Self-Assembly, Crystal Structure, and Magnetic Properties of a Phenoxo-Bridged Tetranuclear Cu^{II} Complex of the [2 × 2] Grid Type

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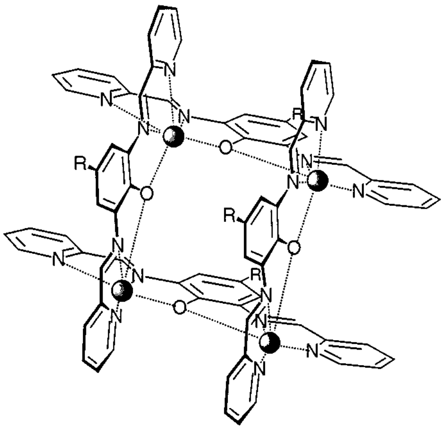
The ditopic ligand **3** has been synthesized. In its deprotonated form, it reacts with copper(II) ions to form a tetranuclear complex **1** of the [2 × 2] Cu$^{II}_4$ grid type, the structure of which has been confirmed by X-ray crystallography. Magnetic studies of complex **1** indicate a very weak antiferromagnetic coupling between the phenoxo-bridged Cu^{II} ions.

Self-assembly of suitably designed ligands with transition-metal ions allows the creation of inorganic architectures with well-defined structures in a spontaneous but directed manner.[1] One of the aims of supramolecular chemistry is the formation of assemblies that may possess interesting physical properties.

Previously, we have reported the self-assembly of metal complexes of rack-[2] and grid-type[3] geometries, where the metal ions are bridged by pyrimidine rings. The metallic centers in these arrays are located at appropriate distances (6.16−6.50 Å) such as to allow electronic interaction, which is manifested in the physical properties of the complexes such as redox potentials,[2,3] optical,[4] and magnetic[5] features. In order to enhance the coupling between the metal-ion centers compared to that provided by a pyrimidine group, and to obtain inorganic architectures exhibiting new properties, we have explored the use of ligands that introduce oxygen bridges between the coordination binding sites.

Oxo-bridged binuclear copper(II) complexes have been extensively studied as a result of the magnetic properties arising from ferromagnetic or antiferromagnetic spin-coupling between the copper ions,[6] which depend strongly on the geometry of the Cu−O−Cu bridge (Cu−Cu distances and bridge angles). While a linear correlation of the magnetic exchange parameter J with bridge angle Φ is well-established for dihydroxo-bridged copper(II) complexes with square-pyramidal $d_{x^2-y^2}$ electronic ground states, this might not be the case for monohydroxo-bridged complexes with a different electronic ground state (i.e. trigonal-bipyramidal, d_{z^2}).[7] The antiferromagnetic coupling observed for most monohydroxo-bridged complexes is larger than that found for di-μ-hydroxocopper(II) complexes and normally occurs through a super-exchange mechanism, with the hydroxo bridge acting as the primary pathway for exchange.[8] Most hydroxo-bridged copper(II) complexes are pentacoordinated and typically exhibit square-pyramidal or trigonal-bipyramidal geometries. Here, we report the synthesis, structural details, and magnetic properties of **1**, [**L**Cu]$_4$(CF$_3$SO$_3$)$_4$, a tetrametallic copper(II) complex of the [2 × 2] grid type, where the copper atoms adopt a distorted bipyramidal geometry and are bridged by the phenolate oxygen atom of the ionized form **L**$^-$ of ligand **3**. Recently, an Mn^{2+} complex of the [2 × 2] grid type with a ligand similar to **3**, but where the metal centers are bridged by non-conjugated alkoxide-type oxygen atoms, has been reported.[9]



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Results and Discussion

Ligand **3** was prepared by condensation of two equivalents of 2-pyridinecarboxaldehyde with one equivalent of 2,6-diamino-4-*tert*-butylphenol in methanol solution in the

