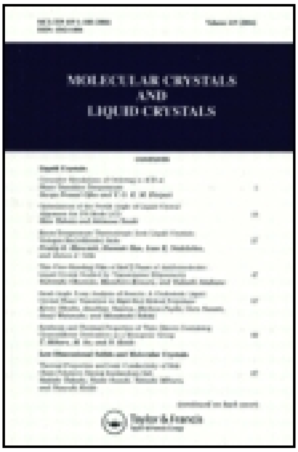

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Polymetallic, Self Assembled Grids and Clusters - Structural and Magnetic Properties

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Polymetallic, Self Assembled Grids and Clusters – Structural and Magnetic Properties

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Polytopic alkoxy-diazine ligands with contiguous coordination pockets, self assemble in high yield to produce [2x2] M_4 grids, M_5 trigonal-bipyramidal clusters, and [3x3] M_9 grids, with alkoxide bridges between the metal centers. Large M-O-M bridge angles lead to antiferromagnetic exchange in all cases except copper, where magnetic orbital orthogonality leads to dominant ferromagnetic exchange.

Keywords self assembly; grid; cluster; structure; magnetism

INTRODUCTION

Strategies for the successful ordered self assembly of paramagnetic transition metal ion centers into magnetically interesting grids and clusters using polyfunctional ligands require that essential coordination environments be incorporated into the ligands, with appropriate geometrical arrangements. Polytopic ligands based on pyridazine, pyrimidine, phenoxide, and alkoxide bridging fragments, have produced 2x2, 3x3, and even 4x4 high nuclearity grids [1-5]. In those cases where paramagnetic transition metal ion centers were involved anti-ferromagnetic coupling was found to predominate.

The present paper summarizes recent approaches using polytopic

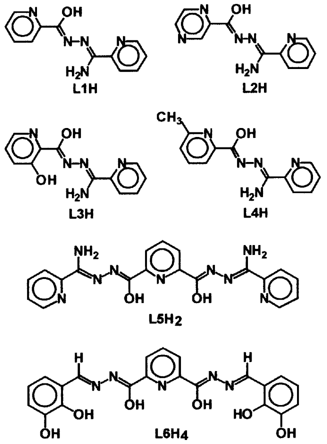


Chart 1

ligands (L1H-L4H, L5H$_2$, L6H$_4$; Chart 1) with contiguous, 'linear' arrangements of coordination pockets that generate five-membered chelate rings, and incorporate alkoxide bridging groups, which serve to link the metal centers in close proximity, and provide the bridging magnetic interactions. Examples of square $[M_4(\mu\text{-}O)_4]$ [2x2] grids (M=Mn(II), Co(II), Ni(II), Cu(II); L1H, L2H, L4H)[5,6] , trigonal bipyramidal $[M_5(\mu\text{-}O)_6]$ clusters (M=Mn(II)[7], Co(II); L1H, L3H), and $[M_9(\mu\text{-}O)_{12}]$ [3x3] grids (M=Mn(II)[8], Cu(II)[9,10]; L5H$_2$) will be discussed. Antiferromagnetic exchange occurs in all cases except for copper, where, through an unusual twist of the copper magnetic planes within the grid structures, strict orthogonality leads to dominant ferromagnetic exchange. L5H$_2$, and the related ligand L6H$_4$, can also produce trinuclear copper(II) complexes. Structural and magnetic properties are highlighted.

EXPERIMENTAL

Preparations

$[Ni_4(L2)_4(H_2O)_4]$ $(ClO_4)_4\bullet H_2O$ (**1**) was prepared as reported previously.[5] $[Co_5(L1)_6](ClO_4)_4\bullet 3H_2O$ (**2**). L1H (1 mmol) was dissolved in a hot stirred solution of $Co(ClO_4)_2.6H_2O$ (1 mmol) in water (20 mL). A pale orange solid formed (Yield 75%), which was recrystallized from acetonitrile to give dark orange crystals. Anal. Calcd for $[Co_5(C_{12}H_{10}N_5O)_6](ClO_4)_4\bullet 3H_2O$: C, 39.52; H, 3.02; N, 19.21. Found: C, 39.58; H, 2.81; N, 19.43.$[Mn_5(L3)_6](ClO_4)_4\bullet CH_3CH_2OH\bullet 3H_2O$ (**3**) was prepared similarly using $Mn(ClO_4)_2.6H_2O$ and L3H. The orange solid formed was recrystallized from methanol/ethanol (50/50) to give orange crystals. (Yield 55%). Anal. Calcd for $[Mn_5(C_{12}H_{10}N_5O_2)_6]$

