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THE CHEMISTRY AND THE STEREOCHEMISTRY OF POLY(*N*-ALKYLIMINOALANES)

XVIII *. THE PREPARATION AND CRYSTAL STRUCTURE OF THE PENTAMER $\{(HAlN—i\text{-}Pr)_2(H_2AlNH—i\text{-}Pr)_2[HAlNCH(CH_3)CH_2N(CH_3)_2]\}$ AND THE CRYSTAL STRUCTURE OF $[HAlN(CH_2)_3N(CH_3)_2]_6 \cdot 2\ LiH$

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Summary

The crystal and molecular structures of the pentamer $\{(HAlN—i\text{-}Pr)_2(H_2AlNH—i\text{-}Pr)_2[HAlNCH(CH_3)CH_2N(CH_3)_2]\}$ (I) and of the hexamer $[HAlN(CH_2)_3N(CH_3)_2]_6 \cdot 2\ LiH$ (II) have been determined by direct methods from diffractometer data (Cu-K_α) and refined by block-matrix least-squares to $R = 0.052$ (I) and 0.084 (II) for 1743 and 1977 independent observations, respectively. The molecular structure of I is built up of four $(AlN)_3$ and two $(AlN)_2$ rings; the nitrogen atom of the side—$N(CH_3)_2$ group is bonded to an aluminum atom which displays five coordination. The molecular structure of II consists of an "open cage" $(AlN)_6$, to which two LiH molecules are linked through Li—H—Al hydrogen bridges; the tetrahedral coordination of Li is completed by a nitrogen atom of the cage and by two nitrogens of the side —$N(CH_3)_2$ groups. The Al—N bond distances range from 1.859(5) to 2.162(5) Å in I and from 1.845(6) to 1.947(8) Å in II; the overall average Al—N bond lengths, involving four-coordinate atoms only, are 1.916(11), I, and 1.901(13) Å, II.

Crystal data: I, orthorhombic, space group $P2_12_12_1$, $a = 19.935(6)$, $b = 11.087(2)$, $c = 13.230(3)$ Å, $Z = 4$, calcd. density 1.073 g cm^{-3}; II, triclinic, space group $P\bar{1}$, $a = 10.162(5)$, $b = 12.989(4)$, $c = 12.030(5)$ Å, $\alpha = 101.58(4)$, $\beta = 118.46(3)$, $\gamma = 109.18(3)$ Å, $Z = 1$, calcd. density 1.095 g cm^{-3}.

Introduction

In recent years an extensive research program has been implemented on the stereochemistry of poly(*N*-alkyliminoalanes) (PIA) [1—10], synthesized from

* For parts I—XVII see refs. 1—11.

TABLE 1

SUMMARY OF CRYSTAL DATA

Molecular formula	$\{(HAlN{-}i\text{-}C_3H_7)_2(H_2AlNH{-}C_3H_7)_2\text{-}[HAlNCH(CH_3)CH_2N(CH_3)_2]\}$	$[HAlN(CH_2)_3N(CH_3)_2]_6 \cdot 2\ LiH$
Molecular weight	472.5	784.8
Space group	$P2_12_12_1$	$P\bar{1}$
Molecules/unit cell	4	1
Unit cell constants (Å, °) (Mo-K_α radiation, λ = 0.71069 Å)	a = 19.935(6), b = 11.087(2), c = 13.230(3) Å	a = 10.162(5), b = 12.989(4), c = 12.030(5) Å α = 101.58(4), β = 118.46(3), γ = 109.18(3)
Unit cell volume (Å^3)	2924.1	1190.3
Calculated density (g cm^{-3})	1.073	1.095
Linear absorption coefficient μ (cm^{-1})	2.0	1.6
Crystal shape	Irregular	Irregular
Crystal size (approximate) (mm)	0.4 × 0.4 × 0.5	0.15 × 0.4 × 0.5

primary amines. It has been shown that these PIA are oligomers, mostly with a "closed cage" structure involving a H_{act}/Al atomic ratio equal to 1.

In contrast, the PIA obtained recently from dimethylamino- or methoxy-substituted primary amines show a tendency to form "open cage" molecular structures [11] ($H_{act}/Al > 1$). New compounds were obtained starting from these primary amines [11], among which the title compounds $\{(HAlN—i\text{-}Pr)_2$-$(H_2AlNH—i\text{-}Pr)_2[HAlNCH(CH_3)N(CH_3)_2]\}$ (I) and $[HAlN(CH_2)_3N(CH_3)_2]_6 \cdot 2\,LiH$ (II) were isolated in the form of single crystals. I is the first example of PIA containing different substituents at nitrogen atoms in the same molecule; II is the first isolated LiH derivative of an hexamer $(HAlNR)_6$. The paper reports the crystal and molecular structures of I and II; the synthesis of I is also described.

