

## Hydrogen-bonded adducts of ferrocene-1,1'-diylbis(diphenylmethanol): monomeric and dimeric 1:1 adducts with 1,2-bis(4-pyridyl)ethane and 1,2-diaminoethane

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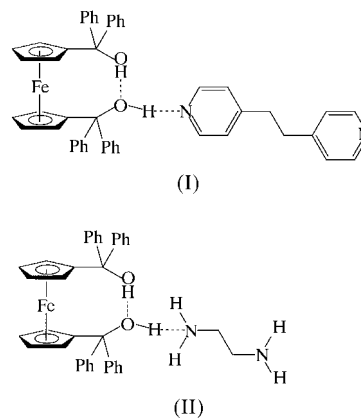
In ferrocene-1,1'-diylbis(diphenylmethanol)-4,4'-ethylenedipyridine (1/1),  $[\text{Fe}(\text{C}_{18}\text{H}_{15}\text{O})_2] \cdot \text{C}_{12}\text{H}_{12}\text{N}_2$ , there is an intramolecular  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bond in the ferrocenediol component and a single  $\text{O}-\text{H} \cdots \text{N}$  hydrogen bond linking the two components into a finite monomeric adduct. Ferrocene-1,1'-diylbis(diphenylmethanol)-ethylenediamine (1/1),  $[\text{Fe}(\text{C}_{18}\text{H}_{15}\text{O})_2] \cdot \text{C}_2\text{H}_8\text{N}_2$ , crystallizes with  $Z' = 2$  in space group  $P\bar{1}$ , and there are two independent four-component aggregates in the structure, both of which are centrosymmetric. In the first type of aggregate, the molecular components are linked by  $\text{O}-\text{H} \cdots \text{N}$  and  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds, in which both diamine N atoms participate; in the second type of aggregate, the diamine component is disordered over two sets of sites, but only one N atom is involved in the hydrogen bonding.

### Comment

The organometallic diol ferrocene-1,1'-diylbis(diphenylmethanol),  $[\text{Fe}(\text{C}_5\text{H}_4\text{CPh}_2\text{OH})_2]$ , forms hydrogen-bonded adducts with a wide range of hydrogen-bond acceptors, particularly cyclic and cage amines (Ferguson *et al.*, 1993, 1995; Glidewell *et al.*, 1994). Thus with piperazine,  $\text{HN}(\text{CH}_2\text{-CH}_2)_2\text{NH}$ , an adduct of 1:1 stoichiometry is formed in which the supramolecular aggregation consists of spiral  $C_2^2(13)$  chains of alternating diol and diamine units containing two distinct  $\text{O}-\text{H} \cdots \text{N}$  hydrogen bonds (Glidewell *et al.*, 1994); by contrast, in the 1:1 adduct formed with 4,4'-bipyridyl, only half of the bipyridyl molecules are involved in the supramolecular aggregation, which takes the form of the centrosymmetric three-component aggregate diol-diamine-diol, while the

remainder of the bipyridyl molecules simply occupy isolated sites in the structure (Glidewell *et al.*, 1994). While a wide range of supramolecular structures has been observed in adducts formed by this ferrocenediol (Ferguson *et al.*, 1993, 1995; Glidewell *et al.*, 1994), no one structure type is predictable from knowledge of the remainder; in particular, the hydrogen-bond donor and acceptor behaviour of the non-ferrocenediol components is not yet readily predictable. However, a frequently observed pattern, found in the adducts formed with 4,4'-bipyridyl, 1,4-dioxan, dimethylformamide and hexamethylenetetramine, is that of a single intramolecular  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bond in the ferrocenediol component forming an  $S(8)$  ring, together with a single  $\text{O}-\text{H} \cdots \text{A}$  hydrogen bond to the acceptor atom A, which may be N or O, in the second component.

In the adduct with 1,2-bis(4-pyridyl)ethane, (I) (Fig. 1), there is an intramolecular  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bond (Table 2) and, in addition, O1 acts as hydrogen-bond donor to N71; N81, on the other hand, does not act as a hydrogen-bond acceptor, even of soft  $\text{C}-\text{H} \cdots \text{N}$  hydrogen bonds, so that (I) is a simple finite adduct, whose hydrogen bonding can be characterized by the graph-set descriptor  $S(8)D$ , precisely as for the 1:1 adduct formed by the ferrocenediol with dimethylformamide (Glidewell *et al.*, 1994). The constitution of (I) is thus entirely different from that of the analogous 1:1 adduct formed with 4,4'-bipyridyl itself.



