www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 620 (2001) 249–255

Thiocyanato-bridged platinum heterocycles: structure and properties of disc-like metallomesogens☆

Belkız Bilgin Eran [a],*, Dirk Singer [b], Joachim Pickardt [c], Klaus Praefcke [d]

[a] Department of Chemistry, Yıldız Teknik Üniversitesi, TR-34210 Istanbul, Turkey
[b] Department of Chemistry, Howard University, Washington, DC 20059, USA
[c] Faculty of Chemistry, Technische Universität Berlin, D-10623 Berlin, Germany
[d] Technische Universität Berlin, J4, D-10623 Berlin, Germany

Received 7 June 2000; received in revised form 16 October 2000

Abstract

The synthesis and liquid crystalline properties of novel disc-like di- and tetra-platinum organyls have been described recently. Here, the synthesis and mesomorphic properties of the first thiocyanato-bridged, sheet-shaped di- and tetra-platinum complexes are described. Structural features of these sheet-shaped thiocyanato-bridged di- and tetra-platinum organyls based on various methods (e.g. ^{1}H-, ^{13}C-, ^{195}Pt-NMR) are discussed and related to the mesomorphic properties of these compounds. In addition, the molecular structure of a new thiocyanato-bridged diplatinum organyl carrying eight hexyl chains has been elucidated by single crystal X-ray diffraction analysis. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cycloplatination; Liquid crystals; Metallomesogens; Thiocyanato-bridged platinum organyls; X-ray structure analysis

1. Introduction

Cyclometallated compounds have been a particularly fertile area of research in recent times, with many different examples from different groups, especially within the field of liquid crystals [1]. Palladium(II) and platinum(II) complexes of this type are stable in air, of sufficient thermal stability, and allow the design and realization of unusual molecular geometries owing to the square-planar coordination of these metals.

H-shaped mesogenic dinuclear ortho-metallated palladium(II) complexes, mainly derived from aromatic Schiff bases or azines, first attracted attention and were shown to form nematic and smectic phases [1]. More recently, our group has shown that just by increasing the number of peripheral aliphatic chains to eight such dinuclear palladium organyls have a more elliptical or sheet-like shape, resulting in the formation of the nematic-discotic (N_D) type of mesophase [2]. Moreover, tetranuclear palladium(II) complexes derived from ortho-palladated Schiff bases of *p*-phenylene diamine carrying 12 peripheral chains form columnar $Col_{ob,d}$ mesophases with an oblique two-dimensional arrangement of the columns and a highly disordered intracolumnar stacking [2–4].

In principle, structurally related halogeno-bridged platinum organyls [5,6] show the same mesomorphic behavior as their palladium analogues. In particular, dinuclear platinum complexes with halogeno bridges and eight aliphatic chains form, if any, the N_D type of mesophase, whereas the tetranuclear platinum organyls with 12 peripheral chains exhibit $Col_{ob,d}$ mesophases.

Here, the synthesis and characterization of the mesogenic properties of the first thiocyanato-bridged ortho-platinated compounds **1**–**4**, derived from imines and bisimines, are described.

2. Results and discussion

The thiocyanato bridged platinum organyls **1**–**4** were prepared from their chloro-bridged analogues [5–7] by

---

☆ This paper is number 127 on liquid-crystalline compounds of the Berlin Research Group; paper 126: B. Bilgin Eran, D. Singer, K. Praefcke, J. Inorg. Chem. in press.

* Corresponding author. Tel.: +90-212-4491750; fax: +90-212-4491514.

E-mail address: bilgin@yildiz.edu.tr (B. Bilgin Eran).

0022-328X/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(00)00782-8

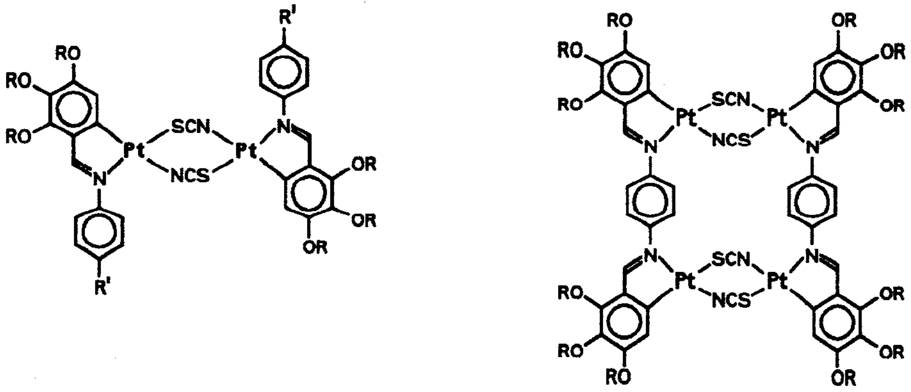
simple exchange reactions with potassium thiocyanate in dichloromethane–acetone under argon at room temperature (see Section 4).

