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Acta Cryst. (1977). **B33**, 931–934

Tri- μ -(trimethylarsine oxide)-hexakis(trimethylarsine oxide)dicalcium(II) Tetraperchlorate — a Dinuclear Calcium Complex

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(Received 21 May 1976; accepted 2 November 1976)

Abstract. $\{Ca_2[(CH_3)_3AsO]_6\}(ClO_4)_4$, hexagonal, $P6_3/m$, $a = 11.762(1)$, $c = 27.279(2)$ Å; $M_r = 1702.198$, $D_m = 1.71$ (by flotation), $D_x = 1.73$ g cm $^{-3}$, $Z = 2$; $F(000) = 1696$, $\mu(Cu K\alpha) = 91.91$ cm $^{-1}$. Four-circle diffractometer intensity data were refined by the full-matrix least-squares method to give $R = 0.061$ for 1072 data with $F_o^2 \geq 3\sigma(F_o^2)$. The structure consists of Ca atoms each coordinated to six trimethylarsine oxide ligands, three of which bridge to similar adjacent groups forming a dinuclear cationic complex with crystallographically imposed m symmetry. There are three crystallographically distinct perchlorate counter anions, two of which are disordered.

Introduction. Colourless, hexagonal crystals were recrystallized from powder samples (Jameson & Rodley, 1975, 1976) in methanol–triethyl orthoformate solution in the presence of acetonitrile vapour. Weissenberg and precession photography revealed the crystal to be hexagonal. Systematic absences ($00l$: $l = \text{odd}$) are consistent with space groups $P6_3$ and $P6_3/m$. On the basis of the statistical distribution of intensities, $P6_3/m$ was selected and successful refinement verified the choice.

The transparent crystal chosen for data collection had a maximum dimension of about 0.38 mm. Cell dimensions and their e.s.d.'s were determined from least-squares refinement of the setting angles of 12

Table 1. *Final parameters for non-group atoms*

The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Parameters without standard deviations are fixed by symmetry. Variable parameters have been multiplied by 10^4 .

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	$\frac{1}{3}$	$\frac{2}{3}$	1860 (1)	61 (2)	$\beta_{22} = \beta_{11}$	7 (0)	$2\beta_{12} = \beta_{11}$	0	0
As(1)	1205 (1)	3806 (1)	1018 (1)	112 (2)	106 (2)	14 (0)	37 (2)	-9 (1)	-15 (1)
As(2)	4677 (3)	4861 (3)	$\frac{1}{4}$	214 (4)	188 (4)	12 (0)	172 (3)	0	0
O(1)	1673 (8)	4984 (8)	1434 (3)	110 (10)	110 (10)	16 (1)	39 (9)	-7 (3)	-19 (3)
O(2)	3630 (10)	5409 (9)	$\frac{1}{4}$	110 (10)	60 (10)	7 (1)	50 (10)	0	0
C(11)	-230 (30)	2230 (20)	1224 (8)	470 (50)	150 (30)	36 (5)	10 (30)	40 (10)	-30 (10)
C(12)	2590 (20)	3510 (20)	850 (10)	200 (30)	390 (50)	100 (10)	170 (30)	-10 (10)	-120 (20)
C(13)	750 (30)	4250 (30)	430 (7)	720 (80)	430 (50)	24 (4)	390 (60)	-70 (10)	-40 (10)
C(21)	6460 (20)	6370 (30)	$\frac{1}{4}$	90 (30)	470 (60)	24 (5)	170 (40)	0	0
C(22)	4410 (20)	2790 (20)	1929 (5)	490 (50)	300 (40)	18 (3)	320 (40)	0 (10)	-23 (8)
Cl(1)	0	0	0	132 (7)	$\beta_{22} = \beta_{11}$	17 (1)	$2\beta_{12} = \beta_{11}$	0	0
Cl(2)	0	0	$\frac{1}{4}$	350 (20)	$\beta_{22} = \beta_{11}$	49 (4)	$2\beta_{12} = \beta_{11}$	0	0
Cl(3)	$\frac{2}{3}$	$\frac{1}{3}$	783 (7)	230 (10)	$\beta_{22} = \beta_{11}$	58 (4)	$2\beta_{12} = \beta_{11}$	0	0
O(31)	6640 (40)	2220 (30)	700 (10)	780 (80)	680 (90)	160 (20)	470 (80)	30 (30)	-150 (30)
O(32)	$\frac{2}{3}$	$\frac{1}{3}$	1210 (20)	800 (100)	$\beta_{22} = \beta_{11}$	100 (20)	$2\beta_{12} = \beta_{11}$	0	0

carefully centred reflections. 1763 independent reflections were collected in the range $0^\circ \leq \theta \leq 57^\circ$ on a Hilger & Watts diffractometer with Cu $K\alpha$ (Ni-filtered) X radiation. The data were corrected for Lorentz and polarization effects. Absorption corrections were not made because of difficulties in accurately defining the crystal habit. The structure was solved by normal Patterson and Fourier syntheses. Difficulties were encountered in attempting to locate the perchlorate O atoms.

