is then partially converted to the tetrakis(pyridine)-platinum(II) salt upon continual refluxing in the presence of excess pyridine.

Analysis of the crude products and extraction procedures with methylene chloride indicated an approximate mole ratio of 2 moles of platinum-olefin complex to 1 mole of cycloheptatrienylium compound were formed when cycloheptatriene reacted with platinum-(IV) bromide, bromoplatinic acid, or chloroplatinic acid. The equations below represent the stoichiometry of these reactions.

$$4C_7H_8 + 3PtBr_4 \longrightarrow (C_7H_7)_2PtBr_6 + 2C_7H_8PtBr_2 + 2HBr$$

$$4C_7H_8 + 3H_2PtX_6 \longrightarrow (C_7H_7)_2PtX_6 + 2C_7H_8PtX_2 + 8HX$$

The reactions of cycloheptatriene with the platinum-(IV) compounds in boiling acetic acid occur rapidly, and the product isolated about 1 min. after addition of the olefin did not differ materially in composition or quantity from a similar product separated 3 hr. after the addition of the olefin to a solution of the platinum(IV) compound.

Although a clear insight into the mechanism of the reaction between platinum(IV) and 1,3,5-cycloheptatriene is not possible from our limited study of the system, it appears that the initial step involves the abstraction of hydride ion from the olefin and the concomitant reduction of platinum from a +4 to a +2 oxidation state. The subsequent coordination of the platinous ion to the olefin and the simultaneous formation of the cycloheptatrienylium compound occur with extreme rapidity.

Recently Chatt and Guy reported[19] an unsuccessful attempt to prepare a triphenylcyclopropenium ion derivative in which this ion was bonded covalently to platinum. In view of the known ability of cycloheptatriene to undergo protonation[20] and hydride ion abstraction reactions[21] while coordinated in certain metal carbonyl complexes, similar reactions were examined as possible methods for obtaining carbonium ion species attached to platinum.

The reaction of dichloro(cycloheptatriene)platinum-(II) with tritylium tetrafluoroborate generated *in situ*[22] or in a dichloromethane medium[23] did not produce the desired cycloheptatrienylium ion species *via* hydride ion abstraction, but instead a nearly quantitative recovery of starting material was realized. The attempted protonation of dichloro(cycloheptatriene)platinum(II) with tetrafluoroboric acid in an acetic anhydride medium also yielded starting material upon purification of the reaction mixture.

In summary, neither the present investigation nor previous reports has yielded any evidence for carbonium species bonded in a coordinate fashion to a platinum atom.

Acknowledgment.—We wish to acknowledge the support of the Army Research Office (Durham), Grant DA-ARO(D)-31-124-G26.

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Metal-Olefin Compounds. VI. The Crystal Structure of Catena-μ-chloro-(cyclooctatetraene)copper(I)

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Received April 27, 1964

A single crystal, three-dimensional X-ray study of catena-μ-chloro-(cyclooctatetraene)copper(I) has been carried out. The structure consists of continuous chains formed by the copper and chlorine atoms extending through the crystal in the *a* direction with one olefinic bond closely bound to each copper atom. The carbon atoms of the bonded olefinic group are approximately coplanar with the copper and adjacent chlorine atoms of the chain, and the coordination about the copper(I) may be described as a distorted trigonal arrangement. The bond distances and the bond angles associated with the closely bound atoms are: Cu-Cl, 2.288 ± 0.002 Å., 2.284 ± 0.002 Å.; Cl-Cu-Cl, 106.4 ± 0.1°; Cl-Cu-(C_1-C_2 center), 123.1 ± 0.2°, 130.1 ± 0.2°; Cu-C_1, 2.073 ± 0.010 Å.; Cu-C_2, 2.097 ± 0.007 Å. A variety of weighting schemes was used in the least-squares data refinement procedures to test the sensitivity of the resulting interatomic distances to the weighting scheme and thus provide a test for systematic errors.

Introduction

By means of a new method of preparation of copper-(I)-olefin compounds,[1] a number of well-crystallized complexes have recently become available for structural studies. A preliminary report has been made on the structure of one of these compounds, di-μ-chloro-bis-(1,5-cyclooctadiene)dicopper(I),[2] in which the co-

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ordination about each copper atom was found to be approximately tetrahedral. The structure of the 1:1 complex formed between cyclooctatetraene and copper(I) chloride, which is reported below, is different, since the coordination about copper is triangular.

Experimental

Crystals.—The crystals of C_8H_8CuCl were prepared by previously described procedures,[1] and two crystals were used in acquiring the data. Crystal number one was ground to a near perfect cylinder, 0.2 mm. in diameter by 0.5 mm. long (μ = 65/cm.; μR = 0.65). The second crystal was rectangular, 0.25 × 0.125 × 0.5 mm. (on equivalent volume basis, μR = 0.78). The crystals were coated with a clear plastic coating to retard decomposition.

X-Ray Data.—All data were obtained using the multiple film (three films) equi-inclination Weissenberg technique at 80°K. (Cu Kα radiation) by means of a specially designed cryostat.[3] The first crystal was used to record ($0kl$) to ($3kl$); the second crystal was used to obtain ($h0l$) to ($h6l$). Three-hour exposure times were adequate to obtain excellent diffraction patterns over the full angular scattering range. The intensities were estimated visually by comparison with calibrated intensity strips made from the crystals at room temperature. Intensity estimates from duplicate reflections, multiple films, and by independent estimators resulted in as many as a dozen observations for each reflection. The standard deviation in the mean value of these estimates was used as an estimate of $s(I)$ later used in the weighting scheme in the least-squares refinement. Independent scale factors for each layer were used until the refinement had converged to an R value of 0.12, after which duplicate reflection intensities were averaged. At a later stage in the refinement a common scale was adopted for all reflections. Absorption corrections were made by a computer program combined with the Lorentz and polarization corrections. Reciprocals of the absorption correction values of Bond[4] were fit to a simple polynomial function in $\sin^2 \theta$ for given values of μR.

