remaining double bonds are not significantly different from 1.34 Å. The average value of all the single bonds is 1.475 Å., in reasonable agreement with the average value found for cyclooctatetraene by electron diffraction methods, 1.462 Å.[9] The distances are significantly shorter than the normal single bond distance of 1.54 Å.

Acknowledgment.—This research work was supported by a grant from the Army Research Office (Durham), DA-ARO(D)-31-124-G26. The authors are indebted to Dr. H. L. Haight for the preparation of the crystal specimens and to Messrs. Mark and Phillip Richards for the estimates of the intensities.

---

(8) N. C. Baenziger, J. R. Doyle, G. F. Richards, and C. L. Carpenter, "Advances in the Chemistry of the Coordination Compounds," The Macmillan Company, New York, N. Y., 1961, p. 131.

(9) O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE STATE UNIVERSITY OF IOWA, IOWA CITY, IOWA

Metal–Olefin Compounds. VII. The Crystal and Molecular Structure of Cyclo-tetra-μ-chloro-tetrakis[bicyclo[2.2.1]hepta-2π,5-dienecopper(I)]

BY N. C. BAENZIGER, H. L. HAIGHT, AND J. R. DOYLE

Received April 27, 1964

A crystal structure determination of the compound formed by the reaction of copper(I) chloride and bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) shows that the complex exists as a tetramer, $(C_7H_8CuCl)_4$, in the solid state with $\bar{4}$ symmetry. The copper and chlorine atoms form an eight-membered tube-shaped ring with one double bond of the olefin coordinated to the copper atom and lying in the plane defined by the copper atom and adjacent chlorine atoms. The copper atom is coordinated to the olefin in an *exo* configuration; one double bond of the olefin is not coordinated. The distorted trigonal planar coordination about copper is similar to that found for potassium dicyanocuprate(I), cyclooctatetraenecopper(I) chloride, and 2-butynecopper(I) chloride.

Introduction

The compound dichloro(norbornadiene)palladium(II) has been studied crystallographically,[1,2] and the 1:2 complex of norbornadiene with silver nitrate had been prepared and the structure determination was in progress[3] when a method for preparing olefin complexes containing copper(I) chloride was developed.[4]

The preparation of norbornadienecopper(I) chloride, hereafter abbreviated as NBD-CuCl, and the subsequent structure determination was made to add another member to a series in which the olefin was kept the same, but the metal to which it was coordinated was varied. The structure determination reveals an interesting coordination arrangement for copper(I) which is very similar to that reported for 2-butynecopper(I) chloride by Carter and Hughes.[5] The companion paper[6] in this series contains a summary of other earlier work and a report on the structure determination of cyclooctatetraenecopper(I) chloride (COT-CuCl).

Experimental

Preparation of Crystals.—Crystals of norbornadienecopper(I) chloride were made by reducing an ethanol solution of copper(II) chloride and the olefin with sulfur dioxide. The crystals which precipitated were separated by filtration and washed with methanol containing a small amount of norbornadiene. The crystals used for X-ray diffraction measurements were mounted in two different ways. For the early work on the structure determination, the crystals were coated with a polystyrene–alkyd copolymer resin immediately after being glued to the glass fiber support. A thin-walled glass capillary was then mounted over the glass fiber and crystal and cemented to the brass pin base. By maintaining the crystal at −10° continuously throughout all the exposures (dry air stream cooled by a Dry Ice–acetone bath) crystal decomposition was retarded. For the measurements made with the G.E. single crystal orienter, an uncoated crystal was mounted in a thin-walled capillary, containing a small amount of norbornadiene, in a drybox, and the capillary was sealed off with a glass seal. Crystals mounted in this fashion did not decompose at room temperature during the approximately 2-week period needed to obtain the intensity data. The crystal used to obtain all of the intensity data was a tetragonal rod, 0.17 × 0.17 × 0.80 mm., bounded by 1,1,0 faces.

Crystal Data.—The cell dimensions were determined from the settings needed for the single crystal orienter. Norbornadienecopper(I) chloride has a tetragonal unit cell with $a = 12.27 \pm 0.03$ Å., $c = 9.62 \pm 0.02$ Å. at room temperature. Cell dimensions obtained from precession camera films at −10° are $a = 12.21 \pm 0.05$ Å., $c = 9.58 \pm 0.04$ Å. From precession films, $(h0l)$ through $(h6l)$, and Weissenberg films, $(hk0)$ through $(hk5)$, the systematic extinctions, (hhl) present only when $l = 2n$, $(h00)$ present only when $h = 2n$, lead to the unique space group $P\bar{4}2_1c$.

The early work on the structure used visually estimated film

---

(1) N. C. Baenziger, J. R. Doyle, and C. L. Carpenter, *Acta Cryst.*, **14**, 303 (1961).

(2) N. C. Baenziger, J. R. Doyle, G. F. Richards, and C. L. Carpenter, "Advances in the Chemistry of the Coordination Compounds," The Macmillan Company, New York, N. Y., 1961, pp. 131–138.

(3) H. L. Haight, Dissertation, University of Iowa, Feb., 1963.

(4) H. L. Haight, J. R. Doyle, N. C. Baenziger, and G. F. Richards, *Inorg. Chem.*, **2**, 1301 (1963).

(5) F. L. Carter and E. W. Hughes, *Acta Cryst.*, **10**, 801 (1957).

(6) N. C. Baenziger, G. F. Richards and J. R. Doyle, *Inorg. Chem.*, **3**, 1529 (1964).

TABLE I

ATOMIC PARAMETERS FOR $[C_7H_8CuCl]_4$

	x $s(x)$ $s(X)^b$	y $s(y)$ $s(Y)^b$	z $s(z)$ $s(Z)^b$	B_{11} $s(B_{11})$	B_{22} $s(B_{22})$	B_{33} $s(B_{33})$	B_{12} $s(B_{12})$	B_{13} $s(B_{13})$	B_{23} $s(B_{23})$
						($\times 10^5$)			
Cu	0.1391	0.0189	0.1192	698	869	986	−62	−260	152
	0.00009	0.00009	0.0001	8	10	11	13	18	18
	0.0011	0.0010	0.0010						
Cl	0.1692	0.9719	0.8938	743	832	1021	−116	54	−40
	0.00015	0.00016	0.00018	13	15	17	22	27	29
	0.0018	0.0019	0.0017						
C_1	0.3462	0.9754	0.2882	606	1095	961	226	152	−71
	0.0006	0.0007	0.0008	56	82	74	118	102	128
	0.007	0.008	0.007						
C_2	0.3624	0.9514	0.4436	726	897	1031	172	−205	26
	0.0007	0.0007	0.0007	57	64	76	110	116	126
	0.008	0.008	0.007						
C_3	0.2926	0.0108	0.5150	769	915	917	75	−180	−260
	0.0007	0.0007	0.0006	62	70	67	106	106	128
	0.008	0.009	0.006						
C_4	0.2243	0.0757	0.4023	786	747	1542	249	−250	−343
	0.0006	0.0006	0.0009	56	55	105	94	153	147
	0.008	0.008	0.008						
C_5	0.1604	0.9880	0.3269	547	950	1314	−16	−204	702
	0.0006	0.0007	0.0008	54	70	82	97	111	138
	0.008	0.009	0.007						
C_6	0.2345	0.9272	0.2594	927	697	869	−202	−209	−22
	0.0007	0.0006	0.0008	64	54	70	102	119	103
	0.008	0.008	0.007						
C_7	0.3171	0.0960	0.2986	726	1148	974	−620	−48	−127
	0.0006	0.0007	0.0008	56	80	75	119	116	131
	0.008	0.009	0.007						
				B^a					
H_1	0.41	0.96	0.22	5.00					
H_2	0.42	0.89	0.50	5.00					
H_3	0.27	0.01	0.62	5.00					
H_4	0.19	0.15	0.44	5.00					
H_5	0.10	0.94	0.38	5.00					
H_6	0.20	0.86	0.20	5.00					
H_7	0.28	0.10	0.21	5.00					
H_8	0.39	0.13	0.36	5.00					

[a] In Å.^{2}. [b] In Å.

data. The final refinement of the structure used only the data obtained by means of the single crystal orienter with Cu Kα radiation and a proportional counter. All accessible reflections with 2θ less than 147.5° were measured in one octant of the reciprocal lattice and the equivalent reflections were averaged. Intensities were measured using the 2θ scan; Lorentz, polarization, and absorption corrections (assuming an equivalent cylinder) were made.

