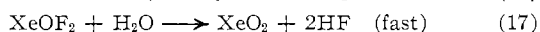
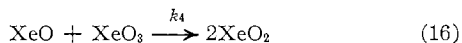
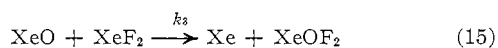


This mechanism could be tested by examining the reactions of XeF_2 and XeO_3 with H_2O_2 . Detailed studies of these reactions are now underway and will be published separately. Preliminary results, however, are not quantitatively consistent with the identification of intermediate A as hydrogen peroxide.

An alternate possibility is that A is the hydrolyzed divalent xenon species, to which we must then attribute reducing properties. In that case, after formation of the hydrolyzed species by rate-determining reaction 10, we may write



followed by reaction 14. The lack of xenon exchange between XeF_2 and XeO_3 rules out reversibility of reaction 16. The H_2O_2 remaining after reaction of XeF_2 with water could arise from a side reaction of XeO or XeO_2 with the solvent, while benzenesulfonic acid could be oxidized by either the XeO or the XeO_2 .

These reaction schemes can hardly be considered unique, but a tetravalent xenon species appears to be an essential intermediate in any satisfactory mechanism, while a hydrolyzed divalent species, though not essential, seems highly probable.

At this time we can say little about the effect of changes in the medium on the stoichiometry of the XeF_2 - XeO_3 reaction (Table II). In all cases the consumption of XeO_3 is decreased, indicating a change in the nature of the reducing intermediate or in its reactivity or both. The lack of a strong H^+ dependence is consistent with either of our proposed mechanisms, but in alkaline solution the situation is complicated by the oxidation of XeO_3 to perxenate by the XeF_2 .² It is worthy of note that when the oxidation of water by XeF_2 is catalyzed by Th^{4+} , no XeO_3 is consumed. At the time it is being reduced, the divalent xenon may be coordinated to the thorium through a fluoride bridge and therefore may be unable to attack an XeO_3 molecule.

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Alkyl- and Arylaluminum Complexes. I. The Reaction of Trialkyl- and Triarylaluminum with Bidentate Ligands

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A series of dialkyl- and diarylaluminum complexes have been prepared through the reactions of trialkyl- and triarylaluminum compounds with bidentate ligands featuring hydroxyl and amino functional groups. The dimeric nature of these compounds is explained on the basis of stereochemical considerations and nmr and infrared spectroscopy, upon which evidence it is concluded that, in all but one case, bridging occurs through the terminal oxygen and nitrogen atoms of the bidentate ligands. The exception is diethylaluminum 3-aminopropoxide, in which bridging occurs through the oxygen bonded to the metal ion.

Introduction

While there have been extensive investigations pertaining to the reactions of triaryl- and trialkylaluminum compounds with alcohols¹ and amines,² relatively few studies have been reported concerning the interaction of such aluminum compounds with chelating agents containing both of these functional groups. In fact, whereas there have been recent reports of the preparation of dialkylaluminum complexes of bis-oxygen bidentate ions such as acetylacetonate³ or diphenylphosphinate,⁴ the only well-documented ex-

ample of aluminum, featuring oxygen and nitrogen bonding, is aluminum tris-8-quinolinate.⁵ Several types of aluminum complexes with nitrogen- and oxygen-containing bidentate ligands are reported herein together with the structural elucidation of these compounds.

Results and Discussion

In the interests of comparing stabilities, characteristics, and stereochemistry, we have prepared a series of dialkyl- and diarylaluminum complexes with bidentate ligands featuring hydroxyl and amino functional groups. The empirical formula of the series is R_2Al -

(1) F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958).

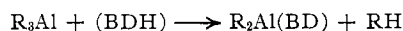
(2) H. C. Brown and N. R. Davison, *J. Am. Chem. Soc.*, **64**, 316 (1942).

(3) B. Bogdanovic, *Angew. Chem. Intern. Ed. Engl.*, **4**, 954 (1965).

