

Investigation of Al–C Bond Reactivity in a Bidentate Ligand System: Structure and Reactivity Studies of $[\text{Al}(\text{8-quinolinol})(\text{C}_2\text{H}_5)_2]_2$

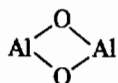
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Abstract

The reaction of triethyl aluminum, $\text{Al}_2(\text{C}_2\text{H}_5)_6$ with 8-quinolinol yields the dimeric dialkyl aluminum complex $[\text{Al}(\text{8-quinolinol})(\text{C}_2\text{H}_5)_2]_2$. The X-ray crystal structure, monoclinic, $P2_1/c$, $a = 18.132(3)$, $b = 9.784(5)$, $c = 15.191(2)$ Å, $\beta = 112.06(1)^\circ$, $V = 2497.6(22)$ Å³, $Z = 4$, shows that the complex dimerizes through the oxygen atoms, forming a four-membered



ring. The 8-quinolinol moiety functions as a bidentate ligand and the coordination environment about the aluminum center is a distorted trigonal-bipyramid. The ¹H NMR spectrum indicates that the complex undergoes a conformational rearrangement in solution, removing the equivalence of the alkyl protons. This complex is reactive in both the solid state and solution to air and moisture.

Introduction

Recently, we reported the synthesis of a series of aluminum alkyl complexes of tetradentate Schiff base ligands having both nitrogen and oxygen donor atoms [1]. These compounds are to our knowledge the first examples of tetradentate non-macrocyclic aluminum mono-alkyls, and bridge the gap between simple chelate complexes and the aluminum alkyl macrocyclic compounds previously reported. Aluminum alkyl compounds have been prepared with three macrocyclic ligands: tetraphenylporphyrin (TPP), cyclam and the $\text{C}_{22}\text{H}_{22}\text{N}_4$ dianion [2–4]. These compounds all exhibit remarkable stability to hydrolysis both in the solid state and in moist solvents. The $[\text{C}_{22}\text{H}_{22}\text{N}_4]^{2-}$ and cyclam complexes are stable in hydroxylic solvents [3, 4] and the cyclam species can be recrystallized from water [4]. The tetradentate Schiff base aluminum alkyl complexes have a greater degree of reactivity than the macrocyclic systems, but also resist hydrolysis

in the solid state [4]. In solution, the susceptibility of the aluminum carbon bond to protonolysis depends on the nature of the ligand, but is still a slow process as compared with the hydrolysis of simple aluminum alkyl systems. In the tetradentate Schiff base system, the reactivity of the aluminum ethyl bond is directly related to the flexibility of the ligand environment and appears unrelated to the aluminum–carbon bond length. Thus, the observed stability is attributed to kinetic, rather than thermodynamic considerations.

In both the macrocyclic and tetradentate Schiff base ligand systems, the ligand donor atoms adopt a planar conformation about the metal center. The overall coordination geometry about the aluminum center is approximately square pyramidal with the alkyl moiety occupying the apical position with an ‘empty’ site *trans* to the alkyl group. This lack of an available coordination site adjacent to the ethyl group may contribute to the lessened reactivity of the aluminum–carbon bond.

In an extension of the above research, an aluminum alkyl complex with the bidentate 8-quinolinol ligand has been prepared. While 8-quinolinol also contains both nitrogen and oxygen donor atoms, the inherent increased flexibility of a bidentate chelate complex should contribute to an increased reactivity of the aluminum–carbon bond if our previous conclusions concerning the ligand are correct. Also, the aluminum center is not constrained by ligand requirements to adopt a square-pyramidal configuration, allowing the coordination geometry about the aluminum to approximate trigonal-bipyramidal. A structural and reactivity study of this complex should further elucidate the role that coordination geometry and ligand flexibility play in affecting the reactivity of the aluminum–carbon bond.

Experimental

Materials

Triethylaluminum (93%) and 8-quinolinol were purchased from the Aldrich Chemical Company

and were used without further purification. All solvents were reagent grade and were dried and purified before use.

