

Stereochemistry of a Friedel-Crafts Intermediate. The Crystal Structure of the Aluminiumchloride-Benzoyl Chloride Complex

SVEND ERIK RASMUSSEN and NIELS CHRISTIAN BROCH

Department of Inorganic Chemistry, University of Aarhus, Aarhus C, Denmark

$\text{AlCl}_3 \cdot \text{C}_6\text{H}_5\text{COCl}$ crystallizes in the monoclinic system with $a = 8.68 \text{ \AA}$, $b = 7.28 \text{ \AA}$, $c = 9.33 \text{ \AA}$, $\beta = 104.33$ and space group $P2_1/m$.

The crystal structure was determined from the three dimensional Patterson function and refined by least squares analysis using anisotropic temperature factors. The adduct is composed of an AlCl_3 group coordinated with the oxygen of the benzoyl chloride group. The adduct has symmetry m . The benzoyl chloride group is coplanar with the aluminium atom and one chlorine atom bound to Al. Two other chlorine atoms coordinated with Al are located above and below the molecular plane. The aluminium atom is essentially tetrahedrally coordinated. Aspects of Friedel-Crafts acylations are discussed.

Friedel-Crafts and related reactions have recently been reviewed in a series of books edited by Olah.¹ References about earlier work on the molecular complex of aluminium chloride and benzoyl chloride can be found in Ref. 1.

This paper aims at establishing the geometrical structure of $\text{C}_6\text{H}_5\text{COCl}$, AlCl_3 . A preliminary account has been given earlier.²

EXPERIMENTAL

The complex was prepared pure and colourless by using thoroughly purified components. AlCl_3 was prepared from dry gaseous HCl and 99.995 % Al from Ver. Aluminium Werke, Bonn. Benzoyl chloride was distilled at 4–5 mm Hg. Reaction of redistilled benzoyl chloride with 3 mole % of AlCl_3 removed tarry impurities. The purified benzoyl chloride was distilled once more and the treatment with AlCl_3 followed by distillation was repeated. Reaction between AlCl_3 and $\text{C}_6\text{H}_5\text{COCl}$ was carried out in redistilled CS_2 in a dry nitrogen atmosphere. (Found: Cl 51.8 ± 0.3 , Al 9.86 ± 0.04 . Calc.: Cl 51.79; Al 9.85).

Recrystallisation from CS_2 yielded needle-shaped colourless crystals looking lamellar under the microscope. A crystal of dimensions $2 \times 0.4 \times 0.1 \text{ mm}^3$ was sealed in a capillary. Oscillation photographs, rotation-retigraph and precession photographs established lattice type and space group extinctions.

Intensities were measured using a linear diffractometer of the Arndt-Phillips design³ manufactured by Hilger and Watts. Molybdenum radiation was employed. Balanced filters SrO, ZrO₂ in conjunction with a scintillation counter and a pulse height discriminator ensured a practically monochromatic MoK α beam. Diffractometer output was on punched cards. The intensities measured were symmetry related in pairs. 4000 reflexions were registered. 947 of the 2000 independent reflexions showed intensities greater than twice their standard deviation. This was estimated as the square root of the total number of counts in an intensity measurement.

STRUCTURE DETERMINATION

The diffractometer output was fed into a GIER computer and an ALGOL program was employed which evaluated intensities, calculated averages, Lp corrections and standard deviations. The output gave Miller indices, squared structure amplitudes and standard deviations. The program was written by Grønbaek.⁴

AlCl₃·C₆H₅COCl has a monoclinic lattice. The only systematic extinctions found were $0k0$ for k odd. The possible space groups are $P2_1$ (No. 4) and $P2_1/m$ (No. 11).

The density of the crystal was not measured as no suitable flotation mixture was found. The calculated densities indicated two rather than four formula units per unit cell: d calc. for $z = 2$: 1.54 g/cm³, d calc. for $z = 4$: 3.08 g/cm³. No piezoelectricity could be detected by the Giebe-Scheibe method.

