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Planar [Ni₇] Discs as Double-Bowl, Pseudo Metallacalix[6]arene Host Cavities

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We report three heptanuclear [Ni₇] complexes with planar disc-like cores, akin to double-bowl metallacalix[6]arenes, which form molecular H-bonded host cavities.

Polymetallic complexes of paramagnetic 1st row transition metal ions are of great current interest since they often exhibit fascinating physical properties such as spin-crossover behaviour,¹ long range ordering (*i.e.* in 1, 2 and 3D coordination polymers²) and Single-Molecule Magnet (SMM) behaviour.³ Ni^{II} in particular, has shown much promise in the synthesis of both Single-Molecule Magnets (SMMs) and spin phonon traps; the former taking advantage of its significant single-ion anisotropy and the latter its paramagnetic nature when confined within a highly symmetric cage.⁴⁻⁶ In addition, the use of magnetic clusters as building blocks to create supramolecular architectures (*i.e.* discrete polyhedra⁷ and 1, 2 and 3D polymers⁸) using both covalent and non-covalent interactions has led to materials whose physical properties can be rather different to that of their parent paramagnetic building blocks.⁹

An important factor in the construction of such assemblies is the choice of ligand, since this dictates not only cluster symmetry, topology and the number of paramagnetic metal ions present, but also the inter-molecular interactions between clusters in the crystal. Our own interest in this area has recently led us to investigate the coordination chemistry of the Schiff-base ligand 2-iminomethyl-6-methoxy-phenol (HL₁)[†] and its bromo-analogue 2-iminomethyl-4-bromo-6-methoxy-phenol (HL₂) (Fig. 1)[†] and herein report its initial coordination and supramolecular chemistry with Ni^{II}.

Reaction of Ni(NO₃)₂·6H₂O and HL₁ in the presence of NaOH in EtOH produces the heptanuclear complex [Ni₇(μ₃-OH)₆(L₁)₆](NO₃)₂ (**1**) in 30 % yield. The green hexagon shaped crystals of **1** crystallize in the trigonal space group P-3c1 (Fig. 1).[‡] Heptanuclear complex **1** possesses a core comprising a hexagon of Ni^{II} ions surrounding a central Ni^{II} centre. The central Ni^{II} ion (Ni1) is located at a site with imposed $\bar{3}$ symmetry while the nitrogen atom (N2) of the NO₃⁻ group lies on a threefold axis. The remainder of the asymmetric unit comprises a second Ni^{II} centre (Ni2) along with one L⁻ unit and one hydroxy group (O1-H1) occupying general positions. Although topologically analogous [Mn₇],¹⁰ [Fe₇]¹¹ and [Co₇]¹² complexes are known, the synthesis of **1** represents the first nickel complex to possess a planar hexagonal disc-like structure. All the Ni ions are in distorted

octahedral geometries with the six μ₃-bridging OH⁻ ions (O1) linking the central nickel (Ni1) to the six peripheral nickel ions (Ni2); each trigonal pyramidal OH⁻ ion being situated alternately above and below the [Ni₇] plane (Fig. 1).

