Discussion. La caractéristique la plus intéressante de cet arrangement atomique est l'existence d'un anion complexe tridimensionnel $Be_2P_3O_{10}$ formé de tétraèdres PO_4 et BeO_4. On peut le décrire de la manière suivante: des groupements P_3O_{10} sensiblements alignés selon la direction **a** dans des plans situés en $z = \frac{1}{4}$ et $\frac{3}{4}$ sont reliés entre eux par l'intermédiaire des tétraèdres BeO_4 qui en assurent la liaison à la fois dans les plans et entre les plans. La Fig. 1 donne une représentation de cet anion en projection selon **b**. La Fig. 2 donne une représentation en projection selon **c** mettant en évidence la position des ions ammonium dans des canaux dirigés selon la direction **c**.

Le Tableau 3 donne les principales distances interatomiques et angles de liaison dans cet arrangement. Le Tableau 4 donne les amplitudes et les directions des axes principaux des ellipsoïdes thermiques.

Référence

BAGIEU-BEUCHER, M., DURIF, A. & AVERBUCH-POUCHOT, M. T. (1976). *J. Appl. Cryst.* **9**, 52.

Acta Cryst. (1977). B**33**, 205–207

Diiodotricarbonylbis(diphenylarsino)methanetungsten(II)

BY MICHAEL G. B. DREW AND ANDREW P. WOLTERS

Department of Chemistry, The University, Whiteknights, Reading RG6 2AD, England

(*Received* 1 *June* 1976; *accepted* 19 *July* 1976)

Abstract. $C_{28}H_{22}As_2I_2O_3W$, $M_r = 994{\cdot}0$, monoclinic, $a = 11{\cdot}281\,(5)$, $b = 16{\cdot}880\,(6)$, $c = 16{\cdot}519\,(6)$ Å, $\beta = 111{\cdot}51\,(20)°$, $U = 2926{\cdot}5$ Å^3, $d_m = 2{\cdot}23\,(3)$, $Z = 4$, $d_c = 2{\cdot}23$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, μ (Mo $K\alpha$) = 86·2 cm^{-1}, space group $P2_1/c$ from systematic absences $0k0$: $k = 2n + 1$, $h0l$: $l = 2n + 1$. In the monomeric complex, the W atom is seven-coordinate with a capped octahedral environment and is bonded to one carbonyl group in the capping position [1·93 (2) Å], two carbonyls [1·96 (2), 1·93 (2) Å] and one As atom [2·605 (3) Å] in the capped face, and two I atoms [2·859 (2), 2·830 (2) Å] and an As atom [2·680 (2) Å] in the uncapped face. 2312 independent reflexions, measured by counter methods, have been refined to R 0·058.

Introduction. Crystals of $WI_2(CO)_3$(dpam), dpam = bis(diphenylarsino)methane, were prepared as described by Colton & Rix (1970). A crystal with dimensions *ca* 0·2 × 0·1 × 0·1 mm was mounted with **c*** parallel to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. It was equipped with a manual goniostat, scintillation counter and pulse-height discriminator. Mo X-radiation was used, filtered with Zr. 3832 reflexions with $2\theta < 45°$ were measured by the stationary-crystal stationary-counter method of which 2312 with $I > 2\sigma\,(I)$ were used in subsequent calculations. An absorption correction was applied to the data (Stewart, 1972).

The structure was solved from the Patterson function and successive Fourier syntheses. Refinement by full-matrix least squares gave R 0·058. W, I and As atoms were refined anisotropically and C and O isotropically. In the final cycle of refinement no shift was $>0{\cdot}10\sigma$. Final positions are listed in Table 1 and the thermal parameters in Table 2. The weighting scheme which was chosen to give average values of $w\Delta^2$ for groups of reflexions independent of values of F_o and $\sin\theta/\lambda$ was $\sqrt{w} = 1$ for $F_o < 43$ and $43/F_o$ for $F_o > 43$. Calculations were performed on a CDC 7600 computer at the University of London Computer Centre with the X-RAY system (Stewart, 1972). Atomic scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1974) as were the corrections for the real and imaginary parts of the anomalous dispersion for the W, I and As. The anisotropic thermal parameters are defined as $\exp(-2\pi^2 \sum_i \sum_j U_{ij}\, h_i\, h_j\, b_i\, b_j)$ $(i,j = 1,2,3)$, where b_i is the ith reciprocal cell dimension. The isotropic thermal parameters are defined as $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)$. The unobserved reflexions showed no large discrepancies and a final difference Fourier map showed no significant peaks. The molecular dimensions are listed in Table 3.*