Structure Determination

From the film data the copper and chlorine positions were easily found from a three-dimensional Patterson function. An indication of the position of the olefinic portion of the molecule was obtained from an electron density projection on the 001 plane. A model of the complex was constructed to correspond to this projection, and a least-squares refinement starting with this model gave an R value of 0.19 for all data. The copper and chlorine atoms formed an eight-membered tub-shaped ring. The copper atom was coordinated to one double bond of the norbornadiene molecule, the other double bond lying much further away in an *endo* configuration. Minor variations in this arrangement, including a more nearly tetrahedral configuration, always led to essentially the same arrangement upon least-squares refinement. Since several crystals had been used in obtaining the intensity data, and some crystal decomposition had been noted to occur, it was felt that the poor agreement might be due to the intensity data rather than an incorrect structure. Thus, at this stage new intensity data were obtained by use of the proportional counter.

A continuation of the refinement with the new intensity data did not lead to any significant reduction in the discrepancy factor. By altering the positions of three of the carbon atoms the configuration of the copper atom with respect to the olefin was changed from *endo* to *exo*. The double bond coordinated to the copper atom remained the same, but the other double bond no longer was in the vicinity of the copper atom. This arrangement refined rapidly to $R = 0.11$. At this point, seven reflections which appeared to be strongly influenced by extinction (1, 0, 1; 2, 0, 0; 1, 1, 0; 2, 2, 0; 3, 3, 0; 4, 4, 0; 3, 3, 10) were removed from the refinement. The R value decreased to 0.098. Individual anisotropic temperature factors were then refined and hydrogen atoms were included at fixed positions and not allowed to refine. The R value decreased to 0.056. Removal of about a half-dozen

TABLE II

INTERATOMIC DISTANCES AND ANGLES FOR $[C_7H_8CuCl]_4$

	Distance, Å.	Std. dev., Å.		Angle, deg.	Std. dev., deg.
Cu–Cl	2.296	0.002	Cl–Cu–Cl′	104.4	0.1
Cu–Cl′	2.275	0.002	Cl–Cu–$(C_5{=}C_6)_c$	124.7	0.2
Cu–Cl″	3.091	0.002	Cl′–Cu–$(C_5{=}C_6)_c$	130.9	0.2
Cu–$(C_5{=}C_6)_c$	1.971	0.008	C_2–C_1–C_6	102.7	0.7
Cu–C_5	2.051	0.007	C_3–C_4–C_5	104.1	0.4
Cu–C_6	2.111	0.008	C_7–C_1–C_2	98.7	0.7
C_1–C_2	1.537	0.010	C_7–C_4–C_3	97.6	0.4
C_1–C_6	1.518	0.011	C_7–C_1–C_6	100.2	0.6
C_1–C_7	1.526	0.012	C_7–C_4–C_5	100.9	0.5
C_2–C_3	1.317	0.011	C_1–C_2–C_3	108.6	0.8
C_3–C_4	1.587	0.011	C_2–C_3–C_4	105.3	0.4
C_4–C_7	1.534	0.011	C_4–C_5–C_6	105.9	0.3
C_4–C_5	1.516	0.011	C_5–C_6–C_1	107.8	0.6
C_5–C_6	1.345	0.011	C_1–C_7–C_4	93.3	0.6
C_2–C_6	2.386	0.011	Cu–Cl–Cu′	94.1	0.1
C_3–C_5	2.448	0.010			
C_2–C_7	2.324	0.011			
C_3–C_7	2.350	0.010			
C_5–C_7	2.353	0.011			
C_6–C_7	2.338	0.012			
C_1–C_3	2.321	0.010			
C_2–C_4	2.314	0.011			
C_4–C_6	2.286	0.011			
C_5-C_1	2.316	0.111			
C_1–C_4	2.226	0.011			
Cl–Cl′	3.611	0.003			

additional reflections which appeared to have some extinction errors did not further decrease the R value but did decrease the sum $\Sigma w(\Delta F^2)^2$ by 5%. The atom parameters did not change significantly. The final R value is 0.057. The refinement continued until the changes in the parameters were less than 1 in the fifth decimal place, on the average. The atom parameters are listed in Table I. Interatomic distances and bond angles are given in Table II together with their standard deviations. The equations of pertinent planes and vectors are given in Table III. The calculated and observed structure factors are summarized in Table IV.

TABLE III

EQUATIONS OF IMPORTANT PLANES AND VECTORS (IN NORMAL FORM WITH COMPONENTS IN Å.) FOR $[C_7H_8CuCl]_4$

(Cu, Cl, Cl′)	$0.8050x + 0.5929y - 0.0204z = 1.488$
(Cu, Cl, Cl′, C_5, C_6)	$0.7806x + 0.6242y - 0.0314z = 1.474$
Dev. from plane (Å.)	−0.03, −0.04, 0.06, −0.13, 0.14
(C_1, C_6, C_5, C_4)	$-0.0907x + 0.5960y - 0.7979z = -2.780$
Dev. from plane (Å.)	−0.003, 0.005, −0.004, 0.003
(C_1, C_2, C_3, C_4)	$-0.6602x - 0.7494y - 0.5021z = -2.713$
Dev. from plane (Å.)	0.005, −0.009, 0.008, −0.005
Cu→Cl vector	$0.1627\mathbf{i} - 0.2536\mathbf{j} - 0.9535\mathbf{k}$
Cu→Cl′	$-0.5930\mathbf{i} + 0.8033\mathbf{j} - 0.0544\mathbf{k}$
Cu→($C_5{=}C_6$ center)	$0.3635\mathbf{i} - 0.3817\mathbf{j} - 0.8498\mathbf{k}$
C_5→C_6	$0.6769\mathbf{i} - 0.5549\mathbf{j} - 0.4835\mathbf{k}$
Cu→C_5	$0.1271\mathbf{i} - 0.1848\mathbf{j} + 0.9745\mathbf{k}$
Cu→C_6	$0.5547\mathbf{i} - 0.5329\mathbf{j} + 0.6390\mathbf{k}$
(Cu, Cl, Cl′, C_5, C_6) and (C_1, C_6, C_5, C_4) plane intersection	$-0.5071\mathbf{i} + 0.6619\mathbf{j} + 0.5520\mathbf{k}$

Angle between (Cu, Cl, Cl′, C_5, C_6) and (C_1, C_6, C_5, C_4) plane normals = 70.9°
Angle between (C_1, C_6, C_5, C_4) and (C_1, C_2, C_3, C_4) plane normals = 89.2°
Angle between Cu→($C_5{=}C_6$ center) and C_5→C_6 = 87.3°
Angle between C_5→C_6 and (Cu, Cl, Cl′, C_5, C_6) and (C_1, C_6, C_5, C_4) plane intersection = 12.2°

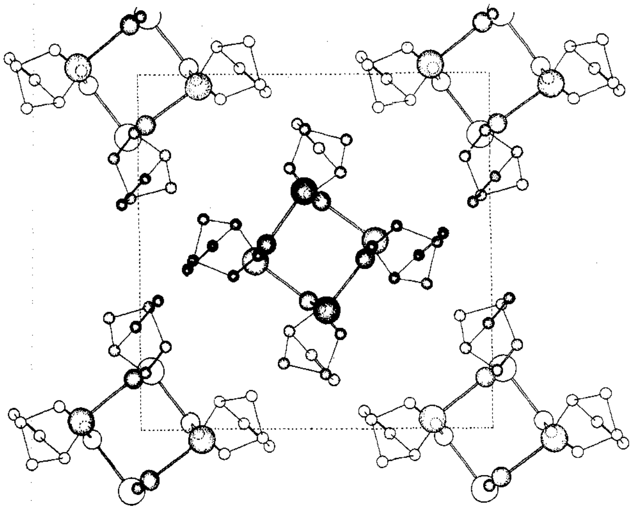


Fig. 1.—Projection of the structure of $[C_7H_8CuCl]_4$ on (001). The small spheres are carbon atoms; the largest spheres are chlorine atoms.

