

***anti*-Bis(μ -2-ammonioethanethiolato- κ^2 S:S)bis[dichloropalladium(II)] dihydrate**

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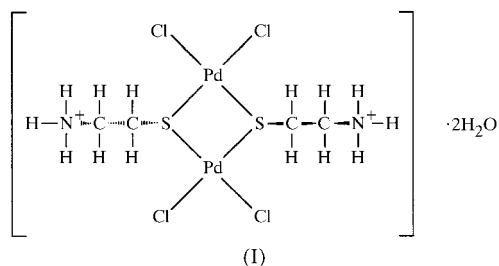
Received 5 June 2001

Accepted 25 September 2001

Each of two square-planar Pd^{II} ions in the title compound, [Pd₂Cl₄(μ -Haet-S)₂] \cdot 2H₂O (Haet = 2-ammonioethanethiolate, C₂H₇NS), which was obtained by rearrangement of [Pd₂{Pd(aet-N,S)₂}₄]⁴⁺ in acidic solution, is coordinated by two bridging S atoms from two Haet ligands and by two terminal Cl atoms, forming the dinuclear structure. Since the complex is situated on a center of symmetry, the two monodentate Haet arms are located on opposite sides of the central Pd₂S₂ square plane, *i.e.* the present complex is the *anti* isomer. The S—C—C—N torsion angle is 177.3 (6) $^\circ$ and some intermolecular hydrogen bonds are observed.

Comment

It has been recognized that the Pd^{II} ion readily forms an S-bridged Pd₂S₂Cl₄ core by reaction with disulfide compounds, such as diphenyl disulfide (Karet & Kostić, 1998). Using the corresponding reaction with cystamine, the dinuclear complex with 2-ammonioethanethiolate (Haet; Efimenko *et al.*, 2000) has been synthesized. This complex exhibits some intramolecular hydrogen bonds involving the ammonio groups of the bridging ligands. On the other hand, during the course of our synthetic investigation of S-bridged polynuclear complexes



containing square-planar [Pd(aet-N,S)₂] units as building blocks (Yamada *et al.*, 2000*a,b*), we found a geometrically different structure of the Haet complex. We describe here, therefore, the crystal structure of [Pd₂Cl₄(μ -Haet-S)₂] \cdot 2H₂O, (I), which occupies a center of symmetry in the unit cell.

The complex molecule in (I) consists of two square-planar Pd atoms, two S-bridging monodentate ligands and four terminal Cl atoms (Fig. 1). The fact that there are no counterions in the crystal implies that the dinuclear complex is neutral, *i.e.* the terminal N atoms of the S-bridging ligands are protonated during the reaction and exist as NH₃⁺ groups. This unusual monodentate coordination mode resulting from the protonation of the aet ligands influences the stereochemistry of the dinuclear complex (see below).

Although the overall S-bridged Pd^{II} dinuclear structure, [Pd₂Cl₄(μ -Haet-S)₂], of the complex in (I) is similar to that of the complex reported by Efimenko *et al.* (2000), notable differences are observed in the geometry for the bridging Haet ligands. The two monodentate Haet arms of the previously reported complex are located on the same side of the central Pd₂S₂ square plane, *i.e.* the complex adopts a *syn* form with a twofold axis through the center of the Pd₂S₂ square plane. On the other hand, in the present complex, the two monodentate Haet arms are located on opposite sides of the central Pd₂S₂ square plane (Fig. 1), *i.e.* the complex adopts an *anti* form with an inversion center at the center of the Pd₂S₂ square plane. According to the differences in the geometry, the two PdS₂Cl₂ planes are bent over the S—S line (dihedral angle = 138 $^\circ$) in the *syn* isomer and adopt a coplanar conformation in the *anti* isomer. The two bridging benzenethiolate ligands in [Pd₂Cl₄(μ -SPh)₂]²⁻ (Karet & Kostić, 1998) are located on the same side of the central Pd₂S₂ square plane, but the Pd₂S₂Cl₄ core is nevertheless essentially planar. Hence, it can be considered that the dihedral angle between two PdS₂Cl₂ planes depends not only on the geometry of the bridging S atoms, but also on weak interactions, such as π - π -stacking or hydrogen-bonding interactions.

The bond distances and angles of the Pd₂S₂Cl₄ core in *syn*- and *anti*-[Pd₂Cl₄(μ -Haet-S)₂] are almost the same (Table 1), although the Pd—S—Pd angle [97.54 (9) $^\circ$] in the *anti* isomer, (I), is somewhat larger than that [91.73 (3) $^\circ$] in the *syn* isomer (Efimenko *et al.*, 2000). Moreover, the Pd—S and Pd—Cl distances are comparable with those in other Pd^{II} complexes, such as [Pd₂Cl₄(μ -SPh)₂]²⁻ (Karet & Kostić, 1998) or [PdCl₂{Co(aet)₂(en)}]⁺ (Konno *et al.*, 1998), which can be regarded as a fixed *anti* form. The Pd \cdots Pd distance [3.423 (1) Å] in the *anti* isomer is considerably longer than that [3.271 (1) Å] in the *syn* isomer; there is no evidence of a Pd—Pd bond in these cases. The bond distances involving the bridging Haet ligands in *syn*- and *anti*-[Pd₂Cl₄(μ -Haet-S)₂] also agree with one another. However, the angles of the Haet arms in these complexes are clearly different, that is, the S—C—C—N torsion angles are 55 $^\circ$ for the *syn* isomer and 177.3 (6) $^\circ$ for the *anti* isomer. Consequently, the S and N atoms take a '*trans* form' with respect to the C—C bond in the *anti* isomer, (I), and a '*cis* form' in the *syn* isomer.

