cell dimensions and the distribution of lattice points on (001), but it does not appear to explain the dehydration reactions. Two-dimensional sheets parallel to (001) would be likely to move in directions either perpendicular to, or parallel to, the (001) plane, during the low temperature dehydration of nekoite, but it is difficult to see how they could tilt out of this plane without setting up unacceptable strains in the crystal. The observed behaviour of nekoite on dehydration, namely the retention of the **c** direction and the shift of the *a* axis, requires just such a tilt. Moreover, the structure proposed by Mamedov & Belov does not permit of the existence of Si–OH groups, which appear to be required to explain the dehydration reactions.

It is possible, however, that the structure of Mamedov & Belov requires only modification. The repeat distance of 7·32 Å along the fibre axis suggests the presence of dreierketten chains in the structure, and the pattern of lattice points suggests that these chains are stacked so as to be displaced by *b*/2 along the *a* axis and by *b*/4 along the **c** direction. The proposed sheet may be 'de-condensed' to give either single or double dreierketten chains, of empirical compositions $Si_3O_9H_3^{3-}$ or $Si_6O_{17}H_4^{6-}$, which are hydrogen bonded into a pseudo-sheet very similar to the original in projection on (001). Such a structure will have similar dimensions to the condensed sheet but will be more flexible and will be able to undergo the required low-temperature re-arrangements without needing to tilt a rigid structure. Also, there will be Si–OH groups on the dreierketten chains, as required.

The author would like to thank Professor H. F. W. Taylor for suggesting this study and for valuable discussions throughout. The infrared spectra were very kindly obtained by Dr V. C. Farmer of the Macauley Institute for Soil Research, and part of the work was carried out under a grant from the Department of Scientific and Industrial Research.

References

BALL, M. C. & TAYLOR, H. F. W. (1961). *Miner. Mag.* **32**, 754.
BUCKLE, E. R., GARD, J. A. & TAYLOR, H. F. W. (1958). *J. Chem. Soc.* p. 1351.
CARPENTER, A. B. (1959). Private communication.
CHALMERS, R. A., NICOL, A. W. & TAYLOR, H. F. W. (1962). *Miner. Mag.* **33**, 70.
DENT, L. S. (1959). Ph. D. Thesis, Aberdeen University.
DENT, L. S. & TAYLOR, H. F. W. (1956). *Acta Cryst.* **9**, 1002.
EAKLE, A. S. (1917). *Univ. Cal. Bull. Dept. Geol.* p. 327.
GARD, J. A. (1960). *Proc. European Regional Conference on Electron Microscopy, Delft*, Ed. A. L. HOUWINK & B. J. SPIT, Vol. 1, 203. Den Haag: Nederlanse Vereniging voor Electronenmicroscopie.
GARD, J. A. & TAYLOR, H. F. W. (1956). *Miner. Mag.* **31**, 5.
GARD, J. A. & TAYLOR, H. F. W. (1960). *Acta Cryst.* **13**, 785.
HELLER, L. & TAYLOR, H. F. W. (1956). *Crystallographic Data for the Calcium Silicates*, p. 24. London: H.M.S.O.
HOWISON, J. & TAYLOR, H. F. W. (1957). *Mag. Concr. Res.* **9**, 13.
LACY, E. D., NICOL, A. W. & TARNEY, J. (1970). In preparation.
MAMEDOV, KH. S. & BELOV, N. V. (1958). *Doklady Akad. Nauk* SSSR, **121**, 720.
MACIVER, E. J. (1962). Ph. D. Thesis, Cambridge University.
NICOL, A. W. (1962). Ph. D. Thesis, Aberdeen University.
TAYLOR, H. F. W. (1955). *Acta Cryst.* **8**, 440.
TAYLOR, H. F. W. (1959). *Progr. Ceram. Sci.* **1**, 89.

Acta Cryst. (1971). B**27**, 476

The Molecular and Crystal Structure of Trifluoromethylarsenic Tetramer $(AsCF_3)_4$

BY NEIL MANDEL AND JERRY DONOHUE

Department of Chemistry and Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania 19104, *U.S.A.*

(*Received* 13 *March* 1970)

Crystals of trifluoromethylarsenic tetramer, $(AsCF_3)_4$, are tetragonal, with 2 molecules in a unit cell with symmetry $P4_2/nmc$ and lattice constants $a=10{\cdot}483$ (2), $c=6{\cdot}381$ (1) Å. The required molecular symmetry is $\bar{4}2m$. Three-dimensional data were collected at 25°C with an automated diffractometer. The heavy atoms were located by Patterson synthesis, and Fourier and least-squares refinement were used to obtain optimum values for the nine positional and eighteen thermal parameters. The value of R is 6%. The bond distances found are: As–As $2{\cdot}454 \pm 0{\cdot}001$, As–C $2{\cdot}012 \pm 0{\cdot}015$, average C–F $1{\cdot}296 \pm 0{\cdot}022$ Å. The four-membered arsenic ring is not planar, having bond angles of 83·6° and torsion angles of 36·8°. These and other molecular quantities are compared with the isostructural $(PCF_3)_4$, and with other arsenic compounds.

