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Author(s)	Noro, Shin-ichiro; Akutagawa, Tomoyuki; Nakamura, Takayoshi
Citation	Chemical Communications, 46(25), 4619-4621 https://doi.org/10.1039/c001718c
Issue Date	2010-07-07
Doc URL	https://hdl.handle.net/2115/46779
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Type	journal article
File Information	CC46-25_4619-4621.pdf



Orthogonality of Jahn–Teller axes in a dinuclear Cu(II) complex bridged by one F[−] anion

Shin-ichiro Noro,*^a Tomoyuki Akutagawa^a and Takayoshi Nakamura*^a

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

First published on the web Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

The dinuclear Cu(II) complex bridged by a single F[−] anion has orthogonal Jahn–Teller axes, which induce a ferromagnetic interaction between the intramolecular Cu(II) ions.

The Cu(II) ion, which has a d⁹ configuration, shows a Jahn–Teller distortion that enables the addition of interesting properties such as flexibility,¹ unsaturated coordination sites,² unprecedented bonding modes derived from electrostatic interactions,^{3,4} and polar structures,⁵ to metal complexes. For example, we have recently developed a synthetic method to introduce polar structures in coordination polymers using Cu(II) ions and weak Lewis-base PF₆[−] anions. The resulting polar coordination polymers showed highly selective CO₂ adsorption properties with structural transformations.⁵ In this paper, we report the synthesis, crystal structure, and physical properties of the dinuclear Cu(II) complex [Cu₂F(BF₄)₃(4-phpy)₇] (**1**, 4-phpy = 4-phenylpyridine) bridged by a single F[−] anion, in which a Jahn–Teller distortion contributes to the formation of a unique structure and properties.

Blue crystals of **1** were obtained by slow diffusion of a methanol solution containing Cu(BF₄)₂·xH₂O and a toluene solution containing 4-phpy in an H-type glass cell.⁶ The bridged F[−] anion originates from the hydrolysis of one equivalent of the BF₄[−] anion,⁷ a well-documented phenomenon that has also been utilized to yield coordination compounds with bridged F[−] anions.^{8,9}

Fig. 1 ORTEP drawing of **1** (thermal ellipsoids drawn at 50% probability). The hydrogen atoms are omitted for clarity.

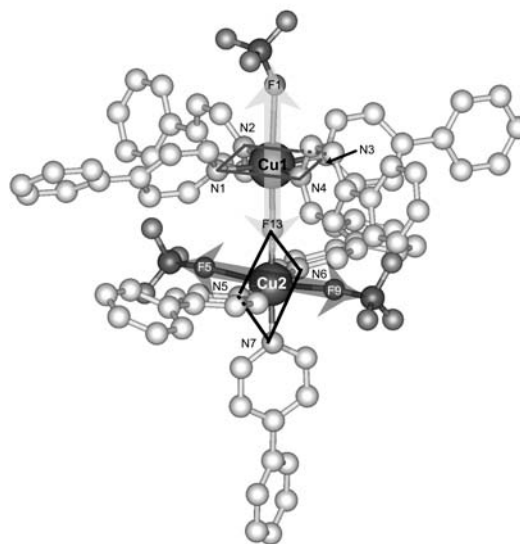
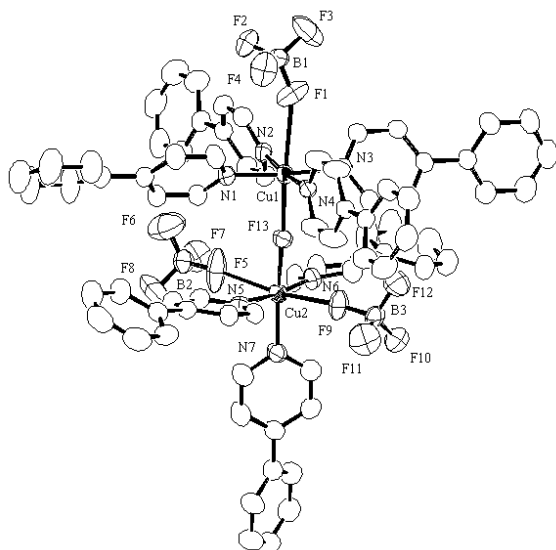


Fig. 2 Schematic view of the orthogonality of the Jahn–Teller axes in **1**. The Jahn–Teller axes of the Cu1 and Cu2 ions are shown by light and dark grey arrows, respectively. The xy planes of the Cu1 and Cu2 ions are therefore defined by N1N2N3N4 and F13N6N7N5 atoms, respectively.



