Comparison of the Dimensions and Conformation of the Sulfaguanidine Moiety in Sulfaguanidine Monohydrate and *trans*-Dichlorobis(sulfaguanidine)palladium(II)

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The crystal structures of sulfaguanidine monohydrate [SG.H$_2$O; C$_7$H$_{10}$N$_4$SO$_2$.H$_2$O; monoclinic, $a=$ 7·515 (1), $b=5·554$ (1), $c=24·592$ (5) Å, $\beta=90·47$ (3)°, $P2_1/c$, $Z=4$] and *trans*-dichlorobis(sulfagua-nidine)palladium(II) [Pd(SG)$_2$Cl$_2$; PdCl$_2$(C$_7$H$_{10}$N$_4$SO$_2$)$_2$; monoclinic, $a=11·590$ (10), $b=10·476$ (1), $c=8·783$ (2) Å, $\beta=100·8$ (1)°, $P2_1/n$, $Z=2$] have been solved by standard methods and refined by full-matrix least squares (based on F^2) to R values of 0·069 and 0·047 respectively (goodness-of-fit 4·52 and 1·20 respectively). The H$_2$N–C (ring) distances are 1·383 Å in SG.H$_2$O and 1·442 Å in Pd(SG)$_2$Cl$_2$, showing that bonding of N to Pd reduces the double-bond character of the N–C bond in the coordination complex. Both moieties have six-membered rings formed by intramolecular hydrogen bonding of one of the sulfone O atoms to one of the amino N atoms of the guanidine group. This bonding is stronger in Pd(SG)$_2$Cl$_2$ than in SG.H$_2$O. The guanidine groups in both moieties are in the amino form, with considerable electron delocalization. There are conformational differences between the two sulfaguanidine moieties, consequent on different amounts of rotation about the C(ring)–S bonds. In SG.H$_2$O there is extensive intermolecular hydrogen bonding involving the guanidine group and the water molecule, but the arylamino group is not involved in hydrogen bonding. In Pd(SG)$_2$Cl$_2$ there is a fairly isotropic arrangement of intermolecular NH$\cdots$Cl, NH$\cdots$O and NH$\cdots$N hydrogen bonds. The sulfone and guanidine groups in these two molecules have dimensions very similar to those found in other molecules. Pd–Cl bond lengths for a number of molecules show a clear dependence of distance on the nature of the group *trans* to Cl, but no such dependence has been found for the Pd–N bond distances.

1. Introduction

The influence of environment on molecular shape and dimensions can be investigated by studying a particular molecule in different phases or by studying a particular moiety in different chemical (and therefore also different crystallographic) environments. We have chosen the second of these routes using sulfaguanidine as the moiety to be studied, firstly as sulfaguanidine monohydrate and secondly in the *trans*-dichlorobis-(sulfaguanidine)palladium(II) coordination complex. The sulfaguanidine moiety in the two environments can

have its guanidine group in the amino (I) or imino (II) form, the effects of metal complexation may be discernible and there may be conformational differences due to different amounts of rotation about formally single bonds. Our results show that the amino form occurs in both environments, that complexation to Pd has an appreciable effect on the bonding at the N atom of the arylamino group, and that there are conformational differences due to different amounts of rotation about the C(ring)–S bonds. Brief accounts of various parts of this research have appeared (Alléaume & Marsh, 1968; Gulko, Herbstein, Kapon & Schmuckler, 1971; Herbstein, Gulko, Kapon, Alléaume & Marsh, 1973).
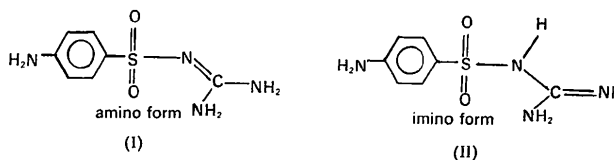
2. Sulfaguanidine monohydrate (SG.H₂O)

2.1. Structure determination and refinement

Crystals were grown from methanol. Standard methods were used for data collection and refinement of the structure [see *e.g.* Sherfinski & Marsh (1973)]; the structure was solved by Patterson methods. Pertinent details are summarized in Tables 1 and 2. Final atomic parameters are given in Table 3; observed and calculated structure factors are in Table 4.*

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* Tables 4, 7, 10 and 13, and Figs. 9 and 10 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31261 (30 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester, CH1 1NZ, England.

2.2. Crystal structure

A projection down the [010] direction is shown in Fig. 1. The principal intermolecular bonding is due to a network of hydrogen bonds in and across the (001)

Table 1. *Crystallographic results and other data for sulfaguanidine monohydrate* (SG.H₂O)

Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digits.

$a = 7.515$ (1) Å	$C_7H_{10}N_4O_2S.H_2O$
$b = 5.554$ (1)	F.W. 232.27
$c = 24.592$ (5)	Space group $P2_1/c$
$\beta = 90.47$ (3)°	$Z = 4$
$V = 1026.4$ Å³	$F(000) = 488$
$\lambda(\text{Cu } K\alpha) = 1.5418$ Å	$D_m = 1.50$ g cm⁻³
	$D_x = 1.502$
	$\mu(\text{Cu } K\alpha) = 27.3$ cm⁻¹

Table 2. *Pertinent information about data collection, and structure refinement for both substances*

	Item	SG.H₂O	Pd(SG)₂Cl₂
1.	Crystal size and shape	Cube approximately 0.1 mm on edge	Plate 0.29 × 0.22 × 0.04 mm, mounted about [100] direction
2.	X-radiation for intensity measurements	Cu $K\alpha$ (Ni-filtered)	Mo $K\alpha$ (graphite monochromator)
3.	Scan method	θ–2θ, 2° 2θ min⁻¹, 30s background at scan extremities	θ–2θ, 1° 2θ min⁻¹, 30s background at scan extremities
4.	Number of reflections measured	2203 ($2\theta < 155°$)	3055 ($2\theta < 60°$)
5.	Number of reflections used in last refinement stage	2122 (all $F_o > 0$)	3010 (45 unreliable reflections given zero weight)
6.	Standard reflections	408, measured every 20 reflections	11̄2, 121, 130, 14̄1, 222 measured in sequence at intervals of 20 reflections
7.	Behaviour of standard reflections	No significant variation	No significant variation
8.	Absorption corrections	Not applied ($\mu R \sim 0.17$)	Transmission factors range from 0.78–0.95
9.	Refinement	Full matrix on F^2	
10.	Atomic scattering factors	C, N, O, S (*International Tables for X-ray Crystallography*, 1962). H (Stewart, Davidson & Simpson, 1965).	Pd (Cromer & Waber, 1955), corrected for anomalous dispersion (real part) (*International Tables for X-ray Crystallography*, 1962)
11.	Extinction correction (Zachariasen, 1963; Larson, 1968, equation 3)	Applied $[g = 5.8 \text{ (4)} \times 10^{-6} \text{ e}^{-2}]$	Not required
12.	R	0.06	0.049
13.	Goodness-of-fit	4.52	1.20
14.	Estimated standard deviations σ(C–C), σ(C–N)	0.005–0.009 Å	0.007 Å
	σ(C–H), σ(N–H)*	0.03–0.05	0.03–0.05
	σ(S–X)	0.003	0.003
	σ(Pd–Cl)	–	0.002
	σ(Pd–N)	–	0.003
	σ(C–C–C)	0.2°	0.2°
	σ(C–C–H)*	1.7	1.7
	σ(X–S–Y)	0.1	0.1
	σ(C–N–H)*	1.9	1.9
	σ(H–N–H)* guanidine	2.5	2.5
	amino	4.2	2.5

* random errors only, see §4.

