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Design and Construction of a New Class of Scaffolding-like Materials Comprising Infinite Polymeric Frameworks of 3D-Linked Molecular Rods. A Reappraisal of the $Zn(CN)_2$ and $Cd(CN)_2$ Structures and the Synthesis and Structure of the Diamond-Related Frameworks $[N(CH_3)_4][Cu^{I}Zn^{II}(CN)_4]$ and Cu^{I}[4,4′,4″,4‴-tetracyanotetraphenylmethane]$BF_4 \cdot xC_6H_5NO_2$

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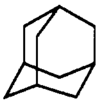
Abstract: It is proposed that a new and potentially extensive class of scaffolding-like materials may be afforded by linking together centers with either a tetrahedral or an octahedral array of valences by rodlike connecting units. Some simple general principles concerning the design and construction of these frameworks are presented together with reasons for expecting them to show unusual and useful properties. Two of the simplest conceivable systems of this type are isomorphous $Zn(CN)_2$ and $Cd(CN)_2$ whose structures have been reexamined by single-crystal X-ray diffraction, confirming the earlier description based on powder diffraction data of two interpenetrating diamond-related frameworks: cubic with space group $P\bar{4}3m$, $Z = 2$; $a = 5.9002\ (9)$ Å ($Zn(CN)_2$) and 6.301 (1) Å ($Cd(CN)_2$); two unique metal centers, one surrounded tetrahedrally by 4 C and the other by 4 N donors; MCNM rods linear; ZnC, 1.923 (6) Å; ZnN, 2.037 (5) Å; CdC, 2.099 (5) Å; CdN, 2.196 (4) Å; CN, 1.150 (5) Å in $Zn(CN)_2$ and 1.162 (5) Å in $Cd(CN)_2$. The interpenetration of separate frameworks demonstrated in these archetypal structures is likely to be a major concern in future studies of more complex scaffolding materials. The material $[N(CH_3)_4][CuZn(CN)_4]$ was deliberately designed to demonstrate one conceivable way of preventing interpenetration; its structure was determined by single-crystal X-ray diffraction: cubic, $F\bar{4}3m$, $a = 11.609\ (3)$ Å, $Z = 4$. The structure contains a single diamond-related framework with alternating tetrahedral Cu(I) and Zn(II) centers and linear rods that are very likely of the type CuCNZn with bond distances CuC, 1.877 (8) Å; and ZnN, 2.069 (15) Å. $N(CH_3)_4^+$ ions occupy half the adamantane cavities generated by the framework, the remaining cavities being vacant. Cu^{I}[4,4′,4″,4‴-tetracyanotetraphenylmethane]-$BF_4 \cdot xC_6H_5NO_2$ ($x \geq 7.7$) represents the first attempt to generate an infinite 3D framework with rods of some complexity. The structure was determined by single-crystal X-ray diffraction; tetragonal, $I\bar{4}m2$, $a = 13.620\ (2)$ Å, $c = 22.642\ (2)$ Å, $Z = 2$. The structure contains a diamond-related cationic framework with $C \cdot C_6H_4 \cdot CN \cdot Cu$ rods of length 8.856 (2) Å. The framework is tetragonally elongated along the *c* axis apparently as a result of nonbonded interactions between the eight ortho-hydrogen atoms around the methane carbon centers. There is no interpenetration. The framework generates very large admanantane-like cavities occupied by disordered $C_6H_5NO_2$ (at least 7.7 molecules per Cu) together with BF_4^- ions. The crystals undergo ready anion exchange. The material is unusual in that approximately two-thirds by volume of what is undoubtedly a crystal is effectively liquid. The results provide confidence that a wide range of scaffolding-like solids should prove accessible.

In this section we present some simple structural ideas that appeared to us to have far-reaching implications with regard to the deliberate design and construction of a new and potentially extensive class of solid materials with infinite framework structures resembling scaffolding. We also put forward sensible reasons for expecting these new materials to show unusual and useful properties. The synthetic and crystallographic results presented in later sections represent some of our early attempts at the deliberate construction of infinite 3D frameworks. The results obtained provide considerable encouragement that a wide range of materials with scaffolding-like structures should prove synthetically accessible.

We propose that infinite, ordered frameworks may form spontaneously, if ways can be devised of linking together centers with either a tetrahedral or an octahedral array of valencies by rodlike connecting units. Some classes of centers and molecular rods that could conceivably be linked together to form these frameworks are considered below. We were mindful of the distinct risk that such polymerizing systems could lead to irregular linking up of units, giving amorphous materials of indefinite composition (e.g., with many internal "loose ends"). Nevertheless, the probability that ordered, truly crystalline structures might spontaneously assemble appeared to us sufficiently high to make some trial syntheses worthwhile. Frameworks constructed from tetrahedral centers might reasonably be expected to adopt a structure based on either the cubic diamond lattice or the hexagonal Lonsdaleite lattice with each C–C bond of the prototype replaced by a molecular rod; those constructed from octahedral centers should yield a simple cubic lattice related to α-polonium.

These frameworks would generate a regular array of cavities, interconnected by windows. The cavities could be described as adamantane-like (I) in the cubic diamond-related lattices and iceane-like (II) in the hexagonal Lonsdaleite-related lattices.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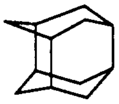
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When models of 3D networks based on tetrahedral centers are constructed, a very striking feature is the relatively large size of the cavities and windows produced even by rods of only modest length. For rods of a given length and "radius" the frameworks built from tetrahedral centers generate much bigger cavities and access windows than those based on octahedral centers. For this reason we have chosen in our initial studies to concentrate on tetrahedral-based systems, but the considerations presented below can readily be applied to the systems based on octahedral centers.

Lattices of this general type appeared to offer a number of features, listed below, of sufficient potential interest and utility to warrant attempting some exploratory syntheses:

(a) Diffusion of various species, molecular or ionic, throughout the structure may be facile, and such materials may therefore have interesting molecular sieve properties and, with rods carrying

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charges, may show ion-exchange properties.

(b) Despite Nature's abhorrence of a vacuum it may be possible to devise rods with sufficient rigidity to support the existence of solids with relatively huge empty cavities. Materials combining good or even high thermal, chemical, and mechanical stability with unusually low density may thereby be afforded.

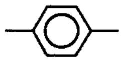
(c) Relatively unimpeded migration of species throughout the lattice may allow chemical functionalization of the rods subsequent to the construction of the framework. The introduction of one or more catalytic centers per rod may thereby be straightforward. The very open structure should again ensure both easy access of substrates to catalytic sites and ready release of catalytic products. Materials for heterogeneous catalysis of great potential utility may thereby be provided. Even with only one catalytic center attached to each rod, each chamber would on average enclose more than one catalytic center (e.g., in the diamond-related lattice there would on average be two catalytic centers per adamantane chamber and in the simple cubic lattice three catalytic centers per chamber). Cooperative action between sites may therefore be feasible.

The materials proposed here have some features in common with existing cross-linked polymers. However, they promise ordered structures with the distinct advantage of being amenable to X-ray crystallographic analysis and offer much better prospects for precise control of the environment of individual catalytic sites, since they possess site reproducibility in contrast to the random, variable local environments provided by cross-linked polymers. They clearly have features in common with zeolites, which have attracted intense interest arising from their diverse applications as catalysts and molecular sieves. The materials we propose here in principle offer bigger cavities, better access, a greater "concentration" of active sites and more widely variable functionalization of the matrix than cross-linked polymers or zeolites.

The mere demonstration that it is possible deliberately to assemble rodlike components into a scaffolding structure with chambers and windows of considerable size seemed to us to constitute a very significant first step in attempts to open up this new area of chemistry.

Some general approaches to the construction of frameworks based on tetrahedral centers are (a) to link together units with a prefabricated array of tetrahedrally disposed minirods by some appropriate linear end-to-end connecting process, (b) to use rodlike units reactive at both ends to link together tetrahedral centers by some appropriate substitution process occurring at the tetrahedral center, and (c) to link together units with an already intact tetrahedral array of minirods by a substitution process at a second sort of tetrahedral center.

With regard to the choice of rods, the following simple molecular units, or combinations thereof, which provide the required collinear bonds might be considered and others no doubt could be readily conceived: (1) *p*-phenylene units (III) or related heterocyclic units such as IV and V; (2) acetylene units (–C≡C–) and related linear triply bonded systems such as –C≡N→M or –N≡C–M; (3) fused 5/6/5 planar ring systems such as VI; (4) metal centers disubstituted in a linear fashion, –X→M←X–, where the two monodentate donors, X, are trans and are linear at X (e.g., a nitrile, an isonitrile, or a 4-substituted pyridine) and where the metal, M, is either two-coordinate, square planar, or octahedral; (5) bis-chelated metal centers such as VII (where M could be square planar or tetrahedral) and VIII (where M is octahedral).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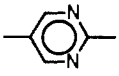

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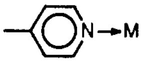

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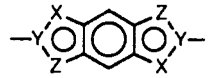

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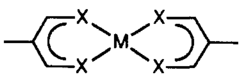
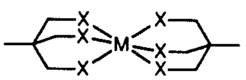


VII



VIII

Many of these possible candidates suffer from the potential deficiency of too readily undergoing some reaction or other to become nonlinear, leading to collapse of the framework; e.g., the linear two-coordinate metal centers may take on extra ligands or the acetylene units may undergo some reaction at the reactive C≡C.

