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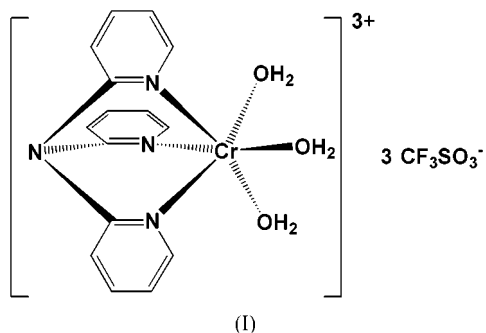
Key indicators

Single-crystal X-ray study
T = 173 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.032
wR factor = 0.089
Data-to-parameter ratio = 17.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.*fac*-Triaqua[tris(2-pyridyl)amine- $\kappa^3\text{N}$]chromium(III) tris(trifluoromethanesulfonate)

In the title compound, *fac*-[Cr(tpa)(H₂O)₃](CF₃SO₃)₃ [tpa is tris(2-pyridyl)amine; C₁₅H₁₂N₄], the Cr^{III} ion is coordinated by the symmetry-related N atoms of tpa, which acts as a tripodal ligand, and O atoms of water; a threefold rotation axis passes through the Cr and amine N atoms, with Cr–N_{pyridyl} and Cr–O distances of 2.0403 (12) and 1.9815 (11) Å, respectively. A three-dimensional network is formed by intermolecular O–H···O hydrogen bonds between coordinated water molecules and sulfonate groups of the anions.

Comment

In our previous papers, the dependence of ligand-field parameters on the solvent coordination sphere has been demonstrated by measuring the ligand-field absorption spectra and/or ²H NMR spectra for several types of chromium(III) complexes (Kaizaki, 1999; Kaizaki & Takemoto, 1990; Kaizaki & Legg, 1994; Terasaki & Kaizaki, 1995; Terasaki *et al.*, 1999). The correlation of the remarkable solvatochromism and solvent-dependent ²H NMR spectra of *fac*-[CrF₃(tpa-d₁₂)], belonging to the C_{3v} symmetry point group, with the acceptor numbers for solvents demonstrated the sensitivity of the Cr–ligand bond lengths or the angular overlap model (AOM) parameters to the embedding solvent, and also suggested a significant trigonal splitting in the first ligand-field band (Terasaki *et al.*, 1999).



As a part of a systematic investigation of solvatochromism and solvent-dependent NMR in terms of the AOM parametrization of chromium(III) complexes, we report here the crystal structure of the title compound, *fac*-[Cr(tpa)(H₂O)₃](CF₃SO₃)₃, (I). The complex cation *fac*-[Cr(tpa)(H₂O)₃]³⁺ in (I) is octahedrally coordinated by three symmetry-related N atoms of tpa and O atoms of water molecules. A threefold rotation axis through atoms Cr and N2 is parallel to the *c* axis, as illustrated in Figs. 1 and 2. Selected bond lengths and angles are given in Table 1. The Cr1–N1 bond length [2.0403 (12) Å] is in the range found for related

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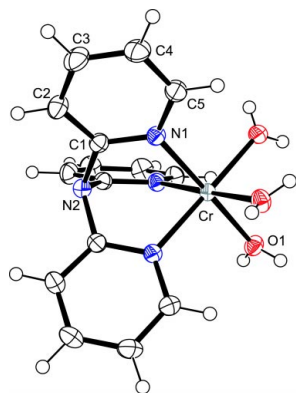


Figure 1
View of the complex cation $fac\text{-}[\text{Crtpa}(\text{H}_2\text{O})_3]^{3+}$ in (I), with 50% probability displacement ellipsoids and the atom-numbering scheme.

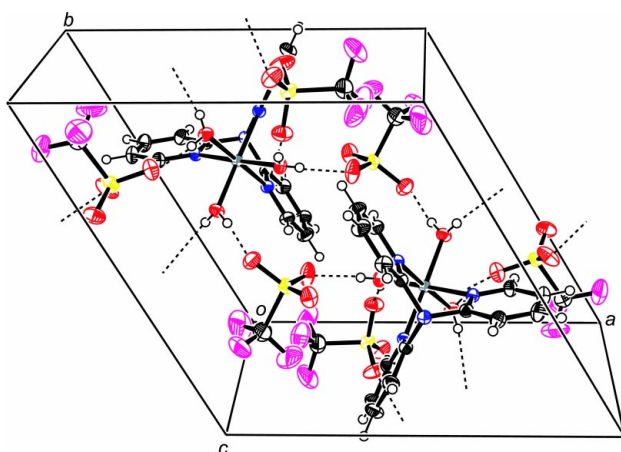


Figure 2
Crystal structure of (I). Broken lines show hydrogen bonds.

polypyridine-coordinated chromium(III) complexes (Casellato *et al.*, 1986; Fujihara *et al.*, 1995). The Cr1—O1 bond length [1.9815 (11) Å] is comparable to that of the bipyridine (bpy) analogue $cis\text{-}[\text{Cr}(\text{H}_2\text{O})_2(\text{bpy})_2]^{3+}$ (1.987 Å; Casellato *et al.*, 1986). The O atom of the coordinated water ligand seems to have an sp^2 character. All bond distances and angles in the pyridine ring are within normal ranges. The pyridine ring (N1/C1—C5) is planar, the largest deviation from the plane being that of atom C4 [0.0049 (2) Å]. The twist angle of opposite triangles consisting of three N and three O atoms is 59 (1)°, insignificantly different from the octahedral value (60°). Sulfonate atoms O2 and O3 act as hydrogen-bond acceptors, forming intermolecular hydrogen bonds with coordinated water molecule O1 (Fig. 2 and Table 2) and forming a three-dimensional network.

