Inorganica Chimica Acta, 84 (1984) L13–L14

Crystal Structure of Tris(*o*-ethylxanthato)arsenic(III): a Redetermination

BERNARD F. HOSKINS, PAUL M. PIKO, EDWARD R. T. TIEKINK and GEORGE WINTER

Department of Inorganic Chemistry, University of Melbourne, Parkville, Vic. 3052, Australia

Received November 29, 1983

Introduction

Recent X-ray structure determinations of group V *o*-alkylxanthato derivatives [1–4] have indicated that the original structure determinations of M(exa)$_3$, [where M = As, Sb and exa = ethylxanthate], [5, 6], suggest features which are inconsistent with those now expected. In order to unambiguously ascertain the nature of the arsenic environment and the ligand geometry in As(exa)$_3$, we have redetermined its structure by contempory X-ray methods.

Experimental

Preparation: As(exa)$_3$ was prepared by adding the appropriate stoichiometric amount of potassium ethylxanthate to an acidified solution of sodium arsenite in a method similar to that used by Carrai and Gottardi [6]. Suitable crystals for X-ray diffraction studies were grown by slow evaporation from a benzene/light petroleum (40–60 °C) solution.

Structure Determination

Intensity data were collected on an Enraf-Nonius four circle CAD-4F diffractometer controlled by a PDP8/A computer using MoK$_\alpha$ radiation (graphite monochromator) λ 0.71069 Å. The ω:2θ scan technique was employed to measure the intensity profiles for 2377 reflections for which $1° \leqslant \theta \leqslant 26.5°$. Using the $I \geqslant 2\sigma(I)$ criterion of observability on 1280 unique reflections there were 1020 reflections remaining. No decomposition of the crystal occurred during the data collection and correction was made for Lorentz and polarization effects and for absorption [7a].

Crystal Data

$C_9H_{15}O_3S_6As$, M = 438.5, Trigonal, (hexagonal setting, $R\bar{3}$ (C_{3i}^2, no. 148), a = 15.681(4), c = 12.909(3) Å, U = 2749.0 Å^3, D_m = 1.57, Z = 6, D_c = 1.589 Mg m^{-3}, $F(000)$ = 1332, μ = 24.67 cm^{-1}, no. parameters/variables = 18.

The three-dimensional Patterson synthesis indicated the position of the arsenic atom, which sits on a site of symmetry 3, and subsequent diffference maps enabled the location of all other atoms constituting the dithiocarbonate moiety. The structure was refined using a full-matrix least squares method in which the function $\Sigma w\Delta^2$ was minimized, where w was the weight applied to each reflection and $\Delta = ||F_o| - |F_c||$. Refinement of all atomic positions and isotropic thermal parameters yielded R 0.092 where $R = \Sigma\Delta/\Sigma|F_o|$. Refinement was continued with anisotropic thermal parameters for all non-hydrogen atoms, hydrogen atom positions were not refined and were given thermal parameters $1.25 \times U_{iso}$ (parent methylene carbon) and $1.5 \times U_{iso}$ (parent methyl carbon). A weighting scheme was applied for which w was modified according to the expression $w = [\sigma^2(F) + 0.0001|F|^2]^{-1}$, at convergence final R 0.024 and R_w 0.026, where $R_w = [\Sigma w\Delta^2/\Sigma wF^2]^{1/2}$.

The analysis of variance showed no special features indicating a satisfactory weighting scheme had been used. A final difference map revealed an electron density peak of 0.28 e Å^{-3}. The scattering factors used for H, C, O, and S were those collected by Sheldrick [8], while the scattering factors and anomalous dispersion terms for neutral arsenic were those given in ref. [7b, 7c]. Structure determination and refinement were performed using the SHELX-76 program system [8] and the University of Melbourne's Cyber 170–730 computer system.

Fractional atomic coordinates and their estimated standard deviations are given in Table I and the numbering scheme used is shown in Fig. 1. All relevant interatomic distances and angles are given in Table II. Materials deposited: anisotropic thermal parameters, all hydrogen atom parameters and the observed and calculated structure factor tables.

TABLE I. Fractional Atomic Co-ordinates for As(exa)$_3$. Estimated Standard Deviations in Parentheses.

Atom	*x/a*	*y/b*	*z/c*
As	0.0	0.0	0.32910(2)
S(1)	0.13901(4)	0.08672(5)	0.22854(4)
S(2)	0.13205(5)	0.20038(5)	0.40974(3)
C(1)	0.1913(2)	0.1882(1)	0.3113(1)
O(1)	0.2832(1)	0.2495(1)	0.2838(1)
C(2)	0.3438(2)	0.3359(2)	0.3486(2)
C(3)	0.4435(2)	0.3862(2)	0.3065(2)

Results and Discussion

Crystals of As(exa)$_3$ consist of enantiomorphous pairs of discrete molecules of As(exa)$_3$ which are centred about a 3 fold axis and are related to each other through a site of symmetry $\bar{3}$, at (0,0,1/2).

0020-1693/84/$3.00

TABLE II. Bond Distances (Å) and Bond Angles (°). Estimated Standard Deviations in Parentheses.

