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The Crystal Structure of Copper(II) 2-(*o*-Hydroxyphenyl)-benzoxazole

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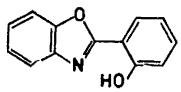
The structure of copper(II) 2-(*o*-hydroxyphenyl)benzoxazole is built up of parallel and almost planar molecules $Cu(C_{13}H_8NO_2)_2$, linked together by weak Cu—O bonds along the *b*-axis. The coordination about copper is a distorted (4+2) octahedron. Two nitrogen and two oxygen atoms form a square plane with a copper atom in the centre and two more oxygen atoms are situated at a comparatively large distance, 2.81 ± 0.01 Å, from the plane. Thus endless chains of octahedra, sharing opposite edges, extend along the *b*-axis.

The crystal structure has been determined from X-ray data and refined by full matrix least-squares methods, giving the *R*-value 0.111 for 777 observed independent reflections. The crystals are monoclinic (space group $C2/c$) with $a = 24.171 \pm 0.004$ Å, $b = 3.7609 \pm 0.0003$ Å, $c = 21.553 \pm 0.003$ Å, and $\beta = 98.85° \pm 0.02°$. The cell contains four formula units.

2-(*o*-Hydroxyphenyl)benzoxazole, 

is known as a chelating agent for quite a number of bivalent metal ions.[1] Stability investigations indicate the presence of complexes of the types MeA^+ and MeA_2 in solution[1,2] (Me = metal, A = ligand). The metal chelates are, however, practically insoluble in aqueous media, which together with a pronounced thermal stability[3] indicate their possible use in gravimetry. Analyses of Cd^{2+}, Pd^{2+}, and Cu^{2+} with 2-(*o*-hydroxyphenyl)benzoxazole as a complexing agent have been reported in the literature.[4–6]

The crystal structure of the palladium compound has been determined by Urdy.[7] Because of the widely accepted use of 2-(*o*-hydroxyphenyl)benzoxazole in gravimetric and fluorometric analyses of Cd^{2+}, the present investigation was started with the cadmium chelate. However, it has so far not been possible to make crystals of this compound suitable for single-crystal work. The relative intensities of the lines in the Guinier photographs and the cell dimensions obtained from powder data (reported in this paper), indicate that the copper and cadmium chelates are isotypical.

The present determination of the crystal structure of copper(II) 2-(*o*-hydroxyphenyl)benzoxazole will be followed by structure reports on 2-(*o*-hydroxyphenyl)benzoxazole and some other metal chelates of this compound.

EXPERIMENTAL

Preparation. 2-(*o*-Hydroxyphenyl)benzoxazole was prepared from *o*-aminophenol and salicylamide.[8] It was vacuum-distilled, recrystallized several times from ethyl alcohol-water mixtures and dried in a vacuum desiccator. The nearly colourless crystals show a bright yellowish-green fluorescence in ultraviolet light.

The copper(II) compound was prepared by mixing stoichiometric quantities of $CuCl_2$ and 2-(*o*-hydroxyphenyl)benzoxazole in hot propyl alcohol. The crystals, appearing when the solution was allowed to cool very slowly, were light brown, non-fluorescent needles.

Analysis. Elemental analyses of $Cu(C_{13}H_8NO_2)_2$ were performed by AB Analytica, Sollentuna. Copper was determined spectrophotometrically after ignition and with oxalyldihydrazide as reagent. The carbon and hydrogen contents were determined after ignition and absorption in ascarite and in magnesium perchlorate, respectively. Nitrogen was determined according to Dumas as free nitrogen gas. (Found: Cu 12.6; C 64.9; H 3.3; N 5.6. Calc.: Cu 13.1; C 64.5; H 3.3; N 5.8.)

STRUCTURE DETERMINATION

Cell dimensions and density. The dimensions of the unit cell were determined from powder photographs recorded in a Guinier-Hägg focusing camera, using $CuK\alpha_1$ radiation and potassium chloride as an internal standard. The data were refined by a least-squares program. The cell dimensions of the corresponding cadmium chelate have also been determined in connection with the present work, and it has been found that the unit cells of the two chelates are very much alike.

$Cu(C_{13}H_8NO_2)_2$	$Cd(C_{13}H_8NO_2)_2$
$a = 24.171 \pm 0.004$ Å	$a = 25.081 \pm 0.005$ Å
$b = 3.7609 \pm 0.0003$ Å	$b = 3.697 \pm 0.001$ Å
$c = 21.553 \pm 0.003$ Å	$c = 21.437 \pm 0.007$ Å
$\beta = 98.85° \pm 0.02°$	$\beta = 98.80° \pm 0.04°$

Table 1. Computer programs used in the calculations.

Program	Subject	Authors
PIRUM	Least-squares refinement of unit cell parameters	Werner, P.-E.[9]
DRF	Lorentz and polarization factors, Fourier summations	Zalkin, A. Modified by Liminga, R. and Lundgren, J.-O.
OR FLS	Full-matrix least-squares refinement of crystal structure parameters	Busing, W. R., Martin, K. O., and Levy, H. A.[10]
LALS	Full-matrix least-squares refinement of crystal structure parameters	Zalkin, A. Modified by Liminga, R., Lundgren, J.-O., and Brändén, C.-I.[11]
DISTAN	Interatomic distances and angles	Zalkin, A.
PLANE	Plane-fitting	Brändén, C.-I.

The density of the copper compound was determined by flotation to be 1.62 g/cm³. Assuming a cell content of 4 formula units, the calculated density is 1.66 g/cm³.

Single crystal work. Weissenberg multi-film (three films) photographs corresponding to the reflections *h0l* to *h3l* were recorded, using Ni-filtered Cu$K\alpha$ radiation. The approximate dimensions of the crystal were $0.40 \times 0.03 \times 0.03$ mm³ and the crystal was mounted with its needle-axis as rotation axis. The intensities of 777 independent reflections were measured photometrically and corrected for Lorentz and polarization effects. No absorption correction was made as the value of the maximum absorption ($\mu \cdot R$) was found to be only about 0.06.

Computer programs. The calculations were carried out by means of the digital computers IBM 7090 of the *Northern Europe University Computing Center*, in Lyngby, Denmark, and CD 3600 of the *Computer Division of the National Swedish Rationalization Agency* in Uppsala. The crystallographic programs used are listed in Table 1.

