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

XV*. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE COMPOUNDS [((THF)Mg)(HA1N-t-Bu)$_3$] AND [((THF)$_3$Ca)(HA1N-t-Bu)$_3$] · THF

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Summary

The compounds [((THF)Mg)(HA1N-t-Bu)$_3$] (I) and [((THF)$_3$Ca)(HA1N-t-Bu)$_3$] · THF (II) have been structurally characterized from single-crystal diffraction data. The molecular structures are based on an (A1N)$_4$ "cubane" type framework in which an aluminum is replaced by an alkaline earth metal. According to the size and the coordination of the "foreign" atom (four for Mg, six for Ca) the cubic geometry of the cage is increasingly distorted. Coordination is completed by one molecule of THF to the Mg atom and three molecules to the Ca atom; in II a molecule of THF crystallizes with a cage molecule. Mean Mg—N and Ca—N bond distances are 2.090(4) and 2.490(2) Å. Crystal data: I, orthorombic, space group *Pbca*, *a* 17.107(2), *b* 17.305(4) and *c* 20.220(5) Å, $Z = 8$, calculated density 1.031 g/cm^3; II, orthorombic, space group *Pbca*, *a* 20.48(1), *b* 20.38(1), *c* 20.51(1), $Z = 8$, calculated density 1.081 g/cm^3.

Introduction

All poly(alkyliminoalane) derivatives (PIA), previously described in this series of papers have a cage structure built up of a framework formed essentially by aluminum and nitrogen atoms, corresponding in the most simple compounds to the (A1N)$_n$ formula ($n = 4,6,8$). Just two atomic species are present also in the skeleton of many other cage compounds, recently reviewed by Hitchcock

* For parts I—XIV see refs. 2, 3, 9.

et al. [1], including a variety of pairs of main group elements, as $(BN)_n$, $(MgO)_n$, $(BeO)_n$, $(CdS)_n$, $(MgS)_n$, etc. with n ranging from 1 to 8.

In this paper we describe the crystal structure of the title compounds, in which there is an unusual replacement of an aluminum atom of a cubic $(AlN)_4$ skeleton by an alkaline-earth metal such as Mg or Ca. In the preceding paper [2] of this series the preparation and some physical properties of these compounds have been reported. The calcium and magnesium derivatives will be referred to as CaPIA and MgPIA, respectively.

Experimental

Crystals of the compounds, colourless and prismatic in shape, were sealed in thin-walled capillaries under dry nitrogen owing to their high sensitivity to moisture. Weissenberg photographs were used to find space group and initial cell dimensions, which were later refined by application of least-squares procedure to a 25 reflections (for both compounds) accurately centered on the diffractometer.

Intensity data collection was carried out using Mo-K_α radiation (β filtered), on an automated Siemens AED diffractometer by the procedure previously described [3]. A total of 6440 reflections ($3° < \theta < 27°$) were measured from a crystal of MgPIA (average dimensions 0.3 × 0.7 × 1.0 mm), but 2680 with $I > 3\sigma(I)$ were used for the structural determination. The maximum decay monitored by a standard reflection, measured every 15 reflections, was 32% at the end of the run. A data set in the 3—21° angular range was gathered from a crystal of CaPIA (av. dimensions 0.6 × 0.7 × 0.9), yielding 3851 reflections of which 1515 with $I > 2\sigma(I)$ were used for the structural determination; the maximum decay in intensity was 11%. No correction for absorption was found to be necessary. The crystal data are summarized in Table 1.

Structure determination and refinement

The crystal structure of MgPIA was solved by direct methods using the program MULTAN [4]. As input data 300 reflections with $E > 1.84$ and 50 with $E < 0.5$ were used. The program gave 16 independent solutions, of which the one having "figures of merit" ABSFOM = 1.19, PSIZERO = 1365 and RESID

TABLE 1

CRYSTAL DATA FOR $[((THF)Mg)(HAlN\text{-}t\text{-}Bu)_3]$ AND $[((THF)_3Ca)(HAlN\text{-}t\text{-}Bu)_3] \cdot THF$

Molecular formula:	$[(C_4H_8O)Mg(HAlN\text{-}C_4H_9)_3]$	$[(C_4H_8O)_3Ca(HAlN\text{-}C_4H_9)_3] \cdot C_4H_8O$
Molecular weight:	464.9	697.0
Space group:	*Pbca*	*Pbca*
Molecules/unit cell:	8	8
Cell constants:	$a = 17.107(2)$, $b = 17.305(4)$,	$a = 20.48(1)$, $b = 20.38(1)$,
(Mo-K_α rad., $\lambda = 0.71069$ Å)	$c = 20.220(5)$ Å	$c = 20.51(1)$ Å
Cell volume:	5985.9 Å^3	8560.9 Å^3
Calculated density:	1.031 g cm^{-3}	1.081 g cm^{-3}
Linear absorption coefficient μ:	1.75 cm^{-1}	2.56 cm^{-1}

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TABLE 2

FINAL ATOMIC FRACTIONAL COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^2$) FOR [((THF)Mg)(HAlN-t-Bu)$_3$].

