Anal. Calcd. for $B_3H_6(SC_2H_5)_3$: C, 32.5; H, 9.5; B, 14.6; S, 43.4; mol. wt., 222. Found: C, 33.0; H. 9.4; B, 14.5; S, 44.1; mol. wt., 223 (cryoscopic, benzene).

The infrared spectrum of $B_3H_6(SC_2H_5)_3$ had the following absorptions: 3000 (w), 2480 (s), 2420 (s), 2250 (w), 1450 (m), 1375 (m), 1265 (m), 1130 (m), 1110 (w), 1070/1040/1025 (s), 975 (m), 920 (w), 775 (w) cm.$^{-1}$.

$(C_2H_5SBH_2)_3$ was easily prepared in larger amounts as follows. The C_2H_5SH–B_2H_6 reaction was carried out in ether as described above using a 2:1 ratio of reactants. The product was then distilled in a molecular still at 1 μ or less at a pot temperature of less than 60° to give a 70% yield of the fluid trimer.

$(C_4H_9S)_2B_2H_4$.—A 500-ml. flask with side arm and magnetic stirrer was connected through a reflux condenser to a mercury leg and flushed with nitrogen. A solution of 49 ml. (0.45 mole) of 1-butanethiol in 50 ml. of absolute ether was stirred in the flask under nitrogen as 3.4 g. (0.126 mole) of diborane was introduced by a gas inlet just under the surface of the liquid. The addition took 2 hr., and a viscous solution resulted. After 16 hr., the volatiles were removed, and the viscous residue was distilled in a 24-in. spinning-band column. A viscous distillate (12–13 g.) was collected, b.p. 98° (1 mm.), n^{24}D 1.5153 (lit.[3] 98–102° (1 mm.), n^{20}D 1.5170). The viscous distillate became mobile after several hours.

Anal. Calcd. for $[BH(SC_4H_9)_2]_x$: C, 50.5; H, 10.1; B, 5.7; S, 33.7. Found: C, 50.4; H, 10.5; B, 6.7; S, 33.5.

A sample of this product was stirred with water for several hours. The white solid which formed (boric acid) was filtered off, and the filtrate was extracted with petroleum ether. The organic layer was dried and distilled under vacuum in a molecular-type still. Solvent was removed and a fluid liquid distilling at 90–100° at 3 μ was collected.

Anal. Calcd. for $(BH_2SC_4H_9)_3$: C, 47.1; H, 10.9; B, 10.6; S, 31.4; mol. wt., 305. Found: C, 47.8; H, 10.7; B, 10.9; S, 31.7; mol. wt., 301 (cryoscopic, benzene).

The infrared spectrum of this compound showed the following absorptions: 2960 (s), 2860 (s), 2470 (s), 2410 (s), 2245 (w), 1460 (m), 1428 (m), 1379 (m), 1275 (m) triplet, 1227 (w), 1130 (m), 1105 (m), 1040 (s), 980 (m), 910 (w), 875 (w), 785 (w), 745 (m), shoulder at 725 cm.$^{-1}$.

CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY,
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The Crystal Structure of Lithium Aluminum Tetraethyl[1a]

BY R. L. GERTEIS, R. E. DICKERSON, AND THEODORE L. BROWN[1b]

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The crystal structure of $LiAl(C_2H_5)_4$ has been determined by X-ray diffraction methods. The structure of the compound is analogous to that of dimethylberyllium and consists of linear chains of alternating lithium and aluminum. The locations of the ethyl groups are such that the structure can be largely accounted for in terms of Li^+ and $Al(C_2H_5)_4^-$ ions, although there is some evidence of weak covalent interaction involving lithium. The proton and lithium n.m.r. spectra in ether demonstrate that extensive dissociation into ethyllithium and triethylaluminum does not occur.

The concept of electron-deficient, or multi-center, bonding in covalent alkyl and hydride compounds of group I, II, and III elements is widely recognized.[2–6] For the most part, however, examples of such bonding are restricted to symmetrical cases of the form A–M$_n$, where A is the bridging atom (hydrogen or carbon) and M are the atoms joined by the multi-center bond (B, Be, Mg, Al, Li, etc.). Some asymmetry in the bridge bond may occur where M atoms, although of the same element, are in slightly different environments, as in the B–H–B bridge bonds in tetraborane-10.[3]

Lithium aluminum tetraethyl, $LiAl(C_2H_5)_4$, provides an example in which asymmetric bridge bonding joining two different elements may occur. As a naïve but suggestive way of viewing the compound, it may be compared with beryllium dialkyls. Dimethylberyllium in the solid state consists of linear chains of beryllium atoms joined by bridging carbon atoms. The arrangement of four carbon atoms about each beryllium is roughly tetrahedral. A similar structure may be predicted for lithium aluminum tetraethyl, with alternate atoms replaced by aluminum and the remainder by lithium. The bridge bonding in such a structure should be quite asymmetric, since aluminum possesses much greater bond-forming capacity than lithium. The structure may in fact approach a limiting ionic form of alternating Li^+ and AlR_4^- ions.

