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$[M\mathrm{Ph}_4][\mathrm{BPh}_4]$, M = P, As and Sb

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Abstract

The structures of $[M\mathrm{Ph}_4][\mathrm{BPh}_4]$, M = P, As and Sb, crystallize in a superstructure ($I\bar{4}$, Z' = 1/2) of the $P\bar{4}2_1c$, Z' = 1/4, structure known for $M\mathrm{Ph}_4$, M = C, Si, Ge, Sn and Pb. The arrangement of the ions is the same as for $CaWO_4$ (scheelite; $I4_1/a$, Z' = 1/4), which is typical of many other ionic XYO_4 structures. Crystals of $[M\mathrm{Ph}_4][\mathrm{BPh}_4]$ turn a pinkish amber when exposed to UV light; ESR spectra confirm that free radicals are generated.

1. Introduction

Symmetric tetraaryl derivatives of group 14 atoms and metal atoms often crystallize in high-symmetry space groups with the molecules occupying $\bar{4}$ sites. The tetraphenyl molecules ($M\mathrm{Ph}_4$, M = C, Si, Ge, Sn, Pb and Os) all crystallize in $P\bar{4}2_1c$ with Z' = $Z/8$ = 1/4 (see Table 1). The persistence of the crystallographic $\bar{4}$ axis in this classic series of compounds is notable (see *e.g.* Bel'skii, 1975; Karipides, 1978; Wharf & Simard, 1987). We wondered whether salts composed of the cation $[\mathrm{PPh}_4]^+$ and the anion $[\mathrm{BPh}_4]^-$ would follow the same pattern. The two ions are almost the same size ($<d_{\mathrm{P-C}}>/<d_{\mathrm{B-C}}>$ = 1.79/1.64 = 1.09; Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) so that the major difference between the molecular compounds and the salt $[\mathrm{PPh}_4][\mathrm{BPh}_4]$ is the need for an ionic arrangement that is electrostatically favorable. Even though the charge/volume ratio for the ions is small, we expected that the electrostatic interactions would be strong enough to prevent disorder of the cations and anions.

If the $[\mathrm{PPh}_4]^+$ cation is replaced by one of the other two tetraphenylpentelonium ions the mismatch of the cation and anion sizes is larger. For $[\mathrm{AsPh}_4]^+$, $<d_{\mathrm{As-C}}>/<d_{\mathrm{B-C}}>$ = 1.91/1.64 = 1.16 (Allen, Kennard, Watson, Bramıner, Orpen & Taylor, 1987) and for $[\mathrm{SbPh}_4]^+$, $<d_{\mathrm{Sb-C}}>/<d_{\mathrm{B-C}}>$ = 2.10/1.64 = 1.28 (Sb—C distance as found in $[\mathrm{SbPh}_4]\mathrm{ClO}_4$; Ferguson, Glidewell, Lloyd & Metcalfe, 1988).

Both the P- and As-containing salts are photoactive. Crystals grown in the dark are colorless, but develop a pale pinkish amber color when exposed to light.

After solving the structures of the $[\mathrm{PPh}_4]^+$ and $[\mathrm{AsPh}_4]^+$ salts we discovered that several other groups had worked on this series of compounds (*e.g.* Aubagnac, Cano, Claramunt, Elguero, Faure, Foces-Foces & Raj, 1988; Ferguson, Glidewell, Lloyd & Metcalfe, 1988). Professor Ferguson was able to supply us with data collected some years ago for the $[\mathrm{SbPh}_4]^+$ salt.

2. Experimental

Tetraphenylphosphonium and tetraphenylarsonium tetraphenylborate were synthesized by combining ethanol solutions of $[\mathrm{PPh}_4]\mathrm{Cl}$ (Aldrich) or $[\mathrm{AsPh}_4]\mathrm{Cl}$ (Lancaster) and $\mathrm{Na}[\mathrm{BPh}_4]$ (Aldrich). The $[M\mathrm{Ph}_4][\mathrm{BPh}_4]$ precipitate was obtained easily, but it proved difficult to grow satisfactory crystals. We eventually tried dimethylformamide after discovering that it had been mentioned in a patent for the use of $[\mathrm{PPh}_4][\mathrm{BPh}_4]$ (Uehara, Hiyamizu & Sakaguchi, 1974).† Evaporation from DMF gave good-sized crystals with morphological symmetry $\bar{4}2m$ (see Fig. 1).

The Laue group of the $[\mathrm{PPh}_4][\mathrm{BPh}_4]$ crystal appeared to be $4/mmm$; R_{int} for $4/mmm$ (0.020; 1196 unique reflections; forms hkl, $\bar{h}kl$, khl, $\bar{k}hl$) was only slightly larger than R_{int} for $4/m$ (0.016; 2126 unique reflections). The volume of the I-centered tetragonal unit cell (Z = 4) was consistent with the proposed chemical formula. Only one possible systematic-absence condition was found ($00l$, $l \neq 4n$, indicative of a 4_1 screw axis), but the intensities of only five $00l$, $l \neq 4n$ reflections had been measured [$(\sin\theta/\lambda)_{\max}$ = 0.65 Å^{-1}] and one of them (002) was 3.8 times as large as its e.s.d.