The new compounds presented here were characterized by various spectroscopic methods, e.g. ^{1}H-, ^{13}C-NMR, IR, and (in part) also ^{195}Pt-NMR ($CDCl_3$). The proposed structures are in full agreement with these spectroscopic data and with elemental analyses. In addition, for the dinuclear thiocyanato-bridged platinum organyl **2** the molecular structure was determined by single crystal X-ray diffraction.

The ^{1}H- and ^{13}C-NMR data for the platinum organyls **1**–**4** are similar to those of the analogous multinuclear platinum(II) complexes with halogeno bridges [5–7] (Fig. 1). In particular, the $\delta(^{195}Pt)$ value of -3599.5 ppm for the methoxy-substituted compound **1** is well within the range expected for organoplatinum(II) compounds with ortho-metallated nitrogen donor ligands [6–8].

In principle, for dinuclear ortho-metallated palladium and platinum complexes of the type investigated here, two isomers are possible based on the parallel or anti-parallel orientation of the two imine ligands to each other. In addition, asymmetric bridging groups like the SCN-moieties used here can introduce further isomerism: these bridging groups can be oriented parallel or anti-parallel to each other. In addition, in the case of anti-parallel orientations of both the ligands and SCN bridging group, two isomeric forms of the square-planar coordination sphere of the platinum atoms can be distinguished: one in which the sulfur atoms are trans to the imine nitrogen atoms and one in which they are trans to the coordinating carbon atom. Unlike the analogous halogeno-bridged dipalladium organyls [2], which show no isomerism, the previously described dinuclear halogeno-bridged platinum organyls [5,7] exist as mixtures (17:83) of the isomers with parallel (syn) and anti-parallel (anti) orientation of their imine ligands; attempts to separate these two isomers were unsuccessful. The ^{1}H-NMR spectra of the thiocyanato-bridged dinuclear platinum organyls **1** and **2**, however, show neither the syn/anti isomerism of their previously described halogeno-bridged diplatinum analogues [5,7], nor isomerism resulting from *parallel* or *anti-parallel* orientation of the thiocyanato bridging groups to each other, as observed for sheet-like and calamitic thiocyanato-bridged dipalladium organyls [2,9]. Even more important, the X-ray single crystal structure analysis of the new platinum organyl **2**, having eight flexible hexyl chains, shows clearly the anti-parallel orientation of the thiocyanato bridging groups. The sulfur atoms of the thiocyanato bridges are trans to the imine nitrogen atoms of the two ligands.

Crystals suitable for X-ray analysis were grown by slow evaporation of a solution of **2** in methanol–acetone. The platinum compound **2** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$ molecule per unit cell. Fig. 2 shows a DIAMOND [10] plot of the molecule. The molecule is centrosymmetric; its inversion center lies on an inversion center of the unit cell. The carbon chains exhibit a slightly increasing distortion at the periphery. The non-bonding Pt–Pt distance is 564.0(2) pm. The thiocyanato groups act as μ_2 bridging ligands. The 'core' is almost planar, only the ring C9···C14 is turned out of the plane of the molecular core by approximately 49°. The bridging thiocyanato group forces the molecule into a completely coplanar geometry of the two square-planar platinum centers. The Pt–C distance, at 199. (5) pm, is slightly larger than that in the analogous chloro-bridged platinum organyl



1, 2

3, 4

1: R = CH_3, R′ = C_6H_{13}, **2**: R = R′ = C_6H_{13}

3: R = C_6H_{13}, **4**: R = $C_{12}H_{25}$

Fig. 1. Structural formulas of the new multi-nuclear platinum organyls **1**–**4** showing their thiocyanato bridges in anti-parallel arrangement; see discussion (Section 2) about the NMR spectra of the macrocycles **3** and **4**.

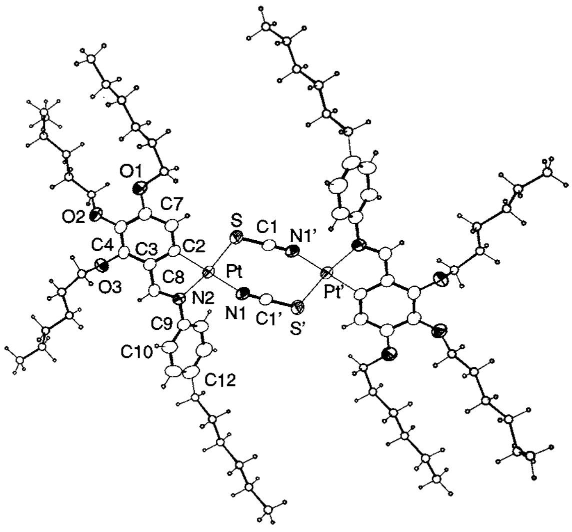


Fig. 2. Crystal structure of **2**. For clarity the carbon atoms of the side chains are represented by open circles with an arbitrary radius, as the outer C atoms have increasing and comparatively large thermal parameters. See Table 3 concerning the symmetry code for equivalent atoms.

