The Co—C(9) and Co—N(5) distances, 2·062 (5) and 2·074 (4) Å, respectively, are approximately the same as the corresponding ones in the ce and mce complexes. The Co—C and Co—N distances in (*R*-ce)(*S*-1-phenylethylamine)cobaloxime (Ohashi, Sasada, Takeuchi & Ohgo, 1980*a*), (*S*-ce)(*S*-1-phenylethylamine)cobaloxime (Ohashi, Sasada, Takeuchi & Ohgo, 1980*b*), (*R*-mce)(*R*-1-phenylethylamine)cobaloxime (Ohashi & Sasada, 1977) and (*S*-mce)(*R*-1-phenylethylamine)cobaloxime (I) and (II) (Kurihara, Uchida, Ohashi & Sasada, 1984) are 2·036 (8) and 2·088 (8) Å, 2·070 (8) and 2·054 (5) Å, 2·067 (8) and 2·066 (6) Å, 2·080 (7) and 2·075 (5) Å, and 2·086 (5) and 2·074 (4) Å, respectively. Other bond distances are not significantly different from the corresponding ones of the related complexes. The torsion angle of C(10)—C(9)—C(12)—C(13) is 60·4 (4)°. This causes the dmce group to take an L-shape.

The crystal structure viewed along the *c* axis is shown in Fig. 2. The molecules are connected by a hydrogen bond N(5)—H(5)···O(7) and make a spiral chain along the *c* axis. The N(5)···O(7) and H(N1)···O(7) distances and N(5)—H(N1)···O(7) angle are 3·174 (7), 2·20 (5) Å and 166 (4)°, respectively. There are no unusually short contacts between the molecules except the hydrogen bonds.

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Structure of (η^5-Cyclopentadienyl)(1,2,3,4,4a,10a-η^6-2-methyldibenzo[*b*,*e*][1,4]dioxine)iron(II) Hexafluorophosphate at 163 K

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Abstract. $[C_{18}H_{15}FeO_2][PF_6]$ (I), $M_r = 464·13$, monoclinic, $P2_1/c$, $a = 7·976$ (1), $b = 8·959$ (3), $c = 24·936$ (8) Å, $\beta = 99·00$ (2)°, $V = 1760$ (1) Å^3, $Z = 4$, $D_x = 1·751$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 10·153$ cm^{-1}, $F(000) = 936$, $T = 163$ (2) K, full-matrix least-squares refinement of (I) converged to $R = 0·047$ and $wR = 0·044$ with 3103 reflections [$I > 3\sigma(I)$] of 4065 total unique reflections. The dihedral angle between the arene rings of the dioxine ligand is 173·8 (1)°; the C—O bond distances to the coordinated ring are significantly shorter than those of the uncoordinated ring. Inclusion of electronegative atoms (*i.e.* N) in the arene rings of thianthrenes and complexation of iron cyclopentadienyl (FeCp) to the arene rings, resulted in flattening of the dihedral angle. The effect was similar, but more pronounced, in phenoxathiins. The effect of an electron-releasing group (methyl) substituent on the arene ring of a thianthrene FeCp complex was to decrease the dihedral angle; but, inconsistently, two methyl groups (in the 2 and 7 positions) increased the angle. Dibenzodioxine and other dibenzodioxines with varying numbers of chloro substituents are planar. The dihedral angle of the title compound is 173·8°. It

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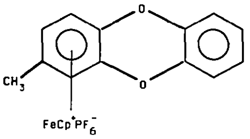
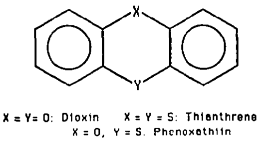
is not clear whether this is owing to the influence of the substituent methyl group, complexation, or packing forces.

