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Mesophase behaviour and thermal stability of octa-alkoxy substituted phthalocyaninatocobalt(II) complexes

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Cobalt(II) phthalocyanines substituted with eight alkoxy chains in the peripheral (2, 3, 9, 10, 16, 17, 23, 24) positions were prepared. The alkoxy chain length was varied between *n*-butyloxy (C_4H_9O) and *n*-octadecyloxy ($C_{18}H_{37}O$). Studies by polarizing optical microscopy and high temperature X-ray diffraction revealed that all the complexes are liquid crystalline and that they exhibit a hexagonal columnar mesophase (Col_h). Transition enthalpies were determined by differential scanning calorimetry. The clearing point could only be observed for compounds with a chain length longer than $C_{13}H_{27}O$. Both the melting and clearing points decrease with increasing chain length. The transition temperatures of these discotic metallomesogens are higher than those of the corresponding metal-free phthalocyanines, but are comparable with those of the corresponding copper(II) compounds. The thermal decomposition of the compounds was studied by thermogravimetry.

1. Introduction

The first liquid crystalline phthalocyanine was a copper(II) compound with eight peripheral alkoxymethyl chains, prepared by Piechocki *et al.* in 1982 [1]. Since this first example, many different mesogenic phthalocyanine compounds have been synthesized [2–4]. Most of the compounds are octasubstituted in the peripheral (2, 3, 9, 10, 16, 17, 23, 24) positions. Many fewer compounds contain four peripheral substituents or are octasubstituted in the non-peripheral (1, 4, 8, 11, 15, 18, 22, 25) positions. Typical for these discotic mesogens is that they form columnar mesophases, with the rigid phthalocyanine cores stacked into columns. In general, these columns are hexagonally ordered in the mesophase with respect to one another, although other two-dimensional lattices are possible, e.g. rectangular columnar mesophases. The transition from the solid state to the liquid crystalline phase (melting point) corresponds to the melting of the flexible side chains. The aromatic cores keep their positional and orientational order. The transition from the mesophase to the isotropic liquid (clearing point) corresponds to the breakdown of the columns. Liquid crystalline phthalocyanines offer the possibility of combining the optoelectronic properties of the phthalocyanines with the orientational control of conventional liquid crystal systems. Because of the columnar architecture of the mesophase and because of electrical conduction along the column axis, these compounds can be considered as one-dimensional semiconductors [5]. Charge transport along the columns is facilitated by the substantial π–π orbital overlap of the aromatic cores, whereas conductivity perpendicular to the columnar axes is hindered by the isolating molten alkyl chains.

Although a large variety of liquid crystalline phthalocyanine compounds has been prepared in the past, little work has been done on the influence of the chain length on the mesomorphic behaviour of these compounds. Van der Pol *et al.* prepared a series of metal-free and copper(II) phthalocyanines with eight peripheral alkoxy

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chains ranging between $C_6H_{13}O$ and $C_{12}H_{25}O$ [6, 7]. We extended these data for metal-free phthalocyanines by preparing all the metal-free phthalocyanines with eight alkoxy chains, where the chain length was varied between CH_3O and $C_{20}H_{41}O$ [8]. Liquid crystalline cobalt(II) phthalocyanines have been much less studied than the corresponding copper(II) phthalocyanines. Severs *et al.* described the synthesis of a cobalt(II) phthalocyanine with eight dodecyloxy chains [9]. The compound was reported to exhibit an unidentified discotic mesophase between 85 and 345°C. Cook prepared cobalt(II) phthalocyanines with eight non-peripheral alkyl chains [10]. For instance the compound with decyl chains in the (1, 4, 8, 11, 15, 18, 22, 25) positions shows a hexagonal columnar mesophase between 75 and 189°C. Sakomoto and Ohno-Okumura synthesized mesogenic cobalt(II) phthalocyanines substituted with eight short alkoxymethyl groups, but the compounds exhibited no liquid crystalline behaviour [11].

In this paper, we describe the synthesis and mesophase behaviour of a series of cobalt(II) phthalocyanine complexes with eight alkoxy chains (figure 1). The influence of the alkoxy chain length on the thermal properties of the complexes has been investigated.

