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Synthesis, Structure, and Magnetism of a Novel Alkoxide Bridged Nonacopper(II) (Cu_9O_{12}) [3 × 3] Square Grid Generated by a Strict Self-Assembly Process**

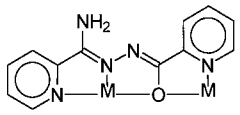
Liang Zhao, Zhiqiang Xu, Laurence K. Thompson,* Sarah L. Heath, David O. Miller, and Masaaki Ohba

Single ligands with repeating linear arrays of coordination pockets have the potential to create gridlike arrangements of metal centers by self-assembly processes. Linear polytopic ligands of this sort with pyridazine and pyrimidine bridging subunits have produced essentially flat [2 × 2] homotetranuclear grids with Cu^{I} and Co^{II} salts,[1, 2] and a flat [3 × 3] nonanuclear grid with Ag^{I} salts.[3]

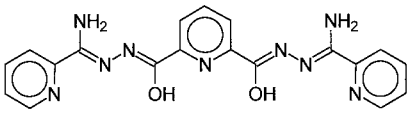
The Co^{II} complex has been shown to exhibit antiferromagnetic coupling within the cluster, despite long distances of separation between the metal centers (6.5 Å).[4] The ordering of paramagnetic metal ions in gridlike arrays presents the possibility of extended spin communication within a lattice of closely spaced metal ion centers, generated from a single preprogrammed ligand. The nuclearity of these clusters is clearly based on the polytopic nature of the ligand and the ability of the metal to read and interpret the coordination options presented by the ligand in the most efficient way, depending on its own coordination algorithm.[3]

Tetradentate ligands (e.g. poap) built on a flexible diazine (N–N) backbone have been shown to self-assemble Mn^{II}, Co^{II}, Ni^{II}, and Cu^{II} centers into square, tetranuclear clusters, with just alkoxide bridges between the metal ions.[5] These systems have close metal – metal spacings (≈4 Å) and display dominant antiferromagnetic intramolecular exchange, except in the copper(II) cases where ferromagnetic coupling, associated with orthogonal magnetic connections, prevails. Spin-coupled, homoleptic trigonal-bipyramidal alkoxo-bridged Mn^{II}_5[6] and Co^{II}_5[7] clusters have also been produced, in which there is an exact match between the ligand donor pocket groupings and the coordination requirements of the six-coordinate metal centers.

Extension of poap using a 2,6-disubstituted pyridine central fragment generates the ligand 2poap, which has an approximately linear array of coordination pockets that produce five-membered chelate rings on coordination. The ligand 2poap behaves as a nonadentate ligand in reaction with



poap



2poap

copper(II) acetate, producing a linear trinuclear complex **1**, in which a central copper center is bound to the other copper centers through N–N diazine single bond bridges.[7] However with copper(II) nitrate and copper(II) sulfate 2poap behaves as a heptadentate ligand, providing donors for nine metal coordination sites through oxygen bridging, and nonanuclear complexes are formed in both cases. Reaction of 2poap with $Cu(NO_3)_2 \cdot 3H_2O$ in water produced a brown crystalline product **2** (71% yield), suitable for structural analysis.[8] A similar reaction with $CuSO_4 \cdot 5H_2O$ produced the dark green crystalline product **3** (75% yield).[7]

$[Cu_3(2poap\text{-}2H)CH_3COO)_4] \cdot 3H_2O$ **1**

$[Cu_9(2poap\text{-}H)_6](NO_3)_{12} \cdot 9H_2O$ **2**

$[Cu_9(2poap\text{-}H)_6](SO_4)_6 \cdot 18H_2O$ **3**

The structure of **2** (Figure 1) involves a novel [3 × 3] grid of nine pseudo-octahedral Cu^{II} centers coordinated by two groups of three roughly parallel ligands arranged above and below the metal pseudo-plane, with the metals bridged just by alkoxide oxygen atoms. The ligands are roughly eclipsed, but have a slight stagger. The parallel grouping of the ligands is associated with π interactions between the aromatic rings (ring separations ≈3.6 – 4.2 Å). Three different pseudo-octahedral copper(II) centers are found; the central Cu atom has a

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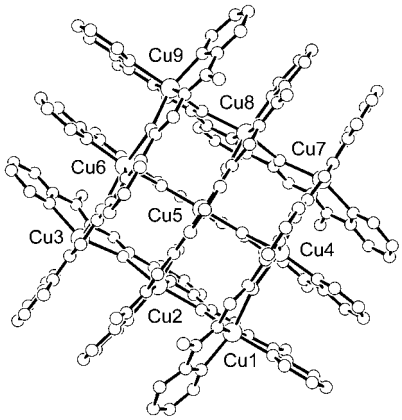

