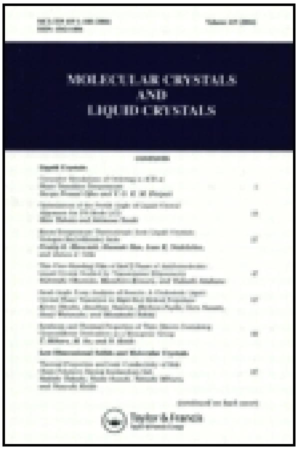

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Novel Thermotropic Mesophases of Copper Complexes with Long-Chain Aliphatic Amines

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NOVEL THERMOTROPIC MESOPHASES OF COPPER COMPLEXES WITH LONG-CHAIN ALIPHATIC AMINES

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Abstract A novel class of liquid crystalline complexes was prepared by the interaction of copper nitrate with long-chain primary amines (such as octyl-, decyl-, dodecyl- and octadecylamine) or with the secondary didodecylamine. Analysis has shown that primary amines form tetracoordinated complexes, whereas, with the secondary one the ratio of copper to ligand was 1:2. The mesomorphic phase behavior of the complexes was established by optical microscopy and differential scanning calorimetry and it was found to depend, as expected, on the amine employed for their synthesis. Further work with X-ray diffraction and other techniques is in progress for a more complete identification of these new mesophases.

INTRODUCTION

A critical investigation of the molecular features of compounds exhibiting thermotropic liquid crystalline behavior reveals that it is not only the rigid anisotropic structure that induces their thermotropic mesomorphism. It has, in addition, been established that a crucial parameter for the compounds to show liquid crystallinity, and specifically smectic phases, is the existence of two distinct immiscible portions in their molecules. This structural feature is fulfilled in surfactants which have a polar head and a long aliphatic chain or chains and therefore the formation of a lamellar structure by alternating polar and lipophilic sublayers is achieved. Thus smectic behavior has been exhibited by metal carboxylates[1-3], n-alkylammonium halides[4,5],bis(n-alkylammonium) salts[6] and quaternary ammonium salts[7,8].

In this connection it has also been found lately that if long lipophilic chains were functionalizing a rigid disk-like core,liquid crystals called discotic were obtained. Thus long-chain substituted metallophthalocyanines[9-11], dicopper[12] or dirhodium[12] long-aliphatic carboxylates exhibiting discotic mesophases have been prepared.

It is well-known that strong Jahn-Teller distortion[14] of Cu(II) (d^9-configuration) favors the formation of square planar amine complexes. In this context, and because of the potential of these complexes for forming liquid crystalline phases which could show interesting magnetic ground states in an ordered array,the preparation of complexes of Cu(II) with long-chain primary aliphatic amines, for instance, octyl-, decyl-, dodecyl-, octadecylamine, as well as the secondary didodecylamine was undertaken. In these first experiments the mesomorphic behavior of the complexes was investigated by optical microscopy and differential scanning calorimetry.

EXPERIMENTAL

Synthesis of Copper Complexes

To 0.01 mole of $Cu(NO_3)_2 3H_2O$ dissolved in acetonitrile, 0.04 mole of octylamine (or decyl-,dodecyl or octadecylamine) dissolved in the same solvent were added. Immediate precipitation occurred and the material was collected by filtration and dried. When the secondary didodecylamine was used as ligand it was dissolved in ether and reacted with $Cu(NO_3)_2 3H_2O$, which was dissolved in the minimum quantity of acetonitrile. The molar ratio of the copper salt to amine was the same as the one employed with the primary amines. The immediately precipitated material was isolated and dried. As established by elemental analysis, tetracoordinated complexes (CuL_4) were formed by the interaction of long-chain primary amines with copper nitrate while with the secondary didodecylamine a two coordinated copper (II) complex (CuL_2) was formed, apparently due to steric hindrance. However with C_8 primary amine, analysis fits better the formula $CuL_4 2H_2O$.

Optical microscopy studies were performed on a Reichert "Thermopan" polarizing microscope.

