Structures Involving Unshared Electron Pair.
The Crystal Structures of As(OCOCH₃)₃ and As₂O(OCOCH₃)₄

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Abstract. $As_2O(OCOCH_3)_4$, reported now for the first time, was obtained, besides $As(OCOCH_3)_3$ by dissolving As_2O_3 in acetic anhydride. The crystals of $As(OCOCH_3)_3$ (A) (monoclinic, space group Cc, Z = 4, a = 9.970(2), b = 13.203(2), c = 8.272(1) Å, β = 117.01(2)°) and of $As_2O(OCOCH_3)_4$ (B) (monoclinic, space group $P2_1/n$, Z = 4, a = 13.966(5), b = 8.127(4), c = 12.706(4) Å, β = 95.14(1)°) are built up from discrete molecules defined by chemical formulae $As(OCOCH_3)_3$ and $(CH_3OCO)_2As—O—As(OCOCH_3)_2$, respectively. The molecular structure of both compounds is based on the AsO_3 pyramid: in (A) with the As—O bonds of 1.841(6) Å and the O—As—O angle of 89.9(3)° as a mean, in (B) with slightly different values and with the As—O—As angle of 127.7(4)° at the bridging oxygen atom. The additional weak chelating contacts are at the distances As···O from 2.625(9) to 2.745(10) Å in (A) and from 2.72(1) to 2.84(2) in (B). The actual arsenic coordination can be described as very distorted octahedral in (A) and square-pyramidal in (B).

Keywords: Arsenic(III) acetates; crystal structures

Über Strukturen mit freiem Elektronenpaar. Kristallstruktur von As(OCOCH₃)₃ und As₂O(OCOCH₃)₄

Inhaltsübersicht. Das bisher unbekannte $As_2O(OCOCH_3)_4$ wurde neben $As(OCOCH_3)_3$ aus einer Lösung von As_2O_3 in Essigsäureanhydrid erhalten. Beide Verbindungen kristallisieren monoklin mit 4 Formeleinheiten in der Elementarzelle: $As(OCOCH_3)_3$ (A), Raumgruppe Cc mit a = 9,970(2), b = 13,203(2), c = 8,272(1) Å; β = 117,01(2)° und $As_2O(OCOCH_3)_4$ (B), Raumgruppe $P2_1/n$ mit a = 13,966(5), b = 8,127(4), c = 12,706(4) Å, β = 95,14(1)°. Die beiden Kristallstrukturen wurden von Einkristallen des $As(OCOCH_3)_3$ bzw. $(CH_3OCO)_2As—O—As(OCOCH_3)_2$ erhalten und entsprechen strukturell der AsO_3-Pyramide: in (A) mit der Kante As—O von 1,841(6) Å und dem Winkel O—As—O von 89,9(3)°, in (B) sind die Werte von diesen wenig verschieden, Winkel As—O—As von 127,7(4)° am gemeinsamen Sauerstoffatom. Infolge der schwachen Chelat-Kontakte As···O von 2,625(9) bis 2,84(2) Å kann die gesamte Arsen-Koordination als sehr verzerrte Polyeder betrachtet werden, das Oktaeder in (A), die quadratische Pyramide in (B).

Introduction

It is well known that the lone electron pair at the arsenic atom in As^{III} compounds is stereochemically "active" concerning not only the covalent bonds but also the intermolecular contacts [1] as evident from the structure of the halides [2], of different forms of the oxide [3] and or organoarsenic compounds [4]. In this respect the structure of As^{III} carboxylates is interesting and we decided to study the structure of the acetate. Using the known method of preparation [5] we obtained the acetate $As(OCOCH_3)_3$ (A) and the hitherto unknown basic acetate $As_2O(OCOCH_3)_4$ (B). Determination of the crystal structures of both compounds showed that the structures are based on almost identical AsO_3 pyramids, which in (B) form pairs with a common corner but with a geometrically different surrounding. Both compounds are extremely hygroscopic.

