and BF$_4^-$ salts, and also in type I (DMCTTF) stacking of the triclinic ClO$_4^-$ salt β phase (for details see Granier, Gallois & Fabre, 1989), as in the latter case C16 and C17 have very high U equivalent temperature factors. Fourier map analysis did not provide evidence for two distinct statistical positions. The As atom is on the inversion center and the whole octahedron is generated starting from the positions of three F atoms. Dispersion of bond lengths and bond angles from an ideal regular octahedron is commonly observed in this type of compound. Large temperature factors account for a strong rotational disorder of the anion; this is supported by the fact that no distinct statistical positions of F atoms could be deduced from Fourier map analysis. DMCTTF$^+$ cations build independent columns along the a axis; these columns form layers parallel to the ab plane, which alternate with AsF$_6^-$ anions (Fig. 1). The DMCTTF columns are weakly dimerized, the interplanar distances within and between dimers being $d_1 = 3{\cdot}49$ and $d_2 = 3{\cdot}72$ Å respectively (Fig. 2a). The mean molecular plane makes an angle $\delta = 23{\cdot}42°$ with the stacking a axis. The one-dimensional character of the structure is reinforced by the overlapping mode of the DMCTTF$^+$ cations within each stack: the projection of three consecutive DMCTTF units $(\bar{1} + b + c)$, (I) and $(\bar{1} + a + b + c)$ in the mean molecular plane of molecule I shows very small transverse shifts of their longitudinal axes (Fig. 2b), $\Delta t_1 = 0{\cdot}014$ Å between (I) and $(\bar{1} + b + c)$, and $\Delta t_2 = 0{\cdot}139$ Å between (I) and $(\bar{1} + a + b + c)$ (these shifts are calculated relative to the center of the C3=C13 double bond; see Granier, Gallois & Fabre, 1989, for a detailed description). On the other hand, alternate longitudinal shifts, $\Delta l_1 = -1{\cdot}261$, $\Delta l_2 = +1{\cdot}864$ Å allow the formation of cavities in which AsF$_6^-$ anions are located. This structural arrangement is very reminiscent to that found in type 1 DMCTTF layers of β-ClO$_4^-$ salts (Vaca, Granier, Gallois, Coulon, Gouasmia & Fabre, 1989).

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Structure of a Palladium(II) Complex with a Non-Symmetrical Tetradentate Schiff Base

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Abstract. (1-Phenyl-3-{2-[(2-aminoethyl)amino]ethylimino}-1-buten-1-olato-*O*,*N*,*N*′,*N*″)palladium(II) perchlorate, [Pd($C_{14}H_{20}N_3O$)]ClO$_4$, $M_r = 452{\cdot}18$, monoclinic, $P2_1/c$, $a = 10{\cdot}339\ (1)$, $b = 19{\cdot}901\ (1)$, $c = 8{\cdot}4629\ (9)$ Å, $\beta = 98{\cdot}74\ (1)°$, $V = 1721{\cdot}1\ (3)$ Å^3, $Z = 4$, $D_m = 1{\cdot}732\ (3)$, $D_x = 1{\cdot}745$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}247$ mm^{-1}, $F(000) = 912$, $T = 296$ K, $R = 0{\cdot}034$ for 2656 unique observed reflections. The complex cation which includes the baden ligand, 1-phenyl-3-{2-[(2-aminoethyl)amino]ethylimino}-1-buten-1-olato-*O*,*N*,*N*′,*N*″, contains two five-membered and one six-membered chelate ring, and the phenyl ring. The coordination polyhedron around Pd is a distorted square formed by three N

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and one O atoms of the baden ligand. The O atoms of the perchlorate anion are disordered. No hydrogen contacts were found in the structure, which is held together predominantly by electrostatic interactions.

