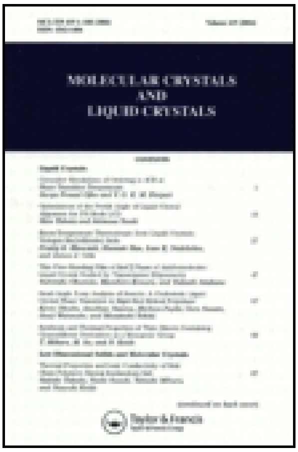

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Mesomorphic Metal Complexes Derived from 4-Alkyl-oxystilbazoles

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Mesomorphic Metal Complexes Derived From 4-Alkyloxystilbazoles

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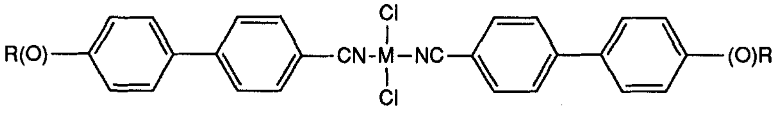
Abstract The weakly mesomorphic *trans*-4-alkyloxy-4'-stilbazoles (*n*-OPhVPy) are readily synthesised from alkyloxyiodobenzenes and 4-vinylpyridine in a palladium-catalysed Heck reaction. While the highly symmetric palladium and platinum complexes *trans*-[MCl_2(*n*-OPhVPy)$_2$] show mesophases only at very high temperatures, the lower symmetry platinum complexes *trans*-[$PtCl_2(\eta^2$-olefin) (*n*-OPhVPy)] melt below 100°C. Similarly, the complexes [MCl$(CO)_2$(*n*-OPhVPy)] (M = Rh, Ir) are low melting. The silver complexes [Ag(*n*-OPhVPy)$_2$][X] (X = $C_{12}H_{25}OSO_3$, $C_8H_{17}OSO_3$, CF_3SO_3) can be obtained by direct reaction of the stilbazole with AgX. These ionic materials show a rich thermotropic polymorphism, including nematic and cubic mesophases. Some fluorinated stilbazoles have also been synthesised and complexed to silver; the mesomorphism of these complexes is also reported.

Keywords: metallo-mesogens, iridium, rhodium, silver, cubic mesophase, ionic nematic

Introduction

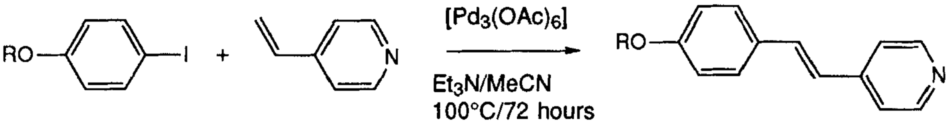
Since the synthesis of the mesomorphic dithiolene complexes of Ni by Giroud-Godquin and Mueller-Westerhoff in 1977[1], work in the area of metal-containing liquid crystals has grown enormously[2]. Much of the interest in metallomesogens stems from the possibilities offered by the inclusion of an electron-dense centre into an ordered medium, such as high birefringence, large hyperpolarisability and enhanced dielectric properties; these are in addition to the properties of colour and paramagnetism which are easily incorporated into metal complexes. Furthermore, many new geometries are offered by metal centres (octahedral; trigonal bipyramidal etc) which may in turn lead to new phase types. The recent report of mesomorphic materials based on a tetrahedral carbon[3] are particularly relevant in this regard.

Our work in this area began with the synthesis of the palladium and platinum complexes of the well-known organonitriles (**1** and **2**) which we found to show predominantly nematic phases[4].



1 M = Pd
2 M = Pt

However, one of the problems associated with materials of this type is the relatively labile metal-nitrile linkage which limits the stability of the complexes, especially for palladium. In order to overcome this problem, the 4-alkyloxystilbazoles (*n*-OPhVPy - where *n* represents the number of carbon atoms in the alkyloxy chain) were synthesised[5] as metal-pyridine bonds are generally less labile, particularly for elements at the right hand side of the periodic table. Initially, the ligands were synthesised by reaction of 4-picoline with a 4-alkyloxybenzaldehyde in acetic anhydride[6], but such conditions gave only tiny yields after long reactions. A better procedure was subsequently developed which used Heck-type vinylic addition reactions[7] catalysed by palladium as described in Scheme 1.