$(ClO_4)_4$•CH_3CH_2OH •$3H_2O$: C, 38.47; H, 3.12; N, 18.19. Found: C, 38.34; H, 2.87; N, 18.21. $[Cu_4(L4)_4](ClO_4)_4$ (**4**) was prepared in a similar manner from L4H (1mmol) and $Cu(ClO_4)_2$•$6H_2O$ (2 mmol) in aqueous methanol. Green crystals were obtained directly from the mother liquor (Yield 82%). Anal. Calcd for $[Cu_4(C_{13}H_{12}N_5O)_4]$ $(ClO_4)_4$: C, 37.42; H, 2.90; N, 16.78. Found: C, 37.20; H, 2.90; N, 16.71. $[Cu_4(L4)_3(L4')]$ $(NO_3)_5$•$5H_2O$ (**5**) was prepared from L4H (1 mmol) and $Cu(NO_3)_2$•$3H_2O$ (2 mmol) in aqueous methanol. Green crystals were obtained from the mother liquor (Yield 75%). Anal. Calcd for $[Cu_4(C_{13}H_{12}N_5O)_3(C_{13}H_{10}N_5)](NO_3)_5$• $3H_2O$•0.75 CH_3OH: C, 38.60; H, 3.38; N, 21.33. Found: C, 38.42; H, 3.41; N, 21.18. $[Cu_3(L6)(H_2O)_3(CH_3OH)](NO_3)_2$ (**6**) was prepared from $L6H_4$ (1 mmol) and $Cu(NO_3)_2$•$3H_2O$ (3 mmol) in aqueous methanol. Dark, almost black crystals were obtained (Yield 70%) from the mother liquor.

Physical measurements

Variable temperature magnetic data (2-300K) were obtained using a Quantum Design MPMS5S SQUID magnetometer with field strengths of 0.1-5.0 T. Diamagnetic corrections were applied.

RESULTS AND DISCUSSION

The tetradentate ligands L1H-L4H self assemble in the presence of transition metal ions (Mn(II), Co(II), Ni(II), Cu(II)) in high yield to produce predominantly tetranuclear 2x2 grid complexes, in which four metal centers are bridged in a square $[M_4(\mu\text{-}O)_4]$ arrangement.[5,6] Each ligand provides five donor sites, and with six-coordinate metal ions (Mn, Co, Ni) extra ligand sites are filled adventitiously by solvent (e.g. water) or anions (e.g. NO_3). The structure of $[Ni_4(L2)_4(H_2O)_4]$ $(ClO_4)_4$•H_2O (**1**)