Discussion. The structure of $WI_2(CO)_3$(dpam) is shown in Fig. 1. The W atom is seven-coordinate in a capped

---

* Lists of structure factors and phenyl ring dimensions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31996 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

octahedral environment with C(1) in the capping position, C(2), C(3) and As(1) in the capped face and As(2), I(1), I(2) in the uncapped face. The arrangement of atoms in the coordination sphere is in accord with a number of similar structures reviewed by Drew (1977) including $MoBr_2(CO)_3(dppe)$, dppe = bis(diphenylphosphino)ethane (Drew, 1972*b*), $MoBr_2(CO)_2(dpam)_2$ (Drew, 1972*a*) and $WI_2(CO)_3(dmpe)$, dmpe = bis(dimethylphosphino)ethane (Drew & Rix, 1975). As in these other compounds the geometry of the present complex is distorted from the ideal C_{3v} symmetry by the chelate ring. In the four-membered ring, the As—W—As angle is 67·2 (1)° compared with an angle of 77° usually found for this edge in the capped octahedron. Only one other angle of this type is significantly different from the mean, *viz* C(2)—W—As(2) at 85·8 (5)°. This enlargement is necessary to ensure a reasonable C(2)···C(21) distance, the C(2)—W—As(2)—C(21) torsion angle being −14·8°. This also occurs in other capped octahedra and Drew & Rix (1975) have shown that this small torsion angle is a necessary consequence of the orientation of atoms with respect to the W—As(2) bond, it being impossible for the four atoms at W and the three C atoms at As to be staggered without one torsion angle being close to 0°. The other angles in the coordination sphere are very similar to the expected values (Drew, 1977).

The W—I bond lengths [2·859 (2), 2·830 (2) Å] are similar to those usually found in this geometry. Ten independent values between 2·859 (3) and 2·885 (3) Å were found for the five molecules of $WI_2(CO)_3(dmpe)$ (Drew & Rix, 1975). It is not apparent why the W—I(2) bond is significantly shorter than these values although

Table 1. *Final positional coordinates* (×10⁴) *and isotropic thermal parameters* (×10³), *with estimated standard deviations in parentheses*

	x	*y*	*z*	*U*
W	2097 (1)	1623 (1)	−0128 (1)	
I(1)	2341 (2)	3275 (1)	−0414 (1)	
I(2)	4078 (2)	1335 (1)	−0754 (1)	
As(1)	1018 (2)	2268 (1)	0860 (1)	
As(2)	3754 (2)	1949 (1)	1477 (1)	
C(1)	0493 (20)	1099 (12)	−0332 (13)	32 (5)
O(1)	−0464 (18)	0745 (11)	−0558 (12)	63 (5)
C(2)	2562 (19)	0512 (12)	0160 (13)	29 (5)
O(2)	2807 (16)	−0139 (10)	0346 (11)	51 (4)
C(3)	1180 (25)	1709 (16)	−1369 (17)	56 (7)
O(3)	0636 (20)	1740 (13)	−2145 (14)	79 (6)
C(4)	2569 (22)	2605 (13)	1797 (14)	38 (5)
C(11)	5242 (22)	2610 (14)	1737 (15)	43 (6)
C(12)	5768 (27)	2848 (17)	2628 (18)	62 (7)
C(13)	6851 (33)	3392 (21)	2850 (22)	84 (10)
C(14)	7357 (35)	3593 (22)	2276 (24)	89 (10)
C(15)	6817 (33)	3355 (21)	1406 (23)	84 (9)
C(16)	5708 (25)	2847 (16)	1136 (17)	55 (7)
C(21)	4384 (22)	1113 (13)	2341 (15)	40 (5)
C(22)	5061 (24)	0520 (15)	2141 (16)	51 (6)
C(23)	5599 (29)	−0137 (17)	2730 (20)	69 (6)
C(24)	5262 (28)	−0135 (17)	3465 (18)	62 (7)
C(25)	4637 (27)	0440 (17)	3690 (18)	61 (7)
C(26)	4131 (23)	1076 (14)	3098 (16)	47 (6)
C(31)	0112 (19)	1579 (13)	1348 (13)	32 (5)
C(32)	0683 (26)	0869 (15)	1779 (17)	52 (6)
C(33)	−0002 (30)	0386 (19)	2152 (21)	73 (9)
C(34)	−1163 (31)	0600 (21)	2152 (20)	76 (9)
C(35)	−1635 (31)	1257 (27)	1813 (28)	111 (13)
C(36)	−0997 (33)	1819 (21)	1367 (22)	86 (10)
C(41)	−0088 (21)	3155 (13)	0469 (14)	38 (5)
C(42)	0097 (23)	3861 (15)	0937 (16)	46 (6)
C(43)	−0712 (28)	4501 (17)	0619 (19)	65 (8)
C(44)	−1818 (25)	4440 (16)	−0172 (17)	55 (7)
C(45)	−1968 (29)	3724 (18)	−0673 (19)	67 (8)
C(46)	−1100 (25)	3093 (16)	−0307 (17)	55 (7)

