149.5 (py$_a$-C6), 139.4 (py$_a$-C4), 139.3 (py$_b$-C4), 136.5 (BAr-C2), 126.4 (q, ^3J(C,B) = 2.8 Hz, BAr-C3), 125.5 (py$_b$-C3), 125.4 (py$_a$-C3), 124.2 (py$_b$-C5), 122.6 (BAr-C4), 121.9 (py$_a$-C5), 72.9 (NCH_2-py$_a$), 70.2 (NCH_2-py$_b$ and RhCH$_2$$CH_2$O), 35.0 (d, ^1J(C,Rh) = 25.0 Hz, RhCH_2CH$_2$O); ESI-MS (CD$_3$CN): 453 $[M - \mathrm{BPh_4}]^+$, 425 $[M - \mathrm{C_2H_4} - \mathrm{BPh_4}]^+$, 409 $[M - \mathrm{C_2H_4O}\text{-}\mathrm{BPh_4}]^+$, 393 $[M - \mathrm{C_2H_4O_2} - \mathrm{BPh_4}]^+$, 391 $[M - \mathrm{C_2H_4O_2} - \mathrm{H_2} - \mathrm{BPh_4}]^+$.

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[5] NaBPh$_4$ was used instead of KPF$_6$ to precipitate the ethene complex.

[6] Transparent yellow crystals of **2b**BPh$_4$ were obtained by slow diffusion of diethylether into a 1,2-dichloroethane/acetonitrile solution. The X-ray diffraction data were collected at 150(2) K on an Enraf-Nonius CAD4 diffractometer with rotating anode and CCD area detector using graphite monochromatized Mo$_{K\alpha}$ radiation (λ = 0.71073 Å). The structure was solved by the PATTY[12] option of the DIRDIF[13] program system. Crystal data: $C_{48}H_{50.50}BClN_{4.50}O_{2.50}Rh$, M_r = 879.60, monoclinic, space group $C2/c$, a = 35.8999(8), b = 10.7567(3), c = 24.2379(5) Å, β = 116.4699(12), V = 8378.6(3) Å^3, Z = 8, ρ_{calcd} = 1.395 Mg m^{-3}. All non-hydrogen atoms that could be located were refined with anisotropic temperature factors. The hydrogen atoms were placed at calculated positions and refined isotropically in riding mode. The 5-membered dioxolane ring has the envelope form and occurs in two conformations. As expected there is considerable positional overlap for some of the atoms (C1A and C1B, C2A and C2B, O1A and O1B). Therefore some geometrical constraints had to be applied: the two conformations were "SAMEd" and the anisotropic thermal displacement parameters were tied. Calculations (PLATON, Spek 1995)[14] showed two distinct voids, one of 228 Å^3, containing 68 electrons, around a two-fold axis (position 4e, 0, y, 1/4; y = −0.037), and one of 151 Å^3, containing 51 electrons, around an inversion center (position 4b: 1/2, 0, 0). Based on the synthetic route and evidence from NMR spectroscopy it is assumed that these electron densities possibly stand for one molecule diethylether ($C_4H_{10}O$, 42 electrons) plus one molecule acetonitrile (CH_3CN, 22 electrons) in the first void (64 electrons, 28.5 Å^3/atom), and one molecule dichloroethane ($C_2H_4Cl_2$, 50 electrons) in the second void (30.2 Å^3/atom). It was not possible to assign any physically meaningful parameters to the electron densities found in the difference fourier map. Therefore the SQUEEZE procedure was applied to account for these electron densities. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157414. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[7] O$_\beta$ and C$_\beta$ (O2 and C2) are positioned above and below the O1-M-C1 plane: the displacement of O2 from this plane is +0.51 Å in **2b**A$^+$ and −0.46 Å in **2b**B$^+$, compared to +0.49 Å in the 3-platina-1,2-dioxolane. The displacement of C2 is −0.21 Å in **2b**A$^+$ and +0.27 Å in **2b**B$^+$, compared to −0.29 in the 3-platinadioxolane.

[8] This range is based on O−O bonds in 48 crystal structures containing a M-O-O-C fragment (M = any metal); 4 outliers were not taken into account.

[9] This range is based on O−C bonds in 48 crystal structures containing a M-O-O-C fragment (M = any metal); 9 outliers were not taken into account.

