Redetermined Crystal Structures of $PdAs_2$, $PdSb_2$, PtP_2, $PtAs_2$, $PtSb_2$, α-$PtBi_2$, and $AuSb_2$

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The compounds $PdAs_2$, $PdSb_2$, PtP_2, $PtAs_2$, $PtSb_2$, α-$PtBi_2$, and $AuSb_2$ with pyrite type crystal structure have been reinvestigated by X-ray powder methods. The redetermined lattice constants and parameters are

$$PdAs_2: a = 5.9855 \pm 0.0005 \text{ Å}, \, x = 0.383 \pm 0.001$$
$$PdSb_2: a = 6.4584 \pm 0.0005 \text{ Å}, \, x = 0.371 \pm 0.002$$
$$PtP_2 \, : a = 5.6956 \pm 0.0005 \text{ Å}, \, x = 0.394 \pm 0.004$$
$$PtAs_2: a = 5.9665 \pm 0.0004 \text{ Å}, \, x = 0.383 \pm 0.002$$
$$PtSb_2: a = 6.4400 \pm 0.0004 \text{ Å}, \, x = 0.375 \pm 0.002$$
$$\alpha\text{-}PtBi_2: a = 6.7022 \pm 0.0006 \text{ Å}, \, x = 0.371 \pm 0.002$$
$$AuSb_2: a = 6.6583 \pm 0.0005 \text{ Å}, \, x = 0.376 \pm 0.002$$

The shortest pnigogen-pnigogen interatomic distances found in these compounds are compared with corresponding distances in other compounds.

Accurate quantum mechanical calculations on solids will eventually reveal the electronic band structure and the charge distribution throughout the crystals. In the meantime, it is worthwhile endeavouring to make reasonably accurate estimates of the chemical bonding from electrical, optical, magnetic, and structural data. Some of the most fundamental information on the interaction of the atoms in the solid state is provided by structural data, which give knowledge regarding coordination and interatomic distances. A detailed empirical or semiempirical discussion of the bond lengths (the shortest metal-metal $(M-M)$, metal-metalloid $(M-X)$, and metalloid-metalloid $(X-X)$ interatomic distances) is difficult without knowledge of the possible interactions (especially the charge distribution) in the crystals.

The present study is a link in continued studies of transition metal polyanionic compounds (*i.e.* compounds with $X-X$ bonds; for more detailed definitions of the terms polyanionic, normal valence, and polycationic compounds, see Pearson[1]) with the purpose of collecting values for pnigogen-pnigogen bond distances. The present paper is concerned with a redetermina-
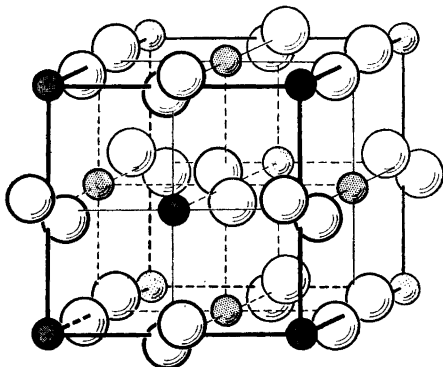
Fig. 1. The pyrite type structure. The smaller and larger circles represent the metal and the metalloid atoms, respectively. Space group: *Pa*3. Equivalent positions: 4 metal atoms in (*a*); 8 metalloid atoms in (*c*).

tion of the pyrite type crystal structures of $PdAs_2$, $PdSb_2$, PtP_2, $PtAs_2$, $PtSb_2$, α-$PtBi_2$, and $AuSb_2$. The pyrite type structure (Fig. 1) is characterized by pairs of metalloid atoms and compounds with this type of structure are thus polyanionic compounds. While the positions of the metal atoms in this type of structure are fixed, a variable parameter (x) is necessary to establish the positions of the metalloid atoms. As the pyrite type structure is cubic with only one variable parameter, compounds having this crystal structure should be favourable for accurate determination of interatomic distances. By comparing the $X-X$ bond distances in these compounds with those of other pnigogen compounds it should be possible to decide to what extent a suggested covalent $X-X$ bond distance is modified by interaction phenomena.

EXPERIMENTAL

The samples were prepared from 99.9 + % Pt (Falconbridge Nikkelverk A/S), 99.99 % Pd (L. Light & Co., Ltd.), 99.999 % Au (L. Light & Co., Ltd.), 99.5 % red P (The British Drug Houses Ltd.), 99.999 + % As and Sb (Johnson, Matthey & Co., Ltd.), and 99.99 + % Bi (American Smelting and Refining Co.) by heating accurately weighed quantities of metal and pnigogen in evacuated, sealed silica tubes for 30 days at 650°C. The samples were then cooled to room temperature over a period of 30 days. The $AuSb_2$ sample was reannealed for 20 days at 300°C and quenched in ice water.

