and valency angles also conform to symmetry *m*, and the mean distances and angles are shown in Fig. 1.

The C–C bond distances are all equal within experimental error, the average value of 1·386 ± 0·004 Å not being significantly different from the distance in benzene (1·392 Å). The mean C–N length of 1·493 ± 0·006 Å is similar to that in nitrobenzene, 1·486 ± 0·02 Å (Trotter, 1959). The N–O bond distances average 1·271 ± 0·006 Å for N(1)–O(1) and N(2)–O(4), and 1·225 ± 0·006 Å for N(1)–O(2) and N(2)–O(3). Since these averages differ by 5σ, the structure contains two types of N–O bond, one longer and the other shorter than, with their mean (1·248 Å) equal to, the N–O distance in, for example *p*-nitroaniline, 1·247 ± 0·005 Å (Trueblood, Goldish & Donohue, 1961). The valency angles are all quite similar to those in other nitro compounds. The hydrogen atom parameters are not very accurate; the mean C–H distance is 0·95 Å.

All the calculations were performed with our own programs on the IBM 7040 computer, and we are indebted to the staff of the U.B.C. Computing Centre for assistance, and the National Research Council of Canada for financial support and for the award of a research studentship to C.S.W.

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Structure of *P*,*P*′,*P*″,*P*‴-Tetrakistricarbonylnickel-tetraphosphorus hexaoxide, $P_4O_6[Ni(CO)_3]_4$.

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The reaction of P_4O_6 with an excess of nickel carbonyl produces $P_4O_6[Ni(CO)_3]_4$, a white powder, with evolution of four equivalents of CO. As described elsewhere (Riess & Van Wazer, 1965) the symmetric bird-cage structure of P_4O_6, which has four unshared pairs of electrons (one on each phosphorus atom) coordinates four nickel tricarbonyl groups.

Since satisfactory single crystals of this substance could not be grown, an attempt has been made to determine the structure from powder intensity data. A General Electric XRD-5 diffractometer with Cu $K\alpha$ radiation was used. Of the 27 measurable diffraction peaks observed up to a maximum $\sin\theta$ value of 0·62, only 19 were due to the diffracted spectrum from a single set of planes.

The pattern could be indexed on the basis of a cubic unit cell with $a = 8{\cdot}811 \pm 0{\cdot}003$ Å. The absence of systematic extinctions indicated four possible space groups: $P23$, $Pm3$, $P\bar{4}3m$, and $Pm3m$. The density, determined on the powdered sample with a Beckman air comparison pycnometer, is 1·865 g.cm^{-3}. This value may be compared with a calculated density of 1·919 g.cm^{-3} for one molecule in each unit cell. Accordingly, two of the possible space groups can be eliminated if it is assumed that no disorder is present, since $Pm3$ and $Pm3m$ do not have four equivalent positions.

For the initial trials it was assumed that the correct space group was $P\bar{4}3m$ with the atoms placed in the Wyckoff positions indicated in Table 2. This still leaves two possible molecular configurations which differ merely in a rotation by 60° of the $Ni(CO)_3$ groups. Standard bond lengths and angles (*Tables of Interatomic Distances*, 1958) were taken to calculate a set of coordinates. The only doubtful distance is the length of the Ni---P bond. Instead of a value of 2·26 Å as previously reported (Scatturin & Turco, 1958), a bond length of 2·15 Å corresponding to the sum of the covalent radii (Pauling, 1960) was selected. Consequently

Table 1. *Assumed molecular dimensions*

P---O	1·64 Å	OPO	101°
C---O	1·14	POP	124
Ni---C	1·82		
Ni---P	2·15		

Table 2.

	Wyckoff positions		Atomic coordinates (Å)		
			X	*Y*	*Z*
Ni	4 (*e*)	$X_1X_1X_1$	2·265	2·265	2·265
P	4 (*e*)	$X_2X_2X_2$	1·024	1·024	1·024
O(1)	6 (*f*)	X_300	1·794	0	0
O(2)	12 (*i*)	$X_4X_4Z_1$	1·672	1·672	5·104
C	12 (*i*)	$X_5X_5Z_2$	1·904	1·904	4·012

the values shown in Table 1 were adopted with linear Ni---C---O groups and tetrahedral valencies around the nickel atom. These parameters yield the coordinates shown in Table 2.

