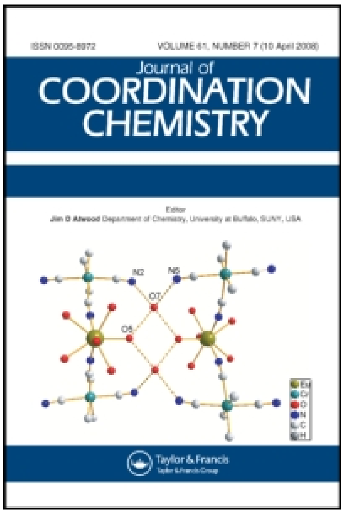

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TETRA-, PENTA- AND HEXACOORDINATED ALUMINIUM: NMR AND X-RAY DIFFRACTION STUDIES OF THE COMPLEXES OF ETHYLENEDIAMINE WITH ALUMINIUM ISOPROPOXIDE AND ITS FLUORO ANALOGUES

Jean-Pierre Laussac[a]; Renee Enjalbert[a]; Jean Galy[a]; Jean-Pierre Laurent[a]
[a] Laboratoire de Chimie de Coordination du C.N.R.S. 205, Toulouse, France

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TETRA-, PENTA- AND HEXACOORDINATED ALUMINIUM: NMR AND X-RAY DIFFRACTION STUDIES OF THE COMPLEXES OF ETHYLENEDIAMINE WITH ALUMINIUM ISOPROPOXIDE AND ITS FLUORO ANALOGUES

JEAN-PIERRE LAUSSAC†, RENEE ENJALBERT, JEAN GALY
and JEAN-PIERRE LAURENT

Laboratoire de Chimie de Coordination du C.N.R.S. 205, route de Narbonne 31400 TOULOUSE, France

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The products resulting from the complexation of $Al[OCH(CH_3)_2]_3$ (*A*) and $Al[OCH(CF_3)_2]_3$ with ethylenediamine have been studied. Four complexes en. $Al[OCH(CH_3)_2]_3$ (*B*); en.$Al[OCH(CF_3)_2]_3$ (*D*); $[en]_2$. $Al[OCH(CF_3)_2]_3$ (*E*) and en. $Al(OH)[OCH(CF_3)_2]_2$ (*F*) were isolated and identified by elemental analysis and NMR spectroscopy. The occurence of a further complex (*C*) en.2$Al[OCH(CH_3)_2]_3$ in solution is suggested by the NMR data. A crystal structure determination is reported for the species (*F*). The structure consists of en. $Al(OH)[OCH(CF_3)_2]_2$ dimers with characteristic (N_2O_4) ligand donor sets. The Al-Al distance (2.939 Å indicates that no metal-metal interaction occurs. For the other complexes, the NMR, and in particular the ^{27}Al NMR, data are shown to be consistent with a tetracoordinated aluminium atom in an (O_3N) environment (compounds *B* and *D*) or with a penta-coordinated aluminium in an (O_4N) environment (*C*) or in an (O_3N_2) environment (*E*).

INTRODUCTION

It is generally accepted that, with bases,[1] aluminium alkoxides form polymers[2,3,4] in preference to addition compounds. Only a few complexes are mentioned in the literature which involve bidentate ligands such as ethylenediamine, hydrazine[5,6,7] or monofunctional bidentate Schiff bases.[8] The electron-acceptor power of aluminium in these compounds can be greatly strengthened when halogen atoms are introduced in the alkoxide radicals[9] which results in a reduction of the degree of polymerization of the alkoxide. For example, fairly stable complexes D.$Al[OCH(CF_3)_2]_3$[10] have been obtained with conventional monodentate ligands (D = Et_2O, Et_2S, Et_3N and Et_3P).

It should be emphasized that phosphorus bidentate ligands reacted with $Al[OR(F)]_3$ lead to monomeric 1/1 adducts which involve a tetra-coordinated aluminium atom, the ligands being monodentate.[11] This result appears rather surprising when compared to the bidentate behaviour of ethylenediamine (en) in the compound en.$\{Al[OR(H)]_3\}_2$ and should be viewed with respect to the more general problem of the coordination number[1,12,13] displayed by aluminium in such complexes.

According to Bains and Bradley[5] the compound containing two molecules of $Al[OR(H)]_3$ monomer to one of en would involve tetra- and/or hexacoordinated aluminium. Further investigations favour either tetra- or pentacoordination.[6,7] However evidence supporting hexa- and pentacoordination has been provided by NMR studies (^1H, ^{13}C and ^{27}Al) of both $\{Al[OR(H)]_3\}_4$ and 2D.$AlCl_3$ (D = Et_3N, Et_3P, etc).[11]

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† To whom correspondance should be addressed.

