

Bis(2,4,7-trimethylindenyl)cobalt(II) and *rac*-2,2',4,4',7,7'-hexamethyl-1,1'- biindene

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The crystal and molecular structures of bis(η^5 -2,4,7-trimethylindenyl)cobalt(II), [Co(C₁₂H₁₃)₂], (I), and *rac*-2,2',4,4',7,7'-hexamethyl-1,1'-biindene, C₂₄H₂₆, (II), are reported. In the crystal structure of (I), the Co atom lies on an inversion centre and the structure represents the first example of a bis(indenyl)cobalt complex exhibiting an eclipsed indenyl conformation. The (1*R*,1'*R*) and (1*S*,1'*S*) enantiomers of the three possible stereoisomers of (II), which form as by-products in the synthesis of (I), cocrystallize in the monoclinic space group *P*2₁/*c*. In the unit cell of (II), alternating (1*R*,1'*R*) and (1*S*,1'*S*) enantiomers pack in non-bonded rows along the *a* axis, with the planes of the indenyl groups parallel to each other and separated by 3.62 and 3.69 Å.

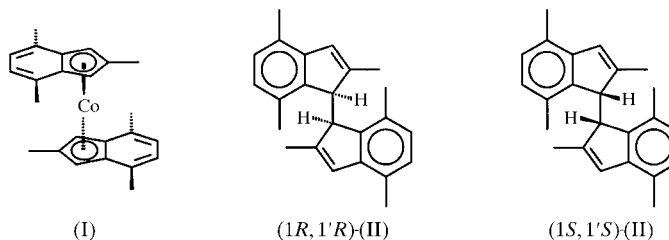
Comment

Late transition metal complexes have been shown to be active catalysts for hydrogenations, hydroformylations, isomerizations or cycloadditions (Eisen *et al.*, 1991; Leitner, 1995; Castellanos-Páez *et al.*, 1997; Zhu & Zhang, 1998; Witulski & Stengel, 1999; Beller *et al.*, 1999). In comparison with the analogous cyclopentadienyl complexes, the more electrophilic transition metal complexes with indenyl ligands often show enhanced reactivities (Kakkar *et al.*, 1992). This was attributed to the ability of indenyl complexes to undergo ring slippage of the five-membered indenyl ring coordinated to the metal from a η^5 - to a η^3 -coordination mode (Trost & Kulawiec, 1993). Currently, only one X-ray structure of a neutral bis(indenyl) complex of cobalt has been described (Westcott *et al.*, 1990).

Biindene compounds are potential precursors for the synthesis of dibenzfulvenes (Lustenberger *et al.*, 1979), biindane compounds (Grindley *et al.*, 1996) or bimetallic complexes (Arce *et al.*, 1999), and can generally be conveniently synthesized by oxidative coupling of the corresponding indenyl salts (Escher *et al.*, 1987). Due to two asymmetric centres at the bridging C atoms, three stereoisomers occur, of which two form a pair of enantiomers with (1*R*,1'*R*) or (1*S*,1'*S*)

configurations at their stereogenic centres. Currently, only two crystal structures of biindene compounds have been reported (Lustenberger *et al.*, 1979; Maouche *et al.*, 1985).

In the course of our investigations regarding the synthesis of indenyl-transition metal complexes (Halterman *et al.*, 2000; Schumann, Stenzel, Dechert, Girgsdies & Halterman, 2001), we isolated bis(2,4,7-trimethylindenyl)cobalt(II), (I), and *rac*-2,2',4,4',7,7'-hexamethyl-1,1'-biindene, (II), as side products in the formation of dicarbonyl(2,4,7-trimethylindenyl)cobalt(I) in the presence of iodine, starting from octacarbonyldicobalt(0) and (2,4,7-trimethylindenyl)lithium.



Chromatographic separation of the crude mixture in an inert atmosphere with *n*-hexane as eluent followed by crystallization from *n*-hexane resulted in the isolation of the pure compound (I) and the diastereomerically pure compound (II). The pure crystalline compound (I) and its solutions are sensitive to air and moisture, while (II) is stable under these conditions. The high thermal stability of (I) and (II) can be shown by mass spectrometry as the molecular ions form the peaks of highest intensity. Compounds (I) and (II) are soluble in polar solvents such as tetrahydrofuran (THF), pyridine and diethyl ether, as well as in aromatic solvents such as benzene or toluene, and non-polar solvents such as *n*-hexane.

