Highly Fluxional Blue Luminescent Aluminum Complexes: $Al(CH_3)(7\text{-azain-2-Ph})_2(7\text{-azainH-2-Ph})$, $Al_3(\mu_3\text{-O})(CH_3)_3(7\text{-azain-2-Ph})_4$, and $Al_3(\mu_3\text{-O})(CH_3)_3(7\text{-azain-2-CH}_3)_4$ (7-azain = 7-Azaindole Anion)

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The new aluminum complexes $Al(CH_3)(7\text{-azain-2-Ph})_2(7\text{-azainH-2-Ph})$ (**1**), $Al_3(\mu_3\text{-O})(CH_3)_3(7\text{-azain-2-Ph})_4$ (**2**), and $Al_3(\mu_3\text{-O})(CH_3)_3(7\text{-azain-2-CH}_3)_4$ (**3**), where 7-azain = 7-azaindole anion, have been synthesized and characterized structurally. The three aluminum atoms in compounds **2** and **3** are bridged by an oxo ligand. Compounds **2** and **3** have an asymmetric structure in the solid state that results in a distinct chemical environment for each aluminum atom and each 7-azain-2-R ligand in the compounds. All compounds emit a blue color, when irradiated by UV light. The blue emission is attributed to the coordinated 7-azain-2-CH_3 and 7-azain-2-Ph ligands. Variable-temperature 1D and low-temperature 2D EXSY ^{1}H NMR experiments established that compounds **2** and **3** are highly fluxional in solution, attributable to an unusual intramolecular migration of the coordinated 7-azain-2-R ligands.

Introduction

We have demonstrated recently that 7-azaindole forms various complexes readily upon reaction with trialkylaluminum.[1] Depending on the reaction conditions, the resulting 7-azaindole aluminum complexes display versatile and complex structural features. The most interesting and important property of these complexes is blue luminescence, because of the potential application in electroluminescent displays.[2] We have reported that the blue emission from these aluminum complexes is originated from the coordinated 7-azaindole anion, where the aluminum ion plays a key role in stabilizing the complex and promoting the blue emission. We have also observed that nonemitting ligands around the aluminum do not have any significant effect on the blue emission of the complex, but they do influence the stability and volatility of the complex. One factor that could have direct impact on luminescent properties and other physical properties such as stability and volatility of the complex is substituents on the 7-azaindole ligand. In fact, it has been demonstrated previously in 8-hydroxyquinoline-based aluminum complexes that the introduction of a substituent on the emitting 8-hydroxyquinoline ligand has a dramatic effect on emission energy.[3] For example, (8-hydroxyquinoline)aluminum complexes typically emit in the yellow-green region. However, with the introduction of appropriate substituents on the 2- and 4-positions of the quinoline, the emission energy of 8-hydroxyquinoline complexes can be shifted to the blue region via mostly electronic effects.[3] Because 8-hydroxyquinoline complexes usually emit in the yellow-green region and elaborate ligand modification has to be carried out in order to achieve a blue emission, the application of 8-hydroxyquinoline-based complexes as blue emitters in electroluminescent displays is therefore rather limited.[3] To determine the effect a substituent on the 7-azaindole ligand has on the properties of aluminum complexes, we initiated the investigation of aluminum complexes containing 7-azaindole derivatives, specifically those that have a subsitituent such as CH_3, CF_3, and phenyl at the 2-position (2-R-7-azaindole). We were able to synthesize 2-phenyl-7-azaindole and 2-methyl-7-azaindole (Chart 1) but were unsuccessful in the attempted synthesis of 2-trifluoromethyl-7-azaindole. Using the 2-R-7-azaindole ligands, we have synthesized three new aluminum compounds, two of which are trinuclear complexes and exhibit an unusual dynamic behavior in solution. The syntheses, crystal structures, luminescent properties, and dynamic solution behavior of these new aluminum compounds are presented herein.

Experimental Section

All manipulations were carried out under an atmosphere of nitrogen using either the standard vacuum line techniques or inert-atmosphere dryboxes. All solvents were freshly distilled over the appropriate drying agent under a nitrogen atmosphere. Trimethylaluminum and 2-amino-3-picoline were purchased from Aldrich. 2-Aminopicoline was further purified by distillation. All NMR samples were prepared in the drybox. 2-Phenyl-7-azaindole and 2-methyl-7-azaindole were prepared

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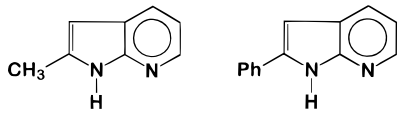
Chart 1. 2-Methyl-7-azaindole and 2-Phenyl-7-azaindole



by a modified procedure reported by Herbert and Wibberley.[4] ^{1}H NMR spectra were recorded on Bruker AM 400 and ACF 200 spectrometers. ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer at 100.6 MHz. The two-dimensional (2D) exchange experiment (EXSY) was performed at 243 K with the standard three-pulse sequence 90°−t1−90°−mixing−90°−ACQ(t2). The mixing time was 100 ms. A total of 256 t1 increments were acquired and zero-filled to 512 in the t1 dimension prior to the 2D Fourier transformation (2D FT). For each t1, eight scans were accumulated. Sine-bell window functions were applied in both dimensions. The spectral width was 4808 Hz, and the digital resolution in the 2D spectrum was 9.39 Hz/point in both dimensions. The total time to record the 2D free-induction decay (FID) was about 2.5 h. Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia, Canada. Excitation and emission spectra were recorded on a Photon Technologies International QM1 spectrometer.

Synthesis of 2-Phenyl-7-azaindole. (1) Preparation of 2-Benzamido-3-picoline. To a solution of benzoyl chloride (15 g, 0.107 mol) in 25 mL of pyridine and 35 mL of chloroform was added 2-amino-3-picoline (12 g, 0.107 mol) with stirring. After the mixture was refluxed overnight, the reaction mixture was cooled to room temperature. The resulting precipitate was removed by filtration. The filtrate was evaporated to dryness, and the residue was redissolved in ethanol. Yellowish crystals of 2-benzamido-3-picoline were obtained and dried under vacuum at 90 °C for 1 h. Yield: 7.50 g (33%). Mp: 130−131 °C. ^{1}H NMR (DMSO-d_6; δ, ppm): 9.10 (br, 1H, NH), 8.55 (d, 1H, CH), 8.24 (d, 1H, CH), 8.10 (d, 2H, CH), 7.80−7.40 (m, 4H, CH), 2.40 (s, 3H, CH_3).

(2) Preparation of 2-Phenyl-7-azaindole. Sodium hydride (3.2 g) was added to *N*-methylaniline (10 g), and the solution was stirred and heated under reflux with nitrogen for 30 min and then cooled to room temperature. 2-Benzamido-3-picoline (3.3 g) was added to the cooled solution, and the mixture was heated at 280 °C for 7 min with stirring. After the mixture was cooled to room temperature, acetic acid was added to the residue until all solids were dissolved. The solution was then made basic with sodium hydroxide and extracted with chloroform. The extract was dried over Na_2SO_4 and then concentrated under reduced pressure. After the addition of hexane (5 mL), the crystals of 2-phenyl-7-azaindole were collected by filtration and washed with hexane (1.75 g, yield 58%). ^{1}H NMR ($CDCl_3$; δ, ppm): 12.11 (br, 1H, NH), 8.29 (d, 1H, CH), 7.94 (d, 1H, CH), 7.84 (d, 2H, CH), 7.54−7.34 (m, 3H), 6.95 (m, 1H, CH), 6.77 (s, 1H, CH).

