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The Crystal Structures of Some Metallo-Organic Chelate Compounds. I. The Ligand, 5-Chlorosalicylaldoxime

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The structure of 5-chlorosalicylaldoxime has been determined by a two-dimensional projection, and trial-and-error methods. The final parameters were evaluated by differential syntheses of the *h*0*l* data and by least-squares refinement of the *hk*0 data. The crystals are monoclinic,

$$a = 14{\cdot}35,\ b = 3{\cdot}90,\ c = 13{\cdot}69\ \text{Å};\ \beta = 100°\ 00'.$$

The space group is $P2_1/c$ with four molecules per unit cell. The molecules are planar except for the =N–OH group which lies below the plane of the benzene ring due to rotation of the oxime group around the single C–C bond. The molecules join in pairs through hydrogen bonds to form dimers, with two hydrogen bonds for each dimer.

Introduction

Despite the importance of metallo-organic chelate compounds in all areas of chemistry only a few crystal structures of the complex and of the ligand have been determined by X-ray methods. Because information concerning various factors (Merritt, 1953), influencing the formation, stability, and specificity of chelate compounds, can be gained only by the study of a number of complexes and ligands, this investigation of the structure of 5-chlorosalicylaldoxime was undertaken. Structure determinations of nickel(II) 5-chlorosalicylaldoximate, palladium(II) 5-chlorosalicylaldoximate, and palladium(II) salicylaldoximate are under way, so that the effect of metal ions on the ligand can be ascertained.

Experimental

5-Chlorosalicylaldoxime, $C_7H_6O_2NCl$, was prepared by chlorinating salicylaldehyde, and by treating the resulting 5-chlorosalicylaldehyde with hydroxylamine hydrochloride (Welcher, 1947). Well-formed, single crystals were obtained by slow evaporation of a saturated solution of the compound in carbon tetrachloride.

The unit-cell dimensions and space group (Simonsen & Pfluger, 1957) were determined from rotation, Weissenberg, and precession photographs, using copper $K\alpha$ radiation. The unit cell is monoclinic with

$$a = 14{\cdot}35,\ b = 3{\cdot}90,\ c = 13{\cdot}69\ \text{Å};\ \beta = 100°\ 00'.$$

Characteristic extinctions were noted which are those required by the space group $P2_1/c$. The unit cell contains four molecules suggesting, because of the assumed formula, that all atoms are in the general positions. The observed density (by flotation) was 1·510 g.cm.$^{-3}$, and the calculated density with four molecules per unit cell was 1·510 g.cm.$^{-3}$.

The intensities were evaluated by a direct photometric measurement (Hoss, 1957) of multiple-film Weissenberg photographs. The *h*0*l* data were taken from two crystals, both needles having very nearly square cross sections of 0·154 mm. and 0·178 mm., respectively. For crystals of this size no absorption corrections were necessary. The two sets of data were corrected for extinction by the method of Pringle (1954) and averaged. The *hk*0 data were collected from one crystal. All intensities were corrected by the usual Lorentz and polarization factors, and relative $|F_o|$ values obtained.

Determination of atomic positions

The corrected *h*0*l* intensities were used to compute a Patterson projection. Because of the presence of the

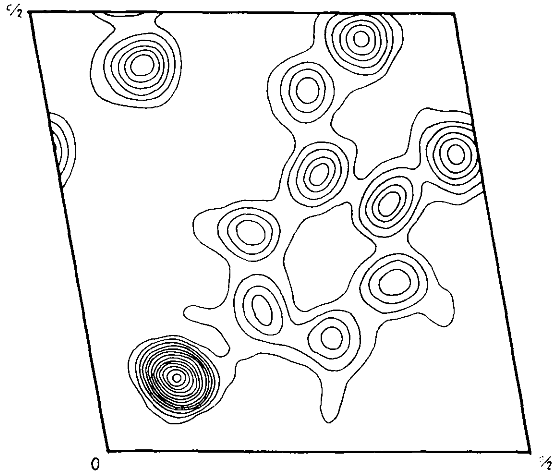

Fig. 1. Fourier projection on (010). Contours at arbitrary intervals.

