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Blue Luminescent Organoaluminum Compounds: $Al_2(CH_3)_4$(7-azain)$_2$, $Al_2(CH_3)_2$(7-azain)$_4$, $Al_2(CH_3)(OCH(CF_3)_2)_3$(7-azain)$_2$, $Al_2(\mu$-$OCH(CF_3)_2)(CH_3)$(7-azain)$_2((OCH(CF_3)_2)_2$, $Al_3(\mu_3$-$O)(CH_3)$(7-azain)$_4(OCH(CF_3)_2)_2$, and $Al_4(\mu_3$-$O)_2$(7-azain)$_6(OCH(CF_3)_2)_2$ (7-azain = Deprotonated 7-Azaindole)

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The reactions of 7-azaindole with $Al(CH_3)_3$ have been investigated. Two new 7-azaindole complexes, $Al_2(CH_3)_4$(7-azain)$_2$ (**1**) and $Al_2(CH_3)_2$(7-azain)$_4$ (**2**) have been isolated and structurally characterized. Both complexes display a blue luminescence upon irradiation by UV light. The introduction of alcohol and water into the reaction of 7-azaindole with $Al(CH_3)_3$ resulted in the formation of several dinuclear and polynuclear complexes which also emit in the blue region. The crystal structures of three new complexes from these reactions, $Al_2(\mu$-$OCH(CF_3)_2)(CH_3)$(7-azain)$_2(OCH(CF_3)_2)_2$ (**3**), $Al_3(\mu_3$-$O)(CH_3)$(7-azain)$_4(OCH(CF_3)_2)_2$ (**4**), and $Al_4(\mu_3$-$O)_2$(7-azain)$_6(OCH(CF_3)_2)_2$ (**5**), have been determined by X-ray diffraction analyses. The 7-azaindole ligand in compounds **1**−**5** has the same bonding mode, i.e., bridging two aluminum ions. The quantum yields for compounds **2** and **4** were determined to be 0.54 and 0.31, respectively, relative to that of 9,10-diphenylanthracene in cyclohexane. The emission lifetime for these compounds is in the order of 10−100 ns. Molecular orbital calculations using Gaussian 94 methods on the neutral free ligand (7-azainH), the deprotonated ligand (7-azain$^-$), and compound **1** were performed, which revealed that the aluminum ions in the complexes play a key role in stabilizing the ligand and promoting the blue luminescence.

Introduction

The chemistry of organoaluminum amido and imido compounds has attracted much attention due to not only their interesting structural and chemical properties but also their applications in materials science.[1] The application of aluminum amido and imido compounds in aluminum nitride has been the primary focus of much of the previous work. During our investigation of polynuclear organoaluminum complexes containing polydentate aromatic amido or imido ligands,[2] we discovered that some of our aluminum compounds display interesting luminescence, ranging from red to blue, the most interesting of which is the blue luminescence. Blue luminescent compounds are among the most sought-after materials by scientists around the world because of their potential applications in electroluminescent (EL) displays.[3,4] Unlike the other two key components in EL displays, red and green, which are readily available, useful blue luminescent materials for EL displays are still scarce. Because the electronic transitions involved in electroluminescence correspond to the same transitions in photoluminescence, the prerequisite for a compound to have electroluminescence is that it has to be photoluminescent in the same energy region.[3,4] Most

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of the previously reported blue luminescent compounds are aromatic organic molecules or polymers.[4] Blue luminescent materials based on inorganic semiconductors are known, but their application is limited because of their processing difficulty.[3] Blue luminescent inorganic and organometallic complexes are rather rare and have been limited to 8-hydroxyquinoline- or azomethine-based complexes where either aluminum or zinc ions are involved.[5] In order for a compound to emit in the blue region, it has to be excited in the UV region, therefore requiring the materials to be colorless. The advantage of employing an aluminum ion in the complex is at least two-fold. First, the Al(III) ion is colorless and contains no d electrons, thus not interfering with the blue luminescence. Second, the Al(III) ion has versatile coordination geometries, ranging from three-coordinate to six-coordinate, therefore capable of accommodating various ligands.[1,2,6] Third, as a hard Lewis acid, the Al(III) ion binds well to hard donor atoms such as nitrogen and oxygen atoms, thus stabilizing the ligand.[6] For these reasons, we initiated series studies on the syntheses and structures of blue luminescent organoaluminum compounds. Of the ligands examined by our group, we have found that di-2-pyridylamine and 7-azaindole ligands are the best in producing blue luminescent aluminum compounds. Some of the preliminary work has been described in a communication.[7] In this report, the systematic syntheses of various blue luminescent compounds and their crystal structures and luminescent properties in addition to theoretical studies on the origin of the blue luminescence of the 7-azaindole-based aluminum compounds are described. The results of our comprehensive study on blue luminescent aluminum compounds based on di-2-pyridylamine will be described in a subsequent paper.

Experimental Section

All reactions were carried out under a nitrogen atmosphere using either standard Schlenk line techniques or the inert atmosphere drybox. $Al(CH_3)_3$ and 7-azaindole were purchased from Aldrich Chemical Co. Solvents were freshly distilled from the appropriate drying agents under nitrogen. ^1H NMR were recorded on either a Bruker AM 400 or a Bruker ACF 200 spectrometer. Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia. Excitation and emission spectra were recorded on Photon Technologies International QM1 spectrometer. The quantum yield and emission lifetime were measured on a Time Master spectrometer of Photon Technologies International. The time-resolved measurements were recorded with the single-photon counting method. NaX zeolite was used to record the lamp profile. The sample was placed at 45° to both the excitation and emission beams.

Synthesis of $Al_2(CH_3)_4$(7-azain)$_2$ (1). A 0.50 mmol amount of 7-azaindole was dissolved in 10 mL of toluene under nitrogen. A 0.50 mmol amount of $Al(CH_3)_3$ (0.25 mL of 2 M $Al(CH_3)_3$ solution in hexane) was added to the solution at 23 °C. The mixture was stirred for 1.5 h. The solution was concentrated to about 5 mL. After a few days standing at 23 °C, the product, $Al_2(CH_3)_4$(7-azain)$_2$, was isolated as colorless crystals in 60% yield. ^1H NMR (δ, toluene-d_8, ppm, 293 K): -0.20 (s, 6H, CH_3), 6.39 (d, 1H, 7-azain), 6.48 (t, 1H, 7-azain), 7.50 (m, 1H, 7-azain), 7.60 (m, 1H, 7-azain), 8.00 (m, 1H, 7-azain). Anal. Calcd for **1**: C, 62.06; H, 6.36; N, 16.08. Found: C, 61.91; H, 6.36; N, 16.08.

Synthesis of $Al_2(CH_3)_2$(7-azain)$_4$ (2). A 200 mg (1.70 mmol) amount of 7-azaindole in 8 mL of toluene was reacted with 423 mL (0.846 mmol) of $Al(CH_3)_3$ (2.0 M in hexane) at 23 °C under nitrogen. The reaction mixture was stirred for 3 h. The volume of the solution was reduced to approximate 2 mL by vacuum. A 2 mL amount of hexane was added to crystallize the product. After a few days standing at 23 °C, colorless crystals of compound **2** were obtained in 62% yield. ^1H NMR (δ, $CDCl_3$, ppm, 293 K): 0.64 (s, 3H, CH_3), 6.20 (m, 2H, 7-azain), 6.75 (m, 2H, 7-azain), 7.65 (m, 4H, 7-azain), 8.20 (m, 2H, 7-azain). Anal. Calcd for $C_{30}H_{26}N_8Al_2$: C, 65.22; H, 4.71; N, 20.29. Found: C, 65.05; H, 4.74; N, 20.22.

