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The Crystal and Molecular Structure of Diiodobis-(dimethyl-*o*-methylthiophenylarsine)palladium(II)

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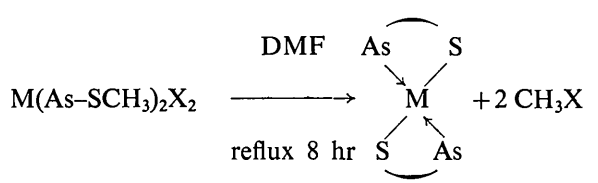
The crystal structure of the compound $Pd(AsSC_9H_{13})_2I_2$ has been examined by X-ray diffraction methods. The complex crystallizes in the monoclinic space group $P2_1/c$ with two molecules in a unit cell of dimensions: $a=10{\cdot}01$, $b=11{\cdot}12$, $c=13{\cdot}32$ Å, $\beta=123{\cdot}25°$ (all to $\pm 0{\cdot}5\%$). The structure consists of a central palladium atom surrounded by a square-planar arrangement of iodine and arsenic atoms in a *trans* configuration. The chelating agent, dimethyl-*o*-methylthiophenylarsine acts as a monodentate ligand with bonding through the arsenic atom. The Pd–As distance is short indicating $d\pi$–$d\pi$ bonding between the palladium and arsenic atoms. The Pd–S distance is elongated to the extent that it is comparable with the sum of the van der Waals radii of palladium and sulphur atoms and therefore can be considered as being non-bonded.

Introduction

The ligand dimethyl-*o*-methylthiophenylarsine, abbreviated (As–SCH), forms mono and bis chelated complexes of the type $Pd(As–SCH_3)X_2$ and $M(As–SCH_3)_2X_2$ (M = Pd, Pt; X = Cl, Br, I) (Livingstone, 1958; Chiswell & Livingstone, 1960).

S-Demethylation of the ligand occurs when these compounds are heated under reflux in dimethylformamide (DMF), as shown below



M = Pd; X = Cl, Br and M = Pt; X = Cl, I. (Lindoy, Livingstone & Lockyer, 1967).

The crystal structure of one of these *S*-demethylated products, bis(dimethyl-*o*-thiophenylarsine)platinum-(II), $Pt(As–S)_2$, has been examined and will be reported at a later date. The molecule is a *trans* isomer in which the thiol group functions as a bidentate ligand. If the parent thiol ($As–SCH_3$) also functions as a bidentate ligand, compounds of the form $M(As–SCH_3)_2X_2$ become of interest because, being diamagnetic and non-electrolytes, they must be examples of low-spin, octahedral complexes of divalent platinum and palladium. Such examples are rare (Stephenson, 1962, 1964*a*, *b*; Stephenson & Jeffrey, 1964; Duckworth & Stephenson, 1970) and have been confined to complexes involving the ligand *o*-phenylenebisdimethylarsine or diarsine where both coordinating atoms are arsenic.

We report below the crystal structure of one of these apparently low-spin octahedral complexes of palladium(II), *viz.* diiodobis(dimethyl-*o*-methylthiophenylarsine)palladium(II), $Pd(As–SCH_3)_2I_2$.

Experimental

The compound was prepared according to the method of Livingstone (1958) and is brownish-orange in colour. Small crystals are shaped as parallelepipeds with (100), (011) and (01$\bar{1}$) faces most prominently developed. A crystal with dimensions $0{\cdot}0050 \times 0{\cdot}0125 \times 0{\cdot}01$ cm was used to collect X-ray data. Unit-cell dimensions were obtained from zero-level precession photographs taken with Mo $K\alpha$ radiation.

Crystal data

Diiodobis (dimethyl- *o*- methylthiophenylarsine) palladium(II):

$C_{18}H_{26}I_2S_2As_2Pd$ F. W. = 816·58

Monoclinic, $a=10{\cdot}01\pm0{\cdot}05$, $b=11{\cdot}12\pm0{\cdot}05$, $c=13{\cdot}32\pm0{\cdot}06$ Å, $\beta=123{\cdot}25=0{\cdot}3°$, $U=1376$ Å^3, $Z=2$, $D_m=1{\cdot}95$ g.cm^{-3} (by flotation), $D_c=1{\cdot}97$ g.cm^{-3}. Space group $P2_1/c$ from systematic absences. The linear absorption coefficient, μ for Cu $K\alpha$ radiation is 281·65 cm^{-1}.

The intensity data were collected on multiple-film equi-inclination Weissenberg photographs (Cu $K\alpha$) taken around [010], ($k=0,1,2\ldots,8$). A total of 1301 independent intensities were estimated by visual comparison with a calibrated strip.

Lorentz and polarization corrections were applied to these data on an IBM 360/50 computer using the programs of Craig (1969). Absorption corrections were applied using the method of Coppens, Leiserowitz & Rabinovich (1965) with a grid of 256 points ($4\times8\times8$). Extinction corrections were not applied to these data.

The final observed structure amplitudes are listed in Table 1.

Determination of the structure

Solution

Iodine and arsenic atomic positions were obtained straightforwardly from a three-dimensional Patterson function and to a first approximation these coordinates were ($0\frac{1}{4}0$) and (0·10, 0, 0·20). These atoms, therefore, only contribute to data with $k = 4n$ and $k = 2n$ respectively. In addition, the palladium atoms in position 2(*a*) of the space group $P2_1/c$ contribute to only a fraction of the data. The amount of data reliably phased by the iodine, arsenic and palladium atoms was therefore severely limited and the resulting Fourier syntheses contained false symmetry. However, a single heavy peak appeared consistently at a distance of approximately 4 Å from the palladium atom and vectors between this

Table 1. *Observed and calculated structure factors for diiodobis(dimethyl–o–methylthiophenylarsine) palladium* (II)

The columns, from left to right read *h*, *k*, *l*, *F*(obs) and *K* . *F*(calc), where the constant *K* is a factor by which the absolute values of *F*(calc) have been multiplied to bring them onto the same scale as the values of *F*(obs) for a particular Weissenberg level. For the various levels, each with a constant *k* index, the values of *K* are 1·413, 2·283, 1·491, 1·336, 1·668, 1·558, 1·808, 1·923, 1·558.

The symbol *U* denotes an unobserved reflexion which has been assigned an *F*(obs) value corresponding to half the minimum observed intensity.

