Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

High Connectivity Networks: Characterization of the First Uninodal 9-Connected Net and Two Topologically Novel 7-Connected Nets

J. Jacob Morris, Bruce C. Noll, Kenneth W. Henderson*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556

* To whom correspondence should be addressed.

E-mail: khenders@nd.edu

General Methods

All experimental manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques, or in an argon-filled glovebox.[1] All glassware was flame-dried under vacuum before use. Hexane was dried immediately before use by passage through columns of copper-based catalyst and alumina (Innovative Technology), and stored over 4 Å molecular sieves. 1,4-Dioxane (diox) was distilled over sodium benzophenone prior to use. $[RbOBu^t{\cdot}Bu^tOH]_\infty$ and RbHMDS (HMDS = hexamethyldisilazide) were prepared by literature methods.[2,3] KHMDS was purchased from Aldrich and used as received. 4-Cl-2,6-Dimethylphenol and 2,4,6-trimethylphenol were purchased from Aldrich and were recrystallized from hexane. 2-Pr^i-phenol was distilled over CaH_2 and stored over 4 Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were dried by storage over 4 Å molecular sieves. ^1H and ^{13}C NMR spectra were recorded on either a Varian Unity Plus 300 MHz or a Bruker AVANCE DPX-400 spectrometer at 293 K, and were referenced internally to the residual signals of the deuterated solvents.

Synthesis of $[4\text{-Cl-2,6-Me}_2\text{-C}_6\text{H}_2\text{OK})_2{\cdot}(\text{diox})_{3.5}]_\infty$, 1: KHMDS (5 mmol, 1.0 g) was added to a stirred solution of 4-Cl-2,6-dimethylphenol (5 mmol, 0.78 g) in dioxane (10 mL) to give a white precipitate. Complete dissolution was achieved by dilution with dioxane (20 mL) and heating the solution to reflux temperature. X-ray quality crystals were obtained by slowly cooling the resulting solution in a hot water bath. Crystalline yield: 582 mg, 55.6 %. δ_H (d_6-DMSO, 293K) 1.86 (s, 6H, *o*-Me), 3.57 (s, 14H, CH_2, dioxane), 6.50 (s, 2H, *m*-H). δ_c (d_6-DMSO, 293K) 18.31 (*o*-Me), 66.37 (CH_2, dioxane), 124.77 (*o*-C, Ph), 125.87 (*m*-C, Ph).

Synthesis of [4-Cl-2,6-Me_2-$C_6H_2ORb)_2$·$(diox)_{3.5}]_\infty$, 2: RbHMDS (1 mmol, 1.0 g) was added to a stirred solution of 4-Cl-2,6-dimethylphenol (1 mmol, 0.16 g) in dioxane (10 mL) to give a white precipitate. Complete dissolution was achieved by heating the solution to reflux temperature. X-ray quality crystals were obtained by slowly cooling the resulting solution in a hot water bath. Crystalline yield: 260 mg, 65.8 %. δ_H (d_6-DMSO, 293K) 1.85 (s, 6H, *o*-Me), 3.57 (s, 14H, CH_2, dioxane), 6.50 (s, 2H, *m*-H). δ_c (d_6-DMSO, 293K) 66.34 (CH_2, dioxane).

Synthesis of [(2,4,6-Me_3-$C_6H_2OK)_5$·$(diox)_5]_\infty$, 4: KHMDS (3 mmol, 0.6 g) was added to a stirred solution of 2,4,6-trimethylphenol (3 mmol, 0.41 g) in dioxane (10 mL) to give a white precipitate. Complete dissolution was achieved by heating the solution to reflux temperature. X-ray quality crystals were obtained by slowly cooling the resulting solution in a hot water bath. Crystalline yield: 173 mg, 33.3 %. δ_H (d_6-DMSO, 293K) 1.86 (s, 6H, *o*-Me), 1.98 (s, 3H, *p*-Me), 3.57 (s, 8H, CH_2, dioxane), 6.50 (s, 2H, *m*-H, Ph). δ_c (d_6-DMSO, 293K) 18.73 (*o*-Me), 20.61 (*p*-Me), 66.36 (CH_2, dioxane), 111.09 (*p*-C, Ph), 122.58 (*o*-C, Ph), 127.72 (*m*-C, Ph).

