Summary

The ordered assembly of paramagnetic transition metal ions into closely spaced, two-dimensional grid-like arrangements can lead to the formation of a flat and precise array of an exact number of spin centers. This has great appeal in terms of potential applications in information storage and processing technology. Self-assembly processes using ‘polytopic’ ligands have achieved significant success in producing magnetic grids, where design elements relevant to the grid/cluster outcome are pre-programmed into the ligands themselves. The important contributions to this emerging area will be surveyed, and prospects for magnetically significant systems discussed.

1.1 Introduction

An euphoric view of the future of chip technology expressed by Gordon Moore in the 1960’s indicated that ‘The complexity [of cheap integrated circuits] has increased at a rate of roughly a factor of two per year’ [1]. The view was held for quite a few years, until it became revised to a doubling every 1-1/2 years. The explosion in computer power in the 1980’s and beyond hinged dramatically on the ability of industry to miniaturize chips, and it appeared that there was no limit (e.g. 64 transistors per chip in 1965 versus 28 million transistors in a Pentium III processor). In recent years the realization that Moore’s Law would finally fail has led to the
search for new devices not constrained by the physical limitations of chip size. Current chip ‘pitches’ in the 150 nm range can lead to electron tunneling through the chip ‘gates’, and so a realistic size limit is fast approaching. Magnetic data storage faces similar scaling problems, although at a lower dimension. It is estimated that magnetic grain size cannot be scaled below 10 nm without the occurrence of thermal self-erasure problems. Thus in both areas the time is ripe for new approaches or even ‘new physics’ [1-3].

Paramagnetic metal ions with covalent radii of the order of 1 Å (0.1 nm) can be brought into close proximity with suitable diamagnetic, single atom bridging ligands, and with appropriate magnetic orbital overlap situations can produce parallel or antiparallel alignment of the metal centered spins (ferromagnetic or antiferromagnetic behavior respectively). For simple dinuclear systems many examples of such spin coupled systems are known, but most are antiferromagnetically coupled. Increasing the number of spin centers in a polynuclear, bridged arrangement is more of a challenge, but can be achieved using polydentate ligands of various types. One approach uses well-defined, polydentate ligands to impose specific geometries on the resulting arrays, while another approach uses simple ligands, and essentially is controlled by properties of the metal ion (e.g. in cyanide or carbonyl clusters). An intermediate approach uses coordinatively flexible ligands.

Grid-like 2-dimensional arrangements of spin centres offer significant benefits to random clusters, in that flat surface arrays are possible (vide infra), and so the prospects for addressing individual molecules or even metal atoms are enhanced. The organization of paramagnetic metal centers into regular grid-like arrangements has
been achieved using the ligand directed, self-assembly approach [4], and examples of [2x2] and [3x3] grid structures have been produced. The success of this approach relies on the fact that the structural attributes necessary for the formation of a specific grid arrangement are pre-programmed into the ligand itself, and the grid forms by a self assembly process in which the donor groupings of the ligand are read by the metal ions in terms of their *coordination algorithms* as the polynuclear structure is built [5].

A number of these [2x2] and [3x3] grid structures have shown a remarkable variety of magnetic properties, with isotropic coupling characterized by examples of both antiferromagnetic and ferromagnetic exchange. Evidence for anisotropic and biquadratic exchange couplings has been reported, systems with pronounced magnetic anisotropy and/or strong interplay between ligand-field and exchange interactions have been identified, and even cooperative spin-crossover effects have been observed. In this review, the structural and magnetic properties of such systems will be described with a focus on the isotropic coupling situation. A brief theoretical treatment of the magnetism will be presented.

Section 2 deals with a survey of the ligands and ligand types found to be suitable for self-assembly into grids, with examples of structures of typical complexes. Section 3 examines the magnetic properties, in relation to structure, and section 4 examines possible applications of such systems to information storage, and the problem of addressing such systems in the nanoscale realm.
1.2 Polytopic Ligands and Grid Complexes

The complexes described in this chapter will be based on the definition of a metallic coordination grid as an “array of metal centers positioned at the vertices of a (approximate) square lattice”, with the number of occupied rows and columns greater than one. This implies a 2-dimensional flat or close to flat polynuclear array. From the magnetic perspective only systems with paramagnetic metal centers that are linked by diamagnetic monatomic or poly-atomic bridges, with metal-metal separations <10 Å, will be discussed. The characteristic feature of such structures is the parallel ligand groupings connecting the metal centers.

Regular grids have been successfully produced from polytopic ligands with ‘n’ coordination pockets, which self-assemble with metal ions to form [nxn] grids [5]. The smallest members of such a series would be [2x2] tetranuclear complexes (Scheme 1). The distinction between grids, squares and small metalla-cycles in this class is essentially semantic, and from a magnetic perspective there is no symmetric difference (vide infra). Systems with higher nuclearity will be restricted to grids, as formerly defined, with single metal ion periodicities, and so will not include metalla-cyclic rings per se. The definition does not require that all vertices of a [nxm] grid have to be occupied by a metal ion, and so incomplete grid structures, e.g. with a ‘pin wheel’ shape, are also included. An extensive review of ‘self-assembled structural motifs in coordination chemistry’ [6] highlights the structural features of some examples of ‘grids’ and ‘squares’ in this class.
1.2.1 [2x2] Ligands

Building grids of nanoscopic dimensions from individual subunits using sequential bond formation methodologies is time-consuming and results in low yields. Supramolecular architectures can conveniently be approached using self assembly chemistry by including key design elements in the ligands that allow the metal ions to read the ultimate structural outcome as the system builds [4,5]. Typical ligands that produce [2x2] square grids are shown in Figure 1, with examples of their primary coordination modes. They all have two potential coordination pockets (ditopic) and involve monatomic, diatomic, tri-atomic and tetra-atomic bridging groups. In each example [2x2], thermodynamically favoured, grid complexes are formed by self assembly processes in high yield, with homoleptic and non-homoleptic examples.

1.2.2 Representative [2x2] complexes

Ligand 1 has a linear arrangement of coordination pockets, and forms five-membered chelate rings on coordination. The complex \([\text{Cu(L1)}]_4(\text{PF}_6)_4 \) (17) [7] (Figure 2) forms in 80% yield and has a [2x2] square grid structure with two pairs of parallel ligands above and below the \([\text{Cu}_4(\mu-O)_4]\) plane. The copper atoms are separated by 4.04 Å, with Cu-O-Cu angles of 140.6 °. Ligands of type 2 have a similar arrangement of coordination pockets, and self assemble in the presence of Ni(II) and Co(II) ions to produce \([\text{Ni(L2)}]_4(\text{PF}_6)_4 \cdot 4\text{EtOH} \cdot \text{H}_2\text{O} \) (18) (R=phenyl) [8] and \([\text{Co(L2)}]_4(\text{CH}_3\text{COO})_4 \cdot \text{H}_2\text{O} \) (19) (R=pyridyl) [9] (Figure 3 shows the core structure only for 18; 19 has an identical core), with square \([\text{M}_4(\mu-S)_4]\) cores, and two
pairs of parallel ligands above and below the metal plane. The M-M distances are 4.8 Å and 4.43 Å respectively and the M-S-M angles are 163° and 151° respectively.

