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Homo- and Heterochiral Aggregations of Samarium(III) Complexes with Acetate and Tripod Ligand Containing Three Imidazole Groups

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Three Sm^{III} complexes with tripod heptadentate N_7 ligands containing three imidazole groups, $[Sm(H_3L^{2\text{-}Me})(ac)](ClO_4)_2\cdot 2MeOH\cdot H_2O$ (**1**), $[Sm(H_3L^{2\text{-}Me})(ac)](ClO_4)_2\cdot 2EtOH$ (**2**), and $[Sm(H_3L^{4\text{-}Me})(ac)](ClO_4)_2\cdot MeOH$ (**3**), were synthesized and the crystal structures were determined, where $H_3L^{2\text{-}Me}$ and $H_3L^{4\text{-}Me}$ are the 1:3 condensation products of tris(2-aminoethyl)amine and either 2-methyl-4-formylimidazole and 4-methyl-5-formylimidazole, respectively, and ac denotes acetate ion. Each Sm^{III} ion is coordinated by a tripod heptadentate N_7 ligand and two oxygen atoms of the acetate ion. Due to the screw coordination arrangement of the achiral tripod ligand to the Sm^{III} ion, the complex-cation $[Sm^{III}(H_3L^{2\text{- or }4\text{-}Me})(ac)]^{2+}$ gives Δ- and Λ-enantiomorphs. In compounds **1** and **2**, two adjacent $[Sm(H_3L^{2\text{-}Me})(ac)]^{2+}$ species with the same chirality are linked by an intermolecular imidazole···acetate hydrogen bond to form a homochiral 1D chain structure. Adjacent chains with the same chirality are stacked to give a conglomerate crystal in **1**, while adjacent chains with opposite chiralities are stacked to give a racemic crystal in **2**. In compound **3**, two adjacent $[Sm(H_3L^{4\text{-}Me})(ac)]^{2+}$ species with the opposite chiralities are doubly bridged by two intermolecular imidazole···acetate hydrogen bonds to form a heterochiral dimer and the adjacent dimers are connected by ClO_4^- ion through the hydrogen bonds to form a racemic crystal.

Since the historic discovery of spontaneous resolution in ammonium sodium tartrate by Pasteur, chirality has been an important subject in science.[1] Chirality is expressed at both the molecular and supramolecular levels.[2–6] When a chiral molecule aggregates and crystallizes, it can form either (1) a racemic compound, (2) a conglomerate (racemic mixture), or (3) a racemic solid solution.[7,8] If enantioselective homochiral molecular discrimination arising from substantially strong, selective, and directional interactions, such as a coordination bond or a hydrogen bond, can be extended from two adjacent molecules to one-dimensional (1D), 2D, and 3D systems, then a conglomerate exhibiting 3D intermolecular homochiral interaction would be achieved. Jacques et al. reported that, statistically, between 5 and 10% of all racemates form conglomerate crystals, indicating that homochiral interaction in the formation of crystalline racemates is usually weaker than heterochiral interaction.[7] The first step toward the realization of conglomerate is to find an intermolecular enantioselective interaction in a molecular system.

Previously, we have found such intermolecular enantioselective interactions.[9] (1) Mono-deprotonated copper(II) complex $[Cu^{II}(HL^1)]ClO_4$ with an achiral pentadentate strand-type ligand involving two imidazole groups, (H_2L^1: bis{3-[(2-methylimidazol-4-yl)methylideneamino]propyl}methylamine.[10–12] The complex gives either Δ (clockwise) or Λ (anticlockwise) enantiomers, due to the spiral coordination arrangement of their achiral ligands. The mono-deprotonated complex $[Cu^{II}(HL)]ClO_4$ has one imidazole and one imidazolate moiety per molecule, which functions as a chiral self-complementary building component, and aggregates into heterochiral (…$\Delta\Lambda\Delta\Lambda$…) and homochiral (…$\Delta\Delta\Delta\Delta$… and …$\Lambda\Lambda\Lambda\Lambda$…) 1D zigzag chains due to the intermolecular imidazole–imidazolate (NH···N) hydrogen bond. Compounds with the less bulky substituent at the 2-position of the imidazole moiety, yielded homochiral chain, while compounds with the bulky substituent yielded heterochiral chains. (2) Hemi-deprotonated cobalt(III) complex with achiral tripod-type ligands involve three imidazole groups, $[Co^{III}(H_{1.5}L^2)](ClO_4)_{1.5}$ (H_3L^2: tris{2-[(imidazol-4-yl)methylideneamino]ethyl}amine).[13] The complexes induce the chirality of the Δ- and Λ-enantiomers due to the screw coordination arrangement of the achiral tripod-type ligand around the Co^{III} ion. The formally hemi-deprotonated complex $[Co^{III}(H_{1.5}L^2)](ClO_4)_{1.5}$ functions as a self-complementary chiral building block to form an extended 2D homochiral layer structure due to the intermolecular imidazole···imidazolate (NH···N) hydrogen bonds. These two examples demonstrate that the metal complexes with multidentate ligand involving imidazole groups have a high-probability for enantioselective interaction.[14–20]

The lanthanide(III) complexes of the tripod-type ligands involving three imidazole groups can be interesting both in luminescence[21] and enantioselective discrimination. In this study, we report a new intermolecular enantioselective interaction in lanthanide(III) complexes with an acetate and tripod ligand, $[Sm(H_3L^{2\text{-}Me})(ac)](ClO_4)_2\cdot 2MeOH\cdot H_2O$ (**1**), $[Sm(H_3L^{2\text{-}Me})(ac)](ClO_4)_2\cdot 2EtOH$ (**2**), and $[Sm(H_3L^{4\text{-}Me})(ac)](ClO_4)_2\cdot MeOH$ (**3**), where $H_3L^{2\text{-}Me}$ denotes tris{2-[(2-methylimidazol-4-yl)methylideneamino]ethyl}amine, $H_3L^{4\text{-}Me}$ de-

