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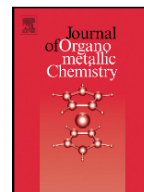
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Comparative analysis of self-aggregation of liquid crystalline Pt(II) complexes in solution and in neat films

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ABSTRACT

Two novel cycloplatinated complexes that differ by the presence/absence of a lateral fused cyclopenteno ring, respectively, were prepared. Although contributing to only a few percentage of the whole molecular volume, the presence of this aliphatic protuberance appears to be essential for the emergence of liquid crystalline behaviour. The pair of two similar compounds, non-mesomorphic complex **5** and mesomorphic complex **6**. Was prepared as a model to assess the possible link of the self-aggregation in solution with the appearance of the liquid crystallinity in molten state. NMR dilution studies in CDCl₃ solution and X-ray diffusion study in neat films show qualitative similarity of the aggregated structures formed by liquid crystalline complex. Solution studies may therefore be a useful additional tool to the characterization of the liquid crystalline properties and other self-association processes of Pt(II) complexes.

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1. Introduction

Cycloplatinated Pt(II) complexes that display liquid crystalline behaviour have attracted much attention in materials chemistry [1]. Such complexes are often phosphorescent and can be used to fabricate organic light-emitting diodes with improved charge mobilities and polarised emission [2]. The square-planar geometry of the Pt complexes is somewhat similar to traditionally used planar cores found in purely organic liquid crystals and not surprisingly, similar design strategies have been used to induce liquid crystalline properties. Usually, several aliphatic chains are attached to the complex to achieve the appropriate disk-like or rod-like geometries compatible with the emergence of one particular mesophase. Following this basic design, liquid crystal properties were successfully induced in bidentate [3], terdentate [4] and tetradentate [5] cyclometallated Pt(II) complexes.

Apart from the liquid crystal properties, it is known that cycloplatinated complexes display apparent tendency to aggregation (self-association) in solution. The self-association is considered as pre-requisite to formation of ordered structures on transition to liquid crystal phase.

Moreover, the self-association/aggregation of liquid crystalline Pt(II) complexes can go beyond the molten state of the mesophase and the same molecules can effectively interact in solution. Self-association in solution can be of interest to a variety of applications from chemical sensors to the design of supramolecular gel-like structures and lyotropic liquid crystals [6]. However, the solution behaviour of thermotropic liquid crystals is rarely investigated [7]. In this paper we compare the self-association properties of two novel cyclometallated Pt(II) complexes in molten state and in solution in order to assess if the solution studies can be useful in understanding the self-organisation behaviour in the bulk of the molten state (Scheme 1).