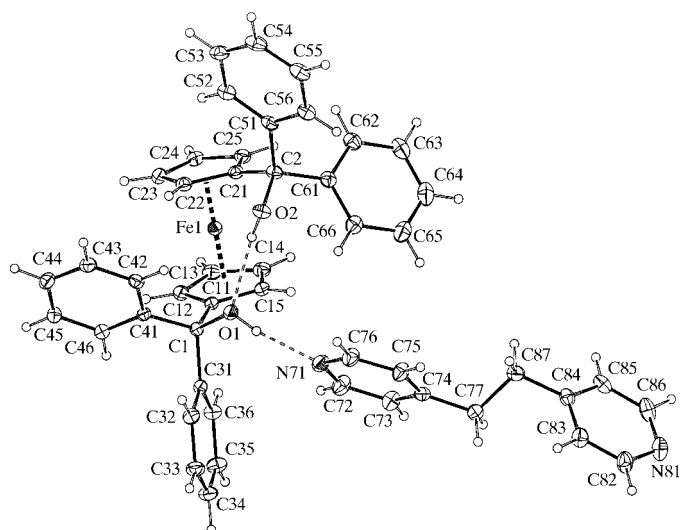
The 1,2-diaminoethane adduct, (II), also exhibits 1:1 stoichiometry, but in this case the diamine component is potentially a fourfold donor of hydrogen bonds, as well as potentially a twofold acceptor; adduct (II) crystallizes with  $Z' = 2$  and there are two distinct finite centrosymmetric aggregates in the structure which exhibit different patterns of hydrogen-bonding behaviour. In the aggregate of type 1, which contains ferrocenediol 1, based on Fe1, and diamine 1, containing N1 and N4, the neutral molecular components are all fully ordered. In addition to the intramolecular  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bond in the ferrocenediol, which generates the usual  $S(8)$  motif, the individual molecular components are linked by both  $\text{O}-\text{H} \cdots \text{N}$  and  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds, but there are no  $\text{N}-\text{H} \cdots \text{N}$  hydrogen bonds present. Hydroxyl O11 acts as a hydrogen-bond donor to N1 within the asymmetric unit (Fig. 2); N1 in the diamine at  $(x, y, z)$  acts as a

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hydrogen-bond donor, *via* H1A and H1B, to O11 and O12, respectively, in the ferrocenediol at  $(-x, 1 - y, 1 - z)$ , and N4 at  $(x, y, z)$  also acts as donor, *via* H4A, to O12 at  $(-x, 1 - y, 1 - z)$  but H4B plays no part in the hydrogen bonding. In this manner, a four-component aggregate is formed, centred at  $(0, \frac{1}{2}, \frac{1}{2})$  (Fig. 3) and containing a central  $R_4^4(8)$  ring and pairs of both  $R_3^2(6)$  and  $R_2^1(7)$  rings, in which O11 and O12, respectively, are the double acceptors.

