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The Crystal Structure of *catena*-μ-(*N*-Salicylidene-L-tyrosinato-*O*,*O*′)copper(II)

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The crystal structure of the Schiff base-type complex *catena*-μ-(*N*-salicylidene-L-tyrosinato-*O*,*O*′)-copper(II) {$a = 12.310(8)$ Å, $b = 5.838(5)$ Å, $c = 20.357(11)$ Å, $Z = 4$ and space group $P2_12_12_1$} has been solved by three-dimensional Patterson and Fourier methods and refined by block-diagonal least-squares technique, hydrogen atoms included, to the R value 0.052. The coordination sphere around the copper(II) atom is square pyramidal (4+1). The basal plane consists of the tridentate *N*-salicylidene-L-tyrosine group and an oxygen atom of the adjacent carboxylate group [Cu–O1 = 1.915(8), Cu–O4 = 1.874(9), Cu–N1 = 1.938(8) and Cu–$O2_1$ = 1.986(7) Å]. The other oxygen atom of the carboxylate group occupies the axial position [Cu–$O1_1$ = 2.490(8) Å]. The oxygen atoms of the carboxylate group (in *syn-anti* configuration) coordinate to different copper(II) atoms, joining the adjacent complex units together so that a chain-like structure is formed in the direction of the *b*-axis.

Although a substantial amount of information is available about transition metal complexes of Schiff bases,[1] those derived from salicylaldehyde and amino acids are less well-known.[2-11] Transition metal complexes of salicylaldehyde-amino acid Schiff bases are analogous to those of pyridoxal-amino acid Schiff bases, which are of considerable importance in nonenzymatic catalysed transamination reactions.[12-14] We have used three-dimensional X-ray data to investigate the crystal structures of copper(II) complexes of Schiff bases derived from salicylaldehyde, L-tyrosine and L-phenylalanine. In this study we present the structure of *catena*-μ-(*N*-salicylidene-L-tyrosinato-*O*,*O*′)copper(II).

EXPERIMENTAL

Preparation. Equimolar quantities of salicylaldehyde (2.12 cm^3) and copper(II) acetate monohydrate (4.0 g) were dissolved in a mixture of hydrochloric acid (1 M, 70 cm^3) and ethanol (30 cm^3) according to the method of Laurie.[15] After heating to 50 °C, L-tyrosine (3.62 g), dissolved in a minimum volume of the same acidified ethanol mixture was added, and then 0.2 M sodium hydroxide until a pH of 4.5 was obtained. The crude product was filtered, washed with water and dried in air. The compound was recrystallized from hot water and dark green, prismatic crystals were obtained. Copper was analysed electrolytically, carbon and nitrogen by microanalytical methods. Calc. for $CuC_{16}H_{13}NO_4$ (F.W. 346.81): Cu 18.32; C 55.41; N 4.04. Found: Cu 18.28; C 54.34; N 3.91 %. The crystals were thermally stable to about 240 °C (236 °C given by Laurie), after which they turned brown.

Unit cell and intensity measurements. Weissenberg photographs showed systematic absences of $h00$, $0k0$ and $00l$ reflections with h, k and l odd, indicating the orthorhombic space group $P2_12_12_1$.[16] The approximate cell parameters were refined by the least-squares technique with data obtained from a powder film (Cu$K\alpha$ radiation; $\lambda = 1.5418$ Å), using CaF_2 as internal standard ($a = 5.4630$ Å). Lattice parameters were $a = 12.310(8)$ Å, $b = 5.838(5)$ Å, $c = 20.357(11)$ Å and $V = 1463.0$ Å^3. Density measurements by flotation method showed that there were four formula units per unit cell ($d_{obs} = 1.56$ g cm^{-3} and $d_{calc} = 1.575$ g cm^{-3}).