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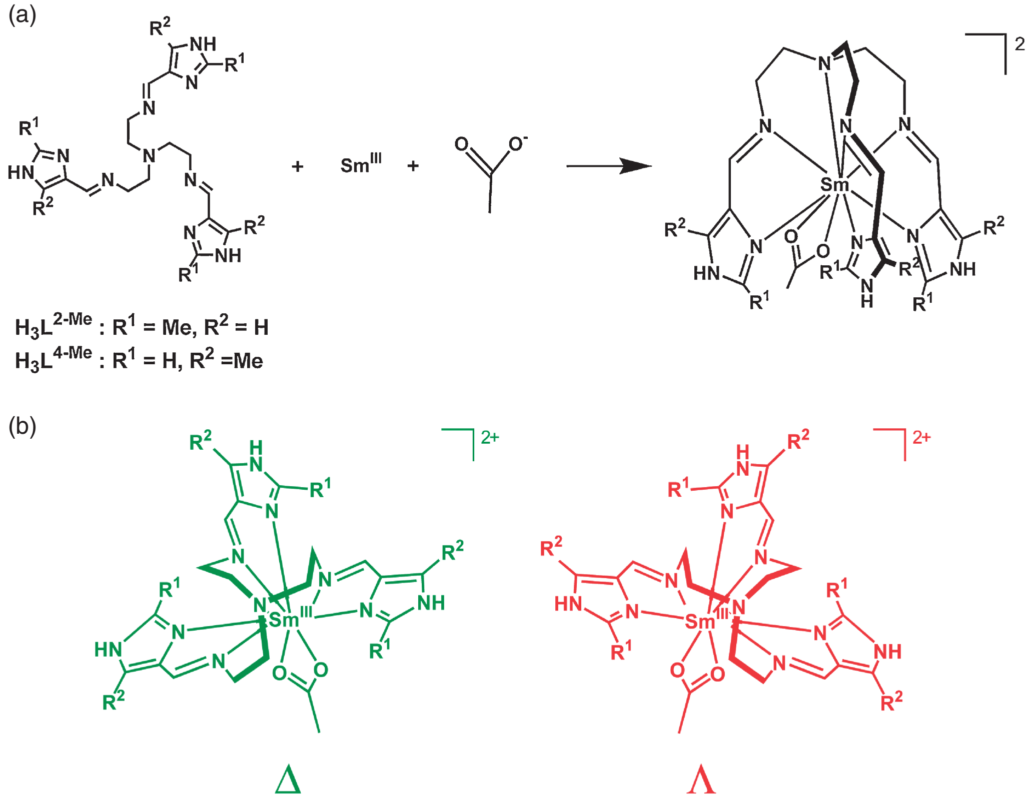

Scheme 1. (a) Structures of tripod ligands (H_3L^R) and $[Sm^{III}(H_3L^R)(ac)]^{2+}$ and (b) *Δ*- and *Λ*-enantiomorphs of $[Sm^{III}(H_3L^R)(ac)]^{2+}$.

notes tris{2-[(4-methylimidazol-4-yl)methylideneamino]ethyl}amine, and ac denotes acetate ion (Scheme 1). Instead of the imidazole···imidazolate hydrogen bonds in the former two examples, imidazole···acetate hydrogen bonds play a central role for enantioselective discrimination in the present complexes. We report here an intermolecular homochiral discrimination of **1** and **2**, an intermolecular heterochiral discrimination of **3** and a spontaneous resolution of **1**.

Results and Discussion

Synthesis. The tripod heptadentate N_7 Schiff-base ligands $H_3L^{2\text{-}Me}$ and $H_3L^{4\text{-}Me}$ were prepared by the 1:3 condensation reaction of tris(2-aminoethyl)amine with either 2-methyl-4-formylimidazole and 4-methyl-5-formylimidazole, respectively, according to literature reported previously.[13] To the ligand solution was added a solution of $Sm^{III}(ac)_3\cdot4H_2O$ and then a solution of $NaClO_4$ in a 1:1:2 molar ratio. From the reaction mixture colorless crystals precipitated. For the syntheses of **1** and **3**, methanol was used as the reaction solvent. For the synthesis of **2**, ethanol was used as the reaction solvent. Single-crystal X-ray analysis revealed the formulas of $[Sm(H_3L^{2\text{-}Me})(ac)](ClO_4)_2\cdot2MeOH\cdot H_2O$ (**1**), $[Sm(H_3L^{2\text{-}Me})(ac)](ClO_4)_2\cdot2EtOH$ (**2**), and $[Sm(H_3L^{4\text{-}Me})(ac)](ClO_4)_2\cdot MeOH$ (**3**). The crystals easily eliminate crystal solvents in ambient atmosphere showing efflorescence. The elemental analyses of the dried samples agreed with the chemical formula $[Sm(H_3L^{2\text{-}Me})(ac)](ClO_4)_2\cdot H_2O$ (**1**), $[Sm(H_3L^{2\text{-}Me})(ac)](ClO_4)_2\cdot0.5EtOH$ (**2**), and $[Sm(H_3L^{4\text{-}Me})(ac)](ClO_4)_2$ (**3**), showing the elimination of some crystal solvent.

Crystal Structures of $[Sm(H_3L^{2\text{-}Me})(ac)](ClO_4)_2\cdot2MeOH\cdot H_2O$ (1), $[Sm(H_3L^{2\text{-}Me})(ac)](ClO_4)_2\cdot2EtOH$ (2), and $[Sm(H_3L^{4\text{-}Me})(ac)](ClO_4)_2\cdot MeOH$ (3). To prevent the elimination of the crystal solvents, a crystal with a suitable size is selected from the solution and coated with epoxy resin quickly, and then used for the X-ray diffraction. The crystal structures for complexes **1–3** were determined by single-crystal X-ray diffraction analyses at 296 K. Their crystallographic data are given in Table 1. The relevant coordination bond distances and angles are given in Table 2. The intermolecular hydrogen bond distances are given in Table 3. The structural features of the complex-cations $[Sm^{III}(H_3L^R)(ac)]^{2+}$ (R = 2-Me or 4-Me) show essentially similar coordination environment.