(4) G. Coates and R. Mukherjee, *J. Chem. Soc.*, 1295 (1964).

(5) J. E. Tackett and D. T. Sawyer, *Inorg. Chem.*, **3**, 692 (1964).

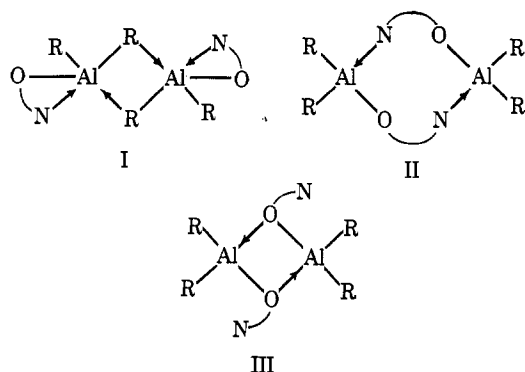
(BD), where BD = 8-quinolate, $O(CH_2)_nNH_2$, or $O(CH_2)_nN(CH_3)_2$ ($n = 2$ or 3), and $R = CH_3$, C_2H_5 , $i-C_4H_9$, or C_6H_5 . The general reaction is illustrated schematically as



by which the combinations below have been synthesized. Molecular weight determinations of benzene

R	BD
CH_3 , C_2H_5 , $i-C_4H_9$, C_6H_5	$OCH_2CH_2NH_2$
C_2H_5	$OCH_2CH_2N(CH_3)_2$
C_2H_5	$OCH_2CH_2CH_2NH_2$
C_2H_5	$OCH_2CH_2CH_2N(CH_3)_2$
CH_3 , C_2H_5 , $i-C_4H_9$, C_6H_5	OC_6H_5N

solutions showed these compounds to be dimeric. Solubility limitations prevented experimental verification of three compounds (see Experimental Section) but it has been assumed that their molecularity will conform to that of the other members of the series. On the basis of elemental analyses and the molecularity of these compounds, three possible arrangements may be proposed (I, II, III), where ON = a potentially



bidentate ligand and $R = CH_3$, C_2H_5 , $i-C_4H_9$, or C_6H_5 . Structure I is plausible in light of our knowledge of alkyl bridging in aluminum chemistry, but nuclear magnetic resonance studies preclude its existence in solution through the following argument. Nuclear magnetic resonance studies of trimethyl-⁶ and triethylaluminum⁶ have shown that, as the temperature is lowered, the exchange between terminal and bridging alkyl groups is slowed. At -40° a splitting of the methylene resonance into two series of bands is observed, differentiating between the two types of alkyl groups. Application of this method to the compounds we are reporting herein failed to indicate any splitting of resonance bands down to -80° (see Table I), implying that there is only one type of alkyl group, which must be terminal since it is stereochemically impossible to have four alkyl groups bridged between two aluminum atoms.

Further corroboration is found in a study of the infrared spectra of the methyl derivatives of the compounds in question. Gray⁷ has reported that trimethylaluminum and chlorodimethylaluminum both exhibit an absorption in the $720\text{--}700\text{-cm}^{-1}$ range which arises from the Al-C stretching vibration. An addi-

(6) K. C. Ramey, J. F. O'Brien, I. Hasegawa, and A. E. Borchert, *J. Phys. Chem.*, **69**, 10, 3418 (1965).

(7) A. P. Gray, *Can. J. Chem.*, **41**, 1512 (1963).