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mg	5262(1)	2151(1)	3463(1)	337(3)	378(3)	377(3)	34(3)	9(3)	-38(3)
Al(1)	3648(1)	2237(1)	3282(1)	350(3)	485(4)	349(3)	-31(3)	-58(3)	-46(3)
Al(2)	4286(1)	2942(1)	4335(1)	354(3)	385(3)	275(2)	8(3)	0(2)	-16(2)
Al(3)	4511(1)	3518(1)	3118(1)	519(4)	395(3)	335(3)	22(3)	16(3)	55(3)
N(1)	4256(1)	1904(1)	4017(1)	367(8)	356(8)	338(8)	-44(7)	-18(7)	48(7)
N(2)	4501(1)	2516(1)	2722(1)	463(9)	482(9)	270(8)	4(9)	-4(7)	-47(7)
N(3)	5174(1)	3268(1)	3849(1)	356(8)	359(8)	340(8)	-65(7)	-12(7)	-43(7)
N(4)	3596(1)	3264(1)	3635(1)	387(9)	463(10)	349(9)	117(8)	-12(7)	3(7)
C(1)	4108(1)	1210(1)	4425(1)	497(13)	459(13)	558(15)	-89(11)	-14(11)	98(11)
C(2)	3301(2)	1258(2)	4744(2)	767(19)	802(20)	703(19)	-229(17)	172(16)	254(16)
C(3)	4133(2)	492(2)	3982(2)	868(22)	401(13)	890(22)	-122(14)	-62(17)	58(14)
C(4)	4715(2)	1143(2)	4969(1)	868(20)	610(17)	608(17)	8(15)	-104(16)	206(14)
C(5)	4541(2)	2365(2)	1999(1)	621(15)	730(16)	281(11)	20(13)	9(10)	-90(11)
C(6)	4490(2)	1495(2)	1877(2)	1109(25)	826(20)	501(16)	115(19)	-50(16)	-325(15)
C(7)	5319(2)	2671(2)	1728(2)	933(23)	1066(26)	454(15)	-16(20)	236(16)	-12(16)
C(8)	3857(2)	2774(2)	1649(1)	902(21)	1108(26)	317(13)	126(19)	-177(13)	0(15)
C(9)	5822(2)	3763(2)	4106(1)	527(14)	515(13)	553(15)	-177(11)	7(11)	-119(11)
C(10)	6101(2)	3456(2)	4765(2)	674(18)	1033(25)	791(20)	-252(18)	-337(17)	-63(19)
C(11)	6480(2)	3798(2)	3601(2)	731(20)	1113(27)	992(25)	-534(20)	251(19)	-224(21)
C(12)	5516(3)	4593(2)	4221(2)	1170(29)	567(18)	1059(28)	-214(18)	-139(24)	-297(18)
C(13)	2881(2)	3747(2)	3733(1)	504(13)	671(16)	543(15)	223(12)	-64(12)	-44(13)
C(14)	3134(2)	4534(2)	3995(2)	892(23)	758(21)	1337(32)	437(18)	-155(22)	-416(21)
C(15)	2466(2)	3847(2)	3058(2)	715(19)	1153(26)	732(19)	458(19)	-191(18)	102(19)
C(16)	2320(2)	3347(2)	4196(2)	471(15)	1267(27)	753(20)	274(17)	150(14)	-3(20)
O(1)	6208(1)	1471(1)	3426(1)	464(9)	653(11)	666(11)	222(8)	-17(8)	-127(9)
C(17)	6825(3)	1484(3)	3906(3)	955(28)	1306(33)	1629(42)	569(25)	-594(28)	-579(31)
C(18)	7216(3)	761(3)	3861(3)	1225(34)	1153(31)	1547(39)	705(28)	-459(31)	-202(30)
C(19)	7016(4)	447(3)	3259(3)	2045(52)	1562(43)	1825(50)	1374(41)	-917(42)	-884(38)
C(20)	6418(3)	909(3)	2949(2)	1184(31)	1348(33)	1054(29)	786(28)	-253(25)	-488(26)

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
H(Al1)	2918(16)	1815(16)	3036(15)	785(79)	H'(C11)	6674(18)	3288(19)	3669(16)	989(91)
H(Al2)	4160(14)	3208(14)	5054(12)	573(61)	H''(C11)	6379(21)	3904(21)	3219(18)	1143(110)
H(Al3)	4535(12)	4270(13)	2754(11)	543(56)	H'''(C11)	6863(20)	4169(21)	3688(18)	1162(108)
H'(C2)	3195(18)	821(17)	5009(14)	911(85)	H'(C12)	5316(20)	4824(21)	3811(20)	1286(117)
H''(C2)	2855(17)	1355(17)	4428(15)	956(88)	H''(C12)	5022(22)	4558(19)	4541(19)	1259(111)
H'''(C2)	3256(18)	1753(18)	5020(15)	962(89)	H'''(C12)	5906(21)	4936(23)	4464(20)	1423(126)
H'(C3)	4628(14)	433(14)	3814(13)	641(68)	H'(C14)	3622(23)	4750(24)	4026(22)	1643(136)
H''(C3)	4004(15)	45(15)	4205(14)	674(72)	H''(C14)	2784(21)	4894(22)	3942(19)	1351(121)
H'''(C3)	3820(16)	566(16)	3663(14)	702(74)	H'''(C14)	3148(25)	4476(25)	4510(24)	1845(156)
H'(C4)	5185(15)	1044(15)	4741(13)	614(67)	H'(C15)	2693(24)	4232(24)	2840(20)	1330(128)
H''(C4)	4592(18)	674(19)	5216(17)	929(98)	H''(C15)	2414(26)	3519(23)	2735(19)	1468(127)
H'''(C4)	4737(17)	1622(17)	5227(15)	855(80)	H'''(C15)	1924(22)	4171(23)	3098(19)	1195(124)
H'(C6)	4022(19)	1269(19)	2054(16)	1042(95)	H'(C16)	1871(20)	3685(19)	4304(18)	1212(107)
H''(C6)	4522(17)	1364(17)	1430(15)	868(85)	H''(C16)	2599(18)	3262(18)	4649(16)	970(84)
H'''(C6)	4892(16)	1239(16)	2104(14)	750(77)	H'''(C16)	2245(17)	2840(16)	4024(15)	839(85)
H'(C7)	5349(16)	3139(17)	1757(14)	692(77)	H'(C17)	7347(29)	1984(28)	3846(26)	2369(175)
H''(C7)	5644(20)	2336(21)	1874(19)	1168(114)	H''(C17)	6586(21)	1619(21)	4425(19)	1443(116)
H'''(C7)	5380(17)	2591(19)	1232(17)	950(89)	H'(C18)	7632(24)	772(24)	3925(20)	1525(131)
H'(C8)	3888(18)	3382(18)	1708(15)	798(86)	H''(C18)	6981(24)	425(23)	4198(23)	1929(146)
H''(C8)	3795(19)	2674(20)	1213(17)	1056(98)	H'(C19)	7353(27)	453(23)	2985(22)	1796(144)
H'''(C8)	3291(17)	2564(19)	1820(15)	908(84)	H''(C19)	6918(20)	-30(22)	3261(19)	1342(114)
H'(C10)	5664(21)	3429(21)	5176(19)	1312(115)	H'(C20)	6568(27)	1066(29)	2586(25)	2034(164)
H''(C10)	6236(17)	2929(16)	4691(16)	796(80)	H''(C20)	6028(24)	652(24)	2919(21)	1729(134)
H'''(C10)	6504(22)	3773(21)	4912(18)	1214(113)					

