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## The Structure of 2,2'-Dimercaptodiethylsulphidepalladium(II): A Trimeric Molecule Containing Bridging Sulphur Atoms

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2,2'-Dimercaptodiethylsulphidepalladium(II) crystallizes in the monoclinic system, space group  $P2_1/c$ ; with lattice constants  $a = 10.69 \pm 0.05$ ,  $b = 24.40 \pm 0.13$  and  $c = 9.44 \pm 0.05$  Å,  $\beta = 111.5 \pm 0.5^\circ$ . The intensities of the three-dimensional equi-inclination Weissenberg data were estimated visually and the structure was solved by Patterson and Fourier techniques. Refinement of atomic parameters was carried out by difference Fourier methods and full-matrix least-squares procedures. The molecules are trimeric with a formula unit  $\text{Pd}_3\text{S}_9\text{C}_{12}\text{H}_{24}$ . Each palladium atom is surrounded by four sulphur atoms in approximately square-planar arrangement. The three sulphur atoms of one ligand molecule form three corners of each square and the squares are completed by one thiol sulphur of each ligand molecule being shared by two palladium atoms, forming a sulphur bridge. The molecule is not flat but bent at the bridging atoms so that the three squares are inclined towards each other and the molecule may be regarded as basin-shaped. There is considerably less strain in this trimeric structure than in the corresponding dimeric 2,2'-dimercaptodiethylsulphidenickel(II).

### Introduction

The ligand 2,2'-dimercaptodiethylsulphide has been shown to form complexes with a variety of metals including palladium(II) (Mathias, 1946). Apart from the nickel complex these compounds are extremely insoluble, which led Harley-Mason (1952) to suggest polymeric structures for these molecules involving bridging sulphur atoms.

Spectroscopic and magnetic studies of some of these complexes (Barclay, McPartlin & Stephenson, 1968) were consistent with sulphur-bridged molecules and a recent X-ray crystal structure analysis (Barclay, McPartlin & Stephenson, 1969) on the nickel(II) compound confirmed the existence of bridging sulphur atoms in a dimeric molecule of formula  $\text{Ni}_2\text{S}_6\text{C}_8\text{H}_{16}$ .

X-ray powder photographs showed that the palladium complex is not isomorphous with the dimeric nickel complex. This and the very low solubility of the

palladium compound suggested that there may be more than two palladium atoms in the polymeric molecule.

### Experimental

Crystals of 2,2'-dimercaptodiethylsulphidepalladium(II) were very difficult to grow and the best results were obtained by taking a solution of potassium tetrachloropalladate in water and acetone (at  $0^\circ\text{C}$ ) and slowly adding, with stirring, a solution of the ligand and sodium acetate in water and acetone (at  $0^\circ\text{C}$ ). The precipitate which formed slowly during the next 10 hours was then alternately boiled with the solution for two hours followed by cooling at  $0^\circ\text{C}$  overnight. After some days the precipitate looked crystalline and yielded thin, fragile, orange plates of irregular shape. The unit-cell dimensions were obtained from zero level precession photographs taken with Mo  $K\alpha$  radiation.

Density measurements indicated that there were twelve monomeric units of composition  $\text{PdS}_3\text{C}_4\text{H}_8$  in the unit-cell. As there are four general equivalent positions in the space group  $P2_1/c$  (determined uniquely

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Table 1. Observed and calculated structure factors for 2,2'-dimercaptodiethylsulphidepalladium(II)

Scale: ½ absolute. The columns are: the index  $l$ ,  $|F_o|$  and  $F_c$ . Unobserved data have been omitted.

