Cluster Compounds

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Azine-Bridged Octanuclear Copper(II) Complexes Assembled with a One-Stranded Ditopic Thiocarbohydrazone Ligand**

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Multinuclear metal complexes are of interest in different fields of research. They are found in biological systems such as ferritin,[1,2] those with high-spin ground states can act as superparamagnets[3,4] and molecular nanomagnets,[5,6] and

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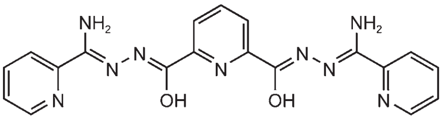
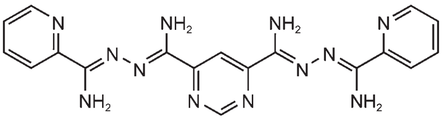
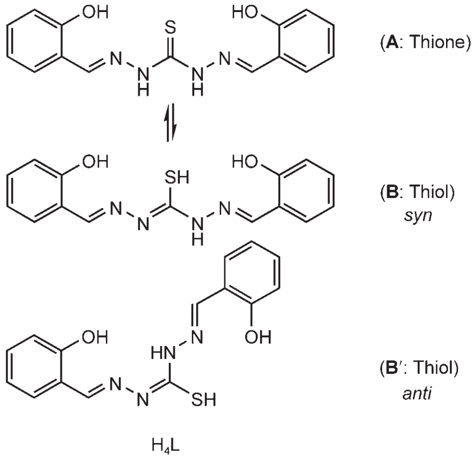
some exhibit spin-transition behavior[7] or manifest catalytic activity.[8] Like metal-template techniques,[9] self-assembly[10] can be used to build up beautiful molecular architectures,[6,11–13] often containing paramagnetic ions and endowed with unique properties.[14] A few octanuclear copper(II) complexes have been reported,[8,15–21] mostly synthesized in an "uncontrolled" assembly process starting from a large number of components in the presence of small bridging ligands such as hydroxide, oxide, methoxide, or halide.[21] A more attractive approach is the use of tailored single-stranded ligands for self-assembly, which makes the involvement of small bridging fragments unnecessary.[21,22] Two remarkable recent examples, reported by Thompson et al.[23] and Matthews et al.,[21] relied on linear ligands, one of which, $2poapH_2$, is tritopic, and the other, L′, tetratopic. Here we use a ditopic single-stranded thiocarbohydrazone ligand and show that further unusual multinuclear systems can be formed.



$2poapH_2$



L′



Thiocarbohydrazones have previously served as building blocks in the self-assembly of tetranuclear molecular square structures. In particular, mixed-valent iron(II)–iron(III), nickel(II), zinc(II), and cadmium(II) clusters have been synthesized starting from 1,5-bis(2-acetylpyridine)thiocarbohydrazone or related derivatives.[24–26] Reactions of the same ligands with copper(II) produced dimers of dinuclear units held together by extraneous bridging ligands.[26,27]

We discovered that 1,5-bis(2-hydroxybenzaldehyde)thiocarbohydrazone (H_4L) reacts with copper(II) acetate monohydrate or copper(II) sulfate in dimethylformamide (DMF)/ethanol (1:10) in the presence of triethylamine to give the green-brown complex $[Cu_8L_4(DMF)_8(H_2O)]\cdot 3.5\,DMF\cdot 3\,H_2O$ ($\mathbf{1}\cdot 3.5\,DMF\cdot 3\,H_2O$) with absorbance features at λ_{max} (ε_M) = 320 (118285), 413 (114660), 437 (136860), and 461 nm (113610 $M^{-1}cm^{-1}$). Recrystallization of the reaction product from dimethyl sulfoxide afforded the complex $[Cu_8L_4(dmso)_7]\cdot 6\,DMSO\cdot 1.32\,H_2O$ ($\mathbf{2}\cdot 6\,DMSO\cdot 1.32\,H_2O$).

As for the parent thiocarbohydrazide, two tautomeric forms are possible for H_4L: thione form **A** and thiol form **B**, which are in equilibrium.[28] The thiol tautomer can adopt a syn (**B**) or anti (**B′**) configuration as a consequence of the double-bond character of the central N–C linkage.