The anisotropic thermal vibrational parameters were analyzed by the method of Cruickshank[7] into translational and torsional motions of the tetramer unit. The assumption that intramolecular vibrations can be neglected appears to be reasonable for this molecule at room temperature. The translational and torsional tensors are

$$T \times 10^2 \text{ (in Å.}^2\text{)}$$

$$\begin{array}{ccc} 5.53 \pm 0.51 & 0.00 \pm 0.45 & 0.00 \pm 0.38 \\ & 5.53 \pm 0.51 & 0.00 \pm 0.38 \\ & & 4.99 \pm 0.45 \end{array}$$

$$\omega \text{ (in deg.}^2\text{)}$$

$$\begin{array}{ccc} 0.08 \pm 0.98 & 0.00 \pm 0.85 & 0.00 \pm 0.62 \\ & 0.08 \pm 0.98 & 0.00 \pm 0.92 \\ & & 4.08 \pm 1.3 \end{array}$$

The full matrix least-squares program used in the refinement was developed for the IBM 7040 in our laboratory. The program minimizes $\Sigma w(F_o^2 - F_c^2)^2$ and is sufficiently flexible to allow any coordinate or temperature parameter to be held fixed or allowed to vary. Individual anisotropic or isotropic temperature factors may be intermixed. Both real and imaginary dispersion corrections may be included for any atom but only the real corrections were made for the copper and chlorine in this refinement. Uncorrected atom scattering factors are obtained by interpolation from the tabulated values in the International Tables for Crystallography, Vol. 3.

Discussion of the Structure

The structure consists of a tetrameric unit $(C_7H_8CuCl)_4$ with $\bar{4}$ symmetry. The copper and chlorine atoms form an eight-membered tub-shaped ring. A projection of the structure is shown in Fig. 1. One of the double bonds of the norbornadiene molecule

---

[7] D. W. J. Cruickshank, *Acta Cryst.*, **9**, 754, 757 (1956).

Table IV

Calculated and Observed Structure Factors for $[C_7H_8CuCl]_4$[a]

