2] Al₇₇,^[3] and Ga₈₄^[4] clusters are examples of inorganic counterparts of fullerenes. The synthesis of metal phosphonates using organo-metallic routes in recent years has led to the realization of a series of oligomeric transition-metal and main-group-metal phosphonates.^[5,6] In all these reports, the size of the oligomeric structure is highly dependent on the substituent on the metal center as well as at the phosphorus center. The metal phosphonates can be synthesized either using metal precursor-phosphonic acid interactions via an acid exchange or by starting from metal alkyls/amides/alcoholates by elimination of alkanes/amines/alcohols.^[5-7] It has been demonstrated that metals belonging to the same group of the periodic table yield molecular phosphonates of the same topology if the substituents on the metal and phosphorus centers are kept the same. Although examples of zinc phosphonates following both the synthetic methodologies have been reported, there have been no examples of molecular cadmium phospho-

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nates.^[8] The known examples of cadmium phosphonates are either polymeric or layer-type structures.^[9]

Molecular cadmium clusters, analogous to those of zinc, should in principle be realizable by the use of a cadmium alkyl precursor, such as CdR_2 , and phosphonic acid, such as *tert*-butylphosphonic acid. Our recent synthesis of a dodecanuclear zincophosphonate containing a $\{\text{Zn}_4(\mu_4\text{-O})\}$ core has been an extension of a cluster-building strategy via organo-metallic routes.^[8a] Surprisingly, the application of a similar strategy for the reaction of dimethylcadmium with *tert*-butylphosphonic acid in a THF solution afforded a still larger aggregate as colorless crystals, which contains 68 heteroatoms arranged in the form of a hollow sphere (see below). Although the initial yield of this reaction was poor, the addition of a stoichiometric amount of water during the reaction significantly enhanced the yield (20%). The ^1H NMR intensities of the solid-state CP-MAS NMR spectrum reveal that the methyl protons on each cadmium atom resonate at $\delta = 0.6$ ppm while the methyl protons of *tert*-butyl groups attached to phosphorus appear at $\delta = 1.7$ ppm. However, the ^{31}P NMR spectrum of **1** in the solid state (Figure 1) displays at least four well-resolved signals in the range $\delta = 30$ –50 ppm, which can be assigned to phosphorus atoms having four different environments.

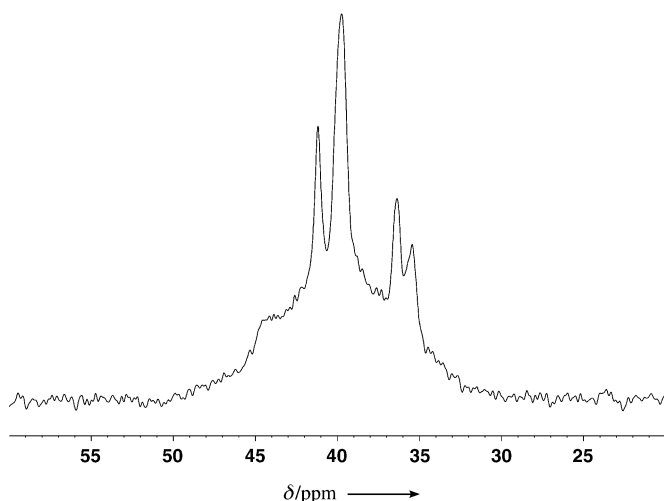


Figure 1. ^{31}P CP-MAS NMR spectrum of $[(\text{MeCd})_{10}\{(\text{thf})\text{Cd}\}_4\text{Cd}_6(\mu_4\text{-O})_2(\mu_3\text{-OH})_2(\text{tBuPO}_3)_{12}]$.

The single-crystal X-ray diffraction study^[10] reveals that compound **1** is the largest cadmium phosphonate aggregate known, $[(\text{MeCd})_{10}\{(\text{thf})\text{Cd}\}_4\text{Cd}_6(\mu_4\text{-O})_2(\mu_3\text{-OH})_2(\text{tBuPO}_3)_{12}]$ (**1**), which contains a skeleton made up of 20 cadmium atoms and 12 phosphorus atoms that are held together by 36 surface oxygen atoms along with a pair of oxo and hydroxo groups in the interior of the sphere (Figure 2). The packing diagram of **1** (Figure 3) shows the arrangement of $\text{Cd}_{20}\text{P}_{12}$ polyhedra in the solid state. Compound **1** appears to have an inversion center, which however is absent in the final structure due to the small variations observed in the coordination geometry of the cadmium centers. The inorganic core of this molecule is embedded in the organic sheath made

