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Trans-Fused Macrobicycle “Betweenanene” around a Planar $Cu_2(\mu\text{-}CH_3O)_2$ Core Showing Remarkable Antiferromagnetic Interaction

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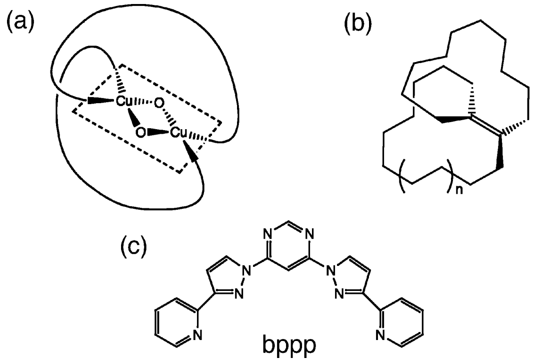
Complexation of 4,6-bis{3-(2-pyridyl)-1*H*-pyrazol-1-yl}pyrimidine (bppp) and copper(II) tetrafluoroborate in methanol gave a self-assembled $[Cu_2(CH_3O)_2(bppp)_2]^{2+}$ ion having a betweenanene-type structure. Each bppp spans across the common Cu_2O_2 plane in a trans fashion to ligate each copper center. The antiferromagnetic interaction observed in the Cu_2O_2 core is ascribable to the superexchange along the Cu–O–Cu linkage and found to be one of the largest among the analogous compounds, owing to the large Cu–O–Cu angle perturbed with the two bppp molecular tweezers.

Chart 1. (a) Schematic Drawing of a Trans-Fused Macrobicycle Having a Cu_2O_2 Core; (b) [10.10]- and [10.8]betweenanenes ($n = 1$ and 0, Respectively); (c) Molecular Structure of bppp



Materials involving novel molecular and electronic structures oriented to electronic, magnetic, and photonic devices are available from various self-assembly techniques;[1] single-molecule magnets are an instance of current interest.[2] Application of unique organic skeletons to transition-metal coordination compounds is assessed extensively. Munakata et al.[3] reported the cyclophanes in which the alkyl bridges were replaced with Ag(I) ions, and Fujita et al.[4] utilized the organic−inorganic hybrid hosts as nanosized reaction vessels in place of conventional cyclodextrins and calixarenes. The synthetic efforts can be drastically decreased by means of a self-assembled coordination process.[3−5] Here we report the construction of a trans-fused macrobicycle wherein the two rings share a common four-membered Cu_2O_2 core, which can be regarded as a coordination compound version of a “betweenanene”,[6,7] as shown in Chart 1. These compounds attract attention of topological isomerism, steric shielding of the core, molecular dynamics, and chirality.[8] Because the present complex contains an exchange-coupled copper(II) ($S = {}^1/_2$) dimer at the center, we then focused on a magnetic study, in connection with the magnetostructural correlation demonstrated impressively in several reports.[9−11]

We prepared a new linear pentakis(azaaryl) compound, 4,6-bis{3-(2-pyridyl)-1*H*-pyrazol-1-yl}pyrimidine (bppp), as a polydentate ligand.[12] The aromatic nucleophilic substitution of the present study was proved to occur under milder conditions than those of the previous reports on 4,6-bis(1*H*-pyrazol-1-yl)pyrimidine.[13] Complexation of bppp with copper(II) tetrafluoroborate in methanol afforded dark green crystals of $[Cu^{II}_2(CH_3O)_2(bppp)_2](BF_4)_2{\cdot}CH_3OH$.[14] The Cu/bppp ratio was elucidated as 1:1 from elemental analysis and X-ray crystal structure analysis.

