

## Two hydration products of 3,4,5,6-tetrachloro-*N*-(methyl-2-pyridyl)-phthalmic acids

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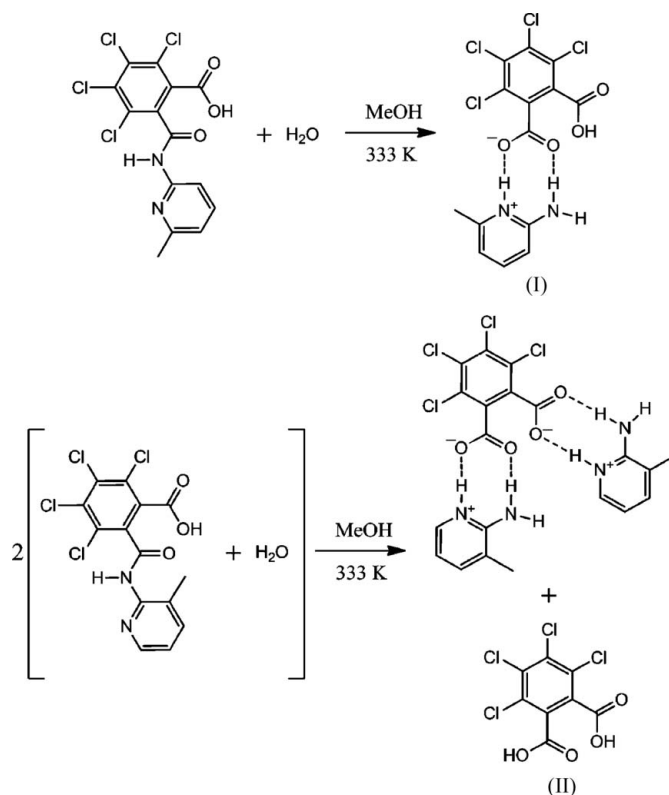
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In 2-amino-6-methylpyridin-1-ium 2-carboxy-3,4,5,6-tetrachlorobenzoate,  $C_6H_9N_2^+ \cdot C_8HCl_4O_4^-$ , there are two perpendicular chains of hydrogen-bonded ions, one arising from the interaction between 2-carboxy-3,4,5,6-tetrachlorobenzoate ions and the other from the interaction between the 2-amino-6-methylpyridin-1-ium and 2-carboxy-3,4,5,6-tetrachlorobenzoate ions. These chains combine to form a two-dimensional network of hydrogen-bonded ions. Cocrystals of bis(2-amino-3-methylpyridin-1-ium) 3,4,5,6-tetrachlorophthalate–3,4,5,6-tetrachlorophthalic acid (1/1),  $2C_6H_9N_2^+ \cdot C_8Cl_4O_4^{2-} \cdot C_8H_2Cl_4O_4$ , form finite aggregates of hydrogen-bonded ions.  $\pi$ – $\pi$  interactions are observed between 2-amino-3-methylpyridin-1-ium cations. Both structures exhibit the characteristic  $R_2^2(8)$  motif as a result of the hydrogen bonding between the 2-aminopyridinium and carboxylate units.

