Thermally induced paramagnetism of spiropyran salts

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An increase in the effective magnetic moments and linewidths in ESR spectra caused by the presence of crystallization water molecules in crystals of tris(oxalato)chromium(III) complexes with spiropyran cations Sp^+ was found. Dehydration (rehydration) of crystals causes a reversible decrease (increase) in thermally induced paramagnetism of Sp+. Thermally induced paramagnetism of crystals appears in the compounds synthesized in oxygen atmosphere but is not found in the compounds synthesized under argon atmosphere. The contributions of chromium oxalates and thermally excited spiropyran molecules to the magnetization were separated using ESR spectroscopy. The enthalpies of the biradical states of some types of spiropyran cations in crystals were determined.

Key words: spiropyrans, tris(oxalato)chromium(III), photochromism, magnetic properties, thermally induced paramagnetism.

Photomagnetic crystals based on spiropyrans (Sp) can reversibly change their magnetic properties when exposed to light; they are promising for the design of devices for information storage and recording.[1—3] Examples of such hybrid compounds are provided by crystals composed of spiropyran (Sp^+) cations forming a sublattice located between two-dimensional networks of transition metal oxalates $M^{II}(M')^{III}(C_2O_4)_3$.[4—6]

Possible mechanisms of the effect of light on the magnetic properties of Sp^+ cations are as follows:

1) photoinduced charge redistribution between the Sp^+ cations and transition metal ions;[7—9]

2) modulation of crystal fields and exchange interactions in the course of photoisomerization of Sp^+ cations;[10,11]

3) formation of radiation effects on spiropyran cations to preclude the motion of domain walls and to increase the coercive force;[4] and

4) appearance of light-induced paramagnetic radiation defects contributing to magnetization.

When considering these mechanisms, it is *a priori* believed that unirradiated photochromic cations Sp^+ are diamagnetic and not involved in exchange interaction. At the same time, many organic compounds with the singlet ground state (spin $S = 0$) have low-lying triplet levels ($S = 1$); therefore, an increase in temperature may cause thermal filling of triplet or biradical states of molecules and the onset of paramagnetic properties.[12—15] Such kind of thermally induced paramagnetism was also discovered in photochromic spiropyran molecular ions in the crystals[16] in which at high temperatures, the Sp^+ ions have nonzero spins and exhibit paramagnetic properties. The latter suggests that photoisomerization will immediately affect the magnetization of the sample. The mechanisms of photomagnetic effects (see above) can be significantly modified and augmented in studies of electron-spin processes involving Sp^+. Paramagnetic spiropyran molecules can serve as "carriers" of exchange interaction between metal complexes, thus increasing the Curie temperature and providing the photoswitching of magnetic properties of the compounds. Practical applications of paramagnetic spiropyran cations require information on the influence of their crystal environment on the activation energy and population of their biradical states.

In this study, we used the fact that solvent molecules present in the crystal lattice produce additional mechanical strain that can influence the magnetic and electrical properties of organometallic compounds.[17—19] If the energy gap between the singlet and lowest triplet levels of spiropyran molecular ions in crystals is sufficiently narrow, small variations of the crystal field can significantly change the populations of the biradical states of Sp^+. In this case, one can expect that the crystallization water molecules in the Sp^+-based crystals will change their magnetic properties.

The aim of the present study was to establish the role of crystallization water in the formation of magnetic properties and features of the spin dynamics in the $Sp_3Cr(C_2O_4)_3$ crystals based on molecular ions of spiropyrans **1—4**.

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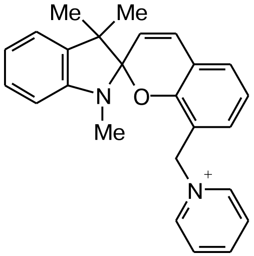

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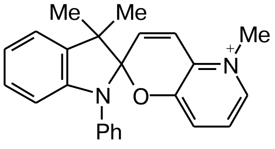

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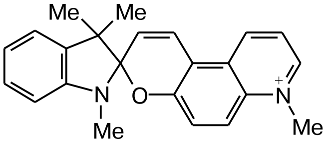

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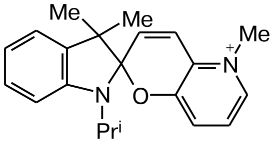

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Experimental

Polycrystalline samples $Sp_3Cr(C_2O_4)_3 \cdot nH_2O$ based on the molecular ions of spiropyrans **1**—**4** with different number of crystallization water molecules per formula unit (hereafter, the crystallization water content) were used. The syntheses and the crystal structures of the compounds were reported in details elsewhere.[20]

A Quantum Design MPMS 5XL SQUID magnetometer was used to obtain the dependences of the magnetic moment M of $Sp_3Cr(C_2O_4)_3$ powder samples on temperature ($2 \le T \le 300$ K) in a magnetic field of $H = 1$ kOe and on the magnetic field ($0 \le H \le 50$ kOe) at $T = 2$ K. For each temperature, the effective magnetic moment μ_{eff} was calculated from the relation $\mu_{eff} = (8MT/\nu H)^{1/2}\mu_B$, where μ_B is the Bohr magneton, T is absolute temperature, ν is the sample mass, and $M/\nu H$ is the static molar magnetic susceptibility.

