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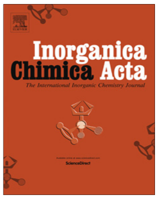

Thyminato-bridged cyclic tetranuclear rhodium(III) complexes containing a sodium, calcium or lanthanoid ion as a template metal core

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ABSTRACT

Reactions of $[(\mathrm{Cp^*Rh})_2(\mu\text{-OH})_3]\mathrm{OH}$ ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5^-}$) and thymine (=$\mathrm{H_2thym}$) in methanol in the presence or absence of a certain metal salt were examined. From the reaction mixture without any template metal salt, a dinuclear hydroxido-bridged complex bearing monodentate monodeprotonated thyminato ligands, $[\{\mathrm{Cp^*Rh}(\mathrm{Hthym}\text{-}\kappa N^1)\}_2(\mu\text{-OH})_2]$, was isolated after recrystallization from water. In the presence of a metal salt MX_n {=$\mathrm{NaPF_6}$, $\mathrm{NaBF_4}$, $\mathrm{NaNO_3}$, $\mathrm{Ca(NO_3)_2}$, $\mathrm{Ca(ClO_4)_2}$, $\mathrm{La(NO_3)_3}$, $\mathrm{Eu(NO_3)_3}$, $\mathrm{Dy(NO_3)_3}$ and $\mathrm{Er(NO_3)_3}$} were deposited orange crystals (**1P**, **1B**, **1N**, **2N**, **2C**, **3N**, **4N**, **5N** and **6N**, respectively) which consist of a thyminato(2-)-bridged tetranuclear Cp*Rh complex incorporating a M^{n+} cation, $[(\mathrm{Cp^*Rh})_4(\mu\text{-thym})_4\mathrm{M}]^{n+}$. All complexes were characterized by the single-crystal X-ray diffraction method, which revealed that homochiral aggregations of four $\mathrm{Rh^{III}}$ centers were achieved to give metallacalix[4]arene-type clusters. It was also observed that the bridging modes of thym^{2-} ligands were dependent on the template metal ion. In the $\mathrm{Na^+}$-incorporated clusters (**1X**, **X** = **P**, **B** or **N**) a thym^{2-} ligand bridged two $\mathrm{Rh^{III}}$ and the third $\mathrm{Na^+}$ ions with a $\mu_3\text{-}1\kappa N^1{:}2\kappa^2 N^3,O^2{:}3\kappa O^2$ mode, while in the $\mathrm{Ln^{3+}}$ analogs (Ln = La, Eu, Dy or Er: **3N**–**6N**) thym^{2-} exhibited a different bridging mode, $\mu_3\text{-}1\kappa N^1{:}2\kappa^2 N^3,O^4{:}3\kappa O^2$. In the cases of $\mathrm{Ca^{2+}}$-incorporated clusters, the bridging mode is further dependent on the associated anion; only the $\mu_3\text{-}1\kappa N^1{:}2\kappa^2 N^3,O^2{:}3\kappa O^2$-type cluster was obtained in the $\mathrm{NO_3^-}$ salt (**2N**), but the $\mathrm{ClO_4^-}$ salt (**2C**) afforded both types of the bridging clusters piled up alternatively in the crystals. The tetranuclear structures with a template metal cation, $[(\mathrm{Cp^*Rh})_4(\mu\text{-thym})_4\mathrm{M}]^{n+}$, are maintained in solution. The magnetic behaviors of the $\mathrm{Dy^{3+}}$- and $\mathrm{Er^{3+}}$-incorporated complexes (**5N** and **6N**) are also reported.

1. Introduction

Metallacalix[*n*]arenes [1–7] are a promising class of compounds because of their fascinating properties for the size- and charge-selective capture of a specific molecule or ion, in addition to their magnetic, electrochemical and catalytic functionalities originated from the cyclic multi-metallic fragments. The most characteristic feature of metallacalix[*n*]arenes, as compared to the other matallamacrocycles or metallacrowns [8–14], is originated from the conformational flexibility of the bridging ligands [1]. In addition, since the unsymmetrical ligands bearing more than two donor sites are often utilized to construct the cyclic frameworks, there are many possible linkage isomers and tautomers [1–5], and it is often difficult to control the products by a self-assembling reaction. Lippert et al. reported an interesting synthesis of cytosinato(1-)-bridged cyclic tetra- or hexanuclear $\mathrm{Pt^{II}/Pd^{II}}$ complexes which have the 1,3- or 1,3,5-alternate conformation [1,2]. In the cases of half-sandwich organometallic fragments (e.g., $\mathrm{Cp^*Rh^{III}}$, $\mathrm{Cp^*Ir^{III}}$ and $(\mathrm{arene})\mathrm{Ru^{II}}$) [15–18] with suitable bridging ligands (e.g., 2,3-dihydroxypyridine and its derivatives) [8–10,17–20], the resulting cyclic trinuclear complexes have a cone-type (i.e., metallacalix[3]arene) conformation due to a homochiral aggregation of three metal centers, and capture specific ionic pairs (e.g., LiF and $\mathrm{Na_2SiF_6}$) in the cavity [16–19]. In contrast, similar cyclic tetranuclear complexes with half-sandwich fragments and suitable bridging ligands [15,16,21–31] formed mostly the 1,3-alternate conformers by heterochiral aggregations. So far, there is no explicit evidence for the formation of metallacalix[4]arene framework with tetranuclear $\mathrm{Cp^*Rh^{III}}$ fragment to our best knowledge.