plane, linking water molecules, guanidine groups and sulfone groups (Fig. 2). The 'aniline' portions of the molecules protrude perpendicularly from the hydrogen-bond network and are interleaved, with opposite orientations so that dipole–dipole interactions contri-

bute to the cohesion in these regions of the crystal. The large temperature factors of the atoms of the aryl-amine group show that this bonding is rather weak and thus the crystals would be expected to cleave along the (001) planes. A generally similar arrangement of
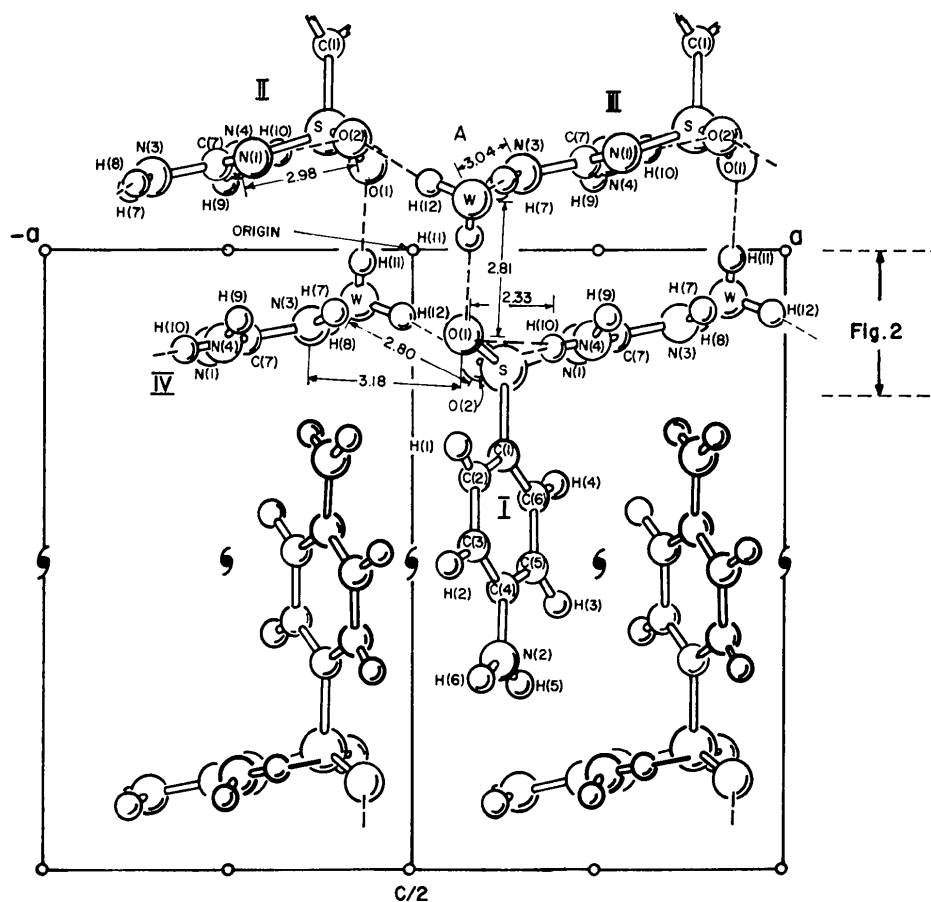

Fig. 1. SG.H_2O in projection down [010]; the slice of the structure shown in Fig. 2 lies between the dashed lines.

Table 3. SG.H_2O – *fractional coordinates and anisotropic temperature factors for the non-hydrogen atoms* ($\times 10^4$); *fractional coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å^2) *for the hydrogen atoms*

The atoms listed belong to SG molecule I and water molecule A in Fig. 1; for numbering of atoms see Fig. 7. Estimated standard deviations are in parentheses. Anisotropic temperature factors have the form exp $\{-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2klb^*c^*U_{23})\}$. Isotropic temperature factors have the form exp $\{-8\pi^2U_{iso}\sin^2\theta/\lambda^2\}$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2406 (3)	857 (4)	1654 (1)	296 (11)	315 (13)	357 (12)	−15 (10)	21 (9)	10 (10)
C(2)	1615 (3)	2942 (5)	1847 (1)	464 (14)	359 (16)	437 (15)	27 (13)	38 (12)	11 (13)
C(3)	1618 (4)	3419 (6)	2396 (1)	534 (17)	452 (19)	497 (16)	28 (15)	72 (13)	−110 (14)
C(4)	2392 (3)	1862 (6)	2764 (1)	421 (14)	691 (22)	398 (14)	−86 (15)	13 (11)	−60 (15)
C(5)	3225 (4)	−214 (7)	2569 (1)	457 (15)	665 (21)	433 (14)	70 (17)	−45 (11)	111 (17)
C(6)	3225 (4)	−699 (5)	2022 (1)	438 (14)	433 (18)	466 (15)	88 (13)	−39 (11)	17 (13)
C(7)	5394 (3)	2089 (5)	701 (1)	318 (11)	372 (15)	352 (12)	−29 (11)	23 (10)	−1 (12)
N(1)	4423 (2)	72 (4)	768 (1)	291 (9)	293 (11)	442 (11)	−33 (10)	57 (8)	−15 (11)
N(2)	2332 (5)	2294 (9)	3317 (1)	764 (22)	1161 (35)	434 (15)	68 (24)	0 (15)	−154 (21)
N(3)	7121 (3)	1761 (5)	615 (1)	333 (12)	384 (15)	708 (17)	−66 (11)	151 (11)	6 (13)
N(4)	4791 (3)	4344 (4)	734 (1)	392 (12)	268 (13)	699 (16)	−35 (10)	75 (12)	9 (11)
O(1)	1349 (2)	2012 (3)	689 (1)	355 (9)	421 (11)	388 (8)	35 (8)	−58 (7)	77 (9)
O(2)	1756 (2)	−2291 (3)	899 (1)	353 (8)	275 (10)	544 (10)	−107 (8)	−22 (8)	55 (9)
O(3) (W)	1536 (2)	3327 (4)	−413 (1)	378 (10)	485 (13)	414 (11)	−74 (9)	−13 (9)	37 (10)
S	2414 (1)	170 (1)	958 (0)	250 (2)	253 (3)	327 (3)	−30 (3)	−11 (2)	5 (3)

Table 3 (cont.)

	x	y	z	U_{iso}
H(1)	1120 (32)	3903 (47)	1594 (10)	0·053 (9)
H(2)	1009 (36)	4795 (55)	2517 (11)	0·070 (10)
H(3)	3838 (37)	−1301 (54)	2852 (12)	0·078 (10)
H(4)	3768 (35)	−2079 (55)	1891 (11)	0·069 (10)
H(5)	2987 (54)	1394 (84)	3469 (17)	0·130 (21)
H(6)	1799 (59)	3659 (82)	3395 (18)	0·136 (21)
H(7)	7721 (35)	3000 (55)	522 (11)	0·062 (10)
H(8)	7555 (39)	92 (59)	561 (12)	0·081 (11)
H(9)	5581 (37)	5594 (53)	623 (11)	0·072 (10)
H(10)	3677 (35)	4766 (49)	776 (10)	0·054 (8)
H(11)	1485 (35)	3006 (52)	−88 (10)	0·055 (10)
H(12)	501 (38)	3029 (54)	−584 (11)	0·070 (10)

alternating polar and non-polar sheets of material has been found in the crystals of S-benzylisothiouronium hexachloroplatinate(IV) and tetrachloroaurate(III) (Pope & Boeyens, 1974).

Each water molecule (W) makes hydrogen bonds to three different SG molecules; in two of these [W–H(11) $\cdots$O(1)^I; W–H(12) $\cdots$O(2)^{II}] the water molecule is a hydrogen-bond donor, while in the third [N(3)–H(7)$^{III}\cdots W$] it acts as an acceptor. The first two bonds are of medium strength [d(O$\cdots$O)=2·81, 2·80 Å respectively] while the third is rather weaker [d(N$\cdots$O)=3·04 Å]. There is one hydrogen bond of type W–H(11)$\cdots$O(1)^I per SG molecule and these bonds provide the only hydrogen bonding in the [001] direction. The hydrogen bonding in the (001) plane is due to bonds of W–H(12)$\cdots$O(2) type, roughly along

[100], N(3)–H(7)$^{III}\cdots W$ type, roughly along [010], and N(4)–H(10)$\cdots$O(2) type [for the latter d(N$\cdots$O)= 2·98 Å], roughly along [1$\bar{1}$0]. H(10) also participates in an intramolecular hydrogen bond N(4)–H(10)$\cdots$O(1) [d(N$\cdots$O)=2·90 Å]. There are also two longer contacts which are presumably van der Waals interactions: N(3)–H(7)$^{IV}\cdots$O(1)^I, d(N$\cdots$O)=3·18 Å, roughly along [100] and N(4)–H(9)$\cdots$N(1), d(N$\cdots$N)=3·19 Å, roughly along [010]. Thus only four of the eight potential donor hydrogen atoms participate in hydrogen bonding – the two hydrogens of the water molecule and one each of the hydrogens of the two guanidine amino groups.

The molecular structure will be discussed below, together with that of Pd(SG)$_2$Cl$_2$.