$l$	$ F_o $	$F_c$	$l$	$ F_o $	$F_c$	$l$	$ F_o $	$F_c$	$l$	$ F_o $	$F_c$
0	0	0	3	70.6	-84.6	1	13	0	0	25.9	-26.9
4	139.4	-182.1	5	33.8	-41.8	-5	74.6	52.7	1	102.5	105.5
-8	33.8	-34.8	1	2	0	-3	47.8	36.8	2	70.6	-55.7
-7	39.9	-22.1	-3	14.0	-14.9	-2	25.9	-33.8	3	35.8	-33.8
2	17.7	17.9	-2	50.6	60.7	0	52.7	39.8	4	51.7	-38.8
3	25.9	-28.1	0	46.8	-46.8	1	121.3	-120.4	5	43.6	-40.8
4	24.9	-36.8	1	07.7	65.8	2	83.6	76.5	-5	32.8	25.9
5	27.9	-46.8	2	23.9	-30.8	3	71.6	-59.7	-4	22.5	-23.6
1	157.2	-158.2	3	17.2	-19.9	5	50.7	36.8	-3	117.4	-87.6
2	61.7	-54.7	1	5	0	1	14	0	-2	61.7	60.7
3	29.0	-26.4	-5	57.7	54.7	-3	49.7	-40.6	3	48.8	48.8
4	31.6	-41.8	-4	112.4	113.4	-2	54.7	-46.8	2	39.9	22.9
5	27.9	-32.8	-3	32.8	-47.8	0	74.6	-71.6	3	46.8	-44.8
1	0	0	-1	169.2	-146.3	3	69.7	70.6	4	8	0
2	46.8	43.8	0	141.3	-134.3	4	91.5	73.6	5	93.5	72.6
3	57.7	67.7	1	32.5	-40.6	5	51.7	39.8	-4	61.7	56.7
4	109.5	-103.5	2	25.2	-35.8	3	15	0	-2	165.2	119.4
0	4	0	4	42.8	35.7	-1	60.7	-62.7	3	161.2	-146.3
1	53.7	-48.8	1	39.8	30.7	1	88.6	81.6	2	41.8	35.9
2	45.8	-36.8	5	55.7	63.7	0	77.6	-61.7	1	89.6	-88.6
3	142.3	141.3	5	14.9	73.6	1	39.8	36.8	2	129.4	-107.5
4	37.8	18.9	-3	18.9	-27.9	2	62.7	-56.7	3	64.7	57.7
5	152.2	-130.3	-1	18.9	-39.8	4	24.3	83.6	4	87.6	-78.6
0	4	0	1	181.1	-175.1	1	16	0	5	64.7	51.7
1	62.7	-50.7	0	39.8	29.9	-2	19.7	-41.3	-3	75.6	-51.7
2	11.9	2.0	1	21.5	-87.5	0	42.8	34.8	-4	99.5	77.6
3	53.7	-53.7	2	58.7	-65.7	1	50.7	53.7	-3	85.0	62.7
4	39.8	32.8	3	40.8	29.9	2	29.9	-27.9	-2	146.3	122.3
5	148.3	-142.3	5	72.6	51.7	3	97.5	79.6	1	70.6	-47.8
1	43.6	40.6	1	5	0	4	33.8	-37.8	2	22.9	-16.9
2	57.7	59.7	-4	115.4	-119.4	3	17	0	3	07.7	-00.7
3	83.6	-61.7	-2	86.6	-67.6	-3	36.8	-30.8	5	116.4	96.5
4	20.9	32.8	-1	15.9	19.9	0	51.7	-46.8	-5	55.7	-51.7
5	62.6	81.6	1	74.0	74.0	0	31.8	-27.8	-3	45.8	42.8
0	8	0	3	71.6	00.7	4	34.8	30.8	-2	44.8	-26.9
1	26.9	30.8	4	61.7	61.7	-5	44.6	40.8	2	130.3	-127.4
2	37.8	-77.0	1	6	0	-3	33.8	30.8	1	35.8	38.8
3	21.9	15.9	-4	147.5	-121.4	2	47.8	44.8	2	109.5	-106.5
4	05.7	-46.8	-3	29.9	-22.9	0	46.8	32.8	3	97.5	82.6
5	25.9	-3.0	-2	56.7	-49.7	2	31.8	-28.9	-5	62.7	52.7
1	47.8	45.8	1	89.6	-64.7	4	20.9	-18.9	5	84.6	62.7
2	43.6	73.6	0	140.3	140.3	1	20	0	1	11	0
3	57.7	-42.7	2	69.7	60.7	-2	47.0	-52.7	-4	91.5	87.6
4	41.8	37.8	3	92.5	-91.5	3	33.8	40.8	-3	29.9	-24.9
5	49.7	-39.9	-4	57.7	-48.8	5	24.9	-27.9	-1	22.9	-27.9
0	10	0	-5	45.8	-34.8	-5	42.8	-38.8	1	45.8	-29.3
1	21.9	7.0	1	23.9	26.9	1	34	0	0	45.8	-48.8
2	39.9	-17.9	-2	150.2	115.4	2	0	0	1	27.9	28.9
3	27.9	-20.9	0	57.7	56.7	0	93.5	100.5	4	61.7	48.6
4	42.8	-29.9	1	79.6	83.6	2	41.8	-40.8	5	50.7	47.8
5	11	0	2	22.9	-20.9	4	31.8	-29.9	1	12	-48.8
1	54.7	30.7	3	61.7	-56.7	1	1	0	-3	31.8	25.9
2	51.7	-22.8	5	69.7	-64.7	-9	41.6	39.8	2	110.4	-99.6
3	49.7	-39.8	1	8	0	-8	32.8	-28.9	-1	17.6	60.7
4	77.6	-60.7	-5	36.8	-28.9	-7	40.8	45.8	0	25.9	-26.9
0	12	0	-4	88.6	-73.6	0	67.7	-69.7	-4	22.9	-26.9
1	42.8	-39.8	-3	22.9	-22.9	-3	82.6	-98.5	5	50.7	-40.8
2	32.8	24.9	-2	18.9	-10.0	-2	48.8	62.7	4	78.6	74.6
3	42.8	-36.8	1	133.3	112.4	-1	46.8	59.7	5	34.8	-24.9
4	90.5	59.7	1	54.7	45.8	0	52.7	52.7	3	81.6	-62.7
5	31.8	22.9	2	39.8	78.6	1	39.8	51.7	4	40.8	47.6
0	13	0	3	15.9	-22.9	2	59.7	-52.7	-5	51.7	-55.7
1	29.9	-25.9	4	24.9	-25.9	4	93.5	-101.5	-4	26.9	-15.9
2	57.7	-46.8	5	42.8	-70.6	5	46.8	-34.8	1	73.6	67.7
3	46.8	25.9	1	9	0	2	2	0	3	114.4	104.5
4	16	0	-5	46.8	-31.8	-5	25.9	37.8	4	56.7	51.7
0	00.7	73.6	-4	57.7	59.7	-4	21.9	-31.8	1	14	0
1	25.9	31.8	-3	40.8	45.8	-3	37.8	36.8	-5	68.7	-58.7
2	37.8	30.8	-2	40.8	22.9	-2	39.8	-36.8	3	101.5	-72.6
3	40.8	33.8	0	54.7	42.6	1	14.9	22.9	-2	26.9	-23.9
4	52.7	-45.8	1	100.5	-80.6	3	31.0	-37.8	4	12.2	-12.2
0	15	0	3	16.9	11.9	3	3	0	-1	37.8	35.8
1	63.7	62.7	4	64.7	-60.7	-5	70.6	77.6	0	28.9	25.9
2	45.8	34.8	5	61.7	-45.8	-4	20.9	-18.9	1	79.6	74.6
3	72.6	-56.7	1	10	0	-3	73.6	87.6	5	7.0	3.0
4	17	0	-2	20.9	16.9	-1	92.5	90.5	-4	64.7	-57.7
5	36.8	-38.8	-1	102.5	140.3	1	14.9	100.0	3	15	-15
0	17	0	0	21.9	15.9	1	71.6	-74.6	-4	50.7	32.6
1	36.8	-31.8	4	52.7	-56.7	4	52.7	-56.7	-3	50.7	-50.7
2	36.8	-29.9	3	103.5	-22.5	5	40.8	20.9	0	127.4	119.4
3	65.7	-64.7	4	67.7	-59.7	2	4	0	1	57.7	63.7
4	33.8	-40.8	5	72.6	-52.7	-5	62.7	-91.5	3	35.6	30.6
0	19	0	-5	52.7	30.8	-5	130.5	-20.9	2	10.9	10.9
1	45.8	-50.7	-4	37.8	37.8	0	91.5	-12.4	4	59.7	-63.7
2	45.8	-55.7	-2	54.7	46.8	2	79.6	66.7	5	44.8	-42.8
3	44.8	37.8	-1	156.2	-132.3	3	51.7	-66.7	1	16	0
4	20	0	2	45.8	33.8	5	41.8	-41.8	-4	33.6	-14.9
5	22.9	25.9	1	65.7	-60.7	2	26.9	40.8	-5	26.9	20.9
1	21	0	3	47.8	-37.8	-5	60.7	61.7	4	77.6	68.7
2	49.7	-52.7	4	157.2	124.4	-4	70.6	-60.7	3	42.8	49.7
3	33.6	26.9	4	117.4	-99.5	-3	27.9	-25.9	2	8.0	1.0
4	47.8	39.8	3	57.0	07.7	-2	00.7	-00.7	-4	41.8	-36.8
-6	55.7	-34.8	1	12	0	-1	116.4	105.5	-3	80.6	73.6
-8	32.8	-16.9	-4	97.5	62.0	1	10.9	0.0	-1	40.8	42.8
-7	65.7	-61.7	-3	67.7	55.7	1	17.9	-12.9	0	06.6	79.6
-6	47.8	39.8	-1	40.8	45.8	2	18.9	23.9	-5	30.8	22.9
-4	72.6	116.4	0	133.3	-122.4	2	6	0	-2	52.7	-43.6
0	124.4	-124.4	4	29.9	49.8	-2	130.3	-123.4	4	55.7	-56.7
2	93.5	-104.5	5	59.7	37.6	-1	124.4	116.4	3	34.8	-26.9

