Synthesis, Spectroscopic, and Structural Studies of the Methylpalladium(II) Complexes $[\{PdMe(SMe_2)X\}_2]$ (X = Cl, Br, or I); Crystal Structure of *trans*-$[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$ †

Peter K. Byers and Allan J. Canty
Chemistry Department, University of Tasmania, Hobart, Tasmania, Australia 7001
Lutz M. Engelhardt and Allan H. White
Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A., Australia 6009

The complexes $[\{PdMe(SMe_2)X\}_2]$ (X = Cl, Br, or I) have been prepared by reaction of *trans*-$[Pd(SMe_2)_2X_2]$ with halide-free methyl-lithium (X = Cl or Br), and reaction of *trans*-$[Pd(SMe_2)_2Cl_2]$ with methyl-lithium containing lithium iodide (X = I) in diethyl ether at −60 to −15 °C under nitrogen. Other synthetic routes to the bromo- and iodo-complexes are also described. The crystal structure of the chloro-complex $[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$ has been determined by single-crystal *X*-ray diffraction at 295 K and refined by least-squares methods to $R = 0.025$ for 1 914 independent 'observed' reflections [space group $P2_1/n$, $a = 10.792(4)$, $b = 7.373(2)$, $c = 9.131(5)$ Å, $\beta = 109.03(3)°$, and $Z = 2$]. The centrosymmetric dimeric molecules have *trans* stereochemistry with bridging chloro-groups and square-planar geometry for palladium(II). ^{1}H N.m.r. and far-i.r. spectra, and molecular weight determinations are consistent with similar structures for the bromo- and iodo-complexes.

Palladium(II) chloride and bromide complexes of dimethyl sulphide with a $PdX_2:SMe_2$ ratio of 1:1 are known to be dimeric with bridging halogeno-groups, *trans*-$[\{PdX(SMe_2)(\mu\text{-}X)\}_2]$ (**1a**), from vibrational and ^{1}H n.m.r. spectroscopic studies (X = Cl or Br),[1,2] and an *X*-ray crystallographic study (X = Br).[3,4] Platinum(II) exhibits different behaviour, with vibrational spectra indicating bridging iodo-groups for *trans*-$[\{PtI(SMe_2)(\mu\text{-}I)\}_2]$ (**1b**),[5] as for the palladium(II) chloro- and bromo-complexes, but bridging thioether for $[\{PtX_2(\mu\text{-}SMe_2)\}_2]$ (X = Cl or Br) (**2**),[3,5] as shown crystallographically for $[\{PtBr_2(\mu\text{-}SEt_2)\}_2]$.[3,4]

Methylmetal(II) complexes $[\{MMe(SMe_2)X\}_2]$ (M = Pd or Pt) may conceivably show related structural isomerism, and indeed ^{1}H n.m.r. spectroscopic studies have shown that $[\{PtMe(SMe_2)I\}_2]$, which could not be isolated as a solid, has iodo-bridging in chloroform with *cis*-(**3a**) and *trans*-(**3b**) isomers in equilibrium.[6] Analogous palladium(II) complexes have been obtained during development of syntheses of methylpalladium(II) poly(pyrazol-1-yl)methane complexes from *trans*-$[Pd(SMe_2)_2Cl_2]$,[7] and we report here the synthesis of $[\{PdMe(SMe_2)X\}_2]$ (X = Cl, Br, or I), an *X*-ray structural study of *trans*-$[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$, and vibrational spectroscopic studies indicating that the bromo- and iodo-derivatives have the same structure as the chloro-derivative in the solid state.

Results

Preparation and Characterization of Complexes.—The complexes $[\{PdMe(SMe_2)X\}_2]$ (X = Cl or Br) were prepared in diethyl ether under nitrogen at low temperature (−60 °C initially, slowly warmed to *ca.* −15 °C) by reaction of *trans*-$[Pd(SMe_2)_2X_2]$ with one mol equivalent of 'halide-free methyl-lithium' (containing 0.4% LiCl), followed by hydrolysis and isolation of the complexes from diethyl ether [equation (1)]. *trans*-$[Pd(SMe_2)_2I_2]$ has low stability,[2] and it was found that $[\{PdMe(SMe_2)I\}_2]$ may be conveniently prepared by reaction of *trans*-$[Pd(SMe_2)_2Cl_2]$ with methyl-lithium–lithium iodide (from MeI + 2Li) under similar conditions to those used for the chloro- and bromo-complexes [equation (2)]; the bromo-complex may also be obtained in this manner using methyl-lithium–lithium bromide.