Experimental

$fac\text{-}[\text{CrCl}_3(\text{tpa})]$ (3.5 g, 8.6 mmol), synthesized according to the published procedure (Kaizaki & Legg, 1994), was added to $\text{CF}_3\text{SO}_3\text{H}$ (25 ml). The mixture was heated for 2 h at 343 K under an atmosphere of nitrogen, yielding a violet solution. To the viscous violet solution, diethyl ether (500 ml) was added with vigorous stirring to obtain a violet powder, $fac\text{-}[\text{Cr}(\text{CF}_3\text{SO}_3)_3(\text{tpa})]$, which was collected by filtration, washed repeatedly with diethyl ether and dried *in vacuo* (6.2 g, 96%). To a solution of $fac\text{-}[\text{Cr}(\text{CF}_3\text{SO}_3)_3(\text{tpa})]$ (1.22 g,

1.6 mmol) in acetone (20 ml) was slowly added an aqueous 1 M $\text{CF}_3\text{SO}_3\text{H}$ solution (0.4 ml). The resulting mixture was stirred for 24 h at room temperature. Pinkish precipitates of (I) separated from the solution, and were collected by filtration and washed with diethyl ether (yield 1.83 g, 71%). Red crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetone solution at room temperature. Analysis found: C 27.05, H 2.27, N 7.05%; calculated for $\text{C}_{18}\text{H}_{18}\text{CrF}_9\text{N}_4\text{O}_{12}\text{S}_3$: C 26.97, H 2.26, N 6.99%.

Crystal data

$[\text{Cr}(\text{C}_{15}\text{H}_{12}\text{N}_4)(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_3$
 $M_r = 801.54$
 Trigonal, $P\bar{3}$
 $a = 13.0562$ (3) Å
 $c = 10.4754$ (5) Å
 $V = 1546.45$ (9) Å³
 $Z = 2$
 $D_x = 1.721$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 8816 reflections
 $\theta = 2.7\text{--}28.3^\circ$
 $\mu = 0.69$ mm⁻¹
 $T = 173$ (2) K
 Block, red
 $0.52 \times 0.51 \times 0.32$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.716$, $T_{\max} = 0.810$
 11 598 measured reflections

2563 independent reflections
 2413 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\text{max}} = 28.3^\circ$
 $h = -11 \rightarrow 17$
 $k = -17 \rightarrow 13$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.089$
 $S = 1.07$
 2563 reflections
 150 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 0.7758P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.35$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.47$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|--|-------------|----------|-------------|
| Cr1—O1 | 1.9815 (11) | N2—C1 | 1.4402 (15) |
| Cr1—N1 | 2.0403 (12) | C1—C2 | 1.375 (2) |
| N1—C5 | 1.3461 (18) | C5—C4 | 1.378 (2) |
| N1—C1 | 1.3478 (18) | C2—C3 | 1.391 (2) |
| O1 ⁱ —Cr1—O1 ⁱⁱ | 87.71 (5) | N1—C1—C2 | 122.65 (13) |
| O1 ⁱ —Cr1—N1 ⁱⁱ | 178.45 (5) | N1—C1—N2 | 116.83 (13) |
| N1 ⁱⁱⁱ —Cr1—N1 ⁱ | 86.22 (5) | N1—C5—C4 | 121.73 (14) |
| O1 ⁱ —Cr1—N1 | 93.83 (5) | C1—C2—C3 | 118.22 (14) |
| O1—Cr1—N1 | 92.24 (5) | C5—C4—C3 | 119.25 (14) |
| C5—N1—C1 | 118.77 (12) | C4—C3—C2 | 119.38 (14) |

Symmetry codes: (i) $1 - y, x - y, z$; (ii) $1 - x + y, 1 - x, z$.

Table 2

Hydrogen-bonding geometry (Å, °).

| $D\text{—}H\cdots A$ | $D\text{—}H$ | $H\cdots A$ | $D\cdots A$ | $D\text{—}H\cdots A$ |
|--|--------------|-------------|-------------|----------------------|
| O1—H10 ⁱⁱⁱ ⋯O2 ⁱⁱⁱ | 0.71 (3) | 1.89 (3) | 2.5995 (17) | 176 (3) |
| O1—H11 ⁱⁱⁱ ⋯O3 | 0.79 (3) | 1.94 (3) | 2.7308 (17) | 172 (2) |

Symmetry code: (iii) $1 + x - y, x, 1 - z$.

Water H atoms were located in difference Fourier maps and refined isotropically. Other H atoms in tpa were placed in calculated positions, with $C\text{—}H = 0.95$ Å, and refined in a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$.

Data collection: *SMART-W2K/NT* (Bruker, 2003); cell refinement: *SAINTE-W2K/NT* (Bruker, 2003); data reduction: *SAINTE-W2K/NT*; program(s) used to solve structure: *SHELXTL-NT* (Bruker, 2003); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL-NT*.

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