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Separation properties of bis(β -diketonato)–copper(II) complexes in capillary gas chromatography

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Abstract

The bis[1-4'-(octyloxybiphenyl-4-yl)-3-(1'-methylpropyl)-1,3-dionato]– and bis[1-4'-(nonyloxybiphenyl-4-yl)-3-(1'-methylpropyl)-1,3-dionato]–copper(II) complexes were synthesized and successfully coated onto a fused-silica capillary column. The results obtained from differential scanning calorimetry and the melting point apparatus equipped with a polarization microscopy showed that they present a nematic phase and have a very limited liquid crystalline temperature range under cooling conditions. The chromatographic experiments show that these metal complexes possess good separation abilities for many different kinds of di- and tri-substituted benzene isomers, polycyclic aromatic hydrocarbons and constituents of volatile oils. In order to illustrate the influence of the presence of copper in the molecules of the stationary phase, the selectivities of 1,3-diones were compared with their corresponding bis(β -diketonato)–copper(II) complexes. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Coated columns; Stationary phases, GC; Complexation; Bis(β -diketonato)–copper stationary phases; Liquid crystals; Aromatic compounds; Halogenated compounds

1. Introduction

Complexation GC is a highly selective chromatographic technique using metal coordination complexes as stationary phase [1]. Its separation mechanism is based on the formation of metastable complexes to metal atoms. It can separate many compounds which possess only slight differences in structure or configuration (positional and chiral isomers) [2–6]. On the other hand, liquid crystals have been used as GC stationary phases for about 35 years [7,8] and a large number of monomeric and polymeric liquid crystals were synthesized and applied to GC [9–14]. In

recent years, the number of investigations of metal-containing liquid crystals is growing fast. Many metal complex liquid crystals have been synthesized [15].

To date, only a few papers have presented the use of metal complex liquid crystals as GC stationary phases; these metal complex liquid crystals combine the properties of metal coordination complexes with liquid crystals and exhibit high selectivity for GC separation [16–19]. In 1995, Berdagué et al. [17] used nematic liquid crystals (LH) and its cupric complex (CuL_2) as a GC stationary phase. They commented that 'Because of the steric effect around the metal, no Cu(II) complexation of aromatic compounds is observed ... the plate number of

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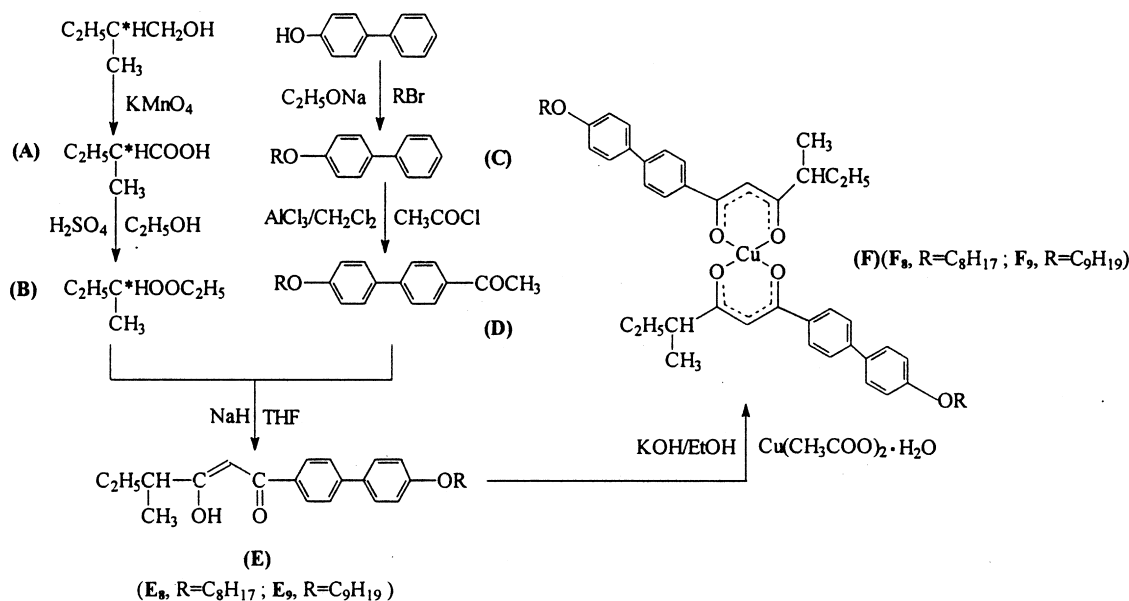


Fig. 1. Outlines of the synthesis route of 1,3-diones and their bis(β -diketonato)-copper(II) complexes.