All attempts to solve the structure (Sheldrick, 1990) in a space group of Laue symmetry $4/mmm$ were unsuccessful. Possible packing arrangements in the other tetragonal space groups were then considered. Most groups could be excluded because they required either unfavorable conformations (see Dunitz, 1979, and references therein) or unfavorable electrostatic arrangements; of the groups remaining, $I\bar{4}$ seemed the

† Tetraphenylphosphonium tetraphenylborate has been investigated for its ability to promote crosslinking and accelerate curing of epoxy resins (*Chem. Abstr.* **79**:43337p, **107**:P237010u; **123**:355806m), particularly for electronic sealants with high dielectric constants (*Chem. Abstr.* **96**:P124647t; **103**:P23536p) or high heat resistance (*Chem. Abstr.* **114**:P44474j). It has also been used in the polymerization of aromatic polycarbonates (*Chem. Abstr.* **66**:P11401v; **123**:P229297h) and in UV-sensitive photoresists (*Chem. Abstr.* **82**:P44397g; **83**:P19031w) and photoconductive materials (*Chem. Abstr.* **121**:121670u).

Table 1. *Structures of MPh_4 and M(thienyl)$_4$ molecules located in the Cambridge Structural Database (Allen, Kennard & Taylor, 1983)*

Compound	Refcode	M—C (Å)	a (Å)	c (Å)	Reference
CPh_4	TEPHME	1.47	10.87	7.23	Sumsion & McLachlan (1950)
CPh_4	TEPHME02	1.551 (3)	10.894 (2)	7.280 (1)	Robbins, Jeffrey, Chesick, Donohoe, Cotton, Frenz & Murillo (1975)
CPh_4	TEPHME03	1.550 (3)	10.899 (2)	7.279 (1)	Robbins *et al.* (1975)
CPh_4	TEPHME11	1.550 (3)	10.916 (3)	7.287 (2)	Robbins *et al.* (1975)
$SiPh_4$	TPENSI	1.872 (7)	11.46 (1)	7.09 (3)	Glidewell & Sheldrick (1971)
$SiPh_4$	TPENSI03	1.877 (2)	11.450 (2)	7.063 (1)	Gruhnert, Kirfel, Will, Wallrafen & Recker (1983)
$GePh_4$	TPENGE	1.956 (1)	11.613 (4)	6.904 (2)	Chieh (1971)
	TPENGE01	1.952 (1)			
$GePh_4$	TPENGE02	1.957 (4)	11.656 (11)	6.928 (7)	Karipides & Haller (1972)
$SnPh_4$	TPHESN	2.144 (14)	12.058 (1)	6.568 (1)	Chieh & Trotter (1970)
$SnPh_4$	TPHESN01	2.143 (10)	11.97 (3)	6.60 (2)	Akhmed & Aleksandrov (1970)
$SnPh_4$	TPHESN02	2.139 (4)	12.058 (1)	6.581 (1)	Belsky, Simonenko, Reikhsfeld & Saratov (1983)
$SnPh_4$	TPHESN03	2.143 (5)	12.068 (3)	6.558 (2)	Engelhardt, Leung, Raston & White (1982)
$PbPh_4$	TPHEPB	2.19 (3)	12.092 (3)	6.589 (2)	Busetti, Mammi, Signor & Pra (1967)
$PbPh_4$	TPHEPB01	2.194 (6)	12.151 (2)	6.545 (1)	Preut & Huber (1993)
$PbPh_4$	TPHEPB02	2.202 (9)	12.144 (1)	6.547 (1)	Schneider-Koglin, Mathiasch & Draeger (1994)
$OsPh_4$	FEFTOZ	1.994 (12)	11.674 (2)	6.820 (1)	Stavropoulos, Savage, Tooze, Wilkinson, Hussain, Motevalli & Hursthouse (1987)
$Si(C_4H_3S)_4$	TENYSI	1.888 (3)	11.368 (9)	6.535 (5)	Karipides, Reed & Thomas (1974)
$Ge(C_4H_3S)_4$	THIEGE	1.94 (1)	11.46 (2)	6.53 (1)	Karipides, Reed, Haller & Hayes (1977)
$Sn(C_4H_3S)_4$	THIESN	2.15 (1)	11.78 (2)	6.54 (1)	Karipides *et al.* (1977)
$Pb(C_4H_3S)_4$	THIEPB	2.20 (1)	11.805 (16)	6.537 (9)	Karipides *et al.* (1977)

most likely. Structure solution in that group proceeded smoothly. The unit cell contains two independent cations and two independent anions, each located on a $\bar{4}$ axis (see Figs. 2 and 3). Careful examination of the solved structure confirmed the relatively low symmetry.

After isotropic refinement the U_{iso} value for the P atom located at 1/2,0,1/4 (see Fig. 2) was much too large and the value for the B atom located at 0,1/2,1/4 was too small. Random disorder of the PPh_4^+ cation and BPh_4^- anion seemed unlikely, however, because such disorder would greatly increase the electrostatic energy; in any event refinement of a disorder model was unsatisfactory. An alternate explanation was a limited disorder that could be described as twinning, which would also explain the increase in Laue symmetry from $4/m$ to $4/mmm$. A twin matrix (010, 100, 00$\bar{1}$) corresponding to the interchange of the **a** and **b** axes and consistent with the crystal morphology (point symmetry $\bar{4}2m$) was proposed.

