Notiz / Note

Liquid-crystalline Compounds, 86[1]

The First Disc-Shaped Dinuclear Platinum Mesogen

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The cycloplatination of the tetrasubstituted imine **1** leads to the diplatinum organyl **3** as the main reaction product, which represents the first example of a new class of metallomesogens exhibiting monotropically a nematic-discotic phase. An X-ray crystal structure of this *anti*-isomer **3** has been performed. Furthermore, this platinomesogen also shows the induction of a hexagonal columnar mesophase (D_{ho}) on doping with 2,4,7-trinitrofluorenone as an electron acceptor. Compared to the analogous palladomesogen the two mesophases observed are more stable in the case of the platinum liquid crystal.

Although the first metal-containing thermotropic liquid crystals were already described in 1910[2], most of the manifold known examples have been synthesized and studied only in recent times[3-5]. The majority of these mesogens are conventional coordination compounds having metal-heteroatom bonds. However, a relatively small number of examples with at least one metal-carbon bond, so-called metalloorganyls, are also known[3-5]. In this latter group, in particular of the disc-shaped type[6-8], palladium is a perfect building unit because of its square-planar geometry of coordination. Thus, recently two disc-shaped series of liquid crystalline palladodiscogens containing two or even four palladium atoms have been obtained by *ortho*-palladation of multisubstituted aromatic imines or bisimines[6-8].

On the other hand, analogous cycloplatinations have neither widely been studied nor readily been accomplished. It has been proposed that the problems arising in *ortho*-platination reactions are at least partly attributed to the poor reactivity of platinum(II) salts compared to those of palladium(II), leading to slower reaction rates and poorer yields. However, these preparative problems have recently been reduced by the application of an allylchloroplatinum precursor[9].

Hence, in this paper we report on the synthesis, the X-ray molecular structure, and the mesomorphic properties of the first two platinum atom-containing disc-shaped liquid crystal.

Results and Discussion

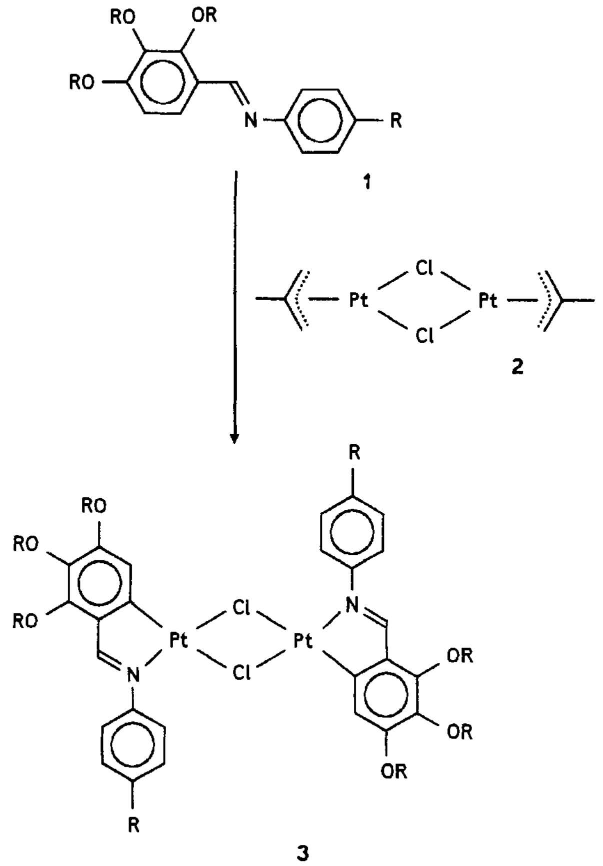
The known[6] imine **1** reacts smoothly under mild conditions with di-μ-chloro-bis[(η^3-2-methylallyl)platinum] (**2**)[10] with the formation of a liquid crystalline material containing the new chloro-bridged dinuclear platinum organyl **3** having eight flexible side chains (see Scheme 1)[11]. This product was characterized by ^{1}H-, ^{13}C-NMR spectroscopy, X-ray diffraction, and elemental analysis. In consequence of its ^{1}H-NMR data ($CDCl_3$ solutions) it is important to note that this platinum mesogen is assumed to be a mixture of two isomers (*syn* and *anti*) due to different orientations of the two ligands in the molecule, parallel or antiparallel to each other; attempts to separate the two isomers by TLC or column chromatography were unsuccessful because of decomposition processes. The ratio of the two isomers calculated from the intensity of two types of their proton signals is 83 (*anti*) to 17 (*syn*), see Experimental. Due to their positions in the molecular periphery of both isomers the chemical shifts of the N=CH protons are nearly identical (δ = 8.15 or 8.12). As expected, a really substantial difference does exist for the protons (δ = 6.64 or 6.46) of the two platinated phenyl rings, located in the inner region of the molecules of both isomers, caused by the shielding effect of the disubstituted phenyl ring on the opposite side of the mentioned aromatic protons in case of the *anti*-isomer **3**. The *syn*-isomer shows this effect in the up-field shift (see Experimental) of the protons of these two aromatic rings now facing each other.