TABLE 3

FINAL ATOMIC FRACTIONAL COORDINATES ($\times 10^4$) AND THERMAL PARAMTERS ($\times 10^2$) FOR $[((THF)_3Ca)(HAlN\text{-}t\text{-}Bu)_3] \cdot THF$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	1985(1)	1985(1)	1985(1)	267(11)	280(11)	287(17)	-18(11)	-10(11)	4(12)
Al(1)	2258(2)	2729(2)	3321(2)	346(18)	304(19)	258(24)	23(17)	84(17)	-8(17)
Al(2)	3318(2)	2265(2)	2722(2)	276(17)	363(19)	294(26)	48(16)	-11(18)	15(18)
Al(3)	2728(2)	3324(2)	2265(2)	270(17)	243(16)	317(24)	2(15)	45(19)	38(16)
N(1)	2548(5)	1869(4)	3056(5)	352(50)	202(48)	285(59)	74(38)	44(45)	132(41)
N(2)	1879(4)	3064(4)	2548(5)	278(49)	234(42)	459(72)	76(38)	49(45)	-13(48)
N(3)	3062(5)	2539(5)	1889(5)	310(46)	438(54)	280(68)	41(45)	49(45)	41(47)
N(4)	3105(5)	3105(4)	3108(5)	360(51)	271(47)	236(63)	-1(41)	24(45)	-5(44)
C(1)	2559(7)	1318(6)	3501(7)	475(76)	241(68)	398(87)	53(56)	-47(64)	-33(60)
C(2)	2983(10)	1473(8)	4118(9)	1136(139)	660(106)	575(123)	138(98)	-165(107)	138(85)
C(3)	2834(7)	719(6)	3159(7)	614(86)	314(65)	418(96)	-18(59)	-61(73)	-3(63)
C(4)	1876(8)	1172(8)	3771(8)	668(105)	662(97)	411(104)	-167(79)	172(79)	140(78)
C(5)	1321(6)	3506(6)	2576(7)	386(72)	344(68)	369(94)	84(56)	41(63)	-109(61)
C(6)	1461(7)	4105(6)	2989(8)	463(79)	266(70)	855(124)	194(57)	-53(74)	-229(72)
C(7)	1145(8)	3764(8)	1893(8)	548(88)	512(87)	729(120)	14(71)	-4(82)	148(83)
C(8)	718(7)	3179(7)	2860(8)	457(78)	546(91)	757(120)	230(68)	115(76)	-78(77)
C(9)	3523(5)	2567(6)	1310(6)	263(63)	476(72)	85(81)	-101(52)	-67(53)	39(56)
C(10)	4109(7)	2997(8)	1446(8)	523(86)	871(111)	396(107)	-60(82)	-48(72)	-201(85)
C(11)	3793(8)	1866(7)	1175(8)	792(103)	403(90)	470(104)	138(74)	243(82)	-51(72)
C(12)	3181(8)	2843(8)	692(8)	696(101)	680(95)	364(106)	-131(78)	96(75)	-31(77)
C(13)	3545(6)	3541(6)	3539(7)	339(68)	394(71)	277(90)	-88(53)	23(57)	-110(59)
C(14)	3652(7)	3192(7)	4160(7)	515(80)	472(85)	375(99)	-10(65)	-115(68)	-4(68)
C(15)	4178(6)	3659(7)	3176(8)	307(74)	648(90)	670(112)	-163(67)	-81(71)	-49(82)
C(16)	3184(8)	4173(7)	3649(8)	725(108)	300(78)	728(122)	-88(69)	-153(86)	-30(72)
O(1)	1237(4)	2244(4)	1024(5)	378(48)	527(53)	529(65)	125(43)	-110(42)	25(47)
C(17)	1418(7)	2660(8)	473(8)	617(92)	803(112)	409(112)	135(79)	-63(78)	205(87)
C(18)	784(10)	2724(12)	143(12)	843(135)	1729(219)	1384(199)	344(137)	83(129)	887(168)
C(19)	317(10)	2272(11)	370(11)	880(140)	1577(184)	994(174)	-39(131)	-463(126)	302(143)
C(20)	563(8)	2045(8)	975(8)	477(85)	860(108)	552(108)	-1(81)	-281(73)	254(87)
O(2)	2243(5)	1033(4)	1244(5)	624(58)	468(51)	411(59)	13(46)	89(50)	-75(42)
C(21)	2051(8)	961(8)	582(9)	754(106)	584(92)	608(113)	172(84)	-33(91)	-30(78)
C(22)	2284(11)	371(11)	326(10)	1461(175)	1417(175)	821(153)	397(146)	-79(133)	-777(135)
C(23)	2728(11)	140(10)	784(10)	1506(199)	838(134)	863(147)	239(135)	177(130)	21(111)
C(24)	2631(9)	465(8)	1410(8)	885(114)	630(95)	477(110)	190(87)	0(90)	-105(80)
O(3)	1023(4)	1240(4)	2241(5)	489(50)	476(51)	431(62)	-108(39)	57(46)	122(46)
C(25)	472(8)	1412(8)	2661(9)	653(102)	754(102)	896(134)	-294(84)	465(99)	-155(94)
C(26)	123(12)	793(11)	2775(12)	1166(166)	1033(150)	1636(221)	-194(127)	627(160)	-195(145)
C(27)	374(11)	361(10)	2356(12)	1124(165)	826(132)	1869(204)	-654(124)	427(154)	-215(136)
C(28)	986(8)	576(8)	2060(9)	517(88)	644(98)	802(127)	-177(72)	194(85)	-154(85)

