## The Crystal Structure of Bis-(2,2'-dipyridyliminato)palladium(II), Pd(C<sub>10</sub>H<sub>8</sub>N<sub>3</sub>)<sub>2</sub>

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#### (Received 7 August 1964)

The structure of bis-(2,2'-dipyridyliminato)palladium(II) has been solved and has been refined by three-dimensional least-squares methods. The complex is centrosymmetrical. The coordination of the palladium is square-planar. Strong inter-ligand repulsions are accommodated by a folding of each ligand so that the normals to the planes of its two pyridyl rings meet at an angle of  $38\cdot2^\circ$ . The pyridyl rings themselves are distorted from planarity. The structural type, in which a resonating system is deformed by inter-ligand repulsions, is novel among chelate compounds, but is characteristic of overcrowded aromatic molecules like bianthronyl.

The bond-lengths in the pyridyl rings parallel those in pyridine, although the carbon-nitrogen bonds appear to be an average of 0.026 Å longer. The imino-nitrogen-carbon bond-length is similar to those found in aromatic nitrogen compounds. The palladium-nitrogen bonds are of normal length, 2.02 Å.

#### Introduction

Square planar coordination of palladium(II) is well established. In bis-(2,2'-dipyridyliminato)palladium(II)<sup>†</sup> a planar arrangement should result in considerable inter-ligand repulsions between hydrogen atoms. The structure analysis of this complex was undertaken to determine the way in which these repulsions are accommodated. The complex was originally prepared by Geldard & Lions (1963); the crystal structure analysis has been briefly reported previously (Freeman, Geldard, Lions & Snow, 1964).

#### Experimental

Crystals were prepared by cooling saturated solutions of the complex in ethylene glycol monomethylether/nhexane mixtures. The small pale yellow needles of rhombic cross-section often appeared as interpenetration twins. The unit-cell data (with the maximum errors in their last decimal places) are:

$C_{20}H_{16}N_6Pd$	F.W. = 446.7
Monoclinic,	a = 15.405(6), b = 12.770(3),
	$c = 9.046(1)$ Å, $\beta = 96.75(8)^{\circ}$ ,
	$U = 1767(2)$ Å <sup>3</sup> , $D_m = 1.70$ (by flotation),
	$Z=4, D_x=1.68 \text{ g.cm}^{-3},$
	$\mu$ Cu $K\alpha = 91.5$ cm <sup>-1</sup> .
Space-group,	C2/c or $Cc$ by systematic absences,

C2/c by structure analysis.

The  $\beta$  angle was found from an hol Weissenberg photograph, allowance being made for film-shrinkage by measuring the separations of a number of pairs of reflexions separated by  $\beta$  and by 180°, respectively. The other unit-cell dimensions were fitted by least-squares to 18 reflexions on Weissenberg photographs (hk0, 0kl) calibrated with platinum powder lines (a=3.9231 Å, Cu  $K\alpha_1$ ,  $\alpha_2$  radiation). A variant of Cohen's analytical extrapolation procedure (Buerger, 1942) was used, parameters being introduced to correct for systematic absorption and eccentricity errors (Freeman & Taylor, 1965). The inclusion of these two corrections in the least-squares calculation affected the resultant celldimensions by 0.01 to 0.02 Å, and eliminated  $\theta$ -dependent systematic errors.

A crystal 0.12 mm long and having an approximately square cross-section (0.04 mm<sup>2</sup>) was rotated about its needle c axis to obtain multiple-film, equi-inclination Weissenberg data for hkL (Cu K $\alpha$  radiation for  $0 \le L \le 7$ , Cu K $\beta$  for L=8). The reflexions with l odd were much weaker than those with l even. Exposures of up to 25 days were required to record the layers with L odd, compared with 2 to 3 days for the layers with L even. Exposures of 7 days were made to record Hkl data ( $0 \le H \le 2$ , Cu K $\alpha$ ) from a similar small crystal.

The intensities were estimated visually and corrected for Lorentz-polarization and Tunell effects, but not for absorption. For the crystal used, the maximum variation of the transmission factor with  $\theta$  was 4% within the zero level and 9% within the seventh level. The 195 reflexions recorded independently twice were used to correlate 1515 non-symmetry-related reflexions of which 161 (all with odd *l* indices) were too weak to observe.

#### Solution and refinement

The conditions limiting possible reflexions (hkl: h+k = 2n, h0l: l=2n) combined with the relative weakness of the reflexions with odd *l* suggested that the palladium was at the origin in space group *Cc* or *C2/c*. A Fourier

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synthesis in which the  $F_o$  with l=2n were given positive signs revealed only one unique image of the ligand atoms. The deduction that the molecule was centrosymmetrical in space group C2/c rather than noncentrosymmetrical in space group Cc (which would require two unique ligand images) was confirmed by the subsequent refinement.

The structure was refined on an IBM 7090 computer with the full-matrix least-squares program of Busing & Levy (1961). Ten cycles of calculations were carried out in five stages. A synopsis is given in Table 1. Stage 1 represents the trial structure.

In Table 1, R(all) is the conventional reliability factor summed over all reflexions.  $[\Sigma w \Delta^2/(M-N)]^{\ddagger}$  is  $[\Sigma w (F_o - G_i F_c)^2/(N-M)]^{\ddagger}$ , where w is the weight given to the observed structure factors  $F_o$ ,  $G_i$  is the scale factor to place the calculated structure factors  $F_c$ on the scale of  $F_o$  and (N-M) is the excess of reflexions N over the number M of parameters refined. In addition to the general scale-factor  $G_1$ , a separate scale  $G_2$  was needed for the hk7 reflexions. These reflexions were too weak to appear on any of the Hkl films which had provided the correlation between the other L layers.

The refinement weights w of the  $F_o$  were equated to  $1/\sigma^2(F)$ , the population standard deviations  $\sigma(F)$  of the  $F_o$  being estimated from the 195 reflexions for which scaled structure factors  $F_1$  and  $F_2$  were available from two independent observations (Davies & Pearson, 1934). Here  $\sigma(F)$  was taken to be  $\overline{\Delta F_o}/\sqrt{2} = \overline{F_1 - F_2}/\sqrt{2}$ , where  $\Delta F_o$  is the mean discrepancy over a range of  $F_o$  values. The variation of  $\overline{\Delta F_o}$  with  $F_o$  is shown in Fig. 1.



Fig. 1. Variation of  $\overline{\Delta F_o}$  (mean difference between scaled amplitudes in an  $F_o$  range) with  $F_o$ .

For the unobserved reflexions  $F_u$ , the relations of Hamilton (1955) for centrosymmetrical space groups  $(F_u = F_{min}/\sqrt{3}, \sigma(F_u) = F_{min}/\sqrt{15})$  were used.  $F_{min}$  values were not recorded beyond values of  $\theta$  for which observed values occurred.

The scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used for carbon and nitrogen, and that of Thomas & Umeda (1957) for singly ionized palladium was used for palladium(II). The real part of the anomalous scattering by palladium [0.5 electron (Dauben & Templeton, 1955)] was subtracted over the whole  $\sin \theta$  range. The error due to neglecting the imaginary part of the anomalous scattering was calculated to be less than 1% by the method of Patterson (1963).

After stage 3. a few gross errors in the reflexion data and an incorrect extrapolation of Fig. 1 to the origin were corrected. The refinement was resumed with scale and isotropic temperature factors from stage 2 and the positional parameters from stage 3. Convergence was reached in stage 5, the final r.m.s. shifts in the coordinates ( $\delta x$ , 0.0006 Å;  $\delta y$ , 0.0012 Å;  $\delta z$ , 0.0012 Å) all being less than one-eighth of the corresponding r.m.s. standard deviations. The final changes in the thermal parameters were negligible. The final value of  $[\Sigma w \Delta^2/(M - M)]$ N]<sup> $\pm$ </sup> — which should be unity for correctly weighted data — lies within the range of values found with the use of weighting schemes based on  $F_o$  discrepancies [e.g. 4.07 for heavy ice (Peterson & Levy, 1957), 2.0 for N-acetylglycine (Donohue & Marsh, 1962), 2.14 for bisglycinocopper(II) monohydrate (Freeman, Snow, Nitta & Tomita, 1964)].