The type of the paramagnetic particles contributing to the magnetic properties of compounds was determined using a Bruker EMX X-band ESR-spectrometer (operating frequency about 9.4 GHz) with an H_{102} rectangular cavity and a modulation frequency of 100 kHz. ESR spectra were recorded as the first derivatives of the microwave absorption dI/dH.

Dehydration of samples was studied by thermogravimetry with a Perkin—Elmer Pyris 1 TGA programmed analyzer. To determine the critical dehydration temperature, a linear increase in temperature in the range 20—100 °C was specified. Magnetic measurements were performed with dehydrated samples dried *in vacuo* for 24—48 h at 60 °C.

Results and Discussion

At $T = 2$ K, the effective magnetic moment μ_{eff} of the initial compound $(\mathbf{1})_3Cr(C_2O_4)_3$ is $3.7\mu_B$ (Fig. 1, *a*, curve *1*), which is close to the calculated value $\mu_{eff} = g\sqrt{S(S+1)} = 3.9\ \mu_B$ for Cr^{3+} paramagnetic ions ($S = 3/2$). To determine the spin of magnetic centers at low temperatures, the dependence of the magnetic moment M on external magnetic field H at $T = 2$ K was obtained (Fig. 1, *b*). It is with high accuracy (dispersion is about 0.99) described by the Brillouin function for noninteracting paramagnetic centers with the spin $S = 3/2$

$$M = N_A g\mu_B \left\{ \left(S + \frac{1}{2}\right) \coth \frac{g\mu_B H\left(S = \frac{1}{2}\right)}{kT} - \frac{1}{2} \coth \frac{g\mu_B H}{2kT} \right\}, \quad (1)$$

where N_A is the Avogadro constant, g is the g-factor, and k is the Boltzmann constant. Therefore, only the Cr^{3+} paramagnetic ions ($S = 3/2$) contribute to the magnetic moment at $T = 2$ K. This result is consistent with the μ_{eff} value obtained at $T = 2$ K. As temperature increases to 300 K, the μ_{eff} of compound $(\mathbf{1})_3Cr(C_2O_4)_3$ gradually increases to 7.17 μ_B (see Fig. 1, *a*, curve *1*), which is much larger

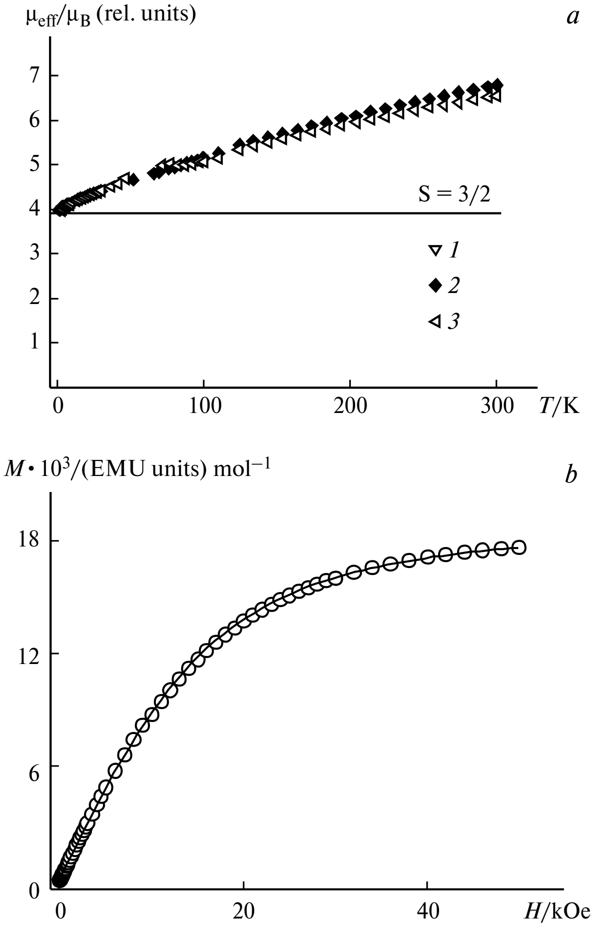

Fig. 1. *a* — Temperature dependences of the effective magnetic moment μ_{eff} of compound $(\mathbf{1})_3Cr(C_2O_4)_3$ before (*1*) and after dehydration over a period of 18 (*2*) and 48 (*3*) h. Solid line denotes the value calculated for $S = 3/2$. *b* — Magnetic field dependence of the magnetic moment M of compound $(\mathbf{1})_3Cr(C_2O_4)_3$ at $T = 2$ K. Circles denote experimental data, the solid line is approximation by the Brillouin function (1).

than the value calculated for Cr^{3+} owing to the contribution of Sp^+ paramagnetic ions.

