Columnar mesophases from tetrahedral copper(1) cores and Schiff-base derived polycatenar ligands

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Received (in Basel, Switzerland) 26th May 1999, Accepted 1st September 1999

In the presence of copper(I), certain di- and tri-topic ligands derived from reaction of substituted anilines with 2-pyridinecarbaldehyde or 2,6-pyridinedicarbaldehyde form a new type of polycatenar metallomesogen around the tetrahedral metallic centre.

Metal complexes derived from Schiff-bases are known to form a large variety of molecular architectures, ranging from macrocyclic helicates to infinite coordination polymers.^{1,2} In particular, 2-iminopyridines, readily formed via reversible reaction between an (achiral or chiral) amine and an appropriate aldehyde, are attractive building blocks for assembling intricate supramolecular species³ and active polymerization catalysts.^{4,5} These ligands can display unusual binding behaviour towards certain cations, leading to the formation of highly stable metallohelicates.⁶ The main advantage of such ligands, however, relates to the availability of a free imino site that can be functionalized with a wide variety of appendages. Indeed, the structural attributes provided by 2-iminopyridines look highly promising for the assembly of metallomesogens by attaching flexible paraffinic tails and subsequent rigidification of the head-group by complexation with copper(I) cations. It is worth noting that silver complexes constructed from polycatenar scaffoldings and which exhibit columnar liquid-crystalline mesophases have previously been studied.7



Ligands L¹ and L² were prepared in 99 and 86% isolated yield, respectively by refluxing 2-formylpyridine or 2,6-diformylpyridine and the corresponding aniline⁸ in ethanol containing a trace amount of acetic acid. Each ligand has a well defined melting point at 58 °C (L¹) on 56 °C (L²). Ligand L³, which serves as a reference compound, was synthesized by a similar route and has a melting point of 159 °C.

Reaction of either ligand in dichloromethane with 0.5 equiv. of [Cu(MeCN)₄]BF₄ leads to immediate formation of a deepred colouration indicative of complexation of copper(I) to four nitrogen donor ligands⁹ { $\lambda_{max} = 505, 500$ (sh) and 500 (sh) nm with $\varepsilon = 5100, 2600$ and 3000 dm³ mol⁻¹ cm⁻¹, respectively for $[Cu(L)^n)_2]BF_4$ (n = 1-3) **1-3**}. Mass spectrometry is consistent with the isolated products being monomeric without contamination from polynuclear structures. These products, therefore, may be assigned the general formula $[Cu(L^n)_2]BF_4.^{\dagger}$ A schematic representation of the complexes and a computer generated CPK model of one of the structures is shown in Fig. 1.



Fig. 1(a) Idealized pictoral representation of complex 2 representing the disk-shape and (b) CPK energy-minimised conformation.

Direct involment of the terminal imino groups in the coordination sphere was confirmed by solid-state and solutionphase FTIR studies and by both ¹H and ¹³C NMR spectroscopy. The NMR studies also indicate that the two ligands bound to Cu(I) are equivalent while the relatively broad signals belonging to the aromatic protons, together with a broad imine signal (for complexes 1 and 2) are attributed to a fast exchange process between coordinated and free imino N atoms. Similar internal flexibility has been observed previously for related macrocyclic¹⁰ and terpyridine¹¹ based copper(I) complexes. Solid state FTIR studies of complex 2 reveal the presence of two imino stretching vibrations; one lying close to that of the free ligand ($v_{C=N}$ 1626 cm⁻¹) and the second occurring at lower frequency ($v_{C=N} = 1588 \text{ cm}^{-1}$) owing to coordination to the metal centre. X-Ray crystallography made for a single crystal of complex 3 indicates that two L^3 ligands are wrapped around a single copper cation, each ligand being coordinated via a pyridine-imine fragment, while the pendant imino arm is directed away from the metal centre in a trans configuration (Fig. 2).‡

It is noteworthy that, despite the *cis* arrangment of the coordinated py-CH=N- fragment and the *trans* conformation of the uncoordinated imino subunit, the overall ligand adopts an almost planar structure. The four-coordinate copper(I) cation shows Cu–N(py) and Cu–N(imine) distances of *ca* 2.085 and 2.021 Å, respectively with chelate bite angles of 81.6 and 81.1°. The uncoordinated imino fragment lies *ca.* 4.706 Å from the cation. There is obvious distortion around the metallic centre that might explain why the molecule stacks into columns, favouring a liquid-crystalline phase (*vide infra*), a situation which is also clearly observed in the CPK energy-minimised conformation [Fig. 1(*b*)].