The final positional parameters for the asymmetric unit at  $(\frac{1}{2}, \frac{1}{2}, 0)$  are given in Table 2, final temperature parameters in Table 3 and the final observed and calculated structure factors are compared in Table 4.

A difference synthesis calculated from the final structure factors contained a hole of  $4.7 \text{ e.} \text{Å}^{-3}$  at the palladium site with smaller holes varying between 0 and  $0.5 \text{ e.} \text{Å}^{-3}$  at the light atom positions. Peaks of between 0.4 and  $0.6 \text{ e.} \text{Å}^{-3}$  appeared in positions where hydrogen atoms were expected, but no claim to have located them unambiguously is made. The presence of considerable holes in the final difference synthesis and the observation from Table 4 that, for large *F*,  $F_c$  exceeds  $F_o$ by amounts up to and exceeding  $3\sigma(F_o)$  suggested the presence of an extinction effect. A plot of  $I_c/I_o$  against  $I_c$  (Pinnock, Taylor & Lipson, 1956) for the *hk*0 data was indeed linear. In the absence of absorption corrections to the original data, a correction for extinction was not applied at this stage.

#### Table 1. Synopsis of the refinement

Stage	Cycles	parameters	R(all)	$[\Sigma w \Delta^2/(M-N)]^{\frac{1}{2}}$	$G_1$	$G_2$
1	0	_	0.141	4.63	1.91	2.31
2	1-3	isotropic	0.114	3.25	1.94	2.35
3	4-5	anisotropic	0.095	2.60	1.98	2.52
4	6	isotropic	0.110	2.39	1.91	2.46
5	7–10	anisotropic	0.082	1.88	1.94	2.60

# Table 2. Final positional parameters, their standard de-viations (in parentheses) and shifts in the final least-squares cycle

The standard deviations and shifts correspond to the least significant digits in the coordinates.

Atom	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$	Estimated s.d.
Pd	0.5000	0.5000	0.0000	
N(1)	0.4771(4)0	0.3475(4)1	0.0412(07)1	0·009 Å
N(2)	0.6163(5)0	0.4777(5)0	0.1247(09)2	0.011
N(3)	0.6290(4)0	0.3011(5)1	0.0413(08)0	0.011
C(1)	0.5420(6)0	0.2759(5)1	0.0348(09)0	0.012
C(2)	0.5213(7)0	0.1693(8)1	0.0281(12)1	0.016
C(3)	0.4357(7)1	0.1379(7)2	0.0477(12)2	0.012
C(4)	0.3709(6)0	0.2119(7)2	0.0655(11)1	0.014
C(5)	0.3948(5)0	0.3158(6)0	0.0613(10)2	0.013
C(6)	0.6631(5)0	0.3882(5)0	0.1035(08)1	0.011
C(7)	0.7529(5)0	0.3854(7)0	0.1551(09)0	0.013
C(8)	0.7915(7)1	0.4686(9)0	0.2393(11)2	0.016
C(9)	0.7387(6)0	0.5540(8)1	0.2736(10)1	0.014
C(10)	0.6528(5)0	0.5555(7)0	0.2149(08)1	0.012

The standard deviations of the coordinates of the light atoms, as calculated from the final least-squares cycle, were 0.01 Å or less (Table 2). These standard deviations seemed to be too small, in view of (1) the presence of a heavy atom (even though 25% of the reflexions contain no contribution from it) and (2) the known existence of extinction errors. An internal check was possible because the ligand molecule contains pairs of bonds which are chemically identical but crystallographically non-equivalent. Although the ratios  $(l_A - l_B)/[\sigma^2(l_A) + \sigma^2(l_B)]^{\frac{1}{2}}$  were near unity or smaller for all but one of such bond pairs, an apparent underestimate of  $\sigma(l)$  did occur for the bonds C(1)–N(3) and N(3)-C(6). The difference between their lengths was 0.046 Å. The standard deviation of this difference (calculated from the least-squares s.d.'s of the atomic coordinates and taking into account that N(3) was common to both bonds) was 0.017 Å.

To be conservative the standard deviations of the atomic positions, averaged over the three axial directions, were therefore multiplied by an arbitrary factor of 1.5 (last column of Table 2). These adjusted values were used in calculating the bond-length s.d.'s of Table 5.

#### Description of the structure

Table 5 contains the bond lengths and angles with their estimated standard deviations. A trimetric projection of the molecule is shown in Fig. 2. Planes were fitted by least-squares to the pyridyl rings A (plane 1) and B (plane 2) and to the atoms N(1), N(2), C(1) and C(6) (plane 3). Details of these planes are listed in Table 6.

The molecule is centrosymmetrical with approximate symmetry 2/m. It may be visualized by starting with a planar configuration. The upper ligand in Fig. 2 is folded upwards (say) about the line Pd · · · N(3) until the angle between the normals to the pyridyl rings is  $38 \cdot 2^{\circ}$ . The chelate ring — PdN(1)C(1)N(3)C(6)N(2) — thus achieves a boat configuration and the atoms Pd and N(3) lie on the same side of plane 3 ('below' it in the present description). The two C-N(3) bonds are shorter than the two N-Pd bonds, so that the deviation of N(3) from plane 3 (0.21 Å) is smaller than that of the palladium atom (0.89 Å). Part of the difference be-



Table 3. The final vibrational parameters from the isotropic (B) and anisotropic  $(B_{ij})$  refinements and their estimated standard deviations (in parentheses)

Anisotropic temperature factor: exp  $\{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)\}$ . (*B*<sub>150</sub> values are in Å<sup>2</sup>. The anisotropic temperature parameters have been multiplied by 10<sup>4</sup>).

Atom	В	<i>B</i> <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	<i>B</i> <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
Pd	2.48(.03)	28(0)	31(1)	96(1)	0(0)	12(0)	0(0)
N(1)	2.68(.12)	34(3)	26(3)	116( 9)	-6(2)	16(4)	4(4)
N(2)	2.81(.13)	34(3)	40(4)	114(11)	1(3)	9(4)	- 5(5)
N(3)	3.57(.16)	36(3)	46(4)	143(11)	4(3)	16(4)	- 8(5)
C(1)	3.09(.16)	38(4)	30(4)	136(11)	4(3)	15(5)	3(5)
C(2)	4.30(.21)	50(1)	40(5)	190(16)	1(4)	2(7)	-12(7)
C(3)	4.66(.19)	56(5)	52(6)	200(17)	-13(5)	-14(7)	- 2(8)
C(4)	4.60(.24)	54(5)	56(6)	172(15)	-14(4)	11(6)	14(7)
C(5)	3.51(.16)	42(4)	50(5)	116(12)	- 8(4)	19(5)	16(6)
C(6)	2.84(.15)	33(3)	40(4)	99(10)	9(3)	17(4)	7(5)
C(7)	3.75(.18)	34(4)	68(6)	128(12)	0(4)	9(5)	21(6)
C(8)	4.09(.19)	41(5)	74(6)	132(14)	-4(5)	5(6)	16(8)
C(9)	4.06(.20)	41(4)	72(7)	124(13)	- 9(4)	9(1)	2(7)
C(10)	3.30(.18)	45(4)	63(6)	71(10)	-15(4)	5(5)	2(5)

Table 4. Observed and calculated structure amplitudes for bis-(2,2'-dipyridyliminato)palladium(II) Each group is headed by h and k. Subsequent lines contain l,  $F_c$  and  $F_o$ . The  $F_c$  values have been scaled by a factor of 1.94. The  $F_u$  values have been tagged with an X. ۲<sup>8</sup> к Fc 2 K Fc O K Fe 81.92 7.45 43.14 ۴. ۲ 16 H K Fo -1 -.26 3.71x 0 107.73 90.35 1 11.96 13.90 H K L Fc 13 3 H K L Fc Fo -7 5.05 3.70x -6 47.94 48.59 10 F4 73.35 5.84 47.56 Fe , 2 278.51 219.22

