ESI

Uranium(IV) amido-borohydrides as highly active diene polymerisation catalysts

Stephen M. Mansell,[a] Fanny Bonnet, *[b] Marc Visseaux,* [b] and Polly L. Arnold*[a]

a. EaStCHEM School of Chemistry, University of Edinburgh, Joseph Black Building, The King's Buildings, Edinburgh, EH9 3JJ, U. K. Email address: polly.arnold@ed.ac.uk

b. CNRS, UMR8181, ENSCL, UCCS, CCM, F-59652 Villeneuve d'Ascq, Univ. Lille Nord de France, F-5900 Lille, France

Contents

Experimental Details

Data for $(N'')_2U\{\kappa^2\text{-}N(SiMe_3)SiMe_2CH_2BBN\text{-}H\}$ 2

^{1}H NMR (400 MHz, 298 K, C_6D_6) δ (ppm) 142.6 (br.s, 2 H, $SiCH_2B$), 8.46 (br. s, 6 H, $SiMe_2$), 6.27 (br. s, 2 H, BBN), 1.89 (m, 1 H, BBN), 0.69 (br. s, 2 H, BBN), -4.91 (m, 1 H, BBN), -5.35 (s, 9 H, $SiMe_3$), -5.78 (br. s, 36 H, N''), -12.92 (m, 1 H, BBN), -15.42 (s, 2 H, BBN), -19.08 (br. s, 2 H, BBN), -20.38 (m, 1 H, BBN), -38.55 (s, 2 H, BBN), -125.09 (br. s, 1 H, BH).
I.R. υ (nujol, cm^{-1}) 1794 (br., B-H), 1306 (m), 1252 (s, Si-Me), 1202 (w), 1133 (w), 1070 (w), 1052 (w), 1007 (m), 928 (s), 904 (s), 847 (Si-Me), 774 (s).
μ_{eff} (Evans' NMR method) 3.16 μ_B per molecule.
Analysis calculated for $C_{26}H_{68}BN_3Si_6U$: C, 37.17; H, 8.16; N, 5.00. Found: C, 36.95; H, 8.23; N, 4.94.

Crystals suitable for X-ray crystallography were grown from a saturated *n*-hexane at -20°C. All the crystals tried were found to be non-merohedrally twinned and much of the structure was also found to be disordered over two positions.

