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Nous apprenons que la structure de LiCl.2en vient d'être décrite brièvement par Brusset, Gillier-Pandraud & Delcroix (1966) dans une communication au Bulletin de la Société Chimique de France. Retenons que les distances interatomiques indiquées par les auteurs, bien que moins précises (écart-type moyen de 0,04 Å; $R=0{,}172$) sont comparables à celles que nous donnons ci-dessus, à l'exception toutefois des liaisons avec le lithium dont la position proposée est manifestement inexacte.*

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* *Note ajoutée aux épreuves:* – Cette position est corrigée dans un article plus detaillé de Mme Jamet-Delcroix qui vient de paraître (Jamet-Delcroix, 1967).

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Two Independent Determinations of the Crystal and Molecular Structure of *trans*-Dichlorobis(dimethyl sulfoxide)palladium(II)

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The crystal and molecular structure of dichlorobis(dimethyl sulfoxide)palladium(II), $PdCl_2(DMSO)_2$, has been determined from three-dimensional X-ray data in two independent studies. The complex crystallizes in the space group $P2_1/c$ of the monoclinic system with two molecules in a unit cell of dimensions (averages of the two studies) $a=6{\cdot}460$, $b=9{\cdot}380$, $c=9{\cdot}555$ Å and $\beta=111{\cdot}8°$. Since the palladium atoms lie on crystallographic centers of symmetry the compound assumes a *trans* planar configuration. The dimethyl sulfoxide is found to be sulfur-bonded to the palladium atom in accordance with infrared spectral data. Anisotropic least-squares refinements led to residuals of 0·031 (with hydrogen atoms held fixed) and 0·118 (hydrogen atoms omitted) for the M.I.T. and Texas Christian studies, respectively. Some important dimensions (weighted averages) are: Pd–Cl 2·287 Å, Pd–S 2·298 Å, S–O 1·475 Å, S–C 1·778 Å, angle CSO 109·1°.

Introduction

The isolation of well-defined complexes containing dimethyl sulfoxide, $(CH_3)_2SO$ (hereafter abbreviated DMSO), was first reported relatively recently (Lindquist & Einarsson, 1959; Cotton & Francis, 1960), though the powerful solvent properties of DMSO were generally recognized much earlier. A number of other reports have appeared in which the formation of metal complexes of DMSO (Meek, Straub & Drago, 1960; Cotton & Francis, 1961) and other sulfoxides (Francis & Cotton, 1961) has been described. Attempts were made very early to establish the structures of these compounds indirectly on the basis of various physical measurements. One study of this sort, utilizing infrared spectra, led to the proposal (Cotton, Francis & Horrocks, 1960) that from shifts in the SO stretching frequency it could be concluded that in nearly all the known complexes the sulfoxide was attached to the metal (or other Lewis acid) through the oxygen atom. The exceptions postulated were complexes formed by Pd(II) and Pt(II), in which coordination by the sulfur atom was proposed.

The investigations described in this paper were undertaken to determine conclusively whether this postulate of sulfur bonding was correct and, in any event, to provide precise structure details upon which basis a close analysis of the metal to sulfoxide bonding could be founded. For various reasons the compound $PdCl_2(DMSO)_2$ appeared to be very well suited to the purpose. A brief report of the M.I.T. study has been published earlier (Bennett, Cotton & Weaver, 1966).

Only after the two studies were complete, or very nearly so, was it realized that both had been carried out. It was therefore agreed, at the suggestion of Dr R. E. Marsh, that the two investigations should be published jointly, taking this somewhat unusual opportunity to compare the results of two entirely independent investigations which are comparable in the range and degree of refinement of the data. In the *Experimental* section, the two studies are described entirely separately [the M.I.T. work in part (1) and the Texas Christian work in part(2)]. Comparison and combining of results is done in the later sections.

Experimental (1)

Preparation

$PdCl_2(DMSO)_2$ was prepared by the method of Cotton & Francis (1960) and crystals suitable for X-ray studies were obtained by slow diffusion of benzene into a solution of the complex in methylene chloride. The physical properties of the sample were in good agreement with those reported previously for the compound.

Collection and reduction of data

The crystals were examined by the precession method and found to belong to the uniquely determined space group $P2_1/c$ (C_{2h}^5, no. 14) from the systematic absences $h0l$, $l=2n+1$, and $0k0$, $k=2n+1$. From precession photographs and measurements made with a General Electric Single Crystal Orienter the following unit-cell dimensions were found:

$$a=6\cdot450\pm0\cdot005,\ b=9\cdot38\pm0\cdot01,\ c=9\cdot54\pm0\cdot01\ \text{Å},\ \beta=111\cdot8^\circ\pm0\cdot1^\circ\ (\lambda\text{Cu}\ K\alpha,\ 1\cdot5418;\ \lambda\text{Mo}\ K\alpha_1,\ 0\cdot70926\ \text{Å}).$$

The measured density was found to be $2\cdot07\pm0\cdot05$ g.cm^{-3} by flotation in a mixture of methyl iodide and ethyl iodide; this compares favorably with a calculated density of $2\cdot066$ g.cm^{-3} for two $PdCl_2(DMSO)_2$ molecules in the unit cell.

Intensity data were collected on a single crystal in the form of an orange needle of dimensions $0\cdot1\times0\cdot1\times0\cdot4$ mm at room temperature. The crystal was mounted on the diffractometer with **a*** in the nonstandard setting $B2_1/a$ parallel to the spindle or φ axis. A modified version of Furnas's moving-crystal, moving-counter method was used (Cotton & Elder, 1964); the mosaic spread of the crystal led to a choice of $2\cdot66^\circ$ in 2θ for the scan. The 836 independent reflections accessible in the spherical range $\theta_{\text{Mo}}\le24\cdot4^\circ$, were collected at room temperature ($\sim22^\circ$C) and corrected for the Lorentz and polarization factors. The profile of intensity *versus* φ was plotted for several $h00$ reflections, which occurred at $\chi=90\cdot0^\circ$, and found to show a maximum variation of $\pm5\%$. Since at this orientation there was a maximum variation in the X-ray path and because the angular dependence of the transmission factor is small for the range over which the data were collected ($\mu r_{\text{max}}=0\cdot5$; $0\le\theta\le24\cdot4^\circ$), absorption corrections were neglected. The data, indexed for $B2_1/a$, were transformed into the standard setting $P2_1/c$.

Solution and refinement of the structure

Since there are two molecules in the unit cell of space group $P2_1/c$, the Pd atoms are required to lie on centers of symmetry. From a three-dimensional Patterson function the sulfur and chlorine atoms were readily located, although not distinguished from each other. Two cycles of least-squares refinement phased on these three atoms led to a residual R_F [equation (1)] of 0·23%.

$$R_F=\Sigma\ |F_o-F_c|/\Sigma\ |F_o| \tag{1}$$

A difference Fourier synthesis was then calculated and the oxygen and carbon atoms were readily located. Further isotropic refinement phased on all these atoms resulted in a residual of 0·096%.