4 172.61 161.46 6 56.59 59.78 8 51.92 47.23 4 2 0	4 130,29 99,11 5 19,91 22.88 6 79,59 67,39 7 26,67 27,48 8 57,24 55,25	<ul> <li>2 2</li> <li>−10 39.93 43.44</li> <li>−9 2.52 5.38x</li> </ul>	-6 41.88 42.55 -4 34.34 36.51 -2 43.00 43.46 0 43.57 46.19 2 45.98 49.54	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 96,78 89,62 3 13,91 15,58 4 91,61 78,25 5 4,58 4,53x 6 48,95 4,60
-8 35.41 42.08 -6 85.75 84.55 -4 116.94 120.39 -2 408.34 341.79 0 182.74 147.32	• 5 1 -8 62.09 69.99 -7 -1.40 2.55×	-8 40.41 40.29 -7 3.34 2.03× -6 31.55 80.10 -5 -50.08 53.35 -4 63.07 63.90 -3 29.07 17 55	4 29.68 29.41 • 18 2 -5 23.65 16.03	-1 18.72 22.35 0 73.06 65.81 2 51.03 46.49 3 10.42 9.28 4 38.66 38.21	1 22.16 22.25 2 48.69 50.80 3 -22.52 20.75 4 41.52 36.46 5 12.09 12.91	8 33.77 32.66 9 5 -3 43.82 53.88
2 302,99 260,45 4 163,44 154,34 6 112,19 104,93 8 44,84 44,99	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-2 219.40 201.04 -1 77.40 71.02 0 14.04 28.06 1 39.15 34.97 2 85.86 83.69	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6 18,55 17.07 • 15 3 -5 26.38 30.63	6 49.96 45.20 8 32.86 35.74 4 12 4	-7 6.82 7.16 -6 62.42 64.76 -5 15.19 18.21 -4 74.18 68.41 -318 3.98×
-8 69.70 71.22 -6 101.76 109.53 -4 140.09 126.68	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3 -10.56 10.60 4 62.51 57.26 5 .40 2.67x 6 99.77 96.04 7 9.42 10.73	-9 57,43 69,27 -7 15,15 15,22 -6 82,61 81,22 -5 7,33 10,52	-6 47.37 50.66 -4 41.57 43.71 -3 18.04 19.23 -2 64.58 66.54 0 53.72 57.64	-8 27,88 31.20 -7 -15.82 18.59 -6 46.95 50.17 -5 1.57 4.71x -4 73.11 75.01	-2 96.74 94.92 -1 -2.33 4.17 0 105.90 99.17 1 2.67 4.25x 2 78.86 77.42
-2 62.88 64.15 0 126.12 104.42 2 129.37 105.96 4 181.06 139.91 6 102.94 96.94	5 3.40 3.45x 6 84.95 73.70 7 .55 3.30x 8 21.31 21.43	8 62.13 64.62 945 8.17× 10 35.77 39.95 4 2	-4 79.62 74.94 -3 -51.24 65.32 -2 102.96 97.69 -1 54.59 55.67 0 152.25 136.11	2 93.97 96.37 4 29.36 25.79 6 13.15 7.94 17 3	-3 $-5.42$ $8.45-2$ $68.00$ $63.97-1$ $39.63$ $39.900$ $30.23$ $31.961$ $16.90$ $14.652$ $50.44$ $50.43$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
-8 57.54 66.74 -6 70.25 68.64	• 7 1 -9 34.71 43.90 -7 -11.05 14.02 -6 76.33 91.21	-8 40.04 45.90 -7 -11.94 13.56 -6 55.16 58.23 -5 25.14 31.20	1 15.85 14.79 2 127.99 124.39 3 -35.63 36.14 4 109.28 93.46 5 -45.59 45.75	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 24,59 21,78 4 55,83 54,96 5 2,34 4,44× 6 41,61 34,04	<ul> <li>11 5</li> <li>-8 31.47 35.45</li> <li>-6 33.81 34.40</li> <li>-3 -3.39 4.71x</li> </ul>
-4 145.54 124.20 -2 119.23 105.21 0 132.61 117.60 2 176.02 154.27 4 95.04 73.77	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6 90.16 95.94 7 -9.28 10.14 9 69.21 59.65 9 1.42 6.95× 10 35.23 37.72	4 26.07 24.09 • 19 3 -2 36.39 37.30	14 4       -8     29.56     33.45       -6     44.80     56.50       -5     -9.14     12.21	-4 59.66 64.36 -3 6.00 8.37 -2 83.83 87.50 -1 9.08 12.54 1 18.86 22.90
6 61,97 54,33 8 39,41 34,45 9 0	1 37.03 36.43 2 126.35 113.65 3 43.29 39.66 4 97.41 30.31 5 3.67 4 06×	2 131.11 123.66 3 -23.79 26.20 4 139.67 102.45 5 2.16 3.27x 6 61.85 57.43	<ul> <li>3 3</li> <li>-9 54.85 65.27</li> <li>-7 -6.14 6.15</li> <li>-6 62.23 62.60</li> </ul>	0 25.71 25.22 • 0 4 0 133.25 105.99 1 22.27 24.24	-4 43,33 48,14 -3 13,44 14,59 -2 38,72 43,16 -1 18,85 22,34 0 57,75 56,04	2 32.20 29.75 3 -23.60 19.10 4 52.54 47.63 6 41.10 37.36
-8 31.36 45.93 -6 92.09 89.16 -4 88.62 90.51 -2 162.39 153.50 0 200.70 175.99	6 40.04 37.93 7 -3.55 3.62x 8 60.31 54.46 9 1	7 8.04 7.99 8 39.48 42.77 # 6 2	-5 -59.34 63.42 -4 111.87 95.74 -3 30.90 37.99 -2 189.06 157.75 -1 -72.50 75.91	2 93.60 54.16 3 9.92 10.65 4 130.45 106.31 5 -42.84 46.57 6 66.89 66.45	1 22.22 24.87 2 50.66 54.20 3 14.84 14.89 4 43.98 46.34 5 12.17 14.31 6 25 14 17 15	-8 23.64 18.82 -6 38.65 44.41 -4 42.28 50.56 -3 2 56 40.40
4 69.50 63.49 6 41.46 35.76 8 47.00 44.06	-8 44.63 60.87 -7 -1.23 3.52x -6 57.54 59.45 -5 -3.83 4.06x	-8 52.23 62.71 -7 2.17 2.97x -6 67.07 67.57 -5 -18.03 25.59 -4 105.26 96.31	0 156.76 137.43 1 -6.69 8.25 2 113.55 102.62 3 -24.55 23.15 4 142.04 110.85	7 -19.97 19.37 8 59.24 64.98 9 .91 5.65× 10 31.31 34.49	<ul> <li>16 4</li> <li>-9 21.84 13.91</li> <li>-6 26.91 29.68</li> </ul>	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
-8 55.91 64.09 -6 49.02 47.05 -4 78.91 74.94 -2 93.91 95.92	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-2 66.95 65.97 -1 -33.21 42.53 0 109.37 102.01 1 -37.19 35.45 2 156 13 139 89	6 81.39 78.42 7 11.50 12.90 9 52.12 49.35	2 4 -10 40.65 43.80 -8 66.73 69.28 -7 18.12 19.97 -7 18.12 19.97	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3 3.13 4.24x 4 55.76 53.30 6 38.08 26.62
0 63.15 61.94 2 86.27 80.80 4 57.91 52.57 6 46.19 41.25 8 24.54 19.67	2 97.82 99.32 3 13.39 15.94 4 71.93 66.35 5 12.42 4.53× 6 65 65 59.92	3 2.37 7.59 4 96.31 77.69 5 18.50 19.87 6 66.10 63.12 7 -13.22 11.87	-8 45.35 57.62 -7 -12.28 14.55 -6 90.33 96.53 -5 23.34 27.19	-5 -23.67 24.14 -4 80.62 67.58 -3 9.83 10.33 -2 139.93 127.75 -1 -22 05 25 89	<ul> <li>18</li> <li>4</li> <li>-4</li> <li>29,13</li> <li>36,99</li> <li>-2</li> <li>36,39</li> <li>40,02</li> </ul>	-8 27.24 28.41 -6 32.23 34.03 -4 31.38 36.91 -2 43.29 44.12
<ul> <li>12 0</li> <li>-3 38.29 48.67</li> <li>-6 41.86 43.39</li> <li>-6 40.0118</li> </ul>	7 11.20 11.71 8 34.32 29.49 4 11 1	8 32.26 35.06	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 121.41 111.57 1 -10.83 10.67 2 96.78 88.53 3 -38.92 45.21 4 67.76 50.99	2 23.79 26.15 4 1 5 -R 48 28 58 05	2 48.46 51.12 4 38.07 41.46 4 17 5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-8 34.69 43.96 -7 13.39 14.69 -6 43.91 47.49 -5 24.21 27.15 -4 52.98 52.68	-7 $-13.77$ $15.04-6$ $79.22$ $73.93-5$ $-21.18$ $26.42-4$ $49.90$ $53.41-3$ $-40.05$ $50.98-29$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-7 10.32 10.69 -6 88.22 85.56 -5 37.49 40.75 -4 129.79 108.17 -3 21.54 23.96	-6 27.58 23.96 -4 40.24 44.89 -2 39.37 44.47 0 43.83 37.50 2 28.47 30.58
