Self-assembled polymetallic square grids ($[2 \times 2] M_4$, $[3 \times 3] M_9$) and trigonal bipyramidal clusters (M_5)—structural and magnetic properties †‡

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New self-assembled grids and clusters are reported, with square $[2 \times 2] M_4$ (M = Mn(II)₄, Cu(II)₄), trigonal-bipyramidal Mn(II)₅, and square $[3 \times 3] M_9$ (M = Mn(II), Cu(II)) examples. These are based on a series of ditopic and tritopic hydrazone ligands involving pyridine, pyrimidine and imidazole end groups. In all cases the metal centres are bridged by hydrazone oxygen atoms with large (>125°) bridge angles, leading to antiferromagnetic exchange for all the Mn systems (J = -2 to -5 cm⁻¹), which results in S = 0 (Mn₄), and S = 5/2 (Mn₅, Mn₉) ground states. The copper systems have a 90° alternation of the Jahn–Teller axes within the Cu₄ and Cu₈ grid rings (Cu₉), which leads to magnetic orbital orthogonality, and dominant ferromagnetic coupling. For the Cu₉ grid antiferromagnetic exchange between the ring and the central copper leads to a S = 7/2 ground state, while for the Cu₄ grids S = 4/2 ground states are observed. The magnetic data have been treated using isotropic exchange models in the cases of the Cu₄ and Cu₉ grids, and the Mn₅ clusters. However due to the enormity of a fully isotropic calculation a simplified model is used for the Mn₉ grid, in which the outer Mn₈ ring is treated as the equivalent of an isolated magnetic chain, with no coupling to the central metal ion.

Introduction

The ability to control molecular assembly through a programmed approach of creating the substituents with desired features, and then allowing the products to form essentially unassisted, offers enormous advantages over other methods of synthesis, where reaction outcomes are frequently left largely to chance, or the end product is the result of a complex sequence of individual steps. Yields by such methods are frequently very low. High yield self-assembly reactions can be very effective for the formation of $[n \times n]$ poly-metallic grids, where the donor content of the ligand pockets is designed to match the Lewis acid nature, and geometric preference, of a transition metal ion. Examples of self-assembled $[2 \times 2]^{1-3}$ and $[3 \times 3]^4$ grids have been reported based on pyridazine and pyrimidine ligands, and in rare cases extension of such ligands has led to larger $[4 \times 4]^{5-7}$ grids.

Ditopic ligands, *e.g.* poap (Chart 1), built on a picolinic hydrazone core fragment, have a bidentate and a tridentate coordination pocket, with a hydrazone oxygen atom, which can act as a bridge between two metal centres. The formation of five-membered chelate rings on coordination ensures that a roughly linear M–O–M coordination fragment results.

Reaction of ligands in this class with a variety of transition metal salts (MX₂, M = Mn, Co, Ni, Cu, Zn) leads to $[2 \times 2]$ self assembled heteroleptic or homoleptic M₄ grids in high yield (Scheme 1).^{8–13} The close proximity of the metal ions leads to spin exchange coupling within the grids, with



[R'=NH₂] 2poap (R=H,X=CH),2poapz (R=H,X=N) Cl2poap (R=CI,X=CH),S2poap (R=S⁻,X=CH) SEt2poap (R=SEt,X=CH), SMe2poap (R=SMe,X=CH); [R'=CH₃] 2pomp (R=H,X=CH),Cl2pomp(R=CI,X=CH); [R'=Ph] Cl2popp (R=CI,X=CH)



2pmoap



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[‡] Electronic supplementary information (ESI) available: Fig. S1: plot of μ mol as a function of temperature for 4; Fig. S2: magnetization data as a function of field at 2 K for 4; Fig. S3: plot of μ mol as a function of temperature for 6. See DOI: 10.1039/b602595a



Scheme 1

anti-ferromagnetic and ferromagnetic examples. Homoleptic self-assembled $[M_5L_6]$ (M = Mn, Co, Zn)^{11,14} clusters can also form, in rare cases, with ditopic ligands in this class, when coligand competition is minimized.

Extension of this ligand type with an extra pocket produces a linear tritopic entity, e.g. 2poap and related derivatives (Chart 1), with the ability to bind to three metal ions. Selfassembly of ligands in this class leads to homoleptic $[3 \times 3]$ M₉ grids (Scheme 1) in high yield (M = Mn, Fe, Ni, Cu, Zn).¹⁵⁻²⁵ The short M–M distances (~ 4 Å) and large M–O–M bridge angles (>125°) in these grids lead to spin exchange with antiferromagnetic (Mn, Fe, Ni) and ferromagnetic (Cu) examples. The Mn₉ grids exhibit a unique suite of reversible redox processes in the range 0.5-1.5 V vs. Ag/AgCl leading to an eight electron redox window associated with eight Mn(II) centers oxidizing to Mn(III). The electronic bistability of these systems, and the fact that they can be attached to gold (Au(111))²³ and HOPG²⁶ surfaces to form self-assembled monolayers in some cases, and probed using STM and CITS (current imaging tunneling spectroscopy) techniques, has clearly indicated their potential for molecular device behaviour in the nanoscale realm.

Related ditopic and tritopic ligands are under study, with the objective of creating increased donor functionality at strategic locations on the ligand backbone. This has been a focus in some recent work where thioether, and sulfide R groups (Chart 1)^{23,26} have been introduced as additional sites for grid elaboration, and for enhanced surface attachment. In the present study some new ditopic and tritopic ligands have been developed with imidazole and pyrimidine end groups (e.g. ioapm, 2pmoap), and their coordinating ability with Mn(II) and Cu(II) salts examined. These ligands are of interest because of the potential for additional extended coordination ability of the imidazole and pyrimidine groups after primary ligand coordination. This 'complex as ligand' approach has been shown to lead to extended coordination successfully with complexes of, for example, oxamate based ligands.^{27,28} In the present study examples of $[2 \times 2]$ and $[3 \times 3]$ square grids, and Mn₅ trigonal bipyramidal clusters involving just primary ligand coordination, are reported. Structural and magnetic properties are highlighted.

Experimental

Commercially available solvents and chemicals were used without further purification.

Physical measurements

Infrared spectra were recorded as Nujol mulls using a Mattson Polaris FT-IR instrument, and UV/Vis spectra were obtained using a Cary 5E spectrometer. Micro-analyses were carried out by Canadian Microanalytical Service, Delta, Canada. Variable temperature magnetic data (2–300 K) were obtained using a Quantum Design MPMS5S SQUID magnetometer using field strengths in the range 0.1 to 5 T. Background corrections for the sample holder assembly and diamagnetic components of the complexes were applied. NMR measurements were taken with a Bruker AVANCE 500 MHz spectrometer. LCMS measurements were taken using an Agilent 1100 Series LC/ MSD in APCI mode with methanol as the solvent.

Synthesis of ligands

mpoap. 6-Methyl-2-picolinic acid was prepared by partial oxidation of 2,6-lutidine with KMnO₄,²⁹ and converted to the ethyl ester (abs. EtOH/c. H₂SO₄; 60%).³⁰ The ethyl ester (9.9 g, 60 mmol) was dissolved in methanol (30 mL) and added slowly to a chilled solution of hydrazine hydrate (7.5 g, 120 mmol) in dry methanol (30 mL), and the mixture allowed to stir overnight. The corresponding hydrazide was obtained as a white solid, and recrystallized from benzene (yield 4.2 g, 47%). Mp 93-94 °C. The methyl ester of imino-2-picolinic acid was prepared in situ by reaction of 2-cyanopyridine (2.08 g, 20 mmol) with sodium methoxide solution, produced by dissolving sodium metal (0.05 g, 2.2 mmol) in dry methanol (100 mL). 6-Methyl-2-picolinic acid hydrazide (3.02 g, 20 mmol) was added to the above solution and the mixture refluxed for 24 h. A yellow crystalline solid was obtained, which was filtered off, washed with water, methanol and diethyl ether and dried under vacuum (yield 3.8 g, 75%). Mp 198–200 °C. ¹H NMR (500 MHz, DMSO-d₆, 25 °C): 10.5 (s, 1H, OH), 8.64 (d, 1H, Ar), 8.22 (d, 1H, Ar), 7.90 (m, 3H, Ar), 7.50 (m, 2H, Ar), 6.95 (s, 2H, NH₂), 2.60 (s, 3H, CH₃). Mass spectrum (major mass peaks, m/z): 255 (M), 239, 238, 237, 208, 163, 107, 105. IR (Nujol mull, cm⁻¹): 3376, 3312 (vNH); 1684, 1677 (vC=O); 1589, 1565 (vC=N). Anal. calcd (%) for C13H13N5O: C, 61.16; H, 5.13; N, 27.43. Found: C, 61.47; H, 4.71; N 27.38.

pomp. 2-Acetyl pyridine (1.8 g, 15.0 mmol) was added dropwise to a solution of picolinic hydrazide (1.35 g, 10.0 mmol) in 15 mL of methanol. The resulting solution was refluxed for 6 h. A noticeable cloudiness of the solution was observed within 1 h. A white precipitate formed, which was filtered off, washed with methanol and ether, and vacuum dried (yield 2.0 g, 83%). Mp 195–197 °C. Mass spectrum (*m/z*): 241.3 (M⁺⁺), IR (Nujol mull, cm⁻¹) 3316 (*v*NH), 1701 (*v*CO), 995 (*v*py). NMR (DMSO-d₆, ppm) 2.5 (s, CH₃), 7.45 (t), 7.72 (t), 7.90 (t), 8.11 (t), 8.16 (t), 8.64 (d), 8.75 (d), 11.15 (s, OH). Anal. calcd (%) for C₁₃H₁₂N₄O: C, 64.98; H, 5.03; N, 23.31. Found: C, 64.69; H, 5.10; N, 23.07.

