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The Crystal Structures of Au_2P_3 and $Au_7P_{10}I$, Polyphosphides with Weak Au—Au Interactions

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Abstract

Gold phosphides which were previously reported with composition Au_2P_3 correspond to different compounds with stoichiometries Au_2P_3 and $Au_7P_{10}I$. Au_2P_3 is monoclinic, space group $C2/m$, $a = 5·863$ (1), $b = 14·439$ (3), $c = 4·674$ (1) Å, $\beta = 108·39$ (1)°, $Z = 4$. $Au_7P_{10}I$ has trigonal symmetry, space group $P\bar{3}1m$, $a = 6·180$ (1), $c = 11·122$ (2) Å, $Z = 1$. Single crystals were prepared for both compounds and their structures were determined and refined from single-crystal diffractometer data. Final conventional R values were 0·054 (878 reflections) for Au_2P_3 and 0·053 (699 reflections) for $Au_7P_{10}I$. In both structures the P atoms can be formulated as polyanions. This results in formal oxidation numbers of $+1$ for all Au atoms. Most P atoms are tetrahedrally coordinated by P and Au atoms and most of the Au atoms have two close P neighbors at distances between 2·321 and 2·339 Å and P—Au—P angles of 171 and 180°. Exemptions are one set of P atoms in Au_2P_3, where a lone pair of electrons of the P atoms may be considered as interacting with secondary Au valences, and one set of Au atoms in $Au_7P_{10}I$, where the Au atoms have C_{3v} symmetry with one I and three P atoms as close neighbors. In both structures secondary weak Au—Au interactions (with distances of 2·932 to 3·136 Å) occur; these seem to be responsible for the metallic conductivity of both compounds. The I atoms are coordinated by a hexagonal bipyramid of Au atoms. Magnetic measurements indicate diamagnetism for both compounds. Bonding in these and related compounds is briefly discussed.

Introduction

A compound with composition Au_2P_3 was reported by Haraldsen & Biltz (1931) and characterized as mono-clinic by Olofsson (1970). While these authors had prepared this gold phosphide by direct reaction of the elemental components, Beck & Stickler (1972) have used vapor transport with iodine to prepare a compound with similar composition and a hexagonal cell. We have now determined the crystal structures of both compounds and find their compositions to be Au_2P_3 and $Au_7P_{10}I$ respectively. Binnewies (1978) has determined the structure of $Au_7P_{10}I$ independently. Our results, however, disagree concerning the space group and the positions of a set of P atoms (Möller, 1978).

Sample preparation and crystal growth

Starting materials were red P (Merck, 'rein') [which was boiled for 12 h in an aqueous solution of NaOH, washed, and dried (Brauer, 1975)], iodine (Merck, 'reinst'), and an ingot of Au (99·99%) which was dissolved in *aqua regia* and precipitated by hydrazine chloride (Brauer, 1954).

Monoclinic Au_2P_3 was prepared by annealing powders of Au and red P in evacuated silica tubes. Au : P atomic ratios varied between 1:1 and 1:10. The samples were annealed for between 3 and 30 d at temperatures from 1300 to 700 K respectively. The optimal temperature was around 1100 K; at higher temperatures the decomposition pressure of Au_2P_3 was sometimes exceeded, especially in relatively large tubes with small P content. Complete reaction was obtained at lower temperatures, even at 700 K. Apart from Au, monoclinic Au_2P_3, and P, no other reaction product was observed. The Au_2P_3 samples thus prepared were essentially microcrystalline. Au_2P_3 crystals suitable for the structure determination were prepared by chemical transport from 1200 to 1100 K using 2 at.% bromine

as a transporting agent. The bromine was added to the starting mixture in thin closed silica tubes which broke when the temperature was raised.

'Hexagonal Au_2P_3', which later turned out to be trigonal with composition $Au_7P_{10}I$, was obtained over the whole temperature range from 700 to 1300 K whenever iodine was used as transporting agent. With small additions of iodine the reaction product contained monoclinic Au_2P_3 and $Au_7P_{10}I$. When the starting composition contained the necessary 7 wt% iodine, only $Au_7P_{10}I$ was found. Well developed crystals of $Au_7P_{10}I$ were obtained by chemical transport from 970 to 920 K after only two days. Their habit varied from hexagonal plates to hexagonal prisms with diameters of up to 1 mm. Occasionally thin foils ($3 \times 5 \times 0.01$ mm) and needles (up to 5 mm long and 0.01 mm thick) were found. The crystals of Au_2P_3 and $Au_7P_{10}I$ are black with a metallic lustre.

