

The Crystal Structure of Silver Tetraborate, $\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3$

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Crystalline $\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ has been prepared and found to be monoclinic with unit-cell dimensions $a = 6.550 \pm 0.003$, $b = 8.671 \pm 0.004$, $c = 17.511 \pm 0.008$ Å; $\beta = 90^\circ 18' \pm 6'$.

The space group is $P2_1/c$. A crystal structure investigation was carried out on a solid solution of this phase, where 40 mol. % of the silver atoms were substituted by sodium atoms. This solid solution had unit-cell dimensions $a = 6.521 \pm 0.003$, $b = 8.624 \pm 0.004$, $c = 17.549 \pm 0.008$ Å; $\beta = 90^\circ 20' \pm 5'$.

A total of 829 reflexions were recorded. The structure was determined by a three-dimensional Fourier synthesis, and refined by a least-squares analysis, including all observed reflexions. A reliability index of $R = 11.0\%$ was obtained.

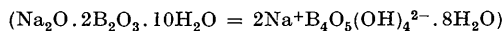
The borate anion in the structure consists of two separate, identical, three-dimensional, interlocking networks. Each of these networks is composed of units which have previously been found in anhydrous triborates and pentaborates. A structural relationship of silver tetraborate to sodium tetraborate is indicated.

Introduction

As part of a systematic study of the crystal structures of anhydrous borates with a ratio of metal oxide to boron oxide smaller than one, a determination of the structure of silver tetraborate,* $\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3$, is presented here. Previously the structures of $\text{Rb}_2\text{O} \cdot 5\text{B}_2\text{O}_3$ and $\text{K}_2\text{O} \cdot 5\text{B}_2\text{O}_3$ (Krogh-Moe, 1959, 1964), $\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ (Krogh-Moe, 1960) and $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ (Krogh-Moe, 1962a) have been reported. The latter structures, *i.e.* the pentaborates, triborates and diborates, all have hydrated counterparts. In potassium pentaborate tetrahydrate (Zachariassen & Plettinger, 1963) a borate polyion is found, which is retained in the anhydrous compound as part of a three-dimensional network. The hydroxyl groups of the polyion, however, are replaced by oxygen atoms bridging two borons in the anhydrous compound. Similar circumstances are found for the structure of sodium diborate decahydrate, (Morimoto, 1956) as compared with anhydrous lithium diborate.

The only hydrated triborate, for which the structure

* The mineral borax



is usually known as a sodium tetraborate, since it has four boron atoms in the 'molecule'. Other borates of a different composition with four boron atoms in the 'molecule' are conceivable, however. (As an example it could be mentioned that a cage structure reminiscent of the urotropine molecule has been suggested for certain hydrated metaborates.) Thus the usual nomenclature is somewhat ambiguous. According to the IUPAC recommendations, borax should be called a disodium tetraborate. The present author has taken the view that a consistent nomenclature can at the moment only be based on the stoichiometry, since neither are all borate structures known, nor do they all contain 'molecules'. The name disodium tetraborate may therefore be simplified to sodium diborate, leaving the name tetraborate to those compounds having a 1:4 ratio of other oxide to boron oxide.

is known, is the mineral tunellite, $\text{SrO} \cdot 3\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ (Clark, 1963). This structure, however, does not follow the pattern. Instead it consists of a larger borate polyion, not related to the simple triborate group found in $\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$.

A few reports about hydrated tetraborates, $\text{M}_2\text{O} \cdot 4\text{B}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, can be found in the older literature, but the existence of any such compound has not been firmly established. In several anhydrous systems, on the other hand, the tetraborates appear to be particularly stable phases. There is also evidence that the structural configuration of the crystalline sodium tetraborate is largely retained in the molten phase and the glass phase of the same chemical composition (Krogh-Moe, 1962b). A crystal structure investigation of an anhydrous tetraborate is therefore of considerable interest.

Experimental

Single crystals of $\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ were grown from a silver borate melt kept in a silica crucible for a few hours at 730°C . The melt was prepared from the stoichiometric amounts of silver oxide and boric acid. The chemicals were first allowed to react in the solid state by gradual heating from 100°C to 300°C so as to prevent decomposition of the silver oxide, and then fused at temperatures around 800°C . The melt could easily be supercooled to a glass.

