

3,3',5,5'-Tetramethyl-4,4'-bipyrazole–  
pentafluorophenol (2/3)

Konstantin V. Domasevitch

Inorganic Chemistry Department, Kiev University, Volodimirska Street 64, Kiev  
01033, Ukraine

Correspondence e-mail: dk@univ.kiev.ua

Received 30 January 2008

Accepted 7 May 2008

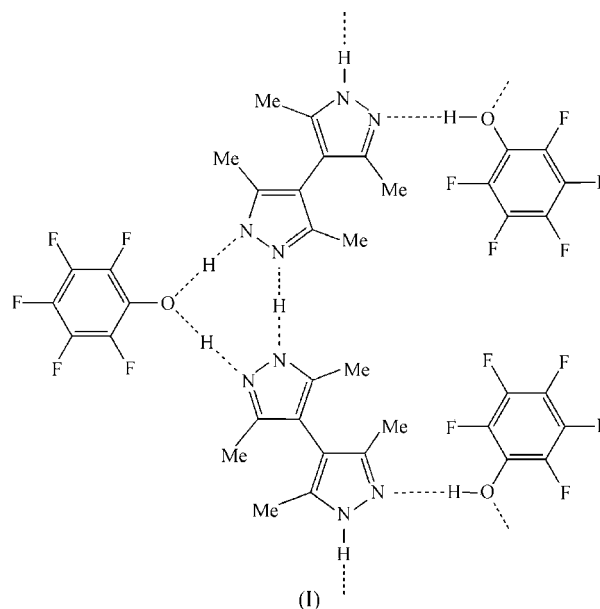
Online 14 May 2008

In the title compound,  $2C_{10}H_{14}N_4 \cdot 3C_6HF_5O$ , one of the pentafluorophenol molecules resides on a mirror plane bisecting the  $O \cdots F$  axis. The components aggregate by  $N-H \cdots N$ ,  $N-H \cdots O$  and  $O-H \cdots N$  hydrogen bonds involving equal disordering of the H atoms into molecular ensembles based on a 2:1 pyrazole–phenol cyclic pattern [ $O \cdots N = 2.7768$  (16) Å and  $N \cdots N = 2.859$  (2) Å], crosslinked into one-dimensional columns *via* hydrogen bonding between the outer pyrazole groups and additional pentafluorophenol molecules. The latter yields a 1:1 pyrazole–phenol catemer with alternating strong  $O-H \cdots N$  [2.5975 (16) Å] and weaker  $N-H \cdots O$  [2.8719 (17) Å] hydrogen bonds. This is the first reported molecular adduct of a pentafluorinated phenol and a nitrogen base, and suggests the utility of highly acidic phenols and pyrazoles for developing hydrogen-bonded cocrystals.