Crystal structure of Au_2P_3

Single-crystal Weissenberg and precession photographs of Au_2P_3 confirmed the monoclinic C-centered cell as found by Olofsson (1970). Lattice constants were refined from Guinier powder data (Table 1) with α-quartz ($a = 4.9130$, $c = 5.4046$ Å) as standard: $a =$

5·863 (1), $b = 14.439$ (3), $c = 4.674$ (1) Å, $\beta = 108.39$ (1)°, $V = 375.5$ Å³. These agree well with Olofsson's data:* $a = 5.8651$ (5), $b = 14.435$ (1), $c = 4.6712$ (4) Å, $\beta = 108.399$ (7)°, $V = 375.3$ Å³. Of the possible space groups, the centrosymmetric $C2/m$ was found to be correct during the structure determination. With four formula units per cell the calculated density is 8·61 Mg m⁻³.

The crystal used for the collection of the intensity data had an approximately globular shape with an average radius of 23 μm. The data were measured on an automated four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation, a scintillation counter and a pulse-height discriminator. Scans were along 2θ with a speed of 0·08° s⁻¹ and a scan angle of between 1·0 and 1·3°, depending on the splitting of the $K\alpha$ doublet. Background was counted for 23 s at both ends of the scan. 4274 reflections within a half-sphere of reciprocal space up to $2\theta = 80°$ were measured which, after averaging, yielded 1186 unique reflections. An absorption correction was made on the assumption of a spherical crystal [μ(Mo $K\alpha) = 76.2$ mm⁻¹].

The structure was determined and refined with Sheldrick's (1976) program system. The positions of the Au atoms were deduced from Patterson maps and the P atoms were located in a difference synthesis. The structure was refined by full-matrix least squares. Scattering factors for neutral atoms were used (Cromer & Mann, 1968), and corrected for anomalous dispersion (Cromer & Liberman, 1970). Weights were assigned according to $w = 1/[\sigma^2(F_o) + 0.0021F_o^2]$ and an extinction correction was applied to the F_c values by refining a parameter x which is defined by $F_c = F(1 - xF^2/\sin \theta)$. Reflections which were overcorrected by this procedure, as well as reflections with $F_o < 6\sigma$, were assigned zero weight in the final least-squares cycles. For a refinement with isotropic thermal parameters the conventional R value was 0·075. The introduction of anisotropic thermal parameters reduced this value to 0·054 for the 878 reflections with nonzero weight in the final least-squares cycles.† For the 1186 reflections $R = 0.089$. A difference synthesis revealed no features lower than -8.6 e Å⁻³ or higher than 12·7 e Å⁻³. All values higher than 4 e Å⁻³ were within 0·8 Å of the Au positions and thus no evidence was found for filling of interstitial sites. Final parameters, interatomic distances and angles are listed in Tables 2 and 3. A stereo-drawing of the structure is shown in Fig. 1.

Table 1. *Powder patterns of* Au_2P_3 *and* $Au_7P_{10}I$

A Guinier camera and Cu $K\alpha$ radiation were used to obtain the experimental powder patterns. The calculated patterns were generated with a computer program (Yvon, Jeitschko & Parthé, 1977) using data for the refined structure. The Q values are defined by $Q = 10^4/d^2$ (Å⁻²).