An unidentified silver borate phase was formed in the solid state reaction at 300°C in a couple of weeks. The same phase also crystallized as a finely grained mass from the fused silver borate. At 650°C only this phase was obtained from the melt; at 730°C up to millimeter large crystals of $\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ grew simultaneously. These crystals could be separated by hand

under a microscope from the glass and the unidentified phase.

Equatorial and non-equatorial Weissenberg exposures of $\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ about the a and b axes showed the space group to be $P2_1/c$. The following unit-cell dimensions were determined with a least-squares fit of powder diffraction data, employing lead nitrate as internal standard:

$$a = 6.550 \pm 0.003, \quad b = 8.671 \pm 0.004, \\ c = 17.511 \pm 0.008 \text{ \AA}; \quad \beta = 90^\circ 18' \pm 6'.$$

These dimensions correspond to a calculated density of 3.41 g.cm^{-3} with four formula units of $\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ in the unit cell.

During the course of this work, it was discovered that silver tetraborate could hold a considerable amount of sodium tetraborate in solid solution. For the subsequent structure determination, the solid solution offers the dual advantage of a lower absorption coefficient and a higher relative contribution of boron and oxygen to the diffracted intensities. Crystals were therefore grown from molten mixtures of silver tetraborate with sodium tetraborate.

Since a complete crystallization of the melt to the tetraborate phase did not occur, the extent of solid solution had to be determined directly on the crystals. This was accomplished by different methods. With an electron microprobe X-ray analyser (from Applied Research Laboratories, Inc.), the silver content of the solid solution crystals was determined, using pure silver tetraborate crystals as a standard. (A uniform distribution of silver in the crystals was also verified, indicating a well defined composition. In agreement with this, the solid solution gave a sharp powder pattern.) A hand picked 2-mg sample of crystals was

analysed for sodium with a spectrophotometer. Both methods gave consistent results, corresponding to replacement of 40 mol. % of the silver oxide by sodium oxide. This result was further checked by measuring the density of the solid solution crystals by the flotation method. The heaviest fraction appeared to have a density slightly above 2.9 g.cm^{-3} as compared with 2.98 g.cm^{-3} calculated for 40 mol. % substitution by sodium oxide and 3.41 g.cm^{-3} for the pure silver compound.

The unit-cell dimensions for the solid solution crystalline phase $(\text{Ag}_{0.6}\text{Na}_{0.4})_2\text{O} \cdot 4\text{B}_2\text{O}_3$ were found to be:

$$a = 6.521 \pm 0.003, \quad b = 8.624 \pm 0.004, \\ c = 17.549 \pm 0.008 \text{ \AA}; \quad \beta = 90^\circ 20' \pm 5'.$$

X-ray intensity data were collected for this phase with the Weissenberg multiple film technique, using $\text{Mo } K\alpha$ radiation. A crystal of prismatic shape with a cross section of $0.0067 \times 0.0060 \text{ cm}^2$ was used. The crystal was rotated about the b axis and data were collected for the equatorial and six non-equatorial layers. An equatorial exposure about the a axis was also secured. Intensities were estimated by visual comparison with a calibration strip for 829 reciprocal lattice points. No absorption corrections were considered necessary, the linear absorption coefficient being only 25 cm^{-1} (as compared with 40 cm^{-1} for pure silver tetraborate). A list of observed structure factors is available upon request.

The structure determination

The structure contains 2 cations, 13 oxygen atoms and 8 boron atoms in the asymmetric unit, all atoms

Table 1. *Atomic position parameters, with standard deviations*

Values are given as fractions multiplied by 10^4 , of the unit cell edge. The last two columns give the parameter B (together with its standard deviation) of the temperature factor $\exp[-B(\sin \theta/\lambda)^2]$

