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Unidentate nitrogen base adducts of aluminium trichloride †

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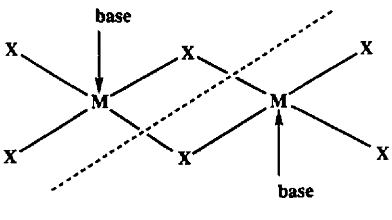
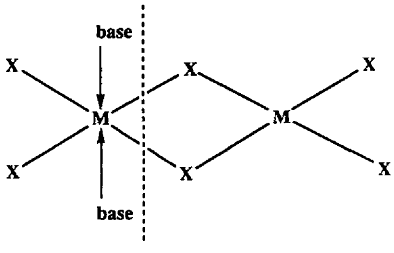
A number of adducts of aluminium(III) chloride with unidentate nitrogen bases have been synthesized and their room-temperature single-crystal structures determined. With piperidine (pip) a mononuclear 1 : 2 adduct is formed, $AlCl_3 \cdot 2pip$, in which the nitrogen atoms are axial in a trigonal-bipyramidal array about the metal: Al–N 2.070(5), Al–Cl 2.162(3)–2.190(3) Å. Attempts to crystallize the material from acetonitrile resulted in the formation of $[Al\{HN{=}C(Me)N(CH_2)_5\}_4]Cl_3 \cdot MeCN$ which has implications in the formation of amidines catalysed by $AlCl_3$; Al–N 1.851–1.857(4) Å. With 2-methylpyridine, 2-diphenylmethylpyridine and quinoline, 1 : 1 adducts are obtained, the latter being also monosolvated: Al–N 1.942(4), 1.954(4), 1.959(6); Al–Cl (over all three), 2.082(2)–2.112(4) Å. The structure of $AlCl_3(thf)$ (thf = tetrahydrofuran) was also determined: Al–O 1.798(6), Al–Cl 2.098(4), 2.095(3) (× 2) Å.

While long regarded as providing examples of classical donor–acceptor dative-bond complexes of the Lewis acid–base Group III–Group V type, the available substantive single-crystal X-ray structural evidence on complexes formed between aluminium trichloride and unidentate N-donor bases is sporadic and diverse. The only such study on material obtained by the crystallization of $AlCl_3$ from the 'linear' base acetonitrile, MeCN, shows the compound to be $AlCl_3 \cdot 2MeCN$, but ionic solvated $[AlCl(NCMe)_5][AlCl_4]_2 \cdot MeCN$ rather than a neutral mononuclear or other covalent complex.[1] Similarly, the adduct obtained from pyridine (py) of the same stoichiometry, $AlCl_3 \cdot 2py$, is also ionic, *trans*-$[AlCl_2(py)_4][AlCl_4]$, while a 1 : 3 complex also isolated is neutral *mer*-$[AlCl_3(py)_3]$.[2] In all of these complexes the aluminium atom in the nitrogen-base complexed component is six-co-ordinate. By contrast, the adduct with trimethylamine, also of 1 : 2 stoichiometry, is presumed to be a neutral mononuclear complex $[AlCl_3(NMe_3)_2]$, on the basis of it being isomorphous with the early determination of $CrCl_3 \cdot 2NMe_3$,[3] and X-ray powder pattern.[4] Symmetrical cleavage of M_2X_6 systems such as Al_2Cl_6 arises when two molecules of a Lewis base attack different metal atoms as in **I**, whereas unsymmetrical cleavage occurs when the Lewis bases attack the same metal atom as in **II**.[5]



