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Synthesis of a new series of chiral Schiff's bases and their copper complexes

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A new series of chiral Schiff's bases containing 2-hydroxybenzilideneaniline moieties and their copper complexes were synthesized and studied by differential scanning calorimetry, polarized optical microscopy, X-ray diffraction and EPR measurement. The results show that most of the Schiff's bases and only two of the copper complexes exhibited chiral smectic liquid crystal phases.

1. Introduction

Over the past few years the study of liquid crystals containing paramagnetic transition metals has increased considerably because of their special combination of liquid crystalline and metal ionic properties which can give rise to special electro-optical and magnetic characteristics [1–10]. Though many paramagnetic metallomesogens have been reported, only a few papers discuss the synthesis and investigation of chiral paramagnetic liquid crystals [7–10]. On the other hand, EPR spectroscopy has been identified to be a very useful method to study paramagnetic liquid crystals because EPR spectra can also provide information about the liquid crystalline molecular arrangements, but few EPR studies on chiral paramagnetic liquid crystals [10] have been reported. In this paper a new series of chiral copper complexes are presented and studied by using DSC, polarized optical microscopy, X-ray diffraction and EPR spectroscopy.

In our previous paper [11], some chiral Schiff's base (see the scheme) with $n=2, 4, 6, 8, 10$ and 12 were reported in order to study the effect of intramolecular hydrogen bonding on the phase behaviour. The aim of this paper is to report the related series of chiral copper complexes with $n=3-8, 10$ and 12 and investigate the effect of introducing a copper centre on the S_C^* phase. The results show that almost all of these Schiff's base (except when $n=1$) exhibit chiral phases (Ch or S_C^*) and only two of the copper complexes show the S_C^* phase.

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2. Experimental

2.1. Techniques

^1H NMR spectra were measured by a Unity 400 NMR instrument operating at 400 MHz in CDCl_3 . Infrared spectra were obtained by using a Nicolet-5DX FTIR spectrometer with a maximum resolution of 2 cm^{-1} . Elemental analyses were performed with a Perkin-Elmer 240C microanalyser.

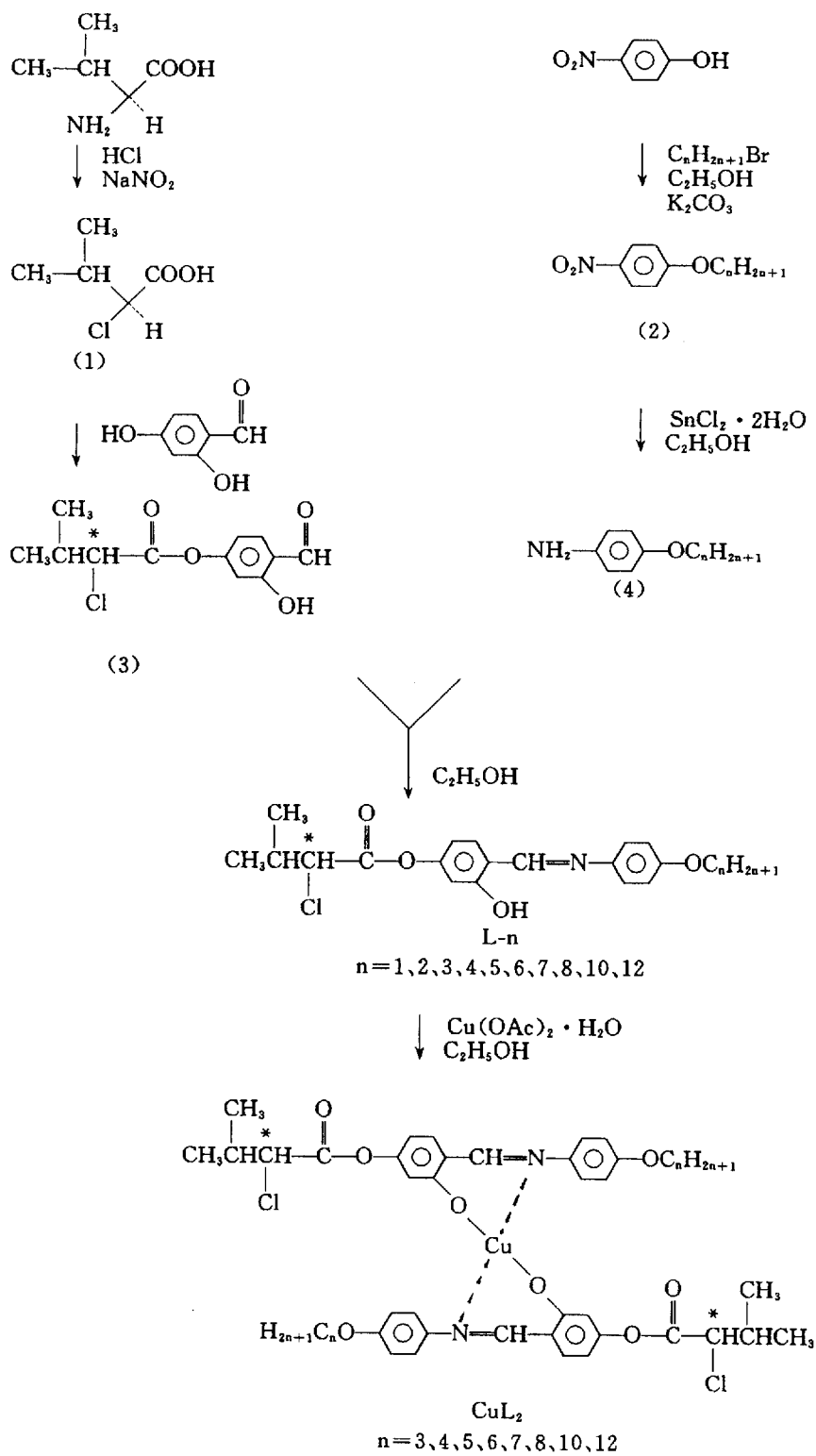
The textures of the mesophases were studied with a Zeiss Jena polarized optical microscope equipped with a hot stage. Measurements of temperatures and enthalpies of transition were carried out using a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating and cooling rate of 5°C min^{-1} . X-ray diffraction studies were performed with a Netherland Philip PW-1700 instrument with monochromatic CuK_α ($\lambda=1.5418\text{ \AA}$) X-ray beam using unoriented samples. EPR measurements were taken with a Bruker Electron Spin Resonance EP 200D-SRC system, working in the X-band mode.