8 24,75 22,09 • 14. 0 -8 19.60 19.31	-3 20,39 20,00 -2 75,16 90,50 -1 -7,00 4,23x 0 75,09 75,79 2 99,72 89,40	-1 -12.37 14.93 0 109.95 92.94 1 4.34 3.56x 2 88.14 73.23	7 1.84 3.46× 8 30.71 28.99 7 3	10 28,29 25,36 4 4 -8 54,51 66,30	-2 147.93 146.34 -1 40.11 42.51 0 175.72 158.95 1 -14.21 16.15 2 160.84 142.51	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3 -5.59 4.27× 4 61.94 59.72 5 -1.37 4.71× 6 52.39 54.09 8 31.42 26.59	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-8 61,66 75,11 -7 14.28 15,14 -6 88.92 99,66 -5 -6,38 3,74~ -4 93,94 85,18	-7 -21.17 22.55 -6 71.19 71.24 -5 -4.19 13.64 -4 162.69 138.74 -3 2.52 11.99	3 -4.71 2.93x 4 99.91 81.35 5 -34.46 34.45 6 64.81 62.70 7 -15.09 16.13	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
4 54 72 52.69 6 29.01 20.02 # 16 0	<ul> <li>13</li> <li>-8</li> <li>32,12</li> <li>34,18</li> <li>-7</li> <li>13,88</li> <li>18,15</li> <li>-6</li> <li>22,53</li> <li>27</li> <li>37</li> </ul>	<ul> <li>IO 2</li> <li>-8 46,76 56,23</li> <li>-7 .52 3,66×</li> </ul>	-3 13.42 14.23 -2 77.89 69.65 -1 -42.75 48.67 0 116.54 92.12 1 -28.92 34.93	-2 139.77 125.96 -1 17.59 25.67 0 66.37 61.81 1 16.63 18.33 2 50.89 53.44 1 -53.60 2000	8 42,16 43.74 986 6.53 10 19,33 20,12 # 3 5	7 9.28 10.77 8 43.56 47.12 9 11.21 11.52 10 20.50 20.83
-8 23.21 26.70 -6 44.09 41.06 -4 28.08 36.37 -2 41.15 48.95 0 47.88 47.48	-5 9.88 11.13 -4 59.74 57.77 -3 -5 52 4.35v -2 46.22 49.36 0 66.09 60.69	-6 44.99 47.74 -5 -17.86 19.95 -4 75.62 73.33 -3 1.28 3.83× -2 107.79 105.60	2 89.27 73.82 3 -1.65 8.00 4 87.63 79.15 5 -21.10 22.60 6 35.96 34.30	4 88.39 73.74 5 20.98 22.50 6 47.16 47.43 7 4.24 3.44× 8 45.67 44.59	-8 60.99 71.27 -7 24.50 23.93 -6 51.32 51.93 -5 -14.40 19.46 -4 105 90 91 20	-10 28.96 30.10 -9 -9.39 7.53x -8 47.38 49.08 -7 7.55 3.44x
4 31,60 30,34 4 18 0 -8 24 52 20.85	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-1 -30.46 32.71 0 97.00 90.65 1 -16.35 20.86 2 84.61 93.19 3 -21.71 21.12	7 -7.80 3.68× 8 39.47 39.19 9 3	<ul> <li>€ 4</li> <li>-a 50.68 65.82</li> <li>-7 -1.92 3.32x</li> </ul>	-3 62.02 59.57 -2 139.21 137.74 -1 26.06 26.07 0 137.75 139.64 1 70.24 69.21	-6 55 49 56 69 -5 -1.17 3.84x -4 95.07 84.31 -3 2.73 3.19x -2 140.69 124.70
-6 15.49 12.41 -4 25.52 33.22 -2 30.90 37.20 0 33.17 35.23 2 33.17 35.41	<ul> <li>15</li> <li>-8</li> <li>15.89</li> <li>18.22</li> <li>-6</li> <li>52.93</li> <li>55.98</li> <li>-6</li> <li>-6<td>5 19.47 19.30 6 61.63 55.90 8 37.38 30.95</td><td>-7 -86 3.62× -6 68.63 65.10 -552 4.26× -4 59.24 61.16 -3 -11.05 14.65</td><td>-6 100,19 105.02 -5 7.39 3.72x -4 125.05 107.24 -3 16.43 16.18 -2 106.71 96.06</td><td>2 70.64 69.22 3 -29.20 33.62 4 96.03 80.86 5 -14.20 16.54 6 62.43 58.39</td><td>-1 <math>-4</math> <math>12</math> <math>6.24 0 <math>181.85</math> <math>166.12</math> 1 <math>58.35</math> <math>69.32</math> 2 <math>151.52</math> <math>131.69</math> 3 <math>30.59</math> <math>34.53</math></math></td></li></ul>	5 19.47 19.30 6 61.63 55.90 8 37.38 30.95	-7 -86 3.62× -6 68.63 65.10 -552 4.26× -4 59.24 61.16 -3 -11.05 14.65	-6 100,19 105.02 -5 7.39 3.72x -4 125.05 107.24 -3 16.43 16.18 -2 106.71 96.06	2 70.64 69.22 3 -29.20 33.62 4 96.03 80.86 5 -14.20 16.54 6 62.43 58.39	-1 $-4$ $12$ $6.240 181.85 166.121 58.35 69.322 151.52 131.693 30.59 34.53$
<pre>1 1 -3 55.79 43.53 -5 -69.89 83.65</pre>	-2 45,28 50,70 0 33,42 34,39 2 55,53 55,45 4 39,16 39,15 6 29,02 24 65	-9 28,99 33,26 -7 10,95 14,15 -6 49,43 53,31 -5 15,98 19,30	-2 97 40 92 45 -1 7 40 3.95 0 97 60 89 93 1 -15 97 20 29 2 96 55 91 94	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7 -3.24 3.52x B 37.05 41.90 # 5 5	5 -7.05 3.99x 6 82.29 80.01 7 13.95 13.09 9 37.18 39.05 9 -7.54 7 14x
-4 91.75 101.50 -3 -156.59 167.75 -2 248.75 218.12 -1 -47.20 45.41 0 255.50 192.50	<ul> <li>17 1</li> <li>-8 32.00 31.44</li> <li>-6 24.83 27.16</li> </ul>	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	3 -26 42 23.70 4 42 56 37.52 5 -16 53 21.05 6 52 96 47.97 7 8.57 11.14	5 20.71 23.64 6 54.84 48.50 7 -11.91 13.63 8 28.45 27.50	-5 30.65 35.40 -7 -26.84 25.18 -6 72.97 69.73 -5 29.60 37.54 -4 90.66 81.44	10 24 29 17 58 4 6 -8 36 51 41 13
1 96,29 77,90 2 65,51 61,93 3 108,87 99,79 4 101,21 96,76 5 75,57 71,91	-4 34,38 40.78 -2 32,96 36,72 0 46,97 47,02 2 31,85 32,66 4 28,09 25,70	1 -29.22 29.53 2 74.40 71.64 3 -10.39 12.05 4 57.37 58.11 5 -14.31 14.09	8 40,19 57.05 11 3 -8 43.68 50.57 -7 43.68		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-7 8,02 6,83 -6 54,35 49,08 -5 -3,12 3,79x -4 92,08 86,07 -3 8,40 3,36x
6 85,46 52.70 7 44.71 40.24 8 59,44 53.37 9 14.74 7.09× 10 29,69 30.53	<ul> <li>19 1</li> <li>-4 23.10 23.22</li> <li>-2 35.11 41.42</li> </ul>	6 41,62 37,36 14 2 -9 29,18 30,12 -9 29,18 30,12	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-5 19.42 22.20 -4 73.73 72.75 -3 2.19 3.60× -2 104.62 105.67 -1 9.47 5.61	3 13.49 13.30 4 90.11 82.24 5 6.40 4.19x 6 72.93 67.05 7 -16.82 18.17	-2 124.33 115.54 -1 29.64 35.83 0 115.89 105.78 1 -6.62 8.30 2 128.55 108.48
<ul> <li>✓ 3 1</li> <li>-8 42.29 42.32</li> <li>-7 -2.50 1.84x</li> <li>-6 89.68 84 92</li> </ul>	0 29.61 25.06 4 0 2 0 140.74 125.37	-5 -5,70 10,54 -4 67.25 65.09 -310 3.84x -2 57.25 62.69	-1 -25.54 26.72 0 74.42 77.90 1 9.41 4.47x 2 45.96 43.02 3 4.84 4.33x	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8 49.00 44.67	5 - 67 . 38 19.50 4 116.55 97.44 5 6.42 4.26× 6 73.22 67.22 7 -10.79 12.34
-5 -7,14 990 -4 143,24 125,43 -3 52,60 63,34 -2 173,57 137,63 -1 -38,42 46,12	4 92.26 93.62 5 -9.67 12.30 6 72.80 75.61	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 49,70 45,59 5 13,95 14,08 6 43,59 35,35 8 24,41 22,73	23.76 23.41 6 25.66 21.78 8 30.79 31.42 10 4	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
0 93,77 82,70	7 2,59 2.18×			-5 49.08 61.31	-2 01.01 13.89	-6 72.72 72.82

