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Reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with *p*-*tert*-butylthiacalix[4]arene ($\text{H}_4\text{TC}[4]\text{A}$) affords a $[\text{Cu}_{24}^{\text{II}}]$ cage whose metallic skeleton conforms to a truncated octahedron in which the metal ions are strongly antiferromagnetically coupled. A structurally related $[\text{Cu}_8^{\text{II}}]$ cluster can be made using CuBr_2 in an otherwise identical reaction.

Polymetallic complexes of Cu^{II} represented the gateway to the field of molecular magnetism, beginning with studies of copper acetate¹ in the 1950s through to the development of magneto-structural correlations in hydroxide- and halide-bridged dimers in the 1970s and 80s.² Later research revealed the presence of spin frustration in equilateral Cu^{II} triangles and prompted detailed studies into the mechanisms of magnetic exchange.³ Indeed, high symmetry molecules are often ideal model complexes to examine geometric spin frustration, and for larger nuclearity cages this can lead to some exotic behaviour including enhanced ground-state degeneracy, low-lying singlets, non-collinear ground states and unusual magnetisation plateaus/jumps.⁴ The synthesis of high symmetry molecules is however not trivial.⁵ One approach is to build small nuclearity, high symmetry complexes such as triangles or squares, since these are the building blocks of certain Archimedean and Platonic (or Keplerate) polyhedra, and assemble them into larger species often at high temperatures and pressures.⁶ An additional challenge comes in designing an organic ligand capable of stabilising such building blocks, and an excellent candidate is *p*-*tert*-butylthiacalix[4]arene ($\text{H}_4\text{TC}[4]\text{A}$, Fig. 1). This versatile molecule was first synthesised in 1997 and has since proved to be a highly successful platform for a breadth of

supramolecular and coordination chemistry.^{7–13} In the latter area, the $[\text{S}_4\text{O}_4]$ donor atom set typically leads to the formation of square $[\text{M}_4]$ building blocks that can self-assemble to form aesthetically pleasing molecular cages exhibiting a variety of nuclearities and topologies.¹⁴ This versatility is particularly appealing to chemists interested in constructing high nuclearity cages of paramagnetic metal ions with a view to developing magneto-structural correlations and/or uncovering novel magnetic phenomena. Surprisingly however, a search of the Cambridge structural database for $\text{TC}[4]\text{A}$ -supported Cu^{II} cages reveals just five hits: four $[\text{Cu}_4]$ squares and one $[\text{Cu}_{13}\text{Na}_2]$ cluster.¹⁵ Herein, we outline the synthesis, structure and magnetic behaviour of a $[\text{Cu}_{24}^{\text{II}}]$ cage and a structurally related $[\text{Cu}_8^{\text{II}}]$ building block.

Reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with $\text{H}_4\text{TC}[4]\text{A}$ in a basic dmf/MeOH solution (see ESI,† for full details) leads to the formation of brown single crystals after 3 days, upon slow evaporation of the mother liquor. Crystals of $[\text{Cu}_{24}(\mu_4\text{-TC}[4]\text{A})_6(\mu_4\text{-Cl})_6(\mu_6\text{-CO}_3)_6(\mu\text{-OH})_6(\text{dmf})_6] \cdot 22\text{dmf}$ (**1**·22dmf) were found to be in a triclinic cell and structure solution was performed in the *P*1 space group (see Fig. S1, ESI,† shows the PXRD). The asymmetric unit (ASU) contains two distinct half clusters (*i.e.* the unit cell contains two $[\text{Cu}_{24}]$ clusters which lie about independent inversion centres)

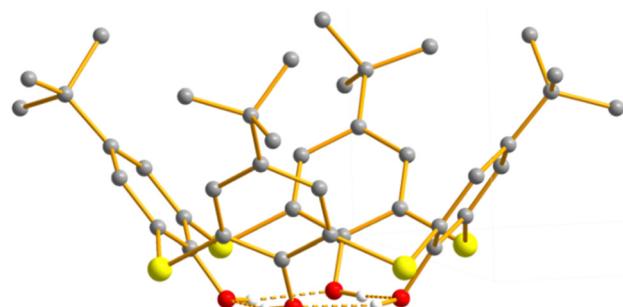


Fig. 1 The structure of *p*-*tert*-butylthiacalix[4]arene ($\text{H}_4\text{TC}[4]\text{A}$). Colour code: C = grey, O = red, S = yellow, H = white. Only the phenolic H atoms are shown.

