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A supramolecular hydrogen-bonded complex between 1,3,5-tris(diisobutylhydroxysilyl)benzene and *trans*-bis(4-pyridyl)ethylene

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The trisilanol 1,3,5-(HOi-$Bu_2Si)_3C_6H_3$ (7), prepared in three steps from 1,3,5-tribromobenzene via the intermediates 1,3,5-(Hi-$Bu_2Si)_3C_6H_3$ (8) and 1,3,5-(Cli-$Bu_2Si)_3C_6H_3$ (9) forms an equimolar complex with *trans*-bis(4-pyridyl)ethylene (bpe), 7·bpe, whose structure was investigated by X-ray crystallography. The hydrogen-bonded network features a number of SiO–H···O(H)Si and SiO–H···N hydrogen bridges. Evidence was found for cooperative strengthening within the sequential hydrogen bonds. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: supramolecular chemistry; hydrogen bonding; silanol; silicon

INTRODUCTION

The design of solid-state architectures on a molecular level requires the judicious choice of rigid building blocks ('synthons') possessing adhesive functional groups ('tectons') with a pre-fixed directionality.[1–5] 1,3,5-Trimesic acid, 1,3,5-($HO_2C)_3C_6H_3$ (**1**), the prime synthon of supramolecular organic chemistry, fulfils these criteria, giving rise to the formation of hydrogen-bonded networks containing hexagonal nano-dimensional cavities that are useful for applications in host–guest chemistry.[6–12] Organometallic chemistry can extend the range of building blocks for applications in supramolecular chemistry by a wealth of adhesive functional groups.[13] Organometallic congeners of 1,3,5-trimesic acid **1** may for instance include 1,3,5-benzenetriboronic acid (**2**)[14] and 1,3,5-benzenetriphosphonic acid (**3**),[15,16] which offer interesting possibilities for the design of novel supramolecular complexes (Scheme 1).

Recently, we have investigated the self-organization of 1,3,5-tris(diorganohydroxysilyl)benzenes, 1,3,5-($HOR_2Si)_3C_6H_3$ (**4**, R = Me; **5**, R = Ph; **6**, R = *i*-Pr) in the solid state (Scheme 1) and studied the assembly of supramolecular complexes of the trisilanol **6** with 4,4′-bipyridine (bpy), *trans*-bis(4-pyridyl)ethylene (bpe), 4,4′-azopyridine (azpy) and bis(4-pyridyl)aceylene (bpa), respectively.[17,18] Interestingly, the overall supramolecular motif was similar for all four complexes. The trisilanol molecules form one-dimensional strings via SiO–H···O(H)Si hydrogen bonds, whereas the 4,4′-bis(pyridines) are linked approximately perpendicularly by SiO–H···N hydrogen bonds, giving rise to the formation of two-dimensional grid structures. In an extension of our previous work,[17,18] we now describe the synthesis of 1,3,5-(HOi-$Bu_2Si)_3C_6H_3$ (**7**) and its supramolecuar complex with *trans*-bis(4-pyridyl)ethylene (bpe). The comparison of **6**·bpe and **7**·bpe reveals that the organic substituents of the silicon atoms, e. g. isopropyl and isobutyl groups, have a large bearing on the supramolecular motifs.

RESULTS AND DISCUSSION

The synthesis of 1,3,5-(HOi-$Bu_2Si)_3C_6H_3$ (**7**) has been achieved in three steps starting with 1,3,5-tribromobenzene, and resembles that of 1,3,5-(HOi-$Pr_2Si)_3C_6H_3$ (**6**).[17,18] Thus, the *in situ* Grignard reaction of 1,3,5-tribromobenzene with *i*-Bu_2SiHCl and Mg provided 1,3,5-(Hi-$Bu_2Si)_3C_6H_3$ (**8**) as a distillable oil. The chlorination of **8** with SO_2Cl_2 afforded 1,3,5-(Cli-$Bu_2Si)_3C_6H_3$ (**9**) as an oil. The base hydrolysis of **8** yielded the trisilanol 1,3,5-(HOi-$Bu_2Si)_3C_6H_3$ (**7**), which was obtained as crystalline hemi-hydrate **6**· 0.5 H_2O after recrystallization from toluene (Scheme 2).