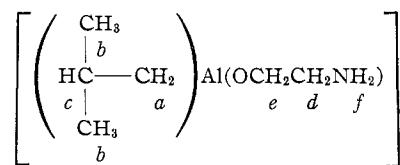
TABLE I

Chem shift (δ)	Splitting pattern			Intens
	[[$(CH_3CH_2)_2AlOCH_2CH_2NH_2$] ₂]			
	b	a	d c e	
a -0.08	Quartet		7.6 Hz	4
b 1.22	Triplet		7.6 Hz	6
c 2.01	Quintet		~5.5 Hz	2
d 3.28	Triplet		5.4 Hz	2
e ~0.90	Broad peak			2

Solvent, benzene; reference, tetramethylsilane

Chem shift (δ)	Splitting pattern					Intens
	[[$(CH_3CH_2)_2AlOCH_2CH_2CH_2NH_2$] ₂]					
	b	a	d	c e f		
a -0.078	Quartet			7.5 Hz	4.0	
b 1.01	Triplet			7.6 Hz	Indeterminate	
c Between 0.6 and 1.4	Indeterminate				Indeterminate	
d 3.41	Triplet			~5.2 Hz	2.0	
e 1.89	Broad multiplet				2.1	
f Between 0.6 and 1.4	Indeterminate				Indeterminate	

Note: total intensity of b, c, and f is 10. Solvent, benzene; reference, tetramethylsilane.



a -0.25	Doublet		6.7 Hz	4
b 0.90	Doublet		6.0 Hz	12
c Between 2.1 and 3.2	Indeterminate			Indeterminate
d 2.86	Quintet		6.0 Hz	2
e 3.63	Triplet		~5.5 Hz	2
f Between 2.1 and 3.2	Indeterminate			Indeterminate

Note: Total intensity of c and f is 3. Solvent, $CDCl_3$; reference, tetramethylsilane

tional band at 780-cm^{-1} , evident in the spectrum of trimethylaluminum but not in that of chlorodimethylaluminum, is a result of the Al-C-Al bridge. Since chlorodimethylaluminum is bridged through the chlorine atoms, not through the alkyl groups,⁸ this latter band would obviously be absent. The infrared spectrum of dimethylaluminum 2-aminoethoxide shows a band in the $720\text{--}700\text{-cm}^{-1}$ region but none in the vicinity of 780-cm^{-1} . The same holds true for dimethylaluminum 8-quinolate; four bands, due to the quinolate ring, appear in this region (Table II), but they would not obscure the Al-C-Al band if it were present. The results of infrared spectroscopy confirm that all of the methyl groups are terminal and, therefore, dimerization of these complexes must result from bridging through the bidentate ligand.

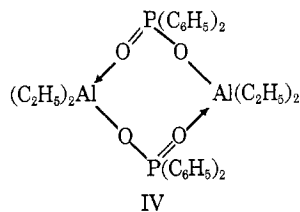
The remaining structures (II and III) both have counterparts which have been reported in the literature. Thus, diethylaluminum diphenylphosphinate,⁴ a dimeric eight-membered ring compound (IV), arises by bonding through two sites on the ligand molecule (analogous to II). In contrast to this is diethylaluminum 2-methoxyethoxide. Here, coordination

(8) G. P. van der Kelen and M. A. Herman, *Bull. Soc. Chim. Belges*, **65**, 362 (1956).

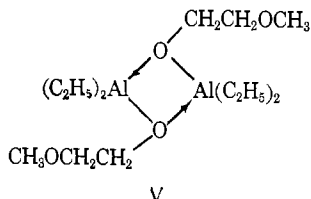
TABLE II
 INFRARED ABSORPTIONS IN THE 820-750-CM⁻¹ REGION^a

