Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE CRYSTAL AND MOLECULAR STRUCTURE OF THE DIPHENYLETHYLPHOSPHINE OXIDE ADDUCT OF TETRAKIS-(μ_3-HYDROXOTRICARBONYLHYDRIDOTUNGSTEN), $[W(OH)(CO)_3H]_4 \cdot 4\ OPPh_2Et$

VINCENZO G. ALBANO, GIANFRANCO CIANI, MARIO MANASSERO AND MIRELLA SANSONI

Istituto di Chimica Generale e Inorganica dell'Università degli Studi, 21, via Venezian, 20133 Milano (Italy)

(Received July 16th, 1971)

SUMMARY

The compound $[W(OH)(CO)_3H]_4 \cdot 4\ OPPh_2Et$ crystallizes in the monoclinic space group *C2/c* with the following unit cell constants: $a = 25.06(2)$, $b = 14.08(1)$, $c = 24.60(2)$ Å, $\beta = 120°20'(10')$ and $Z = 4$. The structure has been determined from a set of 1246 independent non-zero reflections, measured with counter methods, and refined by least-squares to a final *R* index of 0.049. It consists of tetrameric units $[W(OH)(CO)_3H]_4$, lying around the two-fold crystallographic axes. The tungsten atoms, which occupy the corners of a regular tetrahedron, are held together by four μ_3-hydroxo groups, so that the W_4O_4 moiety forms a distorted cube. The W...W distances (mean value 3.48 Å) are definitely non-bonding. The stereochemical arrangement of the ligands around the tungsten atoms identifies the hydridic hydrogen positions. The resulting coordination polyhedron in each $(OH)_3W(CO)_3H$ moiety can be described as a combination, by apex sharing, of one triangular and one square pyramid, the triangle being formed by the OH oxygen atoms and the square by the CO carbon atoms plus the hydridic hydrogen. The four $OPPh_2Et$ molecules are joined to the tetramer through strong hydrogen bonds with the μ_3-hydroxo groups (O...O contacts of 2.47 and 2.48 Å).

INTRODUCTION

This work is part of a crystallographic investigation on a series of polynuclear hydroxocarbonyl- and hydroxocarbonylnitrosyl complexes of molybdenum and tungsten, which derive from an acidic species formulated by Hieber *et al.* as $H_3M_2(CO)_6(OH)_3$ with M equal to Mo[1] or W[2] [compounds (I) and (II) respectively]. We have already described the structure of a derivative, (III), obtained by Canziani *et al.* by reaction of (I) with triphenylphosphine oxide and nitrogen oxide, and originally formulated as dimeric $[Mo(OH)(CO)_2(NO)(OPPh_3)]_2$[3]; the crystal structure determination showed (III) to be tetrameric, the resulting formulation being that of a fourfold $OPPh_3$ adduct of tetrakis-(μ_3-hydroxodicarbonylnitrosylmolybdenum), $[Mo(OH)(CO)_2(NO)]_4 \cdot 4OPPh_3$[4]. The phosphine oxides are linked to the tetramer only through hydrogen bonds with the μ_3-hydroxo groups.

Another species, obtained by reaction of (I) with triphenylphosphine oxide only, and formulated as $Mo(CO)_3OPPh_3$[1], (IV), has been found to be strictly isomorphous with (III) (both crystallize in the cubic space group $P\bar{4}3n$)[4]. The isomorphism indicates that (III) and (IV) have a similar molecular framework, but formulation of (IV) as $[Mo(OH)(CO)_3]_4 \cdot 4OPPh_3$ is not correct because it is not consistent with the diamagnetism of the compound. A subsequent complete determination on (IV) did indeed reveal a similar structure to (III), but some degree of disorder, present in both crystals[4], probably obscured fundamental structural details.

To get more precise information on type (IV) compounds we have undertaken the investigation of an adduct with a less symmetric tertiary phosphine oxide in order to lessen the crystallographic symmetry and possibly to avoid the observed disorder in the cubic species. We describe below the structure of the compound which separates when (II) is allowed to react in ethanol with diphenylethylphosphine oxide at 70–80° for several minutes[5]. (The corresponding molybdenum adduct cannot be obtained.)

NMR spectra of type (IV) compounds, recorded while the present structure determination was in progress, revealed the presence of hydrogen atoms directly bonded to the metals in a ratio 1/1 with the hydroxylic hydrogens[5]. Thus the complete formulation of the compound is $[W(OH)(CO)_3H]_4 \cdot 4OPPh_2Et$. Full structural evidence for the presence of the hydridic hydrogens has been obtained in the present investigation.

EXPERIMENTAL SECTION

The complex $[W(OH)(CO)_3H]_4 \cdot OPPh_2Et$, $M = 2063.3$, crystallizes in green-yellow monoclinic crystals stable in the air at least for the time necessary for data collection. The crystallographic constants are: $a = 25.06(2)$, $b = 14.08(1)$, $c = 24.60(2)$ Å, $\beta = 120°20'(10')$, $U = 7492$ Å^3, $D_m = 1.85(2)$ g/cm^3 (by picnometry), $Z = 4$, $D_c = 1.83$ g/cm^3, $F(000) = 3968$. The cell parameters were determined by use of precession photographs taken with Mo-$K\alpha$ radiation (λ 0.7107 Å). On the basis of systematic absences (hkl for $h+k = 2n+1$ and $h0l$ for $l = 2n+1$) two space groups were possible, Cc (No. 9) and $C2/c$ (No. 15).

The intensities were measured at room temperature on a Pailred single-crystal diffractometer using Mo-$K\alpha$ radiation with a silicon monochromator. The crystal sample, of size 0.51 × 0.26 × 0.34 mm, was mounted along the c axis and a set of reciprocal lattice layers from $hk0$ to $hk20$ up to an equi-inclination angle of 16°28′ was recorded by the ω-scan technique. The total number of collected reflections was about 3400. After the Lorentz and polarization factors had been applied, the resulting F_0^2 were corrected for absorption (μ 67.6 cm^{-1}) using a computational procedure described elsewhere[6]. The transmission factors ranged from 0.22 to 0.37. The structure resolution and refinement were based on 1246 independent non-zero reflections having a relative statistical counting error less than 0.23.

STRUCTURE SOLUTION AND REFINEMENT

By inspection of a tridimensional Patterson function it was possible to determine the coordinates of the tungsten atoms and to accept $C2/c$ as the true space group.

This choice was confirmed by the succesful refinement of the whole structure. In this space group the four molecules contained in the cell are in special positions around the two-fold axes and the only independent part is the $W_2(OH)_2(CO)_6H_2(OPPh_2Et)_2$ moiety. A difference Fourier map phased only with the tungsten atoms showed the phosphorus atoms positions. Isotropic refinement of tungsten and phosphorus atoms gave, at this stage, a conventional R factor of 0.17. The remaining atoms were subsequently located on a difference Fourier except for the phenyl rings of the phosphine oxide molecules which were treated as rigid bodies and located by means of a trial-and-error program[7].

