

Two polymorphic forms of a mixed zinc/copper biquinoline dihydrogenphosphate

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Received 27 February 2007

Accepted 22 April 2007

Online 11 May 2007

Two polymorphic forms of a mixed zinc/copper biquinoline dihydrogenphosphate are presented, showing almost identical monomeric units, *viz.* (2,2'-biquinoline- κ^2N,N')bis(dihydrogenphosphato- κO)copper(II)/zinc(II), formulated as $[Zn_xCu_{1-x}(H_2PO_4)_2(C_{18}H_{12}N_2)]$, with $x = 0.88$ (1) and 0.90 (2). The cation is tetrahedrally coordinated to a chelating biquinoline system and two diprotonated phosphate anions. The structures differ mainly in their intermolecular hydrogen-bonding interactions, leading to different packing schemes. No significant evidence of stress due to the Zn/Cu solid solution formation was detected.

Comment

The synthesis of hybrid organic–inorganic open-framework materials has been a subject of intense research owing to their interesting structural chemistry and potential applications in such different areas as ion exchange, adsorption and catalysis, the search for new physical properties, *etc.* (Hagman *et al.*, 1999; Férey, 2001; Eddaoudi *et al.*, 2001; Davis, 2002). A particular and effective method to obtain these compounds is hydrothermal synthesis, as the generation of a product by a chemical reaction in a sealed heated solution above ambient pressure is usually referred to. The mechanisms involved are not fully understood yet, but the ability of the process to generate novel products unattainable otherwise is well known, and the products can possess peculiar characteristics regarding, for instance, binding affinity (Feng & Xu, 2001; Moghimi *et al.*, 2003; Walton, 2002). The present report on two polymorphic forms of a mononuclear biquinoline dihydrogenphosphate, obtained from a reaction between zinc, copper, phosphate and biquinoline, might serve as an example of such capability. A search of the January 2007 release of the

Cambridge Structural Database (CSD; Allen, 2002) revealed that the few reported zinc or copper phosphates that include chelating dinitrogenated bases in their structures are poly-, oligo- or at least dimeric entities; no mononuclear zinc or copper phosphate including bipyridine, phenanthroline, biquinoline, *etc.*, seems to have been structurally characterized, and the present compound [zinc/copper biquinoline dihydrogenphosphate, $Zn_xCu_{1-x}(biq)(H_2PO_4)_2$; biq is biquinoline] appears to be the first reported occurrence of such a structure. The title compound was obtained serendipitously as a by-product of a hydrothermal synthesis (see *Experimental*) in the form of two different polymorphic varieties, *viz.* a triclinic form (I) [space group $P\bar{1}$, $x = 0.88$ (1)] and a monoclinic form (II) [space group $P2_1/n$, $x = 0.90$ (2)].

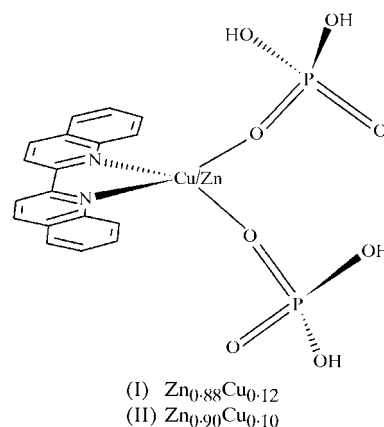


Fig. 1 shows that the two forms are structurally very similar, with the mixed cation chelated by a biquinoline unit through its two N atoms, and two monocoordinated dihydrogenphosphates completing the distorted tetrahedral environment. No meaningful differences regarding coordination distances and angles exist between the two polyhedra (see Tables 1 and 4, and Fig. 2 for a direct comparison), nor is there any significant evidence of structural stress due to solid solution formation, short of a minor transverse elongation of the displacement ellipsoids of the bound phosphate O atoms, which might represent a slight positional disorder.