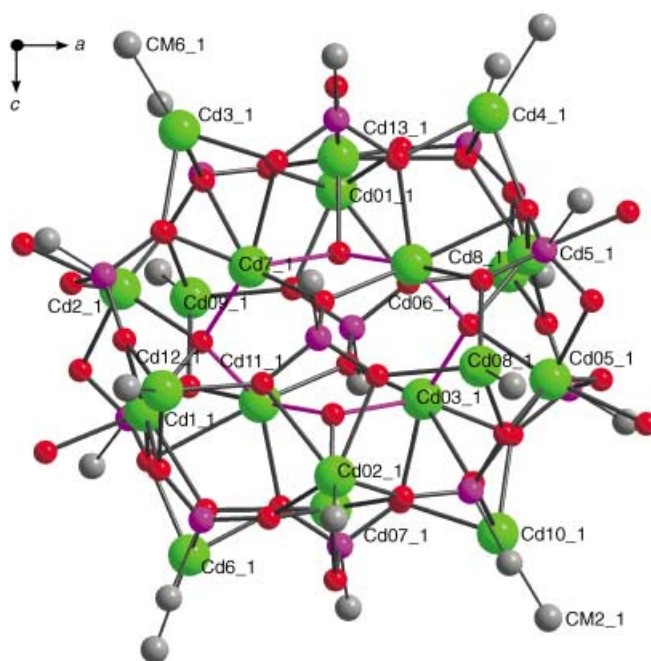


Figure 2. Molecular structure of **1** showing the $\text{Cd}_{20}\text{P}_{12}$ polyhedra (the solvent THF molecules, hydrogen atoms, and the methyl groups of the *tert*-butylphosphonate group are omitted for the sake of clarity).

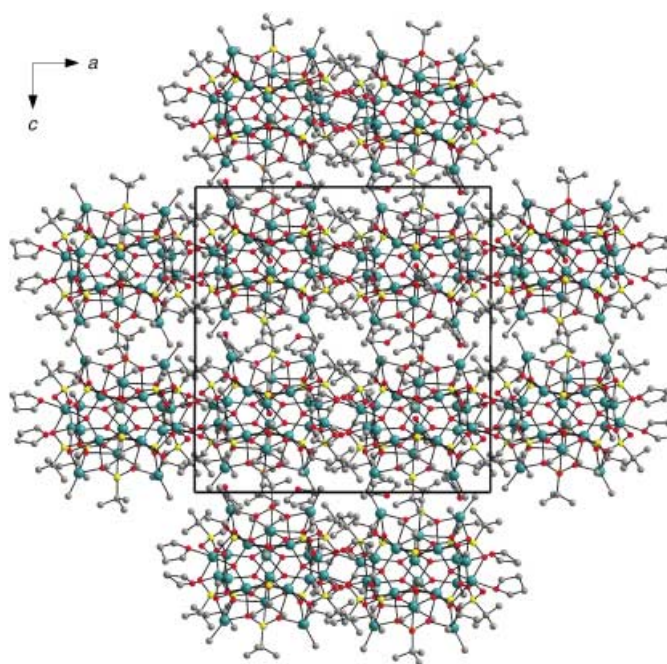


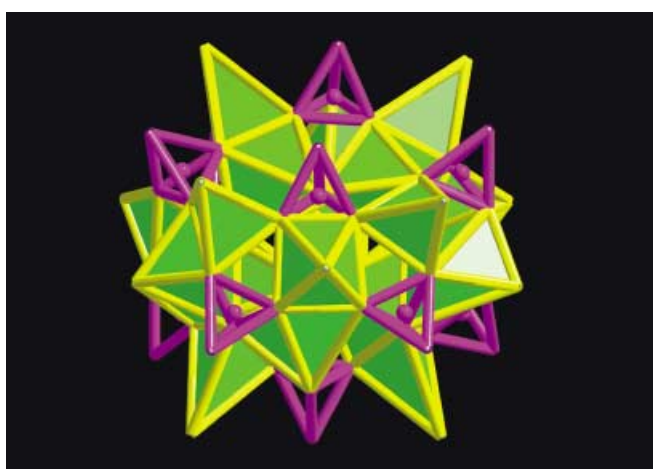
Figure 3. Packing diagram of **1** showing the arrangement of the $\text{Cd}_{20}\text{P}_{12}$ polyhedra in the solid state.

up of ten methyl groups (attached to ten cadmium atoms), four THF molecules (attached to four cadmium atoms) and twelve *tert*-butyl groups (attached to the twelve phosphorus atoms). The twenty cadmium atoms can be categorized into six classes (1–6) depending on the coordination geometry and the environment around them (Table 1). In the molecule, there are 32 polyhedra in total: 20 tetrahedra (12 from

Table 1: Arrangement of cadmium atoms within the molecule 1.

