Electronic Supplementary Information (ESI)

A 1:1 intercluster compound consisting of +6 and –6 charged $Rh^{III}_4Zn^{II}_4$ octanuclear cations and anions with aminothiolate ligands

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Experimental Section.

Preparation of compounds.

$(\Delta)_4$-K_6[Zn_4O{Rh(L-cys)$_3$}$_4$] ($(\Delta)_4$-K_6[1]) and $(\Delta)_4/(\Lambda)_4$-[Zn_4O{Rh(aet)$_3$}$_4$]Br_6 ($(\Delta)_4/(\Lambda)_4$-[2]Br_6). These complexes were prepared as described in the literature.[11] For $(\Delta)_4$-K_6[**1**]: Anal. Calcd for K_6[**1**]·47.5H_2O = $C_{36}H_{155}N_{12}O_{72.5}Rh_4S_{12}Zn_4$: C, 13.47; H, 4.87; N, 5.24%. Found: C, 13.18; H, 4.58; N, 5.10%. For $(\Delta)_4/(\Lambda)_4$-[**2**]Br_6: Anal. Calcd for [**2**]·Br_6·NaBr·8H_2O = $C_{24}H_{88}Br_7N_{12}Na_1O_9Rh_4S_{12}Zn_4$: C, 12.38; H, 3.81; N, 7.22%. Found: C, 12.33; H, 3.76; N, 6.97%.

$(\Delta)_4$-[Zn_4O{Rh(aet)$_3$}$_4$]$(NO_3)_6$ ([2]$(NO_3)_6$). To a solution containing $(\Delta)_4$-[Zn_3OH{Rh(aet)$_3$}$_4$]$(NO_3)_5$ [S1] (27 mg, 15 μmol) in water (10 mL) was added an aqueous solution of $Zn(NO_3)_2$ (66 mM, 0.22 mL, 14 μmol). The mixture was heated at 50°C for 2.5 h and then evaporated to dryness. The orange-yellow residue was dissolved in water (2 mL) and filtered off, followed by the addition of several drops of a saturated aqueous solution of $NaNO_3$ to the filtrate. After the orange solution was stood in a refrigerator for a week, the resulting yellow crystalline powder was collected by filtration. Yield: 10 mg (32%). Anal. Calcd for [**2**]$(NO_3)_6$·5H_2O = $C_{24}H_{82}N_{18}O_{24}Rh_4S_{12}Zn_4$: C, 13.96; H, 4.00; N, 12.21%. Found: C, 13.91; H, 3.96; N, 12.17%.

$(\Delta)_4/(\Lambda)_4$-[Zn_4O{Rh(aet)$_3$}$_4$]$(\Delta)_4$-[Zn_4O{Rh(L-cys)$_3$}$_4$] (3)

A solution containing $(\Delta)_4$-K_6[**1**]·49H_2O (26 mg, 10 μmol) in an aqueous NaOAc/HOAc buffer solution (75 mM, pH 4.5, 10 mL) was slowly layered under an aqueous NaOAc/HOAc buffer solution (75 mM, pH 4.5, 10 mL). Then, a solution containing $(\Delta)_4/(\Lambda)_4$-[**2**]Br_6·NaBr·8H_2O (24 mg, 10 μmol) in an aqueous NaOAc/HOAc buffer solution (7.5 mM, pH 4.5, 10 mL) was layered on the top of the two-layered solution. The three-layered solution was stood at room temperature for 2 weeks, and the resulting yellow block crystals were collected by filtration. Yield: 19 mg (44%). Anal. Calcd for [**2**][**1**]·35H_2O = $C_{60}H_{202}N_{24}O_{61}Rh_8S_{24}Zn_8$: C, 16.56; H, 4.68; N, 7.72%. Found: C, 16.37; H, 4.59; N, 7.51%. IR (KBr disk, cm^{-1}): 1616 (COO^-).

$(\Delta)_4$-[Zn_4O{Rh(aet)$_3$}$_4$]$(\Delta)_4$-[Zn_4O{Rh(L-cys)$_3$}$_4$] (3')

Yellow block crystals for **3'** was obtained by a method used for **3**, employing $(\Delta)_4$-[**2**]$(NO_3)_6$·5H_2O instead of $(\Delta)_4/(\Lambda)_4$-[**2**]Br_6·NaBr·8H_2O in a half scale. Yield: 12

mg (56%). Anal. Calcd for [**2**][**1**]·40H_2O = $C_{60}H_{212}N_{24}O_{66}Rh_8S_{24}Zn_8$: C, 16.22; H, 4.81; N, 7.57%. Found: C, 15.93; H, 4.64; N, 7.38%.

X-ray crystallography.