The intensities of 1372 reflections from six layers ($h0l - h5l$) were collected on a semi-automatic STOE-Güttinger diffractometer with Cu$K\alpha$ radiation. A crystal of dimensions about $0.2 \times 0.4 \times 0.2$ mm was mounted along the b axis. The $10\bar{0}1$ reflections having $I > 2\sigma(I)$ were included in the structure determination. The data were corrected for Lorentz

Table 1. Fractional atomic coordinates ($\times 10^4$; for hydrogen atoms $\times 10^3$) and thermal parameters[a] ($\times 10^3$) with their standard deviations.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	1315(1)	2494(3)	2509(1)	32(1)	58(1)	21(1)	3(1)	5(1)	13(1)
O1	279(5)	4907(12)	2376(3)	38(4)	48(5)	21(4)	−2(4)	8(3)	6(3)
O2	−596(5)	6868(13)	1637(3)	37(3)	58(5)	20(3)	25(4)	−3(3)	−9(3)
O3	3272(6)	3305(16)	−1564(3)	59(5)	77(6)	42(4)	−27(5)	30(4)	−36(4)
O4	2335(5)	148(16)	2607(3)	31(4)	78(6)	31(4)	10(4)	2(3)	27(4)
N1	1741(6)	3230(15)	1617(3)	39(4)	36(5)	19(3)	−1(4)	−6(3)	6(3)
C1	178(7)	5631(17)	1806(4)	29(4)	29(6)	19(4)	1(5)	12(4)	−7(4)
C2	1077(8)	5000(19)	1310(4)	37(5)	46(7)	11(4)	6(5)	3(4)	−5(4)
C3	532(7)	4142(20)	659(4)	33(5)	51(8)	15(4)	12(5)	−1(4)	−2(5)
C4	1310(8)	3906(20)	84(4)	27(4)	56(7)	20(4)	10(5)	4(4)	9(4)
C5	1289(8)	1964(19)	−298(4)	48(6)	39(7)	21(4)	−14(6)	2(4)	1(4)
C6	1936(9)	1749(20)	−857(5)	46(6)	35(7)	44(6)	−2(6)	14(5)	−13(5)
C7	2624(9)	3448(23)	−1020(5)	41(6)	69(8)	32(5)	−14(6)	10(5)	−13(6)
C8	2681(9)	5355(23)	−644(5)	57(7)	47(7)	35(5)	−21(7)	5(5)	−10(6)
C9	2002(9)	5651(21)	−109(5)	51(6)	36(7)	33(5)	−1(6)	1(5)	−14(5)
C10	3069(8)	−498(22)	2186(5)	27(5)	51(7)	41(5)	2(6)	−7(4)	16(6)
C11	3732(9)	−2417(24)	2310(6)	52(6)	50(7)	65(7)	2(8)	−21(5)	12(7)
C12	4557(9)	−3120(23)	1873(7)	53(7)	48(9)	99(10)	43(7)	−29(7)	−3(8)
C13	4721(11)	−1953(25)	1292(7)	69(8)	64(10)	71(9)	36(8)	−11(7)	−5(7)
C14	4091(11)	−96(28)	1171(6)	57(7)	83(11)	58(8)	13(8)	8(6)	1(9)
C15	3265(8)	635(21)	1576(5)	27(5)	54(7)	35(5)	1(6)	15(4)	1(5)
C16	2605(7)	2536(23)	1338(4)	23(4)	48(6)	37(5)	5(6)	9(4)	−15(6)
H1	858(6)	135(15)	377(4)	18(23)					
H2	983(6)	44(16)	444(4)	26(23)					
H3	1005(9)	822(23)	427(6)	52(41)					
H4	922(8)	595(18)	518(5)	53(31)					
H5	791(6)	512(14)	594(3)	23(19)					
H6	689(6)	719(15)	683(4)	25(21)					
H7	690(8)	197(18)	568(4)	50(28)					
H8	790(6)	165(15)	488(4)	1(23)					
H9	345(13)	707(33)	247(8)	199(69)					
H10	491(6)	577(14)	202(4)	3(22)					
H11	559(8)	733(19)	98(5)	44(30)					
H12	433(8)	114(19)	75(5)	59(33)					

[a] The anisotropic thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+\ldots+2hka^*b^*U_{12}+\ldots)]$.

and polarization effects but not for absorption [μ(Cu$K\alpha$) = 23.1 cm^{-1}].