Table 4 (cont.)

Н К L Fc Fa -5 25.37 23.42	H K L F2 F0 S 7	H K L Fc Fo 4 S	H K L Fc Fo	H K L Fc Fo 6 10	H K L Fc Fo ≠ 11 11	H K L F <sub>C</sub> Fo 9 13
-4 93,63 77,34 -3 27,46 33,47 -2 93,99 93,59 0 113,63 96,34 1 -610,05 11,97 0 12,65 16,34 1 -23,75 16,34 4 20,75 16,34 4 20,767 31,15 5 -3,92 10,76 6 6 33,35 60,23 8 43,35 42,16	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	- 8 28.06 31.29 -7 -5.59 3.72% -6 63.71 55.56 -5 -20.22 29.5 -4 7165 75.94 -3 -5 99.09 -1 1.21 42.39 0 115.59 10C.19 1 -19.02 20.72 2 105.10 49.49 3 -29.21 22 22	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-q 34,51 35.42 -7 4,32 11.12 -6 49,37 50.44 -5 1.62 4,63× -4 56,39 55.60 -2 70.04 63.04 -1 2.33 4,71× 0 63.90 59.93 1 2,219 57.51× 2 26,05 23.04 3 60 23.04	-6 29.99 29.04 -4 40.35 46.01 -2 43.95 42.69 0 49.63 49.34 2 41.17 36.62 4 35.72 31.23 1 13 11 -4 32.14 34.04 -2 45.14 49.56 0 35.00 35.11	-4 24.91 25.41 -2 25.97 35.27 0 42.64 41.55 2 40.12 42.47 4 33.76 25.52 111 13 -2 33.97 35.71 0 50.12 62.16 2 25.04 21.25
$\begin{array}{c} & 5 & 6 \\ & -5 & 41,67 & 44,03 \\ & -5 & 42,93 & 57,36 \\ & -5 & 12,001 \\ & -6 & 54,93 & 57,36 \\ & -5 & 12,011 \\ & -6 & 54,93 & 57,36 \\ & -5 & 12,011 \\ & -6 & 57,13 & 22,93 \\ & -1 & 27,13 & 22,95 \\ & -1 & 27,13 & 22,95 \\ & -1 & 27,13 & 22,95 \\ & -1 & 27,13 & 22,95 \\ & -1 & 27,13 & 22,95 \\ & -1 & 27,13 & 22,95 \\ & -1 & 27,13 & 22,95 \\ & -1 & 27,13 & 22,95 \\ & -1 & 27,13 & 22,95 \\ & -1 & 27,13 & 22,95 \\ & -1 & 27,13 & 22,95 \\ & -1 & 27,13 & 22,95 \\ & -1 & 27,13 & 22,95 \\ & -1 & -5 & -1,055 & 45,35 \\ & -9 & -1,055 & 44,135 \\ & -2 & -1,055 & 44,135 \\ & -3 & -1,055 & 44,135 \\ & -3 & -1,055 & 26,13 & 4,405 \\ & -7 & 31,49 & 90,17 \\ & -6 & 57,74 & 43,11 \\ & -2 & 42,27 & 15,14 & 3,28 \\ & -7 & 34,51 & 44,273 \\ & -7 & 34,51 & 44,273 \\ & -7 & 34,51 & 44,273 \\ & -2 & 62,396 & 23,11 \\ & 12 & 6 \\ & -7 & 24,22 & 23,28 \\ & -7 & 34,51 & 42,73 \\ & -3 & 1,335 & 44,273 \\ & -3 & 1,335 & 44,273 \\ & -3 & 1,335 & 44,273 \\ & -3 & 1,335 & 44,273 \\ & -2 & 63,96 & 63,007 \\ & -1 & 35,96 & 63,007 \\ & -2 & 52,51 & 42,53 \\ & -2 & 63,96 & 63,007 \\ & -2 & 53,96 & 63,007 \\ & -2 & 53,96 & 63,007 \\ & -2 & 53,96 & 63,007 \\ & -2 & 53,96 & 63,007 \\ & -2 & 53,96 & 63,007 \\ & -2 & 53,96 & 63,007 \\ & -2 & 53,96 & 63,007 \\ & -2 & 52,32 & 33 \\ & -2 & 63,96 & 63,007 \\ & -2 & 52,33 & 43,076 \\ & -2 & 52,33 & 43,076 \\ & -2 & 52,33 & 43,076 \\ & -2 & 52,33 & 43,076 \\ & -2 & 52,33 & 43,076 \\ & -2 & 52,33 & 43,076 \\ & -2 & 52,33 & 43,076 \\ & -2 & 52,33 & 43,076 \\ & -2 & 52,33 & 43,076 \\ & -2 & 52,33 & 43,076 \\ & -2 & 52,33 & 43,076 \\ & -2 & 52,33 & 43,076 \\ & -2 & 52,33 & 43,076 \\ & -2 & 52,33 & 43,076 \\ & -2 & 52,33 & 43,076 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & -2 & 52,33 & 52,11 \\ & $	4 95.74 75.64 5 .92 4.59 6 47.32 46.61 8 39.37 36.61 8 39.37 36.61 	$ \begin{array}{c} 4 \\ 84 \\ 6 \\ 525 \\ 7 \\ 8 \\ 25 \\ 37 \\ 25 \\ 37 \\ 25 \\ 37 \\ 25 \\ 37 \\ 37 \\ 37 \\ 37 \\ 37 \\ 37 \\ 37 \\ 3$	$\begin{array}{c} 171.49 & 59.53 \\ 516.66 & 22.0.36 \\ 62.23.95 & 22.0.01 \\ 711.25.7 & 23.69 \\ 752.67 & 25.67 \\ 79 \\ -8 & 44.72 & 47.64 \\ -7 & 9.05 & 3.65 \\ -5 & 51.67 & 53.09 \\ -5 & 11.40 & 174.12 \\ -7 & 71.40 & 174.12 \\ -2 & 69.57 & 62.74 \\ -7 & 71.20 & 29.23 \\ 1.40 & 174.12 \\ -2 & 69.57 & 62.74 \\ -2 & 71.20 & 63.14 \\ -7 & 71.20 & 63.14 \\ -7 & 51.30 & 63.14 \\ -7 & 51.30 & 63.14 \\ -6 & 57.7 & 23.12 \\ -7 & 51.67 & 31.66 \\ -5 & 51.67 & 23.12 \\ -7 & 51.30 & 63.14 \\ -7 & 51.30 & 63.14 \\ -7 & 51.30 & 63.14 \\ -7 & 51.20 & 27.15 \\ -7 & 51.20 & 27.15 \\ -7 & 51.20 & 27.15 \\ -7 & 51.20 & 27.25 \\ -7 & 51.20 & 27$	5 19:51 24.59 6 22:50 22.12 8 32.97 27.75 9 10 - R 31.45 33.32 - 4 11.63 31.32 - 4 11.63 41.95 - 1 7.15 - 1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c} 0 & 14 \\ 0 & 49, 29 & 52, 96 \\ 1 & 9, 66 & 4, 107 \\ 2 & 57, 23 & 61, 257 \\ 3 & -3, 37 & 3, 547 \\ 4 & 49, 03 & 51, 257 \\ 5 & 51, 73 & 22, 37 \\ 2 & 14 \\ -6 & 33, 71 & 25, 36 \\ -5 & -1, 42 & 3, 207 \\ -6 & 33, 71 & 25, 36 \\ -5 & -1, 42 & 3, 007 \\ -4 & 37, 76 & 38, 80 \\ -3 & -19, 53 & 19, 63 \\ -3 & -19, 53 & 19, 63 \\ -3 & -19, 53 & 19, 63 \\ -4 & 37, 76 & 38, 80 \\ -3 & -19, 53 & 19, 63 \\ -4 & 37, 76 & 38, 80 \\ -4 & 37, 76 & 38, 80 \\ -4 & 37, 76 & 38, 80 \\ -2 & 42, 30 & 4, 40 \\ 0 & -22, 67 & 65, 40 \\ 0 & -22, 67 & 65, 40 \\ 0 & 516 & 65, 40 \\ 0 & 4 & 14 \\ -5 & -15, 89 & 16, 79 \\ -4 & 51, 89 & 16, 79 \\ -4 & 51, 89 & 39, 44 \\ -4 & 35, 88 & 33, 94 \\ -1 & -1, 95 & 3, 597 \\ 0 & 42, 123 & 39, 58 \\ 2 & 37, 33, 58 & 33, 594 \\ -1 & -139 & 33, 587 \\ 0 & 42, 123 & 39, 587 \\ 4 & 36, 73 & 28, 357 \\ -4 & 25, 78 & 43, 577 \\ -4 & 26, 78 & 26, 327 \\ -4 & 26, 78 & 26, 327 \\ -2 & 27, 95 & 33, 557 \\ -2 & 27, 95 & 33, 577 \\ -2 & 27, 95 & 33, 577 \\ -2 & 27, 95 & 33, 577 \\ -2 & 27, 95 & 33, 577 \\ -2 & 27, 95 & 33, 577 \\ -2 & 27, 95 & 33, 577 \\ -2 & 27, 95 & 33, 577 \\ -2 & 27, 95 & 33, 577 \\ -2 & 27, 95 & 33, 577 \\ -2 & 27, 95 & 33, 577 \\ -2 & 27, 95 & 33, 577 \\ -2 & 27, 95 & 33, 577 \\ -2 & 27, 95 & 33, 577 \\ -$
2 61.01 61.90 3 -3.60 4.29× 4 54.75 56.54 6 39.69 33.23 4 13 6 -4 -45.13 55.73 4 14 6 -8 27.41 29.44		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-6 46.76 47.22 -5 -34 12.87 -4 55.13 65.31 -3 -6.33 4 12.87 -2 43.73 49.01 0 53.70 49.01 2 39.70 40.70 3 -5.55 40.70 3 -5.55 15.02 • 13 9	0 32.57 2 32.59 3 1.90 1 11 -9 29.74 25.18 -7 11.08 10.09 -5 11.91 30.87 -5 11.86 45.59 -4 43.54 43.59 -3 -17.40 17.29 -3 29.15 37.40 -1 8.55 12.258	- 2 02263 02260 0 62263 9226 1 -15,97 14,62 1 -252,59 74,13 4 45,03 48,53 6 34,47 31,16 9 12 -6 30,20 34,07 -4 45,75 50,92 -2 45,96 53,46 0 46,79 45,95	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-# 25.26 29.94 -5 41.43 46.66 -5 4.937 10.027 -2 40.19 10.027 -2 60.19 53.99 1 -24.34 27.66 4 31.00 27.92 6 26.29 23.47 14 5 -8 18.79 17.48 -6 26.54 30.37 -4 4.50 51.28 0 39.05 4.59 10.28 29.01 16 8 -4 23.92 29.01 17.87 -5 50.67 -7 .28 5.647 -6 77.28 5.647 -7 .857 -8 5.647 -7 .857 -8 5.647 -8	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	- 0 67,65 67,03 - 0 77,65 67,03 - 27,2,16 65,76 - 3,-3,91 4,40 - 4,53,50 57,59 - 6 426,52 28,55 - 3 11 - 7 33,04 29,17 - 7 2,12 5,27 - 3 1,44 29,17 - 7 2,12 5,27 - 3 1,14 29,17 - 7 33,06 34,02 - 3 32,00 - 1 42,72 45,42 - 3 82,100 32,07 - 2 37,00 32,07 - 3 45,72 - 3 82,00 - 1 45,72 45,42 - 3 82,00 - 1 45,72 45,42 - 3 82,00 - 1 45,72 45,42 - 3 55,53 52,00 - 3 25,54 53,56 - 5 31 - 6 43,01 27,75 - 5 11 - 6 43,01 27,75 - 5 11 - 7 36,49 40,29 - 7 36,49 40,29 - 7 41,477 - 1 4,47,47 - 5 43,49 40,29 - 7 41,477 - 1 4,477 - 4 46,72 - 7 5 11 - 7 36,49 40,29 - 7 41,477 - 7 36,49 40,29 - 7 41,477 - 7 41,477 - 7 41,477 - 7 4,477 - 7 5,477 - 7 14,477 - 7 4,477 - 7 5,477 - 7 14,477 - 7 5,477 - 7 14,477 - 7 5,477 - 7 14,477 - 7 36,499 - 7 2,477 - 7 34,497 - 7 5,477 - 7 14,477 - 7 36,499 - 7 2,477 - 7 34,477 - 7 34,497 - 7 35,479 - 7 3	$ \begin{array}{c} 1 & 15 & 165 & 18 & 21 \\ 2 & 52 & 61 & 50, 70 \\ 4 & 40, 67 & 40, 32 \\ 10 & 12 \\ -6 & 26, 37 & 21.93 \\ -4 & 33, 92 & 42.79 \\ -2 & 47.65 & 57.63 \\ 0 & 57.65 & 34.12 \\ 2 & 44.79 & 42.79 \\ 2 & 47.73 & 42.79 \\ -2 & 47.65 & 57.63 \\ 2 & 44.79 & 42.79 \\ -2 & 47.65 & 57.63 \\ 2 & 44.79 & 42.79 \\ -2 & 47.65 & 57.63 \\ -2 & 45.73 & 42.79 \\ -2 & 47.65 & 57.63 \\ -3 & 57.63 & 57.63 \\ -4 & 54.28 & 57.63 \\ -3 & 57.63 & 57.63 \\ -3 & 57.63 & 57.63 \\ -4 & 54.45 & 57.63 \\ -3 & 41.49 & 57.63 \\ -3 & 41.49 & 57.63 \\ -3 & 41.49 & 57.63 \\ -2 & 46.93 & 47.52 \\ -1 & 46.93 & 47.52 \\ -2 & 46.93 & 47.52 \\ -2 & 46.93 & 47.52 \\ -2 & 46.93 & 47.52 \\ -2 & 46.93 & 47.52 \\ -2 & 46.93 & 47.52 \\ -2 & 46.93 & 47.52 \\ -2 & 46.93 & 47.52 \\ -2 & 46.93 & 47.52 \\ -2 & 46.93 & 47.52 \\ -2 & 46.93 & 47.52 \\ -2 & 46.93 & 47.52 \\ -2 & 46.93 & 47.52 \\ -2 & 47.53 & 57.25 \\ -2 & 57.53 & 57.25 \\ -2 & 57.53 & 57.25 \\ -3 & 57.25 & 37.12 \\ -3 & 13 \\ -3 & 13 \\ -3 & 13 \\ -3 & 10 \\ -3 & 10 \\ -3 & 10 \\ -3 & 10 \\ -3 & 10 \\ -3 & 10 \\ -3 & 10 \\ -3 & 10 \\ -3 & 10 \\ -4$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
0 103 94 90.39 1 -6.02 \$,19 2 105 41 95.55 3 33 -7 35 64 45 5 16 20 17,95 6 74 20 66 80 7 11.36 10,13 9 9 9 8 5 7 25.02 7 -5 75 75 75 75 75 75 75 75 75 75 75 75 75	$\begin{array}{c} & 2 & 7 & 7 & 5 & 25 \\ & 3 & -3 & 25 & 25 \\ & 4 & -3 & 27 & 47 & 49 \\ & 5 & -3 & .13 & 4 & 47v \\ & 6 & 66 & 675 & 65 & 57 \\ & 7 & -10 & 70 & 11 & 771 \\ & 7 & 9 & 29 & 21 & 4 & 37y \\ & 10 & 26 & 10 & 21 & 21 \\ & 2 & g \\ & -10 & 21 & 98 & 22 & .96 \\ & -10 & 21 & 98 & 22 & .96 \\ & -10 & 21 & 98 & 13 & .59 \\ & -5 & 564 & 6 & .37x \\ & -7 & 13 & .34 & 13 & .59 \\ & -5 & 564 & 6 & .37x \\ & -7 & 13 & .34 & 13 & .59 \\ & -5 & 564 & 6 & .37x \\ & -7 & 13 & .34 & 13 & .59 \\ & -6 & 36 & .29 & 23 & .65 \\ & -7 & -31 & .57 & 40 & .22 \\ & -7 & 13 & .34 & 13 & .59 \\ & -6 & 36 & .29 & 23 & .65 \\ & -7 & -31 & .58 & 53 & .438 \\ & -1 & -31 & .58 & 53 & .438 \\ & -1 & -31 & .58 & 53 & .438 \\ & -1 & -31 & .58 & 53 & .438 \\ & -1 & -31 & .58 & 53 & .438 \\ & -1 & -31 & .58 & 53 & .438 \\ & -1 & -31 & .58 & 53 & .438 \\ & -1 & -31 & .58 & .58 & .438 \\ & -1 & -31 & .58 & .58 & .438 \\ & -1 & -31 & .58 & .58 & .438 \\ & -1 & -31 & .58 & .58 & .438 \\ & -1 & -31 & .58 & .58 & .438 \\ & -1 & -31 & .58 & .58 & .438 \\ & -1 & -31 & .58 & .58 & .438 \\ & -1 & -31 & .58 & .58 & .438 \\ & -1 & -31 & .58 & .58 & .438 \\ & -1 & -31 & .58 & .58 & .438 \\ & -1 & -31 & .58 & .58 & .438 \\ & -1 & -31 & .58 & .58 & .438 \\ & -1 & -31 & .58 & .58 & .438 \\ & -1 & -31 & .58 & .58 & .438 \\ & -1 & -31 & .58 & .58 & .58 \\ & -1 & -31 & .58 $	$\begin{array}{c} -5 & -1 & -1 & -4 & -5 \\ -4 & -4 & -5 & -5 & -5 & -5 & -5 & -5 \\ -5 & -5 &$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<ul> <li>2 16</li> <li>-2 24.94 24.33</li> <li>0 24.49 22.039</li> <li>1 7.99 2.239</li> <li>2 27.54 22.39</li> <li>4 16</li> <li>0 26.09 24.32</li> <li>1 2.64 1.67x</li> </ul>

