STRUCTURE OF AND BONDING IN 1,5-CYCLOOCTADIENE-DUROQUINONE-NICKEL[a]

MILTON D. GLICK[b] AND LAWRENCE F. DAHL[c]
The Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (U.S.A.)
(Received August 3rd, 1964)

INTRODUCTION

Schrauzer and Thyret[1-4] have recently synthesized and characterized from spectral and magnetic measurements bis-duroquinone-nickel, and a number of derivatives in which one duroquinone is replaced by various diolefinic groups. On the basis of the ultraviolet spectra of these complexes, Schrauzer and Thyret[4] concluded that the symmetry of bis-duroquinone-nickel(0) is D_{2h}, and therefore that the nickel is square planar (*i.e.*, the two sets of double bonds are parallel) in the complex. Although no direct predictions of the configurations of 1,5-cyclooctadiene-duroquinone-nickel or other mono-duroquinone-nickel complexes were made[1-4], it is expected that these closely related compounds should possess a similar conformation. Our subsequent single crystal X-ray investigation of the 1,5-cyclooctadiene-duroquinone-nickel complex, hence, was undertaken to confirm or disprove the existence of a square planar "zerovalent" nickel in these complexes and to obtain detailed information about the deformation of the ligands due to their interaction with the nickel. Of further interest is that no X-ray analysis of a metal complexed with duroquinone has been reported.

EXPERIMENTAL

Crystals of cyclooctadiene-duroquinone-nickel ($NiC_{18}H_{24}O_2$) were generously supplied to us by Dr. SCHRAUZER. The density was obtained by the flotation method. A deep-red, needle like crystal of dimensions 0.05 cm × 0.03 cm × 0.03 cm was chosen for obtaining intensity data and aligned with the 0.05 cm needle axis as the rotation axis.

Sixteen layers of multiple-film equi-inclination Weissenberg data (*hk*0 to *hk*15), containing 1757 independent diffraction maxima, were obtained with Mo-K_α radiation. After Lorentz-polarization and spot extension corrections[5], these data were correlated and merged via least squares[6] with 750 Lorentz-polarization corrected diffraction

---

[a] Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.

[b] Based in part on a dissertation submitted by M. D. Glick to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[c] Fellow of the Alfred P. Sloan Foundation.

maxima obtained from multiple-exposure precession photographs of reciprocal layers *h0l*, *h1l*, *h2l*, and *0kl*. A final total of 1880 independent structure amplitudes were placed on a common scale with a weighted reliability index of 4.2 %. Lattice constants were determined from precession photographs. The Weissenberg and precession intensity data were visually estimated by comparison with calibrated standard strips. Absorption corrections were neglected due to the low absorption coefficient ($\mu R_{max} =$ 0.2). The standard deviations of the structure amplitudes [*i.e.*, $|F_0|^2 \sim I(hkl)_0$] were estimated according to the following scheme:
If $I(hkl)_0 < \sqrt{10}\, I(hkl)_{min}$, then $\sigma(|F_0|) = |F_0|\,[I(hkl)_{min}/\sqrt{2}\, I(hkl)_0]^2$.
If $I(hkl)_0 \geq \sqrt{10}\, I(hkl)_{min}$, then $\sigma(|F_0|) = |F_0|/20$.

CRYSTAL DATA

The unit cell is monoclinic with $a = 14.26 \pm 0.05$ Å, $b = 7.95 \pm 0.03$ Å, $c = 14.17 \pm 0.05$ Å, and $\beta = 94°27' \pm 10'$. The experimental density of 1.44 g/cc is in acceptable agreement with the value of 1.37 g/cc calculated for four molecules per unit cell.

The systematic absence of $h + l = 2n + 1$ for *h0l* data indicates the probable space groups *Pn* and *P2/n*. The structural determination showed the correct space group to be *P2/n*. The four molecules were found to be on two-fold axes with the four nickel atoms thereby in the two sets of special two-fold positions: $\pm(1/4, y, 1/4)$ and $\pm(3/4, y, 1/4)$. All carbon atoms are in the general four-fold set of positions: $\pm(x, y, z;\ 1/2 - x, y, 1/2 - z)$. The asymmetric unit, hence, comprises two half-molecules.

In addition to the C_{2h}–$2/m$ Laue symmetry required in the monoclinic system, the X-ray photographs also revealed two *quasi*-mirror planes normal to the *a* and *c* crystallographic axes, which were explained by the final structure.

SOLUTION OF STRUCTURE

The solution of a calculated three-dimensional Patterson synthesis resulted in the placing of two nickel atoms not related by crystallographic symmetry at the fractional coordinates, $x_1 = 0.75$, $y_1 = 0.29$, $z_1 = 0.25$ and $x_2 = 0.25$, $y_2 = 0.059$, $z_2 = 0.25$. The two independent nickel positions with an x separation of 0.5 and the same z coordinate require that either the actual space group is *Pn* and the asymmetric unit consists of two molecules, or the correct space group is *P2/n* and both nickel atoms are located on 2-fold axes. If the latter is true, it is necessary to determine atomic positions corresponding to two half-molecules. Since a Fourier map based upon only the phases of heavy atoms will possess the symmetry of the heavy atoms in the unit cell regardless of the true symmetry, this first approximation to the electron density distribution may have a number of extra "image" peaks if *Pn* is the true space group. A three-dimensional Fourier synthesis phased only on the nickel atoms was computed, and no extra peaks were observed. Examination of the map yielded the 22 non-hydrogen peaks required for the two half-molecules. The peaks corresponding to the two asymmetric oxygen atoms were readily distinguished on the basis of peak heights, chemical conformation, and distances between peaks.

A three-dimensional isotropic least-squares refinement based on the space group *P2/n* resulted in discrepancy factors of $R_1 = [\Sigma||F_0| - |F_c||/\Sigma|F_0|] \times 100 =$

12.3% and $R_2 = [(\Sigma w ||F_0| - |F_c||^2)^{1/2}/(\Sigma w |F_0|^2)^{1/2}] \times 100 = 15.0\%$. In order to ascertain the possible presence of systematic error in the merging of the intensity data, two cycles of least-squares refinement with separate scale factors for each Weissenberg and precession layer were carried out on the parameters obtained from this refinement; no significant parameter changes were obtained.

A three-dimensional difference map, in which the atomic contributions of all atoms in the positions obtained from the isotropic least-squares refinement were subtracted out, showed no areas of residual electron density except for that in the vicinity of the nickel atoms, which was attributed to anisotropy of the heavy atoms. In order to compensate for this effect with a minimum use of computer time, we have modified the Busing-Martin-Levy full matrix least-squares program[7] such that anisotropic refinement of an arbitrary number of atoms and isotropic refinement of the remaining atoms can be carried out simultaneously. The utilization of such a refinement with anisotropic thermal coefficients for the two nickel atoms and isotropic temperature factors for the eighteen carbon and two oxygen atoms yielded final discrepancy factors of $R_1 = 10.1\%$ and $R_2 = 12.7\%$. A final difference map based on this refinement showed no significant residual electron density. Since no peaks characteristic of hydrogen atoms were clearly resolved in the regions where they might be expected, no further attempt was made to locate their coordinates.

Positions and thermal parameters obtained from the final anisotropic–isotropic refinement are given in Table 1. The structure factors calculated from these parameters are listed with observed structure factors (with phases based on those of the calculated structure factors) in Table 2. Bond lengths and angles, calculated with the Busing-Martin-Levy ORFFE program with errors obtained from the full inverse matrix, are listed in Tables 3 and 4. The Fourier maps were calculated on the CDC 1604 with a program[9] written by J. BLOUNT of this laboratory.

The Smith least-squares plane program[11] was utilized to obtain the equations of "best" planes formed by several sets of atoms and the perpendicular distances of these and other atoms from the planes. Unit weighting was used in the calculation of these planes. The equation of the least-squares plane is expressed in orthogonal coordinates X, Y, and Z, which are related to the monoclinic cell coordinates for each atom "k" by the transformation: $X_k = ax_k + cz_k\cos\beta$, $Y_k = by_k$, and $Z_k = cz_k\sin\beta$.

DESCRIPTION AND DISCUSSION OF STRUCTURE

Cyclooctadiene-duroquinone-nickel exists in the solid state as discrete monomeric molecules with each molecule (Fig. 1) consisting of a nickel atom sandwiched between a boat-form 1,5-cyclooctadiene ring and a duroquinone ring (*i.e.*, tetramethyl-*p*-benzoquinone). Since the asymmetric unit contains two half-molecules (packed in the manner indicated in Fig. 2), two independent values of each intramolecular bond length and angle are obtained. Significant distortions (*vide infra*) of the cyclooctadiene ring which are common to each of the independent half-molecules permit the pairing of the chemically equivalent parameters. The atoms are numbered such that C(n) and C(n + 10) are equivalent atoms (*e.g.*, bond lengths C(1)–C(2) and C(11)–C(12) are presumed chemically equivalent); C(1) through C(9), O(10), and Ni(1) belong to the first half-molecule and the remaining atoms to the second half-molecule. Of the 29 resulting pairs of common bond lengths and angles in the two half-molecules,

TABLE I

FINAL ATOMIC PARAMETERS WITH STANDARD DEVIATIONS

Atom	x	y	z	$B(\text{Å}^2)$	$10^4\sigma_x$	$10^4\sigma_y$	$10^4\sigma_z$	$\sigma_B(\text{Å}^2)$
Ni(1)	0.2500	0.0594	0.2500	**	0*	2	0*	
Ni(2)	0.7500	0.2911	0.2500	**	0*	2	0*	
C(1)	0.1312	0.3437	0.1876	5.84	11	24	12	0.34
C(2)	0.1998	0.2278	0.1441	4.28	8	20	10	0.27
C(3)	0.2928	0.2350	0.1498	3.76	9	19	9	0.24
C(4)	0.3480	0.3718	0.2036	6.58	12	26	13	0.41
C(5)	0.0681	−0.1495	0.1358	4.35	9	19	9	0.27
C(6)	0.1591	−0.1544	0.1953	2.51	7	15	7	0.19
C(7)	0.2459	−0.1664	0.1470	2.39	7	14	7	0.18
C(8)	0.3358	−0.1527	0.2048	2.59	7	15	7	0.20
C(9)	0.4247	−0.1461	0.1522	4.17	8	19	9	0.26
O(10)	0.2432	−0.1789	0.0603	4.33	6	13	6	0.19
C(11)	0.6777	0.0052	0.1345	5.52	11	23	11	0.33
C(12)	0.6434	0.1236	0.2076	3.91	9	18	9	0.26
C(13)	0.6547	0.1160	0.3013	4.25	9	19	10	0.28
C(14)	0.7133	−0.0280	0.3488	6.31	12	25	12	0.40
C(15)	0.6378	0.5012	0.0668	4.39	9	20	9	0.27
C(16)	0.6972	0.5068	0.1612	2.50	7	15	7	0.19
C(17)	0.6487	0.5192	0.2468	2.31	7	13	7	0.18
C(18)	0.7052	0.5069	0.3350	2.67	7	16	7	0.19
C(19)	0.6515	0.5029	0.4255	4.14	8	19	9	0.25
O(20)	0.5618	0.5338	0.2430	4.02	6	12	6	0.18

* These standard deviations are required to be identically zero by the special two-fold positions of the nickel atoms.

** For the nickel atoms anisotropic temperature factors of the form: $\exp\{-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})\}$ were used: the resulting thermal coefficients (with standard deviations in parentheses) are:

	10^4B_{11}	10^4B_{22}	10^4B_{33}	10^4B_{13}
Ni(1)	30(1)	36(3)	26(1)	4(1)
Ni(2)	27(1)	33(3)	30(1)	4(1)

Since the nickel atoms lie on two-fold axes, B_{12} and B_{23} are required by the crystallographic symmetry to be identically zero[10].

the largest difference in a given pair is only 1.7 σ's with 21 differences less than 1 σ.

These results confirm the equivalence of the two half-molecules and support the estimates of the standard deviations. This discussion henceforth will use only the atomic designations of the first molecule and will in all cases refer to the average value of the molecular parameters for the two half-molecules with the standard deviation of the average given by the usual statistical formula for independent parameters.

The two sets of parallel double bonds in the cyclooctadiene and duroquinone rings are perpendicular so that, if we assume the nickel to be bonded to the four approximately equidistant double bond centers, the nickel is in an *idealized* tetrahedral configuration. The dihedral angle between the plane containing the nickel and the duroquinone olefinic midpoints and the plane comprising the nickel and the cyclooctadiene olefinic midpoints is essentially 90°. It should be noted that the assumed tetrahedral "zerovalent" nickel in this complex is isoelectronic with the tetrahedral nickel(0) in $Ni(CO)_4$[12]. Of course, the nickel can be formally considered as forming covalent sigma bonds to each of the eight olefinic carbons, but this resulting eight-fold

TABLE 2

COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	FO	FC
2	0	0	-278.2	-270.7
4	0	0	27.0	38.0
6	0	0	-44.4	-44.7
8	0	0	38.7	46.4
10	0	0	-80.9	-87.7
12	0	0	48.8	47.7
16	0	0	20.4	21.4
18	0	0	-19.3	-22.2
5	0	1	-15.1	-13.2
-5	0	1	43.8	33.6
7	0	1	7.1	13.6
-7	0	1	-29.8	-32.8
-12	0	1	13.1	0.0
-13	0	1	16.7	20.2
-15	0	1	-20.0	-6.8
0	0	2	-231.2	-269.3
2	0	2	101.4	102.2
-2	0	2	134.7	143.1
4	0	2	-49.6	-36.8
-4	0	2	-38.0	-31.8
6	0	2	49.6	45.1
-6	0	2	38.3	31.3
8	0	2	-44.3	-42.2
-8	0	2	-31.0	-30.7
10	0	2	60.7	42.5
-10	0	2	66.6	65.9
12	0	2	-35.9	-40.8
-12	0	2	-39.6	-40.5
14	0	2	22.6	21.8
-14	0	2	15.2	13.1
16	0	2	-17.7	-14.2
-16	0	2	-20.6	-20.7
-18	0	2	17.4	21.3
5	0	3	-72.1	-66.2
-5	0	3	69.8	71.1
7	0	3	16.8	16.9
-7	0	3	-22.4	-16.6
11	0	3	24.9	18.9
0	0	4	28.4	38.8
-2	0	4	-37.4	-33.2
4	0	4	43.7	46.2
-4	0	4	35.1	27.8
6	0	4	-51.1	-63.0
-6	0	4	-35.0	-38.5
8	0	4	69.9	82.6
-8	0	4	59.1	66.3
10	0	4	-67.3	-72.2
-10	0	4	-64.6	-73.9
12	0	4	39.9	42.0
-12	0	4	37.6	42.4
14	0	4	-26.3	-27.3
-14	0	4	-22.7	-23.5
16	0	4	15.3	14.1
-16	0	4	17.1	15.2
1	0	5	17.2	14.5
-1	0	5	-41.4	-34.8
3	0	5	66.6	64.6
-3	0	5	-77.8	-71.8

