TABLE I

MAGNETIC RESULTS AND INFRARED DATA ON THE COMPLEXES

Compd	Formula	χ, cgs/g $\times 10^6$	NO stretch, cm^{-1}	Relative conductivity
A-1	$[Co(C_2H_5N)_4NO]Cl_2 \cdot H_2O$	−0.18	1630	...
A-2	$[Co(C_2H_5N)_4NO](NO_3)_2$	−0.32	1645	...
A-3	$[Co(C_2H_8N_2)_2NO](NO_3)_2$	+0.04	1645	...
A-4	$[Co(C_2H_8N_2)_2NO](ClO_4)_2$	...	1660	194[a]
A-5	$[Co(C_5H_5N)_4NO](ClO_4)_2$	...	1700	...
A-6	$[Co(C_6H_8N_2)_2NO](ClO_4)_2$	+0.05	1690	160[a]
B-1	$[Co(C_7H_9N)_2(NO)_2]ClO_4$	+0.16	1770, 1850	114[b]
B-2	$[Co(C_6H_7N)_2(NO)_2]ClO_4$	−0.13	1770, 1850	114[b]
B-3	$[Co(C_{18}H_{15}P)_2(NO)_2]ClO_4$	−0.16	1800, 1850	100[b]

[a] Compared to $CaCl_2$ (as 162) at same concentration. [b] Compared to $NaClO_4$ (as 102) and NaI (as 80) at same concentration.

Compounds A-4 and A-6 had conductivities in the range expected for a 2:1 electrolyte; other A class compounds gave erratic conductivity results—possibly due to decomposition. Compounds of class B had conductivities in the range expected for a 1:1 electrolyte.

The compounds are deeply colored, ranging from red-brown to black. It was difficult to obtain satisfactory electronic spectra.

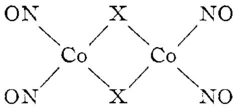
Discussion

The infrared spectra and conductivities suggest that the nitrate and perchlorate anions are not in the coordination sphere. Therefore we have given the name and coordination sphere assignments to be found in the Experimental Section and in Table I.

The compounds reported (with one exception) are new, but they are not without precedent. Booth and Chatt[8] prepared compounds $CoX_2(NO)[P(C_2H_5)_3]_2$, where X = Cl, Br, or I. These may be analogous to our class A complexes; however, the ligands are different and the anions are in the coordination sphere.

After completion of our study, the paper by Feltham and Nyholm[9] was published. In only one case (A-4) was a compound of similar stoichiometry made by both groups. Their data have been interpreted in terms of a polymer with six-coordination about the cobalt atom.

Our class B complexes may be related to the dimeric



(black, diamagnetic crystals) of formula $CoXL(NO)_2$, molecules with X = Cl, Br, or I and to the monomers where L can be phosphines, arsines, stibines, or secondary amines, prepared by Hieber and co-workers.[10,11]

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[8] G. Booth and J. Chatt, *J. Chem. Soc.*, 2099 (1962).

[9] R. D. Feltham and R. S. Nyholm, *Inorg. Chem.*, **4**, 1334 (1965)

[10] W. Hieber and W. Beck, *Z. Naturforsch.*, **13b**, 194 (1958).

[11] W. Hieber and K. Heincke, *ibid.*, **14b**, 819 (1959); **16b**, 553 (1961).

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Aluminum-27 Nuclear Magnetic Resonance Studies of Sodium Fluoride–Aluminum Alkyl Complexes

BY HAROLD E. SWIFT AND JOHN F. ITZEL, JR.

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Aluminum compounds of the general formula $AlR_{3-N}X_N$ (N = 2–0) will react with certain alkali metal salts to form complex compounds of the types $MX \cdot AlR_3$ and $MX \cdot Al_2R_6$ where M is the metal, X can be hydrogen, halogen, etc., and R is an alkyl such as C_2H_5.[1] The ability to form such complexes depends on several factors such as the size of the alkali and halide ions and the nature of the organoaluminum compound. For example, the tendency of the alkali halides to add to aluminum alkyls increases with the size of the alkali ions and decreases with that of the halogen ions. The stabilities of these complex compounds also decrease as the size of the alkyl group bonded to the aluminum increases.[1]

These complexes are of industrial importance. For example, they can be used for the separation of aluminum alkyls from materials such as olefins and hydrocarbons,[2-5] they can be used as electrolytes for the electroplating of metal objects with aluminum,[6] and they can be used as a source of highly reactive alkyl radicals which can in turn be used in the synthesis of compounds such as tetraethyllead.[7]

This note reports the results of Al^{27} nuclear magnetic resonance (nmr) line-width measurements of several sodium fluoride–aluminum alkyl complexes.