Nuclear magnetic resonance is a well-established technique for studying metal-ligand interactions, since the position of the resonance lines is sensitive to electronic changes which can occur within molecular frameworks. Furthermore, aluminium-27 is an attractive nucleus on account of its high sensitivity and a 100% isotopic abundance. However, its spin number, I = 5/2, results in a nuclear quadrupolar moment which strongly interacts with electric field gradients originating from an asymmetrical arrangement of the ligands around the Al^{3+} cation. Thus if the aluminium atom is situated in a region of high molecular symmetry, its NMR absorption line can be less than 10 Hz at half-height ($Al(H_2O)_6{}^{3+}$, $\Delta\ \nu_{1/2} \simeq 10$ Hz.) In less symmetrical environments, a broader absorption line is observed.[14, 15]

The present work was undertaken to obtain a comparison between the acceptor properties of normal and fluoro-alkoxides of aluminium towards en. Such a comparison was expected to provide a new approach to the problem of the coordination number of aluminium in such complexes.

EXPERIMENTAL

Materials and Syntheses. En (*Fluka*) and $\{Al[OR(H)]_3\}_4$ (*A*) (*Fluka*) were used after further purification by distilling. All reactions and syntheses were carried out in an atmosphere of pure dry nitrogen or *in vacuo*. All solvents were dried by standard procedures.

Compound (B). Ehtylenediamine (1.23 g) was added to a solution of aluminium isopropoxide (4.20 g) in benzene (stoichiometric ratio 1 : 1). After the mixture was allowed to stand for some time, the benzene was removed under vacuum. The residue was a white crystalline powder and quantitative analysis (by the "Service Central de Microanalyse" of the C.N.R.S.) gave results corresponding to a 1 : 1 stoichiometry, en. $Al[OR(H)]_3$. Calcd. : C, 49.98; H, 10.06; N, 10.59; Al, 10.20%. Found: C, 49.05; H, 10.86; N, 9.84; Al, 10.07%.

Compound (D) (ratio 1 : 1). This compound was prepared by allowing $Et_2O.Al[OR(F)]_3$ (13.6 g) to react with en (0.36 g) at room temperature in 50 cm^3 of benzene. It is a white product. *Anal.* Calcd. for en. $Al[OR(F)]_3$: C, 22.46; H, 1.88; F, 58.14; N, 4.76; Al, 4.58%. Found: C, 22.25; H, 1.98; F, 57.15; N, 4.90; Al, 4.70%.

Compound (E) (ratio 2 : 1). Prepared similarly to (*D*) using $Et_2O.Al[OR(F)]_3$ (2.82 g) and an excess of en (1.10 g). Calcd for 2[en].$Al[OR(F)]_3$: C, 24.00; H, 2.95; F, 52.73; N, 8.60; Al, 4.16%. Found: C, 24.01; H, 3.00; F, 51.78; N, 8.71; Al, 4.20%.

Compound (F). A benzene solution of (*E*) (0.95 g) was kept during several days at room temperature. The crystals were separated by filtration and washed with small quantities of alcohol and acetone. They were dried at room temperature under vacuum. These crystals were only slightly soluble in C_6D_6. Calcd. for $\{en.Al(OH)[OR(F)]_2\}_2$: C, 21.91; H, 2.51; F, 52.05; N, 6.39; Al, 6.16%. Found: C, 22.02; H, 2.54; F, 50.90; N, 6.64; Al, 5.80%.

NMR spectroscopy. Proton fluorine-19 spectra were recorded on a Perkin-Elmer R 12 spectrometer at 60 MHz (^1H) and 56.46 MHz (^{19}F) with Me_4Si and CF_3COOH as internal references. Carbon-13 NMR spectra were obtained at 22.63 MHz with a Bruker WH 90 instrument equipped with a Bruker-Nicolet data system, model B-NC-12. At the concentrations used (10% in CD_2Cl_2 or C_6D_6), 10000–20000 pulses generally resulted in satisfactory signal intensity. Me_4Si was used as an internal standard. We measured the aluminium-27 spectra on a WH 90 spectrometer using the ^{13}C resonance frequency (22.63 MHz). The magnetic field was lowered to 2.04 T to find the ^{27}Al resonance. No field-frequency lock could be used under these conditions; consequently chemical shifts are measured with an error or ± 2 ppm. Increasing positive values of chemical shifts are toward higher field. Chemical shifts are expressed in parts per million (ppm) from the resonance of $Al(H_2O)_6{}^{3+}$ contained in a 5 mm tube immersed in a 10 mm tube filled with the solution being studied.

Crystallography. The crystal used for the X-ray study was introduced in a dry Lindemann capillary. Examination by precession method using Mo K_α radiation showed that the compound crystallizes in the monoclinic system. The systematic absences ($h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$) lead to the space group $P2_1/c$. All crystal constants and the conditions of data collection on an Enraf-Nonius CAD-4 computer-controlled diffractometer are summarized in Table I.

