Supporting information belonging to the paper

"A new hexakis(isocyanato)silicate(IV) and the first neutral Lewis-base adducts of silicontetraisocyanate"

Content:

1) General

KNCO and KNCS (Aldrich) were dried at 105°C and 130°C, respectively, in high vacuum. $SiCl_4$ was treated with K_2CO_3, trap-to-trap condensed and degassed prior to use. (PPN)NCO, m.p. 212-214°C and (PPN)NCS, m.p. 186-189°C were prepared according to published procedures.[28] 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) were sublimed. Solvents were obtained from a Grubbs column, stirred over CaH_2 and trap-to-trap condensed prior to use. Schlenk tube and Glove box techniques were used under Argon throughout. Fourier transform infrared (FTIR) spectra were obtained from a Galaxy 2000 spectrometer at 4 cm^{-1} resolution between NaCl (nujol suspension) or CaF_2 (solution, d = 0.2 mm) windows. NMR spectra were recorded at r.t. on Bruker spectrometers and are calibrated against the signal of the residual proton content (^1H, 1.94 ppm and 5.32 ppm) or natural abundance (^{13}C, 53.8 ppm) of the solvents CD_3CN and CD_2Cl_2. Thermogravimetry (TGA) and differential scanning calorimetry (DSC) were performed under N_2 using the Perkin Elmer Pyris 1 apparatus at a heating rate of 10 K min^{-1}. Elemental analyses were obtained from the Centre for chemical instrumentation and analytical services at Sheffield. Mass spectra were recorded on a VG Autospec, calibrated against PFK. The positive ion current was recorded between 50 < m/z < 700 at temperatures of ca. 200ºC. Peaks below 10% of base intensity are omitted for m/z < 200. Fragmentation indicated as ***bpy*** and ***phen*** closely resembles published data on genuine samples of the diimines.

2) Syntheses and full spectroscopic data

Preparation of **1b**. KNCS (2.385 g, 24.54 mmol) was suspended in MeCN at 0°C. Under stirring $SiCl_4$ (0.20 ml, 1.7 mmol) were added using a syringe upon which the suspension turned cloudy immediately. The reaction mixture was stirred at r.t. for 4 d, during which the reaction solution, obtained upon sedimentation, was monitored by IR spectroscopy. The diluted, supernatant, clear and colourless solution revealed the presence of two bands in the NCS stretch region at 2101 and 2058 cm^{-1} which arise from the presence of $Si(NCS)_6^{2-}$ and KNCS, respectively. Afterwards the reaction mixture was filtered (0.203 g residue). The filter solution collected in a new Schlenk tube and diminished three times to ca. one half of the respective original volume which caused precipitation each time, while the ratio of $Si(NCS)_6^{2-}$ over NCS^- increased. A total of 1.38 g filter residues were obtained, IR spectra of which feature

mainly KNCS. Evaporation of the final filter solution resulted in oily slush (nujol: 2257 (MeCN), 2099 (ν_{as}(NC)), 910 (ν(CS))cm^{-1}), which was dried until mass remained almost constant, resulting in 1.297 g of white powder that still contains MeCN.
IR (nujol, cm^{-1}): 2297vw (MeCN), 2263vw (MeCN), 2130vs (ν(CN)), 2093vw, sh, 907w (ν(CS)).
IR (MeCN, cm^{-1}): 2101, ν(CN).
IR (THF, cm^{-1}): 2105, ν(CN).

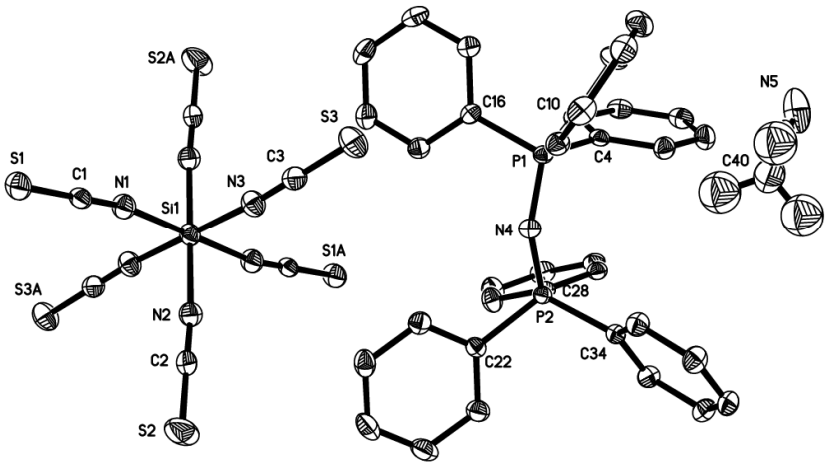
Preparation of **(PPN)$_2$[Si(NCS)$_4$]·2MeCN**, **2b·2MeCN**. A Schlenk tube was charged with **1b** (0.228 g) and (PPN)NCS (0.430 g, 0.721 mmol). MeCN (50 ml) was added at –20°C and the resulting suspension was rapidly stirred and allowed to warm to r.t., after which the suspension was left to settle. An IR spectrum of the colourless supernatant solution in the region of the NCS stretch showed the presence of only two bands at 2101 cm^{-1} (weak) and 2059 cm^{-1} (very strong) due to the presence of $[Si(NCS)_6]^{2-}$ and NCS^- ions, respectively. The solution, containing mainly (PPN)NCS and KNCS, was filtered off and discarded (0.290 g non-volatile content). The white filter residue was dried, resulting in a raw product (0.364 g) which was dissolved in MeCN (55 ml) at 50°C and filtered at this temperature, which afforded a clear solution. Cooling to –30°C caused the formation of crystals, which were filtered off in the cold and dried *in vacuo*. Recrystallisation was repeated using slightly less solvent, which afforded 0.294 g of colourless, sparkling crystals (0.191 mol, 53% with respect to (PPN)NCS), mp. 257 - 261°C. Anal. calcd. for $C_{82}H_{66}N_{10}P_4S_6Si$ (1535.87 g mol^{-1}): C, 64.13; H, 4.33; N, 9.12%. Found: C, 63.97; H, 4.22; N, 9.00 %. IR (nujol, cm^{-1}) ν = 3086, 3056, 2286 and 2249vw, MeCN, 2098vs, ν(CN), 1588, 1572, 1481, 1467, 1437, 1314, 1302, 1284, 1268, 1181, 1160, 1116, 1071, 1025, 998, 916, 797, 760, 745, 724, 691, 617, 549; THF: 2105; CH_2Cl_2: 2106; MeCN: 2101. DSC T_{on} = 83°C (MeCN loss), 256°C (melting). TGA T_{on} = 82 °C (MeCN loss, $\Delta m/m_0$ found 5.4%, calcd. 5.3% for loss of two equivalents of MeCN), 223 °C (dec.).

Si(NCO)$_4$(phen)·MeCN (**4**·MeCN). A Schlenk tube was charged with **1a** (0.200 g) and phen (0.100 g, 0.554 mmol). The tube was immersed in a cold bath (–40°C) and MeCN (ca. 35 ml) was added via cannula transfer. Upon rapid stirring a mixture of fully dissolved **1a** and crystalline phen resulted. The cold bath was removed and phen completely dissolved while the temperature of the reaction mixture approached ambient conditions. The resulting clear reaction solution turned cloudy within several minutes. Stirring was continued for 24 h after which the white suspension was allowed to settle. An IR spectrum of an evaporated sample of the reaction solution (nujol) showed the presence of **4** (2318 cm^{-1} m, 2260 cm^{-1} vs). The white precipitate (66 mg), consisting mainly of KNCO (IR: 2161 cm^{-1}), was filtered off and the filtrate diminished to ca. 3 ml causing crystallisation, which was completed at –28 °C for 2 h. The supernatant was filtered off and the remainder, 0.215 g, raw off-white **4**, recrystallised from a minimal volume of warm MeCN (ca. 50°C) at –28 °C over-

night, and washed in the cold (3.5 ml MeCN). The residue was dried in vacuo at the same temperature, which afforded fine, colourless and electrostatic sheets (0.151 g, 66% with respect to phen) mp 224 °C (DSC). Anal. calcd. for $C_{16}H_8N_6O_4Si$ (376.36 g mol^{-1}): C, 51.06; H, 2.14; N, 22.33%. Found C, 50.59; H, 2.35; N, 22.82%. IR (nujol, cm^{-1}) ν = 3645vw, 2334, 2329, 2279, 2261, 2242, 1456, 1436, 1413, 1318, 1229, 1208, 1151, 1114, 1114, 1062, 1042, 881, 853, 752, 7, 660, 615; THF: 2311m, 2255vs; CH_2Cl_2: 2315m, 2283w, sh, 2256vs. ^{1}H NMR (250 MHz, CD_3CN, ppm): *d* = 1.94 (s, C*H*$_3$), 8.25 (dd, 2H), 8.37 (s, 2H), 9.01 (dd, 2H), 9.70 (dd, 2H); ^3J(H2,H3) = 5.4, ^4J(H2,H4) = 1.3, ^3J(H3,H4) = 8.3 Hz; CD_2Cl_2 (400 MHz) *d* = 1.97 (s, C*H*$_3$), 8.21 (dd, 2H), 8.28 (s, 2H), 8.86 (dd, 2H), 9.70 (dd, 2H); ^3J(H2,H3) = 5.3, ^4J(H2,H4) = 1.3, ^3J(H3,H4) = 8.3 Hz; ^{13}C{^{1}H} (100 MHz, CD_2Cl_2) *d* = 126.8, 127.8, 129.5, 134.0, 141.4, 144.4 (resonances due to carbon in NCO could not be observed as a result of insufficient solubility). EI MS m/z = 196 (40) [M^+ – phen], 181 (27) [*phen*], 180 (100) [*phen*], 179 (37) [*phen*], 155 (14) [*phen*], 154 (73) [M^+ – phen – NCO], 153 (23) [*phen*], 152 (14) [*phen*], 127 (13) [*phen*], 112 (13) [M^+ – phen – 2NCO], 90 (29) [*phen*], 76 (20) [*phen*], 70 (56) [M^+ – phen – 3NCO], 63 (14) [*phen*].

3) Single crystal X-ray diffraction analyses of 1a, 2a,b and 4

Single crystals were grown from acetonitrile solution of pure **1a**, **2a**,**b** and **4** upon cooling saturated solutions in MeCN to –28°C. Diffraction data were collected on a Bruker Smart CCD area detector[28] with an Oxford Cryosystems low temperature unit and Mo-K_α radiation ($\bar{l}$ = 0.71073 Å). Crystallographic and experimental details are summarized in Table 3. All measured reflections were corrected for Lorentz and polarisation effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full matrix least squares methods on F^2. H atoms were placed geometrically and refined with a riding model and with U_{iso} constrained to be 1.2 times (1.5 for CH_3 groups) U_{eq} of the carrier atom. Complex scattering factors were taken from the program package SHELXTL as implemented on a Viglen Pentium computer.[29] The weighting schemes $w = 1/[s^2(F_o^2) + (a\cdot P)^2 + b\cdot P]$, $P = (F_o^2 + 2F_c^2)/3$, a = 0.0485, b = 3.0619 (**1a**), 0.0498, 1.1541 (**2a**), 0.0440, 0.7175 (**2b**), 0.0499, 0.0291 (**4**), were used in the later stages of refinement. Mean and max. δ / σ were 0.000 / 0.000 throughout. Plots were created with SHELX XP and are set at the 50% probability level. **2a** has a residual electron density peak of 1.317 e·Å^{-3} at a distance of 0.71 Å from O2. All structures were investigated for κ*N* / κ*O* NCO bond isomerism. Alternative solutions were invariably associated with an increase of R_1 and wR_2 values.



Structure of the asymmetric unit in a single crystal of **2a**·**2MeCN**, Ph hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: Si-N1 1.823(2), Si-N2 1.829(2), Si-N3 1.831(2), N1-C1 1.170(2), N2-C2 1.168(2), N3-C3 1.170(2), C1-S1 1.607(2), C2-S2 1.608(2), C3-S3 1.611(2), N1-Si-N2 90.41(6), N1-Si-N3 90.11(6), N2-Si-N3 90.06(7), P2-N4-P1 139.97(9), Si-N1-C1 168.20(14), Si-N2-C2 170.13(15), Si-N3-C3 175.12(15), N1-C1-S1 179.03(15), N2-C2-S2 178.44(17), N3-C3-S3 179.53(18).

Table 1 A selection of recently published structural data on related silicon complexes in relation to **1a**, **2a,b** and **4**.

Complex		Si-N [Å]	N-C [Å]	C-E [Å]	Si-N-C [°]	N-C-E [°]	Ref.
$[K(MeCN)_2]_2[Si(NCO)_6]$(**1a**)		1.81-1.84	1.14-1.16	1.19-1.20	171-173	178-179	a
$(PPN)_2[Si(NCO)_6]$ (**2a**)		1.83-1.86	1.16-1.17	1.19-1.20	155-162	177-178	a
$[K(crown)]_2[Si(NCO)_6)]\cdot 2MeCN$		1.82-1.83	1.15	1.18	157-165	177-179	b
$[Si(NCO)_4(phen)]$ (**4**)	eq.	1.78-1.79	1.15-1.17	1.18-1.20	178-179	178-179	a
	ax.	1.82-1.83	1.18-1.19	1.19	177-178	177-178	
$(PPN)_2[Si(NCS)_6]\cdot 2MeCN$ (**2b**)		1.82-1.83	1.17	1.61	168-175	178-180	a
$(NEt_4)_2[Si(NCS)_6]$		1.82-1.83	1.17	1.59-1.60	170-180	179-180	b
$[K(crown)]_2[Si(NCS)_6]\cdot 2MeCN$		1.82-1.84	1.16-1.17	1.59-1.61	159-171	177-180	b

a) this paper, b) Seiler, O.; Burschka, C.; Goetz, K.; Kaupp, M.; Metz, S.; Tacke, R., *Z. Anorg. Allg. Chem.* **2007,** 633, 2667-2670.

