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Direct Synthesis, Crystal Structure, High-Field EPR, and Magnetic Studies on an Octanuclear Heterometallic Cu(II)/Cd Complex of Triethanolamine

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The reaction of zerovalent copper with cadmium iodide and triethanolamine (H_3L) in dimethylformamide (dmf) carried out under open-air conditions afforded a novel heterometallic complex $[Cu_3(HL)_3CdI_2]_2 \cdot 4dmf$. The crystal lattice consists of an octanuclear molecule $[Cu_3(HL)_3CdI_2]_2$, which has an inversion center at the midpoint of the central Cu_2O_2 unit, and of two non-coordinating dmf molecules. Eight metal atoms linked by alkoxide arms of triethanolamine ligands form a zigzag Cd−Cu1−Cu2−Cu3−Cu4−Cu5−Cu6−Cd chain with the separations between bridged Cu atoms in the range 2.935(2)−3.403(2) Å. The complex is further stabilized by intramolecular O−H···O hydrogen bonds. High-field electron paramagnetic resonance (EPR) spectra of the $S = 1$ spin state with $D_{(S=1)} = -0.843$ cm^{-1}, $E_{(S=1)} = -0.081$ cm^{-1} were observed. Fitting the magnetic susceptibility temperature dependence by using the exchange Hamiltonian $H_{HDVV} = J_1(\boldsymbol{S}_1\boldsymbol{S}_2 + \boldsymbol{S}_5\boldsymbol{S}_6) + J_2(\boldsymbol{S}_2\boldsymbol{S}_3 + \boldsymbol{S}_4\boldsymbol{S}_5) + J_3\boldsymbol{S}_3\boldsymbol{S}_4$, to which terms expressing the zero-field splitting and Zeeman splitting of the ground $S = 1$ state were added, resulted in $J_1 = 68$, $J_2 = 19$, $J_3 = -57$ cm^{-1}. "Broken symmetry" DFT calculations correctly predicted the triplet ground state of the hexa-copper system.

Introduction

The interest in multinuclear copper complexes has been driven in recent years to a large extent by the possibility of using them as convenient model systems to test the physical theories and models of magnetism, as well as of establishing useful magneto-structural correlations.[1] The flexibility of the Cu(II) coordination sphere in combination with the steric and crystal packing forces leads to a tremendous structural diversity of multicopper complexes. Small structural changes in such systems can have far-reaching effects on the magnetic properties. Incorporation of different metal ions into a multinuclear skeleton is an effective approach for creating new topologies of complicated intramolecular interactions.

The most successful synthetic strategy for heterometallic complexes is using a preformed metal-containing ligand which subsequently binds to a second type of metal ion via its free coordination donors. In our synthetic procedure, a metal-containing ligand is formed from a zerovalent metal and, subsequently, it self-assembles with a second metal present in the same reaction vessel. In the Cu^0/metal salt/aminoalcohol/solvent system that has been used in our work in the past, metallic copper readily dissolves in the reaction mixture which is heated mildly under open air. In this work, we have employed trieethanolamine which is a very versatile ligand and is known to form polynuclear copper complexes acting either as a bridging ligand,[1f] or as a terminal one.[1g] The idea that the free Lewis basic sites (O, NH_2, NMe_2) of the metal aminoalkoxo species generated in situ could bind a suitable Lewis-acidic ion of the second metal to produce heterometallic molecules was confirmed in a series of Cu/M (M = Pb, Co, Zn, and Cd) compounds.[2,3]

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The Cu/Cd/halide/aminoalcohol system has produced complexes of wider structural diversity compared to those obtained with other metals (Pb, Co, Zn)[2] in place of Cd, and it was suggested that bonding demands of the Cd atoms had a primary role in dictating the ultimate structure of the Cd/Cu heterometallic assemblies.[3] Since the system Cu^0/CdX_2/aminoalcohol (X = halide, CH_3COO) was proven to be a rich source of interesting species, we have reacted copper powder and cadmium iodide in the presence of triethanolamine (H_3L) in dmf, and obtained a novel Cu^{II}/Cd^{II} complex with a peculiar topology of 6 copper centers bridged by oxygen atoms, arranged in a zigzag chain that is terminated on each end by a cadmium atom. We report here the crystal structure and magnetic behavior of this compound.