Experimental

A. Chemical preparation

From the solution of As_2O_3 in acetic anhydride [5] two kinds of crystals were separated: those of $As(OCOCH_3)_3$ and, in small proportion, those of a compound the formula

Table 1 Experimental crystallographic data

Formula	As(OCOCH₃)₃	As₂O(OCOCH₃)₄
Formula	$As(OCOCH_3)_3$	$As_2O(OCOCH_3)_4$
Formula weight	252.6	504.11
Crystal system	monoclinic	monoclinic
Space group	Cc	P2₁/n
Cell parameters		
a (Å)	9.970(2)	13.966(5)
b (Å)	13.203	8.127(4)
c (Å)	8.272(1)	12.706(4)
$\beta(°)$	117.01(2)	95.14(1)
Cell volume, V (Å³)	970.1	1436.4
No. formula units, Z	4	4
D_{calc} (g cm⁻³)	1.726	2.331
F(000)	504	1008
Crystal dimensions (mm)	0.30×0.22×0.76	0.90×0.32×0.17
μ(MoKα) (cm⁻¹)	34.9	47.1
Radiation	MoKα	MoKα
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
θ range (°)	2–30	2–30
Reflection measured	1030	2189
Reflection refined, I > 4σ(I)	853	1626
Refined parameters	153	172
Reliability index, R	0.031	0.051

(CH₃OCO)₂As—O—As(OCOCH₃)₂ of which was subsequently established as the final result of the X-ray diffraction analysis. We were not successful in collecting crystals of (B) by visual selection from the crystals of (A) in the quantity adequate for a chemical analysis or to carry out the preparation in order to obtain (B) only. All operations were carried out in a dry-box under dry nitrogen. The crystal specimens for X-ray data measurements were sealed in Lindemann glass capillaries.

B. Crystal data, Intensity data collection and crystal structure determination

Table 1 gives the crystallographic data and information concerning the data collection and the refinement procedure.

Table 2 Positional (×10⁴) and thermal (Å²×10⁴) Parameters for As(OCOCH₃)₃

Atom	x	y	z	U_{eq}[a])
As	2500(0)	2499(1)	0(0)	470(2)
O(1)	4100(6)	3183(4)	106(8)	488(23)
O(2)	2518(8)	4452(5)	−726(11)	734(32)
O(3)	3650(7)	1372(4)	1001(7)	487(23)
O(4)	3051(10)	1110(5)	−1890(9)	763(35)
O(5)	2980(6)	2967(4)	2364(8)	504(25)
O(6)	1096(9)	1942(5)	2051(10)	740(33)
C(1)	3737(11)	4142(6)	−446(11)	481(41)
C(2)	4941(12)	4706(7)	−654(16)	551(44)
C(3)	3693(10)	802(6)	−327(13)	489(45)
C(4)	4494(13)	−183(7)	304(15)	566(42)
C(5)	2057(8)	2564(7)	2963(10)	483(28)
C(6)	2251(10)	2962(6)	4744(13)	548(46)

ª) $U_{eq} = 1/3(U_{11} \cdot a^{*2} \cdot a^2 + \ldots + U_{23}b^*c^*bc \cos \alpha)$

Table 3 Positional (×10⁴, for C atoms ×10³) and Thermal (Å²×10⁴) Parameters for As₂O(OCOCH₃)₄

Atom	x	y	z	U_{eq}[a])
As(1)	1567(1)	1219(1)	325(1)	395(3)
As(2)	2458(1)	3644(1)	2124(1)	358(3)
O(9)	2161(5)	1650(8)	1561(5)	396(20)
O(1)	2097(5)	3071(9)	3413(5)	426(25)
O(2)	649(6)	3822(14)	2741(8)	765(37)
O(3)	583(5)	2706(9)	325(6)	475(28)
O(4)	−139(6)	811(10)	1219(7)	572(32)
O(5)	3646(5)	2998(9)	2685(5)	447(24)
O(6)	4117(7)	3602(17)	1119(7)	903(46)
O(7)	2144(6)	2809(10)	−419(6)	512(29)
O(8)	3028(10)	810(18)	−1072(12)	287(64)
C(1)	115(1)	335(2)	349(1)	520(43)
C(2)	83(1)	292(2)	455(1)	778(62)
C(3)	−16(1)	213(1)	76(1)	476(41)
C(4)	−101(1)	321(2)	63(1)	721(56)
C(5)	432(1)	311(2)	199(1)	498(42)
C(6)	530(1)	250(2)	243(1)	528(42)
C(7)	283(1)	231(2)	−100(1)	682(58)
C(8)	330(1)	366(2)	−155(1)	883(63)

ª) $U_{eq} = 1/3(U_{11} \cdot a^{*2} \cdot a^2 + \ldots + U_{23}b^*c^*bc \cos \alpha)$

