Crystal structure of hexakis(*N*,*N*-dimethylformamide-*O*)silicon(IV) tris(tribromide) chloride, $[Si\{(CH_3)_2NCHO\}_6][Br_3]_3Cl$

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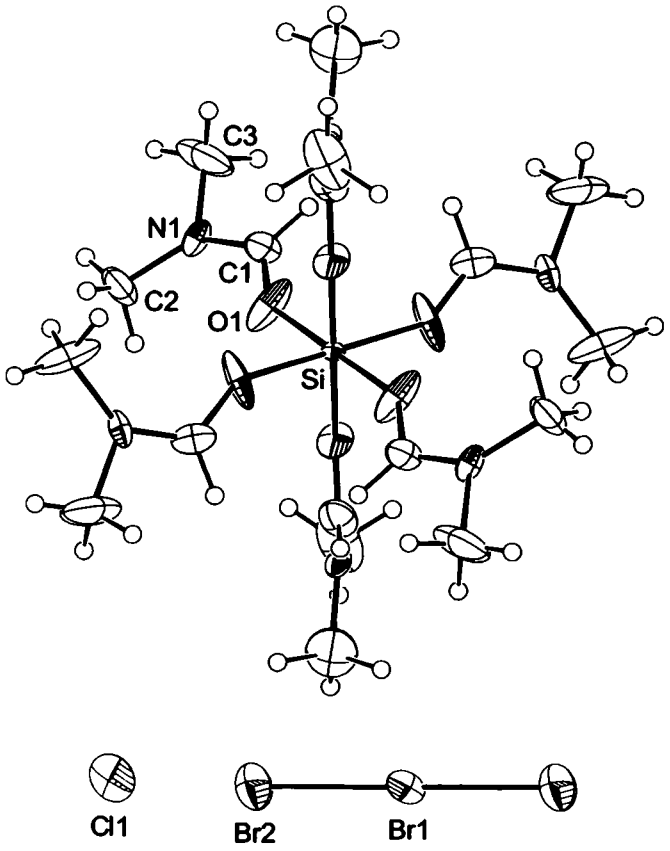

Abstract

$C_{18}H_{42}Br_9ClN_6O_6Si$, trigonal, $R\bar{3}$ (no. 148), a = 18.496(3) Å, c = 9.939(2) Å, V = 2944.7 Å^3, Z = 3, $R_{gt}(F)$ = 0.056, $wR_{ref}(F^2)$ = 0.176, T = 180 K.

Source of material

1.7 g silicon tetrachloride (0.01 mol, 1.15 mL) was added to 10 mL of dimethylformamide. The reaction was strongly exothermic; decreasing of temperature let fall white hygroscopic crystals. Careful addition of 3.2 g bromine (0.02 mol) gave raising of temperature (ca 60 °C) and dissolution of white crystals. The dark brown solution turned slowly (4 h) to an orange one. *n*-Hexane (about 50 mL) was allowed to diffuse slowly into this solution. Orange crystals were obtained in a period of two weeks. The complex is stable for months at room temperature.

Discussion

Bromination is a real challenge in organic substrates chemistry due to elemental bromine reactivity excess. *N*,*N*-dimethylformamide is a member of aprotic solvents and can be considered as a model in the study of the amidic bond. Previous works concerned tribromide anions associated with amides and metallic cations B^{III} [1] and Al^{III} [2]. Moreover, silicon(IV) as $SiCl_4$ is a chemical reagent used in the syntheses of siloxanes. Following our studies, a new crystalline complex based on silicon(IV), dimethylformamide as oxygen-donor ligand and tribromide ions was prepared to clarify the strength of amide-*X* (*X* = B^{III}, Al^{III}, Si^{IV}) cation complex associated with tribromide anion.

