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Further Insights into the Role of Temperature in the Synthesis of the Lanthanide(III)-Pyrazine-Octacyanotungstate(V) System: an Example of Discrete Materials

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Abstract. Slow diffusion reactions of Ln^{3+} (Ln = Ce, Eu, Tb) ions, pyrazine, and the $[W(CN)_8]^{3-}$ unit at 0 °C produced three discrete coordination compounds $[Ln(H_2O)_5(CH_3CN)_2][W(CN)_8] \cdot 0.5$pyrazine$\cdot$ $CH_3CN \cdot 2H_2O$ [Ln = Ce (**1**), Eu (**2**)] and $[Tb(H_2O)_6(CH_3CN)_2][W(CN)_8] \cdot$ pyrazine$\cdot 2CH_3CN \cdot 3H_2O$ (**3**). Single crystal X-ray diffraction analysis revealed that compounds **1** and **2** are isomorphous and adopt a rare centrosymmetric tetranuclear square unit, while compound **3** exhibits

an ion-pair moiety, in which unique tetramer water clusters $(H_2O)_4$ are involved. The presence of different types of hydrogen-bonding interactions is responsible for the formation of three-dimensional supramolecular networks. The isolations of compounds **1**–**3** provide a further insight into the effect of temperatures on constructions and structures of the lanthanide(III)-pyrazine-octacyanotungstate(V) system.

Introduction

The design and synthesis of coordination compounds have grown rapidly in recent years due to their diversity of intriguing architectures and fascinating potential applications.[1] In particular, octacyanide-bearing precursors $[M(CN)_8]^{3-/4-}$ (M = Mo, W) have been employed usually to construct coordination compounds with unique topologies and promising properties, such as single-molecule or single-chain magnets, photomagnetism, spin-crossover magnetism, luminescence, and so on.[2,3] With respect to synthesis, various strategies have been applied to construct these materials, comprising the direct reactions of precursors,[4–6] aids of secondary reagent or assisting molecules or bridging spacers,[7–9] employ of clusters,[10] the electrochemical synthesis,[11] and microwave-assisted self-assembly.[12] However, how to control rationally the desired structures of such system with specific properties still remains a great challenge.

In our previous work, the effect of temperatures on the octacyanide-based 4f-5d system has been demonstrated to play a crucial role in the formation of final products.[13,14] Studies revealed that slow diffusion of starting precursors Ln^{3+} (Ln = La – Tb) ions, pyrazine, and $[W(CN)_8]^{3-}$ unit at slightly high temperatures (ca. 38–40 °C) in the acetonitrile solution produced three-dimensional (3D) pillared frameworks $Ln(H_2O)_4(pyrazine)_{0.5}W(CN)_8$, while 2D layers $Ln(H_2O)_5W(CN)_8$ were generated at slightly low temperatures (<33 °C). The continuation of this theme and relatively few studies on the relationship between temperatures and structures in octacyanide-based system prompt us to investigate further what will happen at extremely low temperatures. Our research presented in this contribution indicated that self-assemblies of the identical starting materials at 0 °C and under synthetic procedures similar to those described for 2D and 3D materials have isolated three discrete compounds $[Ln(H_2O)_5(CH_3CN)_2][W(CN)_8] \cdot 0.5$pyrazine$\cdot CH_3CN \cdot 2H_2O$ [Ln = Ce (**1**), Eu (**2**)] and $[Tb(H_2O)_6(CH_3CN)_2][W(CN)_8] \cdot$ pyrazine$\cdot 2CH_3CN \cdot 3H_2O$ (**3**). Obviously, the overall structural dimensionalities for the Ln^{III}-pyrazine-$[W^V(CN)_8]$ (Ln = Ce, Eu, Tb) system decreased gradually upon lowing diffusion temperatures.