Experimental

Synthesis

I. A solution of isopropylamine (28.75 mmol) and 2-dimethylamino-isopropylamine (5.75 mmol) in diethyl ether (30 ml) was added dropwise to a stirred solution of AlH_3 (34.5 mmol) in diethyl ether (100 ml) at room temperature. Hydrogen evolution took place immediately. The mixture was stirred for 2 h and traces of solid material filtered off. The residue remaining after the complete evaporation of the solution was redissolved in diethyl ether. This solution was set aside for a day and the crystals were removed, dried and analyzed. (Found: Al, 28.6; N, 17.8%; H_{active}, 14.8 meq/g. $C_{17}H_{39}N_6Al_5$ calcd.: Al, 28.5; N, 17.8%; H_{active}, 14.8 meq/g).

II. The preparation of II has been previously reported [11].

X-ray analysis

Crystals of the title compounds were sealed in thin-walled glass capillaries under an inert gas. The space groups were determined from Weissenberg photographs; $P\bar{1}$ was assumed for II and the successful refinement confirmed this assignment. Intensities were measured for $\theta < 25°$ (I) and $\theta < 23°$ (II) by a Siemens AED diffractometer, following the $\theta - 2\theta$ scan method and "five-points" technique [12] and using zirconium-filtered Mo-K_α radiation. A total of 2897 (I) and 3291 (II) reflections were collected, of which 1743 and 1977, respectively, having $I > 3\,\sigma(I)$, were used in the structure determinations. No absorption correction was necessary. The main crystal data are listed in Table 1.

Structure determination and refinement

The structure of both compounds was solved with the MULTAN program [13], using 130 reflections with $E > 1.7$ (I) and 170 reflections with $E > 1.8$ (II) for phase generation.

The lithium and hydrogen atoms were located from ΔF maps; the positions of the hydrogen atoms not clearly evident from these maps were calculated according to the expected geometry. Block-matrix least-squares refinement

TABLE 2

ATOMIC FRACTIONAL COORDINATES (X 10^4) AND THERMAL PARAMETERS [a] (X 10 FOR NON-HYDROGEN ATOMS) FOR COMPOUND I

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al(1)	2210(1)	3153(2)	6116(1)	32(1)	37(1)	38(1)	1(1)	-2(1)	-1(1)
Al(2)	2066(1)	541(2)	5009(1)	41(1)	39(1)	51(1)	6(1)	3(1)	-6(1)
Al(3)	965(1)	2075(2)	6061(1)	29(1)	48(1)	42(1)	-5(1)	13(1)	-1(2)
Al(4)	1772(1)	3081(2)	4168(1)	39(1)	44(1)	34(1)	-10(1)	-2(1)	13(1)
Al(5)	671(1)	1034(2)	3971(2)	37(1)	70(1)	49(1)	-24(2)	-10(2)	-27(2)
N(1)	2390(2)	2166(4)	4932(3)	25(2)	44(2)	37(2)	-4(3)	2(3)	-12(4)
N(2)	3256(2)	2817(5)	6441(4)	34(2)	56(3)	62(3)	1(4)	-17(4)	-22(5)
N(3)	1296(2)	3403(4)	5363(4)	33(2)	43(2)	37(2)	9(3)	-6(3)	5(3)
N(4)	1711(2)	2120(4)	7034(3)	43(2)	43(2)	35(2)	14(4)	3(3)	6(4)
N(5)	1335(2)	1993(5)	3241(3)	40(2)	54(3)	38(2)	-8(4)	-11(3)	-2(4)
N(6)	1115(2)	690(4)	5234(4)	38(2)	43(2)	48(2)	-19(4)	-16(4)	-3(4)
C(1)	3132(3)	2064(6)	4697(5)	39(3)	52(3)	56(3)	12(5)	15(4)	4(6)
C(2)	3291(3)	2311(8)	3606(6)	42(3)	104(5)	59(4)	-6(7)	36(5)	-10(8)
C(3)	3495(3)	2926(6)	5368(5)	24(2)	64(3)	67(4)	-14(5)	1(4)	-21(7)
C(4)	3442(4)	1670(8)	6883(6)	60(4)	86(5)	62(4)	40(7)	-31(6)	-11(8)
C(5)	3568(3)	3805(9)	7031(7)	39(3)	110(6)	93(5)	-19(7)	-30(7)	-89(10)
C(6)	978(3)	4633(5)	5408(5)	54(3)	40(3)	46(3)	29(5)	1(5)	7(5)
C(7)	791(4)	4984(7)	6465(6)	68(4)	58(4)	67(4)	56(6)	14(6)	-18(7)
C(8)	377(5)	4710(8)	4743(8)	99(6)	78(5)	105(6)	108(9)	-59(10)	-6(10)
C(9)	1500(3)	2556(6)	8069(5)	57(3)	71(4)	31(3)	10(6)	19(5)	8(5)
C(10)	2085(4)	3091(9)	8649(5)	91(5)	92(5)	45(3)	-31(10)	11(7)	-36(8)
C(11)	1194(4)	1523(8)	8647(5)	75(4)	82(5)	45(4)	10(7)	22(6)	19(6)
C(12)	1134(4)	2582(8)	2284(5)	79(5)	104(6)	37(3)	-18(9)	-19(6)	-3(7)
C(13)	1726(5)	2781(9)	1607(5)	100(5)	120(6)	36(3)	9(11)	9(7)	3(8)
C(14)	575(5)	1999(13)	1750(7)	84(5)	185(9)	67(5)	-77(14)	-49(8)	61(13)
C(15)	866(4)	-446(7)	5747(6)	76(4)	56(4)	76(5)	-53(7)	56(7)	-17(7)
C(16)	1120(5)	-1570(7)	5319(9)	125(7)	61(4)	108(7)	-65(10)	49(12)	-4(9)
C(17)	107(5)	-500(9)	5776(8)	91(5)	92(5)	99(6)	-77(10)	57(10)	-30(11)