H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)
-6	0	16	152	77	7	0	-6	555	599	1	1	6	336	318	2	1	-5	1200	1251
-5	0	16	183	157	6	0	-6	284	329	2	1	6	182	177	11	1	-6	138	-116
-4	0	16	311	261	5	0	-6	996	927	U 3	1	6	95	35	10	1	-6	167	-136
0	0	16	297	311	4	0	-6	1117	1259	4	1	6	173	147	9	1	-6	329	-310
-1	0	16	370	338	3	0	-6	2066	2396	5	1	6	78	47	8	1	-6	388	-294
-2	0	16	300	239	2	0	-6	1815	2165	U 6	1	6	129	-36	7	1	-6	847	-822
U -3	0	16	133	109	12	0	-8	127	126	1	1	5	1315	1415	6	1	-6	560	-477
U -4	0	16	139	91	2 11	0	-8	262	156	3	1	5	1371	1461	5	1	-6	573	-615
-5	0	14	201	223	U 10	0	-8	145	93	1	1	5	725	743	4	1	-6	805	-800
-6	0	14	296	256	2 9	0	-8	167	157	2	1	5	700	572	3	1	-6	812	-522
-7	0	14	287	333	8	0	-8	830	837	3	1	5	258	165	2	1	-6	552	-560
-8	0	14	286	111	7	0	-8	535	577	4	1	5	215	198	12	1	-7	181	173
-9	0	14	292	288	6	0	-8	1301	1400	5	1	5	156	141	11	1	-7	177	186
-6	0	12	675	576	5	0	-8	1202	1253	6	1	5	335	341	10	1	-7	301	274
-5	0	12	627	561	4	0	-8	1552	1508	7	1	5	261	262	U 9	1	-7	97	28
-4	0	12	794	748	3	0	-8	609	628	8	1	5	156	132	8	1	-7	200	183
-3	0	12	671	618	2	0	-8	752	862	0	1	4	132	220	U 7	1	-7	95	-25
-2	0	12	827	835	10	0	-10	309	282	1	1	4	351	299	6	1	-7	476	449
-1	0	12	209	241	9	0	-10	560	491	U 2	1	4	41	28	5	1	-7	957	919
U 0	0	12	137	122	8	0	-10	521	536	3	1	4	259	223	4	1	-7	1239	1238
1	0	12	373	388	7	0	-10	563	661	0	1	3	737	554	3	1	-7	1130	1249
2	0	12	247	279	U 6	0	-10	134	35	1	1	3	1038	1101	2	1	-7	533	500
-4	0	10	268	300	5	0	-10	857	859	2	1	3	351	866	1	1	-7	400	417
-3	0	10	976	919	-7	1	16	95	148	3	1	3	1512	1518	11	1	-8	149	-132
-2	0	10	916	804	-6	1	16	93	132	4	1	3	675	565	10	1	-8	180	-195
-1	0	10	1191	1062	-5	1	16	83	142	5	1	3	838	838	9	1	-8	255	-216
0	0	10	925	861	-4	1	16	77	131	U 6	1	3	93	-20	8	1	-8	332	-198
1	0	10	533	494	U -3	1	16	167	131	U 7	1	3	75	37	7	1	-8	891	-875
2	0	10	118	295	-13	1	15	380	178	8	1	3	61	39	6	1	-8	881	-674
3	0	10	146	117	-12	1	15	197	217	0	1	2	133	128	5	1	-8	602	-583
4	0	10	275	232	-8	1	15	159	172	1	1	2	556	521	4	1	-8	551	-518
-1	0	8	813	730	U -4	1	15	73	83	2	1	2	197	58	3	1	-8	679	-771
0	0	8	781	885	-3	1	15	252	238	U 3	1	2	78	-139	9	1	-9	361	298
1	0	8	1191	1140	-2	1	15	222	210	4	1	2	110	-83	8	1	-9	399	342
2	0	8	969	1032	U -1	1	15	201	212	5	1	2	162	-188	7	1	-9	737	725
3	0	8	855	901	-9	1	14	128	142	2	1	1	533	461	6	1	-9	604	555
4	0	8	342	377	-8	1	14	174	190	U 3	1	1	69	-73	5	1	-9	262	246
5	0	8	348	274	-7	1	14	214	213	4	1	1	933	889	U 4	1	-9	76	74
6	0	8	131	98	-6	1	14	178	213	5	1	1	539	516	11	1	-10	109	-129
-1	0	6	1353	1297	-5	1	14	176	227	6	1	1	978	924	10	1	-10	192	-188
0	0	6	1493	1275	-4	1	14	248	241	7	1	1	370	451	9	1	-10	286	-268
1	0	6	966	919	-3	1	14	202	191	8	1	1	257	217	8	1	-10	231	-247
2	0	6	579	880	-2	1	14	195	186	1	1	0	320	311	7	1	-10	414	-411
3	0	6	839	702	U -1	1	14	148	127	2	1	0	588	-612	6	1	-10	892	-832
4	0	6	852	818	0	1	14	138	153	3	1	0	218	-190	5	1	-10	884	-866
5	0	6	695	603	-7	1	13	327	381	4	1	0	323	-259	12	1	-11	136	132
6	0	6	571	530	-6	1	13	417	388	5	1	0	259	-285	11	1	-11	153	171
7	0	6	297	284	-5	1	13	321	329	6	1	0	278	-207	10	1	-11	279	308
0	0	4	3176	2991	-4	1	13	292	271	7	1	0	236	-176	9	1	-11	197	226
1	0	4	2619	2584	U -3	1	13	91	55	U 11	1	-1	121	115	8	1	-11	190	201
2	0	4	2158	2222	U -2	1	13	88	42	10	1	-1	255	199	U 7	1	-11	92	-20
3	0	4	1466	1492	U -1	1	13	82	42	9	1	-1	319	317	6	1	-11	127	83
4	0	4	763	679	1	1	13	191	209	8	1	-1	311	296	10	1	-12	136	-149
5	0	4	545	398	0	1	13	273	242	7	1	-1	235	236	9	1	-12	193	-201
6	0	4	805	768	-6	1	12	351	375	6	1	-1	278	-172	8	1	-12	332	-287
7	0	4	940	868	-5	1	12	386	382	5	1	-1	376	384	7	1	-12	268	-253
8	0	4	285	217	-4	1	12	329	359	U 4	1	-1	69	61	7	1	-15	161	131
1	0	2	2077	2127	-3	1	12	296	302	3	1	-1	1394	1294	6	1	-15	227	50
2	0	2	1671	1551	-2	1	12	266	283	U 2	1	-1	1358	1900	5	1	-15	157	58
3	0	2	1908	1805	-1	1	12	253	258	1	1	-1	2257	2377	-9	2	16	158	162
4	0	2	1892	1799	0	1	12	170	167	U 11	1	-2	85	-72	-9	2	14	196	202
5	0	2	1328	1395	1	1	12	161	128	10	1	-2	138	-89	-8	2	14	192	207
6	0	2	1001	991	2	1	12	133	110	9	1	-2	159	-140	-7	2	14	272	303
7	0	2	121	289	-5	1	11	335	339	8	1	-2	240	-234	-6	2	14	192	184
8	0	2	333	297	-4	1	11	505	495	7	1	-2	313	-339	U -5	2	14	134	38
9	0	2	120	127	-3	1	11	761	716	6	1	-2	298	-266	-4	2	14	195	-104
2	0	0	2578	2925	-2	1	11	478	499	5	1	-2	346	-586	U -3	2	14	124	-28
3	0	0	1509	1330	-1	1	11	580	492	4	1	-2	253	-278	U -2	2	14	114	44
4	0	0	1175	1257	U 0	1	11	94	27	3	1	-2	684	-614	U -1	2	14	48	93
5	0	0	885	871	1	1	11	45	58	U 2	1	-2	239	-256	0	2	14	137	143
6	0	0	956	916	2	1	11	65	53	1	1	-2	597	-715	-6	2	12	246	219
7	0	0	996	905	3	1	11	144	137	10	1	-3	132	118	-5	2	12	237	243
8	0	0	711	637	-8	1	10	483	483	9	1	-3	83	-23	-4	2	12	495	401
9	0	0	406	438	-3	1	10	465	454	8	1	-3	345	233	-3	2	12	148	123
10	0	0	203	117	-2	1	10	670	650	7	1	-3	295	251	U -2	2	12	184	-28
11	0	-2	259	206	-1	1	10	323	326	6	1	-3	1366	1320	-1	2	12	279	-171
10	0	-2	407	349	0	1	10	273	271	5	1	-3	1141	1357	0	2	12	142	-104
9	0	-2	363	297	1	1	10	192	191	4	1	-3	1564	1423	-13	2	11	212	160
8	0	-2	332	387	2	1	10	161	150	3	1	-3	974	952	-8	2	10	389	-176
7	0	-2	861	828	3	1	10	127	113	2	1	-3	331	217	U -3	2	10	133	-63
6	0	-2	716	842	-3	1	9	172	-87	U 1	1	-3	213	-257	-2	2	10	196	196
5	0	-2	1295	1071	-2	1	9	199	156	13	1	-4	217	-139	-1	2	10	393	239
4	0	-2	1990	2179	-1	1	9	133	198	3	1	-4	172	162	U 0	2	10	149	150
3	0	-2	3211	3510	0	1	9	986	893	8	1	-4	333	-244	1	2	10	237	-149
11	0	-4	131	131	1	1	9	550	544	7	1	-4	352	-371	2	2	10	171	-157
10	0	-4	175	106	2	1	9	983	943	6	1	-4	474	-511	3	2	10	143	-162
9	0	-4	333	331	-2	1	8	340	359	5	1	-4	537	-552	-2	2	9	181	157
8	0	-4	729	751	-1	1	8	498	548	6	1	-4	630	-625	-1	2	9	193	143
7	0	-4	1051	1072	0	1	8	302	273	3	1	-4	431	-475	U 0	2	9	145	74
6	0	-4	1836	1568	1	1	8	127	323	2	1	-4	633	-644	1	2	9	150	90
5	0	-4	1601	1611	2	1	8	273	231	1	1	-4	742	-745	2	2	9	202	21
4	0	-4	1393	1453	0	1	7	274	-155	11	1	-5	133	30	-2	2	8	545	-454
3	0	-4	762	784	1	1	7	250	246	10	1	-5	151	183	-1	2	8	727	-677
2	0	-4	1726	1915	2	1	7	271	242	9	1	-5	455	430	0	2	8	334	-288
1	0	-4	1904	2038	3	1	7	750	635	4	1	-5	934	881	U 1	2	8	187	55
12	0	-6	158	186	4	1	7	816	638	7	1	-5	761	690	2	2	8	215	179
11	0	-6	274	221	5	1	7	329	307	6	1	-5	197	132	3	2	8	145	164
10	0	-6	467	469	6	1	7	184	129	5	1	-5	173	38	8	2	8	156	-94
9	0	-6	514	536	-1	1	6	528	521	8	1	-5	253	-174	-1	2	7	158	145
8	0	-6	448	502	0	1	6	583	553	3	1	-5	170	315	0	2	6	595	-431