Ligands of type 3 have produced numerous [2×2], [M₄(µ-O)₄] grids (M = Cu(II), Ni(II), Mn(II), Co(II)) in high yield with similar dimensions. Figure 4 shows the structure of the cation in [Cu₄(L3)₄(H₂O)](NO₃)₄·3H₂O (20) (R₁ = pyridine; R₂ = pyrazine) [10a], with Cu-Cu distances of 4.01-4.05 Å, and Cu-O-Cu angles 139.8-141.0°. A striking feature of this and related Cu₄ grid complexes is the strictly orthogonal bridging arrangement between the dₓ²−y² ground state copper centers (vide infra). Figure 5 shows the structure of the cation in [Ni₄(L3)₄(H₂O)₄] (NO₃)₄·8H₂O (21) (R₁ = R₂ = pyridine), with Ni-Ni distances in the range 3.95-3.98 Å, and Ni-O-Ni angles in the range 136.2-140.1° [10a]. Figure 6 shows the structure of the cation in [Mn₄(L3)₄(H₂O)₄](NO₃)₄·H₂O (22) (R₁ = pyridine; R₂ = pyrazine), with Mn-Mn distances in the range 3.91-3.97 Å and Mn-O-Mn angles in the range 127.9-129.3° [10b]. Figure 7 shows the structure of the cation in [Co₄(L3)₄(H₂O)₄] (ClO₄)₄·3H₂O (23) (R₁ = R₂ = pyrazine), with Co-Co distances in the range 3.88-3.95 Å, and Co-O-Co angles in the range 133.5-136.0° [10b]. Mixed metal grids of this ligand type can also be produced, and the related structure of a [Fe(III)Cu₃(µ-O)₄] square grid cation in the complex [Cu₃Fe(L3)₄(NO₃)₂](ClO₄)₄·(NO₃)₄ (24) (R₁ = R₂ = pyridine) is shown in Figure 8 [10c]. Ligands of type 3 exist in a number of different conformational forms e.g. 4, and can accordingly coordinate in a number of different ways. In the complex [Cu₄(L4)₄(H₂O)₂] (NO₃)₄·4H₂O (25) (Figure 9) [10a] a flat rectangular grid is observed involving two pairs of ligands with different coordination modes, one pair bridging by their alkoxide oxygen atoms, and the other pair via the N-N diazine...
single bonds. Cu-Cu distances are 4.097 Å and 4.759 Å, with a Cu-O-Cu angle of 139.9°. Cu(1) and Cu(2) are disposed in an almost trans arrangement around the N-N bonds (Cu-N-N-Cu torsional angle 158.8°).

Ligand 5 contains a rotationally flexible N-N bond, and self assembles to produce the \([\text{Cu}_4(\mu-\text{N-N})_4]\) homoleptic \([2\times2]\) grid complex \([\text{Cu}(\text{L5})_4(\text{NO}_3)_4\cdot8\text{H}_2\text{O}] (26)\) [11]. Figure 10 shows the structure of the cation. An interesting 90° twist of the ligand around the N-N bond leads to effective magnetic isolation of the Cu(II) centers (vide infra), but this produces a significant tetrahedral distortion of the cluster. Ligand types 6 combine terminating pyridine and bridging pyrazole groups, and self assemble to form \([2\times2]\) grids with pyrazolate N-N bridges. With 6 \((R=\text{pyridyl})\) the complex \([\text{Cu}_4(\text{L6})_6(\text{MeOH})_2](\text{PF}_6)_2\cdot2\text{MeOH} (27)\) [12] (Figure 11) is formed and involves six pyrazole bridges with two pairs bridging Cu(1) and Cu(2) equatorially, and the other pair bridging Cu(1) and Cu(2a) axially. This leads to an essentially square grid with Cu-Cu separations of 3.939 Å and 3.984 Å. Ligand 6 \((R=\text{H})\) behaves differently, and forms \([\text{Cu}_4(\text{L6})_4(\text{dmf})_4](\text{PF}_6)_4\cdot6\text{dmf} (28)\) [12]. Figure 12 shows that the \([2\times2]\) grid has two pairs of parallel, mutually perpendicular ligands arranged above and below the Cu4 grid, as in the earlier examples. Each adjacent pair of copper centers is bridged equatorially by one pyrazole N-N linkage. Terminal copper sites are occupied by solvent molecules in both cases.

Ligands 7 self assembles in the presence of Cu(II) ions to produce square \([2\times2]\) grids with one terminal and one bridging imidazolate group per copper center. Figure 13 shows the structure of the cation in \([\text{Cu}(\text{L7})_4(\text{NO}_3)_2\text{Cl}_2\cdot1.25\text{H}_2\text{O} (29)\) [13]. Cu-Cu distances are in the range 6.10-6.15 Å. The four copper centers are connected
equatorially by the imidazolate bridges in a flat array (Cu-Cu-Cu-Cu torsional angle 18.3°). Ligand 8 (1,3-dimethylvioluric acid) acts in a bis-bidentate fashion and forms a flat, square \([\text{Cu}_4(\mu-\text{NO})_4]\) ‘oximate’ bridged \([2\times 2]\) grid complex \([\text{Cu(L8)(H}_2\text{O})_2]_4(\text{ClO}_4)_4\cdot 2\text{H}_2\text{O}\) \((30)\) [14] (Figure 14; bridging oximate groups are disordered over two positions) with Cu-Cu distances of 4.764(3) Å, and the copper centers all linked equatorially.

