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Crystal and Molecular Structure of Trichloro[1,3-dimethyl-2(3*H*)-imidazolethione]arsenic(III)

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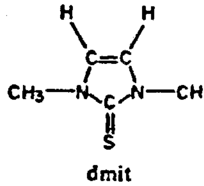
The crystal and molecular structure of $AsCl_3$dmit (dmit = 1,3-dimethyl-2(3*H*)-imidazolethione) has been determined. The compound, $C_5H_8AsCl_3N_2S$, crystallizes in space group $P2_1/c$ with four formula units in a cell of dimensions $a = 8.787$ (2) Å, $b = 10.207$ (1) Å, $c = 12.723$ (3) Å, and $\beta = 108.41$ (3)°. The calculated and observed densities are 1.898 and 1.89 (1) g cm^{-3}, respectively. The structure of $AsCl_3$dmit consists of pseudo-trigonal-bipyramidal molecules (sulfur equatorial) weakly joined into dimeric units of C_i symmetry via axial chlorine bridging. This is in contrast to the known structure of $AsCl_3N(CH_3)_3$ which is best described as a pseudo trigonal bipyramid with the amine bonding in the axial position.

The majority of structural work on adducts of group 5A trihalides has been on complexes with Lewis bases that possess donor sites of relatively high electronegativity and small size such as nitrogen[1,2] and oxygen.[3,4] From the idealized structure[5] for AX_3LE (A = central atom, X = halogen, L = two-electron donor, E = lone pair of electrons), a trigonal-bipyramidal array of substitutents would be predicted assuming a stereoactive lone pair (E). Structures I and II (Figure 1) show the energetically favorable isomeric possibilities for an AX_3LE system.

Both $AsCl_3NMe_3$[6] (Me = methyl) and $SbCl_3NH_2C_6H_5$[2] exhibit structure I due to the relatively high electronegativity and small size of nitrogen.[7] Since all structural studies for AX_3L adducts to date have been concerned with bases of relatively high electronegativity, we were interested in whether a Lewis base with a larger donor site of relatively low electronegativity such as sulfur would give rise to an adduct possessing structure II. The arsenic trichloride adduct of 1,3-dimethyl-2(3*H*)-imidazolethione (dmit) was therefore prepared, and the crystal and molecular structures were determined.



dmit

Experimental Section

The preparation of $AsCl_3$dmit has already been reported.[8] Crystals for X-ray study were grown from a saturated methylene chloride solution at room temperature. A suitable crystal was mounted in a glass capillary, and preliminary precession photography indicated space group $P2_1/c$ from systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. The cell dimensions were obtained using Mo Kα_1 radiation (0.709 300 Å) at 25 °C by a least-squares refinement to fit the $\pm 2\theta$ values for 10 high-angle reflections centered on the Picker FACS-1 four-circle diffractometer. The cell parameters are $a = 8.787$ (1) Å, $b = 10.207$ (1) Å, $c = 12.723$ (3) Å, $\beta = 108.41$ (2)°, and $V = 1083$ Å^3. For a formula weight of 309.48 ($C_5H_8AsCl_3N_2S$) and by assuming $Z = 4$, the calculated density is 1.898 g cm^{-3} which agrees well with the observed density of 1.89 g cm^{-3} obtained by flotation in a mixture of *n*-hexane and dibromomethane.

Collection and Reduction of Data. The same crystal used for the unit cell determination was used for data collection. The approximate dimensions were 0.45 mm × 0.65 mm × 0.35 mm with the $[\bar{1}05]$ direction coincident with the goniometer rotation axis. Diffractometer data were obtained using Zr-filtered Mo Kα radiation by the θ–2θ scan technique at a takeoff angle of 1.5°. The peaks were scanned at a rate of 1.0°/min from 1.0° on the low-angle side of the Kα_1 peak to 1.0° on the high-angle side of the Kα_2 peak. A scintillation counter was employed to count the diffracted beam, and a Ni foil attenuator was used whenever the count rate exceeded 8000 counts. Stationary-crystal, stationary-counter background counts of 10-s duration were taken at each end of the scan.

A unique data set was collected up to $2\theta = 55°$. The intensities of three reflections were monitored as standards every 100 reflections, and no loss in intensity was observed. Intensities were corrected for background, and standard deviations were assigned according to the equations $I = C - 0.5(t_c/t_b)(B_1 + B_2)$ and $\sigma(I) = [C + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$, where C is the integrated peak count obtained in time t_c and B_1 and B_2 are the background counts obtained in time T_b, all corrected for scalar truncation. A value of 0.05 was used for p. The data were also corrected for Lorentz and polarization effects and subsequently for absorption. A linear absorption coefficient of 41.7 cm^{-1} was calculated to give transmission coefficients ranging from 0.14 to 0.32. Of the 2518 unique reflections collected, 2049 with $I \geq 2\sigma(I)$ were used in the refinement.

