

THE PREPARATION AND CRYSTAL STRUCTURE OF BIS(μ -*N,N'*-DIETHYLETHYLENEDIAMIDO)BIS(DIHYDRIDOALUMINUM)HYDRIDOALUMINUM, $\text{HAl}[(\text{EtN}(\text{CH}_2)_2\text{NEt})\text{AlH}_2]_2$, AND ITS CHLORINATED DERIVATIVE, $(\text{H}_{0.85}\text{Cl}_{0.15})\text{Al}[(\text{EtN}(\text{CH}_2)_2\text{NEt})\text{AlH}(\text{H}_{0.7}\text{Cl}_{0.3})]_2$

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Summary

The compounds $\text{HAl}[(\text{EtN}(\text{CH}_2)_2\text{NEt})\text{AlH}_2]_2$ (I) and $(\text{H}_{0.85}\text{Cl}_{0.15})\text{Al}[(\text{EtN}(\text{CH}_2)_2\text{NEt})\text{AlH}(\text{H}_{0.7}\text{Cl}_{0.3})]_2$ (II) have been prepared and their crystal structures determined by X-ray analysis. Block-matrix least-squares refinement led to a final *R* values of 0.050 and 0.095 for I and II, respectively. The molecular structure of I is built up of two AlH_2 groups and one AlH group, connected to each other through two diethylethylenediamine bridging groups. In II, a similar molecular conformation contains hydrogenated and chlorinated molecules randomly co-crystallized. Two different types of Al—H bond distances (1.66(4)—1.70(4) and 1.48(6)—1.51(6) Å) are observed for AlH_2 groups in I; the longer bonds are probably higher in ionic character. The Al—N bond distances range from 1.918(3) to 2.068(3) Å in I and from 1.914(5) to 2.078(5) Å in II. Crystal data. I: triclinic, space group *PT*, *a* 7.433(2), *b* 7.436(2), *c* 18.810(7) Å, α 95.8(1), β 109.9(1), γ 82.6(1)°, *Z* = 2; II: triclinic, space group *P* $\bar{1}$, *a* 7.645(3), *b* 7.574(3), *c* 19.069(9) Å, α 95.6(1), β 111.3(1), γ 81.1(1)°, *Z* = 2.

Introduction

In our programme of study of amino and imino alanes, particular attention has been paid to a class of oligomers of formula $(\text{HAlNR})_n$ ($n = 4-10$), which are active cocatalysts in the polymerization of isoprene [1]; a series of papers has appeared describing the chemistry and stereochemistry of these compounds [2–10, 19–22].

Recently, a product of the reaction of AlH_3 with *N,N'*-diethylethylenediamine, exhibited high cocatalytic activity in the polymerization of ethylene [11]. This product consists mainly of bis(μ -*N,N'*-diethylethylenediamido)bis(dihydridoaluminum)hydridoaluminum, $\text{HAl}[(\text{EtN}(\text{CH}_2)_2\text{NEt})\text{AlH}_2]_2$, which was isolated

as single crystals. A partly chlorinated product was obtained when an excess of AlCl_3 was used; in this case a compound of the formula $(\text{H}_{0.85}\text{Cl}_{0.15})\text{Al}[(\text{EtN}(\text{CH}_2)_2\text{NEt})\text{AlH}(\text{H}_{0.7}\text{Cl}_{0.3})]_2$ was isolated as single crystals. In this paper we report the crystal structures of both compounds, referred to as DIAL1 and DIAL2 respectively.

Experimental

Synthesis

DIAL1. A solution of *N,N'*-diethylethylenediamine (152 mmol) in diethyl ether (100 ml) was added dropwise to a suspension of AlH_3 polymer (152 mmol) in boiling diethyl ether/heptane (in volume ratio 1/2) (AlH_3 was synthesized in situ by the reaction $3 \text{NaH} + \text{AlCl}_3$). The N/Al molar ratio in solution was monitored during the addition of the amine; it remained constant at 1 up to the addition of 65% of the total amine and then increased to ca. 1.3 by the end of addition. After the addition was complete, the mixture was stirred for 1 h at the boiling point and then evaporated under moderate vacuum until the diethyl ether was completely removed. The remaining heptane solution was set aside for three days; the crystals which formed were separated by decantation, dried and analyzed. (Found: Al, 25.70; N, 17.70; H_{active} , 1.55. $\text{C}_{12}\text{H}_{33}\text{N}_4\text{Al}_3$ calcd.: Al, 25.79; N, 17.83; H_{active} , 1.59%):

DIAL 2. This compound was prepared by the same method except that a molar ratio NaH/AlCl_3 of 3/1.08 was used in the preparation of AlH_3 , in order to give $\text{AlCl}_x\text{H}_{3-x}$ species in the reaction mixture. The crystals which formed were analyzed. (Found: Al, 23.50; N, 16.21; Cl, 7.40; H_{active} , 1.20. $\text{C}_{12}\text{H}_{32.25}\text{Cl}_{0.75}\text{N}_4\text{Al}_3$ calcd.: Al, 23.82; N, 16.47; Cl, 7.80; H_{active} , 1.23%).