Atom	x/a	$\sigma_{x/a}$	y/b	$\sigma_{y/b}$	z/c	$\sigma_{z/c}$	B	σ_B
Ag(1)	616	5	4855	4	1184	2	1.59 \AA^2	0.05
Ag(2)	4671	5	645	4	994	2	1.50	0.05
O(1)	4272	28	7798	24	336	10	1.3	0.3
O(2)	4523	27	5508	24	1151	10	1.2	0.3
O(3)	2493	25	1673	22	4275	9	0.6	0.3
O(4)	4604	28	3117	23	3407	11	1.4	0.3
O(5)	589	25	9740	22	1174	9	0.7	0.3
O(6)	1685	26	1855	23	424	10	1.0	0.3
O(7)	9884	28	2332	25	1596	10	1.3	0.3
O(8)	1966	25	6277	22	4445	9	0.5	0.3
O(9)	860	27	6750	23	307	10	1.0	0.3
O(10)	347	27	5244	24	2572	10	1.4	0.3
O(11)	609	27	7700	24	2064	9	1.0	0.3
O(12)	4587	26	955	24	2533	10	1.3	0.3
O(13)	4618	26	3428	23	2018	9	0.9	0.3
B(1)	4615	44	1958	40	4066	16	0.8	0.5
B(2)	9964	48	1181	43	920	17	1.3	0.6
B(3)	1176	38	2273	37	4822	13	0.2	0.4
B(4)	385	51	6811	47	2659	18	1.7	0.6
B(5)	2371	47	7736	43	63	17	1.2	0.5
B(6)	224	42	9187	41	1883	15	0.9	0.5
B(7)	4805	51	5009	45	1879	18	1.5	0.5
B(8)	4690	42	2492	42	2664	14	0.8	0.5

occupying general fourfold positions in the lattice. The positions of the two cations were determined from Patterson projections about the a and b axis. Based on signs from these positions, a three-dimensional Fourier difference summation (with the cation contribution subtracted) was calculated. These calculations were carried out on an ALWAC III E electronic computer. The three-dimensional Fourier synthesis gave a unique set of parameters for all the boron and oxygen atoms. The initial set of parameters obtained in this manner, was subjected to a least-squares refinement analysis, including all observed structure factors. A program written by Åsbrink & Brändén for the Facit EDB computer was utilized. The Cruickshank weighting scheme was used. Atomic form factors were taken for the neutral atoms from *International Tables for X-ray Crystallography* (1962). The atomic form factor for the cation was obtained by compounding the values for silver and sodium.

After 11 cycles, no further improvement in the parameters was evident. The residual index R , including only observed reflexions, remained at 11.0% during the last few cycles. Table 1 gives the parameter values and isotropic temperature factors, all with standard deviations. The cations are referred to as Ag in the table, though treated in the calculations as a hypothetical atom with 32.6 electrons.

Description of the structure

The structure consists of two separate, identical, interlocking, three-dimensional networks. This phenomenon of two independent networks has previously been encountered in the structures of potassium pentaborate (Krogh-Moe, 1959, 1964) and lithium diborate (Krogh-Moe, 1962*a*). Apparently the bond angles and the structural groups of a single borate network do not in general permit an efficient packing of the atoms. Instead a double network is formed so as to avoid a very open, low-density structure.

Fig. 1 gives an idealized view of one of the twin networks. It is seen that in the direction of the a axis the network may be described as built up alternately of triborate and pentaborate groups. The triborate group is essentially a six-membered ring structure with three oxygen atoms and three boron atoms in the ring. Four additional oxygen atoms are linked to the boron atoms of the ring. Thus one boron atom is tetrahedrally coordinated and the two others are planar triangularly coordinated by oxygen. In cesium triborate (Krogh-Moe, 1960) the anion polymer is simply a three-dimensional network of these triborate groups.