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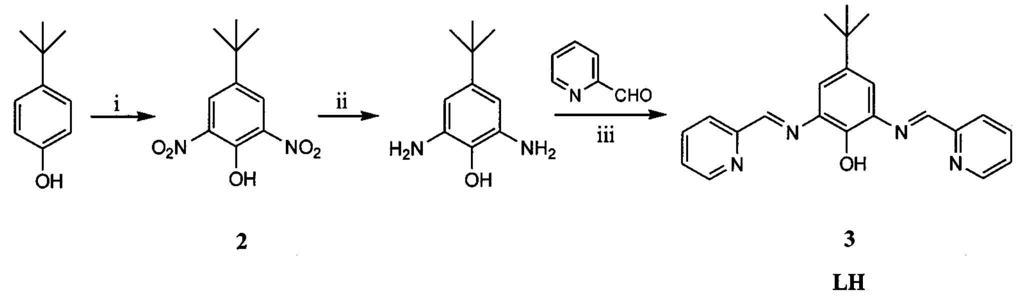
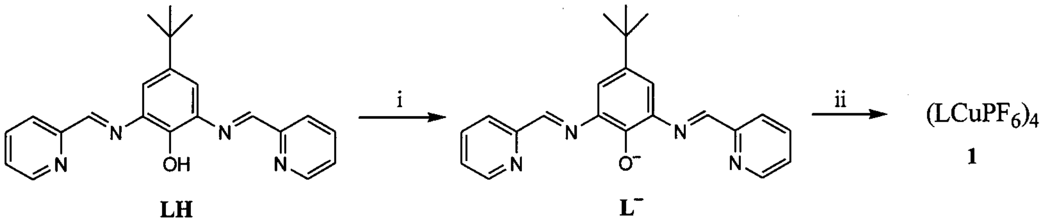


Scheme 1. Synthesis of ligand **3**, **LH**: i) HNO_3, HOAc, −15°C to room temp. − ii) Pd/C, H_4NHCO_2. − iii) 4-Å molecular sieves



Scheme 2. Formation of the tetranuclear copper(II) complex **1**: i) NaOMe, MeOH, room temp. − ii) $Cu(CF_3SO_3)_2$; NH_4PF_6

presence of 4-Å molecular sieves. The latter was obtained by dinitration of 4-*tert*-butylphenol[10] to give **2** and subsequent reduction of the nitro groups to amino groups[11] (Scheme 1). Reaction of ligand **3** with one equivalent of sodium methoxide in anhydrous methanol at ambient temperature led to the immediate formation of a deep-red colour, characteristic of the ligand anion $\mathbf{L}^-$, which consists of two tridentate coordination subunits. One equivalent of copper triflate was then added, resulting in a colour change to purple, indicating complex formation (Scheme 2). After 3 h, the copper complex was precipitated by adding a saturated methanolic solution of ammonium hexafluorophosphate, isolated by centrifugation, purified by recrystallization from acetonitrile/diethyl ether, and characterized by its spectral and analytical properties. Its structure was confirmed by X-ray crystallography.

Crystal Structure of Complex 1

Single crystals of complex **1** were obtained by slow vapor diffusion of diethyl ether into an acetonitrile solution of the complex. Crystal structure determination by X-ray diffraction analysis (Figure 1) revealed that the complex consists of a metallic core composed of four copper(II) atoms, four ligands placed in an orthogonal orientation defining a distorted square, and four counteranions (PF_6^-) delocalized in the unit cell, along with two CH_3CN solvent molecules. The arrangement of the metal ions shows approximate C_4 symmetry and is of the [2 × 2] grid type, analogous to the recently described Co_4 grids.[3]

Each copper atom has a distorted bipyramidal geometry and is bound to two pyridine nitrogen atoms, two imine nitrogen atoms, and two phenoxo oxygen atoms belonging to two orthogonal ligands. The Cu−O distances in the complex correspond to those in other Cu^{II}−O(phenolate) complexes, amounting to 2.29 Å for the phenolate in the apical position and 1.98 Å for the phenolate in the equatorial position. Cu−N bond lengths are between 2.06 and 1.96 Å for the equatorial nitrogen atoms and 2.38 Å for the apical nitrogen atoms (Table 1). The tetranuclear center is characterized by metal−metal separations of 4.04 Å for the μ-phenoxo-bridged copper atoms Cu(1)−Cu(2) and of 5.35 Å for Cu(1)−Cu(3), and a bridge angle Cu−O−Cu of 140.58°.