CuL_2 column is higher.' [17]. More recently, Liu and co-workers [18,19] used metal complex liquid crystals for the separation of polycyclic aromatic hydrocarbons (PAHs). They proved that the separation mechanism of metal complex liquid crystals involved both ligand exchange and shape selectivity.

β -Diketonate metal complexes have been widely used as GC stationary phases [9,20] and as successful mobile phase additives for HPLC [21]. Liquid crystals containing a bis(β -diketonato)-copper(II) core have received more attention since it was first reported in 1981 [22–25]. In this study, two bis(β -diketonato)-copper(II) complexes (as shown in Fig. 1) were synthesized by a method similar to that in [25]. They were successfully coated onto the fused-silica capillary column and their chromatographic characteristics were investigated.

2. Experimental

2.1. Reagents

S-(–)-2-Methylbutanol was purchased from Fluka. All other compounds used for the syntheses were analytical or chemically pure reagents. Volatile essen-

tial oil constituents were kindly supplied by the Department of Chemistry, Beijing University, China.

2.2. Apparatus

The GC separations were carried out on a SP-3700 gas chromatograph (Beijing Analytical Instrument Factory, Beijing, China) equipped with a flame ionization detector (FID). The carrier gas was nitrogen. The output of the detector was connected to a LDC/Milton Roy CI-10 integrator and a graph recorder. The injection split ratio was (80:1).

Temperature transitions were determined by Perkin-Elmer DSC-7 and X-6 precision melting point apparatus equipped with a polarization microscope. A Bruker 400 1H NMR Instrument, Heraeus Rapid C.H.N elemental analysis instrument and a Perkin-Elmer 1600 IR spectrometer were also used.

2.3. Synthesis

Fig. 1 outlines the route of synthesis of the bis(β -diketonato)-copper(II) complexes.

The *S*-(+)-2-methylbutyric acid (A) was synthesized according to the method described in [26]: b.p. 172–176°C, $[\alpha]_D^{20} +19.65$ (c 0.10, C_2H_5OH), IR