Compound (II) can be obtained independently by reacting stoichiometric amounts of (2,4,7-trimethylindenyl)lithium with iodine in THF at 338 K without the presence of the cobalt complex. In the absence of iodine, however, no product is formed. Under the reported reaction conditions the corresponding diastereomeric *meso* compound, (1*R*,1'*S*)-2,2',4,4',7,7'-hexamethyl-1,1'-biindene, is formed in approximately 20% yield, as determined by ¹H NMR spectroscopy of the crude reaction mixture.

The molecular structure of (I) (Fig. 1) exhibits a Co^{II} atom coordinated in a η^5 -fashion to two 2,4,7-trimethylindenyl ligands. As the Co atom of (I) lies on an inversion centre, the indenyl planes in (I) are exactly parallel to one another and the main axes of the indenyl ligands form a rotation angle (RA) of exactly 180°. This is the first example of a bis-(indenyl)cobalt compound where this is observed. In the less sterically hindered bis(η^5 -indenyl)cobalt(II) (Westcott *et al.*, 1990), a nearly eclipsed conformation of the indenyl ligands (RA = 10.4°) is found, whereas in the more sterically hindered bis(η^5 -heptamethylindenyl)cobalt(III) hexafluorophosphate (O'Hare *et al.*, 1993), a nearly perpendicular conformation (RA = 89°) occurs. Rotation angles of 9.1 and 151.3° have been observed for bis(η^5 -indenyl)iron(II) and bis(η^5 -heptamethylindenyl)iron(II), respectively, the latter increased angle being attributed to orbital effects (Crossley *et al.*, 1989). In

(+)-bis(η^5 -2-methylindenyl)iron(II), a rotation angle of 134° has been ascribed to additional steric interactions of the terpene units with the indenyl ligands (Schumann, Stenzel, Dechert & Halterman *et al.*, 2001). A completely staggered indenyl ligand conformation, similar to that found in (I), has been observed for bis(η^5 -heptamethylindenyl)chromium(II), with the metal atom also situated on a crystallographic inversion centre (O'Hare *et al.*, 1993).

The average Co—C bond length in both five-membered rings is 2.119 (2) Å. This correlates well with the average Co—C bond length of 2.077 (8) Å in bis(η^5 -heptamethylindenyl)cobalt(III) hexafluorophosphate (O'Hare *et al.*, 1993) and 2.121 (4) Å in bis(η^5 -indenyl)cobalt(II) (Westcott *et al.*, 1990). The five-membered rings of the indenyl systems are not

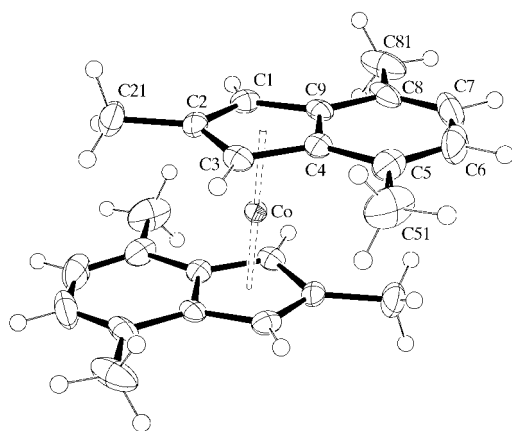


Figure 1
ORTEP-3 (Farrugia, 1997) plot of (I) showing the atomic numbering scheme.