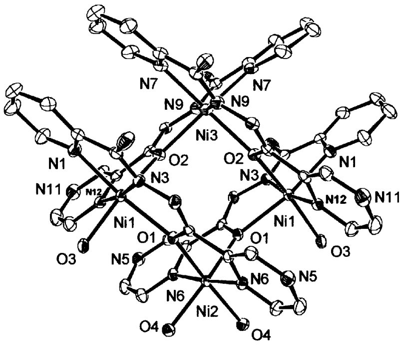


FIGURE 1. Structure of **1**

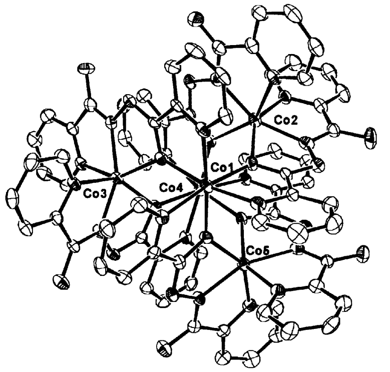


FIGURE 2. Structure of **2**

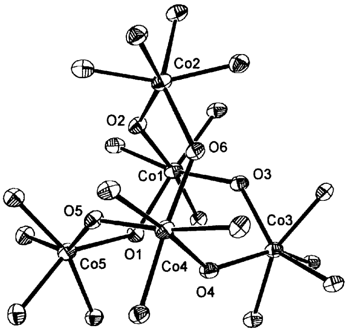


FIGURE 3. Core structure of **2**

is illustrated in Figure 1. For complexes of Mn(II) and Co(II) the self assembled product depends on the anion present. Tetranuclear 2x2 grids are produced with L1H-L3H, and other related ligands, in all cases with nitrate anions, whereas with perchlorate salts homoleptic, trigonal bipyramidal $[M_5(\mu\text{-}O)_6]$ clusters have been produced (M=Mn(II), Co(II)). This may be associated with the stronger coordinating ability of NO_3^- compared with ClO_4^-, and the likely involvement of nitrate as a ligand in the self assembly process.

Figure 2 illustrates the structure of $[Co_5(L1)_6](ClO_4)_4{\bullet}3H_2O$ (**2**)[11] in which six ligands are arranged in three parallel pairs around the central trigonal bipyramidal, alkoxide bridged core, producing a homoleptic cluster. The core is illustrated in Figure 3. Co-O-Co bridge angles fall in the range 133.6-134.9°, and separations between the six-coordinate Co(II) centers fall in the range 3.89-3.93 Å.

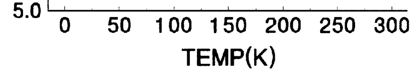


FIGURE 4. Magnetic data for **3**

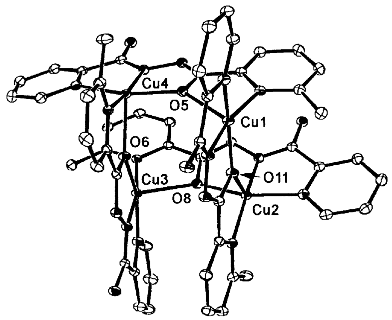
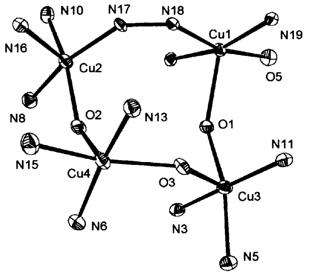
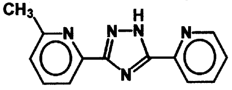


FIGURE 5. Structure of **4**.





L4'H

FIGURE 6. Core structure of **5**.

An identical structure was obtained for $[Mn_5(L3)_6]$ $(ClO_4)_4$•CH_3CH_2OH• $3H_2O$ (**3**),[12] with Mn-O-Mn angles in the range 125.1-131.8°, and Mn-Mn separations in the range 3.86-4.05 Å. The magnetic moments for **1** drops from 10.6 μ_B at 300 K to 2.7 μ_B at 2 K, indicating intramolecular anti-ferromagnetic exchange. Variable temperature magnetic data for **3** show a similar profile (Figure 4) and were fitted to an isotropic exchange expression based on the Mn_5O_6 core, with a single $J_{(Mn\text{-}O\text{-}Mn)}$ value. A reasonable fit gave g=2.02(2), J=-1.0(1) cm^{-1} (Figure 4; solid line, corrected for 0.1 % para-magnetic impurity), indicating overall intra-molecular anti-ferromagnetic coupling, consistent with the alkoxide bridged structure.

$[Cu_4(L4)_4]$ $(ClO_4)_4$ (**4**) has a square 2x2 $[Cu_4\text{-}(\mu\text{-}O)_4]$ grid structure[13] (Figure 5), with two pairs of opposed, parallel ligands arranged above and below the Cu_4 plane, similar to previously reported Cu_4 grids.[5] Cu-Cu distances fall in the range 3.94-3.97 Å, with Cu-O-Cu angles in the range 138.5-140.0°. All connections between copper

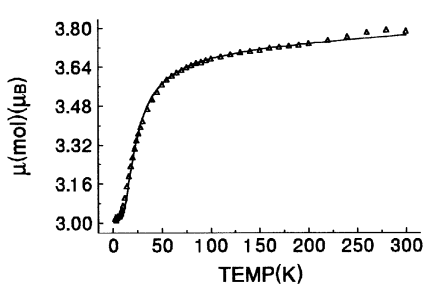


FIGURE 7. Magnetic data for **5**.

