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Tetrabutylammonium isobutyl silsesquioxane monochloroferrate(III)

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The title compound, tetrabutylammonium chloroheptaisobutyldodeca-μ-oxo-heptasiliconiron, $[(C_4H_9)_4N][FeSi_7ClO_{12}(C_4H_9)_7]$, is an ionic species consisting of a tetrabutylammonium cation and an isobutyl silsesquioxane monochloroferrate(III) anion. The Fe^{III} atom in the anion is tetrahedrally coordinated by a single Cl atom and three silanoxides from the tridentate isobutyl silsesquioxane ligand, while the cation exists also in a tetrahedral arrangement.

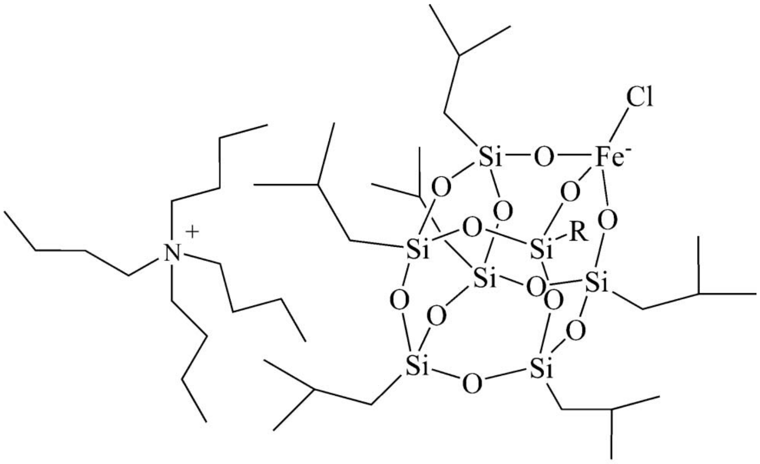
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.008 Å
R factor = 0.067
wR factor = 0.170
Data-to-parameter ratio = 20.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

A variety of iron(III)-containing silsesquioxane compounds have previously been prepared (Liu *et al.*, 2000; Lorenz *et al.*, 2000; Hay *et al.*, 2003; Shapley *et al.*, 2003). It was during the crystal structure analysis of $[Bu_4N][\{(CH_3)_2CHCH_2\}_7Si_7O_{12}FeCl]$ that we serendipitously discovered an equivalent of γ-butyrolactone (GBL) which had crystallized with (I). Since GBL had not been added to the reaction mixture, we hypothesized that it was formed from the aerobic oxidation of the solvent, tetrahydrofuran (THF) (Hay *et al.*, 2003). For reasons of completeness, we present the redetermination of the crystal structure of (I), which has been synthesized and crystallized from toluene, a solvent that is resistant to oxidation. As a result, the crystal structure does not contain GBL.



(I)

The title compound, (I), consists of a tetrabutylammonium cation and an isobutyl silsesquioxane monochloroferrate(III) anion (Fig. 1). The Fe^{III} atom in the anion, $C_{28}H_{63}Si_7O_{12}FeCl^-$, is four-coordinate with a tetrahedral arrangement of a chloride and three silanoxides from the tridentate isobutyl silsesquioxane ligand. The Cl—Fe—O bond angles range between 107.91 (8) and 108.93 (8)°, while the O—Fe—O bond

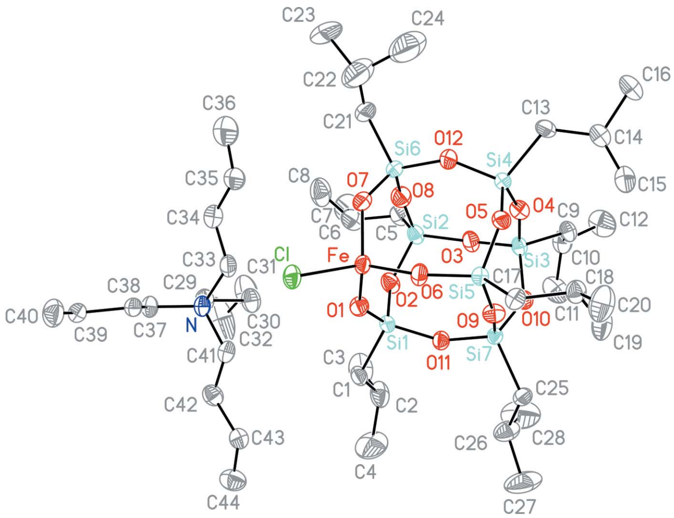


Figure 1

The structure of (I), showing 35% probability displacement parameters. H atoms have been omitted for clarity.

angles range from 108.57 (12) to 113.50 (11)°. The Fe—O bond lengths are in the range 1.832 (2)–1.848 (2) Å. The Fe—Cl bond length is 2.2537 (10) Å. The tetrabutylammonium cation also has a tetrahedral arrangement around the central N atom, with C—N—C bond angles in the range 105.2 (3)–111.7 (3)° and N—C bond lengths in the range 1.508 (4)–1.523 (5) Å. This is consistent with the structure previously reported for (I)·$C_4H_6O_2$ (Hay *et al.*, 2003).

Experimental

A colorless solution of $[(CH_3)_2CHCH_2]_7Si_7O_{12}H_3$ (0.379 mmol, 0.300 g) in toluene (3–4 ml) was treated with three equivalents of triethylamine (1.14 mmol, 159 ml). The mixture was stirred for 5 min at room temperature before one equivalent of solid $[Bu_4N][FeCl_4]$ (0.379 mmol, 0.167 g) was added. The yellow solid did not immediately dissolve. After stirring for 20 min, the solution had turned yellow and a white precipitate had formed. This was collected by filtration. The yellow filtrate was concentrated *in vacuo* giving a yellow oil, which was then extracted with acetonitrile. Most of the yellow oil dissolved, except for a small amount of insoluble white precipitate. This was removed by filtration, and the filtrate was concentrated *in vacuo* to give a yellow crystalline material, which was then extracted with hexane. The yellow hexane extracts were filtered to remove a small amount of insoluble material, and then concentrated *in vacuo* to afford 0.240 g (77.2%) of (I) as yellow powder which was dried under vacuum. The yellow powder was crystallized from toluene at 243 K before being analysed. Analysis calculated for $C_{44}H_{99}FeClNO_{12}Si_7$: C 47.09, H 8.89, N 1.25%; found: C 46.87, H 9.17, N 1.32%.

Crystal data

$(C_{16}H_{36}N)[FeSi_7ClO_{12}(C_4H_9)_7]$
M_r = 1122.17
Monoclinic, $C2/c$
a = 23.6451 (11) Å
b = 32.1149 (15) Å
c = 18.3528 (9) Å
β = 116.586 (1)°
V = 12462.8 (10) Å^3
Z = 8
D_x = 1.196 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.47 mm^{-1}
T = 150 (2) K
Block, yellow
0.36 × 0.28 × 0.14 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{\min}$ = 0.849, $T_{\max}$ = 0.937
54262 measured reflections
12260 independent reflections
8887 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.050
$\theta_{\max}$ = 26.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.170
S = 1.29
12260 reflections
595 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.078P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.011
$\Delta\rho_{\max}$ = 1.06 e Å^{-3}
$\Delta\rho_{\min}$ = −0.39 e Å^{-3}

H atoms were placed in idealized positions and refined using a riding model, with C—H = 0.98–1.00 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) or 1.5$U_{\rm eq}$(methyl C). The highest residual density peak is located 0.89 Å from atom H21a of the disordered butyl group.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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