2.2. Synthesis

The synthesis of the ligands and copper complexes is shown in the scheme.

These Schiff's bases were prepared according to the method detailed in our previous paper [11] by the condensation of the chiral aldehyde and *p*-alkoxyaniline in ethanol, and purified by recrystallization three times from ethanol. The purity of all of the Schiff's bases was confirmed by IR spectroscopy, ^1H NMR spectra (400 MHz) and elemental analysis.

The copper complexes were obtained according to a general method [3, 7, 12] as follows:



Scheme 1.

An ethanolic solution containing 1 mmol copper acetate was added to a hot ethanolic solution containing 2 mmol of the appropriate Schiff's base. The mixture was heated at reflux on a water bath for 1 h, after which it was cooled, the precipitate filtered off and recrystallized twice from chloroform/ethanol (1:3). The brown copper complexes were characterized by IR spectra and elemental analysis. The yields and elemental analyses are shown in table 1.

3. Results and discussion

3.1. Mesomorphisms of ligands and complexes

DSC, polarized optical microscopy and X-ray diffraction methods were employed to study the phase transition behaviours of L and CuL₂. The transition temperatures, enthalpies and mesomorphic properties for L and CuL₂ are shown in table 2.

From table 2, we can see that nearly all of the ligands (except *n*=1) are liquid crystalline. Using polarized

Table 1. Yield, the most relative IR data and elemental analyses of the copper complexes.

<i>n</i>	Yield per cent	Elemental analysis Calculated (found)/per cent			$\nu_{C=O}/\text{cm}^{-1}$	$\nu_{C=N}/\text{cm}^{-1}$
		C	H	N		
3	73	59.97 (60.15)	5.51 (5.32)	3.33 (3.41)	1756.0	1615.3
4	64	60.79 (60.60)	5.80 (5.89)	3.22 (3.58)	1755.3	1616.2
5	71	61.16 (61.02)	6.02 (5.83)	3.12 (3.27)	1757.0	1616.3
6	62	62.30 (62.67)	6.32 (6.53)	3.03 (3.06)	1755.3	1616.6
7	72	63.00 (62.84)	6.50 (6.39)	2.94 (2.83)	1757.0	1616.4
8	68	63.63 (63.45)	6.78 (7.03)	2.85 (2.81)	1758.6	1616.2
10	58	64.82 (64.98)	7.19 (7.50)	2.70 (2.62)	1758.6	1615.8
12	67	65.88 (65.88)	7.56 (7.95)	2.56 (2.52)	1766.5	1614.7

Table 2. Transition temperatures and enthalpies (in italics) for the ligands (L) and their copper complexes (CuL₂).

