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Article

A Novel Bis Tridentate Bipyridine Carboxamide Ligand and Its Complexation to Copper(II): Synthesis, Structure, and Magnetism

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A new bis tridentate ligand 2,2′-bipyridine-3,3′-[2-pyridinecarboxamide] H_2L_1 which can bind transition metal ions has been synthesized via the condensation of 3,3′-diamino-2,2′-bipyridine together with 2-pyridine carbonyl chloride. Two copper(II) coordination compounds have been prepared and characterized: $[Cu_2(L_1)(hfac)_2]\cdot 3CH_3CN\cdot H_2O$ (**1**) and $[Cu_2(L_1)Cl_2]\cdot CH_3CN$ (**2**). The single-crystal X-ray structures reveal that complex **1** crystallizes in the triclinic space group $P\bar{1}$, with the unit cell parameters $a = 12.7185(6)$ Å, $b = 17.3792(9)$ Å, $c = 19.4696(8)$ Å, $\alpha = 110.827(2)°$, $\beta = 99.890(3)°$, $\gamma = 97.966(3)°$, $V = 3868.3(3)$ Å^3, $Z = 4$, $R = 0.0321$ and $R_w = 0.0826$. Complex **2** crystallizes in the monoclinic space group $P2_1/n$ with the unit cell parameters $a = 12.8622(12)$ Å, $b = 9.6100(10)$ Å, $c = 19.897(2)$ Å, $\beta = 102.027(3)°$, $V = 2405.3(4)$ Å^3, $Z = 4$, $R = 0.0409$ and $R_w = 0.1005$. In both complexes the ligand is in the dianionic form and coordinates the divalent Cu^{II} ions via one amido and two pyridine nitrogen donor atoms. In **1**, the coordination geometry around both Cu^{II} ions is best described as distorted trigonal bipyramidal where the remaining two coordination sites are satisfied by hexafluoroacetylacetonate counterions. In **2** both Cu^{II} ions adopt a (4 + 1) distorted square pyramidal geometry. One copper forms a longer apical bond to an adjacent carbonyl oxygen atom, whereas the second copper is chelated to a neighboring Cu–Cl chloride ion to afford a μ-Cl-bridged dimerized $[Cu_2(L_1)Cl_2]_2$ complex. The magnetic susceptibility data for **1** (2 –270 K), reveal the occurrence of weak antiferromagnetic interactions between the Cu^{II} ions. In contrast, variable-temperature magnetic susceptibility measurements for **2** reveal more complex magnetic properties, with the presence of a weak antiferromagnetic exchange ($J = -10.1$ K) between the copper ions in each dinuclear copper complex and a stronger ferromagnetic exchange interaction ($J = 32.9$ K) between the Cu^{II} ions of the $Cu(\mu\text{-}Cl)_2Cu$ dimeric bridging units.

Introduction

There has been great interest in supramolecular transition metal coordination chemistry since self-assembly through coordinate bond formation has proven to be a powerful tool for constructing rings, chains, and networks.[1] The carboxamide group, with its biological significance in the primary structure of proteins, is also an important building block for coordination chemists. A promising class of multidentate ligands containing this linkage are pyridine carboxamides that are available from condensation reactions between pyridyl-bearing amine or carboxylic acid precursors. In recent years, symmetric as well as asymmetric ligands with equal or different pyridine rings have been prepared.[2] Upon deprotonation of the carboxamide nitrogen atom, this center and the pyridyl ring(s) of the anion chelate to metal ions. Deprotonated amide groups generally coordinate via the nitrogen atom, whereas coordination via oxygen is most commonly observed for the neutral ligands. In this respect, metal complexes with high-, low-, and zerovalent metals have

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been prepared.[2] Given the wealth of coordination chemistry, pyridine carboxamide ligands have found useful applications in asymmetric catalysis,[3] molecular receptors,[4] dendrimer synthesis,[5] and the preparation of platinum(II) complexes with antitumor properties.[6] The behavior of pyridine carboxamides toward biologically relevant d-block metals has been widely investigated.[2] Copper complexes have been particularly fruitful since pyridine dicarboxamide ligands support a range of coordination numbers, geometries, and nuclearities for copper(II).[7] Although primarily studied for their biological[8] and catalytic applications,[9] these ligands have also found applications as precursors to molecule-based magnetic materials.[10] In contrast, carboxamide ligands containing the 2,2′-bipyridine moiety are much more rare and have not realized their full potential as versatile ligands in the field of coordination chemistry. In earlier studies, we reported a synthetic strategy for the preparation of 3,3-diamino-2,2′-bipyridine together with an overview of its coordination chemistry.[11] We have now turned our attention to exploit the amine functionality of this ligand. We describe herein, the preparation of a new tridentate 2,2′-bipyridine dicarboxamide ligand prepared from 3,3′-diamino-2,2′-bipyridine and 2-pyridine carbonyl chloride,[12] together with an investigation of the coordination chemistry and magnetic properties of two dinuclear copper(II) complexes.

Experimental Section

Physical Measurements. Elemental analyses were carried out at Guelph Chemical Laboratories, Guelph, Ontario. ^{1}H- and ^{13}C NMR spectroscopy were carried out on a Bruker Advance DPX 300 spectrometer. IR spectra were measured with a Mattison Research Series FT-IR spectrometer with a KBr pellet. Magnetic susceptibility measurements were made on a Quantum Design SQUID magnetometer in an applied field of 500 G between 2 and 270 K for **1** and in an applied field of 100 G between 5 and 270 K for compound **2**.

Synthesis. All chemicals and solvents used during the syntheses were reagent grade. 3,3′-Diamino-2,2′-bipyridine and 2-pyridine carbonyl chloride were prepared via literature procedures.[11,12]