Introduction. Previous studies of the synthesis, structure and reactivity of tricyclic heterocycles (II) complexed with an FeCp moiety indicated that both the location of the FeCp moiety [inside or outside of the heterocycle fold (III)] and the presence of a substituent on the heterocycle may influence the dihedral angle between the arene rings. In the thianthrene complex (Abboud, Lynch, Simonsen, Piórko & Sutherland, 1990) the FeCp moiety was located inside the fold in one molecule of the asymmetric unit and outside the fold in the other; in the 2-methylthianthrene complex (Simonsen, Lynch, Sutherland & Piórko, 1985) it was located inside the fold. However, there were significant differences in the dihedral angles of the thianthrene skeletons. This difference may result from the action of packing forces in the crystal, or it may be owing to the presence of the methyl substituent in the 2-methylthianthrene complex. To extend the investigation of the influence of the substituents and complexation with FeCp upon the geometry of the three-ring heterocyclic ligand, (I) was synthesized and its crystal structure determined.



(I)



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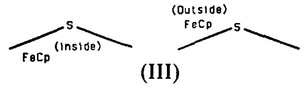

(III)

Experimental. The title compound was synthesized by the reaction of catechol with (η^6-3,4-dichlorotoluene)(η^5-Cp)iron(II) hexafluorophosphate following the described procedure (Sutherland, Piórko, Lee, Simonsen & Lynch, 1988). Crystals of the complex were grown from an acetone–diethyl ether–methylene chloride solution at *ca* 255 K. A needle-shaped orange-yellow crystal, 0·12 × 0·23 × 0·47 mm, was mounted and transferred to a Syntex $P2_1$ diffractometer equipped with a graphite monochromator (Mo $K\alpha$ radiation), where it was maintained in an environment of dry N_2 at 163 (2) K with a Syntex LT-1 low-temperature delivery system. Preliminary investigations revealed the crystal system to be monoclinic. 45 strong reflections, $25·33 \leq 2\theta \leq 34·73°$, were used to refine the unit-cell parameters. 8420 reflections (h, $0\rightarrow10$; k, $-11\rightarrow11$; l, $-32\rightarrow32$) were collected by the ω-scan method, 4065 unique reflections, $R_{\rm int} = 0·023$; 2θ range 4–55° (max. $\sin\theta/\lambda = 0·6497$ Å^{-1}), 1° ω scan at 4–8° min^{-1}, depending upon intensity. Background measurements were taken at both ends of the scan with ω displaced by 1·0° from the $K\alpha_{1,2}$ peak; each measurement was made for one-half of the scan time. Intensities of four reflections ($13\bar{5}$, $14\bar{1}$, 148, 126) were remeasured every 96 reflections to monitor instrument stability and crystal decay; max. correction was 1·6%. Absorption corrections based on measured crystal faces (Riley & Davis, 1976) were applied; min., max. transmission coefficients 0·695, 0·874. An extinction correction was not applied. The structure was solved by the heavy-atom (Patterson) method (*SHELX76*; Sheldrick, 1976) which revealed the position of the Fe atom; the remainder of the atoms were located from difference Fourier maps. Refinement was carried out by full-matrix least squares in *SHELX76* with anisotropic thermal parameters for the non-H atoms and isotropic thermal parameters for the H atoms. $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/(\sigma|F_o|)^2$, $\sigma(F_o) = 0·5kI^{-1/2}\{[\sigma(I)]^2 + (0·02I)^2\}^{1/2}$, $I = (I_{\rm peak} - I_{\rm bkg})$(scan rate) and $\sigma(I) = (I_{\rm peak} + I_{\rm bkg})^{1/2} \times$ (scan rate). k is the correction due to decay and Lp effects, and 0·02 is a factor used to downweight intense reflections and to account for instrument instability. Convergence was attained with R and wR of 0·047 and 0·044, respectively, for 3103 reflections of intensity larger than $3\sigma(I)$; 962 reflections were considered to be unobserved. In the last cycyle of refinement, 313 variables were refined to a goodness-of-fit of 2·88; the largest shift/e.s.d. did not exceed 0·08; min. and max. peaks in the difference Fourier map were −0·44 and 1·43 e Å^{-3}, respectively. The largest residual peak was 0·88 Å from the Fe atom and thus was attributed to its anisotropy. The linear absorption coefficient was calculated with values from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 55). Scattering factors for non-H atoms were taken from Cromer & Mann (1968) with anomalous-dispersion corrections from Cromer & Liberman (1970); those of H atoms were from Stewart, Davidson & Simpson (1965). The least-squares-planes program was supplied by Cordes (1983); other programs used are cited in reference 11 of Gadol & Davis (1982). Positional parameters of all non-H atoms with their equivalent isotropic thermal parameters are given in Table 1. Bond lengths and angles for the non-H atoms are listed in Table 2.[*] Fig. 1 shows the thermal-ellipsoids drawing of (I) with the atom-numbering scheme.