## Comment

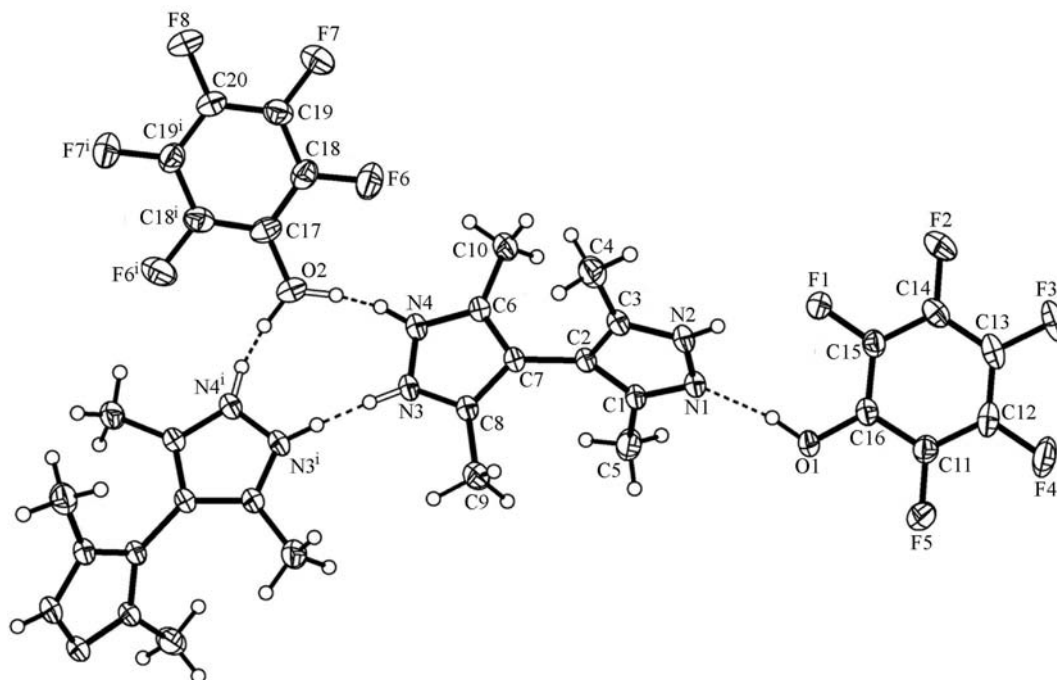
N-Unsubstituted pyrazoles provide rich and versatile possibilities for engineering of hydrogen-bonded solids (Desiraju, 1989), since the molecular frame combines bond donor (NH) and acceptor (N) sites for self-association (Foces-Foces *et al.*, 2000) or for exploitation of characteristic interactions in multicomponent systems. Thus, the hydrogen-bonding functionalities of pyrazoles and phenols complement one another, and these species commonly cocrystallize forming binary adducts in which the components are rationally integrated by  $N-H \cdots O$  and  $O-H \cdots N$  bonding (Boldog *et al.*, 2004). Such incorporation of a strong OH bond-donor unit within the pyrazole catemer is interesting in view of the solid-state tautomerism of pyrazoles (*e.g.*  $N-H \cdots N$  to  $N \cdots H-N$ ; Aguilar-Parrilla *et al.*, 1992) as a tool for enhancing the strength of partial bonding contributions (Steiner, 2002) and the promotion of the proton dynamics leading to long-range fast proton transfer. Therefore, it is of interest to explore whether the highly acidic phenols are applicable for the design of molecular adducts with pyrazoles and if the catemeric motif dominates the structure over the formation of different cyclic

patterns. In this context, we examined 3,3',5,5'-tetramethyl-4,4'-bipyrazole ( $Me_4bpz$ ), the only pyrazole exhibiting catemer/trimer supramolecular isomerism (Boldog *et al.*, 2003), and pentafluorophenol, where the acidity is comparable to that of carbonic acids ( $pK_a = 5.50$  versus 9.95 for phenol).



Compound (I) is the first structurally examined genuine molecular adduct formed by pentafluorophenol and a nitrogen base, unlike the ionic pentafluorophenolate of highly basic 1,8-bis(dimethylamino)naphthalene (Odiaga *et al.*, 1992). The asymmetric unit of (I) includes molecular components lying in general positions and a molecule of pentafluorophenol with the  $O2 \cdots F8$  axis located on a mirror plane (Fig. 1). The primary interaction of the pyrazole and phenol functions occurs by means of  $N-H \cdots N$ ,  $N-H \cdots O$  and  $O-H \cdots N$  hydrogen bonding, which yields a combination of two distinct supramolecular motifs.