No.	Compound	Absorptions in 820-750-cm ⁻¹ region	Al-O-Al band
1	Trimethylaluminum	780 m ^b	...
2	Triethylaluminum
3	Triisobutylaluminum	818 m, 770 m ^b	...
4	Triphenylaluminum	769 vw, 742 w, sh	...
5	Diethylaloxane ¹²	...	755-770 vs, 790-815 vs
6	Diethylaloxane ¹²
7	Chloroethylaloxane ¹²	...	755-770 vs, 780-821 vs
8	Diethylaluminum ethoxide	...	820 w
9	Ethylethoxyaloxane ¹²	...	820 vs
10	Methyldichloroaluminum
11	2-Aminoethanol
12	Dimethylaluminum 2-aminoethoxide
13	Diethylaluminum 2-aminoethoxide
14	Diisobutylaluminum 2-aminoethoxide	815 m ^b	...
15	Diphenylaluminum 2-aminoethoxide
16	8-Quinolinol	820 m, 810 w, 783 s, 740 s ^c	...
17	Dimethylaluminum 8-quinolate	825 s, 812 w, 787 s, 750 vs ^c	...
18	Diethylaluminum 8-quinolate	825 s, 810 m, 789 s, 750 vs ^c	...
19	Diisobutylaluminum 8-quinolate	827 s, 810 m, 790 s, 754 s ^c	...
20	Diphenylaluminum 8-quinolate	830 s, 812 m, 792 s, 748 s ^c	...
21	2-Dimethylaminoethanol	855 w, 772 w, 752 w	...
22	Diethylaluminum 2-dimethylaminoethoxide	792 m, 772 w, sh	<i>d</i>
23	3-Aminopropanol
24	Diethylaluminum 3-aminopropoxide	...	820 m
25	3-Dimethylaminopropanol	840 m, 770 vw, 750 vw	...
26	Diethylaluminum 3-dimethylaminopropoxide	840 m, sh, 830 m, 770 m	<i>d</i>

^a vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. ^b Owing to alkylaluminum skeletal vibration. ^c Owing to phenyl group. ^d No definitive assignment could be made.



and bridging occur on the same site⁹ giving rise to a four-membered ring (V) which is analogous to III.



The preference for the four-membered ring can be readily understood when one compares the donor strength of the oxygen attached to the metal to that of the oxygen bonded between two carbons. The donor strength of the former is so enhanced because of the electropositivity of the metal ion that it coordinates with that ion in preference to the other available oxygen in the ligand.^{9,10} An extreme case of this type of behavior is found in the reaction of trimethylgallium with 2-dimethylaminoethanol, where, owing to the electropositive nature of the gallium ion, bridging occurs through the oxygen, in preference to the amino nitro-

gen, giving rise to a four-membered chelate ring.¹¹ However, although the effect of the metal ion cannot be minimized, the deciding factor may be the steric requirements of the multimembered ring as well as the thermodynamics involved therein.

In the complexes reported herein, only diethylaluminum 3-aminopropoxide appeared to form the four-membered ring; the other complexes contained ten-membered chelate rings with the possible exception of diethylaluminum 2-dimethylaminoethoxide and diethylaluminum 3-dimethylaminopropoxide, where no decision as to the configuration could be made. Structural elucidation was based on elemental analyses (Table III), molecular weight determinations (Table III), and infrared and nmr spectroscopy. The molecular formula obtained from elemental analyses and molecular weight determinations was verified by nmr spectroscopy (Table I) by which the expected proton ratios were established.

A comparison of the infrared spectra, in the 820-750-cm⁻¹ region, of the compounds under discussion with those reported for appropriate aloxanes^{12,13} (Table II) can be employed to show the presence or absence of the Al-O-Al bridge, thus distinguishing between the two possible structures (II, III). If bridging occurs through the oxygen, an intense absorption, tentatively assigned by Laubengayer and Storr¹² to the Al-O-Al stretch, should appear in the 820-750-cm⁻¹ region.

(9) E. G. Hoffmann, *Ann.*, **629**, 104 (1960).

(10) G. E. Coates and D. Ridley, *J. Chem. Soc., Sect. A*, 1064 (1966).

(11) G. E. Coates and R. G. Hayter, *J. Chem. Soc.*, 2519 (1953).

(12) A. W. Laubengayer and A. Storr, private communication.

(13) E. G. Hoffmann, *Z. Elektrochem.*, **64**, 616 (1960).