Experimental Section

The Al^{27} nmr measurements were made on a Varian V-4200-A wide-line nmr spectrometer, a Varian 31-cm electromagnet, and a V-2100 power supply. A Varian V-FR2100 Fieldial was used to regulate and scan the magnetic field. A BC-221-D Bendix Radio Corp. frequency meter and Fieldial were used to calibrate and measure the line widths. Temperature at the sample was monitored by passing controlled current through an electric heater in a gas stream directed to the sample in the probe. A resistance-type temperature sensor, near the sample, monitored the gas stream temperature. The temperature control loop was closed around the controller, heater, gas stream, and sensor. The temperatures at the actual sample position were precalibrated with thermocouple and potentiometer. Line widths were measured at 10.0 Mcps and at a magnetic field strength near 9000 gauss. The first derivative of the resonance absorption was recorded using audio modulation (40 cps) of the magnetic field, and the peak-to-peak modulation amplitudes used were between 0.1 and 0.5 gauss. The absorption mode resonances were

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[1] H. Zeiss, "Organometallic Chemistry," American Chemical Society Monogram No. 147, Reinhold Publishing Corp., New York, N. Y., 1960, pp 199, 200.

[2] K. Ziegler, German Serial Patent 1,153,369 (1963).

[3] W. R. Kroll, U. S. Patent 3,153,075 (1964).

[4] W. B. Carter and J. A. Acciarri, Canadian Patent 696,867 (1964).

[5] Reference 1, p 231.

[6] K. Ziegler, Belgian Patent 540,411 (1955).

[7] "Metal-Organic Compounds," Advances in Chemistry Series, No. 23, American Chemical Society, Washington, D. C., 1959, p 167.

recorded at a radiofrequency field strength of approximately 100 mgauss.

The aluminum alkyls were obtained from Texas Alkyls Inc. and were used as received. Sodium fluoride was obtained from Fisher (Certified reagent). The sodium fluoride was heated for 4 hr at 400° under vacuum (10^{-6} torr) and then transferred to an nmr tube in a nitrogen-controlled-atmosphere glove box. The nmr tubes had been previously baked at 130° for at least 24 hr and then dried under a nitrogen atmosphere.

The tubes were approximately 20 cm long and the inside diameter was 8 mm. The tubes had a side arm with a stopcock so that nitrogen could be flushed through the tube. After the metal fluoride compound was added, a syringe cap was used to seal the tube. The sample tube was then taken from the drybox and reweighed to obtain the weight of the metal fluoride; then the required amount of aluminum alkyl was added with a hypodermic syringe and needle. The mixture was then heated to ~130° until all of the metal fluoride disappeared and the resulting hot liquid contained one visible phase. All of the complexes studied were very viscous liquids at room temperature. During the reaction, the stopcock on the side arm was opened and dry nitrogen was flushed through the tube. The same procedure was used when the nmr spectra were obtained at elevated temperatures.

Results and Discussion

Line Widths of the Complexes.—Variable-temperature Al^{27} nuclear magnetic resonance line-width measurements were carried out on the complexes formed by the reaction of sodium fluoride with triethylaluminum, $Al(C_2H_5)_3$; tri-*n*-propylaluminum, $Al(C_3H_7)_3$; and tri-*n*-butylaluminum, $Al(C_4H_9)_3$. These $NaF \cdot 2AlR_3$ complexes are exceptional in that they can be studied at relatively high temperatures without boiling or decomposing. For convenience triethylaluminum, tri-*n*-propylaluminum, and tri-*n*-butylaluminum will be abbreviated as TEA, TNPA, and TNBA throughout the remainder of the paper.

The variable temperature Al^{27} nmr data obtained are given in Table I. As can be seen from the data, the line widths (ΔH) increase in the order $NaF \cdot 2TNBA > NaF \cdot 2TNPA > NaF \cdot 2TEA$ at a given temperature and decrease as the temperature increases for each complex.

TABLE I

Al^{27} NMR LINE WIDTHS (GAUSS) OF SODIUM FLUORIDE–ALUMINUM ALKYL COMPLEXES

Temp, °C	NaF· 2TEA	NaF· 2TNPA	NaF· 2TNBA	NaF· (TEA + TNBA)
102.0	...	...	...	18.4
110.5	...	13.2	29.7	13.5
119.0	6.70	11.3	23.5	11.5
127.5	5.95	9.7	18.4	...
136.0	4.90	8.5	13.0	8.1
144.0	4.50	7.7	11.2	...
152.0	4.05	7.2	9.7	6.8
160.0	3.80	...	...	...
168.0	3.45	...	...	...