Coordinate bond formation seemed a most attractive process, at least for initial studies, for the framework building step, especially when advantage could be taken of the stability offered by chelate ring formation. A particularly favorable aspect of the coordinate bond forming step is that it is generally reversible; this feature could be important in the building up of an ordered, truly crystalline arrangement, the growing structure being able, if a "wrong" step is taken, first to "backtrack" to eliminate the error and then to continue the orderly build up.

The choice of tetrahedral centers would depend in part on the framework building process to be used. For the approaches using centers with an already intact tetrahedral array of minirods, approaches a and c above, both 4,4′,4″,4‴-tetrasubstituted tetraphenylmethanes (or silane analogues etc.) and 1,3,5,7-tetrasubstituted adamantanes (or adamantane analogues) show promise. For initial studies we have set aside the adamantane possibilities because the required functionalization appeared to be potentially more difficult than with the tetraphenylmethanes; however, in the long term the adamantane-linked frameworks may prove very useful because of the great intrinsic stability of this C_{10} nucleus. For the framework building approach, approach b above, via substitution at a tetrahedral center by rodlike species reactive at both ends, metal centers with a preference for tetrahedral coordination are obvious choices; however, it is not easy to find metal centers for which one can be certain of generating the intended tetrahedral array, for often alternative coordination numbers are adopted unpredictably.

We describe below what we believe to be the first example of a deliberately designed and constructed single infinite framework consisting of tetrahedral centers linked together by polyatomic rodlike segments of some complexity. A brief, preliminary report concerning this structure has already been published.[1] The considerations presented above indicate how enormous is the range of different conceivable approaches to these infinite frameworks. For our first attempt the approach we chose on the basis of its apparent simplicity and lack of obvious pitfalls was to substitute the acetonitrile ligands of $Cu^I(CH_3CN)_4^+$ by the previously unknown 4,4′,4″,4‴-tetracyanotetraphenylmethane.

One of the simplest imaginable approaches to the sorts of frameworks proposed here is to use a diatomic bifunctional rod such as C_2^{2-} or CN^- with a considerable preference for binding metals at each end in a linear fashion, together with a metal center with a preference for a tetrahedral arrangement of ligands. Such a combination is to be found in $Zn(CN)_2$ and $Cd(CN)_2$ whose isomorphous structures were proposed on the basis of X-ray powder diffraction data almost 50 years ago.[2,3] Because of the archetypal importance of these structures and because of their important implications with regard to the construction of more elaborate frameworks, we have undertaken the determinations of the crystal structures of $Zn(CN)_2$ and $Cd(CN)_2$ using contemporary single-crystal X-ray diffraction methods. Diamond-based frameworks with linear MCNM rods and tetrahedral metal centers are indeed present, but the crystal consists of *two* such frameworks, entirely independent of one another and interpenetrating on a grand scale. Each framework effectively fills all the adamantane chambers of the other. Details of these structures are described below.

The fact that zinc and cadmium cyanides prefer to crystallize in the form of two independent interpenetrating frameworks rather than a single framework suggests that such interpenetration may well be a common outcome of the framework building attempts proposed here, in which case the large chambers of so much potential interest would be lost (or at least drastically reduced in size). Nevertheless, the interpenetrating structures themselves would constitute a significant new class of solids that may for example show unusual physical and mechanical properties and

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[1] Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1989**, *111*, 5962.
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that would undoubtedly be worth constructing and studying.

The length to radius ratio of the rods will clearly have an influence on whether or not interpenetrative growth occurs; in general, it would be expected that the larger this ratio, the more likely would interpenetration be. It may be possible in some cases to control whether crystal growth is interpenetrative or not by the deliberate imposition of chosen constraints on the system. Thus, a material that otherwise would crystallize in the form of interpenetrating frameworks could possibly be induced to form a single framework of either the cubic diamond-related type or the hexagonal Lonsdaleite-related type by providing in the crystallizing medium suitable templating molecules of the correct shape and size to fit snugly into the appropriate chambers. With frameworks carrying an overall charge the possibility of influencing the mode of crystal growth is more obvious; large counterions may make interpenetration of a second framework simply impossible, while smaller counterions may allow it.

The relative simplicity of metal cyanide systems makes them attractive models for the exploration of some of these possible factors that may influence or control interpenetration. For example, it may be possible to induce the Zn^{2+}/CN^- system or the Cd^{2+}/CN^- system to grow as single frameworks of either the cubic diamond type or the hexagonal Lonsdaleite type by crystallizing them from a medium containing molecular templates designed to fit snugly into the adamantane or iceane cavities, respectively. Since we embarked on this exploratory tinkering with 3D cyanide structures, a report has recently appeared of a single diamond-related $Cd(CN)_2$ framework with CCl_4 molecules occluded in the adamantane cavities.[4] We have been conducting similar experiments with $Cd(CN)_2$ and have discovered a single 3D framework that generates infinite channels of large cross section.[5] Extensive studies have been carried out on host-guest structures involving cyanide containing 3D frameworks.[6,7] We report below an example of a single, diamond-related, cyanide-linked framework that carries an overall negative charge, achieved by substituting every other Zn^{2+} of a single $Zn(CN)_2$ framework by Cu^+. Simple space-filling considerations suggested that the tetramethylammonium ion might be accommodated nicely within the framework. The structure of $[N(CH_3)_4][Cu^IZn^{II}(CN)_4]$ is described below.

Experimental Section

Zinc Cyanide Crystals. A solution of $Zn(CH_3CO_2)_2 \cdot 2H_2O$ (0.47 g) in water (10 mL) was placed in a glass tube (10 mm × 600 mm). A "buffer zone" of water (3 mL) was carefully introduced on top of the zinc solution, keeping mixing to a minimum. A solution of acetone cyanohydrin (1 mL) in water (10 mL) was likewise carefully introduced on top of the buffer zone. After the mixture had been standing for 2 days, zinc cyanide crystals grew in the mixing zone generally as octahedra truncated at one apex but in some cases as untruncated octahedra or as square pyramids.

Cadmium Cyanide Crystals. $Cd(NO_3)_2 \cdot 4H_2O$ (6.32 g, 22 mmol) in water (40 mL) was added to a stirred solution of NaCN (2.21 g, 45 mmol) in water (20 mL) at room temperature whereupon an amorphous colorless solid precipitated. When the suspension was filtered under gravity through a fluted Whatman no. 1 filter paper, the filtrate emerged turbid. The filtrate was returned to the filter paper repeatedly until it emerged clear and free from turbidity. On standing at room temperature the clear filtrate deposited large single crystals of $Cd(CN)_2$ generally as octahedra truncated at one apex but in some cases as untruncated octahedra.

$[N(CH_3)_4][CuZn(CN)_4]$. A solution of $Cu(CH_3CN)_4BF_4$ (0.314 g, 1 mmol) in acetonitrile (4 mL) was added to a stirred, boiling solution containing zinc cyanide (0.117 g, 1 mmol), sodium cyanide (0.155 g, ca. 3.2 mmol), and tetramethylammonium tetrafluoroborate (0.186 g, 1.16 mmol) in water (30 mL). A colorless precipitate formed immediately. After the mixture had cooled to room temperature, the solid was collected, washed well with water, and dried under vacuum at room temperature. Yield, 0.269 g. Recrystallization from water gave $[N(CH_3)_4][CuZn(CN)_4]$ as highly refracting, regular tetrahedra suitable for crystallography. Anal. Calcd for $C_8H_{12}N_5CuZn$: C, 31.3; H, 3.9; N, 22.8. Found: C, 31.5; H, 3.9; N, 23.0.