			rings with	correspon	ung vonus	in pyriaine.			
Py	ridyl ring A		Ру	ridyl ring B		Aver	age	Pyrid	line†
Bond	Length $l_A$	$\sigma(l_A)$	Bond	Length $l_B$	$\sigma(l_B)$	$\overline{l=\frac{1}{2}(l_A+l_B)}$	σ(1)*	Bond	Length l
N(1)-C(1)	1·361 Å	0·015 Å	N(2)-C(6)	1•377 Å	0∙016 Å	1·369 Å	0∙011 Å	N - C(a)	1•340 Å
C(1) - C(2)	1.398	0.016	C(6)-C(7)	1.408	0.017	1.403	0.011	C(a)-C(b)	1.390
C(2) - C(3)	1.409	0.020	C(7) - C(8)	1.399	0.021	1.404	0.014	C(b)-C(c)	1.400
C(3) - C(4)	1.398	0.022	C(8) - C(9)	1.417	0.021	1.407	0.012	C(c)-C(b)	1.400
C(4) - C(5)	1.379	0.020	C(9)-C(10)	1.367	0.018	1.373	0.013	C(b)-C(a)	1.390
C(5) - N(1)	1.363	0.017	C(10)–N(2)	1.364	0.016	1.364	0.011	C(a)-N	1.340
C(1) - N(3)	1.373	0.016	C(6) - N(3)	1.327	0.016	1.35	0.01		
Pd - N(1)	2.022	0.009	Pd - N(2)	2.022	0.011	2.022	0·007‡		