[5]. Relevant X-ray data of the structure analysis of **2** are given in Tables 1–3.

The ^{1}H-NMR spectra of the thiocyanato-bridged tetraplatinum organyls **3** and **4** show no isomerism. Based on the NMR data, see Section 4, two isomers are possible. The first isomer is centrosymmetric, as depicted in Fig. 2, with an antiparallel orientation not only of the two SCN bridges within each $Pt(SCN)_2Pt$ unit, but also of those moieties to each other. In the second isomer the two $Pt(SCN)_2Pt$ substructures are parallel to each other and, therefore, only a C2 axis exists. However, which one of these conceivable antiparallel thiocyanato-bridged isomers has been formed in the ortho-metallation reaction cannot be deduced from these NMR data. The only way to elucidate this problem is a single crystal X-ray analysis of these two dimeric macrocyclic molecules. Unfortunately, this possibility is hampered by the unsatisfactory crystallization of both compounds.

In contrast to their palladium analogues [2], the thiocyanato-bridged dinuclear compounds **1** and **2** show *no* liquid crystalline behavior; no mesophase could be detected even with a cooling rate as high as 100 K min^{-1}. In general, the effect of the metal atom (Pd or Pt) on the mesomorphism of such dinuclear metal organyls is usually small. Thus, a possible reason for the non-existence of a liquid crystalline phase could be that the di-platinum organyl **2**, in contrast to the palladium analogue, does not exist as an isomeric mixture. However, the melting temperature of **2** is also about 10 K lower than that of the analogue palladium complex, cf. Table 4 and Ref. [2]. In N_D phases no strong attractive interactions exist between the mesogen molecules; specifically, there are no significant attractive interactions perpendicular to the molecular plane. Therefore, the formation of this type of mesophase is very sensitive to small changes in the interaction profile of the constituent molecules. Here, either a small difference in the electron density distribution resulting from the replacement of palladium with platinum or lack of a second isomer with a different interaction profile suppresses the formation of an N_D phase.

However, the dinuclear platinum organyl **2** shows induced/stabilized mesomorphism with the strong electron acceptor 2,4,7-trinitro-fluorenone (TNF). Contact mixtures of the non-liquid-crystalline thiocyanato-bridged complex **2** with TNF shows a fluid mesophase with Schlieren texture and visible thermal fluctuations typical for a nematic phase. The maximum of the clearing temperature is 98°C, which is 14°C lower than that of the charge transfer complex of the corresponding palladium compound with TNF [11a]. Thus, the

Table 1
Crystal and data collection parameters for **2**[a]

Formula	$C_{76}H_{116}N_4O_6Pt_2S_2$
Formula weight	1636.02
Crystal size (mm)	$0.1 \times 0.25 \times 0.6$
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
Z	1
a (Å)	9.625(2)
b (Å)	12.017(3)
c (Å)	18.329(5)
α (°)	73.79(2)
β (°)	78.41(2)
γ (°)	76.32(2)
V (Å^3)	1957.2(8)
d_c (g cm^{-3})	1.39
Radiation, λ (Å)	Mo–K_α, 0.710 69
μ (cm^{-1})	36.7
$2\theta_{max}$ (°)	50.0
hkl range	$0 \le h \le 11$, $-13 \le k \le 14$, $-21 \le l \le 21$
Scan type	ω-scan
Scan speed (° min^{-1})	min 1.0, max 29.3
No. of data measured	7343
No. of unique data	6892
No. of data with $I > 2\sigma(I)$	5856
No. of parameters	406
R	0.067
R_w (on F^2)	0.055
w	$1/[\sigma^2(F_o)^2 + (0.1311P)^2 + 3.18P]$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$
Res. electron density (e$^-$ Å^{-3})	$-3.67/5.69$

[a] Estimated standard deviations are given in parentheses.