equally bound to the Co atom, but resemble an unsymmetrical η^5 -coordination with slip distortions ($\Delta M-C$) of 0.153 Å [$\Delta M-C$ = difference in the average metal to carbon distances: $0.5(M-C4 + M-C9) - 0.5(M-C1 + M-C3)$] and ring slippage towards C2 of 0.157 Å (ring slippage = distance from the normal of the least-squares ring plane defined by C1/C2/C3/C4/C9 to the metal atom and the centroid of the five-membered ring). This tendency towards a slight η^3 -coordination accounts for a hinge angle (HA) of 7.4° (HA = angle between normals to the least-squares planes defined by C1–C3 and C1/C9/C4/C3) as well as a fold angle (FA) of 6.3° (FA = angle between normals to the least-squares planes defined by C1–C3 and C4–C9). Similar values of $\Delta M-C$ = 0.119, 0.074, 0.043 and 0.030 Å, HA = 7.6, 4.5, 2.2 and 2.5° , as well as FA = 6.0, 4.8, 1.0 and 4.4° , are found in the 19 valence-electron complexes bis(η^5 -indenyl)cobalt(II) and bis(η^5 -heptamethylindenyl)cobalt(III) hexafluorophosphate, and the 18 valence-electron complexes bis(η^5 -indenyl)iron(II) and bis(η^5 -heptamethylindenyl)iron(II), respectively. Significantly increased distortions of $\Delta M-C$ = 0.418 Å, HA = 13.9° and FA = 13.1° are found in the 20 valence-electron complex bis(η^5 -indenyl)nickel(II) (Westcott *et al.*, 1990) to avoid 20 valence-electron counts.

The molecular structure of the (1*R*,1'*R*) stereoisomer of (II) is shown in Fig. 2. Bond lengths and angles compare well with those found in *meso*-1,1'-bis(indenyl) (Lustenberger *et al.*, 1979) and *rac*-1,1'-bis(1,3-dimethylindene) (Maouche *et al.*, 1985). The tetrahedral geometries of the stereogenic centres (C1 and C1') are slightly distorted due to steric constraints as a

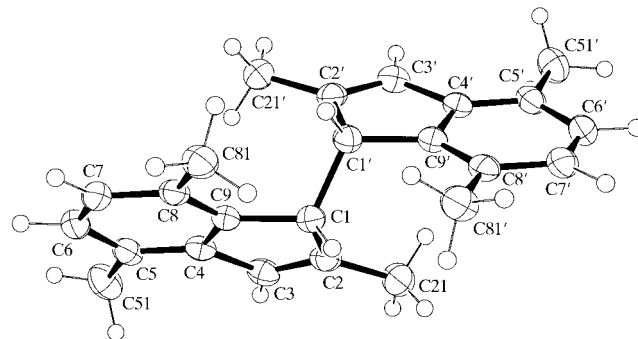


Figure 2
ORTEP-3 (Farrugia, 1997) plot of (II), the (1*R*,1'*R*) stereoisomer, showing the atomic numbering scheme.

result of the opposing 2,4,7-trimethylindenyl fragment [C2—C1—C1' = $113.77(13)^\circ$ and C2'—C1'—C1 = $113.52(12)^\circ$]. Both 2,4,7-trimethylindenyl ring fragments are close to planarity, with the largest deviations from their least-squares planes being 0.066 (1) and 0.057 (1) Å towards the opposing indenyl fragments for C1 and C1', respectively. The C1—C1' bond length is 1.572 (2) Å. The length of the double bonds between C2 and C3, and between C2' and C3' [1.340 (2) and 1.335 (2) Å, respectively] are not affected by the coupling of the two indenyl fragments. The least-squares planes through

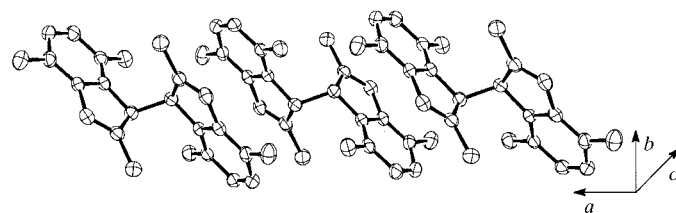


Figure 3
ORTEP-3 (Farrugia, 1997) plot of (II) showing the stacking effect along the *a* axis (H atoms have been omitted for clarity).

the 2,4,7-trimethylindenyl rings lie at an angle of $56.62(3)^\circ$ to one another. The C2—C1—C1'—C2' torsion angle is $48.0(2)^\circ$.