The orthorhombic unit cell dimensions are: at room temperature, a = 6.858 ± 0.010 Å., b = 12.107 ± 0.001 Å., c = 18.040 ± 0.004 Å.; at 80°K., a = 6.806 ± 0.0009 Å., b = 11.920 ± 0.0008 Å., c = 17.925 ± 0.002 Å. All the cell dimensions, except a at room temperature, were obtained from back-reflection Weissenberg photographs using an analytical extrapolation technique to eliminate systematic errors. The calculated density for eight formula weights of C_8H_8CuCl at room temperature is 1.802 g./cm.^{3}; the observed value is 1.763 g./cm.^{3}. Systematic absences, ($0kl$) if k is odd, ($h0l$) if l is odd, and ($hk0$) if h is odd, lead to the unique space group, Pbca.

Determination of Structure

Copper and chlorine positions were determined from a three-dimensional Patterson. These positions corresponded to an infinite polymer chain of –Cu–Cl– which extended along the a axis. Using the positions of these two atoms alone, an R value of 0.32 was obtained from all the data. A three-dimensional electron density map was then evaluated using 925 out of 1089 observable amplitudes. This map, in addition to the chlorine and copper peaks, contained many peaks which might correspond to carbon atoms. Peaks were selected which would correspond to a model of the structure in which the cyclooctatetraene was coordinated to the Cu atom in a roughly tetrahedral orientation. Carbon atoms were added to the calculation one at a time. If the addition of the carbon atom made the agreement worse or on a few least-squares cycles the associated temperature factor became large, the atom was discarded. Based on a number of carbon positions so located, a tetrahedral model was constructed and the remainder of the carbon positions determined from the model. With all the carbon atoms included, the agreement became worse; in fact, the more nearly the model approached the tetrahedral configuration, the poorer the agreement became. The attempt to fit a tetrahedral model was then dropped, and likely carbon atom positions, based on the appearance of peaks in the electron density map, were selected with no attempt at keeping the cyclooctatetraene molecule in a tetrahedral orientation about the copper atom. The arrangement included several of the carbon positions which had been found previously to improve the intensity agreement but did not correspond to the tetrahedral model. A few cycles of least-squares refinement using ($0kl$) data and coupled with the information from the electron density map gave an R value of 0.07 for this zone of data. The remaining x coordinates were then determined by fitting to a model of the cyclooctatetraene molecule, and the least-squares refinement based on all the data was begun. The R value at this stage was 0.15.

Least-Squares Refinement.—The initial least-squares refinement was performed using a program written for an LGP-30 computer. This program used unit weights, individual isotropic temperature parameters, the diagonal approximation, and independent scale factors for each layer of data. The program minimized $\Sigma||F_o| - |F_c||^2$. Successive iterations with this program reduced the discrepancy value, R, to 0.11. Further refinement was done with a different least-squares program written for an IBM 7070 computer. This program allows a wide variety of weighting schemes, individual or anisotropic temperature factors, and inverts the full least-squares matrix. Atom scattering factors are found by interpolation from the values listed in the International Tables of Crystallography, Vol. 3. The real part of the dispersion correction was made for the Cu and Cl atoms. The program minimizes $\Sigma w||F_o^2| - F_c^2|^2$. Reflections common to different layers were averaged and all data were put on a common scale before refinement with this program. Only an over-all scale constant was then allowed to vary. Different weighting schemes were used to test the sensitivity of the resulting interatomic distances to the weights used, thus providing a test for systematic errors. If errors are purely random, the parameters should be independent of the weighting scheme although the estimates of the errors in the parameters should not be. The weighting schemes used were: unit weights, minimizing $\Sigma(\Delta F)^2$; unit weights, minimizing $\Sigma(\Delta F^2)^2$; $w = I_{\max}^2/16I^2$ for I greater than $I_{\max}/4$, and $w = 16I^2/I_{\max}^2$ for values of I less than $I_{\max}/4$; $w = 1/s^2(I)$, where $s^2(I)$ had been obtained from the agreement of intensity estimates. After

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TABLE I

BOND LENGTHS IN C_8H_8CuCl

Bond	Bond dist., Å.	Std. dev. in bond dist., Å.
Cu–Cl	2.288	0.002
	2.284	0.002
C_1–C_2	1.392	0.013
C_2–C_3	1.441	0.012
C_3–C_4	1.378	0.012
C_4–C_5	1.504	0.012
C_5–C_6	1.325	0.012
C_6–C_7	1.493	0.011
C_7–C_8	1.373	0.011
C_8–C_1	1.463	0.013
Cu–C_1	2.073	0.010
Cu–C_2	2.097	0.007
Cu–C_3	2.978	
Cu–C_4	3.239	
Cu–C_5	2.755	
Cu–C_6	2.775	
Cu–C_7	3.241	
Cu–C_8	2.993	

TABLE II

ATOMIC PARAMETERS (Å.)