X-ray diffraction studies showed the metal-free compound to crystallize in the thione form **A**.[29] Both thiol forms have been observed in metal complexes: in $[MoO_2(H_2L)(dmso)]$ the dianionic ligand adopts the *syn* configuration **B**,[28] while the *anti* configuration **B′** was found in $[MoO_2(H_2L)(CH_3OH)]$.[30] X-ray diffraction[31] revealed that in $\mathbf{1}\cdot 3.5\,DMF\cdot 0.7\,H_2O$ the four thiocarbohydrazone ligands adopt the thiol *anti* configuration **B′** and thus provide two contiguous tridentate pockets, one with NNO and the other with ONS donor atoms, each of which can accommodate one copper(II) ion (Figure 1). Thus, six of the seven donor atoms of a fully deprotonated ligand L^{4-} are linked with two metal ions to give a dicopper(II) unit $\{Cu_2L\}^0$. The assembly of four such units into a metallomacrocyclic array takes place by coordination of the seventh donor atom of each $\{Cu_2L\}$ unit to the copper(II) atom of the adjacent unit which resides in the ONS

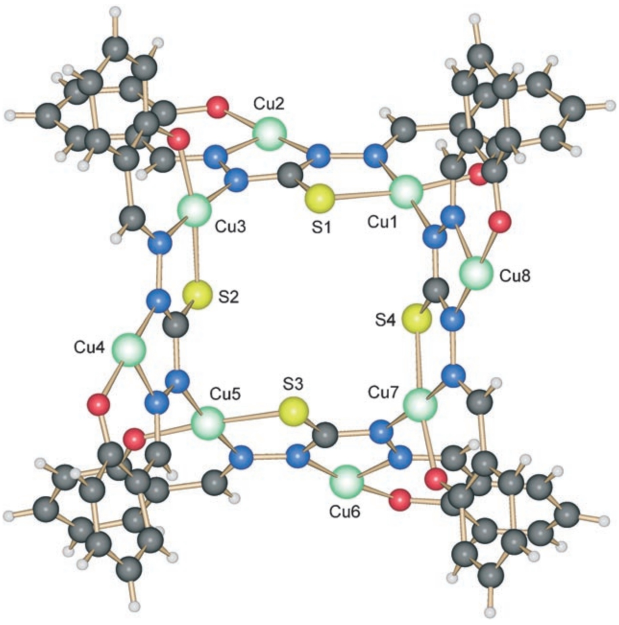


Figure 1. SCHAKAL representation of the charge-neutral copper(II) octanuclear species $\{Cu_8L_4\}^0$ with four ligands in nonparallel pairs in the crystal structure of $\mathbf{1}\cdot 3.5\,DMF\cdot 0.7\,H_2O$. The DMF molecules coordinated to Cu2, Cu4, Cu6. and Cu8 are omitted for clarity. Gray C, red O, blue N, yellow S, white H, green Cu.

ligand pocket to achieve a square-planar geometry. In the resulting architecture (see Figure 1) four copper(II) atoms, Cu1, Cu3, Cu5, and Cu7, are four-coordinate, with two ligands L^{4-} filling all four coordination positions, while the other four copper(II) centers, Cu2, Cu4, Cu6, and Cu8, each accommodated in an ONN ligand pocket, require additional ligands (DMF or DMF and H_2O) to complete their coordination spheres, as shown for Cu2 in Figure 2. The coordination polyhedron for Cu2 is a trigonal bipyramid, while those for Cu4 and Cu8 can be better described as distorted square pyramids. Depending on the positions of the disordered components of DMF and H_2O molecules around Cu6 its coordination geometry changes between distorted trigonal-bipyramidal and distorted octahedral. In both cases a water molecule is involved in coordination to Cu6. The charge balance is in agreement with formation of species **1**. Sixteen negative charges provided by four fully deprotonated ligands are balanced by the sixteen positive charges of eight copper(II) ions. This unique assembly of eight copper(II) centers, four of which are four-coordinate and the other four five-coordinate, into an azine-bridged 24-membered metallomacrocycle is to our knowledge the first example in copper(II) coordination chemistry. It requires four heptadentate ligands which use their donor capacity in an unprecedented manner for thiocarbohydrazone coordination chemistry to bind eight metal ions with the number of solvent molecules required to fully satisfy the coordination preferences of the eight copper(II) centers. We note that **1**·3.5 DMF·3 H_2O has an insular molecular structure in which the shortest intermolecular copper–copper separation is about 7.6 Å.