The metal−metal separations and the oxygen bridge angle are larger than those typically found in bridged bimetallic copper(II) complexes.[6] However, there are other cases where longer distances of 4.09 and 4.13 Å have been reported.[7c,7d]

Electronic Absorption Spectrum of Complex 1

The electronic absorption spectrum of complex **1** in acetonitrile solution shows two maxima centered at 224 nm ($\varepsilon = 5.6 \times 10^4$ $\text{M}^{-1}\text{cm}^{-1}$) and 328 nm ($\varepsilon = 6.1 \times 10^4$ $\text{M}^{-1}\text{cm}^{-1}$), corresponding to ligand-centered (LC) π-π^* transitions. An absorption band in the visible region at 521 nm ($\varepsilon = 4.7 \times 10^4$ $\text{M}^{-1}\text{cm}^{-1}$) can be ascribed to a metal−ligand charge-transfer transition (MLCT). The strong intensity of this MLCT band suggests a good overlap between the phenolate and the metal orbitals. It is known that charge-transfer transitions of phenolate−Cu^{II} groups are more intense when the phenolate oxygen orbital overlaps with the copper $d_{x^2-y^2}$ orbital.[7c]

Magnetic Studies

Figure 2 depicts the temperature dependence of the susceptibility of **1** plotted as χT (Figure 2a) and the field dependence of the magnetic moment at $T = 2$ K (Figure 2b).

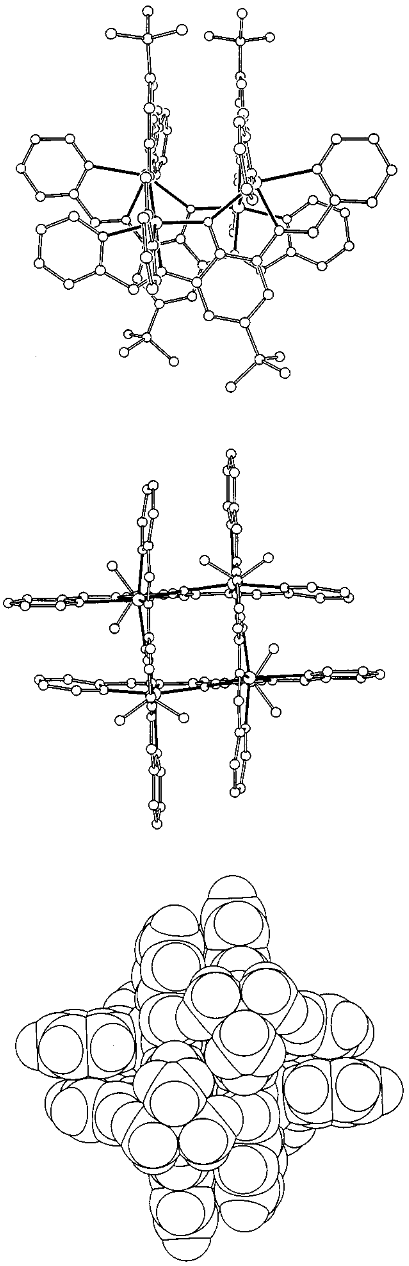


Figure 1. X-ray structure of the [2 × 2] Cu^{II}_4 grid-type complex **1**: (top) side view, (center) top view, (bottom) top view in space-filling representation

The data can be characterized by the following three features:

1. χT decreases slightly with decreasing temperature. The effective moment per copper ion is determined to be $\mu_{eff} = 1.913$ at 250 K and $\mu_{eff} = 1.786$ at 30 K, corresponding to $g = 2.21$ and $g = 2.06$, respectively. However, this decrease in χT cannot simply be ascribed to a temperature-independent paramagnetic contribution μ_0 as the decrease is not linear, as can be seen in Figure 2a. Furthermore, the value of μ_0 would have to be of the order of 10^{-3} cm^3 mol^{-1}, a value which is far beyond the scope of experimental uncertainty.

Table 1. Selected bond lengths [Å] and angles [°] from the X-ray structure of the grid complex **1**; the numbering of the atoms corresponds to that given in Figure 3

