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Refinement of the Structure of Metastable Phosphonitrilic Chloride, $(PNCl_2)_4$

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The crystal structure of $(PNCl_2)_4$ has been refined by three-dimensional Fourier syntheses. The crystallographically non-equivalent P–N bonds in the puckered eight-membered ring have an equal length of $1{\cdot}57_0$ Å, s.d. 0·01 Å. The average value for the P–Cl bond lengths is 1·989 Å, s.d. 0·004 Å. The configuration of the molecule is compatible with Craig's or Dewar's theory in which a delocalization of the p–π and d–π electrons is assumed.

Introduction

In an early structure determination of the metastable modification (Lund, Paddock *et al.*, 1960) of $(PNCl_2)_4$ by Ketelaar *et al.* (1939), the lengths of the P–N bonds in the eight-membered ring were found to be equal within rather large experimental error. However, a theoretical prediction (Craig, 1959) of equal S–N bond lengths in the analogous case of $(NSF)_4$ proved to be incorrect (Wiegers & Vos, 1961). Therefore it seemed desirable to refine the structure of $(PNCl_2)_4$ by three-dimensional methods in order to obtain more conclusive evidence about the P–N bond lengths in this compound.

In connection with our work on the thiazylhalides, an investigation of some more phosphonitrilic compounds is in progress. A preliminary structure determination of the stable form of $(PNCl_2)_4$ by two-dimensional syntheses has already shown that the $(PNCl_2)_4$ molecules in this modification are centrosymmetrical. In addition the crystal structures of $(PNCl_2)_6$, $[PN(OH)_2]_4.2H_2O$ and $[PN(OH)(ONa)]_3.4H_2O$ are being investigated. The above structures will be refined by three-dimensional methods.

Experimental

The substance was prepared by the method of Schenk & Römer, described by Ketelaar (1939). Crystals were obtained from a solution in benzene. For the intensity measurements cylindrical crystals were used; they were made by touching a rotating crystal lightly with filter paper soaked with benzene.

Table 1. *Crystallographic data*

Ketelaar *et al.*	Present work
Tetragonal, space group $P4_2/n$	With $\lambda(\text{Cu } K\alpha_1) = 1{\cdot}54050$ Å
Two mol. $(PNCl_2)_4$ per cell	$\lambda(\text{Cu } K\alpha_2) = 1{\cdot}54434$ Å
$a = b = 10{\cdot}82 \pm 0{\cdot}01$ Å	$a = b = 10{\cdot}844 \pm 0{\cdot}002$ Å
$c = 5{\cdot}95 \pm 0{\cdot}01$ Å	$c = 5{\cdot}961 \pm 0{\cdot}005$ Å

The crystallographic data are listed in Table 1. Accurate cell dimensions were obtained from back-reflexion photographs.

The intensities were measured from the following integrated equi-inclination Weissenberg photographs, taken with zirconium-filtered molybdenum radiation.

Crystal	μR	Layer line
1	0·50	0–6 about [001]
2	0·34	0–3 about [001]
3	0·13	0–4 about [110]

The multiple-film technique was applied, Ilford-Industrial G, Industrial B and Industrial C film being used. Corrections for absorption were calculated from Bond's table (Bond, 1959).

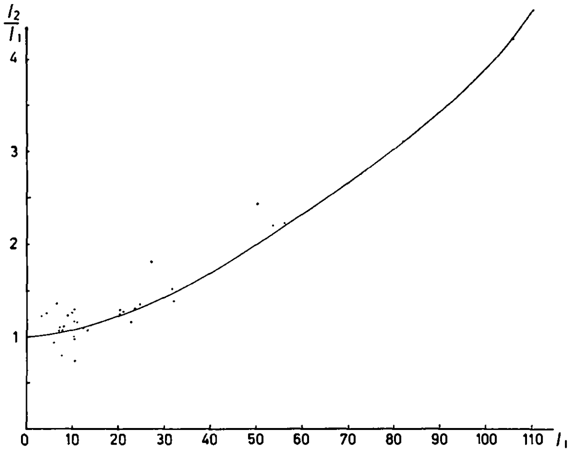

Fig. 1. Correction for extinction (see text). I_1 and I_2 are on the same relative scale.