Results and Discussion

Single crystal X-ray diffraction studies revealed that compounds **1** and **2** are isostructural and crystallize in the monoclinic space group $P2_1/c$ (Table 1). Only the structure of compound **1** was described in detail (Figure 1), which consists of neutral four-centric molecules $\{[Ce(H_2O)_5(CH_3CN)_2]_2$-$[W(CN)_8]_2\}$, uncoordinated pyrazine ligands, crystallized CH_3CN, and H_2O molecules. The $[W(CN)_8]^{3-}$ group adopts a distorted square antiprismatic arrangement, where two *cis* CN ligands acting as linear two-connectors bridge to two adjacent $[Ce(H_2O)_5(CH_3CN)_2]^{3+}$ moieties, while the remaining six are

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Table 1. Crystallographic data and structural refinement for compounds **1**–**3**.

	1	**2**	**3**
Formula	$C_{16}H_{25}N_{12}O_7CeW$	$C_{16}H_{25}N_{12}O_7EuW$	$C_{20}H_{34}N_{14}O_9TbW$
M_r	821.45	833.29	957.38
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a /Å	13.529(6)	13.3479(6)	10.2596(15)
b /Å	12.983(6)	12.8803(6)	12.7761(18)
c /Å	16.986(8)	16.7877(8)	14.096(2)
α /°	90.00	90.00	96.8040(10)
β /°	99.832(5)	99.5720(10)	103.729(2)
γ /°	90.00	90.00	94.749(2)
V /Å^3	2940(2)	2846.0(2)	1770.5(4)
Z	4	4	2
$\rho_{calcd.}$ /g·cm^{-3}	1.856	1.945	1.796
μ /mm^{-1}	5.492	6.277	5.289
Total, unique	21323, 5467	20964, 5290	25678, 6494
Observed [$I > 2\sigma(I)$]	5205	5118	6322
GOF on F^2	1.084	1.135	1.137
R_1, wR_2 [$I > 2\sigma(I)$]	0.0291, 0.0739	0.0134, 0.0303	0.0346, 0.0993
R_1, ωR_2 (all data)	0.0308, 0.0749	0.0143, 0.0306	0.0355, 0.1001

terminal. The mean W1–C and C–N bond lengths are 2.161 and 1.146 Å, respectively, and all W1–CN units exhibit almost linear with the maximum deviation from linearity of 5.2° (Table 2, Table 3). The metric parameter of the central W1 atom is typical for octacyanotungstates(V).[15–19]
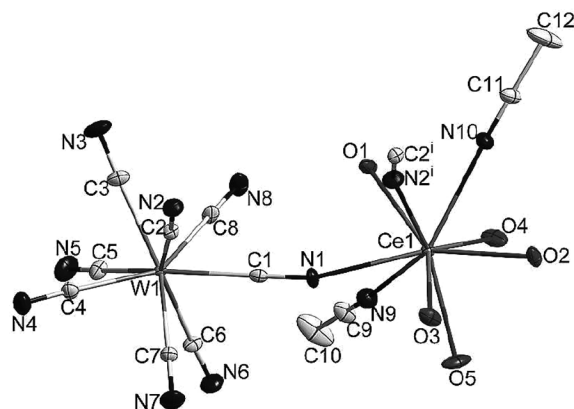
Figure 1. ORTEP diagram of compound **1** with thermal ellipsoids at the 30% probability level. Uncoordinated pyrazine ligands, crystallized H_2O, and CH_3CN molecules, and all hydrogen atoms are omitted for clarity. Symmetry code: (i) –x, –y + 1, –z.

The Ce^{III} atom exhibits a nine-coordinate environment with two cyano nitrogen atoms, two nitrogen atoms from CH_3CN ligands, and five oxygen atoms from water molecules. The coordination arrangement around the central cerium atom is a tricapped trigonal prismatic with the capping positions occupied by N1, N10, and O5 atoms. The average Ce1–N and Ce1–O bond lengths are 2.653 and 2.498 Å, respectively, while the Ce1–NC bonds are significantly bent [155.5(3) and 158.3(4)°], opposition to the linear W1–CN units. The geometrical data of the central Ce^{III} are practically identical to those observed in other cyanide-based Ce^{III} systems.[20,21]

Thus, the $[W(CN)_8]^{3-}$ and $[Ce(H_2O)_5(CH_3CN)_2]^{3+}$ units are linked alternatively by the –Ce–N≡C–W– linkages to generate a centrosymmetric tetranuclear square unit

Table 2. Selected bond lengths /Å and angles /° for compound **1**.

