

average to 105.8° , those centred at the bridgehead C atoms average to 101.5° , and the angle centred at the carbon atom of the bridging apex, *i.e.* C(42)–C(48)–C(45), is $92.3(8)^\circ$.

The Rh–P bond distances are significantly different from one another [Rh–P(1) = $2.357(2)$, Rh–P(2) = $2.332(2)$, Rh–P(3) = $2.311(2)$ Å] and fall in the middle to high part of the Rh–P range generally observed in tertiary phosphine complexes of Rh^I.

Dimensions in the C₃triphos ligand are normal. Deviations from an ideal geometry are present in the bond angles and mainly resemble those observed for the triphos ligand in the [Rh(nbd)(triphos)]⁺ complex except for the Rh–P–C_{alkyl} angles which average 103.4° , while they average 110.0° in the triphos complex.

The relative orientations of the phenyl groups are shown in Fig. 1. The phenyl rings φ_4 and φ_5 are roughly parallel [the dihedral angle between their planes is $14.6(3)^\circ$] and give rise to a graphite-like interaction (about 3° Å spacing). This type of non-bonded interaction, which tends to occur between phenyl groups in phenylphosphines (Tolman, 1977), can only be established between φ_4 and φ_5 because they are 1,3-axial substituents in the basal part of the boat-like six-membered ring Rh–P(2)–C(2)–C(3)–P(3) (scheme, Fig. 2). The other phenyl rings, even if free to rotate, could not interact similarly: φ_1 and φ_6 are 1,3-axial substituents in the five-membered ring Rh–P(1)–C(1)–C(3)–P(3) in a twist conformation with P(1) and

C(1) at the maximum puckering; φ_2 is axial and φ_3 is bisectonal in the five-membered ring Rh–P(1)–C(1)–C(2)–P(2) in an envelope conformation with P(1) at the tip (scheme, Fig. 2). A graphite-like interaction is also observed in the triphos complex [IrCl(CO)(triphos)] (Bachechi, Janser & Venanzi, 1985).

The bond lengths and angles in the PF₆⁻ anion are normal with P–F bond lengths between 1.55 and 1.59 Å and F–P–F angles between 88 and 92° (Lang & Hope, 1976).

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Bis{4-(*n*-heptyloxy)-*N*-[*p*-(*n*-hexyloxy)phenyl]salicylideneaminato}palladium(II)

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Abstract. [Pd(C₂₆H₃₆NO₃)₂] (*M_r* = 927.6) is a tetra-coordinate square-planar complex of Pd^{II}, with a salicylideneaminato bidentate ligand (*L*) having two long-chain substituents, which displays thermotropic behaviour. [Pd^{II}(*L*)₂] is *trans* square planar with C₂ molecular symmetry in the crystalline state. Crystals are monoclinic, *P*2₁/*a*, *a* = 5.961 (5), *b* = 15.018 (4), *c* = 27.881 (7) Å, β = 94.80 (4)°, *V* = 2487 (2) Å³, *Z* = 2, *D_m*(floatation) = 1.25 (5), *D_x* = 1.237 g cm⁻³, λ(Cu Kα) = 1.54178 Å, μ = 35.3 cm⁻¹, *F*(000) = 984,

T = 298 K, *R* = 0.065 for 3737 observed independent reflections. The molecule has a flattened shape with the long-chain substituents in zigzag planar conformation roughly parallel to each other. The dihedral angle between the planar salicylideneaminato group and the *N*-bonded phenyl group is 62 (2)°.

Introduction. The study of the relationships between molecular structure and liquid-crystal properties of organic compounds is based on the crystal struc-

Table 1. Atomic fractional coordinates and equivalent isotropic thermal parameters

The standard errors estimated from the least-squares refinement are given in parentheses. For atom labelling see Fig. 1.

