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Structure of *trans*-[OsH(η^2-H$_2$)(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$][BF$_4$]

By David H. Farrar,* Patricia A. Maltby and Robert H. Morris*

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

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Abstract. Bis[1,2-bis(diphenylphosphino)ethane](η^2-dihydrogen)hydridoosmium(II) tetrafluoroborate, [OsH(C$_{26}$H$_{24}$P$_2$)$_2$(H$_2$)][BF$_4$], $M_r = 1076.9$, monoclinic, $P2_1/n$, $a = 17.711\,(3)$, $b = 16.937\,(3)$, $c = 15.982\,(4)$ Å, $\beta = 102.85\,(2)°$, $V = 4674\,(3)$ Å^3, $Z = 4$, $D_m = 1.54$ (flotation in CCl$_4$/C$_6$H$_{12}$), $D_x = 1.53$ g cm^{-3}, graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, $\mu = 29.2$ cm^{-1}, $F(000) = 2160$, T = room temperature, $R = 0.049$, $wR = 0.054$, for 4642 observed independent reflections. The crystal structure consists of an OsH(η^2-H$_2$)(dppe)$_2$ cation and a disordered BF$_4$ anion. The 1,2-bis(diphenylphosphino)ethane ligands (dppe) coordinate to the Os atom creating an apparent pseudo-square-planar complex, if the H$^-$ and η^2-H$_2$ ligands are disregarded. A hydride ligand has been located in one of the two remaining coordination sites associated with an octahedral coordination geometry although the Os—H1 distance refined to an unacceptably long value of 2.26 (7) Å. Electron density believed to be associated with the η^2-H$_2$ ligand has been located *trans* to the hydride ligand at approximately 1.7 Å from the Os atom. All attempts to refine the η^2-H$_2$ ligand were unsuccessful.

Introduction. An important current problem is the elucidation of the structures of η^2-dihydrogen complexes which are suspected of having H—H distances longer than the usual value of 0.82 (1) Å found in neutron diffraction studies of the complexes W(CO)$_3$(H$_2$)(P^{i}Pr$_3$)$_2$ (Kubas, Ryan, Swanson, Vergamini & Wasserman, 1984), *trans*-[FeH(H$_2$)(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$][BPh$_4$] (Ricci, Koetzle, Bautista, Hofstede, Morris & Sawyer, 1989) and Fe(H)$_2$(H$_2$)(PEtPh$_2$)$_3$ (van der Sluys *et al.*, 1990). For example, a recent X-ray structure determination of the complex [Re(H)$_4$(H$_2$){PPh(CH$_2$CH$_2$CH$_2$PCy$_2$)$_2$}][SbF$_6$] indicates an elongated H—H distance of 1.08 (5) Å (Kim, Deug, Meek & Wojcicki, 1990). NMR studies of the complexes [OsH(H$_2$)(PR_2CH$_2$CH$_2$PR_2)$_2$]$^+$ suggested that when R is Et, the H—H distance could range from 1.0 to 1.4 Å (Bautista, Earl, Maltby, Morris, Schweitzer & Sella, 1988). Unfortunately, crystals of this complex were disordered and hydrogen ligands could not be located (Earl, Morris & Sawyer, 1989). A more recent NMR study gave an H—H distance of 0.99 Å for the complex when R is Ph (Earl, Jia, Maltby & Morris, 1991). The X-ray structure of this complex, as the BF$_4$ salt, is described here. This complex is a good candidate for a neutron diffraction study.

