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Secondary interactions in *n*-(chloromethyl)pyridinium chlorides (*n* = 2, 3, 4)

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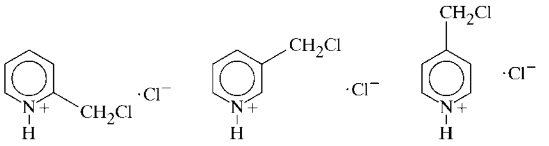
In the isomeric title compounds, *viz*. 2-, 3- and 4-(chloromethyl)pyridinium chloride, $C_6H_7ClN^+\cdot Cl^-$, the secondary interactions have been established as follows. Classical N—H···Cl^- hydrogen bonds are observed in the 2- and 3-isomers, whereas the 4-isomer forms inversion-symmetric N—H(···Cl^-···)$_2$H—N dimers involving three-centre hydrogen bonds. Short Cl···Cl contacts are formed in both the 2-isomer (C—Cl···Cl^-, approximately linear at the central Cl) and the 4-isomer (C—Cl···Cl—C, angles at Cl of *ca* 75°). Additionally, each compound displays contacts of the form C—H···Cl, mainly to the Cl^- anion. The net effect is to create either a layer structure (3-isomer) or a three-dimensional packing with easily identifiable layer substructures (2- and 4-isomers).

Comment

We are interested in secondary bonding interactions (generally hydrogen bonds and halogen–halogen contacts) in halides of simple halogenated nitrogen bases, such as anilines (Gray & Jones, 2002, and references therein) and pyridines (Freytag & Jones, 2001, and references therein). Here, we present the structures of the series of isomers 2-, 3- and 4-(chloromethyl)pyridinium chloride, denoted (I), (II) and (III), respectively.



2-isomer, (I) 3-isomer, (II) 4-isomer, (III)

All three structures crystallize without imposed symmetry. For reasons discussed below, each is shown as a hydrogen-bonded dimer in Figs. 1–3. The numbering is standard; C7 is the methylene C atom and Cl2 the Cl^- anion.

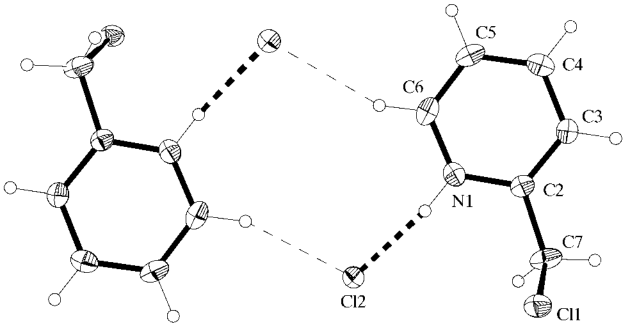


Figure 1
A view of the dimeric unit of the 2-isomer in the crystal. Only the asymmetric unit is numbered. Ellipsoids represent 50% probability levels and H-atom radii are arbitrary. Classical hydrogen bonds are shown as thick dashed lines and C—H···Cl hydrogen bonds as thin dashed lines.

The structures of the cations of (I), (II) and (III) are unexceptional. Common features, consistent with previous observations (Freytag & Jones, 2001), include wider ring angles at the N atom (*ca* 122–123°), slightly narrow ring angles at the CH_2Cl substituent (*ca* 119°) and C—N bond lengths of *ca* 1.32–1.35 Å. For the 2- and 3-isomers, the substituent is rotated by *ca* 70° out of the ring plane, but for the 4-isomer, it is approximately coplanar with the ring. This may explain the wide C3—C4—C7 angle (for values, see Tables 1, 3 and 5).

As in the series of chloropyridines (Freytag & Jones, 2001; Freytag *et al.*, 1999), the main interest centres on the packing

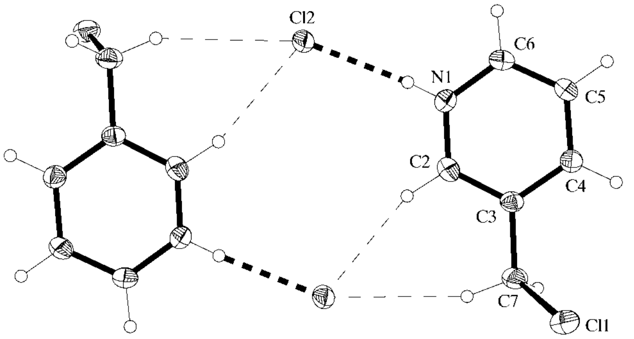


Figure 2
A view of the dimeric unit of the 3-isomer in the crystal. Only the asymmetric unit is numbered. Ellipsoids represent 50% probability levels and H-atom radii are arbitrary. Classical hydrogen bonds are shown as thick dashed lines and C—H···Cl hydrogen bonds as thin dashed lines.