Space group and atomic positions. From Weissenberg data the Laue symmetry $2/m$ was found. The systematic extinctions of reflections *hkl* for $h+k$ odd and *h0l* for h, l odd suggested one of the space groups Cc (No. 9) or $C2/c$ (No. 15), in both cases b as unique axis.[12] The discussion of these two space groups will start with $C2/c$.

The cell content of four molecules implies 4 Cu atoms and 8 organic groups in the unit cell. If space group $C2/c$ is the correct one the copper atoms have to occupy one of the five special positions. From the observed F-values (Table 3) it can be seen that strong reflections appear only for $k+l$ even, which led to the choice of the point position 4(*c*) for Cu.

Table 2. Positional and thermal parameters with estimated standard deviations. The anisotropic thermal parameters for copper are based on the expression

$$\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\}.$$

	x	y	z	B Å²
Cu	¼	¼	0	
C(1)	0.2081 (6)	0.6253 (32)	0.1025 (7)	3.2 (3)
C(2)	0.2233 (6)	0.7883 (36)	0.1610 (7)	3.6 (3)
C(3)	0.1833 (7)	0.8186 (39)	0.2012 (8)	4.3 (3)
C(4)	0.1298 (7)	0.6810 (35)	0.1842 (7)	3.9 (3)
C(5)	0.1132 (7)	0.5282 (36)	0.1276 (7)	3.9 (3)
C(6)	0.1533 (6)	0.4962 (32)	0.0849 (6)	3.2 (3)
C(7)	0.1360 (6)	0.3348 (29)	0.0257 (6)	2.6 (2)
C(8)	0.0752 (7)	0.8585 (35)	0.4474 (7)	3.7 (3)
C(9)	0.0252 (7)	0.9548 (39)	0.4104 (8)	4.3 (3)
C(10)	0.0331 (7)	0.0764 (43)	0.3517 (8)	4.6 (3)
C(11)	0.0847 (7)	0.0998 (38)	0.3318 (8)	4.4 (3)
C(12)	0.1356 (7)	0.9960 (37)	0.3724 (8)	4.2 (3)
C(13)	0.1281 (6)	0.8781 (32)	0.4304 (7)	3.1 (3)
O(1)	0.2460 (4)	0.6031 (24)	0.0646 (5)	3.8 (2)
O(2)	0.0794 (4)	0.2842 (23)	0.0071 (4)	3.8 (2)
N	0.1656 (5)	0.7628 (29)	0.4831 (5)	3.6 (2)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.0013 (1)	0.0945 (43)	0.0022 (1)	−0.0011 (6)	0.0004 (1)	−0.0033 (7)

Table 3. Observed and calculated structure factors.