Figure 1a shows the molecular structure of $[Cu^{II}_2(CH_3O)_2(bppp)_2]^{2+}$. The entire molecule corresponds to a crystallo-

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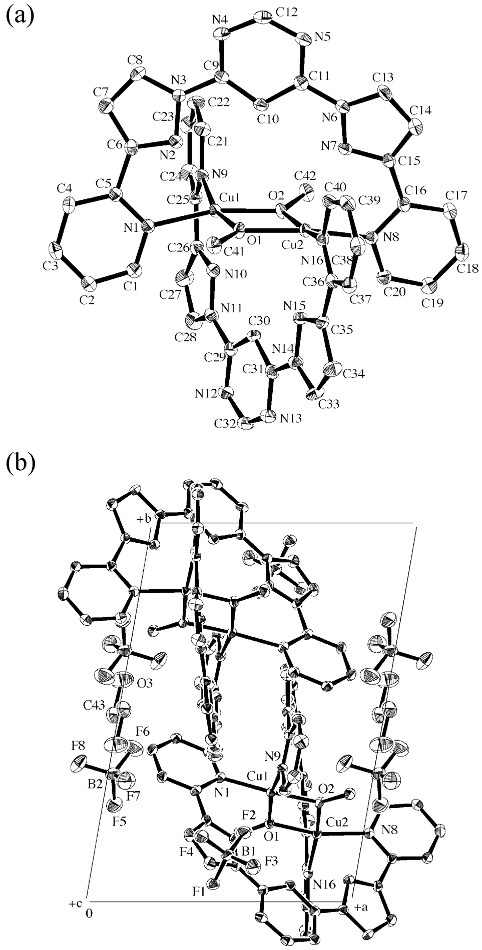

Figure 1. (a) ORTEP drawing of $[Cu^{II}_2(CH_3O)_2(bppp)_2]^{2+}$. Hydrogen atoms, tetrafluoroborate anions, and solvated methanol molecules are omitted for the sake of clarity. Atomic numbering is shown. (b) Molecular arrangement of $[Cu^{II}_2(CH_3O)_2(bppp)_2](BF_4)_2{\cdot}CH_3OH$ viewed along the *c* axis. Hydrogen atoms are omitted. Selected atoms are numbered.

graphically independent unit. Both copper(II) ions (Cu1 and Cu2) were tetracoordinate. Two methoxide oxygens (O1 and O2) are coordinated on a dinuclear copper(II) basal plane with Cu1−O1, Cu1−O2, Cu2−O1, and Cu2−O2 distances of 1.933(3), 1.936(2), 1.926(2), and 1.946(3) Å, respectively. The methoxide anion was introduced from the reaction solvent under the basic conditions due to the bppp base. A four-membered ring Cu1−O1−Cu2−O2 was formed with Cu1−O1−Cu2 and Cu1−O2−Cu2 angles of 106.1(1) and 105.3(1)°, respectively. The interatomic Cu1- - -Cu2 separation is 3.0846(6) Å. The Cu_2O_2 core is practically planar, as indicated by small torsion angles (<0.53(7)°) defined among the Cu1, O1, Cu2, and O2 atoms.

The terminal pyridine nitrogen atoms (N1, N8, N9, and N16) are also coordinated to the copper(II) ions at the equatorial positions with distances of 2.030(3)−2.056(4) Å. There seem to be weak interactions, as indicated by rather long Cu1- - -N2, Cu1- - -N10, Cu2- - -N7, and Cu2- - -N15 distances (2.583(3)−2.647(3) Å). The pyrimidine nitrogen atoms (N4, N5, N12, and N13) are free from coordination. These nitrogen atoms are helpful for coplanar configuration between the pyrazole and pyrimidine rings by reducing steric hindrance between the ortho positions.

The mutual positions of N1- - -N8 and N9- - -N16 can be named as trans such as ethylenes. Each bppp has a U-shaped form and spans across the Cu_2O_2 core in a trans fashion, as illustrated in Chart 1a. The two pyridine nitrogen atoms catch the size-matched dinuclear core, just like supramolecular receptors named as molecular tweezers.[15] The four long axial N- - -Cu interactions may play an auxiliary role in building the domes up above the Cu_2O_2 base.

We have to make a comment on the trans bridge favored over a possible cis bridge. The distances across the trans positions, i.e., interatomic N1- - -N8 and N9- - -N16 distances, were experimentally determined to be 6.530(4) and 6.566(5) Å, respectively. On the other hand, those of the cis positions were 5.968(4) and 5.891(4) Å. The geometry of a metal-free bppp was optimized on a DFT method at the B3LYP/6-311+G(2d,p) level.[16,17] The calculated N1- - -N8 distance was 6.867 Å, which is closer to those for the trans positions than those for the cis ones. Thus, the bridge across the trans position is favored because of matching of the N- - -N distances; the rigid π-conjugated structure of bppp stands against bending deformation.

