

New Columnar Metallomesogens Derived from 1,3,4-Oxadiazole

Beamline

17A X-ray Powder Diffraction beamline

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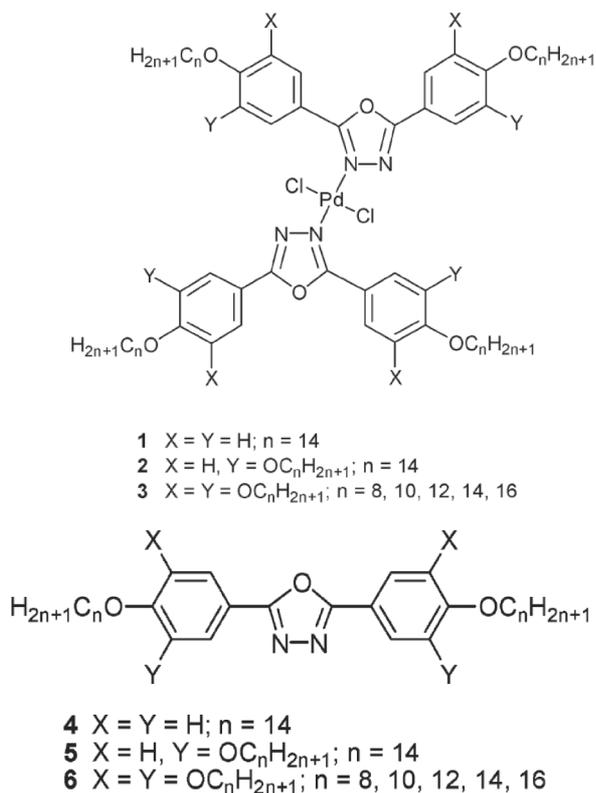
Three series of palladium(II) complexes 1-3 derived from 1,3,4-oxadiazoles exhibiting mesogenic properties are prepared and characterized. It was found that the formation of mesophases was sensitive to the number of alkoxy side chains. The compounds 3 appended with twelve side chains exhibited columnar (Col) phases, however, all other compounds 1-3 appended with four or eight side chains formed crystalline phases. Some derivatives ($n = 8, 10, 12$) of the series 3 were in fact mesogenic at room temperature. Powder XRD data indicated that the columnar mesophase varied from rectangular (Col_r) to hexagonal arrangements (Col_h) as the carbon chain length increases.

A new series of 1,3,4-oxadiazole-based compounds, 2,5-bis(3,4,5-trialkoxyphenyl)-1,3,4-oxadiazoles that exhibited hexagonal columnar phases (Col_h) were reported in our previous paper, and most of them were in fact room-temperature liquid crystals. On the other hand, the two heteroatoms such as N and O with free electron pairs on the five-member rings could provide active potential coordination site for metal ions. Nonmesogenic metal complexes such as Ag, Ru, or Cu were long known, however, mesogenic metal complexes derived from 1,3,4-oxadiazoles still remained unknown.

In this work, as part of our continuing research in metallomesogens we describe herein the preparation and mesomorphic studies of a new series of palladium(II) complexes derived from symmetric 1,3,4-oxadiazole core. These palladium(II) complexes exhibit columnar phases, and some of these compounds 3 ($n = 8, 10, 12$) are room temperature liquid crystals. To our knowledge, this is the first metal complex derived from 1,3,4-oxadiazole that exhibited columnar phases.

The mesophase observed for the derivatives $n = 8, 10, 12, 14$ was identified as rectangular columnar (Col_r) based on optical textures observed under the optical microscope. A mosaic texture with prominent wedge-shaped defect or leaf-plate like was easily observed under the polarized microscope. On the other hand, as the carbon chain length increased to higher homologue ($n = 16$) a hexagonal columnar phase (Col_h) was then observed. POM shows the typical optical textures of Col_r and Col_h phases by 3 ($n = 8$ and 16). This type of columnar mesophase changing from rectangular to hexagonal columnar phases as carbon chain length increased was occasionally observed in other discotic systems. A transition from a Col_r to Col_h superstructure resulted when the molecules projected an elliptical shape along the column's axis, and the molecules are generally tilted within the columns in such phase. Three types of symmetry of the Col_r phase are long known, $C(2/m)$, $P(2/a)$, and $P(21/b)$ depending on the structure of the molecules. The transition from a Col_r to Col_h phase was often accomplished with longer side chains. In

Scheme 1



some cases (Scheme 2), this type of Col_r → Col_h transition occurred when temperature was raised.

Variable-temperature powder XRD diffraction was also employed to confirm the structure of the columnar phases. A summary of the diffraction peaks and lattice for compounds **3** is listed in Table 1. For the derivatives with $n = 10, 12, 14$, two stronger and one weaker diffraction peaks at lower angle and one diffuse broad peak at wide-angle were typically observed. This type of diffraction pattern corresponded to rectangular columnar arrangement (Col_r), and these peaks are corresponding to Miller indices (200), (110), and (310). For example (Figure 1), the derivative **3** ($n = 10$) gave a diffraction of two strong reflections at d 25.64 Å and 18.59 Å, a weaker peak at 12.95 Å, and also a broad diffuse peak at 4.38 Å at 70°C. The two strong low-angle peaks are indexed as (200) and (110) and the third weaker peak at slightly higher angle is indexed as (310).

