Synthesis, Structural Characterization and Mesogenic Behavior of Copper(I) *n*-Alkylthiolates

Pablo Espinet,* M. Carmen Lequerica, and José M. Martín-Alvarez[a]

Abstract: Copper(I) thiolates [$CuSC_nH_{2n+1}$] ($n = 4$, 6, 8, 10, 12, 16, 18) have been prepared, and their liquid crystal behavior has been studied. Contrary to previous reports the compounds possess a lamellar structure in the solid state, which has been characterized by X-ray diffraction analysis of polycrystalline samples. Melting leads to a columnar mesophase which is stable within a range of 50–60 °C for most of the derivatives, and has been characterized for [$CuSC_{10}H_{21}$]: the X-ray diffraction pattern is consistent with a hexagonal columnar mesophase ($a = 2.15$ nm) composed of [$Cu_4(\mu_2\text{-}SC_{10}H_{21})_4$] aggregates, and suggests that additional S$\cdots$Cu interactions between the disklike tetramers induce a fairly ordered intracolumnar arrangement of these aggregates.

Keywords: copper • liquid crystals • metallomesogens • S ligands • thiolates

Introduction

Metal thiolates in general, and copper(I) thiolates $(CuSR)_n$ in particular, are of fundamental interest.[1] Copper arenethiolates have recently found application in organic synthesis.[2] They offer a great diversity of structures.[3] They are also important in connection with the active sites in metalloproteins, such as the blue copper proteins, which involve Cu–S binding.[4] Moreover, copper thiolate complexes can sometimes behave as semiconductors,[5] and can be used as precursors for the synthesis of solid-state chalcogenide materials through thermolysis.[6]

Copper thiolates CuSR are still incompletely characterized structurally, largely due to their insolubility and poor crystal habit, which are presumed to be the result of polymeric structures.[1] One approach to the problem has been to increase the steric bulk of the substituent R, which leads to soluble complexes but is also a major factor in determining the structure of the complex.[7] In some cases it has been shown that the steric pressure between large substituents R can be alleviated by simple structural modifications involving a change in metal coordination from trigonal-planar towards digonal.[8]

This behavior in the solid state is somewhat analogous to that observed for silver alkylthiolates when they are heated and melted. We reported previously that, when the steric pressure of the substituents R increases as a consequence of the appearance of *gauche* conformations upon melting, the silver thiolates change from their bilayer μ_3-bridged structure in the solid state or in the lamellar mesophase to a cyclic μ_2-bridged structure in the columnar mesophase.[9]

In recent years metallomesogens (metal-containing compounds displaying liquid crystalline behavior) have undergone systematic research and development.[10] Copper(II) complexes are paramagnetic and have been studied extensively. The most commonly reported copper(II) mesogens are complexes with β-diketonate ligands, with carboxylate ligands, or with Schiff-base imines.[11] As far as we know, there is only one very recent report on copper(I) mesogens,[12] although examples of mesogens with other d^{10} complexes are known: silver(I) with stilbazoles,[13] alkylamines,[14] and thiolates;[9] gold(I) with isonitriles;[15] zinc(II) and cadmium(II) with porphyrins;[16] zinc(II) with dithiobenzoates;[17] cadmium(II) with alkanoates;[18] and mercury(II) with aryls.[19]

Preliminary tests on long-chain copper(I) *n*-alkylthiolates showed that they had layered structures in the solid state, and melted to give mesophases. We therefore undertook the systematic study presented here.

Results and Discussion

Several methods of preparing copper(I) thiolates have been reviewed recently.[3] A fairly general method is the deprotonation of thiols in the presence of a suitable copper source

---

[a] Prof. Dr. P. Espinet, Dr. M. C. Lequerica, Dr. J. M. Martín Alvarez
Departamento de Química Inorgánica, Facultad de Ciencias
Universidad de Valladolid, E-47005 Valladolid (Spain)
Fax: (+34) 983423013
E-mail: espinet@qi.uva.es

Supporting Information for this contribution is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author. The file contains microanalytical data, details of the powder diffraction technique, and peaks found in the X-ray diffraction experiments on polycrystalline samples.

