mothiophene it is impossible to derive from the electron diffraction data whether the thiophene ring deviates from C_{2v}-symmetry or is distorted at all upon halogen substitution.

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The Crystal and Molecular Structure of cis-Dichloro(meso-2,3-diaminobutane)palladium(II)

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The crystal and molecular structure of cis-dichloro(meso-2,3-diaminobutane)palladium(II), [PdCl$_2$(C$_4$H$_{12}$N$_2$)], has been determined from three-dimensional X-ray diffractometer data. The compound crystallizes in the orthorhombic space group *Pbca* with eight molecules in a unit cell of dimensions $a = 10\cdot072$, $b = 16\cdot093$ and $c = 10\cdot932$ Å. The structure was refined by block-diagonal least-squares methods using 1628 independent reflexions to give $R = 0\cdot038$. The complex molecule has square-planar coordination. Two chlorine atoms are in cis positions with Pd-Cl distances of $2\cdot316$ and $2\cdot318$ Å. The five-membered chelate ring is puckered. One of the two substituted methyl groups is equatorial with respect to the chelate ring, whereas the other is axial. The molecule is dissymmetric and two enantiomeric molecules exist in the crystal. Each enantiomer is linked by a N–H---Cl hydrogen bond to form a chain parallel to the *c* axis. These chains are also bound laterally by N–H---Cl bonds. Thus the molecules make up a two-dimensional network parallel to the plane (010). The Pd–Pd distance is $3\cdot34$ Å, suggesting a weak interaction between the *d* orbitals.

Introduction

meso-2,3-Diaminobutane usually coordinates to a metal atom to form a puckered chelate ring. Consequently one of the two C–CH$_3$ bonds will be in the equatorial position with respect to the chelate ring, whereas the other will be in the axial position. The nuclear magnetic resonance spectra of the Pt(II) or Co(III) complex containing this ligand in heavy water show only one signal corresponding to the methyl group, suggesting a puckering motion of the chelate ring in solution (Yano, Ito, Koike, Fujita & Saito, 1969). The structure determination of cis-dichloro-(*meso*-2,3-diaminobutane)palladium(II) has been undertaken to obtain structural details of the chelate ring in crystals, since the crystals of this palladium analogue are extremely suitable for X-ray analysis.

However, the crystals were sparingly soluble in water and measurement of nuclear magnetic resonance was unsuccessful.

Experimental

A sample of the complex was kindly supplied by Dr H. Ito and Professor K. Saito of Tohoku University. Suitable crystals were grown by slow evaporation of an aqueous solution. Preliminary oscillation and Weissenberg photographs showed that the crystals are orthorhombic with systematic absences given by 0*kl*: $k = 2n + 1$, *h0l*: $l = 2n + 1$, *hk0*: $h = 2n + 1$. These absences are consistent with the space group *Pbca* (No. 61). A specimen for intensity measurements was selected from the recrystallized sample without further treatment; the crystal was approximately cubic (about 0·2 mm in dimension). The intensity data were meas-

ured on a Rigaku automatic four-circle diffractometer by the ω–2θ scan method. Mo $K\alpha$ radiation and a scintillation counter were used. 1628 independent reflexions up to $2\theta = 55°$ were measured. The data were converted to $|F|$ by applying Lorentz and polarization corrections. No corrections were made for absorption.

The unit-cell dimensions and their estimated probable errors, measured on the Rigaku diffractometer (Mo $K\alpha = 0.7107$ Å), are $a = 10.072 \pm 0.005$, $b = 16.093 \pm 0.005$ and $c = 10.932 \pm 0.005$ Å at 15°C: $U = 1772.0$ Å^3; $D_m = 2.006$ g.cm^{-3} at 15°C; $D_x = 1.991$ g.cm^{-3} for 8 molecules, $F(000) = 1040$, M.W. $= 265.46$, linear absorption coefficient for Mo $K\alpha$ radiation $\mu = 25.6$ cm^{-1}.

Determination and refinement of the structure

The positions of the palladium atoms were easily determined from the prominent peaks in the three-dimensional Patterson function. Other lighter atoms except hydrogen were located by routine application of the heavy-atom method. The atomic positions and the isotropic thermal parameters were refined by the least-squares method with a block-diagonal program *HBLS* written by Dr Ashida. All reflexions were given unit weight and the scattering factors for Pd, Cl, C and N were those listed in *International Tables for X-ray Crystallography* (1962). After five cycles the structure converged with $R = 0.067$. Five further cycles of least-squares refinements were performed in anisotropic modes. R then reduced to 0.043. Two successive difference syntheses at this stage revealed the position of all hydrogen atoms. After inclusion of the hydrogen atoms a final set of least-squares calculations was carried out, but temperature factors of the hydrogen
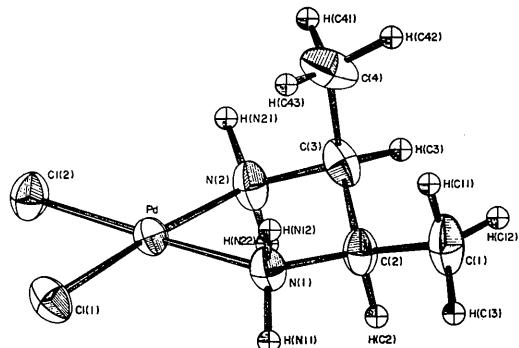