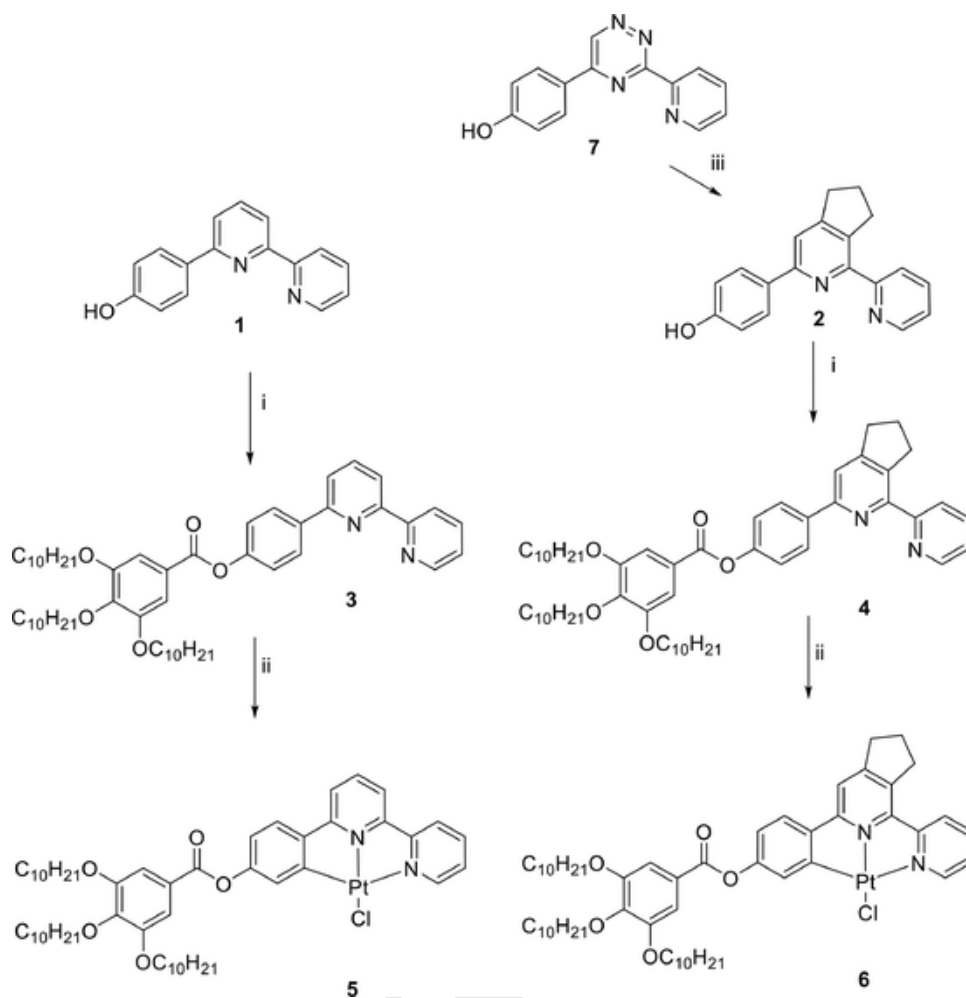
2. Results and discussion

2.1. Synthesis

In search for a good model for our studies we were interested in identifying a pair of none mesomorphic and mesomorphic Pt(II) complexes that are structurally similar. We therefore prepared complexes **5** and **6** that differ only by the small cyclopenteno fragment. It has been shown previously that the introduction of the cyclopenteno fragment is an effective way to modify or even induce liquid crystallinity in Pt(II) complexes [4b,8]. In order to do this, we used the synthetic methodology involving 1,2,4-triazines that are often used in the synthesis of polypyridine ligands and their cyclometallated analogues. In our recent

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Scheme 1. Synthesis of the cycloplatinated complexes 5 and 6. Reaction conditions: (i) 3,4,5-tri(decyloxy)benzoic acid, DCC, DMAP, DCM, RT; (ii) K₂PtCl₄, AcOH, reflux, 24-45h; (iii) 1-morpholinocyclopentene, neat, 150°C, 15 min.

study, we described the synthesis of the phenolic compounds 1 and 2 without and with the fused cyclopentene unit [9]. 4-methoxyphenyl glyoxal was used as a starting material therefore the last step was demethylation in molten pyridinium chloride. Alternatively, the phenol 2 can be prepared from known triazine 7 [10]. Indeed, despite the electron rich nature of 4-hydroxyphenyl substituent, the triazine 7 can still be used in inverse electron demand Diels-Alder reaction with 1-morpholinocyclopentene and gave phenol 2 in good yield. In order to further promote mesomorphism, the phenols 1 and 2 were coupled with the strongly lipophilic gallic derivative, 3,4,5-tri(decyloxy)benzoic acid, under standard conditions to give bipyridine-containing proligands 3 and 4, respectively. Pt(II) complexes were then obtained by the reaction of the ligands with potassium tetrachloroplatinate in boiling acetic acid. The target complexes 5 and 6 were characterised by ¹H, ¹³C NMR spectroscopy, mass spectrometry and elemental analysis. It should be noted, that in this study we did not aim to prepare novel luminescent materials but rather concentrate our attention on self-organisation behaviour in solution and the molten state.

