Technical Physics Letters, 2026, Vol. 52, No. 2

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Effect of dehydration on the magnetism of tetranuclear cobalt(II) cluster $Li_{10}[Co_4(H_2O)_2\cdot(\alpha\text{-}VW_9O_{34})_2]\cdot 34H_2O$

© A.I. Dmitrieva, M.V. Zhidkov, Z.M. Dzhabieva, G.V. Shilov, T.A. Savinnykh,
M.S. Dmitrieva, N.N. Denisov, T.S. Dzhabiev

Federal Research Center for Problems of Chemical Physics and Medical Chemistry, Russian Academy of Sciences,
Chernogolovka, Moscow region, Russia
E-mail: aid@icp.ac.ru

Received August 11, 2025
Revised October 5, 2025
Accepted October 11, 2025

The effect of dehydration on the spin state of Co^{2+} ions and the exchange interaction between them in a new tetranuclear cobalt(II) cluster $Li_{10}[Co_4(H_2O)_2\cdot(\alpha\text{-}VW_9O_{34})_2]\cdot 34H_2O$ is examined. Magnetometric methods are used to demonstrate that the removal of crystallization water leads to a transition from the low-spin state ($S = 1/2$) to the high-spin one ($S = 3/2$) and an intensification of antiferromagnetic exchange. The following key mechanisms of influence of dehydration are identified: a change in geometry of the coordination sphere and a modification of parameters of the ligand field. The obtained results open up prospects for the development of hygrosensitive materials for sensors and spintronics.

Keywords: molecular magnets, hydration, dehydration, spin state, cobalt(II), high-spin state, low-spin state, crystal field, magnetometry.

DOI: 10.61011/TPL.2026.02.63041.20466

Crystallization water (water that is part of the crystal lattice) plays a significant part in modulating the magnetic behavior of molecular magnets, allowing for fine-tuning of their magnetic properties through controlled dehydration/hydration processes [1–4]. The presence and specific arrangement of water molecules in the crystal lattice may alter the electronic structure of magnetic ions and the interactions between them, affecting the magnetic ordering temperature and magnetic anisotropy [5–8]. Removed or added water molecules may change the geometry of bonds between magnetic ions, resulting in switching of the dominant magnetic interactions (e. g., from ferromagnetic interactions to antiferromagnetic ones) [4]. Water molecules may act as ligands, affecting the electronic structure and magnetic anisotropy of magnetic ions. The orientation and positioning of water molecules may exert a significant influence on the energy levels and magnetic properties of complexes [5,6]. Water molecules form a network of hydrogen bonds in the crystal structure, which also has the potential to affect the arrangement and interaction of magnetic ions and, consequently, the magnetic properties [7]. The specific orientation of a water molecule coordinated to a magnetic ion may induce changes in the electronic structure and magnetic anisotropy [5]. The presence of water molecules may influence the magnetization reversal barrier (the energy needed to switch the magnetization of a molecule) [8]. The removal of water molecules may alter the crystal structure and interionic spacing, potentially affecting the magnetic ordering temperature [3,4]. Certain molecular magnets behave as „magnetic sponges“, providing an opportunity to tune their magnetic properties reversibly in a controlled dehydration/hydration process [3]. These unique properties open up new prospects for development of smart magnetic materials with adjustable properties, non-volatile data storage devices, humidity sensors, and magnetic switches.

In the present study, we synthesize and examine a new molecular magnet, which is a tetranuclear cobalt(II) cluster $Li_{10}[Co_4(H_2O)_2\cdot(\alpha\text{-}VW_9O_{34})_2]\cdot 34H_2O$, with the aim of searching for the mechanisms of influence of dehydration on the spin state of Co^{2+} ions in coordination compounds and establishing the relation between the hydration state, structural changes, and magnetic properties.

