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Crystal and Molecular Structure of (Trifluoromethanesulfonato)(3-(diethylamino)propionyl)(diethylamine)palladium(II): An Example of a Very Large Trans Influence

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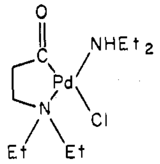
The crystal and molecular structure of (trifluoromethanesulfonato)(3-(diethylamino)propionyl)(diethylamine)palladium(II) has been determined from three-dimensional single-crystal X-ray diffraction data, collected by counter techniques. The colorless crystals are monoclinic, space group $P2_1/c$ (No. 14), with four formula units in a unit cell of dimensions $a = 8.351$ (4) Å, $b = 15.591$ (8) Å, $c = 15.279$ (8) Å, and $\beta = 104.01$ (2)°. The structure was refined by full-matrix least-squares methods to an R value of 0.047 ($R_w = 0.049$) for 1756 independent reflections with $F^2 > 3\sigma(F^2)$. Although it was expected that the compound might be three-coordinate, the monomeric molecules were found to exhibit a four-coordinate, approximately square-planar geometry, with an oxygen atom of the trifluoromethanesulfonate anion bound in the position trans to the acyl carbon atom. The Pd–C(acyl) bond length of 1.938 (11) Å is extremely short, and the very large trans influence associated with the acyl group results in the trifluoromethanesulfonate anion being bound to the metal through the longest known palladium–oxygen bond (Pd–O = 2.271 (7) Å). As a result of this study and previous work, the acyl group of the chelating β-aminoacyl ligand has been found to exhibit the highest degree of trans influence known for ligands bound to palladium(II).

Introduction

Study of the syntheses, modes of reaction, and structures of β-aminoacylpalladium(II) complexes has been a recent topic of interest in these laboratories.[1-3] Structural studies performed on the compounds chloro(3-(diethylamino)propionyl)(diethylamine)palladium(II) (**1**)[2] and chloro(3-(diethylamino)propionyl)[(diethylamino)(methylamino)carbene]palladium(II) (**2**)[3] have shown these molecules to involve a very short, strong palladium–carbon bond which exerts an unprecedentedly large trans influence on the chloro ligand of the approximately square-planar ligand array. In particular, the two above compounds exhibit the longest known palladium(II)–chlorine bond lengths, and this observation underscores the powerful and well-documented[4] trans influence associated with σ-bonded carbon ligands in transition-metal complexes.



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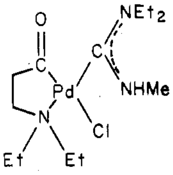
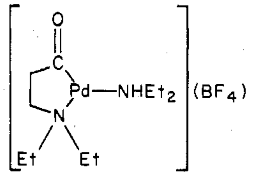


2

Recently, a report detailed the synthesis and structure of the first formally three-coordinate d^8 compound, tris(triphenylphosphine)rhodium(I) perchlorate,[5] and nuclear magnetic resonance evidence has been obtained to support the existence of a similar three-coordinate rhodium(I) compound.[6] The high degree of trans influence of the acyl group in compounds **1** and **2** makes it difficult even for ligands of moderate nucleophilicity to occupy the site trans to the acyl carbon in these compounds, as mentioned above. Therefore, it seemed reasonable to exploit this situation in an attempt to synthesize a three-coordinate palladium(II) complex.

Compound **1** was found to react with several silver salts containing noncoordinating anions (i.e., anions of very low nucleophilicity), including tetrafluoroborate, trifluoromethanesulfonate, and tetraphenylborate. The reaction of **1** with silver tetrafluoroborate has been previously reported.[2] The product of this reaction gave an elemental analysis consistent with formulation as **3**, which was suggestive of the desired three-coordinate complex. Single crystals of **3** suitable for X-ray structural study could not be obtained, however. The tetraphenylborate anion was found to react with the palladium(II) center of **1** after chloride ion abstraction, yielding not the desired three-coordinate cation above but a product which has not yet been characterized.



