Sponge-like Reversible Transformation of a Bimetallic Cyanometallate Polymer

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ABSTRACT: Two new cyano-bridged Ru−Cu polymers, the one-dimensional chain $\{[Cu(tnH^+)_2(H_2O)_2][Ru(CN)_6] \cdot 2H_2O\}_\infty$ (**1**) (where tn = 1,3-diaminopropane) and the pseudo-two-dimensional network $\{[Cu(tnH^+)_2][Ru(CN)_6]\}_\infty$ (**2**), have been prepared and fully characterized. Compounds **1** and **2** both crystallize in the same monoclinic space group, $P2_1/n$. Complex **1** was characterized by single crystal X-ray analysis, and compound **2** was characterized by X-ray powder diffraction (XRPD) techniques. Compound **2** was prepared by dehydration of **1**; structure **1** can be regenerated by rehydration of **2**. The "sponge-like" behavior of this molecular transformation is accompanied by a color change and has been shown by in situ X-ray powder diffraction and immersion calorimetry to be completely reversible.

Introduction

The design and synthesis of nanoporous materials mimicking zeolities has drawn a great deal of attention due to their potential applications as gas adsorbents,[1–4] ion-exchanger,[5–8] chemical adsorbents,[4,9–11] and heterogeneous catalysts.[11,12] Some examples of these materials include cyano-bridged coordination polymers prepared by assembling cyanometallate anions [for example, $M(CN)_2^{2-}$ (M = Au, Ag), $Ni(CN)_4^{2-}$, $M1(CN)_6^{3-}$ (M1 = Fe(III), Cr), $M2(CN)_6^{4-}$ (M2 = Fe(II), Ru)] and transition metal complexes as building blocks. Since copper(II) ion exhibits great stereochemical plasticity, a variety of compounds with hexacyanometalates can be prepared, using ligands such as 1,2-ethylendiamine (en) $Cu(en)_2[Au(CN)_4]_2$,[13] cyclohexane-1,2-diamine (chxn) $[Ni(cis\text{-}chxn)_2]_3[Fe(CN)_6]_2$,[14] or 1,3-diaminopropane (tn) $[Cu(tn)]_3[Cr(CN)_6]_2 \cdot 3H_2O$.[15] Cyano groups are useful owing to their ability to link metal atoms for the construction of multidimensional systems. Currently, hexacyanometallates have been used to develop a wide range of architectures, some of which exhibit interesting magnetic properties.[16–19] The Prussian blue family are among the earliest known coordination compounds, and their diverse magnetic and electronic properties have been extensively studied.[20] Up till now the gas sorption properties of such systems have remained largely unexplored.[21] Only a few examples of cyano-bridged inorganic coordination polymers based on hexacyanometallates have been reported as being porous materials.[22–24] We have focused our efforts on the study of crystalline materials since the attainment of well-defined structures is intimately linked to an understanding of the design, synthesis, and properties of these materials.

Experimental Section

Elemental analyses of carbon, hydrogen, and nitrogen were performed by the Microanalysis Service of the Laboratory of Pharmaceutical and Organical Propedeutical Chemistry at the University of Geneva (Geneva, Switzerland). Infrared spectra were measured using KBr pellets in the interval of $4000-400$ cm^{-1} and were recorded on a Perkin-Elmer 1720X FT-IR spectrometer. Thermogravimetric (TG) analyses were carried out using a Mettler 4000 module. DSC measurements were done with a modified differential scanning calorimeter (Mettler Toledo DSC 822e). Samples were introduced in a closed aluminum oxide crucible and heated at a rate of 0.1 °C min^{-1} under nitrogen at atmospheric pressure. Immersion calorimetry experiments were carried out at 293 K on samples of $0.150-0.200$ g using a TIAN-CALVET type calorimeter.[25,26] The outgassed samples were placed in the calorimetric cells, which were immersed in a water bath controlled by a thermo-regulator system LUDA MS. The thermal flow was provided by 180 thermocouples of Cu/constantan connected to a nanovoltmeter PREMA 8017. The integral of the curve, $V = f(t)$, is proportional to the energy generated during the immersion process, $\Delta_i H$. The normal calibration of the calorimetry system was carried out with an electric resistance. The accuracy varies between 4 and 5% depending on the absolute energy liberated in the process and on the amount of solid used.