2-Methyl-7-azaindole. (1) Preparation of 2-Acetamido-3-picoline. Acetyl chloride (1.96 g, 25 mmol) in 5 mL of toluene was added to the solution of 2-amino-3-picoline (2.32 g, 21 mmol), pyridine (3 mL), and toluene (15 mL) under nitrogen at 0 °C with stirring. After the mixture was warmed to room temperature, the solution was stirred for an additional 1 h. The resulting white solid was collected by filtration and washed with diethyl ether. Recrystallization from ethanol/toluene yielded colorless crystals of 2-acetamido-3-picoline (2.04 g, yield 65%). ^{1}H NMR (DMSO-d_6; δ, ppm): 11.27 (br, 1H, NH), 8.39 (d, 1H, CH), 8.25 (d, 1H, CH), 7.54 (m, 1H, CH), 2.43 (s, 3H, CH_3), 2.31(s, 3H, CH_3).

(2) Preparation of 2-Methyl-7-azaindole. Sodium hydride (5.12 g) was added to *N*-methylaniline (16 g), and the solution was stirred and refluxed under nitrogen for 30 min. After the solution was cooled to room temperature, 2-acetamido-3-picoline (3.6 g) was added to the cooled solution and the mixture was heated at 280 °C for 5 min with stirring. After the mixture was cooled to room temperature, acetic acid was added until all solids were dissolved. The solution was then made basic with sodium hydroxide and extracted with chloroform. The extract was dried over Na_2SO_4 and concentrated. The residue was separated by column chromatography on silica gel with a solution of ethyl acetate/hexane in a 1:1.5 ratio. The crude product was recrystallized from cyclohexane to give a crystalline product (0.72 g, yield 23%). Mp: 135−136 °C. ^{1}H NMR ($CDCl_3$; δ, ppm): 11.12 (br, 1H, NH), 8.19 (d, 1H, CH), 7.80 (d, 1H, CH), 7.01 (m, 1H, CH), 6.15 (s, 1H, CH), 2.50 (s, 3H, CH_3).

Al(CH$_3$)(7-azain-2-Ph)$_2$(7-azain-2-Ph-H) (1). 2-Phenyl-7-azaindole (0.175 g, 0.9 mmol) in 15 mL of toluene was heated to 60 °C. After all 2-phenyl-7-azaindole was dissolved in toluene, $Al(CH_3)_3$ (0.15 mL, 2 M, 0.3 mmol) was added to the solution. After the solution was stirred for 20 h at room temperature, it was concentrated to about 2 mL by vacuum. Colorless crystals of compound **2** were obtained. Yield: 0.125 g (66%). ^{1}H NMR ($CDCl_3$; δ, ppm, 298 K): 14.76 (s, 1H, NH), 8.40−6.75 (br, m, 24H, Ar H), 6.50 (s, 3H, Ar H), −0.50 (s, 3H, Al−CH_3). ^{13}C NMR ($CDCl_3$; δ, ppm, 298 K): 139.3, 129.0, 128.2, 127.9, 127.3, 125.5, 125.2, 114.9, 101.8, 97.6 (aromatic carbon); −9.0 (br, CH_3). Anal. Calcd for $C_{40}H_{31}N_6Al$: C, 71.15; H, 5.00; N, 13.50. Found: C, 71.11; H, 4.83; N, 13.48.

Al$_3$(CH$_3$)$_3$(μ_3-O)(7-azain-2-Ph)$_4$ (2). 2-Phenyl-7-azaindole (0.078 g, 0.4 mmol) in 10 mL of toluene was heated to 60 °C. After all 2-phenyl-7-azaindole was dissolved in toluene, $Al(CH_3)_3$ (0.15 mL, 2 M, 0.3 mmol) was added to the solution and the solution was stirred for 5 h at room temperature with water-saturated nitrogen gas being passed through the flask. After the solution was stirred for an additional 15 h, the mixture was concentrated to about 2 mL by vacuum. Colorless crystals of compound **1** were obtained. Yield: 0.140 g (77%). ^{1}H NMR ($CDCl_3$; δ, ppm, 298 K): 7.80−6.20 (m, 36 H, Ar H), −0.50 (broad, 9H, Al−CH_3). Anal. Calcd for $C_{55}H_{45}N_8OAl_3 \cdot C_7H_8$: C, 73.94; H, 5.30; N, 11.13. Found: C, 73.91; H, 5.38; N, 10.59. (The sample of **2** was evacuated under vacuum to remove the solvent molecules before it was sent for elemental analysis. However, the result of elemental analysis indicated that there is still one toluene molecule per complex.)

Al$_3$(CH$_3$)(μ_3-O)(7-azain-2-CH$_3$)$_4$ (3). 2-Methyl-7-azaindole (0.159 g, 1.2 mmol) in 8 mL of toluene was reacted with $Al(CH_3)_3$ (0.45 mL, 2 M, 0.9 mmol) for 5 h at room temperature with water-saturated nitrogen gas being passed through the flask. After the solution was stirred for another 15 h under nitrogen, it was concentrated to about 2 mL by vacuum. Colorless crystals of compound **3** were obtained. Yield: 0.142 g (71%). ^{1}H NMR ($CDCl_3$; δ, ppm, 298 K): 7.69−6.10 (m, 16H, Ar H); 2.34, 2.15 (s, 12H, C−CH_3), −0.35, −0.72 (broad, 9H, Al−CH_3). Anal. Calcd for $C_{35}H_{37}ON_8Al_3 \cdot 0.5$(toluene): C, 64.89; H, 5.76; N, 15.73. Found: C, 64.45; H, 5.74; N, 15.76.

X-ray Diffraction Analyses. All crystals were obtained either from concentrated toluene solutions or from solutions of toluene/hexane. The crystals were sealed in glass capillaries under nitrogen. All data were collected on a Siemens P4 single-crystal diffractometer with graphite-monochromated Mo Kα radiation, operated at 50 kV and 40 mA at 23 °C. The data for **1** and **3** were collected over $2\theta = 3-45°$ while the data for **2** was collected over $2\theta = 3-50°$. Three standard reflections were measured every 197 reflections. No significant decay was observed for any sample during the data collection. Data were processed on a Pentium PC using the Siemens SHELXTL software package (version 5.0)[5] and corrected for Lorentz and polarization effects. Neutral atom scattering

(4) Herbert, R. and Wibberley, D. G. *J. Chem. Soc. C* **1969**, 1505.

(5) SHELXTL Crystal Structure Analysis Package; Version 5; Bruker Axs, Analytical X-ray System; Siemens: Madison, WI, 1995.