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Table 1. *Observed and calculated structure factors*

hkl	$\lvert F_o \rvert$	F_c
100*	—	−12·66
200	6·63	−7·89
300	21·96	−22·37
400	31·92	−30·34
500	45·12	−46·54
600	25·46	−21·26
700	2·95	−2·27
800	31·17	−29·81
900	4·40	6·44
10,0,0	3·70	2·12
11,0,0	13·89	14·98
12,0,0	17·28	17·25
13,0,0	6·81	6·50
14,0,0	4·90	3·68
15,0,0	4·96	4·96
16,0,0	—	−2·15
17,0,0	3·75	2·34
18,0,0	5·96	−5·60
002	29·47	−29·34
102	17·78	20·29
202	25·46	−26·91
302	23·61	−24·33
402	25·93	−21·20
502	43·13	−46·20
602	—	−2·97
702	10·80	−12·61
802	6·63	5·26
902	23·78	21·09
10,0,2	10·53	10·41
11,0,2	40·77	37·53
12,0,2	3·61	−1·16
13,0,2	—	−2·09
14,0,2	12·50	−10·15
15,0,2	4·20	−2·94
16,0,2	13·03	−8·99
17,0,2	4·28	−2·77
004	56·66	−59·02
104	3·84	1·28
204	59·67	−60·39
304	21·61	−20·81
404	41·86	−40·55
504	7·61	5·79
604	35·48	35·81
704	21·36	20·47
804	32·79	31·91
904	29·76	26·45
10,0,4	14·55	−15·57
11,0,4	21·32	−19·78
12,0,4	5·68	6·98
13,0,4	7·50	−6·39
14,0,4	8·15	−6·77
15,0,4	3·46	−3·23
16,0,4	3·54	−2·31
006	25·95	−27·37
106	23·33	−28·52
206	33·80	−33·79
306	61·83	64·96
406	19·61	17·16
506	17·83	14·86
606	21·96	18·52
706	9·43	7·45
806	5·38	−6·80
906	9·71	−6·16
10,0,6	8·90	10·46
11,0,6	20·72	−18·78
12,0,6	5·54	−5·30
13,0,6	12·25	−8·63
008	14·44	14·80
108	10·19	10·60
208	20·68	19·99
308	8·86	6·37
408	29·23	31·35
508	—	3·75
608	8·28	7·58
708	10·57	−9·91
808	18·71	−16·92
908	7·15	−5·88
10,0,8	12·31	−10·67
11,0,8	5·90	−4·03
12,0,8	2·77	−3·12
13,0,8	7·08	3·95
14,0,8	11·13	7·00
0,0,10	39·25	43·72
1,0,10	14·74	15·85
2,0,10	9·42	9·88
3,0,10	—	−3·46
4,0,10	5·29	2·25
5,0,10	22·79	−19·82
6,0,10	9·24	−8·42
7,0,10	—	0·55
8,0,10	14·15	−13·22
9,0,10	—	−2·74
10,0,10	—	−0·97
11,0,10	8·80	6·87
12,0,10	8·83	6·31
13,0,10	6·63	2·61
0,0,12	15·10	−14·97
1,0,12	17·15	16·73
2,0,12	10·57	−8·60
2,0,12	4·71	−3·35
4,0,12	7·50	−7·64
5,0,12	7·69	−7·35
6,0,12	8·74	−8·49
7,0,12	3·83	−3·01