The three-dimensional Patterson was calculated using a Fourier program written by Lauesen.⁵

The Patterson function exhibited a concentration of peaks at y -levels 0, 1/4 and 1/2. x, z coordinates were deduced for Cl and Al atoms from the Harker section and confirmed by non-Harker vectors which also yielded y -coordinates. After the heavier atoms were found, it was realized that most of the atoms must lie in one plane and all atoms except hydrogens were located from the Patterson function by image seeking methods.

The benzoyl chloride group was found to be coplanar with the aluminium atom and one chlorine atom bound to aluminium. Two chlorine atoms bound to aluminium were located above and below the molecular plane.

The structure can be described in space group $P2_1/m$ assuming all atoms except two chlorine atoms to occupy two fold positions: $x, 1/4, z$. The two chlorine atoms belong to the general fourfold position x, y, z with y close to 0.5. This allocation of atoms yields two formula units of C₆H₅COCl, AlCl₃ per unit cell.

CRYSTAL DATA

The crystal data obtained are reported below. Crystal system: monoclinic, $a = 8.68_1 \text{ \AA}$, $b = 7.28_8 \text{ \AA}$, $c = 9.33_0 \text{ \AA}$, $\beta = 104.33^\circ$ space group $P2_1/m$ (No. 11).

The coordinates found and their estimated standard deviations are given in Table 1. Table 2 gives the coefficients employed in the structure factor calculations. Table 3 gives interatomic and van der Waals distances. The distances are not corrected for thermal vibration effects. A table of observed

Table 1a. Geometric parameters and their standard deviations as fractions of cell edges.

Atom	X	σ_x	Y	σ_y	Z	σ_z
Cl(1)	0.08544	0.00044	0.51217	0.00045	0.71925	0.00042
Cl(2)	0.17954	0.00051	0.25000	0.00000	0.12160	0.00054
Cl(3)	0.54924	0.00058	0.25000	0.00000	0.04976	0.00057
Al	0.95868	0.00056	0.25000	0.00000	0.17446	0.00053
O	0.81874	0.00118	0.25000	0.00000	0.99350	0.00114
C(1)	0.67576	0.00173	0.25000	0.00000	0.93461	0.00166
C(2)	0.61018	0.00166	0.25000	0.00000	0.77921	0.00165
C(3)	0.71617	0.00196	0.25000	0.00000	0.68977	0.00181
C(4)	0.65969	0.00250	0.25000	0.00000	0.54307	0.00211
C(5)	0.49663	0.00276	0.25000	0.00000	0.47826	0.00201
C(6)	0.39513	0.00226	0.25000	0.00000	0.56765	0.00225
C(7)	0.44758	0.00184	0.25000	0.00000	0.71862	0.00195
H(3)	0.81730	0.01950	0.25000	0.00000	0.73142	0.01827
H(4)	0.72602	0.01963	0.25000	0.00000	0.48595	0.01827
H(5)	0.43937	0.01905	0.25000	0.00000	0.36643	0.01785
H(6)	0.26484	0.01979	0.25000	0.00000	0.50821	0.01830
H(7)	0.36498	0.01941	0.25000	0.00000	0.77745	0.01772

Table 1b. Thermal parameters as u_{ij} . Mean square amplitudes, \AA^2 .

Atom	$\overline{u_{11}^2}$	$\overline{u_{22}^2}$	$\overline{u_{33}^2}$	$\overline{u_{12}^2}$	$\overline{u_{13}^2}$	$\overline{u_{23}^2}$
Cl(1)	0.092	0.090	0.098	-0.008	0.034	-0.027
Cl(2)	0.043	0.146	0.076	0.000	0.018	0.000
Cl(3)	0.061	0.169	0.080	0.000	0.037	0.000
Al	0.043	0.115	0.051	0.000	0.011	0.000
O	0.045	0.098	0.056	0.000	0.008	0.000
C(1)	0.046	0.074	0.055	0.000	0.021	0.000
C(2)	0.041	0.063	0.054	0.000	0.008	0.000
C(3)	0.056	0.081	0.061	0.000	0.014	0.000
C(4)	0.088	0.120	0.075	0.000	0.030	0.000
C(5)	0.106	0.130	0.049	0.000	0.006	0.000
C(6)	0.059	0.133	0.087	0.000	0.010	0.000
C(7)	0.039	0.092	0.079	0.000	0.004	0.000
	$\overline{u^2}$					
H(3)	0.060					
H(4)	0.060					
H(5)	0.060					
H(6)	0.060					
H(7)	0.060					

Table 2. Coefficients employed in structure factor calculations.