However, and in spite of their similarities, polymorph (I) appears slightly more strained than (II), as suggested by a comparison of the dihedral angles between the N/Zn/N and the O/Zn/O coordination planes, that in (I) being significantly larger [98.7 (1) *versus* 91.8 (1) $^\circ$]. The same applies for the angles between the lateral wings of the biquinoline ligand [8.7 (1) *versus* 1.2 (1) $^\circ$].

The dihydrogenphosphate anions coordinate through one of their unprotonated O atoms, the other being the acceptor of an intramolecular hydrogen bond linking both dihydrogenphosphate groups into a single unit. The interaction of this O atom seems to be strong enough to partially weaken its bond to the P atom. In fact, and contrary to what would be expected, the $P=O_{uncoord}$ distances are slightly longer than the $P-O_{coord}$ bonds in all four independent units, and even though these differences are rather small in terms of the individual s.u. values, the fact that all four behave in the same way seems to

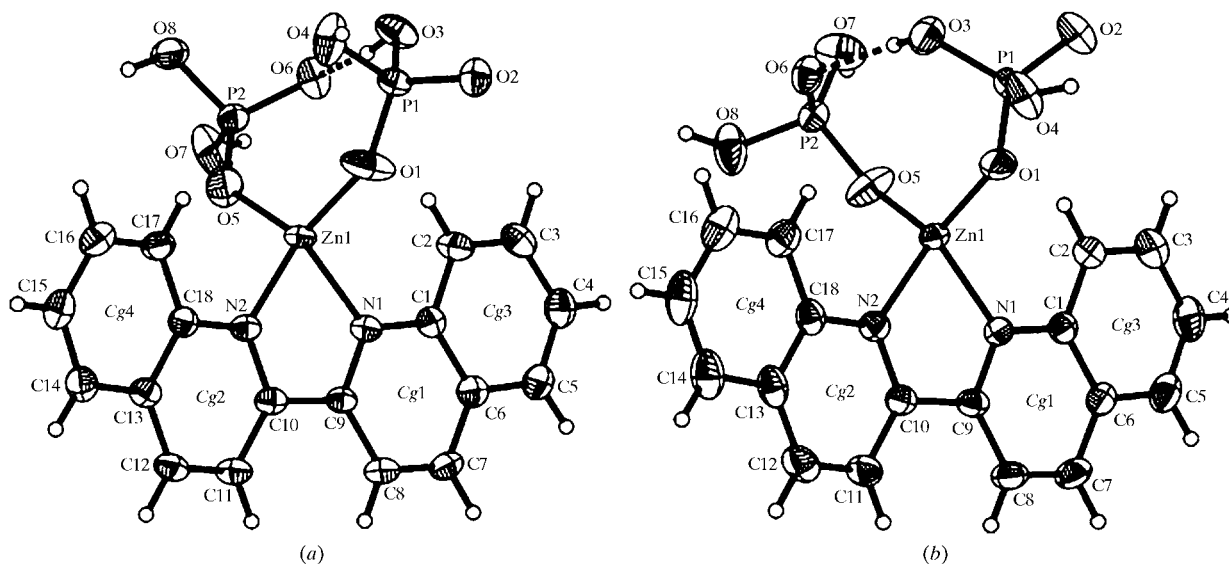


Figure 1
The molecular structures of (a) polymorph (I) and (b) polymorph (II), showing the numbering schemes used. The cation has been labelled according to the major component in the mixture. Displacement ellipsoids are shown at the 40% probability level.

