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Coordinatively saturated cyclometallated Pt(IV) azobenzene complexes: synthesis and mesomorphic behaviour

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The mesomorphic 4,4′-bis[4-*n*-octyloxybenzoyloxy]azobenzene dinuclear chloro-bridged cycloplatinated complex $[(\mathrm{Azo})\mathrm{Pt}(\mu\text{-Cl})]_2$ (smectic C between 263 and 342°C) has been reacted with different chelating ligands, giving rise to a family of square-planar *ortho*-platinated derivatives, $[(\mathrm{Azo})\mathrm{Pt}(L)]$ (L = tropolonate, 8-hydroxyquinolinate and 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate). Thermotropic mesomorphism is preserved for these mononuclear complexes which exhibit at least a nematic mesophase and transition temperatures lower by over 100°C than that of the corresponding dimeric precursor. Oxidative addition to the Pt(II) $[(\mathrm{Azo})\mathrm{Pt}(L)]$ species of electrophilic substrates such as I_2 or CH_3I eventually led to the corresponding octahedral $[(\mathrm{Azo})\mathrm{Pt}(L)(\mathrm{I})(X)]$ products. The introduction of two further ligands leads to Pt(IV) derivatives showing smectic and nematic mesophases for all L ligands. For the hexacoordinated $[(\mathrm{Azo})\mathrm{Pt}(L)(\mathrm{I})(\mathrm{CH}_3)]$ complexes it has been verified that the oxidative addition of methyl iodide is a thermally reversible process, indicating that these species have potential applications as switchable systems.

1. Introduction

Over the last decade, the target most pursued in the field of metallomesogens has been to take advantage of the presence of a transition metal centre in order to obtain increasingly anisotropic molecular architectures with their related novel physical and optical properties [1].

Rapid growth in the number of rod-like thermotropic high coordination number complexes has been achieved using various strategies. One approach towards coordinatively saturated metal-containing liquid crystals is the synthesis of hexacoordinated Re(I) and Mn(I) carbonyl complexes of imines [2], 1,4-diazabutadienes [3] or 2,2′-bipyridines [4] and Rh(III) acetylenes [5]. In addition, butadiene iron-tricarbonyl complexes [6] and formally octahedral systems such as metallocene-based species [7] and (η^6-arene)tricarbonyl chromium [8] have been synthesized. It has also been shown that square-planar 18-electron complexes, namely (cyclopentadienyl)cyclometallated azobenzene derivatives, exhibiting calamitic mesophases, can be designed [9]. All these results have improved the understanding of structure–mesomorphism relationships; it is now known, for example, that in order to balance perturbations produced by bulky organometallic frameworks, the organic ligand needs at least three aromatic rings to achieve the anisotropy necessary for the occurrence of calamitic mesophases.

Recently, we successfully devised an alternative methodology for the synthesis of coordinatively saturated metallomesogens following the speculation that in a coordinatively unsaturated complex the reactivity of the metal centre may allow the modification of the molecular structure. Thus, we reported the synthesis of the first examples of Pt(IV) cyclometallated azobenzenes, shown in the figure, obtained by oxidative addition of electrophilic substrates such as I_2 and CH_3I to the Pt(II) square-planar acetylacetonate (*acac*) precursors [10].

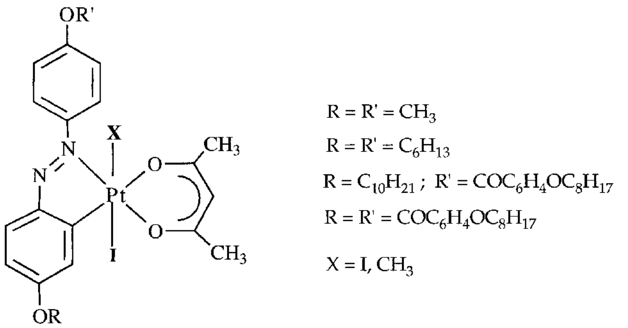

Figure. General formula of the Pt(IV) acetylacetonate derivatives [10].

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The resulting octahedral complexes were found to exhibit disordered calamitic mesophases (namely nematic (N) and smectic C (SmC) phases), at temperatures lower than for the corresponding organic ligands. Also worth noting here is that oxidative addition of methyl iodide, for these complexes, is a thermally reversible process.