Synthesis of $Al_2(\mu\text{-}OCH(CF_3)_2)(CH_3)$(7-azain)$_2(OCH(CF_3)_2)_2$ (3). A 200 mg (1.70 mmol) amount of 7-azaindole in 8 mL of toluene was reacted with 847 mL (1.70 mmol) of $Al(CH_3)_3$ (2.0 M in hexane) at 23 °C under nitrogen for 1 h. A 386 mg (2.30 mmol) amount of hexafluoro-2-propanol in 2 mL of toluene was added to the reaction mixture. This mixture was stirred for additional 3 h at 23 °C. The volume of the solution was then concentrated to about 2 mL by vacuum. After several days standing at 23 °C, colorless crystals of **3** were obtained in 65% yield. ^1H NMR (δ, $CDCl_3$, ppm, 293 K): -0.11 (s, 3H, CH_3), 4.48 (br, 1H, CH), 4.55 (m, br, 1H, CH, $^3J_{HF} = 6.0$ Hz), 6.34 (sept br, 1H, CH, $^3J_{HF} = 7.2$ Hz), 6.74 (m, 2H, 7-azain), 7.30 (m, 2H, 7-azain), 7.44 (d, 1H, 7-azain), 7.84 (m, 1H, 7-azain), 8.17 (d, 1H, 7-azain), 8.24 (d, 1H, 7-azain), 8.33 (m, 2H, 7-azain). Anal. Calcd for **3**, $C_{24}H_{16}N_4O_3F_{18}Al_2$: C, 35.80; H, 1.99; N, 6.96. Found: C, 35.51; H, 2.06; N, 7.03. After the separation of compound **3** from the solution, the minor product, $Al_2(O)(CH_3)_2$(7-azain)$_2$ (**6**), was isolated in low yield (<10%). ^1H NMR (δ, $CDCl_3$, ppm, 293 K): -0.10 (s, 6H, CH_3), 6.49 (d, 2H, 7-azain), 7.04 (m, 2H, 7-azain), 7.49 (d, 2H, 7-azain), 8.06 (m, 2H, 7-azain), 8.19 (m, 2H, 7-azain). Anal. Calcd for **6**, $C_{16}H_{16}N_4OAl_2$: C, 57.05; H, 4.73; N, 15.98. Found: C, 57.48; H, 4.73; N, 16.76.

Synthesis of $Al_3(\mu_3\text{-}O)(CH_3)$(7-azain)$_4(OCH(CF_3)_2)_2$ (4). A 200 mg (1.70 mmol) amount of 7-azaindole in 7 mL of toluene was reacted with 0.423 mL (0.85 mmol) of $Al(CH_3)_3$ (2.0 M in hexane) at 23 °C under nitrogen for 3 h. A 142 mg amount of hexafluoro-2-propanol (0.85 mmol) in 3 mL of toluene was added. The mixture was stirred for another 3 h and concentrated to about 2 mL by vacuum. A 2 mL amount of THF and 1 mL of hexane were added to the solution to crystallize the product. After 2 days, colorless crystals of **4** were obtained in 60% yield. ^1H NMR for **4** (δ, $CDCl_3$, ppm, 25 °C): -0.31 (s, 3H, CH_3), 4.57 (m, 2H, CH), 6.30−8.60 (m, 20H, 7-azain). Anal. Calcd for the vacuum-dried THF-free sample, $C_{35}H_{25}N_8O_3F_{12}Al_3$: C, 45.91; H, 2.73; N, 12.24. Found: C, 46.28; H, 3.28; N, 11.51.

Synthesis of $Al_4(\mu_3\text{-}O)_2$(7-azain)$_6(OCH(CF_3)_2)_2$ (5). A 400 mg (3.40 mmol) amount of 7-azaindole in 10 mL of toluene was reacted with 1.13 mL (2.26 mmol) of $Al(CH_3)_3$ (2.0 M in toluene) at 23 °C under nitrogen for 3 h. To the solution, 30 mg of H_2O (1.67 mmol) mixed with 120 mL of hexafluoro-2-propanol (1.17 mmol) was added. The mixture was stirred for another 2 h and concentrated to about 3 mL by vacuum. A 1 mL amount of THF and 1 mL of hexane were added to the solution to crystallize the product. After a few days, colorless crystals of **5** were obtained in 26% yield (200 mg, 0.147 mmol). ^1H NMR for **5** (δ, $CDCl_3$, ppm, 25 °C): 4.52 (br, 2H, CH), 5.50 (d, 4H, 7-azain), 5.64 (d, 4H, 7-azain), 6.52 (br, 4H, 7-azain),

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Table 1. Crystallographic Data

compound	**1**	**2**	**3**	**4**	**5**
formula	$C_{18}H_{22}N_4Al_2$	$C_{30}H_{26}Al_2N_8$	$C_{24}H_{16}N_4O_3F_{18}Al_2$	$C_{39}H_{33}N_8O_4F_{12}Al_3$	$C_{48}H_{32}N_{12}O_4F_{12}Al_4/2C_7H_8$
fw	348.36	552.55	804.38	986.68	1361.06
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/m$	$Pna2_1$
a (Å)	9.145(2)	8.953(2)	9.847(2)	8.429(6)	15.864(4)
b (Å)	15.04(3)	9.179(2)	10.171(4)	20.464(8)	13.486(3)
c (Å)	7.2044(14)	9.836(2)	17.012(13)	12.799(4)	28.945(5)
α (deg)	99.70(3)	65.48(3)	76.75(6)	90	90
β (deg)	102.95(3)	69.13(3)	77.32(3)	91.22(4)	90
γ (deg)	98.54(3)	89.65(3)	81.51(3)	90	90
V (Å^3)	933.8(3)	677.6(2)	1609.5(14)	2207(2)	6193(2)
Z	2	1	2	2	4
D_c (g cm^{-3})	1.24	1.35	1.66	1.48	1.46
T (°C)	23	23	23	23	23
radiation, λ (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
μ (cm^{-1})	1.62	1.44	2.29	1.87	1.71
$2\theta_{max}$ (deg)	50	45	45	45	50.1
no. of reflns measd	2954	1810	4428	3121	5511
no. of reflns used	2717	1679	4139	2899	5497
no. of variables	218	173	460	312	767
largest shift/esd in final cycle	0.00	0.00	0.00	0.00	0.00
largest electron density peak (e$^-$/Å^3)	0.54	0.39	1.08	0.33	1.18
final R [$I > 2\sigma(I)$]	R1 = 0.0722 wR2 = 0.1788	R1 = 0.0666 wR2 = 0.1910	R1 = 0.0806 wR2 = 0.2154	R1 = 0.0918 wR2 = 0.1946	R1 = 0.0799 wR2 = 0.1996
R (all data)	R1 = 0.0912 wR2 = 0.2189	R1 = 0.0750 wR2 = 0.2110	R1 = 0.1178 wR2 = 0.2614	R1 = 0.2251 wR2 = 0.2931	R1 = 0.1232 wR2 = 0.2501
goodness-of-fit on F^2	1.58	1.11	1.10	1.10	1.09

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

6.87 (m, 4H, 7-azain), 6.94 (d, 2H, 7-azain), 7.72 (m, 4H, 7-azain), 8.13 (m, 4H, 7-azain), 8.29 (m, 2H, 7-azain), 8.62 (d, 2H, 7-azain). Anal. Calcd for the vacuum-dried sample, $C_{48}H_{32}N_{12}O_4F_{12}Al_4$: C, 48.98; H, 2.72; N, 14.28. Found: C, 50.55; H, 3.25; N, 13.17. The poor CHN agreement with the calculated value is due to the incomplete removal of the toluene solvent molecules in the crystal lattice, despite the fact that sample was repeatedly dried in a vacuum. The calculated values for $C_{48}H_{32}N_{12}O_4F_{12}Al_4 \cdot 0.6$ toluene (C, 50.88; H, 2.98; N, 13.64) agree well with the experimental values.