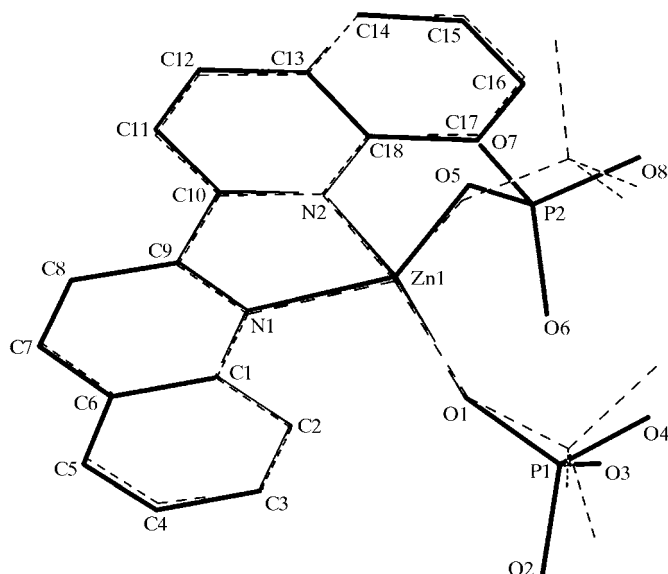


Figure 2
A superposition diagram of the two molecules, showing the coordination polyhedra to be almost identical. Structure (I) is shown with full lines and structure (II) is shown with dashed lines.

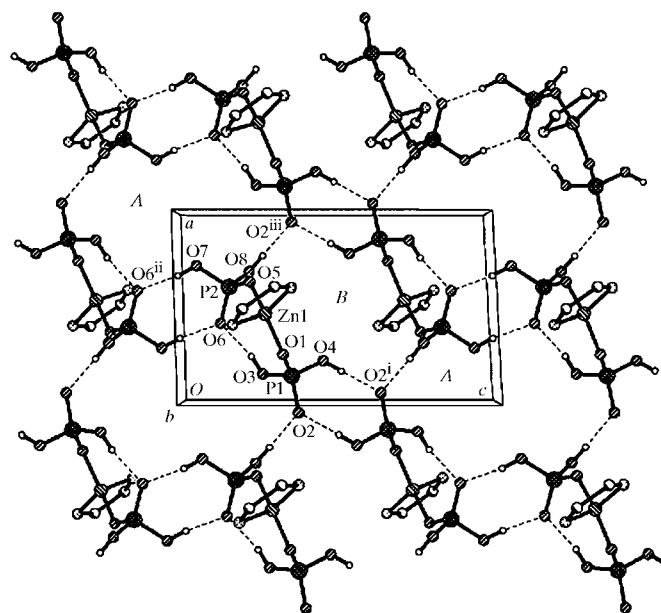
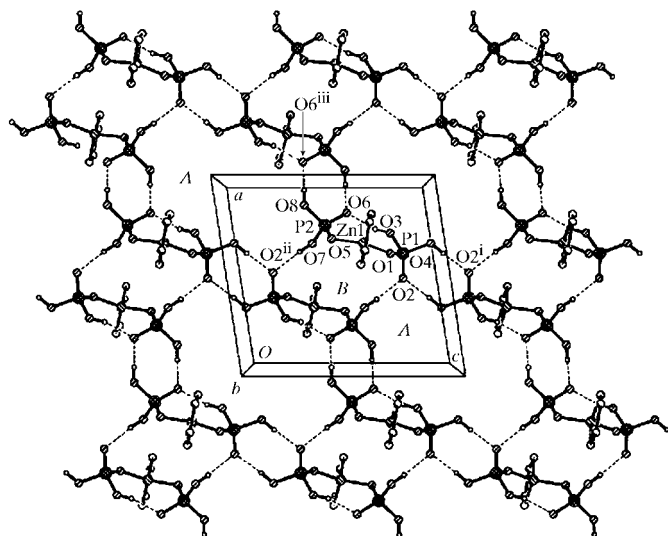


Figure 3
A view of the packing of (I), showing the hydrogen-bonding pattern in one of the sheets. Non-intervening biquinoline units have been idealized by their N1—C9—C10—N2 loop.

give this behaviour some significance. On the other hand, this fact does not appear to be unusual; a search of the CSD showed some 50 cases of singly coordinated phosphates, in half of which a similar situation arises.