3. *trans*-Dichlorobis(sulfaguanidine)palladium(II) (Pd(SG)$_2$Cl$_2$)

3.1. *Structure determination and refinement*

Preparation of the crystals of Pd(SG)$_2$Cl$_2$ and related compounds is described in the Appendix. The crystals of Pd(SG)$_2$Cl$_2$ are light yellow parallelepipedal plates with the [100] and [010] directions as long and short diagonals of the principal face (001). The crystal structure was first solved in Haifa by standard Patterson and Fourier methods and then refined further on the basis of new intensity measurements made at Caltech, using the methods described above for SG.H$_2$O (see also Table 2). Crystal data are given in Table 5, final
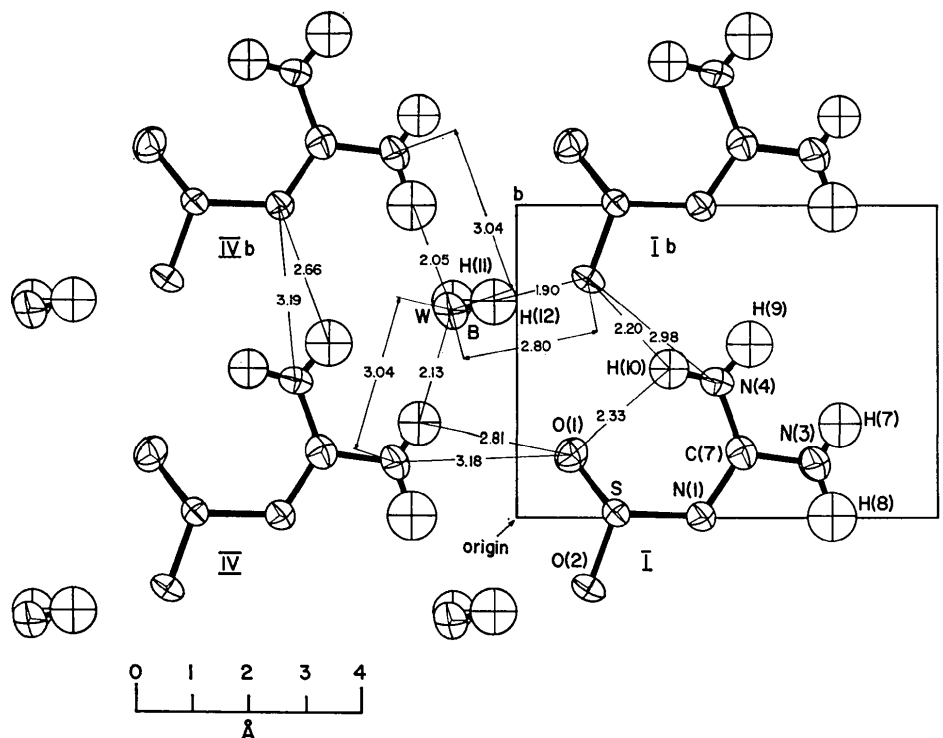

Fig. 2. SG.H$_2$O – the arrangement of the hydrogen bonds in and about the (001) plane.

atomic parameters in Table 6 and observed and calculated structure factors in Table 7.*

3.2. Crystal structure

The crystals are composed of centrosymmetric Pd(SG)$_2$Cl$_2$ molecules packed in criss-cross fashion (Figs. 3 and 4). The sulfaguanidine moiety acts as a monodentate ligand covalently bonded to Pd through its aryl N atom, thus resembling the molecular crystals of *trans*-dichlorobis(nitrosobenzene)palladium(II) (Little & Doedens, 1973) and *trans*-dichlorobis(diamino-maleonitrile)palladium(II) (Miles, Hursthouse & Robinson, 1971); these three complexes have similar arrangements of N and Cl atoms around the central Pd atom. Not all PdCl$_2$ complexes are molecular; for

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* See footnote on p. 670.

example the crystals of bis(ethylenediamine)palladium dichloride contain ionic [Pd(en)$_2$]$^{2+}$ and Cl$^-$ units (Wiesner & Lingafelter, 1966).

The stereoview (Johnson, 1965) along [010] (Fig. 3) shows that the molecules, which are themselves far

Table 5. *Crystallographic results and other data for* trans-dichlorobis(sulfaguanidine)palladium(II) [Pd(SG)$_2$Cl$_2$]

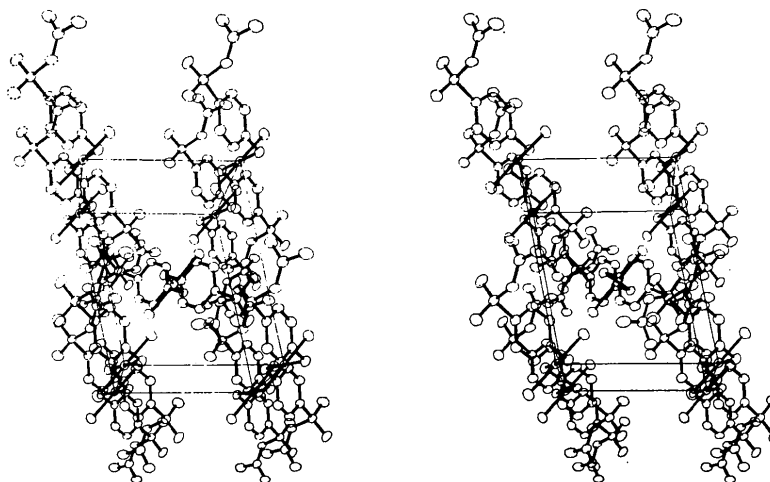|	
$a = 11\cdot590$ (10) Å	$PdCl_2.(C_7H_{10}N_4O_2S)_2$
$b = 10\cdot476$ (1)	F.W. 605·8
$c = 8\cdot783$ (2)	Space group $P2_1/n$
$\beta = 100\cdot8$ (1)°	$Z = 2$
$V = 1047\cdot5$ Å^3	$F(000) = 608$
λ(Cu $K\alpha_1) = 1\cdot54050$ Å	$D_m = 1\cdot877$ g cm^{-3}
λ(Cu $K\alpha_2) = 1\cdot54434$	$D_x = 1\cdot921$
	μ(Mo $K\alpha) = 13\cdot61$ cm^{-1}

Fig. 3. *ORTEP* stereo view of Pd(SG)$_2$Cl$_2$ structure. The origin is at the lower left-hand corner of the unit cell, c runs to the right and the b axis comes up towards the observer. The arrangement of the non-planar molecules in and about the (101) planes can be seen.

Table 6. Pd(SG)$_2$Cl$_2$ - *fractional coordinates and anisotropic temperature factors for the non-hydrogen atoms* ($\times 10^4$); *coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å^2) *for the hydrogen atoms*

The numbering of the atoms is shown in Fig. 6. Estimated standard deviations are in parentheses. Anisotropic temperature factors have the form exp $\{-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2klb^*c^*U_{23})\}$. Isotropic temperature factors have the form exp $\{-8\pi^2 U_{Iso}\sin^2\theta/\lambda^2\}$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	0	0	0	293 (2)	186 (1)	263 (1)	10 (1)	88 (1)	31 (1)
Cl	1505 (1)	−389 (1)	2060 (1)	412 (4)	357 (4)	341 (4)	66 (3)	−8 (3)	32 (3)
C(1)	1290 (2)	4606 (3)	−1722 (3)	299 (14)	196 (12)	293 (13)	−5 (10)	75 (11)	−17 (10)
C(2)	2031 (2)	3864 (3)	−642 (3)	244 (14)	334 (15)	364 (15)	−31 (12)	41 (12)	13 (12)
C(3)	1568 (3)	2951 (3)	187 (3)	315 (15)	272 (14)	321 (15)	33 (12)	4 (12)	44 (11)
C(4)	377 (2)	2768 (2)	−45 (3)	342 (15)	176 (12)	267 (13)	−4 (10)	17 (12)	−32 (10)
C(5)	−376 (3)	3485 (3)	−1131 (3)	267 (14)	255 (14)	404 (16)	−4 (11)	77 (12)	23 (12)
C(6)	96 (3)	4410 (3)	−1970 (3)	311 (15)	249 (14)	372 (15)	33 (12)	36 (12)	77 (12)
C(7)	3398 (3)	7132 (3)	−718 (3)	340 (15)	207 (13)	355 (15)	−16 (12)	101 (12)	29 (11)
N(1)	2300 (2)	6885 (2)	−1399 (3)	260 (12)	236 (12)	417 (13)	−24 (10)	93 (10)	−45 (10)
N(2)	−91 (2)	1817 (2)	852 (3)	342 (13)	228 (11)	298 (12)	47 (10)	111 (10)	18 (9)
N(3)	3542 (2)	8002 (3)	428 (4)	344 (15)	409 (16)	590 (18)	−10 (12)	39 (13)	−150 (14)
N(4)	4360 (2)	6595 (3)	−998 (3)	288 (14)	545 (14)	508 (17)	21 (12)	30 (12)	−146 (14)
O(1)	2909 (2)	5361 (2)	−3247 (3)	452 (12)	376 (14)	441 (12)	−65 (9)	244 (10)	−93 (9)
O(2)	1004 (2)	6349 (2)	−3839 (2)	408 (13)	451 (13)	441 (12)	−97 (10)	−24 (10)	168 (10)
S	1927 (1)	5815 (1)	−2689 (1)	302 (4)	244 (3)	303 (4)	−38 (3)	90 (3)	6 (3)

Table 6 (cont.)

	x	y	z	U_{Iso}
H(1)	2844 (23)	3943 (26)	526 (29)	0·043 (8)
H(2)	1994 (24)	2437 (28)	839 (31)	0·043 (8)
H(3)	−1150 (26)	3357 (28)	−1331 (31)	0·053 (8)
H(4)	−368 (22)	4833 (24)	−2642 (28)	0·036 (7)
H(5)	−772 (21)	2032 (24)	932 (27)	0·035 (6)
H(6)	311 (25)	1777 (27)	1708 (31)	0·054 (8)
H(7)	4138 (31)	8163 (34)	735 (38)	0·065 (10)
H(8)	3020 (30)	8399 (31)	507 (36)	0·082 (10)
H(9)	4864 (24)	6774 (27)	−549 (30)	0·052 (9)
H(10)	4270 (23)	6103 (26)	−1687 (30)	0·042 (8)

from planar (see below), are located in slices of the crystal parallel to (101) planes. There are N–H···Cl and NH···N bonds between molecules in the same (101) plane and also a Pd···O contact of 3·12 Å which is probably attractive. There is a N–H···O bond between molecules in adjacent (101) planes (Table 8 and Fig. 4). Because of systematic errors in the positions of the H atoms (§ 4), the geometries given for the hydrogen bonds are indicative only. There are appreciable deviations from a linear N–H···X arrangement, especially for N(4)–H(10)···Cl, where the H(10)···Cl

distance of 3·09 Å suggests that this is a van der Waals contact.