3

Reaction of **1** with silver trifluoromethanesulfonate, in a manner analogous to that used for the preparation of **3**, yielded a crystalline product, which was formulated as the trifluoromethanesulfonate analogue of **3**. Since the trifluoromethanesulfonate anion is similar to the perchlorate ion in its low coordinating ability and lack of nucleophilic character,[7] it seemed reasonable to suppose that this product might also contain the desired three-coordinate cation. Since conductivity studies were not likely to provide unambiguous information concerning the true nature of this product, and the infrared spectrum was not straightforwardly assignable, a structural study of this trifluoromethanesulfonate analogue of **3** by means of X-ray diffraction was deemed necessary to establish the nature of the coordination about the metal ion. The results of that study are reported.

Experimental Section

Preparation. The preparation of the title compound was carried out in a manner similar to that of compound **3** (3-(diethylamino)propionyl)(diethylamine)palladium(II) tetrafluoroborate), which has been previously reported.[2] The silver trifluoromethanesulfonate employed was prepared by reaction of reagent grade silver carbonate with trifluoromethanesulfonic acid (3M Co.) and recrystallized from ethanol. Reaction of the silver trifluoromethanesulfonate with **1** in THF, followed by treatment with dry petroleum ether, yielded colorless crystals of the product, (trifluoromethanesulfonato)(3-(diethylamino)propionyl)(diethylamine)palladium(II).

Crystal Data. For Pd($C_{12}H_{25}N_2O_4SF_3$) (mol wt 456.8): monoclinic, $a = 8.351$ (4) Å, $b = 15.591$ (8) Å, $c = 15.279$ (8) Å, $\beta = 104.01$ (2)°, $V = 1930$ Å^3, $\rho_{obsd} = 1.56$ g/cm^3, $\rho_{calcd} = 1.57$ g cm^{-3}, $Z = 4$, $F(000) = 928$; space group $P2_1/c$ (No. 14), Mo Kα radiation, λ_1 0.709 30 Å, λ_2 0.713 59 Å, μ(Mo Kα) = 10.9 cm^{-1}.

Data Collection and Reduction. Due to the hygroscopic nature of the compound, crystals of the title compound which were to be examined by means of X-ray diffraction were sealed under a dry atmosphere in thin-walled glass capillaries. Examination of the colorless crystals by Weissenberg and precession photography revealed only Laue symmetry $2/m$, and the conditions for the observation of reflections proved to be $h0l$, $l = 2n$, $0k0$, $k = 2n$. These observed conditions require that the space group be assigned as $P2_1/c$ (No. 14).[8]

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On the basis of the quality of the diffraction pattern exhibited in the photographic work, a crystal was chosen for data collection and mounted on the Enraf-Nonius CAD-3 diffractometer. The *a* axis of the crystal was nearly coincident with the diffractometer ϕ axis. After careful centering of the crystal, the orientation matrix for data collection and the unit cell parameters reported above were obtained from least-squares calculations on the automatically determined[9] 2θ, χ, and ϕ settings of 25 reflections (at ambient temperature, 20 ± 1 °C) with 2θ values in the range 18–22°.

The intensities of all reflections for which $4.5° < \theta < 25°$ and $h,k \geq 0$ were measured by θ–2θ scans. Zr-filtered Mo Kα radiation was used. The scan range employed was 0.5° (in θ) to either side of the calculated K$\bar{\alpha}$ position, and a constant scan rate of 10° min^{-1} was used for all reflections. Weak reflections were scanned a maximum of three times, while very strong reflections would require fewer scans to reach a preset intensity maximum of 4000 counts. Background was counted at both ends of the scan, and the total background counting time was equal to the scanning time. The takeoff angle was 3.5°, and Zr foil attenuators were inserted automatically (to avoid coincidence losses) if the peak count rate exceeded 2500 counts s^{-1}. The intensity of one of three reference reflections ($3\bar{3}2$, $0\bar{3}\bar{6}$, and $08\bar{1}$) was measured every 25 reflections. These reference intensities were found to decrease in a roughly linear fashion by approximately 13% during the course of data collection, and the crystal simultaneously became brownish. The raw data were scaled so that all the reference reflections were returned to the initial intensity level before further data processing was carried out.

