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A Nanoporous Metal–Organic Framework Based on Bulky Phosphane Ligands**

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Metal–organic frameworks are polymer networks consisting of metal ions connected by organic bridging ligands, and they represent a new approach to the synthesis of nanoporous materials.[1–11] Applications are therefore anticipated as novel molecular sieves, sensors, ion-exchangers, and catalysts.[1–10] However, mutual interpenetration of the polymer networks, whereby the vertices of one occupy the cavities of another,[8, 12] often frustrates attempts to generate large accessible pores. Whereas all previous work in this field has featured N- or O- donor bridging ligands, we report novel results with a bulky triphosphane 1,3,5-tris(diphenylphosphanyl)benzene (**L**; see Figure 1 a).[13, 14] The use of the ligand **L** unexpectedly gave a non-interpenetrating network polymer $[\mathrm{Ag_4}\mathbf{L}_3(\mathrm{O_3SCF_3})_4]$ (**1**) with remarkably wide (1.60–1.84 nm) channels. In the as-synthesized state these channels appear to be saturated with solvent, which can be exchanged for other solvents, which can be removed by heating under vacuum without collapse of the metal–phosphane framework. The network bulk, imparted by the phenyl groups of **L**, seems to disallow network interpenetration. Because a P-donor ligand was used, ^{31}P NMR spectroscopy gives insight into solution-state precursors, which appear to be discrete coordination cages.

We have investigated the coordination-cage and polymer chemistry of multidentate phosphane silver complexes.[15a–d] For example, the flexible triphosphane $\mathrm{CH_3C(CH_2PPh_2)_3}$ (triphos) unexpectedly gave the hexasilver adamantanoid cage $[\mathrm{Ag_6(triphos)_4(triflate)_4}]^{2+}$ (triflate = trifluoromethanesulfonyl).[15a] Given the differences in behavior of flexible[16] and rigid[15b,c] diphosphanes, we were interested in how the rigid triphosphane **L** would behave. Polymer **1** was obtained by diffusing diethyl ether into a chloroform–nitromethane solution containing a 3:2 molar ratio of silver trifluoromethanesulfonate (silver triflate, AgOTf) and **L**. Polymer **1** was initially isolated as hexagonal crystals in 10% yield, the remainder of the product being a powder which X-ray diffraction showed to be amorphous.[17] A single-crystal X-ray analysis of **1**,[18] performed on a crystal which was mounted rapidly after removal from the supernatant, and cooled to 120 K, revealed a two-dimensional network of hexagonal rings (Figure 1 b). The large 72-atom rings contain 18 silver atoms and 12 **L** units. The network nodes are trigonal-planar silver centers bonded to three **L** units, with neighboring triflate anions which are too distant for significant bonding interactions (Ag⋯O distance 3.25(1) Å). The connectors between the nodes are $\mathrm{Ag_2}\mathbf{L}_2$ groups which have a 12-membered ring structure. The pairs of silver centers in these smaller rings each bond to two P atoms and are bridged by two weakly coordinated triflate anions, each making two Ag⋯O contacts of 2.73(1) and 2.93(1) Å. The $\mathrm{CF_3}$ groups of these triflate anions point towards the centers of the large rings, to give a transannular F⋯F distance of 19.01(3) Å, which corresponds to approximately 16.0 Å when the van der Waals radius of fluorine (1.47 Å[19]) is taken into account. The transannular H⋯H distance between phenyl groups is 20.8 Å, which gives a major ring diameter of around 18.4 Å when the H van der Waals radius of 1.20 Å[19] is taken into account. The honeycomb layers stack in an eclipsed fashion, so that a three-dimensional structure of approximately cylindrical channels is generated. A space-filling representation of a segment of the framework (nine channels and five layers), which includes the phenyl groups, is shown in Figure 1 c. These channels are amongst the widest reported so far for a coordination network. In fact, the calculated "free sphere" (i.e. the largest sphere which could move freely throughout the structure, a parameter introduced by Yaghi and co-workers[20]) of diameter 16.0 Å may be the largest of any characterized crystal. Of note is the superficial similarity of **1** to the liquid crystal templated $\mathrm{SiO_2}$-framework MCM-41s,[21, 22] which have channel diameters of around 15 to 100 Å, but are not ordered at the atomic level. Based on a spherical