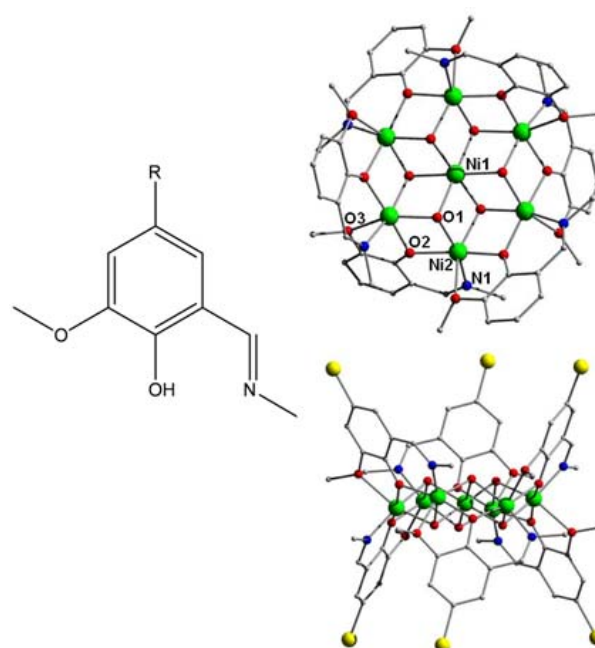


Figure 1 (left) Structure of the ligands HL₁ and HL₂ (R = H (L₁), Br (L₂)). (right) Molecular structures of complexes **1** (top) and **2** (bottom) viewed perpendicular and parallel to the [Ni₇] plane respectively.

The anionic ligands L₁⁻ (singly deprotonated at the phenolate site) bridge the peripheral Ni^{II} centres adopting a μ₂-η¹:η²:η¹ coordination motif, lying alternately above and below the [Ni₇] plane. The result is a double-bowl conformation in which the [Ni₇] core is the basal plane, reminiscent of a metallacalix[6]arene concave unit (Fig. 1). Close inspection of the double-bowl conformation shows approximate bowl dimensions of (base × depth × rim diameter) 6.20 × 4.21 × 11.70 Å. In the crystal the [Ni₇] units stack on top of one another resulting in a unit cell possessing four pseudo-superimposable 1D columns of [Ni₇] units with each unit linked by a 120° rotation. The [Ni₇] units are held into 1D columnar arrays *via* zig-zag shaped belts of NO₃⁻

anions (each comprising six NO_3^- ions) which sit above and below the individual heptanuclear complexes with C-H \cdots O bonding interactions between the NO_3^- oxygen atoms (one unique, O4) and protons (H1A and H5) of the L_1^- ligands (H1A \cdots O4 = 2.59 Å and H5 \cdots O4 = 2.44 Å). These NO_3^- belts thus effectively ‘zip-up’ pairs of $[\text{Ni}_7]$ moieties to form molecular cavities (each of approximate volume $\sim 155.9 \text{ \AA}^3$ with a $[\text{Ni}_7]_{\text{plane}}\text{-}[\text{Ni}_7]_{\text{plane}}$ distance of 11.635 Å)¹³, formed by two juxtaposed pseudo metallocalix[6]arene $[\text{Ni}_7]$ bowl units. In addition they also H-bond to adjacent 1D $[\text{Ni}_7]$ columns thus completing the 3D connectivity in the unit cell (Fig. S11). From a topological point of view, each $[\text{Ni}_7]$ is H-bonded to twelve NO_3^- with the latter being connecting six $[\text{Ni}_7]$ units thus creating a (6,12)-connected net with a $(4^{15})_2(4^{48}.6^{18})\text{-alb}$ topology (Fig. S12).^{14,15}

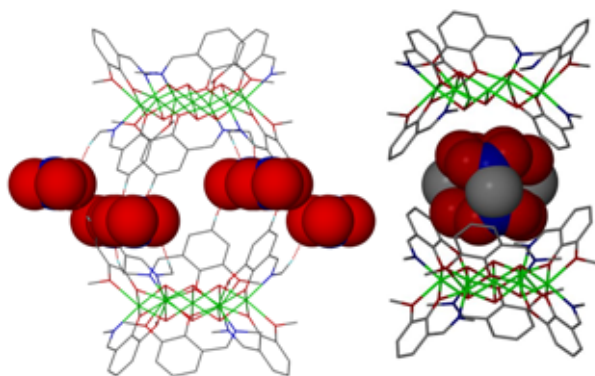


Fig. 2 Molecular structures of **1** and **2** in the crystal highlighting the empty cavity and belt of NO_3^- anions in **1** (left) and the disordered guest MeNO_2 molecules in **2** (right) within the host cavities.

