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Supporting Information

Heterometallic 3d-4f Cluster-Containing Polyoxotungstate Obtained by Partial Disassembly of Preformed Large Clusters

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Experimental Section

Materials and methods. The $[N(CH_3)_4]_{10}Na_{12}[Na_2Sb_8W_{36}O_{132}(H_2O)_4]\ 26H_2O$ precursor was synthesized according to the literature[S1] and characterized by IR spectrum. All chemicals were commercially purchased and used without further purification. Elemental analysis for W, Cu, Dy, Sb, K and Na were determined by a Leaman inductively coupled plasma (ICP) spectrometer. UV-Vis absorption spectra were obtained using a 752 PC UV-Vis spectrophotometer.

General Electrochemical Materials and Methods. Thrice-distilled water was used throughout the experiments. A pH = 4.0 0.4 M $CH_3COONa+CH_3COOH$ solution was used during the experiments. Solutions were deaerated by pure argon bubbling prior to the experiments and the electrochemical cell was kept under an argon atmosphere throughout the experiment. A CHI 760 electrochemical workstation connected to personal computer was used for control of the electrochemical measurements and for data collection. A conventional three-electrode system was used. The working electrode was a glassy carbon (GC), the reference electrode was the Ag/AgCl electrode, and platinum wire was used as a counter electrode. A pHS-25B type pH meter was used for pH measurement. All the experiments were carried out at room temperature (25–30 ℃). The aqueous solution stability of polyoxoanion **1** was investigated by the CV and UV-vis spectra. Compound **1** was dissolved in a pH 4.0 buffer solution, which was kept at room temperature. The cyclic voltammetric behaviors of the buffer solution were detected per 1 h for five times. These solutions can be well stored and no voltammetric characteristics have ever changed. Further, the UV-vis spectra of the above solutions were checked simultaneously and no changes were observed during 5 h. These characterizations can confirm that polyoxoanion **1** is structurally stable in the buffer solution used for the electrochemical measurement.

Synthesis of 1. Dy_2O_3 (0.50 g, 1310 μmol) was added into 7.5 mL of distilled water. Then 2.5 mL of concentrated nitric acid was added. The mixture was boiling for 1 h resulting in solution A. $\{Sb_8W_{36}\}$ (0.30 g, 26.5 μmol) was added into 10 mL of distilled water, which was stirred for 5 min. Then, 0.1 g $CuCl_2$•$2H_2O$, 1.0 mL aq A and 1.0 ml 2 M K_2CO_3 aqueous solution were added in the reaction system one by one. Then, the mixture was stirred or anther 10 min resulting solution B. $\{Sb_8W_{36}\}$ (0.45 g, 39.75 μmol) was added into 15 mL of distilled water, which was stirred for 5 min. Then, 0.15 g $CuCl_2$•$2H_2O$, 1.5 mL aq A and 2.4 ml 2 M K_2CO_3 aqueous solution were added in the reaction system one by one. Then, the mixture was stirred or anther 10 min resulting solution C. The solution B was slowly added into the solution C. The resulting mixture was further stirred for 10 min. Then, 50 mL distilled water and 0.15 g L or D-alanine were added into the mixture, which was further stirred for 5 hours at 40 ℃. Afterwards the solution was cooled down to ambient temperature and filtered. After three weeks, green block crystals suitable for X-ray diffraction were obtained (Yields: 21 % based on W). Anal. Found (%): Dy, 5.43; K, 1.96; Cu, 2.09; Na, 2.12, Sb, 4.38; W, 57.26; Calcd: Dy, 5.66; K, 2.04; Cu, 2.21; Na, 2.00, Sb, 4.24; W, 57.61.

Synthesis of 2. Compound **2** was synthesized similarly to that of **1** in the absence of Dy_2O_3.