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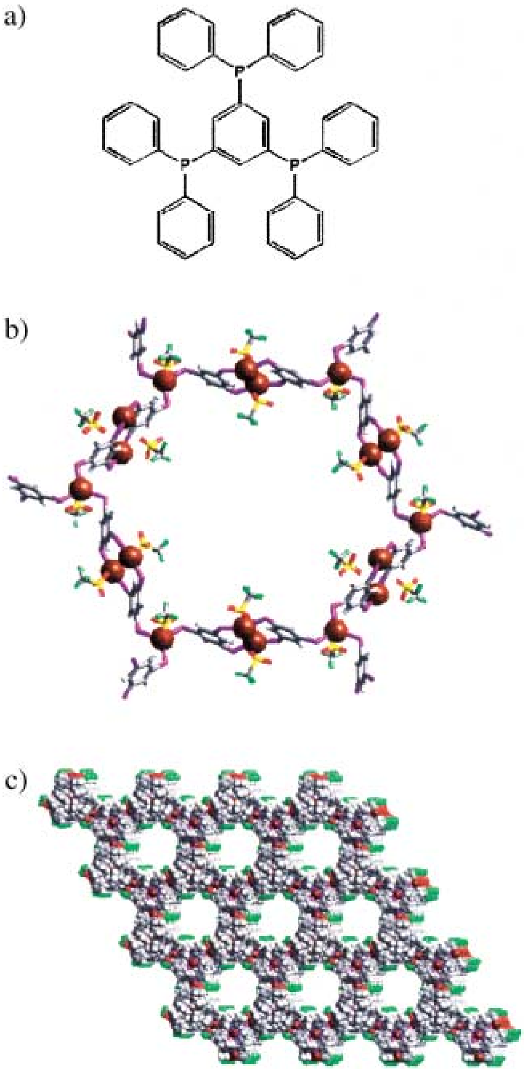

Figure 1. a) Structure of ligand **L**; b) hexagonal network structure of polymer **1** (the bulky phenyl substituents are omitted for clarity); c) space-filling view of a crystal segment of **1** showing the channel structure (C = gray, H = white, P = pink, F = green, Ag = brown, S = yellow, O = red).

1.20 Å probe, the accessible volume is 35.7% ($0.37\ cm^3 g^{-1}$) of the total, and the accessible channel surface area is 2015 $Å^2$ per unit cell ($1032\ m^2 g^{-1}$). The X-ray analysis revealed only electron-density peaks corresponding to less than one electron $Å^{-3}$ in the channel space. These peaks presumably result from disordered solvent molecules (see below), the presence of which is supported by the relatively high R factor of 0.0906. Yields of polymer **1** increased to 50–80% by using the appropriate 4:3 AgO_3SCF_3:**L** stoicheiometry in 3:7 nitromethane:ethanol as solvent. This solution was partially evaporated at 88 °C to give a mixture of block and hexagonal crystals together with some amorphous material.[17] After removing these crystals from their supernatant solution, they were washed with ethanol and kept under ambient conditions for 48 h. A single-crystal X-ray analysis on a block[23] yielded essentially the same structure as **1** in which the largest electron-density peak within the channels was 0.86 electrons $Å^{-3}$, although with a slightly lower R factor of 0.0632. The structural homogeneity of the crystalline product was supported by powder X-ray diffraction, which gave a pattern matching that calculated from the single-crystal structure determination. The crystals appeared indefinitely stable when immersed in alcohols, diethyl ether, water, aromatic, and chlorinated solvents, but were dissolved by acetonitrile.

Although the elemental analysis of the as-synthesized compound could be fitted to the formula $[Ag_4\mathbf{L}_3(O_3SCF_3)_4]\cdot(CH_3NO_2)_{1-2}$, it should be noted that since the carbon content of ethanol is very close to that of the framework, this formula likely to be misleading (see below). Thermogravimetric analysis (TGA) showed 2% weight loss on heating to 80 °C (at a heating rate of $10\,^{\circ}C\,min^{-1}$), which corresponds to the loss of one nitromethane molecule per $[Ag_4\mathbf{L}_3(O_3SCF_3)_4]$ formula unit, before rapid weight loss began at 400 °C. The disparity between this result and those from the prolonged heating experiments (see below) may indicate that thermally induced loss of solvent was too slow to register fully in the TGA experiment.

The thermal stability of as-synthesized **1** was tested by heating samples to a given temperature, at a rate of $10\,^{\circ}C\,min^{-1}$, maintaining them at this temperature for 1 h, and then analyzing them by powder X-ray diffraction. This approach revealed that between 170 and 200 °C a change did indeed take place to a give material which showed some evidence of a second crystalline phase, which we will report more fully in due course.