The molecular arrangement provides an explanation for the prominence of the (101) and (10$\bar{1}$) faces on the crystals.

4. Bond distances involving hydrogen

Hydrogen positions have been determined for both structures. Churchill (1973) has found that, for inorganic coordination complexes, C–H distances lie in the range 0·91–0·99 Å, with a mean of 0·95 Å, N–H distances in the range 0·82–0·95 Å, with a mean of 0·87 Å. Our values for SG.H$_2$O agree well with those of Churchill but those for Pd(SG)$_2$Cl$_2$ (C–H, range 0·85–0·93 Å, mean 0·89 Å; N–H range 0·67–0·84, mean 0·76 Å) are appreciably smaller. Thus the H positions given in Table 6 can differ from the nuclear positions by as much as 0·25 Å, which should be taken into account in considering all distances reported here that involve H atoms. We do not have an explanation for the systematic shortening of C–H and N–H bonds in Pd(SG)$_2$Cl$_2$.

Table 8. *The shorter intermolecular distances in* Pd(SG)$_2$Cl$_2$ *(only single examples of each set of symmetry-related distances are given)*

Atom in reference asymmetric unit*	Neighbor designation	Atom/group located in asymmetric unit at		Distances (Å) $D···A$	$D···H$	Angle (°) $D···H–A$	Notes
Pd	O(1)	$-\frac{1}{2}+x, \frac{1}{2}-y,$	$\frac{1}{2}+z$	3·117	–	–	1
Cl	H(8)—N(3)	$x, y-1,$	z	3·427	2·73	156	1
Cl	H(10)-N(4)	$\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$		3·503	3·09	116	1, 2
N(1)	H(5)—N(2)	$-x, 1-y, -z$		3·016	2·20	163	1
O(2)	H(7)—N(3)	$-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$		2·886	2·19	168	3

* Coordinates in Table 6.

Notes: (1) Between molecules in the same (101) plane. (2) Probably not a hydrogen bond. (3) Between molecules in adjacent (101) planes.

Table 9. *Deviations from planarity for various atoms in* Pd(SG)$_2$Cl$_2$ *and* SG.H$_2$O *(calculations are for the reference molecules whose coordinates are given in Tables 6 and 3 respectively)*

Asterisked atoms were not included in calculation of best plane.

Deviations (Å) from plane through phenyl ring			Deviations (Å) from plane through guanidine group			Deviations (Å) from plane through six-membered hydrogen-bonded ring		
	Pd(SG)$_2$Cl$_2$	SG.H$_2$O		Pd(SG)$_2$Cl$_2$	SG.H$_2$O		Pd(SG)$_2$Cl$_2$	SG.H$_2$O
C(1)	0·006	−0·010	N(1)	−0·004	0·005	O(1)	0·046	−0·216
C(2)	−0·003	0·005	C(7)	0·012	−0·014	S	−0·063	0·302
C(3)	−0·003	0·005	N(3)	−0·004	0·004	N(1)	0·034	−0·133
C(4)	0·006	−0·011	N(4)	−0·004	0·005	C(7)	0·017	−0·108
C(5)	−0·003	0·006	H(7)*	0·06	−0·131	N(4)	−0·034	0·154
C(6)	−0·003	0·004	H(8)*	0·13	−0·082	H(10)*	−0·004	0·274
H(1)*	−0·07	0·009	H(9)*	−0·03	−0·151	N(3)*	0·005	−0·313
H(2)*	−0·05	−0·040	H(10)*	0·03	−0·037	H(7)*	0·06	−0·424
H(3)*	−0·04	0·036				H(8)*	0·16	−0·584
H(4)*	−0·02	0·008				H(9)*	−0·07	0·004
N(2)*	0·024	−0·064				O(2)*	0·862	−0·063
H(5)*	0·39	0·076				R.m.s.	0·039	0·211
H(6)*	0·45	−0·053				deviation		
S*	0·085	−0·025				of non-		
O(1)*	−0·905	−0·144				starred		
O(2)*	−0·053	−1·116				atoms		
Plane No. I	Ia		II	IIa		IV	IVa	

Table 9 (cont.)

Equations of planes (X, Y, Z in Å; coefficients are direction cosines with respect to a,b,c of respective crystals).

Pd(SG)$_2$Cl$_2$

(I)	$-0.2092X + 0.6759Y + 0.7334Z = 1.833$ Å
(II)	$0.1938X + 0.7159Y - 0.6952Z = 6.539$ Å
(III)	(Pd and its first neighbors N(2), Cl)
	$0.7992X + 0.3106Y - 0.6807Z = 0$
(IV)	$0.1657X + 0.7211Y - 0.6919Z = 6.460$ Å

SG.H$_2$O

(Ia)	$0.8635X + 0.4959Y - 0.0984Z = 1.407$ Å
(IIa)	$0.1756X + 0.0138Y + 0.9829Z = 2.435$ Å
(IVa)	$0.0238X + 0.1527Y + 0.9878Z = 2.083$ Å

Angles between plane normals (°)

	Pd(SG)$_2$Cl$_2$				SG.H$_2$O		
	I	II	III	IV	Ia	IIa	IVa
I		91.8	109.7	91.3	Ia		86.1	89.7
II			42.4	1.7	IIa			11.8
III				44.0	IVa			
IV								

5. The molecular structures

5.1. Molecular conformations

The Pd(SG)$_2$Cl$_2$ molecule (Fig. 3) can be described in terms of a number of planar or nearly planar groups of atoms (Table 9; planes and interplanar angles calculated by the methods of Schomaker, Waser, Marsh & Bergman (1959) and Waser, Marsh & Cordes (1973)].
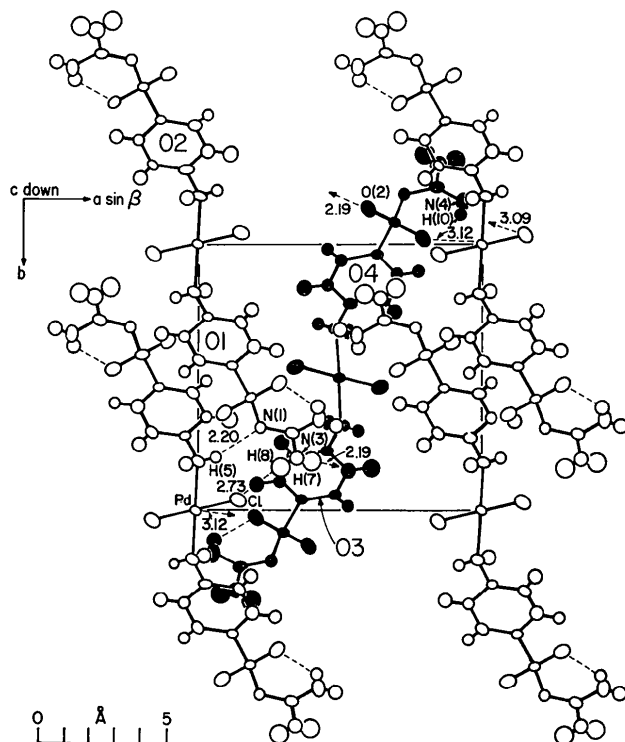

Fig. 4. Pd(SG)$_2$Cl$_2$ in projection down [001] [single examples of hydrogen bonds and other close intermolecular approaches (see Table 8) have been inserted. Arrows indicate that an atom involved in the bond actually belongs to a molecule not included in the diagram].

The phenyl ring is planar (plane I) and its two substituents in the para positions [N(2) and S] and O(2) are close to this plane. The atoms of the guanidine group [N(1), C(7), N(4), N(3) and H(9), H(10), H(7), H(8)] are nearly coplanar (plane II). The central PdN$_2$Cl$_2$ group of atoms is necessarily planar (plane III). The six-membered ring [S···N(1)] (IV) is also nearly planar, the deviations from planarity being small but significant. The sulfaguanidine moiety in SG.H$_2$O can be described in terms of similar planar or nearly planar portions of the molecule (Table 9).

