Acta Cryst. (1964). **17**, 1058

The Crystal Structure of bis-(*N*-phenylsalicylaldiminato)copper(II)

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(*Received* 30 *August* 1963)

The crystal structure of bis-(*N*-phenylsalicylaldiminato)copper(II), $[OC_6H_4CHNC_6H_5]_2Cu$, has been determined from three-dimensional X-ray diffraction data, *h*0*l* through *h*5*l*. The cell has dimensions $a=12{\cdot}15$, $b=7{\cdot}96$, $c=11{\cdot}94$ Å, $\beta=111°\,44'$, space group $P2_1/n$, and contains two molecules.

The coordination of the copper(II) ion is planar with Cu–O = 1·88 Å and Cu–N = 1·99 Å. The molecule, although centrosymmetric, is markedly non-planar, the two salicylaldimine groups being parallel but not coplanar, with a separation of 0·89 Å. The phenyl groups are roughly perpendicular to the remainder of the molecule.

Introduction

The cell dimensions and space group of bis-(*N*-phenylsalicylaldiminato)copper(II), $[OC_6H_4CHNC_6H_5]_2Cu$, have been reported by von Stackelberg (1947) and a report on a preliminary study of the structure has been given by Block (1958). We have now completed a three-dimensional determination of the crystal structure from X-ray diffraction data.

Experimental

The Schiff base, *N*-phenylsalicylaldimine, was prepared by the reaction between aniline and salicylaldehyde in ethanol–water solution. To this solution was added the stoichiometric amount of copper(II) acetate and the mixture was refluxed for one hour. The product, separated as a dark brown powder, was recrystallized from ethanol, yielding rhomb-shaped monoclinic plates on $\{10\bar{1}\}$, bounded by $\{110\}$.

Cell dimensions were determined from rotation, zero-level Weissenberg, and precession photographs, with Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å). Calibration was made by superposition of diffraction patterns of NaCl ($a=5{\cdot}6394$ Å) on the films used for measurement. The cell dimensions are:

$$a=12{\cdot}145,\ b=7{\cdot}956,\ c=11{\cdot}935 \text{ Å (all } \pm 0{\cdot}01 \text{ Å)};$$
$$\beta=111°\,44'.$$

The cell contains two molecules. Density calculated is 1·412 g.cm^{-3}, observed 1·396 g.cm^{-3}. Systematic absence of *h*0*l* for $h+l$ odd and of 0*k*0 for k odd indicate the space group to be $P2_1/n$. With appropriate changes of axes, these results agree satisfactorily with those reported by earlier investigators.

Intensities were obtained from a set of integrated equi-inclination Weissenberg photographs, *h*0*l* through *h*5*l*, with Cu $K\alpha$ radiation. Camera integration was carried out in one direction only, normal to the rotation axis. Diffraction spots were then 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 areas under the densitometer tracings were measured with a planimeter and used as relative intensities. The range of intensities, 1 to 10,000 was obtained by the use of multiple films and a range of exposure times. The intensities from the several films for a given level were placed on the same scale by comparison of common spots. The several levels were then placed on a common scale by the use of intensities from an integrated *hk*0 Weissenberg photograph.

Of the 2451 reflections within the limiting sphere, 1682 (68·4%) were examined and intensities measured for 1475. 207 reflections were found to be too weak for measurement.

Lorentz and polarization factors were applied and observed structure factors calculated by data reduction programs for the IBM 709 computer written in this Laboratory. No correction was made for absorption.

The atomic scattering factors used were those of Viervoll & Øgrim (1949) for copper, Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for nitrogen and carbon, and McWeeny (1951) for oxygen and hydrogen. No correction was made for anomalous dispersion.

Structure determination

The presence of two copper atoms in a cell of space group $P2_1/n$ requires that they be in a twofold set of special positions. They were therefore placed at 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and an electron-density projection on (010) was calculated with all *h*0*l* phases equal to zero. All of the atoms appeared clearly, although not completely resolved, on this projection and their x and z parameters were refined by a series of two-dimensional difference syntheses to $R_{h0l}=11{\cdot}5\%$. R is defined throughout as $\Sigma||F_o|-|F_c||/\Sigma|F_o|$, where the summation is over the unique, observed reflections

only. Consideration of the projected bond lengths made possible the estimation of approximate y coordinates. With these coordinates and an overall isotropic temperature factor, a series of four three-dimensional Fourier syntheses and two difference syntheses reduced R to 14·9%.