Cu−N(2)	1.9650	O−Cu−N(1)	160.54
Cu−O	1.9872	N(3)#1−Cu−N(1)	101.94
Cu−N(3)#1	2.0390	N(2)−Cu−O#1	118.33
Cu−N(1)	2.0600	O−Cu−O#1	93.36
Cu−O#1	2.2973	N(3)#1−Cu−O#1	76.71
Cu−N(4)#1	2.3890	N(1)−Cu−O#1	87.21
O−Cu#2	2.2973	N(2)−Cu−N(4)#1	90.01
N(3)−Cu#2	2.0390	O−Cu−N(4)#1	94.92
N(4)−Cu#2	2.3890	N(3)#1−Cu−N(4)#1	75.00
		N(2)−Cu−O	82.68
		N(1)−Cu−N(4)#1	93.81
		N(2)−Cu−N(3)#1	164.96
		O#1−Cu−N(4)#1	151.28
		O−Cu−N(3)#1	97.11
		Cu−O−Cu#2	140.58
		N(2)−Cu−N(1)	79.96

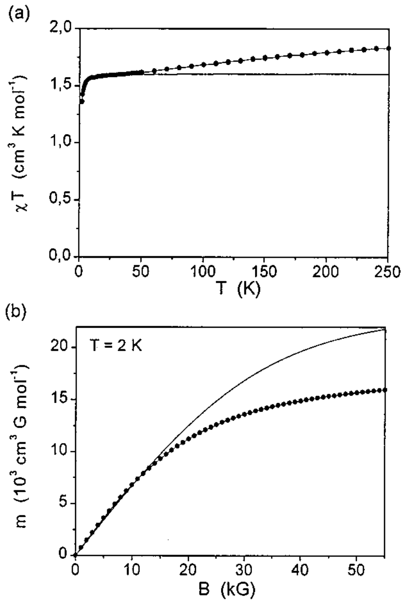


Figure 2. (a) Temperature dependence of the susceptibility of **1** plotted as χT and (b) field dependence of the magnetic moment at $T = 2$ K; the solid lines represent the curves calculated for the hamiltonian (Equation 1) with parameters $J = -0.4$ cm^{-1} and $g = 2.07$

2. Below ca. 10 K, the onset of a sharp decrease of χT can be seen (Figure 2a), indicating a weak antiferromagnetic coupling of the copper ions. In order to obtain an estimate of the coupling strength, we fitted the data below 25 K to the susceptibility given by the spin hamiltonian:

$$H = -J(S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_4 \cdot S_1) + \mu_B g B \cdot S \qquad (1)$$

The parameters were determined to be $J = -0.4$ cm^{-1} and $g = 2.07$. The calculated susceptibility is drawn as a solid line in Figure 2a.

3. The magnetic moment at $T = 2$ K exhibits a strong field dependence, resulting in unusually low values of the magnetic moment at high fields (Figure 2b). This can clearly be seen if the data are compared to the curve calculated for the hamiltonian (Equation 1) using the above parameters. However, the field dependence is paramagnetic-

like, indicating that the magnetic coupling of the copper ions is at best of the order of -0.1 to -1 $\mathrm{cm^{-1}}$.

As yet, we have been unable to provide a satisfactory interpretation of the magnetic data that would explain both the slight decrease of χT and the unusually strong magnetic field dependence. Nevertheless, although these two peculiarities of the data obviously necessitate further investigation, it can be unambiguously concluded that the exchange coupling in **1** is very weak.

Considering the coupling strengths, monohydroxo-bridged copper(II) dimers may be roughly divided into two classes. The systems belonging to the first class exhibit strong antiferromagnetic coupling of the order of several -100 $\mathrm{cm^{-1}}$. This can be attributed to the arrangement of the square-pyramidal coordination spheres of the copper ions, which leads to $d_{x^2-y^2}$ ground states with the orbital lobes directed towards each other, thereby providing a good σ-type exchange pathway.[7a,8b,12,13] Dimers of the second class are characterized by very weak ferro- or antiferromagnetic couplings of just a few $\mathrm{cm^{-1}}$. In these systems, several coordination geometries are realized, e.g. two square pyramids with the bridging oxygen atom in the apical position,[7c] two trigonal bipyramids with the oxygen atom in the equatorial planes,[13] or a combination of a square pyramid and a trigonal bipyramid with the oxygen atom in the equatorial planes,[12] which lead to negligible overlap and thus to weak coupling.

