



Cite this: *Chem. Commun.*, 2017, 53, 4398

Received 15th March 2017,
Accepted 31st March 2017

DOI: 10.1039/c7cc01959a

rsc.li/chemcomm

Highly selective CO₂ vs. N₂ adsorption in the cavity of a molecular coordination cage†

James S. Wright,[‡] Alexander J. Metherell,[‡] William M. Cullen,^{id} Jerico R. Piper, Robert Dawson^{id} * and Michael D. Ward^{id} *

Two M₈L₁₂ cubic coordination cages, as desolvated crystalline powders, preferentially adsorb CO₂ over N₂ with ideal selectivity CO₂/N₂ constants of 49 and 30 at 298 K. A binding site for CO₂ is suggested by crystallographic location of CS₂ within the cage cavity at an electropositive hydrogen-bond donor site, potentially explaining the high CO₂/N₂ selectivity compared to other materials with this level of porosity.

Porous solid-state materials are attractive for gas adsorption purposes, with several classes of porous material gaining increasing attention in recent years. These include metal–organic frameworks (MOFs)/coordination polymers;^{1–17} covalent organic frameworks (COFs)/microporous organic polymers (MOPs);^{18–24} molecular cages;^{25–35} and other molecular crystals.^{36–43}

In the case of MOFs and MOPs, impressive gas uptake capacities have been reported, and extremely highly porous materials described.^{12,14,21} However, higher uptake capacity in porous materials can come at the expense of selectivity between small gaseous molecular guests, as shown in previous work comparing porous organic cages of different pore sizes with each other, and with MOFs.³² Adsorbents which are selective for the desired adsorbate are desirable, but not necessarily at the expense of uptake capacity. For this purpose, the design of flexible adsorbents whose pores may open under the influence of an external stimulus has been demonstrated, both in MOFs^{1,7,13} and extrinsically porous materials;^{17,37,42} this is still an emerging field.

Perhaps better developed is the functionalisation of the pore space of intrinsically porous materials, to enhance selectivity for binding of different gaseous guests. In particular, the improvement of CO₂ adsorption selectivity in MOFs has been

demonstrated by the addition of hydrogen-bonding sites^{3,11} or the fluorination of pores.^{5,44,45} These internal surface modifications can however come at the expense of uptake capacity by occupying some of the interior space, so an adsorbent in which a binding site is built into the ‘walls’ of the cavity is desirable.

We have previously reported the structures and guest binding properties of the cubic coordination cages [M₈L₁₂]X₁₆, in which M are transition metal dications [usually Co(II)] located at the vertices of the cage, and L are bis(pyrazolyl-pyridine) bridging ligands which connect a pair of metal ions along every edge of the assembly (Fig. 1).^{46–52} The ligand L may be unsubstituted (L⁰: R = H in the figure) in which case the cages are soluble in polar organic solvents;^{47,48} or may be substituted (L^W: R = CH₂OH in the figure) to make the cages water-soluble.^{49–52} These cages have been shown to bind a wide range of organic guests in the central cavity. In organic solvents guest binding is partly driven by hydrogen-bonding of electron-rich regions of guests to H-bond donor pockets located on the interior surface of the cage, in regions of high positive electrostatic potential; this affords binding constants in the range 10²–10³ M^{–1}.⁴⁷ In water, the hydrophobic effect provides the dominant driving force for strong binding of hydrophobic guests with binding

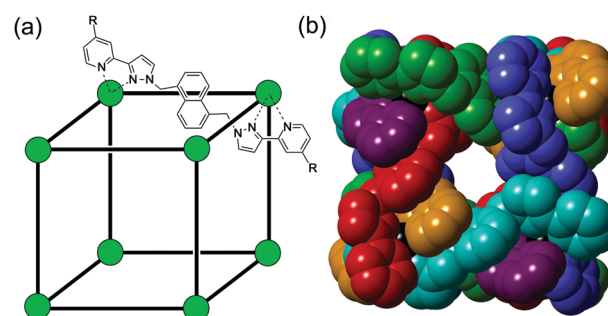


Fig. 1 General structure of host cages [M₈L₁₂](BF₄)₁₆: types **A** (R = H, M = Cd) and **B** (R = CH₂OH, M = Co). (a) A sketch emphasising the cubic array of M(II) ions and the disposition of a bridging ligand spanning an edge; (b) a space-filling representation of the complex cation with ligands coloured separately for clarity (see ref. 46–53).