Solution and Refinement of Structure. The structure was initially solved by direct methods using a data set collected with Cu Kα radiation and uncorrected for absorption. The details of this data collection and structural solution are reported separately.[9,10] The positions of the nonhydrogen atoms derived from the data set taken with Cu Kα radiation were used as starting positions in refinement of the data set described above. One cycle of isotropic and three cycles of anisotropic least-squares refinement yielded $R_1 = 0.043$ and $R_2 = 0.059$, where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. In this refinement the function minimized was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$.

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Table I. Positions and Thermal Parameters of Atoms with Estimated Standard Deviations

atom	*x*	*y*	*z*	$10^4\beta_{11}$[a]	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
As	0.2159 (1)	0.3969 (1)	0.5646 (1)	114.7 (9)	65.5 (5)	49.3 (4)	−22.6 (5)	31.8 (5)	−9.7 (4)
Cl(1)	0.4772 (2)	0.4339 (2)	0.6266 (2)	120.9 (21)	112.9 (15)	59.7 (10)	−35.0 (14)	16.3 (11)	0.1 (9)
Cl(2)	0.2558 (3)	0.1711 (2)	0.6159 (2)	254.1 (33)	81.7 (14)	53.4 (10)	−38.7 (16)	32.9 (14)	8.7 (9)
Cl(3)	0.1545 (2)	0.6244 (2)	0.4820 (2)	137.9 (22)	68.4 (12)	117.4 (15)	−17.5 (12)	57.9 (15)	−19.9 (10)
S	0.1874 (2)	0.3594 (2)	0.3810 (1)	122.7 (19)	53.0 (10)	44.4 (8)	−10.2 (11)	18.1 (10)	1.6 (7)
C(1)	0.2165 (6)	0.1930 (5)	0.3707 (4)	122 (8)	57 (4)	37 (3)	−15 (5)	18 (4)	−2 (4)
C(2)	0.3243 (8)	0.0011 (6)	0.3576 (5)	173 (12)	73 (6)	65 (4)	12 (6)	25 (6)	6 (4)
C(3)	0.1672 (8)	−0.0184 (5)	0.3417 (5)	191 (12)	62 (5)	69 (5)	−17 (6)	22 (6)	−16 (4)
C(4)	−0.0698 (8)	0.1223 (6)	0.3371 (6)	121 (9)	104 (7)	98 (6)	−34 (6)	30 (6)	−23 (5)
C(5)	0.5096 (7)	0.2012 (6)	0.3966 (5)	102 (8)	94 (6)	71 (5)	−10 (6)	18 (5)	−6 (4)
N(1)	0.3543 (6)	0.1336 (4)	0.3750 (4)	137 (8)	68 (4)	45 (3)	7 (4)	20 (4)	−2 (4)
N(2)	0.0998 (6)	0.1001 (4)	0.3488 (4)	131 (7)	58 (4)	55 (4)	−27 (4)	24 (4)	−14 (3)
H(1)	0.383 (13)	−0.039 (11)	0.351 (10)	5.0[b]					
H(2)	0.092 (13)	−0.078 (10)	0.292 (9)	5.0[b]					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Isotropic temperature factor, *B*, in Å^2.

Table II. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations

Bond Lengths

As-Cl(1)	2.213 (2)	C(1)-N(2)	1.359 (6)
As-Cl(2)	2.388 (2)	C(2)-C(3)	1.346 (9)
As-Cl(3)	2.539 (2)	C(2)-N(1)	1.383 (7)
As-Cl(3)	3.125 (2)	C(3)-N(2)	1.363 (7)
As-S	2.301 (2)	C(4)-N(2)	1.467 (8)
C(1)-S	1.729 (5)	C(5)-N(1)	1.476 (7)
C(1)-N(1)	1.339 (7)		

Bond Angles

Cl(1)-As-S	99.1 (1)	N(1)-C(1)-N(2)	107.9 (4)
Cl(2)-As-S	91.2 (1)	N(1)-C(1)-S	126.5 (4)
Cl(3)-As-S	77.9 (1)	N(2)-C(1)-S	125.5 (4)
Cl(3)′-As-S	91.3 (1)	C(1)-N(1)-C(2)	108.2 (5)
Cl(1)-As-Cl(2)	91.3 (1)	C(1)-N(1)-C(5)	124.5 (4)
Cl(1)-As-Cl(3)	92.9 (1)	C(2)-N(1)-C(5)	127.2 (5)
Cl(1)-As-Cl(3)′	168.7 (1)	C(1)-N(2)-C(3)	108.5 (5)
Cl(2)-As-Cl(3)	171.8 (1)	C(1)-N(2)-C(4)	126.1 (5)
Cl(2)-As-Cl(3)′	92.3 (1)	C(3)-N(2)-C(4)	125.4 (5)
Cl(3)-As-Cl(3)′	84.9 (1)	C(3)-C(2)-N(1)	107.6 (5)
C(1)-S-As	105.5 (2)	C(2)-C(3)-N(2)	107.8 (5)