In order to investigate both the role played by the organometallic fragment on the molecular geometry and mesomorphism of the square-planar precursors, and its influence on the stability of the Pt(IV) derivatives towards reductive elimination reactions, we wished to extend this work to other families of square-planar *ortho*-platinated derivatives, by replacing the *acac* group with different chelating ligands, *L*, tropolonate (*trop*), 8-hydroxyquinolinate (*8-q*) and 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate (*hfacac*).

We report here the synthesis and liquid crystalline behaviour of further examples of Pt(II) cyclometallated complexes derived from 4,4′-bis[4-*n*-octyloxybenzoyloxy]-azobenzene (HAzo), [(Azo)Pt(*L*)], (scheme 1), as precursors to the mesogenic octahedral derivatives [(Azo)Pt(*L*)(I)(*X*)] (scheme 2) which can be obtained through oxidative addition reactions.

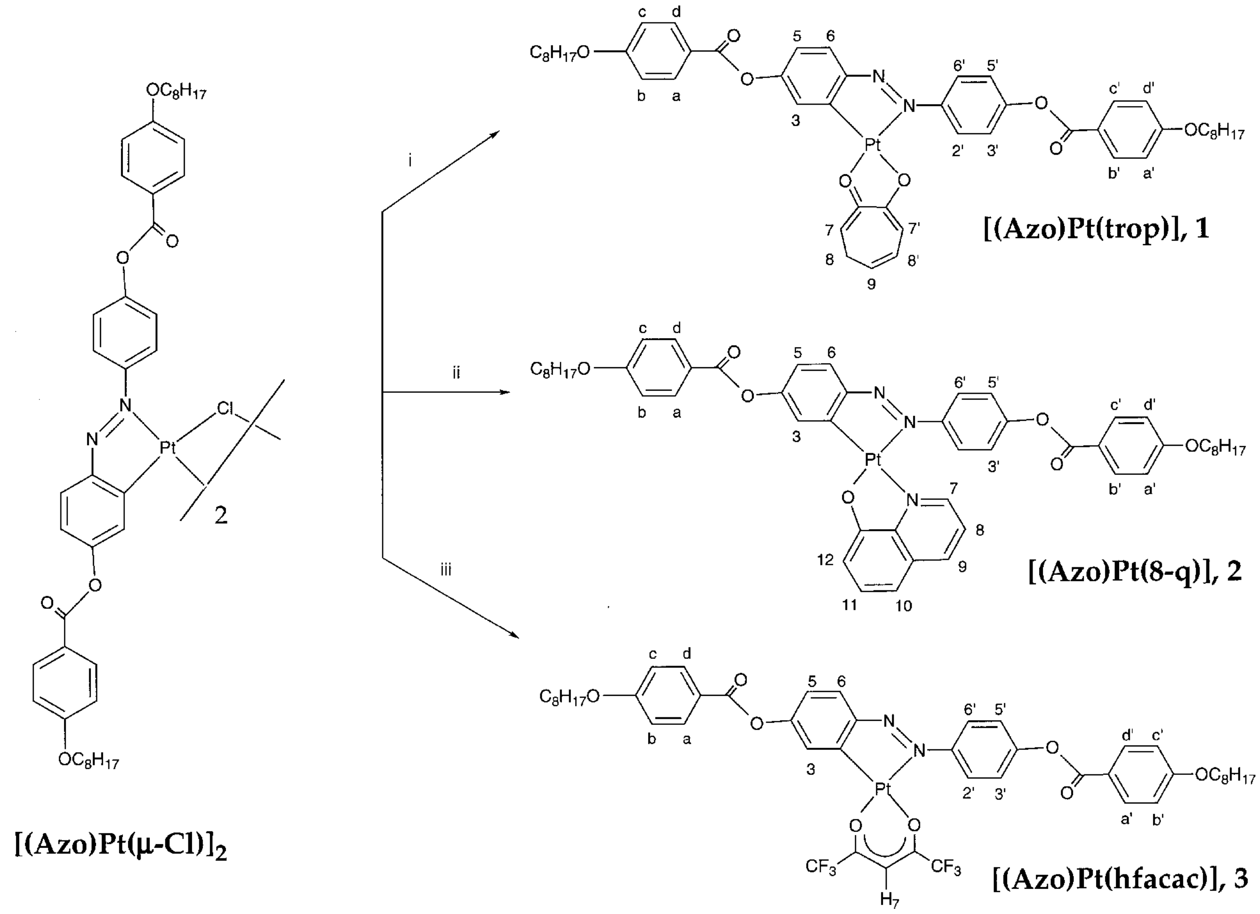
2. Experimental

2.1. *General*

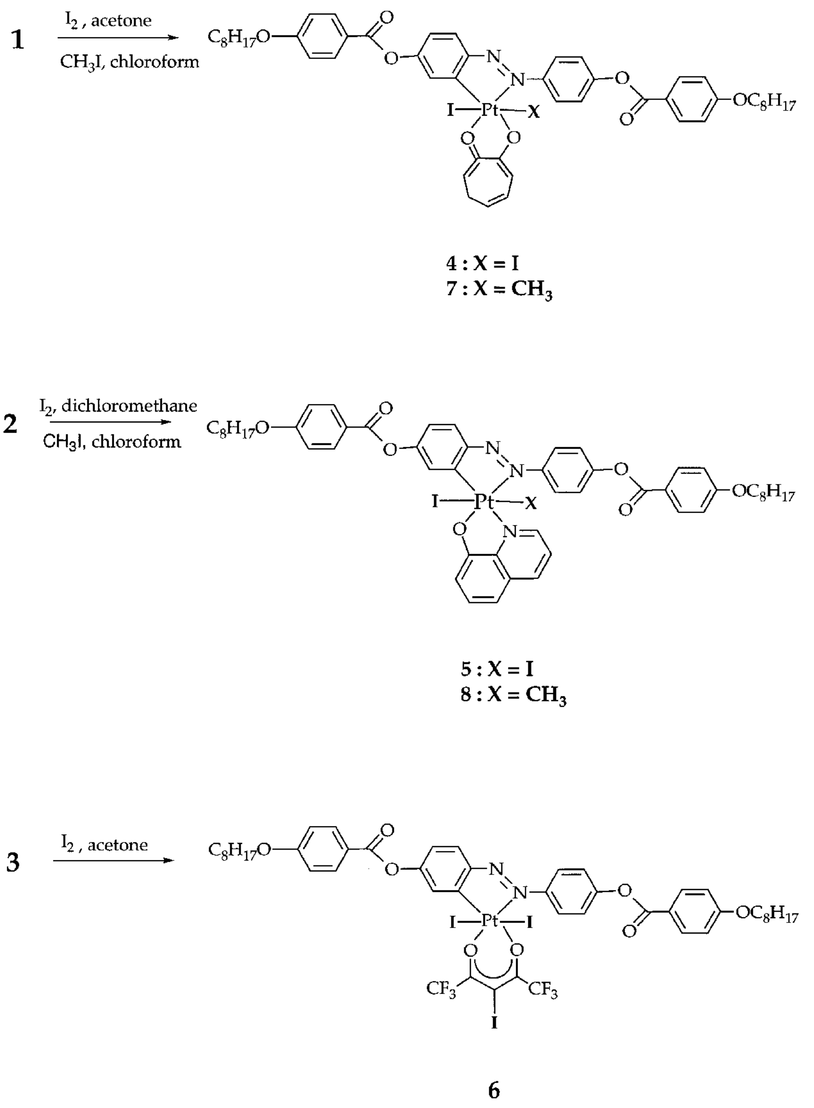
