gest some attractive contact between the carbonyl and phosphine groups, although the effect of the many repulsive interactions within and between the triphenylphosphine ligands is hard to assess.

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Bis-(2,2,6,6-tetramethylheptane-5-thiolo-3-onato)palladium(II)

BY L. E. POPE AND J. C. A. BOEYENS

National Institute for Metallurgy, Applied Structural Chemistry Research Group, Rand Afrikaans University, P.O. Box 524, Johannesburg, South Africa

Abstract. $Pd(C_{11}H_{19}OS)_2$, monoclinic, $P2_1/c$, $a = 11\cdot15$ (1), $b = 21\cdot22$ (1), $c = 12\cdot40$ (1) Å, $\beta = 119\cdot3$ (1)°, $Z = 4$. The two S and two O atoms occur in *cis* arrangement in a distorted square-planar configuration around Pd at distances of $2\cdot232$ (2) and $2\cdot028$ (6) Å respectively. The bond lengths in the chelate rings indicate partial double bonds and hence incomplete delocalization.

Introduction. Shkol'nikova, Yutal, Shugam & Knyazeva (1973) found a surprisingly short Pd–S bond ($2\cdot235$ Å), which they ascribed to $d\pi$–$p\pi$ back donation in palladium monothiodibenzoylmethanate. The Pd–O bond ($2\cdot10$ Å) was also considered short, and this was ascribed to the strong *trans* effect of S. Because both observations have significant implications, an independent investigation of these effects is desirable.

Table 1. *Final fractional positional* ($\times 10^4$)
and anisotropic thermal parameters ($\text{Å}^2 \times 10^3$) *with e.s.d.'s in parentheses*

$$T = \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\right].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ring I									
Pd	−493 (1)	1184 (0)	226 (1)	34 (0)	44 (0)	32 (0)	−6 (0)	18 (0)	−4 (0)
S	1547 (2)	1645 (1)	1371 (2)	37 (1)	59 (2)	44 (1)	−14 (1)	23 (1)	−8 (1)
O	−1394 (6)	1580 (3)	1142 (6)	40 (4)	54 (5)	45 (4)	−14 (3)	24 (3)	−5 (3)
C(1)	1502 (9)	2119 (4)	2461 (8)	37 (5)	41 (6)	38 (5)	−3 (4)	16 (4)	−3 (4)
C(2)	405 (9)	2233 (6)	2657 (9)	38 (5)	49 (6)	51 (6)	−10 (5)	25 (4)	−3 (4)
C(3)	−939(9)	1963 (5)	2032 (8)	41 (5)	41 (6)	42 (5)	−2 (5)	21 (4)	1 (5)
C(4)	2888 (10)	2430 (5)	3361 (10)	37 (5)	69 (8)	55 (6)	−21 (5)	24 (5)	−13 (5)
C(5)	−1984 (10)	2159 (5)	2446 (9)	42 (5)	51 (7)	51 (5)	−7 (5)	28 (4)	1 (5)
M(1)	4039 (12)	2345 (8)	3033 (13)	54 (6)	141 (12)	93 (8)	−53 (8)	45 (5)	−33 (7)
M(2)	2718 (15)	3140 (8)	3495 (21)	71 (11)	74 (10)	248 (28)	−67 (9)	66 (12)	−20 (8)
M(3)	3405 (17)	2078 (11)	4628 (14)	101 (13)	236 (20)	65 (9)	20 (11)	21 (11)	−64 (12)
M(4)	−3279 (11)	1743 (6)	1802 (12)	47 (5)	88 (8)	94 (7)	−39 (6)	46 (5)	−25 (5)
M(5)	−1324 (12)	2078 (7)	3871 (10)	68 (7)	108 (11)	47 (6)	2 (6)	39 (5)	5 (7)
M(6)	−2384 (12)	2865 (6)	2072 (12)	66 (7)	57 (7)	87 (8)	6 (6)	41 (6)	17 (5)
Ring II									
S	416 (2)	751 (1)	−849 (2)	40 (1)	59 (2)	41 (1)	−13 (1)	24 (1)	−8 (1)
O	−2362 (6)	776 (3)	−775 (6)	39 (3)	59 (5)	46 (4)	−13 (3)	25 (3)	−8 (3)
C(1)	−832 (9)	363 (4)	−2105 (8)	47 (5)	35 (5)	30 (4)	−2 (3)	21 (3)	1 (4)
C(2)	−2170 (10)	246 (5)	−2384 (8)	45 (5)	52 (6)	40 (4)	5 (4)	26 (4)	3 (4)
C(3)	−2848 (9)	433 (5)	−1724 (8)	34 (4)	50 (6)	38 (5)	−2 (4)	17 (4)	1 (4)
C(4)	−374 (10)	147 (5)	−3044 (8)	54 (5)	47 (6)	41 (4)	1 (4)	31 (4)	0 (4)
C(5)	−4318 (10)	224 (6)	−2161 (9)	38 (5)	70 (7)	49 (6)	18 (5)	20 (4)	8 (4)
M(1)	1211 (11)	34 (6)	−2424 (10)	54 (5)	83 (8)	63 (5)	14 (5)	40 (4)	−1 (5)
M(2)	−1110 (12)	−473 (6)	−3700 (10)	73 (6)	64 (7)	60 (5)	−26 (5)	41 (5)	−14 (5)
M(3)	−796 (13)	695 (6)	−4002 (10)	99 (7)	70 (8)	53 (5)	−12 (5)	51 (5)	−12 (6)
M(4)	−4836 (16)	−319 (10)	−3148 (19)	74 (6)	185 (11)	169 (11)	89 (9)	73 (7)	54 (7)
M(5)	−5212 (18)	778 (10)	−2714 (33)	65 (8)	115 (15)	487 (30)	1 (17)	106 (15)	−5 (9)
M(6)	−4527 (18)	15 (17)	−1128 (15)	93 (6)	499 (20)	67 (7)	25 (9)	36 (5)	123 (7)

