

Tetragonal

*P*4₂*c**a* = 15.747 (1) Å*c* = 13.148 (1) Å*V* = 3260.3 (4) Å³*Z* = 2*D*_x = 1.268 Mg m⁻³*D*_m not measured

Cell parameters from 35 reflections

 $\theta = 24.7\text{--}25.0^\circ$ $\mu = 0.492\text{ mm}^{-1}$ *T* = 173 (2) K

Prism

0.80 × 0.70 × 0.46 mm

Colorless

SHELXL93. Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1313). Services for accessing these data are described at the back of the journal.

Data collection

Siemens diffractometer

 ω scan

Absorption correction: none

12 559 measured reflections

3237 independent reflections

2777 reflections with

 $I > 2\sigma(I)$ *R*_{int} = 0.046 $\theta_{\text{max}} = 32.50^\circ$ *h* = -23 → 23*k* = -23 → 23*l* = 0 → 19

4 standard reflections

every 96 reflections

intensity decay: 2%

Refinement

Refinement on *F*² $R[F^2 > 2\sigma(F^2)] = 0.035$ $wR(F^2) = 0.089$ *S* = 1.06

3237 reflections

181 parameters

H atoms not refined

 $w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.5476P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = -0.04$ $\Delta\rho_{\text{max}} = 0.29\text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.27\text{ e \AA}^{-3}$

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0125 (10)

Scattering factors from

International Tables for Crystallography (Vol. C)

Absolute structure: Flack

(1983)

Flack parameter = 0.00 (3)

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Acta Cryst. (1998). **C54**, 476–479Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Mn	0	0	0	0.02046 (12)
Cl2	-0.11804 (3)	-0.05617 (4)	0.08839 (5)	0.03157 (13)
C1	0.34898 (15)	-0.09177 (14)	-0.2155 (2)	0.0273 (4)
C2	0.3723 (2)	-0.17418 (15)	-0.1616 (2)	0.0353 (5)
C3	0.3048 (2)	-0.1993 (2)	-0.0846 (2)	0.0415 (6)
C4	0.2916 (2)	-0.1269 (2)	-0.0101 (2)	0.0366 (5)
C5	0.26981 (14)	-0.04437 (15)	-0.0645 (2)	0.0293 (5)
C6	0.32578 (12)	0.06796 (13)	-0.19102 (14)	0.0193 (3)
C7	0.31490 (13)	0.13391 (13)	-0.10540 (15)	0.0233 (4)
C8	0.31498 (15)	0.22439 (14)	-0.1483 (2)	0.0290 (4)
C9	0.3960 (2)	0.24432 (15)	-0.2057 (2)	0.0314 (5)
C10	0.41190 (15)	0.17850 (14)	-0.2887 (2)	0.0266 (4)
C11	0.40945 (13)	0.08783 (14)	-0.2461 (2)	0.0221 (3)
C12	0.24903 (13)	0.06421 (13)	-0.26199 (14)	0.0220 (4)
C13	0.16673 (13)	0.07913 (15)	-0.2259 (2)	0.0271 (4)
C14	0.0971 (2)	0.0767 (2)	-0.2902 (2)	0.0342 (5)
C15	0.1082 (2)	0.0584 (2)	-0.3923 (2)	0.0383 (6)
C16	0.1888 (2)	0.0417 (2)	-0.4294 (2)	0.0384 (6)
C17	0.25884 (15)	0.0451 (2)	-0.3658 (2)	0.0294 (4)
Cl1	0	-1/2	-0.00298 (5)	0.02837 (14)
N	0.33815 (10)	-0.02079 (10)	-0.13987 (13)	0.0213 (3)

The labels of the *x* and *y* axes were chosen to minimize the absolute Flack parameter (Sheldrick *et al.*, 1985).