Fig. 1. A perspective drawing of *cis*-dichloro(*meso*-2,3-diaminobutane)palladium(II) and numbering scheme of atoms. The ellipsoids show the thermal motions of the atoms with a probability of 50%.
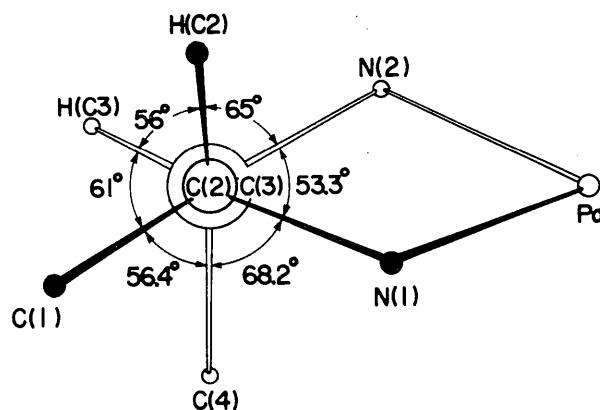
Fig. 2. A Newman projection of a *meso*-2,3-diaminobutane molecule along the C(2)–C(3) bond.
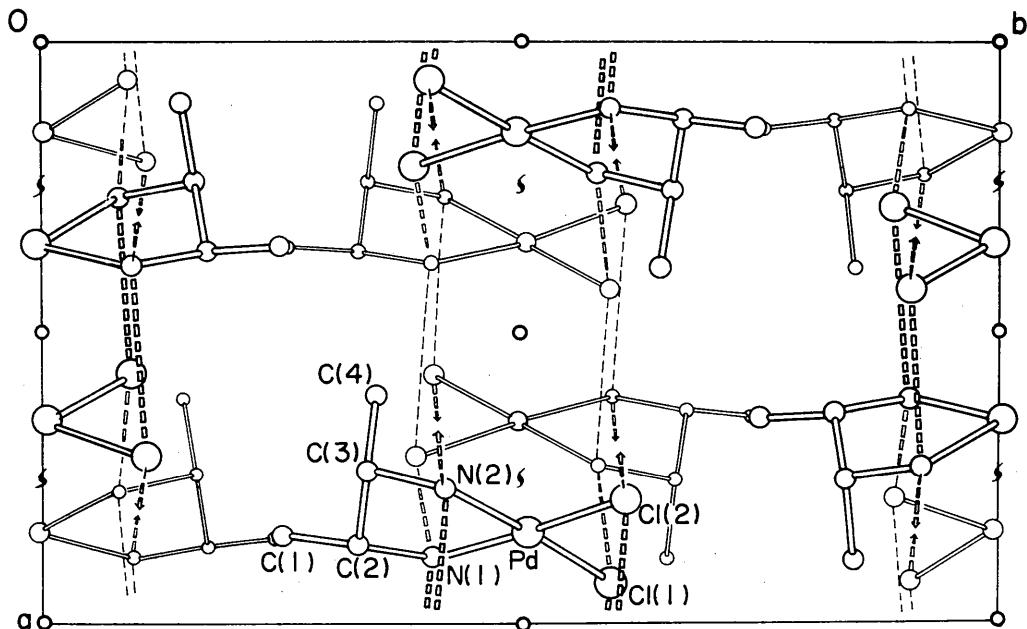
Fig. 3. A projection of the crystal structure along the c axis (from $z = 0$ to $z = 1$).

atoms were assumed to be isotropic and were given the same values as those of the atoms to which the hydrogen atoms were attached. In the last cycle of least-squares, all the parameter shifts were well within the corresponding standard deviations. Table 1 gives the observed and calculated structure factors. The *R* value was 0·038 for all the 1628 observed reflexions. Fractional coordinates and thermal parameters are listed in Tables 2 and 3, respectively, together with their estimated standard deviations.

