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Syntheses, Structures, Solution, and Solid-State ^{27}Al NMR Studies of Blue Luminescent Mononuclear Aluminum Complexes: Al(7-azain)$_2$(7-azain-H)(CH$_3$), Al(7-azain)$_3$(7-azain-H), and Al(7-azain)(7-azain-H)(OCH(CF$_3$)$_2$)$_2$ (7-azain-H = 7-azaindole)

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Abstract: Three novel mononuclear aluminum complexes, Al(7-azain)$_2$(7-azain-H)(CH$_3$) (**1**), Al(7-azain)$_3$(7-azain-H) (**2**), and Al(7-azain)(7-azain-H)(OCH(CF$_3$)$_2$)$_2$ (**3**), where 7-azain-H = 7-azaindole, have been synthesized and fully characterized structurally. The aluminum ion in all three compounds is in a tetrahedral environment. The neutral 7-azaindole ligand is coordinated to the aluminum center through the indole nitrogen site, resulting in a zwitterion form for all three compounds in the solid state. ^{1}H NMR studies established that in solution these compounds are dynamic, caused by an interconversion between the zwitterion isomer and a nonzwitterion isomer. All three compounds produce a blue light (λ_{max} = 430−450 nm) upon irradiation by UV light. ^{27}Al solution and solid-state NMR studies on all three compounds were performed. The data of ^{27}Al solution NMR are in agreement with those of ^{27}Al solid NMR. Quadrupole parameters of ^{27}Al in all three compounds have been obtained.

Introduction

The synthesis and characterization of compounds resulting from the reaction of 7-azaindole and trialkylaluminum have been a continuing subject of research in our laboratory.[1] Depending on reaction conditions, the resulting 7-azaindole aluminum complexes display a rich variety of structural features. Of particular interest are the blue luminescent properties of deprotonated 7-azaindole (7-azain) complexes, because of their potential applications in electroluminescent display devices.[2] We recently reported the synthesis and properties of dinuclear, trinuclear, and tetranuclear aluminum complexes containing 7-azaindole anions.[1a,c] These polynuclear compounds are bright blue emitters, but they are either unstable due to the presence of alkyl ligands or do not sublime under vacuum due to their large molecular weight. We have been therefore interested in the synthesis of mononuclear 7-azaindole aluminum compounds because they may have improved stability and volatility, compared to those of polynuclear compounds. In addition, we have been investigating the characterization of 7-azaindole aluminum complexes by solid-state ^{27}Al NMR to address issues such as isomerism versus disordering in the solid state[1a,g] that cannot be resolved by either solution NMR or crystallographic methods. The simplicity of mononuclear 7-azaindole aluminum complexes makes them ideal model compounds for solid-state ^{27}Al NMR studies in order to establish connections between solid-state ^{27}Al NMR parameters and chemical bonding in this important class of compounds. We report herein the syntheses, structures, luminescent properties, solution, and solid-state ^{27}Al NMR studies of three mononuclear aluminum complexes containing terminal 7-azain ligands.

Experimental Section

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Al(CH$_3$)$_3$, 7-azaindole, and HOCH(CF$_3$)$_2$ were purchased from Aldrich Chemical Co. Solvents were freshly distilled from the appropriate drying agents under nitrogen. ^{1}H NMR spectra were recorded on Bruker AVANCE 400 and AVANCE 300 spectrometers. Elemental analyses were performed by Canadian Microanalytical Services (Delta, British Columbia, Canada). Excitation and emission spectra were recorded on Photon Technologies International QM1 spectrometer. Solution ^{27}Al NMR spectra were obtained on a Bruker AVANCE 400 spectrometer operating at 104.26 MHz for ^{27}Al nuclei using [Al(H$_2$O)$_6$]$^{3+}$ as a reference. Solid-state ^{27}Al NMR spectra were recorded on a Bruker AVANCE 500 operating at 130.32 MHz for ^{27}Al Nuclei. Spectral simulations were performed using the WSOLIDS program kindly provided by Dr. Klaus Eichele and Prof. Rod Wasylishen (Dalhousie University, Halifax, Canada). The powder averaging routine of Alderman et al.[3] was used.

Synthesis of Al(7-azain)$_2$(7-azain-H)(CH$_3$) (1). To a solution of 15 mL of toluene and 354 mg (0.003 mol) of 7-azaindole in a Schlenk flask was added 0.5 mL of a 2.0 M solution of Al(CH$_3$)$_3$ in toluene (0.001 mol). The mixture was stirred for 5 h at ambient temperature and turned cloudy upon evacuation to ~8 mL. The remaining solution was decanted and 270 mg of a white powder was obtained. The powder was washed with toluene and then recrystallized from a CH$_2$Cl$_2$/hexane system. After ~3 days, colorless, block crystals of **3** appeared (yield = 69%). Anal. Calcd for C$_{22}$H$_{19}$N$_6$Al: C, 67.00; H, 4.86; N, 21.31.