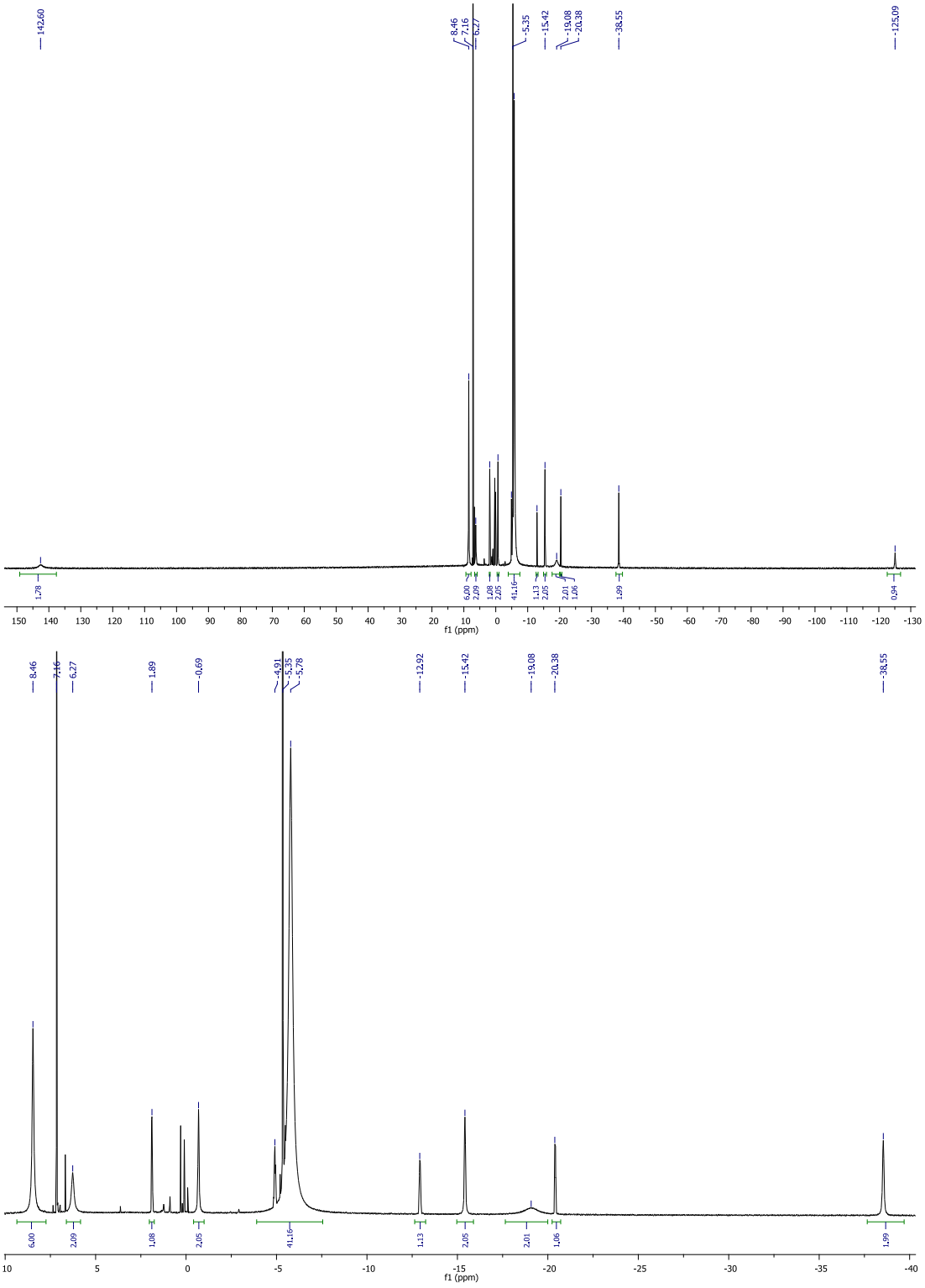

Figure S 1. ^{1}H NMR spectrum of U{N(SiMe$_3$)$_2$}$_2${N(SiMe$_3$)SiMe$_2$CH$_2$BBNH} (top) with enlargement (bottom).

Data for U{N(SiMe$_3$)SiMe$_2$CH$_2$BBNH}$_2$ 3

^{1}H NMR (400 MHz, 298 K, C_6D_6) δ (ppm) 81.81 (s, 1 H, SiC(***H***)HB), 61.23 (s, 1 H, SiC(H)***H***B), 48.16 (s, 3 H, SiMe), 32.47 (s, 1 H), 5.59 (s, 1 H), 3.21 (s, 3 H, SiMe), -3.32 (m, 1 H), -5.94 (m, 1 H), -7.59 (m, 1 H), -9.78 (s, 9 H, $SiMe_3$), -10.05 (m, 1 H), -10.24 (s, 1 H), -12.14 (m, 1 H), -16.12 (m, 1 H), -29.53 (m, 1 H), -30.31 (m, 1 H), -31.40 (m, 1 H), -36.71 (s, 1 H), -76.60 (s, 1 H), -120.51 (br. s, 1 H, BH).
I.R. υ (nujol, cm^{-1}) 1851 (m, B-H), 1292 (m), 1245 (s, Si-Me), 1167 (w), 1117 (m), 1072 (w), 1054 (w), 1023 (m), 939 (s), 841 (Si-Me), 799 (m), 783 (s), 766 (m).
μ_{eff} (Evans' NMR method) 3.12 μ_B per molecule.
Analysis calculated for $C_{28}H_{64}B_2N_2Si_4U$: C, 41.99; H, 8.06; N, 3.50. Found: C, 41.93; H, 8.19; N, 3.43.

Crystals suitable for X-ray crystallography were grown from a saturated *n*-hexane at room temperature.