Introduction

Cowley & Burg (1966) reported for the first time the synthesis of a compound which contained a four-membered arsenic ring. Compounds having five- and six-membered arsenic rings have been previously characterized (Burns & Waser, 1957; Hedberg, Hughes & Waser, 1961). The synthesis of a molecule with a four-membered phosphorus ring and four trifluoromethyl groups was reported by Mahler & Burg (1958); the crystal structure analysis of this substance was reported by Palenik & Donohue (1962). The crystal structure analysis of the corresponding arsenic compound and the comparison of the molecular geometry with the phosphorus ring system is therefore of interest. We report here the results of an X-ray crystallographic study of trifluoromethylarsenic tetramer.

Experimental

The arsenic tetramer is a slightly volatile solid with a melting point of 98·2 °C. The crystals are colorless, but decompose in the X-ray beam to a dark brown. The crystals must be stored in sealed capillaries under dry nitrogen to avoid reaction with the atmosphere. The crystal growth inside the sealed capillaries is in general very irregular, and two possible methods were found to grow suitably shaped crystals. The first method involved sublimation of the sample inside a large test tube with the aid of a heat gun. The sealed capillary was put inside the test tube and the heat was applied at only one end of the capillary, causing the crystals to sublime and move with the temperature gradient. The second method was found to be superior to the first, in that larger and better shaped crystals were formed: the capillaries were again put into test tubes, the tubes inserted in a heating mantle with sand at 43°C, and after two days the sand was allowed to cool to room temperature.

Weissenberg photographs taken with the crystal rotating about the a axis ($h=0,1,2,3$) and about the c axis ($l=0,1,2$), along with an $0kl$ precession photograph gave Laue symmetry $4/mmm$ (D_{4h}). The systematic absences indicated that the probable space group was $P4_2/nmc$ (D_{4h}^{15}). Preliminary lattice constants were obtained by measurement of these photographs. The crystal was transferred to a Picker Nuclear FACS I automated diffractometer where more accurate lattice constants were obtained by a least-squares treatment of twelve 2θ values observed with Cu $K\alpha$ radiation. The lattice constants thus obtained are $a=10\cdot483\pm0\cdot002$, $c=6\cdot381\pm0\cdot001$ Å. The calculated density with two molecules per unit cell is 2·73 g.cm^{-3} and is reasonable compared with the value of 2·00 g.cm^{-3} for $(PCF_3)_4$. The linear absorption coefficient is 213·1 cm^{-1}. The crystal used measured $0\cdot35\times0\cdot20\times0\cdot25$ mm.

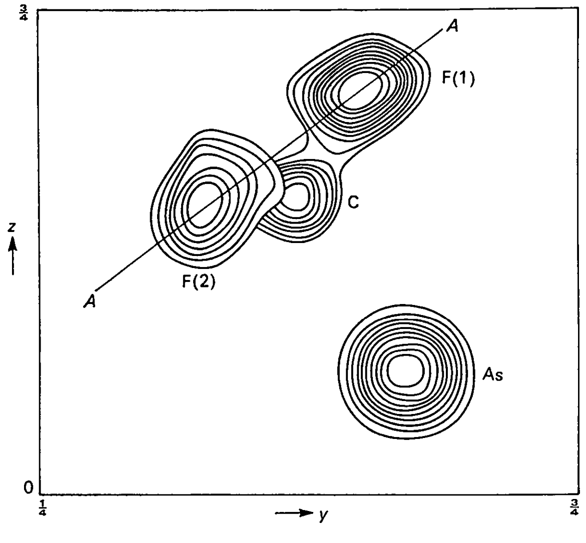


Fig. 1. Sections of $\varrho(xyz)$ at $x=0$ and $x=0\cdot2$ Å.

With two molecules per unit cell the required symmetry is $\bar{4}2m$ (D_{2d}). Of the equivalent positions, one of the two sets of eightfold positions, $8(f)$, is eliminated for placement of the arsenic, carbon, and eight fluorine atoms because of the objectionable 180° As–C–F bond angle. Position $8(g)$, point symmetry m, must therefore accommodate these atoms, with the remaining sixteen fluorine atoms in the general position $16(h)$. The number of positional parameters is thus nine.