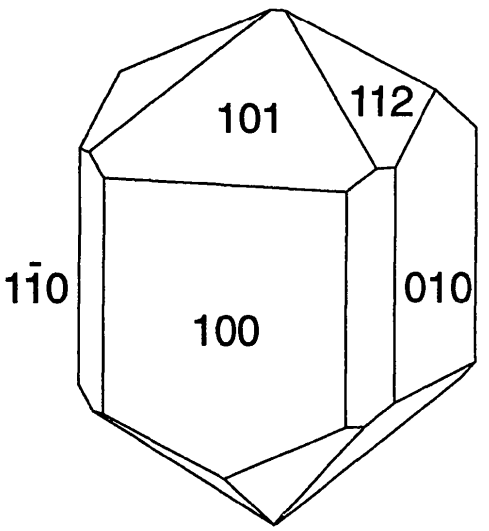

Fig. 1. Typical habit of crystals of [MPh$_4$][BPh$_4$], M = P and As.

Unconstrained least-squares refinement (Sheldrick, 1993) gave satisfactory agreement factors [wR_2 = 0.072 for 2264 reflections and 226 variables; R_1 = 0.036 for the 1889 reflections with $I > 2\sigma(I)$], satisfactory atomic ellipsoids and an acceptable range of C—C bond lengths (1.34–1.42; typical e.s.d. 0.007 Å). The refinement could not, however, be coaxed to converge; $(\Delta/\sigma)_{max}$ was always in the range 0.5–0.9. The instability in the refinement was traced to the pronounced pseudosymmetry (see below) in the cell. Several sets of constraints were evaluated. In the end it seemed best to idealize the four phenyl rings ($R_{C—C}$ = 1.390, $R_{C—H}$ = 0.93 Å; all angles 120°), but to allow independent anisotropic displacement parameters for each C atom. The U_{iso} values for the H atoms were set at $1.2U_{eq}$ for the attached C atom.

Refinements of the structures of the As and Sb structures proceeded in the same way. Correlation coeffients between positional parameters were in general smaller but correlation coefficients between U^{11} and U^{33} values of the As (or Sb) atoms and of the B atoms were larger. Although these coefficients are large (0.83–0.88) for the P-containing structure, the refinement was stable. In the As- and Sb-containing salts it became necessary to require that pairs of U^{11} and U^{33} values for atoms of the same type be equal.

Crystallographic data and the details of the structure determinations are given in Table 2, atomic coordinates and U_{eq} values in Tables 3–5, and selected geometric parameters in Table 6. The atom-numbering scheme is defined and the displacement ellipsoids are displayed in Fig. 4. Tables of anisotropic displacement parameters and of observed and calculated F^2 values have been deposited,† as has an alternate view of the ellipsoids.

† Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: CR0521). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

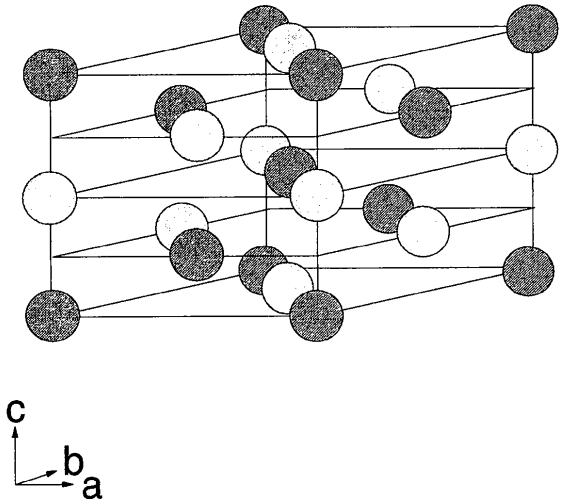

Fig. 2. Schematic drawing of the arrangement of the ions in the salts [MPh$_4$][BPh$_4$], M = P, As and Sb. The darker circles represent the ions containing group 14 atoms and the lighter circles represent the BPh_4^- ions.

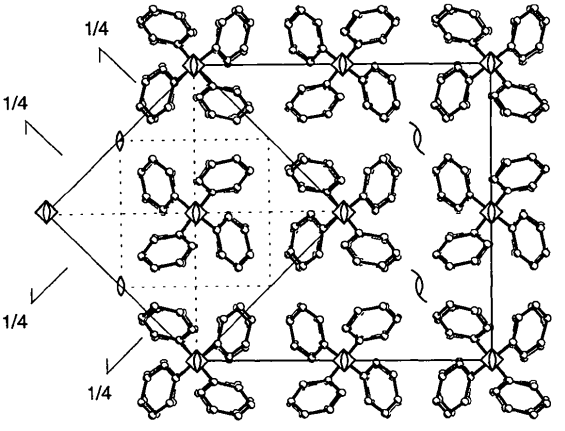

Fig. 3. Projection of the [MPh$_4$][BPh$_4$] structures, M = P, As and Sb, along the **c** axis. The **a** axis points from left to right and the **b** axis points upwards. The subcell is also shown. The only symmetry elements of the subcell that survive are the $\bar{4}$ axes; the glide planes and perpendicular 2_1 axes are lost and the twofold rotation axes become 2_1 axes.