1

|			
W1–C1	2.160(5)	C6–N6	1.146(6)
W1–C2	2.156(4)	C7–N7	1.141(6)
W1–C3	2.168(4)	C8–N8	1.134(6)
W1–C4	2.152(5)	Ce1–O1	2.502(3)
W1–C5	2.151(5)	Ce1–O2	2.463(3)
W1–C6	2.166(4)	Ce1–O3	2.539(3)
W1–C7	2.163(4)	Ce1–O4	2.480(4)
W1–C8	2.172(4)	Ce1–O5	2.504(3)
C1–N1	1.152(6)	Ce1–N2^i	2.627(4)
C2–N2	1.139(6)	Ce1–N10	2.626(4)
C3–N3	1.148(6)	Ce1–N1	2.633(4)
C4–N4	1.159(7)	Ce1–N9	2.726(4)
C5–N5	1.149(7)		
N1–C1–W1	174.8(4)	N6–C6–W1	177.3(4)
N2–C2–W1	175.2(4)	N7–C7–W1	178.2(5)
N3–C3–W1	178.1(5)	N8–C8–W1	176.4(4)
N4–C4–W1	177.6(4)	C1–N1–Ce1	155.5(3)
N5–C5–W1	177.8(5)	C2–N2–Ce1^i	158.3(4)

Symmetry code: (i) –x, –y + 1, –z.

$\{[Ce(H_2O)_5(CH_3CN)_2]_2[W(CN)_8]_2\}$ (Figure 2) with diagonal dimensions of the tetramer of about 7.93 Å (W1···W1) and 8.41 Å (Ce1···Ce1), in which the tungsten and cerium atoms are located on the vertexes, whereas the cyanide groups form the sides. To the best of our knowledge, compounds **1** and **2** represent the first structurally characterized examples of discrete octacyanometalate-based lanthanide molecular squares, although several transition metal compounds based on octacyanometalates building blocks with discrete square structures have been documented so far, most of which consists of an anionic square core co-crystallized with a charge-balance cation.[16,17,22–26]

Terminal cyanide ligands, coordinated and uncoordinated water molecules, and CH_3CN solvents are all involved in the well-defined hydrogen-bonding network (Table 4, Table 5). Six terminal CN groups interact with coordinated and lattice H_2O molecules through the O–H···N hydrogen bonds. Simulta-

Table 3. Selected bond lengths /Å and angles /° for compound **2**.

2			
W1–C1	2.166(2)	C6–N6	1.144(3)
W1–C2	2.159(2)	C7–N7	1.146(3)
W1–C3	2.166(2)	C8–N8	1.146(3)
W1–C4	2.166(2)	Eu1–O1	2.4062(16)
W1–C5	2.164(2)	Eu1–O2	2.4213(16)
W1–C6	2.167(2)	Eu1–O3	2.3843(16)
W1–C7	2.171(2)	Eu1–O4	2.4721(16)
W1–C8	2.159(2)	Eu1–O5	2.4232(16)
C1–N1	1.143(3)	Eu1–N1	2.5431(19)
C2–N2	1.144(3)	Eu1–N2^i	2.540(2)
C3–N3	1.148(3)	Eu1–N9	2.662(2)
C4–N4	1.145(3)	Eu1–N10	2.545(2)
C5–N5	1.148(3)		
N1–C1–W1	173.8(2)	N6–C6–W1	177.8(2)
N2–C2–W1	173.91(19)	N7–C7–W1	177.8(2)
N3–C3–W1	178.0(2)	N8–C8–W1	177.9(2)
N4–C4–W1	177.2(2)	C1–N1–Eu1	157.49(18)
N5–C5–W1	176.8(2)	C2–N2–Eu1^i	158.72(18)

Symmetry code: (i) –x, –y + 3, –z.
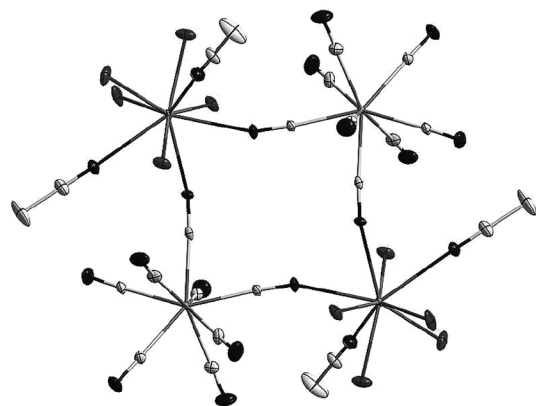
Figure 2. The tetranuclear square unit of compound **1**.