Determination of the structure

The data for this structure determination were collected on the diffractometer using the moving-crystal moving-counter technique. The 2θ scan rate was 1°min^{-1} and a 20 second background count was used. Sets of hkl and khl reflections out to a maximum $\sin\theta/\lambda=0\cdot6$ were collected to observe the effect of the large absorption coefficient. The space group requires that the intensities for these two sets be equal. Comparison of them revealed notable discrepancies. In an attempt to correct for absorption, intensity data were collected on various sets, hkl, $\bar{h}kl$, $h\bar{k}l$, $hk\bar{l}$, $\bar{h}\bar{k}l$, *etc.* reflections, along with the corresponding khl sign combination set. Plots were made of the intensity *versus* the value of φ. Five such plots were made but no reproducible curve was found. The attempted fitting of the data to an absorption curve was hindered by the lack of a $\chi=90°$ reflection in both precession and diffractometer geometries, and also by the somewhat irregular shape of the crystal inside the sealed capillary. To make some sort of correction for the absorption the intensities of the hkl, khl sets of data were compared. The reflection of each hkl, khl pair which showed less absorption was chosen, and a unique set was thus assembled. The final unique set of data chosen was therefore a composite of the two original sets. The 40 unobserved reflections were considered insignificant based on a $2\cdot33\sigma(I)$ rule (designated by * in Table 1).

The intensities are computed as $I=(1/\mathrm{Lp})q[N-(b_1+b_2)(t_s/2t_b)]$ and the standard errors of intensities are computed as $\sigma(I)=(1/\mathrm{Lp})q[N+(t_s/2t_b)^2(b_1+b_2)+(p\mathrm{C})^2]^{1/2}$ where Lp is the Lorentz and polarization term, q is the filter factor, N the number of counts during the 2θ scan, b_1 the first background count in time t_b,b_2 the second background count in time t_b, t_s the total scan time of each peak, $C=N-(b_1+b_2)/(t_s/2t_b)$, and p is a constant dependent of measurements of symmetry-related reflections (usually, $p=0{\cdot}05$).