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Table 1. Crystallographic Data

compd	**1**	**2**	**3**
formula	$C_{22}H_{19}N_6Al$	$C_{28}H_{21}N_8Al \cdot 0.5CH_2Cl_2$	$C_{20}H_{13}N_4O_2F_{12}Al$
fw	394.41	538.97	596.32
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	11.410(4)	13.741(6)	11.374(3)
b/Å	12.508(5)	12.156(5)	12.659(6)
c/Å	14.102(6)	15.965(9)	16.509(5)
β/deg	98.97(1)	98.71(4)	90.376(9)
V/Å^3	1988.0(13)	2619(2)	2377.0(14)
Z	4	4	4
D_c, g cm^{-3}	1.318	1.367	1.66
T (°C)	23	23	23
μ, cm^{-1}	1.23	2.15	2.07
$2\theta_{\max}$, deg	46	45	46
reflns measured	2925	3305	2938
reflns used (R_{int})	2767 (0.0257)	3145 (0.0433)	2938 (0.0500)
no. of variables	266	374	326
final R [$I > 2$ **s(I)**]	$R_1 = 0.0415$	$R_1{}^a = 0.0733$	$R_1 = 0.0550$
	$wR_2 = 0.0897$	$wR_2{}^b = 0.1341$	$wR_2 = 0.1227$
R (all data)	$R_1 = 0.0639$	$R_1 = 0.1341$	$R_1 = 0.0901$
	$wR_2 = 0.1004$	$wR_2 = 0.2040$	$wR_2 = 0.1529$
goodness-of-fit on F^2	1.11	1.07	1.03

[a] $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$. $wR_2 = [\sum w[(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$.

Found: C, 66.46; H, 4.92; N, 20.70. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298K, δ (ppm)): −0.12 (s), 0.02 (s), 6.49−6.53 (m), 6.99−7.05 (m), 7.10 (dd), 7.93 (d), 8.03 (d), 8.07 (d), 8.12 (d), 8.17(d), 8.26 (d) (Note: Compound **1** exists in two isomeric forms in solution.) ^{27}Al NMR spectrum (CH_2Cl_2, 104.26 MHz, 298K): 125 ppm ($\Delta_{1/2} = 2000$ Hz).

Synthesis of Al(7-azain)$_3$(7-azain-H) (2). To a solution of 16 mL of toluene and 472 mg (0.004 mol) of 7-azaindole in a Schlenk flask was added 0.5 mL of a 2.0 M solution of $Al(CH_3)_3$ in toluene (0.001 mol). After the addition, the solution turned pale yellow. After 3 h of stirring at ambient temperature the volume was reduced to approximately 8 mL, and 1 mL of hexane and 1 mL of THF were added to the solution. After sitting overnight, 372 mg of fine white crystals of Al(7-azain)$_3$(7-azain-H) (**2**) formed in solution (75%). Compound **2** can be recrystallized from CH_2Cl_2/hexane. Anal. Calcd for $C_{28}H_{21}N_8$-Al: C, 67.73; H, 4.26; N, 22.57. Found: C, 63.17; H, 4.38; N, 20.50 (consistent with 0.50 CH_2Cl_2 per molecule of **2**: C, 63.52; H, 4.08; N, 20.80). ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298K, δ (ppm)): 6.48 (d, 1H), 6.99 (dd, 1H), 7.10 (d, 1H), 7.97 (d, 2H), 7.99 (d, 1H). ^{27}Al NMR spectrum (toluene, 104.26 MHz, 298K): 97.6 ppm ($\Delta_{1/2} = 160$ Hz).

Synthesis of Al(7-az)(7-azH)(OCH(CF$_3$)$_2$)$_2$ (3). To a solution of 9 mL of toluene and 472 mg (0.004 mol) of 7-azaindole was added 1.0 mL of a 2.0 M solution of $Al(CH_3)_3$ in toluene (0.002 mol) in a Schlenk flask. After 2 h of stirring at 23 °C, the pale yellow solution turned cloudy. A solution of 0.300 mL (0.003 mol) of hexafluoro-2-propanol in 3 mL of toluene was added to the reaction flask, whereupon the solution became clear again. The mixture was stirred for another 3 h at ambient temperature and subsequently evacuated to ∼2 mL. To this was added 2 mL of hexane and 1 mL of THF. After 3 days, two different types of crystals were noted—long, fibrous, white crystals[1a] of $Al_3(O)(OCH(CF_3)_2)_2$(7-azain)$_4$(CH_3) and large, clear, block crystals of **3**. Separation of the block crystals yielded 235 mg of compound **1**. (∼40%). Anal. Calcd for $C_{20}H_{13}N_4O_2F_{12}Al$: C, 42.64; H, 2.15; N, 9.95. Found: C, 42.11; H, 2.28; N, 9.48. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz, 298K, δ (ppm)): 4.55 (2H), 6.65 (d, 2H), 7.18 (dd, 2H) 7.72 (d, 2H), 8.16−8.19 (m, 4H). ^{27}Al NMR spectrum (toluene, 104.26 MHz, 298K) 72.8 ppm ($\Delta_{1/2} = 120$ Hz).

