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The Crystal Structure of Bis-(5-chlorosalicylaldoximato)copper(II)

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The crystal structure of bis-(5-chlorosalicylaldoximato)-copper(II), $[OC_6H_3(Cl)CHNOH]_2Cu$, has been determined from partial three-dimensional X-ray diffraction data, *h0l* through *h2l*. The cell has dimensions $a = 13{\cdot}38$, $b = 3{\cdot}84$, $c = 7{\cdot}31$ Å, $\alpha = 81°\,30'$, $\beta = 98°\,3'$, $\gamma = 98°\,3'$, space group $P\bar{1}$, and contains one molecule.

The copper(II) ion has a distorted octahedral coordination, with Cu–N = 1·96, Cu–O = 1·91 and 3·01 Å. The molecule shows considerable deviation from complete planarity. The chlorine atoms form layers with a distorted hexagonal close packing.

Introduction

The structure of the ligand, 5-chlorosalicylaldoxime, $HOC_6H_3(Cl)CHNOH$, has recently been determined (Simonsen, Pfluger & Thompson, 1961). The determination of the structure of bis(salicylaldoximato)-copper(II), $[OC_6H_4CHNOH]_2Cu$, and bis-(*N*-phenylsalicylaldiminato)copper(II), $[OC_6H_4CHNC_6H_5]_2Cu$, was underway in this laboratory (U. of W.). The investigation of the bis-(5-chloro-) complex, $[OC_6H_3(Cl)CHNOH]_2Cu$, was initiated for comparison of the effects of substituents on the salicylaldehyde-like residues and for comparison with the crystalline ligand.

Experimental

Bis-(5-chlorosalicylaldoximato)copper(II) was prepared by the addition of an aqueous solution of 5-chlorosalicylaldoxime to an aqueous solution of copper(II) chloride. Needle-shaped crystals elongated along the *b* axis were grown from a solution in a mixture of Methyl Cellosolve and acetone.

b-Axis rotation, *h0l* Weissenberg and (*hk*0) and (0*kl*) precession pictures were taken with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). All cell dimensions were obtained by superimposing the rotation pattern of NaCl ($a = 5{\cdot}6378$ Å) to calibrate these films. The results are:

$$a = 13{\cdot}38,\ b = 3{\cdot}84,\ c = 7{\cdot}31\ \text{Å};$$
$$\alpha = 81°\,30',\ \beta = 98°\,03',\ \gamma = 98°\,03'.$$

Each ligand molecule occupies a volume of 188 Å^3 in the free ligand crystal (Simonsen, Pfluger & Thompson, 1961) and not more than two ligand molecules (*i.e.* one complex molecule) can be accommodated in the present unit cell of 358 Å^3 volume. We therefore assumed one molecule per cell with a calculated density of 1·88 g.cm^{-3}, and assumed the probable space group to be $P\bar{1}$.

A needle of 0·05 mm diameter was selected for intensity measurements. Equi-inclination Weissenberg photographs of *h0l* through *h2l* were obtained with nickel-filtered Cu $K\alpha$ radiation on a Nonius camera. The unidirectionally integrated multiple film sets were scanned normal to the integration direction with a Moll type densitometer feeding into a Leeds & Northrup amplifier and recorder having a logarithmic slide wire.

The planimetered areas under the densitometer tracings were taken to be proportional to the intensity for those diffraction spots in the linear response range of the films. The scale of the *h0l* structure factors was determined by comparing with the calculated structure factors. In the initial three-dimensional calculations, the levels were approximately sealed together by comparing with a set of structure factors calculated from the copper position only. These approximate scale factors were used to prepare a set of *hk*0 reflections from these three-dimensional data. During the later stages the various levels were scaled independently by comparing the observed and calculated structure factors.

A total of 773 reflections of measurable intensity were observed and an additional 293 reflections had intensities too weak to be recorded. The $\bar{1}10$, $\bar{1}1\bar{1}$, and $\bar{2}10$ reflections were too intense to be densitometered and were assigned the intensity of the 011 reflection which was the most intense measurable *h1l* reflection. These three reflections were not included in the successive refinement cycles except that values of F_c were used in place of F_o in electron-density maps. The range of relative intensities was 1 to 1000.

Lorentz and polarization factors were applied to

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observed structure factors calculated using the data reduction program written in this laboratory (U. of W.) for the IBM 650 computer. No correction was made for absorption. The atomic scattering factors used were those of Thomas & Umeda (1957) for copper, Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for chlorine, oxygen, nitrogen, and carbon, and McWeeny (1951) for hydrogen. No correction was made for anomalous dispersion.

The structure determination

The choice of space group of $P\bar{1}$ was corroborated by the structure determination. With one molecule per cell, the copper atom was assigned the position 0, 0, 0.

