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The AsF_6^- Salt of a 1,2-Dithia-4-azolylium Cation with Sterically Demanding Substituents

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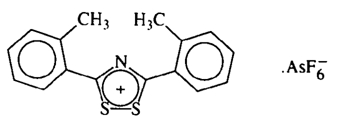
Abstract

The cation of the title compound, 3,5-bis(2-methylphenyl)-1,2,4-dithiazolylium hexafluoroarsenate(V), $C_{16}H_{14}NS_2^+.AsF_6^-$, has a central planar five-membered NCSSC ring with two *o*-tolyl substituents lying 29.11 (9)° out of this plane because of the steric hindrance of the methyl groups. The cation has a twofold rotation axis through the N atom and the midpoint of the S—S bond. Interionic interactions include short S···F and N···F contacts, but the cations are well separated with no S···S or N···S interactions.

Comment

As part of a continuing investigation of derivatives of 1,2-dithia-3,5-diazolyl (SSNCN) and 1,3-dithia-2,5-diazolyl (SNSCN) ring systems [see Rawson, Banister & Lavender (1995) for a general reference to this area], we have prepared and characterized a number of 1,3-dithia-2,5-diazolyl derivatives with *ortho*- and *meta*-substituted phenyl groups attached to the ring C atom (Banister, Hibbert, Aherne, Rawson, Clegg & Elsegood, 1996; Hibbert, 1993). The AsF_6^- salt of the 4-*o*-tolyl-1,3-dithia-2,5-diazolylium cation has been satisfactorily characterized by elemental analysis, IR spectroscopy and mass spectrometry (Hibbert, 1993), but in attempts to produce single crystals suitable for X-ray diffraction studies, further reaction with a small excess of the starting material, *o*-tolyl cyanide, in solution in liquid SO_2 led to a very small amount of the title compound, (I).



(I)

Both the cation and anion have crystallographic twofold rotation symmetry (Fig. 1). The five-membered ring is essentially planar [r.m.s. deviation 0.012 (1) Å]. The steric bulk of the *o*-methyl groups on the aromatic substituents prevents coplanarity and full delocalization of the three rings; each of the planar six-membered rings [r.m.s. deviation 0.006 (2) Å] forms a dihedral angle of 29.11 (9)° with the central ring. This out-of-plane twist puts the C8 atom 2.873 (8) Å from the N atom and 4.20 (2) Å from the C8^{i} atom [symmetry code: (i) $1-x$, y, $\frac{1}{2}-z$]; coplanarity would significantly reduce these distances and give unacceptably short contacts for the methyl H atoms.

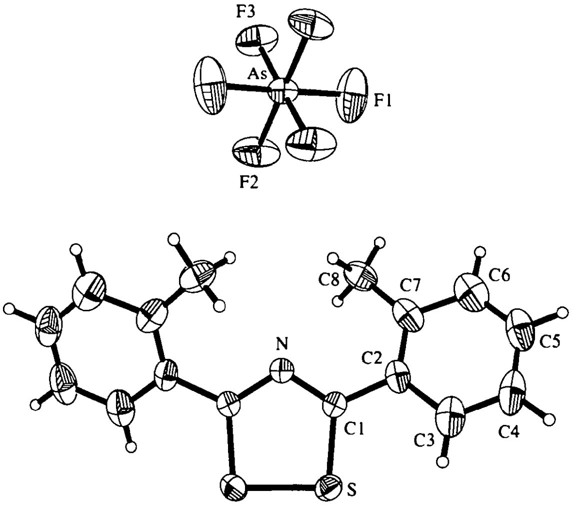


Fig. 1. The structure of the cation and anion of (I) with the atom labels (unique atoms) and 50% probability ellipsoids for non-H atoms.

The geometry of the *o*-tolyl substituent is unexceptional, with ring C—C bonds in the range 1.360 (6)–1.438 (5) Å and a C7—C8 distance of 1.473 (6) Å.