Synthesis



In a typical preparation, 1.2 ml of a 1.0 M solution of $Al(C_2H_5)_3$ in benzene (1.2 mmol) was placed in a deaerated test tube which was sealed with a serum cap. To this was added a deaerated solution of 29 mg of 8-quinolinol (0.20 mmol) dissolved in 2.0 ml of benzene via a syringe through the serum cap. The reaction is exothermic and the system was vented to allow escape of the ethane formed. The solution was heated to boiling for several minutes until the volume was reduced by 50%. On standing, pale yellow air-sensitive needle-like crystals were produced. The crystals were collected and maintained under a nitrogen atmosphere.

Physical Measurements

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer between 4000 and 500 cm^{-1} as Nujol mulls on NaCl plates. ^1H NMR spectra were recorded on a Bruker/IBM 270 MHz spectrometer equipped with variable temperature capabilities.

Growth and Selection of X-ray Data Crystals

X-ray quality single crystals were obtained directly from the reaction mixture. The pale yellow square needles are air and moisture sensitive and are visibly decomposed after a two hour exposure to the atmosphere. They also react with the epoxy resin frequently used to mount crystals. Consequently, the crystal was sealed in a glass capillary for data collection. Visual examination revealed that the crystals have a strong tendency to twin along the long needle axis. The crystal chosen for data collection was a cleaved twin crystal, approximately $0.3 \times 0.2 \times 0.4\text{ mm}^3$.

Collection and Reduction of the X-ray Diffraction Data

The diffraction data were obtained on an Enraf-Nonius CAD-4 diffractometer controlled by a Digital PDP 11/34 computer with the use of graphite monochromatized $Mo\ K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at room temperature. The unit cell parameters and orientation matrix were refined by least-squares fit of the position of 25 reflections in the range of $15 \leq 2\theta \leq 30^\circ$. The preliminary study showed the crystal belongs to the monoclinic crystal system and the space group was uniquely determined by the systematically absent reflections and found to be $P2_1/c$. Data were collected in the $+h, +k, \pm l$ quadrant. Details of data collection are summarized in Table I. The crystal alignment and degree of

TABLE I. Data Collection Parameters

Formula	$Al_2C_{26}H_{32}N_2O_2$
Molecular weight	458.5
Crystal system	monoclinic
Space group	$P2_1/c$
Crystal color	pale yellow
a (Å)	18.132(3)
b (Å)	9.784(5)
c (Å)	15.191(2)
β ($^\circ$)	112.06(1)
V (Å ³)	2497.6(22)
Z	4
D_{calc} (g/cm ³)	1.219
Radiation	$Mo\ K\alpha$
Diffractometer	Enraf-Nonius CAD-4
Absorption coefficient (cm ⁻¹)	1.356
Scan speed ($^\circ$ /min)	2
2θ Scan range ($^\circ$)	2–40
Scan technique	$\theta - 2\theta$
Data collected	2632
Unique data	1794
Unique data with $I > 2\sigma$	1496
Data/Parameters ($I > 1\sigma$)	6.2
R (%) (F_o)	8.4
R_w (%) (F_o)	8.3

deterioration were monitored by the periodic measurement of three standard reflections. No significant intensity deviations were observed. The data were corrected for Lorentz and polarization effects, but no correction for absorption was necessary ($\mu = 1.356$).

Solution and Refinement of the Structure

The structure was solved by direct methods using MULTAN 78 [5]*. The initial MULTAN solution located both 8-quinolinol groups of the dimer and both aluminum atoms. The ethyl carbon atoms were located from a difference Fourier map. The structure was refined by successive block-diagonal least-squares and Fourier techniques. Full-matrix least-squares techniques were used in the final cycles of refinement where anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atom positional coordinates were calculated assuming idealized geometries and standard C–H bond distances of 0.95 Å; their thermal parameters were fixed at 5.0. Hydrogen atoms were fixed at their calculated positions and were included in structure factor calculations, but were not refined. Table II lists the positions of all non-hydrogen atoms with their standard deviations. The final weighted and unweighted R indices are 8.3 and

*All computations were performed on a PDP 11/34 computer with the aid of the Structure Determination Crystallographic Program Library purchased with the Enraf-Nonius X-ray crystallographic system.