The refinement was continued with the Busing & Levy (1959) full matrix least-squares program. A modified Hughes weighing scheme was used, with $\sqrt{w}=0$ for unobserved reflections for which $F_c \leq F_{\min}$, $\sqrt{w}=1$ for unobserved reflections for which $F_c > F_{\min}$ and for observed reflections with $F_o \leq 8$, and $\sqrt{w}=8/F_o$ for reflections with $F_o > 8$. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$. Individual atom anisotropic temperature factors were used. Two cycles of refinement reduced R to 8·0%. At this point the hydrogen atoms were introduced in calculated positions and 20 reflections (marked E in Table 3) were omitted from subsequent calculations because of secondary extinction effects. Three cycles of least-squares refinement followed by adjustment of scale factor reduced R to the final value of 5·8%. During the last cycle no parameter shifted by more than $0{\cdot}1\sigma$.

The final parameters and their estimated standard deviations are given in Tables 1 and 2. Final values of observed and calculated structure factors are given in Table 3.

Table 1. *Atomic coordinates and their e.s.d.'s*

($\times 10^4$)

Atom	x/a	σ_x	y/b	σ_y	z/c	σ_z
Cu	0000	0	0000	0	0000	0
O	−0036	3	−0256	4	1550	3
N	1008	3	−2042	5	0211	3
C(1)	0248	5	−3703	8	−1628	5
C(2)	0384	7	−4377	10	−2656	6
C(3)	1368	7	−4139	10	−2871	6
C(4)	2268	7	−3268	10	−2071	6
C(5)	2183	5	−2547	8	−1010	5
C(6)	1170	4	−2775	6	−0819	3
C(7)	1607	4	−2706	6	1257	3
C(8)	1531	4	−1478	7	4662	3
C(9)	2338	4	−2630	8	4576	4
C(10)	2351	4	−2985	8	3457	4
C(11)	1558	3	−2204	6	2393	3
C(12)	0735	3	−1032	6	2482	3
C(13)	0722	4	−0689	7	3646	3
H(1)	−0542		−3901		−1472	
H(2)	−0292		−5147		−3247	
H(3)	1449		−4571		−3677	
H(4)	3080		−3133		−2204	
H(5)	2889		−1832		−0398	
H(7)	2190		−3700		−1284	
H(8)	1513		−1189		5517	
H(9)	2927		−3239		5350	
H(10)	2976		−3847		3382	
H(13)	0103		0159		3744	

Discussion

The presence of only two molecules in the cell of space group $P2_1/n$ requires that the molecule be centrosymmetric. Intramolecular distances and angles are

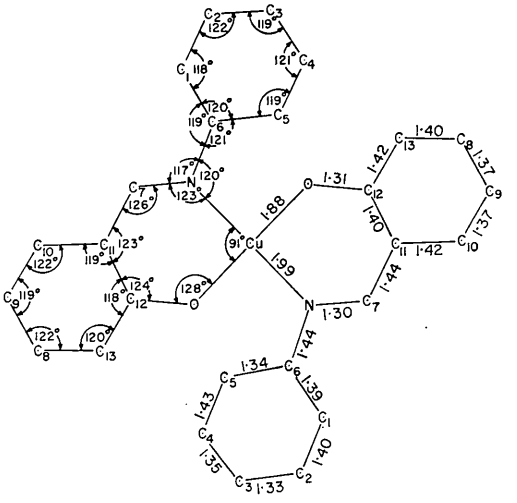

Fig. 1. Bond lengths and angles.