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† Electronic supplementary information (ESI) available: Experimental procedures, XRD and magnetometry collection/analysis details, additional figures. CCDC 2417304 and 2417305. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5cc00532a>



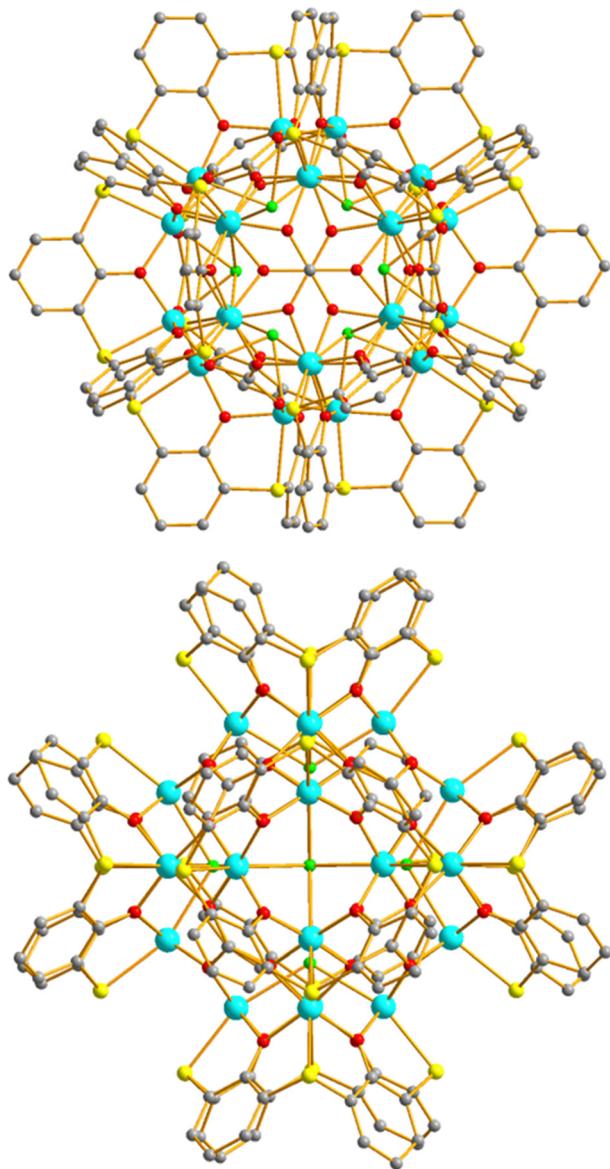


Fig. 2 Different views of the molecular structure of complex **1**. Colour code: Cu = pale blue, O = red, S = yellow, Cl = green, C = grey. ¹Bu groups, H atoms and solvent molecules of crystallisation are omitted for clarity.

and symmetry expansion affords the cage shown in Fig. 2. The metallic skeleton (Fig. 3) of **1** describes a $[\text{Cu}_{24}^{\text{II}}]$ truncated octahedron. The fully deprotonated TC[4]A ligands sit atop the six square faces, bonding to the four Cu ions through four $\mu\text{-O}$ atoms and four terminal S atoms, as expected. Below the square lies a $\mu_4\text{-Cl}^{1-}$ ion, creating the $[\text{Cu}_4(\text{TC}[4]\text{A})\text{Cl}]$ building block. Six of these building blocks are self-assembled into the $[\text{Cu}_{24}]$ unit by a disordered combination of six $\mu_6\text{-CO}_3^{2-}$ ions and six $\mu\text{-OH}^{1-}$ ions (see the CIF file/ESI,[†] for full details), which lie in the hexagonal faces of the truncated octahedron. The carbonate anions originate from CO_2 fixation. Perhaps counter-intuitively, the deliberate addition of CO_3^{2-} ions to the reaction mixture, in the form of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$, prevents crystal formation.

