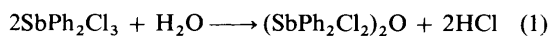


Reaction of Methanol with Diphenylantimony(v) Trihalides: Crystal Structure of $[\text{SbPh}_2\text{Br}_2(\text{OMe})\cdot\text{MeOH}]_2^\dagger$

T. Tunde Bamgboye, Michael J. Begley, I. Gary Southerington and D. Bryan Sowerby*
Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK

A re-examination of the reaction between diphenylantimony trichloride and methanol showed that the initial product is a methanol adduct of the monomethoxide, $\text{SbPh}_2\text{Cl}_2(\text{OMe})$, rather than the oxide $(\text{SbPh}_2\text{Cl}_2)_2\text{O}$, which is a hydrolysis product formed during recrystallisation. The corresponding tribromide, and the mixed halides, $\text{SbPh}_2\text{Br}_{3-n}\text{Cl}_n$, where $n = 1$ or 2 , react similarly with methanol, losing a bromine atom to give solvated monomethoxy products. X-Ray diffraction analysis revealed that $\text{SbPh}_2\text{Br}_2(\text{OMe})$ crystallises as a centrosymmetric dimer, incorporating two molecules of methanol, which are attached *via* strong hydrogen bonds to the oxygen atoms of the methoxy groups. Co-ordination of the methanol oxygen to a symmetry-related antimony atom completes the distorted-octahedral co-ordination about antimony and forms a central eight-atom ring system in the chair conformation. Two unusual features are the similarity of the two Sb–O distances [2.101(4) and 2.121(4) Å], even though the former is formally a normal σ bond and the latter a donor linkage, and the presence of a weak π -arene \cdots H–C hydrogen bond, which probably accounts for the orthogonality of the phenyl groups at antimony.

Treatment of diphenylantimony trichloride with methanol is reported^{1–3} to produce $(\text{SbPh}_2\text{Cl}_2)_2\text{O}$, melting at 140 °C. The compound is considered to arise either by loss of dimethyl ether from an intermediate monomethoxy compound,¹ or as a result of hydrolysis by traces of moisture in the methanol^{2,3} [eqn. (1)]. The yield can be greatly improved if the reaction is carried



out at reflux, passing the condensate through a Soxhlet cup containing sodium carbonate to neutralise the HCl produced,² or by adding either sodium methoxide³ or potassium hydroxide to the original methanol solution.

The production of $(\text{SbPh}_2\text{Cl}_2)_2\text{O}$ in a direct reaction with methanol is surprising as the Sb–O–Sb bonds in both $(\text{SbPh}_3\text{O})_2$ and $(\text{SbPh}_3\text{Cl})_2\text{O}$ are known to be cleaved by methanol giving $\text{SbPh}_3(\text{OMe})_2$ and $\text{SbPh}_3\text{Cl}(\text{OMe})$ respectively.⁴ Our interest in this reaction stems from the fact that we obtained a sample of $(\text{SbPh}_2\text{Cl}_2)_2\text{O}$, by oxidising $(\text{SbPh}_2)_2\text{O}$ with chlorine, with a substantially higher melting point (195 °C) than the 140 °C reported previously.^{1–3}

Results and Discussion

We have re-examined the reaction of SbPh_2Cl_3 with anhydrous methanol to show that at both room temperature and reflux the initial product is indeed a white solid, melting at 140 °C, soluble, among other solvents, in methanol, benzene, toluene and chloroform. The compound does not, however, show the infrared band at *ca.* 770 cm^{-1} associated with an Sb–O–Sb system,^{2,3} but there is a band at 491 cm^{-1} which can be assigned to a simple Sb–O stretching vibration. In addition there are bands at 2935 and 1017 cm^{-1} , associated with C–H stretching and deformation, and the proton resonance spectrum in CDCl_3 clearly shows a peak at δ 3.5. The product is therefore likely to be the monomethoxide, $\text{SbPh}_2\text{Cl}_2(\text{OMe})$.