X-ray Crystallography. The crystallographic data of **1** was performed on a Rigaku R AXIS RAPID IP diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Suitable crystals were affixed to the inner of capillary tube and transferred to the goniostat. The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 crystallographic software package.[S2] During the refinement, all H atoms on water molecules were directly included in the molecular formula. The restraint command 'isor' was employed to restrain the oxygen atoms so as to avoid the ADP and NPD problems on them. This command leads to a final restraint value of 390. The 'omit -3 50' command was used to omit the

weak reflections above 50 degree. The highest residual peak 4.5 eÅ^3 is close to W2 (0.970 Å), and no element is suitable for this residual peak. The crystal data and structure refinement are summarized in Table S1. CSD reference number 429941 contains the supplementary crystallographic data for this paper. This data could be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de).

Table S1 Crystal data and structure refinement for **1.**

Compound	**1**
Empirical formula	$H_{50}Cu_2Dy_2K_3Na_5O_{91}Sb_2W_{18}$
λ / Å	0.71073
Mr	5743.53
T / K	293(2)
Crystal dimensions / mm	0.16×0.15×0.06
Crystal system	Triclinic
Space group	*P-1*
A / Å	12.101(2)
B / Å	18.624(4)
C / Å	22.956(5)
α / °	104.53(3)
β / °	97.88(3)
γ / °	107.70(3)
V / Å^3	4641.6(16)
Z	2
Dc / Mg m^{-3}	4.110
μ / mm^{-1}	25.074
F(000)	5028
θ range / °	3.10-25.00
Data / restraints / parameters	16246 / 390 / 1189
R_1 ($I > 2\sigma$(I))[a]	0.0689
wR_2 (all data)[a]	0.1695
Goodness-of-fit on F^2	1.00

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$; $wR_2 = \Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]^{1/2}$

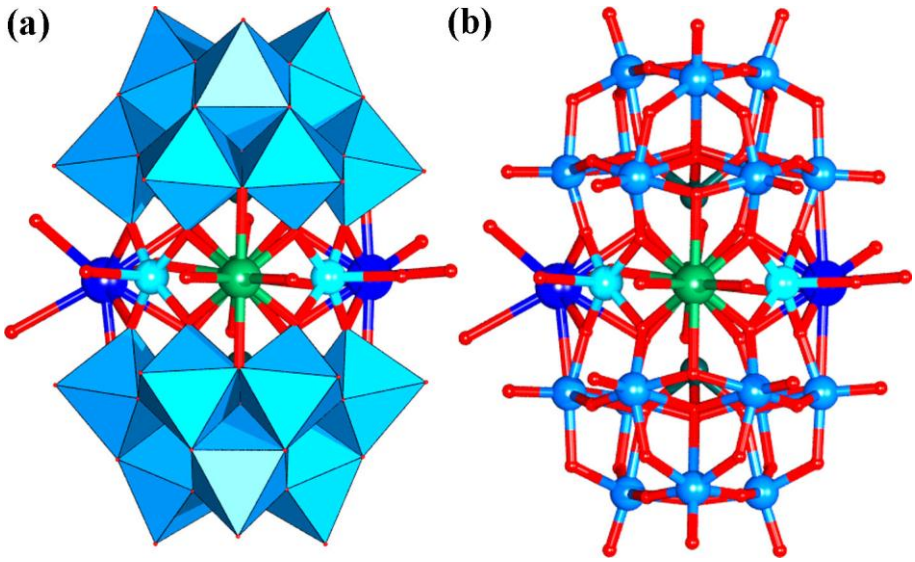

Fig. S1. (a) Polyhedral and ball-and-stick representation of polyoxoanion **1** sandwiching a $\{K_2Dy_2Cu_2(H_2O)_8\}$ cluster; (b) ball-and-stick representation of polyoxoanion **1** sandwiching a $\{K_2Dy_2Cu_2(H_2O)_8\}$ cluster.