To establish whether the structure was stable in the absence of guests, a number of samples were subjected to reduced pressure and/or heated. X-ray powder diffraction patterns were then obtained to examine the integrity of the structure. Part of each sample was also dissolved in $[D_3]$acetonitrile, and ^1H NMR spectra were recorded and used to check for residual solvents by comparing the integrated intensity of solvent peaks with that of the aromatic signals of the ligand. After 12 h at 0.1 mmHg, the powder diffraction pattern was unchanged, but ^1H NMR spectroscopy revealed that the sample still contained large amounts of ethanol (ca. 14 molecules per $Ag_4\mathbf{L}_3(OTf)_4$ formula unit, which corresponds to ca. 75% occupation of the available channel volume). When a sample was immersed in diethyl ether for 12 h, then heated to 130 °C at 0.1 mmHg for 12 h, the diffraction pattern was again unchanged, but approximately three molecules of diethyl ether and three molecules of water were still present per $Ag_4\mathbf{L}_3(OTf)_4$ formula unit, which corresponds to a total of around 60% of the available channel volume. Interestingly, no ethanol was detected, which shows that included guests can be exchanged by immersing the crystals in a second liquid. A third sample was immersed in dichloromethane for 12 h, then heated to 170 °C, at 0.1 mmHg, for 24 h. The powder diffraction pattern was again unchanged, and no dichloromethane was detected by NMR spectroscopy, although there were apparently about two molecules of water present per $Ag_4\mathbf{L}_3(OTf)_4$ formula unit, this corresponds to around 4% of the available channel space. Therefore, it seems possible to obtain virtually solvent- and water-free **1**, without collapse of the framework.

The large-diameter rings in **1** are very striking, given the frequent occurrence of network interpenetrating in coordination polymers.[12] Interpenetration may be prevented in this case by the unusually high steric bulk of the network. A solid cylindrical ring with internal diameter d, edge width w, and depth p can be considered as a simple model for the ring structure of polymer **1** (Figure 2a). Interpenetrating orthogonal rings are shown in Figure 2b, and again in Figure 2c, with one ring in cross-section. This model reveals that the relationship $d^2 \geq w^2 + p^2$ must be satisfied for interpenetration to occur.[24] There is some ambiguity in defining d, w, and p for compound **1**, because it is not perfectly regular, nor perfectly rigid, and so some intermeshing of the surfaces of interpenetrating networks would occur. However, accepting this caveat, w was taken as 13.9 Å (non-transanular F(1)$\cdots$F(1) distance of 10.99 Å plus 2.94 Å for van der Waals radii[19]) and a lower estimate of p taken as 12.9 Å (which is half of the unit cell dimension c, and allows for intermeshing of the layer surfaces). This model requires a minimum "interpenetrating" d value of 18.9 Å at the in-pointing triflates. The actual value of 16.0 Å is only 85% of this, which suggests that the dimensions of **1** are probably transgressing their permitted values for interpenetration. A geometric model for interpenetrated cubic metal–organic frameworks with bulky spherical vertices has been described by Yaghi and coworkers.[8] The structure of **1** points to an alternative general situation, in which the network as a whole is too bulky to permit interpenetration.

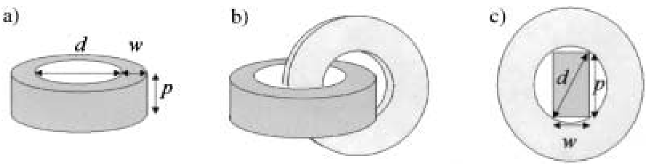

Figure 2. a) Labeling system for dimensions of a solid circular ring, d = inner diameter, w = edge width, p = depth; b) two such rings interpenetrating; c) limiting situation for the two interpenetrating rings, revealing the geometric constraint $d^2 \geq w^2 + p^2$.[24]

