Crystal Structure of cis-Bis(2,2′-bipyridyl)dichlorocobalt(III) Nitrate Methanol Solvate

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A cobalt(III) complex with two 2,2′-bipyridine (bpy) and two chloride ligands, cis-[CoCl$_2$(bpy)$_2$](NO$_3$)$_2$-CH$_3$OH, was prepared, and the crystal structure at 173 K was elucidated by the single-crystal X-ray diffraction method. The complex crystallized in the triclinic space group $P$-1 with $a = 7.0850(2)$, $b = 12.1656(3)$, $c = 13.2186(4)$Å, $\alpha = 87.106(2)$, $\beta = 87.830(3)$, $\gamma = 77.714(3)$, $Z = 2$, $V = 1111.41(6)$Å$^3$. The $R$1 and wR2 values were 0.0496 and 0.1268, respectively; for 4038 reflections.

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The coordination chemistry of cobalt(III) has been investigated because of their redox and magnetic properties. On the basis of these properties, recently there are many reports concerning cobalt(III) complexes for applications in biology, medicine, and photocatalysts. Especially cobalt(III) complexes with two polypyridyl ligands at the cis-position of each other, such as cis-[CoCl$_2$(N-N)$_2$]$^+$ or cis-[Co(CO$_3$)(N-N)$_2$]$^+$ (N-N = 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) etc.), have been prepared. These are not only used as starting materials for many functional complexes, but also the cis-bis(N-N)cobalt(III) complexes have been investigated concerning their chemical and biological properties. In 2016, the crystal structure of antancer activity of cis-[CoCl$_2$(bpy)$_2$](NO$_3$)$_2$-2H$_2$O were reported by Das and co-workers. The structure parameters of a cation part were similar to those of the previously reported crystal structure, [CoCl$_2$(bpy)$_2$]Cl.2H$_2$O. Das and co-workers focused on 1-D water-anion chains, which were ladder-shape hydrogen bonding networks between counter ions, NO$_3$–, and methanol molecules in the crystal. We particularly describe the relationship among cation, NO$_3$– anions, and methanol molecules in the crystal.

Single crystals of cis-[CoCl$_2$(bpy)$_2$](NO$_3$)$_2$-CH$_3$OH were obtained by vapor diffusion of diethyl ether into a mixed solution of CH$_3$OH-DMSO (5:1 [v/v], DMSO = dimethyl sulfoxide) of [Co(CO$_3$)(bpy)$_2$]Cl, which was prepared following literature, with conc-HNO$_3$. From the crystallization, we expected to obtain single crystals of cis-[CoCl$_2$(bpy)$_2$(solv)](NO$_3$)$_2$ or cis-[Co(bpy)$_2$(solv)$_2$](NO$_3$)$_2$ (solv = MeOH or dmos-O), but only single crystals of cis-[CoCl$_2$(bpy)$_2$](NO$_3$)$_2$-CH$_3$OH were obtained, suggesting that a disproportionation reaction had occurred and cis-[CoCl$_2$(bpy)$_2$](NO$_3$)$_2$ would have the lowest solubility among products in the reaction solution.

X-ray crystallography was performed at 173 K on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-K$_\alpha$ radiation. The structure was solved by direct methods, 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-[CoCl$_2$(bpy)$_2$](NO$_3$)$_2$-CH$_3$OH is shown in Fig. 2. The Co had a distorted octahedral geometry with four nitrogen atoms of pyridyl groups of two bipyridine ligands and two Cl atoms; this complex had a nitrate as a counter ion and a CH$_3$OH molecule as a lattice solvent in a unite cell. The bond

