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Crystal structure of phenarsazine chloride dimethylsulfoxide solvate, $C_{14}H_{15}AsClNOS$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	$0.50 \times 0.40 \times 0.30$ mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.55 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.3° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6536, 3458, 0.015
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3278
$N(\text{param})_{\text{refined}}$:	212
Programs:	Bruker [1], SHELX [2], WinGX/ORTEP [3], Mercury [4], PLATON [5]

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Abstract

$C_{14}H_{15}AsClNOS$, monoclinic, $P2_1$ (no. 4), $a = 5.2852(2)$ Å, $b = 13.3035(6)$ Å, $c = 10.7522(5)$ Å, $\beta = 90.130(2)^\circ$, $V = 756.00(6)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0200$, $wR_{\text{ref}}(F^2) = 0.0503$, $T = 200(2)$ K.

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The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
As1	−0.09517 (4)	0.48504 (3)	0.15347 (2)	0.03070 (8)
Cl1	0.15457 (17)	0.37728 (7)	0.04100 (8)	0.0564 (2)
N1	0.2992 (4)	0.5005 (2)	0.38523 (19)	0.0305 (5)
C11	0.1646 (5)	0.58025 (19)	0.1905 (2)	0.0276 (5)
C12	0.3254 (4)	0.57271 (19)	0.2939 (2)	0.0263 (5)
C13	0.5254 (5)	0.6424 (2)	0.3066 (3)	0.0313 (6)
H13	0.637250	0.637527	0.375589	0.038*
C14	0.5598 (6)	0.7166 (2)	0.2209 (3)	0.0391 (6)
H14	0.696935	0.762179	0.230016	0.047*
C15	0.3948 (6)	0.7261 (3)	0.1197 (3)	0.0448 (7)
H15	0.416279	0.778848	0.061109	0.054*
C16	0.2009 (6)	0.6578 (2)	0.1063 (3)	0.0392 (6)
H16	0.088926	0.664068	0.037469	0.047*
C21	−0.0752 (5)	0.41224 (19)	0.3068 (2)	0.0285 (5)
C22	0.1151 (5)	0.4282 (2)	0.3951 (2)	0.0294 (5)
C23	0.1230 (5)	0.3652 (2)	0.5008 (3)	0.0371 (6)
H23	0.252429	0.374264	0.561185	0.045*
C24	−0.0542 (6)	0.2912 (2)	0.5171 (3)	0.0447 (7)
H24	−0.044685	0.249049	0.588250	0.054*
C25	−0.2487 (6)	0.2767 (2)	0.4306 (3)	0.0453 (8)
H25	−0.372825	0.226099	0.443029	0.054*
C26	−0.2566 (5)	0.3373 (2)	0.3272 (3)	0.0383 (6)
H26	−0.388363	0.328178	0.268040	0.046*
H1	0.405 (5)	0.508 (2)	0.438 (2)	0.030 (7)*
S3 ^a	0.8146 (3)	0.55342 (12)	0.67438 (15)	0.0454 (5)
O3 ^a	0.598 (5)	0.5610 (12)	0.5898 (17)	0.060 (3)
C31 ^a	0.7704 (17)	0.6574 (5)	0.7760 (7)	0.069 (2)
H31A ^a	0.801214	0.720047	0.730626	0.104*
H31B ^a	0.889156	0.652337	0.845900	0.104*

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Table 2: (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H31C ^a	0.596627	0.657015	0.807583	0.104*
C32 ^a	0.749 (3)	0.4560 (6)	0.7822 (7)	0.109 (4)
H32A ^a	0.731727	0.392078	0.737781	0.164*
H32B ^a	0.590680	0.471054	0.825928	0.164*
H32C ^a	0.887473	0.451193	0.842560	0.164*
S4 ^b	0.7087 (5)	0.50598 (18)	0.7137 (2)	0.0537 (9)
O4 ^b	0.605 (7)	0.5364 (18)	0.596 (2)	0.060 (3)
C41 ^b	0.9955 (18)	0.5644 (11)	0.7441 (10)	0.089 (4)
H41A ^b	1.118214	0.545731	0.679965	0.133*
H41B ^b	1.058349	0.543067	0.825761	0.133*
H41C ^b	0.971965	0.637488	0.743802	0.133*
C42 ^b	0.535 (2)	0.5638 (14)	0.8342 (8)	0.094 (5)
H42A ^b	0.471946	0.629117	0.805607	0.140*
H42B ^b	0.644969	0.573529	0.906740	0.140*
H42C ^b	0.391934	0.520852	0.857113	0.140*

^aOccupancy: 0.578(4).^bOccupancy: 0.422(4).

