

Monoclinic
 $C2/c$
 $a = 17.998 (4) \text{ \AA}$
 $b = 11.627 (2) \text{ \AA}$
 $c = 13.690 (3) \text{ \AA}$
 $\beta = 96.75 (2)^\circ$
 $V = 2844.9 (10) \text{ \AA}^3$
 $Z = 4$
 $D_r = 1.823 \text{ Mg m}^{-3}$
 D_m not measured

Cell parameters from 25 reflections
 $\theta = 11.5\text{--}14.5^\circ$
 $\mu = 5.63 \text{ mm}^{-1}$
 $T = 298 \text{ K}$
 Prism
 $0.50 \times 0.30 \times 0.20 \text{ mm}$
 Red-brown

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: empirical via ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.263$, $T_{\max} = 0.324$
 2506 measured reflections
 2506 independent reflections

1928 reflections with $I_{\text{net}} > 2\sigma(I_{\text{net}})$
 $\theta_{\max} = 25.0^\circ$
 $h = -21 \rightarrow 21$
 $k = 0 \rightarrow 13$
 $l = 0 \rightarrow 16$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R = 0.029$
 $wR = 0.044$
 $S = 2.49$
 1928 reflections
 140 parameters
 H atoms not refined
 $w = 1/[\sigma^2(F) + 0.0001F^2]$
 $(\Delta/\sigma)_{\max} = 0.0002$

$\Delta\rho_{\max} = 0.79 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.65 \text{ e \AA}^{-3}$
 Extinction correction: Larson (1970)
 Extinction coefficient: $2.7 (4) \times 10^4$
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (II)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq} |
|-----|--------------|--------------|---------------|-----------------|
| Pt | 1/4 | 3/4 | 0 | 0.0247 (2) |
| S1 | 0.12444 (11) | 0.76196 (18) | -0.05278 (15) | 0.0350 (10) |
| C2 | 0.0983 (5) | 0.8837 (7) | 0.0178 (6) | 0.043 (5) |
| C3 | 0.1291 (5) | 0.8791 (7) | 0.1239 (7) | 0.045 (5) |
| S4 | 0.22961 (12) | 0.85135 (17) | 0.13845 (14) | 0.0329 (10) |
| C5 | 0.2425 (5) | 0.7543 (7) | 0.2417 (6) | 0.040 (5) |
| C6 | 0.2019 (5) | 0.6393 (8) | 0.2325 (6) | 0.044 (5) |
| S7 | 0.23531 (13) | 0.54148 (18) | 0.14441 (17) | 0.0413 (12) |
| C8 | 0.1499 (5) | 0.4746 (7) | 0.0858 (7) | 0.049 (5) |
| C9 | 0.1132 (5) | 0.5280 (8) | -0.0087 (7) | 0.048 (5) |
| C10 | 0.0770 (5) | 0.6437 (8) | 0.0019 (6) | 0.045 (5) |
| Cl | 0 | 0.3595 (4) | 3/4 | 0.080 (3) |
| OCl | 0.1947 (2) | 0.1620 (4) | 0.0196 (3) | 0.072 (3) |
| O2 | 1 | 1.0263 (8) | 1/4 | 0.068 (7) |
| O3 | 0 | 0.3830 (10) | 1/4 | 0.085 (8) |
| O4 | 0.0695 (4) | 0.1967 (6) | 0.1487 (5) | 0.069 (5) |
| O5 | 0.0686 (5) | 0.1482 (7) | 0.8624 (6) | 0.091 (6) |

Table 4. Selected geometric parameters (\AA , $^\circ$) for (II)

| | | | |
|-----------|-----------|-----------|-----------|
| Pt—S1 | 2.294 (2) | Pt—S7 | 3.159 (2) |
| Pt—S4 | 2.298 (2) | | |
| S1—Pt—S4 | 88.96 (8) | S1—Pt—S7 | 84.73 (7) |
| S1—Pt—S4' | 91.04 (8) | S4—Pt—S7 | 81.03 (6) |
| S1—Pt—S7 | 95.27 (7) | S4—Pt—S7' | 98.97 (6) |

Symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, -z$.

The title structures were solved by the heavy-atom method, subsequent Fourier syntheses based on the heavy atoms revealing the positions of all the non-H atoms. Least-squares

refinement, including anisotropic parameters for the non-H atoms, was performed. H atoms were placed at calculated positions with $U_{\text{iso}}(\text{H}) = U_{\text{eq}}(\text{attached atom}) + 0.01 \text{ \AA}^2$. The absolute values of $\Delta\rho_{\min}$ and $\Delta\rho_{\max}$ for compound (I) were further than 1 e \AA^{-3} from the Pt atom.

