Supporting Information

Thyminate(2–)-bridged cyclic tetranuclear rhodium(III) complexes formed by a template of a sodium, calcium or lanthanoid ion

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Contents:

Preparation of Complexes

The starting hydroxide complex, $[(Cp^*Rh)_2(\mu\text{-}OH)_3]OH$ was prepared by the literature method.[1]

$[\{Cp^*Rh(\mu\text{-thym})\}_4(NaPF_6)]$ (**1**)

A suspension of H_2thym (13 mg, 0.10 mmol) in methanol (10 mL) was added to a methanol solution (10 mL) of $[(Cp^*Rh)_2(\mu\text{-}OH)_3]OH$ (27 mg, 0.050 mmol), and the mixture was stirred for 3 h at ambient temperature. A methanol solution (10 mL) of $NaPF_6$ (4.2 mg, 0.025 mmol) was added and the mixture was further stirred for 2 h. The resulting solution was evaporated to dryness under reduced pressure, and the residue was extracted with dichloromethane (20 mL). The filtered extract was evaporated, again, to dryness under reduced pressure. The crude product was recrystallized from a methanol solution by vapor diffusion of diethyl ether, and the resulting orange crystals were collected by filtration and dried in vacuo. Yield: 7.8 mg (21%). ^1H NMR (CD_3OD, 300 MHz, 22 °C): δ 1.79 (s, 15H, Cp*), 1.81 (s, 3H, thym CH_3), 7.28 (s, 1H, thym $C^6\text{-}H$). ESI-MS (MeOH): *m*/*z* 1471.12 ($[\{Cp^*Rh(\mu\text{-thym})\}_4Na]^+$). Anal. Found (after drying in vacuo): C, 44.91; H, 5.12; N, 6.64%. Calcd for $C_{60}H_{76}F_6N_8NaO_8PRh_4$ = $[\{Cp^*Rh(\mu\text{-thym})\}_4(NaPF_6)]$: C, 44.57; H, 4.74; N, 6.93%. The crystals of **1**•Et_2O•MeOH suitable for X-ray analysis were obtained from a methanol solution by vapor diffusion of diethyl ether.

$[\{Cp^*Rh(\mu\text{-thym})\}_4(NaBF_4)]\bullet 2CH_3OH$ (**2**•$2CH_3OH$)

This compound was prepared by a similar method to that for **1**, using $NaBF_4$ (4.8 mg, 0.025 mmol) instead of $NaPF_6$. Yield: 13 mg (33%). ^1H NMR (CD_3OD, 300 MHz, 22 °C): δ 1.79 (s, 15H, Cp*), 1.81 (s, 3H, thym CH_3), 7.27 (s, 1H, thym $C^6\text{-}H$). ESI-MS (MeOH): *m*/*z* 1471.18 ($[\{Cp^*Rh(\mu\text{-thym})\}_4Na]^+$). Anal. Found: C, 44.60; H, 5.16; N, 6.60%. Calcd for $C_{62}H_{84}BF_4N_8NaO_{10}Rh_4$ = $[\{Cp^*Rh(\mu\text{-thym})\}_4(NaBF_4)]\bullet 2CH_3OH$: C, 45.73; H, 5.36; N, 6.77%. The crystals of **2**•Et_2O•MeOH•H_2O suitable for X-ray analysis were obtained from a methanol solution by vapor diffusion of diethyl ether.

$[\{Cp^*Rh(\mu\text{-thym})\}_4(NaNO_3)]\bullet H_2O$ (**3**•H_2O)

A suspension of H_2thym (26 mg, 0.20 mmol) in methanol (10 mL) was added to a methanol solution (10 mL) of $[(Cp^*Rh)_2(\mu\text{-}OH)_3]OH$ (55 mg, 0.10 mmol), and the mixture was stirred for 3 h at ambient temperature. A methanol solution (10 mL) of $NaNO_3$ (7.0 mg, 0.08 mmol) was added and the mixture was further stirred for 2 h. The resulting solution was evaporated to dryness under reduced pressure, and the residue was extracted with dichloromethane (20 mL). The filtered extract was evaporated, again, to dryness under reduced pressure. The crude product was recrystallized from an acetonitrile solution by layering of diisopropyl ether, and the resulting orange crystals were collected by filtration and dried in air. Yield: 29.4 mg (35%). ^{1}H NMR (CD_3CN, 400 MHz, 21 °C): δ 1.79 (s, 15H, Cp*), 1.81 (s, 3H, thym CH_3), 7.28 (s, 1H, thym C^6-*H*). $^{13}C\{^1H\}$ NMR (CD_3CN, 100.6 MHz, 22 °C): δ 9.9 (s, Cp* *C*H_3), 13.4 (s, thym CH_3), 95.3 (d, J = 9.1 Hz, Cp**C**Me), 115.4 (s, thym), 116.8 (s, thym), 152.9 (s, thym), 173.4 (s, thym). Anal. Found: C, 46.21; H, 5.01; N, 8.30%. Calcd for $C_{60}H_{78}N_9NaO_{12}Rh_4 = [\{Cp^*Rh(\mu\text{-thym})\}_4(NaNO_3)]\cdot H_2O)$: C, 46.05; H, 4.90; N, 8.50%. The crystals of $\mathbf{3}\cdot 3MeCN\cdot H_2O$ suitable for X-ray analysis were obtained from a mixture of acetonitrile and diisopropyl ether.

$[\{Cp^*Rh(\mu\text{-thym})\}_4\{(CaNO_3)(MeCN)\}](NO_3)_{0.5}(OH)_{0.5}\cdot 9H_2O$ ($\mathbf{4}\cdot 9H_2O$)

A suspension of H_2thym (26 mg, 0.20 mmol) in methanol (10 mL) was added to a methanol solution (10 mL) of $[(Cp^*Rh)_2(\mu\text{-}OH)_3]OH$ (54 mg, 0.10 mmol), and the mixture was stirred for 3 h at ambient temperature. A methanol solution (10 mL) of $Ca(NO_3)_2\cdot 4H_2O$ (12 mg, 0.050 mmol) was added and the mixture was further stirred for 2 h. The resulting solution was evaporated to dryness under reduced pressure, and the residue was extracted with dichloromethane (20 mL). The filtered extract was evaporated, again, to dryness under reduced pressure. The crude product was recrystallized from an acetonitrile solution by vapor diffusion of diisopropyl ether, affording orange crystals suitable for X-ray analysis. Yield: 26.5 mg (30%). ^{1}H NMR (CD_3CN, 400 MHz, 21 °C): δ 1.57 (s, 3H, thym CH_3), 1.70 (s, 15H, Cp*), 7.09 (s,1H, thym C^6-*H*). ESI-MS (MeCN): *m*/*z* 1551.00 ($[\{Cp^*Rh(\mu\text{-thym})\}_4(CaNO_3)]^+$), 744.50 ($[\{Cp^*Rh(\mu\text{-thym})\}_4(Ca)]^{2+}$). Anal. Found (partially efflorescent sample): C, 42.15; H, 4.45; N, 8.21%. Calcd for $C_{62}H_{93.5}N_{10.5}O_{20}CaRh_4$ = $[\{Cp^*Rh(\mu\text{-thym})\}_4(CaNO_3)(MeCN)](NO_3)_{0.5}(OH)_{0.5}\cdot 7H_2O$: C, 42.37; H, 5.36; N, 8.37%.

