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Structure of *cyclo*-Hexakis[*bis*- μ -(methoxycarbonylmethylthiolato)-palladium(II)], [Pd(SCH₂COOCH₃)₂]₆

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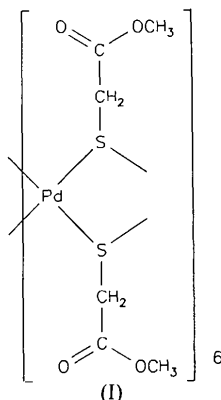
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Abstract

The title compound, [Pd(C₃H₅O₂S)₂]₆, results from the reaction of PdCl₄²⁻ and thioglycolic acid in CH₃OH. It forms a centrosymmetric hexameric structure of a cyclic ribbon in which the square-planar-coordinated Pd²⁺ ions are bridged by the S atoms of the deprotonated thioglycolic acid methyl esters. The Pd—S distances are in the range 2.309 (1)–2.324 (1) Å.

Comment

In connection with our attempts to use thioglycolic acid as a ligand in metal complexes we investigated the reaction of thioglycolic acid with PdCl₄²⁻ and obtained the new hexameric complex (I).



In the hexanuclear complex (I), the Pd^{II} centres are bridged by the S atoms of the deprotonated thiolate group of the thioglycolic acid methyl ester ligand, SCH₂COOCH₃⁻, forming a centrosymmetric cyclic ribbon of PdS₄ groups (Fig. 1). The coordination of the Pd²⁺ ions is approximately square planar with a maximum deviation from the best planes through the PdS₄ groups of 0.169 (1) Å (S2 in the coordination plane of Pd2) and bond angles S—Pd—S between 81.74 (5) and 98.56 (5)° (Table 2). The Pd—S distances within the symmetrical Pd—S—Pd bridges are in the narrow range 2.309 (1)–2.324 (1) Å and correspond to covalent single bonds. The PdS₄ coordination planes forming the cyclic ribbon are inclined to each other by 113.47 (3)–124.36 (4)°, resulting in Pd...Pd distances of 3.0495 (6)–3.1439 (6) Å. Hexa-

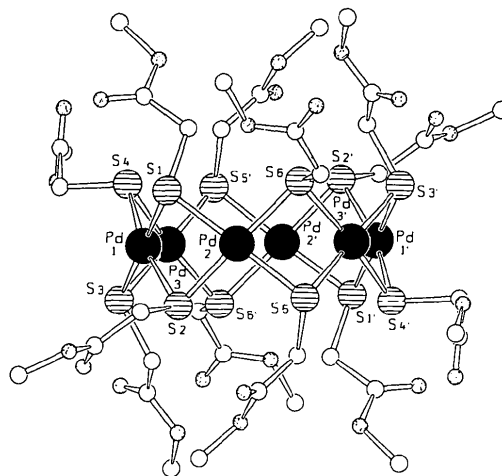


Fig. 1. A perspective view of [Pd(SCH₂COOCH₃)₂]₆ with atomic numbering.

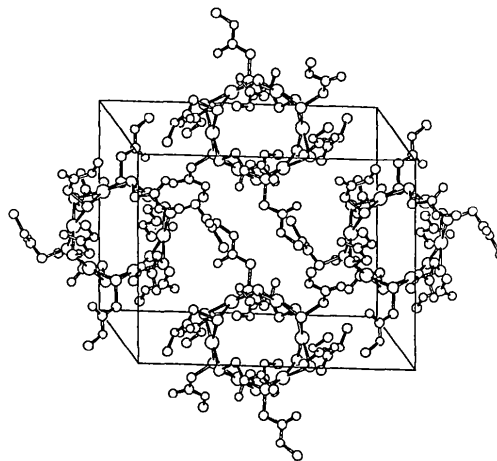


Fig. 2. Packing diagram.

nuclear cyclic ribbons of similar structure have been observed for the Ni^{II} complexes [Ni(SR)₂]₆ with R = Et and CH₂CH₂OH, and [Ni{S(CH₂)₃NH(CH₃)₂}₂]₆¹²⁺. In addition, cyclic Ni^{II} complexes [Ni(SR)₂]_n with n = 4, 5, 7 and 8 are known. Complexes of this type have been reviewed by Krebs & Henkel (1991).