The discrepancy in results arises because, unless care is taken

during recrystallisation, the monomethoxide is hydrolysed by atmospheric moisture to the oxygen-bridged $(\text{SbPh}_2\text{Cl}_2)_2\text{O}$. In the open laboratory, crystallisation from either benzene or chloroform readily yields $(\text{SbPh}_2\text{Cl}_2)_2\text{O}$, but the monomethoxide can be recovered from either pure methanol or chloroform–methanol mixtures as a methanol adduct. The compound is hydrolytically unstable and is slowly hydrolysed even on standing at room temperature. It should be noted that although the carbon and hydrogen contents of the methanol adduct of the monomethoxide and its hydrolysis product are very similar, their melting points differ by 55 °C.

The proton resonance spectrum of the methoxide, on the other hand, is somewhat confusing. In addition to the expected phenyl multiplets at δ 7.3–8.3 there are singlets at δ *ca.* 2.3 and 3.5, both of which are enhanced on addition of methanol. The high-field peak, however, disappears on shaking with D_2O and is probably best assigned to the hydroxy proton of a molecule of methanol of solvation. However, the ready hydrolysis of this compound in the absence of methanol makes it difficult to be certain there is no hydrolysis in the CDCl_3 solution used to obtain the NMR spectrum. At this stage the data, including microanalysis, imply that the product is a monomethoxy derivative, to which a molecule of methanol is incorporated presumably by hydrogen bonding.

Reaction of methanol with either the corresponding bromide, SbPh_2Br_3 , or the mixed bromide chlorides $\text{SbPh}_2\text{Br}_2\text{Cl}$ and $\text{SbPh}_2\text{BrCl}_2$, follows an equivalent route and the white solids obtained by preferential bromine substitution are respectively, $\text{SbPh}_2\text{Br}_2(\text{OMe})$, $\text{SbPh}_2\text{BrCl}(\text{OMe})$ and $\text{SbPh}_2\text{Cl}_2(\text{OMe})$, again most probably as methanol addition compounds. Perhaps rather surprisingly, none of the trihalides reacts with higher primary alcohols, ROH for R = Et, Pr, Prⁱ or Bu^t.

All the compounds can be recrystallised satisfactorily either from methanol, in which they are only slightly soluble, or better from a chloroform–methanol mixture, giving the pure monomethoxides as methanol addition compounds. As with the chloride, recrystallisation from benzene or chloroform with no precautions against atmospheric moisture yields the appropriate hydrolysis product, $[\text{SbPh}_2(\text{Br},\text{Cl})_2]_2\text{O}$, and these are also obtained, presumably as a result of slow hydrolysis, after monomethoxide samples have been standing for long periods at room temperature. Their IR spectra all show, in

[†] Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

addition to methyl stretching and deformation modes, bands at *ca.* 490 cm^{-1} due to Sb–O stretching.

The electron-impact mass spectra of the three products are very similar and, although there is extensive fragmentation, the presence of a methoxy group in, for example, the tribromide product is confirmed by peaks at *m/z* 387 [SbPhBr₂(OMe)], 385 [SbPh₂Br(OMe)], 310 [SbBr₂(OMe)], 308 [SbPhBr(OMe)] and 306 [SbPh₂(OMe)]. The proton NMR spectra of SbPh₂Br₂(OMe) and SbPh₂BrCl(OMe) in CDCl₃ are broadly similar to that of the chloride and show the same set of signals, implying similar structures, incorporating extra methanol.

Owing to ambiguities in the proton NMR spectra and in order to investigate how the methanol is incorporated, we attempted to determine the crystal structure of the diphenylantimony trichloride reaction product. Apparently good-quality crystals were obtained from methanol–chloroform mixtures and, from preliminary oscillation and Weissenberg photographs, reasonable cell dimensions, subsequently refined, were obtained (space group, monoclinic either *C2/c* or *Cc*, *a* = 15.813, *b* = 10.004, *c* = 16.106 Å, β = 92.50° with *Z* = 8). Intensity data were collected and although a number of structural features could be recognised during the attempted solution the *R* value never fell below 0.25 with either space group. Re-examination of the Weissenberg photographs revealed diffuse intensity between the diffraction maxima, indicative of disorder, but attempts to model this were unsuccessful. The determination was therefore abandoned and attention turned to the related dibromide methoxide, for which well behaved crystals were obtained.