We report here the results of a study of lithium aluminum tetraethyl, undertaken with the above considerations in mind. Preparative procedures have been reported for both $LiAl(CH_3)_4$[8] and $LiAl(C_2H_5)_4$.[9] The ethyl derivative is more conveniently worked with and is more desirable also in that location of the β-carbon atom of the alkyl group provides very useful information.

Experimental

All preparative work involving metal alkyls and their solutions was carried out in an inert atmosphere glove box, under a

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(1) (a) Presented at the International Conference on Organometallic Chemistry, Cincinnati, Ohio, June, 1963; (b) Alfred P. Sloan Foundation Fellow. Address correspondence and requests for reprints to T. L. Brown.

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nitrogen atmosphere. Precautions were taken to obtain low water vapor and oxygen levels.[10]

Preparation and Preliminary X-Ray Examination.—Lithium aluminum tetraethyl ($LiAl(C_2H_5)_4$) is conveniently prepared by addition of a 0.1 *F* solution of triethylaluminum to an equivalent amount of ethyllithium in benzene. The desired compound precipitates as a rather gelatinous mass and is further purified by repeated recrystallizations from benzene. Well-formed crystals of suitable size (needles about 0.2 mm. thick) are obtained by slow crystallization from a benzene solution. The crystals were mounted in 1.0-mm. borosilicate glass capillaries which had previously been coated with a thin layer of Duco cement everywhere except for a small area for admittance of the X-ray beam. The coating is beneficial in reducing diffusion of oxygen and moisture into the capillary. After the crystal had been inserted, the capillaries were sealed with Apiezon wax.

X-Ray Data.—All photographic data were collected with the *c*-axis normal to the X-ray beam. Data were collected using a Buerger precession camera, with Zr-filtered Mo Kα radiation. Timed exposures of the $h0l$, $h1l$, $h2l$, hhl, $h(h+1)l$, and $h(h+2)l$ reciprocal planes were taken. Accurate unit cell dimensions were determined from a powder specimen using α-quartz as internal standard and employing Co Kα radiation.

The crystal is tetragonal, $a = 9.99 \pm 0.01$, $c = 5.411 \pm 0.005$ Å. Assignment to the space group $P4_2/nmc$, No. 137,[11a] is indicated by the following systematic absences among the reflections: $hk0$ with $h + k$ odd; hhl with l odd. It was not found possible to obtain accurate density measurements of the compound because of its great reactivity, but from the density of liquid triethylaluminum (0.837 g./ml.) and solid ethyllithium (0.883 g./cm.^{3}) it would appear that the density should be in the vicinity of 0.9 g./cm.^{3}. The behavior of the solid in benzene is that of a substance only slightly denser than the solvent. From these observations we conclude that $Z = 2$, which gives $d_{\text{calcd}} = 0.941$ g./cm.^{3}.

Intensity measurements were made with the aid of a Mark III double-beam automatic recording microdensitometer (Joyce Loebl and Co., Ltd.). Six separate sets of films were scaled by comparison of common reflections occurring in the linear range of the film, after applying Lorentz and polarization corrections. Employing only reflections with intensity values known to within 5%, the intensity ratios of common reflections between two films were averaged to obtain direct ratios. In this manner direct ratios were obtained for all pairs of films except for the $h(h+1)l$–hhl and $h(h+1)l$–$h(h+2)l$ pairs. Indirect ratios between these were obtained by scaling each member of the pair to a third reciprocal plane film. All possible ratios, direct and indirect, between films were thus obtained and averaged to yield final interfilm scaling constants. The estimated standard deviations of the scaling factors were in all cases less than 5%. Of a total of 300 reflections allowed by symmetry within the volume of reciprocal lattice examined, 212 possessed a measurable intensity.

Nuclear Magnetic Resonance Spectra.—Both the proton and ^7Li resonances of $LiAl(C_2H_5)_4$ were examined for the compound in ether solutions. Proton resonance spectra were obtained on a Varian Associates Model A-60 spectrometer. The ^7Li spectra were obtained as described elsewhere.[6] A 70% aqueous lithium bromide solution was employed as external standard by inserting a sealed 1-mm. capillary tube in the sample tube.

