

OPTICAL PROPERTIES OF MESOPHASES AND MESOMORPHIC GLASSES OF Co²⁺ ALKANOATES HOMOLOGOUS SERIES

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Abstract. *The results of spectral studies of thermotropic ionic liquid crystals (TILC) of homologous series of cobalt alkanoates and their mesomorphic glasses are presented. It is shown that the dominant coordination of the cobalt ions in the investigated media is an octahedron. A significant decrease the absorption coefficient with increasing of the aliphatic chain length in the homologous series of cobalt alkanoates is caused by the decrease of the volume concentration of the cobalt cation complexes and the dipole moments of d-d-transitions.*

Keywords: cobalt alkanoates; ionic thermotropic liquid crystals; mesomorphic glasses; optical absorption spectra.

1. Introduction

Modern tendencies in holographic recording of information mostly associated with the developing of new multifunctional materials. One of such materials is metalalkanoates which form TILC during their melt. TILC are the universal matrixes for great number of organic and nonorganic materials. In particular, they are used for introduction of the different dyes in order to create medium for holographic grating recording.

Cobalt alkanoates are standing out of metalalkanoates series due their ability to absorb light in visible spectral region. Also, the important feature of these materials is ability to overcool with vitrification. Received glass state is characterized by preserving Liquid Crystal (LC) structure. Materials with preassigned characteristics can be established by varying length of cobalt alkanoates hydrocarbon chains.

2. Analysis of research and publications

Recently metalalkanoates are used for developing of new optical and nonlinear-optical materials [Bordyuh et al. 2009; Klimusheva et al. 2006; Binnemans 2005]. In particular, metalalkanoates serve as matrixes in composites for dyes and photosensitive impurities with great and fast nonlinear response.

Another perspective way of developing materials with improved nonlinear-optical characteristics on the basis of metalalkanoates is establishing of LC compounds with ions of d- and f-metals [Binnemans 2005; Bordyuh et al. 2009; Hartmut 2004]. It is common knowledge that ions of d- and f-metals are widely used for developing of nonlinear-optical materials [Binnemans 2005; Bordyuh et al. 2009].

Therefore it is necessary to study optical properties of cobalt alkanoates TILC and mesomorphic glasses.

Aim of the work is:

- development of preparation methods of liquid crystal cells and mesomorphic glasses based on cobalt alkanoates;
- determination of cobalt ions coordination, it's possible change depending on the temperature and physical state of matter (mesophase, mesomorphic glass).

3. Methods and objects of research

Electronic spectroscopy was used to study optical properties of cobalt alkanoates. Measurements were taken in the temperature range 20–150°C, towards increase and decrease of the temperature, with measurement pitch 3°C. Temperature was regulated by using specially constructed oven, which was situated in the monochromator chamber on the light path.

Electronic absorption spectra of cobalt alkanoates samples were studied in visible optical wavelengths diapason (400–700 nm) using automatic spectral setup CSOS-6 on the basis of monochromator MDG-6.

As the radiation detector for wavelength range $\lambda = 650\text{--}1200$ nm was used PED-62. Scanning of the spectrum was carried out using step engine, scanning pitch - 2.00 nm. Number of averaging was 1000.

Obtained spectrum of the intensity-transmittance wavelength relation was converted to the optical density wavelength relation using expression

$$D = \lg(I_0/I),$$

where D – optical density;

I_0 – intensity of incident beam;

I – intensity of the beam after passing the sample.

Mentioned below representatives of homologous series of cobalt alkanooates Co^{2+} were used for spectral studies:

– cobalt caprylate $(\text{C}_7\text{H}_{15}\text{COO}^-)_2\text{Co}^{2+}$
($T_{\text{melt}}=93^\circ\text{C}$, $T_{\text{clar}}\approx 164^\circ\text{C}$);

– cobalt decanoate $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Co}^{2+}$
($T_{\text{melt}}=82^\circ\text{C}$, $T_{\text{clar}}>300^\circ\text{C}$);

– cobalt laurate $(\text{C}_{11}\text{H}_{21}\text{COO}^-)_2\text{Co}^{2+}$
($T_{\text{melt}}=88^\circ\text{C}$, $T_{\text{clar}}>300^\circ\text{C}$).