Table 1. *Observed and calculated structure factors*

K	FO	FC
H,L= 0 0		
2	323	342
4	43	32
6	105	93
8	275	272
10	272	274
12	220	220
14	61	61
16	58	60
18	83	82
20	73	74
H,L= 2 0		
0	221	-242
1	18	-23
2	111	-105
3	158	-156
4	61	-56
5	9	6
6	101	-99
7	6	-8
8	114	-114
9	49	-51
10	66	-66
11	99	-100
12	38	-40
13	55	-55
14	23	-24
15	61	-66
16	48	-50
17	30	-31
18	51	-54
19	42	-43
20	10	-15
H,L= 4 0		
0	190	-190
1	22	-19
2	148	-147
3	0	0
4	192	-187
5	11	-9
6	158	-156
7	42	43
8	126	-127
9	85	84
10	97	-97
11	81	82
12	108	-109
13	15	17
14	65	-65
16	53	-58
17	30	29
18	34	-33
19	59	61
H,L= 6 0		
0	99	104
1	62	-61
2	152	155
3	61	-59
4	232	238
5	15	15
6	193	195
7	71	73
8	136	138
9	31	33
10	82	83
11	18	-15
12	78	76
13	23	-22
14	84	85
15	29	32
16	95	95
17	29	30
18	51	51
H,L= 8 0		
1	34	34
2	26	-27
3	9	7
4	10	9
5	46	-47
6	33	33
7	61	-61
9	24	-23
10	32	-33
11	14	-14
12	8	5
13	24	-24
15	58	-57
16	12	5
H,L= 10 0		
0	89	-90
1	11	8
2	87	-88
3	23	21
4	105	-106
5	25	25
6	89	-86
8	55	-55
9	14	-10
10	54	-55
11	12	8
12	77	-76
13	33	31
H,L= 12 0		
0	42	42
2	53	52
3	20	22
4	62	58
6	51	47
8	38	37
H,L= 0 1		
2	17	11
4	90	-86
6	52	-48
8	17	17
10	19	19
12	17	-15
14	44	-47
16	46	-46
H,L= 1 1		
1	230	245
2	19	11
3	161	150
4	94	-89
5	98	91
6	14	13
7	98	93
9	130	130
10	121	-119
11	125	126
12	99	-99
13	63	62
14	20	-20
15	36	35
16	20	-21
17	44	46
18	42	-43
19	37	35
20	51	-53
H,L= 2 1		
1	166	-161
2	87	-85
3	79	-72
4	38	-37
5	13	-14
6	56	54
7	15	-15
8	56	55
9	69	-67
11	93	-92
12	26	-25
13	50	-49
16	23	23
18	18	16
19	12	-15
H,L= 3 1		
1	291	-323
2	39	37
3	231	-225
4	24	-23
5	191	-185
6	53	-49
7	198	-198
8	13	-13
9	198	-200
10	30	29
11	159	-160
12	17	17
13	95	-94
14	29	-31
15	78	-79
16	33	-33
17	89	-90
19	60	-59
H,L= 4 1		
1	45	-43
2	14	-8
3	79	77
4	12	13
5	154	149
6	6	-6
7	79	76
9	12	-11
10	32	32
11	17	-16
12	26	23
13	29	29
15	47	45
17	28	28
H,L= 5 1		
1	84	79
2	10	-13
3	21	22
4	16	15
6	59	57
7	51	50
8	67	66
9	57	56
10	42	42
11	16	17
12	24	24
14	47	47
15	15	17
16	58	61
17	25	25
18	44	42
19	15	13
H,L= 6 1		
1	35	33
2	32	30
4	19	18
5	17	7
6	16	-19
7	26	24
8	42	-41
9	33	31
10	28	-27
11	16	12
13	12	-9
16	12	-12
17	21	23
18	19	-18
H,L= 7 1		
1	88	90
2	45	-44
3	136	137
4	10	-10
5	173	175
6	7	-9
7	116	117
8	29	-28
9	55	56
10	15	-15
11	66	66
12	22	-22
13	82	83
14	39	-37
15	67	65
16	25	-27
17	43	41
H,L= 8 1		
1	50	-49
2	38	36
3	34	-34
4	22	21
5	38	-37
7	40	-40
8	22	-23
9	33	-31
10	18	-16
11	19	-21
12	15	13
13	21	-19
14	24	24
15	24	-22
H,L= 9 1		
1	83	-85
2	29	28
3	97	-98
5	115	-112
6	21	-21
7	91	-90
8	16	-15
9	55	-53
10	16	-16
11	54	-53
13	67	-67
15	50	-48
H,L= 10 1		
1	34	36
2	20	22
4	15	17
5	12	-15
7	8	2
9	23	24
11	20	21
H,L= 11 1		
1	20	-22
4	17	13
5	8	-4
6	21	20
8	16	18
10	16	14
H,L= 12 1		
1	21	21
2	20	-18
5	9	8
H,L= 13 1		
1	60	58
H,L= 0 2		
0	280	307
2	235	228
4	190	184
6	323	315
8	182	175
10	120	116
12	98	98
14	100	100
16	91	91
18	86	84
20	33	31
H,L= 1 2		
0	159	-147
1	17	14
2	88	-79
3	59	-55
4	207	-197
5	9	-7
6	160	-151
7	16	-15
8	83	-78
10	51	-52
11	17	-19
12	107	-105
13	17	-16
14	64	-62
15	42	-43
16	34	-34
17	14	-14
18	17	-13
20	31	-31
H,L= 2 2		
0	233	-249
1	21	-20
2	136	-131
3	20	15
4	9	8
5	25	-23
6	29	-26
7	36	-37
8	69	-67
9	96	-92
10	90	-89
11	48	-49
12	67	-69
13	28	-29
14	24	-24
15	30	-31
16	8	-7
17	46	-46
18	26	-26
19	43	-42
20	18	-19
H,L= 3 2		
0	242	-257
1	77	-73
2	62	-58
3	16	-15
4	104	97
5	25	22
6	71	65
7	80	76
8	43	-45
9	38	38
10	80	-77
11	15	15
12	39	-39
14	21	21
15	54	55
17	36	38
18	10	-12
19	24	22
20	17	-16
H,L= 4 2		
0	79	-77
1	56	55
2	131	-127
3	79	78
4	167	-163
5	30	30
6	158	-154
7	23	-21
8	87	-88
9	11	10
10	69	-71
11	51	53
12	63	-63
13	61	62
14	70	-70
15	33	34
16	55	-55
17	17	19
18	33	-33
19	19	19
H,L= 5 2		
0	161	158
1	38	37
2	100	99
3	42	39
4	110	110
5	31	-32
6	107	107
7	49	-48
8	97	98
10	66	66
11	28	27
12	66	67
14	38	39
15	24	-25
16	53	54
17	23	-23
18	41	39
H,L= 6 2		
0	147	151
2	159	162
3	18	18
4	126	128
5	28	29
6	97	98
7	9	4
8	107	108
9	7	-8
10	122	122
11	10	-7
12	84	84
13	19	19
14	57	57
15	32	32
16	44	42
17	17	18
18	38	36
H,L= 7 2		
0	35	-35
1	8	6
2	55	-55
3	7	-10
4	69	-70
5	13	10
6	44	-43
8	30	-31
9	38	-37
10	29	-32
11	47	-47
12	29	-32
14	31	-32
16	21	-22
17	11	-8
H,L= 8 2		
0	33	33
2	16	1
4	24	-25
5	37	-36
6	11	-10
7	22	-23
8	11	-13
9	20	-19
10	7	4
11	25	-24
12	19	21
13	35	-35
15	34	-34
16	17	-15
H,L= 9 2		
0	43	-43
1	19	19
2	26	-25
3	38	38
4	32	-33
6	40	-40
7	16	-16
8	34	-34
10	18	-18
11	35	36
12	17	-18
13	35	33
H,L= 10 2		
0	68	-66
1	13	-15
2	69	-70
3	20	-18
4	78	-77
5	11	11
6	80	-80
7	28	29
8	54	-54
9	16	17
10	47	-47
12	50	-46
H,L= 11 2		
0	65	65
1	11	-9
2	52	52
4	33	32
6	26	26
8	45	46
10	48	47
H,L= 12 2		
0	34	32
2	41	40
4	51	49
6	44	43
H,L= 0 3		
2	171	167
4	33	-33
6	145	-136
8	83	-81
10	31	-29
12	11	6
14	43	-43
16	85	-85
18	50	-50
20	19	-20
H,L= 1 3		
1	7	-3
2	49	43
3	130	123
4	37	-33
5	192	182
6	43	-40
7	115	109
8	24	-25
9	29	29
10	50	-47