3. Results

The salts [MPh$_4$][BPh$_4$] crystallize in a supercell of the $P\bar{4}2_1c$, Z' = 1/4, structure known (see Table 1) for MPh$_4$, M = C, Si, Ge, Sn, Pb and Os and for M(2-thienyl)$_4$, M = Si, Ge, Sn and Pb (thienyl group disordered). In the [MPh$_4$][BPh$_4$] salts the cations and anions have the same conformations; there is little to distinguish them except the number of electrons present and bond length to the central atom (see Table 6).

The subcell/supercell relationship (see Fig. 3) is given by the equation

$$a_{I\bar{4}} = \begin{bmatrix} 1 & \bar{1} & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 2 \end{bmatrix} a_{P\bar{4}2_1c}.$$

The l odd reflections should be systematically weak, because there is a pseudotranslation of 1/2 along **c** (see

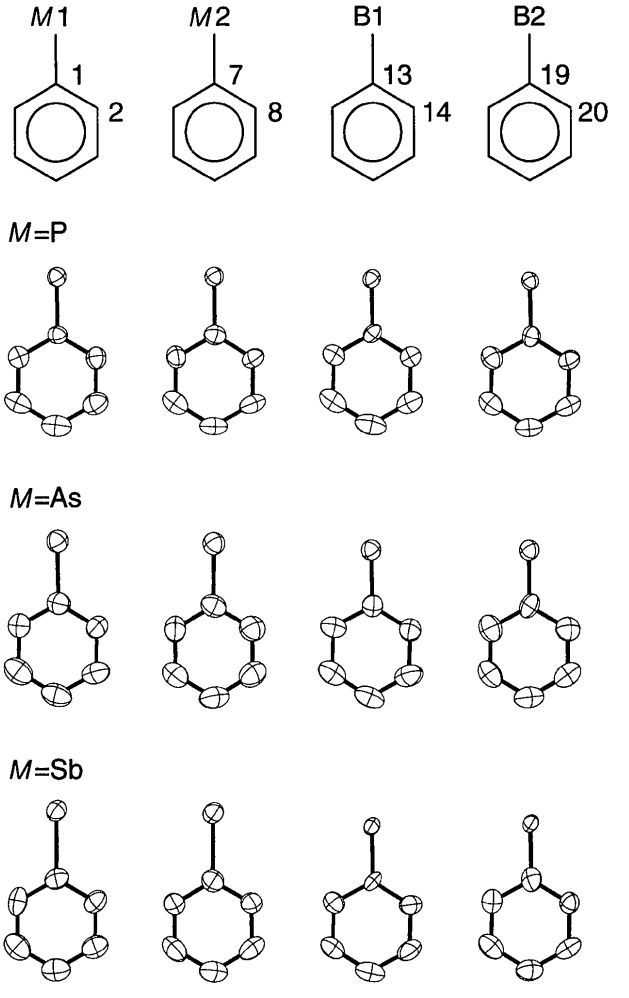

Fig. 4. Perspective view of the displacement ellipsoids (50% probability level) for the seven independent atoms in each of the four independent ions of the three salts [MPh$_4$][BPh$_4$], M = P, As and Sb. The atomic numbering system is also defined.

