

Non-discoidal copper(II) and nickel(II) binuclear complexes forming columnar mesophases

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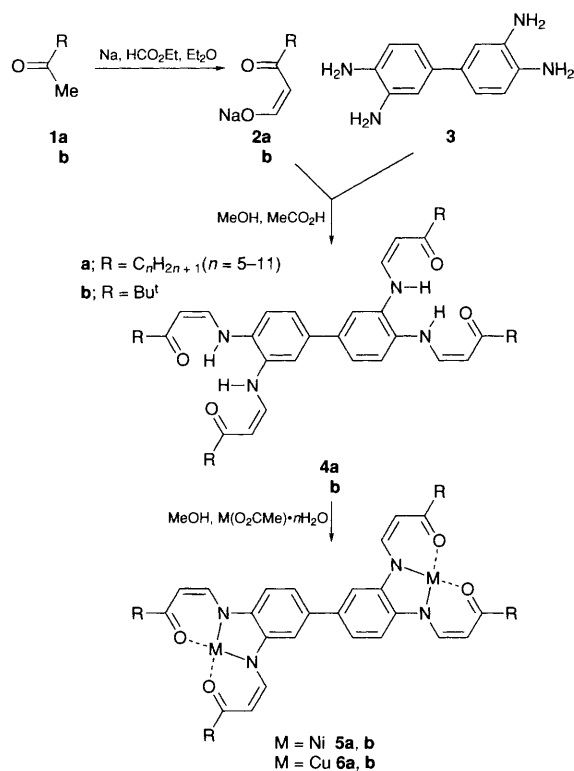
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Nickel(II) and copper(II) *cis*-enaminoketone complexes with two chelating units linked by a biphenyl moiety are found to form the rectangular columnar D_r phase; the columnar phase is produced by the disc-like assemblies of non-discoidal molecules; the existence of molecular dimers is confirmed by EPR measurements where doubling of the Cu^{II} electron and nuclear spin numbers is detected.

Bimetallic mesogens attract considerable attention as potential ferromagnetic liquid crystals.¹ It has been shown that, depending on the bridging groups joining the two metal centres, molecules can adopt either a flat or a 'partially open book' structure.² Although having nearly disc-like molecular geometry these compounds give rise to conventional nematic and smectic rod-like mesophases. On the other hand, columnar phases have been recently observed for elongated or half-disc shaped molecules, where columnar aggregation is produced by disc-shape dimers of the non-discoidal molecules.³ Here, we report the properties of non-discoidal metallomesogens which produce columnar superstructures.

Binuclear nickel(II) and copper(II) complexes **5a**, **6a** were synthesised (Scheme 1), following a procedure similar to that described in ref. 4.



Scheme 1

The ¹H NMR spectrum in CDCl₃ for [3,3',4,4'-tetrakis(2''-heptanoylcarbonylvinylamino)biphenylene]dinickel(II)[‡] was consistent with the assumed molecule structure.

Compounds with modified molecular structures **5b**, **6b** with branched terminal chains did not reveal any mesogenic properties.

The nickel(II) complexes were chosen for systematic studies, owing to their better thermal stability. For the copper(II) complexes some decomposition was observed above 200 °C. A phase diagram for the homologous series of nickel(II) complexes **5a** is shown in Fig. 1.

Complexes **5a**, **6a** exhibit enantiotropic columnar mesophases (D_r). DSC studies show comparable values of enthalpy changes (ca. 20 J g⁻¹) at crystal–liquid crystal and liquid crystal–isotropic phase transitions. The mesophase could easily be supercooled and was stable at room temperature over several days.

Phase identification was based on microscopic and X-ray studies. On cooling the isotropic phase a filament texture was observed. Well developed textures reveal fans with numerous radial disclinations. This type of texture is usually associated with a columnar phase of rectangular symmetry (D_r).⁵

X-Ray studies of the mesophase structures showed strongly disturbed hexagonal crystalline lattices. The appearance of a few Bragg reflections (Table 1) indicates a high degree of molecular organisation and the intracolumnar distance was found to be ca. 4.8 Å in all the studied compounds. A relatively sharp peak related to this spacing, accompanied by a diffused halo, indicates considerable translational order of the mesogenic cores but liquid-like order of the alkyl chains within the column. The presence exclusively of reflections with indexes *h, k* ≠ 0 and *l* = 0 indicates a lack of positional correlation between

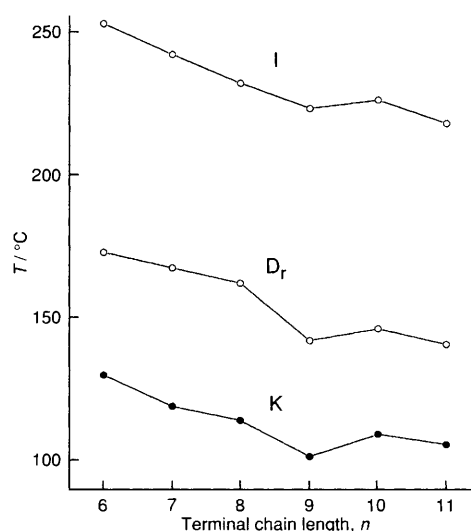


Fig. 1 Phase diagram for the homologous series of nickel(II) complexes **5a**. Filled circles indicate an exothermic process.