The data were collected on a Philips PW 1100 diffractometer with a graphite monochromator. The unit-cell parameters were determined and refined by a least-squares procedure on the positions of 20 reflections in a range 8 < θ < 14° and 8 < θ < 16° for (A) and (B), respectively. Crystal stabilities were monitored by recording three check reflections every two hours. The data were corrected for Lorentz and polarization factors and those of (B) due to better defined crystal faces, also for absorption [6]. Solutions of the structures were achieved through Patterson and Fourier syntheses. The structures were refined by a full-matrix least-squares procedure assuming

anisotropic thermal parameters for non-hydrogen atoms and unit weights for all observations. Hydrogen atom positions were generated on geometrical grounds (C—H 1.08 Å) and their coordinates introduced in the structure factor calculations. The atomic scattering factors and anomalous dispersion corrections were taken from the literature [7, 8]. All calculations were performed on the IBM PC/AT compatible microcomputer using the SHELX programme system [9]. The drawings were made by using the PLUTO programme [10]. Final atomic coordinates are listed in Tables 2 and 3. Further details of the structure investigations are available on request, from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information, W-7514 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD-57115, the authors, and full citation of the journal.

Description of the structure

The structures of (A) and (B) are shown in Figs. 1 and 2, respectively. Selected interatomic distances and angles are listed in Tables 4 and 5.

Both crystals are composed of discrete molecules. Their molecular structure is based on the AsO_3 pyramid as a consequence of the presence of the lone pair of electrons at the arsenic atom [1, 3]. There are three sets of arsenic-oxygen interatomic distances: (i) the covalent As—O bond length with the mean value of 1.841(6) Å in (A) and 1.825(8) Å in (B), (ii) the additional As · · · O contacts with the mean value of 2.673(8) Å in (A) and 2.76(1) Å in (B), and (iii) the bridging As—O covalent bonds in (B) with lengths of 1.745(6) and 1.805(7) Å.

The O—As—O angles at the apex of the AsO_3 pyramid differ only slightly from 90° in (A), while these angles in (B) vary from 84.2 to 99.4° with the largest values for angles formed by the bridging As(1)—O(9) and As(2)—O(9) pyramid edges, caused by the influence of the As · · · As approach of 3.186(2) Å as evident also from the higher value of the bridging
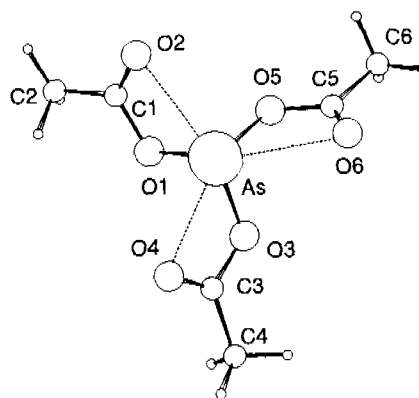

Fig. 1 PLUTO drawing of As(OCOCH₃)₃ showing the atom numbering scheme

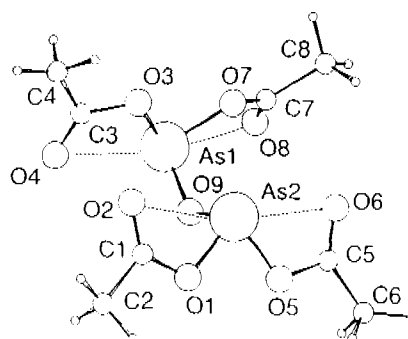**Fig. 2** PLUTO drawing of As₂O(OCOCH₃)₄ showing the atom numbering scheme

Table 4 Selected interatomic distances (Å) and angles (°) for As(OCOCH₃)₃ with e.s.d.s in parentheses