4a) Crystallographic information file for compound 1a (data_chppx55m)

```
data_chppx55m
_audit_creation_method            SHELXL-97
_chemical_name_systematic
;
 ?
;
_chemical_name_common             ?
_chemical_melting_point           ?
_chemical_formula_moiety          'C14 H12 K2 N10 O6 Si'
_chemical_formula_sum
 'C14 H12 K2 N10 O6 Si'
_chemical_formula_weight          522.63

loop_
 _atom_type_symbol
 _atom_type_description
 _atom_type_scat_dispersion_real
 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'C'  'C'   0.0033   0.0016
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Si'  'Si'   0.0817   0.0704
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'K'  'K'   0.2009   0.2494
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting            Monoclinic
_symmetry_space_group_name_H-M    P2(1)/n

loop_
 _symmetry_equiv_pos_as_xyz
 'x, y, z'
```

```
 '-x+1/2, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x-1/2, -y-1/2, z-1/2'
_cell_length_a                    8.427(3)
_cell_length_b                    12.522(4)
_cell_length_c                    11.404(4)
_cell_angle_alpha                 90.00
_cell_angle_beta                  102.948(4)
_cell_angle_gamma                 90.00
_cell_volume                      1172.8(7)
_cell_formula_units_Z             2
_cell_measurement_temperature     120(2)
_cell_measurement_reflns_used     2797
_cell_measurement_theta_min       3.399
_cell_measurement_theta_max       26.16
_exptl_crystal_description        block
_exptl_crystal_colour             colourless
_exptl_crystal_size_max           0.32
_exptl_crystal_size_mid           0.28
_exptl_crystal_size_min           0.27
_exptl_crystal_density_meas       ?
_exptl_crystal_density_diffrn     1.480
_exptl_crystal_density_method     'not measured'
_exptl_crystal_F_000              532
_exptl_absorpt_coefficient_mu     0.506
_exptl_absorpt_correction_type    multi-scan
_exptl_absorpt_correction_T_min   0.8547
_exptl_absorpt_correction_T_max   0.8754
_exptl_absorpt_process_details    sadabs
_exptl_special_details
;
 ?
;
_diffrn_ambient_temperature       120(2)
_diffrn_radiation_wavelength      0.71073
_diffrn_radiation_type            MoK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
_diffrn_measurement_device_type   'CCD area detector'
_diffrn_measurement_method        'omega scans'
_diffrn_detector_area_resol_mean  100
_diffrn_standards_number          0
_diffrn_standards_interval_count  ?
_diffrn_standards_interval_time   ?
_diffrn_standards_decay_%         0
_diffrn_reflns_number             6946
_diffrn_reflns_av_R_equivalents   0.0572
_diffrn_reflns_av_sigmaI/netI     0.0635
_diffrn_reflns_limit_h_min        -8
_diffrn_reflns_limit_h_max        10
_diffrn_reflns_limit_k_min        -15
_diffrn_reflns_limit_k_max        15
_diffrn_reflns_limit_l_min        -14
_diffrn_reflns_limit_l_max        14
_diffrn_reflns_theta_min          3.40
_diffrn_reflns_theta_max          26.80
_reflns_number_total              2291
_reflns_number_gt                 1713
_reflns_threshold_expression      >2sigma(I)
_computing_data_collection        'Bruker SMART'
_computing_cell_refinement        'Bruker SMART'
```

```
_computing_data_reduction         'Bruker SAINT'
_computing_structure_solution     'Bruker SHELXTL'
_computing_structure_refinement   'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics     'Bruker SHELXTL'
_computing_publication_material   'Bruker SHELXTL'
_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor
wR and
 goodness of fit S are based on F^2^, conventional R-factors R are
based
 on F, with F set to zero for negative F^2^. The threshold expression
of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc.
and is
 not relevant to the choice of reflections for refinement.  R-factors
based
 on F^2^ are statistically about twice as large as those based on F,
and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0485P)^2^+3.0619P] where
=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     constr
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          2291
_refine_ls_number_parameters      153
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.1018
_refine_ls_R_factor_gt            0.0729
_refine_ls_wR_factor_ref          0.1495
_refine_ls_wR_factor_gt           0.1395
_refine_ls_goodness_of_fit_ref    1.081
_refine_ls_restrained_S_all       1.081
_refine_ls_shift/su_max           0.000
_refine_ls_shift/su_mean          0.000
loop_
 _atom_site_label
 _atom_site_type_symbol
 _atom_site_fract_x
 _atom_site_fract_y
 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
K1 K 0.65538(11) 0.01626(7) 0.41452(8) 0.0218(3) Uani 1 1 d . . .
Si1 Si 1.0000 0.0000 1.0000 0.0170(4) Uani 1 2 d S . .
```

```
O2 O 0.6107(4) -0.0035(3) 0.1690(3) 0.0348(8) Uani 1 1 d . . .
O3 O 0.6907(4) -0.0203(3) 0.6603(3) 0.0441(10) Uani 1 1 d . . .
O1 O 0.5009(4) -0.1691(3) 0.4675(3) 0.0410(9) Uani 1 1 d . . .
N3 N 0.8683(4) 0.0002(3) 0.8483(3) 0.0270(9) Uani 1 1 d . . .
N1 N 0.5109(4) -0.3547(3) 0.4972(4) 0.0283(9) Uani 1 1 d . . .
C3 C 0.7817(5) -0.0103(4) 0.7569(4) 0.0229(10) Uani 1 1 d . . .
N2 N 0.8206(4) -0.0078(3) 0.0627(3) 0.0284(9) Uani 1 1 d . . .
N4 N 0.7924(5) 0.2063(3) 0.3542(4) 0.0404(11) Uani 1 1 d . . .
C1 C 0.5067(5) -0.2634(4) 0.4826(4) 0.0221(10) Uani 1 1 d . . .
C4 C 0.9183(5) 0.2361(4) 0.3510(4) 0.0272(10) Uani 1 1 d . . .
C2 C 0.7192(5) -0.0057(3) 0.1164(3) 0.0211(9) Uani 1 1 d . . .
N5 N 0.9119(6) -0.1133(4) 0.3927(4) 0.0584(15) Uani 1 1 d . . .
C6 C 0.9853(6) -0.1779(4) 0.3606(4) 0.0323(11) Uani 1 1 d . . .
C5 C 1.0815(5) 0.2743(4) 0.3495(5) 0.0364(12) Uani 1 1 d . . .
H5A H 1.1150 0.3280 0.4128 0.055 Uiso 1 1 calc R . .
H5B H 1.0811 0.3062 0.2710 0.055 Uiso 1 1 calc R . .
H5C H 1.1580 0.2142 0.3639 0.055 Uiso 1 1 calc R . .
C7 C 1.0806(5) -0.2607(4) 0.3219(4) 0.0373(12) Uani 1 1 d . . .
H12A H 1.1932 -0.2565 0.3686 0.056 Uiso 1 1 calc R . .
H12B H 1.0785 -0.2514 0.2363 0.056 Uiso 1 1 calc R . .
H12C H 1.0349 -0.3306 0.3345 0.056 Uiso 1 1 calc R . .

loop_
 _atom_site_aniso_label
 _atom_site_aniso_U_11
 _atom_site_aniso_U_22
 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
K1 0.0267(5) 0.0180(5) 0.0230(5) 0.0008(4) 0.0101(4) 0.0005(4)
Si1 0.0155(7) 0.0164(9) 0.0193(8) -0.0011(7) 0.0042(6) -0.0024(6)
O2 0.0251(15) 0.048(2) 0.0357(18) -0.0060(17) 0.0168(14) -0.0035(15)
O3 0.0302(17) 0.078(3) 0.0211(17) 0.0038(18) -0.0008(15) -0.0017(18)
O1 0.054(2) 0.019(2) 0.058(2) -0.0041(17) 0.030(2) -0.0060(16)
N3 0.0230(18) 0.034(2) 0.0220(19) 0.0022(18) 0.0000(15) -0.0013(16)
N1 0.032(2) 0.017(2) 0.036(2) 0.0002(18) 0.0069(16) 0.0019(16)
C3 0.019(2) 0.028(3) 0.024(2) 0.001(2) 0.0106(19) 0.0016(19)
N2 0.0235(18) 0.033(2) 0.030(2) 0.0027(18) 0.0097(16) -0.0027(17)
N4 0.028(2) 0.038(3) 0.050(3) 0.010(2) -0.0005(19) -0.0086(19)
C1 0.019(2) 0.026(3) 0.023(2) -0.006(2) 0.0097(17) -0.0032(18)
C4 0.027(2) 0.025(3) 0.026(2) 0.004(2) -0.0011(19) 0.001(2)
C2 0.023(2) 0.026(3) 0.0141(19) 0.0017(19) 0.0036(17) -0.0031(18)
N5 0.072(3) 0.064(4) 0.037(3) 0.000(3) 0.008(2) 0.040(3)
C6 0.030(2) 0.044(3) 0.022(2) 0.002(2) 0.003(2) 0.004(2)
C5 0.027(2) 0.038(3) 0.046(3) 0.004(2) 0.011(2) -0.002(2)
C7 0.024(2) 0.048(3) 0.038(3) -0.013(3) 0.004(2) 0.003(2)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s.
planes)
 are estimated using the full covariance matrix.  The cell esds are
taken
 into account individually in the estimation of esds in distances,
angles
 and torsion angles; correlations between esds in cell parameters are
only
 used when they are defined by crystal symmetry.  An approximate
(isotropic)
 treatment of cell esds is used for estimating esds involving l.s.
```

```
planes.
;

loop_
 _geom_bond_atom_site_label_1
 _geom_bond_atom_site_label_2
 _geom_bond_distance
 _geom_bond_site_symmetry_2
 _geom_bond_publ_flag
K1 O2 2.752(3) . ?
K1 N5 2.758(5) . ?
K1 O3 2.789(3) . ?
K1 O1 2.793(3) . ?
K1 N4 2.798(4) . ?
K1 O1 2.829(3) 3_656 ?
K1 O3 2.850(3) 3_656 ?
Si1 N2 1.814(3) 1_556 ?
Si1 N2 1.814(3) 3_756 ?
Si1 N1 1.822(4) 4_656 ?
Si1 N1 1.822(4) 2_656 ?
Si1 N3 1.834(4) 3_757 ?
Si1 N3 1.834(4) . ?
O2 C2 1.201(5) . ?
O3 C3 1.200(5) . ?
O3 K1 2.850(3) 3_656 ?
O1 C1 1.192(6) . ?
O1 K1 2.829(3) 3_656 ?
N3 C3 1.139(5) . ?
N1 C1 1.155(6) . ?
N1 Si1 1.822(4) 2_646 ?
N2 C2 1.157(5) . ?
N2 Si1 1.814(3) 1_554 ?
N4 C4 1.133(6) . ?
C4 C5 1.460(6) . ?
N5 C6 1.128(6) . ?
C6 C7 1.440(7) . ?
C5 H5A 0.9800 . ?
C5 H5B 0.9800 . ?
C5 H5C 0.9800 . ?
C7 H12A 0.9800 . ?
C7 H12B 0.9800 . ?
C7 H12C 0.9800 . ?

loop_
 _geom_angle_atom_site_label_1
 _geom_angle_atom_site_label_2
 _geom_angle_atom_site_label_3
 _geom_angle
 _geom_angle_site_symmetry_1
 _geom_angle_site_symmetry_3
 _geom_angle_publ_flag
O2 K1 N5 77.67(12) . . ?
O2 K1 O3 165.30(11) . . ?
N5 K1 O3 94.85(12) . . ?
O2 K1 O1 100.46(10) . . ?
N5 K1 O1 86.74(15) . . ?
O3 K1 O1 66.17(11) . . ?
O2 K1 N4 78.23(12) . . ?
N5 K1 N4 95.93(16) . . ?
O3 K1 N4 115.46(12) . . ?
O1 K1 N4 176.66(12) . . ?
```

```
O2 K1 O1 124.93(11) . 3_656 ?
N5 K1 O1 154.00(13) . 3_656 ?
O3 K1 O1 65.78(11) . 3_656 ?
O1 K1 O1 99.81(10) . 3_656 ?
N4 K1 O1 78.64(12) . 3_656 ?
O2 K1 O3 78.45(9) . 3_656 ?
N5 K1 O3 138.91(15) . 3_656 ?
O3 K1 O3 100.10(8) . 3_656 ?
O1 K1 O3 65.44(11) . 3_656 ?
N4 K1 O3 111.23(12) . 3_656 ?
O1 K1 O3 64.90(11) 3_656 3_656 ?
O2 K1 K1 125.97(8) . 3_656 ?
N5 K1 K1 131.17(12) . 3_656 ?
O3 K1 K1 50.79(7) . 3_656 ?
O1 K1 K1 50.34(7) . 3_656 ?
N4 K1 K1 128.04(10) . 3_656 ?
O1 K1 K1 49.47(7) 3_656 3_656 ?
O3 K1 K1 49.31(7) 3_656 3_656 ?
N2 Si1 N2 180.000(1) 1_556 3_756 ?
N2 Si1 N1 90.18(17) 1_556 4_656 ?
N2 Si1 N1 89.82(17) 3_756 4_656 ?
N2 Si1 N1 89.82(17) 1_556 2_656 ?
N2 Si1 N1 90.18(17) 3_756 2_656 ?
N1 Si1 N1 180.0(3) 4_656 2_656 ?
N2 Si1 N3 90.56(16) 1_556 3_757 ?
N2 Si1 N3 89.44(16) 3_756 3_757 ?
N1 Si1 N3 89.60(17) 4_656 3_757 ?
N1 Si1 N3 90.40(17) 2_656 3_757 ?
N2 Si1 N3 89.44(16) 1_556 . ?
N2 Si1 N3 90.56(16) 3_756 . ?
N1 Si1 N3 90.40(17) 4_656 . ?
N1 Si1 N3 89.60(17) 2_656 . ?
N3 Si1 N3 180.000(1) 3_757 . ?
C2 O2 K1 124.4(3) . . ?
C3 O3 K1 143.9(3) . . ?
C3 O3 K1 132.3(3) . 3_656 ?
K1 O3 K1 79.90(8) . 3_656 ?
C1 O1 K1 148.0(3) . . ?
C1 O1 K1 127.6(3) . 3_656 ?
K1 O1 K1 80.19(10) . 3_656 ?
C3 N3 Si1 172.7(4) . . ?
C1 N1 Si1 172.3(4) . 2_646 ?
N3 C3 O3 179.3(5) . . ?
C2 N2 Si1 170.5(4) . 1_554 ?
C4 N4 K1 136.8(4) . . ?
N1 C1 O1 179.4(4) . . ?
N4 C4 C5 178.8(5) . . ?
N2 C2 O2 178.1(4) . . ?
C6 N5 K1 161.6(5) . . ?
N5 C6 C7 178.9(5) . . ?
C4 C5 H5A 109.5 . . ?
C4 C5 H5B 109.5 . . ?
H5A C5 H5B 109.5 . . ?
C4 C5 H5C 109.5 . . ?
H5A C5 H5C 109.5 . . ?
H5B C5 H5C 109.5 . . ?
C6 C7 H12A 109.5 . . ?
C6 C7 H12B 109.5 . . ?
H12A C7 H12B 109.5 . . ?
C6 C7 H12C 109.5 . . ?
H12A C7 H12C 109.5 . . ?
```

```
H12B C7 H12C 109.5 . . ?

_diffrn_measured_fraction_theta_max    0.913
_diffrn_reflns_theta_full              25.00
_diffrn_measured_fraction_theta_full   0.996
_refine_diff_density_max    0.542
_refine_diff_density_min   -0.467
_refine_diff_density_rms    0.090
```