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
O(4)	-399(13)	239(13)	4511(13)	1675(85)	O(5)	518(16)	-171(17)	-285(17)	2003(122)
C(29)	95(20)	562(20)	4637(20)	1448(133)	C(33)	33(29)	301(28)	-477(27)	2276(230)
C(30)	86(22)	418(21)	5329(22)	1939(155)	C(34)	-400(30)	490(30)	-3(30)	2471(258)
C(31)	-364(21)	-102(21)	5479(21)	1743(147)	C(35)	-345(27)	-231(28)	381(28)	2232(220)
C(32)	-557(19)	-336(19)	4879(20)	1346(127)	C(36)	292(28)	-344(27)	304(28)	2211(217)
H(A11)	2042(35)	2831(35)	3934(37)	201(192)	H'''(C14)	3915(46)	3493(48)	4442(50)	985(284)
H(A12)	3924(42)	1987(42)	2810(43)	591(244)	H'(C15)	4088(38)	3913(39)	2800(41)	516(222)
H(A13)	2753(41)	3938(41)	2081(41)	669(236)	H''(C15)	4362(44)	3286(43)	3148(45)	743(259)
H'(C2)	3383(41)	1349(38)	3884(40)	415(226)	H'''(C15)	4484(53)	4032(53)	3482(52)	1261(343)
H''(C2)	2763(38)	1688(40)	4272(39)	457(224)	H'(C16)	2905(41)	3943(41)	3919(41)	560(239)

TABLE 3 (continued)

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
H'''(C2)	2993(38)	966(39)	4393(42)	410(223)	H''(C16)	3096(43)	4426(43)	3177(44)	698(261)
H'(C3)	2576(42)	453(39)	2842(38)	430(233)	H'''(C16)	3471(45)	4522(47)	3812(47)	675(287)
H''(C3)	3099(40)	804(38)	2655(41)	505(230)	H'(C17)	1588(45)	3062(44)	698(46)	548(272)
H'''(C3)	3148(46)	508(49)	3414(49)	937(294)	H''(C17)	1753(44)	2495(48)	268(49)	785(273)
H'(C4)	1823(51)	705(51)	3909(52)	1187(331)	H'(C18)	586(50)	3081(49)	266(52)	1039(313)
H''(C4)	1574(51)	1053(52)	3514(53)	819(329)	H'''(C18)	798(37)	2754(37)	-304(41)	379(220)
H'''(C4)	1926(47)	1329(48)	4228(50)	960(305)	H'(C19)	-108(42)	2333(43)	225(45)	663(271)
H'(C5)	1500(41)	3839(42)	3429(43)	478(245)	H''(C19)	383(50)	1922(51)	99(50)	1155(338)
H''(C6)	1772(38)	4351(38)	2897(39)	393(213)	H'(C20)	528(44)	1631(42)	1038(44)	586(250)
H'''(C6)	1056(40)	4380(40)	2992(41)	449(226)	H''(C20)	319(49)	2235(47)	1345(47)	883(302)
H'(C7)	715(48)	3710(48)	2024(48)	1174(300)	H'(C21)	1552(42)	948(43)	570(46)	644(263)
H''(C7)	1217(55)	4236(54)	1892(54)	1562(354)	H'''(C21)	2233(39)	1290(38)	357(40)	413(227)
H'''(C7)	1333(49)	3525(51)	1574(52)	1040(318)	H'(C22)	1908(53)	132(54)	326(55)	1322(359)
H'(C8)	580(35)	2867(34)	2569(38)	339(194)	H''(C22)	2406(52)	289(49)	-125(47)	940(309)
H''(C8)	909(45)	2730(46)	3164(48)	895(286)	H'(C23)	2616(55)	-253(56)	829(55)	1295(361)
H'''(C8)	456(52)	3439(49)	3089(50)	1116(317)	H''(C23)	3114(51)	196(53)	594(54)	1220(336)
H'(C10)	3945(45)	3431(45)	1595(46)	686(268)	H'(C24)	3015(41)	704(41)	1587(43)	517(247)
H''(C10)	4333(40)	2766(40)	1672(44)	510(241)	H''(C24)	2368(41)	213(41)	1769(41)	448(232)
H'''(C10)	4409(38)	3048(36)	998(38)	316(210)	H'(C25)	691(41)	1653(41)	2993(42)	494(241)
H'(C11)	3963(52)	1432(52)	1425(51)	1150(327)	H''(C25)	225(48)	1805(44)	2428(50)	802(275)
H''(C11)	3402(43)	1637(42)	1120(42)	544(245)	H'(C26)	192(61)	641(59)	3234(61)	1535(407)
H'''(C11)	3881(49)	1951(48)	732(50)	1140(313)	H''(C26)	-355(59)	851(55)	2693(56)	1350(382)
H'(C12)	3499(32)	2854(34)	322(36)	111(180)	H'(C27)	456(45)	-59(43)	2594(48)	843(278)
H''(C12)	3020(41)	3297(41)	782(42)	579(252)	H''(C27)	49(56)	284(55)	2001(53)	844(370)
H'''(C12)	2804(43)	2555(44)	574(45)	895(279)	H'(C28)	1066(45)	558(45)	1524(46)	614(272)
H'(C14)	3238(39)	3170(38)	4346(40)	483(222)	H''(C28)	1382(43)	366(46)	2262(47)	731(274)
H''(C14)	3941(41)	2763(42)	4088(42)	544(241)					