Difference Fourier syntheses calculated through sections around the Cl atoms yielded peaks of the partially disordered perchlorate O atoms. Full-matrix positional and anisotropic temperature parameter refinement of all atoms converged at $R = 0.057$. At this stage two of the three perchlorate anions had unreasonable stereochemistries. To resolve these problems, several models were investigated. The structure was refined in the non-centrosymmetric space group $P6_3$ to relieve the constraints on the perchlorate anions, but no electron densities for the O atoms were found at reasonable positions around the Cl atoms. The final model used described the perchlorate O atoms as tetrahedral rigid groups with a Cl—O distance of 1.44 Å in space group $P6_3/m$. Refinement converged with $R = 0.061$. There are only negligible changes (in the order of 0.01 Å) in the cation geometry with different models for the perchlorate anions. The largest shift in the final cycle was 0.27σ. The highest peak from the final difference Fourier was about half the electron density of the most disordered perchlorate O atoms.

Programs used were modified versions of *ORFLS* (Busing, Martin & Levy, 1962), *FORDAP* (Zalkin,

1965) and *ORTEP* (Johnson, 1965). Calculations were carried out at the University of Canterbury on a Burroughs B6718 computer.

Atomic coordinates and temperature factors of all non-hydrogen atoms are listed in Tables 1 and 2. Selected bond distances and angles are given in Tables 3 and 4 respectively.*

Discussion. Various Ca and Mg complexes of substituted arsine and phosphine oxides were recently synthesized and characterized in this laboratory (Jameson & Rodley, 1975, 1976). X-ray powder photographs showed that the Ca analogue of $\{\text{Mg}[(\text{CH}_3)_3\text{AsO}]_3\}(\text{ClO}_4)_2$ did not have exactly the same structure as that reported for the Mg complex (Ng, Rodley & Robinson, 1976). The structure of the Ca arsine oxide complex was determined in order to gain further insight into the effects of metal ion character on the stereochemistries of Ca and Mg complexes.

The structure consists of discrete dimeric cationic units well separated in space. Fig. 1 shows an edge-on

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32273 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Selected interatomic distances (Å)

Cation			
Ca—O(1)	2.284 (7)	As(1)—O(1)	1.657 (7)
Ca—O(2)	2.424 (7)	As(1)—C(11)	1.865 (20)
		As(1)—C(12)	1.886 (19)
Ca...Ca ^{IV}	3.491 (6)	As(1)—C(13)	1.845 (20)
Ca...As(1)	3.800 (2)	As(2)—O(2)	1.649 (10)
Ca...As(2)	3.661 (2)	As(2)—C(21)	1.957 (26)
		As(2)—C(22)	1.926 (14)

Anion			
Cl(3)—O(31)	1.32 (3)	Cl(3)—O(32)	1.16 (6)

The Roman numeral superscripts represent the symmetry transformations given below. Where there is no further qualification, symmetry (i) is implied.

(i)	x, y, z	(iii)	$y-x, -x, z$
(ii)	$-y, x-y, z$	(iv)	$x, y, \frac{1}{2}-z$

Table 2. Final parameters for group atoms

Positional parameters have been multiplied by 10^4 .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Perchlorate group 1				
O(11)	-1320 (10)	-810 (80)	-132 (0)	15 (1)
O(12)	0	0	528 (0)	17 (2)
Perchlorate group 2				
O(21)	-1110 (30)	80 (60)	2368 (0)	19 (1)
O(22)	0	0	3028 (0)	33 (6)

Table 4. Selected bond angles (°)