By comparing the $|F|^2$-values of the reflexions from crystal 1 with those of corresponding reflexions from crystal 3, we found that the intensities obtained from crystal 1 showed strong extinction. These extinction errors could greatly be reduced by comparing, for each layer line about the c axis, the intensities I_1 of the medium and strong reflexions from crystal 1 with the intensities I_2 of the reflexions from crystal 2. A plot of I_2/I_1 versus I_1 for the zero layer line is shown in Fig. 1. It is seen that the correction factor in the intensities I_1 amounts to about 3 for the strongest reflexions $hk0$. The extinction effect appeared to decrease rapidly for increasing values of l, and is vanishingly small for the reflexions $hk3$. For 8 strong reflexions no reliable correction for extinction was obtained.

During the refinement 623 independent reflexions with reliable intensity were taken into account.

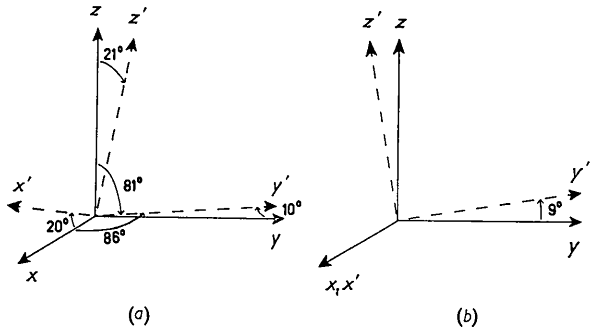

Fig. 2. Directions of x', y' and z' for Cl_1 (a) and Cl_2 (b).

Refinement

The approximate structure is described by Ketelaar (1939). The two $(PNCl_2)_4$ molecules in the unit cell lie on a two-fold special position with symmetry $\bar{4}$, so that the structure contains only one independent $PNCl_2$ group. Starting from Ketelaar's final coordinates, we refined the structure in successive cycles of structure-factor calculations and difference Fourier syntheses. For P and Cl, the atomic scattering factors, calculated by Tomiie & Stam (1958) and for N those calculated by Berghuis *et al.* (1955) were used. The scale factor was determined by comparing observed and calculated structure factors. The atomic shifts were calculated in the usual way (Cochran, 1951).

To obtain accurate values for the bond lengths and angles a certain amount of anisotropic refinement was necessary. We did not aim at a complete refinement of the thermal parameters, however. As no machine-program for the calculation of structure factors with anisotropic temperature factors was available, the structure factors were computed by substituting the anisotropically vibrating atoms by a number of fractional atoms (Vos & Smits, 1961).

During the refinement of the [001] projection, the principal axes of vibration were assumed to coincide with the x and y axis, so that only the parameters B_x and B_y in the temperature factor $\exp -(B_x\xi^2/4 + B_y\eta^2/4)$ (Kartha & Ahmed, 1960) were determined. Corrections in B_x and B_y were first calculated with Hamilton's formula (1955), the parameters α being determined from the curvatures in $\ln \varrho$ at the atomic maxima in a Fourier synthesis of the calculated structure factors. When it appeared that the required corrections were underestimated in this way, further corrections were estimated by comparing successive difference Fourier syntheses.

From the [100] projection we only obtained approximate values for the z-coordinates, because of overlap.

As initial values for the three-dimensional refinement, the final parameters from the projections and estimated B_z values were taken. The directions of the principal axes of vibration x', y' and z', were determined from the first three-dimensional difference map and were kept constant during the refinement. The main directions of vibration of P and N coincide with the crystal axes. For Cl_1 and Cl_2 the directions of x', y' and z' are shown in Figs. 2(*a*) and (*b*) respectively. Corrections in the temperature factor parameters were calculated by using Cochran's formula 4·8 (Cochran, 1951).

At the end of the refinement the residual R amounted to 6·8%. Only a rough estimate of the standard deviations in the coordinates could be made. As the final difference map still shows slight errors in the temperature-factor parameters, Cruickshank's formula (Cruickshank, 1949) will only give a lower limit for the possible errors. The estimated 'standard deviations' listed in Table 2 are twice the values calculated with Cruickshank's formula. The atomic shifts from the final difference Fourier map were small in comparison with these standard deviations.

Table 2. *Final coordinates**

	x	S.d.	y	S.d.	z	S.d.
P	0·2049	0·0002	0·0750	0·0002	0·8094	0·0004
N	0·1119	0·0007	0·1556	0·0006	0·6706	0·0018
Cl_1	0·1477	0·0003	0·0500	0·0004	0·1225	0·0006
Cl_2	0·1924	0·0003	0·9064	0·0002	0·6784	0·0006

* The coordinates refer to the centre of symmetry as origin.