Three more cycles of least-squares refinement were attempted during which both positional and thermal parameters began to oscillate by more than an e.s.d. The 87 weak reflections for which counting statistics were unsatisfactory were omitted from further refinements. The atoms were reset at the centers of their oscillations and isotropic least-squares refinement using a unit weighting scheme converged to $R_F=0\cdot068$ in three cycles. A difference Fourier map calculated from the final isotropic structure factors showed evidence of anisotropic thermal motion. Four cycles of least-squares refinement with inclusion of anisotropic temperature factors of the form

$$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$$

for all atoms led to a residual of 0·035.

An analysis of the variation of $(F_{\text{obs}}-F_{\text{calc}})^2$ with F_{obs} revealed very little divergence from unit weights.

Table 1. *Observed and calculated structure factors for the two investigations*

The five columns contain values of h, $10F_o$(M.I.T.), $10F_c$(M.I.T.), $10F_o$ (Texas Christian) and $10F_c$ (Texas Christian).

H 0 0				
1	1357	1391		
2	1107	1078		
3	1266	1218		
4	121	146	176	150
5	336	326	331	327
6	310	305	320	314
7			0	34
8			134	182
H 0 2				
-11			121	75
-9			190	248
-8			94	108
-7	256	245	235	272
-6	340	340	331	340
-5	73	-61	65	-60
-4	483	450	501	440
-3	521	490	484	448
-2			47	-16
-1	1020	1081		
0	608	566	389	432
1	377	377	363	378
2			1025	983
3	535	511	477	504
4	738	731	732	701
5	636	643	630	598
6	217	230	194	206
7			260	314
8			117	149
H 0 4				
-10			144	194
-9			152	165
-8			260	262
-7	412	410	372	407
-6	286	290	270	267
-5	570	547	563	529
-4	557	535	595	517
-3	291	287	275	288
-2	735	750	779	681
-1	75	83	0	77
0	242	228	214	199
1	840	803	741	745
2	193	197	179	176
3	540	532	487	482
4	640	646	626	579
5	175	175	144	151
6			354	344
7			267	261
H 0 6				
-10			123	71
-9			121	138
-8			225	249
-7	242	240	237	240
-6	580	570	626	583
-5	738	731	777	700
-4	557	538	591	537
-3	955	965	934	957
-2	685	647	606	576
-1	300	293	275	263
0	747	723	694	679
1	161	157	152	156
2	110	102	91	98
3	337	330	240	302
4	46	-30	0	-1
5			144	146
6			164	188
H 0 8				
-8			96	59
-7			94	145
-6	230	207	225	233
-5	97	85	91	87
-4	345	346	313	341
-3	536	507	462	473
-2	515	495	416	464
-1	831	817	762	782
0	650	648	571	600
1	510	516	492	474
2	516	531	477	473
3			146	174
4			179	205
5			129	174
H 0 10				
-8			85	148
-7			121	154
-6			94	80
-5	145	145	159	159
-4	157	160	149	172
-3	155	160	141	175
-2	355	351	308	352
-1	245	246	240	233
0	262	266	249	243
1			404	383
2			170	213
3			229	251
4			232	261
H 0 12				
-8			164	191
-7			144	167
-6			172	224
-5			164	206
-4			0	95
-3			144	138
-2			0	57
-1			83	1
0			121	130
H 0 14				
-7			121	174
-6			182	244
-5			187	244
-4			205	262
-3			211	239
-2			179	182
-1			134	171
0			96	108
H 1 0				
1	375	-332		
2	192	-190	152	-249
3	361	-336	347	-320
4	418	-400	419	-385
5	242	-240	195	-224
6	102	-106		
H 1 1				
-7	116	108		
-6	442	443	487	435
-5	226	228	188	212
-4	396	385	427	374
-3	898	865	942	838
-2	182	190	180	154
-1	970	995		
0	1103	1205		
1	512	500	515	423
2	1408	1425		
3	815	772	810	720
4	380	375	359	325
5	651	652	503	604
6	185	181	144	187
8			212	245
H 1 2				
-7	75	-73		
-6	125	-123	104	-98
-5	171	-172	156	-141
-4	90	-81	0	-67
-3	48	-48	0	-54
-2	57	-26	0	-3
-1	695	680	678	578
0	780	763		
1	323	310	339	294
2	413	376	419	313
3	150	133	131	137
4	91	-93	0	-80
5			0	-33
6	50	-55	0	-40
H 1 3				
-7	393	400	364	400
-6	276	275	275	267
-5	345	332	324	318
-4	790	755	766	720
-3	235	237	172	200
-2	705	708	658	661
-1	1063	1125		
0	267	283	303	223
1	1032	1021	898	911
2	758	725	738	652
3	245	243	207	217
4	645	650	622	600
5	271	280	292	275
6			140	145
7			263	310
H 1 4				
-7	50	-32	0	-17
-6	135	-140	104	-139
-5	252	-241	203	-242
-4	138	-131	119	-116
-3	103	-100	72	-106
-2	100	-85	88	-83
-1	221	191	220	205
0	157	137	116	115
1	51	43	0	12
2	213	205	203	179
3	185	183	167	180
4	130	140	119	121
5	128	125	104	101
6			0	49
H 1 5				
-7	270	265	235	272
-6	265	265	252	281
-5	613	586	667	589
-4	336	332	296	302
-3	470	480	519	462
-2	770	795	686	759
-1	222	235	216	215
0	633	612	474	569
1	543	527	538	484
2	131	131	116	122
3	527	523	510	482
4	256	266	220	254
5			136	160
6			319	314
H 1 6				
-7	118	117	0	109
-6	71	85	0	67
-5			0	25
-4			0	1
-3	200	-196	184	-187
-2	458	-436	387	-410
-1	492	-458	470	-426
0	405	-372	415	-357
1	310	-307	307	-271
2	135	-117	97	-98
3			0	33
4			0	28
5			0	35
H 1 7				
-7			144	156
-6	365	361	311	369
-5	325	320	283	308
-4	453	460	483	455
-3	725	735	838	719
-2	450	448	427	430
-1	661	645	555	617
0	636	617	474	568
1	220	223	180	211
2	483	482	491	444
3	272	283	299	266
4			123	109
5			231	260
H 1 8				
-6	140	142	108	140
-5	168	171	184	173
-4	237	241	188	238
-3	245	242	228	228
-2	125	120	0	107
-1	107	107	0	98
0	62	60	0	59
1	97	-101	96	-91
2	113	-108	0	-108
3			0	-93
4			0	115
H 1 9				
-7			165	229
-6	182	171	148	188
-5	187	200	203	225
-4	365	360	351	374
-3	193	195	191	197
-2	325	313	267	309
-1	437	431	427	407
0	215	217	180	214
1	408	412	339	385
2			319	317
3			136	160
4			195	249
5			140	126
H 1 10				
-5	60	-56	0	-60
-4			0	14
-3	108	85	0	70
-2	98	93	0	85
-1	166	161	144	150
0	151	150	131	134
1			0	55
3	-0	-0		
H 1 11				
-5			184	230
-4			131	147
-3			144	181
-2			207	263
-1			116	168
0			220	255
1			176	237
3			159	204
H 2 0				
0	558	531		
2	475	455	494	409
3	778	753	772	721
4	260	240	256	239
5	587	591	604	550
6	435	438	479	423
7			181	164
8			338	309
H 2 1				
-7			0	-59
-6			0	-18
-5	75	66	82	46
-4	72	71	0	57
-3	412	382	451	349
-2	650	628	693	536
-1	355	341		
0	392	378		
1	238	220	245	202
2	65	-57	0	-26
3			0	11
4	57	-50	0	-65
5	96	-92	110	-98
6	81	-72	96	-77
7			0	-76
H 2 2				
-10			135	82
-9			128	180
-8			0	116
-7	305	311	344	307
-6	482	485		
-5	398	396	472	377
-4	988	961	913	923
-3	970	838	764	753
-2	663	671	714	627
-1	1463	1600	1244	1486
0	497	500	487	470
1	665	646	619	562
2	998	966	640	918
3	36	31	0	19
4	310	311	303	270
5	356	365	376	358
6			0	34
7			270	249
8			178	185
H 2 3				
-8			113	-43
-7	77	-75	0	-72
-6	41	-30	0	-24
-5	71	-57	0	-57
-4	83	-67	0	-39
-3	45	-36	60	-5
-2	142	-142	146	-128
-1	162	-157	185	-120
0	68	-56	0	-28
1	101	95	100	103
2	197	185	213	194
3	98	96	93	84
4	75	80	0	52
5			0	24
6			0	-51
H 2 4				
-8			160	168
-7	263	262	281	271
-6	72	76	93	91
-5	446	480	565	496
-4	595	595	590	554
-3	330	347	398	310
-2	1166	1185	1116	1131
-1	932	960	818	859
0	660	655	604	599
1	1142	1135	821	1029
2	446	435	494	397
3	406	397	451	366
4	460	462	384	431
5	58	72	113	93
6			253	215
7			131	150
H 2 5				
-8			0	29
-7			0	36
-6	42	-27	0	-10
-5	85	-87	82	-74
-4	193	-192	210	-195
-3	295	-305	387	-312
-2	180	-175	213	-189
-1	90	-88	63	-110
0			0	-32
1	156	156	143	144
2	111	100	113	71
3			0	25
4	95	110	0	91
5			0	42
6			0	27
H 2 6				
-10			104	113
-9			138	155
-8			238	253
-7	105	97	1126	110
-6	178	167	170	190
-5	232	230	238	233
-4	57	56	82	58
-3	408	407	519	399
-2	381	388	441	380
-1	400	397	423	383
0	790	768	810	719
1	458	450	491	408
2	551	557	444	514
3	633	645	533	580
4	241	250	235	229
5			406	324
6			238	236
H 2 7				
-8			0	75
-7			0	77
-6	90	101	0	107
-5	153	148	153	135
-4	77	80	88	65
-3	78	80	100	84
-2	63	61	0	69
-1	116	-115	113	-100
0	168	-163	178	-147
1	192	-190	206	-177
2	196	-210	174	-189
3	115	-117		
4			0	-48
5			0	-10
H 2 8				
-8			213	204
-7			327	310
-6	345	351	401	357