Determination of the Structure

For space group $P4_2/nmc$, with $Z = 2$, it is required that the lithium and aluminum atoms occupy special positions with $\bar{4}2m$ point symmetry. Their coordinates are completely determined with selection of the origin (Li: $^3/_4, ^1/_4, ^3/_4$; $^1/_4, ^3/_4, ^1/_4$; Al: $^3/_4, ^1/_4, ^1/_4$; $^1/_4, ^3/_4, ^3/_4$ with origin at $\bar{1}$.) The carbon atoms of the alkyl groups lie in two sets of eightfold positions, the site symmetry of which is m.

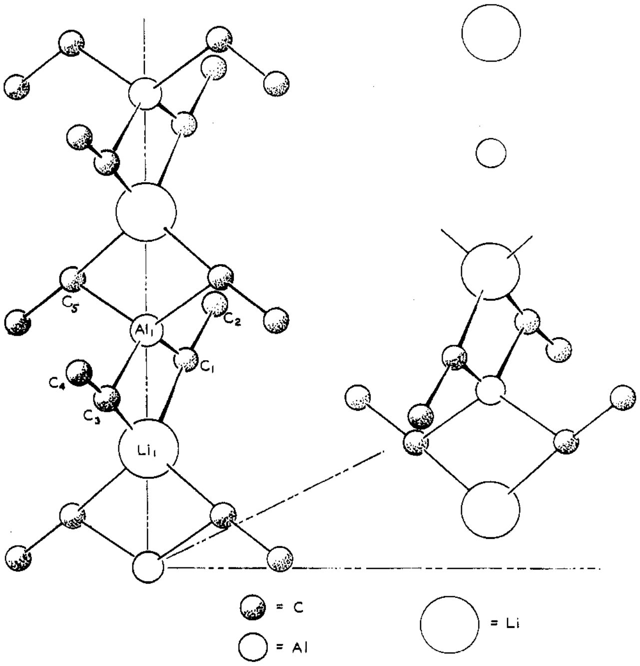

Fig 1.—A portion of the structure of $LiAl(C_2H_5)_4$, *c* axis vertical. The hydrogen atoms attached to carbon are not shown.

A Patterson vector map of the $h0l$ projection revealed the locations of the carbon atoms relative to Al and permitted assignment of a trial structure. From this, structure factor calculations with least-squares refinement were employed to refine thermal parameters for the metal atoms and both coordinates and thermal parameters for the carbon atoms.[12] A three-dimensional difference synthesis then revealed the locations of both methylene hydrogens, symmetrically disposed about the mirror plane (H_1), and two of the three methyl hydrogens, also symmetrically disposed about the mirror plane (H_2). The position of the third methyl hydrogen (H_3) was estimated. The isotropic temperature factor of the off-plane hydrogens is estimated to be 7.0 Å.^{2} and a value of 10 Å.^{2} is estimated for the in-plane hydrogen. With the estimated hydrogen positions and thermal parameters held fixed, the structure was refined through three cycles. The final parameters obtained are listed in Table I together with the standard deviations as computed in the least-squares program. It should be noted that the anisotropic temperature factors are of the form

$$\exp-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$$

Covalent atomic scattering factors were employed in the structure factor calculations.[11b] Values of F_o

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[10] T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instr.*, **33**, 491 (1962).

[11] (a) International Tables of X-Ray Crystallography, Kynoch Press, Birmingham, England, Vol. I, 1952, p. 237; (b) *ibid.*, Vol. III, 1962, p. 201.

[12] The Fourier summation program employed is a modified version of that of W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende ("Two and Three-dimensional Crystallographic Fourier Summation Program for IBM 7090 Computer"). We are indebted to Dr. Van den Hende for supplying us with a copy of this program. The structure factor and least-squares computations were performed with the program by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, "Structure Factor and Least Squares Refinement Program (UCLALS1)," University of California, Los Angeles, Calif., 1962.

TABLE I

ATOMIC POSITIONS AND THERMAL PARAMETERS FOR $LiAl(C_2H_5)_4$

Atom	Parameter	Value	σ	Atom	Parameter	Value	σ
Al_1	x	0.2500	...	C_2	x	0.5401	0.0007
	y	0.7500	...		y	0.7500	...
	z	0.7500	...		z	0.7099	0.0012
	B_{11}, B_{22}	0.0085	0.0002		B_{11}	0.1017	0.0007
	B_{33}	0.0120	0.0007		B_{22}	0.0307	0.0015
Li_1	x	0.2500	...		B_{33}	0.0401	0.0023
	y	0.7500	...		B_{13}	0.0064	0.0022
	z	0.2500	...	H_1	x	0.412	...
	B_{11}, B_{22}	0.0163	0.0017		y	0.658	...
	B_{33}	0.0132	0.0039		z	0.450	...
C_1	x	0.4180	0.0005		B	7.0	...
	y	0.7500	...	H_2	x	0.525	...
	z	0.5411	0.0009		y	0.658	...
	B_{11}	0.0074	0.0005		z	0.810	...
	B_{22}	0.0192	0.0009		B	7.0	...
	B_{33}	0.0243	0.0014	H_3	x	0.626	...
	B_{13}	0.0014	0.0014		y	0.750	...
					z	0.584	...
					B	10.0	...