11	9	9
12	32	-32
13	33	34
14	16	-17
15	61	61
16	30	-30
17	48	46
18	36	-37
19	16	16
20	20	-19
H,L= 2 3		
1	136	-130
2	6	-6
3	223	-217
4	36	33
5	258	-255
6	74	68
7	163	-157
8	13	12
9	87	-88
10	29	-28
11	102	-104
12	9	-9
13	93	-92
14	48	47
15	80	-78
16	56	55
17	64	-64
19	38	-36
H,L= 3 3		
1	162	-157
2	13	12
3	164	-159
4	29	28
5	139	-133
6	11	-13
7	115	-113
8	36	-37
9	99	-100
10	7	-6
11	91	-90
12	11	11
13	70	-72
15	59	-60
16	9	-2
17	41	-40
18	12	-10
19	31	-30
H,L= 4 3		
1	115	113
2	15	-11
3	143	140
4	35	33
5	148	147
7	93	91
8	7	8
9	56	57
10	63	63
11	83	83
12	45	44
13	90	89
15	52	51
17	18	17
18	22	22
19	22	19
H,L= 5 3		
1	68	65
2	76	74
3	19	18
4	43	44
5	18	-13
6	7	7
8	6	-2
9	37	35
11	39	39
12	41	42
13	15	13
14	56	58
16	29	29
18	16	12
H,L= 6 3		
1	111	112
2	35	-36
3	23	24
4	34	-33
5	14	-10
7	25	26
8	11	-11
9	72	71
10	39	-38
11	62	62
12	47	-46
14	42	-41
16	27	-20
17	28	28
18	22	-17
H,L= 7 3		
1	105	109
3	68	68
4	8	8
5	42	42
6	12	-13
7	55	56
8	33	-35
9	72	71
10	16	-16
11	68	68
13	43	44
14	14	-15
15	23	20
16	14	-12
17	16	16
H,L= 8 3		
1	144	-146
2	15	-14
3	77	-79
4	24	-24
5	61	-63
6	12	12
7	90	-92
8	28	30
9	101	-101
11	80	-77
13	42	-43
15	37	-35
H,L= 9 3		
1	54	-55
2	17	-16
3	54	-54
4	18	-20
5	64	-64
7	62	-61
8	14	14
9	43	-41
10	15	-10
11	32	-30
12	22	-21
13	29	-29
H,L= 10 3		
1	42	39
2	18	18
3	27	27
4	12	11
5	20	20
7	33	32
9	32	31
10	31	31
11	16	14
12	21	22
H,L= 11 3		
1	15	-9
2	11	-15
6	16	16
8	27	26
10	22	22
H,L= 12 3		
1	26	25
2	17	-16
3	32	32
5	50	47
7	42	41
H,L= 0 4		
0	27	23
2	92	85
4	129	124
6	139	128
8	40	39
10	20	23
12	59	58
14	70	70
16	19	19
18	15	12
20	15	13
H,L= 1 4		
0	66	-60
1	21	20
2	169	-165
3	60	59
4	268	-262
5	28	-24
6	300	-294
7	55	-53
8	110	-108
9	78	-76
10	65	-67
11	13	-10
12	97	-96
14	113	-112
15	23	-24
16	73	-72
17	42	-41
18	49	-49
19	24	-26
20	29	-28
H,L= 2 4		
1	31	-26
2	14	-13
3	14	-13
4	62	-58
5	31	-28
6	78	-74
7	13	-14
8	10	-9
10	12	9
12	24	-25
13	36	-37
14	32	-29
15	28	-29
17	22	-20
H,L= 3 4		
0	58	-53
1	11	11
2	21	-20
3	19	15
4	24	-23
5	76	72
6	85	-79
7	36	37
8	39	-38
9	44	41
10	6	-4
11	20	21
12	10	6
13	57	57
14	19	-20
15	71	73
16	39	-39
17	57	57
18	32	-29
19	18	18
H,L= 4 4		
0	17	-21
1	14	-16
2	78	-73
3	42	-43
4	52	-51
5	11	11
6	31	-32
7	48	47
8	48	-48
9	27	27
10	50	-50
12	9	-8
14	19	-22
15	17	19
16	24	-24
17	21	21
18	17	-18
H,L= 5 4		
0	244	258
1	14	12
2	198	204
3	6	0
4	106	107
5	37	-34
6	119	119
7	24	-24
8	122	123
9	17	15
10	151	153
12	118	118
13	23	-24
14	71	71
15	32	-31
16	46	44
17	11	-14
18	53	52
H,L= 6 4		
0	41	42
1	23	23
2	66	65
3	17	17
4	55	55
6	41	40
7	19	-19
8	45	47
10	49	47
11	23	23
12	21	21
13	19	18
14	26	25
15	16	-13
16	25	23
H,L= 7 4		
0	79	-78
1	40	-42
2	89	-89
3	63	-63
4	81	-78
5	17	-19
6	57	-56
7	28	37
8	60	-61
9	12	-13
10	63	-66
11	47	-54
12	43	-44
13	51	-52
14	33	-33
15	19	-20
16	27	-27
H,L= 8 4		
1	12	-9
3	15	-9
4	8	-3
6	12	12
9	13	-14
11	22	-22
H,L= 9 4		
0	81	-83
2	58	-59
4	21	-25
6	39	-40
7	19	20
8	50	-47
9	41	41
10	57	-58
11	43	42
12	39	-36
13	19	18
14	15	-13
H,L= 10 4		
0	49	-50
2	35	-34
3	9	8
4	9	-11
6	22	-19
8	30	-29
10	28	-29
12	19	-19
H,L= 11 4		
0	64	63
1	7	-4
2	70	70
4	71	70
6	70	69
8	65	64
H,L= 12 4		
0	33	30
2	19	17
6	13	12
H,L= 0 5		
2	6	6
4	81	-74
6	76	-69
8	26	-28
10	33	-34
12	44	-46
14	68	-70
16	74	-73
18	44	-45
H,L= 1 5		
1	57	54
2	24	23
3	6	7
4	16	-15
5	42	-41
6	46	-46
7	24	-26
9	21	23
10	36	38
11	32	31
12	10	9
13	18	20
14	23	-21
16	27	-30
17	21	-22
18	9	-3
H,L= 2 5		
1	172	-173
3	219	-219
4	16	18
5	237	-235
6	35	34
7	170	-171
8	20	21
9	115	-123
11	108	-115
12	8	11
13	93	-101
14	26	31
15	84	-91
16	30	34
17	65	-70
18	13	17
19	42	-43
H,L= 3 5		
1	39	38
2	118	-116
3	42	-42
4	25	-22
5	55	-53
6	55	54
7	15	-16
8	42	40
9	12	11
11	16	16
12	39	-40
13	17	-18
14	25	-25
15	17	-18
16	24	21
18	21	19
H,L= 4 5		
1	142	141
2	9	9
3	140	136
4	35	31
5	137	134
6	7	10
7	118	116
9	96	97
10	48	47
11	86	87
12	46	47
13	73	73
14	26	28
15	50	51
16	18	21
17	37	38
18	20	23
H,L= 5 5		
1	63	-61
3	32	32
4	45	-45
5	71	70
7	7	4
8	46	46
9	42	-42
10	10	15
11	18	-17
13	18	15
14	13	-11
15	18	19
16	10	-14
H,L= 6 5		
1	66	65
2	8	-11
3	50	52
4	17	-14
5	41	43
6	20	-19
7	46	48
8	35	-38
9	45	49
10	46	-49
11	39	39
12	37	-42
13	18	21
14	34	-35
15	22	24
16	28	-31
17	31	30
H,L= 7 5		
7	26	24
9	18	18
10	10	7
11	15	-16
H,L= 8 5		
1	143	-147
2	8	-5
3	103	-104
4	10	-12
5	85	-88
7	98	-100
8	21	19
9	99	-101
11	85	-86
13	62	-61
H,L= 9 5		
1	36	-38
4	8	7
5	28	29
8	10	-9
9	20	-21
11	19	-22
H,L= 10 5		
1	47	47
3	31	32
4	15	9
5	21	23
6	12	10
7	28	29
8	21	20
9	31	31
10	24	24
11	27	25
H,L= 11 5		
1	7	9
2	22	23
4	19	20
6	9	-12
8	22	-22
H,L= 12 5		
1	41	41
3	39	37
H,L= 0 6		
0	89	-83
2	66	-63
6	58	-57
8	46	-45
10	52	-51
14	11	-13
16	37	-38
18	38	-36
H,L= 1 6		
0	200	-201
1	43	-41
2	179	-176
3	79	-77
4	148	-147
5	28	-26
6	143	-141
7	17	15
8	136	-138
9	8	6
10	119	-120
11	30	-30
12	99	-98
13	52	-55
14	67	-67
15	43	-42
16	54	-52

