Two Interpenetrating 3D Networks Which Generate Spacious Sealed-Off Compartments Enclosing of the Order of 20 Solvent Molecules in the Structures of $Zn(CN)(NO_3)(tpt)_{2/3}$·solv (tpt = 2,4,6-tri(4-pyridyl)-1,3,5-triazine, solv = ~$^3/_4C_2H_2Cl_4$·$^3/_4CH_3OH$ or ~$^3/_2CHCl_3$·$^1/_3CH_3OH$)

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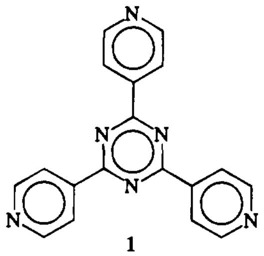
Received December 9, 1994

The results reported here form part of a wide-ranging exploration of the structures of coordination polymers derived from a family of metal-bridging building blocks containing 4-pyridyl donors in simple geometrical dispositions. Family members studied include the "linear" 2-connectors 4,4′-bipyridyl[1] and 1,4-bis(4-pyridyl)butadiyne,[2] the "trigonal" 3-connector 2,4,6-tri(4-pyridyl)-1,3,5-triazine (**1**, hereafter called tpt)



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tpt

discussed below, and the "square-planar" 4-connectors 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphinepalladium(II)[3] and its copper(II) analogue.[4] Some tpt-metal derivatives, including one shown to involve tpt bridging three zinc centers, have been described previously.[5] We report here a remarkable interpenetrating tpt-derived 3D network which contains completely isolated compartments of unprecedented size.

A reaction mixture containing tpt (1.0 g, 3.2 mmol) in 1,1,2,2-tetrachloroethane (400 mL) combined with zinc nitrate (1.12 g, 3.8 mmol) in methanol (200 mL) and tetraethylammonium cyanide (0.588 g, 3.8 mmol) in methanol (200 mL) upon standing at room temperature for several days deposited well-formed cubic crystals (many with edges 0.1–0.2 mm) of composition $Zn(CN)(NO_3)(tpt)_{2/3}$·$^3/_4C_2H_2Cl_4$·$^3/_4CH_3OH$. Anal. Calcd for $C_{15.25}H_{12.5}Cl_3N_6O_{3.75}Zn$: C, 35.8; H, 2.5; N, 16.4; Cl, 20.8; Zn, 12.8. Found: C, 35.7; H, 2.2; N, 16.7; Cl, 20.9; Zn, 12.5.

The structure was determined by single crystal X-ray diffraction.[6] All zinc centers are equivalent, as are all tpt units, all cyanides, and all nitrates. The zinc centers appear in $Zn_4(CN)_4(NO_3)_4$ "squares" (Zn⋯Zn, 5.182(1) Å), as shown in Figure 1, which also indicates the metal environment consisting of two trans tpt pyridines, one bidentate nitrate, and two cis cyanides.[7] Six such Zn_4 square units are linked together by eight μ_3-tpt units to generate a cage structure (hereafter called a type A cage), eight of which can be seen in Figure 2a. These type A cages are highly symmetrical, the normals to the three pairs of Zn_4 squares lying along orthogonal axes and the eight trigonal tpt units having their centers located at the corners of a cube with their normals directed toward the center of the cube (and the cage).

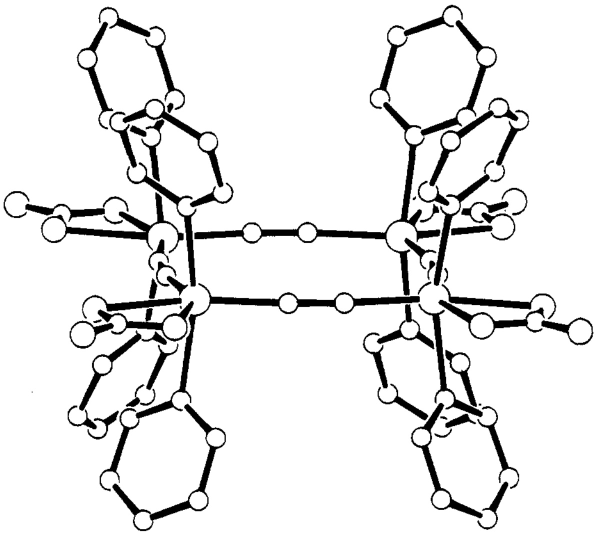

Figure 1. Zinc environment and the $Zn_4(CN)_4(NO_3)_4$ square units. Circles in order of decreasing size represent Zn, O, and C/N. The C and N atoms of the cyanide groups are crystallographically disordered across a mirror plane. Only one pyridine ring of each tpt is shown.

