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Bis(morpholine)aluminium Trichloride, $[Al(C_4H_9NO)_2]Cl_3$

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Abstract. $M_r = 307{\cdot}585$, triclinic, $P\bar{1}$, $a = 7{\cdot}3110\,(5)$, $b = 8{\cdot}0598\,(5)$, $c = 12{\cdot}8353\,(4)$ Å, $\alpha = 80{\cdot}583\,(3)$, $\beta = 89{\cdot}959\,(3)$, $\gamma = 71{\cdot}148\,(4)°$, $V = 705{\cdot}005$ Å^3, $Z = 2$, $D_x = 1{\cdot}449$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å (Ni filter), $\mu = 65{\cdot}64$ cm^{-1}, $F(000) = 320$, $T = 294$ K. Final $R = 0{\cdot}059$ for 2632 unique observed reflections. The structure consists of discrete molecules, all intermolecular distances being longer than 2·8 Å. The coordination geometry around aluminium is slightly distorted trigonal bipyramidal with chlorine in equatorial and nitrogen in axial positions. The Al—N bond lengths are 2·093 (3) and 2·064 (3) Å, Al—Cl 2·173 (1), 2·197 (1) and 2·181 (1) Å.

Introduction. Alkylaluminium halides, in conjunction with Group V*b* Lewis bases, notably phosphines, play an important role as cocatalysts in the oligomerization of olefins catalysed by nickel compounds (Wilke, 1979; Bogdanovic, Spliethoff & Wilke, 1980; Brandes, Goddard, Jolly, Krüger, Mynott & Wilke, 1983). Recent results indicate that morpholine, which is a cofactor in nickel-based catalytic systems even in the absence of aluminium alkyls (Heimbach & Schenkluhn, 1980), may be important in controlling the stereochemical course and product distribution of olefin oligomerizations with homogeneous nickel/aluminium catalysts (Heimbach & Sturm, 1983, unpublished observations). In order to gain more insight into the nature of the active species P. Heimbach and H. Sturm reacted $Al(C_2H_5)_3$ with an excess of morpholine and obtained a material which was tentatively formulated as the 1 : 1 morpholine adduct of aluminium tris(morpholide). Its very low solubility in common solvents indicates a polymeric structure with morpholine acting as a bridging ligand with both of its heteroatoms as donor functions. Unfortunately, no single crystals suitable for X-ray diffraction could be obtained due to the insolubility of the compound. However, the observation that the compound reacted slowly with $CHCl_3$ led to the isolation of a 2 : 1 adduct of morpholine with aluminium trichloride whose structure was determined subsequently to establish the mode of bonding exhibited by morpholine in such complexes.

Experimental. Plate-like crystals (0·5 × 0·4 × 0·2 mm) grown from chloroform; Enraf–Nonius CAD-4 diffractometer; cell dimensions obtained by least squares from setting angles of 75 reflections ($18{\cdot}86 \le \theta \le 64{\cdot}22°$); 2988 measured reflections (θ–2θ scans, $5{\cdot}89 \le \theta \le 76{\cdot}48°$, $-10 \le h \le 10$, $-12 \le k \le 12$, $-17 \le l \le 17$) merged to give 2970 unique reflections ($R_{\mathrm{int}} = 0{\cdot}019$) of which 338 unobserved [$I < 2{\cdot}0\,\sigma(I)$]; orientation (every 250 reflections) and intensity control (every 4000 s of X-ray exposure) by means of three standard reflections ($2\bar{3}\bar{2}$, $0\bar{1}\bar{5}$, $\bar{2}\bar{3}\bar{2}$), no detectable decomposition;

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solution of structure by direct methods using *SHELX*76 (Sheldrick, 1976); second-best solution gave positions of the Al and the three Cl atoms as well as of nine out of the 12 other non-H atoms of the asymmetric unit, location of remaining atoms by difference Fourier synthesis.

In order to obtain minimum ambiguity in assigning the right element (O *vs* N) to the donor function in morpholine the following approach for the refinement of the structure was used. In the first stages of refinement on F all O atoms were treated as N. Isotropic refinement of all non-H atoms with the uncorrected data set converged at $R = 0{\cdot}172$. An empirical absorption correction was undertaken using the program *DIFABS* (Walker & Stuart, 1983) whereupon R dropped to 0·134. After several cycles of anisotropic refinement with the so-corrected data set all H atoms could be located from a difference Fourier synthesis. Anisotropic refinement (H atoms at C isotropic, H atoms at N not included) then converged at $R = 0{\cdot}064$. A subsequent difference Fourier synthesis again clearly revealed the H atoms at N (N bonded to Al) and gave only spurious peaks around the O atoms. Four cycles of anisotropic refinement with the correct scattering factors assigned to the O atoms and all H atoms included (H atoms isotropic) converged at $R = 0{\cdot}059$ for 2632 observed reflections (217 parameters, unobserved reflections not included in refinement); $R_w = 0{\cdot}074$ with $w = 1/\sigma^2(F_o)$.

