

Bis(1-phenylethylammonium) hexachloridostannate(IV) and bis(2-phenylethylammonium) hexachloridostannate(IV)

David G. Billing,^a Andreas Lemmerer^{a*} and Melanie Rademeyer^b

^aMolecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, PO Wits 2050, South Africa, and ^bSchool of Chemistry, University of KwaZulu-Natal, Pietermaritzburg Campus, Private Bag X01, Scottsville 3209, South Africa

Correspondence e-mail: anderl@chem.wits.ac.za

Received 21 December 2006

Accepted 30 January 2007

Online 17 February 2007

The crystal structures of the two isomers bis(1-phenylethylammonium) hexachloridostannate(IV) and bis(2-phenylethylammonium) hexachloridostannate(IV), both $(C_8H_{12}N)_2[SnCl_6]$, exhibit alternating organic and inorganic layers, which interact *via* N—H...Cl hydrogen bonding. The inorganic layer contains an extended two-dimensional hydrogen-bonded sheet. The Sn atom in the 1-phenylethylammonium salt lies on an inversion centre.

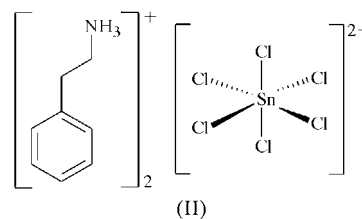
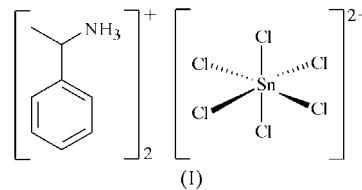
Comment

A significant number of organic/inorganic compounds of the formula $(R-NH_3)_2[SnX_6]$ (where X is F, Cl, Br or I) have previously been investigated structurally because of their interesting magnetic and optical properties (Mitzi *et al.*, 1998; Raptopoulou *et al.*, 2002). In contrast, compounds of the formula $(R-NH_3)_2[SnX_6]$ have not been studied extensively. The crystal structures of only four primary *n*-alkylammonium hexachloridotin(IV) compounds – with organic chain lengths ranging from one to six (Kitahama *et al.*, 1979; Knop *et al.*, 1983; Eulleuch *et al.*, 1996; Lemmerer *et al.*, 2007) – and two primary arylammonium hexachloridotin(IV) organic–inorganic hybrid compounds (Rademeyer, 2004*a,b*) have been reported in the literature.

In the present investigation, two novel crystal structures of organic–inorganic hybrid materials are reported, namely bis(1-phenylethylammonium) hexachloridostannate(IV), (I), and bis(2-phenylethylammonium) hexachloridostannate(IV), (II). A comparison of the structures reveals the effect of a slight change in the cation and the introduction of a chiral cation on the packing of molecular ions in the crystal structures.

The structures of (I) and (II), in which the cations are structural isomers, can be compared with that of bis(benzyl-

ammonium) hexachloridostannate(IV), (III) (Rademeyer, 2004*a*), as they form a logical series; relative to (III), (I) has an additional methyl group on the C atom adjacent to the ammonium group, while the arylammonium chain in (II) is longer by one methylene group than that in (III).



The molecular geometry and atomic numbering schemes employed for (I) and (II) are illustrated in Fig. 1. In the solid state, (I) and (II) self-assemble into structures consisting of alternating organic layers, made up of the ammonium cations bis(1-phenylethylammonium) [for (I)] and bis(2-phenylethylammonium) [for (II)], and inorganic layers, made up of isolated $SnCl_6$ octahedra. The layers stack along the a axis in (I) and along the b axis in (II), as illustrated in Figs. 2 and 3, respectively. In both structures, the inorganic layer and organic layer interact *via* hydrogen bonds to form a two-dimensional network parallel to the bc plane in (I) and parallel to the ac plane in (II).