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
2	0	0	63.8	67.0	16	0	-4	39.8	42.0	1	1	5	27.8	40.7	1	1	-4	85.3	69.9
4	0	0	24.9	22.0	18	0	-4	48.9	47.2	3	1	5	45.3	46.8	7	1	-4	13.5	9.9
6	0	0	65.0	65.9	24	0	-4	15.9	11.5	5	1	5	44.8	51.9	9	1	-4	16.0	16.7
8	0	0	82.9	79.8	2	0	-6	15.1	19.2	7	1	5	31.4	34.6	11	1	-4	26.4	25.2
10	0	0	61.5	68.7	6	0	-6	61.3	66.5	9	1	5	33.6	36.3	19	1	-4	18.4	19.3
12	0	0	43.8	40.7	8	0	-6	40.3	45.9	11	1	5	56.8	59.5	1	1	-5	69.5	72.0
14	0	0	17.8	16.5	12	0	-6	46.1	40.5	13	1	5	25.7	27.6	3	1	-5	25.0	26.3
16	0	0	25.7	27.9	14	0	-6	22.7	25.3	17	1	5	18.3	15.6	5	1	-5	41.6	44.4
18	0	0	51.8	51.7	16	0	-6	23.4	24.7	19	1	5	14.1	15.4	7	1	-5	37.4	42.4
22	0	0	23.4	18.1	20	0	-6	25.3	24.4	21	1	5	18.4	21.0	11	1	-5	35.6	36.7
24	0	0	26.8	25.9	24	0	-6	26.9	24.0	23	1	5	18.0	15.9	13	1	-5	31.2	33.4
0	0	2	140.6	152.9	2	0	-8	44.7	37.1	3	1	6	24.8	22.8	15	1	-5	18.4	17.8
2	0	2	57.3	62.1	4	0	-8	29.4	35.5	5	1	6	24.6	25.4	17	1	-5	20.7	17.4
4	0	2	107.8	112.1	6	0	-8	38.3	42.8	7	1	6	26.2	26.0	19	1	-5	20.0	23.8
6	0	2	51.5	62.1	10	0	-8	24.4	20.5	9	1	6	10.8	7.4	23	1	-5	22.9	24.3
8	0	2	87.7	90.7	12	0	-8	13.9	14.6	11	1	6	17.3	19.1	25	1	-5	19.4	20.8
10	0	2	80.9	79.5	14	0	-8	26.9	28.2	13	1	6	13.8	11.3	11	1	-6	30.0	27.7
12	0	2	75.8	77.6	22	0	-8	14.1	16.3	1	1	7	64.8	60.7	13	1	-6	10.0	10.1
16	0	2	35.1	40.1	24	0	-8	21.4	19.5	3	1	7	19.3	26.8	15	1	-6	12.5	12.5
18	0	2	27.1	28.1	2	0	-10	25.9	31.5	5	1	7	15.7	18.7	17	1	-6	13.1	16.0
22	0	2	35.2	34.5	4	0	-10	59.0	56.5	7	1	7	31.1	32.9	1	1	-7	58.9	60.5
24	0	2	21.0	21.9	8	0	-10	19.0	13.4	9	1	7	23.9	26.6	3	1	-7	55.4	59.4
2	0	4	23.2	23.0	10	0	-10	15.3	14.4	11	1	7	41.3	44.5	5	1	-7	30.4	37.4
6	0	4	47.8	50.3	12	0	-10	47.5	48.6	13	1	7	29.2	31.1	7	1	-7	25.0	25.5
10	0	4	30.6	35.4	14	0	-10	25.6	28.7	15	1	7	17.9	16.3	11	1	-7	53.1	54.0
12	0	4	85.5	83.7	16	0	-10	27.2	30.2	17	1	7	14.3	10.9	13	1	-7	47.2	44.5
14	0	4	32.3	35.2	18	0	-10	13.7	12.5	19	1	7	17.1	16.6	15	1	-7	30.4	34.9
16	0	4	26.2	29.2	22	0	-10	22.6	21.6	21	1	7	14.6	16.3	17	1	-7	43.1	42.1
20	0	4	21.1	15.8	24	0	-10	13.3	11.9	1	1	8	26.5	20.0	19	1	-7	20.9	22.8
22	0	4	21.7	19.0	4	0	-12	61.1	52.4	3	1	8	19.9	20.0	23	1	-7	15.5	13.8
24	0	4	22.7	19.5	6	0	-12	47.4	47.9	5	1	8	17.1	15.2	3	1	-8	28.2	21.5
0	0	6	74.4	78.4	8	0	-12	21.0	20.4	7	1	8	14.5	11.5	5	1	-8	15.3	11.3
2	0	6	31.7	33.5	10	0	-12	20.9	19.2	9	1	8	16.9	16.4	7	1	-8	22.2	25.9
4	0	6	12.6	14.5	12	0	-12	32.3	32.5	11	1	8	15.2	16.1	11	1	-8	15.8	12.4
6	0	6	43.0	49.7	14	0	-12	38.0	34.3	1	1	9	78.0	74.5	1	1	-9	31.0	33.3
8	0	6	19.8	16.0	16	0	-12	26.6	22.9	3	1	9	35.8	36.9	3	1	-9	20.5	21.6
10	0	6	34.9	35.8	18	0	-12	17.1	16.3	5	1	9	37.1	36.9	5	1	-9	55.5	52.9
12	0	6	36.5	40.7	22	0	-12	24.4	24.3	7	1	9	31.4	31.6	7	1	-9	43.5	48.3
18	0	6	17.9	22.9	24	0	-12	19.1	18.6	9	1	9	37.6	37.4	9	1	-9	24.5	25.6
20	0	6	19.5	21.0	2	0	-14	18.0	18.3	11	1	9	44.7	41.9	11	1	-9	31.4	31.7
8	0	8	23.5	25.4	4	0	-14	30.1	29.9	13	1	9	19.0	20.7	13	1	-9	45.2	45.7
10	0	8	45.5	46.1	6	0	-14	41.9	37.9	19	1	9	22.0	24.2	15	1	-9	26.6	28.9
12	0	8	20.9	24.5	8	0	-14	14.6	15.1	1	1	10	28.9	23.7	17	1	-9	21.4	21.3
18	0	8	18.6	18.9	10	0	-14	32.3	31.0	3	1	10	19.3	14.4	23	1	-9	17.0	16.7
20	0	8	18.0	18.7	14	0	-14	39.3	33.7	11	1	10	17.3	16.1	1	1	-10	7.7	8.1
0	0	10	48.9	48.1	16	0	-14	42.9	39.3	13	1	10	17.6	15.9	5	1	-10	22.8	21.8
2	0	10	48.7	48.6	18	0	-14	23.0	21.2	1	1	11	29.0	26.8	7	1	-10	10.1	9.1
4	0	10	25.9	20.0	22	0	-14	17.0	13.7	3	1	11	17.0	19.1	11	1	-10	12.5	7.8
8	0	10	28.7	27.2	24	0	-14	16.2	13.5	5	1	11	15.3	17.3	1	1	-11	23.3	22.0