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A Striking, Multifaceted, Decalithium Aggregate with Carbanion, Organoamide, and Alkoxide Functionalities[**]

Philip C. Andrews, Glen B. Deacon,[*] Craig M. Forsyth, and Natalie M. Scott

Mixed-anion alkali metal complexes are of significant interest because of their ability to act as superbases.[1] Normally superbase aggregates are composed of two anions and two differing metals, $[\mathrm{R'M \cdot M'OR}]_n$ (R′ = alkyl, aryl, amide; R = alkyl; M = Li; M′ = Na, K), and it is these complexes that display greatest reactivity and have the widest application in synthetic processes.[1d,e] Solid-state structural information on mixed-anion systems is of vital importance to provide a more complete understanding of the reasons behind their differing reactivity. However, such complexes have historically proved extremely difficult to crystallize,[1a, 2] hence solid-state structures are scarce despite the emergence of some data for each class of mixed-anion alkali metal complexes.[3]

Unimetallic mixed-anion aggregates (M = M′), though usually less effective, are also of significant synthetic importance since, with suitable anions and metal, they can also show increased reactivity over that of the two separate starting reagents, for example $[n\mathrm{BuLi \cdot LiO(CH_2)_2NMe_2}]$.[4]

Herein, we report the crystallization and structure determination of the remarkable multifeatured unimetallic complex $[\{\mathrm{N(SiMe_3)(2\text{-}(2'\text{-}C_6H_4O)C_6H_4)}\}_2\mathrm{Li_4 \cdot LiOEt \cdot (Et_2O)}]_2 \cdot$ hexane, **1** · hexane, which contains *three* different superbase anionic components, amide, carbanion, and alkoxide. The presence of *ethoxide* is particularly striking since Lochmann has indicated that the most stable mixed-anion aggregates are

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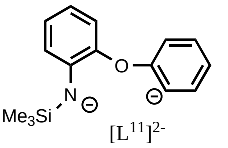
formed with bulky alkoxides, as exemplified by the presence of tBuO$^-$ in many known alkoxo solid-state structures.[1a]

Deprotonation of N-(2-phenoxyphenyl)-N-(trimethylsilyl)amine generates a highly useful lithium organoamide Li(L^1) (L^1 = N(SiMe$_3$)(2-PhOC$_6$H$_4$))[5] which reacts further with nBuLi to form Li$_2$(L^{11}) (L^{11} = N(SiMe$_3$)(2-(2′-C$_6$H$_4$O)C$_6$H$_4$)), containing a Li-carbanion derived from abstraction of the proton from the *ortho* position of the phenyl substituent.[5b] Remarkably, on attempted reaction of Li$_2$(L^{11}) with LaCl$_3$ in diethyl ether, a decalithium assembly, **1** · hexane, comprising four Li$_2$(L^{11}) units and two LiOEt groups (Figure 1) was serendipitously crystallized. The lithium ethoxide is presumably derived from ether cleavage, and is dependent upon the presence of the lanthanoid halide. In the absence of LaCl$_3$, the formation of a product that incorporated a lithium alkoxide unit was not observed.[5b] We have previously observed aryl ether cleavage with formation of [Yb(L^1)$_2$OPh(thf)] on decomposition of [Yb(L^1)$_2$(thf)$_2$], hence an intermediate unstable La complex is implicated in the present system.



[L^{11}]$^{2-}$

Determination of the structure of **1** · hexane by X-ray crystallography[6] revealed a centrosymmetric decalithium aggregate (Figure 1) located at each of the eight unit cell vertices, with a molecule of hexane positioned in a channel parallel to the a axis in the center of the unit cell. The asymmetric unit encompasses five unique Li atoms, two L^{11} ligands and an ethoxide group. Each of the chelating L^{11} ligands binds through bridging amide and aryl ether moieties. One ligand is coordinated by both to Li1 and Li3, whilst the other has the amide nitrogen (N2) bridging Li2 and Li4 and the aryl ether oxygen (O2) bridging Li4 and Li5A. The Li–N(amide) distances (av 2.05 Å) are typical of these structural features, whilst the less common bridging aryl ether oxygen atoms have one long (av 2.42 Å) and one shorter (av 2.08 Å) Li–O(ether) bond length.[7a] Characteristic of lithium amides,[7] Li1 is also coordinated by a molecule of diethyl ether which presumably inhibits further agglomeration of the aggregate. The ethoxide group is bound to three lithium atoms, Li1, Li2, and Li3 with one shorter (Li2–O3 1.839(5) Å) and two longer (Li1–O3 1.918(5), Li3–O3 1.890(5) Å) Li–O distances, though all are in the reported RO–Li range.[8b] A μ_3-alkoxide-Li$_3$ arrangement is characteristic of lithium clusters with bulky alkoxides, [Li(OR)]$_n$ (n = 4,6)[3b, 7a] and presumably the rare incorporation of the much smaller OEt anion in the current structure is facilitated by the steric protection provided by the two nearby bulky SiMe$_3$ groups (Figure 1). The third anionic component is derived from the phenyl carbanion that bridges three lithium atoms in different modes. One phenyl group binds to Li2, Li4, and Li5 through a single

