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Diastereomeric separations and crystal structures of rhodium(III) and iridium(III) complexes containing adenosine and related nucleosides †

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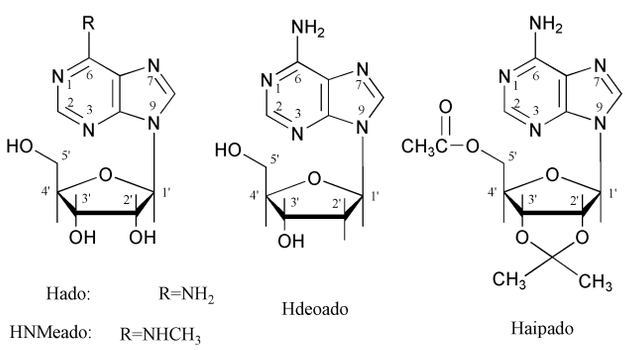
Six C_3 cyclic trinuclear complexes $[\{M(Cp^*)(L)\}_3]^{3+}$ (M = Rh^{III} and Ir^{III}; $Cp^* = \eta^5$–C_5Me_5) containing adenosine nucleosides [L: adenosine (Hado), 2′-deoxyadenosine (Hdeoado) and 5′-acetyl-2′,3′-isopropylideneadenosine (Haipado)] were prepared and characterized by UV/Vis and circular dichroism (CD) spectra, NMR spectroscopy, electrospray ionization mass spectroscopy and X-ray crystal structure analysis. The isolations of one and/or two diastereomers were successfully carried out for the four systems by second-order asymmetric transformation and/or fractional crystallization. Interestingly, a striking kinetic difference was found between the present Rh^{III}– and Ir^{III}–ado systems. The crystal structure of *CCC*-$[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3 \cdot 2.5H_2O \cdot CH_3OH$ revealed that the ado ligand adopts a μ-1κN^1:2$\kappa^2 N^6,N^7$ bridging mode and the three purine rings forming a triangle dome-like cavity can include one methanol molecule into its cavity. The absolute configurations were assigned to these complexes based on the crystal structural result and CD spectral arguments. The Rh^{III}–*N*-methyl adenosine (HNMeado) system exceptionally gave a di-μ-hydroxy *anti*-dinuclear structure because of the weak coordination ability of the N(6) donor.

Introduction

Self-assembly processes are based on the spontaneous reaction between transition metals and ligands. This method has been successfully applied to the formation of a variety of complex structures such as triangles, squares, rectangles and so on.[1] In comparison with square assemblies there have been relatively few reports on triangular macrocycles.

Adenosine (Hado) is an important DNA/RNA nucleosides and a rare triangle-directing ligand in the field of supramolecular chemistry. In 1992 Fish and co-workers reported the synthesis of a C_3 cyclic trimeric complex containing this ligand: $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3$ **1** ($Cp^* = \eta^5$–C_5Me_5).[2] Some related Rh(III) complexes with adenosine derivatives such as 2′-deoxyadenosine, 2′,3′-dideoxyadenosine and adenosine 5′-monophosphate were assigned to have the same cyclic trimeric structure based on their ^{1}H NMR spectra.[3] Interestingly, these complexes have been known to be useful hosts for some kinds of amino acids.[4] However all the complexes were a mixture of two diastereomers due to chiralities of the ribose group and no crystal structures have been reported so far. Hence the isolation of one and/or both diastereomers and then the structure determination of these systems are very intriguing and challenging subjects.

Here we first report the stereoselective isolation of one diastereomer of $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3$ through second-order asymmetric transformation and the determination of its structure by X-ray crystal analysis. In the corresponding iridium(III) complex, both diastereomers were obtained by fractional crystallization. Some related Rh^{III} and Ir^{III} complexes with adenosine derivatives, 2′-deoxyadenosine (Hdeoado), 5′-acetyl-2′,3′-isopropylideneadenosine (Haipado) and *N*-methyl adenosine (HNMeado), were also prepared and the separations of two diastereomers were attempted for these systems. The establishment of the correlations between the structures and



circular dichroism (CD) spectra for the metal complexes containing adenosine and the related nucleosides will be a very useful tool for the future stereochemical studies. Preliminary results of this work have been reported elsewhere.[5]

Experimental

Preparation and isolation of diastereomers

(a) $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3$ (1 and 1a)[6]. To a suspension of $[\{Rh(Cp^*)Cl_2\}_2]$[7] (0.2 g, 0.32 mmol) in water (30 cm^3) was added silver triflate (0.33 g, 1.3 mmol) and the mixture was stirred at 40 °C for 1 h. The resulting precipitate of silver chloride was removed by filtration and to the filtrate was added an aqueous solution (50 cm^3) of Hado (0.18 g, 0.64 mmol) adjusted to *ca.* pH 7 by adding aqueous NaOH. The mixed solution was stirred at room temperature for 1 d and then the resultant solution **1** was evaporated. Fractional crystallization of **1** always gave one diastereomer **1a** until the end of evaporation: that is, second-order asymmetric transformation was found in this Rh^{III} system. Hence the isolation of **1b** was impossible by using $CF_3SO_3^-$. The yield was 70–85%. Found: C, 36.72; H, 4.49; N, 10.12%. Calcd. for $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3 \cdot 6H_2O$ **1a** ($C_{63}H_{93}F_9N_{15}O_{27}Rh_3S_3$): C, 36.58; H, 4.53, N, 10.16%. UV/Vis (water): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}):

† Electronic supplementary information (ESI) available: ^{1}H NMR and CD spectra. See http://www.rsc.org/suppdata/dt/b2/b209148h/

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450sh(300), 385(7470), 305sh(*ca.* 26000), 275(32400). NMR: δ_H (DMSO-d_6): 9.081(H^8; s, 1H), 7.716(H^2; s, 1H), 5.687($H^{1'}$; d, 1H), 5.467($OH^{2'}$; d, 1H), 5.254($OH^{3'}$; d, 1H), 5.052($OH^{5'}$; t, 1H), 4.531(NH^6; s, 1H), 4.462($H^{2'}$; q, 1H), 4.092($H^{3'}$; q, 1H), 3.948($H^{4'}$; q, 1H), 3.703($H^{5'}$; m, 1H), 3.551($H^{5''}$; m, 1H), 1.827(Cp*; s, 15H); δ_C (dmso-d_6): 158.91(C6), 156.83(C2), 143.47(C4), 140.02(C8), 125.58(C5), 121.73(CF_3SO_3), 119.60(CF_3SO_3), 96.12(Cp*), 89.37(C1′), 85.68(C4′), 73.33(C2′), 69.48(C3′), 60.81(C5′), 9.27(Cp*). ESI MS: *m/z* (CH_3OH): 504.1([3M − 3X]$^{3+}$), 830.7([3M − 2X]$^{2+}$), 1811.1([3M − X]$^+$). The crystals for X-ray crystal structure analysis were obtained from a methanol/ether solution. **1b**: NMR: δ_H (DMSO-d_6): 9.057(H^8; s, 1H), 7.743(H^2; s, 1H).