	Au_2P_3						$Au_7P_{10}I$			
h k l	Q_c	Q_o	I_c	I_o		h k l	Q_c	Q_o	I_c	I_o
0 2 0	192	192	325	s		0 0 1	81	82	192	w
1 1 0	371	371	310	s		0 0 2	323	324	337	m
0 0 1	508	–	0	–		1 0 0	349		5	–
1 1-1	624	623	160	m		1 0 1	430	430	31	vw
0 2 1	700	700	475	vs		1 0 2	672	673	1380	vvs
1 3 0	755	753	70	w		0 0 3	728	729	29	vw
0 4 0	767	–	1	–		1 1 0	1047	1046	817	vs
1 3-1	1007	–	11	–		1 0 3	1077	1077	320	m
1 1 1	1135	1135	242	m		1 1 1	1128	1128	1000	vvs
0 4 1	1276	1276	1000	vvs		1 1-1	1128	1128	416	
2 0-1	1289	1290	529	vs		0 0 4	1293	1294	880	vs
2 0 0	1292	–	8	–		1 1 2	1371	1372	34	vw
2 2-1	1481	–	73	–		1 1-2	1371	1372	0	
2 2 0	1484	1482	200	m		2 0 0	1396	1396	849	vs
1 3 1	1519	–	39	–		2 0 1	1477	1477	1074	vs
1 5 0	1522	1523	135	m		1 0 4	1643	–	0	–
0 6 0	1727	1729	149	m		2 0 2	1720	1720	40	vw
1 5-1	1775	1775	62	w		1 1 3	1775	1774	320	vs
1 1-2	1893	1895	56	w		1 1-3	1775	1774	520	
0 0 2	2033	2035	208	m		0 0 5	2021	2019	39	vw
2 4-1	2057	–	0	–		2 0 3	2124	2123	164	w
2 4 0	2060	2061	367	s		1 1 4	2341	2340	384	s
0 2 2	2225	2227	42	vw		1 1-4	2341	2340	157	
0 6 1	2235	–	6	–		1 0 5	2370	–	40	–
1 3-2	2277	–	14	–		2 1 0	2444	–	6	–
1 5 1	2286	2287	98	m		2 1 1	2525	–	0	–
2 0-2	2303	–	1	–		2 1-1	2525	–	13	
2 0 1	2312	2316	145	m		2 0 4	2690	2689	642	s
2 2-2	2495	2495	97	m		2 1 2	2767	2767	268	s
2 2 1	2504	–	43	–		2 1-2	2767	2767	352	
1 7 0	2673	–	1	–		0 0 6	2910	2910	136	w
3 1-1	2697	2696	43	vw		1 1 5	3068	3067	169	m
0 4 2	2801	2800	12	vvw		1 1-5	3068	3067	178	
1 1 2	2916	2918	52	vw		3 0 0	3142	3141	405	s
1 7-1	2926	–	0	–		2 1 3	3171	3172	126	w
3 1 0	2956	2956	83	w		2 1-3	3171	3172	84	
2 6-1	3016	3013	139	m		3 0 1	3223	3224	332	m
2 6 0	3019	–	7	–		1 0 6	3259	3262	186	w
1 5-2	3044	–	48	–		2 0 5	3417	3418	840	vs

Crystal structure of $Au_7P_{10}I$

The single-crystal diffraction patterns of $Au_7P_{10}I$ were indexed with the hexagonal cell given by Beck & Stickler (1972). The lattice constants, refined from Guinier powder data (Table 1) with α-quartz as

Table 2. *Atomic parameters of* Au_2P_3

Variable positional parameters are multiplied by 10^4. The last column contains B values ($Å^2$) as obtained from a least-squares refinement with isotropic thermal parameters.

	$C2/m$	x	y	z	B
Au(1)	4(f)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	0·85 (2)
Au(2)	4(g)	0	1086 (1)	0	0·96 (2)
P(1)	8(j)	1737 (6)	3789 (2)	1812 (7)	0·66 (6)
P(2)	4(i)	6848 (9)	0	4740 (11)	0·79 (8)

Table 3. *Interatomic distances* (Å) *and angles* (°) *in* Au_2P_3

All distances <3·4 Å are listed. Standard deviations are all less than 0·008 Å and 0·25°.