All commercially available starting materials—$AgBF_4$ (Fluka, A.G.), tropolone [H(*trop*)], 8-hydroxyquinoline [H(*8-q*)] and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione [H(*hfacac*)] (all Aldrich Chemical Co.)—were used without further purification. [$K_2(PtCl_4)$] was purchased from Johnson-Matthey Inc. Literature methods were used to prepare [$(\eta^3\text{-}C_4H_7)Pt(\mu\text{-}Cl)]_2$ [11] and sodium hexafluoroacetylacetonate [Na(*hfacac*)] [12].

4,4′-Bis-[4-(*n*-octyloxy)benzoyloxy]azobenzene, HAzo [9*b*], [(Azo)Pt(μ-Cl)]$_2$ [10], potassium tropolonate [K(*trop*)] [13] and [(Azo)Pt(MeCN)$_2$]BF_4 were synthesized as previously reported [14].

^1H NMR spectra were recorded using a Bruker WH-300 spectrometer and $CDCl_3$ solutions, with TMS



Scheme 1. Synthetic route to the Pt(II) [(Azo)Pt(*L*)] complexes, **1**–**3** and related proton numbering scheme. Reagents and conditions: i, [K(*trop*)], dichloromethane; ii, $AgBF_4$, CH_3CN, [H(*8-q*)], ethanol; iii, [Na(*hfacac*)], dichloromethane.