Introduction. The complexes with non-symmetrical tetradentate Schiff bases are interesting model systems for investigation of various oxygen-transfer metalloenzymes (Jones, Summerville & Basolo, 1979). So far the structures of this type of complex have been described with the so-called saden, saltrien and aden ligands. The saden ligand {2-[2-(2-aminoethylamino)ethylimino]methylphenolato-*O*,*N*,*N*′,*N*″} was found to be in three Ni complexes with different anions, [Ni(saden)]B(C_6H_5)$_4$ (Rotondo, Cusmano Priolo, Romeo, Bruno & Bombieri, 1983), [Ni(saden)]ClO_4 (Podlahová, Knížek, Loub & Hašek, 1988), [Ni(saden)]NCS (Loub, Podlahová, Kopf & Weiss, 1989) and in [Pd(saden)]ClO_4 (Kratochvíl, Nováková, Haber, Ondráček & Hájek, 1989). The coordination around Ni and Pd is a distorted square formed by three N and one O atoms of the saden ligand.

A crystal-structure study of [Cu(saden)H_2O]PF_6 (Cusmano Priolo, Rotondo, Rizzardi, Bruno & Bombieri, 1983) showed the coordination around Cu to be a square pyramid where the supplementary apical position is occupied by the water O atom. The structure of [Cd(saden)C_2H_5OH]ClO_4 (Loub, Podlahová, Haber, Kopf & Weiss, 1990) contains the dinuclear complex cation where two Cd polyhedra are connected through a double oxygen bridge. The coordination number of Cd is six with an irregular coordination polyhedron. The protonated saltrien ligand (2-{2-[2-(2-ammonioethylamino)ethylamino]-ethylimino}methylphenolato-*O*,*N*,*N*′,*N*″) together with the perchlorate ligand form an irregular square pyramid around Cu in [Cu(saltrien)ClO_4]ClO_4 (Rotondo, Cusmano Priolo, Bombieri & Bruno, 1984). The terminal N atom of the saltrien ligand is protonated and the apical position is occupied by an O atom of the perchlorate ligand. The structures of two complexes including the aden ligand {4-[2-(2-aminoethylamino)ethylimino]-2-penten-2-olato-*O*,*N*,*N*′,*N*″} have been reported, [Ni(aden)]I.H_2O (Knížek, 1989) and [Cu(aden)]ClO_4.H_2O (Haber, Loub, Podlahová, Kopf & Weiss, 1988). In both cases a distorted square coordination around the metal was found.

In this paper the structure of a complex which includes the so-called baden ligand, 1-phenyl-3-{2-[(2-aminoethyl)amino]ethylimino}-1-buten-1-olato-*O*,*N*,*N*′,*N*″, is reported.

Experimental. The title compound was prepared by mixing $PdCl_2$ with stoichiometric amounts of the baden ligand and NaOH in aqueous methanol (1:1), followed by reaction with $NaClO_4$. The filtered solution was allowed to stand in air for a few days. Dark-yellow crystals were obtained. The density was determined by flotation in methylene iodide/toluene mixture.

A crystal, 0·35 × 0·4 × 0·8 mm, recrystallized from methanol was used for data collection. An Enraf–Nonius CAD-4–SDP73 diffractometer, equipped with a graphite monochromator and a 1 mm collimator, was employed. Lattice parameters were determined by least squares from the setting angles of 23 reflections in the range $18·7 < \theta < 20·3°$. The intensity data were collected with ω–2θ scans, *hkl* range −12 to 12, 0 to 23, 0 to 10, $2\theta \leq 50°$ and two intensity reference reflections (max. fluctuation 1·3%). A total of 3334 reflections were measured of which 2656 unique observed reflections ($R_{\rm int} = 0·014$) were used with $I > 1·96\sigma(I)$. Empirical absorption correction was carried out, transmission factor 0·90–1·00. The structure was solved by the heavy-atom method. The H atoms were found from the difference electron density synthesis. The structure was refined by the block-diagonal least-squares method minimizing $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F_o) + 0·0009F_o^2]^{-1}$. The positional and anisotropic thermal parameters of non-H atoms (isotropic for H atoms) and occupancy factors of O atoms in the perchlorate anion were refined to final $R = 0·034$, $wR = 0·041$ and $S = 1·435$. A total of 244 parameters were refined. Final $(\Delta/\sigma)_{\rm max} = 0·084$ for non-H atoms, and max. and min. heights 0·52 and −0·59 e Å^{-3} were obtained on the final $\Delta\rho$ map. Programs used were *SDP* (B. A. Frenz & Associates, Inc., 1985), *SHELX76* (Sheldrick, 1976) and *PARST* (Nardelli, 1984). The atomic scattering factors used were those incorporated in *SHELX76* with the scattering factors and anomalous-dispersion corrections for Pd taken from *International Tables for X-ray Crystallography* (1974). The calculations were performed with PDP 11/73 and ECD 1033 computers.

