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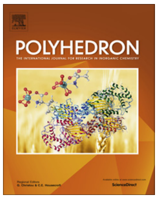

A ground triplet dinuclear copper(II) spiro-complex involving tetraiminoneopentane

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Tetrakis(2-pyridylmethyleneimino)neopentane (**L**) was designed to form a spiro-structure after complex formation, where **L** plays a role of a double tetradentate bridging ligand. The X-ray diffraction study of [Cu_2**L**$(CF_3SO_3)_4$] clarified that the molecular structure was topologically spiro but the two coordination basal planes were not orthogonal with the dihedral angle of 49.8(1)°. The $\chi_m T$ value of [Cu_2**L**$(CF_3SO_3)_4$] showed a small increase on cooling below 10 K, indicating the presence of ferromagnetic coupling. Fitting to a singlet–triplet model gave $2J/k_B = +0.293(7)$ K. The density-functional-theory calculation of the [Cu_2**L**]$^{4+}$ core reproduced the ferromagnetic coupling. Furthermore, from another calculation after removal of the neopentyl skeleton, through-bond interaction is clarified to be major in the exchange mechanism. The intervening sp^3-hybridized carbon atoms may be spin-polarized.

1. Introduction

The spiro junction has been utilized to the geometrically perpendicular structure in bichromophoric π-conjugate molecules oriented to molecular electronic devices [1–3]. The orthogonal arrangement of singly-occupied molecular orbitals attracts much attention in magnetochemistry for development of ground high-spin molecules [4–9]. In particular, 9,9′(10*H*,10′*H*)-spirobiacridine-*N*,*N*′-dioxyl and related compounds have been studied with respect to ground triplet multiplicity [4,5]. We have applied the spiro skeleton to coordination compounds, and already reported dinuclear complexes [{$M^{II}(hfac)_2\}_2(py_4C)$] (Scheme 1a) exhibiting intramolecular antiferromagnetic coupling for M^{II} = Mn^{II} ($3d^5$) [10] and ferromagnetic coupling for M^{II} = Ni^{II} ($3d^8$) [11], where Hhfac stands for 1,1,1,5,5,5-hexafluoropentane-2,4-dione and py_4C for tetrakis(2-pyridyl)methane. The ferromagnetic coupling observed in the Ni^{II} derivative was plausibly explained in terms of orbital orthogonality between σ-type spins [11]. However, unfortunately, preparation of dinuclear Cu^{II} ($3d^9$) complexes with py_4C was unsuccessful, only giving mononuclear compounds [12].

The Schiff bases are well known chelating ligands and supposed to be suitable for such studies on magnetic orbital engineering because of the easily accessible nature. Here we will report successful preparation of a tetrakis(Shiff-base) ligand, tetrakis(2-pyridylmethyleneimino)neopentane (abbreviated as **L**, hereafter). After complete complexation, a whole molecule may form a spiro-fused structure, where **L** plays a role of a double tetradentate bridging ligand (Scheme 1b). By using Cu^{2+} ions carrying a σ-type $3d_{x^2-y^2}$ spin, the σ-electron system in the neopentane skeleton is spin-polarized, and the metal spins might be ferromagnetically exchange-coupled. In this paper the structure and magnetic properties of a novel compound [Cu_2**L**$(CF_3SO_3)_4$] will be reported.

2. Experimental section

2.1. Preparation of [Cu_2**L**$(CF_3SO_3)_4$]·CH_3OH·H_2O

A methanol solution (3 mL) containing 0.013 g (0.098 mmol) of pentaerythrityl tetraamine [13], 0.043 g (0.401 mmol) of 2-pyridinecarboxaldehyde and 0.072 g (0.199 mmol) of $Cu(CF_3SO_3)_2$ were refluxed for 2 d. After the solution was concentrated under reduced pressure, the resulting material was recrystallized from methanol, to give 0.040 g (0.032 mmol) of [Cu_2**L**$(CF_3SO_3)_4$]·CH_3OH·H_2O (**1**) as a green crystalline product in 33% yield. Mp. 301–303 °C. *Anal.* Calc. for $C_{34}H_{34}Cu_2F_{12}N_8O_{14}S_4$: C, 32.36; H, 2.72; N, 8.88; S, 10.16%. Found: C, 32.08; H, 2.41; N, 9.22; S, 10.38%. IR (neat, attenuated total reflection): 422, 515, 573, 630, 771, 1022, 1053, 1145, 1220, 1271, 1453, 1604, 1647 cm^{-1}.

2.2. Crystallography

Single-crystal XRD data of **1** were collected on a Rigaku Saturn70 CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved and

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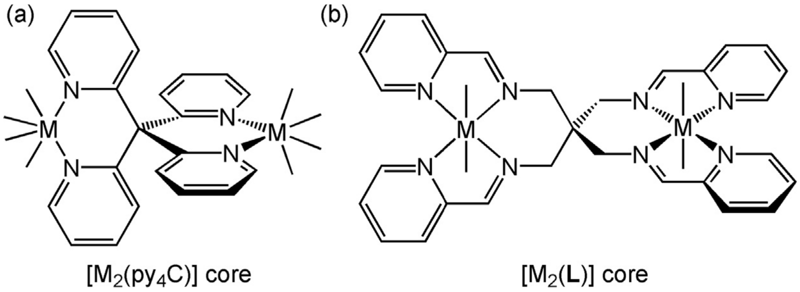


Scheme 1. Structural formulas of dinuclear complexes having (a) py$_4$C and (b) **L**.

