Synthesis, Crystal Structures, and Magnetic Properties of Two New 1D Copper(II) Coordination Polymers Containing Fumarate(−2) and Chelating N,N′-Donor as Ligands

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Two new polynuclear complexes of Cu^{II}, $[Cu_2(fum)(\mu\text{-}OH)(bpy)_2(H_2O)](NO_3)\cdot 2H_2O$ (**1**) (fum = fumarate dianion, bpy = 2,2′-bipyridine) and $[Cu(fum)(tmen)]\cdot 2H_2O$ (**2**) (tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine), have been synthesized and structurally characterized by X-ray crystallography. Complex **1**, $C_{24}H_{27}Cu_2N_5O_{12}$, crystallizes in a triclinic system, space group $P\bar{1}$, with a = 10.168(14), b = 11.347(14), c = 14.74(2) Å, and Z = 2; complex **2**, $C_{10}H_{22}CuN_2O_6$, crystallizes in an orthorhombic system, space group *Pbca*, with a = 14.701(19), b = 14.899(19), c = 26.90(3) Å, and Z = 16. Compound **1** is an alternating chain compound, with alternate repetition of bis(monodentate) (μ_2) and bis(bidentate) (μ_4) bridging modes of fumarate, showing ferromagnetic interaction between Cu^{II} ions through hydroxo bridges with a Cu–O–Cu angle of 108.5°. Compound **2** is a linear 1D zig-zag polymer. There are two copper(II) ions with equivalent coordination and geometry in the asymmetric unit, each of them bonded to a bidentate tmen ligand and to two different fumarate moieties. Magnetic susceptibility data were measured in the 300–2 K temperature range. The magnetic data for **1** were fitted by use of a ferromagnetic/antiferromagnetic alternating S = 1/2 chain system and show the following results: J_F = +5.4 cm^{-1}, J_{AF} = −0.25 cm^{-1}, g = 1.96. The susceptibility data of **2** were fitted by use of the Bonner–Fisher expression for antiferromagnetically coupled S = 1/2 local spins, giving the parameters J = −1.81 cm^{-1}, g = 2.03.

Introduction

The chemistry of metal complexes containing paramagnetic metal ions and exhibiting extended structures is at the forefront of modern research, due to these compounds' potential applications in molecular magnetism.[1−4] The most useful strategy by which to construct such extended systems is to employ appropriate bridging ligands capable of binding metal centers through direct bond formation, promoting magnetic interactions. Di- and polycarboxylates are good candidates as bridging ligands for the construction of such extended systems. Previous reports have revealed that dicarboxylic acids can coordinate to metal centers either in the chelating bis(bidentate) mode or as bridging bis(monodentate) ligands.[5−7] Although the use of various dicarboxylic acids to form bridges between paramagnetic metal centers has been extensively studied with terephthalate, malonate, oxalate, maleate, etc.,[8−12a] systems with fumarate as bridging ligand are much fewer in number,[12b] due to their poor solubilities in all common organic solvents. Our current attention to the use of fumarate dianion as an organic coupler with which to obtain polymetallic complexes[1,4,13,14] is due to its versatile coordination mode (Scheme 1). We have recently reported a few fumarate-bridged Cu^{II} and Ni^{II} systems.[13,14] Here we report the synthesis and structural characterization of two different kinds of copper(II) fumarate systems that make use of N-donor ligands − 2,2′-bipyridine (bpy) and *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (tmen) − as blocking ligands. Both were magnetically characterized, interestingly showing different kinds of magnetic behavior. Complex **1** is a chain of $[Cu_2(fum)(\mu\text{-}OH)(bpy)_2(H_2O)](NO_3)\cdot 2H_2O$ (fum = fumarate dianion, bpy = 2,2′-bipyridine) with alternate repetition of bis(monodentate) (μ_2) and bis(bidentate) (μ_4) fumarate bridging modes. It represents the first molecular system with both bis(monodentate) and bis(bidentate) bridging fumarate. Magnetic studies show the existence of ferromagnetic exchange coupling between the Cu^{II} ions through the hydroxo bridge. To the best of our knowledge, this is the first report of a ferromagnetic interaction between Cu^{II} ions through a hydroxo bridge with a Cu−O−Cu angle as large