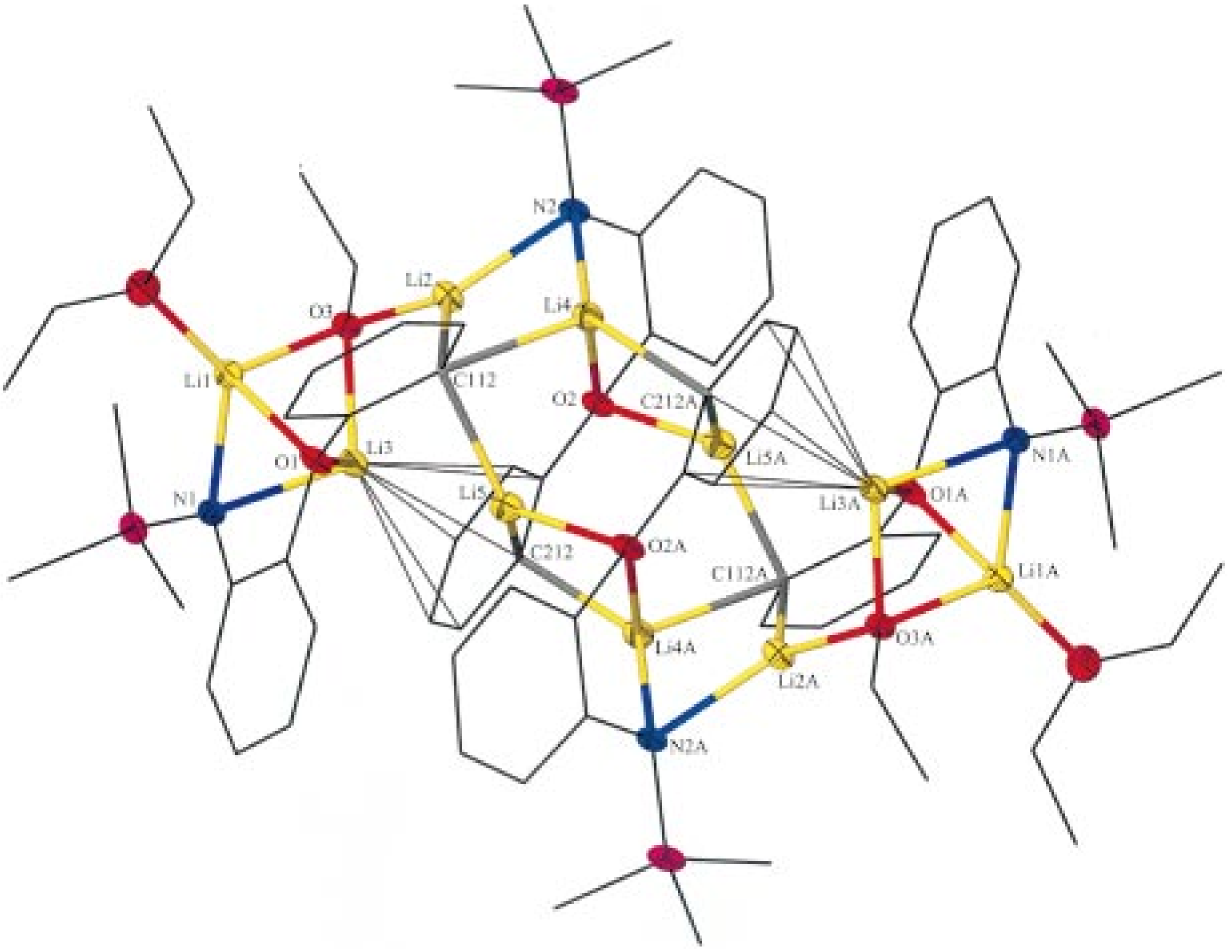


Figure 1. Molecular structure of **1** · hexane with the thermal ellipsiods shown at 30 % probability level for the non-carbon atoms. For clarity, the molecule of hexane and the hydrogen atoms have been omitted and the carbon atoms are represented by lines.

