Crystal Structure Analysis and NMR Spectra of N-(Pentafluorobenzoyl)-4-dimethylaminopyridinium Hexachloroantimonate(V)[#]*

*Sandro Hollenstein, Christian Lohse and Thomas Laube****

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule Zürich, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich, Switzerland

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The crystal structure analysis of *N*-(pentafluorobenzoyl)-4-dimethyl-aminopyridinium hexachloroantimonate(V) (space group: $P1$, measurement at -80 °C; high-order refinement; $R = 0.035$, $R_w = 0.035$ with all data) shows, that the carbonyl group and the dimethylaminopyridine (DMAP) fragment have a practically coplanar arrangement, while the pentafluorophenyl group is twisted by *ca.* 69° out of that plane. The resulting CO-DMAP-π-interaction allows a charge delocalization towards the dimethylamino group, *i.e.* the cation may be best described as an iminium ion. The crystal packing reveals cation-anion interactions only in the formal iminium fragment. The carbonyl-C atom, which is attacked by a nucleophile in the course of an acylation reaction, has two intramolecular and one intermolecular van der Waals contacts to fluorine atoms. The structure is also interpreted in terms of a beginning dissociation into an acyl cation and DMAP. The ^{1}H, ^{13}C and ^{19}F NMR spectra are compared with those of related molecules.
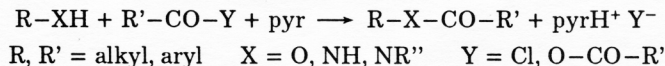
INTRODUCTION

The acylation of alcohols or amines with acyl chlorides or acid anhydrides is catalyzed by pyridines (pyr), which are sometimes added in equimolar amounts in order to bind the acid generated in the reaction (Schotten-Baumann reaction, especially the Einhorn variant; the acid may also be removed by addition of aqueous alkali hydroxide solution).

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* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday.
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** Author to whom correspondence should be addressed.

$$R-XH + R'-CO-Y + pyr \longrightarrow R-X-CO-R' + pyrH^+ Y^-$$
$$R, R' = \text{alkyl, aryl} \quad X = O, NH, NR'' \quad Y = Cl, O-CO-R'$$

One of the best catalysts for this reaction is 4-dimethylaminopyridine (DMAP).[1] It is assumed, that *N*-acylpyridinium cations (**1**) are formed as reactive intermediates, which are attacked by a nucleophile (alcohol or amine) in a second step.

1   **2**
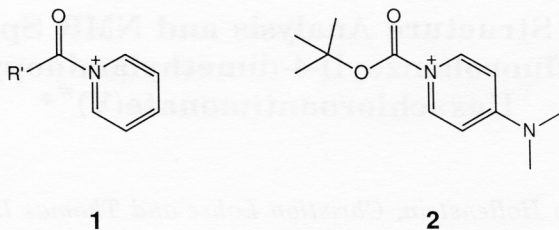
Ions of the type **1** were studied by Olah *et al.*[2] (NMR spectroscopy) and by Jones *et al.*[3] (crystal structure analysis). We have recently described the crystal structure analysis of *N*-BOC-4-dimethylaminopridinium tetrafluoroborate (**2**·BF$_4$)[4] and described in this work the first crystal structure analysis of an *N*-aroyl-pyridinium salt[5] and compare its structure and NMR data with those of **2** and related molecules.

EXPERIMENTS AND RESULTS

Pentafluorobenzoyl chloride (**3**) is used as a derivatizing agent for the gas-chromatographic analysis of amines, amides and phenols.[6] The electron-withdrawing pentafluorophenyl group makes this reagent very reactive towards nucleophilic attack at the carbonyl-C atom. The acylation reactions with **3** are carried out in the presence of trimethylamine or imidazole (amongst others) as acid-removing reagents. In order to prepare an *N*-acylpyridinium ion with a low tendency to dissociate into the acyl cation and the pyridine, we reacted **3** with the highly nucleophilic DMAP. The recombination of the acyl cation (always present in the equilibrium) with the counterion Cl$^-$ is prevented by the introduction of a nonnucleophilic counterion (like BF$_4^-$, CF$_3$-SO$_3^-$, SbF$_6^-$, SbCl$_6^-$ *etc.*), which in addition allows growing different crystals in order to get well diffracting single crystals. This target was achieved by the reaction of equimolar amounts of **3**, SbCl$_5$ and DMAP at low temperature to give N-(pentafluorobenzoyl)-4-dimethylaminopyridinium hexachloroantimonate(V) (**4**·SbCl$_6$).