For thermal analysis a DuPont 910 Differential Scanning Calorimeter was employed.

RESULTS AND DISCUSSION

The complexes with the primary amines (CuL_4) dissolve in dimethylsulfoxide and in this solvent their step-wise formation was followed. Thus in Fig. 1 are shown typical spectra of the copper-complex formation with octylamine for Cu:L ratios 1:1 to 1:4 and excess ligand. The characteristic blue shift of Cu-amine complexes with complexation is observed[15]. An analogous experiment with didodecylamine complex (CuL_2) was not performed since this compound is insoluble in most solvents including dimethyl sulfoxide, in which it is almost insoluble.

In Fig. 2-6 are shown mesomorphic textures of the copper-amine complexes obtained under cooling. A distortion of the long aliphatic chains will be possibly required for the layer structure of smectic-mesophases to be formed. However, for the complete identification of the mesophases

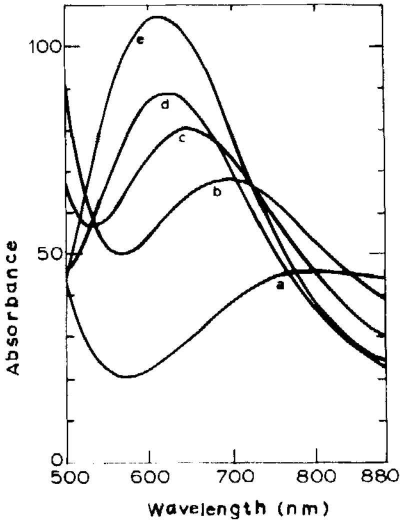

FIGURE 1. Stepwise formation of CuL_4 complex (L=octyl amine) for Cu:L ratios; 1:1, a; 1:2, b; 1:3, c; 1:4, d; 1:8, e.

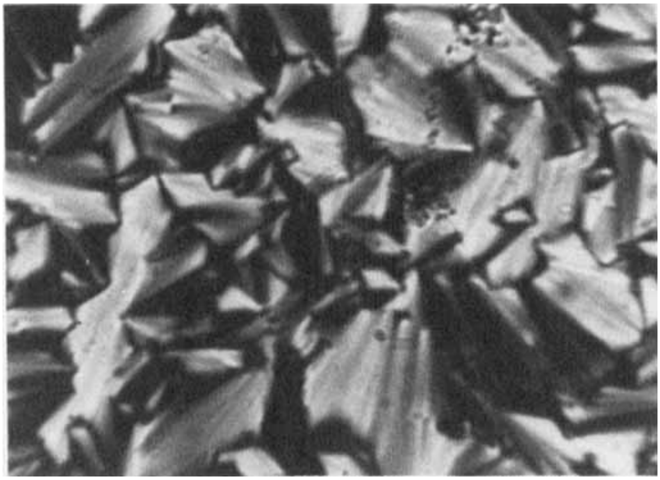

FIGURE 2. Mesomorphic texture of Cu-octylamine complex. See Color Plate V.

of the complexes, X-ray diffraction studies will be performed. The thermal stability of these mesophases was

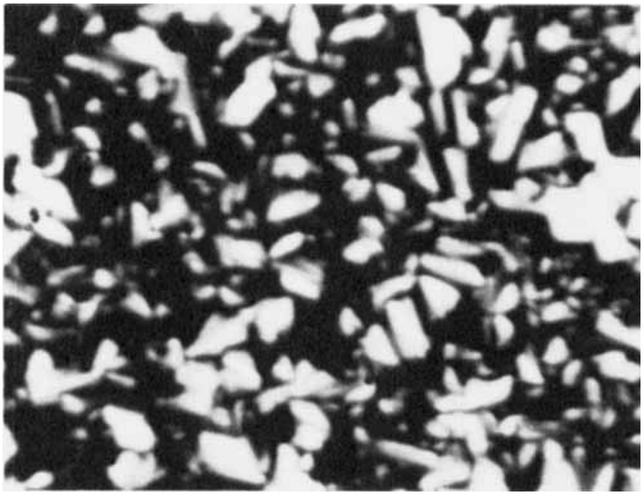

FIGURE 3. Mesomorphic texture of Cu-decylamine complex. See Color Plate VI.