The six-membered rings in Pd(SG)$_2$Cl$_2$ and SG.H$_2$O are differently oriented with respect to the phenyl rings and this constitutes the main conformational difference between the two moieties. In Pd(SG)$_2$Cl$_2$ atom O(2) lies close to the phenyl ring plane (deviation -0.054 Å) while O(1) is further away (-0.905 Å). The opposite situation occurs in SG.H$_2$O. The appropriate torsion angles (calculated from the coordinates of Tables 3 and 6) are:

	Pd(SG)$_2$Cl$_2$	SG.H$_2$O
C(6)–C(1)–S–O(2)	$-7.7°$	$51.6°$
C(2)–C(1)–S–O(1)	48.2	-5.1

The two moieties have been compared using Nyburg's (1974) molecular fit routine (Fig. 6).

An individual sulfaguanidine moiety will be chiral, the tetrahedral sulfur atom being bonded to four dissimilar groups [O(1) and O(2) are not equivalent in the crystal]. In SG.H$_2$O both enantiomorphs crystallize together in the centrosymmetrical crystals, while in Pd(SG)$_2$Cl$_2$ both enantiomorphs are found in the centrosymmetrical molecule.

5.2. Molecular dimensions

The shapes of the sulfaguanidine moieties in Pd(SG)$_2$Cl$_2$ and SG.H$_2$O have an overall similarity (compare Figs. 5 and 7) despite the considerable differences in the molecular arrangements in the respective crystals. However there are conformational differences (Fig. 6) and differences of detail in the arylamino groups and in the six-membered rings with intramolecular hydrogen bonds.

5.2.1. The arylamino group. In Pd(SG)$_2$Cl$_2$ a covalent bond is formed between Pd and N, giving an approximately tetrahedral arrangement of atoms about N with the Pd–N–C angle slightly enlarged at 113°. In SG.H$_2$O, on the other hand, the arrangement of atoms about the arylamino N is nearly planar, although the H–N–H bond angle appears to be appreciably larger than 120°. The arylamino C–N bond in Pd(SG)$_2$Cl$_2$ is significantly longer than the analogous bonds in SG.H$_2$O and similar compounds (1.442 Å as compared to 1.38 Å, see Table 12) and approaches the value of 1.49 Å found for the C–NH$_2$ single bond in cis-dichloro-(meso-2,3-diaminobutane)palladium(II) (Ito, Marumo & Saito, 1971). A similar lengthening of a C–NH$_2$ bond is found in trans-dichlorobis(diaminomaleonitrile)palladium(II) (Miles, Hursthouse &

Robinson, 1971) where the C–NH₂ bond in the coordination complex is 1·49 (3) Å compared to 1·393 (5) Å in diaminomaleonitrile itself (Penfold & Lipscomb, 1961). An unexpected feature of this latter complex is a Pd–NH₂–C angle of 121 (2)°, which appears to be significantly larger than our value of 113°. However, this latter structure was based on visually estimated intensities and the H atoms were ignored, so the e.s.d.'s may be somewhat optimistic.

Weakening of the arylamino N–H bonds on complex formation is shown by the infrared spectra (Gulko, Rittner, Ron, Weissman & Schmuckler, 1971) where the symmetric N–H stretching frequency falls from 3385 cm⁻¹ in sulfaguanidine to 3120 cm⁻¹ in Pd(SG)₂Cl₂. Our present measurements of N–H bond lengths are not accurate enough to permit a check of this interpretation of the infrared spectra.

5.2.2. The intramolecular hydrogen-bonded six-membered ring.

A second major difference between the sulfaguanidine moieties in Pd(SG)₂Cl₂ and SG.H₂O lies in the detailed structures of the intramolecular hydrogen-bonded six-membered rings. The deviations from planarity in this ring are much greater in SG.H₂O than in Pd(SG)₂Cl₂ (Table 9). H(10) participates only in the intramolecular hydrogen bond in Pd(SG)₂Cl₂ {d[N(4)···O(1)] = 2·735 Å, d[H(10)···O(1)] = 2·08 Å, S–O(1)–H(10) = 98·9°} but in SG.H₂O this H participates not only in a corresponding, but weaker, intramolecular hydrogen bond {d[N(4)···O(1)] = 2·895 Å, d[H(10)···O(1)] = 2·33 Å, S–O(1)–H(10) = 90·5°} but also in an intermolecular hydrogen bond N(4)–H(10)···O(2) [d(N···O) = 2·98 Å)]. Thus H(10) participates in a typical 'bifurcated' hydrogen bond [see e.g. Ramakrishnan & Prasad (1971)]. Rather similar ring systems based on the formation of intramolecular hydrogen bonds are found in o-sulfanilamide (Le Bars & Alléaume, 1972) and in 2-amino-3-methylbenzoic acid (Brown & Marsh, 1963).

5.2.3. Coordination about palladium.

Pd–Cl and Pd–N bond lengths and appropriate bond angles have been collected together in Table 10.* The only moiety with ideal square-planar dsp^2 hybridization is (PdCl₄²⁻) in K₂PdCl₄; the deviations of X–Pd–Y bond angles from 90° are due in some instances to the constraints imposed by ligand geometry, but such deviations also occur in trans-Pd[(CH₃)₂SO]₂Cl₂ and trans-Pd(SG)₂Cl₂ where no such constraints exist.

The Pd–Cl bond lengths provide an excellent illustration of the trans influence† (Appleton, Clark &

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* See footnote on p. 670.

† The trans influence of a ligand in a metal complex is the extent to which that ligand weakens the bond trans to itself in the equilibrium state of that complex. The trans effect is the effect of a coordinated group A upon the rate of substitution reactions of the group opposite to A. Thus the trans influence depends on thermodynamic factors and the trans effect on kinetic factors; this distinction was first introduced by Piddock, Richards & Venanzi (1966).

Manzer, 1973), their values depending on the nature of the group trans to chlorine. This is shown in Fig. 8, where the trans groups have been ordered along the abscissa to give a smooth, approximately linear, in-
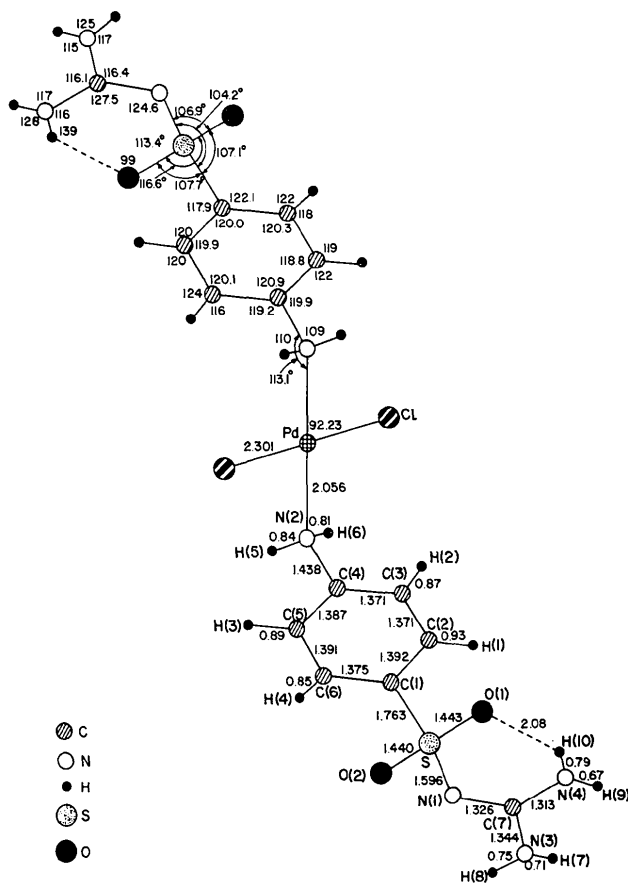

Fig. 5. Pd(SG)₂Cl₂: numbering of atoms and molecular dimensions. The molecule is shown in projection down [001]. The e.s.d.'s are given in Table 2.
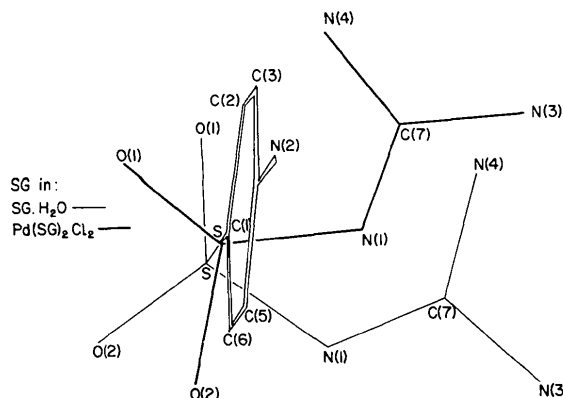

Fig. 6. Comparison of the conformations of the two SG moieties using Nyburg's (1974) molecular fit routine to match the phenyl groups. The sulfaguanidine moiety for Pd(SG)₂Cl₂ is the enantiomorph of that given in Table 6.