H_2L_1. To a solution of 2-pyridine carbonyl chloride[12] (1.19 g, 8.41 mmol) in dry dichloromethane (10 mL) was added 3,3′-diamino-2,2′-bipyridine (0.78 g, 4.20 mmol), and the resulting clear, colorless solution was slowly dropped into triethylamine (1.80 mL, 12.60 mmol) at 0 °C to afford a yellow precipitate. The mixture was kept at 0 °C for 2 h after which time it was heated to 45 °C for 3 h. The solution was cooled, and the resulting precipitate was collected by filtration, washed with saturated aqueous $NaHCO_3$ solution, water, acetone, and diethyl ether. Drying under vacuum afforded the desired product as a pale-yellow solid. Yield 1.25 g, 51%. Mp. 218 °C dec. $C_{22}H_{16}N_6O_2$: calcd C 66.65, H 4.07, N 21.20; found C 66.74, H 3.72, N 20.80. δ_H($CDCl_3$): 14.71 (s, 2H, NH), 9.36 (d, 2H, $J = 8.3$ Hz 6,6′-H_{bipy}), 8.79 (d, 2H, $J = 1.8$ Hz 4,4′-H_{bipy}), 8.65 (dd, 2H, $J = 1.8$ Hz 6,6′-H_{py}) 8.29 (d, 2H, $J = 7.65$ Hz 3,3′-H_{py}) 7.92 (t, 2H, $J = 7.42$ Hz 4,4′-H_{py}), 7.50 (m, 4H, 5,5′-H_{py}, 5,5′-H_{bipy}). δ_C ($CDCl_3$): 164.01 (C═O), 152.65 (2-C_{py}), 148.52 (6-C_{py}), 143.22 (2-C_{bipy}), 141.46 (6-C_{bipy}), 137.37 (4-C_{py}), 136.01 (3-C_{bipy}), 129.95 (4-C_{bipy}), 126.37 (5-C_{py}), 124.03 (5-C_{bipy}), 122.73 (3-C_{py}). IR (cm^{-1}) 2925.63, 1674.86 (C═O), 1518.75, 1432.67, 1385.18, 1293.6. 1224.41, 804.70, 738.01, 691.60. HRMS (EI): calcd for $C_{22}H_{16}N_6O_2$ 396.4017, found 396.1332.

$[Cu_2(L_1)(hfac)_2]\cdot 3CH_3CN\cdot H_2O$ (1). Amide ligand H_2L_1 (0.198 g, 0.50 mmol) was added to a stirred solution of $Cu^{II}(hfac)_2$ (0.248 g, 0.50 mmol) in MeOH (5 mL). The mixture was stirred for 1 day at room temperature, and the resulting precipitate was collected by filtration, washed with *n*-pentane, and dried to afford a green crystalline solid. Yield 0.305 g, 65%. The compound was recrystallized from acetonitrile to afford single crystals of **1** suitable for X-ray diffraction experiments. IR (KBr, cm^{-1}): 3408, 2361, 1638 (C═O), 1600, 1557, 1528, 1495, 1476, 1423, 1349, 1300, 1257, 1209, 1147, 1088, 1047, 996, 902, 803, 753, 691, 669, 587; MS (FAB): *m*/*z* 727 $[Cu_2(L_1)(hfac)]^+$, 100%; $C_{38}H_{27}N_9O_7Cu_2F_{12}$: calcd C42.39, H 2.53, N 11.71; found C 42.02, H 2.41, N 11.65.

$[Cu_2(L_1)Cl_2]\cdot CH_3CN$ (2). Amide ligand H_2L_1 (0.198 g, 0.50 mmol) was added to a solution of copper(II) chloride (0.010 g, 1.00 mmol) in MeOH (5 mL). The mixture was stirred for 1 day at room temperature, and the resulting precipitate was filtered, washed with *n*-pentane, and dried to afford the green crystalline solid $[Cu_2(L_1)Cl_2]$. Yield 0.084 g, 28%. IR (KBr, cm^{-1}): 3751 w, 3472 w, 3073 w, 2673 w, 2363 m, 1624 (C═O) s, 1589 m, 1528 s, 1466 s, 1440 s, 1405 s, 1357 s, 1324 s, 1299 s, 1233 s, 1154 s, 1082 m, 1022 s, 888 s, 812 s, 750 m, 682 s, 644 s. MS (FAB): *m*/*z* 593 $[Cu_2(L_1)Cl_2]^+$, 20%; 557 $[Cu_2(L_1)Cl]^+$, 70%; $C_{22}H_{14}N_6O_2Cu_2Cl_2$: calcd C44.61, H 2.38, N 14.19; found C 44.82, H 2.41, N 14.25. Recrystallization of the green powder from acetonitrile afforded suitable single crystals for X-ray crystallography which were characterized to be the acetonitrile solvate $[Cu_2(L_1)Cl_2]\cdot CH_3CN$, **2**.

Crystallography. Crystallographic data for complexes **1** and **2** are summarized in Table 1. X-ray crystallographic data were collected on a Bruker Apex II CCD system with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz-polarization effects, and an empirical absorption correction was applied. The structures were solved by direct methods using the SHELXTL V6.14 package[13] and the SHELXS-97 program.[14] The refinement and all further calculations were

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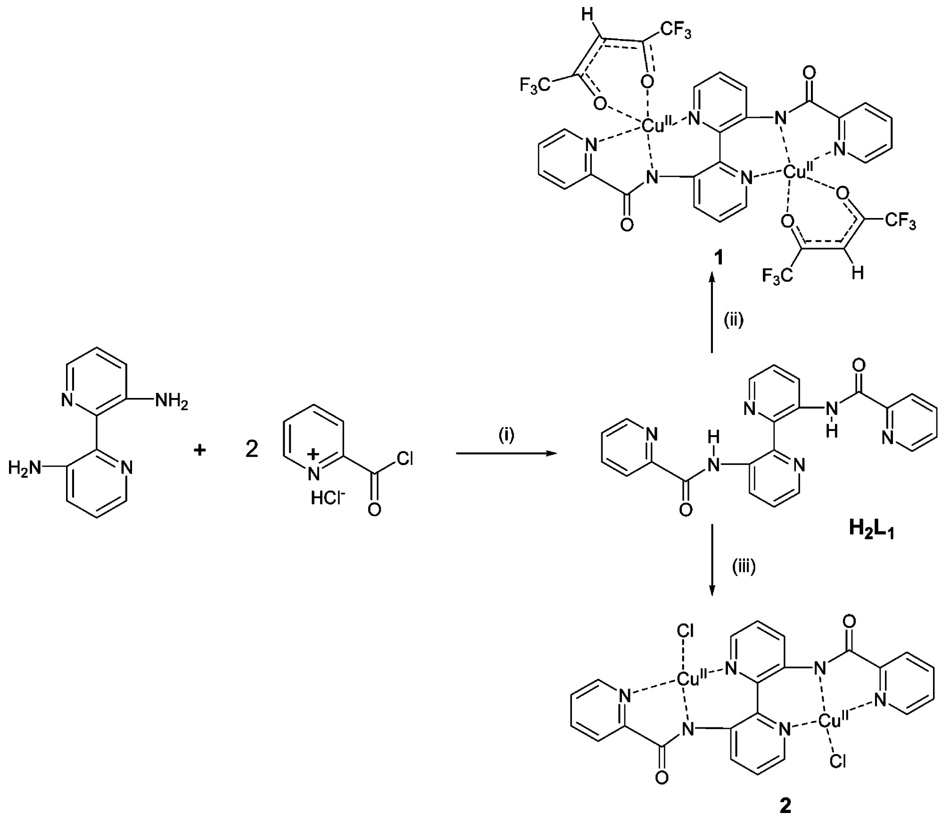
Scheme 1. Preparation of the Amide Ligand H_2L_1 and Coordination Complexes **1** and **2**[a]



[a] Reagents and Conditions: (i) Et_3N, CH_2Cl_2, 0 °C and then 80 °C for 3 h; (ii) 2 equiv of $Cu(hfac)_2$, MeOH; (iii) 2 equiv of $CuCl_2$, MeOH.