h	k	l	Fobsd.	|Fcalcd|
0	0	2	12.82	9.58
0	0	6	59.02	59.69
0	0	8	69.93	71.11
0	0	10	35.61	37.23
1	0	2	59.76	58.55
1	0	3	86.13	91.17
1	0	4	9.98	9.63
1	0	5	129.45	138.19
1	0	6	30.87	27.96
1	0	7	34.56	34.40
1	0	8	14.05	16.00
1	0	9	51.32	49.40
1	0	10	5.48	4.44
1	0	11	1.54	2.86
2	0	2	16.20	15.48
2	0	3	18.42	19.23
2	0	4	69.19	66.75
2	0	5	16.02	14.16
2	0	6	9.37	8.62
2	0	7	11.21	13.09
2	0	8	23.78	21.69
2	0	9	4.56	6.53
2	0	10	6.16	7.04
2	0	11	* 1.48	1.04
3	0	1	59.58	58.67
3	0	2	39.49	39.31
3	0	3	5.98	4.90
3	0	4	5.91	5.54
3	0	5	30.01	27.56
3	0	6	39.06	35.97
3	0	7	8.38	10.60
3	0	8	5.98	5.19
3	0	9	4.31	5.12
3	0	10	22.49	21.66
3	0	11	* 1.42	0.44
4	0	0	20.70	21.47
4	0	1	70.42	72.75
4	0	2	16.02	14.53
4	0	3	55.82	56.84
4	0	4	5.24	5.13
4	0	5	55.39	49.34
4	0	6	4.00	2.97
4	0	7	12.38	13.19
4	0	8	10.10	9.77
4	0	9	15.96	14.00
4	0	10	2.40	3.34
4	0	11	7.09	8.87
5	0	1	53.73	55.53
5	0	2	84.96	88.09
5	0	3	30.93	31.80
5	0	4	28.96	27.35
5	0	5	44.36	42.03
5	0	6	39.80	38.37
5	0	7	4.68	0.34
5	0	8	6.59	5.01
5	0	9	26.86	25.23
5	0	10	16.14	17.33
5	0	11	2.96	4.06
6	0	1	4.00	5.45
6	0	2	16.94	17.61
6	0	3	20.46	21.62
6	0	4	83.30	83.10
6	0	5	14.73	14.98
6	0	6	8.87	8.53
6	0	7	19.47	17.54
6	0	8	26.00	24.27
6	0	9	3.08	3.40
6	0	10	18.30	21.07
6	0	11	* 1.05	0.48
7	0	1	75.54	79.42
7	0	2	19.65	19.46
7	0	3	54.22	55.58
7	0	4	* 1.73	0.96
7	0	5	70.24	70.65
7	0	6	5.91	4.42
7	0	7	1.91	0.79
7	0	8	1.85	1.68
7	0	9	28.83	28.18
7	0	10	3.08	4.53
8	0	0	40.48	43.07
8	0	1	21.63	22.13
8	0	2	3.94	3.34
8	0	3	28.83	28.93
8	0	4	35.18	35.74
8	0	5	7.39	6.18
8	0	6	1.91	1.83
8	0	7	17.01	16.33
8	0	8	17.25	17.03
8	0	9	6.35	7.19
8	0	10	* 1.17	0.74
9	0	1	6.41	5.08
9	0	2	2.22	2.42
9	0	3	5.73	4.50
9	0	4	8.01	8.41
9	0	5	1.91	1.44
9	0	6	6.72	7.32
9	0	7	8.69	7.57
9	0	8	2.34	2.49
9	0	9	7.52	7.96
10	0	0	24.71	23.93
10	0	1	26.68	27.43
10	0	2	5.42	1.13
10	0	3	17.07	14.60
10	0	4	16.76	16.74
10	0	5	11.15	10.64
10	0	6	11.34	11.73
10	0	7	10.29	10.11
10	0	8	3.64	3.83
10	0	9	2.09	1.82
11	0	1	11.46	11.51
11	0	2	32.96	33.15
11	0	3	8.69	7.74
11	0	4	14.11	15.40
11	0	5	2.90	3.75
11	0	6	19.90	18.24
11	0	7	7.21	7.12
11	0	8	4.81	5.14
12	0	0	5.42	5.09
12	0	1	15.10	14.90
12	0	2	7.46	7.25
12	0	3	21.13	21.36
12	0	4	2.16	1.25
12	0	5	7.27	7.71
12	0	6	4.37	2.95
12	0	7	16.02	16.12
13	0	1	3.57	1.86
13	0	2	4.62	4.03
13	0	3	3.39	2.16
13	0	4	2.46	1.05
13	0	5	3.64	2.19
13	0	6	1.66	0.76
14	0	0	6.22	5.74
14	0	1	7.09	5.56
14	0	2	2.59	1.62
14	0	3	9.18	9.10
14	0	4	1.54	0.02
15	0	1	2.65	0.92
15	0	2	10.17	11.21
1	1	2	19.28	19.10
1	1	6	29.39	27.06
1	1	8	49.91	49.62
1	1	10	14.36	14.76
2	1	0	6.22	3.04
2	1	1	75.97	85.07
2	1	2	8.87	9.52
2	1	3	64.82	61.81
2	1	4	14.36	12.82
2	1	5	19.47	18.90
2	1	6	17.62	17.80
2	1	7	19 16	17.34
2	1	8	10.17	10.45
2	1	9	12.63	13.34
2	1	10	11.40	10.54
2	1	11	5.30	9.20
3	1	0	32.53	36.78
3	1	1	40.73	38.91
3	1	2	46.52	47.25
3	1	3	42.51	41.49
3	1	4	47.87	47.17
3	1	5	55.20	52.22
3	1	6	25.45	22.01
3	1	7	18.36	16.96
3	1	8	14.66	14.95
3	1	9	21.81	22.86
3	1	10	7.58	8.34
3	1	11	5.55	7.77
4	1	0	21.75	21.26
4	1	1	28.28	28.83
4	1	2	56.38	58.97
4	1	3	34.44	33.33
4	1	4	23.54	22.19
4	1	5	33.70	31.88
4	1	6	55.76	54.51
4	1	7	20.70	19.64
4	1	8	9.55	7.52
4	1	9	10.17	10.49
4	1	10	16.51	17.71
4	1	11	4.19	8.11
5	1	0	48.43	49.94
5	1	1	42.20	42.98
5	1	2	40.48	41.04
5	1	3	37.65	37.03
5	1	4	42.14	40.88
5	1	5	35.24	32.33
5	1	6	25.26	22.44
5	1	7	20.89	20.65
5	1	8	8.93	9.70
5	1	9	5.42	4.82
5	1	10	8.81	9.28
5	1	11	8.38	11.60
6	1	0	2.09	0.93
6	1	1	61.61	67.11
6	1	2	27.60	28.37
6	1	3	50.52	52.16
6	1	4	10.72	10.84
6	1	5	75.66	72.74
6	1	6	8.44	8.39
6	1	7	28.83	27.32
6	1	8	12.08	11.60
6	1	9	29.94	29.16
6	1	10	2.16	3.52
6	1	11	4.50	6.27
7	1	0	74.80	78.73
7	1	1	11.95	13.06
7	1	2	58.35	57.81
7	1	3	20.09	20.87
7	1	4	64.39	64.48
7	1	5	23.23	21.89
7	1	6	20.95	20.37
7	1	7	10.41	9.69
7	1	8	29.88	28.67
7	1	9	2.09	2.84
7	1	10	9.73	11.88
8	1	0	7.82	6.40
8	1	1	29.20	31.63
8	1	2	32.65	31.08
8	1	3	38.14	37.51
8	1	4	6.22	4.51
8	1	5	15.03	14.87
8	1	6	16.88	16.69
8	1	7	28.77	27.86
8	1	8	7.82	9.00
8	1	9	12.63	12.15
8	1	10	5.30	5.69
9	1	0	5.73	5.01
9	1	1	11.95	11.39
9	1	2	46.02	46.89
9	1	3	9.80	8.24
9	1	4	9.30	8.34
9	1	5	3.39	3.88
9	1	6	14.48	15.08
9	1	7	8.44	9.27
9	1	8	8.19	9.20
9	1	9	2.34	1.97
10	1	0	4.00	5.14
10	1	1	23.41	24.39
10	1	2	14.54	14.20
10	1	3	18.67	18.36
10	1	4	8.63	7.49
10	1	5	17.99	17.86
10	1	6	18.30	17.44
10	1	7	15.03	15.35
10	1	8	10.91	8.28
10	1	9	7.27	7.52
11	1	0	12.75	12.50
11	1	1	26.00	26.64
11	1	2	22.49	22.23
11	1	3	25.82	25.54
11	1	4	10.47	10.54
11	1	5	9.80	10.11
11	1	6	11.21	11.60
11	1	7	18.24	17.07
11	1	8	8.26	8.90
12	1	0	9.67	9.41
12	1	1	10.66	9.10
12	1	2	21.38	20.85
12	1	3	11.71	12.15
12	1	4	4.37	2.28
12	1	5	6.84	5.42
12	1	6	9.80	9.88
12	1	7	9.06	9.40
13	1	0	10.72	10.10
13	1	1	4.68	3.23
13	1	2	11.46	11.33
13	1	3	5.55	5.65
13	1	4	6.72	5.81
13	1	5	4.13	3.35
13	1	6	7.70	7.24
14	1	0	5.73	4.55
14	1	1	6.53	6.01
14	1	2	11.64	11.33
14	1	3	8.69	8.70
14	1	4	3.20	2.80
15	1	0	4.93	4.08
15	1	1	4.50	4.24
15	1	2	6.04	5.68
2	2	2	61.12	64.86
2	2	4	38.82	35.15
2	2	6	39.19	37.29
2	2	8	26.31	25.00
2	2	10	19.10	18.02
3	2	0	14.79	14.50
3	2	2	41.71	42.16
3	2	3	62.72	64.85
3	2	4	11.89	11.86
3	2	5	81.39	80.21
3	2	6	9.98	11.83
3	2	7	24.77	23.05
3	2	8	8.32	7.87
3	2	9	37.34	37.24
3	2	10	6.04	6.87
3	2	11	2.22	4.03
4	2	1	60.07	61.87
4	2	2	36.04	38.56
4	2	3	45.16	45.61
4	2	4	76.71	78.36
4	2	5	22.49	22.28
4	2	6	24.52	25.80
4	2	7	17.44	15.50
4	2	8	25.82	24.65
4	2	9	7.21	7.16
4	2	10	12.26	13.28
4	2	11	7.95	10.21
5	2	0	24.03	23.10
5	2	1	27.11	28.54
5	2	2	40.79	41.78
5	2	3	51.20	51.78
5	2	4	14.05	13.12
5	2	5	25.20	23.74
5	2	6	19.65	19.38
5	2	7	10.84	9.50
5	2	8	10.35	9.55
5	2	9	1.85	3.01
5	2	10	7.21	7.52
5	2	11	4.74	6.66
6	2	0	63.09	64.40
6	2	1	8.63	11.30
6	2	2	37.71	37.40
6	2	3	20.02	20.00
6	2	4	31.55	29.35
6	2	5	23.23	22.22
6	2	6	27.29	26.23
6	2	7	24.21	23.87
6	2	8	9.80	10.71
6	2	9	3.33	4.61
6	2	10	9.67	10.06
7	2	0	24.46	26.27
7	2	1	61.30	63.02
7	2	2	48.92	49.61
7	2	3	41.71	42.88
7	2	4	25.14	24.70
7	2	5	25.26	25.01
7	2	6	11.09	11.95
7	2	7	24.15	23.84
7	2	8	9.80	8.65
7	2	9	11.77	11.29
7	2	10	11.95	12.98
8	2	0	15.16	16.27
8	2	1	25.88	27.18
8	2	2	52.37	53.68
8	2	3	32.72	32.65
8	2	4	17.56	17.28
8	2	5	17.56	16.03
8	2	6	38.32	37.62
8	2	7	19.90	18.72
8	2	8	12.63	11.69
8	2	9	3.88	3.24
8	2	10	7.46	9.60
9	2	0	11.58	12.75
9	2	1	29.88	30.13
9	2	2	19.47	19.68
9	2	3	31.98	32.86
9	2	4	6.65	8.21
9	2	5	24.58	24.80
9	2	6	12.69	12.07
9	2	7	21.50	21.54
9	2	8	1.60	1.87
9	2	9	8.93	10.91
10	2	0	34.13	35.54
10	2	1	14.85	14.66
10	2	2	25.26	25.68
10	2	3	9.18	8.61
10	2	4	20.39	19.71
10	2	5	* 1.91	1.18
10	2	6	21.75	20.70
10	2	7	4.87	4.41
10	2	8	6.16	6.57
11	2	0	2.71	0.30
11	2	1	19.41	18.45
11	2	2	24.95	24.48
11	2	3	13.37	13.00
11	2	4	4.25	5.56
11	2	5	6.26	7.27
11	2	6	13.19	12.86
11	2	7	11.58	11.02
11	2	8	5.79	5.60
12	2	0	2.34	0.16
12	2	1	7.09	6.66
12	2	2	21.56	20.70
12	2	3	14.73	13.93
12	2	4	5.55	5.23
12	2	5	7.15	6.92
12	2	6	8.56	8.28
12	2	7	8.44	8.05
13	2	0	7.39	7.80
13	2	1	11.46	11.64
13	2	2	2.71	1.43
13	2	3	10.84	10.16
13	2	4	9.30	8.85
13	2	5	7.64	7.53
13	2	6	2.22	1.70
14	2	0	7.39	7.33
14	2	1	14.60	14.03
14	2	2	10.91	10.11
14	2	3	13.12	12.89
14	2	4	6.35	6.33
15	2	0	3.27	1.61
15	2	1	5.42	6.24
3	3	2	49.78	50.24
3	3	6	37.34	36.88
3	3	8	50.09	48.75
4	3	0	15.40	15.10
4	3	2	14.73	14.98
4	3	3	63.34	65.69
4	3	4	7.70	7.77
4	3	5	88.11	88.92
4	3	6	16.88	16.06
4	3	7	26.68	27.27
4	3	8	8.63	8.50
4	3	9	45.29	43.46
4	3	10	4.62	6.47
4	3	11	3.33	3.78
5	3	0	66.79	71.20
5	3	1	39.12	39.98
5	3	2	18.05	18.44