The H-bonded molecular cavities formed in the crystals of **1** are empty. Investigation of these enclosures as potential host cavities towards small molecule guest inclusion led to the formation of the analogous hexanuclear complex $[\text{Ni}_7(\text{OH})_6(\text{L}_1)_6](\text{NO}_3)_2 \cdot 3\text{MeNO}_2$ (**2**), formed by dissolution of **1** in MeNO_2 in $\sim 15\%$ yield.[†] Complex **2** crystallises in the same trigonal $P\text{-}3c1$ space group as **1** and thus also possesses a central Ni^{II} (Ni1) with imposed $\bar{3}$ symmetry and a N atom (of the NO_3^- counter anion) lying on a threefold rotation axis (N2). Complex **2** also exhibits similar bowl dimensions of $6.20 \times 4.08 \times 12.04 \text{ \AA}$ while the $[\text{Ni}_7]_{\text{plane}}\text{-}[\text{Ni}_7]_{\text{plane}}$ distance of 11.371 Å in **2** is only marginally larger than observed in **1** (11.635 Å). Indeed complex **2** differs with respect to **1** only in that the H-bonded cavities in **2** are of the required size and shape (calculated volume of $\sim 322.8 \text{ \AA}^3$) to accommodate three guest MeNO_2 solvent molecules (Fig. 2). These are related crystallographically via a three fold rotation and interact within the cavity via H-bonding interactions between their O atoms (O5 and O6) and the nearby $\mu_3\text{-OH}^-$ groups on each of the two $[\text{Ni}_7]$ units which form the cavity floors (O1 \cdots O5 = 3.08 Å; O1 \cdots O6 = 3.25 Å). As commonly observed when small molecules are located within such highly symmetrical molecular cavities,¹⁶ there is crystallographic disorder of the trigonal planar MeNO_2 molecules whereby the methyl carbon atom (C10) lies on a twofold axis (see CIF for

full details). When taking steric effects into account, these orientations are most likely to exist in the up-down-up anti-parallel configuration with respect to the three fold rotation symmetry they share (Fig. 2). In a similar manner to that found in **1** the NO_3^- ions and $[\text{Ni}_7]$ units are connected by means of C-H \cdots O H-bonds (H1A \cdots O4 = 2.58 Å, H2 \cdots O4 = 2.56 Å and H5 \cdots O4 = 2.43 Å) to create the **alb** network (Fig. S12).

In an attempt to alter the size and shape of our molecular cavities and to probe whether we are able to control or alter its subsequent guest preferences, we decided to increase the bowl depth (*cf.* **1** and **2**) by employing the Br-analogue of HL_1 in the form of the pro-ligand 2-iminomethyl-4-bromo-6-methoxy-phenol (HL_2).[†]

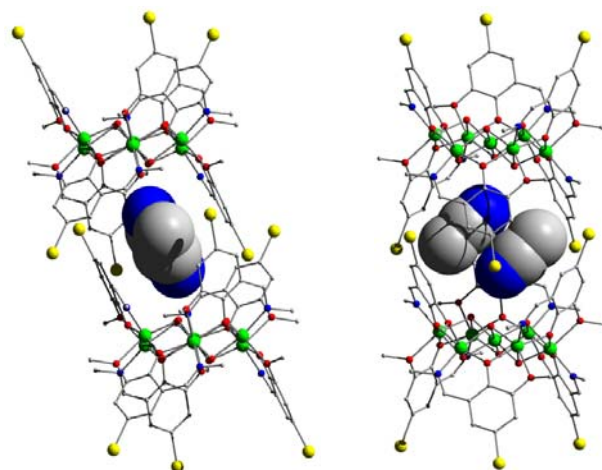


Fig. 3 Molecular structures of **3** in the crystal showing the slightly tilted molecular cavity accommodating guest MeCN pairs (space-filled).

