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## Liquid Crystals

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### Transition metals complexed to ordered mesophases. VI. Synthesis, mesomorphic behaviour and X-ray molecular structure of the cyclopalladated dimer [(L)PdCl]<sub>2</sub> (HL = *N*-(4-methoxybenzylidene)-4'-butylaniline)

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## Transition metals complexed to ordered mesophases†

### VI. Synthesis, mesomorphic behaviour and X-ray molecular structure of the cyclopalladated dimer [(L)PdCl]<sub>2</sub> (HL = *N*-(4-methoxybenzylidene)-4'-butylaniline)

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The reaction between [Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>] and the liquid crystalline ligand *N*-(4-methoxybenzylidene)-4'-butylaniline, (MBBA indicated here as HL) affords the new metallo-mesogen [(L)PdCl]<sub>2</sub>, (1). The main feature of the molecular structure (single crystal X-ray analysis) of the dinuclear cyclopalladated complex (1) is the Cl---Cl hinged dihedral angle, 141.3(1)°, which the Pd<sub>2</sub>Cl<sub>2</sub> core forms. The Pd---Pd separation is 3.36(2) Å. Complex (1) in the solid state forms a columnar array and upon heating shows a solid-to-solid transition at 160°C, a smectic A mesophase, at 218°C, a nematic mesophase at 245°C (with minor decomposition) and the clearing point at 251°C (with large decomposition). By comparison with similar palladium mesogens, the increase in the transition temperatures by (1) with respect to MBBA, has been tentatively ascribed to the fully anisotropic ellipsoidal molecular shape resulting from palladium complexation.

#### 1. Introduction

In the past few years much synthetic effort has been devoted to the preparation of new liquid-crystalline materials to be of use in practical applications. Among these materials, the metallo-mesogens, metal containing liquid crystals, have been considered [1-12]. The preparation of a number of these compounds is conveniently achieved through metallation or coordination of transition metals to appropriate mesogenic ligands. Following such a synthetic approach we have now reacted [Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>] with *N*-(4-methoxybenzylidene)-4'-butylaniline (HL), a well-known thermotropic liquid-crystalline species usually denoted by MBBA [13]. In this paper we report the synthesis, mesomorphic properties and X-ray determined molecular structure of the palladated compound [(L)PdCl]<sub>2</sub> (1). Complex 1 is a *bis*-chloro-bridged dimer having cyclometalated rings containing both Pd-N(*sp*<sup>2</sup>) and Pd-C(*sp*<sup>2</sup>) bonds. Remarkably, up to date, only a few examples of compounds like (1) have been structurally characterized [14, 15].

#### 2. Discussion

The HL molecule is characterized by a benzylideneamine fragment for which cyclopalladation is a straightforward process [3 (a)]. Accordingly, treating a methanolic solution of HL with the stoichiometric amount of [Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>], the dinuclear cyclopalladated derivative [(L)PdCl]<sub>2</sub> (1) is obtained.

† For parts I to V see [1 (a)] to [1 (e)].

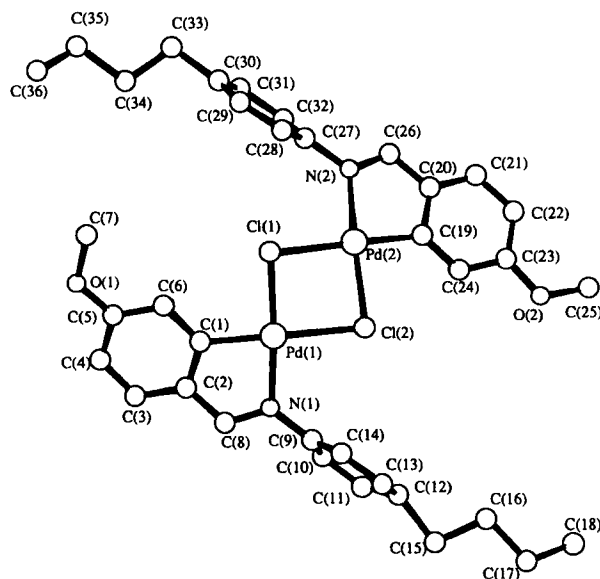


Figure 1. View of complex (1) with the atomic numbering scheme.