X-ray analysis

Irregularly shaped crystals of DIAL1 and DIAL2, chosen for crystallographic analysis, were sealed in thin-walled glass capillaries under dry nitrogen; their approximate dimensions were $0.5 \times 0.4 \times 0.5$ and $0.5 \times 0.7 \times 0.8$ mm, respectively. Weissenberg photographs showed both crystals to be triclinic; the $P\bar{1}$ space group was chosen and subsequently confirmed by the successful refinement of both structures. Accurate cell dimensions were determined by least-squares fit to the setting angles of 25 reflections, carefully centered on the diffractometer; they are given with other pertinent data in Table 1. Experimental intensities were measured up to $\theta = 26^\circ$ by a Siemens AED diffractometer, using Zr-filtered Mo-K_α radiation and following the $\theta - 2\theta$ scan method and "five points" technique [12]. For DIAL1 a total of 3390 independent reflections were collected, of which 2338 with $I > 2.5\sigma(I)$ were used for the structure determination; for DIAL 2, a total of 3547 independent reflections were measured, 1853 having $I > 2.5\sigma(I)$ were used in the subsequent calculations. A correction, based on a simple linear interpolation method, was performed by taking into account the intensity decay, monitored by a standard reflection; the maximum long-term variation was ca. 7% for DIAL1 and 13% for DIAL2. No correction for absorption was found necessary for either compound.

TABLE 1
SUMMARY OF CRYSTAL DATA

| | DIAL1 | DIAL2 |
|---------------------------------|---|---|
| Molecular formula | $\text{HA}[(\text{C}_2\text{H}_5\text{N}(\text{CH}_2)_2\text{NC}_2\text{H}_5)\text{AlH}_2]_2$ | $(\text{H}_{0.85}\text{Cl}_{0.15})\text{Al}[(\text{C}_2\text{H}_5\text{N}(\text{CH}_2)_2\text{NC}_2\text{H}_5)\text{AlH}(\text{H}_{0.7}\text{Cl}_{0.3})]_2$ |
| Molecular weight | 314.4 | 340.3 |
| Space group | $\overline{P1}$ | $\overline{P1}$ |
| Molecules/unit cell | 2 | 2 |
| Cell constants ^a | | |
| a | 7.433(2) Å | 7.645(3) Å |
| b | 7.436(2) Å | 7.574(3) Å |
| c | 18.810(7) Å | 19.069(9) Å |
| α | 95.8(1) ^o | 95.6(1) ^o |
| β | 109.9(1) ^o | 111.3(1) ^o |
| γ | 82.6(1) | 81.1(1) ^o |
| Cell volume | 967.4 Å ³ | 1015.3 Å ³ |
| Calculated density | 1.079 g cm ⁻³ | 1.112 g cm ⁻³ |
| Linear absorption coeff., μ | 2.0 cm ⁻¹ | 2.9 cm ⁻¹ |

^a Mo-K α radiation, λ 0.71069 Å.

TABLE 2
ATOMIC FRACTIONAL COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^2$ Å²) OF DIAL1^a