above a threshold of $4F_o$ (min.) were weighted as $\sqrt{w} = 1/F_o$. Below this threshold all F_o values were given a weight of $^1/_4$. The value of R for the final structure, including all reflections, is 0.087.

The important interatomic distances and angles are listed in Table II, which is keyed to the numbering in Fig. 1. The estimated standard deviations were calculated from the formulas given by Cruickshank.[13]

TABLE II

INTERATOMIC DISTANCES AND ANGLES WITH ESTIMATED STANDARD DEVIATIONS

Distance	Value, Å.	σ	Angle	Value	σ
Al_1–C_1	2.023	0.006	C_3–Al_1–C_1	112.1°	0.6°
Al_1–Li_1	2.706	...	C_3–Al_1–C_5	108.2°	0.3°
Al_1–Li_2[a]	7.061	...	Al_1–C_1–C_2	109.2°	0.5°
C_1–C_2	1.523	0.012	Al_1–C_1–Li_1	77.2°	0.3°
C_1–C_3	3.360	0.011	C_1–Li_1–C_3	93.6°	0.3°
Li_1–C_1	2.302	...	Al_1–C_1–H_1[b]	105°	...
C_1–H_1[b]	1.04	...	C_1–C_2–H_2[b]	101°	...
C_2–H_2[b]	1.08	...	C_1–C_2–H_3[b]	105°	...
C_2–H_3[b]	1.10	...			

[a] This is the distance between chains, normal to the chain axes.
[b] See text for identification of the hydrogen atoms.

Discussion

The structure of lithium aluminum tetraethyl is shown in Fig. 1. A formal similarity with the structure of dimethylberyllium is quite evident. The $LiAl(C_2H_5)_4$ units are aligned in linear chains; a distance of about 7 Å. separates nearest-neighbor chains. It may be assumed that only van der Waals interactions exist between chains.

Despite the formal similarity with the dimethylberyllium structure, it seems quite clear that the alkyl groups are bonded predominantly to aluminum. The Al–C_1 distance of 2.02 Å. is to be compared with the terminal Al–C distances of 1.99 and 2.00 Å. in the trimethylaluminum dimer[2,14] and with the Al–C_1 distance of 2.00 Å. in $KF \cdot 2Al(C_2H_5)_3$.[15] The Al–C_1 bond is thus very little longer than the distances anticipated for a single Al–C bond. The Li–C_1 distance of 2.30 Å., on the other hand, is longer than the values observed in ethyllithium, 2.25 and 2.19 Å.[16] As a first approximation, therefore, the structure may be interpreted as consisting of alternating Li^+ and $Al(C_2H_5)_4^-$ ions.

There is evidence, however, which suggests that there may be some delocalization of the Al–C bonding electrons to include covalent bonding to lithium. The C_2–C_1–Al angle of 109° is somewhat smaller than one would expect if the bonding carbon atomic orbital were directed along the Al–C internuclear axis. ^{13}C–H coupling constant data for methyl derivatives of metals such as lithium or aluminum are characteristically low—in the range of 90–100 c.p.s. From empirical relationships which correlate the ^{13}C–H coupling constant with % s-character in the C–H bond,[17,18] it can be concluded that the s-character in the M–C bond is high, and correspondingly lower in the C–H or C–C bonds of a carbon atom attached to the metal. Assuming orthogonality of the orbitals employed by carbon, the M–C–H (or M–C_1–C_2) angle should be larger than the tetrahedral angle. Using the ^{13}C–H coupling constant found for trimethylaluminum, about 32% s-character is predicted for the carbon orbital employed in the Al–C bond. This value should be higher in the present case, since the aluminum is strongly bonded to four alkyl groups, and the effective nuclear charge presented to the bonding electrons is surely lower. From orthogonality considerations,[19] an angle of 112–114° is then expected between the C–C bond and the direction of the hybrid orbital directed from carbon toward aluminum. The observed C_2–C_1–Al angle is 109°; this means that the carbon orbital is probably directed 3–5°

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(17) N. Muller, *J. Chem. Phys.*, **36**, 359 (1962).
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off the internuclear axis and toward lithium. If the deviations from orthogonality observed by Juan and Gutowsky[18] are assumed to be operative in the present case, the angle is more like 8 to 10°.