Experimental Section

Materials and Instrumentation. Commercially available chemicals were used as received, and all experiments were carried out in air. Elemental analyses for metals were performed by atomic absorption spectroscopy and with a Carlo Erba Strumentazion Analyzer for carbon, hydrogen, and nitrogen. The infrared spectrum of a KBr disk was recorded on a UR-10 spectrophotometer in the 4000−400 cm^{-1} range using conventional techniques. High-frequency EPR spectra were recorded on a home-built spectrometer at the EMR facility of NHMFL.[4] The instrument was a transmission-type device in which waves are propagated in cylindrical lightpipes. The microwaves were generated by Gunn oscillators, operating at 95 ± 3 GHz or at 110 ± 4 GHz. Frequencies higher by a factor 2, 3, or 4 were obtained using a Schottky diode-based multiplier and appropriate high-pass filters. A hot-electron InSb bolometer cooled by liquid helium was used as a microwave detector. The instrument used no resonance cavity. A superconducting magnet (Oxford Instruments) capable of reaching a field of 17 T was employed. The temperature was controlled with an Oxford Instruments CF1200 continuous-flow liquid-helium cryostat and an ITC503 controller. The magnetic susceptibility of a powdered sample was determined on a SQUID-magnetometer MRMS-5S Quantum Design over the temperature range 5−300 K. Corrections for the sample holder were applied, and diamagnetic corrections for the octanuclear molecule were determined from Pascal's constants.[5]

Preparation of $[Cu_3(HL)_3CdI_2]_2\cdot 4dmf$. Copper powder (0.32 g, 5 mmol), CdI_2 (1.83 g, 5 mmol), dmf (20 cm^3), and H_3L (1.5 cm^3) were heated to 50−60 °C and stirred until Cu dissolved completely (120 min). The resulting blue solution was allowed to stand at the room temperature. Blue crystals suitable for X-ray crystallography deposited within 2 weeks after successive drop by drop addition of Pr^iOH and diethyl ether. They were collected by filter-suction and dried in vacuo. Mass collected: 2.01 g, yield 52% (with respect to copper). $C_{48}H_{106}I_4Cu_6N_{10}O_{22}Cd_2$ (2289.36): calcd. Cu 16.16, Cd 9.82, I 22.18, C 25.19, H 4.67, N 6.12; found Cu 16.5, Cd 9.8, I 21.9, C 25.2, H 4.3, N 6.4. IR (KBr, cm^{-1}): 3550−3400br, 2990w, 2960w, 2910−2850br, 1610s, 1465 m, 1375w, 1280 m, 1220 m, 1160 m, 1090s, 1070sh, 1020 m, 950 m, 910w, 890w, 790 m, 720br, 635 m, 530w, 490w, 470w.

Table 1. Crystallographic Data and Relevant Data Referring to the Structure Solution and Refinement

empirical formula	$C_{48}H_{106}Cd_2Cu_6I_4N_{10}O_{22}$
formula weight	2289.07
crystal system	triclinic
space group	$P\bar{1}$
a [Å]	10.729(3)
b [Å]	11.980(4)
c [Å]	15.773(5)
α [deg]	74.588(5)
β [deg]	73.661(5)
γ [deg]	89.396(5)
V [Å^3]	1871.0(10)
Z	1
μ [mm^{-1}]	3.949
measured reflections	17247
observed ($I > 2\sigma(I)$) reflections	4991
R_{int}	0.073
R ($I > 2\sigma(I)$)	0.077
wR (all data)	0.252

The compound is soluble in dmf under heating and insoluble in water. It is stable in air for months.

X-ray Crystallographic Investigation. The diffraction measurements were performed on a Bruker SMART CCD (ω rotation scans with narrow frames) diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Data were corrected for Lorentz polarization effects and for the effects of absorption (multiscan). The structure was solved by direct methods by full-matrix least-squares on F^2 with all reflections using SHELXL.[6] Details of the structural investigation and crystallographic data are summarized in Table 1.

The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The OH protons of the doubly deprotonated triethanolamine ligands were located in the difference Fourier map and refined with geometrical restraints. The geometries of one solvent dmf molecule were restrained to ideal values.

Results and Discussion

Analytical and Spectroscopic Characterization. Elemental analysis of the blue crystalline product revealed a 1 to 3 ratio of Cd(II) to Cu(II). The structural features of the title compound were determined by IR spectroscopy and by single-crystal X-ray diffraction studies (see below). Its formation can be understood considering the following reaction scheme:

$$6Cu^0 + 2CdI_2 + 6H_3L + 3O_2 + 4dmf \rightarrow [Cu_3(HL)_3CdI_2]_2\cdot 4dmf + 6H_2O \qquad (1)$$

In the process, dioxygen from the air was reduced to give water, and Cu^0 was oxidized to Cu(II).

The IR spectrum of the complex that was measured over the range 4000−400 cm^{-1} showed characteristic triethanolamine peaks and indicated the presence of hydrogen-bonded (3400−3500 cm^{-1}) OH groups. An intense band corresponding to ν(CO) vibrations of dmf was clearly observed at 1610 cm^{-1}.