I



II

In this context, and that of recent local exercises concerned with achieving control of stoichiometry, co-ordination number and stereochemistry in complexes of metal salts crystallized from solution in unidentate nitrogen bases, by variation of the steric profile of the latter, we were interested to ascertain the extent to which variation of the stoichiometry and metal co-ordination number of similar complexes of Group III metals might be similarly susceptible to ligand variations. Accordingly, a number of complexes of aluminium(III) chloride were obtained by its crystallization from or with a variety of unidentate nitrogen bases of various steric profiles. We record in this work the synthesis and structural characterization of such complexes of 1 : *n* $AlCl_3$: N-base stoichiometry, all mononuclear, for piperidine (a 1 : 2 complex), 2-methylpyridine (mpy; a 1 : 1 complex), 2-diphenylmethylpyridine (dpmpy; a 1 : 1 complex), and quinoline (quin; a 1 : 1 complex, further solvated by a second quinoline). Also reported are structural characterizations of a pair of interesting by-products. One was obtained from an attempt to obtain better crystals of the piperidine adduct by crystallization from acetonitrile solution, the consequence being a complex of the piperidine–acetonitrile condensate, $[Al\{HN{=}CMeN(CH_2)_5\}_4]Cl_3 \cdot MeCN$; the other, obtained from an attempted synthesis of an octahydroacridine adduct from tetrahydrofuran (thf) solution followed by sublimation, was the structurally unknown 1 : 1 $AlCl_3 \cdot thf$ adduct, also mononuclear.

Experimental

Nitrogen bases and aluminium chloride were from Aldrich Chemical Co. Aluminium chloride was freshly sublimed and diethyl ether and thf were freshly distilled from sodium–benzophenone prior to use. All preparations were conducted under an inert atmosphere involving Schlenk techniques. Repeated attempts at obtaining consistent microanalyses for all compounds were foiled by either their high affinity for moisture and/or the ease of loss of solvent/base.

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† *Non-SI unit employed:* mmHg ≈ 133 Pa.

Synthesis

$AlCl_3$·2pip. To a solution of $AlCl_3$ in thf (*ca.* 20 cm^3) was carefully added an excess of piperidine (pip). A white precipitate immediately formed and would not dissolve upon heating to boiling. The solvent was removed *in vacuo* and the residue sublimed. Colourless crystals sublimed at *ca.* 190 °C (1 mmHg) after the residue had melted at a lower temperature, m.p. 135–138 °C.

[Al{HN=CMeN(CH_2)$_5$}$_4$]Cl_3·MeCN. An excess of piperidine was added to $AlCl_3$, whereupon a vigorous exothermic reaction occurred and a white material precipitated. Acetonitrile was added in an attempt to dissolve the precipitate, and upon heating there was a further vigorous reaction. Colourless crystals were deposited on cooling. They were collected and dried *in vacuo*, m.p. 206–208 °C.

$AlCl_3$·mpy. An excess of 2-methylpyridine was added to $AlCl_3$, whereupon a vigorous exothermic reaction occurred and a white material precipitated. Upon heating the precipitate dissolved and cooling at room temperature yielded colourless crystals. They were collected and dried *in vacuo*, m.p. 72–75 °C.

$AlCl_3$·dpmpy. To a stirred solution of $AlCl_3$ (0.25 g, 1.9 mmol) in diethyl ether (*ca.* 25 cm^3) was added 2-(diphenylmethyl)pyridine (0.47 g, 1.9 mmol). After concentration and cooling of the solution colourless crystals were deposited. They were collected and dried *in vacuo*.

[$AlCl_3$(quin)]·quin. An excess of quinoline was added to $AlCl_3$ whereupon a vigorous exothermic reaction occurred and a white material precipitated. Upon heating the precipitate dissolved and slow cooling yielded colourless plates. They were collected and dried *in vacuo*, m.p. 74–77 °C.

$AlCl_3$·thf. To a stirred solution of $AlCl_3$ (0.25 g, 1.9 mmol) in thf (*ca.* 10 cm^3) was added octahydroacridine (0.35 g, 1.9 mmol). A colourless solution was obtained and after concentration and cooling, colourless rod-shaped crystals were formed. These crystals were extremely sensitive to loss of solvent, and attempts to obtain a structure were fruitless. Subsequent sublimation of this residue (100 °C, 1 mmHg) afforded colourless crystals, m.p. 70–71 °C.