The above argument indicates the possibility of some small degree of covalent bonding involving lithium. It is quite clear from the sharp C_1–Li–C_3 angle of 93.6°, however, that lithium does not employ all of its valence shell orbitals in such covalent bonding as may exist. As a tentative scheme, we suggest that lithium sp-hybrid orbitals directed along the chain axis may overlap to some extent with the aluminum and carbon atomic orbitals.

Lithium aluminum tetraethyl is soluble to some extent in benzene; the solubility increases rapidly with temperature. It was not possible to obtain useful n.m.r. spectra of the compound in benzene, but both proton and ^{7}Li resonances were observed for ether solutions. The proton spectrum is typical of an A_2X_3 system, with the CH_3 triplet largely obscured by solvent absorption. The chemical shift of the CH_2 quartet lies at 7.71 p.p.m. upfield from benzene as internal standard; J_{AX} = 8.0 c.p.s. The corresponding values for ethyllithium in ether are 8.12 p.p.m. and 8.4 c.p.s.[6] The quartet lines are quite broad; the line widths are not appreciably affected by concentration change nor by lowering of the temperature to −48°. Since ^{27}Al possesses a sizable quadrupole moment, it is possible that the broadening arises from a spin–spin interaction between aluminum and the protons. This in turn would require that the rate of exchange of alkyl groups between metal atoms be slow in relation to the *Al*-C-*H* coupling constant. A slow exchange of alkyl groups in a system of this type in ether would be novel, and the matter is under further study.

The ^{7}Li resonance line is quite sharp (half-width about 1.5 c.p.s. in the temperature range 30 to −48° and appears at a chemical shift of 1.47 p.p.m. upfield from 70% aqueous lithium bromide. This is to be compared with a chemical shift of −1.00 p.p.m. from the same standard for ethyllithium in the same solvent.

The structure of lithium aluminum tetraethyl in a coordinating solvent such as ether is a matter of considerable interest. Among the more likely possibilities are (a) extensive dissociation into ethyllithium and triethylaluminum, which are individually solvated, (b) formation of solvated Li^+ and $Al(C_2H_5)_4^-$ ion pairs, and (c) partial retention of the structure of the solid, with short chains terminated by coordinated solvent. The ^{7}Li n.m.r. result rules out (a), but no further conclusions regarding the ether solutions are justified at this time.

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CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS, AND BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, NEW YORK

Stereochemistry of Metal β-Diketonates. Complexes with Two Different Ligands

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For cobalt and chromium β-diketonates of the series $M(CF_3COCHCOCH_3)_n(CH_3COCHCOCH_3)_{3-n}$ where *n* is 1 or 2, the isomers have been separated and characterized. The dipole moments and both fluorine and proton n.m.r. spectra of the cobalt compounds with n = 1, 2, and 3 are reported and interpreted. Coalescence of fluorine n.m.r. lines as a function of temperature for the corresponding aluminum compounds in the presence of excess of the β-diketones indicates that exchange of CF_3 groups between different chemical environments for a given value of *n* occurs by an intramolecular mechanism.

Introduction

In a recent study of the tristrifluoroacetylacetonates of trivalent metals, Fay and Piper have shown the utility of n.m.r. spectroscopy in the assignment of configuration to the two geometrical isomers[2] as well as in studies of the kinetics and mechanisms of their interconversion.[3] This work suggested a study of the complete series of compounds $M(CF_3COCHCOCH_3)_n(CH_3COCHCOCH_3)_{3-n}$ where *n* is 0, 1, 2, or 3. We will abbreviate these compounds hereafter as M(tfac)$_n$(acac)$_{3-n}$ where (tfac)$^-$ indicates the anion of 1,1,1-trifluoro-2,4-pentanedione and (acac)$^-$ indicates the anion of 2,4-pentanedione. These compounds afford another interesting set of geometrical isomers when *n* is 2. Furthermore, one may study the equilibrium distribution of products and the mechanisms of reactions such as isomerization, racemization, and ligand exchange with free β-diketone in solution.

In this paper we report the synthesis, separation, and characterization of the three isomeric M(tfac)$_2$(acac) complexes and of M(tfac)(acac)$_2$ for both cobalt(III) and chromium(III). The assignment of configuration

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[1] (a) University of Illinois; (b) Cornell University; (c) Alfred P. Sloan Foundation Fellow.

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