For both compounds, data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *NRCVAX DATRD2* (Gabe *et al.*, 1989); program(s) used to solve structures: *NRCVAX SOLVER*; program(s) used to refine structures: *NRCVAX LSTSQ*; molecular graphics: *NRCVAX ORTEP*; software used to prepare material for publication: *NRCVAX TABLES*; computer: DEC-3500.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1253). Services for accessing these data are described at the back of the journal.

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A Tetranuclear Complex of Palladium(II) with Cysteine

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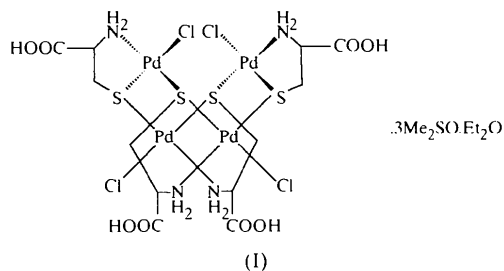
Abstract

The title compound, tetrakis(μ -cysteinato-*N,S,S*)tetrakis-[chloropalladium(II)]-dimethyl sulfoxide-diethyl ether (1/3/1), $[\text{Pd}_4\text{Cl}_4(\mu\text{-C}_3\text{H}_6\text{NO}_2\text{S})_4] \cdot 3(\text{CH}_3)_2\text{SO} \cdot (\text{CH}_3\text{-CH}_2)_2\text{O}$, contains four nearly square-planar units in each of which the palladium(II) ion is bound to two

doubly-bridging thiolate anions from two *N,S*-bidentate cysteinate ligands, the amino group from one of these ligands, and a chloride anion. The two Pd··Pd distances in the pairs that are not bridged by the thiolate ligands are 3.203 (1) and 3.239 (1) Å. If there is any covalent bonding across these distances, it must be very weak.

Comment

The study of palladium(II) complexes with amino acids was spurred by two discoveries. Firstly, that some of these complexes have carcinostatic effects (Rosenberg *et al.*, 1969), and secondly, that palladium(II)-aqua complexes bind to side chains of methionine and histidine in peptides and proteins, and catalyze regioselective hydrolytic cleavage of the adjacent peptide bond (Zhu & Kostic, 1992, 1993, 1994; Zhu *et al.*, 1994; Parac & Kostic, 1996*a,b*; Korneeva *et al.*, 1996; Chen *et al.*, 1996, 1998). The molecular structures of a number of palladium(II) complexes with amino acids have been determined (Pettit & Bezer, 1985; Caubet *et al.*, 1992), but, to our knowledge, all of these complexes were mononuclear. Complexes with cysteine have been studied for some time (Levason & McAuliffe, 1977; Pneumatikakis & Hajilidis, 1979), and a binuclear structure has been proposed on the basis of IR spectra only (Levason & McAuliffe, 1977). We report here what we believe to be the first molecular structure of a polynuclear palladium(II) complex with an amino acid, (I).



The complex lies on a crystallographic twofold axis. The four metal atoms have similar coordination spheres, with somewhat distorted square-planar geometry. Each cysteine amino group coordinates to one of the metal atoms, and each thiolate anion of the cysteine bridges two metal atoms, so that each metal atom has two bridging thiolate ligands. The fourth ligand is a chloride anion. The metal-ligand bond distances are normal. The square-planar units are pairwise parallel. This arrangement is apparently imposed by the structural requirements of the cysteinate ligands. The Pd··Pd distances of 3.203 (1) and 3.239 (1) Å in these pairs correspond to little, if any, covalent bonding. Metal-metal bonding would be accompanied by pyramidal distortion (Aullon *et al.*, 1996), which is absent; the metal atoms lie essentially in the least-squares mean planes of their respective ligands.

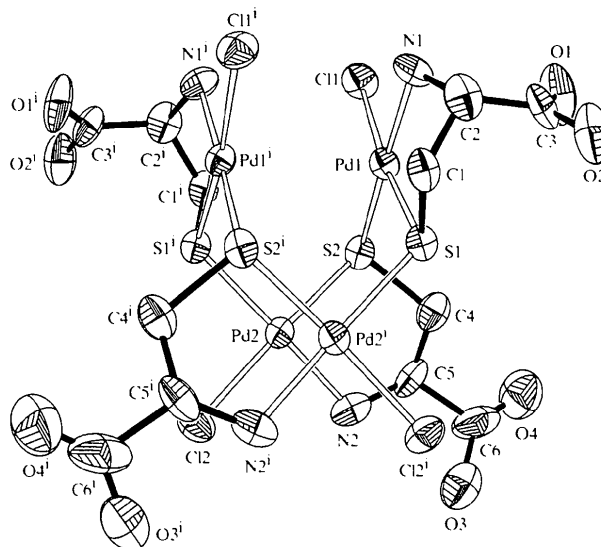


Fig. 1. Plot of the title complex with the atomic numbering scheme. Displacement ellipsoids are shown at the 30% probability level. The H atoms and solvent molecules have been omitted for clarity. [Symmetry code: (i) $-x, -y + 1, z$.]

