

Complexes of Ag^I with cationic ligands: bis[(2-pyridylmethyl)-ammonio]silver(I) salts

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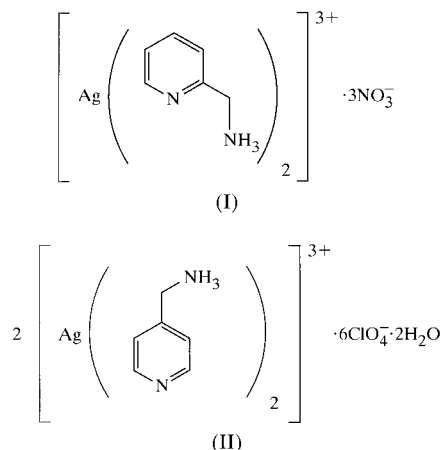
Bis[(2-pyridylmethyl)ammonio]silver(I) trinitrate, [Ag(C₆H₉N₂)₂](NO₃)₃, (I), and bis[bis[(4-pyridylmethyl)ammonio]silver(I)] hexakis(perchlorate) dihydrate, [Ag(C₆H₉N₂)₂]₂(ClO₄)₆·2H₂O, (II), are rare examples of complexes with cationic ligands. In (I), the Ag⁺ cation has a T-shaped [2+1] coordination involving the pyridine N atoms and a nitrate O atom, while in (II) there are three independent two-coordinate Ag complex cations (two with the Ag atoms on independent inversion centres) and disordered ClO₄⁻ ions. The crystal structures reveal the role of hydrogen bonding in stabilizing these complexes.

Comment

Cationic ligands are much less common than anionic or neutral ligands. Examples of structurally characterized metal complexes belong to four categories: (i) the well known tropylium cation (Cotton & Wilkinson, 1988), (ii) thiamine-substituted ligands (Louloudi & Hadjiliadis, 1994), (iii) the quaternary ammonium ion, N(CH₂CH₂)₃NH⁺ (Stucky & Ross, 1969), and (iv) the protonated phosphinoalkyl amine, (Ph₂PCH₂CH₂)₃NH⁺ (Cecconi *et al.*, 1984). Protonation of the primary amine side chain of an N-heterocyclic compound leads to another class of such ligands. Complexes of these ligands are expected to have added stability due to hydrogen bonding with anions. In this paper, we report the crystal structures of two such complexes, namely bis[(2-pyridylmethyl)ammonio]silver(I) trinitrate, (I), and bis[bis[(4-pyridylmethyl)ammonio]silver(I)] hexakis(perchlorate) dihydrate, (II).

The asymmetric unit of compound (I) is made up of two protonated ligands bound to Ag with a near-linear geometry [N1—Ag—N3 = 165.76 (11)°]. A nitrate O atom is also weakly bonded to Ag, leading to a T-shaped AgN₂O coordination, with all four atoms nearly coplanar [r.m.s. deviation for the mean plane = 0.041 Å]. All non-H atoms in the two aromatic ligands, except for one ammonium N atom (N2) and the Ag atom, form another mean plane, with an r.m.s. deviation of 0.056 Å. What is remarkable is that the two ligands are in a

'syn' configuration, which brings the two NH₃⁺ groups close together. This seemingly less stable arrangement is stabilized by an array of NO₃⁻ ions arranged in a semicircular fashion around the NH₃⁺ groups, forming numerous hydrogen bonds (Table 2).



The asymmetric unit of compound (II) contains three Ag atoms. Ag1 and Ag3 are situated on inversion centres and are coordinated to two protonated ligands, whereas Ag2 is coordinated to two crystallographically independent protonated ligands, with a linear geometry [N3—Ag2—N5 = 174.8 (3)°] around Ag2. There are six anions in the unit cell and all were found to be disordered. The disorder was modelled by splitting