(b) [{Ir(Cp*)(ado)}$_3$](PF$_6$)$_3$ (2, 2a and 2b). The corresponding Ir^{III} complex was prepared in the same manner as that for **1** by the use of [{Ir(Cp*)Cl_2}$_2$][7] without adding aqueous NaOH. The reaction solution was stirred at room temperature for 6 d and then the resultant solution was evaporated. Since the desired complex is too soluble, addition of an excess amount of NH_4PF_6 led to give the crystals of **2** (85% yield). When the aqueous solution of **2** was fractionally recrystallized, **2a** was obtained first as the less soluble diastereomer (37% yield) and the more soluble diastereomer **2b** was obtained as a second crop (10% yield; **2a** : **2b** = 1 : 4). The second-order asymmetric transformation in the Rh^{III}–$CF_3SO_3^-$ system was not observed in this Ir^{III}–PF_6^- system. Found: C, 31.37; H, 3.77; N, 9.17%. Calcd. for [{Ir(Cp*)(ado)}$_3$](PF_6)$_3$·4H_2O **2a** ($C_{60}H_{89}F_{18}Ir_3N_{15}O_{16}P_3$): C, 31.50; H, 3.92, N, 9.18%. UV/Vis (water): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 340sh(*ca.* 10600), 285(23400). NMR: δ_H (DMSO-d_6): 9.142(H^8; s, 1H), 7.731(H^2; s, 1H), 5.746($H^{1'}$; d, 1H), 5.523($OH^{2'}$; d, 1H), 5.296($OH^{3'}$; d, 1H), 5.081($OH^{5'}$; t, 1H), 4.651(NH^6; s, 1H), 4.469($H^{2'}$; q, 1H), 4.119($H^{3'}$; q, 1H), 3.972($H^{4'}$; q, 1H), 3.728($H^{5'}$; m, 1H), 3.568($H^{5''}$; m, 1H), 1.815(Cp*; s, 15H); δ_C (DMSO-d_6): 161.38(C6), 157.93(C2), 144.19(C4), 139.36(C8), 128.06(C5), 93.80(CF_3SO3), 89.65(C1′), 87.77(Cp*), 85.64(C4′), 73.55(C2′), 69.30(C3′), 60.62(C5′), 9.09(Cp*). ESI MS: *m/z* (CH_3CN): 594.7([3M − 3X]$^{3+}$), 963.4([3M − 2X]$^{2+}$). **2b**: NMR: δ_H (DMSO-d_6): 9.115(H^8; s, 1H), 7.775(H^2; s, 1H), 5.742($H^{1'}$; d, 1H), 5.541(s, 1H), 5.352(s, 1H), 4.970(s, 1H), 4.611(s, 1H), 4.555(s, 1H), 4.488(s, 1H), 4.220(s, 1H), 3.967(d, 1H), 1.808(Cp*; s, 15H). The concentration of **2b** for CD measurement was determined from the molar absorption coefficients of **2a**.

(c) [{Rh(Cp*)(deoado)}$_3$](PF$_6$)$_3$ (3 and 3′). The $CF_3SO_3^-$ salt of this complex has been already reported by Fish and coworkers, but we found that the PF_6^- salt crystallizes as an imbalanced composition. The complex was prepared in the same way as that for **1**. Since the $CF_3SO_3^-$ salt is too soluble in water, an excess amount of NH_4PF_6 was added to give an orange oil. The oil was redissolved in methanol, and then diethylether was added to give a yellow powder (**3**). When an aqueous solution of **3** was recrystallized, an imbalanced product **3′** (**3a** : **3b** = 26 : 74%) was mainly obtained. **3′**: Found: C, 35.77; H, 4.55; N, 10.35%. Calcd. for [{Rh(Cp*)(deoado)}$_3$](PF_6)$_3$·6H_2O ($C_{60}H_{93}F_{18}N_{15}O_{15}P_3Rh_3$): C, 35.89; H, 4.67, N, 10.46%. ESI MS: *m/z* (CH_3CN): 488([3M − 3X]$^{3+}$), 804.3([3M − 2X]$^{2+}$). **3b**: NMR: δ_H (DMSO-d_6): 9.005(H^8; s, 1H), 7.751(H^2; s, 1H), 6.126(s, 1H), 5.351(d, 1H), 4.847(t, 1H), 4.457(s, 2H), 3.843(s, 1H), 1.815(Cp*; s, 15H).

(d) [{Ir(Cp*)(deoado)}$_3$](PF$_6$)$_3$ (4 and 4a). The complex was prepared in the same way as that for **2** except for the use of Hdeoado and NaOH. The mixed solution was stirred at 60 °C for 3 h and then concentrated to a small volume. An excess amount of NH_4PF_6 was added to it and fractional crystallization was repeated. The first crop was the mixture of the diastereomers (**4**, 30% yield; **4a** : **4b** = 1 : 1). The pure diastereomer **4a** was obtained as a second crop (10% yield). The stabilities of **4** and **4a** were extremely low and significant discoloration due to decomposition was observed after short storage. **4**: Found: C, 31.00; H, 3.82; N, 9.13%. Calcd. for [{Ir(Cp*)(deoado)}$_3$](PF_6)$_3$·7H_2O ($C_{60}H_{95}F_{18}N_{15}O_{16}P_3Ir_3$): C, 31.41; H, 4.17, N, 9.16%. ESI MS: *m/z* (CH_3OH): 939.3([3M − 2X]$^{2+}$).

4a: NMR: δ_H (DMSO-d_6): 9.076(H^8; s, 1H), 7.711(H^2; s, 1H), 6.168(t, 1H), 5.370(d, 1H), 4.969(t, 1H), 4.623(s, 1H), 4.355(s, 1H), 3.880(d, 2H), 1.808(Cp*; s, 15H). **4b**: NMR: δ_H (DMSO-d_6): 9.057(H^8; s, 1H), 7.783(H^2; s, 1H), 1.808(Cp*; s, 15H). The CD spectrum of **4a** was strong but only qualitative: a (−) band at 342 and a (+) one at 296 nm.