Table 2. *Anisotropic thermal parameters* (×10³)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	42·8 (6)	27·6 (5)	30·0 (5)	0·3 (4)	17·7 (4)	−0·6 (4)
I(1)	70 (1)	34 (1)	67 (1)	2 (1)	38 (1)	11 (1)
I(2)	79 (1)	65 (1)	76 (1)	5 (1)	55 (1)	−3 (1)
As(1)	36 (1)	24 (1)	34 (1)	3 (1)	15 (1)	0 (1)
As(2)	36 (1)	30 (1)	30 (1)	2 (1)	15 (1)	−1 (1)

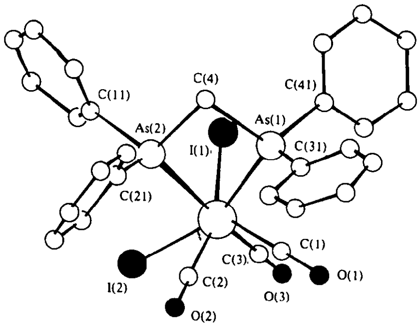

Fig. 1. The structure with atom numbering.

Table 3. *Molecular dimensions*

W—I(1)	2·859 (2) Å	C(1)—W—C(2)	75·8 (9)°
W—I(2)	2·830 (3)	C(1)—W—C(3)	75·3 (11)
W—As(1)	2·605 (3)	C(1)—W—As(1)	71·2 (7)
W—As(2)	2·680 (2)	C(1)—W—I(1)	124·0 (6)
W—C(1)	1·93 (2)	C(1)—W—I(2)	132·3 (7)
W—C(2)	1·96 (2)	C(1)—W—As(2)	122·4 (6)
W—C(3)	1·93 (3)	C(2)—W—C(3)	108·7 (10)
C(1)—O(1)	1·17 (3)	C(2)—W—As(1)	113·2 (7)
C(2)—O(2)	1·15 (3)	C(2)—W—I(1)	160·2 (6)
C(3)—O(3)	1·20 (3)	C(2)—W—I(2)	75·4 (7)
As(1)—C(4)	1·95 (2)	C(2)—W—As(2)	85·8 (5)
As(1)—C(31)	1·91 (2)	C(3)—W—As(1)	116·2 (9)
As(1)—C(41)	1·90 (2)	C(3)—W—I(1)	78·4 (8)
As(2)—C(4)	1·96 (3)	C(3)—W—I(2)	79·1 (9)
As(2)—C(11)	1·93 (2)	C(3)—W—As(2)	160·3 (8)
As(2)—C(21)	1·94 (2)	As(1)—W—I(1)	77·9 (1)
W—C(1)—O(1)	171 (2)°	As(1)—W—I(2)	156·1 (1)
W—C(2)—O(2)	178 (2)	As(1)—W—As(2)	67·2 (1)
W—C(3)—O(3)	178 (3)	I(1)—W—I(2)	88·3 (1)
W—As(1)—C(4)	97 (1)	I(1)—W—As(2)	83·8 (1)
W—As(1)—C(31)	117 (1)	I(2)—W—As(2)	92·2 (1)
W—As(1)—C(41)	121 (4)	C(31)—As(1)—C(41)	104 (1)
W—As(2)—C(4)	95 (1)	C(31)—As(1)—C(4)	108 (1)
W—As(2)—C(11)	125 (1)	C(41)—As(1)—C(4)	109 (1)
W—As(2)—C(21)	121 (1)	C(11)—As(2)—C(21)	102 (1)
As(1)—C(4)—As(2)	97 (1)	C(11)—As(2)—C(4)	104 (1)
		C(21)—As(2)—C(4)	108 (1)