This led to the formation of $[\text{Ni}_7(\text{OH})_6(\text{L}_2)_6](\text{NO}_3)_2 \cdot 2\text{MeCN}$ (**3**) which was formed in $\sim 23\%$ yield and crystallises in the monoclinic $C2/c$ space group.[‡] The Ni^{II} ion (Ni4) located at the centre of $[\text{Ni}_7]$ disk lies on an inversion centre while the remaining three metal centres (Ni1-3) and all other atoms in the asymmetric unit occupy general positions. Our hypothesis regarding changing cavity size was proved correct as the crystal structure shows the formation a deeper bowl of dimensions $6.22 \times 6.18 \times 11.90 \text{ \AA}$. Also apparent is that the individual $[\text{Ni}_7]$ units again stack into superimposable 1D columns, in this instance propagating along the b direction of the unit cell (Fig. S13). The stacking of the $[\text{Ni}_7]$ units along b is supported by two complementary O-H \cdots Br interactions which involve one $\mu_3\text{-OH}^-$ (H1) of a $[\text{Ni}_7]$ unit and the Br1 of a neighbouring cluster (H1 \cdots Br1 = 2.82 Å). More interestingly these 1D columnar stacks of $[\text{Ni}_7]$ units are linked by means of C-H \cdots Br interactions via the Br atoms (Br2 and Br3 and *s.e.*) of the bridging ligands (L_2^-) and $-\text{CH}_3$ (H18B and H27B) protons of juxtaposed $[\text{Ni}_7]$ moieties (H18B \cdots Br3 = 2.93 Å, H27B \cdots Br2 = 2.70 Å and *s.e.*) giving rise to a 10-connected net with a $(3^{12}.4^{28}.5^5)\text{-bct}$ topology (Fig. S14).^{14,15} These interactions give rise to molecular cavities which are tilted with respect to the $[\text{Ni}_7]$ planes and are interlocked in a staggered arrangement (Fig. 3). The

[Ni₇]_{plane}-[Ni₇]_{plane} distance inside the cavity is 11.135 Å and represents a cavity height reduction of ~0.5 Å *cf.* **1** and **2**. This may be attributed to the H-bonding affinity of the pendant Br atoms (Br1) in **3**, leading to a more tightly bound cavity. The approximate area of this enclosure is ~265.9 Å³ which is larger than that within **1** (155.9) and smaller than that within **2** (322.8). As in **2**, these H-bonded molecular cavities act as hosts for the encapsulation of guest solvent molecules. In this case, each cavity accommodates two MeCN molecules (large spheres in Fig. 3) which exhibit a head-to-tail conformation and are held in place through H-bonding *via* their N atoms (N5) with the proton (H3A) of an μ₃-OH⁻ bridging ion belonging to the nearby paramagnetic [Ni₇(OH)₆] core (N5...H3A(O3) = 2.36 Å). Efforts to encapsulate MeCN and MeNO₂ solvent guests inside the cavities of **2** and **3**, respectively, were unsuccessful. We may therefore hypothesise that guest molecules can only be placed within these cavities if and when they are able to orientate themselves into certain topologies comprising symmetry elements compatible with their hosts crystal lattices.