Table 3. *Corrections of Ketelaar's final coordinates*

	Δx	Δy	Δz
P	−0·039 Å	+0·016 Å	−0·123 Å
N	−0·142	+0·115	+0·212
Cl_1	−0·003	−0·011	−0·104
Cl_2	−0·001	+0·010	−0·039

Table 4. *Temperature factor parameters*

	$B_{x'}$	$B_{y'}$	$B_{z'}$
P	1·57 Å²	1·77 Å²	2·57 Å²
N	1·99	1·94	2·74
Cl_1	2·71	5·21	2·21
Cl_2	4·09	1·71	4·01

The final coordinates are listed in Table 2 and are compared with Ketelaar's coordinates in Table 3. Table 4 shows the temperature factor parameters $B_{x'}$, $B_{y'}$ and $B_{z'}$. The observed and calculated structure factors are listed in Table 5.

Table 5. *Observed and calculated structure factors*

In order to obtain F_o and F_c on the absolute scale, the values in the table must be multiplied by ¼
The reflexions which could not be corrected for extinction are marked *

h	k	l	F_o	F_c
2	0	0	52	-37
4	0	0	264*	-315
6	0	0	85	-78
8	0	0	205	-211
10	0	0	90	87
14	0	0	73	70
16	0	0	46	-41
1	1	0	200*	-169
3	1	0	478*	-678
5	1	0	187	172
7	1	0	65	-70
11	1	0	57	43
13	1	0	48	52
2	2	0	346*	-421
4	2	0	146	152
6	2	0	458*	512
8	2	0	145	156
10	2	0	124	-131
12	2	0	144	-141
1	3	0	251*	283
3	3	0	91	-74
5	3	0	37	-40
7	3	0	104	-106
9	3	0	144	-147
13	3	0	108	105
4	4	0	59	-54
6	4	0	191	-206
12	4	0	177	183
14	4	0	68	64
16	4	0	75	-66
1	5	0	294*	-365
3	5	0	229	251
5	5	0	127	128
7	5	0	281	289
11	5	0	110	-115
15	5	0	96	-83
2	6	0	112	121
4	6	0	60	54
6	6	0	150	-173
10	6	0	91	-98
12	6	0	41	36
14	6	0	45	-52
18	6	0	71	56
1	7	0	118	-124
3	7	0	126	126
5	7	0	226	-247
7	7	0	91	-73
11	7	0	88	87
13	7	0	94	92
2	8	0	75	-80
4	8	0	132	138
6	8	0	130	133
8	8	0	52	48
1	9	0	103	-99
5	9	0	71	70
13	9	0	82	-80
2	10	0	50	43
8	10	0	135	-130
10	10	0	74	72
12	10	0	52	52
1	11	0	102	99
3	11	0	69	-66
5	11	0	111	112
7	11	0	72	-53
11	11	0	84	76
13	11	0	37	-40
2	12	0	67	-57
4	12	0	70	-64
6	12	0	83	74
10	12	0	59	49
12	12	0	71	-55
1	13	0	140	135
3	13	0	50	-43
1	15	0	70	-68
4	16	0	70	58
1	0	1	320	294
2	0	1	201	-186
3	0	1	266	-285
4	0	1	154	-153
6	0	1	85	85
7	0	1	97	102
8	0	1	85	88
9	0	1	160	-172
13	0	1	71	-72
1	1	1	150	130
2	1	1	210	207
3	1	1	246	256
4	1	1	236	-257
5	1	1	164	175
8	1	1	167	-183
9	1	1	92	-79
10	1	1	121	129
11	1	1	85	-78
12	1	1	169	165
2	2	1	234	-249
3	2	1	102	102
4	2	1	86	-83
5	2	1	120	121
6	2	1	79	-81
1	3	1	264	-277
2	3	1	301	-329
3	3	1	180	-190
4	3	1	49	50
5	3	1	55	61
6	3	1	104	112
7	3	1	42	43
8	3	1	51	51
9	3	1	92	98
12	3	1	141	-129