$[Sm(H_3L^{2\text{-}Me})(ac)](ClO_4)_2\cdot2MeOH\cdot H_2O$ (1): The crystal structure of **1** consists of $[Sm^{III}(H_3L^{2\text{-}Me})(ac)]^{2+}$, two counter anions ClO_4^-, and two methanol molecules, and one water molecule as the crystal solvents. A molecular structure of $[Sm^{III}(H_3L^{2\text{-}Me})(ac)]^{2+}$ with the selected atom numbering scheme is shown in Figure 1. The Sm^{III} ion is coordinated by seven nitrogen atoms of a tripod heptadentate N_7 ligand ($H_3L^{2\text{-}Me}$) and two oxygen atoms of an acetate ion, in which the Sm–N(1) distance of 2.751(6) Å (N(1) is the central amine nitrogen) is longer than the other six distances of Sm–N (2.512(5)–2.655(5) Å), and an acetate ion coordinates to Sm^{III} ion as a bidentate ligand (2.482(3) and 2.503(4) Å). The tripod ligand encapsulates a Sm^{III} ion by the seven nitrogen atoms, but the geometry is distorted significantly from C_3 symmetry as shown in Figure 1b. Three N(imdazole)–Sm–N(imidazole) angles of N(3)–Sm–N(6) = 79.54(15), N(3)–Sm–N(9) =

Table 1. X-ray Crystallographic Data for $[Sm^{III}(H_3L^{2\text{-}Me})(ac)](ClO_4)_2 \cdot 2MeOH \cdot H_2O$ (**1**), $[Sm^{III}(H_3L^{2\text{-}Me})(ac)](ClO_4)_2 \cdot 2EtOH$ (**2**), and $[Sm^{III}(H_3L^{4\text{-}Me})(ac)](ClO_4)_2 \cdot MeOH$ (**3**) at 296 K

	Complex		
	$[Sm(H_3L^{2\text{-}Me})(ac)]$-$(ClO_4)_2 \cdot 2MeOH \cdot H_2O$ (**1**)	$[Sm(H_3L^{2\text{-}Me})(ac)]$-$(ClO_4)_2 \cdot 2EtOH$ (**2**)	$[Sm(H_3L^{4\text{-}Me})(ac)]$-$(ClO_4)_2 \cdot MeOH$ (**3**)
Formula	$C_{25}H_{43}O_{13}N_{10}Cl_2Sm$	$C_{27}H_{45}O_{12}N_{10}Cl_2Sm$	$C_{24}H_{37}O_{11}N_{10}Cl_2Sm$
Formula weight	912.98	923.02	862.92
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$ (No. 4)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a/Å	10.339(3)	19.3382(6)	16.607(6)
b/Å	11.657(4)	9.1538(3)	12.732(4)
c/Å	16.403(6)	23.4140(6)	16.634(4)
β/deg	107.45(2)	109.3420(8)	103.37(2)
V/Å^3	1886(1)	3910.8(2)	3422(2)
Z	2	4	4
D_{calcd}/g cm^{-3}	1.608	1.568	1.675
μ/cm^{-1}	17.732	17.093	19.452
Flack parameter	0.000(11)		
$R^{a)}$, $R_w^{b)}$	0.0365, 0.0741	0.0562, 0.1491	0.0794, 0.2061

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $Rw = [\Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w|F_o{}^2|^2]^{1/2}$.

110.90(15), and N(6)–Sm–N(9) = 76.68(13)° are not equivalent, while those of the Fe^{II} and Co^{III} complexes are equivalent and the angle of ca. 90° is reported.[14–19] The spread angle of N(3)–Sm–N(9) is due to the inserted coordination of an acetate ion between N(3)–Sm–N(9).

Of three imidazole groups, two imidazole groups N(7) and N(4) of three imidazole groups of a $[Sm^{III}(H_3L^{2\text{-}Me})(ac)]^{2+}$ are hydrogen-bonded to a water molecule O(3) with N(7)···O(3) = 2.833(10) Å and to two oxygen atoms of a perchlorate anion with N(4)···O(6) = 3.043(11) and N(4)···O(7) = 3.028(10) Å as bifurcated hydrogen bonds, respectively. There is no further hydrogen bonding from the water O(3) and the perchlorate ion Cl(1). The remaining imidazole group N(10) is hydrogen-bonded to one of the acetate oxygen atoms $O(2)^{*1}$ of the adjacent $[Sm^{III}(H_3L^{2\text{-}Me})(ac)]^{2+}$ unit related by a symmetry operation of twofold screw axis along the b axis with the distance of N(10)···$O(2)^{*1}$ = 2.814(7) Å (*1; $-x + 2$, $y - 1/2$, $-z + 2$). The other oxygen atom of the acetate ion O(1) is hydrogen bonded to a methanol molecule with O(1)···O(4) = 2.864(9) Å and there is no further hydrogen bonding from the methanol molecule O(4).

As shown in Figure 2a, the intermolecular imidazole–acetate hydrogen bond of N(10)···$O(2)^{*1}$ is repeated to produce a one-dimensional chain running along the b axis. Due to the screw coordination arrangement of the three-armed tripod ligand to the Sm^{III} ion, there are two possible optical isomers, Δ- and Λ-enantiomorphs for $[Sm^{III}(H_3L^{2\text{-}Me})(ac)]^{2+}$. As adjacent two units are related by a symmetry operation of 2_1 screw rotation along the b axis, the one-dimensional chain is a homochiral chain. Further, as shown in Figure 2b, the adjacent chains with the same chirality are stacked to give a homochiral crystal (conglomerate), indicating that the spontaneous resolution occurs during the crystallization. Compound **1** crystallizes into a non-centrosymmetric monoclinic space group $P2_1$, being consistent with **1** being a conglomerate. Flack parameter analysis of complex **1** suggested that the measured crystal was chiral with Δ form enantiomer.

$[Sm(H_3L^{2\text{-}Me})(ac)](ClO_4)_2 \cdot 2EtOH$ (2): The crystal structure of **2** consists of $[Sm^{III}(H_3L^{2\text{-}Me})(ac)]^{2+}$, two counter anions $ClO_4{}^-$, and two ethanol molecules as the crystal solvents. A molecular structure of $[Sm^{III}(H_3L^{2\text{-}Me})(ac)]^{2+}$ projected from the central amine nitrogen to Sm^{III} ion with the selected atom numbering scheme is shown in Figure 3. The structural features of the coordination environment of the complex-cations $[Sm^{III}(H_3L^{2\text{-}Me})(ac)]^{2+}$ of complex **1** and **2** are essentially the same.