Table 5(a). Bond lengths in bis-(2,2'-dipyridyliminato)palladium(II). Comparison of dimensions of averaged pyridyl rings with corresponding hands in puriding

\*  $\sigma^2(I) = \frac{1}{2}[\sigma^2(l_A) + \sigma^2(l_B)]$ .  $\ddagger \sigma^2(I_{1-2, 2-3}) = \frac{1}{2}[\sigma^2(1) + \sigma^2(3) + 4\sigma^2(2)\cos^2\frac{1}{2}\beta]$ . † Bak *et al.* (1954). S.d.'s of all bond-lengths = 0.005 Å.

## Table 5(b). Bond angles in bis-(2,2'-dipyridyliminato) palladium(II)

Pyridyl ring A		Pyridyl ring B		A	Pyridine	
Angle	$\theta_A$	Angle	$\theta_B$	$\bar{\theta} = \frac{1}{2}(\theta_A + \theta_B)$	Angle	θ
Pd - N(1) - C(1)	119·6°	Pd - N(2) - C(6)	118·9°	119·3°		
Pd - N(1) - C(5)	119.7	Pd = N(2) - C(10)	120.5	120.1		
C(1) - N(1) - C(5)	120.4	C(6) - N(2) - C(10)	120.1	120.3	C(a)-N - C(a')	116·7°
N(1)-C(1)-N(3)	124.0	N(2) - C(6) - N(3)	124.6	124.3	—	
N(1)-C(1)-C(2)	119•4	N(2) - C(6) - C(7)	119.0	119-2	N - C(a) - C(b)	124.0
N(3)-C(1)-C(2)	116.5	N(3) - C(6) - C(7)	116.4	116.5		
C(1) - C(2) - C(3)	118-9	C(6) - C(7) - C(8)	120.0	119.5	C(a)-C(b)-C(c)	118.6
C(2) - C(3) - C(4)	120.9	C(7) - C(8) - C(9)	119-1	120.0	C(b)-C(c)-C(b')	118.1
C(3) - C(4) - C(5)	116.8	C(8) - C(9) - C(10)	118.7	117.8	C(c)-C(b)-C(a)	118.6
C(4) - C(5) - N(1)	123.0	C(9) - C(10) - N(2)	122.3	122.7	C(b)-C(a)-N	124.0
C(1)-N(3)-C(6)	123.4	_		123.4		
N(1)-Pd - N(2)	85.6			85.6		

Estimated standard deviations,  $\sigma(\theta)$ : Light atom-light atom-light atom, 1·2°; Pd-light atom-light atom, 0·9°; light atom-Pd-light atom, 0·6°.

## Table 6. Details of least-squares planes

The planes lx' + my' + nz' + k = 0 are referred to orthogonal axes. The transformation from fractional cell coordinates (x, y, z)is  $x' = ax + cz \cos\beta$ , y' = by,  $z' = cz \sin\beta$ . The weight w of an atom in the calculation varies as its (coordinate s.d.)<sup>-2</sup>. Starred values correspond to deviations of atoms not included in the least-squares calculation.