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK.

E-mail: m.d.ward@sheffield.ac.uk, r.dawson@sheffield.ac.uk

† Electronic supplementary information (ESI) available: Details of the crystal structure of [Co₈(L^W)₁₂](BF₄)₁₆·CS₂·5H₂O; powder XRD analyses; gas sorption data at 273 K; NMR titration data for binding of CS₂ into **B** in aqueous solution; additional figures. CCDC 1537994. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc01959a

‡ Equal first authors.



constants of up to 10^8 M^{-1} .^{49–51} Here we report an investigation into the gas sorption capability of these materials, demonstrating a high selectivity for CO_2 uptake over N_2 in the solid state, which we ascribe to the presence of the same H-bond donor sites on the cage interior surface that facilitate guest binding in solution.^{47,53}

We used the cages $[\text{Cd}_8(\text{L}^{\text{O}})_{12}](\text{BF}_4)_{16}$ (**A**)⁴⁸ and $[\text{Co}_8(\text{L}^{\text{W}})_{12}](\text{BF}_4)_{16}$ (**B**),⁴⁹ both of which have been reported before. The compounds were prepared as methanol solvates, and then dried and thermally desolvated. Powder X-ray diffraction analysis of the dried materials (ESI†) showed that **B** retains the same phase that was observed in the single crystal structure of the methanol solvate, whereas **A** loses crystallinity and becomes amorphous. This is likely related to the fact that in **B** the presence of hydroxymethyl groups on the exterior surface of the cages results in a formation of an intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding network of cage molecules which allows crystallinity to be retained even when solvent molecules are lost (ESI†). In **A** in contrast there are no such interactions between the exterior surfaces of adjacent cages and crystallinity is lost on desolvation. However, ^1H NMR and mass spectrometric analyses confirmed that the integrity of the molecular cages is retained even when the crystals are desolvated.

The cages were found to be non-porous having BET surface areas $< 20 \text{ m}^2 \text{ g}^{-1}$. The volumetric gas sorption isotherms were measured for uptake of CO_2 and N_2 by both cages at 298 K (Fig. 2) and also at 273 K (ESI†). Both cages demonstrate highly selective uptake for CO_2 vs. N_2 at both temperatures. The gas uptake comparisons and selectivity constants are summarised in Table 1, and Henry's law calculation data is presented in the ESI.† The capacity for CO_2 uptake is very similar for both cages. Although the cages have identical internal cavities, as we mentioned above the supramolecular structure of the cages is different because of the presence (cage **B**) or absence (cage **A**) of inter-cage hydrogen-bonding interactions between peripheral

Table 1 Gas sorption quantities for CO_2 and N_2 , and CO_2/N_2 selectivity constants, for both cages

Cage	T (K)	1 bar CO_2 uptake (mmol g^{-1})	1 bar N_2 uptake (mmol g^{-1})	CO_2/N_2 selectivity constant	
				Simple (ideal)	Henry's law
B	273	1.003	0.0309	32	156
	298	0.672	0.0138	49	165
A	273	1.005	0.027	37	59
	298	0.673	0.022	30	32

functional groups. This suggests either that CO_2 uptake in the interstitial spaces between cages is very low, or that the void space between cages is similar in both materials (which in the case of the desolvated cage **B** is known to be small due to the hydrogen bonding, and therefore uptake here would be low anyway). We have noted in previous work that when crystalline cage samples are soaked in solutions of guests, quite large guest molecules can permeate the crystals and enter the cage cavities,^{50,52} even when the windows are occluded in the crystal structure and when the guest dimensions are larger than the 4 Å windows⁴⁷ in the cage faces. Thus, for guest molecules as small as N_2 or CO_2 , differences in crystal packing are unlikely to prevent adsorption: the similarity in CO_2 uptake for both cage types therefore most plausibly relates to the similarity of the cavity inside cages **A** and **B**.⁴⁹ Adsorption/desorption of CO_2 is reversible in both cases with only a slight hysteresis, as is common for porous materials, which diminishes at low pressures.