Firstly, two pyrazole and one phenol group form a rare cyclic pattern, which is related to characteristic pyrazole trimers (Foces-Foces *et al.*, 2000) with the substitution of phenol for one of the pyrazole units. A similar hydrogen-bonded ring incorporating a water molecule was observed for the series of isostructural adducts  $(Me_4bpz)_3(H_2O)(L)$  ( $L$  is acetone, ethyl acetate and tetrahydrofuran; Boldog *et al.*, 2001). Since the two bipyrazole molecules of the  $(Me_4bpz)_2 \cdot (C_6F_5OH)$  cyclic unit are related by a mirror plane (symmetry code:  $x, -y + \frac{3}{2}, z$ ), the donor and acceptor sites of the hydrogen bond are not distinguishable and the H atoms are equally disordered over two positions (Fig. 1). Accordingly, the two  $N \cdots O$  separations are equivalent by symmetry [ $N4 \cdots O2 = 2.7768$  (16) Å] and are intermediate between the lengths of  $N-H \cdots O$  (2.92 Å) and  $O-H \cdots N$  (2.70 Å) bonds in a 1:1 adduct of 3,5-dimethylpyrazole and phenol (Boldog *et al.*, 2004). The pentafluorophenol unit is oriented at  $30.69$  (5)° to the plane of the two adjacent pyrazole rings, while the bipyrazole molecule has a twisted conformation with a dihe-



**Figure 1**

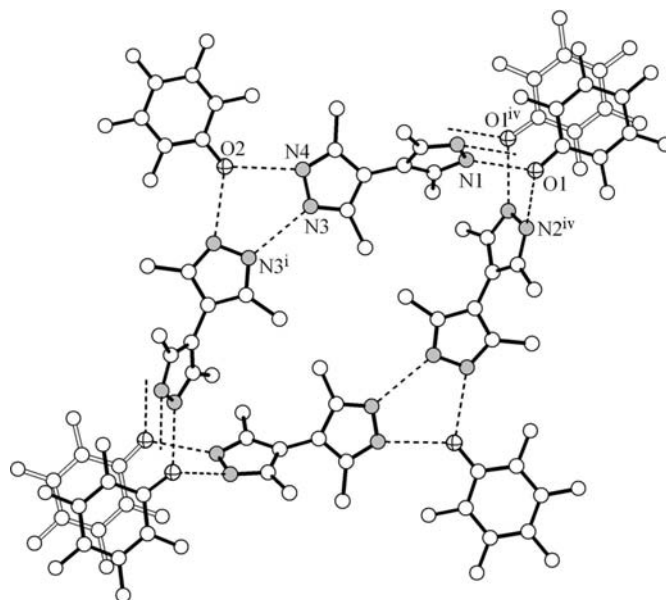
A view of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. Atoms O2, C17, C20 and F8 are located on a mirror plane and therefore the H atoms within the pyrazole/phenol rings are equally disordered by symmetry. [Symmetry code: (i)  $-x, -y + \frac{3}{2}, z$ .]

dral angle of  $72.16(6)^\circ$  between the two pyrazole groups [torsion angle  $C1-C2-C7-C8 = 72.8(2)^\circ$ ].

Secondly, the hydrogen bonding between the outer pyrazole groups and the second pentafluorophenol molecule yields an infinite alternating  $-A(BA)_n-$  motif, which may be viewed as a typical pyrazole catemer expanded by inclusion of a second component. Successive aggregates of  $(Me_4bpz)_2(C_6F_5OH)$  are related by a  $2_1$  axis (symmetry code:  $x + \frac{1}{2}, -y + \frac{3}{2}, -z + \frac{1}{2}$ ), and the phenol linkers provide integration of the units into columns along the  $x$ -axis direction (Figs. 2 and 3). There is a clear differentiation in the  $N \cdots O$  separations, suggesting two distinct types of hydrogen bonding and ordering of the H atoms. The first indicates a strong interaction [ $O1-H10 \cdots N1 = 2.5975(16) \text{ \AA}$ ], while for the bond involving the pyrazole NH donor, the N and O atoms are much more distal [ $N2-H2N \cdots O1^{iv} = 2.8719(17) \text{ \AA}$ ; symmetry code: (ii)  $x - \frac{1}{2}, y, -z + \frac{1}{2}$ ]. The only precedent for an  $O-H \cdots N$  interaction of fluorinated phenols is a  $2.64 \text{ \AA}$  intermolecular bond in 4'-(4-hydroxy-2,3,5,6-tetrafluorophenyl)-2,2':6',2''-terpyridine (Constable *et al.*, 2003).