4b) Crystallographic information file for compound 2a (data_chppx69_0m)

```
data_ch1ppx69_0m
_audit_creation_method            SHELXL-97
_chemical_name_systematic
;
 ?
;
_chemical_name_common             ?
_chemical_melting_point           ?
_chemical_formula_moiety          '2(C36 H30 N P2), C6 N6 O6 Si1'
_chemical_formula_sum
 'C78 H60 N8 O6 P4 Si'
_chemical_formula_weight          1357.31

loop_
 _atom_type_symbol
 _atom_type_description
 _atom_type_scat_dispersion_real
 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
 'C'  'C'   0.0033   0.0016
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Si'  'Si'   0.0817   0.0704
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'P'  'P'   0.1023   0.0942
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting            Triclinic
_symmetry_space_group_name_H-M    P-1

loop_
 _symmetry_equiv_pos_as_xyz
 'x, y, z'
 '-x, -y, -z'

_cell_length_a                    11.6037(5)
_cell_length_b                    12.9974(5)
_cell_length_c                    13.4729(6)
_cell_angle_alpha                 63.885(2)
_cell_angle_beta                  70.577(2)
_cell_angle_gamma                 75.503(2)
_cell_volume                      1707.67(12)
_cell_formula_units_Z             1
_cell_measurement_temperature     120(2)
```

```
_cell_measurement_reflns_used     9886
_cell_measurement_theta_min       2.19
_cell_measurement_theta_max       27.20
_exptl_crystal_description        block
_exptl_crystal_colour             colourless
_exptl_crystal_size_max           0.29
_exptl_crystal_size_mid           0.23
_exptl_crystal_size_min           0.22
_exptl_crystal_density_meas       ?
_exptl_crystal_density_diffrn     1.320
_exptl_crystal_density_method     'not measured'
_exptl_crystal_F_000              706
_exptl_absorpt_coefficient_mu     0.190
_exptl_absorpt_correction_type    multi-scan
_exptl_absorpt_correction_T_min   0.9471
_exptl_absorpt_correction_T_max   0.9595
_exptl_absorpt_process_details    sadabs

_exptl_special_details
;
 ?
;

_diffrn_ambient_temperature       120(2)
_diffrn_radiation_wavelength      0.71073
_diffrn_radiation_type            MoK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
_diffrn_measurement_device_type   'CCD area detector'
_diffrn_measurement_method        'omega scans'
_diffrn_detector_area_resol_mean  100
_diffrn_standards_number          0
_diffrn_standards_interval_count  ?
_diffrn_standards_interval_time   ?
_diffrn_standards_decay_%         0
_diffrn_reflns_number             34308
_diffrn_reflns_av_R_equivalents   0.0296
_diffrn_reflns_av_sigmaI/netI     0.0282
_diffrn_reflns_limit_h_min        -15
_diffrn_reflns_limit_h_max        15
_diffrn_reflns_limit_k_min        -16
_diffrn_reflns_limit_k_max        16
_diffrn_reflns_limit_l_min        -17
_diffrn_reflns_limit_l_max        17
_diffrn_reflns_theta_min          1.74
_diffrn_reflns_theta_max          27.50
_reflns_number_total              7811
_reflns_number_gt                 6570
_reflns_threshold_expression      >2sigma(I)
_computing_data_collection        'Bruker SMART'
_computing_cell_refinement        'Bruker SMART'
_computing_data_reduction         'Bruker SAINT'
_computing_structure_solution     'Bruker SHELXTL'
_computing_structure_refinement   'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics     'Bruker SHELXTL'
_computing_publication_material   'Bruker SHELXTL'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor
wR and
```

```
 goodness of fit S are based on F^2^, conventional R-factors R are
based
 on F, with F set to zero for negative F^2^. The threshold expression
of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc.
and is
 not relevant to the choice of reflections for refinement.  R-factors
based
 on F^2^ are statistically about twice as large as those based on F,
and R-
 factors based on ALL data will be even larger. The residual electron
density
 (1.317) was found to be 0.71 Angstroms from O2. DFIX Restraints were
applied
 to atoms N2 C2 and C2 O2 and refinement converged successfully.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0498P)^2^+1.1541P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     constr
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          7811
_refine_ls_number_parameters      440
_refine_ls_number_restraints      2
_refine_ls_R_factor_all           0.0520
_refine_ls_R_factor_gt            0.0423
_refine_ls_wR_factor_ref          0.1118
_refine_ls_wR_factor_gt           0.1046
_refine_ls_goodness_of_fit_ref    1.030
_refine_ls_restrained_S_all       1.030
_refine_ls_shift/su_max           0.000
_refine_ls_shift/su_mean          0.000

loop_
 _atom_site_label
 _atom_site_type_symbol
 _atom_site_fract_x
 _atom_site_fract_y
 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
Si1 Si 0.0000 1.0000 0.0000 0.02593(16) Uani 1 2 d S . .
P1 P 0.19131(4) 0.30352(3) 0.26845(4) 0.01753(10) Uani 1 1 d . . .
P2 P 0.36555(4) 0.40965(3) 0.30098(3) 0.01587(10) Uani 1 1 d . . .
N1 N 0.04729(15) 0.84553(14) 0.07263(15) 0.0327(4) Uani 1 1 d . . .
N2 N -0.02516(15) 1.02014(14) 0.13406(10) 0.0345(4) Uani 1 1 d D . .
N3 N 0.16025(14) 1.02722(15) -0.04307(16) 0.0351(4) Uani 1 1 d . . .
```

```
N4 N 0.24460(12) 0.39925(12) 0.27821(12) 0.0198(3) Uani 1 1 d . . .
O1 O 0.04718(15) 0.64924(12) 0.19769(14) 0.0452(4) Uani 1 1 d . . .
O2 O -0.0564(2) 0.96685(19) 0.33178(10) 0.0811(7) Uani 1 1 d D . .
O3 O 0.33921(13) 1.06520(13) -0.02469(15) 0.0443(4) Uani 1 1 d . . .
C1 C 0.04622(16) 0.74906(16) 0.13546(17) 0.0276(4) Uani 1 1 d . . .
C2 C -0.0428(2) 0.99279(17) 0.23222(10) 0.0389(5) Uani 1 1 d D . .
C3 C 0.24770(16) 1.04556(15) -0.03170(16) 0.0280(4) Uani 1 1 d . . .
C4 C 0.17353(15) 0.35139(14) 0.12660(14) 0.0205(3) Uani 1 1 d . . .
C5 C 0.19124(15) 0.46389(15) 0.04856(14) 0.0234(3) Uani 1 1 d . . .
H5 H 0.2166 0.5145 0.0688 0.028 Uiso 1 1 calc R . .
C6 C 0.17154(16) 0.50194(17) -0.05949(15) 0.0290(4) Uani 1 1 d . . .
H6 H 0.1833 0.5787 -0.1129 0.035 Uiso 1 1 calc R . .
C7 C 0.13483(17) 0.42783(18) -0.08911(17) 0.0329(4) Uani 1 1 d . . .
H7 H 0.1223 0.4538 -0.1630 0.040 Uiso 1 1 calc R . .
C8 C 0.11635(18) 0.31594(18) -0.01121(18) 0.0344(4) Uani 1 1 d . . .
H8 H 0.0909 0.2657 -0.0319 0.041 Uiso 1 1 calc R . .
C9 C 0.13492(17) 0.27725(16) 0.09653(17) 0.0293(4) Uani 1 1 d . . .
H9 H 0.1216 0.2008 0.1500 0.035 Uiso 1 1 calc R . .
C10 C 0.03900(15) 0.28493(14) 0.36265(14) 0.0217(3) Uani 1 1 d . . .
C11 C -0.01050(17) 0.18216(16) 0.40452(18) 0.0325(4) Uani 1 1 d . . .
H11 H 0.0383 0.1181 0.3885 0.039 Uiso 1 1 calc R . .
C12 C -0.13183(18) 0.17362(19) 0.4700(2) 0.0415(5) Uani 1 1 d . . .
H12 H -0.1656 0.1034 0.4994 0.050 Uiso 1 1 calc R . .
C13 C -0.20308(17) 0.26736(19) 0.49228(18) 0.0379(5) Uani 1 1 d . . .
H13 H -0.2858 0.2612 0.5371 0.045 Uiso 1 1 calc R . .
C14 C -0.15474(17) 0.37023(18) 0.44972(17) 0.0349(4) Uani 1 1 d . . .
H14 H -0.2047 0.4345 0.4648 0.042 Uiso 1 1 calc R . .
C15 C -0.03356(16) 0.37989(16) 0.38510(15) 0.0270(4) Uani 1 1 d . . .
H15 H -0.0002 0.4503 0.3564 0.032 Uiso 1 1 calc R . .
C16 C 0.28510(14) 0.16518(13) 0.30269(14) 0.0197(3) Uani 1 1 d . . .
C21 C 0.36531(17) 0.12816(16) 0.21757(16) 0.0276(4) Uani 1 1 d . . .
H21 H 0.3617 0.1699 0.1402 0.033 Uiso 1 1 calc R . .
C20 C 0.45023(18) 0.03011(17) 0.24656(19) 0.0351(4) Uani 1 1 d . . .
H20 H 0.5038 0.0044 0.1891 0.042 Uiso 1 1 calc R . .
C19 C 0.45672(18) -0.02997(16) 0.35905(19) 0.0354(5) Uani 1 1 d . . .
H19 H 0.5161 -0.0958 0.3782 0.042 Uiso 1 1 calc R . .
C18 C 0.37686(18) 0.00552(16) 0.44393(18) 0.0313(4) Uani 1 1 d . . .
H18 H 0.3814 -0.0364 0.5210 0.038 Uiso 1 1 calc R . .
C17 C 0.29037(16) 0.10209(14) 0.41650(15) 0.0240(4) Uani 1 1 d . . .
H17 H 0.2348 0.1253 0.4750 0.029 Uiso 1 1 calc R . .
C22 C 0.35121(15) 0.36343(13) 0.45169(13) 0.0185(3) Uani 1 1 d . . .
C23 C 0.24970(16) 0.30930(15) 0.53244(15) 0.0242(4) Uani 1 1 d . . .
H23 H 0.1875 0.2985 0.5078 0.029 Uiso 1 1 calc R . .
C24 C 0.23941(18) 0.27119(17) 0.64867(15) 0.0305(4) Uani 1 1 d . . .
H24 H 0.1709 0.2333 0.7032 0.037 Uiso 1 1 calc R . .
C25 C 0.32889(18) 0.28836(16) 0.68517(15) 0.0295(4) Uani 1 1 d . . .
H25 H 0.3217 0.2619 0.7646 0.035 Uiso 1 1 calc R . .
C26 C 0.42918(17) 0.34424(15) 0.60584(15) 0.0252(4) Uani 1 1 d . . .
H26 H 0.4898 0.3567 0.6312 0.030 Uiso 1 1 calc R . .
C27 C 0.44061(15) 0.38184(14) 0.48945(14) 0.0209(3) Uani 1 1 d . . .
H27 H 0.5090 0.4201 0.4353 0.025 Uiso 1 1 calc R . .
C28 C 0.39065(15) 0.55890(13) 0.23677(13) 0.0179(3) Uani 1 1 d . . .
C29 C 0.29125(15) 0.64149(15) 0.25535(15) 0.0228(3) Uani 1 1 d . . .
H29 H 0.2125 0.6183 0.3006 0.027 Uiso 1 1 calc R . .
C30 C 0.30849(17) 0.75740(15) 0.20721(16) 0.0276(4) Uani 1 1 d . . .
H30 H 0.2412 0.8134 0.2196 0.033 Uiso 1 1 calc R . .
C31 C 0.42378(17) 0.79198(15) 0.14097(15) 0.0269(4) Uani 1 1 d . . .
H31 H 0.4349 0.8713 0.1079 0.032 Uiso 1 1 calc R . .
C32 C 0.52237(16) 0.71020(15) 0.12336(14) 0.0239(4) Uani 1 1 d . . .
H32 H 0.6011 0.7337 0.0785 0.029 Uiso 1 1 calc R . .
C33 C 0.50633(15) 0.59379(14) 0.17120(14) 0.0208(3) Uani 1 1 d . . .
```

```
H33 H 0.5741 0.5381 0.1592 0.025 Uiso 1 1 calc R . .
C34 C 0.50304(14) 0.33274(13) 0.24089(14) 0.0182(3) Uani 1 1 d . . .
C35 C 0.52368(15) 0.35012(15) 0.12614(14) 0.0218(3) Uani 1 1 d . . .
H35 H 0.4661 0.4003 0.0840 0.026 Uiso 1 1 calc R . .
C36 C 0.62811(16) 0.29419(15) 0.07406(15) 0.0251(4) Uani 1 1 d . . .
H36 H 0.6418 0.3062 -0.0036 0.030 Uiso 1 1 calc R . .
C37 C 0.71231(17) 0.22086(16) 0.13533(16) 0.0293(4) Uani 1 1 d . . .
H37 H 0.7834 0.1824 0.0997 0.035 Uiso 1 1 calc R . .
C38 C 0.69292(18) 0.20358(16) 0.24856(16) 0.0321(4) Uani 1 1 d . . .
H38 H 0.7512 0.1537 0.2901 0.039 Uiso 1 1 calc R . .
C39 C 0.58810(16) 0.25918(15) 0.30190(15) 0.0255(4) Uani 1 1 d . . .
H39 H 0.5749 0.2468 0.3796 0.031 Uiso 1 1 calc R . .

loop_
 _atom_site_aniso_label
 _atom_site_aniso_U_11
 _atom_site_aniso_U_22
 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
Si1 0.0187(3) 0.0229(3) 0.0350(4) -0.0122(3) -0.0049(3) -0.0014(3)
P1 0.01709(19) 0.0169(2) 0.0200(2) -0.00753(16) -0.00591(16) -
0.00220(15)
P2 0.01621(19) 0.0162(2) 0.0161(2) -0.00680(16) -0.00464(15) -
0.00189(15)
N1 0.0316(8) 0.0236(8) 0.0407(9) -0.0117(7) -0.0105(7) 0.0003(6)
N2 0.0333(9) 0.0345(9) 0.0363(10) -0.0172(8) -0.0079(7) -0.0004(7)
N3 0.0221(8) 0.0343(9) 0.0475(10) -0.0164(8) -0.0054(7) -0.0049(7)
N4 0.0201(7) 0.0182(7) 0.0240(7) -0.0091(6) -0.0087(6) -0.0012(5)
O1 0.0489(9) 0.0281(8) 0.0554(10) -0.0017(7) -0.0292(8) -0.0055(7)
O2 0.141(2) 0.0795(14) 0.0251(9) -0.0245(9) -0.0035(10) -0.0342(14)
O3 0.0306(8) 0.0329(8) 0.0692(11) -0.0125(8) -0.0190(7) -0.0090(6)
C1 0.0216(8) 0.0315(10) 0.0351(10) -0.0165(9) -0.0115(7) 0.0002(7)
C2 0.0405(11) 0.0329(11) 0.0477(13) -0.0170(10) -0.0203(10) 0.0028(9)
C3 0.0243(9) 0.0179(8) 0.0335(10) -0.0052(7) -0.0044(7) -0.0023(7)
C4 0.0187(8) 0.0233(8) 0.0220(8) -0.0107(7) -0.0076(6) 0.0000(6)
C5 0.0192(8) 0.0276(9) 0.0234(8) -0.0105(7) -0.0050(6) -0.0025(7)
C6 0.0231(9) 0.0338(10) 0.0231(9) -0.0073(8) -0.0050(7) -0.0001(7)
C7 0.0281(9) 0.0466(12) 0.0273(10) -0.0183(9) -0.0140(8) 0.0066(8)
C8 0.0350(10) 0.0400(11) 0.0428(11) -0.0254(10) -0.0221(9) 0.0052(8)
C9 0.0321(10) 0.0268(9) 0.0354(10) -0.0132(8) -0.0170(8) -0.0014(7)
C10 0.0187(8) 0.0229(8) 0.0228(8) -0.0077(7) -0.0055(6) -0.0033(6)
C11 0.0225(9) 0.0261(9) 0.0472(12) -0.0133(9) -0.0060(8) -0.0060(7)
C12 0.0261(10) 0.0355(11) 0.0559(14) -0.0106(10) -0.0052(9) -
0.0130(8)
C13 0.0199(9) 0.0484(12) 0.0387(11) -0.0141(10) -0.0015(8) -0.0066(8)
C14 0.0255(9) 0.0395(11) 0.0365(11) -0.0186(9) -0.0024(8) 0.0012(8)
C15 0.0265(9) 0.0260(9) 0.0268(9) -0.0105(8) -0.0049(7) -0.0028(7)
C16 0.0180(7) 0.0159(7) 0.0264(8) -0.0079(7) -0.0075(6) -0.0024(6)
C21 0.0281(9) 0.0256(9) 0.0301(9) -0.0132(8) -0.0063(7) -0.0019(7)
C20 0.0284(9) 0.0301(10) 0.0483(12) -0.0230(9) -0.0051(9) 0.0021(8)
C19 0.0282(9) 0.0210(9) 0.0538(13) -0.0121(9) -0.0147(9) 0.0035(7)
C18 0.0325(10) 0.0199(9) 0.0374(11) -0.0027(8) -0.0152(8) -0.0043(7)
C17 0.0244(8) 0.0202(8) 0.0269(9) -0.0068(7) -0.0072(7) -0.0053(7)
C22 0.0219(8) 0.0169(7) 0.0163(7) -0.0070(6) -0.0052(6) -0.0004(6)
C23 0.0232(8) 0.0277(9) 0.0232(9) -0.0115(7) -0.0037(7) -0.0056(7)
C24 0.0315(9) 0.0361(10) 0.0203(9) -0.0102(8) 0.0016(7) -0.0110(8)
C25 0.0396(10) 0.0307(10) 0.0181(8) -0.0099(7) -0.0072(7) -0.0037(8)
C26 0.0311(9) 0.0255(9) 0.0239(9) -0.0118(7) -0.0115(7) -0.0020(7)
C27 0.0228(8) 0.0194(8) 0.0204(8) -0.0077(7) -0.0048(6) -0.0037(6)
```

```
C28 0.0214(8) 0.0177(7) 0.0173(7) -0.0066(6) -0.0077(6) -0.0039(6)
C29 0.0212(8) 0.0233(8) 0.0253(9) -0.0105(7) -0.0070(7) -0.0018(6)
C30 0.0305(9) 0.0201(8) 0.0349(10) -0.0118(8) -0.0138(8) 0.0019(7)
C31 0.0391(10) 0.0176(8) 0.0272(9) -0.0049(7) -0.0159(8) -0.0063(7)
C32 0.0277(9) 0.0271(9) 0.0196(8) -0.0064(7) -0.0080(7) -0.0105(7)
C33 0.0213(8) 0.0234(8) 0.0193(8) -0.0084(7) -0.0064(6) -0.0036(6)
C34 0.0185(7) 0.0167(7) 0.0198(8) -0.0082(6) -0.0039(6) -0.0024(6)
C35 0.0221(8) 0.0242(8) 0.0207(8) -0.0093(7) -0.0065(6) -0.0033(6)
C36 0.0278(9) 0.0293(9) 0.0213(8) -0.0142(7) -0.0026(7) -0.0055(7)
C37 0.0266(9) 0.0270(9) 0.0294(9) -0.0140(8) -0.0014(7) 0.0027(7)
C38 0.0298(9) 0.0288(10) 0.0280(10) -0.0087(8) -0.0089(8) 0.0100(8)
C39 0.0275(9) 0.0249(9) 0.0194(8) -0.0076(7) -0.0056(7) 0.0021(7)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s.
planes)
 are estimated using the full covariance matrix.  The cell esds are
taken
 into account individually in the estimation of esds in distances,
angles
 and torsion angles; correlations between esds in cell parameters are
only
 used when they are defined by crystal symmetry.  An approximate
(isotropic)
 treatment of cell esds is used for estimating esds involving l.s.
planes.
;

loop_
 _geom_bond_atom_site_label_1
 _geom_bond_atom_site_label_2
 _geom_bond_distance
 _geom_bond_site_symmetry_2
 _geom_bond_publ_flag
Si1 N3 1.8305(16) . ?
Si1 N3 1.8305(16) 2_575 ?
Si1 N1 1.8345(16) . ?
Si1 N1 1.8345(16) 2_575 ?
Si1 N2 1.8556(12) 2_575 ?
Si1 N2 1.8556(12) . ?
P1 N4 1.5910(14) . ?
P1 C4 1.7982(17) . ?
P1 C10 1.8013(17) . ?
P1 C16 1.8040(16) . ?
P2 N4 1.5811(14) . ?
P2 C28 1.7984(16) . ?
P2 C34 1.8042(16) . ?
P2 C22 1.8064(16) . ?
N1 C1 1.164(2) . ?
N2 C2 1.1661(17) . ?
N3 C3 1.169(2) . ?
O1 C1 1.195(2) . ?
O2 C2 1.1940(18) . ?
O3 C3 1.194(2) . ?
C4 C5 1.392(2) . ?
C4 C9 1.405(2) . ?
C5 C6 1.395(2) . ?
C5 H5 0.9500 . ?
C6 C7 1.388(3) . ?
C6 H6 0.9500 . ?
```

```
C7 C8 1.388(3) . ?
C7 H7 0.9500 . ?
C8 C9 1.385(3) . ?
C8 H8 0.9500 . ?
C9 H9 0.9500 . ?
C10 C11 1.392(2) . ?
C10 C15 1.401(2) . ?
C11 C12 1.392(3) . ?
C11 H11 0.9500 . ?
C12 C13 1.382(3) . ?
C12 H12 0.9500 . ?
C13 C14 1.385(3) . ?
C13 H13 0.9500 . ?
C14 C15 1.389(3) . ?
C14 H14 0.9500 . ?
C15 H15 0.9500 . ?
C16 C17 1.399(2) . ?
C16 C21 1.402(2) . ?
C21 C20 1.392(3) . ?
C21 H21 0.9500 . ?
C20 C19 1.385(3) . ?
C20 H20 0.9500 . ?
C19 C18 1.387(3) . ?
C19 H19 0.9500 . ?
C18 C17 1.388(2) . ?
C18 H18 0.9500 . ?
C17 H17 0.9500 . ?
C22 C23 1.398(2) . ?
C22 C27 1.405(2) . ?
C23 C24 1.391(2) . ?
C23 H23 0.9500 . ?
C24 C25 1.386(3) . ?
C24 H24 0.9500 . ?
C25 C26 1.392(3) . ?
C25 H25 0.9500 . ?
C26 C27 1.391(2) . ?
C26 H26 0.9500 . ?
C27 H27 0.9500 . ?
C28 C33 1.397(2) . ?
C28 C29 1.404(2) . ?
C29 C30 1.391(2) . ?
C29 H29 0.9500 . ?
C30 C31 1.394(3) . ?
C30 H30 0.9500 . ?
C31 C32 1.388(3) . ?
C31 H31 0.9500 . ?
C32 C33 1.394(2) . ?
C32 H32 0.9500 . ?
C33 H33 0.9500 . ?
C34 C39 1.392(2) . ?
C34 C35 1.404(2) . ?
C35 C36 1.390(2) . ?
C35 H35 0.9500 . ?
C36 C37 1.386(3) . ?
C36 H36 0.9500 . ?
C37 C38 1.387(3) . ?
C37 H37 0.9500 . ?
C38 C39 1.398(2) . ?
C38 H38 0.9500 . ?
C39 H39 0.9500 . ?
```

```
loop_
 _geom_angle_atom_site_label_1
 _geom_angle_atom_site_label_2
 _geom_angle_atom_site_label_3
 _geom_angle
 _geom_angle_site_symmetry_1
 _geom_angle_site_symmetry_3
 _geom_angle_publ_flag
N3 Si1 N3 180.000(1) . 2_575 ?
N3 Si1 N1 89.65(7) . . ?
N3 Si1 N1 90.35(7) 2_575 . ?
N3 Si1 N1 90.35(7) . 2_575 ?
N3 Si1 N1 89.65(7) 2_575 2_575 ?
N1 Si1 N1 180.0 . 2_575 ?
N3 Si1 N2 89.75(8) . 2_575 ?
N3 Si1 N2 90.25(8) 2_575 2_575 ?
N1 Si1 N2 90.26(7) . 2_575 ?
N1 Si1 N2 89.74(7) 2_575 2_575 ?
N3 Si1 N2 90.25(8) . . ?
N3 Si1 N2 89.75(8) 2_575 . ?
N1 Si1 N2 89.74(7) . . ?
N1 Si1 N2 90.26(7) 2_575 . ?
N2 Si1 N2 180.00(10) 2_575 . ?
N4 P1 C4 110.15(8) . . ?
N4 P1 C10 109.35(8) . . ?
C4 P1 C10 105.89(8) . . ?
N4 P1 C16 113.67(7) . . ?
C4 P1 C16 108.83(8) . . ?
C10 P1 C16 108.65(8) . . ?
N4 P2 C28 109.16(7) . . ?
N4 P2 C34 114.00(7) . . ?
C28 P2 C34 106.48(7) . . ?
N4 P2 C22 111.82(8) . . ?
C28 P2 C22 105.86(7) . . ?
C34 P2 C22 109.06(7) . . ?
C1 N1 Si1 162.35(16) . . ?
C2 N2 Si1 156.63(17) . . ?
C3 N3 Si1 155.37(17) . . ?
P2 N4 P1 136.83(9) . . ?
N1 C1 O1 178.3(2) . . ?
N2 C2 O2 177.1(3) . . ?
N3 C3 O3 177.3(2) . . ?
C5 C4 C9 119.87(16) . . ?
C5 C4 P1 120.13(12) . . ?
C9 C4 P1 119.90(13) . . ?
C4 C5 C6 119.72(16) . . ?
C4 C5 H5 120.1 . . ?
C6 C5 H5 120.1 . . ?
C7 C6 C5 120.11(18) . . ?
C7 C6 H6 119.9 . . ?
C5 C6 H6 119.9 . . ?
C6 C7 C8 120.26(17) . . ?
C6 C7 H7 119.9 . . ?
C8 C7 H7 119.9 . . ?
C9 C8 C7 120.23(18) . . ?
C9 C8 H8 119.9 . . ?
C7 C8 H8 119.9 . . ?
C8 C9 C4 119.81(18) . . ?
C8 C9 H9 120.1 . . ?
C4 C9 H9 120.1 . . ?
C11 C10 C15 120.08(16) . . ?
```

```
C11 C10 P1 121.21(13) . . ?
C15 C10 P1 118.47(13) . . ?
C10 C11 C12 119.77(18) . . ?
C10 C11 H11 120.1 . . ?
C12 C11 H11 120.1 . . ?
C13 C12 C11 120.00(19) . . ?
C13 C12 H12 120.0 . . ?
C11 C12 H12 120.0 . . ?
C12 C13 C14 120.46(18) . . ?
C12 C13 H13 119.8 . . ?
C14 C13 H13 119.8 . . ?
C13 C14 C15 120.27(18) . . ?
C13 C14 H14 119.9 . . ?
C15 C14 H14 119.9 . . ?
C14 C15 C10 119.41(17) . . ?
C14 C15 H15 120.3 . . ?
C10 C15 H15 120.3 . . ?
C17 C16 C21 119.48(15) . . ?
C17 C16 P1 117.91(12) . . ?
C21 C16 P1 121.92(13) . . ?
C20 C21 C16 119.91(18) . . ?
C20 C21 H21 120.0 . . ?
C16 C21 H21 120.0 . . ?
C19 C20 C21 120.11(18) . . ?
C19 C20 H20 119.9 . . ?
C21 C20 H20 119.9 . . ?
C20 C19 C18 120.30(17) . . ?
C20 C19 H19 119.8 . . ?
C18 C19 H19 119.8 . . ?
C17 C18 C19 120.19(18) . . ?
C17 C18 H18 119.9 . . ?
C19 C18 H18 119.9 . . ?
C18 C17 C16 119.99(17) . . ?
C18 C17 H17 120.0 . . ?
C16 C17 H17 120.0 . . ?
C23 C22 C27 119.15(15) . . ?
C23 C22 P2 119.98(13) . . ?
C27 C22 P2 120.86(12) . . ?
C24 C23 C22 120.30(16) . . ?
C24 C23 H23 119.8 . . ?
C22 C23 H23 119.8 . . ?
C25 C24 C23 120.13(17) . . ?
C25 C24 H24 119.9 . . ?
C23 C24 H24 119.9 . . ?
C24 C25 C26 120.26(16) . . ?
C24 C25 H25 119.9 . . ?
C26 C25 H25 119.9 . . ?
C27 C26 C25 119.95(16) . . ?
C27 C26 H26 120.0 . . ?
C25 C26 H26 120.0 . . ?
C26 C27 C22 120.18(16) . . ?
C26 C27 H27 119.9 . . ?
C22 C27 H27 119.9 . . ?
C33 C28 C29 119.65(15) . . ?
C33 C28 P2 121.72(12) . . ?
C29 C28 P2 118.62(12) . . ?
C30 C29 C28 119.72(16) . . ?
C30 C29 H29 120.1 . . ?
C28 C29 H29 120.1 . . ?
C29 C30 C31 120.46(16) . . ?
C29 C30 H30 119.8 . . ?
```

```
C31 C30 H30 119.8 . . ?
C32 C31 C30 119.85(16) . . ?
C32 C31 H31 120.1 . . ?
C30 C31 H31 120.1 . . ?
C31 C32 C33 120.25(16) . . ?
C31 C32 H32 119.9 . . ?
C33 C32 H32 119.9 . . ?
C32 C33 C28 120.07(15) . . ?
C32 C33 H33 120.0 . . ?
C28 C33 H33 120.0 . . ?
C39 C34 C35 119.45(15) . . ?
C39 C34 P2 123.47(12) . . ?
C35 C34 P2 117.08(12) . . ?
C36 C35 C34 120.20(16) . . ?
C36 C35 H35 119.9 . . ?
C34 C35 H35 119.9 . . ?
C37 C36 C35 120.07(16) . . ?
C37 C36 H36 120.0 . . ?
C35 C36 H36 120.0 . . ?
C36 C37 C38 120.11(16) . . ?
C36 C37 H37 119.9 . . ?
C38 C37 H37 119.9 . . ?
C37 C38 C39 120.32(17) . . ?
C37 C38 H38 119.8 . . ?
C39 C38 H38 119.8 . . ?
C34 C39 C38 119.84(16) . . ?
C34 C39 H39 120.1 . . ?
C38 C39 H39 120.1 . . ?

_diffrn_measured_fraction_theta_max    0.996
_diffrn_reflns_theta_full              25.00
_diffrn_measured_fraction_theta_full   0.997
_refine_diff_density_max    1.320
_refine_diff_density_min   -0.500
_refine_diff_density_rms    0.056
```

