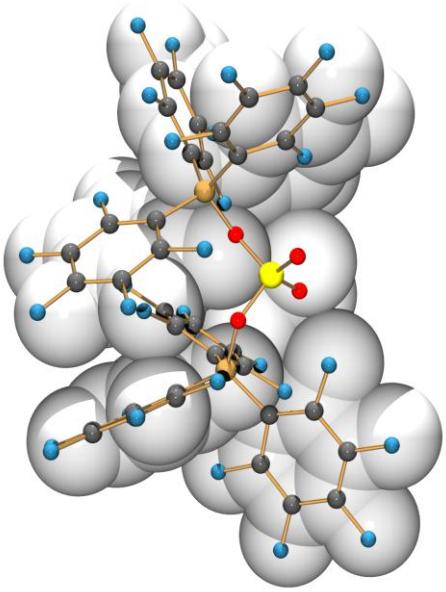
Electronic Supplementary Material (ESI) for RSC Advances

Sulfate and Nitrate Adduct Anions

Martin Becker,[a] Axel Schulz,*[a,b] Alexander Villinger[a] and Karsten Voss[a]

[a] Universität Rostock, Institut für Chemie, Albert-Einstein-Str. 3a, 18059 Rostock; [b] Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany

E-mail: axel.schulz@uni-rostock.de



Contents **page**

Experimental

General Information. All manipulations were carried out under oxygen- and moisture-free conditions under Argon using standard Schlenk or drybox techniques.

Dichloromethane was purified according to a literature procedure[1], dried over CaH_2 and freshly distilled prior to use. diethylether was dried over Na/benzophenone and freshly distilled prior to use. *n*-hexane was dried over Na/benzophenone/tetraglyme and freshly distilled prior to use. Tetrahydrofuran (THF) was dried over Na/benzophenone/tetraglyme and freshly distilled prior to use. $B(C_6F_5)_3$ was prepared by a modified literature procedure originally developed by Massey *et al*[2]. $AgNO_3$ (99%, VEB Feinchemie Sebnitz), KNO_3 (99%, Roth), KOH (>84%, Merck), K_2SO_4 (>99%, Merck), were dried in high vacuo for 3 hours prior to use.

NMR. $^{19}F\{^1H\}$, $^{11}B\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker spectrometers AVANCE 250, 300, or 500. The ^1H and ^{13}C NMR chemical shifts were referenced to the solvent signals (^{13}C δ_{CDCl3} = 77.0 ppm; ^1H δ_{CDCl3} = 7.25 ppm; ^{13}C δ_{CD2Cl2} = 54.0 ppm; ^1H δ_{CD2Cl2} = 5.31 ppm). The ^{19}F and ^{11}B chemical shifts are referred (δ = 0) to $CFCl_3$ and $B(OH)_3$ respectively.

IR. Nicolet 6700 FT-IR with Smart Endurance ATR device or Nicolet 380 FT-IR with Smart Orbit ATR module.

Raman. Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd:YAG laser (1064 nm).

MS. Finnigan MAT 95-XP from Thermo Electron.

CHN analyses. Analysator Flash EA 1112 from Thermo Quest.

DSC. Thermoanalytical measurements were performed with a DSC 823e from Mettler-Toledo instrument. Two point calibrations with In (mp 156.6°C) and Zn (mp 419.6°C) were carried out. About 2-6 mg of the samples were weighed and contained in sealed aluminium crucibles. They were studied with a heating rate of 5°C/min; throughout this process the furnance was flushed with dry nitrogen. For the evaluation of the output the Star^e software was employed.

X-ray Structure Determination. X-ray quality crystals of different samples were selected in Fomblin 1800 oil (Alfa Aesar) at ambient temperatures. All measurements were carried out at 173(2) K. The data were collected on a Bruker-Nonius Apex X8 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (*SHELXS-97*)[5] and refined by full-matrix least squares procedures (*SHELXL-97*)[6]. Semiemperical absorption corrections were applied. All non-hydrogen atoms were refined anisotropically, an hydrogen atoms were included in the refinements at calculated positions using riding models.