H	K	L	FO	FC
6	0	12	-32.8	-33.8
-6	0	12	-45.7	-46.2
8	0	12	23.6	22.1
-8	0	12	25.3	25.1
10	0	12	-17.4	-14.9
-10	0	12	-20.7	-18.3
-12	0	12	15.8	14.5
-1	0	13	-17.3	-23.9
2	0	14	21.3	21.0
-2	0	14	15.7	15.3
4	0	14	-25.1	-24.5
-4	0	14	-23.6	-26.4
6	0	14	23.9	22.7
-6	0	14	25.5	26.0
8	0	14	-21.3	-21.1
-8	0	14	-20.2	-19.7
10	0	14	20.3	15.8
-10	0	14	18.9	16.4
-12	0	14	-15.0	-12.3
0	0	16	25.3	24.4
2	0	16	-17.2	-15.3
-2	0	16	-19.5	-20.9
6	0	16	-16.5	-14.8
-6	0	16	-17.1	-16.3
8	0	16	13.7	21.0
-8	0	16	21.1	20.5
-10	0	16	-20.0	-24.4
0	0	17	-24.5	-0.0
0	0	18	-22.1	-24.1
-2	0	18	14.2	21.1
0	1	0	29.9	25.6
3	1	0	-15.1	-21.8
4	1	0	77.7	66.3
6	1	0	-39.3	-42.1
7	1	0	-37.7	-36.5
8	1	0	27.7	24.2
9	1	0	36.6	39.5
10	1	0	-18.7	-19.4
11	1	0	-42.9	-49.5
12	1	0	30.0	32.5
13	1	0	24.2	26.5
14	1	0	-18.8	-20.5
15	1	0	-17.9	-9.1
0	1	1	-64.9	-64.8
3	1	1	39.1	41.3
-3	1	1	-32.0	-37.4
4	1	1	-29.0	-37.5
-4	1	1	-27.9	-32.8
5	1	1	-85.9	-79.8
-5	1	1	88.0	82.8
6	1	1	30.4	27.8
-6	1	1	15.2	13.0
7	1	1	23.2	24.1
-7	1	1	-34.2	-36.7
8	1	1	-47.1	-49.7
-8	1	1	-44.8	-46.3
9	1	1	-20.7	-16.6

H	K	L	FO	FC
-14	1	3	-19.8	-17.9
15	1	3	-16.8	-13.5
-15	1	3	19.4	16.7
16	1	3	16.1	18.4
-16	1	3	17.4	17.8
0	1	4	-39.3	-24.1
1	1	4	48.9	46.6
-1	1	4	-33.2	-34.6
2	1	4	-47.1	-49.3
-2	1	4	-29.7	-35.9
3	1	4	-53.1	-50.8
-3	1	4	55.7	53.1
4	1	4	33.6	27.0
-4	1	4	27.0	25.9
5	1	4	-9.5	-6.3
6	1	4	-22.1	-13.7
7	1	4	-11.3	-9.1
8	1	4	34.4	30.9
-8	1	4	35.2	29.2
9	1	4	15.7	11.5
-9	1	4	-14.7	-10.6
14	1	4	-15.8	-12.7
5	1	0	51.1	43.7
0	1	5	-34.2	-40.3
1	1	5	-68.0	-67.2
-1	1	5	72.2	78.6
2	1	5	17.7	19.1
-2	1	5	23.7	26.3
3	1	5	14.9	16.8
-3	1	5	-36.1	-39.0
4	1	5	-52.9	-44.2
-4	1	5	-36.8	-30.1
5	1	5	-18.2	-14.0
-5	1	5	30.7	30.8
6	1	5	50.7	52.4
-6	1	5	52.2	52.7
7	1	5	37.9	34.9
-7	1	5	-32.7	-28.7
8	1	5	-33.0	-29.8
-8	1	5	-43.9	-42.0
9	1	5	-49.3	-56.1
-9	1	5	38.6	40.6
10	1	5	31.5	31.1
-10	1	5	39.5	41.8
11	1	5	37.6	37.0
-11	1	5	-37.2	-35.2
12	1	5	-26.0	-28.8
-12	1	5	-34.2	-34.3
13	1	5	-14.9	-11.8
-13	1	5	21.3	19.7
14	1	5	16.6	18.6
-14	1	5	16.8	17.4
-15	1	5	-17.9	-14.4
-16	1	5	-16.2	-16.4
0	1	6	20.4	20.9
1	1	6	-37.0	-35.3
-1	1	6	28.3	30.6
2	1	6	46.7	48.7

H	K	L	FO	FC
4	1	9	-31.6	-30.5
-4	1	9	-45.9	-51.2
5	1	9	-38.8	-42.3
-5	1	9	34.7	36.2
6	1	9	18.0	19.2
-6	1	9	23.9	21.5
7	1	9	19.6	22.6
-7	1	9	-28.4	-34.2
8	1	9	-18.7	-17.1
-8	1	9	-23.2	-20.9
9	1	9	-22.7	-22.5
-9	1	9	19.8	21.2
-10	1	9	20.6	17.7
11	1	9	21.9	19.1
-11	1	9	-24.0	-24.4
-12	1	9	-18.0	-17.7
-13	1	9	12.7	10.9
14	1	9	15.8	11.3
-14	1	9	18.1	19.2
2	1	10	14.6	14.3
-2	1	10	20.8	20.8
3	1	10	15.6	14.9
4	1	10	-28.5	-29.5
-4	1	10	-32.2	-34.1
5	1	10	-30.9	-36.7
-5	1	10	26.6	29.3
6	1	10	28.4	32.1
-6	1	10	28.8	30.3
7	1	10	25.4	27.4
-7	1	10	-26.8	-30.2
8	1	10	-16.7	-15.6
-8	1	10	-22.5	-19.3
9	1	10	-15.8	-13.1
-9	1	10	17.8	16.0
-10	1	10	15.4	4.9
-11	1	10	-19.1	-14.9
-13	1	10	16.2	11.7
0	1	11	21.1	20.6
1	1	11	42.7	49.9
-1	1	11	-51.8	-59.8
2	1	11	-25.9	-27.0
-2	1	11	-24.7	-29.4
3	1	11	-20.6	-21.1
-3	1	11	19.9	19.0
4	1	11	19.5	18.8
-4	1	11	27.3	31.5
5	1	11	18.7	18.5
-5	1	11	-19.3	-17.4
6	1	11	-12.6	-13.6
-6	1	11	-15.4	-13.6
7	1	11	-17.6	-12.1
-7	1	11	24.3	24.1
8	1	11	17.2	14.3
9	1	11	18.6	16.7
-9	1	11	-24.2	-25.8
-11	1	11	24.5	24.1
-14	1	11	-17.9	-14.3
0	1	12	-18.8	-16.9

H	K	L	FO	FC
-9	2	1	52.7	54.5
11	2	1	29.6	29.4
-11	2	1	-29.7	-31.9
13	2	1	-32.5	-34.6
-13	2	1	35.9	40.6
15	2	1	19.1	23.3
-15	2	1	-24.6	-25.6
0	2	2	-11.8	-18.7
3	2	2	-102.1	-94.6
-3	2	2	108.2	92.7
4	2	2	-25.0	-17.0
-4	2	2	-14.7	-11.3
5	2	2	84.8	89.7
-5	2	2	-95.4	-92.6
6	2	2	14.7	15.1
7	2	2	-58.7	-59.9
-7	2	2	54.4	55.2
8	2	2	11.0	9.5
-8	2	2	21.9	22.3
9	2	2	24.8	26.2
-9	2	2	-17.0	-14.5
11	2	2	-14.4	-15.7
13	2	2	22.7	21.4
-13	2	2	-22.6	-21.0
15	2	2	-17.6	-19.1
-15	2	2	23.3	21.9
0	2	3	37.0	38.6
1	2	3	118.5	112.5
-2	2	3	-8.4	-11.2
3	2	3	-96.2	-104.2
-3	2	3	94.2	97.4
4	2	3	26.2	21.2
-4	2	3	29.1	28.0
5	2	3	49.2	51.2
-5	2	3	-53.9	-60.1
6	2	3	-36.9	-27.7
-6	2	3	-46.2	-40.2
7	2	3	-40.1	-48.7
-7	2	3	61.9	70.2
-8	2	3	12.5	12.9
9	2	3	30.4	31.0
-9	2	3	-52.7	-58.2
10	2	3	-13.0	-15.1
11	2	3	-21.6	-19.7
-11	2	3	32.7	34.0
13	2	3	25.2	23.7
-13	2	3	-32.3	-31.9
15	2	3	-18.0	-20.1
-15	2	3	19.6	21.7
-17	2	3	-15.4	-15.4
0	2	4	15.0	14.4
1	2	4	-32.7	-37.9
-1	2	4	36.3	38.3
2	2	4	26.7	23.1
-2	2	4	30.8	26.8
3	2	4	40.7	42.3
-3	2	4	-47.1	-47.4
5	2	4	-59.2	-61.5

-11	0	5	23.8	22.4
0	0	6	-40.9	-41.7
2	0	6	38.6	39.2
-2	0	6	37.6	32.1
4	0	6	-49.2	-61.1
-4	0	6	-34.7	-39.0
6	0	6	62.4	67.4
-6	0	6	56.2	58.0
8	0	6	-57.2	-58.5
-8	0	6	-78.1	-84.3
10	0	6	48.8	49.6
-10	0	6	79.2	88.1
12	0	6	-32.4	-31.0
-12	0	6	-44.1	-49.3
14	0	6	20.0	24.3
-14	0	6	23.2	24.7
16	0	6	-16.8	-18.8
-16	0	6	-16.5	-15.3
-1	0	7	29.8	30.2
3	0	7	-16.8	-19.8
-3	0	7	29.1	20.2
-9	0	7	19.1	15.8
-11	0	7	-21.7	-27.8
0	0	8	37.5	44.5
2	0	8	-39.8	-36.3
-2	0	8	-42.0	-36.5
4	0	8	69.3	84.6
-4	0	8	63.0	67.5
6	0	8	-58.7	-64.7
-6	0	8	-72.9	-82.1
8	0	8	17.6	11.4
-8	0	8	41.0	35.3
10	0	8	-20.2	-17.8
-10	0	8	-36.4	-34.6
12	0	8	20.7	18.7
-12	0	8	32.0	32.8
14	0	8	-17.7	-21.0
-14	0	8	-18.5	-21.6
16	0	8	20.7	23.2
-16	0	8	21.4	19.6
3	0	9	15.6	16.4
5	0	9	-18.6	-19.3
0	0	10	-81.7	-85.5
2	0	10	53.2	56.3
-2	0	10	75.0	74.0
4	0	10	-60.9	-73.6
-4	0	10	-71.9	-76.5
6	0	10	48.4	56.7
-6	0	10	74.0	82.0
8	0	10	-22.1	-22.4
-8	0	10	-31.0	-28.6
10	0	10	24.7	22.5
-10	0	10	22.8	18.8
-12	0	10	-20.8	-23.2
14	0	10	15.6	13.8
-14	0	10	19.5	17.5
16	0	10	-19.4	-20.3
-16	0	10	-19.5	-23.0
-1	0	11	20.0	22.1
3	0	11	-20.4	-22.3
5	0	11	20.1	19.3
-5	0	11	-24.2	-22.4
-7	0	11	23.7	27.5
0	0	12	51.1	44.8
2	0	12	-33.7	-35.9
-2	0	12	-48.8	-44.2
4	0	12	37.4	40.6
-4	0	12	44.0	46.5
-9	1	1	28.1	29.7
10	1	1	23.1	22.2
-10	1	1	20.1	17.2
11	1	1	29.9	31.0
-11	1	1	-38.9	-42.7
12	1	1	-18.0	-12.1
13	1	1	-15.6	-14.2
-13	1	1	13.8	14.4
14	1	1	19.6	17.0
-14	1	1	15.8	11.2
15	1	1	16.9	14.1
-15	1	1	-14.7	-11.6
16	1	1	-16.0	-15.3
-16	1	1	-12.6	-11.6
17	1	1	-16.1	-11.9
-17	1	1	15.5	14.2
0	1	2	-33.8	-26.8
2	1	2	44.3	42.0
-2	1	2	51.9	50.5
3	1	2	11.2	7.9
-3	1	2	-16.5	-9.9
-4	1	2	-18.5	-16.8
5	1	2	12.3	10.6
6	1	2	10.0	0.2
7	1	2	-10.0	-0.0
-7	1	2	-14.5	-13.1
8	1	2	-40.7	-39.3
-8	1	2	-25.9	-23.5
9	1	2	-16.5	-14.1
-9	1	2	23.9	21.9
10	1	2	22.4	23.6
-10	1	2	17.4	15.3
11	1	2	15.5	15.4
-11	1	2	-29.5	-30.9
12	1	2	-16.3	-16.4
-12	1	2	-21.6	-21.7
13	1	2	-13.9	-10.0
-13	1	2	20.3	20.1
14	1	2	14.5	7.0
-14	1	2	14.2	15.4
0	1	3	93.2	95.2
1	1	3	31.9	35.5
-1	1	3	-24.4	-35.0
2	1	3	-65.1	-67.6
-2	1	3	-80.1	-80.2
3	1	3	-53.2	-43.4
-3	1	3	52.0	46.1
4	1	3	59.3	64.9
-4	1	3	56.4	61.1
5	1	3	50.3	53.1
-5	1	3	-71.5	-76.7
6	1	3	-69.5	-71.9
-6	1	3	-66.8	-65.7
7	1	3	-15.6	-15.5
-7	1	3	25.5	27.1
8	1	3	50.1	52.6
-8	1	3	61.0	65.4
9	1	3	23.7	19.0
-9	1	3	-21.5	-13.5
10	1	3	-38.2	-40.0
-10	1	3	-41.4	-46.9
11	1	3	-27.2	-24.7
-11	1	3	24.3	20.4
12	1	3	28.4	31.1
-12	1	3	24.9	27.0
13	1	3	18.6	17.0
-13	1	3	-19.8	-22.0
14	1	3	-19.5	-21.5
-2	1	6	28.1	29.9
3	1	6	36.9	38.7
-3	1	6	-47.2	-50.6
4	1	6	-39.3	-44.5
-4	1	6	-51.9	-54.2
5	1	6	-18.6	-15.2
-5	1	6	19.9	20.7
6	1	6	22.3	22.8
-6	1	6	22.8	23.2
7	1	6	23.5	20.4
-7	1	6	-20.5	-19.7
8	1	6	-15.5	-10.9
-8	1	6	-24.2	-22.2
9	1	6	-13.6	-9.1
-9	1	6	13.5	14.4
10	1	6	-15.3	-15.4
14	1	6	16.2	12.2
-14	1	6	15.3	16.6
0	1	7	41.8	43.9
-1	1	7	-39.3	-46.2
2	1	7	-48.1	-53.8
-2	1	7	-45.0	-52.9
4	1	7	50.9	52.8
-4	1	7	49.6	53.2
5	1	7	34.0	35.0
-5	1	7	-26.6	-28.9
6	1	7	-34.9	-39.7
-6	1	7	-37.1	-41.0
7	1	7	-29.4	-31.9
-7	1	7	32.2	30.9
8	1	7	29.5	29.8
-8	1	7	34.6	33.7
9	1	7	29.4	36.9
-9	1	7	-31.2	-35.2
10	1	7	-22.9	-22.8
-10	1	7	-30.3	-31.0
11	1	7	-24.4	-28.1
-11	1	7	28.2	32.6
12	1	7	21.6	23.4
-12	1	7	25.9	30.0
-13	1	7	-15.4	-13.5
14	1	7	-18.2	-18.4
-14	1	7	-17.8	-20.0
-15	1	7	15.4	10.5
-16	1	7	15.8	13.0
0	1	8	25.3	22.3
2	1	8	-25.9	-24.9
-2	1	8	-27.7	-33.8
3	1	8	-28.1	-3.5
4	1	8	16.0	13.8
-4	1	8	21.6	24.5
5	1	8	23.8	26.4
-5	1	8	-15.7	-15.8
6	1	8	-20.7	-16.9
-6	1	8	-17.7	-13.4
7	1	8	-22.9	-22.4
-7	1	8	17.6	17.1
8	1	8	21.6	12.8
-8	1	8	18.9	17.2
9	1	8	9.5	9.0
12	1	8	15.9	3.1
0	1	9	-28.2	-30.3
1	1	9	-34.5	-37.0
-1	1	9	35.3	44.4
2	1	9	44.8	48.6
-2	1	9	39.7	49.1
3	1	9	25.3	23.6
-3	1	9	-14.2	-10.2
3	1	12	-13.3	-10.8
4	1	12	19.0	18.9
-4	1	12	25.6	24.5
-5	1	12	-19.2	-17.9
6	1	12	-18.2	-22.3
-6	1	12	-24.3	-22.6
7	1	12	-14.9	-10.7
-7	1	12	18.6	16.0
-8	1	12	17.2	16.8
10	1	12	-17.6	-2.5
-10	1	12	-15.3	-3.8
0	1	13	-27.9	-26.3
-1	1	13	24.5	28.9
2	1	13	22.6	21.2
-2	1	13	24.5	27.1
3	1	13	18.6	18.0
-3	1	13	-22.0	-18.7
4	1	13	-22.8	-23.8
-4	1	13	-25.7	-26.1
5	1	13	-17.5	-11.6
-5	1	13	19.1	15.9
6	1	13	23.0	23.2
-6	1	13	25.5	25.5
-7	1	13	-16.1	-15.6
8	1	13	-19.6	-18.9
-8	1	13	-18.9	-18.1
-9	1	13	19.6	14.6
10	1	13	18.6	18.9
-10	1	13	17.4	16.4
-11	1	13	-15.4	-12.0
12	1	13	-17.9	-13.9
-12	1	13	-20.1	-19.4
-14	1	13	15.8	15.6
8	1	14	-17.9	-9.4
0	1	15	18.1	15.6
-2	1	15	-15.7	-15.5
3	1	15	-10.0	-10.5
-3	1	15	15.7	13.6
5	1	15	10.8	9.8
-5	1	15	-12.0	-13.8
6	1	15	-11.6	-16.1
-6	1	15	-12.9	-19.8
7	1	15	-11.9	-10.8
0	2	0	65.5	52.1
1	2	0	78.3	72.7
3	2	0	117.5	90.4
4	2	0	-54.3	-44.3
5	2	0	-59.0	-66.3
6	2	0	41.9	36.8
7	2	0	38.9	39.9
8	2	0	-26.9	-21.7
11	2	0	-13.2	-11.7
12	2	0	-10.2	-12.3
13	2	0	-14.7	-15.8
15	2	0	19.9	18.4
17	2	0	-12.1	-9.7
0	2	1	60.0	45.5
1	2	1	61.9	56.6
-1	2	1	-79.0	-75.7
3	2	1	65.9	67.0
-4	2	1	-10.3	-8.8
5	2	1	-59.4	-65.6
-5	2	1	73.1	70.7
7	2	1	71.2	73.6
-7	2	1	-71.7	-81.8
9	2	1	-50.5	-49.5
-5	2	4	78.1	78.9
-6	2	4	-18.0	-19.5
7	2	4	42.2	42.1
-7	2	4	-55.9	-55.2
9	2	4	-26.2	-27.0
-9	2	4	18.5	19.2
10	2	4	-14.3	-14.1
11	2	4	28.5	28.6
-11	2	4	-21.9	-21.4
13	2	4	-19.6	-17.1
-13	2	4	25.3	25.4
-15	2	4	-22.0	-21.7
-17	2	4	11.8	16.4
0	2	5	-37.2	-36.4
1	2	5	-87.6	-93.2
-1	2	5	81.9	90.7
2	2	5	-22.2	-18.5
-2	2	5	-10.5	-7.7
3	2	5	99.4	98.9
-3	2	5	-99.8	-109.9
5	2	5	-60.7	-55.7
-5	2	5	72.4	72.5
6	2	5	18.8	14.0
-6	2	5	28.8	23.1
7	2	5	28.6	27.1
-7	2	5	-39.6	-39.6
13	2	5	-22.6	-21.5
-13	2	5	25.7	21.9
15	2	5	18.6	18.5
-15	2	5	-18.0	-21.6
-17	2	5	14.4	18.0
0	2	6	-29.0	-24.3
1	2	6	49.1	49.6
-1	2	6	-52.6	-54.0
2	2	6	-28.5	-21.2
-2	2	6	-28.2	-23.0
3	2	6	-29.3	-25.6
-3	2	6	29.8	32.2
4	2	6	28.9	22.3
-4	2	6	42.2	41.7
5	2	6	26.7	21.7
-5	2	6	-37.9	-35.5
7	2	6	-27.9	-28.2
-7	2	6	33.3	34.9
9	2	6	31.1	31.4
-9	2	6	-21.5	-21.5
-10	2	6	17.2	19.2
11	2	6	-26.0	-27.6
-11	2	6	24.6	24.4
13	2	6	18.2	15.7
-13	2	6	-21.6	-21.5
-15	2	6	15.9	15.3
0	2	7	36.0	31.2
1	2	7	61.0	69.1
-1	2	7	-60.7	-67.0
-2	2	7	-22.2	-17.0
3	2	7	-62.9	-67.2
-3	2	7	70.0	82.3
5	2	7	37.6	39.3
-5	2	7	-50.6	-53.0
7	2	7	-39.7	-43.9
-7	2	7	33.4	38.3
9	2	7	27.7	32.7
-9	2	7	-20.6	-19.0
11	2	7	-21.3	-21.4
-11	2	7	23.8	8.3
13	2	7	19.0	20.3
-13	2	7	-20.5	-20.8