In the unit cell, molecules of (II) pack along the *a* axis in zigzag chains of alternating (1*R*,1'*R*) and (1*S*,1'*S*) stereoisomers as a result of π and geometrical stacking effects (Fig. 3). The parallel planes through the indenyl moieties are 3.62 and 3.69 Å apart.

Experimental

(2,4,7-Trimethylindenyl)lithium was prepared according to published procedures (Kaminsky *et al.*, 1995). Octacarbonyldicobalt(0) was sublimed prior to use. Iodine was used without further purification.

For the preparation of bis(2,4,7-trimethylindenyl)cobalt(II), (I), a solution of iodine (2.03 g, 8.00 mmol) in THF (40 ml) was reacted slowly at 273 K with $\text{Co}_2(\text{CO})_8$ (2.73 g, 7.98 mmol) (gas evolution).

After stirring for 30 min, (2,4,7-trimethylindenyl)lithium (2.66 g, 16.2 mmol) was added slowly to the green solution. The brown suspension was stirred for 20 h at this temperature before the solvent was removed under vacuum. Purification by column chromatography (Al_2O_3 , *n*-hexane) and recrystallization from warm *n*-hexane gave 1.11 g (37%) of deep-red crystals of (I); m.p. 440 K. MS (353 K): m/z 373 (100) $[M]^+$, 358 (18) $[\text{C}_{23}\text{H}_{23}\text{Co}]^+$, 343 (10) $[\text{C}_{22}\text{H}_{20}\text{Co}]^+$, 215 (28) $[\text{C}_{12}\text{H}_{12}\text{Co}]^+$, 186.5 (30) $[M]^{2+}$, 157 (45) $[\text{C}_{12}\text{H}_{13}]^+$, 141 (42) $[\text{C}_{11}\text{H}_9]^+$, 127 (10) $[\text{C}_{10}\text{H}_7]^+$, 115 (11) $[\text{C}_9\text{H}_7]^+$; IR (KBr): ν 3022 (*w*), 2911 (*w*), 1806 (*m*), 1618 (*w*), 1591 (*m*), 1497 (*s*), 1451 (*s*), 1436 (*s*), 1371 (*m*), 1330 (*m*), 1269 (*m*), 1164 (*m*), 1129 (*m*), 1031 (*s*), 948 (*s*), 826 (*m*), 800 (*w*), 731 (*m*), 613 (*m*), 559 (*m*) cm^{-1} . For the preparation of *rac*-2,2',4,4',7,7'-hexamethyl-1,1'-biindene, (II), a yellow solution of (2,4,7-trimethylindenyl)lithium (1.68 g, 10.23 mmol) in THF (30 ml) was reacted slowly at room temperature with iodine (1.43 g, 5.63 mmol). The brown solution was stirred for 40 h at this temperature before being hydrolysed with water (10 ml). The mixture was acidified with 1 M HCl and extracted three times with diethyl ether (20 ml). The combined organic fractions were dried with magnesium sulfate and purified by column chromatography (Al_2O_3 , *n*-hexane). Recrystallization from *n*-hexane at 245 K gave 1.63 g (51%) colourless crystals of (II); m.p. 445 K. ^1H NMR (CDCl_3): δ 6.99 (*d*, $^3J = 7.7$ Hz, 2H, $\text{H}^{5,5'}$, $\text{H}^{6,6'}$), 6.89 (*d*, $^3J = 7.7$ Hz, 2H, $\text{H}^{5,5'}$, $\text{H}^{6,6'}$), 6.44 (*s*, 2H, $\text{H}^{3,3'}$), 4.41 (*s*, 2H, $\text{H}^{1,1'}$), 2.62 (*s*, 6H, $\text{H}^{11,11'}$, $\text{H}^{12,12'}$), 2.31 (*s*, 6H, $\text{H}^{11,11'}$, $\text{H}^{12,12'}$), 1.19 (*s*, 6H, $\text{H}^{10,10'}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 148.11, 144.09, 143.88, 129.87, 126.33 ($\text{C}^{2,2'}$, $\text{C}^{4,4'}$, $\text{C}^{7,7'}$, $\text{C}^{8,8'}$ and $\text{C}^{9,9'}$), 128.24, 126.45, 125.73 ($\text{C}^{3,3'}$, $\text{C}^{5,5'}$ and $\text{C}^{6,6'}$), 50.57 ($\text{C}^{1,1'}$), 19.63, 17.91, 16.05 ($\text{C}^{10,10'}$, $\text{C}^{11,11'}$ and $\text{C}^{12,12'}$); MS (473 K): m/z 315 (58) $[\text{C}_{24}\text{H}_{27}]^+$, 314 (100) $[M]^+$, 299 (6) $[\text{C}_{23}\text{H}_{23}]^+$, 157 (94) $[\text{C}_{12}\text{H}_{13}]^+$, 142 (78) $[\text{C}_{11}\text{H}_{10}]^+$, 127 (10) $[\text{C}_{10}\text{H}_7]^+$, 115 (32) $[\text{C}_9\text{H}_7]^+$; IR (KBr): ν 3038 (*m*), 2955 (*m*), 2905 (*m*), 1870 (*w*), 1617 (*m*), 1594 (*m*), 1495 (*s*), 1440 (*s*), 1375 (*s*), 1248 (*w*), 1143 (*w*), 1029 (*m*), 909 (*m*), 850 (*m*), 801 (*s*), 737 (*s*), 708 (*m*), 552 (*w*), 522 (*m*) cm^{-1} . Analysis calculated for $\text{C}_{24}\text{H}_{26}$ (314.47 g mol $^{-1}$): C 91.67, H 8.33%; found: C 92.06, H 7.98%.