Of three imidazole groups, N(4) is hydrogen-bonded to one of the acetate oxygen atoms $O(1)^{*2}$ of the adjacent $[Sm^{III}(H_3L^{2\text{-}Me})(ac)]^{2+}$ unit with the distance of N(4)···$O(1)^{*2}$ = 2.766(7) Å (*2; x, $y - 1$, z). Another two imidazole groups N(7) and N(10) per complex-cation are hydrogen-bonded to two ethanol molecules with N(7)···O(3) = 2.846(11) and N(10)···O(4) = 2.800(18) Å, respectively. Furthermore, two ethanol molecules are weakly hydrogen-bonded to two perchlorate anions with O(3)···O(5) = 3.10(5) and O(4)···O(9) = 3.11(3) Å, respectively. There is no further hydrogen bonding from the ethanol molecules O(3) and O(4) and the perchlorate ions Cl(1) and Cl(2).

The crystal packing diagram of **2** is shown in Figure 4. Two adjacent $[Sm(H_3L^{2\text{-}Me})(ac)]^{2+}$ species are linked by an intermolecular imidazole···acetate hydrogen bond of N(4)···$O(1)^{*2}$ to form a homochiral chain structure running along the b axis. Adjacent chains with opposite chiralities are stacked to give a racemic crystal.

It is interesting to compare the crystal structure of **1** with that of **2**. Since the complexes **1** and **2** were crystallized from methanol and ethanol, respectively, these two complexes with the formulas of $[Sm^{III}(H_3L^{2\text{-}Me})(ac)](ClO_4)_2 \cdot 2MeOH \cdot H_2O$ (**1**) and $[Sm^{III}(H_3L^{2\text{-}Me})(ac)](ClO_4)_2 \cdot 2EtOH$ (**2**) involve different crystal solvents. These two complexes have the same homochiral 1D structure constructed by an intermolecular imidazole–acetate hydrogen bond. There is a difference in packing manner of the chiral chains between **1** and **2**. Adjacent chains with the same chirality are stacked to give a conglomerate crystal in **1**,

Table 2. Relevant Coordination Bond Distances (Å) and Angles (°) for $[Sm^{III}(H_3L^{2\text{-}Me})(ac)](ClO_4)_2\cdot 2MeOH\cdot H_2O$ (**1**), $[Sm^{III}(H_3L^{2\text{-}Me})(ac)](ClO_4)_2\cdot 2EtOH$ (**2**), and $[Sm^{III}(H_3L^{4\text{-}Me})(ac)](ClO_4)_2\cdot MeOH$ (**3**) at 296 K

	Complex		
	1	**2**	**3**
Bond distance			
Sm–N(1)	2.751(6)	2.741(7)	2.720(7)
Sm–N(2)	2.527(6)	2.530(6)	2.533(8)
Sm–N(3)	2.591(6)	2.574(5)	2.589(7)
Sm–N(5)	2.518(5)	2.547(7)	2.544(7)
Sm–N(6)	2.655(5)	2.702(5)	2.538(6)
Sm–N(8)	2.512(5)	2.509(6)	2.545(7)
Sm–N(9)	2.588(4)	2.571(8)	2.647(7)
Sm–O(1)	2.482(3)	2.523(5)	2.454(6)
Sm–O(2)	2.503(4)	2.485(5)	2.476(5)
Bond angle			
N(1)–Sm–N(2)	62.74(18)	62.99(18)	62.8(3)
N(1)–Sm–N(3)	122.72(15)	123.42(19)	119.8(3)
N(1)–Sm–N(5)	63.30(16)	63.07(19)	63.8(2)
N(1)–Sm–N(6)	116.93(14)	115.86(18)	122.09(19)
N(1)–Sm–N(8)	65.59(15)	65.7(2)	65.3(3)
N(1)–Sm–N(9)	126.00(14)	127.15(18)	124.6(3)
N(2)–Sm–N(3)	66.6(2)	67.28(18)	65.4(3)
N(2)–Sm–N(5)	74.41(17)	74.01(19)	78.3(3)
N(2)–Sm–N(6)	131.70(16)	129.76(19)	128.9(3)
N(2)–Sm–N(8)	127.3(2)	128.0(2)	127.7(3)
N(2)–Sm–N(9)	146.61(15)	148.6(2)	151.0(2)
N(3)–Sm–N(5)	79.16(16)	79.04(19)	77.8(2)
N(3)–Sm–N(6)	79.54(15)	77.85(16)	72.58(19)
N(3)–Sm–N(8)	160.94(15)	158.41(16)	155.80(19)
N(3)–Sm–N(9)	110.90(15)	109.3(2)	115.63(19)
N(5)–Sm–N(6)	65.91(16)	64.5(2)	65.3(2)
N(5)–Sm–N(8)	91.74(15)	90.4(2)	85.0(3)
N(5)–Sm–N(9)	138.94(14)	137.25(18)	130.67(19)
N(6)–Sm–N(8)	81.45(16)	80.61(17)	84.8(2)
N(6)–Sm–N(9)	76.68(13)	76.19(19)	73.97(19)
N(8)–Sm–N(9)	65.68(15)	66.4(3)	64.2(2)
O(1)–Sm–O(2)	52.10(13)	51.76(15)	53.09(19)
O(1)–Sm–N(1)	75.53(12)	75.97(18)	79.9(2)
O(1)–Sm–N(2)	79.83(19)	80.99(17)	78.9(3)
O(1)–Sm–N(3)	119.74(16)	120.96(15)	117.64(19)
O(1)–Sm–N(5)	137.97(16)	138.29(19)	143.0(2)
O(1)–Sm–N(6)	148.43(17)	149.24(18)	149.2(2)
O(1)–Sm–N(8)	78.09(17)	79.25(16)	86.3(2)
O(1)–Sm–N(9)	73.08(16)	74.53(17)	75.60(19)
O(2)–Sm–N(1)	117.05(13)	116.19(17)	125.0(2)
O(2)–Sm–N(2)	74.74(16)	74.0(2)	79.9(2)
O(2)–Sm–N(3)	71.00(13)	71.70(16)	70.90(18)
O(2)–Sm–N(5)	143.50(15)	142.93(18)	147.2(2)
O(2)–Sm–N(6)	126.01(15)	127.86(19)	112.66(19)
O(2)–Sm–N(8)	122.66(13)	124.33(19)	127.8(2)
O(2)–Sm–N(9)	73.32(12)	75.4(2)	73.88(18)