Table 1 (*cont.*)

H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)
1	2	6	794	-868	-6	3	14	210	-231	2	3	-2	669	595	7	0	0	337	313
2	2	6	572	-695	-5	3	14	208	-220	1	3	-2	523	373	6	0	0	256	258
3	2	6	418	-462	-4	3	14	183	-189	0	3	-2	245	-33	5	0	0	398	351
4	2	6	133	-58	-3	3	14	190	-193	6	3	-3	699	729	4	0	0	886	519
5	2	6	118	70	-7	3	13	223	223	5	3	-3	729	638	3	0	0	910	1029
6	2	6	193	150	-6	3	13	390	403	4	3	-3	775	685	2	0	0	1316	1881
-1	2	5	173	189	-5	3	13	316	247	3	3	-3	368	217	1	0	0	2024	2230
0	2	4	177	108	-4	3	13	221	153	2	3	-3	420	-462	0	0	0	1814	1965
1	2	4	155	52	-7	3	12	226	-252	1	3	-4	206	228	0	0	3	309	-296
2	2	4	180	150	-6	3	12	318	-280	0	3	-4	155	190	9	0	2	82	92
3	2	4	402	-368	-5	3	12	228	-231	7	3	-4	315	336	8	0	2	211	183
4	2	4	664	-690	-4	3	12	322	-331	6	3	-4	307	320	7	0	2	296	303
5	2	4	370	-372	-3	3	12	228	-203	5	3	-4	574	592	6	0	2	664	668
6	2	4	299	-377	-2	3	12	319	-299	4	3	-4	850	870	5	0	2	903	1005
0	2	3	269	-220	-1	3	12	153	-151	3	3	-4	364	392	4	0	2	1171	1425
1	2	3	445	477	0	3	12	196	-210	2	3	-4	565	552	3	0	2	1395	1483
2	2	3	294	-317	-4	3	11	316	325	1	3	-5	304	320	2	0	2	1298	1135
0	2	2	2187	2607	-3	3	11	453	571	0	3	-5	323	330	1	0	2	925	793
1	2	2	1398	-1611	-2	3	11	326	361	7	3	-5	476	451	0	0	2	1283	1103
2	2	2	1098	-1226	-6	3	10	369	-387	6	3	-5	197	-148	5	0	1	162	176
3	2	2	248	-252	-5	3	10	358	-357	5	3	-5	238	-212	4	0	1	219	142
4	2	2	122	88	-4	3	10	293	-337	4	3	-5	426	-480	3	0	1	104	-61
5	2	2	127	126	-3	3	10	432	-461	3	3	-5	129	-125	2	0	1	372	383
6	2	2	129	-96	-2	3	10	223	-222	2	3	-6	365	389	1	0	1	300	-241
7	2	2	174	-169	-1	3	10	329	-325	1	3	-6	317	352	0	0	1	271	239
0	2	1	407	505	-4	3	9	191	-108	0	3	-6	573	485	1	0	0	2504	2384
1	2	1	287	-397	-3	3	9	340	-311	5	3	-6	408	426	2	0	0	1876	2060
2	2	1	152	140	-2	3	9	147	-97	4	3	-6	681	633	3	0	0	908	926
1	2	0	199	-139	-1	3	9	221	228	3	3	-6	547	568	4	0	0	730	638
2	2	0	538	-517	0	3	9	571	577	2	3	-6	161	398	5	0	0	774	652
3	2	0	983	-1216	1	3	9	238	273	1	3	-6	548	586	6	0	0	753	819
4	2	0	1064	-1172	2	3	9	220	260	6	3	-7	328	371	7	0	0	673	653
5	2	0	870	-624	-4	3	8	431	-479	5	3	-7	451	482	8	0	0	467	478
6	2	0	250	-161	-3	3	8	433	-481	4	3	-7	847	792	9	0	0	339	347
7	2	0	258	190	-2	3	8	463	-519	3	3	-7	249	290	10	0	0	110	108
8	2	0	124	60	-1	3	8	289	-278	2	3	-7	159	178	8	0	1	158	148
9	2	0	148	108	0	3	8	113	-123	1	3	-8	370	419	7	0	1	118	80
4	2	1	217	-195	-3	3	7	659	668	6	3	-8	116	381	6	0	1	116	91
3	2	1	103	-16	-2	3	7	289	325	5	3	-8	842	890	5	0	1	222	226
2	2	1	341	-335	-1	3	7	188	-157	4	3	-9	254	213	4	0	1	105	-28
1	2	1	265	237	0	3	7	457	-435	3	3	-9	332	342	3	0	1	206	173
0	2	1	602	-504	1	3	7	159	-80	2	3	-9	530	496	2	0	1	75	-81
10	2	-2	142	140	2	3	7	170	51	1	3	-9	286	330	1	0	1	807	812
9	2	-2	121	-56	3	3	7	314	350	0	3	-9	117	170	11	0	2	122	169
8	2	-2	261	-215	4	3	7	272	266	5	3	-10	233	340	10	0	2	275	272
7	2	-2	451	-456	0	3	6	371	-329	4	3	-10	313	304	9	0	2	252	226
6	2	-2	847	-496	1	3	6	298	-317	-1	4	14	178	213	8	0	2	284	306
5	2	-2	169	-170	-2	3	5	319	321	-2	4	14	140	201	7	0	2	293	304
4	2	-2	153	40	-1	3	5	816	783	-3	4	14	132	117	6	0	2	871	884
3	2	-2	227	202	0	3	5	1079	1033	-4	4	14	112	100	5	0	2	1122	1235
2	2	-2	931	-1055	1	3	5	138	59	-5	4	14	118	111	4	0	2	1625	1745
1	2	-2	883	-861	2	3	5	156	112	-6	4	14	153	213	3	0	2	2018	2303
5	2	-3	236	-206	3	3	5	335	-337	-7	4	14	328	323	2	0	2	1777	1667
4	2	-3	92	-23	4	3	5	152	-99	-8	4	14	225	229	1	0	2	1958	1902
3	2	-3	145	-134	5	3	5	141	39	-9	4	14	151	177	7	0	3	174	132
2	2	-3	60	97	6	3	5	121	153	2	4	12	165	233	6	0	3	123	139
1	2	-3	355	-261	7	3	5	227	199	1	4	12	134	187	5	0	3	232	136
7	2	-4	277	250	-1	3	4	533	-439	0	4	12	104	144	4	0	3	882	897
6	2	-4	125	292	0	3	4	213	-239	-1	4	12	237	251	3	0	3	146	72
5	2	-4	393	-323	1	3	4	179	-127	-2	4	12	317	253	2	0	3	829	803
4	2	-4	348	-456	2	3	4	206	-289	-3	4	12	848	859	1	0	3	126	84
3	2	-4	1401	-1648	-1	3	3	372	-325	-4	4	12	706	687	0	0	3	363	297
2	2	-4	799	-922	0	3	3	1001	-929	-5	4	12	539	551	9	0	4	280	278
1	2	-4	1072	-1131	1	3	3	432	411	-6	4	12	471	357	8	0	4	865	901
4	2	-5	219	-261	2	3	3	583	624	-4	4	11	253	-172	7	0	4	830	951
3	2	-5	269	-234	3	3	3	657	731	4	4	10	114	154	6	0	4	1168	1187
2	2	-5	110	-166	1	3	2	507	-471	3	4	10	75	104	5	0	4	1009	1056
11	2	-6	145	101	2	3	2	454	383	2	4	10	242	255	4	0	4	934	975
10	2	-6	180	218	3	3	2	143	-154	1	4	10	435	427	3	0	4	773	763
9	2	-6	201	198	4	3	2	280	259	0	4	10	434	458	2	0	4	1311	1301
8	2	-6	154	-21	0	3	1	600	591	-1	4	10	771	855	1	0	4	1113	1199
7	2	-6	275	-246	1	3	1	293	71	-2	4	10	832	811	7	0	5	133	282
6	2	-6	677	-699	2	3	1	739	-721	-3	4	10	583	615	6	0	5	117	126
5	2	-6	848	-818	3	3	1	748	-705	-4	4	10	334	218	5	0	5	133	142
4	2	-6	525	-524	4	3	1	373	335	-1	4	9	131	-155	4	0	5	85	-18
3	2	-6	571	490	5	3	1	198	830	-2	4	9	122	-55	3	0	5	137	522
2	2	-6	193	-122	6	3	1	457	449	-3	4	9	279	-285	2	0	5	155	-105
1	2	-6	141	71	7	3	1	232	257	5	4	8	223	215	12	0	6	111	108
7	2	-7	266	-219	1	3	0	93	122	4	4	8	319	379	11	0	6	204	191
6	2	-7	116	-77	2	3	0	108	-123	3	4	8	653	636	10	0	6	333	353
5	2	-7	254	-260	3	3	0	497	436	2	4	8	745	772	9	0	6	394	428
4	2	-7	97	22	4	3	0	125	29	1	4	8	786	835	8	0	6	477	462
3	2	-7	234	-210	5	3	0	383	359	0	4	7	772	817	7	0	6	323	272
2	2	-7	165	-75	6	3	0	143	53	-1	4	7	434	469	6	0	6	388	354
6	2	-8	553	474	7	3	0	205	231	-2	4	7	534	536	5	0	6	479	708
5	2	-8	223	212	1	3	-1	104	219	-3	4	7	253	-286	4	0	6	937	976
4	2	-8	214	193	2	3	-1	142	132	-4	4	7	332	-397	3	0	6	1436	1579
3	2	-8	494	-465	3	3	-1	146	161	7	4	6	153	220	2	0	6	1470	1658
6	2	-9	247	-191	5	3	-1	401	-409	6	4	6	458	424	1	0	7	273	295
5	2	-9	119	-40	6	3	-1	268	-253	5	4	6	867	881	5	0	7	143	134
4	2	-9	237	-234	4	3	-1	126	-130	4	4	6	535	534	4	0	7	381	315
3	2	-9	122	-24	1	3	-1	478	769	3	4	6	524	513	3	0	7	48	101
13	2	-10	205	182	2	3	-1	469	798	2	4	6	466	478	2	0	7	459	338
12	2	-10	117	113	3	3	-1	990	710	1	4	6	437	522	1	0	7	264	247
4	2	-10	207	213	8	3	-2	296	213	0	4	6	761	872	4	0	8	337	331
7	2	-10	138	189	7	3	-2	296	218	-1	4	6	1733	1733	7	0	8	583	632
0	2	-10	121	-206	6	3	-2	351	375	1	4	5	329	-332	6	0	8	404	496
5	2	-10	483	-251	5	3	-2	276	256	2	4	5	292	314	5	0	8	1128	1141
5	2	-11	198	-167	4	3	-2	439	442	-1	4	5	359	-351	4	0	8	1210	1134
-2	3	15	104	157	3	3	-2	355	356	3	4	4	237	233	3	0	8	631	619

atom and the atoms already located were found quite clearly on the Patterson function. This position was correctly allocated to the sulphur atom and successive cycles of structure factors and difference Fourier syntheses (in which the false symmetry gradually disappeared) resulted in the location of the remaining carbon atoms.

