cis-Bis(2,2'-bipyridine)difluorochromium(III) perchlorate

Yukiko Yamaguchi-Terasaki,[a] Takashi Fujihara,[b] Akira Nagasawa[b] and Sumio Kaizaki[c]*

[a]National College of Toyama Maritime Technology, Shin-minato, Toyama 933-0293, Japan, [b]Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Shimo-Okubo 255, Sakura-ku, Saitama 338-8570, Japan, and [c]Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Correspondence e-mail:
kaizaki@chem.sci.osaka-u.ac.jp

In the title compound, cis-[CrF$_2$(C$_{10}$H$_8$N$_2$)$_2$]ClO$_4$, the Cr^{III} ion is coordinated by the four N atoms [Cr—N = 2.0480 (14)–2.0842 (14) Å] from two 2,2'-bipyridine ligands and two F$^-$ ions [Cr—F = 1.8409 (10) and 1.8541 (10) Å] in a distorted octahedral arrangement. The crystal packing is stabilized by π–π interactions and weak intermolecular C—H$\cdots$F and C—H$\cdots$O hydrogen bonds.

Comment

In our previous papers, the dependence of ligand-field parameters on the solvent coordination environment has been demonstrated by measuring the ligand-field absorption spectra and/or ^{2}H NMR spectra for several types of chromium(III) complexes (Kaizaki, 1999; Kaizaki & Legg, 1994; Kaizaki & Takemoto, 1990; Terasaki & Kaizaki, 1995; Terasaki *et al.*, 1999, 2004). The correlation of the remarkable solvatochromism and solvent-dependent ^{2}H NMR spectra of cis-[CrF$_2$N$_4$]-type complexes with the acceptor numbers for solvents demonstrated the sensitivity of the Cr—ligand bond lengths or the angular overlap model (AOM) parameters to the solvent (Terasaki & Kaizaki, 1995). As part of our systematic investigation of solvatochromism and solvent-dependent NMR in terms of the AOM parameterization of chromium(III) complexes, we report here the crystal structure of the title compound, (I).

(I)
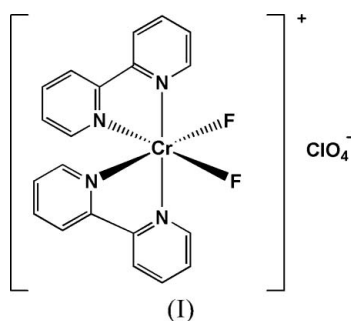
The central Cr^{3+} atom in (I) has an octahedral coordination geometry formed by two F$^-$ ions and two bpy ligands with a *cis* configuration (Fig. 1). Selected bond lengths and angles are given in Table 1. The average Cr—F bond length is 1.848 (7) Å. The Cr—N bond lengths for atoms N2 and N3 [2.0680 (13) and 2.0842 (14) Å, respectively] *trans* to the F atoms are significantly longer than those for atoms N1 and N4 [2.0480 (14) and 2.0511 (14) Å, respectively], which are *cis* to the F atoms. The average Cr—F and Cr—N bond lengths are significantly shorter than those in the aliphatic diamine complex cis-[CrF$_2$(en)$_2$]$^+$ [Cr—F = 1.883 (1) Å, Cr—N(*trans*-
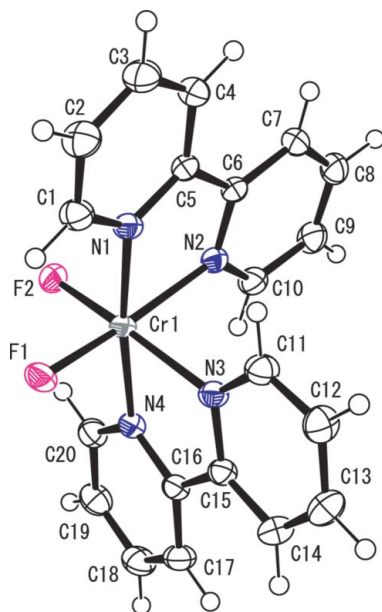
Figure 1
The molecular structure of cis-[CrF$_2$(bpy)$_2$]$^+$ in (I), with 50% probability displacement ellipsoids and the atom-numbering scheme.
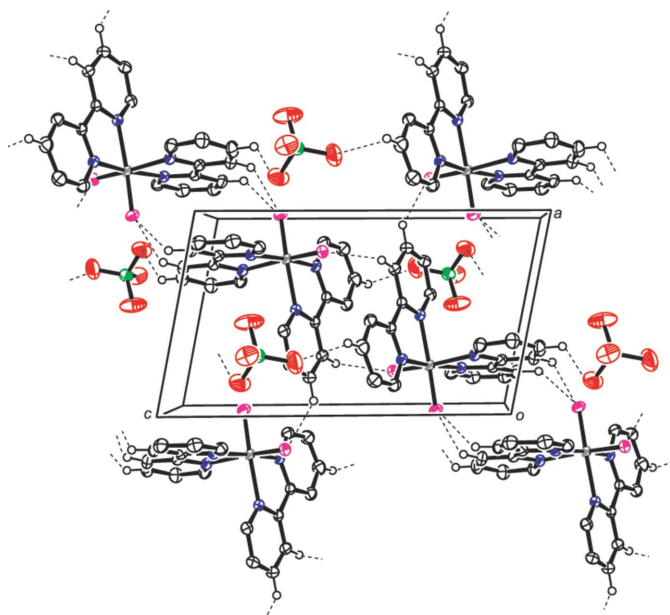
Figure 2
A crystal-packing diagram, viewed along the *b* axis. Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted for clarity.

