

Fig. 3. Projection of the crystal structure of  $\alpha$ -CD-GABA<sup>-</sup>.K<sup>+</sup>.10H<sub>2</sub>O along the *c* axis. Only the carboxyl O atoms of the guest GABA molecules (*A* to *F*) are shown in the  $\alpha$ -CD cavity. ---- and ——— indicate hydrogen and coordinate bonds, respectively.

the first six disordered GABA molecules (*A*, *B*, *C* and their equivalents related by a twofold rotation axis) and those of the second six (*D*, *E*, *F* and their equivalents), separated from each other by about 1 Å along the *c* axis.

The GABA molecules are connected infinitely by intermolecular NH $\cdots$ O hydrogen bonds through the  $\alpha$ -CD cavity. Such GABA molecules are fixed in the cavities in such a way that each carboxyl O atom of the disordered GABA molecules, except the GABA *C* molecule, is engaged in more than one hydrogen bond with the primary hydroxyl O(6*A*) of the host  $\alpha$ -CD molecule, as evidenced by the O $\cdots$ O or O $\cdots$ N

distances. Other parts of the guest molecule are in normal van der Waals contact with the host  $\alpha$ -CD. The  $\alpha$ -CD molecules are arranged into a channel-type structure, which is commonly found in  $\alpha$ -CD complexes, e.g. that with sodium 1-propanesulfonate (Harata, 1977). The intermolecular OH $\cdots$ O hydrogen bond between the secondary hydroxyl O(3) and the primary hydroxyl O(6*A*), which has a *trans-gauche* conformation, connects each  $\alpha$ -CD molecule to form a head-to-tail-type arrangement along the *c* axis as shown in Fig. 2. The K<sup>+</sup> cation is coordinated to six O atoms, constructing a disordered octahedron as shown in Fig. 3, where O(*W*1), O(*W*3), O(5) and O(6*B*) are roughly in a plane and the remaining two atoms, O(2) and O(*W*2), occupy the apices.

The coordination sphere around K<sup>+</sup> and the hydrogen-bond network formed by molecules of water of crystallization seem to be important in the stabilization of the host matrix structure. One  $\alpha$ -CD channel is surrounded by four neighboring channels with opposite channel direction.

#### References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1978). ORXFLS4. Oak Ridge National Laboratory, Tennessee.  
 HARATA, K. (1977). *Bull. Chem. Soc. Jpn*, **50**, 1259–1266.  
 HYBL, A., RUNDLE, R. E. & WILLIAMS, D. E. (1965). *J. Am. Chem. Soc.* **87**, 2779–2788.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 SAENGER, W. (1980). *Angew. Chem. Int. Ed. Engl.* **19**, 344–362.  
 TOMITA, K. (1965). *Joken Hansha (Jpn. J. Brain Physiol.)*, **61**, 1–4.  
 TOMITA, K., HIGASHI, H. & FUJIWARA, T. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2199–2204.  
 UNICS (1979). *The Universal Crystallographic Computing System—Osaka*, The Computation Center, Osaka Univ.

*Acta Cryst.* (1981). B37, 447–450

## Structure of Acetylacetonato[*N*-(methyl)thiobenzamidomethyl]palladium(II)

BY KUNIO MIKI, NOBUO TANAKA AND NOBUTAMI KASAI

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565, Japan

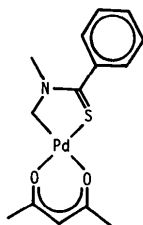
(Received 27 July 1980; accepted 23 September 1980)

**Abstract.** [Pd(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)(C<sub>9</sub>H<sub>10</sub>NS)], C<sub>14</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>Sd, *M<sub>r</sub>* = 369.8, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 11.200 (2), *b* = 6.972(1), *c* = 19.034 (3) Å, *V* = 1486.4 (4) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.652 Mg m<sup>-3</sup>, *F*(000) = 744,  $\mu$ (Mo *K* $\alpha$ ) =

1.36 mm<sup>-1</sup>. *R* = 0.024 for 1837 non-zero reflexions. The geometry around the Pd atom is square planar. The *N*-(methyl)thiobenzamidomethyl group is bound to the Pd atom through the Pd–C  $\sigma$  bond and the dona-

tion of electrons from the S to the metal atom [Pd–C(7) = 1.988 (4) and Pd–S = 2.245 (1) Å].

**Introduction.** As part of a series of Pd-catalysed reactions of thioamides, a Pd complex containing an *N*-(methyl)thiobenzamidomethyl (hereafter abbreviated as thioamidomethyl) group has been prepared by Tamaru, Kagotani & Yoshida (1979).