The structure was refined by the least-squares method using the block-diagonal approximation. Tungsten and phosphorus atoms were assigned anisotropic thermal parameters, oxygen and carbon atoms isotropic ones. The phenyl rings were constrained in a rigid-body motion (D_{6h} symmetry, C–C 1.392 Å). The minimized function was $\Sigma w \cdot (F_0 - |F_c|)^2$ and the weights were assigned following the Cruickshank criterion $w = 1/(a + b \cdot F_0 + c \cdot F_0^2)$ with $a = 10^2$, $b = 0.5$ and $c = 3 \times 10^{-4}$. The atomic scattering factors for all atoms are those given in ref. 8, the value for tungsten and phosphorus atoms being corrected for the real part of the anomalous dispersion[9]. The imaginary part[9] was also taken into account in the refinement of the same atoms. The agreement indices were, at the end, $R = 0.049$ and $R_w = [\Sigma w \cdot (F_0 - |F_c|)^2 / \Sigma w \cdot F_0^2]^{1/2} = 0.066$.

The results of refinement are reported in Tables 1–4: Table 1 shows the final agreement between the observed and calculated structure factors. Tables 2 and 3 list, respectively, the positional and thermal parameters of non-group anisotropic and

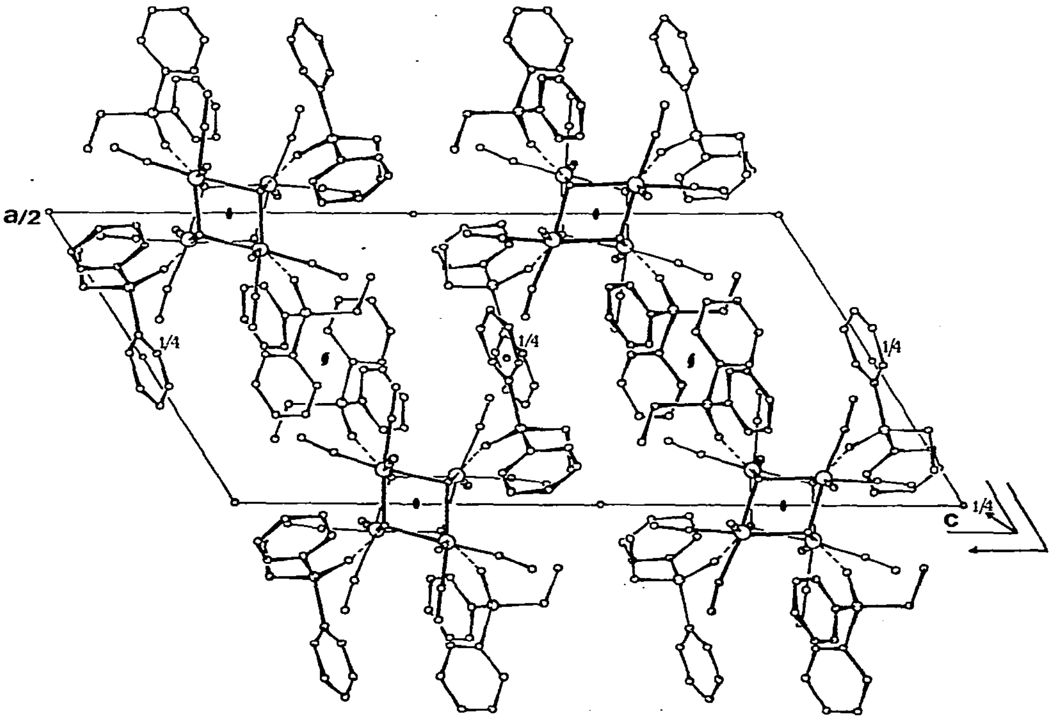

Fig. 1. Projection of the cell content down the b axis.

TABLE 1

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	FO	/FC/
L = 0			
0	2	295	112
0	4	317	329
0	6	246	256
0	10	237	209
0	12	331	329
1	5	935	932
1	7	712	691
1	11	315	303
2	2	515	507
2	4	214	201
2	6	310	296
2	10	185	177
2	12	218	223
3	3	162	154
3	5	494	449
3	7	214	224
4	2	225	213
[illegible]	[illegible]	108	107
[illegible]	[illegible]	109	122
6	4	418	408
6	6	145	171
6	9	197	175
7	1	333	327
7	5	510	510
7	7	353	343
7	11	228	211
8	0	896	870
8	2	315	313
8	4	279	291
9	5	577	583
9	7	488	466
9	9	168	150
10	0	724	730
10	4	166	165
10	6	165	181
10	10	171	176
11	3	283	279
11	5	367	364
11	7	257	270
12	0	581	570
12	2	211	232
13	8	141	141
13	10	149	177
13	1	159	163
13	3	237	242
14	4	182	188
14	8	212	222
15	1	269	267
15	3	310	311
16	0	293	[illegible]
16	4	169	169
17	5	149	184
17	7	205	197
18	0	271	279
19	2	116	101
20	0	160	137
22	2	139	142
-11	-7	127	109
-11	-9	154	161
-12	-2	164	164
-12	-6	236	235
-12	-8	129	117
-13	-1	265	271
-13	-3	223	214
-13	-7	165	174
-13	-9	273	278
-14	2	129	154
-14	-2	352	355
-14	6	203	207
-15	1	236	234
-15	-3	201	191
-15	-5	167	175
-15	-7	209	204
-15	-9	216	209
-16	-2	260	264
-16	4	151	139
-16	6	244	284
-16	-6	182	144
-17	1	293	312
-17	-1	180	179
-17	-3	105	119
-17	5	136	120
-18	4	131	140
-18	6	234	247
-18	-6	200	186
-19	1	210	226
-19	-1	139	140
-20	-4	152	156
L = 2			
0	2	236	207
0	4	700	673
0	12	266	275
1	3	663	689
-1	-3	174	174
1	5	715	722
-1	-5	676	654
1	7	315	335
-1	-3	553	557
1	9	179	177
1	11	219	224
-1	-11	250	247
2	0	176	166
2	2	137	151
-2	-2	281	265
2	4	327	355
-2	-6	250	241
2	8	321	325
-2	-10	221	229
3	1	350	338
3	3	335	314
-3	-1	461	452
-3	-5	458	437
-3	-7	375	361
4	0	381	405
4	2	255	247
-4	-2	351	341