Au(1)—2 P(1)	2·339	P(1)—Au(1)—P(1)	180·0
2 Au(1)	2·932		
2 Au(2)	3·101	P(1)—Au(2)—P(1)	171·2
Au(2)—2 P(1)	2·331	Au(1)—P(1)—Au(2)	106·2
2 P(2)	3·009	Au(1)—P(1)—P(1)	115·8
2 Au(1)	3·101	Au(1)—P(1)—P(2)	105·8
1 Au(2)	3·136	Au(2)—P(1)—P(1)	112·8
		Au(2)—P(1)—P(2)	107·3
P(1)—1 P(1)	2·199	P(1)—P(1)—P(2)	108·4
1 P(2)	2·208		
1 Au(2)	2·331	Au(2)—P(2)—Au(2)	62·8
1 Au(1)	2·339	Au(2)—P(2)—P(1)	89·1 (2×)
		Au(2)—P(2)—P(1)	144·0 (2×)
P(2)—2 P(1)	2·208	Au(2)—P(2)—P(2)	106·0 (2×)
1 P(2)	2·255	P(1)—P(2)—P(2)	103·0 (2×)
2 Au(2)	3·009	P(1)—P(2)—P(1)	104·6
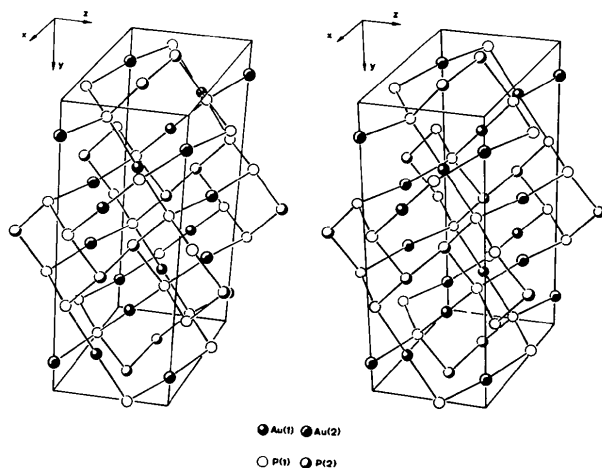
standard, are: $a = 6·180$ (1), $c = 11·122$ (2) Å, $V = 367·9$ Å³. The variations in the lattice constants of the compound in samples with greatly differing starting compositions were all within the error limits. This suggests that the compound has a narrow homogeneity range. In particular, we did not find any indication of partial occupancy of the iodine position.

At first sight our Weissenberg and precession photographs suggested diffraction symmetry $6/mmm$ as proposed by Binnewies (1978). However, a thorough inspection, especially of the single-crystal diffractometer data, clearly showed that the symmetry is trigonal $3m$. No systematically absent reflections were found. Of the six possible space groups, $P\bar{3}1m$ was finally found to be correct during the refinement of the structure.

Intensity data were collected from a prismatic crystal with an average diameter of 0·12 mm. All reflections of one quadrant in reciprocal space up to $2\theta = 76°$ were measured with the experimental set-up as described above for Au_2P_3, except that the scan speed was 0·05° (2θ) s⁻¹. An absorption correction was applied for a spherical crystal after the structure and the composition of the crystals were known [μ(Mo $K\alpha$) = 69·95 mm⁻¹].

The structure was determined from subsequent Patterson and difference syntheses and refined with computer programs as described above for Au_2P_3. Of the 2190 measured intensities, 756 remained after averaging for group $3m$ (the groups $6/mmm$, $6/m$, and $\bar{3}$ could clearly be ruled out). A refinement where all atoms had isotropic thermal parameters resulted in an R value of 0·102 for 699 reflections, excluding those which were overcorrected for secondary extinction, those with $F_o < 3\sigma$ and all 00l reflections (for various reasons). The final conventional R value for these 699 reflections was 0·053 for a refinement where all heavy atoms were allowed anisotropic thermal parameters and the P atoms were refined with isotropic U values.*

* See previous footnote.

Fig. 1. Stereodrawing of the Au_2P_3 structure.
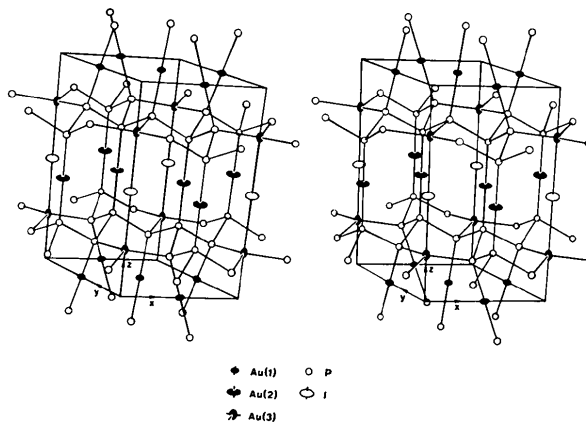
Fig. 2. Stereodrawing of the $Au_7P_{10}I$ structure. Atoms are drawn (Johnson, 1965) at the 67% probability limit.

