Cluster Compounds

# Self-Assembly of a Spin-Coupled Octanuclear Copper(II) Circular Array from a Single-Stranded Ligand[**]

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Cyclic metal arrays containing multiples of spin-coupled paramagnetic metal centers are frequently synthesized from a large number of components in an uncontrolled assembly process that employs relatively simple bridging ligands in conjunction with smaller bridging fragments, such as hydroxide, oxide, halide, and methoxide.[1] A controlled approach that excludes these extraneous bridging fragments can be adopted when designed polytopic ligands are employed, as

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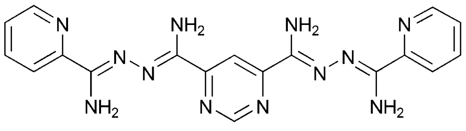
then a self-assembly process proceeds through an algorithm defined by the coordination preferences of the metal ion and the steric information contained within the ligand structure.[2] Cyclic metal arrays formed using this latter approach are a relatively rare class of supramolecular coordination compound.[3] Consequently, they have yet to offer the high nuclearities, the variety of metal centers, or the attractive magnetic phenomena that are associated with those formed from simple bridging ligands.[4] One route to bridge the gap between these two extremes is to use flexible polytopic bridging ligands that exclude the need for extraneous bridging fragments whilst maintaining enough flexibility to explore the potential-energy hypersurface of a system before the formation of a thermodynamically stable metal array. Polytopic diazine ligands with alternating sequences of rigid and flexible bridging groups, previously employed in self-assembly processes,[5] can be readily synthesized to meet these criteria, as exemplified by the recent isolation of a unique $Cu_{12}$ picture-frame assembly.[6] We describe herein the preparation and characterization of the first spin-coupled circular array to be formed from a single-stranded ligand.

The circular motif is formed through the self-assembly of the polytopic diazine ligand **L** with each of $Cu(ClO_4)_2{\cdot}6\,H_2O$, $Cu(BF_4)_2{\cdot}6\,H_2O$, and $Cu(CF_3SO_3)_2$ in high yields to give $[Cu_8L_4(H_2O)_8](X)_{16}$: $X = ClO_4^-$ (**1**), $BF_4^-$ (**2**), and $CF_3SO_3^-$ (**3**) respectively. Ligand **L** (for its preparation see the Supporting Information) is structurally comparable to a pyridazine analogue that has been successfully employed to generate a series of spin-coupled $[M_4L_3]$ tetranuclear triple helicates.[7] However, substitution of the pyridazine for the pyrimidine heterocycle confers a bowed arrangement of bridging bidentate binding sites on the ligand framework. This conformation precludes a linear arrangement of metal ions, as illustrated in the structure[8] of the cation in **2** (Figure 1). The circular array possesses an $S_4$ axis and can be best described as a circular single-stranded side-by-side complex[9] or as a circular single-stranded mesocate.[10] It holds eight copper(II) centers in a bowl-shaped, octagonal array that is composed of two bowed pairs of parallel ligands and eight coordinated water molecules; it has an external dimension of approximately 20 Å and a central cavity with a 4–5 Å diameter. The cavity has a sheath of hydrogen-bonding donors appropriate for the encapsulation of anions and/or solvent molecules, which is quite common for structures of this type.[11] In this particular case, an anion lies at the center of the cavity, and two others above and below this; further anions and uncoordinated water molecules are hydrogen bonded to other $NH_2$ groups of the cation. Each ligand **L** coordinates four adjacent copper centers through the contiguous bridging bidentate binding sites (N-$N_{diazine}$ and N-$N_{pyrimidine}$), to give Cu···Cu separations of 3.742 Å and 6.594 Å, respectively. Each copper ion is coordinated by two chelating subunits, one terminal $N_{py}$-$N_{diazine}$ (py = pyridine) and one central $N_{diazine}$-$N_{pyrimidine}$, belonging to two different ligand strands. This arrangement of ligands forms four equivalent dinuclear double-helical units located at the corners of the cyclic octagonal array that are related to each other through fourfold inversion–rotation symmetry ($S_4$ or $\bar{4}$). The ligands experience a significant amount of twist (Figure 2) within the dinuclear unit, as defined by the two Cu-N-N-Cu torsion angles of 47.0° and 46.3°, which orients the pyridine rings almost perpendicular to the central rigid pyrimidine ring. These rigid rings form the sides of the octagon and bridge the dinuclear units generating the cyclic array, with adjacent essentially coplanar N-$N_{pyrimidine}$ bridged Cu centers. Each copper(II) center adopts a square-based pyramidal geometry with the basal sites occupied by a diazine and pyridine nitrogen pair from one ligand, a pyridine nitrogen from a second ligand, and an oxygen donor atom from a coordinated water molecule; the in-plane bond lengths are short (< 2.0 Å). Longer axial bonds (2.253 and 2.269 Å) to pyrimidine nitrogen atoms complete the five-coordinate environment.