Refinement

The difference Fourier syntheses enabled corrections to be made to the positional parameters of atoms. Once all atoms had been located ($R=0{\cdot}21$) the positional parameters were refined by full-matrix least-squares methods in which the values of $\sum W(|F_{obs}|-|F_{calc}|)^2$ were minimized. Isotropic thermal parameters and interlayer scale factors were refined in addition to the positional parameters. Unit weights were used initially to speed convergence and these were later replaced with weights calculated using Cruickshank's (1965) weighting scheme. The final reliability index (R) obtained was 0·13.

One further refinement cycle using anisotropic temperature parameters for each atom reduced the index, R, to 0·10. There is no justification for this procedure since the data were not rigidly internally scaled. However, the signs and magnitudes of the tensor com-

Table 1 (*cont.*)

H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)
7	4	-9	250	229	1	5	0	102	-50	-4	5	10	157	-197	-3	7	12	136	-97
6	4	-9	118	106	2	5	0	213	-232	-3	5	10	114	59	-3	7	11	206	180
5	4	-9	391	307	3	5	0	157	-114	-2	6	10	169	128	-2	7	11	144	192
4	4	-9	157	170	4	5	0	235	-300	-1	6	10	158	206	-1	7	11	95	89
11	4	-10	131	116	5	5	0	123	-51	0	6	10	150	152	0	7	11	81	-78
10	4	-10	292	215	6	5	0	178	-136	-3	6	9	154	197	1	7	11	90	-87
9	4	-10	440	416	10	5	-1	157	199	-2	6	9	229	263	-5	7	10	143	-177
8	4	-10	460	388	9	5	-1	229	288	-1	6	9	171	133	-4	7	10	102	-129
7	4	-10	477	438	8	5	-1	279	327	0	6	9	171	215	-3	7	10	208	-197
6	4	-10	298	279	7	5	-1	251	273	-1	6	8	295	-292	-2	7	10	108	-79
5	4	-10	237	235	6	5	-1	179	228	0	6	8	122	-161	-1	7	10	150	-153
7	4	-11	180	90	5	5	-1	301	356	1	5	8	123	111	-2	7	9	106	-102
6	4	-11	125	200	4	5	-1	576	559	2	6	8	113	132	-1	7	9	111	-28
5	4	-11	124	95	3	5	-1	1379	1281	3	6	8	179	170	0	7	9	154	175
-4	5	14	219	175	2	5	-1	1958	1984	0	6	5	223	-235	-3	7	8	137	-159
-3	5	14	100	97	1	5	-1	2214	1643	1	6	6	140	-137	-2	7	8	232	228
-2	5	14	83	150	7	5	-2	315	-258	2	6	6	139	-146	-1	7	8	108	-96
-1	5	14	101	68	6	5	-2	129	-109	3	6	6	150	-175	0	7	8	160	-186
-7	5	13	251	267	5	5	-2	358	-381	1	6	4	260	225	-1	7	7	250	-241
-6	5	13	160	141	4	5	-2	121	-61	2	6	4	156	151	0	7	7	276	-224
-5	5	13	117	103	3	5	-2	347	-312	3	5	4	121	-80	1	7	7	280	-328
-4	5	13	179	194	2	5	-2	248	-147	4	5	4	217	-217	-1	7	6	230	-212
-3	5	13	121	131	1	5	-2	152	-75	5	6	4	241	-240	0	7	6	105	-92
-2	5	13	112	68	0	5	-2	212	-209	6	6	4	118	-111	1	7	6	227	-175
-1	5	13	95	122	8	5	-3	253	217	1	5	3	279	253	-1	7	5	269	279
0	5	13	64	171	7	5	-3	265	332	0	6	2	1015	-896	0	7	5	96	61
-7	5	12	262	209	6	5	-3	827	885	1	6	2	881	-775	1	7	5	109	7
-6	5	12	261	218	5	5	-3	1090	1139	2	6	2	376	-378	2	7	5	230	-165
-5	5	12	266	269	4	5	-3	1177	1319	3	6	2	112	-91	3	7	5	261	-261
-4	5	12	272	192	3	5	-3	808	841	4	5	2	152	151	4	7	5	225	-248
-3	5	12	268	232	2	5	-3	757	737	0	6	1	176	139	0	7	3	503	-425
-2	5	12	129	129	1	5	-3	620	664	1	6	0	233	67	1	7	3	137	-121
-1	5	12	170	168	8	5	-4	263	-279	2	5	0	271	-350	2	7	3	108	87
-5	5	11	268	277	7	5	-4	139	-93	3	6	0	511	-567	3	7	3	155	152
-4	5	11	465	490	6	5	-4	346	-343	4	5	0	333	-498	4	7	3	100	59
-3	5	11	588	576	5	5	-4	164	-158	5	6	0	265	-281	5	7	3	130	-58
-2	5	11	437	478	4	5	-4	478	-529	5	6	-1	158	-184	6	7	3	159	-152
-1	5	11	380	381	3	5	-4	268	-258	4	5	-1	238	-320	0	7	1	327	-268
0	5	11	178	208	2	5	-4	415	-381	3	6	-1	107	89	1	7	1	512	-524
-4	5	10	368	311	1	5	-4	512	-484	2	5	-1	818	-839	2	7	1	581	-573
-3	5	10	267	276	10	5	-5	145	186	1	6	-1	59	33	3	7	1	387	-453
-2	5	10	279	236	9	5	-5	302	341	7	6	-2	219	-217	4	7	1	99	-140