neously, coordinated H_2O molecules interact with lattice H_2O, CH_3CN solvents, and uncoordinated pyrazine ligands by the O–H···O or O–H···N hydrogen bonds. In addition, the lattice water molecules are also interlinked by O–H···O hydrogen bonds. As a result, the neighboring $\{Ce_2W_2\}$ tetranuclear units are well separated through above hydrogen-bonding interactions, forming a 3D supramolecular network (Figure 3).

An ion-pair compound **3** was isolated upon changing the lanthanide ions from Ce (or Eu) to Tb, in spite of the same synthetic conditions as compounds **1** and **2**. To the best of our knowledge, only one example of octacyanometalate-based lanthanide compounds with ion-pair structures $[Tm(terpy)(DMF)_2(H_2O)_3][W(CN)_8]\cdot4H_2O\cdot DMF$ was characterized structurally to date, in which the central thulium(III) and tungsten(V) atoms were linked in an alternating arrangement by hydrogen-bonding interactions.[20] Compound **3** crystallizes in the triclinic space group $P\bar{1}$ and the asymmetric unit contains $[Tb(H_2O)_6(CH_3CN)_2]^{3+}$ cation, $[W(CN)_8]^{3-}$ anion, and solvent molecules (Figure 4). Both the central terbium(III) and tungsten(V) atoms display a slightly distorted square antiprism. The tungsten atom is coordinated by eight terminal CN

Table 4. Hydrogen-bond arrangement /Å,° for compound **1**.

D–H···A	D–H	H···A	D···A	D–H···A
O1–H1A···N8	0.85	2.09	2.934(6)	174
O1–H1B···N6^{iii}	0.85	1.99	2.832(5)	172
O2–H2A···O7	0.85	1.87	2.706(6)	167
O2–H2B···N4^{iv}	0.85	2.00	2.852(6)	175
O3–H3A···N3^i	0.85	2.50	3.190(6)	139
O3–H3B···N11	0.85	1.99	2.823(6)	165
O4–H4A···N12^{iv}	0.85	2.07	2.875(8)	159
O4–H4B···N3^v	0.85	2.00	2.839(6)	169
O5–H5A···N8^v	0.85	2.19	2.940(6)	148
O5–H5B···O6	0.84	1.97	2.764(5)	156
O6–H6A···N7^{ii}	0.85	2.21	2.900(6)	138
O6–H6B···N5^v	0.85	2.23	3.064(7)	167
O7–H7A···O6	0.85	2.04	2.834(6)	154
O7–H7B···N5^{vi}	0.85	2.25	3.023(6)	152

Symmetry codes: (i) –x, –y + 1, –z; (ii) –x, –y, –z; (iii) –x, y + 1/2, –z + 1/2; (iv) x – 1, y, z; (v) –x, y – 1/2, –z + 1/2; (vi) x – 1, –y + 1/2, z – 1/2.

Table 5. Hydrogen–bond arrangement /Å,° for compound **2**.

D–H···A	D–H	H···A	D···A	D–H···A
O1–H1A···N7^{iii}	0.85	1.99	2.843(3)	176
O1–H1B···N11^{iv}	0.85	2.02	2.859(3)	171
O2–H2A···N5	0.85	2.09	2.928(3)	171
O2–H2B···N4^v	0.85	2.00	2.825(3)	164
O3–H3A···O6	0.85	1.85	2.694(3)	175
O3–H3B···N8^{vi}	0.85	2.01	2.849(3)	170
O4–H4A···N12	0.85	1.96	2.793(3)	168
O4–H4B···N7^i	0.85	2.33	3.146(3)	162
O5–H5A···N5^{iii}	0.85	2.18	2.940(3)	150
O5–H5B···O7	0.85	1.95	2.771(2)	163
O6–H6A···O7	0.85	2.11	2.780(3)	135
O6–H6B···N6^{vii}	0.85	2.20	2.999(3)	156
O7–H7A···N6^{iii}	0.85	2.19	3.034(3)	171
O7–H7B···N3^{ii}	0.85	2.05	2.874(3)	162