Crystal Structure of SbPh₂Br₂(OMe)·MeOH.—The molecular structure and atom numbering scheme are shown in Fig. 1 and important bond distances and angles are listed in Table 1. Fig. 1 shows that the compound crystallises from solutions containing methanol as a solvated centrosymmetric dimer, in which two molecules of methanol are incorporated *via* hydrogen bonds, giving [SbPh₂Br₂(OMe)·MeOH]₂ as the overall formula.

The antimony atoms are in distorted octahedral coordination, with pairs of bromine and oxygen atoms occupying *cis* positions and the phenyl groups *trans* to each other. The largest deviation from octahedral geometry is at the angle between the two oxygen atoms (84.6°), a consequence presumably of their incorporation into the ring system. In spite of this the Br₂SbO₂ system is close to planarity, with the four angles at antimony summing to exactly 360°. The three *trans* angles are, however, all less than 180°, with the phenyl groups displaced towards the two oxygen atoms.

Although it is not unusual for two phenyl groups at antimony to occupy *trans* positions [C(11)–Sb(1)–C(21) 175.0(2)°], it is surprising that their ring planes are almost orthogonal [the Br(1)–Sb(1)–C(11)–C(12) and Br(1)–Sb(1)–C(21)–C(22) torsion angles are 137.7 and –53.1°, respectively; see Fig. 1], begging the question of some kind of stabilising interaction. The closest contacts between the two rings are those between H(26) and the C(11)–C(16) carbon atoms (primed atoms are related by the symmetry operation 1 – *x*, – *y*, – *z*) at 3.00–3.35 Å and on this basis it is possible to postulate the presence of a weak hydrogen bond between H(26) and the π cloud of the C(11) phenyl group. This is supported by a separation of 2.87 Å between H(26) and the centre of the phenyl group and an angle of 152° at H(26) between C(26) and the ring centre.

Weak non-covalent interactions are now recognised as having an important influence on the solid-state structures of many organic compounds,^{5,6} and recently⁷ the first example of a C–H... π -arene hydrogen bond, similar to that suggested here, has been identified as stabilising the inclusion of dichloromethane in the cavity of a calix[4]resorcinarene.

The bonds between antimony and the two bromine atoms are similar in length and fall towards the top end of the range (2.446–2.605 Å) usually found in antimony(v) systems. The two

Table 1 Bond distances (Å) and angles (°), with estimated standard deviations (e.s.d.s) in parentheses, for [SbPh₂Br₂(OMe)·MeOH]₂

Sb(1)–Br(1)	2.582(1)	O(1)–C(1)	1.421(8)
Sb(1)–Br(2)	2.589(1)	O(1)···O(2')	2.483(6)
Sb(1)–O(1)	2.121(4)	O(2)–C(2)	1.439(8)
Sb(1)–O(2)	2.101(4)	O(1)–H(1)	1.07(9)
Sb(1)–C(11)	2.130(6)	O(2)–H(1')	1.43(9)
Sb(1)–C(21)	2.123(6)		
Br(1)–Sb(1)–Br(2)	93.99(4)	Sb(1)–O(1)–C(1)	124.7(4)
Br(1)–Sb(1)–O(1)	175.5(1)	Sb(1)–O(1)–H(1)	131(5)
Br(1)–Sb(1)–O(2)	91.0(1)	Sb(1)–O(1)–O(2')	131.1(2)
Br(1)–Sb(1)–C(11)	92.3(2)	C(1)–O(1)–H(1)	104(5)
Br(1)–Sb(1)–C(21)	91.8(2)	C(1)–O(1)–O(2')	104.1(4)
Br(2)–Sb(1)–O(1)	90.4(1)	Sb(1)–O(2)–C(2)	125.9(4)
Br(2)–Sb(1)–O(2)	175.0(1)	Sb(1)–O(2)–H(1')	129(4)
Br(2)–Sb(1)–C(11)	91.3(2)	Sb(1)–O(2)–O(1')	123.8(2)
Br(2)–Sb(1)–C(21)	91.1(2)	C(1)–O(2)–H(1')	106(4)
O(1)–Sb(1)–O(2)	84.6(2)	C(2)–O(2)–O(1')	110.1(4)
O(1)–Sb(1)–C(11)	87.0(2)	Sb(1)–C(11)–C(12)	120.3(5)
O(1)–Sb(1)–C(21)	88.6(2)	Sb(1)–C(11)–C(16)	119.5(5)
O(2)–Sb(1)–C(11)	88.1(2)	Sb(1)–C(21)–C(22)	120.6(5)
O(2)–Sb(1)–C(21)	89.1(2)	Sb(1)–C(21)–C(26)	118.9(4)
C(11)–Sb(1)–C(21)	175.0(2)	O(1)–H(1)–O(2')	168(8)

Atoms carrying a prime are related to unprimed atoms by the symmetry operation 1 – *x*, – *y*, – *z*.