Crystallography

Unique room-temperature diffractometer data sets ($T \approx 295$ K; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å 2θ–θ scan mode) were measured, yielding N independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the large-block least-squares refinements after Gaussian absorption correction.

Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were treated as described below. Conventional residuals R, R' on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4\ (I_{diff})$ being used. Neutral atom complex scattering factors were employed, and computation was by the XTAL 3.2 program system,[6] implemented by S. R. Hall. Unless otherwise indicated, H atoms were constrained in (x, y, z, U_{iso}). Specific details are as follows.

$AlCl_3$·2pip. $C_{10}H_{22}AlCl_3N_2$, M 303.6, monoclinic, space group $P2_1/c$ (C^5_{2h}, no.14), a 9.673(2), b 11.027(4), c 16.949(5) Å, β 121.67(2)°, U 1539 Å^3, D_c ($Z = 4$) 1.31 g cm^{-3}, $F(000)$ 640, μ_{Mo} 6.3 cm^{-1}, specimen 0.12 × 0.42 × 0.25 mm, $A^*_{min,max}$ 1.07, 1.21, $2\theta_{max}$ 55°, N 3519, N_o 1554, R 0.064, R' 0.063.

As with all determinations described herein, specimens were capillary mounted. High ligand thermal motion is frequently evident, probably the cause of somewhat high residuals.

$AlCl_3$·mpy. $C_6H_7AlCl_3N$, M 226.5, monoclinic, space group $C2/m$ (C^3_{2h}, no.12), a 16.577(8), b 7.300(3), c 8.76(1) Å, β 105.97(7)°, U 1020 Å^3, D_c ($Z = 4$) 1.48 g cm^{-3}, $F(000)$ 456, μ_{Mo} 9.2 cm^{-1}, specimen 0.48 × 0.70 × 0.75 mm, $A^*_{min,max}$ 1.51, 1.75, $2\theta_{max}$ 50°, N 981, N_o 847, R 0.047, R' 0.059; $(x, y, z, U_{iso})_H$ were refined.

$AlCl_3$·dpmpy. $C_{18}H_{15}AlCl_3N$, M 378.7, triclinic, space group $P\bar{1}$ (C^1_i, no.2), a 11.603(7), b 9.910(9), c 9.160(7) Å, α 62.48(6), β 74.18(6), γ 84.18(6)°, U 898 Å^3, D_c ($Z = 2$) 1.40 g cm^{-3}, $F(000)$ 388, μ_{Mo} 5.6 cm^{-1}, specimen 0.2 × 0.3 × 0.3 mm, no absorption correction, $2\theta_{max}$ 50°, N 3131, N_o 2131, R 0.050, R' 0.039.

$AlCl_3$·2quin ≡ [$AlCl_3$(quin)]·quin. $C_{18}H_{14}AlCl_3N_2$, M 391.7, triclinic, space group $P\bar{1}$, a 15.20(1), b 8.910(9), c 7.200(4) Å, α 93.02(6), β 96.04(5), γ 106.05(7)°, U 928 Å^3, D_c ($Z = 2$) 1.40 g cm^{-3}, $F(000)$ 400, μ_{Mo} 5.4 cm^{-1}; specimen 0.12 × 0.60 × 0.36 mm, $A^*_{min,max}$ 1.07, 1.21, $2\theta_{max}$ 45°, N 2571, N_o 1126, R 0.058, R' 0.047.

A sphere of data was measured, merging R 0.035.

[Al{HN=CMeN(CH_2)$_5$}$_4$]Cl_3·MeCN. $C_{28}H_{58}AlCl_3N_8$·CH_3CN, M 679.2, triclinic, space group $P\bar{1}$, a 14.973(6), b 14.027(5), c 10.94(1) Å, α 74.12(6), β 82.71(6), γ 63.15(3)°, U 1972 Å^3, D_c ($Z = 2$), 1.14 g cm^{-3}, $F(000)$ 732, μ_{Mo} 2.9 cm^{-1}, specimen 0.30 × 0.60 × 0.95 mm, $A^*_{min,max}$ 1.09, 1.22, $2\theta_{max}$ 50°, N 6714, N_o 3750; R 0.061, R' 0.063.