Attempts to locate CO_2 guests within the cages were made using X-ray crystallography on single crystals under a CO_2 atmosphere, but the crystals fractured rapidly into micro-crystalline powder upon desolvation. Instead, using the method that has worked with other guests, single crystals of **B** (still solvated to prevent cracking) were soaked in liquid CS_2 – as a structural analogue of CO_2 – at 40 °C for 2 hours. This resulted in uptake of CS_2 into the cage cavity.

Crystallographic analysis (ESI†) showed the structure to be $[\text{Co}_8(\text{L}^{\text{W}})_{12}](\text{BF}_4)_{16}\cdot\text{CS}_2\cdot 5\text{H}_2\text{O}$ (Fig. 3) in which a molecule of CS_2 is located such that it interacts with one of the hydrogen-bond donor pockets on the interior surface which are located at the two *fac* tris-chelate sites at either end of the long diagonal of the approximately cubic assembly.^{47–49}

The site occupancy of the CS_2 in each of the two pockets is 0.5, *i.e.* in the crystal structure there is one guest molecule per cage but it is disordered equally over the two possible sites. The CS_2 guest is oriented such that the S atom [S(11S)] that is directed into the corner pocket is involved in several $\text{CH}\cdots\text{S}$ contacts ($\text{C}\cdots\text{S}$ distances in the range 3.5–3.7 Å) with H atoms from CH_2 groups and naphthyl groups that converge around the guest binding site; the (non-bonded) $\text{Co}(1)\cdots\text{S}(11\text{S})$ separation is 5.65 Å. The other S atom of the guest S(13S) is also involved in a short $\text{CH}\cdots\text{S}$ contact (3.51 Å) with an inwardly-directed naphthyl CH proton. This set of interactions is emphasised in Fig. 3(b).

The quadrupole moment of CS_2 is opposite in sign to that of CO_2 so in terms of point charges it is denoted $(\delta^+)-(\delta^-)-(\delta^+)$.^{55,56}

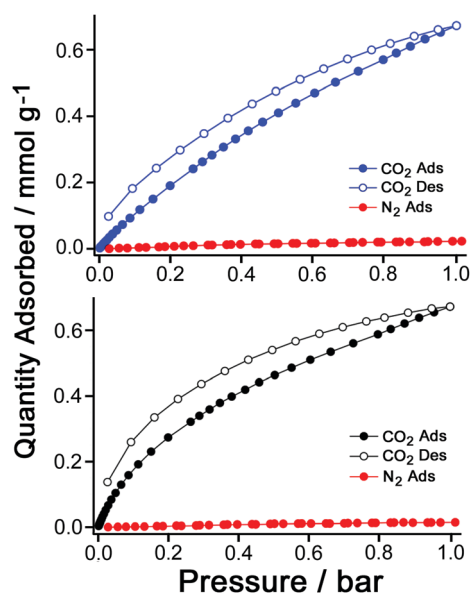


Fig. 2 Volumetric gas sorption profiles for CO_2 and N_2 in cages **A** (top) and **B** (bottom) at 298 K. Filled circles represent adsorption and hollow circles represent desorption.



