Crystal Structure of 2-(Pyridin-2-ylamino)pyridinium Trifluoromethanesulfonate

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The crystal structure of a 2-(pyridin-2-ylamino)pyridinium trifluoromethanesulfonate, H2dpa(OTf) (OTf = CF3SO3−), which consisted of a protonated 2-(pyridin-2-ylamino)pyridine (Hdpa) cation and a trifluoromethanesulfonate anion, was elucidated at 173 K by the single-crystal X-ray diffraction method. The compound crystallized in the monoclinic space group P21/m with a = 7.6770(4), b = 9.6170(5), c = 9.2748(5)Å, β = 106.201(6)°, Z = 2, V = 657.56(6)Å³. The R1 and wR2 values were 0.0461 and 0.1223, respectively, for 1887 reflections.

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Table 1 Crystal and experimental data

| Chemical formula: C11H10F3N3O3S | Formula weight = 321.27 |
| Crystal system: monoclinic |
| Space group: P21/m |
| a = 7.6770(4)Å | α = 90° |
| b = 9.6170(5)Å | β = 106.201(6)° |
| c = 9.2748(5)Å | γ = 90° |
| V = 657.56(6)Å³ | Z = 2 |
| Dcalc = 1.622 g/cm³ |
| Radiation: Mo Kα (λ = 0.71073 Å) |
| μ(Mo Kα) = 2.965 cm⁻¹ | F(0 0 0) = 328.00 |
| Crystal size = 0.25 × 0.25 × 0.05 mm |
| No. of reflections collected = 8217 |
| No. of independent reflections = 1887 |
| θ range for data collection = 2.287 to 30.174 |
| Data/Restraints/Parameters = 1887/2/150 |
| Goodness-of-fit on F² = 1.073 |

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conformation of H$_2$dp$a^+$ is significantly different from those in bidentate Hdpa ligands in transition metal complexes, but the amino group of each Hdpa molecules (Figs. S2(a) and S2(b)).

Interactions between a pyridyl N atom and an H atom of tetramers, which are bound with some hydrogen bonding molecules form intermolecular hydrogen-bridged dimers or the literature. In crystals of neutral Hdpa, two or four Hdpa pyridine rings of H$_2$dp$a^+$ is 0.2, which is similar to the dihedral angle, 0.25, of Hdp$a$ in Hdp$a$[Sn(CF$_3$COO)$_2$(CH$_3$)$_3$] (C$_2$H$_5_1$ = cyclohexyl), and which is close to 0.0$^\circ$ of the cisoid arrangement, H$_2$dp$a^+$, in seven compounds, such as (Hdp$a$)$_2$-[MoCl$_3$(H$_2$O)$_2$]Cl$_2$H$_2$O (Table S1). The angles of the remaining seventy-three cisoid arrangement of H$_2$dp$a^+$ compounds were 0.9 - 10.3$^\circ$ (Table S1), and the non-planar conformations of H$_2$dp$a^+$ might be demanded from the counter anionic complexes in the crystal. On the other hand, all bidentate Hdpa ligands in transition metal complexes also are cisoid arrangements and bent conformations.$^{1,3,4}$ The dihedral angles of two pyridine rings of Hdpa are various in different complexes; [Cu(Hdp$a$)$_2$]-

![Fig. 2 ORTEP structure of the title compound, H$_2$dp$a$(OTf), showing 50% probability ellipsoids. [Symmetry code: (*) x, 1/2–y, z; (**) x, -1/2–y, z]. Overlapped atoms in a cation part are omitted for clarify.](image)

**Fig. 2** ORTEP structure of the title compound, H$_2$dp$a$(OTf), showing 50% probability ellipsoids. [Symmetry code: (*) x, 1/2–y, z; (**) x, -1/2–y, z]. Overlapped atoms in a cation part are omitted for clarify.

respectively, were located in the difference Fourier map and refined isotropically, with the N–H distance restrained to 0.85(2)$\text{Å}$ and $U_{iso}(H) = 1.5U_{eq}(N)$. The crystal data are summarized in Table 1.

An ORTEP view of H$_2$dp$a$(OTf) is shown in Fig. 2. The compound is symmetrical to the mirror, and thus a half of the compound is independent. In the anion part four atoms, C7, F2, S1, and O1, are located on the mirror. In the cation part, N1 and H1 are disordered with occupancies of 0.5, and (C1 or N2) and (C4 or N3) are overlapped with occupancies of 0.5, respectively. The H7a and H7b are disordered with occupancies of 0.25 (Figs. 2 and S1). The distorted H7a and H7b atoms indicates that the hydrogen atom, H7, is located between two N atoms of each pyridine rings of Hdpa to form an intra-cation hydrogen bond N–H$^\ddagger$···N and, consequently, the Hdpa possesses a cisoid arrangement.

The bond lengths and bond angles of the cationic part in our compound are similar to those of the neutral Hdpa$^{2,6}$ and of the bidentate Hdpa ligands in transition metal complexes,$^{1,3,4}$ but the conformation of H$_2$dp$a^+$ is significantly different from those in the literature. In crystals of neutral Hdpa, two or four Hdpa molecules form intermolecular hydrogen-bridged dimers or tetrarers, which are bound with some hydrogen bonding interactions between a pyridyl N atom and an H atom of an amino group of each Hdpa molecules (Figs. S2(a) and S2(b)).$^{2,5,6}$ The dihedral angles of two pyridine rings of Hdpa are 7.9 - 39$^\circ$,$^{2,5,6}$ and the structures of a non-protonated Hdpa are transoid arrangements with non-planar conformation. However, the cation part H$_2$dp$a^+$ in our crystal is a cisoid arrangement and a planar conformation (Fig. S2(c)). The dihedral angle of two pyridine rings of H$_2$dp$a^+$ is 0.2$^\circ$, which is similar to the dihedral angle, 0.25$^\circ$, of Hdp$a$ in Hdp$a$[Sn(CF$_3$COO)$_2$(CH$_3$)$_3$] (C$_2$H$_5_1$ = cyclohexyl), and which is close to 0.0$^\circ$ of the cisoid arrangement, H$_2$dp$a^+$, in seven compounds, such as (Hdp$a$)$_2$-[MoCl$_3$(H$_2$O)$_2$]Cl$_2$H$_2$O (Table S1). The angles of the remaining seventy-three cisoid arrangement of H$_2$dp$a^+$ compounds were 0.9 - 10.3$^\circ$ (Table S1), and the non-planar conformations of H$_2$dp$a^+$ might be demanded from the counter anionic complexes in the crystal. On the other hand, all bidentate Hdpa ligands in transition metal complexes also are cisoid arrangements and bent conformations.$^{1,3,4}$ The dihedral angles of two pyridine rings of Hdpa are various in different complexes; [Cu(Hdp$a$)$_2$]-

![Fig. 3 Tube mode in the crystal of the title compound with showing the view along the a axis. [Symmetry code: (*) x, 1/2–y, z; (**) x, -1/2–y, z]. Overlapped atoms in a cation part are omitted for clarify.](image)

**Fig. 3** Tube mode in the crystal of the title compound with showing the view along the a axis. [Symmetry code: (*) x, 1/2–y, z; (**) x, -1/2–y, z]. Overlapped atoms in a cation part are omitted for clarify.

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Supporting Information

A CIF format file, Tables S1 - S2, and Figs S1 - S4. These materials are available free of charge of the Web at http://www.jsac.or.jp/xraystruct/.

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