The electron-density projection $\varrho(x, z)$ was calculated with the use of the unscaled observed $h0l$ structure factors as coefficients with phase angles equal to zero, using an IBM 1620 computer (at E.J.C.). All of the atoms were resolved and a calculation of the $h0l$ structure factors based on these trial parameters with an overall temperature factor of 2·5 had an R_{h0l} of 0·245; the discrepancy index, R, is defined as $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for observed non-zero reflections only.

After one further electron-density projection $\varrho(x, z)$ and two difference syntheses the value of R_{h0l} was reduced to 0·129 with the use of individual atom isotropic temperature factors.

The very short b axial length and excellent resolutions of the atoms in $\varrho(x, z)$ indicated that the molecule is lying approximately in the plane of the electron-density map. This orientation was utilized to determine approximate y coordinates for the atoms. An electron-density projection $\varrho(x, y)$ was calculated using the approximately scaled observed $hk0$ structure factors as coefficients with phase angles equal to zero. Only the heavy copper and chlorine atoms were resolved; however, these proved sufficient to solve the structure. A line was drawn on the electron-density map connecting the copper atom at 0, 0, 0 with the peak maximum of the chlorine atom, ($x=0{\cdot}5119$, $y=0{\cdot}7800$). The y coordinates for the other atoms were read from this line using the final x coordinates obtained from the $h0l$ data. These y coordinates were used, along with the x, z, and individual atom isotropic temperature factor parameters from the $h0l$ data, as input for continued refinement by the Busing & Levy (1959) least-squares method using an IBM 709 computer. These input data had an overall R of 0·389.

A modified Hughes weighting scheme was used with:

$\sqrt{w}=0$ for unobserved reflections with $F_c \le F_{\min}$
$\sqrt{w}=1$ for unobserved reflections with $F_c > F_{\min}$
$\sqrt{w}=1$ for observed reflections with $F_o \le 16$
$\sqrt{w}=16/F_o$ for $F_o > 16$.

The function minimized was $\Sigma w(|F_o|-|F_c|)^2$. Five cycles of least-squares refinement were carried out, which gave R values of 0·314, 0·237, 0·145, 0·120, and 0·119. Hydrogen atoms were introduced in calculated positions (C–H distance = 1·04 Å), with isotropic temperature factors of 3·0, and two additional cycles were run with R values of 0·111 and 0·107.

The behavior of the first three cycles of least-squares refinement gives a very good illustration of the power of the Busing–Levy program and of the tendency for a least-squares calculation greatly to increase the temperature factors of atoms which are far from their correct positions. In Table 1 are listed the temperature factors suggested by the program in the first three

Table 1. *Least-squares refinement of B*

	Input	Cycle 1	Cycle 2	Cycle 3	δ
Cu	2·40	1·34	1·63	2·14	—
Cl	3·10	2·36	2·62	2·71	0·14 Å
O(1)	2·25	3·88	6·27	3·56	0·78
O(2)	2·50	3·56	4·62	2·19	0·63
N	2·10	1·09	1·51	1·26	0·32
C(1)	2·60	1·12	1·07	1·36	0·11
C(2)	2·30	3·21	3·56	1·74	0·62
C(3)	3·50	6·12	9·82	1·97	0·95
C(4)	1·20	3·17	5·26	3·63	0·83
C(5)	2·40	2·02	1·58	1·93	0·22
C(6)	3·00	2·50	2·14	2·64	0·09
C(7)	2·50	3·08	2·21	1·68	0·26

Table 2. *Atomic positions and temperature factors*

	x/a	y/b	z/c	B
Cu	0·0000	0·0000	0·0000	2·58
Cl	0·5101	0·8156	0·2634	2·77
O(1)	0·0741	0·3041	0·1695	2·00
O(2)	0·0872	−0·0404	−0·3347	2·53
N	0·1090	0·0900	−0·1601	1·62
C(1)	0·2352	0·3883	0·0449	1·61
C(2)	0·1731	0·4130	0·1867	1·80
C(3)	0·2175	0·5665	0·3452	2·30
C(4)	0·3195	0·6894	0·3679	2·56
C(5)	0·3797	0·6552	0·2318	1·82
C(6)	0·3389	0·5144	0·0737	2·14
C(7)	0·1982	0·2355	−0·1241	1·77
H(1)	0·173	0·589	0·449	3·00
H(2)	0·352	0·812	0·484	3·00
H(3)	0·386	0·499	−0·029	3·00
H(4)	0·249	0·249	−0·222	3·00
H(5)	0·024	−0·143	−0·270	3·00