Hydrogen atoms on the HN=CMe fragment were unambiguously defined in difference maps.

$AlCl_3$·thf. $C_4H_8AlCl_3O$, M 205.5, monoclinic, space group $P2_1/m$ (C^2_{2h}, no.11), a 6.244(5), b 10.397(5), c 7.452(3) Å, β 106.99(5)°, U 462.$_6$ Å^3, D_c ($Z = 2$) 1.48 g cm^{-3}, $F(000)$ 208, μ_{Mo} 10.1 cm^{-1}, specimen 0.25 × 0.35 × 0.30 mm, $A^*_{min,max}$ 1.20, 1.30, $2\theta_{max}$ 55°, N 999, N_o 578, R 0.068, R' 0.074.

Very high 'thermal motion' apparent in the ligand is almost certainly a foil for disorder, which was not resolvable.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/141.

Discussion

A number of adducts of aluminium(III) chloride with unidentate nitrogen bases of various types and steric aspects have been synthesized and structurally characterized by room-temperature single-crystal X-ray studies. Although of simple stoichiometries, $AlCl_3$·nB where n is a single integer, comparable with those found in the present study, previous species obtained from the archetypical bases acetonitrile and pyridine have proved to be less than simple in their formation, undergoing ligand disproportionation to yield ionic species of different types. However, a mononuclear covalent array has been obtained from pyridine in the form of the 1:3 complex. In all of these species the co-ordination number of the complex array containing the base rises to six, above that found in the present halide complexes or the common $[AlCl_4]^-$ anion. A further covalent array has been recorded in the adduct with trimethylamine, $AlCl_3$·$2NMe_3$, the co-ordination number being five in a *trans*-trigonal-bipyramidal array.

Among the present complexes, all of which are mononuclear, neutral species, the maximum co-ordination number found is five in the 1:2 adduct with piperidine, with the two base ligands disposed *trans*; one molecule, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. Regrettably, the study of the trimethylamine complex is old, and is unable to offer metal environment data of a precision

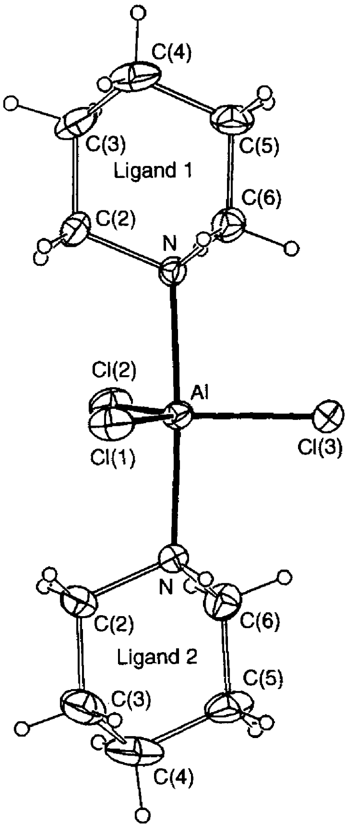

Fig. 1 The compound [$AlCl_3(pip)_2$], projected normal to the pseudo-trigonal-bipyramidal array principal axis. In all figures, non-hydrogen atoms are shown with 20% probability amplitude thermal ellipsoids, hydrogen atoms having arbitrary radii of 0.1 Å

