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On the design of high co-ordination number metal-based liquid crystals: mesomorphic bipyridine complexes of rhenium(I)

Kathryn E. Rowe and Duncan W. Bruce *

Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, UK

Based on studies of bipyridine complexes of Re^I, design criteria for the construction of liquid-crystalline complexes of high co-ordination number metal centres have been proposed.

As part of our studies of metal-based liquid-crystalline materials, we have become interested in the problems associated with the inclusion of metals with high co-ordination number requirements into calamitic liquid crystals.[1]

Our first success in this area was represented by the synthesis and mesomorphism of orthometallated manganese(I)[2] and rhenium(I)[3] carbonyl complexes of imine ligands (Fig. 1). Here we found that in the main, a liquid-crystalline ligand containing at least four rings in its structure was required in order that the subsequent complex was mesomorphic. However, we did see some examples where only three rings were needed, although the liquid-crystal phases were less thermally stable than the crystalline phase.[3]

We subsequently extended the approach to the examination of complexes of mesomorphic diazabutadienes and here, we also found that a four-ring ligand successfully led to mesomorphic complexes of octahedral Re^I.[4] A further example was provided by the co-ordination of two mesomorphic, three-ring acetylene ligands to octahedral Rh^{III}, generating liquid-crystalline complexes (although these systems suffered from thermal instability).[5]

Encouraged by the success of this approach, we turned our attention to the synthesis and design of mesomorphic ligands based on 2,2′-bipyridines, with a view to their subsequent complexation to form further examples of octahedral, metal-based liquid crystals. Thus, we have previously reported[6] the synthesis and liquid-crystal properties of some four-ring, 5,5′-diesters of 2,2′-bipyridine (Fig. 2). However, attempts to obtain mesomorphic complexes based on these compounds were remarkably unsuccessful and complexation to $[ReBr(CO)_3]$ simply gave complexes which melted at rather high temperatures. Thus, it seemed that our four-ring strategy for the generation of high co-ordination number systems had broken down.

The inherent problem in making liquid-crystalline metal complexes containing high co-ordination number metal centres is one of anisotropy. Structurally anisotropic molecules are needed in order to realise liquid-crystalline behaviour and hence, planar metal centres represent excellent molecular components as the global anisotropy is unperturbed by their inclusion [Fig. 3(*a*)]. However, the addition of two additional ligands [Fig. 3(*b*)] serves to reduce this anisotropy and hence, the formation of liquid-crystalline complexes of six-co-ordinate metals becomes much less likely.

Closely related to the search for octahedral systems is the work on ferrocene-based liquid crystals (Fig. 4), most ably pioneered in the recent literature by Deschenaux.[7] Ferrocene may formally be regarded as six-co-ordinate, and in these systems it is also found that at least four rings in the bound groups are necessary in order to realise liquid-crystal properties. However, it is here that a clue is obtained, as in these systems it becomes clear that four rings *in addition to the core* are present, leading to mesomorphism. This situation is also found in the diazabutadienes, the acetylenes and, to a lesser extent, in the manganese and rhenium imines. However, in the case of the bipyridines, the bipyridine unit co-ordinated to the metal centre represents a part of the core and viewed as such, then the complex possesses a core plus only two rings. On the basis of the arguments above, this is clearly insufficient.

In order to test this idea, larger bipyridines (**1**) were synthesised containing six (in this case aromatic) rings, starting from 2,2′-bipyridine-5,5′-dicarboxylic acid and 4′-alkoxy-