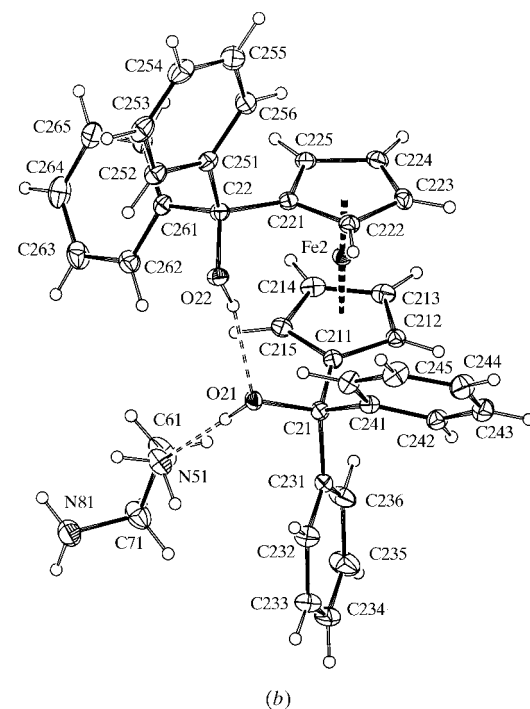
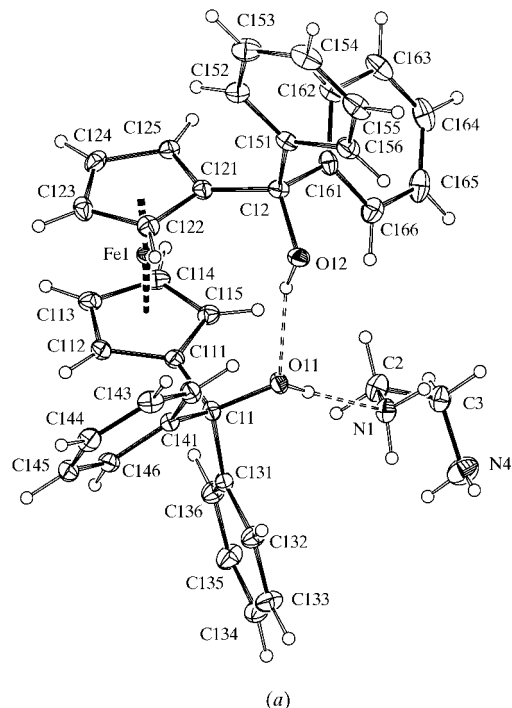
The aggregate of type 2 contains the fully ordered ferrocenediol 2, based on Fe2, and the disordered diamine 2 (Fig. 2); in both orientations of this diamine, only one N atom participates in the hydrogen bonding, so that the rest of the chain, untethered at the distal end, is free to adopt more than one conformation. By contrast, in the type 1 aggregate, both N atoms are engaged in ring formation, so locking the diamine component into a single conformation. The two amine conformers in the type 2 aggregate have refined site-occupation factors of 0.756 (5) and 0.244 (5). In addition, in the minor conformer, there is rotational disorder of the terminal  $\text{NH}_2$  group based on N82; the partial H atoms on N82 could not be unambiguously located from difference maps, and hence they were omitted from the refinements. This type 2 aggregate contains the same  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bond as in the type 1 aggregate, and O21 in the ferrocenediol acts as hydrogen-bond donor to N51 within the asymmetric unit; N51 at  $(x, y, z)$  in turn acts as hydrogen-bond donor, *via* H51A, to O21 in the ferrocenediol at  $(1 - x, -y, -z)$ , so generating an  $R_4^4(8)$  ring centred at  $(\frac{1}{2}, 0, 0)$  (Fig. 4). None of the other N—H bonds in this aggregate participate in hydrogen bonding, and there are no interactions between aggregates of the two types. The hydrogen-bonding patterns within these two types of aggregate (Figs. 3 and 4) may be contrasted with the very simple  $R_6^6(12)$  ring in the four-component aggregate formed by the ferrocenediol in its adduct with methanol (Ferguson *et al.*, 1993). Equally, the behaviour of the diamine component in (II) may be contrasted with that of piperazine in its adduct



**Figure 1**  
The molecular aggregate in (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

with the ferrocenediol (Glidewell *et al.*, 1994), where the diamine acts only as a hydrogen-bond acceptor and the ferrocenediol only as a hydrogen-bond donor.

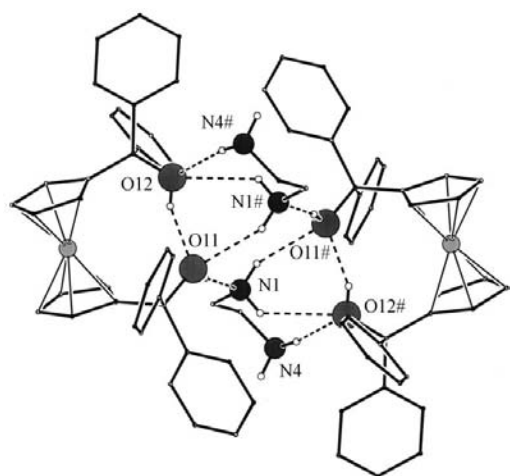
In the ferrocenediol components of (I) and (II), the cyclopentadienyl rings are nearly eclipsed. A convenient measure



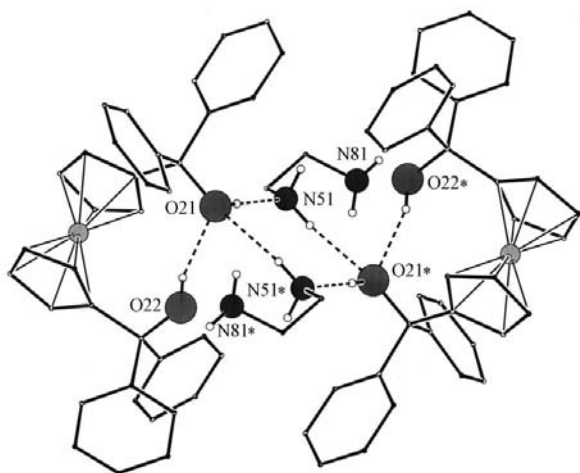
**Figure 2**  
The molecular components of (II) showing the atom-labelling scheme of (a) ferrocenediol 1 and diamine 1, and (b) ferrocenediol 2 and diamine 2. Displacement ellipsoids are drawn at the 30% probability level, but in (b), the minor conformer (N52–N82) of the diamine has been omitted for clarity.

