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Spin Transition in the Cobalt(II) Clathrochelate Films from Electron Spectroscopy Data

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Abstract—The spin states of three earlier described cobalt(II) clathrochelates as films on the quartz supports are studied for the first time. The magnetochemical study shows that the temperature-induced spin transition observed previously in the crystalline samples is retained in the films, which makes it possible to consider this class of coordination compounds with high chemical and thermal stability as promising components for molecular spintronic devices.

Keywords: clathrochelates, cobalt complexes, molecular spintronics, films, spin state, temperature-induced spin transition, electronic spectroscopy (UV-VIS range)

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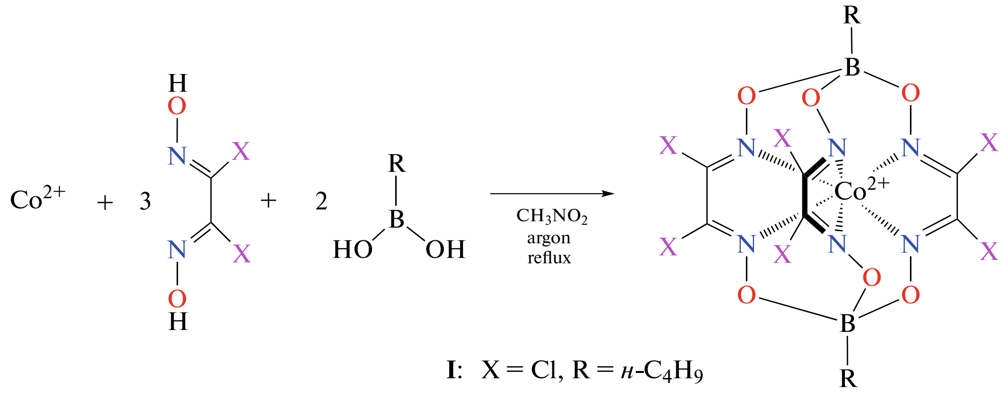
INTRODUCTION

Selected transition metal complexes can exist in two spin states and switch between them under the application of an appropriate external stimulus (for example, temperature or pressure) [1] accompanied by significant changes in the magnetic and optical properties, some of which (for instance, color change) can be observed with the naked eye. This allows one to produce from them various molecular devices and materials [2, 3], including temperature or pressure sensors [4], and (recently) elements of molecular spintronic devices [5] capable of "switching" spin conductivity under the action of the indicated external perturbations. In the last case, the corresponding complexes are immobilized on the surface of various supports [6] as thin films [7, 8]. For this purpose, it is desirable to use neutral complexes stable at high temperatures that are necessary for the immobilization of their molecules on the support by vacuum sublimation [9].

One of the classes of compounds experiencing the spin transition when triggered by temperature [10, 11] and potentially satisfying all indicated requirements is the macrobicyclic tris(dioximate) cage complexes (clathrochelates [12]) of cobalt(II) (Scheme 1). Along with high thermal and chemical stability, these compounds are characterized by the simple synthesis and wide possibilities of chemical modification (at two apical and four ribbed positions of the cage ligand), which make it possible to control their magnetic properties [13] and immobilize them on diverse supports [14]. Owing to this, the cobalt(II) clathrochelates became excellent candidates as single-molecule magnets [13, 15, 16] and compounds with spin transitions [10, 11] for devices of molecular spintronics.

However, in spite of numerous presently known clathrochelates of various transition metals [12], their magnetic properties in films were not studied so far. Among the presently available methods of analysis of spin transitions in film materials (such as X-ray absorption spectroscopy [9, 17] or X-ray photoelectron spectroscopy [17, 18]), electron spectroscopy is most accessible in chemical organizations [19]. Using this method, the spin state of the metal ion can be determined from the presence of characteristic absorption bands in the corresponding spectra and their change with temperature [20]. In some cases, the spin transition temperature can directly be estimated by this method [21, 22].

