Crystal Structure of a Dinuclear Co Complex with Doubly Bridged Fluorides: Di-μ-fluoride Bis{(2-pyridylmethyl)bis(2-quinolylmethyl)amine} Dicobalt(II) Bis(tetrafluoroborate), [Co₂(μ-F)₂(pbqa)₂](BF₄)₂

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The reaction of a methanol solution containing Co(BF₄)₂·6H₂O and (2-pyridylmethyl)bis(2-quinolylmethyl)amine (pbqa) afforded a dinuclear cobalt(II) complex, [Co₂(μ-F)₂(pbqa)₂](BF₄)₂, where the two metal centers are doubly bridged by two fluoride ions. BF₄⁻ is a fluoride source. A temperature-dependent magnetic susceptibility measurement reveal the strong spin orbit contribution with a zero-field splitting effect of two high-spin Co(II) ions. It crystallizes in the monoclinic space group C2/c with a = 24.9600(9) Å, b = 11.1533(3) Å, c = 20.0757(6) Å, α = 90°, β = 109.439(4)°, γ = 90°, V = 5265.4(3) Å³, Dcalcd = 1.535 g/cm³, and Z = 4. The R1 [I > 2σ(I)] and wR2 (all data) values are 0.0403 and 0.1018, respectively, for all 7897 independent reflections.

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Crystal structure and an ORTEP view of the complex are shown in Figs. 1 and 2. The two Co²⁺ ions are bridged by

Dioxo-, dihydroxo- and difluoro-bridged dinuclear metal complexes are well known. Their research concerning the complexes plays an important role in understanding the properties of metal-metal interaction such as energy, electron transfer, valence intermolecular charge-transfer, magnetic coupling. Also, these complexes have been interesting regarding organic synthesis catalysis and photosynthesis catalysis. The fluorine source have an origin from hydrolysis of the tetrafluoroborate ions. The difluoro bridged dinuclear cobalt complex described in this manuscript has tetrafluoroborate ions too. However, the cobalt-cobalt distance is closed due to strong π-π interactions between two quinoline rings of ancillary ligands. In 2014, we reported on the study of a fluorine crosslinked dinuclear cobalt complex has been reported by Cho et al. The fluorine source in an origin from hydrolysis of the tetrafluoroborate ions. The difluoro bridged dinuclear cobalt complex described in this manuscript has tetrafluoroborate ions too. However, the cobalt-cobalt distance is closed due to strong π-π interactions between two quinoline rings of ancillary ligands. In 2014, we reported on the crystal structure of [Co₂(μ-F)₂(Me₃tpa)₂](BF₄)₂ (Me₃tpa = tris(6-methyl-2-pyridylmethyl)amine), which involves μ-fluoro bridged between two cobalt(II) ions; the distance of Co–Co was 3.158 Å. We expected a greater steric hindrance and electronic effect of the ancillary ligand than Me₃tpa (n = 1, 2, 3), and chose pbqa (pbqa = (2-pyridylmethyl)bis(2-quinolylmethyl)amine)³ containing quinoline groups. In this paper we describe the synthesis and crystal structure of a μ-fluoro di-cobalt(II) complex using a simpler ancillary ligand, and have also compared it with [Co₂(μ-F)₂(Me₃tpa)₂](BF₄)₂. (Fig. 1).

Crystals suitable for the single-crystal X-ray structure analysis were obtained as follows. A solution of Co(BF₄)₂·6H₂O in dry methanol was added to a methanol solution of (2-pyridylmethyl)bis(2-quinolylmethyl)amine (pbqa). The resulting solution was stirred for 30 min. The methanol solution was transferred to some glass tubes, and diethyl ether was added to the solution slowly. After this sealed glass tube was left standing at ambient temperature, over a period of 9 days, brown microcrystals of [Co₂(μ-F)₂(pbqa)₂](BF₄)₂ separated from the solution. Characterization was on the basis of ESI-MS, a satisfactory elemental analysis and single crystal crystallographic data.

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Fig. 1 Chemical diagram of the title compound.

X-ray diffraction data for one of these crystals were collected at 100 K on a Rigaku XtaLAB P200 using multi-layer mirror monochromated Mo-Kα radiation. Crystal data and details concerning the data collection are given in Table 1. The structure was solved by direct methods, and refined by full-matrix least-squares methods. Hydrogen atoms were refined using the riding model with C–H = 0.95 or 0.98 Å and with Uiso(H) = 1.2 Ueq(C).

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposit number CCDC-1882663. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html), or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk.)

The chemical structure and an ORTEP view of the complex are shown in Figs. 1 and 2. The two Co²⁺ ions are bridged by
The Co–Ce separation is 3.071 Å. The Co···Co separation is 3.071 Å. The Co –N bond lengths are in the range from 1.9768(15)Å and 2.0776(15)Å are slightly shorter than that of \([\text{Co}2(\text{F})_2(\text{Me}_3\text{tpa})_2](\text{BF}_4)_2\). Lastly, the quinolyl rings stack (3.326 – 3.521 Å) with stacking (3.326 – 3.521 Å) with π-π stacking with the moiety from the other ancillary ligand on the Co center. The separation of the Hamiltonian in higher order matrices; at present, no analytical formula is available for the Co(II) dimer with significant zero-field splitting contributions. The application of the van Vleck equation to the Kambe’s vector coupling scheme allows for the determination of an analytical expression of the magnetic susceptibility from the following spin Hamiltonian.

\[
H = -\frac{1}{2}J|S_1|S_2|S_1S_2|+\Delta|S_1S_2|\]

The susceptibility data were fitted based on the above Hamiltonian. These results have a similarity to those found for \([\text{Co}(\mu-\text{F})_2(\text{pnN4-PhCl})_2](\text{BF}_4)_2\) showing 50% probability ellipsoids. Hydrogen atoms counter anions are omitted for clarity.

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Supporting Information

Synthesis of the complex (S.I.); top and side view of the complex (Fig. S1); ESI-MS (Fig. S2); SQUID (Fig. S3). These materials are available free of charge on the Web at http://www.jsac.or.jp/xraystruct/.

References