Structure and Magnetism of a New Dodecanuclear Cu^{II} Complex with Acetato and Imidazolato Bridges, Formed by Oxidation of the Chelating Ligand 1,1,7,7-Tetrakis(imidazol-2-yl)-2,6-diazaheptane

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A novel dodecanuclear copper(II) complex $[Cu_{12}(tidhd)_4(MeOH)_8(CH_3COO)_8](MeOH)_{0.8}$ (Htidhd = 1,1,7,7-tetrakis-(imidazol-2-yl)-2,6-diaza-1,6-heptadiene) with imidazolato and acetato bridging ligands was synthesized by reaction of polyimidazole 1,1,7,7-tetrakis(imidazol-2-yl)-2,6-diazaheptane (Htidahp) with copper acetate in a methanol solution. The complex crystallized in the triclinic space group $P\bar{1}$ with a = 9.1204(1), b = 13.5139(2), c = 27.6925(5), α = 76.8006(6)°, β = 82.8066(7)°, γ = 76.4594(9)°, Z = 1. Structure analysis shows that the unit cell of the complex contains twelve copper(II) ions in three different coordination environments. The complex is centrosymmetric and the two hexanuclear units are linked by two μ_3-acetate anions [the Cu1–Cu1a distance is 3.5507(7) Å]. The magnetic superexchange interaction via the bridging imidazolate ligand appears to be the most important magnetic interaction in this complex. Magnetic susceptibility measurement vs. temperature in the range of 6–300 K were fitted to the parameters g = 2.05, J_a = –32.0 cm^{-1} and J_b = –5.45 cm^{-1}.

Introduction

There has been great interest in the magnetostructural studies carried out on polynuclear divalent first-row transition metal complexes in recent years.[1] One of the main interests in this field comes from the need for the design and synthesis of novel functional materials with highly ordered structures in order to provide new molecular-based magnets.[2] Furthermore, many such systems are potential model compounds of multi-metal proteins.[3] This is especially relevant when imidazole is used as a ligand, since it is ubiquitous in proteins.[4]

Over the past decades, much progress has been made in the structural characterisation of copper proteins by different methods,[5] although the specific reaction pathways and mechanisms of action have remained unclear. In order to understand their catalytic mechanisms and their unusual spectroscopic characteristics, the development of relatively simple synthetic models of the active sites of copper proteins is of considerable interest.[6] The ligands most frequently used are based on pyrazole, imidazole and pyridine moieties.[7,8] Since imidazole is present in many natural enzyme and proteins, we have chosen to design and synthesize model compounds of copper proteins with imidazole-containing ligands.[9]

The reaction of 1,1,7,7-tetrakis(imidazol-2-yl)-2,6-diazaheptane (Htidahp) with $Cu(OAc)_2$ leads to an unprecedented imidazolato- and acetato-bridged dodecanuclear complex. In this paper, the synthesis, crystal structure, spectroscopic and magnetic properties of this compound are discussed. Figure 1 shows the schematic structure of the ligand Htidahp.

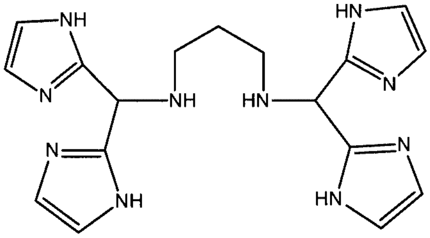

Figure 1. The structure of the ligand1,1,7,7-tetrakis(imidazol-2-yl)-2,6-diazaheptane (Htidahp)

Results and Discussion

The dodecanuclear complex was obtained by reaction of one equivalent of Htidahp with three equivalent of copper(II) acetate in methanol. Diethyl ether diffusion into the methanolic solution led to the formation of deep green,