Experimental. Colourless crystals were grown by the slow diffusion of diethyl ether into a concentrated solution of the complex in acetone. A hexagonal prismatic crystal of approximate dimensions 0.20 × 0.30 × 0.10 mm was mounted inside a capillary because of the air sensitive nature of the complex. Accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $11 < \theta < 14°$. Intensities of reflections with indices h 0 to 19, k 0 to 18, l −17 to 17, and with $1 < \theta < 23°$ were measured; ω–2θ scans, ω scan width $(0.8 + 0.35\tan\theta)°$; graphite-monochromated Mo $K\alpha$ radiation; intensities of two reflections measured every 4 h showed no decrease in intensity. The 6719 reflections measured were corrected for Lorentz and polarization effects. Data were corrected for absorption effects using an empirical absorption correction based on ψ scans of six reflections with $1 < \theta < 18°$. Transmission coefficients for the absorption correction varied from 0.9186 to 0.9703. Crystal faces could not be clearly observed in the capillary and thus the crystal was not indexed. 5619 unique data ($R = 0.014$ on averaging $F_{\rm obs}$); 4642 data with $I > 3\sigma(I)$ were observed and used in the structure solution and refinement. Space group $P2_1/n$ was determined uniquely by systematic absences ($0k0$ absent if $k = 2n + 1$, $h0l$ absent if $h + l = 2n + 1$). The structure was solved by the heavy-atom method. Refinement was by full-matrix least-squares calculations (on F), initially with isotropic and then with anisotropic thermal parameters for Os, P, F and B. Rigid-group constraints were applied to the C atoms of the eight phenyl rings (D_{6h} symmetry and C—C = 1.395 Å; the phenyl ring C atoms labelled C11 through C16 are associated with ring 1, *etc.*).

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* E-mail addresses:
DFARRAR@ALCHEMY.CHEM.- UTORONTO.CA
RMORRIS@ALCHEMY.CHEM.- UTORONTO.CA

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A second orientation of the BF_4 anion associated with an approximately 60° rotation about the B–F1 C_3 axis was observed in a subsequent difference Fourier synthesis. Atoms F2, F3 and F4 were refined with anisotropic thermal parameters and an occupancy of 85%, while F5, F6 and F7 were refined isotropically at 15% occupancy. An *ORTEP*II diagram showing the disordered BF_4^- anion is given in Fig. 1. A difference Fourier synthesis showed maxima in positions consistent with the expected locations of H atoms of the phenyl rings. A hydride ligand was located and the atom was refined isotropically. Electron density 0.53 to 0.34 e Å^{-3} believed to be associated with the η^2-H_2 ligand was located *trans* to the hydride ligand at approximately 1.7 Å from the Os atom. All attempts to refine the η^2-H_2 ligand were unsuccessful. In the final rounds of calculations the phenyl-group H atoms were positioned on geometric grounds (C—H = 0.95 Å) and included (as riding atoms) in the structure factor calculation. These atoms were assigned general isotropic thermal parameters; $U_{iso} = 0.07$ Å^2. The final cycle of refinement included 219 variable parameters; $R = 0.049$, $wR = 0.054$, goodness of fit = 1.31, $w = 1/[\sigma^2(F_o) + 0.00157(F_o)^2]$. Max. shift/e.s.d. in final refinement cycle = 0.05; density in the final difference map in the range −0.23 to 0.53 e Å^{-3}; there were no chemically significant features with the exception of the aforementioned density thought to be associated with the η^2-H_2 ligand. No correction for secondary extinction. The atomic coordinates are given in Table 1. All calculations carried out on a PDP 11/23 computer using *SDP* (Frenz, 1982) and an Apollo computer using *SHELX*76 and *SHELXS*86 (Sheldrick, 1976, 1986).* Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) were stored in the programs.

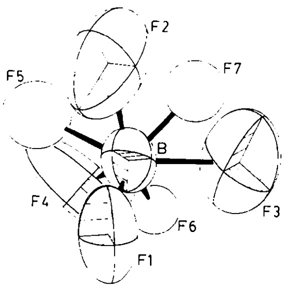

Fig. 1. An *ORTEP* drawing of the BF_4^- anion showing the disorder about the B–F1 axis.