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXL93 (Sheldrick, 1993). Program(s) used to refine structure: SHELXL93. Molecular graphics:

Diiodotetrakis[tris(dimethylamino)-phosphine oxide-*O*]bismuth(III) Pentaiodide, [Bi₂{OP(NMe₂)₃}₄][I₅]

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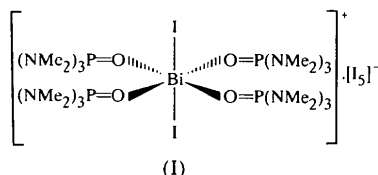
(Received 14 April 1997; accepted 5 November 1997)

Abstract

The title compound, [Bi₂(C₆H₁₈N₃OP)₄](I₅), contains the pseudo-octahedral Bi^{III} cation [Bi₂{OP(NMe₂)₃}₄]⁺, which has crystallographic $\bar{4}$ symmetry, and *trans* iodide ligands. The central I atom of the disordered [I₅]⁻ anion is also situated on a site of $\bar{4}$ symmetry and the atoms of this anion form an infinite three-dimensional network, resulting in a 'cage'-type structure. The cations are situated within the 'cage' cavities.

Comment

The title compound, (I), was prepared as a minor product from the reaction of BiI_3 with $\text{OP}(\text{NMe}_2)_3$ (hmpa), as described previously (Clegg *et al.*, 1993). The diffraction data for this compound were collected in 1992, but the structure could not be solved at that time. Micro-analytical data suggested the formulation $[\text{BiI}_2\{\text{OP}(\text{NMe}_2)_3\}_4]^+ \cdot [\text{I}_5]^-$. The BiL_{III} EXAFS data (Clegg *et al.*, 1993) indicated that the proposed cation had a similar geometry to that observed in a single-crystal X-ray diffraction study of the closely related compound $[\text{BiI}_2\{\text{OP}(\text{NMe}_2)_3\}_4]^+ \cdot [\text{I}_3]^-$, (II). The refined $\text{Bi} \cdots \text{I}$ [3.075 (8) Å], $\text{Bi} \cdots \text{O}$ [2.277 (4) Å] and $\text{Bi} \cdots \text{N}$ [4.27 (3) and 4.75 (2) Å] distances obtained from the EXAFS data for (I) were quite comparable with those from the single-crystal study of (II). However, the EXAFS model afforded two $\text{Bi} \cdots \text{P}$ separations of 3.378 (8) and 3.818 (8) Å, with the former distance being rather shorter than those observed in (II) (3.72–3.81 Å). This result appears to be inconsistent with the proposed structure of the cation in (I), though no comment to this effect was made at the time.



The $[\text{BiI}_2\{\text{OP}(\text{NMe}_2)_3\}_4]^+$ cation in (I) has crystallographically-imposed $\bar{4}$ (S_4) symmetry, and the inter-bond angles about the central Bi atom are very close to 90° . The cation, therefore, displays no evidence of stereochemical activity of the lone pair. Table 2 shows that the $\text{Bi}-\text{I}$ and $\text{Bi}-\text{O}$ distances found in the present study are very similar to those determined both from the EXAFS data for (I) and from the single-crystal X-ray diffraction study of $[\text{BiI}_2\{\text{OP}(\text{NMe}_2)_3\}_4]^+ \cdot [\text{I}_3]^-$ (Clegg *et al.*, 1993). The latter cation does not have crystallographically-imposed symmetry and the inter-bond angles about the Bi atom range from $88.0(2)^\circ$ to $93.1(2)^\circ$. The $\text{Bi} \cdots \text{P}$ distance in (I) is 3.752 (3) Å, which is consistent with the longer such distance found from the EXAFS study, but the origin of the shorter $\text{Bi} \cdots \text{P}$ separation obtained from the EXAFS study is presently unclear. The $\text{Bi} \cdots \text{N}$ distances, ranging from 4.40 (1) to 4.78 (1) Å, with an average value of 4.57 Å, are also very similar to those derived from the EXAFS data.