(e) [{Rh(Cp*)(aipado)}$_3$](CF$_3$SO$_3$)$_3$ (5, 5′ and 5″). This complex was prepared in the same way as that for **1**. The reaction mixture was stirred at room temp. for 1 d. The resulting orange–yellow solution was evaporated with a rotary evaporator and kept standing to give an orange–yellow powder of the CF_3SO_3 salt (**5**, 13% yield; **5a** : **5b** = 1 : 1). When the powder of **5** was recrystallized from water, **5′** (4% yield; **5a** : **5b** = 7 : 3) was mainly obtained. Addition of NH_4PF_6 to the filtrate of **5** gave the second crop of the PF_6 salt (**5″**, 46%). **5**: Found: C, 40.40; H, 4.67; N, 9.23%. Calcd. for [{Rh(Cp*)(aipado)}$_3$](CF_3SO_3)$_3$·4.5H_2O ($C_{78}H_{108}F_9N_{15}O_{28.5}Rh_3S_3$): C, 40.95; H, 4.76, N, 9.18%. **5″**: Found: C, 39.15; H, 4.65; N, 9.36%. Calcd. for [{Rh(Cp*)(aipado)}$_3$](PF_6)$_3$·4.5H_2O ($C_{75}H_{108}F_{18}N_{15}O_{19.5}P_3Rh_3$): C, 39.59; H, 4.78, N, 9.23%. ESI MS: *m/z* (CH_3CN): 586.1([3M − 3X]$^{3+}$), 952.6([3M − 2X]$^{2+}$). **5a**: NMR: δ_H (DMSO-d_6): 8.966(H^8; s, 1H), 7.754(H^2; s, 1H), 6.066(s, 1H), 5.611(d, 1H), 4.800(d, 1H), 4.567(s, 1H), 4.436(s, 1H), 3.975(q, 1H), 3.872(q, 1H), 1.815(Cp*; s, 15H), 1.480(CH_3; s, 3H), 1.289(CH_3; s, 3H), 1.014(CH_3; s, 3H).

(f) [{Ir(Cp*)(aipado)}$_3$](PF$_6$)$_3$ (6 and 6a). This complex was prepared in the same way as that for **2**. The reaction mixture was stirred at room temp. for 1 d. The resulting pale-yellow solution was evaporated with a rotary evaporator and an addition of NH_4PF_6 to the solution gave the first crop of the PF_6 salt (**6**, 35% yield; **6a** : **6b** = 4 : 6). The pure diastereomer **6a** was obtained as a second crop (**6a**: 10%). **6**: Found: C, 36.23; H, 4.18; N, 8.29%. Calcd. for [{Ir(Cp*)(aipado)}$_3$](PF_6)$_3$·3H_2O ($C_{75}H_{105}F_{18}Ir_3N_{15}O_{18}P_3$): C, 35.80; H, 4.21; N, 8.35%. **6a**: Found: C, 35.48; H, 4.25; N, 8.21%. Calcd. for [{Ir(Cp*)(aipado)}$_3$](PF_6)$_3$·4.5H_2O ($C_{75}H_{108}F_{18}Ir_3N_{15}O_{19.5}P_3$): C, 35.42; H, 4.28; N, 8.26%. NMR: δ_H (DMSO-d_6): 9.056(H^8; s, 1H), 7.808(H^2; s, 1H), 6.119(s, 1H), 5.624(d, 1H), 4.834(d, 1H), 4.603(s, 1H), 4.458(s, 1H), 4.053(q, 1H), 3.948(q, 1H), 1.824(Cp*; s, 15H), 1.500(CH_3; s, 3H), 1.305(CH_3; s, 3H), 1.156(CH_3; s, 3H). ESI MS: *m/z* (CH_3CN): 677.2 ([3M − 3X]$^{3+}$), 1089.6 ([3M − 2X]$^{2+}$).

(g) [{Rh(Cp*)(μ-OH)(HNMeado)}$_2$](CF$_3$SO$_3$)$_3$ 7. The complex was prepared in the same way as that for **2** except for the use of HNMeado. The reaction solution was stirred at room temperature for 1d and then the resulting solution was evaporated. After the solution was stood at room temperature for 1d, orange crystals of **7** were obtained. The yield was 40%. **7**: Found: C, 36.51; H, 4.69; N, 9.91%. Calcd. for [{Rh(Cp*)(μ-OH)(HNMeado)}$_2$](CF_3SO_3)$_2$·3H_2O ($C_{44}H_{70}F_6N_{10}O_{19}Rh_2S_2$): C, 37.03; H, 4.94, N, 9.82%. UV/Vis (water): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 450sh(300), 385(7470), 305sh(*ca.* 26000), 275(32400). NMR: δ_H (DMSO-d_6): 8.860(H^8; s, 1H), 7.998(H^2; s, 1H), 3.339(NCH_3; s, 3H), 1.729(Cp*; s, 15H). ESI MS: *m/z* (CH_3OH): 504.1([3M − 3X]$^{3+}$), 830.7([3M − 2X]$^{2+}$), 1811.1([3M − X]$^+$). The crystals for X-ray crystal analysis were obtained from an aqueous solution.

ESI mass spectral measurements

ESI mass spectra were obtained by a sector-type mass spectrometer (JEOL-D300) connected with a laboratory made ESI interface.[8] A sample solution was sprayed from the tip of a needle

Table 1 Crystallographic data for $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3\cdot 2.5H_2O\cdot CH_3OH$ (**1a**·CH_3OH) and $[\{Rh(Cp^*)(\mu\text{-}OH)(HNMeado)\}_2](CF_3SO_3)_2\cdot 3H_2O$ **7**

	1a	**7**
Formula	$C_{64}H_{90}F_9N_{15}O_{24.5}S_3Rh_3$	$C_{44}H_{68}F_6N_{10}O_{19}S_2Rh_2$
FW	2037.38	1425.00
Space group	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)
Crystal system	Orthorhombic	Monoclinic
a/Å	21.0185(4)	12.1434(3)
b/Å	21.3660(4)	16.3817(4)
c/Å	19.4924(3)	15.6214(4)
β/°		107.9928(5)
V/Å^3	8753.7(3)	2955.6(1)
Z	4	2
ρ(calcd.)/g cm^{-3}	1.546	1.601
μ(Mo Kα)/cm^{-3}	7.26	7.24
Temp/K	296	296
*R*1 [a]	0.0441	0.0483
*wR*2 [a]	0.1373	0.1378

[a] Quantity minimized = $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $R1 = \Sigma||F_o - F_c||/\Sigma|F_o|$.

by applying a voltage 3.5 kV higher than that of a counter electrode. The distance between the needle and the counter electrode was 1 cm. The counter electrode consisted of a 12 cm-long stainless steel capillary tube (0.5 mm id). A stream of heated N_2 gas (70 °C) was used to aid desolvation of sprayed charged droplets. The flow rate of the sample solution was 2 mL min^{-1} and the cone voltage was 50 eV. The samples were dissolved in freshly distilled acetonitrile or methanol, and nothing was added to promote ionization. The concentrations of samples were kept at *ca.* 10^{-4} mol dm^{-3}.