In the [2 × 2] grid **1** a new situation is seen, which leads to negligible exchange coupling. The coordination geometries of the copper ions can be described as distorted bipyramidal, with the equatorial planes lying perpendicular to the plane of the grid. The ground state of the copper ions is thus $d_{x^2-y^2}$, with the lobes directed towards N_1, N_2, N_3 and the equatorial phenoxy oxygen atom (Figure 3). However, in view of the approximate C_4 symmetry of the grid, the bipyramids of neighboring copper ions are rotated by 90°, such that the overlap of the orbitals is negligible (Figure 3). This accounts for the almost zero exchange coupling found for the present $\mathrm{Cu^{II}}_4$ grid complex **1**. On this basis, we predict that exchange coupling in the analogous nickel grid should be quite strong, as in this case both $d_{x^2-y^2}$ and d_{z^2} would be occupied and thus a $d_{x^2-y^2}$ − d_{z^2} exchange path would exist.

Conclusions

A [2 × 2] $\mathrm{Cu^{II}}_4$ grid-type complex **1** has been synthesized and characterized. The crystal structure data reveal a complex of C_4 symmetry, where the copper centers adopt a distorted bipyramidal geometry. Cu−N bond lengths and Cu−O−Cu bridge angles are typical for complexes of this type, which usually exhibit antiferromagnetic spin coupling. However, in the present case, magnetic measurements indicate only a very weak antiferromagnetic coupling of the copper ions due to insufficient overlap of the orbitals, which can be rationalized by considering the crystal structure of this grid complex.

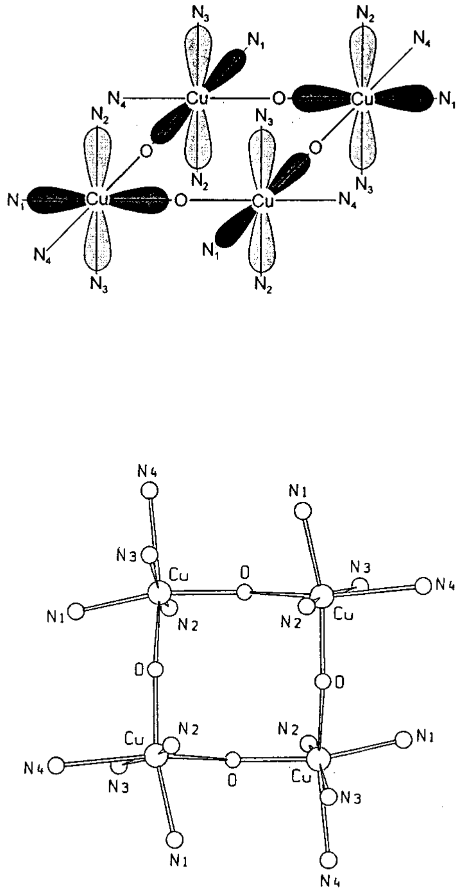


Figure 3. Schematic representation of the orientation of the magnetic $d_{x^2-y^2}$ orbitals in the [2 × 2] grid **1** (top) and X-ray structure of the metallic core of complex **1** and the N,O heteroatoms coordinated to the $\mathrm{Cu^{II}}$ ions (bottom)

Experimental Section

Unless otherwise noted, ^{1}H-NMR spectra were recorded in $CDCl_3$ solution with respect to the residual solvent peak at 200 MHz with a Bruker AC 200 spectrometer. − Melting points were obtained with a digital Thomas Hoover (Electrotherma) apparatus and are uncorrected. − Infrared absorption spectra were recorded with a Perkin-Elmer 1600 series FT-IR spectrometer and electronic absorption spectra with a Cary 219 spectrometer in acetonitrile; λ_{max} in nm and ε in $\mathrm{M^{-1}\,cm^{-1}}$. − Fast-atom bombardment (FAB) mass spectrometry was performed with a ZAB-HF VG spectrometer with *m*-nitrobenzyl alcohol as the matrix; electronic impact (EI) was performed with a Fisons Instruments VG trio 2000 spectrometer, and electrospray (ES) mass spectrometry with a ZAB-HF VG spectrometer. All spectroscopic studies were performed in spectroscopic-grade solvents. All other solvents were reagent grade and were used without further purification.