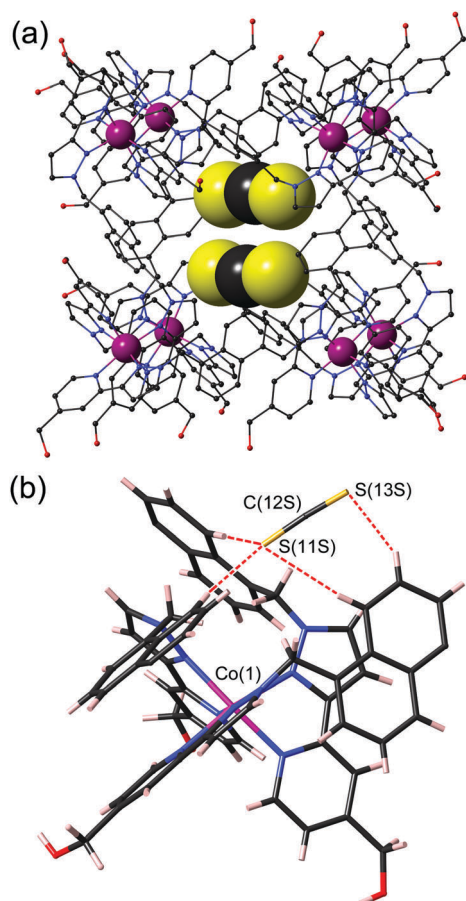


Fig. 3 Crystal structure of the complex cation $[\text{Co}_8(\text{L}^{\text{W}})_{12}](\text{BF}_4)_{16} \cdot \text{CS}_2 \cdot 5\text{H}_2\text{O}$: (a) a view of the entire cage (in wireframe) with the CS_2 guest (50% site occupancy in each of two positions) shown space-filling; (b) a close-up of the hydrogen-bonding environment around the CS_2 guest, with the shortest $\text{CH} \cdots \text{S}$ contacts shown with red dashed lines.

in this respect CS_2 is not electronically analogous to CO_2 although it is a reasonable geometric model. Nonetheless the ability of the S atoms of CS_2 to act as hydrogen-bond acceptors, based on the local electron density at the S atoms associated with lone pairs, is well established.^{57–60} We showed a while ago that the convergent array of CH donors located close to the Co(II) ions at the *fac* tris-chelate cage corners, in a region of high positive electrostatic potential, provides cumulatively an H-bond donor site to guests that is comparable in strength to phenol.⁴⁷ Given that phenol has been shown to be a sufficiently strong H-bond donor to form $\text{S} \cdots \text{H-X}$ hydrogen bonds with CS_2 ,⁵⁷ we propose that this structure of the **B**- CS_2 complex provides (i) a reasonable structural model for CO_2 binding in the cavity,⁵⁴ and (ii) a rationale for the strong preference of the cages for CO_2 vs. N_2 binding. We note also that CS_2 binds weakly in the cavity of **B** in aqueous solution; a standard ^1H NMR titration showed that CS_2 binds in fast exchange, with incremental shifts in the positions of some of the ^1H NMR signals of **B** during addition of CS_2 fitting a 1:1 binding isotherm with $K = 2 \text{ M}^{-1}$ (ESI^\dagger).

The balance between absolute CO_2 uptake, and CO_2/N_2 uptake selectivity, is amongst the best known in any kind of

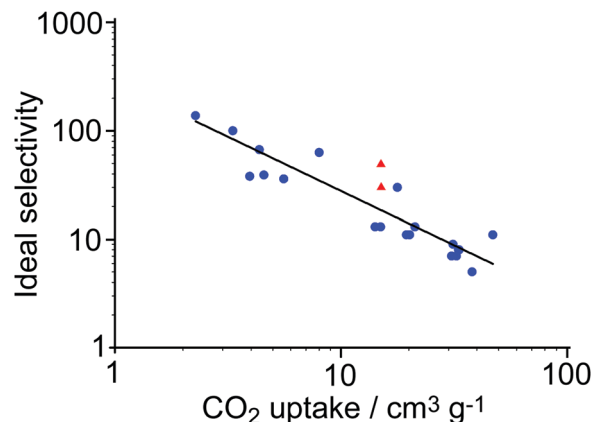


Fig. 4 Logarithmic plot of ideal CO_2/N_2 selectivity vs. CO_2 uptake capacity for a variety of porous materials. The linear trendline in black shows the general inverse relationship between gas uptake capacity and CO_2/N_2 selectivity. Data for the coordination cages in this work are shown as red triangles. Data for porous materials from other groups are shown for comparison as blue circles (Cooper group, ref. 32; Zhang group, ref. 34 and 35; various selected MOFs, see references within ref. 32).

porous material. Fig. 4 shows data for a range of other porous materials: on this graph the results for cages **A** and **B** are clearly better than the average performance for selectivity vs. uptake for many other materials, with the results for cage **B** at 298 K lying furthest above the trend-line of any of the representative set of examples included in the figure.