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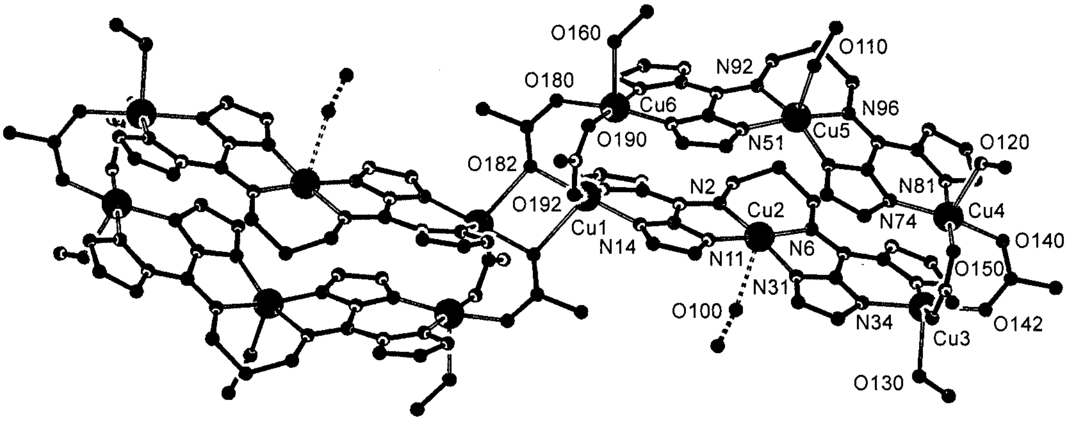

Figure 2. Platon projection[14] of the crystal structure of $[Cu_{12}(tidhd)_4(CH_3OH)_8(CH_3COO)_8](CH_3OH)_{0.8}$; hydrogen atoms are omitted for clarity; only the major component of the disordered methanol molecule at O130 is shown; the methanol molecule at O100 is only partially occupied

square crystals suitable for X-ray crystal structure determination (Figure 2).

The unit cell of the structure encloses one dodecanuclear unit, which is centrosymmetric. The asymmetric unit of the complex contains one $[Cu_6(tidhd)_2]^{4+}$ cation, five methanol molecules, of which one is disordered and one only partially occupied, and four $[CH_3COO]^-$ anions. Disordered solvent molecules occupy 13.5% of the unit cell volume, and they were treated as diffuse electron density (see Exp. Sect.). In the asymmetric unit, the six copper atoms are in different environments. Four dehydronated imidazole groups bridge Cu1 and Cu2 [5.6889(8) Å], Cu2 and Cu3 [5.6731(8) Å], Cu4 and Cu5 [5.7224(8) Å], and Cu5 and Cu6 [5.7148(7) Å], while the acetate anions bridge Cu1 and Cu6 [2.9926(8) Å], and Cu3 and Cu4 [3.0393(8) Å]. Cu1 is coordinated by a bridging imidazolate nitrogen atom, an imidazole nitrogen atom and three bridging acetate oxygen atoms in a distorted square-pyramidal geometry {O192−Cu1−N21 170.23(14)°, O182−Cu1−N14 175.87(14)°; $\tau_1 = 0.094$, where $\tau = 0$ and 1 are for the perfect square pyramidal and trigonal bipyramidal geometries, respectively[10]}, with a N_2O_3 donor set. Cu2 and Cu5 are each coordinated by a bridging imidazolate nitrogen atom, an imidazole nitrogen atom, two nitrogen atoms from the diamine unit, and one oxygen atom from a methanol molecule (N_4O donor set; $\tau_2 = 0.057$, $\tau_5 = 0.194$). The Cu3, Cu4 and Cu6 atoms are coordinated by a bridging imidazolate nitrogen atom, an imidazole nitrogen atom, two oxygen atoms from acetate oxygen atoms and one oxygen from a methanol molecule (N_2O_3 donor set; $\tau_3 = 0.170$, $\tau_4 = 0.123$, $\tau_6 = 0.124$). All the coordination spheres of these six copper atoms are distorted square-pyramidal. The Cu−O distances for the coordinated methanol molecules are in the range of 2.265(3) to 2.294(3) Å. On Cu2 the methanol molecule is only very weakly bound with a Cu−O distance of 2.706(10) Å. It can therefore easily evaporate, which explains the partial occupancy in the crystal. In all cases the methanol ligand is in an axial position. The complex consists of two hexanuclear units bridged by two acetate groups; the distance between Cu1 and Cu1a is 3.5507(7) Å.

It has to be pointed out that the C−N bonds in the original ligand have been oxidized to C=N upon coordination with copper acetate. Such oxidation and dehydrogenation reactions are not uncommon.[9,11] This compound is further stabilized by intramolecular and intermolecular hydrogen bonds. The different molecules are linked by intermolecular stacking between the imidazole rings, and by several hydrogen bonds.