Table 1. Crystallographic Data

	1	2	3
formula	$C_{40}H_{31}N_6Al$	$C_{55}H_{45}N_8OAl_3/2C_7H_8$	$C_{35}H_{37}N_8OAl_3/0.5C_7H_8$
fw	622.7	1099.2	712.7
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	11.070(2)	14.008(6)	10.172(1)
b/Å	11.447(3)	14.232(5)	10.910(3)
c/Å	15.625(3)	17.715(4)	17.136(3)
α/deg	92.68(2)	106.02(2)	99.03(2)
β/deg	110.32(1)	99.23(3)	98.865(5)
γ/deg	116.61(1)	112.68(3)	91.01(2)
V/Å^3	1611.1(6)	2987(2)	1853.9(7)
Z	2	2	2
D_c/g cm^{-3}	1.28	1.22	1.28
T/°C	23	23	23
radiation, λ/Å	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
μ/cm^{-1}	10.3	11.4	14.5
no. of rflns measd	4838	7785	5106
no. of rflns used (R_{ini})	4522 (0.016)	7409 (0.032)	4770(0.062)
no. of variables	425	695	440
final R^a ($I > 2\sigma(I)$)	R1 = 0.0377, wR2 = 0.0944	R1 = 0.0589, wR2 = 0.1572	R1 = 0.1649, wR2 = 0.3810
R (all data)	R1 = 0.0497, wR2 = 0.1063	R1 = 0.0731, wR2 = 0.1843	R1 = 0.2200, wR2 = 0.4529
goodness of fit on F^2	1.04	1.05	1.16

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w[(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$.

factors were taken from Cromer and Waber.[6] The crystals of **1**−**3** belong to the triclinic space group $P\bar{1}$. The structures were solved by direct methods. In the crystal lattices of **2** and **3**, there are toluene solvent molecules (2 toluene molecules per molecule of **2** and 0.5 toluene molecule per molecule of **3**). One of the toluene molecules in **2** displays some degree of rotational disordering which could not be modeled, while the toluene molecule in **3** resides on an inversion center and is disordered over the two sites related by the inversion center. Crystals of **3** suitable for X-ray diffraction analysis were difficult to grow and displayed significant twinning. Twinning and the disorder of the toluene molecule could account for the poor quality of the structural data of **3** (the diffraction data for **3** were collected several times by using several different crystals, but the quality of the resulting data was similar). The positions for all hydrogen atoms except those attached to the disordered solvent molecules were calculated, and their contributions in structural factor calculations were included. All non-hydrogen atoms in **1**−**3** were refined anisotropically, except the carbon atoms of the disordered toluene molecules. The crystallographic data for compounds **1**−**3** are given in Table 1.

Results and Discussion

Synthesis and Crystal Structures of Al(CH$_3$)(7-azain-2-Ph)$_2$(7-azainH-2-Ph) (1) and Al$_3$(μ_3-O)(CH$_3$)$_3$-(7-azain-2-Ph)$_4$ (2). Compounds **1** and **2** were obtained initially as mixtures from a reaction of 2-phenyl-7-azaindole with Al(CH$_3$)$_3$ in a 1:1 ratio. Both compounds were then synthesized successfully from independent stoichiometric reactions. The synthesis of compound **1** is straightforward by simply reacting Al(CH$_3$)$_3$ with 2-phenyl-7-azaindole in a 1:3 ratio in toluene. The independent synthesis of **2** was somewhat challenging, due to the involvement of water in the reaction. We found that the best way to synthesize **2** is by introducing water-vapor-saturated nitrogen gas into the reaction mixture of Al(CH$_3$)$_3$ with 2-phenyl-7-azaindole in a 3:4 ratio in toluene. When exposed to air, compound **1** decomposes rapidly, while compound **2** retains its light yellow crystalline appearance for a few hours. Both compounds were fully characterized by NMR, elemental, and X-ray diffraction analyses.

Selected bond lengths and angles for **1** and **2** are given in Table 2. As shown in Figure 1, the aluminum ion in compound **1** has an approximately tetrahedral geometry, as evidenced by the bond angles around Al(1), ranging from 101.73(7)° to 117.68(9)°. There are two 7-azain-2-Ph anions bound to Al(1) through the negatively charged indole nitrogen atom. The neutral 7-azain-2-Ph ligand, however, is bound to Al(1) via the pyridyl nitrogen atom. The Al(1)−N(indole) bond lengths (1.885(2), 1.889(2) Å) are much shorter than that of Al(1)−N(pyridyl) (1.957(2) Å), reflecting the fact that the negatively charged indole nitrogen is a better donor than the neutral pyridyl nitrogen toward the aluminum ion, consistent with our previous observation.[1] Compound **1** has an asymmetric structure with the three 7-azain-2-Ph ligands in an approximately propeller arrangement. Mononuclear aluminum complexes containing one alkyl ligand are often stabilized by chelating ligands where the aluminum is either five- or six-coordinate.[7] Examples of four-coordinate monoalkylaluminum complexes where only terminal ligands are involved similar to compound **1** have been reported previously.[8] We believe that the steric bulkiness of the ligands in **1** plays a key role in stabilizing the structure of **1**. The phenyl ring is not coplanar with the 7-azaindole ring, apparently due to steric interactions. There is an intramolecular hydrogen bond between the pyridyl nitrogen atom N(6) and the proton on the indole nitrogen atom N(1), as indicated by the distances of N(6)···H(1) (1.695 Å) and N(6)···N(1) (2.831(3) Å). This intramolecular hydrogen bond is believed to further enhance the structural stability of compound **1**.

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Table 2. Selected Bond Lengths (Å) and Angles (deg)