Table 3. Relevant Hydrogen Bond Distances (Å) for $[Sm^{III}(H_3L^{2\text{-}Me})(ac)](ClO_4)_2\cdot 2MeOH\cdot H_2O$ (**1**), $[Sm^{III}(H_3L^{2\text{-}Me})(ac)](ClO_4)_2\cdot 2EtOH$ (**2**), and $[Sm^{III}(H_3L^{4\text{-}Me})(ac)](ClO_4)_2\cdot MeOH$ (**3**) at 296 K[a)]

	Complex		
	1	**2**	**3**
N(4)–O(6)	3.043(11)		
N(4)–O(7)	3.028(10)		
N(7)–O(3)	2.833(10)		
N(10)–O(2)*1	2.814(7)		
O(1)–O(4)	2.864(9)		
N(4)–O(1)*2		2.766(7)	
N(7)–O(3)		2.846(11)	
N(10)–O(4)		2.800(18)	
O(3)–O(5)		3.10(5)	
O(4)–O(9)		3.11(3)	
N(4)–O(2)*3			2.871(10)
N(7)–O(3)*4			2.963(12)
N(10)–O(3)			2.915(14)
N(10)–O(7)			2.948(18)
O(8)–O(11)			2.92(3)

a) Symmetry operations: $*^1$: $-x+2$, $y-1/2$, $-z+2$; $*^2$: x, $y-1$, z; $*^3$: $-x+1$, $-y+1$, $-z+2$; $*^4$: x, $-y+3/2$, $z-1/2$.

while adjacent chains with opposite chiralities are stacked to give a racemic crystal in **2**. In the complexes, there is no noteworthy interchain interaction and the packing manner depends on the crystal solvent or counter anion which occupy the space between the chains.

$[Sm(H_3L^{4\text{-}Me})(ac)](ClO_4)_2\cdot MeOH$ (3): The crystal structure of **3** consists of $[Sm^{III}(H_3L^{4\text{-}Me})(ac)]^{2+}$, two counter anions ClO_4^-, and one methanol molecule as the crystal solvent. The molecular structure of $[Sm^{III}(H_3L^{4\text{-}Me})(ac)]^{2+}$ with the selected atom numbering scheme is shown in Figure 5. The Sm^{III} ion is coordinated by seven nitrogen atoms of a tripod heptadentate N_7 ligand ($H_3L^{4\text{-}Me}$) and two oxygen atoms of an acetate ion. The structural features of the coordination environment of the complex-cations $[Sm^{III}(H_3L^R)(ac)]^{2+}$ (R = 2-Me and 4-Me) are essentially the same.

Of three imidazole groups, N(4) is hydrogen-bonded to one of the acetate oxygen atoms $O(2)^{*3}$ of the adjacent $[Sm^{III}(H_3L^{4\text{-}Me})(ac)]^{2+}$ unit related by an inversion center with the distance of $N(4)\cdots O(2)^{*3} = 2.871(10)$ Å. N(7) is hydrogen-bonded to an oxygen atoms $O(3)^{*4}$ of a perchlorate anion of $Cl(1)^{*4}$ with $N(7)\cdots O(3)^{*4} = 2.963(12)$ (*3; $-x+1$, $-y+1$, $-z+2$: *4; x, $-y+3/2$, $z-1/2$). The oxygen atom O(3) is further hydrogen-bonded to $N(10)^{*4}$ of the adjacent molecular unit to form a dimensional structure, in which two adjacent $[Sm^{III}(H_3L^{4\text{-}Me})(ac)]^{2+}$ cations have different chirality. N(10) is hydrogen-bonded to two perchlorate anions with $N(10)\cdots O(3) = 2.915(14)$ Å of Cl(1) and $N(10)\cdots O(7) = 2.948(18)$ Å of Cl(2) as a bifurcated hydrogen bond. The oxygen atom O(8) of Cl(2) is hydrogen-bonded to a methanol with $O(8)\cdots O(11) = 2.92(3)$ Å. There is no further hydrogen bonding from the methanol molecule O(11) and the perchlorate ions Cl(1) and Cl(2).

Figure 6 shows crystal structure of **3**. Compound **3** crystallizes into a centrosymmetric monoclinic space group $P2_1/c$, and the Δ- and Λ-enantiomorphs coexist in a crystal. The crystal structure can be described as two adjacent $[Sm^{III}(H_3L^{4\text{-}Me})$-

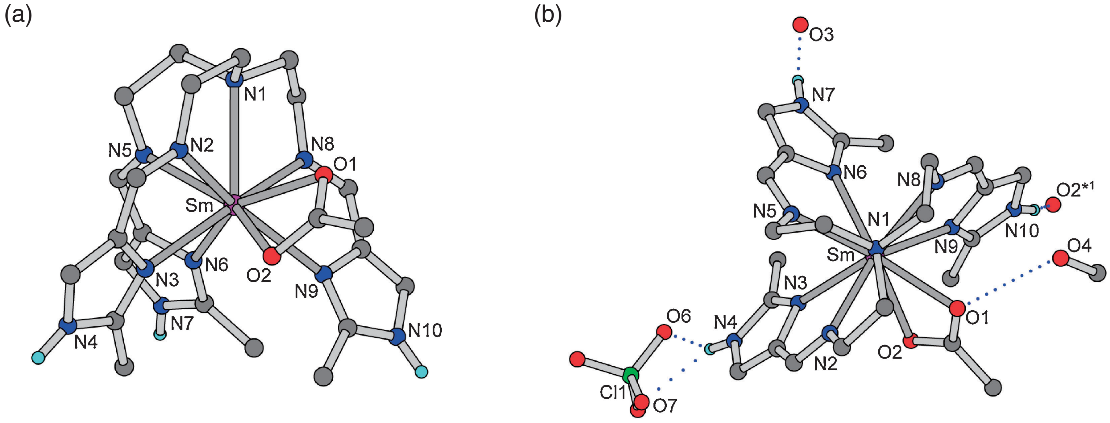

Figure 1. (a) Molecular structure of $[Sm^{III}(H_3L^{2\text{-}Me})(ac)]^{2+}$ of $[Sm^{III}(H_3L^{2\text{-}Me})(ac)](ClO_4)_2 \cdot 2MeOH \cdot H_2O$ (**1**) with the selected atom numbering scheme. Hydrogen atoms except for the imidazole hydrogen atoms are omitted for clarity. (b) Molecular structure of $[Sm^{III}(H_3L^{2\text{-}Me})(ac)]^{2+}$ projected from the central amine nitrogen to Sm^{III} ion and the hydrogen bonds from $[Sm^{III}(H_3L^{2\text{-}Me})(ac)]^{2+}$ to ClO_4^-, H_2O, and MeOH.