X-ray Diffraction Analyses. Crystals of **1** and **2** were grown from a CH_2Cl_2/hexane solution while crystals of **3** were obtained from a toluene/hexane solution. The crystals were sealed in glass capillaries under nitrogen. All data were collected on a Siemens P4 single-crystal X-ray diffractometer with graphite-monochromated Mo−Kα radiation, operating at 50 kV and 35 mA at 23 °C. The data for **1**, **2**, and **3** was collected over the range of 2θ 3−46°. No significant decay was observed for all samples. Data were processed on a Pentium PC using Siemens SHELXTL software package (version 5.0)[4] and corrected for Lorentz and polarization effects. Neutral atom scattering factors were taken from Cromer and Waber.[5] The crystals of **3** belong to the monoclinic space group $P2_1/c$, while the crystals of **1** and **2** belong to the monoclinic space group $P2_1/n$, uniquely determined by systematic absences. All structures were solved by direct methods. In the crystal lattice of **2** there is a CH_2Cl_2 solvent molecule which is disordered over two sites related by an inversion center (0.5 CH_2Cl_2 per molecule of **2**). The positions of hydrogen atoms, except those on nitrogen atoms, were calculated. The acidic proton on the nitrogen atom for all three compounds was located directly from a difference Fourier map and refined successfully. The crystallographic data for compounds **1**−**3** are given in Table 1.

Results and Discussion

Synthesis and Structures. We reported previously that the reaction of 7-azaindole with $Al(CH_3)_3$ in a 1:1 ratio and a 2:1 ratio led to the formation of dinuclear compounds Al_2(7-azain)$_2$-(CH_3)$_4$ and Al_2(7-azain)$_4$(CH_3)$_2$, respectively.[1a] One of the strategies we used to obtain mononuclear 7-azaindole aluminum compounds is the use of excessive 7-azaindole ligands to prevent the formation of polynuclear species. When the reaction of 7-azaindole with $Al(CH_3)_3$ was carried out in a 3:1 ratio, a new mononuclear compound, Al(CH_3)(7-azain)$_2$(7-azain-H) (**1**), was obtained. Upon further increasing the amount of 7-azaindole (4:1 ratio) in the reaction, another mononuclear compound, Al-(7-azain)$_3$(7-azain-H) (**2**), was obtained. The other strategy we employed to achieve stable mononuclear compounds is the use of alkoxo ligands to replace methyl groups on the aluminum center. The alkoxo ligand used in our study is hexafluoro-2-propanol. In the presence of excess hexafluoro-2-propanol (the hexafluoro-2-propanol/7-azaindole/$Al(CH_3)_3$ ratio = 3:2:1), a new mononuclear compound, Al(7-azain)(7-azain-H)(OCH-(CF_3)$_2$)$_2$ (**3**), along with the previously known compound[1a] Al_3-(O)(OCH(CF_3)$_2$)$_2$(7-az)$_4$(CH_3) was obtained. All three compounds are more stable than the corresponding dinuclear compounds. They do however undergo decomposition in the solid state when exposed to air for a few days. Unfortunately, none of them could be successfully sublimed under N_2 under our vacuum conditions (∼0.01 Torr).

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

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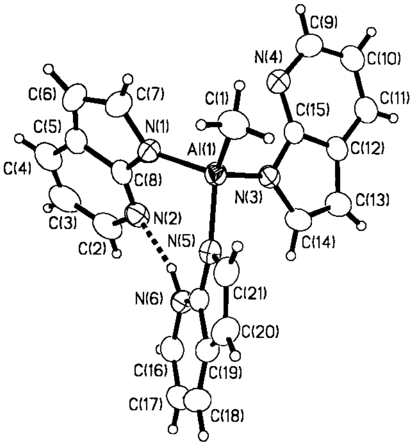

Figure 1. A diagram showing the molecular structure of compound **1** with 40% thermal ellipsoids and labeling schemes.

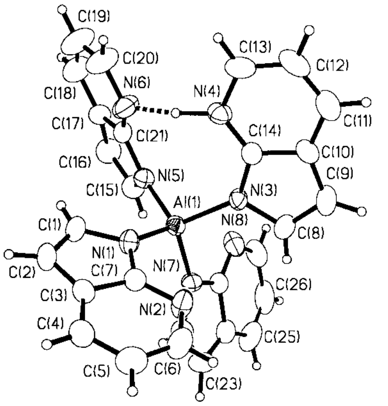

Figure 2. A diagram showing the molecular structure of compound **2** with 40% thermal ellipsoids and labeling schemes.

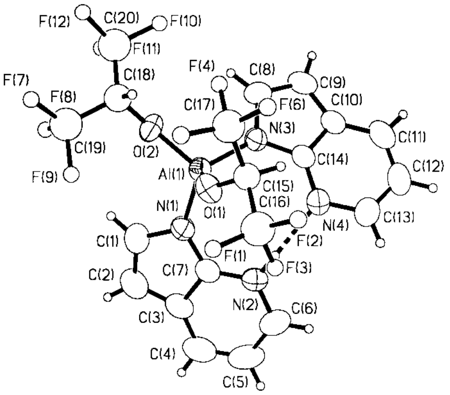

Figure 3. A diagram showing the molecular structure of compound **3** with 40% thermal ellipsoids and labeling schemes.

