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Thin Films of Cobalt(II) Clathrochelate for Molecular Spintronic Devices

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Abstract—The possibility of preparing thin films of cobalt(II) cage complex (clathrochelate) that undergoes a temperature-induced spin transition by thermal sublimation was demonstrated using UV spectroscopy. The films were more uniform and more thermally stable than the films formed by centrifugation of the solution on a substrate surface. In combination with scanning electron microscopy data, this revealed the dependence of the spin transition temperature on the method of film preparation and dependence of the supramolecular organization in the films on the substrate material, indicating that transition metal clathrochelates show the spinterface effect at the interface with a metal electrode. In addition to the possibility of controlling the magnetic properties of this unique class of coordination compounds by molecular design methods, this effect opens up broad opportunities for creating molecular spintronic devices with characteristics tailored for the researcher requirements.

Keywords: clathrochelate, cobalt(II) complexes, crystalline films, molecular spintronics, molecular magnetism, spin state, UV/Vis spectroscopy

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INTRODUCTION

The discovery of giant magnetoresistance at the end of 1980s [1, 2] enabled the application of electron spin for data storage and processing. This gave rise to a new area of microelectronics called spintronics and dealing with spin currents in various devices [3, 4]. The heterostructures designed within this research area, which can change their conductivity depending on the magnitude and direction of the external magnetic field [5], formed the basis of spin logic devices [6, 7], quantum computer components [8, 9], and elements for data recording and reading in modern computers [10–13].

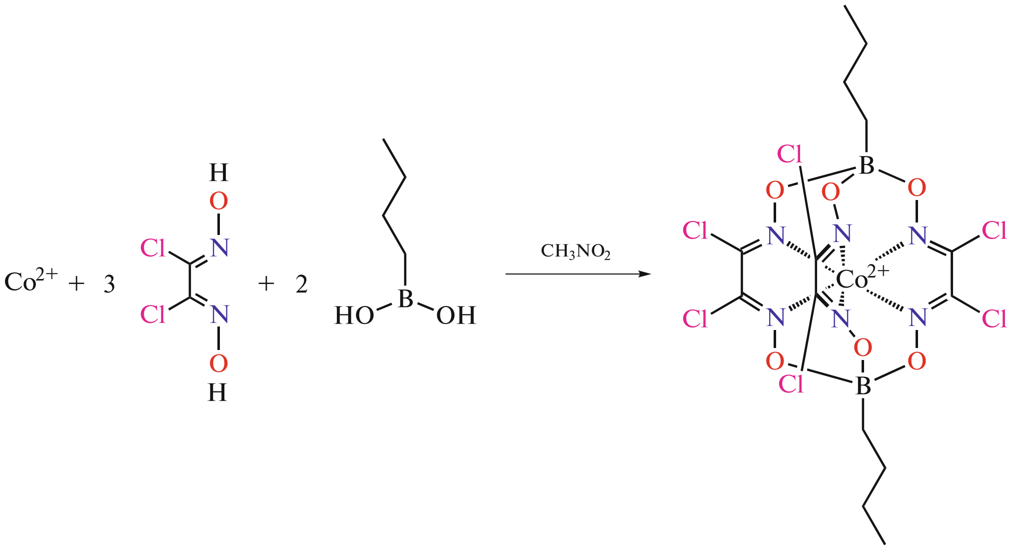
For a long time, only inorganic materials were used in all spintronic devices [14]. However, the implementation of organic materials possessing much longer spin relaxation times [15, 16] and able to change the type of conduction on exposure to external stimuli (e.g., temperature or light irradiation [16–19]) markedly extended the range of potential applications of spintronic devices [20–26]. One of the most important achievements in this area is the discovery of so-called spinterface effect, which is responsible for the pronounced dependence of the spin transport in a spintronic device [23, 27–29] on the interaction between the electrode material and molecules of the chosen compound. A branch of spintronics addressing devices based on organic and molecular materials has been called "molecular spintronics" [14, 30].

