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Structure of {*N*-[2-(2-Aminoethylamino)ethyl]salicylideneaminato-*O,N,N′,N″*}-palladium(II) Perchlorate

BY B. KRATOCHVÍL

Department of Mineralogy, Institute of Chemical Technology, Suchbátarova 5, 166 28 *Praha* 6, *Czechoslovakia*

M. NOVÁKOVÁ

Department of Inorganic Chemistry, Institute of Chemical Technology, Suchbátarova 5, 166 28 *Praha* 6, *Czechoslovakia*

V. HABER

Department of Inorganic Chemistry, Charles University, Albertov 2030, 128 40 *Praha* 2, *Czechoslovakia*

J. ONDRÁČEK

Department of Mineralogy, Institute of Chemical Technology, Suchbátarova 5, 166 28 *Praha* 6, *Czechoslovakia*

AND B. HÁJEK

Department of Inorganic Chemistry, Institute of Chemical Technology, Suchbátarova 5, 166 28 *Praha* 6, *Czechoslovakia*

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Abstract. $[\mathrm{Pd}(\mathrm{C_{11}H_{16}N_3O})]\mathrm{ClO_4}$, $M_r = 412{\cdot}12$, monoclinic, $P2_1/c$, $a = 8{\cdot}960\,(3)$, $b = 13{\cdot}541\,(6)$, $c = 11{\cdot}887\,(2)$ Å, $\beta = 98{\cdot}88\,(2)^\circ$, $V = 1424{\cdot}9\,(8)$ Å^3, $Z = 4$, $D_m = 1{\cdot}913\,(3)$, $D_x = 1{\cdot}921$ Mg m^{-3}, $\lambda(\mathrm{Mo}\;K\alpha) = 0{\cdot}71073$ Å, $\mu = 1{\cdot}50$ mm^{-1}, $F(000) = 824$, $T = 296$ K, $R = 0{\cdot}047$ for 2776 unique observed reflections. The $[\mathrm{Pd^{II}}(\mathrm{C_{11}H_{16}N_3O})]^+$ complex cation with the saden ligand contains two five-membered and two six-membered rings. The coordination polyhedron around the Pd atom is a slightly distorted square (one O and three N) with Pd—O = 1·980 (4) Å and Pd—N in the range 1·951 (4)–2·075 (6) Å. The perchlorate anion is disordered. The structure is predominantly held together by electrostatic interactions.

Introduction. Some complexes containing tetradentate Schiff bases have received a great deal of attention owing to their ability to undergo reversible adduct formation with oxygen and serve as simple models for various metalloenzymes. As a rule the tetradentate Schiff bases which have been utilized up till now are symmetric, they are coordinated as anions with charge 2−. On the other hand, complexes with non-symmetrical tetradentate Schiff bases are almost unknown, owing to the difference in their charge as well as to the number of donor atoms that can suitably modify the properties of the complexes. So far two structures of Ni$^{\mathrm{II}}$ complexes with the saden ligand, {*N*-[2-(2-aminoethylamino)ethyl]salicylideneaminato-*O,N,N′,N″*},

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have been described by Rotondo, Cusmano Priolo, Romeo, Bruno & Bombieri (1983) and Podlahová, Knížek, Loub & Hašek (1988). In both cases a distorted square coordination around Ni (one O and three N) was found. The saden ligand forms a square pyramid around Cu in $[Cu^{II}(C_{11}H_{16}N_3O)(H_2O)]PF_6$, where the supplementary apical position is occupied by the water O atom (Cusmano Priolo, Rotondo, Rizzardi, Bruno & Bombieri, 1983). The protonated ligand (*N*-{2-[2-(2-ammonioethylamino)ethylamino]ethyl}-salicylideneaminato-*O,N,N',N''*) forms an irregular square pyramid around Cu. The apical position is occupied by one O atom of the perchlorate ion (Rotondo, Cusmano Priolo, Bombieri & Bruno, 1984). A crystal-structure study of the title complex was undertaken as part of the investigation of non-symmetrical tetradentate Schiff bases.