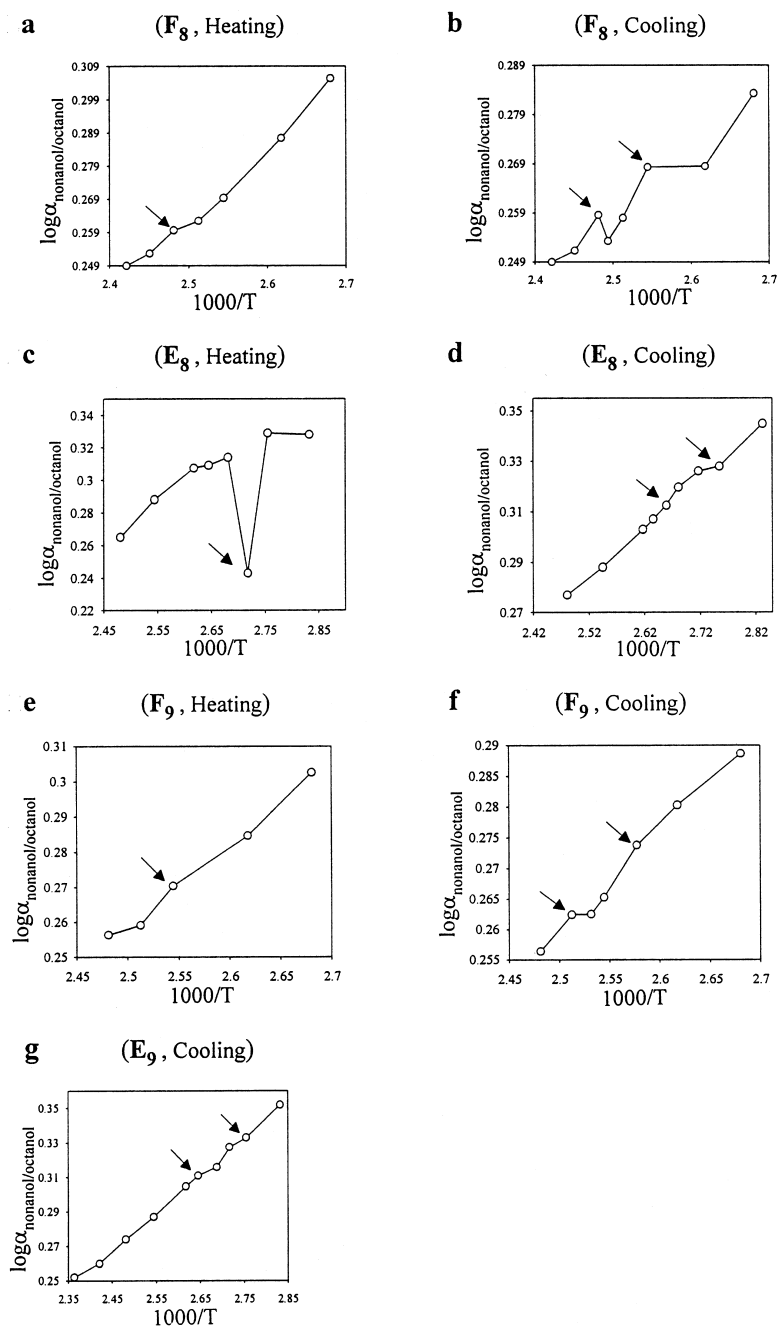


Fig. 2. Curves of $\log \alpha_{\text{nonanol/octanol}}$ versus $1000/T$ for nonanol and octanol probes. Transition temperatures are shown by arrows in the curves. (a) Heating curve for F_8 ; (b) cooling curve for F_8 ; (c) heating curve for E_8 ; (d) cooling curve for E_8 ; (e) heating curve for F_9 ; (f) cooling curve for F_9 ; (g) cooling curve for E_9 .

ν_{\max} (liquid film, cm^{-1}): 3500~2500 (vs, $-\text{COOH}$), 1707 (s, $-\text{C}=\text{O}$).

S-(+)-2-methylbutyrate (B) was also obtained as in [26]: b.p. 130–133°C, $[\alpha]_{\text{D}}^{20} +17.78$ (c 0.10, $\text{C}_2\text{H}_5\text{OH}$), IR ν_{\max} (liquid film, cm^{-1}): 1736 (s, $-\text{C}=\text{O}$).

Compound (D) was obtained according to [27] and compound (E) was obtained by a method similar to [25]. Racemization took place in this reaction step because of the over addition of sodium hydride.

For 1-(4'-octyloxybiphenyl-4-yl)-3-(1'-methylpropyl)-1,3-dione (E_8) a light-yellow powder crystal was obtained: IR ν_{\max} (KBr, cm^{-1}): 1608 (s, $-\text{C}=\text{O}$). ^1H NMR (400 Hz, CDCl_3 , δ ppm, TMS): 0.89 (3H, t,

Table 1

Transition temperatures of liquid crystals E_8 , E_9 and metal complexes F_8 , F_9 measured by Perkin-Elmer DSC-7 and X-6 precise melting point apparatus equipped with a polarization microscopy

| Tested compounds | Conditions | Transition temp. (°C) |
|------------------|------------|---|
| E_8 | Heating | $K \xrightarrow{105.8} I$ |
| | Cooling | $K \xleftarrow{100.5} S_A \xleftarrow{104.1} I$ |
| E_9 | Heating | $K \leftrightarrow S_A \xrightarrow{105.1} I$ |
| | Cooling | |
| F_8 | Heating | $K \xrightarrow{134.7} I$ |
| | Cooling | $K \xleftarrow{117.4} N \xleftarrow{128.6} I$ |
| F_9 | Heating | $K \xrightarrow{122.5} I$ |
| | Cooling | $K \xleftarrow{112.2} N \xleftarrow{120.7} I$ |

Table 2

Evaluation of column efficiency at different column temperatures for E_8 , E_9 , F_8 and F_9 in cooling conditions

Column 1 14.2 m×0.25 mm; film thickness (μm): 0.125

| E_8 | Isotropic | | | | | Smectic A | | Solid | | |
|---------------|--------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | Cooling (°C) | 150 | 140 | 130 | 120 | 110 | 105 | 100 | 95 | 90 |
| Test probe | | C_{12} | C_{12} | C_{12} | C_{12} | C_{12} | C_{12} | C_{12} | C_{12} | C_{12} |
| k | | 0.74 | 1.02 | 1.48 | 2.04 | 2.26 | 2.70 | 2.39 | 2.56 | 3.5 |
| N (plate/m) | | 2709 | 2267 | 2194 | 2259 | 3110 | 2417 | 1595 | 1846 | 835 |

Column 2 14.2 m×0.25 mm; film thickness (μm): 0.125

| E_9 | Isotropic | | | | | | Smectic A | | Solid | |
|---------------|--------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | Cooling (°C) | 160 | 150 | 140 | 130 | 120 | 110 | 105 | 100 | 90 |
| Test probe | | C_{14} | C_{14} | C_{14} | C_{12} | C_{12} | C_{12} | C_{12} | C_{12} | C_{12} |
| k | | 1.84 | 2.82 | 3.67 | 1.54 | 2.18 | 2.64 | 2.64 | 2.82 | 4.27 |
| N (plate/m) | | 1924 | 1328 | 1734 | 1328 | 1701 | 1433 | 1068 | 1147 | 1168 |