Discussion. The final atomic coordinates and equivalent isotropic temperature factors of non-H atoms are given in Table 1.* Bond distances and angles are listed in Table 2. The complex cation is shown in Fig. 1(*a*) and the disordered perchlorate anion in Fig. 1(*b*).

In the [Pd($C_{14}H_{20}N_3O$)]$^+$ cation, the coordination polyhedron around Pd is approximately a square.

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* Lists of structure factors, H-atom positions and isotropic thermal parameters, bond distances and angles involving H atoms, anisotropic thermal parameters and O—Cl—O angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52738 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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

	x	y	z	U_{eq} (Å^2)
Pd	1919·2 (2)	5370·7 (1)	7317·7 (3)	377 (1)
Cl	1580 (1)	8594·0 (5)	7732 (1)	537 (3)
O1	2150 (2)	4488 (1)	6268 (3)	474 (8)
O11*A**	2617 (8)	8344 (5)	6983 (8)	1001 (39)
O11*B*†	2810 (15)	8448 (11)	7782 (42)	3319 (233)
O22*A**	626 (10)	8924 (6)	6743 (13)	1547 (57)
O22*B*†	1325 (14)	9163 (5)	6680 (14)	846 (50)
O33*A**	1064 (10)	8119 (4)	8564 (15)	1378 (45)
O33*B*†	878 (13)	8058 (5)	6848 (19)	1380 (60)
O44*A**	2224 (8)	9066 (4)	8923 (9)	1261 (35)
O44*B*†	1121 (29)	8698 (13)	9058 (15)	2897 (182)
N1	3797 (3)	5564 (1)	7855 (3)	426 (8)
N2	1704 (3)	6257 (1)	8358 (4)	422 (9)
N3	− 119 (4)	5372 (1)	6859 (5)	498 (11)
C1	4058 (3)	6222 (2)	8615 (5)	472 (11)
C2	2857 (4)	6664 (2)	8143 (5)	499 (12)
C3	403 (3)	6525 (2)	7725 (5)	482 (12)
C4	− 573 (4)	5951 (2)	7768 (5)	506 (12)
C5	3305 (3)	4228 (2)	6295 (4)	432 (10)
C6	4477 (4)	4506 (2)	6951 (5)	476 (12)
C7	4731 (3)	5149 (2)	7666 (4)	466 (11)
C8	6137 (5)	5331 (2)	8198 (9)	644 (18)
C9	3278 (3)	3540 (2)	5555 (4)	435 (10)
C10	2182 (4)	3143 (2)	5496 (4)	535 (12)
C11	2134 (5)	2499 (2)	4867 (5)	660 (22)
C12	3199 (5)	2247 (2)	4293 (5)	655 (16)
C13	4299 (5)	2630 (2)	4322 (5)	677 (16)
C14	4362 (4)	3279 (2)	4956 (4)	549 (13)

* Occupancy factor 0·62 (1).
† Occupancy factor 0·38 (1).