carbon atom (C112), whilst the other has a μ_2-C (C212) interaction to Li5 and Li4A but also coordinates more weakly with Li3 by means of an η^6-π-Ph interaction. The range of the shorter carbon–lithium bond lengths (2.128(5)–2.367(5) Å) has some longer than those observed in aryllithium clusters which similarly contain a μ_3-aryl-Li_3 arrangement (e.g. $[\{Li(3,5\text{-}t Bu_2C_6H_3)\}_6]$: Li–C 2.119(7)–2.247(7) Å[9]). The relative positions of the lithium atoms Li2, Li4, and Li5 (Figure 2a) and Li4A and Li5 (Figure 2b) and of the associated phenyl rings in **1** (Li–C to C_6 ring plane angles 0.4–59.2°) suggest predominantly σ-Li–C bonding. The π-Ph coordination to Li3 (Li–C_6 centroid to C_6 ring plane angle 84.3°) occupies a vacant tetrahedral coordination site on this lithium atom. The average Li–C separation (av Li–C 2.62 Å) is at the longer extreme of the range (2.28–2.77 Å)[10a–c] previously observed for Li complexation by a neutral arene. Presumably a closer approach to Li3 is prevented by the bonding of the phenyl ring to Li2A and Li5 as well as being fixed to the L^{11} backbone through the aryl ether oxygen O2. All Li–C(π-phenyl) distances are much less than the sum (3.30 Å) of the metallic radius for Li[10d] and the van der Waals radius of an arene ring.[10e]

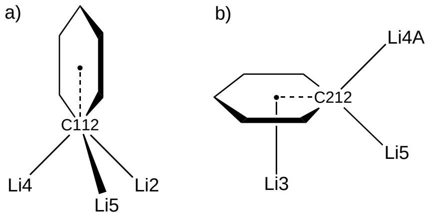


Figure 2. Schematic representation of Li–aryl bonding in **1**·hexane. a) Relative positions of Li2, Li4, and Li5 (a) and Li4A and Li5 (b) to the associated phenyl rings.

The above bonding arrangements give five distinct lithium environments: Li1 four-coordinate (distorted tetrahedral), Li2 three-coordinate (trigonal planar Σ(°) 359.9), Li3 three-coordinate (pyramidal) augmented by the η^6-π-Ph interaction to become pseudo-tetrahedral, Li4 four-coordinate (the donor atoms at the vertices of a triangular pyramid), and Li5 three-coordinate (near trigonal-planar Σ(°) 351.0). The Li2 environment is unique in lithium coordination chemistry being ligated by three "superbase" anions, amide, alkoxide, and carbanion with three different donor atoms (see also a Li/Na bimetallic complex with Li coordinated by hydroxide, alkoxide, and amide[11]). The ^{7}Li NMR spectrum of a $[D_8]$toluene solution of **1**·hexane showed only four separate broad peaks at room temperature, but on cooling, these resolved into the expected five sharp resonance signals. Similarly, variable-temperature ^{1}H NMR spectroscopy indicated some fluxional behavior that could be frozen at low temperature (see Experimental Section). However, two distinct L^{11} environments were detected (even at room temperature) which suggests that the gross structure may remain largely intact in solution as was also observed in the unimetallic mixed-anion complex $[(i Pr)_2NLi\cdot\{(Me_2NCH_2)_2CHOLi\}]_2$.[3e] The unexpected stability may be attributed to the integrity of $[Li_2(L^{11})]_2$ units, which under appropriate conditions can sequester small LiX entities in solution, and appears to support the observations of Schleyer et al. on the conformational stability of mixed aggregates in "superbase" mixtures.[12] Indeed we have also isolated a *n*BuLi adduct from these systems.[5b] Although it is premature to speculate on the possible behavior of triple anion aggregates as superbases, the successful isolation of **1**·hexane should encourage their more deliberate synthesis and hence investigation of their superbase role. The presence of chelation in **1** may be, but is not necessarily, a deterrent to superbase behavior (see ref. [4a]), especially since coordination fluxionality has been detected at room temperature.