The P—OH distances lie in a narrow range, as do the P=O distances, and the P—OH and P=O bonds have well differentiated values in both structures, with means of 1.546 (7) and 1.495 (7) Å for (I), and 1.541 (16) and 1.492 (6) Å for (II). There is a subtle difference between the polymorphs, however, which is influential because of its effects upon the otherwise

very similar packing schemes; this difference is the rotation of the phosphate groups around the P1—O1 and P2—O5 axes, in opposite directions, as a result of the restraint imposed by the very strong intramolecular hydrogen bond (O3—H3P...O6) linking the two phosphate groups. This relative rotation, as measured by the differences in the relevant torsion angles (Zn1—O1—P1—O3 and Zn1—O5—P2—O6), is 52 (1) and 5 (1)° for the P1 and P2 phosphate groups, respectively, and its main consequence is the different orientation in space of the


Figure 4

A view of the packing of (II), showing the hydrogen-bonding pattern in one of the sheets. Non-intervening biquinoline units have been idealized by their N1–C9–C10–N2 loop.

remaining three phosphate H atoms prone to intermolecular hydrogen bonding, which in both structures determines the formation of two-dimensional structures parallel to (010). The first interactions listed in Tables 2 and 5 consist of intramolecular hydrogen bonds (see Fig. 1); the following two define chains that run along $[\bar{1}01]$, in turn connected (roughly along $[101]$) *via* the fourth interaction. Figs. 3 and 4 show a simplified view of these two-dimensional structures. The diverse phosphate orientations can be seen reflected in the size of the ‘holes’ built up around the symmetry centres at $(0, \frac{1}{2}, 1)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(1, \frac{1}{2}, 0)$, labelled as *A* and *B*, respectively, in Figs. 3 and 4; those in (I) are large and even, while those in (II) alternate in size along the $[101]$ direction.

In the two-dimensional structures, the biquinoline groups (schematized in Figs. 3 and 4) protrude outwards at both sides, in such a way as to interdigitate when the planes stack along *b*. The interaction between adjacent planes is achieved through π – π contacts involving aromatic rings in neighbouring biquinoline groups, the main interactions being summarized in Tables 3 and 6.

Experimental

The original scope of the synthesis was to obtain a hybrid organic–inorganic compound, that is, one with an inorganic structure as a host ($\cdots\text{P}—\text{O}—\text{V}\cdots$) and a metal–biquinoline complex as a guest (Feng & Xu, 2001). In the process of adjusting the hydrothermal conditions, the mixed zinc/copper complex reported here was obtained serendipitously. For the synthesis, a mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.5 mmol), V_2O_5 (0.25 mmol), 2,2-biquinoline (1.0 mmol), H_3PO_4 (5 ml, 0.0087 mmol) and Zn (0.5 mmol) was sealed in a Teflon-lined acid digestion bomb, heated at 393 K for 6 d under autogenous pressure and then cooled slowly at a rate of 20 K h^{-1} to room temperature. The resulting solid product consisted of a mixture of

orange crystals pertaining to both polymorphs, which could be clearly distinguished because of their different crystal shapes. A combination of UV–vis spectroscopy and EDAX analysis confirmed the existence of mixed cationic sites with similar occupancies in both polymorphs [polymorph (I) $\text{Zn}_{0.88}\text{Cu}_{0.12}$ and polymorph (II) $\text{Zn}_{0.90}\text{Cu}_{0.10}$].

Polymorph (I)

Crystal data

$[\text{Zn}_{0.88}\text{Cu}_{0.12}(\text{H}_2\text{PO}_4)_2(\text{C}_{18}\text{H}_{12}\text{N}_2)]$	$\gamma = 106.632 (3)^\circ$
$M_r = 515.42$	$V = 972.0 (3) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.8089 (12) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.5225 (17) \text{ \AA}$	$\mu = 1.46 \text{ mm}^{-1}$
$c = 12.3618 (19) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\alpha = 91.787 (2)^\circ$	$0.26 \times 0.12 \times 0.08 \text{ mm}$
$\beta = 91.722 (2)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	7214 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	4216 independent reflections
$T_{\min} = 0.79$, $T_{\max} = 0.89$	3529 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.136$	$\Delta\rho_{\text{max}} = 0.68 \text{ e \AA}^{-3}$
$S = 1.14$	$\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$
4216 reflections	
292 parameters	
4 restraints	

Table 1

Selected bond lengths (\AA) for (I).

