Crystal Structure of a Mononuclear Iron(III) Complex, Chloridopentakis-(dimethylsulfoxide- κO)iron(III) Bis(tetraphenylborate)

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A mononuclear iron(III) complex $[\text{FeCl}(\text{dmsO})_5](\text{BPh}_4)_2$ [chloridopentakis(dimethylsulfoxide- κO)iron(III) bis(tetraphenylborate)] was synthesized, and characterized by a single-crystal X-ray method. The compound crystallized in the monoclinic space group $P2_1/n$ and $Z = 2$ with cell parameters $a = 10.4961(16)\text{\AA}$, $b = 14.260(2)\text{\AA}$, $c = 19.166(3)\text{\AA}$, $\beta = 94.512(2)^\circ$, $V = 2859.8(7)\text{\AA}^3$. The R_1 [$I > 2\sigma(I)$] and wR_2 (all data) values were 0.1149 and 0.2930, respectively, for all 6552 independent reflections. The analysis revealed an octahedral geometry with ClO_5 donor set.

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The orientations of ligands in coordination compounds often play an important role in interactions with substrates. In addition, it sometimes influences the coordination geometry. It is not always easy to predict the orientation; however, we conducted a conformational analysis to understand the observed conformation.¹ In the case of the $[\text{Zn}(\text{dmsO})_6](\text{BPh}_4)_2$ complex (dmsO: dimethylsulfoxide), the crystallographically obtained structure was different from the predicted most stable structure, but it was understood that this structure would be appropriately deformed to reduce the volume. In this study, with the aim of expanding the hexakis-dmsO system¹⁻³ to the pentakis-dmsO system, $[\text{FeCl}(\text{dmsO})_5](\text{BPh}_4)_2$ [chloridopentakis(dimethylsulfoxide- κO)iron(III) bis(tetraphenylborate)] was prepared, and its crystal structure was determined by the single-crystal X-ray method.

Single crystals of $[\text{FeCl}(\text{dmsO})_5](\text{BPh}_4)_2$ were prepared as follows: a dmsO solution (12 mL) of iron(III) chloride hexahydrate (0.85 g, 3.1 mmol) was stirred at room temperature for 15 min, to which was added a dmsO solution (8 mL) of sodium tetraphenylborate (2.07 g, 6.0 mmol). After stirring for 10 min, to this was added 2-PrOH (15 mL) to give yellow precipitation [yield: 2.41 g (72%)]. The compound was recrystallized from dmsO/2-PrOH, which produced red single-crystals that were used for an X-ray diffraction study. Crystal data are included in Table 1. The structure was solved by direct 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 $R_1 = 0.1149$ [$I > 2\sigma(I)$].

The crystal structure consists of $[\text{FeCl}(\text{dmsO})_5]^{2+}$ complex cations, tetraphenylborate anions in a 1:2 molar ratio (Figs. 1 and 2). For each $[\text{FeCl}(\text{dmsO})_5]^{2+}$ complex cation, a pair of centrosymmetrically related cation are superimposed with an occupancy factor of 0.5. In the complex cation (Fig. 3), one

chloride anion and five dmsO molecules coordinate to the central iron(III) ion to form an octahedral coordination geometry with a ClO_5 donor set. The Fe-O distances fall in a short range of 1.986(8) – 2.043(8) Å (Table 2), indicating that the FeClO_5 coordination geometry can be approximated as C_{4v} symmetry.

In some related hexakis-dmsO complexes,¹⁻³ the central MO_6S_6 units [$M = \text{Co(II)}$, Ni(II) , and Zn(II)] can be approximated as S_6 symmetry. In the case of the $[\text{FeCl}(\text{dmsO})_5]^{2+}$ complex cation in this study, the structure of the FeClO_5S_5 unit appears to be

