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Crystal and Molecular Structure of 1,3,5,7-tetraarsa-2,4,6,8-tetraoxaadamantane

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The colourless crystals of the title compound are monoclinic, a = *679.0(10),* b = *1003.0(9),* c = *1191.4(8) pm, β = 105.14(8)°, space group $P2_1/c$. A three dimensional X-ray analysis of the structure was made with counter data (1903 unique reflections with $|F_o| > 3\sigma$). The structure was determined by direct methods and refined anisotropically by full matrix least squares methods to a conventional unweighted R of 0.059. The structure consists of discrete molecules $As_4O_4(CH_2)_2$ which can be described as penetrating distorted As_4-tetrahedra and* trans-*O_4C_2-octahedra. The mean bond lengths and angles are: AsO = 179.5, AsC = 196.2 pm, OAsO = 101.8, CAsO = 99.3, AsOAs = 129.0, AsCAs = 119.4°.*

Introduction

During our work on cyclic chelating ligands [1] we investigated the complexing behaviour of organo-oxoarsines $[RAsO]_n$ [2]. An interesting example of this class is $[CH_2(AsO)_2]_n$, of which an insoluble

TABLE I. Final Positional and Thermal Parameters for *1*.

Atom	X/a(σ)	Y/b(σ)	Z/c(σ)
As1	0.7032(2)	0.1040(1)	−0.0532(1)
As2	0.7965(2)	0.1053(1)	0.2301(1)
As3	0.6007(2)	0.3723(1)	0.0947(1)
As4	1.0609(2)	0.3006(1)	0.0888(1)
O12	0.7262(13)	0.0305(8)	0.0878(9)
O23	0.6381(11)	0.2501(9)	0.2100(7)
O34	0.8551(13)	0.4135(9)	0.0936(8)
O14	0.9415(12)	0.1949(10)	−0.0267(7)
C13	0.5240(15)	0.2552(11)	−0.0389(9)
C24	1.0546(19)	0.1875(15)	0.2234(11)
H131	0.4022(15)	0.1834(11)	−0.0484(9)
H132	0.4629(15)	0.3480(11)	−0.0793(9)
H241	1.1207(19)	0.2588(15)	0.2907(11)
H242	1.1578(19)	0.1046(15)	0.2280(11)

Atom	U_{11}(σ)	U_{22}(σ)	U_{33}(σ)	U_{12}(σ)	U_{13}(σ)	U_{23}(σ)
As1	0.0260(5)	0.0306(6)	0.0362(6)	−0.0014(4)	0.0108(4)	−0.0103(5)
As2	0.0287(6)	0.0427(7)	0.0343(6)	0.0095(5)	0.0095(5)	0.0139(5)
As3	0.0196(5)	0.0249(5)	0.0313(5)	0.0046(4)	0.0067(4)	−0.0017(4)
As4	0.0156(5)	0.0474(7)	0.0417(7)	−0.0067(5)	0.0102(4)	−0.0076(6)
O12	0.0301(40)	0.0253(39)	0.0582(57)	0.0015(33)	0.0124(38)	−0.0005(38)
O23	0.0229(35)	0.0437(46)	0.0287(38)	0.0075(33)	0.0118(29)	0.0048(35)
O34	0.0295(39)	0.0323(42)	0.0452(49)	−0.0097(33)	0.0113(35)	−0.0129(37)
O14	0.0247(37)	0.0522(54)	0.0334(43)	−0.0049(36)	0.0148(32)	−0.0126(39)
C13	0.0196(43)	0.0296(50)	0.0260(46)	0.0030(37)	0.0048(36)	0.0044(40)
C24	0.0264(53)	0.0560(81)	0.0315(59)	0.0121(54)	−0.0040(44)	−0.0037(56)

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TABLE II. Bond Lengths (pm) and Angles (°) in *1*, Standard Deviations.