	x $s(x)$ $s(X)$	y $s(y)$ $s(Y)$	z $s(z)$ $s(Z)$	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} $s(B_{23})$
Cu	0.1830	0.0771	0.2083	0.00518	0.00133	0.00041	0.00008	−0.00010	0.00042
	0.0002	0.0001	0.00006	0.00025	0.00007	0.00003	0.00023	0.00018	0.00008
	0.0013	0.0012	0.0011						
Cl	0.8898	0.9834	0.2130	0.00452	0.00142	0.00054	0.00004	0.00020	−0.00038
	0.0003	0.00014	0.00011	0.00037	0.00011	0.00005	0.00035	0.00023	0.00013
	0.0020	0.0017	0.0019						
C_1	0.1240	0.2154	0.1419	1.49[a]					
	0.0016	0.0008	0.0005	0.16					
	0.011	0.010	0.010						
C_2	0.3063	0.2306	0.1756	0.46					
	0.0012	0.0006	0.0004	0.12					
	0.008	0.007	0.007						
C_3	0.4938	0.2188	0.1391	0.79					
	0.0014	0.0007	0.0005	0.13					
	0.010	0.008	0.008						
C_4	0.5638	0.1237	0.1044	0.89					
	0.0013	0.0007	0.0005	0.13					
	0.009	0.008	0.008						
C_5	0.4497	0.0158	0.1001	0.70					
	0.0014	0.0007	0.0004	0.13					
	0.009	0.008	0.008						
C_6	0.2785	0.0042	0.0658	0.69					
	0.0012	0.0006	0.0004	0.13					
	0.008	0.008	0.008						
C_7	0.1651	0.0951	0.0280	0.75					
	0.0013	0.0006	0.0004	0.13					
	0.009	0.007	0.008						
C_8	0.0957	0.1898	0.0628	0.95					
	0.0012	0.0007	0.0005	0.14					
	0.008	0.008	0.009						

	x	y	z	B
H_1	0.000	0.218	0.173	1.00
H_2	0.300	0.240	0.235	1.00
H_3	0.520	0.295	0.105	1.00
H_4	0.650	0.140	0.053	1.00
H_5	0.470	0.970	0.150	1.00
H_6	0.262	0.928	0.034	1.00
H_7	0.087	0.069	0.978	1.00
H_8	0.960	0.230	0.038	1.00

[a] In Å.^{2}.

a 7040 computer with a 32,768-word memory replaced the 7070 computer, anisotropic parameters for all atoms were refined and H atoms included at fixed positions. The final R obtained was 0.10. The bond lengths from these parameters are listed in Table I.

The interatomic distances obtained using the different weighting schemes did not differ significantly from one another. The weighting scheme with weights inversely proportional to the standard deviations of the means of the intensity estimates gave the lowest error terms for the parameters. Parameters and estimates of errors obtained from this weighting scheme are given in Table II. The calculated and observed structure factors based on these parameters are given in Table III.

Discussion of the Structure

The coordination about the Cu atom is shown in Fig. 1, and the packing arrangement in the unit cell is shown by projection onto (100) in Fig. 2. (The atom parameters on which the following discussion is based are given in Table II. Table IV gives pertinent angles and equations of planes based on this same set of parameters.) The Cu and Cl atoms form continuous chains running through the crystal in the a direction. The Cl–Cu–Cl angle in the chain is 106°. Only one of the double bonds in cyclooctatetraene ($C_1{=}C_2$) is closely bound to the Cu atom, and the atoms of this double bond lie in the same plane as the Cu and adjacent Cl atoms of the chain. The coordination about the Cu atoms may be described as a distorted trigonal planar one, since the remaining angles in the plane between the Cu–Cl vectors and the vector from Cu to the midpoint of the associated double bond are 123 and 130°.

TABLE III

CALCULATED AND OBSERVED STRUCTURE FACTORS FOR C_8H_8CuCl[a]