10	0	10	19.7	15.3	2	0	-16	16.7	15.2	7	1	11	23.4	21.9	3	1	-11	29.7	29.3
16	0	10	23.0	18.5	4	0	-16	23.3	16.7	9	1	11	38.6	35.8	5	1	-11	53.2	53.2
20	0	10	17.4	16.2	6	0	-16	44.1	44.4	11	1	11	38.9	40.0	7	1	-11	18.1	19.0
0	0	12	53.6	54.9	8	0	-16	22.7	20.8	13	1	11	32.4	34.7	11	1	-11	10.4	10.6
2	0	12	59.7	55.8	10	0	-16	43.0	40.6	19	1	11	19.0	17.6	13	1	-11	25.5	23.7
4	0	12	33.1	29.5	12	0	-16	23.9	20.7	3	1	12	14.7	14.2	15	1	-11	29.9	27.4
6	0	12	25.7	25.3	14	0	-16	17.2	14.4	5	1	12	14.0	14.6	17	1	-11	14.3	12.2
8	0	12	26.8	22.8	16	0	-16	44.2	42.7	13	1	12	17.6	16.9	23	1	-11	13.5	14.9
10	0	12	34.5	34.8	24	0	-16	11.7	11.3	1	1	13	40.3	36.4	1	1	-12	13.1	10.6
12	0	12	32.2	32.7	2	0	-18	22.5	19.8	5	1	13	5.8	7.4	3	1	-12	16.4	11.7
16	0	12	18.6	18.5	4	0	-18	55.1	49.1	7	1	13	24.7	21.6	7	1	-12	12.9	12.9
18	0	12	18.1	17.3	6	0	-18	47.5	43.6	13	1	13	16.5	16.2	9	1	-12	25.4	24.5
20	0	12	13.3	14.7	12	0	-18	28.8	28.6	7	1	14	25.5	23.3	15	1	-12	17.1	19.1
0	0	14	44.4	40.7	2	0	-20	19.1	16.8	1	1	15	36.8	30.9	1	1	-13	28.9	20.1
2	0	14	29.8	26.1	4	0	-20	32.3	33.6	7	1	15	26.2	22.5	3	1	-13	15.1	13.8
4	0	14	21.5	20.9	8	0	-20	18.1	16.4	11	1	15	13.4	13.6	5	1	-13	34.7	32.5
6	0	14	22.6	22.2	12	0	-20	19.1	16.5	3	1	16	14.0	8.1	7	1	-13	14.9	12.8
8	0	14	34.5	32.1						1	1	17	17.1	11.8	9	1	-13	13.7	12.5
10	0	14	29.5	26.0	1	1	0	38.8	34.8	5	1	17	19.9	20.6	11	1	-13	24.1	23.3
12	0	14	45.4	46.4	3	1	0	34.7	40.7	7	1	17	17.4	20.5	13	1	-13	14.4	12.2
14	0	14	23.3	20.4	5	1	0	11.4	4.3	11	1	17	12.5	12.3	15	1	-13	24.0	27.9
0	0	16	26.6	28.5	19	1	0	17.3	19.0	13	1	17	13.3	15.2	17	1	-13	21.2	21.2
2	0	16	24.7	26.9	1	1	1	38.4	40.4	1	1	18	7.2	12.0	23	1	-13	13.5	12.4
6	0	16	28.6	27.9	3	1	1	70.6	63.9	5	1	18	15.2	15.6	1	1	-14	15.4	8.2
8	0	16	32.3	32.1	5	1	1	10.1	6.5	7	1	19	17.4	18.8	7	1	-14	17.6	14.5
12	0	16	21.0	17.4	7	1	1	18.7	26.4	5	1	21	13.2	12.4	13	1	-14	12.2	15.9
14	0	16	18.3	17.4	11	1	1	43.5	45.0	7	1	21	18.2	8.4	1	1	-15	11.8	12.5
16	0	16	20.6	18.8	13	1	1	31.3	30.5	5	1	23	16.9	14.3	3	1	-15	17.6	14.3
0	0	18	16.5	14.1	15	1	1	14.4	15.7	1	1	-1	94.0	73.9	5	1	-15	50.4	40.5
6	0	18	40.9	35.7	23	1	1	19.2	19.0	3	1	-1	16.8	19.9	7	1	-15	28.2	19.8
12	0	18	13.2	13.7	1	1	2	87.3	74.6	5	1	-1	29.9	33.5	17	1	-15	18.2	13.6
4	0	20	24.7	22.9	3	1	2	74.0	65.3	7	1	-1	29.3	33.4	23	1	-15	11.6	13.2
6	0	20	28.9	26.6	5	1	2	12.1	8.7	9	1	-1	34.2	40.2	3	1	-16	18.3	16.9
2	0	-2	40.9	47.8	9	1	2	40.8	40.6	11	1	-1	68.1	66.8	9	1	-16	24.8	22.2
4	0	-2	66.9	65.0	17	1	2	20.1	14.4	13	1	-1	16.9	24.8	1	1	-17	18.4	14.0
6	0	-2	64.7	70.0	1	1	3	126.4	115.2	17	1	-1	36.7	39.4	3	1	-17	17.3	17.2
10	0	-2	66.5	63.6	5	1	3	24.8	28.4	1	1	-2	123.7	85.0	5	1	-17	20.5	19.3
12	0	-2	52.2	55.5	7	1	3	23.3	23.2	3	1	-2	35.9	34.0	11	1	-17	13.3	12.1
14	0	-2	19.0	23.8	11	1	3	30.1	34.7	7	1	-2	24.6	21.1	17	1	-17	17.9	16.2
16	0	-2	15.4	12.3	13	1	3	15.6	16.9	9	1	-2	34.4	36.9	7	1	-18	20.2	16.8
18	0	-2	40.3	41.0	17	1	3	23.7	26.9	1	1	-3	170.2	142.8	5	1	-19	26.7	18.5
20	0	-2	28.6	29.2	19	1	3	13.2	12.8	3	1	-3	7.4	2.6	11	1	-19	24.0	22.7
22	0	-2	19.1	17.2	23	1	3	11.6	13.7	5	1	-3	31.2	33.4	17	1	-19	20.5	16.7
24	0	-2	25.2	22.4	1	1	4	28.1	25.2	7	1	-3	47.2	48.8	3	1	-21	17.8	17.8
2	0	-4	78.8	81.3	3	1	4	43.5	37.6	9	1	-3	29.5	31.1	5	1	-21	33.8	29.3
4	0	-4	33.8	39.6	7	1	4	20.5	12.1	11	1	-3	40.1	46.5	7	1	-21	18.2	14.8
6	0	-4	42.8	48.2	9	1	4	24.1	23.1	13	1	-3	28.2	30.0	11	1	-21	14.8	13.2
10	0	-4	52.3	56.9	17	1	4	14.9	16.1	17	1	-3	25.5	28.4	3	1	-23	14.4	13.6
12	0	-4	66.9	73.0	19	1	4	12.1	14.8	23	1	-3	20.2	17.9	5	1	-23	13.0	14.2

