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THE STRUCTURE OF THE SOLID CRYSTALLINE PALLADIUM SULFAGUANIDINE COMPLEX

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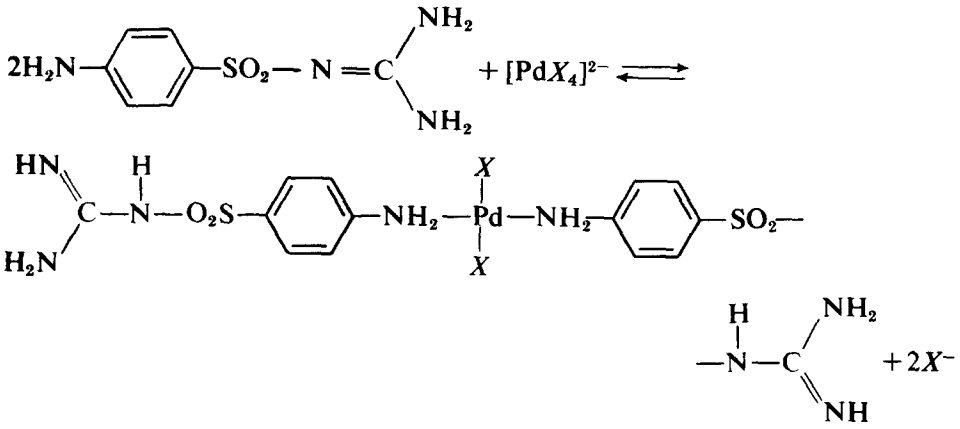
Abstract – Sulfaguanidine forms trans square planar complexes with palladium halides. The general formula of the complexes is $[PdL_2X_2]$. I.R. spectra in the regions 600–140 cm^{-1} and 3000–1500 cm^{-1} were used for their complete structural elucidation. For the sake of comparison the interaction of palladium with paraaminosulfonamide was also studied.

INTRODUCTION

IN A previous paper[1] the water-soluble complex of palladium chloride with sulfaguanidine (SG) was described, and stability constants were determined by a variety of methods. The solid product obtained by the interaction of SG with $[PdX_4]^{2-}$ (where X is a chloride or bromide) has the general formula $Pd(SG)_2X_2$.

The aim of the present work was to establish the structure of the solid product, there being several bonding alternatives, arising from the fact that the ligand, SG, contains four potential donor nitrogen atoms. In addition there are a number of possibilities for resonant and tautomeric structures of the molecule itself and for its interaction with palladium.

X-ray diffraction analysis showed that the subject complex is of the *trans* type; this was confirmed by IR spectroscopy, which further showed that there is a shift in the location of the double bond from its position in the free ligand to its palladium complex as follows:



X-being a chloride or bromide.

1. W. F. Rittner, A. Gulko and G. Schmuckler, *Talanta*, In press.

EXPERIMENTAL

Materials

$(NH_4)_2PdCl_4$	Fluka's Puriss reagent
K_2PdBr_4	A K. & K. Laboratories product
Sulfaguanidine (SG)	A B.D.H. product, which was recrystallized from water
Benzenesulfonamide	An Eastman Organic Chemicals' product, which was recrystallized from ethanol
Benzene sulfonylguanidine	Prepared by the interaction of guanidine nitrate with sulfonyl chloride, after Clarke and Gillespie [2].

Preparation of compounds

$Pd(SG)_2Cl_2$. Well defined crystals were obtained by slowly cooling a mixture consisting of 150 ml HCl 0·01 N, 120 mg SG, and 38 mg $(NH_4)_2PdCl_4$ from an initial temperature of 90°C. The crystals were vacuum dried at 80°C.

Anal.	C	H	N	O	Cl	S	Residue
Calc.	27·7	3·3	18·5	10·5	11·7	10·5	17·6
Found	27·52	3·64	18·12	10·78	12·06	10·59	18·14

$Pd(SG)_2Br_2$. Was slowly precipitated from a solution consisting of 200 ml HBr 0·01 N, 120 mg SG, and 62 mg K_2PdBr_4 at 90°C. Elemental analysis was carried out after drying the precipitate in vacuum at 60°C.

Anal.	C	H	N	O	Br	S	Residue
Calc.	24·2	2·9	16·1	9·2	23·0	9·2	15·4
Found	23·99	3·09	15·92	9·32	23·12	9·08	15·01

$Pd(SA)_2Cl_2$. Was slowly precipitated from a mixture at 90°C containing 250 ml HCl 0·01 N, 120 mg SA*, and 30 mg $(NH_4)_2PdCl_4$ and vacuum dried at 80°C.

Anal.	C	H	N	O	Cl	S	Residue
Calc.	27·6	3·1	10·7	12·3	13·6	12·3	20·4
Found	27·5	3·31	10·55	12·12	12·07	12·14	23·08

Spectra

The near i.r. spectra were recorded from 3000 cm^{-1} to 1500 cm^{-1} with a Perkin–Elmer model 237 Grating Spectrophotometer. The crystals were examined in KBr discs.