H	K	L	FO	FC
-15	2	7	18.6	20.8
0	2	8	13.6	5.6
1	2	8	-57.6	-61.3
-1	2	8	55.6	59.4
3	2	8	37.5	34.5
-3	2	8	-47.4	-49.6
-5	2	8	18.9	15.1
7	2	8	24.2	21.0
-7	2	8	-23.6	-23.4
9	2	8	-31.6	-31.1
-9	2	8	33.8	35.5
11	2	8	20.7	19.7
-11	2	8	-24.2	-24.1
-13	2	8	19.7	19.3
-15	2	8	-14.3	-12.6
0	2	9	-12.5	-9.0
1	2	9	-27.1	-28.6
-1	2	9	23.6	22.5
-2	2	9	14.6	17.2
3	2	9	31.0	34.2
-3	2	9	-32.5	-37.9
5	2	9	-25.6	-24.8
-5	2	9	23.6	22.3
7	2	9	41.6	41.6
-7	2	9	-35.9	-33.0
9	2	9	-34.3	-34.1
-9	2	9	43.0	42.6
11	2	9	22.5	22.9
-11	2	9	-28.1	-26.8
13	2	9	-20.6	-20.9
-13	2	9	25.0	23.2
15	2	9	14.8	10.7
0	2	10	-13.0	-11.8
1	2	10	34.6	38.4
-1	2	10	-33.6	-34.0
2	2	10	-11.6	-11.3
3	2	10	-20.4	-18.0
-3	2	10	29.2	29.3
4	2	10	17.3	19.1
6	2	10	-15.6	-15.0
-6	2	10	-14.8	-13.9
9	2	10	19.9	19.1
-9	2	10	-27.5	-27.1
-11	2	10	18.0	15.9
3	2	11	-28.9	-29.3
-3	2	11	19.8	23.8
5	2	11	28.1	27.5
-5	2	11	-26.1	-26.4
7	2	11	-28.5	-28.3
-7	2	11	30.9	29.9
9	2	11	19.1	19.1
-9	2	11	-31.2	-30.5
11	2	11	-19.5	-18.3
-11	2	11	24.6	23.2
13	2	11	21.0	20.1
-13	2	11	-23.0	-25.0
-15	2	11	19.1	17.0
0	2	12	19.0	19.4
1	2	12	-33.1	-31.5
-1	2	12	33.6	33.1

H	K	L	FO	FC
14	3	1	12.7	4.3
1	3	2	67.0	59.2
-1	3	2	-64.1	-56.8
2	3	2	54.0	50.3
-2	3	2	53.2	54.6
3	3	2	-56.9	-57.9
-3	3	2	53.8	49.3
4	3	2	-54.3	-52.7
-4	3	2	-59.8	-56.8
5	3	2	70.0	70.1
-5	3	2	-66.8	-65.4
6	3	2	56.4	56.8
-6	3	2	51.4	43.3
7	3	2	-51.8	-46.7
8	3	2	-57.4	-58.3
-8	3	2	-51.0	-49.0
9	3	2	32.6	35.9
-9	3	2	-41.1	-38.7
10	3	2	21.4	25.9
11	3	2	-32.5	-30.8
-11	3	2	31.5	32.2
12	3	2	-18.6	-19.2
13	3	2	18.3	20.6
-13	3	2	-21.3	-24.1
14	3	2	17.9	18.6
-14	3	2	22.0	22.7
15	3	2	-15.6	-18.8
-15	3	2	18.7	21.8
16	3	2	-12.3	-14.8
-16	3	2	-12.1	-15.4
17	3	2	12.7	14.2
0	3	3	16.3	14.3
1	3	3	25.4	18.4
-1	3	3	-31.9	-24.2
2	3	3	-24.4	-19.7
-2	3	3	-18.6	-16.4
-3	3	3	-12.0	-11.3
5	3	3	25.4	26.3
-5	3	3	-17.6	-16.1
-8	3	3	15.1	14.0
-13	3	3	13.9	9.1
0	3	4	47.4	44.2
1	3	4	-73.8	-76.8
-1	3	4	78.9	80.1
2	3	4	-48.6	-46.1
-2	3	4	-52.5	-51.7
3	3	4	53.7	54.5
-3	3	4	-53.2	-50.1
4	3	4	52.8	59.8
-4	3	4	51.8	53.9
5	3	4	-58.7	-63.0
-5	3	4	60.9	63.9
6	3	4	-52.8	-55.0
-6	3	4	-53.4	-53.3
7	3	4	34.0	36.3
-7	3	4	-41.6	-43.5
8	3	4	21.6	21.0
-8	3	4	37.9	36.9
9	3	4	-27.5	-30.0
-9	3	4	25.8	28.6

H	K	L	FO	FC
-1	3	8	50.0	46.1
2	3	8	-55.3	-56.7
-2	3	8	-56.2	-52.9
3	3	8	36.2	34.9
-3	3	8	-36.4	-34.0
4	3	8	25.4	19.1
-4	3	8	42.6	37.4
5	3	8	-32.3	-30.0
-5	3	8	37.0	37.5
-6	3	8	-19.8	-14.8
7	3	8	30.0	27.1
-7	3	8	-32.0	-35.1
8	3	8	25.2	23.4
-8	3	8	26.7	28.5
9	3	8	-33.3	-32.1
-9	3	8	35.1	34.2
10	3	8	-19.8	-18.0
-10	3	8	-21.7	-21.9
11	3	8	27.0	27.6
-11	3	8	-30.4	-30.6
12	3	8	20.2	18.6
-12	3	8	22.5	18.0
13	3	8	-15.8	-16.7
-13	3	8	21.9	19.5
-14	3	8	-19.0	-16.8
-15	3	8	-18.0	-15.1
0	3	9	21.4	19.8
1	3	9	20.6	15.8
-1	3	9	-23.3	-19.6
5	3	9	12.1	11.1
7	3	9	-14.9	-11.2
-7	3	9	15.7	14.3
11	3	9	-14.7	-4.5
1	3	10	37.2	39.7
-1	3	10	-36.3	-39.0
2	3	10	23.2	24.7
-2	3	10	18.1	16.3
3	3	10	-30.0	-31.4
-3	3	10	30.6	28.8
-4	3	10	-20.2	-20.7
5	3	10	29.9	25.5
-5	3	10	-27.8	-28.1
7	3	10	-27.7	-24.6
-7	3	10	31.1	29.8
8	3	10	-18.8	-16.5
-8	3	10	-17.7	-18.2
9	3	10	27.5	28.8
-9	3	10	-33.7	-33.3
-10	3	10	17.9	15.7
11	3	10	-24.1	-23.5
-11	3	10	27.5	29.1
12	3	10	-18.9	-17.3
13	3	10	17.7	14.1
-13	3	10	-21.0	-18.9
14	3	10	14.4	10.1
15	3	10	-14.2	-9.1
5	3	11	-21.4	-19.4
-5	3	11	22.9	20.7
6	3	11	-13.8	-6.7
7	3	11	17.4	24.9

H	K	L	FO	FC
10	4	1	49.9	52.4
-10	4	1	53.5	61.1
11	4	1	-21.6	-19.7
-11	4	1	25.3	21.6
12	4	1	-34.6	-36.9
-12	4	1	-43.4	-44.6
14	4	1	21.2	21.2
-14	4	1	25.0	24.2
16	4	1	-17.5	-17.1
-16	4	1	-20.2	-20.3
2	4	2	16.6	14.2
-2	4	2	25.2	24.0
4	4	2	-51.9	-46.6
-4	4	2	-60.8	-53.6
-5	4	2	13.6	16.2
6	4	2	42.6	38.5
-6	4	2	38.5	34.5
-10	4	2	-15.0	-11.8
0	4	3	74.2	76.5
2	4	3	-46.7	-48.0
-2	4	3	-57.0	-61.7
3	4	3	12.4	9.9
-3	4	3	-14.7	-15.5
4	4	3	40.1	40.3
-4	4	3	40.2	44.3
5	4	3	-12.5	-14.7
-5	4	3	23.6	19.9
6	4	3	-36.7	-37.2
-6	4	3	-40.7	-39.2
8	4	3	33.1	33.4
-8	4	3	34.3	35.7
10	4	3	-32.7	-33.9
-10	4	3	-40.3	-42.2
12	4	3	20.4	23.2
-12	4	3	31.4	30.2
14	4	3	-17.1	-17.7
-14	4	3	-18.5	-18.2
-16	4	3	18.1	14.8
2	4	4	24.8	17.3
-2	4	4	18.3	11.6
3	4	4	15.2	14.0
-3	4	4	-18.7	-18.0
4	4	4	15.8	14.6
-4	4	4	21.2	18.8
-5	4	4	-17.7	-15.9
6	4	4	-35.3	-35.8
-6	4	4	-45.3	-44.2
-7	4	4	13.2	10.0
8	4	4	23.3	25.0
-8	4	4	14.8	12.8
10	4	4	-33.6	-35.2
-10	4	4	-16.0	-14.2
12	4	4	19.8	18.3
-12	4	4	17.4	15.9
0	4	5	-75.4	-73.9
1	4	5	15.6	13.8
-1	4	5	-12.6	-10.0
2	4	5	67.0	63.4
-2	4	5	68.8	70.6
4	4	5	-58.2	-58.4