useful for comparative purposes; nevertheless, of interest is the similarity of the base type. Secondary or tertiary aliphatic nitrogens form mononuclear adducts, whereas 'one'- or 'two'-dimensional bases such as acetonitrile or pyridine form ions or extended arrays. In the present complex the trigonal-bipyramidal array is only approximately so; the molecule has a quasi-2 axis passing through Al–Cl(3), with the opposite angle Cl(1)–Al–Cl(2) considerably enlarged [128.6(1)°] relative to the other pair [Cl(3)–Al–Cl(1,2) 114.6(1), 116.8(1)°], with N–Al–N [176.1(3)°] deviating from linearity by virtue of the increase in Cl(3)–Al–N above 90° [92.6(2), 91.4(2)°], possibly consequent upon the disposition of H(6), one from each ligand, in proximity to Cl(3) [(Cl(3) ··· H(6b), *ca.* 2.7 Å], and suggests the molecule to be more crowded than Fig. 1 indicates. The existence of five-co-ordination in the above two complexes may be contingent upon the comparative efficiency of aluminium–aliphatic N-base interactions *vis-à-vis* their aromatic counterparts (base strength considerations), which appear to favour four-co-ordination, at least in the neutral mononuclear arrays. Interestingly the bidentate compound 1,4-dimethylpiperazine also forms a monomeric five-co-ordinate trigonal-bipyramidal species but by virtue of the presence of a chelate ring one of the chloro groups is in an axial position. For all the chloro groups to be in a trigonal plane a polymeric structure would result with the N-donors of one ligand spanning two metal centres.[7] Indeed, such polymeric structures are prevalent for 'bidentate' tertiary amine adducts of AlH_3.[8]

Table 1 Aluminium environments: *r* is the aluminium–ligand distance (Å); other entries in the matrices are the angles (°) subtended by the relevant atoms at the head of the rows and column. Where N(*n*) are designated *n* is the ligand number. Primed atoms are generated by intramolecular mirror planes and symmetry related angles are enclosed in square brackets

(*i*) [$AlCl_3(pip)_2$]

Atom	*r*	N(2)	Cl(1)	Cl(2)	Cl(3)
N(1)	2.070(5)	176.1(3)	89.1(2)	88.6(2)	92.6(2)
N(2)	2.070(5)		88.9(2)	89.9(2)	91.4(2)
Cl(1)	2.190(3)			128.6(1)	114.6(1)
Cl(2)	2.174(3)				116.8(1)
Cl(3)	2.162(3)				

(*ii*) [$AlCl_3(mpy)$]

Atom	*r*	Cl(1)	Cl(2)	Cl(2′)
N	1.942(4)	106.6(1)	107.10(8)	[107.10(8)]
Cl(1)	2.112(4)		110.45(6)	[110.45(6)]
Cl(2)	2.109(1)			114.74(7)

Cl(1) ··· H(21b), Cl(2) ··· H(21a) are 2.96(7), 2.85(3) Å.

(*iii*) [$AlCl_3(dpmpy)$]

Atom	*r*	Cl(1)	Cl(2)	Cl(3)
N	1.954(4)	109.2(1)	107.4(1)	107.5(1)
Cl(1)	2.093(2)		108.10(9)	111.7(1)
Cl(2)	2.100(2)			112.8(1)
Cl(3)	2.082(2)			

Cl(1,3) ··· H(1) are 2.$_7$, 3.$_1$, Cl(2) ··· H(13) 2.$_6$ Å (estimated).

(*iv*) [$AlCl_3(quin)$]

Atom	*r*	Cl(1)	Cl(2)	Cl(3)
N	1.959(6)	107.4(2)	109.4(2)	106.4(2)
Cl(1)	2.104(4)		112.2(2)	110.8(2)
Cl(2)	2.096(4)			110.4(2)
Cl(3)	2.105(4)			

Cl(1,2) ··· H(18) are 3.$_0$, 2.$_9$; Cl(3) ··· H(12) 2.$_7$ Å (estimated).