Single-crystal X-ray diffraction measurements were made on a Rigaku RAXIS VII or a Rigaku RAXIS-RAPID imaging plate area detectors with a graphite monochromated Mo-Kα radiation. The intensity data were collected by the ω scan mode. Empirical absorption corrections were applied. The structures were solved by a direct method using SHELXS-97.[S2] All calculations were performed by using the Yadokari-XG software package [S3] except for the refinement which was performed by using SHELXL-97.[S2]

For K_6[**1**], five of six potassium ions were disordered into two positions, the occupancies of which were fixed to 0.5. The non-hydrogen atoms except for disordered atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms except those of water molecules were placed at calculated positions but were not refined.

For **3**, one cluster anion $(\Delta)_4$-$[\mathbf{1}]^{6-}$ and one cluster cation $[\mathbf{2}]^{6+}$, besides solvated water molecules, were crystallographically independent. The cluster cation was disordered into two positions. Although not all C and N atoms in **3** were determined, the two disordered cation units were characterized as the $(\Delta)_4$ and $(\Lambda)_4$ isomers of $[\mathbf{2}]^{6+}$. The crystallographic data of **3** were summarized in Table S1, and the cluster cation and anion found in **3** illustrated in Fig. S1.

For **3'**, two methylene groups of aet ligand of cationic cluster were disordered into two positions, the occupancies of which were refined. The non-hydrogen atoms except for disordered atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms except those of water molecules were placed at calculated positions but were not refined.

[S1] (a) S. Aizawa, Y. Sone, S. Yamada, M. Nakamura, *Chem*. *Lett*. 1998, 775. (b) T. Konno, K. Haneishi, M. Hirotsu, T. Yamaguchi, T. Ito, T. Yoshimura, *J*. *Am*. *Chem*. *Soc*. 2003, **125**, 9244.

[S2] G. M. Sheldrick, *Acta Cryst*. 2008, **A64**, 112.

[S3] C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *Yadokari-XG 2009*, *Program for the Refinement of Crystal Structures, Nihon Kessho Gakkaishi*, 2009, **51**, 218.

Table S1. Crystal data of **3**.

	rac-[**2**][**1**]·41H_2O (**3**)
empirical formula	$C_{60}H_{132}N_{24}O_{67}Rh_8S_{24}Zn_8$
fw	3508.77
size / mm^3	0.12 x 0.12 x 0.08
crystal system	Orthorhombic
space group	$P2_12_12_1$ (No.19)
a /Å	24.113(2)
b /Å	26.524(2)
c /Å	28.3341(17)
V /$Å^3$	18122(3)
Z	4
T /K	200(2)
R(int)	0.1978
$\rho_{calcd.}$ /g cm^{-3}	1.681
μ (Mo Ka), mm^{-1}	2.103
$2\theta_{Max}$	55.0
total no. of data	173199
no. of unique data	41471
no. of parameters	1300
flack	0.069(19)
R (I>2σ(I))[a]	0.0981
Rw[b]	0.2831

[a] $R_1 = \Sigma|(|Fo|-|Fc|)| / \Sigma(|Fo|)$.

[b] $Rw = [\Sigma w(Fo^2-Fc^2)^2 / \Sigma w(Fo^2)^2]^{1/2}$.

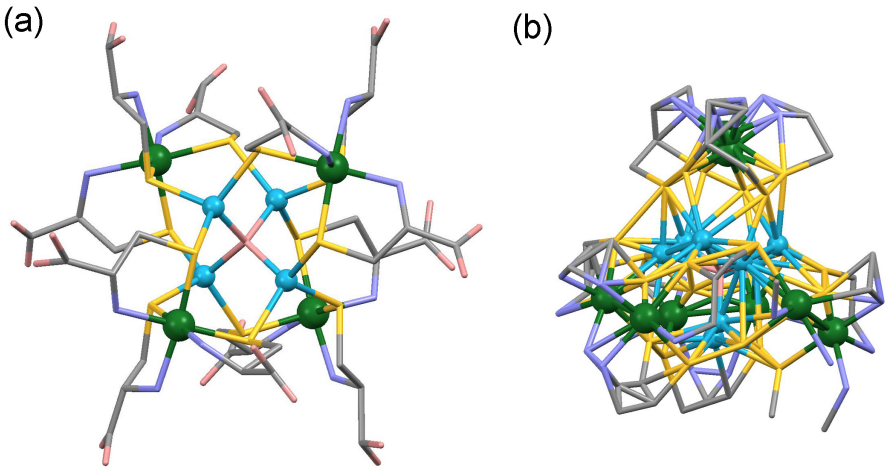

Fig. S1. Molecular structure of (a) the cluster anion and (b) the cluster cation in **3**. Color code; Rh: blue-green, Zn: blue gray, S: yellow, O: pink, N: blue, C: gray.