4,4′,4″,4‴-Tetrabromotetraphenylmethane. Iron powder (2.55 g, 46 mmol) was added to a stirred suspension at room temperature of tetraphenylmethane (12.3 g, 38 mmol) in carbon tetrachloride (100 mL) containing dissolved bromine (9.3 mL, 29 g, 180 mmol). After 1–2 min evolution of HBr was apparent and all the tetraphenylmethane dissolved. After 30 min the reaction was quenched by adding ethanol (400 mL). The precipitated solid was collected, washed with ethanol, and dried in air. The crude product in boiling carbon tetrachloride (350 mL) was treated with decolorizing charcoal (2 g) for 10 min. The suspension was filtered while hot and the filtrate was evaporated to 150 mL when boiling ethanol (600 mL) was added. After the mixture had been allowed to cool and stand, the crystals that had separated were collected and recrystallized from boiling xylene (mixture of isomers). (Dimethylformamide was found to be an equally satisfactory recrystallizing medium.) Yield, 15.9 g, 65%. Anal. Calcd for $C_{25}H_{16}Br_4$: Br, 50.3. Found: Br, 50.3. ^1H NMR ($CDCl_3$): clean symmetrical 12-component AA′BB′ pattern indicative of para substitution with the major "quartet" components at 7.44, 7.35, 7.05, and 6.96 ppm. MS (*m/e*) (70 eV, EI): a group of peaks of 632 (3.9%), 633 (1.1%), 634 (17.2%), 635 (4.9%), 636 (24.7%), 637 (6.0%), 638 (16.0%), 639 (4.2%) showed a pattern consistent with the presence of four Br in $C(C_6H_4Br)_4^+$, calcd for $^{12}C_{25}{}^1H_{16}{}^{79}Br_4$, 632; a group of peaks at 477 (35.5%), 478 (7.4%), 479 (96.6%), 480 (18.9%), 481 (100%), 482 (19.6%), 483 (31.7%), 484 (6.3%) showed a pattern consistent with the presence of three Br in $C(C_6H_4Br)_3^+$, calcd for $^{12}C_{19}{}^1H_{12}{}^{79}Br_3$, 477.

4,4′,4″,4‴-Tetracyanotetraphenylmethane. A mixture of cuprous cyanide (0.95 g, 10.6 mmol) and 4,4′,4″,4‴-tetrabromotetraphenylmethane (1.28 g, 2.0 mmol) in DMF (2.5 mL) was heated with stirring under reflux for 3.5 h. A mixture of ethanol (8 mL) and aqueous ferric chloride (60% solution, 8 mL) was added to the reaction mixture after it had cooled to room temperature. The resulting mixture was heated to the boiling point briefly (2 min), cooled, and then added to stirred dilute aqueous hydrochloric acid (20 mL of concentrated HCl + 80 mL of H_2O). The product was extracted with dichloromethane (100 mL, then 4 × 30 mL), and the combined extracts were washed with aqueous sodium ethylenediaminetetraacetate. The organic layer was dried over sodium sulfate, filtered, and evaporated to dryness under vacuum. The residue was purified by flash chromatography on silica gel (column diameter, 3 cm, length 15 cm, Merck Kieselgel 60) with chloroform as eluent. Recrystallization from dichloromethane–benzene gave lustrous platy needles with a bluish tinge which were collected, washed with benzene, and dried under vacuum at 100 °C. Yield, 0.53 g. Anal. Calcd for $C_{29}H_{16}N_4$: C, 82.8; H, 3.8; N, 13.3. Found: C, 82.7; H, 3.7; N, 13.0. ^1H NMR ($CDCl_3$): AA′BB′ pattern with main "quartet" components at 7.69, 7.60, 7.32, and 7.23 ppm. MS (*m/e*) (70 eV, EI): 420 (M^+, 66.4%), 318 ($M^+ - C_6H_4CN$, 100%), 215 ($M^+ - C_6H_4CN - C_6H_5CN$, i.e., the dicyanofluorenyl cation, 52.2%).

Cu^I[4,4′,4″,4‴-tetracyanotetraphenylmethane]$BF_4 \cdot xC_6H_5NO_2$. A solution of $Cu(CH_3CN)_4BF_4$ (22×10^{-3} g) and 4,4′,4″,4‴-tetracyanotetraphenylmethane·ca. $0.5C_6H_6$ (40×10^{-3} g) in acetonitrile (1.5 mL) was diluted with nitrobenzene (40 mL). The solution was allowed to evaporate at room temperature in an open beaker. Colorless transparent crystals grew over a period of 2–3 days. Some crystals were set aside for crystallographic analysis and kept moist with mother liquor. The remaining crystals were collected, washed with nitrobenzene, and dried in a stream of air until a free-running crystalline solid was obtained. Anal. Calcd for $C_{29}H_{16}BCuF_4N_4 \cdot 8.4C_6H_5NO_2$: Cu, 4.0, weight loss on removal of $C_6H_5NO_2$, 64.4%. Found: Cu, 4.2, weight loss on drying at 100 °C under vacuum, 65.4%. The dried residue was analyzed. Anal. Calcd for $C_{29}H_{16}BCuF_4N_4$: C, 61.0; H, 2.8; N, 9.8; Cu, 11.1. Found: C, 60.9; H, 3.1; N, 9.5; Cu, 11.3.

Physical Measurements and Microanalyses. NMR spectra were recorded on a JEOL FX 100 spectrometer, mass spectra on a VG70-70 spectrometer, and infrared spectra on a JASCO A-302 spectrometer. Microanalyses were performed by the Australian Microanalytical Service.

X-ray Crystallography. Crystal structure analyses, using single-crystal X-ray diffraction methods, were performed on $Zn(CN)_2$, $Cd(CN)_2$, $[N(CH_3)_4][CuZn(CN)_4]$, and Cu^I[4,4′,4″,4‴-tetracyanotetraphenylmethane]$BF_4 \cdot xC_6H_5NO_2$ ($x \geq 7.7$). The details of the data collection and structure refinement for each compound are given in Table I. Accurate cell dimensions were obtained from the setting angles of 25 carefully centered reflections using a least-squares procedure.[8] The

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[8] Enraf-Nonius. Program System for CAD-4F Diffractometer. Delft, The Netherlands, 1980.

Table I. Crystal Data Together with Details of the Data Collections and Structure Refinements for $Zn(CN)_2$, $Cd(CN)_2$, $[N(CH_3)_4][CuZn(CN)_4]$, and Cu^I[4,4′,4″,4‴-tetracyanotetraphenylmethane]$BF_4 \cdot xC_6H_5NO_2$ ($x \geq 7.7$)

compd	$Zn(CN)_2$	$Cd(CN)_2$	$[N(CH_3)_4][CuZn(CN)_4]$	$Cu[C(C_6H_4CN)_4]BF_4 \cdot xC_6H_5NO_2$ ($x \geq 7.7$)
formula	C_2N_2Zn	C_2CdN_2	$C_8H_{12}CuN_5Zn$	$C_{29}H_{16}BCuF_4N_4 \cdot xC_6H_5NO_2$ ($x \geq 7.7$)
M_r	117.41	164.44	307.14	1518.8 ($x = 7.7$)
description of crystal	colorless truncated octahedra	colorless octahedra	colorless octahedra	colorless platelike
crystal system	cubic	cubic	cubic	tetragonal
space group	$P\bar{4}3m$ (No. 215)	$P\bar{4}3m$ (No. 215)	$F\bar{4}3m$ (No. 216)	$I\bar{4}m2$ (No. 119)
a, Å	5.9002 (9)	6.301 (1)	11.609 (3)	13.620 (2)
c, Å				22.642 (2)
vol, $Å^3$	205.4 (1)	250.2 (1)	1565 (1)	4200 (2)
Z	2	2	4	2
ρ(measd), g cm^{-3}	1.852 (ref 2)	2.23 (ref 3)	1.306 (5)	>1.20
ρ(calcd), g cm^{-3}	1.898	2.183	1.304	1.20 ($x = 7.7$)
crystal dimensions (distance in mm from centroid)	±(111) 0.171 ±($\bar{1}$11) 0.135 ±(1$\bar{1}$1) 0.121 ±(11$\bar{1}$) 0.143 (010) 0.086	±(111) 0.086 ±($\bar{1}$11) 0.171 ±(1$\bar{1}$1) 0.129 ±(11$\bar{1}$) 0.150	±(111) 0.093 ±($\bar{1}$11) 0.100 ±(1$\bar{1}$1) 0.071 ±(11$\bar{1}$) 0.071	±(011) 0.025 ±(101) 0.0625 ±($\bar{1}$01) 0.0625 (001) 0.0875
temp, K	295 (1)	295 (1)	295 (1)	295 (1)
radiation and wavelength, Å	Mo Kα (graphite monochromator), $\lambda = 0.71069$			
instrument	Enraf-Nonius CAD-4F diffractometer			
no. of intensity control reflections	3 every 10000 s; no significant variation	3 every 4800 s; no significant variation	3 every 4800 s; no significant variation	3 every 10000 s; no significant variation
$F(000)$	112.0	148.0	588.0	1561.6
μ, cm^{-1}	59.0	41.8	29.0	3.0
transmission factors				
min	0.194	0.344	0.606	0.966
max	0.345	0.477	0.697	0.988
2θ limits				
min	2.0	2.0	2.0	2.0
max	65.0	65.0	55.0	36.0
hkl range				
h	$-8 \rightarrow 8$	$-9 \rightarrow 9$	$-15 \rightarrow 15$	$-1 \rightarrow 11$
k	$-8 \rightarrow 8$	$-9 \rightarrow 9$	$-15 \rightarrow 15$	$-1 \rightarrow 11$
l	$-8 \rightarrow 8$	$-9 \rightarrow 9$	$0 \rightarrow 15$	$0 \rightarrow 19$
no. of reflections measd	2520	3694	1882	1042
no. of unique reflections	171	210	222	455
R_{int}	0.042	0.018	0.018	0.028
no. of reflections used in refinement	150 [$I \geq 3\sigma(I)$]	87 [$I \geq 3\sigma(I)$]	194 [$I \geq 3\sigma(I)$]	345 [$I \geq 2\sigma(I)$]
no. of parameters	10	10	14	23
refinement	full-matrix least squares; function minimized $\sum w\Delta^2$ (SHELX-76[9])			
weighting scheme	$w = k/(\sigma_F^2 + g\lvert F_o\rvert^2)$			
final value of k	15.1	26.1	2.86	1.0
final value of g	4.8×10^{-5}	0.0	3.3×10^{-4}	5×10^{-3}
isotropic extinction param, x ($\times 10^6$)	6.3 (6)	1.6 (7)		
final R ($= \sum \lvert \Delta F \rvert / \sum \lvert F_o \rvert$)	0.028	0.036	0.034	0.170
final R_w ($= \sum w^{1/2} \lvert \Delta F \rvert / \sum w^{1/2} \lvert F_o \rvert$)	0.030	0.015	0.034	0.157
max shift/esd	0.001	0:159	0.005	0.006
max residual electron density, e $Å^{-3}$	0.46	1.00 (0.001 Å from Cd(2); elsewhere <0.6)	0.64	1.0 (0.03 Å from Cu; elsewhere <0.6)