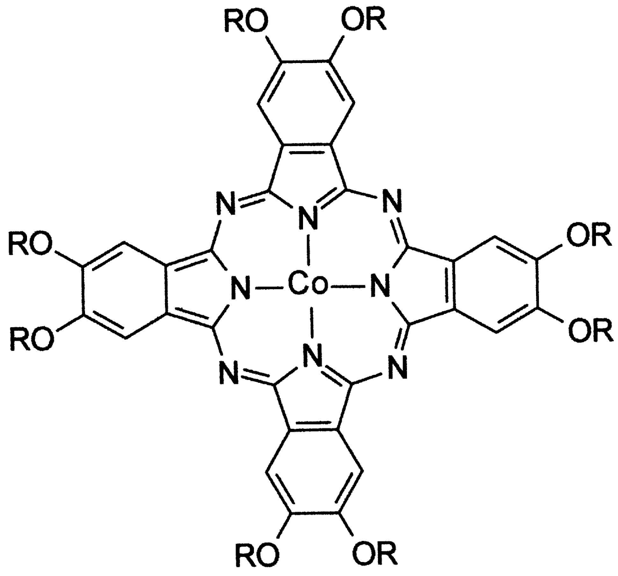


Figure 1. Structure of the cobalt(II) complexes with eight peripheral alkoxy chains. *R* ranges from C_4H_9 to $C_{18}H_{37}$.

2. Experimental

2.1. *Characterization*

Elemental analyses (CHN) were performed using a CE-Instrument EA-1110 elemental analyser. Mass spectra of the organic precursors were recorded using a low resolution electron-impact Hewlett-Packard 5989A for low molecular mass substances. For the phthalocyanines a Micromass Quattro II (triple quadrupole) was used. MALDI-TOF mass spectra of the cobalt(II) complexes were measured using a VG Tofspec SE (Micromass, UK) equipped with a N_2-laser (337 nm). UV-Vis spectra were recorded using a Shimadzu UV-3100 spectrophotometer, with spectrograde chloroform as the solvent. Differential scanning calorimetry (DSC) measurements were made using a Mettler-Toledo DSC821e module (scan rate 10°C min^{-1} under a nitrogen flow, aluminium cups). Optical textures of the mesophases were observed with an Olympus BX60 polarizing microscope equipped with a Linkam THMS600 hot stage and a Linkam TMS93 programmable temperature controller.

High temperature X-ray diffraction (XRD) was measured on a STOE transmission powder diffractometer system STADI P, with a high temperature attachment version 0.65.1 (temperature range from room temperature to 1000°C). Monochromatic Cu $K_{\alpha1}$ radiation ($\lambda = 1.5406$ Å) was obtained with the aid of a curved germanium primary monochromator. Diffracted X-rays were measured by a linear position sensitive detector (PSD). The sample was placed in a quartz glass capillary (outer diameter 0.3 mm, wall thickness 0.01 mm) and spun during the measurement. In general, data were collected in the range $1 < 2\theta < 40°$.

Thermogravimetric analyses were made with a TA Instruments Hi-Res TGA 2950 thermogravimetric analyser (argon flow). The experiments were carried out in the high resolution mode. The principle used was that when a reaction started, the heating rate was decreased in accordance with the mass loss. The maximum heating rate was set at 10°C min^{-1}. As a consequence, the temperatures at which the transitions occurred were better defined. In order to identify the evolved gases TG-MS experiments were performed by coupling a TG 951-2000 thermogravimeter (TA Instruments) to a quadrupole mass spectrometer (Model Thermolab of VG Fisons Instruments), using a flexible, heated, silica-lined steel capillary and a molecular leak. Platinum cups were used as sample holder.

2.2. *Synthesis of the complexes: general procedure*

The 1,2-dicyano-4,5-bis(alkoxy)benzenes were synthesized according to a literature procedure [6, 8]. A mixture of 2 mmol of 1,2-dicyano-4,5-bis(alkoxy)benzene, 0.54 mmol of $CoCl_2 \cdot 6H_2O$, 5 ml of 2-dimethylaminoethanol (DMAE) and 4 drops of 1,8-diazobicyclo[5.4.0]-undec-7-ene (DBU) was stirred under reflux conditions at 150°C for 48 h under a nitrogen atmosphere. After evaporation to dryness, the green residue was dissolved in a few ml of chloroform and reprecipitated by adding 50 ml of acetone. The precipitate was filtered off on a Gooch crucible (porosity 4) and washed with acetone, methanol and ethyl acetate. Further purification was done by chromatography over neutral alumina (Merck 90) using $CHCl_3$ as the eluent. After collection and evaporation the compound was recrystallized from ethyl acetate and dried overnight. The complexes were characterized by MALDI-TOF mass spectrometry, UV/Vis spectroscopy and CHN microanalysis.