h	k	l	F_o	F_c
0	4	0	1109	1169
0	6	0	934-	762
0	8	0*	128-	92
0	10	0	955	936
0	12	0	794	789
0	14	0	797	758
0	0	4	427	482
0	0	6	349-	340
0	0	8	1112-	1179
0	0	10	1428	1566
0	0	12	1836-	1872
0	0	14	1486	1529
0	0	16	932-	921
0	0	18	315	236
0	0	20	383	317
0	0	22	670-	701
0	2	3	97-	83
0	2	5	408-	399
0	2	6	1001-	997
0	2	7	383-	373
0	2	8	753-	781
0	2	9	636	603
0	2	10	1637	1639
0	2	11	1005-	1057
0	2	12	1233-	1258
0	2	13	699	692
0	2	14	879	897
0	2	15	529-	481
0	2	16	835-	864
0	2	17	238	136
0	2	18	364	341
0	2	19	277	200
0	2	20	267	257
0	2	21	456-	420
0	2	22	690-	684
0	4	1	670-	687
0	4	2	519-	536
0	4	3	937	1015
0	4	4	369-	344
0	4	5	568-	602
0	4	6*	87-	43
0	4	7	252-	264
0	4	8	238-	209
0	4	9	845	833
0	4	10	296-	212
0	4	11	1136-	1235
0	4	12*	126	35
0	4	13	427	370
0	4	14	558	468
0	4	15	480-	413
0	4	16*	135-	15
0	4	17	291	195
0	4	18	233	206
0	4	19	291	289
0	4	20	165-	135
0	4	21	383-	390
0	4	22	189	172
0	6	1	291-	326
0	6	2	753	899
0	6	3	330-	350
0	6	4	476-	446
0	6	5	466	429
0	6	6	738-	729
0	6	7	296-	236
0	6	8	223	212
0	6	9	170-	71
0	6	10	539-	523
0	6	11	456	392
0	6	12	611	617
0	6	13	155	163
0	6	14	155-	126
0	6	15*	140	126
0	6	16	228	206
0	6	17	349-	381
0	6	18	325	385
0	6	19	179	168
0	6	20	131-	124
0	8	1	1546	1608
0	8	2	403	414
0	8	3	836-	858
0	8	4	392-	402
0	8	5	135	137
0	8	6	226-	212
0	8	7	453	503
0	8	8	275	300
0	8	9	304-	270
0	8	10	170-	111
0	8	11	850	886
0	8	17	236-	203
0	8	18	229	262
0	10	1	974	1004
0	10	2*	146-	58
0	10	3	1246-	1295
0	10	4	147	164
0	10	5	821	797
0	10	6	284-	216
0	10	7	420	419
0	10	8	147-	167
0	10	9	824-	793
0	10	10*	143	106
0	8	12	468	406
0	8	13	925-	969
0	8	14	373-	381
0	8	15	755	791
0	8	16	161-	110
0	10	11	982	1022
0	10	12	458-	393
0	10	13	1081-	1171
0	10	14	472	446
0	10	15	774	800
0	10	16	216-	229
0	10	17	287-	298
0	12	1	887	858
0	12	2	631-	593
0	12	3	847-	835
0	12	4	710	667
0	12	5	139-	131
0	12	6	136-	94
0	12	7	231	209
0	12	8	582-	565
0	12	9	391-	347
0	12	10	553	596
0	12	11	516	525
0	12	12	540-	588
0	12	13	628-	655
0	12	14	485	495
0	14	1*	110	7
0	14	2	602-	548
0	14	3	175-	134
0	14	4	104	71
0	14	5	164	150
0	14	6*	95	46
0	14	7	193-	177
0	14	9	194-	226
1	0	4	576	565
1	0	6	1311-	1409
1	0	8	295	270
1	0	10*	126-	68
1	0	12*	140-	2
1	0	14	493	448
1	0	16	545-	602
1	0	18	300	234
1	0	20	329-	281
1	0	22*	92	54
1	1	1	87	81
1	1	2	115	121
1	1	3	600-	698
1	1	4	130-	112
1	1	6	711-	683
1	1	7	1084-	1196
1	1	8*	96	52
1	1	9	590	589
1	1	10*	115-	15
1	1	11	706-	659
1	1	12	217	176
1	1	13*	135	17
1	1	14	213	146
1	1	15	629	564
1	1	16	256-	215
1	1	17	668-	604
1	1	18	135	53
1	1	19	484	438
1	1	20	183-	156
1	1	21	624-	625
1	1	22*	82	36
1	2	2	92	62
1	2	3	832	912
1	2	4	503-	447
1	2	5	1476-	1625
1	2	6	450-	448
1	2	7	1041	1229
1	2	8	459	433
1	2	9	644-	661
1	2	10*	115-	83
1	2	11	523	418
1	2	12	213-	150
1	2	13	309	202
1	2	14	334	237
1	2	15	610-	540
1	2	16	358-	293
1	2	17	765	713
1	2	18	213	169
1	2	19	513-	462
1	2	20	154-	106
1	2	21	498	471
1	2	22	154-	149
1	3	1	217-	148
1	3	2	111-	94
1	3	3	711-	771
1	3	4	716	688
1	3	5	842	899
1	3	6	542-	608
1	3	7	445-	418
1	3	8*	101-	24
1	3	9	658	639
1	3	10	300-	231
1	3	11	334-	293
1	3	12*	130-	30
1	3	13*	135-	38
1	3	14	319	182
1	3	15	251	142
1	3	16	396-	353
1	3	17	411-	336
1	3	18*	135	117
1	3	19	338	303
1	3	20*	111	2
1	3	21	363-	317
1	3	22	213	175
1	4	1	338-	350
1	4	2	217-	135
1	4	3	750	825
1	4	4	827-	889
1	4	5	1432-	1576
1	4	6	963	1089
1	4	7	1234	1409
1	4	8	678-	709
1	4	9	1016-	1128
1	4	10	852	843
1	4	11	377	325
1	4	12*	135-	31
1	4	13	391	319
1	4	14	237-	123
1	4	15	498-	469
1	4	16	508	495
1	4	17	832	866
1	4	18	619-	598
1	4	19	644-	649
1	4	20	391	355
1	4	21	532	506
1	4	22	421-	403
1	5	1	106-	69
1	5	2*	82	55
1	5	3*	96	3
1	5	4	101	64
1	5	5	130-	25
1	5	6*	96-	57
1	5	7	295-	236
1	5	8*	111	94
1	5	9*	115	28
1	5	10*	121-	50
1	5	11	237-	167
1	5	12	247-	169
1	5	13	247	169
1	5	14	154	94
1	5	15*	130	61
1	5	16*	135-	66
1	5	17	154	122
1	5	18*	121	92
1	5	19	237	206
1	5	20*	92-	9
1	5	21	160-	173
1	6	1	513-	445
1	6	2	774	781
1	6	3	784	731
1	6	4	1544-	1738
1	6	5	402-	390
1	6	6	1350	1542
1	6	7	513	514
1	6	8	920-	974
1	6	9	295-	256
1	6	10	881	894
1	6	11	135	110
1	6	12	149	162
1	6	13*	149-	3
1	6	14	319-	274
1	6	15	222-	240
1	6	16	614	684
1	6	17	222	169
1	6	18	692-	834
1	6	19	304-	318
1	6	20	411	511
1	6	21	154	160
1	7	1	392-	324
1	7	2	149	85
1	7	3*	131	15
1	7	4	507-	406
1	7	5	137	125
1	7	6	533	469
1	7	7	301	246
1	7	8	471-	379
1	7	9	152-	113
1	7	10	486	401
1	7	11	205-	186
1	7	12*	160	
1	7	13	244	176
1	7	14*	157	57
1	7	15*	151	19
1	7	16	275	224
1	7	17*	132	69
1	7	18	383-	333
1	7	19	167-	142
1	7	20	158	177
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1	8	2	529	452
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1	8	6	935	898
1	8	7	153-	164
1	8	8	927-	858
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1	8	11*	160-	57
1	8	12*	159-	36
1	8	13	156-	184
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1	8	17	331-	270
1	8	18	630-	664
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1	9	2	644	683
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1	9	6	792	738
1	9	7*	158-	88
1	9	8	841-	726
1	9	9*	160	56
1	9	10	432	385
1	9	11	157-	192
1	9	12*	153-	19
1	9	13*	148	82
1	9	14*	140-	112
