Russian Chemical Bulletin, International Edition, Vol. 50, No. 5, pp. 805—808, May, 2001

Synthesis and liquid-crystalline properties of substituted β-aminovinyl ketones and their complexes with copper(II)

O. A. Turanova,[a] Yu. G. Galyametdinov,[a,b★] and I. V. Ovchinnikov[a]

[a]E. K. Zavoisky Kazan Physical-Technical Institute, Russian Academy of Sciences,
10/7 ul. Sibirsky Trakt, 420029 Kazan, Russian Federation.
Fax: +7 (843 2) 76 5075. E-mail: turanova@sci.kcn.ru
[b]Kazan State Technological University,
68 ul. K. Marksa, 420015 Kazan, Russian Federation

Mesogenic complexes were synthesized by the reaction of β-aminovinyl ketones with copper(II) acetate. On going from the ligands to complexes, the temperature of phase transitions increases and the nematic phase disappears. The initial members of the homological 1-(4-nonyloxyphenyl)-3-(4-methoxyphenylamino)-1-propen-1-one series demonstrate the alternation of clearing temperatures, which is absent for the corresponding copper(II) complexes.

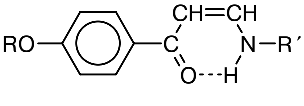
Key words: β-aminovinyl ketones, copper(II) acetate, complexes, liquid crystals, metallomesogens, polythermal polarization microscopy, differential scanning calorimetry.

Chemistry of metallomesogens is being intensely studied for recent 20 years.[1] The synthesis of liquid-crystalline complexes was described, where diketones,[2] Schiff's bases,[3] and aminovinyl ketones[4] were used as ligands. Application of the latters as ligands is of interest because a considerable delocalization of a π-electron pair of the N atom along the five-membered chains of atoms enables tautomeric transformations and the appearance of some physicochemical peculiarities of these compounds. It is also known[5,6] that the variation of metal atoms in a complex or substituents in ligands can substantially change their mesogenic properties and physical parameters. For example, complexes with lanthanides possess high values of magnetic susceptibility anisotropy and magnetic double refringence (Cotton—Muthon effect).[7] Some complexes of β-aminovinyl ketones with copper(II) have a cubic mesophase, whose structure and properties are presently under intense study.[8] Preparation of metallomesogens with specific properties requires data on a relation of their structure to the liquid-crystalline properties.

The purpose of this work is the synthesis of complexes of β-aminovinyl ketones with Cu^{II} and study of their liquid-crystalline properties.

Results and Discussion

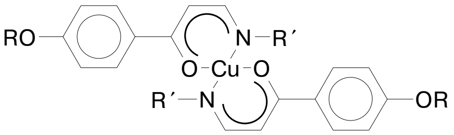
We synthesized several β-aminovinyl ketones with various alkoxyphenyl and alkyl terminal substituents, which are ligands in the complexes under study, with the general formula



1a—p, 2a—e

R = C_nH_{2n+1}; R′ = $PhOC_nH_{2n+1}$ (**1**), C_nH_{2n+1} (**2**)

and the corresponding complexes with Cu^{II}



3a—p, 4a—e

R = C_nH_{2n+1}; R′ = $PhOC_nH_{2n+1}$ (**3**), C_nH_{2n+1} (**4**)

Ligands **1** and **2** were synthesized by refluxing in EtOH of hydrochloride of the corresponding substituted aniline (or amine) with the Na salt of β-hydroxymethylene-4-alkoxyacetophenone. The precipitate that formed on cooling of the reaction mixture was recrystallized from ethanol similarly to a previously described procedure.[9] The products are soluble in $CHCl_3$ and benzene. Solubility of the substances in EtOH decreases with an increase in the chain of the carbon radical R′. The β-aminovinyl ketones prepared are stable in air and on heating.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 771—773, May, 2001.

The ^{1}H NMR and IR spectral parameters of β-aminovinyl ketones are close to those described previously[9,10] and correspond to their enaminoketone form. The IR spectrum of ligands **1** and **2** exhibits the shift of frequencies of stretching vibrations of the N—H (3310 and 3435 cm^{-1}), C—O and C—C (1640 and 1605 cm^{-1}, respectively) bonds. It is due, most likely, to the strong intramolecular bonding appeared upon the formation of a stable pseudo-aromatic cycle. The chemical shift of the signal from the proton of the NH group (~12.00 ppm) and splitting of the signal on the proton of the vinyl fragment (~12 Hz) also confirm this assumption.