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Pd	0.5000	0.5000	0.5000	0.0404 (4)
O1	0.4292 (9)	0.4520 (4)	0.5630 (31)	0.055 (3)
N	0.7271 (10)	0.4035 (4)	0.4921 (2)	0.044 (3)
C1	0.8356 (13)	0.3630 (5)	0.5287 (3)	0.041 (4)
C2	0.7866 (13)	0.3848 (5)	0.4440 (3)	0.042 (4)
C3	0.6228 (14)	0.3425 (6)	0.4132 (3)	0.047 (5)
C4	0.6669 (14)	0.3325 (6)	0.3648 (3)	0.050 (5)
C5	0.8624 (15)	0.3652 (6)	0.3486 (3)	0.049 (5)
C6	1.0252 (14)	0.4058 (6)	0.3803 (3)	0.052 (5)
C7	0.9842 (14)	0.4156 (6)	0.4289 (3)	0.049 (5)
O2	0.8855 (11)	0.3516 (5)	0.3007 (2)	0.063 (4)
C8	1.0790 (17)	0.3869 (7)	0.2803 (3)	0.065 (4)
C9	1.0721 (18)	0.3544 (7)	0.2297 (3)	0.068 (7)
C10	1.2593 (20)	0.3909 (8)	0.2025 (4)	0.076 (8)
C11	1.2387 (21)	0.3564 (8)	0.1523 (4)	0.084 (9)
C12	1.4440 (24)	0.3928 (10)	0.1238 (4)	0.10 (1)
C13	1.4441 (28)	0.3584 (12)	0.0734 (5)	0.14 (1)
C14	0.7840 (13)	0.3705 (6)	0.5779 (3)	0.041 (4)
C15	0.5913 (14)	0.4119 (5)	0.5918 (3)	0.048 (5)
C16	0.5399 (15)	0.4097 (6)	0.6417 (3)	0.048 (5)
C17	0.6983 (14)	0.3683 (6)	0.6744 (3)	0.047 (5)
C18	0.8928 (14)	0.3296 (6)	0.6610 (3)	0.052 (5)
C19	0.9356 (13)	0.3301 (6)	0.6143 (3)	0.049 (4)
O3	0.6630 (11)	0.3620 (4)	0.7225 (2)	0.061 (4)
C20	0.4511 (16)	0.3923 (7)	0.7383 (3)	0.059 (6)
C21	0.4418 (18)	0.3614 (8)	0.7892 (3)	0.070 (7)
C22	0.2383 (18)	0.3940 (8)	0.8119 (3)	0.071 (7)
C23	0.2338 (21)	0.3625 (8)	0.8629 (4)	0.084 (9)
C24	0.0397 (21)	0.3952 (9)	0.8895 (4)	0.092 (9)
C25	0.0414 (25)	0.3644 (12)	0.9409 (5)	0.12 (1)
C26	-0.1477 (27)	0.3905 (12)	0.9663 (5)	0.14 (1)

Table 2. Relevant bond distances (Å) and bond angles (°)

The standard errors estimated from the least-squares refinement are given in parentheses.