To confirm the coexistence of two types of magnetic centers (paramagnetic Cr^{3+} ions and thermally excited Sp^+ cations) in compound $(\mathbf{1})_3Cr(C_2O_4)_3$, the ESR spectra were recorded. The ESR spectrum of compound $(\mathbf{1})_3Cr(C_2O_4)_3$ exhibits two lines in the regions 1.6 and 3.5 kOe (see Fig. 2, *a*, curve *1*). To establish the nature of these lines, the ESR spectrum of Cr^{3+} ions was calculated with the crystal field parameters $g = 1.956$, $D = 0.619$ cm^{-1} and $E = 0.024$ cm^{-1} measured[21] for $(\mathbf{3})_3Cr(C_2O_4)_3$ single crystals. A powder ESR spectrum was calculated by averaging the ESR spectra of chromium oxalates at different orientations. The initial ESR spectra of chromium oxalates at fixed orientations of the complexes were obtained by calculating the spin level positions in the crystal field and in external magnetic field.[22] This algorithm was practically implemented in the "EasySpin" program.[23] The simulated ESR spectrum exhibits an intense line in the region nearly 1.6 kOe and a weak line at 3.5 kOe (see Fig. 2, *a*, curve *2*). A comparison of the simulated spectrum and the experimental spectrum of compound $(\mathbf{1})_3Cr(C_2O_4)_3$ suggests that line 1 (see Fig. 2, *a*) corresponds to the Cr^{3+} ions (S = 3/2). In the simulated spectrum, the amplitude of line 2 in the region 3.5 kOe is an order of magnitude lower than the amplitude of line 1 in the region 1.6 kOe. In the experimental spectra of compounds $(\mathbf{1})_3Cr(C_2O_4)_3$, the lines from series 1 and 2 have comparable amplitudes. Differences between the experimental and theoretical spectra can be explained by the presence of additional ESR line in the region of about 3.5 kOe (near $g = 2$) originating from the signal of thermally excited paramagnetic cations Sp^+.

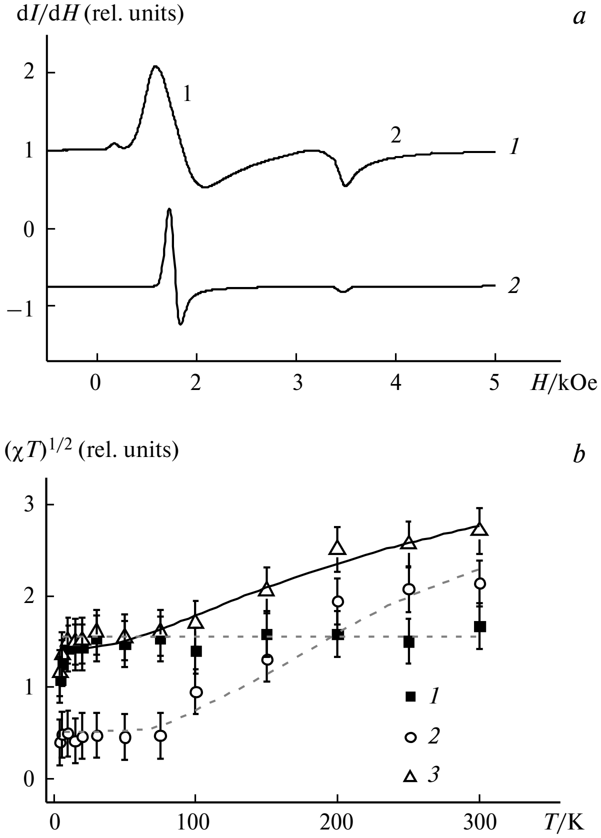

Fig. 2. *a* — Experimental (*1*) and simulated (*2*) ESR spectra of compound $(\mathbf{1})_3Cr(C_2O_4)_3$ at $T = 100$ K. *b* — Temperature dependences of the parameters $\sqrt{\chi_1 T}$ (*1*), $\sqrt{\chi_2 T}$ (*2*), and $\sqrt{\chi T} = \sqrt{(\chi_1 + \chi_2)T}$ (*3*). Lines are drawn for clarity.