Table 2
Atom positions and U_{eq} values for **2**[a]

Atom	x	y	z	U_{eq} [b] (Å^2)
Pt	0.0449(1)	0.3137(1)	0.4273(1)	0.052(1)
S	−0.1001(4)	0.4947(3)	0.3851(2)	0.081(1)
N(1)	0.0827(11)	0.3651(8)	0.5174(5)	0.072(2)
N(2)	0.1667(9)	0.1450(7)	0.4499(4)	0.053(2)
O(1)	−0.1546(8)	0.3265(6)	0.1623(4)	0.068(2)
O(2)	0.0017(8)	0.1156(6)	0.1579(4)	0.066(2)
O(3)	0.1675(9)	−0.0130(6)	0.2750(4)	0.070(2)
C(1)	0.0906(12)	0.5761(9)	0.4416(6)	0.063(3)
C(2)	0.0134(11)	0.2625(8)	0.3385(5)	0.055(2)
C(3)	0.0885(10)	0.1466(8)	0.3364(5)	0.053(2)
C(4)	0.0873(12)	0.0972(8)	0.2769(5)	0.059(2)
C(5)	0.0037(11)	0.1600(9)	0.2175(5)	0.055(2)
C(6)	−0.0748(10)	0.2726(8)	0.2221(5)	0.055(2)
C(7)	−0.0729(11)	0.3235(9)	0.2802(5)	0.058(2)
C(8)	0.1673(11)	0.0880(8)	0.3992(5)	0.054(2)
C(9)	0.2398(11)	0.0853(9)	0.5156(5)	0.055(2)
C(10)	0.2265(11)	−0.0273(10)	0.5559(6)	0.063(2)
C(11)	0.3048(14)	−0.0859(11)	0.6170(7)	0.076(3)
C(12)	0.3967(12)	−0.0311(12)	0.6367(6)	0.076(3)
C(13)	0.4121(13)	0.0815(12)	0.5947(7)	0.081(3)
C(14)	0.3331(12)	0.1390(10)	0.5346(6)	0.068(3)
C(15)	−0.2371(13)	0.4445(10)	0.1596(6)	0.071(3)
C(16)	−0.3112(12)	0.4800(12)	0.0888(6)	0.074(3)
C(17)	−0.2124(13)	0.4845(12)	0.0138(7)	0.075(3)
C(18)	−0.2832(14)	0.5104(12)	−0.0562(7)	0.080(3)
C(19)	−0.1958(18)	0.5169(19)	−0.1309(9)	0.112(5)
C(20)	−0.2740(20)	0.5360(20)	−0.1980(9)	0.144(8)
C(21)	0.0969(14)	0.1617(12)	0.0888(7)	0.079(3)
C(22)	0.0596(15)	0.1380(12)	0.0211(6)	0.080(3)
C(23)	0.1375(16)	0.1989(13)	−0.0547(8)	0.091(4)
C(24)	0.1046(19)	0.1766(14)	−0.1248(7)	0.098(4)
C(25)	0.1660(30)	0.2520(20)	−0.2013(11)	0.145(8)
C(26)	0.3080(30)	0.2490(30)	−0.2147(15)	0.190(13)
C(27)	0.0882(18)	−0.1014(14)	0.2831(14)	0.133(8)
C(28)	0.1780(30)	−0.2216(14)	0.2957(14)	0.155(10)
C(29)	0.2670(30)	−0.2659(19)	0.3550(15)	0.154(9)
C(30)	0.3370(50)	−0.3940(30)	0.3600(20)	0.250(20)
C(31)	0.4380(50)	−0.4600(40)	0.3880(30)	0.310(30)
C(32)	0.4980(30)	−0.5830(20)	0.3914(18)	0.205(15)
C(33)	0.4827(16)	−0.0933(16)	0.7040(7)	0.105(5)
C(34)	0.3932(15)	−0.0990(14)	0.7817(7)	0.089(4)
C(35)	0.4777(16)	−0.1401(14)	0.8479(7)	0.095(4)
C(36)	0.3879(17)	−0.1424(16)	0.9267(8)	0.106(5)
C(37)	0.4620(20)	−0.1770(20)	0.9939(9)	0.130(7)
C(38)	0.3730(20)	−0.1761(19)	1.0699(9)	0.132(6)

[a] Estimated standard deviations are given in parentheses.

[b] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

stability of the deeply monotropic and unobserved N_D phase is increased through the charge transfer interactions of the electron donor **2** with the electron acceptor TNF — a similar behavior has already been observed in the thiocyanato-bridged palladium analogues [11]. However, this stabilized/induced N_D phase of the system **2**/TNF mirrors the lower stability of the mesophase of neat **2** compared with that of the analogous palladium mesogen.

Interestingly, the exclusive stabilization of the N_D phase by charge-transfer interactions up to now has only be observed for thiocyanato-bridged di-palladium and di-platinum compounds. In all the other examples of mesophase induction/stabilization between disc-shaped electron donors (including dinuclear palladium and platinum complexes [11]) and strong electron acceptors the formation of columnar aggregates occurs, either arranged into nematic-columnar (N_C) mesophases or forming columnar phases with a two-dimensional lattice, most commonly a hexagonal one (Col_h phase) [11,12].