(1) Fischer, C.B.; Xu, S.; Zipse, H. *Chem. Eur. J*. **2006**, *12*, 5779.
(2) Massey, A. G.; Park, A. J.; Stone, F. G. A. Proc. *Chem. Soc*. **1963**, 212.
(3) Jürgens, B.; Irran, E.; Schneider, J.; Schnick, W. *Inorg. Chem*. **2000**, *39*, 665.
(4) Mukai, T.; Yoshio, M.; Kato, T.; Ohno, H. *Chem. Lett*. **2004**, *33*, 1630
(5) Sheldrick, G. M. *SHELXS-97: Program for the Solution of Crystal Structures*; University of Göttingen; Göttingen, Germany, 1997.
(6) Sheldrick, G. M. *SHELXL-97: Program for the Solution of Crystal Structures*; University of Göttingen; Göttingen, Germany, 1997.

Synthesis

Synthesis of $[Ag(Et_2O)_3]^+[NO_3{\bullet}B(C_6F_5)_3]^-$ (**1**)

To a solution of $B(C_6F_5)_3$ (2.04 g, 4 mmol, 4 equiv) in 40 ml diethylether is added $AgNO_3$ (170 mg, 1 mmol, 1 equiv) at room temperature. After stirring for 30 min a clear colorless solution was observed. Removal of the solvent led to a white solid, which was washed with 60 mL of *n*-hexane (removal of the $B(C_6F_5)_3$ excess). After discontinuation of the precipitate the excess *n*-hexane is removed with a syringe and discarded. The process is repeated one more time. Recrystallization from diethylether yields pure colorless crystals. Yield: 440 mg (65%). DSC: 76.3 °C (dec.). $C_{18}AgBF_{15}NO_3{\cdot}Et_2O$ (756.0): calcd C 34.95, H 1.33, N 1.85; found C 34.90, H 1.66, N 1.84. ^{11}B-NMR (CD_2Cl_2, 96 MHz, 25°C): δ = 0.23 (s). ^{13}C-NMR (CD_2Cl_2, 75 MHz, 25°C): δ = 148.3 (d, *o*-C, 2C, $^1J_{CF}$ = 241.8 Hz); 139.8 (d, *p*-C, 1C, $^1J_{CF}$ = 249.4 Hz); 137.1 (d, *m*-C, 2C, $^1J_{CF}$ = 247.2 Hz); 118.4 (br, C-B, 1C). ^{19}F-NMR (CD_2Cl_2, 282 MHz, 25 °C): δ = –134.7 (d, *o*-F, 2F, $^3J_{FF}$ = 19.9 Hz); –160.6 (m, *p*-F, 1F); –166.4 (“t”, *m*-F, 2F, $^3J_{FF}$ = 19.9 Hz). IR (ATR, cm^{-1}): ν = 2965 (w), 1645 (w), 1516 (s), 1465 (vs), 1381 (m), 1282 (s), 1261 (m), 1180 (w), 1088 (s), 1069 (s), 977 (vs), 854 (s), 871 (w), 782 (m), 748 (w), 717 (w), 984 (m), 662 (w), 607 (w), 575 (w). Raman (100 mW, 475 Scans, 25 °C, cm^{-1}): ν = 2960 (7), 2912 (10), 2876 (7), 1648 (4), 1453 (3), 1290 (2), 1045 (4), 580 (6), 491 (4), 447 (4), 415 (4).

Synthesis of $[K(Et_2O)_2]^+[NO_3{\bullet}B(C_6F_5)_3]^-$ (**2**)

To a solution of $B(C_6F_5)_3$ (2.04 g, 4 mmol, 4 equiv) in 40 ml diethylether is added KNO_3 (101 mg, 1 mmol, 1 equiv) at room temperature. After stirring for 30 min a clear colorless solution was observed. Removal of the solvent led to a white solid, which was washed with 60 mL of *n*-hexane (removal of the $B(C_6F_5)_3$ excess). After discontinuation of the precipitate the excess *n*-hexane is removed with a syringe and discarded. The process is repeated one more time. Recrystallization from diethylether yields pure colorless crystals. Yield: 331 mg (54%). DSC: 134.8 °C (dec). $C_{18}BF_{15}KNO_3{\cdot}2Et_2O$ (761.33): calc C 41.02, H 2.65, N 1.84; found C 40.93, H 1.74, N 1.88. ^{11}B-NMR ($CDCl_3$, 96 MHz, 25°C): δ = –1.28 (s). ^{13}C-NMR ($CDCl_3$, 75 MHz, 25°C): δ = 147.8 (d, *o*-C, 2C, $^1J_{CF}$ = 243.5 Hz); 140.3 (d, *p*-C, 1C, $^1J_{CF}$ = 240.3 Hz); 137.0 (d, *m*-C, 2C, $^1J_{CF}$ = 246.7 Hz); 116.5 (br, C-B, 1C). ^{19}F-NMR ($CDCl_3$, 282 MHz, 25 °C): δ = –135.0 (“d”, *o*-F, 2F, $^3J_{FF}$ = 24.2 Hz); –156.2 (t, *p*-F, 1F, $^3J_{FF}$ = 19.7 Hz); –163.2 (“t”, *m*-F, 2F, $^3J_{FF}$ = 22.4 Hz). IR (ATR, cm^{-1}): ν = 3578 (w), 2986

