An Octanuclear Copper(II) Complex Containing the *gem*-Diol Anionic Form of Di-2-pyridyl Ketone (dpd-2H) and 2-Hydroxypyridine: Synthesis, Crystal Structure, and Properties of $[Cu_8(dpd\text{-}2H)_4(\mu_2\text{-}O_2CMe)_4\{2\text{-}(OH)C_5H_4N\}_4](ClO_4)_4\cdot4H_2O$

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Introduction

Recently, considerable research effort has been focused on studies of polynuclear complexes having novel polyhedral structures and interesting physical properties, such as magnetic and optical behavior.[1,2] The coordination behavior of di-2-pyridyl ketone (dpk) has also attracted much attention. Its hydrolyzed derivatives, namely, the *gem*-diol $(C_5H_4N)_2C(OH)_2$ (dpd), the monoanion of the *gem*-diol (dpd-H), and the dianion of the *gem*-diol (dpd-2H), are potential chelating or chelating-bridging ligands. Although a number of mononuclear complexes[3] of Pd(II),[3a] Pt(II),[3a] Au(III),[3a] Ni(II),[3b] Cu(II),[3b] Cr(III),[3c] Ru(II),[3c] and Co(III)[3d] and oligomeric polynuclear complexes[4] derived from these ligands have been isolated and crystallographically characterized, several more interesting complexes have recently been prepared and structurally characterized in our laboratories. In a recent communication, we reported a facile synthetic route to a series of discrete cubane-type complexes having a $[M_4O_4]^{n+}$ core [M = Zn(II), Cd(II), Mn(II), Co(II), Ni(II)].[5] Herein we report a novel paddle-wheel-like octanuclear Cu(II) complex, namely, $[Cu_8(dpd\text{-}2H)_4(\mu_2\text{-}O_2CMe)_4\{2\text{-}(OH)C_5H_4N\}_4](ClO_4)_4\cdot4H_2O$ (**1**) [$2\text{-}(OH)C_5H_4N$ = 2-hydroxypyridine], which contains the dianionic ligand dpd-2H.

Experimental Section

All reagents were used as received from commercial sources. C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. EPR spectra were recorded on a Bruker EMX spectrometer operating at X-band and equipped with a variable-temperature helium flow cryostat system (Oxford Instruments). Variable-temperature magnetic susceptibility data were obtained on a Quantum Design SQUID magnetometer. Experimental magnetic susceptibility data were corrected for diamagnetism of the constituent atoms.[6] The effective molar magnetic moments were calculated with the equation $\mu_{\mathrm{eff}} = 2.828(\chi_M T)^{1/2}$.

Synthesis of $[Cu_8(dpd\text{-}2H)_4(\mu_2\text{-}O_2CMe)_4\{2\text{-}(OH)C_5H_4N\}_4](ClO_4)_4\cdot4H_2O$ (1). An MeCN−H_2O solution [2:1 (v/v); 5 cm^3] of dpk (0.092 g, 0.5 mmol) was added dropwise to a stirred MeCN−H_2O solution (5 cm^3) of $Cu(O_2CMe)_2\cdot H_2O$ (0.200 g, 1.0 mmol) over 15 min at room temperature. An MeCN−H_2O solution (5 cm^3) of $2\text{-}(OH)C_5H_4N$ (0.095 g, 0.5 mmol) was then added, followed by NaO_2CMe (0.164 g, 2.0 mmol) and $NaClO_4$ (0.282 g, 2.0 mmol). The resulting solution was allowed to stand in air at room temperature for 2 weeks, yielding deep green polyhedral crystals (ca. 85% yield based on dpk). Anal. Calc for $C_{72}H_{72}N_{12}O_{40}Cl_4Cu_8$: C, 36.10; H, 3.03; N, 7.02. Found: C, 36.04; H, 2.98; N, 6.96.