Pd—O1	1.976 (6)	Pd—N	2.009 (6)
N—C1	1.31 (1)	N—C2	1.44 (1)
O1—C15	1.347 (9)	C1—C14	1.43 (1)
C2—C3	1.40 (1)	C2—C7	1.37 (1)
C3—C4	1.40 (1)	C4—C5	1.38 (1)
C5—O2	1.37 (1)	C5—C6	1.40 (1)
C6—C7	1.40 (1)	O2—C8	1.43 (1)
C8—C9	1.49 (1)	C9—C10	1.50 (1)
C10—C11	1.49 (1)	C11—C12	1.52 (1)
C12—C13	1.50 (1)	C14—C15	1.39 (1)
C14—C19	1.44 (1)	C15—C16	1.45 (1)
C16—C17	1.40 (1)	C17—C18	1.37 (1)
C18—C19	1.35 (1)	C17—O3	1.38 (1)
O3—C20	1.45 (1)	C20—C21	1.50 (1)
C21—C22	1.50 (1)	C22—C23	1.50 (1)
C23—C24	1.51 (1)	C24—C25	1.50 (2)
C25—C26	1.44 (1)		
Pd—N—C1	122.8 (5)	Pd—N—C2	117.6 (5)
Pd—O1—C15	119.9 (5)	O1—Pd—N	91.8 (3)
O1—C15—C14	127.0 (7)	O1—C15—C14	112.7 (7)
N—C2—C3	116.5 (7)	N—C2—C7	120.5 (7)
N—C1—C14	125.2 (7)	C1—N—C2	119.4 (6)
C1—C14—C15	123.4 (7)	C1—C14—C19	118.0 (7)
C2—C3—C4	117.5 (8)	C2—C7—C6	119.2 (8)
C3—C4—C5	120.6 (8)	C3—C2—C7	122.6 (8)
C4—C5—C6	120.8 (8)	C4—C5—O2	115.1 (8)
C5—C6—C7	119.1 (8)	C5—O2—C8	118.8 (7)
C6—C5—O2	124.0 (8)	O2—C8—C9	107.2 (8)
C8—C9—C10	113.2 (9)	C9—C10—C11	113.7 (9)
C10—C11—C12	115 (1)	C11—C12—C13	115 (1)
C14—C15—C16	120.3 (7)	C14—C19—C18	121.7 (8)
C15—C16—C17	116.7 (8)	C15—C14—C19	118.5 (7)
C16—C17—C18	123.3 (8)	C16—C17—O3	120.9 (8)
C17—C18—C19	119.5 (8)	C17—O3—C20	118.8 (7)
C18—C17—O3	115.8 (8)	O3—C20—C21	107.0 (8)
C20—C21—C22	113.3 (9)	C21—C22—C23	112.2 (9)
C22—C23—C24	116 (1)	C23—C24—C25	115 (1)
C24—C25—C26	116 (1)		

ture of mesogens both of low molecular mass and polymeric. A comparatively small number of compounds exhibiting thermotropic mesomorphism are known among metal coordination compounds with organic mesogenic ligands.

For these compounds the nature of the metal atom plays its most important role in defining the basic geometrical shape of the molecular core, which is a very important factor for the onset of liquid-crystal properties. The square-planar coordinative geometry has proved to favour the production of nematic, smectic or discotic mesomorphism in several Cu^{II} and Pd^{II} complexes (Ghedini, Longeri & Bartolino, 1982; Ghedini, Licocchia, Armentano & Bartolino, 1984; Ghedini, Pellegrino, Armentano, De Munno & Bruno, 1986; Ovchinnikov, Galyametdinov, Ivanova & Yagfarova, 1984; Sadashiva & Ramesha, 1986; Ohta, Muroki, Takagi, Hatada, Ema, Yamamoto & Matsuzaki, 1986).

A comparative study of some mesogenic compounds of these two metals has shown (Caruso, Roviello & Sirigu, 1988) that the Pd^{II} compounds have higher isotropization temperatures and larger thermal stability ranges for the mesophase than the Cu^{II} homologues. For some *trans* square-planar complexes of the type *ML*₂, where *L* (bidentate ligand) is a salicylidene-aminato with two long-chain substituents, the thermotropic behaviour is known for *M* = Cu and Pd and the crystalline phase has been studied for the Cu^{II}

homologue of the title compound. We have therefore undertaken a structural study of PdL₂ with the aim of ascertaining if the different thermotropism corresponds to a different shape of the molecule and/or a different packing in the crystalline phase.

Experimental. The title compound has been prepared according to a procedure described elsewhere (Caruso, Roviello & Sirigu, 1988). Single crystals (thin orange platelets 0.8 × 0.5 × 0.02 mm) suitable for X-ray diffraction measurements were crystallized from chloroform-ethanol mixtures. X-ray diffraction measurements were performed with an Enraf-Nonius CAD-4 automated single-crystal diffractometer, Ni-filtered Cu K α radiation, and standard *SDP* procedure (Enraf-Nonius, 1981). Lattice constants were obtained from the angular coordinates of 25 carefully centred strong reflections. Integrated intensities were measured according to the 2 θ - ω scan mode, with $(\sin\theta)/\lambda \leq 0.274 \text{ \AA}^{-1}$ and Miller indices *hkl* with $-7 \leq h \leq 7$, $0 \leq k \leq 17$, $0 \leq l \leq 33$. Two standard reflections monitored every 2 h showed only random deviations. 4536 independent reflections were collected, of which 799 having $I < 3\sigma(I)$ were not used for structure refinement. Corrections for Lorentz and polarization factors were applied. Absorption correction was performed according to the