Symmetry codes: (i) –x, –y + 3, –z; (ii) –x, –y + 2, –z; (iii) –x, y – 1/2, –z – 1/2; (iv) x, –y + 5/2, z – 1/2; (v) –x, y + 1/2, –z – 1/2; (vi) x + 1, y, z; (vii) x + 1, –y + 5/2, z + 1/2.
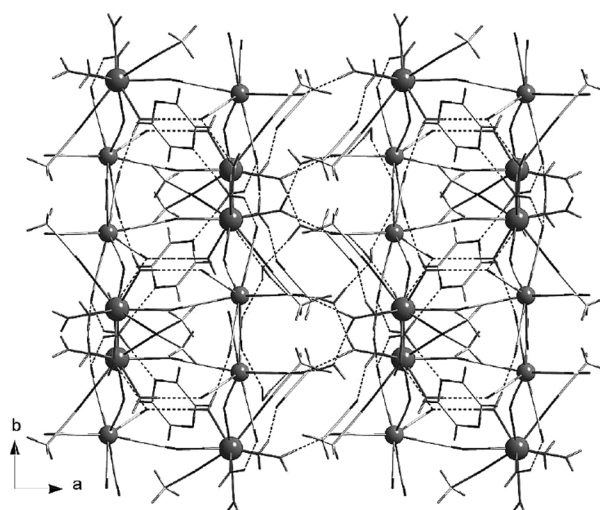
Figure 3. The 3D supramolecular network of compound **1** viewed from the c axis.

groups with the W1–C and C–N bond lengths falling in the range of 2.144–2.175 and 1.133–1.158 Å, respectively (Table 6). The W1–CN linkages are all close to linearity with angles spanning from 177.7 to 179.7°. The terbium atom is surrounded by six oxygen atoms arising from water molecules and two nitrogen atoms from CH_3CN ligands, and the average Tb1–O and Tb1–N bond lengths are 2.351 and 2.548 Å, respectively. The geometrical data of the central Tb^{III} atom are similar to those found in the hexacyanometalate-based compound $Tb(DMF)_6Fe(CN)_6$.[27]
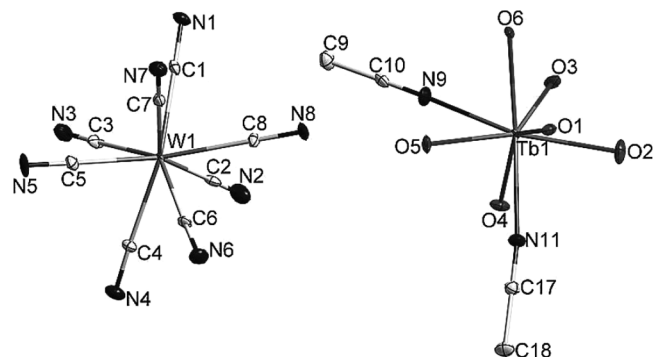
Figure 4. ORTEP diagram of compound **3** with thermal ellipsoids at the 30% probability level. Lattice H_2O and CH_3CN molecules, uncoordinated pyrazine ligands, and all hydrogen atoms are omitted for clarity.

Table 6. Selected bond lengths /Å and angles /° for compound **3**.

3			
W1–C1	2.144(5)	C5–N5	1.152(8)
W1–C2	2.162(6)	C6–N6	1.133(7)
W1–C3	2.175(5)	C7–N7	1.151(7)
W1–C4	2.173(5)	C8–N8	1.138(7)
W1–C5	2.154(6)	Tb1–O1	2.356(4)
W1–C6	2.168(5)	Tb1–O2	2.349(4)
W1–C7	2.164(5)	Tb1–O3	2.364(4)
W1–C8	2.167(5)	Tb1–O4	2.348(4)
C1–N1	1.158(7)	Tb1–O5	2.350(4)
C2–N2	1.147(8)	Tb1–O6	2.337(3)
C3–N3	1.141(7)	Tb1–N9	2.553(5)
C4–N4	1.135(7)	Tb1–N11	2.542(5)
N1–C1–W1	178.9(5)	N5–C5–W1	178.3(5)
N2–C2–W1	179.4(6)	N6–C6–W1	178.2(5)
N3–C3–W1	178.2(6)	N7–C7–W1	178.8(5)
N4–C4–W1	177.7(5)	N8–C8–W1	179.7(5)