The crystal structure is built up from discrete $[Si(DMF)_6]^{4+}$ cations, three $[Br_3]^-$ and one Cl^- anions. The Si atom, located at the inversion point (site symmetry $\bar{3}$), is surrounded by the DMF molecules in a nearly regular octahedral arrangement with O–Si–O angle of 86.6(3)°. The stereochemistry of this $[Si(DMF)_6]^{4+}$ cation is similar to previous observations in $[Si(DMF)_6]I_4$ [3] with a Si—O bond distance slightly shorter than those found in this one (1.724(4) Å and 1.765(5) Å, respectively). The DMF molecule is essentially planar; the maximum deviation out of the best plane of O1/C1/N1/C2/C3 is 0.041(6) Å for C1. The torsion angle Si–O1–C1–N1 is equal to 179.5(5)°, and the distance of Si atom 0.067(9) Å from above mentioned plane show that the silicon is approximately coplanar with the DMF molecule and in the lone-pair direction of the carbonyl group (*trans* to the N atom). The O—C bond (1.217(9) Å) similar to that found in non-coordinating DMF (1.221(7) Å) [3] is significantly shorter than in $[Si(DMF)_6]I_4$ [4] (1.274(9) Å). The C—N_{amide} bond distance of 1.292(9) Å lies within the corresponding range observed for other metal-DMF complexes: $[Si(DMF)_6]I_4$ [4], average of 1.28(1) Å; $[Al(DMF)_6](ClO_4)_3$: 1.290(3) Å [5]. The N—C_{methyl} bonds of 1.43(1) Å and 1.45(1) Å are similar to those found in non-coordinating case (1.425(8) Å and 1.441(8) Å [4]). Each chloride anion is surrounded by six H1(C1) atoms forming six hydrogen bonds (C1–H1···Cl1: 3.514(7) Å and 156°) in the hexagonal geometry of group. Since the central bromine atom of the $[Br_3]^-$ ion is located at an inversion centre, the geometry of this three atomic system is linear. The Br1—Br2 distance of 2.5254(8) Å is in good agreement with the values reported for a symmetric $[Br_3]^-$ anion in $[(CH_3)_3NH^+]_2[Br]^-[Br_3]^-$ (average: 2.535 Å [6]). Six tribromide ions are laid out around the silicon atom according to a octahedral geometry (d(Si···Br2) = 4.875(1) Å, ∠Br2···Si···Br2 = 85.77(2)°). Each $[Br_3]^-$ anion forms a bridge between two silicon atoms. The crystalline cohesion is ensured by many van der Waals contacts, the shortest being 3.547(4) Å.

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Table 1. Data collection and handling.

Crystal:	orange, parallelepipedic, size 0.18 × 0.25 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	93.26 cm^{-1}
Diffractometer, scan mode:	Oxford-Diffraction XCALIBUR, ω/φ
$2\theta_{max}$:	50.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5896, 1123
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1000
$N(param)_{refined}$:	65
Programs:	SIR92 [7], SHELXL-97 [8], CAMERON [9], WinGX [10]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	18*f*	0.7379	0.3243	0.5560	0.12
H(21)	18*f*	0.9741	0.4045	0.6261	0.12
H(22)	18*f*	0.9180	0.3526	0.7517	0.12
H(23)	18*f*	0.9397	0.4469	0.7287	0.12
H(31)	18*f*	0.9217	0.3789	0.4399	0.12
H(32)	18*f*	0.8485	0.3996	0.4143	0.12
H(33)	18*f*	0.8270	0.3047	0.4285	0.12

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	9*e*	⅓	⅙	⅔	0.0252(5)	0.0391(6)	0.0306(6)	0.0121(4)	−0.0019(3)	−0.0098(3)
Br(2)	18*f*	0.23404(5)	0.02401(5)	0.76150(8)	0.0417(5)	0.0457(6)	0.0586(6)	0.0113(4)	0.0032(3)	0.0070(3)
Si(1)	3*b*	⅔	⅓	⅚	0.016(1)	U_{11}	0.011(1)	½U_{11}	0	0
Cl(1)	3*a*	⅔	⅓	⅓	0.074(2)	U_{11}	0.010(2)	½U_{11}	0	0
O(1)	18*f*	0.7518(3)	0.3496(3)	0.7393(6)	0.049(3)	0.041(3)	0.087(4)	0.024(2)	0.055(3)	0.014(3)
N(1)	18*f*	0.8534(3)	0.3658(3)	0.6037(5)	0.023(2)	0.019(2)	0.042(3)	0.010(2)	0.013(2)	0.000(2)
C(1)	18*f*	0.7767(5)	0.3447(4)	0.6282(7)	0.049(4)	0.044(4)	0.032(3)	0.017(3)	−0.009(3)	0.001(3)
C(2)	18*f*	0.9271(6)	0.3947(5)	0.6839(9)	0.073(6)	0.054(5)	0.066(6)	0.002(5)	−0.049(5)	0.006(4)
C(3)	18*f*	0.8635(8)	0.3619(7)	0.4600(9)	0.122(9)	0.088(7)	0.039(5)	0.055(7)	−0.040(5)	−0.014(5)

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