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Diastereomeric separation of $[\{M(Cp^*)(ado)\}_3]^{3+}$ (M = Rh^{III}, Ir^{III}; ado = adenosinato): crystal structure of an inclusion compound $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3\cdot MeOH$

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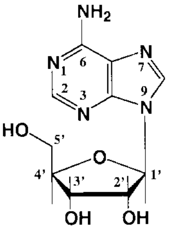
A diastereomer with a C_3 cyclic trimer $[\{Rh(adenosine)(Cp^*)\}_3](CF_3SO_3)_3$, which was obtained selectively by a second-order asymmetric transformation, can include one methanol molecule into its triangle dome-like cavity.

Adenosine (Hado, **1**) is an important DNA/RNA nucleoside. In 1992 Fish and coworkers reported the synthesis of an interesting C_3 cyclic trimer complex containing the ligand $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3$ **2** (Cp* = η^5-C_5Me_5).[1] However this complex was a mixture of two diastereomers (**2a** and **2b**) due to chiralities of the ribose group in **1** and the pure diastereomers had not been isolated. Hence the structure of **2** was deduced from NMR spectroscopy and the crystal structure $[\{Rh(Cp^*)(Me\text{-}ade)\}_3](CF_3SO_3)_3$ (Me-ade = 9-methyladeninato).[1]



Hado

Here we report diastereomeric separations of **2** and the corresponding Ir^{III} complex $[\{Ir(Cp^*)(ado)\}_3](PF_6)_3$ **3** (**3a** and **3b**) and a novel crystal structure of an inclusion compound $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3\cdot MeOH$ (**2a**·MeOH). The absolute configurations of all complexes can be assigned based on circular dichroism (CD) spectra.

A self-assembling reaction between $[Rh(Cp^*)(H_2O)_3]^{2+}$ and **1** gave **2**† in high yield. Fig. 1(a) shows the ^{1}H NMR spectrum of the reaction solution, which indicates the presence of two diastereomers. However fractional crystallization of this reaction solution gave only one diastereomer **2a** up to the end of evaporation [Fig. 1(b)]. This phenomenon, the selective crystallization of one of the diastereomers under conditions of relatively rapid isomer equilibration in solution, is denoted second-order asymmetric transformation,[2] as observed in fac(*S*)-$[Co\{(R)\text{-cysteinato-}N,S\}_3]^{3-}$.[3] Though shifts of the diastereomeric equilibria have been known in many organometallic systems, the above phenomenon is quite rare.[4] The electrospray ionization (ESI) mass spectrum of **2a** showed dominant peaks at *m/z* 504.1, 830.7 and 1811.1, which correspond to the ions $[3M-3X]^{3+}$, $[3M-2X]^{2+}$ and $[3M-X]^+$, respectively, where 3M and X represent the complex and $CF_3SO_3^-$, respectively. The result indicates that **2** has a cyclic trinuclear structure.

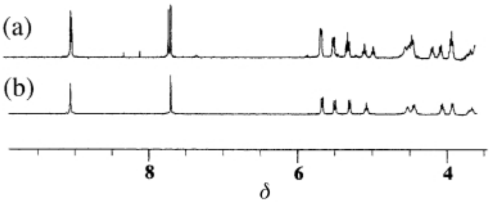


Fig. 1 Proton NMR spectra of **2** (a) and **2a** (b) in $(CD_3)_2SO$.

Fig. 2 shows a view of $[\{Rh(Cp^*)(ado)\}_3][CF_3SO_3]_3\cdot 2.5H_2O\cdot MeOH$ (**2a**·MeOH).‡ This complex has a 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 in a bidentate manner *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 rings are located at the same side and form a triangular dome-like cavity. Interestingly one molecule of methanol 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 types of interactions stabilize the inclusion of the methanol. The side length of the triangle formed by C(6), corresponding to a bottom of the cavity in Fig. 2, is 3.86 Å (av.) and the length by C(1′), at the top of the cavity, is 8.18 Å (av.). Three ribose groups close the cavity by acting as a cap. The side stereoview and the space-filling structure in Fig. 3 clearly show this triangle dome-like cavity. Fish and