The central I atom (I2) of the $[\text{I}_5]^-$ anion (Fig. 1b) is situated at the site of $\bar{4}$ symmetry at the origin. The discrete anions have C_2 symmetry and two independent and unequal I—I distances. This bent geometry is found in the vast majority of cases (*e.g.* Tebbe & Gilles, 1996; Bailey & Pennington, 1995; Hills *et al.*, 1991), while a

linear geometry is more rarely observed (*e.g.* Dong *et al.*, 1991). The anion is statistically disordered over two sites, with the central I atom in common, resulting in the crystallographic $\bar{4}$ symmetry. There are two independent I21—I2—I21 angles, of $80.09(11)$ and $125.88(7)^\circ$, and it is not possible to unequivocally determine which angle belongs to the discrete $[\text{I}_5]^-$ anion. Since the majority of examples of discrete ordered $[\text{I}_5]^-$ anions have central I—I—I angles of around 90° , we tentatively suggest that the corresponding angle in the title compound

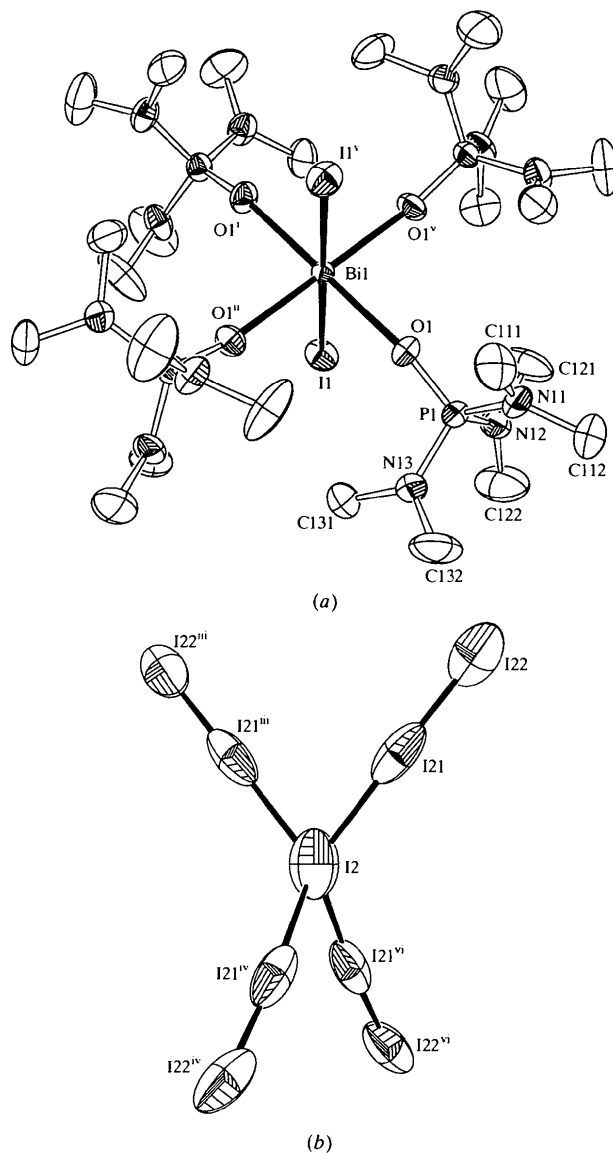


Fig. 1. View of (a) the $[\text{BiI}_2\{\text{OP}(\text{NMe}_2)_3\}_4]^+$ cation (30% probability displacement ellipsoids) and (b) the disordered $[\text{I}_5]^-$ anion (50% probability displacement ellipsoids). Atoms I21 and I22 have occupancies of 0.5. Symmetry codes: (i) $1-x, -y, z$; (ii) $\frac{1}{2}-y, x-\frac{1}{2}, \frac{1}{2}-z$; (iii) $-x, -y, z$; (iv) $-y, x, -z$; (v) $\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}-z$; (vi) $y, -x, -z$.

is 80.09 (11)°. Atoms I21 and I22 are overlapped by the corresponding atoms from neighbouring anions (see Table 2 and Fig. 2), and this is presumably the major reason for their large displacement parameters. Because of this statistical disorder, the anion effectively forms a three-dimensional infinite network when the average contents of the unit cell are considered, resulting in an open 'cage' structure with large cavities, which are occupied by the cations. A similar case of a metal complex encapsulated inside a three-dimensional iodine 'cage' has been reported recently (Blake *et al.*, 1995).