Molecular Structure. The system consists of the octanuclear complex molecule $[Cu_3(HL)_3CdI_2]_2\cdot 4dmf$, located at the crystallographic inversion center, and of four non-coordinated dmf molecules (Figure 1). Eight metal atoms linked by alkoxo bridges form a zigzag Cd−Cu−Cu−Cu−Cu−Cu−Cu−Cd chain with bridged

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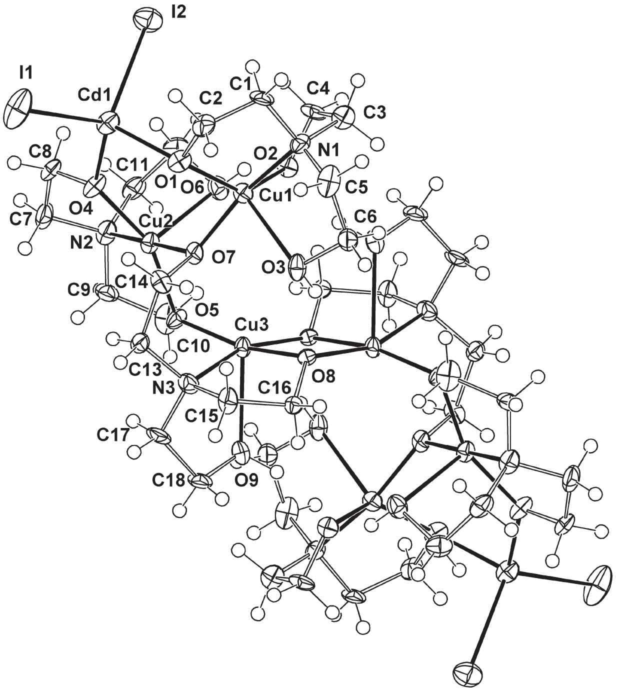

Figure 1. Molecular structure of $[Cu_3(HL)_3CdI_2]_2\cdot 4dmf$ with the non-H atoms drawn with 50% probability ellipsoids.

Table 2. Selected Bond Distances (Å) and Angles (deg)

Cd(1)−I(1)	2.7238(11)	Cu(2)−O(4)	1.957(5)
Cd(1)−I(2)	2.7622(11)	Cu(2)−O(5)	1.956(5)
Cd(1)−O(1)	2.171(5)	Cu(2)−O(6)	2.311(6)
Cd(1)−O(4)	2.161(6)	Cu(2)−O(7)	1.921(5)
Cu(1)−O(1)	1.954(5)	Cu(2)−N(2)	2.002(7)
Cu(1)−O(2)	1.952(5)	Cu(3)−O(5)	1.891(5)
Cu(1)−O(3)	2.263(5)	Cu(3)−O(8)	1.940(5)
Cu(1)−O(7)	1.918(6)	Cu(3)−O(9)	2.425(6)
Cu(1)−N(1)	2.008(7)	Cu(3)−N(3)	2.071(6)
		Cu(3)−O(8)[a]	1.965(5)
Cd(1)···Cu(1)	3.4277(12)	Cu(2)···Cu(3)	3.1565(12)
Cd(1)···Cu(2)	3.723(2)	Cu(1)···Cu(3)	4.084(2)
Cu(1)···Cu(2)	3.403(2)	Cu(3)···Cu(3)[a]	2.935(2)
I(1)−Cd(1)−I(2)	115.26(3)	O(4)−Cu(2)−O(7)	94.5(2)
I(1)−Cd(1)−O(1)	104.2(1)	O(4)−Cu(2)−N(2)	86.7(2)
I(1)−Cd(1)−O(4)	117.4(2)	O(5)−Cu(2)−O(6)	94.6(2)
I(2)−Cd(1)−O(1)	109.1(2)	O(5)−Cu(2)−O(7)	92.3(2)
I(2)−Cd(1)−O(4)	105.8(2)	O(5)−Cu(2)−N(2)	86.8(2)
O(1)−Cd(1)−O(4)	104.4(2)	O(6)−Cu(2)−O(7)	98.6(2)
O(1)−Cu(1)−O(2)	136.6(2)	O(6)−Cu(2)−N(2)	80.2(2)
O(1)−Cu(1)−O(3)	115.4(2)	O(7)−Cu(2)−N(2)	178.4(2)
O(1)−Cu(1)−O(7)	94.6(2)	O(5)−Cu(3)−O(8)	165.4(2)
O(1)−Cu(1)−N(1)	87.6(2)	O(5)−Cu(3)−O(9)	101.2(2)
O(2)−Cu(1)−O(3)	106.1(2)	O(5)−Cu(3)−N(3)	92.1(2)
O(2)−Cu(1)−O(7)	99.3(2)	O(5)−Cu(3)−O(8)[a]	102.4(2)
O(2)−Cu(1)−N(1)	86.8(2)	O(8)−Cu(3)−O(9)	92.5(2)
O(3)−Cu(1)−O(7)	87.8(2)	O(8)−Cu(3)−N(3)	86.5(2)
O(3)−Cu(1)−N(1)	80.9(2)	O(8)−Cu(3)−O(8)[a]	82.6(2)
O(7)−Cu(1)−N(1)	168.3(2)	O(9)−Cu(3)−N(3)	75.6(2)
O(4)−Cu(2)−O(5)	157.3 (2)	O(9)−Cu(3)−O(8)[a]	89.1(2)
O(4)−Cu(2)−O(6)	105.7(2)	N(3)−Cu(3)−O(8)[a]	160.8(2)