(w), 1645 (m), 1517 (s), 1463 (vs), 1371 (s), 1283 (m), 1096 (s), 973 (s), 873 (w), 833 (w), 786 (m), 774 (m), 766 (m), 746 (w), 680 (m), 673 (m), 607 (w), 575 (w). Raman (100 mW, 1000 Scans, 25 °C, cm^{-1}): ν = 2938 (1), 2880 (1), 2757 (1), 2487 (10), 2477 (10), 1647 (1), 1458 (1), 1308 (1), 582 (2), 492 (2), 414 (2), 392 (1).

Synthesis of $K(18\text{-crown-6})(CH_2Cl_2)]_2^+[SO_4 \bullet 2\ B(C_6F_5)_3]^{2-}$ (**3**)

To a solution of $B(C_6F_5)_3$ (2.56 g, 5 mmol, 5 equiv) in 60 ml diethylether is added K_2SO_4 (174 mg, 1 mmol, 1 equiv) and 18-Crown-6 (528 mg, 2 mmol, 2 equiv) at room temperature. After stirring for 30 min a clear colorless solution was observed. Removal of the solvent led to a white solid, which was washed with 60 mL of *n*-hexane (removal of the $B(C_6F_5)_3$ excess). After discontinuation of the precipitate the excess *n*-hexane is removed with a syringe and discarded. The process is repeated one more time. Recrystallization from dichloromethane yields pure colorless crystals. Yield: 950 mg (55%). DSC: 223.5 °C (dec). $C_{60}H_{48}B_2F_{30}K_2O_{16}S$ (1726.8): calc C 41.73, H 2.80; found C 41.64, H 2.26. ^{1}H-NMR (CD_2Cl_2, 300 MHz, 25°C): δ = 3.55 (s, CH_2). ^{11}B-NMR (CD_2Cl_2, 96 MHz, 25°C): δ = -3.33 (s). ^{13}C-NMR (CD_2Cl_2, 75 MHz, 25°C): δ = 148.7 (d, *o*-C, 2C, $^1J_{CF}$ = 240.0 Hz); 139.3 (d, *p*-C, 1C, $^1J_{CF}$ = 242.9 Hz); 136.9 (d, *m*-C, 2C, $^1J_{CF}$ = 248.8 Hz); 122.2 (br, C-B, 1C); 70.5 (s, CH_2, 12C). ^{19}F-NMR (CD_2Cl_2, 282 MHz, 25 °C): δ = –132.7 (d, *o*-F, 2F, $^3J_{FF}$ = 21.4 Hz); –163.4 (t, *p*-F, 1F, $^3J_{FF}$ = 21.2 Hz); –167.7 (“t”, *m*-F, 2F, $^3J_{FF}$ = 21.3 Hz). IR (ATR, cm^{-1}): ν = 2891 (w), 1644 (w), 1514 (m), 1463 (s), 1353 (w), 1279 (m), 1175 (w), 1104 (s), 1085 (s), 839 (w), 805 (w), 763 (m), 677 (m), 621 (w), 576 (w), 550 (m). Raman: decomposition.

ORTEP representation of all species not shown in the manuscript. Thermal ellipsoids with 50% probability at 173 K, H atoms are partly omitted for clarity:

a) $(H_2O)_3$•$B(C_6F_5)_3$ (**4**)