Since diffraction-quality crystals of the related title compound, obtained by the method of Chaston, Livingstone, Lockyer, Pickles & Shannon (1965), were available to us, we undertook this analysis.

The material was recrystallized from n-hexane and, after preliminary examination by photographic methods, cell constants and diffraction intensities were measured on a Stoe Stadi 2 diffractometer with Mo $K\alpha$ radiation at room temperature. The instrument is equipped with an incident-beam graphite crystal monochromator. To compensate for spot elongation, a variable range was scanned in ω-mode at a rate of 1s per 0·02°. No absorption corrections were applied ($\mu R = 0·3$). After Lp correction the structure was solved by the Patterson method and refined by full-matrix least squares with the program *SHEL-X* written by G.M. Sheldrick.

The refinement of the two t-butyl groups in *trans* disposition converged very poorly. Although aniso-

tropic refinement of their thermal parameters eliminated most of the spurious difference Fourier peaks in their vicinity, the extremely high U_{ij} reflect some disorder rather than pure thermal motion. Despite this, the bond parameters calculated for these groups are fairly reasonable. Weighting was applied according to counting statistics, and at the termination of refinement R was 0·05. The refined parameters are listed in Table 1, and the atom numbering is shown in Fig. 1.*

Discussion. All intramolecular bond lengths are collated in Table 2. Bond parameters averaged over chemically equivalent, but crystallographically independent, entities are shown in Fig. 1. The coordination is very close to planar. The least-squares plane through the four ligand atoms is given by $0·0062u + 0·7794v - 0·6265w = 1·8104d$, where $u = xa + zc \cos \beta$, $v = yb$, and