Scheme 2. Synthetic route to the Pt(IV) [(Azo)Pt(*L*)(I)(CH_3)] complexes, **4**–**8**.

as internal standard. Elemental analyses were made with a Perkin-Elmer 2400 analyser. The textures of the mesophases were studied with a Zeiss Axioscope polarizing microscope equipped with a Linkam C0 600 heating stage. The transition temperatures and enthalpies were measured using a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating and cooling rate of 10°C min^{-1}. The apparatus was calibrated with indium. Two or more heating/cooling cycles were performed on each sample.

2.2. *Synthesis of the square-planar [(Azo)Pt(L)] complexes 1–3*

2.2.1. *[(Azo)Pt(trop)], 1*

A mixture of [(Azo)Pt(μ-Cl)$]_2$ (100 mg, 0.055 mmol) and [K(*trop*)], (18 mg, 0.11 mmol) in dichloromethane (15 ml) was stirred at room temperature for 24 h; the resulting red solution was filtered through Celite to remove a white insoluble residue (salt), concentrated and then added to methanol to give a dark red solid; yield 104 mg (95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45 (d, 2H, $H^{2',6'}$, $J = 9.3$ Hz), 8.19 (d, 4H, $H^{a,d,a',d'}$, $J = 9.0$ Hz), 8.06 (d, 1H, H^6, $J = 8.3$ Hz), 7.66–7.59 (m, 5H, $H^{3,7,8,7',8'}$), 7.42 (d, 2H, $H^{3',5'}$, $J = 9.3$ Hz), 7.16 (m, 1H, H^9), 7.10 (dd, 1H, H^5, $J = 8.3$, 2.4 Hz), 7.01–6.99 (m, 4H, $H^{b,c,b',c'}$), 4.06 (m, 4H, $-OCH_2$). Elemental analysis: calc. for $C_{49}H_{54}N_2O_8Pt$, C 59.20, H 5.47, N 2.82; found, C 59.07, H 5.43, N 3.21%.

2.2.2. *[(Azo)Pt(8-q)], 2*

A suspension of [(Azo)Pt(MeCN)$]_2BF_4$ (246 mg, 0.24 mmol) in ethanol (30 ml) was stirred at room temperature with an equimolar amount of 8-hydroxyquinoline (34 mg). After 2.5 h a dark red solid was filtered off and purified by recrystallization from chloroform/methanol to give the pure product in 78% yield (187 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, 4H, $H^{a,d,a',d'}$, $J = 8.9$ Hz), 8.05 (d, 1H, H^6, $J = 8.5$ Hz), 7.79 (d, 1H, H^3, $J = 2.4$ Hz), 7.76 (d, 2H, $H^{2',6'}$, $J = 8.8$ Hz), 7.42 (d, 2H, $H^{3',5'}$), 7.12 (dd, 1H, H^5, $J = 8.5$, 2.4 Hz), 7.02 (d, 2H, $H^{b,c}$, $J = 8.9$ Hz), 6.98 (d, 2H, $H^{b',c'}$, $J = 8.9$ Hz), 4.06 (m, 4H, $-OCH_2$). Elemental analysis: calc. for $C_{51}H_{55}N_3O_7Pt$, C 60.23, H 5.45, N 4.13; found, C 59.80, H 5.39, N 3.83%.

2.2.3. *[(Azo)Pt(hfacac)], **3***

This compound (orange solid) was synthesized following the procedure described for **1**, by reacting $[(Azo)Pt(\mu\text{-}Cl)]_2$ (119 mg, 0.065 mmol) with two equivalents of [Na(*hfacac*)] (30 mg, 0.13 mmol); yield 120 mg (86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, 2H, $H^{a',d'}$, $J = 9.0$ Hz), 8.16 (d, 2H, $H^{a,d}$, $J = 9.0$ Hz), 8.05 (d, 1H, H^6, $J = 8.0$ Hz), 7.91 (d, 2H, $H^{2',6'}$, $J = 8.9$ Hz), 7.36 (d, 2H, $H^{3',5'}$, $J = 8.9$ Hz), 7.15 (m, 2H, $H^{3,5}$), 6.98 (d, 4H, $H^{b,c,b',c'}$, $J = 9.0$ Hz), 6.31 (s, 1H, H^7), 4.05 (t, 4H, $-OCH_2$). Elemental analysis: calc. for $C_{47}H_{50}F_6N_2O_8Pt$, C 52.57, H 4.67, N 2.59; found, C 51.88, H 4.52, N 2.78%.