In this work, we synthesized three earlier described cobalt(II) clathrochelates **I**–**III** (Scheme 1) with different apical (R) and ribbed (X) substituents in the ligand that experience the temperature-induced spin transition in the bulk crystalline samples [10, 23, 24] and studied the spin states of their films on the quartz support by electron spectroscopy.



I: X = Cl, R = *н*-C_4H_9

II: X = Br, R = *н*-C_4H_9

III: X = Cl, R = *н*-$C_{16}H_{33}$

Scheme 1.

EXPERIMENTAL

All procedures of the synthesis of the complexes were carried out in air using commercially available *n*-butyl- and *n*-hexadecylboric acids, $CoCl_2$, organic solvents, and sorbents. Complexes **I–III** were synthesized according to previously described procedures [10, 23, 24]. Analyses for carbon, nitrogen, and hydrogen were carried out on a Carlo Erba microanalyzer (model 1106). ^1H NMR spectra were recorded in CD_2Cl_2 on Bruker Avance 400 and Bruker Avance 600 spectrometers with the working frequencies for protons 400 and 600.22 MHz, respectively. The chemical shifts in the spectra were determined relative to the residual signal of the indicated solvent.

Complex I [10]. ^1H NMR (CD_2Cl_2, 400 MHz), δ, ppm: 9.03 (br.s, 6H, CH_3), 15.18 (br.s, 4H, CH_2), 25.82 (br.s, 4H, CH_2), 36.52 (br.s, 4H, CH_2B).

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

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

Complex II [23]. ^1H NMR (CD_2Cl_2, 400 MHz), δ, ppm: 9.08 (br.s, 6H, CH_3), 15.01 (br.s, 4H, CH_2), 26.00 (br.s, 4H, CH_2), 35.14 (br.s, 4H, CH_2B).

For $C_{14}H_{18}B_2N_6O_6Br_6Co$

Anal. calcd., %	C, 18.12	H, 1.94	N, 9.06
Found, %	C, 18.10	H, 1.88	N, 8.95

Complex III [24]. ^1H NMR (CD_2Cl_2, 600 MHz), δ, ppm: 0.76 (m, 6H, CH_3), 1.31 (m, 8H, 14,15-CH_2), 1.45 (m, 4H, 13-CH_2), 1.80 (m, 4H, 12-CH_2), 2.10 (m, 4H, 10-CH_2), 2.53 (m, 4H, 9-CH_2), 3.18 (m, 4H, 8-CH_2), 4.12 (m, 4H, 7-CH_2), 5.52 (m, 4H, 6-CH_2), 7.59 (m, 4H, 5-CH_2), 11.07 (s, 4H, 4-CH_2), 16.69 (s, 4H, 3-CH_2), 29.17 (s, 4H, 3-CH_2), 39.41 (s, 4H, CH_2B).

For $C_{38}H_{66}B_2N_6O_6Cl_6Co$

Anal. calcd., %	C, 45.78	H, 6.63	N, 8.43
Found, %	C, 45.91	H, 6.61	N, 8.36

Synthesis of films of complexes I–III. The dry crystalline powder of the corresponding complex (20 mg) was dissolved in benzene (600 μL), and the resulting solution was filtered through a Celite layer. The films were deposited on quartz supports by the spin-coating of the obtained solution (4.5 μL) at room temperature with a rate of 2000 rpm for 7 s, and then they were dried in vacuo at room temperature for 1 h.

The electron absorption spectra for the synthesized films of complexes **I–III** were recorded in the UV and visible ranges (300–600 nm) on a Specord M400 spectrophotometer (Carl Zeiss Jena) in a vacuum cryostat (10^{-2} Torr) in a temperature range of 83–408 K.

The quantum chemical calculations for the model complexes with methyl substituents in the apical positions of the cage ligand (**I'** and **II'**) were performed using the ORCA, v. 4 program package [25] using the density functional theory (DFT) [26]. The geometry of the complexes was optimized without symmetry restraints using the TPSSh hybrid functional [27] with the def2-TZVP basis set [28], which made it possible to reliably estimate the difference in energies of the spin states for the transition metal complexes with the spin transitions [29]. The structure of complex **I** determined by X-ray diffraction analysis was used as the initial approximation [10]. The spectra were simulated in the framework of the time-dependent density functional theory (TD-DFT) for the first 50 electronic transitions.