1	4	1	129	-127
3	4	1	178	193
4	4	1	222	236
5	4	1	58	58
6	4	1	24	21
7	4	1	220	-242
8	4	1	71	-62
9	4	1	86	100
10	4	1	62	-62
1	5	1	152	-149
3	5	1	116	-127
4	5	1	253	275
6	5	1	230	-261
7	5	1	39	-39
8	5	1	49	-49
9	5	1	67	-68
10	5	1	69	69
14	5	1	74	76
1	6	1	356	-444
2	6	1	150	-162
5	6	1	135	154
6	6	1	71	74
9	6	1	133	140
10	6	1	51	52
11	6	1	92	-92
12	6	1	55	47
3	7	1	94	102
4	7	1	186	212
6	7	1	151	-154
9	7	1	74	-79
10	7	1	58	52
1	8	1	139	142
3	8	1	54	45
5	8	1	139	-151
7	8	1	124	-130
8	8	1	78	-73
2	9	1	111	-136
4	9	1	58	-64
6	9	1	74	85
8	9	1	104	99
11	9	1	54	52
1	10	1	93	91
2	10	1	88	82
3	10	1	62	72
7	10	1	126	130
2	11	1	188	193
4	11	1	130	-143
8	11	1	54	-61
10	11	1	56	-59
12	11	1	73	79
5	12	1	65	-65
7	12	1	95	91
2	13	1	105	95
6	13	1	75	74
1	14	1	82	81
5	16	1	71	56
0	0	2	444*	-543
1	0	2	232	-239
2	0	2	91	81
3	0	2	189	-190
4	0	2	91	92
5	0	2	161	167
6	0	2	91	92
7	0	2	129	132
8	0	2	126	126
9	0	2	73	60
10	0	2	111	-121
11	0	2	72	59
13	0	2	61	-58
2	1	2	246	-245
3	1	2	140	139
4	1	2	145	139
5	1	2	120	-129
6	1	2	47	52
7	1	2	83	82
8	1	2	211	-234
10	1	2	45	51
1	2	2	260	-251
2	2	2	173	162
3	2	2	40	31
4	2	2	85	-83
5	2	2	308	328
6	2	2	143	-146
7	2	2	200	-221
8	2	2	63	-62
9	2	2	89	-95
10	2	2	56	49
11	2	2	67	71
12	2	2	97	102
15	2	2	75	68
1	3	2	81	-82
2	3	2	142	-142
4	3	2	129	132
5	3	2	55	58
6	3	2	93	106
7	3	2	61	62
8	3	2	83	-93
10	3	2	126	126
2	4	2	134	-130
3	4	2	135	-145
6	4	2	163	164
7	4	2	183	-197
9	4	2	69	67
11	4	2	104	107
12	4	2	73	-73
13	4	2	56	-61
1	5	2	198	202
2	5	2	60	66
3	5	2	110	-110
4	5	2	149	141
5	5	2	35	37
7	5	2	139	-142
8	5	2	54	-41
11	5	2	76	81
1	6	2	45	52
2	6	2	117	-117
3	6	2	115	115
6	6	2	76	77
8	6	2	70	-73
10	6	2	53	56
11	6	2	48	-50
1	7	2	50	-44
3	7	2	98	-104
4	7	2	103	-116
5	7	2	167	173
6	7	2	171	-185
7	7	2	38	33
8	7	2	96	101
10	7	2	63	48
1	8	2	110	-105
2	8	2	64	69
3	8	2	205	219
5	8	2	51	-44
6	8	2	48	-55
7	8	2	52	65
8	8	2	47	-45
11	8	2	55	-54
2	9	2	181	188
4	9	2	102	120
5	9	2	58	-63
6	9	2	80	-80
7	9	2	51	-41
10	9	2	79	-85
1	10	2	60	-63
2	10	2	66	-59
4	10	2	53	37
5	10	2	196	-206
8	10	2	90	90
9	10	2	76	76
1	11	2	39	-39
3	11	2	94	99
8	11	2	71	66
1	12	2	76	71
3	12	2	53	56
6	12	2	88	-81
1	13	2	89	-94
2	13	2	57	-57
4	13	2	98	-104
3	14	2	70	-70
5	14	2	57	57
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2	0	3	154	143
3	0	3	98	-89
4	0	3	85	89
6	0	3	79	-77
7	0	3	90	-91
8	0	3	93	-95
13	0	3	48	50
16	0	3	66	62
1	1	3	50	-46