Two independent but identical and interpenetrating 3D nets are present, each composed of type A cages fused together by shared Zn_4 square faces into an infinitely extended cubic arrangement, part of which is shown in Figure 2a. At the center of Figure 2a is a second and much larger type of cage (type B), the nature of which is more clearly revealed in Figure 2b. Each type B cage from one independent framework completely encircles and encapsulates a type A cage from the other framework, as shown in Figure 2b. The two interpenetrating independent networks generate thereby a series of huge identical chambers, each surrounded by a double shell (inner A cage and encapsulating, outer B cage).

The tpt units appear in very closely associated pairs, one from each framework. Any particular tpt forms part of the inner A shell of one chamber and part of the outer B shell of an adjacent chamber. Within each $[tpt{\cdot}Zn_3]_2$ pair, one component is rotated 60° relative to its partner around their shared 3-fold axis. Each tpt is buckled or domed so that the pyridine rings of one are bent toward the spaces between the pyridine rings of its partner. As a consequence, the two Zn_3 triangles become almost coplanar. The distance between the nitrogen of one triazine and the carbon of its partner triazine is 3.56(1) Å. No twisting around the triazine–pyridine links accompanies this "doming"

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(6) Crystal data: $Zn(CN)(NO_3)(tpt)_{2/3}$·$^3/_4C_2H_2Cl_4$·$^3/_4CH_3OH$, MW = 511.56, cubic, space group *Im*3*m* (No. 229), $a = 23.448(4)$ Å, $V = 12892(4)$ Å^3, $Z = 24$, $\varrho_c = 1.58$, $\varrho_m = 1.61(1)$ g cm^{-3}, μ(Mo Kα) = 15.26 cm^{-1}, $F(000) = 6167.65$. Intensity data were measured at 295(1) K with Mo K radiation (graphite monochromator) using an Enraf-Nonius CAD-4MachS diffractometer and employing the $\omega/2\theta$ scan method; absorption corrections were applied. A full-matrix least-squares refinement (SHELX-76) was then employed with anisotropic thermal parameters applied to all non-hydrogen atoms except those of the disordered solvent structure. At convergence, $R = 0.0672$ and $R_w = 0.0656$ for the 883 reflections with $I \geq 3\sigma(I)$, where $R = \sum|\Delta F|/\sum|F_o|$ and $R_w = \sum w^{1/2}|\Delta F|/\sum w^{1/2}|F_o|$.

(7) Plots in this Communication were obtained using the ORTEP program.

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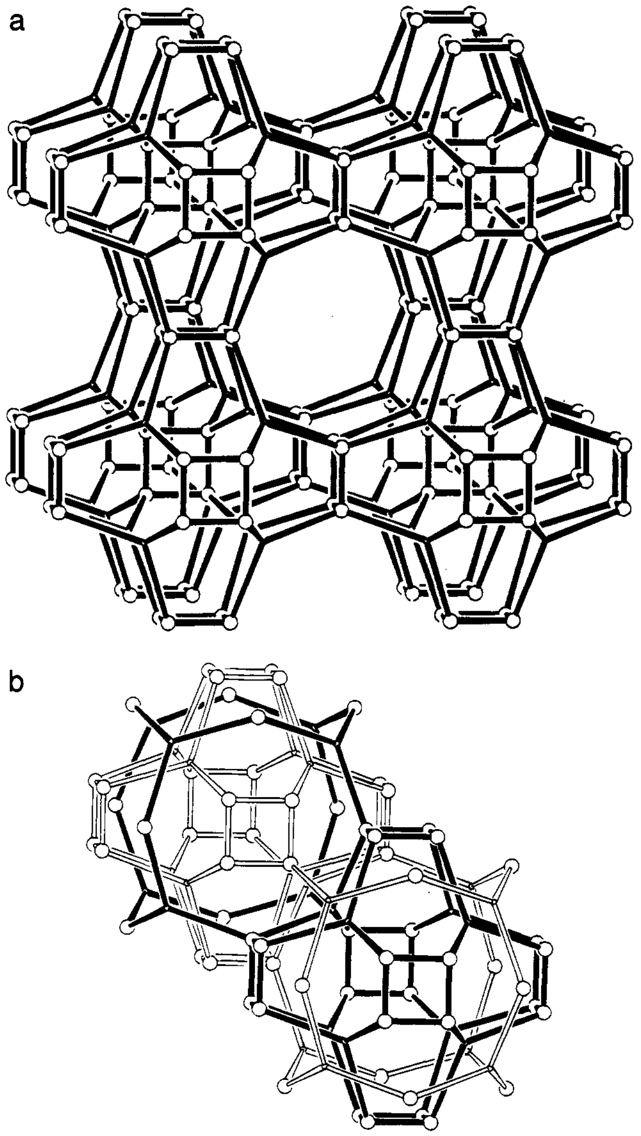