Compound **1**			
Al(1)−N(3)	1.885(2)	N(1)−C(13)	1.361(2)
Al(1)−N(5)	1.889(2)	N(1)−C(7)	1.391(3)
Al(1)−C(40)	1.948(2)	C(39)−N(6)	1.340(2)
Al(1)−N(2)	1.957(2)	N(2)−C(13)	1.354(3)
N(5)−C(39)	1.385(2)	N(2)−C(12)	1.358(2)
N(5)−C(33)	1.397(3)	N(6)−C(38)	1.341(2)
N(3)−C(26)	1.383(3)	N(4)−C(25)	1.333(3)
N(3)−C(20)	1.404(2)	N(4)−C(26)	1.334(3)
N(3)−Al(1)−N(5)	107.93(7)	N(3)−Al(1)−N(2)	108.75(8)
N(3)−Al(1)−C(40)	112.19(8)	N(5)−Al(1)−N(2)	101.73(7)
N(5)−Al(1)−C(40)	117.68(9)	C(40)−Al(1)−N(2)	107.80(9)
Compound **2**			
Al(1)−O(1)	1.818(2)	Al(3)−C(3)	1.944(4)
Al(1)−N(1)	1.940(3)	N(3)−C(29)	1.379(4)
Al(1)−C(1)	1.953(4)	N(3)−C(23)	1.409(4)
Al(1)−N(6)	2.106(3)	N(4)−C(29)	1.344(4)
Al(1)−N(4)	2.166(3)	N(4)−C(28)	1.349(4)
O(1)−Al(2)	1.766(3)	N(5)−C(42)	1.377(4)
O(1)−Al(3)	1.798(2)	N(5)−C(36)	1.406(5)
N(1)−C(16)	1.363(4)	C(5)−C(6)	1.344(13)
N(1)−C(10)	1.407(5)	N(6)−C(41)	1.346(4)
Al(2)−N(5)	1.918(3)	N(6)−C(42)	1.349(5)
Al(2)−C(2)	1.932(4)	C(6)−C(7)	1.328(11)
Al(2)−N(2)	1.942(3)	N(7)−C(55)	1.381(4)
N(2)−C(15)	1.347(5)	N(7)−C(49)	1.401(4)
N(2)−C(16)	1.351(5)	C(7)−C(8)	1.387(7)
Al(3)−N(7)	1.886(3)	N(8)−C(55)	1.329(5)
Al(3)−N(3)	1.901(3)	N(8)−C(54)	1.341(5)
O(1)−Al(1)−N(1)	106.13(12)	O(1)−Al(2)−N(5)	99.48(12)
O(1)−Al(1)−C(1)	128.8(2)	O(1)−Al(2)−C(2)	123.5(2)
N(1)−Al(1)−C(1)	124.7(2)	N(5)−Al(2)−C(2)	112.1(2)
O(1)−Al(1)−N(6)	86.93(11)	O(1)−Al(2)−N(2)	103.45(13)
N(1)−Al(1)−N(6)	91.17(13)	N(5)−Al(2)−N(2)	100.61(13)
C(1)−Al(1)−N(6)	96.9(2)	C(2)−Al(2)−N(2)	114.5(2)
O(1)−Al(1)−N(4)	86.12(11)	O(1)−Al(3)−N(7)	108.08(12)
N(1)−Al(1)−N(4)	88.99(13)	O(1)−Al(3)−N(3)	102.09(12)
C(1)−Al(1)−N(4)	88.9(2)	N(7)−Al(3)−N(3)	102.71(13)
N(6)−Al(1)−N(4)	172.82(12)	O(1)−Al(3)−C(3)	108.3(2)
Al(2)−O(1)−Al(3)	128.28(13)	N(7)−Al(3)−C(3)	119.3(2)
Al(2)−O(1)−Al(1)	115.15(12)	N(3)−Al(3)−C(3)	114.9(2)
Al(3)−O(1)−Al(1)	116.27(13)		
Compound **3**			
O(1)−Al(2)	1.759(7)	Al(3)−N(3)	1.894(8)
O(1)−Al(3)	1.796(7)	Al(3)−N(7)	1.905(9)
O(1)−Al(1)	1.823(7)	Al(3)−C(33)	1.933(11)
C(1)−N(8)	1.35(2)	N(3)−C(16)	1.397(14)
Al(1)−N(1)	1.900(10)	N(3)−C(14)	1.41(2)
Al(1)−C(34)	1.946(11)	N(4)−C(16)	1.293(14)
Al(1)−N(6)	2.121(9)	N(4)−C(9)	1.403(14)
Al(1)−N(4)	2.163(9)	N(5)−C(24)	1.394(13)
N(1)−C(30)	1.409(14)	N(5)−C(22)	1.400(13)
N(1)−C(32)	1.410(14)	N(6)−C(24)	1.325(13)
Al(2)−N(5)	1.859(9)	N(6)−C(17)	1.380(14)
Al(2)−C(35)	1.940(11)	C(6)−N(7)	1.34(2)
Al(2)−N(2)	1.942(10)	N(7)−C(8)	1.41(2)
N(2)−C(25)	1.388(14)	N(8)−C(8)	1.28(2)
N(2)−C(32)	1.409(14)		
Al(2)−O(1)−Al(3)	129.1(4)	O(1)−Al(2)−C(35)	119.8(5)
Al(2)−O(1)−Al(1)	114.9(4)	N(5)−Al(2)−C(35)	118.0(4)
Al(3)−O(1)−Al(1)	116.0(4)	O(1)−Al(2)−N(2)	104.6(4)
O(1)−Al(1)−N(1)	108.8(4)	N(5)−Al(2)−N(2)	102.4(4)
O(1)−Al(1)−C(34)	131.4(5)	C(35)−Al(2)−N(2)	108.8(5)
N(1)−Al(1)−C(34)	119.4(5)	C(25)−N(2)−C(32)	110.7(9)
O(1)−Al(1)−N(6)	86.3(3)	C(25)−N(2)−Al(2)	122.3(7)
N(1)−Al(1)−N(6)	90.5(4)	C(32)−N(2)−Al(2)	123.6(7)
C(34)−Al(1)−N(6)	98.3(5)	O(1)−Al(3)−N(3)	98.5(4)
O(1)−Al(1)−N(4)	83.8(3)	O(1)−Al(3)−N(7)	109.1(4)
N(1)−Al(1)−N(4)	90.5(4)	N(3)−Al(3)−N(7)	107.6(4)
C(34)−Al(1)−N(4)	90.0(5)	O(1)−Al(3)−C(33)	115.8(5)
N(6)−Al(1)−N(4)	169.8(3)	N(3)−Al(3)−C(33)	113.1(5)
O(1)−Al(2)−N(5)	101.1(4)	N(7)−Al(3)−C(33)	111.8(5)

The structure of compound **2** is shown in Figure 2. Compound **2** has three aluminum ions sharing one oxo ligand, resulting from the reaction of H_2O with methyl ligands. The oxo ligand is coplanar with the three aluminum ions (O(1) deviates from the plane defined by the three Al atoms by 0.043 Å; the sum of bond angles around O(1) is 359.7°) with Al−O distances ranging from 1.766(3) to 1.818(2) Å. A similar bonding mode of the oxo ligand has been observed in the complexes[9a,9b] $[(CH_3)_2Al(\mu_3\text{-}O)Al(CH_3)_3]_2^{2-}$, $[Al_3(\mu_3\text{-}O)Cl_8]^-$, $[(AlCl_2)(\mu_3\text{-}O)(AlCl_3)]_2^{2-}$, and[9c] $[(^tBu)_2Al]_4(\mu_3\text{-}O)_2$. There are three methyl groups, which are bound to three aluminum centers, respectively, with three similar Al−C bond lengths. The coordination environment around each aluminum center is, however, different. Al(2) and Al(3) are four-coordinate and approximately tetrahedral,

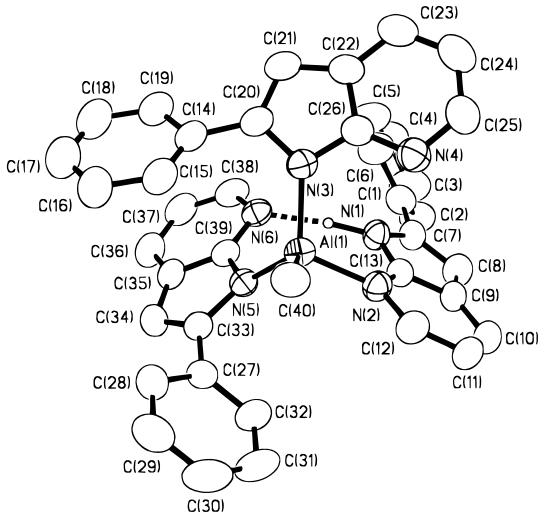


Figure 1. Diagram showing the molecular structure of **1** with 50% ellipsoids and labeling schemes.

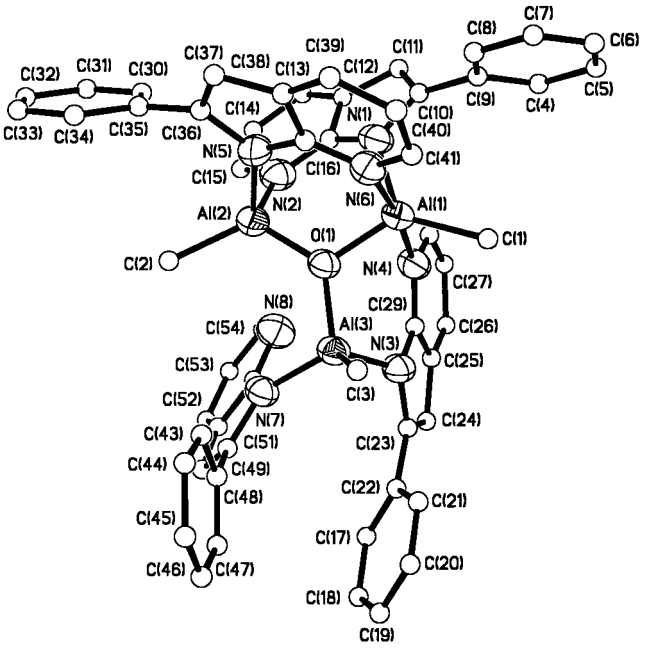
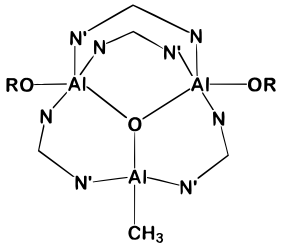


Figure 2. Diagram showing the molecular structure of **2** with 50% ellipsoids and labeling schemes. For clarity, all carbon atoms are shown as ideal spheres.