Synthesis of [(2-*i*-Pr-$C_6H_4ORb)_6$·$(diox)_{4.5}]$, 5: $[RbOBu^t \cdot Bu^tOH]_\infty$ (2 mmol 0.46 g) was added to stirred solution of 2-*i*-propylphenol (2 mmol, 0.27 ml) in dioxane (5 mL) to give a light yellow solution. All of the solvent was completely removed *in vacuo* to give a dark yellow oil. The oil was taken up in hexane (10 mL), which gave a white precipitate after 5 minutes. Complete dissolution was achieved by adding dioxane (5 mL) and heating the solution to reflux temperature. X-ray quality crystals were obtained by slowly cooling the resulting solution in a hot water bath. Crystalline yield: 225 mg, 39.2 %. δ_H (d_6-DMSO, 293K) 1.01 (s, 6H, CH_3, *i*Pr), 3.21 (multiplet, 1H,CH, *i*Pr), 3.56 (s, 6H, CH_2, dioxane), 5.73 (t, $^3J_{H,H}$ = 8.0 Hz, 1H, *m*-H, Ar), 5.90 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, *o*-H, Ar), 6.49 (t, $^3J_{H,H}$ = 8.0 Hz, 1H, *p*-H, Ar), 6.61(d, $^3J_{H,H}$ = 8.0 Hz, 1H, *m*-H, Ar).

X-ray Crystallography

Crystals were examined under Infineum V8512 oil. The datum crystal was either affixed to a thin glass fibre or a Mitegen loop mounted atop a tapered copper mounting-pin and transferred to the 100 K nitrogen stream of a Bruker APEX II diffractometer equipped with an Oxford Cryosystems 700 series low-temperature apparatus. Cell parameters were determined using reflections harvested from three sets of 20 0.3° ω scans. The orientation matrix derived from this was passed to COSMO to determine the optimum data collection strategy.[4] Cell parameters were refined using reflections with $I \geq 10\sigma(I)$ harvested from the entire data collection. All data were corrected for Lorentz and polarization effects, as well as for absorption. The structures were solved and refined using SHELXTL.[5] Structure solution was by direct methods. Non-hydrogen atoms not present in the direct methods solution were located by successive cycles of full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined with parameters for anisotropic thermal motion. Hydrogen atoms were placed at idealized geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to 1.2× the equivalent isotropic U of the parent atom, 1.5× for methyl hydrogens. Details on individual refinements, including descriptions of disorder, can be found in the cif files CCDC-651287-651290, which can be obtained free of charge via the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Supplementary Material (ESI) for Chemical Communications

Crystal Data for **1**: $C_{30}H_{44}Cl_2K_2O_9$, M_r = 697.75 , orthorhombic, *Pbca*, *a* = 10.9385(3), *b* = 19.5849(5), *c* = 32.2466(8) Å, V = 6908.2(3) Å^3, T = 100(2) K, Z =8, ρ_{calc} = 1.342 Mg m^{-3}, F(000) = 2944, μ = 0.477 mm^{-1}, Mo Kα λ = 0.71073, 8172 unique reflections collected, R1 = 0.048 for 7233 reflections with I > 2σ(I), R1 = 0.056 (wR2 = 0.112) for all unique data.

Crystal Data for **2**: $C_{30}H_{44}Cl_2O_9Rb_2$, M_r = 790.49, orthorhombic, *Pbca*, *a* = 11.324(2), *b* = 19.659(4), *c* = 32.308(7) Å, V = 7192(3) Å^3, T = 100(2) K, Z = 8, ρ_{calc} = 1.460 Mg m^{-3}, F(000) = 3232, μ = 2.917 mm^{-1}, Mo Kα λ = 0.71073, 6412 unique reflections collected, R1 = 0.056 for 5011 reflections with I > 2σ(I), R1 = 0.077 (wR2 = 0.136) for all unique data.

Crystal data for **4**: $C_{65}H_{95}K_5O_{15}$, M_r = 1311.91, monoclinic, $P2_1/c$, *a* = 18.380(4), *b* = 21.550(4), *c* = 17.740(4) Å, β = 91.30(3)°, V = 7025(2) Å^3, T = 100(2) K, Z =4, ρ_{calc} = 1.240 Mg m^{-3}, F(000) = 2800, μ = 0.373 mm^{-1}, Mo Kα λ = 0.71073, 20144 unique reflections collected, R1 = 0.043 for 17304 reflections with I > 2σ(I), R1 = 0.053 (wR2 = 0.108) for all unique data.