Fig. 2 ORTEP view of complex 3 showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.

Although non-mesomorphic themselves, ligands L¹ and L² produce thermotropic liquid-crystalline complexes when coordinated to copper(1), as demonstrated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The DSC thermograms of 2, recorded from 20 to 130 °C, contain two sharp peaks, each of which indicates a reversible first-order phase transition. The peak at 49 °C ($\Delta H = 149.2$ kJ mol^{-1}) corresponds to melting of the crystal into a liquidcrystalline phase whereas the peak at 117 °C ($\Delta H = 3.1$ kJ mol⁻¹) can be attributed to clearing of the liquid crystal into an isotropic melt (values are given for the third cycle). The high stability of complex 2 was demonstrated by the absence of significant perturbation of the DSC patterns following several heating-cooling cycles. The optical textures observed for 2 during slow cooling from the isotropic melt are typical of a columnar phase (with pseudo focal-conic textures). This birefringent texture is maintained at room temperature. In contrast, complex 1 melts into the liquid crystal phase at 48 °C $(\Delta H = 84.6 \text{ kJ mol}^{-1})$ and has a clearing point at 75 °C ($\Delta H =$ 10.3 kJ mol⁻¹), but only on the first heating stage. It appears, therefore, that complex 1 is thermally unstable, a feature not entirely unexpected in view of the lack of substituents at the 6-position.

The columnar structure of the liquid crystal phases of 1 and 2 was confirmed by X-ray diffraction studies. It is seen that the rigid aromatic units that comprise the core of the pseudo-tetrahedral copper(I) complexes are superposed on top of one another and embedded in a disordered matrix provided by the molten alkyl chains. These columns are packed laterally into a two-dimensional hexagonal unit cell having parameters of 60 and 47 Å for 1 and 2, respectively as measured at 60 °C from the small-angle reflection. The larger value found for 1 suggests that a 'phosmidic-type' of columnar mesophase is formed (where several individual molecules stack one on top of the other to form columns as in conventional discoid liquid crystalline material.

Liquid crystals obtained from purely organic molecules comprising a tetrahedral carbon atom substituted with four semi-rigid subunits bearing flexible terminal alkyl chains have been reported.¹² However, complexes **1** and **2** are, to the best of our knowledge, the first examples of metallomesogens built around a single tetrahedral metal cation. Many unsuccessful attempts to engineer such metallomesogens have been attempted in the past.^{13,14} As such, these materials differ markedly from the liquid-crystalline metallohelicate built around a central binuclear copper(I) helicate.¹⁵ It should be stressed that the 2-iminopyridine moiety is readily amenable for systematic investigation of how the length and number of

appended alkyl chains influence the liquid-crystalline properties, especially melting temperature, and to establish the structural and thermodynamic factors that assembles the aromatic cores into columns. Such information, which is critical for a proper theoretical description of metallomesogens, is not yet available for any liquid-crystalline material. We are well aware that the polycatenar ligand L^2 is an attractive substrate for reaction with metal cations that favour octahedral coordination geometries.

We thank Professor Anthony Harriman for his critical review of the manuscript and for the energy-mimimised structure and Dr. Benoît Heinrich (IPCMS) for fruitful and helpful discussions.