Because compounds **1**−**3** are a new class of 7-azaindole aluminum complexes, we conducted a full characterization of these compounds by the combination of NMR, elemental, and single-crystal X-ray diffraction analyses. The molecular structures of compounds **1**−**3** are shown in Figures 1−3, respectively. Selected bond lengths and angles for all three compounds are given in Table 2.

All three compounds have an approximately tetrahedral geometry around the aluminum center. The second common feature in all three compounds is that the 7-azaindole anion is coordinated to the Al(III) center as a terminal ligand. In previously reported dinuclear and polynuclear 7-azaindole aluminum compounds, the 7-azaindole anion coordinates to two Al(III) centers as a bridging ligand through both indole and pyridyl nitrogen atoms.[1a,c] As a terminal ligand, the 7-azaindole anion can bind to the Al(III) center through either the indole site or the pyridyl site, as shown in Scheme 1. The 7-azaindole anion in compounds **1**−**3** is bonded to Al(III) by the indole nitrogen only, which could be attributed to the high affinity of the negatively charged indole nitrogen atom to the aluminum center. A similar terminal 7-azaindole bonding mode has been observed[1d] in Hg(CH_3)(7-azain). The third common feature among the three compounds is the presence of a neutral 7-azaindole ligand that is bonded to the Al(III) ion through the indole nitrogen only. The neutral 7-azaindole molecule has two tautomers, as shown in Scheme 1. The binding of the pyridyl site to an aluminum center has been observed in a terminal 2-phenyl-substituted 7-azaindole ligand[1b] and a number of transition metal complexes containing 7-azaindole ligands in the solid state.[1e,f] To our knowledge, the indole binding mode of the neutral 7-azaindole lignad displayed in **1**−**3** has not been observed in the solid state.

In compound **1**, the Al(III) ion is surrounded by three nitrogen atoms and one carbon atom. The Al(1)−C(1) bond length, 1.939(3) Å, is similar to those reported previously.[1,6] The Al−N distances in **1** are similar to the Al−N(indole) distance of 1.885(2) Å in the tetrahedral compound Al(CH_3)(7-azain-2-Ph)$_2$(7-azainH-2-Ph), where the 2-Ph-7-azaindole anion exhibits a similar monodentate binding mode,[1b] but are considerably shorter than the Al−N(indole) distance of 1.942(8) Å displayed by the dinuclear species $Al_2(CH_3)_2$(7-azain)$_4$, where the 7-azaindole anion acts as a bridging ligand.[1a] Presumably the lack of steric hindrance allows for a greater overlap between the atomic orbitals of the Al and N atoms. There is an intramolecular hydrogen bond between the pyridyl nitrogen atoms N(2) and N(6), as indicated by the N(2)−N(6) separation distance of 2.697 Å. The proton appears to be closer to N(6) than N(2), which could explain the relatively long Al(1)−N(5) distance of 1.909(2) Å. Because of the coordination of three negatively charged indole nitrogen atoms and the methyl group, the aluminum center is formally negatively charged. Compound **1** could be therefore described as a zwitterion. The structure of **1** bears much resemblance to that[1b] of Al(CH_3)(7-azain-2-Ph)$_2$(7-azainH-2-Ph), except that Al(CH_3)(7-azain-2-Ph)$_2$(7-azainH-2-Ph) is not a zwitterion because two indole nitrogen atoms and one pyridyl nitrogen atom are coordinated to the Al(III) center. The observed structural difference between these two compounds could be attributed to the steric hindrance imposed by the 2-Ph-7-azaindole ligand in Al(CH_3)(7-azain-2-Ph)$_2$(7-azainH-2-Ph). Mononuclear aluminum compounds with one alkyl ligand are often stabilized by chelating nitrogen-containing ligands, resulting in five- or six-coordinate geometry.[7] Other examples of four-coordinate monoalkylaluminum complexes with terminal ligands only, similar to compound **1**, have been reported previously.[8,9]

In compound **2**, the Al(III) center is surrounded by four indole nitrogen atoms with bond lengths similar to those of **1**. It is

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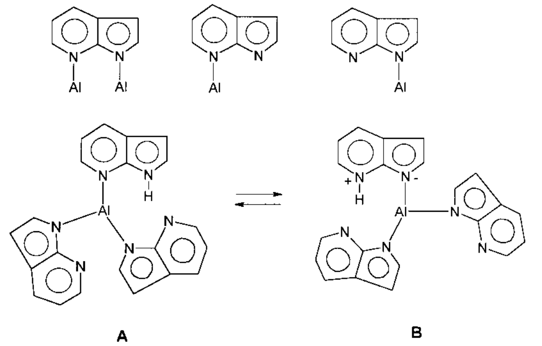
Table 2. Selected Bond Lengths (Å) and Angles (deg)

