Inorganic Chemistry
Communication

Reversible Guest-Induced Magnetic and Structural Single-Crystal-to-Single-Crystal Transformation in Microporous Coordination Network {[Ni(cyclam)]₃[W(CN)₈]₂}ₙ

Beata Nowicka,*,† Michał Rams,‡ Katarzyna Stadnicka,† and Barbara Sieklucka†

Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland, and M. Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Krakow, Poland

Planar honeycomb-like coordination network {[Ni(cyclam)]₃-[W(CN)₈]₂}ₙ (cyclam = 1,4,8,11-tetraazacyclotetradecane) was obtained in the self-assembly reaction of [Ni(cyclam)]²⁺ and [W(CN)]₈³⁻. Its structure is characterized by void channels along the *a* axis. The compound shows reversible water adsorption in the temperature range of 25–40 °C with the formation of {[Ni-(cyclam)]₃[W(CN)₈]₂}ₙ·16nH₂O, accompanied by single-crystal-to-single-crystal transformation. The structural transformation significantly changes the character of intraplane magnetic exchange interactions.

To successfully compete with classical inorganic materials, coordination compounds must offer a variety of functions combined in one material, together with relative robustness and an easy synthetic route. From the point of view of multifunctionality, porosity is a very attractive feature of coordination frameworks.[1] Combining porosity with magnetic properties is a difficult task because high porosity in coordination frameworks is usually realized by the use of long bridging ligands, while magnetic exchange between metal centers is favored by shorter distances. This problem can be addressed by the use of organic radicals instead of diamagnetic molecules as bridging ligands.[2] Another approach is the incorporation of paramagnetic metal ions in both the linker and connector of the structure.[3] [Ni(cyclam)]²⁺ (cyclam = 1,4,8,11-tetraazacyclotetradecane) is known to react with hexacyanometalates to form two-dimensional honeycomb-like structures, which show ferromagnetic coupling at low temperatures and a changeable amount of water of crystallization.[4,5] We have previously observed reversible

dehydration in the materials obtained from [Ni(cyclam)]²⁺ and [Mᴵⱽ(CN)₈]⁴⁻ (M = Mo, W).[6] This prompted us to investigate the reaction of [Ni(cyclam)]²⁺ with [Mⱽ(CN)₈]³⁻. Here we report on microporous magnetic coordination network {[Ni(cyclam)]₃[W(CN)₈]₂}ₙ.

Slow diffusion of an ethanolic solution of [Ni(cyclam)]-Cl₂, prepared in situ from NiCl₂ and cyclam, into an aqueous solution of Na₃[W(CN)]₈ over 2 weeks resulted in a brown crystalline product of the formula {[Ni(cyclam)]₃[W(CN)₈]₂}ₙ·pnH₂O·qnC₂H₅OH (p = 14−15; q = 0.5−1). The amount of solvents of crystallization (determined by elemental analysis)[7] varied, depending on the exact synthesis conditions and the size of the crystals. After drying at 40 °C for 20 min, anhydrous product {[Ni(cyclam)]₃[W(CN)₈]₂}ₙ (**1**) was obtained. When exposed to humid air at room temperature, **1** adsorbed a stoichiometric amount of water, giving {[Ni-(cyclam)]₃[W(CN)₈]₂}ₙ·16nH₂O (**2**). The hydration−dehydration process is fully reversible in the temperature range of 25−40 °C and can be repeated several times without noticeable damage to the crystal structure, which was confirmed by single-crystal X-ray diffraction measurements. Thermogravimetric analysis of **1** (Figure S1 in the Supporting Information) shows that the compound is stable to 180 °C when the first decomposition process begins with a sharp peak in differential thermal analysis at 208 °C and a mass loss of 5.1% corresponding to the removal of three CN groups. At 330 °C, the final decomposition occurs. Differential scanning calorimetry measurement on **2** (Figure S2 in the Supporting Information) reveals an endothermal process between −30 and +45 °C with a minimum at 29 °C. The heat of the process estimated at 706 kJ mol⁻¹ gives 44 kJ mol⁻¹ per water molecule, which is comparable to the sublimation enthalpy of water of 50 kJ mol⁻¹.