Table 1. *Positional and thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}/U_{iso}
Os	-0.01582 (2)	0.18346 (2)	0.23394 (3)	0.03905 (25)
P1	-0.00283 (14)	0.06367 (14)	0.31081 (15)	0.0389 (14)
P2	0.10331 (15)	0.20904 (14)	0.32778 (16)	0.0378 (14)
P3	-0.13762 (15)	0.15542 (14)	0.14689 (15)	0.0376 (14)
P4	-0.02740 (16)	0.29764 (14)	0.14860 (16)	0.0413 (15)
H1	0.032 (4)	0.129 (4)	0.127 (4)	0.026 (20)
C1	0.0732 (6)	0.0743 (6)	0.4114 (7)	0.0536 (27)
C2	0.0978 (7)	0.1609 (6)	0.4287 (7)	0.0532 (27)
C3	-0.1449 (6)	0.2082 (5)	0.0446 (6)	0.0472 (25)
C4	-0.1197 (6)	0.2905 (6)	0.0658 (7)	0.0530 (27)
C12	0.0413 (4)	-0.0957 (4)	0.3177 (4)	0.063 (3)
C13	0.0730 (4)	-0.1625 (4)	0.2877 (4)	0.077 (4)
C14	0.0962 (4)	-0.1598 (4)	0.2098 (4)	0.089 (4)
C15	0.0876 (4)	-0.0903 (4)	0.1619 (4)	0.108 (5)
C16	0.0559 (4)	-0.0234 (4)	0.1919 (4)	0.075 (4)
C11	0.0328 (4)	-0.0261 (4)	0.2697 (4)	0.0443 (25)
C22	-0.1303 (4)	-0.0355 (3)	0.3165 (4)	0.0540 (27)
C23	-0.1977 (4)	-0.0541 (3)	0.3440 (4)	0.081 (4)
C24	-0.2219 (4)	-0.0062 (3)	0.4040 (4)	0.076 (4)
C25	-0.1787 (4)	0.0603 (3)	0.4367 (4)	0.075 (3)
C26	-0.1114 (4)	0.0789 (3)	0.4092 (4)	0.0606 (29)
C21	-0.0872 (4)	0.0310 (3)	0.3492 (4)	0.0385 (22)
C32	0.2002 (4)	0.1767 (4)	0.2174 (4)	0.068 (3)
C33	0.2680 (4)	0.1504 (4)	0.1956 (4)	0.088 (4)
C34	0.3270 (4)	0.1171 (4)	0.2582 (4)	0.085 (4)
C35	0.3183 (4)	0.1102 (4)	0.3425 (4)	0.085 (4)
C36	0.2505 (4)	0.1365 (4)	0.3643 (4)	0.067 (3)
C31	0.1915 (4)	0.1698 (4)	0.3017 (4)	0.0421 (24)
C42	0.0807 (3)	0.3502 (4)	0.4058 (5)	0.0596 (29)
C43	0.0951 (3)	0.4292 (4)	0.4289 (5)	0.076 (4)
C44	0.1584 (3)	0.4680 (4)	0.4091 (5)	0.075 (4)
C45	0.2073 (3)	0.4278 (4)	0.3663 (5)	0.083 (4)
C46	0.1929 (3)	0.3489 (4)	0.3432 (5)	0.0607 (29)
C41	0.1296 (3)	0.3101 (4)	0.3630 (5)	0.0409 (23)
C52	-0.2219 (3)	0.2197 (4)	0.2606 (4)	0.0537 (27)
C53	-0.2889 (3)	0.2490 (4)	0.2816 (4)	0.071 (3)
C54	-0.3589 (3)	0.2479 (4)	0.2208 (4)	0.067 (3)
C55	-0.3619 (3)	0.2175 (4)	0.1390 (4)	0.076 (4)
C56	-0.2949 (3)	0.1882 (4)	0.1180 (4)	0.063 (3)
C51	-0.2249 (3)	0.1893 (4)	0.1788 (4)	0.0393 (22)
C62	-0.1156 (4)	0.0200 (4)	0.0576 (5)	0.077 (4)
C63	-0.1324 (4)	-0.0564 (4)	0.0263 (5)	0.092 (4)
C64	-0.1943 (4)	-0.0978 (4)	0.0460 (5)	0.080 (4)
C65	-0.2394 (4)	-0.0627 (4)	0.0970 (5)	0.079 (4)
C66	-0.2227 (4)	0.0136 (4)	0.1283 (5)	0.0581 (29)
C61	-0.1608 (4)	0.0550 (4)	0.1086 (5)	0.0496 (25)
C72	-0.0296 (5)	0.4614 (5)	0.1374 (4)	0.085 (4)
C73	-0.0451 (5)	0.5372 (5)	0.1632 (4)	0.111 (5)
C74	-0.0719 (5)	0.5479 (5)	0.2382 (4)	0.115 (5)
C75	-0.0832 (5)	0.4827 (5)	0.2873 (4)	0.117 (6)
C76	-0.0677 (5)	0.4069 (5)	0.2615 (4)	0.078 (4)
C71	-0.0409 (5)	0.3962 (5)	0.1865 (4)	0.0545 (27)
C82	0.1133 (5)	0.3525 (5)	0.1232 (4)	0.078 (4)
C83	0.1725 (5)	0.3564 (5)	0.0786 (4)	0.108 (5)
C84	0.1640 (5)	0.3189 (5)	-0.0007 (4)	0.106 (5)
C85	0.0962 (5)	0.2774 (5)	-0.0353 (4)	0.097 (5)
C86	0.0369 (5)	0.2734 (5)	0.0093 (4)	0.073 (3)
C81	0.0455 (5)	0.3110 (5)	0.0885 (4)	0.0538 (27)
B	0.4051 (9)	0.2033 (8)	0.0117 (10)	0.067 (10)
F1	0.4596 (4)	0.2607 (5)	0.0246 (5)	0.097 (6)
F2	0.4139 (10)	0.1584 (8)	0.0774 (8)	0.150 (12)
F3	0.3322 (5)	0.2411 (7)	0.0063 (12)	0.150 (11)
F4	0.4039 (9)	0.1649 (12)	-0.0609 (10)	0.185 (14)
F5	0.438 (3)	0.129 (3)	0.008 (4)	0.082 (15)
F6	0.3628 (26)	0.2092 (23)	-0.0669 (28)	0.047 (10)
F7	0.357 (3)	0.195 (3)	0.054 (3)	0.063 (12)