-1	5	10	281	217	8	5	-5	434	499	6	6	-2	159	-153	5	7	1	98	71
0	5	10	195	178	7	5	-5	563	608	5	6	-2	112	-125	6	7	1	92	133
1	5	10	128	93	6	5	-5	260	321	4	5	-2	270	236	7	7	1	113	140
2	5	10	137	114	5	5	-5	271	319	3	6	-2	271	239	8	7	1	87	-9
-2	5	9	325	372	4	5	-5	333	321	2	6	-2	95	58	5	7	0	141	164
-1	5	9	591	608	3	5	-5	759	637	1	6	-2	801	-581	6	7	-1	200	-248
0	5	9	605	632	2	5	-5	1269	1099	8	6	-3	210	-192	5	7	-1	254	-292
1	5	9	597	555	9	5	-6	182	-148	7	5	-3	227	-199	4	7	-1	205	-236
2	5	9	447	482	8	5	-6	145	-112	6	6	-3	117	-75	3	7	-1	105	-56
3	5	9	230	229	7	5	-6	289	-333	5	6	-3	288	-278	2	7	-1	202	171
-2	5	8	296	242	6	5	-6	249	-217	4	5	-3	134	-76	1	7	-1	485	339
-1	5	8	419	373	5	5	-6	383	-392	3	6	-3	387	-353	6	7	-2	149	161
0	5	8	199	168	4	5	-6	424	-386	2	6	-3	133	136	5	7	-2	107	72
1	5	8	353	274	3	5	-6	404	-386	1	6	-3	422	-321	4	7	-2	217	265
-2	5	7	816	766	2	5	-6	478	-457	0	6	-3	79	40	3	7	-2	86	68
-1	5	7	481	428	1	5	-6	107	-100	7	6	-4	159	139	2	7	-2	194	214
0	5	7	133	118	11	5	-7	120	179	6	6	-4	251	225	1	7	-2	309	237
1	5	7	496	509	10	5	-7	159	196	5	6	-4	135	55	0	7	-2	69	66
2	5	7	818	813	9	5	-7	134	135	4	6	-4	332	-137	6	7	-3	155	95
3	5	7	542	528	8	5	-7	154	117	3	6	-4	733	-698	5	7	-3	229	217
4	5	7	453	466	7	5	-7	195	175	2	6	-4	538	-550	4	7	-3	133	175
5	5	7	311	307	6	5	-7	525	478	1	6	-4	417	-290	3	7	-3	78	-62
6	5	7	142	160	5	5	-7	884	776	0	5	-4	39	-181	2	7	-3	692	-622
0	5	6	429	378	4	5	-7	1131	1052	6	6	-5	232	-259	1	7	-3	808	-702
1	5	6	137	-28	3	5	-7	1191	1128	5	6	-5	100	-138	5	7	-4	206	205
2	5	6	357	309	8	5	-8	213	-283	4	6	-5	305	-352	4	7	-4	176	205
-1	5	5	1512	1374	7	5	-8	272	-237	3	6	-5	257	-228	3	7	-4	258	285
0	5	5	1687	1888	6	5	-8	397	-377	2	6	-5	534	-430	2	7	-4	178	153
1	5	5	902	931	5	5	-8	374	-355	1	6	-5	172	-176	1	7	-4	76	-86
2	5	5	523	497	4	5	-8	359	-330	7	5	-6	140	-118	0	7	-4	212	263
3	5	5	201	246	3	5	-8	361	-334	6	6	-6	273	-299	5	7	-5	140	-137
4	5	5	310	285	9	5	-9	210	212	5	6	-6	241	-272	4	7	-5	494	-443
5	5	5	276	282	8	5	-9	353	379	4	6	-6	91	-61	3	7	-5	279	-276
6	5	5	261	308	7	5	-9	578	529	1	5	-6	325	278	2	7	-5	79	68
7	5	5	222	271	6	5	-9	515	530	2	6	-6	330	279	6	7	-6	263	304
0	5	4	141	116	5	5	-9	522	405	7	6	-7	171	-203	5	7	-6	137	135
1	5	4	372	400	4	5	-9	121	171	6	6	-7	156	-185	4	7	-6	219	201
0	5	3	959	774	3	5	-9	124	133	5	6	-7	436	-385	3	7	-6	170	162
1	5	3	1151	1043	9	5	-10	205	-166	4	6	-7	135	-171	2	7	-6	248	275
2	5	3	1245	1251	8	5	-10	181	-175	3	6	-7	125	-304	6	7	-7	149	-34
3	5	3	1178	1227	7	5	-10	192	-214	2	6	-7	97	-50	5	7	-7	239	218
4	5	3	673	774	6	5	-10	261	-219	1	6	-7	338	-325	4	7	-7	345	327
5	5	3	348	367	5	5	-10	256	-255	6	6	-8	314	290	3	7	-7	182	168
6	5	3	161	213	11	5	-11	118	183	5	6	-8	255	333	7	7	-8	155	151
7	5	3	96	92	10	5	-11	230	221	4	5	-8	131	92	6	7	-8	104	97
8	5	3	99	120	9	5	-11	198	224	3	6	-8	233	-175	5	7	-8	198	225
1	5	2	102	-63	8	5	-11	135	183	2	6	-8	369	-357	4	7	-8	272	248
2	5	2	172	158	7	5	-11	138	99	8	6	-9	215	-171	8	7	-9	219	155
0	5	1	2470	1571	6	5	-11	132	89	7	6	-9	117	-164	7	7	-9	262	274
1	5	1	965	761	5	5	-12	326	-257	5	6	-9	157	-228	6	7	-9	206	163
2	5	1	516	503	-5	6	12	155	236	5	6	-9	107	-123	5	7	-9	100	-81
3	5	1	503	515	-4	6	12	158	221	4	5	-9	260	-292	4	7	-9	199	-174
4	5	1	664	762	-3	6	12	111	137	6	6	-10	158	-92	3	7	-9	203	-155
5	5	1	678	719	-2	6	12	104	50	5	6	-10	220	-170	8	7	-10	146	131
6	5	1	692	745	-1	6	12	134	-94	-7	7	13	120	160	7	7	-10	146	170
7	5	1	395	462	-5	6	11	158	245	-6	7	13	124	158	6	7	-10	208	199
8	5	1	236	241	-4	6	11	113	157	-5	7	13	125	146	-5	8	12	261	251
9	5	1	99	97	-3	6	11	165	208	-3	7	12	134	-137	-4	8	12	261	288