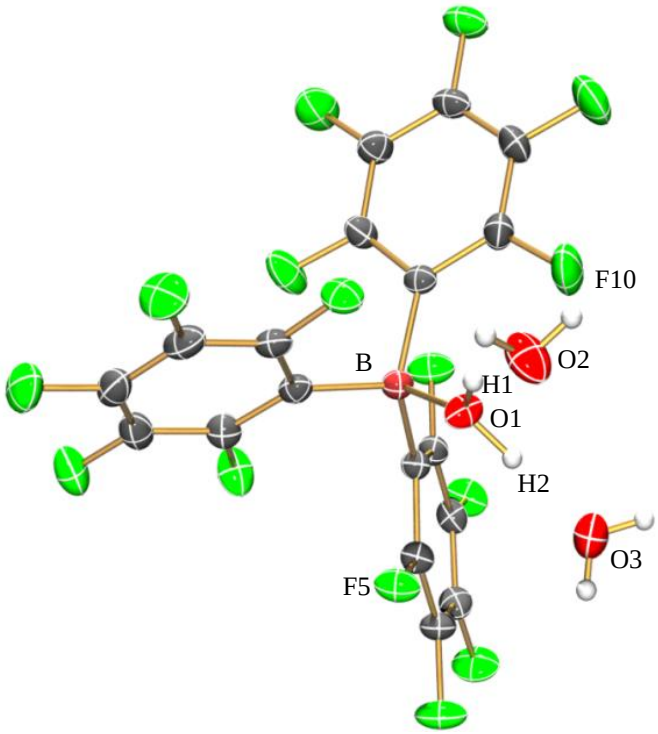


Figure S1. ORTEP drawing of the molecular structure of $(H_2O)_3$•$B(C_6F_5)_3$ (**4**) in the crystal. Thermal ellipsoids with 50% probability at 173 K. Selected bond length (Å) and angles (°): O1–B 1.5816(18), O1–H1 0.98(3), O1–H2 0.83(2), O2–H3 0.79(3), O2–H4 0.82(3), O3–H5 0.82(3), O3–H6 0.85(3); B–O1–H1 124.2(15), B–O1–H2 126.9(16), H1–O1–H2 107(2), H3–O2–H4 112(3), H5–O3–H6 108(3).

b) $[H_2O{\bullet}B(C_6F_5)_3]{\bullet}2(THF)$ (**5**)

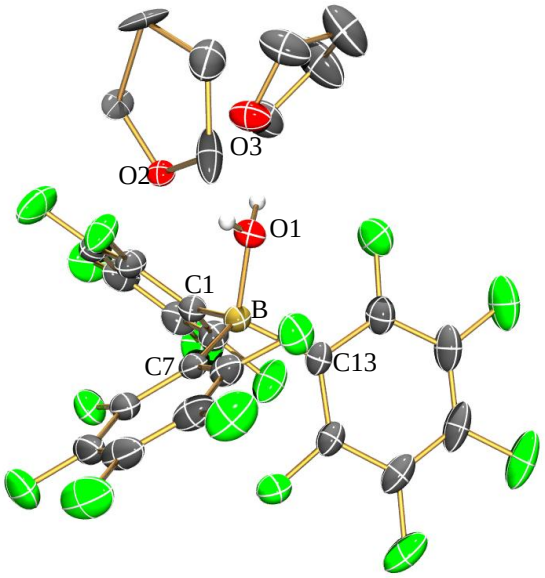


Figure S2. ORTEP drawing of the molecular structure of $[H_2O{\bullet}B(C_6F_5)_3]{\bullet}2(THF)$ (**5**) in the crystal. Thermal ellipsoids with 50% probability at 173 K. Selected bond length (Å) and angles (°): O1–B 1.549(2), B–C1 1.633(3), B–C7 1.639(2), B–C13 1.639(2), C1–C6 1.391(2), C1–C2 1.393(2), C2–F1 1.347(2), C2–C3 1.390(3), C3–F2 1.349(2), C3–C4 1.369(3), C4–F3 1.335(2), C4–C5 1.380(3), C5–F4 1.342(2), C5–C6 1.373(3), C6–F5 1.353(2), C7–C12 1.388(2), C7–C8 1.389(3), C8–F6 1.348(2), C8–C9 1.383(2), C9–F7 1.349(3), C9–C10 1.381(3), C10–F8 1.350(2), C10–C11 1.366(3), C11–F9 1.346(2), C11–C12 1.384(3), C12–F10 1.353(2), C13–C14 1.380(2), C13–C18 1.389(3), C14–F11 1.348(2), C14–C15 1.394(3), C15–F12 1.346(2), C15–C16 1.370(4), C16–F13 1.340(2), C16–C17 1.372(3), C17–F14 1.340(3), C17–C18 1.385(2), C18–F15 1.346(2), O1–B–C1 106.3(1), O1–B–C7 107.59(13), O1–B–C13 104.14(13), C1–B–C7 112.3(1), C1–B–C13 116.3(1), C7–B–C13 116.3(1), C6–C1–C2 119.9(2), C6–C1–B 119.9(2), C2–C1–B 126.3(2), C3–C2–C1 123.2(2), C3–C4–C5 118.9(2), C6–C5–C4 119.3(2), C5–C6–C1 124.76(17), O1–B–C1–C6 50.1(2), C7–B1–C1–C6 167.5(2), C13–B–C1–C6 65.3(2), C7–B–C1–C2 6.9(2), O1–B–C1–C2 124.3(2).

