New metallomesogens core. New copper complexes with calamitic mesophases using tropolone based ligands. Crystal structure of bis(5-octyloxytropolonato)copper

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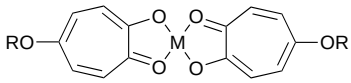
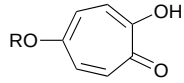
A new class of metallomesogens based on 5-substituted tropolones with both enantiotropic and monotropic mesophase behaviour are prepared, the mesogenic properties are in line with the rod-like, calamitic nature of bis(5-octyloxytropolonato)copper shown in its crystal structure.

Most metallomesogens[1–4] have made use of benzene rings as integral parts of the rigid core. Seven-membered ring cores in metallomesogens are reported here for the first time. Tropolone-based organic liquid crystals have been reported by Uemura *et al.*,[5] and Mori *et al.*[6–9] Tropolone forms complexes with many metals in a manner analogous to acetylacetone,[10] but none were reported to be metallomesogens. We report here the first syntheses and studies of mesogenic complexes **1** based on tropolone.

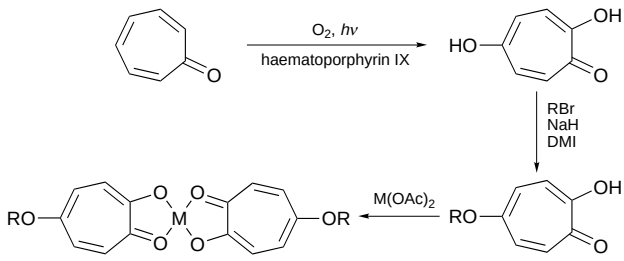


1 R = C_nH_{2n+1} (n = 8, 10, 12, 14, 16); M = Cu, Ni, VO



2a R = H,
b R = alkyl

We have modified the literature method[8] to make 5-substituted tropolones, **2b**, from 5-hydroxytropolone, **2a**, by using dimethylimidazolidinone (DMI) as solvent for alkylation of the 5-position to replace the carcinogenic HMPA.[8] DMI has in the past been reported as replacement for HMPA,[11–14] but we believe that this is the first reported use for tropolone derivatives Scheme 1.



Scheme 1

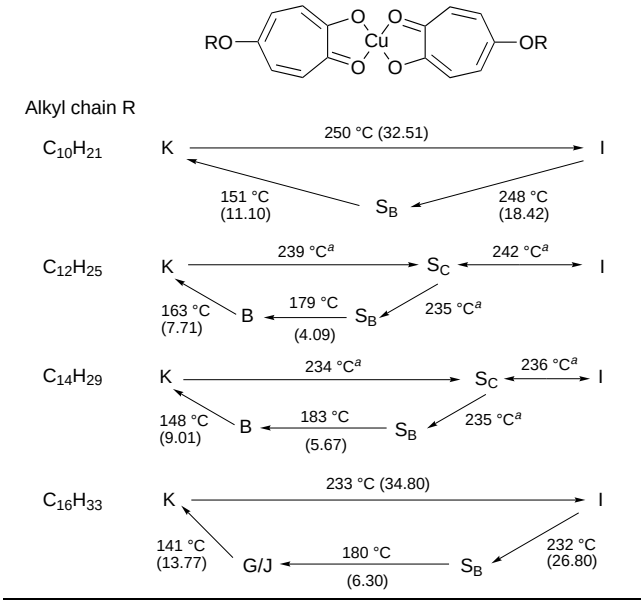
The copper complexes of these 5-substituted tropolones (**1**, M = Cu) have been synthesised in the usual way† and their mesomorphic nature has been studied using polarised optical microscopy and differential scanning calorimetry. Variable temperature X-ray powder studies are in progress.

The decyl substituted copper complex displays a monotropic S_B phase. Both the dodecyl and tetradecyl copper complexes exhibit a short range S_C mesophase (which despite the high temperatures are stable) as well as S_B and crystal G phases. The hexadecyl substituted copper complex exhibits a S_B phase and an anisotropic plastic crystal phase which cannot be pinpointed. The mesogenic data are summarized in Table 1.

