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The crystal structure of diphenylamine hydrochloride antimony trichloride co-crystallizate, $C_{12}H_{12}Cl_4NSb$ – Localization of hydrogen atoms

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Table 1: Data collection and handling.

Crystal:	Green block
Size:	$0.42 \times 0.29 \times 0.20$ mm
Wavelength:	Mo $K\alpha$ radiation ($0.71073 \text{ \AA}$)
μ :	2.34 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	27.5° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	15,212, 3736, 0.021
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3408
$N(\text{param})_{\text{refined}}$:	172
Programs:	Bruker [1, 2], SHELX [3], WinGX/ ORTEP [4], Mercury [5], PLATON [6]

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The compound was obtained upon heating $SbCl_3$ with diphenylamine in toluene. Crystals suitable for the diffraction study were obtained upon storage of the reaction solution at room temperature.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H $0.95 \text{ \AA}$) and were included in the refinement in the riding model approximation, with $U(H)$ set to $1.2U_{\text{eq}}(C)$.

Both nitrogen-bound H atoms were located on a difference Fourier map and refined freely.

Comment

Benzene is one of the most important synthons in chemistry. Via electrophilic substitution reactions a vast variety

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Abstract

$C_{12}H_{12}Cl_4NSb$, monoclinic, $P2_1/n$ (no. 14), $a = 5.6693(2) \text{ \AA}$, $b = 20.2385(7) \text{ \AA}$, $c = 14.3908(5) \text{ \AA}$, $\beta = 100.3830(10)^\circ$, $V = 1624.14(10) \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.0192$, $wR_{\text{ref}}(F^2) = 0.0430$, $T = 200 \text{ K}$.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Sb1	0.60254 (2)	0.42241 (2)	0.62212 (2)	0.02581 (5)
Cl1	0.74776 (11)	0.43708 (3)	0.78814 (4)	0.04689 (14)
Cl2	0.99203 (9)	0.43626 (3)	0.58696 (4)	0.04769 (14)
Cl3	0.63053 (13)	0.30517 (3)	0.62539 (5)	0.06115 (18)
Cl4	0.44458 (8)	0.42553 (2)	0.41040 (3)	0.03228 (10)
N1	0.9128 (3)	0.37738 (8)	0.34111 (11)	0.0274 (3)
H1	1.051 (4)	0.3919 (11)	0.3700 (16)	0.036 (6)*
H2	0.799 (5)	0.3967 (13)	0.3597 (17)	0.046 (7)*
C11	0.9006 (3)	0.39522 (9)	0.24101 (13)	0.0299 (4)
C12	1.0647 (4)	0.36771 (12)	0.19288 (16)	0.0472 (5)
H12	1.182142	0.337393	0.222883	0.057*
C13	1.0538 (6)	0.38548 (16)	0.09964 (19)	0.0637 (8)
H13	1.165023	0.367118	0.064711	0.076*
C14	0.8837 (6)	0.42948 (14)	0.05679 (18)	0.0664 (9)
H14	0.878347	0.441546	−0.007359	0.080*
C15	0.7219 (6)	0.45594 (14)	0.10652 (18)	0.0619 (7)
H15	0.604324	0.486221	0.076552	0.074*
C16	0.7285 (5)	0.43894 (11)	0.19990 (16)	0.0445 (5)
H16	0.616692	0.457088	0.234705	0.053*
C21	0.8949 (3)	0.30587 (9)	0.35992 (14)	0.0302 (4)
C22	0.7125 (5)	0.27045 (12)	0.3087 (2)	0.0594 (7)
H22	0.599787	0.291055	0.260593	0.071*
C23	0.6940 (6)	0.20384 (14)	0.3282 (2)	0.0697 (8)
H23	0.566367	0.178612	0.293553	0.084*
C24	0.8565 (6)	0.17430 (12)	0.3961 (2)	0.0632 (8)
H24	0.844960	0.128359	0.407992	0.076*
C25	1.0362 (6)	0.21075 (14)	0.4471 (3)	0.0792 (10)
H25	1.148017	0.190188	0.495546	0.095*
C26	1.0581 (5)	0.27803 (12)	0.4289 (2)	0.0597 (7)
H26	1.184133	0.303533	0.464108	0.072*