Figure 1. Structural representation of the cation $[Cu_9(2poap\text{-}H)_6]^{12+}$ in **2** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu5-N14 1.941(10), Cu5-N41 1.912(11), Cu5-O3 2.163(7), Cu5-O4 2.197(7), Cu5-O9 2.210(10), Cu5-O10 2.199(9), Cu1-Cu2 4.148(8), Cu2-Cu3 4.198(7), Cu3-Cu6 4.169(8), Cu6-Cu9 4.085(9), Cu9-Cu8 4.2187, Cu8-Cu7 4.106(7), Cu7-Cu4 4.116(8), Cu4-Cu1 4.227(8), Cu2-Cu5 4.069(7), Cu6-Cu5 4.048(8), Cu8-Cu5 4.065(8), Cu4-Cu5 4.032(6); Cu-O-Cu 136.5–143.6.

trans-N_2O_4 donor arrangement, the corner Cu centers have *cis*-N_4O_2 donor arrangements, and the side Cu centers have *mer*-N_3O_3 donor arrangements.

The Cu_9O_{12} core (Figure 2) consists of four fused Cu_4O_4 square subunits, each of which has a puckered bridging arrangement with an alternation of oxygen atoms above and

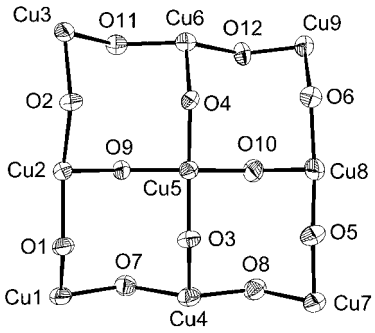

Figure 2. Structural representation of the pseudo-square Cu_9O_{12} core in $[Cu_9(2poap\text{-}H)_6]^{12+}$.

below the Cu_4 pseudo-plane in a boatlike conformation. Each subunit has a similar structure to known square, tetranuclear copper(II) complexes of poap.[5] Adjacent copper–copper separations fall in the range 4.032–4.227 Å, which generates a roughly square grid with overall core dimensions of 8.2 × 8.3 Å. Cu-O-Cu angles fall in the range 136.5–143.6° and Cu–O and Cu–N distances fall in the ranges 2.061–2.314 Å and 1.858–2.231 Å, respectively. Similar nonanuclear grids of octahedral Mn^{II} centers can also be produced with 2poap and related ligands (e.g. $[Mn_9(2poap\text{-}2H)_6](ClO_4)_6 \cdot 18H_2O$).[9] The presence of the acetate anion in **1** causes the ligand to lose two protons, and the acetates also act as ligands leading to the trinuclear structure.[7] However in **2** and **3** the ligands appear to lose just one proton each, and are involved in oxygen bridging only. The formation of the homoleptic grid structure in **2** is a clear consequence of the exact matching of the nine coordination pockets to the coordination requirements of the nine metal centers. However, the formation of a complex with nine pseudo-octahedral copper(II) centers is rather unusual, since copper(II) generally prefers to adopt square or square-pyramidal geometries. This leads to a complicated situation with regard to the magnetic ground states of each copper center. The central copper atom (Cu5) has a compressed tetragonal geometry (d_{z^2} ground state), with four long equatorial Cu–O contacts to O3, O4, O9, and O10 (2.163–2.210 Å), and two short Cu–N bonds to N14 and N41 (1.941(10) and 1.912(11) Å, respectively). Cu3 and Cu7 have similar distorted geometries, while the other copper centers are best described as elongated tetragonal ($d_{x^2-y^2}$ ground state). However in all cases connections between copper centers through the alkoxide bridges appear to be "orthogonal", based on the ground-state assessment.