Experimental Section

1: *n*BuLi (3.1 mL, 4.9 mmol) was slowly added to a stirring solution of *N*-(2-phenoxyphenyl)-*N*-(trimethylsilyl)amine (0.63 g, 2.45 mmol) in Et_2O (40 mL), and the mixture was stirred until it had warmed to room temperature (ca. 1 h). $LaCl_3$ (0.60 g, 2.45 mmol) was added and the reaction mixture was then stirred overnight. After the solvent had been removed under vacuum, hexane (25 mL) was added which gave a white precipitate. The reaction mixture was filtered at −78 °C and the filtrate was reduced under vacuum (ca. 15 mL) whereupon colorless crystals of **1**·hexane deposited (0.15 g, 18%). M.p. 180–184 °C (decomp); IR (Nujol): $\tilde{\nu}$ = 1589 s, 1561 w, 1544 w, 1408 vs, 1281 br s, 1244 s, 1147 vs, 1105 vs, 1162 m, 1044 s, 999 w, 945 s, 929 s, 886 w, 864 w, 828 s, 786 w, 768 s, 749 vs, 727 w, 668 w, 617 w cm^{-1}; ^{1}H NMR (400 MHz, $[D_8]$toluene, 303 K): $\delta = 0.02$ (vbr s, 18 H; $Si(CH_3)_3$), 0.24 (s, 18 H; $Si(CH_3)_3$), 0.78 (t, $^3J = 7.0$ Hz, 12 H; $CH_3(OEt_2)$), 0.81–0.98 (m, 12 H; CH_3(hexane) CH_3(OEt)), 1.23 (br m, 8 H; CH_2(hexane)), 3.03 (q, $^3J = 7.0$ Hz, 8 H; $CH_2(OEt_2)$), 3.39 (br q, 4 H; CH_2(OEt)), 5.70 (br s, 2 H; Ar), 6.08 (br s, 4 H; Ar), 6.29 (br s, 2 H; Ar), 6.45 (br t, 4 H; Ar), 6.66 (br s, 2 H; Ar), 6.80–7.10 (br m, 12 H; Ar), 7.29 (br s, 2 H; Ar), 7.82 (br dd, 4 H; Ar); ^{1}H NMR (400 MHz, $[D_8]$toluene, 213 K): $\delta = 0.35$ (s, 18 H; $Si(CH_3)_3$), 0.37 (s, 18 H; $Si(CH_3)_3$), 0.86–0.99 (m, 18 H; $CH_3(OEt_2)$ CH_3(hexane)), 1.00–1.15 (br m, 6 H; CH_3(OEt)), 1.17–1.38(br m, 8 H; CH_2(hexane)), 2.65 (br m, 4 H; $CH_2(OEt_2)$), 2.82 (br m, 4 H; $CH_2(OEt_2)$), 3.32 (br m, 2 H; CH_2(OEt)), 3.47 (br m, 2 H; CH_2(OEt)), 5.71 (d, $^3J = 7.3$ Hz, 2 H; Ar), 6.05 (d, $^3J = 7.7$ Hz, 2 H; Ar), 6.22 (t, $^3J = 7.0$ Hz, 2 H; Ar), 6.38–6.57 (m, 4 H; Ar), 6.64 (d, $^3J = 8.2$ Hz, 2 H; Ar), 6.70–6.88 (m, 4 H; Ar), 6.93–7.17 (m, 12 H; Ar), 7.20 (br d, 2 H; Ar), 7.37 (d, $^3J = 7.5$ Hz, 2 H; Ar); ^{7}Li NMR (155.51 MHz, $[D_8]$toluene, 303 K): $\delta = -2.57$, 0.68, 1.16, 2.27; (183 K) −3.11, 0.67, 1.72, 1.95, 3.14: A satisfactory C analysis could not be obtained presumably owing to decomposition.[13]