Structure determination. The structure was solved by direct methods;[16] in the first step one aluminium and two nitrogen atoms and two $O–C–(CF_3)_2$ groups were distinguished giving an R factor of 0.27. On a subsequent difference Fourier map, the existence of a new oxygen atom and the diamine ligand N–C–C–N bound to the aluminium atom was confirmed. The symmetry center 1/2, 0, 1/2 implies in fact a dinuclear aluminium complex, 26 atoms defining the half-unit (1 Al, 3 O, 2 N, 8 C and 12 F). A least-squares refinement[16] involving anisotropic thermal parameters for all the atoms led to R = 0.08. On the following difference Fourier map all hydrogen atoms were unambiguously located. A last series of refinements (an isotropic thermal parameter of 5 Å^2 being attributed to

TABLE I

Physical and Crystallographic Data

$Al_2(OH)_2[OCH(CF_3)_2]_4[NH_2CH_2CH_2NH_2]_2$

Monoclinic, space group : $P2_1/c$

a = 9.599 (3) Å V = 1542 Å^3

b = 15.628 (3) β = 110.12°(2) Z = 2

c = 10.949 (2)

ρ_{exp} = 1.85 g cm^{-3} ρ_X = 1.88 g cm^{-3}

Data Collection

Temperature : 22°C

Radiation : Cu_{K_α}

Monochromatization : graphite oriented crystal

Crystal-detector distance : 208 mm

Detector window : height* = 4 mm width* = 3.00 + 0.75 tan θ

Take-off angle* : 4.0°

Scan mode : θ, 2 θ

Maximum Bragg angle : 39°

Scan angle : $\Delta\theta$ = 1.0 + 0.14 tan θ

Conditions for Refinement

Reflections for the refinement of the cell dimensions : 25

Recorded reflections : 3610

Independent reflections : 3230

Utilized reflections : 1012 with I > 2 σ (I)

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*Values definited by A. Mosset, J.-J. Bonnet and J. Galy, *Acta Cryst.*, B33 2639 (1977).

TABLE II

Fractional atomic coordinates and thermal parameters (X 10^4) of the non-hydrogen atoms.*

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al	0.5490(3)	0.0463(2)	0.6244(2)	101(4)	22(1)	60(3)	−2(2)	29(3)	−5(2)
O(1)	0.3608(5)	0.0570(3)	0.6310(5)	81(9)	27(3)	77(6)	1(4)	33(6)	−10(4)
O(2)	0.6080(6)	0.1534(3)	0.6877(5)	100(10)	22(3)	75(7)	−8(4)	32(7)	−5(3)
O(3)	0.4956(5)	−0.0663(3)	0.5527(4)	85(9)	19(2)	50(6)	2(3)	17(5)	−6(3)
N(1)	0.7666(7)	0.0109(4)	0.6373(6)	106(12)	27(3)	67(8)	0(5)	22(8)	−4(4)
N(2)	0.6279(8)	−0.0001(4)	0.8130(6)	107(12)	30(3)	75(8)	8(5)	33(8)	3(4)
C(1)	0.3033(10)	0.1185(6)	0.6882(8)	88(15)	41(5)	70(10)	6(7)	45(11)	−1(6)
C(2J	0.1766(13)	0.1663(7)	0.5878(12)	130(22)	54(7)	144(18)	24(10)	61(16)	8(9)
C(3)	0.2524(13)	0.0802(7)	0.7880(10)	141(22)	57(7)	109(15)	14(10)	38(15)	5(8)
C(4)	0.6879(10)	0.2157(5)	0.6549(8)	121(16)	25(4)	68(10)	−4(7)	38(11)	−1(5)
C(5)	0.5843(13)	0.2873(6)	0.5798(11)	224(25)	25(4)	128(15)	−2(9)	55(16)	1(7)
C(6)	0.8012(13)	0.2523(7)	0.7793(10)	153(21)	47(6)	109(15)	−30(10)	51(15)	−4(8)
C(7)	0.8269(10)	−0.0484(6)	0.7466(9)	136(17)	58(6)	90(12)	30(9)	30(12)	25(8)
C(8)	0.7852(11)	−0.0251(7)	0.8559(9)	161(21)	78(8)	104(13)	26(9)	40(14)	27(8)
F(1)	0.1284(7)	0.2317(4)	0.6377(6)	361(16)	82(5)	218(11)	123(7)	98(10)	10(6)
F(2)	0.2149(7)	0.1940(4)	0.4917(5)	259(13)	78(4)	140(8)	52(6)	81(8)	51(5)
F(3)	0.0593(7)	0.1159(4)	0.5341(6)	132(12)	100(5)	221(11)	0(6)	−28(9)	33(6)
F(4)	0.3664(6)	0.0470(4)	0.8868(5)	207(11)	71(4)	120(7)	19(6)	64(7)	24(5)
F(5)	0.1850(7)	0.1331(4)	0.8457(6)	283(15)	101(5)	186(10)	74(6)	160(10)	13(5)
F(6)	0.1612(7)	0.0140(4)	0.7473(6)	214(13)	90(4)	225(11)	−68(6)	88(9)	8(6)
F(7)	0.4963(6)	0.2572(3)	0.4653(5)	288(13)	41(3)	134(8)	2(5)	−24(8)	7(4)
F(8)	0.6603(7)	0.3528(3)	0.5522(6)	333(16)	35(3)	216(10)	−28(5)	47(10)	30(4)
F(9)	0.5013(7)	0.3186(3)	0.6425(6)	283(15)	50(3)	221(10)	59(5)	99(10)	3(5)
F(10)	0.8951(7)	0.3051(3)	0.7505(6)	196(12)	70(4)	247(10)	−70(6)	65(9)	−9(6)
F(11)	0.7462(7)	0.2907(4)	0.8578(6)	274(14)	95(5)	151(8)	−51(6)	86(9)	−72(5)
F(12)	0.8873(7)	0.1879(4)	0.8461(6)	182(12)	66(4)	219(10)	−19(5)	−54(9)	2(5)