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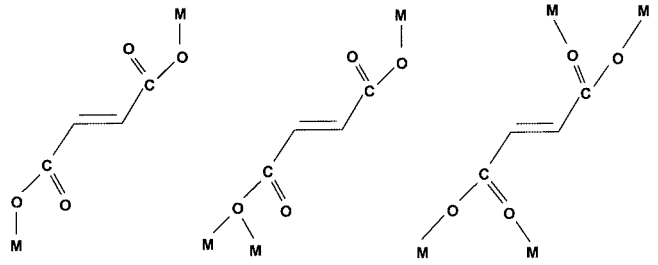
as 108.5°. Complex **2** is a one-dimensional zig-zag polymer of composition $[Cu(fum)(tmen)]\cdot 2H_2O$. Here, fumarate coordinates in bis(monodentate) bridging fashion, and a weak antiferromagnetic interaction (300−2 K) is observed between the two Cu^{II} centers. The attainment of magnetic ordering generally requires the organization of transition metal centers into three-dimensional networks, but reduced dimensionalities (one- and two-dimensional) are preferable for development of the necessary theoretical models required for better interpretation of the magnetic properties of three-dimensional coordination polymers. In this context, one-dimensional systems (such as complexes **1** and **2**) are being thoroughly investigated from both experimental and theoretical viewpoints.



Scheme 1

Results and Discussion

Description of the Structures

$[Cu_2(fum)(\mu\text{-}OH)(bpy)_2(H_2O)]\ (NO_3)\cdot 2H_2O$ (1)

This complex is a one-dimensional polymeric chain made up of dinuclear (bpy)CuOHCu(bpy) units linked together by fumarate anions. The fumarate ligand adopts two bridging coordination modes through the chain, bis(monodentate) and bis(bidentate) (Figure 1). The two Cu^{II} ions in the asymmetric unit are in square-pyramidal environments each with one additional weak bond (shown as dotted line in Figure 1) to complete the octahedron. Thus, Cu(1) is bonded to the bridging hydroxide O(1) at 1.921(5) and to the two nitrogen atoms of the bipyridine ligand at 2.005(5) and 2.030(4) Å. It is also bonded to O(31) [at 2.026(5) Å] and O(41) [at 2.196(5) Å] from bridging fumarate ligands, the latter being the axial position. The second axial site is completed with a weak interaction to O(33) [2.800(2) Å]. The Cu(2) atom is bonded to the bridging hydroxide ion at 1.926(5) Å, to two nitrogen atoms of the bipyridine ligand at 2.010(5) and 2.027(6) Å, to an oxygen atom belonging to the bridging fumarate ligand at 1.940(4) Å, and to a water molecule at 2.420(6) Å in the axial position. The sixth coordination site is completed with a weak bond to a fumarate ligand oxygen atom O(31) at 2.720(2) Å. The Cu···Cu distance in complex **1** is 3.1212 Å. The