X-ray Diffraction Analyses. All crystals were obtained either from concentrated toluene solutions or from the solutions of toluene/hexane. The crystals were sealed in glass capillaries under nitrogen. The data for **1** were collected on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation, operated at 50 kV and 35 mA, while the data for the remaining crystals were collected on a Siemens P4 single-crystal diffractometer with graphite-monochromated Mo Kα radiation, operated at 50 kV and 40 mA. All data were collected at 23 °C. The data for **1** and **5** were collected over $2\theta = 3-50°$, while the data for **2**−**4** were collected over $2\theta = 3-45°$. Three standard reflections were measured every 197 reflections. No significant decay was observed for all samples. Data were processed on a Pentium PC using Siemens SHELX-TL software package (version 5.0). The data were corrected for Lorentz and polarization effects. Neutral atom scattering factors were taken from Cromer and Waber.[8] The crystals of **1**−**3** belong to the triclinic space group $P\bar{1}$, while the crystals of **4** and **5** belong to the monoclinic and orthorhombic crystal system, respectively. The systematic absences of **4** are consistent with both $P2_1$ and $P2_1/m$, while the systematic absences of **5** agree with both $Pna2_1$ and $Pnma$. On the basis of the statistical analysis of the data and consideration of the symmetry of the molecule, the $P2_1/m$ and $Pna2_1$ space groups were chosen for **4** and **5**, respectively. The successful structural solution and refinement confirmed the correctness of these choices. In the crystal lattice of **4**, there is a disordered THF solvent molecule (one THF per molecule of **4**), which was modeled and refined successfully. All four 7-azaindole ligands in compound **3** are disordered. The disordered sites can be considered as related by a mirror plane reflection. The occupancy factor for each site was found to be 50%. A similar disorder was also observed for the two 7-azaindole ligands bridging Al(1) and Al(1′) in **4**. The crystals of **4** suitable for X-ray diffraction analysis are difficult to grow and display some degree of twinning, which, along with the disorder of the THF and the 7-azaindole ligands, could account for the relatively poor quality of the structural data of **4**. In the crystal lattice of **5**, there are two toluene solvent molecules per molecule of **5** that were refined successfully. There are considerable disorders by some of the CF_3 groups in **5**. One of the CF_3 groups which displays a 2-fold rotational disorder was modeled and refined successfully. Due to the limitation of data, some of the carbon atoms in **5** were refined isotropically while all other non-hydrogen atoms were refined anisotropically. The positions for all hydrogen atoms except those attached to the disordered carbon atoms were calculated and their contributions in the structural factor calculation were included. All non-hydrogen atoms in **1** and **3** were refined anisotropically. Aluminum, nitrogen, and some of the nondisordered carbon atoms in **2** were refined anisotropically. Aluminum, oxygen, fluorine, nitrogen, and some of the nondisordered carbon atoms in **4** were refined anisotropically. The crystallographic data for compounds **1**−**5** are given in Table 1.

Results and Discussion

Syntheses and Structures of $Al_2(CH_3)_4$(7-azain)$_2$ (1) and $Al_2(CH_3)_2$(7-azain)$_4$ (2). The reaction of $Al(CH_3)_3$ with 7-azaindole in a 1:1 ratio in toluene yielded compound **1** in good yield. When the ratio of $Al(CH_3)_3$ and 7-azaindole was changed to 1:2, compound **2** was obtained in good yield. Compound **1** is highly unstable when exposed to air in solution and the solid state, while compound **2** is unstable in solution but stable for a few hours in the solid state upon exposure to air. Compound **1** can be sublimed readily at ~190−200 °C and 0.07 mmHg to give a uniform film, while compound **2** became liquid at ~200 °C and 0.06 mmHg. It may be possible to sublime compound **2** under higher vacuum (pressure

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

Compound **1**							
Al(1)−N(2)	1.942(8)	Al(1)−C(1)	1.952(8)	Al(1)−N(1A)	1.976(8)	Al(2)−N(4A)	1.929(8)
Al(1)−C(2)	1.960(10)	Al(2)−C(10)	1.991(9)	Al(2)−N(3)	1.955(9)	Al(2)−C(11)	1.976(9)
N(2)−Al(1)−C(1)	106.3(4)	N(2)−Al(1)−N(1A)	114.0(3)	N(2)−Al(1)−C(2)	107.0(4)	N(3)−Al(2)−C(11)	106.5(4)
C(1)−Al(1)−C(2)	118.8(5)	C(2)−Al(1)−N(1A)	104.5(4)	N(4A)−Al(2)−C(11)	105.7(4)	N(3)−Al(2)−C(10)	105.5(4)
C(1)−Al(1)−N(1A)	106.6(4)	N(4A)−Al(2)−N(3)	113.4(3)	N(4A)−Al(2)−C(10)	107.6(4)	C(11)−Al(2)−C(10)	118.3(5)
Compound **2**							
Al(1)−C(15)	1.978(5)	Al(1)−N(4A)	2.010(4)	Al(1)−N(1)	1.998(3)	Al(1)−N(2A)	2.013(4)
Al(1)−N(3)	2.006(4)						
C(15)−Al(1)−N(1)	103.3(2)	N(3)−Al(1)−N(4A)	150.3(2)	C(15)−Al(1)−N(4A)	106.0(2)	N(3)−Al(1)−N(2A)	85.7(2)
C(15)−Al(1)−N(3)	103.6(2)	C(15)−Al(1)−N(2A)	105.9(2)	N(1)−Al(1)−N(4A)	86.27(13)	N(4A)−Al(1)−N(2A)	83.5(2)
N(1)−Al(1)−N(3)	89.91(14)	N(1)−Al(1)−N(2A)	150.8(2)				
Compound **3**							
Al(1)−O(3)	1.736(4)	O(2)−C(18)	1.400(8)	Al(1)−N(1)	1.935(6)	Al(2)−N(4)	1.891(6)
Al(1)−O(1)	1.765(4)	O(2)−Al(2)	1.790(5)	Al(1)−O(2)	2.288(5)	Al(2)−C(24)	1.924(8)
Al(1)−N(3)	1.896(5)	N(2)−Al(2)	1.864(7)	O(1)−C(21)	1.331(8)	O(3)−C(15)	1.369(8)
O(3)−Al(1)−O(1)	97.2(2)	C(18)−O(2)−Al(2)	131.0(4)	O(3)−Al(1)−O(2)	83.4(2)	O(2)−Al(2)−C(24)	126.6(4)
O(3)−Al(1)−N(3)	116.8(2)	C(18)−O(2)−Al(1)	117.6(4)	O(1)−Al(1)−O(2)	177.5(2)	N(2)−Al(2)−C(24)	111.2(4)
O(1)−Al(1)−N(3)	97.2(2)	Al(2)−O(2)−Al(1)	111.0(2)	N(3)−Al(1)−O(2)	84.6(2)	N(4)−Al(2)−C(24)	110.8(3)
O(3)−Al(1)−N(1)	115.0(2)	O(2)−Al(2)−N(2)	100.2(2)	N(1)−Al(1)−O(2)	81.8(2)	C(15)−O(3)−Al(1)	130.9(4)
O(1)−Al(1)−N(1)	95.8(2)	O(2)−Al(2)−N(4)	99.5(2)	C(21)−O(1)−Al(1)	147.5(5)		
N(3)−Al(1)−N(1)	124.1(2)	N(2)−Al(2)−N(4)	106.5(3)				
Compound **4**							
Al(1)−O(1)	1.711(7)	Al(2)−C(23)	1.83(2)	Al(1)−N(1)	2.007(8)	O(3)−C(27)	1.70(5)
Al(1)−O(2)	1.784(5)	Al(2)−N(4)	1.868(9)	Al(1)−N(3)	2.092(9)	O(1)−C(20)	1.347(11)
Al(1)−N(2)	1.942(9)	O(3)−C(24)	1.29(5)	Al(2)−O(2)	1.798(8)		
C(20)−O(1)−Al(1)	146.0(7)	N(2)−Al(1)−N(3)	90.8(4)	O(2)−Al(1)−N(1)	93.0(4)	N(4)−Al(2)−N(4A)	106.1(6)
O(1)−Al(1)−O(2)	129.2(4)	N(1)−Al(1)−N(3)	176.1(4)	N(2)−Al(1)−N(1)	88.7(3)	Al(1A)−O(2)−Al(1)	117.7(5)
O(1)−Al(1)−N(2)	121.6(4)	O(2)−Al(2)−C(23)	121.3(6)	O(1)−Al(1)−N(3)	88.0(3)	Al(1)−O(2)−Al(2)	121.0(2)
O(2)−Al(1)−N(2)	109.1(4)	O(2)−Al(2)−N(4)	101.3(3)	O(2)−Al(1)−N(3)	90.8(4)		
O(1)−Al(1)−N(1)	89.0(3)	C(23)−Al(2)−N(4)	112.6(4)				
Compound **5**							
Al(1)−O(2)	1.775(7)	O(2)−Al(4)	1.844(8)	O(1)−Al(4)	1.757(7)	O(3)−C(43)	1.28(2)
Al(1)−O(1)	1.844(9)	Al(3)−O(3)	1.798(9)	O(1)−Al(2)	1.765(9)	Al(4)−N(10)	1.930(9)
Al(1)−N(4)	1.931(9)	Al(3)−N(12)	1.894(10)	N(1)−Al(2)	2.020(10)	Al(4)−N(6)	1.944(8)
Al(1)−N(2)	1.928(10)	Al(3)−N(9)	2.016(9)	Al(2)−O(4)	1.776(9)	Al(4)−N(7)	2.055(11)
Al(1)−N(11)	2.026(10)	Al(3)−N(5)	2.049(11)	Al(2)−N(8)	1.895(10)	O(4)−C(46)	1.37(2)
Al(2)−N(3)	2.003(12)	O(2)−Al(3)	1.762(8)				
O(2)−Al(1)−O(1)	84.3(3)	Al(1)−O(2)−Al(4)	95.1(4)	Al(2)−O(1)−Al(1)	124.1(4)	O(1)−Al(4)−O(2)	84.8(3)
O(2)−Al(1)−N(4)	115.6(4)	O(2)−Al(3)−O(3)	165.0(4)	O(1)−Al(2)−O(4)	163.5(4)	O(1)−Al(4)−N(10)	117.3(4)
O(1)−Al(1)−N(4)	90.0(4)	O(2)−Al(3)−N(12)	99.2(4)	O(1)−Al(2)−N(8)	99.0(4)	O(2)−Al(4)−N(10)	89.8(4)
O(2)−Al(1)−N(2)	116.2(4)	O(3)−Al(3)−N(12)	95.8(5)	O(4)−Al(2)−N(8)	97.5(5)	O(1)−Al(4)−N(6)	115.6(4)
O(1)−Al(1)−N(2)	90.6(4)	O(2)−Al(3)−N(9)	87.1(4)	O(1)−Al(2)−N(3)	86.4(4)	O(2)−Al(4)−N(6)	89.9(4)
N(4)−Al(1)−N(2)	127.9(4)	O(3)−Al(3)−N(9)	88.6(4)	O(4)−Al(2)−N(3)	88.4(4)	N(10)−Al(4)−N(6)	126.8(4)
O(2)−Al(1)−N(11)	95.0(4)	N(12)−Al(3)−N(9)	107.7(4)	N(8)−Al(2)−N(3)	108.4(4)	O(1)−Al(4)−N(7)	94.9(4)
O(1)−Al(1)−N(11)	179.0(3)	O(2)−Al(3)−N(5)	86.4(4)	O(1)−Al(2)−N(1)	86.9(4)	O(2)−Al(4)−N(7)	179.7(4)
N(4)−Al(1)−N(11)	91.0(4)	O(3)−Al(3)−N(5)	88.4(4)	O(4)−Al(2)−N(1)	88.2(4)	N(10)−Al(4)−N(7)	90.1(4)
N(2)−Al(1)−N(11)	89.0(4)	N(12)−Al(3)−N(5)	109.4(4)	N(8)−Al(2)−N(1)	107.3(4)	N(6)−Al(4)−N(7)	90.4(4)
Al(4)−O(1)−Al(2)	140.1(5)	N(9)−Al(3)−N(5)	143.0(4)	N(3)−Al(2)−N(1)	144.3(5)	C(46)−O(4)−Al(2)	137.7(10)
Al(4)−O(1)−Al(1)	95.7(4)	C(43)−O(3)−Al(3)	138.2(9)	Al(3)−O(2)−Al(1)	140.0(4)	Al(3)−O(2)−Al(4)	124.9(4)