Unfortunately, only small, weakly diffracting crystals of this material could be obtained of which the most suitable one was selected for a preliminary X-ray analysis[12]. The obtained result is shown in Figure 1. As this molecule possesses a center of inversion, its structure is centrosymmetric, i.e., the compound represents a dinuclear platinum dimer in *anti*-configuration as shown in **3**. Each platinum atom adopts a square-planar geometry, as expected for Pt^{2+}. The Pt–Cl bond lengths are different: Pt–Cl 245(2), Pt–Cl′ 228(2) pm, a result of the different *trans* influences of the phenyl carbon and nitrogen atoms of the imine ligands. The bond length Pt–C is 194(2) pm, vs. Pt–N 219(2) pm.

Investigations of this new platinum complex by polarizing microscopy and differential scanning calorimetry (DSC) show that it exhibits a monotropic nematic phase with the typical Schlieren texture (for the phase transition data see Scheme 1). Based on miscibility studies (contact method) with the analogous (also monotropically thermomesomorphic) dinuclear palladium complex[6], the mesophase of this chloro-bridged platinum liquid crystal was identified as nematic-discotic (N_D).

As expected, mesophase inductions by charge-transfer (CT) interaction found recently in various cases[6,7,13] were also observed in mixtures of this platinum mesogen with 2,4,7-trinitrofluorenone

Scheme 1



Cr 91.7°C {N$_D$ 54.4°C} Iso

1 and **3**: R = C_6H_{13}

(TNF) as an electron acceptor. Thus, contact preparations of it with TNF exhibit a highly viscous induced mesophase up to 195°C. On cooling from the isotropic liquid, droplets with linear defects as well as homeotropic star-shaped domains of a hexagonal symmetry appeared, developing into a mosaic texture similar to that one observed for the D_{ho} phase of TNF complexes of the dinuclear palladium analogue[7].

A comparison of the mesomorphic properties of the platinum liquid crystal with those of its palladium analogue[6,7] shows a stabilization of the N_D as well as of the charge-transfer induced D_{ho} phase by about 11 K in the case of the new platinum complex.

Comparative studies of the thermotropic and lyotropic properties of such pallado- and platinomesogens as a function of the electronic and space-filling influences of these metals or the number of substituents determining, in the latter case, the molecular shape of these metallomesogenes either to be calamitic[4] or discotic[6] are in progress.

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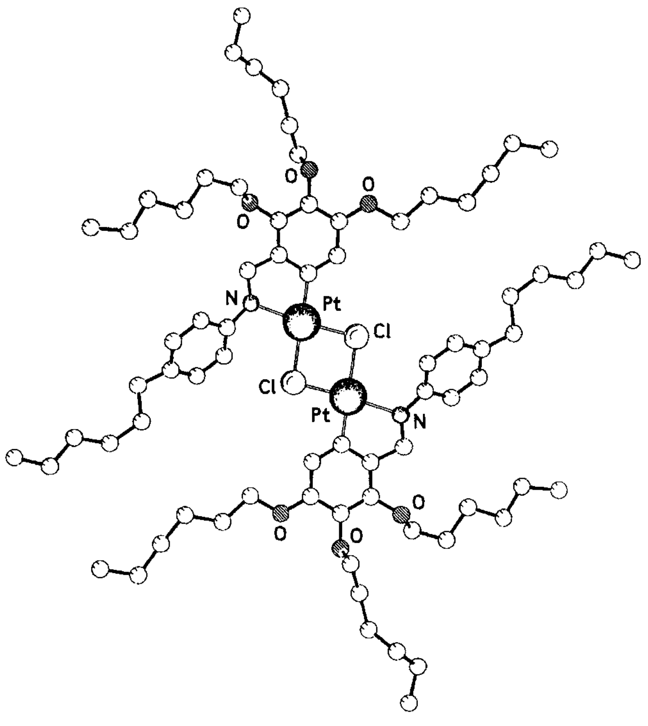

Figure 1. The crystal structure of **3**

Experimental

^1H, ^{13}C NMR: Bruker WH-400 or AM-270 spectrometer, $CDCl_3$ solutions; only structurally relevant resonances are given, see below. – Phase-transition data: Differential scanning calorimetry (Mettler TA 3000/DSC-30 S with a TA 72.5 software; heating rate 5 K/min or 10 K/min) and polarizing microscopy (Leitz Laborlux 12 Pol with a hot stage Mettler FP 82 or Linkam THMS 600; heating rate 5 K/min).

