

The Structure of Dichlorobis[μ -(3-dimethylamino-1-propanethiolato)- μ -*S,N*]-dipalladium(II), (I) [Pd₂(C₅H₁₂NS)₂Cl₂], and *ac, bd, eg, fh*-Tetrakis[μ -(3-piperidinemethanethiolato)- μ -*S,N*]-tripalladium(II) Dichloride Dihydrate, (II) [Pd₃(C₆H₁₂NS)₄]Cl₂·2H₂O

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Abstract. (I): $M_r = 520.15$, monoclinic, $P2_1/n$, $a = 7.207$ (2), $b = 20.616$ (4), $c = 5.854$ (1) Å, $\beta = 96.05$ (1)°, $V = 864.9$ (6) Å³, $Z = 2$, $D_x = 2.00$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 2.553$ mm⁻¹, $F(000) = 512$, 298 K, $R = 0.060$ for 1492 reflections. (II): $M_r = 947.07$, triclinic, $P\bar{1}$, $a = 12.666$ (7), $b = 10.595$ (6), $c = 6.572$ (5) Å, $\alpha = 98.30$ (2), $\beta = 97.04$ (2), $\gamma = 99.84$ (2)°, $V = 850$ (2) Å³, $Z = 1$, $D_x = 1.85$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.958$ mm⁻¹, $F(000) = 490$, 298 K, $R = 0.071$ for 1879 reflections. (I) was solved by direct methods, using *MULTAN* and *DIRDIF*, (II) by the heavy-atom method. The four-membered Pd, S, Pd, S rings have a *syn-exo* conformation, with dihedral angles between the S, Pd, S planes of 154.4 (2) and 133.0 (3)° for (I) and (II), respectively.

Introduction. Synthesis of compounds with di- μ -thiolato-(metal)₂ was carried out by the Department of Inorganic Chemistry of the Free University of Barcelona. In order to elucidate the geometry of the title compounds, X-ray analyses were carried out.

Experimental. Yellow-orange elongated prisms, 0.3 × 0.1 × 0.1 mm (I), 0.7 × 0.2 × 0.2 mm (II), Philips PW-1100 diffractometer, graphite monochromator, ω scan, cell parameters from 25 independent reflections, no significant variation of intensity in three standard reflections, measured each hour; (I) 1518 independent reflections with $\theta \leq 30^\circ$, range of hkl : $\bar{1}0$ to 10, 0 to 25 and 0 to 7, 1492 with $I \geq 2.5\sigma(I)$; (II) 2008 with $\theta \leq 25^\circ$, range of hkl : $\bar{1}4$ to 14, $\bar{1}2$ to 12 and 0 to 8, 1879 with $I \geq 2.5\sigma(I)$; Lp correction, absorption ignored; (I) direct methods [*MULTAN*80, Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson (1980)

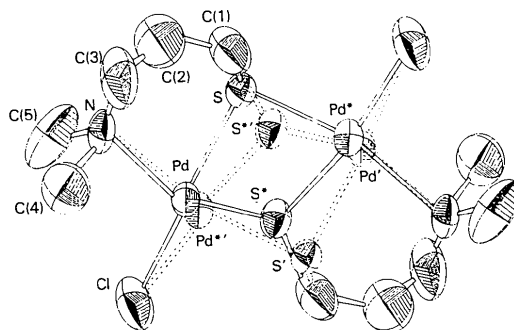
and *DIRDIF*, Beurskens, Bosman, Doesburg, Gould, Van den Hark & Prick (1980)], (II) Patterson (*SHELX76*, Sheldrick, 1976); anisotropic full matrix, $w||F_o| - |F_c||^2$ minimized (*SHELX76*), anomalous-scattering factors for all atoms (*International Tables for X-ray Crystallography*, 1974); hydrogen atoms of (I) from ΔF synthesis; final $R = 0.060$ (I) and 0.071(II), $R_w = 0.063$ (I) and 0.076(II), $\Delta/\sigma = 2.8$ in x of H(C1) (I) and 1.8 in U_{11} of O(W) (II), max. and min. $\Delta\rho$ excursions in final ΔF synthesis 0.1 and -0.3 eÅ⁻³, respectively, in (I) and 0.2 and -0.2 eÅ⁻³ in (II), $w = [\sigma^2(F_o) + k|F_o|^2]^{-1}$, $k = 0.0127$ (I) and 0.0064(II); Digital VAX-750.†