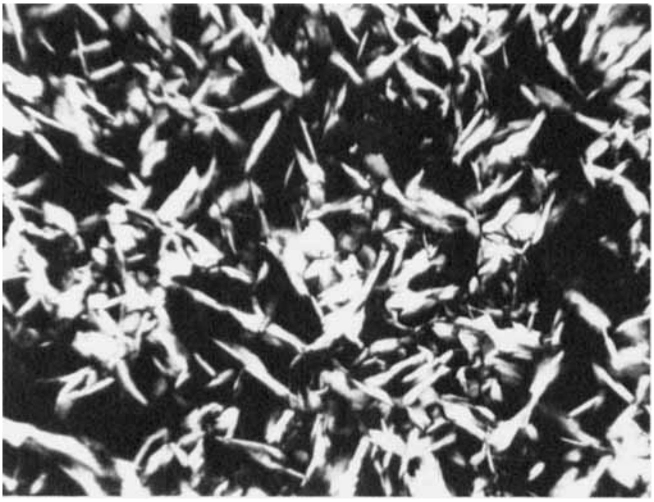

FIGURE 4. Mesomorphic texture of Cu-dodecylamine complex. See Color Plate VII.

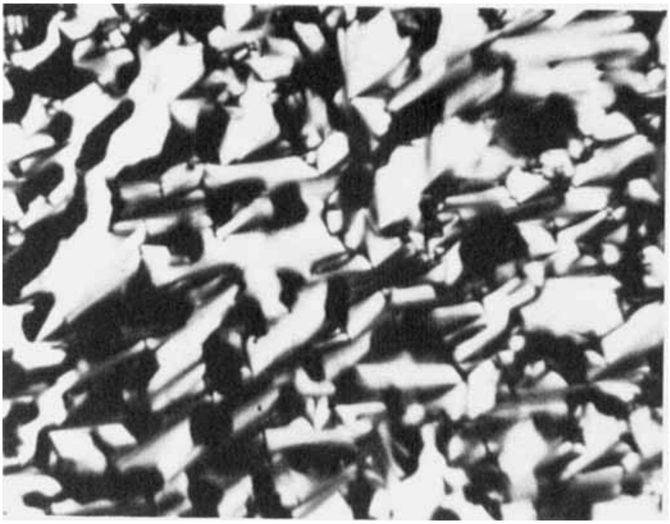

FIGURE 5. Mesomorphic texture of Cu-octadecylamine complex. See Color Plate VIII.

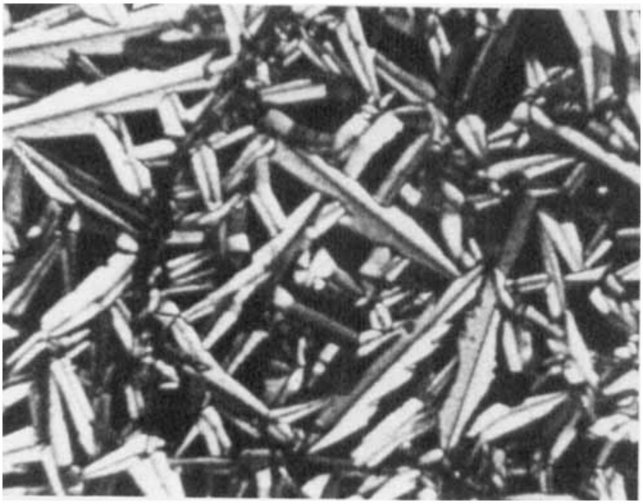

FIGURE 6. Mesomorphic texture of Cu-didodecylamine complex. See Color Plate IX.

enhanced with the length of the aliphatic chains of the amines as was seen by heating-cooling cycles. It is also interesting to notice that on heating these compounds the mesomorphic textures were not observed immediately after the first transition, as determined by DSC. However, mesomorphic phases do appear by pressing the cover slip at temperatures exceeding the first transition of the compounds. By analogy with the smectic-like properties of amphiphilic compounds[16], the first transition is attributed to the conformational melting of the long-aliphatic chain leading to the formation of mesophases while the second transition corresponds to the mesomorphic-isotropic transition.