The methoxy-substituted platinum organyl **1** shows no induced or stabilized mesomorphism with TNF owing to its high melting temperature and rapid decomposition in the isotropic state (see Table 4).

The *tetranuclear* thiocyanato-bridged platinum compounds **3** and **4** both exhibit enantiotropic mesophases. On heating each of the tetraplatinum organyls **3** and **4** above their melting temperatures, highly viscous and birefringent mesophases can be observed under a polarizing microscope between crossed polarizers up to very high clearing temperatures. In their isotropic phases a rapid and strong decomposition takes place; therefore, only on rapid cooling of samples of the platinomesogen **4** are typical textures developed. They resemble those of columnar hexagonal (Col_h) mesophases. However, miscibility studies (contact method) with the mesophases of analogous tetrapalladium organyls [4a] seem to indicate complete miscibility; thus, the mesophase of **4** appears to be of the same type, i.e. Col_{ob}.

Table 3
Selected bond distances (Å) and angles (°) for **2**[a,b]

Pt–C(2)	1.991(9)	C(2)–Pt–N(1)	178.6(4)
Pt–N(1)	2.040(9)	C(2)–Pt–N(2)	81.1(4)
Pt–N(2)	2.064(8)	N(1)–Pt–N(2)	98.0(3)
Pt–S	2.309(3)	C(2)–Pt–S	89.6(3)
S–C(1)	1.637(10)	N(1)–Pt–S	91.3(3)
C(1)–N(1)^i	1.190(14)	N(2)–Pt–S	170.7(2)
C(2)–C(3)	1.416(13)	C(1)–S–Pt	105.9(4)
C(2)–C(7)	1.414(13)	N(1)^i–C(1)–S	179.5(11)
C(3)–C(4)	1.384(13)	C(1)^i–N(1)–Pt	162.4(8)
C(3)–C(8)	1.429(13)	C(8)–N(2)–Pt	113.0(6)
C(4)–C(5)	1.417(14)	C(9)–N(2)–Pt	127.7(6)
C(5)–C(6)	1.401(14)		
C(6)–C(7)	1.375(13)		
C(8)–N(2)	1.298(12)		
C(9)–N(2)	1.442(12)		
C(9)–C(10)	1.371(14)		
C(9)–C(14)	1.369(14)		
C(10)–C(11)	1.401(16)		
C(11)–C(12)	1.372(19)		
C(12)–C(13)	1.383(18)		
C(13)–C(14)	1.391(15)		

[a] Estimated standard deviations are given in parentheses.

[b] Symmetry transformations used to generate equivalent atoms: i, −x+1, −y+1, −z+1.

The thermal phase-transition data of these new thiocyanato-bridged metallocyclic compounds are summarized in Table 4. The clearing temperature of **4** is, at 286°C, nearly identical to that of the respective tetra-pallado mesogen (290°C) [2].

The extremely high viscosity and clearing temperature prevented a detailed study of the thermotropic mesophase of the hexyloxy-substituted platinum compound **3**. In particular, no identifiable textures were obtained; the nature of the mesophase of **3**, therefore, remains unknown.

3. Conclusions

Thiocyanato-bridged di- and tetra-nuclear platinum complexes are easily accessible by simple exchange reactions from their chloro-bridged analogues. Single-crystal X-ray diffraction proves the coplanar arrangement of the two square-planar platinum(II) coordination polyhedral in **2**. The dinuclear compound **2** shows none of the possible forms of isomerism and is not mesomorphic, in contrast to the respective di-palladium organyl. However, with TNF as a strong electron acceptor the induction/stabilization of an N_D mesophase is observed. The mesomorphic properties of the new tetranuclear platinum organyl **4** strongly resemble those of the analogous pallado-mesogen. Thus, here the exchange of platinum for palladium has a significant impact and results in the absence of an N_D mesophase in **2**. However, for the tetranuclear platinum mesogen **4** the switch from palladium to platinum has nearly no impact on the type and stability of the exhibited mesophase.

4. Experimental

The characterizations of the compounds **1**–**4** presented here are based on correct elementary analyses and on various spectroscopic data, e.g. ^{1}H-, ^{13}C-NMR (Bruker WH-400 or AM-270 spectrometers respectively, $CDCl_3$ solutions), ^{195}Pt-NMR (in part) (Bruker ARX 400 spectrometer (86.02 MHz) in $CDCl_3$ solutions using a separate reference sample (0.5 g Na_2PtCl_6 in 2 ml D_2O)), IR (Beckmann 9, CCl_4 solutions) and MS (Varian MAT 711). Only structurally relevant resonances are given; see below.

Phase-transition data were determined by differential scanning calorimetry (Mettler TA 3000/DSC-30 S with TA 72.5 software) and by polarizing microscopy (Leitz Laborlux 12 Pol with a Mettler FP 82 hot-stage or using the Linkam THMS 600 system) with heating rates of 5 or 20 K min^{-1} in both methods.