As—O(1)	1.800(6)	As · · · O(2)	2.650(7)
As—O(3)	1.831(6)	As · · · O(4)	2.625(9)
As—O(5)	1.893(7)	As · · · O(6)	2.745(10)
O(1)—C(1)	1.34(1)	O(1) · · · O(2)	2.187(9)
O(2)—C(1)	1.20(1)	O(1) · · · O(3)	2.602(8)
O(3)—C(3)	1.35(1)	O(1) · · · O(4)	3.121(9)
O(4)—C(3)	1.22(1)	O(1) · · · O(5)	2.591(11)
O(5)—C(5)	1.34(1)	O(3) · · · O(4)	2.213(10)
O(6)—C(5)	1.23(1)	O(3) · · · O(5)	2.615(9)
C(1)—C(2)	1.49(2)	O(5) · · · O(6)	2.233(10)
C(3)—C(4)	1.49(1)	O(2) · · · O(4)	4.59(1)
C(5)—C(6)	1.49(1)	O(2) · · · O(6)	4.61(1)
		O(4) · · · O(6)	4.62(2)
O(3)—As—O(5)	89.2(2)	O(3)—C(3)—O(4)	118.7(8)
O(1)—As—O(5)	89.0(3)	O(4)—C(3)—C(4)	126.9(9)
O(1)—As—O(3)	91.5(3)	O(3)—C(3)—C(4)	114.3(8)
O(1)—C(1)—O(2)	118.8(8)	O(5)—C(5)—O(6)	121.0(8)
O(2)—C(1)—C(2)	127.3(8)	O(6)—C(5)—C(6)	123.9(9)
O(1)—C(1)—C(2)	113.9(8)	O(5)—C(5)—C(6)	115.0(8)

Table 5   Selected interatomic distances (Å) and angles (°) for $As_2O(OCOCH_3)_4$ with e.s.d.s in parentheses

As(1)—O(9)	1.745(6)	As(1)···As(2)	3.186(2)
As(1)—O(3)	1.830(7)	As(1)···O(4)	2.75(1)
As(1)—O(7)	1.830(8)	As(1)···O(8)	2.84(2)
As(2)—O(9)	1.805(7)	As(2)···O(2)	2.72(1)
As(2)—O(1)	1.817(8)	As(2)···O(6)	2.74(1)
As(2)—O(5)	1.823(8)	O(9)···O(1)	2.63(1)
O(1)—C(1)	1.35(2)	O(9)···O(3)	2.73(1)
O(2)—C(1)	1.19(2)	O(9)···O(5)	2.65(1)
O(3)—C(3)	1.30(2)	O(9)···O(7)	2.68(1)
O(4)—C(3)	1.22(1)	O(1)···O(2)	2.21(1)
O(5)—C(5)	1.36(2)	O(1)···O(5)	2.43(1)
O(7)—C(7)	1.32(2)	O(3)···O(4)	2.21(1)
O(8)—C(7)	1.25(2)	O(5)···O(6)	2.21(1)
C(1)—C(2)	1.45(2)	O(7)···O(8)	2.24(2)
C(3)—C(4)	1.48(2)		
C(5)—C(6)	1.51(2)		
C(7)—C(8)	1.49(2)		

O(3)—As(1)—O(7)	84.2(4)	O(3)—C(3)—O(4)	123(1)
O(9)—As(1)—O(7)	97.3(4)	O(4)—C(3)—C(4)	124(1)
O(9)—As(1)—O(3)	99.4(3)	O(3)—C(3)—C(4)	114(1)
O(1)—As(2)—O(5)	83.7(3)	O(5)—C(5)—O(6)	121(1)
O(9)—As(2)—O(5)	93.7(3)	O(6)—C(5)—C(6)	126(1)
O(9)—As(2)—O(1)	93.1(3)	O(5)—C(5)—C(6)	113(1)
As(1)—O(9)—As(2)	127.7(4)	O(7)—C(7)—O(8)	121(1)
O(1)—C(1)—O(2)	121(1)	O(8)—C(7)—C(8)	125(1)
O(2)—C(1)—C(2)	126(1)	O(7)—C(7)—C(8)	114(1)
O(1)—C(1)—C(2)	113(1)		

As(1)—O—As(2) angle of 127.7(4) Å. The values of O—As—O angles are consistent with the values found in analogous structures and are explained by the lone pair-bond-pair repulsion [1, 3, 11, 12, 13].

The surroundings of the arsenic atoms are different and can be best described as strongly distorted octahedral in (A) and square-pyramidal in (B). Due to the steric hindrance of the lone electron pair such geometries were observed in the structures of tris(O-alkylxanthato)-arsenic(III) [11, 12, 13] as well as in the structures of phenylarsenic(III) and phenylantimony(III) bis(dialkyldithiophosphates) [14].

The As···O chelating approaches should be rather weak as can be deduced from their lengths as well as from their IR spectra [5].

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