A crystal structure of a related ligand, namely 1,1,6,6-tetrakis(imidazol-2-yl)-2,5-diazahexane (Htidah) was reported by our group with six copper ions in three different coordination environments.[11] The asymmetric unit in that complex consists of three copper ions, a negative tidah ligand, five chloride ions, two coordinated water molecules involved in hydrogen bonding and three lattice water molecules. The imidazole only bridges two copper atoms and the two trinuclear units are linked by two asymmetric chloride bridges (Cl6 and Cl6a) and two further bridges (Cl4 and Cl4a). The present dodecanuclear copper complex has both imidazolato and acetato bridging ligands. Its magnetic and electronic properties are described below.

Electronic Properties

The ligand field diffusion reflectance spectrum of the complex shows three d-d absorption bands centered at approximately $\lambda = 252$ nm (39.6×10^3 cm^{-1}), $\lambda = 368$ nm (27.2×10^3 cm^{-1}) and $\lambda = 603$ nm (16.6×10^3 cm^{-1}) in agreement with such geometries. The intensity of the absorptions at 368 nm and at 252 nm are assigned to the charge-transfer transition from the imidazolate nitrogen atoms to Cu^{II},[12] while the absorption at 603 nm is assigned to d-d transitions.[13]

EPR and Magnetic Susceptibility

The EPR spectrum of a powered polycrystalline sample of the complex at room temperature shows a broad isotropic copper(II) signal centered around a g value of 2.1034. At 77 K, the signals of the powder and a frozen solution of the complex in CH_3CN/MeOH are sharper, but no resolution of $g_{//}$ and $g_{\perp}$ is observed.

Magnetic susceptibility measurements have been performed on crystals of the complex (m = 34.87 mg) at 0.1 Tesla in the temperature range of 6 to 300 K. The plot of χ^{-1} and χT versus the temperature [with χ being the magnetization per copper(II) ion] is shown in Figure 3. At 300 K, $\chi T = 0.35\ cm^3{\cdot}K{\cdot}mol^{-1}$, which is slightly lower than the expected value for a single, uncoupled copper(II) ion ($\chi T \approx 0.42\ cm^3{\cdot}K{\cdot}mol^{-1}$ for paramagnetic systems). The value of χT decreases upon cooling, with an even sharper decline below 60 K, to a value of $\chi T = 0.06\ cm^3{\cdot}K{\cdot}mol^{-1}$ at 6 K. This decrease indicates the presence of a quite strong antiferromagnetic coupling. The shape of the curve of both χT, and of χ^{-1} vs. the temperature is characteristic for a linear arrangement of three copper(II) ions.[14-16]

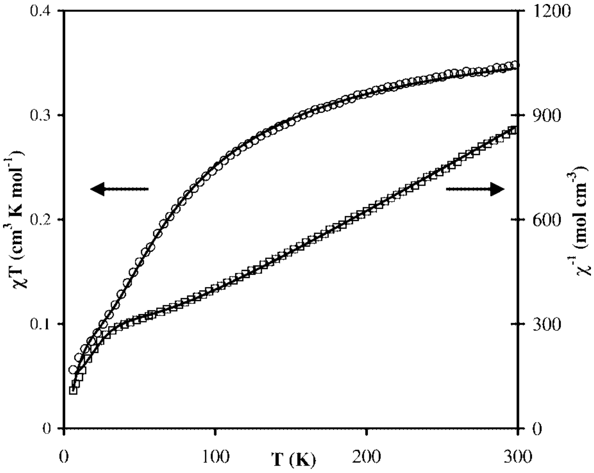

Figure 3. χT vs. T (○) and χ^{-1} vs. T curves (□) of **1**; the solid lines represent the calculated curves with parameters g = 2.05, $J_a = -32.0\ cm^{-1}$, $J_b = -5.45\ cm^{-2}$ and $R = 7.6{\cdot}10^{-5}$ ($J_a = J_1 = J_2 = J_3 = J_4$; $J_b = J_5 = J_6$; $J_7 = 0$)

The fitting of the linear part of the χ^{-1} vs. T curve (between 80 and 300 K) results in a Curie constant, C, of 0.45 $cm^3\ mol^{-1}$ and a Curie Weiss temperature, θ, of −80.0 K with $R < 1.6{\cdot}10^{-4}$. [The fit was accompanied by minimisation of the reliability factor, defined as $R = {}^1/_n{\cdot}\Sigma(\chi_{calc}^{-1}/\chi_{obs}^{-1})^2/(\chi_{obs}^{-1})^2$, by least-squares procedure.] The Curie constant is in good agreement with the g value measured by EPR spectroscopy.[17] To interpret the magnetic data, the possible magnetic-exchange pathways have to be examined in some detail (Figure 4).