* To whom correspondence should be addressed. E-mail: burda@chemia.uj.edu.pl.
† Faculty of Chemistry.
‡ M. Smoluchowski Institute of Physics.

(1) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.
(2) Maspoch, D.; Ruiz-Molina, D.; Wurst, K.; Domingo, N.; Cavallini, M.; Biscarini, F.; Tejada, J.; Rovira, C.; Veciana, J. *Nat. Mater.* **2003**, *2*, 190.
(3) Yanai, N.; Kaneko, W.; Yoneda, K.; Ohba, M.; Kitagawa, S. *J. Am. Chem. Soc.* **2007**, *129*, 3496.
(4) Ferlay, S.; Mallah, T.; Vaissermann, J.; Bartolome, F.; Veillet, P.; Verdaguer, M. *Chem. Commun.* **1996**, 2481.
(5) Colacio, E.; Dominguez-Vera, J. M.; Ghazi, M.; Kivekäs, R.; Lloret, F.; Moreno, J. M.; Stoeckli-Evans, H. *Chem. Commun.* **1999**, 987.
(6) Nowicka, B.; Hagiwara, M.; Wakatsuki, Y.; Kisch, H. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 441.
(7) Anal. Calcd for C₄₇H₁₀₅N₂₈O₁₆Ni₃W₂ (n = 14; m = 0.5): C, 30.44; H, 5.71; N, 21.15. Found: C, 30.55; H, 5.48; N, 21.12. IR (ν_{CN}): 2179m, 2139w, 2107w.
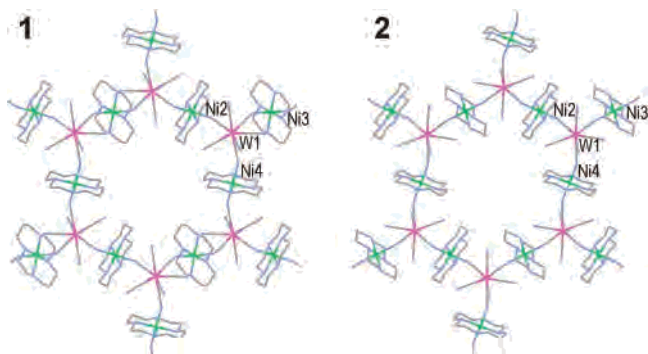
Figure 1. Repeating motif in the structures of **1** and **2**. View along the *a* axis. Water molecules are omitted for clarity. Selected distances [Å] and angles [deg]: W1−Ni2 5.285 (**1**) and 5.290 (**2**), W1−Ni3 5.181 (**1**) and 5.282 (**2**), W1−Ni4 5.233 (**1**) and 5.272 (**2**), W1−C−N(mean) 176.4 (**1**) and 176.8 (**2**), Ni2−N11−C11 157.9(5) (**1**) and 161.0(6) (**2**), Ni3−N13− C13 149.7(4) (**1**) and 159.5(6) (**2**), Ni4−N16−C16 158.1(4) (**1**) and 160.1- (7) (**2**).
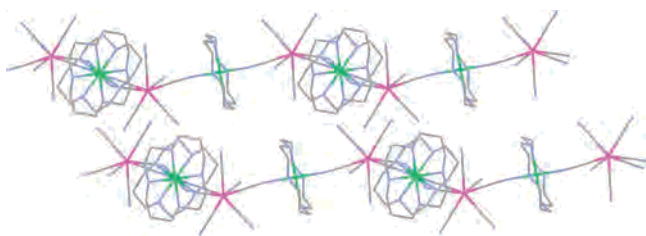

Figure 2. Structure of **1**. View along the *b* axis.