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1	9	18	384-	464
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1	10	2	183-	167
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1	10	11*	149-	74
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1	11	10	410	405
1	11	11	156-	176
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1	11	13*	116-	54
1	11	14*	104-	70
1	11	15	144	152
1	12	1*	154-	93
1	12	2	354-	351
1	12	3	317-	264
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1	12	6	538-	597
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1	13	7	306-	268
1	13	8	432-	401
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1	13	10	160	134
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1	14	5	499-	525
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2	1	7	379-	375
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2	3	7	185-	147
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2	3	12	873	956
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2	3	14	516-	455
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2	3	17	393-	332
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2	4	3	578-	561
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2	4	13	806-	828
2	4	14	351	331
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2	4	19	151-	135
2	4	20	189	161
2	4	21	284	261
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2	5	3	925-	979
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2	5	5	635	570
2	5	6	156-	53
2	5	7	242	208
2	5	8	265	278
2	5	9	811-	792
2	5	10	550-	548
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2	5	12	816	843
2	5	13	631-	596
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2	5	15	707	711
2	5	16	413	412
2	5	17	516-	536
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2	5	19*	109	24
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2	6	3	356-	305
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2	6	8	422-	365
2	6	9	403-	360
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2	7	3	776-	754
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2	7	7	273	262
2	7	8	313	253
2	7	9	591-	596
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2	7	14	347-	349
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2	7	18	229-	222
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2	8	2	551-	588
2	8	3	344	299
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2	8	9	440	378
2	8	10	617	673
2	8	11	428-	407
2	8	12	501-	502
2	8	13*	172-	29
2	8	14	232	176
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2	8	17	178	175
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2	9	1	567	578
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2	9	3	486-	470
2	9	4*	176	91
2	9	5	308	234
2	9	6*	179	86
2	9	7	254	162
2	9	8	294-	303
2	9	9	569-	548
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2	9	12	238-	157
2	9	13	426-	416
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2	9	15	211	222
2	9	16*	123	87
2	9	17	190-	161
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2	10	3	275	160
2	10	4	233-	158
2	10	5*	180-	19
2	10	6*	180	48
2	10	7*	179	119
2	10	8*	177	91
2	10	9	265	208
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2	10	12*	154	37
2	10	13	364	334
2	10	14*	132-	76
2	10	15	287-	292
2	10	16*	97-	19
2	11	0*	179-	124
2	11	1	231-	145
2	11	2*	178-	42
2	11	3*	178	118
2	11	4*	177	7
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2	11	10	217	163
2	11	11	145-	84
2	11	12*	134	22
2	11	13*	121	13
2	11	14	137-	107
2	11	15*	84	7
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2	12	3*	167	67
2	12	4*	165-	104
2	12	5*	162	8
2	12	6*	158	42
2	12	7*	153-	47
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2	12	9	291	297
2	12	10	214-	207
2	12	11	120-	106
2	12	12	337	334
2	12	13	88-	91
2	13	0	369-	359
2	13	1	336-	233
2	13	2	344	319
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2	13	4	470-	478
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2	13	7*	128-	65
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2	13	10	234-	196
2	13	11	334-	376
2	14	0	339-	319
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2	14	2	251	224
2	14	3	225-	159
2	14	4	254-	211
2	14	5	152	137
2	14	6	130	104
2	14	7	175	176
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3	0	8	951-	1016
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3	0	12*	153-	3
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3	0	16	368	311
3	0	18	470-	470
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3	1	8	340-	305
3	1	9	1207-	1198
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3	1	11	452	402
3	1	12	233-	185
3	1	13	405	319
3	1	14	288-	233
3	1	15	447-	408
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3	1	17	923	959
3	1	18	433-	403
3	1	19	820-	723
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3	2	6	960	1009
3	2	7	167-	155
3	2	8	615-	607
3	2	9	326	305
3	2	10	447	432
3	2	11	205	148
3	2	12	591-	611
3	2	13	247-	199
3	2	14	359-	327
3	2	15*	144-	53
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3	2	17	172-	112
3	2	18	377-	314
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TABLE III (*Continued*)