Table 1 Crystal and experimental data

Chemical formula: $\text{C}_{58}\text{H}_{70}\text{B}_2\text{ClFeO}_5\text{S}_5$	
Formula weight = 1120.36	
$T = 90\text{ K}$	
Crystal system: monoclinic	Space group: $P2_1/n$
$a = 10.4961(16)\text{\AA}$	$\beta = 94.512(2)^\circ$
$b = 14.260(2)\text{\AA}$	
$c = 19.166(3)\text{\AA}$	$Z = 2$
$V = 2859.8(7)\text{\AA}^3$	
$D_x = 1.301\text{ g/cm}^3$	
Radiation: Mo K_α ($\lambda = 0.71073\text{ \AA}$)	
$\mu(\text{Mo } K_\alpha) = 0.540\text{ mm}^{-1}$	$F(0\ 0\ 0) = 1182$
Crystal size = $0.40 \times 0.30 \times 0.24\text{ mm}^3$	
No. of reflections collected = 17990	
No. of independent reflections = 6552 [$R_{\text{int}} = 0.0627$]	
θ range for data collection: 1.782 to 27.493°	
Data/Restraints/Parameters = 6552/3/376	
Goodness-of-fit on $F^2 = 1.053$	
R indices [$I > 2\sigma(I)$]: $R_1 = 0.1149$, $wR_2 = 0.2605$	
R indices (all data): $R_1 = 0.1749$, $wR_2 = 0.2930$	
$(\Delta\rho)_{\text{max}} = 0.000$	
$(\Delta\rho)_{\text{max}} = 1.376\text{ e\AA}^{-3}$	$(\Delta\rho)_{\text{min}} = -0.438\text{ e\AA}^{-3}$
Measurement: Bruker Smart APEX CCD diffractometer	
Program system: SHELXTL	
Structure determination: Direct methods (SHELXT 2014/5)	
Refinement: full matrix least-squares (SHELXL-2014/7)	
CCDC deposition number: 1567115	

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Fig. 1 Chemical structure of $[\text{FeCl}(\text{dmsos})_5](\text{BPh}_4)_2$.

Fig. 2 Molecular structure of $[\text{FeCl}(\text{dmsos})_5](\text{BPh}_4)_2$ with atom labeling. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry code: ' (3/2-x, -1/2+y, 1/2-z).

random at a first glance, but a rotational structure is seen from a direction, as shown in Fig. 3. Now the five dmsos ligands are clockwise numbered from (i) to (v). If the FeClO_5S_5 unit is focused, ligands (i) – (iv) are rotationally orientated as a part of the S_6 structure. That is, except for the Cl ion and ligand (v), the FeClO_5S_5 unit can be considered to be a defect S_6 structure. [The $\text{S}(3)\cdots\text{O}(5)$, $\text{S}(5)\cdots\text{O}(4)$, $\text{S}(4)\cdots\text{O}(2)$, and $\text{S}(2)\cdots\text{Cl}(1)$ distances fall in the range from 3.50 to 3.91 Å.]

In conclusion, the $[\text{FeCl}(\text{dmsos})_5]^{2+}$ complex cation was found to have a C_{4v} coordination geometry with a ClO_5 donor set, and the FeClO_5S_5 unit was considered a defect S_6 structure, except for Cl and one dmsos moiety.

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Fig. 3 Molecular structure of $[\text{FeCl}(\text{dmsos})_5]^{2+}$ complex cation with atom labeling.

Table 2 Selected bond distances and angles

Atom Atom		Distance/Å	Atom Atom		Distance/Å
Fe(1)–Cl(1)		2.340(5)	Fe(1)–O(1)		2.013(8)
Fe(1)–O(2)		2.043(8)	Fe(1)–O(3)		2.000(8)
Fe(1)–O(4)		1.986(8)	Fe(1)–O(5)		1.991(9)
Atom Atom Atom		Angle/°	Atom Atom Atom		Angle/°
Cl(1)–Fe(1)–O(1)		93.0(2)	Cl(1)–Fe(1)–O(2)		92.3(3)
Cl(1)–Fe(1)–O(3)		91.4(3)	Cl(1)–Fe(1)–O(4)		92.1(3)
Cl(1)–Fe(1)–O(5)		178.0(2)	O(1)–Fe(1)–O(2)		89.0(3)
O(1)–Fe(1)–O(3)		89.3(3)	O(1)–Fe(1)–O(4)		174.9(4)
O(1)–Fe(1)–O(5)		88.1(4)	O(2)–Fe(1)–O(3)		176.0(4)
O(2)–Fe(1)–O(4)		90.6(4)	O(2)–Fe(1)–O(5)		86.1(3)
O(3)–Fe(1)–O(4)		90.7(4)	O(3)–Fe(1)–O(5)		90.2(4)
O(4)–Fe(1)–O(5)		86.8(4)			

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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