![Chemical diagram of the title complex.](image-url)
1-D cationic chains (Fig. 3 and Fig. S1). Similar Cl···H–C(bpy) adjacent cation complex, were observed in the crystal to form π-stacking contacts between a π-cation complex, and the π-3- and 3′-positions in the bpy(N(1),N(2)) ligand in an adjacent cis similar to those of cis-[CoCl₂(bpy)₂](X)·2H₂O (X = Cl– or NO₃–).6,7

distances and the angles around the Co(III) ion were quite similar to those of cis-[CoCl₂(bpy)₂](X)·2H₂O (X = Cl– or NO₃–),6,7 whereas, the lattice parameters were also similar to those of another previous reported complexes6,7 (Table S1). The distances between the plane of NO₃– in the 1-D water-anion chain was approximately parallel to the 1-D cationic chains (the dihedral angle between the plane of NO₃– and the O(1) or C(21) atom of the CH₃OH molecule was 12.0°), respectively. Therefore, the plane of NO₃– and the O(1) or C(21) atom of the CH₃OH molecule were 1.04 and 1.16 Å, respectively; thus, the NO₃–···HO–CH₃ unit seemed to be like a plate. The NO₃–···HO–CH₃ unit was placed above the pyridyl-N(4) group and staked with a H₂O molecule, although the lattice parameters were similar to each other. These results indicated that cis-[CoCl₂(bpy)₂]⁺ would strongly prefer to build the 1-D cationic chain via Cl–H-C(bpy) interactions in a solid, and the complex would form single chains if counter ions or solvent molecules in the solution were excepted for H atoms, were 11.2 or 4.0°, respectively. Therefore, the NO₃–···HO–CH₃ units were included in the 1-D cationic chains; in the result, the units assisted the 1-D cationic chains to stack each other (Fig. S4).

The plane of NO₃– in this crystal was stacked with the bpy(N(3),N(4)) ligand and in the cis-[CoCl₂(bpy)₂]ⁿ(NO₃)·2H₂Oₖ was placed at a vernicle position for the corresponding bpy ligand to form hydrogen bonding networks with lattice water molecules, although the lattice parameters were similar to each other. These results indicated that cis-[CoCl₂(bpy)₂]⁺ would strongly prefer to build the 1-D cationic chain via Cl–H-C(bpy) interactions in a solid, and the complex would form single crystals if counter ions or solvent molecules in the solution were

Table 1 Crystal and experimental data

| Chemical formula: CoCl₂C₂₅N₅O₄H₂O |
|-------------------------------------|
| Formula weight = 536.26 |
| T = 173 K |
| Crystal system: triclinic |
| a = 7.0850(2)Å |
| b = 12.1656(3)Å |
| c = 13.2186(4)Å |
| α = 87.106(2)° |
| β = 87.830(3)° |
| γ = 77.714(3)° |
| V = 1111.41(6)Å³ |
| Dcalc = 1.602 g/cm³ |
| Radiation: Cu Kα (λ = 1.54187 Å) |
| μCu Kα = 86.160 cm⁻¹ |
| F(0 0 0) = 548.00 |
| Z = 2 |
| Crystal size = 0.30 × 0.04 mm × 0.05 mm |
| No. of independent reflections = 4038 |
| No. of reflections collected = 4038 |
| CCDC deposition number: 1846276 |

Table 2 Selected bond lengths [Å] and angles [°]

| Co1–Cl1 | 2.240(1) |
| Co1–Cl2 | 2.240(1) |
| Co1–N1 | 1.941(2) |
| Co1–N2 | 1.936(3) |
| O1–H1–O4 | 2.11(1) |
| N1–Co1–N2 | 82.98(10) |
| O1–Co1–N3 | 1.934(2) |
| N3–Co1–N4 | 82.69(10) |
| O2–Co1–N4 | 1.950(2) |
| N4–Co1–N3 | 1.941(2) |

Fig. 2 ORTEP structure of the title complex, cis-[CoCl₂(bpy)₂]⁻ \((NO₃)·CH₃OH, showing 50\% probability ellipsoids. \)

Fig. 3 1-D cationic chain in the crystal through a Cl–H–C intermolecular hydrogen-bonding interaction between Cl(2) and two H atoms at the 3,3′-positions in the bpy(N(1),N(2)) ligand, showing the unit axes. Moreover, the location of the pyridyl-N(4) group and sets of NO₃– and methanol molecules in the crystal are shown.

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suitable to fill in gaps in the 1-D cationic chains. It would be also supported by the Cl-salt, because the lattice parameters of the Cl-salt were also similar to those of both NO₃-salts.

Supporting Information

A CIF format file, Table S1, and Figs. S1 - S5. These materials are available free of charge on the Web at http://www.jsac.or.jp/xraystruct/.

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