$$trans\text{-}[Pd(SMe_2)_2X_2] \xrightarrow{LiMe} \tfrac{1}{2}[\{PdMe(SMe_2)X\}_2]\ (X = Cl\ or\ Br) \quad (1)$$

$$trans\text{-}[Pd(SMe_2)_2Cl_2] \xrightarrow{2LiMe\text{-}LiX} \tfrac{1}{2}[\{PdMe(SMe_2)X\}_2]\ (X = Br\ or\ I) \quad (2)$$

In addition, the bromo- and iodo-complexes may be prepared by exchange reactions in diethyl ether–water [equation (3)], and on reaction of MeX with dimethylpalladium(II) species obtained[7] from *trans*-$[Pd(SMe_2)_2Cl_2]$ and two mol equivalents of halide-free methyl-lithium [equation (4)].

$$[\{PdMe(SMe_2)X\}_2] \xrightarrow{2KY} [\{PdMe(SMe_2)Y\}_2]\ (X = Cl,\ Y = Br\ or\ I;\ X = Br,\ Y = I) \quad (3)$$

$$trans\text{-}[Pd(SMe_2)_2Cl_2] \xrightarrow[(ii)\ MeX]{(i)\ 2LiMe} \tfrac{1}{2}[\{PdMe(SMe_2)X\}_2]\ (X = Br\ or\ I) \quad (4)$$

Although the complexes slowly decompose at ambient temperature, and on dissolution in chloroform, they gave satisfactory microanalyses and molecular weight values in chloroform, and both the near-i.r. and ^{1}H n.m.r. spectra are very similar (Table 1). However, far-i.r. spectra (Table 2) are radically different, as expected, since this region contains palladium–halogen stretching frequencies.

Crystal Structure of $[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$.—In the solid state, molecules of *trans*-$[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$ are situated at centres of symmetry in space group $P2_1/n$, with the maximum deviation (0.077 Å) from the $PdCl_2SC$ mean plane being

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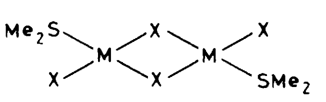
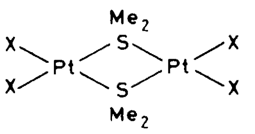
† *trans*-Di-μ-chloro-bis[(dimethyl sulphide)methylpalladium(II)].

Supplementary data available (No. SUP 56527, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

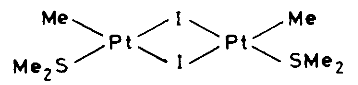


(**1a**) M = Pd; X = Cl or Br

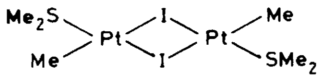
(**1b**) M = Pt; X = I



(**2**) X = Cl or Br



cis-[{PtMe(SMe$_2$)(μ-I)}$_2$] (**3a**)



trans-[{PtMe(SMe$_2$)(μ-I)}$_2$] (**3b**)

Table 1. Characterization data for the complexes

Complex	Colour	Analysis[a] (%) C	Analysis[a] (%) H	$M^{a,b,c}$	^{1}H N.m.r.[c,d] PdMe	^{1}H N.m.r.[c,d] SMe$_2$	I.r.[e] (cm^{-1})
[{PdMe(SMe$_2$)(μ-Cl)}$_2$]	Yellow	16.6 (16.5)	3.7 (4.1)	448 (438)	0.78(1)	2.34(2)	2 952mw, 2 912mw, 2 880mw, 1 428s, 1 320mw, 1 304mw, 1 154m, 1 034m, 988m, 750m, 537w
[{PdMe(SMe$_2$)Br}$_2$]	Orange-tan	13.8 (13.7)	3.4 (3.4)	584 (527)	0.87(1)	2.43(2)	2 988m, 2 912m, 2 892mw, 1 428s, 1 316m br, 1 152m, 1 028m, 986s br, 762mw, 537mw
[{PdMe(SMe$_2$)I}$_2$]	Yellow	11.9 (11.6)	2.8 (2.9)	679 (621)	0.93(1)	2.39(2)	2 976mw br, 2 908mw br, 1 414m br, 1 320m, 1 302mw, 1 142m, 1 028m, 980m br, 753mw, 522w

