STRUCTURE OF A PALLADIUM(II) COMPLEX WITH A NON-SYMMETRICAL TETRADENTATE SCHIFF BASE, [Pd($C_{14}H_{20}N_3O$)]NCS

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The structure of (1-phenyl-3-{2-[(2-aminoethyl)amino]ethylimino}-1-buten-1-olato-O,N,N′,N″) palladium(II) thiocyanate, [Pd(baden)]NCS, was solved by heavy-atom method and refined anisotropically to $R = 0{\cdot}026$ for 2 851 unique observed reflections. The title complex crystallizes in the $Pc2_1b$ space group with $a = 11{\cdot}919(2)$, $b = 14{\cdot}061(2)$, $c = 19{\cdot}769(3)$ Å, $Z = 8$. The structure contains two symmetrical-independent molecules, each includes the palladium complex cation and thiocyanate anion. The cation formed by the baden ligand consists of one six-membered and two five-membered chelate rings and the phenyl ring. The coordination polyhedron around palladium is slightly distorted and puckered N_3O square. The structure is held predominatly by electrostatic forces, but besides there are weak intermolecular hydrogen bonds among baden and thiocyanate nitrogens.

The structure determination of the title compound was undertaken in order to characterize a new series of the complexes containing the baden ligand (1-phenyl-3-{2-[(2-aminoethyl)amino]ethylimino}-1-buten-1-olato-O,N,N′,N″). This type of the ligand belongs to non-symmetrical tetradentate Schiff bases, which can serve as interesting model systems for investigation of various metalloenzymes[1-3]. So far the structures of [Pd(baden)]ClO_4 (ref.[4]) and [Cu(baden)]ClO_4 (ref.[5]) have been described.

EXPERIMENTAL

To the solution of $PdCl_2$ (2·22 g of 40% solution, 0·005 mol) in aqueous methanol was added 0·84 g (0·01 mol) of $NaHCO_3$ dissolved in water and then 0·005 mol of the ethanolic solution of the Schiff base. The mixture was refluxed for 2 h, filtered and evaporated to dryness. The residue was dissolved in methanol, 0·41 g (0·005 mol) of NaSCN dissolved in water was added and resulting solution was slowly evaporated in air. Lustrous yellow crystals were obtained during a few days. The yield was 0·7 g (34%). The density was determined by the flotation method in a mixture of diiodomethane–toluene. For $C_{15}H_{20}N_4OPdS$ (410·8) calculated 43·85% C, 4·91% H, 13·66% N, 25·90% Pd; found 43·62% C, 4·85% H, 13·49% N, 25·38% Pd.

Crystal Structure Determination

Orthorhombic, space group $Pc2_1b$ (No. 29, ***bca*** non-standard setting, the coordinates of equivalent positions are: x, y, z; $\bar{x}, y + 1/2, \bar{z}$; $\bar{x}, y, z + 1/2$; $x, y + 1/2, \bar{z} + 1/2$), $a = 11{\cdot}919(2)$, $b = 14{\cdot}061(2)$, $c = 19{\cdot}769(3)$ Å, $V = 3\,312{\cdot}9(4)$ Å^3, $Z = 8$, $D_o = 1{\cdot}64(1)$, $D_x = 1{\cdot}647$ g cm^{-3}, $\mu(\mathrm{MoK}_\alpha) = 1{\cdot}23$ mm^{-1}, $F(000) = 1\,664$.

The structure was solved by the heavy-atom method and anisotropically refined by the block-diagonal least-squares. The hydrogen atoms were fixed in calculated positions with fixed U_{iso} values of 1·3 times of the U_{eq} value of the attached atoms. Corrections for absorption and extinction were neglected. Data collection and structure refinement parameters are given in Table I.