| Atom | x | y | z | B ₁₁ | B ₂₂ | B ₃₃ | B ₁₂ | B ₁₃ | B ₂₃ |
|-------|----------|----------|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Al(1) | 1398(1) | 8899(1) | 7499(1) | 252(3) | 238(3) | 335(4) | -44(2) | 92(3) | 20(3) |
| Al(2) | -1600(1) | 7844(1) | 6144(1) | 353(4) | 398(5) | 449(5) | -56(4) | 8(4) | -47(4) |
| Al(3) | 1701(2) | 7258(1) | 8858(1) | 453(5) | 445(5) | 458(5) | 16(4) | 191(4) | 151(4) |
| N(1) | -1413(3) | 9593(3) | 6984(1) | 262(10) | 291(10) | 410(12) | -22(8) | 77(9) | 40(9) |
| N(2) | 1157(4) | 7327(3) | 6508(1) | 357(11) | 305(10) | 380(12) | -30(9) | 123(10) | -16(9) |
| N(3) | 821(4) | 9649(4) | 8494(2) | 340(11) | 348(11) | 389(12) | -32(9) | 135(10) | 9(9) |
| N(4) | 2593(4) | 6608(3) | 8013(1) | 311(10) | 270(10) | 410(12) | -14(8) | 111(9) | 42(9) |
| C(1) | -2331(4) | 9293(5) | 7540(2) | 280(13) | 404(15) | 575(18) | -29(11) | 167(13) | 98(13) |
| C(2) | -1269(5) | 10191(5) | 8310(2) | 403(15) | 476(16) | 511(18) | 56(13) | 234(14) | 38(14) |
| C(3) | -1795(5) | 11513(4) | 6770(2) | 419(15) | 319(14) | 515(18) | -25(11) | 132(14) | 69(12) |
| C(4) | -3897(6) | 12119(6) | 6385(3) | 461(19) | 512(20) | 818(28) | 143(16) | 142(18) | 209(19) |
| C(5) | 1873(5) | 5422(5) | 6695(2) | 466(17) | 314(14) | 516(18) | -5(12) | 107(14) | -59(13) |
| C(6) | 1734(5) | 5126(4) | 7452(2) | 413(15) | 248(12) | 561(18) | -70(11) | 130(14) | 12(12) |
| C(7) | 2170(6) | 8023(6) | 6051(2) | 533(19) | 557(19) | 438(17) | -107(15) | 212(15) | -26(15) |
| C(8) | 1925(9) | 6978(8) | 5290(3) | 940(33) | 832(30) | 447(20) | -151(25) | 317(22) | -61(20) |
| C(9) | 1983(6) | 11122(5) | 8952(2) | 561(19) | 462(17) | 425(17) | -118(15) | 173(15) | -60(14) |
| C(10) | 1684(8) | 11621(8) | 9710(3) | 871(31) | 801(29) | 487(22) | -220(24) | 242(21) | -196(20) |
| C(11) | 4745(5) | 6436(5) | 8230(2) | 289(13) | 432(16) | 541(18) | -23(11) | 116(13) | 51(13) |
| C(12) | 5734(6) | 4720(6) | 8629(3) | 410(18) | 500(19) | 796(27) | 121(15) | 73(18) | 144(18) |

| Atom | x | y | z | B | Atom | x | y | z | B |
|----------|-----------|-----------|----------|----------|----------|----------|-----------|-----------|-----------|
| H(A11) | 2754(45) | 10227(42) | 7441(18) | 321(65) | H''(C6) | 2253(60) | 3922(57) | 7579(24) | 648(102) |
| H'(A12) | -2766(55) | 6130(52) | 6261(22) | 553(90) | H'(C7) | 3496(65) | 8028(62) | 6410(26) | 708(108) |
| H''(A12) | -2219(65) | 8784(62) | 5430(25) | 665(111) | H''(C7) | 1699(54) | 9284(51) | 6020(21) | 531(87) |
| H'(A13) | 17(52) | 6026(49) | 8887(21) | 493(84) | H'(C8) | 2522(63) | 5660(60) | 5414(25) | 700(109) |
| H''(A13) | 3308(60) | 7356(57) | 9608(24) | 619(99) | H''(C8) | 490(61) | 7203(58) | 4955(24) | 662(103) |
| H'(C1) | -3847(55) | 9821(52) | 7337(22) | 534(90) | H''(C8) | 2391(80) | 7659(75) | 5002(31) | 1161(160) |
| H''(C1) | -2382(58) | 8057(54) | 7538(22) | 558(96) | H'(C9) | 3400(53) | 10652(50) | 9064(21) | 484(85) |
| H'(C2) | -1477(48) | 11471(46) | 8345(19) | 423(77) | H''(C9) | 1756(58) | 12156(56) | 8682(23) | 600(96) |
| H''(C2) | -1778(60) | 9692(59) | 8745(24) | 633(102) | H'(C10) | 2092(62) | 10459(59) | 10039(24) | 677(106) |
| H'(C3) | -1370(50) | 12291(48) | 197(20) | 436(79) | H''(C10) | 300(71) | 12022(67) | 9646(29) | 830(126) |
| H''(C3) | -955(48) | 11635(46) | 6462(19) | 419(76) | H''(C10) | 2531(81) | 12520(77) | 9907(32) | 1149(166) |
| H'(C4) | -4653(63) | 12164(60) | 6780(25) | 689(107) | H'(C11) | 5030(56) | 6551(54) | 7686(22) | 575(91) |
| H''(C4) | -4415(63) | 11476(60) | 5934(26) | 724(112) | H''(C11) | 5230(53) | 7531(50) | 8618(21) | 519(87) |
| H''(C4) | -4089(74) | 13330(70) | 6275(29) | 867(133) | H'(C12) | 5368(82) | 4528(77) | 9135(34) | 1096(160) |
| H'(C5) | 3142(51) | 5251(48) | 6698(20) | 464(80) | H''(C12) | 5457(76) | 3683(72) | 8272(30) | 894(135) |
| H''(C5) | 1240(61) | 4588(57) | 6359(24) | 643(103) | H''(C12) | 7157(75) | 4647(71) | 8868(30) | 858(138) |
| H'(C6) | 253(63) | 5130(60) | 7353(25) | 713(109) | | | | | |

^a Anisotropic thermal factor defined by $\exp -1/4 (B_{11a}^*h^2 + B_{22b}^*k^2 + B_{33c}^*l^2 + 2B_{12a}^*b^*hk + 2B_{13a}^*c^*hl + 2B_{23b}^*c^*kl)$. Standard deviations in parentheses, in this and following tables, refer to the last digit quoted.