intensity data were corrected for Lorentz, polarization, and absorption effects; absorption corrections[9,10a] were numerically evaluated by Gaussian integration to a precision of 0.5%. In the cases of $Zn(CN)_2$ and $Cd(CN)_2$ an isotropic extinction parameter, x, was included in the refinement so that F_c was modified according to $F_c(\text{cor}) = F_c(1 - xF_c^2/\sin\theta)$.[9] Crystallographic calculations were performed using the SHELX-76 system[9] on a VAX 11/780 computer at the University at Melbourne, and crystallographic diagrams were obtained using the ORTEP program.[11] Parameters for the atomic scattering curves of Cd, Zn, and Cu were taken from ref 10b whereas for the remaining atoms those incorporated in the SHELX-76 system were used. Anomalous dispersion corrections[10c] were applied to the scattering factors of all the non-hydrogen atoms. The full-matrix least-squares refinement procedure used included anisotropic thermal parameters for all of the structure determinations except that of Cu^I[4,4′,4″,4‴-tetracyanotetraphenylmethane]$BF_4 \cdot xC_6H_5NO_2$ ($x \geq 7.7$) for which individual isotropic thermal parameters were employed. Specific details concerning the structure analysis of each compound are given in the following text.

(a) $Zn(CN)_2$. A preliminary single-crystal X-ray study confirmed the primitive cubic unit cell reported by Zhdanov.[2] The diffraction data were of the Laue symmetry group $m3m$. There were no systematic absences, and no superlattice reflections were detected. Of the three space groups consistent with the diffraction data ($Pm3m$, $P432$, and $P\bar{4}3m$), $P\bar{4}3m$ proved to be the correct space group. The metal atoms were placed at the sites of $\bar{4}3m$ symmetry [(000) and ($^1/_2$, $^1/_2$, $^1/_2$)] and the C and N atoms at sites of $3m$ symmetry with coordinates of the type (x, x, x). The coordinates of the C and N atoms for the initial model were those suggested by Zhdanov ($x_C \sim 0.2$, $x_N \sim 0.3$) and the initial least-squares refinement cycles included individual isotropic thermal parameters but after these had converged anisotropic thermal parameters were employed. At convergence the Zn(1)–C and Zn(2)–N distances were 1.923 (6) and 2.037 (5) Å, respectively. Similar refinements were carried out by using as starting models (i) the coordinates suggested by Zhdanov and (ii) the coordinates obtained in the present study, with the atom types C and N reversed for both refinements. These yielded results essentially equivalent to the first with the Zn–C and Zn–N distances not significantly different from those previously obtained and again with Zn–C markedly shorter than Zn–N. A further refinement was carried out by using the coordinates obtained from the first refinement as the initial model with the atom types for C and N reversed but this time allowing only the aniso-

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[9] Sheldrick, G. M. *SHELX-76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, U.K., 1976.

[10] Ibers, J. A.; Hamilton, W. C., Eds. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV: (a) p 55, (b) p 99, (c) p 149.

[11] Johnson, C. K. ORTEP, Report ORNL-3794; Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

tropic thermal parameters to vary. Although there were no significant differences between the R and R_w values obtained for this and the first refinement, the U_{ii} values for C and N atoms were markedly less uniform [0.047 (2) and 0.073 (3) Å^2, respectively] than those obtained from the first refinement [0.053 (1) and 0.065 (2) Å^2, respectively]. This result strongly supports the C and N assignment found from the initial refinement but only a neutron diffraction study would remove all uncertainty on this point.

(b) $Cd(CN)_2$. Crystals of $Cd(CN)_2$ proved to be isomorphous to $Zn(CN)_2$ and again there was no evidence of superlattice reflections; this confirms the result of Shugam and Zhdanov.[3] A similar refinement procedure to that employed for $Zn(CN)_2$ was used employing the parameters obtained from the $Zn(CN)_2$ structure as the initial model. However, in this case attempts to distinguish between the C and N atoms were not conclusive and therefore the cyanide atom which yielded the shorter Cd–cyanide distance was assigned as the carbon atom.

(c) $[N(CH_3)_4][CuZn(CN)_4]$. The diffraction data possessed Laue symmetry *m*3*m*, with the only systematic absences being those required by *F* centering. The space groups *F*432, *F*$\bar{4}$3*m*, and *Fm*3*m* were consistent with the diffraction data; *F*$\bar{4}$3*m* proved to be the correct space group. It did not prove possible to distinguish between the Cu and Zn atoms or between the C and N atoms during the course of the refinement. The shorter metal–cyanide distance was assigned as the Cu–C bond for reasons given in the Discussion. The location of the cations in particular adamantane cavities was also consistent with this assignment, as discussed below.

(d) Cu^I[4,4′,4″,4‴-tetracyanotetraphenylmethane]$BF_4 \cdot xC_6H_5NO_2$ ($x \geq 7.7$). Crystals of this substance, which were sealed in Lindemann glass capillaries together with some mother liquor, were relatively weakly scattering but reflections were obtained to a limit of $(\sin \theta)/\lambda \sim 0.43$, suggesting that atomic resolution would be possible. The diffraction data were of the Laue symmetry group 4/*mmm*, with the only systematic absences being those required by *I* centering. Of the space groups consistent with these data (*I*4/*mmm*, *I*422, *I*$\bar{4}$2*m*, *I*4*mm*, and *I*$\bar{4}$*m*2), only *I*$\bar{4}$*m*2 yielded a solution for the structure. For this space group all of the non-hydrogen atoms of the $Cu[C(C_6H_5CN)_4]$ framework were immediately revealed by the Patterson interpretation routine of the SHELXS-86 system.[12] The positional and individual isotropic thermal parameters were refined by using the procedure stated in Table I; $R = 0.24$. Apart from two ripples (~1.4 e Å^{-3}) associated with the Cu atom, the maximum residual electron density was 0.8 e Å^{-3}. Because of the relatively high R value and poor agreement between the F_o and F_c values of some low-order reflections, all of the space groups consistent with the diffraction data were reconsidered; however, no other solution was found. There is little doubt that the anomalous features result from partial ordering or preferred orientation of the anions and solvent molecules. Six reflections (011, 031, 112, 022, 116, and 224) were excluded from the analysis because of the lack of satisfactory agreement between their calculated and observed structure factors [$\Delta F > 5\sigma(F)$]. The refinement was obtained to convergence; final R and R_w values, together with details of maximum residual electron density, are given in Table I.

Attempts to determine the density of the crystals by flotation were unsuccessful because of the rapid replacement of the nitrobenzene of solvation by the flotation medium. However, it was noted that the density of the crystals appeared marginally greater than that of nitrobenzene (1.20 g cm^{-3}), and taking this value as the minimum possible value for that of the crystals leads to 15.4 molecules of $C_6H_5NO_2$ per unit cell, i.e., at least 7.7 molecules of $C_6H_5NO_2$ per formula unit.

The density of $C_6H_5NO_2$ together with its molecular weight of 123.1 indicates that in the liquid each $C_6H_5NO_2$ molecule occupies ~170 Å^3. The volume occupied by a BF_4^- anion approximates to that of a sphere of a radius that will be close to the sum of the normal B–F covalent distance (~1.40 Å)[13] and the van der Waals radius of fluorine (~1.35 Å).[14] This yields a value of ~87 Å^3.

Therefore the total volume occupied by nonframework atoms is ~ 2790 Å per unit cell, i.e., ~66%. Assuming the residual space is occupied by the framework, the average atomic volume for the non-hydrogen atoms would be ~21 Å^3, a value typical of coordination compounds.