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[*] Lists of structure factors, anisotropic thermal parameters, crystallographic data, bond lengths and angles including H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53854 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *for the non-*H *atoms of* (I)

	x	*y*	*z*	*U**
Fe	0·36640 (6)	0·18949 (5)	0·16340 (2)	0·02946 (13)
P	0·08859 (13)	0·35356 (11)	−0·14762 (4)	0·0453 (3)
F1	0·0857 (4)	0·2337 (3)	−0·10150 (10)	0·0789 (11)
F2	0·0913 (3)	0·4732 (3)	−0·19467 (10)	0·0743 (10)
F3	0·2893 (3)	0·3506 (3)	−0·13868 (12)	0·0934 (12)
F4	0·0861 (4)	0·2238 (3)	−0·19089 (11)	0·0866 (12)
F5	−0·1120 (3)	0·3521 (3)	−0·15857 (15)	0·1035 (14)
F6	0·0908 (6)	0·4823 (3)	−0·10641 (12)	0·127 (2)
O5	0·5741 (3)	0·0205 (2)	0·08315 (9)	0·0405 (8)
O10	0·3468 (3)	0·2486 (3)	0·03666 (9)	0·0438 (8)
C1	0·1636 (4)	0·1886 (4)	0·10051 (13)	0·0375 (10)
C2	0·1220 (4)	0·1025 (4)	0·14398 (13)	0·0366 (11)
C3	0·2361 (5)	−0·0104 (4)	0·16573 (14)	0·0399 (11)
C4	0·3871 (4)	−0·0364 (4)	0·14506 (14)	0·0372 (11)
C4a	0·4257 (4)	0·0472 (3)	0·10069 (13)	0·0338 (10)
C5a	0·6144 (4)	0·1169 (4)	0·04359 (13)	0·0350 (10)
C6	0·7705 (5)	0·0983 (4)	0·02683 (15)	0·0449 (13)
C7	0·8150 (6)	0·1907 (5)	−0·0126 (2)	0·056 (2)
C8	0·7059 (6)	0·2993 (5)	−0·0356 (2)	0·060 (2)
C9	0·5501 (6)	0·3164 (5)	−0·01920 (15)	0·0495 (13)
C9a	0·5058 (4)	0·2267 (3)	0·02068 (13)	0·0363 (11)
C10a	0·3127 (4)	0·1599 (3)	0·07832 (13)	0·0351 (10)
C11	0·4130 (5)	0·4124 (4)	0·1774 (2)	0·0416 (12)
C12	0·5670 (5)	0·3358 (4)	0·1781 (2)	0·0410 (12)
C13	0·5777 (5)	0·2272 (4)	0·2194 (2)	0·0433 (13)
C14	0·4307 (5)	0·2366 (4)	0·24391 (14)	0·0423 (12)
C15	0·3291 (5)	0·3512 (4)	0·2179 (2)	0·0423 (12)
C16	−0·0345 (5)	0·1365 (5)	0·1680 (2)	0·0512 (15)

* For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*A_{ij}$.

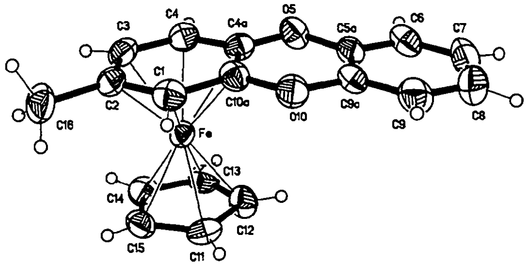

Fig. 1. Molecular structure of (I), with 50% probability ellipsoids, showing the atom-numbering scheme.