Structure determination and refinement

The structure of DIAL2 was determined by direct methods, using the MULTAN program [13]. The 200 strongest and the 50 lowest reflections were used as input data. Of the 32 independent solutions, that having "figures of merit" ABS FOM = 1.10 and PSI ZERO = 2246, was found to be correct. From the *E*-map, all the aluminum and nitrogen atoms were located; from the subsequent Fourier synthesis the positions of the other non-hydrogen atoms were deduced.

Because of the evident isomorphism of the two compounds, the solution of the structure of DIAL1 was performed by Fourier methods, phasing the reflections by means of the positional parameters of aluminum and nitrogen atoms determined for DIAL2. Both structures were refined by block-matrix least-squares methods, minimizing the function $\sum w(F_0 - F_c)^2$ and using

TABLE 3

ATOMIC FRACTIONAL COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^2 \text{ \AA}^2$) OF DIAL2.

| Atom | x | y | z | B ₁₁ | B ₂₂ | B ₃₃ | B ₁₂ | B ₁₃ | B ₂₃ |
|-------|-----------|-----------|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Al(1) | 1391(2) | 8865(2) | 7502(1) | 415(7) | 372(7) | 381(7) | -42(5) | 180(6) | 0(5) |
| Al(2) | -1609(3) | 7981(3) | 6136(1) | 546(10) | 713(12) | 542(10) | -45(9) | 67(8) | -74(9) |
| Al(3) | 1855(4) | 7234(3) | 8862(1) | 827(13) | 604(11) | 569(10) | 75(10) | 350(10) | 180(9) |
| N(1) | -1396(7) | 9594(7) | 6992(3) | 441(23) | 488(24) | 517(24) | 36(18) | 176(19) | 57(19) |
| N(2) | 1101(7) | 7368(6) | 6504(3) | 555(26) | 456(23) | 463(23) | -49(20) | 212(20) | -37(19) |
| N(3) | 857(7) | 9580(6) | 8493(3) | 583(26) | 491(24) | 386(21) | -43(20) | 239(20) | -9(18) |
| N(4) | 2640(7) | 6594(6) | 8014(3) | 491(23) | 407(22) | 486(23) | 46(18) | 190(19) | 23(18) |
| C(1) | -2259(9) | 9326(9) | 7548(4) | 528(32) | 590(34) | 686(37) | -43(26) | 328(29) | 26(29) |
| C(2) | -1174(10) | 10108(9) | 8311(4) | 597(35) | 649(36) | 636(36) | 49(28) | 344(30) | 92(29) |
| C(3) | -1791(11) | 11530(9) | 6787(4) | 774(42) | 427(32) | 692(40) | 155(29) | 244(34) | 159(29) |
| C(4) | -3913(14) | 12153(14) | 6385(6) | 919(58) | 908(59) | 1173(72) | 310(46) | 417(52) | 343(53) |
| C(5) | 1818(10) | 5474(9) | 6688(4) | 688(38) | 517(33) | 606(35) | -10(28) | 218(30) | -94(27) |
| C(6) | 1764(9) | 5172(8) | 7465(4) | 568(33) | 430(28) | 624(34) | 32(25) | 211(28) | 56(25) |
| C(7) | 2054(11) | 8040(11) | 6049(4) | 721(42) | 802(45) | 622(38) | -36(34) | 371(33) | -37(33) |
| C(8) | 1746(15) | 7016(14) | 5289(5) | 1249(70) | 1163(68) | 577(41) | -190(55) | 460(45) | -94(43) |
| C(9) | 2021(12) | 11000(10) | 8946(4) | 900(48) | 627(39) | 542(35) | -130(34) | 294(34) | -119(30) |
| C(10) | 1731(15) | 11450(14) | 9708(5) | 1237(69) | 1127(65) | 572(41) | -375(54) | 360(45) | -283(42) |
| C(11) | 4741(9) | 6385(10) | 8212(4) | 424(31) | 682(38) | 690(39) | 24(27) | 173(28) | 44(31) |
| C(12) | 5750(13) | 4676(13) | 8591(6) | 806(53) | 782(53) | 1167(69) | 283(42) | 264(49) | 174(48) |