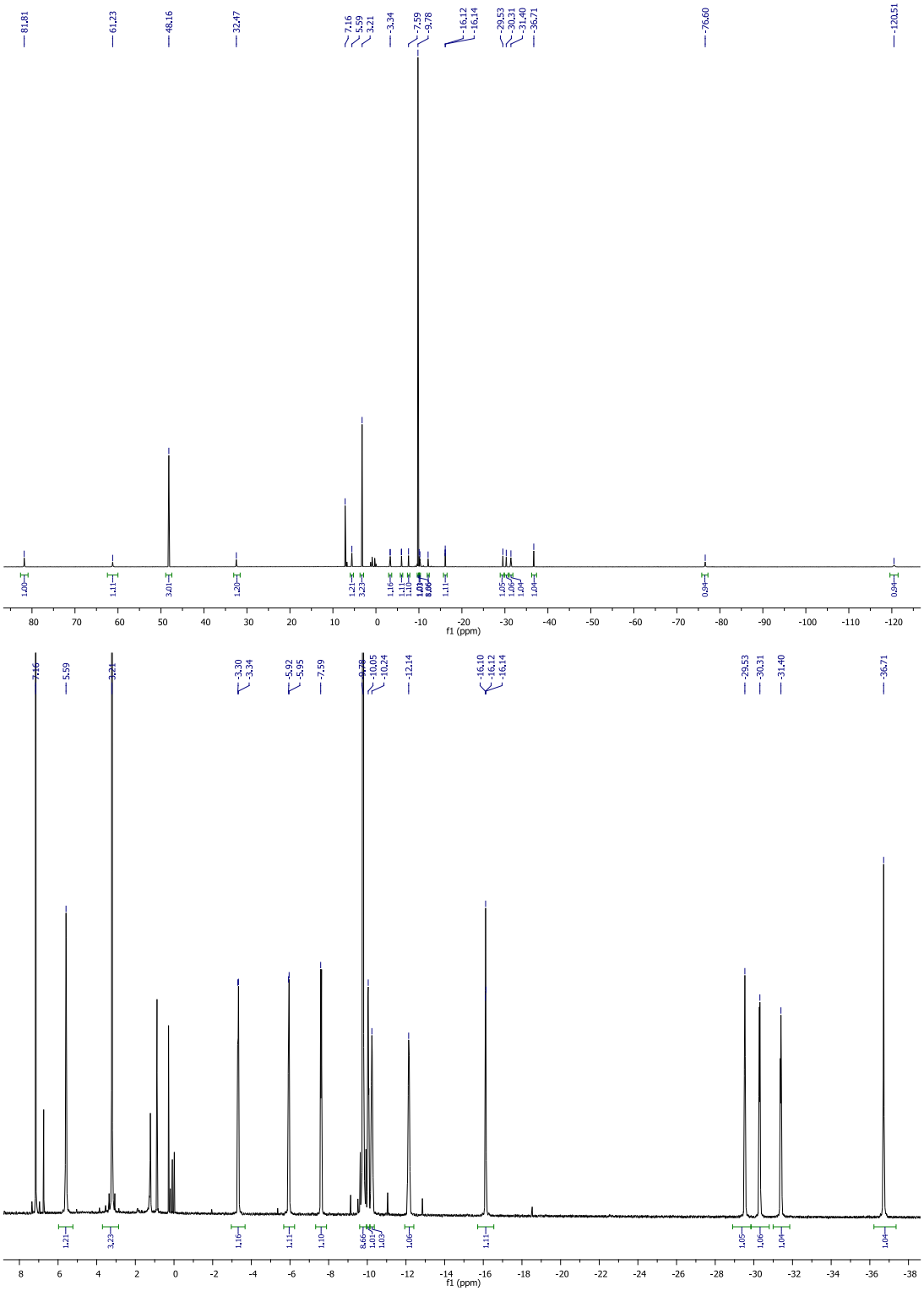

Figure S 2. ^{1}H NMR spectrum of U{N(SiMe$_3$)SiMe$_2$CH$_2$BBNH}$_2$ (top) with enlargement (bottom).

Crystallographic Details

Diffraction experiments on these samples were carried out on single crystals covered in inert oil cooled to 120 or 170 K on either an Oxford diffraction Supernova diffractometer employing Cu-Kα radiation (λ = 1.54184 Å) for **2** or Excalibur four-circle diffractometer employing Mo-Kα radiation (λ = 0.71073 Å) for **3**. The structures were solved by direct methods (XS) and refined by least squares on weighted F^2 values for all reflections (XL).[1] All hydrogen atoms attached to carbon atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. The B-H hydrogens in **3** were located in the Fourier difference map and freely refined with fixed isotropic parameters, but could not be located in **2** so were left unplaced. Several data sets of crystals of **2** were found to be non-merohedrally twinned so the data were refined as two components of ratio 0.67:0.33 using a hklf 5 refinement. In addition, all atoms except U and N were found to be disordered over two positions (occupancy factor of 0.5) and the combination of these challenges resulted in high residual R-factors.