Safety Note. *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.*

X-ray Crystallography. Diffraction intensities for **1** were collected at 21 °C on a Siemens R3m diffractometer using an ω-scan technique, and Lorentz−polarization and absorption corrections were applied.[7] The structure was solved with direct methods and refined with full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97 programs, respectively.[8,9] Non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically (C−H = 0.96 Å), and the aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[10] The crystallographic data for **1** are listed in Table 1, and selected bond lengths and angles are given in Table 2. Structural drawings were produced with SHELXTL.[11]

Results and Discussion

Crystal Structure. Complex **1** is composed of octanuclear $[Cu_8(dpd\text{-}2H)_4(\mu_2\text{−}O_2CMe)_4\{2\text{-}(OH)C_5H_4N\}_4]^{4+}$ cations, perchlorate anions, and lattice water molecules. As illustrated in Figure 1, each octanuclear cation contains two types of copper centers. A group of four Cu(II) atoms [Cu(2), Cu(2a), Cu(2b), Cu(2c)] are located in the inner part of the cation, while another group of four [Cu(1), Cu(1a), Cu(1b), Cu(1c)] are found on the "periphery" around the core. Each inner Cu(II) atom is bound by one nitrogen atom from a dpd-2H ligand, three oxygen atoms,

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Table 1. Crystallographic Data for **1**

empirical formula	$C_{72}H_{72}N_{12}O_{40}Cl_4Cu_8$	Z	2
fw	2395.54	ρ_{calcd} (g cm^{-3})	1.813
space group	$P\bar{4}2_1/c$	T (°C)	22(1)
a (Å)	17.205(2)	μ (mm^{-1})	2.122
b (Å)	17.205(2)	λMo Kα (Å)	0.710 73
c (Å)	14.822(3)	R1^a ($I > 2\sigma(I)$)	0.0546
V (Å^3)	4388(1)	wR2^b (all data)	0.1451

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = [\sigma^2(F_o)^2 + (0.1(\max(0, F_o^2) + 2F_c^2)/3)^2]^{-1}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**^{a}

Cu(2)···Cu(1)	3.434	Cu(2)···Cu(2b)	3.302
Cu(2)···Cu(2a)	3.287	Cu(2)···Cu(2c)	3.287
Cu(1)−O(2*a*)	1.879(4)	Cu(2)−O(1)	1.991(3)
Cu(1)−O(3)	1.934(5)	Cu(2)−O(2*a*)	2.018(4)
Cu(1)−O(4)	1.938(5)	Cu(2)−O(5)	2.127(5)
Cu(1)−N(2*a*)	1.989(5)	N(2)−Cu(1*a*)	1.989(5)
Cu(2)−O(1*b*)	1.950(3)	O(1)−C(6)	1.381(7)
O(1)−Cu(2*c*)	1.950(3)	O(2)−C(6)	1.416(6)
O(2)−Cu(1*a*)	1.879(4)	C(18)−O(4)	1.239(8)
O(2)−Cu(2*a*)	2.018(4)	C(18)−O(5)	1.261(7)
Cu(2)−N(1)	1.984(4)	O(3)−C(12)	1.254(9)
O(2*a*)−Cu(1)−O(3)	176.9(2)	C(5)−N(1)−Cu(2)	115.3(4)
O(2*a*)−Cu(1)−O(4)	96.6(2)	C(1)−N(1)−Cu(2)	124.0(4)
O(3)−Cu(1)−O(4)	86.3(2)	C(11)−N(2)−Cu(1*a*)	126.0(4)
O(2*a*)−Cu(1)−N(2*a*)	83.3(2)	C(7)−N(2)−Cu(1*a*)	113.0(4)
O(3)−Cu(1)−N(2*a*)	93.9(2)	C(6)−O(1)−Cu(2*c*)	123.9(3)
O(4)−Cu(1)−N(2*a*)	176.7(2)	C(6)−O(1)−Cu(2)	115.4(3)
O(1*b*)−Cu(2)−N(1)	173.1(2)	Cu(2*c*)−O(1)−Cu(2)	112.8(2)
O(1*b*)−Cu(2)−O(1)	93.6(1)	C(6)−O(2)−Cu(1*a*)	118.2(3)
N(1)−Cu(2)−O(1)	81.1(2)	C(6)−O(2)−Cu(2*a*)	113.5(3)
O(1*b*)−Cu(2)−O(2*a*)	89.0(2)	Cu(1*a*)−O(2)−Cu(2*a*)	123.6(2)
N(1)−Cu(2)−O(2*a*)	92.6(2)	C(18)−O(4)−Cu(1)	140.1(4)
O(1)−Cu(2)−O(2*a*)	141.4(1)	C(18)−O(5)−Cu(2)	128.2(4)
O(1*b*)−Cu(2)−O(5)	98.0(2)	C(12)−O(3)−Cu(1)	124.1(5)
N(1)−Cu(2)−O(5)	88.4(2)	O(1)−C(6)−O(2)	110.8(4)
O(1)−Cu(2)−O(5)	120.0(2)	O(4)−C(18)−O(5)	125.6(6)
O(2*a*)−Cu(2)−O(5)	97.6(2)		