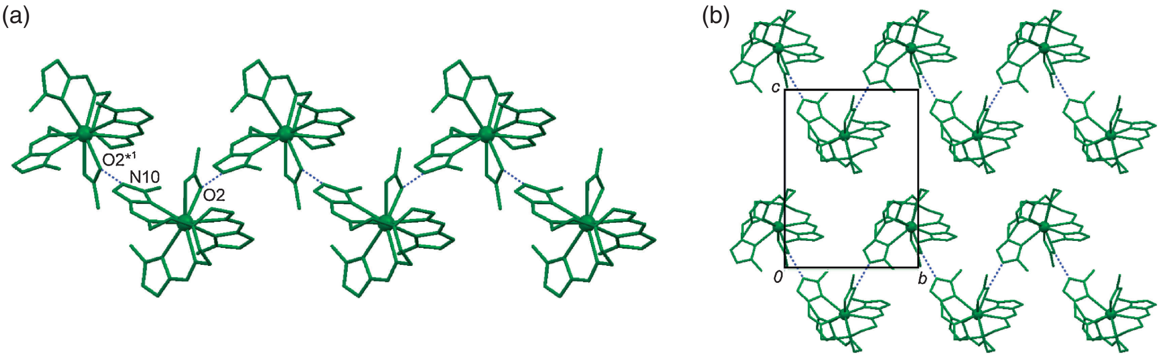

Figure 2. (a) Homochiral one-dimensional structure running along the *b* axis of $[Sm^{III}(H_3L^{2\text{-}Me})(ac)](ClO_4)_2 \cdot 2MeOH \cdot H_2O$ (**1**). Green colored $[Sm^{III}(H_3L^{2\text{-}Me})(ac)]^{2+}$ shows *Δ*-enantiomorph. The intermolecular imidazole···acetate hydrogen bond of N(10)···O(2)*1 = 2.814(7) Å forms the homochiral 1D chain. (b) Crystal packing diagram of **1**, showing that **1** is a conglomerate, where the crystal solvents and the perchlorate anions are omitted for clarity. The adjacent chains with the same chirality are stacked to give a homochiral crystal (conglomerate), indicating that the spontaneous resolution occurs during the crystallization.

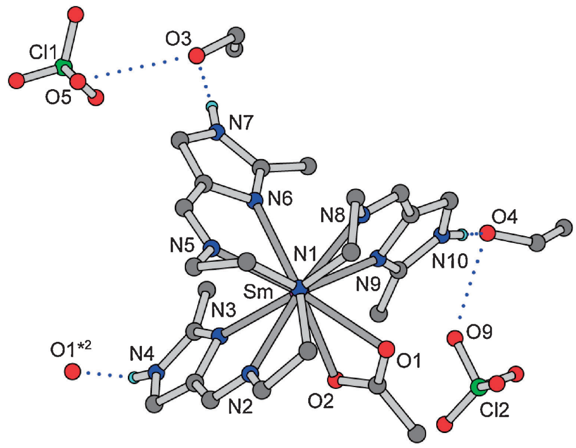

Figure 3. Molecular structure of $[Sm^{III}(H_3L^{2\text{-}Me})(ac)]^{2+}$ of $[Sm^{III}(H_3L^{2\text{-}Me})(ac)](ClO_4)_2 \cdot 2EtOH$ (**2**) projected from the central amine nitrogen to Sm^{III} ion with the selected atom numbering scheme and the hydrogen bonds from $[Sm^{III}(H_3L^{2\text{-}Me})(ac)]^{2+}$ to EtOH and EtOH to ClO_4^-. Hydrogen atoms except for the imidazole hydrogen atoms are omitted for clarity.

$(ac)]^{2+}$ cations with *Δ*- and *Λ*-enantiomorphs doubly bridged by two imidazole···acetate hydrogen bonds of N(4)···O(2)*3 and N(4)*3···O(2) to form a dimeric structure, as shown in Figure 6a. The dimeric structure is further connected to the adjacent dimeric unit through the bridging oxygen atom O(3) of the perchlorate anion by two hydrogen bonds of N(10)···O(3) and N(7)···O(3)*4 to generate a network structure, as shown in Figure 6b.

Conclusion

In summary, three Sm^{III} complexes with an acetate and tripod heptadentate N_7 ligand containing three imidazole groups, $[Sm(H_3L^{2\text{-}Me})(ac)](ClO_4)_2 \cdot 2MeOH \cdot H_2O$ (**1**), $[Sm(H_3L^{2\text{-}Me})(ac)](ClO_4)_2 \cdot 2EtOH$ (**2**), and $[Sm(H_3L^{4\text{-}Me})(ac)](ClO_4)_2 \cdot MeOH$ (**3**), were synthesized and characterized, where **1** and **2** have the methyl substituent at the 2-position of the imidazole moiety, and **3** has the methyl substituent at the 4-position. The crystal structures revealed that each Sm^{III} ion is coordinated by a tripod heptadentate N_7 ligand and two oxygen atoms of the acetate ion. Two adjacent $[Sm(H_3L^{2\text{-}Me})(ac)]^{2+}$ species with the same chirality in **1** and **2** are linked by an intermolecular imidazole···acetate hydrogen bond to form a homochiral 1D chain structure. Although complex **1** and **2** have the same homochiral 1D chain, adjacent chains with the same chirality are stacked to give a conglomerate crystal in **1**, while adjacent chains with opposite chiralities are stacked to give a racemic crystal in **2**. On the other hand, two adjacent $[Sm(H_3L^{4\text{-Me}})(ac)]^{2+}$ species with the opposite chiralities in **3** are doubly bridged by two intermolecular imidazole···acetate hydrogen bonds to form a heterochiral dimer. Furthermore, adjacent dimers are connected by ClO_4^- ion through the hydrogen bonds to form a racemic crystal in **3**. This demonstrates that the intermolecular imidazole···acetate hydrogen bond is a common motif for the assembly in the molecular system of $[Sm^{III}(H_3L^{2\text{-Me or }4\text{-Me}})(ac)](ClO_4)_2$ and plays a central role for enantioselective discrimination in the present system. Figure 7 shows space filling representations of adjacent molecular species bridged by intermolecular imidazole···acetate hydrogen bond for homochiral and heterochiral arrangements. The enantioselectivity is tuned by the position of the methyl substituent of the imidazole moiety.