c) $Et_2O{\bullet}B(C_6F_5)_3$ (**6**)

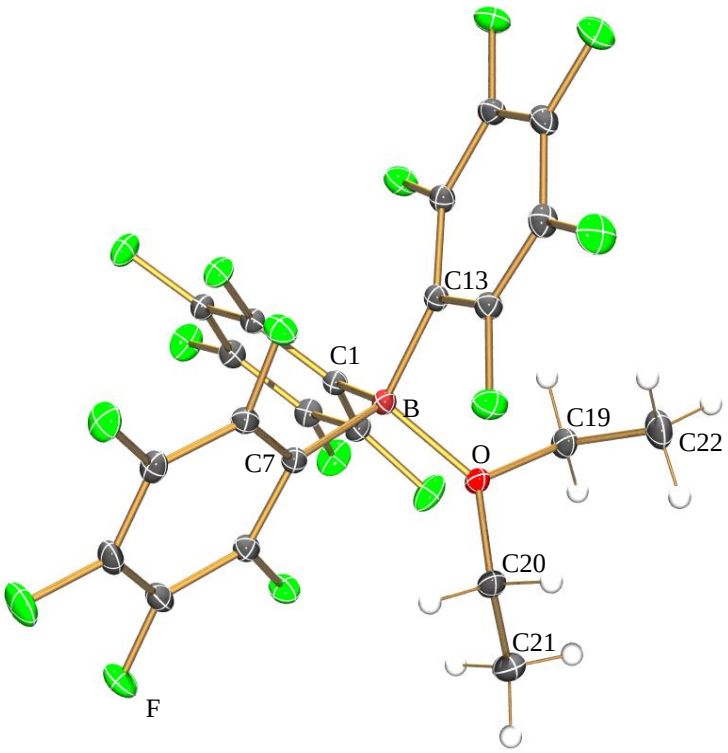


Figure S3. ORTEP drawing of the molecular structure of $Et_2O{\bullet}B(C_6F_5)_3$ (**6**) in the crystal. Thermal ellipsoids with 50% probability at 173 K. Selected bond length (Å) and angles (°): O–B 1.612(1), B–C1 1.645(2), B–C7 1.636(2), B–C13 1.638(2), O–C19 1.474(2), O–C20 1.473(1), C19–C22 1.505(2), C20–C21 1.504(2); C20–O–C19 114.58(8), C20–O–B 126.45(8), C19–O–B 118.14(8), O–B–C7 108.99(8), O–B–C13 102.92(8), C7–B–C13 115.55(9), O–B–C1 109.09(9), C7–B–C1 104.81(9), C13–B–C1 115.32(9), O–C19–C22 114.5(1), O–C20–C21 112.1(1); C20–O–B–C7 8.8 (1), C19–O–B–C7 177.73(9), C20–O–B–C13 114.4(1), C19–O–B–C13 54.6(1), C20–O–B–C1 122.7(1), C19–O–B–C1 68.4(1), C20–O–C19–C22 59(1), B–O–C19–C22 111.3(1), C19–O–C20–C21 64.1(1), B–O–C20–C21 126.6(1).

d) THF•B(C_6F_5)$_3$ co-crystallized with 18-crown-6 (**7**)