Co-crystals of **7**·bpe were obtained by co-crystallization from hexane. The molecular structures of **7** and bpe are

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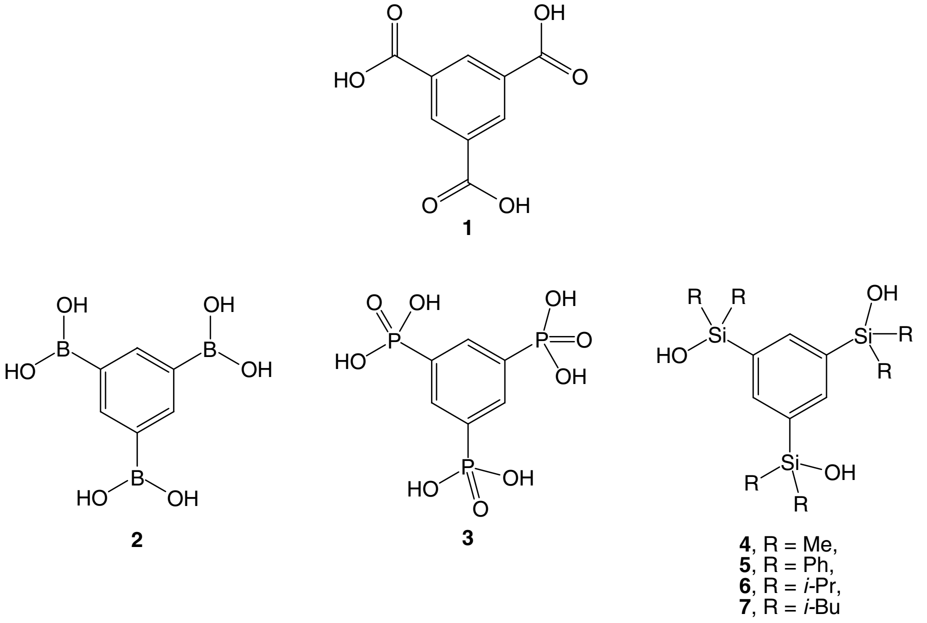
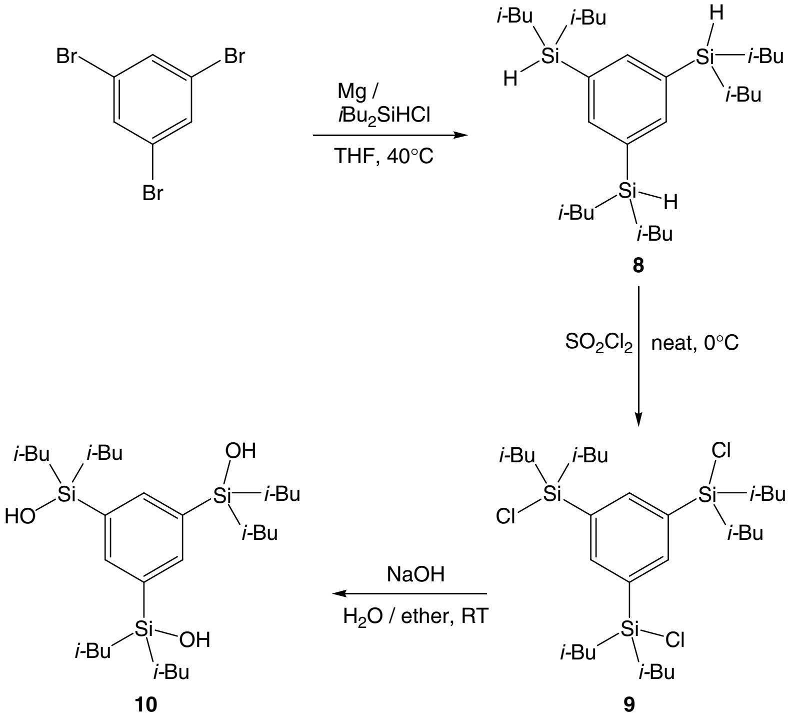


Scheme 1. Supramolecular building blocks : trimesic acid **1** and organometallic congeners **2–7**.