Table 4. *Torsion angles* (°)

(*a*) Of the type *i*—W—As—C where the *i*—W—As angle is < 100°

I(1)—W—As(2)—C(4)	67·1	I(1)—W—As(1)—C(4)	−75·7
I(1)—W—As(2)—C(11)	−43·0	I(1)—W—As(1)—C(31)	169·8
I(1)—W—As(2)—C(21)	−178·0	I(1)—W—As(1)—C(41)	41·8
I(2)—W—As(2)—C(4)	155·2	As(2)—W—As(1)—C(4)	12·6
I(2)—W—As(2)—C(11)	45·0	As(2)—W—As(1)—C(31)	−102·0
I(2)—W—As(2)—C(21)	−90·0	As(2)—W—As(1)—C(41)	130·1
C(2)—W—As(2)—C(4)	−129·7	C(1)—W—As(1)—C(4)	151·7
C(2)—W—As(2)—C(11)	120·2	C(1)—W—As(1)—C(31)	37·2
C(2)—W—As(2)—C(21)	−14·8	C(1)—W—As(1)—C(41)	−90·8
As(1)—W—As(2)—C(4)	−12·5		
As(1)—W—As(2)—C(11)	−122·6		
As(1)—W—As(2)—C(21)	102·5		

(*b*) The minimum torsion angle about each As—C(*n*1) bond

W—As(2)—C(11)—C(16)	−13·1	C(41)—As(1)—C(31)—C(36)	−2·6
C(4)—As(2)—C(21)—C(26)	−7·1	C(4)—As(1)—C(41)—C(42)	−13·8

I(2) is *trans* to As while I(1) is *trans* to carbonyl. A similar difference (of 0·024 Å) is found for Mo—Br bonds in MoBr$_2$(CO)$_2$(dpam)$_2$ (Drew, 1972*a*). The W—As(1) bond is significantly shorter than the W—As(2) bond [2·605 (3), 2·680 (2) Å] and, as in other compounds, this can be related to the *trans* effect of C(3), weakening the π overlap between W and As(2).

The four-membered ring is non-planar, C(4) being 0·42 Å from the plane of W, As(1), As(2); this is less than the distance of 0·60 Å found in MoBr$_2$(CO)$_2$(dpam)$_2$ (Drew, 1972*a*). The orientations of the four phenyl rings are illustrated by the torsion angles quoted in Table 4. Intermolecular contacts are as expected for the normal van der Waals contacts but there are three, not involving H, that are less than 3·20 Å [*viz* O(2)···O(1) ($\bar{x},\bar{y},\bar{z}$) 2·97; O(1)···O(1) ($\bar{x},\bar{y},\bar{z}$) 3·07 and O(3)···C(42) ($x, \frac{1}{2}-y, \frac{1}{2}+z$) 3·17 Å].

We are grateful to the University of Reading for a studentship (APW) and to C. J. Rix for providing the crystals.

References

Colton, R. & Rix, C. J. (1970). *Aust. J. Chem.* **23**, 441–449.

Drew, M. G. B. (1972*a*). *J. Chem. Soc. Dalton*, pp. 626–631.

Drew, M. G. B. (1972*b*). *J. Chem. Soc. Dalton*, pp. 1329–1333.

Drew, M. G. B. (1977). *Progr. Inorg. Chem.* In the press.

Drew, M. G. B. & Rix, C. J. (1975). *J. Organomet. Chem.* **102**, 467–480.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Stewart, J. M. (1972). X-RAY system of programs, Univ. of Maryland Technical Report TR-192.