

Aroylhydrazinatonickel(II) and Copper(II) Complexes; a New Class of Metallomesogens

Mohammed N. Abser,^a Martin Bellwood,^a Michael C. Holmes^b and Richard W. McCabe*^a

^a Department of Chemistry, University of Central Lancashire, Preston, UK PR1 2HE

^b Department of Physics and Astronomy, University of Central Lancashire, Preston, UK PR1 2HE

A series of aroylhydrazinato-nickel(II) and -copper(II) complexes have been synthesised in high yield and shown to form a new class of metallomesogens, which form smectic C and nematic phases; the nickel(II) complexes were found to be highly stable even in the isotropic phase, which contrasted with the rapid decomposition of the copper(II) complexes soon after entering the liquid crystalline phase.

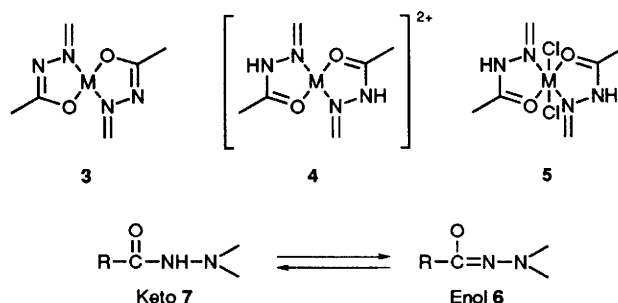
Metal-containing liquid crystals show great promise as materials for building microelectronic devices.¹ They often have the advantage over purely organic liquid crystals in being highly coloured and potentially paramagnetic (if an appropriate metal is chosen), but unfortunately they are usually less thermally stable than their organic counterparts. Thus, a great effort is being made in the design and synthesis of stable metal-containing liquid crystals.

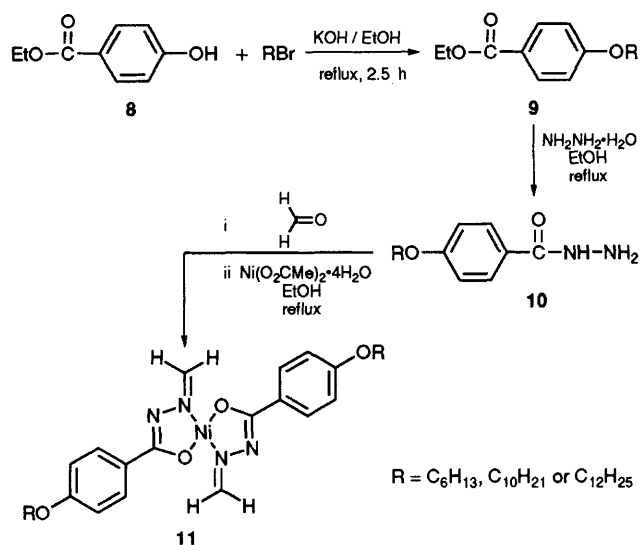
Aroylhydrazones **2** and their parent hydrazines **1** are known to form stable chelates with transition metals.² Such compounds have tuberculostatic activity, which has been attributed to the formation of the stable chelates of these compounds with certain transition metals present in the cell.³⁻⁷

The aroylhydrazones **2** can coordinate to a divalent metal

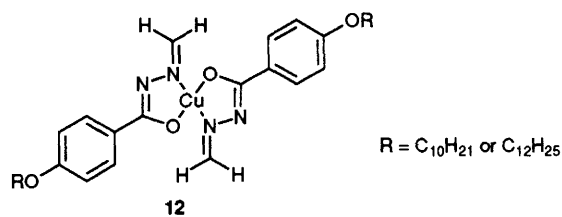
ion either *via* the enolic form (as in **3**) or the ketonic form (as in **4** or **5**).⁸⁻¹⁰

Sacconi¹¹ showed that the tendency of the ligands **2** to react with nickel(II) in the enolic form **6** becomes greater as the conjugating ability of the R group in the hydrazine residue increases. Thus, aryl substituents favour the enolic-tautomer **6**¹² of such ligands.