expanded in the CrystalStructure program package [14]. Numerical absorption correction was applied. All of the hydrogen atoms were located at calculated positions and the parameters were refined as a riding model. Occupancy factors as solvent contents were optimized, and the composition formula is consistent with the result from the elemental analysis. Selected crystallographic data are as follows: $C_{34}H_{34}Cu_2F_{12}N_8O_{14}S_4$ for $[Cu_2\mathbf{L}(CF_3SO_3)_4]\cdot CH_3OH\cdot H_2O$, monoclinic, $C2/c$, $a = 27.745(8)$ Å, $b = 9.048(3)$ Å, $c = 19.118(6)$ Å, $\beta = 103.844(14)°$, $V = 4660(3)$ Å^3, $Z = 4$, $d_{calc} = 1.799$ g cm^{-3}, μ (MoKα) = 1.213 mm^{-1}, $R(F)$ $[I > 2\sigma(I)] = 0.0794$, $R_w(F^2)$ (all data) = 0.2007, G.O.F. = 1.002, and $T = 100$ K for 4111 unique reflections. CCDC reference number 1511337.

2.3. Magnetic study

The magnetic properties of polycrystalline **1** were studied on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T coil in a temperature range 1.8–300 K. The magnetic data were corrected using diamagnetic blank data of the sample holder measured separately. The diamagnetic contribution of the sample itself was estimated from Pascal's constants.

2.4. DFT calculation

Density-functional-theory (DFT) calculation was performed on Gaussian03 [15]. The convergence criterion was below 10^{-8} a.u. in the SCF energy.

3. Results and discussion

3.1. Synthesis and crystal structure

In this work, Schiff-base condensation giving **L** and complex formation giving $[Cu_2\mathbf{L}(CF_3SO_3)_4]$ were conducted in a one-pot procedure. Namely, the reaction of pentaerythrityl tetraamine or tetraaminoneopentane [13], pyridine-2-carboxaldehyde, and Cu $(CF_3SO_3)_2$ with a molar ratio of 1/4/2 afforded polycrystalline $[Cu_2\mathbf{L}(CF_3SO_3)_4]\cdot CH_3OH\cdot H_2O$ (**1**) in 33% yield (Scheme 2).

The X-ray single crystal structure analysis of **1** was performed in 100 K (Fig. 1). A half of the molecule is crystallographically independent, and a twofold axis runs through the central carbon atom (C1) with the crystal $C2/c$ symmetry. The distance of the Cu ions within a molecule is 6.160(2) Å. On the other hand, the nearest distance of Cu ion among the molecules is 8.994(2) Å, and appreciable interaction channel is hardly found among the molecules. Thus, the exchange interaction can be ascribed mainly to the intramolecular one.

The coordination structure is an elongated octahedron. Four shorter bonds are assigned in the Schiff base chelate plane with the Cu1–N1, Cu1–N2, Cu1–N3, and Cu1–N4 bond lengths of 1.989(4), 2.044(5), 2.005(5), and 2.027(4) Å, respectively. The Cu1–O1 and Cu1–O4 bond lengths are 2.589(5) and 2.333(4) Å, respectively, apparently belonging to a boarder class between coordination bonds and weak interaction. The magnetic orbital $3d_{x^2-y^2}$ is located on the chelate plane, as expected from the molecular design.

The dihedral angle between the planes defined with Cu1, N1, N2, N3, and N4 and with Cu1′, N1′, N2′, N3′, and N4′ was 49.8 (1)°, while the ideal spiro junction requires the right angle. The flexible methylene (C2, C9, C2′, and C9′) configuration seems to be responsible for the somewhat small dihedral angle. Although two copper(II) basal planes are not geometrically orthogonal, a possible σ-pathway of magnetic exchange coupling is supposed to work. A topologically spiro-fused structure may play a role of

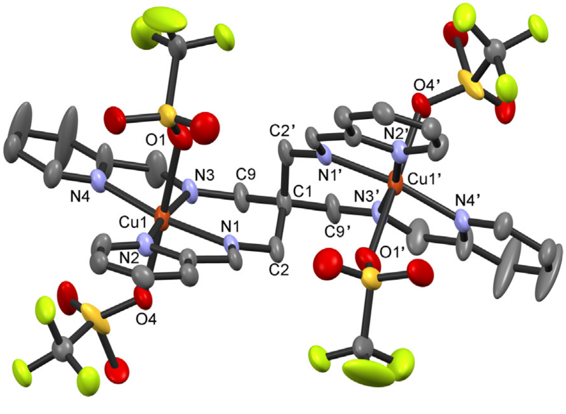
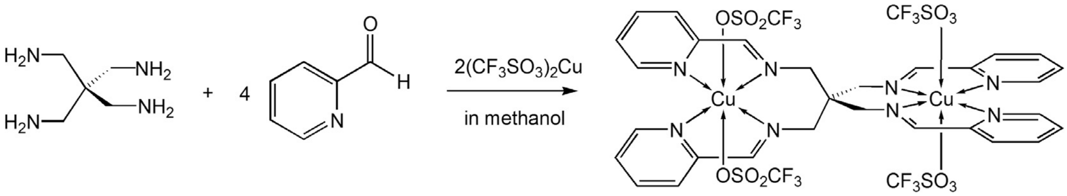


Fig. 1. Crystal structure of **1** with thermal displacement ellipsoids of the 30% probability level. Solvent molecules and hydrogen atoms are omitted for clarity.



Scheme 2. Preparation of $[Cu_2\mathbf{L}(CF_3SO_3)_4]$.