4.1. Single-crystal X-ray diffraction analysis

Data were collected on a Syntex P2_1 diffractometer using Mo–K$_\alpha$ radiation ($\lambda = 0.710\ 69$ Å). The structure was solved after Lp correction by Patterson methods using SHELXS [13] and refined with anisotropic thermal parameters for the non-hydrogen atoms with SHELXL [14]. Hydrogen positions were calculated and refined with a riding model; the methyl groups were refined as rigid groups.

4.2. Preparation of the compounds 1–4

The thiocyanato-bridged platinum organyls **1**–**4** were prepared from the corresponding chloro-bridged precursors [5–7] by the usual exchange reactions with potassium thiocyanate in methylene chloride–acetone under argon at room temperature. The crude products were purified by crystallization.

4.2.1. Synthesis of the dinuclear platinum organyls 1 and 2

The exchange reaction (Cl → SCN) was carried out by stirring either 0.1 mmol (0.12 g) of the methoxy-substituted chloro-bridged platinum organyl [7] or 0.1 mmol (0.16 g) of the hexyloxy-substituted chloro-bridged platinum organyl [5] with 3 mmol (0.29 g) of

Table 4
Phase transition temperatures[a] T and enthalpies ΔH of **1**–**4**

Platinum organyl	Crystalline		Col$_{ob}$[b]		M[b]		I[b]
	T (°C)	ΔH (kJ mol^{-1})	T (°C)	ΔH (kJ mol^{-1})	T (°C)	ΔH (kJ mol^{-1})	T (°C)
1	172.6	42.5	–		–		dec.
2	86.2	20.7	–		–		
3	69.0	11.9	–		308.2	–[c]	dec.
4	17.2	56.9	286.1	–[c]	–		dec.

[a] Mettler TA 3000/DSC-30 S with TA 72.5 software. Heating rates 5 K min^{-1} for the melting and 20 K min^{-1} for the clearing processes.

[b] Col$_{ob}$: columnar oblique; M: a highly viscous phase of unknown type; I: isotropic.

[c] Here, the clearing process is strongly interfered with by decomposition; therefore, the ΔH value obtained of less than 1 kJ mol^{-1} is to be considered with caution.

KSCN in a mixture of 40 ml CH_2Cl_2, and 20 ml of acetone for 6 days under argon. The crude products were purified by removing the solvent under reduced pressure followed by recrystallization from methanol–acetone. The melting points of **1** and **2** are given in Table 4.

Bis[μ-(thiocyanato-*N*:*S*)]bis[3,4,5-tris(methoxy)-2-{[(4-hexylphenyl)imino]methyl}phenyl-*C*,*N*]diplatinum-(II) (**1**). Yield: 87 mg (72%) of yellow crystals. ^{1}H-NMR: $\delta = 8.41$ (s; 2 HC=N), 7.27, 7.22 (2d, $J \approx 8$ Hz each; 4 arom. Hs of the N-substituted phenyl rings), 6.35 (s; 2 arom. Hs of the Pt-substituted phenyl rings), 3.95, 3.89, 3.77 (3s; 6 OCH_3 groups), 2.68 (t, $J \approx 7.5$ Hz; 2 α-CH_2 groups). ^{13}C-NMR: $\delta = 172.03$ (d; 2HC=N), 157.82, 153.84, 147.58, 142.75, 137.71, 137.53, 132.76 (7s; 14 arom. Cs and 2 SCN groups), 128.57, 123.09, 110.05 (3d; 4, 4 and 2 arom. CH respectively), 61.71, 60.71, 56.00 (3q; 6 OCH_3 groups), 35.49 (t; 2 α-CH_2 groups). ^{195}Pt-NMR: $\delta = -3599.5$ (s). IR (CCl_4): $v = 2162$ cm^{-1} (SCN). Anal. Found: C, 45.41; H, 4.63; N, 4.42. Calc. for $C_{46}H_{56}N_4O_6Pt_2S_2$ (1215.3): C, 45.46; H, 4.64; N, 4.61%.