Table 2. *Thermal parameters and their e.s.d.'s*

(All $\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	66(1)	120(3)	57(1)	13(1)	22(1)	3(1)
O	71(2)	118(10)	43(2)	53(3)	28(2)	20(3)
N	70(2)	101(9)	53(2)	13(3)	27(2)	5(3)
C(1)	138(5)	165(17)	95(4)	−14(6)	62(4)	−42(6)
C(2)	244(10)	174(16)	108(6)	−16(10)	95(6)	−50(7)
C(3)	223(9)	187(18)	115(6)	11(10)	117(7)	−16(8)
C(4)	203(8)	227(17)	145(7)	77(10)	137(7)	63(9)
C(5)	115(5)	213(15)	107(4)	28(6)	74(4)	30(6)
C(6)	105(4)	61(11)	72(3)	32(4)	47(3)	15(4)
C(7)	80(3)	114(12)	71(3)	34(4)	36(3)	21(4)
C(8)	111(4)	162(13)	50(3)	8(5)	31(3)	12(4)
C(9)	94(4)	231(15)	61(3)	29(6)	21(3)	38(5)
C(10)	93(4)	213(15)	74(3)	48(5)	33(3)	39(5)
C(11)	62(3)	132(11)	57(3)	11(4)	25(2)	14(4)
C(12)	64(3)	112(12)	49(2)	1(4)	21(2)	7(4)
C(13)	92(4)	133(12)	59(3)	16(5)	33(3)	3(4)

All hydrogen atoms were given isotropic $B=3{\cdot}50$ Å^2

Table 3. *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

Table 3 (*cont.*)

shown in Fig. 1 and listed with their estimated standard deviations in Table 4. The molecule may be described in terms of a set of five planar groups: the coordination group CuN_2O_2; the two salicylaldimine groups, parallel but not coplanar; and the two phenyl groups. The equations for the least-squares planes through these groups are given in Table 5, based on a set of Cartesian axes lying along *a*, *b* and *c**.

The coordination of the copper(II) ion is planar, the more common distorted octahedral coordination being prevented by the bulky phenyl groups. The Cu–O and Cu–N distances of 1·88 and 1·99 Å, respectively, agree well with the corresponding distances of 1·90 and 1·99 Å found in bis-(*N*-methylsalicylaldiminato)copper(II) (Lingafelter, Simmons, Morosin, Scheringer & Freiburg, 1961). The intrachelate angles in the *N*-phenyl and *N*-methyl compounds, 91·4° and 91·1°, are also in agreement.

The benzene ring and the oxygen atom in the salicylaldimine group are strictly coplanar (maximum distance of any atom from the least-squares plane, 0·012 Å), but the external carbon atom, C(7), and the nitrogen atom are slightly but significantly out of the plane. The two salicylaldimine groups are, of course, parallel as required by the centrosymmetry, but are far from coplanar. The perpendicular distance between the two parallel salicylaldimine planes is 0·89 Å, considerably larger than has been reported for any other similar molecule. Each salicylaldimine group makes an angle of 18° with the coordination plane.

Table 4. *Bond distances and angles and their e.s.d.'s*

Bond	(Å)	(Å)	Angle	(°)	(°)
Cu–O	1·878	(0·003)	O–Cu–N	91·4	(0·2)
Cu–N	1·993	(0·004)	Cu–O–C(12)	128·0	(0·4)
O–C(12)	1·313	(0·004)	Cu–N–C(7)	123·4	(0·3)
N–C(7)	1·302	(0·005)	Cu–N–C(6)	119·6	(0·3)
N–C(6)	1·438	(0·006)	C(6)–N–C(7)	116·8	(0·5)
C(1)–C(2)	1·404	(0·010)	N–C(6)–C(1)	118·6	(0·6)
C(2)–C(3)	1·326	(0·014)	N–C(6)–C(5)	120·9	(0·6)
C(3)–C(4)	1·347	(0·010)	C(6)–C(1)–C(2)	119·0	(0·8)
C(4)–C(5)	1·429	(0·010)	C(1)–C(2)–C(3)	121·4	(1·0)
C(5)–C(6)	1·343	(0·008)	C(2)–C(3)–C(4)	119·3	(1·0)
C(6)–C(1)	1·389	(0·007)	C(3)–C(4)–C(5)	121·9	(1·0)
C(7)–C(11)	1·436	(0·006)	C(4)–C(5)–C(6)	117·9	(0·8)
C(8)–C(9)	1·373	(0·008)	N–C(7)–C(11)	126·1	(0·5)
C(9)–C(10)	1·371	(0·007)	C(7)–C(11)–C(10)	118·1	(0·5)
C(10)–C(11)	1·421	(0·005)	C(7)–C(11)–C(12)	122·5	(0·5)
C(11)–C(12)	1·399	(0·006)	C(10)–C(11)–C(12)	119·4	(0·5)
C(12)–C(13)	1·422	(0·006)	O–C(12)–C(11)	123·7	(0·5)
C(13)–C(8)	1·396	(0·006)	O–C(12)–C(13)	118·3	(0·5)
C(1)–O′	3·164				
C(5)–O′	3·308		C(11)–C(12)–C(13)	118·0	(0·5)
C(2)–C(13′)	3·261		C(8)–C(13)–C(12)	120·3	(0·5)
C(3)–C(13′)	3·619		C(9)–C(8)–C(13)	121·9	(0·6)
C(4)–C(13′)	3·984		C(8)–C(9)–C(10)	118·5	(0·6)
			C(9)–C(10)–C(11)	122·1	(0·6)