Table 1 (cont.)

4	10	-5	33.8	-45.8	3	45.8	42.8	-2	102.5	-134.3	-3	26.9	23.9	7	1.2	
-5	79.6	74.6	-3	43.8	-34.7	5	5	-1	25.9	-19.9	-1	07.7	70.0	-4	34.6	-49.7
-4	71.6	60.7	-1	74.6	75.6	-5	66.7	57.7	0	56.7	-75.6	3	75.6	-3	34.0	37.6
-3	51.7	49.7	0	34.8	29.9	-3	32.8	29.9	2	13.9	23.9	6	9	7	1.3	
-2	71.6	63.7	1	43.8	54.7	0	29.9	-24.9	5	40.8	-36.8	-4	30.8	-3	34.8	-47.8
-1	24.9	-29.9	3	21.9	-1.3.9	1	28.9	-34.8	4	35.8	35.8	-3	29.9	34.8	7	1.6
0	26.9	-17.9	5	8		3	46.8	-61.7	6	2		6	1.0	-3	42.8	-45.8
1	54.7	-57.7	-5	58.7	71.6	5	10	81.6	-5	79.6	99.5	-4	44.8	30.7	8	0
3	44.8	-45.8	-1	55.7	-80.6	-5	90.5	81.6	-4	44.8	54.7	0	45.8	-57.7	-2	53.7
5	11		0	50.7	60.7	-4	59.7	-47.8	-3	35.8	45.8	7	105.5	113.4	-2	8
-3	62.7	50.7	8	50.7	61.7	-1	77.6	-90.5	-2	24.9	35.8	-6	105.5	113.4	-2	8
-4	49.7	36.8	8	39.8	39.8	0	6.0	3.0	-1	98.5	-96.5	-2	28.9	-47.8	-1	19.9
-2	25.9	9.0	4	20.0	-8.0	3	67.7	73.6	1	40.8	-41.8	0	63.7	-69.7	3	34.8
-1	93.5	-97.5	5	3		5	11		2	23.9	-25.9	7	1		8	2
0	56.7	-53.7	-2	44.8	69.7	-2	29.9	-50.7	3	36.8	33.8	-6	44.8	39.8	-5	86.6
1	27.9	-28.9	2	55.7	-68.7	0	43.8	-49.7	5	36.8	33.8	-5	20.8	24.9	-2	30.6
3	68.7	69.7	3	21.9	14.0	4	62.7	57.7	6	3		-4	29.9	36.8	-1	64.7
5	12		4	47.8	-42.8	5	12		5	69.7	-81.6	-3	40.8	36.8	8	4
-5	56.7	49.7	5	4		-5	49.7	41.8	-4	31.8	36.8	-2	28.9	3	8	4
-3	49.7	43.8	-4	32.8	-51.7	-4	76.6	-77.6	-2	44.8	-47.8	7	2		8	6
-2	54.7	-59.7	-3	48.8	65.7	-3	24.9	-20.9	-2	52.7	96.5	-5	78.6	-31.6	3	34.0
0	73.6	-70.6	-2	90.5	-107.5	-2	28.9	-33.8	-1	45.8	46.8	-4	29.9	-28.8	8	7
1	34.8	-37.8	-1	90.5	120.4	0	31.8	40.8	0	40.8	-50.7	-3	79.6	-90.5	-1	66.7
3	11		4	29.5	114.4	5	13		1	58.7	74.6	3	35.8	38.8	3	40.8
5	48.8	32.8	3	69.7	-63.7	-3	27.0	66.7	2	23.9	33.8	7	3		8	9
-4	53.7	-48.8	4	47.8	45.8	-4	32.8	-29.9	3	40.8	31.8	-4	35.8	-39.8	-3	24.9
-1	28.9	-37.8	5	5		-3	20.0	-86.6	4	61.7	53.7	-2	45.8	-59.7	-3	42.8
0	33.8	23.9	-5	25.9	37.8	5	14		5	41.8	54.7	-1	30.6	-44.8	9	1
4	14		-3	23.9	42.8	-5	35.8	28.9	-4	20.9	-29.9	3	42.8	30.0	-5	65.7
-3	43.8	-41.8	-1	22.9	24.9	5	15		-1	75.6	-87.6	7	4		-3	34.0
-2	72.6	-74.6	1	35.8	-30.6	-4	34.8	-31.6	1	41.6	-46.6	-5	40.6	-42.6	-2	33.8
-1	16		3	49.7	43.8	0	01.7	63.7	2	36.8	40.8	-1	51.7	62.7	9	2
3	62.7	-57.7	5	6		4	61.7	-66.7	3	23.9	31.8	0	38.8	38.8	-3	34.8
-2	80.6	-76.6	-5	76.6	-82.6	3	16		6	5		-4	53.7	-76.6	-5	36.8
-1	31.8	32.8	-4	79.6	97.5	-4	42.8	42.8	-4	32.8	47.6	0	56.7	66.7	-2	47.8
1	76.6	69.7	-1	108.5	120.4	5	17		-3	46.8	-56.7	7	6		2	4
4	17		0	65.7	85.6	-5	37.8	42.8	-2	53.7	-89.6	3	49.7	-41.6	-3	42.8
-2	38.8	-55.7	1	54.7	65.7	-4	35.8	29.9	-2	53.7	-57.7	7	7		-2	33.8
4	18		2	33.8	-54.7	-3	60.7	69.7	3	23.9	17.9	-4	44.8	29.9	9	5
-5	37.8	21.9	3	44.8	-31.7	0	40.8	-33.8	6	6		-3	37.8	41.8	-5	54.7
5	19		5	27.9	34.8	6	0		-2	68.7	-73.6	-1	61.7	69.7	-3	24.9
-5	44.8	-30.8	-1	29.9	-35.8	-8	66.7	-63.7	0	26.9	-30.8	3	75.6	-77.6	10	0
-4	44.8	36.8	0	26.9	25.9	-6	49.7	-33.8	0	42.8	52.7	7	8		-2	33.8
-3	42.8	39.8	2	40.8	56.7	-4	72.6	67.7	2	47.8	45.8	-4	56.7	30.8	10	1
5	0		5	8		-2	61.7	84.6	3	23.9	20.9	7	10		-3	25.9
-6	38.8	-36.8	-5	58.7	47.8	2	52.7	-46.8	6	7		1	55.7	-75.6	10	2
-8	47.8	-35.8	-4	76.6	74.6	6	1		-4	26.9	-26.9	3	24.9	31.8	-3	44.8
-2	43.8	74.6	-3	26.9	-20.9	-8	46.8	38.8	-2	27.9	52.7	7	11		-3	25.9
0	61.7	62.7	-2	71.6	86.6	-6	25.6	93.5	1	10.8	-35.8	-4	45.8	27.9	10	5
3	47.8	-65.7	-1	74.6	-57.7	-5	25.5	114.4	5	36.8	32.6	-3	27.9	-42.8	-3	35.6
4	46.8	-36.8	0	27.9	-36.8	-4	25.9	15.9	6	6		3	48.8	52.7		38.8
5	1		2	93.5	-103.5	-3	25.6	95.5								