$[\{Cp^*Rh(\mu\text{-thym})\}_4\{La(NO_3)_2(MeCN)\}]NO_3\cdot 2H_2O$ ($\mathbf{5}\cdot 2H_2O$)

A suspension of H_2thym (13 mg, 0.10 mmol) in methanol (10 mL) was added to a methanol solution (10 mL) of $[(Cp^*Rh)_2(\mu\text{-}OH)_3]OH$ (27 mg, 0.050 mmol), and the mixture was stirred for 3 h at ambient temperature. A methanol solution (10 mL) of $La(NO_3)_3{\bullet}6H_2O$ (12 mg, 0.025 mmol) was added and the mixture was further stirred for 2 h. The resulting solution was evaporated to dryness under reduced pressure, and the residue was extracted with dichloromethane (20 mL). The filtered extract was evaporated, again, to dryness under reduced pressure. The crude product was recrystallized from an acetonitrile solution by vapor diffusion of diethyl ether, affording orange crystals suitable for X-ray analysis. Yield: 11 mg (26%). ^1H NMR (CD_3OD, 300 MHz, 22 °C): δ 1.79 (s, 15H, Cp*), 1.81 (s, 3H, thym CH_3), 7.28 (s, 1H, thym $C^6\text{-}H$). ESI-MS (MeCN): *m*/*z* 1711.08 ($[\{Cp^*Rh(\mu\text{-thym})\}_4La(NO_3)_2]^+$), 824.55 ($[\{Cp^*Rh(\mu\text{-thym})\}_4La(NO_3)]^{2+}$). Anal. Found (after drying in vacuo): C, 39.69; H, 3.63; N, 8.94%. Calcd for $C_{60}H_{76}LaN_{11}O_{17}Rh_4$ = $[\{Cp^*Rh(\mu\text{-thym})\}_4 La(NO_3)_2]NO_3$: C, 40.63; H, 4.32; N, 8.69%.

$[\{Cp^*Rh(\mu\text{-thym})\}_4\{Eu(NO_3)_2(MeCN)\}]NO_3{\bullet}2H_2O$ (**6**•$2H_2O$)

This compound was prepared by a similar method to that for **5** using $Eu(NO_3)_3{\bullet}6H_2O$ (11 mg, 0.025 mmol), instead of $La(NO_3)_3{\bullet}6H_2O$. Recrystallization from an acetonitrile solution by vapor diffusion of diethyl ether gave orange crystals. Yield: 7.8 mg (18%). ESI-MS (MeCN): *m*/*z* 1724.98 ($[\{Cp^*Rh(\mu\text{-thym})\}_4Eu(NO_3)_2]^+$), 831.56 ($[\{Cp^*Rh(\mu\text{-thym})\}_4Eu(NO_3)]^{2+}$). Anal. Found (after drying in vacuo): C, 39.61; H, 4.15; N, 8.59%. Calcd for $C_{60}H_{76}EuN_{11}O_{17}Rh_4$ = $[\{Cp^*Rh(\mu\text{-thym})\}_4Eu(NO_3)_2]NO_3$: C, 40.33; H, 4.29; N, 8.62%.

$[\{Cp^*Rh(\mu\text{-thym})\}_4\{Dy(NO_3)_2\}]NO_3{\bullet}MeOH$ (**7**•MeOH)

A suspension of H_2thym (32 mg, 0.25 mmol) in methanol (10 mL) was added to a methanol solution (10 mL) of $[(Cp^*Rh)_2(\mu\text{-}OH)_3]OH$ (54 mg, 0.10 mmol), and the mixture was stirred for 3 h at ambient temperature. A methanol solution (10 mL) of $Dy(NO_3)_3{\bullet}6H_2O$ (24 mg, 0.053 mmol) was added and the mixture was further stirred for 2 h. The resulting solution was evaporated to dryness under reduced pressure, and the residue was extracted with dichloromethane (20 mL). The filtered extract was evaporated, again, to dryness under reduced pressure. The crude product was recrystallized from a methanol solution by layering of diisopropyl ether, affording orange crystals of **7**•MeOH. Yield: 42 mg (42%). ESI-MS (MeCN): *m*/*z* 1736.07 ($[\{Cp^*Rh(\mu\text{-thym})\}_4Dy(NO_3)_2]^+$), 835.53 ($[\{Cp^*Rh(\mu\text{-thym})\}_4Dy(NO_3)]^{2+}$). Anal. Found: C, 40.05; H, 4.41;

N, 8.42%. Calcd for $C_{61}H_{80}DyN_{11}O_{18}Rh_4$ = [{Cp*Rh(μ-thym)}$_4${Dy(NO_3)$_2$}]NO_3•MeOH: C, 40.09; H, 4.26; N, 8.57%. Single-crystals suitable for X-ray analysis were obtained by recrystallization from a mixture of methanol and diisopropyl ether, but the analysis revealed that they contained a free H_2thym ligand per tetrarhodium–dysprosium unit: **7**•H_2thym•MeOH

[{Cp*Rh(μ-thym)}$_4${Er(NO_3)$_2$}]NO_3•MeOH (**8**•MeOH)

This compound was prepared by a similar method to that for **7** using Er(NO_3)$_3$•6H_2O (24 mg, 0.052 mmol), instead of Dy(NO_3)$_3$•6H_2O. Recrystallization from a methanol solution by vapor diffusion of diethyl ether gave orange crystals. Yield: 41mg (42%). ESI-MS (MeCN): *m*/*z* 1740.08 ([{Cp*Rh(μ-thym)}$_4$Er(NO_3)$_2$]$^+$), 837.06 ([{Cp*Rh(μ-thym)}$_4$Er(NO_3)]$^{2+}$). Anal. Found: C, 38.86; H, 4.40; N, 8.61%. Calcd for $C_{61}H_{80}ErN_{11}O_{18}Rh_4$ = [{Cp*Rh(μ-thym)}$_4${Er(NO_3)$_2$}]NO_3•MeOH: C, 39.94; H, 4.40; N, 8.40%. Single-crystals suitable for X-ray analysis were also contained a free H_2thym molecule: **8**•H_2thym•MeOH.

Crystallography

The X-ray diffraction data were obtained using a Rigaku R-axis rapid imaging plate detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A suitable crystal was mounted with a cryoloop and flash cooled using a cold nitrogen gas stream. The data were processed using the Process-Auto software package,[2] and the absorption corrections were applied using the numerical method from the crystal shapes.[3] The structures were solved using the direct method employing the SIR2004 software package[4] or SHELXS97 software package,[5] and refined on F^2 (with all independent reflections) using the SHELXL97 software package.[5] All non-H atoms were refined anisotropically (except for those noted below), and all H atoms in the complexes were introduced at the theoretical positions and treated using riding models. All the calculations were carried out using the CrystalStructure software package.[6] Crystal data of all compound analyzed in this study are summarized in Table S1.

Non-standard techniques used for individual analysis are listed below: **1**•Et_2O•MeOH: H atoms of a solvated methanol molecule were not included in the calculation. **2**•Et_2O•MeOH•H_2O: The ligating F atom of BF_4^- anion and the O atom of hydrated water molecule were disordered over two possible positions with their occupation factors of 0.5. H atoms of a solvated methanol and water molecules were not included in the calculation. **3**•3MeCN•H_2O: The coordinated O atoms of the NO_3^- anion and one of three acetonitrile molecules of crystallization were disordered over two possible positions. H atoms of the disordered acetonitrile molecule and a hydrated water molecule were not included in the calculation. **4**•9H_2O: The anions of NO_3^- and OH^- were treated as the disordered atoms with their occupancies of 0.5, and one of nine water molecules of crystallization was also positionally disordered with occupation factor of 0.333. All H atoms of the hydrated water molecules were not included in the calculation. **5**•2H_2O and **6**•2H_2O: These complexes were crystallized in a chiral space group $P2_12_12$ (no. 18), and a homochiral aggregation of Cp*Rh^{III} fragments and the bridging thym^{2-} ligands were achieved. However, both enantiomers were co-crystallized in the analyzed crystal as disordered atoms. Thus, we analyzed the overlapped model of two structures of cyclic tetramers (with the same $Ln(NO_3)_2$ moiety) in the occupation factors of 0.683:0.317 and 0.779:0.221 for **5**•2H_2O and **6**•2H_2O, respectively. The non-coordinate NO_3^- anion was also treated as disordered atoms over two possible positions. **7**•H_2thym•MeOH: H atoms of a solvated methanol molecule were not included in the calculation. **8**•H_2thym•MeOH: Non-H atoms of a free H_2thym, a non-coordinated NO_3^- anion, and a solvated methanol molecule were treated isotropically, and H atoms of a solvated methanol molecule were not included in the calculation.