For the 756 unique reflections $R = 0.071$. The structure is shown in Fig. 2. Final parameters, interatomic distances and angles are listed in Tables 4 and 5.

A final difference Fourier synthesis resulted in no values higher than 6.8 e $Å^{-3}$ or lower than -4.5 e $Å^{-3}$. The highest values of this analysis were close to the positions of the Au and I atoms and are thus probably due to errors resulting from absorption and extinction. The electron density around the origin, which corresponds to a cavity in the structure, peaks at a value of 4.8 e $Å^{-3}$. This should not necessarily be taken as indicative of partial occupancy of that position by light impurity atoms (N or O, for example), since errors in the data tend to result in relatively large errors in electron density maps at high-symmetry positions (Cruickshank & Rollett, 1953).

Table 4. *Final positional and thermal parameters of* $Au_7P_{10}I$

All variable parameters are multiplied by 10^4. The coefficients of the anisotropic thermal parameters ($Å^2$) are defined by

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)].$$

	Au(1)	Au(2)	Au(3)	P(1)	P(2)	I
$P\bar{3}1m$	3(f)	2(d)	2(e)	4(h)	6(k)	1(b)
x	$\frac{1}{2}$	$\frac{1}{3}$	0	$\frac{1}{3}$	3756 (5)	0
y	0	$\frac{2}{3}$	0	$\frac{2}{3}$	0	0
z	0	$\frac{1}{2}$	2240 (1)	2913 (4)	1982 (3)	$\frac{1}{2}$
U_{11} or U	128 (3)	310 (4)	80 (2)	65 (6)	79 (5)	276 (8)
U_{22}	107 (3)	310 (4)	80 (2)			276 (8)
U_{33}	51 (3)	41 (4)	176 (4)			93 (9)
U_{12}	53 (1)	155 (2)	40 (1)			138 (4)
U_{13}	9 (2)	0	0			0
U_{23}	0	0	0			0

Table 5. *Interatomic distances* (Å) *and related interatomic angles* (°) *in* $Au_7P_{10}I$

All distances <3.6 Å are listed. Standard deviations are all less than 0.007 Å and $0.2°$.

Au(1)–2 P(2)	2.335		P(2)–Au(1)–P(2)	180.0	
4 Au(1)	3.090		P(2)–Au(1)–Au(1)	80.5 (4×)	
4 P(2)	3.553		P(2)–Au(1)–Au(1)	99.5 (4×)	
Au(2)–2 P(1)	2.321		P(1)–Au(2)–P(1)	180.0	
3 I	3.568				
3 Au(2)	3.568				
Au(3)–3 P(2)	2.339		P(2)–Au(3)–P(2)	118.5 (3×)	
1 I	3.070		P(2)–Au(3)–I	97.1 (3×)	
P(1)–3 P(2)	2.201		P(2)–P(1)–P(2)	99.7 (3×)	
1 Au(2)	2.321		P(2)–P(1)–Au(2)	118.1 (3×)	
3 P(1)	3.568				
P(2)–2 P(1)	2.201		P(1)–P(2)–P(1)	108.3	
1 Au(1)	2.335		P(1)–P(2)–Au(1)	109.2 (2×)	
1 Au(3)	2.339		P(1)–P(2)–Au(3)	106.8 (2×)	
4 P(2)	3.365		Au(1)–P(2)–Au(3)	116.3	
2 Au(1)	3.553				
I–2 Au(3)	3.070		Au(3)–I–Au(3)	180.0	
6 Au(2)	3.568				

We considered partial occupancy of the iodine position in $Au_7P_{10}I$ to be possible. We therefore refined our intensity data with variable occupancy of the iodine position by also allowing a simultaneous variation of anisotropic thermal parameters. This resulted in an occupancy value of 0.996 ± 0.018 with essentially unchanged thermal parameters. Thus neither the phase analysis, nor any variation in lattice constants, nor the structure refinement gave evidence for a deviation from the ideal composition $Au_7P_{10}I$.