Table 3. *Estimated standard deviations and final cycle parameter shifts*

		x (Å × 10^4)	y (Å × 10^4)	z (Å × 10^4)	B (Å^2 × 10^3)
Cu	σ	—	—	—	69
	δ	—	—	—	4
Cl	σ	32	43	32	77
	δ	0	0	0	0
N	σ	91	121	88	167
	δ	0	1	1	0
O	$\bar{\sigma}$	86	108	83	162
	$\bar{\delta}$	0	2	1	3
	$\delta_{\max}$	0	2	1	3
C	$\bar{\sigma}$	116	156	114	209
	$\bar{\delta}$	3	2	4	4
	$\delta_{\max}$	7	10	7	7

Table 4. *Observed and calculated structure factors*

The columns are h, $10F_o$ and $10F_c$. Unobserved reflections are marked with *. Reflections omitted because of secondary extinction effects are marked with E

H,0,0		
1	186	245
2	281	300
3	95	-59
4	258	260
5	97	-44
6	276	267
7	333	-273
8	228	206
9	111	115
10	301	285
11	59•	65
12	243	202
13	89	70
14	105	79
15	48•	10
16	82	71

H,0,1		
0	495	498
1	137	146
-1	555	561
2	320	339
-2	88	-48
3	301	336
-3	67	77
4	125	141
-4	222	232
5	383	394
-5	156	161
6	78	-56
-6	365	388
7	82	98
-7	147	158
8	50•	61
-8	269	271
9	211	197
-9	106	110
10	57•	48
-10	130	117
11	263	236
-11	59•	-7
12	112	120
-12	99	69
13	146	113
-13	59•	-12
14	53•	-37
-14	160	130
15	131	104
-15	49•	6
16	34•	0
-16	115	102

H,0,2		
0	271	-244
1	364	369
-1	277	312
2	186	-156
-2	105	-84
3	291	276
-3	791	738
4	38•	4
-4	317	307
5	308	317
-5	512	499
6	45•	63
-6	125	124
7	342	330
-7	333	333
8	53•	58
-8	49•	43
9	254	253
-9	301	315
10	71	86
-10	203	-179
11	214	203
-11	59•	-23
12	59•	58
-12	60•	5
13	61	40
-13	164	139
14	49•	-10
-14	64	65
15	54	42
-15	153	137
-16	39•	0

H,0,3		
0	227	207
1	38•	-5
-1	122	108
2	251	247
-2	76	82
3	310	286
-3	202	195
4	276	270
-4	390	418
5	47•	49
-5	200	203
6	261	242
-6	84	75
7	54•	5
-7	197	189
8	275	261
-8	87	65
9	74	79
-9	264	276
10	75	57
-10	158	147
11	59•	5
-11	60•	-14
12	172	158
-12	60•	24
13	51•	19
-13	182	179
14	139	113
-14	53•	34
15	30•	-31
-15	97	52
-16	35•	-36

H,0,4		
0	111	151
1	114	-117
-1	95	-81
2	421	425
-2	242	258
3	218	211
-3	120	-102
4	303	301
-4	290	290
5	132	123
-5	84	82
6	235	226
-6	244	248
7	111	110
-7	54•	47
8	300	292
-8	264	269
9	109	-99
-9	59•	10
10	59•	-67
-10	233	268
11	55•	2
-11	60•	34
12	67	67
-12	130	118
13	57	55
-13	54•	24
14	77	74
-14	89	61
-15	40•	-31

H,0,5		
0	129	125
1	132	141
-1	247	256
2	55•	60
-2	129	120
3	113	133
-3	225	205
4	57•	19
-4	94	75
5	185	185
-5	101	93
6	60•	19
-8	105	97
7	249	242
-7	59•	28
8	59•	60
-8	60•	55
9	69	58
-9	60•	56
10	53•	-6
-10	110	92
11	91	75
-11	110	88
12	39•	-26
-12	147	141
-13	93	91
-14	48	48

H,0,6		
0	148	125
1	177	183
-1	435	453
2	60•	33
-2	69	44
3	129	124
-3	80	84
4	60•	29
-4	59•	-46
5	63	85
-5	70	98
6	64	-85
-6	60•	-26
7	56•	59
-7	128	142
8	53•	23
-8	60•	-89
9	108	106
-9	111	137
10	52	51
-10	65	64
11	77	68
-11	149	153
-12	46•	13
-13	113	120

H,0,7		
0	59•	62
1	59•	33
-1	131	115
2	123	115
-2	172	199
3	57•	34
-3	59•	-63
4	156	167
-4	59•	47
5	55•	-35
-5	73	78
6	50•	35
-6	83	111
7	45•	-6
-7	119	123
8	88	86
-8	56	63
-9	50•	27
-10	54	60
-11	40•	37