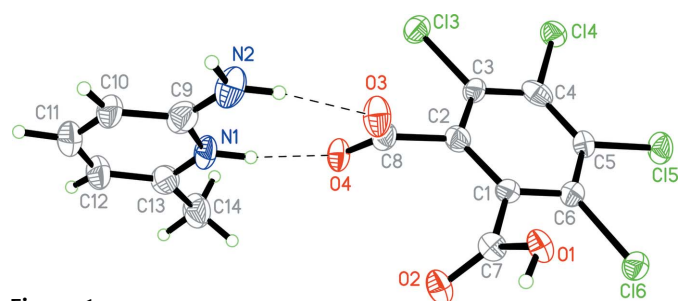
### Comment

*N*-(3-Methyl-2-pyridyl)-3,4,5,6-tetrachlorophthalic acid and *N*-(6-methyl-2-pyridyl)-3,4,5,6-tetrachlorophthalic acid are known to be pharmacologically active having been shown to exhibit a hypertensive effect in biological systems (Dolzhenko *et al.*, 2003). In the context of this study, these materials are of interest for their potential as a UV-active dye for dye-sensitized solar-cell applications. Heating these compounds to 333 K in hydrated methanol produces crystals of two salts, namely 2-amino-6-methylpyridin-1-ium 2-carboxy-3,4,5,6-tetrachlorobenzoate, (I) (Fig. 1), and bis(2-amino-3-methylpyridin-1-ium) 3,4,5,6-tetrachlorophthalate–3,4,5,6-tetrachlorophthalic acid (1/1), (II) (Fig. 2). These salts are the result of the reaction of the starting material with water present in the methanol solution and the equilibrium that exists between amides and water and the corresponding amines and carboxylic acids. In (I) and (II), protonation of the pyridyl N atom results in pyridinium salts stabilized by imino resonance.

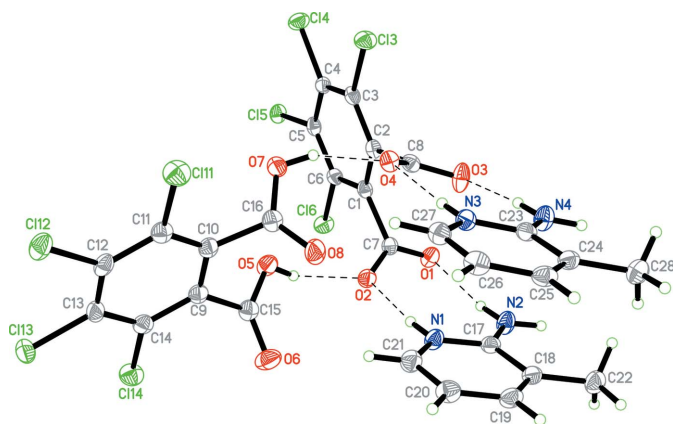
Interestingly, as 3,4,5,6-tetrachlorophthalic acid cocrystallizes with 2-amino-3-methylpyridin-1-ium 3,4,5,6-tetrachlorophthalate all the products of this reaction are represented stoichiometrically in the crystal structure.



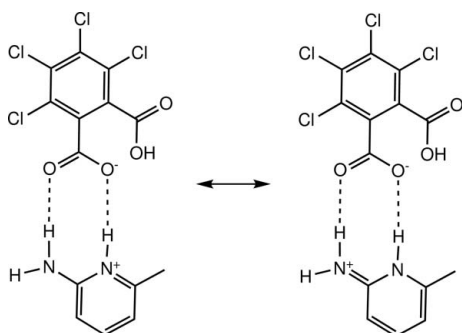
The molecular geometry of the 2-amino-6-methylpyridin-1-ium cation in the structure of (I) (Table 1) can be compared with that of the nonhalogenated 2-amino-6-methylpyridinium 2-formylbenzoate monohydrate (Büyükgüngör & Odabaşoğlu, 2006). This geometry is similar in both compounds, with the characteristic bond-length alternation within the pyridyl ring, which demonstrates the imino resonance stabilizing the positive charge (Fig. 3) (Zhi *et al.*, 2002). The bond geometry of the aromatic ring in the 2-carboxy-3,4,5,6-tetrachlorobenzoate anion in (I) resembles more closely that of the hemihydrate of 3,4,5,6-tetrachlorophthalic acid (Ito *et al.*, 1975) than that of the 2-carboxy-3,4,5,6-tetrachlorobenzoate in a similar salt, 2-methyl-5-ethylpyridinium 3,4,5,6-tetrachlorophthalate (Galloy *et al.*, 1976). This indicates a contribution from the neutral canonical form, which is also observed



**Figure 1**  
The structure of the asymmetric unit of (I), with atomic displacement ellipsoids drawn at the 50% probability level.



**Figure 2**  
The structure of the asymmetric unit of (II), with atomic displacement ellipsoids drawn at the 50% probability level.