TABLE I
Data collection and structure refinement parameters

Parameter	
Crystal dimensions	0·50 × 0·30 × 0·30 mm
Diffractometer and radiation used	Enraf–Nonius CAD4 equipped with a graphite monochromator, MoK_α radiation ($\lambda = 0{\cdot}71073$ Å)
Scan technique	$\omega/2\theta$
No. and θ range of reflections for lattice parameter refinement	20; 19 → 23°
Range of h, k and l	$0 \rightarrow 16$, $-19 \rightarrow 19$, $-26 \rightarrow 26$
Standard reflections and their intensity fluctuation	10 0 0, 0 12 0, 0 0 14, no significant variation
Total number of reflections measured; 2θ range	3 298; 0 → 52°
No. of observed reflections	2 851
Criterion for observed reflections	$I > 1{\cdot}96\sigma(I)$
Function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting scheme	$w = [\sigma^2(F_o) + 0{\cdot}0009F_o]^{-1}$
Parameters refined	397
Values of R, wR and S	0·026, 0·030, 1·090
Ratio of max. LS shift to e.s.d (Δ/σ)	0·006
Max. and min. heights in final $\Delta\varrho$ map	0·82 e Å^{-3} (0·96 Å away from the Pd′ atom); −0·42 e Å^{-3}
Source of atomic scattering factors	(ref.[7] and ref.[9])
Programs used	SDP system (ref.[6]) SHELX-76 (ref.[7]) PARST (ref.[8])
Computers used	DEC PDP 11/73, EC 1033

DISCUSSION

The final parameters of non-hydrogen atoms are summarized in Table II. Bond distances and angles are listed in Table III. Fig. 1 shows the studied complex cations, the crystal packing is depicted in Fig. 2.

As a consequence of absence of an inversion centre, the structure contains two

TABLE II

Final coordinates (.10^4) for non-hydrogen atoms and their equivalent isotropic thermal parameters (.10^4). The equivalent isotropic thermal parameter U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	x	y	z	U_{eq}, Å^2
Pd	3186·2(2)	0*	5388·0(2)	334(1)
S	2794(1)	2635(1)	4478(1)	671(4)
O	1719(2)	166(3)	5838(1)	395(9)
N	5034(5)	2659(3)	4865(2)	557(13)
N1	4049(2)	−108(3)	6233(2)	337(9)
N2	4669(3)	−212(3)	4933(2)	407(10)
N3	2571(3)	220(4)	4426(2)	483(11)
C	4113(4)	2641(4)	4700(2)	443(13)
C1	5289(3)	−131(4)	6104(2)	443(13)
C2	5526(3)	188(5)	5406(2)	507(13)
C3	4618(4)	158(4)	4232(2)	481(13)
C4	3481(4)	−103(5)	3951(2)	532(13)
C5	1604(3)	14(3)	6490(2)	319(10)
C6	2420(3)	−150(4)	6956(2)	389(11)
C7	3616(3)	−172(3)	6818(2)	367(11)
C8	4346(3)	−266(4)	7440(3)	456(13)
C9	385(3)	−18(4)	6698(2)	361(10)
C10	−450(3)	−88(4)	6214(2)	456(13)
C11	−1588(4)	−119(5)	6413(3)	583(13)
C12	−1881(3)	−106(6)	7064(3)	646(13)
C13	−1078(3)	−6(5)	7551(3)	557(13)
C14	57(3)	58(4)	7385(2)	424(11)
Pd′	1764·7(2)	2428·7(4)	885·4(2)	347(1)
S′	2168(1)	5222(2)	6014(1)	765(5)
O′	3222(2)	2196(3)	1344(2)	450(10)
N′	−62(3)	4848(4)	5703(2)	621(13)
N1′	887(3)	2483(3)	1722(2)	419(10)
N2′	320(3)	2774(3)	435(2)	394(10)
N3′	2371(3)	2302(3)	−93(2)	460(10)

TABLE II
(*Continued*)