Structure determination. The Patterson and Fourier programs of the *X-Ray* 76 system were used in solving the structure.[17] From a first Fourier summation, phased on the copper atom, it was possible to locate the nitrogen and oxygen atoms. The carbon atoms were obtained by successive Fourier syntheses. The refinement of the structure was carried out by block-diagonal least-squares method with isotropic thermal parameters to $R=0.124$ and with anisotropic parameters to $R=0.072$ ($R=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$). The hydrogen atoms were located from a difference Fourier map, and after five further cycles, with isotropic parameters for the hydrogen atoms and anisotropic parameters for the others, the R value reached 0.052, the final average shift/error being 0.35. One hydrogen atom (H13) joined to a nitrogen atom could not be located unambiguously and is therefore excluded. The weighting scheme was $w=1/(40.0+|F_o|+0.03|F_o|^2)$ and the function minimized of the form $\Sigma w(|F_o|-|F_c|)^2$. The scattering factors for the non-hydrogen atoms were from Cromer and Mann,[18] and for the hydrogen atoms from Stewart *et al.*[19] Anomalous dispersion corrections were applied for the copper atom, using the values of $\Delta f'$ and $\Delta f''$ from International Tables for X-Ray Crystallography given by Cromer and Liberman.[20] Calculations were carried out on a UNIVAC 1108 computer using the *X-Ray* 76 program system.

Table 2. Interatomic distances (Å) and angles (°). I refers to equivalent position $-x, y-\frac{1}{2}, \frac{1}{2}-z$ and II to position $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Cu – $O1_I$	2.490(8)	C5 – C6	1.392(16)
Cu – O1	1.915(8)	C6 – C7	1.348(19)
Cu – $O2_I$	1.986(7)	C7 – C8	1.357(20)
Cu – O4	1.874(9)	C8 – C9	1.385(17)
Cu – N1	1.938(8)	C9 – C4	1.386(18)
O1 – C1	1.244(12)	C10 – C11	1.408(20)
O2 – C1	1.247(13)	C11 – C12	1.409(20)
O3 – C7	1.369(14)	C12 – C13	1.371(23)
O4 – C10	1.304(14)	C13 – C14	1.365(24)
N1 – C2	1.446(15)	C14 – C15	1.370(19)
C1 – C2	1.537(15)	C15 – C10	1.419(17)
C2 – C3	1.569(14)	C15 – C16	1.462(18)
C3 – C4	1.515(14)	C16 – N1	1.280(14)
C4 – C5	1.374(17)		
Cu – O1 – Cu_{II}	163.1(4)	C4 – C5 – C6	122.5(11)
O1 – Cu – $O2_I$	87.8(3)	C5 – C6 – C7	119.1(12)
O1 – Cu – O4	177.9(3)	C5 – C4 – C9	116.3(10)
O1 – Cu – N1	83.2(3)	C6 – C7 – C8	120.5(12)
O4 – Cu – N1	94.8(4)	O3 – C7 – C6	121.1(12)
O4 – Cu – $O1_I$	94.2(3)	O3 – C7 – C8	118.4(12)
O4 – Cu – $O2_I$	94.1(3)	C7 – C8 – C9	120.1(13)
N1 – Cu – $O1_I$	115.9(3)	C8 – C9 – C4	121.2(13)
N1 – Cu – $O2_I$	169.0(3)	O4 – C10 – C11	120.9(12)
C2 – N1 – C16	120.4(9)	O4 – C10 – C15	123.7(12)
O1 – C1 – O2	122.1(9)	C11 – C10 – C15	115.4(11)
O1 – C1 – C2	117.2(9)	C10 – C11 – C12	122.5(13)
O2 – C1 – C2	120.7(9)	C11 – C12 – C13	119.9(14)
C1 – C2 – C3	108.9(9)	C12 – C13 – C14	118.0(14)
C1 – C2 – N1	107.2(8)	C13 – C14 – C15	123.9(15)
N1 – C2 – C3	112.6(9)	C10 – C15 – C14	120.1(13)
C2 – C3 – C4	114.0(9)	C10 – C15 – C16	123.7(10)
C3 – C4 – C5	120.2(10)	N1 – C16 – C15	123.9(10)
C3 – C4 – C9	123.3(10)		

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters with their standard deviations are given in Table 1. The structure and numbering scheme of the compound is shown in Fig. 1. A list of observed and calculated structure factors is obtainable on request from the authors.