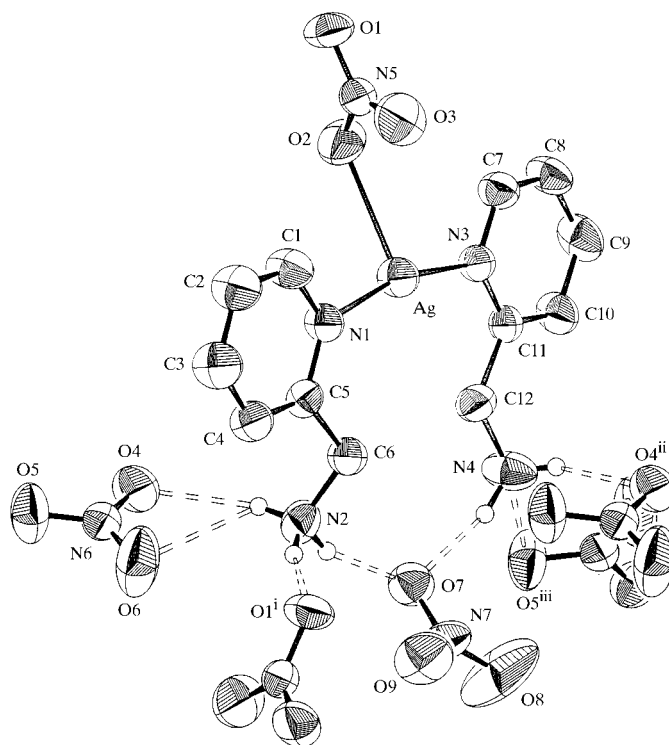


Figure 1 The molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and ring H atoms have been omitted for clarity. Important hydrogen bonds are shown as broken lines [symmetry codes: (i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 + x, y, z$; (iii) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$].