Magnetic Measurements: Magnetic moments of powdered samples of complex **1** were measured with a commercial SQUID magnetometer (Quantum Design). Measurements were made over the temperature range 2−250 K at a maximum field of 5.5 T. Susceptibility was determined on the basis of measurements made at fields of 10 KG. The powder samples were fixed with apiezon grease on a plastic straw. The background signal of the plastic straw was found to be below the resolution of the magnetometer. The signal of the grease was measured independently and the data were corrected accordingly. The data were also corrected for a diamagnetic contribution of -1.5×10^{-3} cm^3 mol^{-1}, taking into account the contribution of the ligands, which was estimated using Pascal's constants and the TIP of the copper(II) ions. The weight of the powder sample used was typically 1.2 mg. The magnetization of the hamiltonian (Equation 1) was calculated in the following way. The well-known formula for the susceptibility of the hamiltonian $-\Sigma J_{ij}\mathrm{S}_i \cdot \mathrm{S}_j + \mu_\mathrm{B} g \mathrm{B} \cdot \mathrm{S}$[14] can be easily generalized to

$$m = N\mu_\mathrm{B} g \frac{\sum_S \Omega(S)\sinh[(2S+1)y]\, S\, B_S(Sy)\exp[-\beta E(S)]}{\sum_S \Omega(S)\sinh[(2S+1)y]\exp[-\beta E(S)]}$$

for the magnetization at arbitrary magnetic field. Here $y = g\mu_\mathrm{B}B/(k_\mathrm{B}T)$, $\mathrm{B_S(Sy)}$ is the Brillouin function,[15] $\beta = 1/(k_\mathrm{B}T)$, $\Omega(S)$ denotes the degeneracy of the states E(S), and other symbols have their usual meanings. For the hamiltonian (Equation 1), the energies E(S) and degeneracies $\Omega(S)$ can be easily calculated using Kambe's vector coupling model.[15,16] The final result for the magnetization is

$$m = N\mu_\mathrm{B} g \frac{\sinh(3/2y)\, B_1(y)\,(x+2x^2) + \sinh(5/2y)\, B_2(2y) 2x^3}{\sinh(1/2y)\,(1+x^2) + \sinh(3/2y)\,(x+2x^2) + \sinh(5/2y)\, 2x^3}$$

with $x = \exp(\beta J)$.

4-*tert*-Butyl-2,6-dinitrophenol (2): A solution of 4-*tert*-butylphenol (0.1797 mol, 27 g) in glacial acetic acid (60 mL) was added dropwise with constant stirring to a mixture of nitric acid 65% (40 mL) and glacial acetic acid (75 mL) cooled to −15°C. After the addition, the mixture was allowed to slowly warm to room temperature over a period of 30 min and then poured onto crushed ice. The resulting yellow solid was filtered off, redissolved in chloroform, and this solution was washed several times with water. The organic phase was dried (Na_2SO_4) and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel, eluting with ethyl acetate/hexane (1:6), to give **2** as a yellow solid (30 g, 70% yield); m.p. 96−97°C (ref.[10] 95°C). − IR (KBr): $\tilde{\nu}$ = 3448, 3173, 2961, 1640, 1533, 1368, 1309, 1266, 922, 729, 651 cm^{-1}. − ^{1}H NMR: δ = 8.32 (s, 2 H, Ar), 1.37 (s, 9 H, *t*Bu). − ^{13}C NMR: δ = 147.2, 143.0, 137.2, 34.7, 30.8. − MS (EI); *m/z* (%): 239.9 (40) [M$^+$], 224.9 (100) [M$^+$ − Me]. − $C_{10}H_{12}N_2O_5$ (240.22): calcd. C 50.00, H 5.04, N 11.66; found C 50.18, H 5.09, N 11.79.