Discussion. Systematic extinctions and density measurements indicated $P2_1/n$ with $Z = 2$ for (I). This would imply a Pd and S planar ring, which does not correspond to other results from the literature. As Fourier synthesis from *DIRDIF* revealed double peaks with equal height for both Pd and S atoms, their positions were considered to be disordered; significant differences between their temperature coefficients were not observed during the refinement (Table 1). The distances between disordered atoms are 0.81 (1) Å for Pd...Pd* and 1.935 (3) Å for S...S* atoms. The ordered atoms of (I) have higher values for anisotropic thermal coefficients (range of B_{eq} 4.8–8.7 Å²), which shows a slight disorder for these atoms; it was not possible to resolve two maxima from difference or

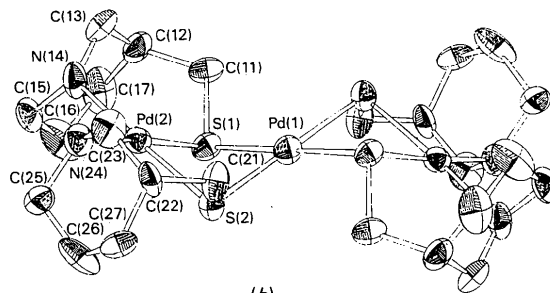
† Lists of structure factors, anisotropic thermal parameters, some bond distances and angles and H-atom parameters for (I) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38818 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fourier syntheses. The disorder consists of two localizations for the PdSPdS ring, according to the distances and angles between peaks (Table 2, Fig. 1).

The Pd atom of each structure is linked to four atoms in a nearly planar fashion [largest deviation of atom from mean plane is 0.02 (1) Å]. The Pd–S bond distances are slightly shorter [mean values: 2.279 (6) Å for (I) and 2.305 (15) Å for (II)] than values observed in the literature [mean value: 2.320 (8) Å, range: 2.301 (7)–2.432 (7) Å] (Ahmed, Itoh, Matsuda, Ueda, Ishii & Ibers, 1977; Chen & Fackler, 1978; Fenn & Segrott, 1972; Fackler, 1976; Bonamico, Dessy &



(a)



(b)

Fig. 1. ORTEP (Johnson, 1965) drawings of (a) molecule of (I) and (b) cation of (II).

Fares, 1977; Piovesana, Sestili, Bellito, Flamini, Tomassini, Zanazzi & Zanzari, 1977; Girling & Amma, 1976; Pope & Boeyens, 1976; Fowler & Griffiths, 1978). The Pd–Cl and Pd–N bond distances are within the ranges observed in the papers of Fowler & Griffiths (1978). The differences observed in (I) are assigned to the disorder of these atoms.

The four-membered rings have a *syn-exo* conformation, with dihedral angles between the S₂PdS₂ planes of 154.4 (2)° in (I) and 133.0 (3)° in (II). These dihedral angles are flatter than those observed in the literature (131.8°, Fackler, 1976), which helps to explain the shortening of Pd–S distances. Moreover, this flattening reduces the S...S bite distances [2.929 (4) in (I), 2.982 (6) in (II) and 3.05 (8) Å in the literature].

The piperidine and the Pd,S,C₃N rings have chair conformations, while the latter type of ring has boat and chair conformations in tetrakis(3-amino-1-propanethiolato)trinickel(II) chloride (Briansó, Perucaud, Suades & Barrera, 1980). The crystal structures consist of discrete molecules or ions linked by van der Waals interactions and, in (II), by ionic forces. The shortest interionic distances are Cl...N(14) 3.237 (7) and Cl...N(24) 3.150 (7) Å.

