

# Metallomesogens presenting blue phases in a glassy state and in metallomesogen/nematic mixtures

Julio Buey,<sup>a</sup> Pablo Espinet,<sup>\*a</sup> Heinz-S. Kitzerow<sup>\*b</sup> and Jochen Strauss<sup>b</sup>

<sup>a</sup> Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid, Spain. E-mail: [espinet@qi.uva.es](mailto:espinet@qi.uva.es)

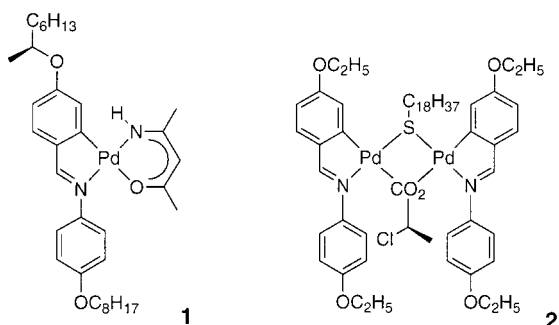
<sup>b</sup> Department of Chemistry, University of Paderborn, Warburger Str. 100, 33098 Paderborn, Germany

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Two palladium complexes are described with very high helical twisting power and producing blue phases, in one case preserved in a glassy state for several days.

Blue phases (BPs)<sup>1</sup> have been the subject of intensive studies during the last decade in the field of chiral liquid crystals because of their anomalous physical and structural features such as Bragg reflections in the visible wavelength, and the occurrence of liquid single crystals (liquid crystal droplets with the shape of solid crystals).<sup>2</sup> These phases are sometimes observed in a narrow range of temperature, typically 2–3 °C, between the cholesteric (N\*) and the isotropic (I) phases, in compounds with very small pitch ( $p$ ). Up to three different phases can be observed at zero field,<sup>3</sup> labelled as BPI (body centered cubic structure), BPII (simple cubic structure) and BPIII (structure still under discussion).<sup>4</sup> Although many organic mesogens displaying BPs are known, the first example of a metallomesogen<sup>5</sup> displaying a blue phase has been reported only recently.<sup>6,7</sup> Here we describe two structural types of metallomesogen leading to blue phases. For one of them the BP is preserved in a glassy state for several days. These compounds have been found in the same family of orthometallated compounds that yielded the first ferroelectric<sup>8</sup> and the first cholesteric metallomesogen.<sup>9</sup>

The new chiral complexes **1** and **2** were prepared as described



elsewhere for similar compounds.<sup>9,10</sup> Their mesogenic properties were studied by optical microscopy and differential scanning calorimetry (DSC) at 5 °C min<sup>-1</sup>, and the pitch ( $p$ ) and handedness of the cholesteric helix were determined using the modified Grandjean–Cano method.<sup>11</sup> All these data are summarized in Table 1. It should be noted that the complexes display

both cholesteric and blue phases in their pure state, but their high viscosity prevents a good alignment of the samples as well as the growing of well shaped BP single crystals to be studied by the Kossel method.<sup>12</sup> For these reasons Cano and Kossel experiments were performed on mixtures of the compounds with the nematic host ZLI-1275 (Merck). The ability of the chiral compounds to induce helical phases on mixing with the nematic host is represented either by the helical twisting power  $htp = 1/pc$  ( $c$  = concentration of the dopant), or by the molecular twisting power,  $mtp = M/px_m r$ ,<sup>13</sup> where  $M$  is the molecular weight,  $p$  the pitch,  $x_m$  the weight fraction of the chiral dopant and  $\rho$  the mass density of the cholesteric solution. The latter quantity is particularly suitable to characterize the twisting power of a molecule.

The mononuclear complex **1** exhibits monotropic BPII and BPI phases at reasonably low temperatures, as well as a very strong selective reflection. The appearance of these phases is in agreement with the estimated pitch of pure **1** ( $\approx$  350 nm). Due to the high viscosity and the low transition temperatures of the material, both phases are retained in a glassy state at room temperature. Thus in contrast to the usual problems, for studying BPs, which require sophisticated temperature control, glassy samples of **1** can be observed, handled, and even stored for days very easily. Kossel experiments could only be carried out on mixtures of **1** and ZLI-1275. For one of the mixtures (62.6 wt% of **1**, deep blue selective reflection at r.t.), three different Kossel diagrams were observed at 47 °C. The first one (Fig. 1a) shows the main ring corresponding to a BPII crystal viewed in its [100] orientation; the second (Fig. 1b) a BPI crystal in the [110] orientation; and the third (Fig. 1c) is the sum of both diagrams, suggesting the coexistence of BPI and BPII crystals in the sample. In order to increase the selective reflection wavelength for the BPII modification, a more dilute mixture was prepared (52.6 wt% of **1**, green selective reflection at r.t.), but in this case only the BPI modification was observed (Fig. 1d).