In conclusion we have demonstrated good CO_2 uptake by a molecular cage complex in which the gaseous guest binds in the central cage cavity even when the bulk materials are not conventionally porous. Such examples of gas sorption into the cavities of molecular cages – in contrast to porous network materials – are very rare.^{61,62} On the basis of the structural model based on CS_2 , we suggest that this arises because of favourable polar interactions between the CO_2 guest and charge-assisted hydrogen-bond donor sites on the interior surface of the cage host;^{47,53,54} these same structural features also result in particularly high selectivity for binding of CO_2 compared to non-polar N_2 .

We thank EPSRC for financial support (grants EP/N031555/1 and EP/K503812/1).

Notes and references

- 1 E. J. Carrington, C. A. McAnally, A. J. Fletcher, S. P. Thompson, M. Warren and L. Brammer, *Nat. Chem.*, 2017, DOI: 10.1038/Nchem.2747.
- 2 S. A. Basnayake, J. Su, X. Zou and K. J. Balkus Jr., *Inorg. Chem.*, 2015, 54(4), 1816–1821.
- 3 P. Deria, S. Li, H. Zhang, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2015, 51, 12478–12481.
- 4 H. Wang, K. Yao, Z. Zhang, J. Jagiello, Q. Gong, Y. Han and J. Li, *Chem. Sci.*, 2014, 5, 620–624.
- 5 H. J. Jeon, R. Matsuda, P. Kanoo, H. Kajiro, L. Li, H. Sato, Y. Zheng and S. Kitagawa, *Chem. Commun.*, 2014, 50, 10861–10863.
- 6 M. Du, C.-P. Li, M. Chen, Z.-W. Gei, X. Wang, L. Wang and C.-S. Liu, *J. Am. Chem. Soc.*, 2014, 136, 10906–10909.
- 7 M. Alhamami, H. Doan and C.-H. Cheng, *Materials*, 2014, 7, 3198–3250.
- 8 J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown and J. Liu, *Chem. Soc. Rev.*, 2012, 41, 2308–2322.



