STRUCTURE OF ANOTHER PHASE OF (1-PHENYL-3-(2-[(2-AMINOETHYL)AMINO]ETHYLIMINO)-1-BUTEN-1--OLATO-O,N,N',N'')PALLADIUM(II) PERCHLORATE

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The structure of the β-phase of (1-phenyl-3-(2-[(2-aminoethyl(amino]-ethylimino)-1-buten-1--olato-O,N,N',N'') palladium(II) perchlorate, β-[Pd(baden)]ClO_4, was solved by the heavy atom method and refined anisotropically to $R = 0{\cdot}035$ for 11 226 unique observed reflections. The title compound is orthorombic, $a = 14{\cdot}152(2)$, $b = 12{\cdot}507(1)$, $c = 20{\cdot}012(2)$Å, $Pca2_1$, $Z = 8$. The structure contains two symmetrically independent molecules both formed by two five-membered and two six-membered rings (one of them is phenyl) and disordered perchlorate anion. The crystal packing is predominantly given by electrostatic interactions accompanied by weak hydrogen bonding among nitrogens and perchlorate oxygens. No structural significant differences between α- and β-phases were found.

A crystal-structure study of the title compound was undertaken as part of an investigation of complexes with a non-symmetrical tetradentate Schiff bases. We recently reported a structure-analysis of [Pd(baden)]ClO_4 (ref.[1]). Here we describe the X-ray structure of another phase of this complex.

EXPERIMENTAL

To 2·25 ml of the 40% solution of $PdCl_2$ (0·005 mol), diluted by aqueous methanol, the equimolar amount of the baden ligand was slowly added. The mixture was refluxed for 2 h and after filtration 0·02 mol of $NaClO_4$ was added. Crystals suitable for a structure analysis were obtained by recrystallization from methanol. The density was determined by flotation in methylene iodide–toluene mixture. For $C_{14}H_{20}ClN_3O_5Pd$ (452.21) calculated: 37·18% C, 4·46% H, 9·29% N and 23·53% Pd; found: 37·93% C, 4·87% H, 9·74% N and 23·02% Pd.

Crystal Structure Determination

Orthorhombic, space group $Pca2_1$ (No.29), $a = 14{\cdot}152(2)$, $b = 12{\cdot}507(1)$, $c = 20{\cdot}012(2)$ Å,

TABLE I

Data collection and structure refinement parameters

Crystal dimension	0·3 × 0·4 × 0·3 mm
Diffractometer and radiation used	Enraf–Nonius CAD4 λ(MoKα) = 0·71073 Å
Scan technique	$\omega/2\theta$
No. and θ range of reflections for lattice parameter refinement	20; 18·91—19·76°
Range of h, k and l	0→ 14, −16→ 16, −22→ 22
Standard reflections	0 2 7, 3 2 2, 1 4 7
Standard reflections monitored in interval; intensity fluctuation	60 min; −0·75%
Total number of reflections measured, 2θ range	14 053, 0—60°
Value of R_{int}	0·024
No. of unique observed reflections	11 226
Criterion for observed reflections	$I \geqq 1{\cdot}96\sigma(I)$
Function minimized	$\Sigma w(\|F_o\| - \|F_c\|)^2$
Weighting scheme	$w = 3{\cdot}2488/[\sigma^2(F_o) + 0{\cdot}0009F_o]$
Parameters refined	425
Values of R, wR and S	0·035, 0·042, 2·258
Ratio of max. least-squares shift to e.s.d. in the last cycle	0·003
Max. and min. heights in final map [eÅ^{-3}]	1·60 [1·15 Å away from Pd(a)] and 1·50 [1·19 Å away from Pd(b)]; −1·24
Source of atomic scattering factors	SHELX 76 and International Tables for X-ray Crystalography (ref.[2])
Programs used	SDP(ref.[3]), SHELX 76 (ref.[4]), PARST (ref.[5])
Computers used	PDP 11/73, PC AT

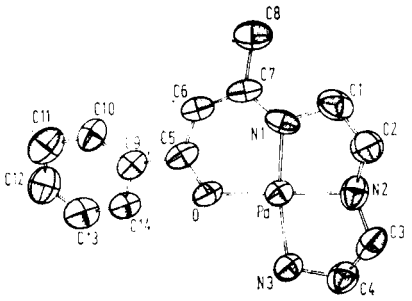

FIG. 1

View of the "a" complex cation. Thermal ellipsoides are scaled to 50% probability

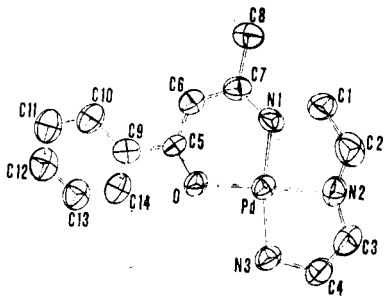

FIG. 2

View of the "b" complex cation. Thermal ellipsoides are scaled to 50% probability

$V = 3\,542{\cdot}1(4)$ Å^3, $Z = 8$, $D_c = 1{\cdot}67(1)$, $D_0 = 1{\cdot}68$ g cm^{-3}, μ(MoKα) = 12·1 cm^{-1}, $F(000) = 1\,824$.