Table 1. Crystallographic Data for Complexes **1** and **2**

	$[Cu_2^{II}(L_1)(hfac)_2]{\cdot}3CH_3CN{\cdot}H_2O$ (**1**)	$[Cu_2^{II}(L_1)Cl_2]{\cdot}CH_3CN$ (**2**)
empirical formula	$C_{70}H_{41}N_{15}O_{13}Cu_4F_{24}$	$C_{24}H_{17}N_7O_2Cu_2Cl_2$
FW	2010.34	633.43
T (K)	150(2)	150(2)
λ (Å)	0.71073	0.71073
crystal system	Triclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/n$
a (Å)	12.7185(6)	12.8622(12)
b (Å)	17.3792(9)	9.6100(2)
c (Å)	19.4696(8)	19.897(2)
α (deg)	110.827(2)	90.00
β (deg)	99.890(3)	102.027(3)
γ (deg)	97.966(3)	90.00
V (Å^3)	3868.3(3)	2405.3
Z	4	4
ρ_{calcd} (g cm^{-3})	1.726	1.749
μ (mm^{-1})	1.215	2.030
$R_1{}^a$/goodness of fit	0.0428/1.034	0.0572/1.026
R_w $(F_o^2)^b$	0.0901	0.1085

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2]/\sum w|F_o|^4|^{1/2}$.

carried out using the SHELXTL package[13] and the SHELXL-97 program.[15] The H atoms were included in calculated positions and treated as riding atoms using default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2.

Results and Discussion

An overview of the synthesis of the ligand and two coordination compounds is presented in Scheme 1. The synthesis of the ligand H_2L_1 was achieved by reaction of 3,3′-diamino-2,2′-bipyridine with the HCl salt of 2-pyridine carbonyl chloride. An excess of triethylamine was used to deprotonate the pyridine, and the resulting triethylamine hydrochloride salt was removed by washing the resulting ligand with water. The synthesis of the dinuclear coordination complexes containing the dinucleating dianion L_1 is shown in Scheme 1. Methanolic solutions of the ligand together with two equivalents of $Cu(hfac)_2$ and $CuCl_2$ in the presence of air followed by recrystallization from acetonitrile produced

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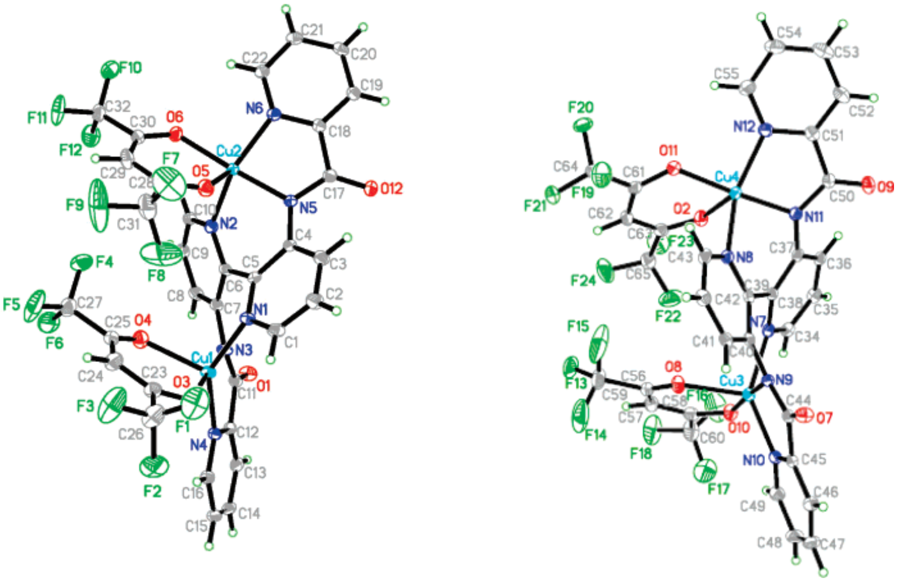

Figure 1. ORTEP[17] views of the molecular structure of the two independent molecules of $[Cu_2(L_1)(hfac)_2]$, **1**, showing the appropriate labeling scheme (thermal ellipsoids are plotted at 50% probability).

Table 2. Selected Bond Angles [deg] for **1**

N(3)−Cu(1)−O(3)	176.85(6)	N(9)−Cu(3)−O(10)	176.21(6)
N(3)−Cu(1)−N(4)	82.60(7)	N(9)−Cu(3)−N(10)	82.87(7)
O(3)−Cu(1)−N(4)	94.27(6)	O(10)−Cu(3)−N(10)	93.77(6)
N(3)−Cu(1)−N(1)	87.30(7)	N(9)−Cu(3)−N(7)	87.48(6)
O(3)−Cu(1)−N(1)	94.97(6)	O(10)−Cu(3)−N(7)	96.24(6)
N(4)−Cu(1)−N(1)	141.07(6)	N(10)−Cu(3)−N(7)	141.26(6)
N(3)−Cu(1)−O(4)	93.14(6)	N(9)−Cu(3)−O(8)	90.05(6)
O(3)−Cu(1)−O(4)	88.58(6)	O(10)−Cu(3)−O(8)	89.84(6)
N(4)−Cu(1)−O(4)	117.30(6)	N(10)−Cu(3)−O(8)	115.63(6)
N(1)−Cu(1)−O(4)	100.67(6)	N(7)−Cu(3)−O(8)	101.75(6)
N(5)−Cu(2)−O(6)	176.69(7)	N(11)−Cu(4)−O(11)	176.67(7)
N(5)−Cu(2)−N(6)	82.74(7)	N(11)−Cu(4)−N(12)	83.30(7)
O(6)−Cu(2)−N(6)	94.60(6)	O(11)−Cu(4)−N(12)	93.45(6)
N(5)−Cu(2)−N(2)	87.84(7)	N(11)−Cu(4)−N(8)	88.39(6)
O(6)−Cu(2)−N(2)	95.46(6)	O(11)−Cu(4)−N(8)	94.76(6)
N(6)−Cu(2)−N(2)	142.91(6)	N(12)−Cu(4)−N(8)	147.58(7)
N(5)−Cu(2)−O(5)	91.40(6)	N(11)−Cu(4)−O(2)	93.78(6)
O(6)−Cu(2)−O(5)	88.20(6)	O(11)−Cu(4)−O(2)	87.18(6)
N(6)−Cu(2)−O(5)	119.49(6)	N(12)−Cu(4)−O(2)	119.39(6)
N(2)−Cu(2)−O(5)	96.45(6)	N(8)−Cu(4)−O(2)	92.33(6)