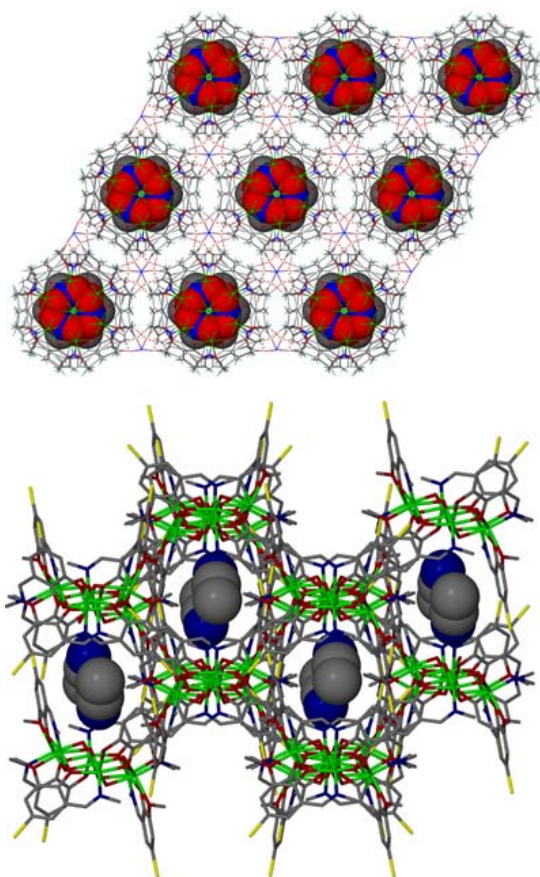


Fig. 4 Crystal packing observed in **2** (top) and **3** (bottom) showing the molecular cavities accommodating guest MeNO₂ (red spheres) and MeCN (grey / blue spheres) solvent molecules respectively. NO₃⁻ counter anions omitted for clarity in both cases.

IR spectroscopic studies on the host complexes **2** and **3** were performed to ascertain whether their guest molecules remained within their respective H-bonded cavities on drying.

CHN analysis of both complexes were consistent with guest residency (ESI). The IR spectrum of **2** gave peaks at 1337 and 1555 cm⁻¹ which are characteristic for the asymmetric and symmetric NO stretching of the guest MeNO₂ molecules respectively. Similarly a weak resonance at 2258 cm⁻¹ (CN stretch) in the IR spectrum of **3** indicated the presence of the enclosed MeCN guest molecules. The TG trace of [Ni₇(OH)₆(L₁)₆](NO₃)₂·3NO₂Me (**2**) exhibits four distinct weight loss regions, with the initial weight loss of 9.82 % corresponding to the loss of the three nitromethane moieties (calculated as 10.17 %) across the temperature range of 112°C to 140°C. The second weight loss step (of 6.30 %) between 178°C and 217°C is consistent with the loss of 2 nitrates (calculated as 6.80 %), while the third weight loss step, beginning at 320°C can be attributed to the loss of two L₁ ligands and upon further heating the decomposition of the remaining combustible materials occurs (SI5).

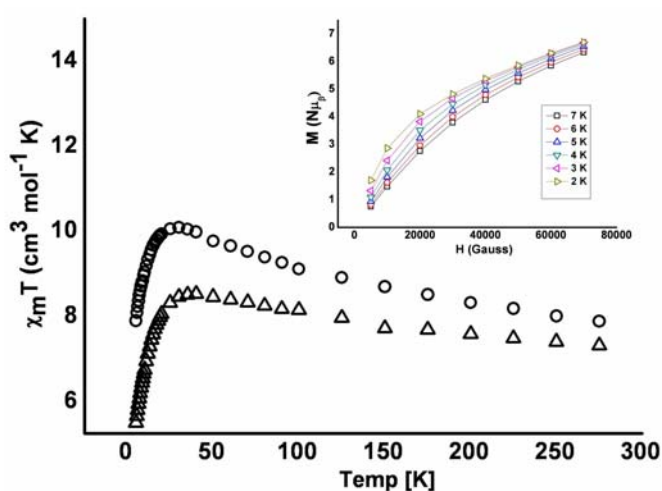


Fig. 5 Plot of $\chi_M T$ vs. T for complexes **1** (Δ) and **3** (\circ) measured in the 300-5 K temperature range in an applied field of 0.1 T. (inset)

Plot of magnetisation ($MN\mu_B$) vs. H (Gauss) for **1** obtained in the 7-2 K temperature range.