3. Results and discussion

The octa-alkoxy substituted phthalocyaninatocobalt(II) complexes were synthesized via a template reaction between one equivalent of cobalt(II) chloride hexahydrate and four equivalents of 1,2-dicyano-4,5-bis(alkoxy)benzene using 2-dimethylaminoethanol as solvent, in the presence of half an equivalent of the sterically hindered base 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) (see the scheme). The crude products were purified by column chromatography and recrystallization. For most of the complexes, it was impossible to obtain reliable data for CHN microanalysis; such problems are generally recognized. The metal complexes were identified by MALDI-TOF mass spectrometry. Although the metal-free phthalocyanine is the main impurity formed during the template reaction, both MALDI-TOF and UV/Vis spectra showed that the purified cobalt(II) phthalocyanines are free from PcH_2 impurities. Purity control can be achieved by UV/Vis spectroscopy, because the spectrum of the cobalt(II) phthalocyanine is markedly different from that of the corresponding metal-free phthalocyanine (different splitting of the Q-band). An overview of the complexes and the mass spectrometric data are given in table 1. In figure 2, the MALDI-TOF spectrum of $(C_{15}H_{31}O)_8PcCo$ is shown.

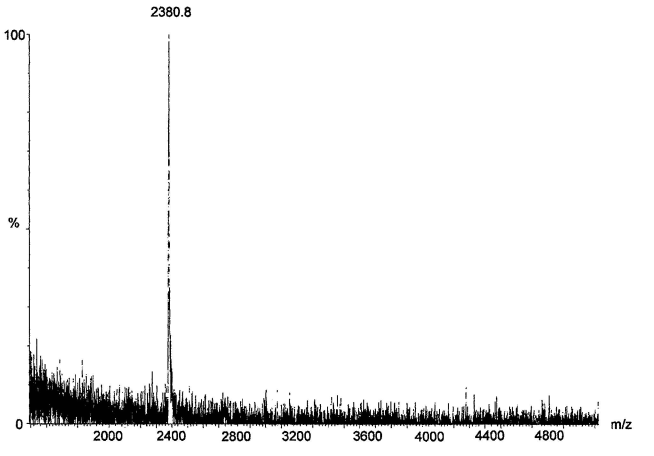
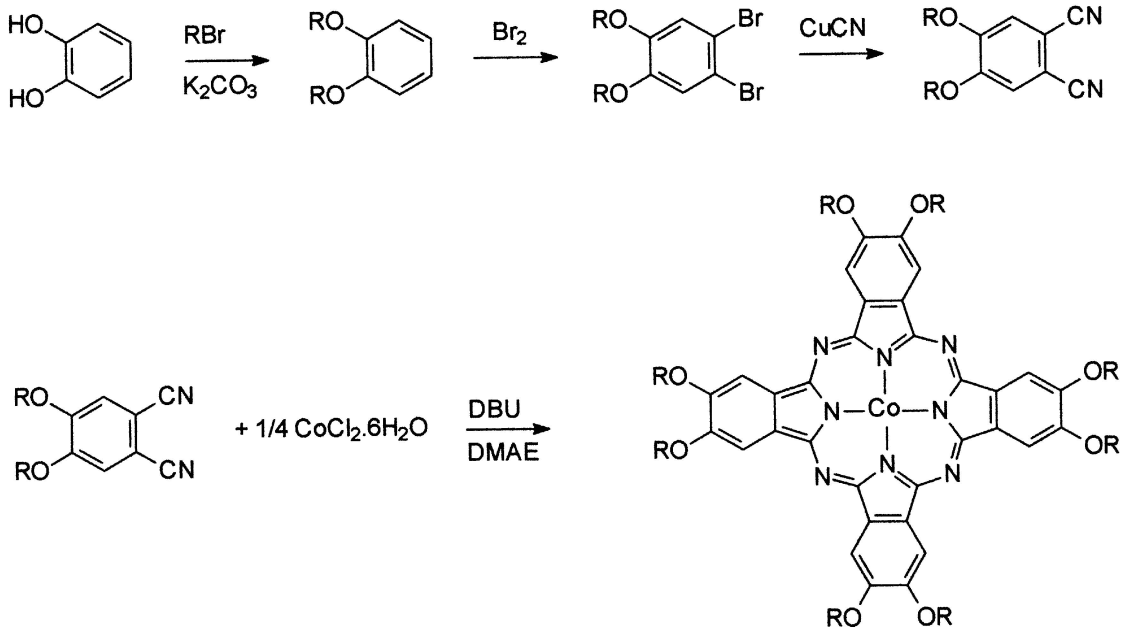


Figure 2. MALDI-TOF spectrum of $(C_{15}H_{31}O)_8PcCo$.