The positions of most atoms in the structure of $Au_7P_{10}I$ correspond to space group $P6/mmm$. Only the positions of the six P(2) atoms violate this group. In $P6/mmm$ they correspond to a half-occupancy of the twelvefold position $x0z$. Full occupancy of this position can be ruled out for reasons of space requirements. In the *translationsgleiche* (Wondratschek & Jeitschko, 1976) maximal subgroups $P\bar{3}1m$ and $P\bar{6}2m$ this twelvefold position splits into two different sixfold sets in such a way that three P positions are the same in $P\bar{3}1m$ and $P\bar{6}2m$, and the other three positions are entirely different from each other. Binnewies (1978) refined the structure in space group $P\bar{6}2m$ and reports unspecified R values of 0.060 and 0.097. We have now refined our data in that group and find an R of 0.100. This compares with an R value of 0.053 as described above for $P\bar{3}1m$ with essentially the same number of variable parameters and reflections. Moreover, the difference Fourier synthesis for the refinement in $P\bar{6}2m$ gave as highest peaks the three positions of the P atoms which we find occupied in $P\bar{3}1m$. Thus space group $P\bar{6}2m$ can clearly be ruled out. Nor should it be considered a possibility for a polymorph of $Au_7P_{10}I$ for structure–chemical reasons since it leads to an angular (141°) twofold P(2) coordination for Au(1) rather than the usual linear coordination for Au in its monovalent state. Nevertheless it seems possible that occasional stacking faults result in multiple-domain crystals such that six-fold overall diffraction symmetry is simulated.

Discussion

Although a large number of organometallic Au–P compounds have been reported in recent years, Au_2P_3 and $Au_7P_{10}I$ are the only solid-state gold phosphides known so far. Their structures show characteristics which can be discussed within the context of the structural chemistry of solid-state transition-metal phosphides and with respect to organometallic gold phosphines.

From the standpoint of solid-state transition-metal phosphides, both Au_2P_3 and $Au_7P_{10}I$ may be regarded as low-coordinated phosphides, where all P atoms are four-coordinated (counting lone pairs of electrons as 'ligands'). High-coordinated phosphides, with coordination numbers greater than four (up to nine) for P, are encountered for phosphides of the early transition

metals (Lundström, 1969). Low-coordinated phosphides are CrP_4 and MoP_4 (Jeitschko & Donohue, 1972), MnP_4 (Jeitschko & Donohue, 1975), ReP_4 (Jeitschko & Rühl, 1979), FeP_4 (Jeitschko & Braun, 1978), RuP_4 and OsP_4 (Braun & Jeitschko, 1978) and all phosphides TP_3 and TP_2 where T indicates Fe- and Pt-group metals (Hulliger, 1968; Jeitschko, 1974a). Au_2P_3 is the low-coordinated transition-metal phosphide with the lowest P content.

To a first approximation the electronic structure of the low-coordinated phosphides is readily rationalized by counting all short near-neighbor interactions as classical two-electron bonds. In order to establish formal oxidation numbers the electrons of the short Au—P bonds are considered as belonging to the P atoms, the P—P bonds are split homolytically and the iodine atom is regarded as the ionic I^{1-}. In this way all Au atoms obtain the formal oxidation number $+1$ and the compounds can be formulated as $Au(1)^{1+}Au(2)^{1+}$-$[P(1)^{1-}]_2P(2)^0$ and $[Au(1)^{1+}]_3[Au(2)^{1+}]_2[Au(3)^{1+}]_2$-$[P(1)^0]_4[P(2)^{1-}]_6I^{1-}$ or (emphasizing the P polyanions) as $Au_2^{1+}(P_3)^{2-}$ and $Au_7^{1+}(P_{10})^{6-}I^{1-}$. Certainly the Au—P bonds are essentially covalent and formal oxidation numbers are introduced here only to count valence electrons.

In Au_2P_3 the P atoms form infinite chains of six-membered rings in the chair conformation which are axially linked to each other via the P(2) atoms (Fig. 3). With the terminology of organic chemistry this chain can be designated as poly(1,4)hexaphosphacyclohexane. These chains, which extend along the z axis, are parallel to each other and connected via the Au atoms which occupy both the equatorial and the axial positions of the P(2) atoms. The equatorial position of the P(1) atom is occupied by a lone pair of electrons which is directed towards two Au(2) atoms. A polyanion P_{3n}^{2n-} in the form of a chain of six-membered rings as in Au_2P_3 is also found in the structure of BaP_3 (von Schnering & Dahlmann, 1971).

