Table 2. *Selected interatomic distances* (Å) *and bond angles* (°)

Au—Cl	2·281 (3)	Au—P	2·243 (2)
P—C(11)	1·840 (9)	P—C(21)	1·815 (8)
P—C(31)	1·835 (8)		
Cl—Au—P	179·4 (1)	Au—P—C(11)	114.5 (3)
Au—P—C(21)	112·8 (3)	Au—P—C(31)	114·2 (3)
C(11)—P—C(21)	104·7 (4)	C(11)—P—C(31)	104·1 (4)
C(21)—P—C(31)	105·6 (4)		

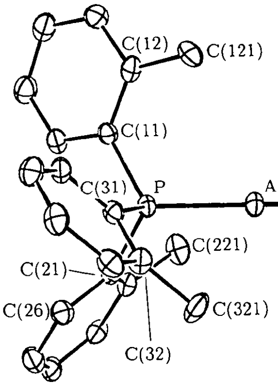

Fig. 1. Molecular structure and numbering scheme for [$(C_{21}H_{21}P)AuCl$] (Johnson, 1971).

Fig. 1 which is drawn with *ORTEP* (Johnson, 1971) with 25% probability ellipsoids.

Related literature. As expected from cone-angle considerations (Tolman, 1977), the Au—P and Au—Cl bond distances in [(*o*-tolyl)$_3$PAuCl] with a cone angle of 194° are comparable to those found for [(cyclohexyl)$_3$PAuCl] of 2·242 (4) and 2·279 (5) Å with a cone angle of 170° (Muir, Muir, Pulgar, Jones & Sheldrick, 1985). In contrast, [(Et)$_3$PAuCl], with a cone angle of 132°, has Au—P and Au—Cl of 2·232 (9) and 2·305 (8) Å, respectively (Tiekink, 1989).

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References

Al-Saády, A. K., McAuliffe, C. A., Parish, R. V. & Sandbank, J. A. (1985). *Inorg. Synth.* **23**, 191–194.
Boer, J. L. de & Duisenberg, A. J. M. (1984). Enraf-Nonius CAD-4F diffractometer software update. February 1984. Groningen and Utrecht, The Netherlands.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Muir, J. A., Muir, M. M., Pulgar, L. B., Jones, P. G. & Sheldrick, G. M. (1985). *Acta Cryst.* **C41**, 1174–1176.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Tiekink, E. R. T. (1989). *Acta Cryst.* **C45**, 1233–1234.
Tolman, C. A. (1977). *Chem. Rev.* **77**, 313–348.

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Structure of a New Iodobismuthate: Tetra(*n*-butyl)ammonium 1,2;1,2;1,2;2,3;2,3;2,3-Hexa-μ-iodo-1,1,1,3,3,3-hexaiodotribismuthate(III) (3:1)

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Abstract. $(C_{16}H_{36}N)_3Bi_3I_{12}$, $M_r = 2877·20$, monoclinic, $P2_1/c$, $a = 17·796$ (4), $b = 20·565$ (6), $c = 23·414$ (8) Å, $\beta = 100·25$ (2)°, $V = 8432$ (4) Å^3, $Z = 4$, $D_x = 2·266$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 10·61$ mm^{-1}, $F(000) = 5208$, room temperature, final $R = 0·140$ for 4850 independent observed reflections with $F_o > 3\sigma(F_o)$. The compound contains a novel $Bi_3I_{12}^{3-}$ anion, consisting of three face-sharing [BiI_6] octahedra. The bridging Bi—I bond lengths average 3·078 Å (inner Bi atom) and 3·330 Å (outer Bi atoms), whereas the bonds to terminal I atoms average 2·910 Å. Bond-length constraints were applied to the refinement of the tetrabutylammonium cation C atoms.