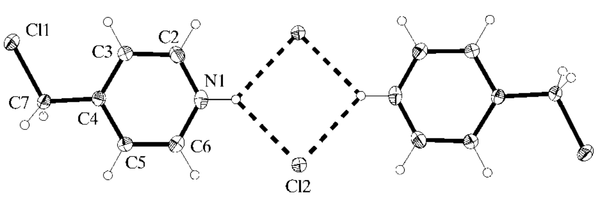


Figure 3
A view of the dimeric unit of the 4-isomer in the crystal. Only the asymmetric unit is numbered. Ellipsoids represent 50% probability levels and H-atom radii are arbitrary. Classical (but three-centre) hydrogen bonds are shown as thick dashed lines.

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features. In the 2-isomer, (I), the classical N—H···Cl$^-$ hydrogen bond combines with the shortest H···Cl interaction, C6—H6···Cl2, to form a centrosymmetric dimer (Fig. 1). The central $R_4^4(10)$ ring is easily recognisable in the extended packing diagram (Fig. 4), which involves three additional H···Cl interactions (Table 2) and a Cl1···Cl2^{i} contact of 3.5505 (7) Å [symmetry code: (i) $2 - x$, $1 - y$, $1 - z$; C—Cl···Cl = 157.26 (4)°]. Although the packing is three-dimensional, vertical layers perpendicular to the *b* axis at $y \simeq \frac{1}{4}, \frac{3}{4}$, *etc*., are easily recognisable and can be seen edge-on in Fig. 4(*a*). Perhaps ironically, these layers involve all the secondary contacts apart from the classical hydrogen bond. The perpendicular view on to such a layer is given in Fig. 4(*b*).

In the 3-isomer, (II), a centrosymmetric dimeric unit can be constructed that involves the classical N—H···Cl$^-$ hydrogen bond, the very short H2···Cl2 interaction and the H7*B*···Cl2 interaction (Fig. 2). The dimers are linked by H6···Cl2 interactions to form layers perpendicular to the *bc* plane at $x \simeq 0, \frac{1}{2}, 1$, *etc*. (Fig. 5). The other H···Cl contacts (Table 4) are all much longer (≥ 2.93 Å). There are no significant Cl···Cl contacts; the shortest contact is Cl1···Cl1^{ii} of 3.9210 (10) Å [symmetry code: (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$].

