DOI: 10.1002/ange.201100880

Switchable Materials

Double Switching of a Magnetic Coordination Framework through Intraskeletal Molecular Rearrangement**

Dawid Pinkowicz, Robert Podgajny, Bartłomiej Gaweł, Wojciech Nitek, Wiesław Łasocha, Marcin Oszajca, Mariusz Czapla, Magdalena Makarewicz, Maria Bałanda, and Barbara Sieklucka**

Molecular systems which undergo reversible structural transformations on application of external stimuli and show additional strongly intertwined physical phenomena are fundamental to the generation of nanoscale multifunctional molecular devices. Multifunctional molecular systems are recognized as potentially revolutionary magnetic,[1] electric,[2] and magneto-optical[3] materials with possible applications in data storage/processing at the molecular level, as molecular switching devices in gas processing systems,[4] and molecular sensors.[5] In the field of porous molecular magnetic materials, the structural versatility of coordination chemistry has allowed the engineering of materials having novel topologies and remarkable properties.[6]

Magnetic coordination compounds with high magnetic ordering temperatures T_c exceeding the boiling point of liquid nitrogen are achievable in cyanido-[7] or tetracyanoethylene-bridged[8] molecular solids. Incorporation of relatively large organic molecules into the structures of the former led to hybrid systems showing multifunctionality but usually with significantly lower T_c due to the lower ratio of bridging/terminal CN ligands.[6c,9] Controlled dehydration of selected cyanido-bridged hybrids may result in substantial increase of T_c due to structural transformations involving terminal CN groups.[1a,b,d,f,j] However, there have been practically no reports on rational utilization of the terminal CN ligands and large organic molecules incorporated into the molecular framework to impart multifunctionality on these materials. Recently, we recognized the great potential of terminal CN groups and successfully exploited it in an Mn^{II}-imidazole–$[Nb^{IV}(CN)_8]$ magnetic spongelike material to reversibly increase its critical temperature from 25 to 62 K.[1f] Here we present a cyanido-bridged molecular magnet in which the coordinated organic molecules and terminal CN ligands are appropriately arranged to provide a unique coexistence of molecule-specific porosity and doubly switchable high ordering temperature in one material.

Orange platelike crystals of $\{[Mn^{II}(pydz)(H_2O)_2][Mn^{II}(H_2O)_2][Nb^{IV}(CN)_8]\cdot 2H_2O\}_n$ (**1**; pydz = pyridazine, $C_4H_4N_2$) were crystallized from an aqueous solution of $MnCl_2\cdot 4H_2O$, pyridazine, and $K_4[Nb(CN)_8]\cdot 2H_2O$ (for details, see Supporting Information). Samples of **1** can be stored in a closed vessel for several months without decomposition. The structure of **1** was determined by single-crystal X-ray diffraction analysis (space group $P2_1/c$; for details, see Supporting Information and CCDC 810685). The cyanido-bridged Mn_2Nb skeleton of **1** (Figure 1a) consists of Mn2-NC-Nb square-grid motifs (in the *bc* plane) cross-linked at Nb^{IV} centers by Mn1-NC-Nb ladders (along the *a* axis). Both Mn1 and Mn2 centers in **1** are octahedral (coordination number cn = 6), but their coordination spheres are different (Figure S2, top in the Supporting Information). Mn1 is coordinated by three nitrogen atoms of CN ligands (*mer*), one nitrogen atom of pyridazine (N11), and two aqua ligands in *trans* geometry. Mn1 belongs exclusively to the ladder motifs. The coordination sphere of Mn2, on the contrary, is purely inorganic and comprises four cyanido ligands in the equatorial plane and two aqua ligands in *trans* geometry. Mn2 belongs to the square-grid motifs. The only terminal CN ligand of the $[Nb(CN)_8]$ moiety (C4N4) is involved in a strong hydrogen bond with oxygen atom O11 of the aqua ligand coordinated to Mn1 (N4···Mn1 4.37 Å). The noncoordinating nitrogen atom of the pyridazine ligand (N16) is involved in a hydrogen-bond to the aqua ligand (O22) of Mn2 (N16···Mn2 4.19 Å; Figure 1a, bottom and Figure S3a in the Supporting Information). The local hydrogen-bonding system is completed by the H_2O molecule of crystallization (O2) bound to O22 and N4. Such an arrangement is very promising from the point of view of topotactic reactivity[1a,b,e,f,10] of the terminal CN and pyridazine ligands.

