tonato). Two other zinc porphyrins with an oxygen-bound axial ligand have been reported, the cation radical [Zn(tpp)(ClO_4)] [Spaulding, Eller, Bertrand & Felton, 1974; Zn—O = 2·079 (8) Å] and the disordered [Zn(tpp)(H_2O)] (Glick *et al.*, 1967; Zn—O ≃ 2·00 Å). All atoms in the macrocycle core are in the mirror plane and hence planar. The phenyl ring, as expected, is also planar.

Other bond distances and angles do not differ significantly from those in other metalloporphyrins (Scheidt, 1978). The phenyl rings are perpendicular to the plane (by symmetry), the C_m—C_p bond [C(5)—C(21)] being a true single bond and showing no interaction between the phenyl and porphyrin aromatic systems (Masuda, Tage, Osaki, Sugimoto & Mori, 1982). We note that our data for the dihedral angle and C_m—C_p bond do not fit on the line of Fig. 6 of Masuda *et al.* (1982). Nor do the data for the other zinc porphyrins listed in Table 3. However, if the line passes through 1·51 Å (C_m—C_p) at a dihedral angle of 90° then the fit is fairly good, but it should be noted that there is no theoretical need for the line to be linear. Also, it has been stated (Bastiansen & Trætteberg, 1962) that for a C—C bond where both C atoms are sp^2 hybrids the expected length is around 1·48 Å and longer values as found for biphenyls (Hargreaves & Rizvi, 1962; Fowweather & Hargreaves, 1950; Smare, 1948) are due to steric repulsion of the H atoms on the ring. Obviously such steric repulsions are present in tetraphenylporphyrins and would mask mesomeric effects.

JS thanks the Iraqi Government for the support of QAAS.

References

Bastiansen, O. & Trætteberg, M. (1962). *Tetrahedron*, **17**, 147–152.

Bobrik, M. A. & Walker, F. A. (1980). *Inorg. Chem.* **19**, 3383–3390.

Collins, D. M. & Hoard, J. L. (1970). *J. Am. Chem. Soc.* **92**, 3761–3771.

Cullen, D. L. & Meyer, E. F. (1976). *Acta Cryst.* B**32**, 2259–2269.

Fleischer, E. B., Miller, C. K. & Webb, L. E. (1964). *J. Am. Chem. Soc.* **86**, 2342–2347.

Fowweather, F. & Hargreaves, A. (1950). *Acta Cryst.* **3**, 81–87.

Frenz, B. A. (1983). *Enraf–Nonius Structure Determination Package; SDP Users Guide.* Version 1.1a, August 1983. Enraf–Nonius, Delft, The Netherlands.

Glick, M. D., Cohen, G. H. & Hoard, J. L. (1967). *J. Am. Chem. Soc.* **89**, 1996–1999.

Golder, A. J., Nolan, K. B., Povey, D. C. & Milgrom, L. R. (1988). *Acta Cryst.* C**44**, 1916–1921.

Hargreaves, A. & Rizvi, S. (1962). *Acta Cryst.* **15**, 365–373.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Killean, R. C. G. & Lawrence, J. L. (1969). *Acta Cryst.* B**25**, 1750–1752.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Masuda, H., Tage, T., Osaki, K., Sugimoto, H. & Mori, M. (1982). *Bull Chem. Soc. Jpn*, **55**, 4–8.

Montgomery, H. & Lingafelter, E. C. (1963). *Acta Cryst.* **16**, 748–752.

Sakurai, T. & Yamamoto, K. (1976). *Sci. Pap. Inst. Phys. Chem. Res. Jpn*, **70**, 31–37.

Schauer, C. K., Anderson, O. P., Eaton, S. S. & Eaton, G. R. (1985). *Inorg. Chem.* **24**, 4082–4086.

Scheidt, W. R. (1978). *The Porphyrins*, Vol. 3, edited by D. Dolphin, pp. 463–511. New York: Academic Press.

Scheidt, W. R., Kastner, M. E. & Hatano, K. (1978). *Inorg. Chem.* **17**, 706–710.