Table 1 (*cont.*)

K	FO	FC
17	17	-16
18	49	-50
H,L=	2	6
0	104	96
1	21	21
2	56	54
3	8	8
4	46	-43
5	14	11
6	47	-44
7	26	-25
8	38	36
9	33	31
10	68	66
11	21	19
14	13	-16
18	12	16
H,L=	3	6
0	90	-86
1	12	10
2	51	-51
3	17	18
5	25	25
7	40	40
8	23	-19
9	50	49
10	43	-42
11	51	51
12	41	-41
13	45	46
14	20	-19
15	42	39
17	39	39
H,L=	4	6
1	30	-30
3	40	-38
4	46	45
6	96	96
7	44	43
10	18	-15
11	39	-40
12	22	21
13	24	-24
14	33	31
15	12	13
17	10	6
H,L=	5	6
0	127	129
1	13	14
2	143	144
3	13	14
4	159	165
5	9	-7
6	160	162
7	24	-24
8	121	122
9	20	-20
10	85	84
11	7	-10
12	75	73
14	76	77
16	72	72
17	15	-15
H,L=	6	6
0	46	-44
1	10	6
2	35	-34
4	15	-15
5	21	-22
6	36	-35
8	21	-20
10	31	-30
11	27	27
12	26	-26
14	11	-9
15	27	-30
H,L=	7	6
0	90	-87
1	14	15
2	81	-80
3	28	27
4	64	-63
5	7	-6
6	48	-46
7	45	-46
8	53	-54
9	46	-47
10	57	-58
11	23	-21
12	49	-48
14	36	-34
15	17	-15
H,L=	8	6
1	14	-11
3	15	-14
5	22	20
7	16	17
11	13	-13
H,L=	9	6
0	28	-31
2	43	-42
3	15	17
4	61	-60
5	20	19
6	60	-59
7	15	13
8	37	-36
10	23	-23
11	25	23
12	27	-26
H,L=	10	6
2	19	19
3	17	18
4	28	28
6	20	18
7	25	-25
10	16	12
H,L=	11	6
0	80	78
2	74	72
4	59	57
6	48	45
H,L=	0	7
2	80	-79
4	54	-52
8	9	5
10	47	-44
12	80	-81
14	52	-50
16	23	-21
18	24	-25
H,L=	1	7
1	85	-83
2	52	52
3	45	-45
4	32	30
5	25	-26
6	29	-29
7	27	-27
8	8	-8
9	46	-46
10	44	41
11	56	-55
12	47	47
13	31	-29
14	21	20
15	16	-12
17	17	-15
H,L=	2	7
1	187	-186
2	13	13
3	132	-133
5	83	-84
7	101	-104
8	18	16
9	138	-139
10	30	31
11	110	-107
12	23	23
13	66	-67
15	41	-42
17	40	-41
H,L=	3	7
1	102	101
3	71	71
4	52	53
5	76	77
6	20	19
7	81	82
8	43	-44
9	70	71
10	27	-25
11	54	54
12	7	7
13	31	31
14	27	26
15	32	34
16	26	26
17	45	45
H,L=	4	7
1	89	90
3	95	95
5	101	99
6	26	26
7	98	99
8	29	30
9	75	76
10	16	16
11	40	42
12	22	22
13	39	38
14	24	23
15	49	48
16	34	24
17	21	47
H,L=	5	7
1	48	-46
2	41	35
4	10	-13
5	12	13
6	31	-29
7	15	-22
8	18	-20
9	31	-30
10	25	-25
11	9	-6
16	28	-28
H,L=	6	7
1	16	16
2	14	12
3	54	55
5	58	61
6	30	-30
7	35	37
8	47	-48
9	15	15
10	32	-31
11	15	14
12	20	-18
13	30	32
14	19	-19
15	28	29
H,L=	7	7
1	11	-8
3	59	-60
5	92	-93
6	12	10
7	52	-54
9	17	-11
11	15	-15
13	29	-28
H,L=	8	7
1	70	-70
3	95	-97
4	21	17
5	96	-102
6	17	-11
7	75	-75
8	19	-17
9	48	-50
11	45	-47
13	59	-59
H,L=	9	7
1	39	40
2	12	-14
3	41	41
5	33	36
7	28	26
8	15	16
9	24	24
11	30	32
H,L=	10	7
1	33	32
3	25	24
4	10	7
5	20	21
6	45	17
7	19	19
8	13	15
H,L=	11	7
1	18	16
H,L=	0	8
0	201	-210
2	141	-146
4	74	-77
6	56	-58
8	104	-107
10	119	-121
12	88	-92
14	42	-45
16	35	-39
H,L=	1	8
0	139	-143
1	7	8
2	102	-103
4	54	-55
6	43	-45
7	31	-30
8	100	-105
9	27	-30
10	81	-85
11	25	-26
12	41	-42
13	7	-6
14	21	-21
16	35	-37
H,L=	2	8
0	40	39
1	24	22
2	48	48
3	52	52
4	52	54
5	13	13
6	37	37
7	8	-6
8	42	42
10	32	31
11	41	42
12	15	12
13	40	40
14	20	22
15	35	35
16	37	35
17	16	15
H,L=	3	8
0	24	24
1	21	19
3	36	36
4	51	-53
6	33	-33
7	16	14
8	10	-10
9	18	18
11	43	45
13	31	33
14	20	-19
15	20	16
H,L=	4	8
0	81	84
1	19	21
2	59	58
3	27	26
4	67	70
6	89	90
7	37	-38
8	57	59
9	43	-44
10	35	36
11	29	-27
12	53	53
14	32	33
16	35	23
H,L=	5	8
0	87	88
1	26	-27
2	86	89
3	40	-40
4	90	91
6	57	57
7	31	33
8	66	66
9	7	-1
10	55	57
11	26	-29
12	61	60
13	17	-19
14	50	49
H,L=	6	8
0	57	-57
2	63	-66
4	103	-103
6	106	-104
7	15	-18
8	62	-63
9	13	-13
10	31	-33
12	42	-46
14	42	-45
H,L=	7	8
0	36	-35
2	33	-34
4	41	-42
5	12	-15
6	47	-47
7	33	-34
8	37	-36
10	22	-22
12	19	-15
13	14	-16
H,L=	8	8
0	20	18
1	7	-10
4	9	-9
5	16	17
7	30	29
9	13	15
10	13	13
H,L=	9	8
0	18	-21
2	29	-29
4	37	-36
6	18	-20
7	18	22
8	20	-20
9	24	15
H,L=	10	8
0	49	48
1	11	-8
2	51	50
3	15	-15
4	49	47
6	36	31
H,L=	0	9
4	32	32
8	49	-49
10	49	-50
12	18	-19
14	17	14
16	10	9
H,L=	1	9
1	75	-75
3	72	-73
5	68	-67
6	25	25
7	61	-61
8	45	47
9	60	-60
10	32	32
11	52	-48
12	20	23
13	35	-36
14	24	24
15	28	-28
16	22	25
H,L=	2	9
1	49	-49
2	54	53
3	55	-55
4	26	25
5	49	-47
6	30	-28
7	59	-58
8	28	-28
9	48	-48
10	19	18
11	16	-15
12	37	37
13	19	-19
15	33	-33
H,L=	3	9
1	125	127
2	6	-8
3	122	124
4	12	11
5	111	111
7	94	96
9	87	87
10	8	10
11	80	81
12	12	12
13	72	74
15	56	55
H,L=	4	9
1	85	87
2	13	-12
3	24	22
4	15	-14
5	21	-22
6	32	30
7	14	15
8	33	33
9	62	61
10	10	-7
11	47	49
13	8	11
14	14	13
H,L=	5	9
1	23	-19
3	22	-23
4	27	-27
5	30	-30
6	23	-25
7	21	-22
8	14	-13
10	21	-21
12	29	-27
13	23	-21
14	25	-26
H,L=	6	9
2	29	-29
3	27	29
4	20	-23
5	20	19
8	12	10
11	13	14
12	25	-23
13	23	27
H,L=	7	9
1	72	-74
3	71	-70
4	8	11
5	63	-61
6	11	12
7	57	-56
9	60	-58
10	15	12
11	49	-50
H,L=	8	9
1	20	-18
2	15	-14
3	45	-45
4	10	-4
5	45	-46
7	27	-28
9	19	-17
H,L=	9	9
1	53	51
3	56	55
5	61	59
7	57	54
H,L=	0	10
0	82	-79
2	117	-118
4	166	-166
6	132	-134
8	97	-97
10	66	-62
12	69	-67
14	78	-80
H,L=	1	10
0	30	-30
2	32	-28
3	7	7
6	11	7
7	10	-7
8	19	-18
10	27	-25
H,L=	2	10
0	48	46
1	23	-21
2	57	58
3	28	-30
4	57	55
6	25	24
7	65	65
8	25	25
9	49	48
10	40	40
11	23	19
12	42	41
14	34	33
H,L=	3	10
0	43	43
1	15	15
4	33	-34
6	18	-19
7	7	-5
9	9	9
10	17	14
11	14	13
13	9	14
14	16	-15
H,L=	4	10
0	98	99
2	75	77
3	23	-25
4	63	62
5	26	-26
6	66	65
7	10	-12
8	71	72
10	56	55
11	15	-15
12	50	51
13	37	-37
H,L=	5	10
1	10	-12
2	16	16
3	14	-16
4	19	18
5	11	10
6	14	14
7	16	18
11	18	-18
H,L=	6	10
0	110	-108
1	18	-18
2	92	-92
3	25	-26
4	72	-72
6	68	-67
7	8	6
8	74	-71
10	71	-70
11	12	-13
H,L=	7	10
5	7	-8
6	12	-10
H,L=	8	10
0	20	-23
1	15	15
3	27	26
4	19	19
5	8	8
6	29	29
H,L=	9	10
1	9	-3
H,L=	0	11
2	39	-37
4	11	-11
6	21	21
8	23	22
12	12	-11
H,L=	1	11
1	44	-44
2	21	-18
3	72	-71
4	9	-11
5	73	-71
6	43	44
7	54	-55
8	52	52
9	36	-35
11	30	-28
13	39	-39
H,L=	2	11
2	13	-17
3	20	19
4	18	-19
5	33	33
7	21	21
8	15	15
10	13	16
H,L=	3	11
1	92	91
3	111	111
5	102	101
7	83	83
9	69	68
10	16	15
11	65	64
H,L=	4	11
1	25	-25
2	15	14
9	11	-12
10	16	-14
11	20	-21
H,L=	5	11
1	13	-9
2	19	-21
3	23	-23
4	22	-20
5	30	-32
7	16	-14
10	24	-24
H,L=	6	11
1	26	-25
2	16	17
4	13	11
5	13	14
7	9	7
8	12	-11
9	10	-10
H,L=	7	11
1	81	-80
3	53	-53
5	28	-27
6	8	10
7	48	-47
H,L=	8	11
1	22	20
2	8	5
H,L=	0	12
0	57	-55
2	98	-97
4	103	-103
6	73	-71
8	53	-53
10	63	-61
H,L=	1	12
0	36	34
2	33	33
3	17	-17
4	34	35
6	41	48
7	21	22
8	37	34
9	19	28
10	23	24
H,L=	2	12
0	13	-9
1	13	12
2	24	24
3	15	11
4	59	60
5	22	22
6	43	44
7	21	18
8	19	18
H,L=	3	12
3	8	-12
4	14	15
6	18	17
H,L=	4	12
0	63	62
1	13	11
2	50	50
3	19	20
4	35	34
6	43	42
7	31	-33
8	50	49
H,L=	5	12
0	57	-58
1	11	13
2	40	-42
3	25	23
4	20	-20
6	14	-18
7	18	-17
H,L=	6	12
0	60	-58
1	16	-12
2	60	-59
4	54	-55
H,L=	7	12
0	12	14
H,L=	0	13
2	25	27
4	22	19
H,L=	1	13
1	42	-42
2	15	17
3	32	-32
5	17	-17
6	14	15
7	21	-21
8	11	11
H,L=	2	13
1	58	61
3	53	52
5	37	36
7	41	40
H,L=	3	13
1	41	39
2	28	29
3	61	61
4	18	17
5	63	64
6	12	-15
7	49	51
H,L=	4	13
1	41	-39
3	32	-31
5	32	-31
H,L=	5	13
3	18	-14
H,L=	0	14
0	15	-13
2	31	-31
H,L=	1	14
0	68	69
1	19	19
2	59	60
3	21	24
H,L=	2	14
2	18	12