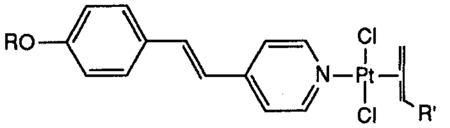
Scheme 1 Synthesis of 4-alkyloxystilbazoles

Using this route, yields in excess of 65% can be routinely obtained and quantities up to 20g can be made in one reaction. The *trans* geometry about the double bond was first assigned using ^{1}H n.m.r. spectroscopy (J = 17 Hz) and was subsequently found in three single crystal determinations[8]. The ligands themselves were found to be weakly mesomorphic and showed a wide range crystal E phase below a narrow range S_B phase; clearing points were typically in the region of 85-90°C.

Results and Discussion

Complexes of the Stilbazoles with Palladium(II) and Platinum(II)

Initially, these stilbazoles were complexed to palladium and platinum to make the complexes *trans*-[MCl_2(*n*-OPhVPy)$_2$], analogous to **1** and **2**. These were high melting materials and only the longest chain homologues (typically $n > 9$) showed any mesomorphism. Thus, the materials would melt above 200°C into an S_C phase and then decompose before clearing. Better results[9] were however obtained from the olefin complexes *trans*-[$PtCl_2$(η^2-olefin)(*n*-OPhVPy)] (**3**).



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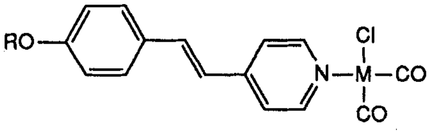
These complexes all melted at temperatures between 60 and 110°C to form S_A phases which cleared at temperatures between 90 and 110°C. These results and those described below for the Rh and Ir complexes of the stilbazoles point to the fact that lower symmetry appears to lower the stability of the crystal phase, allowing mesomorphism at lower temperatures.

Complexes of the Stilbazoles with Rhodium(I) and Iridium(I)

Synthesis and Mesomorphism

Reaction of *n*-OPhVPy with [MCl(η-1,5-cyclooctadiene)]$_2$ (M = Rh, Ir) in dichloromethane under an atmosphere of CO led to the mesomorphic complexes (**4** and **5**)[10]. Related complexes with 4'-alkyloxy-N-(4-pyridylbenzylideneaniline) ligands have been reported by Serrano and co-workers[11].



4 M = Rh
5 M = Ir

The phase behaviour of both series of materials was very similar; the phase diagram for the iridium complexes is shown in Figure 1.

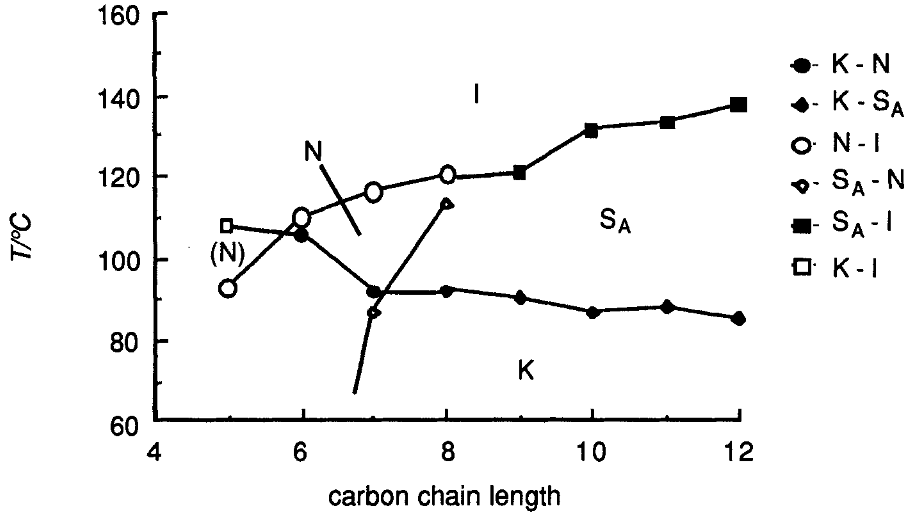


Figure 1 Phase diagram for *cis*-[IrCl(CO)$_2$(*n*-OPhVPy)]
(*Reproduced from reference 10 by kind permission of the Chemical Society*)

Thus in general, the materials melted between 80 - 100°C to give a nematic (*n* = 6 - 7 (Ir), *n* = 5 - 7 (Rh)) or S_A phase (*n* = 8 - 12); the clearing points were in the range 110 - 140°C. For M = Ir, these materials could be cycled in and out of the mesophases with no decomposition problems (unless the isotropic phase was maintained for long periods), while for M = Rh, the materials began to decompose on melting; this decomposition was slowed in an inert atmosphere.