Ligands of type 9 can act in a bis-bidentate bridging mode, and with Ni(II) self assemble to produce a \([2\times 2]\) distorted square grid complex \([\text{Ni}_4(\text{L9Et})_8]_4\cdot 4\text{CH}_2\text{Cl}_2\) \((31)\) [15] (Figure 15). The six-coordinate nickel (II) centers are linked by three atom bridges, and as a consequence Ni-Ni distances are quite long (5.567 Å). Ligands of type 10 create a linear array of coordination pockets, as in 1-3, leading to ideal geometric conditions for self-assembly into square grids. Ligand 10 \((\text{R}_1=\text{phenyl};\text{R}_2=\text{H})\) reacts with Co(BF\(_4\))\(_2\) to produce \([\text{Co(L10)}]_4(\text{BF}_4)_8\) \((32)\) [16] in high yield. Figure 16 shows the cationic structure with four distorted octahedral Co(II) centers bridged by four pyrimidine groups, and two pairs of parallel ligands above and below the metal plane. Co-Co distances are quite long (6.453-6.570 Å), as would be expected, because of the three atom bridges. A corresponding Fe(II) complex \([\text{Fe(L10)}]_4(\text{ClO}_4)_8\) \((33)\) was obtained with ligand 10 \((\text{R}_1=\text{phenyl};\text{R}_2=\text{H})\) with an isostructural, homoleptic pyrimidine bridged Fe\(_4\) cation. Structural studies at 100 K and 293 K reveal significant differences in Fe-N bond distances, some of which are intermediate between those expected for LS and HS Fe(II) systems. This is related to the demonstrated spin crossover behaviour (\textit{vide infra}) [17].
The bis-bidentate ligand 11 undergoes self-assembly in the presence of Ni(II) ions to produce a [2x2] square grid complex $[\text{Ni}_4(L11)_4(CH_3CN)_8](\text{BF}_4)_8$ (34) [18] (Figure 17), with the four octahedral Ni(II) centers bridged on opposite sides of each ligand through the tetrazine subunit, with remaining coordination sites filled by acetonitrile molecules. The inclusion of a BF$_4^-$ ion in the grid cavity is viewed as evidence of an anion cyclization templating effect. The four atom bridging connection between Ni(II) centers leads to quite long Ni-Ni separations (6.84-6.89 Å). An equivalent bridging situation exists in 12 and 13, which both bridge through the pyrazine fragments of the ligands. The complex $[\text{Cu}_4(L12)_4\text{Cl}_7\cdot\text{Cl}_n\cdot\text{H}_2\text{O}]$ (35) [19] (Figure 18) has a [2x2] almost square grid structure with four ligands arranged in two parallel pairs connecting Cu(1) and Cu(2) axially, and Cu(2) and Cu(1a) equatorially. Cu-Cu distances are long (6.89-7.30 Å), due to the four atom pyrazine bridge connections. Cu(1) and Cu(2) form axial bonds to N(6) and N(7) respectively, while the connection between Cu(1) and Cu(2_4) links the d$_{x^2-y^2}$ copper centers equatorially, resulting in a ‘dimer of dimers’ system (vide infra). The complex $[\text{Co}(L13)\text{Cl}_4\cdot27\text{H}_2\text{O}]$ (36) [20] has a similar structure with the ligands bridging through the pyrazine subunits in exactly the same way. Co-Co distances (7.1 Å) are long, as would be expected.

Ligand 14 has two fairly widely spaced N$_2$O coordination pockets, and self assembles with e.g. Fe(ClO$_4$)$_2$ to produce a square [2x2] grid with oxalyl hydrazide bridges between the metal centres. Figure 19 shows the cation structure in the complex $[\text{Fe}_4(L14)_4](\text{ClO}_4)_6\cdot7\text{H}_2\text{O}$ (37) [21]. Fe(II)-Fe(II) distances fall in the range 6.75-7.25 Å, and two oxalyl-hydrazide bridges have a trans configuration, while the
other two are cis. Extension of this ligand to include two additional pyridine rings in place of the NH$_2$ groups (15) allows for a highly novel self-assembly situation where the same primary square grid arrangement can be produced, with additional metal centers attached to the sides of the [2x2] grid. 15 self-assembles in high yield in the presence of Ni(BF$_4$)$_2$ to produce an expanded octanuclear grid [22]. The structure of [Ni$_6$(L15)$_4$(H$_2$O)$_8$](BF$_4$)$_8$·16H$_2$O (38) is shown in Figure 20, revealing the oxalylhydrazide bridged square Ni(II)$_4$ [2x2] grid core (Figure 21; Ni1-Ni3-Ni5-Ni7), with appended Ni(II) centers (Ni2-Ni4-Ni6-Ni8) attached to the external coordination pockets. This effectively creates a large octanuclear ring with almost trans N-N single bond bridges linking adjacent Ni(II) centers (Ni-N-N-Ni torsional angles 152.0-161.0°).

1.2.3 [3x3] Ligands and their complexes

Extensions of the geometric features that successfully led to [2x2] grids with the ligand 3 systems have been programmed into ligand 16. The linear arrangement of three contiguous coordination pockets with the formation of five-membered chelate rings leads successfully to [3x3] square grids in high yields. The complex [Mn$_9$(L16)$_6$(ClO$_4$)$_6$]·18H$_2$O (39) (Figure 22) involves a homoleptic structure with six parallel ligands, arranged in two groups of three, above and below the pseudo-planar grid of nine alkoxide bridged Mn(II) centers. The central [Mn$_9$(µ$_2$-O)$_{12}$] core is shown in Figure 23 [23,24]. The Mn(II) centers are closely spaced (Mn-Mn 3.9-4.0 Å), with Mn-O-Mn angles in the range 126.6-130.0°. An analogous [Cu$_9$(µ$_2$-O)$_{12}$] square grid is found in the complex [Cu$_9$(L16)$_6$](NO$_3$)$_{12}$·9H$_2$O (40) [24, 25]. The core
(Figure 24) has similar dimensions (Cu-Cu 4.03-4.17 Å; Cu-O-Cu 136.5-143.6 °), and all copper centers are connected orthogonally to neighboring metal sites.

In an attempt to introduce lanthanide ions into a nine metal grid assembly 16 was reacted sequentially with Gd(NO$_3$)$_3$ and Cu(NO$_3$)$_2$, with the formation of an unusual octanuclear grid-like cluster (Fig. 25) in the complex [Cu$_8$(L16)$_4$(CH$_3$OH)$_4$
(CH$_3$CN)$_4$][Gd(NO$_3$)$_4$(H$_2$O)$_2$](NO$_3$)$_6$·1.3Cu(NO$_3$)$_2$·10H$_2$O (41), with a ‘pin-wheel’ arrangement of four peripheral Cu(II) centers attached by alkoxide bridges to a typical [Cu$_4$(µ-O)$_4$] central core [26]. Figure 26 shows the core structure. As in previous copper examples of alkoxide bridged grids in this class all bridging connections between adjacent Cu(II) centers are strictly orthogonal, as a result of a twisting of the copper magnetic planes relative to neighboring magnetic planes.

1.3 Magnetic properties of grid complexes

The proximity of the paramagnetic metal ion centers in these grid complexes can lead to spin exchange interactions through the intervening diamagnetic bridge groups. Representative examples of exchange coupling schemes will be described, and related to the symmetry properties of the particular grid arrangement.

