Crystal and Molecular Structure of [Octakisdimethylaminocyclotetraphosphazene]tetracarbonyltungsten

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Crystals of the title compound are monoclinic, a = 18·274(22), b = 18·594(24), c = 10·533(14) Å, β = 90·39(10)°, Z = 4, space group $P2_1/n$. The structure was determined from diffractometer data by Patterson and Fourier methods, and refined by full-matrix least-squares methods to R 0·071 for 2372 observed reflexions. The phosphonitrile is co-ordinated to tungsten through a ring nitrogen atom and an exocyclic dimethylamido-nitrogen atom. The co-ordination geometry about tungsten is distorted octahedral with the nitrogen atoms of the phosphonitrile occupying *cis*-positions and N–W–N angle 65·4°. The bond-length variations in the phosphonitrilic ring caused by co-ordination are explained in terms of π-bonding theory.

PHOSPHONITRILIC derivatives have been shown to form complexes with transition-metal ions, and the structures of some of these compounds have been determined.[1-3] In these complexes co-ordination occurs through the ring nitrogen atoms by donation of lone-pair electrons to the metal. Phosphonitrilic derivatives have also been shown to react with transition-metal carbonyls to yield complexes of unknown co-ordination geometries.[4] The structure of $N_4P_4(NMe_2)_8{\cdot}W(CO)_4$ is unusual in that the metal is co-ordinated to both a ring nitrogen atom and an exocyclic dimethylamido-group. The structure of this compound has been discussed briefly,[5] and a detailed description of the structure analysis is now given.

EXPERIMENTAL

The compound was prepared by the reaction of $N_4P_4(NMe_2)_8$ with $W(CO)_6$ in light petroleum as previously described.[4a] Yellow needles elongated along c grew in the reaction vessel, and were washed several times with light petroleum.

Crystal Data.—$C_{20}H_{48}N_{12}O_4P_4W$, M = 828·43, Monoclinic, a = 18·274(22), b = 18·594(24), c = 10·533(14) Å, β = 90·39(10)°, U = 3579 Å^3, D_m = 1·55 g cm^{-3} (flotation in CCl_4-heptane), Z = 4, D_c = 1·537 g cm^{-3}, $F(000)$ = 1672. Space group $P2_1/n$ (C_{2h}^5) from absent reflexions: $h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$. Mo-K_α radiation, λ = 0·71069 Å, μ(Mo-K_α) = 36 cm^{-1}.

The space group and initial unit-cell parameters were determined from precession and Weissenberg films. Accurate unit-cell parameters were obtained by least-squares refinement of $\sin^2\theta$ values for 30 reflexions measured on a General Electric XRD 6 diffractometer.

Intensity data were collected on a Datex-automated General Electric XRD 6 diffractometer with a scintillation counter, Mo-K_α radiation (zirconium filter and pulse-height analyser), and a θ—2θ scan. The scan width in 2θ was $(1{\cdot}80 + 0{\cdot}86 \tan\theta)°$, and 20 s background counts were taken on either side of every scan. All reflexions with $2\theta(\text{Mo-}K_\alpha) \leqslant 40°$ and some with $40° < 2\theta(\text{Mo-}K_\alpha) \leqslant 45°$ were measured. A check reflexion was monitored every 30 reflexions, and its intensity had fallen off by 15% of its starting value by the end of the data collection. The intensity of this reflexion was used to place the data on the same relative scale. Lorentz and polarisation corrections were applied and structure amplitudes derived. No corrections were made for absorption. The crystal dimensions were approximately 0·2 × 0·1 × 0·4 mm. Of the 3759 independent reflexions measured, 2372 had intensities $>3\sigma(I)$ above background, where $\sigma^2(I) = S + B + (0{\cdot}03S)^2$, with S = scan count and B = background count. These reflexions were classified as observed.