Compound **1**		Compound **2**		Compound **3**	
Al(1)−N(3)	1.868(2)	Al(1)−N(3)	1.889(5)	Al(1)−N(3)	1.826(4)
Al(1)−N(1)	1.882(2)	Al(1)−N(1)	1.853(5)	Al(1)−N(1)	1.883(4)
Al(1)−N(5)	1.909(2)	Al(1)−N(5)	1.863(6)	Al(1)−O(1)	1.723(3)
Al(1)−C(1)	1.939(3)	Al(1)−N(7)	1.845(5)	Al(1)−O(2)	1.700(3)
N(3)−Al(1)−N(1)	110.02(10)	N(7)−Al(1)−N(1)	110.8(2)	O(2)−Al(1)−O(1)	115.5(2)
N(3)−Al(1)−N(5)	102.34(9)	N(7)−Al(1)−N(5)	111.9(2)	O(2)−Al(1)−N(3)	106.5(2)
N(1)−Al(1)−N(5)	110.14(10)	N(1)−Al(1)−N(5)	106.2(2)	O(1)−Al(1)−N(3)	112.0(2)
N(3)−Al(1)−C(1)	115.23(12)	N(7)−Al(1)−N(3)	105.6(2)	O(2)−Al(1)−N(1)	105.6(2)
N(1)−Al(1)−C(1)	109.24(12)	N(1)−Al(1)−N(3)	111.2(2)	O(1)−Al(1)−N(1)	105.0(2)
N(5)−Al(1)−C(1)	109.67(12)	N(5)−Al(1)−N(3)	111.2(2)	N(3)−Al(1)−N(1)	112.3(2)

Scheme 1. Observed Bonding Modes of 7-azaindole in Aluminum Complexes and the Two Structural Isomers of Compound 1[a]



[a] Compounds **2** and **3** exhibit the same isomerism.

therefore again a zwitterion. Mononuclear aluminum complexes with a similar tetrahedral geometry and nitrogen donor atoms only have been reported previously.[10] There is a hydrogen bond between two pyridyl nitrogen atoms N(4) and N(6) (N(4)−N(6) = 2.705 Å), similar to that in **1**. In compound **3**, there are two indole nitrogen atoms and two oxygen atoms from the two alkoxo ligands surrounding the Al atom. The Al(III) center is therefore negatively charged as in **1** and **2**. The Al(III) ion in **3** has a distorted tetrahedral geometry, as evidenced by the bond angles around Al(1) ranging from 105.0(2)° to 115.5(2).° The average Al−O bond length of 1.71 Å in **3** is quite short but similar to those of previously reported polynuclear 7-azaindole aluminum complexes containing the hexafluoro-2-propanolato ligand.[1a] Similar short Al−O distances have also been found in the four-coordinate compounds[8,11] $AlMe(OMes)_2(3,5\text{-}Me_2Py)$, (1.74 Å) and $AlMe(BHT)_2[O{=}C(OMe)Ph]$ (1.71 Å). As observed in **1** and **2**, there is an intramolecular hydrogen bond between two pyridyl nitrogen atoms, N(2) and N(4), as indicated by their separation distance of 2.729 Å.

Solution Behavior of Compounds 1−3. In compounds **1**−**3**, the neutral 7-azaindole ligand is bonded to the aluminum center through the indole nitrogen atom exclusively, resulting in the formation of zwitterions for all three compounds in the solid state. This is quite puzzling for one would predict that the alternative (e.g. isomer **A** for compound **1** in Scheme 1) where the neutral 7-azaindole ligand is bonded to the aluminum by the pyridyl nitrogen atom would be thermodynamically more favorable. We have not, however, seen any evidence supporting the existence of isomer **A** in the solid state for all three compounds. If the energy barrier between isomers **A** and **B** is not very large, both isomers could be observed in solution. We therefore examined the ^1H NMR spectra of compounds **1**−**3** over the temperature range of 200−330 K. The spectra of all three compounds exhibit broad signals at ambient temperature and change with temperature, an indication of the presence of dynamic processes. The absence of chemical shifts due to free 7-azaindole ligands in the spectra lead us to believe that there is no ligand dissociation/association process involved. The dynamic process could be attributed to either an intramolecular proton-hopping process that exchanges the 7-azaindole ligands or an interconversion process between two isomers (**A** and **B**). The information from the spectra of **2** is however, not very informative because of the multiple peaks and spectral overlaps in the aromatic region, making it difficult to analyze the exchange process. The ^1H NMR spectra of compound **1** provided, however, insightful information on the exchange process because the methyl signal can serve as a convenient probe. If the exchange in **1** is caused by an intramolecular proton hopping among all three 7-azaindole ligands, it should have little effect on the chemical shift of the methyl group. On the other hand, if the dynamic process is caused by the isomer **A** and **B** interconversion, as depicted in Scheme 1, at the slow exchange region, two methyl chemical shifts corresponding to **A** and **B** isomers should be observed. That is indeed the case for compound **1**, as shown in Figure 4. At 218 K, two methyl signals (1.5:1) are observed. As the temperature is increased, these two signals become broad, coalesce, and finally become a broad peak at 330 K. The spectral change of the methyl region is reversible with temperature. We therefore concluded that, at 218 K, compound **1** exists in two isomeric forms, **A** and **B,** which interconvert in solution. Due to the overlaps of chemical shifts in the aromatic region, a conclusive peak assignment to **A** and **B** could not be achieved. At temperature above 300 K, some methane formation also becomes evident, indicative of the presence of a partial decomposition of compound **1** at high temperature. One of the decomposition products appears to be