Table 1. *Observed and calculated structure factors*

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
2	0	0	65.6	-65.4	9	4	1	40.8	40.8	4	0	3	86.4	-85.2	5	4	4	25.6	-27.5
4	0	0	22.8	21.4	10	4	1	3.9	-2.6	5	0	3	42.7	42.7	6	4	4	4.8	2.2
6	0	0	139.1	-136.5	11	4	1	11.7	-13.0	6	0	3	4.8	-5.1	7	4	4	40.5	38.9
8	0	0	51.9	45.6	6	5	1	36.8	-38.0	7	0	3	27.4	-28.1	8	4	4	5.3	3.8
•10	0	0	3.0	1.0	7	5	1	6.7	5.7	8	0	3	29.2	-28.4	9	4	4	6.6	6.6
12	0	0	28.8	27.4	8	5	1	6.7	4.4	•9	0	3	2.2	-1.5	•5	5	4	2.7	1.0
1	1	0	97.7	99.9	9	5	1	8.6	9.2	10	0	3	39.9	39.0	6	5	4	16.3	-16.4
3	1	0	15.5	14.5	10	5	1	14.1	15.0	2	1	3	12.6	12.2	•7	5	4	1.6	1.5
5	1	0	78.3	77.3	7	6	1	51.8	-54.1	3	1	3	76.6	77.7	8	5	4	3.7	-1.0
7	1	0	71.5	-71.1	8	6	1	9.1	-9.6	4	1	3	3.7	-2.5	6	6	4	4.9	-5.3
9	1	0	13.3	-12.6	10	6	1	11.3	11.6	5	1	3	13.1	-12.4	•7	6	4	3.4	-2.1
11	1	0	6.8	-5.8	8	7	1	16.6	-17.2	6	1	3	22.5	20.6	•8	6	4	2.7	-.5
2	2	0	150.6	-161.4	9	7	1	9.4	-10.4	7	1	3	16.6	-16.5	•7	7	4	1.7	.7
4	2	0	102.9	92.8	9	8	1	10.2	11.1	8	1	3	3.9	-1.5	1	0	5	17.9	16.2
6	2	0	32.3	31.0	1	0	2	5.7	-5.0	9	1	3	32.1	-31.8	2	0	5	60.0	-59.2
8	2	0	19.8	20.5	2	0	2	54.8	51.2	11	1	3	10.6	10.9	3	0	5	7.2	6.8
10	2	0	39.7	-39.3	3	0	2	162.0	171.4	3	2	3	46.4	-49.4	4	0	5	57.7	58.7
12	2	0	7.1	-7.5	4	0	2	25.6	-24.0	4	2	3	25.5	27.1	5	0	5	12.6	12.6
3	3	0	198.9	-218.4	5	0	2	40.7	-40.5	5	2	3	3.6	1.2	7	0	5	18.0	-18.7
5	3	0	64.2	60.5	6	0	2	78.3	74.7	6	2	3	51.2	51.0	8	0	5	16.6	15.2
7	3	0	11.8	-12.6	8	0	2	21.4	-21.3	7	2	3	5.3	4.9	2	1	5	10.5	11.6
9	3	0	56.0	54.9	9	0	2	43.3	-36.5	8	2	3	15.8	-14.9	3	1	5	55.8	-57.0
11	3	0	18.3	-17.6	11	0	2	15.7	14.9	9	2	3	9.9	8.7	4	1	5	11.0	5.9
4	4	0	80.6	-69.9	1	1	2	94.6	-103.6	10	2	3	14.2	-14.1	5	1	5	5.7	4.9
6	4	0	14.3	-14.8	2	1	2	78.5	-82.5	4	3	3	30.7	-31.5	6	1	5	13.0	13.0
8	4	0	15.6	-15.0	3	1	2	51.6	-50.8	5	3	3	49.8	-52.6	7	1	5	5.2	3.6
10	4	0	35.0	37.3	4	1	2	59.7	56.1	6	3	3	6.9	-7.6	8	1	5	6.5	-5.4
5	5	0	41.9	40.3	5	1	2	38.9	-36.7	7	3	3	56.5	58.4	3	2	5	14.5	-14.5
7	5	0	43.2	-40.4	6	1	2	18.4	19.1	8	3	3	17.0	-15.4	4	2	5	6.9	-5.7
9	5	0	23.4	-23.2	7	1	2	49.5	44.9	•9	3	3	3.4	1.5	5	2	5	6.8	2.9
•11	5	0	2.8	-.5	8	1	2	22.3	19.5	10	3	3	11.7	11.9	6	2	5	31.4	-32.0
6	6	0	60.1	57.9	9	1	2	9.6	9.2	5	4	3	10.2	-10.7	7	2	5	8.9	8.3
8	6	0	25.2	-25.1	10	1	2	24.0	-23.3	6	4	3	47.1	-49.8	8	2	5	5.4	5.6
7	7	0	52.5	53.5	11	1	2	4.8	3.8	7	4	3	6.4	5.8	4	3	5	19.7	-20.5
9	7	0	4.0	1.7	2	2	2	20.6	23.8	8	4	3	20.0	20.4	5	3	5	29.6	31.6
8	8	0	4.0	-3.1	3	2	2	43.1	-44.2	9	4	3	9.0	-8.9	6	3	5	4.1	-3.6
1	0	1	131.0	-149.7	4	2	2	57.7	-61.4	10	4	3	7.2	7.9	7	3	5	33.4	-33.6
2	0	1	59.8	51.2	5	2	2	36.3	-40.6	6	5	3	23.2	22.9	8	3	5	7.6	-6.7