Atom	x	y	z	B	Atom	x	y	z	B
H(Al1)	2301(22)	4280(43)	6259(34)	3(1)	H'(C8)	506(30)	4504(55)	4139(48)	7(2)
H'(Al2)	2219(26)	-32(49)	4190(42)	5(1)	H''(C8)	268(26)	5544(48)	4713(42)	6(1)
H''(Al2)	2407(28)	-74(51)	5804(42)	5(1)	H'''(C8)	84(28)	4054(54)	5085(48)	7(2)
H(Al3)	262(26)	1950(53)	6645(41)	5(1)	H(C9)	1104(33)	3194(69)	7904(58)	10(2)
H(Al4)	1962(39)	4343(80)	3729(62)	12(3)	H'(C10)	2262(32)	3932(62)	8336(51)	8(2)
H'(Al5)	140(31)	1885(61)	4199(51)	7(2)	H''(C10)	2325(34)	2459(58)	8804(53)	9(2)
H''(Al5)	615(34)	-105(60)	3446(54)	8(2)	H'''(C10)	1905(35)	3452(65)	9175(56)	11(2)
H(N4)	1899(30)	1457(57)	7316(48)	7(2)	H'(C11)	804(28)	1056(56)	8248(47)	7(2)
H(N5)	1472(28)	1347(50)	3154(44)	6(1)	H''(C11)	1029(26)	1736(48)	9450(41)	5(1)
H(C1)	3329(23)	1251(39)	4814(35)	3(10)	H'''(C11)	1494(29)	928(54)	8737(46)	7(2)
H'(C2)	3087(23)	1731(45)	3157(37)	3(1)	H(C12)	848(33)	3402(61)	2460(53)	9(2)
H''(C2)	3732(37)	2332(66)	3530(59)	12(2)	H'(C13)	2120(29)	3158(57)	1967(45)	6(2)
H'''(C2)	3136(28)	3207(55)	3511(44)	6(2)	H''(C13)	1595(29)	3088(53)	948(48)	6(1)
H'(C3)	3939(26)	2698(46)	5347(42)	5(1)	H'''(C13)	1935(27)	1915(55)	1368(41)	5(1)
H''(C3)	3503(25)	3785(46)	5293(41)	4(1)	H'(C14)	264(32)	1787(65)	2141(54)	8(2)
H'(C4)	3217(26)	1015(50)	6517(41)	4(1)	H''(C14)	807(35)	1159(67)	1591(58)	11(2)
H''(C4)	3302(29)	1678(52)	7572(44)	6(2)	H'''(C14)	444(37)	2374(59)	1271(58)	10(2)
H'''(C4)	3959(33)	1528(62)	6981(57)	10(2)	H(C15)	977(28)	-554(54)	6560(46)	6(1)
H'(C5)	3332(37)	4673(65)	6744(57)	11(2)	H'(C16)	1529(37)	-1619(61)	5384(55)	10(2)
H''(C5)	4042(30)	3727(59)	7178(54)	8(2)	H''(C16)	1018(32)	-1748(57)	4685(52)	8(2)
H'''(C5)	3401(32)	3662(57)	7815(50)	7(2)	H'''(C16)	904(39)	-2299(69)	5691(61)	12(2)
H(C6)	1360(27)	5272(47)	5224(42)	5(1)	H'(C17)	-105(24)	240(46)	5947(43)	5(1)
H'(C7)	1147(27)	5052(52)	6855(46)	5(2)	H''(C17)	28(39)	-1247(72)	6329(65)	13(3)
H''(C7)	490(30)	4343(56)	6798(46)	6(2)	H'''(C17)	-2(26)	-571(48)	5089(43)	5(1)
H'''(C7)	645(27)	5764(52)	6476(42)	5(1)					

[a] Anisotropic thermal factor defined by $\exp -1/4(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + B_{12}a^*b^*hk + B_{13}a^*c^*hl + B_{23}b^*c^*kl)$.

were applied, the function minimized being $\Sigma w(F_o - F_c)^2$ with Cruickshank's weighting scheme [14].