Experimental

The title compound was prepared by mixing K₂[PdCl₄] (101 mg, 0.31 mmol) and cysteine hydrochloride (48.8 mg, 0.31 mmol) in water (4.0 ml). The yellow precipitate, which formed immediately, was filtered, washed with water and dried *in vacuo*. Diffusion of diethyl ether into the nearly saturated solution of the solid in dimethyl sulfoxide produced the orange single crystals used for the crystallographic analysis.

Crystal data

[Pd₄Cl₄(C₃H₆NO₂S)₄].
3C₂H₆OS.C₄H₁₀O

M_r = 1356.50

Orthorhombic

*P*2₁2₁2

a = 28.048 (2) Å

b = 7.9501 (14) Å

c = 13.6096 (10) Å

V = 3034.7 (6) Å³

Z = 2

D_x = 1.485 Mg m⁻³

D_m not measured

Data collection

Siemens *P4* diffractometer

2θ/ω scans

Absorption correction:

ψ scans (North *et al.*

1968)

T_{min} = 0.238, *T_{max}* = 0.294

5972 measured reflections

5341 independent reflections

3126 reflections with

I > 2σ(*I*)

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 14 reflections

θ = 5.23–9.24°

μ = 1.623 mm⁻¹

T = 293 (2) K

Prism

0.30 × 0.30 × 0.20 mm

Orange

R_{int} = 0.068

θ_{max} = 25°

h = -33 → 33

k = 0 → 9

l = 0 → 16

3 standard reflections

every 97 reflections

intensity decay: 3.89%

RefinementRefinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.067$ $wR(F^2) = 0.238$ $S = 1.204$

5315 reflections

294 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.013$ $\Delta\rho_{\max} = 0.912 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.982 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

Scattering factors from

*International Tables for
Crystallography* (Vol. C)

Absolute structure: Flack

(1983)

Flack parameter = 0.15 (12)

| | | | |
|----------------------------|------------|-------------------------|-------------|
| S2—Pd1...Pd1 ¹ | 93.65 (2) | Pd1—S1—Pd2 ¹ | 115.59 (4) |
| C11—Pd1...Pd1 ¹ | 94.33 (3) | C4—S2—Pd2 | 97.87 (12) |
| N2—Pd2—S2 | 86.26 (9) | C4—S2—Pd1 | 107.08 (12) |
| N2—Pd2—S1 ¹ | 177.68 (8) | Pd2—S2—Pd1 | 114.18 (4) |
| S2—Pd2—S1 ¹ | 93.71 (3) | C2—N1—Pd1 | 110.9 (2) |
| N2—Pd2—C12 | 90.47 (9) | C5—N2—Pd2 | 114.1 (2) |

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

The title structure was solved by direct methods. The three $(\text{CH}_3)_2\text{SO}$ molecule sites are half occupied and the molecules were refined with distance restraints [C—S = 1.550 and S=O = 1.350 Å]. All non-H atoms were refined anisotropically by full-matrix least squares. All the H atoms of the ligands were placed in calculated positions (C—H = 0.96 Å), assigned fixed isotropic displacement parameters ($1.2U_{\text{eq}}$ of the attached atom or $1.5U_{\text{eq}}$ for the methyl groups), and allowed to ride on their respective parent atoms.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1182). Services for accessing these data are described at the back of the journal.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