Along with six different magnetic superexchange interactions within the hexanuclear ring, coupling (J_7) between the two hexanuclear units is possible via the acetate anion bridging between Cu1 and Cu6, Cu1 and Cu1a. This interaction is expected to be small, as no equatorial links are involved, and is therefore not taken into account.[18]

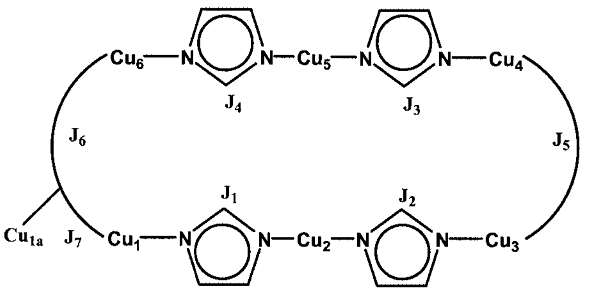

Figure 4. Possible magnetic superexchange pathways of the complex

Magnetic superexchange interaction via a bridging imidazole ligand is known to be relatively strong.[18,19] It is concluded from the short copper-imidazole distances (all between 1.948 Å and 2.022 Å) that the magnetic orbitals of the copper(II) ions are directed in such a way that a considerable electron delocalization occurs over the imidazolate nitrogen atoms. Therefore, an antiferromagnetic interaction is expected between Cu1−Cu2−Cu3 and between Cu4−Cu5−Cu6. Because the difference in Cu−Cu distances and the angles between the copper centers and the C2-atom of the imidazole ring are small (5.698 ± 0.025 Å, 172.12 ± 1.35°), the magnetic-exchange pathways J_{1-4} are considered to be identical (J_a).

These considerations lead to the first part of the expression (1), to describe the magnetic behaviour of this bishexanuclear cluster.

$$\chi = \frac{N\beta^2 g^2}{4kT}\,\frac{1+\exp[-2J_a/kT]+10\exp[J_a/kT]}{3+3\exp[-2J_a/kT]+6\exp[J_a/kT]}\times\exp[J_b/kT] \qquad (1)$$

In this formula, N, β and k have their normal value and g is assumed to be equal for all individual metal ions. The first term is an equation for an A-B-A copper(II) trinuclear species.[14,17] A trinuclear copper(II) species will normally lead to spin frustration, resulting in a χT value at low temperature equivalent to that of one uncoupled copper(II) ion.[17] As can be seen in Figure 3, the value of χT at low temperature is even lower than would be expected for such a trinuclear species. The superexchange interactions over the bridging acetate anions (J_5 and J_6) will be virtually identical and are therefore not expected to be equal to zero, and will be called J_b. This interaction forces the two trinuclear units to behave as two antiferromagnetic coupled units. The coupling constant J_b expresses this intertrinuclear superexchange interaction.

A good fit has been obtained for the parameters g = 2.05, $J_a = -32.0\ cm^{-1}$, $J_b = -5.45\ cm^{-2}$ and $R = 7.6\times10^{-5}$. [$R = {}^1/_n{\cdot}\Sigma(\chi_{calc}^{-1}/\chi_{obs}^{-1})^2/(\chi_{obs}^{-1})^2$, where n is the number of points, χ_{calc} is the magnetic susceptibility calculated by formula 1 and χ_{obs} the measured susceptibility]. The magnetic behaviour of the complex can therefore be described as antiferromagnetic dimers of linear antiferromagnetic linear trimers. The value of J_a is in the range commonly observed for imidazolato-bridged Cu^{II} ions.[17-19]

Conclusions

In this paper, the synthesis and the structural and magnetic study of a novel dodecanuclear copper complex $[Cu_{12}(tidhd)_4(MeOH)_8(CH_3COO)_8](MeOH)_{0.8}$ are presented. The imidazole groups of the Htidhd ligand are dehydronated. The C−N bonds from the starting ligands have been oxidatively converted into C=N bonds upon coordination with copper acetate, which results in an unprecedented complex with a unique architecture. The unit cell of the dodecanuclear complex is centrosymmetric. Each asymmetric unit of the complex is composed by one $[Cu_6(tidhd)_2]^{4+}$, four methanol molecules and four acetate anions, and six copper atoms are in different coordination environment. All the coordination spheres of the six copper atoms are of a distorted square-pyramidal geometry. The two hexanuclear units are linked by two μ_3-acetate groups. The magnetic superexchange interaction via the bridging imidazolate ligand plays an important role in the magnetic interaction. The study here provides not only a novel dodecanuclear complex with imidazolato- and acetato- group as bridges, but also more information about the magnetic and structural data for imidazolato-bridged complexes.

