Other distances of interest are those between the N atom of the pyridine ring and the O atoms of the decavanadate group. The N(30)–O(12) and N(20)–O(18) distances are respectively 2·63 (2) and 2·73 (2) Å. These distances are typical for very strong intermolecular hydrogen bonds.

Our X-ray structural data agree with the results found by Klemperer & Shum (1977), who have determined the protonation positions in the $V_{10}O_{28}^{6-}$ ion by means of ^{17}O NMR, and, according to their work, the sequence of negative charge on the oxygens in our decavanadate ion would be $O(10) = O(14) \simeq O(19) = O(13) < O(7) = O(8) < O(17) < O(9) = O(16) = O(11) = O(18) < O(15) = O(12) < O(16)$. As O(6) is inaccessible to the protons and, of course, to the larger groups such as the 4-ethylpyridinium group, the sequence predicts O(12) and O(18) as the most basic O atoms, O(12) being more basic than O(18). This, added to the steric effects of such a large group, explains why the N–O(12) distance is slightly shorter than the N–O(18) distance.

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catena-μ-[1,2-Bis(diphenylphosphino)ethane]-dicyanomercury(II)

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Abstract. $C_{28}H_{24}HgN_2P_2$, $M_r = 651·05$, triclinic, space group $P\bar{1}$, $a = 9·586 (2)$, $b = 11·793 (2)$, $c = 12·343 (2)$ Å, $\alpha = 104·55 (1)$, $\beta = 107·69 (1)$, $\gamma = 97·74 (1)°$, $V = 1252·6 (4)$ Å^3, $Z = 2$, $d_c = 1·726$, $d_x = 1·70 (1)$ g cm^{-3} (flotation in ZnI_2 solution), Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 62·86$ cm^{-1}, $F(000) = 627·422$. The structure was determined by a least-squares procedure from the measured angular positions of 15 reflections. Final $R = 0·056$ for 3704 independent observed reflections. The structure is built up by packing of infinite chains of $[Hg(CN)_2\{P(C_6H_5)_2CH_2\}_2]_n$. The two Hg–P bonds are significantly different: 2·606 (3) and 2·534 (4) Å. No short contacts occur between the chains in the crystal.

Introduction. Lattice constants and intensity measurements were performed on a computer-controlled automatic Syntex $P2_1$ diffractometer using graphite-monochromatized Mo $K\alpha$ radiation and a colourless crystal of dimensions $0·04 \times 0·12 \times 0·15$ mm.

Intensities of the reflections up to $\theta = 28°$ were measured by the ω-scan technique at a scan rate automatically chosen between 2·0 and 29·3° min^{-1} with a scan range of 1·0°. Background counts were taken, at 1·0° from the peak position, for the scan time. The intensity of three standard reflections, measured for every 100, remained constant throughout the run.

The intensity data were processed as previously described (Bachechi, Zambonelli & Marcotrigiano, 1977), using an uncertainty factor $p = 0·004$, calculated from the variance of the standard reflections (McCandlish, Stout & Andrews, 1975). The values of I and $\sigma(I)$ were corrected for Lorentz, polarization and shape-anisotropy effects.

Of the 6368 unique data collected, 3704 independent reflections, with $I > 3\sigma(I)$, were used in the subsequent solution and refinement of the structure. The structure was solved by the Patterson and Fourier methods and refined by least-squares procedures. The isotropic refinement converged at $R = 0.093$. In the subsequent least-squares cycles the fixed contribution of the H atoms, geometrically positioned, was included, while all the non-H atoms but those of the phenyl groups were allowed to vibrate anisotropically. The H atoms were then repositioned and included in the final structure-factor calculation: $R = 0.056$ ($R_w = 0.071$).

The refinement was carried out with a two-blocks approximation of the normal-equations matrix and the function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = \sin \theta/\lambda$. The four phenyl rings of the molecule of the complex were refined as rigid groups [6/*mmm* symmetry, d(C—C) = 1·392, d(C—H) = 1·0 Å].