Structure Analysis.—The position of the tungsten atom was determined from a three-dimensional Patterson map. A structure-factor calculation with B 5·0 Å^2 gave R 0·378. A three-dimensional electron-density map gave the positions of the ring phosphorus and nitrogen atoms, and with these atoms included R was reduced to 0·304. A three-dimensional difference map was then calculated, and 28 of the remaining 32 non-hydrogen atoms were located. Two cycles of full-matrix least-squares refinement of the positional and isotropic thermal parameters of all atoms located reduced R to 0·126. A difference map gave the positions of the remaining four non-hydrogen atoms. Three cycles of full-matrix least-squares refinement with the tungsten, phosphorus, oxygen, and nitrogen atoms having anisotropic and the carbon atoms isotropic temperature factors reduced R to 0·071 for 2372 observed reflexions.

Least squares refinement was based on the minimisation of $\Sigma w(|F_o| - |F_c|)^2$. The anisotropic thermal parameters are U_{ij} in the expression $f = f_o \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$. The scattering factors f_o were obtained from ref. 6 for all atoms, with correction for anomalous dispersion included for tungsten. The weighting scheme: $\sqrt{w} = 1{\cdot}0$ when $|F_o| \leqslant 75{\cdot}0$ and $\sqrt{w} = 75{\cdot}0/|F_o|$ when $|F_o| > 75{\cdot}0$, gave approximately constant average values of $w(|F_o| - |F_c|)^2$ over ranges of $|F_o|$ and was used in the last cycles of refinement. Unobserved reflexions were given a weight of zero. On the final cycle of refinement no parameter shift was $>0{\cdot}6\sigma$, except for the isotropic temperature factors for C(17) and C(19), for which the shifts were *ca.* $2{\cdot}5\sigma$.

A final difference-Fourier map was calculated and showed maximum fluctuations of up to $\pm 1{\cdot}0$ eÅ^{-3}, but the hydrogen atoms could not be located and were not included in the

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[1] J. Trotter and S. H. Whitlow, *J. Chem. Soc.* (*A*), 1970, 455.

[2] W. C. Marsh and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 1482.

[3] W. Harrison, N. L. Paddock, J. Trotter, and J. N. Wingfield, *Chem. Comm.*, 1972, 23.

[4] (*a*), N. L. Paddock, T. N. Ranganathan, and J. N. Wingfield, *J.C.S. Dalton*, 1972, 1578; (*b*), F. A. Cotton and A. Shaver, *Inorg. Chem.*, 1971, **10**, 2362.

[5] H. P. Calhoun, N. L. Paddock, J. Trotter, and J. N. Wingfield, *Chem. Comm.*, 1972, 875.

[6] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

least-squares refinement. There were also a few larger peaks of up to ± 2 eÅ^{-3} near the tungsten atom.

Final atomic positions and thermal parameters are given in Table 1. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 20831 (7 pp.).*

DISCUSSION

Bond lengths and angles with estimated standard deviations are given in Table 2, and a general view of the molecule is shown in Figure 1. The molecular structure is unusual in two respects: *cis*-co-ordination at tungsten occurs by formation of a four-membered ring, and complex formation involves an exocyclic dimethylamido-group. Protonation usually occurs on the ring nitrogen atoms, though quaternisation of dimethylamidophosphonitriles can occur exocyclically.[7]