The P atoms in $Au_7P_{10}I$ form two-dimensional infinite sheets of twelve-membered rings which contain the Au(3) atoms. The six-membered rings thus obtained (Fig. 4) have a somewhat distorted chair conformation. The axial positions of the P atoms are occupied by the

Au(1) and Au(2) atoms which form the bonds to the adjacent sheets above and below. Although a large number of polyphosphides are known. (von Schnering, 1977), this puckered polyanion seems to be unique to $Au_7P_{10}I$. The P—P bonding distances in Au_2P_3 and $Au_7P_{10}I$ vary between 2·199 and 2·255 Å, which is approximately the range encountered for single P—P bonds (Lee, 1977; Jeitschko & Donohue, 1975).

With the exception of the Au(3) atoms in $Au_7P_{10}I$, the Au atoms are in (at least approximately) linear coordination with two P atoms. This linear coordination is most frequently encountered for Au^I and Hg^{II} compounds. The short Au—P bonding distances vary between 2·321 and 2·339 Å. These correspond to the upper limit of the range of Au—P distances found in molecular compounds: Ph_3P—Au—$Mn(CO)_4P(OPh)_3$, 2·33 (1) Å (Mannan, 1967); $[(Ph_2CH_3P)_2Au]^+(PF_6)^-$, 2·316 (4) Å (Guy, Jones & Sheldrick, 1976); $[Ph_3P$—Au—$C(CF_3)]_2$, 2·28 (1) Å (Gilmore & Woodward, 1971); Ph_3P—Au—C_6F_5, 2·27 (1) Å (Baker & Pauling, 1972); $(\eta$-$C_5H_5)(CO)_3W$—Au—PPh_3, 2·25 (1) Å (Wilford & Powell, 1969); and Ph_3P—Au—$Co(CO)_4$, 2·23 (2) Å (Blundell & Powell, 1971). In these compounds the two ligands of the Au atoms also form approximately linear bonds. Small deviations (up to 15°) from the ideal angle of 180° are probably due to packing effects. It has been argued that some $(d \rightarrow d)\pi$

Fig. 4. The puckered net of six-membered rings containing the P polyanion in the structure of $Au_7P_{10}I$.

Fig. 3. The chain of linked six-membered P rings and their near-neighbor environments in Au_2P_3. Interatomic distances are in Å.

Fig. 5. Near-neighbor environments of the Au atoms in Au_2P_3 (upper part) and $Au_7P_{10}I$ (lower part of the drawing). Small and large light spheres represent P and I atoms. Distances are in Å.

backbonding occurs for such Au—P bonds (Coates & Parkin, 1963), so that they have some double-bond character. There is, however, an important difference between these compounds and the gold phosphides of the present investigation in that the latter seem to form additional secondary bonds to atoms in a plane, approximately perpendicular to the direction defined by the two strongly bonded ligands (Fig. 5).

Usually, a mixture of the $5d_{z^2}$, $6s$, and $6p_z$ orbitals is assumed for the two strong bonds of the Au^I atoms. If electrons are promoted from the $5d$ states of Au to the $6p$ states, the $5d$ states become available for bonding. In the above-mentioned molecular compounds they could interact with the $3d$ states of P. In the Au atoms of Au_2P_3 and the Au(1) atoms of $Au_7P_{10}I$ they apparently interact with $5d$ orbitals of neighboring Au atoms. This is also supported by the metallic conductivity observed for both Au_2P_3 (Juza & Bär, 1956) and $Au_7P_{10}I$ (Binnewies, 1978). The Au—Au distances for these bonds range from 2·932 to 3·136 Å and thus are only slightly longer than the interatomic distances of 2·884 Å in elemental Au. In the molecular compound $[Au(i-C_3H_7O)_2PS_2]_2$ such secondary bonds (from 2·914 to 3·109 Å) are sufficiently strong to cause dimerization in solution and polymerization in the solid state (Lawton, Rohrbaugh & Kokotailo, 1972).

Apparently, the Au(2) atoms of Au_2P_3 form similar secondary bonds of 3·009 Å to the P(2) atoms by interaction with lone pairs of electrons of these P atoms. Similar bonding interactions of lone pairs occur between the Pd and S atoms in PdS_2 and PdPS, where these secondary bonds are the only ones between adjacent layers (Jeitschko, 1974b).