TABLE III
 CHEMICAL AND PHYSICAL DATA FOR THE COMPLEXES

Compound	Mp, °C, or bp, °C (mm)	Mol wt		Elemental analysis							
		Theory, dimer	Found	Calcd, %				Found, %			
				C	H	N	Al	C	H	N	Al
Dimethylaluminum 8-quinolate	330 dec	402	Insol	65.7	6.0	7.0	13.4	64.2	6.0	7.4	...
Diethylaluminum 8-quinolate	262	458	463	68.1	7.0	6.1	11.8	68.3	6.9	6.0	11.6
Diisobutylaluminum 8-quinolate	190	570	547	71.6	8.5	4.9	9.5	70.8	8.4	4.0	...
Diphenylaluminum 8-quinolate	330 dec	650	Insol	77.5	5.0	4.3	8.3	75.2	5.0	4.0	...
Dimethylaluminum 2-aminoethoxide	175	234	233	41.0	10.3	12.0	23.1	41.0	10.4	11.7	...
Diethylaluminum 2-aminoethoxide	105	290	284	49.6	11.1	9.7	18.6	49.4	11.2	9.9	19.0
Diisobutylaluminum 2-aminoethoxide	130	402	407	59.8	11.9	7.0	13.4	59.1	11.8	7.6	...
Diphenylaluminum 2-aminoethoxide	240 dec	482	Insol	69.7	6.6	5.8	11.2	67.8	6.6	6.3	...
Diethylaluminum 2-dimethylaminoethoxide	66	346	355	55.5	11.6	8.1	7.8	53.0	11.6	8.5	...
Diethylaluminum 3-dimethylamino- propoxide	176 (0.6 mm)	374	372	57.7	11.8	7.5	14.5	57.3	11.9	7.3	14.8
Diethylaluminum 3-aminopropoxide	75	318	315	52.9	11.3	8.8	17.0	53.1	11.2	9.0	16.7
Aluminum acetylacetonate di-8-quinolate	300	412 ^a	415	66.7	4.6	6.8	6.5	66.8	4.6	6.7	...

^a Theory for the monomer.

The absence of this absorption denies the existence of oxygen bridging between the two metal ions. In the cases where oxygen bridging is known to occur (no. 5, 7, 8, and 9 of Table II), absorptions in this region are noted; where oxygen bridging is precluded (no. 2, 6, and 10 of Table II), no Al-O-Al stretching vibration appears. In several cases the absorptions appearing in this area are due to Al-C skeletal vibrations (no. 1, 2, and 4 of Table II). The metal-oxygen-metal stretching vibrations for other metal ions also have been shown to fall in this region,¹⁴⁻¹⁶ so the Al-O-Al absorptions fit right into line.

An extension of this approach to the compounds reported herein shows that all members of the dialkylaluminum 2-aminoethoxide series (no. 12-15 of Table II) show no absorption in the 820-750-cm⁻¹ region and are, therefore, assigned structure II. The series of dialkylaluminum 8-quinolates (no. 17-20 of Table II) all have four bands in the aforementioned region but they are vibrations of the 8-quinolinol ring which have been slightly shifted to higher wavelengths owing to complexation. Since no other absorption is noted, bridging must be through the nitrogen atom (II). The spectrum of diethylaluminum 3-aminopropoxide (no. 24 of Table II) exhibits a broad absorption at 820 cm⁻¹ which does not appear in the spectrum of the free ligand. Consequently, the structure of this species is assumed to involve oxygen bridging between the two aluminum ions (III). It should be pointed out that a

modification of structure III, involving coordination of the nitrogen atoms as well as oxygen bridging, is a distinct possibility.

Attempts to resolve whether the amino nitrogen was quaternary or tertiary, by nmr techniques, were unsuccessful because of the masking of the NH₂ peaks by certain aliphatic proton patterns (see Table I). We have demonstrated that the amino groups can be quaternized by treatment with methyl iodide, as evidenced by the shifting of NH₂ stretching vibrations from 3350 and 3200 to 3200 and 3100 cm⁻¹, respectively. It is recognized that this chemical behavior is not conclusive, since it is possible that quaternization by methyl iodide may be occurring through the rupture of an existing N→Al coordinate bond.