-5	251	265	309	273
-4	446	451	544	460
-3	285	286	299	281
-2	88	100	96	107
-1	371	363	366	337
0	78	73	0	70
1	120	112	131	117
2	375	386	356	352
3			113	129
4			228	215
5			253	247
H 2 9				
-7			0	-49
-6			0	-13
-5			0	19
-4	70	63	0	67
-3	117	116	125	118
-2	113	111	128	102
-1	90	87	0	77
0			0	33
1	-0	-0		
H 2 10				
-8			203	168
-7			235	262
-6			231	231
-5			387	377
-4	392	402	484	395
-3	271	263	274	261
-2	382	395	437	387
-1	275	288	306	281
0			156	179
1			259	254
4			138	138
H 2 11				
-4			0	11
-3			0	3
-2			0	37
-1			0	53
H 2 12				
-5			150	206
-4			210	218
-3			381	315
-2			278	305
-1			320	283
0			363	304
1			138	179
H 2 13				
-3			163	-115
H 3 0				
1	296	286		
3	215	210	218	170
4	201	191	198	187
6	63	70		
H 3 1				
-9			202	202
-8			174	203
-7			228	249
-6	585	606	598	579
-5	385	386	434	363
-4	617	593	614	568
-3	1147	1160	834	1054
-2	452	455	474	422
-1	996	1025		
0	1031	1050		
1	191	-162	208	-172
2	396	403	380	361
3	225	223	228	196
4			0	71
5	447	462	388	448
6	215	220	250	213
7			248	216
8			320	258
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H 3 4				
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H 3 5				
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6			290	253
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H 3 7				
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H 3 8				
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4			210	204
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3			132	148
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2			180	186
3			124	128
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H 4 1				
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7			111	25
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H 4 3				
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6			280	271
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6			188	192
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3			188	181
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H 4 14				
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H 5 8				
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1	85	-90		
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2			168	146
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H 5 12				
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H 5 13				
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4	412	422	379	409
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6			115	115
7			122	95
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4			136	-90
H 7 9				
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-4	72	-80	0	-65
-1	130	-125		
0	46	35		
1	95	-90	70	-91
2			0	-44
3	138	147	165	125
H 8 2				
-7			186	179
-6			285	285
-5			250	275
-4	495	510	452	480
-3	471	468	405	454
-2	391	382	332	375
-1	625	611	440	556
0	320	315	233	309
1	288	290	247	264
2	395	393	367	336
3	63	55	75	64
4			144	130
5			165	167
H 8 3				
-6			134	137
-5			0	38
-4	121	121	162	130
-3	71	80	99	84
-2	175	-175	151	-147
-1			56	-30
0	141	-142	146	-114
1	258	-257	250	-212
2	-0	-0		
3	80	-87	70	-77
4			120	-95
H 8 4				
-7			148	137
-6			0	1
-5			268	257
-4	290	293	310	275
-3	250	257	261	259
-2	602	590	508	527
-1	483	487	456	444
0	443	441	395	421
1	582	580	459	509
2	271	270	257	259
3			257	254
4			250	232
5			141	85
6			151	139
H 8 5				
-4	105	95	113	82
-3			0	-22
-2	85	85	123	65
-1	147	150	219	121
0	73	46	0	29
1	111	110	137	82
2			75	-12
3			92	-74
4			0	-28
5			99	-76
H 8 6				
-8			155	151
-7			141	84
-6			116	123
-5			142	112
-4	47	37	0	36
-3	217	210	226	200
-2	191	203	216	196
-1	207	213	226	217
0	402	407	416	380
1	265	275	282	267
2			353	316
3			343	348
4			179	185
5			205	202
6			165	149
H 8 7				
-2	51	50		
0			113	89
H 8 8				
-7			212	193
-6			250	223
-5			216	190
-4			275	240
-3			169	161
-1			198	139
0			0	51
1			106	90
2			250	178
3			134	111
4			158	147
5			169	143
H 8 10				
-7			169	153
-6			195	172
-5			271	250
-4			257	248
-3			184	207
-2			261	246
-1			243	175
0			151	139
1			165	147
H 8 12				
-5			127	135
-4			127	144
-3			206	202
-2			209	202
-1			191	191
0			198	195
1			134	129
2			0	108
H 9 0				
1	158	162		
2	43	23		
3	177	178	151	160
4			157	142
H 9 1				
-7			159	116
-6			188	198
-5			145	154
-4			198	204
-3	365	368	273	322
-2	287	277	200	262
-1	485	475		
0	445	443		
1	236	238	154	220
2	402	401	288	339
3	223	225	212	207
4			174	164
5			249	264
6			131	129
7			133	115
H 9 2				
-8			131	63
-7			0	39
-6			113	112
-5			0	41
-2	160	-163	139	-150
-1	225	-225	131	-194
0	108	-111	90	-115
1	233	-226	183	-226
2	97	-85	102	-96
H 9 3				
-7			186	173
-6			145	119
-5			174	168
-4			290	285
-3	145	140	145	164
-2	290	280	218	278
-1	340	340	235	308
0	100	105	233	121
1	330	330	264	298
2	312	306	255	282
3			177	187
4			290	290
5			215	178
6			131	121
7			154	135
H 9 4				
-6			113	82
-5			98	74
-4			180	181
-3	122	126	143	123
-2	90	82	90	78
-1	107	110	119	101
0	72	-88	125	-84
1	68	-70	78	-79
2			113	-76
3			188	-191
H 9 5				
-8			143	135
-7			149	135
-6			149	157
-5			319	288
-4			261	236
-3	276	265	215	259
-2	342	341	229	305
-1	177	185	198	183
0	281	281	259	263
1			253	255
2			174	177
3			229	230
H 9 6				
-6			104	-46
-2			171	174
-1			119	101
0			143	106
1			157	133
2			0	-3
3			0	2
4			116	-10
H 9 7				
-8			125	112
-7			137	140
-6			206	197
-5			180	168
-4			194	187
-3			233	207
-2			161	147
-1			255	248
0			247	234
1			171	152
2			233	216
3			174	131
4			122	92
5			157	138
H 9 8				
-4			147	-148
-3			73	-80
-2			102	-87
2			0	61
3			96	66
4			139	138
H 9 9				
-7			128	129
-6			128	95
-5			122	116
-4			204	184
-3			171	159
-2			223	229
-1			290	249
0			183	159
1			249	185
2			200	147
3			113	99
4			154	123
H 9 10				
-2			125	-89
-1			113	-70
0			122	-103
1			0	-68
2			0	-21
H 9 11				
-6			125	97
-5			137	136
-4			125	129
-3			131	133
-2			143	132
-1			82	95
0			125	113
1			128	109
2			133	96
H 9 12				
-1			128	-15
H 9 13				
-3			116	104
-2			108	83
-1			108	103
0			149	98
H 10 0				
0	556	550		
1	340	338	228	336
2	336	332	270	323
3			350	339
4			158	166
5			154	153
6			152	115
7			110	54
H 10 1				
-5			92	69
-4			84	-61
-1	145	-137		
2	65	-72		
H 10 2				
-8			98	76
-7			110	125
-6			124	131
-5			70	50
-4			138	131
-3			102	99
-2	75	72	70	70
-1	321	308	200	257
0	286	280	214	248
1	331	335	284	315
2			434	400
3			282	280
4			338	289
5			240	222
6			130	119
7			140	135
H 10 3				
-6			102	56
-5			0	-14
-4			0	5
-3			70	40
-2			0	-18
-1	72	80	68	66
H 10 4				
-8			118	144
-7			192	201
-6			186	172
-5			220	213
-4			200	186
-3			124	119
-2			170	177
-1			76	84
0			76	89
1			180	168
2			82	77
3			166	154
4			232	194
5			110	122
6			170	158
7			154	125
H 10 5				
-4			64	63
-3			0	4
-2			58	74
-1			56	14
0			112	-82
H 10 6				
-8			110	110
-7			118	125
-6			214	202
-5			242	239
-4			242	250
-3			326	344
-2			234	269
-1			220	204
0			288	222
1			129	92
2			82	81
3			136	106
4			78	56
5			90	91
H 10 7				
-3			68	-8
-2			0	-9
-1			90	-49
H 10 8				
-6			112	110
-5			116	121
-4			220	215
-3			236	241
-2			228	241
-1			288	291
0			242	232
1			220	213
2			200	194
3			88	109
4			96	105
H 10 10				
-5			90	63
-4			0	47
-3			0	48
-2			132	103
-1			116	108
0			170	145
1			226	181
2			136	138
3			150	133
4			118	113
H 10 12				
-6			92	110
-5			0	94
-4			0	73
-3			90	83
-2			90	61
-1			92	51
H 10 13				
-5			126	21
-4			0	18
-3			126	20
-2			0	18
H 10 14				
-1			132	74

