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N-Chloro(methyl)arsino-*N*,*N*′-dimethyl-*N*′-(*p*-tolylthio)urea

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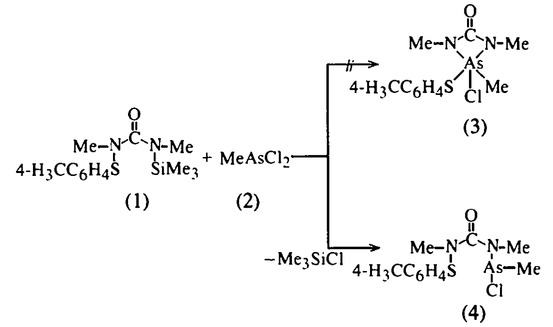
Abstract

The title compound, $C_{11}H_{16}AsClN_2OS$, crystallizes with two independent but closely similar molecules. The pyramidal geometry at arsenic is supplemented by a 1,5-intramolecular interaction with the S atom [2.8682 (13) and 2.8101 (13) Å] and by further weaker intermolecular contacts to oxygen and chlorine.

Comment

We recently reported an intramolecular rearrangement that took place during the phosphorylation of *N*-arylthio-*N*,*N*′-diorgano-*N*′-(trimethylsilyl)ureas with dichlorophosphines. The resulting compounds were shown to be the four-membered cyclic phosphoranes, 2-arylthio-2-chloro-1,2,3-triorgano-1,3,2λ^5-diazaphosphetidin-4-ones (Pinchuk *et al.*, 1994, 1995).

We wished to study the suitability of this synthesis for the preparation of the analogous arsenic derivatives. Some cyclic arsenic compounds based on *N*,*N*′-disubstituted ureas have already been reported (Roesky, Djarrah, Amirzadeh-Asl & Sheldrick, 1981; Vogt, Jones & Schmutzler, 1993). However, the reaction between *N*,*N*′-dimethyl-*N*-(*p*-tolylthio)-*N*′-(trimethylsilyl)urea, (1), and dichloro(methyl)arsine, (2), did not result in the expected derivative, (3), but instead in the acyclic title compound, (4), the structure of which is reported here.



Compound (4) crystallizes with two independent molecules (Fig. 1) which are closely similar (see Table 2); the conformations are almost identical, with all torsion-angle differences < 8°. The geometry at arsenic is pyramidal, with angles ranging from 93.81 (13) to 97.40 (15)°. A search of the Cambridge Structural Database (Allen & Kennard, 1993) revealed no other compound with C, N and Cl substituents at three-coordinate arsenic. The As—N and As—Cl bond lengths in compound (4) are similar to the standard values of 1.858 and 2.268 Å quoted by Allen *et al.* (1987).

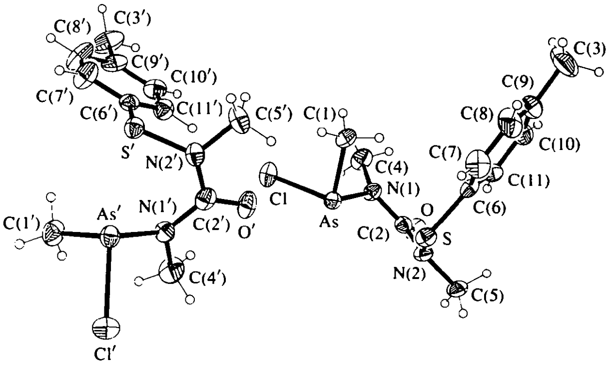


Fig. 1. The two independent molecules of the title compound in the crystal. Ellipsoids correspond to 50% probability levels and H-atom radii are arbitrary.

A feature of both molecules is the short 1,5 contact between the As and S atoms, *trans* to the chlorine substituent [As···S 2.8682 (13) and 2.8101 (13) Å]. These contacts do not lead to obvious perturbations of bond angles. Short intermolecular contacts are observed from As to O′ [3.177 (3) Å] and from As′ to Cl′ [at x, $\frac{3}{2} - y$, $\frac{1}{2} + z$; 3.5243 (16) Å].