[a] Calculated values are given in parentheses. [b] Osmometrically, 3 × 10^{-2} mol dm^{-3} at 37 °C. [c] The complexes slowly decompose in chloroform. [d] Shifts are in p.p.m. from SiMe$_4$ for spectra of complexes in CDCl$_3$; given as chemical shift (relative intensity); all resonances are sharp singlets; unaltered at −60 °C. [e] Nujol and hexachlorobutadiene mulls between KBr plates, 4 000—500 cm^{-1}.

Table 2. I.r. spectra (500—100 cm^{-1}) of [{PdX(SMe$_2$)(μ-X)}$_2$][a] and [{PdMe(SMe$_2$)X}$_2$][b]

	[{PdCl(SMe$_2$)(μ-Cl)}$_2$]	[{PdMe(SMe$_2$)(μ-Cl)}$_2$]	[{PdBr(SMe$_2$)(μ-Br)}$_2$]	[{PdMe(SMe$_2$)Br}$_2$][c]	[{PdMe(SMe$_2$)I}$_2$][d]
Pd–S str. (terminal)	340ms	319w	336s	319w	309w
Pd–X str. (terminal)	360s		274s		
Pd–X str. (bridging)	308ms[e]	275vs	223s[e]	175vs	150vs[h]
Pd–X str. (bridging)	282s[f]	244s, br[g]	195ms[f]	157m	
SC$_2$ def.		~285w (sh)	295ms	288mw	280mw
CSPd def.	209m, br	211vs[i]	185 (sh)	195m	188w, br
Skeletal and lattice modes	151 (sh) 148ms 132wm	154vw 141vw 105vw	124 (sh) 119m 109vw (sh)	134w 119vw 105w	126w 111w

[a] From ref. 2, as mulls in mixtures of Nujol and vaseline. [b] This work, as powdered polyethylene discs. [c] Very weak, broad absorptions at ~273, ~252, and ~224 cm^{-1}. [d] Weak, very broad absorption at 270—240 cm^{-1}. [e] *trans* to S. [f] *trans* to X. [g] Shoulder at ~235 cm^{-1}. [h] Unsymmetrical, broader base at low frequency. [i] Shoulder at 193w cm^{-1}.

observed for the carbon atom C(1) (Table 3, Figure 1). The palladium atoms have square-planar geometry with angles at palladium in the range 87.42(4)—93.6(1)°. The Pd$_2$Cl$_2$ group is almost symmetrical, with Pd–Cl distances differing by 0.14 Å.

Far-i.r. Spectra of the Complexes.—Far-i.r. spectra (500—100 cm^{-1}) of the complexes are shown in Figure 2, and presented together with reported spectra and assignments for the closely related inorganic complexes [{PdX(SMe$_2$)(μ-X)}$_2$] (X = Cl or Br) in Table 2. Spectra are readily assigned by comparison with assignments of Goggin *et al.*[2] for the inorganic complexes, assuming that the bromo- and iodo-complexes have bridging halogeno-groups as found for the chloro-complex [{PdMe(SMe$_2$)(μ-Cl)}$_2$]. Thus, [{PdMe(SMe$_2$)(μ-Cl)}$_2$] has only one absorption above 300 cm^{-1}, at 319 cm^{-1}, assigned as ν(Pd–S)$_{\text{terminal}}$ by comparison with [{PdCl(SMe$_2$)(μ-Cl)}$_2$] which has ν(Pd–S)$_{\text{terminal}}$ at 340 cm^{-1}. Similarly, the bromo- and iodo-derivatives exhibit only one absorption above 300 cm^{-1}, at similar values, 319 and 309 cm^{-1} respectively, and are thus readily assigned as ν(Pd–S)$_{\text{terminal}}$ for halogeno-bridged structures.