3	0	1	19.1	14.1	6	2	2	24.1	-23.8	7	5	3	20.1	-20.5	5	4	5	14.3	-12.0
4	0	1	68.9	65.0	7	2	2	38.0	37.2	8	5	3	4.4	-2.2	6	4	5	31.8	31.6
5	0	1	66.4	-58.0	8	2	2	8.6	-8.5	9	5	3	17.5	-18.5	8	4	5	8.0	-7.6
6	0	1	12.3	-12.9	9	2	2	10.8	10.2	7	6	3	12.4	12.4	6	5	5	10.4	10.3
7	0	1	90.8	85.7	10	2	2	18.0	18.0	8	6	3	13.5	13.3	7	5	5	10.5	10.1
8	0	1	7.4	7.4	•11	2	2	0.0	-.1	•9	6	3	3.0	-.6	0	0	6	42.4	42.7
•9	0	1	0.0	-.1	3	3	2	79.4	90.7	8	7	3	4.6	4.1	2	0	6	13.5	-12.2
10	0	1	14.2	-15.5	4	3	2	11.0	11.9	0	0	4	18.0	-16.9	3	0	6	30.5	29.8
11	0	1	12.5	12.6	5	3	2	22.7	-24.6	1	0	4	47.5	48.1	4	0	6	5.0	4.8
2	1	1	16.1	-14.7	6	3	2	70.4	-73.8	2	0	4	8.3	8.9	5	0	6	9.9	-10.1
3	1	1	74.5	-73.0	•7	3	2	0.0	-.3	3	0	4	94.1	-96.8	6	0	6	26.5	-27.4
4	1	1	25.7	-22.4	8	3	2	20.1	20.1	4	0	4	8.3	-7.4	•7	0	6	0.0	-.2
•5	1	1	1.9	-2.6	9	3	2	36.8	-35.5	5	0	4	36.1	32.6	1	1	6	26.4	26.2
6	1	1	92.3	-86.3	•10	3	2	.8	-.7	6	0	4	6.6	5.1	2	1	6	11.7	-10.3
7	1	1	19.5	17.2	11	3	2	13.0	13.7	7	0	4	5.9	-4.1	3	1	6	8.9	9.2
8	1	1	25.9	24.6	4	4	2	61.1	70.4	•8	0	4	2.7	-1.4	4	1	6	19.4	20.5
9	1	1	22.0	21.0	5	4	2	40.5	45.2	9	0	4	38.9	38.1	5	1	6	10.4	10.5
10	1	1	15.8	15.6	6	4	2	9.9	10.0	2	1	4	55.3	57.7	6	1	6	5.5	5.3
11	1	1	8.0	-7.2	7	4	2	38.4	-39.3	3	1	4	9.2	-9.6	7	1	6	17.2	-17.6
12	1	1	17.0	18.2	8	4	2	22.8	22.4	4	1	4	65.8	-66.4	2	2	6	12.7	-13.9
3	2	1	79.1	90.1	9	4	2	4.0	-0.8	5	1	4	10.4	-12.2	3	2	6	11.2	-11.7
4	2	1	15.5	-17.3	10	4	2	19.9	-20.7	6	1	4	17.8	-16.1	4	2	6	19.0	18.4
5	2	1	14.6	-13.7	5	5	2	5.3	-4.1	7	1	4	4.4	-1.3	5	2	6	4.6	-4.5
6	2	1	26.9	-26.1	6	5	2	23.5	23.0	8	1	4	11.9	-11.9	6	2	6	9.0	8.9
7	2	1	28.0	-26.9	7	5	2	23.8	24.6	10	1	4	25.6	25.7	3	3	6	34.3	-35.5
8	2	1	4.7	-1.9	8	5	2	7.3	7.4	2	2	4	11.0	12.0	4	3	6	3.8	-0.8
9	2	1	39.4	-38.6	9	5	2	7.5	6.4	3	2	4	25.1	26.0	5	3	6	11.2	10.9
11	2	1	9.6	9.6	10	5	2	14.5	-15.3	4	2	4	8.0	-8.1	6	3	6	20.9	-20.9
4	3	1	101.3	114.6	6	6	2	51.5	-56.4	5	2	4	23.5	22.9	4	4	6	22.5	-24.0
5	3	1	4.2	-5.4	7	6	2	6.4	-6.6	6	2	4	3.9	0.8	5	4	6	10.4	10.3
6	3	1	4.9	-5.2	8	6	2	13.0	13.4	7	2	4	38.9	-37.5	5	5	6	5.2	5.5
7	3	1	34.1	-33.1	9	6	2	21.4	22.1	•8	2	4	3.4	-.8	1	0	7	31.1	-31.6
8	3	1	26.3	26.9	•10	6	2	3.0	.1	9	2	4	10.7	-10.5	2	0	7	9.8	10.8
9	3	1	5.9	4.1	7	7	2	21.5	-22.6	3	3	4	10.9	11.5	4	0	7	9.2	-8.9
10	3	1	40.6	-41.5	8	7	2	10.2	-10.2	4	3	4	16.6	-18.1	•2	1	7	2.2	-.5
11	3	1	3.8	-3.5	•9	7	2	3.3	-.2	6	3	4	58.9	61.6	3	1	7	10.8	11.2
5	4	1	26.0	28.1	•8	8	2	0.0	-1.3	7	3	4	4.1	1.5	3	2	7	23.2	23.5
6	4	1	51.1	55.0	1	0	3	53.0	49.7	8	3	4	22.9	-22.6					
7	4	1	13.5	13.3	2	0	3	99.0	99.3	•4	4	4	.9	-1.2					
8	4	1	9.9	-9.1	3	0	3	20.5	17.6										