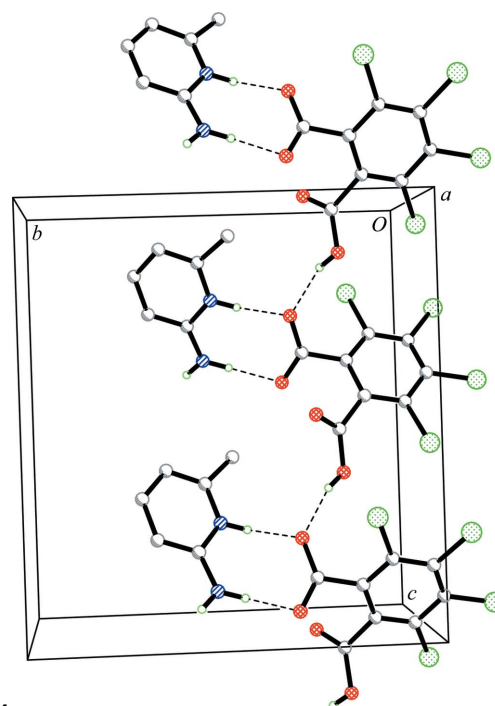


**Figure 3**  
The resonance exhibited by (I).

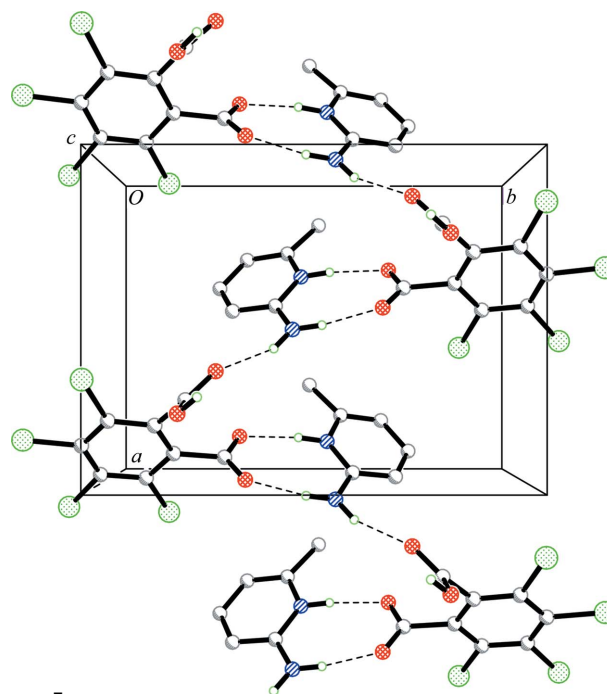
in the carboxylate group, where O3—C8 is observed to be shorter than O4—C8. The bond distances in the aromatic ring of 2-carboxy-3,4,5,6-tetrachlorobenzoate in (I) range from 1.374 (9) to 1.403 (9) Å.

Compound (I) forms continuous sheets of hydrogen-bonded ions parallel to (010) (Table 2). These sheets contain the characteristic rings having graph set  $R_2^2(8)$  (Etter, 1990; Bernstein *et al.*, 1995) with the amine and pyridinium N atoms acting as donors and the two carboxylate O atoms acting as acceptors (N1—H1N $\cdots$ O4 and N2—H2B $\cdots$ O3), as is well documented in this type of compound (Quah *et al.*, 2010; Hemamalini & Fun, 2010). These rings are linked by chain motifs to form the sheets. The 2-carboxy-3,4,5,6-tetrachlorobenzoate anions form chains parallel to the [001] direction through O1—H1 $\cdots$ O4<sup>ii</sup> interactions to give a graph-set motif of  $C(7)$  (symmetry codes as in Table 2). The 2-amino-6-methylpyridin-1-ium cations link *via* the anions forming chains with the graph sets  $C_2^2(9)$  (through N2—H2B $\cdots$ O3 and N2—H2A $\cdots$ O2<sup>i</sup>) and  $C_2^2(11)$  (through N1—H1N $\cdots$ O4 and N2—H2A $\cdots$ O2<sup>i</sup>), giving an overall  $C_2^2(9)C_2^2(11)[R_2^2(8)]$  chain of rings parallel to the [100] direction (Fig. 5).