H,0,8		
0	56	74
1	50•	-3
-1	52•	-43
2	48•	52
-2	105	132
3	46•	26
-3	51•	19
4	57	70
-4	58	132
5	38•	-3
-5	118	74
6	52	73
-6	90	121
-7	44•	9
-9	59	96

H,0,9		
0	32•	-6
1	40	57
-1	33•	44
-2	34•	-15
-3	33•	44
-4	43	31
-5	48	118

H,1,0		
0	75	131
1	173	221
-1	327	434
2	306	300
-2	487E	548
3	24•	32
-3	97	128
4	327	308
-4	101	95
5	328	-236
-5	73	85
6	147	139
-6	74	79
7	112	121
-7	232	222
8	317	299
-8	126	126
9	76	86
-9	99	117
10	356	291
-10	132	130
11	76	90
-11	148	157
12	159	105
-12	63	69
13	45•	-36
-13	83	66
14	145	121
-14	45•	3
15	38	-15
-15	105	83
-16	32•	-3

H,1,1		
0	456	421
1	61	-29
-1	345	-255
2	393	354
-2	313	278
3	144	157
-3	278	-217
4	426	380
-4	421	383
5	70	93
-5	148	157
6	379	336
-6	504	458
7	63	92
-7	137	151
8	251	222
-8	421	399
9	112	111
-9	70	80
10	223	194
-10	404	363
11	71	24
-11	47•	-47
12	47•	-2
-12	48•	9
13	44•	23
-13	54	-69
14	67	57
-14	91	65
15	52	47
-15	40•	0
-16	142	120

H,1,-1		
0	210	-219
1	32	56
-1	599E	1201
2	171	-119
-2	453	439
3	207	198
-3	511	465
4	29•	16
-4	130	140
5	276	249
-5	314	336
6	115	-81
-6	43	35
7	365	332
-7	343	315
8	154	172
-8	213	-207
9	265	245
-9	103	75
10	47•	50
-10	46•	-9
11	157	133
-11	210	190
12	54	52
-12	48•	14
13	93	58
-13	196	180
14	41•	26
-14	64	74
15	77	65
-15	99	85
-16	28•	-0

H,1,2		
0	94	-41
1	365	337
-1	301	260
2	181	180
-2	23•	27
3	311	292
-3	89	94
4	73	54
-4	60	69
5	375	347
-5	543	492
6	38•	28
-6	292	277
7	378	328
-7	181	171
8	45•	58
-8	166	154
9	179	144
-9	69	62
10	49•	35
-10	213	196
11	180	154
-11	205	200
12	46•	-24
-12	48•	-38
13	154	102
-13	48•	-32
14	57	-47
-14	147	127
15	56	72
-15	56	63
-16	124	111

H,1,-2		
0	177	168
1	177	173
-1	297	278
2	231	222
-2	36	58
3	373	341
-3	231	231
4	184	176
-4	157	172
5	410	358
-5	108	117
6	71	81
-6	209	239
7	266	253
-7	63	81
8	68	-43
-8	76	97
9	58	21
-9	59	66
10	48•	-31
-10	112	113
11	127	116
-11	48•	32
12	47•	25
-12	147	138
13	195	176
-13	112	111
14	39•	15
-14	110	102
15	149	125
-15	32•	-30

H,1,3		
0	61	76
1	756	664
-1	228	236
2	297	270
-2	54	-38
3	305	278
-3	308	286
4	112	123
-4	211	-161
5	205	190
-5	214	247
6	102	116
-6	70	77
7	231	208
-7	232	217
8	182	-172
-8	42•	-8
9	48•	-27
-9	263	254
10	114	107
-10	47•	-10
11	129	117
-11	330	303
12	111	103
-12	58	67
13	59	67
-13	119	107
14	33	24
-14	44•	35
-15	112	112

H,1,-3		
0	313	316
1	112	109
-1	33•	-42
2	709	609
-2	316	298
3	168	170
-3	88	-88
4	247	257
-4	207	210
5	39•	25
-5	40•	-10
6	194	193
-6	168	182
7	43•	36
-7	45•	-17
8	210	211
-8	195	209
9	190	-188
-9	48•	-7
10	42•	41
-10	196	201
11	120	119
-11	47•	46
12	159	161
-12	138	141
13	85	77
-13	72	52
14	100	95
-14	85	82
-15	22•	1

H,1,4		
0	240	243
1	124	124
-1	36•	-2
2	246	243
-2	221	233
3	72	70
-3	73	80
4	323	295
-4	271	271
5	62	66
-5	61	65
6	335	344
-6	177	171
7	45•	-39
-7	110	111
8	48•	-3
-8	114	100
9	48•	-27
-9	75	69
10	132	109
-10	67	76
11	42•	-12
-11	58	46
12	174	129
-12	124	93
-13	111	102
-14	118	105
-15	71	70