	Z	a	b	c	d	e
Cl	17	0.00530062	0.00310457	0.0202290399	0.1906431	-0.1599024
Al	13	0.00549639	-0.003092772	0.3782268	-0.5694333	0.3326347
O	8	0.01190571	0.0051983	0.0816816094	0.09526727	-0.04287454
C	6	0.00956688	0.00658085	0.0986952798	0.2463541	-0.1662073
H	1	0.0449699997	0.009711	0.631499995	0.692599995	-0.40295

$$f(z) = Z - s^2/(a + bs + cs^2 + ds^3 + es^4)$$

$$s = \sin\theta/\lambda$$

Table 3a. Bond distances and standard deviations Å.

Bond	l	σ
Cl(1) — Al	2.079	0.002
Cl(2) — Al	2.094	0.003
Cl(3) — C(1)	1.716	0.008
Al — O	1.819	0.005
O — C(1)	1.226	0.008
C(1) — C(2)	1.420	0.009
C(2) — C(3)	1.387	0.011
C(2) — C(7)	1.386	0.009
C(3) — C(4)	1.336	0.011
C(4) — C(5)	1.396	0.013
C(5) — C(6)	1.355	0.015
C(5) — H(5)	1.05	0.070
C(6) — C(7)	1.367	0.012
C(6) — H(6)	1.14	0.070
C(7) — H(7)	1.01	0.080
C(4) — H(4)	0.88	0.08
C(3) — H(3)	0.87	0.08

Table 3b. Van der Waals distances Å.

Atoms involved	l
Cl(1) — Cl(1)	3.47
Cl(1) — H(3)	3.03
Cl(1) — H(7)	3.03
Cl(2) — Cl(3)	3.44
Cl(2) — H(5)	2.78
Cl(3) — Cl(3)	3.80
Cl(3) — H(7)	2.66

and calculated structure factors has been deposited with the editor. The table is not printed to save space. The authors will gladly send tables to interested crystallographers on request.

Since the $h0l$ projection showed little overlapping of atoms this projection was used for the initial refinement. Refinement was therefore started with the $h0l$ data. The method of Bhuiya and Stanley⁶ was employed using a program written by Danielsen.⁷ Convergence was reached at an R -value of 12.3 %. Refinement continued using three-dimensional data and a least-squares program written by Danielsen⁸ and modified by Grønþæk. The program uses the diagonal approximation and isotropic temperature factors. Convergence was reached after 6 cycles at an R -value of 14.6 %. Refinement was carried on using another least squares program employing anisotropic temperature factors. The program employs a block-diagonal approximation with 3×3 matrices for coordinates and 6×6 matrices for temperature factors. This program was written by Grønþæk.⁹ After six cycles an R -value of 7.26 % was obtained. A difference Fourier synthesis revealed then the positions of the hydrogen atoms. Refinement continued with hydrogen atoms included in the calculations with isotropic temperature factors. After three more cycles an R -value of 5.48 % was obtained. The atomic scattering factors used were

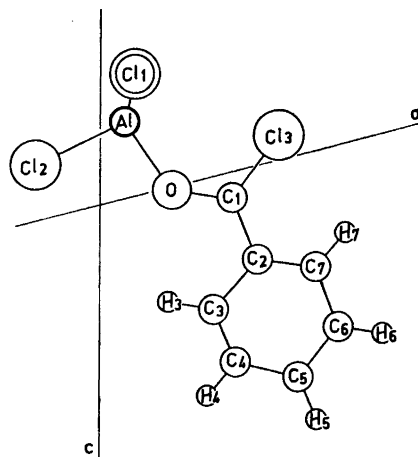


Fig. 1. Projection of an $\text{AlCl}_3 \cdot \text{C}_6\text{H}_5\text{COCl}$ molecule on the a - c plane.

those of *International Tables*. The scattering curves were approximated by Bassi¹⁰ polynomials. The reciprocals of the variances estimated from the counting statistics were used as weights in the least squares analysis.