L = 1			
0	2	185	185
0	4	177	135
0	6	858	848
0	8	258	231
0	10	309	322
0	12	181	180
1	3	321	281
1	5	476	496
-1	-9	397	365
1	11	252	252
-1	-11	259	291
-1	-13	226	278
2	2	245	247
-2	-4	593	577
2	6	469	459
-2	-6	639	648
2	8	343	315
-2	-8	228	208
2	10	248	255
-2	-10	218	231
-2	-12	312	326
3	5	267	248
-3	-7	205	183
-3	-9	248	242
4	2	238	232
-4	-2	465	475
-4	-4	470	468
-4	-6	192	188
5	1	323	335
5	5	169	163
-5	-5	142	151
-5	-7	315	326
-5	-9	286	275
6	2	100	102
-6	-2	375	400
6	4	307	291
6	6	412	406
6	8	170	184
6	10	227	225
7	1	793	760
-7	-3	172	177
7	5	375	398
-7	-5	231	220
-7	-9	174	190
7	11	257	242
8	2	158	144
-8	-2	180	202
8	4	327	317
8	6	663	675
-8	-6	547	516
8	8	199	181
8	10	256	292
-8	-10	255	257
9	1	735	717
-9	-1	528	531
9	5	267	281
-9	-5	148	132
-9	-11	213	223
10	4	235	262
-10	-4	362	335
10	6	554	534
-10	-6	493	473
10	10	195	181
-10	-10	193	186
11	1	372	351
-11	-1	482	457
-11	-3	154	144
11	5	137	139
-11	-5	141	145
-4	-4	294	304
-4	-6	263	270
4	8	251	287
-4	-8	321	338
-4	-10	253	249
5	1	216	212
5	3	224	227
-5	-3	298	327
5	5	369	398
-5	-5	265	247
5	7	226	226
5	11	199	175
6	0	919	878
6	2	486	486
-6	-2	213	228
6	4	245	227
-6	-4	394	348
6	6	216	232
-6	-8	502	496
6	10	260	223
7	1	147	166
-7	-3	179	206
7	5	410	395
7	7	454	458
-7	-7	183	177
-7	-9	211	210
8	0	942	936
8	2	227	219
-8	-2	538	548
8	4	177	195
-8	-4	308	316
8	6	193	204
-8	-8	275	274
-9	-3	233	249
9	5	457	454
-9	-5	261	249
9	7	419	442
-9	-7	296	293
9	9	155	147
-9	-9	154	153
-9	-11	161	133
10	0	674	641
10	2	139	134
10	4	186	184
-10	-4	222	199
10	6	126	146
-11	-1	94	84
11	3	193	191
-11	-5	320	305
-11	-7	191	170
-12	-0	182	196
-12	-8	157	205
-12	-10	223	205
-13	-1	223	246
-13	-3	312	311
13	9	121	115
14	0	287	292
-14	-0	126	108
-14	-2	139	176
-14	-8	399	359
-15	-1	322	296
-15	-3	371	387
15	5	281	278
15	7	199	206
16	0	365	389
16	2	189	198
16	4	182	179
-16	-4	276	279
-16	-8	279	271
-17	-3	186	188
17	5	251	244
-7	-9	461	450
8	2	217	206
-8	-4	281	268
8	6	498	502
-8	-6	222	219
8	10	347	333
-8	-10	173	183
9	1	404	399
9	3	167	173
-9	-3	335	314
9	5	273	261
-9	-5	189	180
-9	-7	207	193
-9	-9	222	210
10	2	288	322
10	6	269	265
-10	-6	144	163
11	3	170	172
11	9	160	156
12	2	215	212
13	1	226	231
-11	-1	141	149
-11	-3	235	234
-13	-7	234	209
-13	-9	214	232
-14	-2	465	456
14	4	224	207
-14	-4	350	353
14	6	247	246
15	1	283	293
-15	-3	315	292
15	5	142	152
-15	-5	181	170
-15	-7	243	273
-15	-9	322	312
-16	-2	392	389
16	4	147	157
-16	-4	225	210
17	1	250	299
-17	-3	254	251
17	5	136	126
-17	-7	180	171
-18	-2	145	151
L = 4			
0	0	596	645
0	2	434	465
0	4	610	616
0	6	148	137
0	8	412	417
0	10	176	156
1	1	639	648
-1	-1	260	231
1	3	551	527
1	5	123	109
-1	-5	224	229
1	7	219	202
-1	-7	140	147
1	9	210	223
2	2	141	157
-2	-2	285	282
2	4	365	368
-2	-4	234	225
2	8	553	556
2	10	230	240
3	1	551	551
3	3	414	449
3	5	174	163
-3	-5	310	294
4	0	371	346
-15	-1	341	344
-15	-3	351	344
15	5	239	235
16	0	321	331
-16	-2	259	269
16	4	136	118
-16	-4	261	258
-16	-8	546	532
-17	-1	143	155
-17	-3	319	313
18	0	176	179
-18	-2	123	114
-18	-4	141	140
-19	-3	133	110
-20	-0	185	186
L = 5			
0	2	482	513
0	6	409	412
0	10	180	155
-1	-1	148	178
1	3	280	313
-1	-3	228	255
1	5	152	178
-1	-5	294	265
1	7	411	415
-1	-7	329	319
1	9	501	486
-1	-9	303	301
2	2	460	437
-2	-2	476	466
2	4	382	401
2	10	169	147
3	1	139	139
-3	-1	120	140
3	3	487	482
-3	-3	154	145
3	5	156	163
3	7	297	301
3	9	423	405
4	2	448	482
-4	-2	318	285
4	4	167	167
4	6	139	128
5	1	182	174
-5	-3	359	347
-5	-5	269	280
5	7	143	124
-5	-7	338	349
5	9	151	155
-5	-9	249	275
-6	-2	484	507
-6	-4	288	275
6	6	169	154
-6	-10	159	160
7	1	192	195
-7	-3	324	330
7	5	213	218
-7	-5	150	172
-7	-7	371	368
-7	-9	473	462
8	2	403	471
-8	-2	489	496
8	4	127	126
-8	-4	369	366
8	6	127	136
-8	-10	190	186
9	1	131	135
9	3	287	315
-9	-3	361	377
-3	-7	167	163
-4	-0	590	604
4	8	250	236
-5	-1	337	352
-5	-3	247	261
-5	-5	162	185
-5	-7	167	172
-6	-0	238	233
-6	-2	338	330
6	4	166	168
-6	-4	337	338
-6	-8	440	456
7	1	244	250
7	3	285	290
-7	-3	611	591
-7	-9	178	179
8	2	177	171
-8	-2	249	251
8	4	297	320
-8	-4	409	421
8	8	309	307
-8	-8	393	420
-8	-10	213	238
9	1	322	328
9	3	377	374
-9	-3	477	466
10	2	223	225
10	4	264	265
-10	-4	201	209
-10	-6	202	200
10	8	321	331
-10	-8	325	318
-10	-10	179	193
11	1	245	218
11	3	313	308
-11	-3	208	205
-11	-5	279	277
-11	-7	234	231
-13	-5	349	325
-13	-7	223	220
-14	-4	351	327
-14	-8	183	171
-15	-3	270	262
-15	-7	170	183
-16	-4	261	247
-16	-8	264	230
-17	-3	243	238
-18	-2	195	189
-19	-3	126	124
-20	-0	316	323
-20	-2	125	123
L = 7			
0	2	462	434
0	4	295	207
-1	-1	527	532
1	3	450	427
-1	-3	274	300
-1	-5	134	124
1	7	277	279
-1	-7	304	331
1	9	417	394
-1	-9	429	399
2	2	406	427
-2	-2	438	478
2	4	139	134
-2	-4	276	291