Bis[μ-(thiocyanato-*N*:*S*)]bis[3,4,5-tris(hexyloxy)-2-{[(4-hexylphenyl)imino]methyl}phenyl-*C*,*N*]diplatinum-(II) (**2**). Yield: 125 mg (76%) of yellow crystals. ^{1}H-NMR: $\delta = 8.38$ (s; 2 HC=N), 7.26, 7.22 (2d, $J \approx 8$ Hz each; 4 arom. Hs of the N-substituted phenyl rings), 6.31 (s; 2 arom. Hs of the Pt-substituted phenyl rings), 4.12, 4.01, 3.85 (3t; $J \approx 6.5$ Hz each; 3 types of OCH_2 group), 2.68 (t, $J \approx 8$ Hz; 2 α-CH_2 groups). ^{13}C-NMR: $\delta = 172.24$ (d; 2 HC=N), 157.79, 153.65, 147.75, 142.66, 137.20, 137.01,133.07 (7s; 14 arom. Cs and 2 SCN groups), 128.60, 123.12, 110.89 (3d; 4, 4 and 2 arom. CH respectively), 74.56, 73.50, 68.62 (3 t; 6 OCH_2 groups), 35.52 (t; 2 α-CH_2 groups). MS: m/z (%) = 1634.8 (15) [M +]. IR (CCl_4): $v = 2161$ cm^{-1} (SCN). Anal. Found: C, 55.09; H, 7.56; N, 3.79. Calc. for $C_{76}H_{116}N_4O_6Pt_2S_2$ (1636.1): C, 55.79; H, 7.15; N, 3.42%.

4.2.2. *Synthesis of the tetranuclear platinum organyls **3** and **4***

The exchange reaction (Cl → SCN) was carried out by stirring 0.1 mmol (0.27 g) of the hexyloxy-substituted chloro-bridged tetra-platinum organyl [6] or 0.1 mmol (0.37 g) of the respective dodeclyoxy-substituted chloro-bridged platinum complex [6] with 10 mmol (0.97 g) of KSCN in a mixture of 60 ml CH_2Cl_2 with 30 ml acetone for 6 days under argon. The crude products were purified by removing the solvent under reduced pressure and recrystallization from methylene chloride–acetone. The melting and clearing temperatures of **3** and **4** are given in Table 4.

Bis{μ-[1,4-phenylenbis[nitrilomethylidyn(3,4,5-tris-(hexyloxy)-2,1-phenylen)]]}tetrakis-[μ-(thiocyanato-*N*:*S*)]tetraplatinum(II) (**3**). Yield: 132 mg (47%) of sticky yellow crystals. ^{1}H-NMR: $\delta = 8.34$, 8.18 (2s; 4 HC=N), 7.34, 7.19 (2d, $J \approx 8$ Hz each; 4 arom. Hs of the 4,4′-di-N-substituted phenyl rings), 6.78, 6.37 (2s; 4 arom. Hs of the benzylidene rings), 4.20–4.11 (m; 6 OCH_2 groups), 4.07, 3.89, 3.86 (3t, $J \approx 6.5$ Hz each; 6 OCH_2 groups). ^{13}C-NMR: $\delta = 176.40$, 172.82 (2d; 4 HC=N), 160.02, 158.42, 154.03, 153.76, 148.87, 148.26, 145.94, 137.98, 136.88, 136.76, 132.96, 130.29, 126.20, 121.70 (14s; 24 arom. Cs and 4 SCN groups), 124.12, 123.74, 112.24, 111.00 (4d; 12 arom. CH situations), 74.55, 73.52, 68.96, 68.70 (4t; 12 OCH_2 groups). IR (CCl_4): $v = 2176$ and 2147 cm^{-1} (SCN). Anal. Found: C, 50.03; H, 6.43; N, 3.88. Calc. for $C_{116}H_{172}N_8O_{12}Pt_4S_4$ (2779.3): C, 50.13; H, 6.24; N, 4.03%.

Bis{μ-[1,4-phenylenbis[nitrilomethylidyn(3,4,5-tris-(dodecyloxy)-2,1-phenylen)]]}tetrakis-[μ-(thiocyanato-*N*:*S*)]tetraplatinum(II) (**4**). Yield: 241 mg (64%) of sticky yellow-brown crystals. ^{1}H-NMR: $\delta = 8.35$, 8.19 (2s; 4 HC=N), 7.34, 7.19 (2d, $J \approx 8$ Hz each; 4 arom. Hs of the 4,4′-di-N-substituted phenyl rings), 6.78, 6.37 (2s; 4 arom. Hs of the benzylidene rings), 4.20–4.11 (m; 6 OCH_2 groups), 4.07, 3.89, 3.86 (3t, $J \approx 6.5$ Hz each; 6 OCH_2 groups). ^{13}C-NMR: $\delta = 176.37$, 172.79 (2d; 4 HC=N), 160.03, 158.42, 154.03, 153.75, 148.86, 148.26, 145.98, 138.01, 136.85, 136.73, 132.95, 130.28, 126.21, 121.76 (14s; 24 arom. Cs and 4 SCN groups), 124.13, 123.75, 112.25, 110.98 (4d; 12 arom. CH situations), 74.55, 73.53, 68.94, 68.71 (4t; 12 OCH_2 groups). IR (CCl_4): $v = 2176$ and 2148 cm^{-1} (SCN). Anal. Found C, 59.35; H, 8.12; N, 2.64. Calc. for $C_{188}H_{316}N_8O_{12}Pt_4S_4$ (3789.2): C, 59.59; H, 8.41; N, 2.96%.