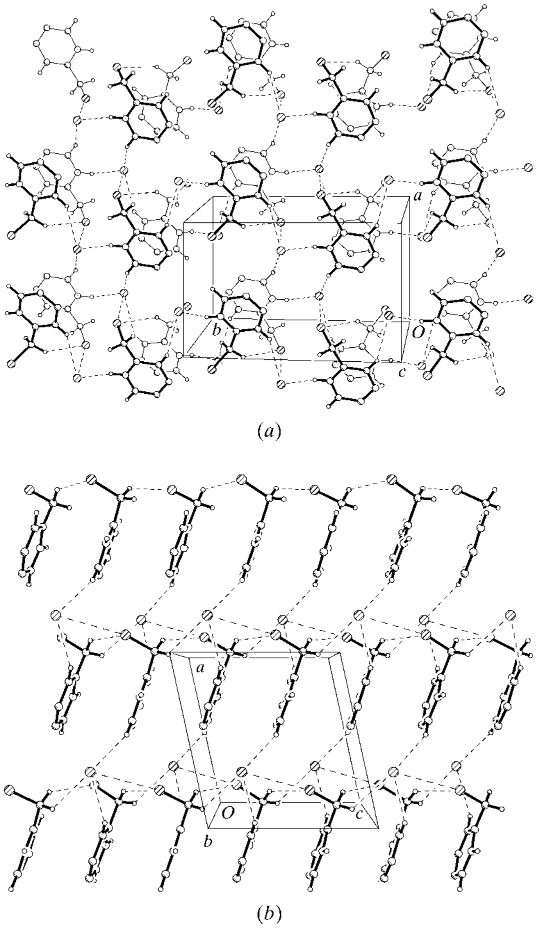

Figure 4
The crystal packing of the 2-isomer. (*a*) The view direction is approximately perpendicular to the *ab* plane. Atom radii are arbitrary and only H atoms participating in hydrogen bonding are included. Hydrogen bonds and Cl···Cl interactions (see text) are shown as dashed lines. Molecules shown with thin bonds are farther away from the viewer. (*b*) Perpendicular view on to the layer at $y \simeq \frac{1}{4}$ (classical hydrogen bonds are not involved in these layers; see text).

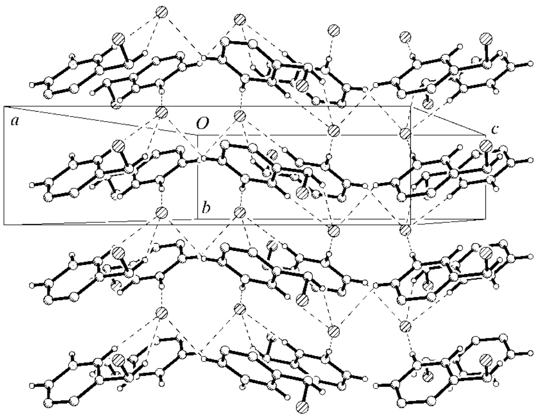

Figure 5
The crystal packing of the 3-isomer. The view direction is approximately perpendicular to the *bc* plane. Atom radii are arbitrary and only H atoms participating in hydrogen bonding are included. Hydrogen bonds and Cl···Cl interactions (see text) are shown as dashed lines. The layer shown is at $x \simeq \frac{1}{2}$.

In the 4-isomer, (III), centrosymmetric dimers (Fig. 3) are built up *via* a three-centre N—H(···Cl)$_2$ hydrogen bond. Within this dimer, the short and highly angled H2···Cl2 and H6···Cl2 contacts are probably imposed by the three-centre hydrogen bond, rather than being of intrinsic significance. Further secondary interactions build up a three-dimensional packing, and the layer shown in Fig. 6 shows most of the salient features. The four-membered rings of Fig. 3 are capped above and below by another three-centre interaction, H7*B*···Cl2, to form distorted octahedra. The H7*A*···Cl2 hydrogen bond and, finally, the Cl1···Cl1^{iii} contact [3.6051 (6) Å, C—Cl···Cl = 74.54 (3)°; symmetry code: (iii) $1 -x, -y, -z$], link the octahedra to form a thick layer with the hydrophilic region at $x \simeq 0$. The next such layer, at $x \simeq 1$,

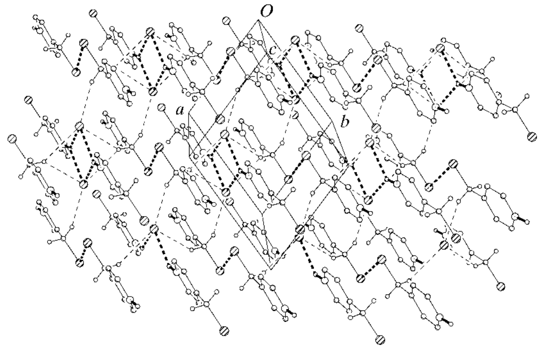

Figure 6
The crystal packing of the 4-isomer, showing a thick layer, centred at $x \simeq 0$, of the three-dimensional structure. The view direction is perpendicular to the *ab* plane. Atom radii are arbitrary and only H atoms participating in hydrogen bonding are included. Three-centre N—H(···Cl)$_2$ hydrogen bonds and Cl···Cl interactions are shown as thick dashed lines and other hydrogen bonds are shown as thin dashed lines.

provides the three-dimensional extension. The other two H···Cl contacts, involving atoms H3 and H6 (Table 6), are long and have narrow angles, but both lie within the layer of Fig. 6 (from which, however, they have been omitted for clarity) and may make a small contribution to the stability of the packing.

It is notable that the crystallographically determined density increases significantly in the order 2-isomer < 3-isomer < 4-isomer, as was also observed for the series of chloropyridines (Freytag & Jones, 2001; Freytag *et al.*, 1999). One might then postulate an increased efficiency of packing in the same sequence, but it is not easy to identify the factors concerned at the molecular level, beyond commenting that the isomer with the highest density also has the greatest number of hydrogen bonds.