X-Ray structure determinations

A yellow columnar crystal (0.15 × 0.15 × 0.35 mm) of $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3\cdot 2.5H_2O\cdot CH_3OH$ **1a** and a red prismatic crystal (0.50 × 0.40 × 0.50 mm) for $[\{Rh(Cp^*)(\mu\text{-}OH)(HNMeado)\}_2](CF_3SO_3)_2\cdot 3H_2O$ **7** were obtained from MeOH–Et_2O and water, respectively, at room temperature. Diffraction data were collected on a Rigaku RAXIS-RAPID Imaging Plate with graphite-monochromated Mo–Kα radiation (λ = 0.71069 Å). Crystallographic data are listed in Table 1. The structure was solved by direct methods. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined for **1a**. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included but not refined for **7**. The final cycle of full-matrix least squares was based on 13527 observed reflections ($I > 2\sigma I$) and 993 variable parameters for **1a**, and on 10728 reflections and 747 parameters for **7**. 20037 reflections for **1a** and 7023 for **7** were collected. Refinement was carried out on *F*. The final values of *R*1 and *wR*2 were 0.044 and 0.137 for **1a**, and 0.048 and 0.138 for **7**. All calculations were performed using the teXsan[9] crystallographic software package of the Molecular Structure Corporation.

CCDC reference numbers 193951 and 157281.

See http://www.rsc.org/suppdata/dt/b2/b209148h/ for crystallographic data in CIF or other electronic format.

Determination of kinetic data

The kinetic measurements by CD spectra were recorded at a fixed wavelength (415 nm). The data treatment was carried out according to the scheme of general reversible unimolecular reaction.[10] The plots of $\ln(\Delta\varepsilon_{eq} - \Delta\varepsilon_t)$ against the time *t* are shown in Fig. 5, where the subscripts "*t*" and "eq" mean at time *t* and at equilibrium, respectively.

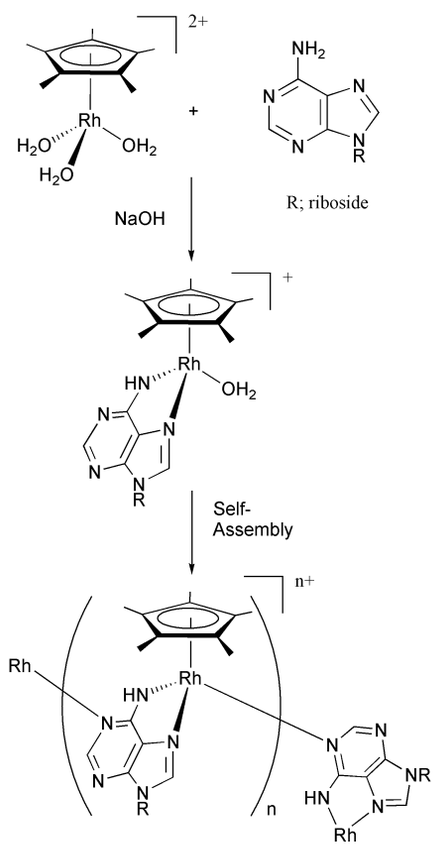
Measurements

UV/Vis absorption spectra were measured with a Hitachi 330 spectrophotometer, CD spectra were measured with a JASCO J-500 spectrophotometer, and ^{1}H and ^{13}C NMR spectra were measured with a JEOL JNM-GSX-270 spectrometer in $(CD_3)_2SO$ at 30 °C. X-ray crystal analysis was made at the X-ray diffraction service of the Department of Chemistry.

Results and discussion

Selective isolation of one diastereomer and crystal structure of $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3$

Self-assembling reaction between $[Rh(Cp^*)(H_2O)_3]^{2+}$ and ado gave $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3$ **1** in a high yield. The reaction is expected to proceed as shown in Scheme 1. Fig. 1a shows



Scheme 1

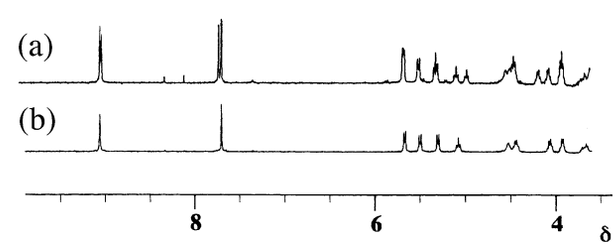


Fig. 1 ^{1}H NMR spectra of $[\{Rh(Cp^*)(ado)\}_3]^{3+}$ [**1** (a) and **1a** (b)] in $(CD_3)_2SO$.

an ^{1}H NMR spectrum of the reaction solution, which indicates the presence of two diastereomers **1a** and **1b**.[6] However every crop of crystallization of this reaction solution gave only one diastereomer **1a** up to the end of evaporation (Fig. 1). This phenomenon, the selective crystallization of one of the diastereomers under conditions of relatively rapid isomer equilibration in solution, is denoted as a second-order asymmetric transformation.[11] We have reported typical examples in *fac*(*S*)-[Co(*R*-cysteinato-*N*,*S*)$_3$]$^{3-}$.[12] Though the shifts of the diastereomeric equilibria have been known in many organometallic systems, the above phenomenon is quite rare.[13]

Electrospray ionization (ESI) mass spectrum of **1a** showed dominant peaks at *m*/*z* = 504.1, 830.7 and 1811.1, which correspond to the ions of $[3M - 3X]^{3+}$, $[3M - 2X]^{2+}$ and $[3M - X]^{+}$, respectively, where [3M] and X represent $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3$ and $CF_3SO_3^-$, respectively. The result means that **1a** has a cyclic trinuclear structure.