1.3.1 [2x2] complexes

In a general case the square (D$_{4h}$) or distorted square (D$_{2d}$) [2x2] grid can be described by an exchange coupling scheme involving two exchange integrals (J1, J2) according to the appropriate Hamiltonian expression (eqn 1) (Figure 27),

\[
H_{ex} = -2J1 \{ S_1 \cdot S_3 + S_1 \cdot S_4 \} -2J2 \{ S_1 \cdot S_2 + S_3 \cdot S_4 \} -2J3 \{ S_1 \cdot S_3 + S_2 \cdot S_4 \}
\] (1)
where \( J_1 \) is the exchange along the vertical sides and \( J_2 \) along the horizontal sides of the square. Diagonal terms (\( J_3 \)) can be set to zero because cross-coupling terms are assumed to be insignificant. Using the conventional spin-vector coupling model \([27, 28]\) eigenvalues of eq. 1 can be obtained analytically for a \( D_{4h} [2\times2] \) grid with \( J = J_1 = J_2 \). The eigenvalues are then given by

\[
E(S', S_{13}, S_{24}) = -J[S'(S'+1) - S_{13}(S_{13}+1) - S_{24}(S_{24}+1)] - J_3[S_{13}(S_{13}+1) + S_{24}(S_{24}+1)]
\]

where \( S_{13} = S_1 + S_3; \ S_{24} = S_2 + S_4; \ S' = S_1 + S_2 + S_3 + S_4. \)

Another coupling situation which arises in the limit \( J_1 = J_3 = 0 \) is that of a “dimer of dimers” (see Figure 27 for model), corresponding to the general Hamiltonian

\[
H_{ex} = -2J_2 \ S_1 \cdot \ S_2 - 2J_2' \ S_3 \cdot \ S_4
\]

where the horizontal coupling strengths might assume different values \( J_2 \) and \( J_2' \). Using the same method the eigenvalues are obtained as

\[
E(S', S_{12}, S_{34}) = -J_2 [S_{12}(S_{12}+1)] - J_2' [S_{34}(S_{34}+1)]
\]

with \( S_{12} = S_1 + S_2; \ S_{34} = S_3 + S_4 \) and \( S' = S_{12} + S_{34}. \) All these results are valid for arbitrary values of the spin quantum numbers \( S_i (i = 1 \ldots 4) \)
Using the addition rules for spin vectors the allowed values for $S'$, and $S_{13}$, $S_{24}$, or $S_{12}$, $S_{34}$ respectively can be obtained. Substituting the appropriate energy terms into the van Vleck equation (eqn. 2), the susceptibility values can be computed for a particular temperature range. In practice this can be achieved by the use of simple programming techniques whereby iterative procedures span the required $S'$ values for fitted values of $J$, in routines that allow regression of the experimental data against equation 3 [29].

Best fit values of $g$ and $J$ are thus obtained, allowing for paramagnetic impurity (fraction ?), TIP (temperature independent paramagnetism), and a Weiss-like corrective term (?) to deal with small intermolecular exchange effects. A review by Murray [30] deals more generally with the magnetic properties of tetruclear complexes.
1.3.2 [3x3] complexes

A similar approach can be adopted to deal with the [3x3] grid cases using an expanded Hamiltonian expression (eqn. 4) that assumes different J values for the interactions within the external ring of eight metal ions (J1), and for the interaction between the central metal and its immediate neighbours (J2) (model based on Fig. 28).

\[
H_{ex} = -J_1 \{ S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_6 + S_6 \cdot S_9 + S_9 \cdot S_8 + S_8 \cdot S_7 + S_7 \cdot S_4 \} \\
- J_2 \{ S_2 \cdot S_5 + S_5 \cdot S_6 + S_5 \cdot S_8 + S_8 \cdot S_5 \} \\
\]

(4)

However, the energy eigenvalues cannot be obtained analytically as for the [2x2] grid examples described in the previous section. Their calculation requires the machinery of irreducible tensor operators [31, 32] and numerical diagonalization routines.

Dealing with such a complex system leads to a situation where, depending on the metal ion spin state, matrix dimensions quickly exceed the capacity of most computers. In the case of Cu(II) (S=1/2) this is not a problem, but for Mn(II) (S=5/2) calculations of the spin state ladder cannot be completed on a Pentium III based computer, even if all symmetries of the Hamiltonian (4) are considered [32]. Simplification of equation 4 assuming J1=J2 does allow for fitting of the experimental data in an acceptable timeframe, since in this case the energy spectrum needs to be calculated numerically only once. We have developed the MAGMUN/ow0L program package, which handles such a situation. It is freely available on request from the authors [33]. In an initial step the energy spectrum is calculated with ow0L and stored as a “.spk” file. This file is then opened with
MAGMUN, which performs the fitting according to eqn. 2 and 3. If not otherwise stated the theoretical curves presented in this review were obtained with these programs.

1.3.3 Magnetic properties of [2x2] and [3x3] grids.

Complex 17 (Fig. 2) appears to be coupled very weakly antiferromagnetically, with a slight drop in $\theta T$ below 25 K, associated with $J = -0.24 \text{ cm}^{-1}$ [7], as determined by data fitting to Eqns. 1-3 for $J = J_1 = J_2$. The very weak coupling is consistent with the orthogonal arrangement of the magnetic $d$ orbitals relative to the phenoxide bridging connections, despite the large Cu-O-Cu angles ($>140.0^\circ$), but surprisingly inconsistent with the properties observed for e.g. 20 and related compounds (vide infra). 18 (Figure 3) appears to exhibit strong intra-molecular anti-ferromagnetic coupling, but the magnetic results are somewhat inconclusive. No magnetic properties are reported for 19 [8,9].

Complex 20 (Figure 4) has a similar orthogonal arrangement to 17 in which the metal ion $d_{x^2-y^2}$ orbitals are twisted relative to their neighbours, with short/long axial/equatorial contacts through the alkoxide bridges. 20 displays magnetic properties typical of an intra-molecular ferromagnet [10a]. Figure 29 shows the variation of $\mu$ (mol) as a function of temperature, with an increase in moment with decreasing temperature to a maximum of 4.8 $\mu_B$ at 5 K. The data were fitted to eqn. 3 ($S_i = \frac{1}{2}$) to give $g = 2.119(7), J = 9.8(4) \text{ cm}^{-1}, \theta = 0.00002, \theta = -0.5 \text{ K}, TIP = 0.000234 \text{ cm}^3 \text{ mol}^{-1}, 10^2 R = 0.48$ ($R = \frac{S(\theta_{\text{obs}} - \theta_{\text{calc}})^2}{S_{\text{obs}}^2}^{1/2}$). The solid line in Figure 29 was calculated with these parameters. Magnetization data as a function of field at 2 K (Figure 30) can be fitted successfully to the appropriate Brillouin function
for \( g=2.119, S=4/2 \), thus confirming the ferromagnetic ground state. The remarkable feature of this compound, and several others like it [10a,b], is the ferromagnetic behaviour. The close spacing of the metal centers, and the very large Cu-O-Cu bridge angles, would normally have dictated strong anti-ferromagnetic exchange, as a result of the usually efficient overlap situation between the copper magnetic orbitals via the alkoxide bridges, if they were connected equatorially [34-36]. However the orthogonal bridging interactions in this case clearly impede this process, as the copper magnetic orbitals orient themselves at right angles to those in neighbouring atoms, leading to the ferromagnetic behaviour.