Compound (I)

Crystal data

$[\text{Co}(\text{C}_{12}\text{H}_{13})_2]$ $Z = 1$
 $M_r = 373.38$ $D_x = 1.283 \text{ Mg m}^{-3}$
 Triclinic, $P\bar{1}$ $\text{Mo K}\alpha$ radiation
 $a = 7.4150$ (3) Å Cell parameters from 4872 reflections
 $b = 7.9299$ (3) Å $\theta = 2.5\text{--}26.0^\circ$
 $c = 8.8881$ (4) Å $\mu = 0.89 \text{ mm}^{-1}$
 $\alpha = 81.578$ (2) $^\circ$ $T = 173$ (2) K
 $\beta = 69.260$ (2) $^\circ$ Prism, black
 $\gamma = 85.453$ (2) $^\circ$ $0.34 \times 0.20 \times 0.10 \text{ mm}$
 $V = 483.27$ (3) Å 3

Data collection

Nonius KappaCCD diffractometer 1903 independent reflections
 φ and ω scans to fill Ewald sphere 1827 reflections with $I > 2\sigma(I)$
 Absorption correction: empirical $R_{\text{int}} = 0.044$
 (*DENZO-SMN*; Otwinowski & Minor, 1997) $\theta_{\text{max}} = 26.0^\circ$
 $T_{\text{min}} = 0.752$, $T_{\text{max}} = 0.916$ $h = -8 \rightarrow 9$
 4872 measured reflections $k = -9 \rightarrow 9$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0242P)^2 + 0.2378P]$
 $R[F^2 > 2\sigma(F^2)] = 0.031$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.074$ $(\Delta/\sigma)_{\text{max}} = 0.001$
 $S = 1.13$ $\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
 1903 reflections $\Delta\rho_{\text{min}} = -0.46 \text{ e \AA}^{-3}$
 118 parameters
 H-atom parameters constrained

Table 1

Selected geometric parameters (Å, $^\circ$) for (I).