The inorganic part of the asymmetric unit of (I) contains an Sn atom on a centre of inversion at $(\frac{1}{2}, 0, \frac{1}{2})$ and three Cl atoms in general positions. The inversion centre generates an $SnCl_6$ octahedron, in which the three unique Sn—Cl bond lengths are 2.4270 (11), 2.4310 (12) and 2.4557 (12) Å (see Table 3), and the *cis* Cl—Sn—Cl bond angles range from 89.56 (4) to 90.44 (4)°, indicating only slight distortion from ideal octahedral geometry. Each unit cell contains one complete inorganic layer [mean plane equation: $12.217(2)x = 6.109(1)\text{Å}$; symmetry operators of atoms used: Sn1 (x, y, z), ($x, 1 + y, z$), ($1 - x, \frac{1}{2} + y, \frac{1}{2} - z$), ($1 - x, \frac{1}{2} + y, \frac{3}{2} - z$)] and successive layers are separated by the unit-cell repeat a of 12.243 (2) Å.

The organic layer of (I) has one independent 1-phenylethylammonium cation on a general position. The aromatic ring plane [C3—C8; mean plane equation: $8.68(3)x - 2.75(2)y - 8.75(6)z = 2.94(4)\text{Å}$] is inclined at an angle of 48.0 (2)° to the plane of the inorganic layer. Within the organic layers, adjacent aromatic rings are separated by a centroid-to-centroid distance of 5.268 Å, clearly far too large to be considered as a π -stacking interaction.

The hydrogen-bonding interactions linking the organic layer and the inorganic layer involve the three H atoms on the ammonium group. There are two simple and one bifurcated hydrogen bond between one cation and three different $SnCl_6$ octahedra (Fig. 4 and Table 1).

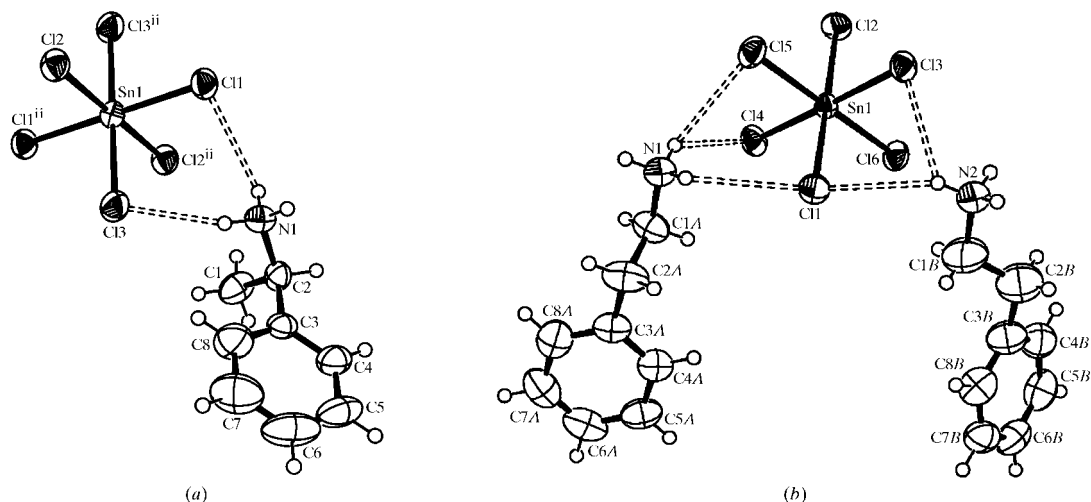


Figure 1
Views of the structures of (a) (I) and (b) (II), showing the atom-numbering schemes. Displacement ellipsoids are shown at the 50% probability level. [Symmetry code: (ii) $-x + 1, -y + 1, -z + 1$.]

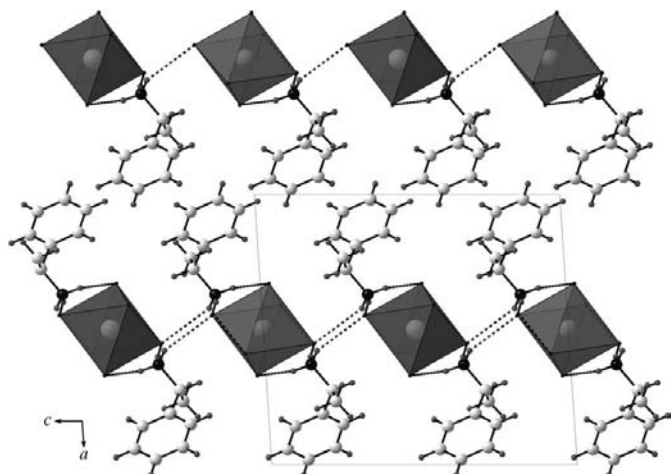


Figure 2
The packing of (I), viewed along the *b* axis. The 1-phenylethylammonium cations are non-interdigitated.