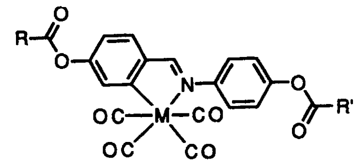


Fig. 1 Mesomorphic Mn^I and Re^I imine complexes

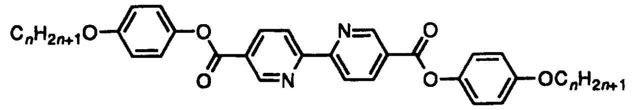


Fig. 2 Four-ring, mesomorphic 2,2′-bipyridines

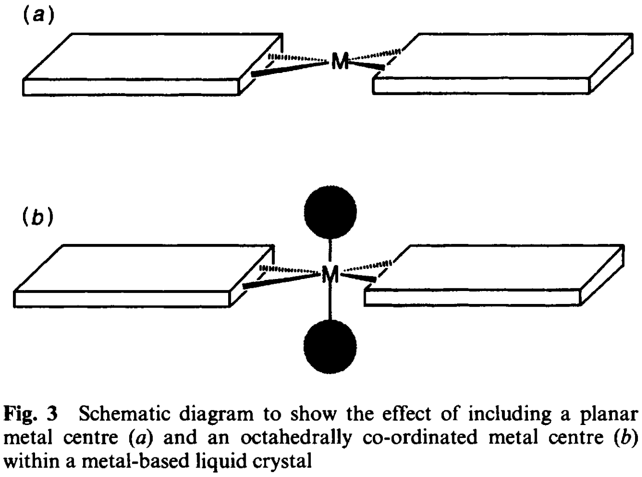


Fig. 3 Schematic diagram to show the effect of including a planar metal centre (*a*) and an octahedrally co-ordinated metal centre (*b*) within a metal-based liquid crystal

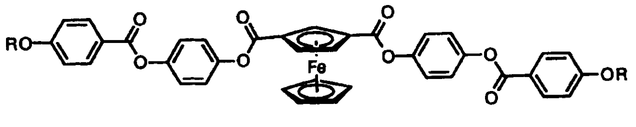
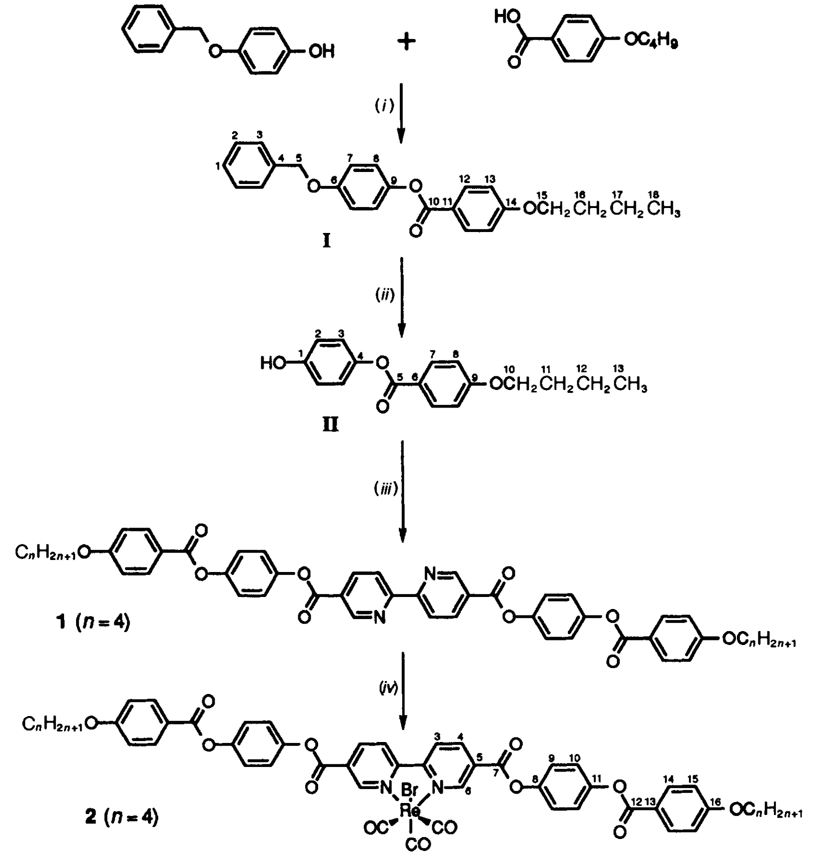