Lorentz and polarization corrections were applied to the data. The uncertainty parameter, *g*, in the formula used for the standard deviation in the intensity[10,11] was taken to be 0.04. Only the 1756 reflections (of 3367 independent reflections measured) which were taken to be observed ($F^2 > 3\sigma(F^2)$) were employed in the solution and refinement of the structure. The crystal used for data collection was extremely small (roughly 0.18 × 0.08 × 0.05 mm), as was the absorption coefficient for Mo Kα radiation, and no absorption correction was applied to the data.

The position of the palladium atom was assigned from the peaks observed in the Harker sections of the Patterson map, and a Fourier synthesis of the electron density phased by the metal ion revealed the positions of all of the nonhydrogen atoms of the compound. Scattering factors for palladium(II), oxygen, nitrogen, carbon, sulfur, and fluorine were taken from ref 12. Scattering factors for spherically bonded hydrogen atoms[13] were also taken from ref 12, as were correction terms $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to palladium and sulfur.

On isotropic refinement of all nonhydrogen atoms, the isotropic thermal parameters for C3, C4, and C6 became abnormally large, while all other atoms refined satisfactorily. Detailed difference Fourier maps calculated about the positions of each of these atoms did not reveal any evidence for resolved disorder at these positions, so all atoms were subsequently refined anisotropically. All hydrogen atoms which could be clearly discerned in the difference Fourier map at this point were included in the model. These hydrogen atoms (including all H atoms of the molecule with the exception of those on the atoms C3, C4, and C6) were placed in fixed, idealized positions 0.95 Å from carbon, with isotropic thermal parameters 1 Å^2 larger than that of the atom to which they were attached. Anisotropic full-matrix least-squares refinement[14] of the model converged at an R ($=\sum||F_o| - |F_c||/\sum|F_o|$) value of 0.047 and an R_w ($=[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$) value of 0.049. The error in an observation of unit weight was 1.28. On the final refinement cycle, no positional or thermal parameter shifted by more than 15% of the estimated standard deviation in that parameter. The NUCLS refinement program minimizes $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factor amplitudes, respectively, and w is the weight for each reflection ($=4F_o^2/\sigma^2(F_o^2)$). No correction for secondary extinction was applied. In a final difference electron density map, no peak higher than 0.55 e Å^{-3} was observed, and the deepest hole in this map was −0.50 e Å^{-3}.

Final atomic positional parameters are listed in Table I, while Table II lists the anisotropic thermal parameters obtained for the nonhydrogen atoms. Table V lists the calculated hydrogen atom positions and Table VI is a listing of the structure factor amplitudes; both of these tables are available as supplementary information.

Results and Discussion

Table III contains bond lengths and angles found in this study for the title compound. A perspective view of the molecule which includes the numbering scheme used in the tables and in the following discussion is displayed in Figure 1.

Table I. Atomic Coordinates (Fractional)[a]