8,0,12	4·07	3·51
9,0,12	4·61	2·60
10,0,12	8·92	6·43
0,0,14	6·54	−7·42
1,0,14	—	−4·05
2,0,14	9·61	−9·67
3,0,14	6·33	−7·81
4,0,14	5·50	−5·03
5,0,14	—	−0·06
6,0,14	—	2·42
7,0,14	6·51	5·32
8,0,14	5·46	6·20
0,0,16	3·06	−3·65
1,0,16	8·27	8·63
2,0,16	—	−0·51
3,0,16	—	2·64
4,0,16	5·33	4·73
$\bar{1}02$	28·09	−29·62
$\bar{2}02$	88·07	90·72
$\bar{3}02$	94·92	97·02
$\bar{4}02$	15·49	16·32
$\bar{5}02$	24·49	20·69
$\bar{6}02$	12·45	10·69
$\bar{7}02$	62·93	−65·03
$\bar{8}02$	25·28	−29·35
$\bar{9}02$	7·09	−7·01
$\overline{10},0,2$	6·09	−9·24
$\overline{11},0,2$	12·87	−11·99
$\overline{12},0,2$	7·08	4·90
$\overline{13},0,2$	—	0·28
$\overline{14},0,2$	23·60	24·53
$\overline{15},0,2$	5·47	5·61
$\bar{1}04$	13·22	12·07
$\bar{2}04$	32·56	−32·56
$\bar{3}04$	86·07	89·53
$\bar{4}04$	2·58	2·92
$\bar{5}04$	28·25	30·34
$\bar{6}04$	26·98	27·65
$\bar{7}04$	10·98	−10·23
$\bar{8}04$	27·10	27·92
$\bar{9}04$	26·75	−27·13
$\overline{10},0,4$	9·53	−11·79
$\overline{11},0,4$	19·29	−19·11
$\overline{12},0,4$	3·87	−6·32
$\overline{13},0,4$	7·67	−6·84
$\overline{14},0,4$	3·52	−2·88
$\overline{15},0,4$	—	2·44
$\overline{16},0,4$	5·65	6·49
$\overline{17},0,4$	9·38	8·68
$\overline{18},0,4$	3·92	3·93
$\bar{1}06$	36·97	−39·31
$\bar{2}06$	2·10	5·04
$\bar{3}06$	35·32	−37·96
$\bar{4}06$	29·57	−31·13
$\bar{5}06$	31·47	34·06
$\bar{6}06$	29·22	34·58
$\bar{7}06$	19·03	23·65
$\bar{8}06$	18·03	22·33
$\bar{9}06$	22·40	22·11
$\overline{10},0,6$	26·88	−25·22
$\overline{11},0,6$	—	−7·57
$\overline{12},0,6$	4·00	−5·54
$\overline{13},0,6$	3·67	−5·82
$\overline{14},0,6$	7·36	−7·47
$\overline{15},0,6$	—	−2·77
$\overline{16},0,6$	6·03	−2·85
$\bar{1}08$	30·16	−30·86
$\bar{2}08$	3·41	−4·81
$\bar{3}08$	27·41	−32·33
$\bar{4}08$	—	−8·38
$\bar{5}08$	5·70	−8·15
$\bar{6}08$	14·78	−14·59
$\bar{7}08$	—	2·57
$\bar{8}08$	6·84	9·46
$\bar{9}08$	11·28	13·82
$\overline{10},0,8$	5·16	8·85
$\overline{11},0,8$	38·62	37·97