Anisotropic refinement for non-hydrogen atoms and isotropic refinement for hydrogens were performed for I; the final R factor was 0.052. For II, the

TABLE 3

ATOMIC FRACTIONAL COORDINATES (X 10^4) AND THERMAL PARAMETERS [a] (X 10 FOR NON-HYDROGEN ATOMS) FOR COMPOUND II

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al(1)	3238(2)	5757(2)	-1495(2)	31(1)	28(1)	34(1)	38(1)	44(1)	40(1)
Al(2)	4152(2)	5137(2)	1198(2)	31(1)	29(1)	32(1)	36(1)	48(1)	36(1)
Al(3)	7194(2)	6726(2)	1193(2)	28(1)	25(1)	30(1)	27(1)	40(1)	33(1)
N(1)	2541(6)	4677(4)	-785(5)	29(2)	34(2)	37(2)	41(4)	50(4)	42(4)
C(1)	864(8)	4521(6)	-1048(8)	27(3)	46(3)	50(4)	35(5)	51(6)	54(6)
C(2)	-611(9)	4107(7)	-2558(8)	34(3)	68(4)	60(4)	66(7)	60(7)	78(7)
C(3)	-1422(9)	2809(7)	-3535(9)	32(3)	63(4)	59(4)	42(6)	50(6)	76(7)
N(2)	-927(7)	2559(5)	-4492(6)	36(3)	39(3)	41(3)	28(5)	27(5)	40(5)
C(4)	-1612(12)	1277(8)	-5173(10)	60(5)	50(4)	66(5)	43(8)	52(9)	46(8)
C(5)	-1672(11)	3003(9)	-5569(10)	55(4)	83(6)	60(5)	71(9)	53(8)	85(9)
N(3)	6228(6)	6546(4)	2156(5)	38(2)	26(2)	32(2)	38(4)	51(4)	36(4)
C(6)	6300(12)	7695(7)	2837(9)	96(6)	42(4)	77(5)	94(8)	140(10)	73(7)
C(7)	6060(15)	7807(9)	3952(10)	136(8)	88(6)	57(5)	175(13)	131(11)	63(9)
C(8)	6462(18)	7170(15)	4817(11)	133(9)	219(14)	64(6)	229(19)	161(14)	130(15)
N(4)	8021(10)	7170(7)	5497(7)	84(4)	72(4)	37(3)	95(7)	75(6)	49(6)
N(5)	5569(6)	6255(4)	-755(5)	33(2)	28(2)	31(2)	34(4)	48(4)	43(4)
C(11)	6168(8)	7083(6)	-1314(7)	47(3)	32(3)	39(3)	39(5)	60(6)	56(5)
C(12)	6343(10)	8304(6)	-789(8)	62(4)	35(3)	52(4)	44(6)	88(7)	58(6)
C(13)	7054(10)	9142(7)	-1328(9)	59(4)	46(4)	81(5)	60(7)	101(8)	100(8)
N(6)	7563(12)	10423(8)	-558(11)	114(6)	74(5)	152(7)	84(9)	194(12)	178(11)

Atom	x	y	z	B	Atom	x	y	z	B
C(9)	7931(29)	6361(19)	6018(24)	185(7)	H'(Al1)	2301(81)	5060(58)	-3057(68)	5(1)
C(10)	9229(27)	8214(18)	6707(22)	171(6)	H''(Al1)	2766(68)	6743(48)	-1212(56)	3(1)
C(14)	6331(19)	10591(13)	-710(16)	117(4)	H(Al2)	3125(74)	5054(52)	1776(61)	4(1)
C(15)	8375(23)	11165(16)	-1055(19)	143(5)	H(Al3)	8707(70)	7923(49)	1896(58)	3(1)
Li	8279(15)	6593(11)	3866(12)	41(2)					

[a] See footnote to Table 2.

lithium atom and some methyl carbon atoms were left isotropic; only the hydridic hydrogens were refined, the contributions of the other hydrogens having been fixed during the refinement, with isotropic thermal parameters equal to those of the related carbon atoms. The final R factor was 0.084.

The atomic scattering factors were from Cromer and Mann [15] for non-hydrogen and from Stewart et al. [16] for hydrogen. With the exception of MULTAN and ORTEP [17], all the computer programs were written by Immirzi [18].

A list of structure factors may be obtained from the authors on request.

Results and discussion

The molecular structure of I (see Figure 1) is built up of a six-membered ring, $(AlN)_3$ [formed by Al(2), N(1), Al(4), N(3), Al(3) and N(6)], crossed by a $-H_2AlNH-$i-Pr$-$ unit on one side and by a $-HAlNH-$i-Pr$-$ unit on the other. The Al(1) atom of the latter bridging unit is connected to two nitrogen atoms of the main $(AlN)_3$ ring, so that three secondary six-membered rings, $(AlN)_3$, and two four-membered rings, $(AlN)_2$ are formed. Both the main and the secondary $(AlN)_3$ rings display a "skew-boat" conformation; significant deviations