The hexanuclear complexes are stacked along [100] to form columns (Fig. 2) which are arranged in a hexagonal rod packing motif (O'Keeffe & Andersson, 1977).

Experimental

Crystal data

[Pd(C₃H₅O₂S)₂]₆

M_r = 1899.98

Monoclinic

P2₁/c

a = 12.878 (5) Å

b = 19.311 (9) Å

c = 14.387 (8) Å

β = 112.56 (4)°

V = 3304.1 Å³

Z = 2

D_x = 1.910 Mg m⁻³

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 9.08–17.64°

μ = 2.0090 mm⁻¹

T = 293 K

Lozenge

0.20 × 0.10 × 0.05 mm

Orange

Data collection

Enraf-Nonius CAD-4 diffractometer

ω/θ scans

Absorption correction:

empirical (DIFABS;

Walker & Stuart, 1983)

T_{min} = 0.895, T_{max} =

1.085

5847 measured reflections

5295 independent reflections

4100 observed reflections

[I > 3σ(I)]

R_{int} = 0.017

(sinθ/λ)_{max} = 0.595 Å⁻¹

θ_{max} = 25°

h = 0 → 15

k = 0 → 23

l = -17 → 17

3 standard reflections

frequency: 60 min

intensity variation: none

Refinement

Refinement on F

R = 0.033

wR = 0.043

S = 1.657

4100 reflections

352 parameters

H-atom parameters not refined

w = 1/σ²

(Δ/σ)_{max} = 0.01

Δρ_{max} = 0.898 e Å⁻³

Δρ_{min} = -1.035 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Data collection: CAD-4 SDP (Frenz, 1978). Molecular graphics: SCHAKAL (Keller, 1990). The structure was solved by direct methods (SHELXS86; Sheldrick, 1986) and refined with anisotropic displacement parameters. The H atoms were calculated at ideal positions and used for the calculation of the structure factors only.

Table 1. Positional parameters and equivalent isotropic displacement parameters (Å²)