Discussion. The crystal structure of (I) was studied in a continuing effort to investigate the variation of the dihedral angles of tricyclic heterocycles by (1) replacing some of the C atoms in the terminal arene rings with more electronegative atoms (*e.g.* N), (2) placing substituents on the rings and (3) complexation of these heterocycles with FeCp. Comparison of the structures of a number of phenoxathiins, Table 3, reveals that the dihedral angle of the heterocycle flattens and approaches 180° with the inclusion of N atoms in the ring. The effect of complexation parallels the influence of electron-withdrawing substituents in the rings. However, in some cases packing effects may be more important than electronic effects.

Table 2. *Bond lengths* (Å) *and angles* (°) *for the non-*H *atoms of* (I)

1	2	3	1–2	1–2–3
C1	Fe		2·069 (3)	
C2	Fe		2·085 (3)	
C3	Fe		2·075 (3)	
C4	Fe		2·087 (3)	
C4a	Fe		2·128 (3)	
C10a	Fe		2·114 (3)	
C11	Fe		2·051 (4)	
C12	Fe		2·056 (4)	
C13	Fe		2·041 (4)	
C14	Fe		2·037 (4)	
C15	Fe		2·039 (4)	
F1	P	F2	1·576 (3)	179·38 (14)
F1	P	F3		90·9 (2)
F1	P	F4		89·83 (14)
F1	P	F5		89·5 (2)
F2	P	F3	1·592 (3)	89·2 (2)
F2	P	F4		89·56 (14)
F2	P	F5		90·5 (2)
F2	P	F6		89·28 (15)
F3	P	F4	1·581 (3)	89·3 (2)
F3	P	F5		177·7 (2)
F3	P	F6		90·7 (2)
F4	P	F5	1·584 (3)	88·4 (2)
F4	P	F6		178·8 (2)
F5	P	F6	1·580 (3)	91·5 (2)
F6	P	F1	1·543 (3)	91·3 (2)
C4a	O5	C5a	1·346 (4)	115·7 (2)
C5a	O5		1·386 (4)	
C9a	O10	C10a	1·401 (4)	115·5 (2)
C10a	O10		1·369 (4)	
C2	C1	C10a	1·412 (5)	121·0 (3)
C10a	C1		1·412 (5)	
C3	C2	C16	1·411 (5)	121·4 (3)
C3	C2	C1		118·2 (3)
C16	C2	C1	1·497 (6)	120·4 (3)
C4	C3	C2	1·401 (5)	121·2 (3)
C4a	C4	C3	1·410 (5)	120·4 (3)
C10a	C4a	O5	1·409 (4)	122·6 (3)
C10a	C4a	C4		119·1 (3)
O5	C4a	C4		118·2 (3)
C6	C5a	C9a	1·385 (5)	119·9 (3)
C6	C5a	O5		117·4 (3)
C9a	C5a	O5	1·374 (4)	122·7 (3)
C7	C6	C5a	1·373 (6)	119·3 (4)
C8	C7	C6	1·370 (6)	120·7 (4)
C9	C8	C7	1·377 (7)	119·8 (4)
C9a	C9	C8	1·367 (5)	119·9 (4)
O10	C9a	C5a		121·4 (3)
O10	C9a	C9		118·2 (3)
C5a	C9a	C9		120·4 (4)
O10	C10a	C1		118·1 (3)
O10	C10a	C4a		121·7 (3)
C1	C10a	C4a		120·1 (3)
C12	C11	C15	1·405 (5)	108·3 (3)
C15	C11		1·406 (6)	
C13	C12	C11	1·408 (5)	107·4 (3)
C14	C13	C12	1·407 (6)	108·5 (3)
C15	C14	C13	1·403 (5)	107·6 (3)
C11	C15	C14		108·2 (3)

Electron-withdrawing groups and complexation have a similar, but smaller, effect on the dihedral angles of thianthrenes [thianthrene (127·1°) and 1-azathianthrene (130·4°), Larson, Simonsen, Martin, Smith & Puig-Torres (1984); (η^5-cyclopentadienyl)(η^6-thianthrene)iron(II) hexafluorophosphate (143·1° and 136·3°), Abboud *et al.* (1990) and 1,4-diazathianthrene (138·9 and 137·0°), Larson, Simonsen, Lam, Martin, Lindsay & Smith (1985)].