The pentaborate group can be derived from the triborate group by adding another two BO_3 triangles to the fourfold coordinated boron, thereby forming a second six-membered ring. This double-ring structure is found as an isolated polyion in potassium pentaborate tetrahydrate (Zachariasen & Plettinger,

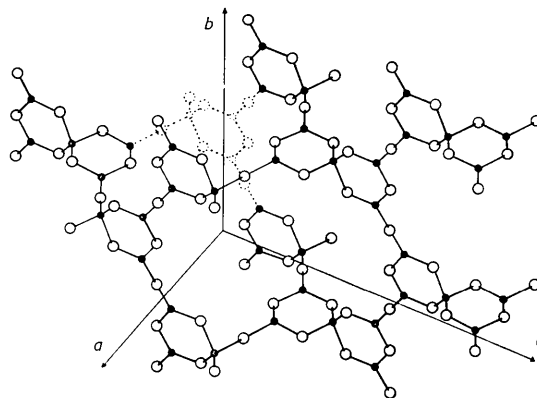


Fig. 1. Idealized view of one of the two three-dimensional networks in silver tetraborate. Large open circles represent oxygen and filled small circles represent boron. The dotted section of the network, a triborate group, is in the rear.

1963). In anhydrous potassium pentaborate, however, each pentaborate group is bonded to four identical groups to form continuous networks. The scarcity (or lack) of hydrated tetraborates is understandable in view of the simultaneous presence of pentaborate and triborate groups, rather than a specific tetraborate group, in the structure of anhydrous tetraborates.

It is seen that two out of every eight boron atoms, *i.e.* 25%, are fourfold coordinated in silver tetraborate. This is the fraction expected from a formula given previously by Krogh-Moe (1960) for the anhydrous alkali borates with less than 34 mol.% alkali. The average boron–oxygen bond lengths in silver tetraborate are 1.47 and 1.37 Å for the tetrahedra and triangles respectively. These values are similar to average values found for many borate structures recently. A list of boron–oxygen bond lengths is given in Table 2. The table shows that the maximum deviations from the average values amounts to no more than twice the estimated standard deviation of ± 0.04 Å.

The oxygen–oxygen distances within the boron coordination polyhedra are also given in Table 2. The consistency of these distances shows that the coordination polyhedra around boron are fairly regular.

The surroundings of the cations, on the other hand, are not symmetrical or regular. This is evident from Table 3. The cation Ag(1) is surrounded by seven closest oxygen neighbours with distances varying from 2.23 to 3.02 Å. The second cation has eight closest oxygen neighbours, with distances ranging from 2.39 to 3.00 Å. Evidently the cation coordination sphere is to a considerable extent governed by the requirements of the borate polymer network and not only by the cation itself. It is understandable that this kind of cation position can accommodate a considerable amount of sodium.

Since the two cation sites are not quite equivalent

Table 2. Boron-oxygen bond lengths (standard deviation ± 0.04 Å) and oxygen-oxygen distances (standard deviation ± 0.03 Å) of the boron coordination polyhedra

The boron atoms numbered 1, 7 and 8 belong to the tetraborate group

Tetrahedra			
B(1)-O(1')	1.47 Å	O(1')-O(2')	2.44 Å
B(1)-O(2')	1.42	O(1')-O(3)	2.42
B(1)-O(3)	1.45	O(1')-O(4)	2.34
B(1)-O(4)	1.53	O(2')-O(3)	2.31
		O(2')-O(4)	2.45
		O(3)-O(4)	2.40
Triangles			
B(3)-O(3)	1.39 Å	O(3)-O(6'')	2.44 Å
B(3)-O(6'')	1.34	O(3)-O(9')	2.31
B(3)-O(9')	1.42	O(6'')-O(9')	2.42
B(5)-O(1)	1.33 Å	O(1)-O(8'')	2.31 Å
B(5)-O(8'')	1.40	O(1)-O(9)	2.40
B(5)-O(9)	1.37	O(8'')-O(9)	2.39
B(7)-O(2)	1.36 Å	O(2)-O(12')	2.41 Å
B(7)-O(12')	1.37	O(2)-O(13)	2.35
B(7)-O(13)	1.39	O(12')-O(13)	2.38
B(2)-O(5)	1.38 Å	B(2)-O(6)	1.53
B(2)-O(6)	1.53	B(2)-O(7)	1.55
B(2)-O(7)	1.55	B(2)-O(8')	1.42
O(5)-O(6)	2.36 Å	O(5)-O(7)	2.40
O(5)-O(7)	2.40	O(5)-O(8')	2.39
O(6)-O(7)	2.40	O(6)-O(8')	2.44
O(6)-O(8')	2.44	O(7)-O(8')	2.37
B(4)-O(7')	1.39 Å	B(4)-O(10)	1.36
B(4)-O(10)	1.36	B(4)-O(11)	1.30
B(4)-O(11)	1.30	O(7')-O(10)	2.32 Å
B(6)-O(5)	1.35 Å	O(7')-O(11)	2.39
B(6)-O(10')	1.37	O(10)-O(11)	2.30
B(6)-O(11)	1.35	O(5)-O(10')	2.32 Å
O(5)-O(10')	2.32 Å	O(5)-O(11)	2.35
O(5)-O(11)	2.35	O(10')-O(11)	2.37
O(10')-O(11)	2.37	O(4)-O(12)	2.41 Å
O(4)-O(12)	2.41 Å	O(4)-O(13)	2.45
O(4)-O(13)	2.45	O(12)-O(13)	2.32