3   **4**·SbCl$_6$
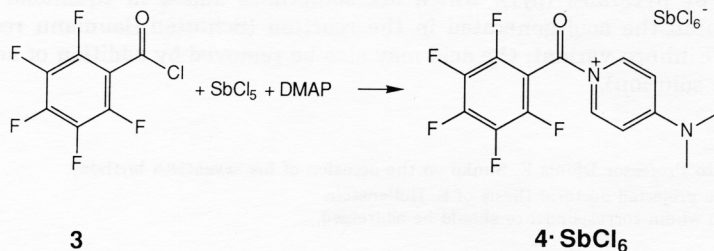
The X-ray measurement was carried out at –80 °C. Data were collected up to $\vartheta = 40°$ with Mo_{K_α} radiation ($\sin \vartheta / \lambda < 0.9045$ Å^{-1}). The anisotropic refinement (space group $P1$, see Experimental Part) with all data yielded an unreasonable bond length C14–C15 = 1.32(1) Å. In order to obtain a more reliable structure, a high-order refinement using only the data with 0.50 Å$^{-1} < \sin \vartheta / \lambda < 0.75$ Å^{-1} (2875 reflections, 2834 with $I > 5 \sigma_I$) and $w = \sigma_F^{-2}$ was carried out. It was necessary to constrain the anisotropic displacement parameters (ADP's) of the antimony atom (Sb1) to the values obtained by the previous refinement with all data, because otherwise the whole cation structure was severely distorted due to the high contribution of the Sb atom to the scattering power in that range. This indicates, that the Gaussian approximation for the probability density function (pdf) of the Sb atom is actually inadequate. A difference Fourier synthesis (with all data) shows the usual strong pairs of difference density peaks around the Sb atom. The difference density is featureless for the cation **4**. Because of the local centrosymmetry around the Sb atom, strong correlations (essentially only between parameters of the SbCl$_6$ anion) occurred during all refinements, but they obviously did not influence the convergence as observed in other cases.[7] The high-order refinement yielded the R values $R = 0.029$, $R_w = 0.031$, and the thus obtained positional and displacement parameters are used in the following discussion. The R values computed with these parameters using all data are $R = 0.035$, $R_w = 0.035$.
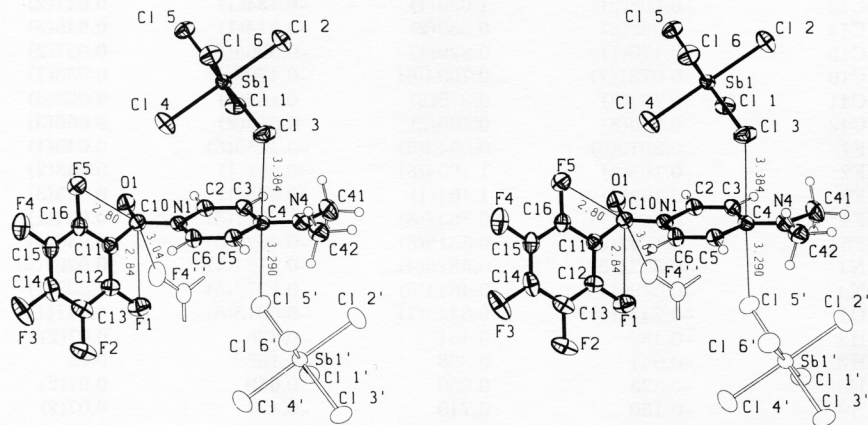

Figure 1. ORTEP Stereodrawing of the asymmetric unit of **4**·SbCl$_6$ (cation and anion with black bonds). A symmetry-related counterion SbCl$_6^-$ (primed labels; $' = x - 1, y + 1, z$) and a fragment of a symmetry-related cation **4** (doubly primed labels; $'' = x - 1, y, z$) are included in order to show the surrounding of C4 and C10 in the crystal. The ellipsoids are drawn on the 50% level; hydrogen atoms are represented by spheres with a radius of 0.1 Å; distances are given in Å.

The result of the crystal structure analysis is shown in Figure 1, the atomic coordinates are given in Table I. The asymmetric unit (the unit cell) contains one ion pair. The bond lengths and angles of **4** are depicted in Figure 2.