2.3. *Synthesis of the octahedral [(Azo)Pt(L)(I$_2$)] complexes **4–6***

2.3.1. *[(Azo)Pt(trop)(I$_2$)], **4***

Three equivalents of I_2 (53 mg, 0.21 mmol) dissolved in 4 ml of acetone were added to a red suspension of **1** (70 mg, 0.07 mmol) in acetone (6 ml). The orange mixture was stirred at room temperature for 1 h, concentrated under reduced pressure and cooled to 0°C to give an orange solid (60 mg) in 69% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.59 (d, 2H, $H^{2',6'}$, $J = 9.0$ Hz), 8.34 (d, 1H, H^6, $J = 8.7$ Hz), 8.19 (d, 4H, $H^{a,d,a',d'}$, $J = 8.8$ Hz), 7.68 (d, 1H, H^3, $J = 2.1$ Hz), 7.64 (d, 2H, $H^{7,7'}$, $J = 4.4$ Hz), 7.55 (m, 2H, $H^{8,8'}$), 7.50 (d, 2H, $H^{3',5'}$, $J = 9.0$ Hz), 7.37 (dd, 1H, H^5, $J = 8.7$, 2.1 Hz), 7.23 (m, 1H, H^9), 7.04–7.01 (m, 4H, $H^{b,c,b',c'}$), 4.08 (m, 4H, $-OCH_2$). Elemental analysis: calc. for $C_{49}H_{54}I_2N_2O_8Pt$, C 47.16, H 4.36, N 2.24; found, C 46.86, H 4.30, N 2.28%.

2.3.2. *[(Azo)Pt(8-q)(I$_2$)], **5***

A solution of I_2 (46 mg, 0.18 mmol) in dichloromethane (10 ml) was added dropwise to the dark red solution of **2** (60 mg, 0.06 mmol) in dichloromethane (6 ml). The resulting red solution was stirred at room temperature for 1 h, then concentrated under vacuum and added to methanol to yield 67 mg (88%) of a dark brown solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (d, 1H, H^6, $J = 8.4$ Hz), 8.24 (d, 4H, $H^{a,d,a',d'}$, $J = 8.9$ Hz), 8.17 (d, 2H, $H^{2',6'}$, $J = 8.8$ Hz), 7.94 (d, 1H, H^3, $J = 2.3$ Hz), 7.53 (d, 2H, $H^{3',5'}$, $J = 8.8$ Hz), 7.47 (dd, 1H, H^5, $J = 8.4$, 2.3 Hz), 7.05 (d, 2H, $H^{b,c}$, $J = 8.9$ Hz), 7.03 (d, 2H, $H^{b',c'}$, $J = 8.9$ Hz), 4.09 (t, 4H, $-OCH_2$). Elemental analysis: calc. for $C_{51}H_{55}I_2N_3O_7Pt$, C 48.20, H 4.36, N 3.31; found, C 47.90, H 4.26, N 3.33%.

2.3.3. *[(Azo)Pt(1,1,1,5,5,5-hexafluoro-3-iodo-2,4-pentanedionate)(I$_2$)], **6***

This compound (brown solid) was synthesized following the procedure described for **5**, by reacting an orange suspension of **3** (54 mg, 0.05 mmol) in acetone (6 ml) with three equivalents of I_2 (38 mg, 0.15 mmol) in acetone (6 ml); yield 56 mg (77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, 1H, H^6, $J = 8.8$ Hz), 8.22 (d, 4H, $H^{a,d,a',d'}$, $J = 8.8$ Hz), 8.19 (d, 2H, $H^{2',6}$), 7.54 (d, 2H, $H^{3',5'}$, $J = 8.2$ Hz), 7.46 (dd, 1H, H^5, $J = 8.8$ Hz), 7.37 (d, 1H, H^3, $J_{Pt\text{-}H} = 25$ Hz), 7.07 (d, 4H, $H^{b,c,b',c'}$, $J = 8.8$ Hz), 4.13 (t, 4H, $-OCH_2$). Elemental analysis: calc. for $C_{47}F_6H_{49}I_3N_2O_8Pt$, C 38.67, H 3.38, N 1.92; found, C 39.26, H 3.97, N 2.02%.