TABLE 1

Final positional parameters (fractional × 10^4) and thermal parameters (anisotropic U_{ij}, Å^2 × 10^4; isotropic U, Å^2 × 10^4), with standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z	U
W	2191·3(6)	0559·6(5)	2198·6(10)	C(17)	3190(12)	0324(10)	2933(20)	637(53)
P(1)	2681(3)	1002(3)	−1087(5)	C(18)	2179(15)	−0395(15)	1592(29)	875(82)
P(2)	2724(3)	1974(3)	1050(5)	C(19)	1933(13)	0239(13)	3827(24)	830(65)
P(3)	4265(3)	2380(3)	0506(5)	C(20)	1061(19)	0572(17)	1778(30)	1027(90)
P(4)	3870(3)	1906(3)	−2100(5)	C(1)	3743(13)	0099(13)	−0148(24)	714(67)
O(1)	2205(12)	−1004(10)	1150(16)	C(2)	3075(15)	−0290(15)	−2065(27)	890(84)
O(2)	3706(10)	0099(11)	3432(20)	C(3)	1664(15)	1281(14)	−2960(26)	843(79)
O(3)	0451(12)	0490(12)	1686(26)	C(4)	1384(16)	0295(15)	−1418(28)	932(87)
O(4)	1711(14)	−0023(10)	4872(17)	C(5)	2484(14)	3393(14)	0581(24)	764(72)
N(1)	2508(9)	1214(8)	0395(16)	C(6)	1558(14)	2512(14)	−0345(25)	808(75)
N(2)	3541(9)	2168(9)	1290(15)	C(7)	1617(14)	2155(13)	2798(24)	793(72)
N(3)	4348(8)	2231(10)	−0934(17)	C(8)	2827(13)	1997(12)	3668(24)	690(66)
N(4)	3063(9)	1630(9)	−1797(16)	C(9)	4425(15)	3562(14)	1993(27)	899(81)
N(5)	3082(9)	0208(8)	−1010(15)	C(10)	4686(17)	3737(16)	−0345(31)	1031(95)
N(6)	1915(11)	0833(10)	−1860(17)	C(11)	4831(18)	1359(18)	2107(34)	1201(111)
N(7)	2278(9)	2621(9)	0357(16)	C(12)	5681(15)	2101(14)	0869(26)	846(76)
N(8)	2349(8)	1808(7)	2547(15)	C(13)	4176(16)	0968(16)	−4003(29)	941(89)
N(9)	4431(10)	3254(11)	0687(17)	C(14)	5184(15)	1139(14)	−2457(27)	893(82)
N(10)	4936(9)	1975(10)	1369(19)	C(15)	3140(14)	3045(14)	−3117(26)	849(77)
N(11)	4402(10)	1300(11)	−2766(18)	C(16)	4444(16)	2845(16)	−3864(29)	973(87)
N(12)	3744(12)	2532(10)	−3244(18)					

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	731(7)	453(6)	590(6)	−30(6)	60(6)	−4(6)
P(1)	509(37)	433(30)	479(34)	8(27)	−91(28)	−41(28)
P(2)	543(37)	381(30)	465(33)	30(26)	0(27)	−38(26)
P(3)	474(36)	485(32)	529(36)	31(27)	−63(29)	−49(28)
P(4)	602(39)	530(35)	415(33)	49(30)	−47(28)	19(27)
O(1)	1639(188)	776(126)	604(118)	−17(124)	163(120)	43(103)
O(2)	970(139)	1278(164)	1086(156)	493(127)	−291(125)	−50(135)
O(3)	878(152)	1402(191)	1984(253)	−120(141)	−226(156)	−214(181)
O(4)	2157(242)	747(129)	748(130)	−344(138)	387(143)	−29(104)
N(1)	448(101)	567(103)	519(107)	54(83)	82(84)	106(85)
N(2)	539(116)	550(102)	493(105)	−40(85)	−215(89)	−4(85)
N(3)	329(100)	893(131)	637(122)	31(90)	−26(88)	−282(105)
N(4)	602(118)	618(112)	522(112)	−80(90)	−182(90)	52(96)
N(5)	727(126)	420(91)	444(102)	109(86)	−108(91)	−121(83)
N(6)	967(154)	734(123)	541(124)	−553(112)	−58(112)	−2(101)
N(7)	687(128)	554(106)	502(112)	87(91)	−3(95)	84(89)
N(8)	588(118)	248(87)	669(113)	49(79)	60(90)	−64(79)
N(9)	696(132)	822(131)	609(123)	−10(106)	16(101)	−56(108)
N(10)	412(110)	833(138)	890(141)	−54(99)	−87(100)	279(119)
N(11)	642(130)	953(147)	634(133)	192(109)	−191(106)	−209(115)
N(12)	1046(164)	770(135)	590(128)	262(122)	122(115)	263(109)

All the evidence suggests that the compound is a simple *cis*-σ-complex, though co-ordination results in appreciable changes in the π-electron distribution. There is a sensitive electronic interconnection between the three donor–acceptor sites: the tungsten atom, the dimethylamido-group, and the phosphonitrilic ring. They will be discussed in this order.