= 31.7 led to correct solution of the structure. From the *E*-map Mg, Al and N atoms were located, and from the next Fourier synthesis the position of all the carbon atoms was obtained (R = 0.237). A least-squares refinement with isotropic thermal parameters converged to R = 0.128. From a Fourier difference all H atoms were located although for some of them, bonded to C atoms, which gave too great a peaks spread, an adjustment of the coordinates was carried out on the bases of usual carbon geometry. A further refinement, including anisotropic thermal parameters of all non-hydrogen atoms, gave a final value of R = 0.057.

The crystal structure of CaPIA was solved by Patterson procedure. The heavy-atom position was readily defined and a Fourier synthesis, phased with this atom gave the location of the nitrogen, aluminum and carbon atoms of the molecular cage. After only a preliminary refinement of these atoms, a *F*-map indicated clearly the atomic positions as of the clathrate molecule of THF, as well of most of the hydrogens of the main molecule. Hydrogen atoms of THF clathrate molecules were disregarded. The last cycles of the least-square refinement were performed with the fixed contribution of the main molecule, using isotropic thermal parameters for THF clathrate molecules and finally with the fixed contribution of all atoms and isotropic thermal parameters for the hydrogens of the carbon atoms. The final R value was 0.082. The function to be minimized was $\Sigma w(F_o - F_c)^2$, using the weighting scheme of Cruickshank [5]. Atomic scattering

factors for all non-hydrogen atoms were taken from Cromer and Man [6] and those for the hydrogen atoms from Stewart et al. [7]. All the computer programs, except the MULTAN, were by Immirzi [8].

The final values of positional and thermal parameters are listed in Tables 2 and 3. Lists of structure factors are obtainable from the authors on request.

Results and discussion

The molecular structure of both compounds is similar to that observed for other tetrameric species, for example $(HAlN\text{-}i\text{-}Pr)_4$ [9], $(MeAlN\text{-}i\text{-}Pr)_4$ [9] and $(PhAlNPh)_4$ [10], whose structure consists essentially of a "cubane" skeleton (AlN). In the present case, one of the four aluminum atoms is replaced by a calcium or magnesium atom. All the t-butyl groups as well as the THF molecules coordinated to the alkaline earth metals point outward from the cage; t-butyl groups in both compounds are in the "staggered" conformation. A perspective view of both molecules and numberings is shown in fig. 1 and the geometrical parameters are reported in Tables 4 and 5.

The replacement of an aluminum by an alkaline earth metal distorts the rather regular cubic geometry observed in previously cited cages, where bond angles at Al and N vary from 89.5° to 90.5° and Al—N bond distances vary for each cage within the e.s.d.'s. The nature of the distortion is similar in both compounds, but the extent of distortion increases on passing from MgPIA to CaPIA with increasing size of the alkaline earth atom and the coordination number (4-coordination for Al and Mg, 6-coordination for Ca). The major cause of distortion arises from the length of Mg—N and Ca—N bonds (means 2.090(4), 2.490(2) Å) compared with Al—N bonds, which in both compounds lie between 1.900 to 1.945 Å. As a result of this lengthening the alkaline earth metals are pushed outward from the cage with a consequent reduction of N—M—N bond angles down to 86.3(2)° for M = Mg and 73.2(2)° for M = Ca. On the other hand, some angles at Al (N(1)—Al(1)—N(2), N(1)—Al(2)—N(3) and N(2)—Al(3)—N(3)) are enlarged to 92.2(1)° and 102.7(1)° in MgPIA and CaPIA, respectively. The general rule [3] by which in 4-membered rings $(Al—N)_2$ bond angles at N are smaller than at Al, is obeyed in spite of the various distortions, as may be appreciated by inspection of Table 3.