Fig. 4 Mesomorphic, 1,3-disubstituted ferrocenes



Scheme 1 (*i*) $C_6H_{11}N{=}C{=}NC_6H_{11}$ (1 equiv.), CH_2Cl_2; $NC_5H_4NMe_2$-4 (1 equiv.), stirred 24 h; (*ii*) freshly distilled tetrahydrofuran, NEt_3 (excess), 10% wet degassed Pd–C catalyst, H_2 atmosphere; (*iii*) 2,2'-bipyridine-5,5'-dicarbonyl dichloride (0.5 equiv.),[6] freshly distilled toluene; NEt_3 (excess), reflux, N_2, overnight; (*iv*) $[ReBr(CO)_5]$ (1 equiv.), toluene–heptane (3 : 2 v/v), reflux, N_2, 3.5 h

Table 1 Thermal data for the new complexes

Compound	*n*	Transition[a]	*T*/°C	Δ*H*/kJ mol^{-1}	Δ*S*/J K^{-1} mol^{-1}
1	4	Crys→N	269	45.8	84.4
		N→decomp.	350	—	—
1	8	Crys→S$_C$	231	52.3	103.9
		S$_C$→N[b]	328	—	—
		N→decomp.	> 328	—	—
1	12	Crys→M	210	2.1	4.4
		M→S$_C$	212	35.5	74.8
		S$_C$→N[b]	341	—	—
		N→decomp.	> 341		
2	4	Crys→N	275	39.2	68.2
		N→I	362	—	—
2	8	Crys→N	224	17.7	35.7
		N→I	315	0.9	1.6
2	12	Crys→S$_C$	238	20.4	40.1
		S$_C$→N	267	0.4	0.7
		N→I	296	0.9	1.7

[a] I = Isotropic phase. [b] These temperatures are sensitive to the thermal history of the sample due to decomposition in the S$_C$ phase.

benzoyloxy-4-phenols.* A sample preparation for the butoxy homologue is given in Scheme 1; other homologues were prepared similarly. Based on the immediately preceding arguments, when complexed two of these would be regarded as the 'core' so that there would then be a core plus four rings. The mesomorphism of these systems clearly showed that there was consistency in the idea and both the bipyridines and their complexes with $[ReBr(CO)_3]$ were found to be mesomorphic. The thermal behaviour of the new compounds and their rhenium complexes is collected in Table 1.

The butoxy derivative (**1**, *n* = 4) showed only a nematic phase (N), while the octyloxy and dodecyloxy derivatives (**1**, *n* = 8 or 12 respectively) melted to a smectic C phase (S$_C$) before giving way to a nematic phase at higher temperatures. The temperature of the S$_C$–N transition was found to vary with heating rate, which we attribute to the fact that decomposition begins in the upper reaches of the S$_C$ phase. Clearing points are therefore not identified as decomposition occurs more rapidly in the nematic phase. Finally, it is noteworthy that on both heating and cooling, the dodecyloxy derivative showed another mesophase between the crystal and S$_C$ phase. On careful cooling, the transition into the phase can be seen, but it persists