Table 2. *The tensor components* ($\times 10^3$) *describing the anisotropic vibration of the atoms in diiodobis(dimethyl-o-methylthiophenylarsine)palladium*(II)

The components U_{ij} are those occurring in the temperature factor $\exp[-2\pi^2(h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots)]$ so that for instance, U_{11} is the mean-square amplitude of vibration parallel to **a***.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	50 Å^2	57 Å^2	38 Å^2	−1 Å^2	11 Å^2	−1 Å^2
I	77	61	62	−1	17	0
As	65	67	52	−2	14	2
S	72	117	76	−6	18	3
C(1)	102	102	77	2	25	3
C(2)	81	53	69	2	18	−19
C(3)	52	148	145	−10	−2	−12
C(4)	65	47	50	5	14	4
C(5)	73	95	53	−9	17	−13

Table 2 (*cont.*)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(6)	113	148	57	−4	18	−23
C(7)	144	31	70	1	8	5
C(8)	54	91	100	1	−14	5
C(9)	74	118	48	9	2	19

ponents listed in Table 2 are reasonable and recent work by Kastalsky & McConnell (1967) has shown that a thermal analysis based upon data collected and treated in the above manner can be meaningful. Furthermore significance tests described by Hamilton (1965) suggest the anisotropic parameters to be meaningful. No attempt has been made at this time to analyse the thermal motions of the molecule.

For the calculation of the structure factors the atomic scattering factors for Pd, I and As of Thomas & Umeda (1957) were used. The atomic scattering factors for sulphur and carbon were those of Dawson (1960) and Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). A correction for the real component of the anomalous dispersion of the heavier atoms for Cu $K\alpha$ radiation was applied (Dauben & Templeton, 1955). An IBM 360/50 computer was used for all calculations, together with local versions of well established programs.

The final atomic parameters for the crystallographically independent atoms, together with estimated standard deviations, are listed in Table 3.