A search of the Cambridge Structural Database (Allen & Kennard, 1993) provided seven compounds containing the same central cationic ring system. The closest comparison is with the diphenyl derivative as its $NP_4S_9^-$ salt (Neels, Ziemer, Meisel & Leibnitz, 1986) and this has essentially the same ring geometry as the title compound. The hydrochloride (Hordvik & Sletten, 1966), hydrobromide (Peyronel, Pignedoli & Malavasi, 1982) and hydroiodide (Rodesiler & Amma, 1971) of thiuret, with two NH_2 substituents, have similar N—C bond lengths (mean 1.330 Å), but longer S—C (mean 1.754 Å) and markedly longer S—S (mean 2.073 Å) bond lengths, which must be a consequence of the electron-donating properties of the NH_2 groups. Three salts have been studied for the cation with one phenyl and one diethylamino substituent, with different anions having transition metals coordinated by chloro ligands, and the cation geometry is essentially invariant in these (Hartung, Beyer, Fernandez, Tudela & Gutierrez-Puebla, 1991; Fernandez, Monge, Gutierrez-Puebla, Beyer, Hartung & Richter, 1990; Kohler, Sieler, Richter, Hoyer, Beyer & Maartmann-Moe, 1989). The mean N—C distance is 1.323 Å, while the mean S—C (1.739 Å) and the S—S (2.031 Å) bond lengths are intermediate between the values found for the bis(aryl)- and bis(amino)-substituted cations, but there is considerable asymmetry in the ring, with the longer N—C (1.350 *versus* 1.296 Å) and longer S—C (1.748 *versus* 1.730 Å) bonds on the amino-substituted side. For all of these cations, with the exception of the title compound, the substituents are essentially coplanar with the central ring in the absence of significant steric obstruction to delocalization.

Apart from coulombic interactions, the cations and anions of the present structure are held together by specific weak S···F and N···F contacts, the shortest of which are given in Table 2. All other S···F distances are greater than 4 Å. The anions are sandwiched between five-membered cation rings. Unlike the case in some nitrogen–sulfur ring compounds, there are no S···S or N···S interactions between rings; all such distances exceed 5.4 and 7.2 Å, respectively. Of the F atoms, F3 is the one most involved in short interionic contacts, and the As—F3 bond is the longest, albeit only marginally so. Distortions from octahedral geometry for the anion are small, with the *cis* angles in the range 88.84 (12)–92.3 (2)° and the *trans* angles deviating from linearity by less than 1.2°. The packing arrangement and the out-of-plane twist of the aryl substituents are shown in Fig. 2.

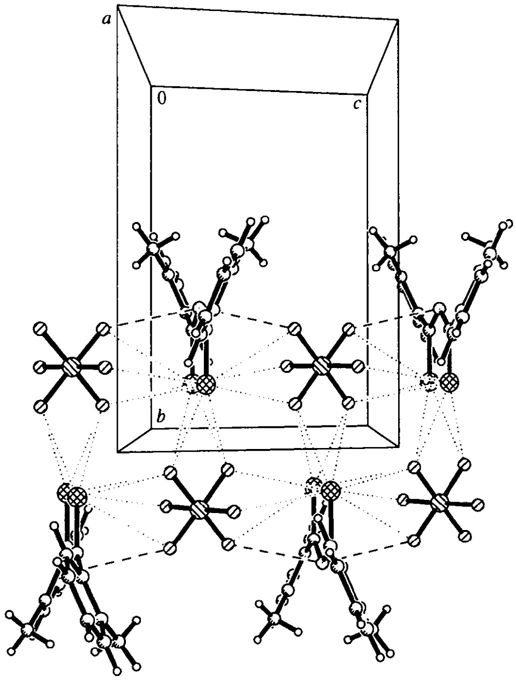


Fig. 2. The packing of cations and anions in projection along **a**. Interionic N···F contacts are shown dashed and S···F contacts dotted.

Experimental

The title compound was prepared unintentionally from 4-*o*-tolyl-1,3-dithia-2,5-diazolylium hexafluoroarsenate(V) and a small amount of *o*-tolyl cyanide in SO_2 solution. Crystals suitable for analysis were obtained directly in very low yield.