A plot of log ΔH *vs.* $1/T$ shows that the line-width data fit the relationship[8,9]

$$\Delta H = \Delta H_0 e^{\Delta E/RT} \qquad (1)$$

where ΔE is the activation energy for nuclear relaxation, ΔH_0 is a constant, and R is the gas constant. The ΔE values obtained for the complexes and for pure TEA are given in Table II. The value of ΔE for pure TEA was determined from line-width data obtained over the temperature range −38 to +50°, whereas the ΔE values for the complexes were determined from line-width data obtained over the temperature range 110–150°. The increase in the value of ΔE as the size of the complexes increases is due in part to the increase in energy required for molecular reorientation.

TABLE II

ΔE VALUES FOR TEA AND $NaF \cdot 2AlR_3$ COMPLEXES

Complex	ΔE, kcal/mole
TEA	3.3
NaF·2TEA	4.5
NaF·2TNPA	5.1
NaF·2TNBA	9.1
NaF·(TEA + TNBA)	7.1

Variable-temperature Al^{27} nmr studies were previously carried out on the pure alkyls and it was found that at a given temperature the line widths are increased in the order TNBA > TNPA > TEA.[8] The line-width variations of the pure alkyls were found to be due to size and viscosity variations.

These terms are introduced by the correlation time (τ_c), which is given by Debye's formula

$$\tau_c = 4\pi\eta a^3/3kT \qquad (2)$$

where a is the effective molecular radius of the complex, k is Boltzmann's constant, T is the absolute temperature, and η is the viscosity. The line width ΔH is directly proportional to the correlation time. This relationship for the case of "extreme narrowing" has been discussed in detail elsewhere.[10]

The increase in line width from NaF·2TEA to NaF·2TNBA at a given temperature is probably due to the increase in the effective molecular radius. The same explanation was used to explain the increase in line width for the pure alkyls.[8]

The decrease in line width for the complexes as the temperature increases is probably due to a decrease in viscosity. A similar line width–viscosity or line width–temperature relationship has also been reported for several pure alkyls.[8]

However, until reliable viscosity and density data are obtained, it is impossible to make definite conclusions as to what extent the line width of these complexes obeys the simple Debye relationship.

At a given temperature the line width of a sodium fluoride–aluminum alkyl complex is much greater than that of the corresponding uncomplexed alkyl. This increase is due to increases in the viscosity and effective molecular radius. Also, considerable line broaden-

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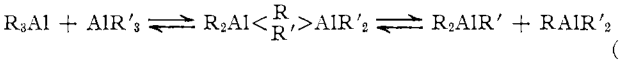
(8) C. P. Poole, Jr., H. E. Swift, and J. F. Itzel, Jr., *J. Phys. Chem.*, **69**, 3663 (1965).

(9) The use of the $\Delta H = \Delta H_0 e^{\Delta E/RT}$ relationship is discussed by D. E. O'Reilly and G. E. Schacher, *J. Chem. Phys.*, **39**, 1768 (1963).

(10) C. P. Poole, Jr., H. E. Swift, and J. F. Itzel, Jr., *ibid.*, **42**, 2576 (1965).

ing will occur upon complexing because of increased quadrupolar interaction of the aluminum nucleus with the molecular electric field gradients.[11]

Alkyl Interchange.—A rapid alkyl interchange on mixing two different aluminum alkyls has been postulated[12] and verified experimentally by Al^{27} nmr.[10] Such an exchange probably results because of the equilibria



$$R_3Al + AlR'_3 \rightleftharpoons R_2Al\langle{}^{R}_{R'}\rangle AlR'_2 \rightleftharpoons R_2AlR' + RAlR'_2 \quad (3)$$

It has been found that an equimolar mixture of TEA and TNBA added to NaF exhibits an Al^{27} nmr line width intermediate to the line widths of the NaF·2TEA and NaF·2TNBA complexes at a given temperature and at all power levels (see Table I). This would only be expected if an alkyl interchange took place upon mixing the TEA and TNBA resulting in a $NaF \cdot 2AlR_3$ complex containing mixed alkyl groups. A plot of the logarithm of the line width of the mixed complex as a function of the reciprocal of the absolute temperature shows that the data fit the relationship given by eq 1. From this relationship a ΔE value of 7.1 kcal/mole was determined, which is intermediate between the ΔE values determined for the NaF·2TEA and NaF·2TNBA complexes.