(9) (a) Atwood, J. L.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 302. (b) Thewalt, U.; Stollmaier, F. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 133. (c) Mason, M. R.; Smith, J. M.; Bott. S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971.

Chart 2. $Al_3(O)(OR)_2(CH_3)(7\text{-azain})_4$



while Al(1) is five-coordinate and approximately trigonal-bipyramidal with two pyridyl nitrogen atoms N(4) and N(6) on the axial positions (N(4)−Al(1)−N(6) = 172.8(1)°). The Al(2) center is coordinated by one carbon, one oxygen, one pyridyl nitrogen, and one indole nitrogen atom, while Al(3) is bound by one carbon, one oxygen, and two indole nitrogen atoms. The Al(1)−N(pyridyl) bond lengths are considerably longer (2.106(3), 2.166(3) Å) than the corresponding ones on Al(2) and Al(3), attributable to the five-coordination and the steric bulkiness around Al(1). The stoichiometry of compound **2** is closely related to that of $Al_3(O)(7\text{-azain})_4(CH_3)(OR)_2$, where R is a terminal hexafluoroisopropoxy ligand.[1] However, in contrast to the symmetric structure (Chart 2) of $Al_3(O)(7\text{-azain})_4(CH_3)(OR)_2$, where only two distinct aluminum environments are present, compound **2** has three distinct aluminum environments. We believe that the asymmetric arrangement of the aluminum centers in **2** is caused by the phenyl substituent on the 7-azaindole, which increases intramolecular nonbonding interactions so substantially that the symmetric structure cannot be achieved (this can be demonstrated readily by a stick and ball molecular model). It is conceivable that the analogous compound $Al_3(O)(7\text{-azain})_4(CH_3)_3$ may have a symmetric structure similar to that of $Al_3(O)(7\text{-azain})_4(CH_3)(OR)_2$, which would be good evidence supporting the notion that the asymmetric structure of **2** is indeed caused by over crowding of the ligands. Unfortunately, this cannot be confirmed because we have not been able to synthesize $Al_3(O)(7\text{-azain})_4(CH_3)_3$ successfully. Again, as observed in **1**, the phenyl portion of the 7-azain-2-Ph ligand in **2** is not coplanar with the 7-azaindole portion, the dihedral angle between these two planes ranging from 42.3 to 59.0°, again attributable to steric interactions. The Al(1)−Al(2), Al(2)−Al(3), and Al(1)−Al(3) separation distances are 3.025(4), 3.207(5), and 3.071(5) Å, respectively. Although Al(2) is four-coordinate, the lone pair of electrons of the noncoordinated pyridyl N(8) atom is oriented toward Al(2) with a separation distance of 3.215(5) Å. Furthermore, N(8) is situated opposite to N(5) atom, with the N(5)−Al(2)···N(8) angle being 169.4°, raising the question of whether Al(2) will remain four-coordinate in solution. Not surprisingly, our NMR investigation on the solution behavior of compound **2** indeed demonstrated unusual dynamic behavior of compound **2** in solution (vide infra).

Synthesis and Crystal Structures of $Al_3(\mu_3\text{-}O)(CH_3)_3(7\text{-azain-2-}CH_3)_4$ (3). Compound **3** was synthesized by a procedure similar to that for compound **2** by reacting $Al(CH_3)_3$ with 2-methyl-7-azaindole in a 3:4 ratio in the presence of water-vapor-saturated nitrogen gas. Compound **3** was fully characterized by elemental, ^1H NMR, and X-ray diffraction analyses. The crystal quality of compound **3** is only marginal. The most serious problems with crystals of **3** are twinning and low diffraction intensity. We collected data for **3** several times by using several different crystals, but the data obtained were similar in quality. The crystal data presented here were from our best effort. Despite the poor quality of the data and refinement, the structure of **3** established by X-ray diffraction analysis is correct. Selected bond lengths and angles of **3** are given in Table 2.

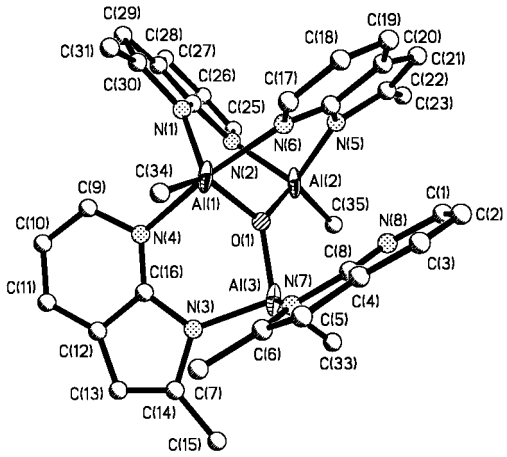


Figure 3. Diagram showing the molecular structure of **3** with 50% ellipsoids and labeling schemes. All atoms except aluminum are shown as ideal spheres.

As shown in Figure 3, the structure of **3** resembles that of **2**. The three Al atoms are bridged by an oxo ligand which is coplanar with the plane defined by the three Al atoms (O(1) is 0.01 Å above the plane; the sum of angles around O(1) is 360°). The variation of Al−O bond lengths in **3** follows the same pattern as that in **2**, i.e., O(1)−Al(2) being the shortest and O(1)−Al(1) being the longest. The Al(1)−Al(2), Al(2)−Al(3), and Al(3)−Al(1) distances are 3.02(1), 3.21(1), and 3.07(1) Å, respectively, also similar to those in **2**. As observed in **2**, the three Al atoms have distinct coordination environments: Al(1), distorted trigonal bipyramidal with two pyridyl nitrogen atoms N(4) and N(6) on the axial positions (N(4)−Al(1)−N(6) = 169.8(3)°); Al(2), tetrahedral with a pyridyl and an indole nitrogen atom; Al(3), tetrahedral with two indole nitrogen atoms. The asymmetric structure of **3** can again be attributed to steric interactions caused by the methyl substituent of the 7-azaindole ligand. The lone pair of electrons of the noncoordinating pyridyl N(8) atom is pointed toward the Al(2) atom, similar to that in **2**. The Al(2)···N(8) distance is, however, much longer (3.99 Å) than that in **2**. In addition, the N(8) atom is situated approximately opposite to N(2) (N(2)−Al(2)···N(8) = 150°), while in **2** N(8) is opposite to N(5). Furthermore, the methyl group (C(33)) on Al(3) is on the opposite side of the methyl group C(34) on Al(1) in **3**, while in **2** these two methyl groups are on the same side. The structural difference between **2** and **3** is most likely caused by steric interactions and packing of the molecules in the crystal lattice. It is very likely that in solution compounds **2** and **3** have a similar structure.