As shown in Figure 5, remarkably dense intermolecular interactions between the neighboring moieties are widely presented in the supramolecular structure (Table 7). All CN ligands of $[W(CN)_8]^{3-}$ units are linked through hydrogen bonds with the surrounding water molecules. The other types of hydrogen-bonding interactions occur between lattice water molecules and coordinated water ligands, and between lattice water molecules and CH_3CN molecules, together between coordinated water molecules and uncoordinated pyrazine ligands. Thus, the $[Tb(H_2O)_6(CH_3CN)_2]^{3+}$ and $[W(CN)_8]^{3-}$ units are well separated by water molecules, uncoordinated pyrazine ligands, and CH_3CN molecules, generating a 3D supramolecular

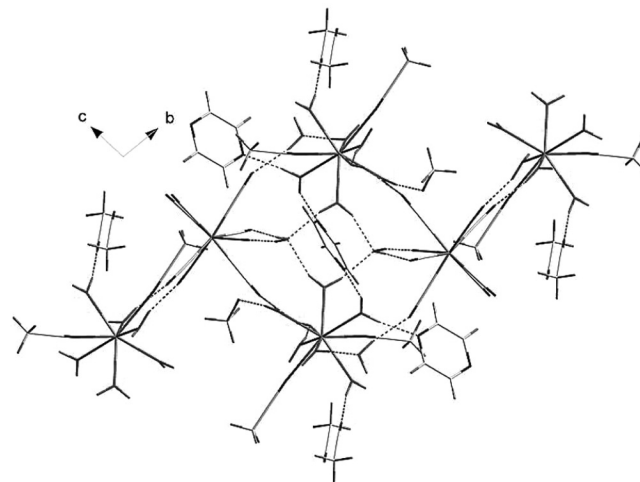network with the Tb···Tb, Tb···W, and W···W contacts of about 8.53, 7.44, and 8.87 Å, respectively.

Figure 5. The 3D supramolecular network of compound **3** viewed from the *a* axis.

Table 7. Hydrogen-bond arrangement /Å,° for compound **3**.

D–H···A	D–H	H···A	D···A	D–H···A
O1–H1A···N6[iii]	0.85	2.01	2.825(6)	160
O1–H1B···O7	0.85	1.86	2.704(5)	176
O2–H2A···N14	0.85	1.91	2.742(8)	166
O2–H2B···N5[vii]	0.85	2.04	2.892(6)	175
O3–H3A···O8	0.85	1.91	2.733(5)	164
O3–H3B···O8[vi]	0.85	1.92	2.741(6)	161
O4–H4A···N4[v]	0.86	1.99	2.813(6)	161
O4–H4B···O9	0.85	1.90	2.731(6)	164
O5–H5A···N13[iii]	0.85	1.98	2.810(8)	167
O5–H5B···N8	0.85	1.97	2.815(6)	171
O6–H6A···N10	0.85	2.00	2.786(7)	154
O6–H6B···N12	0.85	1.92	2.757(6)	168
O7–H7A···N2[viii]	0.85	2.10	2.887(7)	155
O7–H7B···N1[i]	0.85	2.00	2.836(6)	166
O8–H8A···N3[iv]	0.85	1.97	2.823(6)	177
O8–H8B···N7[i]	0.85	2.01	2.854(6)	172
O9–H9X···O7[x]	0.85	2.12	2.914(7)	155
O9–H9Y···N5[ix]	0.85	2.56	3.363(8)	159

Symmetry codes: (i) –x + 1, –y + 1, –z; (iii) –x + 1, –y + 2, –z; (iv) –x + 2, –y + 1, –z; (v) –x + 2, –y + 2, –z; (vi) –x + 1, –y + 1, –z – 1; (vii) x – 1, y, z – 1; (viii) x – 1, y, z; (ix) x, y, z – 1; (x) x + 1, y, z.