<i>n</i>	<i>T</i> /°C and ΔH /kJ mol ⁻¹	
	L	CuL ₂
1	Cr $\frac{107.9}{28.29}$	I
2	Cr $\frac{118.2}{34.93}$	$\left(S_A \frac{95.8}{-1.18} \text{ Ch } \frac{100.6}{-0.70} \right) I$
3	Cr $\frac{108.0}{30.49}$	$\left(S_A \frac{84.2}{-1.33} \text{ Ch } \frac{87.3}{-1.14} \right) I$ Cr $\frac{166.7}{8.01}$ Cr $\frac{173.7}{21.41}$ I
4	Cr $\frac{90.7}{23.62}$	$\left(S_C^* \frac{83.7}{-1.05} \right) S_A \frac{100.9}{3.31} I$ Cr $\frac{147.8}{42.13}$ S _A $\frac{154.1}{7.13} I$
5	Cr $\frac{83.7}{23.77}$ $\left(S_B \frac{73.7}{-4.10} \right)$	S _C [*] $\frac{88.6}{1.38}$ S _A $\frac{96.2}{2.99} I$ Cr $\frac{144.7}{19.90}$ S _A $\frac{159.3}{2.45} I$
6	Cr $\frac{76.5}{25.86}$ $\left(S_B \frac{59.2}{-3.34} \right)$	S _C [*] $\frac{90.7}{0.81}$ S _A $\frac{103.6}{3.88} I$ Cr $\frac{116.9}{1.43}$ Cr $\frac{154.7}{27.13}$ S _A $\frac{156.7}{7.51} I$
7	Cr $\frac{81.8}{26.54}$	S _C [*] $\frac{90.1}{0.36}$ S _A $\frac{101.9}{3.44} I$ Cr $\frac{153.9}{19.31}$ Cr $\frac{163.6}{38.81}$ $\left(S_A \frac{158.0}{-} \right) I$
8	Cr $\frac{76.0}{25.79}$	S _C [*] $\frac{90.3}{0.52}$ S _A $\frac{106.5}{4.28} I$ Cr $\frac{110.7}{1.33}$ Cr $\frac{126.4}{31.22}$ S _C [*] $\frac{132.6}{1.34}$ S _A $\frac{163.3}{7.00} I$
10	Cr $\frac{76.1}{39.69}$	S _C [*] $\frac{90.1}{0.14}$ S _A $\frac{108.1}{4.66} I$ Cr $\frac{137.6}{14.20}$ S _C [*] $\frac{151.7}{6.00}$ S _A $\frac{163.6}{8.13} I$
12	Cr $\frac{80.7}{44.89}$	S _C [*] $\frac{90.0}{0.18}$ S _A $\frac{108.6}{5.20} I$ Cr $\frac{112.1}{51.95}$ S _A $\frac{163.0}{8.64} I$

Parentheses denote a monotropic transition.

optical microscopy, the fingerprint texture (typical texture of the cholesteric phase) and simple fan-shaped texture (S_A phase) could be seen very clearly for the ligands, where $n=2$ and 3, on the cooling sequence. From $n=4$ onwards, a different kind of fan-shaped texture with many strips along the blades (S_C^* texture) appeared. Only for the ligands with $n=5$ and 6 was a monotropic mosaic texture (tentatively identified as smectic B) [11] seen in addition to two kinds of fan-shaped texture (S_C^* and S_A phases).

Figure 1 shows the phase diagram for the ligands. The ligands $Cr-S_C^*$, $S_C^*-S_A$ and S_A-I transitions exhibit an odd-even effect.