The different degree of distortion, markedly increasing on passing from MgPIA to CaPIA, may originate the extent of displacement of the atoms belonging to a 4-membered ring $(AlN)_2$ out of their least-square planes (see Tables 4 and 5). It is worthwhile to note the significant lengthening of the three Al—N bonds converging to N(4), i.e. the atom situated at the corner opposite to that of the alkaline earth metal: the mean of these three Al—N bond distances increases from MgPIA (mean 1.925(1) Å) to CaPIA (mean 1.937(5) Å) while for the other Al—N bonds the mean distance is 1.906(6) Å for MgPIA and 1.902(4) Å for CaPIA: these values are slightly but significantly shorter than the mean values found in previously studied cage molecules (1.916 Å). This effect may be attributed to the enhancement of the ionic character of the M—N′ bond on passing from M = Al to M = Mg and to M = Ca, and the decrease of the polarizability of the metal in the same order. As a consequence high electron charge could be located at the N′ atom and could serve to enhance the covalent

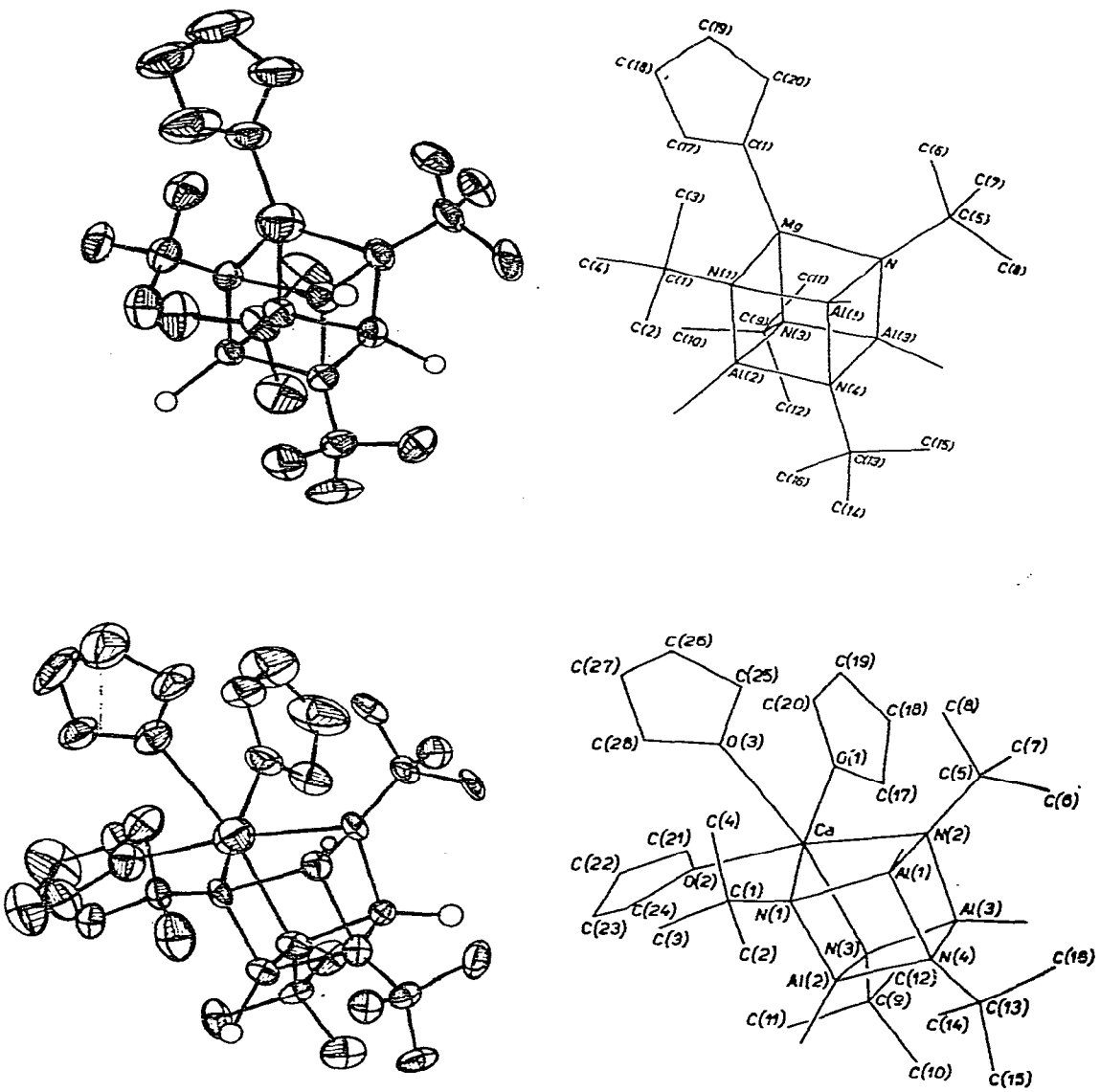

Fig. 1. Perspective view and numbering scheme of the molecules of [((THF)Mg)(HAlN-t-Bu)$_3$] and of [((THF)$_3$Ca)(HAlN-t-Bu)$_3$] · THF.

character of the adjacent N'—Al bonds at expense of electron availability for the next Al—N(4) bonds.

The Mg—N bond distance (mean 2.090(4) Å) is quite close to that found in the dimer $[(CH_3)_2N(CH_2)_2NCH_3MgCH_3]_2$ [11] (means 2.107(3), 2.102(3) Å), while the Mg—O bond distance (2.002(2) Å) may be compared with the values of 2.01(4) and 2.06(4) Å found for the ethyl ether oxygen-t-magnesium dative bond in $C_6H_5MgBr \cdot 2C_4H_{10}O$ [12]. The calcium atom is 6-coordinate with a geometry intermediate between a D_{3d} trigonal antiprismatic (octahedron) and

TABLE 4

SELECTED GEOMETRICAL PARAMETERS FOR [((THF)Mg)(HAlN-t-Bu)$_3$].