5. Supplementary material

Crystallographic data have been deposited at the Cambridge Data Center and may be obtained without charge on quoting the depository number CCDC 143811 from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-1223-336033, e-mail deposit@ccdc.cam.ac.uk).

Acknowledgements

B. Bilgin Eran wishes to thank Yıldız Teknik Üniversitesi Research Fond and Devlet Planlama Teşkilatı (DPT) (State Planning Organization Turkey) for the supply of a polarizing microscope. K. Praefcke is grateful to the Deutsche Forschungsgemeinschaft, Bonn (Sonderforschungsbereich Sfb 335 ‘Anisotrope Fluide’, project C 3), the Fonds der Chemischen Industrie, Frankfurt/Main, the Gesellschaft von Freunden der Technischen Universität Berlin, and to the Technische Universität Berlin, Germany, for financial support of his liquid crystal work as well as to Degussa AG., Hanau, Germany, for the supply of palladium and platinum precursors.

References

[1] (a) J.L. Serrano (Ed.), Metallomesogens, Synthesis, Properties, and Applications, VCH, Weinheim, 1996. (b) A.M. Giroud-Godquin, in: D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds.), Handbook of Liquid Crystals, vol. IIB, Wiley–VCH, Weinheim, 1998, p. 901.

[2] K. Praefcke, D. Singer, B. Gündoğan, Mol. Cryst. Liq. Cryst. 223 (1992) 181.

[3] (a) B. Gündoğan, K. Praefcke, Chem. Ber. 126 (1993) 1253. (b) K. Praefcke, D. Singer, B. Gündoğan, K. Gutbier, M. Langner, Ber. Bunsenges. Phys. Chem. 98 (1994) 118. (c) N. Usol'tseva, K. Praefcke, D. Singer, B. Gündoğan, Liq. Cryst. 16 (1994) 601.

[4] (a) K. Praefcke, S. Diele, J. Pickardt, B. Gündoğan, U. Nütz, D. Singer, Liq. Cryst. 18 (1995) 857. (b) K. Praefcke, J.D. Holbrey, N. Usol'tseva, Mol. Cryst. Liq. Cryst. 288 (1996) 189. (c) N. Usol'tseva, G. Hauck, H.D. Koswig, K. Praefcke, B. Heinrich, Liq. Cryst. 20 (1996) 731. (d) K. Praefcke, J.D. Holbrey, N. Usol'tseva, D. Blunk, Mol. Cryst. Liq. Cryst. 292 (1997) 123. (e) B. Heinrich, K. Praefcke, D. Guillon, J. Mater. Chem. 7 (1997) 1363.

[5] (a) K. Praefcke, B. Bilgin, J. Pickardt, M. Borowski, Chem. Ber. 127 (1994) 1543. (b) B. Bilgin, Neue flächige Mesogene des Palladiums und Platins, Verlag Dr Köster, Berlin, 1996, ISBN 3-89574-155-8.

[6] K. Praefcke, B. Bilgin, N. Usol'tseva, B. Heinrich, D. Guillon, J. Mater. Chem. 5 (1995) 2257.

[7] K. Praefcke, B. Bilgin, J. Pickardt, M. Borowski, J. Organomet. Chem. 592 (1999) 155.

[8] P.S. Pregosin, Coord. Chem. Rev. 44 (1982) 247.

[9] (a) J. Barbera, P. Espinet, E. Lalinde, M. Marcos, J.L. Serrano, Liq. Cryst. 2 (1987) 833. (b) M.A. Ciriano, P. Espinet, E. Lalinde, M.B. Ros, J.L. Serrano, J. Mol. Struct. 196 (1989) 327.

[10] G. Bergerhoff, K. Brandenburg, M. Berndt, DIAMOND, Visuelles Informationssystem für Kristallstrukturen, Bonn, 1996.

[11] (a) D. Singer, A. Liebmann, K. Praefcke, J.H. Wendorff, Liq. Cryst. 14 (1993) 785. (b) K. Praefcke, D. Singer, Mol. Mater. 3 (1994) 265.

[12] (a) K. Praefcke, D. Singer, in: D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds.), Handbook of Liquid Crystals, vol. IIB, Wiley–VCH, Weinheim, 1998, p. 945. (b) S. Zamir, D. Singer, N. Spielberg, E.J. Wachtel, H. Zimmermann, R. Poupko, Z. Luz, Liq. Cryst. 21 (1996) 39.

[13] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, Göttingen, 1997.

[14] G.M. Sheldrick, SHELXL-97, Program for Refinement of Crystal Structures, Göttingen, 1997.