Fluxionality of Compounds 2 and 3 in Solution. As shown in Figures 2 and 3, compounds **2** and **3** exhibit an asymmetric structure, caused by the difference in

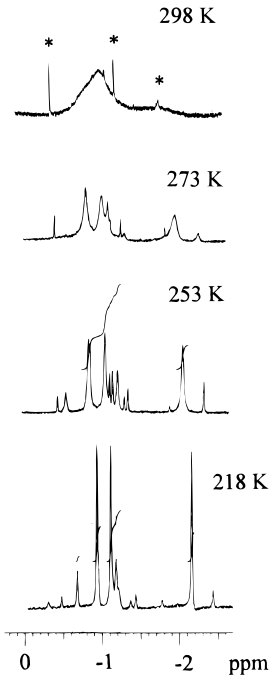


Figure 4. Al−CH_3 region of variable-temperature 1D ^{1}H NMR spectra of compound **2** in $CDCl_3$. The impurity peaks are marked by asterisks.

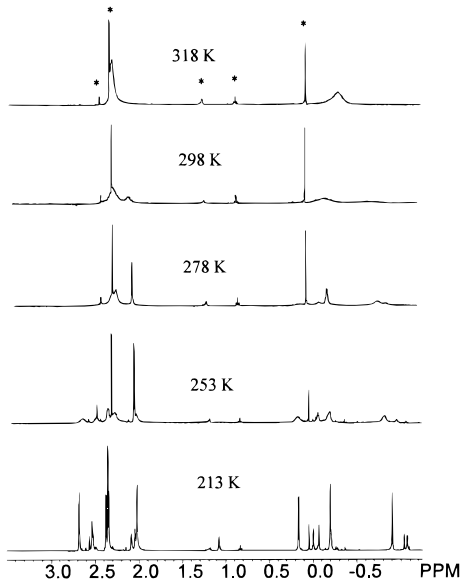


Figure 5. C−CH_3 and Al−CH_3 regions of variable-temperature 1D ^{1}H NMR spectra of compound **3** in $CDCl_3$. The impurity and solvent peaks are marked by asterisks.

coordination environment on Al(1) and Al(2) centers. If the coordinated pyridyl N(4) atom on the Al(1) center were ignored, the Al(1) and Al(2) centers would be very similar (especially in compound **2**). One then must wonder why the two aluminum centers are discriminated by the pyridyl donors and whether the same discrimination exists in solution. To address these questions, we studied the solution behavior of compounds **2** and **3** by ^{1}H NMR spectroscopy. First, we obtained 1D variable-temperature ^{1}H NMR spectra of compounds **2** and **3** over the temperature range 328−213 K. As shown in Figures 4 and 5, compounds **2** and **3** are fluxional in solution. If both compounds retain their solid-state structures in solution, all three methyl groups on the aluminum centers would be different, thus producing three distinct chemical shifts. However, only one broad Al−CH_3 resonance was observed for compounds **2** and **3** at 298 and 308 K, respectively, an indication of the presence of an exchange process. As the temperature decreases, the pattern of chemical shifts in the Al−CH_3 region becomes more complex. At 213 K, three dominant Al−CH_3 resonances were observed for both compounds, which is consistent with the solid-state structure. The four 7-azain-2-CH_3 ligands in compound **3** should have distinct chemical environments, if **3** retains its crystal structure in solution, which should result in four distinct C−CH_3 resonances in the ^{1}H NMR spectra. At 298 K, only two broad resonances of C−CH_3 were observed for compound **3**, which became a broad single resonance at temperatures above 298 K. At 213 K, four dominant C−CH_3 resonances were observed, again consistent with the solid-state structure of **3**. The fact that only one Al−CH_3 and one C−CH_3 resonance (in **3**) were observed above 298 K implies that the dynamic process in solution for compounds **2** and **3** involves exchange of all Al−CH_3 and all 7-azain-2-R ligands, which is very unusual indeed. One important feature in the ^{1}H NMR spectra of **2** and **3** is that at low temperatures, in addition to the dominant resonances, there are additional resonances in both the Al−CH_3 and C−CH_3 (compound **3**) regions. Initially we thought that the minor resonance peaks belong to impurities. However, after several repeated measurements on different batches of samples, we were convinced that these minor peaks are from the samples, not impurities. The fact that these minor peaks disappear at high temperatures further supports that they are not from impurities but belong to the sample. One possible explanation for the minor peaks is that they are resonances of minor isomers of **2** and **3** that are also involved in the dynamic process. The presence of minor peaks is more pronounced in **3** than in **2**.

To further understand the mechanism of the exchange process involved in **2** and **3**, we carried out a ^{1}H 2D EXSY experiment[10] on compound **3** (compound **3** was chosen for 2D EXSY study because it has the C−CH_3 resonance in addition to Al−CH_3 resonance, allowing us to monitor the exchange among 7-azain-2-CH_3 ligands as well). The C−CH_3 region and the Al−CH_3 region of the ^{1}H 2D EXSY spectrum obtained at 243 K are shown in Figures 6 and 7, respectively. Although there are considerable overlaps of peaks in the EXSY spectrum of **3** and some of the cross-peaks are not well resolved due to their broadness, some useful information can be obtained from the spectrum. One important feature in the C−CH_3 region is that cross-peaks are observed between the peak of the major isomer at 2.70 ppm and the peaks of a minor isomer at 1.10 and 2.54 ppm, respectively, an indication of interconversion between minor and major isomers. Further evidence comes from the cross-peaks between the peak of the major isomer at −0.88 ppm and the peaks of a minor isomer at −1.05, −0.06, and 0.00 ppm in the Al−CH_3 region (Figure 7), again consistent with an exchange between minor and major isomers of compound **3** in solution. In both the

(10) (a) Derome, A. E. *Modern NMR Techniques for Chemistry Research*, Pergamon Press: Oxford, U.K., 1987. (b) Collman, J. P.; Hartford, S. T.; Franzen, S.; Eberspacher, T. A.; Shoemaker, R. K.; Woodruff, W. H. *J. Am. Chem. Soc.* **1998**, *120*, 1456.

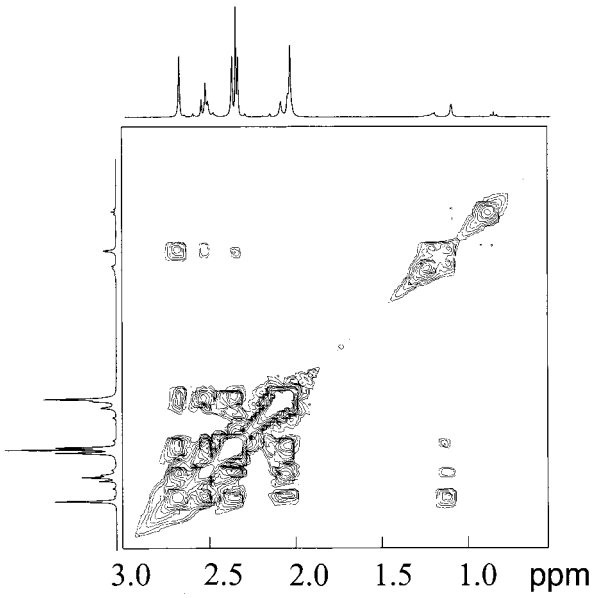


Figure 6. C−CH_3 region of the 2D ^{1}H EXSY spectrum of **3** in $CDCl_3$ at 243 K.