We also compare the transition enthalpies of the ligands. These results are shown in figure 2. The $S_C^*-S_A$ transition enthalpies are relatively small (0.14 to 1.38 kJ mol⁻¹), while the S_A-I transition enthalpies are relatively large (2.99 to 5.20 kJ mol⁻¹). The enthalpies of the S_A-I transitions increase with increasing length of

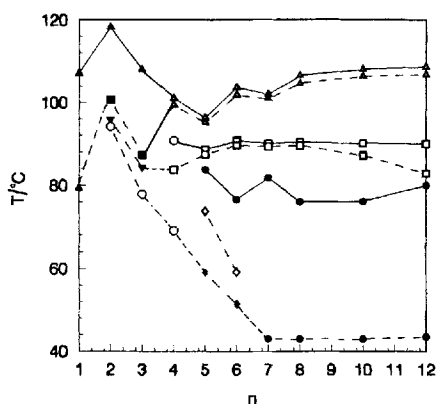


Figure 1. Phase transition diagram for the ligands. Solid line, heating run; dotted line, cooling run. ▲, Cr-I; △, S_A-I ; ■, I-Ch; ○, Cr- S_A ; □, $S_C^*-S_A$; ▼, Ch- S_A ; ◇, $S_C^*-S_B$; ◆, S_B-Cr ; ●, Cr- S_C^* .

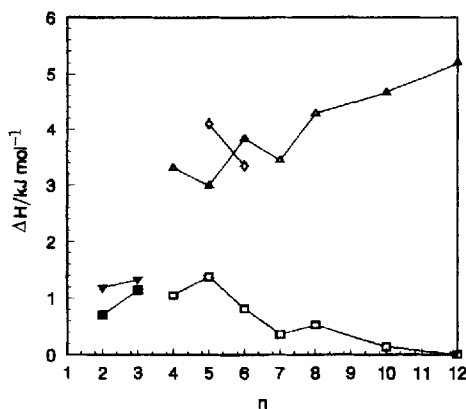


Figure 2. Transition enthalpies for the ligands. ▼, Ch- S_A ; ■, I-Ch; △, S_A-I ; □, $S_C^*-S_A$; ◇, $S_C^*-S_B$.

the alkoxy chains. A similar result can be found in the literature [13].

Wide angle X-ray diffraction was used to identify the phases of the ligands for $n=6, 8, 10$ and 12. As an example, the X-ray diffraction data for the ligand with $n=8$ is shown in figure 3. Figure 4 shows the similar results for the ligand with $n=10$ on cooling.

From figure 3, we can determine that on heating, at 82°C (S_C^* phase) the layer thickness is 29.72 Å, and at 94°C (S_A phase) the layer thickness is 31.33 Å. This result implies that the molecules in the S_C^* phase are more tilted than those in the S_A phase. From figure 4 we can see the results more clearly. In the S_A phase the layer thickness of the ligand with $n=10$ varies only slightly with temperature. However after the temperature drops below the $S_A-S_C^*$ transition, the layer thickness decreases. This is strong evidence for the tilted smectic C phase [14]. We calculated the tilt angle according to $d = d_0 \cos \theta$ [15], where d_0 is the layer thickness near the $S_A-S_C^*$ transition (for L_6 , d_0 is 29.67 Å; for L_{10} , d_0 is 34.32 Å) and d is the layer thickness at any certain temperature [15]. The tilt angles of the two ligands with $n=6$ and 10 as a function of temperature are shown in figure 5.