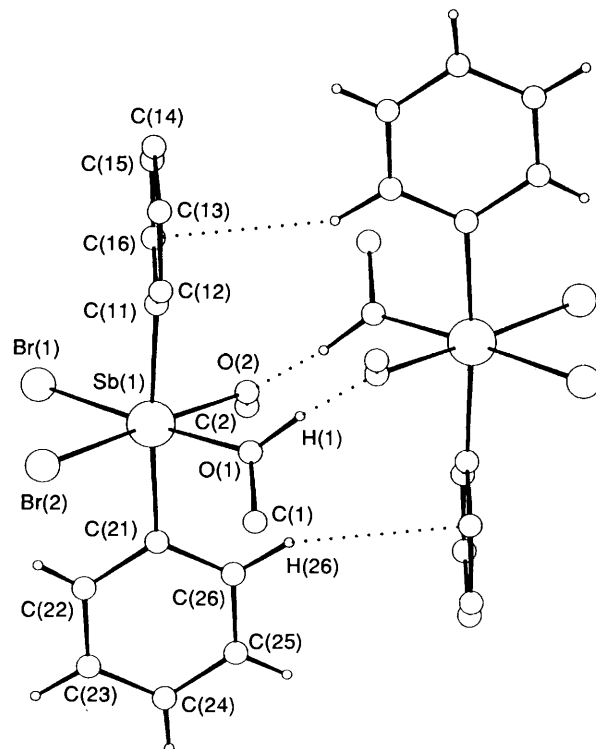


Fig. 1 Molecular structure and atom numbering scheme for [SbPh₂Br₂(OMe)·MeOH]₂. Hydrogen atoms on the methyl groups and on the C(11) phenyl group have been omitted for clarity

antimony–carbon bonds are also effectively equal with normal distances. Perhaps more surprising is the near equivalence of the two antimony–oxygen bonds, even though one is ostensibly a normal σ bond to methoxide [2.101(4) Å] and the second a donor bond from the solvate methanol [2.121(4) Å]. For comparison, bonds to terminal and bridging methoxy groups in dimeric antimony pentamethoxide⁸ are *ca.* 1.94 and 2.10 Å respectively and in the similarly bis(methoxy)-bridged dimer [SbMeBr₂(OMe)₂]₂ the distances are *ca.* 1.96 and 2.14 Å, respectively.⁹ The present distances are clearly comparable

with those for bridging groups. Surprisingly, the geometry at each of the oxygen atoms is planar, with the implication of a stereochemically inactive lone pair of electrons.

After water, methanol is probably the molecule most commonly involved in hydrogen-bond formation and a number of such species are listed in the Cambridge Crystallographic Data Base. In the present structure determination the hydrogen atoms were refined satisfactorily with isotropic thermal parameters to stable positions. The O(1)···O(2) separation at 2.483(6) Å is substantially less than twice the van der Waals radius of oxygen, pointing to strong hydrogen bonding.¹⁰ In such cases hydrogen is usually centrally placed and, if this were the case here, the two Sb–O and Sb–Br separations would be expected to be identical. The hydrogen atom, in fact, refined satisfactorily off centre, with an O–H···O angle of 168(8)° and O–H distances 1.07(9) and 1.43(9) Å. This correlates well with the observed small, but statistically just significant, differences in the two Sb–O and Sb–Br distances, implying that it is probably justifiable to consider the structure in terms of the presence of a methoxy group and a hydrogen-bonded methanol molecule. There is a small *trans* influence as the shorter Sb–O bond is *trans* to the longer Sb–Br bond.

Comparable O···O hydrogen-bonded separations between a methoxy group and methanol have been found in a variety of compounds, including [W₂Cl₄(μ–OMe)₂(OMe)₂(MeOH)₂] (2.49 Å),¹¹ a series of complex Schiff-base complexes containing four nickel atoms (2.44–2.51 Å)^{12,13} and a dicopper complex (2.35 Å).¹⁴

Incorporation of methanol into the centrosymmetric dimeric structure leads to formation of a central eight-membered ring which, as shown by the torsion angles in Table 2, has a chair conformation.