RESULTS AND DISCUSSION

Complexes **I**–**III** were synthesized according to earlier described procedures [10, 23, 24] by the direct template reaction of the corresponding glyoxime, *n*-butyl- or *n*-hexadecylboric acid, and anhydrous cobalt(II) chloride under harsh conditions (on reflux in nitromethane) because of the low donor ability of dichloroglyoximate and dibromoglyoxime (Scheme 1). The partial distillation off of relatively low-volatile boric acids from the reaction mixture was observed during the reaction and, hence, at the first stage the reaction mixture was refluxed with a reflux condenser. The formed water and HCl were azeotropically distilled off together with nitromethane, thus shifting the equilibrium toward the target product.

The films were formed from the synthesized complexes **I**–**III** by spin-coating traditionally used for these purposes in laboratories [7] (including for the compounds with the spin transitions [30]) from a benzene solution on the surface of the quartz supports. The formed films were studied by electron spectroscopy in a range of 83–408 K (Figs. 1–3). The chosen method for the preparation of the films provided their equilibrium character, since no changes in the base line, absorption intensity, and total contrast of the spectra were observed at the same temperature during repeated cooling–heating cycles. The films retained the structure on the surface under the vacuum cryostat conditions (10^{-2} Torr), which was indicated by the unchanged electron spectra at room temperature and their similarity to the corresponding spectra of the solutions [10, 23, 24]. Regardless of the chosen glyoxime or boric acid, the solution spectra contained the metal-to-ligand charge-transfer bands in the visible range with maxima about 430 and 470 nm [10, 23, 24]. However, the slow degradation of the films of complexes **I** and **III** occurred on heating at the temperatures higher than 343 K. In particular, the isosbestic points on the corresponding spectra disappeared at these temperatures (Figs. 1, 3), and the intense band at 356–364 nm corresponds to the predominantly innerligand π–π* transition. Complex **II** turned out to be more thermally stable, since its degradation in the film became appreciable only at 373 K (Fig. 2). This does not exclude the possibility of immobilizing cobalt(II) clathrochelates without loss of the integrity of their molecules upon vacuum sublimation on magnetic supports traditionally used in spintronic devices rather than on optically transparent supports necessary for studies by electron spectroscopy.

At room temperature, the electronic spectra of all three complexes **I**–**III** corresponded to a mixture of the low-spin (LS) and high-spin (HS) states of the cobalt(II) ion. However, the corresponding absorption bands (with maxima in the visible range about 430 and 470 nm) were superimposed (Figs. 1–3), which impeded the interpretation of the electron spectroscopy data on the occurrence of the spin transition in the cobalt(II) complexes [31]. To obtain the necessary additional information about clathrochelates **I**–**III**, we performed the quantum chemical calculations in terms of the TD-DFT method [26] for model compound **I'** in which the conformationally flexible alkyl fragment in the apical position of complex **I** (or its *n*-hexadecyl-substituted analog **III**) was replaced by the methyl group. Thus calculated electron spectra for two spin states confirm that the corresponding absorption bands are overlapped to a significant extent. For the HS state of the chosen model compound (Fig. 4a), they rather closely reproduce the electronic spectra earlier observed for solutions of complexes **I** and **III** [10, 23]. However, in the case of the LS state (Fig. 4b), the agreement is not too good, which is likely due to the known [32] problems of the DFT method in the description of the systems with paired electrons in the case of the states with close energies in which electrons are not paired. A similar quantum chemical calculation for model complex **II'** with the bromine substituents in the edge positions of the cage ligand resulted in the same situation (Figs. 4c, 4d). Interestingly, in both