Measurements

Elemental analyses were performed at Department of Instrumental Analysis, Advanced Science Research Center, Okayama University. ^1H and $^{13}C\{^1H\}$ NMR spectra were acquired on Varian Mercury 300, 400-MR, and VXR 500 spectrometers at 22 °C; the chemical shifts were referenced to residual ^1H and ^{13}C NMR signals of solvents and are reported versus TMS. The ESI mass spectra (positive mode) of complexes in MeOH or MeCN were measured on an ABI QSTAR-Elite mass spectrometer using a turbo spray ionization mode and cone voltage of 20 V. Exact mass numbers were calibrated using plasticizer ($+Na^+$) signals.

References

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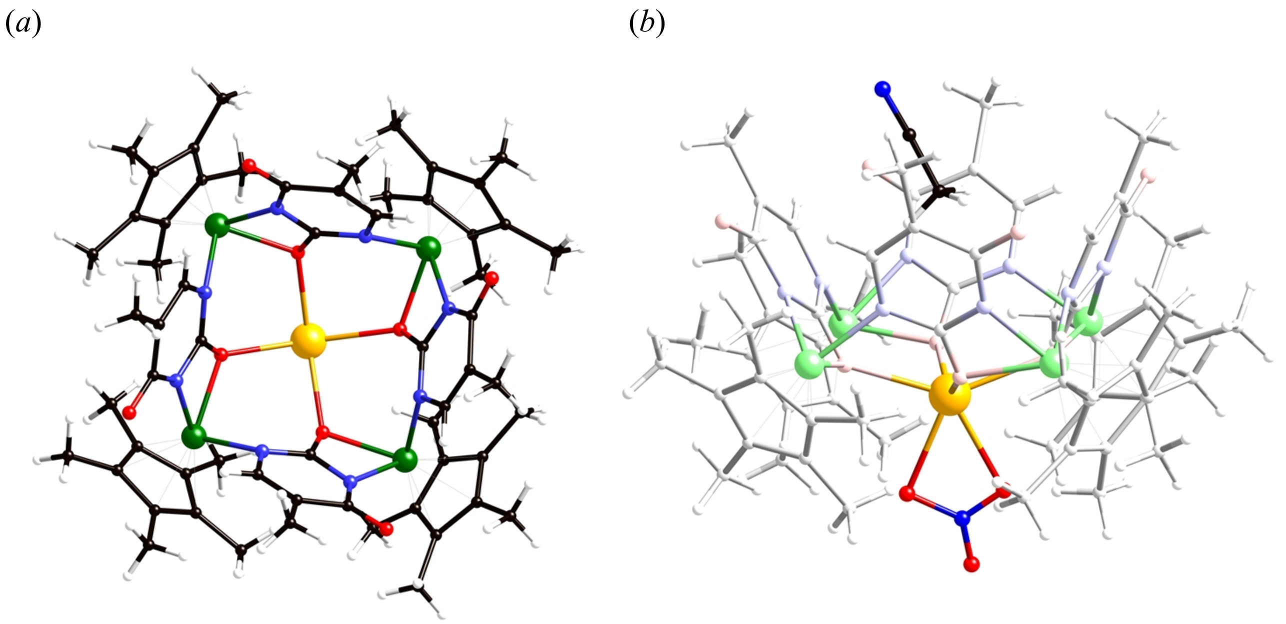

Fig. S1 Perspective views of (*a*) the $[(Cp^*Rh)_4(\mu\text{-thym})_4Na]^+$ moiety and (*b*) the $Na(NO_3)$ and the CH_3CN moieties in **3**•3MeCN•H_2O. Color code: Rh, green; Na, orange; O, red; N, blue; C, black; H, white.

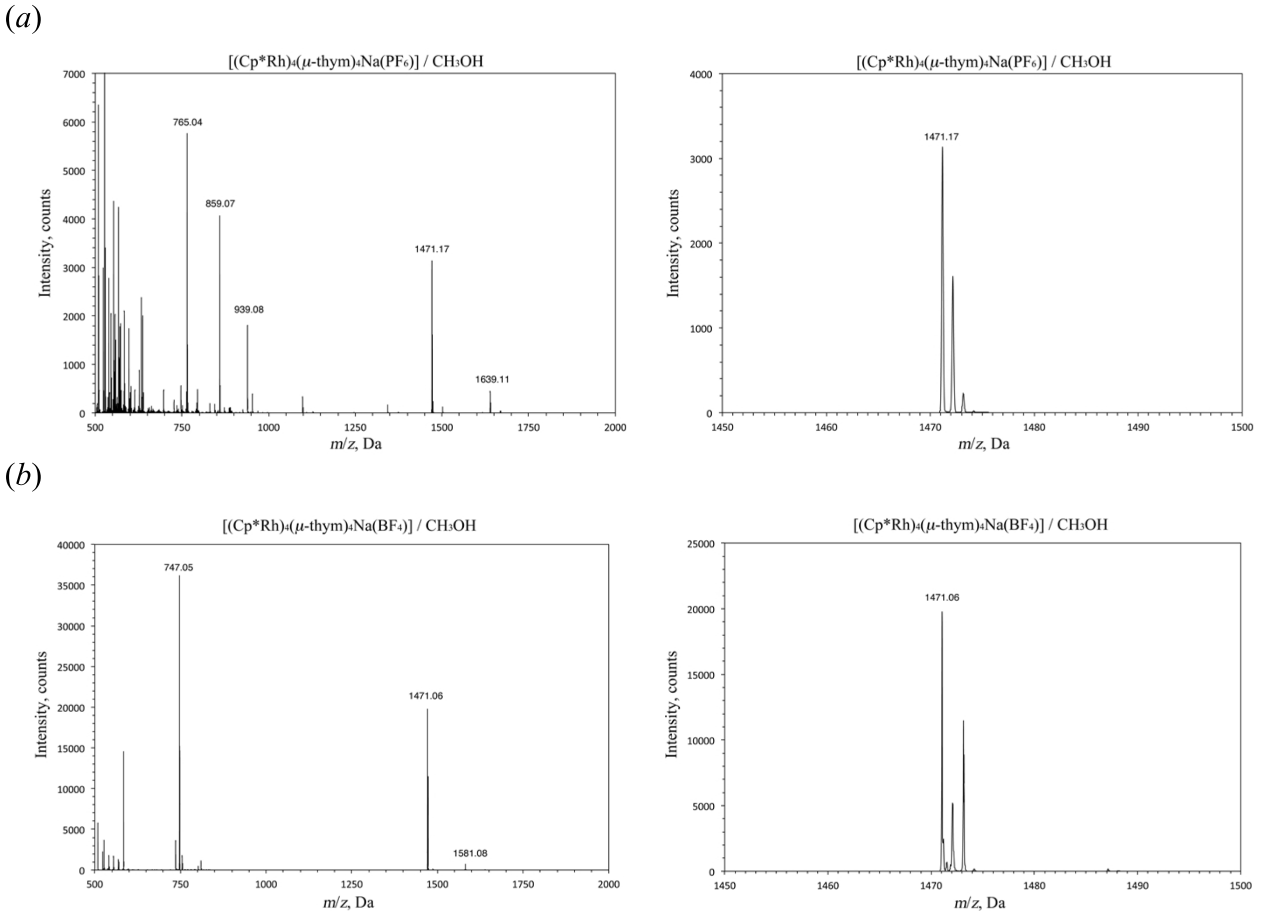

Fig. S2 ESI-mass spectra of complexes (*a*) **1** and (*b*) **2** in MeOH

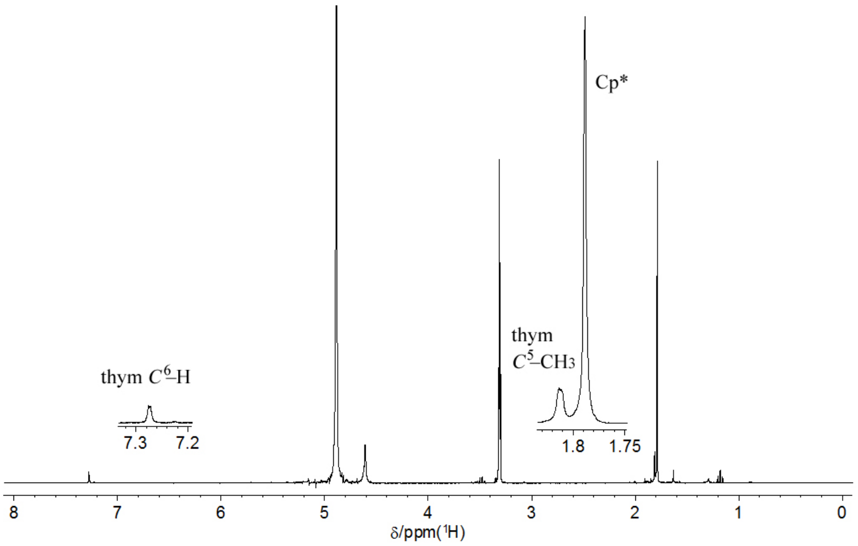

Fig. S3 ^{1}H NMR spectrum of the isolated [(Cp*Rh)$_4$(μ-thym)$_4$Na(PF$_6$)] (**1**) in CD$_3$OD.