In comparing spectra of [{PdMe(SMe$_2$)X}$_2$] the most striking feature is a shift to lower frequency for the major absorption in the region 290—240 cm^{-1} for the chloro-derivative, to 180—150 cm^{-1} (X = Br) and 150 cm^{-1} (X = I). The absorptions are readily assigned as ν(Pd–X)$_{\text{bridging}}$, with the chloro- and bromo-derivatives giving absorptions at similar frequencies to ν(Pd–X)$_{\text{bridging}}$ for [{PdX(SMe$_2$)(μ-X)}$_2$]. The ratios ν(Pd–X)/ν(Pd–Cl) ~0.64 (X = Br) and ~0.57 (X = I) are

Table 3. Non-hydrogen atom molecular geometry for *trans*-$[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$; distances in Å, angles in °; primed atoms are generated by the inversion centre at the centre of the dimer*

Pd–C(1)	2.016(4)	Pd–S	2.265(1)
Pd–Cl	2.358(1)	S–C(2)	1.792(4)
Pd–Cl′	2.498(1)	S–C(3)	1.799(4)
C(1)–Pd–Cl	90.9(1)	Pd–Cl–Pd′	92.58(4)
C(1)–Pd–Cl′	177.3(1)	C(2)–S–Pd	104.5(2)
C(1)–Pd–S	93.6(1)	C(3)–S–Pd	116.2(2)
Cl–Pd–Cl′	87.42(4)	C(2)–S–C(3)	99.3(2)
Cl–Pd–S	175.20(3)		
Cl′–Pd–S	88.16(4)		

* Atom deviations from the mean plane defined by $PdCl_2SC(1)$ are Pd, 0.004; Cl, −0.033; Cl′, 0.005; S, −0.035; C(1), 0.077; C(2), 1.658; C(3), −0.240 Å; the plane is given by $0.6179X - 0.4979Y + 0.3738Z = 0.014$ (standard significance index for coplanarity $\chi^2 = 2\,649$) and the right-hand orthogonal Å frame (X,Y,Z) has X parallel to a, Z in the ac plane.

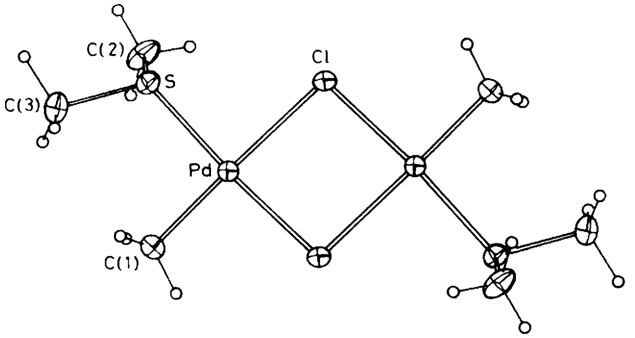


Figure 1. Structure of *trans*-$[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$ projected normal to the $PdCl_2Pd$ plane; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms are shown with an arbitrary radius of 0.1 Å

as expected,[8] *e.g.* ~0.7 for $[\{PdBr(SMe_2)(\mu\text{-}Br)\}_2]$ and ~0.6 for $\nu(Pd\text{–}I)_{terminal}$ in *trans*-$[PdI_2(SMe_2)_2]$.[2]

Experimental

Microanalyses were by the Australian Microanalytical Service, far-i.r. spectra (500—100 cm^{-1}) were recorded with a Digilab FTS.20E Fourier-transform i.r. spectrometer, ^1H n.m.r. spectra in $CDCl_3$ were measured with a JEOL JNM-4H-100 spectrometer, and molecular weights were determined in chloroform at 37 °C with a Knauer vapour pressure osmometer.

Diethyl ether was dried over 4A molecular sieves, followed by reflux and distillation from sodium–benzophenone and storage over sodium. *trans*-$[Pd(SMe_2)_2Cl_2]$ was prepared from *trans*-bis(benzonitrile)dichloropalladium(II) and dimethyl sulphide in benzene followed by recrystallization from hot ethanol; the dibromo-analogue was obtained on reaction of *trans*-$[Pd(SMe_2)_2Cl_2]$ with KBr in acetone–water, and both complexes have far-i.r. spectra in agreement with those reported.[2] Methyl-lithium [diethyl ether solution, containing 0.4% LiCl (Ega) and diethyl ether solution, as complex with LiBr (Aldrich)] was standardized using 1,3-diphenyl-2-propanone tosylhydrazone[9] immediately prior to use in synthesis.