(*v*) [$Al\{HN{=}CMeN(CH_2)_5\}_4]^{3+}$

Atom	*r*	N(2)	N(3)	N(4)
N(1)	1.851(4)	114.8(2)	102.5(2)	112.7(2)
N(2)	1.857(3)		110.6(2)	103.7(2)
N(3)	1.856(4)			113.0(2)
N(4)	1.851(5)			

(*vi*) [$AlCl_3(thf)$]

Atom	*r*	Cl(1)	Cl(2)	Cl(2′)
O	1.798(6)	106.6(3)	106.2(1)	[106.2(1)]
Cl(1)	2.098(4)		111.7(1)	[111.7(1)]
Cl(2)	2.095(3)			113.8(2)

The remainder of the complexes characterized (Fig. 2, Table 1) are effectively 1 : 1 $AlCl_3$: B adducts (the 1 : 2 stoichiometry of the quin adduct being accommodated by its formulation as a monosolvate); in all cases the base is derivative of a planar pyridine array with a substituent of more or less substantial bulk incorporated at the 2 position. For B = dpmpy or quin, one formula unit, devoid of crystallographic symmetry, makes up the asymmetric unit of the structure; for B = mpy, the plane of the base is coincident with a crystallographic mirror plane, which also contains the aluminium and one of the chloride atoms, and relates the other two, so that one half of the formula unit comprises the asymmetric unit of the structure. Although non-crystallographic, the symmetry of the B = dpmpy or quin array is similar, one chlorine atom lying approximately coplanar with the aromatic ring, and the in-plane chloride atom disposed *trans* to the 2-substituent, in relation to the Al–N bond. Variation in ligand bulk appears to have little influence on the $NAlCl_3$ geometry, presumably since, in all cases studied, the bulk of the substituent lies away from the adjacent pair of chlorine atoms. Although the disposition of the 2-substituent hydrogen atoms, established by geometrical necessity in the B = dpmpy or quin complexes, differs from that established by refinement in the mpy adduct and relates to the differences in asymmetry of Al–N co-ordination [Al–N–C (substituted, unsubstituted) are 123.8(3), 118.0(3) when B = mpy, *cf.* 126.6(2), 115.5(3) when B = dpmpy and 122.0(5), 118.6(4)° when B = quin], there appears to be no clear correlation on the basis of