The octahedral geometry about tungsten is distorted, since the angle N(1)–W–N(8) is necessarily small [65·4(6)°]. The other C–W–C angles are not far from 90°, except C(17)–W–C(19), which is 79·3(9)°. The carbonyl groups are bent, as in other compounds with carbonyl groups co-ordinated to tungsten,[8] the

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-size copies.)

[7] J. N. Rapko and G. R. Feistel, *Inorg. Chem.*, 1970, **9**, 1401.

[8] (*a*) E. M. Cradwick and D. Hall, *J. Organometallic Chem.*, 1970, **25**, 91; (*b*) V. A. Semion, Y. A. Chapovskii, Yu. T. Struchkov, and A. N. Nesmeyanov, *Chem. Comm.*, 1968, 666; (*c*) J. B. Wilford and H. M. Powell, *J. Chem. Soc.* (*A*), 1969, 8; (*d*) R. Ros, M. Vidali, and R. Graziani, *Gazzetta*, 1970, **100**, 407; (*e*) M. Elder and D. Hall, *Inorg. Chem.*, 1969, **8**, 1273.

angles at carbonyl carbon ranging from 169·0—176·2° (mean 172·2°). The mean values of the W–C and C–O bond lengths (1·97 and 1·19 Å) are also similar to those in related compounds. They are, however, affected by co-ordination, the W–C bonds *trans* to the W–N bonds being significantly shorter [1·88(3) and 1·89(3) Å] than the *cis*-bonds [2·02(3) and 2·11(4) Å], suggesting greater W $\rightarrow$ CO back-donation to the *trans*-bonds. This interpretation is supported by the lengths of the W–N bonds [2·33(2) and 2·37(1) Å], which are considerably greater than those found in (bipy)$(CO)_3$Br-WGeBr_3 (2·20 Å)[8a] in which some W $\rightarrow$ L (L = bipy = 2,2′-bipyridyl) back-donation may occur. A more detailed estimate is possible. One value for the covalent radius of tungsten can be obtained from the structure of $(\pi\text{-}C_5H_5)W(CO)_3(\sigma\text{-}Ph)$,[8b] in which the W–C(Ph) bond length is 2·32 Å. If the covalent radius of sp^2-hybridised carbon is taken as 0·74 Å, that of the tungsten atom is 1·58 Å. In $N_4P_4(NMe_2)_8W(CO)_4$, N(8) is approximately sp^3-hybridised (0·70 Å), so that the covalent radius of tungsten in this compound is 1·67 Å, nearly 0·1 Å greater than in the bond to phenyl. The interpretation that the phosphonitrilic complex is a simple weak σ-complex, without significant back-donation into the π-levels of the ligand, is supported by a comparison of its carbonyl stretching frequencies (2000, 1870, 1849, and 1809 cm^{-1})[4] with those of (en)$W(CO)_4$ (2006, 1867, 1852, 1809 cm^{-1}).[9]

TABLE 2

Bond lengths (Å) and angles (deg.), with standard deviations in parentheses

(*a*) Distances

W–C(17)	2·02(3)	C(17)–O(2)	1·15(3)
W–C(18)	1·89(3)	C(18)–O(1)	1·23(3)
W–C(19)	1·88(3)	C(19)–O(4)	1·27(3)
W–C(20)	2·11(4)	C(20)–O(3)	1·13(3)
W–N(1)	2·33(2)		
W–N(8)	2·37(1)	N(5)–C(1)	1·52(3)
		N(5)–C(2)	1·45(3)
P(1)–N(1)	1·64(2)	N(6)–C(3)	1·50(3)
P(1)–N(4)	1·55(2)	N(6)–C(4)	1·47(3)
P(2)–N(1)	1·62(2)	N(7)–C(5)	1·50(3)
P(2)–N(2)	1·55(2)	N(7)–C(6)	1·52(3)
P(3)–N(2)	1·61(2)	N(8)–C(7)	1·51(3)
P(3)–N(3)	1·55(2)	N(8)–C(8)	1·50(3)
P(4)–N(3)	1·62(2)	N(9)–C(9)	1·49(3)
P(4)–N(4)	1·60(2)	N(9)–C(10)	1·49(3)
Mean endocyclic P–N	1·59	N(10)–C(11)	1·40(3)
P(2)–N(7)	1·62(2)	N(10)–C(12)	1·48(3)
P(2)–N(8)	1·75(2)	N(11)–C(13)	1·50(3)
P(1)–N(5)	1·65(2)	N(11)–C(14)	1·49(3)
P(1)–N(6)	1·64(2)	N(12)–C(15)	1·47(3)
P(3)–N(9)	1·66(2)	N(12)–C(16)	1·55(3)
P(3)–N(10)	1·70(2)	Mean N–C	1·49
P(4)–N(11)	1·65(2)		
P(4)–N(12)	1·69(2)		