The crystal structure of **1** is shown in Fig. 1.[†] In this crystal, there are two crystallographically independent Cu(II) centres. The Cu1 ion has an elongated octahedral environment with four 4-phpy nitrogen atoms in the equatorial plane and two fluorine atoms from BF₄[−] and F[−] anions in the axial sites. On the other hand, the Cu2 ion is coordinated to three 4-phpy nitrogen atoms and one F[−] anion in the equatorial plane and two BF₄[−] fluorine atoms at the axial positions, resulting in an elongated octahedral environment. The F[−] anion almost linearly bridges the Cu(II) centres (Cu1–F13 = 2.227(2) Å, Cu2–F13 = 1.896(2) Å, and Cu1–F13–Cu2 = 177.5(1)°) to form the dinuclear structure with the Cu1...Cu2 distance of 4.12 Å. Interestingly, the Jahn–Teller axes of the Cu1 and Cu2 ions are not parallel but nearly perpendicular to each other as shown in Fig. 2, suggesting that the magnetic orbitals (d_{x²−y²}) of both Cu(II) ions are orthogonal (dihedral angle of N1N2N3N4 and F13N6N7N5 planes: 88°). A similar orbital arrangement has been observed in inorganic materials such as KCuF₃, K₂CuF₄, and K₃Cu₂F₇, in which there are ferromagnetic interactions between the Cu(II) ions.^{10–12} Therefore, it was expected that **1** would also have a

ferromagnetic interaction between the Cu1 and Cu2 ions.

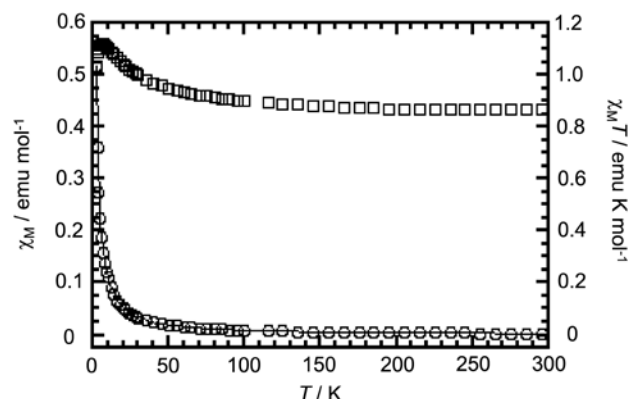


Fig. 3 Temperature dependence of molar magnetic susceptibility (χ_M) of **1**. χ_M vs T (circle) and $\chi_M T$ vs T (square) are plotted using the left and right scales, respectively. Solid line is the fitting result (see text).

The magnetic susceptibility of **1** was measured and is shown in Fig. 3. At 305 K, $\chi_M T$ equals 0.87 emu K mol⁻¹, a value that is already higher than expected for two uncoupled Cu(II) ions. $\chi_M T$ increases upon cooling and appears to reach a maximum equal to 1.12 emu K mol⁻¹ at 6 K, and then to decrease slightly to a value of 1.04 emu K mol⁻¹ at 2 K. This behaviour is characteristic of a ferromagnetic coupling between the Cu(II) ions stabilizing the triplet state with regard to the singlet state. Because the decrease of $\chi_M T$ below 6 K suggests that a very weak antiferromagnetic intermolecular interaction superimposes itself on the intramolecular ferromagnetic coupling, one can account for this intermolecular effect with a Weiss θ correction. The theoretical expression for the magnetic susceptibility of the dimer is then

$$\chi_M = \frac{2N\beta^2 g^2}{k(T-\theta)} [3 + \exp(-J/kT)]^{-1}$$

where the N , β , and k constants have their usual meanings.^{13,14} The values of g , J , and θ parameters, determined by a least-squares procedure, are $g = 2.18$, $J = +13.2$ cm⁻¹, and $\theta = -0.3$ K. It must be noted here that a zero field splitting of the ground triplet state may also contribute to the magnetic behaviour in the very low temperature range. The ferromagnetic interaction can also be confirmed by the field dependence of magnetization measured at 2 K (Fig. S4). The magnetization rapidly increases at low fields beyond the corresponding Brillouin function's curve with the sets of paramagnetic centres, $S = 1/2 + 1/2$ ($g = 2.18$), gradually increasing up to 5 T. The magnetization at 5 T is $2.0\mu_B$, indicating a ferromagnetic arrangement between the magnetic centres. The slightly lower value at 5 T (the expected value calculated from the Brillouin function with $S = 1$ is $2.1\mu_B$ with $g = 2.18$), could be due to the effect of zero field splitting of the ground triplet state. To our knowledge, **1** is the first Cu(II) complex that shows a ferromagnetic interaction derived from F⁻ bridges. ESR spectra (Fig. S5) also support the claim that the ground state is a triplet state.¹⁴