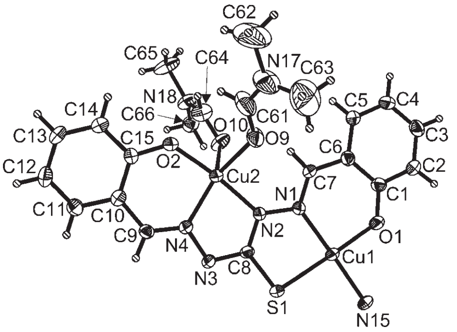


Figure 2. Structural representation of the {$Cu_2L(dmf)_2$} fragment in **1**·3.5 DMF·0.7 H_2O. The atom N15 belongs to the second {Cu_2L} unit, which is arranged perpendicular to the N1–Cu1 vector. Selected bond lengths [Å]: Cu1–O1 1.908(4), Cu1–N1 1.970(4), Cu1–S1 2.2527(15), Cu1–N15 2.007(4), Cu2–O2 1.887(4), Cu2–N2 1.965(4), Cu2–N4 1.957(4), Cu2–O9 2.109(4), Cu2–O10 2.159(4).

Unlike **1**, the molecule of **2** has C_2 symmetry. Of four independent copper(II) atoms two (Cu1 and Cu3) are square-planar coordinated like in **1**, whereas the coordination polyhedra of Cu2 and Cu4 can be described as distorted trigonal-bipyramidal with DMSO molecules occupying the "axial" positions. While both DMSO molecules at Cu2 are bound through oxygen atoms (Cu2–O5 2.002(5), Cu2–O6 2.346(6) Å), the coordination behavior of the two DMSO ligands at Cu4 is different. One of them coordinates to Cu4 through the oxygen atom (Cu4–O8 1.948(6) Å), whereas the second is disordered over two positions, coordinating through O7 (Cu4–O7 2.378(11) Å) or S5 with a weak contact (Cu4–S5 at 3.257(2) Å) in an alternating fashion. As a result, this DMSO acts as a bridging ligand leading to association of the molecules of **2** in one-dimensional chains along [100] (Figure 3).

The magnetic behavior of a polycrystalline sample of **2**·6 DMSO·1.32 H_2O in the temperature range 2–290 K in a field of 1 T is shown in Figure 4. The value of $\chi_M T$ decreases from 1.48 $cm^3 K mol^{-1}$ at 300 K and reaches a plateau of 0.02 $cm^3 K mol^{-1}$ below 20 K. As the room-temperature value of $\chi_M T$ for an octanuclear unit of eight noninteracting $S = {}^1\!/_2$ Cu^{II} ions with $g = 2.0$ would be 3.00 $cm^3 K mol^{-1}$, this clearly reflects that the major interactions in **2**·6 DMSO·1.32 H_2O are antiferromagnetic in nature. To extract the magnitude of exchange interaction between the Cu^{II} ions we applied the spin Hamiltonian $\mathcal{H} = -2J \sum_{i=1}^{8} S_i S_{i+1}$. Best fits to the experimental data down to low temperature were obtained by using g values of 2.2 for the Cu^{II} ions and a coupling constant of $J = -145\ cm^{-1}$, taking additionally into account 0.66% of a paramagnetic impurity ($R = 1.6 \times 10^{-4}$). Since the formation of a dinuclear transition metal species with a related ligand

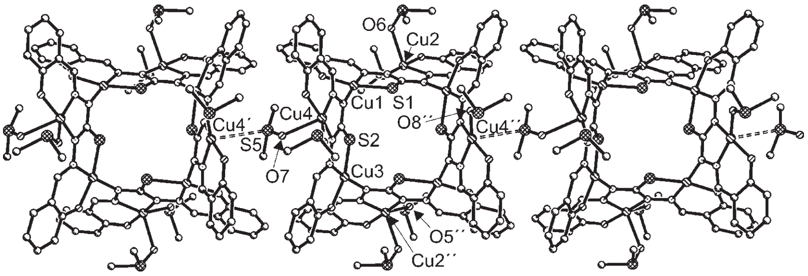


Figure 3. One-dimensional chain of molecules of **2** in **2**·6 DMSO·1.32 H_2O. The second position of the disordered bridging DMSO ligand is omitted for clarity; S5 atoms lie on special positions on twofold axes.

