trans-Dichloro(stilbazole)(methyl *n*-alkyl sulfoxide)platinum(II) complexes: the first examples of metallomesogens containing chiral centres directly bonded to the metal

Francesco Paolo Fanizzi,*[a] Vincenzo Alicino,[a] Cosimo Cardellicchio,[b] Paolo Tortorella[b] and Jonathan P. Rourke*[c]

[a] *Dipartimento Farmaco-Chimico, Università di Bari, via E. Orabona 4, I-70125, Bari, Italy. E-mail: fanizzi@farmchim.uniba.it*
[b] *CNR Centro di Studio sulle Metodologie Innovative di Sintesi Organica, Dipartimento di Chimica, Università di Bari, via G. Amendola 173, I-70126, Bari, Italy*
[c] *Department of Chemistry, University of Warwick, Coventry, UK CV4 7AL. E-mail: j.rourke@warwick.ac.uk*

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The first examples of enantiomerically pure metallomesogens containing the chiral centre directly bonded to the metal are reported; the chiral complexes show different phase behaviour to the racemic modifications.

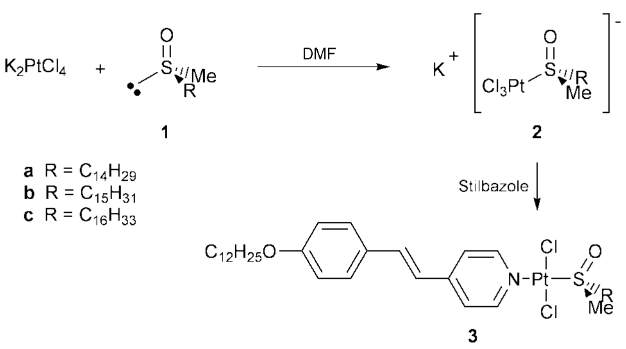
There are many examples of chiral liquid crystals. Since the properties that chirality can confer to liquid crystals, such as ferroelectricity, are very attractive for technological applications, interest in chiral liquid crystals is more than purely academic. Whilst there has been an upsurge of interest in metal containing liquid crystals (metallomesogens) over the last two decades,[1–3] there have been relatively few examples of chiral metallomesogens. Most of these metallomesogens have relied on a chiral centre remote from the central core of the molecule to induce the asymmetry.[4–8] To date, no-one has fully investigated the effect of directly bonding a chiral centre to a metal within the metallomesogen. Early examples include a family of platinum stilbazole alkene complexes which proved to be unresolvable,[9,10] and a family of ruthenium bipyridyl compounds, where no attempt was made to separate enantiomers.[11]

Sulfoxides are widely used as ligands in platinum chemistry, normally bonding through the sulfur. Chiral sulfoxides with two different substituents are configurationally stable, and can be resolved into enantiomers.[12,13] Thus chiral sulfoxides, with two different alkyl chains, present themselves as ideal ligands for platinum based metallomesogens. By using a stilbazole ligand to complete the coordination sphere of the platinum, we can prepare direct analogues of the alkene complexes reported earlier.[9,10] It has been shown that such a highly unsymmetrical structure can be very beneficial, with reductions in the melting and clearing points of up to 100 K.

Enantiomerically pure methyl(*n*-alkyl)sulfoxides are available[14] and the methodology for the synthesis of appropriate platinum complexes is well understood. Crucially, the chirality at the sulfur has been shown to be configurationally stable on coordination to platinum with no racemisation observed even on ligand displacement.[15] Thus, using both racemic and enantiomerically pure sulfoxides we were able to isolate the required neutral complexes in a simple two step procedure, in effectively quantitative yield (Scheme 1).† Recrystallization of the products in diethyl ether–chloroform gave analytically pure samples which were analysed by NMR,‡ elemental analysis,§ polarimetry,¶ DSC and hot-stage polarised optical microscopy (Table 1).

All the new complexes reported here showed mesogenic behaviour at accessible temperatures. The phase behaviour of the new complexes is listed in Table 1 and summarised in Fig. 1. Thus it can be seen that all the complexes showed a melting transition into a mesophase at around 70 °C and cleared into the isotropic between 120 and 135 °C.