All the cobalt(II) complexes form liquid crystals with a wide mesophase range. The mesophase behaviour was investigated by polarizing optical microscopy (POM), DSC and high temperature XRD. The melting points decrease with increasing chain length of the alkoxy substituents, from 218°C for the complex with butyloxy substituents to 64°C for the complex with octadecyloxy substituents (table 2 and figure 3). The homologues with chain lengths up to $C_{13}H_{27}O$ decompose without clearing above 300°C. The clearing point decreases with increasing chain length, from 328°C for the complex with tetradecyloxy substituents to 266°C for the complex with octadecyloxy substituents. The DSC thermogram of the compound $(C_{17}H_{35}O)_8PcCo$ is shown in figure 4.



Scheme. Synthesis of the phthalonitrile precursors and of the alkoxy-substituted cobalt(II) phthalocyanine complexes.

Table 1. MALDI-TOF data for the octa-alkoxy substituted cobalt(II) phthalocyanines.

Compound	Formula	M (isotropic)	M (found)
$(C_4H_9O)_8PcCo$	$C_{64}H_{80}O_8N_8Co$	1147.54	1147.1
$(C_5H_{11}O)_8PcCo$	$C_{72}H_{96}O_8N_8Co$	1259.67	1257.9
$(C_6H_{13}O)_8PcCo$	$C_{80}H_{112}O_8N_8Co$	1371.79	1370.8
$(C_7H_{15}O)_8PcCo$	$C_{88}H_{128}O_8N_8Co$	1483.92	1481.5
$(C_8H_{17}O)_8PcCo$	$C_{96}H_{144}O_8N_8Co$	1596.04	1596.0
$(C_9H_{19}O)_8PcCo$	$C_{104}H_{160}O_8N_8Co$	1708.17	1707.2
$(C_{10}H_{21}O)_8PcCo$	$C_{112}H_{176}O_8N_8Co$	1820.29	1819.3
$(C_{11}H_{23}O)_8PcCo$	$C_{120}H_{192}O_8N_8Co$	1932.42	1929.3
$(C_{12}H_{25}O)_8PcCo$	$C_{128}H_{208}O_8N_8Co$	2044.54	2043.6
$(C_{13}H_{27}O)_8PcCo$	$C_{136}H_{224}O_8N_8Co$	2156.67	2154.6
$(C_{14}H_{29}O)_8PcCo$	$C_{144}H_{240}O_8N_8Co$	2268.79	2267.2
$(C_{15}H_{31}O)_8PcCo$	$C_{152}H_{256}O_8N_8Co$	2380.92	2380.8
$(C_{16}H_{33}O)_8PcCo$	$C_{160}H_{272}O_8N_8Co$	2493.04	2492.0
$(C_{17}H_{35}O)_8PcCo$	$C_{168}H_{288}O_8N_8Co$	2605.17	2604.3
$(C_{18}H_{37}O)_8PcCo$	$C_{176}H_{304}O_8N_8Co$	2717.30	2715.1

Table 2. Mesophase behaviour of the octa-alkoxy substituted cobalt(II) phthalocyanine complexes. All the compounds exhibit a hexagonal columnar mesophase (Col_h).[a]

	T_m/°C	ΔH_m (kJ mol^{-1})	T_c/°C	ΔH_c (kJ mol^{-1})
$(C_4H_9O)_8PcCo$	218	12	Dec[b]	—
$(C_5H_{11}O)_8PcCo$	133	30	Dec	—
$(C_6H_{13}O)_8PcCo$	126	65	Dec	—
$(C_7H_{15}O)_8PcCo$	116	71	Dec	—
$(C_8H_{17}O)_8PcCo$	123	68	Dec	—
$(C_9H_{19}O)_8PcCo$	112	83	Dec	—
$(C_{10}H_{21}O)_8PcCo$	111	94	Dec	—
$(C_{11}H_{23}O)_8PcCo$	102	94	Dec	—
$(C_{12}H_{25}O)_8PcCo$	101	103	Dec	—
$(C_{13}H_{27}O)_8PcCo$	91	91	Dec	—
$(C_{14}H_{29}O)_8PcCo$	95	106	328	10
$(C_{15}H_{31}O)_8PcCo$	91	106	305	7
$(C_{16}H_{33}O)_8PcCo$	92	82	306	10
$(C_{17}H_{35}O)_8PcCo$	96	232	292	16
$(C_{18}H_{37}O)_8PcCo$	64	120	266	35

[a] The melting points (T_m) and clearing points (T_c) were determined by differential scanning calorimetry. The reported temperatures are peak temperatures.