[a] Symmetry operations: $1-x, -y, 1-z$.

metal−metal separations in the range 2.935(2)−3.428(1) Å (Table 2). None of these distances are sufficiently short to imply any metal−metal bonding. The atom Cu(1) is five-coordinate with a distorted trigonal-bipyramidal geometry. The oxygen atoms of triethanolamine [O(1), O(2), O(3)] form the equatorial plane (the Cu−O distances vary between 1.952(5) and 2.263(5) Å). The nitrogen atom from triethanolamine [N(1)] and oxygen atom from another aminoalcohol ligand [O(7)] are coordinated in the axial positions [N(1)−Cu(1)−O(7) = 168.3(2)°]. The NO_4 donor sets of two other crystallographically independent copper centers are arranged in distorted square-pyramidal geometry. The four copper-ligand bonds in the plane fall in the range 1.891(5)−2.071(6) Å, while the axial bonds to oxygen atoms O(6) and O(9) are elongated (Table 2). The longer Cu(1)−O(3), Cu(2)−O(6), and Cu(3)−O(9) distances [2.263(5)−2.425(6) Å] confirm that the corresponding oxygen atoms are protonated. The terminal CdI_2O_2 entity is distorted tetrahedral, with average Cd−I and Cd−O bond lengths of 2.742(11) and 2.165(7) Å, respectively, and angles at the cadmium atom varying from 104.2(1) to 117.4(2)° (Table 2).

The octanuclear molecule is extra stabilized by intramolecular O−H···O hydrogen bonds: O(6)···O(2) = 2.608(8), H(6)···O(2) = 1.93(5) Å, ∠O(6)−H(6)···O(2) = 139(5)°; O(3)···O(8) = 2.731(8); H(3)···O(8) = 1.90(3) Å; ∠O(3)−H(3)···O(8) = 160(4)°; O(9)···O(2)-$\{1-x, -y, 1-z\}$ = 2.605(7); H(9)···O(2)$\{1-x, -y, 1-z\}$ = 1.78(4) Å; ∠O(9)−H(9)···O(2) $\{1-x, -y, 1-z\}$ = 162(6)°. The dmf solvent molecules are non-coordinating and are located in the lattice with no short H-bond contacts.

Magnetic Properties and HF EPR Spectra. The Heisenberg−Dirac−Van Vleck (HDVV) Hamiltonian for our centro-symmetric system should have a form

$$\mathbf{H}_{\mathrm{HDVV}} = J_1(\boldsymbol{S}_1\boldsymbol{S}_2 + \boldsymbol{S}_5\boldsymbol{S}_6) + J_2(\boldsymbol{S}_2\boldsymbol{S}_3 + \boldsymbol{S}_4\boldsymbol{S}_5) + J_3\boldsymbol{S}_3\boldsymbol{S}_4 \tag{2}$$

if one takes into account only the next-neighbor interactions between the copper ions. In a system of six copper ions, there are 64 "microstates" characterized by all possible combinations of the six m_s quantum numbers of individual copper ions, like $|1/2\ 1/2\ 1/2\ 1/2\ 1/2\ 1/2\rangle$, $|1/2\ 1/2\ 1/2\ 1/2\ 1/2\ -1/2\rangle$, and so forth. The eigenfunctions of the Heisenberg Hamiltonian (2) and also of the $\mathbf{S}^2$ operator of the total spin, $\boldsymbol{S} = \boldsymbol{S}_1 + \boldsymbol{S}_2 + \boldsymbol{S}_3 + \boldsymbol{S}_4 + \boldsymbol{S}_5 + \boldsymbol{S}_6$, are formed of these microstates. The exchange interactions give rise to 1 septet state ($S = 3$), 5 quintet states ($S = 2$), 9 triplet states ($S = 1$), and 5 singlets ($S = 0$). The magnetic moment approaching ~3.1 μ_B at the lowest temperatures (Figure 2) indicates that one of the triplets is the ground state. This is also confirmed by the low-temperature EPR spectra showing a pattern characteristic of a spin triplet (Figure 3). The drop of the magnetic moment observed at the lowest temperatures is caused by the combined Zeeman and zero-field splitting (zfs) of the ground triplet state becoming comparable to the thermal energy kT. The magnetic susceptibility can be fitted by using the formula

$$\chi = \frac{Ng^2\mu_B^2}{3kT}\,\frac{\sum_{i=1}^{20}(2S_i+1)(S_i+1)S_i\exp(-E_i/kT)}{\sum_{i=1}^{20}(2S_i+1)\exp(-E_i/kT)} \tag{3}$$

where the summations run over the 20 spin states of the coupled system listed above.