Class	Cd atoms	Geometry	Environment around cadmium
1	Cd3_1, Cd4_1, Cd6_1, Cd8_1, Cd08_1, Cd09_1, Cd10_1, Cd12_1	tetrahedral	3 phosphonate oxygen atoms, 1 methyl group
2	Cd01_1, Cd02_1	square pyramidal	4 phosphonate oxygen atoms, 1 methyl group
3	Cd07_1, Cd13_1	trigonal bipyramidal	1 μ_3 -O atom, 4 phosphonate oxygen atoms
4	Cd2_1	trigonal bipyramidal	1 μ_4 -O atom, 3 phosphonate oxygen atoms, one THF group
5	Cd1_1, Cd5_1, Cd05_1	octahedral	1 μ_4 -O atom, 4 phosphonate oxygen atoms, 1 THF group
6	Cd03_1, Cd06_1, Cd7_1, Cd11_1	octahedral	1 μ_4 -O atom, 1 μ_3 -O atom, 4 phosphonate oxygen atoms

phosphonate groups and eight from cadmium atoms), seven cadmium octahedra, two cadmium square-based pyramids, and three cadmium trigonal bipyramids. The phosphonate tetrahedra are linked to the cadmium polyhedra either by corner sharing via an oxygen atom or by edge sharing through two oxygen atoms (Figure 4). Depending on the coordination

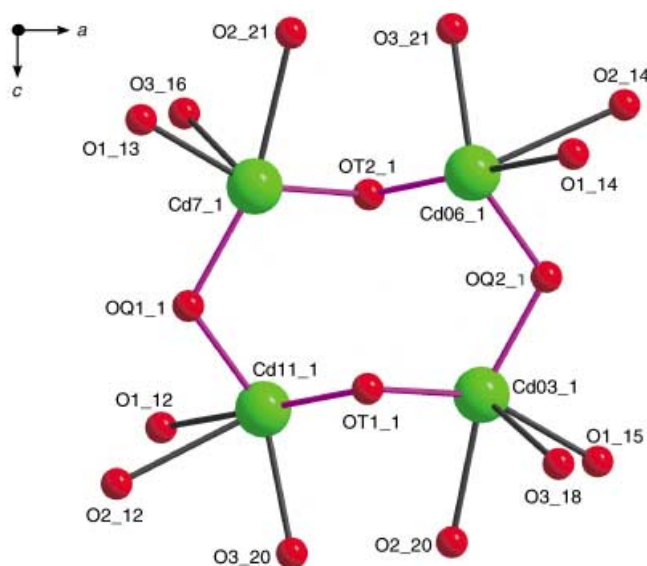

Figure 4. Polyhedral arrangement showing cadmium (as closed polyhedra with green interior and yellow edges) and phosphorus (open polyhedra in pink) atoms.

modes the twelve phosphonate groups can be classified into four different types (A–D; Table 2). This coordination mode of phosphonates in the cluster results in the formation of nine CdO_2P four-membered rings. The two μ_3 -OH and two μ_4 -O groups present in the molecule are located in the space available inside the spherical hollow ball. It appears that the entire cluster is built around these two oxo (OQ1_1 and OQ2_1) and two hydroxo groups (OT1_1 and OT2_1), since

Table 2: Different coordination modes of phosphonate groups in 1.

No. of	No. of	No. of	Type	No. of
$\text{P}-\text{O}-\text{Cd}-$	$\text{P}-\text{O}-\text{Cd}-$	$\text{P}-\text{O}-\text{Cd}-$		P atoms
1	2	–	A	4
1	1	1	B	2
–	3	–	C	3
–	2	1	D	3

these four oxygen centers hold as many as 12 cadmium ions together (Figure 5). Another way of understanding the structure of this molecule is by considering an inner eight-membered $\{\text{Cd}_4\text{O}_4\}$ core, which is surrounded by remaining cadmium and phosphonate moieties (Figure 5). The $\{\text{Cd}_4\text{O}_4\}$ core contains two $\{\text{Cd}(\mu_3\text{-OH})\}$ and two $\{\text{Cd}(\mu_4\text{-O})\}$ moieties and adopts a crown conformation.


Figure 5. Central Cd_4O_4 moiety containing the μ_3 -O (OT1_1 and OT2_1) and μ_4 -O (OQ1_1 and OQ2_1) atoms in 1, around which the phosphonate groups are arranged.