Mg-N(1)	2.098(2)		Mg-N(2)	2.083(3)
Mg-N(3)	2.090(2)		Mg-O(1)	2.002(2)
Mean Mg-N	2.090(4)			
Al(1)-N(1)	1.903(2)		Al(1)-N(2)	1.909(2)
Al(1)-N(4)	1.917(2)		Al(2)-N(1)	1.908(2)
Al(2)-N(3)	1.895(2)		Al(2)-N(4)	1.926(2)
Al(3)-N(2)	1.910(2)		Al(3)-N(3)	1.913(2)
Al(3)-N(4)	1.933(2)			
Mean Al-N(not 4)	1.906(3)		Mean Al-N(4)	1.925(5)
Overall mean		1.913(4)		
Al(1)-H(Al1)	1.53(3)		Al(2)-H(Al2)	1.54(2)
Al(3)-H(Al3)	1.50(2)			
Mean Al-H	1.52(1)			
N(2)-C(1)	1.479(3)		N(2)-C(5)	1.487(3)
N(3)-C(9)	1.494(3)		N(4)-C(13)	1.495(3)
Mean N-C	1.489(4)			
Mean C-C(t-Bu)	1.528(4)			
O(1)-C(17)	1.434(5)		O(1)-C(20)	1.416(5)
C(17)-C(18)	1.422(7)		C(18)-C(19)	1.376(8)
C(19)-C(20)	1.442(8)			

Mean N-Mg-N	86.3(2)	Mean N-Mg-O	128(2)
Mean N-Al-N(not 4)	97.1(1)	Mean N-Al-N(4)	90.9(1)
Mean Mg-N-Al	88.3(1)	Mean Mg-N-C	127.7(5)
Mean Al-N(not 4)-Al	89.5(1)	Mean Al-N(4)-Al	88.4(2)
Mean Al-N(not 4)-C	125.4(2)	Mean Al-N(4)-C	126.4(9)
Mean N-C-C	109.5(2)	Mean C-C-C(t-Bu)	109.4(4)

Deviation of the atoms from the least-squares planes (Å) for four-membered rings in ((THF)Mg)(HAlN-t-Bu)$_3$

Mg	N(1)	Al(1)	N(2)	Mg	N(1)	Al(2)	N(3)
-0.011	0.012	-0.013	0.012	0.011	-0.012	0.014	-0.012
Mg	N(2)	Al(3)	N(3)	Al(1)	N(1)	Al(2)	N(4)
-0.015	0.017	-0.018	0.017	-0.039	0.039	-0.039	0.039
Al(1)	N(2)	Al(3)	N(4)	Al(2)	N(3)	Al(3)	N(4)
0.036	-0.036	0.035	-0.035	-0.036	0.036	-0.035	0.035

a D_{3h} trigonal prismatic form (trigonal prism). The planes containing the three Ca-bonded nitrogen atoms and the three oxygen atoms (of THF molecules) are strictly parallel: the geometrical situation is well defined by the twist angle ϕ, defined by Muetterties and Guggenberger [13], (0° in a regular trigonal prism and 60° in an octahedron) for which a mean of 42° was calculated.

The mean Ca—N value (2.490(2) Å) corresponds fairly closely to the sum of the covalent radii [14] for the two atoms (2.48 = 1.74 + 0.74 Å). The Ca—O bond distance (mean 2.539(9) Å) is close to the highest values reported [15] for this bond (from 2.30 to 2.55 Å).

TABLE 5

SELECTED GEOMETRICAL PARAMETERS FOR $[((THF)_3Ca)(HAlN\text{-}t\text{-}Bu)_3] \cdot THF$.

Ca-N(1)	2.492(10)	Ca-N(2)	2.493(10)	Ca-N(3)	2.486(10)
Mean Ca-N	2.490(2)				
Ca-O(1)	2.552(10)	Ca-O(2)	2.521(10)	Ca-O(3)	2.543(9)
Mean Ca-O	2.539(9)				
Al(1)-N(1)	1.923(10)	Al(1)-N(2)	1.901(11)	Al(1)-N(4)	1.928(10)
Al(2)-N(1)	1.900(10)	Al(2)-N(3)	1.872(12)	Al(2)-N(4)	1.936(10)
Al(3)-N(2)	1.908(10)	Al(3)-N(3)	1.903(11)	Al(3)-N(4)	1.945(11)
Mean Al-N(not 4)	1.901(7)			Mean Al-N(4)	1.936(5)
		Overall mean	1.908(11)		
Mean Al-H	1.35(2)	Mean N-C	1.49(2)	Mean C-C(t-Bu)	1.525(7)
O(1)-C(17)	1.46(2)	O(1)-C(20)	1.44(2)	C(17)-C(18)	1.47(3)
C(18)-C(19)	1.41(3)	C(19)-C(20)	1.42(3)		
O(2)-C(21)	1.42(2)	O(2)-C(24)	1.44(2)	C(21)-C(22)	1.40(3)
C(22)-C(23)	1.39(3)	C(23)-C(24)	1.46(3)		
O(3)-C(25)	1.46(2)	O(3)-C(28)	1.41(2)	C(25)-C(26)	1.47(3)
C(26)-C(27)	1.33(3)	C(27)-C(28)	1.46(3)		
Mean O-C	1.438(8)				
N(1)-Ca-N(2)	73.5(2)	N(1)-Ca-N(3)	72.7(2)	N(2)-Ca-N(3)	73.3(2)
Mean N-Ca-N	73.2(2)				
O(1)-Ca-O(2)	79.6(2)	O(1)-Ca-O(3)	79.5(2)	O(2)-Ca-O(3)	80.0(2)
Mean O-Ca-O	79.7(1)				
N(1)-Ca-O(1)	168.0(2)	N(1)-Ca-O(2)	111.2(2)	N(1)-Ca-O(3)	96.9(2)
N(2)-Ca-O(2)	167.5(2)	N(2)-Ca-O(3)	111.3(2)	N(2)-Ca-O(1)	97.1(2)
N(3)-Ca-O(3)	167.2(2)	N(3)-Ca-O(1)	112.2(2)	N(3)-Ca-O(2)	96.7(2)
Mean N-Al-N(not 4)	102.7(1)	Mean N-Al-N(4)	92.0(2)		
Mean Ca-N-Al	91.7(1)	Mean Ca-N-C	129.3(1)	Mean Ca-O-C	125.2(4)
Mean Al-N(not 4)-Al	88.4(3)	Mean Al-N(4)-Al	86.3(2)	Overall mean Al-N-Al	87.4(5)
Mean Al-N(not 4)-C	122.4(5)	Mean Al-N(4)-C	127.8(2)		
Mean N-C-C(t-Bu)	110.2(5)	Mean C-C-C(t-Bu)	108.6(7)		
Mean O-C-C(THF)	105(1)	Mean C-C-C(THF)	109(2)	C-O-C(THF)	109(1)