Results and Discussion

Zinc and Cadmium Cyanides. Crystal data for isomorphous zinc and cadmium cyanides are presented in Table I. Atomic coordinates are presented in Table II, and bond lengths and angles are given in Table III. The crystal symmetry is such that the MCNM rods are exactly linear and the metal centers precisely tetrahedral. The cubic unit cell shown in Figure 1 (for the particular case of $Zn(CN)_2$) is unusual in that apparently "unattached" metal centers are found at alternate corners. This unit cell implies the presence of two interpenetrating but com-

Table II. Final Fractional Atomic Coordinates and U_{ii}/U_{iso} Values (Å^2) for $Zn(CN)_2$, $Cd(CN)_2$, $[N(CH_3)_4][CuZn(CN)_4]$, and Cu^I[4,4′,4″,4‴-tetracyanotetraphenylmethane]$BF_4 \cdot xC_6H_5NO_2$ ($x \geq 7.7$)

	x	y	z	U_{ii}/U_{iso}
		(a) $Zn(CN)_2$		
Zn(1)	0	0	0	0.0507 (4)
Zn(2)	$^1/_2$	$^1/_2$	$^1/_2$	0.0514 (4)
C	0.1882 (6)	0.1882 (6)	0.1882 (6)	0.053 (1)
N	0.3007 (5)	0.3007 (5)	0.3007 (5)	0.065 (2)
		(b) $Cd(CN)_2$		
Cd(1)	0	0	0	0.1489 (4)
Cd(2)	$^1/_2$	$^1/_2$	$^1/_2$	0.1402 (4)
C	0.1923 (5)	0.1923 (5)	0.1923 (5)	0.1384 (5)
N	0.2988 (4)	0.2988 (4)	0.2988 (4)	0.1321 (5)
		(c) $[N(CH_3)_4][CuZn(CN)_4]$		
Cu	0	0	0	0.0492 (5)
Zn	$^1/_4$	$^1/_4$	$^1/_4$	0.0683 (7)
C(1)	0.0933 (4)	0.0933 (4)	0.0933 (4)	0.064 (2)
N(1)	0.1471 (7)	0.1471 (7)	0.1471 (7)	0.104 (2)
C(2)	0.571 (1)	0.571 (1)	0.571 (1)	0.217 (2)
N(2)	$^1/_2$	$^1/_2$	$^1/_2$	0.081 (2)
		(d) $Cu[C(C_6H_4CN)_4]BF_4 \cdot xC_6H_5NO_2$ ($x \geq 7.7$)		
Cu	0	0	0	0.057 (3)
N	0	0.119 (3)	0.054 (2)	0.114 (9)
C(1)	0	0.176 (4)	0.084 (2)	0.109 (10)
C(11)	0	0.258 (4)	0.124 (3)	0.124 (10)
C(12)	0.095 (3)	0.297 (3)	0.144 (2)	0.121 (9)
C(13)	0.093 (3)	0.380 (3)	0.188 (2)	0.124 (9)
C(14)	0	0.413 (3)	0.210 (2)	0.074 (8)
C(2)	0	$^1/_2$	$^1/_4$	0.065 (10)

Table III. Bond Lengths (Å) and Angles (deg)[a] for $Zn(CN)_2$, $Cd(CN)_2$, $[N(CH_3)_4][CuZn(CN)_4]$, and Cu^I[4,4′,4″,4‴-tetracyanotetraphenylmethane]$BF_4 \cdot xC_6H_5NO_2$ ($x \geq 7.7$)

	(a) $Zn(CN)_2$		
Zn(1)–C	1.923 (6)	Zn(2)–N	2.037 (5)
C–N	1.150 (5)		
	(b) $Cd(CN)_2$		
Cd(1)–C	2.099 (5)	Cd(2)–N	2.196 (4)
C–N	1.162 (5)		
	(c) $[N(CH_3)_4][CuZn(CN)_4]$		
Cu–C(1)	1.877 (8)	Zn–N(1)	2.069 (15)
C(1)–N(1)	1.081 (12)	N(2)–C(2)	1.42 (2)
	(d) $Cu[C(C_6H_4CN)_4]BF_4 \cdot xC_6H_5NO_2$ ($x \geq 7.7$)		
	(i) Distances		
Cu–N	2.02 (4)	C(12)–C(13)	1.51 (5)
N–C(1)	1.05 (6)	C(13)–C(14)	1.44 (4)
C(1)–C(11)	1.43 (6)	C(14)–C(2)	1.49 (4)
C(11)–C(12)	1.47 (4)		
	(ii) Angles[b]		
Cu–N–C(1)	175 (5)	C(13)–C(14)–C(13)^{I}	124 (4)
N–C(1)–C(11)	177 (6)	C(14)–C(2)–C(14)^{II}	112 (2)
C(1)–C(11)–C(12)	118 (3)	C(14)–C(2)–C(14)^{III}	105 (3)
C(12)–C(11)–C(12)^{I}	123 (6)	N–Cu–N^{IV}	111 (1)
C(11)–C(12)–C(13)	117 (4)	N–Cu–N^{V}	107 (2)
C(12)–C(13)–C(14)	119 (4)		

[a] Angles about the metal atoms in $Zn(CN)_2$, $Cd(CN)_2$, and $[N(CH_3)_4][CuZn(CN)_4]$ and N(2) in the last-mentioned compound are strictly tetrahedral (109.47°). The angles about the cyanide C and N atoms are strictly 180°. [b] Symmetry operations for $Cu[C(C_6H_4CN)_4]BF_4 \cdot xC_6H_5NO_2$ ($x \geq 7.7$): (I) $-x, y, z$; (II) $y - {}^1/_2, {}^1/_2 - x, {}^1/_2 - z$; (III) $-x, 1 - y, z$; (IV) $x, -y, z$; (V) $y, x, -z$.

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[12] Sheldrick, G. M. SHELXS-86, Program for Crystal Structure Determination. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., eds.; Oxford University Press: Oxford, U.K., 1985; p 175.

[13] Jordon, T. H.; Dickens, B.; Schroeder, L. W.; Brown, W. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 669.

[14] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

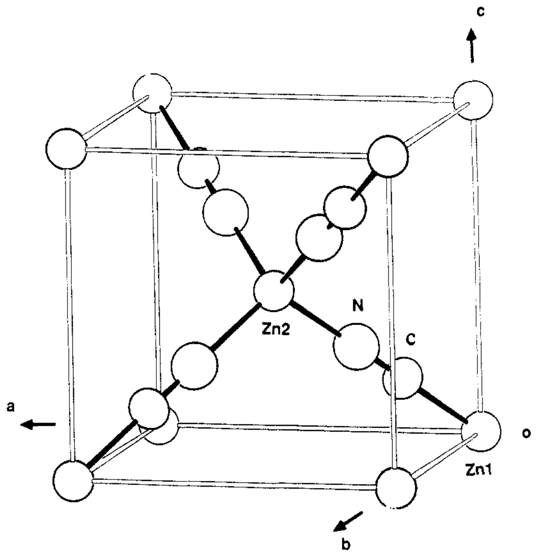

Figure 1. ORTEP for unit cell of $Zn(CN)_2$.

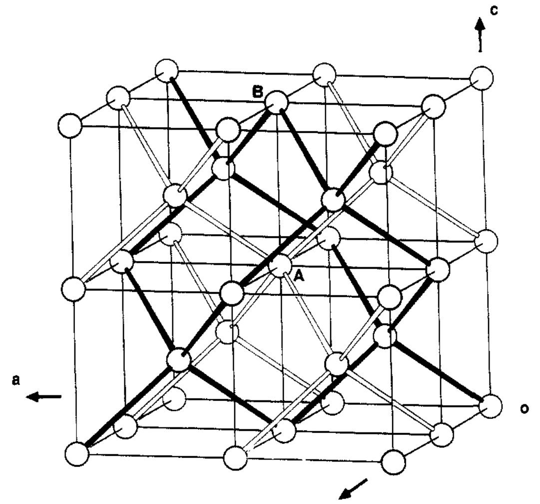

Figure 2. Representation of two independent interpenetrating diamond-related frameworks. (a) The mode of interpenetration observed for $Zn(CN)_2$ and $Cd(CN)_2$ arises when centers A and B are of the same type, i.e., when either both are C bound or both are N bound. (b) An alternative, hypothetical mode of interpenetration arises when centers A and B are of different types.

pletely independent diamond-like frameworks, the "unattached" metal centers of each unit cell belonging to the second framework, as indicated in Figure 2a. A different aspect of this beautiful but generally unappreciated structure that reveals more directly how the separate frameworks interlock is represented in Figure 3a. Every cyanide unit in the crystal projects through the middle of a cyclohexane-like window of the other framework, and at the center of every adamantane cavity of one framework is found a metal center of the second framework. Catenanes, which are single molecules consisting of independent rings interlocking like links in a chain, have attracted much attention.[15,16] The structures of $Zn(CN)_2$ and $Cd(CN)_2$ reveal multiple catenane associations between six-membered rings of independent frameworks repeated in three dimensions (Figure 3b). Passing through every ring in the structure is not one other ring as in "normal" catenanes, but six other rings belonging to the second framework; all six of these rings have in common the rod that passes through the first ring. In a general cyclization process the chance formation of a catenane-associated pair seems an intrinsically improbable event. The detailed mechanism whereby a zinc cyanide crystal assembles itself must be astonishing.