To obtain spectra were used optical quartz cuvettes with a thickness of $30\ \mu\text{m}$. Samples in the form of polycrystalline powder were placed in the cuvette and heated to the temperature of mesophase formation. Orientation of the samples was examined in polarized light using a microscope with a warm stage. In the liquid crystal state samples were mainly homeotropic orientation. In the case of slow cooling the liquid crystal went into a state of smectic glass that obtain at the room temperature for a quite long time (one year), keeping the structure of the liquid crystal.

4. Results of research

The absorption spectra both of cobalt caprylate mesophase $(\text{C}_7\text{H}_{15}\text{COO}^-)_2\text{Co}^{2+}$ (in the temperature range $115\text{--}150^\circ\text{C}$) and mesomorphic glass (room temperature 25°C) are shown in the Fig. 1.

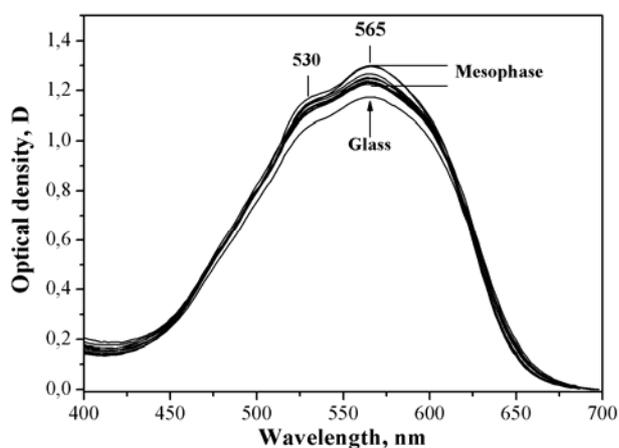


Fig. 1. The absorption spectra of Co^{2+} ions in the mesophase ($100\text{--}150^\circ\text{C}$) and mesomorphic glass (25°C) of cobalt caprylate $(\text{C}_7\text{H}_{15}\text{COO}^-)_2\text{Co}^{2+}$

The spectra of cobalt caprylate consist of a broad absorption band with a maximum at $565\ \text{nm}$ and clearly marked shoulder at $530\ \text{nm}$ due to electronic transitions in complexes of cobalt ions and their coordinating ligands. With increase of the mesophase temperature from 100°C up to 135°C shape and position of the absorption spectrum bands of Co^{2+} ions remained practically constant. But a change of the intensities of the absorption maxima was observed (Fig. 2).

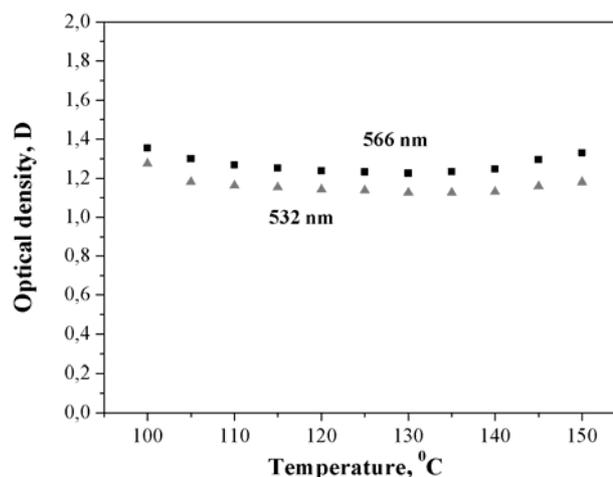


Fig. 2. Temperature dependence of the absorption maxima of Co^{2+} ions in the mesophase ($100\text{--}150^\circ\text{C}$) of cobalt caprylate $(\text{C}_7\text{H}_{15}\text{COO}^-)_2\text{Co}^{2+}$

This is caused by the change of Co^{2+} ions coordination symmetry – they become less centrosymmetric, which is indicated by a decrease of the optical absorption intensity with increasing of the temperature $\Delta D/\Delta T < 0$ [Volkov, Yatsimirskii 1977]. With the further increase of temperature (up to 150°C) an increase in the intensity of optical absorption $\Delta D/\Delta T > 0$ is observed. That is complexes of cobalt ions Co^{2+} become a centrosymmetric again.

The absorption spectra of cobalt decanoate mesophase $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Co}^{2+}$ ($90\text{--}130^\circ\text{C}$) and cobalt decanoate mesomorphic glass (25°C) are shown in the Fig. 3.

The spectra of cobalt decanoate consist of a broad absorption band with a maximum at $560\ \text{nm}$ and clearly marked shoulder at $530\ \text{nm}$ due to electronic transitions in complexes of cobalt ions with the surrounding ligands. As for the sample of cobalt caprylate, with increasing of the temperature shape and position of the absorption spectrum bands of Co^{2+} ions remain almost unchanged.