The far i.r. spectra were recorded from 600 cm^{-1} to 140 cm^{-1} with a Beckman I.R. 11 spectrophotometer. The samples were suspended in Nujol and measured between two polyethylene plates.

X-ray data

Standard X-ray diffraction techniques (oscillation, Weissenberg and precession photographs, CuK_α radiation) were applied in order to determine the cell dimensions and space group of the ligand, sulfaguanidine, and its complexes with palladium halides. Powder photographs were taken with a Debye Sherrer Camera (114·6 mm) using FeK_α radiation.

Crystal densities were measured by the floating crystal method in a solution of toluene and acetylene tetrabromide.

*SA – Para aminosulfonamide.

2. H. T. Clarke and H. B. Gillespie, *J. Am. chem. Soc.* **54**, 1964 (1932).

RESULTS AND DISCUSSION

When preparing the crystalline palladium sulfaguanidine complexes it was evident from the beginning that the process is extremely sensitive to the pH even in very acidic solutions. At pH values lower than 2 yellow plates are obtained. At pH 2·2 and above crystals of different type were obtained (needles), whose crystallography will be reported separately. The crystals studied here were always obtained from solutions of pH range 1·45–1·80 so as to ensure well-defined crystals.

I.R. spectroscopy was also preceded by microscopic and X-ray diffraction study of the samples used to ensure that single-phase samples of known structural type were used.

Crystallographic measurements

The palladium complexes – $Pd(SG)_2Cl_2$ and $Pd(SG)_2Br_2$ – are isomorphous and crystallize in a monoclinic unit cell of space group $P2_1/a$. $Pd(SG)_2X_2$ has 2 molecules in the unit cell and these must necessarily be centrosymmetric. The crystallographic data are summarized in Table 1.

Table 1. X-ray data for palladium complexes of SG

Substance	*b* (Å)	*c* (Å)	(deg)	Density Meas.	Calc.	Diff.
$Pd(SG)_2Cl_2$	39·4	4·90	5·90	91	1·839	1·768	0·071
$Pd(SG)_2Br_2$	39·2	4·90	6·08	91	1·995	1·977	0·018

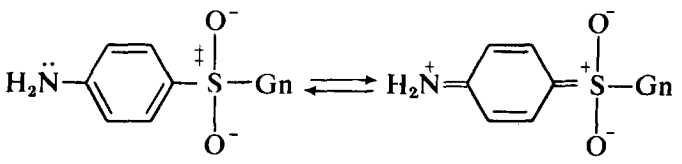
Far i.r. spectra

Spectral assignments of the Pd–*X* (*X* = halide) vibrations in the far i.r. region give immediate information on whether ionic or covalent bonds are formed. According to Durig[3] and Nuttal[4] a Pd–Cl asymmetric stretching vibration for a covalent bond should occur in the region 365–330 cm^{-1}, while for Pd–Br this should be in the 285–265 cm^{-1} region. In this work the vibrations were found to occur at 334 cm^{-1} in the case of $Pd(SG)_2Cl_2$ and at 268 cm^{-1} in that of $Pd(SG)_2Br_2$. These two complexes are of the *trans*-type, since only one vibration could be found for each species, whereas for a cis isomer two vibrations should occur.

A weak Pd–N asymmetric stretching vibration occurs in the complexes at 485 cm^{-1}, the weakness of this peak being explained by the small change in the dipole moment[3].

Another strong peak of interest in this region appears in the pure ligand at 295 cm^{-1} and upon complexation is shifted to 308 cm^{-1}. The same vibration was found at 306 cm^{-1} for benzene sulfonyl guanidine, which indicates that the lone electron pair of the aryl nitrogen of SG is involved in bonding to palladium according to the following scheme. Free SG can assume the following structures:

3. J. R. Durig, R. Layton, D. W. Sink and B. R. Mitchell, *Spectrochim. Acta* **21**, 1367 (1965).
4. R. H. Nuttal, *Talanta* **15**, 157 (1968).



(A) (B)

Gn = Guanidine.

Upon binding to palladium only form (A) can exist, and the ligand structure after bonding is similar to the sulfonylguanidine, and therefore the vibration is shifted from 295 to 308 cm^{-1}.

Two important structural conclusions can be drawn from the far i.r. spectra: (a) covalent bonding of halides in the *trans* form, and (b) complexation via the aryl nitrogen. This argument finds support in the 3000 cm^{-1} i.r. region.

I.R. Region (3000–1500 cm^{-1})

The vibrations of interest in this region are chiefly the stretching and bending vibrations of the aryl and guanidine nitrogens. In order to ascertain whether the band assignments made are the correct ones, the spectra of the sulfaguanidine and of its palladium complexes were compared with the spectra of para-aminosulfonamide and its palladium complex. It is interesting to note that in this case, too, sulfonamides do not react with palladium; only the para-aminosulfonamides do. Table 2 summarizes the important vibrations which were of assistance in determining the structure of the complex.