^{31}P NMR spectroscopy was used to probe the nature of solution-state precursors to network **1**. In 4:1 deuterochloroform:nitromethane as solvent, with a 3:2 molar ratio of silver triflate and **L**, where the concentration of **L** was 25 mmol L^{-1} as in the original synthesis, two species were observed, denoted **A** and **B** (Figure 3a). Both had highly symmetrical structures, as indicated by their single phosphorus chemical environments, and displayed well-resolved one-bond couplings to the spin-1/2 silver isotopes ^{107}Ag and ^{109}Ag. Chemical shift (δ) and coupling (${}^{1}J_{{}^{109}\mathrm{Ag},{}^{31}\mathrm{P}}$ Hz) data, respectively, for **A** are 15.0, 594, and, for **B**, 13.7 and 557. The magnitudes of the coupling constants indicate that each silver center is coordinated to two P atoms.[25] Spectra were concentration-dependent, with dilution increasing the amount of **A** relative to **B**, and causing the appearance of a third species **C**. This species exhibited similar spectroscopic parameters, with $\delta = 16.0$, and ${}^{1}J_{{}^{109}\mathrm{Ag},{}^{31}\mathrm{P}} = 560$ Hz. These observations point to equilibria between symmetrical cage compounds of general formula $[\mathrm{Ag_3}\mathbf{L}_2(\mathrm{O_3SCF_3})_3]_n$. Two examples of possible structures, which correspond to $n = 1$ and 2, are depicted in Figure 3b. Supporting evidence for the precursor cages was provided by electrospray mass spectrometry. A solution similar to that used for NMR spectroscopy, but at a ligand concentration of about 12.5 mmol L^{-1}, with methanol as the mobile phase, gave rise to mass peaks corresponding to the $n = 1$ (trinuclear) cage in which two, one, and zero triflate anions were coordinated (m/z 528, 866, and 1882, respectively). In addition, a peak at 1205 was observed which corresponds to the tricationic $n = 2$ cage with three coordinated triflate anions. A signal also occurred at m/z 1311, which corresponds to the dication $[\mathrm{Ag_4}\mathbf{L}_3(\mathrm{OTf})_2]^{2+}$, which has the same ligand-to-metal stoichiometry as the polymeric framework. Although such a species seems, therefore, to be the most logical precursor to polymer **1**, it is, at most, a minor species in solution since it could not have equivalent phosphorus centers, and so does not correspond to any of the species visible in the NMR spectra. The absence of peaks for higher nuclearity cages may be because of the low sample concentration necessary for the mass spectrometry experiment (lower than for the NMR spectra), and/or the upper m/z detection limit of the mass spectrometer (3000). Although definite identities cannot be assigned to the NMR-visible species **A**, **B**, and **C**, it can be concluded that ring-opening of one or more coordination cage precursors[15c,e,f] constitutes part of the pathway to polymeric **1**.

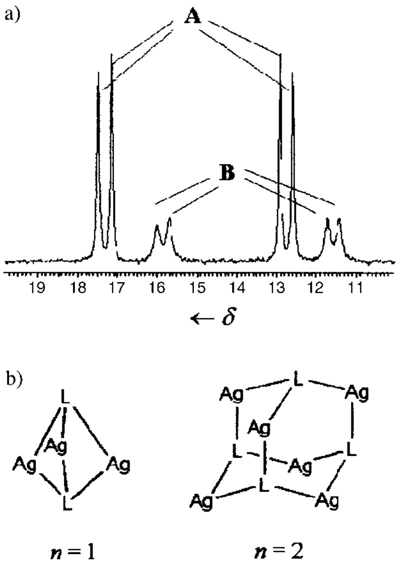

Figure 3. a) ^{31}P NMR spectrum in 4:1 chloroform:nitromethane of a 3:2 $\mathrm{AgO_3SCF_3}$:**L** mixture, at a ligand concentration of 25 mmol L^{-1}; b) Examples of possible $[\mathrm{Ag_3}\mathbf{L}_2]_n$ cage structures formed by $\mathrm{Ag_3}\mathbf{L}_2$ mixtures corresponding to the high molecular symmetry implied by ^{31}P NMR signals.

In summary, **1** is an unusual nanoporous metal–organic framework, which suggests further potential for bulky and NMR-friendly building blocks for synthesizing, and understanding the formation of, stable nanoporous materials.

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[17] Initial synthesis of **1**: A solution of 1,3,5-tris(diphenylphosphanyl)-benzene (**L**; 63 mg, 0.1 mmol) in CH_2Cl_2 (3 mL) was added to a solution of AgOTf (38.5 mg, 0.15 mmol) in CH_3NO_2 (1 mL). Diffusion of diethyl ether vapor into the resulting solution over one week gave colorless hexagonal crystals of **1** in 10% yield, together with powdery amorphous material. Higher yield synthesis: 1,3,5-tris(diphenylphosphanyl)benzene (**L**; 31.5 mg, 0.05 mmol) and AgOTf (17.0 mg, 0.067 mmol) were dissolved in a mixture of ethanol (7 mL) and nitromethane (3 mL), placed in a loosely stoppered polypropylene flask and partially evaporated at 88 °C overnight. Block and hexagonal colorless crystals were manually separated from the powdery amorphous byproduct. Yield: 50–80%; elemental analysis calcd (%) for $[Ag_4\mathbf{L}_3(OTf)_4]\cdot CH_3NO_2$: C 52.79, H 3.42; found: C 52.55, H 3.32.