The structure was solved by the heavy-atom method and anisotropically refined by 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. The oxygen atoms of the perchlorate anions were assumed in two positions (*A* and *B*) with calculated occupancy factor values(0·5) and isotropically refined with constraints. Application of an empirical absorption correction increased the *R*-factor final value to 0·039 and therefore was neglected. Data collection and structure refinement parameters are listed in Table I.

TABLE II

Final coordinates (. 10^4) for non-H atoms and their equivalent isotropic thermal parameters (. 10^3). The isotropic displacement parameter is defined as $U_{eq} = (U_{11} + U_{22} + U_{33})/3$

Atom	*x*	*y*	*z*	U_{eq}, Å^2
		Molecule "a"		
Pd	3360·7(2)	5661·7(2)	2500(2)	50·6(1)
Cl	1105(1)	8187(1)	1179(1)	66·2(4)
O	2324(2)	6404(2)	2969(1)	60·0(8)
O11*A*[a]	532(9)	7299(7)	1189(6)	213(5)
O11*B*[a]	1208(9)	7472(8)	652(6)	275(9)
O22*A*[a]	1108(6)	8762(7)	1771(3)	164(4)
O22*B*[a]	281(6)	8053(10)	1573(6)	203(5)
O33*A*[a]	711(6)	8884(7)	689(4)	148(3)
O33*B*[a]	1156(4)	9253(4)	976(3)	85(2)
O44*A*[a]	2047(5)	7958(7)	983(4)	132(3)
O44*B*[a]	1869(5)	7989(6)	1626(4)	119(2)
N1	4079(2)	5342(3)	3315(2)	59(1)
N2	4407(2)	4890(3)	2019(1)	68(1)
N3	2743(2)	5743(2)	1562(1)	61(1)
C1	4927(3)	4711(4)	3161(2)	76(2)
C2	4810(3)	4127(3)	2530(2)	75(1)
C3	4029(3)	4459(4)	1393(2)	76(2)
C4	3449(3)	5326(4)	1069(2)	76(2)
C5	2352(3)	6594(3)	3596(2)	54(1)
C6	3050(3)	6298(3)	4038(2)	55(1)
C7	3870(3)	5705(3)	3920(2)	54(1)
C8	4518(3)	5463(3)	4490(2)	74(2)
C9	1511(3)	7171(3)	3836(2)	55(1)
C10	1181(3)	7110(4)	4473(2)	68(2)
C11	370(4)	7660(5)	4681(3)	96(2)
C12	−68(4)	8279(4)	4229(3)	91(2)
C13	233(4)	8346(4)	3599(3)	88(2)
C14	1015(3)	7826(3)	3378(2)	59(1)

TABLE II
(*Continued*)

Atom	x	y	z	U_{eq}, Å^2
		Molecule "b"		
Pd	3952·7(2)	−642·3(2)	2435·9(2)	46·8(1)
Cl	3758(1)	3264(1)	6280(0)	61·2(3)
O	4973(2)	−1361(2)	2937(1)	52·0(8)
O11*A*[a]	3212(6)	2364(6)	6281(6)	177(5)
O11*B*[a]	3556(5)	2252(5)	5950(4)	96(2)
O22*A*[a]	3563(4)	3902(5)	5718(3)	80(2)
O22*B*[a]	3822(5)	4215(6)	5938(4)	116(3)
O33*A*[a]	4596(4)	3042(5)	6637(4)	95(2)
O33*B*[a]	4727(4)	3042(6)	6283(4)	106(3)
O44*A*[a]	3571(5)	3897(6)	6868(3)	110(2)
O44*B*[a]	3012(4)	3347(5)	6770(3)	97(2)
N1	3202(2)	−314(2)	3221(1)	51(1)
N2	2930(2)	82(3)	1923(1)	61(1)
N3	4605(2)	−735(2)	1522(1)	59(1)
C1	2354(3)	306(3)	3053(2)	67(1)
C2	2502(3)	871(3)	2403(2)	76(1)
C3	3325(3)	486(4)	1295(2)	76(2)
C4	3923(3)	−390(4)	988(3)	71(2)
C5	4914(2)	−1513(3)	3566(2)	44(1)
C6	4201(3)	−1223(3)	3988(2)	50(1)
C7	3389(3)	−627(3)	3836(2)	52(1)
C8	2725(3)	−370(4)	4389(2)	69(2)
C9	5735(3)	−2126(3)	3840(2)	50(1)
C10	6011(3)	−2083(4)	4508(2)	62(2)
C11	6782(3)	−2669(4)	4730(3)	75(2)
C12	7274(3)	−3271(4)	4291(3)	79(2)
C13	7035(3)	−3344(4)	3637(2)	78(2)
C14	6250(3)	−2770(3)	3413(2)	66(1)