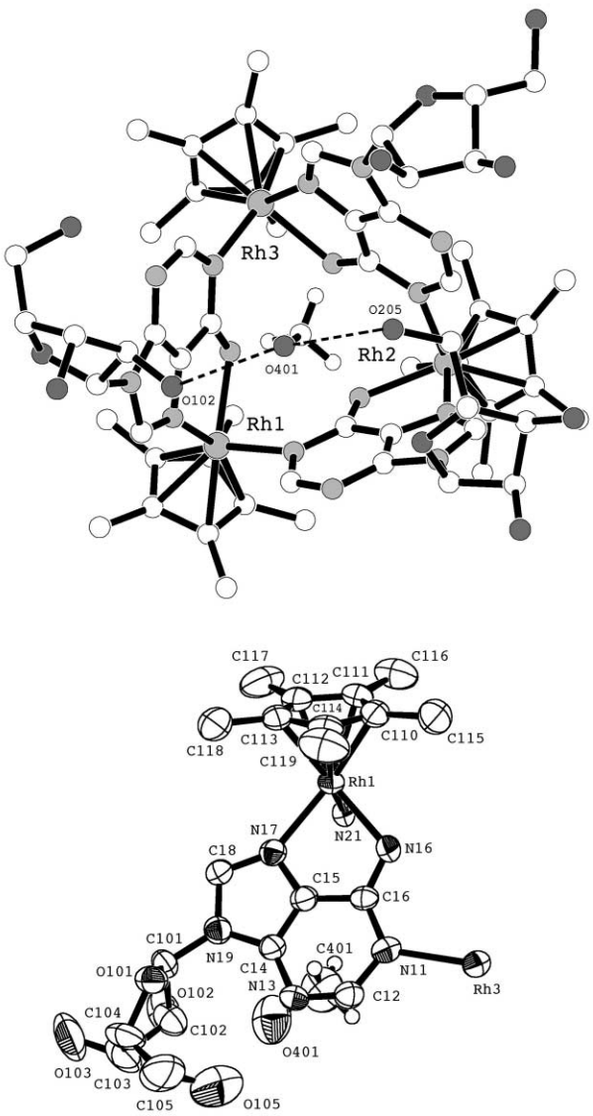


Fig. 2 X-Ray crystal structure of the cation of $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3\cdot 2.5H_2O\cdot CH_3OH$ (top; **1a**·CH_3OH) and the numbering system for the Rh(1) unit (bottom). The numbering system for the Rh(2) or Rh(3) unit is analogous: the first "1" given above in the numbering scheme needs to be replaced by a "2" or "3", respectively.

The top view of Fig. 2 shows the crystal structure of the cation of $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3\cdot 2.5H_2O\cdot CH_3OH$ (**1a**·CH_3OH). The numbering scheme for the Rh(1) unit in **1a** was given in the bottom of Fig. 2. The numbering system for the Rh(2) and Rh(3) units is analogous, *i.e.* always the first "1" given above in the numbering scheme needs to be replaced by a "2" or "3", respectively. The crystallographic data are shown in Table 1 and selected bond distances and angles are listed in Table 2. This complex has a cyclic trinuclear structure. Three Rh^{III} ions are crystallographically independent and form an almost equilateral triangle; Rh(1) ··· Rh(2) = 5.6037(6), Rh(1) ··· Rh(3) = 5.6353(6) and Rh(2) ··· Rh(3) = 5.6285(6) Å. The ado ligand adopts a μ-1κN^1:2$\kappa^2 N^6,N^7$ bridging mode: it coordinates to one Rh^{III} ion bidentatedly *via* the NH^6 and N(7) donors which form a five-membered chelate ring and bridges to another Rh^{III} ion through the N(1) donor. The three purine

Table 2 Selected bond distances (Å) and bond angles (°) for $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3\cdot 2.5H_2O\cdot CH_3OH$ (**1a**·CH_3OH)

Rh(1)–N(16)	2.170(4)	Rh(1)–N(17)	2.142(4)
Rh(1)–N(21)	2.142(4)	Rh(1)–C(110)	2.132(6)
Rh(1)–C(111)	2.152(6)	Rh(1)–C(112)	2.140(6)
Rh(1)–C(113)	2.151(5)	Rh(1)–C(114)	2.127(5)
Rh(2)–N(26)	2.159(4)	Rh(2)–N(27)	2.162(4)
Rh(2)–N(31)	2.171(4)	Rh(2)–C(210)	2.149(4)
Rh(2)–C(211)	2.152(5)	Rh(2)–C(212)	2.180(5)
Rh(3)–C(213)	2.112(6)	Rh(2)–C(214)	2.166(6)
Rh(3)–N(11)	2.151(4)	Rh(3)–N(36)	2.154(4)
Rh(3)–N(37)	2.172(4)	Rh(3)–C(310)	2.148(7)
Rh(3)–C(311)	2.130(7)	Rh(3)–C(312)	2.134(6)
Rh(3)–C(313)	2.159(6)	Rh(3)–C(314)	2.144(5)
N(16)–Rh(1)–N(17)	78.9(2)	N(26)–Rh(2)–N(27)	79.3(2)
N(36)–Rh(3)–N(37)	79.1(2)	Rh(3)–N(11)–C(12)	119.5(3)
Rh(3)–N(11)–C(16)	122.4(3)	Rh(1)–N(16)–C(16)	114.0(3)
Rh(1)–N(17)–C(15)	107.2(3)	Rh(1)–N(21)–C(22)	119.3(3)
Rh(1)–N(21)–C(26)	122.6(3)	Rh(2)–N(26)–C(26)	113.0(3)
Rh(2)–N(27)–C(25)	105.8(3)	Rh(2)–N(31)–C(32)	118.1(3)
Rh(2)–N(31)–C(36)	122.9(3)	Rh(3)–N(36)–C(36)	113.1(3)
Rh(3)–N(37)–C(35)	106.6(3)		

rings are located at the same side and form a triangle dome-like cavity. Interestingly, one methanol molecule just fits this cavity, forming an inclusion compound. There are two O–H ··· O hydrogen bonds between the oxygen of methanol and the hydroxyl groups of ribose [O(102) ··· O(401) = 2.782(8) and O(205) ··· O(401) = 2.748(8) Å]. Moreover three CH/π interactions are found: the three distances between the carbon atom of the methyl group and each of the least-square planes of the three purine rings are 3.53, 3.63 and 3.72 Å. These two kinds of interactions stabilize the inclusion of the methanol. The side length of the triangle formed by C(n6), corresponding to a bottom of the cavity in Fig. 2, is *av.* 3.86 Å and the length by C(n01), a top of the cavity, is *av.* 8.18 Å. Three ribose groups close the cavity by acting as a cap. The side stereoview and the space-filling structure in Fig. 3 show very clearly this triangle dome-like cavity. Fish and co-workers have reported that **1** and analogous cyclic trimer complexes become useful hosts for molecular recognition of aromatic amino acid guests.[4] The