ioapm. 4-Methyl-5-imidazole carboxylic acid hydrazide was generated by the dropwise addition of hydrazine hydrate (85%) (2.34 g, 46.7 mmol) to a stirred solution of ethyl-4-methyl-5imidazole carboxylate (3.39g, 22.0mmol) in 60 mL of 1-butanol and 25 mL of methanol. The resulting clear, yellow solution was refluxed for 72 h. Upon cooling a tan precipitate formed, which was collected by suction filtration and washed with ether (84% yield). The iminoester of 2-pyrimidinecarbonitrile was generated by dissolving 2-pyrimidinecarbonitrile (2.35 g, 22.4 mmol) in methanol (100 mL) with sodium metal (0.10 g, 4.4 mmol). The resulting clear colourless solution was capped with a drying tube and stirred at room temperature for 8 h. Acetic acid was then added until a neutral pH was achieved. 4-Methyl-5-imidazole carboxylic acid hydrazide (2.10 g, 15 mmol) was added to the stirred solution of 2-pyrimidine iminoester, which formed a clear yellow solution. A yellow precipitate formed upon stirring for 5 min. Methanol was added until a total volume of 250 mL was achieved, and the solution was refluxed for 16 h. Upon heating, the precipitate dissolved. The refluxed solution was cooled to room temperature and remained clear and yellow. The volume was reduced under reduced pressure to 20 mL, and 100 mL of diethyl ether was added. A yellow precipitate formed, which was collected by suction filtration, washed with methanol and diethyl ether, and vacuum dried (yield 3.4 g, 93%). Mp 222-225 °C. Mass spectrum (m/z): 246.1 (M^{+•}), IR (v/cm^{-1}) 3332 (vNH), 1654, 1562 (vCN, vCO), 952 (vpym). Anal. Calcd (%) for C₁₀H₁₁N₇O·1.5MeOH·1.2H₂O: C, 43.86 H, 6.17 N, 31.15. Found: C, 43.86; H, 4.80; N, 31.31.

2pmoap. Dimethyl-2,6-pyridinedicarboxylate (10.07 g, 51.60 mmol) was converted to the dihydrazide by reaction with hydrazine hydrate (85%) (2.60 g, 51.9 mmol) in methanol (yield 40%). 2-Pyrimidinecarbonitrile (1.82 g, 17.3 mmol) was reacted with sodium methoxide solution, produced by dissolving sodium metal (0.15 g, 6.5 mmol) in dry methanol (150 mL) to generate the iminoester. The solution was then neutralized using acetic acid, and 2,6-pyridinedicarboxylate dihydrazide (1.52 g, 7.79 mmol) added giving a yellow mixture, which was refluxed for 24 h. A yellow solid was obtained, which was filtered off, washed with methanol and diethyl ether and dried under vacuum. Yield (2.08 g, 66%). Mass spectrum (m/z): 406 (M^{+•}), IR (Nujol mull, cm⁻¹): 3413, 3332, 3181 (vNH); 1685, 1612 (vC=O); 1558, 1519 (vC=N). Anal. calcd (%) for C₁₇H₁₅O₂N₁₁·2.25CH₃OH: C, 48.42; H, 5.06; N, 32.27. Found: C, 48.97; H, 3.71; N 32.27.

Synthesis of complexes

[Mn₄(poap–H)₄(N₃)₄]·2H₂O (1). poap⁸ (0.240 g, 1.00 mmol) was added to a warm solution of Mn(ClO₄)₂·6H₂O (0.360 g, 1.00 mmol) in methanol–water (20 mL : 20 mL) forming an orange solution. A concentrated aqueous solution (2 mL) of sodium azide (0.2 g, 1.3 mmol) was added with stirring, and the resulting orange solution was allowed to stand at room temperature overnight. Dark orange crystals suitable for structural study formed (yield 70%). IR (Nujol mull, cm⁻¹) 2075 (m), 2046 (m) (vN₃), 1651 (m), 1541 (m) (vC=N, vC=O); 1007 (w) (vpy). Anal. calcd (%) for

[Mn₄(pomp–H)₄(H₂O)₃(CF₃SO₃)](CF₃SO₃)₃·CH₃OH (2). pomp (0.100 g, 0.420 mmol) was added to a solution of Mn(CF₃SO₃)₂·*x*H₂O (3.5 mL, 0.03 g mL⁻¹ in MeOH–H₂O 4 : 1) with the addition of 2 drops of Et₃N. The resulting deep red solution was kept for crystallization after stirring for one hour and filtration. Orange crystals were collected after two days (0.055 g, 26% yield). Slow diffusion of ether into a MeOH–CH₃CN solution of the complex gave X-ray quality crystals. Anal. calcd (%) for (C₁₃H₁₁N₄O)₄Mn₄(CF₃SO₃)₄-(CH₃OH)₈(H₂O) (bulk sample): C, 37.54; H, 3.84; N, 10.94. Found (%): C, 37.63; H, 2.85; N, 10.91.

[Cu₄(mpoap–H)₄](ClO₄)₄·8H₂O (3). mpoap (0.255 g, 1.00 mmol) was added to a warm solution of Cu(ClO₄)₂· $6H_2O$ (0.740 g, 2.00 mmol) in methanol–water (30 mL : 5 mL). The resulting suspension was stirred until complete dissolution of the ligand occurred forming a dark green solution. The solution was filtered and allowed to stand at room temperature. X-Ray quality green crystals formed after several days (yield 82%). IR (Nujol mull, cm⁻¹) 1664 (s), 1611 (w), 1590 (m), 1571 (m) (ν C=N, ν C=O); 1085 (s) (ν ClO₄⁻); Vis. (Nujol mull) λ (nm) 696, 800 sh. Anal. Calcd (%) for Cu₄(C₁₃H₁₂N₅O)₄(ClO₄)₄·0.5H₂O (vacuum dried sample): C, 37.22; H, 2.94; N, 16.69. Found: C, 37.20; H, 2.90; N, 16.71.

[Cu₄(ioapm–H)₄](ClO₄)₄·3CH₃CN (4). ioapm (0.21 g, 0.86 mmol) was added to a warm solution of Cu(ClO₄)₂· $6H_2O$ (0.31 g, 0.84 mmol) in methanol–acetonitrile (10 mL : 10 mL). Addition of 3 drops of Et₃N produced a clear, dark green coloured solution, which was stirred for an hour and kept after filtration for crystallization. A green precipitate formed after standing for one week. Dark green crystals, suitable for a structural study, were obtained by recrystallization from 50 : 50 methanol–acetonitrile (0.043 g, 12% yield). Anal. calcd (%) for Cu₄(C₁₀H₁₀N₇O)₄(ClO₄)₄·3H₂O (bulk dried sample): C, 28.61; H, 2.76; N, 23.38. Found (%): C, 28.63; H, 2.59; N, 23.57.

[Mn₅(pomp–H)₆](ClO₄)₄·CH₃CN·1.5CH₃OH (5). pomp (0.100 g, 0.420 mmol) was added to a solution of excess Mn(ClO₄)₂·6H₂O (0.50 g, 2.0 mmol) in a methanol–acetonitrile mixture (10 mL : 10 mL), forming initially a light yellow clear solution. Addition of 2–3 drops of Et₃N produced a clear, deep red coloured solution, which was stirred for an hour and kept after filtration for crystallization. Red, rod like crystals were collected after two days (0.060 g, 38% yield). Slow diffusion of ether into a MeOH–CH₃CN solution of the complex gave X-ray quality crystals. Anal. calcd (%) for (C₁₃H₁₁N₄O)₆Mn₅(ClO₄)₄(CH₃CN)(CH₃OH)₂(H₂O)_{3.5} (bulk sample): C, 43.27; H, 3.72; 15.38. Found (%): C, 43.11; H, 3.46; N, 15.10.

 2 drops of Et₃N produced a clear, deep orange coloured solution, which was stirred for an hour and kept after filtration for crystallization. X-Ray quality, red, prismatic crystals were collected after two days (0.040 g, 30% yield). Anal. calcd (%) for (C₁₀H₁₀N₇O)₆Mn₅(ClO₄)₄·2.5H₂O: C, 33.30; H, 3.00; N, 26.98. Found (%): C, 32.79; H, 2.67; N, 27.40.

[Mn₉(2pmoap-2H)₆](NO₃)₆·28H₂O (7). 2pmoap (0.49 g, 1.2 mmol) was added to a solution of excess $Mn(NO_3)_2 \cdot 6H_2O$ (1.01 g, 3.5 mmol) in methanol-acetonitrile (20 mL : 20 mL) forming initially a light yellow clear solution. This was left to stir with gentle heating for 2 hours. It was then filtered and solvent was removed from the filtrate to yield 0.96 g of a yellow powder. This was dissolved in methanol-acetonitrile (10 mL : 10 mL) to give a clear, yellow solution. NH₄CH₃COO (0.04g, 0.51 mmol) was added producing a clear, deep red coloured solution that was stirred with gentle heating for 1 hour, and at room temperature for three hours. This solution was filtered and allowed to stand at room temperature. X-Ray quality, red prismatic crystals formed after three days (0.86 g, 96% yield). Anal. calcd (%) for (C₁₇H₁₃N₁₁O₂)₆Mn₉(NO₃)₆-(H₂O)₁₃ (bulk dried sample): C, 34.78; H, 2.98; 28.65. Found (%): C, 34.35; H, 2.70; N, 28.94.

 $[Cu_9(2pmoap-2H)_2(2pmoap-H)_4](ClO_4)_{10} \cdot 13.2H_2O$ (8). 2pmoap (0.12 g, 0.30 mmol) was added to a warm solution of Cu(ClO₄)₂·6H₂O (0.13 g, 0.35 mmol) in methanolacetonitrile (10 mL : 10 mL). A clear, dark green solution formed. The solution remained clear and dark green upon the addition of 3 drops of Et₃N. It was stirred with gentle heating for 45 minutes and kept after filtration for crystallization. X-Ray quality, green prismatic crystals formed after standing at room temperature for two weeks (0.030 g, 15% yield). Anal. calcd (%) for (C17H13N11O2)2(C17H14N11O2)4Cu9(ClO4)10-(H₂O)₁₆ (bulk sample): C, 28.62; H, 2.68; N, 21.61. Found (%): C, 29.31; H, 2.34; N, 20.91. The slight discrepancy in analytical data may indicate some solvent (e.g. methanol) in the bulk sample.