The structure of **2** was determined after sudden freezing of the crystal to 100 K. Then the temperature was raised to 313 K to remove water, and the crystal was cooled again to 100 K in the flow of dry nitrogen and the structure of anhydrous compound **1** determined. The structure of **1**[8] consists of honeycomb-like layers spreading in the (101) plane (Figure 1 and S3 in the Supporting Information), with each W ion positioned in grid nodes and surrounded by three CN−Ni−NC connectors, binding it to neighboring nodes. The W−C−N bonds are nearly linear (173.3−178.9°), while Ni−N−C are significantly bent (149.7−158.1°), allowing the Ni−cyclam planes to fit best into the available space. The structure resembles those observed for Ni(cyclam) hexacyanochromate(III)[4] and -ferrate(III);[5] however, a side view (Figure 2) reveals a marked difference: while {[Ni- (cyclam)]$_3$[M(CN)$_6$]$_2$}$_n$ planes are corrugated, forming a stairlike structure with right angles between the folds, {[Ni- (cyclam)]$_3$[W(CN)$_8$]$_2$}$_n$ planes are flattened, with an angle between the folds of 146°. This alteration can be attributed to the difference in the geometrical arrangement of cyano ligands in hexa- and octacyanometalates. The presence of five terminal CN ligands enables the formation of hydrogen bonds to NH groups of cyclam. Eight such bonds additionally link neighboring Ni and W ions, enhancing the stability of the structure (Figure S4 in the Supporting Information). In contrast, the interplane interactions are realized by only two hydrogen bonds. The striking features of the structure are empty channels of 5.4 Å diameter, going through the layers along the *a* axis. The structure of **2**[11] (Figure 1) shows that during the process of water inclusion the bond structure and the conformation of cyclam are retained. The water molecules are located exclusively in the channels, forming a net of
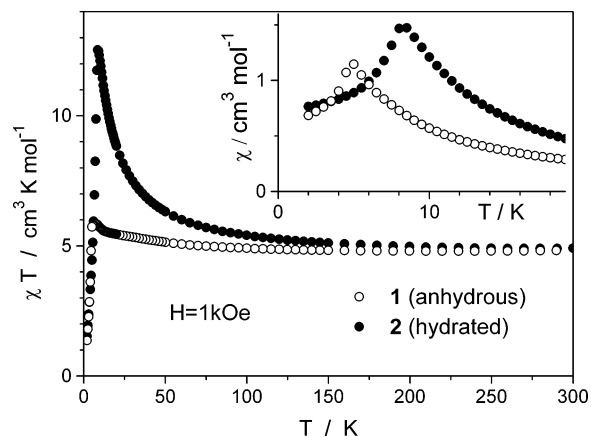

Figure 3. Temperature dependence of χT for **1** and **2**. Inset: low- temperature χ vs T showing distinct antiferromagnetic phase transitions.

hydrogen bonds to N atoms of selected terminal cyano groups. The incorporation of water molecules causes adapta- tion of the structure, which is reflected by the difference in the cell parameters.[8,11] The most noticeable change is the elongation in the [2, −2, 1] direction. The angle of the most bent Ni3−N−C cyano bridge changes from 149.7° to 159.5°, becoming more linear. It causes visible tilting of the cyclam plane on Ni3 (Figure 1) and breaking of two out of the eight intraplane hydrogen bonds. The increase in the cell volume of 2.6% is attributed to the increase in the space occupied by water: 30.3% of the crystal volume for **2** compared to 26.9% void space in **1** (calculated by *PLATON*[12]).

Magnetic measurements[13,14] of **2** were performed on a powdered sample encapsulated in gelatin and inserted into the magnetometer at 150 K to ensure that the water content was intact during purging of the sample space. The suscep- tibility was recorded upon cooling in the field of 1000 Oe (Figure 3), and then the magnetization was measured at 2 K from 50 to 0 kOe (Figure 4). Then the same sample was annealed in the magnetometer (at low pressure of He gas)

