Short Communication

Crystal Structure of $BaSiF_6$ at 180 K

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In a series of attempts to prepare solid aqua complexes of platinum(II) with tetrafluoroborate as counterion, a few very small but well-grown crystals were found on the inside wall of one of the glass vessels. The subsequent X-ray study showed that these crystals contained no platinum ions at all; their composition was $BaSiF_6$. Apparently, the glass had been attacked by HF released from the acidic BF_4^- solution forming SiF_6^{2-} complexes. The glass must also have been the source of the Ba^{2+} ions. A literature survey revealed that no least-squares refinement had been made of the $BaSiF_6$ structure type with anisotropic thermal parameters. It was therefore decided to bring the X-ray study to a proper end.

Experimental

The aqueous solution in which the crystals were found contained originally about 0.2 mol l^{-1} Pt^{2+}, 0.6 mol l^{-1} H^+ and 1.0 mol l^{-1} BF_4^-. It was filtered through a Duran G4 filter and evaporated over P_2O_5 in a Schott and Gen dish for about two weeks. The glass probably contained about 2–3% BaO. A colourless crystal of size 0.05×0.05×0.05 mm was mounted in a Lindemann glass capillary. The X-ray diffraction study was made with an Enraf–Nonius CAD-4 diffractometer with graphite monochromator and Mo$K\alpha$ radiation. The temperature at the crystal was kept at 180(2) K with a N_2 gas stream cooled by liquid N_2. The long-time stability of the cryostat was about ±2 K. The diffraction symmetry indicated one of the space groups: *R*32, *R*3*m* or R3*m*. The unit cell dimensions were determined

Table 1. Crystal data on $BaSiF_6$.

T/K	180(2)	M_r	279.42
a/Å	7.198(1)	Space group	$R\bar{3}m$
c/Å	7.020(1)	*Z*	3
V/Å^3	315.06(7)	λ/Å	0.71069
D_x/g cm^{-3}	4.417(1)	μ/cm^{-1}	101.6

Table 2. Atomic coordinates and thermal parameters (Å^2) for $BaSiF_6$ at 180 K. The form of the temperature factor is $\exp[-2\pi(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + \ldots)]$. $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Atom	*x*	*y*	*z*	U_{eq}		
Ba	0	0	0	0.0084(2)		
Si	0	0	1/2	0.0064(5)		
F	0.2191(4)	0.1095(2)	0.3588(3)	0.0134(8)		
Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba	0.0093(3)	0.0093(3)	0.0064(3)	0.0047(1)	0	0
Si	0.0069(6)	0.0069(6)	0.0055(9)	0.0035(3)	0	0
F	0.0102(9)	0.0102(9)	0.0113(9)	−0.0012(14)	0.0041(8)	−0.0041(8)

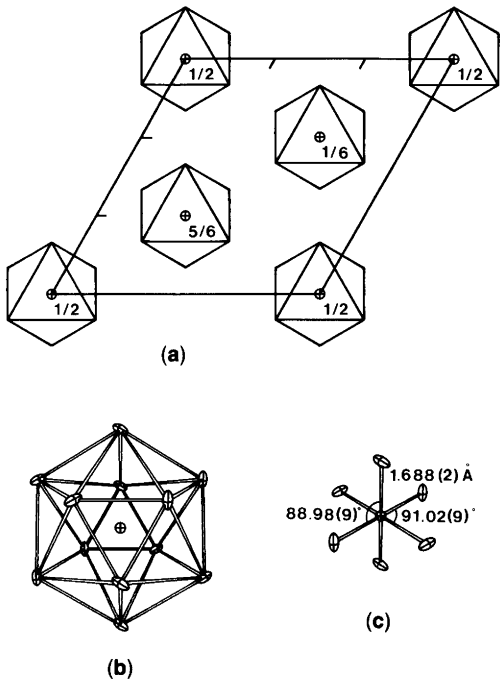

Fig. 1. (**a**) The unit cell content of $BaSiF_6$. The *z* coordinate of Si is given at each octahedron. Ba^{2+} is located at the origin. (**b**) The Ba^{2+} icosahedron. (**c**) The SiF_6^{2-} complex with bond length and bond angles at 180 K. The thermal ellipsoids are scaled to include 75 % probability.

from 23 reflections with $14 \leq \theta \leq 25°$. Crystal data are given in Table 1.

