ChemComm

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

Laurent Douce,[a] Abdelkrim El-ghayoury,[a] Antoine Skoulios[b] and Raymond Ziessel*[a]

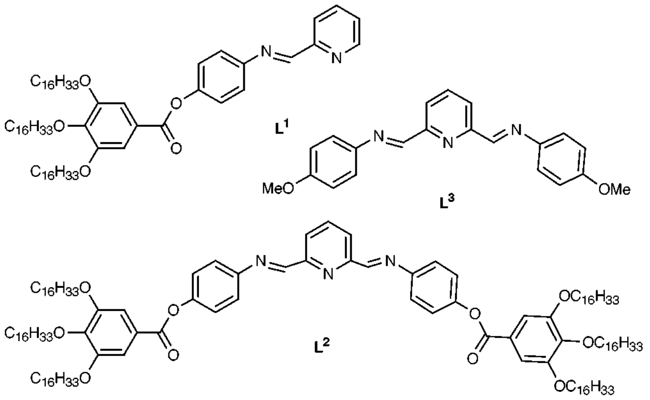
[a] *Laboratoire de Chimie, d'Electronique et de Photonique Moléculaires, Ecole Européenne de Chimie, Polymères et Matériaux, Université Louis Pasteur, ESA 7008 au CNRS, 25 rue Becquerel, F-67087 Strasbourg Cedex 2, France. E-mail: ziessel@chimie.u-strasbg.fr*

[b] *Groupe de Matériaux Organiques, IPCMS, UMR 7504 au CNRS, 23 rue du Loess, F-67037 Strasbourg Cedex , France*

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 species[3] 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 aniline[8] 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 $[Cu(MeCN)_4]BF_4$ leads to immediate formation of a deep-red colouration indicative of complexation of copper(I) to four nitrogen donor ligands[9] {λ_{max} = 505, 500 (sh) and 500 (sh) nm with ε = 5100, 2600 and 3000 dm^3 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 $[Cu(L^n)_2]BF_4$.† A schematic representation of the complexes and a computer generated CPK model of one of the structures is shown in Fig. 1.

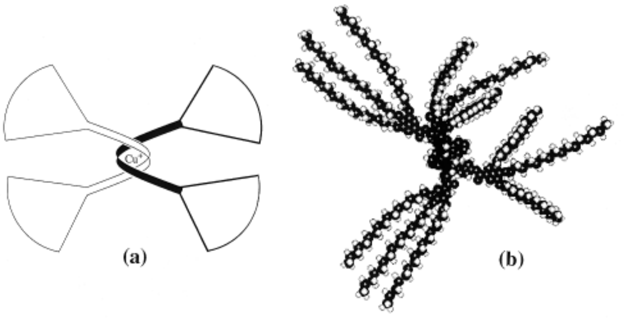


Fig. 1(a) Idealized pictoral representation of complex **2** representing the disk-shape and (b) CPK energy-minimised conformation.

Direct involment of the terminal imino groups in the coordination sphere was confirmed by solid-state and solution-phase FTIR studies and by both ^{1}H and ^{13}C 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 macrocyclic[10] and terpyridine[11] 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 ($\nu_{C=N}$ 1626 cm^{-1}) and the second occurring at lower frequency ($\nu_{C=N}$ = 1588 cm^{-1}) owing to coordination to the metal centre. X-Ray crystallography made for a single crystal of complex **3** indicates that two L³ 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*)].

This journal is © The Royal Society of Chemistry 1999

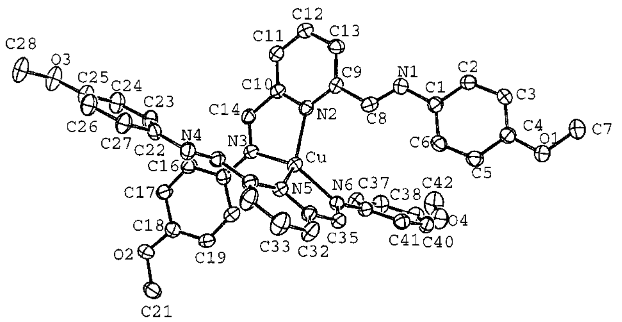


Fig. 2 ORTEP view of complex **3** showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.

Although non-mesomorphic themselves, ligands L^1 and L^2 produce thermotropic liquid-crystalline complexes when coordinated to copper(I), 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 (ΔH = 149.2 kJ mol^{-1}) corresponds to melting of the crystal into a liquid-crystalline phase whereas the peak at 117 °C (ΔH = 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 (ΔH = 84.6 kJ mol^{-1}) and has a clearing point at 75 °C (ΔH = 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 aggregate to form a disk), whereas for **2** the 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*: **L¹**: $\delta_{\mathrm{C=N}}$ 8.64 (CDCl$_3$); $\nu_{\mathrm{C=N}}$ 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%). **L²**: $\delta_{\mathrm{C=N}}$ 8.72 (CDCl$_3$), $\nu_{\mathrm{C=N}}$ 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; $\delta_{\mathrm{C=N}}$ 9.18 (CDCl$_3$); $\nu_{\mathrm{C=N}}$ 1589 cm^{-1} (KBr pellet); FAB$^+$ *m/z* 2109.2 [M-BF$_4$]$^+$, C, 72.98 (73.24), H, 9.73 (10.09), N, 2.23 (2.55%). **2**: 98% yield; $\delta_{\mathrm{C=N}}$ 8.79 (CDCl$_3$); $\nu_{\mathrm{C=N}}$, 1626, 1588 cm^{-1} (KBr pellet); FAB$^+$ *m/z* 3996.8 [M −BF$_4$]$^+$, C, 75.12 (75.50); H, 10.21 (10.61); N, 1.53 (2.05%, calculated with one water molecule).

‡ *Crystal data* for **3**: $C_{42}H_{38}N_6O_4Cu\bullet 2BF_4\bullet H_2O\bullet CH_2Cl_2$, M = 1785.26, triclinic, space group $P\bar{1}$, red crystals, a = 12.6180(7), b = 13.075(1), c = 13.783(1) Å, α = 84.437(9), β = 80.643(9), γ = 70.631(9), V = 2114.4 Å^3, Z = 1, μ = 0.645 mm^{-1}. Data were collected on a Kappa CCD diffractometer (graphite Mo-Kα radiation, λ = 0.71073 Å) at −100 °C. 15930 reflections collected ($2.5 \le 2\theta \le 26.36°$), 4186 data with $I > 3\sigma(I)$. The structure was solved using the Nonius OpenMoleN[16] 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