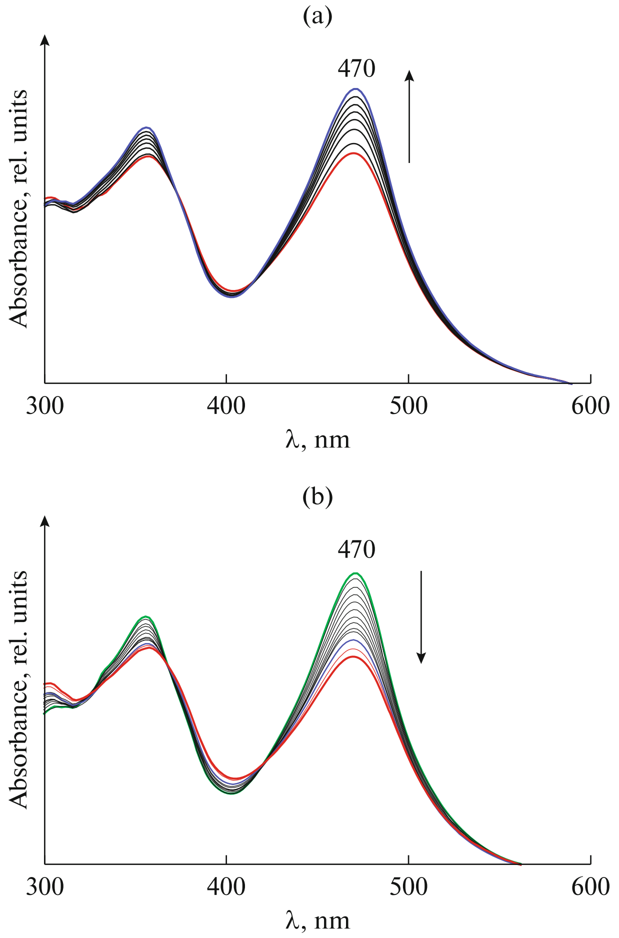


Fig. 1. Temperature dependences of the electron absorption spectrum for the film of complex **I** (a) on cooling from room temperature to 93 K and (b) subsequent heating to 343 K.

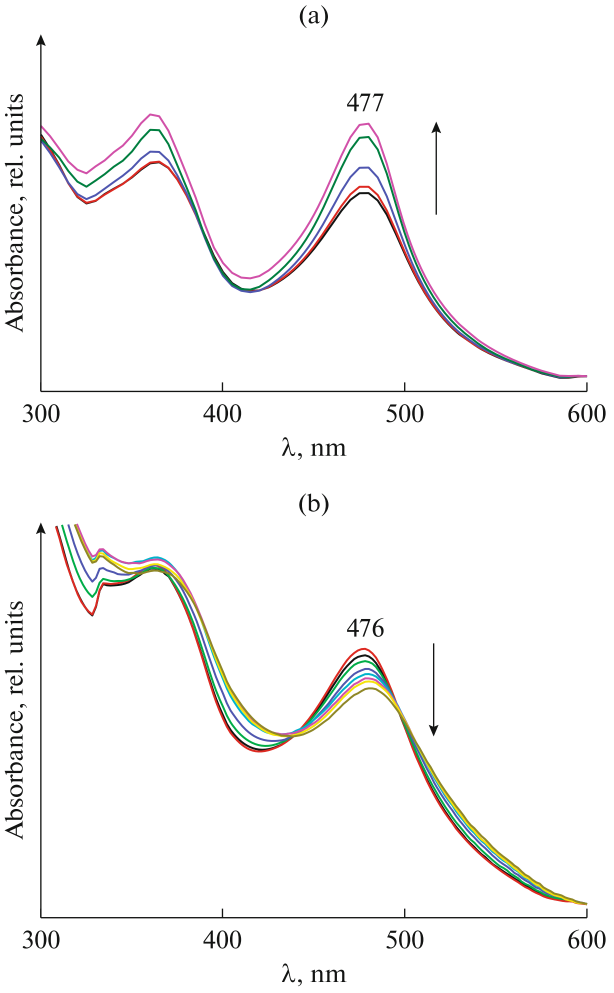


Fig. 2. Temperature dependences of the electron absorption spectrum for the film of complex **II** (a) on cooling from room temperature to 83 K and (b) subsequent heating to 408 K.

cases, the electron spectra of the LS state turned out to be shifted to the long-wavelength range. On the one hand, this agrees with the distinction in color of two spin states, which forms a basis for the use of compounds with spin transitions as sensors of temperature, pressure [4], or other external effects. On the other hand, the LS state of these complexes is colored, as a rule, more intensively, and vice versa for the HS state [1].

The LS state turned out to be more energetically favorable for both model complexes **I'** and **II'**. The difference in energies of two states (2.4 and 3.1 kcal/mol for complexes **I'** and **II'**, respectively) indicated the stabilization of the LS state of the cobalt(II) ion by the bromine ribbed substituents in the ligand, which is consistent with the higher temperature of the spin transition in complex **II** (Fig. 5) according to the results of magnetochemical studies of the crystalline powders of complexes **I**–**III** [10, 23, 24].

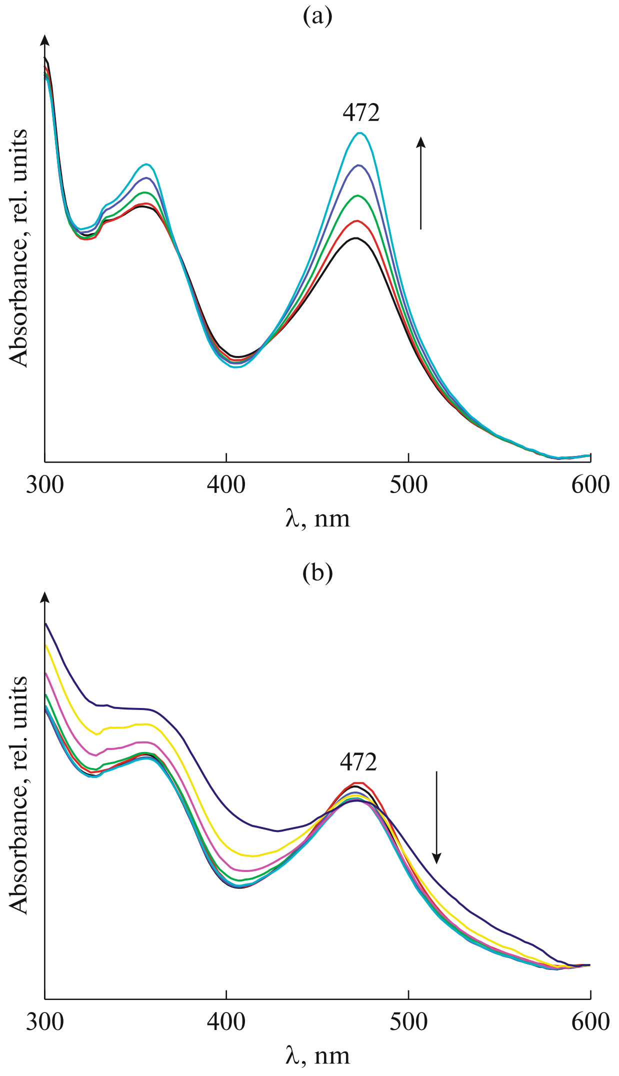


Fig. 3. Temperature dependences of the electron absorption spectrum for the film of complex **III** (a) on cooling from room temperature to 88 K and (b) subsequent heating to 383 K.

According to the electron spectroscopy data for the films of complexes **I**–**III**, a decrease in the temperature to 83–93 K was accompanied by a noticeable increase in the intensity of the metal-to-ligand charge-transfer bands in a range of 470–477 nm (Figs. 1–3), indicating a gradual population of the LS state of the cobalt(II) ion on cooling. Thus, the films of complexes **I**–**III** exhibited the temperature-induced spin transition similar to that observed previously in the crystalline samples of these compounds (Fig. 5) [10, 23, 24]. In the last case, the "backward" spin transition detected for complexes **II** and **III** at ~270 and 230 K (a "jump" of the effective magnetic moment in Fig. 5) was related to the phase transitions caused by the conformationally flexible alkyl substituents in these compounds [23, 24]. As in the case of the crystalline powders, no complete transition to the LS

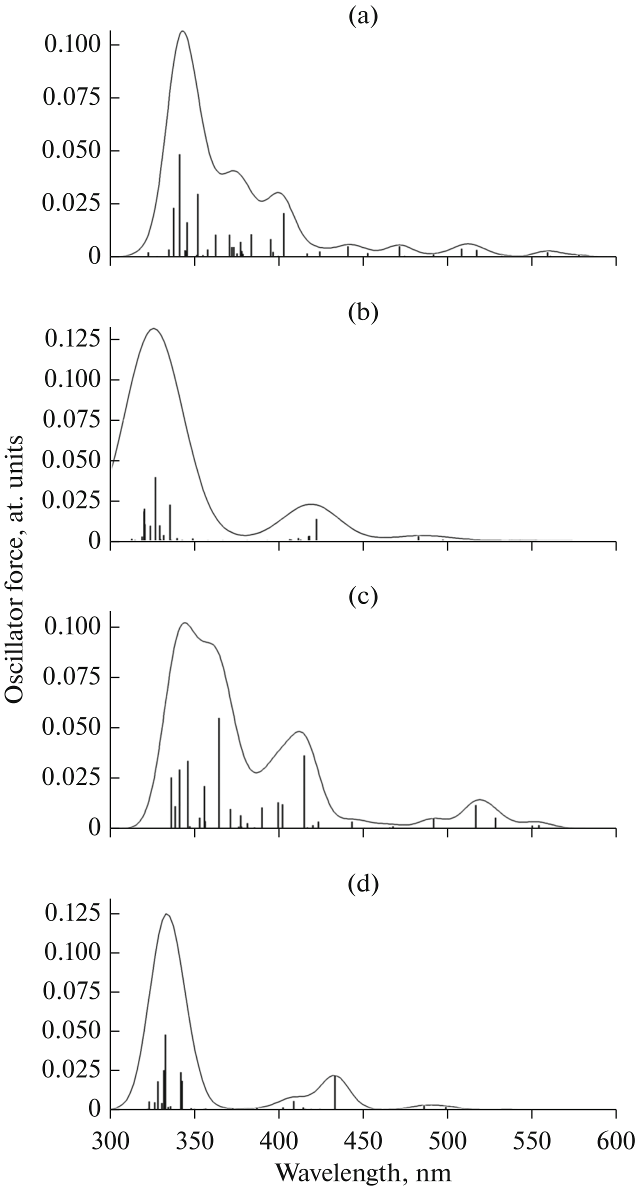


Fig. 4. Electron absorption spectra calculated for model complexes **I'** and **II'** in the (a, c) LS and (b, d) HS states, respectively.

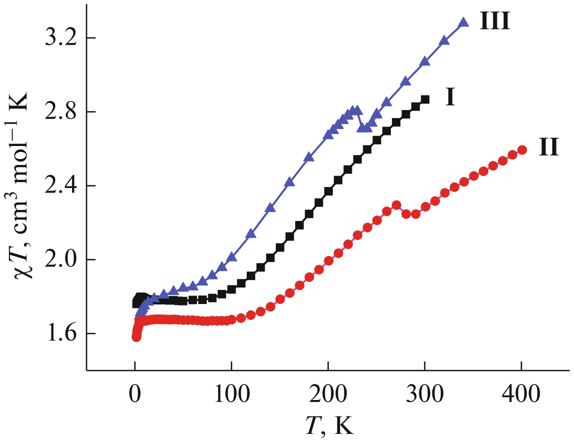


Fig. 5. Temperature dependences of the effective magnetic moment for complexes **I–III**.

state in the films of all three complexes **I–III** occurred even on cooling to 83 K, and the consequent heating to the temperature of degradation onset (up to 373 K) either did not transform them completely into the HS state.

The absence of electron spectra for complexes **I–III** in the individual spin states did not allow one to directly determine the temperature of the observed spin transition ($T_{1/2}$) at which 50% molecules of the complex existed in one spin state and 50% were in another state. However, the temperature can approximately be estimated from the inflection of the curve of changing the intensity of the ligand-to-metal charge-transfer band in a range of 470–477 nm (Fig. 6) during cooling–heating cycles. For the films of complexes **I**, **II**, and **III**, the corresponding inflection was observed at the temperatures about 200, 220, and 170 K, respectively. This estimate proposed (from the data of electron spectroscopy) the following order of changing the temperature of the spin transition: **II** > **I** > **III**. In spite of the known [31] difficulties in interpreting the electron spectroscopy data for the cobalt(II) complexes (Figs. 1–3) because of overlapping of the absorption bands corresponding to two paramagnetic spin states of the cobalt(II) ion (Fig. 4), this order completely reproduces the change in the population of the LS state with temperature (**II** > **I** > **III**) in the crystalline samples of complexes **I–III** (Fig. 5) [10, 23, 24], which is expected [33] for the films with a thickness of nanometers and more used for electron spectroscopy studies [19].

Thus, the temperature-induced spin transition in the films of the cobalt(II) clathrochelates was observed for the first time using electron spectroscopy. This transition has previously been found in the crystalline samples of the complexes by the magnetochemical study. The chosen complexes are fairly resistant to heating (although the existence of other transition metal clathrochelates with higher thermal and chemical stability is doubtless [34]) and retain their integrity when applied onto the surface and keeping in vacuo, which is principally important for the subsequent formation of their thin films on magnetic supports by the vacuum deposition. The possibility of controlling the parameters of the spin transition of the clathrochelates in films by the introduction of various substituents into the apical and ribbed positions of the cage ligand, which can be conducted using numerous elaborated in detail and practically simple synthetic approaches [12], provides wide prospects for the use of compounds of this class in devices of molecular spintronics.

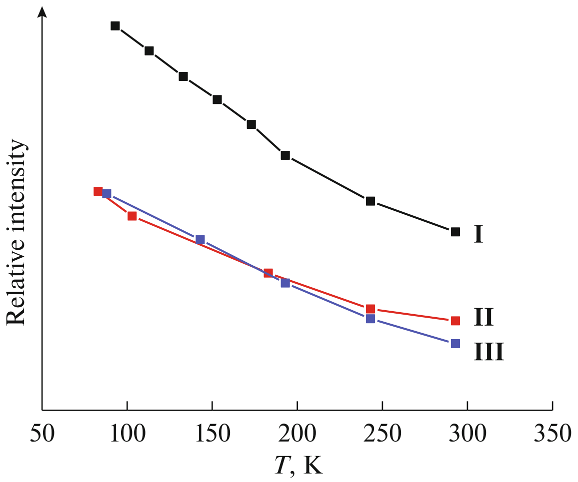


Fig. 6. Changes in the intensity of the band at 470 nm in the electronic absorption spectra of the films of complexes I–**III** on cooling.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

1. *Spin Crossover Materials: Properties and Applications*, Halcrow, M.A., Ed., New York: Wiley, 2013.
2. Molnár, G., Rat, S., Salmon, L., et al., *Adv. Mater.*, 2017, vol. 30, no. 5, p. 1703862.
3. Kumar, K.S. and Ruben, M., *Coord. Chem. Rev.*, 2017, vol. 346, p. 176.
4. Linares, J., Codjovi, E., and Garcia, Y., *Sensors*, 2012, vol. 12, p. 4479.
5. Coronado, E., *Nature Rev. Mater.*, 2020, vol. 5, no. 2, p. 87.
6. Gruber, M., Miyamachi, T., Davesne, V., et al., *J. Chem. Phys.*, 2017, vol. 146, no. 9, p. 092312.
7. Cavallini, M., *Phys. Chem. Chem. Phys.*, 2012, vol. 14, no. 34, p. 11867.
8. Mallah, T. and Cavallini, M., *C. R. Chim.*, 2018, vol. 21, no. 12, p. 1270.
9. Kumar, K.S., Studniarek, M., Heinrich, B., et al., *Adv. Mater.*, 2018, vol. 30, no. 11, p. 1705416.
10. Voloshin, Y.Z., Varzatskii, O.A., Novikov, V.V., et al., *Eur. J. Inorg. Chem.*, 2010, vol. 2010, no. 34, p. 5401.
11. Novikov, V.V., Ananyev, I.V., Pavlov, A.A., et al., *J. Phys. Chem. Lett.*, 2014, vol. 5, no. 3, p. 496.
12. *Cage Metal Complexes: Clathrochelates Revisited*, Voloshin Y., Belaya I., and Krämer R., Eds., Luxemburg: Springer, 2017.
13. Pavlov, A.A., Nelyubina, Y.V., Kats, S.V., et al., *J. Phys. Chem. Lett.*, 2016, vol. 7, no. 20, p. 4111.
14. Voloshin, Y.Z., Belov, A.S., Vologzhanina, A.V., et al., *Dalton Trans.*, 2012, vol. 41, no. 20, p. 6078.
15. Novikov, V.V., Pavlov, A.A., Nelyubina, Y.V., et al., *J. Am. Chem. Soc.*, 2015, vol. 137, no. 31, p. 9792.
16. Pavlov, A.A., Savkina, S.A., Belov, A.S., et al., *Inorg. Chem.*, 2017, vol. 56, no. 12, p. 6943.
17. Atzori, M., Poggini, L., Squillantini, L., et al., *J. Mater. Chem. C*, 2018, vol. 6, no. 33, p. 8885.
18. Wäckerlin, C., Chylarecka, D., Kleibert, A., et al., *Nature Commun.*, 2010, vol. 1, no. 1, p. 61.
19. Gural'skiy, I., Quintero, C., Abdul-Kader, K., et al., *J. Nanophotonics*, 2012, vol. 6, no. 1, p. 063517.
20. Gütlich, P., Gaspar, A.B., and Garcia, Y., *Beilstein J. Org. Chem.*, 2013, vol. 9, p. 342.
21. Tissot, A., Bardeau, J.-F., Rivière, E., et al., *Dalton Trans.*, 2010, vol. 39, no. 33, p. 7806.
22. Naggert, H., Rudnik, J., Kipgen, L., et al., *J. Mater. Chem. C*, 2015, vol. 3, no. 30, p. 7870.
23. Dolganov, A.V., Belov, A.S., Novikov, V.V., et al., *Dalton Trans.*, 2015, vol. 44, no. 5, p. 2476.
24. Vologzhanina, A.V., Belov, A.S., Novikov, V.V., et al., *Inorg. Chem.*, 2015, vol. 54, no. 12, p. 5827.
25. Neese, F., *Wiley Interdiscipl. Rev.: Computat. Mol. Sci.*, 2018, vol. 8, no. 1. e1327.
26. Runge, E. and Gross, E.K.U., *Phys. Rev. Lett.*, 1984, vol. 52, no. 12, p. 997.
27. Tao, J., Perdew, J.P., Staroverov, V.N., et al., *Phys. Rev. Lett.*, 2003, vol. 91, no. 14, p. 146401.
28. Weigend, F. and Ahlrichs, R., *Phys. Chem. Chem. Phys.*, 2005, vol. 7, no. 18, p. 3297.
29. Cirera, J., Via-Nadal, M., and Ruiz, E., *Inorg. Chem.*, 2018, vol. 57, no. 22, p. 14097.
30. Matsuda, M. and Tajima, H., *Chem. Lett.*, 2007, vol. 36, no. 6, p. 700.
31. Goodwin, H.A., *Spin Crossover in Transition Metal Compounds II*, *Topics in Current Chemistry*, Berlin: Springer, 2004.
32. Perdew, J.P., Ruzsinszky, A., Constantin, L.A., et al., *J. Chem. Theor. Comput.*, 2009, vol. 5, no. 4, p. 902.
33. Zhang, X., Palamarciuc, T., Rosa, P., et al., *J. Phys. Chem.*, 2012, vol. 116, no. 44, p. 23291.
34. Voloshin, Y.Z., Novikov, V.V., Nelyubina, Y.V., et al., *Chem. Commun.*, 2018, vol. 54, no. 28, p. 3436.

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