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

Pd—N1	1·964 (3)	C5—C9	1·504 (6)
Pd—N2	1·999 (2)	C6—C7	1·423 (6)
Pd—N3	2·084 (4)	C7—C8	1·499 (6)
Pd—O1	1·999 (2)	C7—N1	1·299 (5)
N1—C1	1·466 (5)	C9—C10	1·376 (5)
C1—C2	1·525 (5)	C10—C11	1·386 (6)
C2—N2	1·475 (5)	C11—C12	1·365 (7)
N2—C3	1·470 (4)	C12—C13	1·366 (7)
C3—C4	1·528 (6)	C13—C14	1·396 (6)
C4—N3	1·500 (5)	C14—C9	1·398 (5)
O1—C5	1·298 (4)		
C5—C6	1·371 (5)		
Cl—O11*A*	1·416 (9)	Cl—O33*A*	1·337 (11)
Cl—O11*B*	1·299 (16)	Cl—O33*B*	1·435 (12)
Cl—O22*A*	1·362 (10)	Cl—O44*A*	1·462 (8)
Cl—O22*B*	1·440 (11)	Cl—O44*B*	1·300 (19)
Pd—N2—C3	108·5 (2)	N1—Pd—N3	168·3 (1)
N2—C3—C4	106·9 (3)	N2—Pd—O1	179·4 (1)
C3—C4—N3	107·6 (3)		
C4—N3—Pd	107·0 (3)	Pd—N1—C1	112·7 (2)
		C7—N1—C1	122·1 (3)
Pd—O1—C5	120·9 (2)	N1—C1—C2	108·2 (3)
O1—C5—C6	126·9 (3)	C1—C2—N2	107·0 (3)
O1—C5—C9	113·4 (3)	C2—N2—Pd	106·5 (2)
C6—C5—C9	119·7 (3)	C2—N2—C3	117·9 (3)
C5—C6—C7	129·1 (4)		
C6—C7—C8	116·9 (4)	C5—C9—C10	120·1 (3)
N1—C7—C8	121·0 (3)	C5—C9—C14	121·6 (3)
C6—C7—N1	122·1 (3)	C10—C9—C14	118·3 (4)
		C9—C10—C11	121·8 (4)
N1—Pd—N2	84·1 (1)	C10—C11—C12	119·5 (4)
N2—Pd—N3	84·5 (1)	C11—C12—C13	120·2 (4)
N3—Pd—O1	96·0 (1)	C12—C13—C14	120·9 (4)
O1—Pd—N1	95·4 (1)	C13—C14—C9	119·3 (4)

The maximum and minimum displacements from the least-squares plane through Pd, N1, N2, N3 and O1 are shown by atoms N3 [0·068 (4) Å] and Pd [0·0008 (3) Å]. Pd—N3 is the longest bond and Pd—N1 the shortest while Pd—N2 and Pd—O1 are of equal lengths, as is the case in [Pd(saden)]ClO_4. This is in contrast to the related Ni, Cu and Cd complexes (see *Introduction*), where *M*—O1 is the shortest bond. The difference follows from the fact that Pd is a soft acceptor atom with a lower affinity to O (the hard donor) than Ni, Cu and Cd. The angles N1—Pd—N2 and N2—Pd—N3 are smaller than O1—Pd—N1 and N3—Pd—O1. The structure contains two five-membered and two six-membered rings. The C atoms of the five-membered chelate ring (Pd, N1, C1, C2 and N2) assume an asymmetric envelope conformation with an N1—C1—C2—N2 torsion angle of 46·5 (4)°. The deviations of C1 and C2 from the Pd, N1, N2 plane are − 0·060 (4) and − 0·673 (4) Å, respectively. The C atoms of the other five-membered chelate ring (Pd, N2, C3, C4 and N3) have a half-chair conformation with an N2—C3—C4—N3 torsion angle of − 55·2 (4)°. The C3 and C4 atoms are displaced from the Pd, N2, N3 plane by − 0·501 (4) and 0·225 (4) Å. The six-membered chelate ring (Pd, N1, C7, C6, C5 and O1) has a boat conformation. The best plane may be fitted through N1, C7, O1 and C5 ($\chi^2 = 1{\cdot}238$), the Pd and C6 atoms being displaced by − 0·1308 (3) and − 0·033 (4) Å. The deviations of the atoms in the phenyl ring (C9, C10, C11, C12, C13 and C14) from the least-squares plane are in the range − 0·005 (4)