Experimental Section

All reagents and solvents were purchased from commercial sources and used as received. C, H and N analyses were carried out in Leiden University. Infrared spectra were recorded on a Perkin−Elmer Paragon 1000 spectrophotometer equipped with a Golden Gate diamond ATR as a sample support. X-band EPR spectra were recorded on a JEOL ESR spectrometer equipped with an Esprit 330 data system, at room temperature and at 77 K, with dpph as internal reference ($g = 2.0036$). The ligand-field spectra of the solid samples were recorded in the 300−2000 nm range on a Perkin−Elmer Lambda 900 UV/Vis/NIR spectrometer in the diffuse reflectance mode with MgO as reference. Bulk magnetizations of polycrystalline samples were measured in the range 6−300 K with a Quantum Design MPMS-5S SQUID magnetometer, in a 1 kG applied field. The data were corrected for the experimentally determined contribution of the sample holder. Corrections for the diamagnetic responses of the complex, as estimated from Pascal's constants, were applied.[20]

The ligand 1,1,7,7-tetrakis(imidazol-2-yl)-2,6-diazaheptane (Htidahp) was prepared as follows: 1,3-Diaminopropane (0.32 g, 4.34 mmol) was added to a solution of the hydrochloride salt of bis(imidazol-2-yl)nitromethane[21] (2.0 g, 8.69 mmol) in 10 mL of ethanol and 10 mL of sodium hydroxide solution (2.0 M). The solution was stirred for 45 min at 80 °C, during which time the product crystallised from the reaction mixture. After cooling to room temperature, the reaction mixture was filtered. The product was washed with water, ethanol and dried with diethyl ether. Yield 76%. ^1H NMR (200 MHz, 1 M DCl, 25 °C): $\delta = 7.40$ (s, 8 H, imidazole), 5.85 (s, 2 H, CH), 2.58 (d, 4 H, CH_2), 1.67 (m, 2 H, CH_2) ppm.

Preparation of the Complex: A solution of the ligand Htidahp (14.64 mg, 0.01 mmol) in 3 mL of methanol was added to a solution of $Cu(CH_3COO)_2$ (24.00 mg, 0.03 mmol) in 5 mL of methanol. The reaction mixture was stirred at room temperature for 10 min and filtered. Diethyl ether diffusion into the filtered solution led to the formation of deep green crystals of sufficient quality for X-ray structure determination. Yield: 11%. $C_{92.8}H_{114.4}Cu_{12}N_{40}O_{24.8}$ (2949.5): calcd. C 37.8, H 3.9, N 19.0; found C 37.5, H 3.7, N 18.4. IR (solid): $\tilde{\nu} = 1557.9, 1455.3, 1414.3, 1373.0, 1199.4, 937.9, 764.4, 623.1, 480.4\ cm^{-1}$. UV/Vis/NIR (solid): $\lambda_{max} = 368$ nm (strong); $\lambda = 252$ nm and $\lambda = 603$ nm (weak). EPR (solid, room temp): $g = 2.1034$.

X-ray Crystal Structure Determination: $C_{92.8}H_{114.4}Cu_{12}N_{40}O_{24.8}$ + solvent, Fw = 2949.52, green needle, $0.30 \times 0.12 \times 0.06\ mm^3$, triclinic, $P\bar{1}$ (no. 2), $a = 9.1204(1)$, $b = 13.5139(2)$, $c = 27.6925(5)$ Å, $\alpha = 76.8006(6)°$, $\beta = 82.8066(7)°$, $\gamma = 76.4594(9)°$, $V = 3221.33(8)$ Å^3, $Z = 1$, $\rho_x = 1.520\ g\ cm^{-3}$, 36255 measured reflections, 11025 unique reflections ($R_{int} = 0.0656$), 7472 observed reflections [$I > 2\sigma(I)$]. 785 refined parameters, 16 restraints. R (obs. refl.): $R1 = 0.0416$, $wR2 = 0.1143$. R (all data): $R1 = 0.0674$, $wR2 = 0.1285$. S = 1.038. Intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (Mo-K_α, $\lambda = 0.71073$ Å) at a temperature of 150 K. An absorption correction based on multiple measured reflections was applied ($\mu = 2.014\ mm^{-1}$, 0.76−0.89 transmission). The structure was solved by direct