centers are strictly orthogonal with alternating axial-equatorial contacts to the alkoxide bridging oxygen atoms. Variable temperature magnetic data for **4** were fitted successfully to an isotropic square model with one J value to give g=2.136(1), J=7.45(5) cm^{-1}, TIP=240*10^{-6} $cm^3.mol^{-1}$. The structure of $[Cu_4(L4)_3(L4')](NO_3)_5•5H_2O$ (**5**)[13] is in complete contrast to **4**, with two different ligands and a tetranuclear structure in the shape of a trapezoid, with three alkoxide bridges, and one triazole bridge (N17-N18) from L4'. The core structure is illustrated in Figure 6. The ring closure reaction occurs commonly through high temperature dehydration with organic molecules of this sort. The present example is clearly a low energy, perhaps metal ion catalyzed, route to the triazole, but only occurs with one ligand. Cu(1)-N(18) and Cu(2)-N(17) are short equatorial contacts, while all other copper connections are orthogonal. To simplify the exchange model, and avoid too many fitting parameters, the variable temperature magnetic data (Figure 7) were fitted to an expression which combined two dinuclear halves of the molecule (Cu(1)-Cu(2) [J1] and Cu(3)-Cu(4) [J2]). The solid line in Figure 7 indicates a good fit of the data for g=2.143(2), J1=-14.9(2) cm^{-1}, J2=7.0(1) cm^{-1}, TIP=240*10^{-6} $cm^3.mol^{-1}$ (0.03% paramagnetic impurity). The ferromagnetic J2 is consistent with compound **4**, and antiferromagnetic J1 is typical for a triazole bridge.

$L5H_2$ effectively doubles some structural elements of L1H-L4H, with the potential to create three contiguous, linear coordination pockets. Self assembly with $L5H_2$ occurs efficiently, and in high yield with Mn(II)[8]

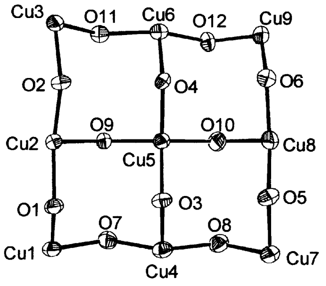


Figure 8. Core structure of **7**.

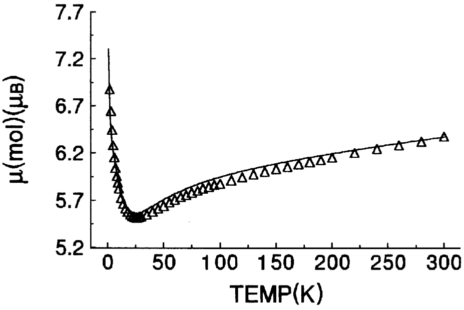


Figure 9. Magnetic data for **7**.

and Cu(II)[9] salts to produce 3x3 nona-nuclear, $[M_9(\mu\text{-}O)_{12}]$, alkoxide bridged grids. The core structure of $[Cu_9(L5H)_6](NO_3)_{12}.9H_2O$ (**7**)[9] is shown in Figure 8 (the Mn complex has the same core structure). Short Mn-Mn distances and large Mn-O-Mn angles lead to antiferromagnetic coupling for the Mn system, but in common with **4**, and other similar examples, the copper system is dominated by ferromagnetic coupling at low temperature. Variable temperature magnetic data (Figure 9) have been modeled successfully[10] with an isotropic exchange expression based on the Hamiltonian: (eqn. 1)

$$\begin{aligned} H= -2J_1 [S_1.S_2 + S_2.S_3 + S_3.S_6 + S_6.S_9 + S_8.S_9 + S_7.S_8 + S_4.S_7 + S_1.S_4] \\ -2J_2 [S_2.S_5 + S_6.S_5 + S_8.S_5 + S_4.S_5] \qquad (1) \end{aligned}$$

The solid line in Figure 9 is calculated with g = 2.30, $J_1 = 0.52\ cm^{-1}$, $J_2 = -24.2\ cm^{-1}$, TIP = $600*10^{-6}\ cm^3.mol^{-1}$. This leads to an overall S=7/2 ground state (confirmed by M/H studies at 2K) resulting from ferromagnetic coupling in the external ring of eight coppers and antiferromagnetic exchange between Cu(5) and the surrounding four copper centers. Cu(5) has a tetragonally compressed d_{z^2} ground state, and all connections between coppers within the grid are orthogonal, with the copper magnetic planes twisted at right angles to the magnetic planes in adjacent copper centers. This is a remarkable feature of this system, and all related $[Cu_4(\mu\text{-}O)_4]$ complexes with L1H-L4H, and similar ligands,[5,6] and leads to dominant ferromagnetic behavior in these cases.