$< 10^{-2}$ mmHg), hence lower temperature. Unfortunately, this cannot be achieved in our laboratory. Both compounds **1** and **2** have been fully characterized by ^1H NMR spectroscopy, elemental, and single-crystal X-ray diffraction analyses. Selected bond lengths and angles for compounds **1** and **2** are given in Table 2.

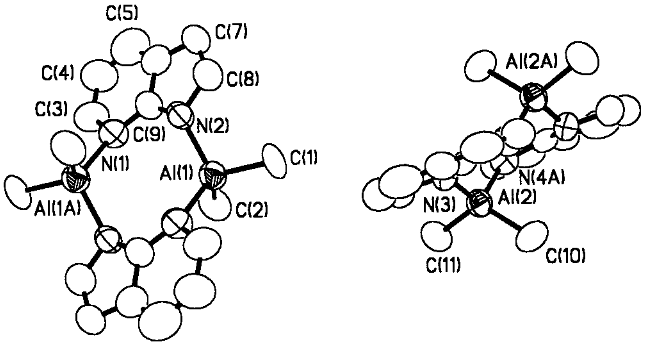

Figure 1. Molecular structures of two independent molecules of compound **1** with labeling scheme and 50% thermal ellipsoids.

In the asymmetric unit of the crystal lattice of **1**, there are two independent molecules with essentially identical structures, as shown in Figure 1. The deprotonated 7-azaindole ligand in **1** functions as a bridging ligand for two $Al(CH_3)_2$ units. Each aluminum ion has an approximately tetrahedral geometry. The Al−N and Al−C bond lengths in **1** are comparable to those reported earlier.[9] The two 7-azain ligands are coplanar, while the two $Al(CH_3)_2$ units are situated above and below the plane, respectively. The Al−Al separation distances in the two independent molecules are 3.828 and 3.784 Å. The Al(1)−N(1) (pyridyl) distance, 1.976(8) Å, is slightly shorter than the Al(1′)−N(2) (indole) distance, 1.942(8) Å, perhaps reflecting that the

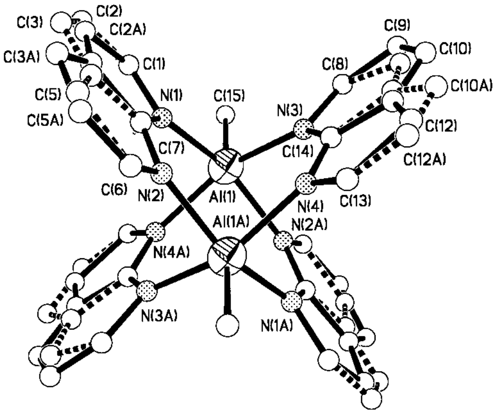

Figure 2. Diagram showing the disordering in **2** with labeling scheme. For clarity, all atoms are shown as ideal spheres.

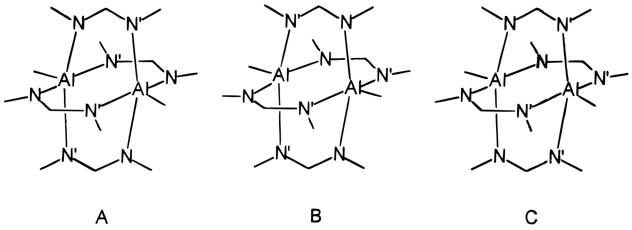

Figure 3. Possible structural isomers of **2**.

negatively charged indole nitrogen forms a somewhat stronger bond with the aluminum than the pyridyl nitrogen atom does. Although the two methyl groups on the aluminum ion do not have the same environment in the crystal lattice (one is approximately parallel to the 7-azain plane while the other is nearly perpendicular to it), they do appear to be equivalent in solution, as confirmed by the presence of a single methyl resonance in the ^{1}H NMR spectra of **1** in $CDCl_3$ at −0.52 ppm in the temperature range from −60 to 23 °C.

The crystal structure of **2** is shown in Figure 2. In contrast to the structure of **1**, compound **2** contains four bridging 7-azain ligands. The two sets of 7-azain planes are perpendicular to each other. The Al−C and Al−N bond lengths are similar to those in **1**. The Al−Al distance (3.398 Å) is, however, much shorter than that in **1**, apparently caused by the steric constraint of the four bridging 7-azain ligands. The geometry of the aluminum ion can be best described as a square pyramid with the Al atom above the basal plane. Examples of five-coordinate organoaluminum compounds have become a common occurrence recently.[1,2,10] The cage-like core structure of compound **2** is uncommon for organoaluminum compounds; it, however, resembles that of $In_2(CyNC(H)NCy)_4Cl_2$ reported by Richeson et al.[11] As shown in Figure 3, compound **2** has a crystallographically imposed inversion center and all the 7-azain ligands are all disordered. Each 7-azain ligand has two sets of positions, which could be considered as related by a mirror plane, with 50% occupancy for each set of positions. The origin of the disorder could be caused by (a) the presence of several different isomers or (b) one isomer which has several different orientations in the crystal lattice. The ^{1}H NMR spectrum of compound **2** shows only one set of 7-azain resonances and a single methyl resonance at − 60 to 23 °C, which led us to suggest that compound **2** is likely to exist as one isomer in solution and the solid state. The disorder displayed by **2** is, therefore, very likely caused by the different orientations of one isomer in the crystal lattice. The ^{1}H NMR data also support that compound **2** has a symmetric structure. Two possible symmetric structures of **2** where each aluminum is bound by two pyridyl nitrogen atoms (N) and two indole nitrogen atoms (N′) in either a cis (**A**) or trans (**B**) fashion are depicted in Figure 3 along with the asymmetric isomers. On the basis of the NMR data and X-ray diffraction data alone, we cannot distinguish **A** from **B**. Solid-state ^{27}Al NMR using MQMAS techniques[12] could provide a conclusive answer to the true structure of **2**, which is being explored currently by us. (If the true structure is **A**, the two Al atoms are related by an true inversion center, hence giving identical solid-state NMR resonances. If, however, the true structure is **B**, the two Al centers are not related by an true inversion center, hence crystallographically inequivalent, giving two different solid-state NMR resonances.)