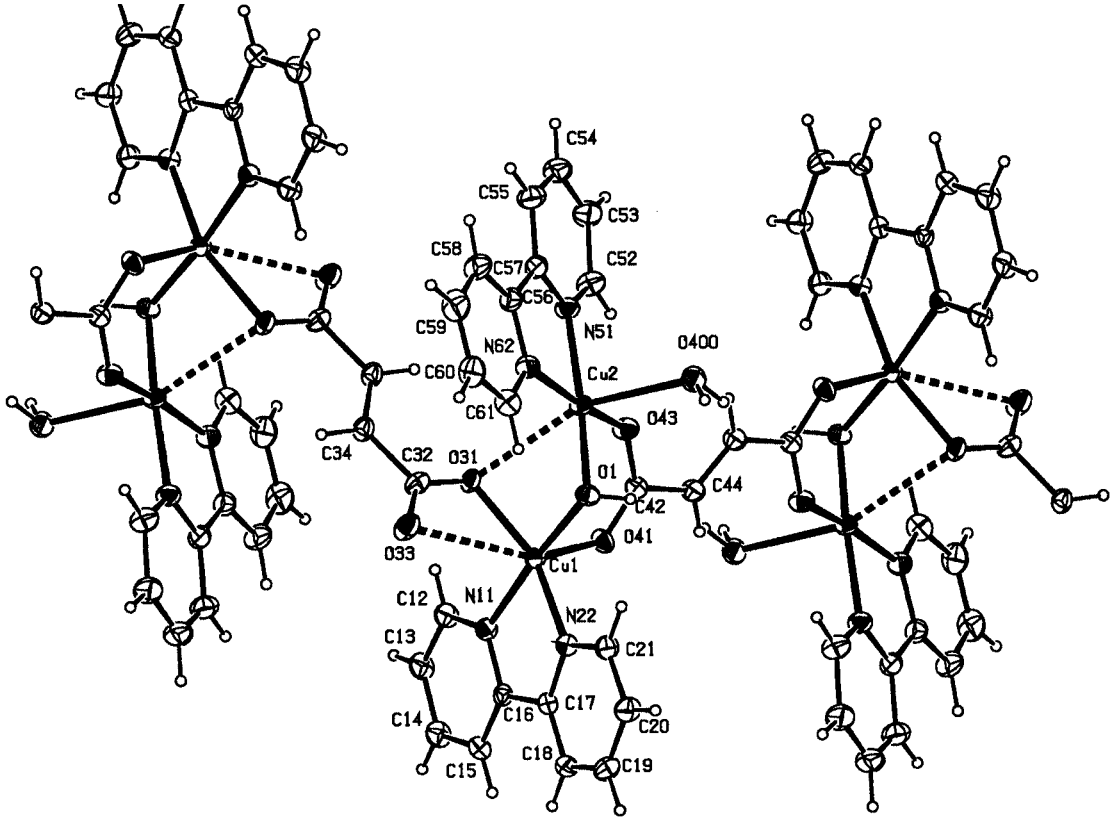


Figure 1. The polymeric structure of **1** at 20% probability; weak bonds in the metal coordination spheres are shown as dotted lines; the nitrate anion and the lattice water molecules in the asymmetric unit are not shown

structure is stabilized by an extensive hydrogen bond network with the water molecules and nitrate anion. The alternate repetition of the bidentate and tetradentate bridging modes of the fumarate makes the compound unique.

[Cu(fum)(tmen)]·2H$_2$O (2)

The structure of **2** is shown in Figure 2, together with its atom numbering scheme. In this complex the copper atoms are each in a four-coordinate square-planar environment, the asymmetric unit possessing two metal atoms. Each has equivalent coordination and geometry and each is part of a self-contained quasi-one-dimensional zig-zag polymer (Figure 3). Each metal ion is bonded to a bidentate tmen ligand and to two different fumarate ligands. The ligands are centrosymmetric. The carboxylate groups can be considered to be monodentate, with distances of 1.985(4)/2.015(4) and 2.001(4)/1.987(4) Å in the two coordination spheres, but the other oxygen atoms are weakly bonded at distances ranging from 2.450(5) to 2.592(5) Å, and could be considered to complete a distorted octahedral coordination sphere. The Cu···Cu distances in complex **2** are Cu−Cu (interchain) 7.3526 Å and Cu−Cu (intrachain) 9.0421 Å.