In the free sulfaguanidine two absorptions were found, at 3450 cm^{-1} and at 3385 cm^{-1}. They are attributed to the asymmetric and symmetric stretching

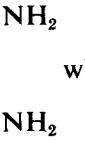
Table 2. A selection of the most important i.r. frequencies of sulfaguanidine and of para-aminosulfonamide and its palladium complexes*

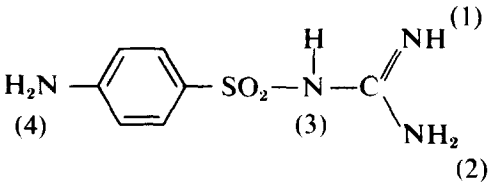
Band assignment		SA	$Pd(SA)_2Cl_2$	SG	$Pd(SG)_2Cl_2$	$_PPd(SG)_2Br$
	—νNH imine				3430	3470
asym.	—νNH_2 aryl	3470	3200	3450	3200	3190
sym.	—νNH_2 aryl	3380	3120	3385	3120	3115
asym.	—νNH_2 amide	3350	3378			
sym.	—νNH_2 amide	3250	3260			
	—νNH amide				3280	3278
asym.	—νNH_2-Gn			3340	3335	3357
sym.	—νNH_2-Gn			3200	3200	3185
	—δNH_2-aryl	1645	1590	1635		
	—$\delta NH_2 + \nu$N—C—N			1635 1530	1630 1530	Shoulder 1533
	—δNH_2 aryl?				1588	1572
ring vib.		1609	1604	1605	1604	1600
ring vib.		1510	1500	1495	1499	1492

SA – Para aminosulfonamide; SG – Sulfaguanidine; Gn – Guanidine.

*All vibrations were very strong ones.

vibrations respectively, the aryl-NH_2 groups, analogous to para-SA, where the vibrations were obtained at 3470 and 3380 cm^{-1}, respectively. The two absorptions at 3340 cm^{-1} and 3200 cm^{-1}, are attributed to the antisymmetric and symmetric stretching vibrations of the guanidine nitrogens which, according to Schwenker[6], are identical when in the free ligand.

In the present work absorptions were found that differ from those given by Schwenker. It is assumed that the reason for this discrepancy is the existence of several crystalline forms of the ligand. This is lent support by the work of Novak *et al.*[5], who found three different crystalline forms of SA, all having different absorptions, and by the work of Hirooka *et al.*[8], who did the same for benzenesulfonylisothioureas. An additional factor that must be considered is the difference between the spectra of SG and of SG·H_2O. Schwenker[6] showed that the free ligand is in the amine form:  whereas in the present work it is shown that the ligand reacting with palladium assumes the imine form, which has the structure:



The finding of six vibrations in the 3000 cm^{-1} region supported the suggested structure. $Pd(SG)_2Cl_2$ manifests first of all the shift of the aryl nitrogen vibrations to 3200 cm^{-1} and to 3120 cm^{-1}; while in $Pd(SG)_2Br_2$ the shifts are to 3190 cm^{-1} and 3115 cm^{-1}. The ratio between the shifts is 1·085, similar to that found in the palladium complex with para-amino-SA. A third vibration occurs at 3280 cm^{-1} for $Pd(SG)_2Cl_2$ and at 3278 cm^{-1} for $Pd(SG)_2Br_2$, attributed to the stretching vibrations of the sulfonamide nitrogen[6]. The symmetric vibrations of the guanidine —NH_2 also occur at 3200 cm^{-1}, shown as a broad band. The antisymmetric vibration is found at 3335 cm^{-1}. The sixth vibration occurs at 3430 cm^{-1} and is attributed to the stretching vibration of the guanidine =N—H. These absorptions are close to those found for guanidine[7].

In addition to these vibrations the asymmetric and symmetric N—C—N skeleton vibrations are of interest. Appearing at 1635 cm^{-1} and 1530 cm^{-1} respectively, they are wide, coupled to the bending deformation of the guanidine —NH_2, and overlapping with the aryl —NH_2 group. These absorptions do not shift with the formation of the $Pd(SG)_2Cl_2$ complex, whence it is concluded that the palladium is not bound to the guanidine nitrogens. Upon deuteration the skeleton vibrations shift, respectively from 1635 to 1565 and from 1530 to 1505 cm^{-1}.

5. A. Novak, J. Lascombe and M. L. Josien, *Coll. J. Phys. Paris.* Suppl. 5–6, 38 (1966).
6. G. Schwenker, *Arch. Pharm.* **295**, 753 (1962).
7. W. J. Jones, *Trans. Faraday Soc.* **55**, 524 (1959).
8. S. Hirooka and K. Hasega *C.A.* **70**, 19765 (1969).

These shifts are too small for the D—H substitution as regards the —NH_2 vibrations, and this is the proof for the coupling between the N—C—N skeleton vibration to the —NH_2 bending mode.

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