(8) Crystal structure of **1**: C$_{46}$H$_{72}$N$_{28}$Ni$_3$W$_2$, fw = 1561.15, triclinic, space group P$\bar{1}$, a = 9.0677(6) Å, b = 15.2210(10) Å, c = 15.8788(10) Å, α = 60.446(5)°, β = 87.419(4)°, γ = 89.916(3)°, V = 1904.0(2) Å^3, Z = 1, D$_{calc}$ = 1.362 g·cm^{-3}, T = 100(2) K. Structure solution: *SIR92*.[9] Least-squares refinement on F^2 using anisotropic thermal parameters for non-H atoms.[10] H atoms were calculated in idealized positions and included in the refinement in a riding model. R1 = 0.0519, wR2 = 0.1099, and GOF = 1.021 for 9397 reflections.
(9) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.
(10) Sheldrick, G. M. *SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.
(11) Crystal structure of **2**: C$_{46}$H$_{104}$N$_{28}$O$_{16}$Ni$_3$W$_2$, fw = 1849.40, triclinic, space group P1, a = 8.7270(2) Å, b = 15.2575(4) Å, c = 15.9146(6) Å, α = 67.406(2)°, β = 87.077(1)°, γ = 87.160(1)°, V = 1952.85- (10) Å^3, Z = 1, D$_{calc}$ = 1.573 g·cm^{-3}, T = 100(2) K. Structure solution: *SIR92*.[9] Least-squares refinement on F^2 using anisotropic thermal parameters for non-H atoms.[10] H atoms were calculated in idealized positions and included in the refinement in a riding model, except for water H atoms, which were ignored. O atoms of water molecules, O2−O9, were disordered and were given an occupancy of 0.2−0.5. R1 = 0.0632, wR2 = 0.1400, and GOF = 1.199 for 11 305 reflections.
(12) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.
(13) Magnetic measurements on a MPMS-5XL squid magnetometer. The results were carefully corrected for the diamagnetic backgrounds coming from the gelatin capsule, its water content, and the calculated sample diamagnetism.[14]
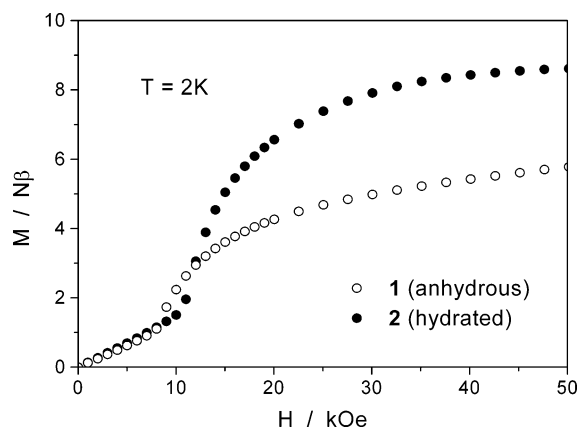(14) Kahn, O. *Molecular magnetism*; Wiley-VCH: New York, 1993.

Figure 4. Magnetization of **1** and **2**.

at 320 K for 15 min, giving anhydrous compound **1**, and the same measurement sequence was repeated (Figures 3 and 4). We have also checked that, following the exposition of **1** sample to humid air at room temperature for 2 days, the originally measured data points of **2** were again reproduced. Finally, the high-temperature susceptibility of **2** was obtained by placing the sample in the magnetometer and evacuating the sample space at 300 K. The low-temperature results were the same as those for frozen **2**, proving that evacuation did not remove water. The high-temperature limit of χT for both **2** and **1** is about 4.8 cm^3 K mol^{-1} at 300 K, which is close to the theoretical value of 4.4 cm^3 K mol^{-1} calculated assuming per formula unit three Ni^{II} ($S = 1$; $g_{Ni} = 2.2$) and two W^V ($S = {}^1/_2$; $g_W = 2.0$). As the temperature is lowered, χT increases significantly for **2** but only slightly for **1**. In both cases, a sharp peak is observed in the $\chi(T)$ curve, at 8.0 K (**2**) and 5.0 K (**1**), which is characteristic for the phase transition to an antiferromagnetically ordered structure. The magnetization data obtained at 2 K show upturns at 12 kOe (**2**) and 9 kOe (**1**), which also is typical for the ordered antiferromagnetic structure undergoing a spin−flip transition. At 50 kOe, the magnetic moment of **2** is almost saturated at a value close to the predicted 8.6β per formula unit of ferromagnetically coupled spins, whereas the curve for **1** is much lower and far from saturation. This striking difference in magnetic behavior between hydrated and anhydrous compounds reflects the structural changes. It is known that the sign and strength of the exchange interaction mediated through −CN− bonds strongly depends on the bridge geometry. The density functional theory calculations for Ni^{II}−N−C−Cr^{III} predict a ferromagnetic interaction between two metal ions when Ni−N−C angles are greater than about 148° and an effective antiferromagnetic exchange for more bent cyanide bridges.[15] A similar situation takes place in the case of Ni^{II}−N−C−W^V bonds;[16] the limiting angle may, however, be different. For **1**, the intraplane exchange interactions can be divided into two groups because of significantly different Ni−N−C angles: J_1 for Ni2−N11−