The maximum tilt angle (30° for L_6 , 28° for L_{10}) is

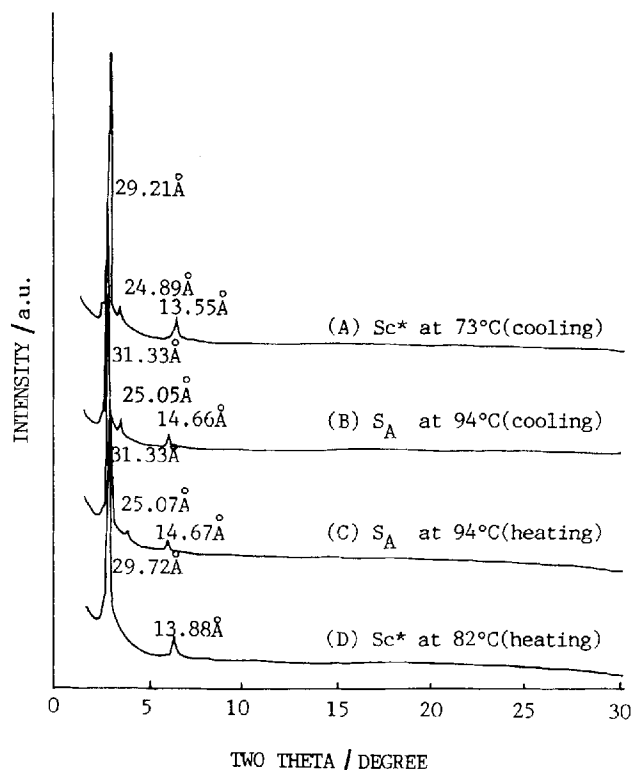


Figure 3. X-ray diffractograms for L_8 at (A) 73°C, S_C^* (cooling), (B) 94°C, S_A (cooling), (C) 94°C, S_A (heating) and (D) 82°C, S_C^* (heating).

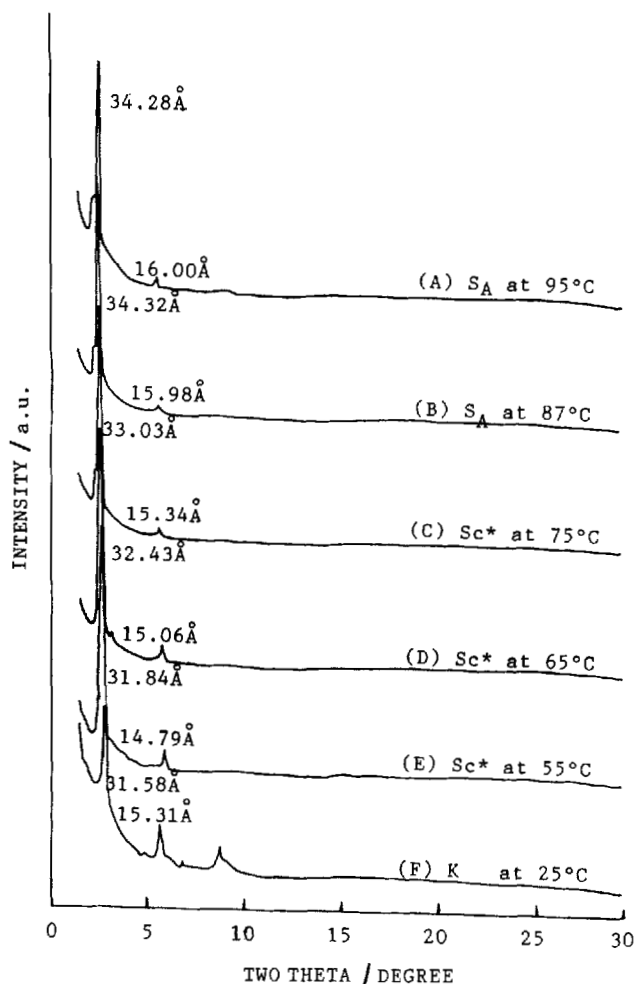


Figure 4. X-ray diffractogram for L_{10} on cooling.

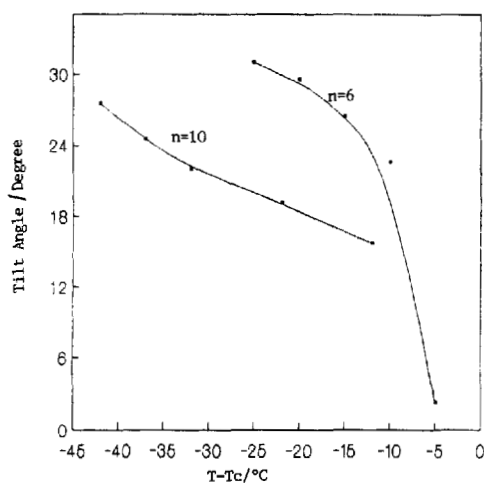


Figure 5. Tilt angle of the ligands with $n=6$ and 10 at different temperatures.

similar to the maximum tilt angle reported for some ferroelectric liquid crystals with the same (*S*)-2-chloro-3-methylbutanoyloxy group [16] and this value is the ideal value for display device applications [15, 16].

Many papers report copper complexes containing two salicylideneaminato derivatives [1, 6, 7, 10, 17, 18], but papers about the chiral copper complexes are quite rare [7, 10].