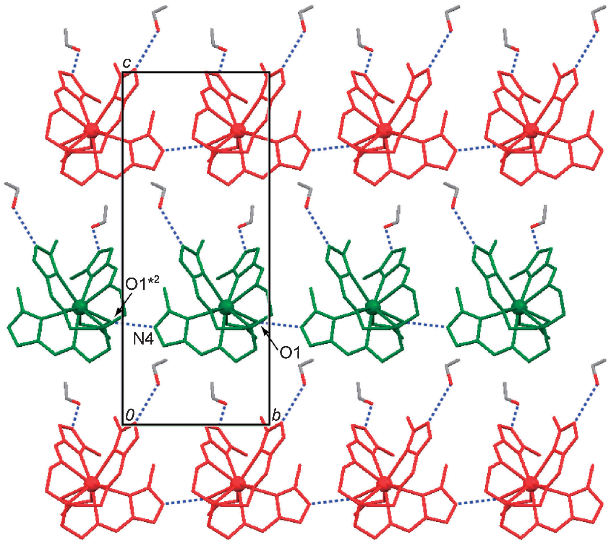

Figure 4. Crystal structure of $[Sm(H_3L^{2\text{-Me}})(ac)](ClO_4)_2\cdot 2EtOH$ (**2**), showing homochiral chain structure running along the *b* axis. The perchlorate anions are omitted for clarity. Δ- and Λ-Enantiomorphs are drawn in green and red, respectively. Adjacent chains with opposite chiralities are stacked to give a racemic crystal.

Experimental

Materials. All reagents and solvents used in this study are commercially available from Tokyo Kasei Co., Ltd. and Wako Pure Chemical Industries, Ltd. and were used without further purification.

CAUTION! The perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of the compound should be prepared, and they should be handled with much care!

Preparations. **$[Sm^{III}(H_3L^{2\text{-Me}})(ac)](ClO_4)_2\cdot 2MeOH\cdot H_2O$ (1):** A solution of tris(2-aminoethyl)amine (0.073 g, 0.5 mmol) in 10 mL of methanol and a solution of 2-methyl-4-formylimidazole (0.165 g, 1.5 mmol) in 10 mL of methanol were mixed, and the mixture was stirred at 50 °C for 1 h and then cooled to room temperature. To the resultant ligand solution ($H_3L^{2\text{-Me}}$) was added a solution of $Sm^{III}(ac)_3\cdot 4H_2O$ (0.200 g, 0.5 mmol) in 10 mL of methanol and the mixture was stirred for 30 min at room temperature. A solution of $NaClO_4$ (0.122 g, 1 mmol) in 10 mL of methanol was added and the resultant mixture was stirred for 30 min and then filtered. The filtrate was left to stand for several days to form colorless crystals. Single-crystal X-ray analysis revealed that the crystal contains two methanol molecules and one water molecule per complex, but crystals efflorescence and the elemental analysis agreed with the chemical formula without the methanol molecules. Yield: 0.122 g (29%). Anal. Calcd for $[Sm^{III}(H_3L^{2\text{-Me}})(ac)](ClO_4)_2\cdot H_2O = C_{23}H_{35}N_{10}O_{11}Cl_2Sm$: C, 32.54; H, 4.16; N, 16.50%. Found: C, 32.56; H, 4.15; N, 16.62%.

$[Sm^{III}(H_3L^{2\text{-Me}})(ac)](ClO_4)_2\cdot 2EtOH$ (2): The complex **2** was prepared in a similar way to **1**, using ethanol, instead of

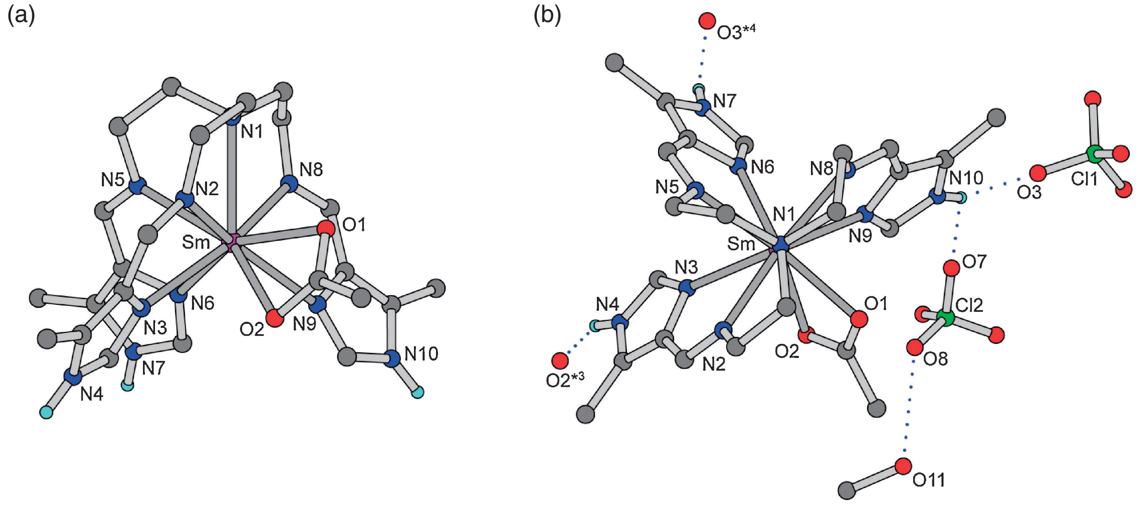

Figure 5. (a) Molecular structure of $[Sm^{III}(H_3L^{4\text{-Me}})(ac)]^{2+}$ of $[Sm(H_3L^{4\text{-Me}})(ac)](ClO_4)_2\cdot MeOH$ (**3**) with the selected atom numbering scheme. Hydrogen atoms except for the imidazole hydrogen atoms are omitted for clarity. (b) Molecular structure of $[Sm^{III}(H_3L^{4\text{-Me}})(ac)]^{2+}$ projected from the central amine nitrogen to Sm^{III} ion and the hydrogen bonds.