21 (Figure 5) has a similar square alkoxide bridged structure, but orbital orthogonality is not an issue in the nickel case. Figure 31 clearly shows that the intramolecular exchange coupling is anti-ferromagnetic, and a data fitting to eqn. 3 \( (S_i=1) \) gives \( g = 2.29(1), J = -13.6(2) \text{ cm}^{-1}, ? = 0.012, ? = 0 \text{ K}, TIP = 0.000800 \text{ cm}^3. \text{ mol}^{-1}, \ 10^2 R = 0.70 \). The solid line in Figure 31 was calculated with these parameters. The moderate anti-ferromagnetic exchange is entirely consistent with the large Ni-O-Ni angles [10a, 37]. 22 (Figure 6) displays similar anti-ferromagnetic properties with a magnetic moment per mole dropping from 11.4 \( \mu_B \) at 300 K to 3.5 \( \mu_B \) at 4.5 K. A similar data treatment using eqn. 3 \( (S_i = 5/2) \) gave \( g = 1.99(1), J = -2.85(4) \text{ cm}^{-1}, ? = 0.014, ? = 0 \text{ K}, TIP = 0 \text{ cm}^3. \text{ mol}^{-1} \ (10^2 R = 1.0) \). Such behaviour is again consistent with the large Mn-O-Mn bridge angles [10b]. 23 (Figure 7) has a similar drop in moment (9.4 \( \mu_B \) at 300 K, 3.5 \( \mu_B \) at 5 K), and surprisingly gave a good fit to eqn. 3 \( (S_i = 3/2) \) for \( g = 2.42(1), J = -6.95(4) \text{ cm}^{-1}, ? = 0.004, TIP = 0.001200 \text{ cm}^3. \text{ mol}^{-1} \ (10^2 R = 0.9) \).
The intra-molecular anti-ferromagnetic coupling is again consistent with the alkoxide bridged square structure, and the large Co-O-Co angles [10b].

**24** (Figure 8) has a unique structural arrangement in which axial connections between both Cu(3) and Cu(1) and Fe(1), and between Cu(2) and Cu(1), and an equatorial connection between Cu(2) and Cu(3) (Cu(2)-O(2)-Cu(3) 142.0°) would suggest a combination of ferromagnetic and anti-ferromagnetic interactions. The plot of $\mu$ (mol) as a function of temperature (Figure 32) shows a drop from 6.68 $\mu_B$ at 300 K to 6.38 $\mu_B$ at 35 K followed by a rise to 7.20 $\mu_B$ at 2 K, suggesting that this is the case. The magnetic data were fitted to an exchange expression based on the Hamiltonian (eqn. 5).

$$H_{ex} = J_1 S_{Cu2} S_{Cu3} - J_2 S_{Fe1} S_{Cu1} - J_3 S_{Fe1} S_{Cu3} - J_4 S_{Cu1} S_{Cu2}$$ (5)

The best fit was obtained when $J_3$ and $J_4$ were set to zero, corresponding to a “dimer of dimers” situation, with $g_{ave.} = 2.04$, $J_1 = -61.5 \text{ cm}^{-1}$, $J_2 = 1.1 \text{ cm}^{-1}$, $TIP = 0.000150 \text{ cm}^3 \cdot \text{mol}^{-1}$. The solid line in Figure 32 was calculated with these values. This is reasonable given the orthogonal Cu-Fe and Cu-Cu connections. The significant anti-ferromagnetic coupling between Cu(2) and Cu(3), in combination with the ferromagnetic interaction between Fe(1) and Cu(1) would of necessity lead to a S = 3 ground state. Magnetization versus field data at 2 K (0-5 T) (Figure 33) confirm this [10c] (solid line calculated from the appropriate Brillouin function with S = 3, $g = 2.04$).
Complex 25 (Figure 9) has an unusual rectangular structure with both alkoxide and diazine bridges. The alkoxide bridges connect adjacent pairs of copper centers orthogonally, while the diazine groups bridge equatorially. The \( \gamma \) (mol)/T profile shows a maximum at 150 K, and a fit of the data to equation 3 (\( S_i = \frac{1}{2} \)) gives an excellent fit with 
\[ g = 2.18(1), J_1 = -168(1) \text{ cm}^{-1}, J_2 = 0 \text{ cm}^{-1}, \gamma = 0.029, \text{TIP} = 0.000240 \text{ cm}^3\text{mol}^{-1} (10^2 R = 0.29). \]
The strong anti-ferromagnetic component is clearly associated with the almost trans N-N bridges [38-40], while \( J_2 = 0 \text{ cm}^{-1} \) is in complete agreement with the orthogonal alkoxide bridges. \( \gamma \)T for 26 (Figure 10) is almost constant in the range 6.5-280 K indicating no significant interaction between the copper(II) centers. Cu-N-N-Cu torsion angles of 97° are consistent with this behaviour, but somewhat larger than anticipated for orthogonal overlap of the copper magnetic orbitals via the N-N single bond connection [38-40].

Magnetic data for 27 and 28 (Figures 11, 12) indicate intramolecular antiferromagnetic coupling within the square grids, \( J = \sim -170 \text{ cm}^{-1} \) and \( -63.5 \text{ cm}^{-1} \) respectively. The orthogonality between Cu(1) and Cu(2) in 27 suggests that a dimer model is more appropriate with Cu(1) and Cu(1)' bridged by two pyrazole groups. In 28 all four copper centers are linked equatorially with a single pyrazole bridge. 29 (Figure 13) has a clearly defined square arrangement of four copper centers bridged by single imidazolate linkages. Variable temperature magnetic data are interpreted with a square model (eqn. 3; \( S_i = \frac{1}{2} ; J = J_1 = J_2 \)) to give 
\[ g = 2.062(4), J = -97.6 \text{ cm}^{-1}. \]
These results are consistent with previous studies involving pyrazole and imidazole bridged complexes [38, 41, 42].
Complex 30 (Figure 14) has a square arrangement of four copper ions bridged equatorially by single N-O linkages. Variable temperature magnetic data indicated strong antiferromagnetic coupling, and a data fit to eqn. 3 ($S_i = \frac{1}{2}; J = J_1 = J_2$) gave $g = 2.15(3), J = -349(5) \text{ cm}^{-1}$, consistent with related aldoxime bridged dicopper(II) complexes [43]. Complex 31 (Figure 15) has four octahedral Ni(II) centers bridged directly by a bifurcated bridge involving two four bond pathways (Ni-N-C-N-Ni and Ni-N-C-O-Ni). The grid is slightly distorted (Ni-Ni-Ni-Ni torsional angle 34.8°, with long Ni-Ni distances (5.567 Å), but exhibits a crystallographically imposed $S_4$ symmetry axis. Variable temperature magnetic data have been interpreted according to eqn. 3 ($S = 1; J = J_1 = J_2$) to give $g = 2.24, J \approx 0.75 \text{ K}$, with inclusion of a uniaxial zero field splitting term $|D| = 3 \text{ K}$ [15]. Given the long distance between the Ni centers the positive J value, indicating ferromagnetic coupling, is quite surprising.