0947-6539/99/0507-1982 $ 17.50+.50/0

(either Cu^I or Cu^{II}) and a base. We have synthesized the copper(I) thiolates reported in this work starting from Cu_2O without any base (method A), or from CuCl with triethylamine as a base (method B). The second procedure is faster and does not require reflux. However, although all the copper(I) thiolates, whether prepared from copper(I) chloride or from copper(I) oxide, gave satisfactory C, H analyses and powder diffraction patterns, after two months of storage (in air, but shielded from light) only the samples prepared from copper(I) oxide again gave satisfactory elemental analyses, remained white, and exactly reproduced the powder diffraction patterns. Those prepared from CuCl had become sticky, had developed colors ranging from greenish to black, and gave elemental analyses low in C. This suggested partial oxidation of the copper and eventual formation of CuO, which could be confirmed by comparison of the powder diffractograms of these samples with that of the original CuO. The difference in stability towards oxidation of the samples obtained by different preparative methods must correspond to small structural differences or catalytic impurities which could not be detected by the characterization methods used. Therefore, we recommend the preparative method A, starting from Cu_2O. The studies reported in this paper were made on compounds prepared by this method.

Dance et al., when studying the layered structure of silver thiolates, did not observe a layer-type diffraction pattern for any CuSR compound,[20] but our X-ray diffraction analysis of polycrystalline samples of the copper(I) thiolates prepared as described in the Experimental Section revealed very clearly a layered structure in the solid state, similar to that found for silver thiolates. In view of the remarkable influence of the conditions of synthesis on the properties of these polymeric thiolates (as discussed above for Cu^I and for Ag^I in our previous paper),[9, 21] we assume that the samples used by Dance et al. were prepared by a different synthetic procedure (not reported in ref. [20]) and were either structurally different, or partially decomposed.

A representative example of the X-ray diffraction patterns of our polycrystalline samples of copper(I) thiolates is shown in Figure 1. All the compounds produce a series of intense reflections, which are successive orders of diffraction from a layer structure, and can be indexed as $(0k0)$ reflections with $k \leq 7$. For each compound, there is excellent agreement between the interlayer spacing measured from the diffraction patterns and that calculated with molecular models assuming a bilayer structure analogous to that of the silver thiolates. The latter consists of a central slab of Ag and S atoms disposed in a quasi-hexagonal network with each silver tricoordinated by three thiolates and each thiolate μ_3-bridging three silver atoms.[20] The chains of the thiolates are distributed randomly on both sides of this slab, roughly perpendicular to it. Observed interlayer spacings, and those calculated assuming this structure, are collected in Table 1.

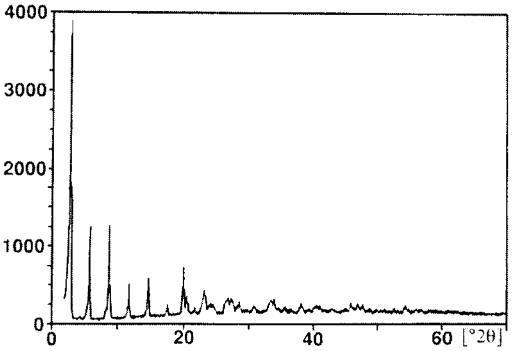

Figure 1. Diffraction pattern of polycrystalline [$CuSC_{10}H_{21}$].

Table 1. Observed and calculated layer thickness for [$CuSC_nH_{2n+1}$].

n	T_{obs}[a] [Å]	T_{calcd}[a] [Å]
4	15.92	15.91
6	20.72	20.89
8	25.74	25.86
10	30.19	30.83
12	36.05	35.81
16	46.04	45.76
18	49.99	50.73

[a] T_{obs} is the layer thickness measured by X-ray diffraction, and T_{calcd} is the calculated one assuming a fully extended conformation of the alkyl chains.