2	6	163	143
-2	-6	165	156
2	10	195	186
-17	-5	137	133
-20	-4	144	118
-20	-6	194	201
L = 8			
0	0	132	148
0	2	237	242
0	4	256	245
0	6	136	147
0	8	352	341
1	1	363	372
-1	-1	252	263
1	3	318	314
-1	-3	479	513
-1	-5	174	202
1	7	181	175
2	0	455	433
-2	-0	277	307
-2	-2	144	118
2	4	252	254
-2	-4	133	146
-2	-6	161	170
2	8	285	302
-2	-8	290	289
-2	-10	189	186
3	1	170	205
-3	-1	387	376
-3	-3	186	163
3	5	260	256
-3	-5	292	296
3	7	262	254
-3	-7	231	259
4	0	300	322
-4	-0	774	732
4	2	171	170
-4	-2	295	293
-4	-4	140	130
-4	-10	203	197
-5	-1	180	201
5	5	290	293
-5	-5	641	652
5	7	197	191
-5	-7	385	376
-5	-11	207	220
6	0	274	259
-6	-0	972	953
6	2	248	247
-6	-2	251	251
-6	-4	302	317
6	8	273	263
7	1	274	279
-7	-1	370	322
7	3	288	287
-7	-3	181	174
7	5	192	184
-7	-5	332	350
-7	-7	324	360
-8	-0	520	498
8	2	195	190
-8	-2	115	107
8	4	253	238
-8	-4	197	202
8	8	300	312
-8	-8	189	193
9	1	220	227
-9	-1	159	161
9	3	318	327
-9	-3	185	171
-10	-0	162	160
-10	-2	232	218
-7	-1	676	647
7	3	129	152
-7	-5	189	177
7	7	207	212
8	2	264	272
-8	-2	167	157
-8	-6	430	433
-8	-10	182	157
-9	-1	219	217
9	3	162	187
-9	-5	123	105
10	2	191	211
10	6	164	162
11	1	155	156
-12	-6	292	320
-12	-10	165	160
11	1	152	134
-11	-5	285	273
-14	-4	229	217
-14	-6	472	452
-15	-5	236	270
-16	-2	337	387
L = 10			
0	0	467	431
-1	-1	139	134
1	3	409	409
1	7	340	346
-1	-7	170	159
2	0	649	684
-2	-0	112	121
2	2	245	231
-2	-2	135	147
2	4	232	235
3	5	433	449
3	7	298	295
-3	-7	191	187
3	11	204	201
4	0	428	447
-4	-0	573	560
4	2	236	249
-4	-2	174	134
4	4	143	136
-4	-4	214	216
4	6	148	149
-4	-6	210	218
-5	-1	236	224
5	5	296	316
-5	-5	494	496
5	7	190	214
-5	-7	453	437
6	0	286	305
-6	-0	899	813
6	2	150	144
-6	-2	337	323
-6	-4	267	307
-7	-1	151	151
7	3	180	170
-7	-5	569	571
-7	-7	458	444
-7	-11	191	214
-8	-0	741	722
-8	-2	251	244
8	4	167	162
-8	-4	146	161
9	1	132	106
9	5	137	114
-9	-5	331	332
-9	-7	209	220
10	0	250	259
-13	-1	169	158
-13	-5	244	219
-13	-9	156	155
-14	-7	247	246
-14	-6	227	218
-14	-1	378	371
-15	-5	165	201
-16	-4	154	130
-16	-6	283	313
-18	-6	167	199
-19	-3	144	173
-20	-2	168	203
L = 12			
0	0	491	509
0	2	242	237
1	3	405	399
-1	-5	293	309
1	7	315	316
-1	-7	174	190
2	0	591	603
-2	-0	142	147
2	2	170	189
-2	-2	135	128
2	4	202	203
3	1	139	141
-3	-3	261	269
3	5	267	254
3	7	262	253
4	0	326	344
-4	-0	155	140
4	4	133	130
-4	-4	298	297
-4	-8	192	194
-5	-1	305	325
-5	-3	192	181
-5	-5	220	217
-5	-7	192	198
-6	-0	493	602
-6	-2	156	168
-6	-4	265	300
-7	-1	212	221
-7	-5	348	372
-7	-7	319	316
8	0	259	274
-8	-0	744	709
-8	-2	133	132
-9	-3	145	172
-9	-5	329	317
-9	-7	257	243
10	0	310	316
-10	-0	317	328
-10	-2	338	327
-10	-8	183	173
-10	-10	169	170
-11	-1	141	146
-11	-3	302	300
-11	-5	179	175
-12	-2	143	133
-12	-8	257	277
-12	-10	149	129
-13	-1	309	300
-13	-3	307	298
-14	-0	283	243
-14	-4	347	347
-14	-8	244	238
-15	-1	188	177
-16	-0	351	332
-16	-2	105	104
-16	-4	166	160
-1	-5	174	199
1	7	209	200
2	0	339	340
-2	-0	149	148
-2	-2	208	205
2	4	205	202
-2	-8	201	189
3	1	213	180
-3	-1	270	276
3	3	184	189
-3	-3	264	251
-4	-2	179	169
-4	-4	231	255
-4	-8	334	345
-5	-1	278	301
5	3	224	208
-5	-5	319	335
-6	-0	141	130
-6	-4	264	278
-6	-8	265	261
-7	-1	140	153
-7	-3	241	214
-8	-0	273	258
-8	-4	195	218
-10	-0	157	144
-10	-2	181	185
-10	-6	144	127
-10	-8	182	175
-11	-1	112	111
-11	-3	126	147
-12	-2	191	208
-12	-8	308	321
-13	-1	322	310
-13	-3	336	340
-14	-2	158	171
-14	-4	270	274
-14	-8	308	316
-15	-1	232	227
-15	-3	252	240
-16	-4	119	121
-17	-3	143	133
L = 15			
2	2	209	21[illegible]
-2	-2	201	185
-2	-6	206	180
3	3	194	207
-3	-3	205	217
-3	-7	205	231
-3	-9	188	200
4	2	280	285
-4	-2	376	397
-4	-4	186	189
-5	-3	218	203
-5	-5	191	188
-5	-7	250	248
-6	-2	373	380
-6	-4	188	197
-7	-3	248	230
-7	-0	272	234
-8	-2	173	184
-10	-2	129	121
-11	-3	184	206
-11	-4	167	158
-12	-2	379	363
-12	-4	180	165
-13	-3	216	236
-13	-5	174	167
-13	-7	220	224
-14	-2	363	352
-14	-2	168	187
-15	-3	146	160
-16	-5	130	130
-17	-3	177	158
-18	-6	173	179
-19	-1	219	221
-20	-6	188	184
L = 18			
0	0	170	164
-2	-0	272	259
3	1	161	150
-4	-0	185	196
-5	-3	183	175
-6	-4	149	151
-7	-3	182	186
-8	-2	165	146
-9	-5	162	169
-10	-0	277	245
-10	-2	166	160
-11	-5	208	214
-11	-7	167	198
-12	-0	155	156
-13	-1	129	135
-13	-5	158	168
-14	-0	272	248
-18	-0	220	217
-20	-0	241	249
L = 19			
-2	-6	183	196
-3	-1	211	198
-5	-1	144	158
-10	-6	165	196
-11	-1	258	264
-12	-6	270	256
-13	-1	210	232
-14	-6	188	199
-19	-1	180	175
-20	-6	186	194
L = 20			
-2	-0	192	187
-3	-5	193	186
-6	-0	233	246
-10	-0	217	223
-11	-5	171	176
-12	-0	298	285
-13	-4	142	172
-13	-5	338	312
-14	-0	214	224
-20	-0	240	215
L = 21			
-3	-1	189	200
-11	-1	187	182
-12	-2	127	104
-13	-1	195	206
L = 22			
-12	-0	214	204