General Synthetic Procedures

$\{[Cu(tnH^+)_2(H_2O)_2][Ru(CN)_6] \cdot 2H_2O\}_\infty$ **(1).** 1,3-Diaminopropane (tn) (1.0 mL, 12.0 mmol) was added under aerobic conditions to a concentrated aqueous solution (10 mL) of $CuSO_4 \cdot 5H_2O$ (2.9g, 12.0 mmol) with continuous stirring, leading to the immediate precipitation of a green powder. After addition of an aqueous solution of potassium hydroxide (12 mmol) the resulting dark-blue solution was warmed (60 °C for about 10 min) and then filtered in order to remove the small amount of precipitate that remained. An aqueous warm solution (10 mL) of $K_4[Ru(CN)_6]$ (2.47 g, 6 mmol) was then added with continuous stirring. Further evaporation afforded hexagonal dark blue crystals of **1** after several weeks under aerobic conditions; these were filtered and air-dried. All the operations for the synthesis were carried out in the dark to avoid the decomposition of $[Ru(CN)_6]^{4-}$. Yield: 80%. The results of elemental analyses (found C, 26.36; H, 5.51; N, 25.67. $C_{12}H_{30}N_{10}Cu_1Ru_1O_4$ requires C, 26.54; H, 5.57 N, 25.79%) were consistent with the formula of the sample used for X-ray analysis.

$\{[Cu(tnH^+)_2][Ru(CN)_6]\}_\infty$ **(2).** Compound **2** was obtained as a green powder by heating crystals of complex **1** to 120 °C. The results of elemental analyses for compound **2** (found C, 30.36; H, 4.52; N, 29.61. $C_{12}H_{22}N_{10}Cu_1Ru_1$ requires C, 30.60; H, 4.71 N, 29.74%) were consistent with the formula of the sample used for powder diffraction analysis.

X-ray Structural Determination. A blue hexagonal shaped crystal of **1** (0.45 × 0.42 × 0.05) was mounted on a Stoe Mark

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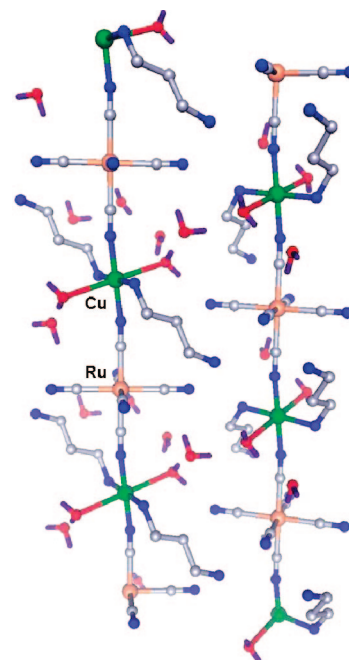† University of Neuchâtel.
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Table 1. Crystal and Structure Refinement Data for 1 (single crystal) and 2 (powder)

	1	2
formula	$C_{12}H_{30}N_{10}O_4CuRu$	$C_{12}H_{22}N_{10}CuRu$
Mw	543.07	470.99
λ (Å)	0.71073	1.54051
T (K)	173	293
crystal size, mm	$0.45 \times 0.42 \times 0.05$	
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	10.3003(9)	9.7292(5)
b (Å)	9.0112(8)	12.0350(5)
c (Å)	12.0042(11)	8.2574(4)
β (°)	105.136(7)	111.701(3)
V (Å^3)	1075.55(17)	898.34(4)
Z	2	2
ρ_{calcd} (Mg/m^3)	1.677	1.741
μ (mm^{-1})	1.730	8.41
reflns collected	12515	
indep reflns	2897	
indep reflns $> 2\sigma(I)$	2318	1078
no. of param	141	84
R1^a [$I > 2\sigma(I)$]	0.027	
wR2^b [$I > 2\sigma(I)$]	0.0574	
no. contributing reflns		1078
no. of struct param		84
no. of restraints		70
R_{wp}^c		0.0716
R_p^d		0.055
R_F^e		0.125
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.576/−0.741	1.041/−0.728

