Crystal Structure of a Dinuclear Co Complex with Doubly Bridged Fluoride and Peroxo Ligands: μ -fluoro μ -peroxo bis{tris(2-pyridylmethyl)amine} dicobalt(III) tris(tetrafluoroborate), $[\text{Co}_2(\mu\text{-F})(\mu\text{-O}_2)(\text{tpa})_2](\text{BF}_4)_3$

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The reaction of a methanol solution containing $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and tris(2-pyridylmethyl)amine (tpa) afforded the unexpected dinuclear cobalt(III)-peroxo complex $[\text{Co}_2(\mu\text{-F})(\mu\text{-O}_2)(\text{tpa})_2](\text{BF}_4)_3$, where the two metal centers are simultaneously doubly bridged by one fluoride ion such that BF_4^- is a fluoride source. It crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.452(3)\text{\AA}$, $b = 12.529(3)\text{\AA}$, $c = 16.708(5)\text{\AA}$, $\alpha = 106.410(4)^\circ$, $\beta = 106.916(4)^\circ$, $\gamma = 90.2807(13)^\circ$, $V = 1999.0(9)\text{\AA}^3$, $D_{\text{calc}} = 1.678\text{ g/cm}^3$, and $Z = 2$. The $R1$ [$I > 2\sigma(I)$] and $wR2$ (all data) values are 0.0450 and 0.1679, respectively, for all 9093 independent reflections.

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Dinuclear peroxo bridged complexes¹⁻⁸ have been well known to play a very important role in many biological systems. In fact, the peroxo-Fe(III) and Cu(II) species were studied for mimicking the dioxygen activation transition metal compounds. The formation of fluoride complexes as a result of the decomposition of transition metal tetrafluoroborate derivatives is well known. These complexes presented in the literature⁹ are particularly facial examples of fluoride ligand abstraction. However, the title dinuclear cobalt(III) complex with doubly bridging fluoride and peroxo (cis-end-on type) ligands represents an almost unknown structure, which offers a unique opportunity to prepare and investigate the properties of the complex. Recently, we reported on the crystal structure of $[\text{Co}_2(\mu\text{-F})_2(\text{Me}_3\text{tpa})_2](\text{BF}_4)_2$ (Me_3tpa = tris(6-methyl-2-pyridylmethyl)amine), with μ -fluoro bridged between two

cobalt(II) ions. In this paper we report on the synthesis and crystal structure of a new μ -fluoro μ -peroxo di-cobalt(III) complex. Interestingly, this compound, which is very stable at room temperature, was isolated without pumping O_2 , or even air through the reaction mixture.

The reactions with $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and tpa (tris(2-

Fig. 1 Chemical diagram of the title compound.

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Table 1 Crystal data and experiments

Chemical formula: $\text{C}_{36}\text{H}_{36}\text{B}_3\text{Co}_2\text{F}_{13}\text{N}_8\text{O}_2$	
Formula weight = 1010.01	
$T = 120\text{ K}$	
Crystal system: triclinic	Space group: $P\bar{1}$
$a = 10.452(3)\text{\AA}$	$\alpha = 106.410(4)^\circ$
$b = 12.529(3)\text{\AA}$	$\beta = 106.916(4)^\circ$
$c = 16.708(5)\text{\AA}$	$\gamma = 90.2807(13)^\circ$
$V = 1999.0(9)\text{\AA}^3$	$Z = 2$
$D_{\text{calc}} = 1.678\text{ g/cm}^3$	
Radiation: Mo K_α ($\lambda = 0.71075\text{\AA}$)	
$\mu(\text{Mo } K_\alpha) = 0.94\text{ mm}^{-1}$	$F(0\ 0\ 0) = 1020$
Crystal size = $0.300 \times 0.200 \times 0.100\text{ mm}^3$	
No. of reflections collected = 23265	
No. of independent reflections = 9093	
θ range for data collection: 3.268 to 27.469°	
Data/Restraints/Parameters = 9093/0/577	
Goodness-of-fit on $F^2 = 1.206$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0450$, $wR2 = 0.1609$	
R indices (all data): $R1 = 0.0532$, $wR2 = 0.1679$	
$(\Delta/\sigma)_{\text{max}} = 0.001$	
$(\Delta\rho)_{\text{max}} = 0.51\text{ e}\text{\AA}^{-3}$	$(\Delta\rho)_{\text{min}} = -0.55\text{ e}\text{\AA}^{-3}$
Measurement: Rigaku Mercury70	
Programs system: SHELXL2013	
Structure determination: SIR2011	
CCDC deposition number: 1023645