[*] Dr. D. Pinkowicz, Dr. R. Podgajny, Dr. B. Gaweł, Dr. W. Nitek, Prof. Dr. W. Łasocha, M. Oszajca, Prof. Dr. B. Sieklucka
Faculty of Chemistry Jagiellonian University
Ingardena 3, 30-060 Kraków (Poland)
Fax: (+48) 12-634-0515
E-mail: pinkowic@chemia.uj.edu.pl
barbara.sieklucka@uj.edu.pl
Homepage: http://www.chemia.uj.edu.pl/znmm/
Dr. M. Czapla, M. Makarewicz, Dr. M. Bałanda
H. Niewodniczański Institute of Nuclear Physics PAN
Radzikowskiego 152, 31-342 Kraków (Poland)
Dr. B. Gaweł
Ugelstad Laboratory, Department of Chemical Engineering
Norwegian University of Science and Technology (NTNU)
7491 Trondheim (Norway)

[**] We thank the Polish Ministry of Science and Higher Education (D.P. 0538/B/H03/2008/35, B.S. 1535/B/H03/2009/36, and M.Cz. 0087/B/H03/2008/34), the European Commission (MAGMANet project, contract no. NMP-3-CT-2005-515767), the European Regional Development Fund (POIG.02.01.00-12-023/08), and Jagiellonian University for financial support of this work.

Supporting information for this article (synthetic procedures, XRD data collection and structure refinement, details of the magnetic measurements, and other physical methods used for the characterization of the presented system) is available on the WWW under http://dx.doi.org/10.1002/anie.201100880.

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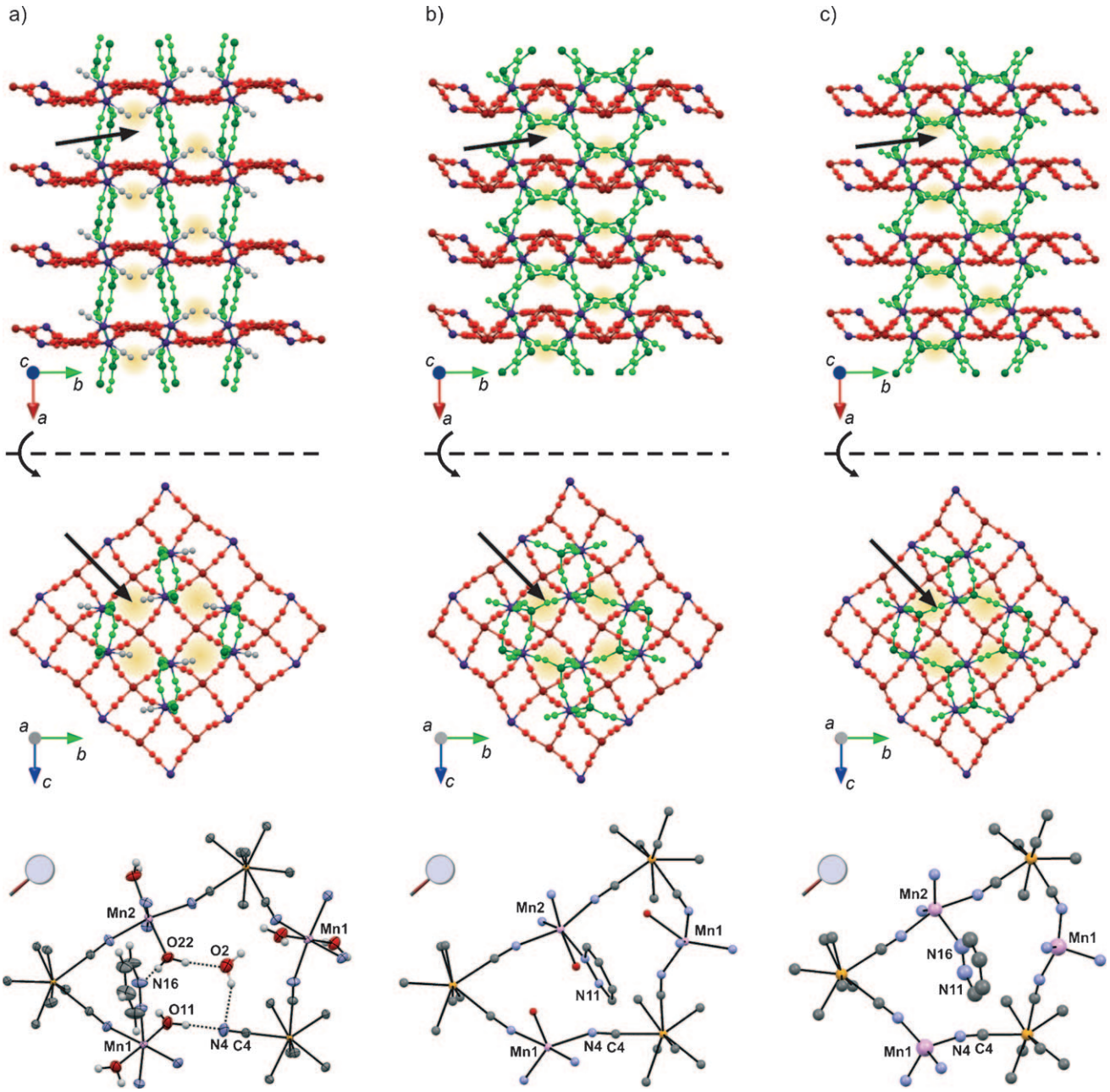