Table 3. Selected Bond Distances [Å] for **1**

Cu(1)−N(3)	1.9212(16)	Cu(3)−N(9)	1.9142(16)
Cu(1)−O(3)	1.9639(13)	Cu(3)−O(10)	1.9486(14)
Cu(1)−N(4)	2.0026(16)	Cu(3)−N(10)	2.0103(16)
Cu(1)−N(1)	2.0246(16)	Cu(3)−N(7)	2.0544(16)
Cu(1)−O(4)	2.1558(15)	Cu(3)−O(8)	2.1339(14)
Cu(2)−N(5)	1.9284(16)	Cu(4)−N(11)	1.9250(16)
Cu(2)−O(6)	1.9592(14)	Cu(4)−O(11)	1.9630(14)
Cu(2)−N(6)	1.9901(16)	Cu(4)−N(12)	1.9970(17)
Cu(2)−N(2)	2.0198(16)	Cu(4)−N(8)	2.0393(16)
Cu(2)−O(5)	2.1873(14)	Cu(4)−O(2)	2.2036(14)

Table 4. Coordination Geometry of the Copper(II) Metal Ions for **1**

	equatorial ligands	axial ligands	% along Berry pseudorotation coordinate from TP to SP
Cu(1)	N(4), N(1), O(4)	O(3), N(3)	40.6
Cu(2)	N(6), N(2), O(5)	O(6), N(5)	41.4
Cu(3)	N(10), N(7), O(8)	O(10), N(9)	38.1
Cu(4)	N(12), N(8), O(2)	O(11), N(11)	50.8

green microcrystalline materials of $[Cu_2(L_1)(hfac)_2]\cdot 3CH_3CN\cdot H_2O$, **1**, and $[Cu_2(L_1)Cl_2]\cdot CH_3CN$, **2**, respectively.

In both cases no base was required to deprotonate the ligand since, when it undergoes complexation, binding of the N atom to the electron-rich metal center facilitates deprotonation.[16] For both complexes **1** and **2**, single crystals suitable for X-ray diffraction experiments were grown via slow evaporation of acetonitrile.

Crystal Structures. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules per unit cell. An ORTEP[17] view of the molecular structure of **1** along with an atom numbering scheme is shown in Figure 1. Selected bond distances and angles are listed in Tables 2 and 3, respectively. The ligand chelates in a dinuclear fashion to two Cu^{II} metal ions through the deprotonated amide N and two pyridine N atoms leaving the carbonyl oxygen atom uncoordinated. Two additional oxygen atoms from the hexafluoroacetylacetonate (hfac) counterions complete the pentacoordinate geometry around both copper(II) centers that is best interpreted as intermediate between trigonal bipyramid (C_{3v}) and square-based pyramid (C_{4v}). According to the procedure described by Addison[18] the Cu^{II} atoms have distortion parameter τ values of 0.60, 0.56, 0.58, and 0.48 for Cu(1) to Cu(4) respectively. ($\tau = (\theta_1 - \theta_2)/60$, where θ_1 and θ_2 are the largest angles in the coordination sphere), where $\tau = 0$ for square pyramidal and 1 for trigonal planar.

This indicates that the coordination geometry for Cu^{II} ions (1) through (3) is best described as distorted trigonal bipyramidal, whereas Cu(4) is distorted square planar with O(11), N(8), N(11), and N(12) occupying the basal plane. Table 4, summarizes the atoms occupying the equatorial and apical positions of the trigonal bipyramid together with the percentage along the Berry pseudorotational coordinate from trigonal bipyramidal (TP) to square pyramidal (SP). In order

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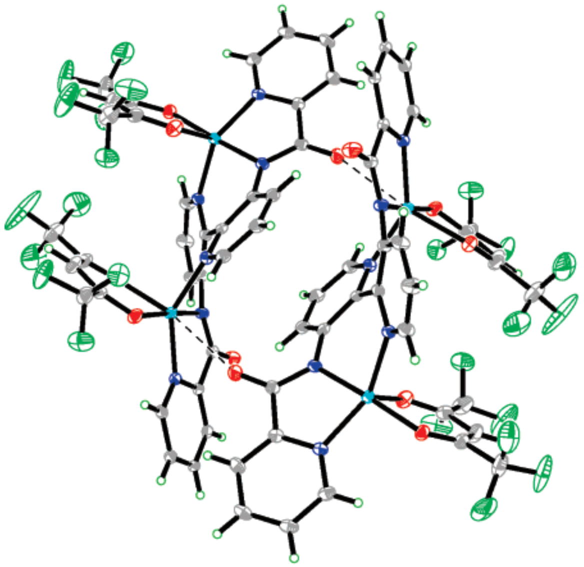

Figure 2. ORTEP[17] view of a centrosymmetric pair of molecules of complex **1** linked via Cu···O═C interactions (dashed lines); thermal ellipsoids are plotted at 50% probability.

to chelate in this manner, the two pyridine rings of the 2,2′-bipyridine are substantially twisted. The dihedral angles between the mean plane of the two bipyridine rings are 38.7° for molecule **1** and 40.6° for molecule **2** relative to the trans coplanar conformation. The molecules pack in a head-to-head arrangement where centrosymmetric pairs of molecules run along the *b*-axis of the unit cell, Figure 2. Intramolecular $Cu^{II}\cdots Cu^{II}$ distances are in the range 5.868−5.958 Å, whereas intermolecular $Cu^{II}\cdots Cu^{II}$ distances are slightly shorter, in the range 5.348−5.487 Å. The packing is such that the carbonyl oxygen atoms of the first independent molecule form short intermolecular contacts to neighboring Cu^{II} ions (O(12)···Cu (4) 3.408 Å, O(1)···Cu(2) 3.382 Å), whereas those contacts involving the carbonyl functionality of the second molecule are longer (O(9)···Cu(4) 4.010 Å, O(7)···Cu(3) 4.010 Å). All four independent carbonyl oxygen atoms form H-bonds to neighboring pyridyl H-atoms that lie in the range 2.41−2.80 Å.