The carbonyl group and the DMAP ring are nearly coplanar (O1–C10–N1–C2 = –10.7(8)°, C11–C10–N1–C6 = –11.9(7)°), so that an interaction between their π systems is possible. The pentafluorophenyl ring, however, does not lie in the same plane

TABLE I

Fractional atomic coordinates and equivalent (non-hydrogen atoms) or isotropic (hydrogen atoms), U values ($Å^2$) of 4·$SbCl_6$. The estimated standard deviations (in brackets) refer to the last given digit. The anisotropic displacement parameters are given in the Supplementary Material.

Atom	x/a	y/b	z/c	U_{equiv} or U
Sb1	0	0	0	0.02727(5)
Cl1	-0.2933(4)	0.0391(3)	-0.1123(3)	0.0400(7)
Cl2	-0.0744(5)	-0.2240(4)	0.1791(3)	0.0454(8)
Cl3	-0.1457(5)	0.1802(4)	0.1484(3)	0.0474(7)
Cl4	0.0727(5)	0.2227(4)	-0.1776(4)	0.0490(9)
Cl5	0.1447(4)	-0.1870(3)	-0.1441(3)	0.0403(6)
Cl6	0.2969(4)	-0.0452(4)	0.1126(4)	0.0425(7)
C2	-0.452(1)	0.4825(9)	-0.2498(9)	0.030(2)
C3	-0.5377(6)	0.4439(5)	-0.1214(6)	0.034(1)
C4	-0.501(2)	0.504(1)	-0.002(2)	0.0307(9)
C5	-0.3609(7)	0.6033(5)	-0.0279(5)	0.032(1)
C6	-0.281(1)	0.641(1)	-0.1597(8)	0.031(2)
C10	-0.2336(7)	0.6173(5)	-0.4122(5)	0.033(1)
C11	-0.1217(7)	0.7478(6)	-0.4391(5)	0.032(1)
C12	-0.207(1)	0.9122(9)	-0.449(1)	0.036(2)
C13	-0.105(2)	1.030(1)	-0.484(1)	0.041(2)
C14	0.089(2)	0.989(2)	-0.514(1)	0.046(3)
C15	0.176(1)	0.829(1)	-0.5065(8)	0.037(2)
C16	0.0731(7)	0.7094(6)	-0.4702(5)	0.033(1)
C41	-0.733(3)	0.375(2)	0.152(2)	0.063(4)
C42	-0.519(3)	0.506(2)	0.254(2)	0.056(3)
F1	-0.3979(6)	0.9543(5)	-0.4185(6)	0.049(1)
F2	-0.199(2)	1.1904(8)	-0.492(1)	0.058(2)
F3	0.193(2)	1.104(1)	-0.549(1)	0.065(3)
F4	0.3675(7)	0.7838(8)	-0.5321(5)	0.054(1)
F5	0.1642(6)	0.5519(5)	-0.4629(5)	0.046(1)
N1	-0.3221(5)	0.5829(4)	-0.2734(4)	0.0297(9)
N4	-0.5796(7)	0.4644(5)	0.1276(5)	0.039(1)
O1	-0.2475(9)	0.5440(7)	-0.5013(5)	0.047(1)
H2	-0.482	0.431	-0.336	0.07(2)
H3	-0.641	0.368	-0.108	0.08
H5	-0.323	0.650	0.059	0.07(2)
H6	-0.180	0.719	-0.177	0.07(2)
H411	-0.780	0.358	0.263	0.08
H412	-0.677	0.256	0.128	0.12(2)
H413	-0.853	0.442	0.082	0.08
H421	-0.607	0.463	0.345	0.08
H422	-0.539	0.637	0.235	0.10(2)
H423	-0.370	0.447	0.277	0.08