Figure 1. Packing diagrams of the cyanido-bridged frameworks of a) **1** and the dehydration products b) **1deh** and c) **1anh** (top: along the *c* axis, middle: along the *a* axis; pyridazine and water omitted for clarity). Mn2-NC-Nb square-grid motifs in the *bc* plane, Mn1-NC-Nb ladder motifs (**1**) transformed into the 3D substructure in **1deh** and **1anh** along the *a* axis. Structural details of molecular rearrangement (indicated by black arrows) are shown at the bottom.

After 4–6 h of dehydration the weight of **1** decreases by 12%, which corresponds to the loss of four water molecules per formula unit, and it is transformed into dehydrated $\{[Mn^{II}(pydz)(H_2O)][Mn^{II}(H_2O)][Nb^{IV}(CN)_8]\}_n$ (**1deh**). The structure of **1deh** was determined by X-ray powder diffraction (XRPD) analysis (space group $P2_1/c$; for details see Supporting Information and CCDC 810686). The crystallographic analysis revealed a huge unit-cell contraction of about 17% and the removal of water of crystallization and two aqua ligands on dehydration. The loss of water destabilizes the well-defined hydrogen-bonding network and allows closer approach of the terminal C4N4 ligand to Mn1 and subsequent formation of an additional bridge with a new N4–Mn1 distance of 2.27 Å (Figure 1b, bottom; Figure S3 in the Supporting Information). Simultaneously, the Mn1–N11 bond connecting pyridazine with Mn1 breaks, and new coordination bond Mn2–N16 is formed with a distance of 2.30 Å indicating well-defined translocation of the organic building block from Mn1 to Mn2. Such intraskeletal molecular rearrangement is unprecedented in the solid-state chemistry of polycyanide-based compounds. As a result of the local formation/cleavage of coordination bonds, the

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overall topology of the cyanido skeleton of **1** changes. The initial Mn1-NC-Nb ladders characteristic of **1** are smoothly transformed into a three-dimensional "subnetwork", which is still cross-linked at Nb centers with the unchanged Mn2-NC-Nb square grids (Figure 1b). In the dehydrated phase the coordination sphere of Mn1 adopts a strongly distorted square-pyramidal geometry (cn = 5) with four nitrogen atoms of the CN bridges and one oxygen atom of the remaining aqua ligand. The coordination geometry of Mn2 is still octahedral (cn = 6) due to translocation of the pyridazine ligand and consists of five N atoms (four CN ligands and one pyridazine ligand) and only one oxygen atom of the remaining aqua ligand (Figure 1b, bottom; Figure S2 in the Supporting Information).