method developed by North, Phillips & Mathews (1968); min., max. transmission coefficients 0.65, 1.00. All calculations performed with the *SHELX76* package (Sheldrick, 1976). The systematic absences and the Patterson function agree with the $P2_1/a$ space group, with Pd atoms lying on inversion centres ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ position was arbitrarily selected). The crystal structure was determined starting from the Pd-atom position and by repeated application of the Fourier method. Structure refinement was carried out with H atoms placed in calculated positions according to standard sp^3 and sp^2 geometries and with a single U_{iso} value of 0.0766 \AA^2 . The full-matrix least-squares procedure minimized $\sum_i w_i (F_{obs,i} - F_{calc,i})^2$ with unit w_i 's and included the

anisotropic vibration for all non-H atoms. Final R , wR and S values are 0.065, 0.065 and 2.6 respectively. Max. $\Delta/\sigma = 0.01$; max., min. heights in final difference Fourier map = 1.46, -1.67 e \AA^{-3} . Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).*

Discussion. Atomic coordinates and equivalent thermal vibration parameters for the crystallographically independent unit are listed in Table 1. The molecular parameters are listed in Table 2 with lettering as in Fig. 1 which shows the molecular model which has crystallographic C_i symmetry. The relevant aspects of the crystal packing are visible in Fig. 2.

It is convenient to compare the molecular geometry obtained in the present case with that of the Cu homologue (Iannelli, Immirzi, Roviello & Sirigu, 1988). The first and most evident difference is that the Pd^{II} compound is characterized by a single molecular conformation with square-planar coordinative geometry of C_i molecular and crystal symmetry, whilst in the Cu^{II} case two crystallographically independent molecules are present: one having C_i molecular and crystallographic symmetry and a second having

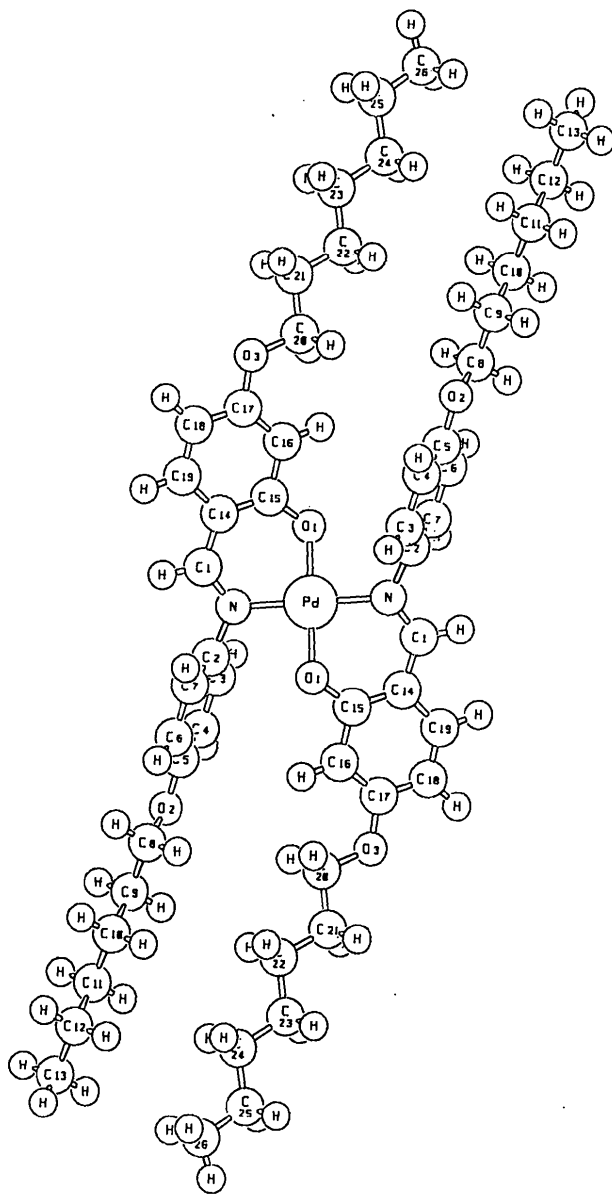


Fig. 1. Molecular drawing for the title compound.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51689 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