(O1–C10–C11–C12 = 112.7(7)°, O1–C10–C11–C16 = –60.5(7)°). The counterion is situated above the DMAP ring, and a symmetry-related counterion lies below the DMAP ring, near to the dimethylamino group. For both counterions, the shortest C···Cl distance occurs with C4 (C4···Cl3 = 3.38(1)Å, C4···Cl5′ = 3.29(1) Å; sum of the van der Waals radii of C and Cl: 1.70 Å + 1.75 Å = 3.45 Å). The carbonyl-C atom C10 is surrounded by three electronegative atoms: the two *ortho* fluorine atoms F1 and F5 (C10···F1 = 2.844(7) Å, C10···F5 = 2.800(6) Å; sum of the van der Waals radii of C and F: 3.17 Å) and a fluorine atom of a symmetry-related cation (C10···F4″ = 3.037(7) Å).
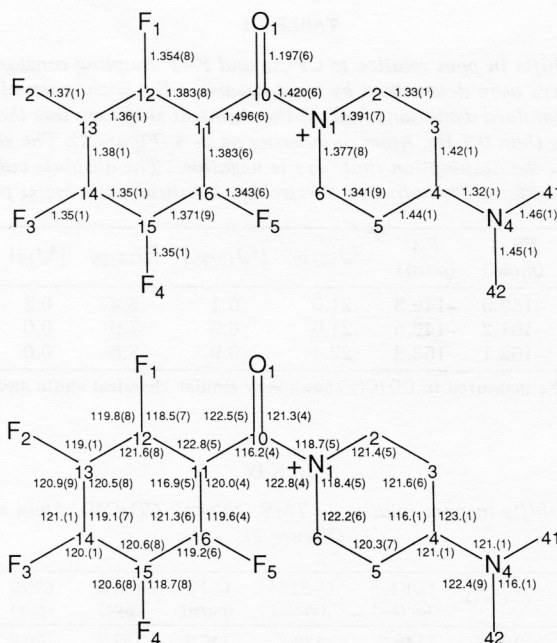
Figure 2. Bond lengths (in Å; top) and bond angles (in °; bottom) of **4** in the crystal structure of **4**·SbCl₆. The standard deviations (in brackets) refer to the last digit of the value.

In order to derive qualitatively the charge distribution in **4**, ¹H, ¹³C and ¹⁹F NMR spectra in solution were measured of **4**·SbCl₆, **4**·BF₄, **2**·BF₄, **3**, *N,N*-dimethylpentafluorobenzamide (**5**), DMAP and 4,4-dimethylaminopyridinium tetrafluoroborate (DMAP-H·BF₄). The results are shown in the Tables II–IV.

The ¹H NMR chemical shifts in the DMAP units of **2** and **4** are very similar, but slightly different from those in DMAP-H·BF₄ and DMAP (Table II). The ¹⁹F NMR data of the pentafluorophenyl groups of **4** and the acid chloride **3** show striking similarity, whilst those of the amide **5** are significantly different (Table III). The ¹³C NMR chemical shifts of **4** show the close relationship to **3** (with the exception of the *ipso* C atom) and to DMAP-H·BF₄ (Table IV). Another hint to the chemical similarity between the pentafluorophenyl groups of **4** and **3** is provided by the ${}^1J_{CF}$ coupling constants shown in Table V.

TABLE II

¹H NMR Chemical shifts in ppm relative to TMS (solvent: a = CD₂Cl₂, else CD₃CN).
*Atom numbering as in **4** (Figure 1).*

Compound	N–CH₃	H–C2/6	H–C3/5
4·SbCl₆	3.37	8.37	6.97
2·BF₄ᵃ	3.40	8.54	6.98
DMAP-H·BF₄	3.18	7.99	6.86
DMAP	2.93	8.12	6.53

TABLE III

^{19}F NMR Chemical shifts in ppm relative to $CFCl_3$ and F—F coupling constants J in Hz (solvent: CD_3CN). All parameters were determined by least-squares adjustment assuming an AA'BCC' system. The estimated standard deviations (esd) of the chemical shifts are less than 0.001 ppm, those of the J values are less than 0.1 Hz. Atom numbering as in **4** (Figure 1). The signs of the coupling constants are based on the assumption that $^3J_{FF}$ is negative.[8] The absolute values are given if the sign is uncertain. The adjusted spectra are identical with $J_{23/34}$ positive.

Compound	F1/5 (ortho)	F2/4 (meta)	F3 (para)	$-^3J_{12/45}$	$\|^4J_{13/35}\|$	$^5J_{14/25}$	$\|^4J_{15}\|$	$-^3J_{23/34}$	$\|^4J_{24}\|$
4·SbCl$_6$[a]	−137.1	−159.9	−146.3	21.9	6.1	8.4	0.2	20.0	7.0
3	−138.7	−161.2	−146.5	21.6	6.9	7.9	0.0	20.3	7.5
5	−143.5	−162.1	−153.3	22.4	0.9	8.5	0.0	19.9	4.6

[a] The spectrum of **4**·BF$_4$ measured in CD$_2$Cl$_2$ shows very similar chemical shifts and coupling constants.