H	K	L	FO	FC
-10	4	9	26.4	28.7
12	4	9	-21.5	-19.7
-12	4	9	-23.9	-24.5
0	4	10	-44.7	-41.2
2	4	10	27.1	23.7
-2	4	10	37.9	33.7
3	4	10	-17.7	-14.9
-3	4	10	12.9	7.4
-4	4	10	-11.3	-5.5
5	4	10	15.8	16.6
-5	4	10	-16.4	-15.0
6	4	10	-15.1	-12.4
7	4	10	-14.8	-11.9
-7	4	10	16.5	16.1
0	4	11	38.2	39.1
1	4	11	-21.2	-20.0
-1	4	11	23.8	23.8
2	4	11	-31.1	-32.9
-2	4	11	-33.1	-34.8
4	4	11	35.6	38.5
-4	4	11	37.1	37.5
6	4	11	-33.6	-32.9
-6	4	11	-41.4	-45.0
8	4	11	26.1	23.5
-8	4	11	32.0	32.6
10	4	11	-21.9	-20.9
-10	4	11	-25.2	-27.3
-12	4	11	23.1	22.7
0	4	12	36.7	34.6
2	4	12	-19.7	-13.6
-2	4	12	-29.0	-23.6
0	4	13	-27.7	-24.4
2	4	13	24.8	22.7
-2	4	13	27.7	22.9
4	4	13	-22.4	-20.6
-4	4	13	-25.1	-23.9
6	4	13	19.0	16.6
-6	4	13	25.8	24.9
-8	4	13	-22.6	-20.4
-10	4	13	19.8	17.0
4	4	15	13.3	13.9
-4	4	15	14.8	19.1
2	4	15	-16.7	-19.4
-2	4	15	-16.9	-21.3
6	4	15	-10.8	-13.8
-6	4	15	-12.5	-17.2
-8	4	15	14.9	13.5
0	5	0	-61.3	-60.8
1	5	0	-81.5	-76.5
2	5	0	32.2	31.7
3	5	0	27.6	23.6
5	5	0	-31.4	-30.8
6	5	0	16.2	17.0
8	5	0	-24.8	-25.6
10	5	0	28.2	28.1
11	5	0	26.2	26.8
0	5	1	-50.1	-46.4
1	5	1	-59.1	-61.1
-1	5	1	64.5	61.0

3	2	12	19.5	18.2
-3	2	12	-25.6	-21.4
5	2	12	-19.8	-10.4
7	2	12	20.7	14.1
9	2	12	-21.6	-17.8
-9	2	12	25.6	20.8
-11	2	12	-20.5	-17.8
0	2	13	-15.7	-13.7
1	2	13	-29.7	-28.8
-1	2	13	28.5	28.4
3	2	13	28.4	26.3
-3	2	13	-32.9	-32.9
5	2	13	-23.1	-20.7
-5	2	13	29.0	26.9
7	2	13	22.2	21.2
-7	2	13	-28.2	-26.0
9	2	13	-21.3	-16.3
-9	2	13	25.5	24.6
-11	2	13	-21.1	-20.0
-13	2	13	22.2	20.1
1	2	14	20.7	21.3
-1	2	14	-23.8	-25.7
3	2	14	-16.0	-17.0
-3	2	14	18.5	16.9
5	2	14	19.8	18.0
-5	2	14	-18.3	-15.4
7	2	14	-18.1	-13.0
-7	2	14	23.1	18.3
9	2	14	16.1	12.4
-9	2	14	-20.0	-16.9
-11	2	14	21.0	18.0
1	2	15	16.7	24.4
-1	2	15	-17.7	-25.0
3	2	15	-15.0	-23.0
-3	2	15	18.2	28.6
5	2	15	11.7	17.2
-5	2	15	-14.3	-22.9
-7	2	15	14.2	18.1
0	3	0	-103.5	-99.0
1	3	0	-59.8	-51.3
3	3	0	63.7	61.1
4	3	0	56.9	49.7
6	3	0	-37.0	-33.7
8	3	0	42.3	39.2
9	3	0	-44.6	-47.1
11	3	0	32.3	34.9
13	3	0	-25.1	-25.8
14	3	0	-23.9	-25.6
15	3	0	20.7	22.4
0	3	1	20.9	18.5
3	3	1	-42.1	-33.7
-4	3	1	11.6	9.5
5	3	1	30.1	30.5
6	3	1	-15.0	-8.6
7	3	1	-12.0	-12.9
-7	3	1	18.6	18.2
8	3	1	-22.3	-19.7
-8	3	1	-27.8	-29.0
10	3	1	15.3	9.2
-10	3	1	18.4	15.4
11	3	1	-17.6	-16.4
-11	3	1	19.3	16.8
12	3	1	-11.6	-9.6
13	3	1	19.3	17.3
-13	3	1	-26.5	-27.3
-10	3	4	-16.4	-18.8
11	3	4	30.5	30.4
-11	3	4	-31.0	-29.9
12	3	4	15.5	16.2
-12	3	4	17.9	16.9
13	3	4	-19.3	-17.5
-13	3	4	22.6	20.1
14	3	4	-18.0	-15.4
-14	3	4	-13.4	-15.5
15	3	4	18.2	15.7
-15	3	4	-20.4	-18.7
16	3	4	17.3	14.4
-16	3	4	17.1	17.6
17	3	4	-17.3	-13.4
-17	3	4	12.0	15.8
5	3	0	-75.6	-72.9
0	3	5	-34.9	-26.7
-1	3	5	31.1	29.3
2	3	5	40.4	31.8
-2	3	5	30.3	25.8
3	3	5	-46.1	-46.2
-3	3	5	38.6	37.4
4	3	5	-22.8	-19.2
-4	3	5	-16.9	-15.0
-5	3	5	-16.9	-13.7
7	3	5	-15.2	-13.2
-7	3	5	14.3	11.3
11	3	5	15.2	12.9
0	3	6	-30.6	-30.0
1	3	6	71.4	67.9
-1	3	6	-78.8	-73.1
2	3	6	51.2	50.3
-2	3	6	40.7	40.2
3	3	6	-50.4	-45.3
-3	3	6	53.1	47.2
4	3	6	-52.9	-53.1
-4	3	6	-50.6	-50.6
5	3	6	43.4	45.3
-5	3	6	-53.2	-55.5
6	3	6	28.4	29.8
-6	3	6	41.1	42.1
7	3	6	-27.8	-29.6
-7	3	6	34.9	42.1
8	3	6	-8.6	-6.7
-8	3	6	-18.7	-16.7
9	3	6	31.3	30.9
-9	3	6	-30.4	-31.1
11	3	6	-29.7	-29.9
-11	3	6	31.4	31.3
12	3	6	-18.0	-16.7
-12	3	6	-18.7	-14.9
13	3	6	18.3	17.0
-13	3	6	-20.8	-19.5
14	3	6	15.9	15.4
-14	3	6	14.3	16.4
15	3	6	-15.2	-12.5
-15	3	6	18.5	16.7
1	3	7	-12.5	-10.0
2	3	7	-12.6	-14.4
-2	3	7	-11.4	-7.1
3	3	7	13.1	13.9
-3	3	7	-14.9	-12.5
4	3	7	13.3	12.6
-4	3	7	13.7	10.8
0	3	8	44.5	44.8
1	3	8	-49.4	-46.0
-7	3	11	-24.4	-23.3
-13	3	11	24.9	4.9
1	3	12	-34.8	-33.9
-1	3	12	36.7	36.7
2	3	12	-22.8	-19.1
-2	3	12	-16.6	-12.6
3	3	12	28.2	24.5
-3	3	12	-29.9	-24.0
5	3	12	-27.2	-20.9
6	3	12	-18.8	-16.9
-6	3	12	-18.9	-16.3
7	3	12	20.3	16.2
-7	3	12	-28.8	-23.1
8	3	12	20.3	19.2
-8	3	12	20.8	17.7
9	3	12	-23.8	-18.7
-9	3	12	28.6	23.6
10	3	12	-19.1	-18.2
-10	3	12	-18.0	-13.5
11	3	12	20.5	16.1
-11	3	12	-25.9	-22.4
1	3	13	-14.4	-8.3
-1	3	13	19.0	17.6
0	3	14	-28.8	-23.5
1	3	14	26.0	25.9
-1	3	14	-32.2	-30.9
2	3	14	21.1	10.0
-2	3	14	22.9	20.1
3	3	14	-22.2	-18.9
-3	3	14	22.3	20.9
-4	3	14	-16.9	-13.4
5	3	14	22.7	17.8
-5	3	14	-22.5	-19.8
6	3	14	17.6	15.7
-6	3	14	19.4	16.6
7	3	14	-18.8	-12.2
-7	3	14	21.8	18.4
-8	3	14	-23.9	-18.6
9	3	14	16.6	12.6
-9	3	14	-21.4	-15.1
-10	3	14	20.1	16.4
-11	3	14	17.5	15.5
-12	3	14	-22.2	-15.7
0	4	0	43.1	40.0
1	4	0	-34.8	-30.3
2	4	0	-50.2	-47.5
3	4	0	21.8	20.5
4	4	0	52.3	38.8
5	4	0	-18.2	-13.0
6	4	0	-16.7	-9.9
7	4	0	29.3	19.6
12	4	0	-13.9	-10.6
0	4	1	-102.1	-120.8
1	4	1	65.7	61.7
-1	4	1	-70.2	-69.9
2	4	1	61.2	65.9
-2	4	1	72.8	70.1
4	4	1	-49.0	-50.4
-4	4	1	-53.9	-56.4
6	4	1	56.0	55.1
-6	4	1	59.2	63.4
8	4	1	-42.5	-43.9
-8	4	1	-49.6	-51.4
9	4	1	10.4	8.9
-9	4	1	-12.2	-8.4
-4	4	5	-62.1	-60.7
6	4	5	48.8	48.4
-6	4	5	46.9	46.2
8	4	5	-37.4	-38.9
-8	4	5	-40.8	-40.2
9	4	5	24.8	21.4
-9	4	5	-23.9	-22.0
10	4	5	30.3	31.6
-10	4	5	38.1	39.0
12	4	5	-21.5	-21.8
-12	4	5	-25.5	-26.9
14	4	5	21.5	18.2
-14	4	5	17.1	18.7
16	4	5	-15.9	-14.0
-16	4	5	-14.6	-14.4
0	4	6	-28.6	-30.7
3	4	6	-13.4	-12.8
-3	4	6	26.4	25.9
-4	4	6	14.5	13.2
6	4	6	15.1	11.1
-6	4	6	18.9	16.4
8	4	6	-26.6	-22.9
-8	4	6	-25.0	-24.4
10	4	6	33.1	33.5
-10	4	6	38.2	37.2
12	4	6	-16.9	-15.7
-12	4	6	-25.5	-25.2
0	4	7	44.1	47.8
2	4	7	-35.4	-39.7
-2	4	7	-39.5	-41.6
4	4	7	40.3	48.7
-4	4	7	41.9	45.2
6	4	7	-39.4	-43.8
-6	4	7	-39.4	-45.4
8	4	7	25.0	28.2
-8	4	7	29.8	33.1
-9	4	7	18.6	19.2
10	4	7	-25.3	-26.4
-10	4	7	-28.8	-32.1
-11	4	7	-13.6	-15.7
12	4	7	17.7	19.0
-12	4	7	21.7	23.8
-14	4	7	-16.1	-17.4
0	4	8	37.8	34.4
1	4	8	13.5	9.3
-1	4	8	-15.0	-11.4
2	4	8	-27.1	-21.2
-2	4	8	-27.8	-22.5
5	4	8	-11.1	-5.8
-10	4	8	-22.6	-21.0
0	4	9	-37.3	-42.5
1	4	9	15.3	10.9
-1	4	9	-17.1	-11.4
2	4	9	30.3	33.5
-2	4	9	33.6	33.9
3	4	9	-15.6	-8.9
4	4	9	-42.0	-47.9
-4	4	9	-39.1	-39.1
5	4	9	23.9	18.9
-5	4	9	-24.6	-19.2
6	4	9	43.2	44.4
-6	4	9	46.6	49.4
-7	4	9	19.0	17.4
8	4	9	-28.5	-28.1
-8	4	9	-33.4	-31.7
10	4	9	27.7	28.1
2	5	1	52.4	49.8
-2	5	1	58.2	52.7
3	5	1	23.9	25.4
-3	5	1	-25.0	-21.7
4	5	1	-47.1	-45.4
-4	5	1	-58.9	-52.9
6	5	1	32.4	33.5
-6	5	1	37.1	42.2
8	5	1	-20.6	-21.8
-8	5	1	-20.1	-23.2
9	5	1	-18.4	-14.5
-9	5	1	23.8	24.6
10	5	1	18.7	20.5
-10	5	1	20.5	21.8
11	5	1	17.6	13.0
-11	5	1	-23.3	-18.1
12	5	1	-25.9	-25.5
-12	5	1	-29.1	-29.9
13	5	1	-11.5	-3.9
14	5	1	18.3	17.2
-14	5	1	21.4	20.5
16	5	1	-14.6	-8.8
17	5	1	-13.8	-6.3
0	5	2	56.5	57.5
1	5	2	49.5	41.9
-1	5	2	-51.7	-41.5
2	5	2	-49.8	-46.6
-2	5	2	-48.2	-42.2
3	5	2	-13.7	-13.6
4	5	2	44.0	43.5
-4	5	2	34.8	34.2
5	5	2	14.1	14.1
6	5	2	-37.0	-38.1
-6	5	2	-29.4	-31.9
8	5	2	26.7	24.9
-8	5	2	29.3	28.4
9	5	2	14.4	14.9
10	5	2	-23.8	-22.9
-10	5	2	-33.0	-30.3
11	5	2	-17.9	-18.2
-11	5	2	23.4	22.0
12	5	2	14.7	18.6
-12	5	2	16.1	18.2
14	5	2	-15.0	-14.9
0	5	3	15.6	12.1
1	5	3	23.5	19.7
-1	5	3	-20.0	-16.4
2	5	3	-40.6	-39.4
-2	5	3	-39.6	-36.3
3	5	3	-10.9	-12.6
4	5	3	32.3	28.4
-4	5	3	41.4	38.7
5	5	3	14.4	12.0
6	5	3	-16.1	-15.6
-6	5	3	-23.9	-24.2
8	5	3	27.7	26.9
-8	5	3	25.1	25.7
9	5	3	14.2	9.9
-9	5	3	-15.7	-12.5
10	5	3	-17.3	-15.6
-10	5	3	-16.3	-15.1
11	5	3	-17.8	-14.7
-11	5	3	18.6	13.9
12	5	3	17.0	16.6
-12	5	3	19.7	19.9
14	5	3	-16.8	-15.0