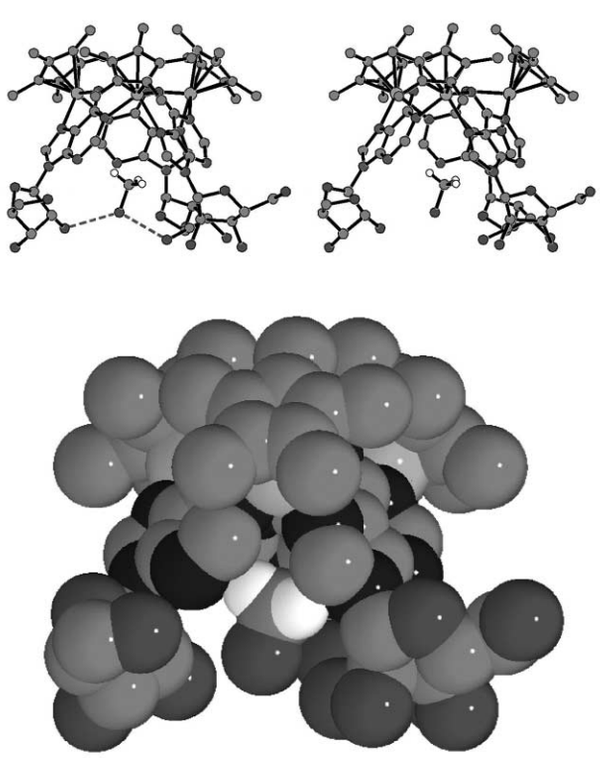


Fig. 3 The stereoview (top) and the space-filling structure (bottom) of **1a**·CH_3OH.

present study gives the structural support for such investigations.

Since the central Rh^{III} ions become chiral, each unit complex has chirality *C* (clockwise) or *A* (anticlockwise).[14] For the cyclic trimer, two diastereomeric pairs, (*CCC* + *AAA*) and (*CCA* + *AAC*), are possible. The latter isomer was only found in $[\{Co(put)(tacn)\}_3]^{3+}$ (H_2put = 6-purinethione; tacn = 1,4,7-triazacyclononane) where the complex adopts a μ-1κN^9:-2κ$^2N^6$,N^7 bridging mode.[15] For the present μ-1κN^1:2κ$^2S^6$,N^7 bridging mode is possible just the former chirality array. In fact, **1a** adopts a chiral array of *CCC*, and the CD spectrum is shown in Fig. 4. The CD intensity is considerably stronger than

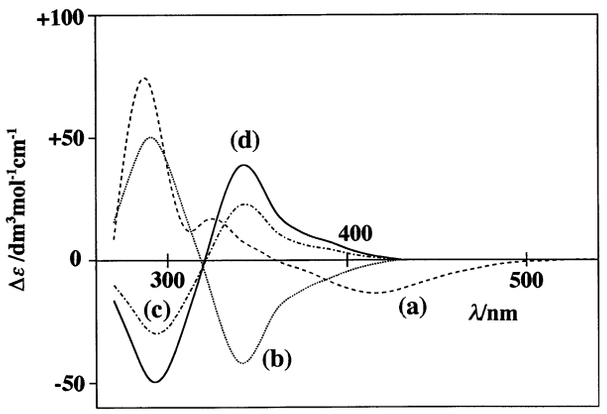


Fig. 4 CD spectra of $[\{Rh(Cp^*)(ado)\}_3]^{3+}$ [**1a** (a)] and $[\{Ir(Cp^*)(ado)\}_3]^{3+}$ [**2a** (b) and **2b** (c)]. The pure CD spectrum of **2b** (d) was calculated from the spectra.

those reported for nucleosido complexes which are the mixture of two diastereomers.[3] It should be noted that the present Rh^{III} system is composed of the single C_3 *CCC*-diastereomer.

Separations of two diastereomers of $[\{Ir(Cp^*)(ado)\}_3]^{3+}$

The corresponding Ir^{III} complex $[\{Ir(Cp^*)(ado)\}_3](PF_6)_3$ **2** was prepared in the same manner and showed a very similar ^1H NMR spectrum to that of **1** which is characteristic for a trimer.[1] By fractional crystallization, both diastereomers **2a** and **2b** were obtained as almost pure isomers as shown in Fig. S1 (ESI).†

The ESI mass spectrum of **2a** showed dominant peaks corresponding to the ions of $[3M - 3X]^{3+}$ and $[3M - 2X]^{2+}$. Therefore we concluded that **2** has the same C_3 cyclic trinuclear structure as **1a**.

As shown in Fig. 4, both CD spectra (b) and (d) are almost enantiomeric. To our knowledge, this is the first example of isolating two diastereomers in nucleosido complexes. The CD spectra of Ir^{III} complexes are blue-shifted by *ca.* 5000 cm^{-1} compared with those of Rh^{III} complexes. **2a** showed (−) and (+) CD peaks from the lower energy side, the pattern of which is similar to that of the Rh^{III} complex **1a**. The ^1H NMR patterns of H^2 and H^8 are also analogous between **1a** and **2a**. Hence **2a** can be assigned to the *CCC* cyclic structure and **2b** to the *AAA* one.

Second-order asymmetric transformation

Kinetic studies on the hexaaquo complexes of Rh^{III} and Ir^{III} have shown extremely slow water exchange rate constants of 2.2 × 10^{-9} and 1.1 × 10^{-10} s^{-1}, respectively. Substitution of three water molecules by the Cp* ligand leads to a dramatic increase of 14 orders of magnitude in the respective rate constants.[16] However, there is the distinct kinetic difference between the present Rh^{III}– and Ir^{III}–ado complexes described below.