Scheme 2. Synthetic route for the preparation of **7**.

shown in Fig. 1. The supramolecular association of **7**·bpe and **6**·bpe are shown in Fig. 2.[17,18] Two molecules of **7** are related by a crystallographic center of inversion and associate via two SiO–H···O(H)Si hydrogen bonds. The centrosymmetric dimers of **7** are linked by two bpe molecules with which they are associated via two SiO–H···N hydrogen bonds. Interestingly, the supramolecular motif of **7**·bpe entirely contrasts with the two-dimensional grid structure of **6**·bpe and those of other inclusion complexes between **6** and 4,4′-bis(pyridines).[17,18] This observation demonstrates the subtle

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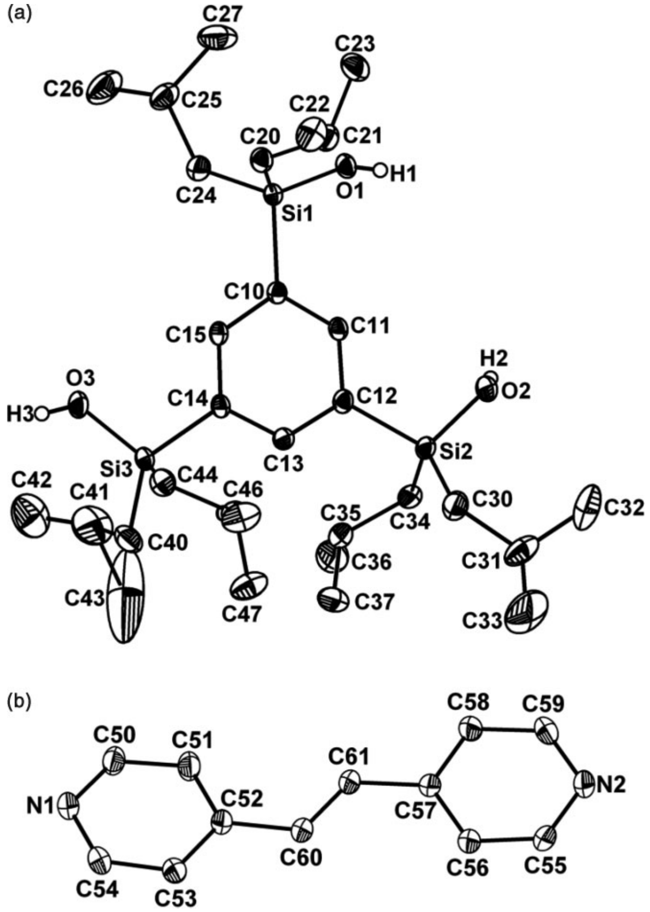

Figure 1. Molecular structures of (a) 1,3,5-(HO*i*-Bu$_2$Si)$_3$C$_6$H$_3$ (**7**) and (b) *trans*-bis(4-pyridyl)ethylene (bpe) in the co-crystals of **7**·bpe showing 30% probability displacement ellipsoids and the atom numbering.

Table 1. Selected hydrogen bond parameters of **7**·bpe

	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (deg)
O2–H2···O1	0.74(3)	2.10(4)	2.835(7)	172(3)
O1–H1···N1	0.80(3)	2.00(3)	2.763(5)	162(3)
O3–H3···N2	0.76(4)	2.04(4)	2.793(6)	172(3)