of the relative twist of the rings in (I) is the torsion angle  $C11-Cg1-Cg2-C21$ , where  $Cg1$  and  $Cg2$  are the centroids of the two rings; to allow for the fact that the rings do not have local  $C_5$  rotational symmetry, because of the variations in the C—C bond distances, the mean value of the torsion angles  $C1n-Cg1-Cg2-C2n$  ( $n = 1-5$ ) provides a better measure. For (II), the relevant values are those of  $C11n-Cg1-Cg2-C12n$  and  $C21n-Cg3-Cg4-C22n$  ( $n = 1-5$ ). For perfect eclipsing, this mean value should be  $(72 \times n)^\circ$  ( $n =$  zero or integer); the observed values are  $65.4(4)^\circ$  in (I), and  $53.7(4)$  and  $-60.0(4)^\circ$  in (II), indicating that each independent ferrocenediol adopts a conformation which is close to eclipsed, with the substituents on the two rings offset from one another by one-fifth of a turn.

The orientation of the exocyclic  $CPh_2OH$  substituents relative to the adjacent rings (Table 1 and 3) is largely deter-



**Figure 3**  
Part of the crystal structure of (II) showing the formation of a type 1 aggregate. For clarity, H atoms bonded to C atoms have been omitted. Atoms marked with a hash (#) are at the symmetry position  $(-x, 1-y, 1-z)$ .



**Figure 4**  
Part of the crystal structure of (II) showing the formation of a type 2 aggregate. For clarity, H atoms bonded to C atoms have been omitted, and only the major conformer of the diamine is shown. Atoms marked with a star (\*) are at the symmetry position  $(1-x, -y, -z)$ .

mined by the formation of the intramolecular  $O-H \cdots O$  hydrogen bonds. In adduct (I), the central aliphatic portion of the diamine has an almost planar skeleton, but the rings are significantly twisted out of this plane (Table 1, Fig. 1). In adduct (II), the synclinal conformation of the diamine component in the type 1 aggregate is most readily ascribed to the hydrogen bonding, but such a simple explanation cannot be valid for the diamine in the type 2 aggregate, where the major and minor components of the amine adopt synclinal and antiperiplanar conformations, respectively (Tables 3 and 4).

## Experimental

For each adduct, stoichiometric quantities of the ferrocenediol and the appropriate amine were separately dissolved in dichloromethane. The component solutions were mixed and the mixtures were set aside to crystallize, producing analytically pure (I) and (II). Analyses: compound (I), found C 78.5, H 5.9, N 3.7%;  $C_{48}H_{42}FeN_2O_2$  requires C 78.5, H 5.8, N 3.8%; compound (II), found C 74.2, H 6.3, N 4.6%;  $C_{38}H_{38}FeN_2O_2$  requires C 74.7, H 6.3, N 4.6%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

### Compound (I)

#### Crystal data

$[Fe(C_{18}H_{15}O_2)] \cdot C_{12}H_{12}N_2$   
 $M_r = 734.69$   
 Triclinic,  $P\bar{1}$   
 $a = 9.7191(3) \text{ \AA}$   
 $b = 11.3281(4) \text{ \AA}$   
 $c = 17.5549(7) \text{ \AA}$   
 $\alpha = 78.6970(16)^\circ$   
 $\beta = 87.8100(15)^\circ$   
 $\gamma = 75.772(2)^\circ$   
 $V = 1837.05(11) \text{ \AA}^3$

$Z = 2$   
 $D_x = 1.328 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 7609 reflections  
 $\theta = 2.7-27.2^\circ$   
 $\mu = 0.45 \text{ mm}^{-1}$   
 $T = 150(2) \text{ K}$   
 Block, orange  
 $0.20 \times 0.18 \times 0.18 \text{ mm}$

#### Data collection

KappaCCD diffractometer  
 $\varphi$  scans, and  $\omega$  scans with  $\kappa$  offsets  
 Absorption correction: multi-scan  
 (DENZO-SMN; Otwinowski & Minor, 1997)  
 $T_{\min} = 0.915$ ,  $T_{\max} = 0.923$   
 23051 measured reflections  
 8061 independent reflections

4882 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.094$   
 $\theta_{\max} = 27.2^\circ$   
 $h = 0 \rightarrow 12$   
 $k = -13 \rightarrow 14$   
 $l = -22 \rightarrow 22$   
 Intensity decay: negligible

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.125$   
 $S = 0.97$   
 8061 reflections  
 481 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.40 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.0031(7)

**Table 1**

Selected torsion angles ( $^\circ$ ) for (I).