Table 1. Selected bond lengths (Å) and angles (°) of $[Cu_{12}(tidhd)_4(CH_3OH)_8(CH_3COO)_8](CH_3OH)_{0.8}$

Bond lengths (Å)			
Cu1−Cu6	2.9925(8)	Cu3−Cu4	3.0392(8)
Cu1−O182	2.007(3)	Cu4−O120	2.294(3)
Cu1−O181a	2.484(3)	Cu4−O140	1.975(3)
Cu1−O192	1.970(3)	Cu4−O150	2.009(3)
Cu1−N14	1.961(4)	Cu4−N74	1.961(3)
Cu1−N21	1.964(4)	Cu4−N81	1.992(3)
Cu1−Cu2	5.6885(8)	Cu4−Cu5	5.7225(8)
Cu2−N2	2.004(4)	Cu5−O110	2.287(3)
Cu2−N6	2.002(3)	Cu5−N51	1.966(3)
Cu2−N11	1.968(3)	Cu5−N71	1.966(3)
Cu2−N31	1.948(4)	Cu5−N92	2.022(4)
Cu2−O100	2.706(10)	Cu5−N96	2.013(3)
Cu2−Cu3	5.6732(8)	Cu5−Cu6	5.7147(8)
Cu3−O130	2.265(3)	Cu6−O160	2.292(3)
Cu3−O142	1.968(3)	Cu6−O180	1.978(3)
Cu3−O152	1.975(3)	Cu6−O190	1.981(3)
Cu3−N34	1.958(4)	Cu6−N54	1.949(4)
Cu3−N41	1.968(4)	Cu6−N61	1.977(4)
Bond angles (°)			
O182−Cu1−O192	87.22(12)	O120−Cu4−O140	92.92(12)
O182−Cu1−N14	175.87(14)	O140−Cu4−O150	88.79(12)
O182−Cu1−N21	93.55(14)	O140−Cu4−N74	170.52(14)
O182−Cu1−O182a	76.01(13)	O140−Cu4−N81	90.72(13)
O192−Cu1−N14	88.94(14)	O150−Cu4−N74	91.40(13)
O192−Cu1−N21	170.23(14)	O150−Cu4−N81	177.93(14)
N2−Cu2−N6	96.86(14)	O110−Cu5−N51	91.69(13)
N2−Cu2−N11	81.77(15)	N51−Cu5−N71	96.82(14)
N2−Cu2−N31	171.82(15)	N51−Cu5−N92	81.82(14)
N2−Cu2−O100	90.8(2)	N51−cu5−N96	170.34(14)
N6−Cu2−N11	175.25(15)	N71−Cu5−N92	158.76(15)
N6−Cu2−O100	93.7(2)	N71−Cu5−N96	81.84(14)
O130−Cu3−O142	89.55(12)	O160−Cu6−N54	96.08(13)
O142−Cu3−O152	88.28(13)	O180−Cu6−O190	86.46(13)
O142−Cu3−N34	177.31(14)	O180−Cu6−N54	171.11(14)
O142−Cu3−N41	91.62(13)	O180−Cu6−N61	92.15(14)
N34−Cu3−N41	89.63(15)	O190−Cu6−N54	91.52(15)
O152−Cu3−N41	167.12(14)	O190−Cu6−N61	178.55(14)

methods using the program SHELXS-97,[22] and refined with the program SHELXL-97[23] against F^2 of all reflections up to a resolution of $(\sin\theta/\lambda)_{max} = 0.59$ Å^{-1}. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. O-H hydrogen atoms were fixed in their located positions, all other hydrogen atoms were refined as rigid groups. One weakly coordinated methanol molecule was only partially occupied in the crystal (occupancy 40%); its O-H hydrogen atom could not be located in the difference Fourier map and was therefore not included in the refinement. The crystal structure contains large voids (435.5 Å^3) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation (program PLATON,[24] CALC SQUEEZE, 56 e$^-$/unit cell). The drawings, structure calculations, and checking for higher symmetry were performed with the program PLATON.[24]

The Platon projection[24] of the crystal structure of $Cu_{12}(tidhd)_4(CH_3OH)_8(CH_3COO)_8](CH_3OH)_{0.8}$ is shown in Figure 2. Selected bond lengths and angles are given in Table 1.

CCDC-213532 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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