*Estimated standard deviations in parentheses. The form of the anisotropic thermal parameters is :

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

TABLE III
Fractional atomic coordinates of the hydrogen atoms.

	x/a	*y/b*	*z/c*
HC(1)	0.389	0.156	0.731
HC(4)	0.741	0.188	0.599
H(1)N(1)	0.832	0.060	0.652
H(2)N(1)	0.767	−0.017	0.557
H(1)N(2)	0.572	−0.052	0.820
H(2)N(2)	0.613	0.042	0.873
H(1)C(7)	0.932	−0.054	0.771
H(2)C(7)	0.782	−0.106	0.719
H(1)C(8)	0.810	−0.071	0.922
H(2)C(8)	0.850	0.025	0.901
HO(3)	0.460	−0.093	0.612

hydrogen atoms) taking into account the secondary extinction ($g = 2.8\ (8) \times 10^{-7}$) led to the reliability index values falling to R = 0.044 and R_W = 0.042. Atomic scattering factors of the atoms were from Cromer and Waber's Tables[17] and corrected, except carbon and hydrogen, for anomalous dispersion. The final atomic and thermal parameters together with their standard deviations are listed in Tables II and III. The main

TABLE IV
Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses.*

Bond lengths			
Al-O(1)	1.840(5)	O(1)-C(1)	1.363(8)
Al O(2)	1.823(6)	O(2)-C(4)	1.370(8)
Al-O(3)	1.923(5)	C(1)-C(2)	1.53(1)
Al-O(3)*	1.863(5)	C(1)-C(3)	1.47(1)
Al-Al*	2.939(5)	C(4)-C(5)	1.53(1)
Al-N(1)	2.118(7)	C(4)-C(6)	1.53(1)
Al-N(2)	2.070(6)	C(7)-C(8)	1.43(1)
N(1)-C(7)	1.467(9)		
N(2)-C(8)	1.47(1)		
C(2)-F(1)	1.31(1)	C(5)-F(7)	1.33(1)
C(2)-F(2)	1.30(1)	C(5)-F(8)	1.35(1)
C(2)-F(3)	1.33(1)	C(5)-F(9)	1.31(1)
C(3)-F(4)	1.35(1)	C(6)-F(10)	1.34(1)
C(3)-F(5)	1.34(1)	C(6)-F(11)	1.30(1)
C(3)-F(6)	1.33(1)	C(6)-F(12)	1.35(1)
Angles			
O(1)-Al-O(2)	94.4(2)	Al-O(1)-C(1)	129.8(5)
O(1)-Al-O(3)	83.4(2)	Al-O(2)-C(4)	132.8(5)
O(1)-Al-O(3)*	98.5(2)	O(1)-C(1)-C(2)	111.3(7)
O(1)-Al-N(1)	168.6(3)	O(1)-C(1)-C(3)	110.2(8)
O(1)-Al-N(2)	91.2(3)	O(2)-C(4)-C(5)	109.7(7)
O(2)-Al-O(3)	176.9(3)	O(2)-C(4)-C(6)	109.0(7)
O(2)-Al-O(3)*	99.9(2)	Al-N(1)-C(7)	108.8(5)
O(2)-Al-N(1)	92.9(2)	Al-N(2)-C(8)	113.2(5)
O(2)-Al-N(2)	89.1(3)	N(1)-C(7)-C(8)	112.0(8)
O(3)-Al-O(3)*	78.2(2)	N(2)-C(8)-C(7)	110.6(8)
O(3)-Al-N(1)	88.9(2)	Al-O(3)-Al*	101.8(2)
O(3)-Al-N(2)	92.4(3)		
O(3)*-Al-N(1)	88.9(2)		
O(3)*-Al-N(2)	166.2(3)		
N(1)-Al-N(2)	80.1(3)		

*Atoms marked with an asterisk are at −*x*, −*y*, −*z*, relative to those at *x*, *y*, *z*.

intramolecular bond distances and bond angles are given in Table IV. Lists of observed and calculated structure factors are available from the editor.