Refinement with an empirical weighting scheme produced no significant variation in either parameters ($<1{\cdot}7\sigma$) or e.s.d.'s ($<10\%$) and unit weights were therefore retained.

A difference Fourier synthesis phased on the last cycle of refinement revealed six peaks around the two carbon atoms of 0·5 to 0·75 e.Å^{-3} at reasonable locations for hydrogen atoms. Since the standard deviation of the electron density of the difference map was estimated to lie between 0·07 e.Å^{-3} (Cruickshank, 1949) and 0·11 e.Å^{-3} (Lipson & Cochran, 1953), these peaks were considered to be real. Thus, six hydrogen atoms were included in four additional cycles of anisotropic refinement leading to a residual of 0·031. The hydrogen atoms were assigned fractional coordinates corresponding to the positions obtained from the difference Fourier synthesis and anisotropic temperature parameters approximately 10% greater than those of the carbon to which they were attached. None of the hydrogen parameters were varied in the refinement.

In the final cycle of refinement the largest shift in the parameters was half of the standard deviation, an average shift being one-fourth of the standard deviation. A final difference Fourier map calculated from the parameters obtained in the last cycle of refinement exhibited no electron density maximum exceeding 0·5 e.Å^{-3}. Atomic scattering factors used throughout for the neutral light atoms were those of Ibers (1962). The neutral Pd scattering factor was obtained from a tabulation by Cromer & Waber (1965) and was corrected for the real part of anomalous dispersion (Dauben & Templeton, 1955). The observed and calculated structure factors are listed in Table 1. The final coordinates and thermal parameters are given in Table 3.

The following programs for the IBM 7094 computer were used and are gratefully acknowledged.