Since the solid-state structures of copper(I) and silver thiolates seem very alike, a similar mesogenic behavior could be expected for both types of compound. Nevertheless, we have found some differences. For $n = 4-10$, melting of the $AgSC_nH_{2n+1}$ compounds leads initially in each case to a metastable lamellar (or S_A) mesophase; above this S_A phase an isotropic phase is formed, and further heating gives rise to a columnar mesophase. For $n \geq 12$, melting of the $AgSC_nH_{2n+1}$ compounds produces the columnar mesophase in each case; presumably the other phases could be formed as transient intermediates, but they have not been detected. In the copper thiolates melting leads directly to the columnar mesophase for every chain length and no intermediate phases were observed. With short aliphatic chains ($4 \leq n \leq 10$) the mesophase observed has a texture with large extinction domains (pseudo-isotropic), and bâtonnets on cooling from the isotropic liquid (Figure 2). With longer chains ($n \geq 12$) a typical fan-shaped focal-conic texture is observed (Figure 3). Both textures are very similar to those found for silver thiolates in their columnar mesophase.

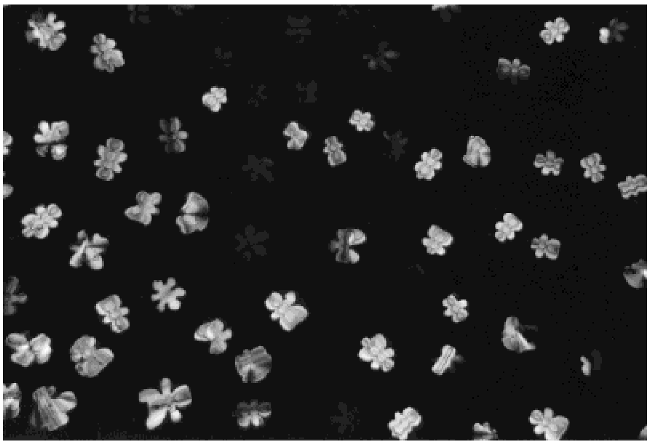

Figure 2. Texture of the columnar phase of [$CuSC_8H_{17}$], on cooling from the isotropic liquid to 150 °C.

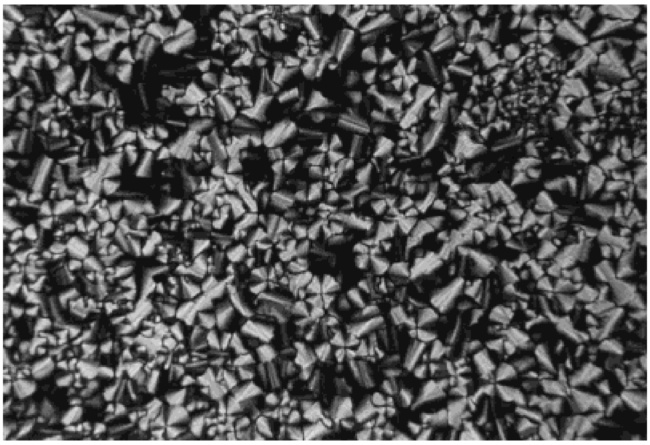

Figure 3. Texture of the columnar phase of [$CuSC_{18}H_{37}$], on cooling from the isotropic liquid to 145 °C.

Thermal parameters (Table 2) were determined by differential scanning calorimetry (DSC), and the thermal behavior was compared with that of the corresponding AgSR compounds (Figure 4). The melting points decrease with increasing length of the alkyl chain to reach a roughly constant value beyond $n = 8$. The clearing points are in the range 195–210 °C for all the derivatives except that with $n = 18$, which undergoes the transition to the isotropic liquid at approximately 150 °C. Thus the range of mesogenic behavior is 50–60 °C for compounds with $6 \leq n \leq 16$, and somewhat smaller for the derivatives with shorter or longer chains (10–15 °C for $n = 4$, 18).

Table 2. Optical, thermal, and thermodynamic data for [$CuSC_nH_{2n+1}$].

n	Transition[a]	Temperature[b] [°C]	ΔH[b] [KJ mol^{-1}]
4	C–M	172.6	9.0
	M–I	188.5	0.6
6	C–Col	148.0	19.4
	Col–I	210.8	3.3
8	C–Col	136.4	25.6
	Col–I	192.7	3.2
10	C–Col	140.8	29.2
	Col–I	203.7	2.7
12	C–Col	143.5	36.8
	Col–I	205.6	2.8
16	C–Col	143.2	42.7
	Col–I	194.8	1.9
18	C–C′	56.1	10.0
	C–Col	140.6	42.0
	Col–I	151.5	0.9

[a] C, C′: crystal; Col: columnar; I: isotropic liquid. [b] Data referred to the second DSC cycle. Temperature data as peak onset.