^{a} R1 $= \Sigma|F_o| - |F_c|/\Sigma|F_o|$. ^{b} wR2 $= [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$. ^{c} $R_{wp} = [\Sigma w(I_o - I_c)^2 / \Sigma w I_o^2]^{1/2}$. ^{d} $R_p = \Sigma|I_o - I_c|\Sigma I_c$. ^{e} $R_F = \Sigma|F_o| - |F_c|/\Sigma|F_o|$.

II-Imaging Plate Diffractometer system equipped with a graphite-monochromator. Data collection was performed using Mo Kα radiation ($\lambda = 0.71073$ Å) at 173 K. The structure was solved by direct methods using the program SHELXS-97[27] and refined by full matrix least-squares on F^2 with SHELXL-97.[28] All non-hydrogen atoms were refined anisotropically. The water hydrogen atoms in 1 were derived from difference Fourier Maps and were refined isotropically, while the remaining hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters.
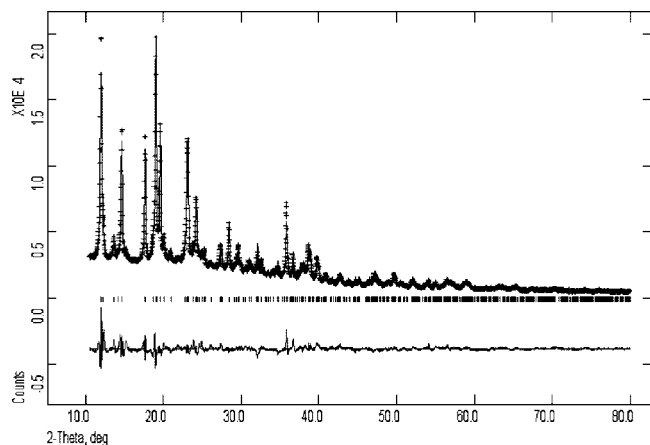
X-Ray Powder Diffraction. X-ray powder diffraction data were collected at room temperature on a computer controlled STOE-STADIP focusing powder diffractometer equipped with a curved Ge(111) monochromator (Cu Kα$_1$; $\lambda = 1.54051$ Å). A STOE linear position sensitive detector was used. The green powder sample of 2 was inserted in a glass capillary of 0.5 mm diameter. The compounds were measured in the range of $4° \leq 2\theta \leq 80°$ using a step width of 0.1°. The indexing procedure was performed using ITO[29] in WinXPow.[30] The structure solution was carried out using the program DASH[31] introducing a structural model.[32] The obtained position of the molecule in the given symmetry and unit cell was used for Rietveld refinement in GSAS/EXPGUI.[33,34] After the initial refinement of the scale and unit cell constants, the atomic positions were refined using soft constraints defining the geometry of the molecule within some allowable errors. Subsequent Rietveld refinement was carried out using gradually relaxing bond restraints. The non-hydrogen atoms were refined isotropically applying an overall temperature factor for the all C and all N atoms. The H-atoms were treated as riding atoms, and their temperature factors were fixed. In the final cycles of refinement, the shifts in all parameters were less than their estimated standard deviations. Further details of the data collection and refinement are given in Table 1.

Figure 1. A partial view of the 1D polymer structure of 1 (H-atoms on the ligand tn have been omitted for clarity).
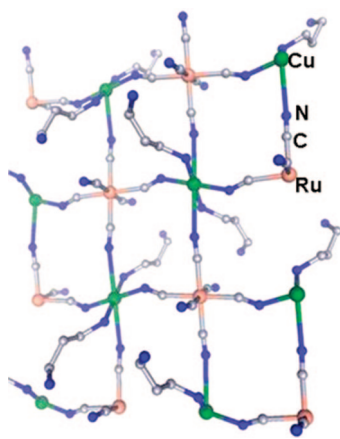
Results and Discussion