| Atom | x | y | z | B | Atom | x | y | z | B |
|-----------|-----------|-----------|----------|----------|-----------|--------|----------|---------|---------|
| Cl(1) | 3208(31) | 10523(29) | 7565(12) | 1153(53) | Cl(3) | 51(11) | 5740(10) | 8925(4) | 783(16) |
| Cl(2) | -3243(11) | 6084(11) | 6067(5) | 825(17) | | | | | |
| H(A11) | 2679 | 10067 | 7527 | 360 | H'(C6) | 2482 | 3998 | 7685 | 550 |
| H''(A12) | -2742 | 6603 | 6081 | 640 | H''(C7) | 3349 | 7893 | 6242 | 700 |
| H'''(A12) | -2609 | 8615 | 5220 | 640 | H'''(C7) | 1240 | 8878 | 5946 | 700 |
| H'(A13) | 530 | 6127 | 8914 | 640 | H'(C8) | 2596 | 6021 | 5384 | 900 |
| H''(A13) | 3373 | 7054 | 9712 | 640 | H''(C8) | 427 | 6708 | 5077 | 900 |
| H'''(C5) | -3700 | 9599 | 7321 | 570 | H'''(C8) | 1958 | 7751 | 4921 | 900 |
| H'(C1) | -2255 | 8159 | 7555 | 570 | H'(C9) | 3441 | 10192 | 9080 | 690 |
| H''(C2) | -1525 | 11436 | 8303 | 560 | H''(C9) | 1582 | 12184 | 8690 | 690 |
| H'''(C2) | -1617 | 9646 | 8695 | 560 | H'(C10) | 1994 | 10352 | 10018 | 890 |
| H'(C3) | -994 | 12378 | 7312 | 650 | H''(C10) | 315 | 11896 | 9496 | 890 |
| H''(C3) | -1088 | 11798 | 6376 | 650 | H'''(C10) | 2488 | 12385 | 10043 | 890 |
| H'(C4) | -4560 | 12334 | 6780 | 960 | H'(C11) | 5049 | 6517 | 7710 | 630 |
| H''(C4) | -4689 | 11356 | 5997 | 960 | H''(C11) | 5267 | 7514 | 8641 | 630 |
| H'''(C4) | -4129 | 13313 | 6144 | 960 | H'(C12) | 4879 | 4031 | 8756 | 950 |
| H'(C5) | 3165 | 5254 | 6694 | 590 | H''(C12) | 6155 | 3819 | 8222 | 950 |
| H''(C5) | 675 | 4844 | 6256 | 590 | H'''(C12) | 6866 | 4885 | 9043 | 950 |
| H'(C6) | 363 | 5482 | 7581 | 550 | | | | | |

Cruickshank's weighting scheme [14]. The hydrogen atoms were located from ΔF -maps and, for DIAL1, included in the refinement with isotropic thermal parameters. In the structure of DIAL2, the contribution of hydrogen atoms was kept fixed during the refinement, with the same B parameters of the atoms to which they are bonded. Positional and isotropic thermal parameters of the chlorine atoms were refined, while their occupancy factors, established on the basis of both the height of the corresponding Fourier peaks and the results of the chemical analysis, were kept fixed. The final R values were 0.050 and 0.095 for DIAL1 and DIAL2, respectively. Atomic scattering factors were those of Moore [15] for non-hydrogen atoms and of Stewart et al. [16] for hydrogen atom. With the exception of MULTAN, all the computer programs were those written by Immirzi [17]. The final values of positional and thermal parameters are reported in Tables 2 and 3. A list of structure factors may be obtained from the authors on request.

Results and discussion

The crystal structures of DIAL1 and DIAL2 are strictly isomorphous, as indicated by the crystal data of both compounds, reported in Table 1; only a slightly higher cell volume is observed in DIAL2, where hydrogenated and chlorinated molecules are randomly co-crystallized. Neither the results of X-ray analysis of DIAL2, nor the method of its preparation allowed us to establish the distribution by type of chlorine atoms in the crystallized molecules; however, assumption of a statistical distribution seems reasonable.

The molecular structure of DIAL1, shown in the Fig. 1, is built up of two AlH_2 groups and one AlH group, connected to each other through two diethylenediamine bridging groups. Two nearly planar four-membered $(\text{AlN})_2$ rings (all the atoms are within 0.07 Å of their mean planes, see Table 4) and two five-membered (AlN_2C_2) rings are formed; the "gauche" conformation of the $\text{CH}_2\text{—CH}_2$ bond (see Table 4) precludes a planar structure in the latter rings.