Further dehydration (ca. 24 h) causes additional weight loss of about 6% corresponding to removal of the two remaining aqua ligands and subsequent formation of the anhydrous phase $\{[Mn^{II}_2(pydz)][Nb^{IV}(CN)_8]\}_n$ (**1anh**). The structure of **1anh** was determined by XRPD analysis in space group $P2_1/c$ but showed no further unit-cell contraction (for details see Supporting Information and CCDC 810687). Removal of the last two aqua ligands does not cause any further topological changes (Figure 1c). The coordination spheres of both Mn atoms adjust their geometries to the reduced coordination numbers (4 and 5). That of Mn1 is distorted tetrahedron with four N atoms of four cyanido bridges at a significantly shorter average interatomic distance of 2.09 Å characteristic of tetrahedral Mn^{II}.[7b,11] Mn2 adopts a distorted trigonal-bipyramidal geometry with four N atoms of CN ligands and one additional N atom of pyridazine (Figure 1, bottom; Figures S2 and S3d in the Supporting Information).

The above-described dehydration process is fully reversible. Rehydration of **1anh** occurs in two well-defined steps. In the first one, two water molecules are reabsorbed over one hour in humid air and **1deh** is fully restored (abbreviated **1reh** for convenience). The second and final step fully restores the original compound **1** after absorption of four water molecules per formula unit over approximately 20 h in water vapor (relative humidity 100%; fully rehydrated **1** is designated **1res**). The full dehydration/rehydration cycle was confirmed by XRPD and IR spectroscopy (Figure 2 and Figure S5 in the Supporting Information). Both methods show full restoration of **1deh** and **1** on rehydration, and the whole cycle can be performed repeatedly. The full transformation involves reversible removal/uptake of six water molecules per formula unit, intraskeletal rearrangement of the terminal CN and organic ligands, and huge unit-cell contraction/expansion.

Magnetic susceptibility measurements were used to determine the magnetic properties and magnetic ordering temperatures of **1** on dehydration. The temperature dependences of molar magnetic susceptibility $\chi(T)$ for powder samples of **1**, **1deh**, **1anh**, and **1res** at 1 kOe are presented in Figure 3. On cooling, $\chi(T)$ of **1** increases slowly, then rises abruptly to reach the highest rate point at about 43 K, and then saturate at low temperatures. The $\chi(T)$ curves of the dehydrated and anhydrous phases are roughly similar but the critical temperatures are much higher: 68 and 100 K, respectively. Such temperature dependences of χ suggest the presence of long-range magnetic ordering below the respective critical temperatures (see the Supporting Information multimedia AVI file for the behavior of **1anh** in the magnetic

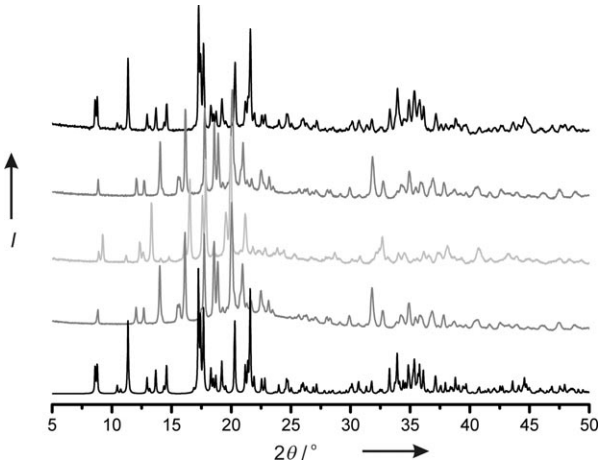

Figure 2. Experimental XRPD patterns of the products of the full dehydration/rehydration cycle (from bottom to top: **1**, **1deh**, **1anh**, **1reh**, and **1res**).