Crystal data for **5**: $C_{72}H_{102}O_{15}Rb_6$, M_r = 1720.36, monoclinic, $P2_1/n$, *a* = 19.0470(4), *b* = 20.6118(5), *c* = 20.0105(5) Å, β = 91.713(1)°, V = 7852.5(3) Å^3, T = 100(2) K, Z =4, ρ_{calc} = 1.455 Mg m^{-3}, F(000) = 3504, μ = 3.768 mm^{-1}, Mo Kα λ = 0.71073, 14914 unique reflections collected, R1 = 0.029 for 11405 reflections with I > 2σ(I), R1 = 0.051 (wR2 = 0.062) for all unique data.

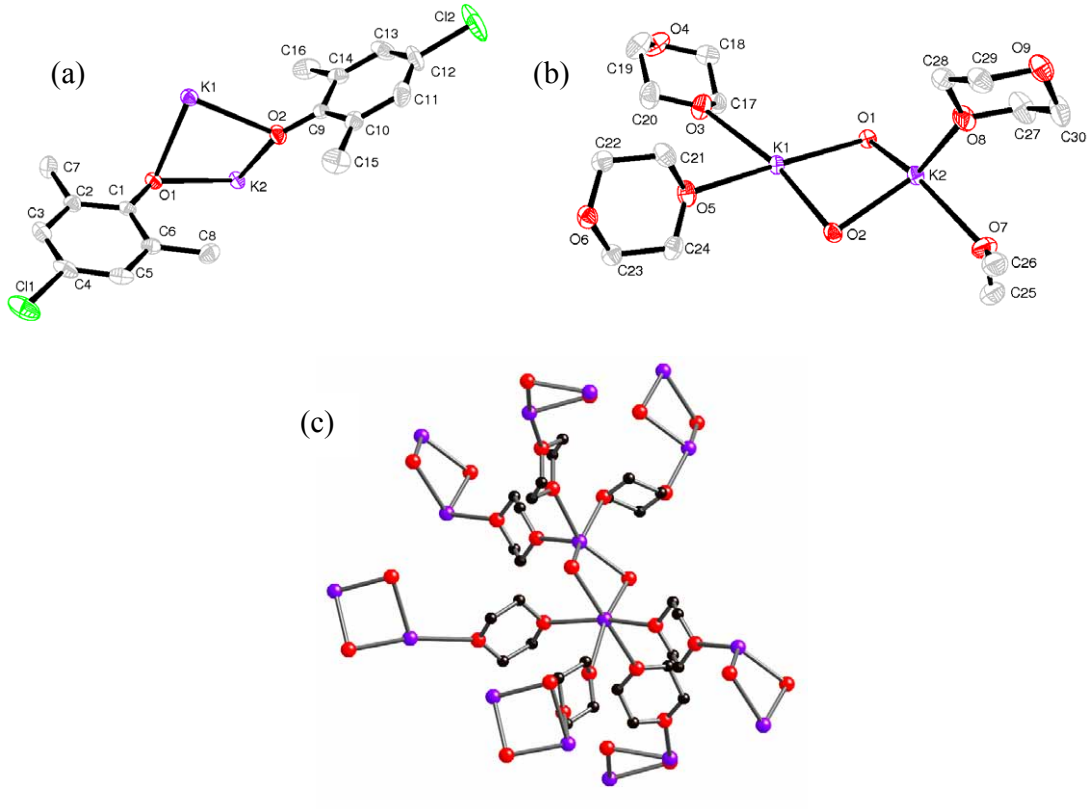

Figure S1. (a) Asymmetric unit of $[4\text{-Cl-2,6-Me}_2\text{-C}_6\text{H}_2\text{OK})_2\bullet(\text{diox})_{3.5}]_\infty$, **1**, highlighting the potassium aryloxide dimer. The dioxane molecules and hydrogen atoms are removed for clarity. (b) Asymmetric unit of **1** highlighting the four unique dioxane molecules coordinated to the potassium dimer. (d) Extended view of **1** showing the potassium dimer coordinated to seven neighbouring dimers through the divergent dioxane molecules.