Table 2 also gives the transition temperatures of these copper complexes. Figure 6 shows the phase diagram of the copper complexes. When $n > 3$, these copper complexes are liquid crystals displaying at minimum a smectic A phase with the simple fan-shaped texture or bâtonnet texture. It is very interesting that the complex with $n=7$ has only a monotropic smectic A phase (from 158°C to 148°C). The complex with $n=8$ has a very narrow S_C^* phase (6.2°C). Increasing the side chain to $n=10$ produces a wider S_C^* phase (14.1°C) with the focal-conic texture, however the $n=12$ complex only exhibits a S_A phase. From table 2 and figure 6, we can see the transition temperatures of all the copper complexes are higher than those of the uncomplexed ligands.

Comparing the mesomorphic behaviour of the ligands and their copper complexes, the copper complexes with $n=4-7$ and 10 narrow the mesomorphic range, whereas complexes with $n=8$ and 12 broaden the mesomorphic range. The great difference is that the ligands with $n > 3$ exhibit the S_C^* phase, but only two of the copper complexes possess the S_C^* phases. Furthermore, the ligands have only one crystalline state but the complexes with $n=3, 6, 7$ and 8 possess two kinds of crystalline state. This difference might be caused by the difference in molecular structures. The centrosymmetrical copper complexes and coordinating interaction with the metal centre make it easy to polymorph [12]. On the other hand, the lesser molecular anisotropies of the complexes

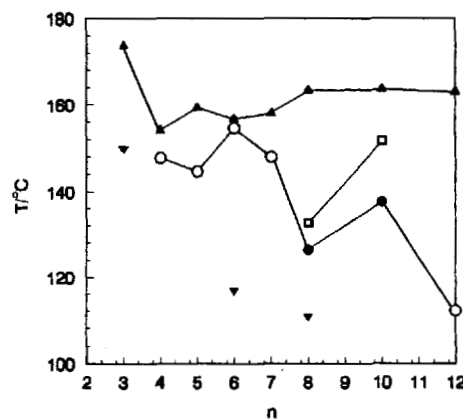


Figure 6. Phase transition diagram for the copper complexes. \blacktriangle , Cr-I; \triangle , S_A -I; \square , S_C^* - S_A ; \circ , Cr- S_A ; \bullet , Cr- S_C^* ; ∇ , Cr₁-Cr₂.

compared with those of ligands [19] affect the S_C^* phase significantly. As a result this series of copper complexes does not favour the formation of the S_C^* phase.

Figure 7 shows the X-ray diffractogram for an unoriented complex with $n=8$ on heating.

The first order reflection peak at 150°C (S_A phase) gives 29.95 \AA , and the first order reflection peak at 130°C (S_C^* phase) is only slightly smaller. The layer thickness of the S_A phase (29.95 \AA) is much smaller than the molecular length (36.3 \AA , using a molecular model with all-*trans* side chains). The difference between d and l is 6.3 \AA , and the ratio of the layer spacing to the molecular length (d/l) is 0.83 . Though many copper complexes are interdigitated [6, 17, 18], for this compound, this arrangement cannot be warranted because of the high value of d/l .

3.2. EPR study of the complex with $n=8$

EPR spectroscopy has proved to be a most useful tool in the study of mesomorphic behaviour of paramagnetic metallomesogenic compounds [3, 10, 20, 21]. It has also been found that the spectra do not depend on the aliphatic chain length, n , and that no modification of the spectrum is observed when temperature is increasing except for the changes induced by the phase transitions [3, 10]. As a result, we investigate the EPR spectra