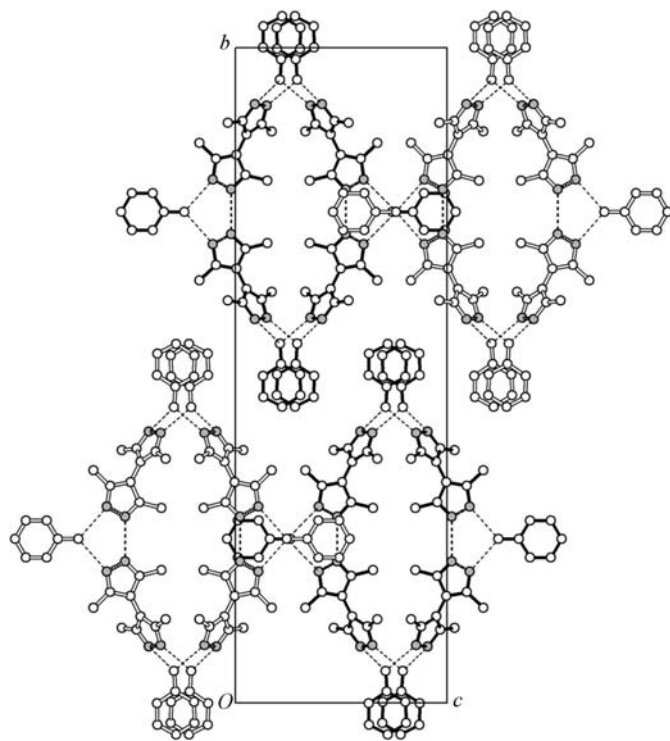
Ordering of the H atoms in the catemer is supported by the internal angles involving the N atoms [ $C1-N1-N2 = 105.46(12)^\circ$  and  $N1-N2-C3 = 112.50(12)^\circ$ ], which are most sensitive to the tautomerism of pyrazole (Alkorta *et al.*, 1999). Such differentiation agrees with the  $C-N-N(H)$  and  $C-N(H)-N$  angles ( $104.0-106.7$  and  $111.1-113.0^\circ$ , respectively) for hydrogen-bonded  $Me_4bpz$  structures (Table 2), while convergence of these parameters is a positive sign for the disordering of the H atoms, as occurs for the cyclic pattern in  $(Me_4bpz)_2(C_6F_5OH)$ .

Several types of weaker interactions are also relevant in the crystal packing. Along the catemer, the pentafluorophenol molecules are situated almost parallel to one another (symmetry code:  $x + \frac{1}{2}, y, -z + \frac{1}{2}$ ; Fig. 2) and afford a weak slipped  $\pi-\pi$  stack with an intercentroid distance of  $3.588(2) \text{ \AA}$ .



**Figure 2**

Interconnection of the  $(Me_4bpz)_2(C_6F_5OH)$  ensembles in (I) by hydrogen bonding involving the outer pyrazole and pentafluorophenol rings with the alternating  $[(pyrazole)/(phenol)]_n$  catemer. Dashed lines indicate hydrogen bonds. H atoms have been omitted for clarity and N atoms are shaded gray. [Symmetry codes: (i)  $-x, -y + \frac{3}{2}, z$ ; (iv)  $x + \frac{1}{2}, y, -z + \frac{1}{2}$ .]