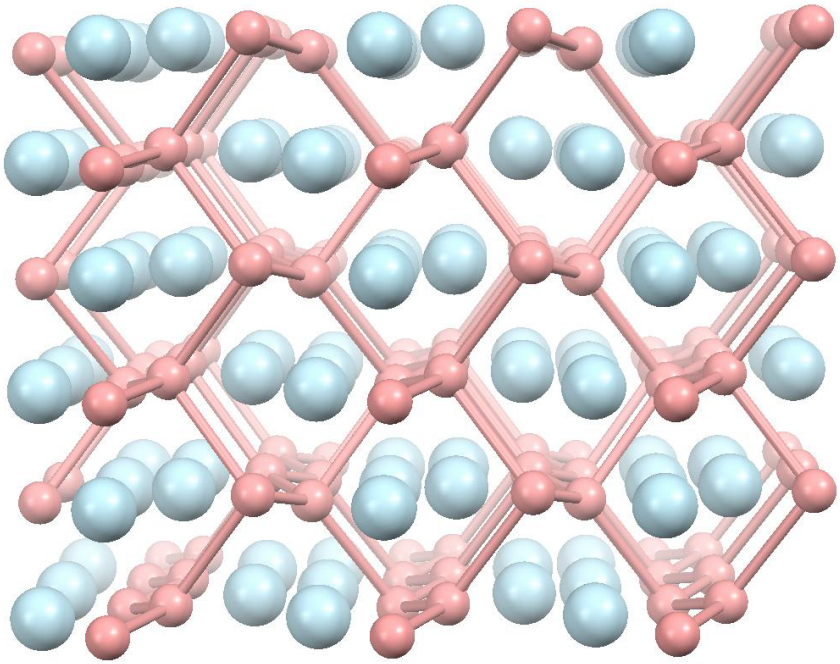

Fig. S2. A schematic drawing of the packing structure of **3'**. The **dia** net of the cluster anions ($[\mathbf{1}]^{6-}$; pink) accommodates cluster cations ($[\mathbf{2}]^{6+}$; blue) in its cavities.

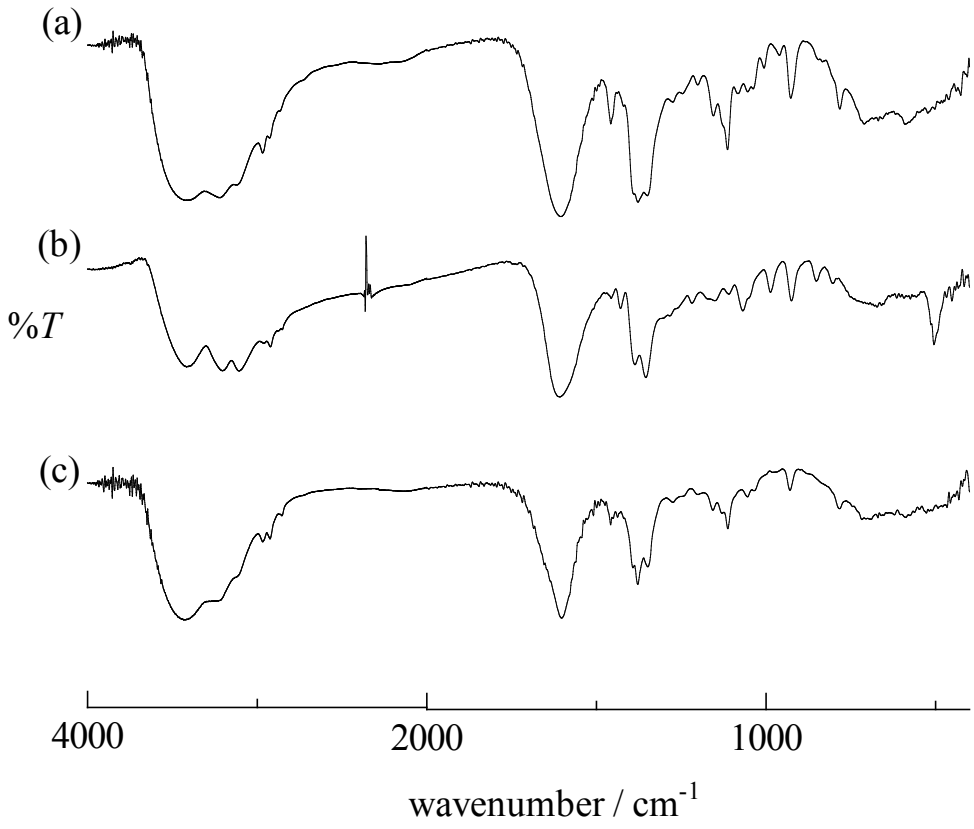

Fig. S3. IR spectra of (a) $(\Delta)_4$-K_6[**1**], (b) **3**, and (c) **3'** (KBr disks).