Transition metal complexes that undergo a spin transition are of particular interest for molecular spintronics [31]. The capability of reversible switching between the low-spin (LS) and high-spin (HS) states under the action of temperature, pressure, radiation, or another external stimulus inherent in these compounds opens up broad prospects for studying the dependence of electron-transport properties of a spintronic device on the magnetic state of the metal ion and for the design of multifunctional devices based on coordination compounds of this type [31, 32]. In addition, molecules of these complexes often behave as permanent magnets, i.e., they show so-called single-molecule magnetism [33]; hence, they can directly interact with electron spin and efficiently affect the spin current mode in the device [19, 22, 34, 35].

However, currently, the molecular spintronic applications of complexes subject to spin transition are limited to theoretical studies of devices consisting of a single molecule of such complexes [36, 37], while practical implementation of these devices is a complicated task [38]. Conversely, the fabrication of devices in which these molecules form a continuous layer is mainly prevented by the possible blocking of the spin transition upon deposition on the substrate [39] and moderate thermal stability of most of the complexes [19], which precludes the use of thermal vacuum deposition, which is traditionally employed to fabricate spintronic devices [16, 40, 41]. In order to use compounds with a spin transition into real molecular spintronic devices, it is necessary to elaborate approaches to their molecular design (taking account of possible change in their properties as they are converted to films) [42–44] and to establish recommended methods for the preparation highly uniform and thermally stable thin films. In addition, study of the properties of such films on metal substrates would make it possible to predict the spinterface effect and to evaluate the efficiency of the selected compounds in molecular spintronic devices [29, 31].

To solve these problems, we chose transition metal cage complexes (clathrochelates) [45], many of which undergo temperature-induced spin transition [46] or possess single-molecule magnetism [47–49]. Furthermore, they are characterized by high thermal and chemical stability, ease of preparation, and wide opportunities for chemical modifications that enable control over their magnetic properties [50] by introducing various substituents into the apical and ribbed positions of the cage ligand and depositing the compounds onto substrates [51].

In this study, we used a representative of this series, the tris-dioximate complex $Co(Cl_2Gm)_3(Bn\text{-}C_4H_9)_2)$ (**I**) [52], in which the cobalt(II) ion is encapsulated into a cage ligand with chlorine atoms and butyl groups as ribbed and apical substituents, respectively (Scheme 1). We obtained thin films of complex **I** on fused quartz and silver substrates by thermal sublimation and studied the supramolecular organization of the complex molecules, depending on the substrate material, by scanning electron microscopy (SEM). The spin state of the complex, which previously underwent a temperature-induced spin transition in bulk crystals and films obtained by centrifugation of a solution [53], was studied by UV–Vis spectroscopy.



(I)

Scheme 1.

EXPERIMENTAL

All operations were carried out in air using commercially available organic solvents, which were distilled under argon. *n*-Butylboronic acid $CH_3(CH_2)_3B(OH)_2$ (Sigma-Aldrich) of 97% purity was used as received. Dichloroglyoxime was obtained by a previously described procedure [52]. Analysis for carbon, nitrogen, and hydrogen was carried out on a Carlo Erba microanalyzer, model 1106. ^1H and ^{13}C NMR spectra were measured in CD_2Cl_2 on a Bruker Avance 400 spectrometer (operating at 400 MHz for protons). The chemical shifts were referred to the residual signal of the solvent.

Synthesis of complex I. Dichloroglyoxime (5.5 g, 35 mmol) and *n*-butylboronic acid (2.6 g, 26 mmol) were dissolved/suspended in dry refluxing nitromethane (50 mL) with stirring under argon, and then $CoCl_2$ (1.3 g, 10 mmol) was gradually added. The resulting reaction mixture was stirred at reflux for 8 h, then the solvent was partially evaporated, and the mixture was cooled down to room temperature. The finely crystalline brown product was collected on a filter, successively washed with ethanol, diethyl ether, and hexane, and then dried in vacuum. The yield was 1.7 g (26%).

^{1}H NMR (CD_2Cl_2; 400 MHz; 290 K: δ, ppm): 9.03 (s, 6H, CH_3), 15.18 (s, 4H, CH_2), 25.82 (s, 4H, CH_2), 36.52 (s, 4H, BCH_2).