2.4. *Synthesis of the octahedral [(Azo)Pt(L)(I)(CH$_3$)] complexes 7 and **8***

2.4.1. *[(Azo)Pt(trop)(I)(CH$_3$)], 7*

CH_3I (9 mmol) was added to a solution of **1** (90 mg, 0.09 mmol) in chloroform (12 ml) and stirred, at room temperature, for 6 days. Concentration of the resulting red solution followed by addition of acetone resulted in the formation of an orange solid which was filtered off and dried under vacuum; yield 62 mg (61%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.63 (d, 2H, $H^{2',6'}$, $J = 9.3$ Hz), 8.26 (d, 1H, H^6, $J = 8.8$ Hz), 8.19 (d, 4H, $H^{a,d,a',d'}$, $J = 7.8$ Hz), 7.67 (d, 1H, H^3), 7.59 (d, 2H, $H^{7,7'}$), 7.52 (m, 2H, $H^{8,8'}$), 7.46 (d, 2H, $H^{3',5'}$, $J = 9.3$ Hz), 7.36 (dd, 1H, H^5, $J = 8.8$ Hz), 7.19 (m, 1H, H^9), 7.01 (d, 4H, $H^{b,c,b',c'}$, $J = 7.8$ Hz), 4.06 (m, 4H, $-OCH_2$), 1.38 (s, 3H, $-CH_3$). Elemental analysis: calc. for $C_{50}H_{57}IN_2O_8Pt$, C 52.86, H 5.06, N 2.46; found, C 53.08, H 5.09, N 2.38%.

2.4.2. *[(Azo)Pt(8-q)(I)CH$_3$)], **8***

CH_3I (9.8 mmol) was added to a magenta solution of **2** (100 mg, 0.098 mmol) in chloroform (12 ml) and stirred for 6 days. The solvent was evaporated and the crude product recrystallized first from diethyl ether and then from methylene chloride–methanol to give a light brown solid; yield 45 mg (40%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (d, 1H, H^6, $J = 8.5$ Hz), 8.22 (d, 4H, $H^{a,d,a',d'}$, $J = 8.5$ Hz), 8.01 (d, 2H, $H^{2',6'}$, $J = 8.2$ Hz), 7.52 (d, 2H, $H^{3',5'}$, $J = 8.2$ Hz), 7.47 (d, 1H, H^3, $J = 2.4$ Hz), 7.41 (m, 1H, H^5), 7.04 (d, 4H, $H^{b,c,b',c'}$, $J = 8.5$ Hz), 4.08 (m, 4H, $-OCH_2$), 1.23 (s, 3H, $-CH_3$). Elemental analysis: calc. for $C_{52}H_{58}IN_3O_7Pt$, C 53.89, H 5.04, N 3.62; found, C 53.93, H 4.92, N 3.47%.

3. Results and discussion

3.1. *Synthesis*

3.1.1. *Square-planar [(Azo)Pt(L)] complexes*

The synthetic pathways to complexes **1**–**3** are shown in scheme 1. Complexes **1** and **3** (dark red and orange solids, respectively) were obtained by reaction of the cycloplatinated chloro-bridged dimer $[(\mathrm{Azo})\mathrm{Pt}(\mu\text{-Cl})]_2$ with two equivalents of [K(*trop*)] or [Na(*hfacac*)] in dichloromethane, at room temperature. For the 8-quinolinate derivative this route was unsuccessful, and complex **2**, a dark red solid, was synthesized in two consecutive steps. The dinuclear precursor was first reacted with four equivalents of silver tetrafluoroborate in acetonitrile to give the corresponding solvato species $[(\mathrm{Azo})\mathrm{Pt}(\mathrm{MeCN})_2]\mathrm{BF}_4$ which was then reacted with an equimolar amount of 8-hydroxyquinoline (in ethanol, at room temperature) to afford the desired product. For all products, purified by crystallization from suitable solvents (see § 2), yields were in the range 78–95%. The ^{1}H NMR spectra of complexes **1**–**3** show the pattern typical for a mononuclear cyclometallated compound with no $J(\mathrm{H}, {}^{195}\mathrm{Pt})$ coupling.

3.1.2. *Octahedral [(Azo)Pt(L)(I)(X)] complexes*

The syntheses of the Pt(IV) complexes **4**–**8** were carried out following the method previously reported [10] for the analogous acetylacetonate derivatives, as shown in scheme 2.