5	3	3	17.37	16.26
5	3	4	51.26	51.38
5	3	5	17.87	19.20
5	3	6	6.22	6.24
5	3	7	18.18	18.07
5	3	8	21.75	20.77
5	3	9	4.44	4.31
5	3	10	3.82	5.73
5	3	11	1.97	2.47
6	3	0	40.97	40.88
6	3	1	7.39	9.05
6	3	2	12.82	11.36
6	3	3	3.14	2.66
6	3	4	20.02	17.48
6	3	5	10.04	10.01
6	3	6	22.06	20.94
6	3	7	4.37	4.22
6	3	8	13.92	11.70
6	3	9	2.46	2.27
6	3	10	7.33	7.60
7	3	0	17.07	17.88
7	3	1	39.93	42.68
7	3	2	23.54	22.86
7	3	3	35.92	37.40
7	3	4	13.74	14.23
7	3	5	33.39	32.16
7	3	6	13.12	13.90
7	3	7	14.54	13.13
7	3	8	14.36	13.42
7	3	9	10.23	10.61
7	3	10	3.02	3.67
8	3	0	9.73	10.15
8	3	1	20.76	20.70
8	3	2	44.05	43.90
8	3	3	19.10	18.72
8	3	4	22.37	22.18
8	3	5	12.45	10.88
8	3	6	33.39	31.47
8	3	7	14.60	14.00
8	3	8	12.51	11.65
8	3	9	5.73	6.84
9	3	0	28.53	28.74
9	3	1	16.94	17.68
9	3	2	22.61	23.50
9	3	3	21.63	22.45
9	3	4	22.49	23.54
9	3	5	2.71	3.21
9	3	6	8.19	7.21
9	3	7	9.73	10.72
9	3	8	5.24	5.01
9	3	9	2.16	2.88
10	3	0	10.54	9.88
10	3	1	19.90	19.75
10	3	2	4.93	0.74
10	3	3	17.68	15.81
10	3	4	5.30	4.57
10	3	5	21.26	19.16
10	3	6	7.21	7.07
10	3	7	6.41	7.46
10	3	8	2.90	3.28
11	3	0	9.92	9.80
11	3	1	11.64	10.20
11	3	2	3.33	0.74
11	3	3	11.03	9.23
11	3	4	13.19	12.97
11	3	5	8.63	8.59
11	3	6	3.02	2.03
11	3	7	8.19	9.10
11	3	8	6.10	6.79
12	3	0	14.17	14.47
12	3	1	6.22	7.14
12	3	2	14.11	13.70
12	3	3	5.67	4.96
12	3	4	13.92	13.26
12	3	5	6.47	6.90
12	3	6	4.50	4.14
12	3	7	3.08	3.02
13	3	0	9.24	8.22
13	3	1	10.66	11.50
13	3	2	5.79	5.17
13	3	3	9.98	10.52
13	3	4	9.06	8.32
13	3	5	5.61	5.64
14	3	0	6.47	5.30
14	3	1	5.73	5.89
14	3	2	10.66	11.36
14	3	3	8.01	7.64
14	3	4	7.09	6.69
15	3	0	3.27	1.98
4	4	2	51.08	49.06
4	4	4	93.96	93.56
4	4	6	34.20	32.35
4	4	8	37.58	35.94
4	4	10	12.01	12.47
5	4	0	7.33	7.42
5	4	1	52.00	53.55
5	4	2	16.27	14.66
5	4	3	53.66	54.17
5	4	4	5.73	5.29
5	4	5	31.42	30.88
5	4	6	11.15	11.79
5	4	7	38.63	35.50
5	4	8	13.00	11.61
5	4	9	10.29	9.74
5	4	10	* 1.48	0.54
6	4	0	* 1.48	2.73
6	4	1	47.13	49.59
6	4	2	39.49	41.47
6	4	3	23.66	23.34
6	4	4	11.64	9.57
6	4	5	28.10	27.60
6	4	6	32.65	32.30
6	4	7	11.34	10.68
6	4	8	8.26	7.04
6	4	9	12.14	12.63
6	4	10	6.28	7.11
7	4	0	17.07	17.41
7	4	1	15.90	14.71
7	4	2	42.27	43.00
7	4	3	22.80	22.50
7	4	4	26.12	25.25
7	4	5	13.00	11.29
7	4	6	24.15	22.40
7	4	7	5.91	6.55
7	4	8	7.39	8.20
7	4	9	5.18	5.80
7	4	10	11.77	13.01
8	4	0	8.44	7.06
8	4	1	39.43	40.23
8	4	2	2.53	2.37
8	4	3	31.24	29.06
8	4	4	6.16	5.13
8	4	5	13.86	14.10
8	4	6	8.44	7.31
8	4	7	22.37	20.65
8	4	8	4.13	4.90
8	4	9	6.04	6.72
9	4	0	2.65	0.01
9	4	1	20.58	20.86
9	4	2	23.47	23.24
9	4	3	6.10	6.16
9	4	4	9.61	10.07
9	4	5	18.79	20.14
9	4	6	13.19	12.42
9	4	7	4.56	5.09
9	4	8	5.55	6.30
9	4	9	8.38	8.90
10	4	0	29.39	28.59
10	4	1	11.21	11.00
10	4	2	23.17	23.92
10	4	3	5.98	5.05
10	4	4	24.83	24.68
10	4	5	6.04	4.86
10	4	6	10.97	10.34
10	4	7	5.18	6.94
10	4	8	9.43	10.41
11	4	0	3.88	2.37
11	4	1	16.45	17.42
11	4	2	15.03	17.22
11	4	3	15.40	17.06
11	4	4	2.22	2.80
11	4	5	6.59	6.49
11	4	6	8.56	7.30
11	4	7	10.60	11.12
12	4	0	6.65	5.49
12	4	1	7.27	6.26
12	4	2	11.46	11.56
12	4	3	8.87	8.50
12	4	4	2.59	1.96
12	4	5	7.09	7.10
12	4	6	9.55	9.99
13	4	0	12.88	12.44
13	4	1	6.10	5.08
13	4	2	4.81	5.26
13	4	3	5.73	5.93
13	4	4	8.56	8.10
13	4	5	4.87	5.08
14	4	0	11.83	12.15
14	4	1	7.39	7.24
14	4	2	5.48	4.34
14	4	3	7.95	7.96
5	5	0	18.24	17.10
5	5	2	94.33	97.60
5	5	4	22.61	21.55
5	5	6	34.50	33.72
5	5	8	23.10	21.84
5	5	10	9.86	11.86
6	5	0	32.65	33.10
6	5	1	42.76	43.67
6	5	2	14.23	13.98
6	5	3	37.65	37.16
6	5	4	3.39	2.56
6	5	5	30.44	28.75
6	5	6	9.24	9.26
6	5	7	27.05	26.25
6	5	8	2.59	2.43
6	5	9	15.16	14.26
6	5	10	4.74	5.49
7	5	0	31.18	32.65
7	5	1	24.03	25.78
7	5	2	30.87	31.62
7	5	3	26.31	26.30
7	5	4	25.82	26.55
7	5	5	20.83	20.83
7	5	6	11.89	10.83
7	5	7	21.19	19.89
7	5	8	9.80	9.46
7	5	9	4.62	5.79
8	5	0	4.25	2.43
8	5	1	13.00	12.60
8	5	2	27.23	26.87
8	5	3	19.28	18.00
8	5	4	11.40	9.15
8	5	5	12.82	12.76
8	5	6	21.07	20.06
8	5	7	10.54	9.23
8	5	8	9.12	8.27
8	5	9	3.27	3.82
9	5	0	29.27	29.93
9	5	1	21.63	22.65
9	5	2	16.57	16.58
9	5	3	19.53	17.94
9	5	4	8.81	7.22
9	5	5	4.07	3.77
9	5	6	8.75	8.65
9	5	7	8.44	7.09
9	5	8	7.27	7.62
10	5	0	20.39	20.42
10	5	1	15.03	15.96
10	5	2	11.46	11.60
10	5	3	22.61	22.59
10	5	4	25.94	25.22
10	5	5	18.42	17.45
10	5	6	8.07	7.76
10	5	7	16.27	16.73
10	5	8	5.18	7.58
11	5	0	5.61	8.30
11	5	1	8.87	8.44
11	5	2	26.31	26.94
11	5	3	17.87	17.58
11	5	4	10.91	9.55
11	5	5	7.76	7.33
11	5	6	11.21	11.04
11	5	7	8.13	8.81
12	5	0	7.09	7.67
12	5	1	11.64	11.28
12	5	2	13.80	12.66
12	5	3	21.13	20.63
12	5	4	2.71	2.03
12	5	5	4.81	6.31
12	5	6	5.98	6.44
13	5	0	4.19	1.81
13	5	1	6.90	7.31
13	5	2	12.45	11.58
13	5	3	3.33	1.00
13	5	4	4.25	3.64
14	5	0	4.62	2.56
14	5	1	5.48	4.61
14	5	2	5.98	5.87
6	6	0	64.88	68.53
6	6	2	33.09	33.30
6	6	4	35.37	35.02
6	6	6	32.04	30.11
6	6	8	16.05	18.34
7	6	0	5.05	5.94
7	6	1	23.60	24.07
7	6	2	14.79	14.48
7	6	3	19.90	18.27
7	6	4	3.57	2.13
7	6	5	28.65	27.96
7	6	6	6.10	6.30
7	6	7	6.04	4.71
7	6	8	4.31	4.39
7	6	9	12.94	13.12
8	6	0	25.38	24.17
8	6	1	9.37	7.68
8	6	2	8.44	7.82
8	6	3	20.83	19.97
8	6	4	19.72	19.03
8	6	5	13.49	12.09
8	6	6	5.42	4.39
8	6	7	9.30	8.33
8	6	8	8.38	7.90
8	6	9	2.53	2.84
9	6	0	31.55	31.88
9	6	1	5.48	5.39
9	6	2	8.69	8.40
9	6	3	5.67	5.86
9	6	4	29.14	27.77
9	6	5	3.20	2.74
9	6	6	3.02	3.50
9	6	7	1.54	1.72
9	6	8	11.52	12.50
10	6	0	11.09	10.81
10	6	1	22.18	21.83
10	6	2	13.37	12.33
10	6	3	19.22	18.91
10	6	4	13.12	12.30
10	6	5	17.01	17.37
10	6	6	6.90	7.06
10	6	7	7.39	7.17
11	6	0	21.32	21.20
11	6	1	12.69	12.65
11	6	2	19.22	19.32
11	6	3	17.68	17.33
11	6	4	13.25	11.51
11	6	5	6.84	6.52
11	6	6	9.00	8.69
12	6	0	3.39	4.04
12	6	1	6.47	6.03
12	6	2	10.84	10.40
12	6	3	8.07	7.55
12	6	4	2.53	0.99
12	6	5	4.62	4.64
13	6	0	3.57	3.97
13	6	1	6.22	5.29
13	6	2	3.27	2.23
13	6	3	2.71	2.02
13	6	4	3.76	3.85
14	6	0	2.34	0.52
7	7	0	61.30	64.00
7	7	2	22.18	23.35
7	7	4	30.07	29.61
7	7	6	9.37	8.88
7	7	8	19.04	20.56
8	7	0	23.78	23.98
8	7	1	18.61	18.71
8	7	2	9.43	8.74
8	7	3	30.01	30.48
8	7	4	8.75	7.54
8	7	5	15.83	14.72
8	7	6	3.08	3.09
8	7	7	18.98	18.41
8	7	8	5.24	5.15
9	7	0	3.64	3.78
9	7	1	26.99	27.85
9	7	2	19.72	20.61
9	7	3	9.61	10.07
9	7	4	4.37	3.71
9	7	5	21.44	20.63
9	7	6	5.18	6.87
9	7	7	6.84	6.97
10	7	0	28.96	28.50
10	7	1	8.50	9.00
10	7	2	6.47	7.41
10	7	3	9.30	8.78
10	7	4	20.70	19.14
10	7	5	3.27	3.25
10	7	6	10.35	10.38
10	7	7	2.16	1.42
11	7	0	3.33	2.29
11	7	1	10.78	9.85
11	7	2	3.88	3.26
11	7	3	12.69	11.83
11	7	4	5.42	5.22
11	7	5	11.95	11.76
11	7	6	2.59	1.43
12	7	0	3.39	0.76
12	7	1	3.14	2.18
12	7	2	8.38	8.82
12	7	3	3.39	1.57
12	7	4	3.02	2.28
13	7	0	2.65	1.23
13	7	1	4.31	4.53
13	7	2	2.90	3.44
13	7	3	2.71	2.65
8	8	0	8.26	5.08
8	8	2	31.73	30.56
8	8	4	19.04	17.65
8	8	6	21.07	20.79
8	8	8	7.76	7.83
9	8	0	9.00	8.17
9	8	1	20.58	21.18
9	8	2	2.96	2.74
9	8	3	19.59	18.73
9	8	4	10.54	10.09
9	8	5	9.86	9.08
9	8	6	4.07	3.73
9	8	7	12.38	13.56
10	8	0	6.47	3.94
10	8	1	13.92	13.74
10	8	2	12.20	11.19
10	8	3	9.80	8.46
10	8	4	4.74	3.52
10	8	5	10.17	10.16
10	8	6	7.58	7.61
11	8	0	5.42	4.68
11	8	1	5.36	4.76
11	8	2	7.76	6.51
11	8	3	4.19	3.99
11	8	4	3.14	1.30
11	8	5	4.37	3.36
12	8	0	2.28	1.60
12	8	1	4.99	5.09
12	8	2	3.20	2.81
12	8	3	5.18	6.03
13	8	0	8.13	10.10
9	9	0	9.92	9.30
9	9	2	21.56	20.75
9	9	4	* 1.60	1.07
9	9	6	10.35	11.22
10	9	0	2.71	2.52
10	9	1	6.96	5.86
10	9	2	2.34	1.83
10	9	3	3.70	2.68
10	9	4	1.79	0.83
10	9	5	5.24	4.83
11	9	0	2.59	3.04
11	9	1	4.93	5.28
11	9	2	2.83	1.81
11	9	3	5.36	5.05
11	9	4	2.65	2.63
12	9	0	10.04	10.99
12	9	1	2.40	0.17
12	9	2	2.22	1.41
10	10	0	5.48	3.99
10	10	2	2.90	2.18
10	10	4	7.64	7.76
11	10	0	4.50	3.27
11	10	1	3.64	3.44
11	10	2	1.85	1.24