The present compound and betweenanenes possess an approximate D_2 symmetry and are basically chiral. However, the crystal of $[Cu^{II}_2(CH_3O)_2(bppp)_2](BF_4)_2{\cdot}CH_3OH$ consists of a racemate of the P and M forms. The enantiomer pair is related with an inversion symmetry due to the $P\bar{1}$ space group with $Z = 2$, as shown in Figure 1b.

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(12) A mixture of 4,6-dichoropyrimidine (376 mg, 2.52 mmol), 3-(2′-pyridyl)-1*H*-pyrazole (869 mg, 5.95 mmol), potassium carbonate (837 mg, 6.06 mmol), and acetone (5 mL) was refluxed for 3 days with vigorous stirring. The mixture was poured into water, and the organic solid was separated on a filter. Purification through silica gel with chloroform as an eluent gave pure bppp (787 mg, 2.15 mmol) in 85% yield. Mp: 239−240 °C. ^{1}H NMR (CDCl$_3$, 270 MHz, 25 °C): δ 7.18 (2H, d, $J = 2.7$ Hz), 7.32 (2H, ddd, $J = 1.2$, 4.9, and 7.6 Hz), 7.83 (2H, dt, $J = 1.7$ and 7.6 Hz), 8.26 (2H, td, $J = 1.1$ and 7.6 Hz), 8.64 (1H, d, $J = 1.1$ Hz), 8.69 (2H, d, $J = 2.7$ Hz), 8.70 (2H, ddd, $J = 1.1$, 1.7, and 4.9 Hz), 8.83 (1H, d, $J = 1.1$ Hz). ^{13}C NMR (CDCl$_3$, 67.8 MHz, 25 °C): δ 95.6, 107.9, 120.9, 123.4, 129.3, 136.7, 149.5, 151.0, 155.9, 158.0, 158.6. MS (EI, 70 eV): *m*/*z* 366 (M$^+$). IR (KBr disk): 777, 1369, 1469, and 1585 cm^{-1}. For the preparation of 3-(2′-pyridyl)-1*H*-pyrazole, see: Amoroso, A. J.; Thompson, A. M. C.; Jeffery, J. C.; Jones, P. L.; McCleverty, J. A.; Ward, M. D. *J. Chem. Soc., Chem. Commun.* **1994**, 2751.

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(14) To a hot mixture of bppp (41 mg, 0.11 mmol) and methanol (10 mL) was added dropwise a methanol solution (1 mL) containing $Cu(BF_4)_2{\cdot}6H_2O$ (41 mg, 0.12 mmol). The resultant mixture was filtered, and the filtrate was allowed to stand at room temperature for 1 week. Green crystalline and colorless powder products were precipitated, and the latter was removed by decantation. The former was collected on a filter (40 mg, 0.035 mmol) in 32% yield as $[Cu_2(CH_3O)_2(bppp)_2](BF_4)_2{\cdot}CH_3OH$ and subjected to elemental and X-ray diffraction analyses and magnetic study. IR (KBr disk): 781, 1059, 1369, 1466, 1589, and 3400 cm^{-1}. Anal. Calcd for $C_{43}H_{38}Cu_2B_2F_8N_{16}O_3$ ($[Cu_2(CH_3O)_2(bppp)_2](BF_4)_2{\cdot}CH_3OH$): C, 45.80; H, 3.40; N, 19.88. Found: C, 45.45; H, 3.42; N, 19.87.

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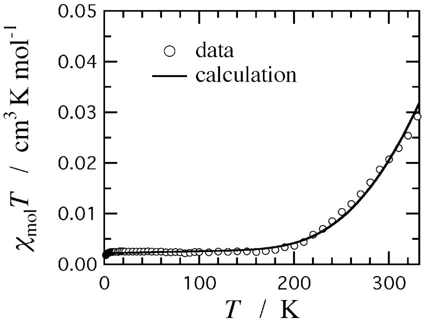

Figure 2. Temperature dependence of the product of molar magnetic susceptibility (χ_{mol}) and temperature (T) measured at 5000 Oe for $[Cu^{II}_2(CH_3O)_2(bppp)_2](BF_4)_2\cdot CH_3OH$. The solid line represents the theoretical fit. See the text for the equation and optimized parameters.