| | $U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j a_i a_j$. | | | |
|------|---------------------------------------------------------------|--------------|--------------|-----------------|
| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq} |
| Pd1 | 0.054610 (9) | 0.44115 (3) | 0.62038 (2) | 0.05073 (7) |
| Pd2 | -0.015042 (9) | 0.30333 (3) | 0.84788 (2) | 0.04967 (7) |
| C11 | 0.04370 (4) | 0.23907 (12) | 0.49729 (7) | 0.0773 (4) |
| C12 | -0.07260 (4) | 0.34959 (14) | 0.96895 (7) | 0.0806 (4) |
| S1 | 0.07186 (3) | 0.64838 (10) | 0.72932 (7) | 0.0537 (3) |
| S2 | 0.04254 (3) | 0.23913 (10) | 0.73715 (7) | 0.0553 (3) |
| O1 | 0.16188 (8) | 0.5990 (3) | 0.5387 (2) | 0.1141 (13) |
| O2 | 0.16790 (9) | 0.8475 (3) | 0.6015 (2) | 0.1126 (13) |
| O3 | 0.11359 (11) | 0.2149 (4) | 1.0649 (2) | 0.1309 (15) |
| O4 | 0.16228 (10) | 0.1027 (5) | 0.9414 (3) | 0.143 (2) |
| N1 | 0.06839 (11) | 0.6219 (4) | 0.5106 (2) | 0.0744 (11) |
| N2 | 0.03519 (11) | 0.2498 (3) | 0.9545 (2) | 0.0746 (11) |
| C1 | 0.06681 (11) | 0.8317 (3) | 0.6442 (2) | 0.0580 (11) |
| C2 | 0.09355 (11) | 0.7763 (4) | 0.5541 (3) | 0.0756 (14) |
| C3 | 0.14501 (9) | 0.7257 (4) | 0.5622 (3) | 0.0803 (14) |
| C4 | 0.09373 (13) | 0.2466 (5) | 0.8210 (3) | 0.0796 (15) |
| C5 | 0.08023 (11) | 0.1644 (5) | 0.9151 (2) | 0.0849 (15) |
| C6 | 0.12692 (11) | 0.1568 (6) | 0.9785 (2) | 0.133 (2) |
| O5 | 0 | 0 | 1.0940 (2) | 0.104 (2) |
| C7 | 0.02891 (9) | -0.0781 (3) | 1.1756 (2) | 0.125 (2) |
| C8 | 0.06065 (12) | -0.1936 (4) | 1.2375 (2) | 0.192 (3) |
| S3† | 0.23799 (6) | 0.6374 (2) | 0.8840 (2) | 0.1434 (11) |
| C10† | 0.20028 (7) | 0.5145 (2) | 0.8435 (3) | 0.107 (4) |
| C9† | 0.23612 (13) | 0.7869 (2) | 0.8137 (2) | 0.168 (5) |
| O6† | 0.27960 (7) | 0.5638 (4) | 0.8906 (4) | 0.192 (4) |
| S4† | 0.28494 (5) | 0.6677 (3) | 0.57352 (12) | 0.1180 (11) |
| S5† | 0.14506 (6) | -0.2957 (2) | 1.2616 (2) | 0.1459 (14) |
| O7† | 0.25841 (8) | 0.7733 (3) | 0.6281 (2) | 0.0523 (13) |
| C12† | 0.33827 (6) | 0.7083 (7) | 0.5939 (2) | 0.069 (2) |
| O8† | 0.11374 (9) | -0.2978 (5) | 1.3349 (2) | 0.153 (4) |
| C11† | 0.27996 (10) | 0.7120 (9) | 0.46314 (12) | 0.144 (5) |
| C14† | 0.17463 (11) | -0.4565 (2) | 1.2580 (5) | 0.194 (7) |
| C13† | 0.18195 (9) | -0.1546 (2) | 1.2785 (5) | 0.169 (6) |

† Site occupancy = 0.50.

Table 2. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|---------------------------|-------------|-----------------------------------------|-------------|
| Pd1—N1 | 2.108 (3) | Pd2—N2 | 2.067 (3) |
| Pd1—S1 | 2.2686 (9) | Pd2—S2 | 2.2671 (9) |
| Pd1—S2 | 2.2847 (9) | Pd2—S1 ¹ | 2.3000 (9) |
| Pd1—C11 | 2.3411 (10) | Pd2—C12 | 2.3359 (10) |
| Pd1...Pd1 ¹ | 3.2031 (5) | Pd2...Pd2 ¹ | 3.2389 (7) |
| N1—Pd1—S1 | 85.92 (8) | S2—Pd2—C12 | 175.31 (4) |
| N1—Pd1—S2 | 177.54 (9) | S1 ¹ —Pd2—C12 | 89.41 (3) |
| S1—Pd1—S2 | 95.02 (3) | N2—Pd2...Pd2 ¹ | 91.21 (8) |
| N1—Pd1—C11 | 89.14 (8) | S2—Pd2...Pd2 ¹ | 91.82 (2) |
| S1—Pd1—C11 | 173.66 (4) | S1 ¹ —Pd2...Pd2 ¹ | 91.11 (2) |
| S2—Pd1—C11 | 89.77 (3) | C12—Pd2...Pd2 ¹ | 91.61 (3) |
| N1—Pd1...Pd1 ¹ | 88.63 (8) | C1—S1—Pd1 | 98.37 (10) |
| S1—Pd1...Pd1 ¹ | 89.53 (2) | C1—S1—Pd2 ¹ | 104.61 (10) |

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