Complex **2** crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell. A perspective view of **2** along with an atom-numbering scheme is shown in Figure 3. Selected bond distances and angles are listed in Tables 5 and 6. The bipyridine carboxamide ligand once again chelates in a tridentate manner to two Cu^{II} metal ions through the deprotonated amide N and two pyridine nitrogen atoms leaving the carbonyl oxygen atom unchelated. The pyridine rings of the 2,2′-bipyridine are twisted by an angle of 44.2° with respect to the trans coplanar conformation.

The two end Cu(1) ions have a CuN_3ClO ligand environment and are (4 + 1) pentacoordinate with a geometry that is intermediate between a trigonal bipyramid (C_{3v}) and a square-based pyramid (C_{4v}). The Cu(1) atom has a τ value of 0.43, indicating that the coordination geometry can be better described as a distorted base pyramid. In this description, the basal coordination sites are occupied by an amide and three pyridine N atoms of the tridentate ligand, with bond distances in the range of 1.919(3)−2.023(3) Å, together with a chloride ion at a distance of 2.2194(8) Å. The apical site is occupied by a neighboring carbonyl oxygen atom at a longer distance of $C{=}O\cdots Cu^{II} = 2.868$ Å, Figure 4 (dashed line). The Cu(1) ion is raised from the mean basal plane toward the apical oxygen ion by 0.1911 Å. The geometry around the Cu(2) ion is also square pyramidal with a τ value of 0.39. Three N atoms from the tridentate ligand together with a chloride ion form the square plane; in this respect bond lengths range from 1.942(2) to 1.997(2) Å with the chloride ion at a distance of 2.2585(8) Å. The apical site is occupied by a chloride ion from another molecule at a longer distance of 2.7994(9) Å and the Cu(2)−Cl(2)−Cu(2)′ angle (φ) is 91.01(10)°. The Cu(2) ion is raised from the mean basal plane toward the apical Cl ion by 0.1871 Å. Pairs of these binuclear species are arranged to form planar $[Cu_2(L_1)_2Cl_2]_2$ dimers linked via chloride bridges formed between Cu(2) and a chloride ion of the adjacent binuclear species, Figure 3. The molecule has a crystallographic center of inversion located between the two central copper atoms which ensures that the four copper atoms are coplanar and the Cu(1a)−Cu(2a)−Cu(2b)−Cu(1b) torsion angle is 180°. The interesting structural feature for $[Cu_2(L_1)_2Cl_2]_2$ is that its Cu_2Cl_2 bridging unit is nearly a square (the two bridging bonds are 2.258 and 2.799 Å, and the Cu−Cl−Cu′ and Cl−Cu−Cl′ angles are 91.01 and 89.99° respectively). This is quite unusual and not observed in other known $Cu(\mu\text{-}Cl)_2Cu$ complexes, where bridging angles generally diverge considerably from 90°.[19] The bridging arrangement of the 2,2′-bipyridine carboxamide ligand gives rise to a Cu(1)−Cu(2) distance of 5.84 Å, substantially longer than the distance of 3.63 Å associated with the Cu_2Cl_2 core. The latter short distance can be considered to be in the range associated with short metal−metal separations similar to those occurring in a number of metalloenzymes containing polymetallic active sites.[20] The Cu(1)−Cu(2)′ and Cu(1)−Cu(1)′ separations are 6.830 and 12.181 Å, respectively. The packing diagram for **2** is shown in Figure 4. Chloro-bridged dimers stack along the *b*-axis of the unit cell. Short intermolecular contacts connect neighboring dimers (Figure 4, dashed lines). For clarity, these contacts are more clearly represented in Figure 5. Figure 5a shows the H-bonding interaction between the hydrogen atom of an acetonitrile solvent molecule and a neighboring pyridyl nitrogen atom, and Figure 5b shows the H-bonding interaction from a pyridyl H atom to the chloride ion of a neighboring molecule and the C═O···Cu contacts. Within the solid-state structure, there are six Cu(1)···Cu(1) separations ranging from 8.422 to 11.023 Å that are shorter than the interdimer Cu(1)−Cu(2) distances.

Magnetic Properties. Figure 6 shows the magnetic behavior of complex **1** in the form of χ_M (χ_M is the molar magnetic susceptibility per two Cu^{II} ions) with $1/\chi$ in the

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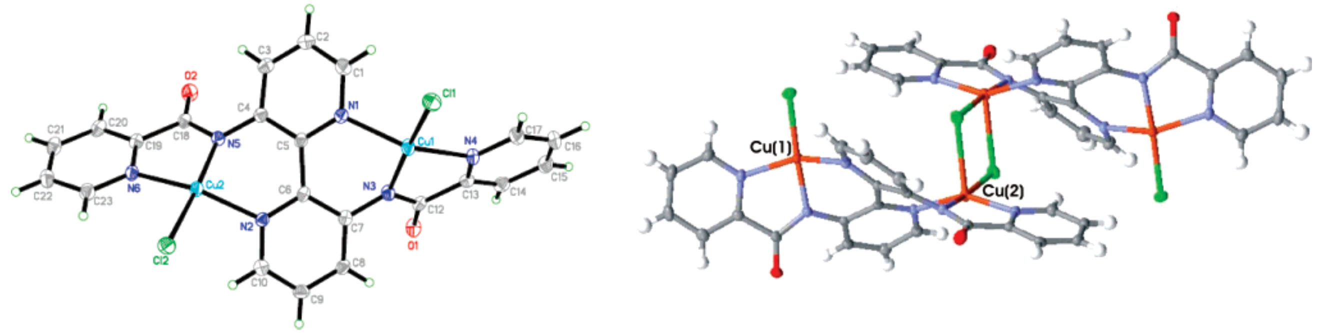

Figure 3. (a) An ORTEP[17] view of the molecular structure of $[Cu_2(L_1)Cl_2]$, **2**, showing the labeling scheme (thermal ellipsoids are plotted at 50% probability); (b) view of the μ-chloro-bridged dimeric complex $[Cu_2(L_1)_2Cl_2]_2$ showing the (4 + 1) coordination around the Cu^{II} metal ion.

