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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Bruce, Duncan W. and Liu, Xiao-Hua(1995) 'Mesomorphic complexes of rhenium(I) and manganese(I)', *Liquid Crystals*, 18: 1, 165 – 166

To link to this Article: DOI: 10.1080/02678299508036607

URL: <http://dx.doi.org/10.1080/02678299508036607>

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Mesomorphic complexes of rhenium(I) and manganese(I)

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(Received 1 August 1994; accepted 9 September 1994)

Following our discovery of liquid crystals based on octahedral manganese(I), we have now extended these studies to the synthesis of what we believe to be unique examples of mesomorphic rhenium-based complexes. These complexes offer advantages over the related manganese(I) systems in that they are more thermally stable. Further, modification of the organic backbone has led to lower melting manganese materials.

For some time, derivatives of ferrocene (and some of ruthenocene) have been the sole examples of six-coordinate complexes forming calamitic mesophases [1] the vast majority of the literature on calamitic metal complexes concentrating on 2- and 4-coordinate complexes of metals taken from groups 9-11 [2].

Informed by these studies on ferrocene, we began to search for rational means by which high coordination number metal centres could be successfully used as the basis for the construction of calamitic materials. Recently, we reported [3] some success in this search with the synthesis of complexes of octahedral manganese(I), based on the orthometallation of some mesogenic imines (see figure 1; M = Mn). The design of these materials was based on the premise that if a large structural perturbation (i.e. 6-coordinate metal centre) were to be tolerated in a mesogen, then the organic part would need to be

sufficiently anisotropic to withstand such disruption. The strategy was successful and the manganese complexes demonstrated nematic mesophases in the range 100-190°C.

One of the problems sometimes encountered in the study of mesomorphic metal complexes is the lack of thermal stability of the materials at the clearing point, which can be a significant drawback if it is intended to study physical properties. In order to try to get round this problem, we decided to synthesize the related complexes of rhenium(I) on account of the fact that metal complexes of 3rd row transition elements are normally much more stable than their 2nd and 1st row counterparts. Another strategy to obtain more stable materials was to modify the metal/ligand combination to access lower melting systems. We now report the results of studies along these lines.

Yellow rhenium complexes analogous to their manganese counterparts were prepared by reaction of $[\text{ReMe}(\text{CO})_5]$ [4] with the relevant imine in boiling toluene, followed by column chromatography in dichloromethane using a neutral alumina stationary phase. Yields were in the range 75-85 per cent. All the new complexes were characterized by elemental analysis, infrared spectroscopy and by conventional ^1H and ^{13}C NMR spectroscopy and 2-D NMR experiments. The new manganese complexes were made, purified and characterized in the same way.

The new complexes are described in figure 2 and table 1, and the mesomorphic properties are given in table 2. Comparison of the results for complexes I-III with those for the related manganese complexes reported in [3] reveals that the mesomorphism is exactly comparable, while the transition temperatures are broadly comparable, most agreeing to within 7° or so. In all cases, the clearing

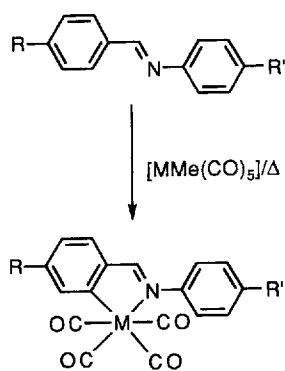


Figure 1. Synthesis of the mesomorphic metal complexes.

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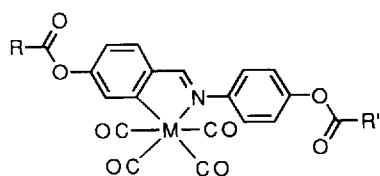


Figure 2. New Mn and Re complexes.

Table 1. Structure of the new complexes.

Complex	M	R	R'
I	Re	C ₅ H ₁₁ -C ₆ H ₁₀ -	-C ₆ H ₄ -OC ₈ H ₁₇
II	Re	C ₇ H ₁₅ -C ₆ H ₁₀ -	-C ₆ H ₄ -OC ₈ H ₁₇
III	Re	C ₈ H ₁₇ O-C ₆ H ₄ -	-C ₆ H ₄ -OC ₈ H ₁₇
IV	Mn	C ₇ H ₁₅ -	-C ₆ H ₄ -OC ₈ H ₁₇
V	Mn	C ₁₁ H ₂₃ -	-C ₆ H ₄ -OC ₈ H ₁₇
VI	Mn	C ₈ H ₁₇ O-C ₆ H ₄ -	C ₇ H ₁₅ -
VII	Mn	C ₈ H ₁₇ O-C ₆ H ₄ -	C ₁₁ H ₂₃ -

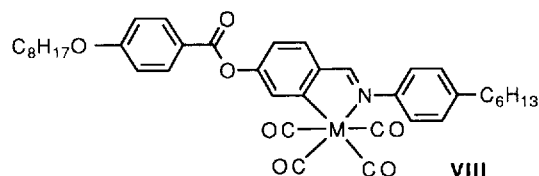
Table 2. Mesomorphism of the new complexes.

Complex	Transition	T/°C
I	C-N	147
	N-I	177
II	C-N	129
	N-I	171
III	C-N	135
	N-I	176
IV	C-I	124
	(N-I)	(85)
V	C-I	92
	(N-I)	(63)
VI	C-I	123
	(N-I)	(83)
VII	C-I	93
	(N-I)	(73)

points of the ligands have been substantially reduced (see [3] for data on some of the free ligands) on complexation, as expected with the introduction of a lateral substituent. For example, complex III clears at 176°C compared to 298°C for the parent free ligand. The similarity between the rhenium and manganese complexes is unsurprising, given that one would expect them to be effectively isostructural in every regard, the only small differences being expected in metal-to-ligand bond lengths and angles, given the large radius of Re versus Mn. However, the major difference is that the

Re complexes appear to be stable in the isotropic phase, whereas their manganese analogues decomposed immediately.

Examination of the data for complexes IV-VII reveals how a change in the ligand can also affect the thermal parameters. Thus, removing a phenoxy group from complex III leads to alkanoyloxy-substituted materials which show monotropic nematic phases. The octanoyloxy derivatives (IV and VI) melted at 124 and 123°C, giving mesophases at 85 and 83°C, respectively, showing that the position of the alkanoyloxy chain on the left or right of the molecule of the complex was unimportant in determining the temperatures of transition. Lengthening the terminal chain to dodecylloxy (complexes V and VII) served to destabilize further both the crystal and nematic phases. An interesting comparison is also made between complex VIII which is structurally analogous to VI and VII except for the nature of the group—alkyl (VIII) of alkanoyloxy (VI and VII)—attached to the aniline-derived ring. Thus, VIII is non-mesomorphic, melting straight to an isotropic fluid at 110°C. Hence the nature of the terminal group is important, even if its position is not.



These new manganese complexes have mesophases approaching room temperature, although for now, the melting points render the nematic phases rather inaccessible. However, we believe that by using mixtures, low-melting preparations can be achieved and such studies are already underway.

We thank the University of Sheffield for a studentship to X.-H.L.

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