Initial magnetic measurements indicate weak ferromagnetic exchange between the metal centres; the data obtained for **1** and **3** is plotted in Figure 5. The room temperature $\chi_M T$ value of 7.76 cm³ mol⁻¹ (**1**) and 7.90 cm³ K mol⁻¹ (**3**) are consistent with that expected for 7 non-interacting Ni(II) ions with $g = 2.1$ (~7.7 cm³ K mol⁻¹). As the temperature is decreased the value of $\chi_M T$ increases slowly, reaching maximum values of ~8.5 cm³ K mol⁻¹ at 40 K for **1** and ~10 cm³ K mol⁻¹ at 25 K for **3**, before decreasing below these temperatures to minimum values of 5.5 cm³ K mol⁻¹ and 7.9 cm³ K mol⁻¹, respectively at 5 K. The observed behaviour is suggestive of very weak ferromagnetic intra-molecular exchange, with the low temperature ($T < 40$ K) decrease in $\chi_M T$ ascribed to relatively strong inter-molecular antiferromagnetic exchange, consistent with the packing of the [Ni₇] molecules in the crystal. Indeed the maxima in $\chi_M T$ for both complexes are well below that expected for an isolated $S = 7$ spin ground state (38 cm³ K mol⁻¹ for $g = 2.00$). A fit of the $1/\chi_M$ versus T using only the 300-50 K data affords Weiss constants (Θ) of +18.7 K (**1**) and

29.0 K (**3**) (Fig. SI6). The exchange interactions are likely much smaller than the single ion zfs (weak exchange limit) and thus the multiple low lying states cannot properly be described as total *S* states. This picture is also reflected in the magnetisation versus field data (collected in the ranges 0.5 – 7.0 T and 2 – 7 K and plotted in the inset of Figure 5) which shows *M* increasing only slowly with *H*, rather than quickly reaching saturation as one would expect for an isolated spin ground state. This is indicative of the population of low lying levels with smaller magnetic moment, which only become depopulated with the application of a large field, and so we cannot describe the system within the giant spin approximation.

Guest detection on **2** and **3** using ¹H NMR proved inconclusive due to significant spectral broadening and therefore the diamagnetic Zn^{II} analogues to the host / guest complexes **2** and **3** are currently being sought in order to assess their dynamic solution behaviour using NMR titration methods.¹⁶ Work on functionalising HL₁ and HL₂ to alter the size and / or shape of the resultant molecular cavities in order to incorporate species such as anions, cations and fluorescent molecules towards molecular sensor materials is currently underway.

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Notes and references

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† Full experimental details on the synthesis of **1-3** and ligands L¹ and L² are available in Electronic Supplementary Information (ESI).

‡ Crystal data for **1**: C₅₄H₆₆N₈O₂₄Ni₇, *M* = 1622.12, trigonal, space group P-3c1, *a* = *b* = 13.806(2), *c* = 23.270(5) Å, α = 90, β = 90, γ = 120°, *V* = 3841.2(11) Å³, *T* = 150(2) K, *Z* = 2, *D*_c = 1.402 g cm⁻³, 2306 reflections collected of which 1376 were unique (*R*_{int} = 0.0802), *R*₁ [*I* > 2σ(*I*)] = 0.1209, *wR*₂ = 0.2446 (*F*², all data). Crystal data for **2**: 3.3NO₂Me: C₅₇H₇₅N₁₁O₃₀Ni₇, *M* = 1709.25, trigonal, space group P-3c1, *a* = *b* = 13.933(2), *c* = 22.742(5) Å, α = 90, β = 90, γ = 120°, *V* = 3823.4(11) Å³, *T* = 150(2) K, *Z* = 2, *D*_c = 1.485 g cm⁻³, 2333 reflections collected of which 1835 were unique (*R*_{int} = 0.0502), *R*₁ [*I* > 2σ(*I*)] = 0.0604, *wR*₂ = 0.1725 (*F*², all data). Crystal data for **3**: 2MeCN: C₅₈H₆₆Br₆N₁₀O₂₄Ni₇, (2(C₂H₃N), 2(NO₃)), *M* = 2177.64, monoclinic, space group C2/c, *a* = 28.8575(14), *b* = 11.1352(3), *c* = 27.4079(13) Å, α = 90, β = 109.603(3), γ = 90.00°, *V* = 8296.6(7) Å³, *T* = 150(2) K, *Z* = 4, *D*_c = 1.743 g cm⁻³, 7348 reflections collected of which 3779 were unique (*R*_{int} = 0.0511), *R*₁ [*I* > 2σ(*I*)] = 0.1090, *wR*₂ = 0.1325 (*F*², all data). **CCDC XXXX-XXXX**