2	1	3	179	-177
3	1	3	340	-347
4	1	3	167	175
5	1	3	203	-203
6	1	3	93	90
7	1	3	133	148
9	1	3	95	92
11	1	3	105	105
13	1	3	59	-63
15	1	3	49	-50
2	2	3	241	245
3	2	3	136	143
5	2	3	69	63
6	2	3	149	158
7	2	3	57	-62
8	2	3	48	-49
9	2	3	61	-60
14	2	3	66	-69
1	3	3	311	309
2	3	3	61	-66
3	3	3	159	170
4	3	3	43	-49
5	3	3	25	-26
6	3	3	96	-105
8	3	3	59	-59
9	3	3	171	-195
12	3	3	79	74
15	3	3	83	76
1	4	3	112	-120
3	4	3	70	67
4	4	3	299	-323
5	4	3	71	74
6	4	3	34	40
7	4	3	59	70
8	4	3	64	60
10	4	3	81	77
1	5	3	131	133
2	5	3	134	139
3	5	3	64	76
4	5	3	42	37
5	5	3	38	-34
7	5	3	41	36
8	5	3	38	-52
9	5	3	77	75
13	5	3	60	-54
2	6	3	178	185
4	6	3	64	63
5	6	3	99	-104
6	6	3	51	-55
7	6	3	53	-52
8	6	3	57	-60
10	6	3	75	-71
11	6	3	65	64
12	6	3	73	-62
14	6	3	70	65
1	7	3	88	-100
2	7	3	52	55
3	7	3	117	-126
5	7	3	32	-28
9	7	3	93	103
1	8	3	44	43
2	8	3	128	-130
3	8	3	49	34
4	8	3	45	48
6	8	3	56	-53
8	8	3	100	99
10	8	3	74	73
12	8	3	55	-60
1	9	3	49	-51
3	9	3	51	40
5	9	3	93	104
6	9	3	42	-49
7	9	3	70	-70
11	9	3	86	-79
2	10	3	101	-105
4	10	3	87	91
2	11	3	41	-34
3	11	3	49	-46
7	13	3	48	40
2	14	3	48	47
4	14	3	94	-89
2	16	3	58	52
0	0	4	250	-271
2	0	4	49	-47
3	0	4	209	212
4	0	4	78	80
5	0	4	69	68
6	0	4	36	-39
7	0	4	66	-72
9	0	4	89	-87
10	0	4	67	68
11	0	4	50	-39
13	0	4	60	63
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2	1	4	84	90
3	1	4	181	186
4	1	4	42	-38
6	1	4	95	-92
7	1	4	46	-42
8	1	4	63	69
9	1	4	51	50
10	1	4	70	-74
15	1	4	30	-36
1	2	4	130	-130
2	2	4	52	52
3	2	4	64	-68
5	2	4	199	-215
6	2	4	160	-168
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8	2	4	29	-35
9	2	4	89	94
10	2	4	35	39
15	2	4	89	-83
1	3	4	63	-59
2	3	4	170	179
3	3	4	80	78
4	3	4	94	99
5	3	4	31	-31
6	3	4	29	-31
8	3	4	43	49
9	3	4	88	95
10	3	4	95	-96
12	3	4	36	31
13	3	4	35	-23
1	4	4	38	-42
2	4	4	121	120
3	4	4	154	169
5	4	4	57	-56
6	4	4	47	-40
7	4	4	31	33
8	4	4	44	41
9	4	4	103	-103
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8	5	4	44	49
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10	5	4	49	48
12	5	4	44	45
14	5	4	47	-43
2	6	4	39	40
3	6	4	25	39
5	6	4	37	39
6	6	4	29	42
8	6	4	65	64
11	6	4	47	47
13	6	4	38	-37
1	7	4	116	122
2	7	4	48	56
4	7	4	58	62
6	7	4	72	67
8	7	4	128	-133
1	8	4	77	67
3	8	4	160	-171
4	8	4	105	-113
5	8	4	27	27
6	8	4	24	-28
7	8	4	47	-45
11	8	4	70	70
13	8	4	40	-42
1	9	4	47	47
2	9	4	76	-71
4	9	4	75	-69
6	9	4	54	60
7	9	4	68	66
10	9	4	76	77
1	10	4	47	56
2	10	4	28	34