- 9 W. M. Bloch, R. Babarao, M. R. Hill, C. J. Doonan and C. J. Sumby, *J. Am. Chem. Soc.*, 2013, **135**(28), 10441–10448.
- 10 J. A. Mason, M. Veenstra and J. R. Long, *Chem. Sci.*, 2014, **5**, 32–51.
- 11 B. Yuan, D. Ma, X. Wang, Z. Li, Y. Li, H. Liu and D. He, *Chem. Commun.*, 2012, **48**, 1135–1137.
- 12 H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. Özgür Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim and O. M. Yaghi, *Science*, 2010, **329**, 424–428.
- 13 S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2010, **1**, 695–704.
- 14 A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 17998–17999.
- 15 T. Itoh, M. Kondo, H. Sakamoto, K. Wakabayashi, M. Kanaïke, K. Itami and S. Masaoka, *Dalton Trans.*, 2015, **44**, 15334–15342.
- 16 Y. Takasaki and S. Takamizawa, *J. Am. Chem. Soc.*, 2014, **136**, 6806–6809.
- 17 W. Kosaka, K. Yamagashi, H. Yoshida, R. Matsuda, S. Kitagawa, M. Takata and H. Miyasaka, *Chem. Commun.*, 2013, **49**, 1594–1596.
- 18 K. Polak-Kraśna, R. Dawson, L. T. Holyfield, C. R. Brown, A. D. Burrows and T. J. Mays, *J. Mater. Sci.*, 2017, **52**, 3862–3875.
- 19 R. T. Woodward, L. A. Stevens, R. Dawson, M. Vijayaraghavan, T. Hasell, I. P. Silverwood, A. V. Ewing, T. Ratvijitvech, J. D. Exley, S. Y. Chong, F. Blanc, D. J. Adams, S. G. Kazarian, C. E. Sharpe, T. C. Drage and A. I. Cooper, *J. Am. Chem. Soc.*, 2014, **136**, 9028–9035.
- 20 S. Fischer, A. Schimanowitz, R. Dawson, I. Senkowska, S. Kaskel and A. Thomas, *J. Mater. Chem. A*, 2014, **2**, 11825–11829.
- 21 Y. Zhu, H. Long and W. Zhang, *Chem. Mater.*, 2013, **25**, 1630–1635.
- 22 R. Dawson, A. I. Cooper and D. J. Adams, *Polym. Int.*, 2013, **62**, 345–352.
- 23 X.-Z. Luo, X.-J. Jia, J.-H. Deng, J.-L. Zhong, H.-J. Liu, K.-J. Wang and D.-C. Zhong, *J. Am. Chem. Soc.*, 2013, **135**(32), 11684–11687.
- 24 H. Ma, H. Ren, S. Meng, Z. Yan, H. Zhao, F. Sun and G. Zhu, *Chem. Commun.*, 2013, **49**, 9773–9775.
- 25 T. Hasell, M. Miklitz, A. Stephenson, M. A. Little, S. Y. Chong, R. Clowes, L. Chen, D. Holden, G. A. Tribello, K. E. Jelfs and A. I. Cooper, *J. Am. Chem. Soc.*, 2016, **138**, 1653–1659.
- 26 Q. Song, S. Jiang, T. Hasell, M. Liu, S. Sun, A. K. Cheetham, E. Sivaniah and A. I. Cooper, *Adv. Mater.*, 2016, **28**, 2629–2637.
- 27 R. Manurung, D. Holden, M. Miklitz, L. Chen, T. Hasell, S. Y. Chong, M. Haranczyk, A. I. Cooper and K. E. Jelfs, *J. Phys. Chem. C*, 2015, **119**, 22577–22586.
- 28 L. Chen, P. S. Reiss, S. Y. Chong, D. Holden, K. E. Jelfs, T. Hasell, M. A. Little, A. Kewley, M. E. Briggs, A. Stephenson, K. M. Thomas, J. A. Armstrong, J. Bell, J. Busto, R. Noel, J. Liu, D. M. Strachan, P. K. Thallapally and A. I. Cooper, *Nat. Mater.*, 2014, **13**, 954–960.
- 29 D. Holden, K. E. Jelfs, A. Trewin, D. J. Willock, M. Haranczyk and A. I. Cooper, *J. Phys. Chem. C*, 2014, **118**, 12734–12743.
- 30 S. Jiang, K. E. Jelfs, D. Holden, T. Hasell, S. Y. Chong, M. Haranczyk, A. Trewin and A. I. Cooper, *J. Am. Chem. Soc.*, 2013, **135**, 17818–17830.
- 31 T. Hasell, J. A. Armstrong, K. E. Jelfs, F. H. Tay, K. M. Thomas, S. G. Kazarian and A. I. Cooper, *Chem. Commun.*, 2013, **49**, 9410–9412.
- 32 S. Jiang, J. Bacsá, X. Wu, J. T. A. Jones, R. Dawson, A. Trewin, D. J. Adams and A. I. Cooper, *Chem. Commun.*, 2011, **47**, 8919–8921.
- 33 T. Mitra, X. Wu, R. Clowes, J. T. A. Jones, K. E. Jelfs, D. J. Adams, A. Trewin, J. Basca, A. Steiner and A. I. Cooper, *Chem. – Eur. J.*, 2011, **17**, 10235–10240.