The thermotropic character of these copper complexes was also established by Differential Scanning Calorimetry and in Fig. 7-11 are shown their DSC diagrams.

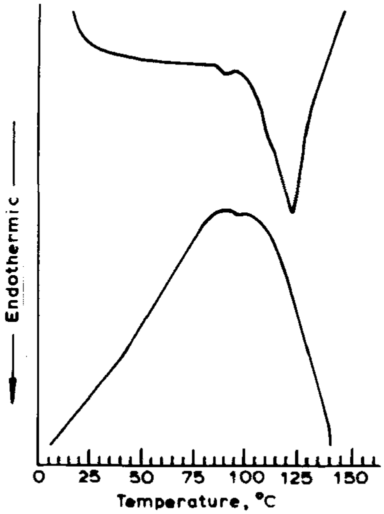

FIGURE 7. DSC diagram of Cu-octylamine complex.

From DSC diagrams a characteristic trend is observed Thus in compounds prepared from C_8-, C_{10}- and C_{12}-amine, the

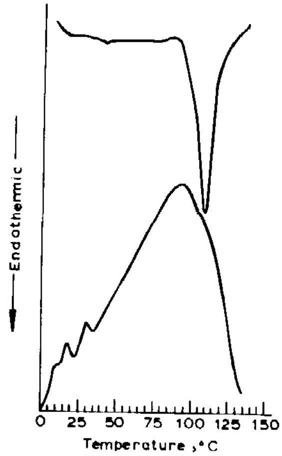

FIGURE 8. DSC diagram of Cu-decylamine complex.

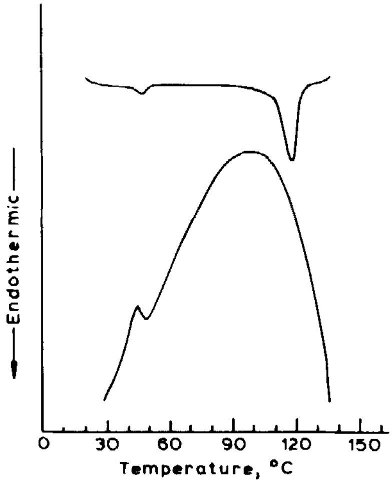

FIGURE 9. DSC diagram of Cu-dodecylamine complex.

major transition, corresponding to a mesomorphic-isotropic transition, is the breakage of the ionic bonding among the complexes and follows the minor transition of the aliphatic

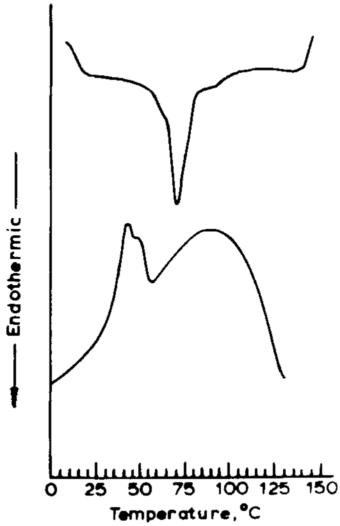

FIGURE 10. DSC diagram of Cu-octadecylamine complex.