Scheidt, W. R., Mondal, J. U., Eigenbrot, C. W., Adler, A., Radonovich, L. J. & Hoard, J. L. (1986). *Inorg. Chem.* **25**, 795–799.

Smare, D. L. (1948). *Acta Cryst.* **1**, 150–154.

Spaulding, L. D., Eller, P. G., Bertrand, J. A. & Felton, R. H. (1974). *J. Am. Chem. Soc.* **96**, 982–987.

Thomas, D. W. & Martell, A. E. (1959). *J. Am. Chem. Soc.* **81**, 5111–5119.

Acta Cryst. (1990). C**46**, 1212–1215

Structure of Piperazinium Tetrachlorocobaltate Monohydrate

By D. Tran Qui and E. Palacios

Laboratoire de Cristallographie, CNRS, Laboratoire associé à l'Université J. Fourier, 166 X,
38042 Grenoble CEDEX, France

(*Received* 16 *February* 1989; *accepted* 6 *October* 1989)

Abstract. $C_4H_{12}N_2^{2+}.CoCl_4^{2-}.H_2O$, $M_r = 304{\cdot}9$, monoclinic, $P2_1/a$, $a = 14{\cdot}017\ (2)$, $b = 12{\cdot}706\ (2)$, $c = 6{\cdot}559\ (1)$ Å, $\beta = 87{\cdot}21\ (2)°$, $V = 1166{\cdot}8\ (5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}736$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7107$ Å, $\mu = 2{\cdot}356$ mm^{-1}, $F(000) = 612$, $T = 298$ K, $R = 0{\cdot}047$, $wR = 0{\cdot}05$ for 2509 reflexions $> 2\sigma(F)$. The structure

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of this complex consists of $C_4H_{12}N_2$ and $CoCl_4$ layers parallel to the *ac* plane. The cobalt and piperazinium layers are alternately stacked along the *b* axis and are held together only by H bonding: N—H···Cl, C—H···Cl and O—H···Cl. The internal bond length and angle values involving C and N atoms in $C_4H_{12}N_2$ are consistent with the chair conformation usually observed for this group. The cobalt ion is tetrahedrally coordinated by four Cl atoms forming a [$CoCl_4$] monomer. Co—Cl distances range from 2·275 (1) to 2·291 (1) Å. [$CoCl_4$] groups are isolated tetrahedra, Co—Co distances are no less than 6·3 Å.

Introduction. The crystal structure determination of the title compound is a continuation of our studies of the coordination geometry of 3*d* transition metals in organometallic complexes in correlation with their magnetic properties. Based on previous structural studies (Willet, Dwiggins, Kruh & Rundle, 1963; Landée & Willet, 1979; Daoud, Ben Salah, Chappert, Renard, Cheikhrouhou, Tran Qui & Verdaguer, 1986; Tran Qui, Daoud & Mhiri, 1989), it is suggested that among [MCl_n] groups (where M is a bivalent Cu, Ni or Co ion) only the [$CuCl_n$] group, due to the ability of Cu^{II} to form a wide bond-length range (2·2 to 2·9 Å) with Cl atoms, is able to adopt different configurations: linear, bibridged or isolated groups of [$CuCl_n$]. The linear configuration of [$CuCl_3$] is of special interest as recently shown in the study of $CuCl_3$ piperazinium. In this latter compound the [$CuCl_3$] groups form a linear chain in which Cu^{II} is located in a highly distorted bipyramidal coordination polyhedron with four short Cu—Cl bonds, 2·265 to 2·321 Å and one longer bridging bond at 2·606 Å giving rise to relatively short intra-chain Cu···Cu distances of 3·423 and 3·446 Å compared with 6·7 Å for inter-chain Cu···Cu distances. For this copper complex it resulted in an alternate antiferromagnetic coupling of Cu···Cu along the [$CuCl_3$] chain observed at $T < 15$ K (Daoud *et al.*, 1986).