Table 5. Selected Bond Distances [Å] for **2**

Cu(1)−N(3)	1.919(2)	Cu(2)−N(5)	1.942(2)
Cu(1)−N(4)	2.002(2)	Cu(2)−N(6)	1.989(2)
Cu(1)−N(1)	2.023(2)	Cu(2)−N(2)	1.997(2)
Cu(1)−Cl(1)	2.2194(8)	Cu(2)−Cl(2)	2.2584(8)
		Cu(2)−Cl(2)*	2.7994(9)

Table 6. Selected Bond Angles (deg) for **2**

N(3)−Cu(1)−N(4)	82.12(10)	N(5)−Cu(2)−N(6)	83.30(10)
N(3)−Cu(1)−N(1)	86.62(10)	N(5)−Cu(2)−N(2)	88.15(10)
N(4)−Cu(1)−N(1)	142.73(11)	N(6)−Cu(2)−N(2)	149.82(10)
N(3)−Cu(1)−Cl(1)	168.78(8)	N(5)−Cu(2)−Cl(2)	173.33(8)
N(4)−Cu(1)−Cl(1)	100.88(8)	N(6)−Cu(2)−Cl(2)	95.86(8)
N(1)−Cu(1)−Cl(1)	96.99(8)	N(2)−Cu(2)−Cl(2)	95.74(7)
		Cu(2)−Cl−Cu(2)[a]	91.01(8)
		Cl(2)−Cu−Cl(2)[a]	89.99(8)

[a] Cl(2) 1 − *x*, 2 − *y*, 2 − *z*.

inset. The susceptibility of the sample increases monotonically as the temperature lowers all the way down to 5 K where it shows a maximum and then drops. At high temperatures the susceptibility follows a typical Curie−Weiss behavior, from which the Curie constant *C* could be determined. The presence of two Cu^{II} ions per molecule is confirmed by a Curie constant of 0.75 emu·K·mol (expected 0.76 for two $S = {}^1/_2$ and $g = 2.10$) and a value for the Weiss constant of $\theta = -6.29$ K, Figure 5. In order to evaluate the exchange interaction between neighboring Cu^{II} atoms, the variable-temperature susceptibility data were analyzed using eq 1 derived[21] from the Heisenberg isotropic spin Hamiltonian ($H = -2JS_1 \cdot S_2$), for two coupled $S = {}^1/_2$ ions, given by the Bleaney−Bowers expression for a dinuclear Cu^{II} compound. *J* is the intradimer coupling constant between Cu^{II} ions, zJ' is the interdimer magnetic exchange, treated in the molecular field approximation. A best fit, which affords the solid line in Figure 6, was obtained with values of $g = 2.10$, $J = -4.93$ K, and $zJ' = -1.28$ K, confirming the antiferromagnetic nature of the coupling.

$$\chi_M = 2Ng^2\beta^2[kT - 2zJ'/(3 + \exp(-2J/kT))]^{-1}[3 + \exp(-2J/kT)]^{-1} \quad (1)$$

The results of magnetic susceptibility measurements for $[Cu_2(L_1)Cl_2]_2$ are given in Figure 7 in the form of a χ_mT versus *T* plot. Upon lowering the temperature from room temperature to about 50 K χ_mT remains practically constant at a value of 1.43 emu K mol^{-1} which is slightly lower than that calculated for four uncorrelated $S = {}^1/_2$ spins (1.50 emu·K·mol^{-1} with $g = 2$). Between 60 and 5 K χ_mT decreases sharply reaching a value of 1.16 emu·K·mol^{-1} which is slightly larger than the value of 1.0 emu·K·mol^{-1} expected for a $S = 1$ ground state arising through a combination of competing ferromagnetic and antiferromagnetic interactions. A schematic view of the bridging framework of the μ-chloro-bridged dimer **2** is presented in Figure 8, where a simplified numbering scheme is useful for the following discussion.

Due to the crystallographic inversion center, the chloro-bridged complex has C_2 symmetry with the two-fold axis perpendicular to the best plane containing the four Cu atoms and passing halfway between the central copper atoms. As a consequence, the copper dimer can be described with four exchange coupling constants, leading to the Hamiltonian described by equation 2:

$$H = -2J_1(S_1S_2 + S_{1'}S_{2'}) - 2J_2(S_2S_{2'}) - 2J_3(S_1S_{2'} + S_{1'}S_2) - 2J_4(S_1S_{1'}) \quad (2)$$

where J_1 describes the nearest-neighbor interactions between the outer pairs of copper atoms, J_2 is the central exchange constant, J_3 describes the next-nearest-neighbor interactions, and J_4 is the exchange constant between the terminal copper atoms. This model has been solved exactly,[22] affording the molar susceptibility expression defined by eq 3:

$$\chi_m(4Cu) = (N\beta^2g^2/kT)\,[10\exp(-E_1/kT) + 2\exp(-E_2/kT) + 2\exp(-E_3/kT) + 2\exp(-E_4/kT)]/[5\exp(-E_1/kT) + 3\exp(-E_2/kT) + 3\exp(-E_3/kT) + 3\exp(-E_4/kT) + \exp(-E_5/kT) + \exp(-E_6/kT)] + 4N\alpha \quad (3)$$

where E_1−E_6 are the energies (expressed as functions of the *J* values) of the various spin states (one quintet, three triplets, and two singlets) and $N\alpha$ is a temperature-independent paramagnetic term. Although not strictly correct theoretically,[23] eq 3 assumes equal *g* values for all of the spin states in order to avoid the presence of too many adjustable parameters.

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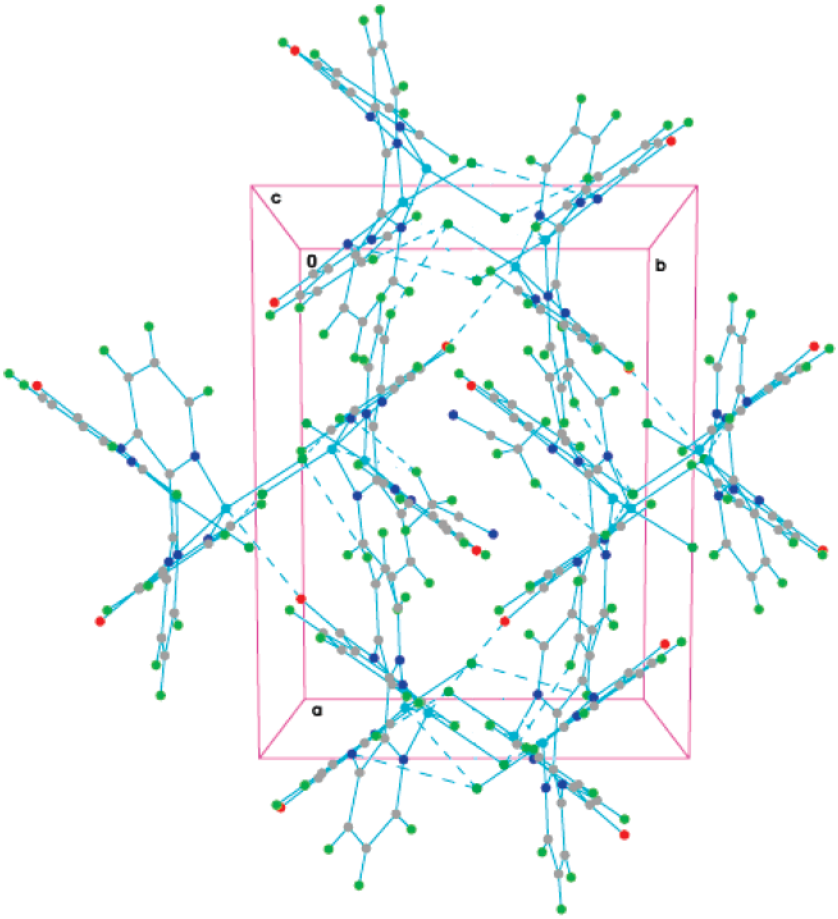

Figure 4. Packing diagram for complex **2**, projection down the *c*-axis.