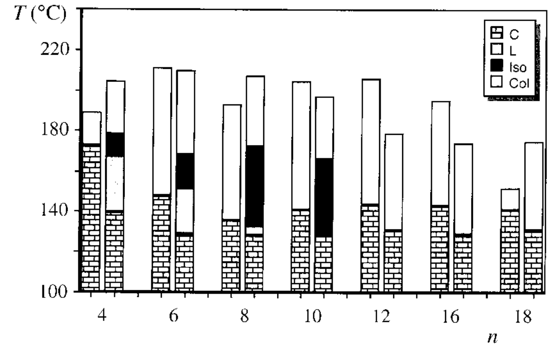

Figure 4. Comparison of the thermal properties of [$AgSC_nH_{2n+1}$] compounds reported in ref. [11] and [$CuSC_nH_{2n+1}$] compounds. The left-hand bar of each pair represents the behavior of the copper thiolates and the right-hand bar those of the silver thiolates. C, crystalline; L, lamellar; Iso, uncharacterized isotropic phase; Col, columnar.

An X-ray analysis of the columnar mesophase of the $CuSC_{10}H_{21}$ derivative was carried out at 170 °C and showed four low-angle rings and two diffuse halos in the corresponding diffraction pattern (Figure 5). The d spacing of the first four diffraction rings scales as $1{:}(1/3)^{1/2}{:}1/2{:}(1/7)^{1/2}$, which is consistent with a hexagonal lattice ($a = 2.15$ nm). The first broad halo (0.46 nm) is indicative of the melting of the chains, and the outer diffuse halo reveals that the columns consist of stacks of disks separated by 0.34 nm. From these data, the composition of the disks can be calculated: they are formed by cyclic [$Cu_4(\mu_2\text{-}SC_{10}H_{21})_4$] units (Figure 6). This result is not

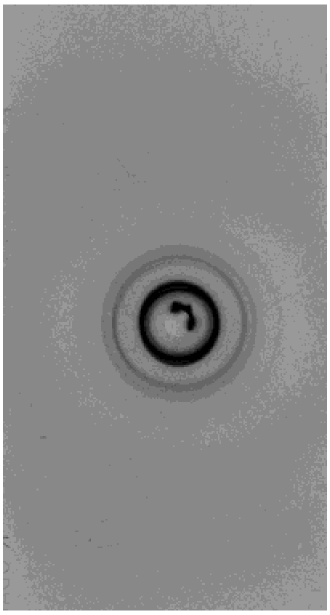

Figure 5. Diffraction pattern of [$CuSC_{10}H_{21}$] in the mesophase (at 170 °C).

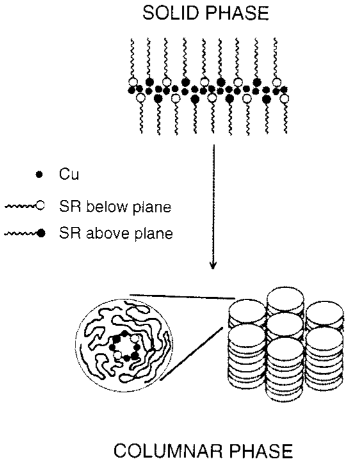

Figure 6. Schematic representation of the structure of copper thiolates in the solid and columnar phases. The tetranuclear aggregates can be assimilated into disks 0.34 nm thick. One disk is viewed in the direction of the columnar axis. For a more detailed description of the solid phase, see ref. [20].

unexpected since tetrameric copper(I) thiolate aggregates are common, not only with intramolecularly coordinating ligands and auxiliary donor ligands,[22] but also without donor ligands of any type.[23]