[b] Dec = decomposition.

The textures observed microscopically between crossed polarizers were the typical mosaic texture of the hexagonal columnar mesophase (figure 5). Between parallel polarizers, a dendritic pattern was observed when the mesophase was formed by cooling the isotropic liquid (figure 6).

The high temperature X-ray patterns consist of: (*a*) a diffuse scattering halo in the wide angle region, corresponding to the liquid-like disorder of the aliphatic chains, at *c.* 4.7 Å; (*b*) another, less broad peak around 3.4 Å, which is the stacking distance between the phthalocyanine cores within the columns; (*c*) up to four sharp, intense reflections in the small angle region, with

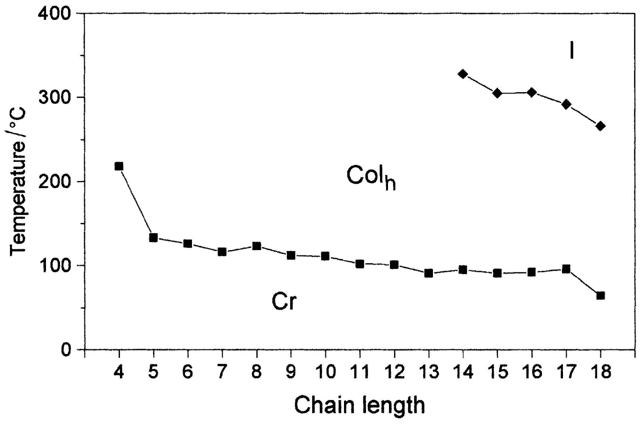


Figure 3. Influence of the alkoxy chain length on the transition temperatures of the substituted cobalt(II) phthalocyanines. Cr = crystalline solid, Col_h = hexagonal columnar mesophase, I = isotropic liquid.

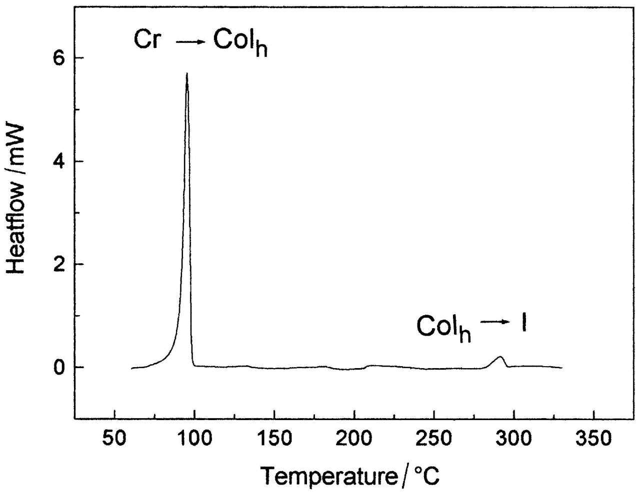


Figure 4. DSC thermogram (first heating run) of the complex $(C_{17}H_{35}O)_8PcCo$. Endothermic peaks point upwards.

Figure 5. Texture of the complex $(C_{16}H_{33}O)_8PcCo$ between crossed polarizers at 290°C.

Figure 6. Texture of the complex $(C_{16}H_{33}O)_8PcCo$ between parallel polarizers at 290°C.

reciprocal spacings in the ratio $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$, corresponding to the indexation $[h\,k]=[1\,0]$, $[1\,1]$, $[2\,0]$ and $[2\,1]$. Such features are characteristic of a two-dimensional hexagonal spacing of columns, that is of a *hexagonal columnar mesophase* (Col_h). The phase is disordered since there is no long range correlative order within the columns, as is evident from the absence of a sharp peak in the wide angle region which would have corresponded to a perfect and regular stacking along the columnar axis. The XRD pattern of the compound $(C_{16}H_{33}O)_8PcCo$ at 175°C is shown in figure 7.

The thermal decomposition of the complexes was studied by a thermogravimeter coupled to a mass spectrometer. The TG-thermogram of the cobalt(II) phthalocyanine complex with eight decyloxy chains, $(C_{10}H_{21}O)_8PcCo$, is shown in figure 8. Thermal decomposition takes place in two distinct steps: one at *c.* 300°C and a sharp set at 600°C. By TG-MS it could be shown that the decomposition step at 300°C corresponds to loss of the eight decyl ($C_{10}H_{21}$) chains. Different alkyl fragments between C_2H_5 and $C_{10}H_{21}$ could be observed. The decomposition step at 600°C corresponds to degradation of the phthalocyanine core (detection of nitrogen in the MS).