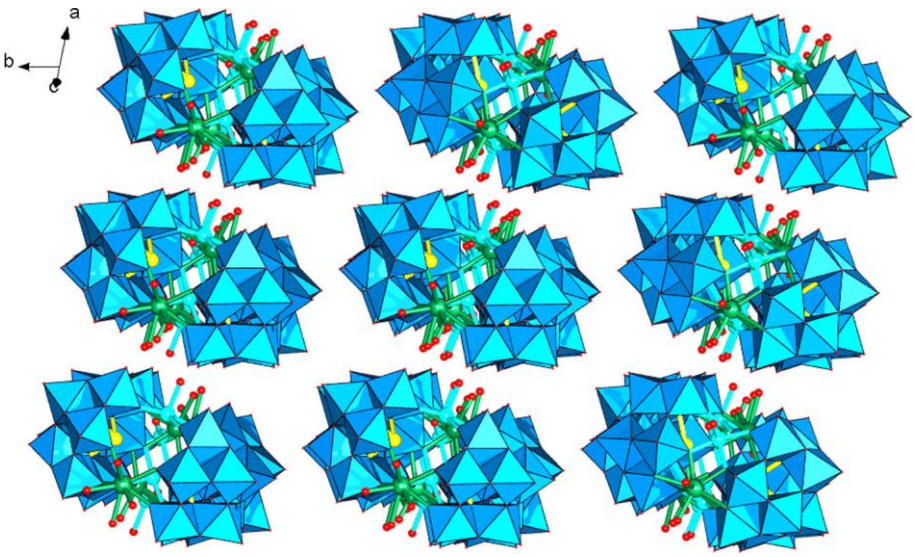

Fig. S2. Polyhedral and ball-and-stick representation of the packing arrangements of **1**. K^+, Na^+ and the lattice H_2O molecules are omitted for clarity.

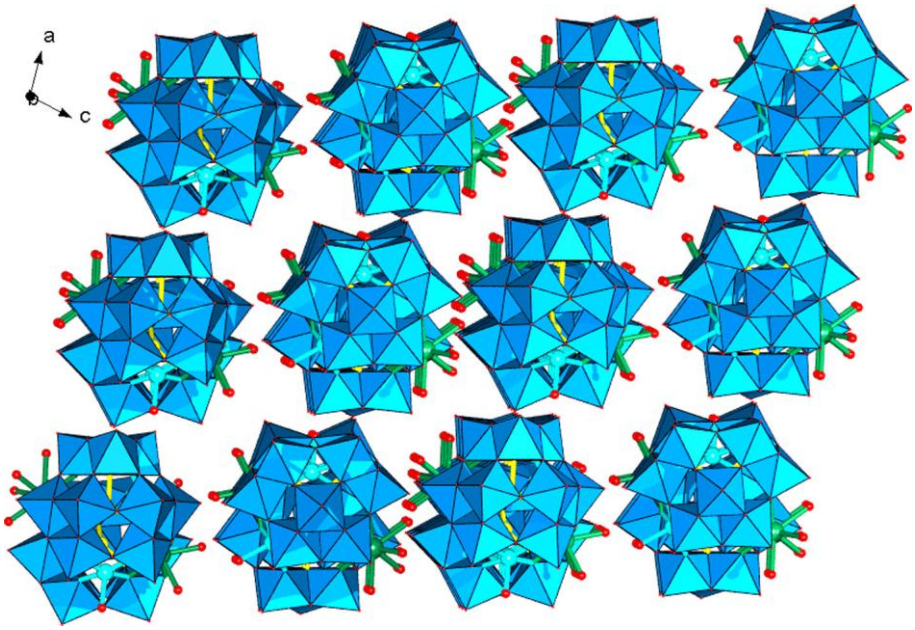

Fig. S3. Polyhedral and ball-and-stick representation of the packing arrangements of **1**. K^+, Na^+ and the lattice H_2O molecules are omitted for clarity.