The presence of the outer diffuse halo is a consequence of a roughly equal distance between disks along the column axis and is observed in copper(I) thiolates but not in silver thiolates. Moreover, in copper(I) thiolates the lamellar or isotropic phases are destabilized compared with the columnar phase, even for the derivative with the shortest aliphatic chain. These observations can be explained by the similarity of the structure of the copper(I) thiolate aggregates inside the column to that found in $[Cu_8(SCMe_2Et)_4(S_2CSCMe_2Et)_4]$.[8] In our case the sulfur atoms of the $[Cu_4(\mu_2\text{-}SC_{10}H_{21})_4]$ rings would be bonded by their lone electron pairs to another Cu atom of another $[Cu_4(\mu_2\text{-}SC_{10}H_{21})_4]$ ring above or below the one with which they are mainly involved. Thus, assuming that the disks are stacked in an alternating fashion along the column as reported for [AuX(CNR)] complexes,[15f] weak $S\cdots Cu$ interactions could be established between the Cu atoms of one tetranuclear aggregate and the S atoms of the neighboring aggregates. Counting this additional interaction, the sulfur atoms would be μ_3-bridging, connecting two Cu atoms of the central ring between them and also one Cu atom of the ring above or below; the Cu atoms would be tricoordinated. The existence of these additional weak interactions may account nicely for the increased stability of the columnar phase in copper(I) thiolates and the ordered intracolumnar character that this mesophase displays.

Conclusion

The preparative method severely influences the stability of copper(I) *n*-alkylthiolates towards oxidation. Contrary to previous reports, they possess a lamellar structure in the solid state. Upon heating they melt to a columnar mesophase based on the stacking of cyclic $[Cu_4(\mu_2\text{-}SC_nH_{2n+1})_4]$ aggregates.

Experimental Section

All the thiols used were of commercial grade (Aldrich) and were not purified further. Their catalogue purities were all greater than 97% except for $HSC_{16}H_{33}$ (92%). No commercial source of $HSC_{14}H_{29}$ was found. Combustion analyses were performed with a Perkin-Elmer 2400 microanalyzer. Microscopic studies were carried out in a Leitz microscope equipped with a hot stage and polarizers, at a heating rate of approximately 10 K min^{-1}. For DSC a Perkin-Elmer DSC7 instrument was calibrated with water and indium; the scanning rate was 10 K min^{-1}, the samples were sealed in aluminum capsules in air, and the holder atmosphere was dry nitrogen.

X-ray diffraction experiments on the mesophase were performed with a Guinier camera with $Cu_{K\alpha}$ radiation and a cylindrical film, diameter 114.6 nm. The samples were held in Lindemann glass tubes situated in the gap of a magnet with a field strength of 0.3–1.7 T. X-ray diffraction experiments on polycrystalline samples were carried out on a Phillips PW1710 diffractometer fitted with a PW1820 goniometer.

Representative synthetic procedures:

Method A: To a solution (or a suspension for $n = 16$, 18) of the corresponding *n*-alkylthiol (2.8 mmol) in ethanol (15 mL) was added Cu_2O (0.7 mmol) under N_2. The resulting suspension was refluxed until the color changed from reddish to white. The resulting fine powder was centrifuged, washed with ethanol (4 × 10 mL; for $n = 4$–12) or dichloromethane (4 × 10 mL) (for $n = 16$, 18), and vacuum-dried. All $CuSC_nH_{2n+1}$ compounds were prepared according to this procedure, but with different reflux times: 48 h for $n = 4$, 6; 96 h for $n = 8$; five days for $n = 10$; eight days for $n = 12$; three weeks for $n = 16$; four weeks for $n = 18$. $CuSC_4H_9$: calcd. C 31.46, H 5.94; found C 31.62, H 6.05. $CuSC_6H_{13}$: calcd. C 39.87, H 7.25; found C 39.74, H 7.18. $CuSC_8H_{17}$: calcd. C 46.01, H 8.21; found C 46.02, H 8.17. $CuSC_{10}H_{21}$: calcd. C 50.70, H 8.94; found C 50.46, H 8.96. $CuSC_{12}H_{25}$: calcd. 54.40, H 9.51; found C 54.03, H 9.38. $CuSC_{16}H_{33}$: calcd. C 59.86, H 10.36; found C 59.98, H 10.26. $CuSC_{18}H_{37}$: calcd. C 61.93, H 10.68; found C 62.22, H 10.77.