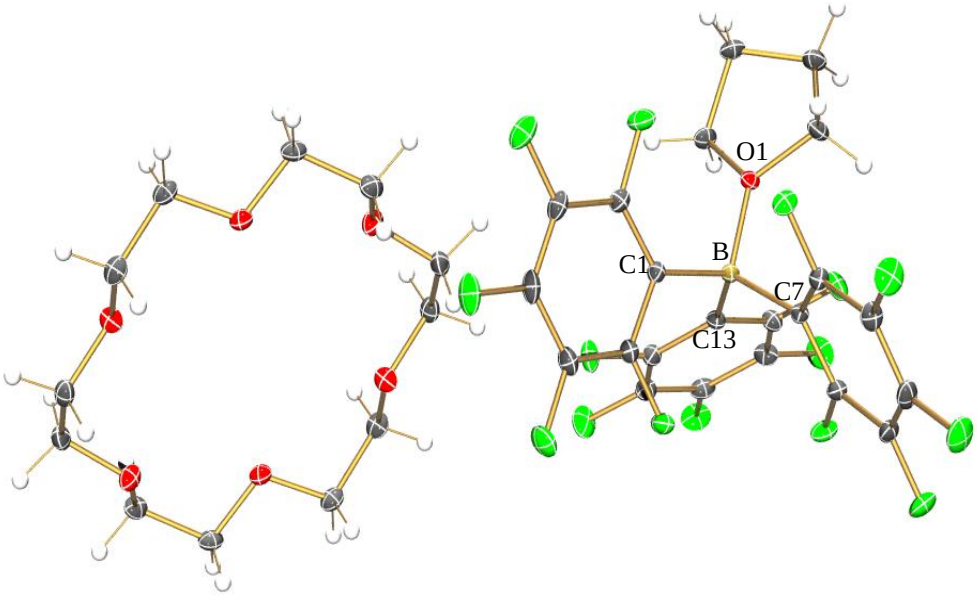


Figure S4. ORTEP drawing of the molecular structure of THF•B(C_6F_5)$_3$ co-crystallized with 18-crown-6 (**7**) in the crystal. Thermal ellipsoids with 50% probability at 173 K. Selected bond length (Å) and angles (°):O1–B 1.572(1), B–C7 1.638(1), B–C13 1.640(1), B–C1 1.643(1), C1–C2 1.383(1), C1–C6 1.398(1), C2–C3 1.394(1), C3–C4 1.373(2), C4–C5 1.374(2), C5–C6 1.382(1), O1–B–C7 109.63(7), O1–B–C13 103.27(7), O1–B–C1 109.26(7), C7–B–C13 114.87(7), C7–B–C1 105.18(7), C13–B–C1 114.57(7), O1–B–C1–C2 6.8(1), C7–B–C1–C2 110.8(1), C13–B–C1–C2 122.1(1), O1–B–C1–C6 179.61(7), C7–B–C1–C6 62.0(1), C13–B–C1–C6 65.1(1).

Table S1. Crystallographic details of **4**, **5**, **6** and **7**.

	4	**5**	**6**	**7**
Chem. Formula	$C_{18}H_6BF_{15}O_3$	$C_{26}H_{18}BF_{15}O_3$	$C_{22}H_{10}BF_{15}O$	$C_{28}H_{20}BF_{15}O_4$
Form. Wght. [g mol^{-1}]	566.04	674.21	586.11	716.25
Colour	colourless	colourless	colourless	colourless
Cryst. system	monoclinic	monoclinic	triclinic	triclinic
Space group	*C*2/*c*	*P*21/*c*	*P*-1	*P*-1
a [Å]	19.367(4)	9.285(4)	10.381(3)	10.110(2)
b [Å]	10.729(2)	30.031(9)	10.673(3)	10.950(4)
c [Å]	19.820(4)	10.049(4)	10.849(3)	13.482(4)
α [°]	90.00	90.00	65.507(17)	75.23(3)
β [°]	96.45(3)	105.14(3)	85.51(2)	81.81(2)
γ [°]	90.00	90.00	75.68(2)	82.94(2)
V [Å^3]	4092(2)	2705(2)	1059.5(5)	1422.6(7)
Z	8	4	2	2
$\rho_{calc.}$ [g cm^{-3}]	1.837	1.656	1.837	1.672
μ [mm^{-1}]	0.213	0.176	0.202	0.175
T [K]	173(2)	173(2)	173(2)	173(2)
Measured reflections	21007	30910	20497	29445
Independent reflections	5088	8102	5582	10676
Reflections with $\underline{I > 2\sigma(I)}$	3946	5479	4828	8229
$R_{int.}$	0.0212	0.0346	0.0366	0.0332
F(000)	2224	1352	580	720
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0387	0.0597	0.0382	0.0415
wR_2 (F^2)	0.1059	0.1884	0.1143	0.1235
GooF	1.046	1.079	1.089	1.050
Parameters	358	466	354	433