C21—C2	1.501 (3)	C9—C4	1.427 (3)
C2—C1	1.413 (3)	C9—Co	2.2056 (17)
C2—C3	1.418 (3)	C4—C3	1.446 (3)
C2—Co	2.0672 (17)	C4—Co	2.2100 (17)
C1—C9	1.445 (3)	C3—Co	2.0562 (17)
C1—Co	2.0553 (18)		
C1—C2—C3	107.39 (16)	C4—C9—Co	71.32 (10)
C1—C2—Co	69.49 (10)	C1—C9—Co	64.66 (10)
C3—C2—Co	69.46 (10)	C9—C4—C3	107.29 (16)
C21—C2—Co	124.70 (14)	C9—C4—Co	70.98 (10)
C2—C1—C9	108.98 (16)	C3—C4—Co	64.54 (9)
C2—C1—Co	70.40 (10)	C2—C3—C4	108.65 (16)
C9—C1—Co	75.90 (10)	C2—C3—Co	70.30 (10)
C4—C9—C1	107.11 (16)	C4—C3—Co	76.04 (10)

Compound (II)

Crystal data

$\text{C}_{24}\text{H}_{26}$ $D_x = 1.162 \text{ Mg m}^{-3}$
 $M_r = 314.47$ $\text{Mo K}\alpha$ radiation
 Monoclinic, $P2_1/c$ Cell parameters from 8928 reflections
 $a = 12.1229$ (4) Å $\theta = 2.5\text{--}27.4^\circ$
 $b = 9.6880$ (4) Å $\mu = 0.07 \text{ mm}^{-1}$
 $c = 15.7045$ (6) Å $T = 173$ (2) K
 $\beta = 102.942$ (2) $^\circ$ $V = 1797.59$ (12) Å 3
 $Z = 4$ Prism, colourless
 $0.39 \times 0.25 \times 0.17 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer 4024 independent reflections
 φ and ω scans to fill Ewald sphere 2298 reflections with $I > 2\sigma(I)$
 Absorption correction: empirical $R_{\text{int}} = 0.040$
 (*DENZO-SMN*; Otwinowski & Minor, 1997) $\theta_{\text{max}} = 27.4^\circ$
 $T_{\text{min}} = 0.975$, $T_{\text{max}} = 0.989$ $h = -15 \rightarrow 13$
 8928 measured reflections $k = -12 \rightarrow 12$
 $l = -18 \rightarrow 20$

Refinement

Refinement on F^2 H atoms treated by a mixture of independent and constrained refinement
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.115$
 $S = 0.95$
 4024 reflections
 255 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0538P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$

Table 2

Selected geometric parameters (Å, $^\circ$) for (II).

C1'—C9'	1.515 (2)	C1—C9	1.512 (2)
C1'—C2'	1.519 (2)	C1—C2	1.531 (2)
C1'—C1	1.572 (2)	C2—C3	1.335 (2)
C2'—C3'	1.340 (2)	C2—C21	1.493 (2)
C2'—C21'	1.491 (2)	C3—C4	1.469 (2)
C3'—C4'	1.458 (2)	C4—C9	1.409 (2)
C4'—C9'	1.404 (2)		
C9'—C1'—C2'	102.35 (13)	C9—C1—C2	102.25 (12)
C9'—C1'—C1	113.84 (12)	C9—C1—C1'	114.12 (12)
C2'—C1'—C1	113.52 (12)	C2—C1—C1'	113.77 (13)
C3'—C2'—C1'	109.81 (15)	C3—C2—C1	109.85 (14)
C2'—C3'—C4'	110.95 (16)	C2—C3—C4	111.15 (15)
C9'—C4'—C3'	107.61 (14)	C9—C4—C3	107.14 (14)
C4'—C9'—C1'	109.08 (14)	C4—C9—C1	109.48 (13)

Although it was possible to locate most of the H atoms in (I) by Fourier map, all H atoms were placed in idealized positions with the isotropic displacement parameters fixed at 1.2 (aromatic H atoms) and 1.5 (methyl H atoms) times the equivalent isotropic displacement parameters of their parent atoms. The H atoms in (II) situated on the aromatic C atoms and the stereocentres (C1 and C1') were found from the Fourier map and were refined isotropically, whereas those on the methyl moieties were placed in idealized positions with the C—C—H torsion angles allowed to rotate and their isotropic displacement parameters fixed at 1.5 times the equivalent isotropic displacement parameters of the parent C atoms.

For both compounds, data collection: *COLLECT* (Nonius, 1999); 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: *ORTEP-3 for Windows* (Farrugia, 1997); 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: DE1172). Services for accessing these data are described at the back of the journal.

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