Complex 32 (Figure 16) involves pyrimidine bridges between Co(II) centers, creating even larger Co-Co separations (6.4-6.6 Å). The magnetic properties of a related, and structurally similar complex $[\text{Co(L10)}]_4(\text{PF}_6)_8$ (L10; $R_1 = \text{H}, R_2 = \text{Me}$) [44] are interpreted in terms of a quantum spin system of four anti-ferromagnetically coupled high spin Co(II) centers with effective spin $S'_i = \frac{1}{2}$. This is confirmed by magnetization studies at 2 K as a function of field. The quantitative analysis of the magnetic properties is impeded in this case by the orbital contribution of the high spin Co(II) ions to the magnetism. The effective exchange integral was estimated to be $J' \approx -13.5 \text{ K}$, corresponding to a microscopic exchange coupling of $J' \approx -1.5 \text{ K}$. The magnetism of the isomorphic $[\text{Ni(L10)}]_4(\text{PF}_6)_8$ complex has been carefully examined by variable temperature magnetic measurements on single crystals [45]. The data
have been analyzed with eqn. 3 ($S_i = 1; J = J_1 = J_2$), expanded by uniaxial zero field splitting terms and anisotropic g-factors ($g = 2.10, g = 2.02, J = -4.2$ K, $D = -8.0$ K). Strong evidence for a sizeable biquadratic exchange contribution ($J' = 0.5$ K) has also been found.

The related iso-structural iron(II) complex 33 is an example of an unusual spin-crossover grid system. Room temperature magnetization data at 1 T suggest three HS Fe(II) ions and one LS Fe(II) ion. $\chi T$ values drop gradually from 2.5 cm$^3$.K.mol$^{-1}$ at 300 K to 1.4 cm$^3$.K.mol$^{-1}$ at 30 K, followed by a further drop towards 4.2 K attributable to zero-field splitting. The gradual decrease in $\chi T$ on lowering the temperature is interpreted in terms of a ‘practically non-cooperative spin crossover situation’, with a residual HS fraction at low temperature. At 4.2 K both HS and LS Fe(II) forms are confirmed by Mössbauer spectroscopy, with a population of 46% and 54% respectively. At 300 K the HS state has a population of 80% [17].

Complex 34 (Figure 17) involves five bond pathways between Ni(II) centers, and not surprisingly exchange coupling is essentially non-existent [18]. 35 (Figure 18) has a similar five bond pyrazine bridging connection between Cu(II) centers, and good fitting of the variable temperature magnetic data to eqn. 3 ($S_i = \frac{1}{2}$) gave $g = 2.09, J_1 = -2.5$ cm$^{-1}, J_2 = -0.2$ cm$^{-1}$ [19]. Given the long copper-copper distances and the effective ‘dimer of dimers’ magnetic structure in 35 this result is very reasonable. 36 has a similar structure and magnetic data are interpreted in terms of ZFS effects only, with insignificant intra-molecular spin exchange [20].

37 (Figure 19) involves a similar sized asymmetric grid to 34-36, with five bond bridges between Fe(II) centers. $\mu$ (mol) drops slightly from 11.5 $\mu_B$ at 300 K to
11.0 µB at 30 K, and then drops precipitously to 6.1 µB at 2 K. These data are consistent with HS Fe(II) and insignificant exchange coupling, with the low temperature drop in µB associated with zero-field splitting [21]. Complex 38 (Figures 20, 21) is a novel expanded square grid with a ring of eight Ni(II) centers linked by trans N-N bond bridges. µ (mol) shows a dramatic drop from 8.2 µB at room temperature to 2 µB at 2 K, indicative of substantial intra-molecular anti-ferromagnetic exchange (Figure 34). The data were fitted, as described earlier [33], to an isotropic exchange expression based on an exchange Hamiltonian (eqn. 6) that assumes a ring of eight Ni(II) centers connected by equivalent bridging groups.

\[ H_{ex} = -J(S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_4 \cdot S_5 + S_5 \cdot S_6 + S_6 \cdot S_7 + S_7 \cdot S_8 + S_8 \cdot S_1) \] (6)

A good data fit to adapted eqn. 3 gave \( g = 2.250(5) \), \( J = -15.0(4) \) cm\(^{-1}\), TIP = 0.00150 cm\(^3\).mol\(^{-1}\). The moderately strong anti-ferromagnetic exchange is associated with the almost trans bridging arrangement of the Ni(II) centers around the N-N single bonds, in complete agreement with earlier studies [38-40]. The solid line in Figure 34 is calculated with these parameters.

Complex 39 (Figures 22, 23) corresponds to a fusion of four square subunits like 22, and as such would be expected to display similar magnetic properties. Figure 35 shows a pronounced drop in magnetic moment (per mole) from 16.9 µB at 300 K to 5.0 µB at 1.8 K, clearly indicating the presence of nine HS Mn(II) centers experiencing intra-molecular anti-ferromagnetic exchange. The low temperature value suggests an \( S = 5/2 \) ground state with a sizeable magnetic anisotropy due to zero
field splitting. This is corroborated by field dependent studies at 1.8 K (Figure 36; solid line calculated from the appropriate Brillouin function with $g = 2, S = 5/2$). The increase of magnetic moment at higher fields reflects the presence of low-lying excited states. Quantifying the exchange integral using eqn. 4 has proved to be difficult since, even if all symmetries of eqn. 4 are exploited [32, 46], the dimensions of the largest matrix to be solved is still as large as 22210 [47]. This exceeds by far the capacity of today’s PCs. However, the somewhat simpler system of a ring of eight $S_i = 5/2$ ions has been solved recently [46]. These results could be used to calculate the susceptibility of eqn. 4 in the limit $|J_1| > |J_2|$. With $J_1 = -3.8 \text{ cm}^{-1}$ a reasonable fit could be obtained (Fig. 35; $g = 2.0$). This value is comparable with that observed for the square [2x2] analogue 22 ($J = -2.85 \text{ cm}^{-1}$) [10b].

40 has an analogous structure (Figure 24 illustrates the core), with a similar disposition of the copper(II) magnetic orbitals to those found in related Cu$_4$ square grids [10, 25]. In the outer ring the eight copper centers are linked with alternating axial/equatorial connections between the copper $d_{x^2-y^2}$ orbitals leading to a situation of strict magnetic orbital orthogonality. Cu(5) has an unusual tetragonally compressed six-coordinate geometry, and nominally a $d_{z^2}$ ground state. This suggests orthogonality between Cu(5) and its neighbors as well. The profile of magnetic moment per mole as a function of temperature (Figure 37) shows a drop from 6.4 $\mu_B$ at 300 K to 5.5 $\mu_B$ at 25 K, followed by a sharp rise to 6.9 $\mu_B$ at 2 K, indicating the presence of fairly strong anti-ferromagnetic exchange, but also ferromagnetic exchange as well. The data were fitted to eqn. 4 to give $g = 2.30, J_1 = 0.52 \text{ cm}^{-1}, J_2 = -24.3 \text{ cm}^{-1}$ [48]. The solid line in Figure 37 is calculated with these parameters. Since
J1 (ferromagnetic) dominates at low temperature this leads to an effective \( S = 7/2 \) low temperature ground state [48], in agreement with magnetization versus field data at 2 K (Figure 38). The dominant exchange term is between Cu(5) and its neighbours, and combined with the nominal \( S_4 \) molecular symmetry, it reveals what can only be described as a fluxional ground state for Cu(5). While Cu(5) appears to have a \( d_{z^2} \) ground state according to the structure it must undergo a dynamic Jahn-Teller distortion effect, where in its relationship with one equivalent neighbouring copper center it appears to be \( d_{x^2-y^2} \), and is anti-ferromagnetically coupled (\( J_2 = -24.3 \text{ cm}^{-1} \)).

