High-connectivity networks: characterization of the first uninodal 9-connected net and two topologically novel 7-connected nets†

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Ring and cage aggregates containing the large alkali metals potassium or rubidium have proven to be excellent building blocks for the creation of high-connectivity nets, as demonstrated by their use as septahedral and nonahedral nodes in synthesis of two new types of 7-connected nets and the first ever example of a 9-connected net.

There is currently a great deal of interest in the synthesis and characterization of metal–organic frameworks and coordination polymers.[1] A subject of central importance within this area is the study of network topology, which precisely describes the structure of extended solid-state materials. This field ties together chemists focused on synthesis, materials science, and crystallography with physicists and mathematicians interested in fundamental aspects of topology such as non-Euclidean geometry.[2] The growing number of framework structures being reported has led to an increasing emphasis towards identifying and classifying their underlying topologies. This systematic enumeration has been greatly aided by the recent construction of searchable databases and computer programs designed for topological analysis.[3]

A compelling illustration of the importance of topological classification comes from the paradigm that a small number of high-symmetry topologies dominate the structures of framework materials.[4] For example, two of the most commonly encountered nets are the diamondoid net (**dia**) and the primitive cubic net (**pcu**), resulting from tetrahedral and octahedral nodes respectively.[5] Thus, the almost limitless potential complexity of extended structures is simplified, bringing at least some level of predictability to the design of new materials.

Networks formed with connectivities greater than six are very unusual, with the large majority adopting either the high symmetry 8-connected body-centered cubic (**bcu**) net or the 12-connected face-centered cubic (**fcu**) net.[6] High-connectivity nets that do not have the highest possible symmetry are extremely rare, with almost all of the examples being low-symmetry 8-connected nets or multinodal nets.[7] In fact, there is only one reported example of a uninodal 7-connected net and no examples of uninodal 9-, 10- or 11-connected nets.[6a] Therefore, there is presently very little experimental data available to predict which, if any, of the many thousands of possible topologies will dominate for each of these nodal types. Furthermore, no general synthetic strategy has emerged to prepare such unusual nodal geometries. Previously, most high-connectivity nets have been formed using either isolated lanthanide ions or polynuclear transition metal clusters (decorated nets) as nodes. Herein, we demonstrate that ring and cage aggregates incorporating large alkali metals are very useful for this purpose. Moreover, the materials prepared are remarkable, including the first ever example of a 9-connected net and two topologically novel 7-connected nets.

We have recently shown that lithium and sodium aryloxide aggregates may be used as secondary building units (SBUs) to direct the assembly of diamondoid and cubic nets.[8] These systems were designed such that each metal center in the soluble aggregate has one or two open sites available for divergent Lewis base ligation. We reasoned that the larger alkali metal analogues were appealing candidates as SBUs for high-connectivity systems since they should allow multiple sites for network extension. Building upon our previous experience we chose to investigate the use of 4-chloro-2,6-dimethylphenolate as a ligand, 1,4-dioxane (diox) as the linker, with potassium and rubidium as the metal ions.

Crystals were successfully prepared following reaction of the metal hexamethyldisilazides with the phenol using 1,4-dioxane as media (ESI†). Single-crystal X-ray diffraction analyses elucidated the structures of the extended frameworks [4-Cl-2,6-Me$_2$C$_6$H$_2$OM)$_2$·(diox)$_{3.5}$]$_\infty$, where M = K (**1**) or M = Rb (**2**).‡ Complexes **1** and **2** are isomorphous, being composed of dimeric alkali metal aryloxide rings solvated by seven dioxane molecules (Fig. 1(a), only complex **1** is shown for brevity). The dimers are asymmetrically solvated, with one metal center coordinated to three dioxane molecules, whereas the second metal is coordinated to four dioxanes. In the extended structure each dioxane acts as a divergent bridging ligand, so that each dimer connects to seven neighbors *i.e.* the dimers are septahedral nodes. Similar to other frameworks constructed from SBUs, the total connectivity from each node is considered, rather than the connectivity from the individual metals within the node.[6–8] This leads to a 7-connected, three-dimensional network.