The molecule possesses a pseudo-binary axis coincident with the $\text{Al}(1)\text{—H}(\text{Al}1)$ bond. The central $\text{Al}(1)$ atom displays a distorted trigonal bipyramidal coordination, with the $\text{N}(2)$ and $\text{N}(3)$ atoms displaced from the axial positions of the bipyramid (the $\text{N}(2)\text{—Al}(1)\text{—N}(3)$ bond angle is in fact $154.3(1)^\circ$). The molecular conformation of DIAL2 is identical, as is evident from a comparison of the molecular structures of both compounds (see Fig. 1) and their geometrical parameters (see Table 4). It must be noted, however, that in DIAL2 the extent of chlorine replacement of the $\text{H}'(\text{Al}2)$ and $\text{H}'(\text{Al}3)$ hydridic hydrogens is double that of $\text{H}(\text{Al}1)$, while no substitution occurs for $\text{H}''(\text{Al}2)$ and $\text{H}''(\text{Al}3)$. This could happen during the preparation of the compound. However, the possibility of intermolecular hydrogen—chlorine exchanges in solution, as established for $(\text{HAIN-}i\text{-Pr})_6$ by NMR spectroscopy [8], must be taken into account; if this occurs, the method of preparation would have no effect. A partial explanation of the above feature could be given by considering the closer intramolecular contacts (minimum $\text{Cl}\cdots\text{C}$ distance 3.06 Å) involving the $\text{Cl}(1)$ atom, which replaces $\text{H}(\text{Al}1)$, with respect to the corresponding ones (minimum $\text{Cl}\cdots\text{C}$ distance 3.50 Å) involving $\text{Cl}(2)$ and $\text{Cl}(3)$. But similar arguments cannot account for the lack of chlorination in the $\text{H}''(\text{Al}2)$ and $\text{H}''(\text{Al}3)$ positions, because a

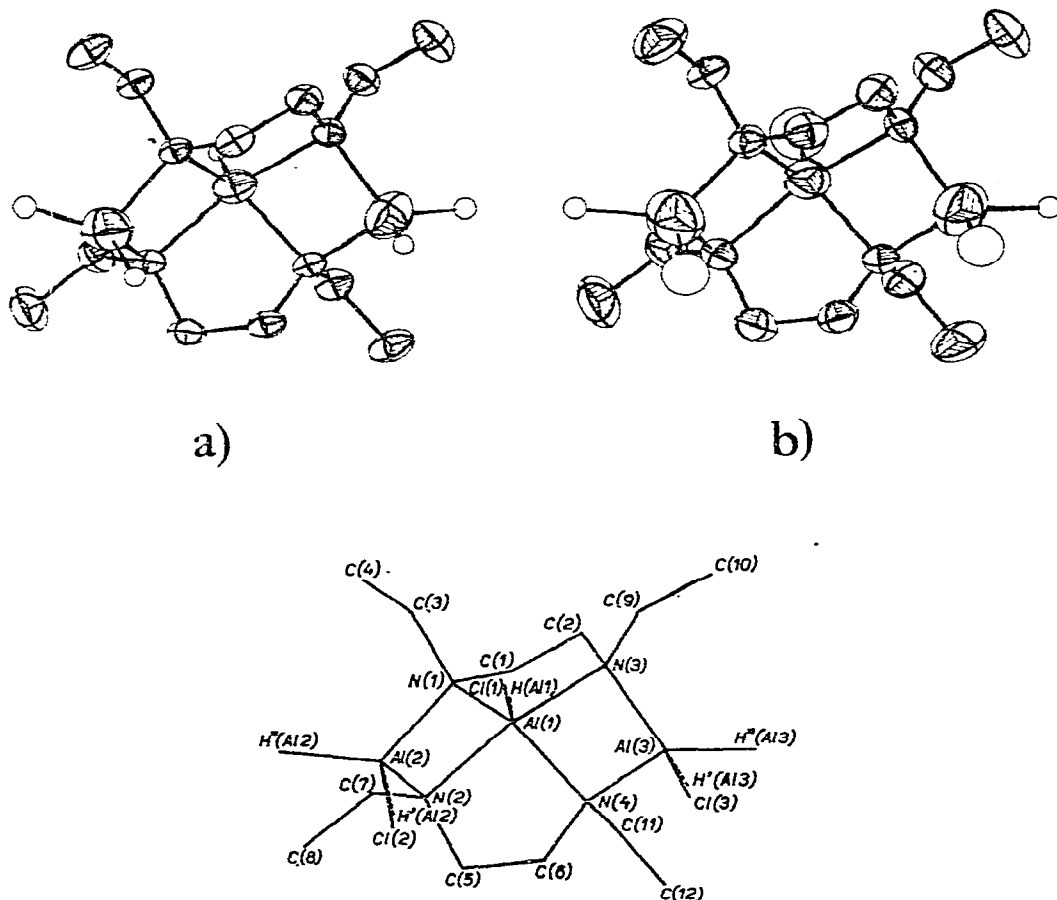


Fig. 1. Molecular structures and labelling scheme of DIAL1 (a), and DIAL2 (b). For clarity, the H(A11), H'(A12) and H'(A13) hydrogen atoms have been omitted in DIAL2.