by systematic absences) there appeared to be three monomeric groups in the asymmetric unit, *i.e.* the molecule might be a trimer. Although other alternatives existed, such as a centrosymmetric hexamer, subsequent structure analysis proved that the molecule was trimeric.

### 2,2'-Dimercaptodiethylsulphidepalladium(II)

(PdS<sub>3</sub>C<sub>4</sub>H<sub>8</sub>)<sub>3</sub>, F.W. = 776.1

Monoclinic;  $a = 10.69 \pm 0.05$ ,  $b = 24.40 \pm 0.13$ ,  $c = 9.44 \pm 0.05$  Å,  $\beta = 111.5 \pm 0.5^\circ$ .  $U = 2292$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 2.30$  g.cm<sup>-3</sup> (by flotation),  $D_c = 2.25$  g.cm<sup>-3</sup>.  $F(000) = 1512$ .

Space group  $P2_1/c$  ( $C_{2h}^5$ , No. 14).

The intensity data were collected on multiple-film equi-inclination Weissenberg photographs (Cu  $K\alpha$ ) taken around [001], ( $l=0, 1, \dots, 5$ ). Correlation data were collected about [010]. The crystals were small and very poorly formed and as a result the intensity data fell markedly with increasing value of  $\theta$ . Exposure times of 200 hours per level were needed and the spots showed considerable distortion in shape, sometimes terminating in broad streaks. Despite the poor quality of the data the structure of this apparently polymeric sulphur bridged complex was considered of sufficient interest to justify a complete structure analysis. However, it seemed unlikely that the structure could be determined with high accuracy.

Intensities were estimated visually with the aid of a calibration strip and data processing was carried out on UTECOM by use of the programs of Rollett (1961). Neither extinction nor absorption corrections were applied to these data. Internal correlation was unreliable owing to spot shape variation, which was not systematic, and inter-layer scale factors were therefore introduced as variables in the structure refinement stages. The final scaling (Table 1) is based upon the calculated structure amplitudes.

### Determination of the structure

The three-dimensional Patterson function contained three very large peaks approximately coplanar with the origin and at distances of about 3.25 Å from it. This distribution verified a trimeric molecular species and the positions of the three palladium atoms and three bridging sulphur atoms were readily obtained. Successive cycles of structure factors and difference Fourier syntheses were used to locate the remaining six sulphur and twelve carbon atoms, the latter with some difficulty. Peak heights for the carbon atoms varied between 3-6 e.Å<sup>-3</sup> and were of the same order of magnitude as some spurious peaks which arose as artefacts owing to the use of very poor data. As a result some false positioning occurred but this became obvious during attempts at refinement.

Full-matrix least-squares methods were not successful in the early stages of refinement ( $R=0.27$ ). The interlayer scale factors and isotropic temperature factors varied irrationally, so much so that a check on the approximately correct values was necessary by the statistical method of Wilson (1942). Parameter refinement was carried out by the use of successive cycles of structure factor and difference Fourier syntheses until the reliability index  $R$  was 0.18. At this stage least-squares methods were recommenced and a successful refinement of positional parameters, isotropic temperature factors and interlayer scale factors was accomplished. The weighting scheme used  $F_o/10$  as the standard deviation in the observed structure amplitudes. The final

$R$  value was 0.15, which was considered satisfactory in view of the very poor data which were available for the structure determination.

The average estimated standard deviations in atomic positions (0.009 Å for Pd, 0.03 Å for S and 0.10 Å for C) are large, as might well be expected and although the errors in bond lengths, particularly those involving carbon atoms, are too large to allow a detailed comparison with similar bond lengths in other compounds, the gross features of the structure are well established and are of considerable interest.

For the calculation of structure factors the atomic scattering factors for Pd, S and C of Thomas & Umeda (1951), Dawson (1960) and Berghuis, Haanappel, Pot-

Table 2. Atomic parameters for 2,2'-dimercaptodiethylsulphidepalladium(II)

Standard deviations are r.m.s. values based upon e.s.d.'s along the three crystallographic directions.

	$x/a$	$y/b$	$z/c$	e.s.d.	$B$
Pd(1)	0.0554	0.1217	0.0905	0.009 Å	3.25 Å <sup>2</sup>
Pd(2)	0.3383	0.1424	0.4041	0.009	3.36
Pd(3)	0.3856	0.0784	0.0975	0.008	2.58
S(1)	0.1726	0.0437	0.0429	0.031	4.08
S(2)	-0.0001	0.1364	-0.1586	0.033	4.65
S(3)	-0.0995	0.1920	0.0961	0.033	4.66
S(4)	0.1341	0.1009	0.3474	0.028	3.09
S(5)	0.2262	0.2199	0.4445	0.031	3.88
S(6)	0.5303	0.1947	0.4796	0.030	3.60
S(7)	0.4344	0.0612	0.3532	0.030	3.98
S(8)	0.6054	0.1068	0.1627	0.029	3.45
S(9)	0.3691	0.0889	-0.1506	0.029	3.12
C(1)	0.0870	0.0369	-0.1915	0.170	9.77
C(2)	-0.0379	0.0748	-0.2590	0.107	4.11
C(3)	-0.1825	0.1784	-0.2461	0.127	5.94
C(4)	-0.1749	0.2186	-0.0894	0.125	5.70
C(5)	0.0299	0.1416	0.4401	0.173	10.25
C(6)	0.1447	0.1910	0.5284	0.098	2.84
C(7)	0.3651	0.2578	0.5947	0.146	4.33
C(8)	0.4875	0.2609	0.5444	0.108	3.95
C(9)	0.6042	0.0640	0.4448	0.109	3.51
C(10)	0.6845	0.0582	0.3470	0.086	1.59
C(11)	0.6357	0.0766	0.0188	0.093	2.27
C(12)	0.5291	0.0973	-0.1520	0.101	5.65

Table 3. Selected interatomic distances (Å) in the molecule of 2,2'-dimercaptodiethylsulphidepalladium(II)

The atomic numbering used is the same as in Table 2. Standard deviations are given in brackets and refer to the last two places of the preceding number.

Pd(1)-Pd(2)	3.407 (12)	S(1)-C(1)	2.07 (17)
-Pd(3)	3.662 (12)	S(2)-C(2)	1.74 (11)
Pd(2)-Pd(3)	3.486 (12)	-C(3)	2.09 (13)
		S(3)-C(4)	1.76 (13)
Pd(1)-S(1)	2.409 (32)	S(4)-C(5)	1.92 (18)
-S(2)	2.234 (34)	S(5)-C(6)	1.55 (10)
-S(3)	2.397 (34)	-C(7)	1.88 (15)
-S(4)	2.313 (30)	S(6)-C(8)	1.84 (11)
Pd(2)-S(4)	2.285 (30)	S(7)-C(9)	1.70 (11)
-S(5)	2.343 (32)	S(8)-C(10)	2.02 (09)
-S(6)	2.296 (31)	-C(11)	1.68 (10)
-S(7)	2.361 (32)	S(9)-C(12)	1.73 (13)
Pd(3)-S(7)	2.314 (31)		
-S(8)	2.307 (30)	C(1)-C(2)	1.55 (20)
-S(9)	2.298 (30)	C(3)-C(4)	1.75 (18)
-S(1)	2.304 (32)	C(5)-C(6)	1.71 (20)
		C(7)-C(8)	1.55 (18)
		C(9)-C(10)	1.48 (14)
		C(11)-C(12)	1.68 (14)

ters, Loopstra, MacGillivray & Veenendaal, (1955) were used. A correction for the real component of the anomalous dispersion by Pd of Cu  $K\alpha$  radiation was applied (Dauben & Templeton, 1955). UTECOM, an English Electric DEUCE computer, was used for all calculations except the least-squares procedure, for which an IBM 7040 computer of the Australian Atomic Energy Commission was used. The programs used were those of Rollett (1961) and Busing, Martin & Levy (1962), respectively.

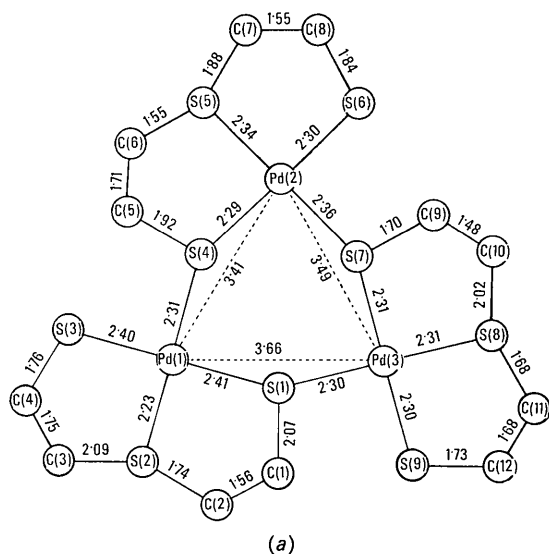
The final atomic coordinates, their average estimated standard deviations and the temperature factors are

listed in Table 2. The coordinates, together with unit-cell dimensions, were used to calculate the *intra-* and *inter-*molecular distances listed in Tables 3 and 5, and the bond angles listed in Table 4.