Variable-temperature magnetic data[10] were obtained for **2** in a 0.1 T field in the temperature range 2–300 K. The magnetic moment (per mole) drops slightly from 6.3 μ_B at 300 K to 5.5 μ_B at 30 K, followed by a rise below this temperature to a value of 6.9 μ_B at 2.0 K (Figure 3). The room-temperature value is consistent with the presence of

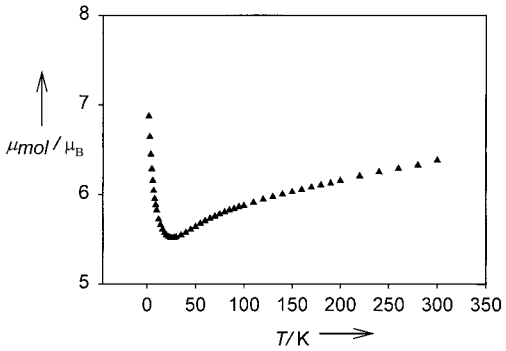

Figure 3. Variable-temperature magnetism for **2** plotted as magnetic moment (μ_B) per mole versus temperature (0.1 T field).

nine Cu^{II} centers, and the small drop towards 30 K suggests the possible presence of a weak antiferromagnetic exchange interaction within the cluster. The rise in μ_B at temperatures below 30 K is associated with a ferromagnetic component, which appears to be dominating the exchange process at low temperatures. Interestingly, for the Cu_4 complexes of poap, which involve orthogonal alkoxide linkages between all copper centers, ferromagnetic coupling dominates the exchange situation.[5] The analogous complex **3** reveals an almost identical profile of magnetic moment versus temperature, indicating a comparable [3 × 3] grid structure.[7]

A preliminary fit of the magnetic susceptibility data was carried out to an exchange expression for an assembly of nine $S = 1/2$ centers with a single exchange integral (J) between each spin center, according to a Hamiltonian expression ($H = -2J(\Sigma S_i S_j)$) based on the Cu_9O_{12} grid structure (Figure 2). Eigenvalues and energy levels were evaluated and substituted into the van Vleck equation. A reasonable data fit was obtained for $g = 2.23(2)$, $J = 3.5(2)$ cm^{-1}, corrected for 0.5% paramagnetic impurity, with a Weiss-like temperature correction (θ) of −9.6 K (TIP = 800×10^{-6} cm^{3}mol^{-1}). The dominant exchange term is ferromagnetic and comparable with

that for the Cu_4 complexes,[5] thus supporting the orbital ground state analysis. The requirement of a significant negative Weiss-like (θ) correction indicates the presence of an antiferromagnetic term as well, which is likely to be intramolecular in nature (no viable intermolecular pathways were identified in the structure).

A magnetization study (Figure 4) at 2 K in the range 0–5 T shows that the system approaches saturation at 5.0 T, but appears not to be fully saturated. The magnetization data compare closely with the theoretical line for an $S = 7/2$ system

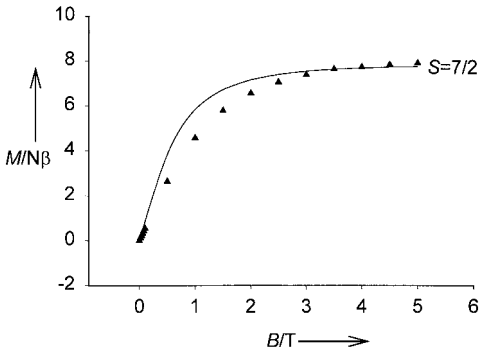

Figure 4. Magnetization data at 2.0 K for **2** in Nβ units (0–5.0 T). ▲ (**2**); theoretical line ($S = 7/2$, $g = 2.23$).

($g = 2.23$), although the lower portion of the profile does not match the theoretical data well. This result confirms the dominant ferromagnetic behavior of **2** at low temperature, but indicates that the magnetic ground state situation within the cluster is complicated, and involves a weak antiferromagnetic component, in agreement with the previous analysis. Significantly, at 30 K a magnetization versus field profile (0–5.0 T) is a straight line, with a constant magnetic moment of 5.5 μ_B. This clearly corresponds to a Curie-like situation, but may reflect a small intramolecular antiferromagnetic exchange component. Compound **3** exhibits an almost identical magnetization profile at 2 K. Further magnetic studies on these complicated systems are underway, including single-crystal measurements.

This unique self-assembly of nine pseudo-octahedral copper(II) centers into an oxygen-bridged, square [3 × 3] grid is, to our knowledge, the first strict self-assembly process to achieve this in copper(II) coordination chemistry. The combined coordination algorithm of the assembly of nine pseudo-octahedral metal centers (fifty-four coordination positions) is exactly matched by the aligned arrangement of the two sets of three "parallel" ligands above and below the metal grid pseudo-plane (fifty-four donor positions). The oxygen-bridging arrangement fixes the metals in an almost completely orthogonal arrangement in the closely spaced grid leading to a complex spin-coupled structure dominated by ferromagnetic exchange. The synthetic strategy has more general application, and antiferromagnetically coupled Mn^{II}[9] and Ni^{II}[7] analogues have also been prepared.