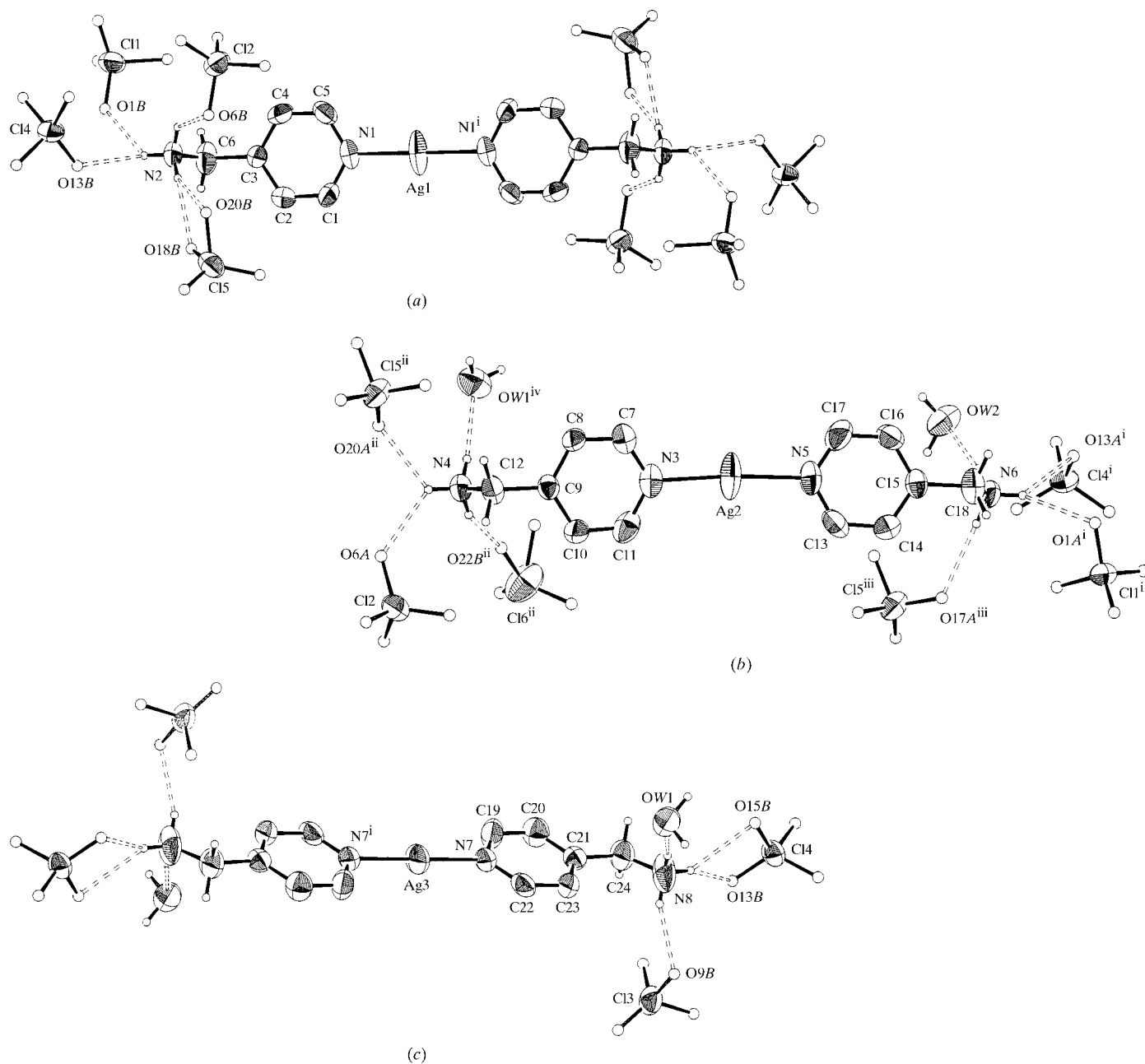


Figure 2

The molecular structures of the three different complex cations in (II) with the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level and ring H atoms have been omitted for clarity. Only part of each disordered ClO_4^- ion is shown, with the disordered O atoms represented by circles. Important hydrogen bonds are shown as broken lines. Symmetry codes: in (a), (i) $-x, 1-y, 1-z$; in (b), (i) $1-x, y-1, z$; (ii) $-x, -x, 1-y, -z$; (iii) $1-x, -y, -z$; (iv) $x-1, y, z$; in (c), (i) $1-x, 1-y, -z$.

each perchlorate O atom into two parts, which were refined isotropically. As in the case of (I), all 18 ammonio H atoms in (II) are involved in hydrogen-bonding interactions with the anions (Table 4).

In both structures, the number of potential hydrogen-bond acceptor atoms is higher than the number of 'acidic' H atoms. This leads to numerous three-centre (bifurcated-donor type) hydrogen bonds. However, the available number of acceptor atoms is limited by crystal-packing constraints. In (I), six out of nine O atoms, and in (II), nine out of 24 ClO_4^- O atoms and

two water O atoms, are able to act as acceptors. In contrast with the usual situation, where hydrogen bonding inhibits positional disorder, all the ClO_4^- ions in (II) are disordered. It appears that this unusual situation is a consequence of the small number of available acceptors.

Experimental

Compound (I) was synthesized by slowly adding, with stirring, a solution of 2-amp [0.2 ml, 1.9 mmol; amp is (aminomethyl)pyridine]

in 0.1 N HNO₃ (5 ml) to an aqueous solution of AgNO₃ (5 ml, 0.108 g, 0.64 mmol). Crystals of (I) were obtained by leaving the solution to stand at 277 K for several days. Identical crystals were also obtained when Ag(2-amp)NO₃ (Swarnabala & Rajasekharan, 1997) was recrystallized from 0.1 N HNO₃. Compound (II) was synthesized by dissolving polymeric Ag(4-amp)ClO₄·0.5H₂O (Sailaja & Rajasekharan, 2000) in 0.1 N HClO₄. Single crystals of (II) were obtained by slow evaporation of the acid solution at 277 K.

Compound (I)

Crystal data

[Ag(C₆H₉N₂)₂](NO₃)₃
M_r = 512.20
 Monoclinic, *P*2₁/*c*
a = 8.854 (2) Å
b = 19.752 (12) Å
c = 10.662 (7) Å
 β = 93.66 (3)°
V = 1860.7 (16) Å³
Z = 4

D_x = 1.828 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 7.8–13.7°
 μ = 1.15 mm⁻¹
T = 293 (2) K
 Rhombic, light yellow
 0.45 × 0.25 × 0.09 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: semi-empirical (North *et al.*, 1968)
T_{min} = 0.831, *T_{max}* = 0.999
 3481 measured reflections
 3259 independent reflections
 2655 reflections with *I* > 2σ(*I*)