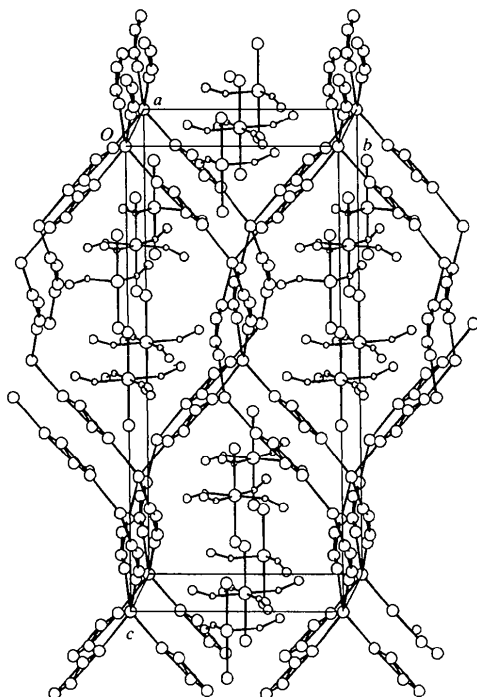


Fig. 2. View of the unit-cell contents of (I) showing the three-dimensional 'cage' structure of the disordered [I₅]⁻ anion encapsulating the cations.

Data collection

Enraf-Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scans [local program based on the method of North *et al.* (1968)]
 $T_{\min} = 0.109$, $T_{\max} = 0.304$
2751 measured reflections
1422 independent reflections

950 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$
 $\theta_{\max} = 25.0^\circ$
 $h = 0 \rightarrow 16$
 $k = 0 \rightarrow 16$
 $l = 0 \rightarrow 36$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.077$
 $S = 1.001$
1422 reflections
133 parameters
H atoms not refined
 $w = 1/[\sigma^2(F_o^2) + (0.0374P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = -0.005$

$\Delta\rho_{\max} = 0.78 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.10 \text{ e } \text{\AA}^{-3}$
(1.08 Å from Bi1)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = -0.029 (11)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Bi1	1/2	0	1/4	0.0347 (2)
I1	1/2	0	0.14958 (3)	0.0686 (3)
P1	0.2616 (2)	-0.1267 (2)	0.23372 (10)	0.0491 (7)
O1	0.3509 (5)	-0.0777 (5)	0.2499 (3)	0.056 (2)
N11	0.1810 (7)	-0.1270 (9)	0.2723 (3)	0.065 (3)
N12	0.2155 (8)	-0.0717 (7)	0.1928 (3)	0.067 (3)
N13	0.2837 (8)	-0.2362 (8)	0.2184 (4)	0.066 (3)
C111	0.2133 (12)	-0.1445 (14)	0.3173 (4)	0.092 (5)
C112	0.0786 (10)	-0.1316 (17)	0.2641 (7)	0.130 (7)
C121	0.2042 (16)	0.0365 (11)	0.1939 (6)	0.131 (9)
C122	0.1865 (17)	-0.1087 (14)	0.1520 (6)	0.147 (8)
C131	0.3709 (11)	-0.2584 (11)	0.1922 (5)	0.084 (5)
C132	0.2223 (14)	-0.3170 (11)	0.2269 (6)	0.122 (7)
I2	0	0	0	0.1741 (13)
I21†	-0.1435 (3)	0.0395 (2)	-0.07989 (12)	0.144 (2)
I22†	-0.2786 (4)	0.0613 (3)	-0.14712 (13)	0.161 (2)

† Site occupancy = 0.5.

Experimental

Compound (I) was prepared as a minor product from the reaction of BiI₃ with OP(NMe₂)₃ (hmpa) (Clegg *et al.*, 1993).

Crystal data

[BiI₂(C₆H₁₈N₃OP)₄](I₅)

$M_r = 1814.1$

Tetragonal

$I\bar{4}2d$

$a = 13.775 (6) \text{ \AA}$

$c = 30.533 (5) \text{ \AA}$

$V = 5793 (3) \text{ \AA}^3$

$Z = 4$

$D_x = 2.08 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 8.2\text{--}15.1^\circ$

$\mu = 6.92 \text{ mm}^{-1}$

$T = 291 (2) \text{ K}$

Prism

$0.30 \times 0.20 \times 0.15 \text{ mm}$

Black

Table 2. Selected geometric parameters (\AA , °)