The synthesis of tetracobalt-substituted polyoxo anion with lithium countercations $Li_{10}[Co_4(H_2O)_2\cdot(\alpha\text{-}VW_9O_{34})_2]\cdot 34H_2O$ was performed in accordance with the procedure detailed in [9]. The sample was examined via elemental and X-ray diffraction analysis, nuclear magnetic resonance and infrared spectroscopy, and thermogravimetric analysis. Temperature dependences of the magnetic moment $M(T)$ for the as-prepared sample and the sample dried in a rotary evaporator were recorded within the $T = 2{-}300\,\mathrm{K}$ temperature range in a constant magnetic field with strength $H = 5\,\mathrm{kOe}$ using a vibration magnetometer of a CFMS multifunctional cryomagnetic measurement system (Cryogenic Ltd., UK). The measured $M(T)$ dependences were recalculated into temperature dependences of the molar magnetic susceptibility using the $\chi = M/(H\nu)$ formula, where ν is the molar amount of substance [10]. The structure of tetranuclear cobalt(II) cluster $Li_{10}[Co_4(H_2O)_2\cdot(\alpha\text{-}VW_9O_{34})_2]\cdot 34H_2O$ is shown in Fig. 1. Its main structural units are as follows: a polyoxo anion framework formed by tungsten-vanadate anions $[\alpha\text{-}VW_9O_{34}]^{10-}$ and consisting of nine WO_6 octahedra

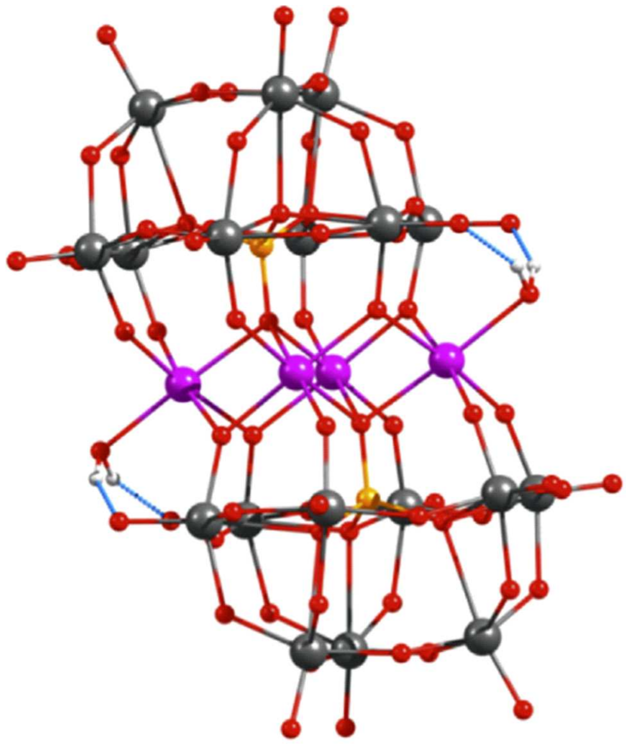

Figure 1. Sample structure. O atoms are shown in red; W atoms, in grey; V atoms, in yellow; H atoms, in white; Co atoms, in purple. A color version of the figure is provided in the online version of the paper.

and one VO_4 tetrahedron; a quasilinear tetracobalt $Co_4O_{14}(H_2O)_2$ core surrounded by $[\alpha\text{-}VW_9O_{34}]^{10-}$ and bound at both ends by Li^+ cations. The Co^{2+} ions are in an octahedral environment: two inner Co^{2+} ions are bound only to the cluster oxygen ions, while two outer Co^{2+} ions are coordinated by five cluster oxygen ions and a water molecule (H_2O). Water molecules include coordination water (two molecules bound to Co^{2+} ions) and crystallization water (32 molecules) that fills lattice cavities and forms hydrogen bonds.

Figure 2 shows the measured temperature dependences of molar magnetic susceptibility $\chi(T)$ of the as-prepared sample and the sample dried in a rotary evaporator (*dehydration*). Dependences $\chi(T)$ were recalculated into temperature dependences of reciprocal magnetic susceptibility $\chi^{-1}(T)$ (Fig. 3). The $\chi^{-1}(T)$ dependences are linear at high temperatures, but deviate significantly from linearity at low temperatures. Extrapolating the high-temperature part of this dependence to point $\chi^{-1} = 0$, we obtain a non-zero intersection. This behavior may be interpreted in the context of the Curie–Weiss law: $\chi^{-1} = (T - \Theta)/C$, where C and Θ are the Curie and Weiss constants, respectively. The values of $\Theta = -40\,\text{K}$ for the as-prepared sample and $\Theta = -110\,\text{K}$ for the sample dried in a rotary evaporator were determined by extrapolation. A non-zero Θ value may be attributed to the exchange interaction between Co^{2+} ions. The negative sign of Θ is indicative of antiferromagnetic exchange. Thus, dehydration of the tetranuclear cobalt(II) cluster leads to an intensification of antiferromagnetic exchange. Dehydration is indeed known to enhance exchange interactions in certain materials (e.g., Cu(II)–Mn(III) coordination networks [11] or cyanide-bridged Fe_2Co chains [12]). This is attributable to the fact that removal of water molecules alters the material structure, bringing magnetic ions closer together and modifying bridging ligands, which enhances exchange interactions. The key changes in the tetranuclear cobalt(II) cluster structure induced by dehydration include a reduction in Co^{2+}–Co^{2+} interionic distances, a change in Co^{2+} coordination geometry, and a reconstruction of the

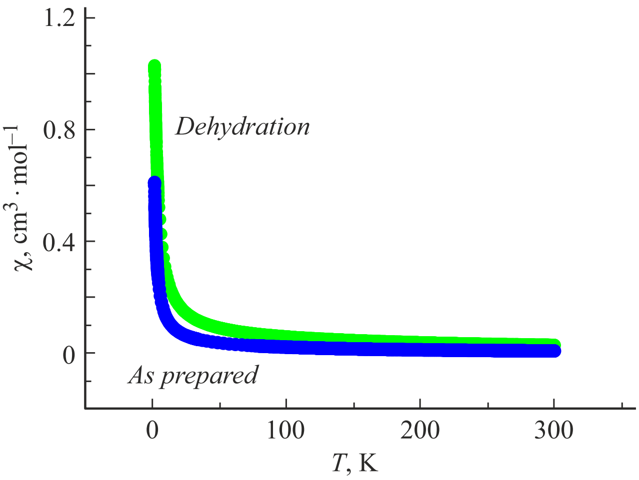

Figure 2. Temperature dependences of molar magnetic susceptibility χ for the sample before (*as prepared*) and after (*dehydration*) drying in a rotary evaporator.

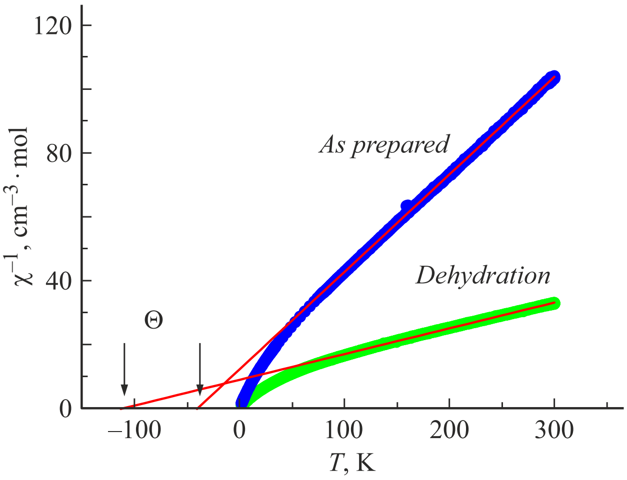

Figure 3. Temperature dependences of reciprocal molar magnetic susceptibility χ^{-1} for the sample before (*as prepared*) and after (*dehydration*) drying in a rotary evaporator. Solid lines represent extrapolations of the high-temperature part of χ^{-1} to the point of intersection with the temperature axis that were performed to determine Weiss constants Θ (marked with arrows).

hydrogen bond network. Crystallization water acts as a spacer, increasing the distances between magnetic centers. When it is removed, the Co^{2+} coordination polyhedra are brought closer together, the Co–O–Co distances shorten, and the Co–O–Co angles increase, which enhances the exchange interaction. Dehydration may remove coordination water (H_2O) from Co^{2+}, leaving only the bridging oxygen ions from [α-VW_9O_{34}], and take Co^{2+} from a distorted octahedron to a more symmetric one, enhancing the overlap of d orbitals. The original H-bonds ($O{-}H\cdots O$) are destroyed in the process of dehydration. New short $O\cdots O$ contacts between Co^{2+} ions establish additional pathways for exchange enhancement.

The measured $\chi(T)$ dependences were recalculated into temperature dependences of effective magnetic moment μ_{eff}, which is expressed in Bohr magnetons μ_B, per one Co^{2+} ion (out of four in the formula unit) in the following way: $\mu_{eff} = (8\chi T/4)^{1/2}$ (Fig. 4). At high temperatures $T > 150$ K, the effective magnetic moment of the sample remains constant prior to drying in a rotary evaporator. When the temperature drops below 150 K, the μ_{eff} value decreases (Fig. 4). After drying in a rotary evaporator, the values of effective magnetic moment of the sample do not plateau and decrease with decreasing temperature. This may be attributed to the antiferromagnetic interaction between Co^{2+} ions. The difference between the as-prepared sample and the sample after drying in a rotary evaporator is evident. The former has a significantly lower effective magnetic moment at room temperature ($\mu_{eff} \approx 2.4\,\mu_B$) than the latter ($\mu_{eff} \approx 4.3\,\mu_B$; see Fig. 4).

The ground state of an isolated Co^{2+} ion with the $3d^7$ electron configuration corresponds to term $^4F_{9/2}$ (spin quantum number $S = 3/2$; orbital quantum number $L = 3$) [10]. If the spin-orbit interaction (LS- coupling) is taken into account, the effective magnetic moment is determined in this case by total angular momentum $J = L + S = 9/2$: $\mu_J = g_J\big(J(J+1)\big)^{1/2} \approx 6.6\,\mu_B$, where $g_J = 4/3$ is the Landé g-factor. The LS coupling is dominant in free ions and $4f$ elements, but is suppressed by the crystal field for $3d$ ions. With the spin-orbit interaction neglected (vectors **L** and **S** behaving independently), the effective magnetic moment is determined by the spin and orbital contributions: $\mu_{HS+L} = \big(L(L+1) + 4S(S+1)\big)^{1/2}$. The corresponding value for $S = 3/2$ and $L = 3$ is $\mu_{HS+L=3} \approx 5.2\,\mu_B$, which is significantly higher than the experimentally obtained values.

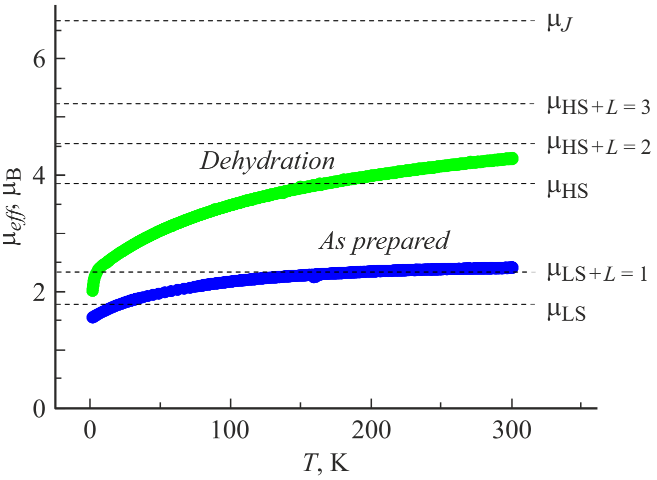

Figure 4. Temperature dependences of effective magnetic moment μ_{eff} per one Co^{2+} ion for the sample before (*as prepared*) and after (*dehydration*) drying in a rotary evaporator. Horizontal dashed lines denote the expected calculated values of μ_J, μ_{HS}, μ_{LS}, etc. (see text).

In octahedral crystal field complexes, five d orbitals of a Co^{2+} ion are split into two sets of orbitals designated as t_{2g} and e_g. If splitting Δ is insignificant, the high-spin (HS) $^4T_1(t_{2g}^5 e_g^2)$ state with a partially „frozen“ orbital angular momentum ($S = 3/2$, $L = 2$) is established. The corresponding value for $S = 3/2$ and $L = 2$ is $\mu_{HS+L=2} \approx 4.5\,\mu_B$, which is very close to the experimentally obtained value of $\mu_{eff} \approx 4.3\,\mu_B$ for the sample dried in a rotary evaporator. This indicates that the ground state of the dehydrated sample is HS-. If the orbital angular momentum is quenched completely ($L = 0$), the effective magnetic moment is determined just by the spin contribution with $S = 3/2$: $\mu_{HS} = 2\big(S(S+1)\big)^{1/2} \approx 3.9\,\mu_B$. In contrast, when splitting Δ is large, the low-spin (LS) $^2E(t_{2g}^6 e_g^1)$ state is established with an even more „frozen“ orbital angular momentum ($S = 1/2$, $L = 1$). The corresponding value for $S = 1/2$ and $L = 1$ is $\mu_{LS+L=1} \approx 2.2\,\mu_B$, which is very close to the experimentally obtained value of $\mu_{eff} \approx 2.4\,\mu_B$ for the as-prepared sample that was not dried in a rotary evaporator. This indicates that the ground state of the hydrated sample is LS-. If the orbital angular momentum is quenched completely ($L = 0$), the effective magnetic moment is determined just by the spin contribution with $S = 1/2$: $\mu_{LS} = 2\big(S(S+1)\big)^{1/2} \approx 1.7\,\mu_B$. Thus, dehydration of the tetranuclear cobalt(II) cluster leads to the LS → HS spin crossover. Dehydration may indeed induce the LS → HS spin crossover in certain materials (e.g., $[Co(pyterpy)Cl_2]\cdot 2H_2O$ [13] or $[Co(terpy)_2]_2[Mo(CN)_8]\cdot 15H_2O$ [14] complexes). This effect is attributable to a modification of the ligand field and a change in the coordination environment of a Co^{2+} ion occurring upon removal of water molecules. H_2O molecules exhibit moderate σ-donor activity, which is the capacity of ligands to transfer electron density to orbitals of the central magnetic metal ion. The stronger the σ-donor properties of a ligand are, the greater is the electron density acquired by the metal and, accordingly, the more profound is the splitting of d orbitals (Δ) in the crystal field, which stabilizes the LS-state. Furthermore, hydrogen H-bonds secure the geometry of the coordination polyhedron, preventing distortions that could reduce Δ. Certain distortions of the octahedral field (tetragonal elongation, trigonal compression) may enhance the splitting of d orbitals. In the process of dehydration, the removal of crystallization water induces hydrogen bond rupture and suppresses the σ-donor influence, causing a corresponding reduction in Δ. Octahedral field distortions (rhombic distortion, tetragonal contraction) may also weaken the splitting of d- orbitals. When coordination water (axial ligand) is removed, the coordination number decreases from 6 to 5 and the geometry transforms to a square pyramid. The energy difference (Δ) becomes smaller. This leads to stabilization of the HS-state.

Thus, hydration stabilizes the LS-state of Co^{2+} in a new tetranuclear cobalt(II) cluster $Li_{10}[Co_4(H_2O)_2 \cdot (\alpha\text{-}VW_9O_{34})_2]{\cdot}34H_2O$ ($\mu_{eff} = 2.4\,\mu_B$), while dehydration induces a transition to the HS state ($\mu_{eff} = 4.3\,\mu_B$). The main mechanisms of influence of dehydration are a reduction in coordination number, suppression of splitting of d orbitals, hydrogen bond rupture, and a change in crystal packing. The reversibility of LS ↔ HS transitions induced by hydration/dehydration confirms that such systems hold much promise for the development of hygrosensitive sensors, fabrication of non-volatile data storage devices, and external control over magnetic properties.

Funding

This study was supported by the Ministry of Science and Higher Education of the Russian Federation under state assignments Nos. 124013100858-3 and 124020200104-8.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by D.Safin