The most significant observation is the difference between the thermal behaviour of the racemic and chiral forms. The racemic compounds clearly exhibit two mesophases: a highly



Scheme 1

Table 1 Thermal behaviour of compounds **3**

	Racemic	*T*/°C	Δ*H*/J g^{-1}	Chiral	*T*/°C	Δ*H*/J g^{-1}
3a	K–SmG	69.9	25.9	K–SmF	87.2	31.6
	SmG–SmF	72.5	25.7	K–I	128.3	38.6
	SmF–I	124.5	101.3			
3b	K–SmG	80.9	20.8	K–K′	75.4	5.4
	SmG–SmF	84.4	20.0	K′–SmF	92.6	24.6
	SmF–I	126.1	76.7	SmF–I	129.3	40.9
3c	K–SmG	74.8	17.6	K–K′	72.3	2.3
	SmG–SmF	85.1	17.4	K′–SmF	84.3	25.4
	SmF–I	118.6	63.3	SmF–I	121.7	28.5

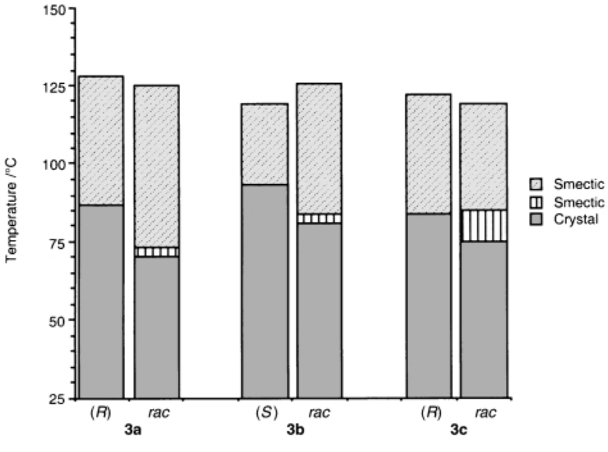


Fig. 1 Phase behaviour of compounds **3**.

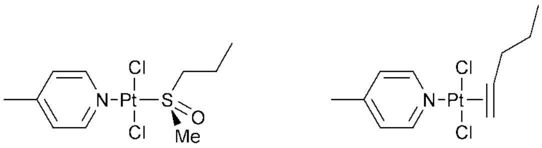


Fig. 2

ordered crystal smectic G followed by a smectic F‖ at higher temperatures, whereas the enantiomerically pure compounds only exhibit the smectic F phase. The melting points of the enantiomerically pure compounds are all about 10 K higher than the racemic compounds, though the clearing points are much more similar.

That the melting points of the chiral and racemic forms show a large difference is not totally unexpected: the packing arrangements within the crystal forms (assuming that the racemic form crystallises with both enantiomers present in the unit cell) must be substantially different—thus the melting points must be different. The presence of a short lived crystal smectic G for the racemic form at a temperature before the enantiomerically pure compound even melts can also be attributed to the differing crystal forms. At higher temperatures the molecules are much more mobile, therefore the intermolecular forces are more of an average, and thus less dependent on the precise structure of the molecule. Hence, the effect of enantiopurity on thermal behaviours is reduced and the final transition to the isotropic liquid is much the same for both racemic and enantiomerically pure compounds.

This type of effect has been seen on a number of occasions with organic compounds, with perhaps the most graphic demonstration being the existence of the so-called twist grain boundary phases,[16] though such a large effect has never been observed before with metallomesogens. This is almost certainly due to the presence of the chiral centre directly bonded to the mesogenic core, rather than remote on a chain. One group have reported the use of chiral carboxylates to bridge palladium centres within a dimeric metallomesogen, which gives rise to blue phases which would not have been present in the racemic mixtures.[8]