Column 3 11 m×0.25 mm; film thickness (μm): 0.10

| F_8 | Isotropic | | | | Nematic | | | Solid | | |
|---------------|--------------|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | Cooling (°C) | 160 | 150 | 140 | 130 | 127 | 124 | 120 | 110 | 100 |
| Test probe | | | C_{14} | C_{14} | C_{14} | C_{14} | C_{14} | C_{14} | C_{14} | C_{12} |
| k | | | 0.50 | 0.70 | 0.81 | 0.91 | 1.07 | 1.83 | 2.86 | 1.09 |
| N (plate/m) | | | 2590 | 1927 | 1954 | 1972 | 1558 | 1259 | 717 | 724 |

Column 4 25 m×0.25 mm; film thickness (μm): 0.10

| F_9 | Isotropic | | | | | Nematic | | Solid | | |
|---------------|--------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | Cooling (°C) | 160 | 150 | 140 | 130 | 120 | 115 | 110 | 100 | 90 |
| Test probe | | C_{14} | C_{14} | C_{14} | C_{13} | C_{13} | C_{13} | C_{12} | C_{12} | C_{11} |
| k | | 1.00 | 1.45 | 1.93 | 1.52 | 1.88 | 2.26 | 1.69 | 2.54 | 2.64 |
| N (plate/m) | | 4820 | 4430 | 3820 | 4440 | 3840 | 3440 | 4010 | 2920 | 2860 |

k : Capacity factor; N : theoretical plate number, (plate/m).

–O(CH₂)₇CH₃), 0.95 (3H, t, –CH₂CH₃), 1.21 (3H, d, –CH₃), 1.30–1.87 (14H, m, (–CH₂)₇), 2.39 (1H, m, –CH(CH₃)–), 4.00 (2H, t, OCH₂), 4.20 (trail, s, –COCH₂CO), 6.20 (1H, m, –CH=C), 6.97–7.95 (8H, m, ArH), 16.30 (1H, s, –OH). Elemental analysis (calc., %): C 79.33 (79.41), H 8.54 (8.82).

For 1-(4'-nonyloxybiphenyl-4-yl)-3-(1'-methylpropyl)-1,3-dione (E₉) a light-yellow plate crystal was obtained: IR ν_{\max} (KBr, cm⁻¹): 1605 (s, –C=O). ¹HNMR (400 Hz, CDCl₃, δ ppm, TMS): 0.89 (3H, t, –O(CH₂)₈CH₃), 0.95 (3H, t, –CH₂CH₃), 1.20 (3H, d, –CH₃), 1.29–1.83 (16H, m, (–CH₂)₈), 2.40 (1H, m, –CH(CH₃)–), 4.00 (2H, t, OCH₂), 4.17 (trail, s, –COCH₂CO), 6.20 (1H, m, –CH=C), 6.97–7.95 (8H, m, ArH), 16.40 (1H, s, –OH). Elemental analysis (calc., %): C 79.95 (79.62), H 9.09 (9.00).

Bis(β -diketonato)-copper(II) complexes (F) were then synthesized. For bis[1-4'-(octyloxybiphenyl-4-yl)-3-(1'-methylpropyl)-1,3-dionato]-copper(II) complex (F₈), the product was a needle-like green powder. IR ν_{\max} (KBr, cm⁻¹): 1615, 1595 (s, –C=O). Elemental analysis (calc., %): C 73.90 (73.85), H 7.85 (7.98). For bis[1-4'-(nonyloxybiphenyl-4-yl)-3-(1'-methylpropyl)-1,3-dionato]-copper(II) complex (F₉), the product was also a needle-like green powder. IR ν_{\max} (KBr, cm⁻¹): 1601, 1582 (s, –C=O). Elemental analysis (calc., %): C 73.93 (74.21), H 7.93 (8.17).

2.4. Column preparation

Fused-silica capillary tubing (0.25 mm I.D., Yong Nian Optical Fibre Factory, Hebei, China) was treated by depositing sodium chloride onto the inner wall of the column [28]. The columns were then statically coated with a solution (0.20% (w/v) for E₈, E₉ and 0.16% (w/v) for F₈, F₉) in dichloromethane at 35°C, the film thickness is approximately 0.125 μ m and 0.10 μ m, respectively. Following coating and flushing with nitrogen for 2 h, the columns coated with E₈ and E₉ stationary phases were conditioned at 80°C, 120°C, 160°C for 1 h each and finally at 180°C for 6 h, the columns coated with F₈ and F₉ stationary phases were conditioned at 100°C, 140°C, 180°C, 200°C for 1 h each and finally at 230°C for 6 h.