Method B: To a solution (or a suspension for $n = 16$, 18) of the corresponding *n*-alkylthiol (3.9 mmol) and triethylamine (3.5 mmol) in ethanol (15 mL) was added copper(I) chloride (3.5 mmol) in small portions. The reaction was complete, giving a very fine white precipitate, in 2 h for $n = 4$, 6, 8; 6 h for $n = 10$, 12; 8 h for $n = 16$; 10 h for $n = 18$. The white solid was centrifuged, washed with ethanol (4 × 10 mL; for $n = 4$–12) or dichloromethane (4 × 10 mL) (for $n = 16$, 18), and vacuum-dried.

Acknowledgments

We are indebted to Dr. Anne-Marie Levelut for the use of the Guinier camera and helpful discussions. We also thank the Comisión Interministerial de Ciencia y Tecnología (Project MAT96-0708) and the Junta de Castilla y León (Project VA23/97) for financial support.

---

[1] a) I. G. Dance, *Polyhedron* **1986**, *5*, 1037; b) B. Krebs, G. Henkel, *Angew. Chem.* **1991**, *103*, 785; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 769.

[2] a) G. H. Posner, C. E. Whitten, J. J. Sterling, *J. Am. Chem. Soc.* **1973**, *95*, 7788; b) D. M. Knotter, D. M. Grove, W. J. J. Smeets, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **1992**, *114*, 3400; c) M. van Klaveren, F. Lambert, D. J. M. F. Eijkelkamp, D. M. Grove, G. van Koten, *Tetrahedron Lett.* **1994**, *35*, 6135; d) Q. Zhou, A. Pfaltz, *Tetrahedron Lett.* **1993**, *34*, 7725; e) A. Haubrich, M. van Klaveren, G. van Koten, G. Handke, N. Krause, *J. Org. Chem.* **1993**, *58*, 5849; f) M. van Klaveren, E. S. M. Persson, D. M. Grove, J.-E. Bäckvall, G. van Koten, *Tetrahedron Lett.* **1994**, *35*, 5931; g) M. van Klaveren, E. S. M. Persson, A. del Villar, D. M. Grove, J.-E. Bäckvall, G. van Koten, *Tetrahedron Lett.* **1995**, *36*, 3059; h) M. van Klaveren, E. S. M. Persson, D. M. Grove, J.-E. Bäckvall, G. van Koten, *Chem Eur. J.* **1995**, *1*, 351.

[3] For a recent review see: M. D. Janssen, D. M. Grove, G. van Koten, *Progress in Inorganic Chemistry*, *Vol. 46*, Wiley, New York, **1997**, p. 97.

[4] D. Swenson, N. C. Baenziger, D. Coucouvanis, *J. Am. Chem. Soc.* **1978**, *100*, 1932.

[5] G. N. Schrauzer, H. Prakash, *Inorg. Chem.* **1975**, *14*, 1200.

[6] D. V. Khasnis, M. Buretea, T. J. Emge, J. G. Brennan, *J. Chem. Soc. Dalton Trans.* **1995**, 45, and references therein.

[7] a) Q. Yang, K. Tang, H. Liao, Y. Han, Z. Chen, Y. Tang, *J. Chem. Soc. Chem. Commun.* **1987**, 1076; b) E. Block, M. Gernon, H. Kang, G. Ofori-Okai, J. Zubieta, *Inorg. Chem.* **1989**, *28*, 1263; c) M. Knotter, G. van Koten, H. L. van Maanen, D. M. Grove, A. L. Spek, *Angew. Chem.* **1989**, *101*, 351; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 341.

[8] I. G. Dance, *Polyhedron* **1988**, *7*, 21, 2205.

[9] M. J. Baena, P. Espinet, M. C. Lequerica, A. M. Levelut, *J. Am. Chem. Soc.* **1992**, *114*, 4182.

[10] For reviews see: a) A. M. Giroud-Godquin, P. M. Maitlis *Angew. Chem.* **1991**, *103*, 370; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 375; b) P. Espinet, M. A. Esteruelas, L. A. Oro, J. L. Serrano, E. Sola, *Coord, Chem. Rev.* **1992**, *117*, 215; c) D. W. Bruce, in: *Inorganic Materials* (Eds.: D. W. Bruce, D. O'Hare), John Wiley, Chichester, **1992**, Chapter 8; d) S. A. Hudson, P. M. Maitlis, *Chem. Rev.* **1993**, *93*, 861; e) *Metallomesogens* (Ed.: J. L. Serrano), VCH, Weinheim, **1996**.