H,1,-4		
0	101	104
1	39•	46
-1	97	94
2	198	203
-2	41•	0
3	237	231
-3	55	66
4	130	148
-4	227	222
5	43•	62
-5	205	217
6	204	216
-6	84	86
7	77	65
-7	146	160
8	250	253
-8	48•	12
9	62	57
-9	167	171
10	43•	15
-10	128	110
11	46•	38
-11	43•	4
12	126	137
-12	39•	-49
13	38•	-21
-13	80	84
14	72	64

H,1,5		
0	148	145
1	43•	-9
-1	76	60
2	83	89
-2	567	500
3	46•	20
-3	232	206
4	73	66
-4	264	240
5	48•	-9
-5	44•	43
6	144	146
-6	146	144
7	103	78
-7	47•	-36
8	155	135
-8	146	156
9	83	80
-9	87	-110
10	70	57
-10	68	87
11	71	67
-11	47•	7
-12	146	149
-13	41•	17
-14	162	151
-15	50	49

H,1,-5		
0	45•	-18
1	197	226
-1	121	145
2	45•	-12
-2	103	-128
3	216	235
-3	145	173
4	73	64
-4	69	62
5	170	188

Table 4 (*cont.*)

H,1,-5		
-5	148	180
6	48*	32
-6	49*	51
7	155	176
-7	124	164
8	48*	-0
-8	59	54
9	157	180
-9	242	269
10	45*	25
-10	41*	11
11	97	102
-11	36*	-19
12	38*	2
-12	29*	-32
H,1,6		
0	47*	48
1	185	174
-1	112	102
2	48*	30
-2	144	125
3	180	177
-3	312	371
4	65	-114
-4	48*	-23
5	48*	62
-5	48*	38
6	47*	10
-6	49*	12
7	158	148
-7	101	101
8	41*	22
-8	106	110
9	168	138
-9	104	113
-10	46*	5
-11	83	92
-12	84	77
-13	47	41
H,1,-6		
0	142	159
1	58	47
-1	203	192
2	77	72
-2	115	121
3	49*	34
-3	51	66
4	48*	20
-4	54	77
5	66	75
-5	47*	9
6	48*	-18
-6	75	97
7	56	72
-7	88	-11
8	66	73
-8	72	91
9	110	125
-9	45	48
10	84	71
-10	30*	59
11	118	127
12	44	41
H,1,7		
0	48*	20
1	82	82
-1	101	84
2	83	86
-2	63	-75
3	74	88
-3	118	149
4	44*	17
-4	48*	31
5	101	100
-5	105	93
6	68	57
-6	93	67
7	55	55
-7	161	172
8	66	68
-8	80	55
9	86	89
-9	145	163
-10	39*	-2
-11	87	104
-12	30*	-30
H,1,-7		
0	179	261
1	72	-92
-1	108	93
2	46*	7
-2	106	135
3	45*	-28
-3	46	32
4	76	97
-4	65	107
5	44*	18
-5	100	40
6	87	113
-6	103	114
7	40*	-41
8	116	140
9	64	57
10	62	87
H,1,8		
0	87	93
1	40*	20
-1	42*	4
2	86	106
-2	75	93
3	37*	-9
-3	42*	-33
4	109	115
-4	65	73
5	30*	1
-5	41*	5
6	72	84
-6	144	154
-7	78	65
-8	62	54
H,1,-8		
0	79	87
1	72	85
2	36*	-21
3	55	70
4	75	87
5	65	64
6	63	77
H,1,9		
0	100	107
1	64	63
2	46	51
H,2,0		
0	87	102
1	269	282
-1	342	347
2	164	172
-2	99	-75
3	176	199
-3	264	279
4	32*	45
-4	26*	-16
5	248	237
-5	121	142
6	76	90
-6	33*	-10
7	168	160
-7	199	220
8	128	130
-8	40*	44
9	164	139
-9	256	282
10	46*	5
-10	46*	50
11	45*	-8
-11	257	274
12	86	70
-12	46*	51
13	35*	53
-13	95	83
14	72	59
-14	40*	-41
-15	33*	30
H,2,1		
0	296	307
1	103	119
-1	12*	-5
2	331	330
-2	237	233
3	73	88
-3	47	-38
4	350	348
-4	63	77
5	37*	25
-5	111	-91
6	312	280
-6	272	296
7	43*	21
-7	183	202
8	199	161
-8	193	209
9	47*	-4
-9	129	133
10	125	87
-10	90	96
11	67	-44
-11	123	115
12	154	101
-12	226	214
13	50	-24
-13	45*	-11
14	130	91
-14	41*	-54
-15	35*	31
H,2,-1		
0	42	33
1	169	156
-1	24*	19
2	45	-36
-2	58	74
3	135	192
-3	605	658
4	206	-157
-4	226	247
5	279	256
-5	170	203
6	176	177
-6	67	84
7	323	299
-7	66	86
8	45*	67
-8	115	115
9	325	226
-9	119	111
10	46*	20
-10	46*	-7
11	103	69
-11	52	48
12	56	-37
-12	84	85
13	122	99
-13	70	78
14	42	-24
-14	51	51
-15	30*	30
H,2,2		
0	644	505
1	140	132
-1	176	192
2	145	146
-2	252	259
3	92	99
-3	50	63
4	132	120
-4	269	270