**L**

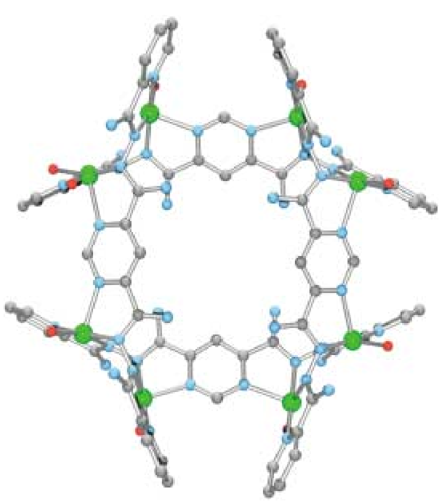


*Figure 1.* POV-Ray representation of the X-ray structure of the $[Cu_8(L)_4(H_2O)_8]^{16+}$ ion in **2** (hydrogen atoms are omitted for clarity). Gray C, red O, blue N, green [$Cu^{II}$].

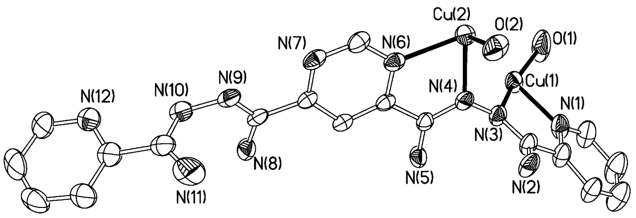


*Figure 2.* Displacement ellipsoid plot (ellipsoids set at 50% probability) of the dinuclear asymmetric unit in **2**. Selected bond lengths [Å]: Cu(1)-N(1) 1.977(5), Cu(1)-N(3) 1.992(4), Cu(1)-N(7A) 2.253(4), Cu(1)-N(9A) 1.998(4), Cu(1)-O(1) 1.970(5), Cu(2)-N(4) 1.999(4), Cu(2)-N(6) 2.269(4), Cu(2)-N(10A) 1.994(4), Cu(2)-N(12A) 1.985(5), Cu(2)-O(2) 1.996(4).

The structure of **2** could be determined successfully only with the use of synchrotron radiation facilities, because of the small crystal size and the weak scattering resulting from a high degree of disorder of the anions and solvent molecules. Data were also obtained for the perchlorate analogue **1**, with a rotating-anode X-ray source, but the diffraction pattern was much weaker, leading to a structure of low precision. The results, however, are sufficient to indicate that the two structures are isomorphous, that the octanuclear cation is essentially identical, and that the packing and hydrogen-bond arrangement is very similar.

Variable-temperature magnetic susceptibility data (Supporting Information) were collected on a single polycrystalline sample of **1** over the range 2–290 K and a fit of these data to the Curie–Weiss law gave $\chi = 0.510(2)\ \mathrm{cm^3\,K\,mol^{-1}}$ and $\theta = +0.273(9)$ K, suggestive of a weak ferromagnetic interaction between $\mathrm{Cu^{II}}$ centers. Structurally we may expect the behavior of **1** to approximate that of simple exchange-coupled dimers. Fitting the data to the Bleaney–Bowers equation[12] gave a good fit with $g = 2.15(1)$ and $-2J = -6.6(2)\ \mathrm{cm^{-1}}$. This ferromagnetic exchange interaction is in broad agreement with other structures that possess two and three Cu-N-N-Cu linkages with dihedral angles below approximately 80°.[13–16]