Max. shift in positional parameters 0·0034 in last cycle. Final difference Fourier map qualitatively featureless (max. electron density 0·49 e Å^{-3}). Details of computing procedures described elsewhere (Brauer & Krüger, 1976). Scattering factors of neutral atoms (except for H) from Cromer & Waber (1965), those of H from Stewart, Davidson & Simpson (1965).

Discussion. Table 1 gives the final atomic parameters, Table 2 selected interatomic distances and angles.* Fig. 1 gives a perspective view of the molecule together with the arbitrary numbering scheme used. Fig. 2 sketches a projection of the molecule down the N(1)—Al—N(2) axis and summarizes important dihedral angles. The unit cell contains discrete molecules of the title compound, the shortest intermolecular distance being 2·82 (4) Å between the H atom at N(1) and Cl(1) of a neighbouring molecule. In view of the respective angle Cl(1)—HN(1)—N(1) of 161 (3)° this interaction might be interpreted as a very weak hydrogen bond.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors for the non-*H *atoms*

$U_{eq} = (U_1U_2U_3)^{1/3}$ where U_i are the eigenvalues of the U_{ij} matrix.

	x	y	z	U_{eq}(Å^2)
Cl(1)	0·2987 (1)	0·0113 (1)	0·4060 (1)	0·043
Cl(2)	−0·0432 (1)	−0·1836 (1)	0·3252 (1)	0·047
Cl(3)	0·0350 (1)	0·2287 (1)	0·1406 (1)	0·052
Al	0·0902 (1)	0·0245 (1)	0·2818 (1)	0·033
O(1)	−0·4565 (3)	0·5192 (2)	0·3595 (1)	0·045
O(2)	0·5165 (4)	−0·2620 (4)	0·0259 (1)	0·060
N(1)	−0·1353 (3)	0·1954 (3)	0·3525 (1)	0·034
N(2)	0·2957 (3)	−0·1479 (3)	0·2049 (1)	0·035
C(1)	−0·1079 (4)	0·3671 (4)	0·3684 (2)	0·041
C(2)	−0·2769 (5)	0·4810 (4)	0·4193 (2)	0·046
C(3)	−0·4905 (5)	0·3556 (4)	0·3543 (3)	0·047
C(4)	−0·3315 (4)	0·2365 (4)	0·2997 (3)	0·046
C(5)	0·2155 (5)	−0·2025 (5)	0·1142 (2)	0·048
C(6)	0·3697 (6)	−0·3335 (5)	0·0627 (3)	0·056
C(7)	0·6056 (5)	−0·2237 (5)	0·1126 (3)	0·054
C(8)	0·4655 (5)	−0·0915 (4)	0·1685 (2)	0·046

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

E.s.d.'s in units of the last significant figure are given in parentheses.

Al—Cl(1)	2·173 (1)	Cl(1)—Al—Cl(2)	110·4 (1)
Al—Cl(2)	2·197 (1)	Cl(2)—Al—Cl(3)	129·2 (1)
Al—Cl(3)	2·181 (1)	Cl(1)—Al—Cl(3)	120·4 (1)
Al—N(1)	2·093 (3)	N(1)—Al—N(2)	175·3 (1)
Al—N(2)	2·064 (3)		
N(1)—C(1)	1·507 (4)	Al—N(1)—C(1)	115·7 (2)
N(1)—C(4)	1·500 (5)	Al—N(1)—C(4)	114·2 (2)
N(2)—C(5)	1·494 (5)	Al—N(2)—C(5)	114·2 (2)
N(2)—C(8)	1·505 (5)	Al—N(2)—C(8)	116·6 (2)
C(1)—C(2)	1·503 (5)	C(1)—N(1)—C(4)	108·9 (3)
C(3)—C(4)	1·504 (5)	C(5)—N(2)—C(8)	108·1 (2)
C(5)—C(6)	1·511 (6)		
C(7)—C(8)	1·498 (6)		
C(2)—O(1)	1·440 (5)		
C(3)—O(1)	1·431 (4)		
C(6)—O(2)	1·420 (6)		
C(7)—O(2)	1·414 (5)		
N(1)—HN(1)	0·874 (38)	Cl(1)—HN(1)—N(1)	160·9 (33)
N(2)—HN(2)	0·886 (41)		
HN(1)···Cl(1)	2·824 (38)		

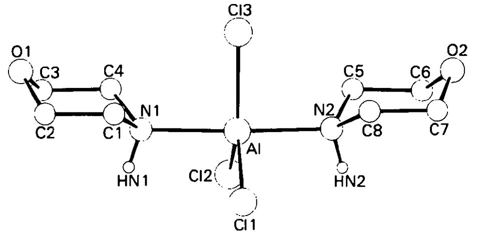

Fig. 1. Perspective view of the molecule with the numbering of atoms.