The structures of the remaining two complexes, diethylaluminum 2-dimethylaminoethoxide (no. 22 of Table II) and diethylaluminum 3-dimethylamino-propoxide (no. 26 of Table II), could not be determined because of the complicated absorption pattern shown by the free ligands.

The fact that these species bridge rather than chelate is, at first, unexpected in view of the greater entropy of 2 moles of chelated monomer as compared to 1 mole of bridged dimer. Further, the aluminum tris-8-quinolate and aluminum tris-2-aminoethoxide derivatives are both monomeric in benzene, a behavior which appears to be in contradiction in the dimeric nature exhibited by dialkylaluminum 8-quinolate and dialkylaluminum 2-aminoethoxide analogs. A plausible explanation for this divergence of behavior lies in the steric requirements of the central aluminum atom and

(14) D. C. Bradley and A. H. Westlake, *Nature*, **191**, 273 (1961).

(15) R. C. Poller, *J. Inorg. Nucl. Chem.*, **24**, 593 (1962).

(16) M. Cousins and M. H. L. Green, *J. Chem. Soc.*, 1567 (1964).

its relation to the size of the chelate ring. If one considers a regular pentagon containing only carbon-carbon bonds, all of the angles are 108° . Substitution of any oxygen or nitrogen atom or inclusion of double bonds does not result in severe perturbations because the bond lengths and, consequently, the angles, are not altered to a great extent. However, incorporation of an aluminum atom in the five-membered ring results in significant strain due to the increased bond length. As a direct result, a tetrahedral aluminum atom with its angular requirements would not, under ordinary circumstances, be accommodated, whereas an octahedral aluminum atom is able to form a five-membered ring, albeit with some degree of strain. This would serve to explain why aluminum tris-8-quinolate is a chelated monomer, while members of the dialkylaluminum 8-quinolate are bridged dimers. The former contains an aluminum surrounded by an octahedral array, whereas the aluminum atoms in the latter compounds are tetrahedral. Identical conclusions result from a comparison of aluminum tris-2-aminoethoxide with dialkylaluminum 2-aminoethoxide analogs.

A somewhat analogous pattern is found with regard to six-membered rings. Here again, strain results upon the incorporation of a tetrahedrally directing aluminum atom into the six-membered ring, but the distortion is significantly less than with a five-membered cycle because of the angle requirements. Consequently, although the bridged arrangement is still preferred as demonstrated by the dialkylaluminum complexes of 3-aminopropanol and *N,N*-dimethylaminopropanol, the chelated arrangement will result when stabilized by extensive π interaction. Consequently, dialkylaluminum acetylacetonate derivatives are monomeric in benzene.

It is also of interest to compare the stabilities of the six-membered rings containing octahedrally and tetrahedrally bonded aluminum, respectively. On the basis of molecular models, one would predict that the ring containing the aluminum in an octahedral environment would be the less strained, and, consequently, the more stable. This is borne out in several ways. We have observed that if diethylaluminum acetylacetonate is permitted to stand in benzene for a period of time, disproportionation occurs, with the resultant formation of aluminum acetylacetonate. Further indication of the greater stability of the six-membered ring involving an octahedrally bonded aluminum is found in the reaction of the dimeric dialkylaluminum 8-quinolate derivatives with acetylacetone. The resulting product, aluminum acetylacetonate bis-8-quinolate, is monomeric in benzene and undoubtedly involves a central atom surrounded by ligands arranged in an octahedral array. There is no indication of any bridge product.

In summary, one may conclude that five-membered rings involving tetrahedrally bonded aluminum in conjunction with atoms of the first period are sterically not preferred; six-membered rings containing tetrahedral aluminum are strained although they will form

if stabilized by extensive π conjugation. Aluminum in an octahedral environment is stable either in a five- or six-membered ring system.