1. (a) K. S. Murray, *Eur. J. Inorg. Chem.*, 2008, **20**, 3101-3121. (b) A. B. Gaspar, M. Munoz, M. Carmen and J. A. Real, *J. Mat. Chem.*, 2006, **16**, 2522-2533. (c) A. Hauser, J. Jetic, H. Romstedt, R. Hineck and H. Spiering, *Coord. Chem. Rev.*, 1999, **190-192**, 471-491.

- (a) R. Robson, *Dalton Trans.*, 2008, 5113. (b) S. R. Batten and K. S. Murray, *Coord. Chem. Rev.*, 2003, **246**, 103-130. (c) C. Janiak, *Dalton Trans.*, 2003, 2781-2804. (d) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705-714.
- (a) R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141. (b) R. Sessoli, H. -L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1993, **115**, 1804.
- (a) J. Krzystek, J.-H. Park, M. W. Meisel, M. A. Hitchman, H. Stratemeier, L.-C. Brunel and J. Tesler, *Inorg. Chem.*, 2002, **41**, 4478. (b) G. Rogez, J. N. Rebilly, A. L. Barra, L. Sorace, G. Blondin, N. Kirchner, M. Duran, J. van Slageren, S. Parsons, L. Ricard, A. Marvilliers and T. Mallah, *Angew. Chem. Int. Ed.*, 2005, **44**, 1876.
- For Nickel based polymetallic complexes (inc. SMMs) see: (a) M. S. El Fallah, E. Rentschler, A. Caneschi, R. Sessoli and D. Gatteschi, *Inorg. Chem.*, 1996, **35**, 3723. (b) T. S. Stamatatos, E. Diamantopoulou, C. P. Raptopoulou, V. Psycharis, A. Escuer and S. P. Perlepes, *Inorg. Chem.*, 2007, **47**, 2350-2352. (c) E. Diamantopoulou, C. P. Raptopoulou, A. Terzis, V. Tangoulis and S. P. Perlepes, *Polyhedron*, 2002, **21**, 2117. (d) M. Murrie, H. Stoeckli-Evans and Hans U. Güdel, *Angew. Chem., Int. Ed.*, 2001, **40**, 1957. (e) S. T. Ochsenein, M. Murrie, E. Rusanov, H. Stoeckli-Evans, C. Sekine and Hans U. Güdel, *Inorg. Chem.*, 2002, **41**, 5133. (f) T. C. Stamatatos, K. A. Abboud, S. P. Perlepes and G. Christou, *Dalton Trans.*, 2007, **35**, 3861.
- S. Caretta, P. Santini, G. Amoretti, M. Affronte, A. Candini, A. Ghirra, I. S. Tidmarsh, R. H. Laye, R. Shaw and E. J. L. McInnes, *Phys. Rev. Lett.*, 2006, **97**, 207201.
- (a) W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson and G. Christou, *Nature*, 2002, **416**, 406. (b) S. Hill, R. S. Edwards, N. Aliaga-Alcalde and G. Christou, *Science*, 2003, **302**, 1015. (c) C. C. Stoumpos, R. Inglis, G. Karotsis, L. F. Jones, A. Collins, S. Parsons, C. J. Milios, G. S. Papaefstathiou and E. K. Brechin, *Cryst. Growth and Design*, 2009, **9**, 24-27.