The temperatures of phase transitions and types of mesophases of several compounds were studied by differential scanning calorimetry (DSC) and polythermal polarization microscopy (Tables 1 and 2). Due to the predomination of the steric effect, ligands **1** with short hydrocarbon groups (see Table 1, compounds **1a—e**) are characterized by a weak intermolecular interaction favoring the formation of both smectic (S) and nematic (N) phases. An increase in the length of the hydrocarbon group enhances the lateral interaction of alkyl substituents, disappearance of the less ordered nematic phase, and appearance of smectic (S_A) mesomorphism[11]; for compounds **2d,e**, this results in the absence of the mesophase. It is of interest that compounds **2a—e** have the smectic phase (see Table 1), although related complexes do not manifest liquid-crystalline properties.

The study of the influence of the number of atoms *n* in the R′ substituent on the phase transition temperature in ligands **1** showed (Fig. 1) that an increase in *n* results in the alternation of clearing temperatures, which is known for many classes of liquid-crystalline compounds,[12] narrowing of the temperature interval of nematic phase existence (it is absent from compounds with $n \geq 7$), and extension of the temperature interval of smectic phase

Table 1. Temperatures of phase transitions (*T*) in ligands **1** and **2**

Compound	*n**	R′	*T*/°C			Δ*T*/°C
			Cr—S	Cr(S)—N	S(N)—I	
1a	9	PhOMe	—	124	185	61
1b	9	PhOEt	130	169	201	71
1c	9	$PhOC_3H_7$	128	176	192	64
1d	9	$PhOC_4H_9$	129	186	195	66
1e	9	$PhOC_5H_{11}$	132	188	191	59
1f	9	$PhOC_6H_{13}$	99	193	194	95
1g	9	$PhOC_7H_{15}$	98	—	189	91
1h	9	$PhOC_8H_{17}$	104	—	190	86
1i	9	$PhOC_9H_{19}$	106	—	188	82
1j	9	$PhOC_{10}H_{21}$	118	—	189	71
1k	9	$PhOC_{11}H_{23}$	86	—	184	98
1l	9	$PhOC_{12}H_{25}$	108	—	181	73
1m	9	PhMe	130	—	169	39
1n	9	PhEt	128	—	162	34
1o	9	PhC_4H_9	112	—	167	55
1p	9	PhC_7H_{15}	122	—	173	51
2a	7	$C_{12}H_{25}$	46	—	55	9
2b	12	$C_{10}H_{21}$	45	—	52	7
2c	12	$C_{12}H_{25}$	59	—	64	5
2d	12	$C_{16}H_{33}$	—	—	74	—
2e	12	$C_{18}H_{37}$	—	—	76	—

Note. Cr is crystalline, S is smectic, N is nematic, and I is isotropic phases.
* *n* is the number of carbon atoms in the alkyl chain of the R substituent.

Table 2. Temperature of phase transitions (*T*) in Cu^{II} complexes **3** and **4**

Compound	*n**	R′	*T*/°C		Δ*T*/°C
			Cr—S	(Cr)S—I	
3a	9	PhOMe	141 (S_1); 144 (S_2)	190	49
3b	9	PhOEt	163 (S_1); 176 (S_2)	192	29
3c	9	$PhOC_3H_7$	167 (S_1); 187 (S_2)	196	29
3d**	9	$PhOC_4H_9$	173	210	37
3e**	9	$PhOC_5H_{11}$	164	209	45
3f	9	$PhOC_6H_{13}$	142	204	62
3g**	9	$PhOC_7H_{15}$	139	197	58
3h	9	$PhOC_8H_{17}$	155	198	43
3i	9	$PhOC_9H_{19}$	156	190	34
3j**	9	$PhOC_{10}H_{21}$	150	192	42
3k**	9	$PhOC_{11}H_{23}$	151	195	44
3l	9	$PhOC_{12}H_{25}$	140	195	55
3m	9	$PhCH_3$	110	167	57
3n	9	PhC_2H_5	112	167	55
3o	9	PhC_4H_9	121	179	58
3p**	9	PhC_7H_{15}	151	182	31
4a	7	$C_{12}H_{25}$	—	83	—
4b	12	$C_{10}H_{21}$	—	77	—
4c	12	$C_{12}H_{25}$	—	79	—
4d	12	$C_{16}H_{33}$	—	94	—
4e	12	$C_{18}H_{37}$	—	130	—

Note. Cr is crystalline, S is smectic, and I is isotropic phases.
* *n* is the number of carbon atoms in the alkyl chain of the R substituent.
** Melting with decomposition.