[11] Representative examples: a) A. C. Ribeiro, A. F. Martins, A. M. Giroud-Godquin, *Mol. Cryst. Liq. Cryst. Lett.* **1988**, *5*, 133; b) S. Chandrasekhar, B. K. Sadashiva, B. S. Srikanta, *Mol. Cryst. Liq. Cryst.* **1987**, *151*, 93; c) K. Ohta, O. Takenaka, H. Hasebe, Y. Morizumi, T.

Fujimoto, I. Yamamoto, *Mol. Cryst. Liq. Cryst.* **1991**, *195*, 135; d) K. Ohta, H. Akimoto, T. Fujimoto, I. Yamamoto, *J. Mater. Chem.* **1994**, *4*, 61; e) N. J. Thompson, J. W. Goodby, K. Toyne, *Mol. Cryst. Liq. Cryst.* **1992**, *214*, 81; f) M. Ibn-Elhaj, D. Guillon, A. Skoulios, A. M. Giroud-Godquin, P. Maldivi, *Liq. Cryst.* **1992**, *11*, 731; g) U. Caruso, A. Roviello, A. Sirigu, *Liq. Cryst.* **1988**, *3*, 1515; h) M. Marcos, P. Romero, J. L. Serrano, C. Bueno, J. L. Cabeza, L. A. Oro, *Mol. Cryst. Liq. Cryst.* **1989**, *167*, 123; i) M. Ghedini, S. Morrone, D. Gatteschi, C. Zanchini, *Chem. Mater.* **1991**, *3*, 752; j) M. Marcos, J. L. Serrano, T. Sierra, M. J. Giménez, *Angew. Chem.* **1992**, *104*, 1523; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1471; k) N. Hoshino, H. Murakami, Y. Matsunaga, T. Inabe, Y. Murayama, *Inorg. Chem.* **1990**, *29*, 1177.

[12] A. El-ghayoury, L. Douce, A. Skoulios, R. Ziessel, *Angew. Chem.* **1998**, *110*, 2327; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 2205.

[13] a) D. W. Bruce, D. A. Dunmur, E. Lalinde, P. Styring, *Nature (London)* **1986**, *323*, 791; b) D. W. Bruce, D. A. Dunmur, P. M. Maitlis, P. Styring, M. A. Esteruelas, L. A. Oro, M. B. Ros, J. L. Serrano, E. Sola, *Chem. Mater.* **1989**, *1*, 479; c) D. W. Bruce, D. A. Dunmur, S. A. Hudson, E. Lalinde, P. M. Maitlis, M. P. McDonald, R. Orr, P. Styring, A. S. Cherodian, A. M. Richardson, J. L. Feijoo, G. Ungar, *Mol. Cryst. Liq. Cryst.* **1991**, *206*, 79; d) H. Adams, N. A. Bailey, D. W. Bruce, S. C. Davis, D. A. Dunmur, P. D. Hempstead, S. A. Hudson, S. Thorpe, *J. Mater. Chem.* **1992**, *2*, 395; e) D. W. Bruce, D. A. Dunmur, S. A. Hudson, P. M. Maitlis, P. Styring, *Adv. Mater. Optics Electron.* **1992**, *1*, 37; f) D. W. Bruce, S. A. Hudson, *J. Mater. Chem.* **1994**, *4*, 479.

[14] J. Barberá, J. L. Serrano, A. C. Albéniz, P. Espinet, M. C Lequerica, F. J. López-Marcos, A. M. Levelut, L. Lièbert, *2nd International Symposium on Metal-Containing Liquid Crystals*, **1991**, Saint Pierre de Chartreuse (France).