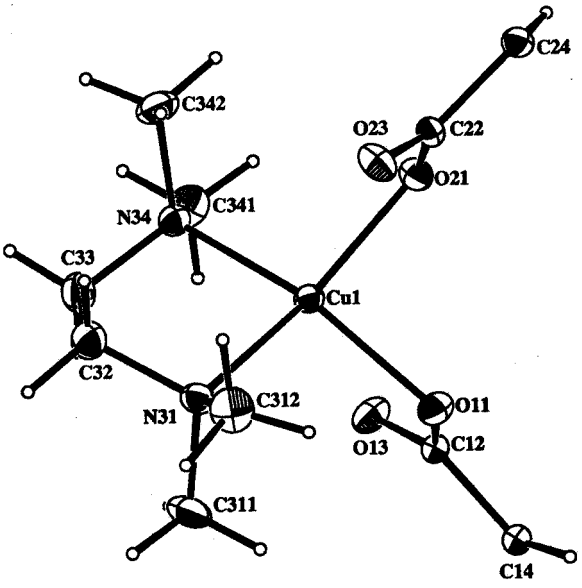


Figure 2. The coordination sphere of Cu^{II} in complex **2**; the ellipsoids are at 15% probability

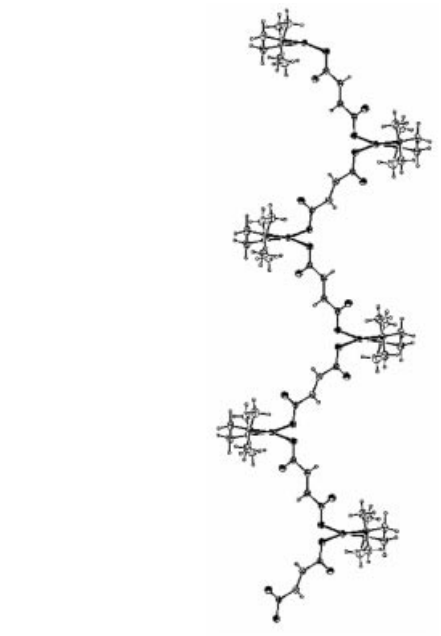


Figure 3. View of the zig-zag chain for complex **2**

Magnetic Results

Variable-temperature magnetic susceptibility data for complexes **1** and **2** were collected in the 300−2 K temperature range with a SQUID magnetometer. For complex **1**, the $\chi_M T$ value at room temperature corresponds to what is expected for isolated $S = 1/2$ spins (0.73 cm^{3}mol^{-1}K, $g = 1.96$). On cooling down, $\chi_M T$ increases, reaches a maximum of 0.83 cm^{3}mol^{-1}K at $T = 4$ K, and then rapidly decreases (Figure 4). This behavior can be explained by the existence of a ferromagnetic interaction between the Cu^{II} ions within the hydroxo- and carboxylato-bridged dinuclear unit and a much weaker antiferromagnetic interaction between the dinuclear units through the fumarate bridges. The magnetic data were therefore fitted by use of a ferromagnetic/antiferromagnetic alternating[15−16] $S = 1/2$ chain system and gave the following results: $J_F = +5.4$ cm^{-1}, $J_{AF} = -0.25$ cm^{-1}, $g = 1.96$, and an agreement factor $R = 6{\cdot}10^{-6}$. The ferromagnetic exchange coupling between the Cu^{II} ions is surprising because of the presence of a hydroxo bridge with a Cu−O−Cu angle of 108.5°. The presence of a carboxylato bridge within the dinuclear unit might produce a counter-complementarity between the two bridges, which could explain the ferromagnetic interaction. However, this cannot reasonably be operative since the oxygen atom O(41) of the bridging carboxylate group linked to Cu(1) is in an apical