Table 3. Continued.

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
2	2	0	61.5	43.6	8	2	12	21.1	22.2	14	2	-10	18.9	20.5	9	3	15	9.5	10.2
4	2	0	28.8	23.6	10	2	12	10.6	10.3	16	2	-10	29.2	29.8	1	3	17	7.8	9.6
6	2	0	43.3	32.6	4	2	13	12.3	12.3	18	2	-10	14.8	17.2	1	3	-1	37.8	26.1
8	2	0	5.8	1.6	6	2	13	8.7	8.4	24	2	-10	11.6	12.5	3	3	-1	16.5	15.8
10	2	0	13.2	15.7	10	2	13	8.9	9.6	10	2	-11	7.9	7.6	5	3	-1	22.6	20.4
12	2	0	35.5	32.2	0	2	14	9.7	10.2	12	2	-11	13.1	16.1	7	3	-1	19.1	17.0
16	2	0	16.1	18.5	2	2	14	9.2	8.7	14	2	-11	12.2	15.2	11	3	-1	20.1	18.9
24	2	0	14.7	12.8	6	2	14	20.1	23.2	16	2	-11	13.9	12.4	13	3	-1	21.4	20.7
0	2	1	8.0	10.7	8	2	14	15.2	13.1	2	2	-12	11.5	15.7	15	3	-1	14.1	12.2
2	2	1	13.0	7.9	10	2	14	12.5	12.3	4	2	-12	16.0	17.9	19	3	-1	10.8	11.2
4	2	1	5.9	2.2	12	2	14	11.5	11.7	6	2	-12	25.9	33.5	21	3	-1	9.2	9.6
6	2	1	14.4	10.1	2	2	15	10.5	10.5	8	2	-12	14.1	13.8	23	3	-1	5.8	7.7
10	2	1	9.5	7.0	4	2	15	8.9	10.2	12	2	-12	9.0	10.4	1	3	-2	2.9	0.0
20	2	1	10.5	10.6	6	2	15	12.6	14.4	14	2	-12	14.2	13.4	5	3	-2	10.3	8.7
0	2	2	47.5	39.3	0	2	16	10.1	11.5	16	2	-12	21.0	20.9	7	3	-2	10.5	10.7
2	2	2	34.5	23.8	6	2	16	11.4	11.1	24	2	-12	8.9	9.3	1	3	-3	11.2	13.9
4	2	2	12.0	9.1	12	2	16	9.1	8.5	8	2	-13	13.2	17.9	3	3	-3	17.4	17.5
6	2	2	52.4	44.2	0	2	18	13.1	15.0	2	2	-14	13.6	14.0	5	3	-3	11.8	11.6
8	2	2	8.0	9.8	8	2	18	10.0	8.6	4	2	-14	29.3	31.1	7	3	-3	9.2	9.8
10	2	2	38.5	35.9	12	2	18	9.3	10.6	6	2	-14	13.4	11.5	11	3	-3	20.1	16.6
12	2	2	34.4	32.1	0	2	20	10.3	11.3	8	2	-14	10.4	11.2	13	3	-3	16.0	13.5
14	2	2	12.8	10.1	2	2	20	9.6	8.9	12	2	-14	18.3	22.6	15	3	-3	10.4	11.2
16	2	2	19.6	19.5	6	2	20	11.6	10.0	12	2	-15	8.9	12.0	17	3	-3	6.7	7.0
20	2	2	13.0	16.4	8	2	20	8.6	9.8	4	2	-16	16.9	20.7	21	3	-3	6.5	6.9
2	2	3	36.7	26.9	6	2	-1	14.5	13.3	12	2	-16	14.0	18.6	23	3	-3	2.6	4.0
4	2	3	40.2	32.9	8	2	-1	13.9	11.4	4	2	-18	12.0	14.4	1	3	-4	12.0	13.3
6	2	3	14.1	10.8	10	2	-1	7.1	8.2	6	2	-18	12.0	14.9	3	3	-4	5.8	5.9
8	2	3	8.6	4.4	2	2	-2	9.7	10.2	16	2	-18	11.1	8.9	5	3	-4	5.0	5.5
10	2	3	8.0	8.0	4	2	-2	15.5	15.7	4	2	-19	9.8	6.7	5	3	-5	13.0	11.7
12	2	3	10.1	10.5	6	2	-2	19.6	20.2	6	2	-20	7.0	10.6	11	3	-5	13.4	11.6
20	2	3	12.5	9.5	8	2	-2	12.6	14.4	16	2	-20	7.2	8.0	13	3	-5	13.9	11.6
0	2	4	122.7	78.4	10	2	-2	5.3	7.1	4	2	-22	5.8	8.9	17	3	-5	11.5	11.2
4	2	4	24.8	17.2	12	2	-2	33.2	32.0	6	2	-22	9.4	11.4	23	3	-5	9.0	8.4
6	2	4	15.9	16.6	14	2	-2	11.7	14.0						1	3	-6	17.2	17.4
8	2	4	26.8	25.5	16	2	-2	22.0	20.7	3	3	0	4.2	4.2	3	3	-6	8.9	8.0
10	2	4	37.5	29.6	22	2	-2	17.2	15.9	7	3	0	5.0	5.0	5	3	-6	17.5	19.3
12	2	4	21.1	17.1	24	2	-2	21.0	20.4	9	3	0	7.1	5.5	9	3	-6	7.1	7.0
14	2	4	14.9	11.6	2	2	-3	30.2	26.5	11	3	0	13.0	9.7	15	3	-6	9.6	9.1
16	2	4	11.0	8.3	4	2	-3	20.5	23.4	1	3	1	24.6	23.2	1	3	-7	24.8	22.7
18	2	4	20.3	15.3	6	2	-3	24.3	26.4	3	3	1	20.5	16.2	5	3	-7	12.4	12.2
20	2	4	5.6	6.3	10	2	-3	14.0	12.0	5	3	1	23.9	18.2	7	3	-7	6.4	4.4
22	2	4	12.2	12.0	14	2	-3	22.7	22.8	7	3	1	14.3	11.3	9	3	-7	9.1	9.9
24	2	4	6.8	9.2	20	2	-3	14.8	13.1	9	3	1	10.5	9.7	11	3	-7	10.2	8.1
0	2	5	29.2	25.3	2	2	-4	36.1	35.6	11	3	1	20.6	19.8	13	3	-7	9.1	9.3
2	2	5	56.9	49.5	4	2	-4	12.7	14.5	13	3	1	14.8	15.3	15	3	-7	7.8	6.9
4	2	5	36.0	32.3	6	2	-4	19.7	17.7	23	3	1	11.9	12.0	23	3	-7	4.8	6.5
6	2	5	16.6	14.0	8	2	-4	23.4	23.2	1	3	2	6.5	4.2	1	3	-8	11.0	11.5
8	2	5	16.6	15.2	10	2	-4	25.7	25.6	9	3	2	10.5	7.7	3	3	-8	5.8	5.6