- (a) E. E. Moushi, T. C. Stamatatos, W. Wernsdorfer, V. Nastopoulos, G. Christou and A. J. Tasiopoulos, *Angew. Chem. Int. Ed.*, 2006, **45**, 7722-7725. (b) H. Miyasaka, K. Nakata, L. Lecren, C. Coulon, Y. Nakazawa, T. Fujisaki, K. Sugiura, M. Yamashita and R. Clerac, *J. Am. Chem. Soc.*, 2006, **128**, 3770-3783. (c) T. C. Stamatatos, K. M. Poole, D. Foguet-Albiol, K. A. Abboud, T. A. O'Brien and G. Christou, *Inorg. Chem.*, 2008, **47**, 6593-6595. (d) L. F. Jones, A. Prescimone, M. Evangelisti and E. K. Brechin, *Chem. Commun.*, 2009, 2023-2025.
- (a) C. Boskovic, R. Bircher, P. L. W. Tregenna-Piggott, H. U. Güdel, C. Paulsen, W. Wernsdorfer, A. -L. Barra, E. Khatsko, A. Neels and H. Stoeckli-Evans, *J. Am. Chem. Soc.*, 2003, **125**, 14046. (b) J. Yoo, W. Wernsdorfer, E.-C. Yang, M. Nakano, A. L. Rheingold and D. N. Hendrickson, *Inorg. Chem.*, 2005, **44**, 3377. (c) H. Miyasaka, K. Nakata, L. Lecren, C. Coulon, Y. Nakazawa, T. Fujisaki, K. Sugiura, M. Yamashita and R. Clerac, *J. Am. Chem. Soc.*, 2006, **128**, 3770.
- (a) T. C. Stamatatos, K. M. Poole, D. Fouget-Albiol, K. A. Abboud, T. A. O'Brien and G. Christou, *Inorg. Chem.*, 2008, **47**, 6593. (b) N. C. Harden, M. A. Bolcar, W. Wernsdorfer, K. A. Abboud, W. E. Streib and G. Christou, *Inorg. Chem.*, 2003, **42**, 7067. (c) M. A. Bolcar, S. M. J. Aubin, K. Folting, D. N. Hendrickson and G. Christou, *J. Chem. Soc., Chem. Commun.* 1997, 1485. (d) B. Pilawa, M. T. Kelemen, S. Wanka, A. Geisselmann and A. L. Barra, *Europhys. Lett.* 1998, **43**, 7. (e) T. C. Stamatatos, K. M. Poole, D. Foguet-Albiol, K. A. Abboud, T. E. O'Brien and G. Christou, *Inorg. Chem.*, 2008, **47**, 6593.
- H. Oshio, N. Hoshino, T. Ito, M. Nakano, F. Renz and H. Gütlisch, *Angew. Chem. Int. Ed.*, 2003, **42**, 223.
- S.-H. Zhang, Y. Song, H. Liang and M.-H. Zeng, *CrystEngComm.*, 2009, **11**, 865.
- L. J. Barbour, MCAVITY: Program for calculating the molecular volume of closed capsules, University of Missouri-Columbia, Columbia, MO, USA, 2003, <http://www.x-seed.net/cavity.html>. The free volume within the cavities of **2** and **3** was calculated in the absence of guests.
- <http://www.topos.ssu.samara.ru>; V. A. Blatov, *IUCr CompComm Newsletter*, 2006, **7**, 4.

-
15. M. O'Keeffe, M. A. Peskov, S. J. Ramsden, O. M. Yaghi, *Acc. Chem. Res.*, **2008**, *41*, 1782.
16. (a) N. P. Power, S. J. Dalgarno and J. L. Atwood, *Angew. Chem. Int. Ed.*, 2007, **46**, 8601-8604. (b) M. Yoshizawa, J. K. Klosterman and M. Fujita., *Angew. Chem. Int. Ed.*, 2009, **48**, 3418-3438 and references herein. (c) M. D. Pluth and K. N. Raymond, *Chem. Soc. Rev.*, 2007, **36**, 161-171. (d) A. Pastor and E. Martínez-Vivente., *Coord. Chem. Rev.*, 2008, **252**, 2314-2345.