Crystal data

$C_{16}H_{14}NS_2^+.AsF_6^-$
$M_r = 473.32$
Monoclinic
$C2/c$
$a = 18.130\,(6)$ Å
$b = 12.194\,(4)$ Å
$c = 8.461\,(3)$ Å
$\beta = 108.82\,(3)°$
$V = 1770.5\,(10)$ Å^3
$Z = 4$
$D_x = 1.776$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 33 reflections
$\theta = 11.82$–$12.43°$
$\mu = 2.22$ mm^{-1}
$T = 160\,(2)$ K
Block
0.40 × 0.21 × 0.16 mm
Yellow

Data collection

Stoe–Siemens diffractometer with Cryostream cooler (Cosier & Glazer, 1986)
ω/θ scans with on-line profile fitting (Clegg, 1981)
Absorption correction: empirical ψ scans (*SHELXTL*; Sheldrick, 1994)
$T_{\min} = 0.65$, $T_{\max} = 0.84$
3258 measured reflections

1558 independent reflections
1407 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.026$
$\theta_{\max} = 25.04°$
$h = -21 \rightarrow 21$
$k = -14 \rightarrow 14$
$l = -8 \rightarrow 10$
5 standard reflections
frequency: 60 min
intensity decay: 1.5%

Refinement

Refinement on F^2
$R(F) = 0.0362$
$wR(F^2) = 0.0971$
$S = 1.091$
1558 reflections
120 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 3.799P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.80$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
S	0.44178 (5)	0.85943 (6)	0.21876 (10)	0.0333 (2)
N	1/2	0.6607 (3)	1/4	0.0247 (7)
C1	0.4349 (2)	0.7184 (2)	0.2185 (3)	0.0248 (6)
C2	0.3575 (2)	0.6696 (3)	0.1843 (4)	0.0333 (7)
C3	0.3008 (2)	0.7322 (4)	0.2318 (5)	0.0488 (9)
C4	0.2285 (2)	0.6907 (4)	0.2097 (6)	0.0571 (11)
C5	0.2113 (2)	0.5880 (4)	0.1390 (5)	0.0538 (11)
C6	0.2630 (2)	0.5265 (4)	0.0890 (5)	0.0530 (10)
C7	0.3395 (2)	0.5669 (3)	0.1116 (4)	0.0421 (8)
C8	0.3934 (2)	0.4999 (3)	0.0540 (5)	0.0498 (9)
As	1/2	0.18651 (4)	1/4	0.0315 (2)
F1	0.4085 (2)	0.1852 (3)	0.1079 (3)	0.0795 (9)
F2	0.5278 (2)	0.2834 (2)	0.1353 (3)	0.0674 (8)
F3	0.5275 (2)	0.0871 (2)	0.1369 (3)	0.0571 (6)

Table 2. *Selected geometric parameters (Å, °)*

S—C1	1.724 (3)	N···F2^{iii}	3.207 (7)
S—S^{i}	2.004 (2)	S···F3^{iv}	3.011 (6)
N—C1	1.326 (3)	S···F3^{ii}	3.297 (6)
C1—C2	1.465 (4)	S···F3^{v}	3.361 (6)
As—F2	1.704 (2)	S···F3^{iii}	3.436 (6)
As—F1	1.706 (3)	S···F1^{iii}	3.575 (6)
As—F3	1.715 (2)	S···F2^{ii}	3.657 (6)
N···F2^{ii}	3.207 (7)		
C1—S—S^{i}	94.04 (10)	N—C1—S	118.0 (2)
C1^{i}—N—C1	115.8 (4)	C2—C1—S	118.1 (2)
N—C1—C2	123.9 (3)		

Symmetry codes: (i) $1-x, y, \frac{1}{2}-z$; (ii) $1-x, 1-y, -z$; (iii) $x, 1-y, \frac{1}{2}+z$; (iv) $1-x, 1+y, \frac{1}{2}-z$; (v) $x, 1+y, z$.

H atoms were placed geometrically and refined using a riding model with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. This produces no additional refined parameters except for the torsional freedom of the methyl group about the C—C bond.

Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and local programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BK1238). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis[methyl N^{β}-(4-dimethylaminophenylmethylene)dithiocarbazato]nickel(II)

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Abstract

There are two independent centrosymmetric and essentially planar molecules in the unit cell of the title compound, $[Ni(C_{11}H_{14}N_3S_2)_2]$, having slightly different ligand conformations and a square-planar coordination of the Ni atom. Within each molecule, the two ligands are linked by a pair of C—H···S hydrogen-bonding interactions.

Comment

Metal complexes of chelating agents derived from dithiocarbazic acid are of considerable interest (West, Liberta, Padhye, Chikate, Sonawane, Kumbhar & Yerande, 1993). The thio derivatives of Schiff bases,

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