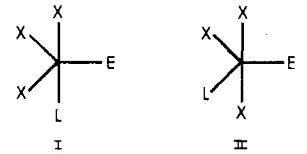

Figure 1. Isomeric possibilities I and II for an AX_3LE trigonal-bipyramidal molecule.

A difference Fourier map revealed the positions of the ethylene protons, but the methyl protons appeared to be disordered. Two more cycles of least-squares including ethylene protons with isotropic thermal parameters gave final values of 0.043 and 0.057 for R_1 and R_2, respectively. Atomic scattering factors and values of anomalous terms $\Delta f'$ and $\Delta f''$ were taken from the literature.[11]

Table III. Distances (Å) of Atoms from Least-Squares Planes[a]

Plane A		Plane B		Plane C		Plane D	
*As	0.110	*As	0.099	*As	0.044	*S	−0.027
Cl(1)	0.568	*Cl(1)	−0.004	*Cl(2)	−0.024	*C(1)	0.025
*Cl(2)	−0.057	*Cl(2)	−0.049	*Cl(3)	−0.023	*C(2)	−0.015
*Cl(3)	−0.056	*Cl(3)	−0.046	*S	0.003	*C(3)	−0.012
*As′	−0.110	rms dev	0.060	rms dev	0.028	*C(4)	0.014
Cl(1)′	−0.568					*C(5)	0.013
*Cl(2)′	0.057					*N(1)	0.003
*Cl(3)′	0.056					*N(2)	0.000
rms dev[b]	0.079					rms dev	0.016

[a] Asterisks mark atoms which were used to define least-squares plane. [b] Root-mean-square deviations in Å of the asterisked atoms from their respective least-squares planes.

Results and Discussion

A stereoview of the molecular structure of $AsCl_3$dmit is shown in Figure 2. Final atomic positions and thermal parameters with estimated standard deviations (esd's) are listed in Table I. Selected bond lengths and angles are given in Table II. The crystal packing is typical for space group $P2_1/c$, and other than those described in Table II there are no approaches of nonbonded atoms closer than 3.6 Å.

The dimeric unit (Figure 2) may be described as two highly distorted square pyramids sharing a common edge via long As–Cl bridging bonds with trans apexes occupied by sulfur. An unweighted least-squares analysis of the plane formed by As, Cl(2), Cl(3), As′, Cl(2)′ and Cl(3)′ (Table III)[12] clearly shows the distortion of the square pyramids. As (0.1 Å) and Cl(1) (0.6 Å) are displaced below the plane while As′ and Cl(1)′ are displaced above the plane by identical distances as required by the C_i symmetry of the dimer. This results in a set of staggered trans basal bond angles. Thus, the Cl(1)–As–Cl(3)′ angle (168.7 (1)°) is bent away from sulfur, while

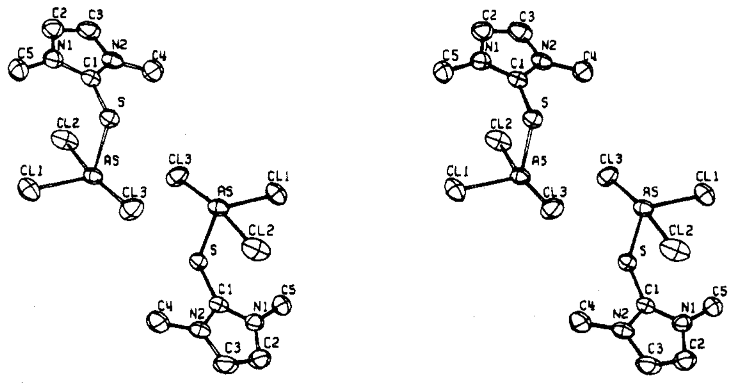

Figure 2. ORTEP stereodrawing of the $AsCl_3$dmit dimer with vibrational ellipsoids drawn at the 50% probability level.