In the present *anti* isomer, no intramolecular hydrogen bonds are observed. This is inconsistent with the fact that the NH₃⁺ group of the Haet ligand in the *syn* isomer is close to both the terminal Cl atom and the bridging S atom [the N \cdots Cl and N \cdots S contact distances are 3.19 (4) and 3.10 (3) Å, respectively; Efimenko *et al.*, 2000]. Alternatively, the NH₃⁺

group in the *anti* isomer is close to the water molecule [the N1...O1 contact distance is 2.81 (1) Å]. Considering that the O1...O1ⁱⁱ contact distance [2.86 (1) Å; symmetry code: (ii)

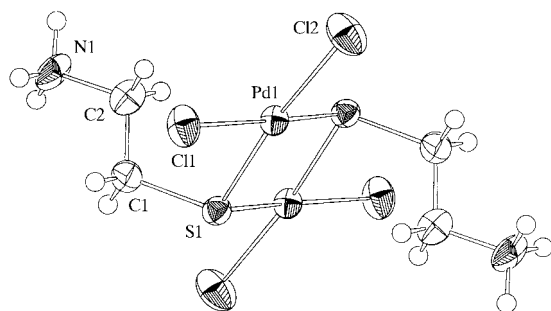


Figure 1

A view of the complex molecule of (I) with the labeling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

$-x + 1, -y + 1, -z]$ is also short, each complex molecule is linked by intermolecular hydrogen bonds through the two water molecules to form a one-dimensional row in the crystal. Further, the NH_3^+ group is close to the Cl atom of the complex molecule in the neighboring row [the N1...Cl1ⁱⁱⁱ contact distance is 3.186 (8) Å; symmetry code: (iii) $x - 1, y, z$]. Accordingly, it has become apparent that the structural differences between the *syn* and *anti* isomers of $[\text{Pd}_2\text{Cl}_4(\mu\text{-Haet-S})_2]$ greatly influence the crystal lattice.

Experimental

An orange solution containing $[\text{Pd}_2\{\text{Pd}(\text{aet})_2\}_4\text{Br}_4 \cdot 6\text{H}_2\text{O}$ (Konno *et al.*, 1994; 0.040 g, 0.024 mmol) in 1.0 mol dm^{-3} HCl (30 ml) was stirred at room temperature overnight. After removing the unreacted materials by filtration, the filtrate was poured onto a gel-filtration column of Sephadex G-10. Two yellow bands were eluted with 1.0 mol dm^{-3} HCl and the first band was concentrated to dryness. The resulting orange powder was redissolved in 1.0 mol dm^{-3} HCl and allowed to stand at room temperature for several days. A small number of orange crystals was collected.

Crystal data

$[\text{Pd}_2\text{Cl}_4(\text{C}_2\text{H}_7\text{NS})_2] \cdot 2\text{H}_2\text{O}$
 $M_r = 544.93$
 Monoclinic, $P2_1/c$
 $a = 7.449$ (1) Å
 $b = 8.941$ (3) Å
 $c = 11.984$ (2) Å
 $\beta = 91.68$ (1)°
 $V = 797.8$ (3) Å³
 $Z = 2$

$D_x = 2.268$ Mg m^{-3}
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 11.2\text{--}14.1^\circ$
 $\mu = 3.17$ mm^{-1}
 $T = 296.2$ K
 Prismatic, orange
 $0.15 \times 0.10 \times 0.08$ mm

Data collection

Rigaku AFC-7S diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.729, T_{\max} = 0.776$
 1970 measured reflections
 1833 independent reflections
 982 reflections with $F^2 > 2\sigma(F^2)$

$R_{\text{int}} = 0.063$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 11$
 $l = -15 \rightarrow 15$
 3 standard reflections every 150 reflections
 intensity decay: 0.1%

Refinement

Refinement on F^2
 $R(F) = 0.044$
 $wR(F^2) = 0.108$
 $S = 0.97$
 1833 reflections
 74 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + [0.03(F_o^2 + 2F_c^2)]^2]$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.11$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.05$ e Å⁻³
 Extinction correction: Zachariasen (1967), type 2, Gaussian isotropic
 Extinction coefficient: 0.0034 (9)

Table 1

Selected geometric parameters (Å, °).

Pd1—Cl1	2.357 (2)	Pd1—S1	2.285 (3)
Pd1—Cl2	2.346 (3)	Pd1—S1 ⁱ	2.267 (2)
Cl1—Pd1—Cl2	93.55 (9)	S1—Pd1—S1 ⁱ	82.46 (9)
Cl1—Pd1—S1	91.62 (9)	Pd1—S1—Pd1 ⁱ	97.54 (9)
Cl1—Pd1—S1 ⁱ	170.40 (9)	Pd1—S1—Cl1	106.8 (3)
Cl2—Pd1—S1	173.35 (9)	Pd1—S1 ⁱ —Cl1 ⁱ	107.3 (3)
Cl2—Pd1—S1 ⁱ	92.94 (9)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

H atoms bonded to C or N atoms were fixed geometrically and allowed to ride on their attached atoms [$\text{C—H} = \text{N—H} = 0.95$ Å; $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C,N})$]. The H atoms of the water molecules were not included in the calculations.

Data collection: *WinAFC* (Rigaku Corporation, 1999); cell refinement: *WinAFC*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

This work was supported by a Grant-in-Aid for Scientific Research (Nos. 12023205 and 11640555) from the Ministry of Education, Science, Sports and Culture, Japan.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1118). Services for accessing these data are described at the back of the journal.

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