3. Results and discussion

3.1. Transition temperature

The transition temperatures were measured by differential scanning calorimetry (DSC) and by using a precision melting point apparatus equipped with a polarization microscope (as shown in Table 1). The results show that E₈, E₉ present smectic A liquid crystal phase and E₈ is monotropic S_A, while F₈, F₉ present monotropic N liquid crystals in cooling condition. The cooling scans for F₈, F₉ show a

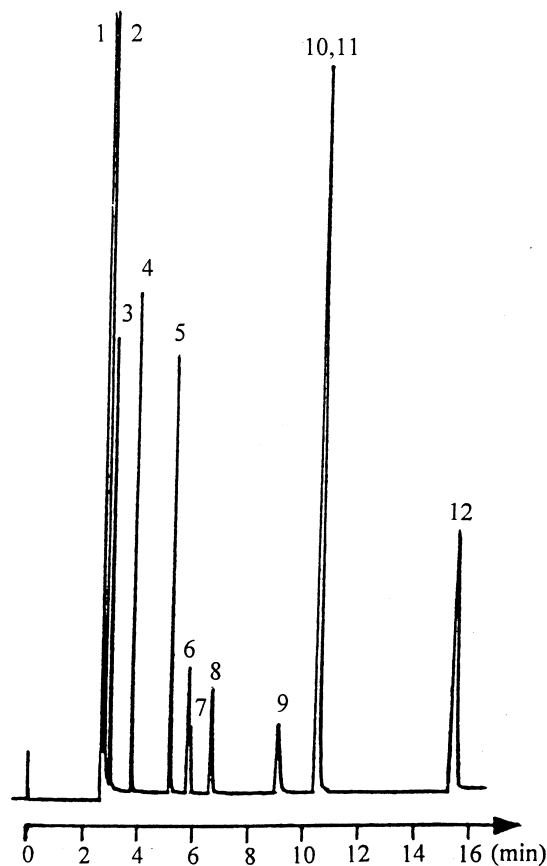


Fig. 3. Chromatogram for aromatic isomers on F₉ stationary phase (column 4). Column temperature: 60°C. N₂ linear velocity: 18.7 cm/s. Peaks: 1=acetone; 2=cyclohexane; 3=benzene; 4=methylbenzene; 5=ethylbenzene; 6=*m*-xylene; 7=*p*-xylene; 8=*o*-xylene; 9=*tert*-butylbenzene; 10,11=isobutylbenzene and 1,3,5-trimethylbenzene; 12=*n*-butylbenzene.

limited nematic mesophase range from 128.6°C to 117.4°C and from 120.7°C to 112.1°C, respectively.

The transition temperatures were also determined by plotting $\log \alpha_{\text{nonanol/octanol}}$ versus $1000/T$ for nonanol and octanol probes in cooling and heating conditions. The results are shown in Fig. 2. The discontinuities are clearly shown by arrows in these curves. These results are in agreement with those obtained by DSC and precision melting point apparatus.

3.2. Column efficiency

n-Alkanes (C_{12} – C_{14}) were used to evaluate column efficiency at different column temperatures in

cooling condition (as shown in Table 2). It is noted that the columns possess high efficiency whether the bis(β -diketonato)-copper(II) complexes are in isotropic, nematic or smectic A phases. Generally, the column efficiency is relatively lower when they are in solid phase.

3.3. Analytical performance

All separation experiments were carried out under cooling conditions, i.e., all the results were obtained at the chosen column temperature that was reached by cooling. These metal complexes present supercooling mesophase properties in their solid-phase temperature range. Because the mesophase range of