Table 2. *Fractional coordinates of the atoms and their standard deviations* (×10⁴)

Numbers in parentheses here and in subsequent tables are estimated standard deviations

	x	y	z
Pd	1569 (1)	57 (0)	480 (0)
Cl(1)	691 (2)	931 (1)	1959 (2)
Cl(2)	2126 (2)	1110 (1)	−869 (2)
N(1)	1117 (6)	−950 (4)	1516 (5)
N(2)	2276 (7)	−808 (4)	−705 (5)
C(1)	1452 (10)	−2478 (5)	1667 (8)
C(2)	1358 (8)	−1739 (4)	822 (6)
C(3)	2580 (9)	−1589 (4)	12 (7)
C(4)	3888 (9)	−1487 (6)	676 (9)
H(N11)	123 (94)	−952 (55)	1769 (83)
H(N12)	1657 (92)	−967 (53)	2311 (86)
H(N21)	3200 (92)	−600 (57)	−1172 (85)
H(N22)	1470 (96)	−946 (56)	−1488 (86)
H(C11)	2290 (105)	−2336 (62)	2206 (96)
H(C12)	1824 (103)	−2926 (62)	1483 (96)
H(C13)	506 (98)	−2536 (66)	2118 (97)
H(C2)	469 (92)	−1872 (55)	286 (85)
H(C3)	2769 (95)	−2101 (55)	−585 (87)
H(C41)	4576 (106)	−1312 (64)	163 (101)
H(C42)	4320 (106)	−2032 (63)	1039 (97)
H(C43)	3666 (108)	−1127 (65)	1421 (98)

Description of the structure and discussion

The structure consists of discrete molecules. The atomic numbering of the molecules is shown in Fig. 1 with the thermal ellipsoids of the individual atoms. The interatomic distances and bond angles within the complex molecule are listed in Tables 4 and 5, respectively. The palladium atom has square-planar coordination. Two chlorine atoms are bonded to the palladium atom in *cis* positions, with Pd–Cl distances of 2·318 and 2·316 Å. The ligand molecule coordinates to the

Table 3. *Anisotropic temperature factors and their standard deviations* ($\times 10^4$)

The temperature factor term is of the form:

$$\exp\left[-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + hk B_{12} + kl B_{23} + hl B_{13})\right]$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	57 (0)	19 (0)	38 (0)	5 (1)	1 (1)	−2 (0)
Cl(1)	86 (2)	29 (1)	49 (1)	29 (2)	−19 (3)	−23 (2)
Cl(2)	93 (2)	23 (1)	57 (1)	−9 (2)	25 (3)	10 (2)
N(1)	76 (7)	22 (2)	43 (5)	7 (6)	27 (10)	3 (5)
N(2)	100 (8)	20 (2)	40 (5)	14 (7)	26 (10)	1 (5)
C(1)	148 (12)	20 (3)	86 (8)	5 (11)	36 (18)	15 (8)
C(2)	89 (9)	18 (2)	44 (5)	2 (7)	12 (11)	−10 (6)
C(3)	89 (9)	21 (3)	51 (6)	28 (8)	−3 (12)	−5 (7)
C(4)	69 (9)	52 (4)	89 (9)	40 (11)	−3 (15)	16 (11)

Table 3 (*Cont.*).