5	127	117
-5	103	-87
6	143	117
-6	179	175
7	172	-106
-7	99	95
8	86	70
-8	138	183
9	187	177
-9	43*	-34
10	105	99
-10	165	160
11	121	99
-11	70	-62
12	38*	24
-12	245	229
13	55	35
-13	79	81
-14	76	68
-15	35*	10
H,2,-2		
0	69	83
1	32*	11
-1	260	-222
2	196	191
-2	399	395
3	109	106
-3	200	190
4	201	201
-4	231	283
5	40*	53
-5	99	114
6	243	242
-6	203	249
7	77	79
-7	43*	48
8	122	114
-8	239	272
9	47*	23
-9	57	-59
10	83	76
-10	47	58
11	69	63
-11	45*	-44
12	54	48
-12	94	97
13	52	49
-13	38*	-30
14	63	61
-14	106	107
H,2,3		
0	177	176
1	266	266
-1	426	400
2	39	64
-2	30*	16
3	308	283
-3	207	202
4	40*	39
-4	33*	16
5	319	276
-5	243	238
6	214	-186
-6	37*	-5
7	46*	-22
-7	159	161
8	47*	29
-8	76	69
9	216	155
-9	110	109
10	43*	32
-10	46*	53
11	209	-153
-11	98	96
12	33*	-6
-12	46*	15
13	163	129
-13	118	106
-14	65	62
-15	94	87
H,2,-3		
0	249	260
1	160	169
-1	95	106
2	189	212
-2	177	197
3	64	53
-3	40*	33
4	194	176
-4	139	152
5	44*	-10
-5	55	60
6	165	156
-6	71	74
7	137	-128
-7	95	87
8	47*	20
-8	62	64
9	46*	41
-9	46*	51
10	165	165
-10	45*	55
11	41*	54
-11	42*	50
12	170	156
-12	38*	31
13	29*	-1
-13	54	61
H,2,4		
0	28*	-7
1	94	85
-1	92	90
2	76	83
-2	37*	-38
3	124	102
-3	312	301
4	150	130
-4	201	191
5	172	166
-5	289	274
6	84	65
-6	142	130
7	130	103
-7	201	189
8	92	82
-8	45*	16
9	43*	27
-9	168	169
10	105	81
-10	47*	-59
11	33*	10
-11	73	65
12	59	45
-12	44*	-38
-13	95	90
-14	36*	-9
-15	128	121
H,2,-4		
0	106	93
1	303	326
-1	165	200
2	44*	23
-2	44*	9
3	71	95
-3	165	198
4	45*	19
-4	46*	-41
5	116	124
-5	112	137
6	87	59
-6	64	28
7	113	117
-7	109	129
8	113	-118
-8	45*	-26
9	116	93
-9	104	114
10	138	140
-10	40*	-45
11	83	92
-11	110	124
12	30*	38
-12	30*	24
H,2,5		
0	165	155
1	44*	-22
-1	43*	10
2	135	128
-2	124	101
3	143	-141
-3	43*	60
4	154	139
-4	467	458
5	47*	62
-5	119	95
6	246	204
-6	124	115
7	44*	46
-7	46*	-8
8	196	147
-8	84	79
9	37*	27
-9	47*	50
10	109	74
-10	120	124
-11	44*	-34
-12	63	68
-13	73	63
-14	74	78
H,2,-5		
0	47*	39
1	149	168
-1	93	99
2	102	114
-2	57	43
3	90	116
-3	47*	5
4	47*	45
-4	46*	-51
5	136	159
-5	83	95
6	45*	17
-6	97	111
7	136	158
-7	57	71
8	42*	-9
-8	73	92
9	39*	30
-9	37*	18
10	34*	20
-10	104	94
11	60	70
-11	108	131
H,2,6		
0	132	114
1	140	133
-1	87	79
2	81	55
-2	116	109
3	46*	28
-3	46*	-74
4	109	102
-4	143	140
5	79	83
-5	87	82
6	41*	53
-6	47*	38
7	109	96
-7	46*	2
8	88	67
-8	130	130
9	27*	21
-9	75	57
-10	187	190
-11	57	35
-12	97	107
H,2,-6		
0	110	145
1	45*	-2
-1	44*	6
2	95	127
-2	109	138
3	44*	26
-3	43*	-42
4	66	91
-4	57	75
5	42*	5
-5	40*	1
6	71	102
-6	59	80
7	37*	15
-7	34*	-3
8	94	114
-8	53	83
9	51	32
-9	22*	-8
10	43	65
H,2,7		
0	45*	24
1	146	139
-1	112	110
2	43*	-4
-2	45*	4
3	170	151
-3	102	104
4	39*	7
-4	45*	-62
5	154	99
-5	83	94
6	32*	10
-6	44*	-30
7	115	106
-7	139	139
-8	95	78
-9	103	106
-10	35*	27
-11	65	66
H,2,-7		
0	36*	-29
1	36*	4
-1	36*	20
2	36*	25
-2	149	145
3	35*	9
-3	85	89
4	48	65
5	32*	-16
6	61	93
7	67	75
H,2,8		
0	80	71
1	51	43
-1	127	117
2	71	68
-2	73	59
3	30*	34
-3	61	60
4	52	52
-4	37*	20
-5	59	44
-6	35*	-31
-7	56	48
-8	65	66
-9	55	63