1. W.G.Sly, D.P.Shoemaker and J.H.Van den Hende. Two- and three-dimensional crystallographic Fourier summation, ERFR-2 (1962).
2. D.P.Shoemaker. M.I.T. X-ray goniometer package, MIXG-2 (1962).
3. C.T.Prewitt. A full matrix crystallographic least squares program, SFLSQ3 (1962).
4. J.S.Wood. Molecular geometry with estimated standard deviations, MGEOM (1964).
5. D.P.Shoemaker. Crystallographic bond distance, bond angle and dihedral angle computer program, DISTAN (1963).
6. D.P.Shoemaker and R.C.Srivastava. Anisotropic temperature factor interpreting program, VIBELL (1963).
7. R.C.Elder. General data reduction and presentation programs, RAWRE, PDATA and PUBTAB (1964).

Experimental (2)

Preparation

Palladium(II) chloride obtained from Englehard Inds. Inc. was used without further purification. Dimethyl sulfoxide obtained from Fisher Scientific Company was dried over calcium hydride and vacuum distilled before use.

trans-$PdCl_2(DMSO)_2$ was prepared by dissolving palladium(II) chloride in DMSO at 100°C and allowing the solution to cool slowly. Single crystals of the bright orange material, suitable for X-ray studies, were obtained upon recrystallization from a DMSO–acetone mixture, m.p. 203–204°C. The crystals showed a tendency to twin, but examination with a polarizing microscope permitted the selection of untwinned specimens.

Collection and reduction of data

A crystal $0{\cdot}23 \times 0{\cdot}13 \times 0{\cdot}13$ mm was used for the collection of all X-ray data. Precession photographs indicated that the crystal belonged to the monoclinic system. Systematic extinctions $0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$ placed the crystal in space group $P2_1/c$ (no. 14) with the b axis unique. The unit-cell dimensions were obtained from the $h0l$ Weissenberg photograph and a b-axis layer line photograph (λMo $K\alpha_1$, 0·70296 Å). The films were calibrated by superimposed sodium chloride powder lines. The unit-cell dimensions are $a = 6{\cdot}48 \pm 0{\cdot}01$, $b = 9{\cdot}380 \pm 0{\cdot}005$, $c = 9{\cdot}562 \pm 0{\cdot}004$ Å, $\beta = 111°49' \pm 10'$. The measured density, $d_0 = 2{\cdot}037$ g.cm^{-3} (flotation method), indicated two molecules per unit cell; $d_c = 2{\cdot}055$ g.cm^{-3}.

Levels $h0l$ to $h10l$ were recorded by the equi-inclination Weissenberg technique. The intensities of the reflections were estimated visually with calibrated strips prepared from reflections of similar area. In this way, 1258 non-zero reflections were obtained. Absorption corrections were applied with the use of Bond's values with $\mu R = 0{\cdot}187$ (*International Tables for X-ray Crystallography*, 1959).

Solution and refinement of structure

Since the space group is $P2_1/c$ with two molecules per unit cell, the palladium atoms are required to occupy special positions which are located at centers of symmetry. This requires like ligands to be *trans* to each other and a *trans* square-planar configuration was assumed. An electron density projection was calculated with the signs derived from the palladium atom positions. Positions corresponding to sulfur and chlorine atoms in a square-planar array were evident although they were indistinguishable at this stage. A series of successive Fourier syntheses was used to locate the lighter atoms and to assign the sulfur and chlorine positions definitely.

The atomic scattering factors used in the structure factor calculations were those computed from relativistic Dirac–Slater wave functions (Cromer & Waber, 1965). Anomalous dispersion corrections of the type $f = f_0 + \Delta f' + i\Delta f''$ were applied to the scattering factors (*International Tables for X-ray Crystallography*, 1962). In all cases, the imaginary term was negligible.

Initial refinement was carried out through use of a difference electron density map. A full-matrix least-squares technique was used for the final refinement. The quantity minimized was $\Sigma w(F_o-F_c)^2$. A few reflections that were obviously affected by extinction were omitted in the final calculations. Several cycles with isotropic temperature factors decreased R ($R=\Sigma(F_o-F_c)/\Sigma F_o$) to 0·137 and three cycles with the anisotropic factors gave the final value of R=0·118.

Three different weighting schemes were used. The resulting parameters all agreed within the estimated standard deviations, and the results for the unit weighting scheme are presented for comparison with the M.I.T. calculations. The other weighting schemes used were $F_o<4|F_{\min}|$, $w=1/(16|F_{\min}|^2)$ and w=1·0; $F_o>4|F_{\min}|$, $w=1/|F_{\text{obs}}|^2$ and $w=|F_{\min}|/4|F_{\text{obs}}|$. The only noticeable change for the latter two schemes was a trend toward equalizing the two S–C distances.

The final shifts in all parameters were well below their estimated standard deviations. Table 1 lists the observed and calculated structure factors while Tables 2 and 3 give the final positional and thermal parameters.

The following computer programs were used:

1. W.H.Watson and R.J.Williams. Data reduction program (IBM 1620).
2. R.Shiono. Structure factor calculations in X-ray crystallography (IBM 1620).
3. R.Shiono. General three-dimensional Fourier synthesis program (IBM 1620).
4. M.E.Pippy. Calculation of bond lengths and bond angles (IBM 1620).
5. H.A.Levy and W.R.Busing. Full-matrix least-squares (IBM 7094, Texas A and M University).

Table 2. *Fractional coordinates of atoms*

	x	y	z
Pd	0·0	0·0	0·0
	0·0	0·0	0·0
S	0·0642 (3)	0·1981 (2)	−0·1200 (2)
	0·0638 (7)	0·1969 (5)	−0·1202 (4)
Cl	0·3628 (3)	−0·0114 (2)	0·1647 (2)
	0·3616 (7)	−0·0125 (7)	0·1652 (5)
O	0·0578 (10)	0·1655 (6)	−0·2729 (5)
	0·0626 (29)	0·1697 (19)	−0·2710 (15)
C(1)	0·3166 (13)	0·2885 (9)	−0·0167 (8)
	0·3122 (34)	0·2851 (28)	−0·0168 (23)
C(2)	−0·1347 (13)	0·3333 (8)	−0·1324 (8)
	−0·1461 (34)	0·3348 (22)	−0·1362 (20)

Description of the structure

Molecular structure

Table 4 gives the molecular dimensions while Fig. 1 shows the molecular structure of $PdCl_2(DMSO)_2$ projected along the *a* axis. Since the Pd atom lies on a crystallographic center of symmetry, the molecule is required to have a *trans* planar configuration.

Table 4. *Intramolecular distances** (Å) *and angles* (°) *together with their estimated standard deviations*

	Determination (1)		Determination (2)	
	Distance	e.s.d.	Distance	e.s.d.
Pd–S	2·299	0·002	2·291	0·005
Pd–Cl	2·287	0·002	2·290	0·006
S—O	1·476	0·005	1·46	0·02
S—C(1)	1·780	0·008	1·75	0·03
S—C(2)	1·776	0·007	1·84	0·03
	Angle	e.s.d.	Angle	e.s.d.
S——Pd–Cl	93·00	0·06	93·3	0·2
Pd —S—C(1)	114·1	0·3	113·4	1·0
Pd —S—C(2)	110·5	0·3	110·0	0·9
Pd —S—O	112·4	0·2	115·0	0·9
O——S—C(1)	109·2	0·3	107·6	1·3
O——S—C(2)	109·1	0·3	107·7	1·2
C(1)–S—C(2)	100·9	0·3	102·3	1·3
C(1)–H(av.)	1·07	†		
C(2)–H(av.)	0·97	†		

* All distances uncorrected for thermal motion.