chlorine atom there would give rise to intramolecular contacts similar to those for Cl(1). It must be pointed out, however, that in DIAL1 different Al—H bond distances are observed for the two hydridic hydrogens of each AlH_2 group. In particular, $\text{H}'(\text{Al}2)$ and $\text{H}'(\text{Al}3)$, which correspond to the chlorinated positions in DIAL2, display Al—H distances (1.70(4) and 1.66(4) Å, respectively) significantly longer than $\text{H}''(\text{Al}2)$ and $\text{H}''(\text{Al}3)$ (1.48(6) and 1.51(5) Å, respectively)*, the latter values are similar to those in iminoalane derivatives [3–6]. If one assumes the lengthening of this bond to be connected to an increase in its ionic character, the tendency of the electronegative chlorine atom to replace preferentially $\text{H}'(\text{Al}2)$ and $\text{H}'(\text{Al}3)$ can be explained. Moreover, the mean distances of the Al—N bonds connecting the AlH_2 or AlHCl groups to the rest of the molecule, are 1.922(2) and 1.918(3) Å in DIAL1 and DIAL2, respectively. These values are significantly lower than that observed in $[\text{H}_2\text{AlN-}i\text{-Pr}_2]_2$ [18], 1.966(2) Å, and are close to the corresponding ones found in $[\text{H}(\text{HAIN-}i\text{-Pr})_5\text{AlH}_2] \cdot \text{LiH/}$

* The disorder in DIAL2 precluded refinement of the positional parameters of the hydrogen atoms, and so the values of the Al—H distances are not significant for this compound.

TABLE 4
GEOMETRICAL PARAMETERS FOR DIAL1 AND DIAL2

| | DIAL1 | DIAL2 | | DIAL1 | DIAL2 |
|-----------------------|----------|-----------|---------------------|----------|-----------|
| Al(1)-N(1) | 2.003(3) | 2.007(6) | Al(1)-H(A11) | 1.54(3) | 1.43 |
| Al(1)-N(2) | 2.063(3) | 2.077(5) | Al(2)-H'(A12) | 1.70(4) | 1.43 |
| Al(1)-N(3) | 2.068(3) | 2.078(5) | Al(2)-H''(A12) | 1.48(6) | 1.72 |
| Al(1)-N(4) | 1.996(3) | 1.991(6) | Al(3)-H'(A13) | 1.66(4) | 1.45 |
| Al(2)-N(1) | 1.920(3) | 1.914(5) | Al(3)-H''(A13) | 1.51(5) | 1.62 |
| Al(2)-N(2) | 1.926(3) | 1.927(7) | Al(1)-C1(1) | | 1.98(2) |
| Al(3)-N(3) | 1.923(3) | 1.915(6) | Al(2)-C1(2) | | 1.96(1) |
| Al(3)-N(4) | 1.918(3) | 1.916(5) | Al(3)-C1(3) | | 1.96(1) |
| N(1)-C(1) | 1.478(5) | 1.480(9) | N(3)-C(2) | 1.482(5) | 1.461(10) |
| N(1)-C(3) | 1.488(5) | 1.511(9) | N(3)-C(9) | 1.495(5) | 1.500(10) |
| N(2)-C(5) | 1.482(5) | 1.482(10) | N(4)-C(6) | 1.491(5) | 1.483(9) |
| N(2)-C(7) | 1.486(5) | 1.484(10) | N(4)-C(11) | 1.501(5) | 1.497(9) |
| Mean N-C ^a | 1.488(3) | 1.487(6) | | | |
| C(1)-C(2) | 1.527(6) | 1.504(12) | C(7)-C(8) | 1.523(6) | 1.531(12) |
| C(3)-C(4) | 1.510(7) | 1.540(16) | C(9)-C(10) | 1.520(6) | 1.546(12) |
| C(5)-C(6) | 1.504(6) | 1.537(11) | C(11)-C(12) | 1.518(7) | 1.503(15) |
| Mean C-C | 1.517(4) | 1.527(8) | | | |
| N(1)-Al(1)-N(2) | 83.4(1) | 83.2(1) | N(2)-Al(1)-N(4) | 85.1(1) | 85.8(1) |
| N(1)-Al(1)-N(3) | 85.3(1) | 84.7(1) | N(3)-Al(1)-N(4) | 83.3(1) | 83.6(1) |
| N(1)-Al(1)-N(4) | 126.7(1) | 127.1(2) | N(1)-Al(2)-N(2) | 89.4(1) | 89.8(1) |
| N(2)-Al(1)-N(3) | 154.3(1) | 154.3(2) | N(3)-Al(3)-N(4) | 89.4(1) | 90.1(1) |
| Al(1)-N(1)-Al(2) | 94.1(1) | 94.5(1) | Al(1)-N(3)-Al(3) | 91.9(1) | 91.5(1) |
| Al(1)-N(2)-Al(2) | 92.1(1) | 91.9(1) | Al(1)-N(4)-Al(3) | 94.4(1) | 94.2(1) |
| Al(1)-N(1)-C(1) | 104.8(1) | 105.3(3) | Al(1)-N(2)-C(5) | 108.9(1) | 108.4(3) |
| Al(1)-N(1)-C(3) | 111.6(2) | 110.8(3) | Al(1)-N(2)-C(7) | 112.2(2) | 112.9(3) |
| Al(2)-N(1)-C(1) | 118.7(2) | 121.5(3) | Al(2)-N(2)-C(5) | 115.4(2) | 116.2(3) |
| Al(2)-N(1)-C(3) | 113.9(1) | 112.3(3) | Al(2)-N(2)-C(7) | 115.1(2) | 114.1(3) |
| Al(1)-N(3)-C(2) | 108.9(2) | 109.2(3) | Al(1)-N(4)-C(6) | 104.8(1) | 104.5(3) |
| Al(1)-N(3)-C(9) | 112.3(2) | 111.3(3) | Al(1)-N(4)-C(11) | 111.5(2) | 111.7(3) |
| Al(3)-N(3)-C(2) | 115.5(2) | 116.8(3) | Al(3)-N(4)-C(6) | 119.2(2) | 119.1(3) |
| Al(3)-N(3)-C(9) | 115.0(2) | 113.2(3) | Al(3)-N(4)-C(11) | 113.2(1) | 113.6(3) |
| N(1)-C(1)-C(2) | 109.8(1) | 110.6(3) | N(4)-C(6)-C(5) | 109.6(1) | 109.8(3) |
| N(3)-C(2)-C(1) | 108.8(1) | 110.2(3) | N(2)-C(7)-C(8) | 114.1(2) | 113.3(3) |
| N(1)-C(3)-C(4) | 114.0(2) | 112.9(4) | N(3)-C(9)-C(10) | 113.5(2) | 111.6(3) |
| N(2)-C(5)-C(6) | 110.0(1) | 110.0(3) | N(4)-C(11)-C(12) | 113.8(2) | 113.8(4) |
| C(1)-N(1)-C(3) | 111.7(1) | 110.7(3) | C(2)-N(3)-C(9) | 111.5(2) | 112.8(3) |
| C(5)-N(2)-C(7) | 111.6(2) | 111.7(3) | C(6)-N(4)-C(11) | 111.9(1) | 111.8(3) |
| N(1)-C(1)-C(2)-N(3) | 311.0 | 313.7 | N(2)-C(5)-C(6)-N(4) | 310.8 | 311.4 |