The asymmetric unit of (II) comprises two crystallographically independent 2-phenylethylammonium cations, labelled cat1 (containing atom N1) and cat2 (containing atom N2), and one octahedral $[\text{SnCl}_6]^{2-}$ anion, the atoms of which lie in general positions. Each unit cell contains two complete inorganic layers [mean plane equation: $25.45(1)y - 1.660(2)z = 11.893(5) \text{ \AA}$; symmetry operators of atoms used: Sn1 (x, y, z), $(1 + x, y, z)$, $(-x, 1 - y, 1 - z)$, $(1 - x, 1 - y, 1 - z)$]. The Sn–Cl bond lengths range from 2.4118 (16) to 2.4342 (17) \AA (see Table 3) and the *cis* Cl–Sn–Cl angles from 88.68 (6) to 91.61 (7) $^\circ$, indicating small distortions from ideal octahedral geometry.

Within the organic layer of (II), the cations pack in an interdigitated fashion. The planes of the aromatic rings of the two cations are tilted by 80.6 (2) [for C3A–C8A; mean plane equation: $6.66(1)x - 0.06(9)y + 5.03(4)z = 9.90(8) \text{ \AA}$] and 86.5 (2) $^\circ$ [for C3B–C8B; mean plane equation:

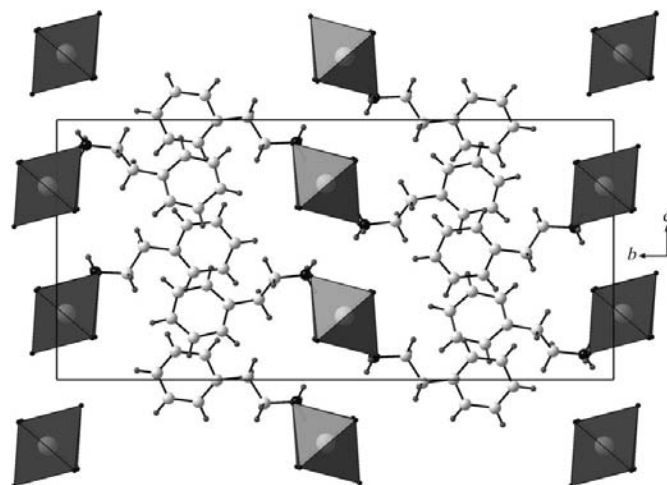


Figure 3
The packing of (II), viewed along the *a* axis. The 2-phenylethylammonium cations are interdigitated.

$6.59(1)x + 2.72(8)y - 5.13(3)z = 2.20(6) \text{ \AA}$] relative to the inorganic layer plane, and by 50.6 (2) $^\circ$ relative to one another. Weak C–H $\cdots\pi$ interactions are present in this layer, with atom C4A interacting with the centroid Cg2 of the aromatic group C3B–C8B (symmetry operator: $x, \frac{3}{2} - y, -\frac{1}{2} + z$) through atom H4A (CH \cdots Cg2 = 2.82 \AA and C–H \cdots Cg2 = 133 $^\circ$), and atom C7A interacting with the centroid Cg2 of another ring (symmetry operator: $-1 + x, y, -1 + z$) through atom H7A (CH \cdots Cg2 = 2.83 \AA and C–H \cdots Cg2 = 136 $^\circ$) (see Fig. 5).

In (II), the two crystallographically independent cations display the same hydrogen-bonding interactions with the $[\text{SnCl}_6]^{2-}$ anions. Atoms N1 and N2 interact with three anions each through three simple hydrogen bonds (Fig. 6 and Table 2). The N1–H1C \cdots Cl2ⁱⁱ hydrogen bond (symmetry code as in Table 2) has a hydrogen–acceptor distance of 2.92 \AA and can be classified as a short contact.