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* Lists of structure factors, anisotropic thermal parameters for the non-H atoms, H-atom parameters and additional interatomic distances and angles as well as a figure of a cell projection have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39119 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The Al atom is trigonal bipyramidally coordinated with three Cl atoms in the equatorial plane and the N atoms of the two morpholine rings in axial positions. The C atoms attached to N are in a staggered conformation with respect to the Cl atoms and in an eclipsed conformation with respect to those in the opposite morpholine ring (Fig. 2). The morpholine rings are in a chair conformation; the O atoms do not participate in any significant intermolecular interaction. Thus the potential difunctionality of morpholine does not result in a polymeric structure (Marconi, Mazzei, Bonati & De Maldè, 1962).

The Al—Cl distances are significantly longer than in gaseous monomeric $AlCl_3$ where an Al—Cl distance of 2·06 (1) Å was observed (Zasorin & Rambidi, 1967). The Al—N distances of 2·093 (3) and 2·064 (3) Å are in good accord with the overall pattern of Al—N distances observed in similar five-coordinated aluminium complexes where Al—N bond lengths between 2·051 (3) and 2·238 (4) Å are found ($AlH_3.2NMe_3$: Heitsch, Nordman & Parry, 1963; $AlH_3.Me_2NCH_2CH_2NMe_2$: Palenik, 1964; $AlCl_3.2NHMe_2$: Ahmed, Schwarz, Weidlein & Hess, 1977; Lobkovskii, Korobov & Semenenko, 1978). Again, these distances are longer than in comparable aluminium–amine complexes with lower coordinated aluminium ($AlCl_3.NMe_3$: Almenningen, Haaland, Haugen & Novak, 1973). Deformations from the ideal trigonal-bipyramidal geometry arise mainly from unequal Al—Cl bond lengths and angles and the nonlinearity of N(1)—Al—N(2) [175·3 (1)°]. As may be seen in Fig. 2, the displacements in the $AlCl_3$ plane can most probably be explained by steric interaction of the Cl atoms and the CH_2 groups C(1), C(4), C(5) and C(8). Both morpholine rings show bond lengths and angles equal to within two standard deviations with those observed for other morpholinium salts with fourfold-coordinated nitrogen (Von Dreele, Bradshaw & Burke, 1983; Swaminathan, Murthy & Lessinger, 1976). The structural results of the title compound are in close analogy with the structure of the bis(dimethylamine) adduct of aluminium trichloride (Ahmed *et al.*, 1977; Lobkovskii *et al.*, 1978). Not only are the overall geometry and the deformations from an ideal trigonal-bipyramidal coordination polyhedron directly comparable but so are the bond lengths and angles. Even very weak hydrogen-bond-type interactions N—H···Cl have also been found in this compound. Surprisingly, not even the etheral function in morpholine exerts any stereochemical influence. However, the larger steric bulk of morpholine over dimethylamine results in the deformations of the Cl—Al—Cl angles being more pronounced. Thus the steric nature of the deformations is indirectly confirmed.

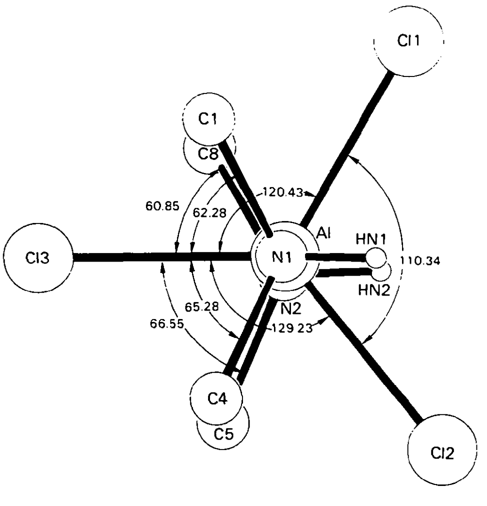

Fig. 2. Projection of the molecule down the N(1)—Al—N(2) axis showing selected dihedral angles (°, e.s.d.'s ~0·2°).

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