The aromatic rings in the 2-amino-3-methylpyridin-1-ium cations of compound (II) exhibit similar geometry to those in (I) with regard to the bond distances (Table 3). The distances in the benzene rings of the 3,4,5,6-tetrachlorophthalate dianion and the 3,4,5,6-tetrachlorophthalic acid molecule are in the ranges 1.387 (3)–1.403 (2) and 1.389 (3)–1.399 (3) Å,

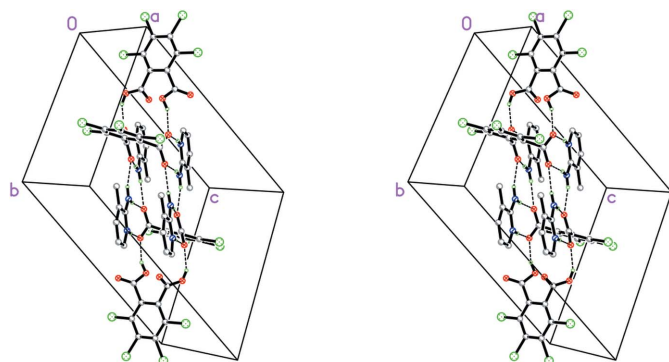


**Figure 4**  
View of the  $C(7)$  hydrogen-bonding motif in the [001] direction in (I). H atoms not involved in hydrogen bonding (dashed lines) have been omitted.



**Figure 5**  
View of the  $C_2^2(9)C_2^2(11)[R_2^2(8)]$  chain of rings along [100] in (I). H atoms not involved in hydrogen bonding (dashed lines) have been omitted.

respectively, altogether more consistent than the bond distances of the 2-carboxy-3,4,5,6-tetrachlorobenzoate anion in (I) or the hemihydrate of 3,4,5,6-tetrachlorophthalic acid. This similarity in bond geometry between the dianion and the neutral acid in (II) strengthens the argument for the contribution of the neutral canonical forms in these compounds. As



**Figure 6**

Stereoview of the finite hydrogen-bonding network in the structure of (II). H atoms not involved in hydrogen bonding (dashed lines) have been omitted.

is observed in similar structures (Ni *et al.*, 2007; Zhi *et al.*, 2002), there are  $\pi$ – $\pi$  interactions between 2-amino-3-methylpyridin-1-ium cations; the dihedral angle between the two pyridinium rings in the selected asymmetric unit is only  $3.8(2)^\circ$  and the corresponding centroid–centroid separation is  $3.834(2) \text{ \AA}$ .

Unlike the two-dimensional network observed in (I), the hydrogen-bonded system in (II) consists of a finite array of four 2-amino-3-methylpyridin-1-ium cations, two 3,4,5,6-tetrachlorophthalate dianions and two molecules of 3,4,5,6-tetrachlorophthalic acid (Fig. 6 and Table 4). The  $R_2^2(8)$  ring motifs formed between the pyridinium and phthalate ions are once again present, with each phthalate dianion forming two such rings parallel to each other because of the  $\pi$ – $\pi$  interactions between the pyridinium cations, *i.e.* through  $\text{N2} \cdots \text{H2A} \cdots \text{O1}$  and  $\text{N1} \cdots \text{H1N} \cdots \text{O2}$  for one ring, and  $\text{N4} \cdots \text{H4A} \cdots \text{O3}$  and  $\text{N3} \cdots \text{H3N} \cdots \text{O4}$  for the other. In addition to this, each of these rings is connected to an adjacent  $R_2^2(8)$  ring through  $\text{N2} \cdots \text{H2B} \cdots \text{O3}^i$  and  $\text{N4} \cdots \text{H4B} \cdots \text{O1}^i$  forming an  $[\text{R}_2^2(8)\text{R}_4^2(8)]$  motif within an outer  $\text{R}_4^4(16)$  ring (symmetry code is as in Table 4). Further motifs are observed when considering that there are two parallel  $[\text{R}_2^2(8)\text{R}_4^2(8)\text{R}_2^2(8)]$  motifs linked by the phthalate dianions; this gives rise to rings with graph sets  $\text{R}_4^4(18)$  and  $\text{R}_4^4(22)$ .

The 3,4,5,6-tetrachlorophthalic acid molecules and 3,4,5,6-tetrachlorophthalate dianions are also connected by hydrogen bonds with the acid protons donating to carboxylate O-atom acceptors through  $\text{O5} \cdots \text{H5O} \cdots \text{O2}$  and  $\text{O7} \cdots \text{H7O} \cdots \text{O4}$  to create  $\text{R}_2^2(14)$  motifs. Though there is no direct hydrogen bonding between the acid molecules and the pyridinium cations, rings with the graph set  $\text{R}_6^6(34)$  are formed between acid molecules through the  $[\text{R}_2^2(8)\text{R}_4^2(8)\text{R}_2^2(8)]$  motif.