The formation of the circular array is quite remarkable as it requires four octadentate ligands and the inclusion of eight solvent molecules to satisfy the coordination algorithm of the eight five-coordinate copper(II) centers. Compounds **1**–**3** also represent a rare example of a polynuclear copper(II) circular array containing more than six copper(II) centers.[17] Examination of a solution of redissolved crystals of **1** and **2** in acetonitrile by electrospray mass spectroscopy, at various cone voltages, displayed four sets of peaks that correspond to the species $[\mathrm{Cu_8}\mathbf{L}_4(\mathrm{X})_n]^{16-n}$ ($\mathrm{X} = \mathrm{ClO_4^-}$, $\mathrm{BF_4^-}$; $n = 10$–13) together with their acetonitrile adducts. No other discernible peaks were observed; this suggests that, once the circular motif is formed, it is preserved in solution. A similar breakdown pattern was observed for the triflate analogue **3** and implies the formation of the circular motif is dominated by metal–ligand interactions[18] and not templated about a central anion, in contrast to some circular systems.[19] The isolation of **1**–**3** in high yields opens up exciting opportunities to build larger arrays through the substitution of the labile water or other solvent molecules with coordination complexes bearing suitable bridging units.

## Experimental Section

**L**: See Supporting Information.

**1**: Reaction of **L** with $\mathrm{Cu(ClO_4)_2{\cdot}6\,H_2O}$ (1:2) in aqueous acetonitrile gave a green precipitate in 70–75 % yield when the solution was left to stand for one week. Elemental analysis (%) calcd for $[\mathrm{Cu_8(C_{18}H_{18}N_{12})_4(H_2O)_8](ClO_4)_{16}{\cdot}6\,H_2O{\cdot}CH_3CN}$: C 22.2, H 2.6, N 17.2; found (vacuum-dried sample): C 21.9, H 2.7, N 17.5; IR (nujol mull): $\tilde{\nu} = 3425$ ($\nu_{\mathrm{H_2O}}$), 3344, 3177 ($\nu_{\mathrm{NH_2}}$), 1679 ($\nu_{\mathrm{CO}}$), 1656 ($\nu_{\mathrm{CN}}$), 1062 $\mathrm{cm^{-1}}$. Crystals suitable for X-ray diffraction were grown by slow evaporation of a concentrated solution of the precipitate in aqueous acetonitrile. **2** and **3** were obtained in similar yields using the same experimental conditions as **1**.

Magnetic susceptibility measurements were made on **1** using a Quantum Design MPMS SQUID magnetometer between 2–290 K in an applied field of 200 G. A diamagnetic correction of $-226 \times 10^{-6}\ \mathrm{cm^3\,mol^{-1}}$ was estimated from Pascal's constants.[20]

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[8] Crystal data for **2**: $[\mathrm{C_{72}H_{88}Cu_8N_{48}O_8}](\mathrm{BF_4})_{16}{\cdot}8\,\mathrm{H_2O}$ (including only the modeled ordered solvent), $M_r = 3795.3$, tetragonal, space group $I\bar{4}2d$, $a = 19.8207(12)$, $c = 38.220(5)$ Å, $V = 15015(2)$ Å$^3$, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.679\ \mathrm{g\,cm^{-3}}$, synchrotron radiation ($\lambda = 0.6888$ Å, $\mu = 1.26\ \mathrm{mm^{-1}}$), $T = 120$ K, $R = 0.064$ ($F^2 > 2\sigma$), $R_w = 0.191$ (for all $F^2$ values) for 10585 data and 511 refined parameters. Some of the anions are disordered, and refinement included partial substitution by other species with a heavier central atom (possibly perchlorate or chloride). Constrained H atoms were included on C and N atoms. Two uncoordinated water molecules were located in the asymmetric unit and refined (without H atoms). Other disordered solvent molecules and 3/16 of the anions lie in regions of diffuse electron density, which were treated by the PLATON/SQUEEZE procedure (A. L. Spek, University of Utrecht, The Netherlands). CCDC-216472 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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