Di-μ-chlorobis[3,4,5-tris(hexyloxy)-2-{[(4-hexylphenyl)imino]-methyl}phenyl-C,N]diplatinum(II) (**3**): A solution of 2.05 mmol (1.16 g) of the imine **1**[6] in 10 ml of acetone was added under Ar to a suspension of 1.0 mmol (0.57 g) of **2** in 20 ml of dry methanol. After stirring the reaction mixture at room temp. for 25 d a yellow precipitate was filtered off. After washing with methanol, drying, and crystallization from methanol/acetone a product containing >83% (based on the following ^1H-NMR data) of **3** was isolated as orange air-stable crystals; yield: 0.29 g (18%). Its yield is poorer (11%) if the reaction is carried out by stirring the mixture at 50°C for 16 h. The phase-transition temperatures of this product are included in Scheme 1; the data in { } indicate a monotropic transition. – ^1H NMR: δ = 8.15, 8.12 [2 s, ratio 1 (*anti*):0.2 (*syn*); HC=N], 7.29, 7.18 as well as ≈7.18, ≈7.08 (2 × 2 d, J = 8 Hz each; arom. Hs of the disubstituted rings), 6.64, 6.46 [2 s, ratio 0.2 (*syn*):1 (*anti*); arom. Hs of the platinated rings], 4.12, 3.96, 3.85 (3 t, J = 6.5 Hz each; 3 types of OCH_2), 2.62 (t, J = 8 Hz; aryl-CH_2). – ^{13}C NMR: δ = 172.52 (d; 2 HC=N), 157.25, 152.89, 146.70, 142.56, 136.63, 134.96, 131.12 (7 s; 14 arom. Cs), 128.48, 123.59, 110.20 (3 d; 4, 4, and 2 arom. CH situations), 74.52, 73.45, 68.55, 35.60 (4 t; 8 α-CH_2). – $C_{74}H_{116}Cl_2N_2O_6Pt_2$

(1590.8): calcd. C 55.87, H 7.35, N 1.76; found C 55.85, H 7.21, N 1.81.

Crystallographic Data of **3**: Formula $C_{74}H_{116}Cl_2N_2O_6Pt_2$, molecular mass 1590.8 g/mol; suitable crystals were obtained from a methanol/acetone solution; the lattice constant determination and intensity measurement were performed at room temperature by using a Syntex $P2_1$ diffractometer (Mo-K_α radiation, graphite monochromator); crystal system triclinic, space group $P\bar{1}$ (no. 2) with lattice constants a = 981.3(7), b = 989.2(8), c = 2082.4(24) pm, α = 90.15(8), β = 101.13(8), and γ = 99.86(9)°, with Z = 1 molecule per unit cell, $V = 1952.7 \cdot 10^{-30}$ m^3, ρ_{calc} = 1.35 gcm^{-3}; 6636 intensities were measured with $2\Theta \leq 50°$, but only 1880 intensities with $F_o \geq 4\sigma(F_o)$ were obtained and used for the structure determination and refinement; the data were corrected for Lorentz and polarization effects, an empirical absorption correction (DIFABS) was applied; the Pt and Cl atoms could be located by the Patterson method using SHELXS-86, the localization of the C, O, and N atoms from difference Fourier maps and refinement were performed with SHELX-76 and SHELXL-93. The hexyl chains show a severe disorder; therefore, the strongest peaks in the difference maps corresponding to possible C positions were chosen and bond length constraints of 154 pm for C–C bonds of the chains were applied. Pt and Cl were refined anisotropically, all other atoms isotropically. The refinement converged at an R value of 0.213, probably a consequence of the disorder of the hexyl chains, which is also reflected in rather high temperature factors of the C atoms under consideration.

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[11] In this connection we are very grateful to Professor *P. Espinet*, Institute of Inorganic Chemistry, Universidad de Valladolid, E-47005 Valladolid, Spain, for his kind and helpful private information (June 1993) about his experience on the *ortho*-platination reaction of other arylimines.

[12] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-400846, the names of the authors, and the journal citation.

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