Crystallography

The diffraction intensities of an orange plate-like crystal of 1 of dimensions $0.52 \times 0.12 \times 0.04$ mm were collected with graphite-monochromatized Mo-Ka X-radiation using a Bruker P4/CCD diffractometer at 193(1) K to a maximum 2θ value of 52.8°. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.^{31,32} All atoms except hydrogens were refined anisotropically. Hydrogen atoms were placed in calculated positions with isotropic thermal parameters set to twenty percent greater than their bonded partners at the time of their inclusion, and were not refined. Neutral atom scattering factors³³ and anomalous-dispersion terms^{34,35} were taken from the usual sources. All other calculations were performed with the teXsan³⁶ crystallographic software package. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.98 and $-0.44 \text{ e}^- \text{ Å}^{-3}$, respectively. Abbreviated crystal data for 1 are given in Table 1. Diffraction intensities for 2 and 5 were collected similarly,

Table 1 Crystal data and	structure refinement	for compounds 1–8						
	1	2	3	4	N.	6	7	×
Chemical formula	$C_{48}H_{44}O_{6}$ -	$C_{57}H_{54}O_{20}$ -	C ₅₂ H ₄₈ O _{28.13} -	$C_{46}H_{49}Cl_4N_{31}$ -	C _{81.5} H ₇₅ O _{23.5} -	$C_{60}H_{74}O_{29}$ -	$C_{102}H_{134}O_{58}$ -	C ₁₀₂ H _{108.4} O _{65.2} -
	$N_{32}Mn_4$	$N_{16}S_4F_{12}Mn_4$	$N_{20}Cl_4Cu_4$	$O_{20}Cu_4$	$N_{25}Cl_4Mn_5$	N ₄₂ Cl ₄ Mn ₅	$N_{72}Mn_9$	$N_{66}Cl_{10}Cu_9$
M	1384.91	1859.16	1799.10	1752.08	2197.17	2264.01	3791.07	4228.43
T/K	193(2)	193(2)	100(2)	153(2)	193(2)	153(2)	153(2)	153(2)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	tetragonal	tetragonal
Space group	$P2_1$	$P\overline{1}$	$P2_1/n$	C2lc	$P2_1/n$	$P2_1/n$	$I4_1/acd$	$P4_2/n$
aiÅ	13.0200(9)	12.4058(8)	19.9608(10)	22.912(9)	13.9992(13)	16.8375(19)	27.9255(13)	20.9857(14)
$b/\text{\AA}$	14.0538(10)	14.4617(10)	17.0907(9)	21.105(7)	22.318(2)	23.483(3)		
c/Å	16.5587(12)	22.1102(15)	21.2188(11)	18.184(7)	29.476(3)	23.610(3)	40.217(2)	17.3731(12)
αl°		72.629(1)						
β/° √/°	100.253(1)	80.747(1) 78.257(1)	96.9830(10)	128.679(7)	93.573(2)	96.970(3)		
V/Å ³	2981.5(4)	3685.3(4)	7185.0(6)	6864(4)	9191.4(15)	9266.1(18)	31362(3)	7651.1(9)
Z	5	2	4	4	4	4	8	5
$D_{\rm c}/{ m g~cm^{-3}}$	1.543	1.675	1.663	1.695	1.588	1.623	1.606	1.834
$\mu(Mo-K\alpha)/cm^{-1}$	9.04	8.94	14.12	14.71	8.73	8.77	8.09	15.17
Reflections total	16310	29338	88214	37116	72073	32353	151450	75957
Reflections unique (Rint)	10903 (0.042)	15043 (0.019)	16521 (0.0163)	9417 (0.082)	18894 (0.120)	16107 (0.031)	11887 (0.059)	10853 (0.053)
$R_1[I > 2\sigma(I)]$	0.0674	0.0449	0.038	0.1101	0.0745	0.0979	0.1278	0.1023
wR_2	0.1790	0.1192	0.1024	0.2878	0.2436	0.2731	0.3008	0.2406
$^{a} R_{1} = \Sigma [F_{0} - F_{c}]/\Sigma F_{0} , n$	$vR_2 = [\Sigma[w(F_0 ^2 - F_0 ^2)]$	$ ^{2} ^{2} /\Sigma[w(F_{0} ^{2})^{2}] ^{1/2}.$						

and structural solutions achieved using the same methods (see Table 1, and ESI‡).

The diffraction intensities of a green prism-like crystal of 4 of dimensions $0.72 \times 0.17 \times 0.11$ mm, were collected with graphite-monochromatized Mo-Ka X-radiation using a Rigaku AFC8 Saturn CCD diffractometer at 153(1) K to a maximum 2θ value of 62.0° . The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods,³⁷ and expanded using Fourier techniques.³⁸ Some non-hydrogen atoms were refined anisotropically, while others were refined isotropically. Hydrogen atoms were introduced in calculated positions with thermal parameters set twenty percent greater than their bonding partners, and were refined on the riding model. Neutral atom scattering factors³³ and anomalous-dispersion terms^{34,35} were taken from the usual sources. All calculations were performed using the CrvstalStructure^{39,40} crystallographic software packages, except for refinement, which was carried out using SHELX-97.³¹ Diffraction intensities for 6-8 were collected similarly, and structural solutions achieved using the same methods (see Table 1, and ESI[‡]).

The data collection for 3 was carried out using graphite monochromated Mo-Ka X-radiation with a Siemens SMART CCD detector diffractometer equipped with a Cryostream⁴¹ N₂ flow cooling device. Series of narrow ω -scans (0.3°) were performed at several φ -settings in such a way as to cover a hemisphere or a full sphere of data to a maximum resolution of 0.7 Å. Cell parameters were determined and refined within SMART⁴² using the centroid values of approximately 500 selected reflections with 2θ values between 20 and 45° . Raw frame data were integrated using the SAINT program.⁴³ The data were corrected for absorption by an empirical psiscan based method.⁴⁴ The structure was solved using direct methods and refined by full-matrix least squares on $F^{2,44}$ All atoms except hydrogen were refined with anisotropic atomic displacement parameters (ADPs). Hydrogen atoms were placed geometrically, with ADPs set at twenty percent of their bonded partners, and were not refined. Abbreviated crystal data for 3 are given in Table 1.

CCDC reference numbers 258937, 299029–299035. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602595a

Results and discussion

Structures

 $[Mn_4(poap-H)_4(N_3)_4]\cdot 2H_2O$ (1). The structure of the neutral $[2 \times 2]$ grid is shown in Fig. 1, and important bond distances and angles are listed in Table 2. The tetradentate ligands are arranged in parallel eclipsed pairs on either side of the $[Mn_4-(\mu-O)_4]$ square core leaving four open coordination sites, which are occupied by four terminally bound azide groups, with one each bound to Mn(2) and Mn(4) and two in a *cis*orientation bound to Mn(1). Mn–L distances are typical of square grids of this type, and the relative positions of the azide ligands are similar to those reported in previous examples.⁹ Mn–Mn distances fall in the range 3.88-4.01 Å, with Mn–O–Mn angles in the range $126.9-129.5^{\circ}$.



Fig. 1 Structural representation of complex 1 (30% probability thermal ellipsoids).

 $[Mn_4(pomp-H)_4(H_2O)_3(CF_3SO_3)](CF_3SO_3)_3 \cdot CH_3OH$ (2). The structure of the cation in 2 is shown in Fig. 2, and important bond distances and angles are listed in Table 3. The square $[2 \times 2]$ grid consists of two eclipsed, parallel tetradentate pomp ligands bound on the upper and lower faces of the $Mn_4-(\mu-O)_4$ core. The four vacant sites in this arrangement are in the same relative positions as in 1, and are occupied by three water molecules, and a triflate anion. Mn-Mn distances fall in the range 3.94-4.00 Å, with Mn-O-Mn angles in the range 128.8-129.9°. C-O distances in the ligands fall in the range 1.298-1.309 Å, indicating a predominance of single CO bond character. The infrared spectrum of the ligand (vide infra) indicates significant ketonic character in this group on the basis of the observation of a vC=O band at 1700 cm⁻¹ and that some ligand rehybridization has occurred on coordination.

 $[Cu_4(mpoap-H)_4](ClO_4)_4 \cdot 8H_2O$ (3). The structural representation of the homoleptic tetranuclear cation in 3 is shown in Fig. 3, and important bond distances and angles are listed in

Table 2 Bond distances (Å) and angles (°) for 1

		e	
Mn(1)–O(4)	2.152(6)	Mn(3)–N(11)	2.310(7)
Mn(1) - N(24)	2.183(7)	Mn(3) - N(10)	2.385(7)
Mn(1) - N(21)	2.196(7)	Mn(4) - N(30)	2.143(8)
Mn(1)-O(1)	2.213(5)	Mn(4) - O(3)	2.167(5)
Mn(1) - N(20)	2.227(7)	Mn(4) - N(18)	2.179(7)
Mn(1)-N(1)	2.241(6)	Mn(4)-O(4)	2.204(5)
Mn(2)-N(3)	2.151(6)	Mn(4) - N(15)	2.274(7)
Mn(2) - N(27)	2.175(7)	Mn(4) - N(16)	2.380(8)
Mn(2)-O(2)	2.212(5)	Mn(1)-Mn(4)	3.919(4)
Mn(2) - O(1)	2.218(5)	Mn(3)-Mn(4)	3.882(4)
Mn(2) - N(6)	2.268(7)	Mn(1)-Mn(2)	4.007(5)
Mn(2) - N(5)	2.411(6)	Mn(2)-Mn(3)	3.977(4)
Mn(3) - N(13)	2.141(6)	Mn(1)-O(1)-Mn(2)	129.5(2)
Mn(3) - N(8)	2.151(6)	Mn(3) - O(2) - Mn(2)	128.5(2)
Mn(3) - O(3)	2.173(5)	Mn(4) - O(3) - Mn(3)	126.9(2)
Mn(3)-O(2)	2.203(5)	Mn(1)–O(4)–Mn(4)	128.2(3)



Fig. 2 Structural representation of complex cation in **2** (30% probability thermal ellipsoids).

Table 3 Bond distances (Å) and angles (°) for 2.