isotropic atoms, while in Table 4 are listed the derived positional parameters of the rigid groups carbon atoms and the mean group isotropic temperature factors.

A difference Fourier synthesis was computed using the final set of calculated structure factors. The highest residual electron density peaks (0.7 and 0.6 e/Å^3) were found at the positions of the carbon atoms C(29) and C(32). The phenyl ring to which these atoms belong [atoms from C(29) to C(34)] has an exceedingly high mean tem-

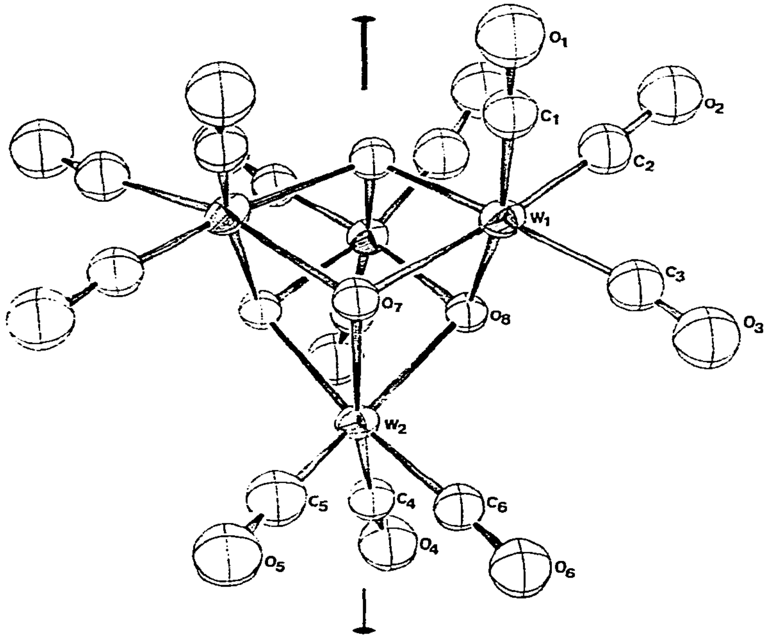

Fig. 2. ORTEP drawing of the tetramer [W(OH)(CO)$_3$H]$_4$ (ellipsoids at 30% probability). The hydridic hydrogens are not reported.

TABLE 2

POSITIONAL AND THERMAL PARAMETERS OF THE NONGROUP ANISOTROPIC ATOMS^{a,b,c}

Atom	*x/a*	*y/b*	*z/c*
W(1)	499 (1)	1962 (1)	3312 (1)
W(2)	623 (1)	3719 (1)	2379 (1)
P(1)	1710 (5)	557 (8)	2336 (6)
P(2)	1277 (5)	5179 (9)	4549 (5)

Atom	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
W(1)	21 (0)	1 (1)	18 (0)	40 (1)	13 (1)	28 (0)
W(2)	21 (0)	−3 (1)	22 (0)	38 (0)	10 (1)	25 (0)
P(1)	29 (3)	24 (9)	39 (6)	68 (9)	18 (10)	45 (4)
P(2)	33 (3)	−24 (9)	21 (5)	77 (9)	−28 (9)	25 (3)

[a] All values × 10^4. [b] The β_{ij} are the coefficients of the form: $h^2 \cdot \beta_{11} + k^2 \cdot \beta_{22} + l^2 \cdot \beta_{33} + h \cdot k \cdot \beta_{12} + h \cdot l \cdot \beta_{13} + k \cdot l \cdot \beta_{23}$. [c] The numbers in parentheses here and in the succeeding tables are the esd's on last significant digits.

perature factor (see Table 4). This effect seems to be the result of a rotational disorder of the phenyl group around the C(29)–C(32) axis; in fact an individual refinement for the temperature factors of the carbon atoms in this group converged to reasonable values for C(29) and C(32) and was divergent for the remaining carbon atoms.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

A projection of the structure down the *b* axis is shown in Fig. 1. It consists of tetrameric groups $[W(OH)(CO)_3H]_4$ which lie around the two-fold axes of space group *C2/c* and are surrounded by four diphenylethylphosphine oxide molecules linked to the tetramers through OH...O bridges. An inspection of all intra- and intermolecular non bonded distances showed only the usual Van der Waals contacts.

The tetramer, which has a rigorous C_2 symmetry, is shown in Fig. 2 with atomic labelling. Interatomic distances and angles are reported in Table 5, along with their standard deviations. The tungsten atoms form a nearly regular tetrahedron held together by four face-bonding hydroxo groups which define a smaller tetrahedron, so that the W_4O_4 core is an irregular cube. The carbonyl groups are linearly bonded, three to each metal atom. The same M_4X_4 arrangement, beside being present in (III), has been also found in the compounds $[Zn(OCH_3)(CH_3)]_4$[10] and $[Pt(OH)(CH_3)_3]_4$[11], and more recently in $[OsO(CO)_3]_4$[12] and $[Re(SCH_3)(CO)_3]_4$[13], in which four $M(CO)_3$ units are linked through triple bridging oxo and respectively methylthio groups. Definite non-bonding intermetallic distances have been observed in all these compounds, so that metal–metal interactions can be assumed to occur only

TABLE 3

POSITIONAL AND THERMAL PARAMETERS OF THE NONGROUP ISOTROPIC ATOMS

Atom	x/a[a]	y/b	z/c	B (Å^2)
C(1)	387 (16)	709 (28)	3343 (16)	6.2 (10)
O(1)	290 (14)	−171 (24)	3333 (13)	9.3 (9)
C(2)	445 (18)	1862 (31)	4003 (17)	6.6 (11)
O(2)	350 (14)	1785 (24)	4459 (14)	9.6 (9)
C(3)	1321 (18)	2177 (32)	4037 (17)	6.9 (11)
O(3)	1826 (14)	2341 (25)	4400 (13)	9.5 (9)
C(4)	682 (15)	5079 (26)	2475 (15)	5.4 (9)
O(4)	754 (14)	5890 (23)	2588 (13)	9.1 (9)
C(5)	877 (20)	3574 (36)	1825 (19)	8.2 (12)
O(5)	1123 (15)	3405 (25)	1497 (14)	10.1 (10)
C(6)	1459 (17)	3918 (28)	2925 (16)	5.8 (10)
O(6)	2001 (13)	4040 (22)	3237 (12)	8.5 (8)
O(7)	453 (9)	2142 (17)	2385 (9)	4.9 (5)
O(9)	1153 (14)	1098 (21)	2216 (13)	8.2 (7)
C(7)	1705 (22)	313 (34)	1612 (21)	8.6 (12)
C(8)	1070 (24)	−115 (37)	1116 (22)	7.2 (13)
O(8)	390 (9)	3474 (16)	3138 (8)	4.4 (5)
O(10)	986 (14)	4720 (22)	3921 (14)	8.6 (8)
C(21)	1262 (20)	4452 (31)	5147 (19)	9.3 (11)
C(22)	577 (29)	4203 (41)	4898 (25)	12.7 (17)

[a] x/a, y/b and z/c $\times 10^4$.