For $C_{14}H_{18}B_2N_6O_6Cl_6Co$

Anal calcd., %	C, 25.42	H, 2.74	N, 12.73
Found, %	C, 25.47	H, 2.73	N, 12.74

Preparation of films of complex I. Before the deposition of films of complex **I**, the substrate was pretreated. For this purpose, silver was sputtered on a substrate covered by half with an impermeable shield (15 mA current and 460 V voltage, 15 min, 10^{-2} Torr pressure, and 30 mm distance from the silver target). The dry crystalline powder of complex **I** (3 mg) was deposited onto a quartz substrate located at a 20 mm distance from the crucible with the powder in a vacuum chamber at a pressure of 10^{-5} Torr and a temperature of 245°C. The dry crystalline powder of complex (3 mg) was deposited on the pretreated silver-coated substrate located at 20 mm distance at a pressure of 10^{-5} Torr and a temperature of 245°C for 20 min. The axis of the crucible with the sample was located in the middle of the silver–glass interface.

The UV–Vis spectra of the obtained films were measured in the 200–900 nm range on a Carl Zeiss Jena Specord M400 spectrophotometer in a vacuum cryostat (10^{-2} Torr) in the temperature range from −178 to 80°C with a step of 20°C.

SEM images of the deposited films placed on a 25-mm aluminum stage and attached with a conductive carbon tape were measured in the backscattered electron mode at an accelerating voltage of 5 kV using a Hitachi TM4000Plus scanning electron microscope.

RESULTS AND DISCUSSION

Cobalt(II) tris-dioximate clathrochelate (**I**) was prepared according to a previously described procedure [52] by direct template reaction of dichloroglyoxime, *n*-butylboronic acid, and anhydrous cobalt(II) chloride under drastic conditions (by refluxing in nitromethane) because of low donor properties of dichloroglyoxime (Scheme 1). The films of this complex were deposited on an optically transparent (quartz) substrate for recording UV–Vis spectra by heating a finely crystalline powder of the complex in a vacuum chamber up to a temperature of 245°C at a pressure of 10^{-5} Torr. This method for film formation ensured the homogeneity and equilibrium state of the films, as evidenced by SEM (Fig. 1) and UV–Vis spectroscopic data in the temperature range from −178 to 80°C (Fig. 2). Indeed, repeated cooling/heating (Fig. 2) did not result in changes in the baseline, the absorption intensity, or the general contrast of the UV-Vis spectrum at the same temperature. The fact that the structure and composition of complex **I** remained unchanged when the complex occurred on the surface in the vacuum cryostat (10^{-2} Torr) was indicated by the invariability of the UV–Vis spectra at room temperature and their similarity with the corresponding spectra of bulk crystalline samples and films obtained previously by solutions centrifugation [53]. In addition, cooling down to −178°C induced no film fracturing caused by crystallization of complex **I**.

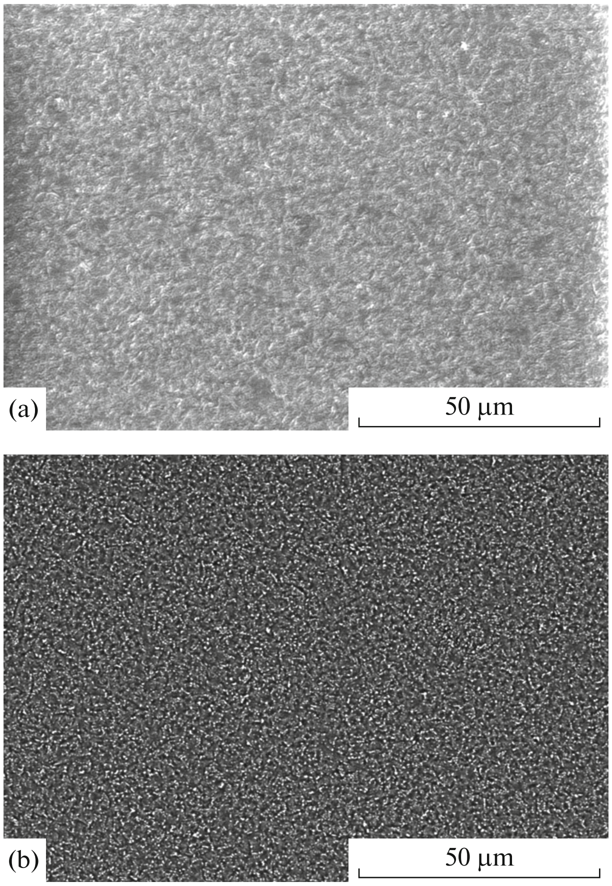


Fig. 1. Scanning electron microscopy image for a part of film surface of complex **I** deposited on (a) quartz and (b) silver substrates.