influence of the organic substitutes attached to the silicon atoms, e.g. isopropyl and isobutyl groups, on the supramolecular structure of these complexes. Selected hydrogen bond parameters of **7**·bpe are collected in Table 1. These values compare well with those reported for similar co-crystals of **6** with bis(pyridines).[17,18] Despite this difference, **6**·bpe and **7**·bpe show the same number of donor acceptor pairs, namely one SiO–H···O(H)Si hydrogen bond and two SiO–H···O(H)Si hydrogen bonds. Moreover, both co-crystals contain one sequential SiO–H···O(Si) –H···N hydrogen bridge as well as one isolated SiO–H···N hydrogen bond. The O···N distances of the sequential hydrogen bridges are by 0.039(5) Å (**6**·bpe)[17,18] and 0.030(6) Å (**7**·bpe) shorter than in the isolated hydrogen bridges, which may be tentatively explained by a strengthening of the SiO–H···N by the SiO–H···O(H)Si hydrogen bond. Cooperative effects have been frequently observed for other hydrogen bond systems, such as various water clusters.[19,20] Concomitant strengthening of SiO–H···N and SiO–H···O(H)Si hydrogen bonds was also found in the gas-phase complex H$_3$SiOH···H$_3$SiOH···NC$_5$H$_5$, whose complex energy E_{Add}(-13.12 kcal mol^{-1}) is by 3.18 kcal mol^{-1} more stable than the complex energies E_{Add} of the isolated complexes H$_3$SiOH···H$_3$SiOH(-3.47 kcal mol^{-1}) and H$_3$SiOH···NC$_5$H$_5$(-6.47 kcal mol^{-1}).[21] Attempts to grow co-crystals of **7** with 4,4′-bipyridine (bpy), 4,4′-azopyridine (azpy) and bis(4-pyridyl)acetylene (bpa) have failed, presumably due to the higher solubility of **7** compared to **6**, which precluded a more detailed comparison of related inclusion complexes with 4,4′-bis(pyridines).

EXPERIMENTAL

1,3,5-Tribromobenzene, diisobutylchlorosilane and *trans*-bis(4-pyridyl)ethylene (bpe) are commercially available. NMR spectra were collected in CDCl$_3$ using a Jeol JNM-LA 400 FT spectrometer and are referenced against Me$_4$Si. IR spectra were recorded with a 5 SXC Nicolet DTGS FT-IR spectrometer. Microanalyses were obtained from a Vario EL elemental analyzer.

Synthesis of 1,3,5-tris(diisobutylsilyl)benzene (8)

A 250 ml flask equipped with a reflux condenser, a dropping funnel and a septum was charged with Mg turnings (2.79 g, 0.11 mol) and covered with THF (20 ml). The Mg was activated by 1,2-dibromoethane (100 μl) before diisobutylchlorosilane (16.4 g, 0.090 mol) was added via a syringe. A solution of 1,3,5-tribromobenzene (8.8 g, 0.028 mol) in THF (80 ml) was slowly added whereby the temperature rose to 50 °C. The reaction mixture was kept at this temperature for 5 h and was then cooled at 0 °C. Water (60 ml) and hexane (40 ml) were added and the organic layer separated and dried over Na$_2$SO$_4$. The crude product was purified by Kugelrohr distillation affording a colorless oil (5.9 g, 0.012 mol, 42%; b.p. 235–250 °C/7.5 × 10^{-3} Torr). ^{29}Si-{^{1}H} NMR: $\delta = -13.5$. ^{13}C-NMR-{^{1}H}: $\delta = 141.9$, 134.8, 26.1, 25.9, 25.4, 23.5. ^{1}H-NMR: $\delta = 7.81$ (s, 3H), 4.56 (m, 3H), 1.99–1.83 (m, 6H), 1.20–0.89 (m, 48H). IR (NaCl, neat): $\tilde{\nu}$(Si–H) = 2116 cm^{-1}. Analysis calcd for C$_{30}$H$_{60}$Si$_3$ (504.59): C 70.99, H 11.82; found: C 71.11, H 12.09%.

Synthesis of 1,3,5-tris(diisobutylchlorosilyl) benzene (9)

A 50 ml Schlenk flask with a gas outlet was charged with **8** (4.48 g, 8.9 mmol) and closed with a septum.