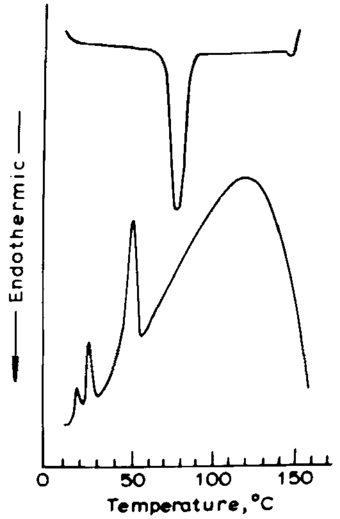

FIGURE 11. DSC diagram of Cu-didodecylamine complex.

chains melting. On the contrary, with C_{18} and secondary amine complexes the melting of aliphatic chains is the major transition. It seems that in this latter case, the strong van der Waals forces predominate over the very weak ionic bonding of the primarily "lipophilic" complexes. Transition temperatures as well as the thermodynamic parameters of the complexes are shown in Table I.

TABLE I. Transition temperatures and thermodynamic parameters of the Copper (II)-amine complexes.

Amine	T_{tr}, K	ΔH, kJ/mol	ΔS, J/mol K
C_8^a	360	0.6	1.8
	371	29.4	79.3
C_{10}^a	314	0.9	2.9
	370	44.9	121.4
C_{12}^a	315	3.2	10.0
	381	56.2	137.1
C_{18}^a	333	93.1	297.7
C_{12}^b	349	134.2	378.9
	421	1.4	3.4

a: Primary Amine
b: Secondary Amine

CONCLUSION

The interaction of long-chain aliphatic amines with Cu(II) nitrate results in the facile formation of copper complexes which exhibit mesomorphic phases. The type of the complexes as well as their mesomorphic phase behavior (mesomorphic range, thermal stability) are dependent, as expected, on the amines employed. Further identification of these novel liquid crystalline phases with X-ray studies is planned as well as additional investigation with other techniques.

REFERENCES

1. A. Skoulios and V. Luzzati, Nature, 183, 1310 (1959).
2. A. Malliaris, C.M. Paleos and P. Dais, J. Phys. Chem., 91, 1149 (1987).
3. A.M. Amorim Da Costa, H.D. Burrows, C.F.G.C. Geraldes, J.J.C. Teixeira-Dias, C.G. Bazuin, D. Guillon, A. Skoulios, E. Blackmore, G.J.T. Tiddy and D.L. Turner, Liquid Crystals, 1, 215 (1986) and references cited therein.
4. V. Busico, P. Cernicchiaro, P. Corradini and M. Vacatello, J. Phys. Chem., 87, 1631 (1983).
5. J.D. Gault, H.A. Gallardo and H.J. Müller, Mol. Cryst. Liq. Cryst., 130, 163 (1985).
6. V. Busico, D. Castaldo, M. Vacatello, Mol. Cryst. Liq. Cryst., 78, 221 (1981).
7. K. Iwamoto, Y. Ohnuki, K. Sawada and M. Seno, Mol. Cryst. Liq. Cryst., 73, 95 (1981).
8. G. Margomenou-Leonidopoulou, A. Malliaris and C.M. Paleos, Thermochim. Acta, 85, 147 (1985).
9. C. Piechocki, J. Simon, A. Skoulios, D. Guillon, and P. Weber, J. Amer. Chem. Soc., 104, 5245 (1982).
10. C. Piechocki and J. Simon, J. Chem. Soc. Comm. 259 (1985).
11. D. Guillon, P. Weber, A. Skoulios, C. Piechocki and J. Simon, Mol. Cryst. Liq. Cryst. 130, 223 (1985).
12. Anne-Marie Giroud-Godquin, Jean-Mark Latour, Jean-Claude Marchon, Inorg. Chem., 24, 4454 (1985).
13. A.M. Giroud-Godquin, J.C. Marchon, D. Guillon and A. Skoulios, J. Phys. Chem., 90, 5502 (1986).
14. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, (Interscience Publishers, New York, 1967), p. 898.
15. B.J. Hathaway and A.A.G. Tomlinson, Coordination Chem. Rev., 5, 1 (1970).
16. V. Busico, A. Ferraro and M. Vacatello, Mol.Cryst.Liq. Cryst., 128, 243 (1985) and references cited therein.