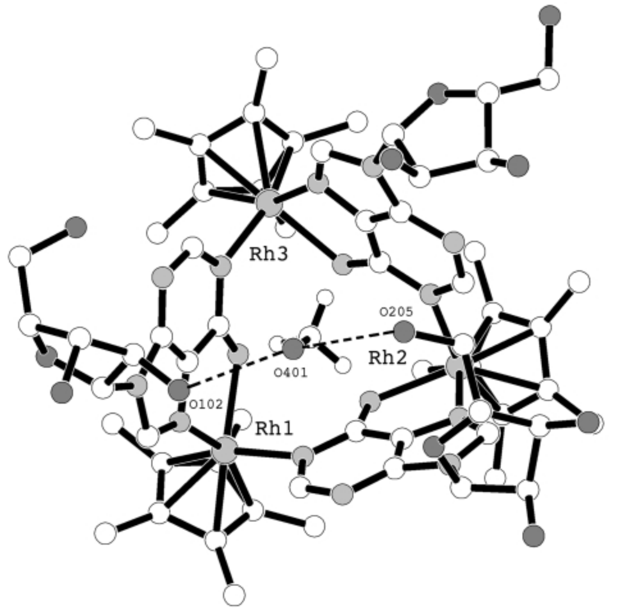


Fig. 2 The structure of the cation in $[\{Rh(Cp^*)(ado)\}_3][CF_3SO_3]_3\cdot 2.5H_2O\cdot MeOH$ (**2a**·MeOH): Selected average bond distances (Å) and angles (°) Rh–N(6) 2.161, Rh–N(7) 2.159, Rh–N(1′) 2.155, C(6)–N(6) 1.306; N(6)–Rh–N(7) 79.1, N(6)–Rh–N(1′) 89.9, N(7)–Rh–N(1′) 84.5, N(6)–C(6)–C(5) 115.6, Rh–N(7)–C(5) 106.5, Rh–N(6)–C(6) 113.4.

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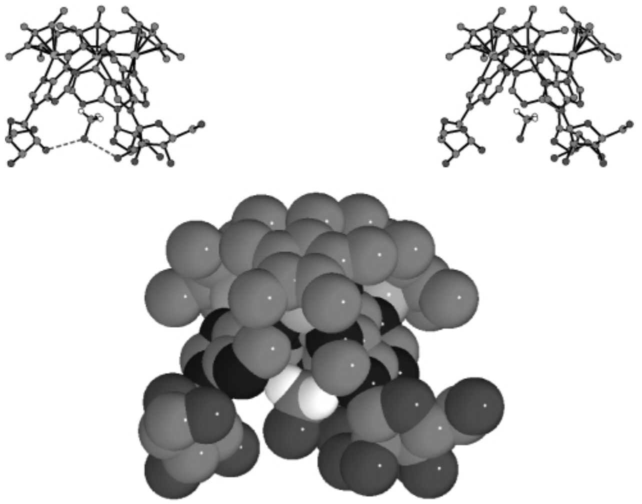

Fig. 3 Side stereoview (top) and the space-filling structure (bottom) of **2a**·MeOH.

coworkers have reported that **2** and analogous cyclic trimer complexes are useful hosts for molecular recognition of aromatic amino acid guests.[5] The present study gives the structural support for such investigations.

Since the central $\mathrm{Rh^{III}}$ ions become chiral each unit complex has chirality C (clockwise) or A (anticlockwise).[6] **2a** has a chiral array of CCC, and the CD spectrum is shown in Fig. 4. The CD intensity is considerably stronger than those reported for nucleosido complexes which are mixtures of two diastereomers.[7] It should be noted that the present $\mathrm{Rh^{III}}$ system contains only the C_3 CCC diastereomer. A D_2O solution of **2a** produced 30% of **2b** at room temperature in ten days.

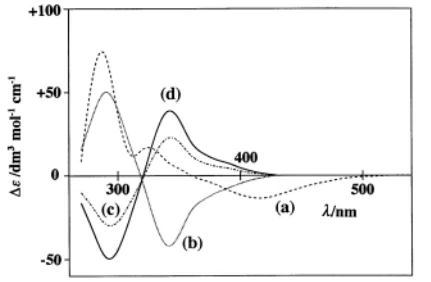

Fig. 4 CD spectra of $[\{Rh(Cp^*)(ado)\}_3](CF_3SO_3)_3$ (a) and $[\{Ir(Cp^*)(ado)\}_3](PF_6)_3$ (b, c and d). The pure CD spectrum (d) of **3b** was calculated from the spectra.

The corresponding $\mathrm{Ir^{III}}$ complex $[\{Ir(Cp^*)(ado)\}_3](PF_6)_3$ **3**§ was prepared in the same manner and showed a very similar ^1H NMR spectrum to that of **2** which is characteristic for a trimer.[1] Upon fractional crystallization, both diastereomers **3a** and **3b** were obtained as almost pure isomers (Fig. 5). The ESI mass spectrum of **3a** showed dominant peaks corresponding to the ions $[3M - 3X]^{3+}$ and $[3M - 2X]^{2+}$. Therefore we concluded that **3** has the same C_3 cyclic trinuclear structure as **2**. 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 for nucleosido complexes. The CD spectra of the $\mathrm{Ir^{III}}$ complexes is blue-shifted by *ca.* 5000 cm^{-1} compared with those of $\mathrm{Rh^{III}}$ complexes. **3a** showed (−) and (+) CD peaks from the lower energy side, the pattern of which is similar to that of the $\mathrm{Rh^{III}}$ complex **2a**. The ^1H NMR patterns of H^2 and H^8 are also analogous for **2a** and **3a**. Hence **3a** can be assigned as a CCC cyclic trinuclear structure and **3b** as AAA.