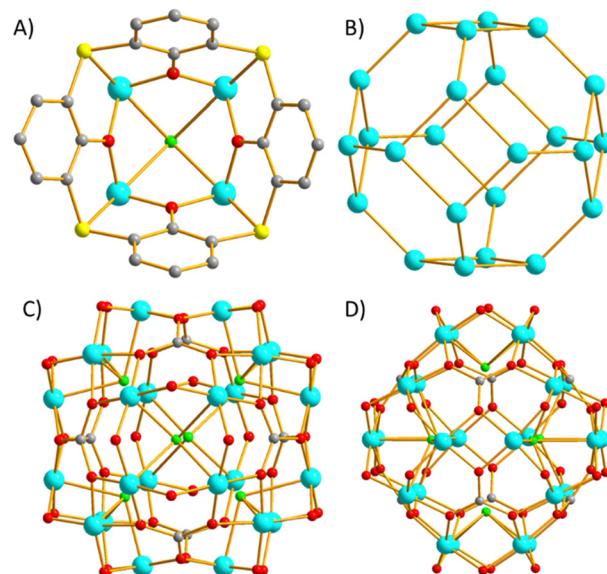


Fig. 3 (A) Bonding modes of the TC[4]A ligand/Cl ion and the formation of the $[\text{Cu}_4(\text{TC}[4]\text{A})\text{Cl}]$ building block. (B) Metallic skeleton of **1** highlighting the truncated octahedron topology. (C) and (D) Different views of the magnetic core of **1**. Colour code: Cu = pale blue, O = red, S = yellow, Cl = green, C = grey. ¹Bu groups, H-atoms and solvent molecules of crystallisation are omitted for clarity.

The Cu ions are all six coordinate and in Jahn–Teller (JT) distorted $\{\text{CuO}_4\text{SCl}\}$ environments with the JT axis directed along the S–Cu–Cl vector (Cu–O , $\sim 1.60\text{--}2.10$ Å, Cu–S , $\sim 2.59\text{--}2.63$ Å, Cu–Cl , $\sim 2.65\text{--}2.67$ Å). A dmf molecule sits in each of the calixarene cavities, although two were handled using a solvent mask during structure refinement. The self-assembly of the six $[\text{Cu}_4(\text{TC}[4]\text{A})\text{Cl}]$ moieties gives rise to a small encapsulated space at the centre of the $[\text{Cu}_{24}]$ cluster that is occupied by three disordered H_2O molecules. These are H-bonded to both the $\mu_4\text{-Cl}^{1-}$ ions and the O-atoms of the $\mu_6\text{-CO}_3^{2-}/\mu\text{-OH}^{1-}$ ions ($\text{O}\cdots\text{O/Cl} \leq 3$ Å) that line the interior wall of the cage. Closest intermolecular interactions occur between the ¹Bu groups of the TC[4]A ligands ($\text{C}\cdots\text{C} \geq 3.5$ Å) and between the ¹Bu groups and the dmf solvate ($\text{C}\cdots\text{O} \geq 3.7$ Å). Examination of the extended structure (Fig. S2, ESI,[†]) confirms that the cluster cores are very well isolated from symmetry equivalents due to the TC[4]A ligands, with the closest $\text{Cu}\cdots\text{Cu}$ distance found being >12.6 Å.

We note that TC[4]A-stabilised truncated octahedra are known for Co^{II} , Ni^{II} and Mn^{II} ,¹⁶ but **1** represents the first example obtained with Cu^{II} . Interestingly a $[\text{Cu}_{24}^{\text{I}}]$ cage was recently synthesised using tetramercaptotetrathiocalix[4]arene,¹⁷ which suggests that control over metal oxidation state can be achieved through choice/variation of lower rim substituent, or through the use of different calix[n]arenes within the same reaction, routes not yet exploited.

A $[\text{Cu}_8^{\text{II}}]$ cluster representing approximately one third of the structure of **1** can be isolated by replacing $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ with CuBr_2 in an otherwise identical reaction. Crystals of $[\text{Cu}_8^{\text{II}}(\mu_4\text{-TC}[4]\text{A})_2(\mu_4\text{-CO}_3)(\mu\text{-OH})(\text{Br})_5(\text{dmf})_3(\text{H}_2\text{O})]\cdot 2\text{dmf}$ (2·2dmf, Fig. S1, ESI,[†] shows the PXRD) were in an orthorhombic cell with