No analytical expressions for the energies are available, and they have thus to be evaluated by numerical diagonalization the Heisenberg Hamiltonian (2).

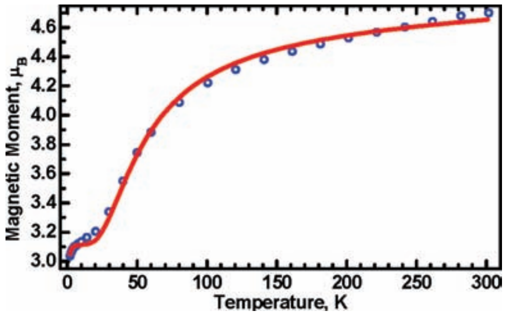

Figure 2. Experimental magnetic moments (blue circles). The solid line was calculated from eq 4 with the best-fit parameters J_1 = 68, J_2 = 19, J_3 = −57 cm^{-1}; g_{average} = 2.2 and with fixed $D_{(S=1)}$ = −0.843 cm^{-1}, $E_{(S=1)}$ = −0.081 cm^{-1}, as found from EPR.

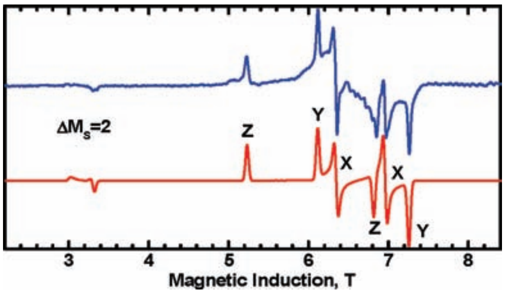

Figure 3. Blue: experimental high-Field EPR spectrum of $[Cu_3(HL)_3CdI_2]_2\cdot 4dmf$ recorded at 10 K with the microwave frequency 195.31 GHz. Red: simulated for S = 1 using g_x = 2.09, g_y = 2.08, g_z = 2.33, D = −0.843 cm^{-1}, E = −0.081 cm^{-1}. Molecular orientations are marked with X, Y, and Z.

The least-squares fitting procedure gave J_1 = 68, J_2 = 20, J_3 = −61 cm^{-1}. Formula 3 above is not applicable at very low temperatures and to explain the drop of the magnetic moment below ~15K it is necessary to express the magnetic susceptibility as

$$\chi = -\frac{N}{B}\frac{\sum_{i=1}^{64}\frac{\partial E_i}{\partial B}\exp(-E_i/kT)}{\sum_{i=1}^{64}\exp(-E_i/kT)} \qquad (4)$$

where the energies as well as their derivatives with respect to the magnetic field have to be calculated numerically by diagonalizing an extended Hamiltonian that includes the HDVV Hamiltonian (2) plus a part (5) containing the zfs and the Zeeman interaction

$$H_{\text{aniso}} = \sum_{i=1}^{5}\sum_{j=i+1}^{6} S_i\{D_{ij}\}S_j + \mu_B\sum_{k=1}^{6} B\{g_k\}S_k \qquad (5)$$

$\{D_{ij}\}$ is a tensor representing the sum of the anisotropic exchange and dipole−dipole interactions between Cu$_i$ and Cu$_j$. $\{g_k\}$ is the g-tensor of Cu$_k$. For the purpose of powder susceptibility calculation it is sufficient to assume the same isotropic g (g_{average}) on each copper ion. The zfs splitting of only the ground state affects magnetic susceptibilities because the effect is only important at the lowest temperatures at which other states are depopulated. The ground state zfs parameters D and E were found from EPR (Figure 3) and were fixed in the fitting procedure, but the g_{average} value was allowed to vary. The fitting resulted in slightly different exchange integrals: J_1 = 68, J_2 = 19, J_3 = −57 cm^{-1} (Figure 2) and an overall better agreement between the calculated and experimental susceptibilities. The fitted g_{average} of 2.20 was slightly higher than obtained from EPR (2.17).

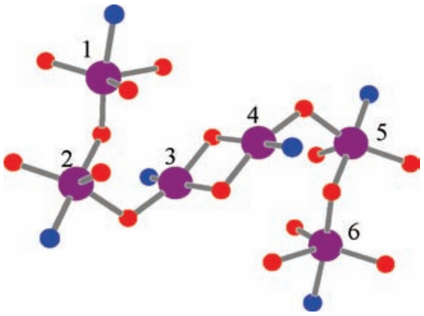

Figure 4. Copper coordination and the system of bridges in $[Cu_3(HL)_3CdI_2]_2\cdot 4dmf$ showing the numbering scheme for the HDVV Hamiltonian. The angles CuOCu in the hexa-copper chain are Cu(1)O-Cu(2) = 124.9°, Cu(2)OCu(3) = 110.3°, and Cu(3)OCu(4) = 97.4°.