A three-dimensional Patterson function was calculated and the As–As vectors were easily located. A three-dimensional electron density function was calculated with all of the observed F_{hkl} values; the phases were assigned based on the As contribution as obtained from the coordinates from the Patterson function. A refined set of As coordinates, together with tentative carbon and fluorine coordinates were obtained, and the coordinates from the final Fourier synthesis used as input for the UCLA full-matrix least-squares refinement routine. The function $\sum w(KF_o-G|F_c|)^2$, where K and G are scale factors of the observed and calculated structure factors respectively, is minimized using a weighting scheme proportional to σ^{-1} where $\sigma=[F_o^2+\sigma(I)]^{1/2}-F_o$. Temperature factors for the isotropic refinement were arbitrarily set at 4·0 and the scale factor was obtained from Wilson statistics. The results after twelve cycles of anisotropic refinement are presented in Tables 2 and 3. The anisotropic temperature factors were used to calculate root-mean-square displacements $[(\bar{r}_i^2)^{1/2}]$ and direction cosines (q_{ij}) for the thermal ellipsoids. These results are presented in Table 4.

Table 2. *Final positional parameters and estimated standard errors (in parentheses) after twelve cycles of anisotropic least-squares (all values* × 10⁴*)*

As	y	5930 (1)	F(1)	y	5499 (12)
	z	1861 (2)		z	6267 (16)
C	y	4906 (14)	F(2)	x	3501 (10)
	z	4514 (23)		y	4155 (12)
				z	4522 (13)

Table 4. *Thermal ellipsoid parameters*

	i	$(\bar{r}_i^2)^{1/2}$	q_{ia}	q_{ib}	q_{ic}
As	1	0·0587	−1·0	0	0
	2	0·0503	0	−0·3817	0·9243
	3	0·0458	0	0·9243	0·3817
C	1	0·1029	−1·0	0	0
	2	0·0838	0	0·3962	0·9182
	3	0·0517	0	0·9182	−0·3962
F(1)	1	0·1702	1·0	0	0
	2	0·1142	0	0·9449	0·3275
	3	0·0485	0	−0·3275	0·9449

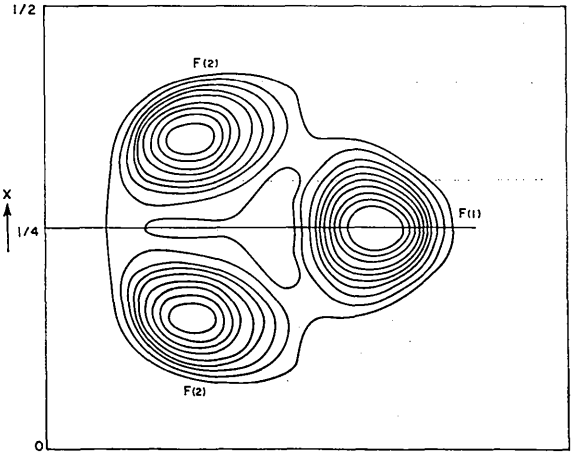


Fig. 2. Section of $\varrho(xyz)$ through the plane of the three fluorine atoms. The trace of the plane is the line AA in Fig. 1.

Table 3. *Final anisotropic temperature factors and estimated standard errors (in parentheses) (all values* × 10⁴*)*

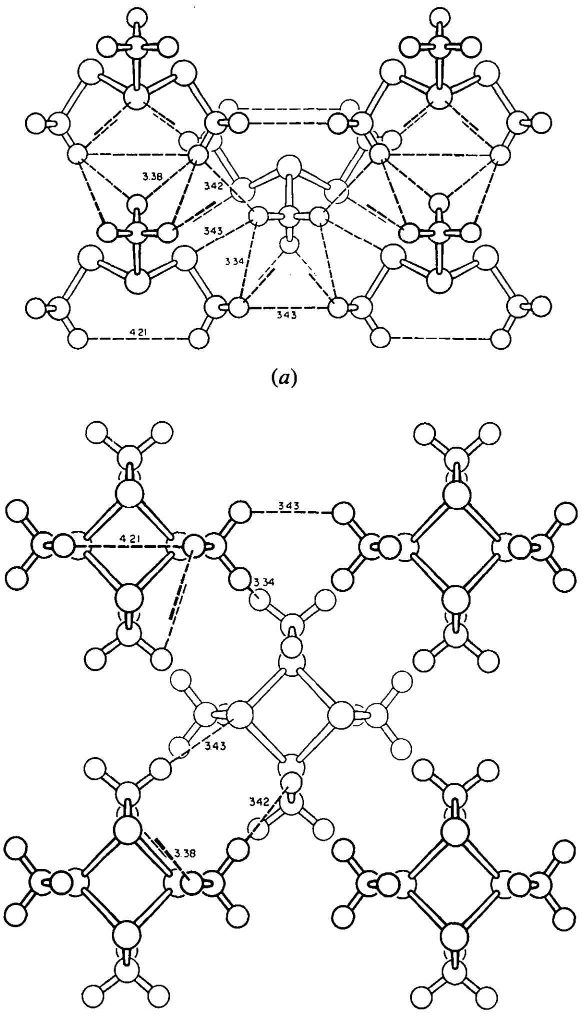
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
As	106 (2)	84 (2)	241 (5)			−10 (3)
C	189 (21)	104 (14)	370 (45)			64 (45)
F(1)	316 (21)	189 (15)	261 (21)			101 (33)
F(2)	248 (13)	280 (13)	681 (35)	284 (19)	152 (32)	448 (39)

Table 4 (*cont.*)