Table 3. Cation-cation separations smaller than 6 Å (standard deviation ± 0.004 Å) and cation-oxygen distances (standard deviation ± 0.02 Å) for the first coordination shell of the cation

The cation is referred to as Ag, though replaced to 40% by sodium

Ag(2)-Ag(2')	3.686 Å	Ag(1)-O(2)	2.60 Å
Ag(1)-Ag(1')	4.238	Ag(1)-O(3')	2.67
Ag(2)-Ag(1)	4.525	Ag(1)-O(6)	3.02
Ag(2)-Ag(1')	5.340	Ag(1)-O(7)	2.37
Ag(2)-Ag(1'')	5.637	Ag(1)-O(9)	2.23
		Ag(1)-O(10)	2.46
		Ag(1)-O(11)	2.88
Ag(2)-O(1)	2.78 Å		
Ag(2)-O(1'')	2.73		
Ag(2)-O(4')	2.47		
Ag(2)-O(5)	2.79		
Ag(2)-O(6)	2.43		
Ag(2)-O(8')	2.39		
Ag(2)-O(12)	2.71		
Ag(2)-O(13)	3.00		

with respect to the surroundings, it is conceivable that the distribution silver-sodium is not entirely random. The Fourier peaks at the two cation positions are very similar in size, however, so that the deviation from random distribution cannot be very large.

Table 3 also gives the cation-cation distances. These are of interest for a comparison with corresponding distances, obtained from radial distribution curves of vitreous tetraborate phases.

The relation of silver tetraborate to other tetraborates

The large range of solid solubility raises the question whether pure sodium tetraborate, $\text{Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$, is isomorphous with the silver tetraborate phase studied in this paper. This is not the case, however, but the similarity in unit-cell dimensions indicates that the

phases are structurally related. Sodium tetraborate is also monoclinic with unit-cell dimensions (Krogh-Moe, 1957):

$$a = 6.50, b = 17.80, c = 8.37 \text{ Å}; \beta = 96.5^\circ.$$

The space group was reported as $P2_1$ or $P2_1/m$, but recent studies indicate that the space group is probably $P2_1/a$. The sodium tetraborate unit cell thus mainly differs from the silver tetraborate cell by the exchange of the unique axis with the c axis, and by a change of the extinction conditions to conform with $P2_1/a$ instead of $P2_1/c$. The cell dimensions are not very different, however. Stronger evidence for a structural relationship of these two phases is found by comparing the infrared spectra in the region from 2 to 15 microns. The spectra are found to be remarkably similar, thus supporting a hypothesis that even crystalline sodium tetraborate is built up from tetraborate groups and pentaborate groups.

From a statistical mechanical analysis of thermodynamic data it was concluded that sodium tetraborate fuses with little decomposition (Krogh-Moe, 1962b). Also it was concluded that the melt does not contain separate tetraborate groups or pentaborate groups, but rather a tetraborate group. This does not contradict the results of the present structure determination, however. Supposing that tetraborate and pentaborate groups exist in the melt, the statistical analysis merely shows that such groups do not exist as independent units, that is units which may be randomly linked with each other to a network in the melt. A tetraborate group must therefore (nearly) always appear associated with a pentaborate group in the melt. This entity can thus, from a statistical point of view, formally be regarded as a tetraborate group, whether or not the constituent units are linked with boron-oxygen bonds.