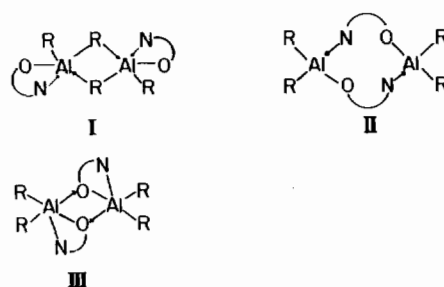
TABLE II. Positional Parameters for Non-hydrogen Atoms

Atom	x	y	z
Al	0.3308(1)	0.1051(2)	0.7093(2)
Al2	0.1772(1)	0.1481(3)	0.5291(2)
O1	0.2354(2)	0.0205(5)	0.6347(3)
O2	0.2706(3)	0.2354(3)	0.6055(4)
N1	0.3462(3)	-0.0920(7)	0.7741(4)
N2	0.1653(3)	0.3375(5)	0.4564(5)
C1	0.2817(4)	-0.1712(10)	0.7297(6)
C2	0.2211(3)	-0.1121(9)	0.6543(5)
C3	0.1526(4)	-0.1821(10)	0.6042(6)
C4	0.1470(4)	-0.3190(9)	0.6318(8)
C5	0.2062(4)	-0.3775(6)	0.7060(8)
C6	0.2763(4)	-0.3067(7)	0.7587(8)
C7	0.3400(5)	-0.3569(7)	0.8331(8)
C8	0.4068(5)	-0.2810(6)	0.8781(8)
C9	0.4054(5)	-0.1439(8)	0.8431(6)
C10	0.4245(6)	0.0885(9)	0.6765(6)
C11	0.4233(7)	-0.0222(8)	0.6071(10)
C12	0.3260(6)	0.2098(6)	0.8160(8)
C13	0.3938(6)	0.2047(8)	0.9097(8)
C14	0.2287(4)	0.4210(8)	0.4992(7)
C15	0.2865(4)	0.3642(8)	0.5822(5)
C16	0.3506(5)	0.4386(7)	0.6316(5)
C17	0.3607(5)	0.5738(9)	0.6018(7)
C18	0.3059(4)	0.6274(7)	0.5227(6)
C19	0.2382(4)	0.5561(9)	0.4703(6)
C20	0.1751(4)	0.5967(7)	0.3866(6)
C21	0.1147(4)	0.5153(12)	0.3413(6)
C22	0.1104(4)	0.3823(9)	0.3792(7)
C23	0.0812(4)	0.1725(10)	0.5551(7)
C24	0.0753(7)	0.2825(10)	0.6141(11)
C25	0.1753(4)	0.0313(9)	0.4208(6)
C26	0.0942(5)	-0.0013(9)	0.3512(6)

8.4%, respectively for data with intensities greater than 1σ . With a 2σ cutoff, the weighted and unweighted R values were 7.6 and 6.3%. A final difference Fourier map was essentially featureless with no peaks greater than $0.20 e/\text{\AA}^3$.

Results and Discussion

$[\text{Al}(\text{8-quinolinol})(\text{C}_2\text{H}_5)_2]_2$ is synthesized by mixing benzene solutions of 8-quinolinol and triethylaluminum in a stoichiometric ratio under an inert atmosphere. Reduction of the volume results in the precipitation of pale yellow air-sensitive needles. This compound was first synthesized by Hurley and co-workers 20 years ago using a similar procedure in their study of a variety of aluminum complexes with nitrogen and oxygen containing bidentate ligands [6]. Molecular weight determination in benzene showed that the 8-quinolinol complex mentioned above is dimeric. While our investigation of this complex also indicates a dimeric species, the reported structural assignment, which was based



Scheme 1. Possible structures for $[\text{Al}(\text{8-quinolinol})(\text{C}_2\text{H}_5)_2]_2$.

on elemental analysis, the molecular weight determination, and infrared and ^1H NMR spectroscopy, is in error. The possible structural arrangements that the 8-quinolinol dimer complex can adopt are presented in Scheme 1. Structure II was originally proposed by Hurley's group, but we have determined that structure III best fits the data. The 8-quinolinol functions as a bidentate ligand with the oxygen atom bridging to a second aluminum center yielding a five-coordinate geometry and not tetrahedral as assumed by Hurley. Since changes in coordination number affect infrared spectra, this may have contributed to Hurley's difficulty with the structural assignment. Our structural assignments are based on both high resolution ^1H NMR and X-ray diffraction, techniques that were not readily available in 1966.