The molecular structure of the title compound has been determined in order to elucidate the coordination behaviour of the thioamidomethyl group to the Pd atom.

A yellow, prismatic crystal with approximate dimensions 0.15 × 0.25 × 0.40 mm was mounted on a Rigaku automated four-circle diffractometer. The crystal system was determined as orthorhombic with the aid of the Rigaku soft-ware system of the diffractometer. Accurate unit-cell dimensions were determined by a least-squares fit of 25 strong reflexions. Intensity data were collected by the  $\theta$ - $2\theta$  scan technique with graphite-monochromatized Mo  $K\alpha$  radiation. The scan speed was 4° min<sup>-1</sup> and the scan width  $\Delta 2\theta = (2.0 + 0.7 \tan \theta)^\circ$ . The background intensities were measured for 7.5 s at each end of the scan. Two sets of  $|F(hkl)|$  and  $|F(\bar{h}\bar{k}\bar{l})|$  reflexions ( $h, k, l > 0$ ), a total of 3720, were collected up to  $2\theta = 54^\circ$ , 198 of which were considered as unobserved. Reflexions were corrected for  $L_p$  factors but not for absorption or extinction.

The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares procedure (HBL5-V, Ashida, 1979). The refinement was carried out without consideration of anomalous-dispersion effects, using 1886 (1837 non-zero) reflexions obtained by averaging  $|F(hkl)|$  and  $|F(\bar{h}\bar{k}\bar{l})|$  reflexions. The agreement factor of equivalent reflexions, defined by  $R_{ref} = \sum (|F| - \langle |F| \rangle) / \sum |F|$ , is 0.014 for 3720 reflexions, where  $\langle |F| \rangle$  is the average value of two or more equivalent reflexions. After the anisotropic refinement for the non-hydrogen atoms, all the H atoms were found at reasonable positions in the difference Fourier map, parameters of which were refined isotropically in the further refinement. At the final stage of the refinement, five strong reflexions (200, 201, 002, 012 and 013), which were considered as affected by extinction, were omitted. The final  $R$  indices are 0.024 and 0.027 for non-zero and all reflexions, respectively, where  $R = \sum (|F_o| - |F_c|) / \sum |F_o|$ .

Table 1. Final atomic parameters

(a) Non-hydrogen atoms

The  $B_{eq}$  values are equivalent isotropic temperature factors calculated from the anisotropic factors (Hamilton, 1959).

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}$ (Å <sup>2</sup> )
Pd	0.17529 (3)	0.03667 (5)	0.064725 (14)	3.09
S	0.21986 (10)	0.15287 (15)	-0.04213 (6)	3.43
O(1)	0.1217 (3)	-0.0374 (5)	0.16431 (14)	4.02
O(2)	0.2825 (3)	-0.2109 (4)	0.05793 (14)	3.52
N	0.0829 (3)	0.4083 (5)	0.01720 (16)	2.91
C(1)	0.1576 (4)	-0.1828 (6)	0.19727 (19)	3.39
C(2)	0.2963 (4)	-0.3277 (7)	0.1084 (3)	3.36
C(3)	0.2402 (4)	-0.3189 (7)	0.1736 (3)	3.68
C(4)	0.1063 (6)	-0.2071 (8)	0.2703 (3)	4.90
C(5)	0.3822 (5)	-0.4907 (7)	0.0950 (3)	4.44
C(6)	0.1453 (4)	0.3649 (6)	-0.0388 (2)	2.95
C(7)	0.0748 (4)	0.2702 (6)	0.0749 (3)	3.28
C(8)	0.0188 (4)	0.5892 (6)	0.0273 (3)	3.39
C(9)	0.1537 (4)	0.4986 (6)	-0.09978 (19)	3.22
C(10)	0.2613 (5)	0.5881 (7)	-0.1155 (3)	4.20
C(11)	0.2681 (6)	0.7119 (8)	-0.1714 (3)	5.19
C(12)	0.1705 (6)	0.7451 (7)	-0.2138 (3)	5.04
C(13)	0.0659 (5)	0.6572 (9)	-0.1993 (3)	5.03
C(14)	0.0537 (5)	0.5293 (8)	-0.1426 (3)	4.34