Scheme 1 Synthesis of the aroylhydrazinatonicel(II) complexes



The preferred form of the chelates is strongly dependent on the coordinating ability of the counterion of the metal salt used.¹ For instance, aroylhydrazones **2** react with nickel(II) acetate yielding the corresponding bis[aroylhydrazinato]nickel(II) complexes **3** with the deprotonation of the secondary imino hydrogen; whereas with nickel(II) chloride it gives the dichlorobis(aroylhydrazone)nickel(II) **5**. The octahedral complexes **5** undergo dehalopronation to the square planar neutral complexes, however, on treatment with alcoholic KOH. The characteristic ability of aroylhydrazones to form stable square planar chelates with transition metals, together with the fact that a molecule with a flat central core attached to a long hydrocarbon chain is an ideal structural arrangement for a compound to be mesogenic, lead us to envisage the possibility of synthesising novel mesogenic inorganic compounds based on these ligands.

In order to maintain a planar central core in the molecule and to minimise molecular broadening, two factors that can profoundly affect the mesogenic behaviour of molecules, it was decided that the simplest substituent, azomethylidene, would be most appropriate. Accordingly, the complex bis[*N*-methylidene(4'-*n*-dodecyloxy)benzoylhydrazinato]nickel(II) (**11**, R = C₁₂H₂₅) was synthesised as outlined in Scheme 1.

A notable feature of the ¹H NMR spectrum of this, and the other complexes **11**, is the unusually large coupling constant (*J* 10.9 Hz) shown by the two separate methylidene proton doublets at δ 7.05 and 6.47. The other features of the ¹H NMR spectrum were as expected and were fully consistent with the structures **11**.

The complex (**11**, R = C₁₂H₂₅) was an orange–yellow microcrystalline solid, which on examination by differential scanning calorimetry (DSC), X-ray diffraction and on a hot-stage polarising microscope, showed a transition from crystal to smectic C phase at 125.5 °C (Δ*H* = 74.89 J g^{−1}). This change was preceded by a crystal to disordered crystal phase transition at 122.8 °C (Δ*H* = 29.40 J g^{−1}). The smectic to isotropic transition occurred at 164–165 °C and on cooling

the smectic phase reappeared at 164 °C, but supercooling to 113–114 °C occurred giving only the disordered crystalline phase. This disordered crystalline material gave only the 125.5 °C phase transition on re-heating and showed an X-ray diffraction pattern similar to that of the smectic phase. On recrystallisation from chloroform the original, ordered crystalline solid was recovered. These observations suggest that solvent recrystallisation produces a kinetically stable crystalline form that transforms to a thermodynamically stable crystalline form on heating. The thermodynamically stable form persists on subsequent cooling.

Two further homologues (**11**, R = C₁₀H₂₁) and (**11**, R = C₆H₁₃) were synthesised to investigate the effects of different alkyl chain lengths on mesophase formation.

The complex bis[*N*-methylidene(4'-*n*-decyloxy)benzoylhydrazinato]nickel(II) (**11**, R = C₁₀H₂₁) was obtained as fine 'floppy' needles whilst the complex bis[*N*-methylidene(4'-*n*-hexyloxy)benzoylhydrazinato]nickel(II) (**11**, R = C₆H₁₃) was a microcrystalline, orange solid.

The decyloxy homologue (**11**, R = C₁₀H₂₁) gave a crystal to smectic C phase transition at 135–135.5 °C and a smectic C to nematic transition at 166–166.7 °C, which on further heating goes to the isotropic liquid at 183.5–184.5 °C. The DSC trace of this complex showed a slight shoulder on the 135 °C peak on first-time heating, which disappeared on subsequent re-heating; once again suggesting a transition from the kinetically stable crystal phase to the less ordered thermodynamic crystal. Similarly, on cooling the complex supercooled to 127 °C. On the other hand, the hexyloxy homologue (**11**, R = C₆H₁₃) forms a nematic phase between 159 and 186.7 °C that supercools to 155 °C before crystallising.

The equivalent copper(II) complexes (**12**, R = C₁₀H₂₁ or R = C₁₂H₂₅) were synthesised in an analogous manner to the nickel(II) complexes **11**; copper(II) acetate being substituted for the nickel(II) acetate.

The brown paramagnetic complexes **12** were shown to be liquid crystalline. The complex (**12**, R = C₁₂H₂₅) showed a transition to a liquid crystalline phase at 139–140 °C; the type of mesophase has not yet been determined as the complex decomposed at *ca.* 147 °C to form a glassy product (without reaching the isotropic phase). The C₁₀ analogue (**12**, R = C₁₀H₂₁) showed parallel behaviour, beginning at the elevated temperature range of 150–152 °C. These promising compounds need careful re-examination.

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