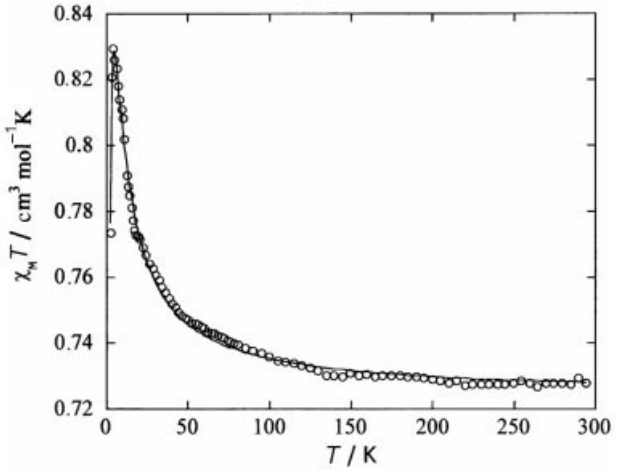
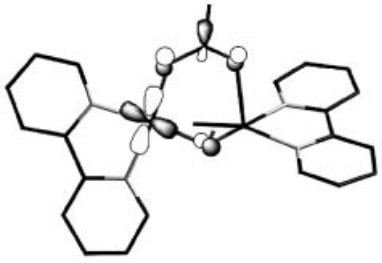
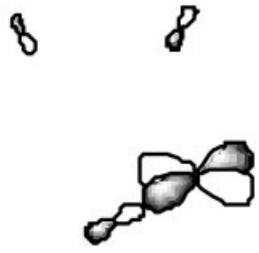


Figure 4. Plot of $\chi_M T$ versus T for complex **1**; the solid line shows the best fit obtained

position and the carboxylate bridge does not participate much in the magnetic coupling. In order to understand the experimentally observed ferromagnetic interaction, we carried out semiempirical calculations on the dinuclear unit.[17] The results show that the two single electrons are described by molecular orbitals (Schemes 2 and 3) mainly localized on each copper atom.[18]



Scheme 2



Scheme 3

From a structural viewpoint, complex **2** is a homogeneous chain of Cu^{II} with fumarate bridging. The geometry of each Cu^{II} is distorted octahedral. A plot of $\chi_M T$ against T is given in Figure 5, and shows a gradual decrease in $\chi_M T$ value with decreasing temperature, revealing the existence of antiferromagnetic interaction within the chain. The temperature dependence of the susceptibility data was analyzed by use of the Bonner−Fisher expression for antiferromagnetically coupled $S = 1/2$ spins.[19]

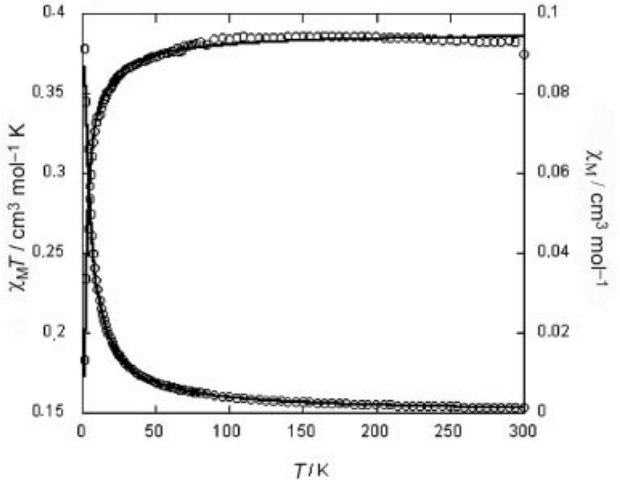


Figure 5. Plot of $\chi_M T$ versus T for complex **2** with solid lines showing the best fit obtained

The Hamiltonian for the isotropic interaction between nearest neighbor ions is

$$H = -J\sum_{i=1}^{n-1} S_i \cdot S_{i+1}$$

and according to Bonner and Fisher[20] the molar susceptibility is given by

$$\chi = \frac{Ng^2\beta^2(0.25 + 0.074975x + 0.075235x^2)}{kT(1 + 0.9931x + 0.172135x^2 + 0.757825x^3)}$$

where $x = |J|/kT$ and J is the exchange coupling parameter describing the magnetic interaction between any two nearest-neighbor $S = 1/2$ spins. The results of the best fit (Figure 5) are $J = -1.81\text{cm}^{-1}$, $g = 2.03$, and $R = 2.9\cdot10^{-5}$ (R is the agreement factor defined as $R = [(\chi_M)_{obsd.} - (\chi_M)_{calcd.}]^2/[(\chi_M)_{obsd.}]^2$). The very low J value is obviously due to a long-range superexchange pathway and this result agrees with previously reported results.[1e,4]