H	K	L	FO	FC
-14	5	3	-19.9	-19.6
-17	5	3	-15.1	-4.2
0	5	4	-51.3	-53.7
1	5	4	-12.0	-12.3
-1	5	4	14.2	9.9
2	5	4	40.5	37.8
-2	5	4	46.6	44.2
4	5	4	-35.0	-29.7
-4	5	4	-37.1	-35.3
6	5	4	28.8	27.7
-6	5	4	31.4	31.2
8	5	4	-26.6	-26.6
-8	5	4	-25.3	-27.3
9	5	4	-24.7	-23.2
-9	5	4	17.1	16.9
10	5	4	24.3	27.3
-10	5	4	29.2	30.2
11	5	4	15.6	13.6
-11	5	4	-19.5	-16.2
12	5	4	-16.8	-18.3
-14	5	4	12.5	14.4
-15	5	4	-12.9	-4.8
-0	5	5	-13.4	-10.8
1	5	5	-26.0	-23.9
-1	5	5	25.2	25.0
2	5	5	44.5	45.0
-2	5	5	35.6	34.3
4	5	5	-36.8	-31.2
-4	5	5	-30.5	-38.6
-5	5	5	12.3	8.3
6	5	5	25.2	21.3
-6	5	5	25.5	22.1
7	5	5	16.9	17.2
-7	5	5	-15.0	-17.9
8	5	5	-37.8	-32.5
-8	5	5	-38.0	-33.4
9	5	5	-29.5	-27.4
-9	5	5	26.9	25.6
10	5	5	16.3	14.1
-10	5	5	19.2	15.7
11	5	5	21.4	22.7
-11	5	5	-24.8	-23.3
-14	5	5	19.5	19.6
0	5	6	41.7	42.3
2	5	6	-22.0	-22.2
-2	5	6	-35.0	-36.0
4	5	6	17.8	17.9
-4	5	6	20.9	21.5
-5	5	6	-14.2	-13.7
6	5	6	-26.7	-24.6
-6	5	6	-21.8	-20.7
7	5	6	-15.4	-15.1
-7	5	6	9.1	15.2
8	5	6	30.5	29.6
-8	5	6	27.5	26.7
9	5	6	16.5	16.3
-9	5	6	-23.1	-20.5
10	5	6	-26.0	-29.1
-10	5	6	-30.2	-31.9
6	5	10	-15.8	-14.8
-6	5	10	-21.2	-16.7
-7	5	10	24.1	19.5
-8	5	10	16.3	12.8
0	5	11	24.5	20.1
1	5	11	25.9	21.0
-1	5	11	-24.3	-26.6
2	5	11	-23.5	-23.7
-2	5	11	-23.6	-22.2
-3	5	11	22.2	18.8
4	5	11	22.7	24.5
-4	5	11	26.4	24.6
6	5	11	-21.5	-22.8
-6	5	11	-28.4	-28.0
8	5	11	18.3	15.8
-8	5	11	26.6	25.0
-10	5	11	-18.4	-14.2
0	5	12	-33.3	-29.9
2	5	12	26.2	21.0
-2	5	12	31.8	26.3
-3	5	12	-16.5	-9.5
-3	5	13	-14.5	-9.8
-4	5	13	-16.5	-16.1
0	5	14	26.9	19.4
2	5	14	-20.0	-16.3
-2	5	14	-26.2	-20.3
-4	5	14	25.3	20.1
-6	5	14	-20.0	-16.9
0	6	0	41.4	37.9
1	6	0	-72.3	-64.8
3	6	0	45.7	46.8
4	6	0	-25.6	-24.1
5	6	0	-27.1	-31.3
6	6	0	20.0	18.8
7	6	0	29.7	34.6
9	6	0	-31.5	-32.7
13	6	0	-16.1	-21.3
0	6	1	-12.6	-14.6
1	6	1	25.2	21.3
-1	6	1	-25.2	-20.9
2	6	1	-12.0	-9.6
3	6	1	-25.7	-22.9
-3	6	1	27.3	23.3
4	6	1	17.3	10.7
-4	6	1	12.5	8.4
5	6	1	14.6	12.9
-5	6	1	-15.6	-9.9
6	6	1	-13.6	-6.9
8	6	1	18.6	15.5
-8	6	1	20.5	16.2
-11	6	1	-11.7	-9.7
1	6	2	62.6	62.0
-1	6	2	-61.0	-59.0
2	6	2	-22.5	-22.8
-2	6	2	-13.1	-9.2
3	6	2	-54.2	-54.2
-3	6	2	48.3	49.4
4	6	2	26.9	25.7
-6	6	6	-25.1	-21.1
7	6	6	-35.8	-33.2
-7	6	6	38.0	35.0
9	6	6	19.8	21.5
-9	6	6	-33.5	-31.3
11	6	6	-16.2	-15.0
-11	6	6	18.1	19.4
13	6	6	18.6	19.8
-13	6	6	-22.3	-21.5
1	6	7	-16.5	-17.5
-1	6	7	19.4	18.3
-9	6	7	21.2	20.7
-11	6	7	-20.6	-21.3
0	6	8	-24.5	-22.0
1	6	8	-35.1	-30.2
-1	6	8	31.1	30.0
2	6	8	19.9	19.1
-2	6	8	24.5	23.3
3	6	8	44.0	40.3
-3	6	8	-45.3	-43.1
5	6	8	-44.7	-39.3
-5	6	8	45.0	42.4
7	6	8	30.6	29.3
-7	6	8	-38.1	-35.8
8	6	8	-15.2	-11.8
-9	6	8	23.5	23.3
-11	6	8	-16.8	-16.3
-13	6	8	16.9	18.7
1	6	9	23.3	19.7
-1	6	9	-26.1	-21.3
-3	6	9	20.5	16.5
1	6	10	23.9	22.3
-1	6	10	-25.0	-21.9
3	6	10	-33.4	-31.6
-3	6	10	34.4	32.9
5	6	10	34.3	33.3
-5	6	10	-39.4	-36.7
7	6	10	-20.9	-24.0
-7	6	10	28.1	29.6
1	6	11	-24.1	-19.6
-1	6	11	30.6	25.0
0	6	12	-17.7	-3.8
1	6	12	-17.8	-17.7
-1	6	12	19.6	14.8
3	6	12	29.1	25.8
-3	6	12	-28.8	-27.0
5	6	12	-26.6	-24.9
-5	6	12	30.4	28.4
7	6	12	20.7	22.2
-7	6	12	-26.9	-23.3
-9	6	12	17.6	16.0
-11	6	12	-17.0	-11.4
0	6	14	17.9	10.0
3	6	14	-21.1	-19.3
-3	6	14	25.3	21.4
5	6	14	19.5	16.3
-5	6	14	-22.2	-20.4
-7	6	14	21.7	17.7
3	7	7	33.7	36.4
-3	7	7	-35.7	-38.4
4	7	7	15.6	15.3
-4	7	7	18.0	16.1
5	7	7	-28.1	-29.5
-5	7	7	31.1	33.8
6	7	7	-14.3	-11.1
7	7	7	19.3	22.5
-7	7	7	-22.0	-25.3
9	7	7	-16.1	-17.7
-11	7	7	-15.9	-20.0
-13	7	7	17.6	18.9
1	7	9	31.8	31.1
-1	7	9	-32.6	-31.4
3	7	9	-28.2	-28.2
5	7	9	19.3	17.6
-5	7	9	-22.0	-23.3
7	7	9	-16.2	-19.1
1	7	11	-17.7	-18.1
-1	7	11	16.8	17.7
3	7	11	23.5	22.2
-3	7	11	-27.0	-26.4
5	7	11	-23.0	-20.3
-5	7	11	25.2	25.2
7	7	11	19.2	18.3
-7	7	11	-20.7	-19.2
-1	7	13	-21.6	-18.2
-3	7	13	20.1	17.3
5	7	13	22.6	18.5
-5	7	13	-22.0	-19.4
1	8	0	34.5	36.9
2	8	0	14.0	22.0
3	8	0	-12.0	-12.5
4	8	0	-39.6	-39.4
6	8	0	40.8	38.6
8	8	0	-25.9	-28.5
9	8	0	12.9	11.3
10	8	0	16.2	20.0
12	8	0	-17.9	-19.3
14	8	0	15.6	18.7
1	8	1	23.0	19.9
-1	8	1	-24.6	-22.6
-2	8	1	14.8	13.1
4	8	1	-20.2	-19.5
-4	8	1	-22.0	-20.3
6	8	1	18.6	18.4
-6	8	1	18.6	19.4
8	8	1	-16.2	-14.6
-8	8	1	-16.4	-15.3
-10	8	1	13.4	10.5
0	8	2	14.5	19.0
1	8	2	-22.9	-22.6
-1	8	2	26.8	27.6
2	8	2	-19.4	-22.2
-2	8	2	-21.2	-22.7
-3	8	2	-14.3	-12.8
4	8	2	26.0	27.4
-4	8	2	28.0	28.8
-11	8	13	21.3	1.2
0	9	0	-37.4	-41.7
2	9	0	32.2	36.5
3	9	0	14.6	12.2
4	9	0	-26.6	-26.8
6	9	0	23.2	25.0
8	9	0	-20.6	-23.5
10	9	0	16.8	22.9
12	9	0	-16.0	-19.1
0	9	1	23.8	24.2
2	9	1	-14.2	-15.0
-8	9	1	12.4	7.2
-11	9	1	16.3	11.6
0	9	2	25.8	29.9
2	9	2	-28.1	-31.0
-2	9	2	-28.2	-30.0
4	9	2	27.4	28.2
-4	9	2	27.2	27.4
6	9	2	-20.8	-21.8
-6	9	2	-22.1	-23.5
8	9	2	15.5	18.2
-8	9	2	16.8	20.3
-10	9	2	-14.5	-18.9
0	9	3	-21.5	-20.3
2	9	3	19.0	16.9
0	9	4	-24.8	-24.8
2	9	4	27.4	27.1
-2	9	4	25.0	26.3
4	9	4	-20.4	-21.6
-4	9	4	-22.7	-24.1
6	9	4	17.3	17.8
-6	9	4	17.8	19.9
8	9	4	-20.2	-20.4
10	9	4	18.6	17.7
-10	9	4	15.1	16.1
0	9	5	21.0	14.3
0	9	6	22.0	21.6
2	9	6	-22.7	-22.9
-2	9	6	-21.2	-23.3
4	9	6	19.4	17.5
-4	9	6	18.2	20.5
6	9	6	-19.8	-18.1
-6	9	6	-18.6	-19.2
8	9	6	19.7	21.5
-8	9	6	22.1	22.5
10	9	6	-17.5	-18.0
-10	9	6	-21.2	-19.4
12	9	6	14.5	13.0
0	9	7	-11.5	-14.4
-6	9	7	13.6	12.0
0	9	8	-16.8	-17.9
2	9	8	16.3	19.8
4	9	8	-19.0	-21.3
-4	9	8	-18.8	-20.5
6	9	8	19.4	20.9
-6	9	8	22.2	22.4
8	9	8	-18.1	-17.6
-8	9	8	-23.2	-20.8