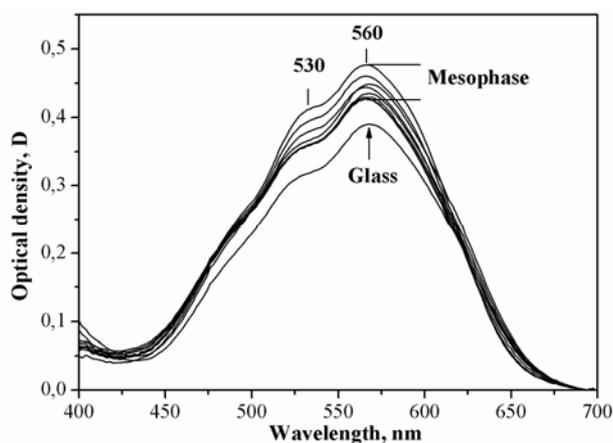


Fig. 3. The absorption spectra of Co^{2+} ions in the mesophase (90–130°C) and mesomorphic glass (25°C) of cobalt decanoate $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Co}^{2+}$

The intensity of absorption maxima changes with increase of the temperature from 90°C up to 125°C (Fig. 4).

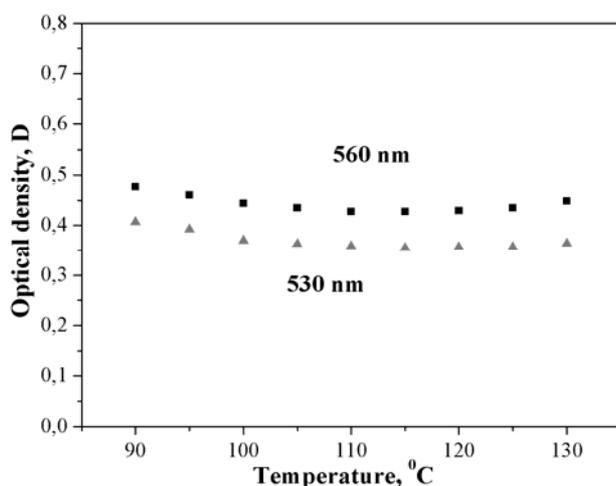


Fig. 4. Temperature dependence of the absorption maxima of Co^{2+} ions in the mesophase (90–130°C) of cobalt decanoate $(\text{C}_9\text{H}_{19}\text{COO}^-)_2\text{Co}^{2+}$

As in the previous case, reduce of the optical absorption intensity with temperature increase ($\Delta D/\Delta T < 0$) indicates that cobalt ion complexes surrounded by decanoate ligands undergo a coordination distortion, becoming less centrosymmetric with temperature increase up to 125°C. The reverse process takes place at the temperature 130°C. The increase of optical absorption intensity with the temperature $\Delta D/\Delta T > 0$ denotes the restoration of cobalt Co^{2+} ion complexes to more centrosymmetrical coordination.

Absorption spectra of cobalt laurate $(\text{C}_{11}\text{H}_{21}\text{COO}^-)_2\text{Co}^{2+}$ at the temperature of mesophase existence (100–130°C) and at the room temperature (25°C – mesomorphic glass) are shown in the Fig. 5.

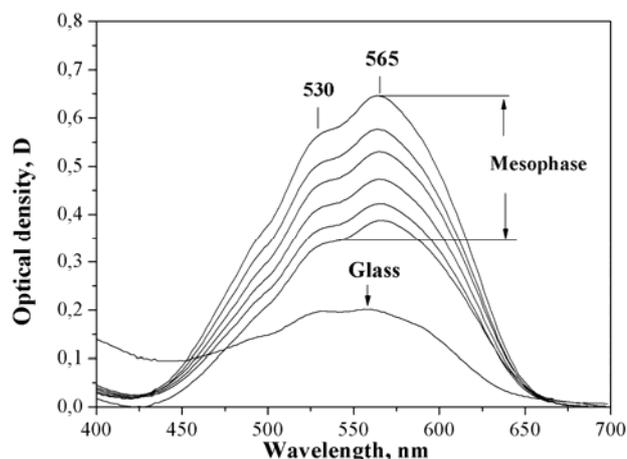


Fig. 5. The absorption spectra of Co^{2+} ions in the mesophase (100–130°C) and mesomorphic glass (25°C) of cobalt laurate $(\text{C}_{11}\text{H}_{21}\text{COO}^-)_2\text{Co}^{2+}$

As for previous samples the spectrum is characterized by a broad absorption band with a maximum at 565 nm and clearly marked shoulder at 530 nm. With temperature increase the shape and position of the absorption spectrum bands of Co^{2+} ions in observed samples remain practically unchanged. But there is a change in the intensities of the absorption maxima (Fig. 6).