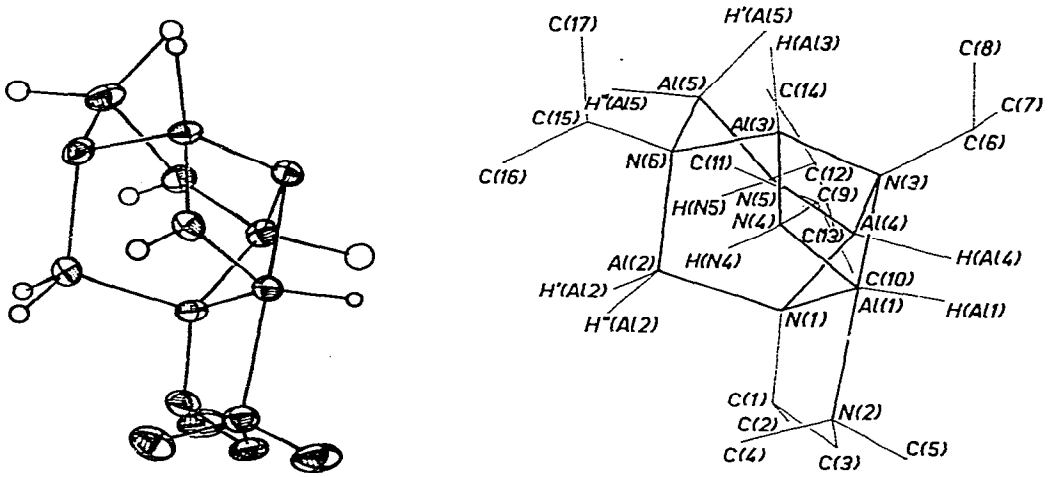

Fig. 1. A perspective view and labelling scheme for the molecule of compound I. For clarity, the isopropyl carbon atoms have been omitted in the view of the molecular structure.

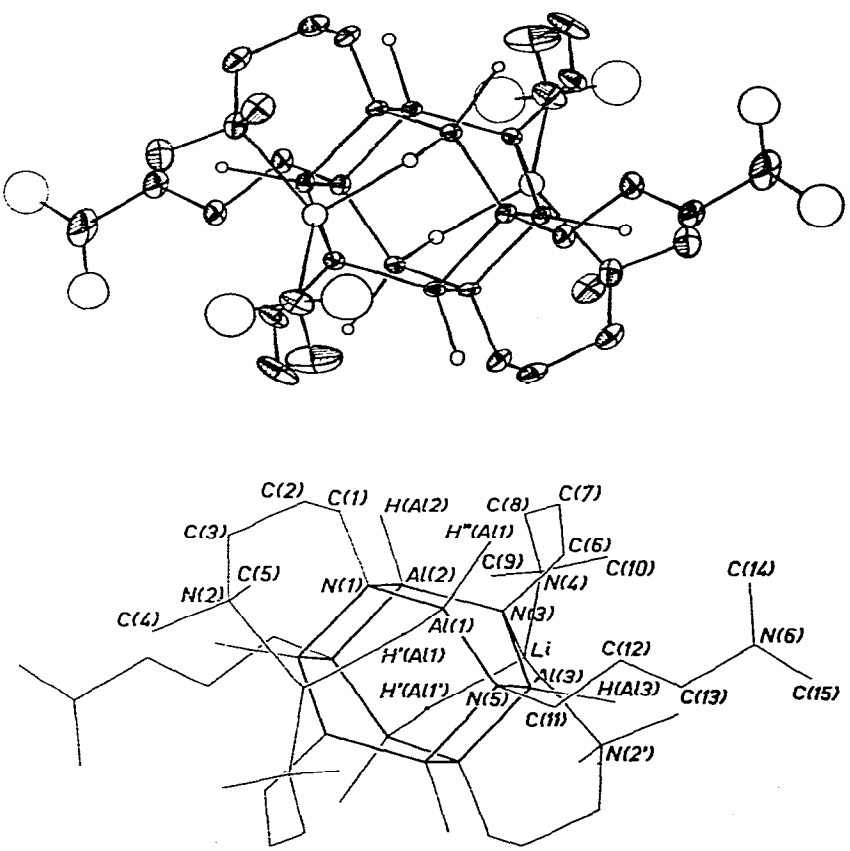

Fig. 2. A perspective view and labelling scheme for the molecule of compound II.

TABLE 4

CALCULATED FRACTIONAL COORDINATES ($\times 10^4$) OF NON-HYDRIDIC HYDROGEN ATOMS OF COMPOUND II

Atom	x	y	z
H'(C1)	528	3979	—646
H''(C1)	1166	5376	—439
H'(C2)	—1531	4254	—2591
H''(C2)	—154	4611	—2978
H'(C3)	—1198	2344	—2973
H''(C3)	—2741	2470	—4169
H'(C4)	—1275	1108	—5820
H''(C4)	—2892	855	—5723
H'''(C4)	—1136	976	—4451
H'(C5)	—1345	2845	—6222
H''(C5)	—1206	3890	—5091
H'''C(5)	—2949	2572	—6104
H'(C6)	7426	8396	3223
H''(C6)	5354	7781	2061
H'(C7)	6784	8668	4637
H''(C7)	4796	7577	3496
H'(C8)	6179	7413	5520
H''(C8)	5468	6250	4150
H'(C9)	9092	6410	6529
H''(C9)	7040	5564	5268
H'''(C9)	7687	6597	6719
H'(C10)	10 357	8252	7183
H''(C10)	8843	8287	7313
H'''(C10)	9342	8924	6428
H'(C11)	7342	7213	—1041
H''(C11)	5350	6677	—2358
H'(C12)	5172	8189	—1128
H''(C12)	7125	8704	240
H'(C13)	8024	9030	—1300
H''(C13)	6119	8853	—2363
H'(C14)	6795	11 466	—157
H''(C14)	5764	10 089	—387
H'''(C14)	5498	10 357	—1727
H'(C15)	8770	12 035	—509
H''(C15)	7539	10 898	—2054
H'''(C15)	9413	11 099	—865

from planarity are observed in the $(AlN)_2$ rings (see Table 5).