[a] The asterisk denotes reflections which were unobserved. The value of F_o for these reflections is the minimum value observable.

lies approximately in the plane of the copper atom and its two adjacent chlorine atoms in a direction giving a distorted trigonal configuration about copper. The plane (C_4, C_5, C_6, C_1) which contains the coordinated double bond makes an angle of 109.1° (180 − 70.9) with the plane (Cu, Cl, Cl′, C_5, C_6); see Fig. 2. For comparison, the comparable angle in COT-CuCl is 109.2°. The reason why the angle is not closer to 90° in NBD-CuCl may be because the hydrogen atom, H_7, attached to the bridgehead carbon atom, C_7, is only 2.18 Å. away from the copper atom. The covalent radii sum (1.17 + 0.30 = 1.47 Å.) indicates that the hydrogen and copper atoms are less than a normal van der Waals distance apart. Thus, repulsion of the hydrogen atom by the copper atom may cause the larger angle. In the NBD-CuCl case the second double bond is not near any copper atom. In an additional comparison with the COT-CuCl structure, the distorted trigonal arrangement of ligands about copper is very similar. The Cl–Cu–Cl chain angle is 106.0° in COT-CuCl; it is 104.4° in NBD-CuCl. The angles between chlorine, copper, and the C=C bond center are 123.1 and 130.1° in COT-CuCl; in NBD-CuCl they are 124.7 and 130.9°. The similarity of the latter two angles is surprising. One might have expected the vector from the copper atom to the double bond center to be symmetrically located, with both angles equal to $(360 - 104.4)/2 = 127.8°$. Packing of the organic portion of the complex might easily cause the asymmetry, but it is unusual to find the asymmetry the same in two different packing arrangements of the complexes.