(b) Hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	$B$ (Å <sup>2</sup> )
H(3)	0.254 (4)	-0.405 (7)	0.206 (3)	1.9 (10)
H(4A)	0.074 (6)	-0.339 (13)	0.279 (4)	7.8 (21)
H(4B)	0.164 (6)	-0.187 (13)	0.304 (4)	8.3 (22)
H(4C)	0.070 (6)	-0.103 (13)	0.274 (4)	8.6 (22)
H(5A)	0.453 (7)	-0.457 (12)	0.080 (4)	9.2 (25)
H(5B)	0.375 (7)	-0.573 (13)	0.123 (4)	8.1 (22)
H(5C)	0.369 (7)	-0.550 (11)	0.063 (3)	7.4 (21)
H(7A)	0.107 (5)	0.345 (8)	0.118 (3)	2.0 (10)
H(7B)	-0.006 (5)	0.224 (9)	0.071 (3)	4.3 (14)
H(8A)	-0.039 (5)	0.589 (9)	0.007 (3)	3.7 (13)
H(8B)	0.028 (5)	0.637 (9)	0.074 (3)	4.2 (14)
H(8C)	0.052 (4)	0.697 (8)	0.002 (3)	3.1 (13)
H(10)	0.331 (4)	0.562 (7)	-0.092 (3)	2.3 (10)
H(11)	0.340 (4)	0.759 (8)	-0.181 (3)	2.6 (11)
H(12)	0.185 (5)	0.824 (8)	-0.260 (3)	3.4 (12)
H(13)	0.004 (6)	0.667 (9)	-0.228 (3)	4.0 (14)
H(14)	-0.027 (5)	0.487 (8)	-0.134 (3)	2.6 (11)

$\sum |F_o|$ . The weighting schemes used are  $w = (\sigma_{cs}^2 + a|F_o| + b|F_o|^2)^{-1}$  for  $|F_o| > 0$  and  $w = c$  for  $|F_o| = 0$ , where  $\sigma_{cs}$  is the standard deviation obtained from the counting statistics and  $a, b$  and  $c$  used in the final stage of the refinement are 0.0012, 0.0004 and 0.1450, respectively. The final weighted  $R$  index  $\{R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}\}$  is 0.031 for all reflexions. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974) for the non-hydrogen atoms and Stewart, Davidson & Simpson (1965) for H atoms. Final atomic parameters are listed in Table 1.\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35689 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

After the refinement was completed, the absolute configuration of the molecule was confirmed by the refinement of both models ( $x, y, z$  and  $x, y, \bar{z}$ ), including H atom contributions, to convergence, although the present molecule contains no asymmetric atoms. For this refinement,  $|F(hkl)|$  and  $|F(\bar{h}\bar{k}\bar{l})|$  reflexions were treated as independent data (a total of 3252 reflexions) and anomalous-dispersion effects were included, the  $f'$  and  $f''$  components of which were taken from *International Tables for X-ray Crystallography* (1974). The chosen model had an  $R$  of 0.0260 while the enantiomeric structure gave an  $R$  of 0.0295. The  $R$ -factor-ratio test (Hamilton, 1965) applied to these  $R$  values showed that the alternative model ( $x, y, \bar{z}$ ) may be rejected at less than the 0.005 significance level.

**Discussion.** Fig. 1 shows an ORTEP drawing (Johnson, 1976) of the molecule together with the atomic-numbering scheme. Bond lengths and angles are listed in Tables 2 and 3.

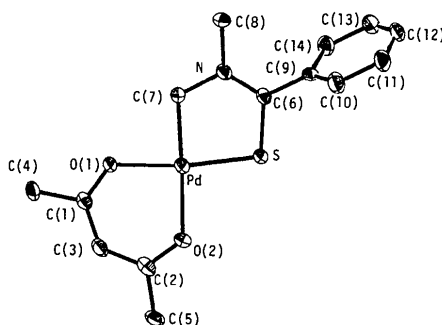


Fig. 1. An ORTEP drawing of the molecule along with the numbering system of the atoms. The thermal ellipsoids correspond to the 30% probability level. H atoms are omitted for clarity.

Table 2. Bond lengths (Å) with their estimated standard deviations in parentheses