Atom	x	y	z	U_{eq}, Å^2
C′	865(5)	4992(4)	5812(2)	545(13)
C1′	−315(3)	2616(4)	1595(2)	456(13)
C2′	−581(3)	2365(4)	861(2)	469(13)
C3′	368(4)	2477(4)	−286(2)	481(13)
C4′	1518(4)	2725(5)	−551(3)	532(13)
C5′	3344(3)	2288(3)	1976(2)	361(10)
C6′	2475(3)	2398(4)	2447(3)	445(11)
C7′	1312(3)	2455(4)	2329(2)	400(11)
C8′	4526(3)	2471(5)	2940(2)	557(13)
C9′	4526(3)	2267(3)	2214(2)	361(11)
C10′	5382(4)	2288(4)	1726(2)	481(13)
C11′	6483(4)	2298(5)	1912(3)	621(13)
C12′	6792(3)	2258(5)	2580(4)	608(13)
C13′	5970(4)	2237(5)	3063(3)	570(13)
C14′	4845(4)	2255(4)	2895(3)	507(13)

* The origin fixed.

crystallographicaly-independent molecules. Therefore, the atom numbering system is divided into unprimed and primed moieties.

The structure consists of palladium complex cations including the baden ligands and thiocyanate anions. The coordination polyhedra around Pd and Pd′ are both slightly distorted (in the plane) and puckered (outside of the plane) squares. The maximum and minimum displacements from the least-squares plane through Pd, N1, N2, N3, O (and corresponding primed atoms) are shown by N3(−0·122(6) Å] and Pd[0·0004(3) Å] and N1′(0·090(4) Å] and Pd′[−0·003(6) Å], respectively. The dihedral angle between these two planes is 2·7(1)°, so both complex cations are oriented nearly parallely. The coordination sphere of complex cations includes one six-membered and two five-membered chelate rings and the phenyl ring. In the both cations the six-membered chelate ring is slightly puckered. The displacements of the Pd, N1, C7, C6, C5, O group and the primed one from least-sqaures plane fitted through all the atoms of the ring are in the range −0·106(4) Å for O and 0·095(6) Å for C6 and −0·103(4) Å for O′ and 0·070(6) Å for C6′, respectively. The six-membered chelate ring is conjugated with the phenyl ring, particulary in the primed cation, as can be seen either from the dihedral angle between least-squares planes through the both rings [172·4(2)°] or from the C5′—C6′ bond length [1·486(5) Å].

TABLE III
Interatomic distances (in Å) and angles (in °)

Atoms	Distance	Atoms	Distance
Pd—N1	1·967(4)	Pd′—N1′	1·958(4)
Pd—N2	2·005(4)	Pd′—N2′	1·998(4)
Pd—N3	2·062(4)	Pd′—N3′	2·072(4)
Pd—O	1·976(2)	Pd′—O′	1·986(3)
N1—C1	1·500(4)	N1′—C1′	1·466(5)
N1—C7	1·270(5)	N1′—C7′	1·303(6)
C1—C2	1·478(6)	C1′—C2′	1·527(6)
C2—N2	1·495(6)	C2′—N2′	1·481(6)
N2—C3	1·482(6)	N2′—C3′	1·486(6)
C3—C4	1·510(7)	C3′—C4′	1·508(7)
C4—N3	1·505(6)	C4′—N3′	1·486(7)
O—C5	1·314(5)	O′—C5′	1·264(6)
C5—C6	1·359(5)	C5′—C6′	1·401(6)
C5—C9	1·511(5)	C5′—C9′	1·486(5)
C6—C7	1·452(5)	C6′—C7′	1·408(5)
C7—C8	1·512(7)	C7′—C8′	1·496(5)
N—C	1·454(8)	N′—C′	1·144(7)
C—S	1·632(5)	C′—S′	1·636(6)
C9—C10	1·384(5)	C9′—C10′	1·404(6)
C9—C14	1·417(6)	C9′—C14′	1·399(7)
C10—C11	1·413(6)	C10′—C11′	1·363(7)
C11—C12	1·334(8)	C11′—C12′	1·372(10)
C12—C13	1·365(7)	C12′—C13′	1·368(8)
C13—C14	1·395(5)	C13′—C14′	1·382(7)