$\overline{12},0,8$	10·64	−7·46
$\overline{13},0,8$	11·61	−12·30
$\overline{14},0,8$	4·69	−6·17
$\overline{15},0,8$	4·66	−5·98
$\overline{16},0,8$	4·58	−4·72
$\bar{1},0,10$	—	5·70
2,0,10	—	−4·38
$\bar{3},0,10$	3·89	−6·33
$\bar{4},0,10$	18·35	−21·25
$\bar{5},0,10$	5·85	−8·29
$\bar{6},0,10$	10·90	−16·44
$\bar{7},0,10$	7·13	−7·64
$\bar{8},0,10$	4·27	2·20
$\bar{9},0,10$	3·03	−3·71
$\overline{10},0,10$	11·17	12·80
$\overline{11},0,10$	6·58	−0·94
$\overline{12},0,10$	3·38	6·55
$\overline{13},0,10$	7·80	9·31
$\overline{14},0,10$	7·05	7·36
$\bar{1},0,12$	—	0·99
$\bar{2},0,12$	26·10	26·79
$\bar{3},0,12$	14·55	20·38
$\bar{4},0,12$	—	3·32
$\bar{5},0,12$	—	−0·02
$\bar{6},0,12$	3·69	−6·67
$\bar{7},0,12$	15·05	−19·61
$\bar{8},0,12$	—	−8·10
$\bar{9},0,12$	4·55	−7·44
$\overline{10},0,12$	—	0·47
$\overline{11},0,12$	—	−1·89
$\overline{12},0,12$	6·66	4·39
$\overline{13},0,12$	—	2·59
$\overline{14},0,12$	8·45	8·41
$\bar{1},0,14$	9·66	10·09
$\bar{2},0,14$	—	2·69
$\bar{3},0,14$	4·40	0·00
$\bar{4},0,14$	4·42	7·33
$\bar{5},0,14$	7·74	9·01
$\bar{6},0,14$	—	3·06
$\bar{7},0,14$	—	2·31
$\bar{8},0,14$	6·46	4·60
$\bar{9},0,14$	7·91	−8·98
$\overline{10},0,14$	8·72	−10·62
$\overline{11},0,14$	—	−2·16
$\overline{12},0,14$	5·12	−3·89
$\overline{13},0,14$	5·39	2·39
$\bar{1},0,16$	7·19	−7·43
$\bar{2},0,16$	—	−0·51
$\bar{3},0,16$	4·12	−3·51
$\bar{4},0,16$	—	0·55
$\bar{5},0,16$	9·01	7·56
$\bar{6},0,16$	—	3·64
$\bar{7},0,16$	7·34	8·12
010	—	0·40
110	59·94	−61·93
210	3·90	−4·67
310	23·05	−26·78
410	31·92	−33·48
510	25·89	−26·92
610	15·61	14·36
710	7·09	6·84
810	12·06	10·25
910	9·22	9·23
10,1,0	15·25	15·27
11,1,0	5·67	6·57
12,1,0	13·48	11·47
13,1,0	13·83	−13·22
14,1,0	4·26	−3·83
15,1,0	6·74	−5·37
16,1,0	3·19	−1·84
020	4·61	3·95
120	—	−3·20
220	8·51	−9·58
320	2·13	1·17
420	15·25	−15·44
520	7·45	8·13
620	11·70	13·68
720	9·93	10·68
820	—	−1·39
920	5·68	3·54
10,2,0	5·68	−4·85
11,2,0	3·55	2·76
12,2,0	7·80	−7·31