Table 2. *Experimental details*

	[PPh$_4$][BPh$_4$]	[AsPh$_4$][BPh$_4$]	[SbPh$_4$][BPh$_4$]
Crystal data			
Chemical formula	$C_{24}H_{20}P^+.C_{24}H_{20}B^-$	$C_{24}H_{20}As^+.C_{24}H_{20}B^-$	$C_{24}H_{20}Sb^+.C_{24}H_{20}B^-$
Chemical formula weight	658.63	702.58	749.41
Cell setting	Tetragonal	Tetragonal	Tetragonal
Space group	$I\bar{4}$	$I\bar{4}$	$I\bar{4}$
a (Å)	15.796 (1)	15.936 (4)	16.272 (3)
c (Å)	14.198 (1)	14.062 (2)	13.703 (3)
V (Å^3)	3542.3 (4)	3571.6 (8)	3628.3 (12)
Z	4	4	4
D_x (Mg m^{-3})	1.235	1.307	1.372
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073
No. of reflections for cell parameters	22	22	25
θ range (°)	13.1–13.9	12.2–12.9	10.2–14.1
μ (mm^{-1})	0.107	0.980	0.796
Temperature (K)	296 (1)	296 (1)	295 (1)
Crystal form	See Fig. 1	See Fig. 1	See Ferguson *et al.* (1988)
Crystal size (mm)	0.4 × 0.35 × 0.35	0.4 × 0.4 × 0.3	Unknown
Crystal color	Initially colorless (see text)	Initially colorless (see text)	Initially colorless (see text)
Data collection			
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans	ω scans	$\omega/2\theta$ scans
Absorption correction	None	Empirical	None
T_{min}	–	0.53	–
T_{max}	–	0.67	–
No. of measured reflections	2274	2277	2202
No. of independent reflections	2264	2267	2184
No. of observed reflections	1889	1842	1916
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0098	0.0265	0.0231
θ_{max} (°)	27.49	27.50	26.97
Range of h, k, l	$0 \rightarrow h \rightarrow 20$ $0 \rightarrow k \rightarrow 20$ $0 \rightarrow l \rightarrow 18$	$0 \rightarrow h \rightarrow 20$ $0 \rightarrow k \rightarrow 20$ $0 \rightarrow l \rightarrow 18$	$0 \rightarrow h \rightarrow 20$ $0 \rightarrow k \rightarrow 20$ $0 \rightarrow l \rightarrow 17$
No. of standard reflections	3	2	3
Frequency of standard reflections (min)	60	60	120
Intensity decay (%)	<0.7	<0.8	No longer available
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.050	0.039	0.028
$wR(F^2)$	0.172	0.112	0.082
S	1.21	1.12	1.17
Twin fraction†	0.521 (6)	0.430 (5)	0.431 (4)
No. of reflections used in refinement	2264	2267	2179
No. of parameters used	178	174	174
H-atom treatment	Riding	Riding	Riding
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1172P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0520P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	−0.008	−0.002	0.010
$\Delta\rho_{max}$ (e Å^{-3})	0.50	0.34	0.94
$\Delta\rho_{min}$ (e Å^{-3})	−0.23	−0.21	−0.21
Extinction method	None	None	None
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)
Absolute configuration	0.1 (2) (Flack, 1977)	0.42 (3) (Flack, 1977)	0.02 (4) (Flack, 1977)
Computer programs			
Data collection	*CAD*-4 (Enraf–Nonius, 1989)	*CAD*-4 (Enraf–Nonius, 1989)	*CAD*-4 (Enraf–Nonius, 1989)
Cell refinement	*CAD*-4 (Enraf–Nonius, 1989)	*CAD*-4 (Enraf–Nonius, 1989)	*CAD*-4 (Enraf–Nonius, 1989)
Structure solution	*SHELXTL/PC* (Sheldrick, 1990)	*SHELXTL/PC* (Sheldrick, 1990)	*SHELXTL/PC* (Sheldrick, 1990)
Structure refinement	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)

† Scattering fraction of the first individual. The second individual is related to the first by the transformation 010/100/00$\bar{1}$.

Fig. 3) that interconverts cations and anions. In the [PPh$_4$][BPh$_4$] structure the l even reflections are about 10 times more intense than the l odd reflections.

The most important difference between the $P\bar{4}2_1c$ and $I\bar{4}$ cells is the absence of the glide planes in the latter. Every second glide operation would convert one ion type

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for [PPh₄][BPh₄]*

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

	x	y	z	U_{eq}
P1	0.0000	0.0000	0.0000	0.0353 (10)
C1	0.0710 (2)	0.0570 (2)	0.0744 (2)	0.0346 (13)
C2	0.0919 (2)	0.1410 (2)	0.0571 (2)	0.0430 (14)
C3	0.1502 (2)	0.1822 (2)	0.1144 (2)	0.057 (2)
C4	0.1876 (2)	0.1392 (3)	0.1890 (2)	0.056 (2)
C5	0.1668 (2)	0.0552 (3)	0.2063 (2)	0.055 (2)
C6	0.1085 (2)	0.0141 (2)	0.1490 (3)	0.047 (2)
P2	0.0000	1/2	1/4	0.0350 (9)
C7	0.0711 (2)	0.4430 (2)	0.3254 (2)	0.045 (2)
C8	0.0879 (3)	0.3575 (2)	0.3114 (2)	0.0475 (15)
C9	0.1434 (3)	0.3152 (2)	0.3710 (3)	0.054 (2)
C10	0.1822 (2)	0.3584 (3)	0.4446 (2)	0.057 (2)
C11	0.1654 (2)	0.4439 (3)	0.4586 (2)	0.055 (2)
C12	0.1098 (2)	0.4862 (2)	0.3990 (3)	0.047 (2)
B1	0.0000	0.0000	1/2	0.029 (3)
C13	0.0684 (2)	0.0515 (2)	0.5706 (2)	0.0332 (12)
C14	0.0821 (2)	0.1383 (2)	0.5642 (2)	0.0451 (14)
C15	0.1375 (2)	0.1778 (2)	0.6263 (3)	0.059 (2)
C16	0.1791 (2)	0.1307 (3)	0.6947 (2)	0.061 (2)
C17	0.1654 (2)	0.0440 (3)	0.7011 (2)	0.058 (2)
C18	0.1100 (2)	0.0044 (2)	0.6391 (3)	0.0458 (12)
B2	0.0000	1/2	3/4	0.033 (4)
C19	0.0666 (2)	0.4455 (2)	0.8220 (2)	0.0371 (13)
C20	0.0817 (2)	0.3594 (2)	0.8114 (2)	0.0458 (15)
C21	0.1393 (3)	0.3187 (2)	0.8701 (3)	0.054 (2)
C22	0.1817 (2)	0.3642 (3)	0.9393 (2)	0.055 (2)
C23	0.1666 (2)	0.4504 (3)	0.9499 (2)	0.051 (2)
C24	0.1091 (2)	0.4910 (2)	0.8912 (3)	0.0489 (14)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for [AsPh₄][BPh₄]*