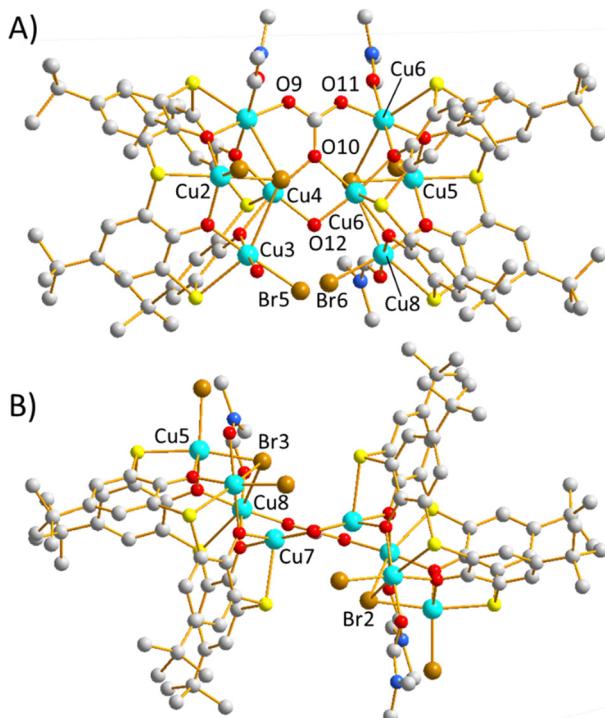


Fig. 4 Orthogonal views of the molecular structure of complex **2**. Down the *b*-axis (A) and *a*-axis (B) of the unit cell. Colour code: Cu = pale blue, O = red, S = yellow, Br = brown, C = grey, N = dark blue. ¹Bu groups, H atoms and solvent molecules of crystallisation are omitted for clarity.

structure solution performed in the space group *Pbca*; the ASU contains the whole formula (Fig. 4). The structure of **2** describes two $[\text{Cu}_4(\text{TC}[4]\text{A})\text{Br}]$ metalloligands bridged by one CO_3^{2-} ligand and one OH^{1-} ion. The $[\text{Cu}_4]$ squares are asymmetric, with one Cu–Br bond length in the range ~ 2.43 – 2.44 Å and three in the range ~ 2.98 – 3.08 Å. As a result, the Cu···Cu distances are also asymmetric, and in the range ~ 3.21 – 3.45 Å. The CO_3^{2-} ion (which as with **1** originates from CO_2 fixation) acts as a μ_4 -bridge between the two $[\text{Cu}_4]$ squares, linking Cu1 and Cu4 on one square with Cu6 and Cu7 on the second square. Cu4 and Cu7 are also bridged by the sole $\mu\text{-OH}^{1-}$ ion (Cu4–O12–Cu7, $\sim 105^\circ$) which itself is H-bonded to the terminal Br^{1-} ion (Br6) attached to Cu8 with 50% occupancy ($\text{O}(\text{H})\cdots\text{Br}$, ~ 3.15 Å). Charge-balance is afforded through the 50% occupancy of another terminal Br^{1-} ion (Br5) attached to Cu3, but at an angle that does not allow for H-bonding with the OH^{1-} ion. The remaining coordination sites on the Cu ions are filled with a dmf molecule (Cu1, Cu3, Cu6), a H_2O molecule (Cu8), and a terminal Br^{1-} ion with full occupancy (Cu2, Cu5). The Cu ions adopt four different geometries/coordination spheres. Cu3 and Cu8 are five-/six-coordinate as the Br^{1-} ion is disordered across the two positions and thus have distorted square pyramidal/octahedral $\{\text{CuO}_3\text{Br}_{1.5}\text{S}\}$ geometries. Cu2 and Cu5 are five-coordinate and are in distorted square pyramidal $\{\text{CuO}_2\text{Br}_2\text{S}\}$ geometries, and Cu1/Cu4/Cu6/Cu7 are all six-coordinate and in distorted octahedral $\{\text{CuO}_4\text{BrS}\}$ geometries. In each case the JT axis of the Cu^{II} ion lies along the S–Cu–Br vector. A molecule of dmf occupies each TC[4]A cavity. Deliberate

introduction of CO_3^{2-} ions to the reaction mixture, in the form of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ results in the formation of insoluble powder.