Notes and references

[†] Full synthetic details will be given elsewhere. All new compounds were authenticated by NMR, FTIR, MS and elemental analyses (required values in parentheses). *Selected data*: **L**¹: δ_{C=N} 8.64 (CDCl₃); v_{C=N} 1626 cm⁻¹ (KBr pellet, FAB⁺ m/z 1023.3 [M + H]⁺, C, 78.59 (78.62), H, 10.62 (10.83), N, 2.57 (2.74%). **L**²: δ_{C=N} 8.72 (CDCl₃), v_{C=N} 1626 cm⁻¹ (KBr pellet); FAB⁺ m/z 1967.3 [M + H]⁺, C, 78.43 (78.72), H, 10.53 (11.01), N, 1.99 (2.13%). **1**: 92% yield; δ_{C=N} 9.18 (CDCl₃); v_{C=N} 1589 cm⁻¹ (KBr pellet); FAB⁺ m/z 2109.2 [M-BF4]⁺, C, 72.98 (73.24), H, 9.73 (10.09), N, 2.23 (2.55%). **2**: 98% yield; δ_{C=N} 8.79 (CDCl₃); v_{C=N}, 1626, 1588 cm⁻¹ (KBr pellet); FAB⁺ m/z 3996.8 [M −BF4]⁺, C, 75.12 (75.50); H, 10.21 (10.61); N, 1.53 (2.05%, calculated with one water molecule).

[‡] *Crystal data* for **3**: C₄₂H₃₈N₆O₄Cu•2BF₄•H₂O•CH₂Cl₂, M = 1785.26, triclinic, space group $P\overline{1}$, red crystals, a = 12.6180(7), b = 13.075(1), c = 13.783(1) Å, $\alpha = 84.437(9)$, $\beta = 80.643(9)$, $\gamma = 70.631(9)$, V = 2114.4 Å³, Z = 1, $\mu = 0.645$ mm⁻¹. Data were collected on a Kappa CCD diffractometer (graphite Mo-K α radiation, $\lambda = 0.71073$ Å) at -100 °C. 15930 reflections collected ($2.5 \le 2\theta \le 26.36^\circ$), 4186 data with $I > 3\sigma(I)$. The structure was solved using the Nonius OpenMoleN¹⁶ package and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms except for the solvent molecules (the latter are disordered). Final results: R(F) = 0.079, wR(F) = 0.105, GOF = 1.189, 542 parameters. CCDC 182/1402.

- 1 S. Brooker, R. J. Kelly and P. Plieger, Chem. Commun., 1998, 1079.
- 2 P. K. Bowyer, K. A. Porter, A. D. Rae, A. C. Willis and S. B. Wild, *Chem. Commun.*, 1998, 1153.
- 3 M. J. Hannon, C. L. Painting, A. Jackson, J. Hamblin and W. Errington, *Chem. Commun.*, 1997, 1807.
- 4 D. M. Haddleton, D. J. Duncalf, D. Kukulj, A. M. Heming, A. J. Shooter and A. J. Clark, J. Mater. Chem., 1998, 8, 1525.
- 5 G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. Mctavish, G. A. Solan, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 849.
- 6 R. Ziessel, A. Harriman, J. Suffert, M.-T. Youinou, A. De Cian and J. Fischer, Angew. Chem., Int. Ed. Engl. 1997, 36, 2509.
- 7 B. Donnio and D. W. Bruce, J. Mater. Chem., 1998, 8, 1993; New J. Chem., 1999, 275.
- 8 H.-T. Nguyen, C. Destrade and J. Malthête, Adv. Mater., 1997, 9, 375.
- 9 A. Juris and R. Ziessel, Inorg. Chim. Acta, 1994, 225, 251.
- 10 R. Ziessel and M.-T. Youinou, Angew. Chem., Int. Ed. Engl., 1993, 32, 877.
- 11 A. El-ghayoury, A. Harriman, A. De Cian, J. Fischer and R. Ziessel, J. Am. Chem. Soc., 1998, **120**, 9973.
- 12 J. Malthête, New J. Chem., 1996, 20, 925.
- 13 A. Pegenau, T. Hegmann, C. Tschierske and S. Diele, *Chem. Eur. J.*, 1999, 5, 1643.
- 14 B. Donnio and D. W. Bruce, Struct. Bonding (Berlin), 1999, 95, 193.
- 15 A. El-ghayoury, L. Douce, A. Skoulios and R. Ziessel, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 2205.
- 16 OpenMoleN, Interactive Structure Solution, Nonius B. V., Delft, The Netherlands, 1997.

Communication 9/04245H