The remarkably improved stability of compound **2**, in comparison with that of compound **1**, could be attributed to five-coordination of the aluminum and the increased number of 7-azain ligands on the aluminum centers, which reduces the electron density on the aluminum, thus stabilizing the $Al-CH_3$ bond. In fact, in the ^{1}H NMR spectrum of **2**, the methyl resonance at $\delta = 0.64$ ppm (in $CDCl_3$) is shifted much further downfield than that of **1** at $\delta = -0.51$ ppm (in $CDCl_3$), further supporting that the stability of **2** is due to the reduced negative charge on the methyl ligand, facilitated by the 7-azain ligands.

Syntheses and Structures of $Al_2(\mu\text{-}OCH(CF_3)_2)(CH_3)(7\text{-azain})_2(OCH(CF_3)_2)_2$ (3), $Al_3(\mu_3\text{-}O)(CH_3)(7\text{-azain})_4(OCH(CF_3)_2)_2$ (4), and $Al_4(\mu_3\text{-}O)_2(7\text{-azain})_6(OCH(CF_3)_2)_2$ (5). Al−O and Al−OR bonds, in general, are less susceptible to the attack of oxygen or water than Al−R bonds, where R is an alkyl group.[2d,15,16] It is, therefore, possible to improve the stability of the 7-azaindole aluminum complex toward air by replacing the alkyl groups with oxo or alkoxo ligands. We, therefore, examined the utility of alkoxo and oxo ligands in

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stabilizing aluminum compounds containing 7-azaindole ligands. The alkoxo ligand we chose was the 1,3-hexafluoro-2-propanolato ligand because the CF_3 groups stabilize the negative charge on the oxygen atom, hence increasing the stability of the complex in addition to providing the high solubility and volatility of the complex.[13] The synthetic approach was simple—just add the alcohol to the reaction mixture of $Al(CH_3)_3$ and 7-azaindole to replace the methyl groups either completely or partially by the OR^- and the 7-azain ligands. We have found that the reaction of 1,3-hexafluoro-2-propanol with $Al(CH_3)_3$ and 7-azaindole yields complex products. The structures and compositions of the products isolated from the reaction are highly dependent on the stoichiometry of the reaction.

Compound **3**, $Al_2(\mu\text{-}OCH(CF_3)_2)(CH_3)(7\text{-azain})_2(OCH(CF_3)_2)_2$, was isolated from the reaction of $Al(CH_3)_3$ with 7-azaindole and 1,3-hexafluoro-2-propanol in about a 2:2:3 ratio in toluene, while compound **4**, $Al_3(\mu_3\text{-}O)(CH_3)(7\text{-azain})_4(OCH(CF_3)_2)_2$, was obtained from the reaction of $Al(CH_3)_3$ with 7-azaindole and 1,3-hexafluoro-2-propanol in about a 1:2:1 ratio in toluene. Compound **5**, $Al_4(\mu_3\text{-}O)_2(7\text{-azain})_6(OCH(CF_3)_2)_2$, was initially isolated as a minor product from the reaction of $Al(CH_3)_3$, 7-azaindole, and 1,3-hexafluoro-2-propanol in a 1:2:1 ratio. The oxo ligands in both **4** and **5** are believed to come from the reaction of a trace amount of water in the 1,3-hexafluoro-2-propanol with $Al(CH_3)_3$. Compound **5** can be obtained by the reaction of $Al(CH_3)_3$ with 7-azaindole, 1,3-hexafluoro-2-propanol, and H_2O in an approximate 4:6:2:2 ratio in toluene in 26% yield. There are other products formed from the same reactions which have not yet been fully characterized. For example, a colorless crystalline compound **6** was obtained as a minor product from the synthesis of compound **3**. The ^1H NMR spectral pattern of the 7-azain ligand in **6** closely resembles that of $B_2(O)(C_2H_5)_2(7\text{-azain})_2$, reported recently by our group,[14] which made us suggest the formula of this compound is $Al_2(O)(CH_3)_2(7\text{-azain})_2$ (**6**). The composition of **6** was further supported by elemental analysis. However, satisfactory crystals of **6** for X-ray diffraction analysis could not be obtained. Attempted independent synthesis of **6** was also unsuccessful. The procedures given in the Experimental Section are the best methods to reproduce compounds **3**, **4**, and **5**, even though some of them may not be stoichiometric due to the formation of byproducts. Compounds **4** and **5** are stable for a few days under air in the solid state, while compound **3** undergoes a rapid hydrolysis when exposed to air in the solid state. Attempts to sublime compounds **4** and **5** have not been successful using our vacuum system (~0.05 mmHg). Compounds **3**−**5** were fully characterized by ^1H NMR, elemental, and X-ray diffraction analyses. Selected bond lengths and angles are given in Table 2.

The structure of compound **3** is shown in Figure 4. As observed in compound **1**, there are two bridging 7-azain ligands in **3**. The Al−Al separation distance in **3** is 3.372 Å, comparable to that of compound **2** but much shorter than that of compound **1**, attributable to the RO^- bridge. In contrast to compound **1** where each aluminum atom has two methyl groups, there is only one methyl group bound to Al(2) in compound **3**. There are three $(CF_3)_2CHO^-$ ligands in **3**, one of them acts as a bridging ligand (O(2)) while the other two function as terminal ligands. The terminal Al−O bond lengths (1.736(4) and 1.765(4) Å) are shorter than those of the bridging Al−O bond lengths (Al(2)−O(2) = 1.790(5) Å, Al(1)−O(2) = 2.288(5) Å), which is consistent with previous observations.[15,16] It is well-known that alkoxo ligands have a tendency to form polymeric compounds via bridging.[17] The nonbridging mode of the hexafluoro-2-propanolato ligand in 3 can be attributed to the steric bulk of the ligand. A similar bonding mode of the hexafluoro-2-propanolato ligand has been observed in[16a] $[(en)Al(OH)(OCH(CF_3)_2)_2]_2$. The long Al(1)−O(2) bond could be attributed to the fact that Al(1) is five-coordinate and surrounded by the bulky alkoxo ligands while Al(2) is four-coordinate and has no terminal alkoxo ligands. The geometry of Al(1) could be best described as a trigonal bipyramid (O(1)−Al(1)−O(2) = 177.5(2)°), while the geometry of Al(2) is approximately tetrahedral. To our knowledge, compound **3** is one of the rare examples of dinuclear organoaluminum compounds where the two aluminum centers have different ligand environments. Compound **3** retains its structure in solution, as evident by the presence of two sets of distinct resonance signals (one at 6.34 ppm and the other at ~ 4.50 ppm), due to the bridging and terminal $(CF_3)_2CHO^-$ ligands, in its ^1H NMR spectrum.

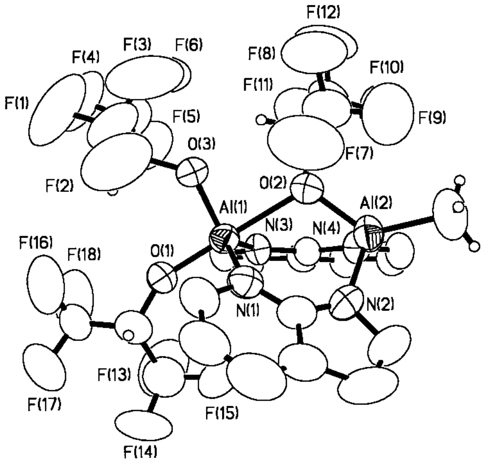

Figure 4. Diagram showing the molecular structure of **3** with labeling scheme and 50% thermal ellipsoids.