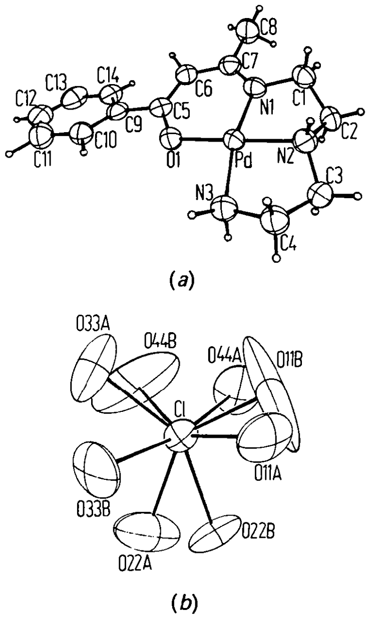

Fig. 1. (*a*) View of the complex cation with thermal ellipsoids scaled to 50% probability. (*b*) View of the disordered perchlorate anion with thermal ellipsoids scaled to 15% probability.

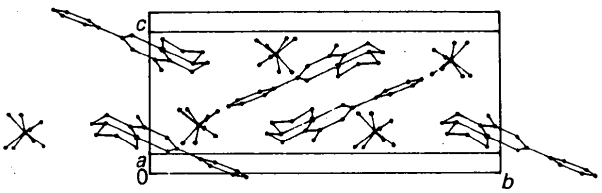

Fig. 2. Packing scheme.

for C12 to 0·004 (4) Å for C13. The O atoms of the perchlorate anion (O11, O22, O33 and O44) are disordered. The R-factor value decreased for a model in which each O atom assumes two positions, A and B, with refined occupancy factors. According to this model the ClO_4 unit apparently oscillates between these two states in the structure.

Fig. 2 shows the crystal packing. No hydrogen bonds are indicated in the structure, which is held together predominantly by electrostatic interactions.

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Synthesis and Structure of Cytosine Dichloride Cuprate: Direct Binding of Copper to Cytosine

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Abstract. Dichlorobis(cytosine)copper(II), [$CuCl_2(C_4H_5N_3O)_2$], $M_r = 356·65$, monoclinic, $P2_1/n$, $a = 8·399$ (2), $b = 13·773$ (2), $c = 10·775$ (2) Å, $\beta = 90·8$ (2)°, $V = 1246·3$ (9) Å^3, $Z = 4$, $D_x = 1·901$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 2·195$ mm^{-1}, $F(000) = 716$, $T = 298$ K, $R = 0·032$, $wR = 0·037$ for 2313 reflections $> 2\sigma(F)$. The crystal structure of the title compound consists of two crystallographically independent cytosine molecules attached together through the direct bonding of a Cu^{2+} ion with two N atoms of the pyrimidine rings. In addition to the N atoms, the Cu ions are coordinated to two Cl atoms forming approximately a square-planar environment. The bond distances of Cu to Cl(1), Cl(2), N(3) and N(3′) atoms are 2·299 (1), 2·267 (1), 1·985 (4) and 1·996 (3) Å, respectively. Packing of the Cyt(I)–$CuCl_2$–Cyt(II) complex in the crystal is ensured by an extensive extramolecular N—H···Cl and N—H···O network. Hydrogen bonds involving Cl, O and H atoms of the neighboring Cyt(I) and Cyt(II) induce a slight distortion in Cu—Cl, C═O distances but do not significantly affect intramolecular bond lengths and angles in the cytosine rings and their flatness.

Introduction. It is established that the stability of the DNA structure is affected by the interaction of a 3*d* transition metal with polynucleic acids by binding to their phosphate groups and/or to their base moieties. Thus, it was reported that Mg^{2+}, Co^{2+}, Ba^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} act as stabilizers of the calf-thymus DNA macromolecule while Cu^{2+} has a reverse effect (Eichhorn, 1962). The binding of metal ions to biomolecules is therefore of interest in helping to understand this mechanism.

Selective binding of an alkaline ion to a GC-rich DNA fragment was first suggested by kinetic studies (Eichhorn & Shin, 1968) and later confirmed by

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