Metal-containing Liquid Crystals: Calamitic Metallomesogens Containing Two Dicarbonyl-rhodium or -iridium Moieties Bound to a Single Salen-type Ligand

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Mesomorphic Schiff base (salen type) ligands H_2L_a–H_2L_c [H_2L_x = $\{C_{10}H_{21}C_6H_3(O)CH{=}N\}_2R_x$; R_a = CH_2CH_2, R_b = 1,4-C_6H_4, R_c = 1,4-C_6H_{10}] complex two square planar *cis*-$M(CO)_2$ moieties (M = Rh, Ir); the complexes [$\{M(CO)_2\}_2L_c$] show smectic A behaviour.

Many metal-containing liquid crystals (metallomesogens) have been made, often by complexing metals with mesomorphic (liquid crystalline) organic ligands.[1] Quite a number are dinuclear, of the type [$LM(\mu\text{-}X)_nML$], where two metal–organic ligand halves are joined by X bridges (L = organic ligand, M = metal, X = halide, carboxylate, *etc.*); related polymeric species are also known. However, so far as we are aware, there have been no reports of calamitic (rod-like) mesomorphic compounds in which a single organic ligand binds two metals. We here describe two examples.

Tetradentate salen type ligands such as H_2L_a [salen = bis(salicylidene)ethylenediamine], which contain N_2O_2 ligand sets, have been widely used to bind a single metal, and some calamitic (smectic A or C) complexes have been made with Cu^{II}, Ni^{II} and VO^{2+}.[2] The ligands themselves showed mesomorphism when they were substituted by long-chain alkyl or alkyloxy substituents in the 4-position (*para* to the CH=NR). However, in the metal complexes examined, where the ligand was bound tetradentate, the substituent had to be in position 5 (*para* to the hydroxy group) for mesomorphic behaviour to be evident.

While modelling the relationship between mesogenic behaviour and molecular shape using computer graphics, we observed that such salen type ligands exhibited a rod-like shape when they were stretched into a form where the two HO···CH=NR functions were *trans* to each other, and that in this conformer two separate transoid *bidentate* N_1O_1 sites became available which could bind the *cis*-positions of *two* square planar metals (Fig. 1). Some (non-mesomorphic) dimetal complexes of the type [$M_2(salen)L_n$] (M = Rh, Ir) are known,[3] and we have therefore synthesised a series of related complexes bearing 4-*n*-alkyloxy substituents on the salen type ligands to determine if such compounds show mesomorphism.

The ligands H_2L_a–H_2L_c [H_2L_x = $\{C_{10}H_{21}C_6H_3(O)\text{-}CH{=}N\}_2R_x$; R_a = CH_2CH_2, R_b = 1,4-C_6H_4, R_c = *trans*-1,4-C_6H_{10}] were synthesised (60% overall yield) by adaptation of established routes from 2,4-dihydroxybenzaldehyde[4] as shown in Scheme 1, and characterised by microanalysis and NMR spectroscopy.† All three were mesomorphic; as already reported,[4] H_2L_a showed a S_C phase. We found that H_2L_b and H_2L_c showed substantial smectic A phases, and H_2L_c also showed a short range (7 °C) S_B phase (Table 1).

The mesogenic stability of the ligand increases when the centre of the molecule becomes more rigid, presumably enforcing a more rod-like shape; thus the mesophase ranges are much greater (145 and 122 °C, respectively) for H_2L_b and H_2L_c, which have a 1,4-phenylene or a *trans*-cyclohexane-1,4-diyl group linking the two Schiff bases, than for H_2L_a (22 °C) where they are linked by the more flexible $–CH_2CH_2–$. The melting and clearing points of H_2L_c, bearing the *trans*-cyclohexane-1,4-diyl, are somewhat lower than those of the 1,4-phenylene, H_2L_b, probably because the latter has a more rigid centre.