The pure diastereomer *CCC*-$[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3$**1a** was selectively isolated through second-order asymmetric transformation. The phenomenon occurs under relatively rapid isomer equilibration in solution. Hence the CD spectral change of **1a** was measured with time. The solution of the *CCC*-diastereomer came to equilibrium with the *AAA* one in *ca.* 5 days at room temperature. The plots of $\ln(\Delta\varepsilon_{eq} - \Delta\varepsilon_t)$ against time gave a straight line as shown in Fig. 5, indicating a

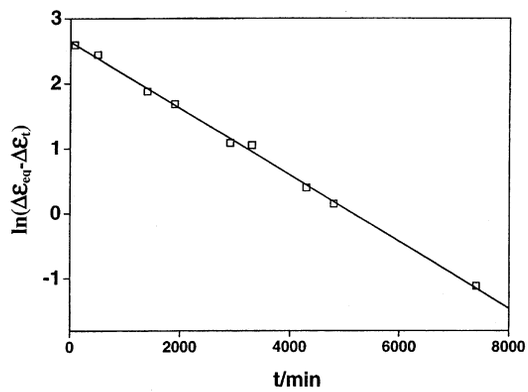


Fig. 5 The relationship between $\ln(\Delta\varepsilon_{eq} - \Delta\varepsilon_t)$ and time.

first-order reversible reaction. The half-life of epimerisation was calculated from the observed rate constant ($k = 5.1 \times 10^{-4}$ min^{-1}): 23 h at room temperature. This phenomenon is also dependent on the counter ion.[11,12] Hence some other salt systems were prepared and examined. The ClO_4^- and PF_6^- salt systems produced only the same *CCC*-diastereomer as $CF_3SO_3^-$, but the BF_4^- salt gave the mixture of two diastereomers. Therefore, second-order asymmetric transformation was observed also in ClO_4^- and PF_6^-.

On the other hand, the two diastereomers were obtained by fractional crystallization in $[\{Ir(Cp^*)(ado)\}_3](CF_3SO_3)_3$. The CD spectrum of **2a** (*CCC*) did not change at all for 7 days at room temperature and hence there is no equilibrium in the Ir^{III} system. This kinetic stability leads to the isolation of both the diastereomers.

Separation of diastereomers in adenosine related nucleoside systems

The Rh^{III} and Ir^{III} complexes containing 2′-deoxyadenosine (Hdeoado) and 5′-acetyl-2′,3′-isopropylideneadenosine (Haipado) were also prepared and attempted to separate the diastereomers. These four complexes were assigned to be cyclic trimer based on the following two grounds. The observed drastic chemical shift changes for both H^2 (upfield) and H^8 (downfield) from free ligand are characteristic of cyclic trimers.[2] ESI mass spectra of these complexes showed dominant peaks corresponding to the ions of $[3M - 3X]^{3+}$ and/or $[3M - 2X]^{2+}$.

The attempts to separate two diastereomers were carried out for these complexes. In all systems, the reaction mixtures were composed of almost equal amounts of two diastereomers. The fractional crystallization often led to the isolation of the pure diastereomer or the imbalanced mixture. The results were clearly indicated by the ^1H NMR spectra of Fig. S2 (ESI) and S3 (ESI).† The pure diastereomer was isolated in two systems; **4a** in $[\{Ir(Cp^*)(deoado)\}_3](PF_6)_3$ and **6a** in $[\{Ir(Cp^*)(aipado)\}_3](PF_6)_3$. The imbalanced mixture was obtained in $[\{Rh(Cp^*)(deoado)\}_3](PF_6)_3$ (**3′**; **3a** : **3b** = 26 : 74%) and $[\{Rh(Cp^*)(aipado)\}_3](CF_3SO_3)_3$ (**5′**; **5a** : **5b** = 7 : 3).

These CD spectra were shown in Fig. S4 (ESI).† According to the CD patterns of **1a** (*CCC*) and **2a** (*CCC*) at the lower energy side, the absolute configurations can be assigned to all of the diastereomers as follows: **3b** can be assigned to *AAA*, **4a** to *CCC*, and **5a** and **6a** to *AAA*. It should be noted that the ^1H NMR spectral pattern of H^8 in the Rh^{III}– and Ir^{III}–aipado complexes is opposite to those in the other adenosine ligand systems.

Elimination of the deoxyribose group from 2′-deoxyadenosine

In the course of the preparations of Rh^{III} and Ir^{III} complexes, we often observed the disappearance of the riboside peaks at δ 3.8–6.2 in ^{1}H NMR spectroscopy. Especially, it was found that the deoxyribose group is easily cleaved in the Ir^{III}–2′-deoxyadenosine system. Fig. 6 shows the ^{1}H NMR spectra of the

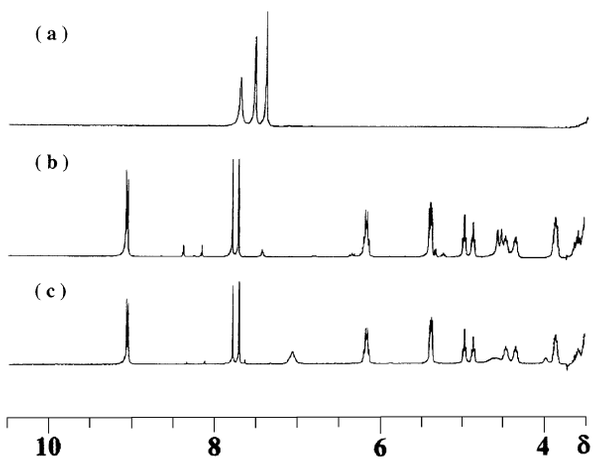


Fig. 6 pH dependence of the reaction products in Ir^{III}–aipado system: (a) pH 2.8, (b) pH 6.9 and (c) pH 9.6.

reaction products at different pH values. The reaction time was 3 h at 60 °C. The deoxyribose group is reserved in the reactions at pH 6.9 (b) and pH 9.6 (c), whereas the complete elimination was found at pH 2.8 (a). These results indicate the occurrence of the facile elimination of riboside group at acidic condition. The product after the elimination reaction showed the same ^{1}H NMR spectrum as that of $[\{Ir(Cp^*)(adeninato)\}_4]^{4+}$ where the N(9) donor becomes a bridging site.[17]

We observed a similar phenomenon in the Co^{III}–6-purinethione riboside (Hputrb) system.[18] The reaction between $[Rh(Cp^*)(H_2O)_3]^{2+}$ (or $[Ir(Cp^*)(H_2O)_3]^{2+}$) and putrb gave a novel cyclic hexanuclear structure of $[\{Rh(Cp^*)(putrb)\}_6]^{6+}$ (or $[\{Ir(Cp^*)(putrb)\}_6]^{6+}$).[19] On the other hand, the reaction between $[CoCl_3(tacn)]$ and putrb gave a cyclic tetramer $[\{Co(put)(tacn)\}_4]^{4+}$ in good yield where the N(9) donor becomes a bridging site. The product showed the same ESI mass spectrum as that obtained previously from the reaction between $[CoCl_3(tacn)]$ and put.[15] In this case, the elimination of the riboside group from 6-purinethione riboside occurred even in neutral condition. Thus, we have to pay our attention to the possibility of the N(9)–riboside bond cleavage on the metal–nucleoside complex formation.