All samples were crushed and X-ray powder photographs taken with filtered CuK-radiation ($\lambda(\alpha_1) = 1.54050$Å) in cameras with 114.6 mm effective diameter and asymmetric film mounting. Lattice constants were determined from high-angle reflections by extrapolation according to the method of Nelson and Riley.[2] X-Ray photographs were also taken in a Guinier type focusing camera of 80 mm diameter using strictly monochromatized $CuK\alpha_1$-radiation. Potassium chloride (Analar, The British Drug Houses Ltd., $a = 6.2919$ Å [3]) was added to the specimen as an internal standard.

The relative intensities of the reflections on Debye-Scherrer photographs were determined from photometric recordings of the films. Multiple-film photographs were used to avoid errors in the estimation of the strongest and weakest reflections. Corrections for the resolution of $K\alpha_1\alpha_2$ doublets were carried out according to the method of Rae and Barker.[4] In the calculation of F_c values, atomic scattering factors were taken from *International Tables*.[5] (The relation between intensities and structure factors is given by the expression $I \propto F^2 \times Lp \times \nu \times T \times A$.) For $PdAs_2$, $PdSb_2$, $PtSb_2$, α-$PtBi_2$, and $AuSb_2$

corrections for absorption and temperature factors had to be carried out, whereas $T \times A$ was almost constant for PtP_2 and $PtAs_2$. Two different reliability indices

$$R = \Sigma \, ||F_o| - |F_c|| / \Sigma |F_o|$$
$$R^* = \Sigma \, |I_o - I_c| / \Sigma I_o$$

were calculated in order to judge the degree of agreement between the observed and calculated data.

RESULTS

The lattice constants of the samples used in this study, are listed in Table 1. (The values were determined from Guinier and Debye-Scherrer photograph data, which showed good internal agreement.)

Sets of structure factors were calculated for values of x in the range $0.35-0.42$. From these sets of F_c, sets of I_c were calculated and compared with the corresponding I_o for the compounds PtP_2, $PtAs_2$, and $PtSb_2$. R^* was then calculated as a function of x. The results are shown in the upper part of Fig. 2. (The observed intensities of the strong high-angle reflections $(\Theta > 70°)$ are, probably because of systematic errors, considerably lower than the calculated ones and are not included in the calculations.)

For compounds with pyrite type structure, F_o values can be obtained from powder photograph data for about half of the possible reflections. Comparison of structure factors by the reliability index R instead of comparison of intensities by R^* simplifies the calculations by allowing extensive use of the available electronic computer programs. R is shown as a function of x for the same three compounds, PtP_2, $PtAs_2$, and $PtSb_2$, in the lower part of Fig. 2. The x value of the minimum in the x,R curve for each compound is not shifted from that of the corresponding x,R^* curve. In accordance with convention, the position of the minimum is used to locate the best value of the variable parameter x. As the minima in the corresponding x,R and x,R^* curves occur at the same value of x, we suggest that the structural x parameter for compounds with pyrite type structure can be determined from the selected reflections which allow the use of x,R curves. The simplified calculations were carried out for $PdAs_2$, $PdSb_2$, α-$PtBi_2$, and $AuSb_2$. The R versus x curves are shown in Fig. 3.

Table 1. Structural data for $PdAs_2$, $PdSb_2$, PtP_2, $PtAs_2$, $PtSb_2$, α-$PtBi_2$, and $AuSb_2$.