Atoms	Distance	Atoms	Angle
As–S(1)	2.3069(7)	As–S(1)–C(1)	93.89(8)
As–S(2)	2.9560(7)	As–S(2)–C(1)	74.93(6)
S(1)–C(1)	1.744(2)	S(1)–C(1)–S(2)	123.1(1)
S(2)–C(1)	1.641(2)	S(1)–C(1)–O(1)	110.1(1)
C(1)–O(1)	1.320(3)	S(2)–C(1)–O(1)	126.8(1)
O(1)–C(2)	1.467(3)	C(1)–O(1)–C(2)	119.1(2)
C(2)–C(3)	1.459(4)	O(1)–C(2)–C(3)	108.1(2)

Atoms	Angle
S(1)–As–S(2)	67.56(2)
S(1)–As–S(1)^{I}	91.43(2)
S(1)–As–S(2)^{I}	158.70(2)
S(2)–As–S(1)^{I}	92.55(2)
S(2)–As–S(2)^{I}	108.30(2)

Where I refers to the symmetry operation –y, x – y, z.

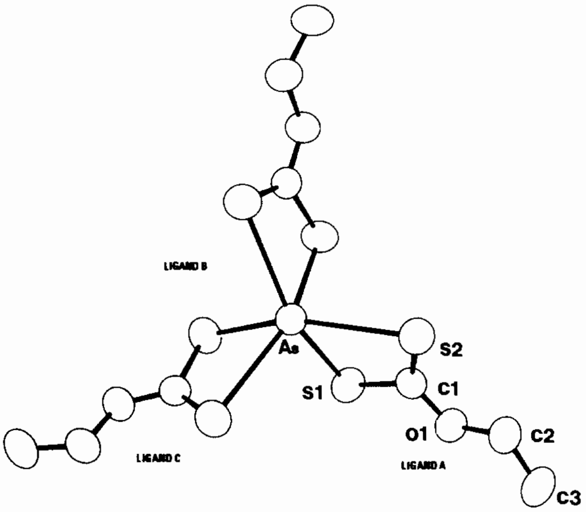

Fig. 1. A view down the three fold axis of As(exa)$_3$, note that ligand B and ligand C are related to ligand A by the symmetry operations (–y, x – y, z) and (y – x, –x, z) respectively. All relevant interatomic parameters are given in Table I.

The xanthate moiety in As(exa)$_3$ bonds asymmetrically with As–S distances 2.3069(6) and 2.9560(7) Å. This asymmetry in bonding is also reflected by two very different C–S distances, *i.e.* 1.641(2) and 1.744(2) Å, the longer C–S distance being associated with the shorter As–S bond. The short C–S distance is only slightly longer than the distance of 1.61 Å [9] estimated for a C–S double bond, indicating a substantial degree of localization of the π-electron density in this bond. The sulphur atoms with the short As–S distances form an equilateral triangle which is separated by 2.3391(8) Å from another and parallel equilateral triangular array formed by the remaining three sulphur atoms involved in the long bond formation to the arsenic atom. One triangle is rotated 41.46(2)° relative to the other so that the geometry is intermediate between trigonal prismatic and octahedral.

The asymmetry of the arsenic environment may arise as a result of the presence of a stereochemically active lone pair of electrons on the arsenic atom, which may be considered to protrude along the three fold axis, through the triangular face of the coordination polyhedra formed by the sulphur atoms involved with the weak As–S interactions. The steric pressure of the lone pair of electrons acting on the S(2) atoms, with the concomitant expansion of the triangular face formed by these atoms requires the xanthate moiety as a whole to pivot on the S(1) atom in such a manner as to move away from the arsenic atom with the interesting result that the 3-fold molecular symmetry is retained.

Recently the crystal and molecular structure of the isomorphous tris methylxanthate derivative, As(mexa)$_3$, was reported [4]. The two As–S distances of 2.298(2) and 2.992(2) Å are comparable to the equivalent bonds in As(exa)$_3$. The major difference between the two structures arises not in the immediate environment of the arsenic atom but in the way the enantiomorphous pairs of molecules are related. Although the As–––As distance in As(exa)$_3$ of 4.4123(4) Å is longer than 4.110(4) Å observed in As(mexa)$_3$, the S(2)–––S(2) contacts between pairs of molecules in As(exa)$_3$ of 3.6173(8) Å is significantly shorter than 3.650(2) Å in As(mexa)$_3$ therefore confirming the original suggestion that pairs of enantiomorphic molecules form loosely associated dimers in the solid state [4].

Acknowledgements

We thank the Commonwealth of Australia for a Post-Graduate Research Award to one of us (E.R.-T.T.).

References

1 R. W. Gable, B. F. Hoskins, R. J. Steen, E. R. T. Tiekink and G. Winter, *Inorg. Chim. Acta, 74*, 15 (1983).
2 B. F. Hoskins, E. R. T. Tiekink and G. Winter, *Inorg. Chim. Acta, L579* (1983).
3 B. F. Hoskins, E. R. T. Tiekink and G. Winter, to be published.
4 T. Ito and H. Hishino, *Acta Cryst., C39*, 448 (1983).
5 C. Carrai and G. Gottardi, *Z. Krist., 113*, 373 (1960).
6 G. Gottardi, *Z. Krist., 115*, 451 (1961).
7 International Tables for X-ray Crystallography; (a) Vol. 4, p. 58; (b) Vol. 4, p. 99; (c) Vol. 4, p. 149, Kynoch University Press, 1974.
8 G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, Cambridge, (1976).
9 L. Pauling, 'The Nature of the Chemical Bond', Ed., Cornell University Press, New York, 1960.