Given the very weakly mesomorphic nature of the stilbazole ligands, the strongly mesomorphic nature of these complexes was at first surprising. However, in the literature of organic liquid crystals, it is known that extension of the molecular length without increase of the breadth of a molecule will increase the thermal stability of a mesophase and that in relation to the nematic phase in particular, certain groups are better than others at stabilising the nematic phase. Given the limited number of complexes yet available, good comparisons are difficult but on the basis of the available materials, we have suggested that the d^8 fragment *cis*-[IrCl(CO)$_2$] is as good as the nitrile group in stabilising the nematic phase while *cis*-[RhCl(CO)$_2$] is appreciably better[10].

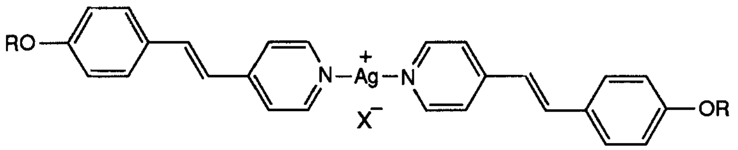
Physical Measurements

For both the stilbazole ligands and their iridium complexes, it was possible to make measurements of the mean polarisability, $\bar{\alpha}$ and the polarisability anisotropy, $\Delta\alpha$[12]. The stilbazoles themselves gave values of $\bar{\alpha}$ of around $35 \pm 4 \times 10^{-40}$ $J^{-1}C^2m^2$ which is broadly similar to materials such the cyanobiphenyls, although $\Delta\alpha/\bar{\alpha}$ was somewhat higher at around 0.8. However, the iridium complexes show a marked increase in both parameters, with $\bar{\alpha} = 60 \pm 8 \times 10^{-40}$ $J^{-1}C^2m^2$ and $\Delta\alpha/\bar{\alpha} \approx 0.9$. This is clear evidence that it is possible to use the highly polarisable electrons of the metal and that they do contribute to the overall polarisability of the materials. These high polarisabilities may also be related to the nematic stability of these complexes.

Birefringence measurements have also been possible[13] and have shown that the iridium complex *cis*-[IrCl(CO)$_2$(8-OPhVPy)] has $\Delta n = 0.166$ at a reduced temperature (T/T_{NI}) of 0.985.

Complexes of the Stilbazoles with Silver(I)

Reaction of the stilbazoles with a variety of silver(I) salts AgX (X = $C_{12}H_{25}OSO_3$ (DOS), CF_3SO_3 (OTf) and $C_8H_{17}OSO_3$ (OS)) led to the linear complexes [Ag(*n*-OPhVPy)$_2$][X] (**6**), all of which were mesomorphic. For each series, the shorter chain homologues all showed a nematic phase, while S_C and S_A phases were seen at longer chain lengths.



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The appearance of the nematic phase in these ionic materials[14] was particularly surprising, given the apparent conflict between the anisotropic nature of the forces associated with the formation of a nematic phase and the isotropic nature of ionic forces. However, if ion-pairing is important in these systems (and conductivity measurements appear to imply that it is), then anisotropic attractive and repulsive interactions could overcome the isotropic coulombic forces.

Mesomorphism in the Triflate Salts

The phase diagram for the triflate salts is shown in Figure 2.

