Crystal Structure of cis-Bis(2,2′-bipyridyl)bis(trifluoromethanesulfonato)cobalt(II)

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A cobalt(II) complex with two 2,2′-bipyrindole (bpy) and two trifluoromethanesulfonato (OTf−) ligands, cis-[Co(OTf)2(bpy)2], was prepared, and the crystal structure at 173 K was elucidated by the single-crystal X-ray diffraction method. The complex crystallized in the monoclinic space group C2/c with a = 9.90587(16), b = 14.2978(2), c = 18.6626(3) Å, α = 90, β = 101.6670(17), γ = 90°, Z = 4, V = 2588.61(7) Å³. The R1 and wR2 values were 0.0397 and 0.1016, respectively, for 2377 reflections.

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Cobalt(II) complexes with polypyridyl ligands were used as photo-catalysts for hydrogen generation from water,¹ sensitizers in dye-sensitized solar cells,² or building blocks for magnetic supramolecules,³ because of their redox and magnetic properties. When synthesizing a new functional cobalt(II) complex with polypyridyl ligands, such as cis-[Co(L-L)(N-N)2] (L = monodentate ligand, L-L = bidentate cis-(phen)-bipyridine (bpy) or 1,10-phenanthroline (phen) etc.), cis-[Co(salonen)(N-N)2]²⁺ or cis-[Co(OTf)2(N-N)2] (OTf = trifluoromethanesulfonato or CF3SO3−) have been utilized as a precursor.³ This is a popular synthetic method for not only cobalt(II) complexes, but also many transition metal complexes. However, there are only four reports concerning the crystal structure of cis-[CoIII(OTf)2(bpy)2]. In 2013, Kurahashi and Fujii reported on a very unique cobalt complex with a salen ligand (Fig. S1, Supporting Information) and an OTf− ligand, [Co(salen)(OTf)], which was characterized by X-ray crystallography, cyclic voltammetry, L-edge X-ray absorption spectroscopy, the temperature dependence of the magnetic moment, X-band EPR spectra, and NMR spectra.⁵ Based on their experiments, they concluded that the complex contained both [CoIII(salen)(OTf)] and [CoIII(salen−)(OTf)] (salen−= salen ligand radical) character, and in the crystal the complex had a significant [CoIII(salen)(OTf)] character compared with the [CoIII(salen−)(OTf)] character.³ This interesting and uncommon complex had been the only reported instance of the Co complex with an OTf− ligand, until our report concerning the common Co²⁺ complex, cis-[Co(OTf)2(bpy)2].

X-ray crystallography was performed at 173 K on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-Kα radiation. The structure was solved by [CoIII(bpy)3](OTf)3 and cis-[CoIII(OTf)2(bpy)2], and a yellow-brown oily product, which would be the CoIII-Hdpa complex, might be produced from a reduction reaction of the Co²⁺ complex, [CoIII(CO3)(bpy)2]+, by EtOH in the reaction solution. We thought that it would be important for coordination chemists, because it is the first report concerning the crystal structure of cis-[CoIII(OTf)2(bpy)2]. In 2013, Kurahashi and Fujii reported on a very unique cobalt complex with a salen ligand (Fig. S1, Supporting Information) and an OTf− ligand, [Co(salen)(OTf)], which was characterized by X-ray crystallography, cyclic voltammetry, L-edge X-ray absorption spectroscopy, the temperature dependence of the magnetic moment, X-band EPR spectra, and NMR spectra.⁵ Based on their experiments, they concluded that the complex contained both [CoIII(salen)(OTf)] and [CoIII(salen−)(OTf)] (salen−= salen ligand radical) character, and in the crystal the complex had a significant [CoIII(salen)(OTf)] character compared with the [CoIII(salen−)(OTf)] character.³ This interesting and uncommon complex had been the only reported instance of the Co complex with an OTf− ligand, until our report concerning the common Co²⁺ complex, cis-[Co(OTf)2(bpy)2].

X-ray crystallography was performed at 173 K on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-Kα radiation. The structure was solved by

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Fig. 1 Chemical diagram of the title complex.
ligands, bpy and OTf –, in our complex were labile, and that the
are different. These Ru –N bond lengths, 2.1037(19) and trans were close to each other, although ligands at the position
atoms of OTf – ligands. Two Ru–N bond lengths in a bpy ligand
were labile. The Co –O bond length (2.1466(15)Å) in the title
complex was significantly longer than those in cis-[Mn(OTf)2(bpy)2] (av. 79.1°, 79.01(10) – 78.68(8)°). On the other hand, the dihedral angle between two pyridyl groups in the bpy ligand (4.0°) was smaller than those in other CoIII-bpy complexes (av. 8.4°, 6.0 – 10.1°), in which bpy ligands had contacts with each other. The elongations of two Ru-N bond lengths in our complex might lead to less contact between the co-ligands. The O1-Co1-O1* angle (85.65(9)°) was smaller than the ideal 90°, although both O atoms were in monodentate ligands, OTf –, due to contact between the O3 atom of the OTF ligand and the pyridyl-N1 group in the bpy ligand (Fig. S2, Supporting Information).

The bond length between the S1 and the O1 atom, which coordinated to the CoII ion, was the longest among three S-O bonds, and the remaining two S-O bond lengths were close to each other, suggesting that the S1-O1 bond was a single bond, and the O1 atom had a slightly negative charge. These structural parameters of OTF ligands were similar to those in cis-[MnIII(OTf)2(bpy)2]. Therefore, the elongation of Co-O bonds in our complex was not caused by delocalization of π electrons around the S=O bonds.