**Figure 3**

A view of (I) along the direction of the hydrogen-bonded columns, showing the interdigitation of the pentafluorophenyl groups (projection on to the *bc* plane). F atoms have been omitted for clarity.

and an interplanar angle of  $12.13(4)^\circ$ . Interdigitation of the columns (Fig. 3) leads to close contacts between the C6–C8/N3/N4 pyrazole ring and atom F7<sup>v</sup> [symmetry code: (v)  $x + \frac{1}{2}, y, -z + \frac{3}{2}$ ], situated almost exactly above the ring centroid [ $\pi \cdots \text{F}^{\text{v}} = 3.287(2) \text{ \AA}$ , with the  $\text{F} \cdots \pi$  axis making an angle to the aromatic plane of  $85.2(2)^\circ$ ]. Such stacking commonly occurs for N-heterocycles and negatively polarized atoms, and is especially characteristic for the most electron-deficient azines and counter-anions (Schottel *et al.*, 2008). The short C10 $\cdots$ F3<sup>vi</sup> separations [ $3.288(2) \text{ \AA}$ ; symmetry code: (vi)  $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$ ] may be attributed to very weak C–H $\cdots$ F bonding ( $\text{H} \cdots \text{F}^{\text{vi}} = 2.59 \text{ \AA}$  and C10–H10B $\cdots$ F3<sup>vi</sup> =  $129^\circ$ ) (Desiraju & Steiner, 1999).

In conclusion, (I) suggests the utility of pyrazoles and highly acidic fluorinated phenols as complementary components for the development of hydrogen-bonded cocrystals. The efficient hydrogen-bond-donor properties of pentafluorophenol allow its integration within either cyclic or infinite supramolecular pyrazole motifs. The (pz)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>OH) ring displays disordering of the NH and OH H atoms, while along the two-component catemer the H atoms are ordered and immobile.

## Experimental

Me<sub>4</sub>bpz was synthesized according to the method reported by Mosby (1957). Large colorless crystals of (I) were prepared by slow evaporation of a solution of Me<sub>4</sub>bpz (0.190 g, 1 mmol) and pentafluorophenol (0.184 g, 1 mmol) in methanol (5 ml).

## Crystal data

2C<sub>10</sub>H<sub>14</sub>N<sub>4</sub>·3C<sub>6</sub>HF<sub>5</sub>O  
*M<sub>r</sub>* = 932.71  
 Orthorhombic, *Pnma*  
*a* = 6.9565 (7) Å  
*b* = 41.727 (4) Å  
*c* = 13.4827 (15) Å

*V* = 3913.6 (7) Å<sup>3</sup>  
*Z* = 4  
 Mo Kα radiation  
 $\mu$  = 0.15 mm<sup>−1</sup>  
*T* = 213 (2) K  
 0.27 × 0.20 × 0.20 mm

## Data collection

Siemens SMART CCD area-detector diffractometer  
 Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.950, *T<sub>max</sub>* = 0.980

13762 measured reflections  
 4321 independent reflections  
 3634 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.021

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.105$   
*S* = 1.03  
 4321 reflections

297 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$

**Table 1**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1O $\cdots$ N1	0.90	1.71	2.5975 (16)	168
O2—H2O $\cdots$ N4 <sup>i</sup>	0.92	1.90	2.7768 (16)	158
N2—H2N $\cdots$ O1 <sup>ii</sup>	0.90	2.10	2.8719 (17)	143
N3—H3N $\cdots$ N3 <sup>i</sup>	0.85	2.01	2.859 (2)	176
N4—H4N $\cdots$ O2	0.89	1.92	2.7768 (16)	161

Symmetry codes: (i)  $x, -y + \frac{3}{2}, z$ ; (ii)  $x - \frac{1}{2}, y, -z + \frac{1}{2}$ .

**Table 2**

Representative hydrogen-bonded structures of Me<sub>4</sub>bpz, involving ordering or disordering of the pyrazole NH atoms.