TABLE IV

^{13}C NMR Chemical shifts in ppm relative to TMS (solvent: CD_3CN). Atom numbering as in **4** (Figure 1).

Compound	C=O	C–C=O	C–F1/5 (ortho)	C–F2/4 (meta)	C–F3 (para)	C2/6 (pyr)	C3/5 (pyr)	C4 (pyr)	N–CH$_3$
4·SbCl$_6$	158.6	106.5	146.2	139.2	146.2	137.7	109.2	159.6	42.4
3	159.5	112.9	145.9	139.2	145.9	–	–	–	–
5	159.1	112.9	143.9	139.0	142.9	–	–	–	a
DMAP-H·BF$_4$	–	–	–	–	–	139.6	107.6	158.6	40.4
DMAP	–	–	–	–	–	150.3	107.3	155.0	39.0

[a] The chemical shifts of the amide methyl groups are 35.1 and 38.2 ppm (Z and E).

TABLE V

$^{13}C—^{19}F$ Coupling constants in the pentafluorophenyl groups in Hz. For the sign see Ref. 9

| Compound	$^1J_{ortho}$	$^1J_{meta}$	$^1J_{para}$
4·SbCl$_6$	−262	−251	−262
3	−259	−252	−260
5	−246	−252	−250

DISCUSSION

The main question behind the crystal structure of **4** is, whether its stability may be explained in terms of resonance formulas **4'** and **4"**.

Therefore, we compare the structure of **4** with those of **2**, DMAP[10] and **6**.[11] Their most important structural parameters are shown in Figure 3.

The pentafluorophenyl ring **4** shows no unusual structural features, probably because it is twisted from the π-system of the carbonyl group and the DMAP ring. The DMAP ring of **4**, however, has a geometry significantly different from that of DMAP (see Figure 3). The C2–C3, C5–C6 and C4–N4 bond of **4** are shorter by 0.05(1), 0.037(9), and 0.05(1) Å, while N1–C2, N1–C6, C3–C4 and C4–C5 are longer by 0.055(7), 0.041(8), 0.02(1) and
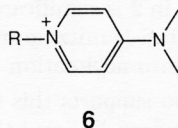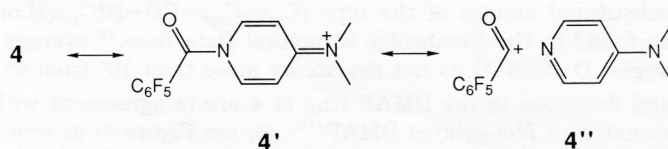
0.04(1) Å, if compared with DMAP. These changes may be interpreted as a strong hint to the importance of the resonance formula **4'** for the description of **4**, and this interpretation is supported by the fact that the counterions have their shortest C···Cl distances with the iminium-like carbon atom C4, *i.e.*, it is possible, that a large amount of the positive charge is located in the iminium group ("C4=N4"). Nevertheless, also the nonbonding resonance formula **4"** deserves some attention, because the C10–N1 bond of **4** is elongated by 0.039(7) Å, if compared with the C–N bond of essentially
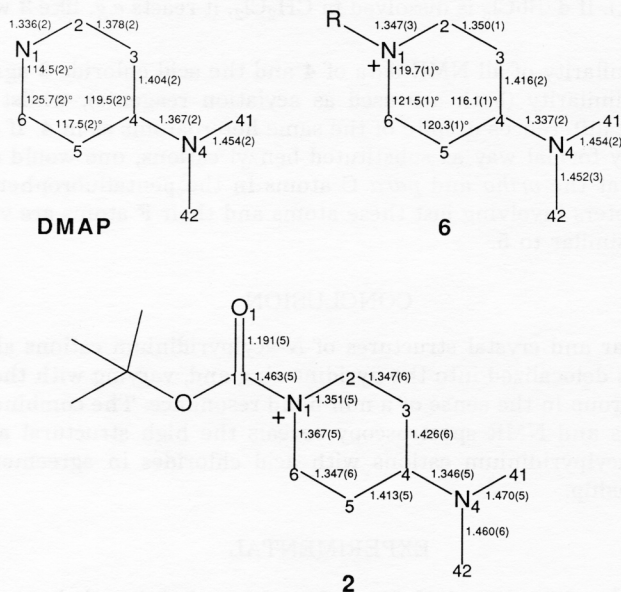