R_{int} = 0.049
 θ_{\max} = 25°
h = 0 → 10
k = 0 → 23
l = -12 → 12
 2 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.034
wR(*F*²) = 0.093
S = 1.11
 3259 reflections
 288 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 1.9184P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.044$
 $\Delta\rho_{\max} = 0.66 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.65 \text{ e \AA}^{-3}$

Table 1

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

Ag–N1	2.217 (3)	Ag–O2	2.526 (3)
Ag–N3	2.224 (3)		
N1–Ag–N3	165.76 (11)	N3–Ag–O2	90.70 (11)
N1–Ag–O2	102.41 (12)		

Table 2

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

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N2–HN21...O7	0.86 (5)	2.04 (5)	2.860 (5)	160 (4)
N2–HN21...O9	0.86 (5)	2.49 (5)	3.129 (6)	132 (4)
N2–HN22...O4	0.83 (6)	2.33 (6)	3.151 (6)	168 (6)
N2–HN22...O6	0.83 (6)	2.40 (6)	2.910 (6)	120 (5)
N2–HN23...O1 ⁱ	0.97 (7)	1.91 (7)	2.858 (6)	165 (5)
N4–HN41...O7	0.90 (6)	1.94 (6)	2.818 (6)	163 (5)
N4–HN42...O4 ⁱⁱ	0.82 (4)	2.35 (4)	3.051 (8)	145 (4)
N4–HN43...O5 ⁱⁱⁱ	0.88 (9)	2.17 (9)	2.867 (5)	137 (7)
N4–HN43...O9 ^{iv}	0.88 (9)	2.55 (8)	3.162 (8)	128 (7)

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

Compound (II)

Crystal data

[Ag(C₆H₉N₂)₂](ClO₄)₆·2H₂O
M_r = 1285.08
 Triclinic, *P*1̄
a = 11.3358 (7) Å
b = 14.5436 (10) Å
c = 14.6015 (17) Å
 α = 77.700 (8)°
 β = 89.519 (6)°
 γ = 74.421 (6)°
V = 2262.5 (3) Å³

Z = 2
D_x = 1.886 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 15.0–17.5°
 μ = 1.32 mm⁻¹
T = 293 (2) K
 Rectangular, colourless
 0.44 × 0.44 × 0.32 mm

Table 3

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

Ag1–N1 ⁱ	2.175 (5)	Ag2–N3	2.136 (5)
Ag1–N1	2.175 (5)	Ag3–N7	2.142 (5)
Ag2–N5	2.133 (5)	Ag3–N7 ⁱⁱ	2.142 (5)
N1–Ag1–N1 ⁱ	180	N7–Ag3–N7 ⁱⁱ	180
N3–Ag2–N5	175.0 (2)		