Aluminum and nitrogen atoms show tetrahedral coordination except for Al(1), which is five-coordinate with a distorted trigonal bipyramidal geometry; the five-coordination is reached by means of the nitrogen, N(2), belonging to the $-CH(CH_3)CH_2N(CH_3)_2$ substituent, which in turn achieves four-coordination.

The Ni(1) and N(4) atoms, which are bonded to the five-coordinate Al(1) atom and lie in the equatorial positions, display Al—N bond distances (1.954(5) and 1.943(5) Å, respectively) which are shorter than those related to the axially-bonded N(2) and N(3) (2.162(5) and 2.095(5) Å, respectively). The values of the remaining Al—N bond lengths are spread over the range 1.859—1.968 Å, as already found in other PIA with an irregular framework structure [3,4].

The molecular structure of II consists of a "open cage" framework $(AlN)_6$ with a crystallographic $\bar{1}$ symmetry, see Figure 2. This framework structure can

TABLE 5

GEOMETRICAL PARAMETER FOR COMPOUND I

Bond lengths (Å) and angles (°)

Al(1)-N(1)	1.945(5)	Al(4)-N(5)	1.927(5)	C(1)-C(2)	1.503(10
Al(1)-N(2)	2.162(5)	Al(5)-N(5)	1.954(5)	C(1)-C(3)	1.491(9)
Al(1)-N(3)	2.095(5)	Al(5)-N(6)	1.930(5)	C(6)-C(7)	1.500(10
Al(1)-N(4)	1.943(5)	N(1)-C(1)	1.514(7)	C(6)-C(8)	1.489(12
Al(2)-N(1)	1.918(5)	N(2)-C(3)	1.503(9)	C(9)-C(10)	1.517(11
Al(2)-N(6)	1.925(5)	N(2)-C(4)	1.448(10)	C(9)-C(11)	1.507(10
Al(3)-N(3)	1.859(5)	N(2)-C(5)	1.481(10)	C(12)-C(13)	1.499(11
Al(3)-N(4)	1.968(5)	N(3)-C(6)	1.505(7)	C(12)-C(14)	1.469(13
Al(3)-N(6)	1.910(5)	N(4)-C(9)	1.512(8)	C(15)-C(16)	1.459(12
Al(4)-N(1)	1.889(4)	N(5)-C(12)	1.480(9)	C(15)-C(17)	1.515(12
Al(4)-N(3)	1.879(5)	N(6)-C(15)	1.515(9)		
Al(1)-H(Al1)	1.28(5)	Al(3)-H(Al3)	1.61(5)	Al(5)-H''(Al5)	1.45(7)
Al(2)-H'(Al2)	1.29(5)	Al(4)-H(Al4)	1.56(9)	N(4)-H(N4)	0.91(6)
Al(2)-H''(Al2)	1.43(5)	Al(5)-H'(Al5)	1.45(6)	N(5)-H(N5)	0.78(6)
N(1)-Al(1)-N(2)	83.4(1)	N(1)-Al(1)-N(3)	81.5(1)	N(1)-Al(1)-N(4)	105.5(1)
N(2)-Al(1)-N(3)	163.0(4)	N(2)-Al(1)-N(4)	105.5(1)	N(3)-Al(1)-N(4)	86.0(1)
N(1)-Al(2)-N(6)	105.0(1)	N(3)-Al(3)-N(4)	92.1(1)	N(3)-Al(3)-N(6)	107.3(1)
N(4)-Al(3)-N(6)	106.1(1)	N(1)-Al(4)-N(3)	88.9(1)	N(1)-Al(4)-N(5)	107.4(1)
N(3)-Al(4)-N(5)	115.2(1)	N(5)-Al(5)-N(6)	102.9(1)		
Al(1)-N(1)-Al(2)	115.1(1)	Al(1)-N(1)-Al(4)	90.5(1)	Al(1)-N(1)-C(1)	112.8(2)
Al(2)-N(1)-Al(4)	108.2(1)	Al(2)-N(1)-C(1)	105.7(2)	Al(4)-N(1)-C(1)	124.6(3)
Al(1)-N(2)-C(3)	96.0(2)	Al(1)-N(2)-C(4)	118.6(4)	Al(1)-N(2)-C(5)	112.5(3)
C(3)-N(2)-C(4)	111.8(3)	C(3)-N(2)-C(5)	107.8(3)	C(4)-N(2)-C(5)	109.2(3)
Al(1)-N(3)-Al(3)	88.1(1)	Al(1)-N(3)-C(6)	117.9(3)	Al(3)-N(3)-Al(4)	116.5(1)
Al(3)-N(3)-C(6)	123.3(3)	Al(4)-N(3)-C(6)	114.7(2)	Al(1)-N(3)-Al(4)	86.3(1)
Al(1)-N(4)-Al(3)	89.6(1)	Al(1)-N(4)-C(9)	121.3(3)	Al(3)-N(4)-C(9)	113.0(2)
Al(4)-N(5)-Al(5)	109.4(1)	Al(4)-N(5)-C(12)	113.0(3)	Al(5)-N(5)-C(12)	118.6(3)
Al(2)-N(6)-Al(3)	108.2(1)	Al(2)-N(6)-Al(5)	109.6(1)	Al(2)-N(6)-C(15)	108.7(3)
Al(3)-N(6)-Al(5)	105.4(1)	Al(3)-N(6)-C(15)	111.1(3)	Al(5)-N(6)-C(15)	113.7(3)
N(1)-C(1)-C(2)	112.9(3)	N(1)-C(1)-C(3)	107.7(2)	C(2)-C(1)-C(3)	110.6(3)
N(2)-C(3)-C(1)	110.9(3)	N(3)-C(6)-C(7)	112.1(3)	N(3)-C(6)-C(8)	111.6(3)
C(7)-C(6)-C(8)	109.7(3)	N(4)-C(9)-C(10)	111.7(3)	N(4)-C(9)-C(11)	109.2(3)
C(10)-C(9)-C(11)	110.6(3)	N(5)-C(12)-C(13)	111.3(3)	N(5)-C(12)-C(14)	115.0(4)
C(13)-C(12)-C(14)	112.0(4)	N(6)-C(15)-C(16)	115.0(4)	N(6)-C(15)-C(17)	111.8(3)
C(16)-C(15)-C(17)	108.8(3)				