cycles and the distance in Å between the initial positions and the final 'true' positions. It will be noted that all atoms which were more than 0·5 Å from their final positions showed marked increases in their temperature factors, the extreme being atom C(3) which moved 0·95 Å and whose temperature factor reached 9·82 Å^2 in the second cycle.

An attempt was made to extend the refinement by the use of anisotropic temperature factors. This attempt was unsuccessful because the standard deviation in β_{22} of the carbon atoms was of the same order of magnitude as the average value of β_{22}. Consequently there was a tendency for some β_{22} values to become negative. It may be noted that R was reduced to 0·071 with no appreciable shift in atomic positions.

The final parameters are listed in Table 2, and the estimated standard deviations and final cycle parameter shifts are listed in Table 3. The final values of observed and calculated structure factors are listed in Table 4, and the agreement of certain classes of reflections is listed in Table 5 where R^* includes $F_{\min}$ and $(F_{\min}-F_c)$ for those unobserved reflections for which $F_c > F_{\min}$.

Table 5. *Agreement of certain classes of reflections*

Class	R	R^*
$hk0$	0·132	0·109
$0kl$	0·119	0·119
$h0l$	0·091	0·108
$h1l$	0·114	0·121
$h2l$	0·110	0·131
Overall	0·107	0·121

Discussion

Bond lengths and angles in the molecule of bis-(5-chlorosalicylaldoximato)copper(II) are listed in Table 6 with their estimated standard deviations and shown in Fig. 1.

The coordination configuration about the copper(II) ion is a rectangle with N–O(1) distance of 2·78 Å and N–O(1′) distance of 2·69 Å. The coordination polyhedron is completed by phenolic oxygen atoms located at $(x, y-1, z)$ and $(-x, 1-y, -z)$ with a distance of 3·01 Å. The phenolic oxygen–copper direction is nearly perpendicular to the Cu–N–O(1) plane, making an angle of 80° along the Cu–O(1) bond direction. The distances and angles within the coordination polyhedron are listed in Table 7. The chelate coordination configuration is identical with that found in bis(salicylaldoximato)copper(II) (Jarski & Lingafelter, 1964). However, the apical oxygen in bis(salicylaldoximato)copper(II) is an oxime oxygen atom from an adjacent molecule rather than a phenolic oxygen atom, and is considerably closer (2·66 Å) to the copper atom. The Cu–O distance of 1·91 Å is similar to the 1·90 Å in bis-(N-methylsalicyl-

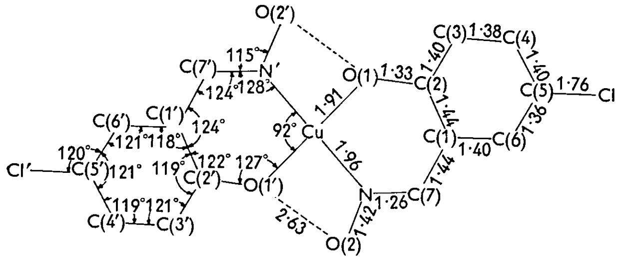

Fig. 1. Bond lengths and angles.