Table 1 (*cont.*)

hkl	$\|F_o\|$	F_c	hkl	$\|F_o\|$	F_c	hkl	$\|F_o\|$	F_c	hkl	$\|F_o\|$	F_c
13,2,0	7·45	−7·92	230	4·61	−6·04	930	2·48	3·29	340	2·84	4·43
14,2,0	5·67	6·24	330	—	−0·40	10,3,0	3·55	5·36	440	4·61	5·09
15,2,0	—	−1·03	430	7·80	−9·78				540	3·90	−1·80
16,2,0	—	−0·88	530	5·32	6·15	040	—	−2·95	640	—	3·38
			630	—	−3·29	140	3·55	−5·96	740	—	2·26
030	—	0·40	730	2·48	3·61	240	3·55	−5·51	840	2·84	4·65
130	7·09	5·90	830	4·97	−5·89						

heavy chlorine atom, the (010) projection showed directly the orientation and location of the molecule. Using x and z coordinates obtained from the Patterson projection, structure factors were calculated. The signs were applied to the observed structure factors and an electron-density projection was computed (Fig. 1). The x and z parameters were then refined by Booth's (1946) differential synthesis method.

The shortening of the benzene bond lengths in the (010) projection showed that the molecules were tilted out of the (010) plane. A trial structure was obtained by assuming planarity of the molecule; by estimating the angle of tilt from the projection; and from accepted bond lengths and angles. An (001) Patterson projection was then computed, despite the expectation of poor resolution, in the hope that a chlorine–chlorine peak could be recognized, thus establishing the y parameter of the chlorine atom and making possible the estimation of all the y parameters. However, the Patterson projection could not be interpreted, so $hk0$ structure factors were calculated, using y parameters estimated from the trial structure. The molecule was then moved up the b axis in intervals of 0·05 y, and the calculated structure factors compared with the observed values. The best reliability factor, R, obtained by this procedure was 0·48. A number of least-squares cycles using the 'best' parameters failed to refine this trial structure appreciably. A trial was then made of a structure in which the axis of tilt was not parallel to the (010) plane. This structure improved rapidly upon least-squares refinement. Because of the small number of reflections available for the $hk0$ refinement, the x parameters, derived from refinement of the $h0l$ data, were held constant during all cycles, and only the y parameters and individual isotropic temperature parameters allowed to vary. Individual isotropic temperature parameters of the form

$$\exp\,[-B\,(\sin\theta/\lambda)^2]$$

were estimated for the ($h0l$) structure factors during the differential synthesis refinement by adjusting the values so that after the final cycle, $\varrho_o=\varrho_c$. Final values of observed and calculated structure factors are given in Table 1, and the final values of the parameters in Table 2.

The atomic scattering factor for chlorine was taken from Thomas & Umeda (1957) and the factors for carbon, oxygen, and nitrogen were taken from Berghuis *et al.* (1955). The final refinements were carried out with an IBM 650 using Shiono's (1957) differential synthesis program modified for two-dimensional projections; and the least-squares LSII program of Senko (1957) as modified by Fitzwater (1958).

Table 2. *Final atomic positional and temperature parameters*

	x/a	y/b	z/c	B ($h0l$)	B ($hk0$)
C_1	0·3146	0·2002	0·3082	4·25	3·59
C_2	0·2832	0·0482	0·3875	4·25	3·59
C_3	0·1916	−0·0914	0·3813	4·25	4·78
C_4	0·1289	−0·0417	0·2893	4·25	5·18
C_5	0·1613	0·1026	0·2099	4·25	4·30
C_6	0·2515	0·2407	0·2167	4·25	4·11
C_7	0·4103	0·3421	0·3113	4·25	3·92
O_1	0·3428	−0·0012	0·4736	5·00	6·09
O_2	0·5591	0·4344	0·3774	5·00	4·66
N	0·4713	0·3032	0·3863	5·00	4·06
Cl	0·0819	0·1535	0·0958	4·50	5·37

Accuracy

The final reliability factors $[R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|]$ were 0·144, including 36 unobserved reflections out of a possible 233, for the $h0l$ zone; and 0·144, including 12 unobserved reflections out of a possible 72, for the $hk0$ zone. Omitting the unobserved reflections, $R=$ 0·113 and 0·110 for the $h0l$ zone and $hk0$ zone, respectively. The standard deviations of the x and z parameters were estimated by Cruickshank's (1949) method; the standard deviations of the y parameters were obtained from the least-squares treatment. There was little difference among the atoms, and $\sigma(x)=\sigma(y)=\sigma(z)$. The average values are given in Table 3, and the standard deviations of the bond lengths in Table 4.