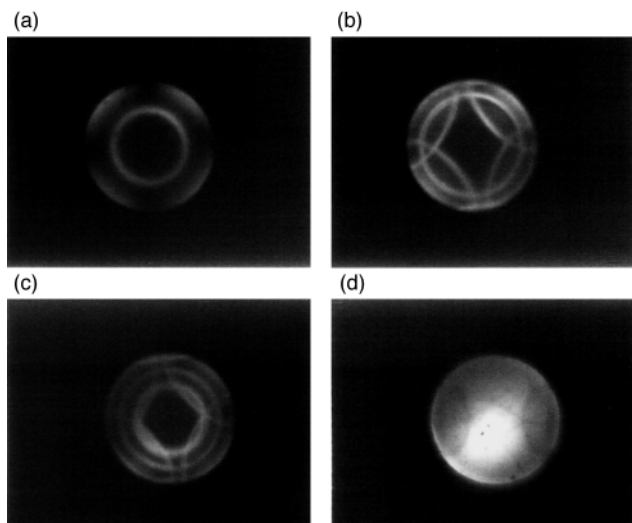
Moreover, **1** has good solubility in the nematic host, very high  $htp$  (i.e. very low pitch), and a  $p$  value almost invariant with temperature (17.43 wt% of **1**, Fig. 2). The value of its molecular twisting power is as high as for most chiral dopants used in commercial applications, but still one order of magnitude below the highest value reported for calamitic chiral dopants (DL21 : 28300 m<sup>2</sup> mol<sup>-1</sup>).<sup>14</sup>

The dinuclear compound **2** also displays a monotropic BPI phase, in the range 98–94 °C, appearing under the microscope

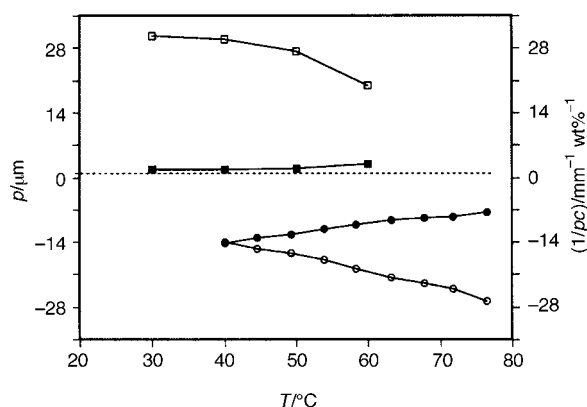
Table 1 Phase transition data and characterisation of the helix for complexes **1** and **2**

Complex	Transition <sup>a</sup>	$T/^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$	$p^d/\mu\text{m}$	$htp^d/(\text{mm wt}\%)^{-1}$	$mtp^d/\text{m}^2 \text{mol}^{-1}$	Handedness
(S)- <b>1</b>	C–I	85.4	36.5	1.9–2.9	20–30	1500–2400	Right
	I–BPII–BPI–N* <sup>b</sup>	46.1	–0.3 <sup>c</sup>				
(R)- <b>2</b>	C–I	134.1	36.8	–7 to –14 <sup>e</sup>	–14 to –26.5 <sup>e</sup>	–1600 to –3000	Left
	I–BPI <sup>b</sup>	98.0	–0.3 <sup>c</sup>				
	BPI–N*	94.0					

<sup>a</sup> See ref. 1. <sup>b</sup> Monotropic transitions not resolved by DSC. <sup>c</sup> Combined enthalpies. <sup>d</sup> In mixtures with ZLI-1275. <sup>e</sup> See text.



**Fig. 1** Kossel diagrams of mixtures of 62.6 wt% of **1** in ZLI-1275 at 47 °C (a–c), and 52.06 wt% at 47 °C (d).



**Fig. 2** Temperature dependence of the cholesteric pitch  $p$  (■, **1**; ●, **2**) and the helical twisting power  $1/pc$  (□, **1**; ○, **2**) in mixtures of 17.43 wt% of **1** in ZLI-1275, or 5.01 wt% of **2** in ZLI-1275.

in its platelet texture. At the lower temperature, some crystallization occurs. Complex **2** gave rather high and temperature-dependent  $p$  values (measured on a 5.01 wt% mixture with ZLI-1275, the amount of **2** being limited by its low solubility), leading to estimated  $p$  values for pure **2** ranging from  $\approx 350$  nm at 76 °C to  $\approx 700$  nm at 40 °C. As previously reported for related systems,<sup>9</sup> this strong temperature dependence of  $p$  is possibly associated with the occurrence of two conformers in a temperature-dependent thermodynamic equilibrium.<sup>15</sup>

In summary, the mononuclear complex **1** shows a very low  $p$  value which is almost temperature independent, and a good solubility in a nematic matrix. Its enantiomer is easily available using the enantiomeric alcohol. These properties are very good

for its application as chiral dopant.<sup>16</sup> Furthermore, the glassy state of **1** allows the stabilization of a blue phase for several days. Further studies on these fascinating materials are in progress.

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