2.2. Self-organization properties in pure films

Mesomorphous structures generally form in the molten state for molecules with incompatible segments nano-segregating into juxtaposed domains [11]. The type and range of the mesophases are primarily ruled by the natural sections of the segments on both sides of the interface, but also depend on domain widths and thus on segment sizes

[12]. These antagonistic parts are constituted by both the Pt-complexes and the aliphatic chains, lengthened by the gallate segment. Despite its amphipathic structure [11], compound 5 is surprisingly not mesomorphous and was found to melt directly in the isotropic liquid at 158°C. However, the homologous complex with the cyclopenteno protuberance exhibits mesomorphic behavior. The characterizations by DSC (Differential Scanning Calorimetry) and S/WAXS (Small/Wide-Angle X-ray Scattering) demonstrated different types of crystalline and mesomorphous self-organizations, whereas POM (Polarized Optical Microscopy) technique was not very helpful in the phase identification. Complex 6 did not develop any precise optical texture nor any textural change could be detected upon either heating or cooling; the sample melts into the isotropic liquid at ca. 245°C. TGA thermogram (Fig. S1) shows no weight loss below the isotropization, suggesting that the sample is stable over the entire studied temperature range. DSC reveals several thermal events on heating at respectively ca 120, 210°C and 245°C (Fig. S2). The absence of transition temperature delay on cooling (at ca. 243°C) also supports the good thermal stability of 6, and the perfectly reversible isotropization temperature and small enthalpy are in agreement with the emergence of a liquid crystalline phase. At lower temperatures, the large energetic events typically correspond to transitions to crystalline and/or highly ordered phases. Another small phase transition was detected by DSC on cooling (183-164°C) between the mesophase and the high-temperature ordered phase, but this monotropic phase could not be further investigated due its kinetical nature. The room temperature phase is expectedly crystalline and the

lamellar phase between 120 and 210°C is another crystalline phase with either structural disorder or with 3D long-range order (Fig. S3).

Apart from the series of sharp reflections (00l) of a lamellar phase (with a layer spacing $d \approx 35.4 \text{ \AA}$ at 212°C, Fig. 1), the S/WAXS pattern in the mesophase also contains broad scattering signals from local-range interactions: the large diffusion with a maximum at $h_{ch} \approx 4.5 \text{ \AA}$ from the undifferentiated contribution of the lateral distances between molten chains and of the gallate extenders, h_{gal} , along with the sharper signal $h_{\pi} = 3.5\text{-}3.6 \text{ \AA}$ from face-to-face piling of complexes, and the mid-angle scattering $D \approx 11 \text{ \AA}$ from lateral distances between piles. The mesophase could be thus assigned to as a smectic-like phase, with some local-range of columnar order (h_{π}), as encountered in sanidic compounds [13].

The molecular volume of **6** at 212°C, $V_{mol} = 1550 \pm 30 \text{ \AA}^3$ ($\rho \approx 1.17 \text{ g}\cdot\text{cm}^{-3}$, as calculated from database of volumetric measurements and from single-crystal structures [14]), divided by the lamellar periodicity, d (see above), provides access to the molecular area $A_{mol} = V_{mol}/d = 43\text{-}45 \text{ \AA}^2$. This value almost coincides with the cross-sectional area of the complex obtained from the product $h_{\pi} \times D$ ($\sigma_{\pi} = 40 \pm 2.5 \text{ \AA}^2$) and confirms that both the piling of the complexes

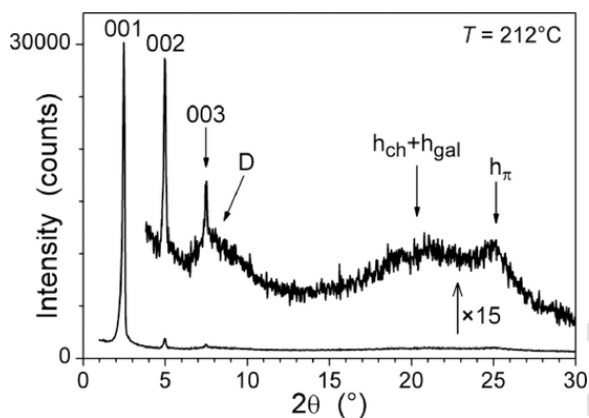


Fig. 1. SAXS patterns of compound **6** at 212°C in the smectic phase.