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B _{eq}
Pd1	0.54416 (3)	0.09976 (2)	0.68976 (3)	2.915 (9)
Pd2	0.54849 (3)	-0.06267 (2)	0.70109 (3)	2.889 (9)
Pd3	0.49542 (3)	0.16252 (2)	0.48273 (3)	2.794 (9)
S1	0.6795 (1)	0.02136 (8)	0.7836 (1)	3.52 (3)
S2	0.4246 (1)	0.01964 (8)	0.7153 (1)	3.23 (3)
S3	0.4093 (1)	0.17837 (7)	0.5958 (1)	3.12 (3)
S4	0.6560 (1)	0.16506 (8)	0.6298 (1)	3.53 (3)
S5	0.4175 (1)	-0.14907 (8)	0.6302 (1)	3.40 (3)
S6	0.6645 (1)	-0.13580 (8)	0.6564 (1)	3.14 (3)
O11	0.9315 (4)	0.0846 (3)	0.7187 (5)	9.3 (2)
O12	0.8805 (4)	0.1169 (3)	0.8423 (4)	7.9 (2)
O21	0.3980 (5)	0.0726 (3)	0.9644 (3)	8.4 (1)
O22	0.3290 (5)	0.1182 (3)	0.8161 (4)	8.3 (1)
O31	0.0953 (4)	0.1446 (3)	0.4276 (5)	8.7 (2)
O32	0.1985 (4)	0.2381 (2)	0.4485 (4)	5.5 (1)
O41	0.6343 (9)	0.3334 (5)	0.5529 (6)	19.2 (3)
O42	0.7951 (7)	0.2922 (4)	0.6140 (6)	17.5 (3)
O51	0.1508 (4)	-0.0353 (3)	0.5784 (4)	6.9 (2)
O52	0.2432 (4)	-0.1017 (3)	0.7103 (4)	6.3 (1)
O61	0.8306 (5)	-0.1421 (3)	0.8600 (5)	9.6 (2)
O62	0.8703 (4)	-0.2515 (3)	0.8578 (4)	7.5 (2)
C11	0.7955 (5)	0.0184 (3)	0.7390 (5)	4.3 (2)
C12	0.8720 (6)	0.0780 (4)	0.7762 (6)	6.1 (2)
C13	1.0089 (8)	0.1428 (6)	0.741 (1)	15.9 (5)
C21	0.4461 (5)	0.0180 (3)	0.8464 (4)	4.1 (1)
C22	0.3847 (5)	0.0758 (3)	0.8718 (4)	4.4 (2)
C23	0.3559 (9)	0.1293 (5)	1.0066 (7)	11.7 (3)
C31	0.2724 (5)	0.1375 (3)	0.5511 (5)	3.8 (1)
C32	0.1876 (5)	0.1810 (3)	0.4715 (5)	4.4 (2)
C33	0.0091 (8)	0.1800 (7)	0.347 (1)	16.8 (4)
C41	0.6682 (6)	0.2527 (4)	0.6779 (5)	5.1 (2)
C42	0.6953 (8)	0.2996 (5)	0.6098 (7)	12.2 (3)
C43	0.702 (2)	0.3539 (9)	0.481 (1)	23.3 (6)
C51	0.2817 (5)	-0.1087 (4)	0.5609 (5)	4.7 (2)
C52	0.2260 (5)	-0.0833 (4)	0.6263 (5)	5.0 (2)
C53	0.0939 (8)	-0.0020 (5)	0.6347 (9)	9.3 (3)
C61	0.6971 (5)	-0.2112 (3)	0.7378 (5)	4.3 (2)
C62	0.8085 (5)	-0.2010 (4)	0.8232 (5)	5.1 (2)
C63	0.936 (2)	-0.132 (1)	0.940 (1)	23.9 (8)

Table 2. Selected geometry (Å, °)

Pd1—S1	2.312 (1)	Pd3—S6 ⁱ	2.313 (1)
Pd1—S2	2.309 (1)	S1—C11	1.839 (6)
Pd1—S3	2.312 (1)	S2—C21	1.800 (5)
Pd1—S4	2.316 (1)	S3—C31	1.809 (5)
Pd2—S1	2.313 (1)	S4—C41	1.813 (6)
Pd2—S2	2.316 (1)	S5—C51	1.823 (6)
Pd2—S5	2.313 (1)	S6—C61	1.814 (5)
Pd2—S6	2.318 (1)	Pd1...Pd2	3.1402 (5)
Pd3—S3	2.314 (1)	Pd1...Pd3	3.0495 (5)
Pd3—S4	2.324 (1)	Pd2...Pd3 ⁱ	3.1439 (6)
Pd3—S5 ⁱ	2.316 (1)		
S1—Pd1—S2	82.39 (5)	S3—Pd3—S6 ⁱ	97.49 (5)
S1—Pd1—S4	97.85 (6)	S4—Pd3—S5 ⁱ	98.05 (6)
S2—Pd1—S3	97.81 (5)	S5 ⁱ —Pd3—S6 ⁱ	82.96 (5)
S3—Pd1—S4	81.95 (5)	Pd1—S1—Pd2	85.51 (4)
S1—Pd2—S2	82.23 (5)	Pd1—S2—Pd2	85.54 (5)
S1—Pd2—S6	98.56 (5)	Pd1—S3—Pd3	82.47 (4)
S2—Pd2—S5	97.10 (5)	Pd1—S4—Pd3	82.18 (4)
S5—Pd2—S6	82.92 (5)	Pd2—S5—Pd3 ⁱ	85.57 (6)
S3—Pd3—S4	81.74 (5)	Pd2—S6—Pd3 ⁱ	85.51 (5)