The molecular structure of (1) (figure 1), determined by single crystal X-ray analysis, consists of a *bis*-chloro-bridged dimer wherein each palladium atom, as part of a metallated five membered ring, is tetracoordinated in a square planar geometry. The bond distances and angles (see table 1) are not unusual and are similar to those observed for related complexes [14–18]. The whole molecule is not planar and forms a Cl...Cl hinged dihedral angle of 141.3(1)° with a Pd–Pd separation of 3.326(2) Å. As far as the geometry of the Pd<sub>2</sub>Cl<sub>2</sub> fragment is concerned, it should be pointed out that for complexes like (1) the planar geometry is usually exhibited [14–16, 18]. A bent geometry (dihedral angle = 122°) has only been found for the cyclometallated oxime compound [ $\{\text{CH}_2\text{C}(\text{CH}_3)_2\text{C}(\text{=NOH})\text{CH}_3\}\text{PdCl}\}_2$  reported by Constable *et al.* [17].

Table 1. Selected bond distances (Å) and angles (°) in complex 1.

|                   |           |                   |           |
|-------------------|-----------|-------------------|-----------|
| Pd(1)–Cl(1)       | 2.457(3)  | Pd(2)–Cl(1)       | 2.327(3)  |
| Pd(1)–Cl(2)       | 2.318(3)  | Pd(2)–Cl(2)       | 2.447(3)  |
| Pd(1)–N(1)        | 2.033(9)  | Pd(2)–N(2)        | 2.040(7)  |
| Pd(1)–C(1)        | 1.974(9)  | Pd(2)–C(19)       | 1.973(8)  |
| C(1)–C(2)         | 1.402(20) | C(19)–C(20)       | 1.406(10) |
| C(2)–C(8)         | 1.404(20) | C(20)–C(26)       | 1.409(10) |
| C(8)–N(1)         | 1.303(20) | C(26)–N(2)        | 1.318(10) |
| Cl(1)–Pd(1)–Cl(2) | 84.9(1)   | Cl(1)–Pd(2)–Cl(2) | 84.9(1)   |
| Cl(1)–Pd(1)–N(1)  | 99.4(3)   | Cl(2)–Pd(2)–N(2)  | 99.4(2)   |
| Cl(1)–Pd(1)–C(1)  | 178.2(3)  | Cl(2)–Pd(2)–C(19) | 179.4(3)  |
| Pd(1)–C(1)–C(6)   | 127.1(8)  | Pd(2)–C(19)–C(24) | 128.0(7)  |
| Pd(1)–C(1)–C(2)   | 112.1(8)  | Pd(2)–C(19)–C(20) | 113.3(7)  |
| C(2)–C(1)–C(6)    | 120.9(9)  | C(20)–C(19)–C(24) | 118.7(8)  |
| C(1)–C(2)–C(3)    | 117.9(13) | C(19)–C(20)–C(21) | 120.9(9)  |
| C(1)–C(2)–C(8)    | 115.9(10) | C(19)–C(20)–C(26) | 114.8(8)  |
| C(3)–C(2)–C(8)    | 126.1(12) | C(21)–C(20)–C(26) | 124.3(9)  |
| Pd(1)–N(1)–C(8)   | 113.5(8)  | Pd(2)–N(2)–C(26)  | 113.0(6)  |
| Pd(1)–N(1)–C(9)   | 125.4(7)  | Pd(2)–N(2)–C(27)  | 125.5(6)  |
| C(8)–N(1)–C(9)    | 120.9(10) | C(26)–N(2)–C(27)  | 121.1(8)  |

The molecules in the unit cell are associated in pairs, with the shortest Pd–Pd distance of 10.028(2) Å. The crystal packing (see figure 2) is characterized by a one dimensional array of pairs of columns parallel to the *b* axis. Between the columns the closest palladium atoms are at 7.038(1) Å, while into the column the shortest Pd–Pd separation is 6.485(5) Å.