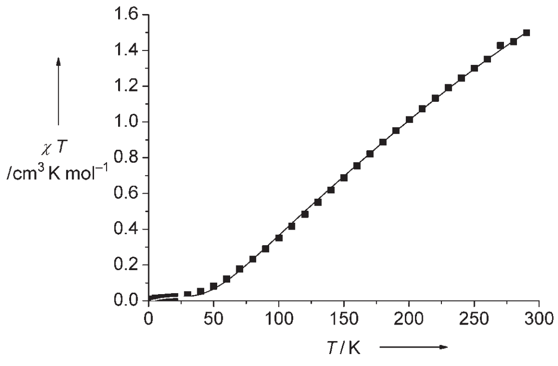


Figure 4. Magnetic data for **2**·6 DMSO·1.32 H_2O (see text for fitting parameters).

has been observed,[32] the low-temperature behavior of the molar susceptibility was regarded not as a simple paramagnetic impurity but rather as 0.3% of a weakly coupled dimer of two copper ions in comparable ligand environments, and hence presumably having the same g values as in the main compound. The simulation of $\chi_M T$ versus T with these data is shown in Figure 4 as a solid line. The magnetic behavior of **1**·3.5 DMF·0.7 H_2O is very similar: the g value is 2.14, and the intramolecular coupling $J = -128\ \mathrm{cm}^{-1}$. Also here an impurity had to be considered. The preparation of **1** is very sensitive, and contributions of between 1 and 7% of a coupled side product were experimentally found. Independent of whether DMF or DMSO completed the coordination sphere for the copper atoms in **1**·3.5 DMF·0.7 H_2O and **2**·6 DMSO·1.32 H_2O, respectively, alternation of the bridging between the metal ions is not reflected in the magnetic measurements. In all cases the fitting of the data with a model containing only one exchange interaction constant was good. This seems reasonable, since all torsion angles Θ_{CuNNCu} (av. 176°) are very close to 180°. Interestingly, the intermolecular arrangement as a one-dimensional chain for **2**·6 DMSO·1.32 H_2O does not influence the magnetic properties of the octanuclear compound; it behaves magnetically like **1**·3.5 DMF·0.7 H_2O, which has shortest intermolecular contacts of about 7.6 Å.

In conclusion, the unprecedented octanuclear clusters **1** and **2** are formed by a unique heptadentate ligand that exhibits particular conformational and configurational flexibility, appropriate spatial arrangement of metal-binding sites, coordination ability, and acid–base properties which allow full use of its donor capacity to satisfy maximally the stereochemical demands of the metal ions with minimum strain energy. The assembled metallomacrocyclic array of eight azine-bridged copper(II) ions, four of which are square-planar and four of which are distorted square-pyramidal or distorted trigonal-bipyramidal, is also unique in copper(II) coordination chemistry. The isolation of **1** and **2** opens up exciting opportunities to construct multinuclear systems with a number of other redox active metal ions with similar stereochemical preferences. The construction of heteronuclear clusters is also a challenge. Substitution of solvent molecules by suitable bridging ligands will also permit the assembly of oligomeric or even polymeric chains of HSNC units. This work is underway in our laboratories.

Experimental Section

All reagents were used as received from Aldrich. 1,5-Bis(2-hydroxybenzaldehyde)thiocarbohydrazone[29] was prepared according to reported procedures.

1·3.5 DMF·3 H_2O: $Cu(CH_3COO)_2 \cdot H_2O$ (0.2 g, 1.0 mmol) in ethanol (20 mL) and triethylamine (3 mL) was added to a hot solution of 1,5-bis(2-hydroxybenzaldehyde)thiocarbohydrazone (0.16 g, 0.5 mmol) in DMF/ethanol (1:10, 22 mL). The resultant brown solution was heated at 100°C for 1 h and allowed to cool to room temperature. The green-brown crude product was collected by filtration, washed with diethyl ether, and then dissolved in hot DMF (10 mL) and filtered. After 5 d the brown product crystallized from this solution at room temperature, was collected by filtration, washed with diethyl ether, and dried in air. Yield: 0.06 g, 19%. Elemental analysis (%): calcd for $C_{94.5}H_{144.5}N_{27.5}Cu_8O_{23.5}S_4$: C 42.38, H 5.44, N 14.38, S 4.79; found: C 41.99, H 5.60, N 14.09, S 4.92. IR (CsI): $\tilde{\nu} = 1651$, 1599, 1537, 1361, 1331, 1199, 757, 571, 527, 495, 472, 364, 323 cm^{-1}. Brown cubic crystals of 1·3.5 DMF·0.7 H_2O suitable for X-ray diffraction were obtained by recrystallization of **1**·3.5 DMF·3 H_2O from anhydrous DMF.