5	10	4	119	118
9	10	4	44	-53
3	11	4	57	-65
3	12	4	31	-29
5	12	4	45	-45
6	12	4	40	39
9	12	4	50	44
4	13	4	68	61
3	14	4	77	76
5	14	4	36	-34
11	14	4	36	-32
6	15	4	52	-44
8	15	4	43	36
1	16	4	54	-53
3	0	5	87	88
4	0	5	98	81
5	0	5	32	15
6	0	5	30	-23
9	0	5	37	38
10	0	5	55	51
11	0	5	42	-33
12	0	5	48	-41
3	1	5	150	154
4	1	5	19	18
5	1	5	45	34
6	1	5	26	-22
7	1	5	167	-170
8	1	5	45	44
10	1	5	43	-37
11	1	5	35	-24
12	1	5	57	-56
15	1	5	43	38
2	2	5	30	-31
3	2	5	63	-68
4	2	5	109	107
5	2	5	50	-38
6	2	5	109	-109
8	2	5	59	63
10	2	5	56	57
12	2	5	29	-39
14	2	5	41	27
1	3	5	87	-81
2	3	5	82	88
3	3	5	25	18
5	3	5	64	-63
7	3	5	56	-56
9	3	5	135	131
15	3	5	39	-31
1	4	5	62	63
3	4	5	76	-75
4	4	5	106	105
6	4	5	87	-93
7	4	5	59	52
8	4	5	32	29
9	4	5	34	-35
11	4	5	32	-21
12	4	5	35	-30
1	5	5	38	35
2	5	5	41	-41
3	5	5	94	88
4	5	5	94	-92
6	5	5	84	83
11	5	5	51	-46
13	5	5	26	22
1	6	5	115	117
4	6	5	123	-120
5	6	5	37	-15
6	6	5	58	-45
8	6	5	66	54
9	6	5	47	-44
4	7	5	57	-60
5	7	5	40	41
6	7	5	50	44
7	7	5	98	81
10	7	5	37	-36
1	8	5	65	-69
2	8	5	163	164
5	8	5	53	44
6	8	5	51	60
7	8	5	32	42
8	8	5	26	-24
10	8	5	75	-68
1	9	5	76	72
3	9	5	76	-77
5	9	5	115	-114
7	9	5	38	32
8	9	5	26	-26
11	9	5	37	32
1	10	5	38	-39
4	10	5	81	-78
6	10	5	69	55
7	10	5	39	-38
8	10	5	41	39
1	11	5	54	53
2	11	5	49	-46
3	11	5	34	42
4	11	5	50	43
5	11	5	54	52
9	11	5	46	-43
2	12	5	34	-29
4	12	5	40	-31
1	13	5	41	-38
2	13	5	36	-37
5	13	5	42	28
9	13	5	33	33
4	14	5	68	66
7	15	5	39	-36
2	16	5	37	-36
0	0	6	156	165
3	0	6	107	-105
4	0	6	37	-40
5	0	6	121	-120
6	0	6	39	-39
8	0	6	59	-53
9	0	6	43	42
10	0	6	49	54
11	0	6	22	15
4	1	6	28	-23
5	1	6	62	62
6	1	6	77	67
7	1	6	35	-32
10	1	6	35	34
12	1	6	39	-34
2	2	6	60	-55
3	2	6	29	33
4	2	6	34	22
5	2	6	37	36
6	2	6	57	61
8	2	6	26	24
9	2	6	50	-43
11	2	6	39	-36
12	2	6	46	-45
15	2	6	48	38
2	3	6	106	-92
3	3	6	21	8
4	3	6	130	-131
5	3	6	21	-23
7	3	6	31	-25
14	3	6	34	29
3	4	6	80	-80
5	4	6	56	54
6	4	6	72	-64
7	4	6	65	65
9	4	6	57	52
12	4	6	32	29
1	5	6	76	-69
2	5	6	33	40
3	5	6	44	44
4	5	6	41	36
7	5	6	61	54
10	5	6	59	-53
11	5	6	35	-33
12	5	6	29	-22
1	6	6	36	-33
2	6	6	58	47
3	6	6	69	-75
5	6	6	41	-37
6	6	6	39	-43
8	6	6	29	35
13	6	6	49	39
2	7	6	51	-45
3	7	6	49	53
5	7	6	84	-76
8	7	6	68	61
2	8	6	31	-35
3	8	6	46	47
6	8	6	35	21
9	8	6	34	-30
11	8	6	38	-30
2	9	6	25	-23
5	9	6	30	24
1	10	6	29	-23
8	10	6	38	-35
3	11	6	38	-37
5	11	6	27	22
6	12	6	35	29
1	13	6	46	44
3	14	6	35	-30
1	16	6	35	26