4c) Crystallographic information file for compound 2b (data_chppx75_0m)

```
data_ch1ppx75_0m

_audit_creation_method            SHELXL-97
_chemical_name_systematic
;
 ?
;
_chemical_name_common             ?
_chemical_melting_point           ?
_chemical_formula_moiety          '2(C36 H30 N P2), C6 N6 S6 Si, 2(C2
H3 N)'
_chemical_formula_sum
 'C82 H66 N10 P4 S6 Si'
_chemical_formula_weight          1535.78

loop_
 _atom_type_symbol
 _atom_type_description
 _atom_type_scat_dispersion_real
 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
```

```
 'C'  'C'   0.0033   0.0016
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Si'  'Si'   0.0817   0.0704
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'P'  'P'   0.1023   0.0942
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'S'  'S'   0.1246   0.1234
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting            Triclinic
_symmetry_space_group_name_H-M    P-1

loop_
 _symmetry_equiv_pos_as_xyz
 'x, y, z'
 '-x, -y, -z'

_cell_length_a                    10.7540(4)
_cell_length_b                    13.4160(6)
_cell_length_c                    14.4498(5)
_cell_angle_alpha                 100.540(2)
_cell_angle_beta                  102.120(2)
_cell_angle_gamma                 96.806(2)
_cell_volume                      1977.01(13)
_cell_formula_units_Z             1
_cell_measurement_temperature     100(2)
_cell_measurement_reflns_used     9985
_cell_measurement_theta_min       2.16
_cell_measurement_theta_max       27.33

_exptl_crystal_description        Block
_exptl_crystal_colour             colourless
_exptl_crystal_size_max           0.19
_exptl_crystal_size_mid           0.16
_exptl_crystal_size_min           0.14
_exptl_crystal_density_meas       ?
_exptl_crystal_density_diffrn     1.290
_exptl_crystal_density_method     'not measured'
_exptl_crystal_F_000              798
_exptl_absorpt_coefficient_mu     0.320
_exptl_absorpt_correction_type    multi-scan
_exptl_absorpt_correction_T_min   0.9417
_exptl_absorpt_correction_T_max   0.9566
_exptl_absorpt_process_details    sadabs

_exptl_special_details
;
 ?
;

_diffrn_ambient_temperature       100(2)
_diffrn_radiation_wavelength      0.71073
_diffrn_radiation_type            MoK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
```

```
_diffrn_measurement_device_type   'Bruker APEX-II CCD'
_diffrn_measurement_method        '\f and \w scans'
_diffrn_detector_area_resol_mean  100
_diffrn_standards_number          0
_diffrn_standards_interval_count  ?
_diffrn_standards_interval_time   ?
_diffrn_standards_decay_%         0
_diffrn_reflns_number             33304
_diffrn_reflns_av_R_equivalents   0.0356
_diffrn_reflns_av_sigmaI/netI     0.0367
_diffrn_reflns_limit_h_min        -13
_diffrn_reflns_limit_h_max        13
_diffrn_reflns_limit_k_min        -17
_diffrn_reflns_limit_k_max        17
_diffrn_reflns_limit_l_min        -18
_diffrn_reflns_limit_l_max        18
_diffrn_reflns_theta_min          1.48
_diffrn_reflns_theta_max          27.45
_reflns_number_total              8974
_reflns_number_gt                 7406
_reflns_threshold_expression      >2sigma(I)

_computing_data_collection        'Bruker APEX2'
_computing_cell_refinement        'Bruker SAINT'
_computing_data_reduction         'Bruker SAINT'
_computing_structure_solution     'SHELXS-97 (Sheldrick, 2008)'
_computing_structure_refinement   'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics     'Bruker SHELXTL'
_computing_publication_material   'Bruker SHELXTL'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor
wR and
 goodness of fit S are based on F^2^, conventional R-factors R are
based
 on F, with F set to zero for negative F^2^. The threshold expression
of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc.
and is
 not relevant to the choice of reflections for refinement.  R-factors
based
 on F^2^ are statistically about twice as large as those based on F,
and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0440P)^2^+0.7175P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     constr
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          8974
_refine_ls_number_parameters      467
```

```
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.0482
_refine_ls_R_factor_gt            0.0372
_refine_ls_wR_factor_ref          0.0968
_refine_ls_wR_factor_gt           0.0905
_refine_ls_goodness_of_fit_ref    1.051
_refine_ls_restrained_S_all       1.051
_refine_ls_shift/su_max           0.001
_refine_ls_shift/su_mean          0.000

loop_
 _atom_site_label
 _atom_site_type_symbol
 _atom_site_fract_x
 _atom_site_fract_y
 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
Si1 Si 0.5000 1.0000 0.0000 0.02045(14) Uani 1 2 d S . .
P1 P 0.31840(4) 0.68070(3) 0.34130(3) 0.01538(9) Uani 1 1 d . . .
P2 P 0.08796(4) 0.78241(3) 0.29552(3) 0.01475(9) Uani 1 1 d . . .
S1 S 0.86494(4) 1.23891(3) 0.06448(3) 0.02817(11) Uani 1 1 d . . .
S2 S 0.37092(7) 1.30078(5) 0.12107(4) 0.05078(17) Uani 1 1 d . . .
S3 S 0.62359(5) 0.94311(4) 0.30871(3) 0.03425(12) Uani 1 1 d . . .
N1 N 0.65492(13) 1.08199(11) 0.01900(10) 0.0245(3) Uani 1 1 d . . .
N2 N 0.43045(13) 1.11319(11) 0.04125(10) 0.0248(3) Uani 1 1 d . . .
N3 N 0.54388(14) 0.98198(11) 0.12461(10) 0.0256(3) Uani 1 1 d . . .
N4 N 0.23412(12) 0.76877(10) 0.32877(9) 0.0184(3) Uani 1 1 d . . .
N5 N 0.2588(2) 0.56236(19) 0.65821(13) 0.0547(5) Uani 1 1 d . . .
C1 C 0.74334(15) 1.14802(13) 0.03735(11) 0.0204(3) Uani 1 1 d . . .
C2 C 0.40439(17) 1.19218(15) 0.07365(12) 0.0262(4) Uani 1 1 d . . .
C3 C 0.57710(15) 0.96524(13) 0.20195(12) 0.0233(4) Uani 1 1 d . . .
C4 C 0.23049(14) 0.55580(12) 0.33733(11) 0.0173(3) Uani 1 1 d . . .
C5 C 0.20931(15) 0.47607(13) 0.25557(11) 0.0198(3) Uani 1 1 d . . .
H5 H 0.2446 0.4861 0.2023 0.024 Uiso 1 1 calc R . .
C6 C 0.13624(15) 0.38191(14) 0.25244(13) 0.0240(4) Uani 1 1 d . . .
H6 H 0.1209 0.3280 0.1967 0.029 Uiso 1 1 calc R . .
C7 C 0.08589(16) 0.36676(14) 0.33052(13) 0.0268(4) Uani 1 1 d . . .
H7 H 0.0360 0.3025 0.3280 0.032 Uiso 1 1 calc R . .
C8 C 0.10805(17) 0.44525(15) 0.41253(13) 0.0285(4) Uani 1 1 d . . .
H8 H 0.0747 0.4341 0.4663 0.034 Uiso 1 1 calc R . .
C9 C 0.17876(16) 0.53985(14) 0.41584(12) 0.0227(3) Uani 1 1 d . . .
H9 H 0.1921 0.5939 0.4713 0.027 Uiso 1 1 calc R . .
C10 C 0.43220(14) 0.71870(13) 0.45743(11) 0.0182(3) Uani 1 1 d . . .
C11 C 0.48420(16) 0.64533(14) 0.50481(12) 0.0248(4) Uani 1 1 d . . .
H11 H 0.4572 0.5742 0.4768 0.030 Uiso 1 1 calc R . .
C12 C 0.57520(16) 0.67641(15) 0.59272(12) 0.0288(4) Uani 1 1 d . . .
H12 H 0.6102 0.6266 0.6247 0.035 Uiso 1 1 calc R . .
C13 C 0.61460(16) 0.77976(15) 0.63349(12) 0.0264(4) Uani 1 1 d . . .
H13 H 0.6769 0.8007 0.6935 0.032 Uiso 1 1 calc R . .
C14 C 0.56391(16) 0.85354(15) 0.58746(12) 0.0257(4) Uani 1 1 d . . .
H14 H 0.5915 0.9245 0.6161 0.031 Uiso 1 1 calc R . .
C15 C 0.47243(15) 0.82317(13) 0.49917(11) 0.0214(3) Uani 1 1 d . . .
H15 H 0.4376 0.8734 0.4676 0.026 Uiso 1 1 calc R . .
C16 C 0.40912(14) 0.66232(12) 0.24983(11) 0.0174(3) Uani 1 1 d . . .
```

```
C17 C 0.51261(16) 0.60794(14) 0.26247(13) 0.0266(4) Uani 1 1 d . . .
H17 H 0.5367 0.5833 0.3202 0.032 Uiso 1 1 calc R . .
C18 C 0.57983(17) 0.59010(16) 0.19064(14) 0.0332(4) Uani 1 1 d . . .
H18 H 0.6491 0.5521 0.1987 0.040 Uiso 1 1 calc R . .
C19 C 0.54620(17) 0.62765(15) 0.10671(13) 0.0309(4) Uani 1 1 d . . .
H19 H 0.5931 0.6158 0.0580 0.037 Uiso 1 1 calc R . .
C20 C 0.44455(17) 0.68219(14) 0.09419(12) 0.0271(4) Uani 1 1 d . . .
H20 H 0.4221 0.7080 0.0369 0.033 Uiso 1 1 calc R . .
C21 C 0.37500(15) 0.69941(13) 0.16523(11) 0.0210(3) Uani 1 1 d . . .
H21 H 0.3047 0.7362 0.1562 0.025 Uiso 1 1 calc R . .
C22 C 0.08693(15) 0.89299(12) 0.24079(11) 0.0177(3) Uani 1 1 d . . .
C23 C 0.19877(16) 0.93684(13) 0.21945(11) 0.0214(3) Uani 1 1 d . . .
H23 H 0.2776 0.9125 0.2387 0.026 Uiso 1 1 calc R . .
C24 C 0.19447(18) 1.01672(13) 0.16960(12) 0.0265(4) Uani 1 1 d . . .
H24 H 0.2704 1.0465 0.1545 0.032 Uiso 1 1 calc R . .
C25 C 0.07960(19) 1.05259(14) 0.14207(13) 0.0308(4) Uani 1 1 d . . .
H25 H 0.0770 1.1067 0.1078 0.037 Uiso 1 1 calc R . .
C26 C -0.03166(18) 1.00994(15) 0.16429(13) 0.0311(4) Uani 1 1 d . . .
H26 H -0.1098 1.0355 0.1458 0.037 Uiso 1 1 calc R . .
C27 C -0.02925(16) 0.92999(13) 0.21347(12) 0.0238(4) Uani 1 1 d . . .
H27 H -0.1055 0.9006 0.2285 0.029 Uiso 1 1 calc R . .
C28 C -0.01296(14) 0.67712(12) 0.20528(11) 0.0173(3) Uani 1 1 d . . .
C29 C -0.02909(16) 0.68146(14) 0.10721(12) 0.0246(4) Uani 1 1 d . . .
H29 H 0.0058 0.7419 0.0898 0.030 Uiso 1 1 calc R . .
C30 C -0.09596(18) 0.59759(15) 0.03586(12) 0.0305(4) Uani 1 1 d . . .
H30 H -0.1070 0.6007 -0.0305 0.037 Uiso 1 1 calc R . .
C31 C -0.14695(16) 0.50896(14) 0.06078(13) 0.0265(4) Uani 1 1 d . . .
H31 H -0.1925 0.4517 0.0115 0.032 Uiso 1 1 calc R . .
C32 C -0.13158(15) 0.50388(13) 0.15761(12) 0.0222(3) Uani 1 1 d . . .
H32 H -0.1663 0.4430 0.1744 0.027 Uiso 1 1 calc R . .
C33 C -0.06537(14) 0.58789(13) 0.23006(12) 0.0190(3) Uani 1 1 d . . .
H33 H -0.0558 0.5847 0.2963 0.023 Uiso 1 1 calc R . .
C34 C 0.01524(15) 0.80780(12) 0.39729(11) 0.0180(3) Uani 1 1 d . . .
C35 C -0.11777(15) 0.78501(13) 0.38744(12) 0.0216(3) Uani 1 1 d . . .
H35 H -0.1726 0.7507 0.3266 0.026 Uiso 1 1 calc R . .
C36 C -0.16967(16) 0.81296(14) 0.46741(12) 0.0256(4) Uani 1 1 d . . .
H36 H -0.2598 0.7965 0.4612 0.031 Uiso 1 1 calc R . .
C37 C -0.09035(17) 0.86452(14) 0.55565(12) 0.0253(4) Uani 1 1 d . . .
H37 H -0.1264 0.8839 0.6096 0.030 Uiso 1 1 calc R . .
C38 C 0.04187(17) 0.88818(14) 0.56581(12) 0.0254(4) Uani 1 1 d . . .
H38 H 0.0959 0.9239 0.6265 0.031 Uiso 1 1 calc R . .
C39 C 0.09495(16) 0.85937(13) 0.48694(11) 0.0222(3) Uani 1 1 d . . .
H39 H 0.1854 0.8747 0.4940 0.027 Uiso 1 1 calc R . .
C40 C 0.3116(2) 0.76076(18) 0.71762(16) 0.0443(5) Uani 1 1 d . . .
H40A H 0.3137 0.7927 0.6621 0.067 Uiso 1 1 calc R . .
H40B H 0.3957 0.7798 0.7640 0.067 Uiso 1 1 calc R . .
H40C H 0.2450 0.7846 0.7491 0.067 Uiso 1 1 calc R . .
C41 C 0.2826(2) 0.6499(2) 0.68462(14) 0.0384(5) Uani 1 1 d . . .

loop_
 _atom_site_aniso_label
 _atom_site_aniso_U_11
 _atom_site_aniso_U_22
 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