RESULTS AND DISCUSSION

Chemical behavior. It is noteworthy that we succeeded not only in isolating and characterizing one adduct of the normal alkoxide, en.Al[OR(H)]$_3$ (*B*), but also two of its fluoro analogues, en.Al[OR(F)]$_3$ (*D*) and [en]$_2$.Al[OR(F)]$_3$ (*E*). All attempts to obtain an (*E*)-like compound from {Al[OR(H)]$_3$}$_4$ were unsuccessful. However, a new species (*C*) was detected in the ^{27}Al NMR spectra of mixtures made up from (*A*) and (*B*). Contrary to the single line in the spectrum of (*B*) (64.7 ppm), (*D*) (56.6 ppm) or (*E*) (13.0 ppm) four absorptions are clearly discernible at 65.0, 58.0, 13.0 and 0 ppm, in the spectrum of the (*A*)/(*B*) mixture. Furthermore the intensities of these adsorptions depend on the composition of the sample. On adding increasing amounts of (*A*) to a solution of (*B*), the absorption at 13 ppm grows at the expense of the 65 ppm line while the 0 and 58 ppm resonances increase only slightly. Since the peak at 65 ppm is due to the (*B*) species and those at 58 and 0 ppm to the free alkoxide (*A*) (*vide infra*), the 13 ppm absorption may be attributed to a new species (*C*). The fact that the 13 ppm adsorption increase until about one mole of (*A*) (calculated as monomer) has been added per mole of (*B*), strongly suggests that (*C*) is the en. 2Al[OR(H)]$_3$ complex previously mentioned by Shiner and Whittaker.[18] We did not succeed in isolating a pure sample of this species (see Table V).

Another interesting feature is related to the behavior of the (*E*) complex in solution. Freshly prepared solutions in CD_2Cl_2 and C_6D_6 display the same ^{27}Al spectrum i.e. a single peak at 13 ppm. On aging, additional peaks appear at 56.8 ppm (CD_2Cl_2 solutions) and at 56.8 ppm and 7 ppm (C_6D_6 solutions) while, in this last instance, a white crystalline compound precipitates progressively. From microanalytical data this compound (*F*) has the crude formulation $C_{13}H_{19}F_{18}O_3N_4Al$ and its structure determined by X-ray diffraction (*vide infra*) involves hexacoordinated aluminium. In spite of its very low solubility, its ^{27}Al NMR spectra has been obtained and a simple resonance (δ^{27}Al = 7 ppm) is observed. From these data it may be inferred that, in solution, the (*E*) complex undergoes dissociation to the (*D*) complex (δ^{27}Al = 56.8 ppm) and, presumably due to trace of water in C_6D_6, to the (*F*) species through hydrolysis.

NMR data and aluminium coordination. The structure of the tetrameric aluminium isoproxide (*A*) originally proposed by Bradley[1] involves a central octahedrally co-

TABLE V
^{27}Al NMR parameters (shifts and linewidths) of the aluminium complexes.

Compound	δ^{27}Al (ppm)	$\Delta\nu_{1/2}$ (Hz)
(*A*)	0 58.0	50 1000
(*B*)	64.7	220
(*C*)	13.0	350
(*D*)	56.6	200
(*E*)	13.0	450
(*F*)	7.0	200

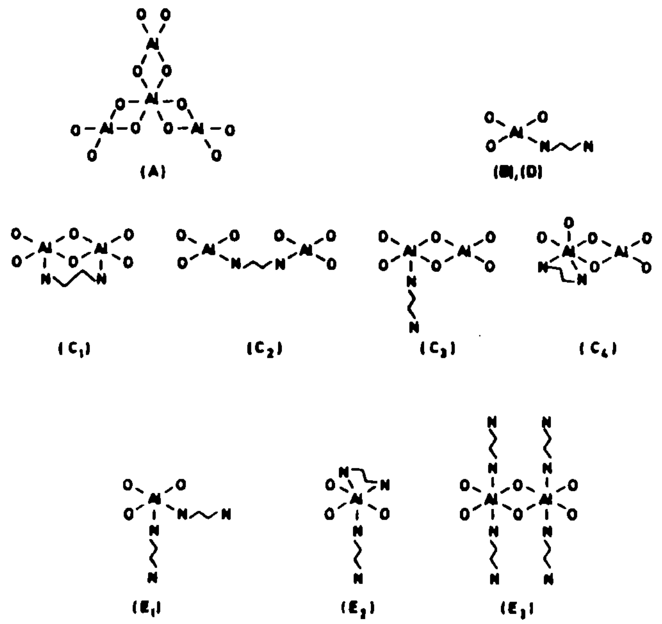

FIGURE 1 Schematic structures of aluminium alkoxides and their adducts with ethylenediamine.