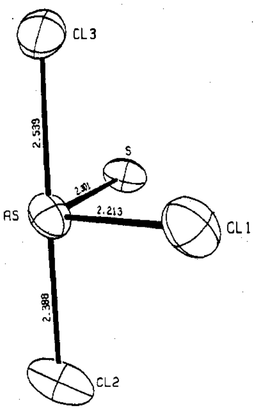

Figure 3. ORTEP drawing of $AsCl_3$dmit monomeric unit showing pseudo-TBP geometry with vibrational ellipsoids drawn at the 50% probability level.

the Cl(2)–As–Cl(3) angle (171.8 (1)°) is bent toward sulfur.

Significant deviations from 90° are seen for bond angles involving bridging chlorines. The acute angles of 84.9 (1)° (Cl(3)–As–Cl(3)′) and 77.9 (1)° (Cl(3)–As–S) are those which involve long As–Cl(3) (2.539 (2) Å) and As–Cl(3)′ (3.125 (2) Å) bonds where bonded pair–bonded pair interactions[13] should be minimized.

The distortion of the square pyramid is also evident from the progression of basal As–Cl bond distances: As–Cl(1) < As–Cl(2) < As–Cl(3) << As–Cl(3)′. The differences in bond distances are 0.175, 0.151, and 0.586 Å, respectively. All As–Cl distances are greater than that observed for $AsCl_3$ (2.161 Å),[14] although As–Cl(1) is only 0.052 Å longer. The long As–Cl(3) distance, which is trans to the shortest As–Cl bond, is more than halfway toward the van der Waals contact (~3.7 Å)[15,16] with reference to the single-bond distance found for $AsCl_3$.[14] This halogen bridging by Cl(3) to As′ disrupts the symmetry of the Cl(2)–As–Cl(3) group and is responsible for lengthening the As–Cl(3) bond. Similar weak bridges are found in $SeBr_2$tmtu[17] and TeX_2tmtu (X = Cl, Br).[18,19]

Another structural feature of interest is the As–S bond length (2.301 (2) Å) which is 0.02 Å shorter than the As–S bond distance in $[Me_2As(tu)]^+ Cl^-\cdot$tu (tu = thiourea).[16] The adjacent C–S bond (1.729 (5) Å is 0.02 Å shorter than the C–S bond length in $SeBr_2$tmtu.[17] The bond lengths and angles for the dmit ring agree very closely with those reported for the uncoordinated molecule,[20] and there is good agreement in lengths observed for chemically equivalent bonds. An unweighted least-squares-plane analysis of all eight nonhydrogen atoms showed the ring to be essentially planar with no atom more than 0.03 Å out of the plane (Table III).

The significant displacement of Cl(1) from the least-squares plane and the resulting Cl(1)–As–S bond angle of 99.1 (1)° reveals the tendency of individual molecules making up the dimeric unit to assume trigonal-bipyramidal (TBP) geometry. A projection of the TBP portion of the structure is shown in Figure 3. This portion of the structure may be compared with the TBP structure of $AsCl_3NMe_3$.[6] The structures are similar but display a notable difference in the position of the donor atom. In $AsCl_3$dmit the sulfur donor atom is in an equatorial position, whereas nitrogen in $AsCl_3NMe_3$ occupies an apical position. Thus, the argument that a donor of low electronegativity could give rise to structure II for an AsX_3LE adduct has some merit.

The equatorial Cl–As–Cl angle (98.6°) in $AsCl_3NMe_3$ compares favorably with the S–As–Cl(1) angle in $AsCl_3$dmit (99.1 (1)°). The axial angle N–As–Cl (178.7°) for $AsCl_3NMe_3$ is closer to 180° than Cl(2)–As–Cl(3) (171.8 (1)°) in $AsCl_3$dmit. This modest disparity and that associated with the long axial As–Cl(3) bond (2.539 (2) Å) reflect the involvement of Cl(3) in chlorine bridging (vide supra). The remaining axial As–Cl(2) (2.388 (2) Å) and equatorial As–Cl(1) (2.213 (2) Å) bond lengths are very close to the respective distances observed in $AsCl_3NMe_3$ (2.385, 2.192, 2.181 Å).

The pseudo-TBP description is useful in comparing the structure of $AsCl_3$dmit and $AsCl_3NMe_3$ as it serves to emphasize that the primary structural effect of changing the donor from N to S is the change in donor position from axial (N, I) to equatorial (S, II). This primary effect is in accord with the electronegativity rule regarding apicophilicity which is based on a wealth of structural information.[7,21,22] Parenthetically, we note an interesting exception in the structure of μ-oxo-bis[bis(2-methyl-8-quinolinato)aluminum(III)],[23] where the nitrogen atoms occupy axial positions and oxygen atoms occupy the equatorial positions—the reverse of that expected in the basis of apicophilicity.

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Supplementary Material Available: A listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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