The Au(3) atoms of $Au_7P_{10}I$ are three-coordinated to P with bonding distances of 2·339 Å. An I atom at 3·070 Å completes the coordination of a distorted tetrahedron. However, the Au atom is displaced out of the plane of the three P atoms towards the I atom by only 0·29 Å. Three-coordinated Au is present in $(Ph_3P)_2AuCl$ with Au—P distances of 2·323 and 2·339 Å (Baenziger, Dittemore & Doyle, 1974) and in $[(CH_3)_2PhP]_2AuSnCl_3$ with Au—P distances of 2·310 and 2·318 Å (Clegg, 1978).

All Au atoms in $Au_7P_{10}I$ show anisotropic thermal motion with the largest displacements, as could be expected, in directions perpendicular to the strong bonds. This is also true for the Au atoms in Au_2P_3, although to a somewhat lesser extent. Since large anisotropic thermal displacements are indicative of displacive phase transitions (see, for instance, Jeitschko, 1972, 1975), we considered the possibility of such a transition occurring in $Au_7P_{10}I$. However, Guinier powder photographs, recorded continuously at temperatures between 123 and 623 K, failed to show any indication of such a transition.

Similar anisotropic thermal motion also occurs for the I atom. This atom (which may also be considered

as an I^{1-} ion) is in the unusual coordination of a hexagonal bipyramid with the Au atoms, with two relatively short I—Au bonds of 3·070 Å at the apices and six bonds of 3·568 Å at the base of the pyramid. In AuI the I atoms are in angular two-coordination to Au with an Au—I—Au angle of 72° and with I—Au distances of 2·62 Å (Jagodzinski, 1959). In $Rb_2AgAu_3I_8$ the short Au—I distances vary between 2·55 and 2·64 Å (Strähle & Werner, 1978), in $Rb_2Au_2I_6$ they are 2·54 and 2·64 Å (Strähle, 1978), and in $(Ph_3P)_2AuI$ the Au—I distance is 2·766 Å (Strähle & Beindorf, 1978). Although the I atoms in these latter compounds are essentially bonded only to one Au atom, the Au—I distances in $Au_7P_{10}I$ are nevertheless rather large. Thus the I atom may be considered as 'rattling' in a cage of Au atoms, the size of which is determined by the rest of the structure.

A similar, somewhat smaller, cage is formed by six Au(1) and two Au(2) atoms around the origin of the $Au_7P_{10}I$ structure. This position, which was found to be essentially unoccupied, has 'bonding' distances of 2·49 Å (2×) and 3·09 Å (6×). It seems possible that at higher temperatures some of the I atoms move into this position. Since there is no easy diffusion channel connecting this position to the normal I position, the I atoms might be trapped in the position around the origin when the sample is quenched.

Au_2P_3 is reported to be diamagnetic (Haraldsen, 1939). We have determined the magnetic susceptibility of Au_2P_3 and $Au_7P_{10}I$ with the Faraday technique and find both compounds to be diamagnetic. Apparently this property dominates over the Pauli paramagnetism associated with the metallic conductivity.

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Die Kristallstruktur von Mangan(III)-hydroxid-sulfat-Dihydrat, Mn(OH)SO₄.2H₂O

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Abstract

$Mn(OH)SO_4.2H_2O$ crystallizes in the space group $P2_1/n$, $a = 10.630$, $b = 7.120$, $c = 7.149$ Å, $\beta = 97.69°$, $Z = 4$. The crystal structure was determined from three-dimensional X-ray data and was refined by least-squares calculations to a conventional $R = 0.025$ with 968 observed reflexions. Two kinds of $[Mn^{3+}O_2(OH)_2(H_2O)_2]$ octahedra share opposite vertices via OH groups to form infinite chains along **b**. Each two adjacent octahedra are also linked via bridging SO_4 tetrahedra. The chains are connected by hydrogen bonds. The structure is very similar to but not isotypic with butlerite, $Fe(OH)SO_4.2H_2O$. Both types of Mn atoms have a Jahn–Teller-distorted octahedral [4 + 2] coordination with bond distances of 1.90 Å to two sulphate oxygens, 1.91 Å to two OH groups, and 2.24 [Mn(1)], 2.20 Å [Mn(2)] to two water molecules. Average bond lengths are Mn—O = 2.011 and S—O = 1.470 Å.

Einleitung

Diese Arbeit ist ein Beitrag zur Kristallchemie von Sulfaten dreiwertiger Übergangselemente. Vorher-

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