F(2)	1	0·2667	−0·5238	−0·6876	−0·5028
	2	0·1134	−0·6801	−0·0178	0·7329
	3	0·0514	−0·5129	−0·7259	−0·4583

The anisotropic motion of the fluorine atoms is seen in the drawing of the cross section of the three fluorine atoms, (Fig. 2). The trace of the three atoms is the line *AA* in the slice of the three-dimensional electron density function plotted in Fig. 1. It can be seen in Fig. 2 that the anisotropic motion of the fluorine atoms in the general position 16(*h*) is apparently more irregular than that of the fluorine atoms in the special position 8(*g*). In Fig. 1 the thermal motion of the arsenic atom is seen to be almost isotropic in nature, and the motion of the carbon and fluorine atoms is anisotropic.

The above results show that $(PCF_3)_4$ and $(AsCF_3)_4$ are isostructural, but the former was described with the origin on $\bar{4}$ rather than at $2/m$ as in the present case.



(*a*)

(*b*)

Fig. 3. The structure projected on (*a*) (010); (*b*) (001).

Discussion

Intramolecular distances and angles are shown in Table 5. The intramolecular contacts are shown in Fig. 3. The As–As bond distance of 2·454 ± 0·001 Å is in satisfactory agreement with the As–As distances of 2·428 ± 0·008 Å in $(AsCH_3)_5$ (Burns & Waser, 1957), of 2·456 ± 0·005 Å in $(AsC_6H_5)_6$ (Hedberg, Hughes & Waser, 1961), of 2·51 in metallic As by Bradley (1924), and of 2·44 in gaseous As_4 (Maxwell, Hendricks & Moseley, 1935).

Table 5. *Intramolecular distances and angles*

	d	*σ*
As—As	2·454 Å	0·001 Å
As—C	2·019	0·015
C—F(1)	1·264	0·018
C—F(II)	1·312	0·009
As—As-As	83·6°	0·1
As—As-C	94·4	0·3
As—C—F(I)	118·5	1·1
As—C—F(II)	109·0	0·8
F(I)—C—F(II)	106·7	0·9
F(II)-C—F(II)	106·4	1·2

As-As-As-As torsion angle: 36·8°.

The As–C distance of 2·012 ± 0·015 Å is comparable with As–C distances of 1·95 ± 0·02 Å in $(AsCH_3)_5$, and 1·97 ± 0·02 Å in $(AsC_6H_5)_6$. Even though the value of 2·012 Å is somewhat longer than the other two reported distances, these differences are only possibly significant.

The carbon–fluorine distances of 1·281 ± 0·018 Å for F(1) and 1·312 ± 0·009 Å for F(2) are shorter than the value of 1·334 ± 0·004 Å reported for the average distance of many polyfluorides (Sutton, 1958). The reason for this apparent discrepancy is probably due to librational motion of the fluorine atoms. In the phosphorus tetramer the two distances are, respectively, 1·326 ± 0·018 and 1·313 ± 0·010 Å.

The As–As–As–As torsion angle of 36·8° is comparable to the value of 35° for $(AsCH_3)_5$ and 34° for the phosphorus tetramer. The As–As–As bond angle of 83·6° is in good agreement with the 84·6° P–P–P bond angle of the $(PCF_3)_4$. It seems likely that the non-planarity of the ring in the tetramer is due largely to the relief of the Pitzer torsion strain, the equilibrium being attained by a balance between the energy loss due to increase in the torsion angle from 0°, and also the energy gain due to bond angle deformation. Fig. 3 shows that all intermolecular contacts less than 4·0 Å are fluorine–fluorine contacts.

This work was supported by the National Science Foundation and by the Advanced Research Projects Agency. We thank Dr C.-C. Tsai for carrying out the calculations on the Wilson statistics, Dr A. B. Burg for his patience and continuous supply of crystals, and Mrs Maryellin Reinecke for the drawings.

References

BRADLEY, A. J. (1924). *Phil. Mag.* **47**, 657.
BURNS, J. H. & WASER, J. (1957). *J. Amer. Chem. Soc.* **79**, 859.
COWLEY, A. H. & BURG, A. B. (1966). *J. Amer. Chem. Soc.* **88**, 3178.
HEDBERG, K., HUGHES, E. W. & WASER, J. (1961). *Acta Cryst.* **14**, 369.
MAHLER, W. & BURG, A. B. (1958). *J. Amer. Chem. Soc.* **80**, 6161.
MAXWELL, L. R., HENDRICKS, S. B. & MOSELEY, V. M. (1935). *J. Chem. Phys.* **3**, 699.
PALENIK, G. & DONOHUE, J. (1962). *Acta Cryst.* **15**, 564.
SUTTON, L. E. (1958). Ed. *Tables of Interatomic Distances and Configuration in Molecules and Ions*. London: The Chemical Society.