Examination of the extended structure of **2** reveals that symmetry equivalent clusters pack to form a bi-layer type structure (Fig. S3, ESI†). This type of self-assembled bi-layer structure is commonly observed¹⁸ in a variety of calixarene solvates and coordination compounds in which the ligands are not forced to pack in a parallel manner, *e.g.* as in the structure of **1**. The result of this is that the closest crystallographically unique Cu···Cu distance between neighbouring clusters is found to be significantly shorter than in **1**, in this case at ~ 8.4 Å as shown in Fig. S3 (ESI†).

De magnetic susceptibility data were measured on powdered polycrystalline samples of **1**–**2** in the $T = 300$ – 2.0 K temperature range, in a field of $B = 0.1$ T (Fig. 5). The χT values of **1**/**2** at 300 K are $4.29/2.49$ $\text{cm}^3 \text{K mol}^{-1}$, both well below the Curie constant expected for 24/8 uncoupled $S = \frac{1}{2}$ ions ($9/3$ $\text{cm}^3 \text{K mol}^{-1}$ for $g = 2.00$). As the temperature is decreased the value of χT decreases rapidly and reaches a value of $0 \text{ cm}^3 \text{K mol}^{-1}$ at $T = 15/5$ K in both cases. This behaviour is clearly indicative of very strong antiferromagnetic exchange between neighbouring Cu^{II} ions in both **1** and **2**, and the presence of well isolated diamagnetic ground states, as corroborated by magnetisation data (Fig. S4, ESI†).

The presence of two different clusters of **1** in the unit cell, the disordered $[\text{CO}_3]/[\text{OH}]$ and a total of twenty four Cu^{II} ions per cluster poses some problems (over-parameterisation, computational limits) for modelling the magnetic behaviour. In order to overcome these issues, we have constructed three $[\text{Cu}_{12}]$ model compounds (models 1–3, Fig. S5, ESI†) that describe half the cluster, and assume the presence of not more than three distinct exchange interactions based on the different bridging atoms and angles present. These are $J_1 = \text{Cu–O/Cl–Cu}$

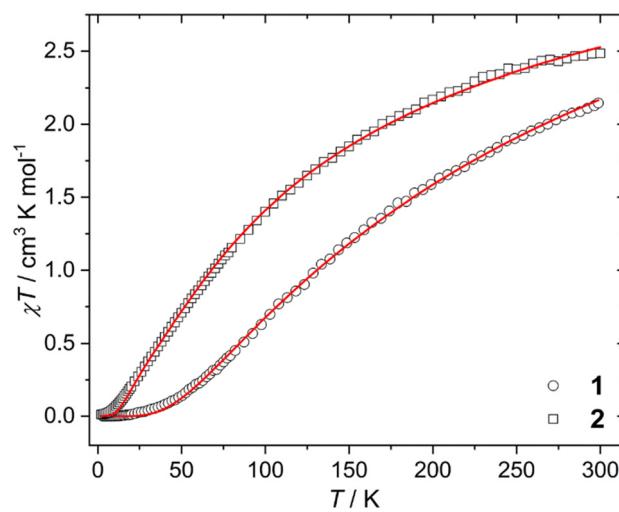


Fig. 5 Experimental χT versus T data for **1** (○) and **2** (□) measured in the $T = 300$ – 2.0 K temperature range in an applied field, $B = 0.1$ T. The experimental data for **1** is divided by two and modelled using spin-Hamiltonian (1) and model 1 shown in Fig. S5 (ESI†). The solid red lines are the best fits to the experimental data. See text for details.



along the sides of the square faces ($\text{Cu}-\text{O}-\text{Cu} = \sim 109\text{--}112^\circ$, $\text{Cu}-\text{Cl}-\text{Cu} = \sim 75^\circ$); $J_2 = \text{Cu}-\text{Cl}-\text{Cu}$ across the diagonal of the square faces ($\text{Cu}-\text{Cl}-\text{Cu} = \sim 118^\circ$); and $J_3 = \text{Cu}-\text{O}-\text{Cu}$ along the edges of hexagonal faces ($\text{Cu}-\text{O}_{\text{hydroxide}}-\text{Cu} = \sim 94^\circ$, $\text{Cu}-\text{O}_{\text{carbonate}}-\text{Cu} = \sim 120^\circ$) through the disordered OH/CO_3 bridges. We ignore any diagonal interactions across the face of the hexagon through the three atom $\text{Cu}-\text{O}-\text{C}-\text{O}-\text{Cu}$ carbonate bridges.