Table 11. *Comparison of bond lengths* (Å) *and angles* (°) *in various compounds*

Compound	H_2N–C(ring)	C–S	S–O	S–N	Angles O–S–O	R_1–S–R_2	Reference
1. Pd(SG)₂Cl₂	1·442	1·763[a]	1·440 1·446	1·596[d]	116·4	104·0	present paper
2. SG.H₂O	1·383	1·752[a]	1·456	1·586[d]	115·5	107·9	present paper
3. Sulfathiazole polymorph I		1·749[a]	1·434	1·614[d]	117·9	107·7	Kruger & Gafner (1971)
4. polymorph II	–	1·759[a]	1·444	1·588[d]	116·2	104·7	Kruger & Gafner (1971)
5. polymorph III	–	1·757[a]	1·445 1·441	1·606[d]	116·5	104·6	Kruger & Gafner (1972)
6. Methanesulfonanilide C_6H_5–NH–SO_2CH_3	(1·438)[h]	–	1·425 1·443	1·633[e]	118·6	107·6	Klug (1968)
7. β-Sulfonilamide p–NH_2–C_6H_4–SO_2–NH_2	1·38 (3)	1·75 (2)[a]	[1·45(2)][h] [1·45(1)][h]	1·62 (2)[f,g]	118·2	110·7	O'Connell & Maslen (1967)
8. Diaminodiphenyl sulfone	1·383 1·385	1·756[a] 1·749[a]	1·455 1·439	–	117·7	106·1	Alléaume (1974)
9. o-Sulfonilamide	1·378	1·756[a]	1·440 1·431	1·594	118·3	110·0	Le Bars & Alléaume (1972)
10. m-Aminobenzene-sulfonamide hydrochloride	1·458 (5) (C–NH₃⁺)	1·765 (4)[a]	1·440 (3) 1·430 (3)	1·582 (8)	119·1	109·1	Le Bars, Alléaume & Hauw (1973)
11. S,S-Diphenyl-N-p-tolylsulfonyl sulfilimine		1·756 (8)[a]	1·430 (8) 1·435 (8)	1·598 (8)	118·1 (5)	107·0 (4)	Kálmán, Duffin & Kucsman (1971)
12. 3-Oxo-5α-androsten-17β-ol toluene-p-sulfonate (at −170°C)	–	1·762 (5)	1·435 (4) 1·435 (4)	–	119·2 (4)	106·2 (6)	de Graaff & Romers (1974)
13. 3α,3β-Dimethoxy-5α-estran-17β-ol toluene-p-sulfonate (at −170°C)	–	1·749 (6)	1·431 (5) 1·449 (5)	–	120·4	103·4	de Graaff, van der Ende & Romers (1974)
14. Methylsulfonic acid monohydrate	–	1·753[a]	1·457 1·450 1·456	–	112·2	–	Arora & Sundaralingam (1971)
15. 1,5-$endo$-Methylene-quinolizidinium toluene-p-sulfonate		1·780 (4)[a]	1·457 (3)	–	–	–	Huber (1969)
16. Picrylsulfonic acid tetrahydrate	–	1·807 (1)[a]	1·431 (1) 1·445 (1) 1·444 (1)	–	114·0	–	Lundgren (1972); Lundgren & Tellgren (1974)
17. Thiepin 1,1-dioxide	–	1·719 (3)[b]	1·439 (2)	–	117·7	103·3	Ammon, Watts & Stewart (1970)
18. 4,5-Dihydrothiepin 1,1-dioxide	–	1·753 (3)[b]	1·440	–	116·9	106·4	Ammon, Smith & Kelso (1972)
19. Butadiene sulfone	–	1·793 (6)[c]	1·440	–	117·0	97·0	Sands & Day (1967)
20. β-Isoprene sulfone	–	1·812 (5)[c]	1·424	–	117·6	97·5	Beall, Herdglotz & Sass (1970)
21. cis-Perhydrocyclopenta-[1,2-c:3,4-c']dithiophen S,S,S',S'-tetroxide	–	1·783 (6)[c] (average of 4 values)	1·428 (6) (average of 4 values)	–	117·1 (1·0)	95·2	Burzlaff (1968)
22. p-Aminobenzoic acid H_2N–C_6H_4–COOH	1·378 1·381	–	–	–	–	–	Lai & Marsh (1967)

(a) C(ring)–S^{VI}. (b) C(sp^2)–S^{IV}. (c) C(sp^3)–S^{IV}. (d) S–N$\diagup$C. (e) S–N$\diagdown$C₆H₅ / H. (f) S–N$\diagdown$H / H. (g) Corrected for thermal motion.

(h) Not exactly comparable.

crease in d(Pd–Cl) from left to right. The order of increasing *trans* influence found here is similar to that deduced by McWeeny, Mason & Towl (1969) from a less-extensive group of Pt(II)–Cl bond lengths (O < Cl, C=C < P < H < Si). These results support the general conclusion of Appleton *et al.* (1973) that, for all the metals studied to date, σ-alkyl groups have a high structural *trans* influence while halide and nitrogen donors have low *trans* influences. The values obtained for Pd–Cl distances *trans* to a particular group (*e.g.* N) from different structures spread over a range of ~0·02–0·03 Å, which includes both the effects of inaccuracies in the various structure determinations and real chemical differences between them. On the other hand, the values for Pd–N distances *trans* to Cl from different structures spread over a range of ~0·1 Å and we have not been able to find any systematic dependence of Pd–N distances on the nature of the *trans* group. Values of d(Pd–N) in addition to those in Table 10 have been given by Clark & Palenik (1970) and by Carty & Chiek (1972).

5.2.4. *The coordination about sulfur.* Table 11 contains relevant bond distances and angles obtained from the more accurate recent determinations of appropriate molecular structures. The sulfaguanidine moieties show an approximation to type II conjugation (Koch & Moffitt, 1951) between the > SO₂ group and the adjoining phenyl ring and N atom [*cf.* our Fig. 6 and Figs. 3 and 4 of Kálmán, Duffin & Kucsman (1971)]. The earlier work of Koch & Moffitt has been extended by Jaffé (1954) and, especially, by Cruickshank (1961), who has shown that there is strong π-bonding in XY_4^{n-} moieties (X=Si,P,S,Cl; Y=O,N) because of overlap between $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals of X and 2pπ orbitals of Y.

In the molecular structures (entries 1–11 of Table 11), the C(ring)–S^{VI} bond lengths have a mean value of 1·756 Å and a range of 0·016 Å. In the sulfonate ions (entries 12–14) this bond length can overlap with the values found for C(sp³)–S (1·796 Å, entries 15–17). [The C(sp²)–S^{IV} bond length, which does not concern us here, is more variable; see Table 6 of Ammon, Watts & Stewart (1970).] The principal cause of the difference of 0·04 Å between the C(ring)–S and C(sp³)–S bond lengths appears to be the difference in the radii of the C atoms in different states of hybridization, and it is not necessary to assume any double-bond character in the C(ring)–S bonds. This is not so for the S–N bonds, which have a mean value of 1·602 Å and a range of 0·051 Å. The S–N single bond in sulfamic acid (Sass, 1960) is 1·764 Å (by neutron diffraction), and thus the present group of S–N bonds must have a considerable amount of double-bond character. The appreciable range is presumably due to variations in the nature of the hybridization at the various N atoms.

The S–O bond lengths do not vary much over the whole series of compounds (mean 1·442 Å, range 0·033 Å). In some of these crystals the O atoms of the sulfone

(or sulfonate) groups participate in hydrogen bonds, but this does not significantly affect the S–O bond lengths [for example, the dimensions of the sulfonate group in the hydrogen-bonded toluene-*p*-sulfonic acid monohydrate (Arora & Sundaralingam, 1971) are very similar to those of the sulfonate group in 1,5-*endo*-methylene quinolizidinium toluene-*p*-sulfonate (Huber, 1969), which is not hydrogen-bonded]. The bond length–order curve given by Cruickshank (1961) indicates that an S–O bond length of 1·44 Å corresponds to a π-bond order of 0·6.