Data of UV–Vis spectroscopy also clearly indicated that the thermal vacuum sublimation produced more stable films of complex **I** than the solution centrifugation. In the latter case, the complex degraded even on heating to 60°C, whereas the films obtained by thermal sublimation showed no signs of such degradation up to 80°C or during the subsequent cooling, and the UV–Vis spectrum returned to the initial form (Fig. 2). This difference between the thermal stabilities may be caused by water that remained in the films of clathrochelate **I** obtained by centrifugation after solvent (acetonitrile) evaporation in air.

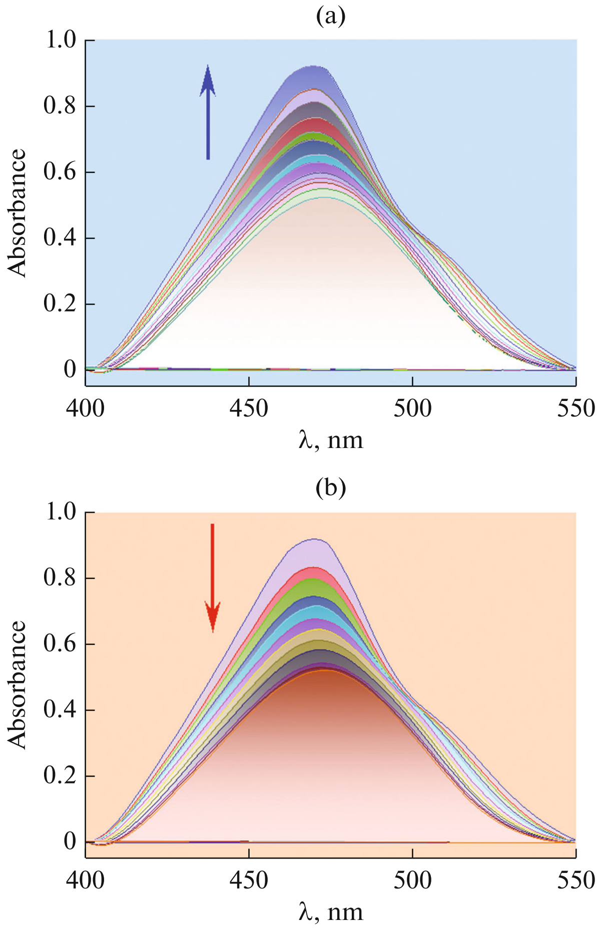


Fig. 2. Temperature dependence of the UV–Vis spectra of a film of complex **I** obtained by thermal sublimation (a) during cooling from 80 to –178°C and (b) subsequent heating.

At room temperature, the UV–Vis spectra of both types of films [53] corresponded to a mixture of LS and HS states of complex **I**; their metal–ligand absorption bands in the visible part of the spectrum with a maximum at about 470 nm overlapped. It is noteworthy that the HS–LS equilibrium established faster in the films formed by vacuum sublimation, since repeated recording of the UV–Vis spectrum at the same temperature fully reproduced the first one after 5 min. This provides additional evidence for advantages of vacuum sublimation over solution centrifugation for the manufacture of uniform equilibrium and thermally stable films, which are necessary for practical application of transition metal clathrochelates in real devices of molecular spintronics [54–56].

To compare the parameters of the temperature-induced spin transition of complex **I** in the two types of films, we analyzed the temperature dependence of the peak intensity of the metal–ligand absorption band in the UV–Vis spectra (Fig. 3). Although in both cases, spin transition is stretched along the temperature and is not completed over the whole temperature range studied, in the case of film obtained by thermal sublimation in vacuum, it is more clear-cut, looks more complete, and takes place at lower temperature (200 versus 220 K). It is worth noting that the hysteresis observed between cooling and heating, amounting to 20–25°C, does not depend on the film formation method.