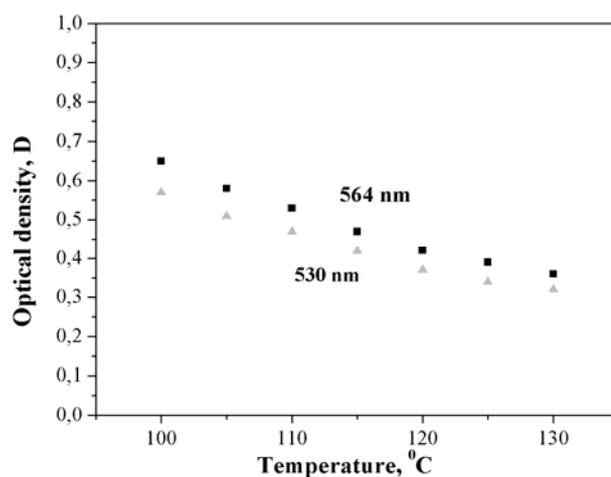


Fig. 6. Temperature dependence of the absorption maxima of Co^{2+} ions in the mesophase (100–130°C) of cobalt laurate $(\text{C}_{11}\text{H}_{21}\text{COO}^-)_2\text{Co}^{2+}$

The typical decrease in absorption intensity with increasing temperature ($\Delta D/\Delta T < 0$) indicates that complexes of cobalt ions undergo conformational distortion becoming less centrosymmetric in the case of temperature increase [Volkov, Yatsimirskii 1977].

Spectra of cobalt alkanooates homologous series can be considered in terms of ligand field theory [Volkov, Yatsimirskii 1977; Crabb et al. 2010], as excitation display of the octahedral coordination (coordination number = 6) of cobalt ions. Two characteristic electronic transitions were observed for this coordination. Maximum on 535 nm corresponds to an electronic transition ${}^4T_{1g}({}^4F) \rightarrow {}^4T_{1g}({}^4P)$ [Volkov, Yatsimirskii 1977; Bersuker 1976], and maximum on 565 nm – ${}^4T_{1g}({}^4F) \rightarrow {}^4A_{2g}({}^4F)$ [Volkov, Yatsimirskii 1977; Bersuker 1976].

Thus, studies of the homologous series of cobalt Co^{2+} alkanooates in the mesophase and in the mesomorphic glass revealed the presence of octahedral Co^{2+} ions. The decrease of the intensity of optical absorption with increasing temperature of the mesophase $\Delta D/\Delta T < 0$ indicates that the octahedral coordination of cobalt ions undergo certain distortions, becoming less centrosymmetric, especially for the longest homolog $\text{Co}(\text{C}_{12})$ (Fig. 6). It is known that for d-metal alkanooates extinction coefficient decreases with increasing number of carbon atoms in the aliphatic chain of the ligand [Volkov, Yatsimirskii 1977]. This is because the increase of alkanooate ligand size promotes the increase of the coordination distortion. We can assume that the larger ligand is located in the coordination sphere of a transition metal cation, the less is centrosymmetric complex. Alkanooate-anions with short chains are able to form more symmetrical surroundings around the cobalt cation unlike the alkanooate-anions with long chains, since they have more spatial barriers. For the studied homologous series modulo the value of $\Delta D/\Delta T$ increases monotonically from short aliphatic chain $\text{Co}(\text{C}_8)$ to the long $\text{Co}(\text{C}_{12})$, i.e. homologues with longer chain are less centrosymmetric.