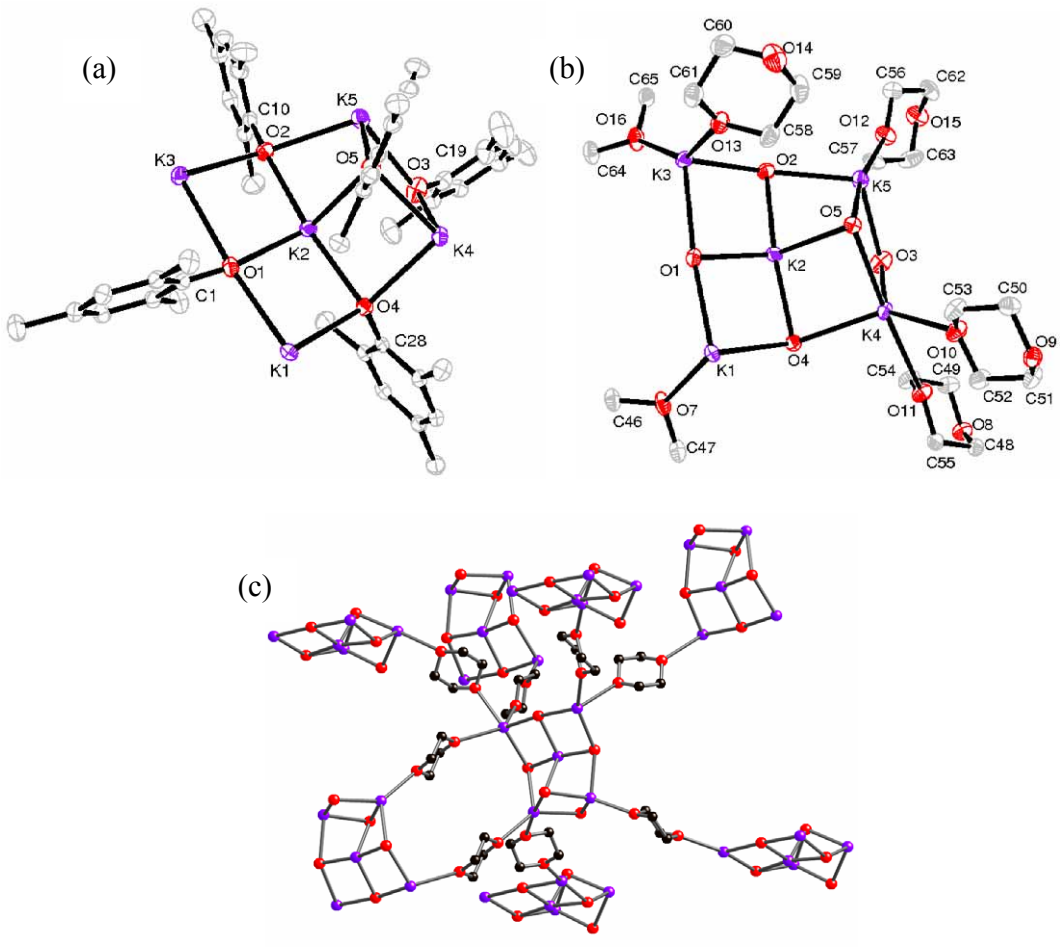

Figure S2. (a) Asymmetric unit of $[2,4,6\text{-}Me_3\text{-}C_6H_2OK)_5\bullet(diox)_5]_\infty$, **4**, highlighting the potassium aryloxide pentamer. The dioxane molecules and hydrogen atoms are removed for clarity. (b) Asymmetric unit of **4** highlighting the six unique dioxane molecules coordinated to the potassium pentamer. (d) Extended view of **4** showing the potassium pentamer coordinated to seven neighbouring pentamers through the divergent dioxane molecules.