The structure of compound **4** has been reported in an earlier communication[7] and shown in Figure 5. Compound **4** has a crystallographically imposed mirror plane where the Al(2), O(2), C(23), C(5), C(6), C(11), and C(12) atoms lie. There are four bridging 7-azain ligands in the molecule, two of which bridge Al(1) and Al(1a) while the other two bridge Al(1) and Al(2), Al(1a) and Al(2), respectively. The two 7-azain ligands bridging Al(1) and Al(1a) are disordered over the two sites related by the mirror plane with 50% occupancy for each site. As a consequence of the disorder, the Al(1)−N(1) and Al(1)−N(2) bond lengths (2.007(8), 1.942(9) Å) can be considered as the average of the Al(1)−N(indole) and Al(1)−N(pyridyl) bonds. The bond lengths between the

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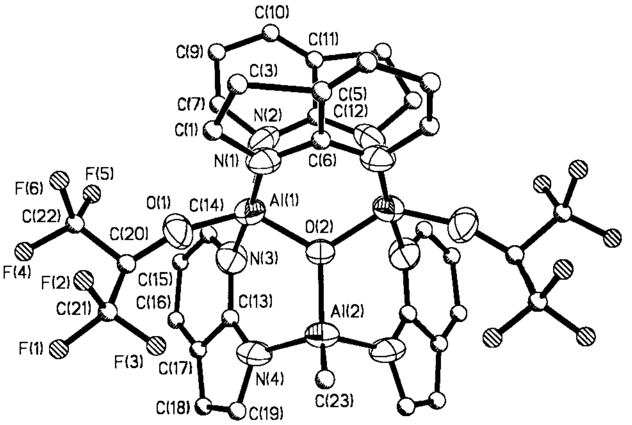

Figure 5. Diagram showing the molecular structure of **4** with labeling scheme and 50% thermal ellipsoids. The symmetry-related disordered atoms of the 7-azaindole ligands are omitted for clarity.

aluminum and the nondisordered 7-azain ligand, Al(1)−N(3) = 2.092(9) Å and Al(2)−N(4) = 1.868(9) Å, demonstrate unambiguously that the negatively charged indole nitrogen atom (N(4)) forms a stronger bond with the aluminum atom than does the neutral pyridyl nitrogen atom (N(3)). The oxo ligand acts as a triply bridging ligand to three aluminum atoms with similar Al−O bond lengths (1.784(5)−1.798(8) Å) and is essentially coplanar with the three Al atoms (0.052 Å above the plane). A similar bonding mode of the oxo ligand has been reported in complexes[18] $[(CH_3)_2Al(\mu_3\text{-}O)Al(CH_3)_3]_2^{2-}$, $[Al_3(\mu_3\text{-}O)Cl_8]^-$, and $[(AlCl_2)(\mu_3\text{-}O)(AlCl_3)]_2^{2-}$. The Al−O bond lengths are in the normal range of the known Al−O bond lengths.[15,16,18] The hexafluoro-2-propanolato ligand is monodentate, coordinating to one aluminum center with a relatively short Al−O bond length (1.711(7) Å). The coordination geometry of Al(1) is that of a slightly distorted trigonal bipyramid, with N(1) and N(3) occupying the axial positions (N(1)−Al(1)−N(3) = 176.1(4)°), while the geometry of Al(2) is tetrahedral, which could account for the bond length difference between Al(1) and Al(2). The Al(1)−Al(1a) separation distance is 3.054 Å, while the Al(1)−Al(2) distance is 3.372 Å. The short Al(1)−Al(1a) distance can be attributed to the oxo and two 7-azain bridges. The Al(2)−C(23) bond length, 1.82(2) Å, is substantially shorter than those in **1**−**3** and the previously reported alkylaluminum amido and imido complexes, attributable to the oxo and the 7-azain ligands which reduce the electron density on the aluminum center by being more electron withdrawing than the methyl group, hence stabilizing the Al−C bond. In fact, compound **4** is so stable that it does not decompose after being exposed to air for several days. The alkoxo ligands and the bridging oxo ligand no doubt contribute to the overall stability of compound **4**. There are no significant π stackings in the crystal lattice of **4**.

The structure of compound **5** is shown in Figure 6. Compound **5** contains two triply bridging oxo ligands, each of which bind to three aluminum atoms in the same manner as that in **4**. The four aluminum atoms and two oxo ligands are almost coplanar with the two 7-azaindole ligands. Al(1) and Al(2) are bridged by two 7-azaindole ligands situated below and above the Al_4O_2 plane, respectively. Al(3) and Al(4) are bridged by two 7-azaindole ligands in the same fashion. The oxo−aluminum bond lengths range from 1.757(7) (Al(4)−O(1)) to 1.844(9) Å (Al(1)−O(1), Al(4)−O(2)). The Al−N(indole) bond lengths ranging from 1.894(10) to 1.944(8) Å (1.920 Å in average) are significantly shorter than that of Al−N(pyridyl) bonds, ranging from 2.003(12) to 2.055(11) Å (2.028 Å in average), again reflecting the fact that the negatively charged indole nitrogen forms a stronger bond with the aluminum than the pyridyl nitrogen atom does. The two 1,3-hexafluoro-2-propanolato ligands in **5** function as terminal ligands, as found in **4**. The Al−O (2-propanolato) bond lengths (1.776(9), 1.798(9) Å) are, however, slightly longer than those in **4** (1.711(7) Å), perhaps due to the increased bulk in **5**. Structurally, compound **5** is closely related to compound **4**. The structure of compound **5** could be rationalized as the fusion of two molecules of compound **4** by sharing one edge of the Al_3 triangle (Figure 7). The Al(1)−Al(4) separation, where the two triangles fuse, is very short (2.672(3) Å), apparently caused by the double oxo bridges. A similar short Al−Al separation distance with double oxo bridges was also found in $Al_4(\mu_3\text{-}O)_2(CH_3)_6$(di-2-pyridylamido)$_2$.[7] The Al(1)−Al(2) and Al(3)−Al(4) distances, 3.189(4) and 3.197(4) Å, doubly bridged by two 7-azaindole ligands are longer than the corresponding one in **4**, attributable to the increased congestion in **5**. The Al(2)−Al(4) and Al(1)−Al(3) distances, 3.311(4) and 3.324(4) Å, bridged by a single 7-azaindole, are similar to those in **4**. The geometry of all four aluminum atoms in **5** can be described as a slightly distorted trigonal bipyramid. The two terminal aluminum atoms, Al(2) and Al(3), have two oxygen atoms on the axial positions, while the two central aluminum atoms, Al(1) and Al(4), have one oxygen and one nitrogen atom in the axial positions. The remarkable stability of **5** can be again attributed to the presence of the bridging oxo ligands and the alkoxo ligands. In contrast to compound **4**, where a methyl group is still present in the complex, compound **5** is methyl-free, which could further contribute to its overall stability.

The syntheses and structures of compounds **3**−**6** demonstrate the complexity and versatility of the reactions of trimethylaluminum with 7-azaindole and alcohol. However, despite the complexity of structures, these compounds all share a common feature, that is, the deprotonated 7-azaindole ligand binds to two aluminum ions in a bridging fashion in all complexes. It is this common feature that is responsible for the remarkable blue luminescent properties of these complexes as addressed below.

Luminescent Properties of Compounds 1−6. The most exciting property of compounds **1**−**6** is that they all emit an intense blue light upon being irradiated by UV light in solution and the solid state. The excitation and emission maxima for these compounds in the solid state are listed in Table 3. The excitation and emission spectra for these compounds are shown in Figures 8−10, respectively. As shown in Table 3, the emission energy for compounds **1**−**6** is similar despite the different geometry and ligand environment of the complexes. This is not surprising because the blue

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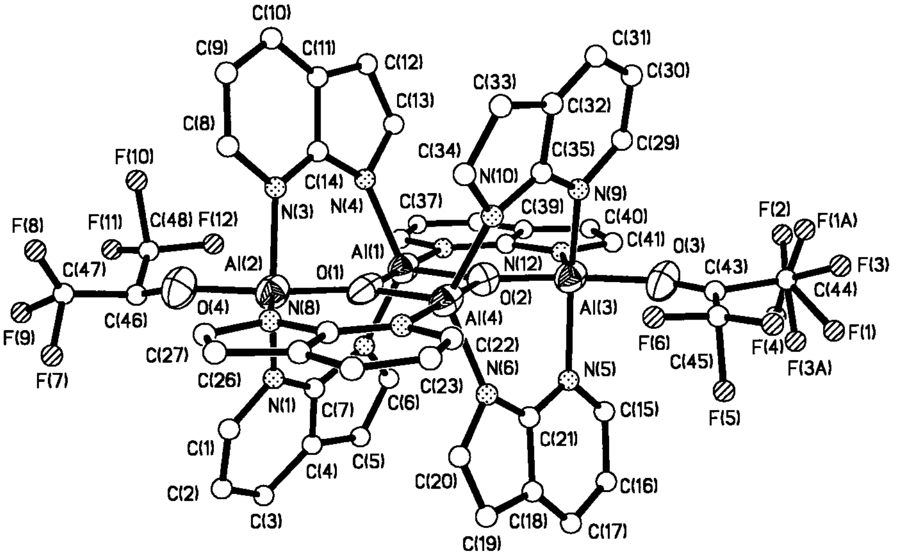

Figure 6. Diagram showing the molecular structure of **5** with labeling scheme. For clarity, carbon and fluorine atoms are shown as ideal spheres while hydrogen atoms are omitted.