Experimental

A solution of MeAsCl$_2$ [(2); 0.58 g, 3.7 mmol] in 3 ml dichloromethane was added dropwise with stirring at 273 K over 15 min to a solution of (1) (1.04 g, 3.7 mmol) in 3 ml dichloromethane. The reaction mixture was stirred for 24 h at room temperature. The solvent was removed under vacuum and 3 ml petroleum ether (303–313 K) was added to the residue. The product was obtained as yellow crystals on cooling this solution to 253 K. M.p. 311–313 K, yield 1.0 g (81%); ^{1}H NMR (CDCl$_3$): δ 1.72 (*s*, CH$_3$As), 2.32 (*s*, 4-CH$_3$C$_6$H$_4$), 3.02, 3.13 (*s*, NCH$_3$), 6.99–7.25 (*m*, C$_6$H$_4$); ^{13}C NMR (CDCl$_3$): δ 20.09, 21.11 (*s*, CH$_3$As, 4-CH$_3$C$_6$H$_4$), 31.82, 40.63 (*s*, NCH$_3$), 124.12–138.68 (*m*, C$_6$H$_4$), 164.80 (*s*, C=O); analysis calculated C 39.47, H 4.82, N 8.37%; found C 39.56, H 4.98, N 8.35%.

Crystal data

$C_{11}H_{16}AsClN_2OS$
$M_r = 334.69$
Monoclinic
$P2_1/c$
$a = 17.784\ (5)$ Å
$b = 18.326\ (4)$ Å
$c = 9.055\ (3)$ Å
$\beta = 104.74\ (3)°$
$V = 2854.0\ (14)$ Å^3
$Z = 8$
$D_x = 1.558$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 58 reflections
$\theta = 10.0$–$11.5°$
$\mu = 2.702$ mm^{-1}
$T = 143\ (2)$ K
Prism
0.80 × 0.60 × 0.30 mm
Pale yellow

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: ΔF (*SHELXA*; Sheldrick, 1993*a*)
$T_{\min} = 0.32$, $T_{\max} = 0.68$
8486 measured reflections
4980 independent reflections
4097 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0301$
$\theta_{\max} = 25.03°$
$h = -21 \rightarrow 21$
$k = -21 \rightarrow 21$
$l = -9 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0344$
$wR(F^2) = 0.0802$
$S = 1.046$
4980 reflections
315 parameters
H atoms: rigid methyl H atoms, others riding
$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 1.862P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ 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)*