Experimental

The starting materials, SbPh₂Cl₃, SbPh₂Br₃ and SbPh₂BrCl₂, were obtained by oxidation of either SbPh₂Cl or SbPh₂Br with the appropriate halogen at 0 °C in dichloromethane solution, and recrystallised from chloroform.¹⁵ The remaining mixed halide, SbPh₂BrCl₂, was prepared by oxidising SbPh₂Br with the stoichiometric amount of suluryl chloride at 0 °C in dichloromethane; this is a more convenient method than the previous method, which used chlorine at –78 °C.¹⁵

Reaction of SbPh₂Cl₃ with Methanol.—(a) A solution of SbPh₂Cl₃ (1 g, 3 mmol) in methanol (50 cm³) at room temperature almost immediately began to deposit a white solid. After 2 h this was filtered off and recrystallised from methanol–chloroform (1:1 v/v). Yield 21%, m.p. 140 °C [Found: C, 40.7; H, 3.9. Calc. for SbPh₂Cl₂(OMe)·MeOH: C, 41.0; H, 4.1; Calc. for SbPh₂Cl₂(OMe)₂: C, 41.3; H, 3.4; Calc. for (SbPh₂Cl₂)₂O: C, 40.7; H, 2.9%].

(b) After 30 min a methanol solution of 1 mol of either sodium methoxide² or potassium hydroxide³ was added to a solution of SbPh₂Cl₃ in methanol as described above. After stirring at room temperature for 2 h, the solid was filtered off and recrystallised as above to give an 88% yield of SbPh₂Cl₂(OMe)·MeOH.

Reaction of SbPh₂Br₃ and SbPh₂(Br,Cl)₃ with Methanol.—In a similar way, a solution of the tribromide (2 g, 4 mmol), in methanol at room temperature after 30 min gave SbPh₂Br₂(OMe)·MeOH (0.9 g, 45% yield), m.p. 135 °C, after recrystallisation from a methanol–chloroform mixture [Found: C, 33.6; H, 3.5. Calc. for SbPh₂Br₂(OMe)·MeOH: C, 33.7; H, 3.5%].

Solutions of SbPh₂Br₂Cl and SbPh₂BrCl₂ similarly gave, respectively, SbPh₂BrCl(OMe)·MeOH, m.p. 148 °C [Found: C, 36.0; H, 3.4. Calc. for SbPh₂BrCl(OMe)·MeOH: C, 37.0; H, 3.7%] and SbPh₂Cl₂(OMe)·MeOH, m.p. 140 °C, the same compound as obtained from SbPh₂Cl₃.

Table 2 Torsion angles (°) describing the ring in [SbPh₂Br₂(OMe)·MeOH]₂

Sb(1)–O(2)–O(1')–Sb(1')	64.3
Sb(1)–O(1)–O(2')–Sb(1')	–64.3
O(2)–Sb(1)–O(1)–O(2')	48.7
O(2')–Sb(1')–O(1')–O(2)	–48.7
O(1')–Sb(1')–O(2')–O(1)	43.0
O(1)–Sb(1)–O(2)–O(1')	–43.0

Atoms carrying a prime are related to unprimed atoms by the symmetry operation 1 – x, – y, – z.

Table 3 Fractional atomic coordinates, with e.s.d.s in parentheses, for the heavy atoms in SbPh₂Br₂(OMe)·MeOH