Pd—O(1)	2.054 (3)	Pd—O(2)	2.106 (3)
Pd—S	2.245 (1)	Pd—C(7)	1.988 (4)
O(1)—C(1)	1.258 (5)	O(2)—C(2)	1.268 (5)
C(1)—C(3)	1.400 (6)	C(2)—C(3)	1.394 (6)
C(1)—C(4)	1.514 (7)	C(2)—C(5)	1.510 (7)
S—C(6)	1.699 (4)	N—C(6)	1.309 (5)
N—C(7)	1.463 (5)	N—C(8)	1.463 (5)
C(6)—C(9)	1.492 (6)		
C(9)—C(10)	1.389 (6)	C(10)—C(11)	1.373 (7)
C(11)—C(12)	1.379 (8)	C(12)—C(13)	1.350 (8)
C(13)—C(14)	1.406 (8)	C(14)—C(9)	1.402 (7)
C(3)—H(3)	0.87 (5)	C(5)—H(5A)	0.88 (9)
C(4)—H(4A)	1.00 (9)	C(5)—H(5B)	0.79 (9)
C(4)—H(4B)	0.92 (9)	C(5)—H(5C)	0.75 (8)
C(4)—H(4C)	0.83 (9)	C(10)—H(10)	0.92 (5)
C(7)—H(7A)	1.03 (6)	C(11)—H(11)	0.89 (5)
C(7)—H(7B)	0.97 (6)	C(12)—H(12)	1.05 (6)
C(8)—H(8A)	0.76 (6)	C(13)—H(13)	0.89 (6)
C(8)—H(8B)	0.96 (7)	C(14)—H(14)	0.96 (6)
C(8)—H(8C)	0.97 (6)		

Table 3. Bond angles (°) involving non-hydrogen atoms with their estimated standard deviations in parentheses

O(1)—Pd—O(2)	90.99 (12)	O(1)—Pd—C(7)	87.19 (15)
S—Pd—C(7)	85.31 (12)	S—Pd—O(2)	96.50 (8)
Pd—O(1)—C(1)	124.7 (3)	Pd—O(2)—C(2)	123.3 (3)
O(1)—C(1)—C(3)	126.7 (4)	O(2)—C(2)—C(3)	126.3 (4)
O(1)—C(1)—C(4)	115.3 (4)	O(2)—C(2)—C(5)	115.7 (4)
C(3)—C(1)—C(4)	118.0 (4)	C(3)—C(2)—C(5)	118.1 (4)
C(1)—C(3)—C(2)	127.9 (5)		
Pd—S—C(6)	99.82 (14)	Pd—C(7)—N	115.5 (3)
S—C(6)—N	119.6 (3)	C(6)—N—C(7)	119.4 (4)
S—C(6)—C(9)	118.9 (3)	C(6)—N—C(8)	124.6 (4)
N—C(6)—C(9)	121.5 (4)	C(7)—N—C(8)	116.0 (3)
C(6)—C(9)—C(10)	120.2 (4)	C(6)—C(9)—C(11)	119.8 (4)
C(10)—C(9)—C(14)	120.0 (5)	C(9)—C(10)—C(11)	119.8 (5)
C(10)—C(11)—C(12)	121.0 (6)	C(11)—C(12)—C(13)	119.5 (6)
C(12)—C(13)—C(14)	121.9 (6)	C(13)—C(14)—C(9)	117.7 (5)

Table 4. Least-squares planes and atomic deviations from them

The equation of the plane is of the form:  $AX + BY + CZ + D = 0.0$ , where  $X, Y$  and  $Z$  are in Å.

(a) Coordination plane of Pd through Pd, O(1), O(2), C(7) and S

$$-0.7750X - 0.5006Y - 0.3858Z + 2.1346 = 0.0$$

(b) Plane of the thioamidomethyl group through S, N, C(6), C(7), C(8) and C(9)

$$-0.8081X - 0.4189Y - 0.4141Z + 2.0804 = 0.0$$

(c) Plane of the acetylacetonato ligand through O(1), O(2), C(1), C(2), C(3), C(4) and C(5)

$$-0.7533X - 0.5469Y - 0.3654Z + 2.0054 = 0.0$$

Deviations of atoms from the plane (Å) with e.s.d.'s in parentheses

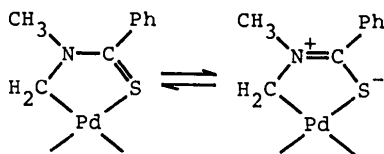
	Plane (a)	Plane (b)	Plane (c)
Pd	0.010 (2)	-0.123 (4)*	-0.063 (5)*
S	0.002 (2)	-0.024 (3)	
N	-0.137 (4)*	0.002 (3)	
C(6)	-0.115 (5)*	0.005 (4)	
C(7)	-0.007 (2)	0.024 (2)	
C(8)	-0.285 (6)*	-0.026 (3)	
C(9)	-0.207 (5)*	0.019 (2)	
O(1)	0.002 (2)		-0.021 (3)
O(2)	-0.007 (2)		0.024 (3)
C(1)	-0.044 (5)*		0.001 (4)
C(2)	-0.090 (5)*		0.001 (4)
C(3)	-0.113 (5)*		-0.013 (4)
C(4)	-0.050 (7)*		0.018 (3)
C(5)	-0.168 (6)*		-0.009 (3)

\* Not included in the least-squares calculation.

The geometry around the Pd atom is essentially square planar. The Pd atom is surrounded by two O atoms of the acetylacetonato ligand and the C and S atoms of the thioamidomethyl group. The equations of the least-squares planes and atomic deviations from the plane are presented in Table 4.

The thioamidomethyl group, bound to the Pd atom through the Pd—C  $\sigma$  bond and the donation of electrons from S to the metal atom, functions as a bidentate ligand forming a Pd—C—N—C—S five-

membered ring. The Pd–C(7) bond length of 1.988 (4) Å is somewhat short but falls into the range 1.97–2.19 Å of the Pd<sup>II</sup>–C(sp<sup>3</sup>) bond lengths reported hitherto. The Pd–S bond length [2.245 (1) Å] in this complex is also one of the shortest Pd<sup>II</sup>–S bonds among Pd complexes whose structures have been determined by the diffraction method (2.23 ~ 2.45 Å). The S, N, C(6), C(7), C(8) and C(9) atoms in the thioamidomethyl group are coplanar. The dihedral angle between this plane and the coordination plane of the Pd atom is 5.3°. Among the three N–C bonds, the N–C(7) and N–C(8) lengths [both 1.463 (5) Å], are considered to be normal lengths for N–C(sp<sup>3</sup>) single bonds. On the other hand, N–C(6) [1.309 (5) Å] is obviously shorter than the other two N–C bonds and may have partial double-bond character. In this connexion, the S–C(6) bond [1.699 (4) Å] is apparently longer than an S=C double bond (1.61 Å, Abrahams, 1956). These facts show the conjugation through the S–C(6) and N–C(6) bonds. Both resonance structures presented below contribute significantly to the bonding of the thioamidomethyl group in this complex, which may be connected with the relatively short Pd–S bond.



The structure of the acetylacetonato ligand, which has high planarity and is coplanar with the Pd atom, is almost the same as that found in [Pd(acac)<sub>2</sub>] (Knyazeva, Shugam & Shkol'nikova, 1970; Sato, Miki, Kai, Tanaka, Yasuoka & Kasai, unpublished). However, both Pd–O bond lengths are longer than that found in [Pd(acac)<sub>2</sub>] (1.989 Å), which may be due to a weak *trans* influence of the O atoms in [Pd(acac)<sub>2</sub>]. The Pd–O(1) bond [2.054 (3) Å] is obviously shorter than Pd–O(2) [2.106 (3) Å]. This shortening may also be caused by a weak *trans* influence of the electro-negative S atom attached to the *trans* position of the Pd–O(1) bond.

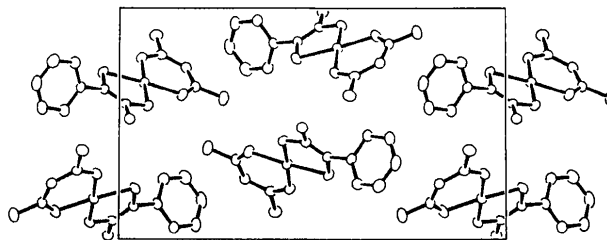


Fig. 2. The crystal structure as viewed down the *b* axis. Atoms are represented by thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.

The crystal structure as viewed down the *b* axis is shown in Fig. 2. All intermolecular distances are considered to be normal van der Waals contacts, the shortest contact between non-hydrogen atoms being 3.218 (5) Å [C(8) (*x*, *y*, *z*) ··· O(2) ( $\frac{1}{2} + x$ ,  $\frac{1}{2} - y$ ,  $-z$ )].

All computations were carried out on an ACOS 700 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University. The authors wish to thank Professor Z. Yoshida, Dr Y. Tamaru and co-workers at Kyoto University for crystals.

#### References

- ABRAHAMS, S. C. (1956). *Q. Rev. Chem. Soc.* **10**, 407–436.  
 ASHIDA, T. (1979). *The Universal Crystallographic Computing System—Osaka*, pp. 53–59. The Computation Center, Osaka Univ.  
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.  
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.  
 KNYAZEVA, A. N., SHUGAM, E. A. & SHKOL'NIKOVA, L. M. (1970). *Zh. Strukt. Khim.* **11**, 938–939.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.  
 TAMARU, Y., KAGOTANI, M. & YOSHIDA, Z. (1979). 40th Nat. Meet. Chem. Soc. Japan, Fukuoka. Abstr. III, pp. 1046–1047.