Table 2. *Intramolecular bond lengths (Å) and angles (°)*

	Ring I	Ring II	Mean
Pd——S	2·233 (2)	2·230 (2)	2·232
Pd——O	2·030 (6)	2·026 (6)	2·028
S——C(1)	1·705 (9)	1·709 (9)	1·707
C(1)–C(2)	1·379 (12)	1·380 (12)	1·380
C(2)–C(3)	1·428 (12)	1·414 (12)	1·421
C(3)–O	1·260 (10)	1·259 (10)	1·260
C(1)–C(4)	1·544 (12)	1·551 (11)	
C(3)–C(5)	1·542 (12)	1·519 (13)	} 1·539
M(1)–C(4)	1·534 (14)	1·563 (14)	
M(2)–C(4)	1·538 (18)	1·554 (14)	
M(3)–C(4)	1·573 (19)	1·562 (15)	
M(4)–C(5)	1·541 (14)	1·571 (24)	} 1·543
M(5)–C(5)	1·556 (14)	1·476 (23)	
M(6)–C(5)	1·567 (15)	1·478 (22)	
O——S	3·152 (5)	3·144 (5)	
			3·148
S(I)—S(II)			3·062 (3)
O(I) –O(II)			2·687 (8)
S——Pd—S			86·6 (1)
O——Pd—O			83·0 (2)
S——Pd—O	95·3 (2)	95·1 (2)	95·2
Pd—S——C(1)	110·3 (3)	109·7 (3)	110·0
S——C(1)–C(2)	127·9 (7)	127·9 (7)	127·9
C(1)–C(2)–C(3)	128·3 (9)	128·5 (9)	128·4
C(2)–C(3)–O	126·9 (8)	126·5 (8)	126·7
C(3)–O——Pd	131·2 (6)	131·6 (6)	131·4
S——C(1)–C(4)	114·7 (6)	114·0 (7)	114·4
C(2)–C(1)–C(4)	117·3 (8)	118·1 (8)	117·7
O——C(3)–C(5)	114·8 (8)	113·5 (8)	114·2
C(2)–C(3)–C(5)	118·3 (8)	120·0 (8)	119·2
C(1)–C(4)–M(1)	115·4 (8)	112·6 (8)	
C(1)–C(4)–M(2)	111·3 (1·0)	111·1 (8)	
C(1)–C(4)–M(3)	105·6 (9)	105·2 (8)	
C(3)–C(5)–M(4)	109·9 (8)	114·5 (9)	} 110·2*
C(3)–C(5)–M(5)	109·5 (8)	107·4 (1·1)	
C(3)–C(5)–M(6)	108·1 (8)	112·2 (1·1)	
M(1)–C(4)–M(2)	107·9 (1·1)	107·9 (9)	
M(1)–C(4)–M(3)	105·3 (1·2)	109·6 (8)	
M(2)–C(4)–M(3)	111·2 (1·4)	110·3 (8)	
M(4)–C(5)–M(5)	109·2 (9)	108·4 (1·5)	} 108·6*
M(4)–C(5)–M(6)	109·6 (9)	107·5 (1·6)	
M(5)–C(5)–M(6)	110·5 (9)	106·5 (1·7)	
O(I) –Pd——S(II)	177·7 (2)		
O(II)–Pd——S(I)		178·2 (2)	178·0

* Overall mean 109·4°.

Table 3. *Deviations (Å × 10³) from the plane through the coordinating atoms*

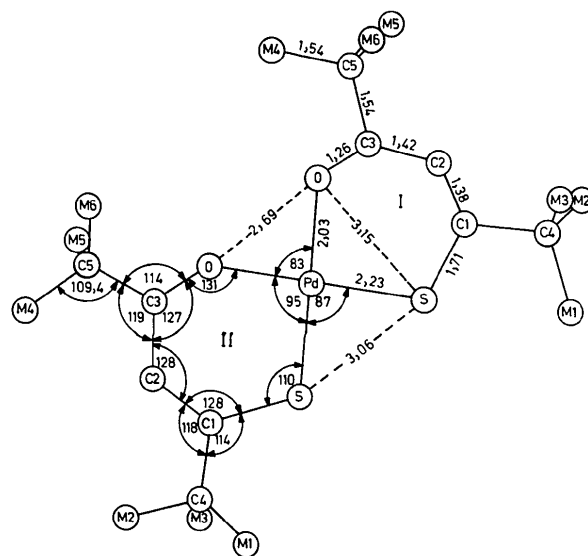|	Ring I	Ring II
Pd		−9
S	−13	13
O	15	−15
C(1)	28	219
C(2)	75	208
C(3)	45	61

Fig. 1. One asymmetric unit drawn in projection on the average plane through the molecule. The bond parameters are averaged over chemically equivalent, but crystallographically distinct, entities.

$w = zc \sin \beta$. The deviations of all the ring atoms from this plane are given in Table 3.