[a] Symmetry codes: (*a*) −*x*, −*y*, *z*; (*b*) −*y*, *x*, −*z*; (*c*) *y*, −*x*, −*z*.

each from a separate dpd-2H ligand, and one oxygen atom from an acetate group [Cu(2)−O(1*b*) = 1.950(3), Cu(2)−N(1) = 1.984(4), Cu(2)−O(1) = 1.991(3), Cu(2)−O(2*a*) = 2.018(4), Cu(2)−O(5) = 2.127(5) Å; O(1*b*)−Cu(2)−N(1) = 173.14(17), O(1*b*)−Cu(2)−O(1) = 93.55(13), N(1)−Cu(2)−O(1) = 81.06(17), O(1*b*)−Cu(2)−O(2*a*) = 89.02(15), N(1)−Cu(2)−O(2*a*) = 92.56(18), O(1)−Cu(2)−O(2*a*) = 141.42(14), O(1*b*)−Cu(2)−O(5) = 97.97(16), N(1)−Cu(2)−O(5) = 88.44(18), O(1)−Cu(2)−O(5) = 120.02(15) = O(2*a*)−Cu(2)−O(5) = 97.60(15)°], forming a distorted square-pyramidal NO_4 geometry around the metal center. Each of the outer Cu(II) centers, on the other hand, is ligated in a square-planar NO_3 coordination environment by one nitrogen atom from a dpd-2H ligand, and three oxygen atoms, one each from a dpd-2H ligand, a 2-(OH)-C_5H_4N ligand, and an acetate ligand [Cu(1)−O(2*a*) = 1.879(4), Cu(1)−O(3) = 1.934(5), Cu(1)−O(4) = 1.938(5), Cu(1)−N(2*a*) = 1.989(5) Å; O(2*a*)−Cu(1)−O(3) = 176.9(2), O(2*a*)−Cu(1)−O(4) = 96.6(2), O(3)−Cu(1)−O(4) = 86.3(2), O(2*a*)−Cu(1)−N(2*a*) = 83.31(18), O(3)−Cu(1)−N(2*a*) = 93.9(2), O(4)−Cu(1)−N(2*a*) = 176.7(2)°]. It should be emphasized that each oxygen atom of the dpd-2H ligand binds in a μ_2-O mode that bridges one inner Cu(II) atom and one outer Cu(II) atom, with a Cu···Cu distance of 3.287−3.434 Å. In other words, the dpd-2H anion coordinates in a μ_4-η^1:η^2:η^2:η^1 ligation mode that bridges one outer Cu(II) center and three inner Cu(II) centers. To our knowledge, this type of coordination mode is rare. Only one other example has been observed in a recently reported heptanuclear Cu(II) complex.[4b]

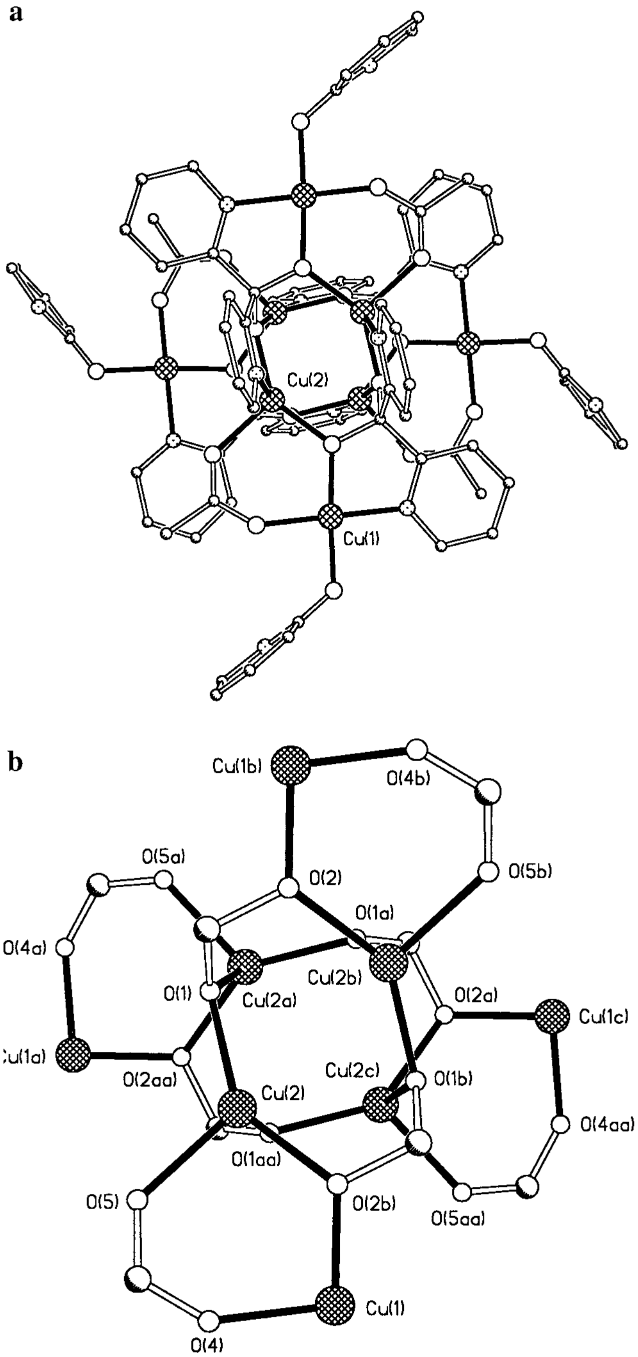

Figure 1. Perspective views of (a) the octanuclear core and (b) the bridging skeleton of the eight Cu(II) atoms in each Cu_8 core in **1**.

Each acetate group in **1** binds in a μ_2-carboxylato-*O*,*O*′ mode, bridging one inner Cu(II) atom and one outer Cu(II) atom (Cu···Cu = 3.434 Å). Although polynuclear copper(II) complexes containing up to six metal atoms are not uncommon, compounds with seven,[12] eight,[4a,13] or more[4b,c,14] copper(II) atoms remain scarce. Thus, **1** represents an excellent example of the latter compounds.

A 2-(OH)C_5H_4N ligand coordinates to an outer Cu(II) atom in a monodentate manner via its hydroxyl group. It is noteworthy

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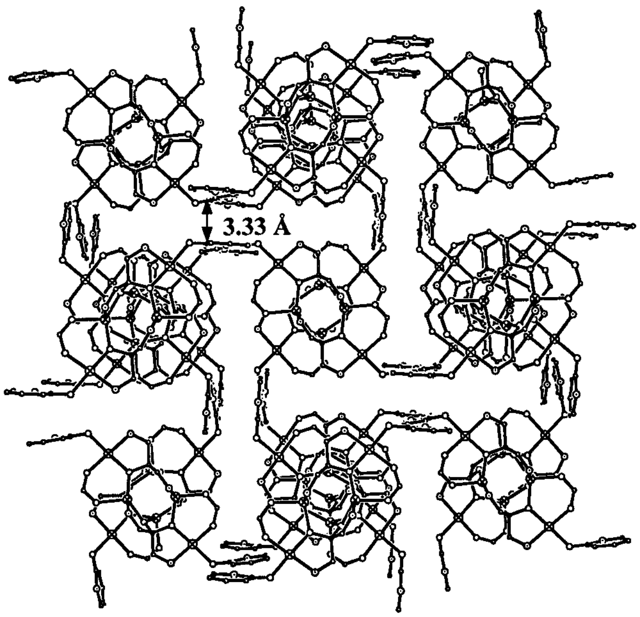

Figure 2. The three-dimensional supramolecular array formed through $\pi-\pi$ interactions in the solid state.

that the shape of the octanuclear cation resembles a paddle wheel with four 2-(OH)C_5H_4N ligands corresponding to the paddles. Close contacts between pyridyl rings of the 2-(OH)C_5H_4N ligands from adjacent Cu_8 cores, with face-to-face separations of ca. 3.33 Å, indicate strong $\pi-\pi$ stacking interactions.[15] These $\pi-\pi$ stacking interactions force the octanuclear cations into an interesting three-dimensional supramolecular array, as shown in Figure 2.

Cyclic Voltammetry. The redox behavior of **1** was studied by cyclic voltammetry in acetonitrile solutions containing 0.1 M Et_4NClO_4 as the supporting electrolyte at a scan rate of 50 mV s^{-1}. **1** displays two quasi-reversible reduction processes ($E_{1/2} \approx -0.93$ and -1.49 V) and one irreversible oxidation ($E_a \approx +0.17$ V) (Figure 3). The irreversible process occurring at $E_a \approx +0.17$ V in the anodic domain corresponds to a single-electron transfer, with its current height being about 0.25 times higher than that of the quasi-reversible wave occurring at -1.01 or -1.55 V. Although the electroactivity of **1** in the solution is thus detected, it seems difficult to ascribe unequivocally any of the waves to metal- rather than to ligand-centered electron transfer.[16] The fact that the anodic wave at $E_a \approx +0.17$ V behaves like a platform suggests that **1** may be oxidized continuously across a wide anodic potential range with the electron-rich dpd-2H ligands as the electron acceptors.[17] It should be noted that when the potential is higher than 1.45 V, the cluster begins to decompose.

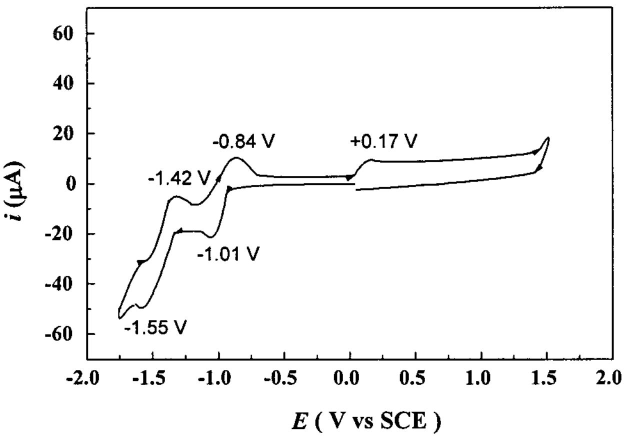

Figure 3. Cyclic voltammetry of **1** in MeCN (1.0×10^{-4} M; 0.1 M Et_4NClO_4, Pt working electrode, Pt counter electrode, SCE reference electrode, scan rate $v = 50$ mV s^{-1}).

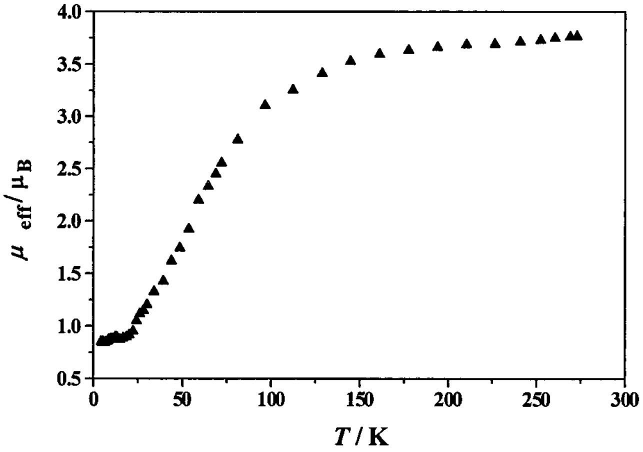

Figure 4. Plot of effective magnetic moment per Cu^{II}_8 vs *T*.

A remarkable pattern in the cathodic domain is observed for **1**. The quasi-reversible process occurring at $E_{1/2} \approx -0.93$ V ($\Delta E_p = 170$ mV, equal current height) can be attributed to the Cu(II)/Cu(I) redox couples corresponding to the four outer Cu(II) atoms. Coulometry of this process indicates a multielectron redox process. This assignment is based on a comparison with the $E_{1/2}$ value reported for [CuL(H_2O)(ClO_4)] (HL = 4-methyl-5-[(imidazol-1-yl)methylidene]-β-alanine).[18] The other quasi-reversible process occurring at $E_{1/2} \approx -1.49$ V ($\Delta E_p = 130$ mV, equal current height) can be assigned to the Cu(II)/Cu(I) redox couples corresponding to the four inner Cu(II) centers of **1**. These observations suggest that the cation of **1** is stable in acetonitrile and that the outer four and inner four Cu(II) atoms of **1** are reduced at different cathodic potentials, as shown in Scheme 1.

Scheme 1

$$\text{decomposition} \xleftarrow{>1.45\text{ V}} \text{a single-electron charge transfer} \xleftarrow{0.17\text{ V}}$$

$$Cu^{II}_8 \underset{-4e}{\overset{+4e}{\rightleftharpoons}} Cu^{II}_8Cu^{I}_4 \underset{-4e}{\overset{+4e}{\rightleftharpoons}} Cu^{I}_8$$

Magnetic Properties and EPR Spectra. Magnetic susceptibility data were measured with a polycrystalline sample of **1** in a 5.0 kG field over the temperature range 4−273 K. Figure 4 shows the effective magnetic moments per Cu_8 unit (μ_{eff})

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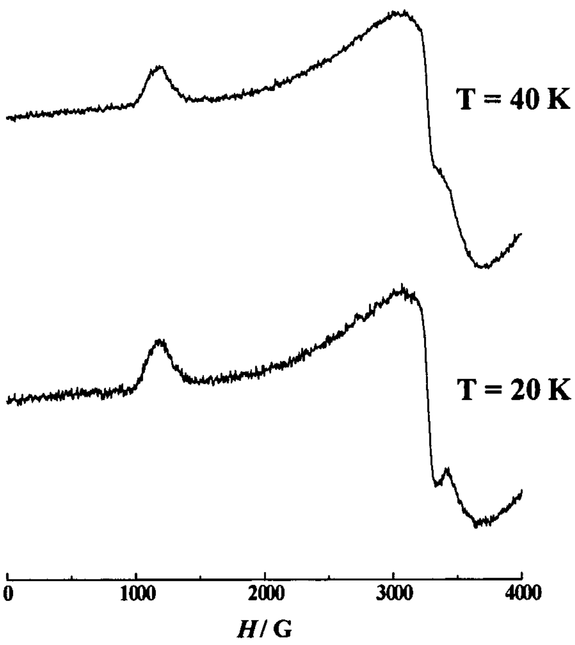

Figure 5. X-Band EPR spectra of **1** in frozen acetonitrile solutions.

versus temperature. The effective moment of 3.77 μ_B per Cu_8 unit at 273 K is greatly below the value $[((\sum 4S_i(S_i + 1))^{1/2} = 4.90\ \mu_B]$ for a noninteracting Cu_8 unit. When the temperature is lowered, the magnetic moment decreases slowly from 3.77 μ_B at 273 K to 3.53 μ_B at 145 K and then decreases dramatically to ca. 0.86 μ_B at 4.2 K, indicating a strong intramolecular antiferromagnetic interaction. Unfortunately, it is difficult to fit the behavior of the eight copper centers to a current theory.

X-Band EPR spectra of **1** in frozen acetonitrile solution were recorded at 20 and 40 K (Figure 5). Two features, one with an intense broad signal centered at $g \approx 1.9$ and the other with a signal at $g \approx 5.7$, are believed to be consequences of a complicated exchange coupling among the eight Cu(II) atoms within the cluster. This suggestion is consistent with the results of the magnetic susceptibility measurements.

Conclusions

A novel paddle-wheel-like octanuclear copper(II) complex, $[Cu_8(dpd\text{-}2H)_4(\mu_2\text{-}O_2CMe)_4\{2\text{-}(OH)C_5H_4N\}_4](ClO_4)_4\cdot 4H_2O$ (**1**), is synthesized by the reaction of $Cu(OAc)_2$ with dipyridyl ketone and 2-hydroxypyridine. X-ray crystallography shows that the octanuclear $[Cu_8(dpd\text{-}2H)_4(\mu_2\text{-}O_2CMe)_4\{2\text{-}(OH)C_5H_4N\}_4]^{4+}$ cationic core contains two types of copper centers that are bridged by oxygen atoms of the dpd-2H ligands and the μ_2-carboxylato-*O,O′* acetate groups. Four of the Cu(II) atoms are located in the inner part of the cationic core, while the other four are found on the “periphery” around the core. The shape of the octanuclear core resembles a paddle wheel with the 2-(OH)C_5H_4N ligands corresponding to the paddles. Cyclic voltammetry indicates that the cation of **1** is stable in acetonitrile and that the outer four and inner four Cu(II) atoms of **1** are reduced at different cathodic potentials. Magnetic susceptibility measurements and EPR spectroscopy suggest that a strong antiferromagnetic interaction among the copper centers is present within the cluster.

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Supporting Information Available: An X-ray crystallographic file, in CIF format for the structure determination of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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