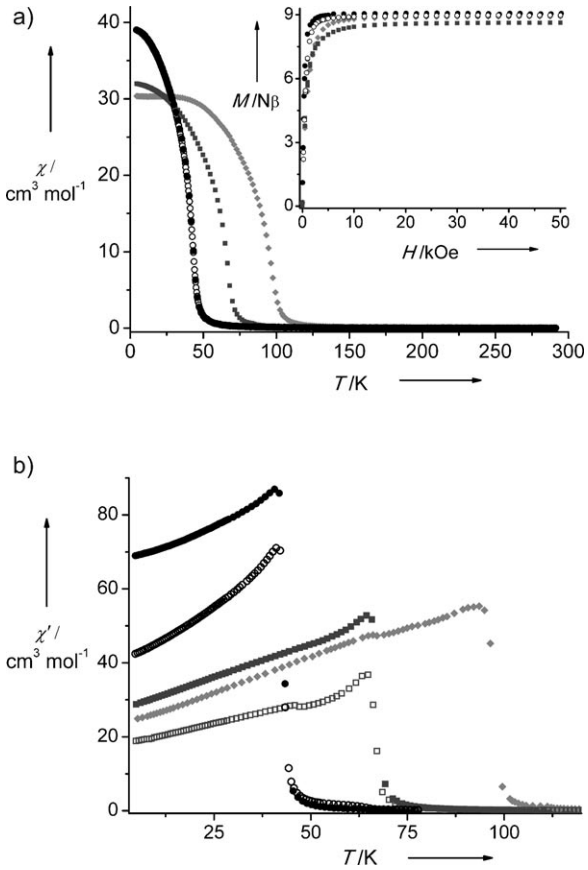

Figure 3. a) Molar magnetic susceptibility versus temperature at $H_{dc} = 1$ kOe and magnetization versus field at $T = 4.2$ K (inset) for **1**, **1deh**, **1anh**, and **1res**. b) In-phase ac magnetic susceptibilities versus temperature ($f = 125$ Hz, $H_{ac} = 3$ Oe) for the products of the dehydration/rehydration cycle of **1** showing the subsequent shifts of the ordering temperature. **1** (filled circles), **1deh** (squares), **1anh** (diamonds), **1reh** (empty squares), and **1res** (empty circles).

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field when cooled below 100 K). Experimental data of $\chi(T)$ above 94 K for **1**, 108 K for **1deh**, and 154 K for **1anh** were fitted by using the mean-field model for two sublattices (Figure S6 in the Supporting Information),[12] neglecting interactions other than Mn–Nb exchange [Eq. (1)]

$$\chi = \frac{(2C_{5/2} + C_{1/2})T + 4\lambda C_{5/2}C_{1/2}}{T^2 - 2\lambda^2 C_{5/2}C_{1/2}} \quad (1)$$

where $C_S = N_A g^2 S(S+1)\beta^2/3k_B$ are the Curie constants for respective spins, $\lambda = 6J_{MnNb}/(N_A g^2 \beta^2)$ is the molecular field constant, and other symbols have their usual meanings. The fitting gives the following average values of the g factor[13] and molecular field constant: $g = 2.03(1)$ and $\lambda = -35.7(8)$ mol cm^{-3} for **1**, $g = 2.00(2)$ and $\lambda = -49.4(9)$ for **1deh**, and $g = 2.00(3)$ and $\lambda = -71(2)$ for **1anh**. The negative values of the molecular field parameter λ indicate predominant antiferromagnetic Mn–Nb interaction in these compounds. The average values of the magnetic coupling constants J_{MnNb} for **1**, **1deh**, and **1anh** can be estimated from the formula defining the λ parameter. The J_{MnNb} values obtained for **1**, **1deh**, and **1anh** of $-9.2(3)$, $-12.4(4)$, and $-17.8(7)$ cm^{-1}, respectively, are in good agreement with those reported and predicted for other cyanido-bridged Mn_2Nb compounds.[1j,14]

Critical temperatures for all phases of the dehydration/rehydration cycle were confirmed by ac magnetic susceptibility measurements (Figure 3b and Figure S7 in the Supporting Information).