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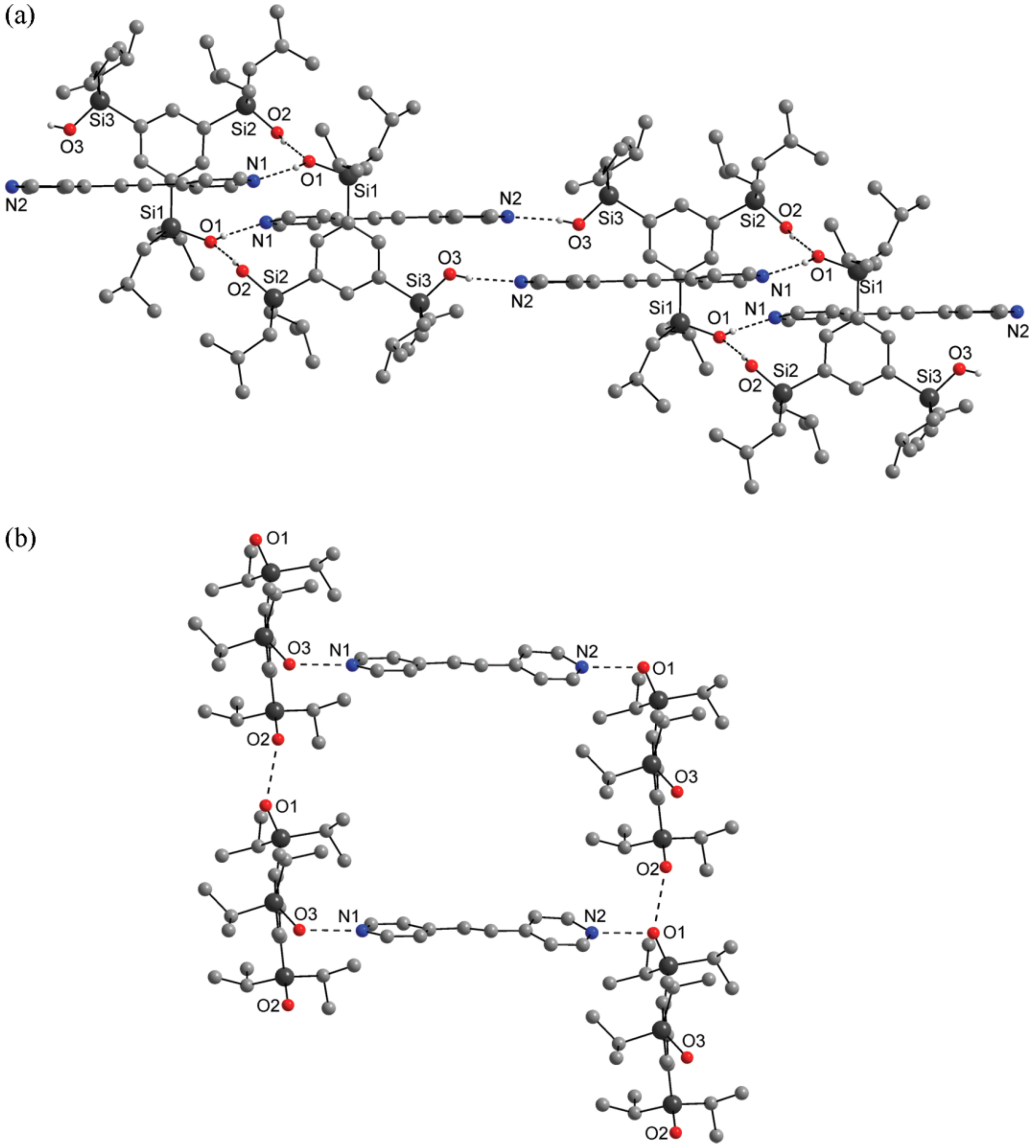

Figure 2. Supramolecular association of (a) **7**·bpe and (b) **6**·bpe. This figure is available in colour online at www.interscience.wiley.com/AOC.

At 0 °C, SO_2Cl_2 (4.05 g, 30.0 mmol) was slowly added via a syringe. After a short delay a vigorous reaction took place and SO_2 gas evolved. After the gas evolution had ceased, the reaction mixture was heated to 40 °C for 1 h. The excess SO_2Cl_2 was condensed off leaving a slightly yellow crude product that was pure by NMR (5.18 g, 8.52 mmol, 96%). An analytical sample was purified by Kugelrohr distillation (b.p. 220–230 °C/7.5 × 10^{-3} Torr) affording a colorless oil that solidified upon standing. ^{29}Si-{^{1}H} NMR: $\delta = 19.8$. ^{13}C-NMR-{^{1}H}: $\delta = 140.1$, 134.5, 27.6, 26.1, 25.9, 24.4. ^{1}H-NMR: $\delta = 7.85$ (s, 3H), 1.84–1.74 (m, 6H), 1.01–0.78 (m, 48H). Analysis calcd for $C_{30}H_{57}Si_3Cl_3$ (607.94): C 59.27, H 9.38; found: C 59.28, H 9.57%.