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In this study we have attempted to prepare $Cp^{*}Rh^{III}$ complexes bearing thyminate(2-) as a bridging ligand (Scheme 1). It was found that Na^{+}, Ca^{2+} and Ln^{3+} (Ln = La, Eu, Dy or Er) cations can act as a template forming a cyclic tetranuclear $[(Cp^{*}Rh)_4(\mu\text{-thym})_4M]^{n+}$ cluster, which has a metallacalix[4]arene framework. Also, it turned out that the bridging mode of $thym^{2-}$ is dependent on the kinds of cation and anion. In particular, in the case that $Ca(ClO_4)_2$ was used as a template salt two kinds of tetranuclear clusters with the $\mu_3\text{-}1\kappa N^1{:}2\kappa^2N^3,O^4{:}3\kappa O^2$ and $\mu_3\text{-}1\kappa N^1{:}2\kappa^2N^3,O^2{:}3\kappa O^2$ bridging modes (Scheme 1) are piled up alternatively in the crystals. A preliminary result of this study has been reported previously [32].

2. Experimental

2.1. Materials

Thymine (H_2thym), 1,2,3,4,5-pentamethylcyclopentadiene (HCp^{*}) and other chemicals and solvents were commercially available, and they were used as received. The starting hydroxido complex, $[(Cp^{*}Rh)_2(\mu\text{-OH})_3]OH$ was prepared by the literature method [33].

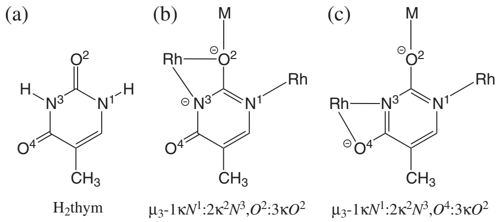
2.2. Preparation of complexes

2.2.1. $[\{Cp^{*}Rh(Hthym)\}_2(\mu\text{-OH})_2]\cdot 6H_2O$

A suspension of H_2thym (13 mg, 0.10 mmol) in methanol (10 mL) was added to a methanol solution (10 mL) of $[(Cp^{*}Rh)_2(\mu\text{-OH})_3]OH$ (28 mg, 0.051 mmol), and the mixture was stirred for 3 h at ambient temperature. The resulting solution was evaporated to dryness under reduced pressure, and the residue was dissolved in water. The filtered solution was allowed to stand at room temperature to concentrate slowly, affording orange crystals of $[\{Cp^{*}Rh(Hthym)\}_2(\mu\text{-OH})_2]\cdot 6H_2O$. Yield: 27 mg (62%). ^1H NMR (CD_3OD, 400 MHz, 21 °C): δ 1.32 (s, 15H, Cp^{*}), 2.01 (s, 3H, thym CH_3), 7.41 (s, 1H, thym $C^6\text{–}H$), 8.17 (s, 1H, thym $N^3\text{–}H$). *Anal.* Calc. for $C_{30}H_{54}N_4O_{12}Rh_2$: C, 41.48; H, 6.27; N, 6.45. Found: C, 41.47; H, 6.10; N, 6.39%.

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

To a mixture of H_2thym (13 mg, 0.10 mmol) and $[(Cp^{*}Rh)_2(\mu\text{-OH})_3]OH$ (27 mg, 0.050 mmol) in methanol (20 mL) was added a methanol solution (10 mL) of $NaPF_6$ (4.2 mg, 0.025 mmol), and the mixture was stirred for 2 h at ambient temperature. 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, affording orange crystals of **1P**$\cdot Et_2O\cdot MeOH$ suitable for X-ray analysis. Yield (after drying in vacuo): 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.* Calc. for $C_{60}H_{76}F_6N_8NaO_8PRh_4$ = **1P**: C, 44.57; H, 4.74; N, 6.93. Found (after drying in vacuo): C, 44.91; H, 5.12; N, 6.64%.



Scheme 1. (a) Thymine (H_2thym) with the atom-numbering scheme used in this paper, and (b) and (c) two bridging modes of $thym^{2-}$ found in the tetranuclear $Cp^{*}Rh$ complexes incorporating a metal cation (M^{n+}).