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3	2	21*	65-	16
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3	3	8	769-	881
3	3	9	457-	436
3	3	10	419	384
3	3	11	167-	78
3	3	12	457	447
3	3	13	177	110
3	3	14	279-	238
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3	3	17	237	198
3	3	18	540-	534
3	3	19	349-	321
3	3	20	531	488
3	3	21	233	204
3	4	1	247	246
3	4	2*	97-	37
3	4	3	121-	76
3	4	4	419-	402
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3	4	7	172-	149
3	4	8	218-	181
3	4	9	186-	130
3	4	10*	135	57
3	4	11	186-	130
3	4	12	414-	363
3	4	14	158-	106
3	4	15	326	313
3	4	16	265	214
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3	5	4	498-	487
3	5	5	797	842
3	5	6	452	443
3	5	7	661-	705
3	5	8	480-	407
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3	5	11	111	88
3	5	12*	139-	47
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3	5	14	293-	272
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3	5	17	223-	224
3	5	18	419-	399
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3	6	4	139-	52
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3	6	14	153	9
3	6	15*	139-	27
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3	6	17	158	146
3	6	18*	97-	25
3	6	19	288-	292
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3	7	2	186-	195
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3	7	5	708	701
3	7	6	470-	470
3	7	7	536-	507
3	7	8	332	279
3	7	9	374	346
3	7	10	470-	466
3	7	11	460-	440
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3	7	13*	156-	81
3	7	14*	150	46
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3	8	9	524-	484
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3	8	12	267-	240
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3	8	14*	139-	66
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3	9	9	159-	145
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3	10	8	267-	248
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3	11	9	320-	289
3	11	10	285-	293
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3	12	11	91	96
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3	13	5	549-	523
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7	0	2	549-	591
8	0	2	210	153
4	0	4	709-	610
5	0	4	487-	416
6	0	4	286	264
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8	0	4	123-	96
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6	0	6	427	442
7	0	6	1014-	1132
4	0	8	229	223
5	0	8*	173-	33
6	0	8*	171-	95
7	0	8	854	900
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6	0	10	267	221
7	0	10	683-	659
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6	0	12	432-	389
7	0	12	219-	151
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5	0	14	157-	88
6	0	14	128	143
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6	0	16	199-	153
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5	1	6	537-	511
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5	1	9	223	208
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5	1	17	238-	251
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6	1	3	797	861
6	1	4	193-	198
6	1	5	208-	195
6	1	6	157	161
6	1	7	174-	137
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6	1	11	660-	768
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6	1	13	528	647
6	1	14*	99-	32
6	1	15	526-	517
6	1	16	135	114
7	1	1	274	223
7	1	2*	128-	35
7	1	3*	127	63
7	1	4*	126-	18
7	1	5	215-	188
[illegible]	1	[illegible]*	[illegible]	55
7	1	7*	118-	52
7	1	8*	113-	41
7	1	9*	108	11
7	1	10*	101	54
7	1	11*	94	68
7	1	12	189-	196
8	1	0*	100	11
8	1	1	419-	388
8	1	2*	99	50
8	1	3	329	258
8	1	4*	95-	77
8	1	5	230-	253
8	1	6	87-	104
8	1	7	194-	173
8	1	8*	74-	12
8	1	9	154	141
4	2	0	596-	520
4	2	1*	98	25
4	2	2	803	808
4	2	3	183	133
4	2	4	574-	469
4	2	5	181	112
4	2	6	206-	127
4	2	7	180	124
4	2	8*	113	13
4	2	9*	116	39
4	2	10	485-	477
4	2	11*	120-	5
4	2	12	538	584
4	2	13*	120	17
4	2	14	374-	390
4	2	15*	113-	21
4	2	16	473	477
4	2	17*	99	62
4	2	18	135-	95
4	2	19*	75-	11
4	2	20	95	47
5	2	1	423	332
5	2	2	293-	187
5	2	3	397-	311
5	2	4	299-	187
5	2	5	487	428
5	2	6	298	211
5	2	7	443-	352
5	2	8*	121	57
5	2	9	414	381
5	2	10	156	105
5	2	11	183-	109
5	2	12*	117	60
5	2	13	206-	178
5	2	14	107-	101
5	2	15*	100	61
5	2	16	90	112
5	2	17	366-	330
5	2	18*	66-	12
6	2	0*	121-	30
6	2	1	675-	605
6	2	2*	121	6
6	2	3	560	538
6	2	4	221	218
6	2	5	209-	149
6	2	6*	120-	14
6	2	7	316-	309
6	2	8	192-	151
6	2	9	210	174
6	2	10	171	126
6	2	11	496-	554
6	2	12	131-	119