Synthesis, IR Analysis, and Structure Description. Complex $\{[Cu(tnH^+)_2(H_2O)_2][Ru(CN)_6] \cdot 2H_2O\}_\infty$ (1) was formed as dark-blue hexagonal platelike crystals by treating $K_4[Ru(CN)_6]$ with a mononuclear copper(II) complex, generated in situ from 1,3-diaminopropane (tn) and copper sulfate. In the IR spectrum the bands expected for both the ligand and the counterions are present (Figure S1 in the Supporting Information). Coordination of the CN ligand to a second metal ion through its nitrogen atom results in a shift of these values to around 2065−2110 cm^{-1} for $[Ru(CN)_6]^{4-}$ [35] Three strong cyanide absorption bands were found at 2106, 2068, and 2044 cm^{-1}; this is in good agreement with the presence of $[Ru(CN)_6]^{4-}$ units having at least one terminal CN ligand, as indicated by the lower wavenumber band.[35,36] For compound 1, the supplementary weak bands observed in the 2700−2500 cm^{-1} region could be tentatively assigned to $\nu(NH)$ stretching vibrations of the uncoordinated NH_3^+ group. The X-ray structural analysis of complex 1 revealed the formation of a one-dimensional polymer (Figure 1), which is isostructural with the $[Fe(CN)_6]^{4-}$ analogue $[Cu(tnH)_2(H_2O)_2][Fe(CN)_6] \cdot 2H_2O$.[37] The structure can be described as a linear chain with alternating $[Cu(tnH^+)_2(H_2O)_2]^{4+}$ and $[Ru(CN)_6]^{4-}$ units, bridged by the CN groups. The asymmetric unit in 1 consists of half a $[Ru(CN)_6]^{4-}$ anion, half a $[Cu(tnH^+)]^{2+}$ cation, and two water molecules, one of which is coordinated to the copper(II) atom (Figure S2 in the Supporting Information). The Cu atom is hexacoordinate with a strong pseudo Jahn−Teller effect. In the equatorial plane it is bonded to two nitrogen atoms of the linear tn ligands, Cu1−N(tn) = 2.049(1) Å, and to two nitrogen atoms from the CN groups, Cu1−N(CN) = 1.973(2) Å. The apical positions are occupied by two water molecules, Cu1−O(H$_2$O) = 2.606(1) Å. The coordination polyhedron of the Cu atoms can be described as Cu(tnH$^+$)$_2$(H$_2$O)$_2$(NC)$_2$ or CuN$_4$O$_2$. It is worth noting that the tn unit is protonated and coordinates in a monodentate manner (Figure 1 and Table 1).

Four of the six CN$^-$ groups are nonbridging, while the other two bond to the Cu atoms giving rise to Ru−C≡N−Cu bridges.

Figure 2. The Rietveld refinement for compound **2**; including the difference curve between the calculated (−) and measured (+) X-ray powder diffractograms.
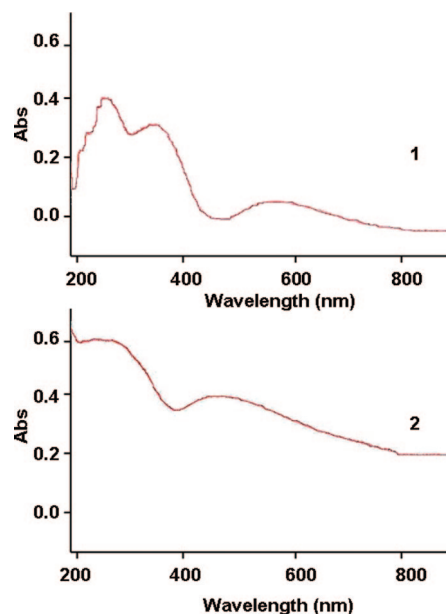

Figure 3. A partial view of the gridlike polymer structure of **2** (H-atoms have been omitted for clarity).