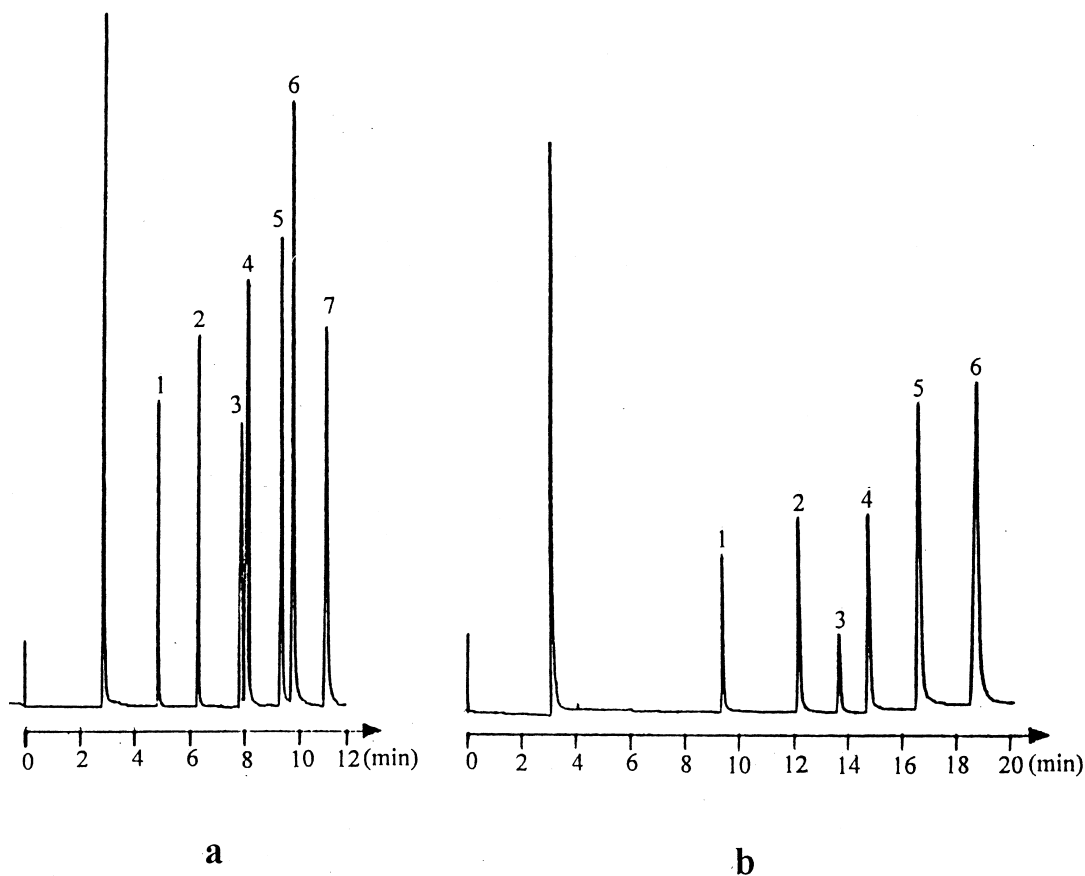


Fig. 4. Chromatograms for tri-substituted benzene isomers on F_9 stationary phase (column 4). (a) Column temperature: 130°C. N_2 linear velocity: 16.7 cm/s. Peaks: 1 = phenol; 2 = 2,6-xyleneol; 3 = 2,4-xyleneol; 4 = 2,5-xyleneol; 5 = 2,3-xyleneol; 6 = 3,5-xyleneol; 7 = 3,4-xyleneol. (b) Column temperature: 180°C. N_2 linear velocity: 15.4 cm/s. Peaks: 1 = 2,6-dinitrotoluene (DNT); 2 = 2,5-DNT; 3 = 2,3-DNT; 4 = 2,4-DNT; 5 = 3,5-DNT; 6 = 3,4-DNT.

F_8 , F_9 is limited, most separations were performed not in the liquid crystals phase but in their supercooling mesophase and isotropic phases. In the case of supercooling mesophase, the separation ability was mainly caused by liquid crystals property, but in the isotropic phase, the good separation ability was mainly caused by complex formation to metal and the difference in volatility and polarity of solute.

The separation abilities of the F_9 stationary phase were investigated in detail. Fig. 3 shows the chromatogram for the aromatic isomers, several alkylbenzene isomers are well separated, although isobutylbenzene and 1,3,5-trimethylbenzene coelute. Some typical disubstituted benzene isomers are also well separated, such as xylene, chlorotoluene, bromotoluene, dichlorobenzene, dibromobenzene and cresol. For xylene isomers, *m*-xylene elutes before *p*-xylene isomer. This reflects the typical property of liquid crystals: the more rod-like a solute molecule is, the easier it should fit into liquid crystals and

hence lengthening the retention time. Fig. 4 shows the chromatogram for the separation of typical explosive substances — dinitrotoluene (DNT) isomers — and for the separation of important industry chemical substances — phenol and xylenols. All these isomers are difficult to resolve on the commonly used columns such as SE-54 and PEG-20M. The F_8 stationary phase also shows a good separation ability for many substituted benzene isomers and naphthalene analogs on a short capillary column (11 m) as shown in Table 3.