Ligand LH 3: To 4-*tert*-butyl-2,6-dinitrophenol (**2**, 4.2 mmol, 1.0 g) in ethyl acetate (10 mL) and dry methanol (20 mL), 5% Pd/C (0.4 g) and 9 equiv. of anhydrous ammonium formate (37.5 mmol, 2.36 g) were added. The resulting mixture was stirred at room temperature under argon for 15 min, according to the standard literature procedure.[11] The catalyst was then removed by filtration through a Celite pad and washed with dry methanol. The combined filtrate and washings were concentrated to dryness, the resulting residue was triturated with water (10 mL), and extracted with chloroform (3 × 50 mL). The combined organic extracts were dried (Na_2SO_4) and the solvent was removed under reduced pressure to leave a dark solid (670 mg). This solid was redissolved in dry THF (10 mL), two equivalents of 2-pyridinecarboxaldehyde (7.4 mmol, 0.7 mL) were added, and the resulting mixture was stirred in the presence of 4-Å molecular sieves for 7 h. The solvent was then removed and the residual oil was triturated with hexane to give **3** as a brownish-yellow solid, which was filtered off and washed with further hexane. Ligand **3** (1.01 g, 81% yield, m.p. 103−105°C) was used without further purification for the complexation studies. − IR (KBr): $\tilde{\nu}$ = 3354, 2954, 1629, 1586, 1467, 1435, 1362, 1288, 1247, 989, 778, 550, 406 cm^{-1}. − ^{1}H NMR: δ = 8.87 (s, 2 H, CH=N), 8.72 (d, 2 H, *J* = 4.3 Hz, Ar), 8.28 (d, 2 H, *J* = 8.0 Hz, Ar), 7.89 (dt, 2 H, *J* = 7.7, 1.4 Hz, Ar), 7.39 (ddd, 2 H, *J* = 7.4, 4.9, 1.0 Hz, Ar), 7.28 (s, 2 H, Ar), 1.35 (s, 9 H, *t*-Bu). − ^{13}C NMR: δ = 159.5, 154.3, 149.5, 143.5, 136.9, 136.6, 136.1, 125.1, 121.6, 115.2, 34.4, 31.3. − MS (FAB): *m/z* (%) = 359.1 (100) [M$^+$ + 1]. − HRMS ($C_{22}H_{23}N_4O$): calcd. 359.1867; found 359.1872. − UV/Vis: λ_{max} ($\varepsilon \times 10^4$) = 226 (0.13), 282 (0.12), 500 nm (0.05).

$(LCu)_4(PF_6)_4$ 1: To ligand LH **3** (0.2789 mmol, 100 mg) in anhydrous methanol (15 mL), 1 equiv. of NaOMe (0.2789 mmol, 15 mg) was added at room temperature. To the deep-red solution obtained, 1 equiv. of $Cu(CF_3SO_3)_2$ (0.2789 mmol, 100 mg) was added, resulting in a color change to purple. The mixture was stirred for 3 h and then filtered through cotton. Addition of a saturated methanolic solution of ammonium hexafluorophosphate led to the precipitation of a solid, which was collected by centrifugation and recrystallized from acetonitrile/diethyl ether to give complex **1** as a deep-purple solid (158 mg, 80% yield); m.p. 240°C (calcination). − IR (KBr): $\tilde{\nu}$ = 3142, 1598, 1484, 1400, 1281, 1248, 838, 559 cm^{-1}. − MS (ES); *m/z*: 2119.3 [M − PF_6], 987 [M − 2 PF_6]. − $C_{88}H_{84}Cu_4F_{24}N_{16}O_4P_4$ (2263.78): calcd. C 46.69, H 3.74, N 9.90; found C 46.68, H 3.82, N 9.73. − UV/Vis: λ_{max} ($\varepsilon \times 10^4$) = 224 (5.6), 328 (6.1), 521 nm (4.7).

Crystal Structure Determination: Crystal data for $C_{88}H_{84}Cu_4F_{24}N_{16}O_4P_4 \cdot (MeCN)_2$, M_r = 2592.18, tetragonal, space group *I*4(1)/*a* (no. 88), *a* = *b* = 26.325(4), *c* = 16.980(3) Å, *V* = 11767(3) Å^3, *Z* = 4, D_c = 1.463 Mg m^{-3}, *F*(000) = 5296, *T* = 200 K, crystal dimensions 0.3 × 0.2 × 0.2 mm, purple; 28039 reflections, of which 5952 were unique (R_{int} = 0.0457), were recorded with an Enraf−Nonius CAD4 diffractometer. Final *R* indices: R_1 = 0.0451, wR_2 = 0.1195; (all data) R_1 = 0.0554, wR_2 = 0.1260 for 463 parameters. Goodness of fit on F^2 = 1.020. Largest diff. peak and hole 0.750 and −0.599 Å^{-3}. Crystallographic data for complex **1** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication CCDC-112945. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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[1] [1a] J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**. − [1b] *Comprehensive Supramolecular Chemistry* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, J.-M. Lehn), Pergamon, Oxford, **1996**; P. N. W. Baxter, vol. 9, ch. 5, p. 165; M. Fujita, vol. 9, ch. 7, p. 253.

[2] G. S. Hanan, C. R. Arana, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1996**, *2*, 1292.