C11−W1 (157.9°) and Ni4−N16−C16−W1 (158.1°) and J_2 for Ni3−N13−C13−W1 (149.7°). In the hydrated compound **2**, the Ni3−N13−C13 bridge is less bent (159.5°) and, consequently, J_2 becomes close to J_1. The ordering temperature and the spin−flip field are determined in the main respect by the weak interplane interaction J' because three-dimensional exchange paths are necessary to obtain a long-range magnetic ordering. In the case of **2**, the positive J_1 and J_2 and negative J' lead to a structure with all spins in one plane ferromagnetically ordered, while two neighboring planes have opposite magnetization directions. In this situation, following the spin−flip transition, the magnetic moment gradually saturates at the maximal value with all spins aligned parallel. On the contrary, in **1** the constants J_1 and J_2 are of opposite signs, which leads to a ferromagnetic or canted antiferromagnetic structure within every plane. Thus, following the spin−flip transition of whole planes, spins within one plane still need to be rotated by a much stronger field to obtain full saturation of 8.6β. The temperature dependence of χT above the phase transition is a net result of all of the J_1, J_2, and J' interactions. Thus, dominant ferromagnetic interactions are observed for **2**, while for **1**, the effects of J_1 and J_2 incidentally almost cancel. The model sketched above qualitatively explains differences between magnetic properties of **1** and **2**. The numerical estimation of J_1 and J_2 from magnetic data is not straightforward because exchange paths create the infinite two-dimensional magnetic network. The net exchange interaction can be obtained by fitting $1/\chi(T)$ with the Curie−Weiss dependence $1/\chi = (T - \theta_{CW})/C$. Using the data above 50 K, we obtained $\theta_{CW} = 14$ K (**2**) and 6 K (**1**).

$\{[Ni(cyclam)]_3[W(CN)_8]_2\}_n$ is a rare example of a coordination network that shows reversible structural single-crystal-to-single-crystal transformation upon inclusion of water and can be classified as a third-generation microporous material.[1] Adsorbing water, the structure expands to accommodate more guest molecules; however, the changes are small enough to allow the compound to retain its crystalline form. Interestingly, the seemingly subtle structural transformation causes significant changes in the magnetic structure: from antiferromagnetically to ferromagnetically ordered planes. The unusual dynamic stability of the framework and easy way of tuning magnetic properties, together with a straightforward synthetic procedure, make $\{[Ni(cyclam)]_3$-$[W(CN)_8]_2\}_n$ an interesting candidate for potential applications. The possibility of different guest molecule incorporations is currently under study.

Supporting Information Available: X-ray crystallographic files in CIF format for **1** and **2** and Figures S1−S4. This material is available free of charge at http://pubs.acs.org.

IC701168X

(15) Marvaud, V.; Herrera, J.-M.; Barilero, T.; Tuyeras, F.; Grade, R.; Sciuller, A.; Decroix, C.; Cantuel, M.; Desplanches, C. *Monatsh. Chem.* **2003**, *134*, 149. (b) Toma, L.; Toma, L. M.; Lescouëzec, R.; Armentano, D.; De Munno, G.; Andruh, M.; Cano, J.; Lloret, F.; Julve, M. *Dalton Trans.* **2005**, 1357.

(16) Visinescu, D.; Desplanches, C.; Imaz, I.; Bahers, V.; Pradhan, R.; Villamena, F. A.; Guionneau, P.; Sutter, J.-P. *J. Am. Chem. Soc.* **2006**, *128*, 10202.