Iridium Liquid Crystal Complexes by Co-ordination of Non-mesogenic Organic Ligands

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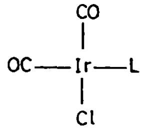
The first family of iridium liquid crystal complexes [IrCl(CO)$_2$L] (L = NC_5H_4–CH=N–C_6H_4R) formed by complexation of a non-mesogenic organic ligand directly to the metal is described.

In the last few years there has been increasing interest in metal-containing liquid crystals owing to their potential applications.[1,2,3] Mesogenic complexes have been reported for Ni,[4,5] Cu,[2,6,7,8] Rh,[9,10,11] Pd,[9,10,12,13] Ag,[3] Pt,[5,9,10] and Au [9] amongst other metals. We now describe a family of iridium complexes that we believe to be of interest not only because they are the first iridium liquid crystal complexes but also because they are formed by direct co-ordination of a non-mesogenic organic ligand to the metal.

The iridium compounds [IrCl(CO)$_2$L] (L = NC_5H_4–CH=N–



(1)

L =

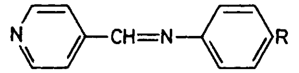


Table 1. Temperature and enthalpy data for IrCl(CO)L complexes.

Complex	Transition[a]	Temperature/°C	ΔH(J g^{-1})[b]
R = H	C–I	108.9	41.3
R = OC_nH_{2n+1}			
n = 2	C–I	104.1	35.8
4	C–I	92.2	33.2
5	C–I	72.1	47.4
6	C–I	88.2	51.2
	I–N[c]	56.9	
7	C–I	85.0	40.8
	I–N[c]	63.1	
	N–S_A[c]	35.3	
8	C–N	68.1	44.8
	N–I	76.2	0.6
	N–S_A[c]	66.2	
9	C–C′	54.5	21.1
	C′–S_A	63.8	28.3
	S_A–I	75.2	1.73
10	C–S_A	62.8	52.7
	S_A–I	84.8	2.0
12	C–S_A	70.1	52.5
	S_A–I	92.1	3.6
14	C–S_A	79.6	68.9
	S_A–I	99.4	3.36
16	C–S_A	84.4	75.2
	S_A–I	104.1	2.4
R = C_nH_{2n+1}			
n = 10	C–I	46.5	17.0
14	C–I	74.9	71.8
	I–S_A[c]	70.5	

[a] C: Crystal, N: Nematic, S_A: Smectic A, I: Isotropic liquid. [b] Measured on Perkin-Elmer differential scanning calorimeter (DSC-2). [c] Monotropic transition.

C_6H_4R) (**1**)† were prepared as yellow–green solids in 60—80% yield by bubbling CO through a solution of the corresponding diolefinic complex [IrCl(cod)L] (cod = cycloocta-1,5-diene) {obtained by reaction of $[IrCl(cod)]_2$ with a stoicheiometric amount of the non-mesogenic ligand}.

Complexes with alkoxylic chains containing more than five carbon atoms show mesogenic properties. The temperatures and enthalpy data are collected in Figure 1 and Table 1. While for the compounds with n = 6 and 7 only monotropic transitions were observed, N and S_A enantiotropic phases were exhibited by the higher members of the series. The mesogenic compounds melt at similar or even lower temperatures than the corresponding ligand and show a clear thermochromism to a red colour at their melting points. When an alkyl chain is present in the organic ligand lower melting points but worse mesogenic properties were obtained (Table 1).

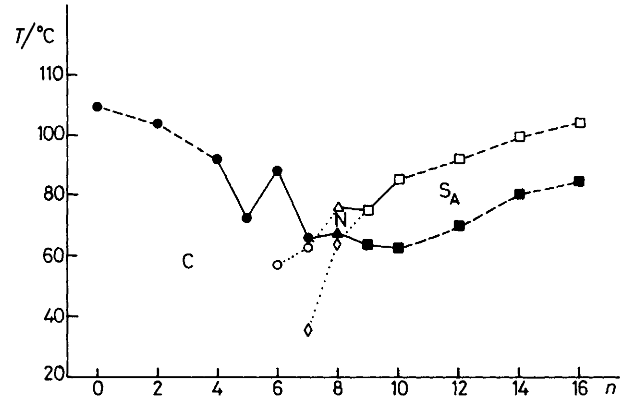


Figure 1. Transition temperatures as a function of alkyl chain length for $IrCl(CO)_2L$ complexes (L = NC_5H_4–CH=N–C_6H_4–OC_nH_{2n+1}). ● C–I, ▲ C–N, ■ C–S_A, ◇ N–S_A, ○ I–N, △ N–I, □ S_A–I transitions.

In order to explore the influence of the metal on the mesogenic behaviour, some similar rhodium complexes have been prepared. Rh Compounds with OC_nH_{2n+1} (n = 8,9) ligands show N and S_A phases, respectively, but they decompose on the microscope just after melting.

To the best of our knowledge, the mesogenic complexes described so far contain a liquid crystal ligand or, alternatively, significant structural changes by co-ordination of the organic ligand (L–M–L structures or formation of dinuclear complexes) are observed. Interestingly, the results reported in this Communication show that new liquid crystals can be obtained by direct co-ordination to a metal of a single molecule of a non-mesogenic organic ligand.

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† The new complexes have been satisfactorily characterized by i.r. and ^1H n.m.r. spectroscopy and C,H,N microanalysis.