Table 3. *Final fractional atomic coordinates for diiodobis(dimethyl-o-methylthiophenylarsine)palladium*(II)

Standard deviations are given in brackets and refer to the last two decimal places in the preceding coordinate.

	x/a	*y/b*	*z/c*
Pd	0·00000	0·00000	0·00000
I	0·00991 (24)	0·23087 (21)	−0·01060 (17)
As	0·12816 (38)	0·00269 (31)	0·21330 (26)
S	0·4522 (11)	−0·0404 (10)	0·22302 (86)
C(1)	−0·0384 (47)	−0·0254 (34)	0·2506 (30)

Table 3 (*cont.*)

	x/a	*y/b*	*z/c*
C(2)	0·2405 (36)	0·1491 (28)	0·2987 (27)
C(3)	0·6561 (43)	0·0168 (46)	0·3214 (52)
C(4)	0·2826 (37)	−0·1286 (26)	0·3111 (25)
C(5)	0·4092 (42)	−0·1346 (37)	0·3079 (26)
C(6)	0·5253 (48)	−0·2335 (39)	0·3692 (29)
C(7)	0·4914 (50)	−0·3094 (27)	0·4495 (33)
C(8)	0·3534 (40)	−0·2918 (45)	0·4434 (36)
C(9)	0·2446 (39)	−0·1924 (33)	0·3780 (22)

Description of the structure

The structure of diiodobis(dimethyl-*o*-methylthiophenylarsine)palladium(II) is one in which individual molecules of $PdI_2As_2S_2C_{18}H_{26}$, depicted in Fig. 1, pack together in a manner portrayed by Fig. 2. The packing is tight with intermolecular contacts less than 4·0 Å as listed in Table 6. Bond distances and angles are listed in Tables 4 and 5.

Table 4. *Bond distances in a molecule of diiodobis(dimethyl-o-methylthiophenylarsine)palladium*(II)

Pd–I	2·576 (13) Å	C(4)–C(5)	1·29 (4) Å
Pd–As	2·392 (14)	C(5)–C(6)	1·48 (5)
As–C(1)	2·01 (4)	C(6)–C(7)	1·54 (6)
As–C(2)	1·95 (3)	C(7)–C(8)	1·35 (6)
As–C(4)	2·00 (3)	C(8)–C(9)	1·46 (5)
S—C(3)	1·83 (4)	C(9)–C(4)	1·35 (4)
S—C(5)	1·76 (4)		

Table 5. *Bond angles defined by three atoms in a molecule of diiodobis(dimethyl-o-methylthiophenylarsine)palladium*(II), *with the central atom as the vertex*

I——Pd–As	92·4 (1)°	C(2)–As—C(4)	104 (2)°
I——Pd–S	95·4 (3)	C(3)–S——C(5)	108 (2)

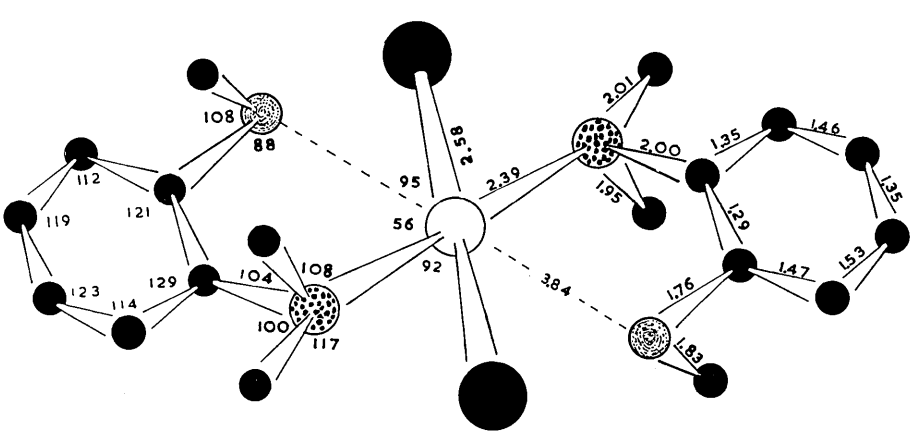


Fig. 1. A diagram illustrating the configuration of the diiodobis(dimethyl-*o*-methylthiophenylarsine)palladium(II) molecule and showing some bond distances (Å) and angles (°).

Table 5 (*cont.*)

As —Pd–S	56·4 (3)	C(4)–C(5)–C(6)	121 (4)
Pd —As–C(1)	108 (1)	C(5)–C(6)–C(7)	113 (3)
Pd —As–C(2)	118 (1)	C(6)–C(7)–C(8)	119 (4)
Pd —As–C(4)	119 (1)	C(7)–C(8)–C(9)	123 (4)
C(1)–As–C(2)	106 (1)	C(8)–C(9)–C(4)	114 (4)
C(1)–As–C(4)	100 (1)	C(9)–C(4)–C(5)	129 (3)

Table 6. *Some interatomic approach distances less than* 4 Å *in the crystal of diiodobis(dimethyl-o-methylthiophenylarsine)palladium*(II)

The superscripts denote the following symmetry transformations of the parameters of Table 3.

No superscript	x	y	z
1	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
2	$\bar{x}$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
3	$1-x$	$\bar{y}$	$1-z$
4	$\bar{x}$	$\bar{y}$	$\bar{z}$

Pd —S	3·84 (02)	S^{1} —C(8)^{3}	3·78 (05)
I^{2}—C(6)^{3}	3·97 (05)	S^{2} —C(6)^{3}	3·68 (04)
C(2)–C(6)^{3}	3·82 (04)	S^{2} —C(7)^{3}	3·69 (04)
C(2)–C(7)^{3}	3·43 (05)	C(3)^{2}–C(6)^{3}	3·52 (06)
C(2)–C(8)^{3}	3·94 (05)	C(3)^{2}–C(7)^{3}	3·62 (07)
S^{4}—C(8)^{2}	3·78 (05)		

Contrary to the expected, the compound is not an example of a six-coordinated low-spin palladium(II) complex but rather a four-coordinated square-planar palladium(II) complex. The palladium atom, lying at the centre of an almost perfect square, is bonded to iodine and arsenic atoms arranged in a *trans* configuration.

The best-fit planes through various atoms in the molecule located at the origin of the unit-cell have been calculated using the programs of Craig (1969). The equation of the plane through the Pd, As and I atoms in this molecule is

$$0{\cdot}991\ X-0{\cdot}063\ Y-0{\cdot}4472\ Z=0$$

where the coordinates X, Y and Z are in Å and refer to the crystallographic axes. The equation of the plane through the Pd, As and S atoms is:

$$0{\cdot}150\ X+0{\cdot}989\ Y-0{\cdot}078\ Z=0\,,$$

and the dihedral angle between these two planes is $85{\cdot}04\pm0{\cdot}23°$.

The equation of the least-squares plane through the benzene ring of the thio-arsenic chelate is:

$$0{\cdot}104\ X+0{\cdot}619\ Y+0{\cdot}594\ Z+1{\cdot}899=0\,.$$

Deviations of the carbon atom positions from this plane (summarized in Table 7) cannot be regarded as significant. The uncertainties associated with the accurate location of light atoms in the presence of heavy atoms are also reflected in the large standard deviations of the carbon–carbon distances in the benzene ring.