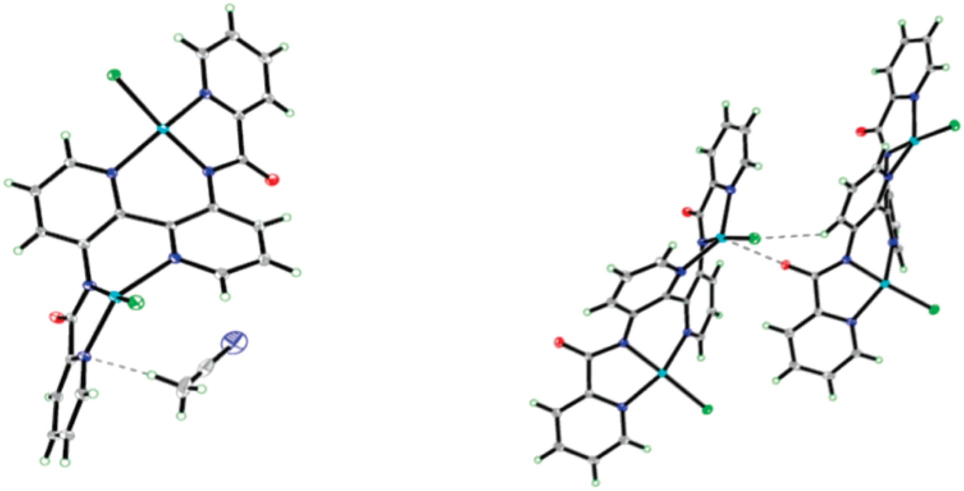

Figure 5. Intermolecular contacts present in the solid-state structure of complex **2**. (a) CH⋯N = 2.17 Å; (b) CH⋯Cl = 2.75 Å, and C═O⋯Cu = 2.868 Å.

The experimental susceptibility data were fit to eq 3 by holding $g = 2.10$ (the value deduced from the Curie−Weiss plot of the high-temperature data) and letting two to four coupling constants vary (the remaining ones being held equal to zero). The function that was minimized in curve fitting was $F = (\chi^{\rm obs} - \chi^{\rm calc})^2(\chi^{\rm obs})^{-1}$. Best-fit parameters and F values are collected in Table 7, where it can be seen that any set of parameters describes equally well the experimental data (a value of 25×10^{-6} emu per Cu atom for the temperature-independent paramagnetism was used). Fit 1 is plotted in Figure 7.

As can be seen, the addition of J_3 and J_4 does not improve the value of the fitting parameter, nor does it have any influence in the sign of J_1 and J_2, with J_2 being strongly ferromagnetic in all cases. This suggests that the magnetic structure of complex **2** can be attributed to nearest-neighbor interactions which is in agreement with previous observations for other tetranuclear systems.[24] From the magnetic data and

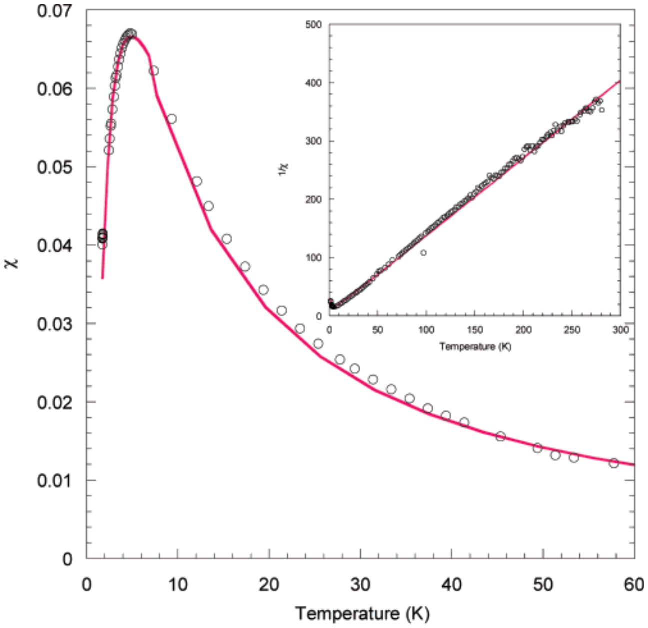

Figure 6. Variation of the molar susceptibility (black circles) and fit according to parameters in text (solid line). Inset 1/χ vs *T* and fit to the Curie Weiss model.

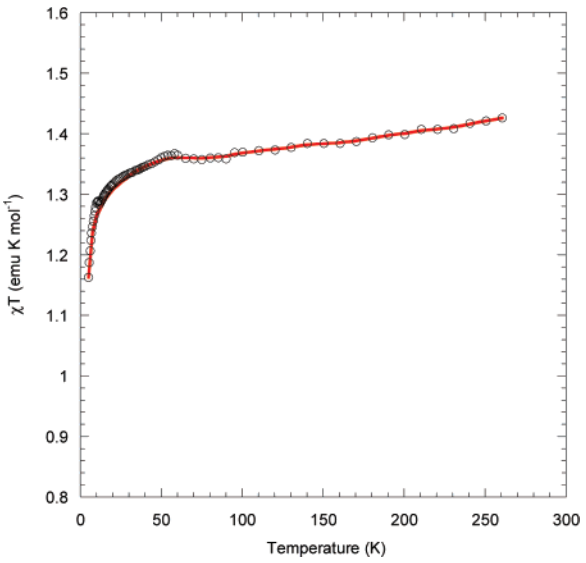

Figure 7. Variation of the χ*T* product (4 Cu) (black circles) and fit according to parameters in text (solid line).

the molecular structure, one can infer that in complex **2**, there is a ferromagnetic coupling between the Cu^{II} metal centers through the μ-chloro bridging ligands ($J_2 = 32.9$ K) and a weaker antiferromagnetic coupling ($J_1 = -10.1$ K) between the two Cu^{II} ions in each half of the $[Cu_2(L_1)Cl_2]_2$ complex that is similar in sign and magnitude to that observed in complex **1**. The sign and magnitude of the coupling constant J_2 for pentacoordinate Cu(μ-Cl)$_2$Cu dimers depends mainly on: (i) the Cu−Cl−Cu bridging angle φ, (ii) the axial Cu−Cl distance, *R*, (iii) the nature of the terminal ligands, and (iv) the distortions of the coordination geometry.[25] A review of the literature reveals that three SP geometries have been experimentally characterized for chloro-bridged Cu^{II} dimers.