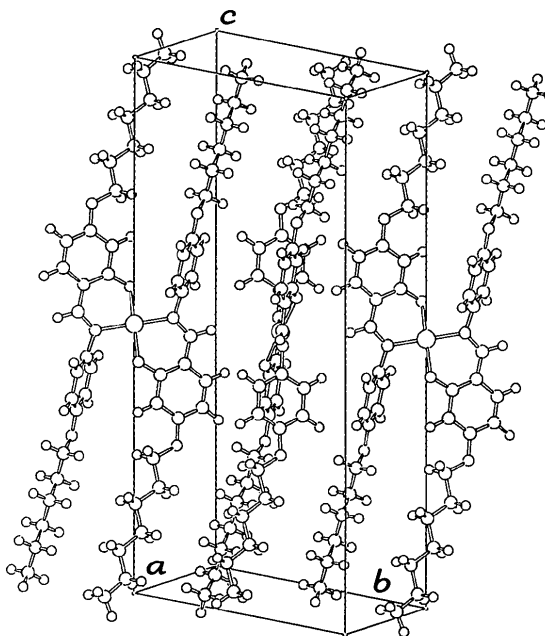


Fig. 2. Packing of molecules in layers parallel to the crystallographic xy plane. For the sake of clarity only some molecules are shown.

approximate C₂ molecular symmetry with the coordination square distorted towards a tetrahedral geometry.

The unique molecular conformation in the Pd^{II} case is very similar to the C_i molecule in the Cu^{II} case. The salicylideneaminato group is planar (within 0.16 Å), but its least-squares plane does not coincide with the least-squares coordination plane, the dihedral angle being 27.0 (5)°. The N-bonded phenyl group is planar (within 0.013 Å) and tilted by 58.1 (2)° with respect to the salicylideneaminato plane. Not very different values were found for the Cu^{II} homologue [46 (2)° for the C_i molecule; 66 (2) and 57 (2)° for the other]. Unlike the Cu^{II} complex, the conformation of the alkoxy groups in the Pd^{II} compound is very close to all-*trans* and no evidence of statistical disorder was detected. The main axes are roughly parallel. The packing indeed seems rather tighter in the Pd^{II} case since the molecular volume is 1243 (1) Å³ for Pd^{II} and 1264 (1) Å³ for Cu^{II}. Evaluation of the central ellipsoid of inertia for the whole molecule (equal weights for all non-H atoms were considered) results in a mean square displacement from the principal plane of inertia of 0.67 (2) Å with a maximum of 1.81 (2) Å for atom C4. The molecular packing along the z axis is characterized by a sequence of molecular layers containing molecules with their elongation axes (*i.e.* the major axis of the central ellipsoid of inertia of the molecule) mutually parallel but tilted by 73 (1)° with respect to the xy plane. No interdigitation of the alkoxy terminals belonging to contiguous layers is observed, while this feature is present to a small extent in the crystal packing of the Cu^{II} homologue. The packing along the y axis within each of the layers is characterized by an alternate sequence at y = 0 and y = ½ of rows of molecules with different orientation. Each row contains strictly parallel molecules while molecules belonging to contiguous rows have their average planes mutually orthogonal.

The shortest metal-metal distance, 5.961 (5) Å, is found between contiguous molecules of the same row. This value is ~1 Å shorter than the shortest Cu-Cu distance measured for the Cu^{II} homologue.

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Structure of Chloro(nitrioltriethanolato)cobalt(II)

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Abstract. [Co(C₆H₁₄NO₃)Cl], *M*_r = 242.6, orthorhombic, *Pnma*, *a* = 16.893 (7), *b* = 7.890 (2), *c* = 6.792 (2) Å, *V* = 905 Å³, *Z* = 4, *D*_x = 1.76 g cm⁻³,

Cu Kα, λ = 1.5418 Å, μ(Cu Kα) = 50.6 cm⁻¹, *F*(000) = 492, room temperature, final *R* = 0.076, *wR* = 0.081 for 720 unique reflections. The triethanolamine ligand

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