O(1)—Ca—O(1) ⁱⁱ	96.4 (3)	O(1)—As(1)—C(11)	112.4 (7)	O(2)—As(2)—C(21)	108.4 (9)
O(1)—Ca—O(2)	99.2 (3)	O(1)—As(1)—C(12)	111.2 (7)	O(2)—As(2)—C(22)	110.2 (6)
O(1)—Ca—O(2) ⁱⁱ	162.8 (3)	O(1)—As(1)—C(13)	112.5 (8)	C(21)—As(2)—C(22)	110.2 (8)
O(1)—Ca—O(2) ⁱⁱⁱ	89.1 (3)	C(11)—As(1)—C(12)	109.2 (12)	C(22)—As(2)—C(22) ^v	107.9 (11)
O(2)—Ca—O(2) ⁱⁱ	73.9 (3)	C(12)—As(1)—C(13)	103.9 (14)	O(31)—Cl(3)—O(32)	100.3 (20)
Ca—O(1)—As(1)	148.8 (5)	C(13)—As(1)—C(11)	107.2 (13)	O(31)—Cl(3)—O(31) ⁱⁱ	116.9 (12)
Ca—O(2)—Ca ^{iv}	92.1 (4)				
Ca—O(2)—As(2)	127.0 (3)				

view of the dinuclear Ca cationic unit and illustrates the labelling scheme adopted in this paper. The structure is relatively 'open' and there are no interionic distances shorter than 3.3 Å (excluding H atoms). The perchlorate anions are symmetrically located around the cations as illustrated in Fig. 2. The Ca atoms are surrounded by six O atoms of the $(\text{CH}_3)_3\text{AsO}$ ligands in an approximately octahedral environment. There are two types of $(\text{CH}_3)_3\text{AsO}$ ligands present in the structure. Three crystallographically equivalent ligands form terminal groups with Ca—O bonds of 2.284 (7) Å. The other three symmetry-related ligands bridge the two Ca centres with a Ca—O distance of 2.424 (7) Å. The present structure appears to be the first of its kind to have been the subject of X-ray analysis. Closely

related structures are $\text{I}_3\text{NiI}_3\text{Bi}[(\text{Ph}_3\text{AsO})_3]$ (Lazarini & Golič, 1975), and the dimeric species $(\text{Zn}\{\text{C}_6\text{H}_4[(\text{CH}_3)_2\text{AsO}]_2\})^{4+}$ (Hunter, Rodley & Emerson, 1976).

Two of the three crystallographically independent perchlorate anions are disordered. The Cl atom at (0,0,0) is in an environment with $\bar{3}$ symmetry while that at $(0,0,\frac{1}{4})$ has $\bar{6}$ symmetry imposed on it. Each Cl atom may be considered to be at the centroid of two possible orientations for its bonded, tetrahedrally arranged O atoms. In the first case the overlapped arrangement is necessarily staggered, and in the second it is eclipsed. The high thermal motions exhibited by the associated perchlorate O atoms hindered further characterization of these disorders.

As—C bond lengths in the present structure are similar to those in $\{\text{Mg}[(\text{CH}_3)_3\text{AsO}]_3\}(\text{ClO}_4)_2$. However, in the Mg complex all the Mg—O distances are shorter than those in the present structure. The stronger Mg—O axial bond in the Mg complex possibly produces a 'trans' effect (via strong $L \rightarrow M$ donation) (Ng, Rodley & Robinson, 1976) which favours the formation of a five-coordinate species. By contrast, the Ca ion is unlikely to exert this type of 'trans' effect to produce five-coordination because $L \rightarrow M \pi$ bonding is less likely to occur for a significantly larger ion (ionic radii are: $\text{Ca}^{2+} = 0.99$ and $\text{Mg}^{2+} = 0.65$ Å). The larger size favours a higher coordination number than five. In fact, many Ca complexes with oxo ligands have coordination numbers of 7 or even 8 (Uchtman, 1972; Einspahr & Bugg, 1974; Kretsinger & Nelson, 1976).

We thank Dr F. C. March for his helpful comments on the solution of this structure and the New Zealand University Grants Committee for research equipment grants.

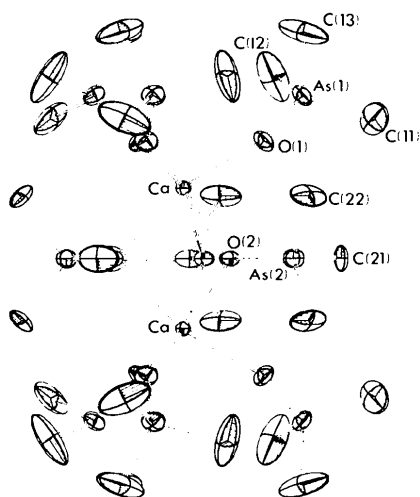


Fig. 1. A perspective view of the $\{\text{Ca}_2[(\text{CH}_3)_3\text{AsO}]_3\}^{4+}$ cation.