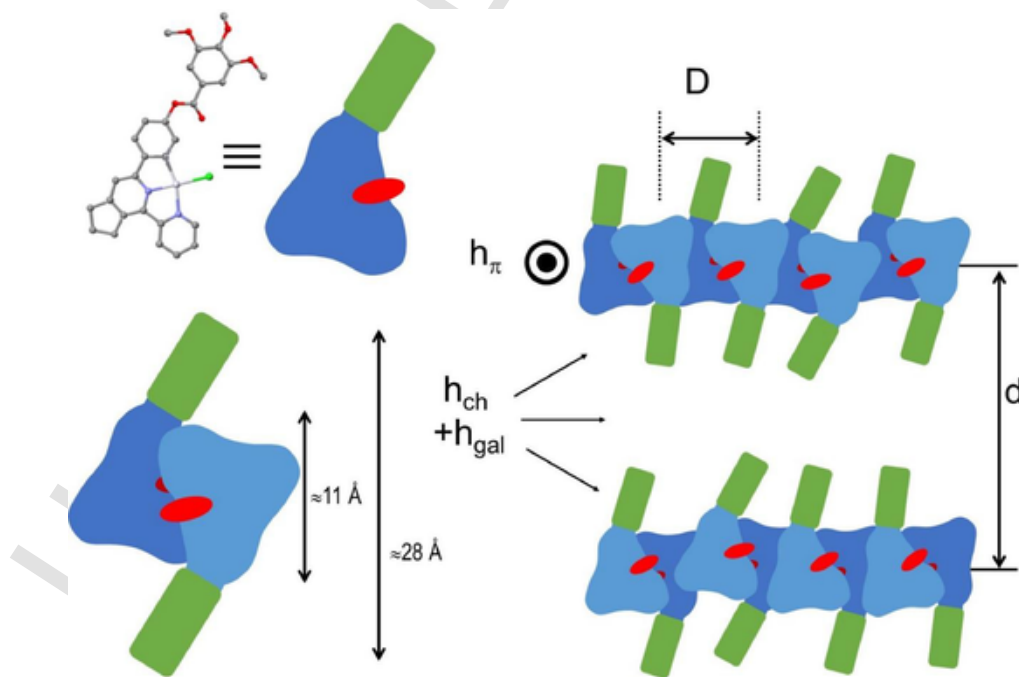


Fig. 2. Model of the supramolecular organization in the smectic-like mesophase of compound **6**. (d , D , h_{π} , h_{ch} , and h_{gal} are defined in the text). Aliphatic chains are not shown for clarity. Molecular model reconstructed from the Cambridge Structural Database [14].

into strips and the lateral-association of the strips into monolayers determine the lateral extension of the lamellae. The self-assembling process rejects the gallate extenders on both sides of the monolayer, with the effect of sharing the bulky tails (of overall cross-sectional area: $3\sigma_{ch} = 73 \text{ \AA}^2 > A_{mol}$) between the two adjacent aliphatic layers (Fig. 2).

The lamellar structure at high temperature persists thanks to the strong interactions between piled complexes, very likely through the metal-chloride or metal-metal interactions (Fig. 2) [3,4,14], but unlike the archetypal calamitic materials, the introduction of nano-segregating alkyl tails leads here only to purely crystalline complex **5**. A smectic-like phase is obtained for **6**, presumably because the insertion of its fused cyclopenteno ring between piled complexes perturbs their lateral arrangement and causes melting to a fluid monolayer of loosely assembled strips. The main effect of extending the complex moiety is therefore the thickening of their layers that theoretically delays the vanishing of the overall supramolecular structures.