A detailed study of the magnetic anisotropy has provided further strong evidence for a complicated ground state of the Cu(II) ions [48]. The thermodynamic spectroscopy of the ground state, obtained by means of high-field torque magnetometry, gave a g-factor anisotropy of \( \Delta g = g_{||} - g_{\perp} = -0.14(2) \) [48]. If the Cu(II) ions assume pure \( d_{x^2-y^2} \) or \( d_{z^2} \) ground states as suggested by the structure, one would expect \( \Delta g > 0 \) in striking contrast to the experimental finding. The zero field splitting factor was also determined to be \( D = 0.009(1) \text{ K} \). Since the dipole-dipole interaction between the nine Cu(II) ions contributes only \( D_{\text{dip}} = 0.012 \text{ K} \) to this splitting, the presence of an anisotropic exchange interaction must be assumed, adding an additional splitting of \( D_{\text{ex}} = -0.003(1) \text{ K} \). Because \( |J_1| << |J_2| \) one expects that only the couplings involving Cu(5) contribute to the anisotropic exchange, with a strength which could be estimated to be \( J_{\text{aniso}} = 0.11(3) \text{ K} \), in satisfying agreement with theoretical expectation [48].
Complex 41 (Figure 25) has an orthogonally bridged expanded [2x2] grid structure in the shape of a ‘pin-wheel’ of eight Cu(II) centers, with two isolated Gd(III) ions and 1.3 Cu(II) ions in the lattice structure, according to the X-ray structural analysis. Magnetic moments (per mole) rise with decreasing temperature from 13.1 \( \mu_B \) at 300K to 14.5 \( \mu_B \) at 2 K (Figure 39), exceeding the spin only value sum associated with two isolated Gd(III) centers and 9.3 isolated Cu(II) centers. This suggests intra-molecular ferromagnetic behaviour within the cluster. The magnetic data were fitted to an isotropic exchange expression based on the Hamiltonian (eqn. 7) for a ‘pin-wheel’ arrangement of eight copper centers (Figure 40), with terms to include two Curie-like Gd(III) centers, and 1.3 isolated Curie-like Cu(II) centers.

\[
\begin{align*}
H_x &= -J(S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_3 \cdot S_4 + S_4 \cdot S_1 + S_1 \cdot S_5 + S_2 \cdot S_6 + S_3 \cdot S_7 + S_4 \cdot S_8) \quad (7)
\end{align*}
\]

A good data fit was obtained with \( g_{av.} = 2.113(2), J = 5.0(2) \text{ cm}^{-1}, \text{TIP} = 0.000500 \text{ cm}^3\text{mol}^{-1}, \Delta = -0.10 \text{ K}, (10^2R = 1.0) \). The solid line in Fig. 39 was calculated with these parameters. Magnetization versus field data at 2K show that at 5 T the system approaches an \( S = 23/2 \) ground state, in agreement with the total spin situation. The dominant intramolecular ferromagnetic exchange is consistent with previous Cu_4 and Cu_9 square grids with orthogonally arranged Cu(II) centers, and highlights the fact that systems of this sort are important models for higher order ferromagnetic grids.
1.4.1 Potential applications of magnetic grids to nanoscale technology

It has been demonstrated that self-assembly procedures can produce ordered grid-like arrays of paramagnetic transition metal ions in close proximity, with magnetic interactions between the spin centers, and in some cases ferromagnetic behavior. Fabricating devices such that individual magnetic subunits can be addressed is a challenge, but could be approached in a number of ways; e.g. chemical incorporation into polymeric substrates, dispersion within a polymer matrix, surface deposition etc. It has recently been demonstrated that grids of type \( \text{10, e.g.} \) \([\text{Co}_4(\text{L10})_4](\text{PF}_6)_8 (\text{R}_1 = \text{H, R}_2 = \text{Me})\) can be deposited from solution in highly ordered monolayers on a pyrolytic graphite surface, and addressed using STM techniques [49], which is a clear indication of the potential in this area. Single grid cations could be addressed and extracted with a \(-0.5\) V pulse at the STM probe. Monolayer deposition of such systems using vacuum technology has not been tried, but recent MALDI-TOF experiments with \( \text{39 and 40} \) indicate prominent molecular species corresponding to the molecular cations, indicative of the high gas phase stability of grids of this sort [50].

The successful use of magnetic grids will depend on many factors, in particular their ability to retain data bits of information once addressed and perturbed at room temperature. We are perhaps a long way from this goal, but the new physics that this type of system may present is as yet largely unexplored, and intensive activity will doubtless follow to e.g. increase grid dimensions by expanding the polytopic nature of the ligands, link magnetic grids together into chains and interlocked 2D and 3D arrays, add redox probes to the magnetic grids such that
magnetic properties can be turned on and off by external electrochemical perturbations etc. These possibilities present exciting opportunities to address e.g. the failure of Moore’s law, the thermal erasure problems with current magnetic data storage media, and the apparent insatiable desire of computer consumers to have faster and larger machines.

Acknowledgments

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References


33. MAGMUN/ow0L is available as a combined package free of charge from the authors (lthomp@mun.ca; waldmann@physik.uni-erlangen.de). MAGMUN has been developed by Dr. Zhiqiang Xu (Memorial University), and ow01.exe by Dr. O. Waldmann. We do not distribute the source codes. The programs may be used only for scientific purposes, and economic utilization is not allowed. If either routine is used to obtain scientific results, which are published, the origin of the programs should be quoted together with a reference to this review.


47. O. Waldmann, L. Zhao and L.K. Thompson, Submitted.


Figure captions.


Figure 1. Polytopic ligands and their coordination modes.

Figure 2. Structural representation of [Cu(L1)]₄(PF₆)₄ (17).

Figure 3. Structural representation of the core in [Ni(L2)]₄(PF₆)₄·4EtOH·H₂O (18).

Figure 4. Structural representation of [Cu(L3)]₄(H₂O)](NO₃)₄·3H₂O (20) (R₁ = pyridine; R₂ = pyrazine).

