Physical properties. The $[bEDOT]^+.AsF_6^-$ salt is semiconducting with a room-temperature conductivity of $2(1) \times 10^{-6} S\,m^{-1}$. Basic low-dimensional physics (*cf.* Söderholm, 1987) shows that a compound with 1:1 stoichiometry cannot be more than semiconducting. In this case every donor has a charge of +1, and in order to move an electron along the stack the repulsive energy between two electrons on the same bEDOT molecule has to be overcome. The electrical, optical and magnetic properties are reported by Söderholm, Noreland, Olovsson, Olovsson, Hellberg & Engman (1989). (In that paper a slightly erroneous X-ray wavelength was used for the lattice parameter refinement, giving rise to a small systematic error in the lattice-parameter values.)

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Di-μ-chloro-bis[(4-hydroxy-4′-methylazobenzenato-C^2,N^2)palladium(II)] Ethanol Solvate

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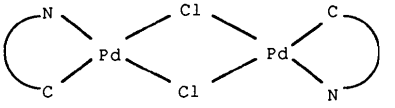
Abstract. $C_{26}H_{22}Cl_2N_4O_2Pd_2.C_2H_5OH$, $M_r = 752{\cdot}2$, triclinic, $P\bar{1}$, $a = 9{\cdot}354\ (2)$, $b = 11{\cdot}926\ (3)$, $c = 13{\cdot}417\ (3)$ Å, $\alpha = 90{\cdot}30\ (2)$, $\beta = 105{\cdot}04\ (2)$, $\gamma = 93{\cdot}00\ (2)^\circ$, $V = 1443{\cdot}3\ (6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}731$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 14{\cdot}52$ cm^{-1}, $F(000) = 748$, $T = 298$ K, $R = 0{\cdot}037$ for 4755 reflections with $I > 3\sigma(I)$. The dimeric complex has an overall *trans* conformation with bridging Cl atoms and a folded Pd_2Cl_2 unit. The Cl---Cl hinged dihedral angle is 14·0 (1)°. The Pd···Pd distance is 3·554 (1) Å.

Introduction. Azobenzenes or aromatic imines easily react with the appropriate source of palladium(II) chloride to give cyclometallated $\overline{C(sp^2)—Pd—N(sp^2)}$ complexes as in (I) (Ryabov, 1990).



(I)

In the solid state the Pd_2Cl_2 fragment can be either planar (Clark, Dyke, Smith, Kennard & White, 1985) or bent (Ghedini, Armentano, De Munno, Crispini & Neve, 1990). The cyclopalladated μ-Cl dimer obtained from 2′,6′-dimethylazobenzene has a strictly planar Pd_2Cl_2 rhomboid (Armentano, Crispini, De Munno, Ghedini & Neve, 1991). Here

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we report on the homologous complex which forms by reaction of $(PhCN)_2PdCl_2$ and 4-hydroxy-(4′-methyl)phenylazobenzene.

Experimental. The title compound was synthesized from $(PhCN)_2PdCl_2$ and 4-hydroxy-(4′-methyl)-phenylazobenzene in ethanol at room temperature. Single crystals (orange, 0·20 × 0·19 × 0·26 mm) of X-ray quality were obtained from ethanol. Siemens *R3m/V* four-circle diffractometer, 2θ–ω scan mode, graphite-monochromated Mo $K\alpha$, scan range 2θ = 3·5–54° ($-1 \le h \le 12$, $-16 \le k \le 16$, $-18 \le l \le 18$). Lattice constants obtained from the angular coordinates of 25 strong reflections. No systematic loss of intensity of three standard reflections ($\bar{2}65$, $1\bar{3}7$, $\bar{4}0\bar{2}$) during data collection. 7893 reflections measured, 4755 having $I > 3\sigma(I)$ used to refine 355 parameters. Corrections for Lorentz and polarization factors applied. No absorption correction. Full-matrix least-squares procedure (on F) applied to minimize $\sum w(F_o - F_c)^2$ with unit weights, anisotropic non-H atoms. The structure was solved by Patterson and Fourier methods. H atoms located towards end of refinement and set at fixed positions with $U = 0{\cdot}08$ Å^2, except for hydroxyl H atoms, which were refined. Final R = 0·037, $wR = 0{\cdot}031$, $S = 1{\cdot}49$. Max. and mean Δ/σ = 0·117, 0·001, min., max. $\Delta\rho = -0{\cdot}81$, 0·66 e Å^{-3}. All calculations performed with *SHELXTL-Plus* (Sheldrick, 1989) and *PARST* (Nardelli, 1983) packages. Atomic scattering factors from *SHELXTL*.

Discussion. Final atomic parameters of non-H atoms are listed in Table 1.* Selected bond lengths and angles are given in Table 2; Fig. 1 gives the molecular scheme with atomic numbering. The Cl---Cl hinged dihedral angle is 14·0 (1)°, smaller than in the analogous derivative of *N*-(4-methoxybenzylidene)-4′-butylaniline [38·7 (1)°] (Ghedini *et al.*, 1990).