6	2	13	437	406
6	2	14*	86-	13
6	2	15	431-	406
6	2	16*	62	31
7	2	1	113-	133
7	2	2	515-	475
7	2	3	337	280
7	2	4	524	522
7	2	5	530-	547
7	2	6	612-	751
7	2	7	363	336
7	2	8	651	773
7	2	9	293-	285
7	2	10	543-	562
7	2	11*	81	52
7	2	12	157	135
7	2	13	174	182
8	2	0	87-	147
8	2	1	481	535
8	2	2*	86-	67
8	2	3	285-	283
8	2	4	202	189
8	2	5	188	192
8	2	6*	75	8
8	2	7	70	70
8	2	8	141-	151
4	3	0	1395	1426
4	3	1	603	579
4	3	2	857-	945
4	3	3	152-	65
4	3	4	692	690
4	3	5	129	44
4	3	6	297	228
4	3	7	192-	139
4	3	8	643-	684
4	3	9	357-	343
4	3	10	658	707
4	3	11	389	376
4	3	12	659-	746
4	3	13	146-	68
4	3	14	498	485
4	3	15	136	119
4	3	16	326-	306
4	3	17	299-	300
4	3	18	90-	70
4	3	19*	75-	16
4	3	20	99	84
5	3	1*	120-	18
5	3	2	877-	916
5	3	3	211	112
5	3	4	933	965
5	3	5	431-	351
5	3	6	897-	929
5	3	7	548	535
5	3	8	620	608
5	3	9	478-	458
5	3	10	481-	472
5	3	11	177	147
5	3	12*	121	75
5	3	13*	117-	36
5	3	14	312	293
5	3	15*	102-	6
5	3	16	546-	530
5	3	17	257	211
5	3	18	469	492
6	3	0	590-	593
6	3	1	466-	446
6	3	2	442	370
6	3	3	510	549
6	3	4*	127	1
6	3	5*	127-	32
6	3	6	178-	153
6	3	7	249-	218
6	3	8	212	189
6	3	9	119	69
6	3	10	267-	200
6	3	11	306-	282
6	3	12	262	221
6	3	13	542	487
6	3	14	194-	156
6	3	15	332-	353
7	3	1	152	132
7	3	2*	117-	37
7	3	3*	116	24
7	3	4	331-	291
7	3	5*	112-	57
7	3	6	179	189
7	3	7	149-	174
7	3	8*	101-	80
7	3	9*	96-	62
7	3	10*	89-	74
7	3	11*	81-	80
7	3	12*	72-	30
7	3	13	96	104
8	3	1	311-	313
8	3	2	87-	89
8	3	3	156	95
8	3	4*	83-	70
8	3	5	242-	236
8	3	6*	74-	24
8	3	7	79-	80
4	4	0	292-	241
4	4	1	211-	165
4	4	2	665	600
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4	4	4	347-	327
4	4	5	214-	140
4	4	6*	114	17
4	4	7*	117	42
4	4	8	120	56
4	4	9	172	133
4	4	10	350-	321
4	4	11*	124	57
4	4	12	379	388
4	4	13	222	203
4	4	14	421-	380
4	4	15	145-	87
4	4	16	352	337
4	4	17	109	102
4	4	18	178-	188
4	4	19	128-	123
5	4	1	207	157
5	4	2	495-	447
5	4	3	287-	232
5	4	4	140-	29
5	4	5	646	595
5	4	6	384-	313
5	4	7	476-	486
5	4	8	449	458
5	4	9	344	311
5	4	10	224-	233
5	4	11	183-	167
5	4	12	190-	145
5	4	13	157-	125
5	4	14*	104-	10
5	4	15	227	206
5	4	16*	85-	72
5	4	17	322-	316
6	4	0	570-	456
6	4	1	711-	662
6	4	2	344	268
6	4	3	470	439
6	4	4	484-	463
6	4	5	465-	434
6	4	6	185	117
6	4	7	294-	254
6	4	8	253	245
6	4	9	442	428
6	4	10	283-	282
6	4	11	535-	554
6	4	12	410	399
6	4	13	478	517
6	4	14	370-	364
6	4	15	333-	360
7	4	1	330-	274
7	4	2	222-	175
7	4	3	285	216
7	4	4	226	218
7	4	5	330-	333
7	4	6	119-	74
7	4	7	358	398
7	4	8	309	314
7	4	9	206-	198
7	4	10	82-	69
7	4	11	141	103
8	4	0	569	539
8	4	1	577	657
8	4	2	319-	334
8	4	3	278-	312
8	4	4	150	181
8	4	5	108	114
8	4	6	66-	71
4	5	0	763	720
4	5	1	736-	645
4	5	2	475-	376
4	5	3	473	438
4	5	4	204	181
4	5	5	417-	364
4	5	6	201-	193
4	5	7	625-	627
4	5	8	184-	149
4	5	9	361	317
4	5	10	538	556
4	5	11	294-	259
4	5	12	536-	516
4	5	13	509	518
4	5	14	316	298
4	5	15	240-	223
4	5	16	205-	222
4	5	17	183-	174
5	5	1	767-	714
5	5	2	320-	174
5	5	3	825	841
5	5	4	569	502
5	5	5	855-	882
5	5	6	825-	847
5	5	7	859	972
5	5	8	693	721
5	5	9	585-	515
5	5	10	433-	406
5	5	11	452	474
5	5	12*	112	90
5	5	13*	106-	23
5	5	14	234	225
5	5	15	534-	539
5	5	16	418-	409
5	5	17	478	513
6	5	0	187	168
6	5	1	265	253
6	5	2*	122	28
6	5	3	591	363
6	5	4	242-	177
6	5	5	138-	81
6	5	6*	118-	8
6	5	7*	116-	2
6	5	8*	113	93
6	5	9	109-	106
6	5	10	104-	35
6	5	11	98-	108
6	5	12	105	112
6	5	13*	82	55
6	5	14	71-	99
7	5	1	107	16
7	5	2*	106	46
7	5	3	105-	135
7	5	4*	103-	67
7	5	5	142	123
7	5	6*	97	9
7	5	7	178-	234
7	5	8	124-	130
7	5	9*	81	1
7	5	10	129	147
8	5	0*	73	20
8	5	1	111-	105
8	5	2	71-	73
8	5	3	170	201
8	5	4*	66	9
4	6	0	349-	229
4	6	1	365-	310
4	6	2	447	420
4	6	3	348	238
4	6	4	249-	165
4	6	5	132-	78
4	6	6*	134	15
4	6	7*	136	13
4	6	8	138	54
4	6	9	139	85
4	6	10	227-	177
4	6	11	286-	298
4	6	12	246	272
4	6	13	212	169
4	6	14	275-	308
4	6	15	209-	234
4	6	16	158	183
4	6	17	156	162
4	6	18	172-	166
5	6	1	138-	128
5	6	2	536-	513
5	6	3	240-	186
5	6	4	385	285
5	6	5	394	345
5	6	6	574-	610
5	6	7*	138-	97
5	6	8	475	454
5	6	9*	134-	9
5	6	10	273-	277
5	6	11	193-	163
5	6	12*	120-	50
5	6	13	113	85
5	6	14	103	92
5	6	15	224	231
5	6	16	253-	276
6	6	0	1048-	1123
6	6	1	415-	390
6	6	2	536	543
6	6	3	245	215
6	6	4	442-	407
6	6	5	131	145
6	6	6*	129	30
6	6	7*	126	53
6	6	8	423	399
6	6	9	116	118
6	6	10	470-	462
6	6	11	298-	257
6	6	12	644	619
6	6	13	228	194
7	6	1*	114	49
7	6	2	207	193
7	6	3*	111	48
7	6	4	190-	172
7	6	5	167	121
7	6	6	394	383
7	6	7	96-	130
7	6	8*	90	21
7	6	9*	82	50