2.3. NMR dilution studies

NMR dilution study is a well-established method to explore intermolecular interactions in solutions. Typical experiments compare NMR spectra of solutions of different concentrations and the change in chemical shifts of protons, or in fact ^{195}Pt [9], provides information on the magnitude and the architecture of the bonding within the aggregates of Pt(II) complexes [15]. Figs. 3 and 4 show ^1H NMR spectra and ^{195}Pt chemical shifts of compound **6** at different concentrations, respectively. It can be seen that the aromatic protons (which are magnetic atoms directly attached to rigid aromatic chromophore and marked by letter in Fig. 3) experience upfield shift on concentration raise, whereas the signals of the aliphatic protons are hardly affected by concentration changes. The ^{195}Pt signals, instead, exert downfield shift. Such pattern is typical of the formation of aromatic stacking-type aggregates in solution and has previously been observed for wide range of aromatic molecules [16], including the Pt(II)-containing complexes [9,17]. It originates from the ring-current effect induced by static mag-

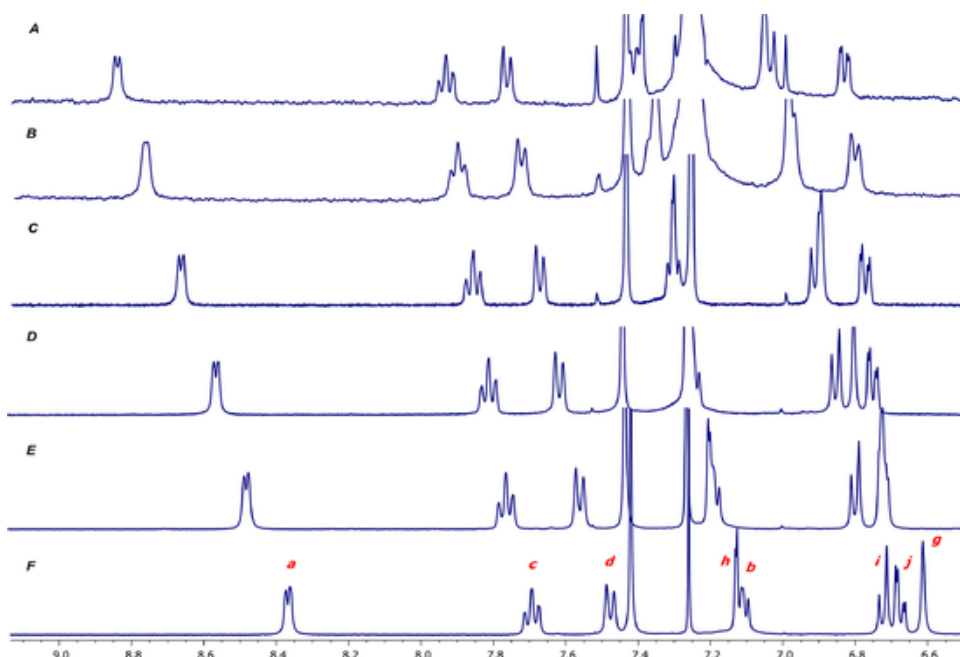


Fig. 3. ^1H NMR spectra of complex **6** in CDCl_3 at concentrations $0.52 \cdot 10^{-3}$ M (A), $1.17 \cdot 10^{-3}$ M (B), $3.12 \cdot 10^{-3}$ M (C), $8.31 \cdot 10^{-3}$ M (D), $15.24 \cdot 10^{-3}$ M (E), $30.48 \cdot 10^{-3}$ M (F).