Discussion of the structure

The arrangement of the molecules is shown in Fig. 4 in Ketelaar's paper. The smallest intermolecular distances are those between chlorine atoms, the minimum distance, 3·68 Å, agreeing well with the sum of the Van der Waals radii, 3·60 Å.

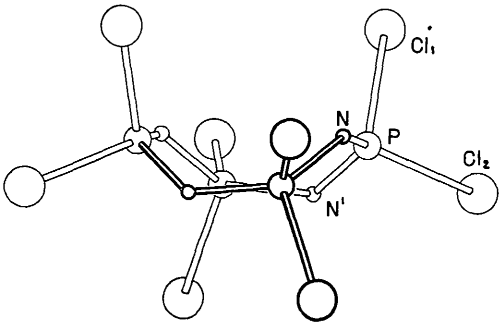

Fig. 3. Molecule of $(PNCl_2)_4$.

The $(PNCl_2)_4$ molecule, which is shown in Fig. 3, contains a fourfold inversion axis. The puckered eight-membered ring of alternating phosphorus and nitrogen atoms has a tub-like form. In Table 6 our intramolecular distances and angles are compared with those given by Ketelaar. No correction for thermal motion was made in calculating the atomic distances. The standard deviations are estimated from the standard deviations in the coordinates, listed in Table 2. The P–Cl bond lengths are equal within experimental error. The average value, 1·989 Å, agrees with the P–Cl bond lengths known from other structures, e.g. 2·03 ± 0·02 Å in PCl_3, PCl_2F and $PClF_2$ and 2·00 ± 0·02 Å in $POCl_3$, $POCl_2F$, $POClF_2$ and $PSCl_3$ (Sutton, 1958).

Table 6. *Intramolecular distances and bond angles*

	Ketelaar *et al.* Distance	Refined value Distance	S.d.
P–N	1·66 Å	$1{\cdot}57_0$ Å	0·009 Å
P–N′	1·69	$1{\cdot}56_9$	0·009
$P–Cl_1$	1·98	1·985	0·004
$P–Cl_2$	2·02	1·993	0·004
$Cl_1 \cdots Cl_2$	3·17	3·109	0·005
$P \cdots P'$	2·93	2·861	0·003
$N \cdots N'$	2·85	2·73	0·01
$N \cdots Cl_1$	3·18	2·953	0·009
$N \cdots Cl_2$	2·71	2·840	0·009
$N' \cdots Cl_1$	2·88	2·838	0·009
$N' \cdots Cl_2$	3·14	2·914	0·009
$Cl_1' \cdots Cl_2$		4·23	0·005
	Angle	Angle	
$Cl_1–P–Cl_2$	105°	102·8°	0·2°
N–P–N	117	121·2	0·5
P–N–P	123	131·3	0·6
$Cl_1–P–N$		111·8	0·4
$Cl_1–P–N'$		105·3	0·4
$Cl_2–P–N$		105·1	0·4
$Cl_2–P–N'$		109·2	0·4

The values found for the lengths of the two crystallographically non-equivalent P–N bonds show that the P–N bonds in the eight-membered ring are essentially equal. The P–N bond length, 1·57 Å, is significantly smaller than the value, 1·67 Å, reported by Ketelaar and is even smaller than the sum, 1·60 Å, of the covalent radii for a double P–N bond (Pauling, 1945). Short P–N bond lengths have also been found in other phosphonitrilic compounds, e.g. 1·59 Å in $[PN(NMe_2)_2]_4$ (Bullen, 1960), 1·53–1·61 Å in $(PNCl_2)_3$ (Wilson & Carroll, 1960; Giglio, 1960) and 1·51 Å in $(PNF_2)_4$ (McGeachin & Tromans, 1960). The phosphorus atom is four-coordinated. The bonds point to the corners of a distorted tetrahedron. The N–P–N bond angle is large in comparison with the tetrahedral value, 109·5°. The P–N–P bond angle is larger than the angle between two p orbitals, 90°, or between two sp^2 hybrid orbitals, 120°.

Theoretical discussions of the electronic structure of the phosphonitrilic chlorides have been given recently (for a review see Paddock, 1960; Dewar *et al.*, 1960). Craig (1958) pointed out that d orbitals may take part in the binding. Besides σ bonds, the phosphonitrilic chlorides will form π bonds due to the interaction between phosphorus d–π and nitrogen p–π orbitals.

Our values for the bond lengths and angles suggest that the σ bonds in $(PNCl_2)_4$ are established by sp^3 hybrid orbitals of phosphorus and sp^2 hybrid orbitals of nitrogen. The relatively planar configuration of the eight-membered ring, corresponding to the large P–N–P and N–P–N bond angles, and the equal lengths of the P–N bonds support the assumption of a delocalization of the p–π and d–π electrons. From our experimental evidence it cannot be concluded, however, whether this delocalization is complete (Craig, 1959) or restricted to a three-centre P–N–P π bond (Dewar, 1960).

The Fourier syntheses and structure factors were calculated on the digital computer ZEBRA, with programs devised by Dr D. W. Smits. Bond lengths and angles were calculated with a program devised by Dr D. Rogers. We wish to thank Prof. E. H. Wiebenga for his interest throughout the course of this investigation, and Dr D. W. Smits and Mr H. Schurer for operating the ZEBRA. The Netherlands Organization for the Advancement of Pure research (ZWO) supported this work indirectly.

References

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Bond, W. L. (1959). *Acta Cryst.* **12**, 375.

Bullen, G. J. (1960). *Proc. Chem. Soc.*, p. 425.