As1–O12	180.3(10)	As1–C13–As3	119.7(5)
As2–O12	180.0(10)	As2–C24–As4	119.0(6)
As2–O23	178.6(8)		119.4 ± 0.4
As3–O23	180.8(8)		
As3–O34	178.0(8)	O12–As1–O14	100.8(4)
As4–O34	181.1(9)	O12–As2–O23	102.1(4)
As1–O14	181.2(8)	O23–As3–O34	102.6(4)
As4–O14	175.8(8)	O14–As4–O34	101.5(4)
	179.5 ± 0.7		101.8 ± 0.4
As1–C13	197.9(11)	C13–As1–O12	98.0(4)
As3–C13	193.7(11)	C13–As1–O14	98.1(4)
As2–C24	195.7(14)	C13–As3–O23	99.6(4)
As4–C24	197.3(15)	C13–As3–O34	100.8(4)
	196.2 ± 0.9	C24–As2–O12	99.1(5)
		C24–As2–O23	99.5(5)
As1–O12–As2	130.1(5)	C24–As4–O14	100.7(5)
As2–O23–As3	127.8(4)	C24–As4–O34	98.8(5)
As3–O34–As4	127.8(5)		99.3 ± 0.4
As1–O14–As4	130.4(4)		
	129.0 ± 0.7		

polymeric and a soluble dimeric form (*1*) have been described [3–5]. For *1* an adamantane-analogue structure has been proposed [5], but has not been characterized unambiguously. Since we obtained well structured crystals on slow evaporation of a benzene solution of *1*, we carried out an X-ray structure determination.

Experimental

Preparation

The starting compound methylene-bis(dichloroarsine) was prepared according to the literature [3], but isolated by extraction with CCl_4 instead of vacuum distillation. Hydrolysis with 2 *N* NaOH and addition of the alkaline solution to a solution of excess NH_4Cl yielded a precipitate of methylene-bis-(oxoarsine). *1* (m.p. 538 K) was obtained by extraction with benzene.

X-ray Study

Intensity data were collected on a Syntex P 2_1 four-circle diffractometer, using Mo-K_α (λ = 71.069 pm) radiation. From a rotation photograph 16 reflections of varying intensities were selected for automatic lattice determination, which showed the crystal to be monoclinic P. Systematic absences h0l with l = 2n + 1 and 0k0 with k = 2n + 1 showed the space group to be $P2_1/c$. The lattice parameters are a = 679.0(10), b = 1003.0(9), c = 1191.4(8) pm, β = 105.14(9)°; Z = 4, V = 783.22 × 10^6 pm^3; crystal dimensions: 0.25 × 0.25 × 0.50 mm^3. During data collection two check reflections were measured after every 98 reflections. A total of 2301 independent reflections with $1 < 2\theta < 60°$ was collected. An empirical absorption correction based on 7 strong reflections was then applied and all data corrected for polarization and Lorentz factors. The solution was carried out with 1903 reflections having $|F_o| > 3\sigma$.

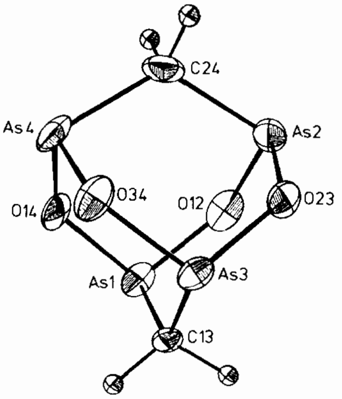


Fig. 1. ORTEP-plot [8] of *1* and numbering scheme of atoms.

Solution and Refinement

The positions of the arsenic atoms were found by direct methods (MULTAN 74, [6]). Oxygen and carbon atoms could then be located on difference Fourier maps and all heavy atoms were refined anisotropically by full matrix least squares methods using the SHEL 76 program system [7]. Unit weights were used throughout. While peaks corresponding to hydrogen appeared near the carbon atoms in the difference Fourier maps, their refinement proved unsatisfactory and their positions were calculated instead, but not included in the refinement except for a common isotropic temperature factor. This led to a final R = 0.059. Tables of $|F_o|$ and $|F_c|$ values are available on request.