In the COT-CuCl complex, two double bonds were located in the directions roughly perpendicular to the (Cu, Cl, Cl′) plane at the apices of a distorted trigonal bipyramid. The ligands were far enough away that their participation in bonding is not certain. In the NBD-CuCl complex, a chlorine atom at 3.091 Å. lies in one apical direction. Nothing exists in the other apical direction except H_7.

In another point of similarity between the COT- and NBD-CuCl complexes, the deviations of the atoms of the coordinated double bond from the (Cu, Cl, Cl′, C=C) plane are similar. In COT-CuCl they are −0.06 and 0.10 Å.; in NBD-CuCl they are −0.13 and 0.14 Å. Both deviations are in the direction of a tetrahedral distortion, but this distortion is very small.

The norbornadiene molecule itself is compared with the dimensions of the free molecule as determined from electron diffraction data[8] and to the dimensions in the NBD-$PdCl_2$ complex[9] in Table V. The bond distances and angles which would be equivalent in the free uncomplexed molecule have been averaged for comparison with the electron diffraction data. In most cases, the apparent differences due to complexing are not significant. As can be seen from the tabular comparison, the complexed norbornadiene molecular dimensions are in reasonable agreement with each other and with Schomaker's values. The reliability of Schomaker's values is unknown, so statements of significant agreement or disagreement with those values are not possible. Assuming that free norbornadiene should have double bond distances of 1.34 Å. and single bond distances of 1.54 Å., one could not claim that any bond distance in NBD-CuCl, except C_4–C_3, is significantly different, using 3.3 × the standard deviation as the criterion. Even as an internal check, the coordinated double bond C_5=C_6 is not significantly longer than the noncoordinated bond.

In the companion structure determination of COT-CuCl, the C=C bond length was found to be lengthened significantly. The particular value found, 1.392 Å., is probably longer than the true value. Based on the shift in the double bond frequencies in the infrared spectrum (about 100 cm.$^{-1}$ toward lower frequencies in both COT-CuCl and NBD-CuCl) a bond length corresponding to the average of the two distances found, $(1.392 + 1.345)/2 = 1.369$ Å., would be more compatible. This bond length compares reasonably well with the value 1.366 Å. found for the C=C bond in dichloro(norbornadiene)palladium(II),[2] in which the change in frequency is about 150 cm.$^{-1}$.

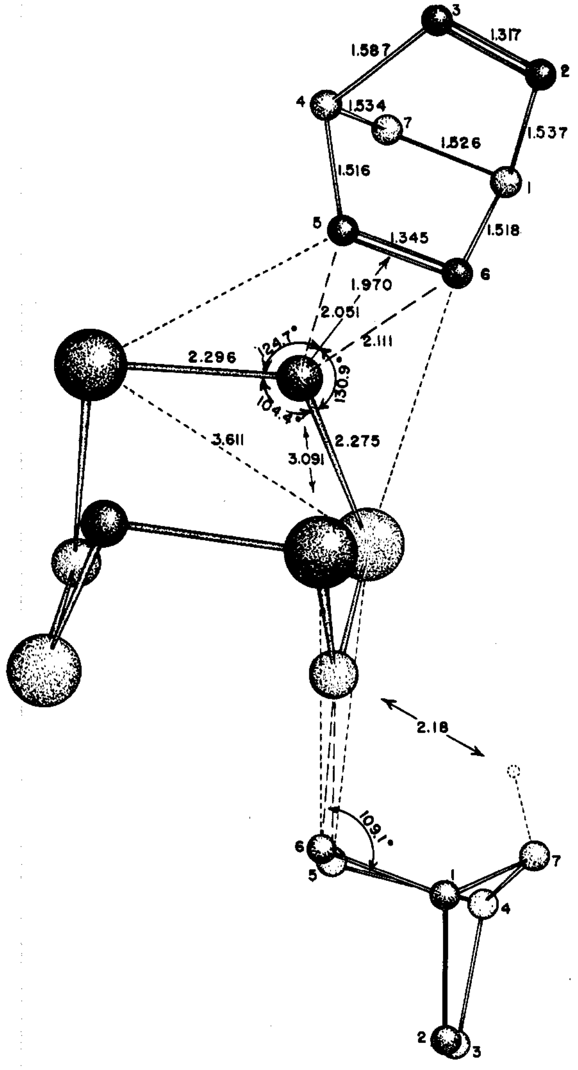


Fig. 2.—View of one tetramer of $[C_7H_8CuCl]_4$. Two C_7H_8 molecules have been omitted for clarity. The tetramer corresponds to the one at the lower left in Fig. 1.

The structure which has been found from the crystallographic studies is compatible with the infrared spectrum and the structure proposed for the complex by Schrauzer and Eichler.[10] They observed a band at 1547 cm.$^{-1}$ in the free olefin which they attributed to the double bond stretching frequency. In the norbornadienecopper(I) chloride complex, bands were observed at 1563 and 1473 cm.$^{-1}$ and attributed to an uncoordinated and a coordinated double bond; the copper atom was proposed to be in an *exo* configuration to the coordinated double bond. Spectral measure-

---

[8] C. F. Wilcox, Jr., S. Winstein, and W. H. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960). The authors refer to a private communication from V. Schomaker.

[9] G. F. Richards, Ph.D. Dissertation, University of Iowa, Feb., 1964.

[10] G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 260 (1962).

Table V

Comparison of Norbornadiene Dimensions with Other Work

Distance, Å.	NBD-CuCl	Av.	NBD-PdCl$_2$[9]	Av.	Free NBD[8]
C_1—C_2	1.537 (0.010)	1.539	1.554 (0.006)	1.553	1.522
C_4—C_3	1.587 (0.011)				
C_1—C_6	1.518 (0.011)		1.552 (0.006)		
C_4—C_5	1.516 (0.011)				
C_1—C_7	1.526 (0.012)	1.530	1.547 (0.006)	1.547	1.558
C_4—C_7	1.534 (0.011)				
C_2=C_3[a]	1.317 (0.011)	1.331	1.366 (0.010)	1.366	1.333[a]
C_5=C_6	1.345 (0.011)		1.366 (0.010)		
Angle, deg.					
C_1–C_2–C_3	108.6 (0.8)	106.9	106.9 (0.4)		
C_2–C_3–C_4	105.3 (0.4)			107.0	109.1
C_4–C_5–C_6	105.9 (0.3)		107.0 (0.4)		
C_5–C_6–C_1	107.8 (0.6)				
C_2–C_1–C_7	98.7 (0.6)	99.4	99.5 (0.4)		
C_3–C_4–C_7	97.6 (0.4)			100.0	96.4
C_6–C_1–C_7	100.2 (0.6)		100.4 (0.4)		
C_5–C_4–C_7	100.9 (0.5)				
C_2–C_1–C_6	102.7 (0.7)	103.4	100.3 (0.3)	100.3	102.2
C_3–C_4–C_5	104.1 (0.4)				

[a] Not coordinated.

ments in this laboratory gave bands at 1460 and 1560 cm.$^{-1}$ for the NBD-CuCl complex.