Interestingly, the overall supramolecular organization consists of tetrameric water clusters $(H_2O)_4$ with the side length (O···O distance) of about 2.74 Å (Figure 6). The O3 and O3[vi] atoms only form two hydrogen bonds (as two donors), while both O8 and O8[vi] atoms form four hydrogen bonds (as two donors and two acceptors) and adopt tetrahedral arrangements. In fact, the water clusters have played an important role in the stabilities of such supramolecular species. It is worth noting that the hydrogen-bonding motif of the water tetramer in our case is different obviously from those predicted theoretically[28] and observed experimentally[29] in the cyclic water cluster $(H_2O)_4$, in which all four water molecules formed two types of hydrogen bonds (acting as both proton donor and acceptor).
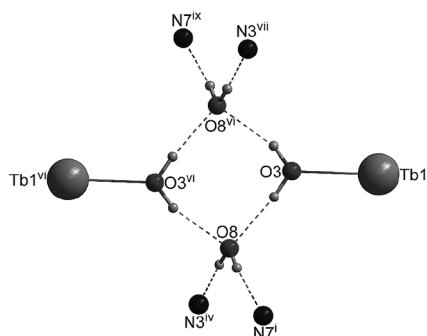
Figure 6. The tetranuclear water cluster $(H_2O)_4$ in the structure of compound **3**. Symmetry codes: (i) $-x + 1, -y + 1, -z$; (iv) $-x + 2, -y + 1, -z$; (vi) $-x + 1, -y + 1, -z - 1$; (vii) $x - 1, y, z - 1$; (ix) $x, y, z - 1$.

Comparison of structures observed for compounds **1–3** shows that the coordination arrangements of the central Ln^{III} atoms undergo an apparent change from Ce (or Eu) to Tb in spite of the same surrounding of the tungsten atom and experimental conditions, which may be ascribed to the systematic ionic radii contraction of the Ln series. Thus, the tendency of replacing coordinated CN groups with sterically less demanding H_2O ligands practically stops the assembling process from extending further into a polymeric network. This phenomenon of structural changes induced by lanthanide ions has also been found in other cyanide-based compounds.[20,30–32]

Conclusions

Two tetranuclear squares and one ion pair were obtained by lowering crystallization temperatures. The successful isolation of these species not only produces intriguing examples of octacyanometalate-based lanthanide supramolecular architectures, but also provides further insights on the intrinsic relationship between synthetic temperatures and structures in the lanthanide(III)-pyrazine-octacyanotungstate(V) system. We believe that the research presented in this paper offer valuable information for the crystal engineering of solid materials with desired structures and specific properties. Further investigations on the temperature-driven self-assemblies of octacyanometalate-based lanthanide compounds with other ligands are underway in our laboratory.

Experimental Section

Materials and General Methods: All chemicals and solvents were of analytical grade. The precursor $[HN(nC_4H_9)_3]_3[W(CN)_8]$ was prepared according to the published procedure.[33] All reactions were carried out under low light condition because of the photosensitivity of octacyanotungstate(V) ions. Red block crystals of compounds **1–3** were obtained after about two months by slow diffusion of an acetonitrile solution (2 mL) of pyrazine (0.15 mmol) into an acetonitrile solution (20 mL) containing $[HN(nC_4H_9)_3]_3[W(CN)_8]$ (0.05 mmol) and $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Ce, Eu, Tb) (0.05 mmol) at 0 °C. It should be noted here that the crystals of compounds **1–3** were easily fragile to powders upon removal from the mother liquor. So single-crystal X-ray structural measurements of all compounds were performed by covering liquid