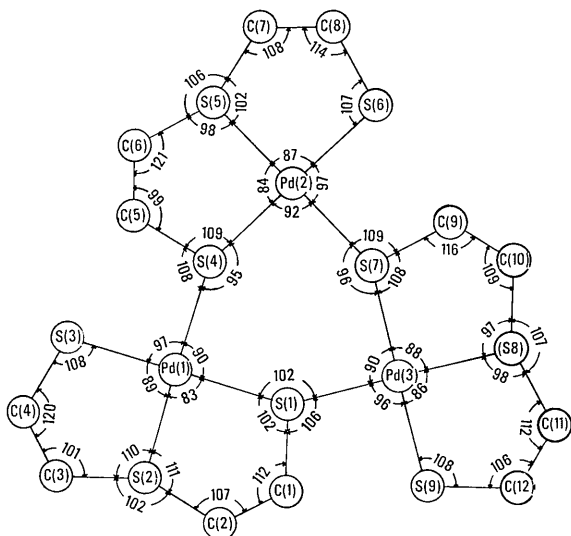
Table 4. Selected bond angles ( $^{\circ}$ ) in the 2,2'-dimercaptodiethylsulphidepalladium(II) molecule

Standard deviations (in brackets) refer to the last two place of the preceding number.

Pd(1)-S(4)-Pd(2)	95.6 (1.1)
Pd(2)-S(7)-Pd(3)	96.4 (1.2)
Pd(3)-S(1)-Pd(3)	102.2 (1.2)
S(1)-Pd(1)-S(2)	83.4 (3.2)
S(2)-Pd(1)-S(3)	89.4 (4.0)
S(3)-Pd(1)-S(4)	97.1 (3.7)
S(4)-Pd(1)-S(1)	90.5 (3.6)
S(4)-Pd(2)-S(5)	83.9 (3.6)
S(5)-Pd(2)-S(6)	87.4 (3.7)
S(6)-Pd(2)-S(7)	97.1 (3.7)
S(7)-Pd(2)-S(4)	91.7 (3.5)
S(7)-Pd(3)-S(8)	87.6 (3.7)
S(8)-Pd(3)-S(9)	85.9 (3.6)
S(9)-Pd(3)-S(1)	96.5 (3.7)
S(1)-Pd(3)-S(7)	89.6 (3.7)
Pd(1)-S(1)-C(1)	101.9 (5.7)
Pd(3)-S(1)-C(1)	106.4 (5.7)
Pd(1)-S(2)-C(2)	110.7 (3.8)
Pd(1)-S(2)-C(3)	110.2 (4.4)
C(2)-S(2)-C(3)	102.3 (5.6)
Pd(1)-S(3)-C(4)	108.1 (4.1)
Pd(1)-S(4)-C(5)	108.4 (5.8)
Pd(2)-S(4)-C(5)	109.1 (5.8)
Pd(2)-S(5)-C(6)	97.7 (3.5)
Pd(2)-S(5)-C(7)	102.2 (5.0)
C(6)-S(5)-C(7)	106.0 (6.0)
Pd(2)-S(6)-C(8)	106.7 (3.8)
Pd(2)-S(7)-C(9)	108.9 (3.9)
Pd(3)-S(7)-C(9)	108.3 (3.9)
Pd(3)-S(8)-C(10)	96.8 (3.1)
Pd(3)-S(8)-C(11)	97.6 (3.2)
C(10)-S(8)-C(11)	107.2 (3.3)
S(1)-C(1)-C(2)	111.6 (9.9)
S(2)-C(2)-C(1)	107.2 (8.6)
S(2)-C(3)-C(4)	101.2 (8.4)
S(3)-C(4)-C(3)	119.7 (9.1)
S(4)-C(5)-C(6)	98.9 (9.6)
S(5)-C(6)-C(5)	120.8 (8.6)
S(5)-C(7)-C(8)	108.4 (9.9)
S(6)-C(8)-C(7)	113.5 (8.3)
S(7)-C(9)-C(10)	115.7 (7.6)
S(8)-C(10)-C(9)	109.0 (6.2)
S(8)-C(11)-C(12)	112.5 (6.9)
S(9)-C(12)-C(11)	106.5 (7.5)



(a)



(b)

Fig. 1. A depiction of the molecule 2,2'-dimercaptodiethylsulphidepalladium(II) showing (a) bond distances and (b) angles.

Table 5. Intermolecular approach distances ( $\text{\AA}$ ) of less than 4  $\text{\AA}$  in the crystal of 2,2'-dimercaptodiethylsulphidepalladium(II)

The atomic numbering used is the same as in Table 2; the number in the second bracket denotes the following symmetry transformation:

No bracket	x	y	z
i	x	$\frac{1}{2} - y$	$\frac{1}{2} + z$
ii	$1 + x$	y	z
iii	x	y	$1 + z$

Table 5 (cont.)

S(3)—C(3) (i)	3.74
—C(4) (i)	4.00
C(6)—C(4) (i)	3.87
C(7)—Pd(2) (i)	3.89
—S(6) (i)	3.60
—C(8) (i)	3.98
C(8)—S(8) (i)	3.50
C(11)—S(3) (ii)	3.87
C(5)—S(2) (iii)	3.92
—C(2) (iii)	3.57
C(6)—S(9) (iii)	3.98

## Description of the structure

The molecule of 2,2'-dimercaptodiethylsulphidepalladium(II) has a trimeric structure which is depicted in Fig. 1. Each palladium atom is surrounded by four sulphur atoms in an approximately square-planar arrangement. The three sulphur atoms of one ligand molecule form three corners of each square and the squares are completed by one thiol sulphur of each ligand molecule being shared by two palladium atoms, forming a sulphur bridge.