-11	5	6	15.2	14.5
12	5	6	17.6	17.8
-12	5	6	20.0	21.1
0	5	7	16.7	20.6
2	5	7	-30.8	-33.2
-2	5	7	-24.8	-26.7
4	5	7	25.8	27.1
-4	5	7	26.1	28.3
5	5	7	15.7	16.2
6	5	7	-23.8	-24.7
-6	5	7	-22.9	-23.9
7	5	7	-17.9	-14.5
-7	5	7	15.8	15.1
8	5	7	23.1	22.0
-8	5	7	28.4	27.4
9	5	7	14.6	12.6
-9	5	7	-20.1	-17.8
10	5	7	-12.9	-10.5
-10	5	7	-14.4	-12.9
-11	5	7	15.1	17.2
0	5	8	-17.7	-21.2
1	5	8	-12.8	-11.4
-1	5	8	20.9	20.5
2	5	8	20.4	19.5
-2	5	8	23.1	24.9
3	5	8	10.8	5.7
4	5	8	-34.3	-31.2
-4	5	8	-33.2	-31.4
5	5	8	-27.0	-23.4
-5	5	8	23.7	22.3
6	5	8	31.7	30.3
-6	5	8	37.7	32.1
7	5	8	19.1	11.3
-7	5	8	-24.1	-17.7
8	5	8	-23.6	-20.7
-8	5	8	-25.2	-23.4
10	5	8	20.3	18.1
-10	5	8	23.2	23.4
12	5	8	-16.3	-13.7
-12	5	8	-19.9	-20.7
0	5	9	-32.8	-30.0
1	5	9	-14.7	-11.3
2	5	9	29.9	28.1
-2	5	9	30.8	27.0
3	5	9	17.2	17.2
4	5	9	-28.4	-29.5
-4	5	9	-27.4	-25.2
5	5	9	-22.5	-21.1
-5	5	9	23.5	20.8
6	5	9	28.4	28.4
-6	5	9	30.0	30.6
7	5	9	18.0	11.7
-7	5	9	-19.1	-12.8
8	5	9	-20.1	-17.3
-8	5	9	-25.1	-24.6
-10	5	9	14.7	12.2
0	5	10	22.7	23.2
1	5	10	23.7	18.5
-1	5	10	-32.2	-28.0
2	5	10	-15.4	-16.1
-2	5	10	-19.2	-19.8
3	5	10	-18.9	-15.0
-3	5	10	18.8	15.0
4	5	10	17.3	15.6
-4	5	10	19.3	16.7
5	5	10	27.6	28.4
-5	5	10	-27.7	-25.7
-4	6	2	21.9	19.2
5	6	2	28.8	34.7
-5	6	2	-26.0	-30.2
6	6	2	-20.9	-21.2
-6	6	2	-21.7	-21.6
7	6	2	-34.9	-39.7
-7	6	2	32.6	36.3
8	6	2	15.7	17.5
-8	6	2	17.0	20.1
9	6	2	35.3	36.0
-9	6	2	-37.2	-37.6
11	6	2	-25.5	-27.3
-11	6	2	27.6	29.9
13	6	2	20.6	24.1
15	6	2	-14.3	-15.5
16	6	2	14.8	7.3
3	6	3	15.3	18.2
-3	6	3	-20.2	-18.9
5	6	3	-31.3	-30.6
-5	6	3	31.0	34.4
7	6	3	22.5	21.6
-7	6	3	-19.8	-21.1
9	6	3	-18.8	-16.2
11	6	3	16.3	16.5
0	6	4	-29.3	-24.2
1	6	4	-41.7	-42.4
-1	6	4	37.5	37.1
2	6	4	29.9	23.6
-2	6	4	19.8	15.9
3	6	4	44.9	51.3
-3	6	4	-44.3	-48.3
4	6	4	-24.9	-23.7
-4	6	4	-20.1	-18.4
5	6	4	-26.7	-31.4
-5	6	4	25.9	29.4
6	6	4	17.1	18.0
-6	6	4	24.3	24.1
7	6	4	37.3	36.9
-7	6	4	-36.0	-36.5
-8	6	4	-15.9	-15.6
9	6	4	-33.4	-30.4
-9	6	4	40.7	39.4
11	6	4	19.7	20.3
-11	6	4	-26.8	-26.2
12	6	4	-18.2	-9.3
13	6	4	-24.0	-23.6
-13	6	4	22.8	24.0
-14	6	4	13.0	8.3
7	6	5	-19.3	-16.6
-7	6	5	21.0	20.3
9	6	5	26.9	24.8
-9	6	5	-21.8	-20.8
11	6	5	-21.3	-21.9
-11	6	5	21.6	21.6
0	6	6	22.0	18.4
1	6	6	28.2	30.7
-1	6	6	-24.7	-26.8
2	6	6	-22.9	-18.9
-2	6	6	-18.8	-17.7
3	6	6	-40.2	-45.0
-3	6	6	41.7	45.7
4	6	6	20.9	18.5
-4	6	6	24.1	21.5
5	6	6	33.6	34.9
-5	6	6	-33.2	-35.4
6	6	6	-14.6	-11.5
12	7	0	15.2	14.6
0	7	1	22.2	13.1
1	7	1	30.3	32.7
-1	7	1	-32.2	-33.8
3	7	1	-40.4	-42.5
4	7	1	-15.6	-16.0
-4	7	1	-22.4	-19.4
5	7	1	35.8	38.0
-5	7	1	-37.6	-40.5
6	7	1	22.1	17.5
-6	7	1	21.0	17.2
7	7	1	-38.4	-30.6
8	7	1	-15.1	-15.3
-8	7	1	-19.9	-14.6
9	7	1	30.3	31.4
-9	7	1	-28.2	-29.9
11	7	1	-18.3	-19.3
-11	7	1	13.0	17.0
13	7	1	15.4	18.3
-13	7	1	-14.8	-19.5
14	7	1	14.4	10.7
15	7	1	-16.4	-16.8
1	7	3	-38.2	-41.1
-1	7	3	42.7	45.0
2	7	3	-19.7	-20.7
-2	7	3	-25.0	-25.8
3	7	3	30.4	34.1
-3	7	3	-37.2	-38.5
4	7	3	24.8	22.9
-4	7	3	35.4	31.3
5	7	3	-36.7	-39.1
-5	7	3	35.2	37.8
6	7	3	-24.8	-20.6
-6	7	3	-25.0	-23.9
7	7	3	35.8	37.0
-7	7	3	-37.4	-38.1
-8	7	3	18.9	17.8
9	7	3	-26.8	-29.1
-9	7	3	31.0	32.8
11	7	3	19.6	23.0
-11	7	3	-22.3	-23.8
1	7	4	-14.4	-12.7
-1	7	4	17.6	16.6
-2	7	4	-15.0	-9.1
-0	7	5	-17.9	-15.7
-1	7	5	-39.3	-39.4
2	7	5	24.4	21.0
-2	7	5	27.7	23.7
3	7	5	-37.4	-39.4
-3	7	5	37.3	37.6
4	7	5	-22.3	-18.6
-4	7	5	-26.5	-23.0
5	7	5	46.1	46.8
-5	7	5	-45.1	-44.5
6	7	5	18.6	13.7
-6	7	5	20.3	14.8
7	7	5	-29.9	-30.1
-7	7	5	36.4	35.3
-9	7	5	-23.2	-23.2
11	7	5	-16.8	-18.9
-11	7	5	20.9	23.6
0	7	7	21.1	16.1
1	7	7	-37.0	-38.4
-1	7	7	36.4	38.9
2	7	7	-21.1	-21.2
-2	7	7	-23.6	-20.1
6	8	2	-26.5	-26.0
-6	8	2	-30.9	-29.6
8	8	2	18.9	20.4
-8	8	2	23.0	24.4
-10	8	2	-14.5	-19.0
-11	8	2	-14.9	-15.3
-12	8	2	15.8	17.6
-14	8	2	-16.6	-16.2
0	8	3	28.1	26.0
2	8	3	-20.6	-18.6
-2	8	3	-19.7	-19.3
4	8	3	21.1	21.7
-4	8	3	25.9	23.5
6	8	3	-24.1	-21.9
-6	8	3	-26.4	-26.2
-10	8	3	-17.3	-13.3
0	8	4	-30.4	-32.1
-1	8	4	-13.5	-13.2
2	8	4	27.8	28.3
-2	8	4	31.1	30.5
-3	8	4	16.4	11.3
4	8	4	-28.9	-28.2
-4	8	4	-29.4	-28.7
6	8	4	21.6	22.8
-6	8	4	23.9	24.5
9	8	4	17.5	13.4
-9	8	4	-17.3	-12.8
-10	8	4	13.1	12.1
0	8	5	-34.7	-32.5
2	8	5	23.3	18.0
-2	8	5	25.7	20.5
4	8	5	-19.7	-16.9
-4	8	5	-19.8	-17.0
6	8	5	17.0	11.4
-6	8	5	21.4	22.2
0	8	6	30.5	30.6
2	8	6	-29.3	-28.1
-2	8	6	-33.1	-30.9
4	8	6	23.8	26.4
-4	8	6	30.7	31.5
6	8	6	-20.4	-20.2
-6	8	6	-22.3	-25.3
0	8	7	28.1	26.8
2	8	7	-17.7	-16.6
-2	8	7	-18.2	-18.8
-4	8	7	17.6	11.2
0	8	8	-25.7	-24.8
-1	8	8	-18.5	-11.8
2	8	8	20.5	21.7
-2	8	8	23.0	22.7
4	8	8	-14.6	-15.6
-4	8	8	-15.5	-18.7
8	8	8	-20.8	-17.7
0	8	9	-20.6	-18.1
0	8	10	16.3	16.8
1	8	10	-19.3	-12.5
2	8	10	-17.5	-19.0
3	8	10	17.2	10.7
6	8	10	-17.8	-17.0
8	8	10	17.2	17.0
-8	8	10	24.2	20.3
0	8	11	18.4	17.1
0	8	13	-21.7	-17.7
-2	8	13	19.3	14.9
-7	8	13	23.6	2.9
-9	8	13	-19.9	-1.1
-10	9	8	20.3	16.6
0	9	10	22.8	22.8
2	9	10	-22.4	-21.7
-2	9	10	-20.6	-20.7
4	9	10	20.5	19.9
-4	9	10	18.8	19.0
6	9	10	-18.9	-18.1
-6	9	10	-24.5	-20.5
-8	9	10	21.4	19.6
11	10	0	-16.5	-0.5
1	10	1	32.2	35.5
-1	10	1	-34.4	-36.3
3	10	1	-21.3	-24.2
-3	10	1	23.4	24.9
4	10	1	18.9	16.4
-4	10	1	15.6	15.3
6	10	1	-17.9	-16.0
-6	10	1	-15.9	-15.3
0	10	3	-16.1	-13.2
1	10	3	-22.1	-23.3
-1	10	3	21.9	23.9
2	10	3	20.4	19.0
-2	10	3	18.0	15.7
3	10	3	22.9	23.0
-3	10	3	-22.4	-24.5
4	10	3	-18.6	-19.4
-4	10	3	-17.9	-18.5
-5	10	3	19.0	18.9
-6	10	3	18.0	16.6
-7	10	3	-17.7	-17.7
9	10	3	-20.1	-18.1
-9	10	3	18.2	17.7
2	10	7	16.3	15.4
-2	10	7	15.5	14.7
3	10	7	17.2	19.2
-3	10	7	-16.8	-17.9
4	10	7	-16.6	-13.2
-5	10	7	18.1	18.4
-6	10	7	15.4	12.9
-7	10	7	-16.9	-19.3
-9	10	7	16.9	18.5
-10	10	7	13.4	7.1
3	11	0	-19.0	-20.9
5	11	0	17.6	20.2
7	11	0	-15.4	-19.6
-3	11	1	15.5	7.9
-5	11	1	-17.7	-10.7
3	11	2	15.6	21.6
-3	11	2	-19.5	-21.4
5	11	2	-16.9	-21.6
-5	11	2	17.6	20.9
7	11	2	15.6	20.0
-7	11	2	-17.0	-19.8
9	11	2	-13.3	-15.0
11	11	2	13.7	11.6
1	11	4	20.8	20.8
-1	11	4	-19.2	-20.8
3	11	4	-21.6	-21.9
-4	11	4	-18.5	-2.6
5	11	4	21.9	22.0
-5	11	4	-21.8	-21.9
5	11	6	-18.9	-18.6
-5	11	6	18.8	20.0
-8	11	6	17.7	5.3

TABLE 3

INTRAMOLECULAR DISTANCES (Å) WITH STANDARD DEVIATIONS

For each chemically distinct distance the two independent values corresponding to the two half-molecules and the average value are given.

Duroquinone		
C=C bonds		
C(6) –C(8^I)	1.413 ± 0.015	1.401 ± 0.010
C(16)–C(18^{II})	1.389 ± 0.014	
C–C bonds		
C(7) –C(8)	1.470 ± 0.014	1.454 ± 0.010
C(17)–C(18)	1.437 ± 0.015	
C(6) –C(7)	1.462 ± 0.015	1.454 ± 0.010
C(16)–C(17)	1.445 ± 0.015	
CH_3–C bonds		
C(5) –C(6)	1.492 ± 0.017	1.510 ± 0.012
C(15)–C(16)	1.527 ± 0.017	
C(9) –C(8)	1.521 ± 0.016	1.533 ± 0.011
C(19)–C(18)	1.544 ± 0.016	
C=O bonds		
C(7) –O(10)	1.231 ± 0.013	1.237 ± 0.009
C(17)–O(20)	1.242 ± 0.011	
Non-bonding ring distances		
C(6) ...C(6^I)	2.916 ± 0.022	2.874 ± 0.016
C(16)...C(16^{II})	2.831 ± 0.021	
C(8) ...C(8^I)	2.848 ± 0.022	2.812 ± 0.016
C(18)...C(18^{II})	2.815 ± 0.022	
C(6) ...C(8)	2.512 ± 0.017	2.485 ± 0.012
C(16)...C(18)	2.457 ± 0.017	
Non-bonding $H_3C...CH_3$ distances		
C(5) ...C(9^I)	2.999 ± 0.021	2.999 ± 0.014
C(15)...C(19^{II})	2.999 ± 0.020	
Non-bonding $H_3C...O$ distances		
C(5) ...O(10)	2.801 ± 0.018	2.805 ± 0.013
C(15)...O(20)	2.809 ± 0.018	
C(9) ...O(10)	2.818 ± 0.015	2.812 ± 0.011
C(19)...O(20)	2.806 ± 0.017	
1,5-Cyclooctadiene		
C=C bonds		
C(2) –C(3)	1.323 ± 0.017	1.325 ± 0.013
C(12)–C(13)	1.326 ± 0.018	
C–C bonds adjacent to olefinic bond		
C(1) –C(2)	1.510 ± 0.021	1.510 ± 0.015
C(11)–C(12)	1.510 ± 0.021	
C(3) –C(4)	1.514 ± 0.023	1.528 ± 0.016
C(13)–C(14)	1.541 ± 0.023	
C–C bonds non-adjacent to olefinic bond		
C(1) –C(4^I)	1.563 ± 0.023	1.570 ± 0.016
C(11)–C(14^{II})	1.576 ± 0.022	

(Continued on page 211).

TABLE 3 *(continued)*

Non-bonding ring distances		
C(2) ...C(3^{I})	2.920 ± 0.025	2.908 ± 0.017
C(12)...C(13^{II})	2.896 ± 0.023	
C(2) ...C(2^{I})	3.229 ± 0.033	3.205 ± 0.023
C(12)...C(12^{II})	3.181 ± 0.031	
C(3) ...C(3^{I})	3.183 ± 0.032	3.185 ± 0.023
C(13)...C(13^{II})	3.187 ± 0.034	
C(1) ...C(4)	3.066 ± 0.028	3.057 ± 0.020
C(11)...C(14)	3.048 ± 0.029	
C(1) ...C(1^{I})	3.663 ± 0.037	3.699 ± 0.026
C(11)...C(11^{II})	3.735 ± 0.037	
C(4) ...C(4^{I})	3.166 ± 0.041	3.114 ± 0.029
C(14)...C(14^{II})	3.061 ± 0.041	
Duroquinone–nickel		
Ni(1)–C(8)	2.207 ± 0.012	2.213 ± 0.010
Ni(2)–C(18)	2.219 ± 0.013	
Ni(1)–C(6)	2.240 ± 0.012	2.232 ± 0.010
Ni(2)–C(16)	2.224 ± 0.012	
Ni(1)–C(7)	2.311 ± 0.012	2.314 ± 0.008
Ni(2)–C(17)	2.317 ± 0.010	
Ni(1)–M(1)	2.108	2.109
Ni(2)–M(2)	2.109	
Cyclooctadiene–nickel		
Ni(1)–C(3)	2.114 ± 0.015	2.114 ± 0.010
Ni(2)–C(13)	2.113 ± 0.015	
Ni(1)–C(2)	2.096 ± 0.015	2.086 ± 0.010
Ni(2)–C(12)	2.075 ± 0.014	
Ni(1)–N(1)	1.998	1.992
Ni(2)–N(2)	1.985	

The midpoints of the olefinic bonds are designated as follows:

M(1): C(8)–C(6^{I}) N(1): C(2)–C(3)
M(2): C(18)–C(16^{II}) N(2): C(12)–C(13)
Superscript I refers to the position $(1/2 - x, \bar{y}, 1/2 - z)$.
Superscript II refers to the position $(3/2 - x, \bar{y}, 1/2 - z)$.

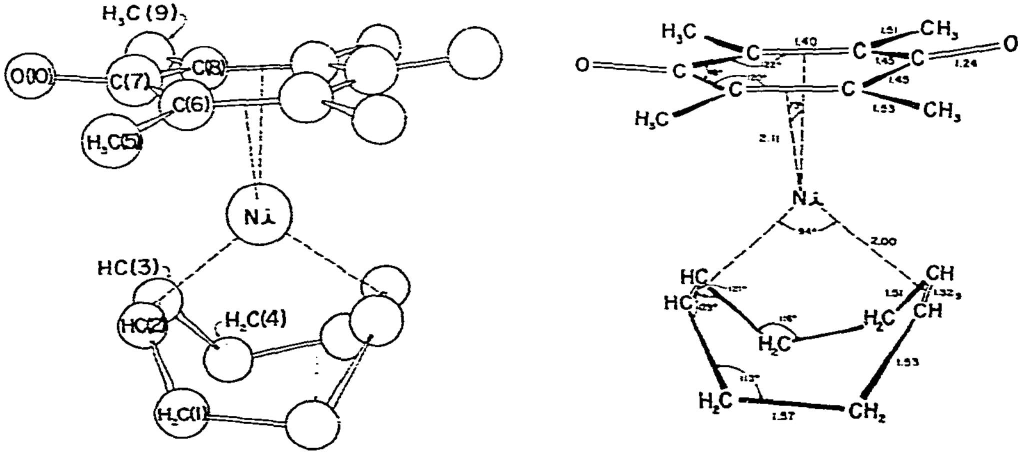

Fig. 1. The configuration of 1,5-cyclooctadiene-duroquinone-nickel with average bond lengths and angles.

TABLE 4

INTRAMOLECULAR ANGLES (DEGREES) WITH STANDARD DEVIATIONS

For each chemically distinct angle the two independent values corresponding to the two half-molecules and the average value are given*.

Duroquinone		
C(6)–C(7)–C(8)	117.9 ± 0.9°	117.5 ± 0.6°
C(16)–C(17)–C(18)	117.0 ± 0.9°	
C(7)–C(8)–C(6^{I})	122.2 ± 0.9°	122.0 ± 0.6°
C(17)–C(18)–C(16^{II})	121.7 ± 0.9°	
C(8)–C(6^{I})–C(7^{I})	119.3 ± 0.9°	120.0 ± 0.6°
C(18)–C(16^{II})–C(17^{II})	120.7 ± 0.9°	
C(7)–C(8)–C(9)	117.0 ± 1.0°	116.7 ± 0.7°
C(17)–C(18)–C(19)	116.4 ± 0.9°	
C(7)–C(6)–C(5)	117.9 ± 1.0°	117.9 ± 0.7°
C(17)–C(16)–C(15)	117.9 ± 0.9°	
C(9)–C(8)–C(6^{I})	120.8 ± 0.9°	121.4 ± 0.7°
C(19)–C(18)–C(16^{II})	121.9 ± 1.0°	
C(8)–C(6^{I})–C(5^{I})	122.8 ± 1.0°	122.1 ± 0.7°
C(18)–C(16^{II})–C(15^{II})	121.3 ± 1.0°	
C(6)–C(7)–O(10)	120.7 ± 0.9°	120.7 ± 0.6°
C(16)–(C17)–O(20)	120.7 ± 0.9°	
O(10)–C(7)–C(8)	121.4 ± 1.0°	121.9 ± 0.7°
O(20)–C(17)–C(18)	122.3 ± 0.9°	
1,5-Cyclooctadiene		
C(1)–C(2)–C(3)	128.8 ± 1.4°	129.3 ± 1.0°
C(11)–C(12)–C(13)	129.7 ± 1.4°	
C(2)–C(3)–C(4)	122.8 ± 1.4°	121.1 ± 1.0°
C(12)–C(13)–C(14)	119.4 ± 1.4°	
C(4^{I})–C(1)–C(2)	114.2 ± 1.3°	113.0 ± 1.0°
C(14^{II})–C(11)–C(12)	111.7 ± 1.3°	
C(3)–C(4)–C(1^{I})	116.5 ± 1.0°	116.2 ± 1.1°
C(13)–C(14)–C(11^{II})	115.9 ± 1.5°	
Cyclooctadiene-nickel		
N(1)–Ni(1)–N(1^{I})	93.7°	93.6°
N(2)–Ni(2)–N(2^{II})	93.5°	
Duroquinone-nickel		
M(1)–Ni(1)–M(1^{I})	73.1°	72.2°
M(2)–Ni(2)–M(2^{II})	71.3°	

* M and N denote the midpoints of the olefinic duroquinone and 1,5-cyclooctadiene bonds, respectively, as defined in Table 3. The superscripts refer to symmetry-related positions as defined in Table 3.

coordination polyhedron of approximately cubic environment has no precedent in that known eight-coordination configurations invariably are based upon less regular polyhedra (*viz.*, the dodecahedral and antiprismatic arrangements)[13]. Hence, both the stereochemistry and electronic configuration of the presumed "zerovalent" nickel[4] in these complexes strongly support a four-coordinated tetrahedral type sigma-orbital bonding representation for the nickel.