5.2.5. *The guanidine group and a comparison of its dimensions with those of the guanidyl group.* Results for four independent determinations of the dimensions of the guanidine group $\left(-N{=}C{\Big\langle}{NH_2 \atop NH_2}\right)$ are given in Fig. 9* [nitroguanidine (Bryden, Burkardt, Hughes & Donohue, 1956); dicyandiamide (Rannev, Ozerov, Datt & Kshnyakina, 1966); Pd(SG)₂Cl₂ and SG.H₂O] and for five determinations of the guanidyl group $\left(-NH^+{=}C{\Big\langle}{NH_2 \atop NH_2}\right)$ in Fig. 10* [L-arginine dihydrate

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* See footnote on p. 670.
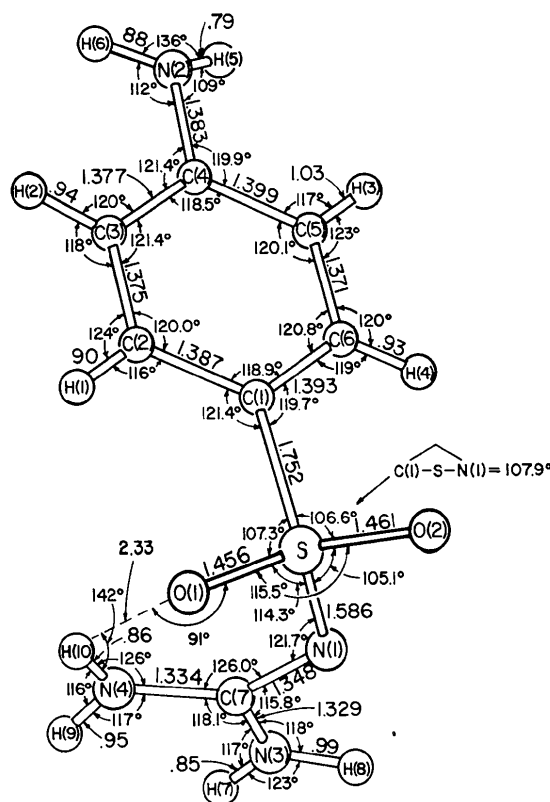

Fig. 7. SG.H₂O: numbering of atoms and dimensions of the SG moiety. The molecule is shown in projection down [100]. The e.s.d.'s are given in Table 2.
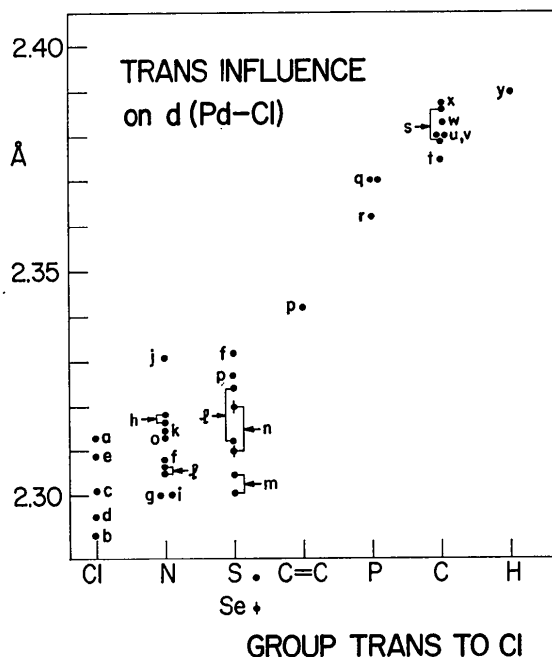
Fig. 8. The *trans* influence on d(Pd–Cl) for the palladium coordination complexes listed in Table 11. The e.s.d.'s of d(Pd–Cl) are ~0·001–0·003 Å. The letters on the diagram refer to the following compounds: (*a*) K₂PdCl₄ (Mais, Owston & Wood, 1972). (*b*) *trans*-Pd[(CH₃)₂SO]₂Cl₂ (Bennett *et al.*, 1967). (*c*) *trans*-Pd(SG)₂Cl₂ (present paper). (*d*) *trans*-Dichlorobis(nitrosobenzene)Pd(II) (Little & Doedens, 1973). (*e*) *trans*-Dichlorobis(diaminomaleonitrile)-Pd(II) (Miles, Hursthouse & Robinson, 1971). (*f*) *cis*-Dichloro-(DL-methionine)Pd(II) (Warren, McConnell & Stephenson, 1970). (*g*) *cis*-(Dimethylpiperazine)Pd(II)Cl₂ (Hassel & Pedersen, 1959). (*h*) *cis*-Dichloro-(*meso*-2,3-diaminobutane)Pd(II) (Ito *et al.*, 1971). (*i*) *cis*-Dichloro-(tetrahydrogenethylenediaminetetraacetate)Pd(II) pentahydrate (Robinson & Kennard, 1970). (*j*) Chloro{methyldi-[(6-methyl-2-pyridyl)methyl]amine}Pd(II) chloride (Drew, Riedl & Rogers, 1972). (*k*) *N*-Methyl-*N*-phenyl-*N′*-methyl-*N′*-(*o*-phenylchloropalladium)biacetyl osazone (Bombieri *et al.*, 1971). (*l*) *cis*-Dichloro-(*S*-methyl-L-cysteine)Pd(II) monohydrate (Battaglia, Corradi, Palmieri, Nardelli & Tani, 1973). (*m*) *cis*-Dichloro-(1,10-diaza-4,7,13,16-tetraoxa-21,24-dithiabicyclo [8,8,8]hexacosane)Pd(II) (Louis, Thierry & Weiss, 1974). (*n*) *cis*-Dichloro-[1,2-bis(isopropylseleno)-ethene]Pd(II) (Whitfield, 1970). (*o*) Chloro-(2,2′,2″-ter-pyridine)Pd(II)Cl₂ dihydrate (Intille, Pfluger & Baker, 1973). (*p*) *cis*-Dichloro-(*O*-methyl-*N*-allylthiocarbonate)Pd(II) (Porta, 1971). (*q*) *cis*-Dichloro[bis(diphenylphosphino)-ethylamine]Pd(II) (Mokuolu, Payne & Speakman, 1973). (*r*) *cis*-Dichlorobis(dimethylphenylphosphine)Pd(II) (Martin & Jacobson, 1971). (*s*) *trans*-Chloro-2-(phenylazo)-phenylbis(triethylphosphine)Pd(II) (Weaver, 1970). (*t*) Triphenylphosphineallyl Pd(II) chloride (Smith, 1969). (*u*) Triphenylphosphinemethylalyl Pd(II) chloride (Mason & Russel, 1966). (*v*) *cis*-Dichlorobis(methylisocyanido)hydrazine Pd(II) (Burke, Balch & Enemark, 1970). (*w*) Bis-(μ-*N*,*N*-dimethylthiocarbamoyl)-bis(chlorotrimethylphosphite)Pd-(II) (Porter, White, Green, Angelici & Clardy, 1973). (*x*) 1,1-Dichloro-1-pallada-2,5-di(methylamino)-3,4-diazacyclopentadiene (Butler & Enemark, 1971). (*y*) *trans*-Pd(H)Cl(PPr₃)₂ [Owston *et al.*, 1973, unpublished results (ref. 79) quoted by Appleton *et al.* (1973)]. Further values of d(Pd–Cl) not included in Table 10 and Fig. 8: *trans* to Cl: 2·24 Å, *trans*-dichlorobis(cyclohexanone oxime)Pd(II) (Tanimura, Mizushima & Kinoshita, 1967). This value seems too low. 2·30 Å, *trans*-dichlorobis(acetoxime)Pd(II) (Kitano, Kobori, Tani-

Fig. 8. (*cont.*)
mura & Kinoshita 1974). *trans* to P(CF₃)₂: 2·311 (4) Å, *trans* to P(PH)₂: 2·370 (4) Å, *cis*-[1-bistrifluoromethyl-phosphino-2-(diphenylphosphino)ethane]dichloropalladium-(II) (Manojlović-Muir *et al.*, 1974).

(Karle & Karle, 1964); L-arginine hydrochloride monohydrate (Dow, Jensen, Mazumdar, Srinivasan & Ramachandran, 1970); L-arginine phosphate monohydrate (Saenger & Wagner, 1972) and morpholine biguanide hydrobromide (Handa & Saha, 1973) and hydrochloride (Handa & Saha, 1971)]. The overall similarity of the dimensions of all these moieties is quite remarkable. Furthermore the dimensions in no way support the existence of distinct C=N and C–N bonds and it is clear that extensive electron delocalization must occur in both types of group. Extensive electron delocalization also occurs in 'tetrazene' (1-amino-1-[(1*H*-tetrazol-5-yl)azo]guanidine hydrate) (Duke, 1971) but the pattern of bond lengths in the guanidinium group differs in detail from the patterns summarized in Figs. 9 and 10.

In SG.H₂O and Pd(SG)₂Cl₂ the H atoms found in the difference syntheses show that the guanidine groups are in the amino and not the imino form. Occurrence of the imino form in Pd(SG)₂Cl₂ was inferred from infrared spectra (Gulko, Rittner, Ron, Weissman & Schmuckler, 1971). Reconsideration of this interpretation seems desirable in the light of the present crystallographic results.