Mn(1) - O(8)	2.171(2)	Mn(3) - N(8)	2.267(2)
Mn(1) - N(15)	2.181(2)	Mn(3)-N(9)	2.328(3)
Mn(1) - O(1)	2.1840(19)	Mn(4) - O(6)	2.139(2)
Mn(1) - O(4)	2.2095(18)	Mn(4) - O(4)	2.1605(18)
Mn(1)-N(1)	2.230(2)	Mn(4) - O(7)	2.178(2)
Mn(1) - N(16)	2.312(2)	Mn(4) - O(3)	2.1857(19)
Mn(2)-N(6)	2.175(2)	Mn(4) - N(12)	2.236(2)
Mn(2)-N(3)	2.176(2)	Mn(4) - N(13)	2.249(2)
Mn(2) - O(1)	2.1938(19)	Mn(1)-Mn(2)	3.948(1)
Mn(2)-O(2)	2.2250(18)	Mn(2)-Mn(3)	3.980(2)
Mn(2)-N(5)	2.278(2)	Mn(3)-Mn(4)	3.999(1)
Mn(2)-N(4)	2.309(2)	Mn(1)-Mn(4)	3.959(1)
Mn(3) - O(5)	2.166(2)	Mn(1)-O(1)-Mn(2)	128.80(9)
Mn(3)-O(2)	2.1791(18)	Mn(3) - O(2) - Mn(2)	129.28(8)
Mn(3) - N(10)	2.191(2)	Mn(4) - O(3) - Mn(3)	129.55(8)
Mn(3)–O(3)	2.2342(19)	Mn(4)-O(4)-Mn(1)	129.87(9)

Table 4. The Cu₄O₄ core is typical for self assembled 'square' grids of this sort, with a boat conformation, Cu–Cu separations in the range 3.943-3.967 Å, and Cu–O–Cu angles in the range $138.5-140.1^{\circ}$. The copper centers have square-pyramidal stereochemistries, with an alternation of short (equatorial) and long (axial) Cu–O contacts around the square (1.895–2.056 Å

Fig. 3 Structural representation of complex cation in 3 (30% probability thermal ellipsoids).

Table 4 Bone	d distances (A) a	and angles (°) for 3	
Cu(1)–N(29)	1.9008(19)	Cu(3)–O(51)	2.2252(17)
Cu(1)–N(76)	1.9942(19)	Cu(4)–N(67)	1.895(2)
Cu(1)–O(32)	2.0050(17)	Cu(4)–N(18)	1.982(2)
Cu(1)–N(26)	2.056(2)	Cu(4)–O(70)	1.9925(17)
Cu(1)–O(70)	2.2441(17)	Cu(4)–N(59)	2.038(2)
Cu(2)–N(48)	1.903(2)	Cu(4)–O(12)	2.1999(17)
Cu(2)–N(38)	1.994(2)	Cu(1)-Cu(2)	3.957(1)
Cu(2)–O(51)	1.9985(17)	Cu(1)–Cu(4)	3.967(2)
Cu(2)-N(40)	2.044(2)	Cu(2)–Cu(3)	3.951(1)
Cu(2)–O(32)	2.2042(17)	Cu(3)–Cu(4)	3.943(1)
Cu(3)–N(9)	1.901(2)	Cu(3)–O(12)–Cu(4)	139.31(8)
Cu(3)–N(57)	1.978(2)	Cu(1)–O(32)–Cu(2)	140.03(8)
Cu(3)–O(12)	2.0047(17)	Cu(2)–O(51)–Cu(3)	138.57(8)
Cu(3)–N(1)	2.045(2)	Cu(4)–O(70)–Cu(1)	138.78(8)

and 2.199–2.245 Å respectively). There are no additional axial contacts to the copper centers within 3.5 Å. This may be due to the presence of the 6-methyl groups, which project enough to at least partially impede the approach of *e.g.* a water molecule at each copper ion center. The ligands are arranged in parallel pairs, with separations close to the metal–metal contacts, above and below the Cu_4 pseudo-plane, but adopt opposed *anti* conformations within each pair.

 $[Cu_4(ioapm-H)_4](CIO_4)_4 \cdot 3CH_3CN$ (4). The structure of the homoleptic tetranuclear cationic fragment in 4 is shown in Fig. 4, and important bond distances and angles are listed in Table 5. The core structure is shown in Fig. 5. Four square-pyramidal copper ions are bound to four tetradentate ligands arranged in two parallel groups above and below the metal



Fig. 4 Structural representation of the complex cation in 4 (POVRAY $^{\circ}$ image).

Table 5 Bond distances (Å) and angles (°) for 4

$C_{1}(1)$ $N(4)$	1.012(5)	C (2) O(2)	1.002(4)
Cu(1)-N(4)	1.912(5)	Cu(2) - O(2)	1.992(4)
Cu(1) - N(8)	1.940(5)	Cu(2) - N(13)	2.051(5)
Cu(1)–O(1)	1.956(4)	Cu(2)–O(1)	2.349(4)
Cu(1) - N(7)	2.057(5)	Cu(1)-Cu(2)	4.035(3)
Cu(1)–O(2)	2.318(4)	Cu(1)– $Cu(2')$	4.056(3)
Cu(2)–N(10)	1.924(5)	Cu(1)-O(1)-Cu(2)	139.00(19)
Cu(2)–N(2)	1.967(5)	Cu(2)–O(2)–Cu(1)	140.42(19)



Fig. 5 Core structural representation of 4 (POVRAY^{\otimes} image). Arrows highlight the Jahn–Teller axes.

pseudo-plane. The ligands have anti arrangements within each pair (unlike 1 and 2). The charge balance in 4 requires that all ligands bear a -1 charge as usual. Cu–Cu distances fall in the range 4.03-4.06 Å, with Cu-O-Cu angles in the range 139.0-140.4°, typical of the square copper grids. The copper square pyramids have three nitrogen atoms and an oxygen atom in the basal plane (Cu(2), N(2), N(10), N(13), O(2'); Cu(1), N(4), N(7), N(8), O(1)) with short Cu-L distances, and a much longer axial contact to a second bridging oxygen atom (Cu(1)-O(2) 2.318(4) Å, Cu(2)–O(1) 2.349(4) Å). This results in a $d_{x^2-v^2}$ magnetic ground state at each copper centre (vide infra), and Cu-O distances around the square core which alternate short (equatorial), long (axial), such that the copper atoms are linked in an orbitally strictly orthogonal fashion. The elongated Jahn-Teller axes are shown in Fig. 5. The same model applies to complex 3.

The non-coordinating nitrogen atoms on the imidazole and pyrimidine groups are arranged on the outer surface of the



Fig. 6 Structural representation of complex cation in **5** (30% probability thermal ellipsoids).

Table 6	Bond d	istances (Å)	and angles (°) for 5	
Mn(1)-O((5)	2.165(4)	Mn(4)–O(3)	2.201(4)
Mn(1)-O((1)	2.168(4)	Mn(4) - N(17)	2.301(5)
Mn(1)-O((6)	2.189(4)	Mn(4) - N(12)	2.311(5)
Mn(1)-N((20)	2.221(5)	Mn(5)-N(22)	2.173(5)
Mn(1)-N((24)	2.230(5)	Mn(5) - N(15)	2.180(5)
Mn(1)-N((1)	2.247(5)	Mn(5)–O(6)	2.189(4)
Mn(2)-N((6)	2.173(5)	Mn(5)–O(4)	2.207(4)
Mn(2)-N((3)	2.183(5)	Mn(5)-N(21)	2.290(5)
Mn(2)-O((1)	2.186(4)	Mn(5) - N(16)	2.321(5)
Mn(2)-O((2)	2.187(4)	Mn(1)-Mn(2)	3.896(3)
Mn(2)-N((4)	2.295(5)	Mn(2)-Mn(3)	3.943(3)
Mn(2)-N((5)	2.330(5)	Mn(3)-Mn(5)	3.941(3)
Mn(3)-O((4)	2.151(4)	Mn(1)-Mn(5)	3.941(2)
Mn(3)-O((2)	2.170(4)	Mn(1)-Mn(4)	3.909(3)
Mn(3)-O((3)	2.177(4)	Mn(3)-Mn(4)	3.991(3)
Mn(3)-N((9)	2.226(5)	Mn(1)-O(1)-Mn(2)	126.92(18)
Mn(3)-N((8)	2.236(5)	Mn(3)-O(2)-Mn(2)	129.66(18)
Mn(3)-N((13)	2.249(5)	Mn(3)-O(3)-Mn(4)	131.51(18)
Mn(4)-N(4)	(11)	2.171(5)	Mn(3)-O(4)-Mn(5)	129.41(18)
Mn(4)-N(4)	(18)	2.183(5)	Mn(1)-O(5)-Mn(4)	127.67(18)
Mn(4)-O((5)	2.191(4)	Mn(1)-O(6)-Mn(5)	128.40(18)

grid, poised appropriately for further coordination. The pyrimidine and imidazole nitrogen atoms (N(5), N(3), N(11) and N(12) and their symmetry related counterparts) form potentially chelating donor pairs.

[Mn₅(pomp–H)₆](ClO₄)₄·CH₃CN·1.5CH₃OH (5). The structure of the homoleptic cation in 5 is shown in Fig. 6, and important bond distances and angles are given in Table 6. The core structural fragment, showing just the metal ions and bridging oxygen atoms, is shown in Fig. 7. Six tetradentate ligands are bound to a trigonal bipyramidal [Mn₅–(μ -O)₆] core cluster, such that there is an exact match between the bonding capacity of the six ligands and the coordination requirements of the five octahedral metal ions. This self-assembled structure has been observed before,^{11,14} and is an alternative to the [2 × 2] heteroleptic Mn₄ structure commonly observed with this class of ligand. Anion and solvent donor competition are regarded as the primary influences in the cluster outcome, with the weakly coordinating perchlorate favouring the formation of the trigonal bipyramidal cluster. Mn–L and Mn–Mn



Fig. 7 Core structural representation of complex 5 (30% probability thermal ellipsoids).



Fig. 8 Structural representation of the complex cation in 6 (POVRAY^{\circ}) image).

distances (3.89–4.00 Å) are similar to those observed in the $[2 \times 2]$ square systems, with Mn–O–Mn angles in the range 126.9–131.6°.