Table 1 X-Ray diffraction data (in Å) for Ni^{II} complex **5** with R = C₆H₁₃, C₈H₁₇ and C₁₀H₂₁ measured 10 K above the melting point

h k l	C ₆ H ₁₃		C ₈ H ₁₇		C ₁₀ H ₂₁	
	Meas-ured	Calcu-lated	Meas-ured	Calcu-lated	Meas-ured	Calcu-lated
0 2 0	26.46	26.46	28.68	28.68	30.83	30.83
1 1 0	15.48	15.48	16.88	16.88	17.98	17.98
0 4 0	13.22	13.23	14.55	14.34	15.48	15.42
1 4 0	10.14	10.24	10.97	11.13	11.90	11.92
1 5 0	8.93	8.86	9.71	9.62	10.39	10.31
2 2 0	7.75	7.74	—	—	9.02	8.99
2 3 0	7.47	7.36	7.98	8.02	8.62	8.55

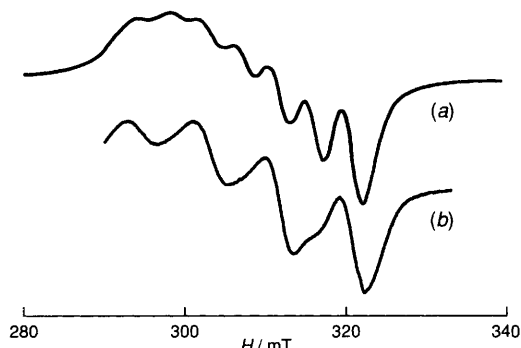


Fig. 2 EPR spectra for (a) **6a** ($n = 1$) at 120 °C, and (b) **6b** in cyanobenzene

molecules belonging to the different columns, and thus the two-dimensional nature of the mesophase. A reasonable density of *ca.* 1.2 g cm⁻³, comparable to that observed in crystal phases,⁶ can be obtained from the X-ray data if four molecules are assumed to exist in the crystal lattice cell.

Interesting behaviour was found within the temperature range of the crystal phase in the nickel(II) complexes. During the first heating cycle the DSC trace exhibits an exothermic process preceding melting to the columnar phase. The room-temperature X-ray diffraction spectrum is characteristic for a poorly organised, possibly glassy or plastic state K.

EPR measurements on the copper(II) complex **6a** ($n = 11$) were performed over a wide temperature range. The spectra of crystalline or liquid-like phases consist of one exchange-narrowed line. When dissolved in cyanobenzene, a gel-like structure was formed and its EPR spectrum exhibited a broad signal with some detectable hyperfine features. On heating (to about 120 °C) the hyperfine pattern became more pronounced and seven lines were visible [Fig. 2(a)]. The spectrum differs from those usually observed for dissolved copper complexes, for which four lines are detected ($S = 1/2$, $I = 3/2$).⁷ For complex **6a** ($n = 11$), the average interline spacing is half that for the standard mononuclear copper complex [1,2-bis(3'-oxo-3'-*p*-toluidino-1'-propenylamino)ethane]copper(II) **7** in which a square-planar configuration was confirmed.⁸ The doubling of the EPR peaks results most probably from an electron exchange interaction between copper ions belonging to neighbouring molecules. Two unpaired electrons from each copper ion create an exchange-coupled system with an effective electron spin number $S = 1$ as well as hyperfine coupling of the nuclei leads to a total spin number $I = 3$.⁹ Thus in solution, **6a** ($n = 11$) freely rotated dimers which display copper-copper interactions are present. Although coupling of unpaired copper electrons in a single molecule could also lead to the multiplying of the EPR spectral lines, this possibility seems to be less plausible owing to the large separation between copper ions (11 Å). Moreover, it has been shown that complex **6b**, with branched terminal chains, when dissolved in cyanobenzene or toluene-chloroform gives an EPR spectrum which, upon heating, gives four hyperfine signals [Fig. 2(b)] as for complex **7**. This confirms the