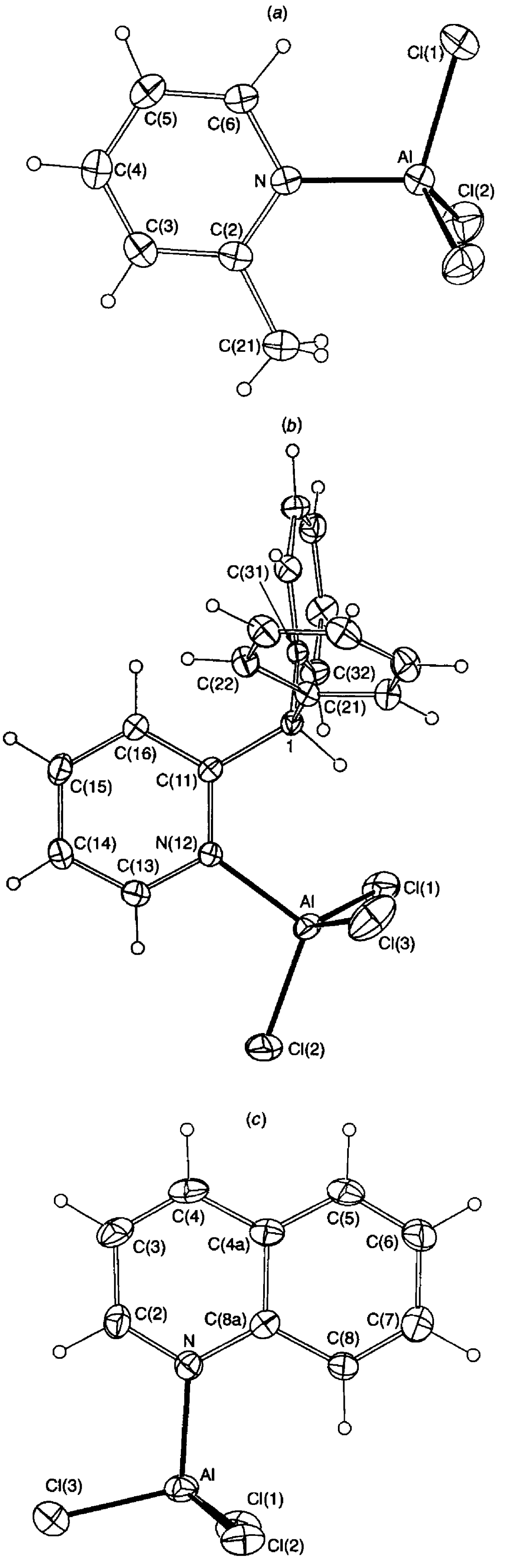

Fig. 2 The structures of (*a*) [$AlCl_3$(mpy)] [the ligand plane coincides with the crystallographic mirror plane, and is tilted slightly with respect to the page to permit viewing of the two Cl(2) atoms], (*b*), [$AlCl_3$(dpmpy)] and (*c*) [$AlCl_3$(quin)] projected normal to the ligand planes

this small sample between the situation where one or two H atoms confront the pair of chlorine atoms disposed to either side of the ligand plane. In all three compounds, Al–N are comparable (1.95 ± 0.01 Å) as are Al–Cl which, overall, span a range 2.082(2)–2.112(4) Å. More variation is found in the Cl–Al–Cl angles, which still, nevertheless, are fairly tightly ranged, generally slightly above the tetrahedral norm, the greatest excursion being 114.74(7)° in between the symmetry-related chlorine atoms of the mpy adduct. The N–Al–Cl angles in general vary little, lying slightly below the tetrahedral norm. There is no indication of any substantial tendency for the co-ordination number of aluminium to deviate from four; we note that achievement of a co-ordination number of five is feasible with 'three'-dimensional bases such as piperidine. Also that in the quinoline adduct the crystal packing is dictated by stacking of the ligand planes, those of the complex molecules being pairwise inversion related, lying approximately parallel to the *ab* plane, while the solvent molecules are related similarly, approximately parallel to the *bc* plane.

In the course of attempting to improve the crystal quality of the piperidine adduct, crystallization was attempted using solvent combinations of ligand and 'inert' support. For many such metal salt–N-base systems acetonitrile has served well in the past, and we had lost sight of the well known propensity of amines to react with nitriles containing electron-withdrawing groups, a reaction for which acetonitrile, in fact, is a common solvent.[9] The compound obtained from this reaction is the co-ordination complex of the base and solvent appearing in bulk as the first homoleptic neutral N-base complex of aluminium(III). The structure of this intermediate also sheds light on the nature of the species involved in the formation of amidines, of which the $AlCl_3$-catalysed reaction is a commonly used route. The Al–N distances in this array are closely ranged at 1.851–1.857(4) Å, shorter than the other such distances recorded herein; the N–Al–N angles range between 102.5(2) and 114.8(2)°. The cation, as displayed in Fig. 3 (see also Table 2), has, at least in respect of the inner [$Al(HN{=}CMeN)_4$] array, quasi-$\bar{4}2m$ symmetry, shown in projection down the quasi-$\bar{4}$ axis, a disposition perhaps dictated by the mutual avoidance of the bulk of the methyl substituents and imine hydrogen. The angular distortions conform to this array also, the two conspicuously small angles being between ligands 1 and 3 and 2 and 4 about the axis [102.5(2), 103.7(2)°]. The four HN=CMeN planes lie approximately parallel to the quasi-$\bar{4}$ axis and in the associated mirror planes, with the metal atoms also reasonably coplanar.