| Compound	a (Å)	x	Metal-pnigogen distance (Å)	Pnigogen-pnigogen distance (Å)
$PdAs_2$	5.9855 ± 0.0005	0.383 ± 0.001	2.498 ± 0.002	$2.42_6 \pm 0.02$
$PdSb_2$	6.4584 ± 0.0005	0.371 ± 0.002	2.671 ± 0.004	$2.88_6 \pm 0.05$
PtP_2	5.6956 ± 0.0005	0.394 ± 0.004	2.401 ± 0.010	$2.09_1 \pm 0.08$
$PtAs_2$	5.9665 ± 0.0004	0.383 ± 0.002	2.490 ± 0.004	$2.41_8 \pm 0.04$
$PtSb_2$	6.4400 ± 0.0004	0.375 ± 0.002	2.669 ± 0.004	$2.78_9 \pm 0.05$
α-$PtBi_2$	6.7022 ± 0.0006	0.371 ± 0.002	2.771 ± 0.004	$2.99_5 \pm 0.05$
$AuSb_2$	6.6583 ± 0.0005	0.376 ± 0.002	2.763 ± 0.004	$2.86_0 \pm 0.05$
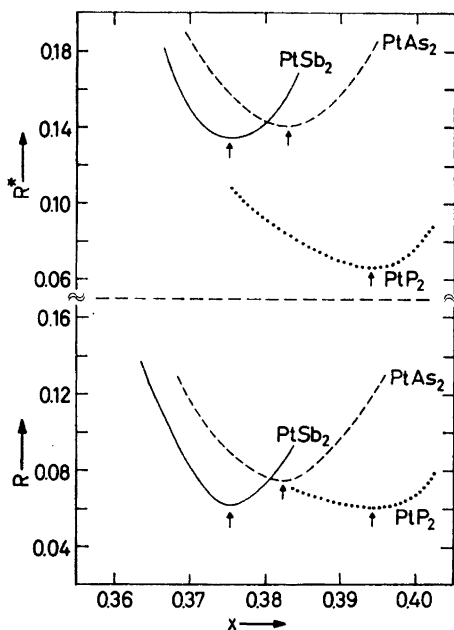
Fig. 2. Reliability indices R^* and R as functions of the x parameter of the metalloid atoms for PtP_2, $PtAs_2$, and $PtSb_2$.
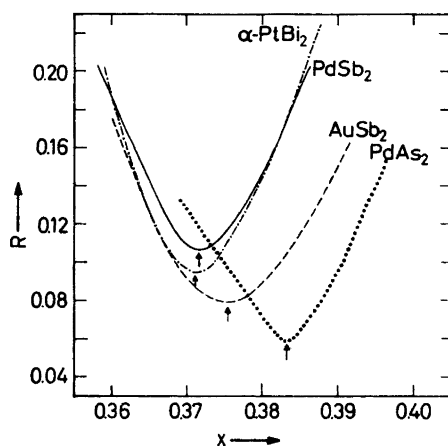
Fig. 3. R versus x for $PdAs_2$, $PdSb_2$, α-$PtBi_2$, and $AuSb_2$.

The final x parameters are listed in Table 1 together with the corresponding error limits in x estimated from the curvature of the x,R curves. The observed and calculated intensities (corresponding to the values of x listed in Table 1) are listed in Table 2. Except for the compounds PtP_2 and $AuSb_2$, the previous determinations [6,7] of the crystal structures of these compounds were based on calculations assuming the "ideal" pyrite parameter $x = 0.38 \approx 3/8$. The parameter $x = 0.390 \pm 0.005$ for PtP_2, determined by Rundqvist,[8] agrees with the present value within the limited accuracies of the two studies. Because of the large difference in scattering factors between Pt and P, R (and R^*) is less sensitive to variation in x (Fig. 2) for PtP_2 than for the other compounds in Table 1. The value $x = 0.386 \pm 0.007$ for $AuSb_2$ reported by Graham and Kaiman [9] is somewhat different from the present value.

The shortest interatomic $M-X$ and $X-X$ distances are calculated and listed in Table 1. A discussion of the $M-X$ distances obtained in this study, is postponed to a later paper and only the $X-X$ distances are considered in the following text. The $X-X$ distances in Table 1 can be compared with corresponding distances reported in the literature. A distinction between pnigogen-pnigogen bond distances found in transition metal polyanionic compounds and those of corresponding non-transition metal compounds is adopted in the construction of Table 3, which contains the results of our

Table 2. Observed and calculated intensities for $PdAs_2$, $PdSb_2$, PtP_2, $PtAs_2$, $PtSb_2$, α-$PtBi_2$, and $AuSb_2$.