Bi1—O1	2.316 (7)	N11—C111	1.47 (2)
Bi1—I1	3.0661 (9)	N12—C122	1.41 (2)
P1—O1	1.488 (7)	N12—C121	1.50 (2)
P1—N12	1.593 (10)	N13—C132	1.42 (2)
P1—N13	1.609 (11)	N13—C131	1.47 (2)
P1—N11	1.618 (10)	I2—I21	3.186 (5)
N11—C112	1.43 (2)	I21—I22	2.787 (8)
O1'—Bi1—O1	179.9 (4)	N12—P1—N11	107.3 (6)
O1—Bi1—O1 ⁱⁱ	90.00 (2)	N13—P1—N11	109.8 (6)
O1—Bi1—I1	89.9 (2)	P1—O1—Bi1	160.6 (5)
O1—P1—N12	112.0 (5)	I21—I2—I21 ⁱⁱⁱ	80.09 (11)
O1—P1—N13	111.4 (5)	I21—I2—I21 ^{iv}	125.88 (7)
N12—P1—N13	107.0 (6)	I22—I21—I2	175.2 (2)
O1—P1—N11	109.1 (5)		

Symmetry codes: (i) $1-x, -y, z$; (ii) $\frac{1}{2}-y, x-\frac{1}{2}, \frac{1}{2}-z$; (iii) $-x, -y, z$; (iv) $-y, x, -z$.

The *E* statistics were generally indicative of a centrosymmetric space group, but the systematic absences were only consistent with the non-centrosymmetric space groups $I4_2d$ and $I4_1md$. From the Patterson function, it seemed highly probable that most or all of the heavy atoms resided on special positions, and a consideration of the possible geometry of the complex led to the likelihood of the former space group. However, all initial attempts to solve the structure led to unsatisfactory refinements, with some of the light-atom positions being undetectable in difference Fourier maps. The structure was finally solved using the *DIRDIF96* package (Beurskens *et al.*, 1996). The rather diffuse, but quite substantial, electron density from the disordered pentaiodide anion and the presence of the heavy atoms on special positions were undoubtedly the major reasons for the original failure to solve the structure completely. Indeed, only when the disordered pentaiodide was satisfactorily modelled was it possible to detect all of the light-atom positions of the hmpa ligand from difference Fourier maps. The final refinement of the structure proceeded smoothly, with the largest correlation matrix element (0.66) relating the displacement-parameter elements of atom I21. Calculations using *PLATON* (Spek, 1990) indicated that there were no further voids in the structure capable of containing solvent molecules.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *XCAD-4* (Harms & Wocadlo, 1996). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP3* for Windows (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993).

The EPSRC is thanked for financial support towards the purchase of a diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1163). Services for accessing these data are described at the back of the journal.

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fac-Triazido(2,2'-bipyridine-*N,N'*)(pyridine-*N*)cobalt(III)

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Abstract

The title complex, [Co(N₃)₃(C₁₀H₈N₂)(C₅H₅N)], adopts *fac*-octahedral coordination geometry. All the azido ligands are terminally coordinated with an average Co—N—N angle of 125°. The pyridine ligand is least strongly coordinated to the Co^{III} atom and forms the longest Co—N bond [1.992 (2) Å]. The bipyridine rings lie in the equatorial plane and are nearly perpendicular to the pyridine ring.

Comment

The number of known first-row transition metal complexes containing azido ligands has markedly increased in the past few years; their number now includes low-dimensional complexes of copper (Thompson *et al.*, 1995, and references therein), nickel (Escuer *et al.*, 1995, and references therein) and manganese (Cortes *et al.*, 1997). The main interest arises from the rich magnetic chemistry of these azido complexes, which depends on whether the coordination mode of the ligand is end-on (Charlot *et al.*, 1986) or end-to-end (Escuer, Vincente, El Fallah *et al.*, 1996). We have become interested in this type of complex recently (Chen, Qiu *et al.*, 1994; Chen, Tang *et al.*, 1994) and now report the crystal structure of a discrete mononuclear Co^{III} complex, (I), containing three azido ligands, with pyridine and bipyridine as co-ligands.