Mean exocyclic P–N [excluding P(2)–N(8)] 1·66

(*b*) Angles

C(17)–W–N(8)	92·5(7)		
C(17)–W–N(1)	101·3(7)	N(5)–P(1)–N(6)	103·3(9)
C(17)–W–C(18)	86·2(10)	N(7)–P(2)–N(8)	109·6(8)
C(17)–W–C(19)	79·3(9)	N(9)–P(3)–N(10)	103·9(10)
C(17)–W–C(20)	163·9(10)	N(11)–P(4)–N(12)	104·2(10)
C(18)–W–N(1)	102·5(10)		
C(18)–W–C(19)	90·5(11)	N(5)–P(1)–N(4)	119·7(9)
C(18)–W–C(20)	85·9(12)	N(5)–P(1)–N(1)	104·9(8)
C(19)–W–N(8)	101·5(8)	N(6)–P(1)–N(4)	106·8(9)
C(19)–W–C(20)	86·7(11)	N(6)–P(1)–N(1)	110·3(10)
C(20)–W–N(8)	98·1(9)	N(7)–P(2)–N(1)	109·5(9)
C(20)–W–N(1)	94·1(9)	N(7)–P(2)–N(2)	112·3(9)
N(8)–W–N(1)	65·4(6)	N(8)–P(2)–N(1)	97·7(8)
		N(8)–P(2)–N(2)	106·0(8)
W–C(17)–O(2)	169·5(19)	N(9)–P(3)–N(2)	109·2(9)
W–C(18)–O(1)	176·2(24)	N(9)–P(3)–N(3)	105·5(10)
W–C(19)–O(4)	174·0(20)	N(10)–P(3)–N(2)	102·1(9)
W–C(20)–O(3)	169·0(29)	N(10)–P(3)–N(3)	111·7(10)
Mean W–C–O	172·2	N(11)–P(4)–N(3)	105·2(9)
P(1)–N(1)–P(2)	124·5(10)	N(11)–P(4)–N(4)	114·4(10)
P(2)–N(2)–P(3)	139·8(11)	N(12)–P(4)–N(3)	110·7(10)
P(3)–N(3)–P(4)	138·8(11)	N(12)–P(4)–N(4)	104·0(10)
P(4)–N(4)–P(1)	139·1(12)		
		W–N(1)–P(2)	99·7(8)
N(4)–P(1)–N(1)	111·5(9)	W–N(1)–P(1)	134·4(9)
N(1)–P(2)–N(2)	120·2(9)		
N(2)–P(3)–N(3)	122·9(9)		
N(3)–P(4)–N(4)	117·6(9)		
P(2)–N(8)–W	94·6(6)		
C(7)–N(8)–W	109·8(12)		
C(8)–N(8)–W	114·8(12)		
C(8)–N(8)–P(2)	115·9(13)		
C(7)–N(8)–P(2)	115·8(14)		
C(7)–N(8)–C(8)	105·8(16)		

Excluding N(8):
C–N–C 111—117, mean 114·5
C–N–P 114—128, mean 121·0
Sum of three angles at exocyclic N 350—360, mean 356·6