Figure 5. Structural representation of [Ni(L3)]₄(H₂O)₄(NO₃)₄·8H₂O (21) (R₁ = R₂ = pyridine).

Figure 6. Structural representation of [Mn₄(L3)]₄(H₂O)₄(NO₃)₄·H₂O (22) (R₁ = pyridine; R₂ = pyrazine).

Figure 7. Structural representation of [Cu₄(L3)]₄(H₂O)₄(ClO₄)₄·3H₂O (23) (R₁ = R₂ = pyrazine).

Figure 8. Structural representation of [Cu₃Fe(L3)]₂(NO₃)₂Cl₂·1.25H₂O (24) (R₁=R₂=pyridine).

Figure 9. Structural representation of [Cu₄(L4)]₄(H₂O)₄(NO₃)₄·4H₂O (25).

Figure 10. Structural representation of [Cu(L5)]₄(NO₃)₄·8H₂O (26).

Figure 11. Structural representation of [Cu₄(L6)]₄(MeOH)₂](PF₆)₂·2MeOH (27) (R=pyridyl).

Figure 12. Structural representation of [Cu₄(L6)]₄(dmf)₄](PF₆)₄·6dmf (28) (R=H).

Figure 13. Structural representation of [Cu(L7)]₄(NO₃)₂Cl₂·1.25H₂O (29).

Figure 14. Structural representation of [Cu(L8)(H₂O)₄]₄(ClO₄)₄·2H₂O (30).

Figure 15. Structural representation of [Ni₄(L9Et)₈]·4CH₂Cl₂ (31).
Figure 16. Structural representation of [Co(L10)]₄(BF₄)₈ (32).

Figure 17. Structural representation of [Ni₄(L11)(CH₃CN)]₄(BF₄)₈ (34).

Figure 18. Structural representation of [Cu₄(L12)₄Cl₄]₄Cl₄·15nH₂O (35).

Figure 19. Structural representation of [Fe₄(L14)₄](ClO₄)₆·7H₂O (37).

Figure 20. Structural representation of [Ni₈(L15)₄(H₂O)₈](BF₄)₈·16H₂O (38).

Figure 21. Structural representation of the octanuclear core in [Ni₈(L15)₄(H₂O)₈](BF₄)₈·16H₂O (38).

Figure 22. Structural representation of [Mn₉(L16)₆](ClO₄)₆·18H₂O (39).

Figure 23. Structural representation of the core in [Mn₉(L16)₆](ClO₄)₆·18H₂O (39).

Figure 24. Structural representation of the core in [Cu₉(L16)₄(CH₂OH)₄(CH₃CN)₄][Gd(NO₃)₄(H₂O)₂]₂(NO₃)₆·1.3Cu(NO₃)₂·10H₂O (41).

Figure 25. Structural representation of the Cu₈ fragment in [Cu₈(L16)₄(CH₂OH)₄(CH₃CN)₄][Gd(NO₃)₄(H₂O)₂]₂(NO₃)₆·1.3Cu(NO₃)₂·10H₂O (41).

Figure 26. Structural representation of the octanuclear core in [Cu₈(L16)₄(CH₂OH)₄(CH₃CN)₄][Gd(NO₃)₄(H₂O)₂]₂(NO₃)₆·1.3Cu(NO₃)₂·10H₂O (41).

Figure 27. Magnetic model for a [2x2] grid.

Figure 28. Magnetic model for a [3x3] grid.

Figure 29. Magnetic data (μmol versus temperature) for [Cu₄(L3)₄(H₂O)](NO₃)₄·3H₂O (20) (see text for fitted parameters).

Figure 30. Magnetization versus field data for [Cu₄(L3)₄(H₂O)](NO₃)₄·3H₂O (20) at 2 K.

Figure 31. Magnetic data (θ° versus temperature) for [Ni₄(L3)₄(H₂O)₄](NO₃)₄·8H₂O (21) (see text for fitted parameters).
Figure 32. Magnetic data ($\mu_{\text{mol}}$ versus temperature) for \([\text{Cu}_3\text{Fe}(L3)_4(\text{NO}_3)]_2(\text{ClO}_4)_4(\text{NO}_3)_4\) (24) (see text for fitted parameters).

Figure 33. Magnetization versus field data for \([\text{Cu}_3\text{Fe}(L3)_4(\text{NO}_3)]_2(\text{ClO}_4)_4(\text{NO}_3)_4\) (24).

Figure 34. Magnetic data ($\mu_{\text{mol}}$ versus temperature) for \([\text{Ni}_8(L15)_4(\text{H}_2\text{O})_8](\text{BF}_4)_8\cdot16\text{H}_2\text{O}\) (38) (see text for fitted parameters).

Figure 35. Magnetic data ($\mu_{\text{mol}}$ versus temperature) for \([\text{Mn}_9(L16)_6](\text{ClO}_4)_6\cdot18\text{H}_2\text{O}\) (39) (see text for fitted parameters).

Figure 36. Magnetization versus field data for \([\text{Mn}_9(L16)_6](\text{ClO}_4)_6\cdot18\text{H}_2\text{O}\) (39) at 1.8 K.

Figure 37. Magnetic data ($\mu_{\text{mol}}$ versus temperature) for \([\text{Cu}_9(L16)_6](\text{NO}_3)_{12}\cdot9\text{H}_2\text{O}\) (40) (see text for fitted parameters).

Figure 38. Magnetization versus field data for \([\text{Cu}_9(L16)_6](\text{NO}_3)_{12}\cdot9\text{H}_2\text{O}\) (40) at 2 K.

Figure 39. Magnetic data ($\mu_{\text{mol}}$ versus temperature) for \([\text{Cu}_8(L16)_4(\text{CH}_3\text{OH})_4(\text{CH}_3\text{CN})_4][\text{Gd}(\text{NO}_3)_4(\text{H}_2\text{O})_2]_2(\text{NO}_3)_6\cdot1.3\text{Cu}(\text{NO}_3)_2\cdot10\text{H}_2\text{O}\) (41) (see text for fitted parameters).

Figure 40. Magnetic model for ‘pin-wheel’ cluster.
Scheme 1
R = Me, Et

R_1 = H, Me, Ph
R_2 = H, Me

R = Me, Et

Cu

Ni

Co

Cu

Ni

Co

M

M

Ni

Ni

Ni

Ni

Co

Co

M

M

Ni

Ni

Ni

Ni

Co

Co

M

M

Ni

Ni

Ni

Ni

Co

Co

M

M
Figure 1.

Figure 2.
Figure 3.

Figure 4.
Figure 10.

Figure 11.

Figure 12.
Figure 13.

Figure 14.
Figure 15.

Figure 16.
Figure 17.

Figure 18.
Figure 19.

Figure 20.
Figure 21.

Figure 22.
Figure 23.

Figure 24.
Figure 27.

Figure 28.
Figure 29.

Figure 30.
Figure 33.

Figure 34
Figure 35.

Figure 36.
Figure 37.

Figure 38.