Finally, the lattice parameters of our crystal were close to those of other reported four comparable complexes, cis-[MnII(OTf)2(bpy)2] (M = Mn, Ni, Cu, or Zn, Table S1), suggesting that cis-[MnIII(OTf)2(bpy)2] (M is the first low transition metal ion) would have a favorable lattice parameter without depending on the kind of metal ion in the complex.

Acknowledgements

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Supporting Information

A CIF format file, Table S1, and Figs. S1 and S2. These materials are available free of charge of the Web at http://www.jsac.or.jp/xraystruct/.

Table 1 Crystal and experimental data

| Parameter | Value |
|-----------|-------|
| Chemical formula: CoC22F6N4O6S2H16 | |
| Formula weight | 669.44 |
| T | 173 K |
| Crystal system | monoclinic |
| Space group | C2/c |
| a | 9.90587(16) Å |
| b | 14.2978(2) Å |
| c | 18.6626(3) Å |
| α | 90° |
| β | 101.6670(17)° |
| γ | 90° |
| V | 2588.61(7) Å³ |
| Z | 4 |
| Dcalc | 1.718 g/cm³ |
| Radiation: Cu Kα (λ = 1.54187 Å) | |
| μ(Cu Kα) | 75.483 cm⁻¹ |
| F(0 0 0) | 1348.00 |
| Crystal size | 0.20 × 0.15 × 0.10 mm |
| No. of reflections collected | 6387 |
| No. of independent reflections | 2377 |
| θ range for data collection | 4.84 to 68.19 |
| Data/Restraints/Parameters | 2377/0/186 |
| Goodness-of-fit on F² | 1.084 |
| R indices [I > 2σ(I)]; R1 = 0.0381, wR2 = 0.1006 |
| R indices (all data); R1 = 0.0397, wR2 = 0.1016 |
| (Δρ)ave | 0.000 |
| (Δρ)max | 0.33 eÅ⁻³ |
| (Δρ)min | –0.66 eÅ⁻³ |
| Measurement: Rigaku XtALAB P200 |
| Programs system: CrysAlisPro8 |
| Structure determination: Direct Methods (SIR2011)9 |
| Refinement: full matrix least-squares (SHELXL Version 2014/7)¹⁰ |
| CCDC deposition number: 1879729 |

Table 2 Selected bond lengths (Å) and angles (°)

| Bond | Length (Å) | Angle (°) |
|------|-----------|-----------|
| Co1-N1 | 2.1037(19) | Co1-N2 | 2.0976(18) |
| Co1-O1 | 2.1466(15) | S1-O1 | 1.4546(16) |
| S1-O2 | 1.4316(18) | S1-O3 | 1.4344(18) |
| Ni-Co1-N2 | 77.84(7) | O1-Co1-O1* | 85.65(9) |

Fig. 2 ORTEP structure of the title complex, cis-[Co(OTf)2(bpy)2], showing 50% probability ellipsoids. [Symmetry code: (*) 2–x, y, 1/2–z].

direct methods (SIR2011), and refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were refined using a riding model. The crystal data and selected bond lengths and angles are summarized in Tables 1 and 2, respectively.

An ORTEP view of cis-[CoIII(OTf)2(bpy)2] is shown in Fig. 2. The Co had a distorted octahedral geometry with four nitrogen atoms of the pyridyl groups of two bpy ligands and two oxygen atoms of OTF ligands. Two Ru-N bond lengths in a bpy ligand were close to each other, although ligands at the trans position are different. These Ru-N bond lengths, 2.1037(19) and 2.0976(18)Å, were longer than those in [CoIII(bpy)2]6+ (av. 2.087 Å, 2.070(2) – 2.109(2)Å), and were significantly longer than those in cis-[CoIII(OH2)2(bpy)2]2+ (av. 2.062 Å, 2.058(2) – 2.065(2)Å), suggesting that the bpy ligands in our complex were labile. The Co-O bond length (2.1466(15)Å) in the title complex was significantly longer than those in cis-[CoIII(OH2)2-(bpy)2]2+ (2.047(2) and 2.093(2)Å), and slightly longer than those in the CoII-OTF complex, [CoII(salen)(OTf)2] (2.134(6) and 2.124(5)Å), which contained two molecules in an asymmetric cell. Thus, our crystal structure revealed that both ligands, bpy and OTF, in our complex were labile, and that the complex would occur the decomposition even under mild conditions. This was in good agreement with what was found by Smith and co-workers. They noted the substitution reactions of cis-[MnIII(OTf)2(bpy)2] (M = Mn, Co) were difficult to control, since even mild conditions often result in a decomposition reaction due to ligand redistribution.

The bite angle of the bpy ligand (77.84(7)°) in this complex was similar to those in other CoIII-bpy complexes (av. 79.1°, 79.01(10) – 78.68(8)°). On the other hand, the dihedral angle between two pyridyl groups in the bpy ligand (4.0°) was smaller than those in other CoIII-bpy complexes (av. 8.4°, 6.0 – 10.1°), in which bpy ligands had contacts with each other. The elongations of two Ru-N bond lengths in our complex might lead to less contact between the co-ligands. The O1-Co1-O1* angle (85.65(9)°) was smaller than the ideal 90°, although both O atoms were in monodentate ligands, OTF –, due to contact between the O3 atom of the OTF ligand and the pyridyl-N1 group in the bpy ligand (Fig. S2, Supporting Information).

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