$$\hat{H} = \mu_B B \sum_i g_i \hat{S}_i - 2 \sum_{i,j > i} J_{ij} \hat{S}_i \cdot \hat{S}_j \quad (1)$$

The best fit parameters using these models and spin-Hamiltonian (1), where the indices refer to the constituent Cu^{II} ions, μ_B is the Bohr magneton, g is the g -factor fixed at $g = 2.00$, \hat{S} is a spin operator and J_{ij} is the pairwise isotropic exchange interaction parameter, are collected in Fig. S4 (ESI†). What is clear is that each model matches the experimental data (Fig. 5 and Fig. S6, ESI†) well but does so with different sets of J values. In other words, there is no unique fit of the susceptibility data and we can only conclude that the J values in **1** range between $-56 < J < -139 \text{ cm}^{-1}$. We disregard model 2 on account of the erroneously large J_2 value. Models based on just 2 J values led to poorer fits and/or erroneously large J values.

The data for **2** can be fitted using the model shown in Fig. S7 (ESI†), which contains two J values, one within each $[\text{Cu}_4]$ square ($J_1 = \text{Cu}-\text{O}/\text{Br}-\text{Cu}$), and one between the two squares through the two single O-atom bridges ($J_2 = \text{Cu}-\text{O}_{\text{CO}_3}/\text{O}_{\text{OH}}-\text{Cu}$). The best fit parameters are $J_1 = -98.6 \text{ cm}^{-1}$ and $J_2 = -40.6 \text{ cm}^{-1}$, with $g = 2.00$. The J values obtained for **1** and **2** are in accordance with previous magneto-structural correlations developed for O/Cl-bridged Cu^{II} dimers with similar $\text{Cu}-\text{O}/\text{Cl}-\text{Cu}$ angles.^{1,2}

In conclusion, reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or CuBr_2 with $\text{H}_4\text{TC}[4]\text{A}$ in basic dmf/MeOH solutions affords $[\text{Cu}_{24}^{\text{II}}]$ and $[\text{Cu}_8^{\text{II}}]$ clusters, respectively. The former possesses a metallic skeleton conforming to a truncated octahedron containing six $[\text{Cu}_4(\text{TC}[4]\text{A})]$ metalloligands, and the latter a dimer of $[\text{Cu}_4(\text{TC}[4]\text{A})]$ squares. In each case the self-assembly process has been facilitated by the presence of carbonate ions, originating from the fixation of CO_2 . Both **1** and **2** are novel structure types in Cu-TC[4]A coordination chemistry, the former joining the family of known TC[4]A-supported $[\text{M}_{24}]$ cages of Ni^{II} , Co^{II} and Mn^{II} . Surprisingly, **1** and **2** are just the sixth and seventh known polynuclear Cu-TC[4]A clusters, with **1** being by far the largest yet reported. Given the clear affinity between M^{II} ions and TC[4]A, one would expect many more such compounds await discovery. Magnetic susceptibility measurements reveal the presence of very strong antiferromagnetic interactions between neighbouring Cu^{II} ions in **1** and **2**, resulting in well isolated $S = 0$ ground states in both cases.

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Data availability

Crystallographic data for compounds **1**–**2** have been deposited at the CCDC under numbers 2417304 and 2417305 and can be obtained from <https://www.ccdc.cam.ac.uk/structures/>.[†] Further data supporting this manuscript have been included as part of the ESI.[†]

Conflicts of interest

There are no conflicts to declare.