Conclusion

Fumarate(−2) has been employed as a bridging ligand, because of its potential for the construction of coordination polymers with different structures and its possible combination with bidentate bridging (and not chelating) N,N′-donors, as in previous work by our group.[1e,4] We present here the synthesis, single-crystal X-ray structure, and magnetic behavior of two fumarate-bridged Cu^{II} complexes. Complex **1** is a one-dimensional polymeric chain made up of dinuclear (bpy)CuOHCu(bpy) units linked together by fumarate anions. The fumarate ion adopts two coordination bridging modes through the chain, bis(monodentate) and bis(bidentate). The magnetic data were thus fitted by use of a ferromagnetic/antiferromagnetic alternating $S = 1/2$ chain system, with the result $J_F = +5.4\ \text{cm}^{-1}$, $J_{AF} = -0.25\ \text{cm}^{-1}$, $g = 1.96$, and an agreement factor $R = 6\cdot10^{-6}$. The ferromagnetic exchange coupling between the Cu^{II} ions is unusual because of the presence of a hydroxo bridge with a Cu−O−Cu angle of 108.5°. Compound **2** is a 1D zig-zag chain of Cu^{II} in which the fumarate ion binds in a bis(monodentate) fashion and the diamine is a blocking ligand. Fitting of the temperature-dependent susceptibility data (300−2 K) by use of the Bonner−Fisher equation gives $J = -1.81\ \text{cm}^{-1}$.

Experimental Section

Synthesis

$[Cu_2(fum)(\mu\text{-}OH)(bpy)_2(H_2O)](NO_3)\cdot2H_2O$ (1): $Cu(NO_3)_2\cdot3H_2O$ (1 mmol) dissolved in water/methanol (50:50) solution (15 mL) was mixed with 2,2′-bipyridine (1 mmol). A water/methanol (50:50) solution (10 mL) of fumaric acid (1 mmol) and triethylamine (2 mmol) was added, and the mixture was heated under reflux for 1 h at 80 °C. A sky-blue solid separated, and this remained insoluble in all common organic solvents. It was dissolved in a minimum amount of dilute (4 N) ammonia and allowed to crystallize. After

a week, suitable green single crystals of X-ray diffraction quality were obtained. Yield ca. 60%. $C_{24}H_{27}Cu_2N_5O_{12}$ (704.59): calcd. C 40.8, H 3.8, N 9.9; found C 40.9, H 3.6, N 9.8.

[Cu (fum)(tmen)]·2H$_2$O (2): A methanolic solution (10 mL) of $Cu(NO_3)_2·3H_2O$ (1 mmol) and tmen (1 mmol) was added dropwise, with constant stirring, to a water/methanol (50:50) solution (10 mL) of fumaric acid (1 mmol) and triethylamine (2 mmol). Suitable blue single crystals of X-ray diffraction quality were obtained after a week on keeping the resulting blue solution in a refrigerator. Yield ca. 65%. $C_{10}H_{22}CuN_2O_6$ (329.81): calcd. C 36.5, H 6.4, N 8.6; found C 36.3. H 6.6, N 8.4.

Crystallographic Data Collection and Refinement: Intensity data were collected with Mo-K_α radiation by use of the MAR research Image Plate System. The crystals were positioned at 70 mm from the Image Plate. 100 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[21] The structures were solved by direct methods with the SHELX-86 program.[22] In both structures, the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structures were refined on F^2 by use of SHELXL-93.[23]. Selected bond lengths and angles are given in Table 1 (complex **1**) and Table 2 (complex **2**). Selected crystallographic data are summarized in Table 3 and hydrogen bonds of complex **1** are shown in Table 4. CCDC-165333 and -185540 for complexes **1** and **2**, respectively, contain 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].

