X-Ray Crystal Structure of the 1:2 Adduct of Aluminium Trichloride with Acetonitrile; an Interesting Example of Auto-complex Formation

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Summary Single crystal *X*-ray studies have shown that the co-ordination complex of aluminium trichloride with acetonitrile of stoicheiometry $AlCl_3$–2MeCN has the ionic structure $[AlCl(MeCN)_5]^{2+}[AlCl_4]_2^-$ and contains one molecule of solvent acetonitrile per asymmetric unit.

MANY attempts have been made to establish the nature of the stable molecular addition compounds in the $AlCl_3$–MeCN system, and to characterize the species present in solution. Schmulbach,[1] from a phase study, reports the presence of three stable complexes with empirical formulae $AlCl_3 \cdot 2MeCN$, $2AlCl_3 \cdot 3MeCN$, and $AlCl_3 \cdot MeCN$.

Solutions of $AlCl_3$ in MeCN are highly conducting, indicating the presence of ionic species,[2–4] and both Raman and n.m.r. experiments suggest that the anionic species present is $AlCl_4^-$.[1,3–7] The n.m.r. solution studies[5–7] have been taken to indicate the presence of only the 1 : 1·5 adduct, the most likely ionic species present being $[Al(MeCN)_6]^{3+}$-$[AlCl_4]^-_3$. The identification of the cationic species in the 1 : 2 adduct has proved very difficult and controversial. To account for the stoicheiometry various structures have been proposed, for example: $[Al_2Cl_5 \cdot 6MeCN]^+[AlCl_4]^-$;[1] $[AlCl_2(MeCN)_4]^+[AlCl_4]^-$;[2] and $[Al(MeCN)_6]^{3+}[AlCl_4]^-_3$-$\cdot 2MeCN$.[8]

Jones and Wood[8] note from their i.r. measurements that there appears to be unco-ordinated MeCN in the unit cell. A single crystal *X*-ray structure determination of the 1 : 2 adduct appeared to be the only unequivocal way of deciding the structure of the solid, and possibly of helping to understand the solution behaviour.

Crystal data: $C_{12}H_{18}Al_3Cl_9N_6$, orthorhombic, space group $P2_12_12_1$; $Z = 4$, $a = 10{\cdot}121(6)$, $b = 14{\cdot}562(12)$, $c = 21{\cdot}055(13)$ Å, $R = 0{\cdot}066$ for 2355 independent reflections (Syntex-$P2_1$ four-circle diffractometer) refined by full-matrix least squares from a direct methods solution of the structure.

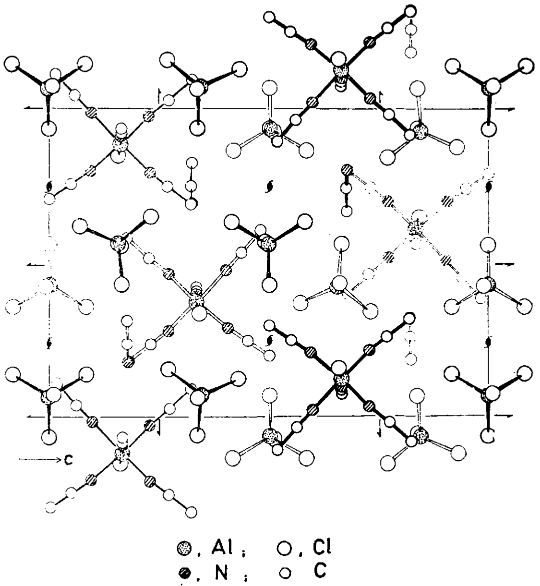

FIGURE. A view of the contents of the unit cell projected on the *b c* plane, viewed along the $-x$ axis towards the origin.

The crystal (Figure; unit cell contents) contains discrete $[AlCl_4]^-$ and $[ClAl(MeCN)_5]^{2+}$ ions together with one unco-ordinated solvent molecule (MeCN) per asymmetric unit.

The $[AlCl_4]^-$ tetrahedra show a mean Al–Cl distance of 2·118(7) Å and ∠Cl–Al–Cl in the range 107·7(3)–112·5(3)°, whereas the Al–Cl distance in the octahedral ion is 2·197(5)Å. The mean parameters for the equatorial acetonitriles in this latter ion are Al–N, 1·983(11); N–C, 1·149(17); and C–C, 1·468(21) Å; but the MeCN *trans* to the chlorine atom gives Al–N, 2·042(10); N–C, 1·105(16); and C–C, 1·483(20) Å. The $[ClAl(MeCN)_5]^{2+}$ ion deviates considerably from regular octahedral symmetry with the average ∠Cl–Al–N (equatorial) being 94·3(3)° and ∠Cl–Al–N (*trans*) 177·7(3)°. The solvent acetonitrile molecule [N–C, 1·16(2) and C–C, 1·46(2) Å] has no contact distance shorter than 3·09 Å.

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