The dimetal complexes [$\{Rh(CO)_2\}_2L_a$] and [$\{Rh(CO)_2\}_2L_b$] [where the linking groups R_x = $(CH_2)_2$, and *p*-C_6H_4] were not mesomorphic but melted at high temperatures with decomposition (300 and 284 °C, respectively). However, [$\{Rh(CO)_2\}_2L_c$], where R_x was derived from *trans*-1,4-diaminocyclohexane, was liquid crystalline and showed a S_A phase over short (4 °C) range. We also made the iridium analogue, [$\{Ir(CO)_2\}_2L_c$] to see if the effect of replacing rhodium by the heavier iridium was to increase the transition temperature because of the larger molar mass, or whether the consequent increase in polarizability would improve the

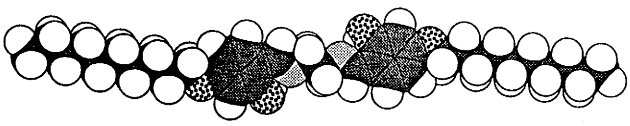
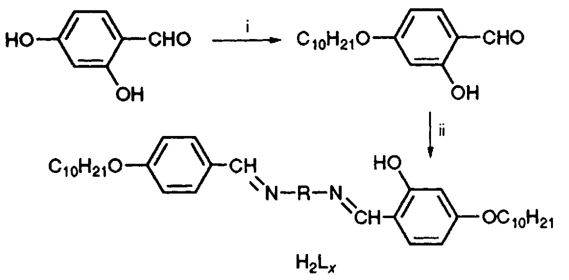
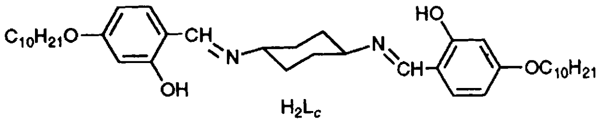


Fig. 1 Chem 3D view of H_2L_a salen(bis-bidentate)



Scheme 1 The synthesis of the ligands H_2L_a, H_2L_b and H_2L_c and of the complexes [$\{M(CO)_2\}_2L_c$], (M = Rh, Ir). i, $C_{10}H_{21}Br$/polyethylene-glycol–dioxane; $KHCO_3$; ii, $H_2N–R–NH_2$/EtOH (*x* = *a*, R = $–CH_2CH_2–$; *x* = *b*, R = 1,4–C_6H_4; *x* = *c*, R = 1,4–C_6H_{10})

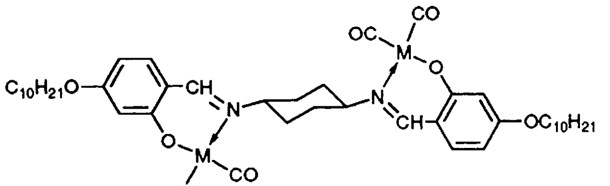


H_2L_c

Table 1 Transition temperatures (°C) and transition enthalpies [kJ mol^{-1}] of the ligands H_2L_a–H_2L_c, and of the complexes [$\{Rh(CO)_2\}_2L_c$] and [$\{Ir(CO)_2\}_2L_c$]

Ligand/ Complex	Phase transition temperatures (°C) and transition enthalpies [kJ mol^{-1}]						
H_2L_a	K	84 [34]	S_C	106 [16]	I		
H_2L_b	K	115 [42]	S_A	260 [9]	I		
H_2L_c	K	92 [38]	S_B	99 [1]	S_A	221 [9]	I
[$\{Rh(CO)_2\}_2L_c$]	K	141 [32[a]]	S_A	145 [40[a]]	I		
[$\{Ir(CO)_2\}_2L_c$]	K	120 [0.3]	K′	142 [16]	S_A	169 [4.5]	I

[a] Approximate; overlapping peaks make the individual Δ*H*'s difficult to estimate.



[$\{M(CO)_2\}_2L_c$]

mesophase behaviour. [$\{Ir(CO)_2\}_2L_c$] was also mesomorphic; after a crystal phase change, it melted at a very similar temperature to [$\{Rh(CO)_2\}_2L_c$], but showed a much larger S_A phase range (27 °C). These complexes may be compared with the known mononuclear mesomorphic rhodium and iridium compounds; again the melting points are similar but the iridium complexes are somewhat more stable.[5]