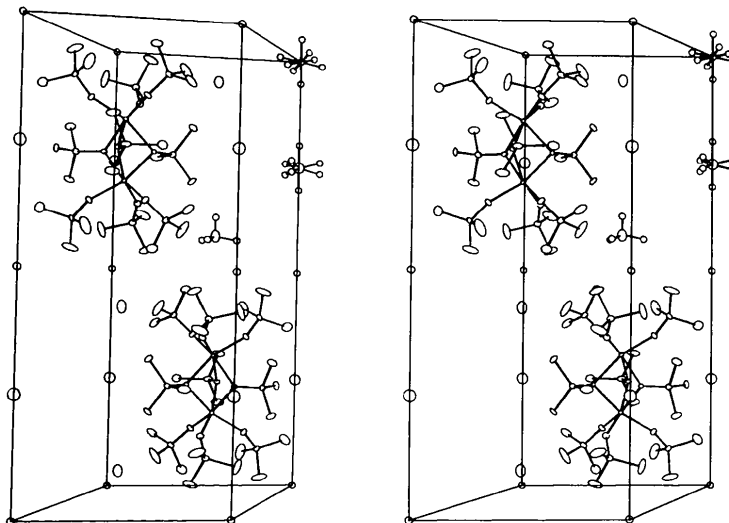


Fig. 2. Stereo diagram of the contents of the unit cell. For clarity only three perchlorate anions are shown with their O atoms attached.

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Acta Cryst. (1977). **B33**, 934–936

6-Methyl-5,6-dihydrouracil, a Highly Disordered Structure

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(Received 3 June 1976; accepted 10 November 1976)

Abstract. $C_5H_8N_2O_2$, monoclinic, $C2$ (with the molecules highly disordered in such a way that an approximate mirror is introduced normal to the b axis; $C2/m$ approximately describes the crystal structure), $a = 10.532(3)$, $b = 6.447(2)$, $c = 9.183(2)$ Å, $\beta = 101.55(3)^\circ$, $Z = 4$, $D_o = 1.39$, $D_c = 1.39$ g cm $^{-3}$, $R = 0.08$. Because of the disorder and ambiguities in the results of least-squares analysis in this structure, the y coordinates of the atoms are indeterminate. The molecules are self-paired across twofold axes by pairs of $N(1) \cdots O(2)$ (2.88 Å) and $N(3) \cdots O(4)$ (2.88 Å) hydrogen bonds. The orientation of the g tensor of the products of radiation damage in the crystal is correlated with the orientation of the molecules in the crystal structure.

Introduction. Transfer-ribonucleic acid molecules contain a variety of modified bases, one of which is dihydrouracil which occurs in a special loop region. The title compound (Fig. 1) (hereafter referred to as 6mhura) is an analog of the naturally occurring 5,6-dihydrouracil. The present investigation was undertaken to study the influence of different substituents upon the hydrogen-bonding pattern of uracil, and also to correlate the results of the crystal structure analysis with ENDOR studies by our colleague Dr H. Box and his co-workers.

Crystals of 6mhura (Sigma Chemical Company)

were obtained by slow evaporation from water solution. Intensity data to the limit $2\theta = 120^\circ$ (little scattering was observed beyond this range) for $Cu K\alpha$ were obtained from a crystal of size $0.65 \times 0.35 \times 0.15$ mm by the stationary crystal-stationary counter technique, with a 5° take-off angle. Of the 770 reflections measured, 186 intensities were less than twice the background in that range and were given zero weight during the refinement. The difference in absorption as a function of the φ angle (Furnas, 1957) was measured for the axial 600 reflection and was used for correcting

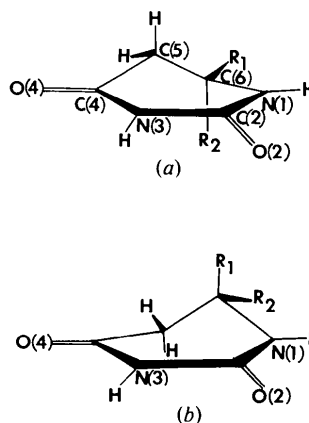


Fig. 1. $R_1 = H$, $R_2 = C(Me)$ yields the (*S*) isomer; $R_1 = C(Me)$, $R_2 = H$ yields the (*R*) isomer. For each isomer, two modes of pucker, (a) and (b), are possible.

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