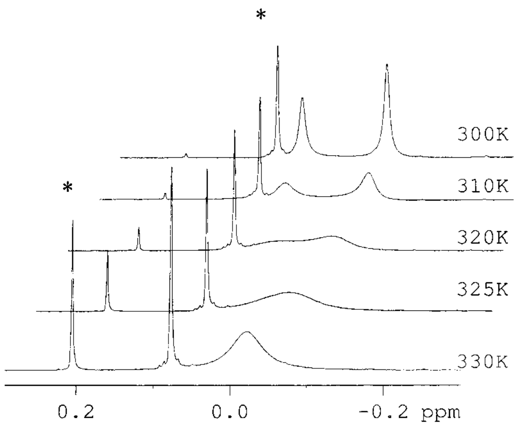


Figure 4. The methyl region of ^1H NMR spectra of compound **1**. The peaks marked by asterisks are from impurity (grease, 0.07 ppm) and methane (0.21 ppm), respectively.

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compound **2** based on solution ^{27}Al NMR data (see next paragraph). At 300 K, the ^{1}H NMR spectrum of compound **3** shows two sets of signals due to the CH group of the hexa2-propanolato ligand in ~4:1 ratio and three sets of signals due to 7-azaindole ligands. The ^{1}H NMR spectrum of **3** can be explained by the presence of two isomers similar to **A** and **B** in a 1:4 ratio in solution. On the basis of the pattern and integration of signals in the aromatic region, the dominating isomer of **3** in solution is determined to be isomer **B**. (Isomer **B** has one set of 7-azaindole signals while isomer **A** has two sets of 7-azaindole signals due to the presence of a indole bound 7-azaindole and a pyridyl bound 7-azaindole.) It is likely that a similar isomerism is also present in solution for compound **2**. The 2-Ph-7-azaindole analogue[1b] of **1**, Al(2-Ph-7-azain)$_2$(2-Ph-7-azain-H)(CH$_3$), reported previously by us exists as isomer **A** only in both solution and the solid state which could be explained by the steric hindrance imposed by the phenyl group. Why only isomer **B** was observed for compounds **1**−**3** in the solid state has not been understood at this time.

Solution ^{27}Al NMR Spectroscopy. The solution ^{27}Al NMR spectrum of **1** shows a broad peak typical of organoaluminum compounds. The signal at 125 ppm is in the expected region for a tetrahedral aluminum coordinated to a single alkyl group.[12] The ^{27}Al spectrum of **2** shows a singlet at 97.1 ppm, nearly identical to the 96 ppm observed[10] for [AlPy$_4$](ClO$_4$)$_3$ with a line width of 160 Hz. The ^{27}Al NMR spectrum of **3** exhibits a single peak at 72.8 ppm with a line width of 120 Hz, consistent with a tetrahedral geometry. Interestingly, the chemical shift for **3**, which has an AlN$_2$O$_2$ environment, is between those observed[13] for AlO$_4$ (59 ppm) and AlN$_4$ (97 ppm). Since solution ^{27}Al NMR spectroscopy has proved useful in the investigation of chemical exchange phenomena,[14] we also carried out variable temperature ^{27}Al NMR experiments. At 320 and 330 K, the ^{27}Al NMR signal of **1** showed the expected sharpening as a result of a decrease in the rotational correlation time[15] but no significant shift toward either the three-coordinate aluminum region ($\delta > 150$ ppm) or the five-coordinate aluminum region ($\delta < 60$ ppm), further confirming that the exchange in **1** occurs between two four-coordinate species. In addition, at 330 K, a small signal starts to appear at 97 ppm, indicative of the presence of compound **2**, perhaps the result of the partial decomposition of compound **1**.

Solid-State ^{27}Al NMR Spectroscopy. Solid-state ^{27}Al NMR spectroscopy has been used extensively to study the properties of glasses, ceramics, cements, and zeolites,[15,16] but very little is known about solid-state ^{27}Al NMR parameters in organoaluminum compounds. Under certain conditions, solid-state NMR spectra can yield valuable information about chemical bonding and molecular structure that may be unavailable from solution NMR spectroscopy. For a quadrupolar nucleus such as ^{27}Al (spin $= 5/2$), the most important NMR parameters are quadrupole and chemical shift tensors. Computer simulation of both MAS and static solid-state ^{27}Al NMR spectra can allow for the determination of these two tensors. Usually, one uses the nuclear quadrupole coupling constant (NQCC) to describe the magnitude of the quadrupole tensor, $\chi = e^2QV_{zz}$, where V_{zz} is the largest component of the electric field gradient (EFG) at the nucleus and Q is the nuclear quadrupole moment. In addition, an asymmetry parameter, η, is used to describe the relation between the three components of the EFG tensor in the form $\eta = (V_{xx} - V_{yy})/V_{zz}$. Symmetric arrangement of charges about the nucleus gives rise to a low electric field gradient, thus producing a smaller value for NQCC.[17]