10	2	5	9.3	7.9	12	2	-4	41.6	34.5	1	3	3	38.7	29.5	5	3	-8	5.8	8.8
12	2	5	13.3	7.9	14	2	-4	23.0	21.7	3	3	3	31.3	22.9	13	3	-8	7.2	8.8
14	2	5	11.7	9.4	16	2	-4	16.5	16.9	5	3	3	12.5	9.6	15	3	-8	8.1	8.9
20	2	5	10.7	12.5	18	2	-4	22.1	19.4	7	3	3	16.7	14.2	19	3	-8	7.7	7.2
0	2	6	81.6	66.2	22	2	-4	12.0	11.9	9	3	3	17.8	17.2	1	3	-9	20.5	20.6
2	2	6	43.7	37.8	24	2	-4	13.1	11.3	11	3	3	21.7	21.0	3	3	-9	8.1	7.1
4	2	6	15.3	14.2	2	2	-5	6.2	4.2	13	3	3	10.6	9.6	5	3	-9	10.6	12.6
6	2	6	9.2	10.3	4	2	-5	25.6	28.0	1	3	4	5.6	5.4	7	3	-9	9.9	6.4
8	2	6	33.3	30.7	6	2	-5	4.0	5.2	5	3	4	16.4	13.5	11	3	-9	9.7	11.2
10	2	6	30.4	26.7	12	2	-5	14.5	11.4	9	3	4	10.0	8.2	15	3	-9	6.0	7.0
12	2	6	21.0	19.4	14	2	-5	12.9	10.2	13	3	4	8.9	6.6	23	3	-9	5.4	5.1
18	2	6	12.5	13.9	16	2	-5	10.3	9.4	1	3	5	27.8	22.4	11	3	-10	7.8	5.9
22	2	6	12.2	10.3	18	2	-5	10.6	9.8	3	3	5	3.9	4.3	15	3	-10	12.3	12.5
24	2	6	7.4	7.0	20	2	-5	9.8	6.7	5	3	5	11.8	8.4	1	3	-11	8.8	9.6
0	2	7	9.0	8.8	2	2	-6	29.3	30.4	7	3	5	16.8	13.5	3	3	-11	10.7	11.8
2	2	7	10.4	10.4	4	2	-6	17.2	19.7	9	3	5	15.2	12.8	5	3	-11	11.7	9.4
4	2	7	10.4	9.8	6	2	-6	26.5	25.6	11	3	5	19.9	19.2	9	3	-11	6.3	7.1
6	2	7	11.9	12.8	8	2	-6	13.1	13.6	13	3	5	16.3	15.8	11	3	-11	12.3	14.0
10	2	7	15.4	16.1	10	2	-6	32.5	30.9	19	3	5	11.4	10.4	13	3	-11	6.5	5.3
12	2	7	14.2	13.9	12	2	-6	35.8	35.1	3	3	6	25.7	22.0	17	3	-11	9.7	12.2
14	2	7	12.9	11.9	14	2	-6	16.9	16.6	5	3	6	5.6	6.6	19	3	-11	7.6	6.2
0	2	8	18.5	23.1	16	2	-6	8.7	7.0	7	3	6	22.9	19.5	5	3	-12	6.5	7.1
2	2	8	29.2	28.3	18	2	-6	13.0	10.4	9	3	6	14.5	14.0	7	3	-12	9.1	8.2
4	2	8	27.3	26.3	24	2	-6	10.8	8.0	13	3	6	11.5	9.9	11	3	-12	11.6	13.1
6	2	8	22.0	20.4	2	2	-7	27.5	29.2	17	3	6	6.2	6.4	13	3	-12	10.1	12.5
8	2	8	14.8	13.2	4	2	-7	18.6	19.2	1	3	7	10.6	8.6	1	3	-13	10.0	11.1
10	2	8	31.4	27.1	10	2	-7	7.8	5.7	3	3	7	14.4	13.3	3	3	-13	9.1	11.3
12	2	8	43.4	43.6	16	2	-7	10.2	8.9	11	3	7	7.0	5.8	5	3	-13	6.6	7.8
14	2	8	10.6	11.7	20	2	-7	10.5	5.9	13	3	7	10.0	10.2	11	3	-13	15.9	13.2
20	2	8	11.6	13.0	2	2	-8	11.2	13.7	17	3	7	9.8	9.0	13	3	-13	14.7	15.6
22	2	8	11.9	10.2	4	2	-8	30.6	31.1	3	3	8	14.7	15.9	15	3	-13	9.0	7.8
24	2	8	7.7	7.4	6	2	-8	26.0	30.1	5	3	8	6.3	7.4	17	3	-13	10.0	12.2
6	2	9	17.0	17.5	10	2	-8	16.7	16.9	7	3	8	7.9	8.4	19	3	-13	5.4	8.2
18	2	9	10.0	7.9	12	2	-8	25.9	23.6	9	3	8	6.5	6.9	3	3	-14	8.7	11.7
0	2	10	31.5	38.5	14	2	-8	12.0	11.1	11	3	8	9.1	5.6	5	3	-14	7.0	7.8
2	2	10	13.6	16.7	16	2	-8	10.5	11.4	17	3	8	7.7	7.4	9	3	-14	3.9	5.5
6	2	10	15.4	15.7	18	2	-8	19.6	17.6	1	3	9	10.9	11.8	11	3	-14	11.4	9.7
10	2	10	11.3	10.4	22	2	-8	12.0	12.3	3	3	9	7.5	6.3	1	3	-15	8.8	9.4
12	2	10	25.1	25.6	24	2	-8	10.7	11.8	7	3	9	12.6	11.2	3	3	-15	10.4	12.7
14	2	10	13.5	12.7	2	2	-9	14.1	15.9	1	3	10	7.4	7.9	5	3	-15	13.6	16.1
18	2	10	10.0	9.9	4	2	-9	8.6	9.7	3	3	10	7.5	4.9	7	3	-15	7.8	9.3
20	2	10	9.1	10.8	14	2	-9	14.1	15.0	5	3	10	7.3	3.3	9	3	-15	5.8	7.9
22	2	10	8.7	8.0	16	2	-9	15.0	14.8	7	3	10	14.2	16.0	11	3	-15	7.8	9.7
4	2	11	8.5	11.3	2	2	-10	17.6	18.2	1	3	11	11.0	13.0	13	3	-15	7.5	10.4
8	2	11	11.4	9.0	4	2	-10	11.6	12.4	5	3	11	7.4	8.5	1	3	-17	6.4	6.0
10	2	11	26.1	19.8	6	2	-10	24.0	28.1	7	3	11	16.9	16.9	3	3	-17	7.9	7.9
0	2	12	17.1	22.9	8	2	-10	15.0	16.2	11	3	11	10.9	11.7	5	3	-17	10.4	13.7
2	2	12	18.5	21.8	10	2	-10	15.9	18.3	1	3	13	5.0	6.3	5	3	-19	6.3	7.6
6	2	12	17.3	21.2	12	2	-10	13.1	11.3	5	3	13	12.9	15.1					