[a] Occupancy factor equals 0·5.

DISCUSSION

The structure contains two symmetrically independent molecules, designated as "a" and "b". The final parameters of non-hydrogen atoms are summarized in Table II*. Bond distances and angles are listed in Table III. Figures 1 and 2 show "a" and "b"

* Lists of structure factors, H-atom parameters, bond distances and angles involving H-atoms and anisotropic thermal parameters may be obtained from authors on request.

complex cations, Figs. 3 and 4 corresponding perchlorate anions. The crystal packing is depicted in Fig. 5.

From the crystal structure analysis it follows that the complex studied (denoted here as β) is another phase of [Pd(baden)]ClO_4. Similarly to the α-phase (see ref.[1]), the coordination polyhedron of β around Pd is approximately a square. A comparison of the least-squares plane geometries of α and β is given in Table IV. No

TABLE III

Bond lenghts (in Å) and angles (in °)

Atoms	Lenghts	
	molecule "a"	molecule "b"
Pd—O	1·974(3)	1·975(3)
Pd—N1	1·963(4)	1·941(2)
Pd—N2	2·013(3)	1·992(3)
Pd—N3	2·073(2)	2·052(2)
O—C5	1·278(5)	1·276(5)
N1—C1	1·469(6)	1·468(5)
N1—C7	1·326(6)	1·318(5)
N2—C2	1·511(5)	1·504(5)
N2—C3	1·465(5)	1·465(5)
N3—C4	1·498(5)	1·503(5)
C1—C2	1·468(6)	1·495(6)
C3—C4	1·507(7)	1·515(7)
C5—C6	1·377(6)	1·365(5)
C5—C9	1·472(6)	1·496(5)
C6—C7	1·397(6)	1·403(6)
C7—C8	1·495(6)	1·487(6)
C9—C10	1·360(6)	1·394(6)
C9—C14	1·416(6)	1·383(6)
C10—C11	1·401(7)	1·388(6)
C11—C12	1·342(8)	1·350(8)
C12—C13	1·333(8)	1·355(7)
C13—C14	1·358(7)	1·396(6)
Cl—O11*A*	1·375(10)	1·365(8)
Cl—O22*A*	1·386(7)	1·406(6)
Cl—O33*A*	1·426(9)	1·412(7)
Cl—O44*A*	1·419(7)	1·443(7)
Cl—O11*B*	1·390(11)	1·456(7)
Cl—O22*B*	1·418(10)	1·375(8)
Cl—O33*B*	1·396(5)	1·399(6)
Cl—O44*B*	1·425(8)	1·445(6)

TABLE III
(*Continued*)

	Angles	
	molecule "a"	molecule "b"
N2—Pd—N3	84·31(8)	83·88(9)
N1—Pd—N3	168·7(1)	168·5(1)
N1—Pd—N2	85·3(1)	85·6(1)
O—Pd—N3	95·4(1)	95·6(1)
O—Pd—N2	179·3(1)	179·50(9)
O—Pd—N1	94·9(1)	94·90(9)
Pd—O—C5	122·1(3)	121·4(2)
Pd—N1—C7	125·0(3)	125·7(3)
Pd—N1—C1	111·0(3)	112·0(2)
C1—N1—C7	123·9(3)	122·3(3)
Pd—N2—C3	108·5(2)	108·8(3)
Pd—N2—C2	104·9(2)	105·2(2)
N1—C7—C8	119·4(4)	120·3(4)
O11*A*—Cl—O11*B*	63·5(7)	34·2(5)
O22*A*—Cl—O22*B*	65·7(6)	28·9(4)
O33*A*—Cl—O33*B*	40·2(4)	30·2(4)
O44*A*—Cl—O44*B*	54·9(4)	43.4(4)