The description of the structure of the complex of copper(I) chloride with 2-butyne[5] appears to be very similar to that of NBD-CuCl. An eight-membered ring with $\bar{4}$ symmetry was found with alternating copper and chlorine atoms. The carbon atoms of the acetylenic group lie in the same plane as the copper atom and the two adjacent chlorine atoms. Sufficient details of this structure are not available to make further comparisons.

The structure of NBD-CuCl may be compared with two other copper(I) complexes which show similarities in configuration as well as a trend toward tetrahedral geometry about the copper atom. In the structure of potassium dicyanocuprate(I), $KCu(CN)_2$,[11] the copper atom is surrounded by three ligands: two carbon atoms from cyanide ions at distances of 1.915 and 1.922 Å. and one nitrogen from a third cyanide ion at 2.052 Å. The angles between these groups are 134.2, 112.3, and 107.3°. The sum, 353.8°, indicates that the ligand groups are not completely coplanar, but deviate in the direction that atoms would be if they occupied three of the four corners of a tetrahedron about the copper. There appear to be no groups in apical positions for a bipyramidal arrangement or a tetrahedral arrangement.

In the structure of azomethanecopper(I) chloride[12] the copper and chlorine atoms form a double alternating chain. The copper atom in one chain has as ligands two chlorine atoms in the chain at 2.319 and 2.368 Å., and the third ligand is a nitrogen atom in the azomethane molecule at 1.993 Å. The angles between these ligands are 109.2 (the chain angle), 107, and 132.1°. Again the sum (348.3°) indicates further deviation from planarity. In this structure the fourth ligand is a chlorine atom from the second chain of the double strand at a distance of 2.547 Å. In this case, the configuration about the copper could equally as well be called a distorted tetrahedral configuration as a distorted trigonal planar arrangement.

In the structure of 1,5-cyclooctadienecopper(I) chloride a slightly distorted tetrahedral configuration was reported for the arrangement about the copper.[13] In the structure of K_2CuCl_3[14] a more nearly symmetrical tetrahedral coordination about copper(I) exists, and in copper(I) chloride, which has the zinc sulfide (zinc blende) structure type, the coordination is perfectly tetrahedral. Thus, it appears that coordination from the extremes of perfectly tetrahedral to trigonal planar (though not symmetrical trigonal planar) arrangements occur with examples in the intermediate configurations. A black and white categorization of the hybridization of the orbitals of copper as either sp^3 or sp^2, etc., is thus not possible. In all the examples with the exception of copper(I) chloride the ligands about copper are not equivalent, so that symmetry requirements do not make the idealized hybrid orbitals mandatory.

In the olefin, acetylene, and azomethane complexes, filled d orbitals of copper(I) may interact with the vacant antibonding π-orbitals of the carbon or nitrogen atoms. This type of interaction would drain away some electron density from the region where the orbitals from the copper are directed toward the chlorine atoms. These orbitals could then adopt more p-character. The orbitals directed toward the olefin could then have

---

(11) D. T. Cromer, *J. Phys. Chem.*, **61**, 1388 (1957).

(12) J. D. Brown and J. D. Dunitz, *Acta Cryst.*, **13**, 28 (1960).

(13) J. H. van den Hende and W. C. Baird, *J. Am. Chem. Soc.*, **85**, 1009 (1963).

(14) C. Brink and C. H. MacGillavary, *Acta Cryst.*, **2**, 158 (1949).

more s-character, which should be more suitable for better overlap with the bonding π-orbital of the olefin.

Acknowledgment.—The authors wish to express their thanks to Prof. J. Hayes of the Geology Department, University of Iowa, for the use of the single crystal orienter, and to Miss Carol Valley and Mr. William Duax, who assisted in the intensity measurements. Part of this work was supported by grant DA-ARO(D)-31-124-G26 from the Army Research Office (Durham). A further grant from the Petroleum Research Fund enabled H. L. H. to obtain the intensity data which led to the solution of the structure.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND ORGANIC CHEMISTRY,
UNIVERSITY OF SYDNEY, SYDNEY, AUSTRALIA

Multidentate Ligand Equilibria. II. Complex Formation between Iron(II) and Some Hydrazones of Pyridine-2-aldehyde

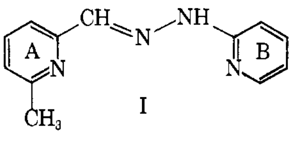
BY ROWLAND W. GREEN, PETER S. HALLMAN,[1] AND FRANCIS LIONS

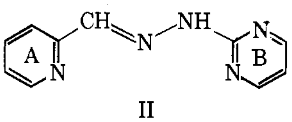
Received June 5, 1964

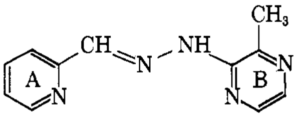
Formation and deprotonation equilibria have been studied for iron(II) complexes of the three tridentate chelates, 6-methylpyridine-2-aldehyde-2′-pyridylhydrazone, pyridine-2-aldehyde-2′-pyrimidylhydrazone, and pyridine-2-aldehyde-3′-methyl-2′-pyrazinylhydrazone. The respective measured stability constants were log β_1: 6.3, 6.0, 7.9; log β_2: 12.6, 14.0, 15.6; and the acid dissociation constants of the respective cationic bis complexes were pK_1: 6.28, 4.56, 4.12; pK_2: 7.95, 6.09, 5.61. A method is described for calculating stability constants and deprotonation constants from pH titration data when the buffer regions of the two equilibria overlap.

Introduction

A class of multidentate ligands has been reported[2] in which each ligand is capable of forming cationic and neutral complexes with bivalent transition metal ions. Addition of alkali to the cationic complexes deprotonates imino groups not involved in coordination to the metal, forming stable uncharged species. The previous paper of this series[3] discussed the equilibria of metal complex formation and deprotonation for the tridentate ligand pyridine-2-aldehyde-2′-pyridylhydrazone (PAPHY). Three related ligands, 6-methylpyridine-2-aldehyde-2′-pyridylhydrazone (I), pyridine-2-aldehyde-2′-pyrimidylhydrazone (II), and pyridine-2-aldehyde-3′-methyl-2′-pyrazinylhydrazone (III) have now been studied in coordination with iron(II).


I


II


III

Experimental

The three ligands were taken from the same specimens prepared by Geldard and Lions.[2] Experimental methods of studying the equilibria have also been described previously.[3]

Results

Acid Dissociation Equilibria of the Free Ligands.—Solutions of each ligand in perchloric acid (4 moles), alone and in the presence of iron(II) (0.5 mole), were titrated with sodium hydroxide solution (10^{-2} *M*). Detailed experimental results are given in the Appendix.[4] In discussing the titrations, in view of the potentially acidic character of the NH group, we shall refer to species I–III as HL. The equilibrium constants are defined in Table I, and for purposes of computation we further define three quantities, L_T, the total ligand concentration in all its forms, b, the number of moles alkali added in the titration, and

$$g = (\Sigma i[H_iL] + \Sigma j[MH_jL_m])/L_T \qquad (1)$$

easily calculable from the titration data. This last quantity, the average number of protons attached to L^-, falls below 1 only when deprotonation of the imino group occurs.

In spite of the presence of four nitrogen atoms in ligand I, its g values were found not to exceed 2.9 even at the beginning of the titration, and there was no spectrophotometric evidence for heavier protonation at lower pH. It could therefore be treated as a diacid base and the first two dissociation constants of the conjugate acid, H_3L^{2+}, could be calculated from the titration in the usual way, with small activity corrections estimated from the Güntelberg formula.[5] They appear in Table I as pK_1 and pK_2.

---

[1] Petroleum Research Fund Fellow, Sydney University.

[2] J. F. Geldard and F. Lions, *Inorg. Chem.*, **2**, 270 (1963).

[3] R. W. Green, P. S. Hallman, and F. Lions, *ibid.*, **3**, 376 (1964).

[4] For Appendix, order Document No. 8059 from the Chief, Photoduplication Service, Library of Congress, Washington 25, D. C., Auxiliary Publications Project, remitting $1.25 for microfilm (35-mm.) or $1.25 for photocopies.

[5] E. Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).