Fig. 2 ORTEP view of μ -fluoro μ -peroxo bis{tris(2-pyridylmethyl)amine} dicobalt(III) tris(tetrafluoroborate), $[\text{Co}_2(\mu\text{-F})(\mu\text{-O}_2)(\text{tpa})_2](\text{BF}_4)_3$, showing 50% probability ellipsoids.

pyridylmethyl)amine) in dry methanol at ambient temperature for 7 days produced brown crystals of $[\text{Co}_2(\mu\text{-F})(\mu\text{-O}_2)(\text{tpa})_2](\text{BF}_4)_3$ in 26% yield. Characterization was on the basis of ESI-MS, a satisfactory elemental analysis, and single-crystal crystallographic data.

X-ray diffraction data for one of these crystals were collected at 120 K on a Rigaku CCD X-ray diffractometer (Mercury 70) using multi-layer mirror monochromated $\text{Mo-K}\alpha$ 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 $\text{C-H} = 0.95$ or 0.98 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The final cycle of a full-matrix least-squares refinement on F^2 was based on 9093 observed reflections and 577 variable parameters, and converged (largest parameters shift was 0.00 times its esd) with unweighted and weighted agreement factors of $R1 = 0.045$ and $wR2 = 0.1609$. The standard deviation of an observation of unit weights was used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.51 and -0.55 $\text{e}/\text{\AA}^3$, respectively. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposit number CCDC-1023645. 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; e-mail: deposit@ccdc.cam.ac.uk).

The chemical structure and an ORTEP view of the complex are shown in Figs. 1 and 2. The two Co(III) ions are bridged by two ligands: the end-on peroxo group and the fluoride atom that abstracts from the tetrafluoroborate anion.

The $\text{Co(1)}\cdots\text{Co(2)}$ separation is 3.220 Å. Each cobalt ion is ligated by one F, one O atom of the peroxo bridge and four N-donor atoms of the tpa coligand to form a distorted CoN_4OF octahedral geometry. The Co-N bond lengths are in the range from 1.889(3) to 1.979(3) Å; these indicate that the Co^{III} state as the bond lengths is similar to the reported Co-N (1.972(10), 1.932(9), 1.944(9), 1.896(10) Å) values for low-spin Co^{III} . The Co(1)-O(1) and Co(2)-O(2) bond distances are 1.860(2) and

1.857(2) Å, respectively. The Co-O-O bond angles of the peroxo bridge (111.5 and 109.6°) fall into the range observed for other similar peroxo-bridging dinuclear cobalt(III) complexes.⁴ The O(1)-O(2) bond distance of 1.431(3) Å is comparable with the corresponding values found in the literature.³

In the positive-ion electrospray mass spectrum (ESI-MS, Fig. 4S, 5S), $[\text{Co}(\text{tpa})\text{F}]^+$ ($m/z = 368$), $[\text{Co}_2(\text{tpa})_2\text{F}_2(\text{BF}_4)]^+$ ($m/z = 823$) and $[\text{Co}_2(\text{tpa})_2\text{F}(\text{BF}_4)_2]^+$ ($m/z = 891$) are observed in the spectrum that corresponds to the fluoride-bridged metallacycles. The ^{19}F NMR spectrum of the complex shown at -151.4 ppm, is assigned to the BF_4^- anions. The smaller resonance at -151.3 ppm can be associated with the isotropic distribution of boron. However, the presence of only the BF_4^- anions signal in the ^{19}F NMR spectrum can be attributed to a fast fluoride exchange, which could be brought about by reversible dissociation in solution, so that the resonance of the bridging fluoride ions can not be observed (Fig. 6S).^{9,10} To examine the presence of μ -peroxo O_2 , TG analysis for the complex was carried out (Fig. 7S). The complex showed two steps for the release of O_2 and the decomposition of the complex. An analysis of the TG curves of the complex shows that a weight loss of 3.06% occurs for the first stage from 190°C to 250°C, which corresponds to an expected value of 3.17% for the loss of all of the O_2 in the complex. The weight loss is more than 300°C, which corresponds to the decomposition of the complex.

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Supporting Information

Synthesis of the complex (S.I.), top and side view of the complex (Fig. 3S). ESI-MS (Fig. 4S, 5S). ^{19}F NMR (Fig. 6S). TG/DTA (Fig. 7S). These material are available free of charge on the Web at <http://www.jsac.or.jp/xraystruct/>.

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