† H atom positions derived from electron difference map.

Refinement (1)

The Pd–Cl distance of 2·30 Å is exactly that found previously in a norbornadienedichloropalladium(II) complex (Baenziger, Doyle & Carpenter, 1961) while the Pd–S distance of 2·30 Å compares quite favorably with that of 2·33 Å in $Pd(SCN_2H_4)_2Cl_2$ (Oi, Kawase, Nakatso & Kuroya, 1960). The two crystallographically independent S–C distances are equal within ex-

Table 3. *Anisotropic thermal parameters* (×10⁴)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	129 (2)	51 (1)	52 (1)	4 (1)	17 (1)	2 (1)
	115 (4)	50 (6)	47 (2)	11 (3)	23 (2)	5 (2)
S	191 (5)	53 (2)	47 (2)	−3 (3)	36 (3)	2 (2)
	212 (11)	52 (8)	55 (4)	−1 (5)	48 (5)	−2 (3)
Cl	151 (5)	85 (2)	111 (2)	−2 (3)	11 (3)	16 (2)
	150 (10)	104 (10)	116 (6)	3 (7)	3 (6)	14 (5)
O	411 (21)	93 (7)	65 (6)	−20 (10)	85 (10)	−13 (6)
	471 (61)	121 (25)	76 (16)	−16 (30)	127 (26)	−24 (15)
C(1)	223 (22)	89 (10)	97 (10)	45 (13)	41 (13)	−1 (8)
	204 (53)	124 (35)	109 (25)	63 (34)	47 (29)	−5 (22)
C(2)	286 (23)	65 (9)	94 (10)	45 (12)	47 (13)	13 (8)
	278 (57)	62 (25)	90 (21)	42 (28)	89 (28)	4 (16)

perimental error at 1·778 ± 0·007 Å, while the S–O distance is 1·475 ± 0·005 Å. The environment around the sulfur atom is nearly tetrahedral with the angles ranging from 100·9 to 114·0°. The average C–H distances are reasonably close to the value of 1·09 Å accepted (Pauling, 1960) for an sp^3 hybridized carbon atom bonded to hydrogen.

Refinement (2)

The Pd–S and Pd–Cl bond lengths are experimentally identical, 2·290 ± 0·006 and 2·291 ± 0·005 Å respectively, and the bond angles around the palladium atom are 87·3 and 92·7°. The sulfur atom in each DMSO group is in an approximate tetrahedral environment with angles ranging from 102·3 to 115·0°. The two independent C–S bond lengths are 1·84 ± 0·03 and 1·75 ± 0·03 Å in the unit weighting scheme and 1·82 ± 0·03 and 1·76 ± 0·03 Å for the others.

Intermolecular distances

All intermolecular contacts up to 4 Å were calculated. The pertinent ones are listed in Table 5. None of these are excessively short and no further significance is attached to them.

Analysis of anisotropic motion

Root mean square amplitudes of the atomic vibrational ellipsoid axes for $PdCl_2.(DMSO)_2$ are given in Table 6 together with their direction cosines. These are referred to principal axes in a cartesian system in which x is parallel to **a**, y parallel to **b** and z parallel to **c***. The anisotropy of the individual atoms is that expected. For example, the Cl minor axis is along the Pd–Cl bond direction, the major axis being perpendicular to the plane of the complex and to the Pd–Cl bond. Similarly the oxygen and two carbon atoms have their minor axes in the S–O bond direction and S–C bond directions respectively. The palladium atom vibrates in such a way that the minor axis lies roughly along the Pd–Cl bond direction. The major axis lies slightly below the plane of the complex and bisects the S–Pd–Cl angle.

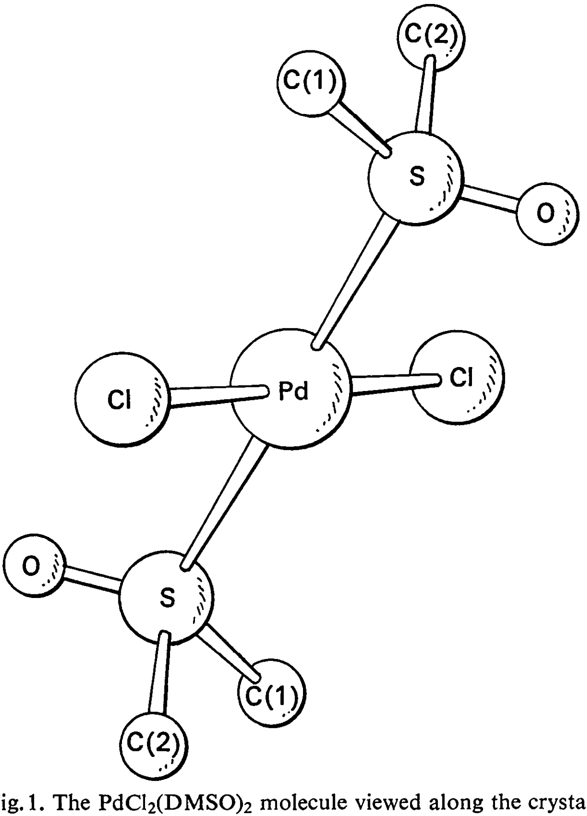

Fig. 1. The $PdCl_2(DMSO)_2$ molecule viewed along the crystallographic *a* axis. The palladium atom lies on an inversion center.

Table 5. *Intermolecular contacts in* $PdCl_2(DMSO)_2$

Atom of reference molecule	Atom in neighboring molecule	Distance
Cl	O $(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·95 Å
	C(1) $(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·79
	C(1) $(\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z)$	3·72
	C(2) $(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·50
S	O $(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3·57
O	C(1) $(x, \frac{1}{2}-y, z-\frac{1}{2})$	3·37
	C(2) $(x, \frac{1}{2}-y, z-\frac{1}{2})$	3·20
	C(2) $(\bar{x}, y-\frac{1}{2}, -\frac{1}{2}-z)$	3·33

Comparison of results

A comparison of the two independent sets of parameters and their estimated standard deviations emphasizes the main factors in the accuracy of crystal structure determinations. The two main features affecting the precision of the determined values are (*a*) accuracy of data measurement, and (*b*) the number of observations. Clearly in this case determination (1), using diffractometer data, gains from criterion (*a*) while determination (2), from film data, is better under criterion (*b*). In this example it would appear that the improved accuracy in the measurement of the intensities more than offsets the larger number of observations to the extent that the values for the estimated standard deviations of the positions in determination (1) are, in general, one third the values of those for determination (2). The agreement between the sets of parameters is satisfying with no discrepancy exceeding 3σ, σ being that in determination (2).