The $M(H)$ dependences for **1**, **1deh**, **1anh**, and **1res** at 4.2 K are presented in the inset of Figure 3a. The saturation magnetizations M_{sat} of 9.0 for **1**, 8.6 for **1deh**, 8.9 for **1anh**, and $9.0\,N\beta$ for **1res** strongly suggest magnetic structures with Mn magnetic moments antiparallel to Nb ones, whereby a saturation value of $9N\beta$ is expected (assuming isotropic $g = 2.0$ for both metal centers). The increase of $M(H)$ signals for all four samples is extremely fast, and about 90% of M_{sat} is reached below $H = 2$ kOe. No magnetic hysteresis is observed at 4.2 K.

The increase of the ordering temperature on two-step dehydration can be roughly explained by means of molecular field theory [Eq. (2)][15]

$$T_c = \frac{2\sqrt{n_{Nb}n_{Mn}}|J_{MnNb}|\sqrt{S_{Mn}(S_{Mn}+1)S_{Nb}(S_{Nb}+1)}}{3k_B} \quad (2)$$

where n_{Nb} is the number of nearest magnetic neighbors bridged to Nb, n_{Mn} the number of nearest magnetic neighbors bridged to Mn, S_{Mn} the effective spin for Mn^{II} (5/2), S_{Nb} the effective spin for Nb^{IV} (1/2), and k_B the Boltzmann constant (0.69372 cm^{-1} K^{-1}). In the first dehydration step an additional molecular connection between magnetic centers is formed, and hence the numbers of nearest neighbors n_{Nb} and n_{Mn} increase from 7 and 3.5 for **1** to 8 and 4 for **1deh**. This contributes significantly to the increase of the T_c of **1deh** by a factor of 1.143. The second contribution, which further increases T_c by a factor of 1.343, is due to the stronger magnetic coupling J_{MnNb} in **1deh** (higher average J_{MnNb} originates from the reduced coordination number of the Mn1 center in **1deh**[7b]). According to Equation (2), the predicted T_c for the dehydrated phase is 66 K, very close to the experimental value of 68 K.

In the second step the system does not undergo transformations changing the numbers of nearest neighbors. The shift of T_c from 68 to 100 K is fully attributed to the increase in coupling constant J_{MnNb}. This can be related to the dramatic reduction of the coordination numbers of both Mn^{II} centers followed by changes of their coordination geometries and significant shortening of the Mn1–N_{CN} bonds in the case of tetrahedral Mn1. All these structural features lead to better overlap of the corresponding magnetic orbitals of Mn^{II} and Nb^{IV} and strengthen the antiferromagnetic Mn–Nb interactions. Again the prediction of an increase of T_c on going from **1deh** to **1anh** by a factor of 1.438 is accurate and gives a value of 97 K, which is comparable with the experimental value of 100 K.

In conclusion, we have shown that it is possible to generate chemically sensitive frameworks that display high ordering temperatures influenced by the reversible exchange of guest molecules, and engineered a molecular magnet responsive to water vapor, namely, $\{[Mn^{II}(pydz)(H_2O)_2][Mn^{II}(H_2O)_2][Nb^{IV}(CN)_8]\cdot 2H_2O\}_n$ **1**. The structure of **1** is based on the flexible $[Nb^{IV}(CN)_8]$ metalloligand with one terminal CN group and blocking pyridazine ligand coordinated to an Mn center. Compound **1** undergoes spectacular structural transformation with large shifts of the critical temperature, which finally reaches 100 K. The unique features of the transformation are its two-step character and reversibility. The dramatic increase of the critical temperature in the first step is caused by the structural changes: hydrogen-bond cleavage, topotactic molecular bridge formation, and relocation of organic ligand. The further increase of the T_c in the second step is attributed to the decrease in coordination numbers of both Mn^{II} ions during complete dehydration. The organic ligands "trapped" within the pores of the compound play the role of a safety lock which prevents the framework from irreversible collapse on dehydration and guarantees reversibility.

The occurrence of the guest molecule driven magneto-structural switching requires a very specific molecular arrangement involving the guest and the magnetic centers. Such an arrangement can be achieved very efficiently through the self-assembly of well-known molecular systems showing long-range magnetic ordering in the presence of appropriate organic blocking ligands.

Experimental Section

CCDC 810685 (**1**), 810686 (**1deh**), and 810687 (**1anh**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: February 3, 2011
Published online: March 22, 2011

Keywords: cyanides · host–guest systems · magnetic properties · manganese · niobium

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