Zn1–O1	1.863 (3)	P1–O4	1.546 (3)
Zn1–O5	1.892 (3)	P1–O3	1.553 (2)
Zn1–N2	2.017 (2)	P2–O5	1.496 (3)
Zn1–N1	2.033 (3)	P2–O6	1.502 (2)
P1–O1	1.486 (3)	P2–O7	1.542 (3)
P1–O2	1.496 (2)	P2–O8	1.542 (3)

Table 2

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O3–H3P \cdots O6	0.82 (3)	1.78 (2)	2.586 (3)	166 (4)
O4–H4P \cdots O2 ⁱ	0.83 (3)	1.79 (2)	2.616 (3)	177 (5)
O7–H7P \cdots O6 ⁱⁱ	0.84 (3)	1.75 (2)	2.592 (4)	173 (4)
O8–H8P \cdots O2 ⁱⁱⁱ	0.83 (3)	1.78 (2)	2.580 (3)	161 (4)

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

Table 3

π – π contacts (\AA , $^\circ$) in (I).

$Cg\cdots Cg$	ccd	sa	ipd
$Cg1\cdots Cg1^{iv}$	3.595 (2)	21.78 (1)	3.338 (1)
$Cg1\cdots Cg3^{iv}$	3.613 (2)	22.92 (8)	3.330 (4)
$Cg1\cdots Cg4^v$	4.248 (2)	38.(3)	3.33 (13)
$Cg2\cdots Cg2^v$	3.911 (2)	27.38 (1)	3.473 (1)
$Cg2\cdots Cg4^v$	3.779 (3)	23.5 (8)	3.46 (2)
$Cg2\cdots Cg4^{vi}$	4.094 (3)	35.0 (7)	3.35 (3)

Symmetry codes: (iv) $-x + 1, -y + 2, -z$; (v) $-x + 1, -y + 2, -z + 1$; (vi) $-x + 2, -y + 2, -z + 1$. For centroid definitions, see Fig. 1. Notes: ccd is the centroid-to-centroid distance, sa is the (mean) slippage angle and ipd is the (mean) interplanar distance.

Polymorph (II)

Crystal data

[Zn _{0.90} Cu _{0.10} (H ₂ PO ₄) ₂ (C ₁₈ H ₁₂ N ₂)]	V = 1959.8 (5) Å ³
M _r = 515.46	Z = 4
Monoclinic, P2 ₁ /n	Mo Kα radiation
a = 9.3801 (12) Å	μ = 1.46 mm ⁻¹
b = 20.528 (3) Å	T = 295 (2) K
c = 10.2991 (13) Å	0.20 × 0.12 × 0.12 mm
β = 98.791 (2)°	

Data collection

Bruker SMART CCD area-detector diffractometer	16359 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	4435 independent reflections
T _{min} = 0.79, T _{max} = 0.84	3060 reflections with I > 2σ(I)
	R _{int} = 0.059

Refinement

R[F ² > 2σ(F ²)] = 0.059	H atoms treated by a mixture of independent and constrained refinement
wR(F ²) = 0.109	Δρ _{max} = 0.75 e Å ⁻³
S = 1.02	Δρ _{min} = -0.39 e Å ⁻³
4435 reflections	
292 parameters	
4 restraints	

Table 4

Selected bond lengths (Å) for (II).