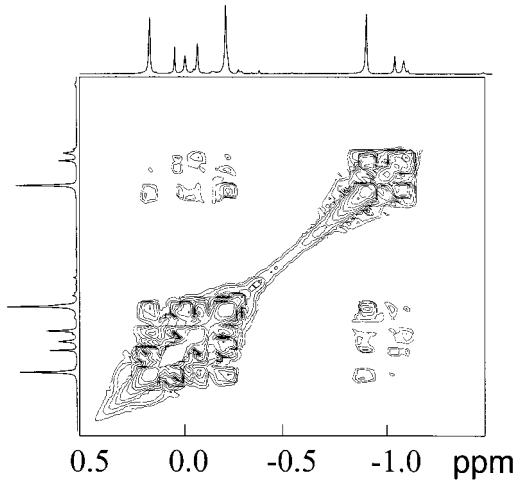
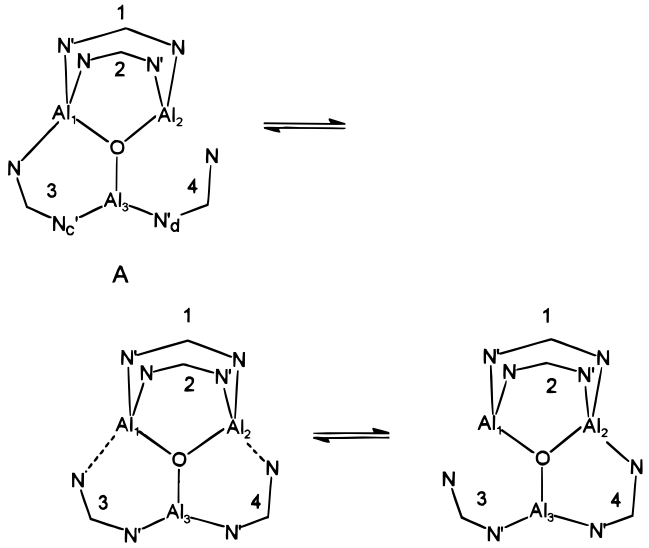


Figure 7. Al−CH_3 region of the 2D ^{1}H EXSY spectrum of **3** in $CDCl_3$ at 243 K.

C−CH_3 and Al−CH_3 regions, there are cross-peaks within the major isomer and cross-peaks within the minor isomers. However, due to the broadness of the peaks, conclusive assignments for all cross-peaks cannot be achieved. On the basis of the 1D and 2D EXSY ^{1}H NMR data, we can therefore conclude that the dynamic process displayed by compounds **2** and **3** involves exchanges among different isomers, as well as within each isomer, and that at 213 K one isomer is dominant.

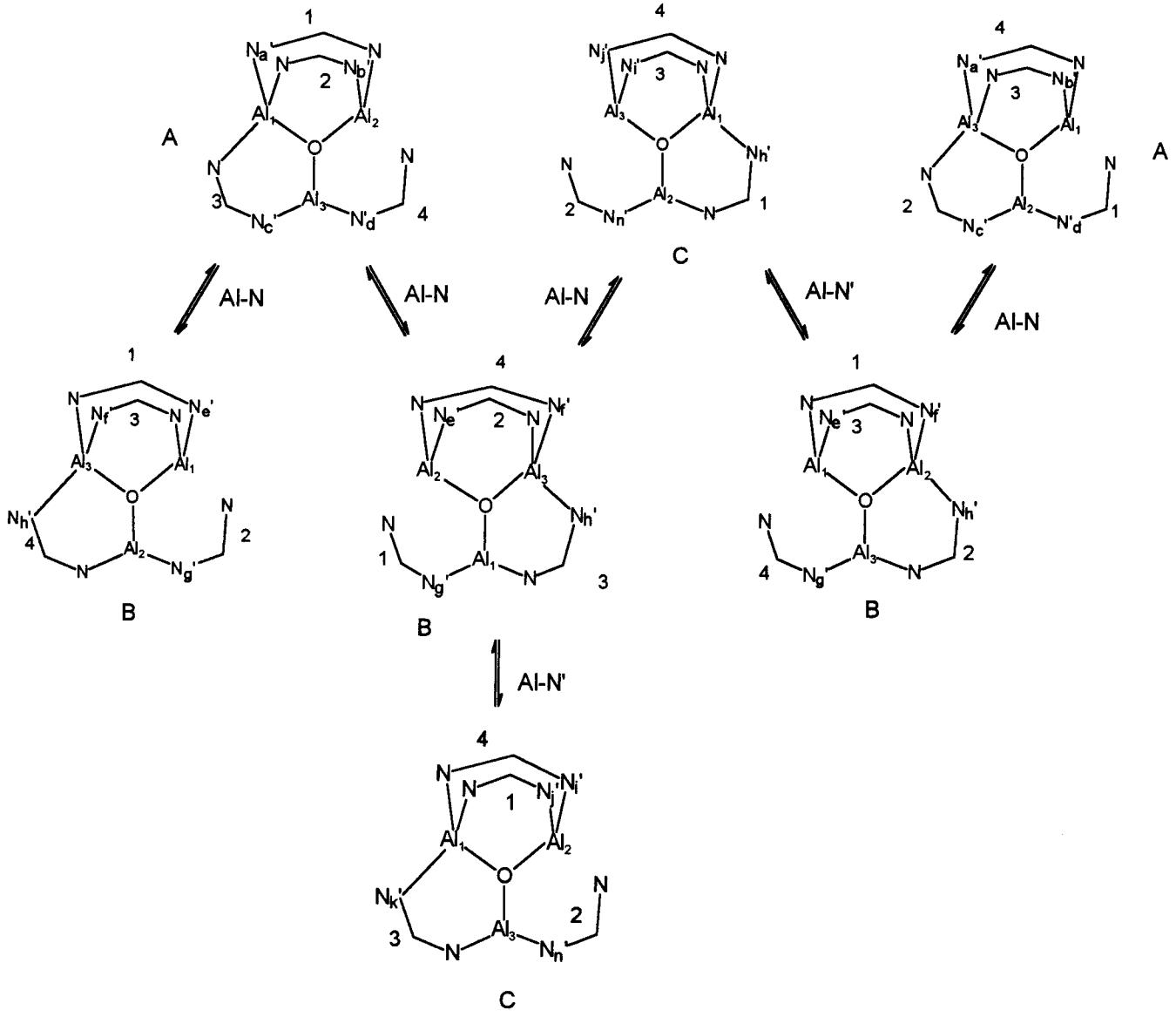
Among many possible isomers for compounds **2** and **3**, the three isomers that we think most likely to exist in solution are shown in Scheme 2 as **A**, **B**, and **C**, where N and N′ represent pyridyl and indole nitrogen atoms, respectively, and the subscript represents each of the distinct C−CH_3 chemical environments. The solid-state structure of compounds **2** and **3** is represented by **A** (the orientation difference of the Al−CH_3 groups in **2** and **3** is ignored to simplify the matter), which we believe is likely the major isomer in solution at 213 K. If all three isomers coexist in solution, one would expect to see at least 12 distinct C−CH_3 chemical shifts and 9 distinct