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

	x	y	z	U_{eq}
As1	0.0000	0.0000	0.0000	0.0478 (2)
C1	0.0750 (3)	0.0611 (3)	0.0782 (4)	0.050 (2)
C2	0.0944 (4)	0.1448 (3)	0.0613 (4)	0.051 (2)
C3	0.1526 (4)	0.1857 (3)	0.1185 (4)	0.064 (2)
C4	0.1914 (4)	0.1429 (4)	0.1925 (4)	0.067 (2)
C5	0.1720 (4)	0.0592 (4)	0.2094 (4)	0.070 (3)
C6	0.1138 (4)	0.0183 (3)	0.1523 (5)	0.056 (2)
As2	0.0000	1/2	1/4	0.0478 (2)
C7	0.0744 (4)	0.4407 (4)	0.3306 (4)	0.054 (3)
C8	0.0885 (4)	0.3558 (4)	0.3143 (4)	0.062 (2)
C9	0.1437 (4)	0.3115 (3)	0.3722 (5)	0.068 (2)
C10	0.1846 (3)	0.3520 (4)	0.4464 (5)	0.068 (3)
C11	0.1705 (4)	0.4369 (4)	0.4627 (4)	0.065 (2)
C12	0.1154 (4)	0.4812 (3)	0.4048 (5)	0.055 (2)
B1	0.0000	0.0000	1/2	0.0398 (9)
C13	0.0684 (3)	0.0518 (3)	0.5710 (4)	0.043 (2)
C14	0.0810 (4)	0.1380 (3)	0.5669 (4)	0.054 (2)
C15	0.1357 (3)	0.1765 (3)	0.6303 (4)	0.066 (2)
C16	0.1778 (3)	0.1288 (4)	0.6979 (4)	0.065 (2)
C17	0.1652 (3)	0.0425 (4)	0.7021 (4)	0.064 (2)
C18	0.1105 (3)	0.0040 (3)	0.6386 (5)	0.055 (2)
B2	0.0000	1/2	3/4	0.0398 (9)
C19	0.0659 (3)	0.4478 (3)	0.8232 (5)	0.046 (2)
C20	0.0792 (3)	0.3621 (3)	0.8125 (4)	0.054 (2)
C21	0.1365 (3)	0.3209 (2)	0.8706 (5)	0.065 (2)
C22	0.1805 (3)	0.3654 (3)	0.9394 (4)	0.065 (2)
C23	0.1673 (3)	0.4511 (3)	0.9502 (4)	0.061 (2)
C24	0.1100 (4)	0.4923 (2)	0.8921 (5)	0.058 (2)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for [SbPh₄][BPh₄]*

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

	x	y	z	U_{eq}
Sb1	0.0000	0.0000	0.0000	0.04338 (12)
C1	0.0816 (3)	0.0659 (3)	0.0868 (3)	0.044 (2)
C2	0.0966 (3)	0.1487 (3)	0.0691 (3)	0.052 (2)
C3	0.1544 (3)	0.1907 (2)	0.1247 (3)	0.059 (2)
C4	0.1971 (3)	0.1499 (3)	0.1981 (3)	0.057 (2)
C5	0.1820 (3)	0.0672 (3)	0.2158 (3)	0.062 (2)
C6	0.1243 (3)	0.0252 (2)	0.1601 (4)	0.054 (2)
Sb2	0.0000	1/2	1/4	0.04338 (12)
C7	0.0816 (3)	0.4344 (3)	0.3370 (3)	0.048 (2)
C8	0.0910 (3)	0.3506 (3)	0.3214 (3)	0.048 (2)
C9	0.1446 (3)	0.3054 (2)	0.3794 (3)	0.059 (2)
C10	0.1889 (3)	0.3442 (3)	0.4529 (3)	0.061 (2)
C11	0.1795 (3)	0.4281 (3)	0.4685 (3)	0.063 (2)
C12	0.1258 (3)	0.4732 (2)	0.4106 (3)	0.049 (2)
B1	0.0000	0.0000	1/2	0.0285 (7)
C13	0.0646 (2)	0.0515 (2)	0.5736 (3)	0.031 (2)
C14	0.0747 (3)	0.1363 (2)	0.5696 (3)	0.050 (2)
C15	0.1292 (3)	0.1750 (2)	0.6327 (3)	0.057 (2)
C16	0.1736 (2)	0.1289 (3)	0.7000 (3)	0.058 (2)
C17	0.1635 (2)	0.0442 (3)	0.7040 (3)	0.049 (2)
C18	0.1090 (3)	0.0055 (2)	0.6409 (3)	0.0455 (14)
B2	0.0000	1/2	3/4	0.0285 (7)
C19	0.0667 (3)	0.4481 (3)	0.8247 (3)	0.045 (2)
C20	0.0785 (3)	0.3637 (3)	0.8173 (3)	0.0435 (15)
C21	0.1340 (3)	0.3244 (2)	0.8786 (3)	0.056 (2)
C22	0.1778 (3)	0.3695 (3)	0.9473 (3)	0.057 (2)
C23	0.1661 (3)	0.4538 (3)	0.9547 (3)	0.057 (2)
C24	0.1106 (3)	0.4932 (2)	0.8934 (3)	0.051 (2)