The Pd–I distance of $2{\cdot}58\pm0{\cdot}04$ Å is appreciably shorter than the sum of the covalent radius of palladium(II) and the normal covalent radius for iodine ($0{\cdot}131+1{\cdot}33=2{\cdot}64$). All diarsine complexes examined have shown a metal–halogen distance significantly greater than the sum of the covalent radii of the atoms concerned. (Stephenson, 1962, 1964*a*, *b*; Stephenson

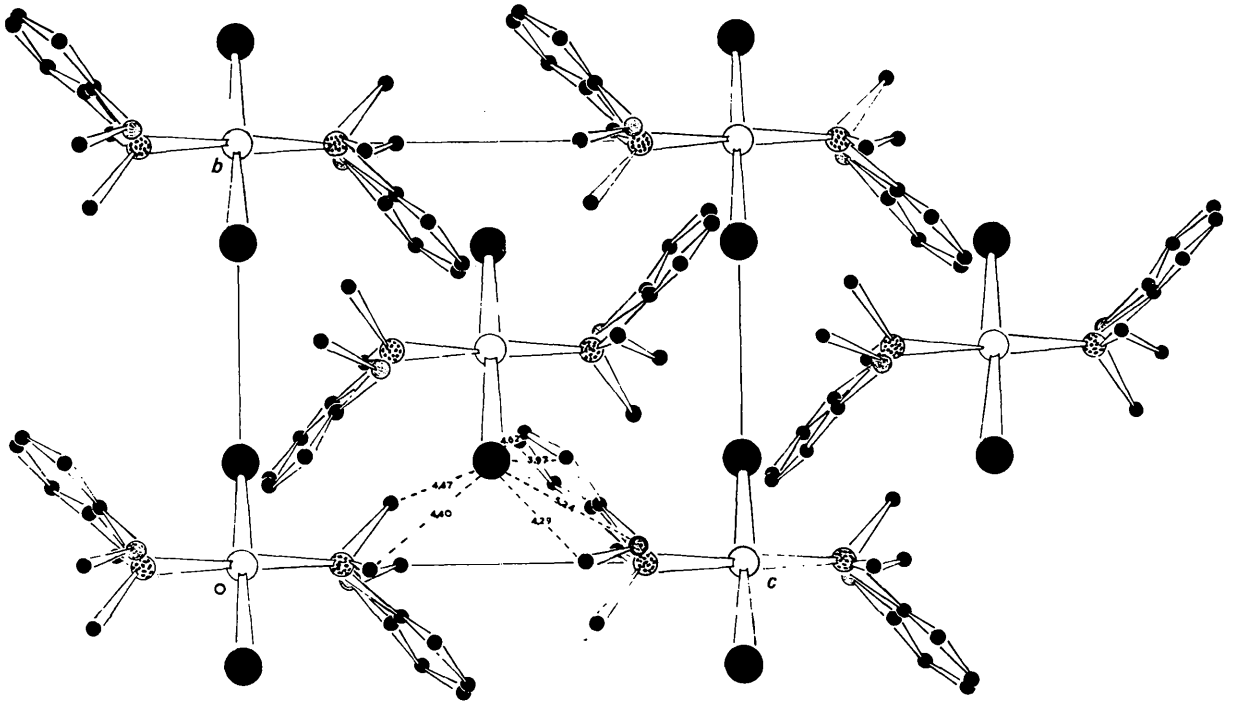


Fig.2. A (100) projection of the unit cell contents of diiodobis(dimethyl-*o*-methylthiophenylarsine)palladium(II), showing some non-bonded approach distances (Å).

& Jeffrey, 1964; Duckworth & Stephenson, 1970). The Pd–I distance in diiodobis-(*o*-phenylenebisdimethylarsine)palladium(II), $Pd(As–As)_2I_2$ is 3·40 Å, an increase of almost 30% on the expected value of 2·64 Å (Stephenson, 1962).

Table 7. *Deviations of atoms from the least-squares plane of the benzene ring*

	Deviation		Deviation
C(4)	−0·03 Å	C(7)	0·04 Å
C(5)	0·04	C(8)	−0·03
C(6)	−0·04	C(9)	0·02

The equation of the least-squares plane through the carbon atoms of the benzene ring is:

$$0{\cdot}104X + 0{\cdot}619Y + 0{\cdot}594Z + 1{\cdot}899 = 0.$$

The Pd–As bond distance of 2·39 ± 0·04 Å, although appreciably shorter than the sum of the square covalent radius for palladium(II) and the tetrahedral radius for arsenic (1·31 + 1·18 = 2·49 Å) (Pauling, 1948), is in good agreement with the Pd–As distance observed in complexes of the type $M(diarsine)_2X_2$, (M = Pd or Pt, X = Cl or I), and $Pt(As–S)_2$. The substantial shortening of the bond length is attributed to $d\pi$–$d\pi$ bonding between the arsenic and palladium atoms. However, a more detailed investigation involving molecular orbital calculations will be undertaken shortly (Gray, 1969).

The Pd–S distance of 3·84 ± 0·01 Å is appreciably greater than the sum of the covalent radius of palladium(II) and the normal covalent radius of sulphur (1·31 + 1·04 = 2·33 Å) and is not significantly less than the non-bonded distance of 3·92 Å. This latter figure is obtained by adding together the van der Waals radii of the sulphur atom (1·85 Å) and the palladium atom, taken as one half of the separation distance between adjacent $PdCl_4^{2-}$ ions (2·07 Å in the compound K_2PdCl_4), (Pauling, 1948; Theilacker, 1937).

Pauling has observed that the van der Waals radii of many elements exceed the corresponding single-bond covalent radii by 0·75–0·83 Å, which in this case would give palladium a van der Waals radius of 2·06–2·14 Å (Pauling, 1948).

The distances of the methylthio carbon atom C(3) and carbon atoms C(7) and C(8) of the aromatic ring system from the iodine atom of an adjacent molecule are 4·29 and 4·34 Å respectively and compare favourably with the sum of the van der Waals radii for a methyl carbon and an iodine atom (2·00 + 2·15 = 4·15 Å) (Pauling, 1948).

Many dissimilarities occur between the crystal structures of $Pd(As–SCH_3)_2I_2$ and $Pd(As–As)_2I_2$. In both cases the Pd^{II} atom is surrounded by six atoms. In the former molecule these are two iodine, two sulphur and two arsenic atoms; in the latter molecule these are two iodine and four arsenic atoms. However, the Pd–S direction in the former complex is inclined 34° to the normal to the plane through the Pd,I and As atoms whilst in the diarsine complex this angle is 5°. Also in the thiol complex the dihedral angle between the Pd, As,S plane and the benzene ring is 50° 52′ whilst in the diarsine complex this angle is 2° 42′. These features, of course, are a result of (or result in) the diarsine complex being an example of a tetragonally distorted molecule involving four strong Pd–As bonds together with two elongated Pd–I bonds whereas the thiol molecule contains only four strong Pd–I and Pd–As bonds. It is apparent that, in these two instances, $d\pi$–$d\pi$ bonding is strongest between Pd and As atoms and when bonded to four arsenic atoms, in a plane, the back donation of electrons from the Pd atom enables it to attract large or polarizable anions, such as iodide ions, into the fifth and sixth positions. Palladium in the presence of only two arsenic atoms (as well as two sulphur and two iodide atoms) cannot sufficiently delocalize its charge by $d\pi$–$d\pi$ bonding and the higher coordination number is not attained.

The complex *trans*-$Pd(As–SCH_3)_2I_2$ is prepared by reacting excess of the ligand dimethyl-*o*-methylthiophenylarsine, $As–SCH_3$, with diiodo(dimethyl-*o*-methylthiophenylarsine)palladium(II), $Pd(As–SCH_3)I_2$. The reaction must therefore involve a considerable rearrangement of bonds about the transition metal atom. The formation of an intermediate six-coordinate complex is obvious.

At the present time a whole series of related compounds are being examined and these results will be reported at a later date.

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