[Mn₅(ioapm–H)₆](ClO₄)₄·7H₂O (6). The structure of the homoleptic pentanuclear Mn₅ cation is shown in Fig. 8, and important bond distances and angles are listed in Table 7. Six ligands are bound in parallel pairs around the Mn₅(μ -O)₆ core, with the ligands opposed (*anti*) in each pair, similar to the arrangement in **5**. The orientation of the cation in Fig. 8 highlights the parallel ligand arrangement. Each ligand adopts a -1 charge, as in **5**, and so the imidazole groups are not deprotonated. The pentanuclear core structure is shown in Fig. 9. Mn–Mn distances fall in the range 3.865–3.950 Å, and Mn–O–Mn angles fall in the range 126.5–128.7°. These compare closely with those found in **5**.

The outer surface of the cluster is comprised of six pyrimidine and six imidazole subunits, which could be involved in further coordination. Potentially chelating N_2

Table 7	Bond	distances	(Å)	and	angles	(°)) for	6
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Mn(1)–N(25)	2.147(4)	Mn(4)–O(5)	2.201(4)
Mn(1) - O(2)	2.182(4)	Mn(4) - N(16)	2.201(5)
Mn(1) - N(11)	2.183(5)	Mn(4)-O(2)	2.211(4)
Mn(1)-O(4)	2.197(4)	Mn(5) - N(18)	2.162(5)
Mn(1) - N(14)	2.392(5)	Mn(5) - N(39)	2.169(5)
Mn(1) - N(28)	2.425(5)	Mn(5)–O(6)	2.172(4)
Mn(2) - N(32)	2.121(5)	Mn(5)-O(3)	2.186(4)
Mn(2)-O(1)	2.135(4)	Mn(5) - N(21)	2.395(5)
Mn(2)-N(4)	2.139(5)	Mn(5) - N(41)	2.423(5)
Mn(2) - O(5)	2.159(4)	Mn(1)-Mn(4)	3.944(3)
Mn(2) - N(7)	2.438(5)	Mn(4)-Mn(5)	3.919(3)
Mn(2) - N(34)	2.460(5)	Mn(4)-Mn(2)	3.921(3)
Mn(3)-O(4)	2.185(4)	Mn(2)-Mn(3)	3.865(3)
Mn(3) - O(1)	2.194(4)	Mn(5)-Mn(3)	3.946(3)
Mn(3)–N(37)	2.200(5)	Mn(1)-Mn(3)	3.950(3)
Mn(3)-N(2)	2.204(5)	Mn(2)-O(1)-Mn(3)	126.46(17)
Mn(3) - N(23)	2.206(5)	Mn(1)-O(2)-Mn(4)	127.73(17)
Mn(3) - O(6)	2.207(4)	Mn(4) - O(3) - Mn(5)	127.50(17)
Mn(4) - O(3)	2.184(4)	Mn(3) - O(4) - Mn(1)	128.69(17)
Mn(4) - N(9)	2.194(5)	Mn(2)-O(5)-Mn(4)	128.18(17)
Mn(4)–N(30)	2.197(5)	Mn(5)–O(6)–Mn(3)	128.61(18)



Fig. 9 Core structural representation of complex 6 (POVRAY^{\circ}) image).

donor pairs from the pyrimidines (*e.g.* N(33)-N(35), N(12)-N(13) and other pairs) are highlighted in Fig. 8.

 $[Mn_9(2pmoap-2H)_6](NO_3)_6\cdot 28H_2O$ (7). The structure of the homoleptic nonanuclear Mn₉ cation in 7 is shown in Fig. 10, and important bond distances and angles are listed in Table 8. The grid comprises a $[Mn_9-(\mu-O)_{12}]$ core encompassed by two groups of three parallel, roughly planar ligands arranged



Fig. 10 Structural representation of the complex cation in 7 $(POVRAY^{\oplus} image)$.

Fable 8 Bond distances (Å	and angles (°) for 7
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Mn(1)–N(8)	2.135(5)	Mn(2)–O(1)	2.222(4)
Mn(1)-N(4)	2.145(5)	Mn(2) - N(12)	2.373(5)
Mn(1)-O(2)	2.162(4)	Mn(3) - N(17)	2.182(5)
Mn(1) - O(1)	2.200(4)	Mn(3)-O(3)	2.199(3)
Mn(1)-N(1)	2.280(5)	Mn(1)-Mn(2)	3.968(3)
Mn(1) - N(11)	2.309(5)	Mn(1)-Mn(2')	3.912(3)
Mn(2) - N(15)	2.145(4)	Mn(2)-Mn(3)	3.924(3)
Mn(2)-O(3)	2.155(4)	Mn(1)-O(1)-Mn2	127.64(17)
Mn(2) - N(6)	2.183(4)	Mn(1)-O(2)-Mn2	127.61(17)
Mn(2) - O(2)	2.197(4)	Mn(2)-O(3)-Mn3	128.65(15)



Fig. 11 Structural representation of the complex cation in 8 (POVRAY $^{\circ}$ image).

above and below the metal pseudo-plane. All metal ions have distorted octahedral geometries. Separations between the aromatic rings on the ligands are around 4 Å, in keeping with the Mn–Mn separations. Mn–N and Mn–O distances are normal for grids in this class and the Mn–Mn distances (ave. 3.921 Å) and Mn–O–Mn angles (ave. 127.8°) are similar to those reported for the parent complex [Mn₉(2poap–2H)₆](ClO₄)₆ involving the equivalent ligand with terminal pyridine groups.¹⁵ The almost flat coordination mode of the ligands brings the non-coordinating pyrimidine nitrogen atom and the NH₂ group at the end of each ligand into a suitable binding mode for secondary metal ion coordination, with N–C–C–N torsional angles of $<7^{\circ}$.

[Cu₉(2pmoap–2H)₂(2pmoap–H)₄](ClO₄)₁₀·13.2H₂O (8). The grid cation structure of 8 is shown in Fig. 11, and important bond distances and angles are given in Table 9. The grid cation has four-fold symmetry, which is unusual among similar copper grids already reported.^{16,45} The overall grid dimensions are typical of M₉ [3 × 3] grids in general with Cu–Cu distances in the range 4.05–4.27 Å, and Cu–O–Cu angles in the range 136.5–142.5°. The core structure is shown in Fig. 12. Each copper ion in the outer eight-membered ring has a distorted, axially elongated octahedral geometry, typical of six-coordinate copper(II). Four Cu(2) short contacts to N(6), N(12),

Table 9 Bond distances (Å) and angles (°) for 8

Cu(1)–N(4)	1.920(4)	Cu(2)–O(1)	2.251(4)
Cu(1) - N(10)	2.020(4)	Cu(2) - O(2)	2.294(4)
Cu(1) - O(1)	2.070(4)	Cu(3)–N(17)	1.936(6)
Cu(1) - N(1)	2.106(5)	Cu(3)–O(3)	2.203(3)
Cu(1) - N(7)	2.248(5)	Cu(1)-Cu(2)	4.075(2)
Cu(1)–O(2)	2.298(4)	Cu(2)-Cu(3)	4.053(2)
Cu(2)–N(15)	1.908(4)	Cu(1)– $Cu(2')$	4.266(2)
Cu(2) - N(6)	1.993(4)	Cu(1) - O(1) - Cu(2)	141.13(18)
Cu(2)–O(3)	2.077(3)	Cu(2) - O(2) - Cu(1)	136.50(18)
Cu(2)–N(12)	2.109(4)	Cu(2)–O(3)–Cu(3)	142.53(17)



Fig. 12 Core structural representation of the complex cation in 8 (POVRAY^{\circ} image). Arrows highlight the Jahn–Teller axes.

N(15), and O(3) define this as the $d_{x^2-y^2}$ orbital plane, with long axial contacts to O(1) and O(2). Cu(1) has short contacts to N(1), N(4), N(10), and O(1), which again define the copper $d_{x^2-y^2}$ orbital. All axial contacts exceed 2.24 Å. Cu(3) has a different axially compressed geometry (d_{z^2} ground state), with long contacts to O(3) atoms, and short bonds to N(17). This has been observed before with other Cu₉ grids in this class, and may result from the way in which the arrangement of the six ligands organizes the central CuN₂O₄ coordination pocket, with four deprotonated oxygen sites.^{16,45} This arrangement sets up an orbitally orthogonal magnetic connection in the outer ring of eight copper ions (vide infra), which is shown in Fig. 12 (arrows) in terms of the way in which the elongated Jahn-Teller copper axes are arranged (90° mutual angles). This is shown clearly in terms of the Cu-Cu distances, where Cu(1)–Cu(2) is 4.075(2) Å, and Cu(1)–Cu(2')is 4.266(2) Å.

The presence of ten perchlorate anions is unusual, but matches the observation made previously with the complex [Cu₉(2poap-H)₆](NO₃)₁₂·9H₂O, which involves mono-deprotonated ligands.¹⁶ As a result the cation charge is +10, which requires that four ligands have a -1 charge and two a -2 charge. The structure reveals four ligand protons (H(21)) in the difference maps, which are located on non-coordinated diazine nitrogen atoms (N(11)). The adjacent CO group (C(12)-O(2)) bridges Cu(1) and Cu(2) with long, axial contacts (2.299 Å, 2.294 Å) respectively, and has a short C-O distance (1.240 Å) consistent with a C=O group, and no formal charge on the oxygen atom. In contrast the C(23)–O(3) CO group is much longer (1.307 Å), signifying a single CO bond and a formal charge of -1 on the oxygen bridging atom. This atom connects Cu(2) and Cu(3) with distances of 2.077 Å and 2.203 Å respectively. This unusual observation is consistent with long and short axial and equatorial contacts typical of sixcoordinate copper(II), where a stronger bridging connection would clearly exist with an equatorial contact, and highlights the subtle effects of charge balance and pH brought to bear in reactions where ligands with ionizable protons compete with

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Fig. 13 Magnetic exchange models for the polynuclear systems.

the polarization effects of metal cations, and their coordination requirements in solvents containing water.