An electron density projection, $\varrho(xpz)$ was then calculated, in which the signs of the observed F-values had been determined assuming 4 Cu atoms in 4(*c*). The projection immediately revealed all the non-hydrogen atoms in the organic molecule and gave the x- and z-parameters of these atoms. The results provide evidence that 4(*c*) is the correct position for the Cu atoms, and also that space group $C2/c$ is to be preferred to Cc.

The zones with higher layer numbers include a few reflections with $h+l$ odd and so the signs of these reflections could not be determined at once. In order to find the y-parameters of the light atoms the reflections with $h+l$ even were used in calculating the generalized Fourier projections $\varrho_1(xz)$ to $\varrho_3(xz)$. By geometrical considerations correct y-values were found by the aid

Table 4. Interatomic distances (Å) and angles (°) with estimated standard deviations.

Cu	—Cu	3.761 (0)	N	—Cu	—O(1)	89.2 (4)
Cu	—N	2.016 (11)	Cu	—O(1)	—C(1)	127.2 (8)
Cu	—O(1)	1.937 (10)	C(1)	—C(2)	—C(3)	118.9 (13)
Cu	—O(1′)	2.812 (9)	C(2)	—C(3)	—C(4)	120.7 (14)
O(1)	—C(1)	1.321 (17)	C(3)	—C(4)	—C)5)	122.1 (15)
C(1)	—C)2)	1.400 (20)	C(4)	—C(5)	—C(6)	118.6 (14)
C(2)	—C(3)	1.397 (21)	C(5)	—C(6)	—C(1)	119.7 (12)
C(3)	—C(4)	1.390 (22)	C(6)	—C(1)	—C(2)	120.0 (13)
C(4)	—C(5)	1.351 (21)	C(13)	—C(8)	—C(9)	126.2 (15)
C(5)	—C(6)	1.440 (21)	C(8)	—C(9)	—C(10	112.4 (15)
C(6)	—C(1)	1.407 (20)	C(9)	—C(10)	—C(11)	124.1 (16)
C(6)	—C(7)	1.416 (18)	C(10)	—C(11)	—C(12)	121.2 (15)
C(7)	—O(2)	1.378 (16)	C(11)	—C(12)	—C(13)	114.9 (15)
C(7)	—N	1.301 (17)	C(12)	—C(13)	—C(8)	121.2 (14)
O(2)	—C(8)	1.383 (18)	O(2)	—C(7)	—N	112.7 (11)
N	—C(13)	1.408 (18)	C(7)	—O(2)	—C(8)	104.6 (10)
C(8)	—C(9)	1.391 (23)	O(2)	—C(8)	—C(13)	109.2 (13)
C(9)	—C(10)	1.385 (23)	N	—C(13)	—C(8)	106.0 (12)
C(10)	—C(11)	1.383 (24)	C(7)	—N	—C(13)	107.4 (11)
C(11)	—C(12)	1.448 (23)	Cu	—N	—C(7)	121.1 (9)
C(12)	—C(13)	1.365 (21)	C(1)	—C(6)	—C(7)	121.7 (13)
C(13)	—C(8)	1.385 (21)	O(1)	—C(1)	—C(6)	121.7 (12)
			N	—C(7)	—C(6)	129.7 (13)

of these projections. The parameters were then refined by the method of least squares. Refinement with isotropic temperature factors for all the atoms resulted in an agreement factor of $R=0.116$. The final refinement was made with anisotropic temperature factors for copper and isotropic ones for the rest of the atoms giving a final R-value of 0.111. The slight improvement in the agreement factor was shown to be significant by Hamilton's significance test on the crystallographic R-factor.[13]

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Final coordinates and thermal parameters with their estimated standard deviations are given in Table 2, and the observed and calculated structure factors in Table 3. Selected interatomic distances and bond angles are listed in Table 4 and also shown in the projection of one molecule on the xz-plane

(Fig. 1). A corresponding projection of the palladium compound, as determined by Urdy,[7] is shown for comparison in Fig. 2.

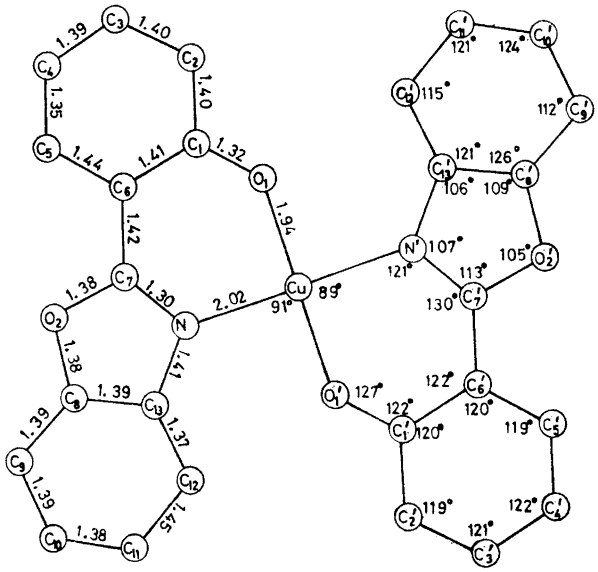


Fig. 1. Bond lengths (Å) and angles (°) in copper(II) 2-(*o*-hydroxyphenyl)benzoxazole.

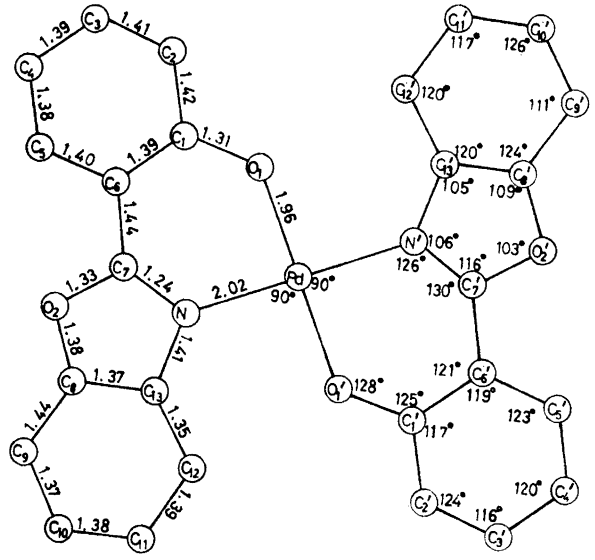


Fig. 2. Bond lenghts (Å) and angles (°) in palladium(II) 2-(*o*-hydroxyphenyl)benzoxazole according to Urdy.[7]

The structure is built up of parallel and almost planar molecules $Cu(C_{13}H_8NO_2)_2$ linked together along the *b*-axis by weak copper-oxygen bonds. In this way copper and its neighbouring nitrogen and oxygen atoms form endless chains of octahedra sharing opposite edges (Fig. 3). Only normal van der Waals forces operate between the molecules in the *a* and *c* directions.