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* **I** (white solid), yield 4.0 g (82%) [Found (calc.): C, 76.6 (76.6); H, 6.5 (6.4)%]. NMR ($CDCl_3$): ^{1}H, δ 8.12 (2 H, AA'XX', H^{12}, $J_{AA'XX'}$ 9), 7.40 (5 H, m, H$^{1-3}$), 7.10 (2 H, AA'XX', H^8, $J_{AA'XX'}$ 9), 7.00 (2 H, AA'XX', H^{13}, $J_{AA'XX'}$ 9), 6.95 (2 H, AA'XX' H^7, $J_{AA'XX'}$ 9), 5.05 (2 H, s, H^5), 4.05 (2 H, t, H^{15}, $^3J_{HH}$ 6.5 Hz), 1.80 (2 H, qnt, H^{16}), 1.50 (2 H, sxt, H^{17}) and 0.98 (3 H, t, H^{18}); ^{13}C, δ 165.3 (C^{10}), 163.5 (C^{14}), 156.4 (C^6), 144.8 (C^9), 136.9 (C^4), 132.3 (C^{12}), 128.6, 128.0, 127.5 (C$^{1-3}$), 122.6 (C^8), 121.7 (C^{11}), 115.5 (C^7), 114.3 (C^{13}), 70.5 (C^5), 68.0 (C^{15}), 31.2 (C^{16}), 19.2 (C^{17}) and 13.9 (C^{18}). Octyloxy homologue. Found (calc.): C, 77.7 (77.8); H, 7.6 (7.5)%. Dodecyloxy homologue. Found (calc.): C, 78.6 (78.7); H, 8.2 (8.3)%. **II** (colourless solid), yield 2.22 g (8%) [Found (calc.): C, 71.5 (71.3); H, 6.5 (6.3)%]. NMR ($CDCl_3$): ^{1}H, δ 8.05 (2 H, AA'XX', H^7, $J_{AA'XX'}$ 9), 6.95 (2 H, AA'XX', H^3, $J_{AA'XX'}$ 9), 6.90 (2 H, AA'XX', H^8, $J_{AA'XX'}$ 9), 6.74 (2 H, AA'XX', H^2, $J_{AA'XX'}$ 9), 5.48 (1 H, s, OH), 3.98 (2 H, t, H^{10}, $^3J_{HH}$ 6.5 Hz), 1.75 (2 H, qnt, H^{11}), 1.45 (2 H, sxt, H^{12}) and 0.93 (3 H, s, H^{13}); ^{13}C, δ 165.4 (C^5), 163.4 (C^9), 154.8 (C^1), 143.5 (C^4), 132.1 (C^7), 122.3 (C^3), 121.7 (C^6), 116.0 (C^2), 114.2 (C^8), 67.9 (C^{10}), 31.1 (C^{11}), 19.2 (C^{12}) and 13.8 (C^{13}). Octyloxy homologue. Found (calc.): C, 71.5 (71.3); H, 6.5 (6.3)%. Dodecyloxy homologue. Found (calc.): C, 73.6 (73.7); H, 7.8 (7.7)%.

only for a degree or so before crystallisation occurs. Due to the thermal instability of the compound in the nematic phase, it was not possible to obtain a good optical texture for the S_C phase, and therefore for the unidentified mesophase, too. However, the relative magnitude of the enthalpy and entropy changes leads us tentatively to assign the phase as being of the crystal smectic type. Finally, we would note that the bipyridines were rather insoluble, making purification difficult. Thus, while we obtained a pure sample of the octyloxy derivative, elemental analysis[*] showed that the other two gave carbon values which were low by about 1%, despite repeated and exhaustive attempts to obtain materials of analytical purity. Thus, we would advise caution in interpreting the exact transition temperatures for these two compounds (which may vary by 1–2 °C compared with the pure material), although we are confident that the small degree of impurity does not affect the mesophases observed. The complexes however, were much more soluble and therefore readily purified.

The compounds were then treated with equimolar $[ReBr(CO)_5]$ in toluene–heptane (3:2 v/v) at reflux under N_2 for 3.5 h to give the desired complexes in isolated yields which were essentially quantitative.[†] Now, the complexes were mesomorphic. Thus, the butoxy and octyloxy derivatives gave only nematic phases, while the S_C phase seen in the dodecyloxy ligand was retained in the complex. We have previously observed suppression of smectic phases on complexation to high co-ordination number metal centres, which we have attributed to reduced intermolecular interactions on account of the reduced structural anisotropy.[2,3]