It has also been found that there is no alkyl interchange when two different $NaF \cdot 2AlR_3$ complexes are mixed. This has been shown by mixing 0.5 ml of NaF·2TEA with 2 ml of NaF·2TNBA, heating to 152°, and recording the Al^{27} nuclear magnetic resonance of the mixture. By successively lowering the modulation amplitude to 0.1 gauss, two fairly distinct resonances were obtained—a narrow line of 4 gauss which is due to NaF·2TEA and a broad line of 10 gauss which is due to the NaF·2TNBA complex.

Also, Al^{27} nmr was used to determine if any exchange takes place when TEA is mixed with NaF·2TNPA. At room temperature TEA forms a separate phase when added to NaF·2TNPA. Upon heating to 120° a single phase forms which exhibits two resonances—a narrow line due to TEA and a broad line corresponding to the NaF·2TNPA complex. Thus, there is very little, if any, exchange when TEA is mixed with NaF·2TNPA at 120° to form NaF·2TEA and TNPA.

All of the $NaF \cdot 2AlR_3$ complexes exhibited single, Lorentzian Al^{27} nmr line widths regardless of temperature. These results indicate that all of the aluminum nuclei are equivalent and support the proposed structure where an aluminum–fluorine–aluminum collinear bond exists[13] instead of the proposed structure, $Na^+[Al(C_2H_5)_3F]^- \cdot Al(C_2H_5)_3$, where the aluminum nuclei are not equivalent.[14] However, more refined techniques will have to be used to obtain conclusive proof of the structure of these liquid complexes.

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(11) D. E. O'Reilly, *J. Chem. Phys.*, **32**, 1007 (1960).

(12) Reference 1, p 208.

(13) G. Allegra and G. Perego, *Acta Cryst.*, **15**, 185 (1963).

(14) Reference 1, p 251.

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Chloride Ion Exchange with *trans*-Dichlorobis(pyridine)platinum(II) in Selected Solvents

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It has been shown[2] that in substitution reactions of square-planar platinum(II) complexes, nucleophilic reactions may be divided into two classes: (a) those that are first order in complex, zero order in nucleophile, and all of similar rate; (b) those that are first order in both complex and nucleophile and, in general, faster than those of class a. In the mechanism proposed for these reactions, it has been assumed that the solvent coordinates on the z axis above and below the primary ligand plane. In this fashion, the complex becomes six coordinate, with the magnitude of the solvent interaction assumed to be of great importance in determining the mechanistic route followed during substitution.

Pearson, Gray, and Basolo[3] have studied the rate of chloride ion exchange with *trans*-$[Pt(py)_2Cl_2]$ (py = pyridine) in a number of solvents. They proposed that the observed rates of chloride ion exchange in the various solvents are consistent with a mechanism based on strong interaction of the solvent with the metal complex in the rate-determining step. It was proposed that this strong interaction facilitates chloride ion displacement from the complex, enhancing the rate for the process that is zero order in chloride (*i.e.*, a slow ionization step followed by fast chloride attack). These authors again state that the reactions are first order in the platinum complex.

Previous work in this laboratory on the coordination model[4] treated anion displacement from metal ions by solvent. The thermodynamic cycle for this reaction contained an energy step for the gas phase reaction corresponding to the anion leaving the coordination sphere and the solvent entering. The enthalpy for this reaction is related to the difference in the donor strength of the anion and solvent. The difference in the ability of the solvent to solvate the products and starting materials (*i.e.*, without entering the coordination sphere) is related to the solvating ability of the solvent. The results of these studies for various nonaqueous solvents have led us to question whether the observed and proposed mechanisms could be attributed solely to solvent donor strength as reported[3] or could also be dependent on the solvating properties of the solvent media. By selecting solvents on the basis of both solvating properties and donor ability, a more

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(1) Abstracted in part from the Ph.D. Thesis of V. A. Mode, University of Illinois, 1965; National Science Foundation Graduate Fellowship, 1964–1965.

(2) D. Banerjea, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **79**, 4055 (1957).

(3) R. G. Pearson, H. B. Gray, and F. Basolo, *ibid.*, **82**, 787 (1960).

(4) R. S. Drago and K. F. Purcell, *Progr. Inorg. Chem.*, **6**, 217 (1965).