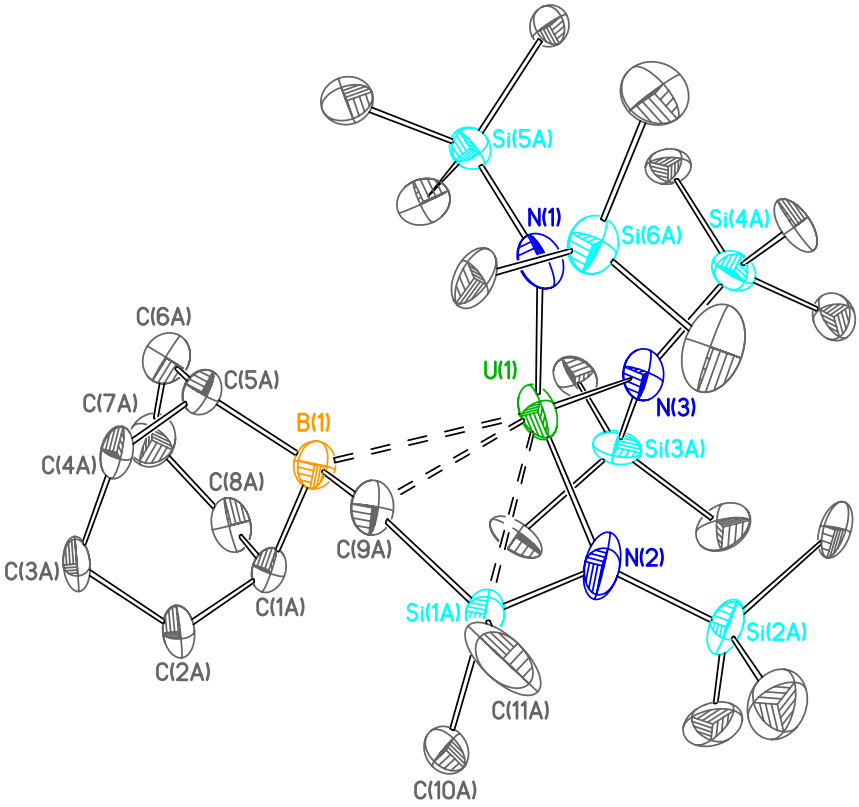

Figure S 3. Thermal ellipsoid plot for one of the two disordered positions in 2 **with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.**

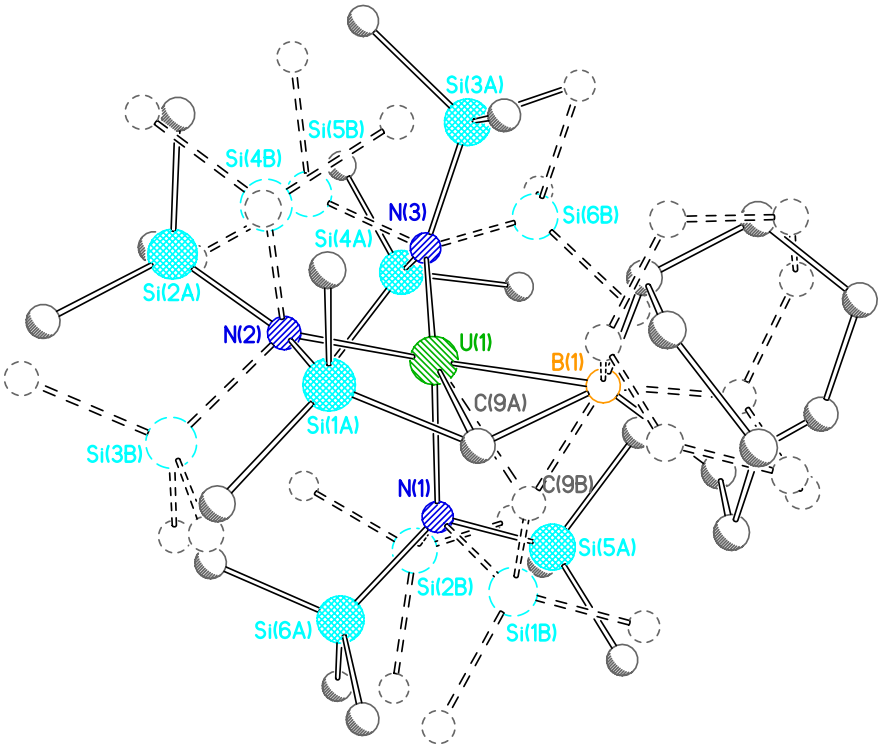

Figure S 4. Plot showing the two overlapping disordered positions in 2. To clarify, N(2) is the amide nitrogen in the amido-borate for the part labeled A (together with Si(1A) and C(9A)), whereas N(1) is the amide nitrogen in the amido-borate in the dashed second-part labeled B (with Si(1B) and C(9B)).