Description of the Solid State Structure

The crystal structure of $[\text{Al}(\text{8-quinolinol})(\text{C}_2\text{H}_5)_2]_2$ reveals a dimeric molecule with the aluminum centers associated through the bridging oxygens of the 8-quinolinol moieties. An ORTEP drawing of the structure with the atom designations is depicted in Fig. 1. The four-membered $(\text{Al}-\text{O})_2$ ring is unsymmetrical with aluminum-oxygen distances of 1.865(9) \AA for the chelate bond and 1.998(10) \AA for the bridging bond. Each aluminum atom is penta-coordinate, forming a distorted trigonal-bipyramid. The equatorial plane is composed of the two Al-C bonds and the shorter Al-O bond of the monomer unit. The nitrogen atom of the chelated 8-quinolinol group and the oxygen atom from the 8-quinolinol unit of the other monomer complex complete the coordination sphere, although at $151.2(4)^\circ$ and $152.1(4)^\circ$, the N-Al-O angles are far from linear. Selected interatomic distances and angles are presented in Tables III and IV, respectively.

Coordination Geometry

The average aluminum-carbon distance of 1.957(15) \AA is of the same order as observed for other alkyl-aluminum complexes. The Al-C bond distance for a variety of compounds is presented

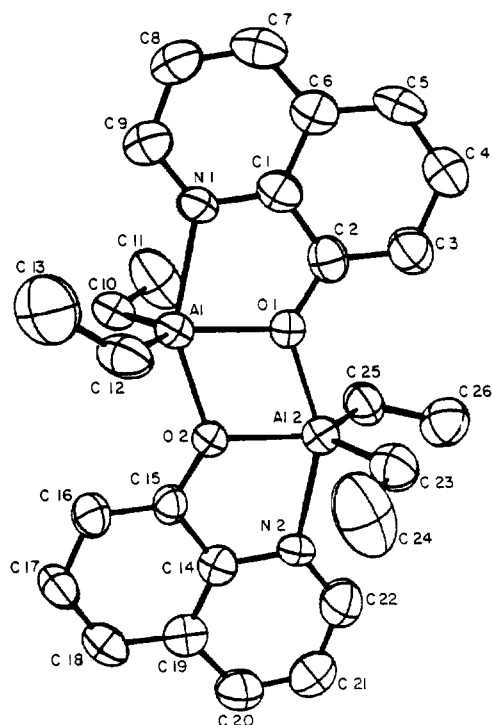


Fig. 1. An ORTEP diagram of $[\text{Al}(\text{8-quinolinol})(\text{C}_2\text{H}_5)_2]_2$, with labeling scheme illustrating the dimerization through bridging oxygen atoms.

TABLE III. Bond Distances for $[\text{Al}(\text{8-quinolinol})(\text{C}_2\text{H}_5)_2]_2$

Bond	Distance	Bond	Distance
Al-O1	1.868(9)	Al2-O1	1.994(10)
Al-O2	2.002(9)	Al2-O2	1.863(9)
Al-N1	2.136(9)	Al2-N2	2.126(10)
Al-C10	1.949(13)	Al2-C23	1.939(14)
Al-C12	1.946(14)	Al2-C25	1.993(14)
O1-C2	1.377(13)	O2-C15	1.369(12)
N1-C1	1.352(14)	N2-C14	1.360(14)
N1-C9	1.291(15)	N2-C22	1.296(16)
C1-C2	1.381(17)	C14-C15	1.416(16)
C1-C6	1.412(16)	C14-C19	1.424(14)
C2-C3	1.372(17)	C15-C16	1.337(16)
C3-C4	1.418(18)	C16-C17	1.432(17)
C4-C5	1.357(19)	C17-C18	1.345(17)
C5-C6	1.404(17)	C18-C19	1.376(17)
C6-C7	1.368(21)	C19-C20	1.411(18)
C7-C8	1.365(21)	C20-C21	1.319(18)
C8-C9	1.439(17)	C21-C22	1.437(19)
C10-C11	1.501(22)	C23-C24	1.430(21)
C12-C13	1.492(22)	C25-C26	1.487(19)

in Table V. As was mentioned above, the complex contains two different Al-O bond distances of 1.866(9) (chelate) and 1.998(10) (bridging) Å. These values fall within the range of distances given for a variety of Al-O compounds presented in Table VI. The average Al-N distance of 2.131(10) Å is