Table 3. *Comparison of structures*

	Dihedral angle (°)	Reference
Phenoxathiin	147·7	Kimura & Simonsen (1981).
3-Azaphenoxathiin	168·8	Caldwell, Martin, Simonsen, Inners & Willcott (1981).
1,3-Diazaphenoxathiin	165·4	Puig-Torres, Martin, Larson & Simonsen (1984).
1,4,9-Triazaphenoxathiin	172·5	Larson, Simonsen, Martin & Smith (1985).
7-Chloro-1-azaphenoxathiin	175·3	Martin, Korp, Turley & Bernal (1978).
8-Chloro-1-azaphenoxathiin	176·8	Martin, Korp, Turley & Bernal (1978).
1-Nitrophenoxathiin (2 molecules/asymmetric unit)	163·8 145·7	Hossain, Dwiggins, van der Helm, Gupta, Turley & Martin (1982).
9-Nitro-1-azaphenoxathiin	178·3	Hossain, Dwiggins, van der Helm, Gupta, Turley & Martin (1982).
1-Dimethylamino-2,3-diazaphenoxathiin	174·0	Womak, Turley, Martin, Kimura & Simonsen (1981).
6,7,9-Trimethyl-4-aza-phenoxathiin	180·0	Lynch, Simonsen, Martin, Puig-Torres & Smith (1984).
η^5-Cyclopentadienyl)(η^6-phenoxathiin)iron(II) Hexafluorophosphate	178·6	Simonsen, Lynch, Sutherland & Piorko (1984).

Electron-releasing groups, however, do not show a similarly consistent trend. Whereas the methyl group in 2-methylthianthrene FeCp complex (Simonsen *et al.*, 1985), is believed to cause the ring to fold [dihedral angle, 127·4 (3)°, compared to 143·1 (2)° in the thianthrene FeCp complex], the dihedral angle in 2,7-dimethylthianthrene [136·96°, Weakley (1982)] is larger than that of thianthrene. Thus, the two methyl groups were accompanied by ring flattening.

Uncomplexed dibenzodioxine is a planar molecule (Singh & McKinney, 1978), and dioxines with two (Boer & North, 1972), four (Boer, van Remoortere, North & Neuman, 1972) or six (Cantrell, Webb & Mabis, 1969) chloro substituents were found to be planar or nearly so. In the title compound the dihedral angle is 173·8 (1)°, which clearly shows that the three-ring heterocycle deviates from planarity in spite of complexation to FeCp. The folding in (I) may be attributed to the presence of the methyl group as an electron-releasing substituent. However, it is not clear yet whether this effect is electronic in nature or due to packing forces.

The Fe atom is centered above the Cp ring; however, bonding between Fe and the arene ring is asymmetrical. The longest Fe—C distances are to C atoms adjacent to O atoms. This phenomenon is also observed in similar compounds reported by Simonsen *et al.* (1985) and Lynch, Thomas, Simonsen, Piórko & Sutherland (1986). The Fe—C4a and Fe—C10a distances are 2·128 (3) and 2·114 (3) Å, respectively, which represent the longest Fe—C distances in (I), indicating that the Fe atoms are not exactly centered upon the arene rings. In addition, the C—C distances of the coordinated ring are longer than the C—C distances of the uncoordinated rings which has also been observed in similar compounds. The distances between the O atoms and the C atoms of the coordinated ring are shorter than those of the uncoordinated one; O5—C4a is 1·346 (4) whereas O5—C5a is 1·386 (4) Å; O10—C10a is 1·369 (4) compared to 1·401 (4) Å for O10—C9a. This may be due to the electron-withdrawing power of the FeCp moiety.

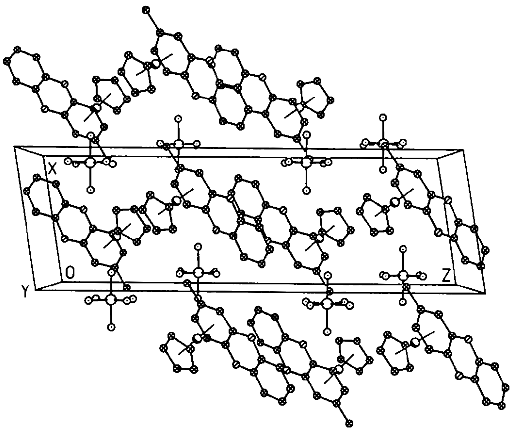

Fig. 2. The packing diagram for (I).