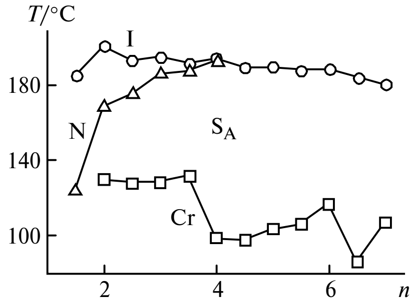


Fig. 1. Plots of the phase transition temperatures of ligands **1** *vs.* number of carbon atoms (*n*) in the alkyl chain of the R′ substituent (Cr is the crystalline phase, S_A is the smectic A phase, N is the nematic phase, and I is the isotropic phase).

existence compared to the first three members of the homologic series of the ketones synthesized.

Complexes **3** and **4** were prepared by heating of the ligand in ethanol or dioxane with Cu^{II} acetate as described in Ref. 10. The products were colored in various shades of brown and green, soluble in $CHCl_3$, moderately soluble in benzene and EtOH, and insoluble in water. Unlike the ligands, not all complexes are stable on heating. Analysis of the IR spectra of the compounds synthesized showed that for complex formation the frequencies of stretching vibrations of C=O (1655 cm^{-1}) and C=C (1602 cm^{-1}) of the vinyl fragment are shifted by 30—40 cm^{-1} toward the long-wave region. The ESR spectra of the complexes (triplet: $g_1 = 2.165$, $g_2 = 2.094$, $g_3 = 2.041$) are identical to the spectra[13] of similar compounds.

On going from the ligands to complexes (see Table 2), the following is observed. The nematic phase was absent from the synthesized complexes, their temperatures of phase transitions were higher, and the interval of S_A mesophase existence was more narrow than that for the ligands. When the complex is formed, the volume of the molecule increases considerably and its length remains unchanged. This results in a decrease in the geometric anisotropy (the ratio of the "length" of the molecule to its "width") of the complex molecules compared to the ligands and leads to additional dispersion interactions between the complex molecules. Thus, this creates conditions for the predominant formation of the smectic phase. The above said explains the absence of the nematic phase from complexes **3** and the complete absence of mesomorphism from compounds **4**.

Resemblance of the structures of Schiff's bases and β-aminovinyl ketones suggests that the physical and chemical properties of related complexes are close. For example, the character of changing the phase transition temperatures of ligands **1** and complexes **3** corresponds to the general regularities described previously for Schiff's bases.[3] At the same time, a distinction in the structure of the coordination unit of the ligand can result in the appearance of new interesting properties. For example, in the complexes with β-aminovinyl ketones. the type of mesophase changes toward high ordering. The phase transition temperatures of the copper(II) complexes with β-aminovinyl ketones exceed, as a whole, by 20—30 °C the corresponding temperatures for Schiff's bases. This phenomenon can be explained, most likely, by the difference in anisometry of the molecules of β-aminovinyl ketones (3.5) and *N*-arylsalicylaldimines (3). Compounds **3**, unlike similar complexes with Schiff's bases,[3] have no alternation effect of clearing temperatures.

When the length of the alkyl group increases to the third homolog, the temperature interval of smectic phase existence is narrowed. Beginning from $n = 4$, the region of S_A mesophase existence extends and reaches a maximum for the complexes with $n = 6, 7$. With the further elongation of the alkyl group, the changes in the interval of mesophase existence become wave-like.

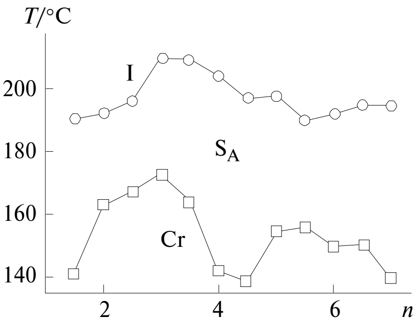


Fig. 2. Plots of the phase transition temperatures of complexes **3** *vs.* number of carbon atoms (*n*) in the alkyl chain of the R′ substituent (Cr is the crystalline phase, S_A is the smectic A phase, N is the nematic phase, and I is the isotropic phase).