A notable difference between the three structures lies in the volume of the unit cell, which is approximately doubled in (II) and (III) compared with (I). The organic cations in (I) and (III) have approximately the same length, but because the cations are non-interdigitated in (I) and interdigitated in (III), the interlayer spacing of (III) is shorter than that of (I) (see the values in Table 3). Although the cation in (II) is longer than that in (I), the two interlayer spacings are similar as a result of the interdigitation of the organic layer of (II), and the fact that the rings are tilted at different angles to the inorganic layer, thus compensating for the different packing arrangements of the organic layer.

In (I), neighbouring cations participate in hydrogen bonding with different inorganic layers, thus alternating in orientation, as shown in Fig. 2. However, in (II), pairs of cations point in the same direction and neighbouring pairs alternate in orientation (Fig. 3), and the same is observed for (III). In all three structures, the hydrogen bonds give rise to a complex hydrogen-bonded network extending in two dimensions. The packing efficiency of (I) is slightly lower than that of (II) and (III) (Table 3), possibly because the sterically hindering methyl group prevents more efficient packing.

In summary, slight changes to the cation cause subtle differences in the structures of compounds (I), (II) and (III),

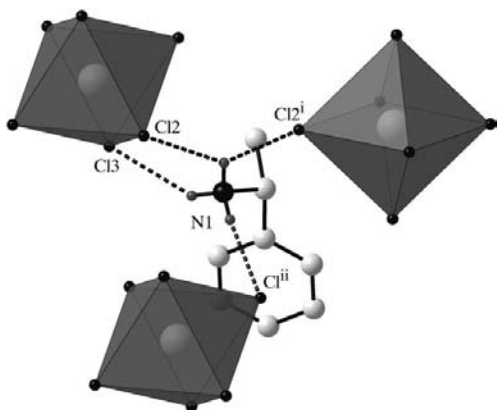


Figure 4
A magnified view of the hydrogen bonding in (I) between the 1-phenylethylammonium cation and three $[\text{SnCl}_6]^{2-}$ anions. [Symmetry codes: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x + 1, -y + 1, -z + 1$.]

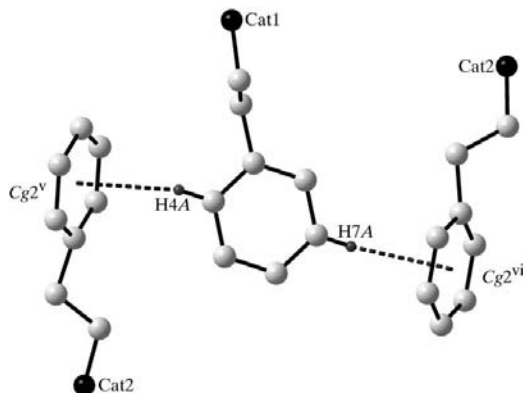


Figure 5
The $\text{C}-\text{H} \cdots \pi$ interactions in (II) between cat1 and cat2 (see *Comment*). [Symmetry codes: (v) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (vi) $x - 1, y, z - 1$.]

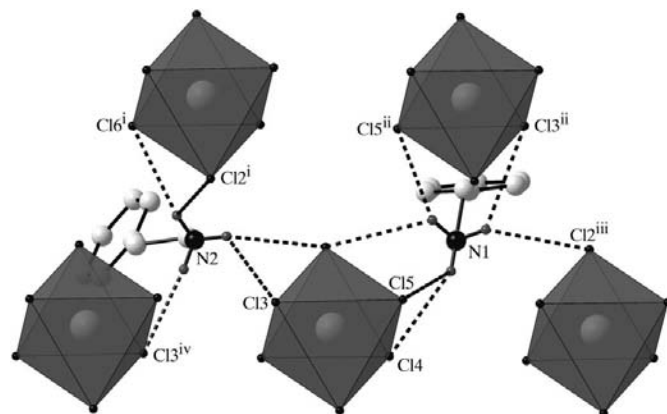


Figure 6
A magnified view of the hydrogen bonding in (II) between the two 2-phenylethylammonium cations and five $[\text{SnCl}_6]^{2-}$ anions. [Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x, -y + 1, -z + 1$; (iv) $-x + 1, -y + 1, -z + 2$.]

involving changes in interdigitation and cation orientation. Overall, however, the structures are still very similar, indicating that self-assembly in the hydrophobic and hydrophilic layers and hydrogen-bond formation are the major driving forces that dictate the packing.