Experimental Section

Reagents.—Trimethyl-, triethyl-, and triisobutylaluminum were obtained from Ethyl Corp. and used without further purification. Triphenylaluminum was obtained from Orgmet Corp. and used as received. The aminoalcohols (Eastman Organic Chemicals) were distilled over calcium sulfate. All solvents were purified and stored over lithium aluminum hydride. 8-Hydroxyquinoline (Mallinckrodt Chemical Corp.) was used as received.

Synthesis.—Since the preparations of most of the compounds of the dialkylaluminum complex type employ essentially the same procedure, only the synthesis of dimethylaluminum 8-quinolate will be described in detail. Table III shows pertinent chemical and physical data for all compounds synthesized.

Preparation of Dimethylaluminum 8-Quinolate.—A solution of 7.2 g of trimethylaluminum (0.1 mole) in 250 ml of dry benzene was placed in a 1-l. three-necked flask under an atmosphere of nitrogen. The reaction flask was equipped with a dropping funnel and a reflux condenser which contained an outlet through an oil bubbler to a wet-test meter. The solution of 14.5 g of 8-quinolinol (0.1 mole) in 100 ml of dry benzene was added dropwise with stirring. The product, which precipitated from the reaction solution while approximately 0.1 mole of gas was evolving, was filtered under a nitrogen atmosphere, washed with benzene, and dried under vacuum. The insolubility of this product prevented recrystallization.

Modifications.—Of the other aluminum 8-quinolates prepared, the diphenyl derivative was also too insoluble to recrystallize. Diethyl- and diisobutylaluminum 8-quinolates were recrystallized from benzene.

In the preparation of the aminoalkoxide complexes, the pure ligand was added directly to a benzene solution of trialkylaluminum. The dimethylaluminum 2-aminoethoxide was recrystallized from benzene; the diethyl- and diisobutylaluminum 2-aminoethoxide and the diethylaluminum 2-dimethylaminoethoxide were recrystallized from petroleum ether (bp $30-60^\circ$). The diphenylaluminum 2-aminoethoxide was so insoluble that recrystallization could not be effected. Diethylaluminum 3-dimethylaminopropoxide was isolated as a liquid and was purified by distillation under reduced pressure. Diethylaluminum 3-aminopropoxide is isolated as a waxy solid from benzene; however, if petroleum ether (bp $30-60^\circ$) is used as the solvent, the material is isolated as a microcrystalline powder.

All reactions proceeded readily at ambient temperature except those involving triphenylaluminum. In the latter cases, it was necessary to reflux the benzene solutions for 1 hr to facilitate complete reaction.

Preparation of Aluminum Acetylacetonate Di-8-quinolate.—A solution of triethylaluminum (23.0 g, 0.2 mole) in 250 ml of dry benzene was prepared in a drybox. To this solution was added a solution of freshly distilled butanol (29.6 g, 0.4 mole) in 50 ml of dry benzene over a period of 1 hr. The reaction temperature was held at $40-50^\circ$. The volume of evolved ethane, measured with a wet-test meter, indicated that monoethyl-di-butoxyaluminum ($C_2H_5Al(OC_4H_9)_2$) had formed. A solution of acetylacetone (20.0 g, 0.2 mole) in 50 ml of dry benzene was added dropwise. No precipitate formed. A solution of 8-hydroxyquinoline (58.0 g, 0.4 mole) in 100 ml of dry benzene was then added and a yellow solid formed. The solution was filtered and the solid was isolated. It was recrystallized from ether and dried under vacuum.

Note: the bis-8-quinolinato derivative results irrespective of the stoichiometry of the reactants, and excess of either ligand is recovered either unchanged or in the form of the corresponding tris-aluminum derivative.

Elemental analyses are recorded in Table III.

Molecular Weights.—The molecular weight determinations

were obtained cryoscopically in benzene. A No. 8163B platinum resistance thermometer and a Mueller temperature bridge, Leeds and Northrup Model No. 8069, were used to measure the temperature differences. The results are listed in Table III.