An interesting point is that on complexation, the transition temperatures do not change very much, whereas in the case of the orthometallated imines (Fig. 1), complexation very much reduced the clearing point. This reduction in temperature was attributed to the reduction in structural anisotropy on inclusion of the $[M(CO)_4]$ group. In this study, the $[ReBr(CO)_3]$ is similarly large, and yet substantial reductions appear absent. The observation that the $[ReBr(CO)_3]$ group does not reduce at least clearing temperatures on complexation was also made in our study of complexes of diazabutadienes,[4] although we did note that the use of the larger iodide ligand did reduce transition temperatures to some degree. In both of the last cases, we suspect that the polarity of the cisoid α-diimine group coupled with the polarity of the Re–Br bond acts to increase intermolecular interactions, thus stabilising both the crystal and the mesophase. Further studies to investigate this point are already underway. It is also interesting to note that the thermal stability of the complexes appeared to be greater than that of the unco-ordinated compounds, with no observable decomposition occurring in the octyloxy or dodecyloxy derivatives.

Thus, we believe that we now have strong evidence that at least four rings plus the molecular core represents a sensible design requirement for the generation of calamitic mesophases of high co-ordinate metal centres.

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[*] $n = 4$. Cream solid, yield 0.43 g (15%) [Found (calc.): C, 67.6 (69.0); H, 4.0 (4.1); N, 4.2 (4.0)%]. m/z: 697 $[M^+]$ (calc. 696.174). No NMR data were obtained due to the insolubility of the product. $n = 8$. Found (calc.): C, 72.4 (72.6); H, 6.3 (6.3); N, 3.0 (3.1)%. $n = 12$. Found (calc.): C, 73.2 (74.1); H, 7.2 (7.2); N, 2.8 (2.8)%.

[†] **2** ($n = 4$) (orange solid), yield 0.075 g (93%) [Found (calc.): C, 51.3 (52.0); H, 3.4 (3.6); N, 2.7 (2.5); Br, 7.2 (7.1)%]. NMR ($CDCl_3$): ^1H, δ 9.79 (2 H, dd, H^6, $^4J_{HH}$ 2, $^5J_{HH}$ 1), 8.81 (2 H, dd, H^4, $^3J_{HH}$ 8.5, $^4J_{HH}$ 2), 8.48 (2 H, dd, H^3, $^3J_{HH}$ 8.5, $^5J_{HH}$ 1), 8.14 (4 H, AA′XX′, H^{14}, $J_{AA'XX'}$ 9), 7.34 (8 H, AA′XX′, H^9, H^{10}), 6.98 (4 H, AA′XX′, H^{15}, $J_{AA'XX'}$ 9), 4.06 (4 H, t, H^{17}, $^3J_{HH}$ 6.5 Hz), 1.81 (2 H, qnt, H^{18}), 1.52 (4 H, sxt, H^{19}) and 0.99 (6 H, t, H^{20}); ^{13}C, δ 195.7, 187.8 (CO), 164.7, 160.9 (C^7, C^{12}), 163.7 (C^{16}), 157.9 (C^2), 154.9 (C^6), 149.3, 147.2 (C^8, C^{11}), 140.3 (C^4), 132.3 (C^{14}), 129.3 (C^5), 124.1 (C^3), 123.2, 122.2 (C^9, C^{10}), 121.1 (C^{13}), 114.3 (C^{15}), 68.0 (C^{17}), 31.1 (C^{18}), 19.2 (C^{19}) and 13.8 (C^{20}); IR (CH_2Cl_2): ν(C≡O) 2028s, 1930s, 1907s, ν(C=O) 1750m and 1734m cm^{-1}. $n = 8$. Found (calc.): C, 54.7 (55.1); H, 4.5 (4.5); N, 2.4 (2.3); Br, 6.2 (6.4)%. $n = 12$. Found (calc.): C, 57.3 (57.6); H, 5.3 (5.4); N, 2.1 (2.1); Br, 6.2 (5.9)%.