In order to illustrate the influence of the presence of copper in the molecules of the F_8 , F_9 stationary phases, the separation abilities of the corresponding E_8 , E_9 stationary phases were also investigated for the same isomers at the same column temperature (Table 3). The results show that the elution orders of these isomers are the same both on E_8 , E_9 and on F_8 , F_9 stationary phases. However, the separation factors for these isomers are significantly different. It can be

Table 3
Comparison of capacity factor (k) and relative retention (α) on E_8 , F_8 and E_9 , F_9 stationary phases

| Compound | E_8 (column 1) | | F_8 (column 3) | | T (°C) | Compound | E_9 (column 2) | | F_9 (column 4) | | T (°C) | | |
|---------------------|---------------------|------------|---------------------|----------|-------------|----------|---------------------|------------|---------------------|---------------|-------------|------------|------|
| | k | α | k | α | | | k | α | k | α | | | |
| | Nitrotoluene | <i>o</i> - | 3.00 | 1.00 | | | 1.56 | 1.00 | 130 | Chlorotoluene | | <i>o</i> - | 1.25 |
| | <i>m</i> - | 4.22 | 1.41 | 2.17 | 1.39 | | | <i>m</i> - | 1.35 | 1.08 | 1.54 | 1.08 | |
| | <i>p</i> - | 5.05 | 1.68 | 2.57 | 1.64 | | | <i>p</i> - | 1.70 | 1.36 | 1.61 | 1.13 | |
| Nitrochlorobenzene | <i>m</i> - | 5.25 | 1.00 | 2.89 | 1.00 | 130 | Bromotoluene | <i>o</i> - | 1.95 | 1.00 | 2.18 | 1.00 | 90 |
| | <i>p</i> - | 5.25 | 1.00 | 3.00 | 1.04 | | | <i>m</i> - | 2.10 | 1.07 | 2.34 | 1.08 | |
| | <i>o</i> - | 5.92 | 1.13 | 3.52 | 1.22 | | | <i>p</i> - | 2.63 | 1.35 | 2.47 | 1.14 | |
| Nitrobromobenzene | <i>m</i> - | 10.00 | 1.001.12 | 5.68 | 1.00 | 130 | Dichlorobenzene | <i>m</i> - | 1.71 | 1.00 | 1.29 | 1.00 | 100 |
| | <i>p</i> - | 11.17 | | 5.96 | 1.05 | | | <i>p</i> - | 1.90 | 1.11 | 1.39 | 1.08 | |
| | | | | | | | | <i>o</i> - | 2.29 | 1.33 | 1.65 | 1.28 | |
| Naphthalene | | 2.33 | 1.00 | 0.79 | 1.00 | 140 | Dibromobenzene | <i>m</i> - | 4.48 | 1.00 | 2.67 | 1.00 | 120 |
| 1-Methylnaphthalene | | 2.58 | 1.96 | 1.45 | 1.84 | | | <i>p</i> - | 4.72 | 1.06 | 2.76 | 1.04 | |
| 2-Methylnaphthalene | | 4.92 | 2.11 | 1.62 | 2.05 | | | <i>o</i> - | 5.43 | 1.21 | 3.22 | 1.21 | |
| Cresol | <i>o</i> - | 6.38 | 1.00 | 2.88 | 1.00 | 100 | Cresol | <i>o</i> - | 3.86 | 1.00 | 2.10 | 1.00 | 105 |
| | <i>p</i> - | 8.81 | 1.38 | 4.11 | 1.43 | | | <i>p</i> - | 5.14 | 1.33 | 2.80 | 1.33 | |
| | <i>m</i> - | 8.95 | 1.40 | 4.11 | 1.43 | | | <i>m</i> - | 5.30 | 1.37 | 2.90 | 1.38 | |
| Phenol | | 1.13 | 1.00 | 0.79 | 1.00 | 130 | Phenol | | 1.14 | 1.00 | 0.73 | 1.00 | 130 |
| Xylenol | 2,6- | 2.00 | 1.76 | 0.84 | 1.34 | | Xylenol | 2,6- | 2.19 | 1.92 | 1.27 | 1.75 | |
| | 2,4- | 2.88 | 2.54 | 1.36 | 2.16 | | | 2,4- | 3.19 | 2.79 | 1.82 | 2.50 | |
| | 2,5- | 2.98 | 2.63 | 1.36 | 2.16 | | | 2,5- | 3.24 | 2.83 | 1.91 | 2.63 | |
| | 2,3- | 3.57 | 3.15 | 1.73 | 2.75 | | | 2,3- | 3.86 | 3.38 | 2.36 | 3.25 | |
| | 3,5- | 3.83 | 3.38 | 1.87 | 2.98 | | | 3,5- | 4.19 | 3.67 | 2.52 | 3.46 | |
| | 3,4- | 4.50 | 3.97 | 2.27 | 3.60 | | | 3,4- | 4.95 | 4.33 | 2.93 | 4.03 | |

reasoned that a different separation mechanism is caused by the introduction of copper into molecules: for E_8 , E_9 , the mechanism of liquid crystals has an effect on their separation process; for F_8 , F_9 , both liquid crystals and complexation mechanisms have an effect on the separation process. Another reason is that although the column temperatures are the same, E_8 , E_9 and F_8 , F_9 present different phases. As to the same elution orders on both stationary phases, it may