Due to the complex nature of visualizing high-connectivity nets, they are most easily described in terms of interconnected simpler subnets. In these terms, the extended structures of **1** and **2** can be described as parallel 4^4-nets that are intersected perpendicularly by a series of 6^3-nets (Fig. 2(a)), *i.e.* four of the seven dioxane molecules connect to other dimers "in-plane" to give a two-dimensional 4^4-net, and the remaining three dioxane molecules bridge to identical 4^4-nets above or below this plane. Each vertex in the 4^4-net bridges to two vertices above and one vertex below (or *vice versa*). The Schläfli symbol for the underlying topology of the 7-connected net is $3^3.4^{12}.5^5.6$ (td10 = 2198),[3c] which is an unprecedented topology for a coordination network.[5] This network is identified by the code **vcn** in the Reticular Chemistry Structure Resource (RCSR) database.[5,9]

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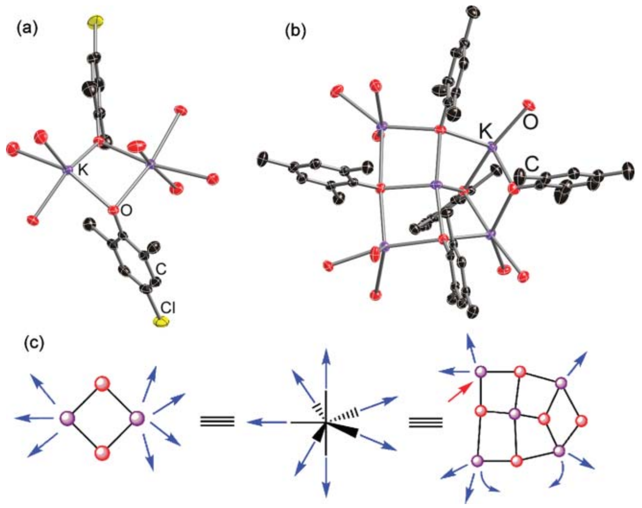

Fig. 1 (a) Dimeric K_2O_2 ring aggregate of **1** coordinated by seven dioxane molecules. (b) Pentameric potassium aggregate of **4** coordinated by eight bridging and one terminal dioxane molecules. The carbon atoms of the coordinated dioxane and all hydrogen atoms are omitted for clarity. (c) Schematic view of the septahedral SBUs in **1** and **4** with the dioxanes shown by red (terminal), straight blue (single bridge), and curved blue (double bridge) arrows.

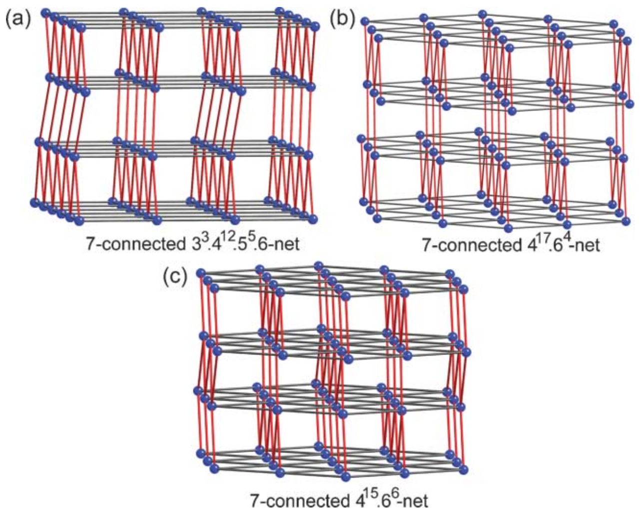

Fig. 2 Simplified network structure of (a) **1** and **2**, (b) **3** and (c) **4**, highlighting the 4^4-nets (gray) and intersecting 6^3-nets (red). Aggregates are represented by blue spheres with dioxane bridges shown as gray or red lines.

Of note here is the only other example of a uninodal 7-connected network, namely $\{[La(L)_4](BPh_4)(ClO_4)_3 \cdot 2.75MeOH\}_\infty$, L = 4,4′-bipyridine *N*,*N*′-dioxide, (**3**).[6a,10] This network, identified by the code **sev** in the RCSR database,[5] is constructed from single La(III) metal centers that are coordinated by eight bridging 4,4′-bipyridine *N*,*N*′-dioxides. Six of the linkers form single bridges to six neighboring metals, while the remaining two form a double bridge to a single metal center. Each of the metals therefore act as a 7-connected node as shown in Fig. 2(b), to give a network with the Schläfli symbol of $4^{17}.6^4$.