TABLE 4

POSITIONAL PARAMETERS OF THE PHENYLIC CARBON ATOMS AND MEAN ISOTROPIC TEMPERATURE FACTORS OF THE PHENYL RINGS

Atom	x/a[a]	y/b	z/c	B (Å^2)
C(9)	2441 (12)	1164 (21)	2858 (13)	8.6 (5)
C(10)	2983 (16)	1022 (20)	2844 (13)	
C(11)	3515 (12)	1527 (24)	3252 (16)	
C(12)	3504 (12)	2174 (21)	3674 (13)	
C(13)	2961 (16)	2318 (20)	3688 (13)	
C(14)	2429 (12)	1812 (24)	3280 (16)	
C(15)	1768 (19)	−594 (20)	2658 (14)	9.9 (6)
C(16)	1255 (14)	−899 (26)	2688 (15)	
C(17)	1279 (14)	−1749 (29)	2989 (16)	
C(18)	1815 (19)	−2293 (20)	3261 (14)	
C(19)	2329 (14)	−1989 (26)	3230 (15)	
C(20)	2305 (14)	−1140 (29)	2931 (16)	
C(23)	910 (14)	6274 (19)	4499 (16)	7.9 (5)
C(24)	977 (13)	6691 (23)	5044 (11)	
C(25)	647 (15)	7512 (23)	5001 (12)	
C(26)	252 (14)	7917 (19)	4415 (16)	
C(27)	185 (13)	7497 (23)	3871 (11)	
C(28)	515 (15)	6677 (23)	3914 (12)	
C(29)	2097 (15)	5398 (41)	4822 (19)	14.7 (8)
C(30)	2406 (23)	4669 (26)	4712 (17)	
C(31)	3022 (23)	4783 (32)	4878 (18)	
C(32)	3329 (15)	5627 (41)	5154 (19)	
C(33)	3020 (23)	6356 (26)	5263 (17)	
C(34)	2404 (23)	6243 (32)	5097 (18)	

[a] x/a, y/b and z/c × 10^4.

through the triple bridging groups. This is certainly the case in the present complex, for which the mean W...W distance (3.48 Å), while very similar to the corresponding Mo...Mo distance observed in (III) (3.43 Å), is much longer than the largest known Mo–Mo and W–W bonding lengths (3.22 and 3.24 Å), which occur in $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$[14] and $[(\pi\text{-}C_5H_5)W(CO)_3]_2$[15]. We also note that a similar value (3.23 Å), found[16] in the dimeric trianion $[W_2(OH)_3(CO)_6]^{3-}$, has been considered to be non-bonding and that a direct Mo–Mo bond is not involved in the complex $[(\pi\text{-}C_5H_5)_2Mo_2H[P(CH_3)_2](CO)_4]$ in which the intermetallic distance is 3.26 Å[17].

The oxygen atoms of the OH groups show distances from the three nearest tungsten atoms which are not equivalent, one being significantly shorter than the other two. Triple bridging hydroxo groups have been previously characterized in the crystal structures of the already cited $[Pt(OH)(CH_3)_3]_4$ and of $Ni_6(CF_3COCHCOCH_3)_{10}(OH)_2(H_2O)_2$[18], and demonstrated spectroscopically in the ionic species in solution $[Pb(OH)]_4^{4+}$ (ref. 19) and $[Ni(OH)]_4^{4+}$ (ref. 20). The mean value of the W–O distances (2.21 Å) can be compared with the Mo–O distance in III (2.20 Å); the value is somewhat greater than that obtained in the case of double bridging hydroxo groups between two tungsten atoms (2.16 Å)[16]. The W–O–W angles have a mean value of 104°. The departure from the tetrahedral angle may be due to the necessity of minimizing the O...O non-bonded interactions (O...O contacts in the range 2.60–2.73 Å). The atomic orbitals of the O atoms, however, are much nearer to an sp^3 hybridization

TABLE 5

SELECTED INTERATOMIC DISTANCES AND ANGLES WITHIN THE TETRAMER $[W(OH)(CO)_3H]_4$

Distances (Å)		Angles (°)	
W(1)...W(1')	3.482 (3)	W(1)–O(7)–W(1')	105 (1)
W(1)...W(2)	3.494 (3)	W(1)–O(7)–W(2)	102 (1)
W(1)...W(2')	3.477 (2)	W(2)–O(7)–W(1')	104 (1)
W(2)...W(2')	3.461 (4)	W(1)–O(8)–W(2)	105 (1)
W(1)–O(7)	2.24 (2)	W(1)–O(8)–W(2')	105 (1)
W(2)–O(7)	2.26 (2)	W(2)–O(8)–W(2')	102 (1)
W(1')–O(7)	2.14 (2)	O(7)–W(1)–O(7')	73 (1)
W(1)–O(8)	2.16 (2)	O(7)–W(1)–O(8)	75 (1)
W(2)–O(8)	2.25 (2)	O(8)–W(1)–O(7')	75 (1)
W(2')–O(8)	2.22 (2)	O(7)–W(2)–O(8)	73 (1)
W(1)–C(1)	1.79 (4)	O(7)–W(2)–O(8')	72 (1)
W(1)–C(2)	1.78 (5)	O(8)–W(2)–O(8')	75 (1)
W(1)–C(3)	1.95 (3)	C(1)–W(1)–C(2)	78 (2)
W(2)–C(4)	1.93 (4)	C(1)–W(1)–C(3)	103 (2)
W(2)–C(5)	1.78 (6)	C(2)–W(1)–C(3)	72 (2)
W(2)–C(6)	1.85 (4)	C(4)–W(2)–C(5)	100 (2)
C(1)–O(1)	1.26 (5)	C(4)–W(2)–C(6)	77 (1)
C(2)–O(2)	1.26 (6)	C(5)–W(2)–C(6)	82 (2)
C(3)–O(3)	1.14 (4)	C(1)–W(1)–O(7)	103 (1)
C(4)–O(4)	1.17 (5)	C(1)–W(1)–O(7')	91 (1)
C(5)–O(5)	1.26 (7)	C(1)–W(1)–O(8)	166 (1)
C(6)–O(6)	1.19 (4)	C(2)–W(1)–O(7)	173 (1)
O(7)...O(7')	2.60 (4)	C(2)–W(1)–O(7')	101 (1)
O(7)...O(8)	2.70 (3)	C(2)–W(1)–O(8)	102 (1)
O(7)...O(8')	2.62 (3)	C(3)–W(1)–O(7)	114 (2)
O(8)...O(8')	2.73 (2)	C(3)–W(1)–O(7')	162 (1)
		C(3)–W(1)–O(8)	90 (1)
		C(4)–W(2)–O(7)	168 (1)
		C(4)–W(2)–O(8)	95 (1)
		C(4)–W(2)–O(8')	103 (1)
		C(5)–W(2)–O(7)	92 (2)
		C(5)–W(2)–O(8)	164 (2)
		C(5)–W(2)–O(8')	107 (1)
		C(6)–W(2)–O(7)	107 (1)
		C(6)–W(2)–O(8)	95 (1)
		C(6)–W(2)–O(8')	171 (2)
		W(1)–C(1)–O(1)	177 (3)
		W(1)–C(2)–O(2)	174 (3)
		W(1)–C(3)–O(3)	170 (4)
		W(2)–C(4)–O(4)	174 (3)
		W(2)–C(5)–O(5)	171 (3)
		W(2)–C(6)–O(6)	175 (4)

in the present case than in the double bridging OH groups of $[W_2(OH)_3(CO)_6]^{3-}$ (mean W–O–W value equal to 97°).