TABLE IV. Selected Coordination Sphere Bond Angles

Al-O1-Al2	107.5(4)	Al-O2-Al2	107.3(4)
O1-Al-O2	72.4(4)	O1-Al2-O2	72.7(4)
O1-Al-N1	79.0(4)	O1-Al2-N2	152.1(4)
O2-Al-N1	151.2(4)	O2-Al2-N2	79.4(4)
O1-Al-C10	120.4(5)	O1-Al2-C23	99.1(5)
O1-Al-C12	114.7(5)	O1-Al2-C25	98.3(5)
O2-Al-C10	97.0(5)	O2-Al2-C23	119.5(5)
O2-Al-C12	98.0(5)	O2-Al2-C25	120.5(5)
N1-Al-C10	93.9(4)	N2-Al2-C23	94.3(5)
N1-Al-C12	97.5(5)	N2-Al2-C25	96.0(5)
C10-Al-C12	124.9(6)	C23-Al2-C25	120.0(5)

substantially longer than that observed for most aluminum nitrogen complexes, regardless of coordination number. The Al-N(cyclam) distance in the six-coordinate $[\text{Al}(\text{cyclam})(\text{C}_2\text{H}_5)(\text{CH}_3\text{CN})]^{2+}$ species is 2.020(7) Å [4]. While the Al-N distance in this complex is constrained by the macrocyclic nature of the ligand, the average distances in the more flexible four-coordinate *cis* $[\text{Al}(\text{CH}_3)_2\text{NHi-Pr}]_2$ and in the five-coordinate μ -oxo aluminum bis 2-methyl-8-quinolinol are 1.950(8) Å [16] and 2.085(15) Å [17], respectively. The Al-N distance in the title complex is also somewhat longer than the sum of the covalent radii (2.05 Å) [18] indicating a weak bonding interaction which may contribute to the observed (*vide infra*) reactivity of this complex. This bond length is, however, substantially shorter than the 2.320(7) Å reported for the weakly coordinated acetonitrile of the six-coordinate $[\text{Al}(\text{cyclam})(\text{C}_2\text{H}_5)(\text{CH}_3\text{CN})]^{2+}$ species.

Description of the Solution Structure

In the solid state, the alkyl groups coordinated to each aluminum are bisected by the plane composed of the four-membered Al-O ring and both 8-quinolinol groups (see Figs. 1 and 3). This arrangement provides an identical coordination environment for all four alkyl groups and thus only one type of methylene resonance should be observed in the ^1H

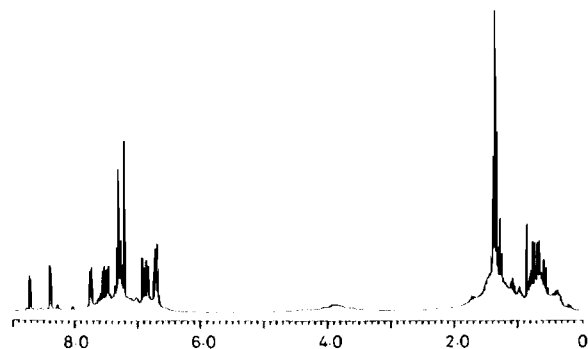


Fig. 2. The 270 MHz ^1H NMR spectrum of $[\text{Al}(\text{8-quinolinol})(\text{C}_2\text{H}_5)_2]_2$ in benzene.

TABLE V. Comparison of Aluminum Alkyl Bond Distances in Selected Compounds

Complex	Al-C distance (Å)	Reference
[Al(8-quinolinol)(C ₂ H ₅) ₂] ₂	1.957(15)	this work
Al ₂ (CH ₃) ₆ -terminal C	1.970	7
Al(C ₂₂ H ₂₂ N ₄)C ₂ H ₅	1.976(3)	3
Al(cyclam)C ₂ H ₅ ·CH ₃ CN	2.01(1)	4
Al(salen)C ₂ H ₅	1.966(7)	1
[(CH ₃) ₂ AlOCPPhNPh·CH ₃ CHO] ₂	1.97, 2.02	8
[{Al(C ₂ H ₅) ₂] ₂ (DPP) ₂ CH ₂] ₂ Cl ^a	1.949(4), 1.959(4) 1.964(7), 1.974(4)	9

^aDPP = diphenylphosphine.