$[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$.—Methyl-lithium (0.4% LiCl solution, 1.85 cm^3, 2.3 mmol) was added to a suspension of *trans*-$[Pd(SMe_2)_2Cl_2]$ (0.674 g, 2.2 mmol) in diethyl ether (70 cm^3) at −70 °C under nitrogen. The suspension was stirred for 1 h at −60 °C giving a colourless solution with some unreacted *trans*-$[Pd(SMe_2)_2Cl_2]$, followed by gradual warming of the solution to −15 °C giving an orange solution with little unreacted reagent. After hydrolysis (2 cm^3) and filtration at −15 °C, subsequent evaporation of solvent in a vacuum at 0 °C gave a black solid. Extraction of the solid with dry acetone (4 × 5 cm^3), followed by addition of hexane (20 cm^3), and slow evaporation at 0 °C gave the product (0.22 g, 45%), m.p. 87 °C (decomp.). Recrystallization was not necessary, but may be achieved using acetone–light petroleum or acetone–water.

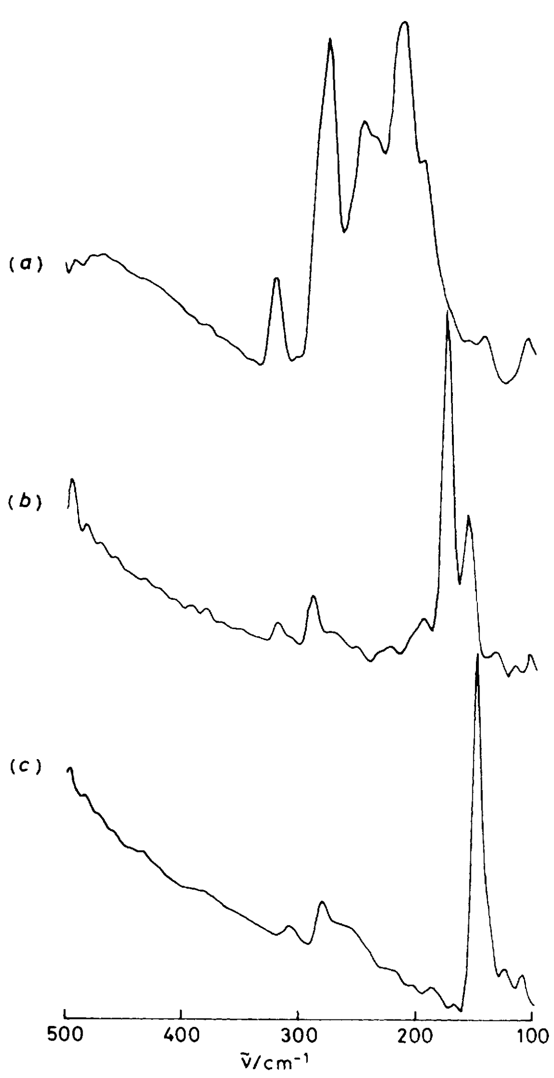


Figure 2. Far-i.r. spectra of $[\{PdMe(SMe_2)X\}_2]$: X = Cl (*a*), Br (*b*), or I (*c*)

$[\{PdMe(SMe_2)Br\}_2]$.—A similar procedure, using *trans*-$[Pd(SMe_2)_2Br_2]$, gave the product in 70% yield, m.p. 104—105 °C (decomp.). Recrystallization was not necessary, but may be achieved using acetone–light petroleum. Alternatively, the bromo-complex may be prepared in a similar manner from *trans*-$[Pd(SMe_2)_2Cl_2]$ and methyl-lithium–lithium bromide.

$[\{PdMe(SMe_2)I\}_2]$.—To a suspension of lithium chips (0.118 g, 17 mmol) in diethyl ether (40 cm^3) under nitrogen was added iodomethane (0.1 cm^3), followed by dropwise addition of iodomethane (0.55 cm^3, 8.5 mmol) in diethyl ether (30 cm^3) over 30 min. The suspension was stirred until the lithium had been consumed or reaction had ceased, followed by standardization.[9] Yields of methyl-lithium were commonly in the range 40–50%, and solutions were used immediately.

A similar procedure to that for the bromide gave an orange solution after hydrolysis (2 cm^3). After filtration, water (30 cm^3) was added and diethyl ether removed in a vacuum at 0 °C to give the product (85%), m.p. 120 °C (decomp.), which did not require recrystallization.