Experimental. Orange, plate-like needles were prepared from equimolar amounts of [$(n\text{-}C_4H_9)_4N$]I and BiI_3, dissolved in hot absolute ethanol, by slow cooling. One of the largest available crystals (0·008 × 0·13 × 0·59 mm) was mounted on a Nicolet *P*3/*F* four-circle diffractometer with graphite monochromator. ω-scan data, 0·9° width, 2–8° min^{-1}, $2\theta < 45°$, $(\sin\theta)/\lambda < 0·538$ Å^{-1} (no observed diffracted intensity beyond that), h: 0 to 19, k: 0 to 22, l: −25

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to 24; lattice parameters from 25 centered reflections, $18 < 2\theta < 22°$. 12 086 reflections collected (two standards, intensities corrected for gradual decay to *ca* 80% of original values); 1115 duplicates or equivalents averaged, $R_{\rm int} = 0{\cdot}050$ (on F); 11 021 unique and allowed by space group; 4850 observed with $F_o > 3\sigma(F_o)$; corrected for Lorentz–polarization and absorption (Gaussian integration; min., max. transmission factors 0·35–0·91). Computer programs supplied by Strouse (1985) and Sheldrick (1976), scattering factors (including anomalous-dispersion contributions) from *International Tables for X-ray Crystallography* (1974).

Structure solved by direct methods (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and completed by Fourier methods. Initially, unconstrained full-matrix least-squares refinement (Strouse, 1985) of 336 variable parameters, based on $|F_o|$. Bi and I atoms refined with anisotropic thermal parameters. Due to the presence of elements with very large atomic number (96·5% of the scattering power is in the anion), and large thermal motion in the tetrabutylammonium cation, C and N atoms were refined isotropically. Even so, free refinement of all carbon atomic coordinates did not converge stably. Therefore, bond-length constraints were applied, d(C—N) = 1·48 (1) and d(C—C) = 1·54 Å with allowed tolerances of 0·01, 0·02 and 0·03 Å, respectively, for successive C—C bonds starting near the center of the molecule, C atom thermal parameters were required to be equal for every four C atoms located an equal number of bonds away from the central N atom, and the 306 variables of the constrained model were refined using program *SHELX76* (Sheldrick, 1976). No H atoms were located. $(\Delta/\sigma)_{\max} = 0{\cdot}10$ in final cycle, with $R = 0{\cdot}140$, $wR = 0{\cdot}082$, $S = 1{\cdot}65$. $w = 1/\sigma^2(F_o)$ and $\sigma(F_o) = [\sigma^2(F_o^2) + (0{\cdot}02F_o^2)^2]^{1/2}/(2F_o)$, with $\sigma(F_o^2)$ based on counting statistics. Largest peaks (3 and -2 e Å^{-3}) on difference Fourier map in the vicinity of Bi atoms. No correction for extinction. Final atomic positions and isotropic (or equivalent isotropic) thermal parameters are given in Table 1.* Relevant geometrical results are listed in Table 2, and a picture of the $Bi_3I_{12}^{3-}$ anion is shown in Fig. 1.

Table 1. *Anion atomic coordinates and equivalent isotropic* (*isotropic for* N1–3) *thermal parameters in* $[(n\text{-}C_4H_9)_4N]_3Bi_3I_{12}$

$$U_{\rm eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å^2 × 10^3)
Bi1	0·4182 (2)	0·2257 (1)	0·3641 (1)	65 (1)
Bi2	0·6437 (2)	0·2401 (1)	0·4507 (1)	62 (1)
Bi3	0·8683 (2)	0·2652 (1)	0·5317 (1)	69 (1)
I1	0·3469 (4)	0·3351 (2)	0·2959 (2)	104 (3)
I2	0·2985 (3)	0·2068 (2)	0·4308 (2)	120 (3)
I3	0·3666 (3)	0·1295 (2)	0·2762 (2)	106 (3)
I4	0·5130 (3)	0·3305 (2)	0·4582 (2)	92 (2)
I5	0·5314 (3)	0·1235 (2)	0·4538 (3)	78 (2)
I6	0·5915 (3)	0·2340 (2)	0·3203 (2)	91 (2)
I7	0·7823 (3)	0·1461 (2)	0·4539 (2)	82 (2)
I8	0·7095 (3)	0·2543 (2)	0·5842 (2)	81 (2)
I9	0·7501 (3)	0·3509 (2)	0·4350 (2)	86 (2)
I10	0·9560 (4)	0·1805 (3)	0·6174 (2)	129 (3)
I11	0·9861 (3)	0·2772 (3)	0·4587 (2)	116 (3)
I12	0·9120 (3)	0·3869 (2)	0·5947 (2)	107 (3)
N1	0·511 (3)	0·097 (3)	0·650 (2)	91 (18)
N2	0·205 (3)	0·411 (3)	0·492 (2)	109 (20)
N3	0·090 (4)	0·649 (3)	0·209 (3)	126 (22)