Experimental. The complex studied was prepared by adding NaOH to a solution of stoichiometric amounts of the saden ligand and palladium in ethanol (0·01 mol in 50 ml solution). After refluxing for several hours the equivalent amount of $NaClO_4$ was added and the solid residue (NaCl) was filtered off. The filtrate was allowed to stand in air for several days, yielding brown crystals.

The determination of density was carried out by flotation in bromoform/toluene mixture at 298 K. Preliminary values of the lattice parameters and space group were found on the basis of Weissenberg patterns. The crystal studied was ground to a sphere with radius $r = 0{\cdot}4$ mm. Syntex $P2_1$ diffractometer, graphite monochromator, lattice parameters from least-squares refinement of 15 reflections with θ in the range 4–22° measured by a centering routine; data collection: $\theta/2\theta$ mode, $2\theta \leq 60°$, $-12 \leq h \leq 12$, $0 \leq k \leq 19$, $0 \leq l \leq 16$; two standard reflections (100, $\bar{1}04$) monitored after every 100 reflections, no significant variation in intensity; 4188 measured reflections, 2776 unique observed reflections $[I > 1{\cdot}96\sigma(I)]$. Absorption correction was neglected. The phase problem was solved using the heavy-atom method, H atoms found from the electron density difference synthesis. Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = 1{\cdot}633/[\sigma^2(F_o) + 0{\cdot}0009F_o^2]$, positional and anisotropic thermal parameters of non-H atoms and isotropic thermal parameters of H atoms refined in three blocks, $R = 0{\cdot}047$, $wR = 0{\cdot}046$, $S = 1{\cdot}123$, $(\Delta/\sigma)_{max} = 0{\cdot}146$ (for non-H atoms), max. and min. heights in final $\Delta\rho$ map 1·06 and $-0{\cdot}57$ e Å^{-3}. Atomic scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974), anomalous-dispersion corrections neglected. Computer programs used: *SHELXS*86 (Sheldrick, 1986), *SHELX*76 (Sheldrick, 1976), *PARST* (Nardelli, 1984); EC 1033 computer.

Table 1. *Final coordinates* ($\times 10^4$) *for non*-H *atoms and their equivalent isotropic thermal parameters* ($\times 10^4$)

$$U_{eq} = \tfrac{1}{3}[U_{22} + 1/\sin^2\beta\,(U_{11} + U_{33} + 2U_{13}\cos\beta)].$$

	x	y	z	U_{eq}(Å^2)
Pd	871·5 (4)	552·6 (3)	1723·0 (3)	370 (1)
Cl	7151 (2)	8485 (1)	3487 (1)	583 (5)
O1	−1150 (4)	1141 (3)	1244 (3)	438 (11)
O11	6987 (7)	9482 (4)	3185 (8)	1352 (35)
O22*A**	8471 (19)	8147 (13)	3301 (18)	1195 (75)
O33*A**	6767 (34)	8274 (17)	4538 (20)	1673 (136)
O44*A**	6049 (28)	8162 (14)	2656 (20)	1823 (103)
O22*B**	8574 (15)	8514 (10)	4202 (15)	1062 (57)
O33*B**	6093 (19)	8096 (16)	4025 (19)	1081 (89)
O44*B**	7338 (22)	7716 (9)	2677 (12)	1006 (57)
N1	1678 (4)	959 (3)	361 (3)	381 (12)
N2	2925 (5)	−37 (4)	2210 (4)	505 (16)
N3	480 (6)	162 (4)	3340 (5)	512 (16)
C1	3271 (6)	641 (5)	387 (5)	506 (18)
C2	3988 (6)	523 (5)	1608 (6)	576 (20)
C3	3198 (8)	−62 (6)	3464 (6)	676 (25)
C4	1790 (8)	−437 (6)	3863 (6)	679 (25)
C5	−1493 (5)	1655 (4)	311 (4)	384 (14)
C6	−2947 (6)	2079 (4)	115 (5)	483 (17)
C7	−3440 (7)	2659 (5)	−831 (5)	546 (20)
C8	−2515 (7)	2833 (5)	−1629 (5)	570 (20)
C9	−1100 (7)	2432 (4)	−1475 (5)	499 (18)
C10	−542 (5)	1836 (3)	−524 (4)	369 (13)
C11	984 (6)	1488 (4)	−449 (4)	420 (15)

* The occupancy factor is 0·5.