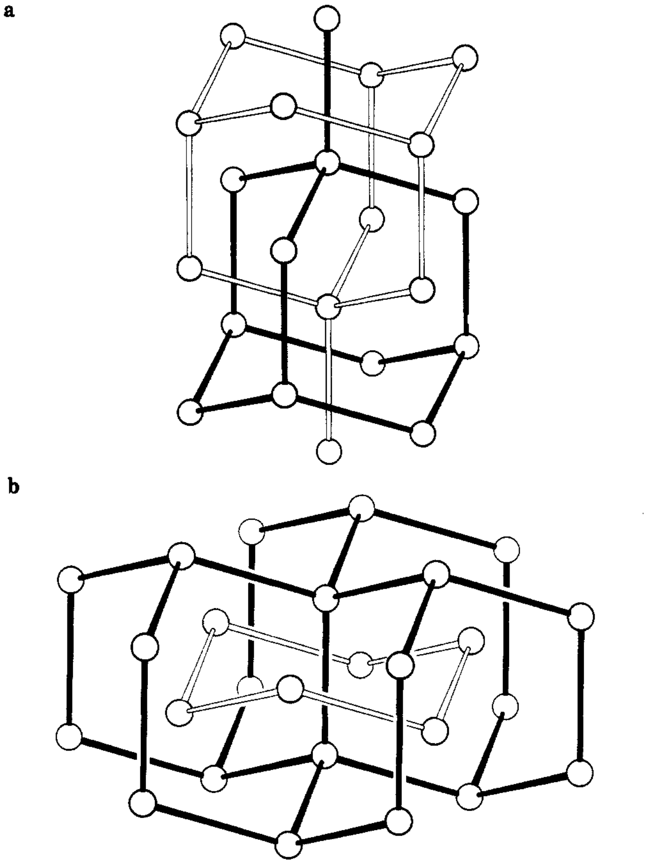

Figure 3. (a) View of interpenetrating adamantane units in $Zn(CN)_2$ and $Cd(CN)_2$. (b) View of $Zn(CN)_2$ and $Cd(CN)_2$ structures revealing multiple catenane associations.

The present structural analysis of $Zn(CN)_2$ allowed discrimination between carbon and nitrogen atoms and indicated the presence of two types of metal centers, one surrounded by four carbons, the other by four nitrogens. This feature was merely assumed in the original study based on powder data.[2] A number of infinite 3D frameworks related to Prussian Blue with octahedral metal centers and linear MCNM rods contain metal centers surrounded either entirely by carbon or entirely by nitrogen.[17] For a given metal the metal–carbon distances were shorter than metal–nitrogen distances; ZnC, 1.923 (6); ZnN, 2.037 (5); CdC, 2.099 (5); CdN, 2.196 (4) Å.

An adamantane cavity is surrounded by ten tetrahedral centers. Four of these are equivalent and are arranged tetrahedrally around the center of the chamber at a distance of one rod length. The other six, which are equivalent to each other, are arranged octahedrally around the center of the chamber at a distance of ca. 1.15 times the rod length. The presence in $Zn(CN)_2$ and $Cd(CN)_2$ of two sorts of metal centers (N bound and C bound) implies then that each separate framework generates two sorts of adamantane cavities in equal numbers. One type of cavity is surrounded by four C-bound metals and six N-bound metals, i.e., a 4C/6N cavity; the other cavities are of the 4N/6C type. The existence of two types of metal centers and two types of adamantane chambers for a given 3D framework implies that two such frameworks could conceivably interpenetrate in two different ways. The structure observed here for $Zn(CN)_2$ and $Cd(CN)_2$ represents one of these ways in which centers A and B in Figure 2 are of the same type, i.e., both C bound or both N bound. In this case every metal center of a given type is surrounded by six members of the second framework of the same type and four of the other type. In the

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[15] Schill, G. *Catenanes, Rotoxanes and Knots*; Academic Press: New York, 1971.

[16] Lipatov, Y. S.; Lipatova, T. E.; Kosyanchuk, L. F. *Adv. Polym. Sci.* **1989**, *88*, 49.

[17] Wells, A. F. *Structural Inorganic Chemistry*, 4th ed.; Clarendon Press: Oxford, U.K., 1975; p 755.

alternative, hypothetical mode of interpenetration in which centers A and B in Figure 2 are of different types, every center of a given type is surrounded by six of the other type and four of the same. Because of the asymmetrical charge distribution that is almost certain to exist within each MCNM rod, it is likely that these two alternative modes of interpenetration will have different total energies. The unit cell of the structure with the hypothetical alternative mode of interpenetration would have 8 times the volume of the observed unit cell in Figure 1.

Although the essentials of the unusual structure of Zn and Cd cyanides have been known for almost 50 years, it receives only the barest mention in many texts concerned with inorganic structure and no attention seems to have been paid to its most outstanding feature, namely, the nature of the interaction between one giant molecule and its intimate neighbor. The regions of closest contact between frameworks are where cyanide units project through a chair-form cyclohexane-like ring of six cyanides of the second framework, several instances of which can be discerned on inspection of Figure 3 (or Figure 2a). The distance of closest contact between the central cyanide and the six cyanides surrounding it is 4.17 Å for $Zn(CN)_2$ and 4.46 Å for $Cd(CN)_2$, large separations indeed for intermolecular contacts. It is likely that each cyanide unit, despite its attachment at both ends to a dipositive metal, will retain an overall partial negative charge. The component of the interframework interaction arising from nearest-neighbor contacts is therefore possibly repulsive, although van der Waals interactions between cyanide π clouds may be important. It is noteworthy that $Zn(CN)_2$ and $Cd(CN)_2$ are strictly isomorphous and that the latter does not distort and buckle in some way so as to take up the additional empty interstitial space that the significantly longer rods must generate. This additional empty space in $Cd(CN)_2$ is apparent in the rather large average volume per atom of 25 Å^3. A theoretical study of these interlocking frameworks and especially of the nature of the interactions between frameworks would be interesting and valuable.

$[N(CH_3)_4][Cu^IZn^{II}(CN)_4]$. One possible way to generate a single framework of the $Zn(CN)_2$ type and prevent interpenetration of a second is to introduce a charge onto the framework so that the required counterions then make interpenetration impossible. Copper(I) is known to give a range of tetrahedral complexes including $Cu(CN)_4^{3-}$[18] and so replacement of every other zinc(II) by copper(I) conceivably could yield a diamond-related $[CuZn(CN)_4]_n^{n-}$ framework. We were aware of the distinct possibility that the synthetic approach to this framework of simply mixing appropriate sources of Cu^I, Zn^{II}, and CN^- in 1:1:4 proportions could yield complex mixtures of insoluble $Zn(CN)_2$ and CuCN together with various cyano complex ions in solution. However, the likely preferences of Cu^I and Zn^{II} for different ends of the cyanide ion suggested that the desired framework might spontaneously assemble. The choice of a countercation that fitted snugly into the adamantane cavities also appeared to be a factor that might facilitate the spontaneous generation of the $[CuZn(CN)_4]_n^{n-}$ framework. Crude space-filling considerations suggested that the $N(CH_3)_4^+$ ion would fit well and in the presence of this ion, $[N(CH_3)_4][CuZn(CN)_4]$ was indeed spontaneously and preferentially formed. Na^+ was also present in the reaction mixture but was not incorporated into the lattice. At this stage we do not know how important the nature of the cation is in promoting the assembly of the anionic framework in preference to alternative arrangements.

The structure of $[N(CH_3)_4][CuZn(CN)_4]$ was determined by single-crystal X-ray diffraction methods. Crystal data are presented in Table I, atomic coordinates in Table II, and bond lengths and angles in Table III. The cubic unit cell is represented in Figure 4a. The $[CuZn(CN)_4]_n^{n-}$ framework is of the diamond type. Although we were unable on the basis of the present data to discriminate definitively between Cu and Zn and between C and N, it is clear that all the rods are of the type Cu–cyanide–Zn and that copper is surrounded by four atoms of the same type and zinc is surrounded by four of the other type. Bond lengths around one metal center are 1.877 (8) Å and those around the second are 2.069 (15) Å; we have tentatively assigned the shorter bond length to a Cu–C association. The four-atom rods are strictly linear.