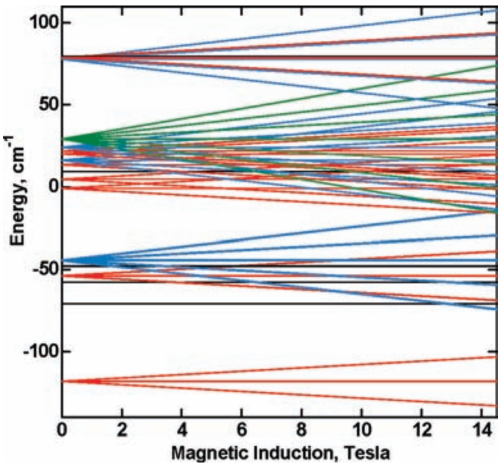

Figure 5. Diagram of the energy levels of the Cu$_6$ assembly in magnetic field parallel to Z, calculated by diagonalizing $H_{\text{HDVV}} + H_{\text{aniso}}$ with the best-fit parameters J_1 = 68, J_2 = 19, J_3 = −57 cm^{-1}, but with no zfs. The singlet, triplet, quintet, and septet levels are drawn in black, red, blue, and green, respectively.

Slight imperfectness of the fit in Figure 2 may be caused by neglecting the Dzialoshinskii−Moriya interactions which are possible in pairs 1−2, 5−6, as well as in 2−3 and 4−5 (Figure 4). It should also be emphasized that our system is very complicated, with many crowded energy levels (Figure 5), and the fit may be expected to be of a lower quality than, for example, in binuclear copper complexes. There is no doubt that the value −57 cm^{-1} resulting from the fitting refers to J_3 because there is only one such a lone interaction, but J_1 and J_2 cannot be distinguished. It is reasonable to assign 68 cm^{-1} to the interaction occurring through the largest CuOCu angle (Figure 4), that is, to the interaction Cu(1)−Cu(2). The angle Cu(3)OCu(4) of 97.4° is just below the borderline separating ferromagnetic and antiferromagnetic interactions in compounds with Cu(OH)$_2$Cu bridges[7], and moderate ferromagnetic interactions are not unexpected. With these J values, one of the triplet states is the ground state, as shown in Figure 5.

The energy levels in Figure 5 were calculated without the zfs. Inclusion of zfs causes mixing of levels that belong to different S states, leading to "anticrossing" effects, and results in a diagram that is difficult to decipher. A centrosymmetric ferromagnetic complex $[Cu_6(bipy)_{10}(\mu\text{-}CO_3)_2(\mu\text{-}OH)_2](ClO_4)_6\cdot 4H_2O$ with a hexa-membered Cu chain has been reported and its magnetic properties were analyzed in a similar manner, although without taking the zfs effects into account.[8] The ground state in the latter case was a septet ($S = 3$). The CuOCu angle in the central dihydroxo-bridged copper pair in that complex is 95°, and the exchange interaction magnitude is very similar to our J_3 (-49 versus -57 cm^{-1}).[9] It is instructive to compare Figure 8 in ref 8 with our Figure 5.

EPR Spectra. No EPR transitions within the excited states were observed (Figure 3). This is rather typical for copper polymers,[3d,10] although both triplet (ground) and quintet (excited) state EPR spectra in a tetrameric copper complex were observed in ref 11. The spin Hamiltonian for $S = 1$ was used in a form

$$H = \mu_B \boldsymbol{B}\cdot\mathbf{g}\cdot\boldsymbol{S} + \boldsymbol{D}[\boldsymbol{S}_z^{\,2} - S(S+1)/3] + E(\boldsymbol{S}_x^{\,2} - \boldsymbol{S}_y^{\,2}) \tag{6}$$

The spin Hamiltonian parameters were found and errors estimated by fitting the resonance field versus the microwave frequency dependencies (Figure 6). The powder spectra taken at different microwave frequencies could not be satisfactorily simulated with one parameter set. One has to understand that the spin triplet state in this system is much more complicated than that in simpler systems, like dimeric paddlewheel copper complexes.[12] In the present system, the **g** and the zfs tensors are unlikely to be coaxial, and the Dzialoshinskii−Moriya interactions may be operative in the copper pairs where copper atoms are not related by the inversion center, that is, in pairs 1−2, 5−6, and 2−3, 4−5.[13] Both effects cannot be further investigated in the absence of large single crystals suitable for high-field EPR. The values of D and E, of the g components, must therefore be considered as approximate. The intensity ratio of the low-field Z line to the high-field Z line (Figure 3) increased with the temperature lowering and proved the negative sign of D.[12]

g Values. In exchange-coupled metal polymers the g tensors of ions combine according to their orientation in space, and the coefficients in expressions for **g** in a coupled spin state depend on the Clebsh-Gordan coefficients used to build that spin state from microstates.[14]