The variance between the topologies of **1** and **2**, and that of **3** is highlighted by their different Schläfli symbols, and can be seen illustratively in Fig. 2(a) and (b). In the extended structures of **1** and **2** the 6^3-subnets are aligned along the ring edges of the 4^4-nets. In comparison, the 6^3-subnets in **3** traverse the face of the aligned 4^4-nets. This topological difference is comparable to that between the 6-connected **pcu** and 8-connected **bcu** nets. The **pcu** and **bcu** networks can be simplified into parallel sheets of 4^4-subnets that are perpendicularly intersected by a similar series of 4^4-subnets. However, in the **pcu** net the perpendicular subnets intersect along the ring edges, whereas in the **bcu** net the subnets intersect across the face of the ring.

With these results in hand, we wished to use the same synthetic approach to target related networks by modifying the substituents on the aryloxide anion. Simply replacing the chloride at the *para*-position in **1** with a methyl substituent led to the unexpected formation of the pentameric aggregate $[(2,4,6\text{-}Me_3C_6H_2OK)_5 \cdot (diox)_5]_\infty$ (**4**), as determined by single-crystal X-ray diffraction.‡ To date, there have only been four reports of homometallic alkali metal pentamers, all of which are lithium salts.[11] Indeed, pentameric aggregates of any metal are rare, with **4** having a unique structural core. The cage can be described as an eight-membered K_4O_4 tetrameric ring with a potassium aryloxide at its center (Fig. 1(b)).

Since the pentameric aggregate is relatively flat and open, it allows for coordination by a large number of solvent molecules. Two of the outer potassium atoms of the aggregate coordinate to three dioxanes, while the remaining two metals coordinate to two and one dioxanes. The interior metal is bonded only to four of the aryloxide anions. This gives a total of nine dioxane molecules per pentamer. Six of the dioxane molecules form single bridges to six neighboring pentameric aggregates, two dioxanes form a double bridge to a single neighboring aggregate, and the final dioxane terminally solvates the aggregate (Fig. 1(c)). In topological terms the pentameric aggregate in **4** acts as a 7-connected node to give an extended network of parallel 4^4-nets that are perpendicularly intersected by parallel 6^3-nets (Fig. 2(c)). The 3D structure adopts a $4^{15}.6^6$ topology (td10 = 2206), which is also an unprecedented topology for coordination networks.

As is illustrated in Fig. 2, the gross topologies of **3** and **4** are quite similar. The Schläfli symbol of $4^{17}.6^4$ for **3** and $4^{15}.6^6$ for **4** indicates that only two of the rings formed at each node differ in size. In both structures, the 6^3-nets perpendicularly intersect the 4^4-nets across the ring face. In **3**, the 6^3-nets are perfectly eclipsed, beginning and ending at the same 4^4-net layer. However, in **4** alternate 6^3-nets are offset from each other, beginning and ending at different 4^4-net layers. The staggered pattern of the 6^3-nets in **4** leads to the novel $4^{15}.6^6$ topology.

Next, we reasoned that decreasing the steric bulk close to the metal center may allow the formation of higher aggregates and/or increased solvation sites for polymer extension. This approach was successful through the synthesis and structural characterization of $[(2\text{-}i\text{-}PrC_6H_4ORb)_6 \cdot (diox)_{4.5}]$, **5**. Compound **5** was prepared by reaction of 2-isopropylphenol with the rubidium base $[t\text{-}BuORb \cdot t\text{-}BuOH]_\infty$ in dioxane.[12] The solid state structure of **5**‡ proved to be remarkable, being composed of hexameric rubidium aryloxide aggregates that are coordinated by nine dioxane molecules (Fig. 3(a)). There are three different rubidium bonding environments within the hexameric aggregate. Three of the four rubidium atoms at the two ends of the aggregate are each coordinated by two dioxane molecules, with the fourth rubidium coordinated by

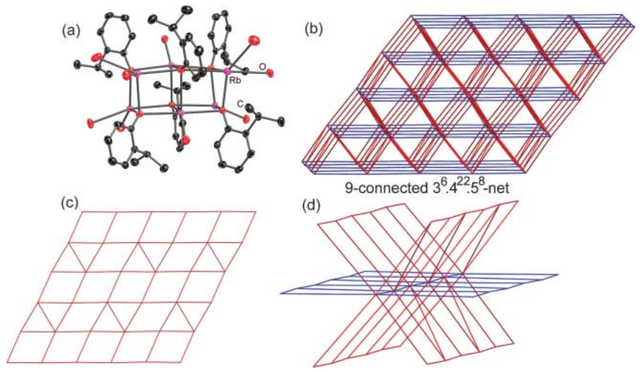

Fig. 3 (a) Hexameric rubidium aggregate of **5**. The carbon atoms of the nine coordinated dioxane and all hydrogen atoms are omitted for clarity. (b) Extended **ncd** network of **5** showing the framework with the 4^4-nets in blue and the $(3.4^3)(3^2.4^3)$-nets in red. (c) Section of the $(3.4^3)(3^2.4^3)$-net. (d) Offset pattern of the two $(3.4^3)(3^2.4^3)$-nets intersecting with a 4^4-net.