Spectra.—Temperature-dependent nuclear magnetic resonance spectra were obtained on a Varian A-60R high-resolution spectrometer. The spectra were run in deuteriochloroform down to -60° and in toluene down to -80° . Proton nuclear magnetic spectra were obtained on a Varian A-60 spectrometer. Tetramethylsilane was used as a standard. Results are listed in Table I.

A Perkin-Elmer Model 21 spectrophotometer was used to obtain the infrared spectra. Mulls of Nujol and Fluorolube were employed for the solids. Solution spectra were obtained in benzene and methylene chloride. The results are listed in Table II.

Melting Points.—Melting points (Table III) were obtained on a Perkin-Elmer Model DSC-1 differential scanning calorimeter under an argon atmosphere.

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Nuclear Resonance Studies of Vanadium(III) Complexes. I. Stereochemistry and Electron Delocalization of Tris β -Diketonates

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The isotropic proton hyperfine contact shifts of a series of five tris(β -diketonate)vanadium(III) complexes, $V(R_\alpha COCR_\beta CO R_\gamma)_3$, have been measured in order to determine structures in solution and to define qualitatively the mode of unpaired spin delocalization predominantly responsible for these shifts. In addition to the known complexes $V(acac)_3$ ($R_\alpha = R_\gamma = CH_3$, $R_\beta = H$) and $V(mmm)_3$ ($R_\alpha = R_\beta = R_\gamma = CH_3$), three complexes having unsymmetrical chelate rings, $V(mhh)_3$ ($R_\alpha = R_\beta = H$, $R_\gamma = CH_3$), $V(mmh)_3$ ($R_\alpha = H$, $R_\beta = R_\gamma = CH_3$), and $V(tfac)_3$ ($R_\alpha = CH_3$, $R_\beta = H$, $R_\gamma = CF_3$), all prepared for the first time, were examined. The *cis* and *trans* isomers of the latter three complexes are readily detected by virtue of their considerably different contact interactions. The isomers of $V(tfac)_3$ are not formed in statistical amounts. From consideration of the signs of the contact shifts of protons and methyl groups of the chelate rings and by comparison of these shifts with calculated spin density distributions for the ligands treated as π radicals, it is concluded that metal-to-ligand parallel spin transfer is the principal mode of spin delocalization. The contact shifts of solutions of $V(H_2O)_3^{3+}$ have been measured and the results interpreted in terms of ligand-to-metal parallel spin transfer by π bonding.

Introduction

A recent investigation of the proton magnetic resonance spectra of paramagnetic tris acetylacetonates by Eaton³ has revealed that of all trivalent ions of the first transition series, vanadium(III) produced the narrowest line width of the chelate ring methyl signal (~ 25 cps at 60 Mc). The observation of nuclear resonances in complexes such as these indicates that $1/T_1 \gg A_i$, the usual criterion for such observation in paramagnetic compounds,⁴ where T_1 is the electronic relaxation time of the coordinated metal ion and A_i is the electron-nuclear coupling constant for the i th nucleus. While T_1 for a given metal ion is certainly dependent upon the details of its structural and electronic environment, Eaton's observation implies that reasonably well-resolved nuclear resonance spectra might be obtainable for vanadium(III) complexes simi-

lar to acetylacetonates, and possibly for vanadium(III) complexes in general.

Compared to the paramagnetic complexes of other metals,⁵ especially those of Co(II) and Ni(II), there have been only a few reports of the nuclear resonance spectra and attendant isotropic contact shifts of vanadium(III) complexes, or of paramagnetic vanadium complexes in any other formal oxidation state. Contact shifts have been observed for polycrystalline vanadocene⁶ and for vanadocene⁷ and 1,1'-dimethylvanadocene⁸ in solution, and the proposed interpretation⁹ of the contact shifts in vanadocene has recently been questioned.⁸ In one of the earliest demonstrations by nuclear resonance of spin delocalization in metal complexes, Forman, Murrell, and Orgel¹⁰

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