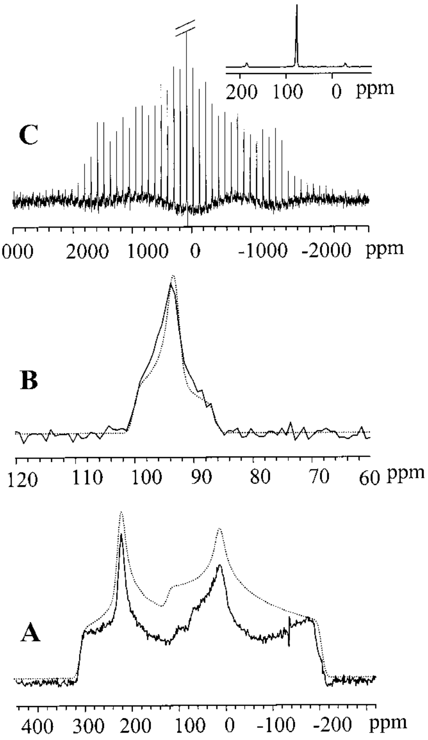

Figure 5. Solid-state ^{27}Al NMR spectra for compounds **1** (A), **2** (B), and **3** (C): (A) 10 s recycle time, 2096 transients, 1.0 μs pulse width; (B) 14 kHz spinning frequency, 10 s recycle time, 32 transients, 1.0 μs pulse width; (C) 14 kHz spinning frequency, 10 s recycle time, 32 transients, 1.0 μs pulse width.

Solid-state ^{27}Al NMR spectra of compounds **1**−**3** are shown in Figure 5. As seen from Figure 5A, the static ^{27}Al NMR spectrum of **1** covers a frequency range of over 65 kHz, indicating a very large ^{27}Al NQCC. In this case, magic-angle spinning (MAS) at any practical spinning speed is not effective for **1**. Analysis of the static ^{27}Al NMR line shape yields the following quadrupole parameters: $\chi = 13.75$ MHz and $\eta = 0.44$. It should also be pointed out that a small chemical shift anisotropy (CSA) must be included in the simulation in order to obtain the best-fit line shape shown. The small ^{27}Al CSA found in **1**, $\Omega = 30$ ppm, is comparable to those recently reported ^{27}Al CSA values.[16e] The large χ value found in **1** can be attributed to the presence of an Al−C bond. To the best of our knowledge, compound **1** represents the first organometallic aluminum compound characterized by solid-state ^{27}Al NMR. Now it is interesting to compare the results for **1** with those obtained from ^{27}Al nuclear quadrupole resonance (NQR) studies. Dewar et al.[18] reported ^{27}Al NQCCs for a wide variety of four-coordinate organoaluminum compounds with halide, alkyl, and alkoxide bridges, as well as monomeric AlMe$_3$ adducts with various group V and VI donors. The NQCC for **1** is uniformly lower than those reported for the bridging organoaluminum compounds, which range between 20 and 40 MHz. The ^{27}Al

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Table 3. Solution and Solid-State ^{27}Al NMR Parameters for Compounds **1**−**3**

	solution ^{27}Al NMR		solid ^{27}Al NMR		
compd	δ/ppm	$\Delta\nu_{1/2}$/Hz	δ_{iso}/ppm	χ/MHz	η
1	125.0	2000	125	13.75	0.44
2	97.1	160	100	3.65	1.00
3	72.1	120	78	1.30	1.00

NQCC of **1** is, however, similar to that reported for Me_3-Al•NMe_3 (χ = 11.52 MHz). Interestingly, a much larger ^{27}Al NQCC value was found in H_3AlNMe_3 as determined by gas-phase high-resolution microwave spectroscopy (χ = 25.0 MHz).[19]

Figure 5B shows the ^{27}Al MAS spectrum of **2**. The spectrum exhibits a typical line shape arising from second-order quadrupole interaction, the narrow line width of which indicates a small ^{27}Al NQCC. Simulation of the line shape yields $\chi = 3.65$ MHz and $\eta = 1.0$. The crystal structure of **2** indicates that the Al center is in a slightly distorted tetrahedron with four indole nitrogen atoms. The Al−N distances vary between 1.845 and 1.889 Å, whereas the N−Al−N angles are in a range from 105.6 to 111.2°.

The ^{27}Al MAS spectrum of **3** is shown in Figure 5C. Since the central transition (shown as the insert) exhibits a sharp, featureless peak, it is difficult to extract information about ^{27}Al NQCC. However, the fact that the second-order quadrupolar interaction is negligible in **3** suggests that the first-order quadrupole interaction might be observable. Therefore, we attempted to detect all ^{27}Al NMR satellite transitions. As shown in Figure 5C, the ^{27}Al satellite transitions cover a much larger frequency range, resulting in a large number of spinning sidebands. Clearly, the envelope of the spinning sidebands resembles the line shape due to the first-order quadrupole interaction. From the observed ^{27}Al spinning sideband manifold, we determined the ^{27}Al NQCC to be 1.30 MHz and the asymmetry parameter to be 1.0 for **3**. The coordination environment at the Al center is also a distorted tetrahedron, similar to the case in **2**. But the Al center in **3** is coordinated by two indole nitrogen atoms and two oxygen ligands. It is somewhat surprising that the ^{27}Al NQCC in **3** is even smaller than that in **2**, where all four ligands are indole nitrogen atoms. It is noted that the Al−O distances in **3** are quite short, 1.700 and 1.723 Å. Since ^{27}Al NQCC is a measure of the change of the electric field at the nucleus, the very small ^{27}Al NQCC found in **3** indicates that the electric fields generated by the Al−N bonds, 1.826 and 1.883 Å, essentially cancel those from the Al−O bonds, 1.700 and 1.723 Å.