Discussion. The final atomic coordinates and equivalent isotropic temperature factors of non-H atoms are listed in Table 1.* Bond lengths and angles are given in Table 2. Fig. 1 depicts a perspective view of the molecule with its atomic numbering. Pd has a distorted square coordination. The maximum and minimum displacement from the plane fitted through Pd, N1, N2, N3 and O1 is shown by the N3 atom [−0·126 (6) Å] and the O1 atom [−0·001 (4) Å], respectively. Similarly, as in the related complexes of Ni^{II} and Cu^{II}, the equivalent Pd—N2 and Pd—N3 bond distances are longer than Pd—N1. The Pd—N1 bond is the shortest of the Pd coordinating bonds, as distinguished from the related complexes where the shortest bond is *M*—O1. Angles N1—Pd—N2 and N2—Pd—N3 are smaller than O1—Pd—N1 and N3—Pd—O1. The complex cation $[Pd^{II}(C_{11}H_{16}N_3O)]^+$ with the saden ligand contains two five-membered and two six-membered rings. The C atoms of the first five-membered ring (Pd, N1, C1, C2, N2) assume an asymmetric envelope conformation, where the N1—C1—C2—N2 torsion angle equals 46·1 (6)°. The deviations of C1 and C2 from the Pd, N1, N2 plane are 0·005 (7) and −0·600 (7) Å, respectively. The C atoms of the second five-membered ring (Pd, N2, C3, C4, N3) have the δ conformation with an N2—C3—C4—N3 torsion angle of −53·2 (7)°. C3 and

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* Lists of structure factors, anisotropic thermal parameters, H-atom positions and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51478 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and angles* (°)

Pd—N1	1·951 (4)	C11—N1	1·281 (6)
Pd—N2	2·007 (5)	C5—C6	1·410 (7)
Pd—N3	2·075 (6)	C6—C7	1·387 (8)
Pd—O1	1·980 (4)	C7—C8	1·373 (9)
N1—C1	1·487 (7)	C8—C9	1·365 (9)
C1—C2	1·502 (9)	C9—C10	1·416 (7)
C2—N2	1·485 (8)	Cl—O11	1·399 (6)
N2—C3	1·473 (9)	Cl—O22*A*	1·318 (18)
C3—C4	1·503 (11)	Cl—O33*A*	1·376 (26)
C4—N3	1·482 (9)	Cl—O44*A*	1·357 (22)
O1—C5	1·305 (6)	Cl—O22*B*	1·420 (14)
C5—C10	1·426 (7)	Cl—O33*B*	1·331 (21)
C10—C11	1·436 (7)	Cl—O44*B*	1·445 (14)