## Experimental

*N*-(3-Methyl-2-pyridyl)-3,4,5,6-tetrachlorophthalic acid (10 mg, 0.026 mmol) and *N*-(6-methyl-2-pyridyl)-3,4,5,6-tetrachlorophthalic acid (10 mg, 0.026 mmol) were heated to 333 K in hydrated methanol (5 ml) until a clear solution was obtained. Colourless plate-like crystals of (I) were grown upon cooling to room temperature and colourless prism-like crystals of (II) grew after the solution was allowed to stand for one week.

## Compound (I)

### Crystal data

$\text{C}_6\text{H}_9\text{N}_2^+ \cdot \text{C}_8\text{HCl}_4\text{O}_4^-$	$V = 1623(4) \text{ \AA}^3$
$M_r = 412.04$	$Z = 4$
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation
$a = 9.441(14) \text{ \AA}$	$\mu = 0.75 \text{ mm}^{-1}$
$b = 12.56(2) \text{ \AA}$	$T = 120 \text{ K}$
$c = 13.69(2) \text{ \AA}$	$0.33 \times 0.16 \times 0.06 \text{ mm}$

### Data collection

Rigaku Saturn724+ ( $2 \times 2$ bin mode) diffractometer	5083 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	2495 independent reflections
$T_{\min} = 0.866$ , $T_{\max} = 0.956$	2302 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.048$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$	H-atom parameters constrained
$wR(F^2) = 0.127$	$\Delta\rho_{\text{max}} = 0.44 \text{ e \AA}^{-3}$
$S = 1.10$	$\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$
2495 reflections	Absolute structure: Flack (1983)
218 parameters	Flack parameter: $-0.31(13)$
1 restraint	

## Compound (II)

### Crystal data

$2\text{C}_6\text{H}_9\text{N}_2^+ \cdot \text{C}_8\text{Cl}_4\text{O}_4^{2-} \cdot \text{C}_8\text{H}_2\text{Cl}_4\text{O}_4$	$\gamma = 72.618(1)^\circ$
$M_r = 824.08$	$V = 1621.7(6) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.6972(17) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 13.762(3) \text{ \AA}$	$\mu = 0.75 \text{ mm}^{-1}$
$c = 15.381(3) \text{ \AA}$	$T = 120 \text{ K}$
$\alpha = 69.388(9)^\circ$	$0.41 \times 0.14 \times 0.12 \text{ mm}$
$\beta = 75.342(10)^\circ$	

### Data collection

Rigaku Saturn724+ ( $2 \times 2$ bin mode) diffractometer	9810 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	5964 independent reflections
$T_{\min} = 0.881$ , $T_{\max} = 0.914$	5551 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.033$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (I).

C7–O2	1.205(7)	C9–N1	1.361(9)
C7–O1	1.413(8)	C9–N2	1.402(10)
C8–O3	1.248(8)	C13–N1	1.427(10)
C8–O4	1.344(8)		
O2–C7–O1	127.0(6)	N1–C9–N2	124.9(6)
O3–C8–O4	134.0(5)	C9–N1–C13	129.2(5)

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I).

$D \cdots H \cdots A$	$D \cdots H$	$H \cdots A$	$D \cdots A$	$D \cdots H \cdots A$
$\text{N2} \cdots \text{H2B} \cdots \text{O3}$	0.86	1.81	2.666(8)	173
$\text{N2} \cdots \text{H2A} \cdots \text{O2}^i$	0.86	2.11	2.931(8)	159
$\text{N1} \cdots \text{H1N} \cdots \text{O4}$	0.86	1.71	2.559(7)	171
$\text{O1} \cdots \text{H1O} \cdots \text{O4}^{ii}$	0.82	1.83	2.604(7)	158

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

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

C7—O1	1.235 (3)	C16—O7	1.301 (3)
C7—O2	1.272 (3)	C17—N2	1.330 (3)
C8—O3	1.245 (3)	C17—N1	1.346 (3)
C8—O4	1.258 (3)	C21—N1	1.358 (3)
C15—O6	1.211 (3)	C23—N4	1.333 (3)
C15—O5	1.303 (3)	C23—N3	1.349 (3)
C16—O8	1.218 (3)	C27—N3	1.363 (3)
O1—C7—O2	125.39 (19)	N2—C17—N1	118.96 (19)
O3—C8—O4	124.88 (19)	C17—N1—C21	123.66 (18)
O6—C15—O5	126.7 (2)	N4—C23—N3	118.35 (18)
O8—C16—O7	126.1 (2)	C23—N3—C27	122.89 (18)