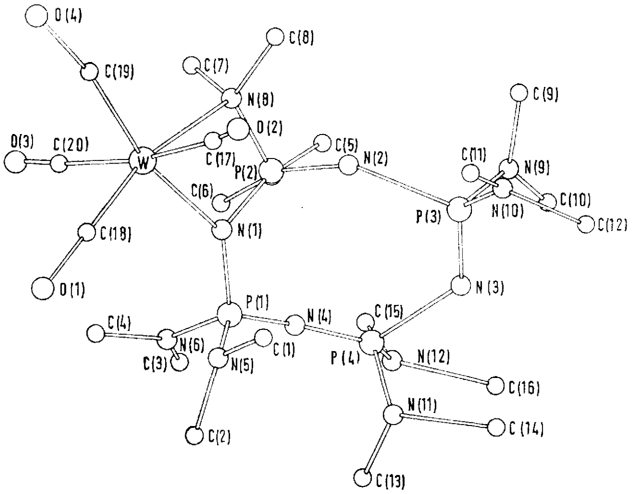

FIGURE 1 General view of the molecule; N(7) is below P(2)

Co-ordination nevertheless has a significant effect on the π-levels of the ligand. The tungsten atom evidently accepts electrons from both a ring and an exocyclic nitrogen atom, sources which in the neutral ligand are competitive donors to phosphorus. Thus, in the unco-ordinated ligand,[10] substantial delocalisation of the lone-pair electrons on the dimethylamido-groups on to phosphorus shortens the exocyclic P–N bonds from 1·77 Å, characteristic of a single bond,[11] to a mean value of 1·678(10) Å, the dimethylamido-groups being nearly planar (mean sum of angles around exocyclic

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[9] C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, 1963, **2**, 533.

[10] G. J. Bullen, *J. Chem. Soc.*, 1962, 3193.

[11] E. Hobbs, D. E. C. Corbridge, and B. Raistrick, *Acta Cryst.*, 1953, **6**, 621; D. W. J. Cruickshank, *ibid.*, 1964, **17**, 671.

N 354°). In the complex, the geometry about N(8) is nearly tetrahedral, the largest difference from the normal tetrahedral angle being that of P(2)–N(8)–W (94·6°). The tungsten evidently acts as a competitive acceptor, the P(2)–N(8) bond length being 1·75(2) Å. The lack of exocyclic π-bonding in this bond is partly compensated by increased donation from the second dimethylamido-group, and in fact the length of the P(2)–N(7) bond is 1·62(2) Å, the sum of the angles round N(7) being 359°. The compensatory effect of the more remote dimethylamido-groups is smaller, the mean of the six P–N bond lengths being 1·665 Å.

The geometry of the phosphonitrilic ring itself shows clearly that tungsten acts both indirectly, through competitive withdrawal from the dimethylamido-group, and directly, by co-ordination to N(1). As a result of complex formation, the conformation of the ring is different from the near-saddle of the uncomplexed ligand.[10] It consists of two nearly planar segments P(2),N(2),P(3),N(3),P(4),N(4) and N(4),P(1),N(1),P(2) making an angle of 48°, the latter set being roughly coplanar with N(1),W,N(8),P(2). The equations of the mean planes through these atoms are given in Table 3. There are also now substantial inequalities in the lengths of the ring bonds, which are shown in Figure 2. Localisation of the lone-pair electrons on N(1) by donation to W is expected to lengthen the P–N bonds meeting at this nitrogen atom, and to induce partial localisation in the more remote parts of the ring. The tungsten atom also affects the electron distribution in the ring by withdrawing charge from P(2) *via* N(8), as indicated by the structural evidence already discussed. As a consequence of the increased electronegativity of P(2), π-bonding from this atom within the ring is strengthened locally; again, the more remote bonds are also influenced. At the co-ordination sites, tungsten therefore has two effects, exerted respectively through N(1) and N(8)–P(2). Their combined effect can be seen by examining the structures of molecules in which the two effects occur separately.

TABLE 3

Mean planes through the molecule

(*a*) Equations of planes: $lX + mY + nZ = p$, where X, Y, Z are orthogonal co-ordinates (Å) with respect to a, b, c^*.