Atomic scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974). The calculations were performed, using local programs, on the Univac 1100/20 computer of the University of Rome (Carruthers & Spagna, 1975) and on the HP 21MX minicomputer of the CNR Research Area (Cerrini & Spagna, 1977).

Discussion. Final atomic coordinates are reported in Table 1.* The Hg atoms are surrounded by two CN groups and two $P(C_6H_5)_2CH_2$ groups in an approximately tetrahedral coordination. These tetrahedra form endless chains of formula

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36836 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
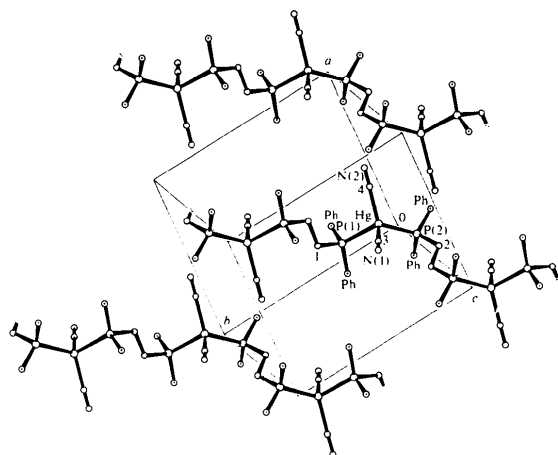

Fig. 1. Packing of the chains of $[Hg(CN)_2\{P(C_6H_5)_2CH_2\}_2]_n$. The phenyl groups are omitted for clarity, only the C atoms directly bound to the P atoms being represented.

$[Hg(CN)_2\{P(C_6H_5)_2CH_2\}_2]_n$ and the structure is built up by the packing of these infinite chains as shown in Fig. 1.

Table 1. *Final positional coordinates and some B_{eq} for the non-H atoms*

Standard deviations are given in parentheses. B_{eq} is defined as $(B_1.B_2.B_3)^{1/3}$, where $B_i = 8\pi^2 U_i^2$ ($i = 1, 2, 3$). The U_i^2 are the mean-square amplitudes of vibration along the principal axes of the thermal ellipsoid.

	x	y	z	B_{eq} (Å²)
Non-group atoms				
Hg	0·3146 (1)	0·1794 (1)	0·4555 (1)	2·44
P(1)	0·2890 (3)	0·3637 (3)	0·3766 (3)	2·03
P(2)	0·0870 (3)	0·0049 (3)	0·3494 (2)	1·89
N(1)	0·3394 (17)	0·2925 (15)	0·7367 (11)	4·16
N(2)	0·6430 (17)	0·1272 (18)	0·4520 (14)	4·64
C(1)	0·4165 (13)	0·5014 (12)	0·4867 (11)	2·53
C(2)	0·0156 (13)	−0·0490 (10)	0·4539 (10)	2·09
C(3)	0·3322 (14)	0·2539 (13)	0·6415 (12)	2·82
C(4)	0·5290 (16)	0·1429 (13)	0·4502 (12)	3·20
Rigid-group atoms				
C(5)	0·3369 (10)	0·3529 (7)	0·2425 (6)	
C(6)	0·3310 (10)	0·2390 (6)	0·1712 (7)	
C(7)	0·3628 (10)	0·2260 (6)	0·0665 (7)	Ph(1)
C(8)	0·4006 (10)	0·3269 (7)	0·0332 (6)	
C(9)	0·4066 (10)	0·4409 (6)	0·1045 (7)	
C(10)	0·3748 (10)	0·4538 (6)	0·2092 (7)	
C(11)	0·1035 (9)	0·3969 (14)	0·3470 (11)	
C(12)	0·0552 (10)	0·4714 (11)	0·2788 (10)	
C(13)	−0·0892 (10)	0·4913 (9)	0·2572 (9)	Ph(2)
C(14)	−0·1853 (9)	0·4369 (14)	0·3037 (11)	
C(15)	−0·1369 (10)	0·3625 (11)	0·3719 (10)	
C(16)	0·0075 (10)	0·3425 (9)	0·3936 (9)	
C(17)	0·1186 (9)	−0·1272 (7)	0·2545 (7)	
C(18)	−0·0055 (7)	−0·2152 (9)	0·1710 (8)	
C(19)	0·0149 (8)	−0·3132 (8)	0·0919 (7)	Ph(3)
C(20)	0·1593 (9)	−0·3232 (7)	0·0961 (7)	
C(21)	0·2834 (7)	−0·2352 (9)	0·1795 (8)	
C(22)	0·2630 (8)	−0·1372 (8)	0·2587 (7)	
C(23)	−0·0683 (10)	0·0386 (18)	0·2437 (11)	
C(24)	−0·0367 (11)	0·0768 (23)	0·1540 (12)	
C(25)	−0·1469 (10)	0·1104 (10)	0·0733 (7)	Ph(4)
C(26)	−0·2887 (10)	0·1059 (18)	0·0824 (11)	
C(27)	−0·3202 (11)	0·0677 (23)	0·1721 (12)	
C(28)	−0·2100 (10)	0·0340 (10)	0·2527 (7)	

