Crystal Structure of a Mononuclear Iron(III) Complex, Hexakis(dimethylsulfoxide- κO)iron(III) Tris(hexafluoridophosphate)

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A mononuclear iron(III) complex, $[\text{Fe}(\text{dmsO})_6][\text{PF}_6]_3$ [hexakis(dimethylsulfoxide- κO)iron(III) tris(hexafluoridophosphate)], was synthesized, and characterized by a single-crystal X-ray method. The compound crystallized in the trigonal space group $R\bar{3}$ and $Z = 3$ with cell parameters $a = 11.598(8)\text{\AA}$, $c = 25.367(18)\text{\AA}$, $V = 2955(4)\text{\AA}^3$. The R_1 [$I > 2\sigma(I)$] and wR_2 (all data) values were 0.0509 and 0.1565, respectively, for all 1630 independent reflections. The symmetry of the complex cation was found to belong to the S_6 point group, possessing a trigonally compressed octahedral coordination geometry with an O_6 donor set.

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Iron(III) complexes have been attracted much interest since a mononuclear iron(III) single molecule magnet was reported.¹ For the purpose of finding new iron(III) complexes, in this study, the structure of a new mononuclear iron(III) complex, $[\text{Fe}(\text{dmsO})_6][\text{PF}_6]_3$ [hexakis(dimethylsulfoxide- κO)iron(III) tris(hexafluoridophosphate)], as shown in Fig. 1, was determined.

Single crystals of $[\text{Fe}(\text{dmsO})_6][\text{PF}_6]_3$ were prepared as follows: an aqueous dmsO solution (dmsO: 3.0 mL; water: 1.0 mL) of iron(III) nitrate–water (1/9) (0.40 g, 1.0 mmol) was refluxed for 30 min; after cooling, to this was added ammonium hexafluoridophosphate (0.50 g, 3.0 mmol). After stirring for 40 min at room temperature, deposited light-yellow micro-crystals were collected and washed with 2-propanol. The product was dissolved in dmsO and recrystallized by slow diffusion of 2-propanol to obtain light-yellow single crystals (yield: 0.79 g, 82%). Elemental analysis (Found: C, 15.10; H, 3.80%. Calcd. for $\text{C}_{12}\text{H}_{36}\text{F}_{18}\text{FeO}_6\text{P}_3\text{S}_6$: C, 15.00; H, 3.80%).

Crystal data are included in Table 1. The structure was solved by intrinsic phasing methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the riding model. The final cycle of a full-matrix least-squares refinement on F^2 was allowed to satisfactory converge with $R_1 = 0.0509$ [$I > 2\sigma(I)$].

The crystal structure consists of the $[\text{Fe}(\text{dmsO})_6]^{3+}$ complex cations and hexafluoridophosphate anions in a 1:3 molar ratio (Figs. 1 and 2). In the complex cation, the six dmsO ligands coordinate to the central iron(III) ion through their oxygen atoms, forming an octahedral FeO_6 coordination geometry. A slight disorder was observed around the dmsO moiety (Fig. 3), and the disordered structure seemed to be consistent with the

sulfur-inversion motion;^{2,3} however, we will discuss only the main structure because the occupancy of the disordered minor unit is very small [0.082(3)]. The complex cation belongs to the S_6 point group, possessing the S_6 axis along the c -axis. Such a conformer is often observed in related divalent metal complexes, including e.g. $[\text{Zn}(\text{dmsO})_6]^{2+}$, $[\text{Fe}(\text{dmsO})_6]^{2+}$ and $[\text{Ni}(\text{dmsO})_6]^{2+}$

Table 1 Crystal and experimental data

Chemical formula: $\text{C}_{12}\text{H}_{36}\text{F}_{18}\text{FeO}_6\text{P}_3\text{S}_6$	
Formula weight = 959.53	
$T = 293\text{ K}$	
Crystal system: trigonal	Space group: $R\bar{3}$
$a = 11.598(8)\text{\AA}$	
$c = 25.367(18)\text{\AA}$	
$V = 2955(4)\text{\AA}^3$	$Z = 3$
$D_x = 1.617\text{ g/cm}^3$	
Radiation: Mo $K\alpha$ ($\lambda = 0.71073\text{ \AA}$)	
$\mu(\text{Mo } K\alpha) = 0.933\text{ mm}^{-1}$	$F(0\ 0\ 0) = 1455$
Crystal size = $0.36 \times 0.32 \times 0.21\text{ mm}^3$	
No. of reflections collected = 6538	
No. of independent reflections = 1630 [$R_{\text{int}} = 0.0338$]	
θ range for data collection: 2.181 to 28.533°	
Data/Restraints/Parameters = 1630/66/135	
Goodness-of-fit on $F^2 = 1.046$	
R indices [$I > 2\sigma(I)$]: $R_1 = 0.0509$, $wR_2 = 0.1343$	
R indices (all data): $R_1 = 0.0853$, $wR_2 = 0.1565$	
$(\Delta/\sigma)_{\text{max}} = 0.000$	
$(\Delta\rho)_{\text{max}} = 0.440\text{ e\AA}^{-3}$	$(\Delta\rho)_{\text{min}} = -0.290\text{ e\AA}^{-3}$
Measurement: Bruker Smart APEX CCD diffractometer	
Program system: SHELXTL	
Structure determination: intrinsic phasing methods (SHELXT 2014/5)	
Refinement: full matrix least-squares (SHELXL-2014/7)	
CCDC deposition number: 1856764	