2·6 DMSO·1.32 H_2O: Recrystallization of the green-brown crude product (obtained as described above) from DMSO (5 mL) afforded green-brown prisms suitable for X-ray diffraction. Yield: 0.04 g. Elemental analysis (%): calcd for $C_{86}H_{120.67}N_{16}Cu_8O_{22.33}S_{17}$: C 37.03, H 4.32, N 8.03; found: C 37.03, H 3.97, N 8.11.

IR spectra were recorded on a Bruker FTIR VERTEX70 instrument in the region 4000–150 cm^{-1}. UV/Vis spectra were recorded on a Perkin-Elmer Lambda 20 UV/Vis spectrophotometer on samples dissolved in DMF. Magnetic susceptibility measurements were carried out with a Quantum Design MPMS SQUID magnetometer between 2 and 290 K in an applied field of 1 T. Diamagnetic corrections of -1370×10^{-6} and $-1340 \times 10^{-6}\ \mathrm{cm^3\,mol^{-1}}$ for **1**·3.5 DMF·3 H_2O and **2**·6 DMSO·1.32 H_2O, respectively, were estimated from Pascal's constants.[33]

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[31] Crystal data for **1**·3.5 DMF·0.7 H_2O: $C_{94.5}H_{139.9}Cu_8N_{27.5}O_{21.2}S_4$, $M_r = 2620.83$, monoclinic, space group $P2_1/c$, $a = 19.431(4)$, $b = 28.279(6)$, $c = 26.838(9)$ Å, $\beta = 129.48(2)°$, $V = 11\,383(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.529$ g cm^{-3}, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $\mu = 1.615$ mm^{-1}), $T = 120$ K, $R = 0.0588$ ($F^2 > 2\sigma$), $R_w = 0.1746$ (for 22 343 data and 1466 refined parameters). Crystal data for **2**·6 DMSO·1.32 H_2O: $C_{86}H_{120.67}Cu_8N_{16}O_{22.33}S_{17}$, $M_r = 2789.35$, monoclinic, space group $P2$/c, $a = 14.228(3)$, $b = 13.863(3)$, $c = 29.827(6)$ Å, $\beta = 102.75(3)°$, $V = 5738(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.614$ g cm^{-3}, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $\mu = 1.833$ mm^{-1}), $T = 120$ K, $R = 0.0820$ ($F^2 > 2\sigma$), $R_w = 0.2562$ (for 11 279 data and 723 refined parameters). Data were collected on a Nonius Kappa CCD diffractometer. Single crystals were placed at 50 mm from the detector and 1267 and 942 frames were measured, each for 60 and 80 s over a 0.75 and 1° scan width for **1**·3.5 DMF·0.7 H_2O and **2**·6 DMSO·1.32 H_2O, respectively. The data were processed using Denzo-SMN software. The structure was solved by direct methods and refined by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were placed at calculated positions and refined as riding atoms in the subsequent least-squares model refinements. Two DMF ligands coordinated to Cu6, as well as one of two DMF molecules coordinated to Cu4 and Cu8, were disordered over two positions, which could be resolved with close 0.5:0.5 occupancy. On the other hand, by taking into account the increased values of the thermal anisotropic factors, one of the DMF molecules of solvation was localized in a single position with 0.5 occupancy. Structure solution and refinement were performed with the SHELX program. CCDC-270851 (**1**·3.5 DMF·0.7 H_2O) and -281722 (**2**·6 DMSO·1.32 H_2O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[32] The reaction of $CuCl_2$ with 1,5-bis(2-hydroxybenzaldehyde)carbohydrazone (H_4L'') in 2:1 molar ratio in DMF/H_2O with subsequent recrystallization of the resulting precipitate from DMSO afforded the dinuclear complex [$Cu_2(HL'')Cl(dmso)_2$]·DMSO.

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