The alkene complexes reported earlier[9,10] typically melt into a smectic A phase at around 50 °C which persists until clearing at a temperature of around 90 °C. Thus the mesogenic range of the new sulfoxide complexes is greater than that of alkene complexes reported earlier, albeit at a slightly higher temperature. However, the major difference is the observation of the more ordered smectic F phases with the sulfoxide complexes, compared to the relatively disordered smectic A phase for the alkene complexes. This difference is highly significant, as it implies much stronger lateral interactions between the sulfoxide complexes than between the alkene complexes. Simplistically, one could ascribe this difference to one or both of two factors: the steric arrangement around the platinum, or the electronic effects of the different ligands. The geometry of a coordinated sulfoxide at platinum is known to approximate to a tetrahedral sulfur,[17] thus resulting in a compact arrangement and allowing the long chains to freely lie along the main axis of the molecule. In contrast, a coordinated alkene bonds *via* a face-like interaction, resulting in the alkyl chain being forced away from the main axis of the molecule (Fig. 2). Thus these steric factors would suggest the sulfoxide complexes would be able to achieve the greater lateral interactions necessary for the smectic F phase, whereas the alkene complexes could not. The major electronic difference between the two families relates to the sulfur–oxygen double bond. However since this bond is known to only be weakly polarised, any dipole that arises is almost certainly insignificant. Changing the sulfoxide for the alkene also has some effect on the melting point—the octadecene (effectively a 16 carbon chain) complex has a melting point of 64 °C compared with 75 °C for the racemic C-16 sulfoxide **1c** and 84 °C for the chiral analogue. The corresponding clearing points are 88 °C for the octadecene, and 119 and 122 °C for the racemic and chiral sulfoxides, respectively. Once again the most probable cause of the variation is the steric effect of the alkene which will destabilise both the crystal and the mesophase, resulting in lower transition temperatures.

We are now investigating the full range of platinum sulfoxide complexes over the full range of enantiopurity in order to see if the effects we observe are accentuated with longer or shorter chain lengths and to fully characterise the effect of enantiopurity on phase behaviour.

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Notes and references

† Methyl alkyl sulfoxide **1** (0.30 mmol) dissolved in DMF (4 ml) was added to a suspension of potassium tetrachloroplatinate (0.30 mmol) in DMF (1 ml). The mixture was stirred (40 °C, 16 h) giving a deep yellow solution. The solution was filtered to remove KCl and **2** precipitated as a yellow compound upon addition of diethyl ether (20 ml) followed by hexane (20 ml).

Alkoxy stilbazole (0.10 mmol) dissolved in acetone (5 ml) was added to a solution of **2** (0.10 mmol) in acetone (50 ml). The solution was stirred (1 h) by which time it had changed to a paler yellow colour. The solution was concentrated to one third of the original volume and **3** precipitated by addition of diethyl ether. The product was collected by filtration, washed with diethyl ether, then methanol and dried in air. Yield: 95% (0.095 mmol).

The chiral sulfoxides used were (*S*)-**1a**, (*R*)-**1b** and (*S*)-**1c**. Note that the priority at sulfur reverses on coordination to platinum, thus an (*R*)-sulfoxide becomes an (*S*)-platinum complex.

‡ δ_H($CDCl_3$, 400.0 MHz): 8.61 (2H, AA′XX′, ^3J 8 Hz), 7.50 (2H, AA′XX′, ^3J 8 Hz), 7.40 (2H, AA′XX′, ^3J 8 Hz), 7.34 (1H, d, ^3J 16 Hz), 6.93 (1H, AA′XX′, ^3J 8 Hz), 6.87 (2H, d, ^3J 16 Hz), 4.00 (2H, t, ^3J 7 Hz), 3.69 (1H, m), 3.40 (3H, s), 3.38 (1H, m), 2.11 (2H, m), 1.79 (2H, m), 1.4–1.3 (m), 0.87 (6H, t, ^3J 7 Hz).

§ Elemental analysis found (calc.): *rac*-**3a**: C 54.2 (53.9), H 7.7 (7.6), N 1.5 (1.6); (*R*)-**3a**: C 53.8 (53.9), H 7.6 (7.6), N 1.6 (1.6); *rac*-**3b**: C 54.0 (54.4), H 7.6 (7.7), N 1.8 (1.6); (*S*)-**3b**: C 54.4 (54.4), H 7.8 (7.7), N 1.4 (1.6); *rac*-**3c**: C 54.6 (54.8), H 7.4 (7.8), N 1.2 (1.5); (*R*)-**3c**: C 55.0 (54.8), H 7.7 (7.8), N 1.6 (1.5)%.

¶ $[\alpha]_D$ values at 20 °C: **3a** − 12.2°; **3b** + 12.5°; **3c** −12.4°

‖ Phases were identified by their optical textures: the smectic F was distinguished from the smectic I by the lack of point disclinations.

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