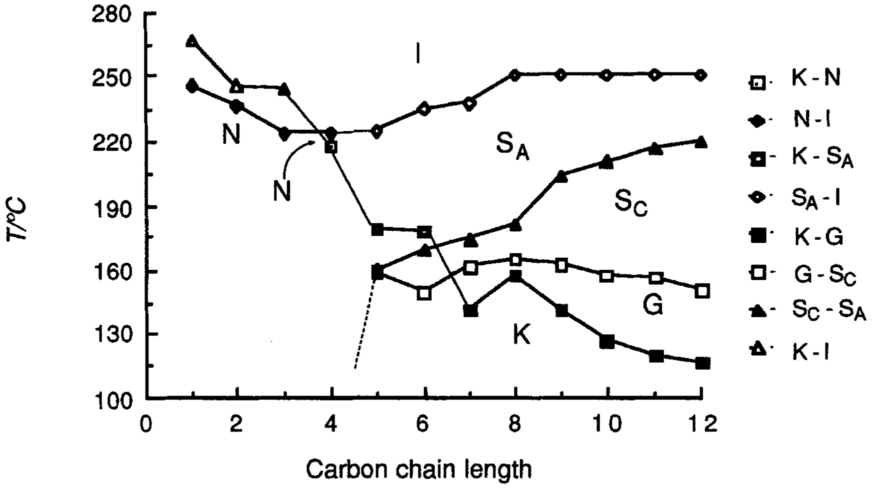


Figure 2 Phase diagram for $[\mathrm{Ag}(n\text{-OPhVPy})_2][\mathrm{CF_3SO_3}]$

The first four homologues show nematic mesophases which were monotropic for $n = 1 - 3$; the temperatures shown for the (N - I) transition are approximate as the materials rapidly decomposed at or around the clearing point. At $n = 5$, the nematic phase disappeared and an S_A phase was seen which then persisted through all other homologues. In addition, monotropic S_C and crystal G phases were seen and as the chain length was increased, these became more stable with respect to the crystal phase so that at $n = 7$, they were both enantiotropic. The S_A and S_C phases were readily identified from their optical textures and the G phase was likewise assigned, on the basis of the large, coloured mosaic plates formed on cooling the schlieren texture of the S_C phase[15]. While these materials were generally quite stable, at high temperatures in the S_A and isotropic phases, decomposition was apparent and the clearing points of the n = 8 - 12 compounds reflect this decomposition.

Mesomorphism in the Alkylsulphate Salts

The phase diagram[16] for the DOS compounds is shown in Figure 3.

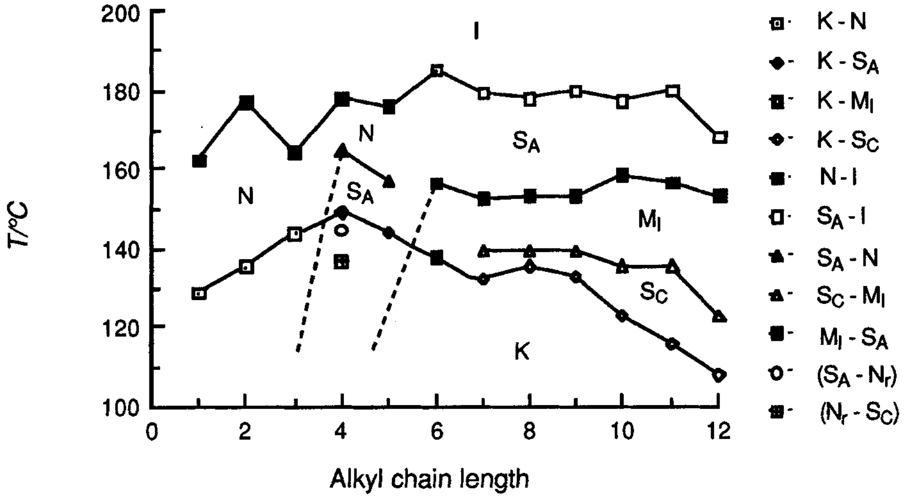


Figure 3 Phase diagram for $[Ag(n\text{-}OPhVPy)_2][C_{12}H_{25}OSO_3]$

The first thing which was immediately apparent was that the transition temperatures into true liquid crystal phases were appreciably lower than those found in the OTf salts and that the crystal smectic phase had disappeared. The destabilisation of the highest temperature phases (N or S_A) and of the crystal phase in the lower homologues is attributed to lower structural anisotropy and poorer crystal packing respectively, caused by the introduction of an amphiphilic anion. That the clearing temperatures of these materials were so much lower than those of the OTf salts provides additional evidence that the mesomorphic unit in the mesophase is a tight-bound ion pair rather than a 'free' bis(stilbazole)silver(I) cation.

The phase diagram shows that the nematic phase persists to the pentyloxy homologue, with the butyloxy homologue showing a monotropic re-entrant nematic phase and a monotropic S_C phase; from $n = 7$ onwards, the phase sequence was $K \rightarrow S_C \rightarrow M_I \rightarrow S_A \rightarrow I$. The phase labelled M_I deserves further comment. The abbreviation M_I stands for *isotropic mesophase* and the phase is very similar in its behaviour and properties to the cubic D phase of the laterally-substituted biphenylcarboxylic acids[17]. Thus, the phase exists between an S_C and a strongly homeotropic S_A phase, it is optically isotropic, viscous and appears with another phase whose optical textures are those of the S_4 phase. X-Ray studies of the phase showed that the phase is face-centred cubic with lattice parameters of 66 and 73Å for the nonyloxy- and dodecyloxy- derivatives respectively. Final assignment as further examples of the D phase must await X-ray studies of monodomain samples.