TABLE VI. Comparison of Al-O Bond Distances in Organo Aluminum Compounds

Compound	Al-O distance (Å)	Reference
[(CH ₃) ₂ AlOC(Ph)N(Ph)]ON(CH ₃) ₃	1.77(7), 1.815(8)	10
K[Al(CH ₃) ₂ (OPh) ₂]	1.79(2)	11
[N(CH ₃) ₄][Al(CH ₃) ₃ CH ₃ COO]	1.83(1)	12
Al(CH ₃) ₂ (ONNCH ₃ O)Al(CH ₃) ₃	1.881(6), 1.909(6), 2.004(6)	13
[As(CH ₃) ₄][Al(CH ₃) ₂ OAl(CH ₃) ₃] ₂	1.78(2), 1.80(2)	11
[(CH ₃) ₂ AlOCH ₃] ₃	1.851(3)	14
[(CH ₃) ₂ AlOC(Ph)N(Ph);CH ₃ CHO] ₂	1.868(6), 1.966(6), 2.047(7)	15

NMR spectrum. In their study, Hurley and co-workers saw no splitting of the alkyl resonances in a 60 MHz field. With a 270 MHz spectrometer, however, we obtain the spectrum shown in Fig. 2. Inspection of the methylene region (upfield from 1.0 ppm) clearly indicates two overlapping quartets of equal intensity centered at 0.75 and 0.65 ppm, assigned to the -CH₂ group. The methyl group appears as a single triplet at 1.35 ppm. Two slightly different chemical environments for the ethyl groups must exist in solution. For stereochemically non-rigid systems, there need not be a direct correlation between the solid state and solution structures as different forces are involved. Crystal packing forces play a major role in determining the solid state structure when energy differences between different solution conformations are small. The more energetically favorable configuration in solution is not necessarily the one that crystallizes. To account for the observed inequivalence of the alkyl groups, dissolution of the 8-quinolinol dimer complex in benzene must produce a configurational change in the molecule. A proposed solution species consistent with the ¹H NMR spectrum is shown schematically (Fig. 3) along with that of the solid state structure for comparison purposes. In the solid state, the Al-N bond, which is rather long, occupies the axial coordination site of a distorted trigonal-bipyramid. On dissolution, this bond could break, leaving a four-coordinate aluminum center which

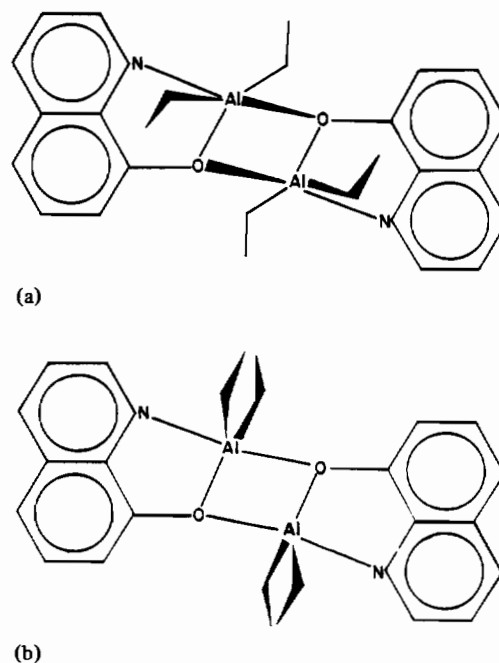


Fig. 3. Schematic representation of the proposed solution conformation (a), and the solid state structure (b), of [Al(8-quinolinol)(C₂H₅)₂]₂.

may rearrange towards a more tetrahedral environment. The nitrogen could then re-coordinate to the aluminum in the equatorial position, forcing

one of the ethyl groups to shift to the axial position. This would provide two different types of coordination sites for the ethyl groups; one axial and one equatorial. (Since trigonal-bipyramidal complexes are often fluxional [19], the same solution configuration could possibly be achieved without breaking the Al–N bond. The dynamics of the rearrangement process could not readily be followed on the NMR time-scale.) From a bonding perspective, the proposed solution species should be the more stable configuration. Typically in trigonal-bipyramidal structures, the most electronegative element or group occupies the apical coordination position. While a nitrogen atom has a higher electronegativity than a carbon atom, the alkyl group actually has a higher electron affinity than the nitrogen of the 8-quinolinol moiety, which functions as a Lewis base. Thus, placing the nitrogen in the equatorial position should reduce strain on the molecule.