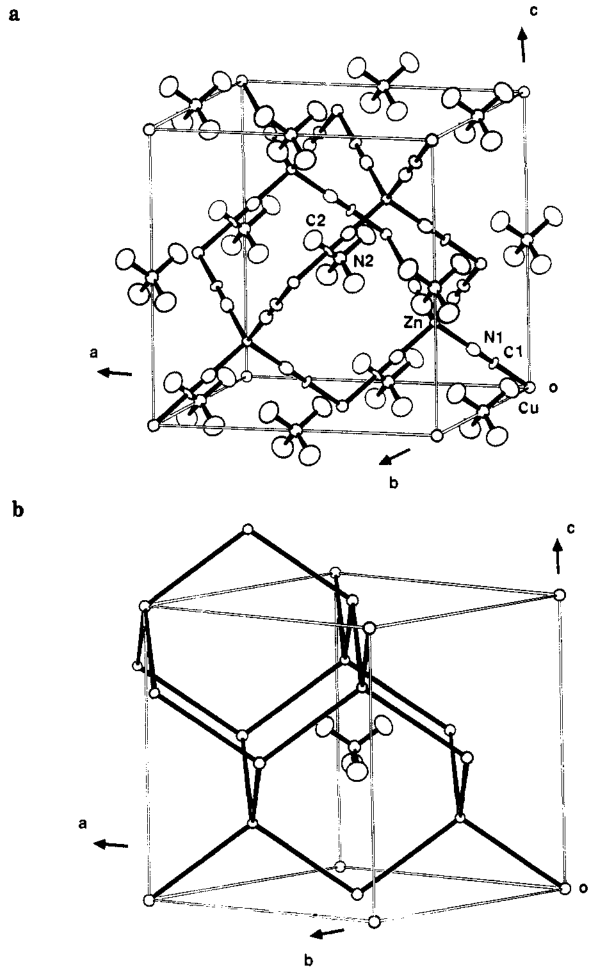

Figure 4. (a) ORTEP for the cubic unit cell of $[N(CH_3)_4][CuZn(CN)_4]$. (b) Part of the contents of the unit cell of $[N(CH_3)_4][CuZn(CN)_4]$ showing one adamantane chamber occupied by $N(CH_3)_4^+$ and one of its four vacant neighboring chambers.

A single diamond-related framework generates as many adamantane cavities as there are tetrahedral centers. Thus, only half the adamantane cavities provided by the $[CuZn(CN)_4]_n^{n-}$ framework need to be filled by $N(CH_3)_4^+$ ions for charge balance. Each adamantane chamber in a diamond-related framework shares a chair-form cyclohexane-like window with each of four neighboring cavities whose centers are arranged tetrahedrally around the center of the first. In $[N(CH_3)_4][CuZn(CN)_4]$ each adamantane cavity containing a $N(CH_3)_4^+$ is surrounded by four vacant ones and each vacant cavity is surrounded by four containing $N(CH_3)_4^+$ ions. This situation is illustrated in Figure 4b in which the central adamantane cavity of the unit cell is occupied by $N(CH_3)_4^+$, and one of its four vacant neighboring cavities is highlighted.

The $[CuZn(CN)_4]_n^{n-}$ framework generates equal numbers of two different kinds of adamantane cavities. One type, the 4Cu/6Zn type, is surrounded by $4Cu^+$ at a distance of one rod length from the center of the cavity and by $6Zn^{2+}$ at a distance of ca. 1.15 rod lengths from the center. The other cavities are of the 4Zn/6Cu type with $4Zn^{2+}$ 1 rod length from the center and $6Cu^+$ ca. 1.15 rod lengths from the center. The average charge associated with the framework surrounding a particular chamber is 0.4− for the 4Cu/6Zn type and 0.6− for the 4Zn/6Cu type. It seems likely therefore that the cations would prefer to occupy the 4Zn/6Cu chambers, although a detailed knowledge of the charge distribution within rods would be required to be certain on this point. If it is true that the cations do actually

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[18] Larson, A. C.; Cromer, D. T. *Acta Crystallogr.* **1968**, *B24*, 269.

occupy the 4Zn/6Cu chambers, the experimental data indicate that the Cu^{I}–ligand distances are 1.877 (8) Å and the Zn^{II}–ligand distances are 2.069 (15) Å. These distances would be consistent with the rod arrangement CuCNZn, which in addition would be expected on the basis of the relative hardness of the four centers involved, Cu^{I} and C being softer, N and Zn^{II} being harder.

The $N(CH_3)_4^+$ ions are oriented within the adamantane chambers with the four NC bonds directed toward the midpoints of the four cyclohexane-like windows of the chamber. The relatively high U_{ii} value for the methyl carbon atoms indicates that the CH_3 groups either are subjected to considerable thermal motion or are possibly disordered; the N centers are much less affected.

It is interesting that the adamantane cavities not occupied by $N(CH_3)_4^+$ ions appear to be totally empty. These cavities afford more than enough room for a molecule of water, the recrystallizing solvent, possibly more than one. Perhaps the cavities are less polar than might be expected on the basis of the charged groups surrounding them and perhaps a water molecule, given the choice, as the crystal is growing, of either entering such an incipient cavity or remaining in solution, prefers the latter. Once the 3D structure is completed the empty cavities are completely isolated, their four cyclohexane-like windows being blocked off by the methyl groups of $N(CH_3)_4^+$ ions in surrounding cavities.

Cu^{I}[4,4′,4″,4‴-tetracyanotetraphenylmethane]$BF_4 \cdot xC_6H_5NO_2$ ($x \geq 7.7$). The iron-catalyzed bromination of tetraphenylmethane afforded selective substitution at the four para centers as judged by ^1H NMR spectroscopy. The required 4,4′,4″,4‴-tetracyanotetraphenylmethane was obtained from the tetrabromo derivative by reaction with CuCN in refluxing *N,N*-dimethylformamide.[19]

Although solid $Cu^{I}(CH_3CN)_4BF_4$ is slowly oxidized in air to Cu^{II} products, it appears to be indefinitely stable toward air oxidation in solution in acetonitrile. Colorless crystals of Cu^{I}[4,4′,4″,4‴-tetracyanotetraphenylmethane]$BF_4 \cdot xC_6H_5NO_2$ suitable for X-ray crystallography were obtained with surprising ease, simply by allowing a solution of the tetranitrile and $Cu(CH_3CN)_4BF_4$ in a mixture of acetonitrile and nitrobenzene to evaporate slowly. Protection from the air was unnecessary. The structure was determined by X-ray crystallography using a single crystal sealed in a Lindemann tube with mother liquor, in the absence of which the crystals visibly degenerated.

Crystal data are presented in Table I. The structure contains an infinite, positively charged, diamond-related framework consisting of $C \cdot C_6H_4 \cdot CN \cdot Cu$ rods linked at somewhat distorted tetrahedral C and Cu centers. It is noteworthy that interpenetration of independent frameworks does not occur in this case. All the rods are equivalent and are 8.856 (2) Å in length. The atom numbering scheme is given in Figure 5a. Atomic coordinates are presented in Table II and selected bond lengths and angles in Table III.

The tetragonal unit cell is represented in Figure 5b. All copper and methane carbon centers are located at sites of symmetry $\bar{4}2m$. Each of the mirror planes intersecting at these sites includes the centers Cu, N, C(1), C(11), C(14), and C(2) for two of the four associated rods, such that the C_6H_4 rings of those rods are perpendicular to the mirror plane.

The framework is tetragonally distorted in the *c* direction (see Figure 5b) such that the "solid diagonal" (C to C or Cu to Cu) across an adamantane unit is 22.64 Å in this direction and is 19.26 Å in the two perpendicular directions. This distortion appears to originate at the methane centers where nonbonded interactions between eight ortho hydrogens dictate the geometry. Of the six bond angles around the methane carbon center, two (those bisected by the *c* axis) are reduced to 105° and four are increased to 112° as indicated in Figure 5b. If the rods were strictly linear, this distortion would be exactly reproduced at the copper centers but slight bending of the rods (see Table III) reduces the distortion at the copper so that the two bond angles bisected by the *c* axis are 107° and the other four are 111°.