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[6] Crystal data for **1**·hexane: colorless crystal, $0.18 \times 0.23 \times 0.38$ mm, triclinic, $P\bar{1}$, $a = 10.7828(3)$, $b = 13.1998(5)$, $c = 16.1826(7)$ Å, $\alpha = 105.724(2)$, $\beta = 103.774(2)$, $\gamma = 92.199(3)°$, $V = 2140.2(7)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.098\,g\,cm^{-3}$, $\mu = 0.120\,mm^{-1}$, $2\theta_{max} = 56.5°$. A total of 10232 ($R_{int} = 0.053$) unique reflections were collected (Enraf Nonius CCD, $Mo_{K\alpha}$ radiation ($\lambda_0 = 0.71073$ Å), $T = 123$ K) and used in least-squares refinement on F^2, 469 refined parameters, GOF = 1.030 (based on F^2), $R1 = 0.073$, $\omega R2 = 0.169$ ($I > 2\sigma(I)$), $R1 = 0.134$, $\omega R2 = 0.198$ (all data), residual electron density $-0.366/0.525\,e\,Å^{-3}$. The hydrogen atoms were placed in calculated positions using a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157276. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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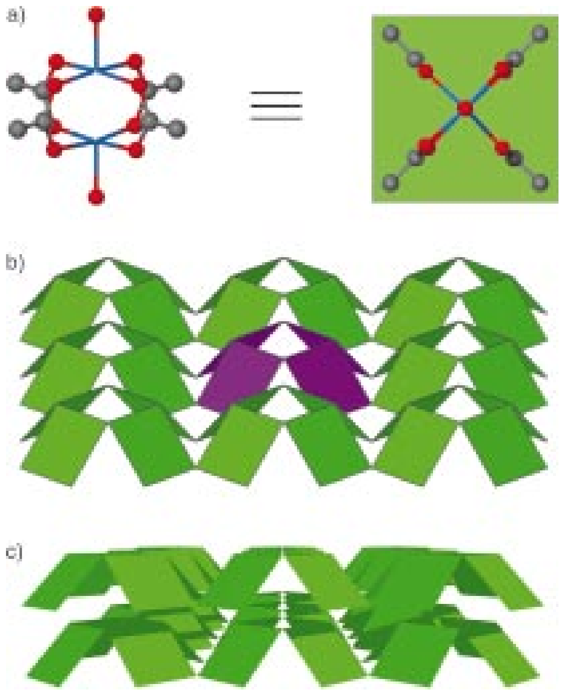
[13] Typical elemental analyses calcd for **1** $C_{72}H_{98}Li_{10}N_4O_8Si_4$ (%): C 65.06, H 7.43, N 4.21 (**1**·hexane $C_{78}H_{112}Li_{10}N_4O_8Si_4$: C 66.19, H 7.98, N 3.96); found: C 62.98, H 7.74, N 4.44.

Self-Assembly of Nanometer-Scale Secondary Building Units into an Undulating Two-Dimensional Network with Two Types of Hydrophobic Cavity**

Susan A. Bourne, Jianjiang Lu, Arunendu Mondal, Brian Moulton, and Michael J. Zaworotko*

By using some of the recently enunciated principles of crystal engineering[1–3] and self-assembly it has become possible to design and construct new classes of crystalline compounds from molecular components that possess useful physical properties including bulk magnetism,[4] nonlinear optical properties,[5] and porosity.[6–9] Open-framework structures can be assembled by using metals or metal clusters as nodes and multifunctional organic ligands to link these nodes. This approach has afforded structures that exhibit high surface areas, affinity for a wide range of organic guest molecules,[10] and some show potential for catalysis.[9] Herein we illustrate how the use of metal-organic secondary building units (SBUs) that are linked by angular ligands can generate nanoscale SBUs (nSBUs) with curvature.

The use of carboxylate-bridged metal clusters as metal-organic SBUs to build extended self-assembled structures has been delineated by Yaghi et al.[8] Scheme 1a illustrates such a cluster—in this case two metal ions are bridged by four carboxylate anions and each metal is bonded to one axial pyridine ligand. When viewed along the axial direction the extension of the carboxylate ligands forms a "square SBU". Such clusters are ubiquitous in the Cambridge Structural Database,[11] but most contain monofunctional carboxylates and, therefore, they will not generate extended structures. However, the use of bifunctional carboxylate ligands such as 1,4-benzenedicarboxylate allows the formation of self-assembled infinite structures that contain channels capable of incorporating a variety of guest molecules.[12–15] 1,3-Benzenedicarboxylate is suitable for the linking of square SBUs at 120° and Scheme 1b shows one of the ways in which square SBUs can pack when there is a 120° angle at their vertices: a two-dimensional (2D) infinite metal-organic framework resembling a layer of upended bowls. In such a structure one bowl



Scheme 1. Schematic illustrations of a) the square SBU (green) based on metal ions bridged by carboxylate anions, b) how the square SBUs can self-assemble at their vertices to generate nanosized bowls (purple) which in turn form curved sheets, and c) how the curved sheets pack because of shape considerations.

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