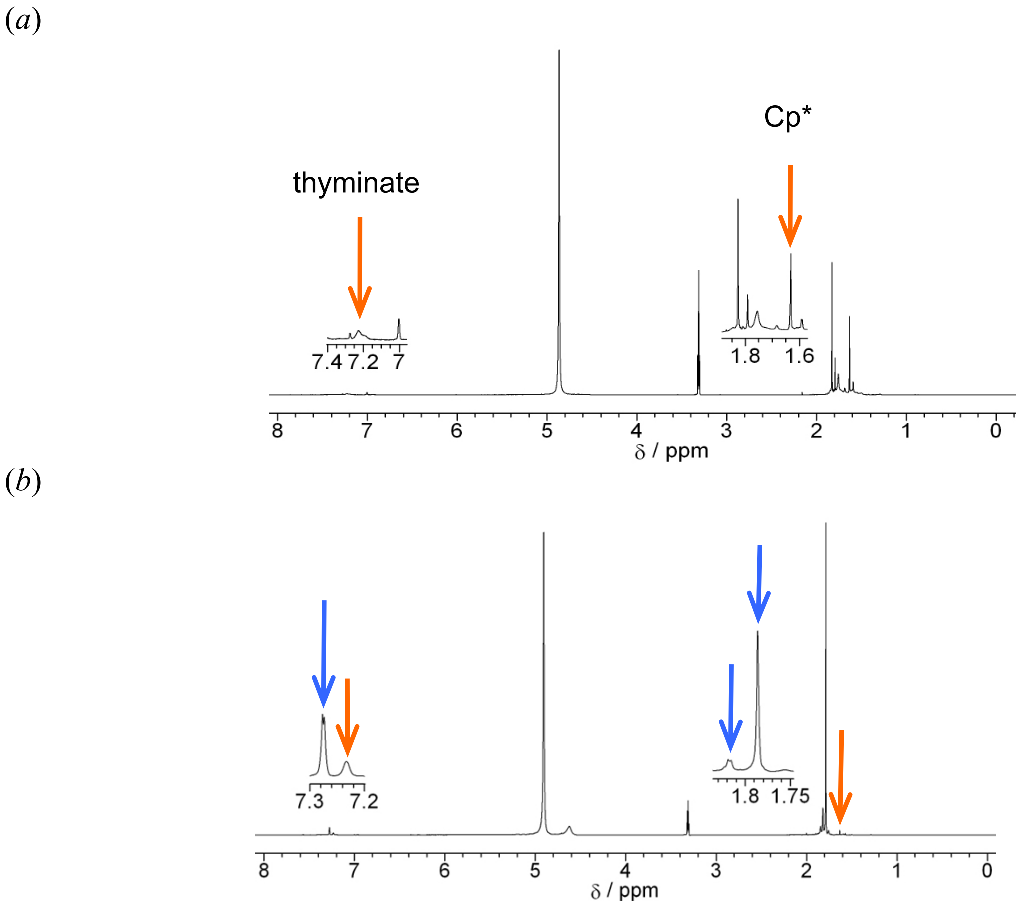

Fig. S4 (*a*) ^{1}H NMR spectrum of a reaction mixture of [(Cp*Rh)$_2$(μ-OH)$_3$]OH and thymine (in 1:2 molar ratio) in CD$_3$OD, and (*b*) that of the same reaction mixture after addition of excess NaPF$_6$. Orange arrows indicated the resonances of starting materials and blue arrows showed the resonances of complex **1**.

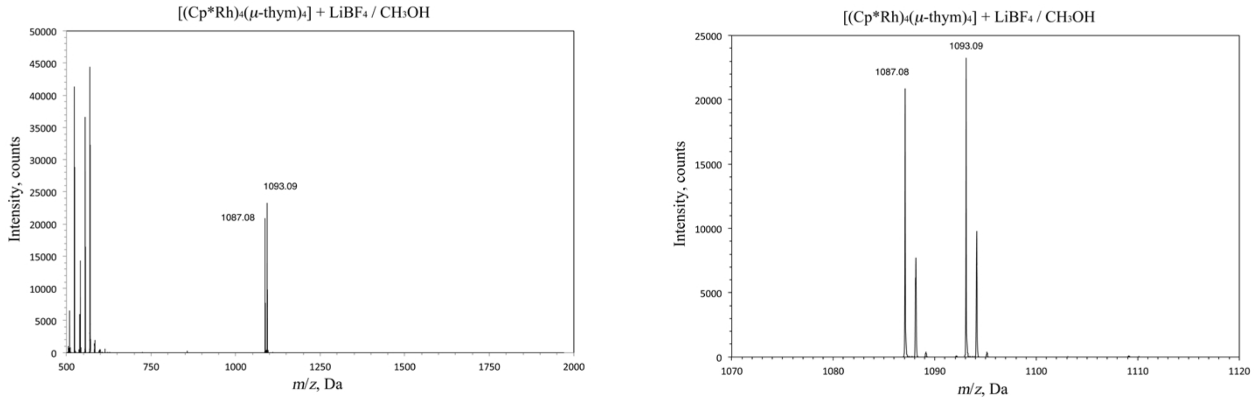

Fig. S5 ESI-mass spectra of the reaction mixture of $[(Cp^*Rh)_2(\mu\text{-}OH)_3]OH$, H_2thym (2 equiv.) and $LiBF_4$ in MeOH.

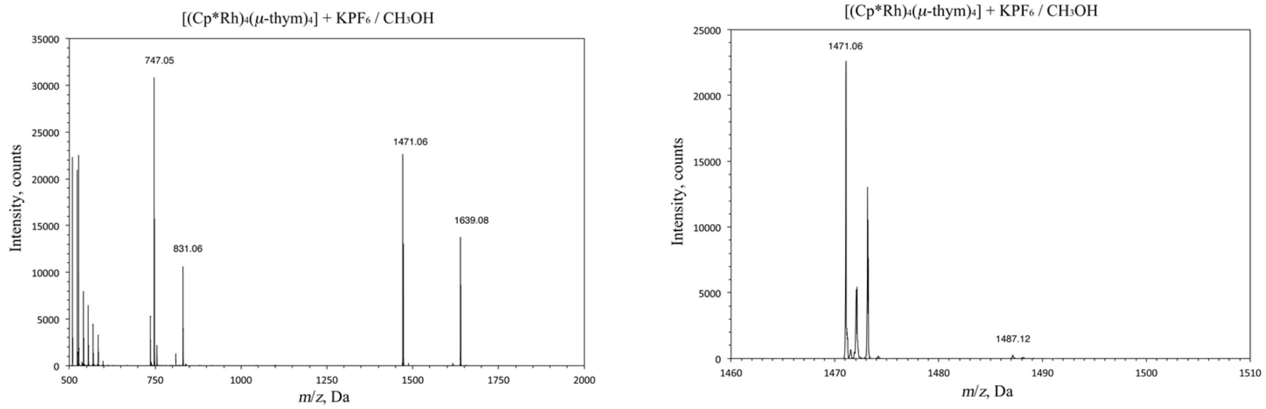

Fig. S6 ESI-mass spectra of the reaction mixture of $[(Cp^*Rh)_2(\mu\text{-}OH)_3]OH$, H_2thym (2 equiv.) and KPF_6 in MeOH.

