

Probing the Origin of Disorder in Polynuclear Aluminum 7-Azaindolyl Complexes by ^{27}Al Multiple-Quantum Magic-Angle-Spinning NMR

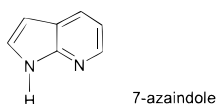
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Received October 8, 1999

Revised Manuscript Received December 20, 1999

In the past decade considerable attention has been devoted to the search for suitable blue luminescent compounds that can be used in electroluminescent (EL) display devices.^{1–4} Polynuclear organoaluminum compounds are among the most interesting candidates for such applications. Recently, we reported the syntheses and structural characterization of a series of new polynuclear aluminum and boron complexes containing the 7-azaindolyl ligand.^{5–8} In these complexes, the 7-azaindolyl group often serves as a bridging ligand between two aluminum centers and, in several cases, is disordered in the crystal lattice as revealed by X-ray diffraction. However, X-ray diffraction studies cannot provide information about the origin of the ligand disorder. In fact, many instances of similar disordering have been reported in the literature concerning polynuclear metal complexes containing the 7-azaindolyl ligand, and the origins of disorder in all these systems have been unidentifiable by the X-ray diffraction method.^{9–16}



Unlike the X-ray diffraction technique, which relies on the long-range order of the crystal lattice, solid-state NMR is sensitive only to the local environment at the nucleus of interest. The utility of solid-state NMR in the study of disorder problems has been previously demonstrated;¹⁷ however, successful applications have been limited to the studies of spin-1/2 nuclei such as ^{13}C . The poor NMR spectral resolution associated with half-integer quadrupolar nuclei such as ^{27}Al has hampered the use of solid-state NMR in the study of disorder phenomena. This situation has been fundamentally changed since the introduction of multiple-quantum

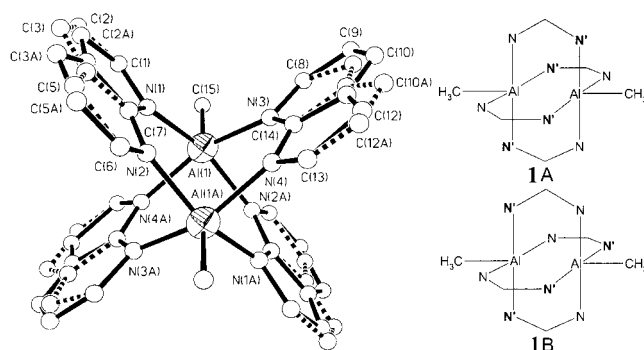


Figure 1. Diagram showing the molecular structure and the two symmetrical isomers for **1**. The negatively charged indole nitrogen atoms are indicated by the symbol N'.

magic-angle-spinning (MQMAS) methodology.¹⁸ In this contribution, we report the first application of ^{27}Al MQMAS spectroscopy to the identification of disorder of two blue luminescent organoaluminum compounds in the solid state, $\text{Al}_2(\text{CH}_3)_2(7\text{-azain})_4$ (**1**) and $\text{Al}_3(\mu_3\text{-O})(\text{CH}_3)(7\text{-azain})_4(\text{OCH}(\text{CF}_3)_2)_2$ (**2**), where 7-azain = 7-azaindolate.

The molecular structure of compound **1** is shown in Figure 1. Compound **1** has a crystallographically imposed inversion center, and all four 7-azaindolyl ligands are disordered in the crystal lattice.⁷ The origin of the disorder could be due to either the coexistence of different structural isomers or the presence of one isomer having different orientations in the crystal lattice. The solution ^1H NMR spectrum of compound **1** exhibits one set of peaks from the 7-azaindolate and a single methyl resonance in the temperature range from -60 to 23 °C. This result suggests that the two Al atoms in compound **1** are chemically equivalent. We refer to this type of isomers as symmetrical isomers in this study. The two possible symmetrical isomers are depicted in Figure 1, one with a C_{2h} symmetry (**1A**) while the other with a D_{2d} symmetry (**1B**). Now the question becomes whether isomers **1A** and **1B** coexist in the crystal lattice or only one of them is present with two different orientations. These three situations are indistinguishable by X-ray crystallography.