Although a large number of Cu(II) complexes with F⁻ bridges have been synthesized, a linear Cu–F–Cu bridge with orthogonal Jahn–Teller axes has been rarely observed to date. Common bent Cu–F–Cu bridges result in antiferromagnetic or no magnetic interactions between the Cu(II) ions. Recently, the linear Cu–F–Cu arrangement in a dinuclear complex has been observed with support of other bridged ligands (poly(pyrazolyl)methane ligands);¹⁵ however, the Jahn–Teller axes in adjacent Cu(II) centres are parallel to each other and a strong antiferromagnetic interaction ($J < -600$ cm⁻¹) is observed. The linear Cu–F–Cu bridge and orthogonality of the Jahn–Teller axes observed in **1** is possibly related to the characteristics of axial bonds in Cu(II) ions. The axial bond distance between a Lewis-acid Cu(II) ion and a Lewis-base molecule is longer than the general coordination bond length because of a Jahn–Teller effect, resulting in a very weak acid–base interaction. Because the F⁻ molecule has a negative charge, an electrostatic interaction exists between the cationic Cu(II) ion and the anionic F⁻ molecule. In Cu(II) complexes, the electrostatic interaction probably cooperates with the acid–base interaction in the formation of the axial bond because the electrostatic interaction is generated over a long distance that is proportional to r^{-1} (r = intermolecular distance). Using this characteristic, capture of weak Lewis-base PF₆⁻ anions has been achieved.^{3,5} The unusual linear Cu–F–Cu bridge with orthogonal Jahn–Teller axes is therefore attributed to the contribution of a directionless electrostatic interaction between the Cu1 and F13 ions.

We next checked the polarity of **1** because weak Cu(II)–anion bonds have local polarity.⁵ The charge distribution of the framework (Fig. S6), which was calculated using the Gaussian program,¹⁶ indicates that coordination-free F atoms of BF₄⁻ anions have large negative charges (−0.54 to −0.58). This result implies that these polar parts may act as adsorption sites for gas molecules.⁵ Therefore, the adsorption isotherms for N₂ (77 K) and CO₂ (195 K and 298 K) on **1** were measured (Fig. S7). However, no adsorption was observed for either gas. The asymmetric dinuclear complex has a large dipole moment (12.5 Debye) along the Cu–F–Cu direction. Therefore, there are dipole–dipole interactions between the dinuclear complexes, which prevents gas adsorption with structural transformations. Such a rigid packing of the dinuclear complexes was also confirmed by dielectric measurements (Fig. S8), in which a large response derived from the displacement of weakly coordinated BF₄⁻ anions was not observed.

In conclusion, we succeeded in the synthesis and crystallographic characterization of a novel dinuclear Cu(II) complex bridged by a single F⁻ anion. A unique structural feature (orthogonality of Jahn–Teller axes of the Cu1 and Cu2 ions) originating from a Jahn–Teller effect produced a ferromagnetic interaction within the dinuclear unit.

We thank Prof. S. Kitagawa and Prof. H.-C. Chang (Kyoto University, Japan) for the single-crystal X-ray diffraction analysis.

Notes and references

^a Research Institute for Electronic Science, Hokkaido University, Sapporo 001-0020, Japan. Fax: +81 11 706 9420; Tel: +81 11 706 9418; E-mail: noro@es.hokudai.ac.jp & tnaka@es.hokudai.ac.jp

† Electronic Supplementary Information (ESI) available: Experimental details, IR, XRD, TG, magnetization curve, ESR, visualized charge distribution, adsorption and desorption isotherms, and temperature-dependent dielectric constants. See DOI: 10.1039/b000000x/

‡ Crystal data of **1**: C₇₇H₆₃B₃Cu₂F₁₃N₇, *M* = 1492.89, monoclinic, *a* = 19.642(6), *b* = 17.709(4), *c* = 19.883(6) Å, β = 93.080(14)°, *U* = 6899(3) Å³, *T* = 173 K, space group *P*2₁/*n* (no. 14), *Z* = 4, 112771 reflection measured, 17078 unique (*R*_{int} = 0.087) which were used in all calculations. The final *wR*(*F*₂) was 0.0798 (*I* > 2σ(*I*)). CCDC-759805.

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