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

	x	y	z	$U_{\rm eq}$
As	0.20290 (2)	0.56754 (2)	0.51449 (4)	0.02599 (10)
Cl	0.24607 (6)	0.48509 (6)	0.70076 (11)	0.0420 (2)
S	0.13508 (5)	0.64979 (5)	0.24390 (11)	0.0290 (2)
O	0.08701 (16)	0.45127 (14)	0.1620 (3)	0.0390 (7)
N(1)	0.12457 (17)	0.50792 (16)	0.3932 (3)	0.0270 (7)
N(2)	0.13133 (17)	0.56673 (16)	0.1655 (3)	0.0266 (7)
C(1)	0.1376 (2)	0.6186 (2)	0.6251 (4)	0.0336 (9)
C(2)	0.1135 (2)	0.50420 (19)	0.2387 (4)	0.0262 (8)
C(3)	−0.1918 (3)	0.7327 (3)	0.2675 (7)	0.0720 (16)
C(4)	0.0897 (2)	0.4480 (2)	0.4593 (5)	0.0420 (10)
C(5)	0.1191 (2)	0.5632 (2)	−0.0017 (4)	0.0360 (9)
C(6)	0.0368 (2)	0.67290 (18)	0.2369 (4)	0.0261 (8)
C(7)	0.0255 (3)	0.7385 (2)	0.3039 (5)	0.0427 (10)
C(8)	−0.0483 (3)	0.7581 (2)	0.3102 (5)	0.0512 (12)
C(9)	−0.1112 (3)	0.7131 (2)	0.2543 (5)	0.0435 (10)
C(10)	−0.0985 (2)	0.6490 (2)	0.1833 (5)	0.0377 (9)
C(11)	−0.0252 (2)	0.6279 (2)	0.1750 (4)	0.0301 (8)
As′	0.53444 (2)	0.70236 (2)	1.04622 (4)	0.02756 (11)
Cl′	0.61886 (6)	0.71283 (6)	0.89874 (12)	0.0460 (3)
S′	0.40863 (5)	0.69041 (5)	1.17988 (10)	0.0294 (2)
O′	0.33499 (16)	0.64935 (14)	0.7615 (3)	0.0379 (6)
N(1′)	0.46003 (17)	0.64522 (16)	0.9099 (3)	0.0291 (7)
N(2′)	0.36211 (17)	0.70384 (16)	0.9952 (3)	0.0305 (7)
C(1′)	0.5908 (2)	0.6225 (2)	1.1656 (5)	0.0404 (10)
C(2′)	0.3834 (2)	0.66459 (19)	0.8787 (4)	0.0306 (8)
C(3′)	0.3125 (3)	0.3950 (2)	1.3719 (6)	0.0586 (14)
C(4′)	0.4810 (3)	0.5927 (2)	0.8051 (5)	0.0476 (11)
C(5′)	0.2840 (2)	0.7346 (2)	0.9628 (5)	0.0412 (10)
C(6′)	0.3783 (2)	0.60259 (19)	1.2238 (4)	0.0271 (8)
C(7′)	0.4032 (3)	0.5821 (2)	1.3745 (5)	0.0481 (11)
C(8′)	0.3825 (3)	0.5151 (2)	1.4208 (5)	0.0536 (13)
C(9′)	0.3371 (3)	0.4673 (2)	1.3195 (5)	0.0382 (10)
C(10′)	0.3134 (2)	0.4882 (2)	1.1679 (5)	0.0351 (9)
C(11′)	0.3339 (2)	0.5554 (2)	1.1192 (4)	0.0332 (9)

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

As—N(1)	1.888 (3)	As′—N(1′)	1.881 (3)
As—C(1)	1.954 (3)	As′—C(1′)	1.941 (4)
As—Cl	2.2490 (11)	As′—Cl′	2.2572 (12)
As···S	2.8682 (13)	As′···S′	2.8101 (13)
As···O′	3.177 (3)	As′···Cl′^{i}	3.5243 (16)
S—N(2)	1.674 (3)	S′—N(2′)	1.684 (3)
S—C(6)	1.784 (4)	S′—C(6′)	1.774 (4)
O—C(2)	1.216 (4)	O′—C(2′)	1.217 (4)
N(1)—C(2)	1.364 (4)	N(1′)—C(2′)	1.366 (5)
N(1)—C(4)	1.463 (4)	N(1′)—C(4′)	1.465 (5)
N(2)—C(2)	1.400 (4)	N(2′)—C(2′)	1.406 (5)
N(2)—C(5)	1.475 (4)	N(2′)—C(5′)	1.458 (5)
N(1)—As—C(1)	97.40 (15)	N(1′)—As′—C(1′)	97.06 (17)
N(1)—As—Cl	96.21 (10)	N(1′)—As′—Cl′	97.00 (9)
C(1)—As—Cl	94.10 (12)	C(1′)—As′—Cl′	93.81 (13)
N(1)—As···S	73.70 (9)	N(1′)—As′···S′	74.63 (9)
C(1)—As···S	90.60 (12)	C(1′)—As′···S′	93.24 (12)
Cl—As···S	169.36 (4)	Cl′—As′···S′	169.67 (4)
N(1)—As···O′	170.71 (10)	N(1′)—As′···Cl′^{i}	154.97 (9)
C(1)—As···O′	80.94 (13)	C(1′)—As′···Cl′^{i}	77.74 (13)
Cl—As···O′	74.87 (6)	Cl′—As′···Cl′^{i}	107.71 (4)
S···As···O′	115.36 (6)	S′···As′···Cl′^{i}	81.18 (4)
N(2)—S—C(6)	105.55 (16)	N(2′)—S′—C(6′)	104.76 (17)
N(2)—S—As	81.21 (11)	N(2′)—S′—As′	78.75 (11)
C(6)—S—As	110.50 (11)	C(6′)—S′—As′	119.19 (11)
C(2)—N(1)—C(4)	114.7 (3)	C(2′)—N(1′)—C(4′)	116.2 (3)
C(2)—N(1)—As	121.2 (2)	C(2′)—N(1′)—As′	119.3 (2)
C(4)—N(1)—As	121.6 (2)	C(4′)—N(1′)—As′	122.5 (3)
C(2)—N(2)—C(5)	117.2 (3)	C(2′)—N(2′)—C(5′)	118.1 (3)
C(2)—N(2)—S	122.2 (2)	C(2′)—N(2′)—S′	120.8 (2)
C(5)—N(2)—S	117.1 (3)	C(5′)—N(2′)—S′	117.3 (3)