Reactivity of the Al–C Bond in [Al(8-quinolinol)(C₂H₅)₂]₂

As indicated previously, the aluminum–carbon bond in this complex is intermediate in reactivity between that of both the tetradentate Schiff base and macrocyclic systems, but not nearly as reactive as monodentate aluminum alkyl species. This complex is also more stable than the diethyl zinc–nickel SALEN adduct recently characterized [20].

Compared with the mono-alkyl aluminum complexes of four-coordinate tetradentate ligand systems, this bidentate system has an enhanced reactivity in both the solid state and in solution. On exposure to moist air, crystals of this complex visibly decompose within a few hours. After a six hour exposure, no active ethyl group remains; addition of concentrated HCl fails to produce the bubbles associated with ethane formation. The ¹H NMR spectrum of the solid compound exposed to air over a three day period has resonances corresponding to alkoxide formation (quartet at 3.65 ppm assigned to the –CH₂ group and a triplet at 0.93 ppm assigned to the –CH₃ group). The upfield quartets which are indicative of an aluminum–carbon bond are replaced by quartets between three and four ppm, the usual alkoxide region. Thus, the oxygen has inserted into the Al–C bond.

As expected, the bidentate 8-quinolinol complex was also more reactive in solution than the mono-alkyl aluminum complexes derived from four-coordinate Schiff base and macrocyclic systems. Solutions of the complex react with dissolved oxygen, as monitored by NMR. The ¹H NMR spectrum of these solutions exhibit ethyl resonances between three and four ppm, indicative once again of alkoxide formation. These solutions also react with traces of moisture in solution, but due to the complexity of the spectra, we are unable to definitively assign

a solution species. On standing the methylene quartet region in deaerated solutions shows the gradual growth of an upfield quartet and the spectrum also indicates the formation of ethane. Presumably, the dialkyl complex is reacting with moisture in solution, producing a hydroxide species. Replacement of an alkyl group with the hydroxyl group would result in a decreased electron density on the aluminum; deshielding the methylene protons on the remaining alkyl group. Reactivity studies of solutions of the title complex with CS₂ or CH₃CHO produces changes in the alkyl region of the ¹H NMR spectra indicating some interaction with the aluminum center, but there is no indication of carbonyl or thio-carbonyl insertion into the aluminum–alkyl bond.

Conclusions

The reaction of 8-quinolinol with triethylaluminum produces [Al(8-quinolinol)(C₂H₅)₂]₂. The complex dimerizes, forming a four-membered (Al–O)₂ ring and the coordination geometry about the aluminum center is a distorted trigonal-bipyramid. This contradicts a previous report which assumed a tetrahedral aluminum coordination environment and a bridging linkage through both the nitrogen and oxygen atoms of the 8-quinolinol molecule [6]. The molecule undergoes a configurational rearrangement in solution, removing the solid state equivalence of the environments about the alkyl groups.

The complex is highly reactive in both the solid state and in solution. Crystals of the complex decompose rapidly (within a few hours), reacting with both moisture and oxygen. This behavior contrasts with the mono-alkyl aluminum tetradentate Schiff base and macrocyclic systems reported previously [1–4]. These systems react slowly with moisture, and no reaction with oxygen has been observed. The aluminum–carbon bond length in the 8-quinolinol complex is comparable to other aluminum alkyl complexes (see Table III) and thus, the greater reactivity of this bidentate complex must be related to kinetic rather than thermodynamic factors. With the tetradentate ligands, the reactivity of the complex was determined to depend on the flexibility of the ligand. The ligand environment about the aluminum in this system is considerably less constrained than the planar tetradentate systems. Also, any loss of an alkyl group is not accompanied by the formation of a high energy square-planar intermediate aluminum species. Instead, the aluminum is free to distort to the more favorable tetrahedral environment. Thus, the kinetic pathways for loss of the alkyl group have a low activation barrier and the complex is quite reactive. The bidentate 8-quinolinol ligand does provide an increased stability

for the complex as compared with monodentate aluminum alkyl systems.

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