$L6H_4$ has three coordination pockets, like $L5H_2$, but the chelate ring sequence (6:5:5:5:5:6) would effectively prevent 3x3 grid formation. Reaction with copper(II) nitrate produces $[Cu_3L6(H_2O)_3(CH_3OH)](NO_3)_2$ (**6**), a trinuclear complex with one internal, and two external pockets (Figure 10).[14] The coppers are bridged equatorially by two trans diazine (N_2) groups (Cu-N-N-Cu torsional angles 172.1 °, 176.7°), rather than alkoxide oxygens, leading predictably to intramolecular antiferromagnetic

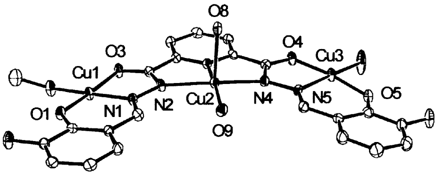


FIGURE 10. Structure of **6**.

coupling. The variable temperature magnetic data were fitted successfully to an isotropic exchange expression for a linear array of S=1/2 centers to give g=2.196(2), J=-57.4(3) cm^{-1}, TIP =$270*10^{-6}$ $cm^3.mol^{-1}$ (R=0.96%). The moderate antiferromagnetic coupling agrees with earlier results on dinuclear Cu(II) complexes bridged by N-N single bonds.[15]

Acknowledgment

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[11] Crystal data: $C_{80}H_{82}N_{34}O_{26}Cl_4Co_5$, formula wt. = 2372.22, monoclinic, space group $P2_1/n$ (#14), a=13.385(1) Å, b=25.797(2) Å, c=28.513(3) Å, β=98.704(2)°, V=9732(1)$Å^3$, Z=4, D_{calc}=1.619g/cm^3, R_1 (wR_2)= 0.068 (0.201) for 18484 data with $I>2\sigma$ and 1343 variables (Bruker P4/CCD with MoKα radiation).

[12] L.K Thompson, C.J. Matthews and S.L. Heath; Preliminary results. Space group $P2_1/n$, a=12.9343(18) Å, b=29.527(7) Å, c=25.828(3) Å, β=98.933(10)°; R1 = 0.0906 for 9844 data with Fo > 4σ(Fo) and 0.1413 for all 17135 data (1335 variables).

[13] L.K. Thompson, M.A. Leech and C. Wilson; Preliminary results. (**3**) Crystal data: $C_{52}H_{48}N_{20}O_{28.13}Cl_4Cu_4$, formula wt. = 1799.1, monoclinic, space group $P2_1/n$, a=19.9608(10) Å, b=17.0907(9)(1) Å, c=21.2188(11) Å, β=96.983(1)°, V=7185.0(6) Å^3, Z=4, D_{calc}=1.663 g/cm^3, R_1 (wR_2)= 0.038(0.1024) for 16521 data ($I>2\sigma$) and 1022 variables (Bruker Smart/CCD system with MoKα radiation). (**4**) Space group $P\bar{1}$, a=14.3519(6) Å, b=15.8406(7) Å, c=16.4653(7) Å, α=62.977(2)°, β=83.572(2)°, γ=89.887(2)°; R1=0.0748 for 8556 data (Fo > 4σ(Fo)) and 0.1059 for all 11636 data (875 variables).

[14] Crystal data: $C_{22}H_{23}N_7O_{16}Cu_3$, formula wt. = 823.10, monoclinic, space group $P2_1/n$ (#14), a=10.0066(7) Å, b=20.675(1) Å, c=13.7619(9) Å, β=90.050(2)°, V=2833.6(3)Å^3, Z=4, D_{calc}=1.950g/cm^3, R_1 (wR_2)= 0.038(0.092) for 4117 data ($I>2\sigma$) and 433 variables (Bruker P4/CCD system with MoKα radiation).

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