Interatomic and intermolecular distances were calculated using a program written by Danielsen and Nyborg.¹¹

DISCUSSION

The space group requires that the molecule has symmetry m . The benzoyl chloride part of the molecule, the Al atom and one Cl atom are all in the symmetry plane and one chlorine atom is above and another one below the plane. A projection of the molecule is shown in Fig. 1. Aluminium is coordinated to three Cl atoms and to the keto-oxygen of the benzoyl group. The four atoms coordinated to aluminium form a distorted tetrahedron. The Al—O bond length is 1.82 Å which is only 0.03 Å longer than, *e.g.* Al—O distances in silicate minerals. The difference between the two sets of crystallographically independent Al—Cl distances is 0.015 Å which is five times the e.s.d. of the bond length. As no correction for thermal vibration has been applied the difference may be ascribed to this systematic error.

Interatomic distances in the benzoyl part of the molecule are close to those expected for the free molecule.

The bond order of the C(1)—C(2) bond is 1.4. The differences between the various bond lengths in the benzene part of the molecule are hardly significant. The mean distance of the six "benzene" distances is 1.371 Å which does not differ significantly from the accepted C—C distance in benzene since the neglect of correction for libration leads to an apparent shortening of distances.

The molecules are chiefly located in layers which are separated $b/2$ (3.64 Å) from each other. The packing of the molecules is largely governed by chlorine contacts.

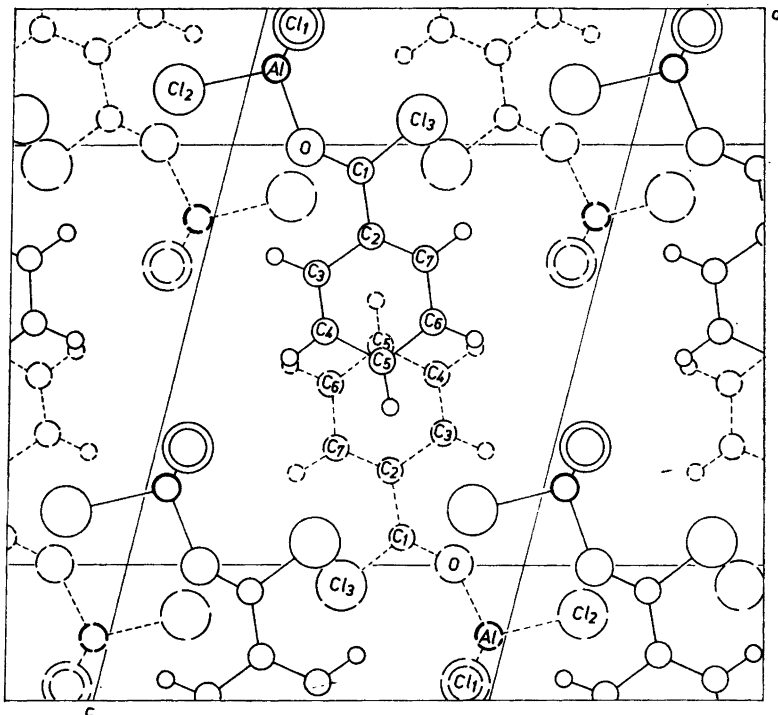


Fig. 2. Projection along the b -axis indicating packing of molecules. Full line atoms are all in one symmetry plane and dotted line atoms all in the other symmetry plane spaced $b/2$ from the first plane.

Within a symmetry plane there is a contact between Cl(2) from one molecule and Cl(3) from a neighbour molecule with a short van der Waals distance of 3.44 Å, Cl(2) is further related with H(5) of another molecule through a distance of 2.78 Å. Molecules related with each other *via* a screw axis have Cl(3)—Cl(3) distances of 3.80 Å.