Plane	l	m	n	!	k
1	+0.11571	-0.01039	+0.9	9323 -1.	19085
2	-0.34527	-0.44320	+0.82	2726 +4.	96150
3	-0.14810	-0.24133	+0.9	5908 + 1·	79118
				Estimated	
	Deviat	ion from plane	(Å)	coordinate	
Atom	1	2	3	s.d.(Å)	w
Pd	-0.3660*	-0.5278*	-0.8904*	0.000	
N(1)	-0.0240			0.009	256
N(2)		-0.0477	+0.0070	0.011	178
N(3)	+0.2538*	+0.2339*	-0.2094*	0.011	
CÌÌ	+0.0449		+0.0097	0.012	154
Č(2)	-0.0369			0.016	89
C(3)	-0.0128			0.012	96
C(4)	+0.0185			0.014	111
C(5)	+0.0104			0.013	142
C(6)		+0.0446	-0.0099	0.011	196
C(7)		-0.0148		0.013	135
C(8)		-0.0343		0.016	85
C(9)	_	+0.0306		0.014	111
Č(10)		+0.0213	<del></del>	0·01 <b>2</b>	158
	Angles be	tween planes:	1	2	
	•	2	38·2°	<u> </u>	
		3	20·3°	17 <b>·9</b> °	

tween these deviations is due to an additional deformation which bends the C-N(3) bonds 'up' and N-Pd bonds 'down' with respect to the pyridyl planes. This causes the deviations of N(3) from planes 1 and 2 to be +0.25 and +0.23 Å respectively, while the palladium lies at -0.37 and -0.53 Å from these planes. The distortions in the bottom ligand of Fig. 3 are in the opposite senses to those described.

The pyridyl rings themselves are not strictly planar. The maximum deviations  $\Delta$  from planes 1 and 2 occur for the four atoms which are common to the pyridyl and chelate rings. For these atoms the ratios of  $\Delta$  to their averaged coordinate s.d.'s lie between 2.6 and 4.3.

Fig. 3 illustrates the arrangement of the complexes and the intermolecular contacts shorter than 3.7 Å. All contacts shorter than 3.7 Å are listed in Table 7. The shortest approach between ligands of the same molecule (3.01 Å) is C(5)–C(10'), indicating overcrowding of the attached hydrogen atoms.

## Table 7. Non-bonded contacts in bis-(2,2'-dipyridyliminato)palladium(II) The superscripts refer to the asymmetric units as follows:

-	
- x, y,	Z F
1 - x, 1 - y,	2
x, 1-y, -	$\frac{1}{2} + Z$
$1-x, y, \cdot$	$\frac{1}{2} - z$
$\frac{1}{2} + x, \frac{1}{2} + y,$	Z
$\frac{y}{2} + x, \frac{1}{2} - y, \frac{y}{2} - y$	$\frac{1}{2} + z$
$v_{1} = \frac{3}{2} - x, \frac{1}{2} - y,$	Ī
Intermolecular contact	s Distance
$C(9) \cdots N(3'')$	3·62 Å
$C(9) \cdots C(6'')$	3.41
$C(9) \cdots C(7')$	3.52
$C(10) \cdots N(3'')$	3.53
$\mathbf{C}(10) \cdots \mathbf{C}(6'')$	3.57
$N(2) \cdots C(5'')$	3.53
$N(3) \cdots C(5'')$	3.66
$C(5) \cdots C(6'')$	3.39
$C(9) \cdots C(4^{iv})$	3.56
$C(8) \cdots C(3^{iv})$	3.68
$C(8) \cdots C(3^{v})$	3.62
$C(7) \cdots N(3^{vi})$	3.59
Interligand contacts	
C(5) + C(10')	3.01 Å
$N(1) \dots C(10')$	3.13
N(1) + C(10)	3.12
$N(2) \cdots C(5)$	2.07
$N(1) \cdots N(2)$	2-91

#### **Discussion of the structure**

## Molecular geometry

The palladium-nitrogen bond length in this complex is 2.02 Å, which is in agreement with the sum of the single-bond radii of palladium(II) and nitrogen, 1.31 and 0.70 Å (Pauling, 1960). Similar values of 2.01 and 1.99 Å respectively have been reported in bis-(*N*-nbutylsalicylaldimino)palladium(II) by Frasson, Panattoni & Sacconi (1963) and in bis-(3-hydroxy-1,3-diphenyltriazine)palladium(II) by Meyer & Simonsen (1963).

The right-hand side of Table 5(a) contains comparisons between the bond lengths in pyridine (Bak, Hausen & Rastrup-Anderson, 1954) and the averaged bond lengths in the pyridyl rings of this complex. As in



Fig. 3. Packing and contacts in the crystal of bis-(2,2-'dipyridyliminato)palladium(II). Atoms of the dotted complex are at  $\frac{1}{2} \pm z$ .

pyridine, the bond lengths in the averaged pyridyl ring increase with increasing distance from the nitrogen. The effect is not symmetrical, no doubt owing to the effect of the bond to the imide nitrogen on one side of the ring. The averaged pyridyl nitrogen-carbon bonds are 0.029 and 0.024 Å longer than the corresponding bond in pyridine. On the basis of the present conservative calculation of the bond-length s.d.'s, this lengthening is only at the threshold of statistical significance ( $t_0 = 2.4, 2.0$ ) (Cruickshank & Robertson, 1953).

The correlation between the bond-angles in the pyridyl ring and pyridine is poor. This is to be expected in view of the unsymmetrical environment of the pyridyl rings.

The averaged imino-nitrogen-carbon bond-length, 1.35 Å, is normal for C-N in aromatic compounds (cf. 1.346 Å in acridine (Phillips, Ahmed & Barnes, 1960); 1.335, 1.355 Å in phenazine (Herbstein & Schmidt, 1955); 1.340 in pyridine (Bak *et al.*, 1954)).

## Relation to similar overcrowded molecules

The configuration of the title compound (I, below) is found also in (II) the  $\beta$  form of 9,9'-bixanthenylidene (Mills & Nyburg, 1963), in (III), bianthronyl (Harnik & Schmidt, 1954) and in (IV), 9,9'-bifluorenylidene (Nyburg, 1954). In each of these four compounds, repulsion between hydrogen atoms causes the folding of a system of three linearly fused rings.

A comparison of (I) and (II) reveals a remarkable similarity of their space groups, unit-cell dimensions and atomic arrangements. The crystals are isomorphous, the ethylenic bridge in (II) being replaced by the palladium in (II). The distance between the carbon atoms bearing the conflicting hydrogen atoms is 2.97 Å in (II) (cf. 3.01 Å in I). The angle between the normals to the benzene rings in (II) is calculated to be  $40.5^{\circ}$ from the coordinates listed by Mills & Nyburg (1963)



(cf.  $38 \cdot 2^{\circ}$  in I). Finally, the angles in (II) corresponding to C(7)–C(6)–N(3) and C(2)–C(1)–N(3) in (I) are both 116° (cf. 116·4°, 116·5°) indicating a similar combination of 'crushing' and 'folding' distortions.

The aromatics (II), (III) and (IV) are thermochromic. For example, 9,9'-bixanthenylidene is colourless at -180 °C but hot solutions are deep blue-green (Day, 1963). No such marked effect has been observed for compound (I). Its toluene solution at -180 °C is pale yellow; the colour deepens on warming to a light orange.

#### Relation to other chelate compounds

A centrosymmetrical arrangement of donor atoms, approximately square with considerable ligand distortion, has also been found by Dale (1963) for bis-(3,3'-p-tolylformazylo)nickel(II). In this complex the chelate rings are boat-shaped in a similar way to that described for (I).

This structural type seems to have been overlooked when structures for similar compounds have been proposed. Specifically, the claim by Porter (1938) that bis-(3,3,5,5-tetramethyl-4,4,dicarbethoxypyrrometheneato)palladium(II) must be a sterically forced tetrahedral structure is thrown into doubt. Here an  $\alpha$ -methyl-substituted pyrrole nucleus essentially replaces pyridine in (I). Implicit in Porter's conclusion is the assumption that conjugated ligands of formal aromaticity remain planar in coordination compounds. The present work shows this assumption to be unnecessary; it can be shown geometrically that a centrosymmetrical configuration — involving no greater distortion and steric hindrance than in (I) — is feasible for the pyrromethene complex.

The authors gratefully acknowledge financial assistance from the U.S. Public Health Service through the National Institutes of Health, Bethesda, Md. (Grant GM10867), and the award of a Research Scholarship from the Commonwealth of Australia (to M.R.S.). The computations were carried out with the help of Professor J. M. Bennett and the staff of the Basser Computing Laboratory, University of Sydney, on SILLIAC and Mr P.N.L. Goddard and the staff of the computing centre of the Weapons Research Establishment at Salisbury, South Australia on the IBM 7090 computer. The SILLIAC programs were



written by Dr F. M. Lovell and Dr J. G. Sime, who also assisted in carrying out the other calculations.

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