Table 6. *Selected geometric parameters (Å, °) for [MPh₄][BPh₄]*

	M = P	M = As	M = Sb
*M*1—C1	1.784 (3)	1.894 (4)	2.080 (3)
*M*2—C7	1.794 (3)	1.894 (5)	2.079 (3)
B1—C13	1.684 (3)	1.693 (4)	1.681 (3)
B2—C19	1.701 (3)	1.690 (4)	1.714 (3)
$< d_{M-C} > - < d_{B-C} >$	0.096 (5)	0.202 (6)	0.382 (4)
C1—*M*—C1′†	107.4 (2)	109.0 (4)	110.3 (2)
	110.5 (1)	109.7 (2)	109.1 (1)
C7—*M*2—C7′	106.7 (2)	106.5 (4)	110.0 (3)
	110.9 (1)	111.0 (2)	109.2 (1)
C13—B1—C13′	106.9 (2)	107.7 (4)	106.2 (3)
	110.8 (1)	110.4 (2)	111.1 (1)
C19—B2—C19′	106.1 (2)	105.0 (5)	106.7 (3)
	111.2 (1)	111.8 (2)	110.9 (2)
*M*1—C1—C2	121.8 (2)	122.3 (3)	120.8 (3)
*M*2—C7—C8	121.4 (2)	119.3 (4)	119.1 (3)
B1—C13—C14	122.5 (2)	123.4 (3)	123.0 (2)
B2—C19—C20	122.5 (2)	120.8 (3)	122.0 (3)
*M*1—C1···C4	177.1 (3)	176.7 (4)	177.1 (3)
*M*2—C7···C10	178.6 (2)	179.1 (4)	178.9 (3)
B1—C13···C16	177.0 (2)	175.9 (4)	177.0 (2)
B2—C19···C22	176.8 (3)	177.4 (4)	177.9 (3)

† Angle for C atoms related by twofold rotation is first; angle for C atoms related by $\bar{4}$ is second.

into the other; alternate glide operations would relate two independent ions of the same type (*e.g.* two independent BPh_4^- ions). Since half these glide operations are almost correct and the other half are at least approximately correct for the C and H atoms, the reflections in $I\bar{4}$

that correspond to the extinction condition hhl, $l \neq 2n$, in $P\bar{4}2_1c$ should be systematically weak. In the [PPh$_4$][BPh$_4$] structure only 5 of the 52 $h0l$, $h = 2n$ and $l \neq 4n$ reflections (see equation above relating the two unit cells) have $I > 2\sigma(I)$, but four of those five reflections are definitely present [$I/\sigma(I)$ = 24, 13, 11 and 7].

The pseudoglide operations result in the phenyl rings for the two independent ions of each type being related by the approximate operation $x' = x$, $y' = 1/2 - y$, $z' = 1/4 + z$. This relationship is the source of the instability in the independent-atom refinement and of the large correlations between the U^{ii}, $i = 1$ and 3, values for the two M and for the two B atoms. A second application of the pseudoglide operation relates a cation and an anion, but these have at least somewhat different central M—C bond lengths (see Table 6).

4. ESR experiment

ESR measurements were carried out on powder samples of [MPh$_4$][BPh$_4$], M = P and As. A preliminary study of samples exposed to sunlight established the existence and position of a resonance. The samples were then recrystallized from dimethylformamide in the dark, packed into glass capillary tubes (Kimble Products Kimax 51) and stored in the dark. Samples of the starting materials (*i.e.* [PPh$_4$]Cl, [AsPh$_4$]Cl and Na[BPh$_4$]) were also prepared. Spectra measured for these materials, and for an empty capillary, showed no ESR signal.

Capillaries were placed inside a standard NMR round cell within the room-temperature resonator cavity of a Bruker 300 EPR spectrometer operating at 9.78 GHz and 18 mW with a modulation amplitude of 0.4 G, modulation frequency of 100 kHz, time constant of 1.28 ms and conversion time of 10 ms. From 50 to 70 scans of 10.5 s duration were collected, with a field sweep width of 301.17 G around a center field of 3485.64 G. Spectra were measured before and after exposure to UV light; an exposure of 103 h to 15 W Philips Blacklight FT15T8/BL at approximately 10 cm (with periodic sample rotation) produced an obvious color change (colorless to amber). A set of controls was treated similarly, except UV exposure was blocked. No ESR signal was observed from the controls or from the UV-exposed Na[BPh$_4$].

Signals were observed for the four salts containing [MPh$_4$]$^+$ cations; all signals were centered at 3493 (2) G. The number of spins per mol of material was estimated by comparing the double-integrated measured intensity with a calibration curve constructed from a series of standards of the spin label 4-Maleimido-TEMPO in KCl. The two tetraphenylborate salts had *ca* 7.7 (10) $\times$ 10^{-5} mol spins per mole compound. The signals for the two chloride salts were an order of magnitude weaker; they corresponded to only 0.9 (7) $\times$ 10^{-5} mol spins per mol compound. Sample spectra have been deposited.