[15] a) T. Kaharu, R. Ishii, S. Takahashi, *J. Chem. Soc. Chem. Commun.* **1994**, 1349; b) T. Kaharu, R. Ishii, T. Adachi, T. Yoshida, S. Takahashi, *J. Mater. Chem.* **1994**, *4*, 859; c) S. Coco, P. Espinet, S. Falagán, J. M. Martín-Alvarez, *New J. Chem.* **1995**, *19*, 959; d) P. Alejos, S. Coco, P. Espinet, *New J. Chem.* **1995**, *19*, 799; e) M. Benouazzane, S. Coco, P. Espinet, J. M. Martín-Alvarez, *J. Mater. Chem.* **1995**, *5*, 441; f) S. Coco, P. Espinet, J. M. Martín-Alvarez, A. M. Levelut, *J. Mater. Chem.* **1997**, *7*, 19; g) R. Bayón, S. Coco, P. Espinet, C. Fernández-Mayordomo, J. M. Martín-Alvarez, *Inorg. Chem.* **1997**, *36*, 2329.

[16] a) B. A. Gregg, M. A. Fox, A. J. Bard, *J. Chem. Soc. Chem. Commun.* **1987**, 1134; b) B. A. Gregg, M. A. Fox, A. J. Bard, *J. Am. Chem. Soc.* **1989**, *111*, 3024; c) S. Kujimiya, M. Takemura, *Tetrahedron Lett.* **1990**, *31*, 3157; d) R. Ramasseul, P. Maldivi, J. C. Marchon, M. Taylor, D. Guillon, *Liq. Cryst.* **1993**, *13*, 729; e) Y. Shimizu, M. Miya, A. Nagata, K. Ohta, I. Yamamoto, S. Kusabayashi, *Liq. Cryst.* **1993**, *14*, 795; f) P. Doppelt, S. Huille, *New J. Chem.* **1990**, *14*, 607; g) F. Lejl, G. Morelli, G. Ricciardi, A. Roviello, A. Sirigu, *Liq. Cryst.* **1992**, *12*, 941.

[17] a) H. Adams, A. C. Albéniz, N. A. Bailey, D. W. Bruce, A. S. Cherodian, R. Dhillon, D. A. Dunmur, P. Espinet, J. L. Feijoo, E. Lalinde, P. M. Maitlis, R. M. Richardson, G. Ungar, *J. Mater. Chem.* **1991**, *1*, 843; b) D. Guillon, D. W. Bruce, P. Maldivi, M. Ibn-Elhaj, R. Dhillon, *Chem. Mater.* **1994**, *6*, 182; c) D. W. Bruce, R. Dhillon, D. A. Dunmur, P. M. Maitlis, *J. Mater. Chem.* **1992**, *2*, 65; d) K. Ohta, Y. Morizumi, H. Ema, T. Fujimoto, I. Yamamoto, T. Sakurai, *Mol. Cryst. Liq. Cryst., Sci. Technol., Sect. A* **1992**, *214*, 151.

[18] P. A. Spegt, A. E. Skoulios, *Acta Crystallogr.* **1963**, *16*, 301.

[19] D. Vorländer, *Z. Phys. Chem.* **1923**, *105*, 211.

[20] I. G. Dance, K. J. Fisher, R. M. H. Banda, M. L. Scudder, *Inorg. Chem.* **1991**, *30*, 183.

[21] H. G. Fijolek, J. R. Grohal, J. L. Sample, M. J. Natan, *Inorg. Chem.* **1997**, *36*, 622.

[22] a) D. M. Knotter, M. D. Janssen, D. M. Grove, W. J. J. Smeets, E. Horn, A. L. Spek, G. van Koten, *Inorg. Chem.* **1991**, *30*, 4361; b) I. G. Dance, L. J. Fitzpatrick, D. C. Craig, M. L. Scudder, *Inorg. Chem.* **1989**, *28*, 1853; c) M. A. Khan, R. Kumar, D. G. Tuck, *Polyhedron* **1988**, *7*, 49.

[23] a) I. Schröter-Schmid, J. Strähle, *Z. Naturforsch. Teil B* **1990**, *45*, 1537; b) E. Block, H. Kang, G. Ofori-Okai, J. Zubieta, *Inorg. Chim. Acta* **1990**, *167*, 147; c) B. Becker, W. Wojnowski, K. Peters, E.-M. Peters, H. G. von Schnering, *Polyhedron* **1990**, *9*, 1659.

Received: October 23, 1998
Revised version: February 8, 1999 [F1410]