Acta Cryst. (1971). B**27**, 480

The Crystal Structures of Compounds Analogous to Magnus' Green Salt

BY M. ELISABETH CRADWICK, D. HALL* AND R. K PHILLIPS
Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada

(*Received* 26 *October* 1969 *and in revised form* 8 *May* 1970)

Tetra(methylamine)platinum(II) chloroplatinate(II) and tetra(ethylamine)platinum(II) bromoplatinate(II) are confirmed as being isostructural with Magnus' green salt, $Pt(NH_3)_4PtCl_4$. The dimensions of the tetragonal cells are $a=10{\cdot}32$, $c=6{\cdot}58$, and $a=12{\cdot}27$, $c=6{\cdot}71$ Å respectively; the space group is $P4/mnc$. Tetra(ethylamine)platinum(II) chloroplatinate(II) forms triclinic crystals, space group $P\bar{1}$, with $a=7{\cdot}56$, $b=9{\cdot}78$, $c=7{\cdot}24$ Å, $\alpha=98{\cdot}3°$, $\beta=113{\cdot}1°$, $\gamma=103{\cdot}4°$; it has a similar structure in that cation and anion alternate in chains, but the cation is non-planar and orbital overlap between adjacent platinum atoms is inhibited. The differing optical properties of this compound are thus explained. The variation in structure is ascribed to packing effects.

The crystal structure of Magnus' green salt, $Pt(NH_3)_4PtCl_4$ and hereafter MGS, comprises chains of square-planar cations and anions stacked directly over one another, with a Pt–Pt separation of 3.26Å (Atoji, Richardson & Rundle, 1957). Both the green colour and the dichroism exhibited by these crystals are distinct from those characteristic of the constituent ions (Yamada, 1951), and have been attributed to weak metal–metal bonding. The compound $Pt(NH_2CH_3)_4PtCl_4$ is also green and similar in dichroism to MGS, but the analogues with higher amines are pink, and show only the dichroism of the chloroplatinate(II) ion. The methylamine compound is similar in powder diffraction pattern to MGS, whereas the ethylamine compound is not (Miller, 1961), and it has been assumed that steric effects inhibit the chain structure and thus prevent the metal–metal bond interaction. Subsequently it has been shown (Yamada, 1962, 1965) that crystals of $Pt(amine)_4PtBr_4$ and $Pt(amine)_4PtI_4$ are all abnormally coloured and dichroic, whether amine be ammonia, methylamine, ethylamine or various higher amines. This clearly indicated that the difference in structure of the higher amine chloroplatinates(II) is not caused by intra-chain steric interference, and Yamada (1965) suggested that it may be due to a weakening influence of the chlorine ligand on the metal–metal bond. This view is not supported by reflectance spectra studies (Miller, 1965), nor indeed by Yamada's own single-crystal spectra, from which it is apparent that the band shifts are less and not greater in bromoplatinates(II) *vis-à-vis* chloroplatinates(II). Further, the compounds $Pt(NH_3)_4PtCl_4$, $Pt(NH_3)_4PdCl_4$, $Pd(NH_3)_4PtCl_4$ and $Pd(NH_3)_4PdCl_4$ show varying spectral shifts, yet all have the MGS structure, with the same metal–metal separation (Miller, 1961, 1965). It appears that chemical variations affect the optical phenomena far more than the crystal structure, and the difference in behaviour of tetra(ethylamine)platinum(II) chloroplatinate(II) remains anomalous. We have examined crystals of several of these compounds in an attempt to elucidate this problem.

In each case, compounds were prepared by mixing solutions containing the constituent ions.

Tetra(methylamine)platinum(II) chloroplatinate(II)

Green tetragonal needles gave $a=10{\cdot}32\pm0{\cdot}02$, $c=6{\cdot}58\pm0{\cdot}02$ Å, $\varrho_{obs}=3{\cdot}12$, $\varrho_{calc}=3{\cdot}11$ g.cm^{-3} for two molecules of $Pt(NH_2CH_3)_4PtCl_4$ per unit cell. Reflexions were systematically absent for $0kl$ with $k+l$ odd, and for hhl with l odd, and were systematically weak for hkl either with l odd or with l even, $h+k$ odd. These observations give the space group as either $P4/mnc$ or $P4nc$, and indicate that the platinum atoms occupy the positions of twofold multiplicity $0,0,0;\frac{1}{2},\frac{1}{2},\frac{1}{2}$ and $0,0,\frac{1}{2};\frac{1}{2},\frac{1}{2},0$. The structure was thus confirmed as essentially similar to that of MGS, for which the pattern

---

* Present address: Chemistry Department, University of Auckland, Private Bag, Auckland, New Zealand.