To our knowledge no such linear configuration has yet been observed for Ni^{II} or Co^{II}. However, bibridged and isolated configurations exist in [$Ni_2Cl_4(H_2O)_6$].$C_4H_{12}N_2^{2+}$.2Cl^- (Fanchon, Halouani, Daoud, Tran Qui & Vicat, 1987) and in [$NiCl_2(C_{21}H_{22}NP)$] (van Mier, Kanters & Harder, 1987), respectively. Therefore, no magnetic ordering is expected for these latter complexes.

Recently, a 'monomer' [$CoCl_4$] piperazinium was synthesized and its crystal structure is reported.

Experimental. Small indigo-blue parallelepiped crystals of piperazinium were rapidly formed by slow evaporation at ambient temperature in an aqueous saturated equimolar solution of $CoCl_2.2H_2O$ and piperazinium chloride. This latter component was previously prepared by adding a concentrated aqueous solution of HCl to a solution of piperazinium in ethanol. Crystals grown by this method have an overall size generally less than 0·03 mm. Several recrystallizations in saturated HCl solution were, therefore, necessary to obtain single crystals suitable for X-ray analysis: Philips PW1100 diffractometer; crystal size 0·05 × 0·04 × 0·06 mm; random orientation; no absorption correction; 3 standard reflexions, no intensity variation; ω scan, 2° $\min^{-1}$, scan range = 1·1°; $2\theta_{\max} = 30°$, $-18 \leq h \leq 18$, $-17 \leq k \leq 17$, $0 \leq l \leq 9$. Unit-cell parameters from 24 reflexions with $9 \leq 2\theta \leq 21°$; 4409 reflexions measured, averaged to 2663 unique reflexions of which $2509 \geq 2\sigma(F)$, internal agreement factors were 3·2 and 3·9% for observed and all measured reflections, respectively.

The structure was solved by direct methods by application of *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), which revealed the positions of Co and four Cl atoms. The remaining non-H atoms were located by successive refinements alternated with difference-Fourier syntheses. Final difference maps, based on the last anisotropic refinement of all non-H atoms, successfully revealed the presence of one additional water molecule and the 14 H atoms bonded to O, N and C atoms. Three final cycles including all atoms without any constraints on H-atom positions showed significant improvement in R, wR and S factors, 4·9, 5·1% and 1·1 respectively (compare with 5·2, 5% and 1·2 for hydrogen-excluded model). Function minimized $\sum w|F_o - |KF_c||^2$, $w = [\sigma^2(F_o) + 0{\cdot}01|F_o|^2]^{-1}$. f, f' and f'' from *International Tables for X-ray Crystallography* (1974). Final R and wR (for non-H atoms anisotropic and H atoms isotropic) are 4·7 and 5·0%, $(\Delta/\sigma)_{\max} = 0{\cdot}03$, $|\Delta\rho|_{\max}$ 0·3 e $Å^{-3}$ on final difference-Fourier map. *SDP-Plus* package of programs was used on a MicroVAX for structure solution and refinement (Frenz, 1983).

Discussion. Table 1 contains the final positional parameters while selected interatomic distances and bond angles appear in Table 2.*

The crystal structure of 'monomer' [$CoCl_4$] piperazinium consists of a monoclinic cell containing four $C_4H_{12}N_2$ and four [$CoCl_4$] units. The Co atom in the isolated [$CoCl_4$] group is tetrahedrally coordinated by four Cl atoms with Co—Cl bonds from 2·275 (1) to 2·291 (1) Å (Table 2). The piperazinium ion, as expected, is in the chair conformation with internal

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52720 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates and equivalent isotropic thermal factors*

Standard deviations are in parentheses.