Similarly, the crystal structure of compound **2** indicates that the molecule exhibits a crystallographically imposed mirror plane containing Al(2), O(2), C(23), C(5), C(6), C(11), and C(12) atoms, as shown in Figure 2. Two of the four bridging 7-azaindolyl ligands are disordered with a 50% occupancy for each orientation.⁷ The two symmetry-related Al centers, Al(1) and Al(1A), are both five-coordinate with a trigonal bipyramidal geometry. The geometry of the Al(2) site is, however, tetrahedral with one of the ligands being a methyl group. If the orientation of the two bridging 7-azaindolyl ligands is completely random between the two possible directions, two isomers will be possible as depicted in Figure 2, leading to a total of four distinct Al sites. Since individual molecules of **2** do not possess a mirror plane, the two five-coordinate Al sites in any isomer should always have a different chemical environment. For isomer **2A**, the two five-coordinate Al centers bridged by two "antiparallel" 7-azaindolyl ligands differ in the identity of their axial ligand. In contrast, the two bridging 7-azaindolyl ligands in isomer **2B** are "parallel" to one another. Under this circumstance, the two five-coordinate Al sites have a quite different chemical environment. Specifically, whereas one Al site is coordinated to two neutral pyridyl nitrogen atoms, the other is bound to two negatively charged indole nitrogen atoms. Again, X-ray diffraction results are not useful in answering the question as to whether isomers **2A** and **2B** coexist or only one of them is present with two different orientations in the crystal lattice.

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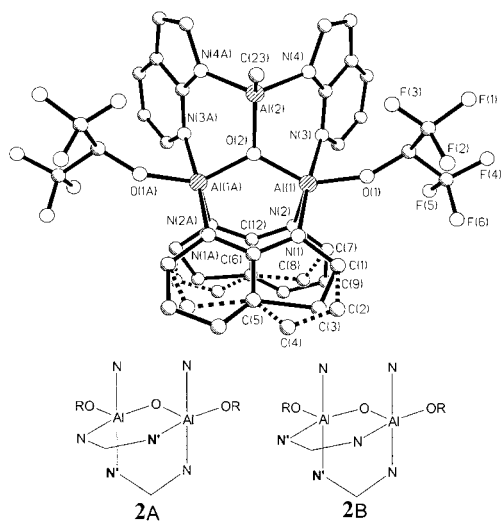


Figure 2. Diagram showing the molecular structure and the four possible Al sites for **2**. The negatively charged indole nitrogen atoms are indicated by the symbol N'.

The two-dimensional ^{27}Al MQMAS spectra of compounds **1** and **2** are shown in Figure 3. The experimental and simulated 1D ^{27}Al MAS spectra are shown on the top of each of the 2D contour plots. It is clear that the ^{27}Al MAS spectra for both compounds exhibit overlapping second-order quadrupolar line shapes, from which it is difficult to extract useful information. The projections shown on the side of the 2D plots are the isotropic ^{27}Al MQMAS spectra. The isotropic ^{27}Al MQMAS spectrum of **1** exhibits two isotropic peaks with an approximate 1:1 intensity ratio, indicating the presence of two types of aluminum centers. Based on the F_2 slice spectra from the 2D ^{27}Al MQMAS spectra, it is straightforward to obtain the following ^{27}Al NMR parameters for **1**: isomer 1A, $e^2qQ/h = 6.5 \pm 0.1$ MHz, $\eta = 0.75$, $\delta_{\text{iso}} = 55 \pm 1$ ppm; isomer 1B, $e^2qQ/h = 6.5 \pm 0.1$ MHz, $\eta = 0.20$, $\delta_{\text{iso}} = 56 \pm 1$ ppm. Since the ^{27}Al NMR parameters for the two isomers are so similar, assignment remains unclear at this time. Nevertheless, the observation of two isotropic peaks in the ^{27}Al MQMAS spectrum of **1** clearly suggests that the 7-azaindolate disorder arises from the coexistence of two symmetrical isomers, **1A** and **1B**, in the crystal lattice.