Also, for the studied homologous series found that the change of the aliphatic chain length of alkanooate anions does not affect form and position of the absorption bands. But there is a significant decrease in the intensity of absorption. The absorption coefficient α decreases monotonically from 450 cm^{-1} to 200 cm^{-1} :

$$\alpha(\text{CoC}_8) > \alpha(\text{CoC}_{10}) > \alpha(\text{CoC}_{12}) \text{ (Fig. 7).}$$

Reduction of optical absorption can be caused mainly by two factors:

- decrease of the concentration of cobalt ions complexes in the homologous series $\text{Co}(\text{C}_8)$, $\text{Co}(\text{C}_{10})$, $\text{Co}(\text{C}_{12})$ with increasing of the aliphatic chain length;
- decrease of the d-d transition dipole moments μ_{d-d} with increasing of the aliphatic chain length:

$$\mu_{d-d}(\text{CoC}_8) > \mu_{d-d}(\text{CoC}_{10}) > \mu_{d-d}(\text{CoC}_{12}) \text{ [Elyashevich 2001].}$$

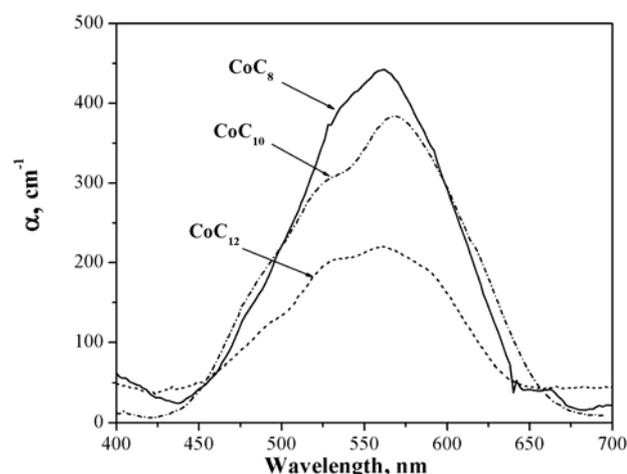


Fig. 7. The absorption spectra of Co^{2+} ions in mesomorphic glasses of homologous series $\text{Co}(\text{C}_8)$, $\text{Co}(\text{C}_{10})$, $\text{Co}(\text{C}_{12})$

It should be noted that observed strong changes in absorbance properties of studied materials can be used for developing of the tunable advanced optical materials. And the main reason for this is the experimental fact that fundamental linear optical properties of the cobalt alkanooates glasses can be tuned by varying of the alkanooate-anion length.

5. Conclusions

A detailed study of the electronic absorption spectra of cobalt Co^{2+} ions complexes in individual samples of the cobalt alkanooates homologous series representatives was done.

It is established that octahedral coordination of ions are present both in mesophase and mesomorphic glass of individual compounds of the cobalt alkanooates homologous series $\text{Co}(\text{C}_8)$, $\text{Co}(\text{C}_{10})$, $\text{Co}(\text{C}_{12})$. It is shown, that octahedral ions become less centrosymmetric with increasing temperature ($\Delta D/\Delta T < 0$) and length of aliphatic chain.

Shown that a significant drop in the absorption coefficient with increase of the aliphatic chain length is caused by the decrease both volume concentration of cobalt cations complexes and magnitudes of dipole moments μ_{d-d} d-d-transition in homologous series $\mu_{d-d}(\text{CoC}_8) > \mu_{d-d}(\text{CoC}_{10}) > \mu_{d-d}(\text{CoC}_{12})$.

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О.В. Грідякіна¹, А.П. Поліщук². Оптичні властивості мезофаз і мезоморфних стекел гомологічного ряду алканоеатів Co^{2+}

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Наведено результати досліджень спектральних властивостей термотропних іонних рідких кристалів алканоеатів кобальту та їх мезоморфних стекел. Показано, що домінуючою координацією іонів кобальту в досліджених середовищах є октаедр. Розглянуто залежність коефіцієнта поглинання від довжини аліфатичного ланцюга в гомологічному ряду алканоеатів кобальту.

Ключові слова: алканоеати кобальту; іонні термотропні рідкі кристали; мезоморфні стекла; оптичні спектри поглинання.

А.В. Гридякина¹, А.П. Полищук². Оптические свойства мезофаз и мезоморфных стекел гомологического ряда алканоеатов Co^{2+}

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Приведены результаты исследований спектральных свойств ионных термотропных жидких кристаллов алканоеатов кобальта и их мезоморфных стекел. Показано, что доминирующей координацией ионов кобальта в исследованных средах является октаэдр. Рассмотрена зависимость коэффициента поглощения от длины аліфатической цепи в гомологическом ряду алканоеатов кобальта.

Ключевые слова: алканоеаты кобальта; ионные термотропные жидкие кристаллы; мезоморфные стекла; оптические спектры поглощения.

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