A calculation of the 19 available structure factors demonstrated that the model represented in Fig. 1 was correct. The scattering factors were taken from *International Tables for X-ray Crystallography* (1962) with the Ni curve corrected for the real part of the dispersion. Attempts were made to refine the model by least-squares but no satisfactory convergence could be obtained. This was due to the paucity of observed reflexions and the inability to measure more accurately the true intensities because of the relative low degree of crystallinity and possible effects induced by preferred orientation during sample preparation. All calculations were carried out on an Elliott 803B computer with the programming system of Daly, Stephens & Wheatley (1966).

Table 3. *Powder pattern of* $P_4O_6[Ni(CO)_3]_4$

N	*hkl*	d_o	d_c	I_o	I_c
1	100	8·835	8·811	1101	985
2	110	6·263	6·231	258	281
3	111	5·108	5·087	1840	1127
4	200	4·414	4·406	609	902
5	210	3·951	3·941	391	413
6	211	3·604	3·598	113	86
8	220	3·121	3·116	75	194
9	300	2·942	2·937	439	556
9	221				
10	310	—	—	—	0
11	311	2·662	2·656	426	351
12	222	2·544	2·544	125	136
13	320	—	—	—	2
14	321	2·360	2·355	60	147
16	400	2·199	2·203	18	51
17	410	2·135	2·137	18	23 (15, 8)
17	322				
18	411	2·074	2·077	18	47 (26, 21)
18	330				
19	331	2·023	2·021	95	195
20	420	1·972	1·970	61	102
21	421	1·926	1·923	7	4
22	332	1·877	1·879	12	13
24	422	1·799	1·799	41	29
25	500	—	—	—	15 (5, 10)
25	430				
26	510	1·726	1·728	14	9 (2, 7)
26	431				
27	511	1·697	1·696	23	57 (47, 10)
27	333				
29	520	1·636	1·636	14	11 (1, 10)
29	432				
30	521	—	—	—	13
32	440	1·557	1·558	42	20
33	522	—	—	—	17 (12, 5)
33	441				
34	530	—	—	—	2 (0, 2)
34	433				
35	531	1·489	1·489	41	50
36	600	1·470	1·469	27	19 (4, 15)
36	442				
37	610	—	—	—	0
38	611	—	—	—	6 (6, 0)
38	532				
40	620	—	—	—	15
41	621	—	—	—	6 (2, 3, 1)
41	540				
41	443				
42	541	—	—	—	3
43	533	—	—	—	4
44	622	1·328	1·328	11	14
45	630	—	—	—	2 (0, 2)
45	542				
46	631	—	—	—	1
48	444	—	—	—	1
49	700	—	—	—	3 (0, 3, 1)
49	632				
50	710				
50	550	—	—	—	6 (4, 1, 6, 7)
50	543				
51	711	1·233	1·234	16	13
51	551				

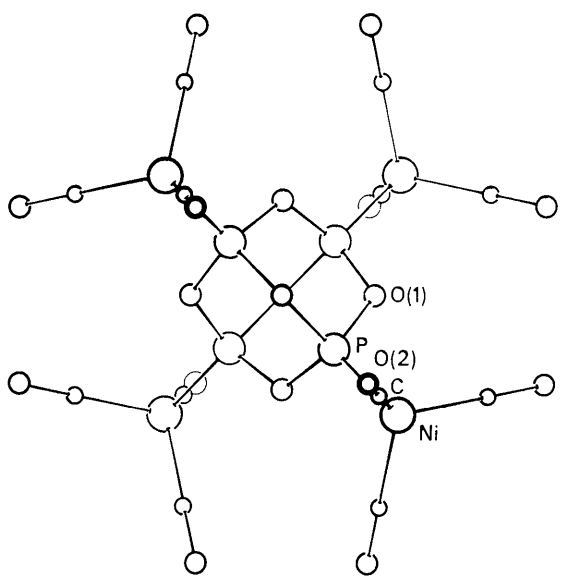

Fig. 1. Structure of the $P_4O_6[Ni(CO)_3]_4$ molecule.

Table 3 shows the powder pattern with the observed and calculated intensities obtained from the coordinates given in Table 2 and with the overall isotropic temperature factor $B=8$ Å^2.

The intensity agreement factor for the 27 observed lines is 16·4%. Thus, although it has not proved possible to obtain exact molecular dimensions, especially the Ni---P bond length, the stereochemistry of $P_4O_6[Ni(CO)_3]_4$ is as shown in Fig. 1.

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