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

D—H...A	D—H	H...A	D...A	D—H...A
O5—H5O...O2	0.84	1.80	2.558 (2)	149
O7—H7O...O4	0.84	1.83	2.593 (2)	151
N1—H1N...O2	0.88	1.83	2.708 (2)	173
N2—H2A...O1	0.88	2.07	2.943 (2)	171
N3—H3N...O4	0.88	2.01	2.891 (2)	175
N4—H4A...O3	0.88	1.93	2.805 (2)	175
N2—H2B...O3 <sup>i</sup>	0.88	1.99	2.823 (2)	157
N4—H4B...O1 <sup>i</sup>	0.88	2.07	2.892 (2)	156

Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$  435 parameters  
 $wR(F^2) = 0.090$  H-atom parameters constrained  
 $S = 1.07$   $\Delta\rho_{\max} = 0.43 \text{ e \AA}^{-3}$   
 5964 reflections  $\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$

H atoms were positioned geometrically and refined as riding on their parent atoms, with C—H = 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ , and N—H = 0.88 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ . Hydroxy and methyl H atoms were modelled in a similar fashion, with O—H = 0.84 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ , and C—H = 0.98 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$ . The most disagreeable reflections were omitted and those exhibiting a  $\Delta(F^2)$  value greater than 5 s.u. were removed; 5 from (I) and 31 from (II). The refinement was further improved by restricting the reflections considered to those with  $\theta \leq 25.68^\circ$ . The Flack parameter for (I) gives the expected values for a correct absolute structure within 3 s.u. Nonetheless since the s.u. is moderate, the inverted structure was tested. This yielded a Flack parameter of  $x = 1.21$  (13)

by the ‘hole-in-one’ method and of  $x = 1.34$  (13) using TWIN/BASF, giving us confidence that we have presented the correct absolute structure with respect to the polar-axis direction. These checks were particularly important given that the precision of the Flack  $x$  parameter is poor owing to a low Friedel coverage of 60%. Refinement for (II) was limited to those reflections with  $\theta < 25.68^\circ$  reducing the number of missing data; however, a number of missing data remain (201 reflections between  $\theta_{\min}$  and  $\sin\theta/\lambda = 0.600$ ). Analysis of reciprocal-space plots reveal that these missing portions are fairly randomly dispersed which gives us confidence that this is not a systematic error. Moreover, the missing data were comprised of high-angle reflections that were just outside the reach of the data collection strategy.

For both compounds, data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3389). Services for accessing these data are described at the back of the journal.

#### References

- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.  
 Büyükgüngör, O. & Odabaşoğlu, M. (2006). *Acta Cryst.* **E62**, o2749–o2750.  
 Dolzhenko, A. V., Syropyatov, B. Ya., Koz’minykh, V. O., Kolotova, N. V., Zakhmatov, A. V. & Borodin, A. Yu. (2003). *Pharm. Chem. J.* **37**, 407–408.  
 Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 121–126.  
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Galloy, J., Putzeys, J.-P., Germain, G. & Van Meerse, M. (1976). *Acta Cryst.* **B32**, 2718–2720.  
 Hemamalini, M. & Fun, H.-K. (2010). *Acta Cryst.* **E66**, o2192–o2193.  
 Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.  
 Ito, K., Moriya, K., Kashino, S. & Haisa, M. (1975). *Bull. Chem. Soc. Jpn.* **48**, 3078–3084.  
 Ni, S.-F., Feng, W.-J., Guo, H. & Jin, Z.-M. (2007). *Acta Cryst.* **E63**, o3866.  
 Quah, C. K., Hemamalini, M. & Fun, H.-K. (2010). *Acta Cryst.* **E66**, o1932.  
 Rigaku (2008). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Zhi, M.-J., Yuan, J.-P., Mao, L.-H. & Liang, S. (2002). *J. Chem. Crystallogr.* **31**, 191–195.