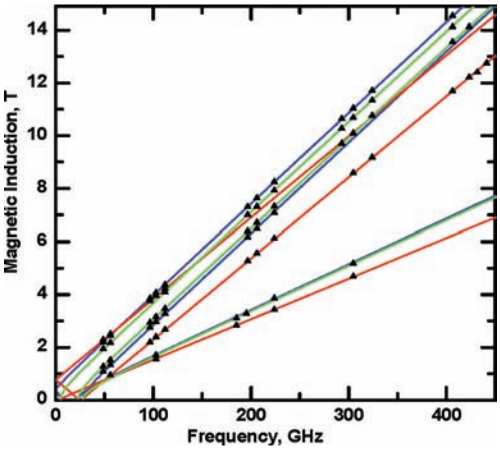

Figure 6. Frequency dependencies of the EPR resonances. Black triangles: experimental points. Green, blue, and red lines were calculated for $S = 1$ with the magnetic field parallel to the X, Y, and Z axes, respectively, by using the spin Hamiltonian parameters $g_x = 2.094$, $g_y = 2.078$, $g_z = 2.329$, $D = -0.843$ cm^{-1}, $E = -0.081$ cm^{-1}. The branches with low slopes correspond to the "forbidden" $\Delta M_S = 2$ transitions (see Figure 3).

As a result, the g values are different in each spin state, and strong reduction of g_z may be observed if the g tensors of interacting ions are non-parallel.[3d,10a,14] For example, $g_z = 2.066$ was found in a μ_4-oxo copper tetramer.[3d] There are no such effect in the present system, where a large g_z of 2.33 was observed in EPR, although the Z axes of copper ions are non-parallel - the angles Z_1-Z_2, Z_1-Z_3, and Z_2-Z_3 are 73°, 57°, and 63°, respectively. (The Z axes are perpendicular to least-squares O_3N planes of respective copper ions). To get insight into that feature, we calculated numerically using the sum of eq 2 and 5 the derivatives of the ground triplet state energies with respect to the g values of each copper ion in the hexanuclear chain to conclude that the **g** tensor observed in EPR is the following combination of the single-ion **g** tensors (in matrix notation):

$$\mathbf{g}_{S=1} = 0.160\mathbf{g}_1 - 0.145\mathbf{g}_2 + 0.985\mathbf{g}_3 \tag{7}$$

where the ions are numbered as in Figure 4. (Note that $\mathbf{g}_1 = \mathbf{g}_6$, $\mathbf{g}_2 = \mathbf{g}_5$, and $\mathbf{g}_3 = \mathbf{g}_4$ and eq 7 applies to the ground triplet state only).[15]

The observed g values thus represent almost exclusively the **g** tensors of the ions 3 and 4 that are related by the inversion center and thus no reduction in g_z is expected. The experimental g_z value of 2.33 still appears too high for copper(II) ions having 3 oxygen and 1 nitrogen atoms in their equatorial planes. This, in conjunction with the difficulties in EPR simulations mentioned above, indicates that spin Hamiltonian (6) dealing with a separate triplet state may be a too crude approximation. One should rather use the sum of eq 2 and 5 with the entire basis of 64 wave functions for EPR simulations. However, this may be doable for single-crystal spectra simulation, but does not appear feasible in the case of powders.

Contributions of the Copper Pairs to the Zero-Field Splitting in the Ground State. The anisotropic interactions in each pair of copper ions are given by the first term in spin Hamiltonian (5), which is expressed by the spins of separate ions. The zfs in a spin state of the coupled system is described by Hamiltonian (6), for which one can write

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an alternative tensor form

$$\mathrm{H} = \boldsymbol{S}\cdot\{\mathrm{D}\}\cdot\boldsymbol{S} \qquad (8)$$

where S is the total spin in a state of the coupled system. The $\{\mathrm{D_{ij}}\}$ tensors (in eq 5) of various pairs contribute to the overall $\{\mathrm{D}\}$ of eq 8 with coefficients that are different for each coupled-spin state.[14] In our case, direct numerical calculation using the sum of eq 2 and 5 shows that the overall $\{\mathrm{D}\}$ tensor in the ground state is almost fully determined by the central copper pair $\mathrm{Cu_3{-}Cu_4}$. Note that $\{\mathrm{D_{12}}\} = \{\mathrm{D_{56}}\}$ and $\{\mathrm{D_{23}}\} = \{\mathrm{D_{45}}\}$:

$$\{\mathrm{D}\} = 0.481\{\mathrm{D_{34}}\} - 0.030\{\mathrm{D_{23}}\} - 0.004\{\mathrm{D_{12}}\} \qquad (9)$$