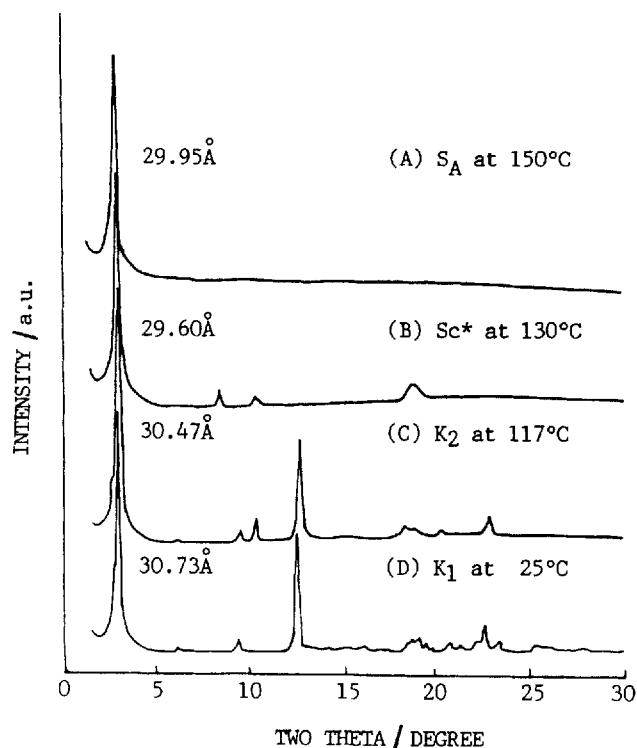


Figure 7. X-ray diffractogram of the copper complex with $n=8$ at (A) 150°C , S_A , (B) 130°C , S_C^* , (C) 117°C , Cr_2 and (D) R.T., Cr_1 .

of the copper complex with $n=8$ at different temperatures. Figure 8 shows the X-band EPR spectra of the complex with $n=8$ from r.t. to 165°C . Curves (a) (50°C , Cr_1) and (b) (90°C , Cr_1) are very unsymmetrical and have no hyperfine structure; these EPR spectra are very rare because of the asymmetry of chiral molecule [10]. When the temperature reaches 115°C (curve (c), Cr_2 state), the spectrum changes, but is still very unsymmetrical. When the temperature rises above 130°C (curve (d), S_C^* phase), the spectrum becomes broad and the magnetic anisotropy of the spectrum markedly decreases. However, no differences were observed between the spectra of the S_C^* and S_A phases. According to the literature [3, 21] this phenomenon is caused by the freedom of motion in the smectic phase, together with the exchange interaction between paramagnetic entities in adjacent molecules whose molecular axes are slightly tilted.

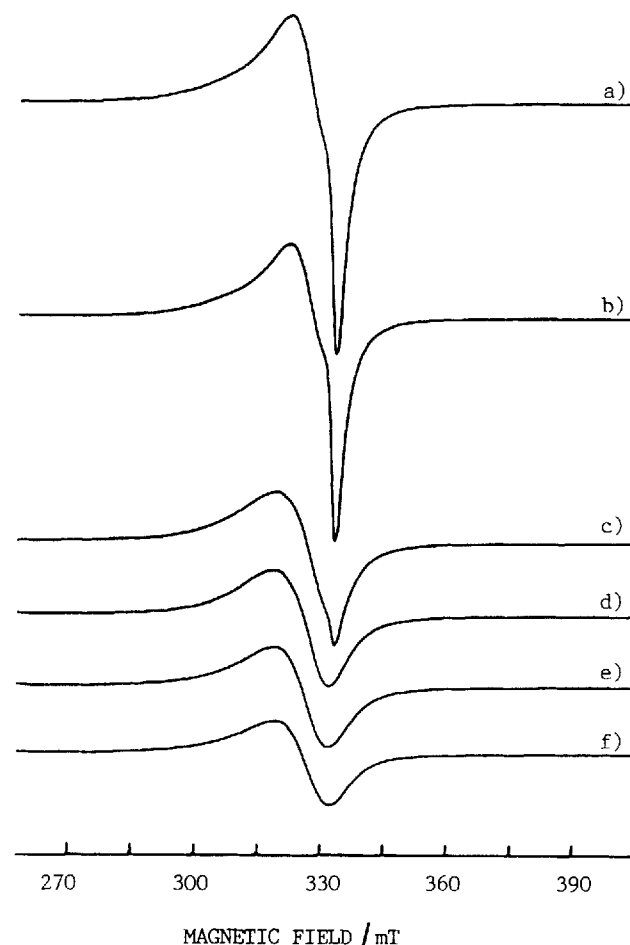


Figure 8. EPR spectra of the copper complex with $n=8$ measured at (a) 50°C , Cr_1 , (b) 90°C , Cr_1 , (c) 115°C , Cr_2 , (d) 130°C , S_C^* , (e) 150°C , S_A and (f) 165°C , isotropic.

4. Conclusions

A series of chiral Schiff's bases and their copper complexes were prepared and studied by DSC, optical microscopy, X-ray diffraction and EPR spectroscopy. X-ray studies show that the maximum tilt angle of the S_C^* phase is about 28° and 30° for the two ligands, respectively. EPR spectroscopy show that the paramagnetic properties of the copper complex are very sensitive to the Cr_1-Cr_2 and $Cr_2-S_C^*$ transitions.

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