Si1 0.0195(3) 0.0177(3) 0.0231(3) 0.0055(3) 0.0034(2) 0.0000(3)
P1 0.01434(19) 0.0166(2) 0.01457(18) 0.00273(16) 0.00197(14)
.00346(15)
P2 0.01480(19) 0.0148(2) 0.01475(18) 0.00333(15) 0.00315(14)
```

```
0.00338(15)
S1 0.0229(2) 0.0201(2) 0.0384(3) 0.00701(19) 0.00325(18) -0.00292(17)
S2 0.0872(5) 0.0430(3) 0.0428(3) 0.0181(3) 0.0360(3) 0.0412(3)
S3 0.0393(3) 0.0359(3) 0.0256(2) 0.0108(2) 0.00031(19) 0.0048(2)
N1 0.0224(7) 0.0218(8) 0.0279(8) 0.0055(6) 0.0043(6) 0.0004(6)
N2 0.0232(7) 0.0217(8) 0.0299(8) 0.0069(6) 0.0069(6) 0.0021(6)
N3 0.0259(7) 0.0229(8) 0.0259(8) 0.0062(6) 0.0031(6) 0.0001(6)
N4 0.0170(6) 0.0172(7) 0.0200(7) 0.0028(5) 0.0029(5) 0.0034(5)
N5 0.0688(14) 0.0618(15) 0.0312(10) 0.0158(10) 0.0108(9) -0.0053(11)
C1 0.0223(8) 0.0206(9) 0.0203(8) 0.0077(7) 0.0049(6) 0.0070(7)
C2 0.0281(9) 0.0312(11) 0.0263(9) 0.0149(8) 0.0122(7) 0.0085(8)
C3 0.0197(8) 0.0192(9) 0.0299(9) 0.0040(7) 0.0052(7) 0.0015(7)
C4 0.0143(7) 0.0187(8) 0.0189(7) 0.0060(6) 0.0011(6) 0.0048(6)
C5 0.0172(7) 0.0214(9) 0.0198(8) 0.0037(7) 0.0020(6) 0.0053(6)
C6 0.0191(8) 0.0204(9) 0.0276(9) 0.0012(7) -0.0015(7) 0.0027(7)
C7 0.0187(8) 0.0210(9) 0.0399(10) 0.0108(8) 0.0028(7) 0.0007(7)
C8 0.0270(9) 0.0317(11) 0.0305(9) 0.0138(8) 0.0097(7) 0.0028(8)
C9 0.0233(8) 0.0247(9) 0.0204(8) 0.0044(7) 0.0057(7) 0.0043(7)
C10 0.0147(7) 0.0230(9) 0.0159(7) 0.0028(6) 0.0025(6) 0.0038(6)
C11 0.0249(9) 0.0216(9) 0.0244(8) 0.0037(7) -0.0017(7) 0.0044(7)
C12 0.0250(9) 0.0355(11) 0.0237(9) 0.0103(8) -0.0022(7) 0.0047(8)
C13 0.0187(8) 0.0385(11) 0.0171(8) 0.0025(7) -0.0008(6) 0.0003(8)
C14 0.0229(8) 0.0269(10) 0.0222(8) -0.0032(7) 0.0038(7) 0.0001(7)
C15 0.0193(8) 0.0231(9) 0.0212(8) 0.0040(7) 0.0045(6) 0.0036(7)
C16 0.0153(7) 0.0174(8) 0.0179(7) 0.0011(6) 0.0038(6) 0.0011(6)
C17 0.0232(8) 0.0334(11) 0.0280(9) 0.0120(8) 0.0086(7) 0.0102(8)
C18 0.0250(9) 0.0422(12) 0.0398(11) 0.0121(9) 0.0148(8) 0.0171(9)
C19 0.0286(9) 0.0369(11) 0.0316(10) 0.0061(8) 0.0172(8) 0.0067(8)
C20 0.0308(9) 0.0293(10) 0.0229(8) 0.0070(7) 0.0093(7) 0.0035(8)
C21 0.0211(8) 0.0206(9) 0.0208(8) 0.0030(7) 0.0049(6) 0.0039(7)
C22 0.0219(8) 0.0153(8) 0.0155(7) 0.0024(6) 0.0039(6) 0.0039(6)
C23 0.0244(8) 0.0178(9) 0.0213(8) 0.0009(7) 0.0068(7) 0.0031(7)
C24 0.0368(10) 0.0185(9) 0.0249(9) 0.0033(7) 0.0128(7) 0.0002(7)
C25 0.0479(11) 0.0208(10) 0.0267(9) 0.0105(8) 0.0095(8) 0.0078(8)
C26 0.0341(10) 0.0293(11) 0.0327(10) 0.0125(8) 0.0046(8) 0.0136(8)
C27 0.0217(8) 0.0229(9) 0.0273(9) 0.0073(7) 0.0048(7) 0.0051(7)
C28 0.0148(7) 0.0164(8) 0.0203(8) 0.0029(6) 0.0033(6) 0.0042(6)
C29 0.0297(9) 0.0222(9) 0.0204(8) 0.0046(7) 0.0044(7) 0.0001(7)
C30 0.0403(11) 0.0288(10) 0.0185(8) 0.0020(7) 0.0038(7) 0.0009(8)
C31 0.0235(8) 0.0229(9) 0.0266(9) -0.0036(7) 0.0016(7) 0.0000(7)
C32 0.0171(8) 0.0184(9) 0.0308(9) 0.0038(7) 0.0064(7) 0.0028(6)
C33 0.0160(7) 0.0202(9) 0.0214(8) 0.0049(7) 0.0042(6) 0.0048(6)
C34 0.0204(8) 0.0174(8) 0.0181(7) 0.0054(6) 0.0061(6) 0.0054(6)
C35 0.0204(8) 0.0236(9) 0.0197(8) 0.0028(7) 0.0036(6) 0.0040(7)
C36 0.0213(8) 0.0306(10) 0.0279(9) 0.0071(8) 0.0102(7) 0.0064(7)
C37 0.0313(9) 0.0273(10) 0.0213(8) 0.0058(7) 0.0127(7) 0.0086(8)
C38 0.0289(9) 0.0277(10) 0.0173(8) 0.0002(7) 0.0049(7) 0.0037(8)
C39 0.0192(8) 0.0252(9) 0.0210(8) 0.0040(7) 0.0036(6) 0.0024(7)
C40 0.0429(12) 0.0530(15) 0.0407(12) 0.0124(11) 0.0150(10) 0.0090(11)
C41 0.0363(11) 0.0578(16) 0.0229(9) 0.0164(10) 0.0084(8) 0.0003(10)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s.
planes)
 are estimated using the full covariance matrix.  The cell esds are
taken
 into account individually in the estimation of esds in distances,
angles
 and torsion angles; correlations between esds in cell parameters are
only
```

```
 used when they are defined by crystal symmetry.  An approximate
(isotropic)
 treatment of cell esds is used for estimating esds involving l.s.
planes.
;

loop_
 _geom_bond_atom_site_label_1
 _geom_bond_atom_site_label_2
 _geom_bond_distance
 _geom_bond_site_symmetry_2
 _geom_bond_publ_flag
Si1 N1 1.8232(14) . ?
Si1 N1 1.8232(14) 2_675 ?
Si1 N2 1.8292(15) 2_675 ?
Si1 N2 1.8292(15) . ?
Si1 N3 1.8311(14) . ?
Si1 N3 1.8311(14) 2_675 ?
P1 N4 1.5854(13) . ?
P1 C16 1.7996(15) . ?
P1 C10 1.8029(16) . ?
P1 C4 1.8086(16) . ?
P2 N4 1.5868(13) . ?
P2 C28 1.8006(16) . ?
P2 C34 1.8036(15) . ?
P2 C22 1.8044(16) . ?
S1 C1 1.6070(17) . ?
S2 C2 1.608(2) . ?
S3 C3 1.6114(17) . ?
N1 C1 1.170(2) . ?
N2 C2 1.168(2) . ?
N3 C3 1.170(2) . ?
N5 C41 1.146(3) . ?
C4 C5 1.400(2) . ?
C4 C9 1.403(2) . ?
C5 C6 1.394(2) . ?
C5 H5 0.9500 . ?
C6 C7 1.386(2) . ?
C6 H6 0.9500 . ?
C7 C8 1.391(3) . ?
C7 H7 0.9500 . ?
C8 C9 1.388(2) . ?
C8 H8 0.9500 . ?
C9 H9 0.9500 . ?
C10 C15 1.397(2) . ?
C10 C11 1.402(2) . ?
C11 C12 1.390(2) . ?
C11 H11 0.9500 . ?
C12 C13 1.381(3) . ?
C12 H12 0.9500 . ?
C13 C14 1.391(3) . ?
C13 H13 0.9500 . ?
C14 C15 1.396(2) . ?
C14 H14 0.9500 . ?
C15 H15 0.9500 . ?
C16 C21 1.398(2) . ?
C16 C17 1.400(2) . ?
C17 C18 1.386(2) . ?
C17 H17 0.9500 . ?
C18 C19 1.392(3) . ?
C18 H18 0.9500 . ?
```

```
C19 C20 1.385(3) . ?
C19 H19 0.9500 . ?
C20 C21 1.394(2) . ?
C20 H20 0.9500 . ?
C21 H21 0.9500 . ?
C22 C23 1.394(2) . ?
C22 C27 1.405(2) . ?
C23 C24 1.396(2) . ?
C23 H23 0.9500 . ?
C24 C25 1.386(3) . ?
C24 H24 0.9500 . ?
C25 C26 1.389(3) . ?
C25 H25 0.9500 . ?
C26 C27 1.391(2) . ?
C26 H26 0.9500 . ?
C27 H27 0.9500 . ?
C28 C33 1.400(2) . ?
C28 C29 1.404(2) . ?
C29 C30 1.385(2) . ?
C29 H29 0.9500 . ?
C30 C31 1.389(3) . ?
C30 H30 0.9500 . ?
C31 C32 1.389(2) . ?
C31 H31 0.9500 . ?
C32 C33 1.392(2) . ?
C32 H32 0.9500 . ?
C33 H33 0.9500 . ?
C34 C35 1.398(2) . ?
C34 C39 1.399(2) . ?
C35 C36 1.396(2) . ?
C35 H35 0.9500 . ?
C36 C37 1.383(2) . ?
C36 H36 0.9500 . ?
C37 C38 1.390(2) . ?
C37 H37 0.9500 . ?
C38 C39 1.392(2) . ?
C38 H38 0.9500 . ?
C39 H39 0.9500 . ?
C40 C41 1.451(3) . ?
C40 H40A 0.9800 . ?
C40 H40B 0.9800 . ?
C40 H40C 0.9800 . ?

loop_
 _geom_angle_atom_site_label_1
 _geom_angle_atom_site_label_2
 _geom_angle_atom_site_label_3
 _geom_angle
 _geom_angle_site_symmetry_1
 _geom_angle_site_symmetry_3
 _geom_angle_publ_flag
N1 Si1 N1 180.00(9) . 2_675 ?
N1 Si1 N2 90.41(6) . 2_675 ?
N1 Si1 N2 89.59(6) 2_675 2_675 ?
N1 Si1 N2 89.59(6) . . ?
N1 Si1 N2 90.41(6) 2_675 . ?
N2 Si1 N2 180.00(9) 2_675 . ?
N1 Si1 N3 90.11(6) . . ?
N1 Si1 N3 89.89(6) 2_675 . ?
N2 Si1 N3 89.94(7) 2_675 . ?
N2 Si1 N3 90.06(7) . . ?
```

```
N1 Si1 N3 89.89(6) . 2_675 ?
N1 Si1 N3 90.11(6) 2_675 2_675 ?
N2 Si1 N3 90.06(7) 2_675 2_675 ?
N2 Si1 N3 89.94(7) . 2_675 ?
N3 Si1 N3 180.00(9) . 2_675 ?
N4 P1 C16 111.30(7) . . ?
N4 P1 C10 108.50(7) . . ?
C16 P1 C10 107.54(7) . . ?
N4 P1 C4 115.85(7) . . ?
C16 P1 C4 106.52(7) . . ?
C10 P1 C4 106.75(7) . . ?
N4 P2 C28 115.14(7) . . ?
N4 P2 C34 111.58(7) . . ?
C28 P2 C34 108.95(7) . . ?
N4 P2 C22 107.06(7) . . ?
C28 P2 C22 106.03(7) . . ?
C34 P2 C22 107.66(7) . . ?
C1 N1 Si1 168.20(14) . . ?
C2 N2 Si1 170.13(15) . . ?
C3 N3 Si1 175.12(15) . . ?
P1 N4 P2 139.97(9) . . ?
N1 C1 S1 179.03(15) . . ?
N2 C2 S2 178.44(17) . . ?
N3 C3 S3 179.53(18) . . ?
C5 C4 C9 119.57(15) . . ?
C5 C4 P1 120.90(12) . . ?
C9 C4 P1 119.49(13) . . ?
C6 C5 C4 119.84(15) . . ?
C6 C5 H5 120.1 . . ?
C4 C5 H5 120.1 . . ?
C7 C6 C5 120.16(16) . . ?
C7 C6 H6 119.9 . . ?
C5 C6 H6 119.9 . . ?
C6 C7 C8 120.28(16) . . ?
C6 C7 H7 119.9 . . ?
C8 C7 H7 119.9 . . ?
C9 C8 C7 120.09(16) . . ?
C9 C8 H8 120.0 . . ?
C7 C8 H8 120.0 . . ?
C8 C9 C4 120.04(16) . . ?
C8 C9 H9 120.0 . . ?
C4 C9 H9 120.0 . . ?
C15 C10 C11 119.57(15) . . ?
C15 C10 P1 119.30(12) . . ?
C11 C10 P1 121.10(13) . . ?
C12 C11 C10 120.17(17) . . ?
C12 C11 H11 119.9 . . ?
C10 C11 H11 119.9 . . ?
C13 C12 C11 119.95(16) . . ?
C13 C12 H12 120.0 . . ?
C11 C12 H12 120.0 . . ?
C12 C13 C14 120.61(16) . . ?
C12 C13 H13 119.7 . . ?
C14 C13 H13 119.7 . . ?
C13 C14 C15 119.91(17) . . ?
C13 C14 H14 120.0 . . ?
C15 C14 H14 120.0 . . ?
C14 C15 C10 119.79(16) . . ?
C14 C15 H15 120.1 . . ?
C10 C15 H15 120.1 . . ?
C21 C16 C17 119.78(14) . . ?
```

```
C21 C16 P1 120.59(12) . . ?
C17 C16 P1 119.60(12) . . ?
C18 C17 C16 119.91(16) . . ?
C18 C17 H17 120.0 . . ?
C16 C17 H17 120.0 . . ?
C17 C18 C19 120.22(16) . . ?
C17 C18 H18 119.9 . . ?
C19 C18 H18 119.9 . . ?
C20 C19 C18 120.10(16) . . ?
C20 C19 H19 120.0 . . ?
C18 C19 H19 120.0 . . ?
C19 C20 C21 120.27(16) . . ?
C19 C20 H20 119.9 . . ?
C21 C20 H20 119.9 . . ?
C20 C21 C16 119.72(15) . . ?
C20 C21 H21 120.1 . . ?
C16 C21 H21 120.1 . . ?
C23 C22 C27 120.14(15) . . ?
C23 C22 P2 120.08(12) . . ?
C27 C22 P2 119.62(12) . . ?
C22 C23 C24 119.70(16) . . ?
C22 C23 H23 120.1 . . ?
C24 C23 H23 120.1 . . ?
C25 C24 C23 120.08(16) . . ?
C25 C24 H24 120.0 . . ?
C23 C24 H24 120.0 . . ?
C24 C25 C26 120.36(16) . . ?
C24 C25 H25 119.8 . . ?
C26 C25 H25 119.8 . . ?
C25 C26 C27 120.32(17) . . ?
C25 C26 H26 119.8 . . ?
C27 C26 H26 119.8 . . ?
C26 C27 C22 119.39(16) . . ?
C26 C27 H27 120.3 . . ?
C22 C27 H27 120.3 . . ?
C33 C28 C29 119.53(15) . . ?
C33 C28 P2 121.62(12) . . ?
C29 C28 P2 118.59(12) . . ?
C30 C29 C28 119.91(16) . . ?
C30 C29 H29 120.0 . . ?
C28 C29 H29 120.0 . . ?
C29 C30 C31 120.35(16) . . ?
C29 C30 H30 119.8 . . ?
C31 C30 H30 119.8 . . ?
C30 C31 C32 120.19(16) . . ?
C30 C31 H31 119.9 . . ?
C32 C31 H31 119.9 . . ?
C31 C32 C33 120.04(16) . . ?
C31 C32 H32 120.0 . . ?
C33 C32 H32 120.0 . . ?
C32 C33 C28 119.97(15) . . ?
C32 C33 H33 120.0 . . ?
C28 C33 H33 120.0 . . ?
C35 C34 C39 119.69(14) . . ?
C35 C34 P2 122.21(12) . . ?
C39 C34 P2 117.91(12) . . ?
C36 C35 C34 119.70(15) . . ?
C36 C35 H35 120.1 . . ?
C34 C35 H35 120.1 . . ?
C37 C36 C35 120.27(15) . . ?
C37 C36 H36 119.9 . . ?
```

```
C35 C36 H36 119.9 . . ?
C36 C37 C38 120.36(15) . . ?
C36 C37 H37 119.8 . . ?
C38 C37 H37 119.8 . . ?
C37 C38 C39 119.89(16) . . ?
C37 C38 H38 120.1 . . ?
C39 C38 H38 120.1 . . ?
C38 C39 C34 120.08(15) . . ?
C38 C39 H39 120.0 . . ?
C34 C39 H39 120.0 . . ?
C41 C40 H40A 109.5 . . ?
C41 C40 H40B 109.5 . . ?
H40A C40 H40B 109.5 . . ?
C41 C40 H40C 109.5 . . ?
H40A C40 H40C 109.5 . . ?
H40B C40 H40C 109.5 . . ?
N5 C41 C40 179.5(3) . . ?

_diffrn_measured_fraction_theta_max    0.994
_diffrn_reflns_theta_full              25.00
_diffrn_measured_fraction_theta_full   0.999
_refine_diff_density_max    0.641
_refine_diff_density_min   -0.529
_refine_diff_density_rms    0.054
```