Magnetic properties

In a general case a square (D_{4h}) or distorted square (D_{2d}) [2 × 2] grid can be described by an exchange coupling scheme involving three exchange integrals (*J*1, *J*2, *J*3) according to the appropriate Hamiltonian expression (eqn (1)) (Fig. 13).

$$H_{\text{ex}} = -2J1\{S_2 \cdot S_3 + S_1 \cdot S_4\} - 2J2\{S_1 \cdot S_2 + S_3 \cdot S_4\} - (1)$$

2J3\{S_1 \cdot S_3 + S_2 \cdot S_4\}

In the case of compounds 1–4 J3 is assumed to be zero, because there is no cross-coupling connection, and it is reasonable to assume that J = J1 = J2 because of similar M–O–M angles within each square grid. Using the conventional spin-vector coupling model,^{46,47} eigenvalues of eqn (1) can be obtained analytically for a D_{4h} [2 × 2] grid with J = J1 = J2 and are given by eqn (2),

$$E(S', S_{13}, S_{24}) = -J[S'(S'+1) - S_{13}(S_{13}+1) - S_{24}(S_{24}+1)]$$
(2)

where $S_{13} = S_1 + S_3$; $S_{24} = S_2 + S_4$; $S' = S_1 + S_2 + S_3 + S_4$. This result is valid for arbitrary values of the spin quantum numbers S_i (i = 1, ...4).

Using the addition rules for spin vectors the allowed values for S', and S_{13} , S_{24} can be obtained. By substituting the appropriate energy terms into the modified van Vleck equation (eqn (3); $E_{(S')}$ refers to the energy of each spin state defined by S'), the susceptibility values can be computed as a function of temperature. Simple programming techniques using iterative procedures spanning the required S' values for fitted values of J allow regression of the experimental data against eqn (3), with applied corrections for paramagnetic impurity (fraction ρ), TIP (temperature independent paramagnetism), and a Weiss-like corrective term (θ) to deal with small intermolecular exchange effects. A comprehensive review by Murray *et al.*⁴⁸ deals more generally with the magnetic properties of tetranuclear complexes.

$$\chi_{\rm M} = \frac{N\beta^2 g^2}{3k(T-\theta)} \frac{\Sigma S'(S'+1)(2S'+1)e^{-E(S')/kT}}{\Sigma(2S'+1)e^{-E(S')/kT}} (1-\rho) + \frac{N\beta^2 g^2 S(S+1)\rho}{3kT} + \text{TIP}$$
(3)

The magnetic exchange model for the trigonal bipyramidal structures observed in complexes 5 and 6 (Fig. 13) involves six exchange pathways, which for simplicity may be regarded as equal, based on the structures. The vector coupling scheme for this model may be summarized using the exchange Hamiltonian (eqn (4)), and the subsequent equations,

$$H_{ex} = -J\{S_1 \cdot S_3 + S_4 \cdot S_3 + S_5 \cdot S_3 + S_1 \cdot S_2 + S_5 \cdot S_2 + S_4 \cdot S_2) \quad (4)$$

= $-J\{S_3 \cdot (S_1 + S_4 + S_5) + S_2 \cdot (S_1 + S_4 + S_5)\}$
= $-J\{(S_2 + S_3) \cdot (S_1 + S_4 + S_5)\}$
= $-J(S_{23} \cdot S_{145})$
= $-J/2(S^2 - S_{23}^2 - S_{145}^2)$

where $S_{23} = S_2 + S_3$; $S_{15} = S_1 + S_5$; $S_{145} = S_{15} + S_4$; $S = S_{23} + S_{145}$ ($S = S_n$ (n = 1-5) = 5/2). The eigenvalues are $E(S, S_{23}, S_{145}) = J/2[S(S+1) - S_{23}(S_{23}+1) - S_{145}(S_{145}+1)]$. The allowed values of S, S_{23} and S_{145} , and their appropriate energies, can then be substituted into the van Vleck equation (eqn (3)) in the usual way to create a susceptibility profile as a function of temperature for a particular J value.

The procedure of generating the exchange equation for such large systems, particularly in the case of Mn(II) (S = 5/2), presents a somewhat daunting task, and so the use of generalized software packages which deal with the calculation of the spin state energy spectrum for a cluster, and substitution into the van Vleck equation in one operation, have some distinct advantages. MAGMUN4.1,⁴⁹ an interactive Windows[®] based program, allows direct fitting of molar susceptibility data based on any exchange model (matrix size limits apply) and vector coupling scheme like those described above.

In the case of the $[3 \times 3]$ Mn(II)₉ grids exchange between adjacent Mn(II) centres in the outer ring of eight metals can be assumed to be the same (J1), on the basis of the similarity in Mn-O-Mn bridge angles, and coupling between the central metal ion and its immediate neighbours would perhaps be slightly different (J2). Therefore the full exchange Hamiltonian (eqn (5)) can be reduced to just two exchange integrals (Fig. 13). The difficulties in dealing with such large systems using a vector coupling approach have been discussed in some detail elsewhere,²⁵ and in this case (45 electrons) the immensity of the matrix calculations required (largest matrix dimension 88 900) to generate the total spin state profile for a system with two J values predicates a simpler approach. D_4 spatial symmetry can be applied to such a grid, which reduces the largest matrix dimension to 22 210, but this is still a challenging calculation with a PC, and even with larger computers.⁵⁰ Another approach, described in previous studies,

involves effectively isolating the outer ring from the central metal ion, and treating it as a spin coupled chain,^{23,25} using the Fisher model (eqn (6), (7)),⁵¹ and assuming that coupling to the central Mn(II) ions (*J*2) can be ignored. This was justified on the basis that the grid has a ground state with S = 5/2 spin in an antiferromagnetic low temperature limit (odd number of spin centres), and that divergence from the fully isotropic exchange model would be relatively small for small values of *J*. For the [Cu(II)₉] grid a full analysis of the exchange within an isotropic model can theoretically be achieved using routines within MAGMUN4.1, since the matrix dimensions are considerably smaller.

$$H_{ex} = -J1 \{ S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_4 \cdot S_5 + S_5 \cdot S_6 + S_6 \cdot S_7 + S_7 \cdot S_8 + S_1 \cdot S_8 \} - J2 \{ S_2 \cdot S_9 + S_4 \cdot S_9 + S_6 \cdot S_9 + S_8 \cdot S_9 \}$$
(5)

$$\chi_{\rm Mn} = \frac{Ng^2\beta^2 S(S+1)(1+u)}{3kT(1-u)}$$
(6)

$$u = \operatorname{coth}\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right]$$
(7)

$$\chi_{\rm mol} = [(8\chi_{\rm Mn} + 1.094g^2)/(T - \theta)](1 - \rho) + (1.094g^2/T)\rho + TIP$$
(8)

Variable temperature magnetic data for **1** are shown in Fig. 14 as a plot of molar susceptibility as a function of temperature. The maximum in χ_{mol} at 22 K indicates the presence of intramolecular antiferromagnetic exchange, clearly the result of oxygen bridging between the Mn(II) centres. The data were fitted to eqn (3) using MAGMUN4.1, assuming J = J1 = J2, and J3 = 0, to give g = 2.02, $J = -3.1 \text{ cm}^{-1}$, $\rho = 0.002$, TIP = 0 cm³ mol⁻¹, $10^2R = 1.9$ ($R = [\Sigma(\chi_{obs.} - \chi_{calc.})^2/\Sigma\chi_{obs}^2]^{1/2}$). The solid line in Fig. 14 was calculated with these parameters. The exchange coupling is consistent with other related Mn(II) [2 × 2] grids, with large Mn–O–Mn bridge angles.⁹

Complex 2 has a similar square structure with similar dimensions. The plot of χ_{mol} as a function of temperature is



Fig. 15 Plot of χ_{mol} as a function of temperature for 2 (the solid line is calculated with g = 1.994(1), J = -3.02(1) cm⁻¹, $\rho = 0.034$, TIP = 0 cm³ mol⁻¹ (10²R = 0.65).

shown in Fig. 15. The expected maximum is overshadowed by a rising low temperature feature associated with paramagnetic impurity (*vide infra*), and so appears as a shoulder. The data were fitted to eqn (3) as before to give g = 1.994(1), J =-3.02(1) cm⁻¹, $\rho = 0.034$, TIP = 0 cm³ mol⁻¹, $10^2R = 0.65$. This exchange integral compares closely with that for 1, as would be expected. The solid line in Fig. 15 was calculated with these parameters. A significant, but small, paramagnetic impurity correction was required to get a good data fit for the magnetic sample, and may reasonably be associated with a mononuclear species, or perhaps a small amount of a pentanuclear complex.

The plot of magnetic moment per mole *versus* temperature for **3** is illustrated in Fig. 16, and shows a marked increase from 3.9 μ_B at 300 K to 5.1 μ_B at 2.0 K, typical of a system dominated by intramolecular ferromagnetic coupling. The experimental data were fitted to eqn (3) using the exchange Hamiltonian given in eqn (1), assuming J = J1 = J2 (J3 = 0). Non-linear regression of the experimental data using



Fig. 14 Plot of χ_{mol} as a function of temperature for **1** (the solid line is calculated with g = 2.02, J = -3.1 cm⁻¹, $\rho = 0.002$, TIP = 0 cm³ mol⁻¹ ($10^2R = 1.9$).



Fig. 16 Plot of μ_{mol} as a function of temperature for 3 (the solid line is calculated with g = 2.134(5), J = 7.45(5) cm⁻¹, $\theta = 0$ K, TIP = 240 × 10^{-6} cm³ mol⁻¹, $\rho = 0$ ($10^2R = 0.81$).

MAGMUN4.1 gave an excellent data fit with g = 2.134(5), $J = 7.45(5) \text{ cm}^{-1}$, $\theta = 0 \text{ K}$, TIP = 240 × 10⁻⁶ cm³ mol⁻¹, $\rho = 0$ $(10^2 R = 0.81)$. The solid line in Fig. 16 was calculated with these parameters. The structure of 3 shows that all the connections between the copper centers are strictly orthogonal (vide supra), which would indicate that antiferromagnetic coupling should not occur, in agreement with the observed exchange situation.