Compound	Motif	C—N(H)—N (°)	C—N—N(H) (°)	H-atom position
α-Me <sub>4</sub> bpz <sup>a</sup>	pz catemer	113.0 (2)	104.1 (2)	Ordered
β-Me <sub>4</sub> bpz <sup>a</sup>	pz catemer	109.9 (2) 108.0 (2)	—	Disordered
γ-Me <sub>4</sub> bpz <sup>b</sup>	pz trimer	111.2 (2)	106.7 (2)	Ordered
(Me <sub>4</sub> bpz)- [ <i>m</i> -C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub> ] <sup>c</sup>	NH $\cdots$ π Catemer [(pz)(OH)]	112.85 (15) 112.76 (17)	104.31 (15) 104.80 (17)	Ordered Ordered
(Me <sub>4</sub> bpz) <sub>2</sub> - (C <sub>6</sub> F <sub>5</sub> OH) <sub>3</sub> <sup>d</sup>	Cycle [(pz) <sub>2</sub> (OH)] Catemer [(pz)(OH)]	108.61 (11) 108.88 (12) 112.50 (12)	— — 105.46 (12)	Disordered — Ordered

References: (a) Boldog *et al.* (2001); (b) Boldog *et al.* (2003); (c) Boldog *et al.* (2004); (d) this paper.

Methyl H atoms were treated as riding in geometrically idealized positions, with C—H distances of 0.97 Å and *U<sub>iso</sub>*(H) values of 1.5*U<sub>eq</sub>*(C), and with equal idealized disordering of the H atoms bonded to atoms C4, C9 and C10. H atoms bonded to N and O atoms were located in difference maps and their coordinates were fixed [with *U<sub>iso</sub>*(H) = 1.5*U<sub>eq</sub>*(O,N)], giving O—H distances of 0.90 and 0.92 Å, and a range of N—H distances of 0.85–0.90 Å. H atoms

bonded to atoms O2, N3 and N4 were included with partial occupancy factors of 0.5, considering a disordering scheme for hydrogen bonding within the cyclic pyrazole/phenol pattern.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-NT* (Bruker, 1999); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Version 1.700.00; Farrugia, 1999).

We acknowledge support from Deutsche Forschungsgemeinschaft (grant No. UKR 17/1/06).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3148). Services for accessing these data are described at the back of the journal.

## References

- Aguilar-Parrilla, F., Gerd Scherer, G., Limbach, H. H., Foces-Foces, C., Cano, F. H., Smith, J. A. S., Toiron, C. & Elguero, J. (1992). *J. Am. Chem. Soc.* **114**, 9657–9659.
- Alkorta, I., Elguero, J., Donnadiou, B., Etienne, M., Jaffart, J., Shagen, D. & Limbach, H.-H. (1999). *New J. Chem.* **23**, 1231–1237.
- Boldog, I., Rusanov, E. B., Chernega, A. N., Siler, J. & Domasevitch, K. V. (2001). *Angew. Chem. Int. Ed.* **40**, 3435–3438.
- Boldog, I., Rusanov, E. B., Siler, J., Blaurock, S. & Domasevitch, K. V. (2003). *Chem. Commun.* pp. 740–741.
- Boldog, I., Rusanov, E. B., Siler, J. & Domasevitch, K. V. (2004). *New J. Chem.* **28**, 756–759.
- Brandenburg, K. (1999). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.
- Bruker (1998). *SMART-NT*. Version 5.0. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *SAINT-NT*. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
- Constable, E. C., Kariuki, B. & Mahmood, A. (2003). *Polyhedron*, **22**, 687–698.
- Desiraju, G. R. (1989). *Crystal Engineering: The Design of Organic Solids*. New York: Elsevier.
- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*. New York: Oxford University Press.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Foces-Foces, C., Alkorta, I. & Elguero, J. (2000). *Acta Cryst.* **B56**, 1018–1028.
- Mosby, W. L. (1957). *J. Chem. Soc.* pp. 3997–4003.
- Odiaga, N., Kanters, J. A., Lutz, B. T. G. & Grech, E. (1992). *J. Mol. Struct.* **273**, 183–195.
- Schottel, B. L., Chifotides, H. T. & Dunbar, K. R. (2008). *Chem. Soc. Rev.* **37**, 68–83.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Steiner, T. (2002). *Angew. Chem. Int. Ed.* **41**, 48–76.