F) = 2.097 (6) Å and Cr—N(*cis*-F) = 2.076 (1) Å; en = ethyl-enediamine, C$_2$N$_2$H$_8$ (Brenčič *et al.*, 1987)]. This notable structural feature is responsible for the additional *trans* influence which is operative, probably resulting from the push–pull action, as observed in the solvent-dependent ^{2}H NMR chemical shifts and ligand-field absorption bands (Terasaki & Kaizaki, 1995).

In the crystal structure of (I), π–π interactions, indicated by the short $Cg1\cdots Cg2^{iii}$ distance of 3.56 (1) Å ($Cg1$ and $Cg2$ are the centroids of the N1/C1–C5 and N2/C6–N10 rings, respec-

tively; for symmetry code see Table 2), link the molecules into centrosymmetric dimers. The crystal packing (Fig. 2) is further stabilized by weak intermolecular C—H$\cdots$F and C—H$\cdots$O hydrogen bonds (Table 2).

Experimental

Compound (I) was synthesized according to the literature method of Glerup *et al.* (1970). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an aqueous solution.

Crystal data

Table 1
Selected geometric parameters (Å, °).

Cr1—F1	1.8409 (10)	Cr1—N4	2.0511 (14)
Cr1—F2	1.8541 (10)	Cr1—N2	2.0680 (13)
Cr1—N1	2.0480 (14)	Cr1—N3	2.0842 (14)
N1—Cr1—N4	172.23 (5)	N1—Cr1—N2	78.72 (5)
F1—Cr1—N2	170.04 (5)	F2—Cr1—N3	169.52 (5)
F2—Cr1—N2	88.59 (5)	N4—Cr1—N3	78.35 (5)

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C17—H17$\cdots$F1^i	0.95	2.43	3.189 (2)	137
C14—H14$\cdots$F1^i	0.95	2.35	3.138 (2)	140
C8—H8$\cdots$F2^{ii}	0.95	2.32	3.067 (2)	135
C7—H7$\cdots$F2^{iii}	0.95	2.43	3.214 (2)	139
C3—H3$\cdots$O4^{iv}	0.95	2.49	3.321 (3)	146
C13—H13$\cdots$O3^v	0.95	2.57	3.264 (2)	130

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

H atoms were placed in calculated positions, with C—H = 0.95 Å, and refined in a riding model, with U_{iso}(H) = $1.2U_{eq}$(carrier atom).

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; 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*.

References

Brenčič, J. V., Leban, I. & Polanc, I. (1987). *Acta Cryst.* C**43**, 885–887.

Bruker (2003). *SAINT* for Windows 2000/NT (Version 5.0), *SMART* for Windows 2000/NT (Version 5.6) and *SHELXTL-NT* (Version 6.14). Bruker AXS Inc., Madison, Wisconsin, USA.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Glerup, J., Josephsen, J., Michelsen, K., Pedersen, E. & Schaeffer, C. E. (1970). *Acta Chem. Scand.* **24**, 247–254.

Kaizaki, S. (1999). *Trends Inorg. Chem.* **6**, 105–136.

Kaizaki, S. & Legg, J. I. (1994). *Inorg. Chim. Acta*, **218**, 179–84.

Kaizaki, S. & Takemoto, H. (1990). *Inorg. Chem.* **29**, 4960–4964.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Terasaki, Y., Fujihara, T., Nagasawa, A. & Kaizaki, S. (2004). *Acta Cryst.* E**60**, m854–m856.

Terasaki, Y., Fujihara, T., Schönherr, T. & Kaizaki, S. (1999). *Inorg. Chim. Acta*, **295**, 84–90.

Terasaki, Y. & Kaizaki, S. (1995). *J. Chem. Soc. Dalton Trans.* pp. 2837–2841.