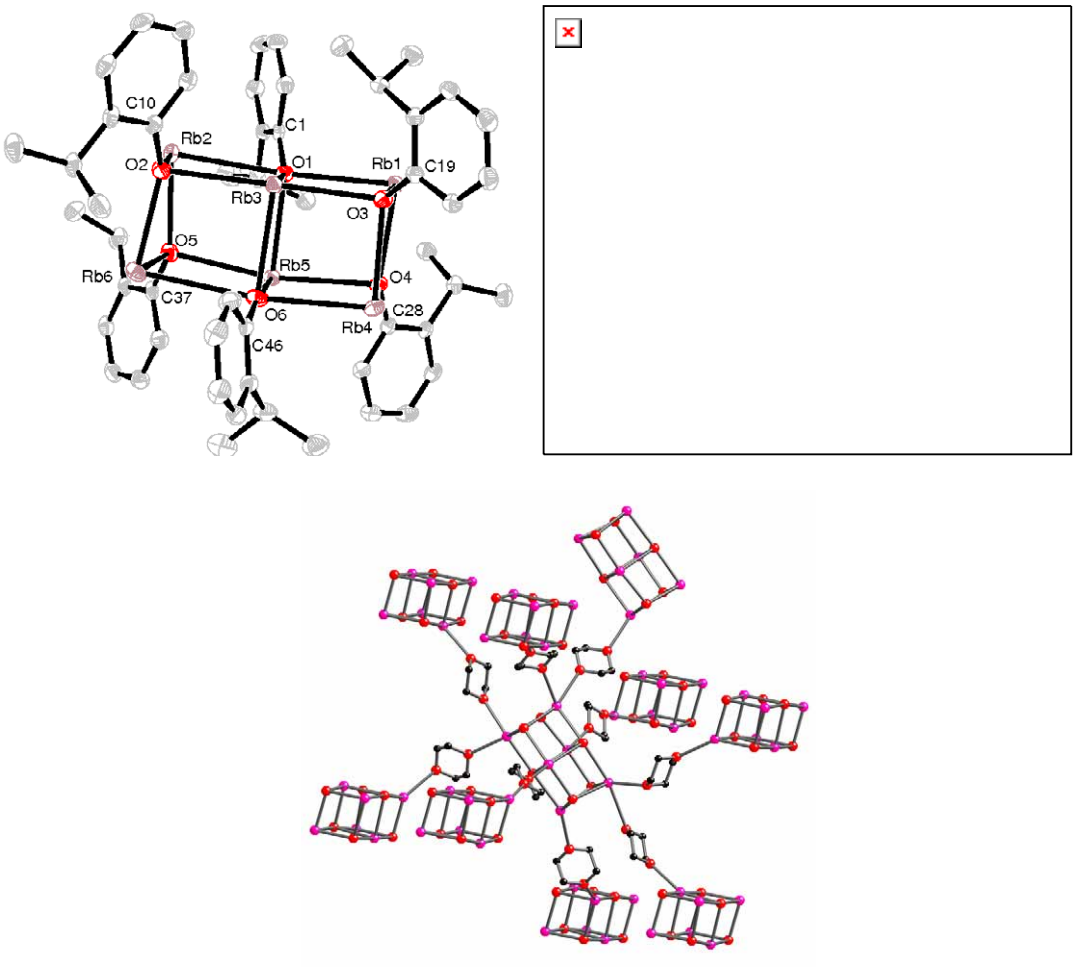

Figure S3. (a) Asymmetric unit of $[2\text{-}i\text{Pr-}C_6H_4ORb)_6\bullet(diox)_{4.5}]_\infty$, **5**, highlighting the rubidium aryloxide hexamer. The dioxane molecules and hydrogen atoms are removed for clarity. (b) Asymmetric unit of **5** highlighting the five unique dioxane molecules coordinated to the rubidium hexamer. (d) Extended view of **5** showing the rubidium hexamer coordinated to nine neighbouring hexamers through the divergent dioxane molecules.

References

[1] D. F. Schriver and M. A. Drezdon, *The Manipulation of Air-Sensitive Compounds*, Wiley, New York, 1986.
[2] M. H. Chisholm, S. R. Drake, A. A. Naiini and W. E. Streib, *Polyhedron,* 1991, **10**, 337.
[3] F. T. Edelmann, F. Pauer, M. Wedler and D. Stalke, *Inorg. Chem*., 1992, **31**, 4143.
[4] J. Kaercher, *COSMO,* Bruker-Nonius AXS, Inc., Madison, Wisconsin, USA, 2003.
[5] G. M. Sheldrick, University of Göttingen, Göttingen (Germany), 2001.