	B^*
H(N11)	2·4 Å²
H(N12)	2·4
H(N21)	2·7
H(N22)	2·7
H(C11)	4·0
H(C12)	4·0
H(C13)	4·0
H(C2)	2·6
H(C3)	2·8
H(C41)	4·2
H(C42)	4·2
H(C43)	4·2

* Isotropic, and given the same values as those obtained at the final stage of the refinement with isotropic temperature factors for the atoms to which the hydrogen atoms are bonded.

palladium atom with two nitrogen atoms. The Pd–N distances, 2·028 and 2·030 Å are in agreement with those found in *bis*-(L-prolinato)-palladium(II) (Ito, Marumo & Saito, 1971) and other palladium complexes. Other interatomic distances and bond angles in

Table 4. *Bond lengths and their standard deviations*

Pd —Cl(1)	2·318 (2) Å
Pd —Cl(2)	2·316 (2)
Pd —N(1)	2·028 (6)
Pd —N(2)	2·030 (6)
N(1)–C(2)	1·499 (9)
N(2)–C(3)	1·513 (9)
C(1)–C(2)	1·508 (11)
C(2)–C(3)	1·536 (11)
C(3)–C(4)	1·513 (12)
N(1)–H(N11)	1·04 (9)
N(1)–H(N12)	1·03 (9)
N(2)–H(N21)	1·11 (9)
N(2)–H(N22)	1·20 (10)
C(1)–H(C11)	1·06 (11)
C(1)–H(C12)	0·84 (10)
C(1)–H(C13)	1·08 (10)
C(2)–H(C2)	1·09 (9)
C(3)–H(C3)	1·07 (9)
C(4)–H(C41)	0·94 (11)
C(4)–H(C42)	1·06 (10)
C(4)–H(C43)	1·03 (11)

the complex molecule are quite normal. The least-squares plane through the palladium atom and the four ligand atoms, and the deviations of other atoms are listed in Table 6. The carbon atoms C(2) and C(3) are off the plane at 0·20 and −0·54 Å, respectively. One of the methyl-carbon bonds, C(2)–C(1), is in the equatorial position relative to the plane of the chelate ring, whereas the other, C(3)–C(4) is in the axial position. A Newman projection of the ligand molecule along the C(2)–C(3) bond is shown in Fig. 2. The dihedral angle formed by the planes N(1)C(2)C(3) and C(2)C(3)N(2) is 53·3°. The C(1)–C(2)–C(3)–C(4) group also takes a *gauche* conformation, the dihedral angle being 56·4°. These results agree well with the conclusion drawn from the conformational analysis of the five-membered chelate rings (Gollogly & Hawkins, 1969).

The azimuthal orientations of the two methyl groups are such that non-bonded hydrogen interactions will be minimized, that is, the dispositions of the bonds around C(1)–C(2) and C(3)–C(4) are both staggered.

The molecule is dissymmetric and two enantiomeric molecules exist in the crystal. Figs. 3 and 4 illustrate projections of the structure along the *c* and *b* axes, respectively. The molecules with the same conformation make an infinite chain along the *c* axis; the molecule is linked to the other (related by a twofold screw axis parallel to the *c* axis) by N(1)–H(N12)---Cl(2) and N(2)–H(N21)---Cl(1) hydrogen bonds of lengths 3·37 and 3·28 Å, respectively. This chain is further bound to the other enantiomeric chains laterally by N(1)–H(N11)---Cl(2) and N(2)–H(N22)---Cl(1) hydrogen bonds of lengths 3·35 and 3·29 Å, respectively, forming a layer parallel to the plane (010). Fig. 4 shows the two-dimensional network by the hydrogen bonds.

Intermolecular distances less than 3·5 Å are tabulated in Table 7. A Pd–Pd distance of 3·34 Å is observed between a pair of molecules related by a centre of symmetry. This is much shorter than the value 3·720 Å observed in the structure of rubidium tetracyanopalladate(II) monohydrate (Dupont, 1970). This rather short distance may be compared with the Pt–Pt distance of 3·39 Å observed in the crystal of dichloro-(ethylenediamine)platinum(II) (Martin, Jacobson, Hunter & Benson, 1970) and the Pt–Pt distance of 3·25 Å in Magnus's green salt (Atoji, Richardson &

Rundle, 1957). The two molecules, which form a pair, are oriented with their coordination planes exactly parallel, and the Pd–Pd vector is approximately perpendicular to the coordination plane (Fig. 4). Such an arrangement of the complex molecules suggests a weak interaction between the d orbitals, and continuing studies on the absorption spectra of single-crystals are in progress by one of the authors (TI).