ordinated aluminium bonded *via* alkoxo bridges to three tetrahedrally coordinated aluminium atoms (*cf.* Figure 1). Such a structure is consistent with the whole set of experimental data (cryoscopy, mass spectroscopy and ^{1}H, ^{13}C and ^{27}Al NMR).[18,19] Our NMR results are in fair agreement with the data in the literature and will be used to discuss the data characterizing the compounds (*B*), (*C*), (*D*), (*E*) and (*F*) in connection with their structures.

The most informative data is gained from the ^{27}Al resonance spectra. In contrast to the two lines (δ = 0 and 58 ppm) in the (*A*) spectrum which are attributed to the tetra- and the hexa-coordinated aluminium atoms respectively, a single absorption is detected in the (*B*), (*D*), (*E*) and (*F*) spectra suggesting the presence of only one kind of aluminium in these species. According to the widely accepted assumption that in a series of closely related compounds the chemical shift (δ^{27}Al) may reflect the coordination number of aluminium,[14,20] similar structures are expected for compounds (*B*) (δ^{27}Al = 64.7 ppm) and (*D*) (56.6 ppm). These δ values compare well, firstly with the shift (58 ppm) attributed to the tetracoordinated aluminium in (*A*) and, secondly, with the shifts of the D.Al[OR(F)]$_3$ complexes which range from 55.5 to 60.0 ppm according to the nature of the donor molecules (D = Et$_2$O, Et$_3$P, etc).[12] Since cryoscopic determinations[21,22] have established the monomeric mature of these adducts and, therefore, the occurence of a tetracoordinated aluminium atom in their structure, a shift δ^{27}Al close to 60 ppm may be associated with an aluminium in an O$_3$N environment (see Figure 1). Since an aluminium atom in an octahedral environment (O$_4$N$_2$) is responsible for the δ^{27}Al = 7 ppm observed in the (*F*) spectrum, the extension of the coordination number of aluminium from 4 (*D*) to 6 (*F*) moves the ^{27}Al resonance by about 50 ppm. A value of ~ 60 ppm is obtained when the two signals of (*A*) are considered.

However it should be kept in mind that, on going from a tetracoordinated (D.AlCl$_3$) to a pentacoordinated aluminium (2D.AlCl$_3$) the ^{27}Al resonance moves upfield by roughly 50 ppm.[11,20] These results show that a very slight difference, if any, is to be expected between the shifts of a pentacoordinated and of a hexacoordinated aluminium and they suggest that the 13 ppm line in (*E*) may be associated to a pentacoordinated rather than to an hexacoordinated aluminium. Hexacoordination would indeed be achieved in structures (E_2) or (E_3) and would imply non-equivalence of either the ethylenediamine molecules or the alkoxo groups. This hypothesis conflicts with the ^{1}H, ^{13}C and ^{19}F spectra which display no sign whatever of non-equivalence.

Regarding the (*C*) species, four structures (C_1,C_2,C_3,C_4) may be considered on the basis of an en.2Al[OR(H)]$_3$ formulation. The structures of (C_3) and (C_4) may be rejected, since we only observed one resonance signal. Furthermore, the position (13 ppm) of this absorption is incompatible with a four-coordinated aluminium (structure C_2) but favours structure (C_1) which contains pentacoordinated aluminium atoms. It may be emphasized that (*C*) and (*E*), the structures, of which may involve a pentacoordinated aluminium arom, are characterized by the same chemical shift value, δ^{27}Al = 13 ppm.

The ^{1}H and ^{13}C study confirms and extends the conclusions previously drawn from ^{27}Al results. Indeed, for ^{1}H, a significant change with concentration is observed for compounds (*B*), (*D*) and (*E*) (Table VI). Thus a 10^{-2}M solution in CD_2Cl_2 of species (*B*) gives a peak corresponding to the NH_2 resonances at $\delta = 2.82$ ppm with a line width at half-height of $\nu_{1/2} \sim 40$ Hz. The concentration change (10^{-3}M) results in a small shift ($\delta = 2.79$ ppm) and in an important sharpening of the NH_2 resonance ($\nu_{1/2} \sim 20$ Hz). However the most striking observation is the appearance of a new peak at 4.01 ppm corresponding to NH_2 bound to aluminium. The same observations can be made for compounds (*D*) and (*E*). The non-equivalence of the NH_2 groups induced by complex formation may be explained by considering that the ethylenediamine actually acts as a monodentate ligand in the three complexes (*B*), (*D*) and (*E*). Similar features appear in the ^{13}C spectrum and are shown in Table VII. Thus the spectra of (*B*) and (*D*) display two resonances; in the case of the (*E*) compound, only one broad signal ($\nu_{1/2} = 20$ Hz) is observed. When these results are considered in conjunction with the other data (^{27}Al, chemical analysis), we are led to the conclusion that the en ligand actually acts as a monodentate in the (*B*), (*D*) and (*E*) compounds. This is consistent with the occurence of a tetracoordinated (O_3N) aluminium in (*B*) and (*D*) and of a pentacoordinated aluminium (O_3N_2) in (*E*).