Figure 3. The most important parameters in the crystal structures of **2**,[4] DMAP[10] and **6**.[11b,c] The bond lengths are given in Å. The structure of **6** is an average of three fragments (R = H or C_{sp^3}).

planar *N,N*-di-substituted amides of the type $(C_{sp}2)_2C_{sp}2-CO-N[C_{sp}2(H\ or\ C)_2]_2$ (two structures[12] were found in the Cambridge Structural Data Base,[13] average = 1.381(3) Å; the torsion angles O=C–N–C do not deviate by more than 10° from 0° or 180°).

The structural deviation in the DMAP ring of **4** are in agreement with those observed in *N*-protonated or *N*-alkylated DMAP[11b,c] (**6**, see Figure 3) as well as those in **2**, but they are in **4** even stronger in the sense of a higher influence of the resonance formula **4'**. This phenomenon may be chemically explained by the fact, that N1 in **4** is substituted by a strongly electron-withdrawing group, and thus a positive charge on N1 destabilizes **4** stronger than **2** (or **6**), which are substituted by less electron-withdrawing groups. Accordingly, N1–C11 in **2** is significantly longer (1.463(5) Å) than N1–C10 in **4** (1.420(6) Å). In terms of the Bürgi-Dunitz approach,[14] **2** is more advanced on the reaction path towards dissociation into acyl cation and DMAP than **4**.

The crystal packing of **2**·BF$_4$ also supports this interpretation, because the shortest cation-anion contact occurs here between F1' and the carbonyl-C atom C11,[4] and this may indicate, that the carbonyl group of **2** bears a higher positive charge than that of **4** and that C4 of **4** is more accessible towards a nucleophilic attack than the carbonyl-C atom C10 (such an attack may occur, but it does not lead to subsequent reactions, and it is probably reversible). It is possible, that the attack of an external nucleophile (in the case of the reaction an alcohol or an amine) is kinetically slightly hindered by the *ortho* fluorine atoms F1 and F5, which act simultaneously as sterical hindrance and as internal nucleophiles which deactivate the carbonyl group by the through-space electron release from the F atoms towards C10. The crystal packing shows also, that another potentially nucleophilic atom (F4") is found in a van der Waals contact with C10 (see Figure 1). If **4**·SbCl$_6$ is dissolved in CH$_2$Cl$_2$, it reacts *e.g.* like **3** with dimethylamine to give **5**.

The close similarity of all NMR data of **4** and the acid chloride **3** agrees well with their chemical similarity (both are used as acylation reagents), whilst the amide **5** shows significant differences despite of the same heteroatoms as in **4**. If one considers **3** and **4** in a very formal way as substituted benzyl cations, one would expect partial positive charges at the *ortho* and *para* C atoms in the pentafluorophenyl rings, and the NMR parameters involving just these atoms and their F atoms are very similar in **3** and **4**, but dissimilar to **5**.

CONCLUSION

The molecular and crystal structures of *N*-acylpyridinium cations show, that the positive charge is delocalized into the pyridine ring and, varying with the acyl moiety, to the carbonyl group in the sense of a non-bond resonance. The combination of X-ray structure analysis and NMR spectroscopy reveals the high structural and electronic similarity of *N*-acylpyridinium cations with acid chlorides in agreement with their chemical relationship.

EXPERIMENTAL

Synthesis and Crystallization off N-*(Pentafluorobenzoyl)-4-dimethylaminopyridinium Hexachloroantimonate(V) (***4**·SbCl$_6$*).

To a solution of pentafluorobenzoylchloride (**3**) (460 mg, 2 mmol) in 15 mL of CH$_2$Cl$_2$ was added SbCl$_5$ (600 mg, 2 mmol) in 8 mL of CH$_2$Cl$_2$ at –80 °C under argon. After 30 min a solution of 4–dimethylaminopyridine (DMAP) (245 mg, 2 mmol) in 10 mL of CH$_2$Cl$_2$ was slowly added

and after another 30 min the solvent was evaporated at –20°C. The dry yellow powder was dissolved in a mixture of 10 mL of CH_2Cl_2 and 4 mL of CH_3CN at 0 °C. After filtration under argon the solution was cooled from 0 °C to –80 °C during 24 hours. The mother liquor was removed and the resulting yellow crystals were washed twice with 3 mL of CH_2Cl_2 and dried in the high vacuum.