- 34 Y. Jin, B. A. Voss, A. Jin, H. Long, R. D. Noble and W. Zhang, *J. Am. Chem. Soc.*, 2011, **133**, 6650–6658.
- 35 Y. Jin, B. A. Voss, R. D. Noble and W. Zhang, *Angew. Chem., Int. Ed.*, 2010, **49**(36), 6348–6351.
- 36 J. Tian, J. Liu, J. Liu and P. K. Thallapally, *CrystEngComm*, 2013, **15**, 1528–1531.
- 37 L. Dobrzańska, G. O. Lloyd, H. G. Raubenheimer and L. J. Barbour, *J. Am. Chem. Soc.*, 2005, **128**, 698–699.
- 38 P. K. Thallapally, G. O. Lloyd, T. B. Wirsig, M. W. Bredenkamp, J. L. Atwood and L. J. Barbour, *Chem. Commun.*, 2005, 5272–5274.
- 39 P. Sozzani, S. Bracco, A. Comotti, L. Ferretti and R. Simonutti, *Angew. Chem., Int. Ed.*, 2005, **44**, 1816–1820.
- 40 L. Dobrzańska, G. O. Lloyd, H. G. Raubenheimer and L. J. Barbour, *J. Am. Chem. Soc.*, 2005, **127**, 13134–13135.
- 41 J. L. Atwood, L. J. Barbour and A. Jerga, *Angew. Chem., Int. Ed.*, 2004, **43**, 2948–2950.
- 42 J. L. Atwood, L. J. Barbour and A. Jerga, *Science*, 2002, **296**, 2367–2369.
- 43 Y. He, S. Xiang and B. Chen, *J. Am. Chem. Soc.*, 2011, **133**, 14570–14573.
- 44 S. D. Burd, S. Ma, J. A. Perman, B. J. Sikora, R. Q. Snurr, P. K. Thallapally, J. Tian, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2012, **134**, 3663–3666.
- 45 S. Galli, N. Masciocchi, V. Colombo, A. Maspero, G. Palmisano, F. J. López-Garzón, M. Domingo-García, I. Fernández-Morales, E. Barea and J. A. R. Navarro, *Chem. Mater.*, 2010, **22**, 1664–1672.
- 46 M. D. Ward, C. A. Hunter and N. H. Williams, *Chem. Lett.*, 2017, **46**, 2–9.
- 47 S. Turega, M. Whitehead, B. R. Hall, A. J. H. M. Meijer, C. A. Hunter and M. D. Ward, *Inorg. Chem.*, 2013, **52**, 1122–1132.
- 48 I. S. Tidmarsh, T. B. Faust, H. Adams, L. P. Harding, L. Russo, W. Clegg and M. D. Ward, *J. Am. Chem. Soc.*, 2008, **130**, 15167–15175.
- 49 M. Whitehead, S. Turega, A. Stephenson, C. A. Hunter and M. D. Ward, *Chem. Sci.*, 2013, **4**, 2744–2751.
- 50 S. Turega, W. Cullen, M. Whitehead, C. A. Hunter and M. D. Ward, *J. Am. Chem. Soc.*, 2014, **136**, 8475–8483.
- 51 W. Cullen, S. Turega, C. A. Hunter and M. D. Ward, *Chem. Sci.*, 2015, **6**, 2790–2794.
- 52 W. Cullen, M. C. Misuraca, C. A. Hunter, N. H. Williams and M. D. Ward, *Nat. Chem.*, 2016, **8**, 231–236.
- 53 A. J. Metherell and M. D. Ward, *Dalton Trans.*, 2016, **45**, 16096–16111.
- 54 C. G. Morris, N. M. Jacques, H. G. W. Godfrey, T. Mitra, D. Fritsch, Z. Lu, C. A. Murray, J. Potter, T. M. Cobb, F. Yuan, C. C. Tang, S. Yang and M. Schröder, *Chem. Sci.*, 2017, **8**, 3239–3248.
- 55 M. R. Battaglia, A. D. Buckingham, D. Neumark, R. K. Pierens and J. H. Williams, *Mol. Phys.*, 1981, **43**, 1015–1020.
- 56 G. L. D. Ritchie and J. Vrbancich, *J. Chem. Soc., Faraday Trans. 2*, 1980, **76**, 1245–1248.
- 57 A. B. Sannigrahi and A. K. Chandra, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 1344.
- 58 A. L. Picone and R. M. Romano, *J. Mol. Struct.*, 2010, **978**, 187.
- 59 M. Wierzejewska and M. Dziadosz, *J. Mol. Struct.*, 1999, **513**, 155.
- 60 K. N. Power, T. L. Hennigar and M. J. Zaworotko, *New J. Chem.*, 1998, 177–181.
- 61 I. A. Riddell, M. M. Smulders, J. K. Clegg and J. R. Nitschke, *Chem. Commun.*, 2011, **47**, 457–459.
- 62 J. Roukala, J. Zhu, C. Giri, K. Rissanen, P. Lantto and V.-V. Telkki, *J. Am. Chem. Soc.*, 2015, **137**, 2464–2467.