atom	*x*	*y*	*z*
Pd(II)	−0.00004 (8)	0.22419 (5)	0.13662 (5)
S1	−0.2545 (3)	0.0923 (2)	0.2410 (2)
F1	−0.1765 (9)	−0.0604 (4)	0.1973 (6)
F2	−0.3948 (9)	−0.0556 (4)	0.2467 (6)
F3	−0.4007 (9)	−0.0127 (5)	0.1155 (5)
O1	0.2841 (9)	0.2936 (5)	0.0987 (5)
O2	−0.1637 (8)	0.1236 (4)	0.1786 (5)
O3	−0.1543 (10)	0.0771 (5)	0.3297 (5)
O4	−0.4087 (8)	0.1329 (5)	0.2347 (6)
N1	−0.1936 (9)	0.3103 (5)	0.0805 (6)
N2	0.2028 (8)	0.1436 (5)	0.1891 (6)
C1	0.1402 (13)	0.3042 (6)	0.0927 (7)
C2	0.0472 (13)	0.3819 (7)	0.0462 (7)
C3	−0.1177 (16)	0.3931 (9)	0.0670 (12)
C4	−0.2797 (18)	0.2826 (11)	−0.0159 (11)
C5	−0.3397 (17)	0.1927 (9)	−0.0231 (9)
C6	−0.3162 (18)	0.3212 (11)	0.1316 (13)
C7	−0.2454 (20)	0.3370 (9)	0.2356 (14)
C8	0.2313 (13)	0.1282 (9)	0.2884 (9)
C9	0.2517 (16)	0.2102 (11)	0.3387 (8)
C10	0.1869 (17)	0.0756 (9)	0.0402 (10)
C11	0.1912 (13)	0.0615 (7)	0.1386 (10)
C12	−0.3079 (14)	−0.0145 (7)	0.1982 (9)

[a] Estimated standard deviations in parentheses.

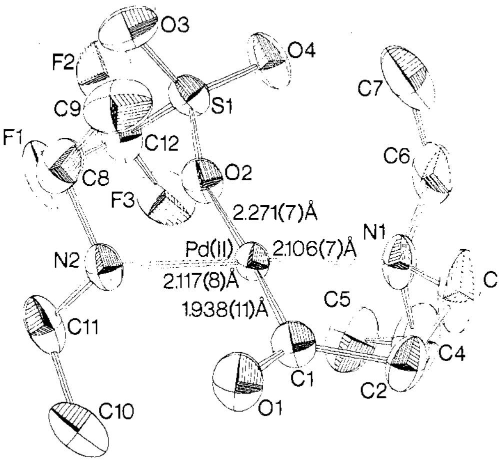

Figure 1. A perspective view of the title compound, showing the atom numbering scheme and the palladium–ligand bond lengths. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

It is clear from Figure 1 that achievement of a three-coordinate palladium(II) system has not been accomplished. Instead of the anticipated vacant coordination site trans to the acyl carbon atom (C1), this position is occupied by an oxygen atom (O2) of the trifluoromethanesulfonate anion. Thus, the geometry about the palladium(II) ion is based on the normal approximately square-planar geometry common for palladium in the dipositive oxidation state.

Although the trans influence of the acyl group has in this case not been sufficient to completely prevent coordination of the metal by the trifluoromethanesulfonate anion, the bonding parameters associated with this interaction underscore the powerful nature of the trans influence in these β-aminoacyl complexes. In the absence of a strongly trans-directing ligand in the trans position, bond lengths between palladium(II) and oxygen can be shorter than 2.0 Å. For example, in the Schiff base complexes bis(*N*-isopropyl-3-methylsalicylaldiminato)palladium(II) and bis(*N*-isopropyl-3-ethylsalicylaldimina-

Table II. Anisotropic Thermal Parameters[a]