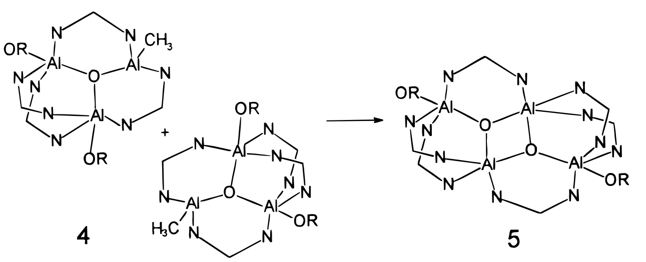

Figure 7. Scheme showing the structural relationship between **4** and **5**.

Table 3. Excitation and Emission Data

	1	2	3	4	5	6
excitation, λ_{max} (nm)	390	397	375	379	365	350
emission, λ_{max} (nm)	430	442	430	430	420	427

luminescence of the complex is believed to originate from a $\pi \rightarrow \pi$ transition of the 7-azaindole ligand. As a consequence, the nonemitting ligands on the complexes have no significant effects on the emission energy. One important and common feature in complexes **1**−**6** is that the 7-azaindole ligand displays only one binding mode, i.e., bridging two aluminum centers, which could also account for the similar blue luminescence displayed by the complexes.

Free 7-azaindole, however, does not have any observable blue luminescence in the solid state. The toluene solution of the free 7-azaindole ligand has an emission band at λ_{max} = 357 nm, which is in the colorless UV region. We, therefore, believe that coordination of the 7-azaindole ligand to the aluminum centers plays an important role in promoting the blue luminescence of the compounds. The major difference between coordinated 7-azaindole and the free ligand is that the coordinated ligand in complexes **1**−**6** is deprotonated. We have observed that the reaction of 7-azaindole with either NaH or Li(butyl) also yielded blue luminescent solutions. The products from these reactions are, however, highly unstable. It is, therefore, conceivable that removal of the proton on the indole nitrogen atom perturbs the π energy levels and shifts the emission energy from UV to blue. The function of the aluminum ions in the complexes appears to be two-fold. First, by forming donor−acceptor bonds with the 7-azaindole ligand, it may also contribute to the perturbation of the π energy levels, thus shifting the transition energy to blue. Second, as a strong Lewis acid, it may stabilize the coordinated 7-azaindole ligands via the formation of a complex.

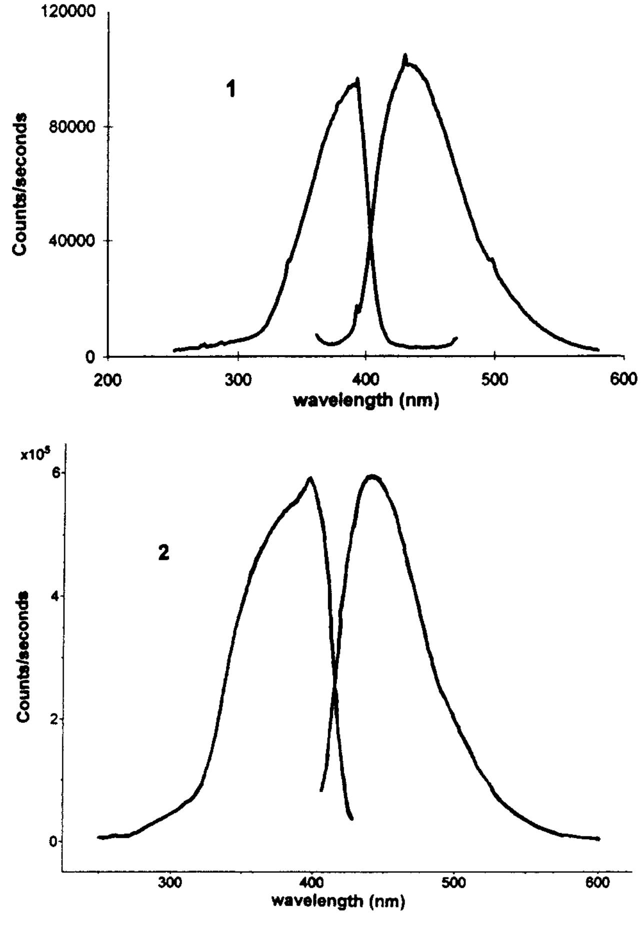

Figure 8. Excitation and emission spectra of **1** and **2**.

Preliminary measurements revealed that the emission lifetime for these complexes is in the order of 10−100 ns. For example, compound **2** was found to have a

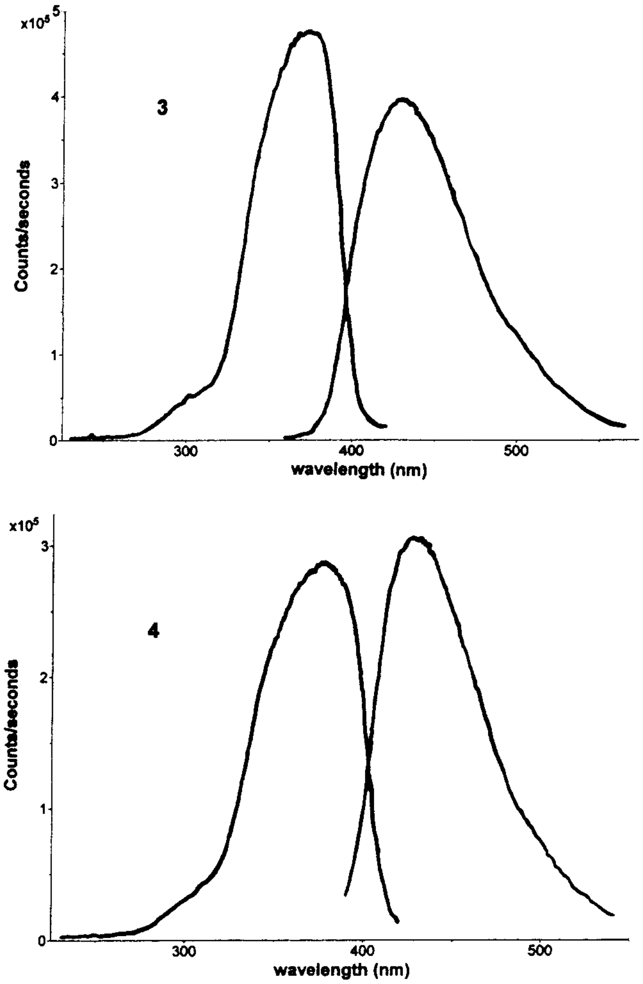

Figure 9. Excitation and emission spectra of **3** and **4**.

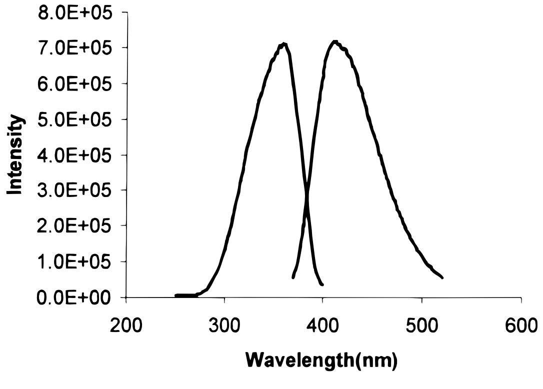

Figure 10. Excitation and emission spectra of **5**.