Figure 2. (a) Part of one individual infinite 3D network showing a cubic arrangement of eight type A cages. Circles represent Zn. Tpt units are represented by three spokes radiating from a point at the center of the triazine. ZnCNZn units are represented by direct Zn••Zn links. (b) The two independent, equivalent, and interpenetrating frameworks distinguished here as "black" and "white" networks. For simplicity, only two adjacent chambers are shown. The lower, front chamber consists of an inner black A cage encapsulated by an outer white B cage. In the adjacent chamber, the roles of the two networks are reversed.

of the tpt units, so the normals to the pyridines intersect the normal to the triazine.

Consideration of nonbonded interactions and the sizes of spaces between components suggests that these double shells provide a barrier impenetrable to even the smallest molecules (with the possible exception of H_2), effectively isolating each chamber from its neighbors and from the outside world. The chambers, sealed-off in this manner, are exceptionally spacious, the distance across the inner A shell from one Zn_4 square to the opposed and parallel Zn_4 square being a unit cell length, 23.448(4) Å. The chamber (one chamber per 12 Zn) is large enough to accommodate approximately nine 1,1,2,2-tetrachloroethane molecules, together with nine molecules of methanol, all of which are highly disordered and essentially liquid. The solid in a conventional solution NMR tube in a normal solution NMR instrument shows broad ^{13}C resonances for $C_2H_2Cl_4$ ($\delta \sim 74$) and CH_3OH ($\delta \sim 52$), indicative of their liquid-like character. The composition of trapped solvent is similar to that of the solution from which the crystals grew.

Solutions of tpt (25 mg, 0.080 mmol) in chloroform (20 mL) combined with solutions of zinc nitrate hexahydrate (28 mg, 0.094 mmol) in methanol (0.5 mL) and tetraethylammonium cyanide (14.7 mg, 0.094 mmol) in methanol (0.5 mL) upon standing at room temperature for several days deposit cubic crystals of approximate composition $Zn(CN)(NO_3)(tpt)_{2/3}\cdot{}^3/_2CHCl_3\cdot{}^1/_3CH_3OH$. Anal. Calcd for $C_{14.83}H_{10.83}Cl_{4.5}N_6O_{3.33}Zn$: C, 32.3; H, 2.0; N, 15.3; Cl, 28.9; Zn, 11.9. Found: C, 32.5; H, 1.8; N, 15.5; Cl, 28.5; Zn, 11.8. These crystals have essentially the same cubic unit cell dimensions (a = 23.488(5) Å) as the tetrachloroethane-containing crystals described above, the cavities each enclosing in this case approximately 18 molecules of chloroform and four of methanol.

The circumstances presented by the framework described here are, we believe, unique. The situation is somewhat reminiscent of the sodalite minerals, but the chambers in the solid reported here are on an altogether more vast scale, containing essentially minute droplets of liquid. By sheer coincidence, 1,1,2,2-tetrachloroethane was one of the species trapped in a new molecular hemicarcerand reported recently in this journal;[8] in that case, however, the cell housed only a single inmate.

The large but sealed-off chambers reported here present unique opportunities not only for trapping all sorts of interesting species but also for conducting unusual pseudosolution chemistry, both photochemical and thermal, in minute pressure cooker reaction vessels.

Acknowledgment. The authors are very grateful to the Australian Research Council for support.

Supplementary Material Available: Crystal data and data collection, structure determination and refinement, numbering scheme, and tables of crystal data, fractional atomic coordinates, isotropic thermal parameters, and interatomic distances and angles (11 pages); observed and calculated structure factors (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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