The final positional and thermal parameters can be found in Table I.

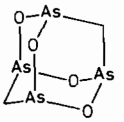
Results and Discussion

The solid state structure of *1* consists of discrete molecules $As_4O_4(CH_2)_2$ (1,3,5,7-tetraarsa-2,4,6,8-tetraoxaadamantane). Fig. 1 shows the molecular structure, the interatomic distances and angles are given in Table II.

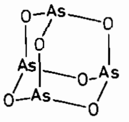
In contrast to cubic arsenic(III) oxid (arsenolite) [9, 10], which crystallizes in Fd3m with the As_4O_6-units (*2*) occupying a diamond-like lattice, $As_4O_4(CH_2)_2$, the molecular structure of which is related to *2*, crystallizes in monoclinic $P2_1/c$ with no recognizable super-structure.

TABLE III. Distances (pm) and Angles (°) in the As_4- and O_4C_2-Units of *1*.

As1••As2	326.7	As2••As1••As3	58.0
As2••As3	322.8	As3••As1••As4	58.2
As3••As4	322.5	As1••As2••As4	58.3
As1••As4	324.1	As3••As2••As4	58.3
	324.0 ± 1.0	As1••As3••As2	59.1
		As1••As3••As4	58.6
As1••As3	338.7	As1••As4••As2	59.0
As2••As4	338.6	As2••As4••As3	58.4
	338.7 ± 0.1		58.5 ± 0.1
O12••O23	279.0	O23••O12••O14	90.0
O23••O34	280.1	O12••O23••O34	89.5
O34••O14	276.5	O23••O34••O14	90.2
O12••O14	278.5	O12••O14••O34	90.4
	278.5 ± 0.8		90.0 ± 0.2
C13••O12	285.6	C13••O12••C24	93.5
C13••O23	286.3	C13••O23••C24	93.3
C13••O34	286.6	C13••O34••C24	92.9
C13••O14	286.5	C13••O14••C24	92.9
C24••O12	286.1		93.2 ± 0.2
C24••O23	286.0		
C24••O34	287.6	O12••C13••O34	86.9
C24••O14	287.7	O23••C13••O14	87.0
	286.6 ± 0.3	O12••C24••O34	86.7
		O23••C24••O14	86.8
As2••As1••As4	62.7		86.9 ± 0.1
As1••As2••As3	62.9		
As2••As3••As4	63.3		
As1••As4••As3	63.2		
	63.0 ± 0.1		



1



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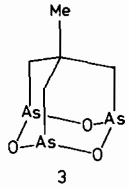

3

1 can be derived from As_4O_6 (*2*), in which the four arsenic atoms are at the corners of a tetrahedron while the six oxygen atoms form an octahedron, by substitution of two *trans*-oxygen atoms by CH_2-groups. However, since the As–C and As–O distances are different, the *trans*-O_4C_2-unit loses the octahedral symmetry being elongated along the CC-axis, and the As_4-unit is distorted from an ideal tetrahedron (Table III). Overall, the T_d symmetry of *2* is lowered to D_{2d} in *1*.

TABLE IV. Comparison of Distances (pm) and Angles (°) in the Adamantane Derivatives *1*, *2* and *3*.

		1	*2* [9]	*3* [11]
Distance	As–O	179.5	180	177
	As–C	196.2	–	196
	As••As'	324.0/338.7	321	316.5
	O••O	278.5	276	273
Angle	O–As–O	101.8	100	100.5
	C–As–O	99.3	–	97.7
	As–O–As	129.0	126	126.7

The structure of *1* also shows certain similarities with that of 5-methyl-1,3,7-triarsa-2,8,10-trioxaadamantane (*3*) [11], in which four mutually bonded carbon atoms remain of the adamantane structure. With reference to As_4O_6, the basic units of *3* are an As_3C- and a *fac*-O_3C_3-unit. Since the atomic radius of carbon is smaller than that of arsenic, the highly symmetric structure of *2* is even more distorted in *3* than in *1* and generally leads to shorter bond lengths (*cf.* Table IV).

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