Plane	l	m	n	p
(1) P(2), N(2), P(3), N(3), P(4), N(4)	−0·2979	0·9284	−0·2223	1·6655
(2) N(4), P(1), N(1), P(2)	−0·8892	0·3690	−0·2705	−3·3642
(3) N(1), W, N(8), P(2)	−0·9410	0·2253	−0·2526	−4·1033

(*b*) Distances (Å) of atoms from the mean planes (σ in parentheses)

Plane (1): P(2) 0·015(5), N(2) −0·149(16), P(3) 0·003(5), N(3) 0·035(18), P(4) 0·006(5), N(4) −0·101(17), P(1) −1·143(5), N(1) −1·027(16)

Plane (2): N(4) 0·007(17), P(1) −0·001(6), N(1) 0·013(16), P(2) −0·001(5)

Plane (3): N(1) 0·198(16), W −0·001(1), N(8) 0·161(16), P(2) −0·027(6)

(*c*) Angles (deg.) between the planes

(1)–(2)	48·1	(2)–(3)	8·8

One effect of co-ordination to tungsten is to cause localisation of the lone-pair electrons on N(1). Comparison can be made with protonated eight-membered phosphonitrilic rings, where complete localisation of one pair of electrons at nitrogen, in an otherwise delocalised system, leaves one (π_a) system intact, but removes all π_s bonding in the bonds which meet at the protonated atom. The calculated bond orders in the remaining N_3P_4 fragment are unequal, and for one simple set of assumptions are shown on Figure 3, in comparison with the successive bond lengths[12] in the cations of $[N_4P_4Me_8H^+]_2[CoCl_4^{2-}]$. The assumption that only one π-system is affected to a major extent is supported by a consideration of the lengths of the bonds from the protonated nitrogen atom (mean 1·695 Å, approximately midway between 1·77 Å and a typical phosphonitrilic bond length of 1·59 Å). These bonds are also comparable in length to exocyclic P–N bonds in uncomplexed dimethylamido-phosphonitriles[10,13] and

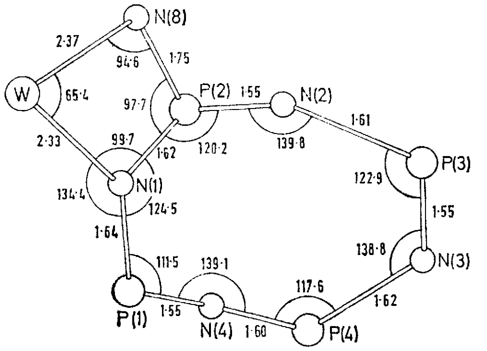

FIGURE 2 Bond lengths (Å) and angles (deg.) in the phosphonitrilic ring: σ(P–N) 0·02 Å, σ(N–P–N) 0·9°, σ(P–N–P) 1·1°

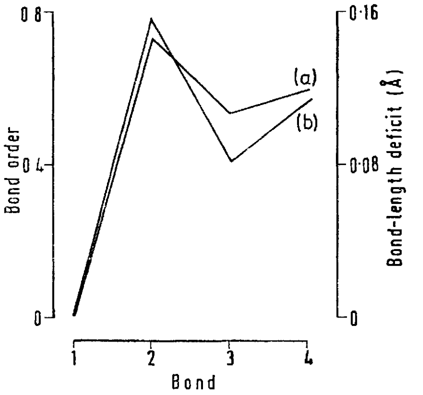

FIGURE 3 (a) Orders of successive symmetrically related pairs of bonds, calculated for a protonated N_4P_4 ring; HMO calculations for single π-system, $\alpha_N = \alpha_P + \beta$, except that the protonated nitrogen atom, taken as the first atom, is assumed to make no contribution to the π-system. (b) Deficit of successive bond lengths from 1·695 Å in the cations of $[N_4P_4Me_8H^+]_2[CoCl_4^{2-}]$

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[12] J. Trotter and S. H. Whitlow, *J. Chem. Soc.* (*A*), 1970, 460.

[13] A. J. Wagner and A. Vos, *Acta Cryst.*, 1968, **B24**, 1423.

in a formally saturated oxophosphazane.[14] Figure 3 shows that the qualitative variation of the three more remote bonds is described correctly by the theoretical treatment, though the magnitude of the variation is larger than expected, possibly because compression effects are ignored.