TABLE VI

^{1}H and ^{19}F NMR data measured for en and its Al[OR(X)]$_3$ complexes with X = H or F.

	Al[OR(X)]$_3$			en^a	
Compound	$\delta(OCHCX_3)$ (ppm)	$\delta(OCHCX_3)$ (ppm)	$^3J(OCHCF_3)$ (Hz)	$\delta(CH_2)$ (ppm)	$\delta(NH_2)$ (ppm)
en				2.68	1.20
(*A*)	4.30	1.12 1.29 1.48			
(*B*)	3.88^{b,c}	1.05^{b,c}	6.2^{b,c}	2.64(20)^b 2.57(3)^c	2.82(40)^b 2.79(20), 4.01(20)^c
(*D*)	4.41^b 4.43^c	1.80	6.6	2.88(10)^b 2.89(4)^c	2.63(40)^b 2.71(20), 4.01(20)^c
(*E*)	4.53^b 4.48^c	1.42	6.5	2.64(6)^b 2.61(3)^c	1.91(40)^b 2.24(8), 4.37(20)^c

^{a}, values incidentally correspond to the line width in Hz; ^{b}, 10^{-2}M solution; ^{c}, 10^{-3}M solution.

TABLE VII
^{13}chemical shifts and coupling constants of en and its aluminium complexes.

	$Al[OR(X)]_3$					en	
Compound	$\delta(OCHCX_3)$ (ppm)	$\delta(CX_3)$ (ppm)	$^2J(CHCF_3)$ (Hz)	$^1J(CHCX_3)$ (Hz)	$^1J(CX_3)$ (Hz)	$\delta(CH_2)$ (ppm)	^1JCH (Hz)
en						45.72	133.06
(*A*)	63.44 66.32	25.87 26.97 28.21 28.43					
(*B*)	63.14	28.04 28.37		131.16	122.40	39.29 44.86	134.12
(*D*)	71.30	123.03	33.16	147.07	283.48	37.79(s)[a] 38.32(s)	142.60
(*E*)	71.95	123.82	31.08	148.10	286.02	40.69(b)	140.20

[a] (s) sharp; (b) broad.

X-ray diffraction study. As previously mentioned attempts to obtain a crystalline sample of (*E*) led to the isolation of a new species (*F*) the structure of which was determined by X-ray diffraction.

The crystals were assigned to the monoclinic system with a space group $P2_1/c$. The lattice constants are $a = 9.599(3)$ Å, $b = 15.628(3)$ Å, $c = 10.949(2)$ Å, $\beta = 110.12(2)°$. The experimental density is 1.85 g cm^{-3} while the density calculated for two formula units per unit cell is 1.88 g cm^{-3}.

The structure is composed of dimeric units $\{en.Al(OH)[OR(F)]_2\}_2$, shown in Figure 2 with the numbering of the different atoms. The two aluminium atoms have an octa-

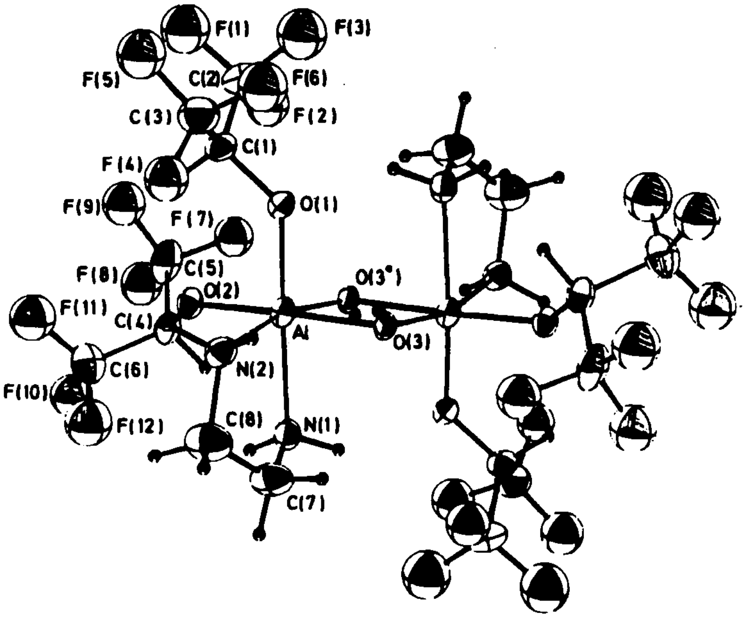

FIGURE 2 A perspective view of dimer unit showing 50% probability ellipsoids for the non-hydrogen atoms.