Now we will consider the temperature dependence of the ESR spectra. Temperature variations have no effect on the ESR lineshape; therefore, for all lines one can determine the value $\chi \sim \Delta H_{pp}{}^2 A$ which is proportional to the corresponding contribution to the magnetic susceptibility (ΔH_{pp} is the peak-to-peak linewidth, A is the amplitude of the line). Figure 2, *b* presents the temperature dependences of the parameters $\sqrt{\chi_1 T}$ and $\sqrt{\chi_2 T}$ for lines 1 and 2, respectively, and of the parameter $\sqrt{\chi T} = \sqrt{(\chi_1 + \chi_2)T}$ proportional to the effective magnetic moment μ_{eff} of the sample. Assuming a constant number of paramagnetic particles obeying the Curie law, in the $\sqrt{\chi T} - T$ coordinates one would observe a horizontal line parallel to the abscissa axis. This is just the case for line 1 which corresponds to ESR on the Cr^{3+} ions (see Fig. 2, *b*, curve *1*). The quantity $\sqrt{\chi_2 T}$ for line 2 increases about five times as the temperature increases from 2 to 300 K (see Fig. 2, *b*, curve *2*). This temperature dependence can not be described by the Curie law for a constant number of paramagnetic centers. Line 2 corresponds to paramagnetic spiropyran cations Sp^+ whose fraction increases with temperature. This confirms the conclusion that two types of particles, namely, Cr^{3+} and Sp^+ cations, contribute to the magnetic moment of compound $(\mathbf{1})_3Cr(C_2O_4)_3$. The quantity $\sqrt{\chi T} = \sqrt{(\chi_1 + \chi_2)T}$ increases by a factor of 1.7 as temperature increases from 4 to 300 K (see Fig. 2, *b*, curve *3*). This result agrees with the SQUID magnetometry data, according to which the $\mu_{eff}(300\ K)/\mu_{eff}(4\ K)$ ratio is 1.7. Thus, ESR spectroscopy and SQUID magnetometry give quantitatively similar results indicating that line 2 in the ESR spectrum corresponds to the Sp^+ cations.

To validate the assumption of the effect of crystallization water on the magnetic properties, the temperature dependences of the effective magnetic moment of compound $(\mathbf{1})_3Cr(C_2O_4)_3$ dehydrated by drying at 60 °C *in vacuo* (at about 10^{-2} Torr) for 18 and 48 h were obtained. It was found that dehydration led to a decrease in the contribution due to paramagnetism of spiropyrans (see Fig. 1, *a*, curves *2* and *3*). Thus, dehydration causes a decrease in thermally induced paramagnetism of spiropyran ions. The magnetic field dependence at 2 K, which characterizes the contribution of Cr^{3+} ions only, remained almost unchanged because at low temperatures the thermally excited triplet states of spiropyran molecules appear to be "frozen".

Therefore, the deviation of μ_{eff} for compound $(\mathbf{1})_3Cr(C_2O_4)_3$ from the value calculated for paramagnetic ions Cr^{3+} is due to the contribution of spiropyran cations. The decrease in the crystallization water content leads to a decrease in the contribution of Sp^+ cations to the total magnetization.

To confirm the results obtained, the temperature and magnetic field dependences for tris(oxalato)chromates based on the spiropyran cations **2** and **3** containing different number of crystallization water molecules were obtained.

The effective magnetic moment of compound $(\mathbf{2})_3Cr(C_2O_4)_3$ at 2 K is 3.8 μ_B (Fig. 3, *a*, curve *1*). This is close to the calculated value μ_{eff} = 3.9 μ_B for paramagnetic ions Cr^{3+} (S = 3/2). The magnetic field dependence of the magnetic moment $M(H)$ at T = 2 K can with high accuracy be described by the Brillouin function for paramagnetic particles with the spin S = 3/2 (Fig. 3, *b*, curve *1*). Therefore, only Cr^{3+} ions contribute to the magnetic moment at T = 2 K. As temperature increases to 300 K, the effective magnetic moment of compound $(\mathbf{2})_3Cr(C_2O_4)_3$ monotonically increases to 5.16 μ_B. This value is greater than that obtained for the contribution of the Cr^{3+} ions only but smaller than the maximum possible effective magnetic moment of 5.7 μ_B calculated assuming that both Cr^{3+} ions and Sp^+ biradicals contribute to the magnetization (two spins with S = 1/2).

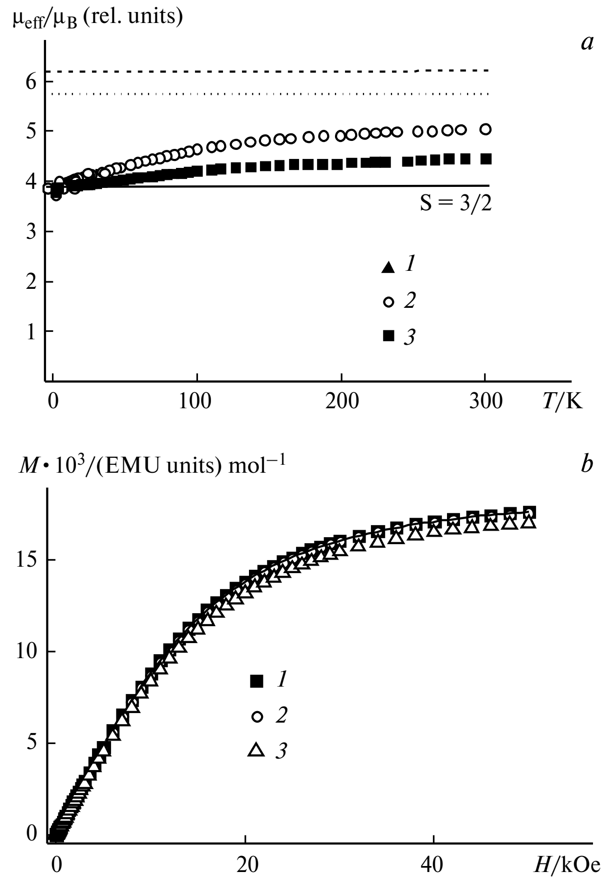

Fig. 3. *a* — Temperature dependences of the effective magnetic moments μ_{eff} of compounds $(\mathbf{2})_3Cr(C_2O_4)_3 \cdot 4H_2O$ (*1*), $(\mathbf{3})_3Cr(C_2O_4)_3 \cdot 1H_2O$ (*2*), and $(\mathbf{3})_3Cr(C_2O_4)_3 \cdot nH_2O$, where $n < 1$, (*3*). The dash-and-dot and dashed lines denote the maximum attainable μ_{eff} values calculated for the biradical (two spins S = 1/2) and triplet states (S = 1) of Sp^+ cations, respectively. *b* — Magnetic field dependences of the magnetic moments M of compounds $(\mathbf{2})_3Cr(C_2O_4)_3 \cdot 4H_2O$ (*1*), $(\mathbf{3})_3Cr(C_2O_4)_3 \cdot 1H_2O$ (*2*) and $(\mathbf{3})_3Cr(C_2O_4)_3 \cdot nH_2O$, where $n < 1$, (*3*) at T = 2 K. The solid line denotes approximation by the Brillouin function (1).

For compound $(\mathbf{3})_3Cr(C_2O_4)_3$, one has μ_{eff}(2 K) = = 3.85 μ_B (see Fig. 3, *a*, curve *2*), which is equal to the calculated value for S = 3/2. The magnetic field dependence of the magnetic moment $M(H)$ at T = 2 K is described by the Brillouin function for paramagnetic ions with S = 3/2 (see Fig. 3, *b*, curve *2*). Thus, only Cr^{3+} ions contribute to the magnetic moment at T = 2 K. As temperature increases to 300 K, the μ_{eff} value of compound $(\mathbf{3})_3Cr(C_2O_4)_3$ monotonically increases to 4.4 μ_B or to 4.7 μ_B depending on the content of crystallization water.

The magnetic moments of the spiropyran salts **1**—**3** described above have contributions of both Cr^{3+} and Sp^+ ions. To select the contribution of the Sp^+ cations only, salt (**4**)I was used in which the chromium oxalate anions $Cr(C_2O_4)_3^{3-}$ were replaced by iodide anions I^-. Since the iodide ion is diamagnetic, the paramagnetism of spiropyran iodide **4** could be due to Sp^+ cations only. It was established that the effective magnetic moment of compound (**4**)I monotonically increases from 0.05 μ_B to 1.9 μ_B as the temperature increases from 2 to 300 K (Fig. 4, *a*). The ESR spectrum of this compound exhibits only an intense broad line (see inset in Fig. 4, *a*) for which the parameter $\chi \sim \Delta H_{pp}{}^2 A$ was determined. The temperature dependence of $\sqrt{\chi T}$ determined by ESR spectroscopy from the integrated intensity of spectral line is in qualitative agreement with the temperature dependence of μ_{eff} obtained from the SQUID magnetometry measurements (see Fig. 4, *a*).

Compound $(\mathbf{4})_3Cr(C_2O_4)_3$ is based on chromium oxalate with the same spiropyran cation (**4**). In this case, one has $\mu_{eff}(T = 2\ K)$ = 3.76 μ_B (Fig. 4, *b*), which is close to the calculated value of 3.87μ_B for S = 3/2. The magnetic field dependence of the magnetic moment $M(H)$ at T = 2 K is correctly described by the Brillouin function for paramagnetic ions with S = 3/2. Consequently, only Cr^{3+} ions contribute to the magnetic moment at T = 2 K. As temperature increases to 300 K, the μ_{eff} value of compound $(\mathbf{4})_3Cr(C_2O_4)_3$ monotonically increases to 8.77 μ_B and thus becomes higher than the calculated value for Cr^{3+}. Qualitatively, the increment to the effective magnetic moment μ^{Sp}_{eff} due to the contribution of spiropyran is analogous for crystals (**4**)I and $(\mathbf{4})_3Cr(C_2O_4)_3$.

The content of crystallization water in compound $(\mathbf{1})_3Cr(C_2O_4)_3$ was changed by the action of external factors (drying *in vacuo*). For $(\mathbf{2})_3Cr(C_2O_4)_3$, $(\mathbf{3})_3Cr(C_2O_4)_3$,

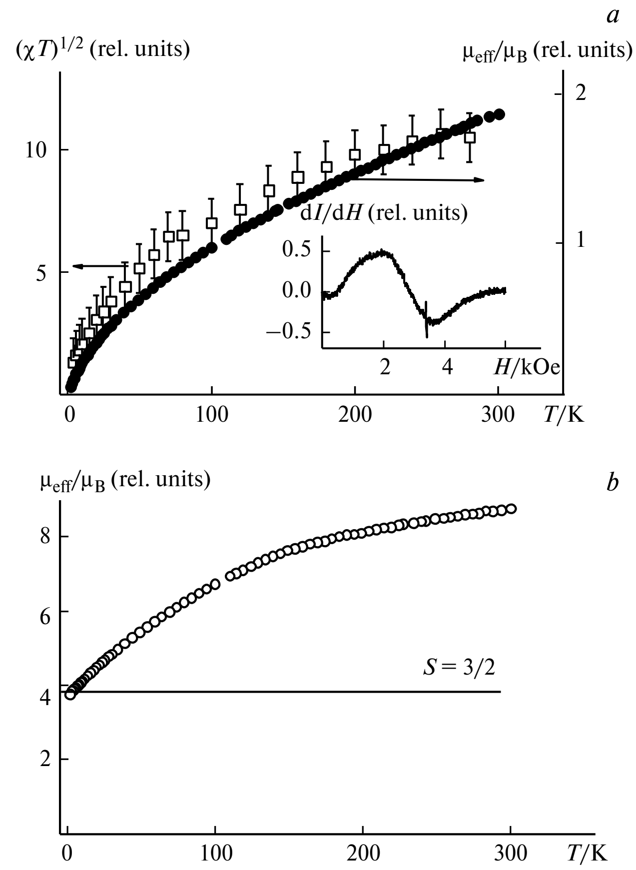

Fig. 4. *a* — Temperature dependences of the parameter $\sqrt{\chi T}$ and the effective magnetic moment μ_{eff} of compound (**4**)I. Inset: the ESR spectrum of compound (**4**)I at $T = 100$ K. *b* — Temperature dependences of the effective magnetic moment μ_{eff} of compound $(\mathbf{4})_3Cr(C_2O_4)_3 \cdot 13H_2O$.

and $(\mathbf{4})_3Cr(C_2O_4)_3$ it was varied during the synthesis. This made it possible to exclude the effects related to heating in the course of dehydration. The number of crystallization water molecules per formula unit determined by IR spectroscopy is 4 for $(\mathbf{2})_3Cr(C_2O_4)_3$, one or less (depending on the synthesis conditions) for $(\mathbf{3})_3Cr(C_2O_4)_3$, and 13 for $(\mathbf{4})_3Cr(C_2O_4)_3$. As the number of crystal water molecules decreases, the increment μ^{Sp}_{eff} decreases (Fig. 5). For the spiropyran cation thermally excited to the biradical state (two unpaired electrons with S = 1/2), the theoretically attainable effective magnetic moment is 2.45 μ_B. Assuming that in complex $Sp_3Cr(C_2O_4)_3$ all three Sp^+ cations are excited to the biradical state, the maximum effective magnetic moment should be equal to 5.74 μ_B. If the spiropyran cations are excited to triplet levels (S = 1), the effective magnetic moment of one cation is equal to 2.8 μ_B and the maximum value expected for the complex $Sp_3Cr(C_2O_4)_3$ is $\mu_{eff} = 6.2$ μ_B. The effective magnetic moments of compounds $(\mathbf{2})_3Cr(C_2O_4)_3$ and $(\mathbf{3})_3Cr(C_2O_4)_3$ are no higher than the values calculated for the biradical and triplet states (see Fig. 3, *a*).

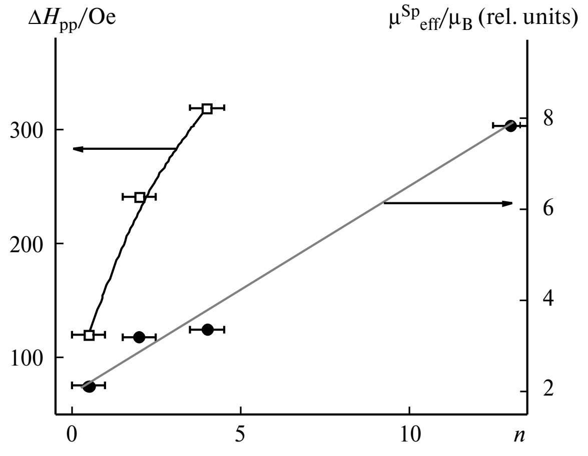

Fig. 5. Dependences of the effective magnetic moments of spiropyran cations μ^{Sp}_{eff} and width ΔH_{pp} line 1 on the number of crystal water molecules *n* in compounds $(Sp)_3Cr(C_2O_4)_3$ at $T = 300$ K. Solid lines are drawn for clarity.

Like the ESR spectrum of $(\mathbf{1})_3Cr(C_2O_4)_3$, those of compounds $(\mathbf{2})_3Cr(C_2O_4)_3$ and $(\mathbf{3})_3Cr(C_2O_4)_3$ exhibit two intense lines (Fig. 6). The temperature dependences of the integrated amplitudes χ_1, χ_2 and the widths of these lines are similar to the dependences $\chi(T)$ and $\Delta H(T)$ for $(\mathbf{1})_3Cr(C_2O_4)_3$. The parameter $\sqrt{\chi_1 T}$ for line 1 is temperature independent in the range from 50 to 300 K, *i.e.*, it obeys the Curie law. It is logical to assume that the lines of series 1 correspond to paramagnetic Cr^{3+} ions. For the lines of series 2, a correct determination of the corresponding magnetic susceptibility is impossible because the lineshape is temperature-dependent. However, based on the position of line 2 in the ESR spectrum, by analogy with the compound $(\mathbf{1})_3Cr(C_2O_4)_3$ one can assume that these lines correspond to the spiropyran cations **2** and **3**.

To establish the effect of the number of crystal water molecules on the shape of ESR spectra, the widths of the lines of series 1 in the ESR spectra of compounds

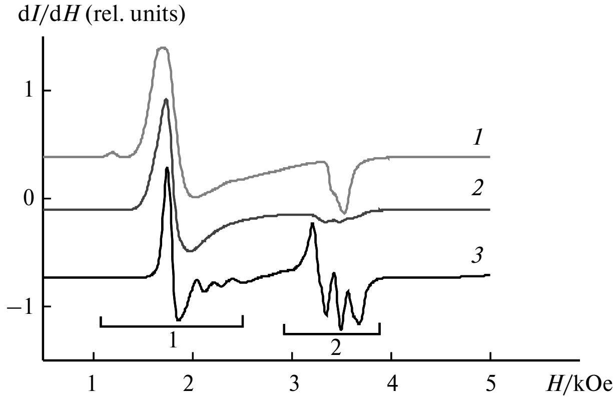

Fig. 6. ESR spectra of compounds $(\mathbf{2})_3Cr(C_2O_4)_3 \cdot 4H_2O$ (*1*), $(\mathbf{3})_3Cr(C_2O_4)_3 \cdot H_2O$ (*2*), and $(\mathbf{3})_3Cr(C_2O_4)_3 \cdot nH_2O$, where $n < 1$ (*3*) at $T = 100$ K.

(**2**)$_3$Cr(C$_2$O$_4$)$_3$ and (**3**)$_3$Cr(C$_2$O$_4$)$_3$ (see Fig. 5) were compared. It was found that an increase in the number of crystal water molecules is accompanied by line 1 broadening and fine structure mixing. A possible reason for ESR line broadening is inhomogeneity of the local crystal fields due to lattice defects. Therefore, the ESR line broadening in the spectra of compounds (**2**)$_3$Cr(C$_2$O$_4$)$_3$ and (**3**)$_3$Cr(C$_2$O$_4$)$_3$ is due to an increase in the concentration of structural defects formed by water molecules.

The experimental results obtained in this work provide an explanation for the difference between the magnetic properties of spiropyran molecules in liquids (where they are diamagnetic at all temperatures) and in the solids where thermally induced paramagnetism of these molecules is observed. The presence of disordered crystal water molecules leads to an increase in internal strain and, therefore, to even greater decrease in the energy of excited paramagnetic levels.

Correlations between the content of crystal water and the magnitude of thermally induced paramagnetism of the compounds under study suggest that mechanical strain fields produced by water molecules can reduce the energy barrier to transition of the Sp$^+$ ion to the biradical state. From thermal activation analysis it is known that mechanical strain causes changes in the enthalpy $E_{ST}^* = -E_{ST} + \gamma\sigma$ (γ is the activation volume and σ is the mechanical strain) rather than activation energy E_{ST}. Here, one should use the initial activation energy values $E_{ST} \approx 1—2$ eV for isolated spiropyran ions. In this case, in order to experimentally obtain $E_{ST}^* = 0.01—0.02$ eV, the product $\gamma\sigma$ should be of the same order of magnitude ~1—2 eV as ΔE_{ST}. Assuming that the activation volume γ should hardly be larger than the molecular volume $(5 \cdot 10^{-10}\ \text{m})^3 \approx 10^{-28}\ \text{m}^3$, one gets the lower boundary of $\sigma \approx 1$ GPa. This mechanical strain is comparable in magnitude with the Young modulus G (usually, G lies between 1 and 10 GPa) and can quite probably be produced in the vicinity of point defects (*i.e.*, bound water molecules). Remind that in the continuum approximation, the mechanical strain at the distance r from a point inclusion defect is given by $\sigma \approx G\Delta V/r^3$, where ΔV is the volume of the inclusion defect. Therefore, the presence of one water molecule per unit cell can, in principle, produce mechanical strain of the order of 0.1—1 GPa, which is sufficient to reduce the activation energy to transition of the molecule to biradical states. Validation of this assumption and experimental determination of the γ and σ values require further studies of the ESR spectra under pressure and under argon atmosphere.

To elucidate the role of the synthesis conditions on thermally induced paramagnetism of spiropyran cations, we compared the temperature and magnetic field dependences of the magnetic moments of compound (**3**)$_3$Cr(C$_2$O$_4$)$_3$ obtained under the oxygen and argon atmospheres.

The effective magnetic moment of compound (**3**)$_3$Cr(C$_2$O$_4$)$_3$ obtained in argon atmosphere is temperature independent and equal to the calculated value for paramagnetic ions Cr^{3+} (S = 3/2), namely, $\mu_{\text{eff}} = 3.9\ \mu_B$ (see Fig. 7, *a*). The magnetic field dependence of the magnetic moment can with high accuracy be approximated by the Brillouin function (1) for the paramagnetic centers with S = 3/2 (Fig. 7, *b*). The concentration of paramagnetic centers determined from this approximation equals the calculated concentration of the Cr^{3+} ions.

The effective magnetic moment of compound (**3**)$_3$Cr(C$_2$O$_4$)$_3$ synthesized under oxygen atmosphere is equal to 3.6 μ_B at $T = 2$ K (see Fig. 7, *a*). As temperature increases, μ_{eff} monotonically increases to 4.4 μ_B at $T = 300$ K, thus being higher than the value calculated for Cr^{3+}. The magnetic field dependence at $T = 2$ K is correctly described by the Brillouin function (1) for S = 3/2, but the concentration of paramagnetic centers is 15% lower

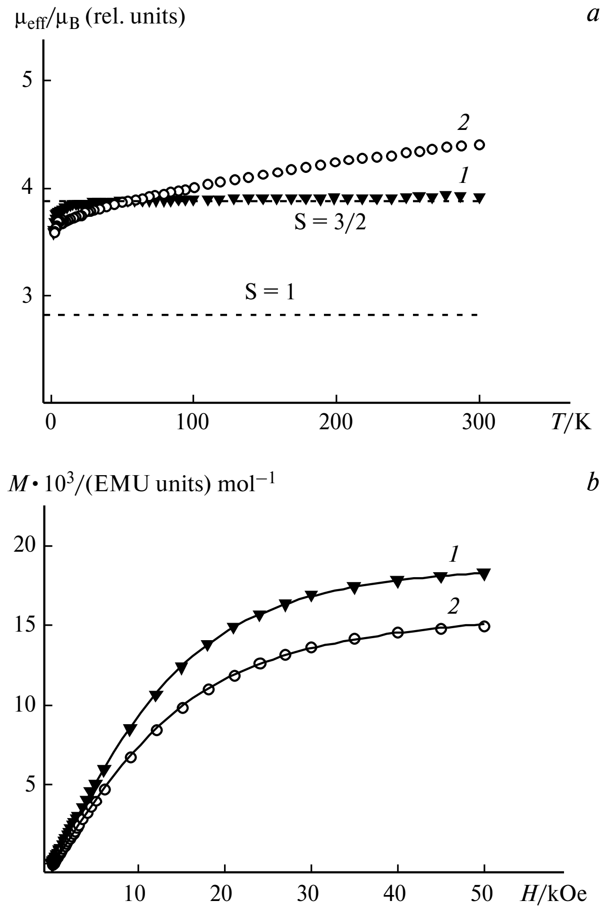

Fig. 7. *a* — Temperature dependences of the effective magnetic moment μ_{eff} of the samples of compound (**3**)$_3$Cr(C$_2$O$_4$)$_3$ obtained under argon (*1*) and oxygen (*2*) atmosphere at $H = 1$ kOe. *b* — Magnetic field dependences of the magnetic moment M of the samples of compound (**3**)$_3$Cr(C$_2$O$_4$)$_3$ obtained under argon (*1*) and oxygen (*2*) atmosphere at $T = 2$ K. Solid lines denote approximation by the Brillouin function for spin S = 3/2.

than the calculated concentrations of Cr^{3+} ions. Equal values of the average spin obtained from approximation of the magnetic field dependence and the spin of Cr^{3+} ions suggest that the contribution of thermally induced paramagnetism is "frozen" at 2 K.

Thus, the magnetic properties of crystals of salt $(\mathbf{3})_3Cr(C_2O_4)_3$ synthesized under inert gas atmosphere are due to paramagnetic Cr^{3+} ions only. As to crystals of salt $(\mathbf{3})_3Cr(C_2O_4)_3$ synthesized under oxygen atmosphere, at high temperatures (~100 K), paramagnetism of chromium oxalates is accompanied by some contribution of thermally induced paramagnetism of spiropyran cations.

The effects of the number of crystal water molecules and the synthesis conditions (atmosphere) on the effective magnetic moments and ESR spectra of tris(oxalato)-chromium(III) complexes with spiropyran cations Sp^+ were disclosed. It was established that an increase in the number of crystal water molecules causes an increase in the effective magnetic moment of spiropyran molecules, produces internal mechanical strain, and leads to a decrease in the activation enthalpy of paramagnetic states of the Sp^+ ions and to broadening of ESR spectral lines due to disordered water molecules responsible for the formation of local regions with scatter of crystal fields. Dehydration of the compounds studied on heating *in vacuo* leads to reversible decrease in the contribution of thermally induced magnetism of spiropyran molecules to the magnetic moments of tris(oxalato)chromium(III) complexes with spiropyran cations. The synthesis of the compounds in question under inert (argon) atmosphere suppresses thermally induced paramagnetism.

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