Table 2. *Interatomic distances* (Å) *and angles* (°) *of the* $Bi_3I_{12}^{3-}$ *anion in* $[(n\text{-}C_4H_9)_4N]_3Bi_3I_{12}$

Bi1···Bi2	4·173 (4)	Bi2—I6	3·030 (5)
Bi2···Bi3	4·140 (4)	Bi2—I7	3·124 (5)
Bi1—I1	2·916 (5)	Bi2—I8	3·151 (5)
Bi1—I2	2·883 (6)	Bi2—I9	3·026 (5)
Bi1—I3	2·885 (5)	Bi3—I7	3·267 (5)
Bi1—I4	3·320 (5)	Bi3—I8	3·284 (5)
Bi1—I5	3·373 (5)	Bi3—I9	3·312 (5)
Bi1—I6	3·423 (6)	Bi3—I10	2·894 (6)
Bi2—I4	3·008 (6)	Bi3—I11	2·942 (5)
Bi2—I5	3·131 (5)	Bi3—I12	2·939 (5)

I1—Bi1—I2	96·3 (2)	I6—Bi2—I9	89·7 (1)
I1—Bi1—I3	95·0 (2)	I7—Bi2—I8	83·2 (1)
I1—Bi1—I4	89·0 (1)	I7—Bi2—I9	87·8 (1)
I1—Bi1—I5	167·2 (2)	I8—Bi2—I9	85·5 (1)
I1—Bi1—I6	97·1 (2)	I7—Bi3—I8	79·0 (1)
I2—Bi1—I3	97·0 (2)	I7—Bi3—I9	80·8 (1)
I2—Bi1—I4	93·8 (2)	I7—Bi3—I10	94·4 (2)
I2—Bi1—I5	89·8 (1)	I7—Bi3—I11	92·9 (1)
I2—Bi1—I6	163·9 (2)	I7—Bi3—I12	167·0 (2)
I3—Bi1—I4	168·0 (2)	I8—Bi3—I9	78·9 (1)
I3—Bi1—I5	95·5 (1)	I8—Bi3—I10	95·4 (2)
I3—Bi1—I6	90·6 (2)	I8—Bi3—I11	166·7 (2)
I4—Bi1—I5	79·3 (1)	I8—Bi3—I12	92·2 (2)
I4—Bi1—I6	77·7 (1)	I9—Bi3—I10	173·1 (2)
I5—Bi1—I6	75·4 (1)	I9—Bi3—I11	89·4 (2)
I4—Bi2—I5	88·2 (1)	I9—Bi3—I12	88·2 (1)
I4—Bi2—I6	89·0 (1)	I10—Bi3—I11	95·8 (2)
I4—Bi2—I7	175·3 (2)	I10—Bi3—I12	95·9 (2)
I4—Bi2—I8	92·3 (1)	I11—Bi3—I12	93·9 (2)
I4—Bi2—I9	92·8 (1)	Bi1—I4—Bi2	82·3 (1)
I5—Bi2—I6	84·8 (1)	Bi1—I5—Bi2	79·7 (1)
I5—Bi2—I7	91·7 (1)	Bi1—I6—Bi2	80·3 (1)
I5—Bi2—I8	100·0 (1)	Bi2—I7—Bi3	80·7 (1)
I5—Bi2—I9	174·4 (1)	Bi2—I8—Bi3	80·1 (1)
I6—Bi2—I7	95·6 (1)	Bi2—I9—Bi3	81·4 (1)
I6—Bi2—I8	175·1 (2)		

Even though the agreement factors are somewhat high, the $Bi_3I_{12}^{3-}$ anion is well defined in its chemical connectivity (the principal aim of this study) and its bond lengths and angles, in this structure determination, regardless of the exact model used for the counter cations. The tetrabutylammonium cations are severely affected by high thermal motion, and many parameters are necessary to model reasonably the electron density in that area of the unit cell. It was outside the interest of our research program to determine precise geometrical information of the