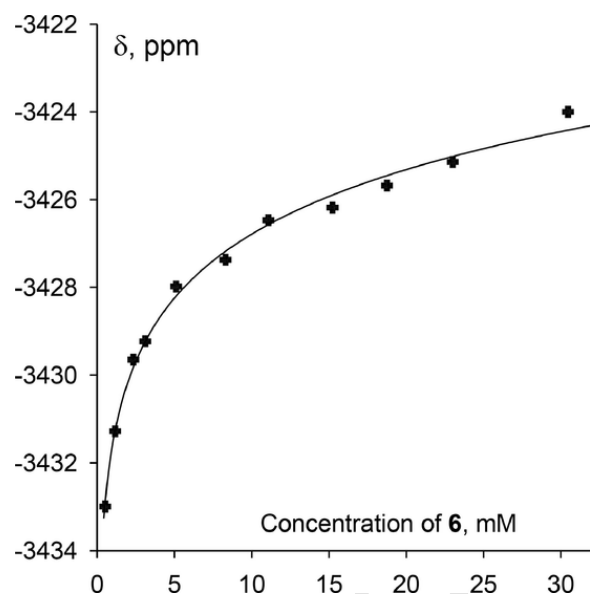


Fig. 4. Experimental concentration dependence of ^{195}Pt NMR chemical shifts of complex **6** in CDCl_3 .

netic field of NMR spectrometer affecting specifically the aromatic protons to larger extent. The systematic upfield shift of aromatic protons and downfield field of the platinum nucleus was noted for both complexes. Comparison of this data with the results reported in previous section enables to conclude that the type of ordered assemblies formed by Pt(II) complexes in solution and crystal phases shares some similarities. Moreover, the distance, $h_\pi = 3.5\text{--}3.6 \text{ \AA}$, between the faces of neighbouring molecules in the mesomorphous state deduced from the SAXS data, matches the interplanar distance, $d_\pi = 3.4 \text{ \AA}$, known for the typical flat heterocyclic molecules which form π -stacked dimers in solution [16].

Considering the observed upfield shift as an apparent indication of the self-association of the studied compounds, this feature of aromatic protons was further used to quantify the aggregation process.

The influence of concentration on signals of aromatic protons of compound **6** is outlined in Fig. 3 (the corresponding spectra for compound **5** are given in supplementary information, Fig. S4). The examples of full ^1H NMR spectra of **5**, **6** covering the aromatic and aliphatic regions, are given in Figs. S5 and S6). Although the concentration range used is relatively wide (two orders of magnitude of variation), the titration curves (Fig. S7), nevertheless, do not feature saturation (i.e. leveling off the asymptotic horizontal line), which could be expected if the aggregation would be limited by simple dimerization. Hence, the aggregation beyond the dimer phase cannot be neglected *a priori*. Because of that, in the present work we used two standard models of indefinite aggregation, viz. the isodesmic equilibrium constant model (the EK-model), assuming equal equilibrium constant K at each stage of the aggregation, and nucleation model, assuming that the dimerization occurs with a constant $K_2 = \sigma K$ different from all the further aggregation stages proceeding with equal $K_i = K$. The description of these models and their application to numerical analysis of the NMR titration data is given in supplementary information. The results of computations of the aggregation parameters are given in Table 1.

For all aromatic protons of both complexes, the induced averaged shielding in dimer, $\langle \Delta\delta_d \rangle$, is equal to ca. $0.19\text{--}0.25$ ppm on average. This value well matches the typical NMR shielding observed before for various aromatic compounds aggregating in the form of π -stacked aggregates [16], including that of aromatic Pt(II) complex in chloroform reported previously [9]. The distribution of $\Delta\delta_d$ over aromatic protons is rather similar for the two compounds, indicating the similarity of the structures of aggregates being formed in solution. The effect of side chains is displayed in the value of the cooperativity parameter, σ (see Table 1). The calculated value $\sigma \approx 2$ for **5** and **6** evidences that the formation of aggregates larger than dimers is disfavoured due to steric hindrance. Moreover, the observed effect of steric hindrance should lead to antiparallel packing of molecules in aggregates with the gallate rings sticking in opposite directions. This conclusion is partly supported by the fact that the gallate protons of **5** and **6** do not experience shielding/deshielding on titration, because these moieties fall out of the volume of aggregate. Such antiparallel orientation is the most typical case observed in solution for flat heterocyclic

Table 1
Calculated parameters of 5, 6 aggregation in CDCl₃.