Atom	X/a	Y/b	Z/c
Sb(1)	0.627 63(4)	0.091 85(3)	0.192 33(4)
Br(1)	0.586 80(9)	0.104 42(7)	0.412 09(7)
Br(2)	0.753 74(9)	0.238 44(4)	0.196 57(9)
O(1)	0.651 2(4)	0.072 8(3)	0.010 5(4)
O(2)	0.526 6(4)	–0.027 8(3)	0.172 9(4)
C(1)	0.780 0(8)	0.089 2(6)	–0.033 4(7)
C(2)	0.541(1)	–0.092 9(6)	0.264 6(7)
C(11)	0.421 8(7)	0.146 9(4)	0.119 1(5)
C(12)	0.408 4(8)	0.205 6(4)	0.027 5(7)
C(13)	0.275 5(8)	0.244 3(5)	–0.012 7(8)
C(14)	0.159 0(9)	0.225 5(6)	0.035 9(9)
C(15)	0.171 6(7)	0.164 1(6)	0.125 9(8)
C(16)	0.302 2(8)	0.125 3(5)	0.168 1(7)
C(21)	0.830 4(6)	0.030 4(4)	0.251 4(5)
C(22)	0.935 9(8)	0.066 6(5)	0.340 2(6)
C(23)	1.066 4(7)	0.026 0(5)	0.378 1(6)
C(24)	1.092 1(7)	–0.051 4(5)	0.328 2(7)
C(25)	0.988 3(8)	–0.086 3(5)	0.238 9(7)
C(26)	0.855 9(7)	–0.046 2(4)	0.198 8(6)
H(1)	0.57(1)	0.061(6)	–0.070(8)

Preparation of (SbPh₂Cl₂)₂O.—(a) By chlorination of (SbPh₂)₂O.¹⁶ Dry chlorine was passed through a solution of (SbPh₂)₂O (2.0 g, 3.5 mmol) in chloroform (50 cm³) at room temperature for 5 min. On cooling to 0 °C, the product was obtained as white crystals (yield 74%, m.p. 198 °C) [Found: C, 40.1; H, 2.8. Calc. for (SbPh₂Cl₂)₂O: C, 40.6; H, 2.8%].

(b) By recrystallisation of diphenylantimony dichloride methoxide. Recrystallisation of this compound from solvents such as benzene, chloroform or dichloromethane, with no precautions to exclude atmospheric moisture, led to hydrolysis of the methoxide and formation of the oxide (m.p. 198 °C).

Preparation of (SbPh₂Br₂)₂O.—(a) By bromination of (SbPh₂)₂O. Slow addition of bromine (1.2 g, 7.5 mmol) to a solution of the oxide (2.0 g, 3.5 mmol) in chloroform (40 cm³) gave with cooling the product (2.6 g, 82% yield). M.p. 201 °C [Found: C, 32.3; H, 2.2. Calc. for (SbPh₂Br₂)₂O: C, 32.5; H, 2.3%].

(b) By recrystallisation of diphenylantimony dibromide methoxide. As for the chloride above, this compound is hydrolysed on recrystallisation in the presence of atmospheric moisture to (SbPh₂Br₂)₂O, m.p. 201 °C.

Crystal Structure Determination of SbPh₂Br₂(OMe)·MeOH.—Crystal data. C₁₄H₁₇Br₂O₂Sb, M = 498.6, monoclinic, space group P2₁/c, a = 9.407(3), b = 15.730(6), c = 11.238(5) Å, β = 101.55(2)°, U = 1629.2 Å³, Z = 4, D_c = 2.03 g cm^{–3}, F(000) = 952, Mo-Kα radiation, λ = 0.7107 Å, μ = 69.1 cm^{–1}, crystal size 0.20 × 0.16 × 0.36 mm.

Structure determination. Intensity data were collected using a Hilger and Watts Y290 four-circle diffractometer for 2θ < 50° and –13 < h < 13, 0 < k < 20 and 0 < l < 15. Of the 2976 reflections measured, 2230 with intensities > 3σ(I) were

considered observed and corrected for Lorentz and polarisation effects; an empirical absorption correction was applied.¹⁷ Data reduction and subsequent calculations used the CRYSTALS programs;¹⁸ scattering factors were those for neutral atoms.¹⁹ The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares. With all the non-hydrogen atoms present, refinement converged at R 0.151 with isotropic and 0.040 with anisotropic thermal parameters. A Fourier-difference map then showed the positions of all hydrogen atoms, which were refined in subsequent cycles with isotropic thermal parameters. Final convergence was at R 0.035 (R' 0.040) after applying a four-coefficient Chebyshev weighting scheme and including the anomalous part of the scattering curve, for 240 least-squares parameters. A final difference synthesis showed, except in the vicinity of the heavy atoms, no peaks with an intensity greater than $0.3 \text{ e } \text{Å}^{-3}$. Table 3 contains the final refined atomic coordinates.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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