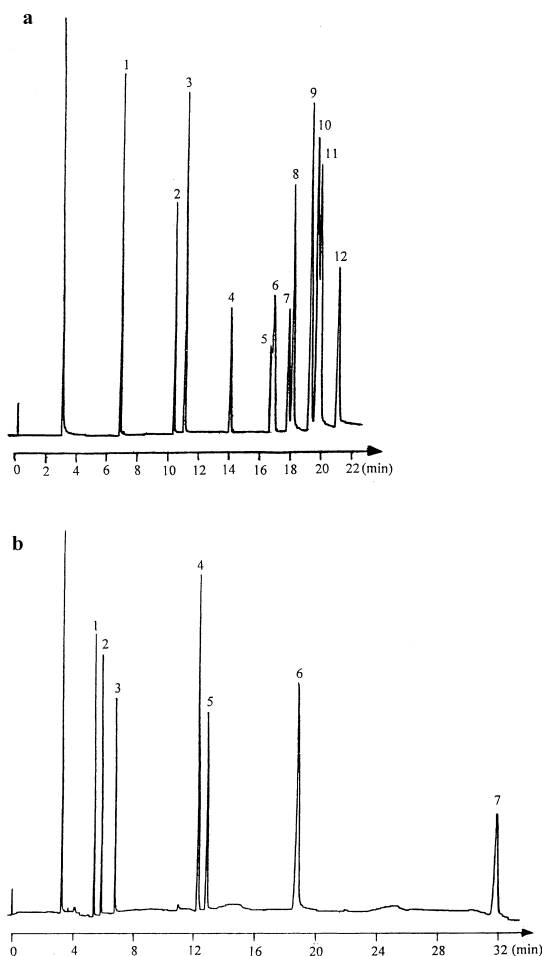


Fig. 5. Chromatograms for PAHs on F_9 stationary phase (column 4). (a) Column temperature: 140°C. N_2 linear velocity: 16.3 cm/s. Peaks: 1 = naphthalene; 2 = 2-methylnaphthalene; 3 = 1-methylnaphthalene; 4 = biphenyl; 5 = 2,6-dimethylnaphthalene (DMN); 6 = 1,7-DMN; 7 = unknown DMN isomer; 8 = 1,6-DMN; 9 = 1,4-DMN; 10 = 1,5-DMN; 11 = 2,3-DMN; 12 = 1,2-DMN. (b) Column temperature: 220°C. N_2 linear velocity: 15.4 cm/s. Peaks: 1 = acenaphthylene; 2 = dibenzofuran; 3 = fluorene; 4 = phenanthrene; 5 = anthracene; 6 = carbazole; 7 = unknown three-ring PAH.

mean that the copper in the molecule does not have a decided influence for the separation because of the steric effect around the metal.

Fig. 5 illustrates the excellent separation for substituted naphthalene isomers and three-ring PAHs. In Fig. 5a, the elution order of 1,4-, 2,5-DMN is different from that obtained on cyclodextrin derivative stationary phase columns [29]. It is considered that the structure of the host molecule has an important effect on the separation of guest molecules. Seven three-ring PAHs are well separated on F_9 (Fig. 5b). The baseline is not so good because the column temperature is high. Acenaphthene and acenaphthylene are baseline separated, as well as phenanthrene and anthracene. All these separations are achieved above the isotropic temperature.

About thirty constituents of volatile essential oils were well separated on F_9 stationary phase (these typical aromatic compounds include α -, β -pinene, camphere, myrcene, linalool, menthol, geraniol, safrol and anethol etc.), in which some *cis*- and *trans*-isomers, such as bornol and citral, are also well separated.

4. Conclusion

Two bis(β -diketonato)-copper(II) complexes were successfully used as stationary phases for capillary GC. DSC and the precise melting point apparatus show that they present nematic phase in cooling condition and their liquid crystals temperature range are very limited. The capillary columns coated by these metal complexes have very good separation ability for many positional aromatic isomers at temperatures from 45°C to 220°C. The influence of the presence of copper in the molecule on the separation is evaluated. Volatile essential oils constituents and some *cis*-, *trans*- isomers are also well separated.

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