The Ru^{II} ion has an almost perfect octahedral RuC6 coordination geometry [Ru—C bond lengths 2.0307(15)−2.0361(15) Å; Ru—C≡N bond angles 178.82(13)−179.55(13)°]. The Ru—C bond distances and C—Ru—C angles are in good agreement with those in similar compounds.[36,38,39]

TG and DSC Analysis. The thermal stability of **1** has been studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Compound **1** contains two coordinated water molecules and two water molecules of crystallization. It was expected that dehydration of **1** would dramatically change the structure. Thermal analysis indicates that the weight loss is 13.52% in the temperature range 45−105 °C, which corresponds to the loss of four water molecules (theoretical value 13.65%) (Figure S3 in the Supporting Information). The DSC studies, after sample incubation at 0 °C followed by heating at a rate of 1° min^{-1} to 150 °C, showed only one endothermic effect at 95 °C (ΔH = 390 J/g). The dehydrated compound, **2**, is green, insoluble in most common solvents, but highly microcrystalline. Powder X-ray diffraction methods were used to determine its three-dimensional structure (Figure 2), which indicates that **1** has been transformed from a 1D polymer into a gridlike polymer structure (Figure 3), with a reduction in the unit cell volume of ca. 16%.

The IR spectra of **2** (Figure S1 in the Supporting Information) confirmed the absence of water bands in the region 3400−3360 cm^{-1} for $\nu_{as,s}$ (OH) and 1650−1600 cm^{-1} for δ (HOH). The
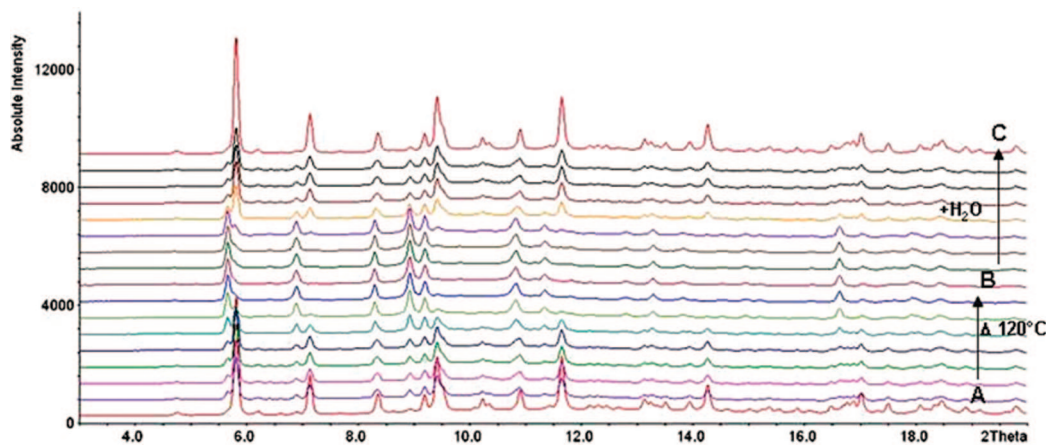

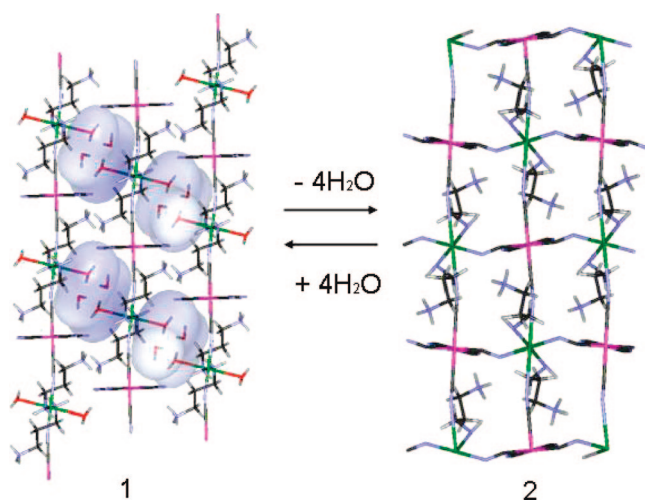**Figure 4.** Solid state UV/vis absorption spectra of compounds **1** and **2**.