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

The title complex (I) results from the reaction of PdCl₄²⁻ with thioglycolic acid, HSCH₂COOH, and recrystallization in CH₃OH-acetone with a small amount of aqueous HClO₄.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71374 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1051]

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Structure of a Tripotassium Pyrroloquinoline Quinone Salt

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Abstract

In $3K^+ \cdot C_{14}H_3N_2O_8^{3-} \cdot 4H_2O$, all three carboxyl groups of pyrroloquinoline quinone (PQQ; 4,5-dihydro-4,5-dioxo-1*H*-pyrrolo[2,3-*f*]quinoline-2,7,9-tricarboxylic acid) are in anion form to neutralize the three potassium cations. Each of the three potassium ions is closely coordinated to polar atoms of the PQQ^{3-} ions and waters of crystallization. Noticeable structural features within the crystal unit are the stacking of the PQQ^{3-} ions and the extensive network of hydrogen-bonding interactions.

Comment

PQQ is known as the coenzyme of a novel class of oxidoreductases (Duine, Frank Jzn & Verwiël, 1980; Duine & Frank Jzn, 1981). To understand its biological behavior, it is important to reveal the molecular structure and atomic charge distribution in the molecule. The structures of the 5-(2-oxopropyl) (Salisbury, Forrest, Cruse & Kennard, 1979; Cruse, Kennard & Salisbury, 1980) and 5-(2,4-dinitrophenylhydrazine) adducts of PQQ (van Koningsveld, Jansen, Jongejan, Frank Jzn & Duine, 1985) and the PQQ disodium salt (Ishida *et al.*, 1989) have been reported already. Ishida *et al.* (1989) demonstrated that the PQQ molecule possesses two sodium-binding sites. This is the first report on the crystal structure of the trianionic form of PQQ.

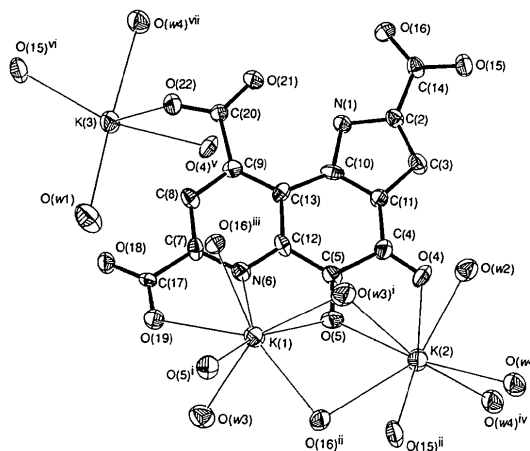


Fig. 1. Perspective view of $K_3(C_{14}H_3N_2O_8) \cdot 4H_2O$ indicating the atom labeling. H atoms are omitted.

Fig. 1 shows a perspective drawing of the structure and indicates the atom-numbering scheme. In an earlier structural study of the PQQ disodium salt, PQQ formed dianions (PQQ^{2-}) (Ishida *et al.*, 1989). The charge on PQQ probably depends on the synthetic conditions. Since the present PQQ crystals were prepared under neutral conditions, the PQQ molecule formed trianions (PQQ^{3-}) with three carboxylate anion substituents. A comparison of the structures of PQQ^{3-} and PQQ^{2-} reveals very similar bond lengths and angles. The carboxylate C(2)—C(14) bond length of 1.498 (8) Å is also significantly shorter than the other two carboxylate C—C bond lengths [1.531 (8) and 1.552 (8) Å for C(7)—C(17) and C(9)—C(20), respectively]. This fact presumably results from the energetic stabilization of the carboxylate group through a resonance effect with the respective aromatic rings (Ishida *et al.*, 1989). Differences between PQQ^{2-} and PQQ^{3-} are manifest in the C(4)=O(4) bond lengths [1.204 (5) and 1.205 (6) Å in PQQ^{2-} (Ishida *et al.*, 1989) and 1.234 (8) Å in PQQ^{3-}]. The longer bond length in