Thus, in the study of β-aminovinyl ketones and their complexes with copper(II), we found that an increase in the number of atoms in the *N*-alkyl chain and alkoxyphenyl substituent results in a loss of the liquid-crystalline properties. The complexes studied have no alternation of clearing temperatures observed for ketones. Higher phase transition temperatures and the disappearance of the nematic phase were established for the complexes with copper (II) compared to β-aminovinyl ketones.

Experimental

Textures and phase transition temperatures were determined on an Boetius polarization microscope supplied with a computer-controlled temperature block. The error of temperature measurement was ±0.1 °C. IR spectra were recorded on a Specord IR-75 spectrometer in Nujol. ^1H NMR spectra were recorded on a Varian Unity-300 spectrometer in $CDCl_3$. Ligands **1**, **2** and complexes **3** were synthesized according to previously described procedures.[3,9] Complexes **4** were prepared by the general procedure presented below.

Bis[1-(4-dodecyloxyphenyl)-3-octadecylamino-1-propen-1-olate]copper (general procedure). A mixture of ligand **2** (0.17 g, 0.3 mmol) and copper(II) acetate (0.029 g, 0.15 mmol) was refluxed for 3 min in EtOH. The green precipitate that formed was filtered off, washed with EtOH, and dried *in vacuo*. The yield was 0.32 g (89%). Found (%): C, 76.18; H, 11.15; N, 2.19; Cu, 5.18. $C_{78}H_{136}CuN_2O_4$. Calculated (%): C, 76.22; H, 11.07; N, 2.28; Cu, 5.21.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 99-03-32716).

References

1. *Metallomesogens: Synthesis, Properties and Applications*, Ed. L. Serrano, VCH, Weinheim, 1996, 498 pp.

2. A. B. Blare, J. R. Chipperfield, S. Clark, and P. G. Nelson, *J. Chem. Soc., Dalton Trans.*, 1991, 1159.
3. Yu. G. Galyametdinov, G. I. Ivanova, I. G. Bikchantaev, L. M. Tinchurina, and I. V. Ovchinnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2833 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 2597 (Engl. Transl.)].
4. A. Krowczynsky, D. Pciecha, J. Szydlowska, P. Przedmojski, and E. Gorecka, *J. Chem. Soc., Chem. Commun.*, 1996, 2371.
5. Yu. G. Galyametdinov, I. G. Bikchantaev, and I. V. Ovchinnikov, *Zh. Obshch. Khim.*, 1988, **58**, 1326 [*J. Gen. Chem. USSR*, 1988, **58**, 1180 (Engl. Transl.)].
6. D. W. Bruce, E. Lalinde, P. Styring, D. A. Dunmur, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1986, 581.
7. I. Bikchantaev, Yu. G. Galyametdinov, O. Kharitonova, I. Ovchinnikov, D. W. Bruce, D. A. Dunmur, D. Gullon, and B. Heinrich, *Liq. Cryst.*, 1996, **20**, 489.
8. S. Diele and P. Goring in *Handbook of Liquid Crystals*, Ed. D. Demus, VCH, Weinheim, 1998, **2**, 887 pp.
9. Yu. G. Galyametdinov, O. A. Kharitonova, and O. N. Kadkin, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1685 [*Russ. Chem. Bull.*, 1994, **43**, 1595 (Engl. Transl.)].
10. Yu. G. Galyametdinov, G. I. Ivanova, and I. V. Ovchinnikov, *Zh. Obshch. Khim.*, 1991, **61**, 234 [*Russ. J. Gen. Chem.*, 1991, **61**, 112 (Engl. Transl.)].
11. Yu. B. Amerik and B. A. Krentsel′, *Khimiya zhidkikh kristallov i mezomorfnykh polimernykh sistem* [*Chemistry of Liquid Crystals and Mesomorphic Polymer Systems*], Nauka, Moscow, 1981, 66 (in Russian).
12. D. Demus, in *Handbook of Liquid Crystals*, Ed. D. Demus, VCH, Weinheim, 1998, **1**, 146.
13. Yu. G. Galyametdinov, A. P. Polishchuk, I. G. Bikchantaev, and I. V. Ovchinnikov, *Zh. Strukt. Khim.*, 1993, **34**, 49 [*Russ. J. Struct. Chem.*, 1993, **34** (Engl. Transl.)].

Received July 24, 2000;
in revised form December 5, 2000