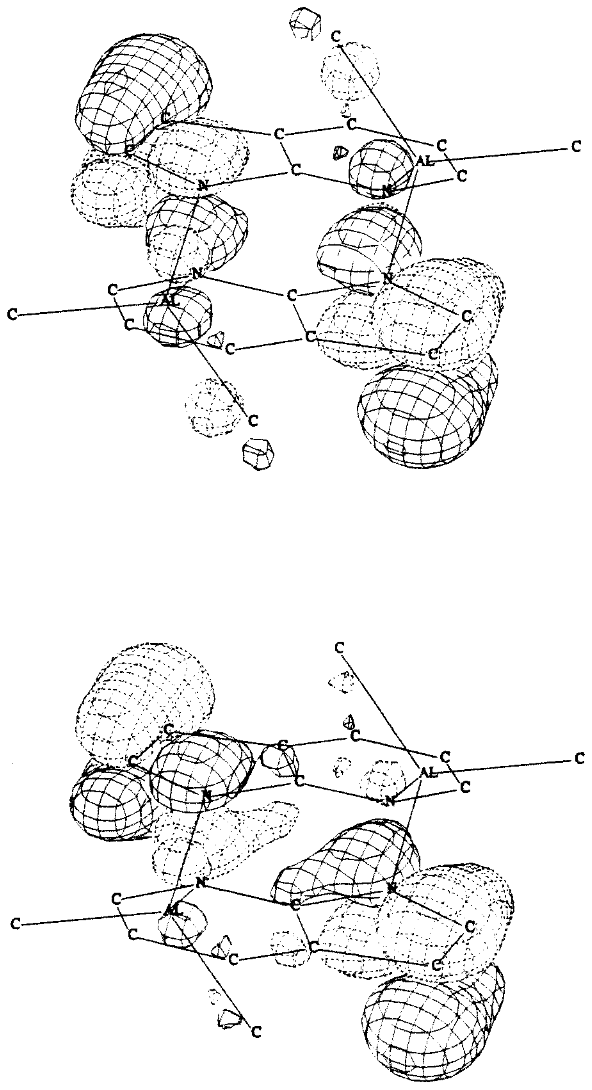

Figure 11. Two degenerate HOMO orbitals obtained from Gaussian 94 calculation (LUMO orbitals are not shown because our package does not produce a graphic representation for virtual orbitals).

single component decay of 33.0(5) ns, consistent with a singlet to singlet fluorescent transition. The kinetics of emission for compounds **1**−**6** is likely to be similar since the emission is centered on the 7-azaindole ligand that has a similar bridging mode through the entire series. Compounds **2** and **4** were selected as representative samples for the quantum yield measurements. The emission quantum yields for compounds **1** and **3** were not measured because of their poor stability in solution. Compound **5** is highly insoluble in the solvents that are suitable for its quantum yield measurement. We, therefore, did not obtain the quantum yield of compound **5**. The emission quantum yields for compounds **2** and **4** in solution were determined to be 0.54 and 0.31, respectively, relative to that of 9,10-diphenylanthracene in cyclohexane,[19] confirming that aluminum complexes of 7-azaindole are indeed efficient emitters. A similarly high quantum yield, 0.50, was also observed in the analogous boron complex of **6**, $B_2(O)(C_2H_5)(7\text{-azain})_2$, previously reported by our group. It is possible that the bridging of 7-azaindole to two aluminum centers (or boron centers) enhances the rigidity of the ligand, thus increasing its emission efficiency by decreasing the loss of energy via thermal vibrational modes.[20]

For practical applications, the emission quantum yields in the solid state for these complexes would be more meaningful. Unfortunately, the measurement of quantum yields of solids is a very difficult task. Our preliminary tests have shown that the aluminum compounds also have electroluminescent properties. The

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[19] Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

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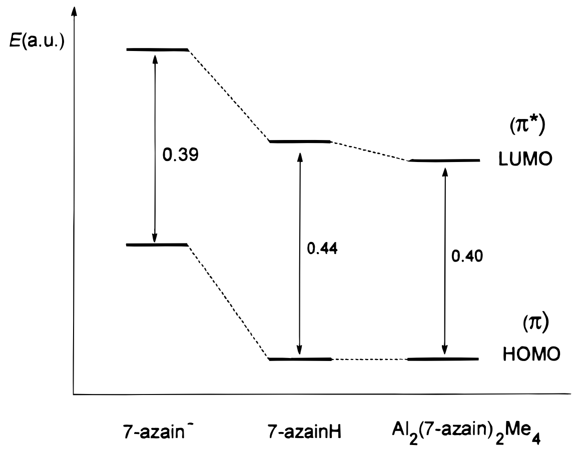

Figure 12. Diagram showing the change of HOMO and LUMO energy in the free neutral ligand, the negatively charged ligand, and complex **1**.

study on electroluminescence of these compounds is currently being conducted extensively in our laboratory and will be reported in due course.

To further understand the observed luminescent properties of these compounds, we conducted a series of molecular orbital calculations for the free ligand, the deprotonated free ligand, and the complex (compound **1** was studied because of its simplicity) by using semiempirical (Zindo)[21] and ab initio (Gaussian 94) methods,[22] employing geometric parameters obtained from X-ray diffraction analyses. The results of the MO calculations from the two different methods consistently showed that the HOMO and LUMO orbitals are π orbitals composed nearly entirely of the 7-azaindole ligand and that the HOMO−LUMO transition is a dipole-allowed transition (Figure 11).[23] In addition, the MO calculation results showed that the energy gap between the HOMO and LUMO is in the following order: deprotonated free ligand $\cong$ the complex < the free ligand. As shown by the results from Gaussian 94 methods in Figure 12, upon deprotonation, the energy levels of both HOMO and LUMO of the 7-azaindole ligand increase. The energy increase of the HOMO is, however, much more pronounced than that of the LUMO due to the increased electronic repulsion. As a result, the negatively charged 7-azain$^-$ is less stable than the neutral free ligand and the energy gap between the HOMO and LUMO of 7-azain$^-$ is smaller than that of the neutral free ligand, consistent with the fact that Na(7-azain) and Li(7-azain) emit in the blue region while the neutral free ligand emits in the UV region. Upon formation of the complex, the HOMO level is essentially the same as that of the neutral free ligand, despite the fact that the 7-azain ligand in the complex is deprotonated. This can be attributed to the donation of the σ lone pair of the indole nitrogen to the Al(III) center, which effectively decreases the negative charge density on the 7-azain ligand, thus stabilizing the ligand. The LUMO energy level of the complex is, however, significantly lower than that of the neutral free ligand, resulting in a smaller HOMO−LUMO energy gap, similar to that of the deprotonated free ligand, again consistent with the fact that the complex emits in the blue while the neutral free ligand emits in the UV region. Although there is little contribution from aluminum in the HOMO of the complex, there is a significant contribution of the aluminum atomic orbitals (3s, 3p, 4s, and 4p) to the LUMO, which could be responsible for the decreasing of the LUMO energy in the complex. The MO calculation results further support that the aluminum ions in the complexes indeed play a key role in stabilizing the complex and promoting the blue luminescence.

Conclusion

7-Azaindole is a good blue emitter upon coordination to aluminum centers. The compositions and structures of 7-azaindole complexes with aluminum(III) ions are versatile, depending on the supporting nonemitting ligands and the reaction conditions. Oxo and alkoxo ligands enhance the stability of the complex without altering the blue luminescence of the complex significantly. The nature of the blue luminescence displayed by our aluminum complexes is fluorescent, due to a $\pi^* \rightarrow \pi$ transition centered on the 7-azaindole ligand. The role of the aluminum ion is to stabilize the deprotonated 7-azaindole ligand via the formation of a donor−acceptor bond and lower the energy gap of the HOMO and LUMO so that the emission occurs in the blue region.

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Supporting Information Available: A diagram showing the entire molecule of **5** and the two toluene solvent molecules in the lattice of **5** and tables of atomic coordinates, complete bond lengths and angles, anisotropic thermal parameters, and unit cell packing diagrams (25 pages). Ordering information is given on any current masthead page.

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[21] *Hyperchem 4.5*, Hypercube Inc.: 1995.

[22] *Gaussian 94, Revision B.3*; Gaussian, Inc.: Pittsburgh, PA, 1995.

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