4d) Crystallographic information file for compound 4 (data_chppx70_0m)

```
data_ch1ppx70_0n

_audit_creation_method            SHELXL-97
_chemical_name_systematic
;
 ?
;
_chemical_name_common             ?
_chemical_melting_point           ?
_chemical_formula_moiety          'C16 H8 N6 O4 Si, C2 H3 N'
_chemical_formula_sum
 'C18 H11 N7 O4 Si'
_chemical_formula_weight          417.43

loop_
 _atom_type_symbol
 _atom_type_description
 _atom_type_scat_dispersion_real
 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
 'C'  'C'   0.0033   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'  'O'   0.0106   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Si'  'Si'   0.0817   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting            Orthorhombic
_symmetry_space_group_name_H-M    Pna2(1)
```

```
loop_
 _symmetry_equiv_pos_as_xyz
 'x, y, z'
 '-x, -y, z+1/2'
 '-x+1/2, y+1/2, z+1/2'
 'x+1/2, -y+1/2, z'

_cell_length_a                    6.9932(9)
_cell_length_b                    18.085(2)
_cell_length_c                    14.1246(15)
_cell_angle_alpha                 90.00
_cell_angle_beta                  90.00
_cell_angle_gamma                 90.00
_cell_volume                      1786.4(4)
_cell_formula_units_Z             4
_cell_measurement_temperature     120(2)
_cell_measurement_reflns_used     2074
_cell_measurement_theta_min       2.25
_cell_measurement_theta_max       27.04
_exptl_crystal_description        sheet
_exptl_crystal_colour             colourless
_exptl_crystal_size_max           0.28
_exptl_crystal_size_mid           0.19
_exptl_crystal_size_min           0.04
_exptl_crystal_density_meas       ?
_exptl_crystal_density_diffrn     1.552
_exptl_crystal_density_method     'not measured'
_exptl_crystal_F_000              856
_exptl_absorpt_coefficient_mu     0.177
_exptl_absorpt_correction_type    multi-scan
_exptl_absorpt_correction_T_min   0.9521
_exptl_absorpt_correction_T_max   0.9929
_exptl_absorpt_process_details    sadabs

_exptl_special_details
;
 ?
;

_diffrn_ambient_temperature       120(2)
_diffrn_radiation_wavelength      0.71073
_diffrn_radiation_type            MoK\a
_diffrn_radiation_source          'fine-focus sealed tube'
_diffrn_radiation_monochromator   graphite
_diffrn_measurement_device_type   'CCD area detector'
_diffrn_measurement_method        'omega scans'
_diffrn_detector_area_resol_mean  100
_diffrn_standards_number          0
_diffrn_standards_interval_count  ?
_diffrn_standards_interval_time   ?
_diffrn_standards_decay_%         0
_diffrn_reflns_number             9835
_diffrn_reflns_av_R_equivalents   0.0464
_diffrn_reflns_av_sigmaI/netI     0.0392
_diffrn_reflns_limit_h_min        -9
_diffrn_reflns_limit_h_max        8
_diffrn_reflns_limit_k_min        -22
_diffrn_reflns_limit_k_max        23
_diffrn_reflns_limit_l_min        -17
_diffrn_reflns_limit_l_max        18
```

```
_diffrn_reflns_theta_min          2.25
_diffrn_reflns_theta_max          27.50
_reflns_number_total              2129
_reflns_number_gt                 1824
_reflns_threshold_expression      >2sigma(I)
_computing_data_collection        'Bruker SMART'
_computing_cell_refinement        'Bruker SMART'
_computing_data_reduction         'Bruker SAINT'
_computing_structure_solution     'Bruker SHELXTL'
_computing_structure_refinement   'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics     'Bruker SHELXTL'
_computing_publication_material   'Bruker SHELXTL'

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor
wR and
 goodness of fit S are based on F^2^, conventional R-factors R are
based
 on F, with F set to zero for negative F^2^. The threshold expression
of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc.
and is
 not relevant to the choice of reflections for refinement.  R-factors
based
 on F^2^ are statistically about twice as large as those based on F,
and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0499P)^2^+0.0291P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     constr
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_abs_structure_details
 'Flack H D (1983), Acta Cryst. A39, 876-881'
_refine_ls_abs_structure_Flack    ?
_refine_ls_number_reflns          2129
_refine_ls_number_parameters      273
_refine_ls_number_restraints      1
_refine_ls_R_factor_all           0.0467
_refine_ls_R_factor_gt            0.0365
_refine_ls_wR_factor_ref          0.0862
_refine_ls_wR_factor_gt           0.0813
_refine_ls_goodness_of_fit_ref    1.028
_refine_ls_restrained_S_all       1.028
_refine_ls_shift/su_max           0.000
_refine_ls_shift/su_mean          0.000

loop_
 _atom_site_label
 _atom_site_type_symbol
 _atom_site_fract_x
```

```
 _atom_site_fract_y
 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
Si1 Si 0.74497(13) 0.98308(4) 0.07612(6) 0.01996(18) Uani 1 1 d . . .
O1 O 0.9965(4) 1.11185(12) -0.12840(17) 0.0396(6) Uani 1 1 d . . .
O2 O 0.6724(7) 1.17369(15) 0.2283(2) 0.0936(15) Uani 1 1 d . . .
O3 O 1.2098(4) 1.01558(15) 0.23571(17) 0.0377(6) Uani 1 1 d . . .
O4 O 0.2697(4) 0.94817(13) -0.08445(17) 0.0368(6) Uani 1 1 d . . .
N1 N 0.8277(4) 1.03364(13) -0.02370(18) 0.0261(6) Uani 1 1 d . . .
N2 N 0.6936(4) 1.06010(13) 0.15093(18) 0.0265(6) Uani 1 1 d . . .
N3 N 0.9848(4) 0.97105(12) 0.12362(17) 0.0231(6) Uani 1 1 d . . .
N4 N 0.4999(4) 0.97998(12) 0.03167(18) 0.0248(6) Uani 1 1 d . . .
N5 N 0.6607(4) 0.91359(13) 0.17638(15) 0.0193(5) Uani 1 1 d . . .
N6 N 0.7874(4) 0.88855(13) 0.00752(17) 0.0201(5) Uani 1 1 d . . .
N7 N 0.6940(5) 0.21322(17) -0.0030(2) 0.0422(8) Uani 1 1 d . . .
C1 C 0.9120(5) 1.07256(15) -0.0746(2) 0.0249(7) Uani 1 1 d . . .
C2 C 0.6841(6) 1.11665(17) 0.1879(2) 0.0383(9) Uani 1 1 d . . .
C3 C 1.0938(5) 0.99370(15) 0.1811(2) 0.0233(6) Uani 1 1 d . . .
C4 C 0.3881(5) 0.96417(15) -0.0272(2) 0.0233(7) Uani 1 1 d . . .
C5 C 0.5927(5) 0.92958(16) 0.26193(19) 0.0239(7) Uani 1 1 d . . .
H024 H 0.5770 0.9799 0.2794 0.029 Uiso 1 1 calc R . .
C6 C 0.5437(5) 0.87430(16) 0.3271(2) 0.0240(7) Uani 1 1 d . . .
H021 H 0.4952 0.8878 0.3875 0.029 Uiso 1 1 calc R . .
C7 C 0.5649(5) 0.80120(15) 0.3047(2) 0.0223(6) Uani 1 1 d . . .
H022 H 0.5340 0.7638 0.3494 0.027 Uiso 1 1 calc R . .
C8 C 0.6338(5) 0.78258(15) 0.2136(2) 0.0206(6) Uani 1 1 d . . .
C9 C 0.6535(4) 0.70856(15) 0.1787(2) 0.0217(6) Uani 1 1 d . . .
H020 H 0.6242 0.6681 0.2191 0.026 Uiso 1 1 calc R . .
C10 C 0.7139(4) 0.69512(16) 0.0880(2) 0.0225(7) Uani 1 1 d . . .
H012 H 0.7239 0.6456 0.0662 0.027 Uiso 1 1 calc R . .
C11 C 0.7622(4) 0.75486(16) 0.0258(2) 0.0205(6) Uani 1 1 d . . .
C12 C 0.8234(5) 0.74652(17) -0.0691(2) 0.0239(7) Uani 1 1 d . . .
H016 H 0.8341 0.6987 -0.0965 0.029 Uiso 1 1 calc R . .
C13 C 0.8671(5) 0.80845(16) -0.1210(2) 0.0250(7) Uani 1 1 d . . .
H017 H 0.9106 0.8035 -0.1844 0.030 Uiso 1 1 calc R . .
C14 C 0.8479(5) 0.87919(16) -0.0808(2) 0.0241(7) Uani 1 1 d . . .
H027 H 0.8789 0.9214 -0.1178 0.029 Uiso 1 1 calc R . .
C15 C 0.7457(4) 0.82757(15) 0.05914(19) 0.0176(6) Uani 1 1 d . . .
C16 C 0.6796(4) 0.84079(15) 0.15277(19) 0.0180(6) Uani 1 1 d . . .
C17 C 0.7200(6) 0.3363(2) 0.0888(3) 0.0484(11) Uani 1 1 d . . .
H11A H 0.8082 0.3696 0.0558 0.073 Uiso 1 1 calc R . .
H11B H 0.7683 0.3264 0.1527 0.073 Uiso 1 1 calc R . .
H11C H 0.5936 0.3594 0.0930 0.073 Uiso 1 1 calc R . .
C18 C 0.7053(5) 0.26764(19) 0.0371(2) 0.0308(8) Uani 1 1 d . . .

loop_
 _atom_site_aniso_label
 _atom_site_aniso_U_11
 _atom_site_aniso_U_22
 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
Si1 0.0279(4) 0.0139(3) 0.0180(3) 0.0003(3) 0.0003(3) -0.0001(3)
```

```
O1 0.0428(16) 0.0338(13) 0.0424(13) 0.0117(11) 0.0072(12) -0.0069(12)
O2 0.219(5) 0.0284(15) 0.0331(14) -0.0080(12) -0.011(2) 0.024(2)
O3 0.0391(17) 0.0482(15) 0.0258(12) -0.0096(10) -0.0056(12) -
0.0045(12)
O4 0.0418(16) 0.0389(14) 0.0298(12) 0.0051(11) -0.0080(12) -
0.0087(11)
N1 0.0370(17) 0.0186(12) 0.0228(12) 0.0015(10) -0.0004(13) -
0.0025(12)
N2 0.0348(17) 0.0175(13) 0.0271(13) -0.0004(10) 0.0015(13) 0.0012(11)
N3 0.0295(16) 0.0192(13) 0.0205(12) -0.0009(10) 0.0003(12) -.0021(11)
N4 0.0290(16) 0.0216(13) 0.0237(12) 0.0014(10) -0.0032(13) 0.0035(11)
N5 0.0231(14) 0.0172(11) 0.0175(11) -0.0004(9) 0.0002(11) 0.0008(10)
N6 0.0217(15) 0.0192(12) 0.0194(11) -0.0002(9) -0.0005(10) -
0.0015(10)
N7 0.053(2) 0.0345(17) 0.0386(16) -0.0031(13) -0.0062(16) 0.0005(15)
C1 0.0311(19) 0.0175(14) 0.0262(14) -0.0013(13) -0.0043(15)
0.0016(13)
C2 0.074(3) 0.0199(16) 0.0208(14) 0.0009(13) -0.0028(17) 0.0061(16)
C3 0.0292(18) 0.0174(13) 0.0235(14) -0.0019(11) 0.0047(14) 0.0005(13)
C4 0.0299(19) 0.0177(14) 0.0222(14) 0.0060(12) 0.0042(15) 0.0005(13)
C5 0.0297(19) 0.0212(14) 0.0207(13) -0.0036(11) 0.0004(14) 0.0009(13)
C6 0.0269(18) 0.0263(15) 0.0189(13) 0.0000(11) 0.0016(13) -0.0006(14)
C7 0.0224(17) 0.0219(14) 0.0226(13) 0.0018(12) -0.0027(13) -
0.0019(13)
C8 0.0200(17) 0.0201(14) 0.0216(14) 0.0018(11) -0.0027(13) 0.0007(12)
C9 0.0200(17) 0.0175(14) 0.0276(15) 0.0051(11) -0.0027(13) -
0.0018(12)
C10 0.0229(17) 0.0153(13) 0.0294(15) -0.0032(12) -0.0037(14)
0.0018(11)
C11 0.0209(16) 0.0180(14) 0.0226(14) -0.0044(11) -0.0021(14)
0.0007(12)
C12 0.0257(17) 0.0217(15) 0.0242(14) -0.0041(12) -0.0012(14)
0.0039(12)
C13 0.0291(19) 0.0255(16) 0.0204(14) -0.0023(12) 0.0016(14)
0.0011(13)
C14 0.0296(19) 0.0242(15) 0.0185(13) 0.0007(12) 0.0022(14) -
0.0016(13)
C15 0.0190(14) 0.0153(13) 0.0185(15) -0.0018(9) -0.0019(12) -
0.0016(12)
C16 0.0182(16) 0.0176(14) 0.0182(13) -0.0013(10) -0.0030(13)
0.0004(11)
C17 0.064(3) 0.0320(19) 0.049(2) -0.0076(17) -0.004(2) 0.0006(18)
C18 0.033(2) 0.0299(19) 0.0295(16) 0.0063(14) -0.0005(15) 0.0042(14)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s.
planes)
 are estimated using the full covariance matrix.  The cell esds are
taken
 into account individually in the estimation of esds in distances,
angles
 and torsion angles; correlations between esds in cell parameters are
only
 used when they are defined by crystal symmetry.  An approximate
(isotropic)
 treatment of cell esds is used for estimating esds involving l.s.
planes.
;

loop_
```

```
 _geom_bond_atom_site_label_1
 _geom_bond_atom_site_label_2
 _geom_bond_distance
 _geom_bond_site_symmetry_2
 _geom_bond_publ_flag
Si1 N1 1.777(3) . ?
Si1 N2 1.785(3) . ?
Si1 N3 1.820(3) . ?
Si1 N4 1.826(3) . ?
Si1 N5 1.983(2) . ?
Si1 N6 1.987(3) . ?
O1 C1 1.197(4) . ?
O2 C2 1.182(4) . ?
O3 C3 1.187(4) . ?
O4 C4 1.193(4) . ?
N1 C1 1.166(4) . ?
N2 C2 1.150(4) . ?
N3 C3 1.186(4) . ?
N4 C4 1.177(4) . ?
N5 C5 1.330(3) . ?
N5 C16 1.365(3) . ?
N6 C14 1.329(4) . ?
N6 C15 1.354(4) . ?
N7 C18 1.138(4) . ?
C5 C6 1.401(4) . ?
C5 H024 0.9500 . ?
C6 C7 1.367(4) . ?
C6 H021 0.9500 . ?
C7 C8 1.415(4) . ?
C7 H022 0.9500 . ?
C8 C16 1.396(4) . ?
C8 C9 1.433(4) . ?
C9 C10 1.370(4) . ?
C9 H020 0.9500 . ?
C10 C11 1.434(4) . ?
C10 H012 0.9500 . ?
C11 C15 1.402(4) . ?
C11 C12 1.414(4) . ?
C12 C13 1.374(4) . ?
C12 H016 0.9500 . ?
C13 C14 1.406(4) . ?
C13 H017 0.9500 . ?
C14 H027 0.9500 . ?
C15 C16 1.421(4) . ?
C17 C18 1.444(5) . ?
C17 H11A 0.9800 . ?
C17 H11B 0.9800 . ?
C17 H11C 0.9800 . ?

loop_
 _geom_angle_atom_site_label_1
 _geom_angle_atom_site_label_2
 _geom_angle_atom_site_label_3
 _geom_angle
 _geom_angle_site_symmetry_1
 _geom_angle_site_symmetry_3
 _geom_angle_publ_flag
N1 Si1 N2 97.68(12) . . ?
N1 Si1 N3 93.09(13) . . ?
N2 Si1 N3 93.47(12) . . ?
N1 Si1 N4 92.79(13) . . ?
```

```
N2 Si1 N4 92.22(13) . . ?
N3 Si1 N4 171.21(11) . . ?
N1 Si1 N5 171.64(12) . . ?
N2 Si1 N5 90.68(11) . . ?
N3 Si1 N5 86.27(11) . . ?
N4 Si1 N5 86.97(11) . . ?
N1 Si1 N6 90.42(11) . . ?
N2 Si1 N6 171.89(12) . . ?
N3 Si1 N6 86.52(11) . . ?
N4 Si1 N6 86.91(11) . . ?
N5 Si1 N6 81.22(10) . . ?
C1 N1 Si1 164.6(3) . . ?
C2 N2 Si1 167.0(3) . . ?
C3 N3 Si1 143.4(2) . . ?
C4 N4 Si1 150.9(3) . . ?
C5 N5 C16 117.8(2) . . ?
C5 N5 Si1 128.1(2) . . ?
C16 N5 Si1 114.08(18) . . ?
C14 N6 C15 118.1(3) . . ?
C14 N6 Si1 128.0(2) . . ?
C15 N6 Si1 113.96(19) . . ?
N1 C1 O1 178.6(3) . . ?
N2 C2 O2 178.0(4) . . ?
N3 C3 O3 176.9(3) . . ?
N4 C4 O4 177.6(4) . . ?
N5 C5 C6 121.9(3) . . ?
N5 C5 H024 119.0 . . ?
C6 C5 H024 119.0 . . ?
C7 C6 C5 120.8(3) . . ?
C7 C6 H021 119.6 . . ?
C5 C6 H021 119.6 . . ?
C6 C7 C8 118.5(3) . . ?
C6 C7 H022 120.8 . . ?
C8 C7 H022 120.8 . . ?
C16 C8 C7 117.3(3) . . ?
C16 C8 C9 118.1(3) . . ?
C7 C8 C9 124.6(3) . . ?
C10 C9 C8 121.1(3) . . ?
C10 C9 H020 119.4 . . ?
C8 C9 H020 119.4 . . ?
C9 C10 C11 120.8(3) . . ?
C9 C10 H012 119.6 . . ?
C11 C10 H012 119.6 . . ?
C15 C11 C12 116.3(3) . . ?
C15 C11 C10 118.8(2) . . ?
C12 C11 C10 124.9(3) . . ?
C13 C12 C11 119.1(3) . . ?
C13 C12 H016 120.4 . . ?
C11 C12 H016 120.4 . . ?
C12 C13 C14 120.3(3) . . ?
C12 C13 H017 119.8 . . ?
C14 C13 H017 119.8 . . ?
N6 C14 C13 121.7(3) . . ?
N6 C14 H027 119.1 . . ?
C13 C14 H027 119.1 . . ?
N6 C15 C11 124.4(2) . . ?
N6 C15 C16 115.7(2) . . ?
C11 C15 C16 119.8(2) . . ?
N5 C16 C8 123.7(3) . . ?
N5 C16 C15 114.9(2) . . ?
C8 C16 C15 121.4(2) . . ?
```