The coordination patterns around the two crystallographically independent tungsten atoms are substantially equivalent. The W–C–O angles show some deviations from linearity up to a maximum of 10°. The metal–carbon bond lengths range between 1.78 and 1.95 Å, the lower values being very short. Correspondingly the carbon-oxygen bond lengths, which fall into the interval 1.14–1.26 Å, vary in such a way that longer W–C correspond to shorter C–O distances and *vice versa*. This strict correlation indicates that the dispersion of values is not a random effect but is due to some disturbing factor which causes irregularities in the d_π–p_{π^*} interactions (see below). Moreover in the Os and Re tetramers previously cited, as in the anion $[W_2(OH)_3(CO)_6]^{3-}$, the coordination around each metal atom is octahedral and the local symmetry is C_{3v}. This is no longer true in the present case, in which the O–W–C angles show deviations from the octahedral values and one of the C–W–C angles is markedly larger than the other two in both the independent $W(CO)_3$ groups (see Fig. 3 and Table 5). As mentioned in the introduction the NMR spectrum of this compound shows a high-field signal (τ 12.34 ppm) which is characteristic of metal-bonded hydrogen atoms. We believe that the presence and the location of one hydrido ligand in the coordination sphere of each tungsten atom is clearly indicated by the opening of one C–W–C angle mentioned above. The resulting heptacoordination polyhedron is therefore a combination of a triangular and a square pyramid sharing their apex, a coordination previously observed around the zirconium atoms in baddeleyite, monoclinic ZrO_2[21], and in the hydrido complex $ReH_3(PPh_3)_2(Ph_2PCH_2CH_2PPh_2)$[22]. Other cases of formally heptacoordinated metal atoms with similar bonding geometries have been found in $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$[14], $[(\pi\text{-}C_5H_5)W(CO)_3]_2$[15], $[(\pi\text{-}C_5H_5)_2Mo_2H[P(CH_3)_2](CO)_4]$[17], $(\pi\text{-}C_5H_5)V(CO)_4$[23] and $(\pi\text{-}C_5H_5)W(CO)_3Au(PPh_3)$[24]. In these complexes the cyclopentadienyl groups are considered to occupy three coordination sites and the (OC)–M–(CO) and (OC)–M–X (X = Mo, W, H and Au) angles are comparable to the (OC)–W–(CO) angles found in the present structure.

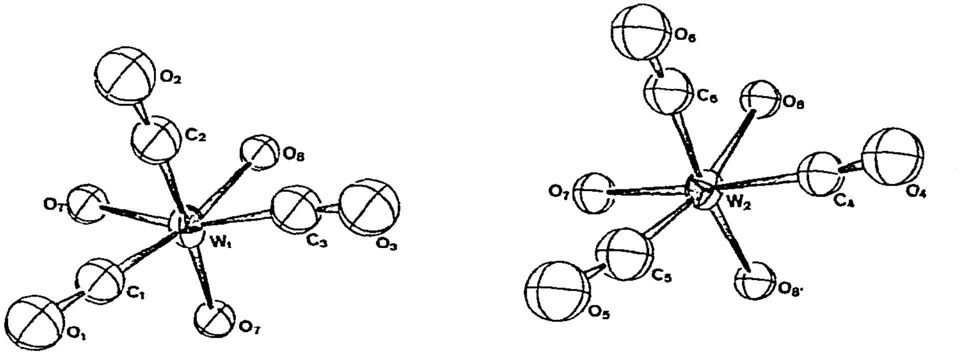

Fig. 3. Coordination pattern around the two independent tungsten atoms projected down the axes of the non-bonded couples W...OH.

The bonding scheme within each $(OH)_3W(CO)_3H$ unit may be rationalized in the following way: seven atomic orbitals (one *s*, three *p*, three *d*) of the W atom are employed in the formation of the seven σ bonds, only two *d* orbitals being therefore available for π-back-donation toward the carbonyl groups. This view is supported by the fact that the mean ν(CO) stretching frequencies in the present compound as well as in similar molybdenum and tungsten hydroxocarbonylhydrides are higher than in *cis*-$M(CO)_3(\sigma\text{-}L)_3$ complexes (M = Mo, W) in which up to three *d* orbitals may be used for π-back-donation[5]. An inspection of the W–C distances in the compound now under study shows that the W→CO back-donation seems to involve to a much smaller extent one of the carbonyl groups which lie in the *cis*-positions with respect to the postulated hydrogen atom location.

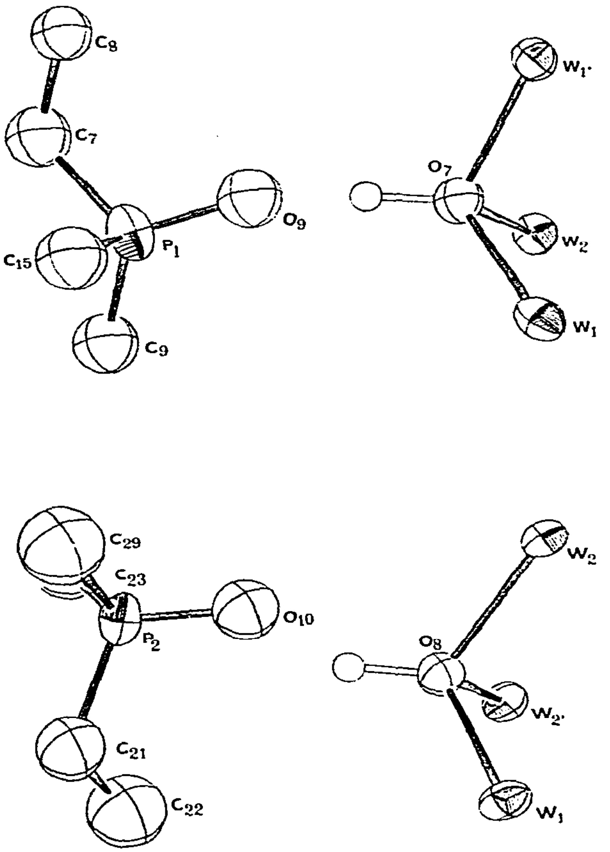

Fig. 4. ORTEP drawing of the two independent diphenyl-ethylphosphine oxide molecules and their linkage with the tetramer, showing only one carbon atom for each phenyl ring. Oxygen and phosphorus atoms lie in the plane of the figure. The postulated positions of the hydrogen atoms are also shown.

THE PHOSPHINE OXIDE MOLECULES AND THE HYDROGEN BONDS

The two independent diphenylethylphosphine oxide molecules are illustrated in Fig. 4; interatomic distances and angles for these molecules are reported in Table 6, along with the estimated standard deviations.