Table 5. *Bond angles and their standard deviations*

|			
Cl(1)–Pd —Cl(2)	95·3 (1)°	H(N21)–N(2)–H(N22)	107 (7)°
Cl(1)–Pd —N(1)	90·6 (2)	H(N22)–N(2)–Pd	110 (5)
Cl(1)–Pd —N(2)	174·1 (2)	H(N22)–N(2)–C(3)	111 (5)
Cl(2)–Pd —N(1)	174·0 (2)	H(C11)–C(1)–C(2)	103 (6)
Cl(2)–Pd —N(2)	90·6 (2)	H(C11)–C(1)–H(C12)	88 (9)
N(1)–Pd —N(2)	83·6 (2)	H(C11)–C(1)–H(C13)	118 (8)
Pd——N(1)–C(2)	111·0 (4)	H(C12)–C(1)–C(2)	124 (7)
Pd——N(2)–C(3)	108·0 (4)	H(C12)–C(1)–H(C13)	116 (9)
N(1)–C(2)–C(1)	111·6 (6)	H(C13)–C(1)–C(2)	107 (5)
N(1)–C(2)–C(3)	106·8 (6)	H(C2)—C(2)–N(1)	108 (5)
C(1)–C(2)–C(3)	115·3 (7)	H(C2)—C(2)–C(1)	103 (5)
N(2)–C(3)–C(2)	105·5 (6)	H(C2)—C(2)–C(3)	112 (5)
N(2)–C(3)–C(4)	109·6 (6)	H(C3)—C(3)–N(2)	111 (5)
C(2)–C(3)–C(4)	116·0 (6)	H(C3)—C(3)–C(2)	112 (5)
		H(C3)—C(3)–C(4)	103 (5)
H(N11)–N(1)–Pd	112 (5)	H(C41)–C(4)–C(3)	113 (7)
H(N11)–N(1)–C(2)	107 (5)	H(C41)–C(4)–H(C42)	100 (9)
H(N11)–N(1)–H(N12)	107 (7)	H(C41)–C(4)–H(C43)	118 (9)
H(N12)–N(1)–Pd	112 (5)	H(C42)–C(4)–C(3)	117 (6)
H(N12)–N(1)–C(2)	109 (5)	H(C42)–C(4)–H(C43)	105 (8)
H(N21)–N(2)–Pd	112 (5)	H(C43)–C(4)–C(3)	105 (6)
H(N21)–N(2)–C(3)	109 (5)		
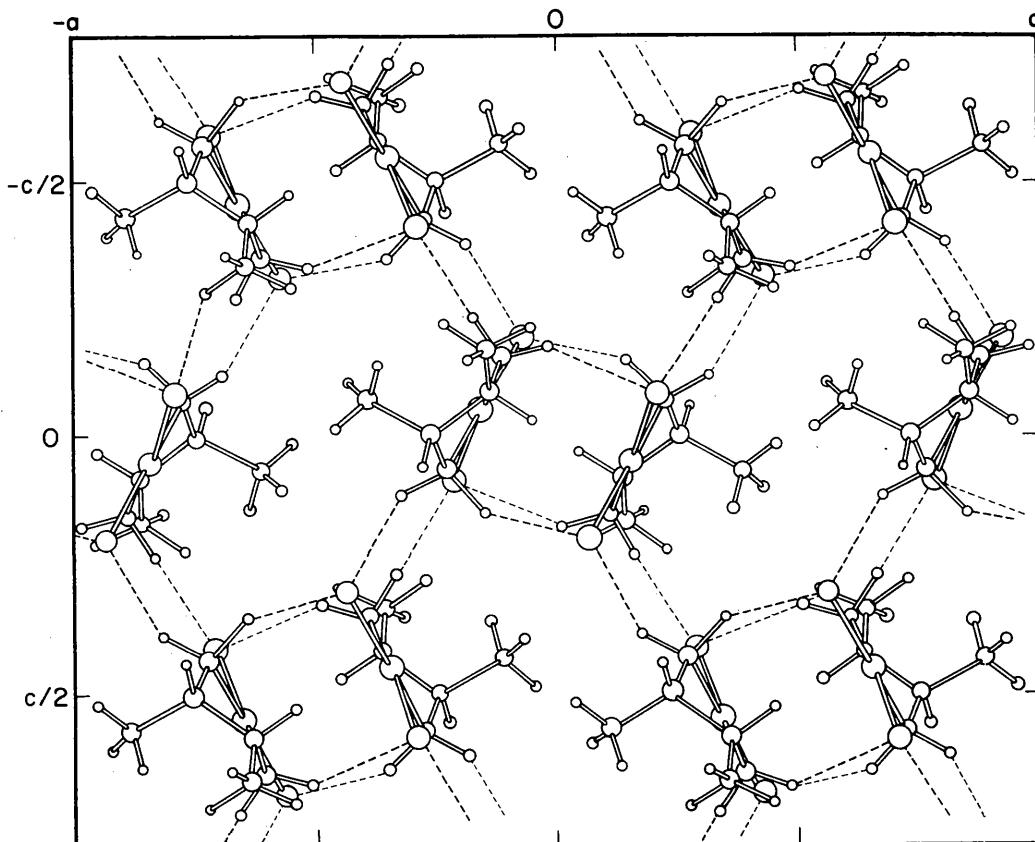
Fig. 4. A partial projection of the crystal structure along the b axis showing the two-dimensional network by hydrogen bonds.

Table 6. *The least-squares plane through the palladium atom and the four coordinating atoms*

$-0.9001x - 0.0639y - 0.4311z + 1.6419 = 0$ where x, y and z are the coordinates in Å referred to the crystal axes a, b and c.

	Pd	Cl(1)	Cl(2)	N(1)	N(2)	C(1)	C(2)	C(3)	C(4)
Displacement (Å)	−0.01	0.00	0.01	0.01	−0.01	−0.20	0.20	−0.54	−2.05

Table 7. *Intermolecular distances less than* 3.5 Å *between non-hydrogen atoms*

Molecule	1	x	y	z
	2	$\frac{1}{2}-x$	$-y$	$\frac{1}{2}+z$
	3	$-x$	$-y$	$-z$

From molecule 1	To atom	In molecule	Distance
Cl(1)	N(2)	2	3.28 Å
N(1)	Cl(2)	2	3.37
Pd	Pd	3	3.34
Cl(1)	N(2)	3	3.29
N(1)	Cl(2)	3	3.35

The computations for the structure analysis were carried out on the HITAC 5020E computer at the Computer Centre of the University of Tokyo using the programs of the *UNICS* system, and also on the electronic computer FACOM 270-30 at this Institute.

Fig. 1 was drawn with a plotter at the C. Ito Electronic Computing Service Co., Ltd. using *ORTEP* (Johnson, 1965).

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The Crystal Structure of a Mixed Valence Copper Cyanide Complex, Cu3(NH3)3(CN)4*

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The green compound $Cu_3(NH_3)_3(CN)_4$ contains Cu(I) and Cu(II) in a ratio of 2:1. The crystals are orthorhombic, space group *Cmca*, with $a = 12.273$ (6), $b = 13.646$ (8) and $c = 12.777$ (7) Å. There are eight formula units per unit cell. Through the use of counter data the structure was solved by the heavy-atom method and was refined by least-squares methods with anisotropic thermal parameters to a conventional R index of 0.055. Two of the three crystallographically different cyanide groups are disordered. If the NH_3 positions were fully occupied, the formula would have four NH_3 groups. However, a 16-fold set appears to be only 75% occupied by NH_3 and one of the 8-fold sets appears to be only 50% occupied by NH_3. Furthermore, a better fit of the data was obtained with a model having freely rotating NH_3 molecules. Each Cu(II) atom is coordinated to three NH_3 molecules distributed over four positions, and to the nitrogen atoms of two cyanide groups in a distorted octahedral geometry. The Cu(I) atoms have a distorted trigonal planar coordination with the carbon atom of the ordered cyanide group and the ends of two disordered cyanide groups. The Cu(II) and four Cu(I) atoms form the apices of a nearly planar pentagon, with cyanide groups bridging the copper atoms. These rings share two edges with adjacent pentagons to form an infinite chain parallel to the a axis.

Introduction

Numerous studies of CuCN complexes have been conducted at this laboratory over the last few years (*e.g.*,

Roof, Larson & Cromer, 1968, and references contained therein). With the single exception of $K_3Cu(CN)_4$, these complexes have exhibited unusual polymeric-type structures. Recently, there have been reports of the preparation and partial characterization of some mixed-valence CuCN complexes with additional nitrogen, phosphorus, and arsenic containing ligands

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