of functionalized derivatives is readily available. The interplay between activating and deactivating substituents as well as the competition and synergism between inductive and mesomeric effects allows for benzene's seemingly endless functionalization. The latter gives rise to a large toolbox of new synthons that can be applied for the production of dyes, medications, catalysts and ligands for novel coordination compounds. The functionalization by means of electrophilic substitution reactions – especially the introduction of hydrocarbonic side chains in the wake of the Friedel–Crafts alkylations and acylations as well as the Gattermann reaction – often requires the use of Lewis acid catalysts such as aluminium chloride to activate the substrate. However, a select number of reagents is able to perform the electrophilic attack on its own. Notable examples are derivatives of arsenic in the production of *para*-arsanilic acid by reacting arsonic acid with aniline [7] or the synthesis of phenarsazine chloride by reacting diphenylamine with arsenic trichloride [8]. In an attempt to

see whether antimony trichloride would show the same ability to directly give rise to electrophilic substitution reactions on activated aromats, diphenylamine was reacted with SbCl₃. A crystalline reaction product was obtained whose crystal structure analysis showed the presence of the title compound (systematic name: diphenylaminium tetrachloridoantimonate). Although the molecular and crystal structure of the latter have been reported earlier [9], the 3D data deposited with the Cambridge Structural Database (ref. code: PAMSBC10) is lacking the two interesting hydrogen atoms on the lighter pnictogen atom. The notes in the database for this set of data explicitly state that these two atoms had to be removed due to erroneous coordinates as they had been shifted towards the chlorine atoms. Furthermore, an incorrect angle is pointed out. And while the remainder of the atom coordinates and their discussion are fine, the absence of the correct position of the hydrogen atoms of the protonated amino group precludes follow up investigations based on the data available as of this moment. This study is intended to close this gap. Apart from the co-crystallizate of the hydrogenchloride of diphenylamine as well as the pnictogen trichloride the molecular and crystal structure of the purely molecular 1:1 [10] and 1:2 [11] adducts between antimonytrichloride and diphenylamine have also been reported in the literature. Furthermore, the crystal structure of one cationic rhodium coordination compound featuring SbCl₄[−] as counterion is apparent [12].

The title compound contains the hydrochloride of diphenylamine. In addition, the solution shows the presence of one equivalent of antimony trichloride present in the crystal structure. The carbon–nitrogen bond lengths are at the lower end of the most-commonly reported ammonium cations that feature two benzene-derived aromatic systems bonded to an NH₂ group [13]. The two phenyl rings are orientated almost perpendicular to one another with the least-squares planes as defined by their respective carbon atoms intersecting at an angle of 86.55(14)°. The antimony atom is directly bonded to three chlorine atoms with the pertaining Cl–Sb–Cl angles spanning a range of 91.85(2)°–95.39(2)°. However, the coordination number of this heavier pnictogen atom can best be described as [3 + 2 + 1] as there is a total of six chlorine atoms around the antimony atom whose Sb–Cl bond lengths can be placed in three different groups with the shortest range of 2.3692(5)–2.4010(5) Å for the covalently-bonded chlorine atoms. Two of the chloride counterions reside at 3.0175(5) and 3.1171(6) Å distance from the antimony atom while the longest Sb–Cl contact with a value of 3.4180(6) Å is established by the covalently-bonded chlorine atom with the shortest Sb–Cl distance in one of the

neighbouring $SbCl_3$ moieties. As a consequence, the coordination polyhedron around the antimony atom could be described as distorted octahedral.

In the crystal structure, classical hydrogen bonds of the $N-H\cdots Cl$ type are observed. These exclusively employ the chloride anion as acceptor and connect the cation and anion to infinite chains along the crystallographic a axis. In terms of graph-set analysis, the descriptor for these interactions on the unary level is DD [14, 15]. While π stacking is not a prominent feature in the crystal structure of the title compound – the shortest distance between two centers of gravity was measured at $5.4085(16)$ Å – a possible $Cl\cdots\pi$ interaction involving one of the chlorine atoms bonded covalently to the antimony atom could be discussed. However, the corresponding $Sb-Cl-C_g$ angle would be rather acute at only $114.82(3)^\circ$.

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