[3] G. S. Hanan, D. Volkmer, U. S. Schubert, J.-M. Lehn, G. Baum, D. Fenske, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1842.

[4] A. Credi, V. Balzani, S. Campagna, G. S. Hanan, C. R. Arana, J.-M. Lehn, *Chem. Phys. Lett.* **1995**, *243*, 102.

[5] O. Waldmann, J. Hassmann, P. Müller, G. S. Hanan, D. Volkmer, U. S. Schubert, J.-M. Lehn, *Phys. Rev. Lett.* **1997**, *78*, 3390; O. Waldmann, J. Hassmann, P. Müller, D. Volkmer, U. S. Schubert, J.-M. Lehn, *Phys. Rev. B* **1998**, *58*, 3277.

[6] [6a] A. R. Davis, F. W. B. Einstein, N. F. Curtis, J. W. L. Martin, *J. Am. Chem. Soc.* **1978**, *100*, 6258. − [6b] Y. Agnus, R. Louis, R. Weiss, *J. Am. Chem. Soc.* **1979**, *101*, 3381. − [6c] L. K. Thompson, F. W. Hartstock, P. Robichaud, A. W. Hanson, *Can. J. Chem.* **1984**, *62*, 2755. − [6d] H. P. Berends, D. W. Stephan, *Inorg. Chem.* **1987**, *26*, 749. − [6e] L. J. Farrugia, P. A. Lovatt, R. D. Peacock, *J. Chem. Soc., Dalton Trans.* **1997**, 911. − [6f] E. Escrivá, J. Server-Carrió, L. Lezama, J. V. Folgado, J. L.

Pizarro, R. Ballesteros, B. Abarca, *J. Chem. Soc., Dalton Trans.* **1997**, 2033. – [6g] E. Ruiz, P. Alemany, S. Alvarez, J. Caro, *Inorg. Chem.* **1997**, *36*, 3683.

[7] [7a] P. L. Burk, J. A. Osborn, M.-T. Youinou, Y. Agnus, R. Louis, R. Weiss, *J. Am. Chem. Soc.* **1981**, 103, 1273. – [7b] M. S. Haddad, S. R. Wilson, D. J. Hodgson, D. N. Hendrickson, *J. Am. Chem. Soc.* **1981**, *103*, 384. – [7c] K. J. Oberhausen, J. F. Richardson, R. M. Buchanan, J. K. McCuster, D. N. Hendrickson, J.-M. Latour, *Inorg. Chem.* **1991**, *30*, 1357. – [7d] Y. Nishida, H. Shimo, H. Maehara, S. Kida, *J. Chem. Soc., Dalton Trans.* **1985**, 1945.

[8] [8a] T. N. Doman, D. E. Williams, J. F. Banks, R. M. Buchanan, H.-R. Chang, R. J. Webb, D. N. Hendrickson, *Inorg. Chem.* **1990**, *29*, 1058. – [8b] E. Spodine, J. Manzur, M. T. Garland, M. Kiwi, O. Peña, D. Grandjean, L. Toupet, *J. Chem. Soc., Dalton Trans.* **1991**, 365.

[9] A. Gelasco, A. Askenas, V. L. Pecoraro, *Inorg. Chem.* **1996**, *35*, 1419.

[10] G. G. S. Dutton, T. I. Briggs, B. R. Brown, M. E. D. Hillman, *Can. J. Chem.* **1953**, *31*, 685.

[11] S. Ram, R. E. Ehrenkaufer, *Tetrahedron Lett.* **1984**, *25*, 3414.

[12] T. N. Sorrell, C. J. O′Connor, O. P. Anderson, J. H. Reibenspies, *J. Am. Chem. Soc.* **1985**, *107*, 4199.

[13] V. McKee, M. Zvagulis, J. V. Dagdigian, M. G. Patch, C. A. Reed, *J. Am. Chem. Soc.* **1984**, *106*, 4765.

[14] F. E. Mabbs, D. J. Machin, *Magnetism and Transition Metal Complexes*, Chapman and Hall, London, **1973**.

[15] O. Kahn, *Molecular Magnetism*, VCH, USA, **1993**.

[16] D. Gatteschi, A. Bencini, *Electron Paramagnetic Resonance of Exchange-Coupled Systems*, Springer-Verlag, Berlin, **1990**.

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