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[a] The asterisk denotes those reflections which were unobserved. The value of F_o in this case represents the minimum observable F_o.

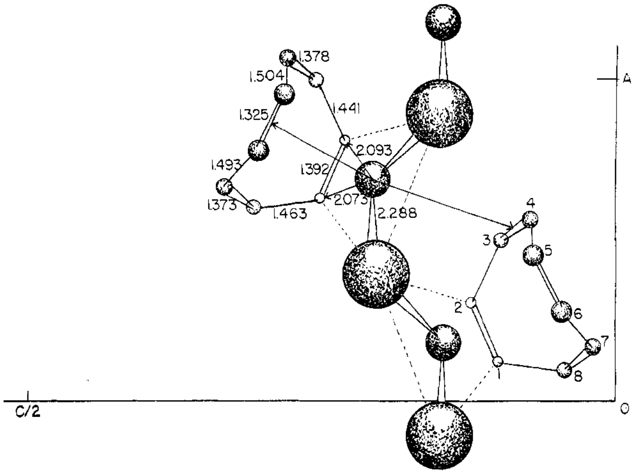

Fig. 1.—Coordination about the copper atoms in C_8H_8CuCl. Small spheres are carbon atoms; large spheres are chlorine atoms.

TABLE IV

EQUATIONS OF PLANES IN NORMAL FORM AND BOND ANGLES

Plane (Cu, Cl, Cl′, C_1, C_2)

$$-0.3276x + 0.5103y + 0.7952z = 3.122 \text{ Å.}$$

Dev. from plane (Å.): −0.092, 0.059, −0.002, −0.065, 0.101

Plane (C_1, C_2, C_3, C_8)

$$-0.0176x + 0.9755y - 0.2194z = 1.943 \text{ Å.}$$

Dev. from plane (Å.): −0.011, 0.011, −0.005, 0.005

Plane (C_4, C_5, C_6, C_7)

$$0.4636x - 0.2184y - 0.8587z = 0.154 \text{ Å.}$$

Dev. from plane (Å.): −0.004, 0.008, −0.009, 0.004

Angle of (Cu, Cl, Cl′, C_1, C_2) with (C_1, C_2, C_3, C_8) = 109.2°

	Angle, deg.	Std. dev., deg.
Cl-Cu-Cl′	106.0	0.1
Cl′-Cu-(C_1-C_2 center)	123.1	0.2
Cl-Cu-(C_1-C_2 center)	130.1	0.2
C_1-C_2-C_3	125.4	0.8
C_2-C_3-C_4	126.3	0.7
C_3-C_4-C_5	123.2	0.7
C_4-C_5-C_6	124.6	0.7
C_5-C_6-C_7	126.1	0.7
C_6-C_7-C_8	124.3	0.7
C_7-C_8-C_1	124.7	0.8
C_8-C_1-C_2	124.6	0.8
Cu-Cl-Cu	108.7	0.1

Angle of (C_1-C_2) with Cu-(C_1-C_2 center) = 88.9°

Two other double bonds are located at points which might be described as the apices of a distorted trigonal bipyramidal configuration about Cu. The atoms in the $C_5{=}C_6$ bond are 2.76 Å. from the Cu atom and are in the same cyclooctatetraene molecule as the closely coordinated $C_1{=}C_2$ bond. The $C_3{=}C_4$ bond in a different molecule is still further away from Cu at about 3.5 Å.

It is not possible to determine from the distances alone whether the $C_5{=}C_6$ bond is involved in an appreciable interaction with the Cu atom. There is some indication that the C_5, C_6 atoms cannot approach closer to the Cu atom because a hydrogen attached to C_5 comes into contact with a Cl atom in the –Cu–Cl– chain. This contact affects the orientation of the whole olefin molecule, so that the plane (C_1, C_2, C_3, C_8) makes an angle of 110° with the (Cu, Cl, Cl′, C_1, C_2) plane. An angle of 90° would give the best overlap between the orbital from the Cu atom and the π-molecular oribital of the olefin. Olefin π-orbitals are sufficiently flattened, however, so that fairly large deviations from 90° for this angle should be tolerated. Since the orientation of the olefin molecule is determined principally by the Cu—($C_1{=}C_2$) interaction, the position of the $C_5{=}C_6$ bond may be incidental. On the other hand, orbitals are available from Cu to form a bond.

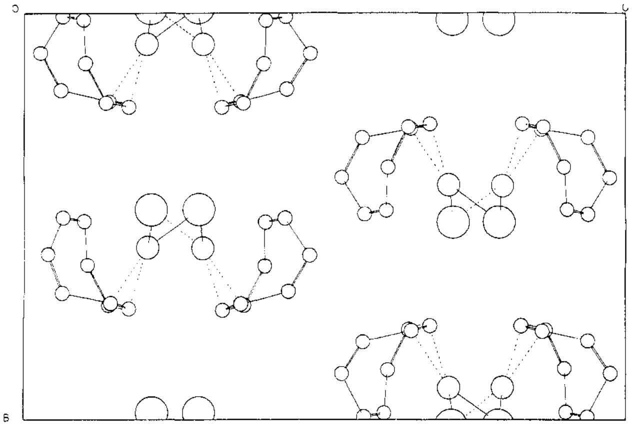

Fig. 2.—Projection of structure of C_8H_8CuCl onto (001). Small circles are carbon atoms; large circles are chlorine atoms.

The trigonal configuration about Cu(I) has been previously reported for $KCu(CN)_2$,[5] and a similar configuration has been found in a complex of norbornadiene with CuCl.[6] The trigonal (or distorted bipyramidal) arrangement has also been found for Ag(I) in the complex of cyclooctatetraene with $AgNO_3$.[7] The structural parallel between C_8H_8CuCl and $C_8H_8AgNO_3$ is rather striking since the silver and nitrate ions form continuous chains through the crystal, the silver atoms forming rather short bonds to two oxygen atoms (2.36, 2.43 Å.), one from each nitrate group. Again one double bond from the cyclooctatetraene molecule is closely bonded to the Ag atom (2.46, 2.51 Å.) and lies in the same plane as the Ag and O atoms. In the apical directions, one double bond from the same cyclooctatetraene molecule is at 2.8 Å. and one from a different molecule is at 3.2 Å.

Although the distances between carbon atoms cannot be accurately determined in the presence of more effective scatterers such as Cu and Cl when an *R* value of only 0.10 has been achieved, nevertheless some significant statements may be made. The $C_1{=}C_2$ bond distance of 1.392 Å. is longer than 1.34 Å. at the 0.1% level of significance (3.3 standard deviations). (Other work on the refinement of norbornadienepalladium chloride indicates that the fact the actual distance may lie between 1.353 and 1.431 Å. should not be disregarded, and the particular numerical value of 1.392 Å. should not be relied on too firmly.[3,8]) The

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

(6) N. C. Baenziger, H. L. Haight, and J. R. Doyle, *Inorg. Chem.*, **3**, 1535 (1964).

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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.

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(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.

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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

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(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.

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