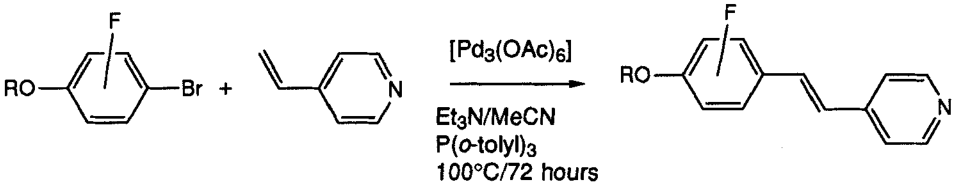
The phase behaviour of the OS salts was broadly similar to that of the DOS salts with the following important differences. First, the nematic phase extended right up to the $n = 6$ homologue and was the only phase observed for the first five homologues, although it was monotropic for $n = 2$ and 3. The mesomorphism of the hexyloxy homologue was interesting as it showed an enantiotropic re-entrant nematic phase, giving the following phase sequence:

$$K\ 136\ S_C\ 140\ N_r\ 151\ S_A\ 163\ N\ 169\ I$$

In general, the melting and clearing points of the two series were comparable and the thermal stability of the S_C phases in each were similar. However, the cubic phase was absent in the OS compounds and thus the S_A range extended to lower temperatures. This raises interesting questions about the factors which stabilise the cubic phase and the mesomorphism of silver complexes of other alkylsulphates is currently under investigation.

Silver(I) Complexes of Fluorinated Alkyloxystilbazoles

While the effects of lateral fluorination in organic systems have been well-studied, they have been largely ignored in the study of metal-containing systems. We therefore undertook the synthesis[18] of 4-alkyloxy-3-fluoro-4'-stilbazoles (*n*-O-3F-PhVPy) and 4-alkyloxy-2-fluoro-4'-stilbazoles (*n*-O-2F-PhVPy) according to the route in Scheme 2. The mesomorphism of the resulting silver complexes is still under investigation[19], but some of the preliminary results are given below.



Scheme 2 Synthesis of fluorinated alkyloxystilbazoles

Complexes of 4-Alkyloxy-3-fluoro-4'-stilbazoles

The salts $[Ag(n\text{-}O\text{-}3F\text{-}PhVPy)_2][DOS]$ are mesomorphic for all *n*, but the nematic phase is strongly destabilised so that it is seen only in the methyloxy homologue. From $n = 2 - 4$, the S_A is the only phase seen and it persists in all homologues, being stabilised by about 20°C relative to the non-fluorinated materials. An enantiotropic S_C phase is stabilised by $n = 6$ and again persists in all homologues; a phase below the S_C has still to be identified. These materials enter the S_C phase at temperatures comparable to their non-fluorinated counterparts and undergo an S_C - S_A transition at temperatures where the M_I phase (now absent) was seen; thus the S_A range is also extended downwards in temperature in these complexes.

The salts $[Ag(n\text{-}O\text{-}3F\text{-}PhVPy)][OTf]$ show a similar pattern. The first three homologues are now non-mesomorphic and no nematic phase is seen in the series. Melting points and S_C - S_A transitions ($n = 8$ onwards) do not deviate much from the non-fluorinated system and the clearing points of the S_A phase are very slightly stabilised.

Preliminary X-ray studies on the S_A phase of these materials show that unlike the non-fluorinated materials, the S_A phase is not interdigitated.

Complexes of 4-Alkyloxy-2-fluoro-4'-stilbazoles

The phase behaviour of the 2-fluoro derivatives is however quite different, although we do not yet have full homologous series. The complexes [Ag(*n*-O-2F-

PhVPy)][OTf] show the nematic phase to be stabilised up to the $n = 6$ derivative, after which only S_C and S_A phases are seen. The S_A phase is destabilised relative to the non-fluorinated derivatives as is the S_C phase; the crystal G phase has been suppressed.

More remarkable changes are observed in the complexes with the DOS anion. All homologues up to and including the heptyloxy complex show a nematic phase and a stable S_C phase is introduced from $n = 5$. From $n = 7$, the M_I phase appears, although now in a new phase sequence sandwiched between a S_C and a N phase, while for the higher homologues, preliminary studies indicate that the M_I phase exists between the S_C and isotropic phases. The clearing temperatures of all of the 2-fluoro derivatives is destabilised relative to the non-fluorinated analogues.

Acknowledgements

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