Notes and references

- B. Bleaney and K. D. Bowers, *Proc. R. Soc. London*, 1952, **214**, 451–465.
- (a) W. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1976, **15**, 2107–2110; (b) W. E. Marsh, K. C. Patel, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, 1983, **22**, 511–515.
- (a) S. Ferrer, F. Lloret, E. Pardo, J. M. Clemente-Juan, M. Liu-González and S. García-Granda, *Inorg. Chem.*, 2012, **51**, 985–1001; (b) M.-A. Bouamalmi, N. Suaud, N. Guihéry and R. Maurice, *Inorg. Chem.*, 2022, **61**, 12138–12148.
- J. Schnack, *Dalton Trans.*, 2010, **39**, 4677–4686.
- M. A. Palacios, E. Moreno Pineda, S. Sanz, R. Inglis, M. B. Pitak, S. J. Coles, M. Evangelisti, H. Nojiri, C. Heesing, E. K. Brechin, J. Schnack and R. E. P. Winpenny, *ChemPhysChem*, 2016, **17**, 55–60.
- L. R. B. Wilson, M. Coletta, M. Evangelisti, S. Piligkos, S. J. Dalgarno and E. K. Brechin, *Dalton Trans.*, 2022, **51**, 4213–4226.
- N. Iki, Thiocalixarenes, in *Calixarenes and Beyond*, ed. P. Neri, J. Sessler and M. X. Wang, Springer, Cham, 2016.
- T. Sone, Y. Ohba, K. Moriya, H. Kumada and K. Ito, *Tetrahedron*, 1997, **53**, 10689–10698.
- H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama and S. Miyano, *Tetrahedron Lett.*, 1997, **38**, 3971–3972.
- N. Morohashi, F. Narumi, N. Iki, T. Hattori and S. Miyano, *Chem. Rev.*, 2006, **106**, 5291–5316.
- R. Kumar, Y. O. Lee, V. Bhalla, M. Kumar and J. S. Kim, *Chem. Soc. Rev.*, 2014, **43**, 4824–4870.
- M. Yamada, M. R. Gandhi, U. Maheswara, R. Kunda and F. Hamada, *J. Inclusion Phenom. Macrocyclic Chem.*, 2016, **85**, 1–18.
- Y. Bi, S. Du and W. Liao, *Coord. Chem. Rev.*, 2014, **276**, 61–72.
- See for example: (a) A. Bilyk, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, B. W. Skelton and A. H. White, *Inorg. Chem.*, 2001, **40**, 672–686; (b) A. Bilyk, J. W. Dunlop, R. O. Fuller, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, G. A. Koutsantonis, I. W. Murray, B. W. Skelton, A. N. Sobolev, R. L. Stamps and A. H. White, *Eur. J. Inorg. Chem.*, 2010, 2127–2152.
- (a) A. Bilyk, J. W. Dunlop, R. O. Fuller, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, G. A. Koutsantonis, I. W. Murray, B. W. Skelton, R. L. Stamps and A. H. White, *Eur. J. Inorg. Chem.*, 2010, 2106–02126; (b) G. Mislin, E. Graf, M. W. Hosseini, A. Bilyk, A. K. Hall, J. M. Harrowfield, B. W. Skelton and A. H. White, *Chem. Commun.*, 1999, 373–374; (c) Y. Bi, W. Liao, X. Wang, R. Deng and H. Zhang, *Eur. J. Inorg. Chem.*, 2009, 4989–4994; (d) C. Zhang, Z. Wang, W.-D. Si, L. Wang, J.-M. Dou, C.-H. Tung and D. Sun, *ACS Nano*, 2022, **6**, 9598–9607.
- (a) M. Liu, W. Liao, C. Hu, S. Du and H. Zhang, *Angew. Chem., Int. Ed.*, 2012, **51**, 1585–1588; (b) K. Xiong, F. Jiang, Y. Gai, D. Yuan, L. Chen, M. Wu, K. Sua and M. Hong, *Chem. Sci.*, 2012, **3**, 2321–2325; (c) K. Su, F. Jiang, J. Qian, Y. Gai, M. Wu, S. M. Bawaked, M. Mokhtar, S. A. Al-Thabaiti and M. Hong, *Cryst. Growth Des.*, 2014, **14**, 3116–3123; (d) K.-C. Xiong, F.-L. Jiang, Y.-L. Gai, D.-Q. Yuan, D. Han, J. Ma, S.-Q. Zhang and M. C. Hong, *Chem. – Eur. J.*, 2012, **18**, 5536–5540.
- N. Frank, A. Dallmann, B. Braun-Cula, C. Herwig and C. Limberg, *Angew. Chem., Int. Ed.*, 2020, **59**, 6735–6739.
- See for example: (a) K. Su, F. Jiang, J. Qian, M. Wu, K. Xiong, Y. Gai and M. Hong, *Inorg. Chem.*, 2013, **52**, 3780–3786; (b) D. Yuan, W.-X. Zhu, S. Ma and X. Yan, *J. Mol. Struct.*, 2002, **616**, 241–246; (c) N. Morohashi, K. Nanbu, A. Tonusaki and T. Hattori, *CrystEngComm*, 2015, **17**, 4799–4808.