The distance between Fe and the Cp ring plane, 1·659 (4) Å, is longer than the distance between Fe and the coordinated arene ring planes, 1·548 (4) Å. These distances are well within the range of similar compounds (Lynch *et al.*, 1986; Simonsen *et al.*, 1985). The dihedral angle between the Cp ring plane and the coordinated arene is 2·1 (1)°.

The PF_6^- group is reasonably well behaved with the P—F bonding distance ranging between 1·543 (3) and 1·592 (3) Å. No F—P—F angle deviates from the octahedral geometry by more than 1·5°.

The packing diagram for (I) is given in Fig. 2.

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Structure of Dinitrato(2-thia-5,8-diazaoctane)copper(II)

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Abstract. $[Cu(NO_3)_2(C_5H_{14}N_2S)]$, $M_r = 321{\cdot}79$, orthorhombic, $P2_12_12_1$, $a = 14{\cdot}883\ (4)$, $b = 8{\cdot}936\ (3)$, $c = 8{\cdot}917\ (3)$ Å, $V = 1185{\cdot}9\ (6)$ Å^3, $Z = 4$, $D_m = 1{\cdot}79$, $D_x = 1{\cdot}802$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 20{\cdot}362$ cm^{-1}, $F(000) = 660$, room temperature, $R = 0{\cdot}036$, $wR = 0{\cdot}038$ for 2201 reflections with $I \geq 3\sigma(I)$. The structure consists of monomeric molecules $[Cu\{2,2\text{-NNS(Me)}\}(NO_3)_2]$, where 2,2-NNS(Me) = 2-thia-5,8-diazaoctane. The coordination polyhedron of Cu^{II} is a tetragonal bipyramid: the tridentate, meridionally coordinated 2,2-NNS(Me) ligand, one bidentate and one monodentate nitrate ligand form a $[CuN_2O_3S]$ chromophore.

Introduction. The complexation properties of α,β- and α,ω-thiadiamines as potential tridentate ligands have been extensively studied with various transition metal ions in solution (Herman & Goeminne, 1977; Herman, Goeminne & Eeckhaut, 1978, 1979). A preference for 1/1 complex formation with Cu^{II} was noted for most of these ligands (Huys, Herman & Goeminne, 1982; Huys, Schaubroeck, Herman & Goeminne, 1982). A difference in complexation activity between the S atoms of α,β- and α,ω-thiadiamines has been observed (Huys, Herman & Goeminne, 1982; Huys, Hoste, Goeminne & Van der Kelen, 1983). As part of a structural study of copper complexes with sulfur–nitrogen chelating ligands the crystal and molecular structure of dinitrato(2-thia-5,8-diazaoctane)copper(II) is presented here.

Experimental. The preparation of 2,2-NNS(Me) and $[Cu\{2,2\text{-NNS(Me)}\}(NO_3)_2]$ has been described elsewhere (Herman & Goeminne, 1977; Herman, Goeminne & Eeckhaut, 1978, 1979). Blue prism-shaped crystals, $0{\cdot}33 \times 0{\cdot}16 \times 0{\cdot}20$ mm; density measured by flotation. Cell parameters refined on Siemens diffractometer (Mo $K\alpha$ radiation) by least squares from 20 reflections with $7{\cdot}00 \leq \theta \leq 8{\cdot}85°$. Absorption and extinction ignored. Intensity measurements from θ–2θ scans carried out for $0 \leq \theta \leq 28°$. h,k,l range h −17 to 17, k 0 to 10, l 0 to 10. Two standard reflections every 98 measurements decreased in intensity by 15% during the course of the experiment. 2201 independent reflections with $I \geq 3\sigma(I)$ (291 unobserved reflections). Average Friedel pairs were used. Cu-atom position from Patterson function, other non-H atoms from Fourier syntheses. H atoms from difference syntheses. Anisotropic full-matrix refinement for non-H atoms based

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