Zn1—O1	1.870 (3)	P1—O3	1.548 (3)
Zn1—O5	1.894 (3)	P1—O4	1.548 (3)
Zn1—N1	2.014 (3)	P2—O5	1.489 (3)
Zn1—N2	2.030 (3)	P2—O6	1.498 (3)
P1—O1	1.488 (3)	P2—O7	1.525 (3)
P1—O2	1.493 (3)	P2—O8	1.544 (3)

Table 5

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

D—H...A	D—H	H...A	D...A	D—H...A
O3—H3P...O6	0.82 (3)	1.79 (2)	2.593 (4)	163 (5)
O4—H4P...O2 ⁱ	0.84 (4)	1.73 (2)	2.567 (4)	174 (5)
O7—H7P...O2 ⁱⁱ	0.83 (3)	1.81 (2)	2.620 (4)	163 (5)
O8—H8P...O6 ⁱⁱⁱ	0.85 (3)	1.76 (2)	2.603 (4)	173 (5)

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

H atoms in the organic ligand were placed at calculated positions (C—H = 0.93 Å) and allowed to ride. Those in the dihydrogenphosphate groups were found in a difference Fourier synthesis and were refined with restrained O—H distances of 0.82 (2) Å. All H atoms were assigned a U_{iso}(H) value of 1.2U_{eq}(host). Owing to the impossibility of differentiating Zn from Cu through refinement methods, the occupancies of the mixed cationic sites were taken as the average result coming out of the compositional analysis (UV-vis spectroscopy

Table 6

π-π contacts (Å, °) in (II).

Cg...Cg	ccd	sa	ipd
Cg1...Cg2 ^{iv}	3.747 (2)	24.42 (1)	3.412 (1)
Cg1...Cg4 ^{iv}	3.522 (2)	14.7 (2)	3.405 (4)
Cg2...Cg3 ^v	4.183 (2)	37.2 (2)	3.33 (1)
Cg2...Cg3 ^{vi}	3.509 (2)	13.9 (3)	3.405 (4)
Cg3...Cg4 ^{vii}	3.574 (2)	18.9 (9)	3.38 (3)

Symmetry codes: (iv) x - 1/2, -y + 1/2, z - 1/2; (v) x + 1, y, z; (vi) x + 1/2, -y + 1/2, z + 1/2; (vii) x - 1, y, z. For centroid definitions, see Fig. 1. Notes: ccd is the centroid-to-centroid distance, sa is the (mean) slippage angle and ipd is the (mean) interplanar distance.

and EDAX), which gave x = 0.88 (5) for (I) and x = 0.90 (4) for (II), values which were kept fixed during the refinement.

For both compounds, data collection: SMART-NT (Bruker, 2001); cell refinement: SAINT-NT (Bruker, 2000); data reduction: SAINT-NT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL-NT (Sheldrick, 2000); software used to prepare material for publication: SHELXTL-NT and PLATON (Spek, 2003).

We acknowledge the Spanish Research Council (CSIC) for providing us with a free-of-charge license to the CSD system. We also thank FONDECYT 1040461 and ECOS/CONICYT-C05E01 for funding, and FONDECYT 1020802 for the purchase of the diffractometer and detector.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3081). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Bruker (2000). *SAINTE-NT*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2001). *SMART-NT*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Davis, M. E. (2002). *Nature (London)*, **417**, 813–821.
 Eddaoudi, M., Moler, D. B., Li, H., Chen, B., Reineke, T. M., O’Keeffe, M. & Yaghi, O. M. (2001). *Acc. Chem. Res.* **34**, 319–330.
 Feng, S. & Xu, R. (2001). *Acc. Chem. Res.* **34**, 239–247.
 Férey, G. (2001). *Chem. Mater.* **13**, 3084–3098.
 Hagrman, P. J., Hagrman, D. & Zubieta, J. (1999). *Angew. Chem. Int. Ed.* **38**, 2638–2684.
 Moghimi, A., Alizadeh, R., Shokrollahi, A., Aghabozorg, H., Shamsipur, M. & Shockravi, A. (2003). *Inorg. Chem.* **42**, 1616–1624.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Sheldrick, G. M. (2000). *SHELXTL-NT*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (2001). *SADABS*. University of Göttingen, Germany.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
 Walton, R. I. (2002). *Chem. Soc. Rev.* **31**, 230–238.