Discussion. Bond lengths and angles for the cation and anion are listed in Table 2. The closest contact between the cation and the anion is 2.21 Å between H33 and F7 while the closest cation–cation contact is 2.33 Å between H15 and H62 at position (−x, −y, −z). Fig. 2 is a view of the cation prepared using *ORTEP*II (Johnson 1976) with H atoms omitted for clarity.

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* Lists of structure factors, thermal parameters, calculated hydrogen coordinates, and mean plane data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54164 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Molecular distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Os—P1	2.356 (2)	P4—C4	1.864 (11)
Os—P2	2.341 (3)	P4—C71	1.810 (9)
Os—P3	2.341 (3)	P4—C81	1.786 (8)
Os—P4	2.349 (2)	C1—C2	1.54 (1)
P1—C1	1.862 (11)	C3—C4	1.48 (1)
P1—C11	1.823 (7)	B—F1	1.35 (2)
P1—C21	1.823 (7)	B—F2	1.28 (2)
P2—C2	1.829 (11)	B—F3	1.43 (2)
P2—C31	1.828 (7)	B—F4	1.33 (2)
P2—C41	1.830 (7)	B—F5	1.39 (5)
P3—C3	1.842 (10)	B—F6	1.32 (5)
P3—C51	1.824 (7)	B—F7	1.20 (6)
P3—C61	1.823 (8)	Os—H1	2.26 (7)