Deviation of the atoms from the least-squares (Å) for $(AlN)_2$ rings

Al(1)	N(3)	Al(3)	N(4)	Al(1)	N(1)	Al(4)	N(3)
- 0.12	0.13	- 0.14	0.13	- 0.21	0.24	- 0.25	0.22

be formally derived from the hexameric "closed cage", observed in compounds of the type $(HAlNR)_6$ (R = i-Pr [1], n-Pr [6]) or $(XAlN—i\text{-}Pr)_6$ (X = Cl, CH_3 [7]), in which two opposite transverse Al—N bonds are broken. The "open cage" is built up of four six-membered rings, $(AlN)_3$, in the boat conformation and of two nearly planar four-membered rings, $(AlN)_2$, see Table 6.

The two LiH molecules are complexed to the cage (which may be regarded as an anion with formal charge 2—) through the Al(1)—H'(Al1)—Li' and the Al(1')—H'(Al1')—Li hydrogen bridges. The tetrahedral coordination of the lithium atom is completed by the N(3) atom of the cage framework and by the side nitrogens N(4) and N(2'). The interactions between Li and these side nitro-

TABLE 6

GEOMETRICAL PARAMETERS FOR COMPOUND II

Bond lengths (Å) and angles (°)

Al(1)–N(1)	1.898(7)	Al(1)–N(5)	1.891(7)	Al(2)–N(1)	1.947(8)
Al(2)–N(3)	1.851(7)	Al(2)–N(5')	1.931(7)	Al(3)–N(3)	1.845(6)
Al(3)–N(5)	1.914(8)	Al(3)–N(1')	1.930(7)	N(1)–C(1)	1.510(11)
N(2)–C(3)	1.481(12)	N(2)–C(4)	1.441(13)	N(2)–C(5)	1.495(15)
N(3)–C(6)	1.511(11)	N(4)–C(8)	1.39(2)	N(4)–C(9)	1.33(3)
N(4)–C(10)	1.37(3)	N(5)–C(11)	1.493(10)	N(6)–C(13)	1.501(15)
N(6)–C(14)	1.29(3)	N(6)–C(15)	1.47(3)	C(1)–C(2)	1.523(17)
C(2)–C(3)	1.507(15)	C(6)–C(7)	1.462(16)	C(7)–C(8)	1.45(3)
C(11)–C(12)	1.500(11)	C(12)–C(13)	1.530(13)		
Li–N(2')	2.19(2)	Li–N(3)	2.09(2)	Li–N(4)	2.12(2)
Li–H''(Al1')	1.92(8)	Al(1)–H''(Al1)	1.52(9)	Al(1)–H''(Al1)	1.54(7)
Al(2)–H(Al2)	1.49(7)	Al(3)–H(Al3)	1.47(8)		
N(1)–Al(1)–N(5)	108.0(2)	N(1)–Al(2)–N(3)	116.1(2)	N(1)–Al(2)–N(5')	90.8(2)
N(3)–Al(2)–N(5')	110.4(2)	N(3)–Al(3)–N(5)	113.8(2)	N(3)–Al(3)–N(1')	105.5(2)
N(5)–Al(3)–N(1')	91.8(2)	Al(1)–N(1)–Al(2)	116.4(1)	Al(1)–N(1)–Al(3')	115.0(1)
Al(2)–N(1)–Al(3')	88.2(1)	Al(1)–N(1)–C(1)	108.8(3)	Al(2)–N(1)–C(1)	107.9(4)
Al(3')–N(1)–C(1)	119.4(4)	Al(2)–N(3)–Al(3)	114.4(1)	Al(2)–N(3)–C(6)	116.3(4)
Al(3)–N(3)–C(6)	112.1(4)	Al(3)–N(3)–Li	95.9(3)	Al(2)–N(3)–Li	114.5(4)
Li–N(3)–C(6)	101.1(3)	Al(1)–N(5)–Al(3)	120.0(1)	Al(1)–N(5)–Al(2')	110.0(1)
Al(3)–N(5)–Al(2')	89.1(1)	Al(1)–N(5)–C(11)	110.1(3)	Al(3)–N(5)–C(11)	114.7(4)
Al(2')–N(5)–C(11)	111.1(4)	N(1)–C(1)–C(2)	116.6(4)	C(1)–C(2)–C(3)	116.0(5)
C(2)–C(3)–N(2)	117.8(4)	C(3)–N(2)–C(4)	109.5(4)	C(3)–N(2)–C(5)	108.2(4)
C(3)–N(2)–Li'	124.4(4)	C(4)–N(2)–Li'	105.9(4)	C(5)–N(2)–Li'	98.4(4)
C(4)–N(2)–C(5)	109.5(4)	N(3)–C(6)–C(7)	118.0(5)	C(6)–C(7)–C(8)	122.7(8)