Deviation of the atoms from their least-squares planes(^oÅ) for four-membered rings.

| DIAL1 | | | | DIAL2 | | | |
|-------|-------|-------|-------|-------|-------|-------|-------|
| Al(1) | N(1) | Al(2) | N(2) | Al(1) | N(1) | Al(2) | N(2) |
| 0.06 | -0.07 | 0.07 | -0.07 | 0.05 | -0.05 | 0.06 | -0.05 |
| Al(1) | N(3) | Al(3) | N(4) | Al(1) | N(3) | Al(3) | N(4) |
| 0.06 | -0.06 | 0.07 | -0.07 | 0.05 | -0.05 | 0.06 | -0.05 |

^a The standard deviation of the means s has been calculated as $s^2 = \frac{\sum_i (x_i - \bar{x})^2}{(n-1)n}$, where \bar{x} is the mean of the x_i values, n their number.

Et_2O [5], 1.911(7) Å, and $(\text{HAIN-i-Pr})_6 \cdot \text{AlH}_3$ [4], 1.896(15) Å; in the last two compounds, one of the two hydridic hydrogens of the AlH_2 groups forms Al-H-Li or Al-H-Al bridge bonds. The N(1) and N(4) nitrogen atoms, which are bonded to the pentacoordinated Al(1) atom and placed in the equatorial positions of the bipyramid, display shorter Al-N bond distances (the mean values are 2.000(5) Å in DIAL1 and 1.999(11) Å in DIAL2) with respect to N(2) and N(3), placed in the axial positions (the corresponding mean values are 2.066(4) and 2.078(1) Å, respectively).

The crystal packing is determined mainly by carbon-carbon contacts (minimum C...C distance 3.82 Å) in DIAL1; close chlorine-carbon contacts arise in DIAL2 (minimum Cl...C distance 3.27 Å), while the minimum C...C distance rises to 3.96 Å as a consequence of the slight increase in cell volume with respect to DIAL1.

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