This diffraction corresponded to a rectangular lattice constants of $a = 51.28$ Å and $b = 19.95$ Å. This lattice might seem to be too long and thin and the disk might incline very steeply to avoid forming a columnar arrangement. A similar lattice constant was observed in other columnar systems. The possibility in forming a tetragonal columnar (Col_{tet}) structure was also considered and the spacing ratio of $1:(1/2)^{1/2}:1/2$ was used to fit all the diffraction peaks. However, the diffraction peaks were not well correlated as the carbon chain length increased (especially for derivatives $n = 12, 14$). Therefore, the structure of columnar phases was tentatively assigned as Col_r phases. The reflection d -spacings of all derivatives were also correlated well with increasing carbon chain length, i.e., 25.64 Å, 18.59 Å ($n = 10$); 27.44 Å, 20.49 Å ($n = 12$); 29.23 Å, 22.42 Å ($n = 14$).

However, the powder XRD diffraction pattern for derivatives $n = 16$ was apparently different, which was also consistent with the textures observed by optical microscope. A diffraction pattern of intense peaks at 54.93 Å, 31.69 Å, and 27.47 Å and a broad diffuse peak (4.57 Å) at wide-angle region was observed and this diffraction pattern corresponded to a hexagonal columnar arrangement. This pattern corresponds to an intercolumnar distance of 63.43 Å. In both Col_h and Col_r arrangements the absence of any distinct peak at higher angle (at $d = 3.3$ -3.5 Å) precluded the observed columnar structures (Col_{ho} or

Table 1: Powder XRD Diffraction Data of Palladium(II) Compounds **3**

compd	n	mesophase	temp (°C)	lattice spacing (Å)	d -Spacing obs. (calcd) (Å)	Miller indices
3	10	Col _r	70	$a = 51.28$ $b = 19.95$	25.64 (25.64)	(200)
					18.59 (18.59)	(110)
					12.95 (12.98)	(310)
					4.38 (br)	(halo)
	12	Col _r	70	$a = 54.88$ $b = 22.09$	27.44 (27.44)	(200)
					20.49 (20.49)	(110)
					14.05 (14.09)	(310)
					4.42 (br)	(halo)
	14	Col _r	70	$a = 58.46$ $b = 24.28$	29.23 (29.23)	(200)
					22.42 (22.42)	(110)
					15.14 (15.20)	(310)
					4.46 (br)	(halo)
16	Col _h	60		$a = 63.43$	54.93 (54.93)	(100)
					31.69 (31.71)	(110)
					27.47 (27.47)	(200)
					4.57 (br)	(halo)

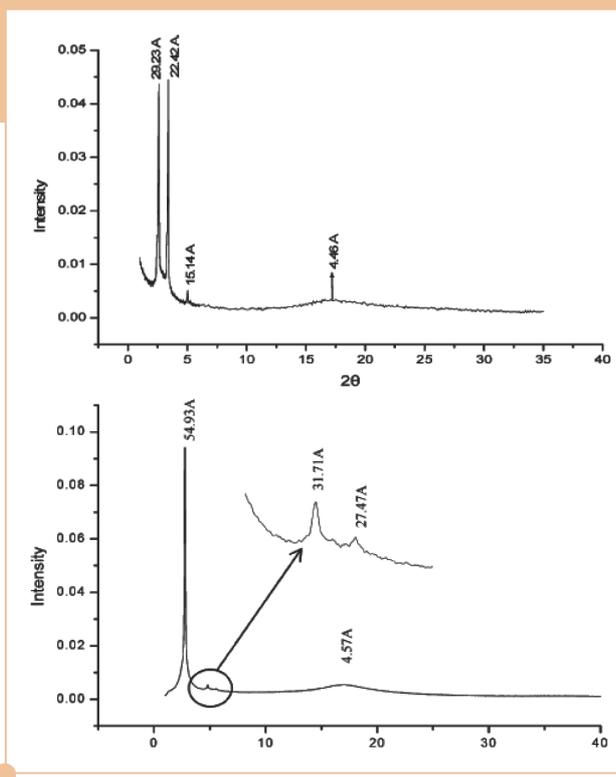
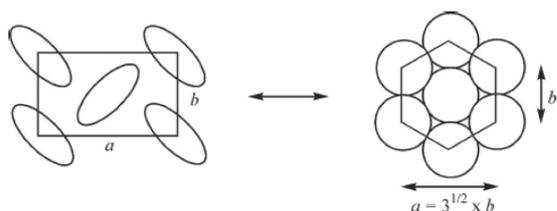


Fig. 1: X-ray diffraction data of the palladium compounds **3**: Col_r phase at 70°C ($n = 14$, top) and Col_h phase at 60°C ($n = 16$, bottom).

Col_o) from a more regular periodicity along the columns. These data were also quite consistent with the relatively small transition enthalpies of columnar-to-isotropic obtained by DSC analysis. A typical example of a diffraction pattern for Col_h ($n = 16$) and Col_r ($n = 14$) phases was depicted in Fig. 1. The pseudo-hexagonal lattice constant, which is a rectangular lattice with an axial ratio of an ideal hexagon of $3^{1/2}$ (as shown in Scheme 2) was also calculated, and this constant ranged from $a/b = 2.57$ (i.e., 51.28/19.95 for $n = 10$) to 2.41 ($n = 14$).

These values indicated that the structural departure from an ideal hexagonal lattice was roughly about 25.7-2.41%. On the other hand, the dependence of a/b value on side chain length also indicates a greater anisotropy or more elliptical exhibited by shorter side chains over longer side chains along the columnar axis.



Scheme 2: Correlation between Lattice Constants a and b Values in Col_h and Col_r Arrangements

Experimental Station

Powder XRD diffraction end station

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