[18] X-ray data were collected on a BrukerAXS SMART diffractometer using the SAINT-NT[26] software with omega/phi scans. A crystal was mounted on to the diffractometer under dinitrogen at approximately 120 K. The structure was solved using direct methods with the SHELXTL program package.[27] Crystal Data for the hexagonal plate crystals $\{C_{130}H_{99}F_{12}Ag_4P_9S_4O_{12}\}_n$ (**1**): $M = 2919.54$, hexagonal, space group $P\bar{3}c$, $a = 29.949(8)$, $c = 25.929(10)$ Å, $V = 20141(11)$ Å^{-3}, $Z = 4$, $\mu = 0.545$ mm^{-1}. A total of 39337 reflections were measured for the angle range $4 < 2\theta < 45$ and 8797 independent reflections were used in the refinement. The final parameters were $wR2 = 0.3009$ and $R1 = 0.0906$ $[I > 2\sigma I]$. Cell parameters for the block crystals $[\{C_{130}H_{99}F_{12}Ag_4P_9S_4O_{12}\}_n]$ (**1'**)[23]: $M = 2919.54$, hexagonal, space group $P\bar{3}c$, $a = 30.076(1)$, $c = 25.791(1)$ Å, $V = 20204(1)$ Å^{-3}. The residual densities (<1 electron Å^{-3}) associated with the voids indicate small amounts of very diffuse solvent molecules. Consequently, the nature of the solvent could not be determined using X-ray diffraction methods. Powder diffraction measurements were performed on a Siemens D5000 powder diffractometer in continuous mode with step size of 0.02° and step time of 20 s. ^{31}P NMR spectra were obtained at 121 MHz and 25 °C and are referenced to external 85% phosphoric acid ($\delta = 0$). CCDC 170632 (**1**) and 176871 (**1'**) 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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[23] A cell check was undertaken on a crystal from a batch that had been washed with ethanol and dried in air for 2 days which gave cell parameters $a = b = 30.076(2)$, $c = 12.8958(8)$ Å $\gamma = 120°$ indicating the presence of a possible polymorph with a *c* axis half that of the original cell. The data was collected and processed using these cell parameters, however, subsequent attempts at structure determination in this cell were unsuccessful. Thus we concluded the apparent halving of the *c* axis in this crystal was incorrect and after transformation to the larger cell $a = b = 30$, $c = 25$ Å, $\gamma = 120°$ the structure was shown to be the same as previously determined with a $wR2 = 0.22$ and $R1 = 0.0632$.

[24] This ignores the effect of curvature within the cavities, which would place slightly more stringent limits on *p* and *w* for a given cavity size.

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A (6-4) Photolyase Model: Repair of DNA (6-4) Lesions Requires a Reduced and Deprotonated Flavin[**]

Michaela K. Cichon, Simone Arnold, and Thomas Carell[*]

Ultraviolet irradiation of cells causes the formation of a variety of DNA lesions with known mutagenic, carcinogenic, and lethal effects.[1, 2] The main UV lesions are cyclobutane–pyrimidine dimers (CPD lesions) formed in a photochemically allowed [2π + 2π] cycloaddition and (6-4) photoadducts; the latter are presumably more mutagenic.[3, 4] The highly mutagenic (6-4) lesions are believed to be formed in a Paternó-Büchi reaction between two adjacent pyrimidines in the DNA duplex to give initially an oxetane intermediate, which rearranges above −80 °C to the (6-4) photoadduct by a proton shift and a C–O bond scission (Scheme 1).[5] Both types of DNA lesions are repaired in many organisms by a special class of repair enzymes, namely DNA photolyases, which cleave both lesions back into the monomers in a light-dependent, single electron transfer based repair reaction.[6] In the last decade, crystallographic,[7, 8] enzymatic,[9, 10] and model compound studies[11–14] showed that the photolyases,[15] which are responsible for the repair of CPD lesions, contain a

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