Source of material

The title compound was synthesized upon the recrystallization of phenarsazine chloride from warm dimethyl sulfoxide. Crystals suitable for the diffraction studies were obtained upon cooling of the solution to room temperature.

Experimental details

The position of the H atom attached to N1 was refined subject to a distance restraint. All other H atoms were placed geometrically and refined as riding with $U_{iso}(H) = 1.2-1.5 U_{eq}(C)$ using the appropriate SHELXL AFIX commands. The dimethylsulfoxide molecule was found to be disordered over two positions with refined occupancies of 0.578(4) and 0.422(4), respectively. The Flack parameter [6] refined to 0.023(10) and was determined using full-matrix least squares.

Comment

The effect of size and steric presence of large ions on chemical and spectroscopic properties of compounds have been a focus of research for many decades. Among the many effects that can be attributed to the spatial requirements of counterions are the glass transition temperature in ionomers [7], surfactant modifying properties [8], the charge transfer in radical ions [9] and polymer-modified electrodes [10], as well as the structural and vibrational spectroscopic behavior

of DNA building blocks [11]. Furthermore, the benefit of choosing the adequate size of counterions to crystallize ionic compounds has been confirmed and reviewed on many occasions [12]. Gaining crystallographic information about a vast variety of large anions has seen significant growth upon the introduction of bulky cations that have simplified the crystallization of these compounds. A remarkable example in this aspect for instance the group of chlorido coordination compounds of gallium that apply cations derived from the phenarsazine scaffold [13, 14]. At the onset of a research project aimed at the characterization of large anionic compounds, we set out to create a novel set of phenarsazine-inspired cations *via* phenarsazine chloride as the starting material. To confirm the successful synthesis of the latter, a diffraction study of the recrystallized compound was conducted. The crystal structures of solvent - free phenarsazine chloride [15, 16] and phenarsazine bromide [15] have been reported earlier; however, no hydrogen atoms had been included in the refinement process. Furthermore, the crystal structure of the *para*-xylene solvate of phenarsazine chloride has been mentioned earlier [16]; however, no structural data has been deposited with the Cambridge Structural Database.

The structure solution from the experimental data collected in this study shows the presence of the desired phenarsazine chloride product as well as one molecule of dimethyl sulfoxide in the asymmetric unit. The solvent molecule is disordered over two positions, as described in the experimental section. The As–Cl bond length of 2.2950(8) Å is slightly longer than the most commonly-reported arsenic–chlorine bond lengths deposited with the Cambridge Structural Database [17]. The angles around the arsenic atom were measured at 96.32(8)° and 96.76(11)° towards the chlorine atom as well as 96.14(8)° for the intracyclic angle thus ruling out classical hybridization of the heavier pnictogen atom. The least-squares planes as defined by the respective atoms of the two aromatic moieties on the one hand as well as the central six-membered heterocyclic ring on the other hand enclose angles of 2.93(11)° and 3.82(12)° while the two planes of the outer aromatic moieties intersect at an angle of 3.99(13)°. A puckering analysis [18] of the central six-membered ring shows the latter to adopt a ⁴C₁ conformation on atoms N1 and As1 [19]. In the crystal structure, classical hydrogen bonds of the N–H...O type as well as C–H...O and C–H...Cl contacts are observed. The classical hydrogen bonds employ the oxygen atom of the disordered solvent molecule as an acceptor. The latter atom also serves as an acceptor for the C–H...O contacts that are supported by a) one of the hydrogen atoms in *ortho*-position to the N–H group and b) one of the hydrogen atoms in *para*-position to the N–H group in the other phenyl ring. The C–H...Cl

contacts stem from one of the hydrogen atoms on one of the methyl groups of the solvent molecule as well as the remaining hydrogen atom in *para*-position to the N–H group. In total, these contacts connect the entities in the crystal structure to a three-dimensional network. In terms of graph-set analysis [20, 21], the classical hydrogen bonds requires a *D* descriptor on the unary level while the C–H...O are to be described by means of a *DD* descriptor on the same level. The graph-set descriptor for C–H...Cl contacts is $DC_1^I(6)$ on the unary level. π -Stacking is not a prominent feature in the crystal structure of the title compound as the shortest distance between two centers of gravity was measured at 4.5864(15) Å. However, one could debate the presence of one C–H... π interaction that is supported by one of the hydrogen atoms on the disordered solvent molecule as donor and one of the phenyl moieties as acceptor.

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