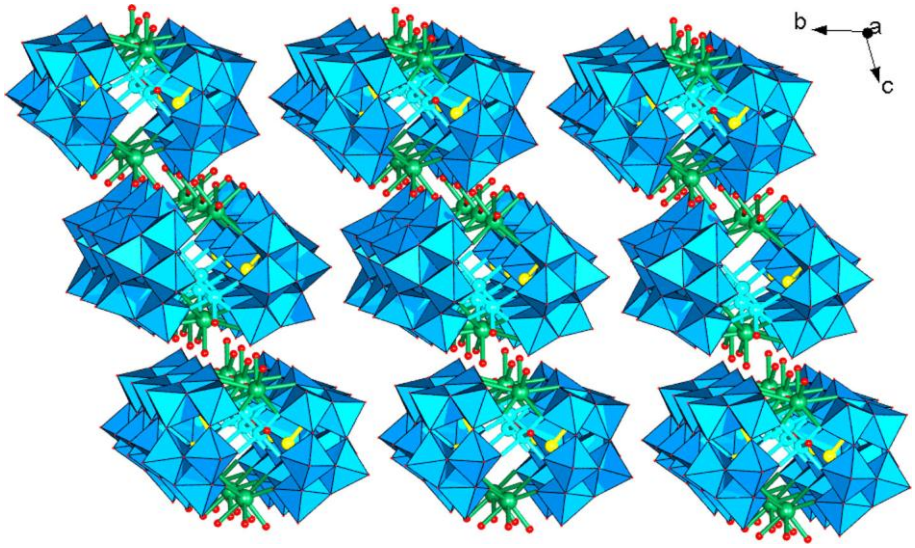

Fig. S4. Polyhedral and ball-and-stick representation of the packing arrangements of **1**. K^+, Na^+ and the lattice H_2O molecules are omitted for clarity.

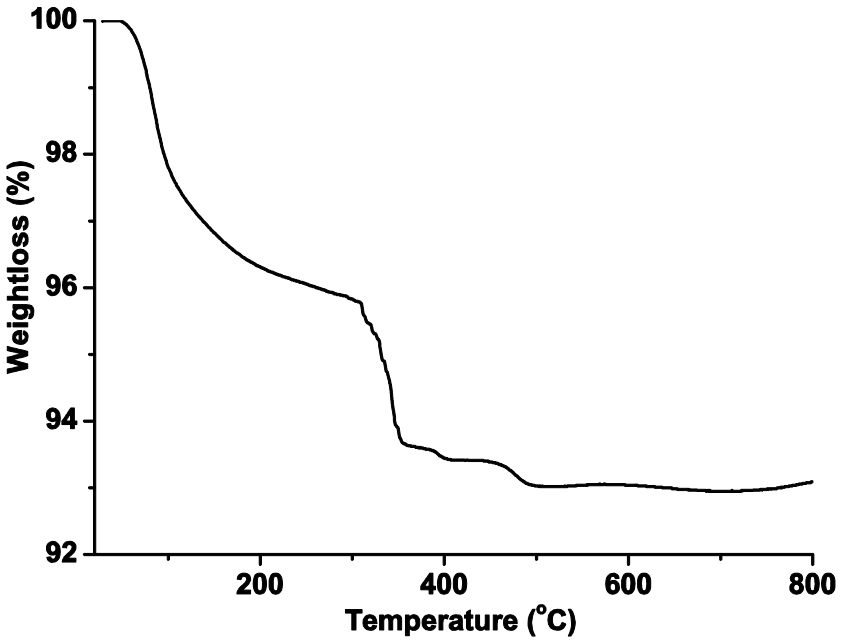

Fig. S5. TG analysis of **1**. The calculated weight loss of 7.83% of the water molecules is in line with the observed weight loss of 7.01%.

[S1] M. Bösing, I. Loose, H. Pohlmann and B. Krebs, *Chem. Eur. J.*, 1997, 3, 1232.

[S2] G. M. Sheldrick, *SHELXL97*, Program for Crystal Structure Refinement, University of Göttingen: Göttingen, Germany, 1997; G. M. Sheldrick, *SHELXS97*, Program for Crystal Structure Solution, University of Göttingen: Göttingen, Germany, 1997.