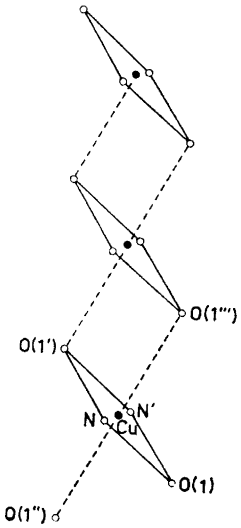
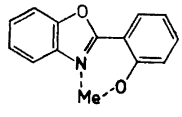
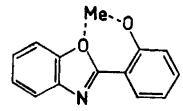


Fig. 3. The chain of distorted octahedra along the *b*-axis. The polyhedra share opposite edges, *e.g.* O(1′)—O(1‴). The weak Cu—O bonds are indicated by dashed lines.

The environment of copper deserves a more detailed discussion. A chelate ring with a metal atom (Me) can in this case be formed in two ways, I or II, with a bridge N—Me—O or O—Me—O.



I



II

As expected, copper prefers the ring which includes nitrogen. Other metals or hydrogen (in the pure organic compound) may choose to close the ring in the other way and these possibilities are at present under investigation. The effect on the chelate of a substitution of the oxygen atom in the five-membered heterocyclic ring for sulphur to give 2-(*o*-hydroxyphenyl)benzothiazole will also be studied.

Coordination about copper(II) can be divided into three principal types (*e.g.* Orgel and Dunitz[14]): a) distorted octahedral with four short and two long bonds; b) square coplanar; c) tetrahedral. There also exist tetragonal-pyramidal

(four short bonds and one long bond) and binuclear types. Type b) can be regarded as a limiting case of a) with two ligands completely removed. The copper coordination in $Cu(C_{13}H_8NO_2)_2$ can be considered to be something between the types a) and b). The copper atom, two nitrogen and two oxygen atoms lie approximately in a square, which is exactly planar as required by the symmetry $\bar{1}$ of the site of the copper atom. Two more oxygen atoms are situated at distances of 2.81 Å from the square plane, thus comprising a distorted (4+2) octahedron of type a). Within the square the distances are 1.94 Å and 2.02 Å for Cu—O and Cu—N, respectively, in good agreement with those reported for numerous other copper(II) complexes. The "long" copper-oxygen distances vary considerably in different structures due to steric effects, *e.g.* the stacking of the organic molecules. The steric effects have been discussed by Wells.[15] In Table 5 the coordination about copper

Table 5. The copper coordination in some organic copper(II) complexes. The distances are given in Å and include available standard deviations.

Compound	Short bonds Cu—O	Short bonds Cu—N	Long bonds	Shortest Cu—Cu distances	Ref.
Copper(II) 2-(*o*-hydroxyphenyl)-benzoxazole	1.937 (10)	2.016 (11)	2.812 (9)	3.761 (0)	This paper
Copper(II) bis-(benzene-azo-*β*-naphthol)	1.93	2.01	3.00	3.90	16
Copper(II) bis-(5-chlorosalicylaldoxime)	1.908 (9)	1.957 (9)	3.013 (10)	3.840 (15)	17

in the present compound is compared with that reported for two similar copper(II) complexes with large organic molecules as ligands. In all three structures the Cu atom is at $\bar{1}$ and the distorted (4+2) octahedra about copper form endless chains along one axis. The molecules are held together by weak Cu—O(phenyl) bonds and the shortest Cu—Cu distances, identical with the *b*-axes, are similar.

The coordination described above is by no means unique for copper(II) compounds. It may be noted, however, that even a metal like cadmium, which does not show a Jahn-Teller effect, might acquire a coordination of this type. The striking similarities of the powder photographs of $Cd(C_{13}H_8NO_2)_2$ and $Cu(C_{13}H_8NO_2)_2$ give a strong indication of this fact.

The distances within the organic molecule are in good agreement with those expected. The angles in the phenyl group are close to the anticipated value of 120°. In the benzoxazole group the divergences are considerably greater in the copper as well as in the palladium chelate. There are significantly low values of the angle C(8)—C(9)—C(10), being $112.4\pm1.5°$ for the copper compound and $111.1\pm2.2°$ for the palladium compound. However,

none of these structures has been determined with an accuracy great enough to confirm the physical significance of this effect.

The planarity of the structure has been determined by a least-squares program and the results are shown in Table 6. As could be expected the

Table 6. Deviations (Å) from calculated least-squares planes (I–V).

	I	II	III	IV	V
O(1)	−0.000				0.153
C(1)	−0.007				0.072
C(2)	−0.001				0.143
C(3)	0.012				0.080
C(4)	−0.015				−0.086
C(5)	0.006				−0.132
C(6)	0.005				−0.056
C(7)		0.011	0.004		−0.110
O(2)		0.035	0.013		0.046
N		−0.041	−0.023		−0.225
C(8)		−0.009	−0.013	0.003	0.017
C(13)		−0.006	0.015	−0.004	−0.100
C(9)		−0.011		0.000	0.132
C(10)		−0.002		−0.002	0.127
C(11)		0.010		0.000	0.022
C(12)		0.011		0.002	−0.096

phenyl group forms a plane, in this structure within ±0.015 Å (plane I). The benzoxazole group (II) is somewhat less planar. The deviations are larger in the five-membered ring (III) due to the tensions in the heterocyclic ring, whereas the benzene ring (IV) is planar within ±0.004 Å. Finally, the best fitting plane for the whole 2-(*o*-hydroxyphenyl)benzoxazole molecule (V) shows a maximum deviation for the nitrogen atom (0.225 Å).

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