6. Summary and conclusions

The structure analysis of Pd(SG)₂Cl₂ shows that the molecules are centrosymmetric and *trans*; the sulfaguanidine moiety is covalently bonded to Pd through the arylamino N, with a consequent weakening of the N–C(ring) bond; there is a tetrahedral distribution of bonds about N. The sulfaguanidine moiety has a folded form, with an intramolecular NH···O hydrogen bond between one of the guanidine N atoms and one of the sulfone O atoms; the guanidine group is in the amino form. The molecules lie in layers in the (101) planes and are bonded together by a fairly isotropic set of NH···Cl, NH···O and NH···N hydrogen bonds. In SG.H₂O the sulfaguanidine moiety has a shape similar to that of the sulfaguanidine in Pd(SG)₂Cl₂ but the conformations of the two moieties differ because of different senses of torsion about the C(ring)–S bonds. Because there is no complexation to metal, the N–C (ring) bond has an appreciable amount of double-bond character and the N has a trigonal disposition of bonds. The guanidine group is again in the amino form. The intramolecular hydrogen-bonded six-membered ring is more puckered in SG.H₂O than in Pd(SG)₂Cl₂, and the intramolecular hydrogen bond is weaker. The SG and H₂O molecules are bonded together in and across (001) planes by a network of OH···O, NH···O and NH···N hydrogen bonds while the aniline rings are interleaved and interact through dipole:dipole and dis-

persion forces, the arylamino groups not participating in any hydrogen bonding.

One important conclusion from this work is that the guanidine groups in both moieties are in the same tautomeric form. Another is that there are small but definite differences in the dimensions of the sulfaguanidine moieties in the two different environments, and in their conformations. Some of these differences are due to chemical effects (complexation to Pd) and some to intermolecular interactions, and particularly to the effects of different sorts and arrangements of intermolecular hydrogen bonds in the two crystals. Analogous conformational differences have been found for the procaine moiety (Dexter, 1972) and for the histidine moiety (Kistenmacher, Hunt & Marsh, 1972). All these results emphasize the essential role of crystal forces in determining solid-state conformations of flexible molecules.

All computations in this paper, except where explicitly noted otherwise, were made using the CRYM system (Duchamp, Trus & Westphal, 1969) on the IBM 370 computers at Caltech and Technion. We are grateful to Professor S. C. Nyburg (Toronto) for a copy of his molecular fit program.

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APPENDIX

Preparation and identification of various sulfaguanidine complexes of $PdCl_2$ and $PdBr_2$

Slow cooling of acidified aqueous solutions (pH 1–2·5) of $(NH_4)_2PdCl_4$ and sulfaguanidine gave three products: a crystalline powder, yellow laths and yellow plates with a distinctive dendritic texture. X-ray diffraction photographs (Table 12) showed that the laths

were α-$Pd(SG)_2Cl_2$.$2H_2O$ and the plates $Pd(SG)_2Cl_2$. Chemical analyses of *vacuum-dried* samples of both laths and plates gave the same composition $Pd(C_7H_{10}N_4O_2S)_2Cl_2$. Analogous studies with $(NH_4)_2PdBr_4$ gave laths and needles of $Pd(SG)_2Br_2$.$2H_2O$. The laths were isormophous with α-$Pd(SG)_2Cl_2$.$2H_2O$, while comparison of Debye–Scherrer patterns showed that the needles of $Pd(SG)_2Br_2$.$2H_2O$ were isostructural with the crystalline powder obtained in the $(NH_4)_2PdCl_4$-sulfaguanidine system. A series of experiments failed to show which factors (*e.g.* pH, cooling rate, crystallization temperature) govern crystal formation in these systems. Indexed Debye–Scherrer patterns of the four samples α- and β-$Pd(SG)_2Br_2$.$2H_2O$, α-$Pd(SG)_2Cl_2$.$2H_2O$ and $Pd(SG)_2Cl_2$ are given in Table 13;* some lines could not be indexed, suggesting the presence of unidentified impurities.

An added complication, not explored in detail, should be mentioned here. The Debye–Scherrer pattern of anhydrous $Pd(SG)_2Cl_2$ obtained by heating α-$Pd(SG)_2Cl_2$.$2H_2O$ *in vacuo* at 100° differs from that of anhydrous $Pd(SG)_2Cl_2$ obtained by crystallization. Compositions of these two different samples were checked by chemical analysis. Infrared spectra show that samples of α- and β-$Pd(SG)_2Cl_2$.$2H_2O$ heated above 100° give very similar spectra which differ from that of $Pd(SG)_2Cl_2$ obtained by crystallization. Thus care must be exercised in comparing the results of crystallographic and spectroscopic studies. However the overall similarity of the various spectra does indicate a close resemblance among the various structures.

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* See footnote on p. 670.

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Table 12. *Crystallographic results for various* $Pd(SG)_2X_2$.mH_2O ($m = 0, 2$) *complexes*

Formula	a (Å)	b (Å)	c (Å)	β(°)	$D_m^{(1)}$ (g cm^{-3})	D_c (g cm^{-3})	Z	Volume of formula unit (Å^3)	Space group	Symmetry of formula unit
$Pd(SG)_2Cl_2$ dendritic laths	11·59 (1)	10·476 (1)	8·783 (2)	100·8 (1)	1·877	1·925	2	523·7	$P2_1/n$	$\bar{1}$
α-$Pd(SG)_2Cl_2$.$2H_2O$	39·4	4·90	5·90	91	1·839	1·872	2	575	$P2_1/a$	$\bar{1}$
α-$Pd(SG)_2Br_2$.$2H_2O$ laths	39·29	4·93	6·14	92	1·995	2·043	2	594	$P2_1/a$	$\bar{1}$
β-$Pd(SG)_2Br_2$.$2H_2O$ needles	16·82	15·82	9·19	99·5	2·016	2·009	4	603	(2)	–

Notes: (1) Flotation in toluene–acetylene tetrabromide solution. (2) The crystals are monoclinic and were all twinned; the only possible absence is $0k0$ for k odd but this was not established beyond doubt because of poor crystal quality.

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The Structure of Decachloropyrene, $C_{16}Cl_{10}$: an Overcrowded Molecule

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Decachloropyrene is monoclinic, space group $P2_1/n$, with $a = 21.462$ (10), $b = 7.494$ (5), $c = 10.803$ (7) Å, $\beta = 92.8$ (1)°, $Z = 4$. Least-squares refinement with 2655 reflexions gave a final R of 0.038 for 236 parameters. The molecule is saddle-shaped, the maximum deviations from planarity being ca 1 Å for Cl and ca 0.5 Å for C atoms. The mean nearest-neighbour $Cl \cdots Cl$ distance in the molecule is 3.003 (1) and the mean C–Cl distance 1.719 (1) Å. The C–C distances are similar to those of pyrene itself. The molecules are stacked in such a way that half the molecule is sandwiched between two neighbouring molecules and the other half is essentially free. The packing forces result in a deviation from $mm2$ molecular symmetry: both the out-of-plane deformations and the $Cl \cdots Cl$ distances are smaller for the half of the molecule which is compressed.

Introduction

Decachloropyrene is an overcrowded molecule; if it were planar there would be $Cl \cdots Cl$ distances, e.g. $Cl(2) \cdots Cl(4)$, of only 2.4 Å whereas the sum of the van der Waals radii is 3.6 Å, and the shortest $Cl \cdots Cl$ distances found in similar compounds are about 3.0 Å, as in octachloronaphthalene (Gafner & Herbstein, 1963). The strain may be relieved by a splaying of angles and by out-of-plane displacements. The ultra-violet spectrum of $C_{16}Cl_{10}$ is quite different from that of other substituted pyrenes (Mosby, 1955) suggesting that the pyrene skeleton is non-planar. Possible ways in which pyrene can deviate from planarity are indicated in Fig. 1. We find the molecule to be saddle-shaped, i.e. model I; packing forces however cause it to deviate from the ideal $mm2$ symmetry.

Crystal data

$C_{16}Cl_{10}$, $M = 546.7$. Monoclinic, $a = 21.462$ (10), $b = 7.494$ (5), $c = 10.803$ (7) Å, $\beta = 92.8$ (1)°, $U = 1735$ Å³,

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$Z = 4$, $D_c = 2.09$ g cm⁻³. Space group $P2_1/n$. Packing coefficient 0.77. μ(Mo $K\alpha$) 15.9 cm⁻¹. The compound crystallizes from dioxane as yellow needles elongated along [010].

Experimental

The crystals were provided by Arne Berg.

A crystal, $0.01 \times 0.14 \times 0.015$ cm, was mounted along b and intensities measured out to $\sin \theta_{max} = 0.5$ with a computer-steered Supper diffractometer (Kryger, 1975). Monochromatic Mo $K\alpha$ radiation was used with a scintillation counter and a pulse-height analyser. 2655 independent reflexions, for which $F_o^2 < 3.0\sigma(F_o^2)$ according to counting statistics, were used in the subsequent calculations. No correction was applied for absorption.

Determination and refinement of the structure

The structure was determined by direct methods (MULTAN, Germain, Main & Woolfson, 1971). Least-squares refinement of atomic coordinates, anisotropic thermal parameters, a scale factor and an isotropic extinction coefficient, g, gave a final R of 0.038 ($R_w = 0.040$) for 236 parameters.

The value obtained for g was 5.2 (6) $\times 10^{-7}$ with t