5. Discussion

The overall ionic arrangement in the [PPh$_4$][BPh$_4$] salts (see Fig. 2) is similar to that of scheelite ($CaWO_4$, $I4_1/a$, $Z' = 1/4$), which is itself closely related to zircon ($ZrSiO_4$, $I4_1/amd$, $Z' = 1/8$). The scheelite structure occurs primarily for M^+X^- and $M^{2+}X^{2-}$ salts (X^{n-}, a tetrahedral anion), while the more symmetrical zircon structure (anions are located at $\bar{4}m2$ rather than $\bar{4}$ sites) occurs for the more covalent $M^{3+}X^{3-}$ and $M^{4+}X^{4-}$ compounds (Wyckoff, 1965). In the scheelite structure there is no restriction on the rotation of the tetrahedral anion around the $\bar{4}$ axis.

Plots of the cell constants a and c against the M—C distance (Fig. 5) for the MPh$_4$ molecules (M = C, Si, Ge, Sn and Pb) and the [MPh$_4$][BPh$_4$] salts reported here (dimensions correspond to the subcell) show that the effect of the ionic charges on the cell dimensions is modest. Compared with predictions based on the average M—C/B—C distance, the dimension a of the salts is about as expected and the dimension c is slightly contracted. The shortest contacts between ions of different charges are along the **c** axis.

Given the ionic arrangement (Fig. 2) and the small effect of the charges on the overall crystal packing, the twinning is no surprise. A layer at $z = 1/4$ (or 3/4) could have the cation at either $x = 1/2$, $y = 0$ or $x = 0$, $y = 1/2$.

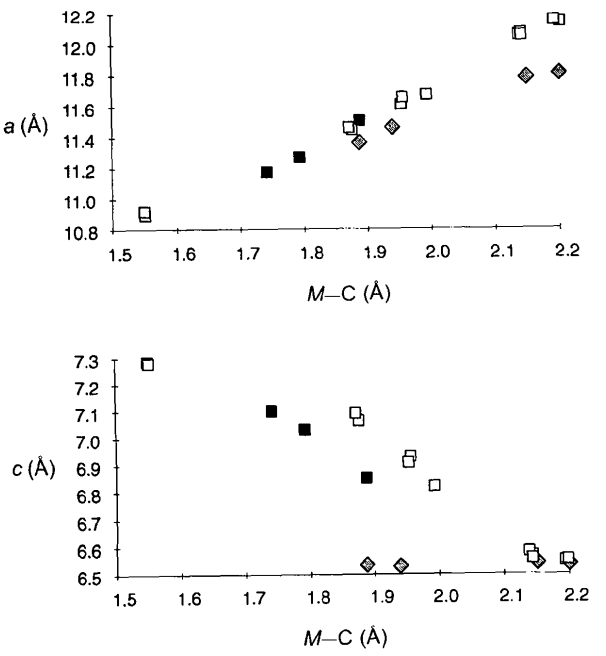

Fig. 5. Plots of the variation of a (above) and c (below) *versus* the M—C bond length for compounds MPh$_4$, M = C, Si, Ge, Os, Sn and Pb (open squares; structures in Table 1 having cell-constant e.s.d.'s < 0.015), [MPh$_4$][BPh$_4$], M = P, As and Sb (filled squares; dimensions correspond to subcell), and M(thienyl)$_4$, M = Si, Ge, Sn and Pb (gray diamonds). In all cases the uncertainties in the cell dimension are much smaller than the height of the marker.

The energies of these two arrangements are the same as far as adjacent layers are concerned; the energies begin to differ only when interactions with second-nearest layers are considered. In a 'salt' composed of ions with such small charge/volume ratios long-range ionic interactions should be weak. Similar 'mistakes' could also occur during growth in the {101} directions.

The pinkish amber color of $[M\mathrm{Ph}_4][\mathrm{BPh}_4]$ crystals that have been exposed to light must be associated with the unpaired electrons. The photolysis of $[\mathrm{PPh}_4]\mathrm{Cl}$ in benzene–ethanol solution yields (Griffin & Kaufman, 1965) biphenyl, diphenylphosphine and triphenylphosphine; the postulated mechanism starts with a photo-induced one-electron transfer from the Cl^- anion to the $[\mathrm{PPh}_4]^+$ cation. In the crystal, the $[M\mathrm{Ph}_4]^\cdot$ radicals are long-lived; the restricted mobility of any phenyl radical produced guarantees recombination with the associated $M\mathrm{Ph}_3$ molecule. The greater number of spins produced in the $[M\mathrm{Ph}_4][\mathrm{BPh}_4]$ salts, M = P or As, compared with the $[\mathrm{MPh}_4]\mathrm{Cl}$ salts reflects the lower oxidation potential of $[\mathrm{BPh}_4]^-$ compared with Cl^-. The existence of free radicals explains the activity of $[\mathrm{PPh}_4][\mathrm{BPh}_4]$ as a polymerization catalyst (see above). The mobility of electrons in $[\mathrm{PPh}_4][\mathrm{BPh}_4]$ is demonstrated by its use in a $[\mathrm{PPh}_4]^+$-sensitive electrode (Satake, Hori & Kaneshina, 1991).

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