Synthesis of N,N-*Dimethylpentafluorobenzamide (5)*.

To a solution of **3** (1.5 g, 6.5 mmol) in 15 mL of CH_2Cl_2 was added DMAP (0.8 g, 6.5 mmol) in 10 mL of CH_2Cl_2 under argon at 0 °C. Through a septum 150 ml of gaseous dimethylamine (6.5 mmol) were added with a gas-tight syringe and the solution was stirred for 15 min at 0 °C and 30 min at room temperature. The reaction mixture was poured into ice water and extracted with ether. The organic layer was washed several times with water, once with *ca.* 0.1 N hydrochloric acid and brine. After drying over anhydrous potassium sulfate the solvent was evaporated and the colourless liquid was distilled under reduced pressure (0.01 Torr, bp *ca.* 100 °C).

NMR Measurements.

All samples were dissolved in CD_3CN (internal standard: tetramethylsilane (TMS) for ^1H /^{13}C NMR and $CFCl_3$ for ^{19}F NMR). The spectra (^1H, 300 and 200 MHz; ^{13}C, 75 MHz and 50 MHz; ^{19}F, 282 MHz) were recorded at room temperature. The ^{19}F spectra were analyzed by least squares adjustments with a modified version of LAOCN-5[15] using practically all lines of the experimental spectra, which are well reproduced if a Lorentz line width of 1.0 to 1.5 Hz is chosen for the computed spectra.

X-ray Crystal Structure Analysis.

A crystal with the shape of a parallelepiped and a size of 0.38 mm × 0.31 mm × 0.15 mm was mounted under dry nitrogen in a Lindemann tube with a diameter of 0.5 mm. The structure was measured on an Enraf-Nonius-CAD4 diffractometer, $Mo_{K\alpha}$ radiation, graphite monochromator, measuring temperature –80 °C, space group $P1$, a = 7.168(3) Å, b = 8.613(1) Å, c = 9.524(2) Å, α = 75.77(1)°, β = 85.88(3)°, γ = 76.03(3)°, V = 553.0(3) Å^3, ρ = 1.957 g cm^{-3}, Z = 1, 7126 measured independent reflections with $\vartheta < 40°$ (6870 with $I > 3\sigma_I$). The position of the Sb atom was determined with the Patterson method of SHELXS-86,[16] and practically all other non-hydrogen atoms were located automatically by partial structure expansion. After locating the residual non-hydrogen atoms and several cycles of isotropic and anisotropic refinements with SHELX-76[17] (at the beginning with w = 1, later with w = σ_F^{-2}; position of Sb1 fixed at 0,0,0), the hydrogen atoms could be located by a difference Fourier synthesis. The hydrogen atoms were refined with the following constraints: all H's riding, H3, H411, H413, H421, H423 with U fixed at 0.08 Å^2 (totally 258 parameters). Figure 1 was drawn with ORTEP-II.[18]

Further details of the crystal structure investigation are available from the Director of the Cambridge Crystallographic Data Centre, Union Road, Cambridge CB2 1EZ, United Kingdom, on quoting the names of the authors and the full journal citation.

Supplementary Material Available:

Crystal packing diagram and lists of atomic coordinates, anisotropic displacement parameters, bond lengths, angles, torsion angles, observed and calculated structure factors of **4**·$SbCl_6$; NMR spectra of **4**·$SbCl_6$ (total 43 pages).

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SAŽETAK

Kristalna strukturna analiza i NMR spektri *N*-(pentafluorbenzoil)-4-dimetilaminopiridin heksaklorantimonata(V)

Sandro Hollenstein, Christian Lohse i Thomas Laube

Kristalna strukturna analiza naslovnog spoja pokazala je da su karbonilna skupina (CO) i dimetilaminopiridinski (DMAP) fragment molekule praktički koplanarni, dok je pentafluorfenilna skupina zaokrenuta za cca 69°. Koplanarnost CO i DMAP omogućuje znatnu delokalizaciju naboja, tako da kationski fragment molekule ima iminsku strukturu. Opisani su također ^{1}H, ^{13}C i ^{19}F NMR spektri analiziranog heksakloroantimonata.