H1—Os—P1	91.8 (17)	H1—Os—P3	85.4 (18)
H1—Os—P2	97.0 (18)	H1—Os—P4	84.1 (17)
P2—Os—P1	81.71 (9)	C4—C3—P3	107.3 (7)
P3—Os—P1	96.05 (8)	C61—P3—C51	104.2 (3)
P4—Os—P1	175.82 (9)	C71—P4—C4	97.9 (4)
C1—P1—Os	109.6 (3)	C81—P4—C4	104.5 (4)
C11—P1—Os	122.1 (2)	C3—C4—P4	113.3 (7)
C21—P1—Os	116.4 (2)	C81—C4—P71	103.2 (4)
P3—Os—P2	176.71 (9)	F2—B—F1	110.5 (14)
P4—Os—P2	99.76 (9)	F3—B—F1	106.9 (11)
C2—P2—Os	105.4 (4)	F4—B—F1	110.8 (14)
C31—P2—Os	118.7 (2)	F5—B—F1	111.0 (26)
C41—P2—Os	120.1 (2)	F6—B—F1	108.9 (21)
P4—Os—P3	82.65 (9)	F7—B—F1	124.6 (29)
C3—P3—Os	107.6 (3)	F3—B—F2	105.2 (15)
C51—P3—Os	119.7 (2)	F4—B—F2	113.8 (14)
C61—P3—Os	119.8 (2)	F5—B—F2	61.7 (29)
C4—P4—Os	108.0 (3)	F6—B—F2	140.4 (23)
C71—P4—Os	124.5 (3)	F7—B—F2	56.4 (28)
C81—P4—Os	115.9 (3)	F4—B—F3	109.2 (15)
C11—P1—C1	98.6 (4)	F5—B—F3	142.1 (26)
C21—P1—C1	103.2 (4)	F6—B—F3	65.9 (22)
C2—C1—P1	111.7 (7)	F7—B—F3	48.9 (28)
C21—P1—C11	104.1 (3)	F5—B—F4	56.3 (29)
C31—P2—C2	104.8 (4)	F6—B—F4	46.1 (21)
C41—P2—C2	101.9 (4)	F7—B—F4	123.8 (30)
C1—C2—P2	109.5 (7)	F6—B—F5	101. (3)
C41—P2—C31	103.8 (3)	F7—B—F5	106. (4)
C51—P3—C3	101.5 (4)	F7—B—F6	103. (3)
C61—P3—C3	100.9 (4)		

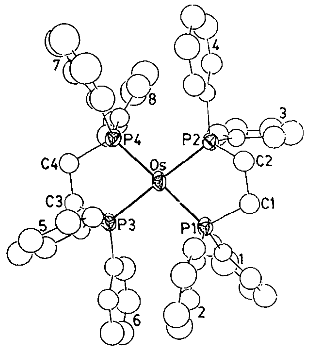

Fig. 2. A perspective view of the cation showing the atom labelling and thermal ellipsoids. The H atoms have been omitted for clarity.

The pseudo-square-planar arrangement of the ditertiaryphosphine ligands results in very uniform Os—P distances which range from 2.341 (3) to 2.356 (2) Å (4σ) and *trans* P—Os—P angles of 175.8 (1) and 176.7 (1)°. The Os atom is 0.016 (1) Å out (away from H1) of a plane defined by the four P atoms. By comparison, the disordered structure of the complex $[OsH(H_2)(PEt_2CH_2CH_2PEt_2)_2][BPh_4]$ has distances that range from 2.32 to 2.36 Å and *transoid* P—Os—P angles in the range 150 to 175° (Earl *et al.*, 1989). Significantly, the *trans* P—Os—P angles of the present structure are similar to one another (6σ) and are not influenced by the different coordination requirements of the dihydrogen and hydride ligands. For example in the complex $[FeH(H_2)(PPh_2CH_2CH_2PPh_2)_2][BPh_4]$, the H_2 ligand lies parallel to a *trans* P—Fe—P unit with an angle of 166.6 (2)° caused by the P atoms moving away from the H_2 ligand and towards the smaller terminal hydride ligand; the other P—Fe—P angle is 172.1 (2)° (Ricci *et al.*, 1989). Apparently H_2 coordination to the larger 5*d* metal, Os, does not perturb the rest of the octahedron. Recent theoretical work suggests that there should be no energy barrier to rotation of the H_2 ligand in a complex *trans*-$[M(H_2)HP_4]^+$ with ideal octahedral coordination (van der Sluys *et al.*, 1990). Thus rotational disorder of the H_2 ligand might explain why it is not located in this structural determination.

Electron density in a reasonable direction from the Os atom for octahedral coordination, refined to a hydride ligand at 2.26 (7) Å from the Os atom. However this bond length is clearly inaccurate judging from the range of Os—H distances, 1.63–1.69 Å, known from neutron diffraction studies (Hart, Bau & Koetzle, 1977; Howard, Johnson, Koetzle & Spencer, 1987). Problems in locating hydride ligands around 5*d* transition metals are well known. An annular region of electron density which could be associated with the η^2-H_2 ligand is located *trans* to this hydride ligand at approximately 1.7 Å from the Os atom. We were not able to refine successfully two H atoms associated with this area of electron density. There is nonetheless unambiguous NMR evidence for the existence of the hydride and dihydrogen ligands (Earl *et al.*, 1991).