Deviation of the atoms from the least-squares planes (Å) for four-membered rings in $((THF)_3Ca)(HAlN\text{-}t\text{-}Bu)_3 \cdot THF$

Ca	N(1)	Al(1)	N(2)	Ca	N(1)	Al(2)	N(3)	Ca	N(2)	Al(3)	N(3)
0.042	-0.056	0.071	-0.057	-0.038	0.051	-0.065	0.052	-0.048	0.065	-0.081	0.065
Al(1)	N(1)	Al(2)	N(4)	Al(1)	N(2)	Al(3)	N(4)	Al(2)	N(3)	Al(3)	N(4)
-0.071	0.072	-0.071	0.070	-0.069	0.069	-0.068	0.067	0.066	-0.067	0.064	-0.063

The conformation of THF coordinate molecules is of the "half-chair" type; the large thermal motion of the carbon atoms in the clathrate THF molecule prevents a good conformational determination. Mean N—C bond lengths are quite close in both compounds (means 1.495(3) in MgPIA and 1.49(2) Å in CaPIA); it is significant that the single highest value correspond in both cases to the N(4)—C bond.

The C ... C intermolecular contacts are greater than 3.75 Å in MgPIA and 3.5 Å in CaPIA; for this last compound a view of the packing is given in Fig. 2.

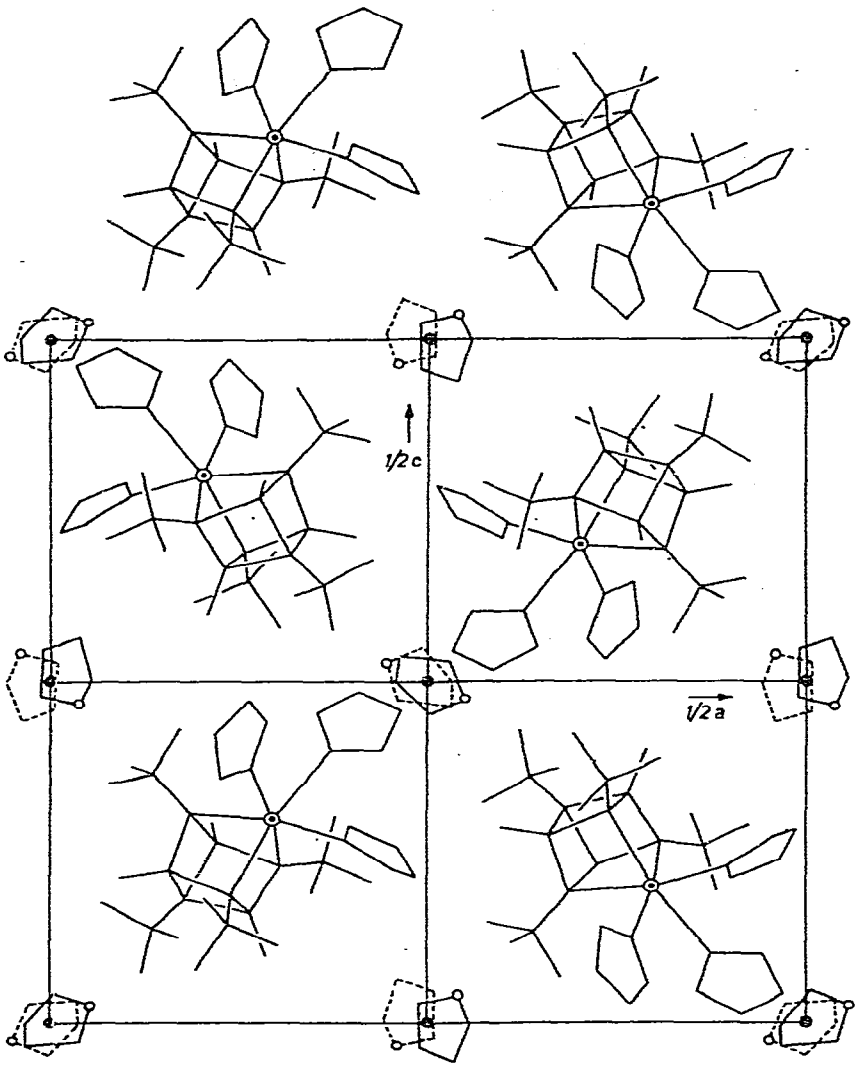

Fig. 2. A prepresentation of the packing of $[((THF)_3Ca)(HAlN\text{-}t\text{-}Bu)_3] \cdot THF$. Projection along the b axis.

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