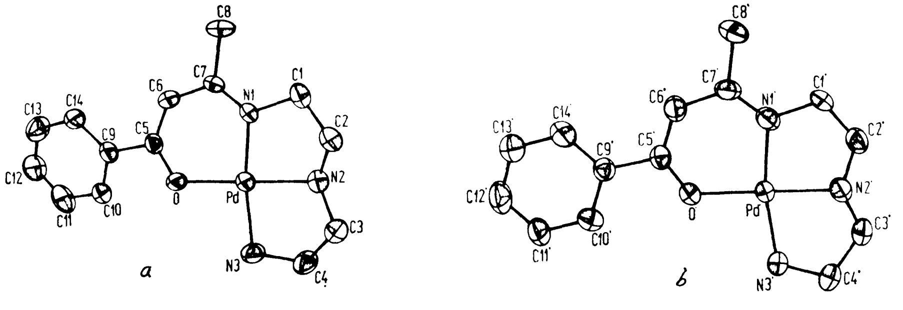


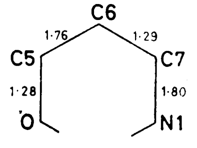
FIG. 1

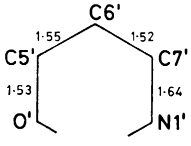
View of the unprimed (*a*) and primed (*b*) complex cations. Thermal ellipsoids are scaled to 50% probability

TABLE III
(*Continued*)

Atoms	Angle	Atoms	Angle
N3—Pd—O	94·7(1)	N—C—S	178·6(5)
N2—Pd—O	178·2(2)	C5—C9—C14	121·6(3)
N2—Pd—N3	85·5(2)	C5—C9—C10	120·4(3)
N1—Pd—O	95·1(1)	C10—C9—C14	118·0(3)
N1—Pd—N3	168·8(1)	C9—C10—C11	120·0(4)
N1—Pd—N2	84·8(1)	C10—C11—C12	121·3(4)
Pd—N1—C7	124·5(2)	C11—C12—C13	119·9(4)
Pd—N1—C1	111·8(3)	C12—C13—C14	121·4(5)
C1—N1—C7	123·6(3)	C9—C14—C13	119·2(4)
N1—C1—C2	109·9(3)	N3′—Pd′—O′	96·1(1)
C1—C2—N2	109·8(3)	N2′—Pd′—O′	175·4(2)
Pd—N2—C2	105·4(3)	N2′—Pd′—N3′	84·6(2)
C2—N2—C3	118·8(4)	N1′—Pd′—O′	95·1(2)
Pd—N2—C3	109·4(3)	N1′—Pd′—N3	167·9(2)
N2—C3—C4	107·2(4)	N1′—Pd′—N2	84·6(2)
C3—C4—N3	110·1(4)	Pd′—N1′—C7′	124·7(3)
Pd—N3—C4	105·9(3)	Pd′—N1′—C1′	112·5(3)
Pd—O—C5	121·0(2)	C1′—N1′—C7′	122·8(4)
O—C5—C9	111·9(3)	N1′—C1′—C2′	109·6(3)
O—C5—C6	128·2(3)	C1′—C2′—N2′	107·5(3)
C6—C5—C9	119·9(4)	Pd′—N2′—C2′	106·1(3)
C5—C6—C7	125·4(4)	C2′—N2′—C3′	117·7(4)
N1—C7—C6	124·7(4)	Pd′—N2′—C3′	109·0(3)
C6—C7—C8	114·5(4)	N2′—C3′—C4′	107·6(4)
N1—C7—C8	120·9(3)	C3′—C4′—N3′	108·5(4)
Pd′—N3′—C4′	107·2(3)	N′—C′—S′	176·5(4)
Pd′—O′—C5′	122·3(2)	C5′—C9′—C14′	124·2(4)
C5′—O′—C6′	28·7(2)	C5′—C9′—C10′	118·1(3)
O′—C5′—C9′	114·8(3)	C10′—C9′—C14′	117·6(4)
O′—C5′—C6′	125·7(3)	C9′—C10′—C11′	121·0(4)
C6′—C5′—C9′	119·5(4)	C10′—C11′—C12′	121·2(4)
C5′—C6′—C7′	128·6(5)	C11l—C12′—C13′	118·7(4)
N1′—C7l—C6′	122·5(4)	C12l—C13′—C14′	121·8(5)
C6′—C7′—C8l	116·6(4)	C9′—C14′—C13′	119·7(5)
N1′—C7′—C8l	120·9(3)		