Complex 4 shows a very similar plot of magnetic moment per mole versus temperature (ESI[‡] Fig. S1) to 3, dropping very slightly from 3.77 μ_B at 300 K to 3.73 μ_B at 140 K, and then rising to 4.90 $\mu_{\rm B}$ at 2.0 K, typical of a system dominated by intramolecular ferromagnetic coupling. Fitting of the data to eqn (3) using the exchange Hamiltonian given in eqn (1), and assuming J = J1 = J2 (J3 = 0) gave an excellent data fit with g = 2.102(3), J = 7.2(5) cm⁻¹, $\theta = -0.2$ K, TIP = 250 × $10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, $\rho = 0$ ($10^2 R = 0.44$). The solid line in Fig. S1 was calculated with these parameters. Magnetization versus field data (ESI[‡] Fig. S2) show a rise in M to a saturation value of 4.17 $\mu_{\rm B}$ at 5.0 T. Fitting of the data to the appropriate Brillouin function gave g = 2.08 for T = 2 K, and S' = 2, clearly corroborating the presence of intramolecular ferromagnetic coupling.

The variable temperature magnetic data for 5 are shown in Fig. 17 as a plot of moment per mole as a function of temperature. The moment drops from 12.7 $\mu_{\rm B}$ at 300 K to 5.82 $\mu_{\rm B}$ at 2 K. The room temperature value is slightly less than the expected spin only moment for a pentanuclear cluster (13.2 $\mu_{\rm B}$), and the drop in moment as temperature is lowered signifies the presence of intramolecular antiferromagnetic exchange. The low temperature value indicates the presence of one uncoupled Mn(II) centre in the ground state (S = 5/2), and is associated with the odd number of spin centres in the cluster. The magnetic data were fitted to eqn (3) using Hamiltonian (4), within MAGMUN4.1 to give g = 2.012(2), $J = -3.01(2) \text{ cm}^{-1}$, TIP = 0 cm³ mol⁻¹, $\rho = 0$, $10^2 R = 0.44$. The solid line in Fig. 17 was calculated with these parameters. The exchange integral is essentially the same as those observed for 1 and 2, and compares closely with that reported for the

complex $[Mn_5(poap-H)_6](ClO_4)_4$,¹¹ which has a similar pentanuclear structure.

Complex **6** shows an almost identical plot of moment (μ_{mol}) as a function of temperature (ESI[‡] Fig. S3), and a fit using the same model gave g = 2.015, J = -2.65 cm⁻¹, $\rho = 0.0001$, TIP = $0 \text{ cm}^3 \text{ mol}^{-1}$, $10^2 R = 0.44$. The solid line in Fig. S3 was calculated with these parameters. The slight difference in J can be attributed to the different ligands, and the differences in Mn-O-Mn angles.

The variable temperature magnetic data for 7 are shown in Fig. 18 as plot of μ_{mol} as a function of temperature. The room temperature value of 17.0 $\mu_{\rm B}$ is typical of the Mn(II)₉ grids, and the value at 2 K (6.7 $\mu_{\rm B}$) indicates that the ground state is S = 5/2, in keeping with related grids in this class, and results from intragrid antiferromagnetic exchange. The data were fitted to eqn (8) to give g = 2.04, $J1 = -4.8 \text{ cm}^{-1}$, $J2 = 0 \text{ cm}^{-1}$, $\rho = 0.003$, TIP = 0 cm³ mol⁻¹, $10^2 R = 2.1$. The solid line in Fig. 18 was calculated with these parameters. Despite the slightly larger than expected g value the exchange coupling is consistent with other Mn(II)₉ grids,^{23,25} and clearly indicates the isotropic nature of the exchange process, with the obvious primary dependence of the exchange on the Mn-O-Mn angles. However it should be emphasized that this is not a rigorous model, since J2 in unlikely to be zero, but is considered to give a reasonable estimate of J1. In this context it is of interest to note that for the mixed oxidation state grid [Mn(II)₅Mn(III)₄-(2poap)₆](ClO₄)₁₀, which involves Mn(III) centres at the corner positions only, $J1 = -8.3 \text{ cm}^{-1}$, and $J2 = -4.5 \text{ cm}^{-1}$ (Fig. 13).⁵⁰ In this case a single fully isotropic calculation (S'/E; based on one set of J1 and J2 parameters) can be completed in about 2 days on a fast PC with 2 GB of RAM. The J2 (Mn(II)–Mn(II)) value is comparable with coupling constants obtained using the chain model (vide supra), and the Mn(II)-Mn(III) exchange is somewhat stronger. This can reasonably be associated with the minor changes in grid dimensions, for example increased Mn(II)-O-Mn(III) bridge angles, which occur on oxidation.

Variable temperature magnetic data for 8 are shown in Fig. 19 as a plot of μ_{mol} as a function of temperature. The

18 16 A A

12

10

8

6

0

50



14 μmol (μB)



100

150

Temp (K)

200

250

300

350





Fig. 19 Plot of μ_{mol} as a function of temperature for **8** (the solid line is calculated with g = 2.28, J2 = -35 cm⁻¹, J1 = 0.35 cm⁻¹ and TIP = 800×10^{-6} cm³ mol⁻¹. Inset: Plot of *M*/*H* at 2 K for **8**. The solid line is calculated for g = 2.2 and S' = 7/2 (2 K) using the appropriate Brillouin function. The dashed line is calculated for g = 2.2, $S' = 7 \times 1/2$ (2 K).

moment drops from 6.0 $\mu_{\rm B}$ at 300 K to a minimum value of 5.4 μ_B at 30 K, followed by a rise to 7.0 μ_B at 2 K. The steady, but small, drop in moment signifies an antiferromagnetic exchange component, while the sharp rise at low temperature is indicative of a ferromagnetic exchange component also. Modeling the exchange in 8, and related grids, using the vector coupling approach described above (based on eqn (5)), in which two J values are evaluated independently using an iterative regression process, is a challenge regardless of any matrix dimensionality constraints. However total spin state/ energy (S'/E) profiles can be calculated easily for fixed values of J1 and J2 for a Cu(II)₉ grid with nine $S = \frac{1}{2}$ spin centres. This can be done using MAGMUN4.1 and set up as a ratio J1/J2, such that for an arbitrarily chosen ratio fitting of the magnetic data for a grid with two J values can be achieved. Such an approach is not strictly rigorous, but can be used to usefully interpret the exchange picture, when an idea of what the exchange should be is revealed from the structure.

The grid in 8, like other copper grids in this group, has nine highly distorted six-coordinate copper(II) ions. The four-fold symmetry apparent in 8 is helpful, in that it simplifies the interpretation of the magnetic connectivity within the grid. The corner copper centres (Cu(1)) have axially elongated geometries with the long axis pointing to O(2), defining their magnetic ground states as $d_{x^2-v^2}$. The side copper centres (Cu(2)) have similar geometries, with the long axis pointing to both O(1) and O(2). The short bonds in the equatorial plane include the connection to O(1) for Cu(1) and O(3) for Cu(2). Such an arrangement therefore shows that the Cu(1)-O(2), Cu(2)–O(1) and Cu(2)–O(2) connections are orthogonal, while the Cu(2)-O(3) connection is not. This effectively isolates Cu(2), and its symmetry related counterparts, from the Cu(1)centres in terms of any antiferromagnetic exchange, but would allow for possible ferromagnetic coupling in the outer Cu₈ ring. One could argue that the different connections between Cu(2) and Cu(1) through O(1) and O(2) (Cu(1)–Cu(2) 4.075 Å,

Table 10 Magnetic analysis for compounds 1-8

Compound	g	J/cm^{-1}	Ground state spin (S')
 (Mn₄ square grid) (Mn₄ square grid) (Cu₄ square grid) (Cu₄ square grid) (Mn₅ trigonal bipyramid) (Mn₉ square grid) (Cu₉ square grid) 	2.02 1.994 2.134 2.102 2.012 2.015 2.04 2.28	$ \begin{array}{r} -3.1 \\ -3.02 \\ 7.45 \\ 7.2 \\ -3.01 \\ -2.65 \\ -4.8 (J1) \\ 0.35 (J1), -35 (J2) \end{array} $	0 0 2 2.5 2.5 2.5 3.5

Cu(1)'-Cu(2) 4.266 Å) could lead to different exchange coupling (both ferromagnetic). However, given the difficulty of fitting magnetic data in general for ferromagnetically coupled systems, and the fact that the difference is likely to be small, a single J value model (Fig. 13) for the outer Cu₈ ring has been chosen.

The central copper, Cu(3), is unusual in that it has an axially compressed six-coordinate geometry, with long contacts to O(3) atoms. This defines its magnetic ground state as d_{z^2} . Since this orbital nominally has some electron density in the *xy* plane (the O(3) plane), then it is reasonable to assume that antiferromagnetic exchange could occur between Cu(3) and the Cu(2) centres. However it would not be expected to be large because of the limited electron density in this spatial region. Therefore, despite the large Cu(3)–O(3)–Cu(2) angles (142.3°), which would otherwise have led to quite strong exchange between copper centres, a relatively small negative exchange coupling would be expected.

Spin state/energy profiles were set up within MAGMUN4.1 for -J2/J1 ratios in the range 10 to 200, and the magnetic data simulated with input for g, the J2/J1 ratio and TIP. The solid line in Fig. 19 was obtained after many trial comparisons with g = 2.28, J2/J1 = -35, and TIP = 800 × 10⁻⁶ cm³ mol⁻¹ for the model in which J2/J1 = 100. This leads to J2 = -35 cm⁻¹ and J1 = 0.35 cm⁻¹. Given the structural features, and the orbital connectivity within the grid, these values are eminently reasonable estimates of the exchange coupling. On the assumption that the exchange situation would be dominated by J1 in the low temperature limit, a magnetization versus field study was carried out at 2 K. Fig. 19 (inset) shows a smooth rise in M with increasing field up to a plateau value of 7.5 $\mu_{\rm B}$ at 5 T (50 000 Oe). The solid line is calculated for g = 2.2 and S' = 7/2 (2 K) using the appropriate Brillouin function. The dashed line is calculated for g = 2.2, $S' = 7 \times 1/2$ (2 K). It is therefore clear that the M/H profile is more typical of a grouped set of copper(II) centres, than isolated ones, supporting not only the coupling scheme, which should result in a 7/2 ground state, but also the ferromagnetic interaction in the outer Cu_8 ring. A closer match in the *M/H* profiles might possibly be expected at a lower temperature.