Cu atom is again hexacoordinated with a strong pseudo Jahn−Teller effect. This time in the equatorial plane it is bonded to two nitrogen atoms of the linear tn ligands (2.057(7) Å) and to two nitrogen atoms from the CN groups (2.025(5) Å) (Figure S4 in the Supporting Information). The apical positions are occupied by two nitrogen atoms of CN groups but with unusually long bonds, 2.902(2) Å. Such long bonds are not uncommon, for example, in [Cu(*cis*-chxn)$_2$]$_3$[Fe(CN)$_6$]$_2$·7H$_2$O^{40} the Cu−N(cyano) distance is 2.818 Å, in [Cu(N-en)$_2$]$_3$[Co(CN)$_6$]$_2$^{41} (where N-en = N-ethylethylene-1,2-diamine) the same distance is 2.828 Å, while in [Cu^{II}(tetrenH$_2$)][Cu^{II}(tetrenH)][W^V(CN)$_8$][W^{IV}(CN)$_8$]·2.5H$_2$O (where tetren = tetraethylenepentamine)^{42} and [Cu-(chxn)$_2$][Ni(CN)$_4$]·2H$_2$O^{43} extremely long Cu−N(cyano) distances are observed, 3.114 and 3.12 Å, respectively. The coordination polyhedron of the Cu atoms can be described as Cu(tnH$^+$)$_2$(NC)$_4$ or CuN6. Hence, in **2** four of the six CN$^-$ are bridging. The Ru^{II} ion has an octahedral RuC6 coordination geometry [Ru−C bonds 2.0307(15)−2.0361(15) Å]. In contrast to **1** the Ru−C≡N bond angles vary from 155.5(14) to 173.8(26)°.

When the green powder (that is, **2**) was exposed to water the color changed to blue, suggesting a change in the coordination geometry of the metal center. Solid-state UV spectra of both **1** and **2** indicate a clear bathochromic shift of the maximum from 380 nm in **1** to 470 nm in **2**, Figure 4. In the IR spectrum the bands associated with the presence of the water molecules reappeared, showing that the water loss is reversible in nature.

The reversibility of this process was also confirmed by in situ synchrotron powder X-ray diffraction (PXRD) measurements (Figure 5 and Table 1). A capillary containing a powdered sample of **1** (Figure 5A) was slowly heated and its transformation to **2** was observed (Figure 5B). By passing a stream of nitrogen gas saturated with water vapor through the capillary, it was possible to regenerate the blue solid (Figure 5C), which has peak positions and intensities fully coincident to those observed for the single crystal of **1** (Figure 5A). Complex **2**, therefore, exhibits "sponge-like" molecular properties: it can easily take up water molecules and return to the original structure, **1**.
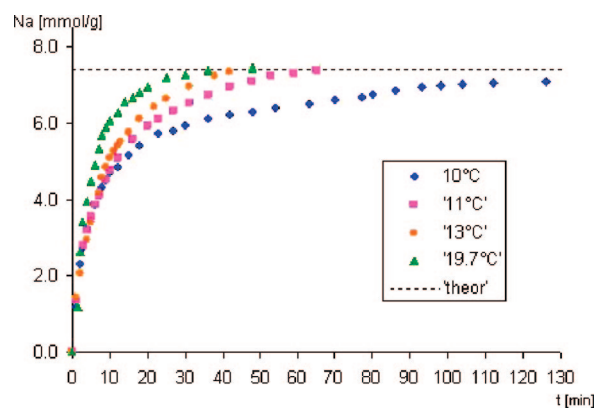
Figure 5. In situ synchrotron powder X-ray diffraction (PXRD) patterns: (A) powdered single-crystals of **1**; (B) after thermal treatment of **1**, that is transforms to compound **2**; (C) after flowing H_2O vapor through the capillary containing **2**, that is, structure **1** is regenerated.

Figure 6. View of the reversible transformation of compound **1** to **2**, as the result of a simple dehydration−rehydration process. The helical chains of hydrogen bonded water molecules are represented by the large white surfaces in **1** (l-h-s).

Figure 7. Kinetics of water vapor adsorption by compound **2** between 10 and 19.7 °C.