The other artefact, obtained by sublimation of the residue

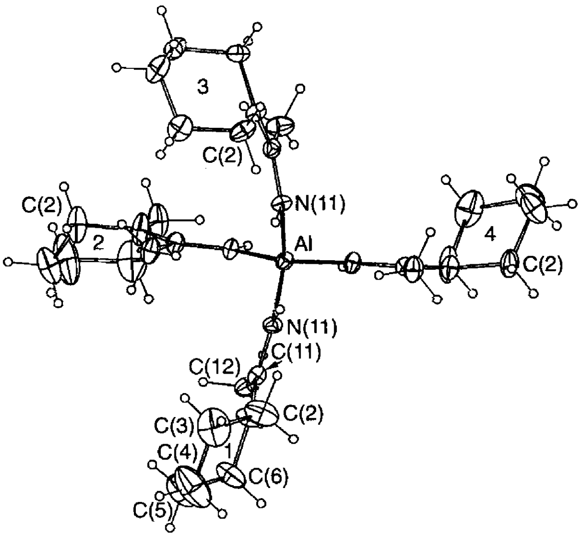

Fig. 3 The [$Al\{HN{=}CMeN(CH_2)_5\}_4]^{3+}$ cation, projected down its quasi-$\bar{4}$ axis

Table 2 Selected ligand geometries (distances in Å, angles in °) of $[Al\{HN{=}CMeN(CH_2)_5\}_4]^{3+}$ pertaining to the $[Al(N{=}CCN)_4]$ fragment

Ligand	1	2	3	4
N=C	1.318(6)	1.331(6)	1.320(6)	1.314(8)
C–N	1.321(7)	1.338(5)	1.324(7)	1.329(5)
C–C	1.493(8)	1.478(9)	1.492(9)	1.487(6)
Al–N=C	129.0(4)	126.9(4)	127.9(4)	129.6(4)
N=C–N	122.4(5)	121.9(6)	123.4(5)	122.9(5)
$N{=}C{-}CH_3$	119.3(5)	119.1(4)	117.5(5)	118.3(5)
$N{-}C{-}CH_3$	118.3(4)	118.9(5)	119.2(4)	118.7(4)
Deviations, δ/Å, of the metal from the N=CCN plane				
	0.007(8)	0.164(8)	0.453(7)	0.007(7)

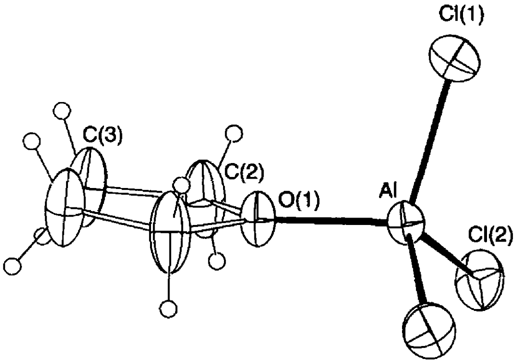

Fig. 4 Structure of $[AlCl_3(thf)]$; the molecule is disposed with a crystallographic mirror plane through OAlCl(1)

obtained after an unsuccessful synthesis using thf as solvent, is the thf monosolvate of aluminium(III) chloride. The 1 : 1 and 1 : 2 $AlCl_3$: thf adducts have been studied in some depth;[10,11] single-crystal X-ray studies have been recorded on two phases of the 1 : 2 adduct, the results mimicking those of such nitrogen-base adducts, one form being a mononuclear neutral trigonal-bipyramidal array,[12] and the other a *trans*-$[AlCl_2L_4][[AlCl_4]$ salt,[13] but there appears to be no record of the structure of the 1 : 1 complex, although this compound has been suggested on the basis of ^{27}Al NMR spectroscopy.[11] Here we show it to be neutral, mononuclear $[AlCl_3(thf)]$, one-half of the molecule comprising the asymmetric unit of the structure, with the molecule disposed on a crystallographic mirror plane (Fig. 4). Thermal motion is very high and the study would obviously benefit from a low-temperature determination. Nevertheless, we find the aluminium(III) environment to be closely comparable with those of the $NAlCl_3$ arrays discussed above, save that Al–O is shorter than Al–N, as is also true in the five- and six-co-ordinate counterparts noted above.

Acknowledgements

We gratefully acknowledge partial support by grants from the Australian Research Council, and fruitful discussion with Assoc. Professor J. R. Cannon.

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Received 19*th March* 1996; *Paper* 6/01916A