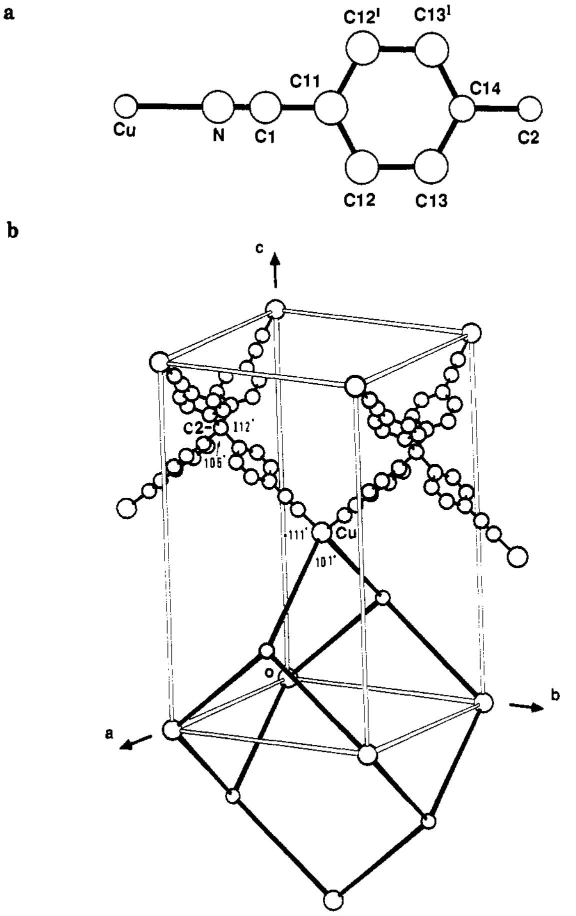

Figure 5. (a) ORTEP and atom numbering scheme for the $\{Cu^{I}$[4,4′,4″,4‴-tetracyanotetraphenylmethane]$\}_n^{n+}$ framework; the superscript I refers to the symmetry operation ($-x$, y, z). (b) Structure of $\{Cu^{I}$[4,4′,4″,4‴-tetracyanotetraphenylmethane]$\}_n^{n+}$ framework. One complete tetragonal unit cell together with parts of adjoining cells is shown. Larger circles denote Cu atoms. An adamantane cavity tetragonally elongated along the *c* axis with its center at the center of the basal face of the complete unit cell is highlighted.

The experimental data were consistent with the presence in the large intraframework spaces of essentially liquid nitrobenzene together with disordered BF_4^- ions. The high *R* value is a direct consequence of the unusual nature of this material, arising from the fact that the relatively large amount of almost liquid nitrobenzene has some slight order which at this stage we are unable to model. This high *R* value gives a misleadingly poor impression of the reliability of the structure of the ordered minor fraction of the crystal, namely, the framework. The framework structure is beyond question because the positions of all the non-hydrogen framework atoms were immediately obtained from the Patterson map for the space group $I\bar{4}m2$ and these atoms were very well resolved in the subsequent electron density maps. Moreover, all the bond distances and angles and the entire 3D arrangement of the framework thus revealed were in complete accord with the intended structure and chemical common sense. The framework structure and the cavities it generates are the aspects of major interest; the uncertainty about the $C_6H_5NO_2$ and BF_4^- ions is a minor concern.

Two different types of adamantane cavities, namely, Cu_4C_6 and Cu_6C_4, are present in equal numbers. The average framework charge per cavity is 0.4+ for Cu_4C_6 and 0.6+ for Cu_6C_4. There are twice as many adamantane cavities as BF_4^- ions. Presumably, the BF_4^- ions would prefer to occupy the more positively charged Cu_6C_4 cavities but no crystallographic evidence for their location was forthcoming. We estimate that the value of *x*, the number of nitrobenzene molecules per formula unit, is at least 7.7 and that the volume occupied by the cationic framework is only approximately one-third of the total. This is an unusual material;

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[19] Friedman, L.; Shechter, H. *J. Org. Chem.* **1961**, *26*, 2522.

it is undoubtedly crystalline, having plane faces and sharp edges and giving an X-ray diffraction pattern and yet approximately two-thirds of its volume is occupied essentially by liquid.

When the crystals of Cu^{I}[4,4′,4″,4‴-tetracyanotetraphenylmethane]$BF_4 \cdot xC_6H_5NO_2$ were collected from the reaction mixture, washed with nitrobenzene, and dried a stream of air until a free-running solid was obtained, the IR spectrum (KBr disk) of the solid so obtained showed a very sharp $\nu_{C\equiv N}$ at 2240 cm^{-1}, major nitrobenzene bands at 705, 1345, and 1520 cm^{-1}, and a strong BF_4^- band at 1060 cm^{-1}. Positions of minor bands arising from the tetranitrile moiety and from the nitrobenzene were very similar to those observed for the tetranitrile alone (KBr disk) and nitrobenzene alone (liquid film). The crystals appeared, under the microscope, to retain their external faces and edges and their internal transparency after suspension in a solution of NBu_4PF_6 (large excess) in nitrobenzene. However, the IR spectrum of the crystals after such treatment showed complete replacement of the initially strong BF_4^- band at 1060 cm^{-1} by an intense band at 830 cm^{-1} together with a medium band at 560 cm^{-1}, both associated with PF_6^-, the rest of the spectrum being essentially unchanged.

Conclusions

It is very likely that interpenetration of independent 3D frameworks of the sort observed for the archetypal $Zn(CN)_2$, and possibly of other types that can be envisaged, will be a major concern in future attempts to construct scaffolding structures with more complex rods. The deliberate construction of a single diamond-related framework in $[N(CH_3)_4][CuZn(CN)_4]$ demonstrates the potential usefulness of simple metal cyanides for the exploration of some of the possible factors influencing or controlling interpenetration. The first deliberately designed material constructed from rods of some complexity, namely, Cu^{I}[4,4′,4″,4‴-tetracyanotetraphenylmethane]$BF_4 \cdot xC_6H_5NO_2$ proves to be unusual, approximately one-third of its volume consisting of an ordered framework which imposes crystallinity on the substance, the other two-thirds being essentially liquid. There is currently much interest in widening the range of the potential catalytic applications of zeolites by synthesizing new examples with larger pores and cavities. We note that the small fraction of space occupied by the Cu–tetranitrile framework in the present example compares most favorably in this respect with available zeolites. This particular framework was designed with the prime purpose of demonstrating general possibilities in a way that combined synthetic simplicity with likelihood of success. A wide range of general synthetic approaches to a variety of different frameworks are presented here. On the basis of this preliminary work the prospects look good for generating many new, unusual and possibly useful materials.

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Supplementary Material Available: Tables S-I to S-IV listing observed and calculated structure factors for $Zn(CN)_2$, $Cd(CN)_2$, $[N(CH_3)_4][CuZn(CN)_4$, and Cu^{I}[4,4′,4″,4‴-tetracyanotetraphenylmethane]$BF_4 \cdot xC_6H_5NO_2$ ($x \geq 7.7$) (7 pages). Ordering information is given on any current masthead page.

(μ-Oxo)(μ-carboxylato)diiron(III) Complexes with Distinct Iron Sites. Consequences of the Inequivalence and Its Relevance to Dinuclear Iron–Oxo Proteins

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Abstract: A new family of (μ-oxo)(μ-carboxylato)diiron(III) complexes has been synthesized with use of the tetradentate tripodal ligand tris(2-pyridylmethyl)amine (TPA) with benzoate, acetate, and diphenyl phosphate as bridging ligands. $[Fe_2(TPA)_2O(OBz)](ClO_4)_3 \cdot 2H_2O$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.669$ (15) Å, $b = 19.568$ (20) Å, $c = 22.285$ (12) Å, and $\beta = 102.24$ (8)°. The structure was determined at −84 °C from 5445 out of a total of 8854 reflections with $R = 0.064$ and $R_w = 0.080$. $[Fe_2(TPA)_2O(OAc)](ClO_4)_3 \cdot H_2O \cdot (CH_3COCH_3)$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 20.774$ (46) Å, $b = 22.312$ (5) Å, $c = 10.372$ (7) Å, and $\beta = 104.14$ (12)°. The structure was determined at −88 °C from 6324 out of a total of 9147 reflections with $R = 0.078$ and $R_w = 0.091$. $[Fe_2(TPA)_2O(O_2P\{OPh\}_2)](ClO_4)_3(CH_3COCH_3)$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.82$ (1) Å, $b = 13.32$ (1) Å, $c = 18.03$ (1) Å, $\alpha = 92.67$ (5)°, $\beta = 94.48$ (5)°, and $\gamma = 94.22$ (5)°. The structure was determined at −83 °C from 6931 out of a total of 9885 reflections with $R = 0.049$ and $R_w = 0.061$. These crystal structures establish the presence of a doubly bridged diiron core with distinct iron sites. On one iron, the amine nitrogen of TPA is trans to the oxo bridge, while one of the pyridines is trans to the oxo bridge on the other iron. These complexes exhibit electronic and Mössbauer spectral features and magnetic properties that are very similar to those of (μ-oxo)diiron(III) proteins as well as (μ-oxo)bis(μ-carboxylato)diiron(III) complexes, demonstrating that these properties are not significantly affected by the number of carboxylate bridges and the inequivalence of the iron sites. The iron(III) sites remain distinct in solution as evidenced by ^{1}H NMR and resonance Raman spectroscopies. The inequivalence is manifested in the resonance Raman spectra as an enhancement of the ν_{as}(Fe–O–Fe) intensity, which is comparable to those found for (μ-oxo)diiron(III) proteins such as methemerythrin and ribonucleotide reductase.

The (μ-oxo)bis(μ-carboxylato)diiron(III) unit is well established in the structure of hemerythrin in its met and oxy forms.[2] The active site of this invertebrate dioxygen carrier has been the focus of an intense modeling effort by several groups with a variety of

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