In particular, the [(Azo)Pt(*trop*)(I_2)] and [(Azo)-Pt(*8-q*)(I_2)] derivatives were obtained by reacting the corresponding square-planar tropolonate and 8-quinolinate precursors, **1** and **2** respectively, with 3 equivalents of iodine in acetone (**4**) or in dichloromethane (**5**), respectively, at room temperature, for 1 h. As in most oxidative additions, these reactions occurred with a colour change, in these cases, from red to orange (**4**) or brown (**5**). All products were obtained in yields in the range 70–90%. Reaction of the Pt(II) hexafluoroacetylacetonate derivative **3** with three equivalents of iodine, in acetone, was performed in an analogous manner, but the formulation of the Pt(IV) product obtained, on the basis of both the ^{1}H NMR spectrum and the elemental analysis, is [(Azo)Pt(1,1,1,5,5,5-hexafluoro-3-iodo-2,4-pentanedionate)(I_2)], **6**. Indeed, the proton spectrum of **6** is lacking the H^7 signal (scheme 2) of the platinum-bonded β-diketonate ring. This outcome suggests that the methinic proton of the *hfacac* fragment has been substituted by an iodine atom, possibly through an electrophilic attack [15] of a halogen atom on the diketone ring and subsequent loss of the H^7 proton. The reaction between the [(Azo)Pt(*hfacac*)] complex and I_2 was carried out by changing the conditions (i.e. lowering the molar ratio of iodine from 3 to 2 or 1.1 and/or performing the reaction in the absence of daylight) and gave a mixture of two isolable products (1:1 ratio) whose ^{1}H NMR spectra and elemental analyses account for the Pt(II) compound [(Azo)Pt(1,1,1,5,5,5-hexafluoro-3-iodo-2,4-pentanedionate)] and for the Pt(IV) complex **6**. Interestingly, these data suggest that the reaction occurs in two stages: a rapid substitution of the H^7 proton of the diketone ring with an iodine atom, followed by a comparatively slower oxidative addition of two iodide ligands to the Pt(II) centre.

However, for all complexes **4**–**6**, the ^{1}H NMR spectra show, when compared with the spectra of the parent Pt(II) complexes, a shift to low field of the cyclometallated ring signals (H^6, H^5, $\mathrm{H}^{2',6'}$); this is in keeping with the trend expected for a deshielded nucleus upon oxidation. The coupling $^3J(\mathrm{PtH})$ to the *ortho*-protons of the azo ligand was not detectable.

The [(Azo)Pt(*trop*)(I)(CH_3)], **7** and [(Azo)Pt(*8-q*)(I)-(CH_3)], **8** derivatives, orange and light brown, respectively, were easily synthesized by treating the appropriate Pt(II) precursor with $\mathrm{CH}_3\mathrm{I}$ in chloroform, at room temperature for 6 days [10]. Contrarily, attempts at oxidatively adding methyl iodide to the Pt(II) hexafluoroacetylacetonate species were unfruitful and even on changing solvents, molar ratio and reaction times, the square-planar starting material **3** was always the only product recovered.

3.2. *Thermal and liquid crystalline properties*

The thermal behaviour of compounds **1**–**8** has been studied by polarizing optical microscopy and differential scanning calorimetry (DSC). The transition temperatures and the corresponding enthalpy changes are listed in the table.

3.2.1. *Square-planar [(Azo)Pt(L)] complexes*

All the Pt(II) [(Azo)Pt(*L*)] complexes are mesomorphic, featuring a N phase (marbled texture) and, for compound **2**, a SmA phase (fan-shaped texture). A crystal to crystal transition is also observed for **1** and **2**. These complexes have very similar melting temperatures (**1** 174°C; **2** 162°C; **3** 165°C), which are lower by about 100°C than that of their dinuclear chloro-bridged parent (Cr 263°C SmC 342°C I). The clearing temperatures range from 209°C (**3**) to 279°C (**2**). Both complexes **2** and **3** undergo decomposition, preventing the possibility of following the cooling cycle scan. The chelating *L* ligand plays an important role in determining the stability and the nature of the mesomorphism; ongoing from the tropolonate derivative (**1**) to the 8-hydroxyquinolinate (**2**) a stabilizing effect is observed and the N phase appears over a temperature range which increases from 90 to 117°C (this last being a broader range than that

Table. Phase transitions of complexes **1**–**6**.