Results for the magnetic analysis for compounds 1-8 are summarized in Table 10.

Conclusions

A series of new polynuclear square [2 \times 2] and [3 \times 3] grids and trigonal-bipyramidal clusters (Mn₅) involving some new

picolinic hydrazone ligands are reported, with copper and manganese examples. Complexes **4**, **6–8** have a large number of extra nitrogen donor sites on the outer surfaces of the grids and clusters, providing the potential for further coordination, an area which is under current investigation. The current structures reveal orthogonal magnetic connections in all copper cases, leading to intramolecular exchange dominated by ferromagnetic components, while for the manganese systems antiferromagnetic exchange prevails. Magnetic data have been rationalized successfully on the basis of structural evidence. The Cu₄ and Cu₉ grid structures clearly show a 90° alternation of the Jahn–Teller axes, leading to orthogonal bridging connections, and in the case of the Cu₉ grid an unusual bridging of carbonyl (C=O) groups between the copper centres through long axial Cu–O connections.

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References

- 1 J. Rojo, F. J. Romero-Salguero, J.-M. Lehn, G. Baum and D. Fenske, *Eur. J. Inorg. Chem.*, 1999, 1421.
- 2 E. Breuning, M. Ruben, J.-M. Lehn, F. Renz, Y. Garcia, V. Ksenofontov, P. Gütlich, E. Wegelius and K. Rissanen, *Angew. Chem., Int. Ed.*, 2000, **39**, 2504.
- 3 E. Breuning, U. Ziener, J.-M. Lehn, E. Wegelius and K. Rissanen, *Eur. J. Inorg. Chem.*, 2001, 1515.
- 4 P. N. W. Baxter, J.-M. Lehn, J. Fischer and M.-T. Youinou, Angew. Chem., Int. Ed. Engl., 1994, 33, 2284.
- 5 A. M. Garcia, F. J. Romero-Salguero, D. M. Bassani, J.-M. Lehn, G. Baum and D. Fenske, *Chem.—Eur. J.*, 1999, **6**, 1803.
- 6 S. T. Onions, A. M. Frankin, P. N. Horton, M. B. Hursthouse and C. J. Matthews, *Chem. Commun.*, 2003, 2864.
- 7 M. Barboiu, G. Vaughan, R. Graff and J.-M. Lehn, J. Am. Chem. Soc., 2003, 125, 10257.
- 8 C. J. Matthews, K. Avery, Z. Xu, L. K. Thompson, L. Zhao, D. O. Miller, K. Biradha, K. Poirier, M. J. Zaworotko, C. Wilson, A. E. Goeta and J. A. K. Howard, *Inorg. Chem.*, 1999, **38**, 5266.
- 9 L. K. Thompson, C. J. Matthews, L. Zhao, Z. Xu, D. O. Miller, C. Wilson, M. A. Leech, J. A. K. Howard, S. L. Heath, A. G. Whittaker and R. E. P. Winpenny, *J. Solid State Chem.*, 2001, **159**, 308.
- 10 Z. Xu, L. K. Thompson, C. J. Matthews, D. O. Miller, A. E. Goeta and J. A. K. Howard, *Inorg. Chem.*, 2001, **40**, 2446.
- 11 C. J. Matthews, L. K. Thompson, S. R. Parsons, Z. Xu, D. O. Miller and S. L. Heath, *Inorg. Chem.*, 2001, 40, 4448.
- 12 Z. Xu, L. K. Thompson and D. O. Miller, J. Chem. Soc., Dalton Trans., 2002, 2462.
- 13 H. Grove, T. J. Kelly, L. K. Thompson, L. Zhao, Z. Xu, T. S. M. Abedin, D. O. Miller, A. E. Goeta, C. Wilson and J. A. K. Howard, *Inorg. Chem.*, 2004, 43, 4278.
- 14 C. J. Matthews, Z. Xu, S. K. Mandal, L. K. Thompson, K. Biradha, K. Poirier and M. J. Zaworotko, *Chem. Commun.*, 1999, 347.
- 15 L. Zhao, C. J. Matthews, L. K. Thompson and S. L. Heath, *Chem. Commun.*, 2000, 265.
- 16 L. Zhao, Z. Xu, L. K. Thompson, S. L. Heath, D. O. Miller and M. Ohba, *Angew. Chem., Int. Ed.*, 2000, **39**, 3114.
- 17 O. Waldmann, R. Koch, S. Schromm, P. Müller, L. Zhao and L. K. Thompson, *Chem. Phys. Lett.*, 2000, **332**, 73.
- 18 O. Waldmann, L. Zhao and L. K. Thompson, Phys. Rev. Lett., 2002, 88, 066401.
- 19 L. Zhao, Z. Xu, L. K. Thompson and D. O. Miller, *Polyhedron*, 2001, **20**, 1359.

- 20 L. K. Thompson, L. Zhao, Z. Xu, D. O. Miller and W. M. Reiff, *Inorg. Chem.*, 2003, 42, 128.
- 21 Z. Xu, L. K. Thompson and D. O. Miller, *Polyhedron*, 2002, 21, 1715.
- 22 L. K. Thompson, Coord. Chem. Rev., 2002, 233-234, 193.
- 23 L. Zhao, Z. Xu, H. Grove, V. A. Milway, L. N. Dawe, T. S. M. Abedin, L. K. Thompson, T. L. Kelly, R. G. Harvey, D. O. Miller, L. Weeks, J. G. Shapter and K. J. Pope, *Inorg. Chem.*, 2004, 43, 3812.
- 24 L. K. Thompson, T. L. Kelly, L. N. Dawe, H. Grove, M. T. Lemaire, J. A. K. Howard, E. C. Spencer, C. J. Matthews, S. T. Onions, S. J. Coles, P. N. Horton, M. B. Hursthouse and M. E. Light, *Inorg. Chem.*, 2004, **43**, 7605.
- 25 L. K. Thompson, O. Waldmann and Z. Xu, Coord. Chem. Rev., 2005, 249, 2677.
- 26 V. A. Milway, S. M. T. Abedin, V. Niel, T. L. Kelly, L. N. Dawe, S. K. Dey, D. W. Thompson, D. O. Miller, M. S. Alam, P. Müller and L. K. Thompson, *Dalton Trans.*, 2006, DOI: 10.1039/b515801j.
- 27 E. Pardo, K. Bernot, M. Julve, F. Lloret, J. Cano, R. Ruiz-Garcia, F. S. Delgado, C. Ruiz-Pérez, X. Ottenwaelder and Y. Journaux, *Inorg. Chem.*, 2004, 43, 2768.
- 28 E. Pardo, I. Morales-Osorio, M. Julve, F. Lloret, J. Cano, R. Ruiz-Garcia, J. Pasán, C. Ruiz-Pérez, X. Ottenwaelder and Y. Journaux, *Inorg. Chem.*, 2004, 43, 7594.
- 29 G. Black, E. Depp and B. B. Corson, J. Org. Chem., 1949, 14, 14.
- 30 H. B. Amin and R. Taylor, J. Chem. Soc., Perkin Trans. 2, 1979, 624.
- 31 (a) SHELX97: G. M. Sheldrick, University of Göttingen, 1997; (b) SIR97: A. Altomare, M. Cascarano, C. Giacovazzo and Z. Guagliardi, J. Appl. Crystallogr., 1993, 26, 343.
- 32 DIRDIF94: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.
- 33 D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography*, vol. IV, The Kynoch Press, Birmingham, England, 1974, Table 2.2 A.
- 34 J. A. Ibers and W. C. Hamilton, Acta Crystallogr., 1964, 17, 781.
- 35 D. C. Creagh and W. J. McAuley, *International Tables for Crystallography*, vol. C, ed. A. J. C. Wilson, Kluwer Academic Publishers, Boston, 1992, Table 4.2.6.8, pp. 219–222.
- 36 teXsan for Windows: Crystal Structure Analysis Package, Molecular Structure Corporation, 1997.
- 37 SIR 92: A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori and M. Camalli, J. Appl. Crystallogr., 1994, 27, 435.
- 38 DIRDIF99: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, The DIRDIF-99 program system, Technical Report of the Crystallography, University of Nijmegen, The Netherlands, 1999.
- 39 CrystalStructure 3.7.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC, 9009, New Trails Dr., The Woodlands, TX 77381, USA, 2000–2005.
- 40 CRYSTALS Issue 10: D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Betteridge, Chemical Crystallography Laboratory, Oxford, UK, 1996.
- 41 J. Cosier and A. M. Glazer, J. Appl. Crystallogr., 1986, 19, 105.
- 42 SMART, Data Collection Software, Ver. 4.050, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- 43 SAINT, Data Reduction Software, Version 4.050, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1996.
- 44 G. M. Sheldrick, SHELXTL 5.04/VMS, An integrated system for solving, refining and displaying crystal structures from diffraction data, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1995.
- 45 V. A. Milway, V. Niel, T. S. M. Abedin, Z. Xu, L. K. Thompson, H. Grove, D. O. Miller and S. R. Parsons, *Inorg. Chem.*, 2004, 43, 1874.
- 46 K. Kambe, J. Phys. Soc. Jpn., 1950, 5, 48.
- 47 R. L. Martin, in *New Pathways in Inorganic Chemistry*, ed. E. A. V. Ebsworth, A. G. Maddock and A. G. Sharpe, Cambridge University Press, Cambridge, 1978, ch. 9.
- 48 K. S. Murray, Adv. Inorg. Chem., 1995, 43, 261-356.

49 MAGMUN4.1/OW01.exe is available as a combined package free of charge from the authors (http://www.ucs.mun.ca/~lthomp/ magmun). 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.

- 50 O. Waldmann, H. U. Güdel, T. L. Kelly and L. K. Thompson, *Inorg. Chem.*, in press.
- 51 M. E. Fisher, Am. J. Phys., 1964, 32, 343.



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