Synthesis of 1,3,5-tris(diisobutylhydroxosilyl) benzene (7)

In a 50 ml flask **8** (3.56 g, 6.86 mmol) was dissolved in ether (30 ml) and a solution of NaOH (1.2 g, 30.0 mmol) in water (30 ml) was added. The mixture stirred for 2 h at room temperature before the layers were separated. The organic layer was washed with water (3 × 20 ml) and dried over Na_2SO_4. After vacuum removal of the solvent the product was obtained as a colorless oil (3.27 g, 5.91 mmol, 86%). ^{29}Si-{^{1}H} NMR: $\delta = 5.4$. ^{13}C-NMR-{^{1}H}: $\delta = 139.3$, 136.4, 26.7, 26.3, 26.2, 24.2. ^{1}H-NMR: $\delta = 7.77$ (s, 3H), 1.84–1.74 (m, 6H), 0.87–0.77 (m, 48H). IR (NaCl, neat): $\tilde{\nu}$(SiOH) = 3645 (free), 3444 (H-bonded) cm^{-1}. From toluene, **7** crystallized as hemi hydrate, **7**· 0.5 H_2O. IR (KBr): $\tilde{\nu}$(SiOH) = 3406 (H-bonded)

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cm^{-1}. Analysis calcd for $C_{30}H_{60}Si_3O_3 \cdot 0.5\,H_2O$ (562.07): C 64.11, H 10.94; found: C 64.32, H 11.07%.

Synthesis of the supramolecular complex 7·bpe

Compound **7**· 0.5 H_2O (60.0 mg, 0.107 mmol) and *trans*-bis(4-pyridyl)ethylene (bpe) (16.4 mg, 0.107 mmol) were dissolved in CH_2Cl_2:hexane (3 : 2). Slow evaporation of the solution furnished colorless crystals (45 mg, 0.061 mmol, 57%). IR (KBr): $\tilde{\nu}$(SiOH) = 3386 (H-bonded) cm^{-1}. Analysis calcd. for $C_{42}H_{68}N_2O_3Si_3$ (733.26): C 64.40, H 9.06, N 4.42; Found: C 64.78, H 9.40, N 4.06%.

Crystallography

Data and structure solution at $T = 173(2)$ K: $C_{42}H_{68}N_2O_3Si_3$, $M_r = 733.26$, triclinic, $P-1$, $a = 10.549(2)$, $b = 13.681(3)$, $c = 16.441(4)$ Å, $\alpha = 107.387(4)°$, $\beta = 94.976(5)°$, $\gamma = 98.492(5)°$, $V = 2217.9(8)$ Å^3, $Z = 2$, $D_{calcd} = 1.098$ mg m^{-3}, $\mu = 0.144\ mm^{-1}$. Intensity data were collected on Bruker Smart 1000 CCD diffractometer fitted with Mo-K_α radiation (graphite crystal monochromator, $\lambda = 0.71073$ Å) to a maximum of $\theta_{max} = 25.0°$ via ω scans. Data were reduced and corrected for absorption using the programs SAINT and SADABS.[22] The structure was solved by direct-methods and difference Fourier synthesis using SHELX-97 implemented in the program WinGX 2002.[23] Full-matrix least-squares refinement on F^2, using all data, was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Disorder of two isobutyl groups was resolved with split occupancies of 0.75 for C45–C47 and 0.25 for C45′–C47′ as well as 0.5 for C42, C42′, C43 and C43′. Hydrogen atoms attached to oxygen atoms were located during the last refinement cycle and refined isotropically. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model and were also refined isotropically. $R_1 = 0.047$ for 6173 $[I > 2\sigma(I)]$ reflections and $wR_2 = 0.139$ for all 7787 independent reflections. The figures were prepared using the DIAMOND program.[24] Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 616 936. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-(0)1223–336033 or e-mail: deposit@ccdc.cam.ac.uk].

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