Experimental

For the preparation of (I), 1-phenylethylamine (0.068 g, 0.561 mmol) was combined with tin(II) chloride (0.054 g, 0.259 mmol) and dissolved in concentrated HCl (5 ml, 0.057 mol, 33%, Aldrich). The resulting solution was left open to the atmosphere and crystals grew by slow evaporation. A colourless plate-like crystal was selected for the X-ray diffraction study. 2-Phenylethylammonium chloride was prepared by the dropwise addition of excess concentrated HCl (4.82 ml, 0.059 mol, 37%, Aldrich) to a solution of 2-phenylethylamine (2.4 ml, 0.020 mol, 99%, Aldrich) in chloroform (10 ml, 99%, Saarchem). The resulting precipitate was filtered off and left to dry. Crystals of (II) were grown by slow evaporation to total dryness of an aqueous solution of stoichiometric amounts (1:2) of tin(II) chloride (0.065 g, 0.340 mmol) and 2-phenylethylammonium chloride (0.107 g, 0.679 mmol). A colourless crystal was selected for the X-ray diffraction study.

Compound (I)

Crystal data

$(\text{C}_8\text{H}_{12}\text{N})_2[\text{SnCl}_6]$
 $M_r = 575.76$
 Monoclinic, $P2_1/c$
 $a = 12.243 (2) \text{ \AA}$
 $b = 7.1124 (13) \text{ \AA}$
 $c = 13.777 (3) \text{ \AA}$
 $\beta = 93.697 (3)^\circ$
 $V = 1197.2 (4) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.597 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 1.74 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Plate, colourless
 $0.48 \times 0.28 \times 0.13 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector diffractometer
 ω scans
 Absorption correction: integration (*XPREP*; Bruker, 1999)
 $T_{\min} = 0.443, T_{\max} = 0.821$

6461 measured reflections
 2228 independent reflections
 1736 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.067$
 $\theta_{\text{max}} = 25.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.097$
 $S = 1.30$
 2228 reflections
 103 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + 2.608P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.96 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.50 \text{ e } \text{Å}^{-3}$

Table 1
 Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1A\cdots Cl2^i$	0.89	2.68	3.302 (4)	128
$N1-H1A\cdots Cl1$	0.89	2.76	3.331 (4)	123
$N1-H1B\cdots Cl2^{ii}$	0.89	2.41	3.289 (4)	170
$N1-H1C\cdots Cl3$	0.89	2.54	3.302 (5)	144

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

Compound (II)

Crystal data

$(C_8H_{12}N)_2[SnCl_6]$
 $M_r = 575.76$
 Monoclinic, $P2_1/c$
 $a = 7.335$ (3) Å
 $b = 25.695$ (4) Å
 $c = 11.974$ (2) Å
 $\beta = 90.03$ (2)°
 $V = 2256.8$ (11) Å³

$Z = 4$
 $D_x = 1.695 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 1.85 \text{ mm}^{-1}$
 $T = 293$ (2) K
 Plate, colourless
 $0.2 \times 0.2 \times 0.15 \text{ mm}$

Data collection

Oxford Excalibur2 CCD area-detector diffractometer
 ω - 2θ scans
 Absorption correction: multi-scan (*WinGX*; Farrugia, 1999)
 $T_{\min} = 0.709, T_{\max} = 0.753$

14565 measured reflections
 4159 independent reflections
 3144 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\max} = 25.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.122$
 $S = 1.05$
 4159 reflections
 202 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 6.342P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.008$
 $\Delta\rho_{\max} = 1.01 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.00 \text{ e } \text{Å}^{-3}$