Rigid-group parameters

The fractional coordinates x, y, and z describe the positions of the rings and the angles θ, φ and ψ (in degrees) describe rotations about an internal coordinate system (Rollett. 1965).

	x	y	z
Ph(1)	0·3688 (6)	0·3399 (5)	0·1379 (5)
Ph(2)	−0·0409 (7)	0·4169 (6)	0·3254 (6)
Ph(3)	0·1390 (7)	−0·2252 (5)	0·1753 (5)
Ph(4)	−0·1785 (7)	0·0722 (5)	0·1630 (5)

	θ	φ	ψ
Ph(1)	−7·7 (3)	0·0 (2)	77·1 (3)
Ph(2)	179·9 (5)	51·0 (4)	−20·0 (5)
Ph(3)	180·4 (3)	−32·4 (3)	−2·6 (4)
Ph(4)	180·3 (8)	70·4 (3)	−18·3 (8)
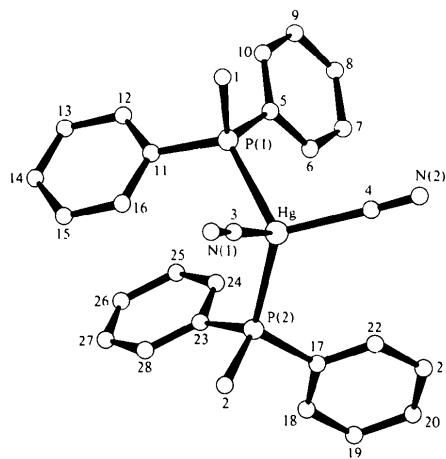
Fig. 2. The monomeric unit [Hg(CN)₂{P(C₆H₅)₂CH}₂].

An analogous polymeric structure was found in the complex *catena-μ*-[1,5-bis(diphenylphosphino)pentane]-diiodomercury(II) (Aurivillius & Wendel, 1976). In this compound each monomeric unit is symmetrical with respect to a binary axis passing through Hg, and is correlated to its next neighbours by twofold axes, parallel to the previous one, passing through the γ-C atoms of the pentane moieties of the ligand. In the present case the monomeric units are correlated in the chain by centres of symmetry situated between the two methylene groups of the 1,2-bis(diphenylphosphino)-ethane ligand.

A diagram of the monomeric unit [Hg(CN)₂{P(C₆H₅)₂CH₂}₂] with the numbering scheme is shown in Fig. 2. The relevant torsion angles of the backbone are given in Table 2, Table 3 gives information about the orientation of the phenyl rings, and a selection of bond lengths and valence angles is reported in Table 4. The two Hg—P bonds are significantly

Table 2. *Relevant torsion angles* (°) *along the chain of* [Hg(CN)₂{P(C₆H₅)₂CH₂}₂]ₙ