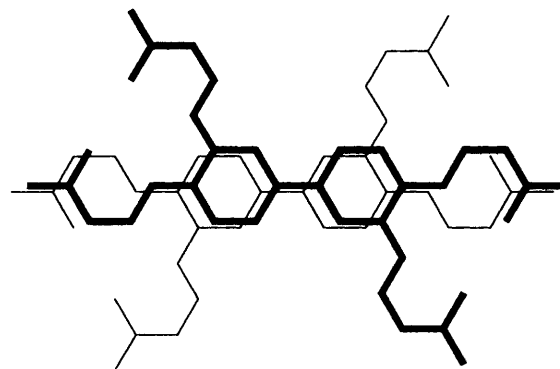


Fig. 3 Schematic representation of the dimer structure of complexes **5a**, **6a**

presence of separated molecules in the solvent as well as the absence of copper-copper interactions in **6b**.

Summarising, new bimetallic *cis*-enaminoketone liquid crystals have been designed. They show a columnar rectangular D_r phase over a wide temperature range, although the isolated molecules do not have the geometry required to form columnar mesophases (length to width ratio of the mesogenic core is *ca.* 2.35). Thus, if the columnar mesophase appears, it is probable that the columns are built up by disc-like dimers. Such dimers may be formed by molecules adopting a parallel orientation of their long axes, as illustrated in Fig. 3. This structure has an estimated length to width ratio of *ca.* 1.5, a more suitable value for columnar aggregation. Based on X-ray measurements and molecular modelling the estimated intermolecular Cu...Cu distance is *ca.* 6 Å, sufficient to cause strong coupling spin interactions, as detected in the EPR studies. Dimers of **5a** and **6a** are present even in strongly polar cyanobenzene, which usually inhibits molecular association. On the other hand the *tert*-butyl derivatives **5b**, **6b** in the same solvent are monomeric. The latter materials do not display any stable mesophase since the bulky chains hinder dimer formation.

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Footnotes

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‡ NMR for **5a** ($n = 6$): δ 0.86–0.92 [m, 12 H, CH₂(CH₂)₄CH₃], 1.26–1.68 [m, 32 H, CH₂(CH₂)₄CH₃], 2.40 [m, 8 H, CH₂(CH₂)₄CH₃], 5.50 (br d, 4 H, HCCO), 7.14 (dd, J 8.30, 1.47 Hz, 2 H, H^{6,6'}), 7.41 (d, J 6.35 Hz, 2 H), 7.50 [d, J 6.83 Hz, 2 H, HCNNi], 7.43 (d, J 8.30 Hz, 2 H, H^{5,5'}), 7.54 (d, J 1.47 Hz, 2 H, H^{2,2'}).

References

- D. W. Bruce and D. O'Hare, *Inorganic Materials*, Wiley, New York, 1992.
- M. Ghedini, S. Armentano and F. Neve, *Inorg. Chim. Acta*, 1987, **134**, 23; M. Ghedini, S. Licoccia, S. Armentano and R. Bartolino, *Mol. Cryst. Liq. Cryst.*, 1984, **108**, 269; P. Espinet, J. Etxebarria, M. Marcos, J. Perez, A. Remon and J. L. Serrano, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1065.
- K. L. Chung, A. G. Serrette and T. M. Swager, *J. Am. Chem. Soc.*, 1992, **114**, 7948; A. G. Serrette and T. M. Swager, *J. Am. Chem. Soc.*, 1993, **115**, 8879; H. Zheng, B. Xu and T. M. Swager, *Chem. Mater.*, 1996, **8**, 907.
- W. Pyzuk, A. Krowczynski, Li Chen, E. Gorecka and I. Bikchantaev, *Liq. Cryst.*, 1995, **19**, 675.
- C. Destrade, P. Foucher, H. Gasparoux, N. Huu Vinh, A. M. Levelut and J. Malthere, *Mol. Cryst. Liq. Cryst.*, 1984, **106**, 121.
- K. Usha, K. Vijayan and B. K. Sadashiva, *Mol. Cryst. Liq. Cryst. Lett.*, 1987, **5**, 67.
- J. A. Weil, J. R. Bolton and J. E. Wertz, *Electron Paramagnetic Resonance*, Wiley, New York, 1992.
- J. Szydłowska, A. Krówczyński and R. Anulewicz, unpublished work.
- P. D. W. Boyd, A. D. Toy, T. D. Smith and J. R. Pilbrow, *J. Chem. Soc., Dalton Trans.*, 1973 1549; T. D. Smith and J. R. Pilbrow, *Coord. Chem. Rev.*, 1974, **13**, 173.

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