The bridging sulphur atoms lie at the corners of a triangle. The molecule is not flat but bent at the bridging atoms, so that the three squares are inclined towards each other, and the molecule as a whole may be regarded as basin-shaped (Fig. 2). The palladium and sulphur bridging atoms form a six-membered ring in which the palladium and sulphur atoms alternate. The palladium atoms form a triangle above the triangle of the sulphur atoms, and nearly parallel to it. The equations of the planes of these triangles are given in Table 6 and the dihedral angle between them is  $2.5^\circ$ .

The triangle formed by the palladium atoms is not equilateral as might be expected, but is approximately isosceles; the distance Pd(1)—Pd(3) of  $3.66 \text{ \AA}$  appears to be significantly longer than the distances Pd(1)—Pd(2) and Pd(2)—Pd(3) of  $3.41$  and  $3.49 \text{ \AA}$  respectively.

The six non-bridging sulphur atoms, which form the upper edges of the squares of coordinated sulphur atoms, form an irregular, approximately planar, hex-

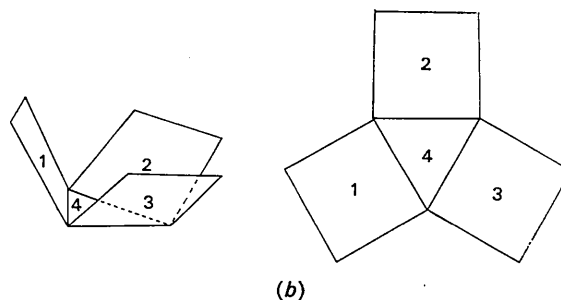
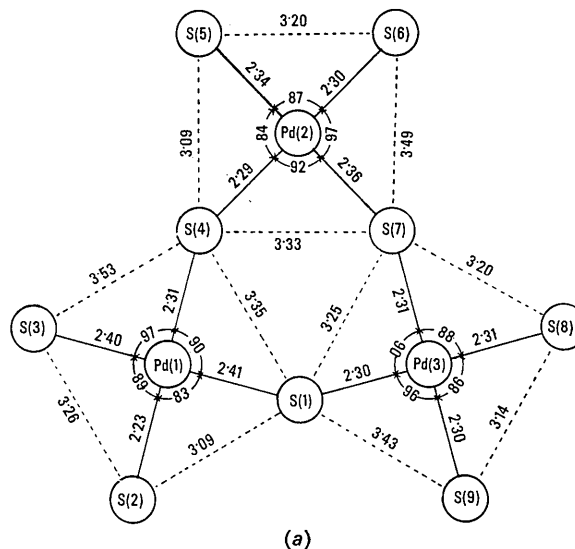


Fig. 2. A diagram showing (a) the environments of the palladium atoms within a molecule and (b) the arrangement of the mean planes through the sulphur atoms.

Table 6. Least-squares planes

Equation in the form  $Ax + By + Cz + D = 0$ , referred to the crystallographic axes, calculated after Schomaker, Waser, Marsh & Bergman (1959) with all weights equal to 1. All values have been multiplied by  $10^3$ .

Plane	A	B	C	D	Atoms defining the plane
I	761	626	171	-2135	S(1), S(2), S(3), S(4)
II	-145	-266	953	-2161	S(4), S(5), S(6), S(7)
III	-356	933	58	-386	S(7), S(8), S(9), S(1)
IV	266	909	-320	-1324	S(1), S(4), S(7)
V	275	892	-358	-2443	Pd(1), Pd(2), Pd(3)

Deviations from planes ( $10^{-3} \text{ \AA}$ )

Plane	Pd(1)	Pd(2)	Pd(3)	S(1)	S(2)	S(3)	S(4)	S(5)	S(6)	S(7)	S(8)	S(9)
I	73			-112	127	-119	105					
II		-24					37	-30	24	-31		
III			104	29						-28	28	-28
I	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)
II	-647	-1008	-1193	-1159								
III					778	1063	876	220				
									-450	-1057	-1026	-448

agon which may be regarded as the rim of the basin-shaped molecule. This hexagon lies above the two triangles formed by the three palladium atoms and the three bridging sulphur atoms, and is approximately parallel to them.

The bond distances and angles in 2,2'-dimercaptodiethylsulphidepalladium(II) are listed in Tables 3 and 4 and the environment of the palladium atoms is shown in Fig. 2. The sulphur atoms around each palladium atom are distorted from the ideal square-planar configuration, as evidenced by significant differences in bond angles at the palladium atoms and in deviations from the best fit planes through these sulphur atoms (Table 6). There are three such 'coordination' planes, numbered 1, 2, and 3 in Fig. 2 and they are inclined at angles of 136°, 126° and 137° respectively to the plane of the triangle of the bridging sulphur atoms. The dif-

ferences in inclination are consistent with Pd-Pd separations mentioned above.

The palladium atoms all show deviation in a direction towards each other from the least-squares planes of the sulphur atoms ( $3 < \Delta/\sigma < 12$ ).

The Pd-S bonds in the trimer can be divided into four different chemical types. In the case of the 2,2'-dimercaptodiethylsulphidenickel(II) dimer (Barclay, McPartlin & Stephenson, 1969), the bonds from the bridging sulphur atoms were longer than those from the terminal sulphur atoms. Unfortunately in the present investigation the large standard deviations in Pd-S bond distances ( $\approx 0.03 \text{ \AA}$ ) prevent any deductions being made concerning the relative lengths of the various Pd-S bonds. However, the mean value of the Pd-S bond lengths in the trimer, *viz.* 2.32 Å, is short when compared with, for example, the Pd-S bond length of 2.44 Å reported for potassium bis(dithiooxalato)palladate(II) (Cox, Wardlaw & Webster, 1935). This agrees with a similar comparison for 2,2'-dimercaptodiethylsulphidenickel(II) where the average Ni-S bond distance of 2.16 Å is again short when compared with, for example, the Ni-S bond distance of 2.30 Å found in bis(dithiooxalato)nickelate(II).