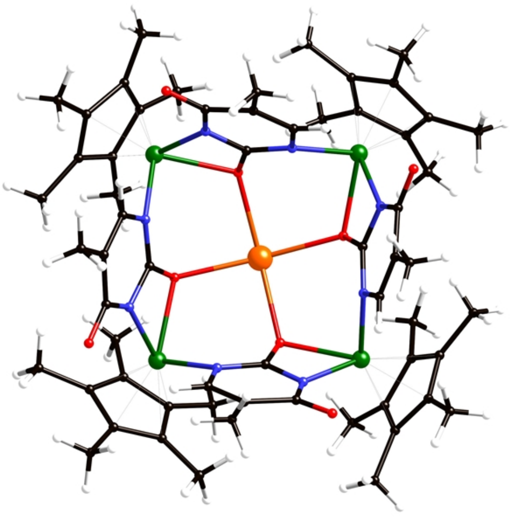

Fig. S7 A perspective view of the $[(Cp^*Rh)_4(\mu\text{-thym})_4Ca]^{2+}$ moiety in **3**•$3CH_3CN$•H_2O. Color code: Rh, green; Ca, orange; O, red; N, blue; C, black; H, white.

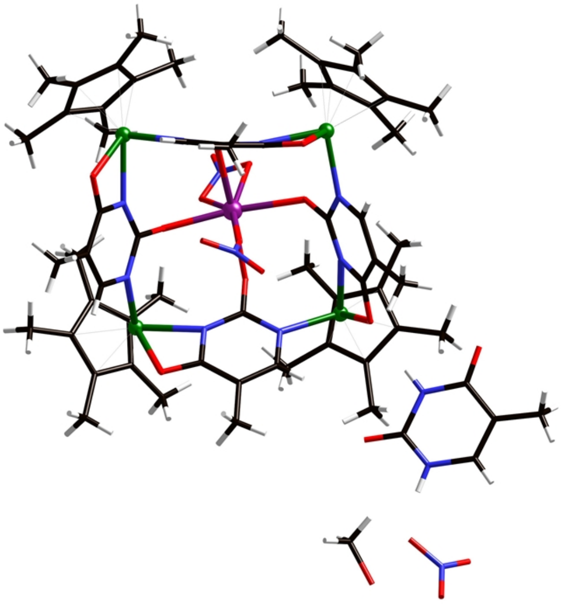

Fig. S8 A perspective view of an unit of $[(Cp^{*}Rh)_4(\mu\text{-thym})_4Dy(NO_3)_2](NO_3)\bullet H_2thym\bullet MeOH$ in **7**•H_2thym•MeOH, illustrating the hydrogen bonds between one of the bridging thym^{2-} and a free H_2thym, and between the free H_2thym and a NO_3^- anion. Color code: Dy, purple; Rh, green; O, red; N, blue; C, black; H, white.

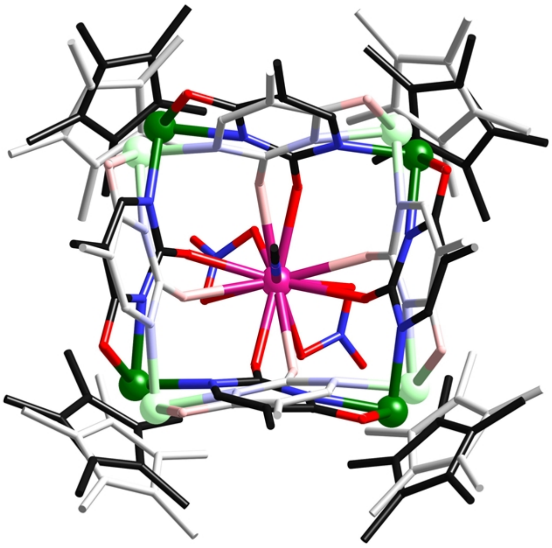

Fig. S9 Perspective view of the overlapped enantiomeric $[(Cp^{*}Rh)_4(\mu\text{-thym})_4Eu(NO_3)_2]^+$ cations found in a non-centrosymmetric crystal of **6**•2MeOH. Color code: Eu, bright pink; Rh, green; O, red; N, blue; C, black; H, white, and the lighter colors are the minor conformer.

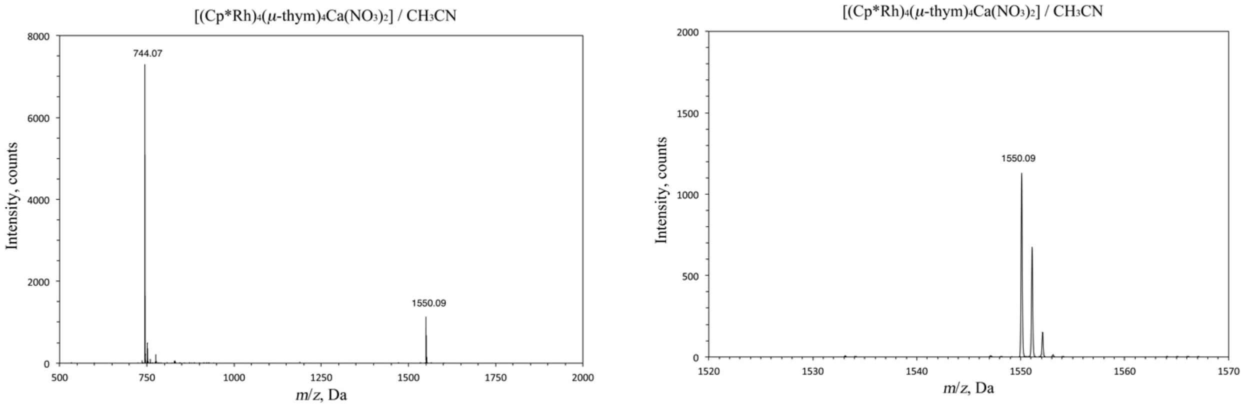

Fig. S10 ESI-mass spectra of complex **4** in MeCN.

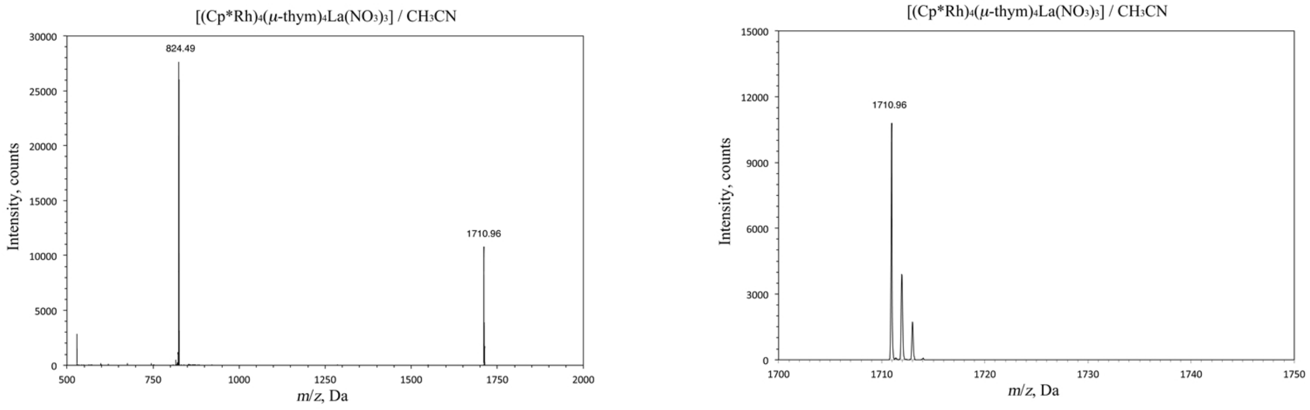

Fig. S11 ESI-mass spectra of complex **5** in MeOH.