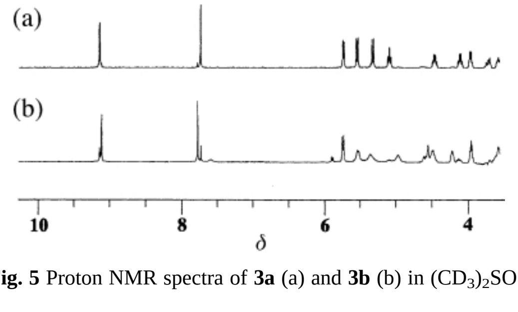

Fig. 5 Proton NMR spectra of **3a** (a) and **3b** (b) in $(CD_3)_2SO$.

Notes and references

† For **2** (**2a**): to a suspension of $[\{Rh(Cp^*)Cl_2\}_2]^8$ (0.2 g, 0.32 mmol) in water (30 cm^3) was added silver triflate (0.33 g, 1.3 mmol) and the mixture stirred at 40 °C for 1 h. The resulting silver chloride precipitate was removed by filtration and to the filtrate was added an aqueous solution (50 cm^3) of **1** (0.18 g, 0.64 mmol) adjusted to *ca.* pH 7 by adding aqueous NaOH. The mixed solution was stirred at room temp. for 1 d and then the resultant solution **2** was evaporated. Fractional crystallization of **2** always gave one diastereomer **2a** until the end of evaporation: that is, a second-order asymmetric transformation was found in this $\mathrm{Rh^{III}}$ system; hence the isolation of **2b** is impossible using $CF_3SO_3^-$. The yield was 70–85%. Found: C, 36.72; H, 4.49; N, 10.12. Calc. for $[\{Rh(Cp^*)(ado)\}_3][CF_3SO_3]_3\cdot 6H_2O$ **2a** ($C_{63}H_{93}F_9N_{15}O_{27}Rh_3S_3$): C, 36.58; H, 4.53, N, 10.16%. UV–VIS (H_2O): λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹) 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 (MeOH): *m/z* 504.1($[3M - 3X]^{3+}$), 830.7($[3M - 2X]^{2+}$), 1811.1 ($[3M - X]^+$). Crystals for X-ray crystal structure analysis were obtained from a methanol–ether solution.

‡ *Crystal data* for $[\{Rh(Cp^*)(ado)\}_3][CF_3SO_3]_3\cdot 2.5H_2O\cdot MeOH$ **2a** were collected on a Rigaku RAXIS-RAPID Imaging Plate with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å); $C_{64}H_{90}F_9N_{15}O_{24.5}Rh_3S_3$, $M_r = 2037.38$, crystal size 0.15 × 0.15 × 0.35 mm; T = 23 °C; orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 21.0185(4)$, $b = 21.3660(4)$, $c = 19.4924(3)$ Å, $V = 8753.7(3)$ Å³, $Z = 4$, $\mu = 7.26$ cm⁻¹, $F(000) = 4156$, $D_c = 1.546$ g cm⁻³, $2\theta_{max} = 55.0°$. 20037 reflections were collected. Final $R1 = 0.044$ ($wR = 0.137$) for 13527 reflections with $I > 2\sigma(I)$ (993 parameters). All calculations were performed using the TEXSAN[9] crystallographic software package. CCDC reference number 157281. See http://www.rsc.org/suppdata/cc/b1/b102870g/ for crystallographic data in CIF or other electronic format.

§ For **3** (**3a** and **3b**): the corresponding $\mathrm{Ir^{III}}$ complex was prepared in the same manner but 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, an excess of NH_4PF_6 was added leading to crystals of **3** (85% yield). When an aqueous solution of **3** was fractionally recrystallized, **3a** was obtained first as the less soluble diastereomer (37% yield) and the more soluble diastereomer **3b** was obtained as a second crop (10% yield; 20% **3a** and 80% **3b**). The second-order asymmetric transformation in the $\mathrm{Rh^{III}}$–CF_3SO_3 system was not observed in the $\mathrm{Ir^{III}}$–PF_6 system. Found: C, 31.37; H, 3.77; N, 9.17. Calc. for $[\{Ir(Cp^*)(ado)\}_3][PF_6]_3\cdot 4H_2O$ **3a** ($C_{60}H_{89}F_{18}Ir_3N_{15}O_{16}P_3$): C, 31.50; H, 3.92, N, 9.18%. UV–VIS (H_2O): λ_{max}/nm (ε/dm³ 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_3SO_3), 89.65(C1′), 87.77(Cp*), 85.64(C4′), 73.55(C2′), 69.30(C3′), 60.62(C5′), 9.09(Cp*). ESI MS (MeCN): *m/z* 594.7($[3M - 3X]^{3+}$), 963.4($[3M - 2X]^{2+}$). **3b**: 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 **3b** for CD measurement was determined from the molar absorption coefficients of **3a**.

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