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Structure of Dichlorobis(1,10-phenanthroline *N*-oxide)copper(II) Dihydrate

By Jozef Kožíšek, Peter Baran and Dušan Valigura

Department of Inorganic Chemistry, Faculty of Chemical Technology, Radlinského 9,
Slovak Technical University, CS - 812 37 Bratislava, Czechoslovakia

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Abstract. $[\mathrm{CuCl_2(C_{12}H_8N_2O)_2}].2\mathrm{H_2O}$, $M_r = 562.90$, triclinic, $P\bar{1}$, $a = 8.586\,(6)$, $b = 8.790\,(8)$, $c = 8.770\,(6)$ Å, $\alpha = 68.23\,(6)$, $\beta = 62.42\,(5)$, $\gamma = 86.08\,(7)°$, $V = 540.5\,(8)$ Å^3, $Z = 1$, $D_m = 1.67\,(2)$, $D_x = 1.729$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0.71069$ Å, $\mu = 1.30$ mm^{-1}, $F(000) = 287$, $T = 293$ K, final $R = 0.0337$ for 1173 unique reflections with $F > 4\sigma(F)$. The crystal structure consists of $\mathrm{Cu(phenO)_2Cl_2}$ (phenO = 1,10-phenanthroline *N*-oxide) and water molecules which are linked *via* hydrogen bonds. The $\mathrm{Cu^{II}}$ atom is situated on a centre of symmetry and is octahedrally coordinated by two N and two O atoms of phenO and by two Cl atoms with Cu—N(1) 1.983 (4), Cu—O(1) 1.903 (5) and Cu—Cl 2.899 (4) Å.

Introduction. The title compound is one of a series containing chelating aromatic *N*-oxide ligands. Studies of these complexes are in progress to determine the various bonding modes of the *N*-oxide ligands. 1,10-Phenanthroline *N*-oxide (hereafter phenO) can form six-membered metallocycles containing an aromatic N and *N*-oxygen donor atoms, and it is more rigid than the previously studied 2,2′-bipyridyl *N,N*′-dioxide (Baran, Koman, Valigura & Mrozinski, 1991; Koman, Baran & Valigura, 1991) since there is no possibility of rotation of the aromatic rings.

Experimental. Green-brown, well shaped crystals were obtained by slow crystallization from an equimolar ethanolic solution of $\mathrm{CuCl_2}$ and phenO; the size of the crystal used was 0.5 × 0.05 × 0.2 mm. D_m was measured by flotation. Crystal system and approximate cell dimensions were determined from Weissenberg and precession photographs. Accurate unit-cell parameters were obtained by a least-squares fit of 15 reflections ($18 < 2\theta < 40°$). Intensity data were measured on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation; θ–2θ-scan mode with $(2\theta)_{\max} = 55°$ and index range h −12/12, k −12/12, l 0/12; two standard reflections (212, 201) were measured every 98 reflections, no significant systematic fluctuations were found. 3335 reflections were measured; 1175 unique reflections with $F_o > 4\sigma(F_o)$ were considered observed; $R_{\rm int} = 0.050$ for 392 unique reflections before absorption correction. Empirical absorption correction based on intensity measurements at different azimuthal angles, transmission range 0.897–0.999. The structure was solved by Patterson methods using *SHELXS*86 (Sheldrick, 1990) and refined on F by least squares with *SHELX*76 (Sheldrick, 1976). A difference map of the partially refined structure gave the positions of all the H atoms. Refinement continued on all 198 positional and thermal parameters (anisotropic for non-H atoms and isotropic for H atoms). In the final cycle $R = 0.034$ and $wR = 0.029$ for 1173 observed reflections [two of the strongest reflections (010 and $2\bar{1}2$) were thought to be affected by extinction and were excluded from the refinement], $w^{-1} = k\sigma^2(F)$, $k = 0.2763$; maximum $\Delta/\sigma = 0.056$ and maximum and minimum heights in final $\Delta\rho$ map were +0.38 and −0.26 e Å^{-3}. The scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

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