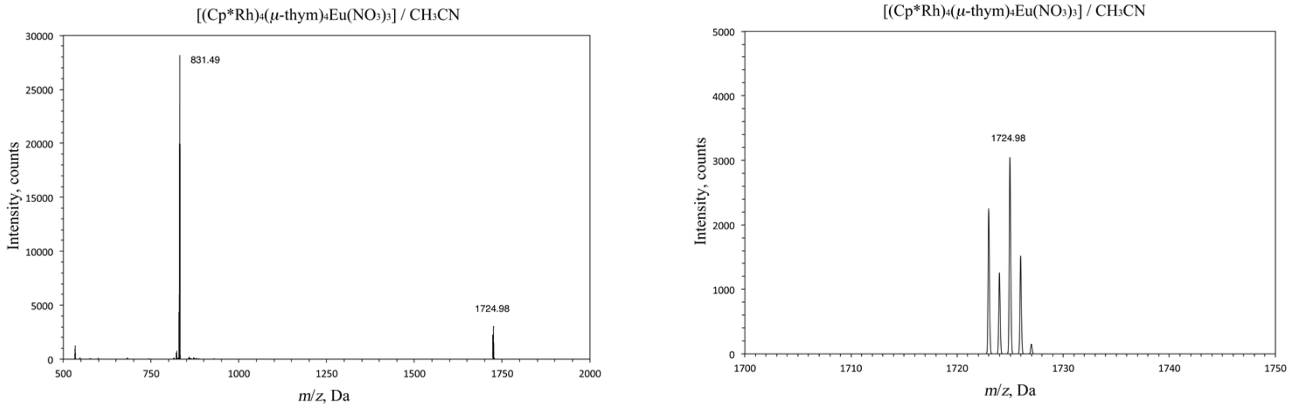

Fig. S12 ESI-mass spectra of complex **6** in MeOH.

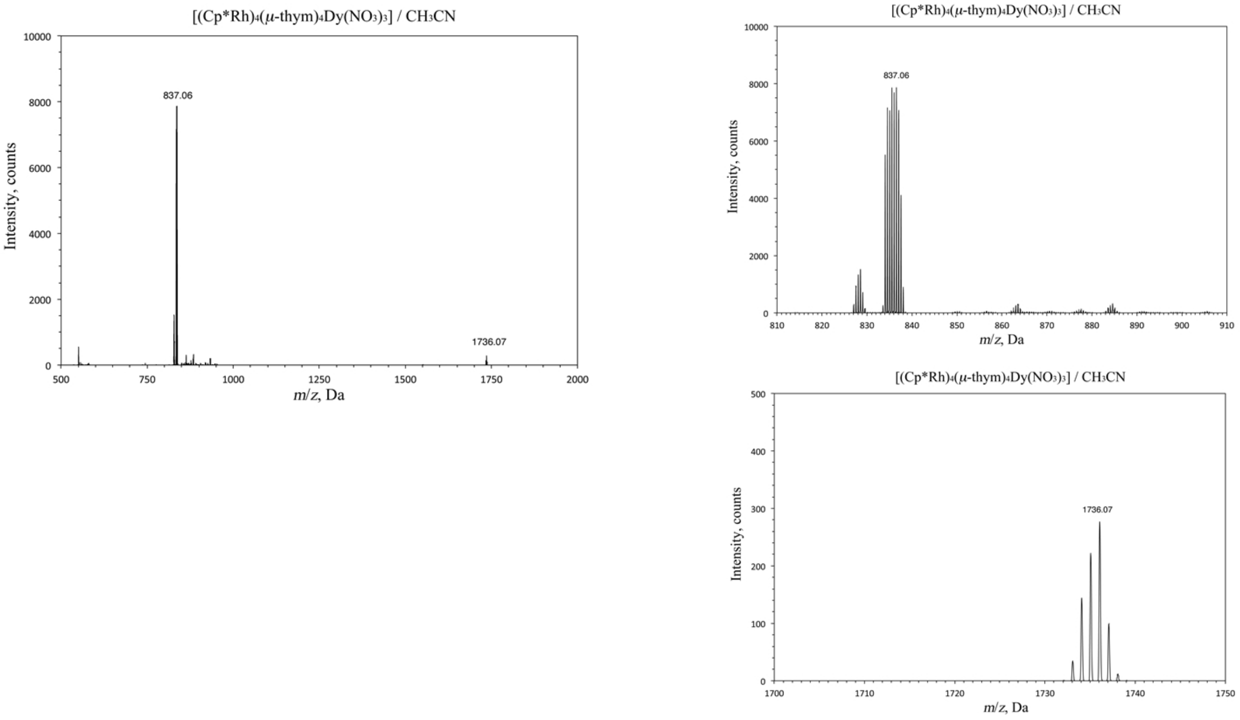

Fig. S13 ESI-mass spectra of complex **7** in MeCN.

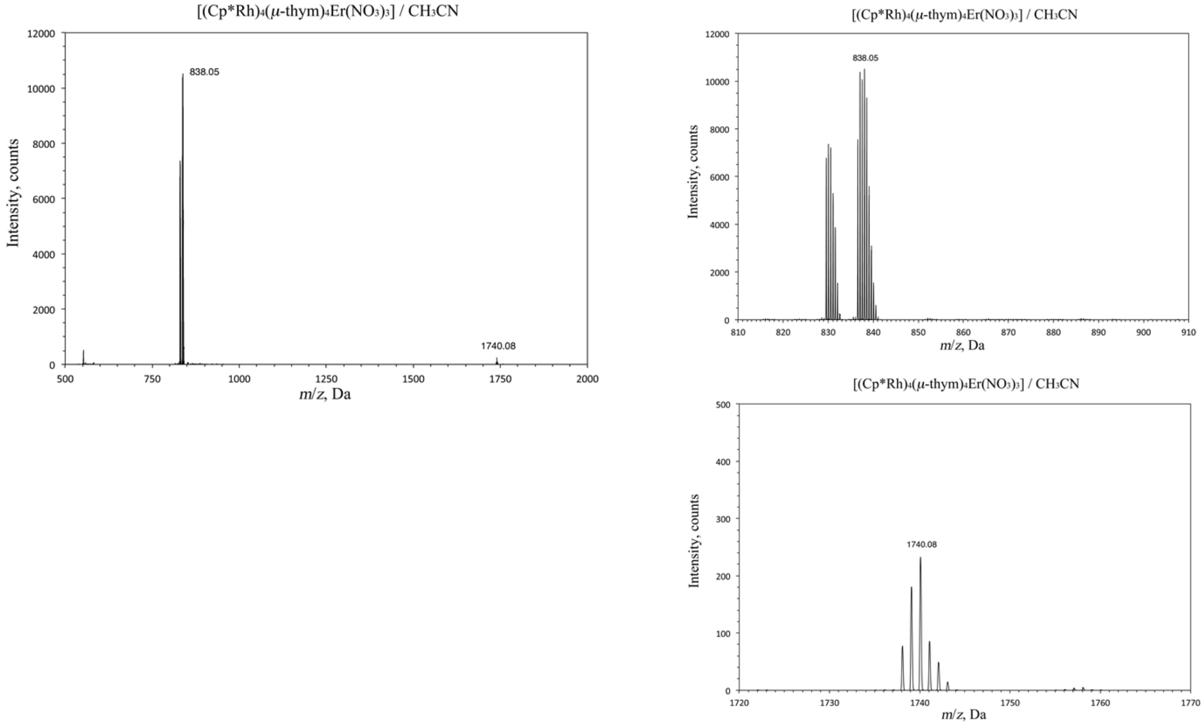

Fig. S14 ESI-mass spectra of complex **8** in MeCN.

Table S1 Crystallographic data for compounds **1**–**8**.