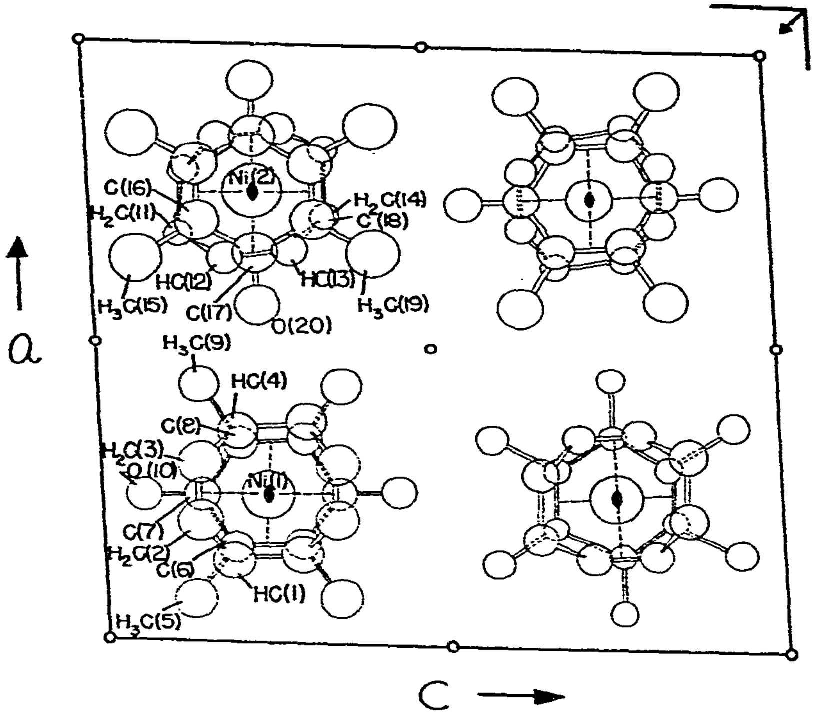

Fig. 2. The packing of 1,5-cyclooctadiene-duroquinone-nickel as viewed down the [010] direction.

These results strongly suggest a similar geometry of the diolefinic bonds with an essentially tetrahedrally coordinated nickel in bicycloheptadiene-duroquinone-nickel, dicyclopentadiene-duroquinone-nickel, cyclooctatriene-duroquinone-nickel, and cyclooctatetraene-duroquinone-nickel. All of the above compounds, each of which has only one duroquinone group per molecule, have electronic spectra similar to that of cyclooctadiene-duroquinone-nickel[4]. It should be noted that no direct predictions of the configurations in cyclooctadiene-duroquinone-nickel or the other mono-substituted duroquinone-nickel complexes were made by Schrauzer and Thyret[4].

The distance from the nickel to the olefinic carbon atoms in the cyclooctadiene ring is 2.10 ± 0.01 Å (av.) and to the double bond center is 1.99 Å. The corresponding nickel–duroquinone distances are 2.24 ± 0.007 Å (av.) and 2.11 Å. Both sets of distances are considerably longer than the nickel–carbon distances of 1.98 ± 0.01 Å and the nickel-midpoint distance of 1.83 Å reported for a nickel–unconjugated olefinic bond in $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$[14]. The angle formed by the two olefinic midpoints of the duroquinone with the nickel as the vertex is 72°, whereas the corresponding angle to the cyclooctadiene is 94°.

Since no abnormally short intermolecular distances are present, the molecular crystals are held together primarily by van der Waals forces; the minimum intermolecular $H_3C...O$ and $H_2C...O$ contact distances of 3.3 Å are approximately equal to the normal van der Waals distances[15].

Geometry of the duroquinone

The duroquinone fragment of crystallographic C_{2v} symmetry possesses *idealized* C_{2v} symmetry as contrasted with the *idealized* D_{2h} symmetries of free planar duroquinone and quinone, as found from X-ray studies by Hirshfeld *et al.*[16] and Trotter[17] respectively. The lower symmetry in the nickel complex is a result of the two carbonyl groups bending back away from the nickel and the four methyl carbons bending slightly toward the nickel. The resultant dihedral angle between the plane of the four central ring carbons and the plane of the carbonyl group and the two carbons to which the carbonyl is attached is 6°. The bending back of a carbonyl group in a ring upon complexing of the ring with a metal has been observed for several cyclopentadienone complexes in which a diene group is coordinated to the metal. These include cyclopentadienyl-tetramethylcyclopentadienone-cobalt (8°)[18], π-cyclopentadienyl-tetrakis(trifluoromethyl)cyclopentadienone-cobalt (21°)[19], and tetrakis(trifluoromethyl)cyclopentadienone-tricarbonyl-iron (16.2°)[19]. The deformation of the carbonyl groups in these compounds may be at least partly attributed to the distortions of the σ-framework of the olefinic carbons coordinated to the metal; this interaction produces an unsymmetrical charge distribution thereby partially destroying the geometrical restrictions which the olefinic bond places upon attached substituents. This explanation has been utilized to account for the considerable deformation of the tetrasubstituted unconjugated olefinic group bonded to nickel in $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$[14].

Of significance is that although the duroquinone group also functions as a four-electron donor system to the metal, the resulting interaction *does not directly involve* a diene system; the average non-bonding intramolecular C(6)...C(8) distance of 2.485 ± 0.012 Å for the two half-molecules certainly implies little if any direct interaction between the two pairs of olefinic groups except for that which can occur indirectly via both the CO and metal linkages.

Schrauzer[20] has suggested that these deviations in the metal-complexed duroquinone may arise from increased stability of the complex due to a decrease in antibonding metal–carbonyl overlap in the π-back-bonding MO combinations. The bending (8°) of the one carbonyl group out of the mean diene plane in the tetramethyl-substituted cyclopentadienone ring in cyclopentadienyl-tetramethylcyclopentadienone-cobalt is not appreciably larger than the symmetry-identical distortions (6°) of the two carbonyl groups out of the mean plane of the other four olefinic ring carbons in the tetramethyl-substituted quinone complex.

The carbonyl groups in these five- and six-membered ring systems function as electron-withdrawing "sinks" by decreasing the overall charge donated to the metal (both directly through decreasing via conjugation in the metal-complexed state the charge contributed to the metal from the μ-bonding olefinic carbons and indirectly through greater back-donation of π-electron charge from the metal to the ring orbitals). Because of the directional nature of the metal orbitals and the "*para*" orientation of the two CO groups in the duroquinone ligand, it may be expected that *each* CO group in duroquinone accepts a smaller portion of charge from a given metal than the one CO group in tetramethylcyclopentadienone thereby causing smaller decreases in the carbon–oxygen bond order and in the carbonyl stretching frequency for the metal-complexed duroquinone.

Examination of the carbonyl stretching frequencies of these compounds reveals a decrease of 133 cm^{-1} in cyclooctadiene-duroquinone-nickel (1553 cm^{-1})[3] from that in free duroquinone (1687 cm^{-1})[3] *vs.* a decrease of 146 cm^{-1} in the tetramethyl- and tetraphenylcyclopentadienone-cyclopentadienyl-cobalt compounds (both at 1569 cm^{-1})[21,22] from that in free tetraphenylcyclopentadienone (1715 cm^{-1})[21,22]. The validity of such a comparison is limited in this case due to the presence of different metals and different ligands (*i.e.*, cyclooctadiene and cyclopentadienyl groups), both of which certainly may influence the carbonyl frequencies by different mixing of the group's bonding and antibonding π-orbitals. It should be noted that the CO frequencies reported by Schrauzer and Thyret[3] for the other *mono*-duroquinone nickel complexes are essentially invariant (~ 1550 cm^{-1}) to the diolefinic group present, but as expected bis(duroquinone)nickel has a higher CO frequency of 1577 cm^{-1}. In any event our structural results, which do not conflict with the proposal made by Schrauzer[20], suggest an approximately similar charge distribution on the tetramethyl-substituted cyclopentadienone and quinone ring systems consistent with the essentially equivalent distortions observed for these rings.

The importance of the nature of the substituents on the ring is demonstrated by the much greater deformations of the carbonyl groups in the two perfluoromethyl cyclopentadienone metal complexes mentioned earlier[19], which may result from increased localized bonding of the diene system to the metal due to a greater inductive or other electrical effect of the perfluoromethyl groups and/or greater steric repulsion of these bulkier groups.

The *idealized* C_{2v} symmetry of the duroquinone fragment is demonstrated by an examination of the 9 pairs of crystallographically independent distances and angles which must be equivalent in each half-molecule for this assumed symmetry. Eight of the nine pairs have differences within 2 σ's with only one pair of non-bonding cross ring distances (*i.e.*, C(6)...C(6^1) *vs.* C(8)...C(8^1)) differing by 2.5 σ's, which is still not a significant difference. The average values of these nine pairs of bond lengths and angles together with the standard deviation of the average are listed in Table 5 along with the other singly-determined ring parameters. A comparison of these molecular parameters with those of free duroquinone and quinone (also presented in Table 5) shows that the only really significant change in the quinone ring parameters upon interaction with the nickel, aside from the decrease of *idealized* symmetry from D_{2h} to C_{2v} due to the carbonyl distortion, is a lengthening of the C=C bond. The average double bond values of 1.33 Å in the free duroquinone[16] and 1.322 ± 0.008 Å in the free quinone[17] have increased to 1.40 ± 0.01 Å in the nickel-complexed duroquinone. The lengthening of a conjugated olefinic bond to 1.40–1.46 Å upon coordination with a metal has been observed in a number of other complexes and is attributed to a decrease in the π-bond order of the olefinic bond due to the interaction with the metal.

The average C–C single bond distance of 1.45 ± 0.007 Å in the nickel complex is somewhat shorter than those found in free duroquinone[16] (1.49 Å) and quinone[17] (1.477 ± 0.006 Å). The C–CH_3 distance of 1.52 ± 0.007 Å is virtually unchanged from that of 1.51 Å found in free duroquinone[16]. The average values of 117 ± 0.6° for the ring angle whose vertex is at the ketonic carbon and 121 ± 0.4° for the other inner carbon ring angle are experimentally equal to those in the two free quinones[16,17].

The carbonyl bond length of 1.24 ± 0.009 Å is in essence unaltered from those observed for free duroquinone[16] (1.23 Å) and quinone[17] (1.222 ± 0.008 Å). A lengthening would be predicted on the basis of the previously mentioned decrease in infra-

TABLE 5

A COMPARISON OF QUINONE DISTANCES* AND OF QUINONE ANGLES

	1,5-cyclooctadiene-duroquinone-nickel	*duro-quinone*[16]	*quinone*[17]
Distances			
C=C	1.401 ± 0.010	1.33	1.322 ± 0.008
C–C	1.454 ± 0.008	1.49	1.477 ± 0.006
$C-CH_3$	1.522 ± 0.008	1.51	
C=O	1.237 ± 0.009	1.23	1.222 ± 0.008
$H_3C...CH_3$	2.999 ± 0.014	2.98	
$H_3C...O$	2.809 ± 0.009	2.82	
M...M	2.48	2.58	2.53
Angles			
C=C–C	121.0 ± 0.4°	121°	121.1 ± 0.45°
C–C–C	117.5 ± 0.6°	120°	117.8 ± 0.6°
$C=C-CH_3$	121.8 ± 0.5°	123°	
$C-C-CH_3$	117.3 ± 0.5°	117°	
C–C=O	121.3 ± 0.5°	121°	121.1 ± 0.45°

* M denotes the olefinic midpoints. In the nickel complex the ring is presumed to have C_{2v} symmetry, while the latter two rings are presumed to have D_{2h} symmetry.

red stretching frequency. A similar carbonyl bond length of 1.23 ± 0.01 Å was found in cyclopentadienyl-tetramethylcyclopentadienone-cobalt[18].

Geometry of the 1,5-cyclooctadiene

Of significance is the absence of any appreciable distortion of the structure of the 1,5-cyclooctadiene fragment from that of the free 1,5-cyclooctadiene. A comparison of molecular parameters obtained for the ring in this complex with those obtained for gaseous 1,5-cyclooctadiene in an electron diffraction study by Hedberg and Hedberg[23] is given in Table 6. Also given in this table are the corresponding parameters for the 1,5-cyclooctadiene rings in the metal complexes $[C_8H_{12}CuCl]_2$ and $[C_8H_{12}RhCl]_2$ as determined from X-ray studies by van den Hende and Baird[24] and by Ibers and Snyder[25], respectively. For clarity the following discussion will refer to the ring atoms by standard IUC nomenclature as designated in Table 6.