Experimental

The title compounds were purchased from Avocado Research Chemicals Ltd and dried carefully under vacuum. Single crystals were obtained by liquid–liquid diffusion at 253 K from ethanol–diethyl ether for (I), and from dimethylformamide–diethyl ether for (II) and (III). Crystals of (I) are hygroscopic and those of (II) were so hygroscopic that they had to be transferred rapidly from the mother liquor to the mounting oil, thence to the glass fibre and finally to the cold gas stream. The crystals of (II), being thin needles, of necessity then lay at the side of the fibre in a moderately large oil drop. The long exposure times precluded the measurement of sufficient equivalents to perform an adequate absorption correction.

Compound (I)

Crystal data

$C_6H_7ClN^+\cdot Cl^-$
$M_r = 164.03$
Monoclinic, $P2_1/c$
$a = 7.9273$ (14) Å
$b = 12.721$ (2) Å
$c = 7.4773$ (14) Å
$\beta = 102.382$ (6)°
$V = 736.5$ (2) Å^3
$Z = 4$

$D_x = 1.479$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7727 reflections
$\theta = 2.6$–30.5°
$\mu = 0.79$ mm^{-1}
$T = 133$ (2) K
Lath, colourless
0.45 × 0.15 × 0.09 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*TWINABS*; Bruker, 2002)
$T_{min} = 0.795$, $T_{max} = 0.928$
15 781 measured reflections

2150 independent reflections
1864 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 30°$
$h = -11 \rightarrow 10$
$k = -0 \rightarrow 17$
$l = -0 \rightarrow 10$

Table 1
Selected geometric parameters (Å, °) for (I).

N1—C6	1.3411 (16)	N1—C2	1.3449 (16)
C6—N1—C2	122.78 (11)	N1—C2—C3	119.04 (11)
C3—C2—C7—Cl1	109.28 (12)		

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.071$
$S = 1.04$
2150 reflections
87 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2 + 0.0509P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H0···Cl2	0.89 (2)	2.08 (2)	2.9578 (12)	166 (2)
C3—H3···Cl2^{i}	0.95	2.75	3.5621 (13)	143
C6—H6···Cl2^{ii}	0.95	2.63	3.4730 (13)	148
C7—H7B···Cl2^{iii}	0.99	2.85	3.5296 (14)	126
C7—H7A···Cl1^{iv}	0.99	2.82	3.6603 (15)	143

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

Compound (II)

Crystal data

$C_6H_7ClN^+\cdot Cl^-$
$M_r = 164.03$
Monoclinic, $C2/c$
$a = 23.037$ (4) Å
$b = 4.3310$ (8) Å
$c = 14.855$ (3) Å
$\beta = 104.441$ (12)°
$V = 1435.3$ (5) Å^3
$Z = 8$

$D_x = 1.518$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3132 reflections
$\theta = 2.8$–30.4°
$\mu = 0.81$ mm^{-1}
$T = 133$ (2) K
Needle, colourless
0.50 × 0.06 × 0.03 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω and φ scans
8435 measured reflections
2098 independent reflections
1582 reflections with $I > 2\sigma(I)$

$R_{int} = 0.179$
$\theta_{max} = 30°$
$h = -32 \rightarrow 31$
$k = -6 \rightarrow 6$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.123$
$S = 1.01$
2098 reflections
86 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

N1—C2	1.326 (3)	N1—C6	1.328 (3)
C2—N1—C6	123.2 (2)	C2—C3—C4	118.05 (19)
C4—C3—C7—Cl1	66.3 (3)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl2	0.81 (3)	2.16 (3)	2.967 (2)	174 (3)
C2—H2···Cl2^{i}	0.95	2.53	3.443 (2)	161
C7—H7B···Cl2^{i}	0.99	2.81	3.720 (3)	153
C6—H6···Cl2^{ii}	0.95	2.69	3.383 (2)	130
C4—H4···Cl1^{iii}	0.95	2.93	3.636 (2)	132
C5—H5···Cl1^{iv}	0.95	2.93	3.640 (2)	133
C7—H7A···Cl1^{iii}	0.99	2.99	3.797 (3)	139
C7—H7A···Cl2^{v}	0.99	2.95	3.323 (2)	103