Crystal structure of $[\{Rh(Cp^*)(\mu\text{-}OH)(HNMeado)\}_2](CF_3SO_3)_2\cdot 3H_2O$ 7

Fig. 7 shows a view of $[\{Rh(Cp^*)(\mu\text{-}OH)(HNMeado)\}_2](CF_3SO_3)_2\cdot 3H_2O$ **7**. The crystallographic data are shown in Table 1 and selected bond distances and angles are listed in Table 3. This complex has an *anti*-dinuclear structure with the di-μ-hydroxy bridge and two HNMeado ligands are located at the opposite side. Two Rh^{III} ions are crystallographically independent. The Rh–O(1) lengths [Rh(1)–O(1) = 2.150(5) and Rh(2)–O(1) = 2.123(4) Å] are slightly longer than the Rh–O(2) ones [Rh(1)–O(2) = 2.101(4) and Rh(2)–O(2) = 2.109(4) Å]. Both HNMeado ligands act only as a monodentate ligand through the N(7) donor: the Rh(1)–N(7) and Rh(2)–N(27) lengths are 2.171(4) and 2.176(5) Å, respectively. This indicates that the deprotonation from the HN^6Me group by the addition of NaOH and the subsequent coordination of the N^6 donor to Rh^{III} are difficult to achieve. Thus the coordination behaviour

Table 3 Selected bond distances (Å) and bond angles (°) for $[\{Rh(Cp^*)(\mu\text{-}OH)(HNMeado)\}_2](CF_3SO_3)_2\cdot 3H_2O$ **7**

Bond distances			
Rh(1)–O(1)	2.150(5)	Rh(1)–O(2)	2.101(4)
Rh(1)–N(7)	2.171(4)	Rh(1)–C(40)	2.152(7)
Rh(1)–C(41)	2.150(6)	Rh(1)–C(42)	2.144(7)
Rh(1)–C(43)	2.128(7)	Rh(1)–C(44)	2.139(7)
Rh(2)–O(1)	2.123(4)	Rh(2)–O(2)	2.109(4)
Rh(2)–N(27)	2.176(5)	Rh(2)–C(50)	2.102(7)
Rh(2)–C(51)	2.162(8)	Rh(2)–C(52)	2.153(7)
Rh(2)–C(53)	2.119(6)	Rh(2)–C(54)	2.124(7)
Bond angles			
O(1)–Rh(1)–O(2)	76.1(2)	O(1)–Rh(2)–O(2)	76.6(2)
O(1)–Rh(1)–N(7)	88.2(2)	O(1)–Rh(2)–N(27)	87.1(2)
O(2)–Rh(1)–N(7)	86.4(2)	O(2)–Rh(2)–N(27)	88.7(2)
Rh(1)–O(1)–Rh(2)	102.5(2)	Rh(1)–O(2)–Rh(2)	104.7(2)

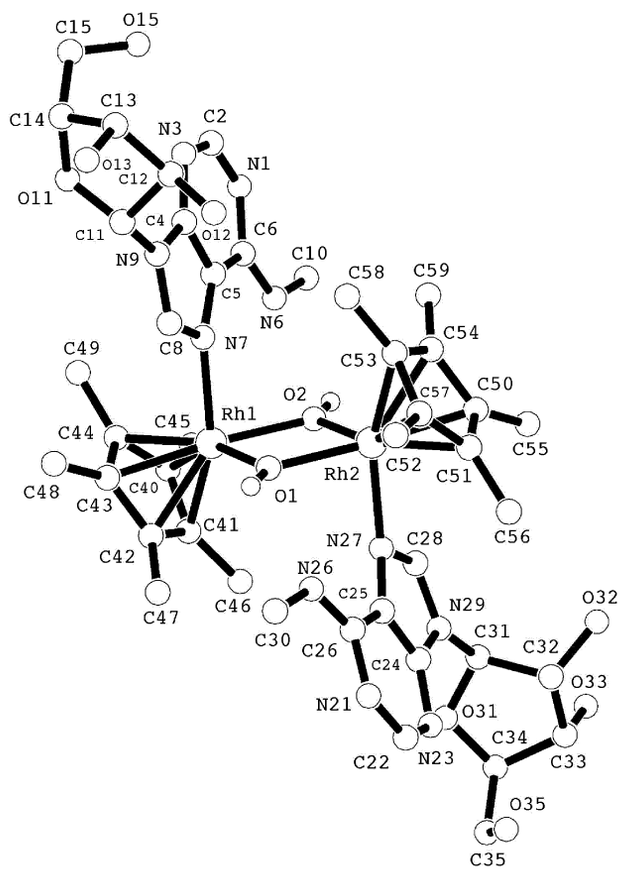


Fig. 7 X-Ray crystal structure of the cation of $[\{Rh(Cp^*)(\mu\text{-}OH)(HNMeado)\}_2](CF_3SO_3)_2\cdot 3H_2O$ **7**.

of HNMeado is quite different from those of adenosine and related nucleoside. Hodgson has found the rules that the most probable site of coordination is N(9) for adenine, guanine, xanthine, and hypoxanthine and N(7) for theophilline. When N(9) is blocked, N(7) is the site of coordination.[20] The present complex is consistent with the general rules for purine coordination.

There are two intramolecular hydrogen bonds between the μ-OH groups and N(6) atoms [N(6) ··· O(2) = 2.885(7) and N(26) ··· O(1) = 2.793(7) Å]. Moreover, two intramolecular hydrogen bonds are found within HNMeado; N(3) ··· O(15) = 2.792(6) and N(23) ··· O(35) = 2.834(6) Å]. These hydrogen bonds stabilize the di-μ-hydroxy *anti*-dimer structure. A similar *anti*-dimer structure has been reported in $[\{Rh(Cp^*)(\mu\text{-}OH)(9\text{-}MH)\}_2]$ (9-MH = 9-methyl hypoxanthinate), though the N(1) site is used for coordination.[21]

Conclusion

The six C_3 cyclic trinuclear Rh^{III} and Ir^{III} complexes containing ado, deoado and aipado were prepared and characterized. The isolations of one and/or two diastereomers were successfully attempted for the four systems by second-order asymmetric transformation and/or fractional crystallization. Their absolute configurations were assigned for the first time based on the crystal structural result and CD spectral arguments. The HNMeado system exceptionally gave a di-μ-hydroxy *anti*-dinuclear complex because of weak coordination ability of the N(6) site.

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6 In this paper, "**a**" denotes the diastereomer which shows a H^8 signal at lower magnetic field and "**b**" denotes the one with a higher field H^8 signal.
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