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}/B_{iso} (Å^2)
Co	0·26486 (3)	0·50318 (3)	0·02702 (7)	2·041 (7)
Cl(1)	0·26988 (6)	0·47944 (4)	−0·3196 (1)	2·52 (1)
Cl(2)	0·12419 (6)	0·44416 (7)	0·1726 (1)	2·91 (1)
Cl(3)	0·39235 (6)	0·41157 (7)	0·1363 (1)	2·88 (1)
Cl(4)	0·27566 (6)	0·68003 (7)	0·0753 (1)	2·85 (1)
O	0·3173 (3)	0·2113 (3)	0·4126 (5)	4·69 (7)
N(1)	−0·0673 (2)	0·2136 (2)	0·7196 (4)	2·37 (5)
N(2)	0·1122 (2)	0·2960 (2)	0·5584 (4)	2·35 (5)
C(1)	0·0628 (3)	0·2086 (3)	0·4512 (6)	2·64 (6)
C(2)	−0·0179 (3)	0·2988 (3)	0·8257 (5)	2·49 (6)
C(3)	0·0025 (3)	0·1447 (3)	0·6020 (6)	2·67 (6)
C(4)	0·0412 (2)	0·3638 (3)	0·678 (3)	2·46 (6)
H(1)*	0·316 (3)	0·260 (3)	0·318 (3)	5·4 (2)
H(2)	0·310 (1)	0·153 (3)	0·356 (3)	5·8 (3)
H(3)	−0·108 (1)	0·237 (2)	0·634 (3)	1·3 (2)
H(4)	0·602 (1)	0·687 (2)	0·193 (4)	4·0 (2)
H(5)	0·350 (2)	0·772 (2)	0·370 (3)	0·3 (1)
H(6)	0·645 (1)	0·162 (2)	0·457 (2)	1·6 (1)
H(7)	0·523 (2)	0·254 (2)	0·358 (3)	0·5 (2)
H(8)	0·612 (1)	0·332 (2)	0·392 (3)	1·6 (1)
H(9)	0·565 (1)	0·841 (2)	0·106 (3)	0·3 (2)
H(10)	0·482 (2)	0·764 (2)	0·073 (2)	1·3 (1)
H(11)	0·528 (2)	0·594 (2)	0·466 (3)	0·3 (2)
H(12)	0·453 (2)	0·611 (2)	0·297 (3)	1·7 (2)
H(13)	0·421 (2)	0.913 (2)	0.254 (3)	1·5 (1)
H(14)	0·498 (2)	0·897 (2)	0·428 (3)	1·3 (1)

*H atoms were refined isotropically.

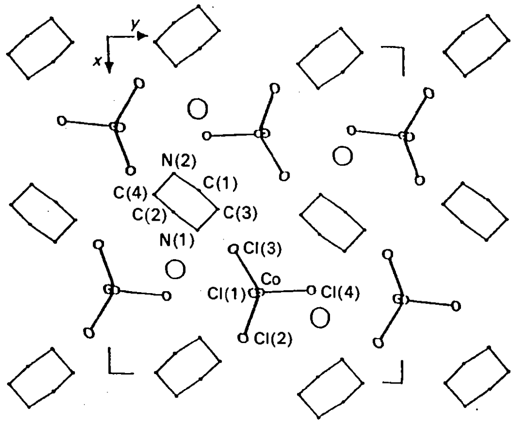

Fig. 1. *ORTEP* plot viewed along the *c* axis (Johnson, 1965). For clarity H atoms are not represented.

Table 2. *Selected bond distances* (Å) *and angles* (°)

Standard deviations are in parentheses.

$CoCl_4$ group

Co—Cl(1)	2·291 (1)	Co—Cl(3)	2·277 (1)
Co—Cl(2)	2·276 (1)	Co—Cl(4)	2·275 (1)
Cl(1)—Co—Cl(2)	110·92 (4)	Cl(2)—Co—Cl(3)	112·13 (4)
Cl(1)—Co—Cl(3)	104·98 (3)	Cl(2)—Co—Cl(4)	109·22 (4)
Cl(1)—Co—Cl(4)	105·65 (4)	Cl(3)—Co—Cl(4)	113·72 (4)

Piperazinium group

N(1)—C(2)	1·478 (5)	N(2)—C(4)	1·396 (5)
N(1)—C(3)	1·498 (5)	C(1)—C(3)	1·507 (5)
N(2)—C(1)	1·501 (5)	C(2)—C(4)	1·509 (5)
N(1)—C(3)—C(1)	110·2 (2)	N(2)—C(4)—C(2)	110·4 (3)
C(3)—C(1)—N(2)	110·4 (4)	C(4)—C(2)—N(1)	110·2 (3)
C(1)—N(2)—C(4)	110·6 (3)	C(2)—N(1)—C(3)	111·2 (3)