atom	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Pd(II)	28.8 (3)	45.2 (4)	52.7 (4)	−1.8 (4)	11.2 (2)	4.2 (5)
S1	41 (1)	58 (1)	70 (2)	−8 (1)	21 (1)	−3 (2)
F1	87 (5)	68 (5)	202 (9)	17 (4)	46 (5)	−13 (5)
F2	109 (6)	79 (5)	182 (8)	−37 (4)	61 (5)	18 (4)
F3	90 (5)	122 (6)	110 (6)	−21 (4)	5 (5)	−41 (5)
O1	54 (5)	88 (6)	126 (7)	−4 (5)	39 (5)	27 (5)
O2	53 (4)	56 (4)	91 (6)	−6 (3)	36 (4)	11 (4)
O3	104 (7)	123 (7)	56 (4)	−21 (6)	5 (5)	−1 (6)
O4	56 (5)	72 (5)	151 (8)	6 (4)	55 (5)	−4 (5)
N1	36 (5)	52 (5)	101 (7)	3 (4)	13 (5)	23 (5)
N2	33 (4)	50 (5)	80 (7)	−2 (4)	19 (4)	2 (4)
C1	47 (6)	57 (7)	74 (7)	−9 (5)	20 (6)	2 (5)
C2	62 (7)	51 (6)	92 (9)	−9 (6)	14 (6)	27 (6)
C3	72 (9)	87 (10)	248 (19)	10 (8)	49 (11)	83 (12)
C4	115 (12)	101 (11)	138 (13)	−5 (11)	−61 (10)	17 (12)
C5	90 (10)	109 (11)	110 (11)	−20 (8)	−28 (9)	12 (8)
C6	80 (10)	152 (15)	132 (16)	74 (9)	79 (11)	81 (13)
C7	139 (14)	68 (9)	206 (18)	9 (8)	111 (14)	−10 (11)
C8	39 (6)	117 (11)	92 (10)	5 (7)	13 (6)	38 (8)
C9	81 (9)	157 (14)	72 (8)	−25 (9)	−3 (7)	−11 (9)
C10	101 (11)	108 (11)	128 (12)	4 (9)	54 (10)	−41 (9)
C11	57 (7)	52 (7)	145 (12)	5 (6)	44 (8)	1 (7)
C12	50 (7)	61 (7)	103 (10)	−8 (6)	20 (7)	3 (8)

[a] Estimated standard deviations in parentheses. The form of the anisotropic thermal ellipsoid is given by $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$.

Table III. Bond Lengths (Å) and Angles (Deg)[a]

Pd(II)-C1	1.938 (11)	C1-O1	1.19 (1)
Pd(II)-N1	2.117 (8)	C1-C2	1.52 (1)
Pd(II)-N2	2.106 (7)	C2-C3	1.50 (2)
Pd(II)-O2	2.271 (7)	C3-N1	1.47 (2)
S1-O2	1.441 (8)	N1-C4	1.54 (2)
S1-O3	1.430 (7)	N1-C6	1.44 (2)
S1-O4	1.417 (8)	C4-C5	1.48 (2)
S1-C12	1.805 (12)	C6-C7	1.57 (3)
C12-F1	1.31 (1)	N2-C8	1.50 (2)
C12-F2	1.32 (2)	N2-C11	1.49 (1)
C12-F3	1.31 (1)	C8-C9	1.48 (2)
		C10-C11	1.51 (2)

C1–Pd^{II}–N1	85.3 (4)	Pd^{II}–N1–C3	107.5 (6)
C1–Pd^{II}–O2	175.4 (4)	Pd^{II}–N1–C4	110.1 (8)
C1–Pd^{II}–N2	91.0 (4)	Pd^{II}–N1–C6	115.4 (8)
N1–Pd^{II}–O2	95.7 (3)	C3–N1–C4	103.2 (11)
N1–Pd^{II}–N2	176.3 (3)	C3–N1–C6	111.1 (11)
O2–Pd^{II}–N2	87.9 (3)	C4–N1–C6	108.9 (10)
Pd^{II}–O2–S1	150.5 (4)	N1–C4–C5	114.1 (12)
O2–S1–O3	113.7 (5)	N1–C6–C7	115.0 (12)
O2–S1–O4	114.8 (5)	Pd^{II}–N2–C8	113.4 (7)
O2–S1–C12	101.3 (6)	Pd^{II}–N2–C11	111.8 (6)
O3–S1–O4	116.9 (5)	C8–N2–C11	111.2 (9)
O3–S1–C12	103.1 (5)	N2–C8–C9	110.9 (10)
O4–S1–C12	104.3 (5)	N2–C11–C10	112.0 (10)
S1–C12–F1	111.9 (8)	Pd^{II}–C1–O1	124.5 (8)
S1–C12–F2	111.4 (9)	Pd^{II}–C1–C2	113.0 (8)
S1–C12–F3	111.5 (8)	O1–C1–C2	122.4 (10)
F1–C12–F2	108.3 (9)	C1–C2–C3	112.7 (10)
F1–C12–F3	107.5 (11)	C2–C3–N1	112.1 (10)
F2–C12–F3	105.9 (9)		