Table 6. *Bond lengths and angles*

	Distance	σ
Cu–O(1)	1·908 Å	0·009 Å
Cu–N	1·957	0·009
O(1)–C(2)	1·326	0·013
N–O(2)	1·418	0·014
N–C(7)	1·256	0·014
C(1)–C(2)	1·438	0·017
C(1)–C(6)	1·402	0·015
C(1)–C(7)	1·441	0·017
C(2)–C(3)	1·397	0·018
C(3)–C(4)	1·376	0·017
C(4)–C(5)	1·395	0·019
C(5)–C(6)	1·360	0·018
C(5)–Cl	1·762	0·011
	Angle	σ
O(1)–Cu–N	91·8°	0·4°
Cu–O(1)–C(2)	127·3	1·0
Cu–N–C(2)	128·0	1·0
O(2)–N–C(7)	115·2	1·2
O(1)–C(2)–C(1)	122·1	1·4
N–C(7)–C(1)	123·8	1·5
C(2)–C(1)–C(7)	124·2	1·5
C(2)–C(1)–C(6)	118·2	1·4
C(1)–C(2)–C(3)	119·1	1·4
C(2)–C(3)–C(4)	121·0	1·6
C(3)–C(4)–C(5)	119·4	1·6
C(4)–C(5)–C(6)	121·4	1·6
C(5)–C(6)–C(1)	120·9	1·5
C(6)–C(5)–Cl	119·9	1·1

Table 7. *Coordination configuration*

	Distance	σ
Cu–O(1)	1·908 Å	0·009 Å
Cu–N	1·957	0·009
Cu–O(1″)	3·013	0·010
N–O(1)	2·775	0·014
N–O(1′)	2·691	0·012
O(1″)–O(1)	3·271	0·011
O(1″)–O(1′)	3·840	0·015
O(1″)–N	3·594	0·015
O(1″)–N′	3·592	0·013
	Angle	σ
O(1)–Cu–N	91·8°	0·4°
O(1)–Cu–O(1″)	79·9	0·3
N–Cu–O(1″)	90·0	0·3

Note: O(1) and N are located at (x, y, z), O(1′) and N′ at $(\bar{x}, \bar{y}, \bar{z})$, and O(1″) at $(\bar{x}, 1-y, \bar{z})$.

aldiminato)copper(II) (Lingafelter, Simmons, Morosin, Scheringer & Freiburg, 1961), the 1·88 Å in bis-(*N*-phenylsalicylaldiminato)copper(II) (Wei, Stogsdill & Lingafelter, 1964), and the 1·92 Å in bis(salicylaldoximato)copper(II) (Jarski & Lingafelter, 1964). There is good agreement between the Cu–N distance of 1·96 Å and the distance of 1·94 Å found in bis-(salicylaldoximato)copper(II). The Cu–O distance of 3·01 Å in the 'long bond' direction is somewhat longer than in most copper(II) coordination compounds, but with the type of molecular packing found in this crystal, the van der Waals radii of the ring atoms and the chlorine atom limit the approach distance.

The hydrogen bond in bis(salicylaldoximato)copper (II) is longer (2·58 Å) than that (2·52 Å) in the nickel(II) compound because of the increased metal–ligand atom distances. The hydrogen bond in bis-(5-chlorosalicylaldoximato)copper(II) is still longer, 2·63 Å, probably because of the increased deviation of the molecule from complete planarity.

There are no significantly different bond distances or angles in the 5-chlorosalicylaldoxime residue from distances reported for similar molecules. The average C–C distance in the benzene ring is 1·395 Å. The C–Cl distance of 1·77 Å is somewhat longer than the average aromatic C–Cl distance of 1·70 Å (Bowen, 1958), but agrees with the distance of 1·78 Å in the ligand 5-chlorosalicylaldoxime (Simonsen, Pfluger & Thompson, 1961), and 1·78 Å in *syn-p*-chlorobenzaldoxime (Jerslev, 1950).

The set of atoms consisting of the benzene ring and C(7), O(1), and Cl which are directly attached to the benzene ring shows no significant deviation from planarity. The nitrogen atom is significantly displaced from this plane by 0·10 Å, the oxime oxygen atom is also displaced from this plane by 0·08 Å, and the copper atom by 0·38 Å. The molecule may be described as consisting of two parallel planes defined by the two phenyl groups and displaced by a perpendicular distance of 0·76 Å, and the coordination plane which joins these two planes and makes an angle of 14° with each of them. This configuration is similar to that found in bis-(*N*-phenylsalicylaldiminato)copper (II) (Wei, Stogsdill & Lingafelter, 1964) in which the perpendicular distance between the phenyl groups is 0·89 Å and the angle is 18°.

The chlorine atoms form layers parallel to (100), the atoms lying alternately 0·014 Å above and below this plane. They form a distorted hexagonal packing with Cl–Cl distances of 3·84, 3·84, 3·89, 3·94, 3·98, and 4·80 Å. All of these distances are greater than the normal van der Waals sum of 3·42 Å reported for the 5-chlorosalicylaldoxime ligand molecule (Simonsen, Pfluger & Thompson, 1961).

Except for the Cu–O(1) distance of 3·01 Å, all intermolecular approach distances are greater than 3·4 Å.

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