The generation of predetermined, large gridlike architectures by self-assembly processes, using preprogrammed ligands, provides a unique opportunity to produce complex nanostructures with the potential for information storage. The recent report of a hexadecanuclear [4 × 4]-Pb^{II}_{16} pyrimidine-bridged grid complex, based on spectroscopic evidence, indicates the viability of such an approach for larger grids.[11] Efforts are currently underway in our laboratory to extend ligands like 2poap with additional five-membered chelate ring compartments to produce [4 × 4] and [5 × 5] grids, and even higher homologues.

Experimental Section

2-poap: The ligand 2poap was prepared in high yield (85%) by reaction of the hydrazide of 2,6-pyridine dicarboxylic acid with the methyl ester of imino-picolinic acid, generated in situ from the reaction of 2-cyanopyridine with sodium methoxide in methanol.

2: 2poap (0.40 g, 1.0 mmol) was added to a hot solution of $Cu(NO_3)_2 \cdot 3H_2O$ (1.44 g, 6.00 mmol) in water (15 mL) and the mixture was stirred for 30 min, filtered, and the yellowish solution allowed to stand at room temperature for several days, during which time brown crystals suitable for X-ray structural determination were deposited (Yield 0.65 g, 71%). Elemental analysis calcd for $[Cu_9(C_{19}H_{16}N_9O_2)_6](NO_3)_{12} \cdot 9H_2O$ (%): C 35.21, H 2.96, N 23.76; found (vacuum dried sample): C 35.33, H 3.05, N 23.31 (repeated on X-ray sample; found: C 35.46, H 2.83, N 23.31); IR (Nujol mull, cm^{-1}): $\tilde{\nu} = 3450$ (sh; ν_{NH/H_2O}), 3293 (ν_{NH/H_2O}); 1670 (ν_{CN}); UV/Vis (Nujol mull): 810 nm; $\mu_{(RT)} = 6.3$ μ_B (mol); 2.1 μ_B (Cu).

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[8] Crystal data for $C_{114}H_{134}Cu_9N_{60}O_{52}$ **2;** $M_r = 3748.67$, triclinic, space group $P\bar{1}$, $a = 18.698(10)$, $b = 18.902(5)$, $c = 27.602(8)$ Å, $\alpha = 95.89(2)$, $\beta = 102.41(3)$, $\gamma = 117.62(2)^\circ$, $V = 8208(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.517$ g cm^{-3}, $T = 150(2)$ K, brown plate ($0.25 \times 0.15 \times 0.01$ mm), $\mu = 1.240$ mm^{-1}. Data were collected with a Bruker Smart three-circle diffractometer, equipped with a CCD area detector using graphite-monochromated $Mo_{K\alpha}$ X-radiation ($\lambda = 0.71073$ Å), and with an Oxford Cryostream low temperature device. SHELXTL (G. M. Sheldrick, SHELXTL 5.10/NT, An integrated system for solving, refining and displaying crystal structures from diffraction data. Siemens Analytical X-ray Instruments Inc.: Madison, WI) was used for the structure solution and the refinement based on F^2. The data were very weak, and only the non-hydrogen atoms of the cation were refined anisotropically. Hydrogen atoms were fixed at idealized positions with isotropic U values set 1.2 times U (atom connected). The nitrate anions that were located were very disordered and were modeled isotropically each with its own free variable. A total of just 5.6 nitrates were found from the final cycle of least squares. Attempts to use a SUMP command to constrain the total nitrate occupancy resulted in unstable refinements. The largest features in the final difference maps occur near to waters of crystallization, but no sensible models could be found. Some of these peaks may account for the discrepancy between the expected number of nitrates from the elemental analysis (12) and the six located with the current structural data. The main cationic fragment is however clearly defined. For 1913 parameters $R1 = 0.1043$, $wR2 = 0.2903$, for 9414 unique reflections

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with $I > 2.0\sigma I$) (28848 independent reflections, $R_{int} = 0.0922$), for 2θ in the range 1.56 to 50.0° ($GOF = 0.900$). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140825. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[10] Variable temperature magnetic measurements were carried out in the range 2–300 K using a SQUID magnetometer (Quantum Design MPMS5S) in fields of 0.1–5.0 T. Background corrections for the sample holder and diamagnetic portions of the complex were applied.