[a] Estimated standard deviations in parentheses.

to)palladium(II) the Pd–O bond lengths were found to be 1.987 (3) Å[15] and 1.991 (2) Å,[16] respectively. In these cases, equivalent oxygen atoms were trans to one another. Several cases are known in which oxygen is bound in a position trans to a more strongly trans-directing ligand atom. When trans to the phosphorus atom of an ethoxydiphenylphosphine ligand, for example, a longer Pd–O bond length of 2.102 (3) Å has been observed.[17] The trans influence of σ-bonded carbon is usually regarded as at least as great as that of a phosphine ligand, and observed Pd–O bond lengths of 2.158 (9) Å (acetylacetonate oxygen trans to sp^3 carbon)[18] and 2.094 (6) Å (trans to sp^2 phenyl carbon)[19] support this view. The short Pd–O bond length of 2.008 (6) Å trans to the isocyanide carbon in 4-[(diethylamino)(*tert*-butylamino)methylene]-4-(*tert*-butyl isocyanide)-2,2,5,5-tetrakis(trifluoromethyl)-1,3,4-dioxapalladolan[20] is a consequence of the very different ligand character of the isocyanide ligand compared to the powerful σ donors above.

As can be readily seen by reference to Figure 1, the bond between palladium and oxygen atom O2 of the trifluoromethanesulfonato ligand is, at 2.271 (7) Å, much weaker than any of the Pd–O bonds cited above. This is due to the combined effects of the very large trans influence of the acyl carbon and the low degree of nucleophilicity of the trifluoromethanesulfonate moiety. In a case involving the trifluoromethanesulfonato ligand bound trans to sp^3 carbon about square-planar gold(III) in *cis*-dimethylgold trifluoromethanesulfonate monohydrate, the Au–O distance was observed to be 2.201 (6) Å.[21] If the crystal radii[22] of 0.82 Å for square-planar Au(III) and 0.78 Å for square-planar Pd(II) are taken as indicative of the relative sizes of these metal ions, the Pd–O distance observed here would have to be approximately 2.15 Å to be similar in strength to that quoted for the gold(III) complex, instead of the 2.271 (7) Å observed. To the best of our knowledge, the Pd–O bond length reported here is the longest such bond length known.

The orientation of the trifluoromethanesulfonato ligand with respect to the Pd–O bond is also somewhat surprising. In the gold(III) compound referred to above,[21] the Au–O–S angle was observed to be 128.7 (2)°. The deviation of this value from the expected tetrahedral angle was there explained as being due to the requirements of hydrogen bonding between the palladium-bound aquo ligand and the trifluoromethanesulfonate oxygen atom. The corresponding angle in the present structure (Pd–O2–S1) is 150.5 (4)°! This very large angle is due to the interaction between hydrogen atoms of the *N*-ethyl groups and the unbound oxygen atoms O3 and O4. A glance at Figure 1 shows that the ethyl groups bound to the two amine nitrogens of the complex are folded back over the metal ion, and, in fact, hydrogen atoms of the terminal methyl groups make van der Waals contacts with the metal. For example, the distances Pd–H3(C9) (=2.8 Å) and Pd–H1 (C7) (=3.1 Å) are approximately equal to the sum of the van der Waals radii for these atoms (H 1.29[23]–1.45[24] Å, Pd 1.6 Å[24]). The position of these hydrogen atoms of the ethyl groups is

Table IV. Least-Squares Planes[a]