The ^{27}Al MQMAS spectrum of **2** also exhibits two isotropic peaks in the isotropic dimension, again indicating the presence of two distinct Al sites. Simulation of the 1D sub-spectra from the 2D MQMAS spectrum yields the following parameters for **2**: site 1, $e^2qQ/h = 5.5 \pm 0.1$ MHz, $\eta = 1.00$, $\delta_{\text{iso}} = 46 \pm 1$ ppm; site 2, $e^2qQ/h = 6.8 \pm 0.1$ MHz, $\eta = 0.80$, $\delta_{\text{iso}} = 43 \pm 1$ ppm. As expected, the Al site associated with a larger value of e^2qQ/h gives rise to a lower intensity for the isotropic peak in the MQMAS spectrum.²⁰ It should be pointed out that the ^{27}Al NMR signal from the tetrahedral Al(2) site was not observed in the MAS spectrum due to the fact that this site has a very large ^{27}Al quadrupolar coupling constant. Our recent study indicates that a tetrahedral Al site containing an Al–C bond exhibits $e^2qQ/h \approx 14$ MHz and $\delta_{\text{iso}} \approx 125$ ppm.²¹ Therefore, at the present sample spinning frequency, the tetrahedral Al(2) site will give rise to negligible signal intensities. It is interesting to note that the two 5-coordinate Al sites have almost identical isotropic chemical shifts, suggesting that these Al centers have a very similar chemical environment. As mentioned above, the two five-coordinate Al sites in isomer **2B** exhibit quite different chemical environment and, therefore, would be expected to give rise to

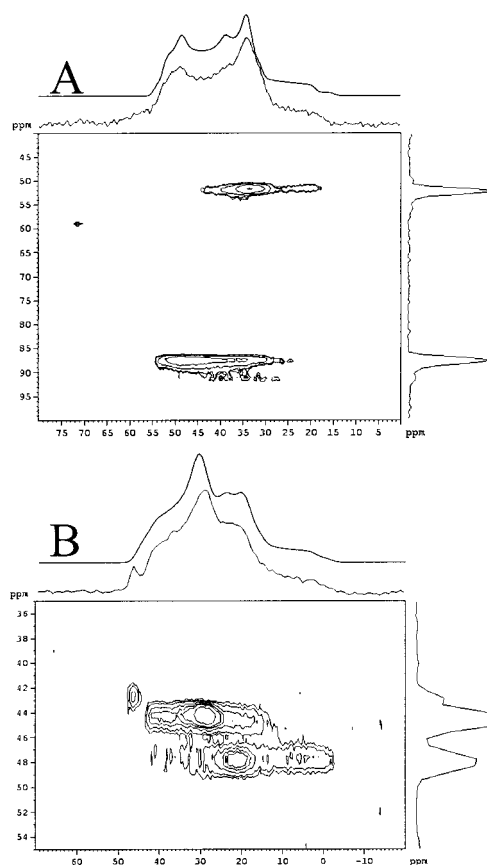


Figure 3. Two-dimensional (2D) ^{27}Al triple-quantum (3Q) MAS NMR spectra of **1** (A) and **2** (B). Simulated ^{27}Al MAS spectra are shown on the top of the spectra. Solid-state ^{27}Al NMR experiments were carried out on a Bruker Avance-500 spectrometer operating at 130.8 MHz for ^{27}Al nuclei. The pulse sequence with a z-filter was used in obtaining ^{27}Al 3QMAS spectra.¹⁹ The excitation and conversion pulse width was 3.0 and 1.0 μs , respectively. The selective ^{27}Al 90° pulse for the central transition was 24 μs . Powder samples were packed into zirconium oxide rotors (4-mm o.d.) in a glovebox under a dry nitrogen environment. The sample spinning frequency was 13 kHz. A total of 180 transients were accumulated for each of the 136 t_1 increments with a recycle delay of 2 s. The small peak at 48 ppm in the spectra of **2** is due to an impurity.

substantially different ^{27}Al chemical shifts. Based on this argument, we tentatively assign the observed NMR signals for **2** to be due to the presence of isomer **2A**. The difference in the ^{27}Al quadrupolar coupling constants for the two sites is probably due to their different axial/equatorial ligand arrangements. Based on the fact that only two 5-coordinate Al sites were observed in **2**, we can conclude that the origin of disordering in **2** arises from the presence of only one isomer in the crystal lattice. The disorder of **2** can be attributed to the coexistence of the enantiomer of isomer **2A** in the crystal lattice, producing the crystallographically imposed mirror plane symmetry detected by X-ray diffraction.

In summary, we have demonstrated that MQMAS is a powerful method of obtaining site-specific information unobtainable with other spectroscopic techniques. Although the MQMAS technique has recently been applied to a diverse range of structural problems in chemistry and materials sciences, the present study represents the first MQMAS application to disorder problems. The methodology demonstrated here is clearly applicable to other systems where half-integer quadrupolar nuclei can be used as a probe of ligand disordering.

Acknowledgment. This research was financially supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada.

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