H_1—X—H_2	X—H_1	X—H_2	H_1—X—H_2
H(2)—O—H(2)	0·87	0·80	104
H(3)—N(1)—H(4)	0·88	0·79	102
H(5)—N(2)—H(6)	0·78	0·95	109
H(7)—C(1)—H(8)	0·96	0·94	116
H(9)—C(2)—H(10)	0·95	0·96	108
H(11)—C(3)—H(12)	0·91	1·02	110
H(13)—C(4)—H(14)	0·95	0·99	113

X—H···Y	X—H···Y	X—H	X···Y
O—H(1)···Cl(1)	0·87	3·258	150
O—H(2)···Cl(2)	0·80	3·268	152
N(1)—H(3)···O	0·88	2·810	170
N(1)—H(4)···Cl(3)	0·79	3·189	144
N(2)—H(5)···Cl(2)	0·78	3·152	143
N(2)—H(6)···Cl(4)	0·95	3·283	163

covalent bond lengths and angles in the range of those usually observed in this form. The bond lengths and angles involving H atoms (Table 2) are consistent with the sp^3 hybridization state of C and N atoms. The $C_4H_{12}N_2$ groups are stacked together forming layers parallel to the *ac* plane (Fig. 1). The distance separating two piperazinium layers is relatively large, 6·35 Å. The cohesion forces of the packing of the piperazinium units in the layer and between two adjacent layers are mostly provided by a three-dimensional H-bond network: N—H···Cl, C—H···Cl and O—H···Cl. The N—H···Cl bonds, as suggested by their relatively short N···Cl contacts compared with C···Cl (Table 2), seem to play a crucial role in packing together $C_4H_{12}N_2$ groups and the counter ions, [$CoCl_4$]. Thus, the [$CoCl_4$] counter ions form monomer groups, isolated from each other by $C_4H_{12}N_2$ molecules, suggesting that any magnetic ordering of Co ions very unlikley, even at low temperature.

The water molecules also contribute to the stability of this complex in forming two O—H···Cl H bonds with [$CoCl_4$] groups. Furthermore, the relatively high thermal factors of their associated hydrogens, H(1) and H(2), may consistently denote their mobility and/or positional disorder in the crystal.

References

Daoud, A., Ben Salah, A., Chappert, C., Renard, J. P., Cheikhrouhou, A., Tran Qui, D. & Verdaguer, M. (1986). *Phys. Rev. B*, **33**, 6253–6260.

Fanchon, E., Halouani, F., Daoud, A., Tran Qui, D. & Vicat, J. (1987). *Acta Cryst.* **C43**, 829–831.

Frenz, B. A. (1983). *Enraf–Nonius Structure Determination Package; SDP Users Guide*. Version 1.1, August 1983. Enraf–Nonius, Delft, The Netherlands.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

LANDÉE, C. P. & WILLET, R. D. (1979). *Phys. Lett.* **43**, 463–469.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MIER, G. P. M. VAN, KANTERS, J. A. & HARDER, S. (1987). *Acta Cryst.* C**43**, 2327–2330.

TRAN QUI, D., DAOUD, A. & MHIRI, T. (1989). *Acta Cryst.* C**45**, 33–35.

WILLET, R. D., DWIGGINS, C. W. JR, KRUH, R. H. & RUNDLE, R. E. (1963). *J. Chem. Phys.* **38**, 2429–2436.