All the P–C distances are equal within experimental error, with a mean value of 1.81 Å. The O–P–C and C–P–C angles exhibit deviations from the tetrahedral angle up to about 6°, with mean values of 112 and 107° respectively. These values are comparable with those found in the free triphenylphosphine oxide (1.76 Å, 112°, 107°)[25] and trimethylphosphine oxide (1.81 Å, 112°, 106°)[26]. The bonding parameters in the ethyl groups, although affected by high uncertainties, show normal values. Both the independent P–O bond lengths are 1.48 Å long, a value which is very close to those of the corresponding bonds in $OPPh_3$ (1.46 Å) and $OPMe_3$ (1.48 Å), whereas some lengthening is usually observed when the oxides are bonded to transition metals. The oxygen–phosphorus bond order, thus seems not to be appreciably influenced by the hydrogen bond formation. This can be also inferred from the ν(OP) stretching fre-

TABLE 6

INTERATOMIC DISTANCES AND ANGLES IN THE DIPHENYLETHYLPHOSPHINE OXIDE MOLECULES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Distances (Å)		Angles (°)	
P(1)–C(7)	1.81 (6)	C(7)–P(1)–C(9)	107 (2)
P(1)–C(9)	1.83 (3)	C(7)–P(1)–C(15)	103 (2)
P(1)–C(15)	1.78 (3)	C(9)–P(1)–C(15)	107 (2)
P(2)–C(21)	1.81 (5)	C(21)–P(2)–C(23)	109 (2)
P(2)–C(23)	1.77 (3)	C(21)–P(2)–C(29)	106 (2)
P(2)–C(29)	1.84 (4)	C(23)–P(2)–C(29)	109 (2)
P(1)–O(9)	1.48 (4)	O(9)–P(1)–C(7)	111 (2)
P(2)–O(10)	1.48 (3)	O(9)–P(1)–C(9)	114 (2)
C(7)–C(8)	1.56 (6)	O(9)–P(1)–C(15)	114 (2)
C(21)–C(22)	1.54 (8)	O(10)–P(2)–C(21)	114 (2)
O(7)...O(9)	2.48 (5)	O(10)–P(2)–C(23)	110 (2)
O(8)...O(10)	2.47 (4)	O(10)–P(2)–C(29)	109 (2)
		P(1)–C(7)–C(8)	110 (4)
		P(2)–C(21)–C(22)	106 (3)
		O(7)...O(9)–P(1)	161 (2)
		O(8)...O(10)–P(2)	155 (2)

quency, which is only slightly lower than that of free OPPh$_2$Et[3,5].

An interesting feature of the present structure determination concerns the hydrogen bonds OH...O. The O...O contacts, 0.3 Å lower than the Van der Waals contact (2.80 Å), are among the shortest ever reported[27]. The reasons for these strong hydrogen bonds must lie on the high acidity of the OH groups, which in turn is due to the large amount of the electron donation from the O atoms to the three nearest W atoms. The nature of these hydrogen bonds can be better understood with the aid of IR data. As expected, in the formation of the OH...O bonds the ν(OH) stretching frequencies shift to lower values (2920w, 2850w, 2730m)[5]. The relationships between ν(OH) values and O...O contacts have been extensively studied and correlation diagrams are available (see ref. 28 and references therein). The present ν(OH) values however are rather high with respect to O...O distances. Although in the range 2.41–2.61 Å both single minimum and double minimum hydrogen bond potentials are possible[28], on the basis of the hydroxyl stretching frequencies we can exclude in the present case the single-minimum type.

Finally it is interesting to note some geometrical aspects of the OH...O bridges. The hydrogen atoms can be approximately located along the axes passing through the O atoms and the baricenters of the three nearest W atoms at a distance from O of about 1.1 Å (see ref. 27 p. 53)*. The resulting O–H...O angles are 175°, O(7)–H...O(9), and 152°, O(8)–H...O(10). In the second case there is a large deviation from linearity; however "linearity is rather the exception than the rule in hydrogen bonding"[27]. The H...O(9)–P(1) and H...O(10)–P(2) angles are respectively 163° and 143°, both values being in the range of the M–O–P angles found when the phosphine oxides are bonded to transition metals (see, for example, ref. 29 and references therein).

---

* Experimental support for the soundness of this value was found in the final difference Fourier for structures (III) and (IV) for which residual electron density peaks (about 0.6 e/Å^3) were found at approximately 1.1 Å from the oxygen atoms.

ACKNOWLEDGEMENTS

This work was financially supported by the Italian Consiglio Nazionale delle Ricerche. We thank U. Sartorelli for a gift of crystal samples and P. L. Bellon and V. Scatturin for their continued interest in this work and for discussions.

REFERENCES

1 W. Hieber, K. Englert and K. Rieger, *Z. Anorg. Allg. Chem.*, 300 (1959) 295.
2 W. Hieber and K. Englert, *Z. Anorg. Allg. Chem.*, 300 (1959) 311.
3 F. Canziani, F. Zingales, U. Sartorelli and A. Chiesa, *Rend. Ist. Lombardo Sci. Lett.*, 98A (1964) 709.
4 V. G. Albano, P. L. Bellon, G. Ciani and M. Manassero, *J. Chem. Soc. D*, (1969) 1242.
5 U. Sartorelli, L. Garlaschelli, G. Ciani and G. Bonora, *Inorg. Chim. Acta*, 5 (1971) 191.
6 G. Ciani, M. Manassero and M. Sansoni, *J. Appl. Crystallogr.*, 4 (1971) 173.
7 V. G. Albano, P. L. Bellon, F. Pompa and V. Scatturin, *Rend. Ist. Lombardo Sci. Lett.*, 100A (1966) 337.
8 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 24 (1968) 321.
9 *International Tables for X-Ray Crystallography*, Vol. III, Kynoch Press, Birmingham, 1962.
10 H. M. M. Shearer and C. B. Spencer, *Chem. Commun.*, (1966) 194.
11 T. G. Spiro, D. H. Templeton and H. Zalkin, *Inorg. Chem.*, 7 (1968) 2165; H. S. Preston, J. C. Mills, C. H. L. Kennard, *J. Organometal. Chem.*, 14 (1968) 447.
12 D. Bright, *J. Chem. Soc. D*, (1970) 1169.
13 E. W. Abel, W. Harrison, R. A. N. McLean, W. C. Marsh and J. Trotter, *J. Chem. Soc. D*, (1970) 1531.
14 F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 27 (1957) 809.
15 F. C. Wilson and D. P. Shoemaker, *Naturwissenschaften*, 43 (1956) 57.
16 V. G. Albano, G. Ciani and M. Manassero, *J. Organometal. Chem.*, 25 (1970) C55.
17 R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 87 (1965) 2576.
18 F. A. Cotton and B. H. C. Winquist, *Inorg. Chem.*, 8 (1969) 1304.
19 V. A. Maroni and T. G. Spiro, *Inorg. Chem.*, 7 (1968) 188.
20 G. B. Kolski, N. K. Kildhal and D. W. Margerum, *Inorg. Chem.*, 8 (1969) 1211.
21 J. D. McCullough and K. N. Trueblood, *Acta Crystallogr.*, 12 (1959) 507.
22 V. G. Albano, P. L. Bellon and V. Scatturin, *Rend. Ist. Lombardo Sci. Lett.*, 100A (1966) 989.
23 J. B. Wilford, A. Whitla and H. M. Powell, *J. Organometal. Chem.*, 8 (1967) 495.
24 J. B. Wilford and H. M. Powell, *J. Chem. Soc. A*, (1969) 8.
25 G. Bandoli, G. Bortolozzo, D. A. Clemente, U. Croatto and C. Panattoni, *J. Chem. Soc. A*, (1970) 2778.
26 H. K. Wang, *Acta Chem. Scand.*, 19 (1965) 879.
27 W. C. Hamilton and J. A. Ibers, *Hydrogen Bonding in Solids*, Benjamin, New York, 1968.
28 R. Blinc, D. Hadzi and A. Novak, *Ber. Bunsenges. Phys. Chem.*, 64 (1960) 567.
29 C. Panattoni, R. Graziani, G. Bandoli, B. Zarli and G. Bombieri, *Inorg. Chem.*, 8 (1969) 320; R. Graziani, B. Zarli, A. Cassol, G. Bombieri, E. Forsellini and E. Tondello, *Inorg. Chem.*, 9 (1970) 2116.