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* Lists of anisotropic thermal parameters, tetrabutylammonium C-atom coordinates, bond angles of the tetrabutylammonium cations and structure factors, and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52823 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

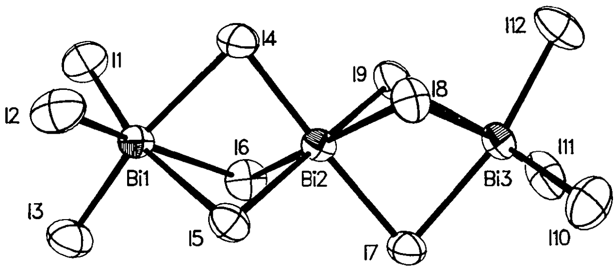

Fig. 1. The $Bi_3I_{12}^{3-}$ anion in $[(n\text{-}C_4H_9)_4N]_3Bi_3I_{12}$. The thermal ellipsoids are drawn at the 50% probability level.

tetrabutylammonium cation, as there are numerous examples in the literature. Otherwise, data would have been collected at cryogenic temperatures. Other factors contributing to the high R values (and residual difference density near the heavy atoms) include a low ($\sin\theta/\lambda$) cut-off due to the extremely small plate thickness of the crystals available, resulting in Fourier series truncation problems.

Related literature. The title compound was prepared as an intermediate in the synthesis of the organic conductor (BEDT-TTF)BiI_4 (Geiser, Wang, Budz, Lowry, Williams, Ren & Whangbo, 1990) [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene, $C_{10}H_8S_8$] as part of an ongoing search for organic superconductors (Williams, Wang, Emge, Geiser, Beno, Leung, Carlson, Thorn, Schultz & Whangbo, 1987). The main interest of the current structure determination was the identification of the bismuth iodide anion species in this intermediate product. During the electrocrystallization of (BEDT-TTF)BiI_4, the anion rearranges to form an infinite, edge-sharing chain of [BiI_6] octahedra (Geiser *et al.*, 1990). The $Bi_3I_{12}^{3-}$ anion has not previously been observed in a crystal structure. However, a dimeric analogue, $Bi_2I_9^{3-}$, exists in $Cs_3Bi_2I_9$ (Lindqvist, 1968) and $[N(CH_3)_4]_3Bi_2I_9$ (Lazarini, 1980).

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References

Geiser, U., Wang, H. H., Budz, S. M., Lowry, M. J., Williams, J. M., Ren, J. & Whangbo, M.-H. (1990). *Inorg. Chem.* **29**, 1611–1614.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Lazarini, F. (1980). *Cryst. Struct. Commun.* **9**, 815–819.

Lindqvist, O. (1968). *Acta Chem. Scand.* **22**, 2943–2952.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Strouse, C. (1985). *UCLA Crystallographic Package.* Univ. of California, Los Angeles, USA.

Williams, J. M., Wang, H. H., Emge, T. J., Geiser, U., Beno, M. A., Leung, P. C. W., Carlson, K. D., Thorn, R. J., Schultz, A. J. & Whangbo, M.-H. (1987). *Prog. Inorg. Chem.* **35**, 51–218.

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{Bis[2-(diphenylphosphino)ethyl]phenylphosphine}chloropalladium(II) Chloride

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Abstract. $[Pd(C_{34}H_{33}P_3)Cl]^+.Cl^-$, $M_r = 711{\cdot}88$, monoclinic, $P2_1/n$, $a = 10{\cdot}248$ (2), $b = 20{\cdot}520$ (4), $c = 15{\cdot}833$ (3) Å, $\beta = 95{\cdot}81$ (1)°, $V = 3312$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}428$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 8{\cdot}73$ cm^{-1}, $F(000) = 1448$, $T = 296$ K, $R = 5{\cdot}17$% for 3561 unique reflections with $F_o \geq 5\sigma(F_o)$ and 311 parameters. The Pd atom has a distorted square-planar geometry formed by the three P atoms of the chelating triphosphine and a Cl atom, with the angles subtending Pd ranging from 83·8 (1) to

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