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

Compound (III)

Crystal data

$C_6H_7ClN^+·Cl^-$
M_r = 164.03
Triclinic, $P\overline{1}$
a = 6.9531 (4) Å
b = 7.4755 (6) Å
c = 7.4978 (4) Å
α = 71.119 (3)°
β = 75.731 (3)°
γ = 72.694 (3)°
V = 347.16 (4) Å^3
Z = 2
D_x = 1.569 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4785 reflections
θ = 2.9–30.5°
μ = 0.84 mm^{-1}
T = 133 (2) K
Tablet, colourless
0.3 × 0.2 × 0.1 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.797, T_{max} = 0.928
6548 measured reflections
2024 independent reflections
1856 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 30°
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -10 \rightarrow 10$

Table 5
Selected geometric parameters (Å, °) for (III).

N1—C2	1.3353 (15)	N1—C6	1.3466 (14)
C2—N1—C6	122.40 (9)	C3—C4—C7	124.51 (9)
C3—C4—C5	118.81 (9)		
C3—C4—C7—Cl1	−5.40 (14)		

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl2^{i}	0.93 (2)	2.54 (2)	3.2301 (10)	131.6 (15)
N1—H1···Cl2	0.93 (2)	2.44 (2)	3.1369 (10)	132.5 (15)
C2—H2···Cl2^{i}	0.95	2.84	3.3592 (11)	115
C6—H6···Cl2	0.95	2.84	3.3393 (11)	114
C7—H7B···Cl2^{ii}	0.99	2.90	3.7286 (11)	142
C7—H7B···Cl2^{iii}	0.99	2.96	3.6809 (12)	131
C7—H7A···Cl2^{iv}	0.99	2.74	3.6589 (11)	155
C6—H6···Cl1^{v}	0.95	2.90	3.5983 (12)	132
C3—H3···Cl2^{vi}	0.95	2.86	3.5141 (11)	127

Symmetry codes: (i) $-x, 1-y, 2-z$; (ii) $x, y, z-1$; (iii) $-x, 1-y, 1-z$; (iv) $1-x, 1-y, 1-z$; (v) $x, 1+y, z$; (vi) $x, y-1, z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.070
S = 1.12
2024 reflections
86 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.0639P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

The acidic H atoms (at N) were refined freely. The remaining H atoms were refined with a riding model, with C—H distances of 0.95 Å for aromatic C—H and of 0.99 Å for CH$_2$, and with U_{iso}(H) = 1.2U_{eq}(C). The crystal of (I) gave diffraction patterns suggestive of twinning; although a unit cell was found without difficulty, an appreciable number of significant reflections remained unindexed. The original data collection involved 12 218 reflections, of which 2138 were unique. The refinement gave satisfactory R values (R_{int} = 0.031 and R_1 = 0.039; however, wR_2 was rather high at 0.118) but unsatisfactory residual electron density (1.05 e Å^{-3}). Inspection with the program *GEMINI* (Bruker, 2002) clearly showed two twin domains related by a rotation of 180° about [00$\overline{1}$]. The data were integrated with *SAINT*32*A* (Bruker, 2002), which allows the use of two orientation matrices for the two twin domains. The program *TWINABS* 1.02 (Bruker, 2002) was used for scaling and merging. Because *SAINT* treats equivalent reflections independently, *ca* 30% of the data were integrated as non-overlapped, although their equivalents were overlapped by a reflection of the second domain. These reflections could not be merged, which led to an artificially high apparent number of data. Therefore, these data were omitted. The fractional contribution of the second domain refined to 0.1854 (12).

For all compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1509). Services for accessing these data are described at the back of the journal.

References

Bruker (1998). *SMART* (Version 5.0), *SAINT* (Version 4.0) and *SADABS* (Version 2.0). Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2002). *GEMINI* (Version 1.02), *SAINT*32*A* (Version 6.31A) and *TWINABS* (Version 1.02). Bruker AXS Inc., Madison, Wisconsin, USA.

Freytag, M. & Jones, P. G. (2001). *Z. Naturforsch. Teil B*, **56**, 889–896.

Freytag, M., Jones, P. G., Ahrens, B. & Fischer, A. K. (1999). *New J. Chem.* **23**, 1137–1138.

Gray, L. & Jones, P. G. (2002). *Z. Naturforsch. Teil B*, **57**, 73–82.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA.