Inorganic Chemistry

Article

pubs.acs.org/IC

Solvent-Induced Change of Electronic Spectra and Magnetic Susceptibility of Co^{II} Coordination Polymer with 2,4,6-Tris(4-pyridyl)-1,3,5-triazine

Ruslan A. Polunin,[†] Nataliya P. Burkovskaya,[‡] Juliya A. Satska,[†] Sergey V. Kolotilov,*[,†] Mikhail A. Kiskin,[‡] Grigory G. Aleksandrov,[‡] Olivier Cador,[§] Lahcène Ouahab,*[,§] Igor L. Eremenko,*[,‡] and Vitaly V. Pavlishchuk[†]

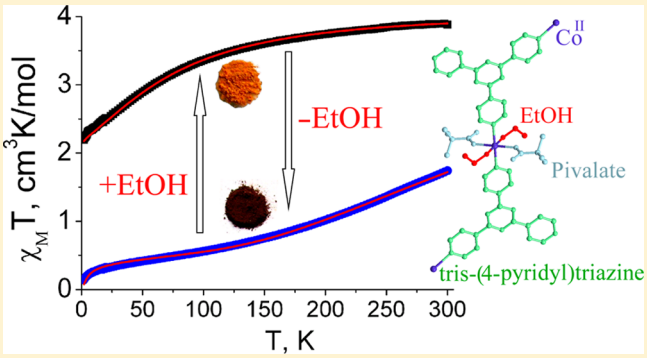
[†]L. V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of the Ukraine, Prospekt Nauki 31, Kiev, 03028, Ukraine

[‡]N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky Prospekt 31, 119991 Moscow, GSP-1, Russian Federation

[§]Equipe Organométalliques Matériaux et Catalyse, Sciences Chimiques de Rennes, UMR UR1-CNRS 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes cedex, France

Supporting Information

ABSTRACT: One-dimensional coordination polymer $[Co(Piv)_2(4\text{-ptz})(C_2H_5OH)_2]_n$ (compound **1**, Piv^- = pivalate, 4-ptz = 2,4,6-tris(4-pyridyl)-1,3,5-triazine) was synthesized by interaction of Co^{II} pivalate with 4-ptz. Desolvation of **1** led to formation of $[Co(Piv)_2(4\text{-ptz})]_n$ (compound **2**), which adsorbed N_2 and H_2 at 78 K as a typical microporous sorbent. In contrast, absorption of methanol and ethanol by **2** at 295 K led to structural transformation probably connected with coordination of these alcohols to Co^{II}. Formation of **2** from **1** was accompanied by change of color of sample from orange to brown and more than 2-fold decrease of molar magnetic susceptibility (χ_M) in the temperature range from 2 to 300 K. Resolvation of **2** by ethanol or water resulted in restoration of spectral characteristics and χ_M values almost to the level of that of **1**. $\chi_M T$ versus T curves for **1** and samples, obtained by resolvation of **2** by H_2O or C_2H_5OH, were fitted using a model for Co^{II} complex with zero-field splitting of this ion.



INTRODUCTION

Coordination compounds with porous crystal lattices, the so-called metal−organic frameworks (MOFs) or porous coordination polymers (PCPs), have been attracting attention as a basis for creation of multifunctional materials due to their ability to adsorb or release guest molecules in combination with other properties, which is promising for practical application.[1] Combination of the porosity with accessible paramagnetic ions or luminescent fragments gives rise to creation of porous magnetic[2] or luminescent[3] materials, respectively; pore filling by guests with labile protons allows researchers to develop systems with high proton conductivity,[4] etc. PCPs are also considered as promising size-selective catalysts,[5] selective sorbents,[6] carriers for chromatography,[7] etc. Physical properties of PCP can be tuned by "addition" or "removal" of guests, which is a unique feature of such systems.[8] However, in the overwhelming majority of cases, when magnetic properties of PCP changed upon guest molecule removal or exchange, the change of magnetic susceptibility, type of exchange interactions (ferro- or antiferromagnetic), or magnetic ordering parameters was observed only at low temperatures.[9] This is an obstacle to potential application of such compounds as new magnetic materials, and development of systems which can show significant change of magnetic response at room temperature.

The probability of magnetic properties change is higher if a guest molecule can induce a significant change in electronic structure of the sorbent (due to coordination to metal site or distortion of coordination polyhedron upon crystal lattice rearrangement), and this ability is usually favored by the presence of a donor group in the guest molecule.[9c,d,10] Capture or removal of such a guest is closer to chemisorption, in contrast to physical adsorption, usually observed for gases like N_2 or Ar.[11]

In addition to the above-mentioned materials, coordination polymers, in contrast to compounds built of discrete units, preserve the method for structural element binding (framework connectivity) upon guest molecule removal or exchange

Received: January 23, 2015
Published: May 14, 2015

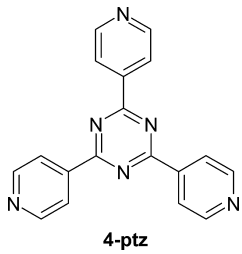
DOI: 10.1021/acs.inorgchem.5b00179
Inorg. Chem. 2015, 54, 5232−5238

(though crystal lattice rearrangements can lead to disorder or change of crystallographic parameters, chemical bonds between metal ions and linkers are preserved[12]). This feature is important for reversibility of changes in physical properties, and it is an advantage of coordination polymers over mononuclear complexes. In particular, several examples of multiple reversible changes of magnetic properties[2b,13] or luminescence[14] were reported; studies of such systems can be considered as a step toward creation of active bodies of sensors.

Spin-crossover compounds are one of the most promising systems for changing magnetic properties at high temperatures (close to room temperature).[15] In contrast to coordination polymers, which have magnetic properties which are controlled by paramagnetic ions with permanent value of spin (or exchange-coupled systems, based on such ions), spin-crossover compounds can undergo an abrupt change of magnetic susceptibility in a narrow temperature range.[15] The study of possibilities to induce spin-crossover in coordination polymers under the influence of guest inclusion or removal is an actual task of modern inorganic chemistry and materials science.

The aim of this study was to elucidate the influence of decoordination (removal) or coordination of ethanol molecules to Co^{II} ions in porous coordination polymer on electronic spectra and magnetic properties of the compound, and to evaluate the range of change of magnetic susceptibility of this compound, induced by such desolvation/resolvation.

In this Article, we present the synthesis and X-ray structure of new PCP $[Co(Piv)_2(4\text{-ptz})(C_2H_5OH)_2]_n$ (compound **1**; Piv^- = pivalate, 4-ptz =2,4,6-tris(4-pyridyl)-1,3,5-triazine, Figure 1), and the changes of its spectral and magnetic properties upon desolvation (formation of $[Co(Piv)_2(4\text{-ptz})]_n$, compound **2**) and resolvation.



4-ptz

Figure 1. Formula of 4-ptz ligand.

EXPERIMENTAL SECTION

Materials and Measurements. Commercially available reagents (Aldrich, Merck) were used as received. Solvents were dried and distilled by standard procedures. $[Co(Piv)_2]_n$ and 4-ptz were prepared according to the literature procedures.[16,17] C,H,N-analyses were performed using a Carlo Erba 1106 analyzer. UV−vis reflectance spectra were measured using Specord 210 spectrometer (Analytik Jena AG) in 380−1100 nm range in pellet in $BaSO_4$. Thermogravimetric analysis (TGA) was performed in air using an MOM Q1500 instrument. Magnetic measurements were performed using a Quantum Design MPMS SQUID magnetometer operating in the temperature range 2−300 K with a dc magnetic field up to 5 T. Samples were measured in Teflon capsules; diamagnetic corrections were calculated using Pascal's constants.[18] Samples of resolvated **2** were prepared by keeping this compound in saturated vapor of corresponding liquids (ethanol, water, etc.) at room temperature to permanent weight (about 1 day). Powder X-ray diffraction experiments were performed on a Bruker D8 instrument with Cu radiation. Measurements of N_2 and H_2 sorption by **2** were performed by Sorptomatic-1990 instrument at 78 K by the volumetric method. Sorption of methanol and ethanol by **2** was measured gravimetrically at 295 K. Each point on the absorption and desorption isotherms corresponds to equilibrium conditions (constant sample weight at given PP_S^{-1}). Prior to all sorption measurements sample of **2** was dried in vacuum 10^{-3} Torr at 120 °C.

Synthesis. Details follow for compound **1**, $[Co(Piv)_2(4\text{-ptz})(C_2H_5OH)_2]_n$. A solution of 0.084 g of $[Co(Piv)_2]_n$ (0.032 mmol) in 15 mL of ethanol was layered on the top of solution of 0.1 g (0.032 mmol) of 2,4,6-tris(4-pyridyl)-1,3,5-triazine (4-ptz) in the mixture of 15 mL of chloroform and 10 mL of ethanol. An orange crystalline precipitate formed in a few days, which was collected by filtration and washed by a hot chloroform−ethanol mixture and dried in air. Yield 0.15 g (about 70%). Anal. Found %: C, 57.6; H, 6.41; N, 12.4. Calcd for $C_{32}CoH_{42}N_6O_6$, %: C, 57.8; H, 6.36; N, 12.6.

Details follow for compound **2**, $[Co(Piv)_2(4\text{-ptz})]_n$. This compound was prepared by heating **1** at 150 °C for 2 days in vacuum 10^{-2} Torr. Deep-brown microcrystals form, with almost quantitative yield. Anal. Found %: C, 58.5; H, 5.45; N, 14.5. Calcd for $C_{28}CoH_{30}N_6O_4$, %: C, 58.6; H, 5.28; N, 14.7.

Details follow for compound **2**·$2H_2O$. Anal. Found %: C, 55.3; H, 5.55; N, 13.7. Calcd for $C_{28}CoH_{34}N_6O_6$, %: C, 55.2; H, 5.62; N, 13.8.

Crystallographic Data Collection and Structure Determination. An X-ray quality crystal of **1** was prepared by slow diffusion of reagents, as described with the synthetic procedures. The X-ray data set for **1** was collected on a Bruker APEX II diffractometer equipped with a CCD camera and a graphite monochromated Mo Kα radiation source (λ = 0.710 73 Å).[19] Semiempirical absorption corrections were applied.[20] X-ray structure was solved using SHELXS-97[21] and refined using SHELXL-97[21] by full-matrix least-squares on F^2, with H atoms treated by a riding model. Crystal data for **1**: $C_{32}H_{42}CoN_6O_6$, M = 665.65, monoclinic, space group $C2/c$, a = 23.826(5) Å, b = 19.696(4) Å, c = 7.4015(14) Å, β = 106.784(4)°, V = 3325.4(11) Å^3, T = 150(2) K, Z = 4, size 0.25 × 0.25 × 0.05 mm^3, D_{calc} = 1.330 g cm^3, μ = 0.567 mm^{-1}, $-23 \le h \le 29$, $-24 \le k \le 23$, $-7 \le l \le 9$, $1.37° \le \theta \le 26.39°$, $F(000)$ = 1404, 7729 reflections measured, 3386 reflections unique (R_{int} = 0.0634) which were used in all calculations (2155 reflections with $I > 2\sigma(I)$), T_{min}/T_{max} = 0.8712/0.9722, 211 number of parameters, GOF = 1.068, R1 ($I > 2\sigma(I)$) = 0.0517, wR2 ($I > 2\sigma(I)$) = 0.1140, R1 (all data) = 0.1053, wR2 (all data) = 0.1593. CCDC 1044834.

RESULTS AND DISCUSSION

Reaction of tripyridine ligand 4-ptz with Co^{II} pivalate in $C_2H_5OH/CHCl_3$ (2:3 v/v) led to formation of coordination polymer **1**, where Co^{II} ions were linked by 4-ptz molecules, acting as the ditopic bridges. One pyridine group from each 4-ptz was not coordinated to Co^{II}, in contrast to previously reported cases when 4-ptz bound three cobalt(II) ions.[22]

Compound **1** possessed the structure of a 1D coordination polymer (Figure 2). Each Co^{II} ion was located in an inversion center in the N_2O_4 donor set, where two N atoms were from pyridine rings, two O atoms were from carboxy groups, and two O atoms belonged to coordinated C_2H_5OH molecules. Bond lengths and angles in **1** were in the range typical for high-spin octahedral Co^{II} complexes with carboxylate and heterocyclic amine ligands.[23] Positive charge of the Co^{II} was compensated by the two coordinated pivalate ions.

One-dimensional chains in the crystal were located parallel to each other along ($c-a$) vector forming dense packing without solvent-accessible voids (Figure S1 in Supporting Information). Separation between mean planes of the adjacent 4-ptz ligands from the neighboring layers is 3.22(1) Å, which can provide evidence for some interactions like π-stacking (Supporting Information Figure S2). About 17% of the crystal volume was occupied by coordinated ethanol molecules, according to estimation by Platon[24] for a probe molecule with r = 1.4 Å.

DOI: 10.1021/acs.inorgchem.5b00179
Inorg. Chem. 2015, 54, 5232−5238

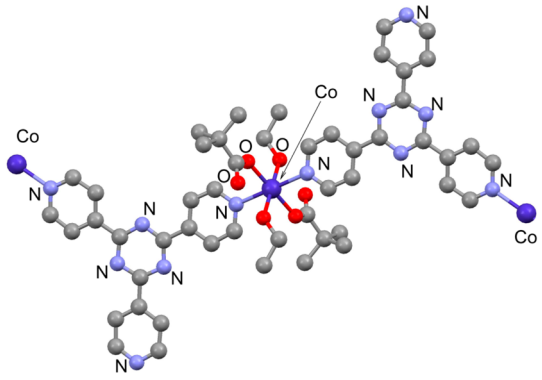


Figure 2. Fragment of 1D polymeric chain of **1**. Hydrogen atoms omitted for clarity.

Similar Co^{II} complexes with 4-ptz, possessing the structure of a zigzag chain where Co^{II} ions are bound by 4-ptz bridges, were reported.[25] Compounds of other metals with structures similar to **1** are known.[26]

Thermal stability of **1** was studied by thermogravimetric analysis (Supporting Information Figure S3). Gradual mass loss started at 40 °C and was completed at 140 °C (at P = 1 atm). Mass loss at this temperature corresponded to elimination of the two ethanol molecules per Co^{II} ion (expt 12%, theor 13.8%). Temperature increase to 215 °C did not lead to weight change, but further heating resulted in abrupt weight loss, associated with thermal decomposition of the sample (total weigh loss was 75% at 600 °C, which probably corresponded to formation of Co oxides as the solid pyrolysis products). The desolvated form of **1** (compound **2**) was prepared by heating of **1** in vacuum at 150 °C (temperature was chosen on the basis of TG data, *vide supra*).

The UV−vis reflectance spectrum of the compound **1** (Figure 3) contained a broad absorption band centered at 825 nm, which could be assigned to the $^4T_{1g} \rightarrow {}^4A_{2g}$ transition in high-spin octahedral Co^{II}.[27] The $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition expected in **1** at higher energy (lower wavelength) was probably obscured by the intense absorption band, which started from 700 nm (to lower wavelengths) and could be caused by several charge transfer transitions (notably, absorption bands of 4-ptz or its coordination polymer with Zn^{II} are located at λ < 400 nm[28]).

Elimination of the ethanol from **1** (formation of **2**) led to color change from orange to brown (Figure 3) and occurrence of a new absorption band (shoulder) at ca. 570 nm. This change could be explained by transformation of Co^{II} polyhedron from octahedral to pentacoordinated (square pyramidal or trigonal bipyramid) or even tetracoordinated tetrahedral Co^{II}.[27] Since transformation of compound **1** to **2** was associated with the loss of two ligands (two ethanol molecules) from the coordination sphere of the Co^{II}, one position could be occupied by the donor atom from the neighboring 1D chain (N atom of noncoordinated pyridine group or O atom of pivalate), similarly to reported cases of crystal rearrangements,[29] but the Co^{II} ion also can remain tetracoordinated.

Resolvation of sample **2** by different compounds (water, alcohols, nitriles, 1,4-dioxane, and amines) was studied (pictures and spectra are presented on Figure 3 and Supporting Information Figure S5 and S6). Interaction of **2** with ethanol resulted in complete restoration of color and electronic spectrum (Figure 3), while exposition to water or other alcohols (methanol, *n*-butanol) led to some color change, but not to formation of orange compound. Among the studied solvents, the most significant change of color was observed for ethanol (as mentioned above) and pyridine, which produced a pink sample. This could be explained by coordination of these substrates to the Co^{II} ion. In contrast, the most insignificant changes were observed at resolvation of **2** by bulky and/or weakly interacting substrates (benzonitrile or triethylamine), which was consistent with less efficient coordination of these compounds to cobalt(II) and even could be explained by interaction of Co^{II} with traces of water, present in these solvents. Notably, results of resolvation of **2** by water and ethanol, methanol, or pyridine were completely different, which could provide evidence that color change in the case of the three latter substrates was not caused by water, present in these solvents. We cannot exclude that reaction of **2** with pyridine could lead to a chemical reaction with formation of new compounds.

Desolvation of **1** led to occurrence of a broad intense band in IR spectrum with maximum at 1611 cm^{-1} (Figure 4 and Figure S4, Supporting Information), which can be assigned to ν_{as}(COO) of bridging or bidentate pivalate ion.[30] Notably, ν(C═C, C═N) vibration of 4-ptz[31] is observed at the same wavenumbers; however, this vibration is not intense compared

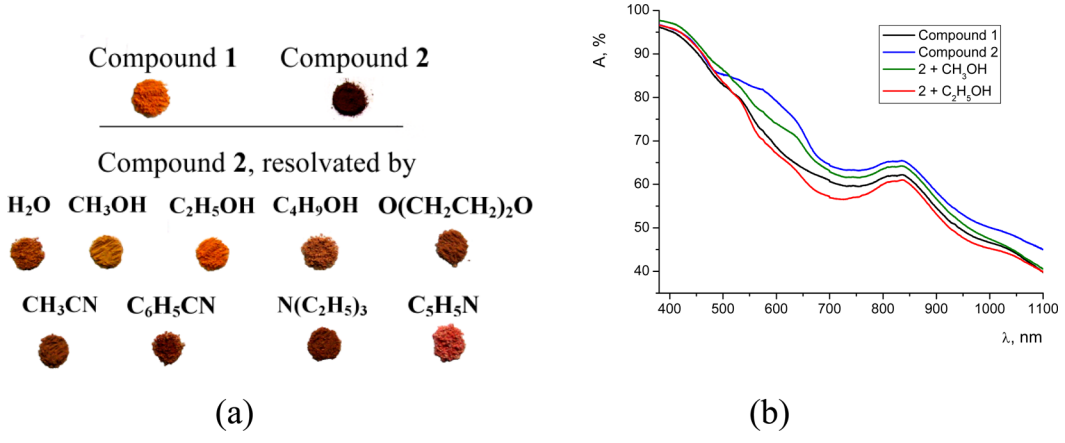


Figure 3. Photo pictures of samples of compounds **1** and **2**, and compound **2** after resolvation by different solvents (a) and electronic spectra of solid samples (b).

DOI: 10.1021/acs.inorgchem.5b00179
Inorg. Chem. 2015, 54, 5232−5238

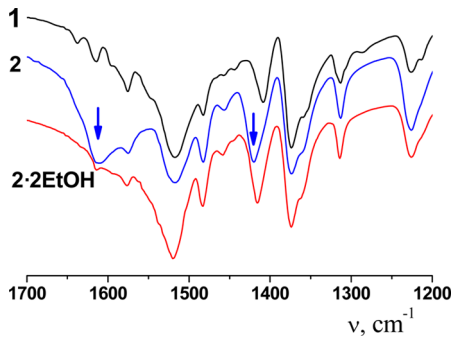


Figure 4. Fragments of IR spectra of **1**, **2**, and **2**·2EtOH. Bands in the IR spectrum of **2**, which differ from corresponding bands in spectrum of **1**, are shown by blue arrows.

to the new band, as can be concluded from comparison of the IR spectra of **1** and **2**. Thus, the occurrence of this new band can be associated with bidentate coordination of the pivalate (instead of monodentate coordination in **1**) or binding of O atom of the pivalate to the Co^{II} ion of the neighboring 1D chain[26a] or, less likely, coordination of the third pyridine group of 4-ptz to Co^{II} ion from another 1D chain [for example, for 4-ptz, bound to three Co^{II} ions, ν(C═C, C═N) was observed[31a] at 1612 cm^{-1}]. In addition, the change of the symmetric band at 1410 cm^{-1} in the IR spectrum of **1** to an asymmetric band at 1420 cm^{-1} in the case of **2** [probably, ν_s(COO)] is also consistent with bridging coordination of some of pivalate ions in **2** (instead of monodentate in **1**).[31] Resolvation of **2** by ethanol resulted in disappearance of the intense band at 1612 cm^{-1} and a red-shift of the band at ca. 1410 cm^{-1}, confirming reversible changes upon desolvation (this conclusion is consistent with analysis of the powder XRD data and magnetic data, *vide infra*).

Significant structural rearrangement of **1** upon desolvation was also confirmed by powder X-ray diffraction: the diffraction pattern of **2** was significantly different compared to the one expected for **1** or for a hypothetical isostructural desolvated form (Figure 5). However, these changes were reversible, and

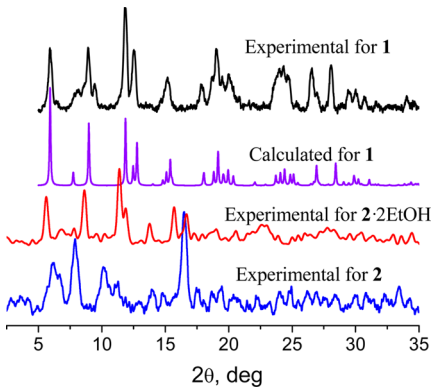


Figure 5. Powder X-ray diffraction patterns for **1**, **2**, and **2**·2EtOH. λ = 1.54 Å.

resolvation of **2** by ethanol led to formation of a phase that is similar to starting compound **1** and even some improvement of crystallinity (as can be concluded by signal-to-noise ratio) (Figure 5). In particular, intense reflection at 2θ = 5.9°, corresponding to the {110} plane in **1** passing through the Co^{II} ions (d = 15.0 Å), upon desolvation shifted to 6.2° (d = 14.2 Å) but returned back to 5.6° after resolvation (d = 15.8 Å). Similarly, reflection at 8.9° [corresponding to the {020} plane passing through triazine and noncoordinated pyridine groups, d = 9.9 Å] shifted to 7.9° upon desolvation (d = 11.2 Å) and almost returned to its initial position at resolvation (2θ = 8.65°, d = 10.2 Å).

Compound **2** possessed a porous lattice, which was confirmed by measurements of N_2 and H_2 adsorption at 78 K (Figure 6). Adsorption isotherms of this compound were typical for microporous sorbents. Sharp growth of nitrogen adsorption isotherm at low pressures was caused by micropore filling, and the micropore volume, estimated by the Dubinin–Radushkevich model,[32] was equal to 0.021 cm^3/g. This value is significantly lower than the volume, filled by solvent in **1** (about 0.15 cm^3/g, estimated by Platon assuming that crystal structure did not change upon elimination of coordinated ethanol), providing evidence for significant rearrangement of the crystal lattice and partial collapse of the porous structure. Estimation of Langmuir and BET surface gives values 80 and 62 m^2/g, respectively. There was some hysteresis between N_2 adsorption and desorption isotherms, which can be caused by the presence of small "windows" in pores or some rearrangement of sorbent upon pore filling.[32,33] Abrupt growth of the isotherm at P close to 760 Torr is caused by interparticle condensation of nitrogen. Hydrogen sorption capacity of **2** was 0.12% at 830 Torr, which seems to be close to the saturation value in the case of this compound.

In contrast to adsorption of gases at 78 K, isotherms of alcohol sorption (methanol and ethanol) at 295 K were not typical for classical adsorption and can provide evidence for structural rearrangements of **2** upon interaction with these substrates. In the case of both alcohols the volume, occupied by substrate, sharply grew at certain P/P_S (where P and P_S are current pressure and pressure of saturated vapor of substrate at 295 K, respectively), which can be caused by phenomenon similar to "gates opening".[2c,34] The quantity of absorbed methanol was close to one molecule per Co^{II} in the P/P_S range 0.1–0.32, but then it sharply increased, reaching more than 10 molecules per Co^{II} at P close to P_S. Ethanol absorption was less than 0.35 molecule per Co^{II} at P/P_S < 0.5, and then it increased to 3.7 molecules per Co^{II} at P/P_S = 0.94; however, decrease of pressure did not lead to elimination of this substrate, and about two molecules of ethanol appeared to be irreversibly captured. Such behavior can be explained by resolvation of **2** (transformation of **1**), which is consistent with the results of spectral studies, *vide supra*, and magnetic measurements, presented below.

Magnetic properties of compounds **1**, **2**, and samples resolvated by water or ethanol were characterized by molar magnetic susceptibility (χ_M) measurements in temperature range from 2 to 300 K. To avoid doubts regarding the influence of desolvation on magnetic properties, the sample of **1** was heated in vacuum at 155 °C after magnetic measurements, and the same capsule was measured again, to make sure that the quantity of sample did not change.

The $\chi_M T$ value for **1** at 300 K was 3.88 $cm^3\ mol^{-1}$ K, which significantly exceeded the theoretical spin-only value for an ion with $S = {}^3/_2$ (1.88 $cm^3\ mol^{-1}$ K). This difference could be caused by spin–orbit coupling (SOC) in the Co^{II} ion. The temperature decrease led to lowering of the $\chi_M T$ value, which was equal to 2.19 $cm^3\ mol^{-1}$ K at 2 K.

Energy levels of Co^{II} ion in axially distorted octahedral field can be treated by Hamiltonian (1), where spin–orbit coupling

DOI: 10.1021/acs.inorgchem.5b00179
Inorg. Chem. 2015, 54, 5232–5238

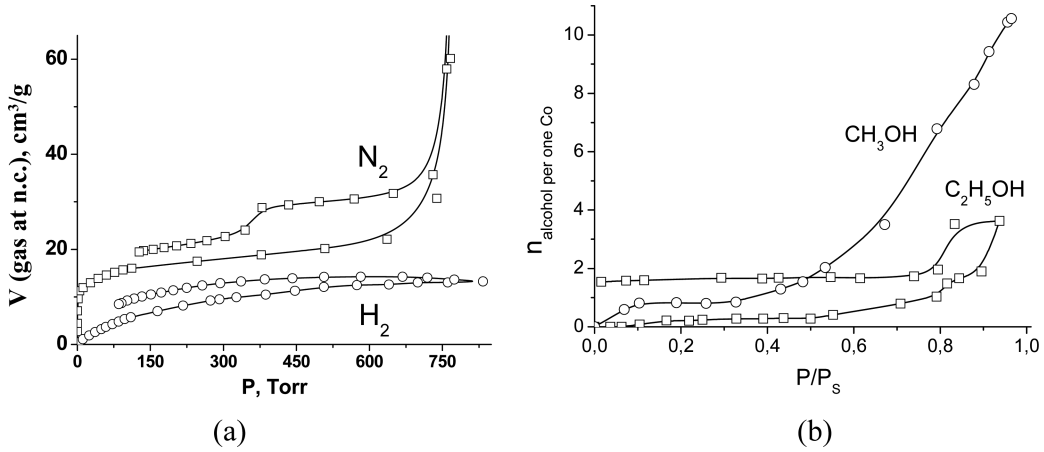


Figure 6. Isotherms of N_2 and H_2 sorption by **2** at 78 K (a), methanol and ethanol sorption by **2** at 295 K (b).

effects are considered to be incorporated in zero-field splitting (ZFS) parameter.[35]

$$\hat{H} = D_{Co}\left(\hat{S}^2_{Co_z} - \frac{1}{3}\hat{S}_{Co}(\hat{S}_{Co} + 1)\right) + g_{Co}\beta\hat{S}_{Co}H \quad (1)$$

D_{Co} is the ZFS parameter of Co^{II}, and other symbols have the usual meanings.

$\chi_M T$ versus T dependency for **1** was simulated using a model for an isolated ion based on the Hamiltonian (eq 1). Calculation was performed by full-matrix diagonalization in Mjöllnir software.[36] The best correspondence between experimental data for **1** and theoretically calculated curve was achieved for $D_{Co} = -60(3)$ cm^{-1}, $g_z = 2.77(5)$, $g_{xy} = 3.04(5)$ ($R^2 = 6.3 \times 10^{-5}$, Figure 7). The values of g_z and g_{xy} for **1** are close to the values reported previously.[35,37]

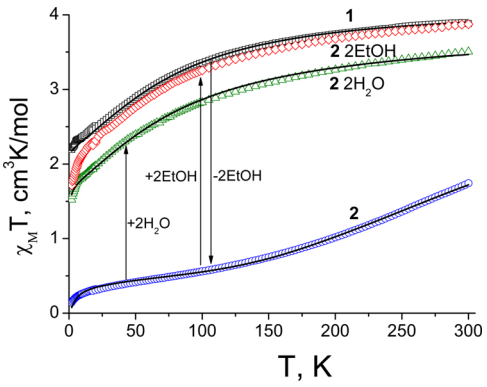


Figure 7. $\chi_M T$ vs T dependencies for compounds **1** (□), **2** (○), **2**·2EtOH (◊), and **2**·2H_2O (Δ) along with calculated curves, corresponding to the best fit parameters (see text). Arrows show interconversion pathways between compounds **1**, **2**, and resolvated forms.

The $\chi_M T$ value for compound **2** at 300 K was 1.74 cm^3 mol^{-1} K, which was lower than the expected spin-only value for a compound with $S = {}^3/_2$. Temperature lowering led to decrease of $\chi_M T$, which became equal to 0.143 cm^3 mol^{-1} K at 2 K (Figure 7). In the whole range of studied temperatures (from 2 to 300 K), $\chi_M T$ values for **2** were significantly lower than the respective values for **1**, so desolvation led to a significant (more than 2-fold) decrease of $\chi_M T$.

As it was shown by the data of TG and elemental analysis, heating of **1** led to elimination of two ethanol molecules, but electronic spectra could correspond to tetra- or pentacoordinated Co^{II} ions. Magnetic susceptibility of high-spin pentacoordinated Co^{II} complexes was found to be significantly higher than spin-only values.[38] So, a decrease of g-factors to the values close to 2 due to quenching of orbital magnetic momentum of Co^{II} seems not to be the probable reason for decrease of $\chi_M T$ of **1** upon desolvation, assuming that coordination number of Co^{II} in **2** is five. One of the other possible reasons is formation of new bonds between the Co^{II} ions and carboxyl or pyridine groups from the neighboring 1D chains, leading to antiferromagnetic exchange interactions between such ions. However, the attempts to fit a $\chi_M T$ versus T curve for **2** using models, which took into account exchange in the frames of models for a dimer of ions with $S = {}^3/_2$ and zero-field splitting effects,[35,39] a model of infinite chain described by the Fisher equation[40] for ions with $S = {}^3/_2$ (which should be suitable for Co^{II} in distorted tetrahedral environment, coordination number 4), were not successful. Finally, a $\chi_M T$ versus T curve for **2** could be fitted using a model of spin-crossover of Co^{II} with crossover temperature above 300 K (see Supporting Information for fitting details), so spin-crossover can be considered as one of the possible explanations for a $\chi_M T$ decrease.

Resolvation of **2** by ethanol (sample **2**·2EtOH) led to restoration of $\chi_M T$ almost to the level of compound **1**. $\chi_M T$ versus T curve for **2**·2EtOH could be fitted as superposition of $\chi_M T$ of the mixture, containing 97% of **1** and 3% of **2**.

Resolvation of **2** by water (formation of **2**·2H_2O) led to increase of $\chi_M T$ to the values, quite close to $\chi_M T$ of compound **1**. At 300 K $\chi_M T$ of **2**·H_2O was equal to 3.51 cm^3 mol^{-1} K (compared to 3.88 cm^3 mol^{-1} K in the case of **1**). Temperature lowering led to decrease of $\chi_M T$ of **2**·2H_2O to 1.52 cm^3 mol^{-1} K (compared to 2.19 cm^3 mol^{-1} K for **1**). In order to fit the $\chi_M T$ versus T curve for **2**·2H_2O, it was assumed that rehydration was complete (as supported by elemental analysis) and the pure compound $Co(Piv)_2(4\text{-ptz})(H_2O)_2$ formed. $\chi_M T$ versus T for **2**·2H_2O was fitted using the model based on the Hamiltonian (eq 1), with the difference that temperature-independent paramagnetism (tip) was introduced and possible interactions between the Co^{II} ions were taken into account within molecular field model (zJ' term).[40] The best correspondence of calculated curve and experimental data for **2**·2H_2O was achieved at $D = -57(6)$ cm^{-1}, $g_z = 2.44(7)$, $g_{xy} =$

DOI: 10.1021/acs.inorgchem.5b00179
Inorg. Chem. 2015, 54, 5232−5238

2.90(5), $zJ' = -0.04(1)$ cm^{-1}, tip = 8.0(5) × 10^{-5} (R^2 = 1.21 × 10^{-4}, Figure 7).

The magnitude of the $\chi_M T$ change upon desolvation/resolvation of **1** at room temperature is higher than the values reported for coordination polymers, where change was caused by reasons other than spin-crossover.[41] It seems that 2-fold change of room-temperature $\chi_M T$ can hardly be achieved by variation of zero-field splitting or spin−orbit coupling parameters only.

CONCLUSIONS

It was shown that magnetic susceptibility of 1D coordination polymer **1** could be decreased by more than 2 times in the whole temperature range between 2 and 300 K upon desolvation. Desolvation also led to a change in the sample's color and electronic spectra, which could be explained by change of Co^{II} coordination environment. It is important to note that these changes were reversible. While magnetic properties of the solvated form (**1**) could be fitted using a model for isolated Co^{II} ions with ZFS, temperature dependence of magnetic susceptibility for the desolvated form (**2**) was governed by more complex effects, among which spin-crossover cannot be excluded. The results of this study can be interesting for creation of magnetic materials with tunable properties, magnetic sensors, etc.

ASSOCIATED CONTENT

Supporting Information

Detailed description of spin-crossover model used for magnetic data fitting for compound **2**, additional figures of crystal structure of **1**, TG curve for **1**, IR and electronic spectra. Crystallographic data in CIF format. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00179.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: svk001@mail.ru.
*E-mail: lahcene.ouahab@univ-rennes1.fr.
*E-mail: ilerem@igic.ras.ru.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank to P. S. Yaremov for sorption measurements. This work was supported by a joint grant of the National Academy of Sciences of Ukraine (No. 03-03-14 (U)) and the Russian Foundation for Basic Research (No. 14-03-90423), Russian Academy of Sciences, and the National Academy of Sciences of Ukraine, CNRS, University of Rennes 1, Région Bretagne, and FEDER. M.A.K., G.G.A., and I.L.E. acknowledge the Russian Scientific Foundation (Project 14-23-00176) for financial support.

REFERENCES

(1) (a) He, Y.; Li, B.; O'Keeffe, M.; Chen, B. *Chem. Soc. Rev.* **2014**, *43*, 5618−5656. (b) Bhattacharjee, S.; Chenab, C.; Ahn, W.-S. *RSC Adv.* **2014**, *4*, 52500−52525. (c) Foo, M. L.; Matsuda, R.; Kitagawa, S. *Chem. Mater.* **2014**, *26*, 310−322. (d) Meek, S. T.; Greathouse, J. A.; Allendorf, M. D. *Adv. Mater.* **2011**, *23*, 249−267.

(2) (a) Dechambenoit, P.; Long, J. R. *Chem. Soc. Rev.* **2011**, *40*, 3249−3265. (b) Coronado, E.; Espallargas, G. M. *Chem. Soc. Rev.* **2013**, *42*, 1525−1539. (c) Horike, S.; Shimomura, S.; Kitagawa, S. *Nat. Chem.* **2009**, *1*, 695−704.

(3) (a) Wang, Y.; Yang, J.; Liu, Y.-Y.; Ma, J.-F. *Chem.—Eur. J.* **2013**, *19*, 14591−14599. (b) Cui, Y.; Chen, B.; Qian, G. *Coord. Chem. Rev.* **2014**, *273−274*, 76−86. (c) Roy, S.; Chakraborty, A.; Maji, T. K. *Coord. Chem. Rev.* **2014**, *273−274*, 139−164.

(4) (a) Shimizu, G. K. H.; Taylor, J. M.; Kim, S. *Science* **2013**, *341*, 354−355. (b) Goesten, M. G.; Juan-Alcañiz, J.; Ramos-Fernandez, E. V.; Gupta, K. B. S. S.; Stavitski, E.; van Bekkum, H.; Gascon, J.; Kapteijn, F. *J. Catal.* **2011**, *281*, 177−187. (c) Horike, S.; Umeyama, D.; Kitagawa, S. *Acc. Chem. Res.* **2013**, *46*, 2376−2384. (d) Solís, C.; Palaci, D.; Llabrés i Xamena, F. X.; Serra, J. M. *J. Phys. Chem. C* **2014**, *118*, 21663−21670.

(5) (a) Lastoskie, C. *Science* **2010**, *330*, 595−596. (b) Ravon, U.; Domine, M. E.; Gaudillère, C.; Desmartin-Chomel, A.; Farrusseng, D. *Stud. Surf. Sci. Catal.* **2008**, *174, Part A*, 467−470. (c) Ravon, U.; Savonnet, M.; Aguado, S.; Domine, M. E.; Janneau, E.; Farrusseng, D. *Microporous Mesoporous Mater.* **2010**, *129*, 319−329. (d) Shultz, A. M.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. *J. Am. Chem. Soc.* **2009**, *131*, 4204−4205. (e) Roberts, J. M.; Fini, B. M.; Sarjeant, A. A.; Farha, O. K.; Hupp, J. T.; Scheidt, K. A. *J. Am. Chem. Soc.* **2012**, *134*, 3334−3337.

(6) (a) Majumder, M.; Sheath, P.; Mardel, J. I.; Harvey, T. G.; Thornton, A. W.; Gonzago, A.; Kennedy, D. F.; Madsen, I.; Taylor, J. W.; Turner, D. R.; Hill, M. R. *Chem. Mater.* **2012**, *24*, 4647−4652. (b) Zheng, B.; Yun, R.; Bai, J.; Lu, Z.; Du, L.; Li, Y. *Inorg. Chem.* **2013**, *52*, 2823−2829. (c) Wiersum, A. D.; Chang, J.-S.; Serre, C.; Llewellyn, P. L. *Langmuir* **2013**, *29*, 3301−3309.

(7) (a) Ahmad, R.; Wong-Foy, A. G.; Matzger, A. J. *Langmuir* **2009**, *25*, 11977−11979. (b) Han, S.; Wei, Y.; Valente, C.; Lagzi, I.; Gassensmith, J. J.; Coskun, A.; Stoddart, J. F.; Grzybowski, B. A. *J. Am. Chem. Soc.* **2010**, *132*, 16358−16361. (c) Zhao, Z.; Ma, X.; Kasik, A.; Li, Z.; Lin, Y. S. *Ind. Eng. Chem. Res.* **2013**, *52*, 1102−1108.

(8) (a) Coronado, E.; Espallargas, G. M. *Chem. Soc. Rev.* **2013**, *42*, 1525−1539. (b) Kolotilov, S. V.; Kiskin, M. A.; Eremenko, I. L.; Novotortsev, V. M. *Curr. Inorg. Chem.* **2013**, *3*, 144−160. (c) Zhang, Z.; Xiang, S.; Zheng, Q.; Rao, X.; Mondal, J. U.; Arman, H. D.; Qian, G.; Chen, B. *Cryst. Growth Des.* **2010**, *10*, 2372−2375.

(9) (a) Kurmoo, M.; Kumagai, H.; Hughes, S. M.; Kepert, C. J. *Inorg. Chem.* **2003**, *42*, 6709−6722. (b) Lytvynenko, A. S.; Kolotilov, S. V.; Cador, O.; Gavrilenko, K. S.; Golhen, S.; Ouahab, L.; Pavlishchuk, V. V. *Dalton Trans.* **2009**, 3503−3509. (c) Cheng, X.-N.; Zhang, W.-X.; Lin, Y.-Y.; Zheng, Y.-Z.; Chen, X.-M. *Adv. Mater.* **2007**, *19*, 1494−1498. (d) Yoshida, Y.; Inoue, K.; Kurmoo, M. *Inorg. Chem.* **2009**, *48*, 10726−10736.

(10) (a) Kaneko, W.; Ohba, M.; Kitagawa, S. *J. Am. Chem. Soc.* **2007**, *129*, 13706−13712. (b) Ohkoshi, S.-I.; Arai, K.-I.; Sato, Y.; Hashimoto, K. *Nat. Mater.* **2004**, *3*, 857−861. (c) Ohkoshi, S.; Tsunobuchi, Y.; Takahashi, H.; Hozumi, T.; Shiro, M.; Hashimoto, K. *J. Am. Chem. Soc.* **2007**, *129*, 3084−3085.

(11) Coronado, E.; Giménez-Marqués, M.; Espallargas, G. M.; Brammer, L. *Nat. Commun.* **2012**, *828*, 1−8.

(12) (a) Kolea, G. K.; Vittal, J. J. *Chem. Soc. Rev.* **2013**, *42*, 1755−1775. (b) Medishetty, R.; Jung, D.; Song, X.; Kim, D.; Lee, S. S.; Lah, M. S.; Vittal, J. J. *Inorg. Chem.* **2013**, *52*, 2951−2957. (c) Qin, T.; Gong, J.; Ma, J.; Wang, X.; Wang, Y.; Xu, Y.; Shen, X.; Zhu, D. *Chem. Commun.* **2014**, *50*, 15886−15889. (d) Piromchoma, J.; Wannaritb, N.; Boonmaka, J.; Pakawatchaic, C.; Youngmea, S. *Inorg. Chem. Commun.* **2014**, *40*, 59−61.

(13) (a) Mohapatra, S.; Rajeswaran, B.; Chakraborty, A.; Sundaresan, A.; Maji, T. K. *Chem. Mater.* **2013**, *25*, 1673−1679. (b) Wriedt, M.; Yakovenko, A. A.; Halder, G. J.; Prosvirin, A. V.; Dunbar, K. R.; Zhou, H.-C. *J. Am. Chem. Soc.* **2013**, *135*, 4040−4050.

(14) (a) Manna, B.; Chaudhari, A. K.; Joarder, B.; Karmakar, A.; Ghosh, S. K. *Angew. Chem., Int. Ed.* **2013**, *52*, 998−1002. (b) Hou, S.; Liu, Q.-K.; Ma, J.-P.; Dong, Y.-B. *Inorg. Chem.* **2013**, *52*, 3225−3235. (c) Zhou, J.-M.; Shi, W.; Li, H.-M.; Li, H.; Cheng, P. *J. Phys. Chem. C* **2014**, *118*, 416−426.