A distinctive structural feature common to all of these compounds[23,24] (except for $[C_8H_{12}RhCl]_2$[25] where the magnitude of the errors does not permit such conclusions) is the skewing of the ring and the resultant *idealized* symmetry (and in the nickel complex, crystallographic symmetry) of C_2. This skewing, illustrated for the cyclooctadiene ring in the nickel complex in Fig. 3, may be visualized as a distortion from a rectangle composed of C_3, C_4, C_7, and C_8 in which C_3 and C_7 move away from each other and toward the nickel. The resulting dihedral angle between the plane containing C_3, C_4, and C_8 and the plane containing C_7, C_4, and C_8 is about 17°. As a consequence of this distortion, the non-bonding distance between the non-olefinic carbons $C_3...C_7$ of 3.70 ± 0.026 Å is almost 0.6 Å greater than the non-bonding distance between the non-olefinic carbons $C_4...C_8$ of 3.11 ± 0.029 Å. In the free 1,5-cyclooctadiene ring[23], the corresponding cross-ring distances of 3.131 and 3.815 Å are representative of a similar skewing. Comparison of the non-bonding cross-ring distances between the olefinic bonds in both the nickel complex (Fig. 3) and in the free

TABLE 6

A COMPARISON OF 1,5-CYCLOOCTADIENE DISTANCES (Å) AND ANGLES*

	1,5-cyclooctadiene (C_2 ring symm.)[23]	*1,5-cyclooctadiene-duroquinone-Ni (C_2 ring symm.)*	*1,5-cyclooctadiene-Rh(I) chloride (C_{2v} ring symm.)*[25]	*1,5-cyclooctadiene Cu(I) chloride (C_1 ring symm.)*[21]
Distances				
C_1–C_2	1.341	1.325 ± 0.013	1.44 ± 0.07	1.41 ± 0.01 (av.)
C_8–C_1	1.502 (av.)	1.510 ± 0.015		1.50 ± 0.01 (av.)
C_2–C_3		1.528 ± 0.016	1.52 ± 0.09	1.50 ± 0.01 (av.)
C_3–C_4	1.554	1.570 ± 0.016		1.58 ± 0.01 (av.)
$C_1 \ldots C_5$	3.302	3.205 ± 0.023		
$C_2 \ldots C_6$	3.318	3.185 ± 0.023		
$C_1 \ldots C_6$	3.047	2.908 ± 0.017	2.82 ± 0.10	
$C_3 \ldots C_7$	3.131	3.114 ± 0.029		
$C_4 \ldots C_8$	3.815	3.699 ± 0.026		
$C_4 \ldots C_7$	3.191	3.057 ± 0.020	3.14 ± 0.14	
metal–C_1		2.086 ± 0.010	2.12 ± 0.03	2.17 ± 0.01
metal–C_5				2.29 ± 0.01
metal–C_2		2.114 ± 0.010		2.21 ± 0.01
metal–C_8				2.38 ± 0.01
metal–N**		1.992	2.00	2.05
metal–N^1**				2.22
$N \ldots N^1$**	3.00	2.91	2.82	
Angles				
C_1–C_2–C_3	127.8° (av.)	121.1 ± 1.0°	123 ± 6°	118° (av.)
C_4–C_5–C_6		129.3 ± 1.0°		
C_2–C_3–C_4	116.8° (av.)	116.2 ± 1.1°	116 ± 10°	113° (av.)
C_3–C_4–C_5		113.0 ± 1.1°		
N–metal–N^1**		93.6°	90°	91.7°

---

* For clarity, the atoms in this table are numbered according to IUC notation. These subscripted chemical designations are related to the crystallographic notation as follows:

$C_1 \sim C(2)$	$C_3 \sim C(4)$	$C_5 \sim C(2^1)$	$C_7 \sim C(4^1)$
$C_2 \sim C(3)$	$C_4 \sim C(1^1)$	$C_6 \sim C(3^1)$	$C_8 \sim C(1)$

** N and N^1 denote the midpoints of the olefinic bonds of the cyclooctadiene.

cyclooctadiene[23] (*i.e.*, 3.19 ± 0.023 Å *vs.* 3.21 ± 0.023 Å in the complex; 3.302 Å *vs.* 3.318 Å in the free organic molecule) shows essentially no skewing in the unsaturated hydrocarbon part of the cyclooctadiene ring in both complexed and uncomplexed forms. The consistency between the cross-ring distances in the nickel complex and those in the free cyclooctadiene leaves little doubt that the skewing is the same in both compounds, and that this distortion is predominant for the non-olefinic carbons.

No observed lengthening of the olefinic bond occurs in the nickel complex. This bond length is 1.33 ± 0.01 Å in the complex and 1.341 Å in the free cyclooctadiene[23]. The 99.9 % fiducial limits for the mean value in the metal complex are 1.28 and 1.37 Å, so there is less than a 0.1 % chance that the true value of this bond length can be greater than 1.37 Å. Most prior X-ray results of unconjugated olefins bonded to metals show a complexed olefinic bond length greater than 1.40 Å (*e.g.*, $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$[14], 1.45 ± 0.02 Å; $[C_8H_{12}CuCl]_2$[21], 1.40 ± 0.01 Å). However, these large magnitudes of lengthening over that of a normal double bond length of 1.33 Å have been questioned in light of the relatively small decreases in C=C stretching frequencies upon complexing[26]. Indeed, a recent low temperature X-ray redetermination with counter date of norbornadiene palladium(II) chloride by Baenziger *et al.*[27], has revealed that the unconjugated, metal-complexed C=C bond length (formerly reported[26] as 1.46 Å) is 1.37 ± 0.01 Å.

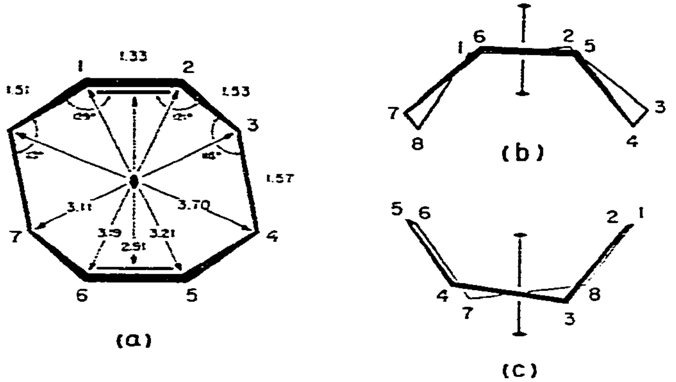

Fig. 3. Three projections of the 1,5-cyclooctadiene fragment illustrating the skewing of the ring. The atoms are designated according to IUC designation.

The two approximately equal single bonds adjacent to the olefinic bond (1.510 ± 0.015 Å, 1.528 ± 0.016 Å) have an average value of 1.52 Å, which is close to those of 1.502 Å (av.) in free cyclooctadiene[23], and 1.50 Å (av., individual e.s.d., 0.01 Å) in 1,5-cyclooctadiene-copper chloride[24]. The value of 1.570 ± 0.016 Å for the single bond non-adjacent to the double bond agrees with those of 1.554 Å, and 1.58 Å (av., individual e.s.d., 0.01 Å) in the free molecule[23] and the copper complex[24], respectively. The average value of 1.52 ± 0.09 Å for all these single bonds reported for the rhodium complex[25] lies experimentally within the range defined by these other cyclooctadiene compounds.

The $HC=CH-CH_2$ angles adjacent to the double bond in the nickel complex of 129.3 ± 1.0° and 121.1 ± 1.0° are considerably larger than the other, non-adjacent, $HC-CH_2-CH_2$ ring angles of 113.0 ± 1.0° and 116.2 ± 1.1°, as would be expected in a comparison of angles whose vertices are *quasi-sp*^{2} carbons with angles whose vertices are *quasi-sp*^{3} carbons. It can be seen that the skewing in the non-olefinic part of the ring is manifested in the different angles adjacent to the olefinic bond.

Examination of the angles given in Table 6 shows the average values of the adjacent $HC=CH-CH_2$ and non-adjacent $HC-CH_2-CH_2$ angles in free cyclooctadiene[23] and the rhodium[25] and copper[24] complexes to be in good agreement with those of the nickel complex. The only reasonably large difference occurs in the adjacent angles in $[C_8H_{12}CuCl]_2$ which have an average value[24] of 118°.

In the nickel complex, C_8, C_1, C_2, and C_3 are coplanar within 0.01 Å, whereas in the free cyclooctadiene[23] the carbons are distorted such that the plane of C_8, C_1, and C_2 makes a dihedral angle of 10° with the plane of C_1, C_2, and C_3. This above mean plane of the four carbons (*i.e.*, C_8, C_1, C_2, C_3) in cyclooctadiene-duroquinone-nickel forms a dihedral angle of 124° with the mean plane of the four olefinic carbons (C_1, C_2, C_5, C_6) and of 68° with its symmetry related plane of C_4, C_5, C_6, and C_7.

In the nickel complex the two nickel-cyclooctadiene olefinic midpoint distances are required by the crystallographic two-fold to be identical (1.99 Å). These distances were also found to be equivalent (2.00 ± 0.04 Å) in the rhodium complex[25]; however, in the copper complex[24] an inexplicable difference in the two metal–midpoint distances (2.05 and 2.22 Å) occurs.

Metal–ring bonding

The significantly short olefinic bonds in the cyclooctadiene ring relative to those in the duroquinone ring (*i.e.*, 4.6 standard deviations difference) may imply weaker bonding from the nickel to the cyclooctadiene than to the duroquinone. Chemical evidence of this is provided by the fact that both the bis-duroquinone-nickel and the cyclooctadiene-duroquinone-nickel are very stable and are synthesized by the reaction of $Ni(CO)_4$ with the appropriate free ligands[1-3], whereas bis-cyclooctadiene-nickel is unstable and can be prepared only indirectly from the compound cyclododeca-1,5,9-triene-nickel(0)[28]. This difference in nickel–ligand bond strength would presumably be due to the stabilization of the duroquinone–nickel bonds through extensive π-electron back-bonding.

In presumed conflict with this is that the nickel is 0.12 Å closer to the olefinic bonds in the cyclooctadiene ring than to those in the duroquinone ring. Although the metal–ring distance has been utilized as a gauge of bond strength[29], this criterion alone would imply stronger nickel–cyclooctadiene bonding than nickel–duroquinone bonding. If it is assumed for conceptual convenience that each metal–ring interaction results primarily from overlap of two tetrahedrally hybridized metal lobes with the corresponding π-bonding molecular orbitals of each double bond, then this apparent conflict may perhaps be rationalized. The normals to the π-nodal planes of the two double bonds in duroquinone are essentially parallel to each other and to the vector through the nickel and the centroids of each of the two rings, whereas the normals of the two π-nodal planes of the double bonds in cyclooctadiene are directed more nearly toward the nickel and form an angle with the above nickel centroid vector (or with the intersecting vector parallel to it) of 56°. In the case of the nickel–duroquinone overlap, the two tetrahedral nickel orbitals, which are oriented toward the midpoints of the two double bonds, intersect the π-orbitals at an angle of approximately 125° and at a distance of about 0.8 Å from the double bonds. In order for the tetrahedral nickel orbitals to obtain significant overlap with the non-parallel cyclooctadiene π-olefinic orbitals (which make an angle of approximately 112° with each other), the nickel must lie closer to the cyclooctadiene ring. Hence, this effect, as well as the difference in separations between the olefinic bonds in the two rings (*i.e.*, 2.84 Å for duroquinone *vs.* 3.20 Å for cyclooctadiene), suggests that the difference in metal–olefin distances may be a consequence of the stereochemical configuration of the ligands rather than a simple function of the metal–olefin bond strengths.

ACKNOWLEDGEMENTS

We wish to thank both the United States Atomic Energy Commission and the National Science Foundation for their generous financial support of this work. The calculations were carried out on the IBM 704 computer at MURA and on the CDC 1604 computer at the University of Wisconsin Computing Center. We are greatly indebted to Dr. G. Schrauzer for samples of this compound and for his interest in this work. Our thanks are extended to Professor K. Hedberg of Oregon State University and Professor G. M. J. Schmidt of the Weizmann Institute of Science (Rehovoth, Israel) for communicating part of their results to us prior to publication.

SUMMARY

The structure of 1,5-cyclooctadiene-duroquinone-nickel, $C_8H_{12}NiC_{10}H_{12}O_2$, has been determined from a three-dimensional X-ray analysis. The compound crystallizes in a monoclinic unit cell of symmetry $P2/n$ and dimensions $a = 14.26$ Å, $b = 7.95$ Å, $c = 14.17$ Å, and $\beta = 94°27'$. There are four molecules per unit cell with each molecule located on a crystallographic two-fold axis. A three-dimensional least-squares refinement yielded a final unweighted discrepancy factor of $R_1 = 10.1\%$. Each discrete monomeric molecule consists of a nickel atom sandwiched between a boat-form 1,5-cyclooctadiene ring and a duroquinone ring. The two sets of parallel double bonds in the cyclooctadiene and duroquinone rings are perpendicular; the nickel therefore can be considered to possess an *idealized* tetrahedral configuration. The cyclooctadiene ring of C_2 symmetry shows significant skeletal skewing similar to that present in free 1,5-cyclooctadiene, whereas the *idealized* D_{2h} symmetry of free duroquinone is reduced to C_{2v} in the nickel-complexed duroquinone due to a deformation of the carbonyl groups out of the plane of the ring. The detailed geometry of the rings, and the nature and implications of the bonding are discussed with respect to related complexes.

REFERENCES

1 G. N. Schrauzer and H. Thyret, *J. Am. Chem. Soc.*, 82 (1960) 6420.
2 G. N. Schrauzer and H. Thyret, *Z. Naturforsch.*, 16b (1961) 353.
3 G. N. Schrauzer and H. Thyret, *Z. Naturforsch.*, 17b (1962) 73.
4 G. N. Schrauzer and H. Thyret, *Theoret. Chim. Acta*, 1 (1963) 172.
5 D. C. Phillips, *Acta Cryst.*, 7 (1954) 746.
6 P. W. Sutton, *A Crystallographic Data Correlation Program for the CDC 1604*, University of Wisconsin, 1962.
7 W. R. Busing, K. O. Martin and H. A. Levy, *A Fortran Crystallographic Least Squares Program*, ORNL-TM-305, Oak Ridge National Laboratory, 1963.
8 W. R. Busing, K. O. Martin and H. A. Levy, *A Fortran Function and Error Program*, ORNL-TM-305, Oak Ridge National Laboratory, 1963.
9 J. Blount, *A Fourier Program for the CDC 1604*, University of Wisconsin, 1963.
10 H. A. Levy, *Acta Cryst.*, 9 (1956) 679.
11 D. L. Smith, *A Least-Squares Planes Program for the CDC 1604 Computer*, Ph.D. Thesis (Appendix IV), University of Wisconsin, 1962.
12 J. Ladell, B. Post and I. Fankuchen, *Acta Cryst.*, 5 (1952) 795; L. O. Brockway and P. C. Cross, *J. Chem. Phys.*, 3 (1935) 828.
13 *Cf.*, J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 2 (1963) 235.
14 L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 2 (1963) 713.
15 L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, New York, 1960, pp. 257–261.
16 F. L. Hirshfeld, D. Rabinovich, G. M. J. Schmidt and E. Ubell, *Acta Cryst.*, 16 (1963) A57.
17 J. Trotter, *Acta Cryst.*, 13 (1960) 86.
18 L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.*, 83 (1961) 752.
19 N. A. Bailey, M. Gerloch and R. Mason, *Nature*, 201 (1964) 72.
20 G. N. Schrauzer, *Abstracts of Papers*, 17L, 147th Meeting, ACS, April, 1963.
21 R. Markby, H. W. Sternberg and I. Wender, *Chem. Ind. (London)*, (1959) 1381.

22 E. WEISS AND W. HÜBEL, *J. Inorg. Nucl. Chem.*, 11 (1959) 42.

23 L. HEDBERG AND K. HEDBERG, *Abstracts of Papers, National Meeting of the American Crystallographic Association*, Bozeman, Montana, July 1964.

24 J. H. VAN DEN HENDE AND W. C. BAIRD, JR., *J. Am. Chem. Soc.*, 85 (1963) 1009.

25 J. A. IBERS AND R. G. SNYDER, *Acta Cryst.*, 15 (1962) 923.

26 N. C. BAENZIGER, J. R. DOYLE, G. F. RICHARDS AND C. L. CARPENTER, in S. KIRSCHNER, *Advances in the Chemistry of the Coordination Compounds*, Macmillan, New York, 1961, pp. 131–138.

27 N. C. BAENZIGER, G. F. RICHARDS, R. C. MEDRUD, H. L. HAIGHT AND J. R. DOYLE, *Abstracts of Papers, National Meeting of the American Crystallographic Association*, Bozeman, Montana, July 1964.

28 G. WILKE, *Angew. Chem.*, 72 (1960) 581.

29 *Cf.*, M. R. CHURCHILL AND R. MASON, *Proc. Chem. Soc.*, (1963) 112.