An important connection between layers is given through Cl(1) atoms. The top Cl(1) atom in one molecule is 3.47 Å from the bottom Cl(1) atom in the equivalent molecule in the next unit cell. Cl(1) is further connected with an H(3) atom in one molecule (3.03 Å) and an H(7) in another molecule (3.03 Å).

Fig. 2 shows the packing of the molecules and the van der Waals distances are given in Table 3.

The structural results lead us to summarize some facts and some speculations on the Friedel-Crafts acylation of benzene: Solid AlCl_3 has a layer structure with octahedrally bonded Al. It is only slightly soluble in CS_2 . Addition of benzoyl chloride to AlCl_3 in the mole ratio 1:1 increases the solubility of AlCl_3 in CS_2 . At 46°C 0.05 mole AlCl_3 and 0.05 mole $\text{C}_6\text{H}_5\text{COCl}$ are dissolved

in 50 ml (1 mole) CS₂. At 20°C most of the two components crystallize as the molecular adduct.

On this evidence we postulate that the adduct is formed also in solutions of CS₂, AlCl₃, and C₆H₅COCl. We suggest that the molecular adduct is also formed in solutions of AlCl₃ in C₆H₅COCl and in other solvents which do not react with either component of the adduct.

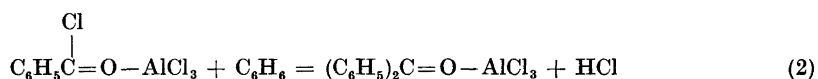
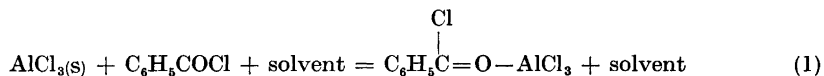
It is a wellknown fact that an adduct, AlCl₃·(C₆H₅)₂CO, can be isolated. We postulate that this adduct has a structure analogous to that of the benzoyl chloride-aluminiumchloride adduct.

Investigations of yields of benzophenone as a function of AlCl₃ addition by Riddel and Noller¹² have shown that maximum yield is obtained with molar ratios of AlCl₃ against C₆H₅COCl a little above 1.

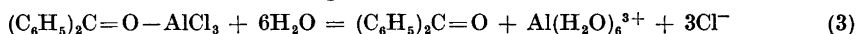
In the Perrier¹³ variation of the acylation reaction aluminium chloride and the acyl component are allowed to react prior to the addition of benzene.

Kinetic studies by Brown and Jensen¹⁴ and by Jensen, Marino and Brown¹⁵ show that the speed of acylation is proportional to AlCl₃ concentration and benzene concentration.

On the basis of the various experimental findings we propose the following description of the Friedel-Crafts acylation:



Benzophenone can be isolated using the reaction:



This reaction scheme is consistent with the stoichiometry and the kinetics of the reaction. Tracer studies using labelled chlorine in AlCl₃ show that a complete exchange of radioactive Cl occurs between the complex and the HCl, (Oulevey and Susz¹⁶). This result shows that in the transition state none of the chlorine atoms can be definitely located.

Strictly speaking the usual Friedel-Crafts acylation is not a catalytic reaction. The AlCl₃ affects the energetics of the reaction by forming well defined, stable compounds with reactant and with reaction product. Isolation of the desired product is carried out using reaction (3) which means that the "catalyst" cannot be recovered without elaborate chemical work.

We have isolated the compound CH₃COCl·AlCl₃. The crystals obtained are however, too small for X-ray work. A Crystal growth equipment is at present under construction for work at low temperature.

The monographs of Olah¹ and of Lindqvist¹⁷ contain a wealth of information about adducts containing the group >C=O. However, as pointed out by Lindqvist,¹⁷ few complete structure determinations of these adducts are reported. The structure determination of Mn(II) (PO₂Cl₂)₂(CH₃-CO-OC₂H₅)₂ by Danielsen and Rasmussen¹⁸ shows that the >C=O group in ethyl-acetate coordinates with Mn²⁺.

The available evidence shows that a great variety of molecules containing $>C=O$ groups acts as complexing agents especially in non aqueous chemistry.

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