The bond angles in the three monomeric units are in reasonable agreement. The three two-covalent sulphur atoms, S(3), S(9) and S(6) have C-S-Pd bonding angles of 108, 108 and 107° respectively, which are in good agreement with the reported values for other two-covalent sulphur atoms, *viz.* 105° in dimethyl sulphide (Allen & Sutton, 1950) and 107° in dimethyltrisulphide (Donohue & Schomaker, 1948).

The three-covalent sulphur atoms, S(2), S(5) and S(8), have pyramidal configurations, and the values of the bond angles all lie in the range 97–111°, and are approximately those expected for this arrangement.

The remaining three sulphur atoms are the bridging atoms which are also three-covalent. As expected, these atoms have a pyramidal configuration. However, unlike the equivalent angles in the nickel dimer, the Pd-S-Pd angles do not appear to be grossly distorted from the approximately tetrahedral values expected for this configuration. These angles, Pd(1)-S(4)-Pd(2), Pd(2)-S(7)-Pd(3) and Pd(3)-S(1)-Pd(1), have values 95, 96 and 102° respectively, whereas the corresponding Ni-S-Ni angles in the dimer have the unusually small value of 77°. There is considerably less steric strain in the trimeric structure than in the dimeric structure.

The chelate rings in the molecule are all bent with the four carbon atoms of each ligand molecule all lying on the same side of the plane formed by the three sulphur atoms of that molecule. The -CH<sub>2</sub>-CH<sub>2</sub>- groups may be regarded as being arranged in pairs round the rim of the basin-shaped molecule, and all are bent outwards away from the centre of the molecule. The perpendicular distances of the carbon atoms from the mean planes through the corresponding sulphur atoms are listed in Table 6, and these deviations are in the opposite sense to those of the corresponding palladium

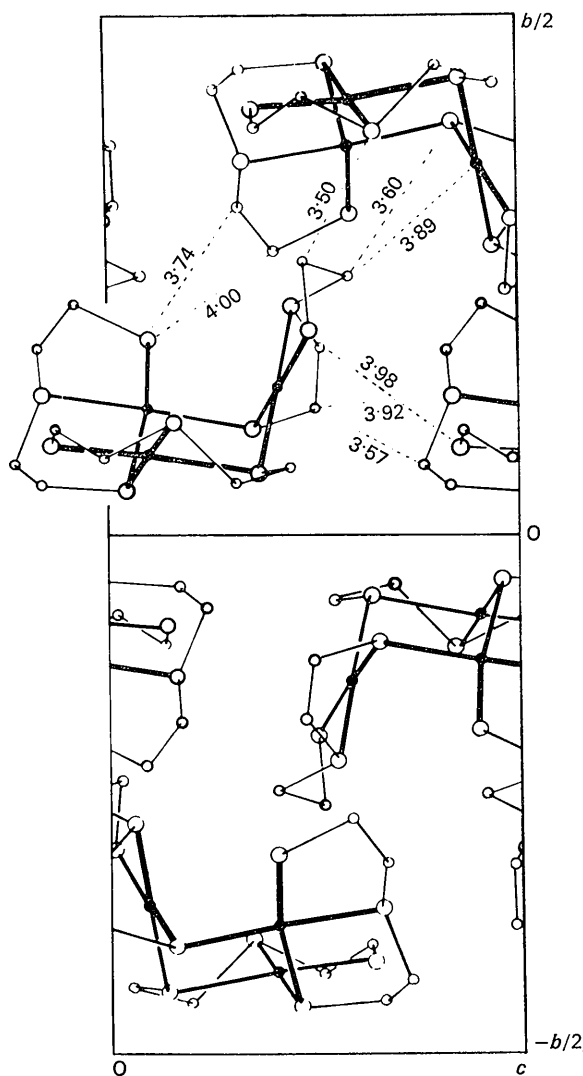


Fig. 3. A (100) projection of the contents of a unit cell of 2,2'-dimercaptodiethylsulphidepalladium(II).

atoms. The bending of the chelate rings, as in the case of the nickel dimer, can be attributed to the pyramidal configuration of the three-covalent thioether sulphur atoms in each ligand molecule. This would be expected to cause both  $-\text{CH}_2-\text{CH}_2-$  groups, in each monomeric unit, to bend in the same direction.

Different orientations of the  $-\text{CH}_2-\text{CH}_2-$  groups would be expected to give rise to several different isomeric forms of the trimer. Adopting Harley-Mason's nomenclature, there is the possibility of two *cis*- and two *trans*-isomers. The two *cis*-isomers have all three pairs of  $-\text{CH}_2-\text{CH}_2-$  groups bent in the same direction. In one, the groups are bent towards the centre of the basin-shaped molecule, whilst in the other they are all bent outwards away from the centre. The two *trans*-isomers have either one or two pairs of  $-\text{CH}_2-\text{CH}_2-$  groups bent in towards the centre of the molecule and the remaining groups bent outwards. The configurations which impose least steric strain on the molecule as a whole are the *cis*-isomers and the results of the present structural investigation have shown that the molecule has a *cis*-configuration with the  $-\text{CH}_2-\text{CH}_2$  groups all bent outwards from the centre of the molecule.

The arrangement of the trimers in the unit cell is shown in Fig. 3. The molecules are arranged in layers perpendicular to the unique axis *b*. Some close approach distances are listed in Table 5. There is no evidence of interaction along the approximately tetragonal axes

of the palladium atoms; the closest intermolecular approach is 3.50 Å between C(8) and S(8)(i), which is a normal van der Waals contact.

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