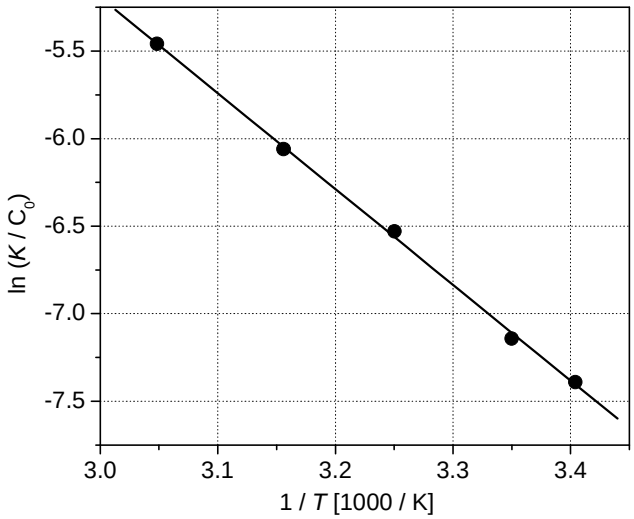
```
C18 C17 H11A 109.5 . . ?
C18 C17 H11B 109.5 . . ?
H11A C17 H11B 109.5 . . ?
C18 C17 H11C 109.5 . . ?
H11A C17 H11C 109.5 . . ?
H11B C17 H11C 109.5 . . ?
N7 C18 C17 179.4(4) . . ?

_diffrn_measured_fraction_theta_max    0.998
_diffrn_reflns_theta_full              25.00
_diffrn_measured_fraction_theta_full   0.998
_refine_diff_density_max    0.265
_refine_diff_density_min   -0.187
_refine_diff_density_rms    0.051
```