Complex	**1**•Et_2O•MeOH	**2**•Et_2O•MeOH•H_2O	**3**•3MeCN•H_2O	**4**•9H_2O
Chemical formula	$C_{65}H_{90}F_6N_8NaO_{10}PRh_4$	$C_{65}H_{92}BF_4N_8NaO_{11}Rh_4$	$C_{66}H_{87}N_{12}NaO_{12}Rh_4$	$C_{62}H_{97.5}CaN_{10.5}O_{22}Rh_4$
Formula weight	1723.05	1682.90	1675.10	1793.72
T / K	185(2)	233(2)	186(2)	192(2)
Crystal color and shape	orange, prism	orange, plate	orange, block	orange, block
Size of specimen / mm	0.30 × 0.20 × 0.10	0.25 × 0.20 × 0.20	0.40 × 0.40 × 0.40	0.25 × 0.25 × 0.40
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic
Space group, Z	$P2_1/c$, 4	$P2_1/c$, 4	*Pbca*, 8	*P*¯, 8
a / Å	16.7562(6)	16.6620(7)	22.6289(7)	11.3211(7)
b / Å	16.3493(8)	16.4372(7)	21.7265(7)	18.6735(10)
c / Å	27.6506(9)	27.4724(10)	29.7275(15)	18.7302(8)
α / °	90	90	90	89.602(2)
β / °	91.707(1)	94.940(1)	90	75.171(2)
γ□/ °	90	90	90	87.676(3)
U / $Å^3$	7571.6(5)	7496.1(5)	14615.4(10)	3824.6(4)
D_{calc} / Mg m^{-3}	1.512	1.491	1.523	1.558
μ(Mo Kα) / mm^{-1}	0.955	0.940	0.959	0.991
R_{int}	0.0484	0.0443	0.0426	0.0699
No. reflns / params.	17312 / 856	17152 / 865	16164 / 871	17268 / 937
$R1$ (F^2: $F_o^2 > 2\sigma(F_o^2)$)	0.0811	0.0605	0.0434	0.0545
$wR2$ (F^2: all data)	0.2495	0.1818	0.1464	0.1585
GoF	1.030	1.028	1.052	1.068
Flack param.	—	—	—	—

Table S1 (Continued) Crystallographic data for compounds **1**–**8**.

Complex	**5**•2H_2O	**6**•2H_2O	**7**•H_2thym•MeOH	**8**•H_2thym•MeOH
Chemical formula	$C_{62}H_{83}LaN_{12}O_{19}Rh_4$	$C_{62}H_{83}EuN_{12}O_{19}Rh_4$	$C_{66}H_{86}DyN_{13}O_{20}Rh_4$	$C_{66}H_{86}ErN_{13}O_{20}Rh_4$
Formula weight	1850.95	1864.00	1955.62	1960.38
T / K	186(2)	186(2)	191(2)	193(2)
Crystal color and shape	orange, block	orange, block	orange, block	orange, prism
Size of specimen / mm	0.28 × 0.23 × 0.20	0.25 × 0.20 × 0.10	0.45 × 0.30 × 0.20	0.10 × 0.10 × 0.10
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group, Z	$P2_12_12$, 2	$P2_12_12$, 2	$P2_1/c$, 4	$P2_1/c$, 4
a / Å	18.7826(10)	18.4641(7)	13.9749(6)	13.8619(4)
b / Å	19.9113(12)	19.8783(8)	18.7743(6)	18.8672(8)
c / Å	10.6111(5)	10.5405(3)	28.0431(10)	28.1155(9)
α / °	90	90	90	90
β / °	90	90	93.975(1)	93.687(1)
γ / °	90	90	90	90
U / Å^3	3968.4(4)	3868.7(2)	7339.9(5)	7338.0(4)
D_{calc} / Mg m^{-3}	1.549	1.600	1.770	1.774
μ(Mo Kα) / mm^{-1}	1.410	1.705	1.966	2.092
R_{int}	0.0661	0.0472	0.0521	0.0917
No. reflns / params.	9089 / 571	8861 / 573	16784 / 937	16780 / 862
$R1$ (F^2: $F_o^2 > 2\sigma(F_o^2)$)	0.0624	0.0493	0.0507	0.0668
$wR2$ (F^2: all data)	0.1827	0.1349	0.1323	0.1810
GoF	1.069	1.077	0.965	0.986
Flack param.	0.50(3)	0.503(16)	—	—

Table S2 Selected bond lengths (*l*/Å) and angles (*ϕ*/°) of complexes **1**–**8**.

	1	**2**	**3**	**4**
Rh1–N1	2.096(6)	2.107(4)	2.096(3)	2.104(3)
Rh2–N3	2.084(6)	2.102(4)	2.096(3)	2.097(3)
Rh3–N5	2.092(7)	2.110(5)	2.083(3)	2.103(3)
Rh4–N7	2.133(6)	2.098(4)	2.091(3)	2.088(3)
Rh1–N8	2.053(8)	2.072(4)	2.075(3)	2.091(3)
Rh2–N2	2.095(6)	2.095(5)	2.071(4)	2.071(3)
Rh3–N4	2.066(7)	2.101(4)	2.075(3)	2.076(3)
Rh4–N6	2.072(7)	2.079(5)	2.067(3)	2.094(3)
Rh1–O7	2.169(5)	2.198(3)	2.204(3)	2.263(3)
Rh2–O1	2.190(5)	2.215(3)	2.214(2)	2.265(3)
Rh3–O3	2.249(5)	2.215(3)	2.206(3)	2.287(3)
Rh4–O5	2.218(5)	2.225(3)	2.201(2)	2.273(3)
Na1(Ca1)–O1	2.497(6)	2.416(4)	2.428(3)	2.356(3)
Na1(Ca1)–O3	2.484(6)	2.387(4)	2.427(3)	2.382(3)
Na1(Ca1)–O5	2.434(6)	2.382(4)	2.425(3)	2.355(3)
Na1(Ca1)–O7	2.496(6)	2.397(4)	2.408(3)	2.372(3)
Na1–F(BF_4 or PF_6)	1.990(11)	2.548(15)	—	—
Na1(Ca1)–O(NO_3)	—	—	2.415(10)–2.499(12)	2.440(5), 2.445(4)
Ca1–N10(CH_3CN)	—	—	—	2.611(4)
O7–Rh1–N8	62.4(2)	62.32(14)	61.61(11)	60.77(11)
O1–Rh2–N2	61.9(2)	61.72(14)	61.48(11)	60.84(11)
O3–Rh3–N4	60.8(2)	61.28(15)	61.80(12)	60.32(11)
O5–Rh4–N6	60.3(2)	61.63(15)	61.78(11)	60.65(12)
O7–Rh1–N1	91.6(2)	89.44(14)	89.32(12)	90.74(11)
O1–Rh2–N3	90.7(2)	89.08(15)	89.51(11)	90.29(11)
O3–Rh3–N5	91.2(2)	90.09(15)	90.47(12)	90.26(11)
O5–Rh4–N7	90.6(2)	91.01(14)	90.05(11)	91.87(11)
N8–Rh1–N1	85.9(3)	84.00(16)	85.54(13)	85.88(13)
N2–Rh2–N3	85.4(2)	86.92(17)	84.37(14)	85.73(13)
N4–Rh3–N5	84.9(3)	84.82(17)	84.27(12)	86.31(13)
N6–Rh4–N7	85.5(3)	86.60(17)	85.29(13)	85.51(13)
O1–Na1(Ca1)–O5	137.8(2)	144.97(14)	143.03(11)	159.25(11)
O3–Na1(Ca1)–O7	139.3(2)	146.57(14)	142.67(10)	158.22(11)
O1–Na1(Ca1)–O3	81.00(19)	82.91(13)	84.42(10)	87.53(9)
O3–Na1(Ca1)–O5	83.2(2)	85.34(14)	83.97(11)	87.19(9)
O5–Na1(Ca1)–O7	84.23(19)	85.73(13)	84.10(10)	88.80(10)
O7–Na1(Ca1)–O1	82.82(18)	86.20(13)	84.22(10)	88.70(9)
Rh2–O1–Na1(Ca1)	118.9(2)	120.67(16)	117.71(13)	116.91(10)
Rh3–O3–Na1(Ca1)	116.8(2)	117.40(15)	118.46(12)	117.44(12)
Rh4–O5–Na1(Ca1)	117.5(2)	117.70(16)	118.17(12)	115.22(11)
Rh1–O7–Na1(Ca1)	117.7(2)	117.55(15)	118.22(12)	116.49(12)

Table S2 (Continued) Selected bond lengths (l/Å) and angles (ϕ/°) of complexes **1**–**8**.