Cruickshank (1960) gives a simple formula for coordinate e.s.d.'s for data that are isotropic in three dimensions and have no atoms on special positions:

$$\sigma(x) \simeq \frac{R}{\bar{S}} \left(\frac{N}{8p}\right)^{\frac{1}{2}} \text{ (centrosymmetric case)}$$

where

R = residual $\Sigma\,|\Delta F|/\Sigma\,|F\mathrm{OBS}|$
$\bar{S}$ = r.m.s. reciprocal radius for the planes observed
p = difference between the number of observations and the numbers of parameters
N = the number of atoms, of the type being considered, that are needed to give a scattering power equivalent to the total asymmetric unit at $\bar{S}$.

Although both data sets are approximately isotropic, clearly the formula is invalid since the palladium atom is on a special position. However, the ratio of the e.s.d.'s of the two determinations should be closely approximated by the expression:

$$\frac{\sigma_1(x)}{\sigma_2(x)} \simeq \frac{R_1\bar{S}_2}{R_2\bar{S}_1}\left(\frac{N_1p_2}{N_2p_1}\right)^{\frac{1}{2}},$$

which on substitution of the relevant values, $R_1=0{\cdot}031$, $R_2=0{\cdot}118$, $\bar{S}_1=0{\cdot}90$, $\bar{S}_2=1{\cdot}05$,* $p_1=744$, $p_2=1198$, $N_1\simeq N_2$, gives $\sigma_1(x)/\sigma_2(x)\simeq 1/2{\cdot}5$, which is in reasonable agreement with the observed results.

A semiquantitative treatment of the β_{ij}'s is more difficult because the lack of isotropy in data set (2) becomes more important. This feature is clearly shown by the disparity in e.s.d.'s for β_{22}'s and β_{33}'s in determination (2), where a straight comparison is reasonably valid, *i.e.* conversion to u_{ij}'s involves approximately the same constant. However, once again the dominant feature in the comparable formula for u_{ij}'s is R, and the lower e.s.d.'s come from determination (1) despite the large amount of high angle data in determination (2).

Discussion

The structure of this compound is of interest chiefly in two respects. First, and most obvious, it shows that the earlier interpretation of infrared spectra, in which binding of the DMSO to palladium is through sulfur is, indeed, correct. The general applicability of the infrared criteria proposed (Cotton, Francis & Horrocks, 1960) is thus strongly suggested.

Second, the detailed structure of DMSO in $PdCl_2(DMSO)_2$ invites comparison with the molecular structure parameters of DMSO itself. Two reports of the DMSO structure, determined by X-ray crystallography have recently appeared (Viswamitra & Kannan, 1966; Thomas, Shoemaker & Eriks, 1966). We shall make comparisons with the molecular parameters of Thomas, Shoemaker & Eriks because their structure is (*a*) based on data collected nearer to room temperature (+5°) than that of Viswamitra & Kannan (−60°), (*b*) their data are more extensive and apparently better scaled, and (*c*) their refinement appears to have been more complete. Moreover, the thermal ellipsoids obtained in the M.I.T. study of $PdCl_2(DMSO)_2$ and those of Thomas, Shoemaker & Eriks for DMSO are comparable in magnitude and shape. Since librational corrections to the bond lengths have not been applied in the present work, comparisons will be made with the uncorrected bond lengths in the DMSO structure.

The weighted mean S–C distance found in the present studies is 1·778(5) Å. This is in good agreement with the values of 1·771(8) and 1·805(11) found by Thomas, Shoemaker & Eriks and the values of 1·80(1) and 1·81(1) found by Viswamitra & Kannan in DMSO itself, as well as with the S–C distances in the $(CH_3)_3SO^+$ ion (Zimmermann, Barlow & McCullough, 1963; Coulter, Gantzel & McCullough, 1963).

The S–O bond length is of particular interest. In resonance terms, the electron distribution can be expressed as a hybrid of the three canonical forms (I), (II) and (III), with (II) presumably predominating.

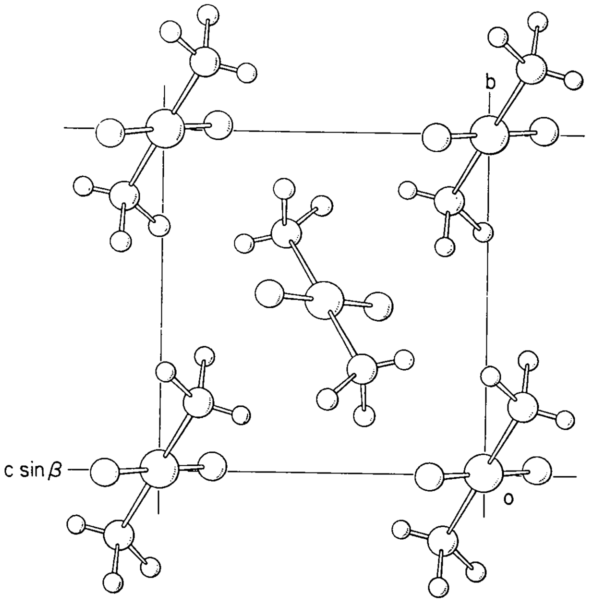

Fig. 2. Molecular packing in $PdCl_2(DMSO)_2$ as shown by a projection down the crystallographic *a* axis.

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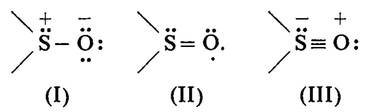
* $\bar{S}_2$ computed assuming an isotropic data set containing 1300 independent reflections.

Table 6. *Root mean square amplitudes and direction cosines of the atomic vibrational ellipsoids*

	$(u^2_{\rm max})^{1/2}$	$(u^2_{\rm med})^{1/2}$	$(u^2_{\rm min})^{1/2}$
Pd	0·168	0·152	0·137
	0·918 0·084, −0·388	0·037, 0·955, 0·296	0·396, −0·286, 0·873
S	0·188	0·154	0·135
	0·982, −0·092, 0·096	0·059, 0·976, 0·213	−0·182, −0·199, 0·946
Cl	0·256	0·191	0·147
	−0·652, 0·254, 0·714	0·277, 0·957, −0·085	0·706, −0·143, 0·695
O	0·276	0·204	0·145
	0·945, −0·156, 0·289	0·205, 0·968, −0·144	−0·255, 0·196, 0·946
C(1)	0·236	0·197	0·166
	0·758, −0·639, −0·134	−0·052, 0·264, 0·962	0·651, 0·723, 0·235
C(2)	0·244	0·199	0·149
	0·934, 0·357, −0·031	−0·151, 0·314, 0·938	−0·324, 0·880, −0·347



(I) (II) (III)

In (III) it must be assumed that sulfur is using at least one *d* orbital for back-accepting π electrons from oxygen.

Clearly, if (III) represents a reasonable electronic distribution but one which is far from predominant in DMSO itself, the attachment of sulfur to an electrophile should increase the contribution of (III) and consequently decrease the S–O bond length. In $(CH_3)_3SO^+$, where the very powerful electrophile CH_3^+ has been attached to the sulfur of DMSO, the S–O bond length has decreased to 1·45(1) Å, from the 1·513(5) Å found in DMSO. In $PdCl_2.(DMSO)_2$, the S–O distance 1·475(5) Å is also shorter than in DMSO by 0·038(10) Å.