Scheme 1



Al−CH_3 signals. Compound **2** appears to contain two major isomers in a 6:1 ratio in solution, while the third isomer is only present in trace amount at 218 K. Compound **3** contains at least three isomers in appreciable amounts at 213 K with an approximate ratio of 6:2:1. Conclusive assignment of the observed peaks to the proposed isomers could not be achieved due to the overlap of peaks. One facile exchange process that averages the environment of Al(1) and Al(2), ligands 1 and 2, and ligands 3 and 4 in all isomers, is shown in Scheme 1, where only the forming and breaking of an Al−N(pyridyl) bond is involved. This process does not, however, exchange all aluminum centers or all 7-azain-2-R ligands as implied by the NMR data. To achieve the exchange of all 7-azain-2-R ligands and all aluminum environments within each isomer, additional Al−N or Al−N′ bond breaking and forming must be involved. A possible mechanism that involves either Al−N or Al−N′ bond breaking and forming at each step is given in Scheme 2. Assuming all three isomers are present, Scheme 2 shows that there is no one-step pathway to exchange all Al−CH_3 and all C−CH_3 groups within each isomer. In order for each isomer to achieve exchange with itself, a multistep process must occur where isomer interconversion is part of the process. For example, the intramolecular exchange of isomer **A** would involve first the migration of ligand 2 from Al(1) and Al(2) to Al(2) and Al(3) by breaking and forming an Al−N bond, thus yielding isomer **B**. The subsequent migration of ligand 4 in isomer **B** to Al(3) and Al(1) via breaking and forming an Al−N bond leads to the formation of isomer **C**, which in turn converts to the new isomer **B** via breaking and forming of an Al−N′ bond, thus achieving the intramolecular exchange of isomer **B**. The further conversion of isomer **B** to **A** by breaking and forming an Al−N bond completes the cycle of all Al−CH_3 and C−CH_3 exchanges in isomer **A**. The mechanism proposed in Scheme 2 is of course not unique but is perhaps the most facile one, since each step involves breaking and forming of only one Al−N or Al−N′ bond. Our understanding of the exchange in compounds **2** and **3** is by no means conclusive, due to the complexity of the system. Dynamic exchanges have been frequently observed in dinuclear organoaluminum compounds,

Scheme 2



where trans and cis isomerizations are often involved.[11] However, the highly fluxional behavior of compounds **2** and **3** is rare in that the process involves exchange of all ligand environments and all aluminum environments.

Luminescent Properties of Compounds 1−3. Blue luminescence is the other important feature of (7-azaindole)aluminum complexes. We have observed that aluminum complexes containing the simple 7-azaindole ligand typically emit in the 420−440 nm region when excited by UV. Compounds **2** and **3** demonstrated that the introduction of a substituent at the 2-position has a dramatic effect on the structure. We have established previously that the blue emission of aluminum compounds containing nonsubstituted 7-azaindole ligand is due to a $\pi^* \rightarrow \pi^*$ transition localized on the 7-azaindole ligand.[1] Because a methyl group is an electron-donating substituent while a phenyl group is an electron-accepting[12] and sterically demanding group, one could anticipate they may have quite different effects on the electronic properties of the complex, in particular, the emission energy. We therefore examined the luminescence of compounds **1**−**3** by measuring their excitation and emission spectra. The data are shown in Figure 8. When irradiated by UV, both compounds **1** and **2** have weak blue luminescence while compound **3** exhibits a blue emission with a brightness comparable to that of $Al_3(O)(7\text{-azain})_4(CH_3)(OR)_2$ (quantum yield 0.31, relative to 9,10-diphenylanthracene). The relatively weak emission of compounds **1** and **2** could be mostly attributed to the phenyl substituent, which increases the thermal vibrations of the emitting 7-azaindole ligand substantially, thus reducing the emission efficiency, in comparison to that of the nonsubstituted 7-azaindole. The other factor that may contribute to the weak emission of **1** and **2** is the interference of π orbitals on the phenyl

(11) (a) Choquette, D. M.; Timm, M. J.; Hobbs, J. L.; Rahim, M. M.; Ahmed, K. J.; Planalp, R. P. *Organometallics* **1992**, *11*, 529. (b) Amirkhalili, S.; Hitchcock, P. B.; Jenkins, A. D.; Nyathi, J. Z.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1981**, 377. (c) Gosling, K.; Smith, J. D.; Wharmby, D. H. W. *J. Chem. Soc. A.* **1969**, 1738. (d) Trepanier, S. J.; Wang, S. *Organometallics* **1996**, *15*, 760. (e) Sierra, M. J.; de Mel, S. J.; Oliver, J. P. *Organometallics* **1989**, *8*, 2486.

(12) Dean, J. A. *Lange's Handbook of Chemistry*, 3rd ed.; McGraw-Hill: New York, 1985.

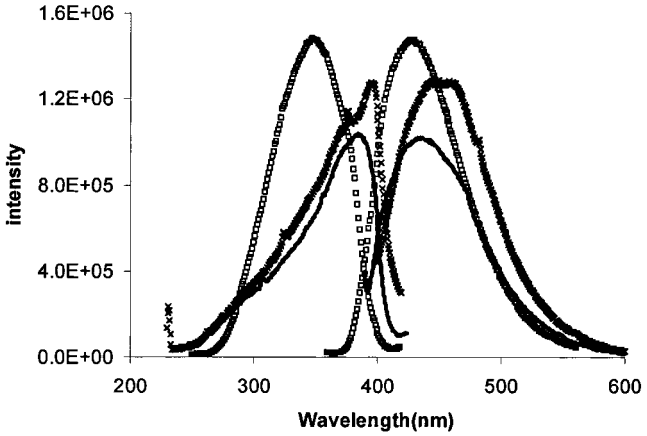


Figure 8. Excitation and emission spectra of **1** (×), **2** (—), and **3** (□).

ring, which could effectively quench the emission by intercepting the electrons returning from the excited state (7-azaindole → phenyl charge transfer). The fact that the excitation and emission bands of compounds **1** and **2** are much broader than those of **3** and nonsubstituted 7-azaindole aluminum compounds, as shown in Figure 8, appears to further support the presence of phenyl interference on the excitation and emission spectra of 7-azaindole. The emission energy ($\lambda_{max} = 431$ nm) of compound **3** is essentially the same as that of $Al_3(O)(7\text{-azain})_4(CH_3)(OR)_2$ ($\lambda_{max} = 430$ nm), indicating that the methyl substituent at the 2-position has little effect on the emission energy of coordinated 7-azaindole. The emission energy of compound **2** ($\lambda_{max} = 443$ nm) has shifted considerably toward a longer wavelength, in comparison to that[1] of $Al_3(O)(7\text{-azain})_4(CH_3)(OR)_2$, which must be caused by the electron-accepting nature of the phenyl substituent. VanSlyke and co-workers have observed a similar effect by introducing substituents at the 2-position (the pyridyl ring) of the emitting 8-hydroxyquinoline ligand in aluminum complexes.[3]

Conclusion

The introduction of a methyl or phenyl group at the 2-position of the 7-azaindole ligand increases the steric bulkiness of the ligand and leads to the formation of two new and asymmetric trinuclear aluminum complexes that are highly fluxional in solution. The unusually complicated dynamic exchange process in the two trinuclear complexes is likely caused by an intramolecular migration of the coordinated 2-R-7-azaindole. There is no significant difference in luminescence between the nonsubstituted 7-azaindole aluminum complex and the 2-methyl-substituted one. The 2-phenyl-substituted 7-azaindole complex appears to have a weaker emission at a wavelength longer than that of the nonsubstituted 7-azaindole complex, attributable to both electronic and steric factors.

Acknowledgment. We are grateful to Professor Stephen Brown and his students for recording the emission and excitation spectra. We thank the NSERC of Canada for financial support. G.W. wishes to thank Queen's University for a Faculty Initiation Grant.

Supporting Information Available: Tables giving X-ray crystallographic data, atomic coordinates, bond lengths and angles, hydrogen parameters, and anisotropic thermal parameters and diagrams showing the complete molecules and solvent molecules of compounds **2** and **3** and a figure giving the complete 2D EXSY spectrum of compound **3** obtained at 243 K (27 pages). Ordering information is given on any current masthead page.

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