Synthesis of [{PdMe(SMe$_2$)X}$_2$] *using Halide-free Methyllithium and Halogenomethane* (X = Br *or* I).—X = I. Methyllithium (0.4% LiCl solution, 3.5 cm^3, 2.9 mmol) was added to a suspension of *trans*-[Pd(SMe$_2$)$_2$Cl$_2$] (0.417 g, 1.4 mmol) in diethyl ether (70 cm^3) at −70 °C under nitrogen. The suspension was stirred for 1 h at −60 °C giving a colourless solution, followed by warming to *ca.* −40 °C, addition of iodomethane (0.5 cm^3, 8 mmol), and gradual warming to −15 °C to give a yellow solution. Hydrolysis, followed by filtration and evaporation of diethyl ether at 0 °C gave the product (0.392 g, 91%).

X = Br. A similar procedure, involving warming to *ca.* 10 °C after addition of bromomethane, gave a black solution. Hydrolysis, followed by filtration gave a yellow solution that gave the product on evaporation of diethyl ether (41%).

Synthesis of [{PdMe(SMe$_2$)X}$_2$] (X = Br *or* I) *from* [{PdMe(SMe$_2$)(μ-Cl)}$_2$] *and* KX.—On suspension of the chloro-complex in diethyl ether at −60 °C, KX (X = Br or I) was added and the resulting suspension allowed to warm slowly to *ca.* −10 °C. Water was added, and the diethyl ether slowly evaporated to yield the products (isolated by filtration).

Crystallography.—Crystals of *trans*-[{PdMe(SMe$_2$)(μ-Cl)}$_2$] were obtained by vapour-phase diffusion of diethyl ether into an acetone solution of the complex at −20 °C.

Crystal data. (C$_3$H$_9$ClPdS)$_2$, M = 438.0, monoclinic, space group $P2_1/n$ (variant of C^5_{2h}, no. 14), a = 10.792(4), b = 7.373(2), c = 9.131(5) Å, β = 109.03(3)°, U = 686.9(5) Å^3, D_c (Z = 2 dimers) = 2.12 g cm^{-3}, $F(000)$ = 424, monochromatic Mo-K_α radiation, λ = 0.710 69 Å, μ = 32 cm^{-1}. Specimen: 0.25 × 0.25 × 0.25 mm, transmission = 0.48 (min.), 0.53 (max.), $T \sim$ 295 K.

Structure determination. A unique data set was measured to $2\theta_{max.}$ = 65° using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ—θ scan mode, yielding 2 441 independent reflections, 1 914 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after analytical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; for the hydrogen atoms the corresponding isotropic form was constrained at an estimated value for each atom. At convergence, R and R' (statistical weights) quoted on $|F|$, were 0.025, 0.023. Neutral complex scattering factors were used.[10] Computation used the XTAL 83 program system[11] implemented by S. R. Hall on a Perkin-Elmer 3240 computer.

Table 4. Atom co-ordinates for *trans*-[{PdMe(SMe$_2$)(μ-Cl)}$_2$]

Atom	*x*	*y*	*z*
Pd	0.094 24(2)	0.199 21(3)	0.035 40(2)
S	0.221 33(8)	0.320 16(10)	−0.094 10(8)
Cl	−0.047 27(8)	0.059 74(11)	0.151 09(8)
C(1)	0.134 1(4)	0.399 6(6)	0.194 2(4)
H(1A)	0.124(3)	0.506(5)	0.143(4)
H(1B)	0.222(4)	0.401(6)	0.238(4)
H(1C)	0.087(3)	0.376(6)	0.268(4)
C(2)	0.371 4(4)	0.194 5(6)	−0.026 6(6)
H(2A)	0.360(4)	0.063(6)	−0.029(5)
H(2B)	0.414(3)	0.198(5)	0.094(4)
H(2C)	0.420(4)	0.223(5)	−0.095(4)
C(3)	0.284 1(4)	0.544 2(5)	−0.035 9(5)
H(3A)	0.340(3)	0.538(5)	0.081(4)
H(3B)	0.223(4)	0.607(6)	−0.045(5)
H(3C)	0.352(4)	0.575(7)	−0.107(6)

Atom co-ordinates are given in Table 4.

Acknowledgements

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