hkl	PdAs₂		PdSb₂		PtP₂		PtAs₂		PtSb₂		α-PtBi₂		AuSb₂	
	I_o	I_c	I_o	I_c	I_o	I_c	I_o	I_c	I_o	I_c	I_o	I_c	I_o	I_c
111	220	136	113	67	1482	1423	833	1020	621	745	0	28	47	91
200	465	514	388	375	1270	1225	1146	1405	1285	1577	98	127	137	166
210	419	472	1299	1876	93	58	451	498	1670	1705	376	581	182	191
211	414	419	1058	1371	87	53	423	415	1297	1366	291	431	134	150
220	278	301	374	366	825	829	841	930	974	1149	111	129	120	129
221	0	4	0	4	42	3	69	4	0	2	0	1	0	0
311	536	735	1493	1461	1119	1131	1564	1770	2725	2897	452	508	334	335
222	95	102	172	129	283	284	325	326	437	413	49	46	43	47
320	130	161	421	369	34	26	168	158	554	474	121	121	57	49
321	396	221	844	775	42	32	232	221	952	755	253	256	113	85
400	0	5	163	91	76	70	0	11	0	11	49	29	0	1
410⎱ 322⎰	0	5	0	3	0	4	0	5	0	2	0	1	0	0
411	0	3	233	217	0	2	0	3	0	1	0	1	0	0
331	59	57	0	2	338	361	294	298	213	217	0	2	26	23
420	80	95	0	1	320	323	377	362	659	492	89	76	79	61
421	87	93	460	394	18	9	112	91	525	362	163	135	56	42
332	41	45	226	173	18	4	74	45	271	172	72	59	27	20
422	84	92	156	120	261	271	340	312	427	396	52	45	51	46
430	0	2	0	1	0	2	0	2	0	1	0	0	0	0
431	0	3	0	3	0	3	0	3	0	2	0	1	0	0
511⎱ 333⎰	191	259	494	403	401	423	674	614	1026	950	170	149	124	106
520⎱ 432⎰	109	99	332	333	18	13	121	98	455	340	125	115	43	38
521	56	60	269	214	10	7	81	60	264	213	88	73	33	24
440	111	172	448	408	163	162	320	325	619	651	140	144	65	72
522⎱ 441⎰	0	2	0	3	0	1	0	2	0	1	0	1	0	0
433	0	1	0	1	0	1	0	1	0	0	0	0	0	0
531	38	30	57	11	285	324	259	226	160	146	0	5	22	17
600⎱ 442⎰	85	82	108	117	234	266	308	274	327	298	37	31	31	32
610	24	22	89	86	0	2	36	22	103	79	34	29	14	9
611⎱ 532⎰	82	84	292	251	22	16	114	84	310	246	90	83	38	26
620	52	55	85	60	182	201	237	200	259	212	23	22	25	23
621⎱ 540⎰ 443	0	8	0	6	0	6	0	8	0	4	0	2	0	0
541	0	2	0	2	0	2	0	2	0	1	0	0	0	0
533	99	120	190	192	225	263	386	321	443	417	54	67	35	44
622	54	61	85	60	212	246	282	220	235	208	18	21	21	22
630⎱ 542⎰	52	61	214	250	0	6	73	61	274	205	62	80	24	22
631	53	54	141	150	0	6	92	54	179	150	44	48	17	15
444	0	1	0	30	51	67	0	9	0	3	0	9	0	0
632	0	8	0	3			0	8	0	2	0	1	0	0
543	0	3	0	2			0	3	0	1	0	1	0	0
711⎱ 551⎰	66	43	0	12			394	304	121	136	0	5	13	14

Table 2. Continued.

640	139	157	60	27			519	436	226	289	9	10	21	24
720⎫ 641⎭	119	124	236	71			149	126	241	260	50	66	24	24
721⎫ 552⎬ 633⎭	134	155	323	328			182	158	381	332	72	98	31	33
642	248	244	131	141			813	888	439	502	32	46	36	48
722⎫ 544⎭	0	4	0	3			0	4	0	1	0	1	0	0
731⎫ 553⎭			697	804					1379	1603				
650⎫ 643⎭			277	305					296	329				
651⎫ 732⎭			317	433					384	451				

search in the literature. For each class of compounds the mean value and the corresponding standard deviation for a single "measurement" are listed. (A weight ranging from 1 to 5 has been given according to the estimated accuracy in the previous structure determination.) With an overall error limit of twice the standard deviation there appears to be no significant difference between the two sets of $X—X$ distances in columns I and II of Table 3. The mean values for both transition and non-transition metal compounds are therefore listed in column III together with the corresponding standard deviations. A comparison of the values in the penultimate columns of Tables 1 and 3 shows that the $X—X$ distances for the compounds $PdSb_2$, $AuSb_2$, and α-$PtBi_2$ are in good agreement with the literature values. The largest discrepancy is found for PtP_2 where the obtained $P—P$ distance is significantly shorter than all the $P—P$ bond distances found in our search of the literature. (However, as pointed out above, PtP_2 is rather unfavourable for accurate determination of the $P—P$ distance.)

As a conclusion of this study we propose that the set of mean values with the appropriate error limits (twice the standard deviation) listed in the penultimate column of Table 3 will give reasonable expectation values for the pnigogen-pnigogen bond distances in a polyanionic compound. The modifying

Table 3. Pnigogen-pnigogen bond distances and standard deviations in Å for transition (I) and non-transition (II) element compounds, together with the mean values of these distances (III).

$X—X$	I		II		III	
$P—P$	2.18_8	0.04	2.24_4	0.05	2.20_9	0.03
$As—As$	2.48_0	0.06	2.48_9	0.05	2.48_5	0.04
$Sb—Sb$	2.84_4	0.07	2.86_5	0.02	2.86_3	0.02
$Bi—Bi$	3.05_4	0.06	—		3.05_4	0.06

influence of the variety of interatomic interactions should however be considered as significant.

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