O1—C1—C11—C12	-155.0 (2)	O2—C2—C21—C22	34.4 (3)
C31—C1—C11—C12	85.7 (3)	C51—C2—C21—C22	-78.2 (3)
C41—C1—C11—C12	-37.2 (4)	C61—C2—C21—C22	156.6 (2)
C73—C74—C77—C87	128.6 (3)	C74—C77—C87—C84	-179.8 (2)
C83—C84—C87—C77	-64.3 (3)		

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

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...N71	0.84	1.92	2.751 (3)	170
O2—H2...O1	0.84	2.07	2.845 (2)	153

**Compound (II)***Crystal data*[Fe(C<sub>18</sub>H<sub>15</sub>O)<sub>2</sub>]<sub>2</sub>·C<sub>2</sub>H<sub>8</sub>N<sub>2</sub> $M_r = 610.55$ Triclinic,  $P\bar{1}$  $a = 9.8551$  (2) Å $b = 11.7183$  (2) Å $c = 27.6810$  (5) Å $\alpha = 82.3495$  (8)° $\beta = 84.4918$  (8)° $\gamma = 73.4846$  (8)° $V = 3031.88$  (10) Å<sup>3</sup> $Z = 4$  $D_x = 1.338$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation

Cell parameters from 12683 reflections

 $\theta = 2.7$ – $27.5$ ° $\mu = 0.54$  mm<sup>-1</sup> $T = 150$  (2) K

Block, orange

0.32 × 0.28 × 0.26 mm

*Data collection*

KappaCCD diffractometer

 $\varphi$  scans, and  $\omega$  scans with  $\kappa$  offsets

Absorption correction: multi-scan (DENZO-SMN; Otwinowski &amp; Minor, 1997)

 $T_{\min} = 0.848$ ,  $T_{\max} = 0.873$ 

39 122 measured reflections

13 826 independent reflections

*Refinement*Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.050$  $wR(F^2) = 0.123$  $S = 0.98$ 

13 826 reflections

795 parameters

8093 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.088$  $\theta_{\text{max}} = 27.5$ ° $h = 0 \rightarrow 12$  $k = -14 \rightarrow 15$  $l = -35 \rightarrow 35$ 

Intensity decay: negligible

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0430P)^2]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\text{max}} < 0.001$  $\Delta\rho_{\text{max}} = 0.38$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -0.42$  e Å<sup>-3</sup>**Table 3**

Selected torsion angles (°) for (II).

O11—C11—C111—C112	-153.6 (2)	O21—C21—C211—C212	161.3 (2)
C131—C11—C111—C112	88.1 (3)	C231—C21—C211—C212	-79.4 (3)
C141—C11—C111—C112	-35.0 (3)	C241—C21—C211—C212	42.5 (3)
O12—C12—C121—C122	41.0 (3)	O22—C22—C221—C222	-36.2 (3)
C151—C12—C121—C122	-73.4 (3)	C251—C22—C221—C222	78.7 (3)
C161—C12—C121—C122	165.0 (2)	C261—C22—C221—C222	-159.7 (2)
N1—C2—C3—N4	61.6 (4)	N52—C62—C72—N82	179.5 (4)
N51—C61—C71—N81	60.5 (13)		

Compounds (I) and (II) both crystallize in the triclinic system; for each, space group  $P\bar{1}$  was assumed and confirmed by the analysis. In (II), the hydrogen-bonded N atoms of the two conformers of amine 2,

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

D—H...A	D—H	H...A	D...A	D—H...A
O11—H11...N1	0.84	1.89	2.715 (3)	169
O12—H12...O11	0.84	1.92	2.687 (2)	152
O21—H21...N51	0.84	1.90	2.743 (3)	178
O22—H22...O21	0.84	2.01	2.790 (2)	154
N1—H1A...O11 <sup>i</sup>	0.91	2.31	3.103 (3)	146
N1—H1B...O12 <sup>i</sup>	0.91	2.49	3.142 (3)	129
N4—H4A...O12 <sup>i</sup>	0.91	2.45	3.358 (3)	172
N51—H51A...O21 <sup>ii</sup>	0.91	2.43	3.252 (3)	151

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

N51 and N52, were constrained to have identical coordinates and identical anisotropic displacement parameters. H atoms were treated as riding atoms with C—H distances of 0.95 (aryl and cyclopentadienyl) or 0.99 Å (aliphatic), an N—H distance of 0.91 Å and an O—H distance of 0.84 Å.

For both compounds, data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1062). Services for accessing these data are described at the back of the journal.

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