6) Variable temperature NMR spectra of compound 3

^{1}H NMR spectra were recorded of a solution of compound **3** in acetonitrile-d^3, c = 0.021(+/-0.006) mol dm^{-3}. The thermodynamic equilibrium constants were calculated from the ratios of integrated peaks arising from **3** and bpy. The following data was obtained:

Exp. No	T [°C]	thermodynamic equilibrium constant
1	20.6	6.17×10^{-4}
2	54.9	4.26×10^{-3}
3	43.7	2.33×10^{-3}
4	34.5	1.46×10^{-3}
5	25.35	7.90×10^{-4}



The standard enthalpy ($\Delta H°$), entropy ($\Delta S°$) and free energy ($\Delta G°$) of the equilibrium reaction, $Si(NCO)_4(bpy) \leftrightarrow Si(NCO)_4$ + bpy, were obtained from the slope and intercept of a van't Hoff plot, $\Delta H°$ = +45 kJ mol^{-1}, $\Delta S°$ = +93 J mol^{-1} K^{-1}, $\Delta G°$ = +18 kJ mol^{-1} (c_0 = 1 mol dm^{-3}). This results in K' = 7.9×10^{-3} mol dm^{-3} at 298 K and the complex stability constant pK = 3 for $Si(NCO)_4(bpy)$, **3**.