Complex	Transition^a	T/°C	ΔH/kJ mol^{-1}
1	Cr–Cr′	165.0	3.0
	Cr′–N	174.2	53.6
	N–I	264.1	0.6
2	Cr–Cr′	148.3	11.5
	Cr′–SmA	162.1	3.8
	SmA–N	189.2	22.6
	N–I	279.6^b	
3	Cr–N	164.7	32.9
	N–I	209.4^b	
4	Cr–I	209.8	39.0
	I–N	209.3	1.5
5	Cr–Cr′	173.0	5.1
	Cr′–SmC	211.2	26.8
	SmC–N	218.3	0.4
	N–I	255.0^b	
6	Cr–Cr′	217.5	24.8
	Cr′–SmC	250.2	18.7
	SmC–N	259.3	1.1
	N–I	289.0^b	

^{a} Cr = Crystal, N = Nematic, Sm = Smectic; I = Isotropic.
^{b} Decomposition.

of its dimeric precursor (80°C)). Differently for the hexafluoroacetylacetonate compound (**3**), the pronounced lowering of the clearing temperature induces a noticeable shortening of the liquid crystalline phase range.

In our previous investigations on cyclopalladated mononuclear complexes, we synthesized a series of 4-hexyloxy-4′-(4-octyloxybenzoyloxy)azobenzene derivatives containing the *hfacac* and the *trop* groups as chelating ligands. As far as the thermal behaviour is concerned, a comparison between these structurally similar mononuclear Pd(II) and Pt(II) complexes shows that changing palladium from platinum increases both the melting and clearing temperatures. Although a general trend could not be accurately established owing to the presence of a further aromatic ring in the HAzo ligand, such behaviour parallels the expected increase in polarizability on substituting Pt(II) for Pd(II).

3.2.2. *Octahedral [(Azo)Pt(L)(I)(X)] complexes*

Ongoing from the Pt(II) to the Pt(IV) species by the oxidative addition of I_2, the liquid crystallinity is preserved although it undergoes irregular changes, both as regards the nature of the mesophase and the thermal behaviour. In particular, it should be pointed out that all the iodo-derivatives preserve the N phase (monotropic in **4** and enantiotropic in **5** and **6**) exhibited by their square-planar precursors. In addition, complexes **5** and **6** show the more ordered SmC mesophase (schlieren texture).

The effect of the oxidative addition of I_2 on the transition temperatures strongly depends on the nature of the chelating ligand L. In particular, complexes **4** and **5** exhibit higher melting points and lower clearing points than their corresponding square-planar parents, and consequently a destabilization of the mesophase range is observed. For the hexafluoroacetylacetonate derivative **6**, an increase of both the melting and clearing temperatures by about 80°C results instead, leaving the thermal stability of the mesophase with respect to the Pt(II) precursor, unchanged.

Substitution of I_2 for CH_3I in the octahedral complexes [(Azo)Pt(L)(I)(CH_3)] gives species with a rather complicated mesomorphism. Thus, optical examination on heating complexes **7** and **8** showed SmC phases (schlieren texture) at 142 and 147°C, respectively. On further heating, both **7** and **8** show the same transition temperatures and the same kind of mesophase as the parent [(Azo)Pt(L)] complexes **1** and **2**. The DSC traces confirm this behaviour and display, after the first transition (at 142 and 147°C) an endothermic peak at 146°C and 154°C, respectively, accounted for by a structural change, namely the loss of the oxidatively added ligands. Remarkably, these results are further confirmed by ^{1}H NMR measurements indicating that the [(Azo)Pt(L)(I)(CH_3)] derivatives quantitatively revert to the respective Pt(II) starting materials, so that the oxidative addition of methyl iodide to [(Azo)Pt(L)] species is a thermally reversible process.

4. Conclusions

New mononuclear square-planar cycloplatinated azobenzene complexes [(Azo)Pt(L)] containing three different chelating ligands, L = tropolonate (*trop*), 8-hydroxyquinolinate (*8-q*) and 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate (*hfacac*), have been synthesized and investigated. A new synthetic procedure leading to straightforward coordinatively saturated metallomesogens has been developed and a series of Pt(IV) complexes, [(Azo)Pt(L)(I)(X)], has been obtained by oxidative addition of electrophilic reagents such as iodine or methyl iodide.

All Pt(II) and Pt(IV) compounds were found to be mesomorphic, exhibiting N and SmA or SmC phases. The influence of the chelating ligand L on the liquid crystalline behaviour seems to indicate that the 8-hydroxyquinolinate derivatives display the most interesting mesomorphism in terms of the nature and thermal stability of the mesophase.

Moreover, as regards the octahedral complexes, the oxidative addition of methyl iodide proved to be a thermally reversible process, suggesting that these species are of potential interest as switchable systems.

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