

Liquid Crystalline Complexes of Octahedral Manganese(I)

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Liquid crystalline metal complexes of Mn^I are reported which comprise an aromatic imine bound in an orthometallated fashion to a $Mn(CO)_4$ moiety; these are unique examples of calamitic thermotropic liquid crystals containing a metal with a simple octahedral coordination environment.

The synthesis and characterisation of metal complexes with liquid crystalline properties is now a well established area of materials chemistry and has been the subject of five recent reviews.¹⁻⁵ An examination of the literature quickly shows that of all the thermotropic liquid crystalline complexes synthesised thus far, the vast majority contain metals in a linear or planar environment and usually with a d^8-d^{10} electronic configuration. Notable exceptions are five-coordinate complexes of the vanadyl and $Fe^{II}-Cl$ moieties,² both bound in a square-pyramidal fashion, some complexes of the $Fe(CO)_3$ unit⁶ and the increasing literature of mesomorphic ferrocene complexes.⁷ However, most metal complexes are not derived from metallocenes or from metals in Groups 8-12 and so there are whole areas of the periodic table for which calamitic liquid crystalline complexes have not yet been synthesised.⁸

This is, however, not a straightforward problem, as it is necessary to match the need of liquid crystals to have

structural anisotropy with the inevitable disruption which will be caused to such anisotropy by the introduction of high-coordinate and therefore bulky metal complex fragments.

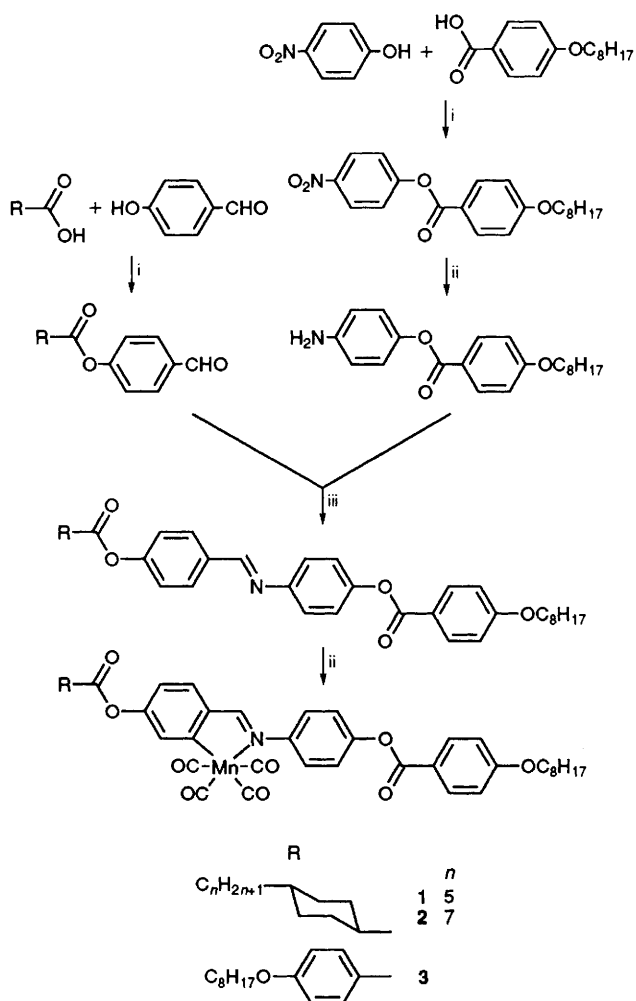
In attempting to devise a strategy for the synthesis of such high-coordination number complexes, we reasoned that the organic fragment would need to be sufficiently anisotropic so that the perturbations produced by the addition of a metal centre could be minimised. A previous attempt to synthesise octahedrally-based liquid crystals was that of Giroud-Godquin and Rassat⁹ who made tris(diketonato)iron(III) complexes which were non-mesomorphic. Our consideration of this problem was informed by the work of Deschenaux *et al.*¹⁰ with 1,3-disubstituted ferrocenes where it was found that four rings (plus the ferrocene unit) were necessary to promote mesomorphism.

We combined our reasoning and Deschenaux's findings and now wish to report liquid crystals derived from octahedral Mn^I bound to orthometallated imine ligands. Orthometallated imines of palladium have previously been reported by Espinet and co-workers,¹¹ but in these complexes the ligands were bound to planar (d^8) palladium centres.