(a) Deviations from the Planes

plane 1 ($n = 5$): Pd(II) (0.001), O2 (−0.071), N1 (−0.005), N2 (−0.006), C1 (−0.088), O1 (−0.172), C2 (−0.089), C3 (0.369), S1 (0.590)

plane 2 ($n = 4$): O2 (−0.030), N1 (0.031), N2 (0.047), C1 (−0.040), Pd(II) (0.046), O1 (−0.119), C2 (−0.046), C3 (0.407), S1 (0.628)

(b) Equations of the Planes[b]

plane 1: $A = -0.612, B = 7.252, C = 13.350, D = 3.448$

plane 2: $A = -0.525, B = 7.182, C = 13.358, D = 3.381$

[a] In section (a), numbers in parentheses refer to the distance (Å) of the given atom from the calculated plane. The first n atoms in each case determine the given plane. [b] In the form $Ax + By + Cz = D$.

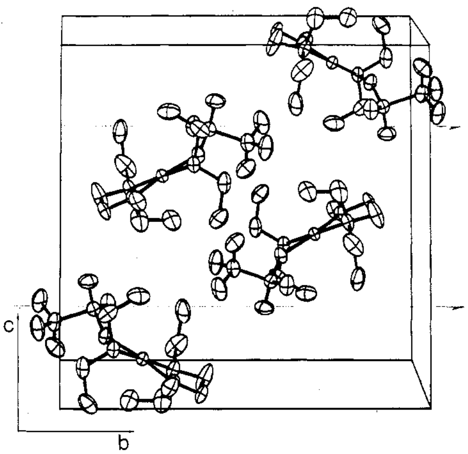

Figure 2. A view of the unit cell contents (down *a*), showing the way in which the twofold screw axis relates molecules within the cell.

such that they also interact strongly with the unbound oxygen atoms O3 and O4 of the trifluoromethanesulfonate anion. For example, O3–H1(C8) = 2.6 Å and O4–H1(C7) = 2.9 Å, which with a van der Waals radius of 1.5 Å[23] for oxygen must essentially involve van der Waals contacts between H and O. This steric interaction is, presumably, the reason that the Pd–O2–S1 angle is so much larger than expected in this complex.

The configuration of the remainder of the trifluoromethanesulfonate ligand is as expected. The S–O, S–C, and C–F distances all agree well with those found in earlier studies involving trifluoromethanesulfonate anions which are both coordinated[21] to transition-metal ions and free.[25] The anion adopts the expected staggered configuration, with the dihedral angle between the planes defined by Pd–O2–S1 and S1–C12–F2 being 170.3°.

Aside from the very long, weak bond to oxygen already discussed, the coordination geometry about the palladium(II) ion is much as expected from earlier work.[2,3] The small bite of the chelating ligand (C1–Pd^{II}–N1 = 85.3 (4)°) results in small but significant deviations from the ideal 90° angles of the square plane. The four coordinating atoms are not perfectly planar (see Table IV), but the small deviations from planarity seen here are also normal for this type of compound.[18-20,26,27] The Pd–C(acyl) bond length of 1.938 (11) Å is the shortest yet seen in this series of compounds, presumably because of the presence of such a weak ligand in the trans position. Bond lengths and angles in the β-aminoacyl and diethylamine ligands are unexceptional, and the Pd–N bond lengths observed agree well with those found in our earlier study.[2] There are no intermolecular contacts of obvious structural significance (see Figure 2).

Thus, the structure of the title compound, while not proving to be three-coordinate as originally hoped for, has once again underscored the very strong σ-donor character and trans influence of the acyl carbon in these β-aminoacylpalladium(II) complexes. On the basis of our earlier studies[2,3] and the present work, the acyl group appears to possess the largest known degree of trans influence for ligands bound to palladium(II).

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Registry No. **1**, 62776-24-3; (trifluoromethanesulfonato)(3-(diethylamino)propionyl)(diethylamine)palladium(II), 69224-99-3.

Supplementary Material Available: Table V, calculated hydrogen atom positions; Table VI, a listing of observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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