2.2.3. $[\{Cp^{*}Rh(\mu\text{-thym})\}_4(NaBF_4)]\cdot 2MeOH\cdot 2H_2O$ (**1B**$\cdot 2MeOH\cdot 2H_2O$)

This compound was prepared by a similar method to that for **1P**, using $NaBF_4$ instead of $NaPF_6$. Yield: 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.* Calc. for $C_{62}H_{88}BF_4N_8NaO_{12}Rh_4$ = **1B**$\cdot 2MeOH\cdot 2H_2O$: C, 44.89; H, 5.35; N, 6.76. Found: C, 44.60; H, 5.16; N, 6.60%. The crystals of **1B**$\cdot Et_2O\cdot MeOH\cdot H_2O$ suitable for X-ray analysis were obtained from a methanol solution by vapor diffusion of diethyl ether.

2.2.4. $[\{Cp^{*}Rh(\mu\text{-thym})\}_4(NaNO_3)]\cdot H_2O$ (**1N**$\cdot H_2O$)

This compound was prepared by a similar method to that for **1P**, using $NaNO_3$ instead of $NaPF_6$. The crude product obtained by extraction with dichloromethane, followed by evaporation of the solvent, was recrystallized from an acetonitrile solution by layering of di(isopropyl) ether, and the resulting orange crystals were collected by filtration and dried in air. Yield: 35%. ^1H 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 $C^6\text{–}H$). $^{13}C\{^1H\}$ NMR (CD_3CN, 100.6 MHz, 22 °C): δ 9.9 (s, Cp^{*} CH_3), 13.4 (s, thym CH_3), 95.3 (d, J = 9.1 Hz, $Cp^{*}CMe$), 115.4 (s, thym), 116.8 (s, thym), 152.9 (s, thym), 173.4 (s, thym). *Anal.* Calc. for $C_{60}H_{78}N_9NaO_{12}Rh_4$ = **1N**$\cdot H_2O$: C, 46.44; H, 5.07; N, 8.12. Found: C, 46.21; H, 5.01; N, 8.30%. The crystals of **1N**$\cdot 3MeCN\cdot H_2O$ suitable for X-ray analysis were obtained from a mixture of acetonitrile and di(isopropyl) ether.

2.2.5. $[\{Cp^{*}Rh(\mu\text{-thym})\}_4\{(CaNO_3)(MeCN)\}](NO_3)_{0.5}(OH)_{0.5}\cdot 9H_2O$ (**2N**$\cdot 9H_2O$)

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 di(isopropyl) ether, affording orange crystals of **2N**$\cdot 9H_2O$ suitable for X-ray analysis. Yield: 26.5 mg (30%). ^1H 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 $C^6\text{–}H$). ESI-MS (MeCN): m/z 1551.00 ($[\{Cp^{*}Rh(\mu\text{-thym})\}_4(CaNO_3)]^{+}$), 744.50 ($[\{Cp^{*}Rh(\mu\text{-thym})\}_4Ca]^{2+}$). *Anal.* Calc. for $C_{62}H_{93.5}N_{10.5}O_{20}CaRh_4$ = **2N**$\cdot 7H_2O$: C, 42.37; H, 5.36; N, 8.37. Found (partially efflorescent sample): C, 42.15; H, 4.45; N, 8.21%.

2.2.6. $[\{Cp^{*}Rh(\mu\text{-thym})\}_4\{(CaClO_4)(CH_3OH)_{0.5}(H_2O)_{0.5}\}]ClO_4\cdot H_2O$ (**2C**$\cdot H_2O$)

This compound was prepared by a similar method to that for **2N**, using $Ca(ClO_4)_2$ instead of $Ca(NO_3)_2\cdot 4H_2O$. The crude product obtained by extraction with dichloromethane, followed by evaporation of the solvent, was recrystallized from a methanol solution by vapor diffusion of di(isopropyl) ether. Yield: 31%. ^1H NMR (CD_3CN, 600 MHz, 21 °C): δ 1.57 (s, 3H, thym CH_3), 1.71 (s, 15H, Cp^{*}), 7.09 (s,1H, thym $C^6\text{–}H$). ^1H NMR (CD_3OD, 600 MHz, 21 °C): δ 1.68 (s, 3H, thym CH_3), 1.78 (s, 15H, Cp^{*}), 7.25 (s,1H, thym $C^6\text{–}H$). ESI-MS (MeOH): m/z 1587.11 ($[\{Cp^{*}Rh(\mu\text{-thym})\}_4(CaClO_4)]^{+}$), 744.09 ($[\{Cp^{*}Rh(\mu\text{-thym})\}_4Ca]^{2+}$). *Anal.* Calc. for $C_{121}H_{162}N_{16}O_{36}Ca_2Cl_4Rh_8$: C, 41.98; H, 4.72; N, 6.47. Found: C, 42.14; H, 4.51; N, 6.35%. Single-crystals used for X-ray analysis were obtained similarly to the above, but the analysis indicated that they contained partially deprotonated methoxido or hydroxide complex with its

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