Nucleus	a	b	c	d	e	f	g	h	i	j
Complex 5										
δ_m , ppm	9.14	7.72	8.06	7.90	7.55	7.84	7.47	7.54	7.44	7.00
δ_d , ppm	8.79	7.52	7.94	7.80	7.46	7.70	7.23	7.31	7.20	6.86
$\Delta\delta_d$, ppm	0.35	0.20	0.12	0.10	0.09	0.14	0.24	0.23	0.24	0.14
EK-model	$K = 865 \pm 435 \text{ M}^{-1}$						$\langle \Delta\delta_d \rangle = 0.19 \text{ ppm}$			
Nucleation model	$K = 450 \pm 220 \text{ M}^{-1}$						$\sigma = 1.9 \pm 0.7$			
Complex 6										
δ_m , ppm	8.87	7.42	7.95	7.77			7.06	7.42	6.96	6.84
δ_d , ppm	8.48	7.16	7.72	7.50			6.76	7.16	6.82	6.70
$\Delta\delta_d$, ppm	0.39	0.26	0.23	0.27			0.30	0.26	0.14	0.14
EK-model	$K = 127 \pm 45 \text{ M}^{-1}$						$\langle \Delta\delta_d \rangle = 0.25 \text{ ppm}$			
Nucleation model	$K = 69 \pm 22 \text{ M}^{-1}$						$\sigma = 2.0 \pm 0.5$			

Note. Parameters δ_m , δ_d , $\Delta\delta = \delta_m - \delta_d$, K are derived from the EK-model.

molecules [16], and was previously reported for Pt(II) complexes as well [9]. It well agrees with the model of ordered structures formed by Pt(II) complexes in liquid crystal phase deduced from SAXS data and depicted in Fig. 2. It suggests that the self-association in solution phase may in principle be used as an instrument to characterise the mutual orientation of Pt complexes in liquid crystal phase.

The calculated values of K in Table 1 can be related to upper range of typical values of aggregation constants in chloroform, i.e. $K \sim 1 \dots 100 \text{ M}^{-1}$ [9,18] and reveal the high strength of aggregation. Complex 5 showed higher aggregation affinity in solution than 6. In chloroform the aggregation is primarily driven by van der Waals interactions between aromatic moieties; however, the solvent significantly influences the magnitude of interaction. Therefore, the balance of physical forces stabilizing ordered structures in pure films and in solution is likely to be different, thus making the existence of such correlation not necessarily meaningful. Nevertheless, as shown above, the geometric features of ordered structures formed by the studied Pt(II) complexes in solution and crystal phases have much in common.

As it follows from Table 1, the aliphatic fused cyclopentane ring in 6 obviously influences the behaviour in solution in a similar way as the alkyl side-chains introduced in molecules or polymers with π -stacking units [19]. These substituents are indeed used to improve the solubility in certain solvents, among which chloroform, with the effect of an early dissociation of the aggregates and dispersion of the isolated molecules. The increased solubility in presence of cyclopentane is thus here indicated by the lowering of K as compared with 5.

3. Conclusions

Somewhat unconventional approach of annealing cyclopenteno fragments was used to induce liquid crystallinity in terdentate cyclometalated Pt(II) complexes of C^NN type. Complex 6 shows a stable smectic mesophase with a lamello-columnar character while complex 5 is not mesomorphic. Annealing of aliphatic rings through the use of 1,2,4-triazine chemistry is likely to be applicable to induce mesomorphism in other Pt(II) complexes. Comparison of structural data shows that the embryonic arrangement of the molecules in the aggregates in solution shows common features to the ordered structures in the liquid crystal phase. Therefore, a simple, non-distractive analysis of self-aggregation in solution is likely to be useful tool in predicting and understanding the behaviour of Pt(II) complexes in mesomorphic states.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorgchem.2021.121750.

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