Acta Cryst. (1990). C**46**, 1215–1217

Structure of Dimethyltetramethylenetetrathiafulvalene Hexafluoroarsenate: $(C_{12}H_{14}S_4)_2AsF_6$

BY T. GRANIER, B. GALLOIS AND J. GAULTIER

Laboratoire de Cristallographie, UA-CNRS 144, *Université de Bordeaux* I, 351 *Cours de la Libération*, 33405 *Talence CEDEX, France*

AND J. M. FABRE

Laboratoire de Chimie Organique Structurale, USTL, Place E. Bataillon, 34060 *Montpellier CEDEX, France*

(*Received* 15 *May* 1989; *accepted* 14 *September* 1989)

Abstract. Bis[2-(4,5-dimethyl-1,3-dithiol-2-ylidene)-4,5,6,7-tetrahydro-1,3-benzodithiol]ium hexafluoroarsenate, $(DMCTTF)_2AsF_6$, $M_r = 761\cdot89$, triclinic, $P\bar{1}$, $a = 7\cdot8665\,(28)$, $b = 7\cdot8575\,(14)$, $c = 13\cdot4458\,(21)$ Å, $\alpha = 95\cdot67\,(1)$, $\beta = 101\cdot36\,(2)$, $\gamma = 111\cdot08\,(2)°$, $V = 747\cdot1$ Å^3, $Z = 2$, $D_x = 1\cdot6934$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1\cdot54178$ Å, $\mu = 68\cdot02$ cm^{-1}, $F(000) = 387$, $T = 298$ K, $R = 0\cdot0489$ for 2743 observed reflections $[I > 3\sigma(I)]$. $DMCTTF^+$ organic cations stack in a zigzag type mode along the a axis and build weakly dimerized conducting columns. AsF_6^- anions are located in cavities left by the organic molecules. The As atom lies on the inversion center.

Introduction. The title compound belongs to a novel series of organic conductors which have been extensively studied recently (Vaca, Granier, Gallois, Coulon, Gouasmia & Fabre, 1988; Vaca, Coulon, Ducasse, Granier, Gallois, Fabre & Gouasmia, 1989). These compounds are based on the new unsymmetrical π donor derived from the tetrathiafulvalene (TTF) backbone: dimethyltetramethylenetetrathiafulvalene (DMCTTF) and its selenium analogue (DMCTSeF) (Giral, Fabre & Gouasmia, 1986). All sulfur compounds [*i.e.* $(DMCTTF)_2X$ where X is a diamagnetic anion such as AsF_6^-, PF_6^-, BF_4^-, ClO_4^- and ReO_4^-] exhibit an antiferromagnetic ground state at low temperature ($T \simeq 10$–30 K), the properties of which are well understood through the structural organization of these compounds. The latter depends on the anion geometry: salts of tetrahedral anions present two organic stacks in the unit cell (Granier, Gallois & Fabre, 1989) while salts of octahedral anions present only one single DMCTTF stack. We discuss here the detailed structure of one of the latter salts: $(DMCTTF)_2AsF_6$.

Experimental. The salt studied was prepared in tetrahydrofuran using oxidative electrocrystallization at constant current (10 μA), in the presence of tetrabutylammonium hexafluoroarsenate and $DMCTTF^+$ (Giral, Fabre & Gouasmia, 1986). The crystals obtained were thin black needles: dimensions 0·50 × 0·08 × 0·02 mm. All measurements were carried out on an Enraf–Nonius CAD-4 diffractometer, determination of the unit-cell parameters was by least-squares refinement of the setting angles of 22 reflections ($10 < \theta < 65°$). 2971 [2743 with $I > 3\sigma(I)$] unique reflections; graphite-monochromated Cu $K\alpha$ radiation, ω–2θ scan, scan angle $(1\cdot2 + 0\cdot15\tan\theta)°$, $1 < \theta < 73°$; ranges of h, k and l: -9 to 9, -9 to 9, 0 to 16 respectively. Three standard reflections were measured every 100 reflections, small random variation was observed (±3%). Data corrected for Lorentz and polarization factors, and empirical absorption correction applied (North, Phillips & Mathews, 1968), max. and min. transmission factors 0·63 and 0·99. All non-hydrogen atoms were positioned by a Patterson map analysis. Full-matrix least-squares refinement achieved on F, using *SHELX76* (Sheldrick, 1976), atomic scattering factors inlaid. Methylene and methyl groups were refined as rigid groups with a C—H bond length of

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