Intensities were measured from all reflections with $0.07 \leq \sin\theta/\lambda \leq 0.63$ Å^{-1}, $-9 \leq h,k \leq 9$, $-8 \leq \ell \leq 8$ using $\omega/2\theta$ scan and $\Delta\omega = 0.60° + 0.50° \tan\theta$. The maximum counting time was 300 s. Three control reflections (0 1 2, −2 1 0, −1 3 2) were measured every hour but no significant variation was detected. Lorentz, polarization and absorption corrections were applied. As the crystal was very small and mounted in a capillary, it was difficult to assign correct indices to its faces. Both rhombohedral and spherical shapes were tested with the former giving slightly more consistent results in the final least-squares refinements (transmission factor between 0.54 and 0.74 for rhombohedron and 0.64 for sphere). The 1036 measured reflections were averaged to 93 unique observations, all with $|F_o|^2 \geq 3\sigma_c(|F_o|^2)$ (σ_c based on counting statistics). The averaging procedure gave $R_{int}(|F_o|^2) = 0.033$.

Structure refinement

The original aim, to locate a platinum complex in the vector and $\Delta\varrho$ maps, could not be met. Crystal Data Determinative Tables[1] then indicated $BaSiF_6$ from $c/a = 0.975$ and the possible space group $R\bar{3}m$.[2] All maxima in the Patterson function could be construed from this structure. There are some solid platinum fluoro complexes which are isomorphous with $BaSiF_6$.[3-6] $SrPtF_6$ has, e.g., $c/a = 0.9810$,[4] $BaPtF_6$ 0.9811,[4,5] and K_2PtF_6 0.9933.[6] The structures of these compounds are, of course, incompatible with the present intensity data set.

The values of the ten parameters of the structural model and a scale factor were improved by full matrix least-squares refinement minimizing $\Sigma w(\Delta F)^2$ with weights $w = [\sigma_c^2(|F_o|) + (0.016|F_o|)^2]^{-1}$. The 1 1 0 reflection had to be excluded from the refinement, due apparently to severe secondary extinction. Inclusion of an isotropic secondary extinction parameter gave $g = 1.8(6) \cdot 10^3$ with an average mosaic particle radius of 0.13 μm.[7] Refinement converged to $R = 0.013$, $R_w = 0.016$, $S = 1.04$ and $\Delta/\sigma < 0.10$. The δR plot[8] has slope 0.97(2), intercept 0.01(2) and correlation coefficient 0.986; i.e., the random errors of $|F_o|$ are on the average correctly estimated and there are only small systematic errors affecting the model. The final $\Delta\varrho$ map was almost without significant features. The max. and min. values were located on the $\bar{3}$ axes: +0.43 e Å^{-3} at points 1.40 Å from Si^{4+} and −1.14 e Å^{-3} at points 0.70 Å from Ba^{2+}. Atomic scattering factors for ions Ba^{2+}, Si^{4+} and F^- and anomalous dispersion corrections were taken from Ref. 9. All computer programs used are described in Ref. 10.

Results

Atomic parameters are given in Table 2, while the structure and its building blocks are shown in Fig. 1.* The structure type is often named after the representative compounds $TlSbF_6$[11] or $KOsF_6$.[12] It was originally described by Hoard

*A list of observed and calculated structure amplitudes can be obtained from one of the authors (J.A.) on request.

and Vincent[2] as a distorted CsCl structure composed of Ba^{2+} and SiF_6^{2-} units. The actual distortion is indicated by the rhombohedral angle. At 180 K, $BaSiF_6$ has $a_R = 4.769(1)$ Å, $\alpha_R = 98.0(1)°$. At the same temperature, the bond distance in the SiF_6^{2-} complex is 1.688(2) Å with bond angles 88.98(9) and 91.02(9)°, (see Fig. 1). The F^- icosahedron about Ba^{2+}, slightly elongated along *c*, has a less puckered equatorial hexagon than the regular polyhedron. The equatorial Ba–F bond distances are 2.796(2) Å; the other six Ba–F bond lengths are 2.865(2) Å. The shortest F–F contact distances between adjacent SiF_6^{2-} complexes, 2.813(3) Å, are in the equatorial hexagon.

In view of the difference in temperature, measuring technique and accuracy, and computational power, there are surprisingly few disagreements between the present results and those obtained by Hoard and Vincent in 1940.[2]

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