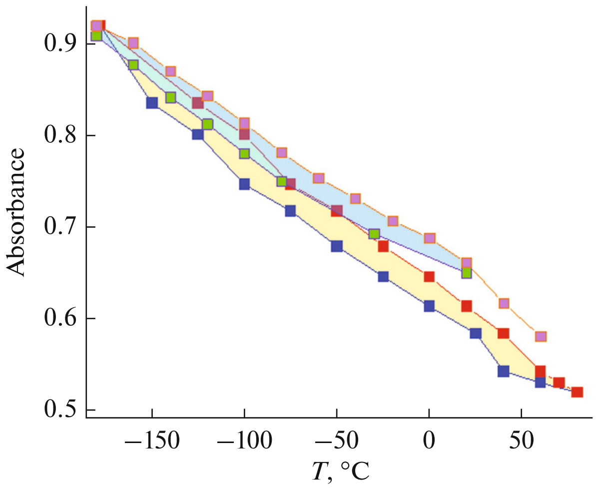


Fig. 3. Temperature dependence of the intensity of the metal–ligand absorption band at about 470 nm during heating and cooling of films of complex **I** obtained by thermal sublimation (red and blue lines) and by solution centrifugation (pink and blue lines).

To gain better understanding of the spinterface effects for the future molecular spintronic devices, we compared the uniformity and supramolecular organization of the films of complex **I** on different substrates (metallic and amorphous). A silver layer was deposited by magnetron sputtering onto a stage glass covered by half with an impermeable shield. In order to ensure equal film thickness on both substrates (~500 nm), the stage glass was mounted above the crucible with a finely crystalline powder of complex **I** in such a way that the crucible axis was located in the middle of the silver–glass interface.

A SEM study of the surface topography of the films revealed a significant difference between the supramolecular organizations of complex **I** on glass (Fig. 1a) and silver (Fig. 1b). Both films were highly uniform and contained no large crystalline fragments or fractures, and the film on silver was much more ordered than the film on the glass substrate. This fact demonstrates a pronounced effect of interaction between molecules of **I** and the substrate on the film character even when the film thickness is macroscopic (~500 nm).

Unfortunately, it is impossible to monitor the temperature-induced spin transitions in the silver-deposited film of **I** and the possible dependence of spin transition parameters on the substrate material using UV-

Vis spectroscopy or attenuated total reflectance spectroscopy, because the emission power of the silver substrate is too high and the signals of complex **I** cannot be distinguished against its background.

Thus, the combined use of UV–Vis spectroscopy and SEM made it possible to demonstrate that thermal sublimation produces uniform thin films of a unique class of transition metal complexes (clathrochelates) that undergo a temperature-induced spin transition. Unlike centrifugation of a solution [53] on a substrate surface, this method for the formation of cobalt(II) clathrochelate film provided a higher thermal stability and more complete spin transition at a lower temperature, which is desirable for most practical applications [54–56] of complexes possessing spin transitions, in particular in molecular spintronics.

In addition, analysis of the films of the chosen complex on silver and glass substrates obtained in this way revealed a significant difference between its supramolecular organizations on the surface of these two materials, indicating an important role of interactions at the substrate–clathrochelate interface in the formation and properties of this molecular layer. This observation prompts the idea that transition metal clathrochelates might exhibit the spinterface effect at the electrode boundary in molecular spintronic devices. However, to verify this hypothesis, it is necessary to carry out more detailed studies of the properties of appropriate thin films on various metal substrates, which are traditionally used in molecular spintronics; now these studies are carried out by our research group.

Since the magnetic properties of transition metal clathrochelates can be varied over a broad range using targeted functionalization of the cage ligand and selection of the transition metal ion, the possibility of the spinterface effect on the surface of a metal electrode may enable the fabrication of various molecular spintronic devices with tailored characteristics for particular purposes based on this unique class of coordination compounds.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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