Cochran, W. (1951). *Acta Cryst.* **4**, 408.

CRAIG, D. P. (1958). Special Publication, no. 12, p. **343**. London: The Chemical Society.
CRAIG, D. P. (1959). *J. Chem. Soc.*, p. 997.
CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
DEWAR, M. J. S., LUCKEN, E. A. C. & WHITEHEAD, M. A. (1960). *J. Chem. Soc.*, p. 2423.
GIGLIO, E. (1960). *Ric. Sci.* **30**, 721.
HAMILTON, W. C. (1955). *Acta Cryst.* **8**, 841.
KARTHA, G. & AHMED, F. R. (1960). *Acta Cryst.* **13**, 532.
KETELAAR, J. A. A. & VRIES, T. A. DE (1939). *Rec. Trav. Chim. Pays-Bas*, **58**, 1081.
LUND, L. G., PADDOCK, N. L., PROCTOR, J. E. & SEARLE, H. T. (1960). *J. Chem. Soc.*, p. 2542.
MCGEACHIN, H. MCD. & TROMANS, F. R. (1960). *Chem. and Ind.*, p. 1131.
PADDOCK, N. L. (1960). *Endeavour*, **19**, 134.
PAULING, L. (1945). *The Nature of the Chemical Bond*, Ithaca: Cornell University Press.
SUTTON, L. E. (1958). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Spec. Publ. no. 11. London: The Chemical Society.
TOMIIE, Y. & STAM, C. H. (1958). *Acta Cryst.* **11**, 126.
VOS, A. & SMITS, D. W. (1961). *Acta Cryst.* **14**, 1299.
WIEGERS, G. A. & VOS, A. (1961). *Acta Cryst.* **14**, 562.
WILSON, A. & CAROLL, D. F. (1960). *J. Chem. Soc.*, p. 2548.

Acta Cryst. (1962). **15**, 543

The Structure of the μ-Phase Co_7Mo_6

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The μ-phase structure of Co_7Mo_6 has been confirmed by making single-crystal measurements. The atomic parameters show some significant changes when compared with those in μFe_7W_6, and the interatomic distances in Co_7Mo_6 are compared with those in other transition-metal phases. The distribution of atoms in the available sites appears to be completely ordered.

1. Introduction

The cobalt–molybdenum system has been investigated by several workers. The phase diagram in the range 0–50 at.% Mo was determined by Raydt & Tammann (1913), Takei (1928), Sykes & Graff (1935) and Haschimoto (1937). Two intermediate phases were found in this range: Co_3Mo at 25 at.% Mo and Co_7Mo_6 at 46·15 at.% Mo. Takei detected the phase Co_2Mo_3 at 60 at.% Mo, which was later confirmed by Sykes & Graff (1935) and Ham (1950). Co_2Mo_3 has a σ-phase structure (Summers-Smith, 1951; Goldschmidt, 1951).

Henglein & Kohsok (1949) showed that the intermediate phase Co_7Mo_6 was isotypic with Fe_7W_6 by comparison of their X-ray powder photographs. The structure of the latter phase had been determined by Westgren (1936) using Arnfelt's (1928) data.

The present work is concerned with the refinement of the structure of Co_7Mo_6.

2. Material

The crystal used in this work was prepared by heating pressed compacts of the two metal powders. The composition of the compacts was 58·25 wt.% Mo (i.e. 46·15 at.% Mo) and each compact was melted in an aluminium boat under 10^{-5} mm. Hg pressure using an induction heater.

Some difficulty was experienced in finding a sufficiently large single crystal and three melts had to be prepared. A few crystals of reasonable size were obtained, the habit being plate-like, with the c_{hex}-axis perpendicular to the plate. X-ray examination showed that every crystal was twinned; however, one of these crystals was successfully used for the refinement of the structure.

3. Unit cell and space group

Accurate lattice parameters were determined by the method of Farquhar & Lipson (1946). The values obtained are compared with those of Henglein & Kohsok in Table 1.

Table 1. *The lattice parameters of* Co_7Mo_6

		Henglein & Kohsok's values	
	Present investigation	58·4 wt.% Mo	Alloy at Co rich end of composition range
a_{hex}	4·762 ± 0·001 Å	4·767 ± 0·005 Å	4·725 ± 0·05 Å
c_{hex}	25·615 ± 0·005	25·65 ± 0·01	25·42 ± 0·02
a_{rh}	8·970	8·980	8·873
α	30° 47′	30° 48′	30° 53′

Laue and Weissenberg photographs were consistent with the space group $R32$, $R3m$ and $R\bar{3}m$. The last

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