The other effect of co-ordination to tungsten is to increase the electronegativity of P(2). An appropriate comparison structure is now that of *gem*-$N_4P_4F_6Me_2$.[15] The successive bond lengths in this compound are well described in terms of atom-bond polarisabilities calculated for a delocalised system by simple perturbation theory, on the basis that the methyl groups decrease the electronegativity of the atom to which they are attached.[16] In the present complex we can expect similar variations, but of opposite sign.

Since the qualitative pattern of bond lengths is not critically dependent on the choice of numerical parameters, we can avoid a detailed theoretical treatment, and deduce an expected bond-length pattern in the carbonyl complex by a superposition of the patterns in $N_4P_4Me_8H^+$ and $N_4P_4F_6Me_2$, as follows: (i) find, in order from the protonated nitrogen atom, the deviations of the lengths of the successive PN bonds in $N_4P_4Me_8H^+$ from the mean; (ii) find, in order from the Me_2P group, the deviations of the lengths of the successive PN bonds in $N_4P_4F_6Me_2$ from the mean; (iii) apply the first series to the successive bonds in $N_4P_4(NMe_2)_8W(CO)_4$, initially assumed all equal to the final average, and starting from N(1); and (iv) apply the second series, with opposite sign, but starting at P(2). The results of the superposition of the localisation and the electronegativity effects are embodied in Figure 4, which shows also the actual bond lengths. The actual pattern is well reproduced by the addition of the two components, with the exception of P(4)–N(4), which would be expected to be longer. P(1)–N(1) is, correctly, the longest, and the three shortest bonds are, again correctly, P(2)–N(2), P(3)–N(3), and N(4)–P(1). The general parallelism of the rather irregular curves seems good evidence that the basic assumptions used are correct. Although the pattern is reproduced satisfactorily, the observed range of variation of bond lengths is smaller than that 'calculated'. This is not surprising, as tungsten would be expected to be a less-good direct acceptor at N(1) than a proton, and, being more remote, would have less effect on P(2) than a pair of methyl groups.

The bond angles in the ring are also different from those in the free ligand, but are less reliably interpreted. The endocyclic angles at N(2), N(3), and N(4) (mean 139·2°) are larger than in $N_4P_4(NMe_2)_8$ [133·0(6)°]. P(1)–N(1)–P(2) is smaller than the other endocyclic ring angles at nitrogen and is similar to that at the nitrogen co-ordinated to Cu in $(N_4P_4Me_8H)CuCl_3$ [123·2(14)°].[1] The endocyclic angles at phosphorus range from 111·5—122·9°, mean 118·0°. The angle at P(1) is significantly smaller than at the other three phosphorus atoms. Some of these variations can be attributed to the distortion of the phosphonitrilic ring caused by co-ordination.

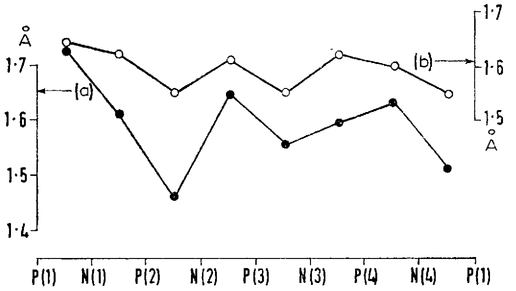

FIGURE 4 Bond lengths (Å) (a) estimated by superposition of inequalities in $N_4P_4Me_8H^+$ and $N_4P_4Me_2F_6$, and (b) in $N_4P_4(NMe_2)_8{\cdot}W(CO)_4$

Intermolecular distances correspond to normal van der Waals contacts. The closest O · · · C(Me) contacts are 3·24 and 3·33 Å, and the closest C(Me) · · · C(Me) contacts are 3·71 and 3·81 Å.

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[3/1039 *Received*, 21*st May*, 1973]

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[14] G. B. Ansell and G. J. Bullen, *J. Chem. Soc.* (*A*), 1968, 3026.

[15] W. C. Marsh and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 573.

[16] T. N. Ranganathan, S. M. Todd, and N. L. Paddock, *Inorg. Chem.*, 1973, **12**, 316.