Solid-state ^{27}Al NMR parameters for compounds **1**−**3** are summarized in Table 3, together with solution ^{27}Al NMR parameters for comparison. The solid-state ^{27}Al chemical shifts are in excellent agreement with the solution values, indicating that molecular structures are retained in solution. Furthermore, the ^{27}Al NQCC values of compounds **1**−**3** observed in the solid-state correlate very well with the line widths observed from solution ^{27}Al NMR. The ^{27}Al chemical shift for **3** is approximately 20 ppm more shielded than that for **2** because of the replacement of two nitrogen ligands by two oxygen ligands. This is also consistent with the previous observation of Fitzgerald et al. in a solid-state ^{27}Al NMR study of four-coordinate aluminum oxynitride ($AlO_{4-x}N_x$) environments in AlON ceramic powders.[20]

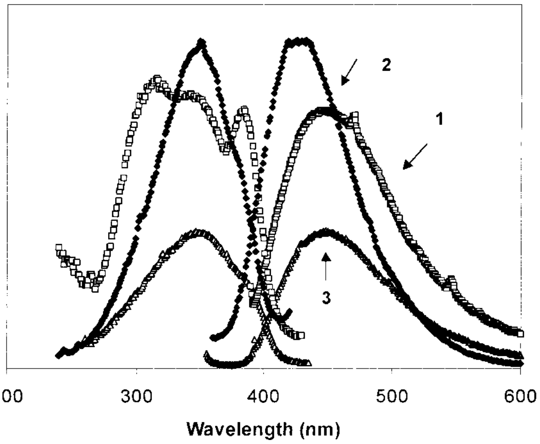

Figure 6. The excitation and emission spectra of compounds **1**−**3** in the solid state.

Luminescent Properties of Compounds 1−3. Compounds **1**−**3** all emit blue light upon being irradiated by UV light in solution and the solid state. The emission maxima for these compounds in the solid state are at λ = 445, 448, and 430 nm, respectively, as shown in Figure 6. The luminescence displayed by compounds **1**−**3** is similar to those of polynuclear 7-azaindole aluminum complexes, where the 7-azaindole anion functions as a bridging ligand only.[1a] Previous theoretical calculations using semiempirical (Zindo)[21] and ab initio (Gaussian 94) methods[22] have shown that the blue luminescence displayed by these compounds originates from a π−π^* transition of the deprotonated 7-azaindole anion.[1a] The role of the aluminum ions is simply to stabilize the 7-azaindole anion. The bridging mode of the 7-azaindole ligand was believed to also play an important role in enhancing the efficiency of the emission in dinuclear and polynuclear complexes. Despite the fact that only the terminal bonding mode of 7-azaindole is present, compounds **1**−**3** do not show significant decrease of emission brightness in comparison to those of polynuclear 7-azaindole aluminum complexes. We, therefore, believe that the formation of intramolecular hydrogen bonds between 7-azaindole ligands in compounds **1**−**3** may have a similar effect on luminescence efficiency as the bridging mode of 7-azaindole because the hydrogen bond locks the two 7-azaindole ligands in position, thus reducing their thermal vibrations.

Conclusions

Our studies have shown that mononuclear aluminum compounds containing 7-azaindole ligands can be obtained by the use of either a stoichiometric ligands/$Al(CH_3)_3$ ratio or an excessive amount of ligands. These new mononuclear compounds display a blue luminescence and an improved stability toward air and moisture in comparison with related dinuclear and polynuclear compounds. Compounds **1**−**3** are fluxional in solution, caused by an interconversion of an indole nitrogen bound isomer and a pyridyl nitrogen bound isomer of a neutral 7-azaindole ligand. The distinct coordination environment around the aluminum ion in compounds **1**−**3**—four nitrogen coordinating atoms in **1**, three nitrogen and one carbon coordinating atoms in **2**, and two oxygen and two nitrogen coordinating atoms in **3**—makes them good model compounds

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for the study of ^{27}Al NMR on tetrahedral aluminum complexes. The parameters obtained from ^{27}Al solid-state NMR spectroscopic studies correlate well with ^{27}Al solution NMR data and the coordination environment of compounds **1**−**3**. These parameters will be very useful for future studies of organoaluminum and aluminum coordination compounds by solid-state NMR spectroscopic methods.

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Supporting Information Available: Tables of crystallographic analysis, atomic coordinates and isotropic thermal parameters, a complete list of bond lengths and angles, anisotropic thermal parameters, hydrogen parameters, a diagram showing the disordered solvent molecule in the crystal lattice of **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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