(When converting the $\{\mathrm{D}\}$ tensor from Hamiltonian (5) to Hamiltonian (8) in binuclear copper systems, a factor of 0.5 appears in place of 0.481 − see ref 14). Thus, the central copper pair contributes overwhelmingly to both the g factors and zfs in the ground triplet state of our copper hexamer. Hence, it is not surprising that the D value of Hamiltonian (6) for our hexamer is similar to the D values observed in dihydroxo-bridged copper(II) dimers,[16] and carries the same sign.[12,16b]

The contribution to D due to the magnetic dipole−dipole interactions is also governed by eq 9; therefore, one can estimate it using the well-known formula

$$D_{\mathrm{dip}} = -(2g_z^{\,2} + (g_x^{\,2} + g_y^{\,2})/2)\mu_{\mathrm{B}}^{\,2}/2r^3_{\mathrm{Cu-Cu}} \qquad (10)$$

which yields $D_{\mathrm{dip}} = -0.13\ \mathrm{cm^{-1}}$ when using the distance between $\mathrm{Cu_3}$ and $\mathrm{Cu_4}$ of 2.93 Å. The main contribution to the zfs splitting of about $-0.73\ \mathrm{cm^{-1}}$ thus comes from the LS coupling effects, like it does in dimeric systems.[3d,10,12,14,16,17]

Estimation of the Exchange Integrals by the DFT Calculations. We have tried to adapt the "broken symmetry" method to estimate the exchange integrals in our system. The method is typically applied to binuclear complexes, and in our case we put 4 zinc atoms on copper atom positions in the X-ray structures thus leaving a system with only one exchange interaction between the remaining two copper atoms. In this way, the exchange within each pair of copper atoms can be calculated.[3d] A free software package "ORCA" developed by F. Neese[18] was used. The calculation utilized the Ahlrichs-VDZ basis and polarization functions from the Ahlrichs polarization basis.[19] The exchange integrals were calculated according to the convention $J = 2(E_{\mathrm{HS}} - E_{\mathrm{BS}})/(S_{\mathrm{HS}}(S_{\mathrm{HS}} + 1))$, where HS and BS denote the high- spin state and the broken-symmetry state, respectively. This convention is equivalent to that of ref 20 where exchange coupling in copper "paddlewheel" dimers was studied by DFT. The original formula for J from ORCA, which uses the exchange Hamiltonian $\mathrm{H} = -2JS_aS_b$, was converted to the notation of this paper by multiplying it by −2. Functional B3LYP was used, which seems to give best results in the "broken symmetry" method.[21,22] The ORCA calculation results were: $J_{\mathrm{Cu1-Cu2}} = J_1 = +27$ (antiferromagnetic), $J_{Cu2-Cu3} = J_2 = -32$ (ferromagnetic), and $J_{\mathrm{Cu3-Cu4}} = J_3 = -84\ \mathrm{cm^{-1}}$ (ferromagnetic). All calculated exchange integrals are smaller (more ferromagnetic) than the experimental ones. These exchange integrals result in one of the triplets being the ground state, but the magnetic moment temperature dependence simulated by using them is far from the experimental results. The trend of the calculated integrals is in accord with expectations: the antiferromagnetic interaction is obtained for the largest CuOCu angle while the stronger ferromagnetic J is associated with the smallest CuOCu angle. Attempts to calculate the exchange integrals between the non-neighboring copper ions resulted in very small numbers: $J_{\mathrm{Cu1-Cu3}} = -1\ \mathrm{cm^{-1}}$, $J_{\mathrm{Cu1-Cu4}} = -0.1\ \mathrm{cm^{-1}}$, $J_{\mathrm{Cu2-Cu4}} = 4\ \mathrm{cm^{-1}}$, $J_{\mathrm{Cu2-Cu5}} = 1.5\ \mathrm{cm^{-1}}$. A systematic theoretical study was performed by Ruiz et al.,[22] in which the exchange integrals in dialkoxo bridged copper dimers were calculated depending on the angle Θ (Cu−O−Cu) and an angle τ (deviation of the O−C bond from the bridge plane $\mathrm{Cu_2O_2}$). In our case, the central bridge unit Cu3−O8−Cu3′−O8′ is perfectly planar with the Θ angle of 97°, while $\tau = 49°$. No calculations in ref 22 were performed for such a large value of τ, but the observed trends (Figure 3 in ref 22) indicate an agreement between our results and those of Ruiz et al.

Conclusions

Exchange interactions in the hexa-copper chain result in a triplet ground state, whose large zfs and the g values are almost exclusively determined by the central copper pair $\mathrm{Cu_3{-}Cu_4}$. The zfs has to be taken into account for accurate description of the magnetic properties at the lowest temperatures. The "broken symmetry" calculations correctly predicted the triplet ground state of the hexanuclear copper entity.

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Supporting Information Available: Crystallographic data in CIF format; energy level diagram showing effect of zfs; shortened output of ORCA calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) For example, in the septet state the relation is $\mathbf{g}_{S=3} = (\mathbf{g}_1 + \mathbf{g}_2 + \mathbf{g}_3)/3$.

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