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

Table 4

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

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N2–HN21...O1B ⁱ	0.87	2.24	2.89 (2)	132
N2–HN21...O13A ⁱ	0.87	2.32	3.002 (10)	135
N2–HN21...O13B ⁱ	0.87	2.38	2.93 (2)	122
N2–HN21...O11A ⁱⁱ	0.87	2.62	3.328 (14)	140
N2–HN22...O5A	0.87	2.19	3.058 (11)	171
N2–HN22...O6B	0.87	2.32	2.93 (2)	128
N2–HN23...O18B ⁱⁱⁱ	0.87	2.10	2.92 (2)	157
N2–HN23...O20B ⁱⁱⁱ	0.87	2.35	3.16 (2)	154
N2–HN23...O18A ⁱⁱⁱ	0.87	2.53	3.33 (2)	153
N4–HN41...O6A	0.87	2.20	2.842 (11)	130
N4–HN41...O20A ⁱⁱⁱ	0.87	2.23	2.844 (13)	128
N4–HN41...O20B ⁱⁱⁱ	0.87	2.29	2.981 (17)	137
N4–HN41...O6B	0.87	2.34	2.973 (18)	130
N4–HN42...O22B ⁱⁱⁱ	0.87	1.86	2.68 (2)	155
N4–HN42...O22A ⁱⁱⁱ	0.87	2.11	2.978 (14)	177
N4–HN43...OW1 ⁱ	0.87	2.02	2.865 (8)	163
N6–HN61...O1B ^{iv}	0.87	2.10	2.91 (2)	155
N6–HN61...O1A ^{iv}	0.87	2.37	3.091 (10)	140
N6–HN61...O13A ^{iv}	0.87	2.48	3.057 (13)	124
N6–HN61...O2A ^{iv}	0.87	2.52	2.954 (10)	112
N6–HN62...OW2	0.87	1.95	2.814 (8)	170
N6–HN63...O17A ^v	0.87	2.19	3.058 (13)	175
N6–HN63...O17B ^v	0.87	2.26	3.118 (16)	171
N8–HN81...O13B ^{vi}	0.87	2.16	2.97 (2)	154
N8–HN81...O15B ^{vi}	0.87	2.25	3.00 (2)	144
N8–HN81...O13A ^{vi}	0.87	2.28	3.081 (11)	153
N8–HN81...O15A ^{vi}	0.87	2.46	3.219 (14)	146
N8–HN82...O9B ^{vii}	0.87	1.96	2.758 (18)	151
N8–HN82...O9A ^{vii}	0.87	2.50	3.225 (12)	142
N8–HN83...OW1	0.87	2.00	2.866 (9)	171
OW1–HW11...O23A ^{viii}	0.93 (5)	2.07 (7)	2.796 (17)	134 (8)
OW1–HW11...O23B ^{viii}	0.93 (5)	2.35 (6)	3.22 (2)	156 (8)
OW1–HW11...O21A ^{viii}	0.93 (5)	2.50 (8)	3.105 (18)	123 (7)
OW1–HW12...O14A ^{viii}	0.95 (5)	2.03 (7)	2.830 (12)	141 (7)
OW1–HW12...O14B ^{viii}	0.95 (5)	2.10 (8)	2.87 (2)	138 (7)
OW2–HW21...O15A ^{vii}	0.91 (5)	2.58 (10)	3.031 (12)	111 (7)
OW2–HW22...O24B ^{vii}	0.88 (5)	2.14 (6)	2.942 (19)	151 (8)
OW2–HW22...O24A ^{vii}	0.88 (5)	2.20 (7)	3.026 (19)	155 (8)
OW2–HW22...O21A ^{vii}	0.88 (5)	2.42 (6)	3.178 (17)	144 (7)

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

Data collection

Enraf–Nonius CAD-4
diffractometer
 $\omega/2\theta$ scans
Absorption correction: semi-
empirical (North *et al.*, 1968)
 $T_{\min} = 0.915$, $T_{\max} = 0.982$
8138 measured reflections
7939 independent reflections
5117 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.009$
 $\theta_{\text{max}} = 25^\circ$
 $h = -4 \rightarrow 13$
 $k = -16 \rightarrow 17$
 $l = -17 \rightarrow 17$
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.063$
 $wR(F^2) = 0.181$
 $S = 1.04$
7939 reflections
605 parameters
H atoms treated by a mixture of
independent and constrained
refinement

$w = 1/[\sigma^2(F_o^2) + (0.1016P)^2 + 1.328P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.021$
 $\Delta\rho_{\text{max}} = 0.78 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.58 \text{ e } \text{\AA}^{-3}$
Extinction correction: *SHELXL97*
(Sheldrick, 1997)
Extinction coefficient: 0.0067 (7)

For compound (I), the ammonio H atoms were located from difference maps and refined isotropically. Other H atoms were located by geometrical considerations and refined using a riding model with common isotropic displacement parameters, which were refined. For compound (II), the water H atoms were located from difference maps and bond-length constraints were applied. All other H atoms were located by geometrical considerations and refined using a riding model. U_{iso} values for ammonio H atoms were refined; other H atoms were assigned fixed U_{iso} values, equal to $1.2U_{\text{eq}}$ of the parent atom for ring atoms and $1.5U_{\text{eq}}$ for CH_2 and H_2O H atoms.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *Xtal3.4* (Hall *et al.*, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1143). Services for accessing these data are described at the back of the journal.

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