only one dioxane. In addition, the two central rubidium atoms are each coordinated by only one dioxane. All nine of the dioxanes bridge to unique neighboring hexamers. Therefore the SBUs in **5** act as nonahedral nodes to give a 9-connected network. To the best of our knowledge compound **5** is the first uninodal 9-connected framework to be reported.[13]

The underlying topology of the network has a Schläfli symbol of $3^6.4^{22}.5^8$ (td10 = 3010) and is identified by the code **ncd** in the RCSR database. Fig. 3(b) shows the overall connectivity, which is composed of parallel sheets of 4^4-nets that are doubly intersected by $(3.4^3)(3^2.4^3)$-nets. The complex $(3.4^3)(3^2.4^3)$-subnets (Fig. 3(c)) are best described by their tiling pattern, rows of squares that alternate with rows of mixed triangles and squares. The intersecting $(3.4^3)(3^2.4^3)$-nets are offset from one another so that between each 4^4-net layer there is an alternating pattern of rows of squares and rows of mixed triangles and squares (Fig. 3(d)). In **1–4** the 6^3-nets intersect the 4^4-nets at 90° but in **5** the two $(3.4^3)(3^2.4^3)$-nets intersect the 4^4-nets at approximately 60°, creating the appearance of triangular windows.

An interesting aspect of 7- and 9-connected networks is that unlike 4-, 6-, 8- and 12-connected nets there is no highest symmetry topology. Surprisingly, three distinct topologies have been discovered from the first four uninodal 7-connected networks **1–4** that have been characterized.[5] Also, the new topology reported here for **4** is not even predicted in the RCSR database.[5] Nets that are 9-connected possess another level of complexity, with compound **5** showing one of the many beautiful topological possibilities for this degree of connectivity.

These early investigations into high-connectivity networks suggest that a fascinating and rich coordination chemistry is waiting to be discovered. Our hope is that underlying structural patterns will emerge from the systematic synthesis and classification of a library of high-connectivity networks, as has evolved for their higher symmetry counterparts.

Notes and references

‡ CCDC 651287–651290. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b711668c

1 (*a*) C. Janiak, *Dalton Trans.*, 2003, 2781; (*b*) A. K. Cheetham, C. N. R. Rao and R. K. Feller, *Chem. Commun.*, 2006, 4780; (*c*) H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O'Keeffe and O. M. Yaghi, *Science*, 2007, **316**, 268.

2 S. T. Hyde, O. Delgado-Friedrichs, S. J. Ramsden and V. Robins, *Solid State Sci.*, 2006, **8**, 740.

3 (*a*) M. O'Keeffe, O. M. Yaghi and S. Ramsden, Reticular Chemistry Structure Resource, Arizona State University, Tempe, AZ, 2007, database available at http://rcsr.anu.edu.au/; (*b*) S. Ramsden, V. Robins, S. T. Hyde and S. Hungerford, 2006, EPINET: Euclidean patterns in non-Euclidean tilings, http://epinet.anu.edu.au; (*c*) V. A. Blatov,2007, http://www.topos.ssu.samara.ru/.

4 N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2005, **38**, 176.

5 The bolded net abbreviations are from the RCSR database. See ref. 3*a* and O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Phys. Chem. Chem. Phys.*, 2007, **9**, 1035.