It was possible to repeat this process a number of times without any loss of crystallinity of either compounds, **1** or **2**. Complex **1** originally forms parallel polymer chains slightly displaced with respect to one another and separated by two water molecules of crystallization (Figure 6). They are linked by O−H···O hydrogen bonds which give rise to the formation of helical chains of water molecules running parallel to the 2-fold crystallographic screw axis (Figure 6, **1** on l-h-s). After heating, a gridlike structure, (**2**), is obtained (Figure 6, **2** on r-h-s). The TG analysis indicates that all four water molecules are lost between 45–110 °C.

We assume that the water molecules of crystallization are lost first, allowing the chains to approach one another. After loss of the coordinated water molecules the chains slip parallel to one another enabling a C≡N⁻ group to fill the free coordination site on the copper atoms. This in turn weakens the original Cu···N≡C bond in **1**. The direction of the pseudo Jahn−Teller effect in **2** is now perpendicular to that in **1**. These changes involve a reduction from 12.004 Å in the length of the *c* axis of **1** to 8.257 Å in the length of the *c* axis of **2** (ratio ca. 4:3), and a corresponding increase from 9.011 to 12.035 Å (ratio ca. 3:4) in the length of the *b* axes (Figure S5 in the Supporting Information).

Evidently, the key to the observed phenomena is the ability to break and reform the network, which is turn results in the change in the copper atom coordination sphere, from CuN_4O_2 to CuN_6 (Figure 6).

Surprisingly, the system **1/2** is selective for water only. Attempts to adsorb other small molecules, like CH_3OH or CH_3CN, were unsuccessful, as shown by PXRD (Figure S6 in the Supporting Information), immersion calorimetry (Table S1 in the Supporting Information), and the color of the solid, which remained green. The unique property of this assembly is the complete reversibility of the molecular structure, as well as the color change, under a simple dehydration−rehydration process.

Immersion Calorimetry. Immersion calorimetric studies were carried out with compound **2**. This technique, applied mainly to carbons, provides an insight into the filling of nanopores.[44–46] The enthalpies of immersion of **2**, Δ_iH, into acetonitrile and methanol are very low, which suggests exclusion from the structure. On the other hand, for water (Table S1 in the Supporting Information) an average value of −99.5 ± 3 J per gram of solid was obtained, which corresponds to −46.6 kJ per mole of **2**. It is likely that this value reflects essentially the heat of transformation of the gridlike structure into the original 1D polymer.

Kinetics measurements for complex **2** at different temperatures have also been carried out by exposing it to H_2O vapor close to the corresponding saturation pressures (Figure 7).

During these isobaric processes, which lasted between 50 and 130 min, the sample color changed from green to blue. The

activation energy for the reaction **2** → **1** obtained from the classical Arrhenius plot (Figure S7 in the Supporting Information) is ca. 60 kJ mol^{-1}. It is also found that complex **2** adsorbs 7.3 mmol of H_2O per gram, which corresponds to ca. 3.5 water molecules per mole of **2**. This is close to the expected number of four water molecules in the resulting complex $\{[Cu(tnH^+)_2][Ru(CN)_6] \cdot 4H_2O\}_\infty$ (**1**).

Conclusion

Compound **1** is, to the best of our knowledge, the first example of a reversible structural transformation in a bimetallic hexacyanoruthenate coordination complex. X-ray powder diffraction analysis confirmed the transformation of the 1D polymer structure (**1**) into a gridlike structure (**2**), giving rise to coexistence of pseudo Jahn−Teller elongation. The unique aspect of this system is the "sponge-like" behavior of the molecular transformation and the color change, which are completely reversible under a simple dehydration−rehydration process. These results also present further evidence that solid materials do not need to be porous to reversibly adsorb small molecules.[47,48] Future investigations of the vapor adsorption properties of **2** using a combination of in situ Raman spectroscopy and powder X-ray diffraction will, we hope, help to explain the mechanism of this reversible process and why it is apparently selective for water only.

Supporting Information Available: Supporting Information for this article is available free of charge via the Internet at http://pubs.acs.org.

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