Table 5. *Equations for least-squares planes*

Coordination	$-0{\cdot}0823x-0{\cdot}0634y-0{\cdot}0424z=$	0
Salicylaldimine No. 1	$-0{\cdot}0871x-0{\cdot}0954y-0{\cdot}0140z=$	0·0581
Salicylaldimine No. 2	$-0{\cdot}0871x-0{\cdot}0954y-0{\cdot}0140z=$	−0·0581
Phenyl No. 1	$-0{\cdot}0481x+0{\cdot}1976y-0{\cdot}1188z=$	−0·4158
Phenyl No. 2	$-0{\cdot}0481x+0{\cdot}1976y-0{\cdot}1188z=$	0·4158

The bond distances and angles within the salicylaldimine group appear to be normal.

The phenyl group shows no significant deviation from planarity (maximum distance of any atom from the least-squares plane, 0·010 Å). The several bond distances and angles in the phenyl group appear to be significantly different, but we are unable to suggest any interpretation of the differences.

The phenyl groups are roughly perpendicular to the remainder of the molecule, making an angle of 82·3° with the coordination group and 64·9° with the salicylaldimine group.

The shortest intermolecular contact distance of each atom is given in Table 6.

Dobler (1962) has recently reported the cell dimensions and space group of the corresponding nickel(II) compound. After making the appropriate transformation of axes, a comparison of the two cells:

Table 6. *Shortest intermolecular distances*

Atom	Distance	Neighbor
C(1)	3·77 Å	C(7) at $-x, -1-y, -z$
C(2)	3·69	C(11) at $-x, -1-y, -z$
C(3)	3·69	C(4) at $\frac{1}{2}-x, -\frac{1}{2}+y, -\frac{1}{2}-z$
	3·69	C(8) at $x, y, -1+z$
C(4)	3·69	C(3) at $\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$
C(5)	3·33	C(13) at $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
C(6)	3·90	C(13) at $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
C(7)	3·45	C(13) at $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
C(8)	3·60	C(5) at $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
C(9)	3·60	O at $\frac{1}{2}+x, -\frac{1}{2}-y, \frac{1}{2}+z$
C(10)	3·45	Cu at $\frac{1}{2}+x, -\frac{1}{2}-y, \frac{1}{2}+z$
C(11)	3·69	C(2) at $-x, -1-y, -z$
C(12)	3·80	C(10) at $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
C(13)	3·33	C(5) at $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
N	3·82	C(10) at $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
O	3·60	C(9) at $-\frac{1}{2}+x, -\frac{1}{2}-y, -\frac{1}{2}+z$
Cu	3·45	C(10) at $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$

Cu: $a=12{\cdot}15$, $b=7{\cdot}96$, $c=11{\cdot}94$ Å, $\beta=111°\,44'$, $V=1073$ Å^3,

Ni: $a=12{\cdot}64$, $b=7{\cdot}63$, $c=11{\cdot}81$ Å, $\beta=112°\,13'$, $V=1054$ Å^3,

indicates that the two molecules are nearly, but not completely, identical in structure.

This investigation was supported in part by the U.S. Public Health Service under Research Grant GM 10842.

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