The Pd—C and Pd—N bond distances (Table 1) are comparable to those reported for similar complexes. In particular, di-μ-chloro-bis[(2′,6′-dimethylazobenzenato-C^2,N^2)palladium(II)] has Pd—C and Pd—N distances in the range 1·96–1·97 and 1·99–2·00 Å, respectively (Armentano *et al.*, 1991).

The chelate ring involving Pd(1) is essentially planar [max. deviation from the plane 0·028 (5) Å at N(1)]. The metallacycle involving Pd(2) is slightly puckered instead [max. torsion angle about Pd(2)—N(3) −6·5°]. The C—Pd—N bite-angle values agree well with those found in cyclometallated azobenzenes (Armentano *et al.*, 1991; Elder, Cruea & Morrison, 1976; Hoare & Mills, 1972).

The Pd—Cl bond lengths (Table 1) reflect the greater *trans* influence of the Pd—C bond *vs* Pd—N bond (Appleton, Clark & Manzer, 1973). The intramolecular Pd---Pd separation [3·554 (1) Å] is similar to that reported for dimeric chloro-bridged cyclopalladated azobenzenes (Armentano *et al.*, 1991) or

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement coefficients* (Å^2 × 10^3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Pd(1)	1343 (1)	1114 (1)	4900 (1)	38 (1)
Pd(2)	534 (1)	2802 (1)	6854 (1)	38 (1)
Cl(1)	2 (2)	2832 (1)	5066 (1)	51 (1)
Cl(2)	2216 (2)	1352 (1)	6687 (1)	57 (1)
N(1)	1452 (5)	−36 (4)	3039 (3)	46 (2)
N(2)	822 (5)	766 (3)	3347 (3)	40 (1)
N(3)	991 (5)	2992 (3)	8412 (3)	40 (1)
N(4)	502 (5)	3835 (3)	8783 (3)	42 (2)
O(1)	5202 (5)	−2062 (4)	6263 (3)	74 (2)
O(2)	−3269 (5)	6154 (4)	5799 (3)	68 (2)
C(1)	2368 (6)	−580 (4)	3843 (4)	43 (2)
C(2)	2544 (6)	−175 (4)	4861 (4)	39 (2)
C(3)	3506 (6)	−689 (4)	5649 (4)	46 (2)
C(4)	4275 (6)	−1597 (4)	5443 (4)	48 (2)
C(5)	4087 (7)	−2001 (5)	4444 (4)	52 (2)
C(6)	3133 (7)	−1490 (5)	3644 (4)	52 (2)
C(7)	−60 (6)	1400 (4)	2527 (4)	40 (2)
C(8)	267 (6)	1472 (5)	1585 (4)	49 (2)
C(9)	−614 (7)	2088 (5)	810 (5)	58 (2)
C(10)	−1811 (7)	2621 (5)	960 (5)	54 (2)
C(11)	−2130 (7)	2517 (5)	1908 (5)	54 (2)
C(12)	−1273 (6)	1922 (5)	2690 (4)	49 (2)
C(13)	1945 (6)	2323 (4)	9171 (4)	39 (2)
C(14)	1838 (7)	1181 (4)	9018 (4)	48 (2)
C(15)	2681 (7)	511 (5)	9771 (4)	54 (2)
C(16)	3619 (7)	981 (5)	10659 (4)	51 (2)
C(17)	3716 (6)	2131 (5)	10786 (4)	52 (2)
C(18)	2891 (6)	2816 (5)	10052 (4)	49 (2)
C(19)	−409 (6)	4434 (4)	8014 (4)	39 (2)
C(20)	−1104 (7)	5356 (5)	8290 (4)	50 (2)
C(21)	−2045 (7)	5923 (5)	7527 (5)	52 (2)
C(22)	−2295 (7)	5580 (5)	6512 (4)	50 (2)
C(23)	−1595 (6)	4665 (5)	6226 (4)	47 (2)
C(24)	−652 (6)	4081 (4)	6980 (4)	39 (2)
C(25)	−2746 (9)	3307 (7)	112 (6)	82 (3)
C(26)	4485 (8)	245 (7)	11490 (5)	77 (3)
O(3)†	6455 (8)	5912 (6)	3828 (4)	116 (3)
C(27)†	6254 (12)	5143 (10)	3071 (8)	120 (5)
C(28)†	5575 (12)	5434 (11)	2072 (8)	135 (6)

†Solvate molecule.