paraffin on the single crystal. Powder X-ray diffraction experiments of polycrystalline samples of compounds **2** and **3** were carried out in order to further investigate if the phase transition occurred when the crystals were picked out from vials and exposed in air at ambient temperature. To our surprise, powder X-ray diffraction patterns of two samples were not in agreement to those simulated from single crystal diffraction data (Figure 7), but well consistent to those of corresponding 3D frameworks $Ln(H_2O)_4(pyrazine)_{0.5}W(CN)_8$ [Ln = Eu (**2a**), Tb (**3a**)] (Figure 8), which were characterized structurally and magnetically by our group.[13,14]
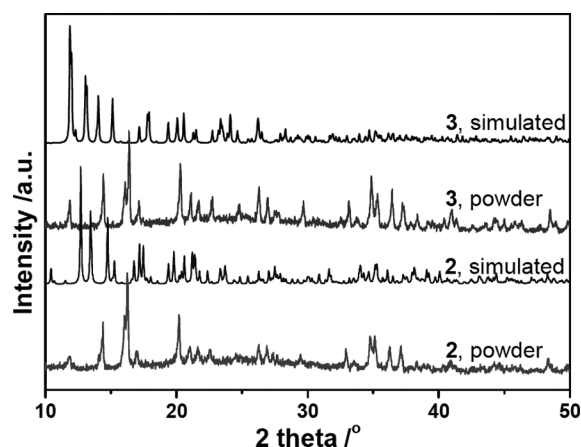

Figure 7. Powder X-ray diffraction patterns of samples of compounds **2** and **3**, compared to those simulated from corresponding single crystal diffraction data.
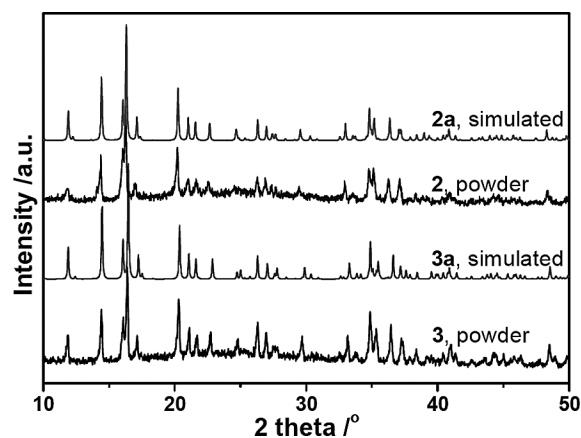

Figure 8. Powder X-ray diffraction patterns of samples of compounds **2** and **3**, compared to those simulated from single crystal diffraction data of 3D compounds **2a** and **3a**.

Above experimental results indicated that the phase has changed when crystals of compounds **2** and **3** were removed from the mother liquor. This phase transition process may be roughly elucidated as follows: the acetonitrile molecules bound to Ln^{3+} ions in structures are easy to lose when both compounds are exposed in air at room temperature. Subsequently the original crystallized pyrazine ligands entered into these coordinatively-unsaturated Ln^{3+} sites left exposed by the removal of coordinated acetonitrile molecules, resulting in the structural rearrangement of both compounds and the formation of 3D pillar-layered frameworks **2a** and **3a**. Based on above considerations, it is very difficult to obtain samples used to magnetic and other characterizations. In fact, this phase transition phenomenon were also observed in octacyan-

ometalate-based hetero-bimetallic materials $[Ln(H_2O)_4(CH_3CN)_2]$-$[M(CN)_8] \cdot CH_3CN$ (Ln = La, Ce; M = Mo, W), which transformed to 2D layers $Ln(H_2O)_5W(CN)_8$ (Ln = La, Ce) upon removal from the mother liquid, with the change of color from yellow to orange.[21]

X-ray Crystallographic Analysis: Diffraction data for compounds **1**–**3** were collected at 173(2) K with a Bruker Smart APEX II diffractometer equipped with Mo-K_α (λ = 0.71073 Å) radiation. Diffraction data analysis and reduction were performed within SMART, SAINT and XPREP.[34] Correction for Lorentz, polarization and absorption effects were performed within SADABS.[35] Structures were solved using Patterson method within SHELXS-97 and refined using SHELXL-97.[36–38] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of pyrazine and acetonitrile molecules were calculated at idealized positions and included in the refinement in a riding mode with U_{iso} for hydrogen assigned as 1.2 or 1.5 times U_{eq} of the attached atoms. The hydrogen atoms bound to water molecules were located from difference Fourier maps and refined as riding with $U_{iso}(H) = 1.5U_{eq}(O)$.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-919462 (**1**), CCDC-919463 (**2**), and CCDC-919464 (**3**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Acknowledgements

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