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Table 1. Positional parameters ($\times 10^4$) for (I) and (II)

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{Å}^2)$
(I)C₁₀H₂₄Cl₂N₂Pd₂S₂				
Pd	-542 (2)	812 (1)	-234 (2)	3.2 (2)
Pd*	732 (2)	-703 (1)	-1062 (2)	3.3 (2)
Cl	-3218 (5)	1328 (1)	-1088 (5)	6.5 (6)
S	2180 (5)	253 (2)	-117 (6)	3.4 (6)
S*	-1404 (6)	3 (2)	-2819 (6)	3.6 (6)
C(1)	3417 (16)	331 (6)	2387 (28)	8 (2)
C(2)	3866 (26)	972 (7)	3420 (28)	8 (2)
C(3)	2179 (25)	1357 (6)	-5996 (29)	9 (2)
N	698 (11)	1545 (3)	-7745 (12)	4 (1)
C(4)	-599 (21)	1896 (7)	-6435 (26)	7 (2)
C(5)	1359 (23)	1997 (8)	637 (22)	8 (6)
(II)C₂₄H₄₈N₄Pd₃S₄·2Cl₂·2H₂O				
Pd(1)	0	0	0	3.1 (3)
Pd(2)	2009 (1)	1345 (1)	8001 (2)	2.7 (2)
Cl	4549 (4)	7387 (6)	829 (14)	8.3 (9)
S(1)	-763 (3)	568 (4)	2944 (6)	2.9 (6)
C(11)	-1485 (14)	1905 (17)	2586 (28)	4 (3)
C(12)	-2542 (13)	1776 (17)	3647 (28)	4 (3)
C(13)	-3466 (13)	654 (20)	2446 (30)	4 (2)
N(14)	-3301 (12)	-593 (14)	3045 (22)	4 (2)
C(15)	-3298 (15)	-555 (20)	5370 (24)	4 (2)
C(16)	-2398 (20)	442 (21)	6577 (27)	6 (5)
C(17)	-2347 (18)	1812 (21)	6008 (31)	5 (3)
S(2)	-546 (3)	-2043 (4)	838 (6)	3.0 (6)
C(21)	-1078 (14)	-3206 (17)	-1541 (27)	4 (2)
C(22)	-2048 (14)	-4314 (16)	-1351 (26)	3 (3)
C(23)	-3050 (16)	-3862 (20)	-1020 (26)	4 (2)
N(24)	-3055 (11)	-3172 (14)	1109 (20)	4 (2)
C(25)	-2883 (14)	-4102 (18)	2637 (27)	4 (2)
C(26)	-1832 (19)	-4534 (17)	2521 (28)	5 (2)
C(27)	-1710 (13)	-5147 (15)	227 (26)	4 (2)
O	4737 (21)	6260 (21)	5246 (36)	10 (5)

Table 2. Bond lengths (Å) and angles (°) for (I) and (II)

	(I)		(II)
Pd–S	2.270 (3)	Pd(1)–S(1)	2.315 (4)
Pd–S*	2.294 (3)	Pd(1)–S(2)	2.322 (4)
Pd–Cl	2.213 (3)		
Pd–N	2.220 (5)		
Pd*–S'	2.271 (3)	Pd(2)–S(1)	2.299 (4)
Pd*–S**	2.282 (3)	Pd(2)–S(2)	2.283 (4)
Pd*–Cl	2.445 (3)	Pd(2)–N(14)	2.086 (6)
Pd*–N	2.101 (5)	Pd(2)–N(24)	2.110 (6)
S...S*	2.929 (4)	S(1)–S(2)	2.982 (6)
Pd...Pd*	3.305 (1)	Pd(1)–Pd(2)	3.217 (1)
S–Pd–S*	79.8 (1)	S(1)–Pd(1)–S(2)	80.0 (1)
S*–Pd–Cl	91.8 (1)	S(1)–Pd(1)–S(2')	100.0 (1)
Cl–Pd–N	95.9 (2)		
S–Pd–N	92.2 (2)		
Pd–S–Pd*	93.4 (1)	Pd(1)–S(1)–Pd(2)	88.4 (1)
Pd–S*–Pd*	92.5 (1)	Pd(1)–S(2)–Pd(2)	88.6 (1)
S'–Pd*–S**	80.1 (1)	S(1)–Pd(2)–S(2)	81.2 (1)
S'–Pd*–Cl'	92.2 (1)	S(1)–Pd(2)–N(14)	95.6 (5)
S**–Pd*–N'	95.3 (2)	S(2)–Pd(2)–N(24)	94.8 (5)

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