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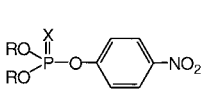
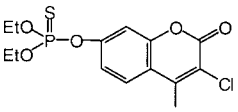
Highly Efficient Degradation of Thiophosphate Pesticides Catalyzed by Platinum and Palladium Aryl Oxime Metallacycles**

Gregory M. Kazankov, Victoria S. Sergeeva, Elena N. Efremenko, Larissa Alexandrova, Sergey D. Varfolomeev, and Alexander D. Ryabov*

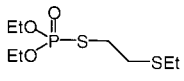
Thiophosphoric acid esters such as **1** and **4**, pesticides with an annual world production of hundred thousands of tons, are strong pollutants and their accumulation in the environment is a recognized ecological threat.[1] Some neurotoxins and V-type chemical warfare agents are chemically similar, and a potential danger is emerging from their aging stockpiles.[2]



1 (R = Et, Z = S; parathion)
2 (R = Me, Z = S; methyl parathion)
3 (R = Et, Z = O; paraoxon)



4 (coumaphos)



5 (demeton-S)

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Needless to say, creation of "green" catalytic processes for degradation of thiophosphoric acid esters is an urgent task of contemporary chemical technology and biotechnology. Significant progress has recently been made by the use of organophosphate hydrolases (OPH), a class of metal-dependent enzymes whose vital virtue is in the detoxification of organophosphoric species by reaction (1).[3] These enzymes

$$RR'P(=X)Z + H_2O \xrightarrow{OPH} RR'P(=X)OH + HZ \quad (1)$$

are superior to their low molecular weight analogues in terms of catalyst specificity and activity, but the latter are often also efficient, more stable, and less subject to inactivation. Chemical catalysts with the features of enzyme active sites are believed to be particularly promising.[4]

Recently, we introduced orthometalated complexes of Pd^{II} and Pt^{II} as mimetics of metal-dependent esterases. The catalysts display regio- and stereoselectivity as well as reasonable rate accelerations at neutral pH values.[5] However, the rates of hydrolysis of amino acid esters were not very striking, although the catalysts had features typical of metallohydrolases.[5b] It could be argued that a square-planar metal configuration, which is not reported in enzymes, is less favorable for catalysis, and that Pd^{II} and Pt^{II} are "soft" acids which require "softer" bases for efficient catalysis. The thiophosphoric acid esters **1**–**5** are examples of such bases, and therefore metallacycles **6** and **7** (dmso = dimethyl sulfoxide, py = pyridine) have been tested as catalysts for the hydrolysis of pesticides **1**–**5**. Here we show that **6** and **7**[6] as well as the Pt^{IV} complex **8**[6] are excellent catalysts for the degradation of thiophosphate pesticides and neurotoxins.

Parathion (**1**) is spontaneously hydrolyzed at pH 8.5 at an immeasurably slow rate. Addition of a catalytic amount of the Pt^{II} complex **6a** enhances the rate of hydrolysis of **1** (by reaction (1)), which proceeds to completion and follows first-order kinetics.[7] Methyl parathion (**2**) and coumaphos (**4**) behave similarly (Figure 1). No intercept is observed in the

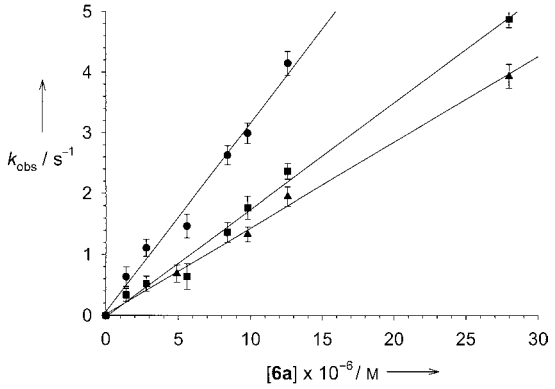

Figure 1. Dependencies of k_{obs} for the hydrolysis of parathion (**1**, ●), methyl parathion (**2**, ■), and coumaphos (**4**, ▲) catalyzed by Pt^{II} complex **6a** at different concentrations. Conditions: [ester] = 1×10^{-4} M, 0.005 M $Na_2B_4O_7$/NaOH buffer, pH 8.5, 0.01 M $NaClO_4$, 25 °C.

plot of the observed rate constant versus the concentration of **6a**, indicating good catalysis according to the rate law (2).

$$k_{obs} = k_2[\text{catalyst}] \quad (2)$$