These changes in the S–O distance appear to be quite consistent with the corresponding changes in the S–O stretching frequency. This varies from 1096 cm^{-1} in gaseous DMSO to 1116 cm^{-1} in $PdCl_2(DMSO)_2$ to 1233 cm^{-1} in $(CH_3)_3SO^+$.

The changes in bond length also seem to correlate in a reasonably semi-quantitative way with the assumed bond orders. Thus for S–N bonds one has a complete range of bond orders. Essentially a triple bond, with a length of 1·416(3) is found in F_3SN (Cotton & Wilkinson (1966) give a summary and references for the S–N bond lengths), while the S–N double bond in $S_4N_4F_4$ has a length of 1·54(1) Å and the single bonds found in $S_4N_4H_4$ have lengths of 1·66(1) and 1·67(1) Å respectively. Thus, for S–N bonds, the change in length per unit change in bond order is about 0·12 Å and a roughly similar value might be expected for S–O bonds. Moreover, the S–O bond of any given order ought to be a little shorter than the corresponding S–N bond due to the inherently smaller radii of O *versus* N.

Thus the S–O bond length of about 1·51 Å is consistent with the assignment of a bond order of about 2·0 when compared with the S–N bonds and the change from 1·51 to 1·45 Å on going from $(CH_3)_2SO$ to $(CH_3)_3SO^+$, that is 0·06 Å, would suggest that a very considerable increase, roughly to a bond order of $2+(0{\cdot}06)/(0{\cdot}12)=2{\cdot}5$ had occurred. In $PdCl_2(DMSO)_2$, on the other hand, a smaller change, 0·04 Å, perhaps to about 2·2, appears to have occurred.

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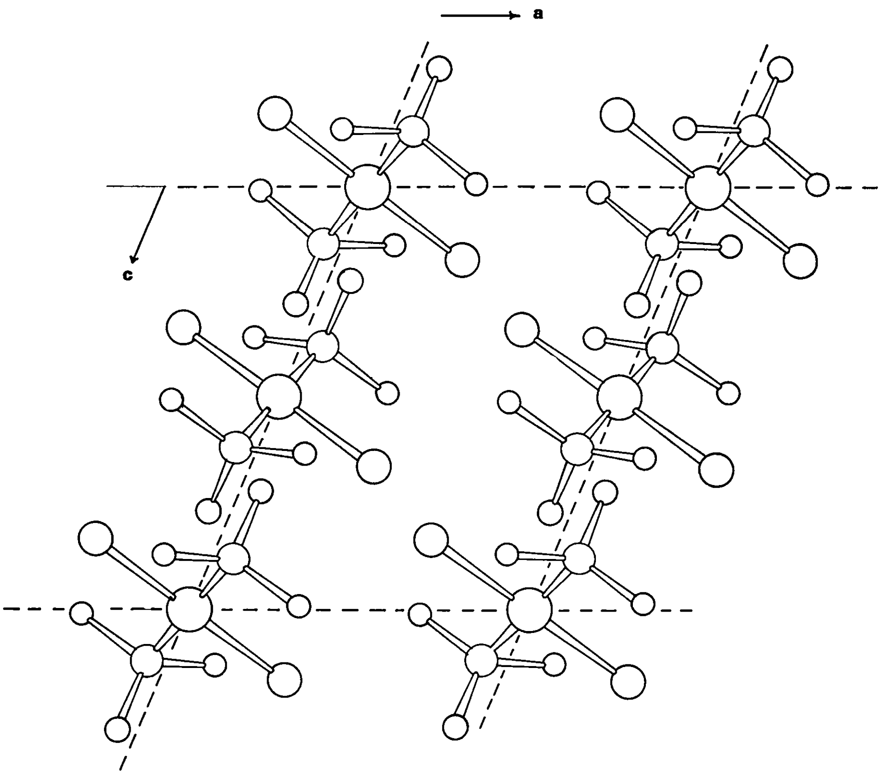

Fig. 3. Molecular packing in $PdCl_2(DMSO)_2$ as shown by a projection down the crystallographic *b* axis.

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The Crystal Structure of Two Modifications of Tetraethylammonium Triiodide, $(C_2H_5)_4NI_3$

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The crystal structures of two modifications, I and II, of $(C_2H_5)_4NI_3$ have been determined by three-dimensional X-ray methods. Modification I crystallizes in space group *Cmca* with $a=14{\cdot}207$, $b=15{\cdot}220$, $c=14{\cdot}061$ Å, e.s.d. 0·05 %, $Z=8$; II crystallizes in space group *Pnma* with $a=14{\cdot}552$, $b=13{\cdot}893$, $c=15{\cdot}156$ Å, e.s.d. 0·05 %, $Z=8$. Anisotropic least-squares refinement was carried out with 909 independent reflexions for I ($R=0{\cdot}045$) and with 1094 reflexions for II ($R=0{\cdot}042$). In I, there are two independent I_3^- ions at special positions with symmetry $2/m$; the bond lengths in the two symmetrical I_3^- ions are 2·928 and 2·943 Å, e.s.d. 0·0025 Å. In II there are two independent I_3^- ions; the ions are nearly linear, but asymmetric with bond lengths of 2·912, 2·961 and 2·892, 2·981 Å, e.s.d. 0·0035 Å. A VESCF molecular orbital study of the electronic structure of the triiodide ions, including the effect of the crystal field, was made. A bond order *versus* bond length curve could be obtained.

Introduction

The nearly linear triiodide ion varies in structure with its environment in the crystal. Symmetric ions with equal bond lengths have, for instance, been observed in $(C_6H_5)_4AsI_3$ (Mooney Slater, 1959) whereas in crystals of CsI_3 (Tasman & Boswijk, 1955), the ions are asymmetric with a difference in I–I bond length of approximately 0·2 Å. From the data available at that time, Rundle (1961) concluded that the asymmetry and the total length of the ions increase with decreasing size of the surrounding cations. Hach & Rundle (1951) as well as Havinga & Wiebenga (1959) ascribe the variations in bond length to the influence of the (electrostatic) crystal field. Their qualitative conclusions have recently been supported by Brown & Nunn (1966) for the triiodide ions in $(C_6H_5)_4AsI_3$ and in CsI_3 by theoretical variable electronegativity self-consistent field (VESCF) molecular orbital calculations in which the crystal field was taken into account. Mooney Slater (1959) and Slater (1959), on the other hand, have suggested that in certain crystals 'pressure' may force the I_3^- ions to become shorter and more symmetric.

Examination of the structural data on which these discussions are based shows that most of the data used do not give reliable information on the lengths of the I–I bonds in I_3^- ions. In $(CH_3)_4NI_5$, $(C_2H_5)_4NI_7$ and Cs_2I_8, the I_3^- ions show strong interaction either with each other or with iodine molecules so that complexes with I_5^-, I_7^- and I_8^{2-} ions respectively occur in these