The most striking feature of the structure is the short Pd–S bond of 2·23 Å. However, the Pd–O bond, although shorter than the 2·10 Å observed by Shkol'nikova *et al.* (1973), appears normal in comparison with the 2·02 Å reported by Ito, Marumo & Saito (1971) for a Pd–O bond *trans* to N. Compared with the structure of the present ligand with Ni (Coetzer & Boeyens, 1971), it is once again the short Pd–S bond that stands out. The 2·14 Å Ni–S bond is not far from corresponding lengths of bonds *trans* to either S or N, and hence the present effect finds no easy explanation in terms of backbonding and/or *trans* effects. The *cis* arrangement that occurs persistently in the chelates of monothiodiketones is probably related to this effect, and further studies are indicated.

The structural formula of the complex is best represented by
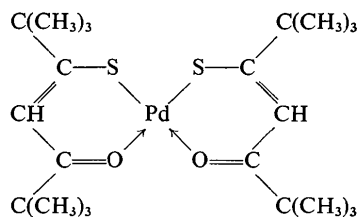
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2-Ethoxycarbonylimino-2*H*-1,2,4-thiadiazolo[2,3-*a*]pyridine Monohydrate

BY IVAN LEBAN

Chemistry Department, University of Ljubljana, 61000 Ljubljana, Yugoslavia

Abstract. $C_9H_9N_3O_2S . H_2O$, a product of the oxidative cyclization of *N*-ethoxycarbonyl-*N'*-(2-pyridyl)thiourea by bromine in acetic acid [Koren, Stanovnik & Tišler, *Org. Prep. Proceed. Int.* (1975), **7**, 55–59] is monoclinic, $P2_1/c$, $a = 6·310$ (4), $b = 37·269$ (22), $c = 4·568$ (4) Å, $\beta = 100·44$ (3)°, $V = 1056·5$ Å³, $D_m = 1·52$ (5) g cm⁻³ (flotation), $Z = 4$, $D_x = 1·517$ g cm⁻³, at 20 (1)°C. The molecule is almost planar, except for the ethoxy group which is bent out of the plane, and exhibits a very strong S···O interaction of 2·294 (5) Å, thus suggesting the presence of a single bond–no bond resonance structure.

Introduction. The compound crystallizes as transparent needles from toluene and dimethylformamide (3:1). The systematically absent reflexions ($0k0$; $k = 2n + 1$ and $h0l$; $l = 2n + 1$) on Weissenberg photographs and the centric distribution of $|E|$ values ($\langle E^2 \rangle = 1·000$; $\langle |E^2 - 1| \rangle = 1·020$; $\langle |E| \rangle = 0·776$) indicate space group $P2_1/c$. Unit-cell dimensions were obtained from a least-squares fit of the 2θ values of 15 reflexions measured on a CAD-4 diffractometer [Mo $K\alpha_1$ radiation, $\lambda = 0·70926$ Å, $t = 20$ (1)°C].

A single crystal with approximate dimensions $0·3 \times 0·1 \times 0·5$ mm was used for data collection on an automatic computer-controlled Enraf–Nonius CAD-4 four-

circle diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. Reflexions were scanned in the $\omega–2\theta$ mode (moving crystal–moving counter) at different rates to obtain a minimum net count of 5000 within a specified maximum scan time of 60 s. The background counts were taken at each of the scan limits for $\frac{1}{4}$ of the scan time. The 2θ scan width in degrees was $0·6 + 0·2 \tan \theta$ and the aperture was $2·4 + 0·9 \tan \theta$. The complete sphere of reflexions (7707 intensities in all) in the range $1·0 < \theta < 25·0°$ was measured. The symmetry-related reflexions were averaged (mean discrepancy on $I = 5·2\%$) to yield 1901 independent reflexions. Of these, 972 with $I > 3·0\sigma(I)$ were considered observed and were included in the refinement. The values of $\sigma(I)$ were based on counting statistics. Absorption corrections were not made [μ(Mo $K\alpha$) = 2·882 cm⁻¹]. The structure was solved by direct methods with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). An E map with the highest combined figure of merit CFOM (2·00) obtained with the unit weighting of ABSFOM (1·13), ψ_0 (2772) and RESID (31·13), computed with 300 phases ($|E| > 1·42$) gave initial coordinates for all the heavy atoms. The structure refinement was by full-matrix least squares, minimizing the function $\sum w(F_o - F_c)^2$, where the weighting function was determined empirically: