

Structure of Tetrakis(μ -1,3-benzothiazole-2-thiolato-*N,S*)-dipalladium(II), [Pd₂(C₇H₄NS₂)₄]

BY MARIA KUBIAK

Institute of Chemistry, University of Wrocław, Joliot-Curie 14, 50–383 Wrocław, Poland

(Received 6 July 1984; accepted 22 April 1985)

Abstract. $M_r = 877.8$, triclinic, $P\bar{1}$, $a = 9.746$ (3), $b = 7.673$ (3), $c = 11.304$ (4) Å, $\alpha = 105.45$ (4), $\beta = 99.05$ (4), $\gamma = 101.02$ (4)°, $U = 780.1$ Å³, $Z = 1$, $D_m = 1.88$ (2), $D_x = 1.87$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.67$ mm⁻¹, $F(000) = 432$, room temperature, final $R = 0.030$ for 1572 reflections. The molecular structure of the title complex consists of binuclear units of composition [Pd₂(C₇H₄NS₂)₄], in which two Pd atoms are linked by four bridging 1,3-benzothiazole-2-thiolato ligands, *via* their exocyclic S and heterocyclic N atoms. The coordination geometry around Pd is square-planar [Pd–S 2.289 (2), 2.285 (2) Å; Pd–N 2.084 (5), 2.078 (5) Å]. The Pd...Pd distance is 2.745 (1) Å.

Introduction. 4,5-Dihydro-1,3-thiazole-2-thiol (Httz) and 1,3-benzothiazole-2-thiol (Hbttz) contain two donor sites capable of interacting with metal ions, *i.e.* exocyclic S and heterocyclic N atoms. These ligands exist, as free molecules in two tautomeric forms, HN–C=S and N=C–SH, in a thione–thiol equilibrium and may also be deprotonated to form thiolato anions (Dehand & Jordanov, 1976; Raper, Oughtred & Nowell, 1983). Spectroscopic studies of the interactions of Pd^{II} and Pt^{II} with 4,5-dihydro-1,3-thiazole-2-thiol (De Filippo, Devillanova, Trogu, Verani, Preti & Viglino, 1973; Dehand & Jordanov, 1976) have suggested that the complexes formed at low pH are N-bonded species.

In an earlier paper we discussed the synthesis and molecular structure of tetrakis(1,3-thiazolidine-2-thione)palladium(II) dichloride–1,3-thiazolidine-2-thione (1/2) and showed that coordination occurs between Pd and exocyclic S (Kubiak & Głowiak, 1982). Spectroscopic investigations of the Pd^{II}–bttz system (Dehand & Jordanov, 1976) have suggested that the complex has a polymeric structure in which a ligand forms a bridge, through N and S, between two metals atoms.

To check this possibility we have determined the crystal structure of the title compound.

Experimental. Clear, brick-like crystal from aqueous solution of K₂PdCl₄ and water–ethanol solution of the

ligand, dimensions 0.09 × 0.12 × 0.18 mm; D_m by flotation in CCl₄/CHBr₃; triclinic geometry from Weissenberg photographs; Syntex P2₁ computer-controlled four-circle diffractometer, scintillation counter, graphite monochromator; cell parameters by least squares from setting angles of 15 reflections with $15 < 2\theta < 24^\circ$ measured on the diffractometer; 2045 independent reflections measured; $2\theta_{\max} = 45^\circ$; variable θ – 2θ scan rate, 2.0–29.3° min⁻¹ (depending on intensity); two standards measured every 50 reflections, variation in their intensities $\pm 2\%$; corrections for Lorentz and polarization effects, but not for absorption; 1572 reflections with $I > 3.0\sigma(I)$ used for structure determination; index range $h 0 \rightarrow 10$, $k -8 \rightarrow 8$, $l -12 \rightarrow 11$; calculations performed on a NOVA 1200 computer with programs supplied by Syntex (1976); neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); structure solved by heavy-atom method; full-matrix least-squares refinement (on F); non-H atoms refined with anisotropic temperature factors; H-atom coordinates and thermal parameters kept fixed (with $B = 5.0$ Å²); 190 variables; $(\Delta/\sigma)_{\max} < 0.005$; $(\Delta\rho)_{\max} \pm 0.4$ e Å⁻³; $R = 0.030$, $wR = 0.029$, $S = 1.56$, $w = 1/\sigma^2(F)$; no correction for extinction.

Discussion. Final atomic parameters are given in Table 1,* interatomic distances and angles in Table 2; Fig. 1 shows the configuration of the binuclear complex and indicates the numbering system used.

The crystal structure consists of dimeric units in which two Pd atoms are linked by four bttz bridges with an inversion center at the midpoint between the two metal atoms. The bttz ligand is coordinated to the Pd atoms *via* exocyclic S and thiazole N. There are no axial ligands and no molecules of solvent of crystallization. The crystal structure thus confirms the spectroscopic evidence (Dehand & Jordanov, 1976) that bttz acts as a bridging S,N ligand.

* Lists of structure amplitudes, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42202 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

	$B_{eq} = \frac{1}{3} \sum_i B_{ii}$			
	x	y	z	$B_{eq} (\text{\AA}^2)$
Pd	0.05514 (5)	0.15085 (7)	-0.03645 (5)	2.45 (3)
S(1)	0.1904 (2)	0.3123 (2)	0.1612 (1)	3.0 (1)
S(2)	0.2437 (2)	0.2474 (2)	0.4074 (1)	3.2 (1)
S(3)	0.1215 (2)	-0.2955 (2)	-0.0139 (2)	3.2 (1)
S(4)	0.3607 (2)	-0.2286 (2)	-0.1391 (2)	4.0 (1)
N(1)	0.0735 (5)	-0.0058 (7)	0.2138 (4)	2.5 (4)
N(2)	0.2169 (5)	0.0193 (7)	-0.0806 (4)	2.3 (4)
C(1)	0.1549 (6)	0.1661 (8)	0.2491 (6)	2.6 (5)
C(11)	0.1739 (7)	0.0311 (9)	0.4242 (6)	3.3 (5)
C(12)	0.0853 (6)	-0.0885 (9)	0.3123 (6)	2.8 (5)
C(13)	0.0219 (7)	-0.2696 (9)	0.3019 (6)	3.4 (6)
C(14)	0.0493 (9)	-0.3317 (10)	0.4046 (7)	4.7 (7)
C(15)	0.1375 (9)	-0.2105 (12)	0.5177 (7)	5.7 (8)
C(16)	0.2011 (8)	-0.0288 (11)	0.5299 (6)	4.2 (7)
C(2)	0.2231 (6)	-0.1497 (9)	-0.0770 (5)	2.6 (5)
C(21)	0.4154 (6)	-0.0191 (9)	-0.1682 (6)	2.9 (5)
C(22)	0.3266 (7)	0.0983 (9)	-0.1309 (5)	2.6 (5)
C(23)	0.3545 (7)	0.2779 (9)	-0.1391 (6)	3.3 (6)
C(24)	0.4696 (8)	0.3351 (10)	-0.1900 (7)	4.3 (6)
C(25)	0.5564 (8)	0.2140 (11)	-0.2305 (7)	4.7 (7)
C(26)	0.5301 (7)	0.0375 (10)	-0.2216 (7)	4.3 (7)

Table 2. *Bond distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses*

A prime indicates a symmetry-related atom at $-x, -y, -z$.			
Pd-S(1)	2.289 (2)	Pd-S(3')	2.285 (2)
Pd-N(2)	2.084 (5)	Pd-N(1')	2.078 (5)
	Pd...Pd'	2.745 (1)	
S(1)-C(1)	1.709 (7)	S(3)-C(2)	1.722 (7)
S(2)-C(1)	1.747 (6)	S(4)-C(2)	1.743 (7)
N(1)-C(1)	1.322 (8)	N(2)-C(2)	1.320 (8)
S(2)-C(11)	1.741 (7)	S(4)-C(21)	1.727 (7)
N(1)-C(12)	1.421 (8)	N(2)-C(22)	1.401 (8)
C(11)-C(12)	1.387 (9)	C(21)-C(22)	1.396 (9)
C(12)-C(13)	1.375 (10)	C(22)-C(23)	1.383 (10)
C(13)-C(14)	1.375 (10)	C(23)-C(24)	1.389 (10)
C(14)-C(15)	1.398 (11)	C(24)-C(25)	1.409 (11)
C(15)-C(16)	1.374 (13)	C(25)-C(26)	1.363 (12)
C(16)-C(11)	1.396 (10)	C(26)-C(21)	1.403 (10)
S(1)-Pd-S(3')	88.4 (1)	S(3')-Pd-N(1')	89.8 (2)
S(1)-Pd-N(1')	178.2 (1)	S(3')-Pd-N(2)	179.5 (1)
S(1)-Pd-N(2)	91.1 (1)	N(1')-Pd-N(2)	90.6 (2)
S(1)-Pd-Pd'	92.7 (1)	N(1')-Pd-Pd'	86.8 (1)
S(3')-Pd-Pd'	93.3 (1)	N(2)-Pd-Pd'	86.5 (1)
Pd-S(1)-C(1)	104.7 (2)	Pd'-S(3)-C(2)	104.0 (2)
Pd'-N(1)-C(1)	126.3 (4)	Pd-N(2)-C(2)	126.1 (4)
Pd'-N(1)-C(12)	121.7 (4)	Pd-N(2)-C(22)	121.7 (4)
C(1)-S(2)-C(11)	89.9 (3)	C(2)-S(4)-C(21)	90.0 (3)
C(1)-N(1)-C(12)	112.0 (5)	C(2)-N(2)-C(22)	111.9 (5)
S(1)-C(1)-S(2)	116.6 (4)	S(3)-C(2)-S(4)	116.4 (4)
S(1)-C(1)-N(1)	129.3 (5)	S(3)-C(2)-N(2)	129.5 (5)
S(2)-C(1)-N(1)	114.0 (5)	S(4)-C(2)-N(2)	114.1 (5)
S(2)-C(11)-C(12)	110.7 (5)	S(4)-C(21)-C(22)	110.4 (5)
C(12)-C(11)-C(16)	121.0 (6)	C(22)-C(21)-C(26)	121.0 (6)
S(2)-C(11)-C(16)	128.3 (6)	S(4)-C(21)-C(26)	128.5 (5)
N(1)-C(12)-C(11)	113.2 (6)	N(2)-C(22)-C(21)	113.5 (6)
N(1)-C(12)-C(13)	125.7 (6)	N(2)-C(22)-C(23)	125.7 (6)
C(11)-C(12)-C(13)	121.0 (6)	C(21)-C(22)-C(23)	120.7 (6)
C(12)-C(13)-C(14)	118.7 (7)	C(22)-C(23)-C(24)	118.2 (6)
C(13)-C(14)-C(15)	120.2 (7)	C(23)-C(24)-C(25)	120.8 (7)
C(14)-C(15)-C(16)	121.8 (8)	C(24)-C(25)-C(26)	121.3 (7)
C(11)-C(16)-C(15)	117.2 (7)	C(21)-C(26)-C(25)	118.0 (7)

Each Pd atom has five neighbors: two S and two N atoms and the other metal atom at a distance of 2.745 (1) \AA. The *cis* PdS₂N₂ units with eclipsed relationship are essentially square-planar with S-Pd-N, S-Pd-S' and N-Pd-N' angles close to 90°. The Pd atom is displaced from the coordination plane by 0.0082 (5) \AA.

The Pd...Pd distance found in the present compound is shorter than the 2.751 \AA observed in metallic Pd (Donohue, 1974) and lies well within the range 2.71-2.79 \AA observed for dimeric complexes of palladium(II) with chelating or bridging S ligands (Piovesana, Bellitto, Flamini & Zanazzi, 1979; Browall, Bursh, Interrante & Kasper, 1972); in such complexes a Pd-Pd bond has generally been assumed.

However, recently, Pd₂(mhp)₄ (where Hmhp = 6-methyl-2-pyridinol) (Clegg, Garner & Al-Samman, 1982) is considered as having no direct M-M bond, though the existence of a bond would be suggested by the Pd...Pd separation of 2.546 (1) \AA, in view of the estimated value of 1.31 \AA for the covalent radius of Pd^{II} (Churchill, 1970).

The two Pd-S bond lengths in Pd₂(bttz)₄ [2.289 (2) and 2.285 (2) \AA] are shorter than the Pd-S distances of 2.322 (2) and 2.327 (2) \AA observed in Pd(Htz)₄Cl₂.2ttz (Kubiak & Głowiak, 1982). The mean Pd-S-C angles in these structures are 104 and 110°, respectively. The two unique Pd-S and Pd-N distances are in the range normally observed for square-planar Pd,S,N systems (Głowiak & Ciszewska, 1982).

Corresponding bond distances and angles of the two crystallographically independent ligands are equivalent within experimental error. They are slightly different from those of the free ligand (Chesick & Donohue, 1971). Coordination of the bttz molecule in the complex involves shortening of the C-N, and elongation of the C-S_{exo} bond of the N-C-S_{exo} system, in comparison with 1.353 (6) and 1.662 (4) \AA in the free molecule (see Table 2).

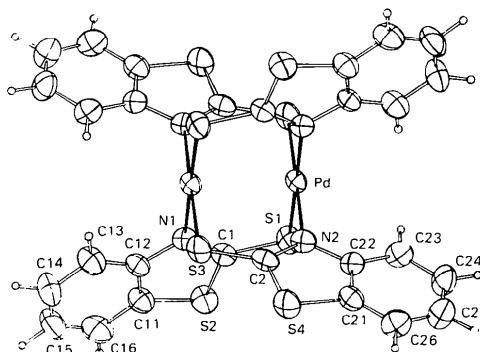


Fig. 1. The structure of the binuclear complex and the numbering system used.

On the basis of the observed bond lengths, it would seem possible to represent formally the ligand as the anion derived from the thiolate form of the ligand, although the thione form is observed in free Hbttz. This change may be related to a strong metal–ligand interaction (Jeannin, Jeannin & Lavigne, 1979). Electron donation from the S atom to the metal may induce a decrease in the π -electron density along the C–S_{exo} bond and this would result in a charge displacement from the N lone pair to the C–N bond, in agreement with the observed C–N shortening.

The bond angles in the bttz ligands indicate a distorted geometry because of the steric hindrance arising from the coordination. The S,N coordination alters the thiazole ring geometry by decreasing the C–N–C and S_{exo}–C–S_{endo} angles (by *ca* 4 and 7° respectively) and opening up the S_{endo}–C–N angle (by 5°).

The thiazole ring is also more non-planar than in uncoordinated Hbttz, the largest deviations from the least-squares planes through the benzene rings being for the thiazole S atoms. It is interesting to note that all atoms of the thiazole ring are out of the benzene plane and on the same side, in agreement with the previously reported structure of Mn(CO)₃(bttz)₂ (Jeannin, Jeannin & Lavigne, 1977). The angles between the benzene and thiazole rings of the ligands are 3.1 (8) and 2.2 (8)°.

The most pronounced distortion is the bending of the exocyclic S(1) and S(3) atoms out of the thiazole-ring planes by 0.191 (2) and 0.131 (2) Å, respectively. This does not appear in free Hbttz and is probably a consequence of the particular, bridged linkage of the ligand.

The author is grateful to Professor Tadeusz Głowiak for his constant interest in this work and for discussions concerning the results. This research was supported by the Polish Academy of Sciences.

References

- BROWALL, K. W., BURSH, T., INTERRANTE, L. V. & KASPER, J. S. (1972). *Inorg. Chem.* **11**, 1800–1806.
 CHESICK, J. P. & DONOHUE, J. (1971). *Acta Cryst.* **B27**, 1441–1444.
 CHURCHILL, M. R. (1970). *Perspect. Struct. Chem.* **3**, 91–164.
 CLEGG, W., GARNER, C. D. & AL-SAMMAN, M. H. (1982). *Inorg. Chem.* **21**, 1897–1901.
 DE FILIPPO, D., DEVILLANOVA, F., TROGU, E. F., VERANI, G., PRETI, C. & VIGLINO, P. (1973). *Can. J. Chem.* **51**, 1172–1178.
 DEHAND, J. & JORDANOV, J. (1976). *Inorg. Chim. Acta*, **17**, 37–44.
 DONOHUE, J. (1974). *The Structure of Elements*, p. 216. New York: John Wiley.
 GŁOWIAK, T. & CISZEWSKA, T. (1982). *Acta Cryst.* **B38**, 1735–1737.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 JEANNIN, S., JEANNIN, Y. & LAVIGNE, G. (1977). *J. Cryst. Mol. Struct.* **7**, 241–249.
 JEANNIN, S., JEANNIN, Y. & LAVIGNE, G. (1979). *Inorg. Chem.* **18**, 3528–3535.
 KUBIAK, M. & GŁOWIAK, T. (1982). *Acta Cryst.* **B38**, 2031–2034.
 PIOVESANA, O., BELLITTO, C., FLAMINI, A. & ZANAZZI, P. F. (1979). *Inorg. Chem.* **18**, 2258–2265.
 RAPER, E. S., OUGHTRED, R. E. & NOWELL, I. W. (1983). *Inorg. Chim. Acta*, **77**, L89–L93.
 SYNTAX (1976). *XTL/XTLE Structure Determination System*. Syntax Analytical Instruments, Cupertino, California.

Acta Cryst. (1985). **C41**, 1290–1295

Structure of a Solvated Nickel(II) Complex of (S)-2'-(N-Benzylpropyl)aminoacetophenone and (R)-Valine Schiff Base, C₂₅H₂₉N₃NiO₃·½C₄H₈O. Conformational Calculation of Diastereomeric Complexes of (R)-Valine and (S)-Valine

BY S. V. LINDEMAN, T. V. TIMOFEEVA, V. I. MALEYEV, YU. N. BELOKON', M. G. RYZHOV, V. M. BELIKOV AND YU. T. STRUCHKOV

A. N. Nesmeyanov Institute of Organoelement Compounds, USSR Academy of Sciences, 28 Vavilov Street, Moscow 117813, USSR

(Received 20 November 1984; accepted 30 April 1985)

Abstract. {(R)-[N-(1-{2-[N-(S)-Benzylpropylamino]phenyl}ethylidene)valinato]nickel(II)-tetrahydrofuran (2/1), *M_r* = 514.3, monoclinic, *P*2₁, *a* = 10.779 (1), *b* = 11.800 (5), *c* = 20.014 (2) Å, β = 95.26 (1)°, *V* = 2535 (2) Å³, *Z* = 4, *D_x* = 1.35 Mg m⁻³, Mo *K*α, λ = 0.71069 Å, μ = 0.796 mm⁻¹, *F*(000) = 1088, room temperature, *R* = 0.055 for 5284 independent reflections. In the crystal

0108-2701/85/091290-06\$01.50

© 1985 International Union of Crystallography