Magnetic susceptibilities of randomly oriented polycrystalline samples of $[Cu^{II}_2(CH_3O)_2(bppp)_2](BF_4)_2\cdot CH_3OH$ were measured on a SQUID magnetometer. Figure 2 shows the results of magnetic susceptibility measurements on the basis of the dinuclear copper(II) unit. The $\chi_{mol}T$ value was extremely smaller than the theoretical value (typically 0.8 cm^3 K mol^{-1}) and gradually increased on heating. This behavior can be interpreted in terms of the singlet−triplet model[18] with considerably strong antiferromagnetic coupling. The $\chi_{mol}T$ value also includes monomeric $^1/_2$ spins with approximately 2.4×10^{-3} cm^3 K mol^{-1}. Therefore, the following equation (eq 1) can be proposed for the analysis of the data. The first term implies the singlet−triplet model and the second term the Curie-type impurity, where the impurity factor (p) is defined as a molar fraction of the monomeric Cu^{II} ions. Assuming a g value of 2.15 for typical Cu^{II} ions,[19] because the present compound was electron spin resonance silent under ambient conditions, we obtained the following optimized parameters: $J/k_B = -793(10)$ K and $p = 0.0051(1)$. The calculated curve is superposed in Figure 2.

$$\chi_{mol} = \frac{N_A g^2 \mu_B{}^2}{k_B T}\left[(1-p)\frac{2}{3+\exp(-2J/k_B T)} + p\frac{1}{4}\right] \quad (1)$$

Hatfield[20] and Haase[21] discussed the magnetostructure relationship, J as a function of the Cu−O−Cu angle (ϕ), in various hydroxo- and alkoxo-bridged dinuclear copper(II) complexes, respectively. As for the latter, a linear relationship between J and ϕ has been proposed with a slope of −82.1 cm^{-1} deg^{-1} and a crossover angle of 95.7°.[21] Very recently, we have reported another example of a doubly methoxide-bridged dicopper(II) core containing 4-aminopyrimidine (4APM), $[Cu(4APM)(NO_3)(OCH_3)]$, which showed $2J/k_B = -1100$ K with $\phi = 102.9(2)°$.[22] The present complex has $\phi = 105.7°$ on average and $2J/k_B = -1600$ K. These ϕ values fell in the antiferromagnetic region according to the Hatfield and Haase formalism.[20,21] Furthermore, the larger angle in the present complex showed the stronger antiferromagnetic coupling, in agreement with the negative slope in the J vs ϕ plot.[21]

However, the empirical linear relationship[21] gave a somewhat underestimation of J. Walz et al. proposed the correction factor[23] for such a deviation reported on the μ-methoxo-μ-phenoxo-bridged dinuclear copper(II) complexes ($\phi = 104.0°$ and $2J/k_B = -1460$ K),[24] but the angle of the present complex lies out of the range for this correction. Nevertheless, the present J value belongs to the largest class among the analogous structures in connection with the considerably large ϕ.

The large ϕ of the Cu_2O_2 rhombus was accompanied by elongated deformation in the Cu- - -Cu direction. Actually, the Cu- - -Cu separation of the present compound is farther than those of any other compounds (2.903(3)−3.063(1) Å) listed in ref 23. From the calculation results shown above, the metal-free bppp has a longer N1- - -N8 (or N9- - -N11) distance than those found in the complex, and accordingly the Cu_2O_2 core is forced to expand in the Cu- - -Cu direction through tension of four equatorial N−Cu bonds.

In summary, the ligand bppp works as molecular tweezers that fit the trans positions of the Cu_2O_2 moiety. The Cu−O−Cu angle seems to be opened with tension of the Cu−N bonds. As a consequence, the superexchange antiferromagnetic interaction observed within the Cu_2O_2 core belongs to the largest class among the analogues. Peripheral derivatization on bppp may bring about tuning of the magnetic interaction because the magnitude of the exchange coupling is highly susceptible to the Cu_2O_2 elongation or compression.

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Supporting Information Available: CIF file for $[Cu_2(CH_3O)_2(bppp)_2](BF_4)_2\cdot CH_3OH$. This material is available free of charge via the Internet at http://pubs.acs.org.

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