Table 2
 Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1A\cdots Cl5$	0.89	2.80	3.421 (6)	128
$N1-H1B\cdots Cl5^{ii}$	0.89	2.74	3.548 (6)	152
$N1-H1C\cdots Cl2^{iii}$	0.89	2.92	3.606 (6)	135
$N2-H2A\cdots Cl3$	0.89	2.81	3.362 (6)	122
$N2-H2B\cdots Cl3^{iv}$	0.89	2.56	3.443 (6)	171
$N2-H2C\cdots Cl6^i$	0.89	2.70	3.546 (6)	159

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

H atoms were placed geometrically and refined in idealized positions in the riding-model approximation, with C—H = 0.93 (ArH), 0.98 (CH), 0.97 (CH₂) or 0.96 Å (CH₃) and N—H = 0.89 Å; $U_{\text{iso}}(\text{H})$ values were set at $1.5U_{\text{eq}}(\text{N})$, $1.5U_{\text{eq}}(\text{methyl C})$ or $1.2U_{\text{eq}}(\text{C})$. The highest residual peaks in the final ΔF syntheses lie 1.07 Å from Cl2 in (I) and 1.67 Å from Cl5 in (II).

Table 3

Comparative geometric parameters (Å, °) in (I), (II) and (III).

Parameter	(I)	(II)	(III) ^a
Sn1—Cl1	2.4270 (11)	2.4244 (16)	2.4242 (12)
Sn1—Cl2	2.4557 (12)	2.4316 (16)	2.4590 (12)
Sn1—Cl3	2.4310 (11)	2.4342 (16)	2.4064 (14)
Sn1—Cl4	—	2.4257 (16)	2.4244 (14)
Sn1—Cl5	—	2.4291 (16)	2.4415 (12)
Sn1—Cl6	—	2.4118 (16)	2.4271 (13)
Interplanar spacing	12.243 (2)	12.848 (4)	11.016 (7)
Packing efficiency	0.648	0.689	0.689

Note: (a) $(C_6H_5CH_2NH_3)_2[SnCl_6]$ [Rademeyer, 2004a; Cambridge Structural Database (Allen, 2002) refcode INIXOS].

For compound (I), data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*. For compound (II), data collection: *CrysAlis CCD* (Oxford Diffraction 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

MR acknowledges funding received for this work from the University of KwaZulu-Natal Research Office and the National Research Foundation (GUN:2054350). DGB thanks the University of the Witwatersrand and the National Research Foundation (GUN:2069064) for funding.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3024). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Brandenburg, K. (1999). *DIAMOND*. Version 2.1e. Crystal Impact GbR, Bonn, Germany.
 Bruker (1998). *SMART-NT*. Version 5.050. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (1999). *SAINT-Plus*. Version 6.02 (including *XPREP*). Bruker AXS Inc., Madison, Wisconsin, USA.
 Eulleuch, H., Kamoun, M., Daoud, A. & Jouini, T. (1996). *Phys. Status Solidi A*, **157**, 3–9.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
 Kitahama, K., Kiriyama, H. & Baba, Y. (1979). *Bull. Chem. Soc. Jpn.*, **52**, 324–328.
 Knop, O., Cameron, T. S., James, M. A. & Falk, M. (1983). *Can. J. Chem.* **61**, 1620–1646.
 Lemmerer, A., Billing, D. G. & Reisinger, S. A. (2007). *Acta Cryst.* **C63**, m97–m100.
 Mitzi, D. B., Liang, K. & Wang, S. (1998). *Inorg. Chem.* **37**, 321–327.
 Oxford Diffraction (2003). *CrysAlis CCD* and *CrysAlis RED*. Version 1.170. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
 Rademeyer, M. (2004a). *Acta Cryst.* **C60**, m55–m56.
 Rademeyer, M. (2004b). *Acta Cryst.* **E60**, m345–m347.
 Raptopoulou, C. P., Terzis, A., Mousdis, G. A. & Papavassiliou, G. C. (2002). *Z. Naturforsch. Teil B*, **57**, 645–650.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.