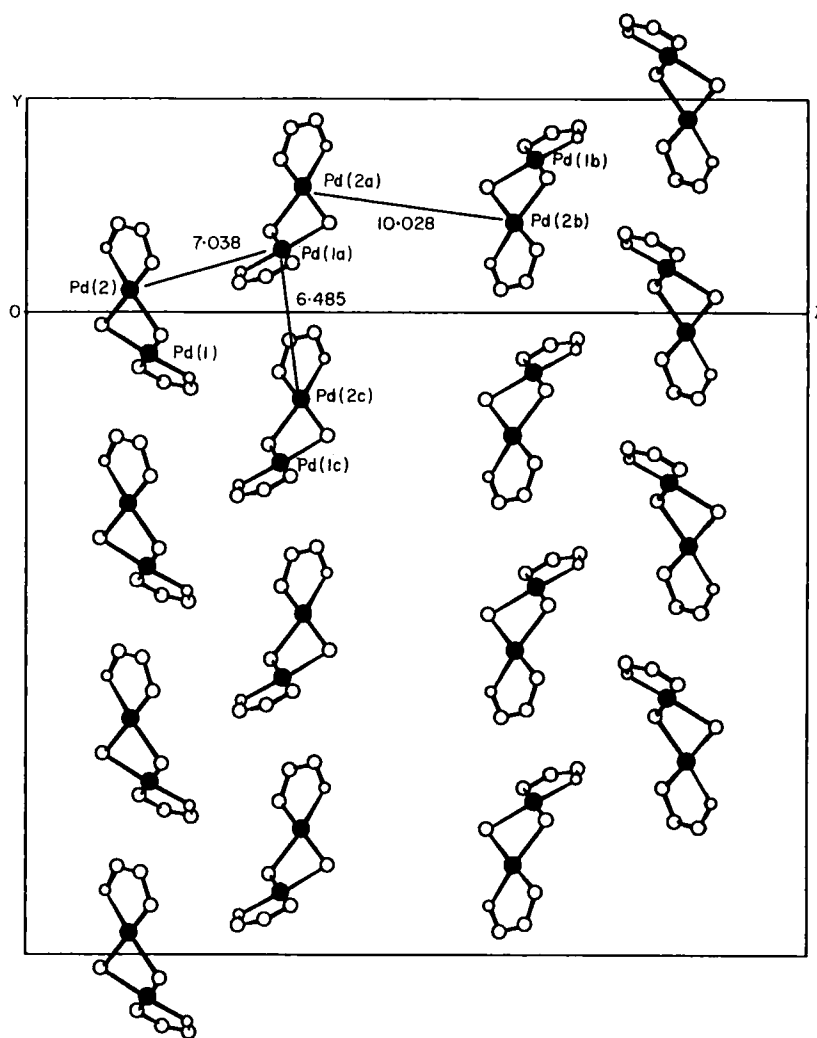


Figure 2. Projection of complex **1** down the *a* axis. Symmetry code: (a)  $1 - x, 0.5 + y, 0.5 - z$ ; (b)  $x, 0.5 - y, 0.5 + z$ ; (c)  $1 - x, -0.5 + y, 0.5 - z$ .

Complex (**1**) is a mesogenic species which, upon heating, shows a solid-to-solid transition at 160°C and then at 218°C, a smectic A phase with a polygonal texture [19]. Such a mesophase is stable until 245°C, thereafter a transition to a nematic phase exhibiting a schlieren texture [19], together with some decomposition, takes place. The clearing point, accompanied by much decomposition, is reached at 251°C.

Recently, with reference to copper containing mesogens it has been proved that the molecular geometry and the crystal packing might account for the mesogenic

behaviour [7 (b), 20], by contrast, in the present case a similar relationship is not apparent. Furthermore, the uncomplexed MBBA is a liquid-crystalline compound which displays a nematic phase at 20°C and a clearing point at 47°C [13] while (1) exhibits a rich mesomorphism as well as significantly higher transition temperatures. Therefore, the thermotropic properties of the ligand are modified in the same way previously found for the mesogenic dinuclear cyclopalladated complexes obtained from *p,p'*-disubstituted-azobenzenes [21]. The data concerning the azobenzene compounds were interpreted by taking into account the higher molecular biaxiality arising from the metal complexation. Unfortunately, (1) decomposes upon heating so that calorimetric data which could provide appropriate information about the biaxiality of the nematic phase [22], are not available. However, since as far as the molecular structure is concerned the MBBA and the azobenzene derivatives are strictly similar, also the thermal behaviour displayed by (1) could be tentatively ascribed to the increased molecular width which should produce a fully anisotropic ellipsoidal molecular shape.