O—C(2)—N(1)	124.0 (3)	O′—C(2′)—N(1′)	124.6 (3)
O—C(2)—N(2)	119.0 (3)	O′—C(2′)—N(2′)	120.4 (3)
N(1)—C(2)—N(2)	117.0 (3)	N(1′)—C(2′)—N(2′)	115.0 (3)
		C(2′)—O′···As	162.7 (2)

Symmetry code: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

H atoms were refined using a riding model or rigid methyl groups. Slow convergence of the methyl group at C(3′) may indicate rotational disorder. Owing to crystal loss, the preferred method of absorption correction (ψ scans) was not available and we were forced to use a ΔF method. This may lead to systematic errors in U values. The additional 18 parameters were taken into account in calculating e.s.d.'s. The matrix 001/201/010 generates a metrically orthorhombic C-centred cell with a = 9.055, b = 34.397 and c = 18.329 Å. However, a high $R_{\rm int}$ value of 0.42 is obtained when the transformed intensities are merged in *mmm*, indicating that the true symmetry is no higher than monoclinic.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993*b*). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1265). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A μ-Oxamidato-Bridged Dinuclear Copper(II) Complex

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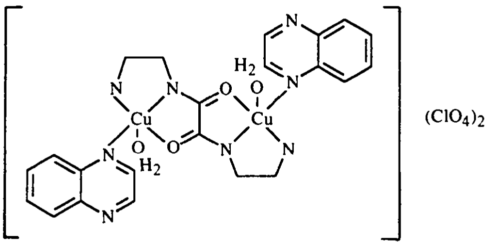
Abstract

The oxen ligand [oxen = N,N'-bis(2-aminoethyl)oxamide] in the title compound, μ-[N,N'-bis(2-aminoethyl)oxamido(2−)-N,N',O:N'',N''',O']-bis[aqua(quinoxaline-N^1)copper(II)] diperchlorate, $[Cu_2(C_6H_{12}N_4O_2)(C_8H_6N_2)_2(H_2O)_2](ClO_4)_2$, is bis-tridentate in a *trans* conformation bridging two copper(II) ions to form a centrosymmetric binuclear molecule. The symmetry-equivalent central copper(II) ions are located in a distorted square-based pyramid, with a water molecule bonded at the axial site.

Comment

As extending bridging ligands transmitting a strong magnetic exchange interaction, oxamidates have played a key role in the design of polymetallic systems (Ojima & Nonoyama, 1988). One of the most important factors for the versatility of these ligands is their easy *cis*–*trans* conformational change affording symmetric or asymmetric oxamidato bridges. In contrast with symmetric oxamidato-bridged copper(II) complexes in the *cis* conformation (Journaux, Sletten & Kahn, 1985), few copper(II) complexes bridged by oxamidato groups displaying the *trans* conformation have been synthesized and characterized structurally by X-ray diffraction (Lloret, Julve, Real, Faus, Ruiz, Mollar, Castro & Bois, 1992). We report here the crystal structure of a dinuclear copper(II) complex with a bridging N,N'-bis(2-aminoethyl)oxamide (oxen) ligand in the *trans* conformation, (I).



(I)