Long chain alkoxy derivatives are very difficult to crystallise in forms suitable for X-ray structure determination. Generally very fine needles are obtained. Crystallisation of bis(5-octyloxytropolonato)copper from 1,4-dioxan containing 10% acetic acid in a similar way to that used for bis(tropolonato)-copper(II)[15] yielded a suitable crystal for an X-ray diffraction study.‡ The CuO_4 centre is required by crystallographic symmetry to be precisely planar, and the entire molecule is planar within 7%. The ligand plane O(1)C(1)C(7)O(2) attached to the Cu makes an angle of 2° with the tropolone ring. The molecular structure shown in Fig. 1 confirms the calamitic nature of the tropolone derivatives, while the packing in the crystal shows a similar arrangement to that in the smectic C phase. No solvent molecules are incorporated into the structure and there is no Cu–Cu interaction, the closest Cu···Cu approach being along the *c*-axis at 6.413(4) Å. The alkyl chain thermal parameters are interesting in that they exhibit partial melting at room temperature.

NMR analysis of 5-alkoxy tropolones confirmed their structure. Satisfactory analyses were obtained for the complexes. Over a period of time, the copper complexes are prone to hydrate, making them difficult to dry. However, because of the high transition temperatures, all water will have evaporated from the copper complex and have no effect on the mesophase behaviour. This is confirmed by uniform phase identification (and transition temperatures) of the copper complexes when dry and hydrated. IR data for bis[5-(decyloxy)tropolonato]-copper(II) (KBr disc): 2918s, 2850s, 1516s, 1432vs, 1350s, 1241s, 1204s, 789w.

Table 1 Phase transition temperatures and corresponding enthalpies (kJ mol^{-1}) of copper tropolonate complexes



[a] Overlapping peaks, enthalpies could not be resolved.

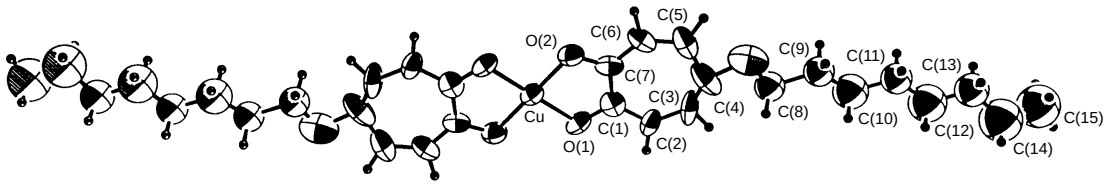


Fig. 1 View of bis(5-octyloxytropolonato)copper(II) from X-ray data

Nickel and oxovanadium(IV) complexes of the 5-substituted tropolone ligands have been prepared. However, despite having melting points which are 50 and 90 °C lower respectively than their copper complex counterparts, none have displayed any mesophases. For the nickel complexes, IR spectra suggest octahedral nickel.

While mesophases are still at high temperatures, appropriate substitution on the tropolone rings enables the length-to-breadth ratio to be adjusted, and initial work gives the promise of metallotropolonates with much lower mesophase transition temperatures. The use of tropolone derivatives in medicine (colchicine is a valuable anti-tumour agent while hinokitiol has strong biocidal properties), indicates potential uses for metal tropolonate derivatives outside the field of display devices.

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Footnotes and References

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† *Example*: bis[5-(decycloxy)tropolonato]copper(II): 5-decyloxytropolone (0.18 g, 0.71 mmol), sodium acetate (0.1 g, 1.4 mmol) and copper acetate (0.072 g, 0.359 mmol) were dissolved in methanol (15 cm^3). The mixture was refluxed for 3 h before cooling and filtration of the copper complex as a green powder. Recrystallisation in dichloromethane yielded bis[5-(decycloxy)tropolonato]copper(II) as green needles.

‡ *Crystal data*: $C_{80}H_{42}CuO_6$, triclinic, space group $P\bar{1}$, a = 7.607(4), b = 15.871(8), c = 6.413(4) Å, α = 96.32(4), β = 105.46(3), γ = 97.449(3)°, U = 731(1) $Å^3$, Z = 1, T = 24 °C, μ(Mo-Kα) = 7.84 cm^{-1}, R, R_w = 0.055 for 990 independent reflections collected on a Rigaku AFC6S diffractometer. The small crystal size led to a relatively small data set. The copper, oxygen and ring carbons were refined with anisotropic thermal parameters. Cu lies on a special position (origin): Cu–O(1) 1.916(2) Å, Cu–O(2) 1.902(9) Å; O(1)–Cu–O(2) 85.0(4)°. CCDC 182/694.

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