### 3. Experimental section

#### 3.1. General procedures

The synthesis of complex 1 was performed under a nitrogen atmosphere. The thermal behaviour was monitored by means of a Mettler FP 800 thermosystem equipped with a FP 84 microscopy cell, at a heating rate of 4°C min<sup>-1</sup>. The textures of the various mesophases were observed with a Zeiss Axioskop polarizing microscope equipped for photography and with a Linkam CO 600 heating stage.

#### 3.2. Preparation of [(L)PdCl]<sub>2</sub> (1)

To a solution of HL (Aldrich Chemical Co.) (267 mg, 1 mmol) in 30 ml of methanol, [Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>] [23] (383 mg, 1 mmol) was added and the resulting orange solution stirred overnight at room temperature. The yellow-greenish precipitate which forms was collected by filtration, washed with diethyl ether, and vacuum dried. The product was recrystallized from dichloromethane-petroleum ether affording (1) as single crystals: yield 250 mg (60 per cent) Anal. Calcd for C<sub>36</sub>H<sub>40</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pd<sub>2</sub>: C, 52.96; H, 4.94; N, 3.44. Found: C, 52.44; H, 4.71; N, 3.28. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS internal standard): 2.63 (br t, 2H, *J* = 6.5 Hz, -CH<sub>2</sub>-C<sub>3</sub>H<sub>7</sub>); 3.75 (br s, 3H, -O-CH<sub>3</sub>); 7.81 (s, 1H, -N=CH-).

#### 3.3. X-ray structure determination

The X-ray data collection was performed by the 'Centro Interdipartimentale di Cristallografia Strutturale' of the Università di Firenze, Italy, on a Nonius Cad-4 using graphite-monochromated MoK $\alpha$  ( $\lambda$  = 0.71069 Å) radiation and a  $\omega/2\theta$  scan. Accurate unit cell dimensions and crystal orientation matrices were obtained from least squares refinement of 25 strong reflections in the 15° < 2 $\theta$  < 30° range. Crystallographic data and other pertinent information are summarized in table 2. Lorentz and polarization corrections were applied to the intensity data. Absorption and extinction corrections were ignored. The structure was solved by using standard Patterson methods and subsequently by using the Fourier maps. Some disorder was found in the aliphatic chains. The refinement was carried out using geometric constraints for the carbon atoms (the distances C-C were assumed = 1.5 Å). Full matrix least squares refinement was carried out by minimizing the function  $\sum_w (|F_o| - |F_c|)^2$ ,

Table 2. Crystallographic data for complex 1.

|                                      |   |
|--------------------------------------|---|
| Formula                              | C <sub>36</sub> H <sub>40</sub> N <sub>2</sub> Cl <sub>2</sub> O <sub>2</sub> Pd <sub>2</sub> |
| Molecular weight                     | 816.43  |
| Colour                               | orange  |
| Space group                          | P2 <sub>1</sub> /c  |
| Temp/K                               | 298   |
| a/Å                                  | 12.641(4)   |
| b/Å                                  | 8.771(7)  |
| c/Å                                  | 32.252(7)   |
| $\beta$ /°                           | 90.69(2)  |
| V/Å <sup>3</sup>                     | 3576(3)   |
| Z                                    | 4   |
| $m(\text{MoK}\alpha)/\text{cm}^{-1}$ | 11.7  |
| R                                    | 0.046   |
| R <sub>w</sub>                       | 0.051   |
| S                                    | 1.198   |

where  $F_o$  and  $F_c$  are the observed and the calculated structure factors. Of 5139 reflections there were 3117 unique with  $I > 3\sigma(I)$ . These data were used in the final refinement of the structural parameters to arrive at a residual of  $R = 0.046$ ,  $R_w = 0.051$  and  $S = 1.198$ . The weighting scheme used in the last refinement cycle was  $w = 1.000/(\sigma^2(F_o) + 0.001622(F_o)^2)$ . The anomalous dispersion corrections and atomic scattering factors were taken from [24]. All calculations were performed with the SHELX 76 [25] and PARST [26] set of programs on the VAX/VMS computer from the 'Università della Calabria'.

Table SI listing complete bond distances and bond angles, and the tables SII–SIV, listing crystallographic data, positional parameters of non-hydrogen atoms, and thermal parameters (10 pages) are available, as a Supplementary Publication, from the British Library Lending Division and may be obtained by using the procedure described at the end of this issue and by quoting the number SUP 16516.

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