C(7)–C(8)–N(4)	123.7(7)	C(8)–N(4)–C(9)	110.6(11)	C(8)–N(4)–C(10)	109.3(11)
C(8)–N(4)–Li	103.7(3)	C(9)–N(4)–C(10)	100.4(9)	C(9)–N(4)–Li	108.2(3)
C(10)–N(4)–Li	124.5(4)	N(5)–C(11)–C(12)	115.4(3)	C(11)–C(12)–C(13)	113.4(3)
C(12)–C(13)–N(6)	112.0(4)	C(13)–N(6)–C(14)	115.1(8)	C(13)–N(6)–C(15)	107.6(7)
C(14)–N(6)–C(15)	108.7(7)				
N(2')–Li–N(3)	124.1(4)	N(2')–Li–N(4)	114.6(4)	N(3)–Li–N(4)	103.1(4)
N(2')–Li–H''(Al1')	98(3)	Al(1')–H''(Al1')–Li	122(3)	N(1)–Al(1)–H''(Al1)	109(3)
N(1)–Al(1)–H''(Al1)	108(2)	N(5)–Al(1)–H''(Al1)	104(3)	N(5)–Al(1)–H''(Al1)	118(2)
H''(Al1)–Al(1)–H''(Al1)	110(2)	N(1)–Al(2)–H(Al2)	105(2)	N(3)–Al(2)–H(Al2)	117(3)
N(5')–Al(2)–H(Al2)	115(3)	N(3)–Al(3)–H(Al3)	113(2)	N(5)–Al(3)–H(Al3)	113(3)
N(1')–Al(3)–H(Al3)	118(3)				

Deviation of the atoms from the least-squares planes (Å) for $(AlN)_2$ ring

Al(2)	N(1)	Al(3')	N(5')
- 0.01	0.01	- 0.01	0.01

gen atoms constrain the related $-(CH_2)_3N(CH_3)_2$ substituents to assume a coiled conformation, while the remaining crystallographically-independent substituent displays a fully extended conformation.

In II, the shortest Al—N bond distances (those at N(3), 1.845(6) and 1.851(7) Å, and at Al(1), 1.891(7) and 1.898(7) Å) are shared by two hexagonal $(AlN)_3$ rings; all the other Al—N bond distances, ranging from 1.914(8) to 1.947(8) Å, are shared by one hexagonal and one square $(AlN)_2$ ring. A similar trend has been observed in $(HAlN—n\text{-}Pr)_8$ [6].

The overall average Al—N bond distance, involving four-coordinate atoms only, is 1.916(11) Å in I and 1.901(13) Å in II; these values agree with the corresponding ones found in other compounds of this series [1,3,5,6]. The other bond distances display the usual values; the shortening of some N—C and C—C distances observed in both compounds, as well as of some Al—H distances

in I, must be ascribed to the strong thermal disorder.

Both of the above structures show that when amines with $-N(CH_3)_2$ terminal groups are used in the synthesis of PIA, the tendency of this nitrogen atom to reach four-coordination leads preferentially to open cages, generally with H_{act}/Al ratios greater than unity, as clearly revealed in previous work [11]. For instance, the preparation procedure of I ($H_{act}/Al = 1.4$) leads to the hexamer $(HAlNR)_6$ ($H_{act}/Al = 1$) if 2-dimethylamino-isopropylamine is replaced by isopropylamine. Moreover, PIA obtained from substituted primary amines show an increasing ability to add other molecules: as a result, no LiH derivative of the hexamer $(HANR)_6$ has been obtained so far.

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