Table 3. *Average standard deviations of atomic coordinates*

$\sigma(x)=\sigma(y)=\sigma(z)$

	σ		σ
C_{1-7}	0·011 Å	N	0·010 Å
$O_{1,2}$	0·009	Cl	0·003

Discussion

The mean plane through the carbon, chlorine, and phenolic oxygen atoms was calculated by the least-squares method of Schomaker *et al.* (1959), and the equation of the plane is:

$$-4\cdot96919X+3\cdot30053Y+4\cdot63442Z-0\cdot534698=0\,,$$
$$\lambda^{(1)}=2\cdot30\times10^{-3}.$$

The average deviation of these atoms from the plane is 0·018 Å, so that the molecule is essentially planar except for the nitrogen, which is −0·086 Å out of the plane, and the oxime oxygen, which is −0·130 Å out of the plane. The departure of the oxime group from the plane can be accomplished without distortion by rotation about the C_1–C_7 single bond.

Table 4. *Bond lengths and angles*

Bond	Length	σ	Atoms	Angle
C_1–C_2	1·379 Å	0·017 Å	C_7–N–O_2	113·9°
C_2–C_3	1·412	0·017	C_1–C_7–N	120·0
C_3–C_4	1·428	0·015	C_2–C_1–C_7	124·7
C_4–C_5	1·375	0·016	C_1–C_2–O_1	120·4
C_5–C_6	1·390	0·016	C_6–C_1–C_2	119·8
C_6–C_1	1·421	0·016	C_1–C_2–C_3	123·1
C_1–C_7	1·474	0·016	C_2–C_3–C_4	116·0
C_7–N	1·237	0·016	C_3–C_4–C_5	120·3
N–O_2	1·385	0·013	C_4–C_5–C_6	123·0
C_2–O_1	1·345	0·015	C_5–C_6–C_1	117·4
C_5–Cl	1·777	0·012	C_4–C_5–Cl	119·2

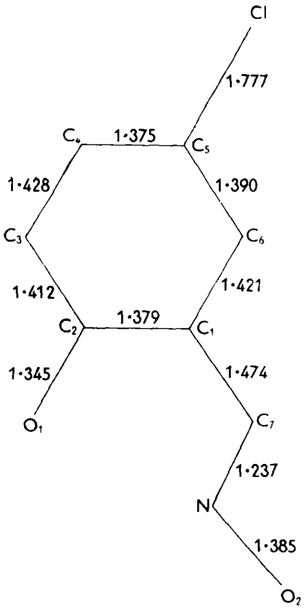

Fig. 2. Bond distances.

The intramolecular bond distances and bond angles are given in Table 4 and in Fig. 2. The bond lengths are all normal and compare reasonably well with those reported in previous structure determinations, except that the C=N distance appears to be a little short. Some comparisons are made in Table 5. The average value of the benzene carbon–carbon distances is 1·401 Å, and the average angle is 119·9°.

The intermolecular distance of 2·828 Å for the O_1–O_2' indicates that molecules join in pairs through hydrogen bonds to form dimers, with two hydrogen bonds for each dimer. The 3·420 Å Cl–Cl distance between two dimers is a normal van der Waals sum.

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Table 5. *Comparison of bond lengths*

Compound	-C=N-	-N-O-	C_1–C_7	C_2–O_1	C_5–Cl
5-Chlorosalicylaldoxime	1·237	1·385	1·474	1·345	1·777
Syn-*p*-chlorobenzaldoxime[1]	1·31	1·36	1·45	—	1·78
Dimethylglyoxime[2]	1·27	1·38	—	—	—
Acetoxime[3]	1·29	1·36	—	—	—
Salicylic acid[4]	—	—	1·458	1·361	—
Benzoic acid[5]	—	—	1·48	—	—
1:5 Dichloronaphthalene[6]	—	—	—	—	1·76

[1] Jerslev (1950).

[2] Merritt & Lanterman (1952).

[3] Bierlein & Lingafelter (1951).

[4] Cochran (1953).

[5] Sim, Robertson & Goodwin (1955).

[6] Kitaigorodskij & Kabalkina (1951).