P(1')—C(1')—C(1)—P(1)	180·0	P(2)—C(2)—C(2')—P(2')	180·0
C(1')—C(1)—P(1)—Hg	64·0 (11)	C(5)—P(1)—Hg—P(2)	−83·1 (3)
C(1)—P(1)—Hg—P(2)	158·9 (5)	C(11)—P(1)—Hg—P(2)	41·3 (5)
P(1)—Hg—P(2)—C(2)	−128·6 (5)	P(1)—Hg—P(2)—C(17)	110·8 (4)
Hg—P(2)—C(2)—C(2')	52·6 (9)	P(1)—Hg—P(2)—C(23)	−5·6 (5)

Table 3. *Orientation of the phenyl rings: dihedral angles formed by their planes and relevant torsion angles* (°)

[C(5)···C(10)] ∧ [C(11)···C(16)]	111·7 (4)
[C(17)···C(22)] ∧ [C(23)···C(28)]	78·8 (3)
[C(5)···C(10)] ∧ [C(17)···C(22)]	107·9 (3)
[C(11)···C(16)] ∧ [C(23)···C(28)]	161·5 (3)
C(12)—C(11)—P(1)—Hg	−164·3 (10)
C(10)—C(5)—P(1)—Hg	−159·8 (7)
C(28)—C(23)—P(2)—Hg	−119·7 (12)
C(18)—C(17)—P(2)—Hg	−164·5 (7)

Table 4. *Selected bond lengths* (Å) *and angles* (°)

Standard deviations are given in parentheses.

Hg—P(1)	2·606 (3)	P(1)—C(5)	1·827 (8)
Hg—P(2)	2·534 (4)	P(1)—C(11)	1·820 (10)
Hg—C(3)	2·188 (17)	P(2)—C(2)	1·835 (11)
Hg—C(4)	2·172 (15)	P(2)—C(17)	1·822 (10)
C(3)—N(1)	1·125 (23)	P(2)—C(23)	1·820 (14)
C(4)—N(2)	1·127 (22)	C(1)—C(1')	1·541 (26)
P(1)—C(1)	1·825 (19)	C(2)—C(2')	1·537 (27)
P(1)—Hg—P(2)	113·5 (1)	C(1)—P(1)—C(5)	104·5 (6)
P(1)—Hg—C(3)	102·2 (4)	C(1)—P(1)—C(11)	104·4 (7)
P(1)—Hg—C(4)	104·9 (4)	C(5)—P(1)—C(11)	107·7 (6)
P(2)—Hg—C(3)	109·1 (4)	Hg—P(2)—C(2)	112·5 (6)
P(2)—Hg—C(4)	116·7 (5)	Hg—P(2)—C(17)	114·8 (4)
C(3)—Hg—C(4)	109·5 (6)	Hg—P(2)—C(23)	113·6 (7)
Hg—C(3)—N(1)	179·1 (14)	C(2)—P(2)—C(17)	105·4 (5)
Hg—C(4)—N(2)	177·2 (20)	C(2)—P(2)—C(23)	108·0 (6)
Hg—P(1)—C(1)	111·2 (4)	C(17)—P(2)—C(23)	101·7 (8)
Hg—P(1)—C(5)	114·4 (3)	P(1)—C(1)—C(1')	113·0 (10)
Hg—P(1)—C(11)	113·8 (5)	P(2)—C(2)—C(2')	114·7 (8)

different (14·4σ); however, their mean length, 2·580 (25) Å, compares well with the value observed in *catena-μ*-[1,5-bis(diphenylphosphino)pentane]-diiodomercury(II) (Aurivillius & Wendel, 1976).

While the mean Hg—P length agrees well with the sum of the covalent radii, the weighted mean of the two Hg—CN bond lengths, 2·179 (14) Å, is much larger than the sum of the covalent radii: 1·48 Å for tetrahedral Hg (Grdenić, 1965), 1·10 Å for P (Pauling, 1960) and 0·687 Å for the *sp* hybridized C (Bastiansen & Skancke, 1961). Some of the angles at the Hg atom deviate from the regular tetrahedral value; however, no particular trend is apparent.

All the other values reported in Table 4 appear satisfactorily regular.

No short contacts occur between the chains in the crystal.

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