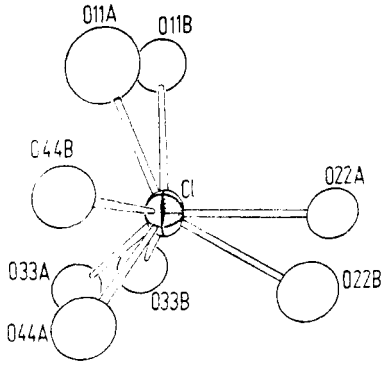

FIG. 3
The "a" disordered perchlorate anion

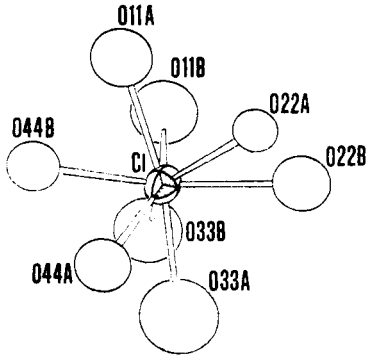

FIG. 4
The "b" disordered perchlorate anion

remarkable differences were found, only the Pd,N1,N2,N3,O plane shows the maximum displacement at N1 for β-phase (in both molecules) and at N3 for α-phase.

The oxygen atoms of the perchlorate anions are disordered. The *R*-factor decreased for a model in which each oxygen atom assumes two positions *A* and *B*, with one half occupancy factor value. According to this model ClO_4 tetrahedra vibrate between two limiting stages *A* and *B* in the structure. An inspection of the crystal packing shows there are some intermocleular N...O contacts in the range from 3·00 to 3·17 Å. But only pairs O44*A*, O44*B* of the "a" molecule and O33*A*, O33*B* of the

TABLE IV

A comparison of the least-squares plane geometries of α- and β-phase

	α-Phase	β-Phase	
		molecule "a"	molecule "b"
Pd,N1,N2,N3,O plane:			
Max. and min. displacements, Å	0·068(4) for N3 0·0008(3) for Pd	−0·104(4) for N1 0·0013(3) for Pd	−0·080(3) for N1 0·0017(3) for Pd
Pd,N1,C1,C2,N2 ring:			
Deviations from Pd,N1,N2 plane, Å	−0·060(4) for C1 −0·673(4) for C2	−0·053(5) for C1 −0·640(4) for C2	−0·070(4) for C1 −0·663(4) for C2
Conformation	asymetric envelope	asymetric envelope	asymetric envelope
N1−C1−C2−N2 torsion angle, °	46·5(4)	46·1(4)	45·4(4)
Pd,N2,C3,C4,N3 ring:			
Deviation from Pd,N2,N3 plane, Å	−0·501(4) for C3 0·225(4) for C4	−0·507(5) for C3 0·170(5) for C4	−0·485(5) for C3 0·216(5) for C4
Conformation	half-chair	half-chair	half-chair
N2−C3−C4−N3 torsion angle, °	−55·2(4)	−52·5(4)	−52·9(4)
Pd,N1,C7,C6,C5,O ring:			
Best plane;	N1,C7,O,C5;	N1,C7,O,C5;	N1,C7,O,C5;
χ^2 test	1·24	11·01	1·84
Displacements, Å	−0·1308(3) for Pd −0·033(4) for C6	0·1251(3) for Pd 0·010(4) for C6	0·0955(3) for Pd 0·036(4) for C6
Conformation	boat	boat	boat

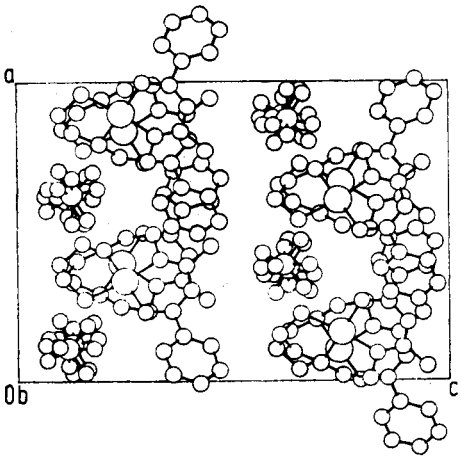

FIG. 5
Molecular packing

"b" molecule can serve as proton acceptors in weak hydrogen bonding. The donor–acceptor lengths and the donor–hydrogen–acceptor angles are following: 3·160(9) Å and 164·8° for N3–H1N3...O44*A* and 3·072(8) Å and 153·8° for N3–H1N3...O44*B* of the "a" molecule and 3·074(8) Å and 177·8° for N3–H1N3...O33*B* and 3·108(7) Å and 158·5° for N3–H1N3...O33*A* of the "b" molecule.

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