N1—Pd—N2	84·9 (2)	C10—C5—C6	116·8 (5)
N2—Pd—N3	84·8 (2)	C5—C6—C7	122·4 (5)
N3—Pd—O1	95·2 (2)	C6—C7—C8	120·5 (6)
O1—Pd—N1	95·0 (2)	C7—C8—C9	119·1 (6)
N1—Pd—N3	167·9 (2)	C8—C9—C10	122·7 (6)
O1—Pd—N2	179·8 (2)	C9—C10—C5	118·6 (5)
Pd—N1—C1	112·2 (3)	C9—C10—C11	116·9 (5)
C11—N1—C1	122·0 (4)	O11—Cl—O22*A*	110·7 (8)
N1—C1—C2	108·5 (5)	O11—Cl—O22*B*	100·1 (6)
C1—C2—N2	108·0 (5)	O11—Cl—O33*A*	113·7 (11)
C2—N2—Pd	106·6 (4)	O11—Cl—O33*B*	116·8 (9)
C2—N2—C3	118·7 (5)	O11—Cl—O44*A*	95·1 (10)
Pd—N2—C3	107·6 (4)	O11—Cl—O44*B*	122·9 (7)
N2—C3—C4	108·1 (6)	O22*A*—Cl—O33*A*	115·9 (14)
C3—C4—N3	109·4 (6)	O22*A*—Cl—O44*A*	109·7 (13)
C4—N3—Pd	107·0 (4)	O33*A*—Cl—O44*A*	109·8 (15)
Pd—O1—C5	122·9 (3)	O22*B*—Cl—O33*B*	111·3 (12)
O1—C5—C10	126·6 (5)	O22*B*—Cl—O44*B*	103·5 (9)
O1—C5—C6	116·6 (5)	O33*B*—Cl—O44*B*	101·5 (11)
C5—C10—C11	124·5 (4)	O22*A*—Cl—O22*B*	50·5 (11)
C10—C11—N1	125·3 (5)	O33*A*—Cl—O33*B*	35·4 (14)
C11—N1—Pd	125·6 (4)	O44*A*—Cl—O44*B*	55.2 (11)

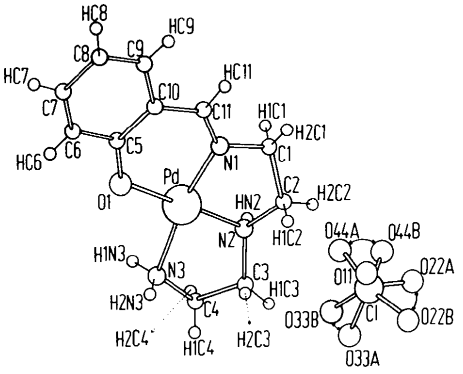

Fig. 1. View of the complex with atom numbering.

C4 are displaced from the Pd, N2, N3 plane by −0·487 (8) and 0·193 (8) Å. The arrangement of the Pd, N1, C11, C10, C5 and O1 atoms, forming the six-membered ring, corresponds to a very flat chair conformation. The best plane may be fitted through N1, C11, C5 and O1 ($\chi^2 = 0{\cdot}024$) the Pd and C10 atoms being displaced by −0·075 (1) and 0·013 (4) Å. The phenyl ring (C5, C6, C7, C8, C9 and C10) is also planar ($\chi^2 = 1{\cdot}587$), the displacements being in the range −0·005 (5) for C5 to 0·004 (6) Å for C6.

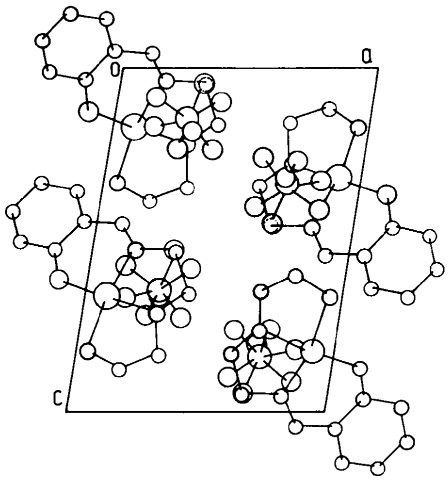

Fig. 2. Packing scheme.

Three O atoms of the perchlorate anion are disordered. A lower *R*-factor value was obtained for the model (Podlahová *et al.,* 1988) in which the O11 atom has an occupancy factor of 1·0 while the three remaining O atoms each assume two positions with fixed occupancy factors of 0·5 (O22*A*, O22*B*; O33*A*, O33*B*; O44*A*, O44*B*). According to this model the perchlorate tetrahedron apparently oscillates in the structure around the Cl—O11 bond.

No hydrogen-bond contacts were found in the complex studied, from which it follows that the structure is held together through electrostatic interactions. The molecular packing is shown in Fig. 2.

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