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

Pd(1)—Cl(1)	2·497 (2)	Pd(1)—Cl(2)	2·333 (1)
Pd(1)—N(2)	2·049 (4)	Pd(1)—C(2)	1·959 (5)
Pd(2)—Cl(1)	2·321 (1)	Pd(2)—Cl(2)	2·446 (2)
Pd(2)—N(3)	2·031 (4)	Pd(2)—C(24)	1·964 (5)
N(1)—N(2)	1·270 (7)	N(1)—C(1)	1·379 (6)
N(3)—N(4)	1·276 (6)	N(4)—C(19)	1·385 (6)
C(1)—C(2)	1·413 (7)	C(19)—C(24)	1·404 (7)
Cl(1)—Pd(1)—Cl(2)	82·8 (1)	Cl(1)—Pd(1)—N(2)	104·8 (1)
Cl(2)—Pd(1)—N(2)	172·0 (1)	Cl(1)—Pd(1)—C(2)	175·0 (1)
Cl(2)—Pd(1)—C(2)	93·3 (1)	N(2)—Pd(1)—C(2)	78·9 (2)
Cl(1)—Pd(2)—Cl(2)	84·2 (1)	Cl(1)—Pd(2)—N(3)	172·7 (1)
Cl(2)—Pd(2)—N(3)	101·4 (1)	Cl(1)—Pd(2)—C(24)	95·1 (2)
Cl(2)—Pd(2)—C(24)	174·1 (2)	N(3)—Pd(2)—C(24)	78·9 (2)
Pd(1)—Cl(1)—Pd(2)	95·0 (1)	Pd(1)—Cl(2)—Pd(2)	96·1 (1)
N(2)—N(1)—C(1)	112·7 (4)	Pd(1)—N(2)—N(1)	117·8 (3)
Pd(2)—N(3)—N(4)	118·5 (3)	N(3)—N(4)—C(19)	111·5 (4)
N(1)—C(1)—C(2)	118·7 (5)	Pd(1)—C(2)—C(1)	111·8 (3)
N(4)—C(19)—C(24)	119·2 (5)	Pd(2)—C(24)—C(19)	111·5 (3)

* Lists of structure factors, anisotropic thermal parameters, full bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54210 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

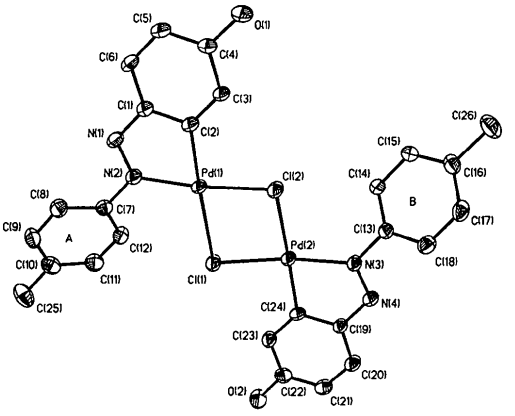

Fig. 1. Molecular structure and atom-numbering scheme. Thermal ellipsoids drawn at 30% probability level.

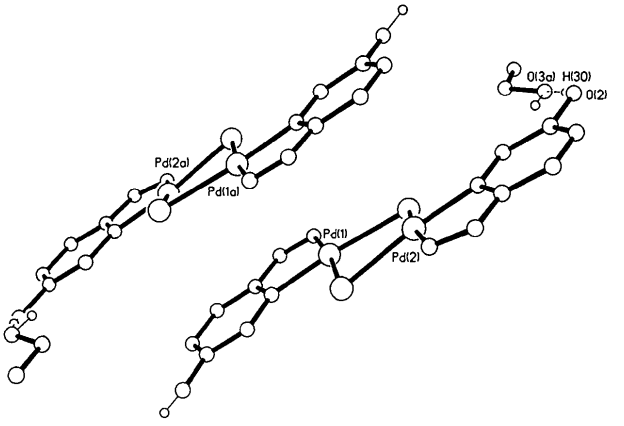

Fig. 2. A molecular dimer viewed along the *c* crystallographic axis ('free' phenyl rings removed for clarity).

dimethylbenzylamines (Barr, Dyke, Smith, Kennard & McKee, 1985).

The phenyl rings *A* and *B* are planar and tilted by 34·6 (2) and 47·4 (2)° with respect to the Pd(1) and Pd(2) mean coordination planes, respectively. The H(12)---Cl(1) and H(14)---Cl(2) distances are normal.

The crystal packing (Fig. 2) is characterized by discrete pairs of dimers which show weak intermolecular association. The shortest metal–metal contact [Pd(1)—Pd(1*a*; $-x$, $-y$, $-z+1$), 3·620 (1) Å] is greater than 3·2 Å, the van der Waals radii sum (Pauling, 1960). There is a hydrogen bond with a solvate molecule [O(2)---O(3*a*; $-x+1$, $-y+1$, $-z+1$) = 2·60 (1), O(2)—H(30) = 0·91 (1) Å; O(2)—H(30)—O(3*a*) = 173 (1)°].

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Structure of a New Form of Octaethylporphyrinato(methyl)rhodium(III)

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Abstract. $C_{37}H_{47}N_4Rh$, $M_r = 650.72$, triclinic, $P\bar{1}$, $a = 10.973$ (1), $b = 11.875$ (1), $c = 14.211$ (1) Å, $\alpha = 108.03$ (1), $\beta = 105.41$ (1), $\gamma = 100.92$ (1)°, $V = 1616.0$ (7) Å^3, $Z = 2$, $D_x = 1.337$ g cm^{-3}, λ(Mo $K\alpha_1$) = 0.7093 Å, $\mu = 5.5$ cm^{-1}, $F(000) = 684$, $T = 295$ K, final $R = 0.044$ for 4775 reflections [$F_o > 3\sigma(F_o)$]. The

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