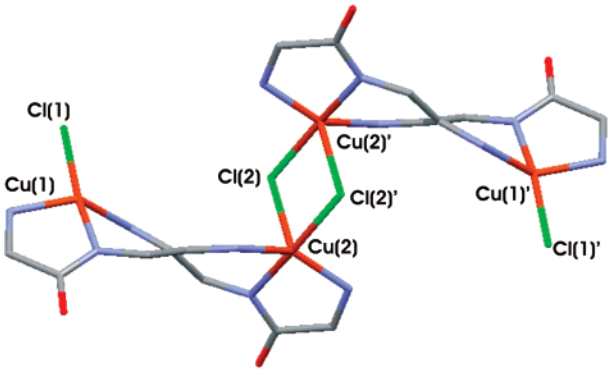

Figure 8. Simplified view of the bridging framework in $[Cu_2(L_1)Cl_2]_2$, with the appropriate numbering scheme.

Table 7. Best Fit Parameters (*K*) and Agreement Factors

fit	J^a	J_2	J_3	J_4	$10^4\,F^b$
1	−10.1	+32.9	c	*c*	3.2
2	−2.6	+43.8	−1.5	*c*	3.1
3	−7.3	+47.0	−2.1	+0.6	3.1

[a] *J* values denoted by *c* were arbitrarily held constant to zero. [b] *F* was calculated as described in the text for 61 observations.

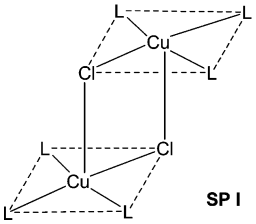

Figure 9. Square planar geometry SP I for which the square pyramids share a base-to-apex edge with parallel basal planes.

In this respect, complex **2** can be classified as SP I since the square pyramids share a base-to-apex edge with parallel base planes, Figure 9.

SP I compounds can show both ferromagnetic or antiferromagnetic coupling constants, depending on the nature of the terminal ligands. There are seven SP I compounds with ferromagnetic coupling reported to date in the chemical literature.[26] The J_2 value obtained for the $[Cu_2(L_1)Cl_2]_2$ dimer **2** is consistent with the 90° angle rule that the coupling is ferromagnetic for the φ value near to 90°. In this respect, the φ value of 91.01° found for **2** is fairly close to 90°, and this induces the ferromagnetic coupling ($J > 0$). Hatfield and co-workers have proposed an empirical correlation between the coupling constant and the φ/*R* ratio (φ is the Cl−Cu−Cl bridging angle, and *R* is the axial Cu−Cl bond length) for chloro-bridged compounds involving axial−

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equatorial dimers.[27] For a value of φ/R lower than 32.6 or higher than 34.8 [deg/Å], the exchange is expected to be antiferromagnetic, and for values falling between these limits the interactions are predicted to be ferromagnetic. In our case the φ/R ratio for complex **2** is 32.5 [deg/Å]. This value just falls slightly short of the limits expected for ferromagnetic exchange and so does not fit the general trend. Interestingly, in recent months Qi and co-workers have magnetically and structurally characterized a chloro-bridged Cu^{II} Schiff-base complex for which a ferromagnetic interaction is reported between two copper centers through a bridging $CuCl_2$.[10e] This complex also does not fit the Hatfield J vs φ/R correlation trend since the compound has a φ/R ratio of 36.51 [deg/Å] which would predict antiferromagnetic coupling between the two copper centers. The reasons for these deviations are not totally clear, but are most likely a consequence of the chemical and structural environment of the copper ions in the two complexes that in turn effect the coefficients of the various orbital functions involved in their superexchange pathways. For complex **2**, it is understood that the superexchange pathway involving the Cu^{II} metal centers will take place mainly through a π^* type of interaction between the Cu $d_{x^2-y^2}$ and the apical p Cl orbitals. For an ideal geometry with a square core, the former overlap integral would be zero, and therefore, there would be no magnetic coupling between the Cu metals. In this respect, complex **2** presents J_2 values which are due to small structural deviations from the ideal squared Cu_2Cl_2 core that are consistent with the molecular structure determined for **2**. Examples of planar copper dimers that have been magnetically characterized are still relatively scarce in the chemical literature.[10e,22,24,26,27] To the best of our knowledge, this is the first example of a dimerized bis dinuclear copper(II) complex that displays ferromagnetic coupling interactions between the $Cu(\mu\text{-}Cl)_2Cu$ dimers and antiferromagnetic coupling interactions between the Cu^{II} centers within each half of the dimerized unit. A detailed search of the literature revealed one other example of a bis dinuclear copper(II) complex assembled from four salen-type ligands.[24] In this case, the ligand acts in a bis bidentate manner bridging two copper atoms which are coordinated to two phenolato and two imino groups of two ligands. Two binuclear moieties are held together through Cu−O interactions between neighboring units to form pseudolinear $[Cu(L)_2]_2$ tetrameric clusters.[24] Detailed magnetic investigations for this compound reveal that the magnetic structure of the compound is fundamentally dominated by nearest-neighbor interactions which are antiferromagnetic.[24]

Conclusion

The preparation of a new multidentate bipyridine carboxamide ligand and its complexation to copper(II) has afforded two new magnetic complexes which demonstrate its potential application as a building block for the self-assembly of molecule-based magnetic materials. Structural characterization of the two Cu^{II} complexes by X-ray crystallography have revealed that this building block is capable of connecting one-dimensionally and in the case of the dimerized bis copper complex, that the spins on neighboring metal centers can be coupled without complete cancellation of the magnetization. The chloride ligands on the terminal copper ions of the dimer provide open sites for alternative bridging ligands such as cyanide to bind. In this respect, this complex is a very useful precursor for targeting the controlled self-assembly of molecule-based magnets. Work along these lines is in progress and will be reported in due course.

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Supporting Information Available: Additional crystallographic data in CIF format for complexes **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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