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Fig. 1 Chemical structure of $[\text{Fe}(\text{dmsO})_6][\text{PF}_6]_3$.

Fig. 2 Molecular structure of $[\text{Fe}(\text{dmsO})_6][\text{PF}_6]_3$ with atom labeling. Hydrogen atoms and minor disordered moieties are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Symmetry code: a $(-y+1, x-y+1, z)$, b $(x-y+2/3, x+1/3, -z+4/3)$, c $(-x+2/3, -y+4/3, -z+4/3)$, d $(-x+y, -x+1, z)$, e $(y-1/3, -x+y+1/3, -z+4/3)$, f $(x-y, x, -z+1)$, g $(-y, x-y, z)$, h $(-x, -y, -z+1)$, i $(-x+y, -x, z)$, j $(y, -x+y, -z+1)$.

complex cations,^{4,5} belonging to the exact S_6 or *pseudo*- S_6 symmetry.

It is of interest to compare the structure of the trivalent $[\text{Fe}(\text{dmsO})_6]^{3+}$ complex cation, observed in this study, with the related divalent $[\text{Fe}(\text{dmsO})_6]^{2+}$ complex cation.⁵ Both cations belong to the exact S_6 point group. In the trivalent complex cation, the Fe(III)–O distance is 1.996(2) Å (Table 2), while the Fe(II)–O distance is 2.121(3) Å. This is normal as the ionic radii for the trivalent and divalent iron ions. The S–O distances in the trivalent and divalent complex cations are 1.536(3) Å (major component) and 1.530(3)–1.532(9) Å, respectively. These distances are similar, but both are longer than the S–O distance in solid dimethylsulfoxide [1.5040(10) Å].⁶ In the trivalent complex cation, a distinct trigonal compression was observed along the S_6 axis [the top O–Fe–O angle = 91.85(11)°; the side O–Fe–O angle = 88.16(11)°]. On the contrary, in the divalent complex cation, a distinct trigonal elongation was observed [the top O–Fe–O angle = 89.55(12)°; the side O–Fe–O angle = 90.45(12)°].

In the crystal structure of the trivalent $[\text{Fe}(\text{dmsO})_6]^{3+}$ complex cation, the intermolecular CH $\cdots$ F interactions (C $\cdots$ F = 3.46 Å) were found to stabilize the highly symmetrical crystal structure by connecting the methyl hydrogen in the dmsO moiety and the fluorine atom in the hexafluoridophosphate ion.

In conclusion, the structure of $[\text{Fe}(\text{dmsO})_6]^{3+}$ complex cation belongs to the S_6 point group, possessing the trigonally compressed octahedral coordination geometry.

Fig. 3 Disordered structure of $[\text{Fe}(\text{dmsO})_6]^{3+}$ complex cation along the S_6 axis. Minor moieties are drawn with thin red bonds.

Table 2 Selected bond distances and angles

Atom	Distance (Å)	Atom	Distance (Å)
Fe(1)–O(1)	1.996(2)	Fe(1)–O(2)	1.95(2)
O(1)–S(1)	1.536(3)	O(2)–S(2)	1.502(16)
Atom	Angle (°)	Atom	Angle (°)
O(1)–Fe(1)–O(1) ^a	91.85(11)	O(1)–Fe(1)–O(1) ^b	88.16(11)
O(1)–Fe(1)–O(1) ^c	180.0	O(2)–Fe(1)–O(2) ^a	89.6(9)
O(2)–Fe(1)–O(2) ^b	90.4(9)	O(2)–Fe(1)–O(2) ^c	180.0

Symmetry code: a $(-y+1, x-y+1, z)$, b $(x-y+2/3, x+1/3, -z+4/3)$, c $(-x+2/3, -y+4/3, -z+4/3)$.

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Supporting Information

A CIF format file. This is available free of charge on the Web at <http://www.jsac.or.jp/xraystruct/>.

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