Table 1. Selected bond lengths [Å] and bond angles [°] in complex **1**

Cu(1)−O(1)	1.921(5)	Cu(1)−O(31)	2.026(5)
Cu(1)−O(41)	2.196(5)	Cu(1)−N(11)	2.005(5)
Cu(2)−O(1)	1.926(5)	Cu(2)−O(43)	1.940(4)
Cu(2)−O(400)	2.420(6)	Cu(2)−N(51)	2.027(6)
Cu(2)−N(62)	2.010(5)	O(1)−Cu(1)−O(31)	89.60(18)
O(1)−Cu(1)−O(41)	91.19(17)	O(1)−Cu(1)−N(11)	175.44(18)
O(1)−Cu(1)−N(22)	96.23(19)	O(31)−Cu(1)−O(41)	93.87(16)
O(31)−Cu(1)−N(11)	94.77(18)	O(31)−Cu(1)−N(22)	157.27(16)
O(41)−Cu(1)−N(11)	87.24(18)	O(41)−Cu(1)−N(22)	107.90(17)
O(400)−Cu(2)−N(51)	92.90(20)	O(400)−Cu(2)−N(62)	96.05(19)
N(51)−Cu(2)−N(62)	80.30(20)		

Table 2. Selected bond lengths [Å] in complex **2**

Cu(1)−O(21)	1.985(4)	Cu(2)−O(48)	1.987(4)
Cu(1)−O(11)	2.015(4)	Cu(2)−O(41)	2.001(4)
Cu(1)−N(34)	2.034(5)	Cu(2)−N(51)	2.040(5)
Cu(1)−N(31)	2.036(5)	Cu(2)−N(54)	2.041(4)
Cu(1)−O(23)	2.592(5)	Cu(2)−O(43)	2.533(5)
Cu(1)−O(13)	2.450(5)	Cu(2)−O(47)	2.546(5)

Table 3. Crystal data and structure determination for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{24}H_{27}Cu_2N_5O_{12}$	$C_{10}H_{22}CuN_2O_6$
Formula mass	704.59	329.81
Space group	$P\bar{1}$	*Pbca*
a [Å]	10.168(14)	14.701(19)
b [Å]	11.347(14)	14.899(19)
c [Å]	14.74(2)	26.90(3)
α, β, γ [°]	109.936(10), 93.334(10), 113.470(10)	90, 90, 90
V [Å^3]	1428	5892(13)
Z	2	16
T [°C]	20	20
λ(Mo-K_α) [Å]	0.71073	0.71073
$\rho_{calcd.}$ [g cm^{-1}]	1.633	1.469
μ(Mo-K_α) [mm^{-1}]	1.6	1.5
R[a]	0.0621	0.0588
$R_w{}^2$ [b]	0.1803	0.1696

[a] $R = \|\|F_o| - |F_c\|\|/|F_o|$. [b] $Rw = [\{w(F_o^2 - F_c^2)^2\}/\{w(F_o^2)^2\}]^{1/2}$.

Table 4. Hydrogen bonds [Å, °] for complex **1**

D−H···A	D−H	H···A	D···A	D−H···A
O400−H401···O101	0.91(2)	2.00(3)	2.895(8)	165(7)
O400−H401···O103	0.91(2)	2.56(6)	3.260(9)	134(6)
O400−H402···O402	0.89(6)	1.88(7)	2.754(10)	166(8)
O402−H421···O102	0.97(10)	1.96(10)	2.892(11)	161(9)
O402−H422···O403	0.84(10)	1.96(11)	2.771(12)	163(10)
O403−H431···O33	0.92(7)	1.97(6)	2.805(8)	150(7)
O403−H432···O401	0.90(8)	1.97(8)	2.808(10)	154(7)

Physical Measurements: Elemental analyses (carbon, hydrogen, and nitrogen) were performed with a Perkin−Elmer 240C elemental analyzer. The magnetic measurements were carried out on polycrystalline samples with a SQUID magnetometer working in the 300−2 K temperature range. Diamagnetic corrections were estimated from Pascal's Tables.

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