The bis(dicarbonyl)rhodium complex [$\{Rh(CO)_2\}_2L_c$] was prepared from H_2L_c by reaction with [$Rh_2(CO)_4Cl_2$] in methanol–THF in the presence of triethylamine (70% yield). The iridium complex [$\{Ir(CO)_2\}_2L_c$] was prepared in two steps (30% overall yield) by reacting H_2L_c first with the cycloocta-1,5-diene (cod) complex [$Ir_2(cod)_2Cl_2$] to give the bis(cyclooctadiene)iridium complex [$\{Ir(cod)\}_2L_c$]; the cyclooctadiene was then replaced by reaction with CO (1 atm, 20 °C). Both the dirhodium and the diiridium complexes were characterised by microanalysis and spectroscopy.†

Thus we conclude that relatively simple ligands can give calamitic metallomesogens containing two metal centres, and that the heavier metal iridium shows a longer mesophase range than rhodium. We are exploring molecular modifications which will allow the complexation of other metals and should also bring down the melting temperatures substantially.[6]

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Footnote

† H_2L_a: ^1H NMR ($CDCl_3$): δ 8.2 (s, 2 H), 7.1 (d, 2 H), 6.35 (m, 4 H), 3.95 (t, 4 H), 3.8 (s, 4 H) 1.2–1.9 (CH_2s), 0.85 (t, 6 H). H_2L_b: ^1H NMR ($CDCl_3$): δ 8.55 (s, 2 H), 7.25 (d, 2 H), 7.2 (s, 4 H), 6.5 (m, 4 H), 4 (t, 4 H), 1.2–1.9 (CH_2s), 0.9 (t, 6 H). H_2L_c: ^1H NMR ($CDCl_3$): δ 8.25 (s, 2 H), 7.1 (d, 2 H), 6.4 (m, 4 H), 3.95 (t, 4 H), 3.25 (m, 2 H), 1.2–1.9 (CH_2s), 0.9 (t, 6 H). [$\{Rh(CO)_2\}_2L_a$]: microanalysis, found (calc.): C, 52.9 (53.6); H, 6.0 (6.1); N, 3.0 (3.1)%. IR ν/cm^{-1} (CO) (Nujol): 2077, 2000. ^1H NMR ($CDCl_3$): δ 7.75 (s, 2 H), 6.8 (d, 2 H), 6.3 (d, 2 H), 6.1 (dd, 2 H), 4.3 (s, 4 H), 3.85 (t, 4 H), 1.2–1.9 (CH_2s), 0.8 (t, 6 H). [$\{Rh(CO)_2\}_2L_b$]: microanalysis, found (calc.): C, 55.7 (55.9); H, 5.5 (5.8); N, 2.7 (3.0)%. IR ν/cm^{-1} (CO) (Nujol): 2083m, 2048m, 2004s. ^1H NMR ($CDCl_3$): δ 8.05 (d, 2 H), 7.25 (s, 4 H), 7.15 (d, 2 H), 6.55 (d, 2 H), 6.4 (dd, 2 H), 4 (t, 4 H), 1.2–1.9 (CH_2s), 0.9 (t, 6 H): [$\{Rh(CO)_2\}_2L_c$]: microanalysis, found (calc): C, 55.0 (55.6); H, 6.35(6.4); N, 2.8 (2.95)%. IR ν/cm^{-1} (CO) ($CHCl_3$): 2080, 1997; ^1H NMR ($CDCl_3$): δ 8.1 (s, 2 H), 7.1 (d, 2 H), 6.5 (d, 2 H), 6.3 (dd, 2 H), 3.95 (t, 4 H), 2.4 (m, 4 H), 1.2–2 (CH_2s), 0.9 (t, 6 H). [$\{Ir(CO)_2\}_2L_c$]: microanalysis, found (calc.): C, 46.7 (46.5); H, 5.4 (5.9); N, 2.3 (2.5)%. IR ν/cm^{-1} (CO) ($CHCl_3$): 2067, 1981; ^1H NMR ($CDCl_3$): δ 8.15 (s, 2 H), 7.1 (d, 2 H), 6.5 (d, 2 H), 6.35 (dd, 2 H), 4.15 (m, 2 H), 3.9 (t, 4 H), 2.4 (m, 4 H), 1.2–2 (CH_2s), 0.9 (t, 6 H).

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