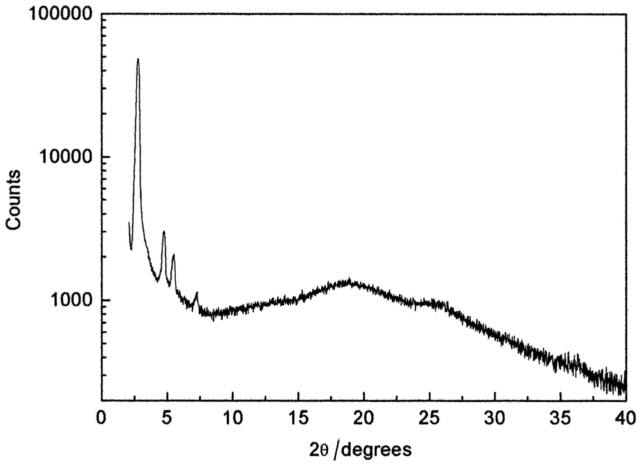


Figure 7. X-ray diffractogram of cobalt(II) complex $(C_{16}H_{33}O)_8PcCo$ at 175°C.

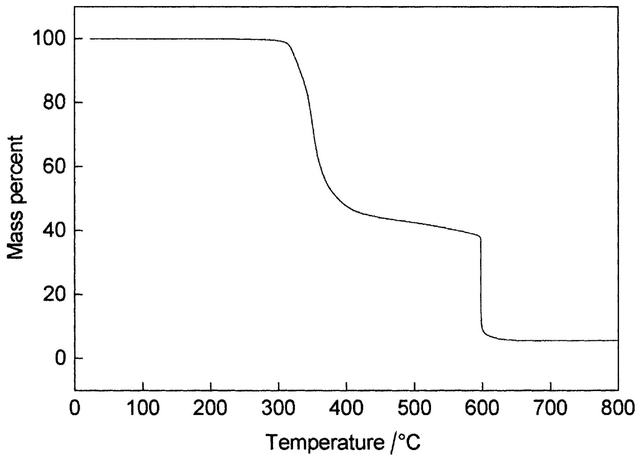


Figure 8. TG-thermogram of cobalt(II) complex $(C_{10}H_{21}O)_8PcCo$.

In comparison with the metal-free phthalocyanines, transition temperatures (both melting and clearing points) of the corresponding cobalt(II) phthalocyanines are higher. For instance for the metal-free phthalocyanine with $C_{14}H_{29}O$ chains, the mesophase behaviour (temperatures in °C) is Cr 69 Col_h 242 I, whereas for the corresponding cobalt(II) complex it is Cr 95 Col_h 328 I. The mesophase stability range of the cobalt(II) phthalocyanines is significantly larger than that of the metal-free phthalocyanines. Thus, the metal ion in the central cavity of the phthalocyanine ring has a stabilizing effect on the mesophase. On the other hand, the melting temperatures of the cobalt(II) phthalocyanines are comparable with those of the corresponding copper(II) phthalocyanines. For the copper(II) series reported by van der Pol *et al.* data are available only for alkoxy chains up to $C_{12}H_{25}O$ and no clearing points are reported [7]; because of this, the clearing points of the copper(II) and cobalt(II) series cannot be compared with one another. However, Ford *et al.* [12] published data for the copper(II) phthalocyanine with eight octadecyloxy chains; the transition temperatures of this compound are Cr 52 M 257 I. This is again comparable with the data for the corresponding cobalt(II) compound: Cr 64 Col_h 266 I.

4. Conclusions

Cobalt(II) phthalocyanines with eight peripheral alkoxy chains have been synthesized. The alkoxy chain length was varied between C_4H_9O and $C_{18}H_{37}O$. Studies by polarizing optical microscopy and high temperature X-ray diffraction revealed that all the complexes exhibit a hexagonal columnar mesophase. The clearing point could only be observed for the compounds with a chain length longer than $C_{13}H_{27}O$. Both the melting and clearing points decrease with increasing chain length. The transition temperatures are higher than those of corresponding metal-free phthalocyanines, but are comparable with those of the corresponding copper(II) compounds. The compounds are one of the few examples of metallomesogens with cobalt(II) as the central metal ion.

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