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The Structure of the Adduct of $\text{Ph}_3\text{P}=\text{N}.\text{Ph}$ and $\text{MeO}_2\text{C}.\text{C}=\text{C}.\text{CO}_2\text{Me}$

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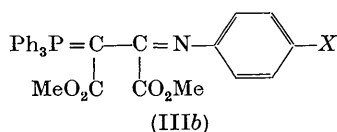
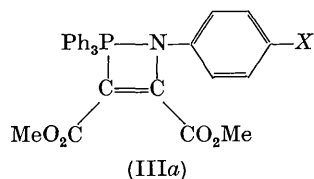
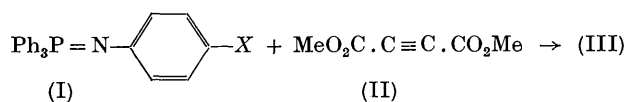
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Tetraphenylphosphine imide, $\text{Ph}_3\text{P}=\text{N}.\text{Ph}$, forms a 1:1 adduct with acetylenedicarboxylic acid dimethyl ester, $\text{MeO}_2\text{C}.\text{C}=\text{C}.\text{CO}_2\text{Me}$; two types of structure may be proposed for this adduct, one containing a four-membered ring of phosphorus, nitrogen and two carbon atoms, the other being an open chain structure with a $\text{>P}=\text{C}-\text{C}=\text{N}-$ unit. The molecular structure of the adduct has been determined by X-ray analysis of the bromo-derivative, prepared from *N-p*-bromophenyl-*PPP*-triphenylphosphine imide, $\text{Ph}_3\text{P}=\text{N}.\text{C}_6\text{H}_4.\text{Br}$. Crystals of the bromo-derivative are monoclinic, $a=11.83$, $b=9.24$, $c=25.43$ Å, $\beta=104^\circ 15'$, $Z=4$, space group $P2_1/c$. The intensities of all reflexions with $d \geq 1$ Å were measured with a scintillation counter and Mo $K\alpha$ radiation, and visual estimates of Cu $K\alpha$ Weissenberg films were made for higher order reflexions. The bromine atom is in a pseudospecial position, and the structure was solved by determining the x and z coordinates from the b -axis projection, and then deducing the y parameters by trials with various models. The parameters were then refined by three-dimensional F_o and (F_o-F_c) syntheses, differential syntheses, and a cycle of least squares; R for 1940 observed reflexions is 0.21.

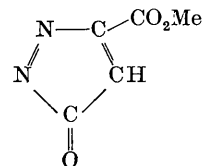
The molecule has the open-chain structure, $\text{Ph}_3\text{P}=\text{C}(\text{CO}_2\text{Me}).\text{C}(\text{CO}_2\text{Me})=\text{N}.\text{C}_6\text{H}_4.\text{Br}$ and all the dimensions are normal; one distance which is worthy of note, since it does not appear to have been measured previously, is $\text{P}=\text{C}$, which is 1.70 ± 0.03 Å.

Introduction

Tetraphenylphosphine imide (I, $X=\text{H}$) forms a 1:1 adduct (III) with acetylenedicarboxylic acid dimethyl



ester (II). Chemically the adduct is very resistant to oxidative, reductive and hydrolytic attack, but $\text{Ph}_3\text{P} \rightarrow \text{O}$, $\text{Ph}.\text{NH}.\text{Me}$ and



can be isolated as degradation products, indicating that in the formation of the adduct there is no extensive rearrangement. Two possible structures may be suggested for the adduct, (IIIa) with a four-membered ring, and the open-chain formulation (IIIb), and the stability of the compound makes it difficult to distinguish between these by chemical methods. We have therefore undertaken an X-ray investigation of the bromo-derivative (III, $X=\text{Br}$), prepared from *N-p*-bromophenyl-*PPP*-triphenylphosphine imide (I, $X=\text{Br}$). This analysis shows that the bromo-derivative has structure (IIIb, $X=\text{Br}$), and hence the unsubstituted adduct is (IIIb, $X=\text{H}$).

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