hedral environment and they are bridged by two hydroxo groups. The distances Al-O(3) and Al-O(3)* are slightly longer than Al-O(1) and Al-O(2). The bite of the angle O(3)-Al-O(3)* (78.2°) and the distance Al-Al (2.939 Å) indicate that no metal-metal interaction occurs. Each ethylenediamine molecule is bonded to one aluminium and acts as a bidentate ligand. The N-C and C-C distances are very close to the ones recently found for example in an isomer of chloro-(*R*, *S*-1, 2-diaminopropanediethlenetriamine)cobalt(III) tetrachlorozincate(II)[24] and also in the mixed ethylenediamine, 1, 3-propanediamine complexes $[Cr(en)_2(tn)]Br_3.H_2O$ and $[Cr(en)(tn)_2]I_3H_2O$.[25] The angle of the C-C bond made with the N-N axis, the angle between the planes N(1)-Al-N(2) and C(7)-Al-C(8) is 22°, in good agreement with the value quoted for $[Cr(en)_2(tn)]Br_3.H_2O$.

Such a group of two octahedra sharing an edge $[Al_2O_4(OH)_2N_4]$ is comparable with the $Al_2(OH)_{10}$ group found in the compound $Ba_2[Al_2(OH)_{10}]$[26]. The Al_2X_{10} units alternatively disposed at *b*/2 levels, form a kind of sheet parallel to (100) and repeated with a period of *a* (Figure 3). The $-C(CF_3)_2$ groups are extended between these slices.

The molecular structure of (*F*) suggest that the formation of this compound from benzene solutions of (*E*) is due to traces of water which would induce a partial hydrolysis of the fluoroalkoxide moiety. The so-formed en.Al(OH)[OR(F)]$_2$ species then dimerises through OH bridges.

The results obtained allow some conclusions to be drawn. The main one concerns the difference in Lewis acidity between normal and fluoroalkoxide, the latter being able to complex up to two ethylenediamine molecules per aluminium atom. In the 1 : 1 complexes en.Al[OR(H)]$_3$ and en.Al[OR(F)]$_3$ the metal centers are in a tetrahedral environ-

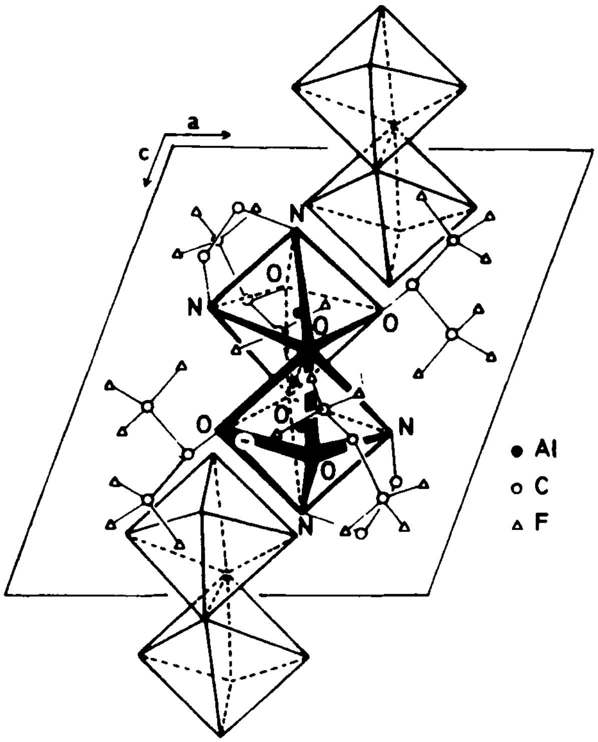

FIGURE 3 Projection onto (010) illustrating the packing of $[Al_2X_{10}]$ along the *C* axis.

ment and ethylenediamine behaves as a monodentate ligand. In the 2 : 1 complex 2 $en.Al[OR(F)]_3$ ethylenediamine is also monocoordinated to the aluminium atom, the coordination of which is raised to the less common value of five. Six-coordination, which is generally assumed to be more stable, is presumably prohibited by steric limitations. This hypothesis is consistent with the fact that hexacoordination is achieved in $\{en.Al(OH)[OR(F)]_2\}_2$ where bridging occurs through OH groups which are less bulky than isopropoxide. It is noteworthy that, in this last compound, ethylenediamine behaves as a monocluear chelating ligand and not as a bridge between two aluminium atoms. The results suggest that the actual coordination number of aluminium in the alkoxide derivatives mainly depends on steric requirements.

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