DOI: 10.1021/acs.inorgchem.5b00179
Inorg. Chem. 2015, 54, 5232−5238

(15) (a) Gaspar, A. B.; Ksenofontov, V.; Seredyuk, M.; Gütlich, P. *Coord. Chem. Rev.* **2005**, *249*, 2661−2676. (b) Ohba, M.; Yoneda, K.; Agustí, G.; Muñoz, M. C.; Gaspar, A. B.; Real, J. A.; Yamasaki, M.; Ando, H.; Nakao, Y.; Sakaki, S.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 4767−4771. (c) Agustí, G.; Cobo, S.; Gaspar, A. B.; Molnár, G.; Moussa, N. O.; Szilágyi, P. Á.; Pálfi, V.; Vieu, C.; Muñoz, M. C.; Real, J. A.; Bousseksou, A. *Chem. Mater.* **2008**, *20*, 6721−6732.
(16) Fomina, I. G.; Aleksandrov, G. G.; Dobrokhotova, Zh. V.; Proshenkina, O. Yu.; Kiskin, M. A.; Velikodnyi, Yu. A.; Ikorskii, V. N.; Novotortsev, V. M.; Eremenko, I. L. *Russ. Chem. Bull.* **2006**, *55*, 1909−1919.
(17) Barrios, L. A.; Ribas, J.; Aromi, G. *Inorg. Chem.* **2007**, *46*, 7154−7162.
(18) Kahn, O. *Molecular Magnetism*; VCH Publishers Inc.: Weinheim, 1993.
(19) Bruker. *APEX2 Software Package*; Bruker AXS: Madison, WI, 2005.
(20) Sheldrick, G. M. *SADABS, Program for Scanning and Correction of Area Detector Data*; Göttingen University: Göttingen, Germany, 2003.
(21) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112−122.
(22) (a) Inokuma, Y.; Arai, T.; Fujita, M. *Nat. Chem.* **2010**, *2*, 780−783. (b) Inokuma, Y.; Yoshioka, S.; Ariyoshi, J.; Arai, T.; Hitora, Y.; Takada, K.; Matsunaga, S.; Rissanen, K.; Fujita, M. *Nature* **2013**, *495*, 461−467. (c) Inokuma, Y.; Kojima, N.; Arai, T.; Fujita, M. *J. Am. Chem. Soc.* **2011**, *133*, 19691−19693. (d) Chang, Z.; Zhang, D.-S.; Hu, T.-L.; Bu, X.-H. *Cryst. Growth Des.* **2011**, *11*, 2050−2053. (e) Tian, D.; Chen, Q.; Li, Y.; Zhang, Y.-H.; Chang, Z.; Bu, X.-H. *Angew. Chem., Int. Ed.* **2014**, *53*, 837−841. (f) Yi, F.-Y.; Zhang, J.; Zhang, H.-X.; Sun, Z.-M. *Chem. Commun.* **2012**, *48*, 10419−10421.
(23) (a) Pan, L.; Liu, H.; Lei, X.; Huang, X.; Olson, D. H.; Turro, N. J.; Li, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 542−546. (b) Kiskin, M. A.; Aleksandrov, G. G.; Bogomyakov, A. S.; Novotortsev, V. M.; Eremenko, I. L. *Inorg. Chem. Commun.* **2008**, *11*, 1015−1018.
(24) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.
(25) (a) Barrios, L. A.; Ribas, J.; Aromí, G.; Ribas-Ariño, J.; Gamez, P.; Roubeau, O.; Teat, S. J. *Inorg. Chem.* **2007**, *46*, 7154−7162. (b) Yoshida, J.; Nishikiori, S.; Kuroda, R. *Chem. Lett.* **2007**, *36*, 678−679.
(26) (a) Polunin, R. A.; Burkovskaya, N. P.; Kolotilov, S. V.; Kiskin, M. A.; Bogomyakov, A. S.; Sotnik, S. A.; Eremenko, I. L. *Russ. Chem. Bull.* **2014**, *63*, 252−266. (b) Hayami, S.; Kawamura, K.; Juhasz, G.; Kawahara, T.; Uehashi, K.; Maeda, Y. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **2002**, *379*, 371−376. (c) Kim, J.; Han, S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2002**, *58*, m521−m522.
(27) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: New York, 1984.
(28) Ohmori, O.; Kawano, M.; Fujita, M. *J. Am. Chem. Soc.* **2004**, *126*, 16292−16293.
(29) (a) Cussen, E. J.; Claridge, J. B.; Rosseinsky, M. J.; Kepert, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 9574−9581. (b) Navarro, J. A. R.; Barea, E.; Rodríguez-Diéguez, A.; Salas, J. M.; Ania, C. O.; Parra, J. B.; Masciocchi, N.; Galli, S.; Sironi, A. *J. Am. Chem. Soc.* **2008**, *130*, 3978−3984. (c) Nagarathinam, M.; Vittal, J. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 4337−4341. (d) Vittal, J. J. *Coord. Chem. Rev.* **2007**, *251*, 1781−1795.
(30) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*, 6th ed.; John Wiley & Sons, Inc.: New York, 2009, pp 64−67.
(31) (a) Biedermann, H.; Wichmann, K. *Z. Naturforsch, B: Anorg. Chem., Org. Chem.* **1974**, *29*, 360−362. (b) Díaz-Ortiz, A.; Hoz, A. de la; Moreno, A.; Sánchez-Migallón, A.; Valiente, G. *Green Chem.* **2002**, *4*, 339−343.
(32) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*, 2nd ed.; Academic Press: London, 1982, p 4.
(33) (a) Fletcher, A. J.; Thomas, K. M.; Rosseinsky, M. J. *J. Solid State Chem.* **2005**, *178*, 2491−2510. (b) Grünker, R.; Senkovska, I.; Biedermann, R.; Klein, N.; Lohe, M. R.; Müller, P.; Kaskel, S. *Chem. Commun.* **2011**, *47*, 490−492.
(34) (a) Kotani, R.; Kondo, A.; Maeda, K. *Chem. Commun.* **2012**, *48*, 11316−11318. (b) Cheng, Y.; Kajiro, H.; Noguchi, H.; Kondo, A.; Ohba, T.; Hattori, Y.; Kaneko, K.; Kanoh, H. *Langmuir* **2011**, *27*, 6905−6909.
(35) Ostrovsky, S. M.; Werner, R.; Brown, D. A.; Haase, W. *Chem. Phys. Lett.* **2002**, *353*, 290−294.
(36) Polunin, R. A.; Kolotilov, S. V.; Kiskin, M. A.; Cador, O.; Mikhalyova, E. A.; Lytvynenko, A. S.; Golhen, S.; Ouahab, L.; Ovcharenko, V. I.; Eremenko, I. L.; Novotortsev, V. M.; Pavlishchuk, V. V. *Eur. J. Inorg. Chem.* **2010**, 5055−5057.
(37) Litvinenko, A. S.; Mikhaleva, E. A.; Kolotilov, S. V.; Pavlishchuk, V. V. *Theor. Exp. Chem.* **2011**, *46*, 422−428.
(38) (a) Gerloch, M.; Kohl, J.; Lewis, J.; Urland, W. *J. Chem. Soc. A* **1970**, 3283−3296. (b) Mani, F.; Scapacci, G. *Inorg. Chim. Acta* **1980**, *38*, 151−155. (c) Stoppioni, P.; Morassi, R.; Zanobini, F. *Inorg. Chim. Acta* **1981**, *52*, 101−106.
(39) Mikhalyova, E. A.; Kolotilov, S. V.; Cador, O.; Zeller, M.; Trofimenko, S.; Ouahab, L.; Addison, A. W.; Pavlishchuk, V. V.; Hunter, A. D. *Dalton Trans.* **2012**, *41*, 11319−11329.
(40) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993.
(41) (a) Ferrando-Soria, J.; Ruiz-García, R.; Cano, J.; Stiriba, S.-E.; Vallejo, J.; Castro, I.; Julve, M.; Lloret, F.; Amorós, P.; Pasán, J.; Ruiz-Pérez, C.; Journaux, Y.; Pardo, E. *Chem.—Eur. J.* **2012**, *18*, 1608−1617. (b) Beauvais, L. G.; Shores, M. P.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 2763−2772. (c) Saha, R.; Kumar, S. *CrystEngComm* **2012**, *14*, 4980−4988.

DOI: 10.1021/acs.inorgchem.5b00179
Inorg. Chem. 2015, 54, 5232−5238