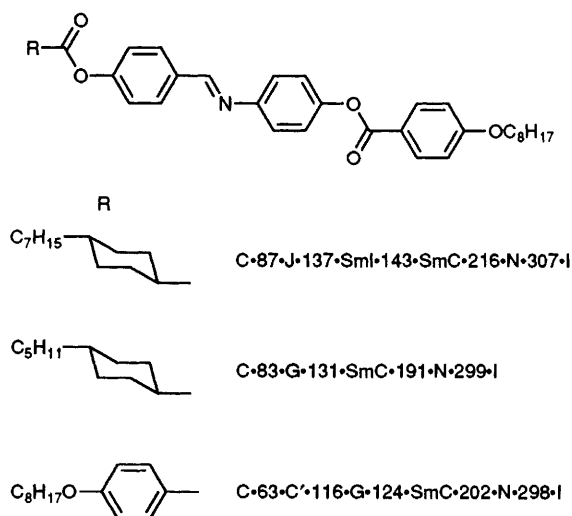
The complexes were synthesised according to the procedures shown in Scheme 1.[†] All of the reactions are based on procedures well-documented in the literature, except that we found that orthometallation¹² was best achieved by reflux in toluene, with yields of about 70% for this stage.

The mesomorphism of the parent ligands is given in Scheme 2 and it can be seen that all are polymorphic with nematic, smectic C (identified unequivocally) and other, more ordered phases. The assignments of the SmI, and crystal smectic J and G phases is on the basis of optical microscopy alone and will be confirmed by other techniques in due course. The high structural anisotropy of these materials is reflected in their very high clearing points.

The orthometallated complexes, however, melted at much reduced temperatures and showed only nematic phases at temperatures typically between about 120 and 190°C as evidence by the characteristic optical texture (see Fig. 1). The complexes began to decompose around their clearing point



Scheme 1 Synthesis of the mesomorphic manganese complexes. Reagents and conditions: i, 1,3-Dicyclohexylcarbodiimide, 4-dimethylaminopyridine, CH_2Cl_2 ; ii, $SnCl_2 \cdot 2H_2O$, EtOH; iii, toluene, HOAc; iv, $[MnMe(CO)_5]$, toluene.



Scheme 2 Thermal behaviour for the parent imine ligands

(darkening seen under the microscope and complex endotherms seen in the DSC), but if cooled from just above the melting point, they showed the nematic phase down to room temperature. The thermal behaviour is collected in Table 1.

That only a nematic phase is seen is entirely consistent with the general effects of lateral substitution of liquid crystals by relatively bulky groups. Such substitution tends to act to reduce lateral interactions and so disfavour smectic phases.

The complexes described are both the first examples of liquid crystalline metal complexes showing simple octahedral coordination and the first examples of calamitic (rod-like) liquid crystalline metal complexes containing manganese.

We thank the University of Sheffield for the award of a

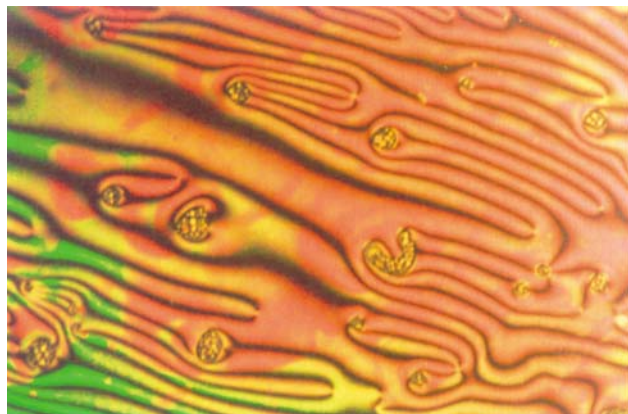


Fig. 1 Optical texture of the nematic phase of one of the manganese complexes ($R = C_8H_{17}OC_6H_4$; Scheme 1) at 166°C on cooling

Table 1 Transition temperatures for the new manganese complexes

Compound	Transition	$T/^\circ C$
1	C-N	135
	N-I	184
2	C-N	122
	N-I	180
3	C-N	154
	N-I	190

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Footnote

† All new complexes were fully characterised by IR, NMR and elemental analysis for which satisfactory results were obtained. For example, ν_{CO} were found at 2078m, 1993vs and 1942s cm^{-1} . Further, in the 1H NMR spectra, the AA'XX' pattern for the ring to be metallated changed to an AMX system on metallation.

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