The corresponding values for the unprimed cation are 167·7(2)° and 1·510(5) Å. The Pd, N1, C1, C2, N2 chelate ring assumes the asymmetric envelope conformation (the same for the primed ring) with the N1—C1—C2—N2 torsion angle of −40·3(5)° [−42·5(5)° for primed atoms]. The other chelate ring (Pd, N2, C3, C4 and N3) has the half-chair shape (the same for the primed ring) with the N2—C3—C4—N3 torsion angle of 52·2(5)° [53·2(5)° for primed atoms]. Comparison of unprimed and primed cations revelas pronounced differences in *bond orders* calculated for O—C5—C6—C7—N1 and O′—C5′—C6′—C7′—N1′ fragments:





In spite of these differences, the stability of the fragments as well as their coordination ability are apparently the same.

The bond lengths and angles for the thiocyanate anions are unexceptional. The structure is held together predominantly by electrostatic interactions, but there are some indications for weak intermolecular hydrogen bridges following from contact-lengths: $\text{N2}\cdots\text{N}^{\text{i}} = 3{\cdot}041(6)$ Å; $\text{N3}\cdots\text{N}'^{\text{ii}} = 3{\cdot}047(5)$ Å; $\text{N2}'\cdots\text{N}'^{\text{iii}} = 3{\cdot}000(7)$ Å; $\text{N3}'\cdots\text{N}^{\text{iv}} = 3{\cdot}134(7)$ Å ($\text{i} = 1 - x, y - 1/2, 1 - z$; $\text{ii} = -x, y - 1/2, 1 - z$; $\text{iii} = -x, y, z - 1/2$; $\text{iv} = 1 - x, y, z - 1/2$).

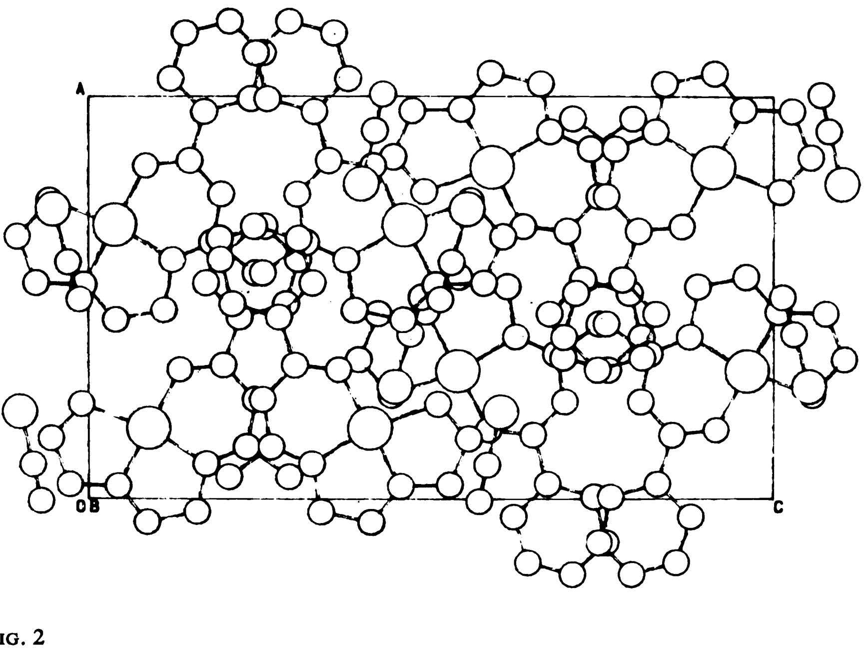


FIG. 2
Crystal packing

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