6 (*a*) D.-L. Long, A. J. Blake, N. R. Champness, C. Wilson and M. Schröder, *Angew. Chem., Int. Ed.*, 2001, **40**, 2443; (*b*) T.-T. Luo, H.-L. Tsai, S.-L. Yang, Y.-H. Liu, R. D. Yadav, C.-C. Su, C.-H. Ueng, L.-G. Lin and K.-L. Lu, *Angew. Chem., Int. Ed.*, 2005, **44**, 6063; (*c*) X.-M. Zhang, R.-Q. Fang and H.-S. Wu, *J. Am. Chem. Soc.*, 2005, **127**, 7670; (*d*) D. Li, T. Wu, X.-P. Zhou, R. Zhou and X.-C. Huang, *Angew. Chem., Int. Ed.*, 2005, **44**, 4175; (*e*) Q.-R. Fang, G.-S. Zhu, Z. Jin, M. Xue, X. Wei, D.-J. Wang and S.-L. Qiu, *Angew. Chem., Int. Ed.*, 2006, **45**, 6126; (*f*) J. Zhang, Y. Kang, J. Zhang, Z.-J. Li, Y.-Y. Qin and Y.-G. Yao, *Eur. J. Inorg. Chem.*, 2006, 2253.

7 (*a*) L. Pan, H. Liu, X. Lei, X. Huang, D. H. Olson, N. J. Turro and J. Li, *Angew. Chem., Int. Ed.*, 2003, **42**, 542; (*b*) D.-L. Long, R. J. Hill, A. J. Blake, N. R. Champness, P. Hubberstey, D. M. Proserpio, C. Wilson and M. Schröder, *Angew. Chem., Int. Ed.*, 2004, **43**, 1851; (*c*) X.-L. Wang, C. Qin, E.-B. Wang, Z.-M. Su, L. Xu and S. R. Batten, *Chem. Commun.*, 2005, 4789; (*d*) X.-L. Wang, C. Qin, E.-B. Wang and Z.-M. Su, *Chem.–Eur. J.*, 2006, **12**, 2680; (*e*) J. Jia, X. Lin, C. Wilson, A. J. Blake, N. R. Champness, P. Hubberstey, G. Walker, E. J. Cussen and M. Schröder, *Chem. Commun.*, 2007, 840; (*f*) X. Qu, L. Xu, G. Gao, F. Li and Y. Yang, *Inorg. Chem.*, 2007, **46**, 4775.

8 (*a*) D. J. MacDougall, J. J. Morris, B. C. Noll and K. W. Henderson, *Chem. Commun.*, 2005, 456; (*b*) D. J. MacDougall, B. C. Noll and K. W. Henderson, *Inorg. Chem.*, 2005, **44**, 1181; (*c*) J. J. Morris, B. C. Noll and K. W. Henderson, *Cryst. Growth Des.*, 2006, **6**, 1071.

9 V. A. Blatov, *Acta Crystallogr., Sect. A*, 2007, **63**, 329.

10 R. J. Hill, D.-L. Long, N. R. Champness, P. Hubberstey and M. Schröder, *Acc. Chem. Res.*, 2005, **38**, 335.

11 (*a*) D. Barr, W. Clegg, R. E. Mulvey and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 226; (*b*) M. G. Davidson, J. A. K. Howard, S. Lamb and C. W. Lehmann, *Chem. Commun.*, 1997, 1607; (*c*) M. A. Beswick, B. R. Elvidge, N. Feeder, S. J. Kidd and D. S. Wright, *Chem. Commun.*, 2001, 379; (*d*) B.-H. Huang, B.-T. Ko, T. Athar and C.-C. Lin, *Inorg. Chem.*, 2006, **45**, 7348.

12 For the synthesis of $[t\text{-BuORb}\cdot t\text{-BuOH}]_\infty$: M. H. Chisholm, S. R. Drake, A. A. Naiini and W. E. Streib, *Polyhedron*, 1991, **10**, 337.

13 We are aware of three recent reports of binodal (3,9)-connected networks, as well as a trinodal (4,5,9)-connected network: (*a*) Y.-J. Shi, X.-T. Chen, Y.-Z. Li, Z. Xue and X.-Z. You, *New J. Chem.*, 2002, **26**, 1711; (*b*) Q.-Q. Kang, L.-S. Long, R.-B. Huang and L.-S. Zheng, *Acta Crystallogr., Sect. E*, 2004, **60**, i12; (*c*) J. Jia, X. Lin, C. Wilson, A. J. Blake, N. R. Champness, P. Hubberstey, G. Walker, E. J. Cussen and M. Schröder, *Chem. Commun.*, 2007, 840; (*d*) X.-M. Zhang, Y.-Z. Zheng, C.-R. Li, W.-X. Zhang and X.-M. Chen, *Cryst. Growth Des.*, 2007, **7**, 980.