Among the reported cadmium phosphinates, phosphonates, phosphates, and oxides, there is no report on the presence of a $\{\text{Cd}(\mu_4\text{-O})\}$ central unit, whereas $\{\text{Cd}(\mu_3\text{-OH})\}$ is a quite well known structural motif in these systems.^[11] The average bond lengths in $\{\text{Cd}-\mu_4\text{-O}\}$ (2.208(7) Å) and $\{\text{Cd}-\mu_3\text{-OH}\}$ (2.256(7) Å) are comparable to those in the reported cadmium complexes containing oxo and hydroxo bridges.^[11] The average distance between the methyl substituents on the diagonally opposite cadmium atoms (CM6_1 to CM2_1; Figure 2) is ≈ 15.4 Å, while the average distance between the opposite carbon atoms of the *tert*-butyl groups is 14.9 Å, and the average distance between the hydrogen atoms of the opposite THF atoms is 20.03 Å. Within the inorganic core, the diagonally opposite $\text{Cd}\cdots\text{Cd}$ and $\text{P}\cdots\text{P}$ distances are 10.9 and 9.8 Å, respectively. Hence, this molecule falls truly into the

nanomolecular regime, as the molecular diagonal distances measured fall in the range of 10 to 20 Å. Thus, this giant molecule can easily encapsulate three C₆₀ molecules at one time.^[1]

Experimental Section

1: Dimethylcadmium (0.65 g, 4.6 mmol) was added dropwise to a solution of *tert*-butylphosphonic acid (0.32 g, 2.3 mmol) in THF (50 mL) at room temperature. After the evolution of methane gas ceased, the resulting solution was stirred for 6 h. The solution was then concentrated to 5 mL and toluene (5 mL) was added. Colorless crystals of **1**, insoluble in common organic solvents, were obtained over the period of a month at room temperature (0.12 g, 14 %); m.p. > 300 °C; solid-state NMR of **1**: ¹H NMR (399.92 MHz, TMS): δ = 0.6 (s, CdCH₃), 1.7 ppm (br, C(CH₃)₃); ³¹P NMR (161.90 MHz, 85 % H₃PO₄): δ = 35.4, 36.3, 39.7, 41.2 ppm; IR (nujol): ν̄ = 3181 vw, 2232 vw, 1615 vw, 1478 s, 1461 s, 1393 m, 1365 s, 1261 w, 1231 w, 1202 w, 1127 m, 1051 vs, 1027 vs, 969 vs, 884 w, 832 m, 804 w, 727 w, 680 vs, 660 vs, 557 s, 520 vs, 508 s, 487 m, 435 cm⁻¹ m; elemental analysis (THF molecules were removed by drying under vacuum) calcd (%) for C₃₈H₁₄₀Cd₂₀O₄₀P₁₂ (4097.61): C 17.00, H 3.44; found: C 16.25, H 3.48.

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- [10] Crystal data for **1**: C₇₄H₁₇₂Cd₂₀O₄₄P₁₂ (1·4 C₄H₈O), *M*_r = 4385.56, monoclinic, space group *P*2₁/*c*, *a* = 24.303(5), *b* = 25.294(5), *c* = 25.107(5) Å, β = 90.14(3)°, *V* = 15434(5) Å³, *Z* = 4, ρ_{calcd} = 1.938 g cm⁻³, *F*(000) = 8694, λ = 0.71073 Å, *T* = 133 K, μ(MoKα) = 28.78 cm⁻¹, min./max. transmission 0.3271/0.5968, crystal dimensions 0.5 × 0.4 × 0.2 mm³, 3.32° < θ < 25.19°; 158685 reflections were collected, of which 28040 were independent (*R*_{int} = 0.1052) and 27363 were used for refinement. For the final refinement of 1550 parameters, 713 restraints were used. The *R* values were: *R*₁ = Σ|*F*_o − *F*_c|/Σ*F*_o = 0.0587 for *I* > 2σ(*I*), and *wR*₂ = [Σ*w*(*F*_o² − *F*_c²)²/Σ*wF*_o⁴]^{1/2} = 0.1483 for all data; max/min. residual electron density: 2.429/−1.956 e Å⁻³. The unit cell contains four molecules of **1** and 16 molecules of THF. The crystal was covered with a drop of inert perfluorinated polyether oil and flash-cooled in a nitrogen stream. Intensity data were collected on a Huber four-circle instrument and a Siemens 1 K-CCD area detector. A semi-empirical absorption correction was employed using the Bruker AXS program SADABS. The observed systematic absences did not correspond to any space group in the apparent orthorhombic crystal system, which suggested the presence of pseudo-merohedral twinning with a twofold rotation about the *c* axis. The structure was solved with direct methods (SHELXS-97)^[12] and refined against *F*².^[13] Non-hydrogen atoms in **1** were refined anisotropically except for atoms with very low (<0.1) occupancy. Eight out of twenty cadmium atoms (Cd1_1, Cd2_1, Cd3_1, Cd4_1, Cd5_1, Cd6_1, Cd7_1, and Cd8_1) were found to adopt a minor second position and the occupancy of these alternative positions varies by <0.1. Solvent molecules were refined isotropically. The riding model was used for the hydrogen atoms. The fractional contribution from the second twin domain was determined as 44 %. CCDC-210527 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
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