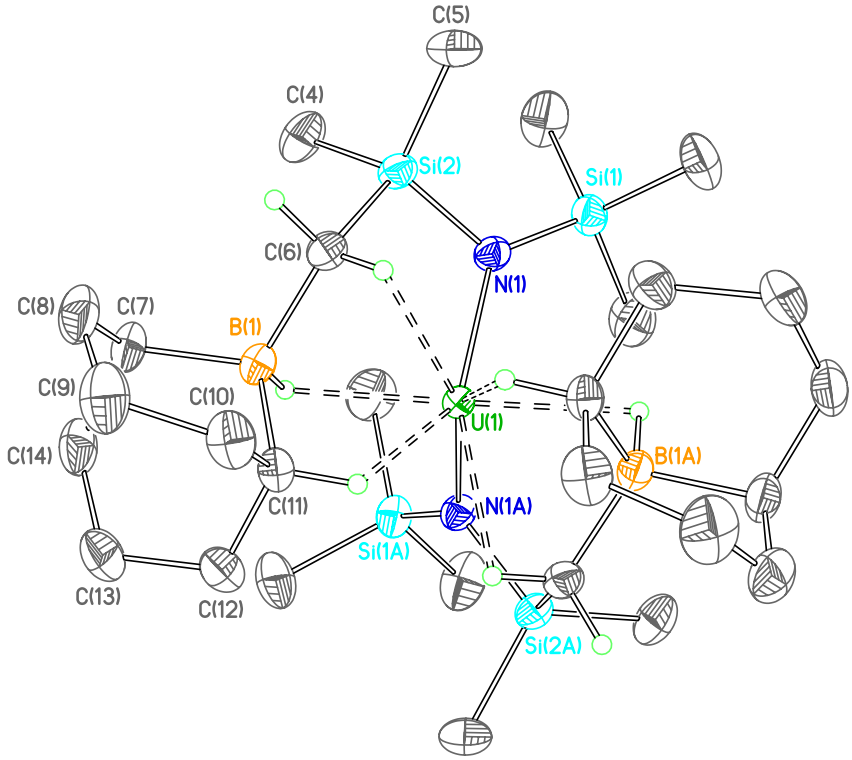

Figure S 5. Thermal ellipsoid plot for 3 with thermal ellipsoids at 50% probability. Most of the hydrogen atoms are omitted for clarity. Symmetry operator used to generate symmetry-generated atoms: *y*, *x*, *-z*. Selected bond lengths (Å) and angles (°): U(1)-N(1) 2.2015(18), U(1)-B(1) 2.644(2), U(1)-C(6) 2.695(2), U(1)-C(11) 2.907(2), U(1)-Si(2) 3.0784(6), U(1)-H(12) 2.30(3), B(1)-H(12) 1.25(3), N(1A)-U(1)-N(1) 106.19(11), N(1)-U(1)-B(1) 98.34(7), N(1)-U(1)-B(1A) 108.56(8).

Table 1. Selected crystallographic details

Compound	**2**	**3**
CCDC number	918119	918120
Chemical formula	$C_{26}H_{67}BN_3Si_6U$	$C_{28}H_{64}B_2N_2Si_4U$
Formula Mass	839.21	800.82
Crystal system	Monoclinic	Tetragonal
a/Å	18.1815(4)	12.6359(1)
b/Å	12.0062(2)	12.6359(1)
c/Å	18.7241(4)	22.6693(2)
α/°	90	90
β/°	101.721(2)	90
γ/°	90	90
Unit cell volume/Å^3	4002.07(14)	3619.52(5)
Temperature/K	120(2)	170(2)
Space group	$P2_1/n$	$P4_12_12$
No. formula units / unit cell, Z	4	4
Density (calculated)/Mgm^{-3}	1.393	1.470
Radiation type	Cu-Kα	Mo-Kα
Absorption coefficient, μ/mm^{-1}	13.269	4.636
No. of reflections measured	215449	141972
No. of independent reflections	16185	8762
Rint		0.0536
Final R_1 values (I > 2σ(I))	0.1109	0.0256
Final $wR_2(F^2)$ values (I > 2σ(I))	0.2793	0.0500
Final R_1 values (all data)	0.1132	0.0311
Final $wR_2(F^2)$ values (all data)	0.2806	0.0515
Flack parameter		0.664(4)

References

1. G. M. Sheldrick, *Acta Crystallographica Section A*, 2008, **64**, 112-122.