	5[a]	**6**[a]	**7**	**8**
Rh1–N1	—		2.104(5)	2.094(7)
Rh2–N3	—		2.085(5)	2.103(7)
Rh3–N5(102)	2.082(10)	2.103(7)	2.092(5)	2.093(7)
Rh4–N7(202)	2.072(9)	2.102(7)	2.098(5)	2.087(7)
Rh1–N8	—	—	2.143(5)	2.130(7)
Rh2–N2	—	—	2.129(5)	2.138(6)
Rh3–N4(201’)	2.119(9)	2.102(7)	2.116(5)	2.123(7)
Rh4–N6(101)	2.104(9)	2.108(7)	2.131(5)	2.114(7)
Rh1–O8	—	—	2.209(4)	2.222(6)
Rh2–O2	—	—	2.186(5)	2.221(6)
Rh3–O4(202’)	2.178(9)	2.171(7)	2.215(5)	2.217(6)
Rh4–O6(102)	2.165(8)	2.158(6)	2.201(4)	2.205(7)
Ln1–O1(101)	2.498(7)	2.378(5)	2.242(4)	2.230(5)
Ln1–O3(201)	2.481(7)	2.354(5)	2.251(4)	2.235(6)
Ln1–O5	—	—	2.290(4)	2.229(6)
Ln1–O7	—	—	2.252(4)	2.277(5)
Ln1–O(NO_3)	2.632(8), 2.722(7)	2.501(7) 2.710(8)	2.385(7), 2.387(6) 2.266(4)	2.410(8), 2.402(7) 2.253(6)
Ln1–N511	2.761(8)	2.663(7)	—	—
O8–Rh1–N8	—	—	59.81(16)	59.7(2)
O2–Rh2–N2	—	—	60.08(17)	59.7(2)
O4(202’)–Rh3–N4(201’)	61.7(3)	61.7(2)	60.14(18)	59.8(2)
O6(102)–Rh4–N6(101)	61.7(3)	61.6(2)	60.30(16)	59.7(2)
O8–Rh1–N1	—	—	91.73(19)	89.9(2)
O2–Rh2–N3	—	—	91.37(19)	91.3(3)
O4(202’)–Rh3–N5(102)	86.2(3)	87.0(2)	91.11(19)	91.3(3)
O6(102)–Rh4–N7(202)	86.2(3)	86.0(2)	89.40(17)	90.8(3)
N8–Rh1–N1	—	—	91.02(18)	88.3(2)
N2–Rh2–N3	—	—	87.32(18)	90.5(2)
N4(201’)–Rh3–N5(102)	83.6(3)	83.2(2)	90.52(19)	87.4(3)
N6(101)–Rh4–N7(202)	85.5(3)	84.8(2)	88.49(17)	90.3(3)
O1(101)–Ln1–O5(101’)	142.5(3)	146.4(3)	163.60(15)	165.58(19)
O3(201)–Ln1–O7(201’)	141.4(3)	144.2(3)	164.55(14)	163.4(2)
O1(101)–Ln1–O3(201)	82.5(2)	83.9(2)	88.19(16)	87.6(2)
O3(201)–Ln1–O5(101’)	85.3(2)	85.9(2)	89.31(16)	88.5(2)
O5–Ln1–O7	—	—	90.78(16)	89.0(2)
O7–Ln1–O1	—	—	87.37(16)	90.7(2)
Ln1–O1(101)–C11(101)	129.7(4)	129.6(4)	132.6(4)	125.6(5)
Ln1–O3(201)–C26(201)	133.8(4)	135.4(4)	126.3(4)	134.0(5)
Ln1–O5–C41	—	—	125.5(4)	125.8(5)
Ln1–O7–C56	—	—	125.4(3)	126.6(5)

[a] Only the parameters in the major isomer was listed.

Table S3 Selected dihedral angles (ϕ/°) and non-bonding distances (l/Å) of complexes **1**–**8**.

	1	**2**	**3**	**4**
Na(Ca)···pl(4O-thym)	0.876(4)	0.704(3)	0.772(2)	0.436(2)
Rh1···Na1(Ca1)	4.039(3)	3.931(2)	3.9589(17)	3.9422(8)
Rh2···Na1(Ca1)	4.033(3)	4.025(2)	3.9746(16)	3.9389(10)
Rh3···Na1(Ca1)	3.979(2)	3.933(2)	3.9826(18)	3.9894(9)
Rh4···Na1(Ca1)	3.996(3)	3.944(2)	3.9706(16)	3.9083(10)
Rh1···Rh2	5.4170(9)	5.4308(6)	5.3835(6)	5.4719(6)
Rh1···Rh3	7.6321(8)	7.6362(7)	7.6067(8)	7.7423(6)
Rh1···Rh4	5.3853(8)	5.3632(6)	5.3866(9)	5.4317(6)
Rh2···Rh3	5.3982(8)	5.3954(7)	5.3852(9)	5.4450(6)
Rh2···Rh4	7.6358(9)	7.6262(6)	7.6251(7)	7.6896(7)
Rh3···Rh4	5.3918(9)	5.4122(7)	5.3859(6)	5.4777(6)
O1–Na1(Ca1)–O5	137.8(2)	144.97(14)	143.03(11)	159.25(11)
O3–Na1(Ca1)–O7	139.3(2)	146.57(14)	142.67(10)	158.22(11)
O1···O5	4.670(7)	4.575(5)	4.603(4)	4.635(4)
O3···O7	4.601(7)	4.582(5)	4.581(4)	4.674(4)
C5···C15	9.311(18)	9.615(12)	9.078(9)	8.772(8)
C10···C20	9.389(19)	9.144(11)	9.262(7)	8.713(8)
Pl (thym1) vs. pl(thym3)	54.9(2)	59.3(1)	54.62(8)	51.67(9)
Pl(thym2) vs. pl(thym4)	56.3(2)	55.0(1)	55.33(9)	50.97(9)

Table S3 (Continued)

	5	**6**	**7**	**8**
La···pl(4O-thym)	0.812(4)	0.706(3)	0.311(2)	0.304(3)
	0.797(8)	0.68(1)		
Rh1···La1	—	—	4.6432(6)	4.6456(8)
Rh2···La1	—	—	4.5871(7)	4.6419(7)
Rh3···La1	4.8208(14)	4.7495(10)	4.6674(6)	4.5799(8)
(Rh8···La1)	4.914(3)	4.852(3)		
Rh4···La1	4.9263(14)	4.8509(10)	4.6601(7)	4.6665(7)
(Rh9···La1)	4.814(4)	4.742(3)		
Rh1···Rh2	—	—	6.3489(6)	6.2795(8)
Rh1(Rh3’)···Rh3	8.884(2)	8.8649(14)	8.8045(7)	8.9738(8)
(Rh8’···Rh8)	9.009(5)	8.965(5)		
Rh1(Rh3’)···Rh4	6.348(2)	6.3351(14)	6.2500(8)	6.2962(8)
(Rh8’···Rh9)	6.342(5)	6.319(5)		
Rh2(Rh4’)···Rh3	—	—	6.2959(8)	6.3326(8)
Rh2(Rh4’)··Rh4	9.023(2)	8.9800(14)	8.9831(8)	8.8184(8)
(Rh9’···Rh9)	8.871(5)	8.839(5)		
Rh3···Rh4	6.316(2)	6.2860(13)	6.3166(6)	6.3105(8)
(Rh8···Rh9)	6.303(5)	6.274(5)		
O1(101)–Ln1–O5(101’)	142.5(3)	146.4(3)	163.60(15)	165.58(19)
O3(201)–Ln1–O7(201’)	141.4(3)	144.2(3)	164.55(14)	163.4(2)
O1(O101)···O5(O101’)	4.730(9)	4.552(7)	4.485(6)	4.426(7)
(O601···O601’)	4.728(19)	4.73(2)		
O3(O201)···O7(O201’)	4.682(10)	4.479(7)	4.463(6)	4.465(7)
(O701···O701’)	4.71(2)	4.66(2)		
C5(C105)···C15(C105’)	8.835(19)	8.930(17)	10.571(10)	9.272(15)
(C605···C605’)	8.85(3)	8.44(3)		
C10(C205)···C20(C205’)	9.567(17)	9.767(15)	9.304(12)	10.566(13)
(C705···C705’)	9.19(3)	9.31(4)		
Pl(thym1) vs. pl(thym3	42.5(2)	44.9(2)	64.5(1)	54.7(2)
or thym1’)	52.1(2)	38.6(5)		
Pl(thym2) vs. pl(thym4	43.4(4)	56.4(2)	54.4(1)	65.1(2)
or thym2’)	47.5(4)	49.5(5)		