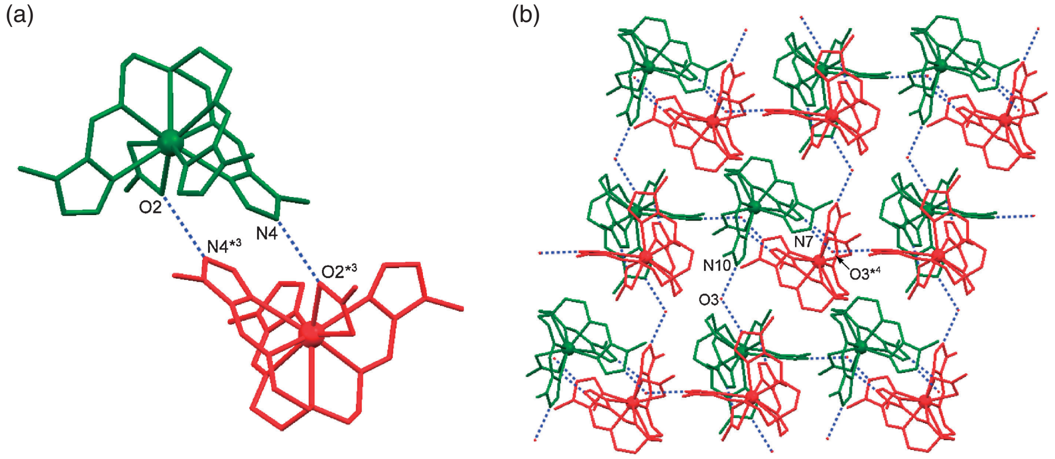

Figure 6. Crystal structure of $[Sm^{III}(H_3L^{4\text{-}Me})(ac)](ClO_4)_2 \cdot MeOH$ (**3**). The counter anions (ClO_4^-), one MeOH molecule, and hydrogen atoms are omitted for clarity. Δ- and Λ-Enantiomorphs are drawn in green and red, respectively. (a) Δ- and Λ-Enantiomorphs are doubly bridged by two imidazole···acetate hydrogen bonds with $N(4) \cdots O(2)^{*3} = 2.871(10)$ Å to form a dimeric structure. (b) The dimeric structure is further hydrogen-bonded to the adjacent dimeric unit through the bridging oxygen atom O(3) of the perchlorate anion with $N(10) \cdots O(3) = 2.915(14)$ and $N(7) \cdots O(3)^{*4} = 2.963(12)$ Å to generate a network structure.

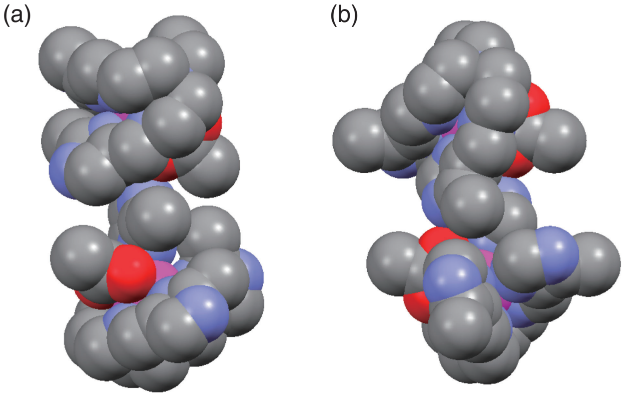

Figure 7. Space filling representations of two adjacent molecular species bridged by imidazole···acetate hydrogen bond, where hydrogen atoms are omitted. (a) Adjacent $[Sm(H_3L^{2\text{-}Me})(ac)]^{2+}$ species with the same chirality. (b) Adjacent $[Sm(H_3L^{4\text{-}Me})(ac)]^{2+}$ species with the opposite chiralities.

methanol as a reaction solvent. Colorless crystals easily lose the crystal solvent under ambient atmosphere to become cloudy white. Yield: 0.054 g (13%). Anal. Calcd for $[Sm^{III}(H_3L^{2\text{-}Me})(ac)](ClO_4)_2 \cdot 0.5EtOH = C_{23}H_{33}N_{10}O_{10}Cl_2Sm \cdot 0.5EtOH$: C, 33.76; H, 4.25; N, 16.40%. Found: C, 33.34; H, 4.51; N, 15.97%.

$[Sm^{III}(H_3L^{4\text{-}Me})(ac)](ClO_4)_2 \cdot MeOH$ (3): The complex **3** was prepared in a similar way to **1**, using 4-methyl-5-formylimidazole, instead of 2-methyl-4-formylimidazole. Colorless crystals. The single-crystal X-ray analysis revealed that the crystal contains one methanol molecule per complex, but the crystals efflorescence under ambient atmosphere and the elemental analysis agreed with the chemical formula without the methanol molecule. Yield: 0.289 g (70%). Anal. Calcd for $[Sm^{III}(H_3L^{4\text{-}Me})(ac)](ClO_4)_2 = C_{23}H_{33}N_{10}O_{10}Cl_2Sm$: C, 33.25; H, 4.00; N, 16.86%. Found: C, 33.33; H, 4.02; N, 17.00%.

Physical Measurements. The elemental C, H, and N analyses were carried out by Miss Kikue Nishiyama at the Center for Instrumental Analysis of Kumamoto University.

X-ray Crystallography. The X-ray diffraction data were collected with a Rigaku RAXIS RAPID imaging plate diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 296 K. The structures were solved by direct methods and expanded using the Fourier technique. Hydrogen atoms except for those of solvent molecules were fixed at the calculated positions and refined using a riding model. All calculations were performed using the Crystal Structure crystallographic software package.[22] Flack parameter of complex **1** was calculated to determine the absolute configuration.[23]

X-ray crystallographic data in CIF format for $[Sm^{III}(H_3L^{2\text{-}Me})(ac)](ClO_4)_2 \cdot 2MeOH \cdot H_2O$ (**1**), $[Sm(H_3L^{2\text{-}Me})(ac)](ClO_4)_2 \cdot 2EtOH$ (**2**), and $[Sm^{III}(H_3L^{4\text{-}Me})(ac)](ClO_4)_2 \cdot MeOH$ (**3**) has been deposited with the deposition number 824693–824695 at CCDC. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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