The oxygen atoms of the same carboxylate group coordinate in *syn-anti* configuration to different copper ions and thereby join the adjacent complex units together to form a chain structure in the direction of the *b*-axis.

The copper(II) ion has a distorted square-pyramidal coordination geometry (4+1). The tridentate *N*-salicylidene-L-tyrosine group occupies three of the square-planar coordination sites and the carboxyl oxygen atom $O2_I$ of the adjacent complex completes the plane. The carboxyl oxygen atom $O1_I$ occupies the apical site at the distance 2.490 Å. The coordination distances and angles around the copper atom are given in Table 2. The values are comparable with those found earlier in related compounds.[10,11]

The complex unit consists of four, approximately planar groups: atoms of the coordination plane, the carboxylate group, and the rings of the tyrosine and salicylidene residues. The displacements of selected atoms from least-squares planes and the angles between the planes are presented in Table 3. The copper atom is situated almost in the coordination plane (deviation <0.06 Å), which is consistent with

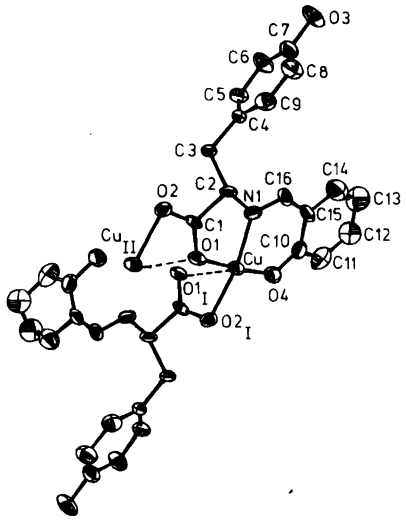

Fig. 1. The structure and numbering scheme of the compound.

the observation that only an oxygen–copper separation of less than ≃2.45 Å results in an interaction sufficient to displace the copper atom from the coordination plane.[21]

The deviation of the nitrogen atom from the carboxylate plane, 0.244 Å, is clearly smaller than the 0.35 Å in *N*-salicylideneglycinatoaquacopper(II) hemihydrate[10] and 0.44, 0.58 and 0.31 Å in α-, β- and γ-glycine, respectively,[22–24] but greater than the deviation 0.12 Å in *N*-salicylideneglycinatoaquacopper(II) tetrahydrate.[11]

The bond distances and angles in the benzene rings fluctuate in the range 1.35–1.42 Å and 115.4–123.9 °, which are fairly large deviations but still comparable with corresponding values in the literature.[25–28] The planarity of both aromatic rings is satisfactory (Table 3) and the exocyclic atoms in the tyrosine residue, C3 and O3, are situated almost in the plane (0.07 Å and 0.03 Å, respectively). The deviations agree, for example, with values of diaquabis(L-tyrosinato)nickel(II) bismethanol.[25]

Ueki *et al.*[11] have examined the bonding around the nitrogen atom in connection with the *N*-salicylideneglycinatoaquacopper(II) tetrahydrate structure and established that the bond lengths are of two different types. In Type I, the bond A between the nitrogen atom and the carbon atom of the amino acid part is shorter than the usual single bond

Table 3. Deviations (Å) from least-squares planes. Atoms indicated with an asterisk were omitted from the calculations.

Plane 1.					
O1	.054	O4	.048	Cu*	.058
$O2_I$	−.050	N1	−.053		
Plane 2.					
O1	.003	C2	.003	N1*	−.244
O2	.003	Cu*	−.409	C16*	−.159
C1	−.008	O4*	−.823	Cu_{II}*	.277
Plane 3.					
C4	.005	C7	−.012	O3*	−.034
C5	.012	C8	.029	C3*	−.069
C6	−.008	C9	−.026		
Plane 4.					
C10	.014	C13	−.009	Cu*	−.069
C11	−.011	C14	.013	O1*	−.200
C12	.008	C15	−.015	O4*	.034
				N1*	−.308

Angle (°) between	
planes 1 and 2	14.6
planes 2 and 3	79.5
planes 2 and 4	19.2
planes 3 and 4	60.7

Table 4. The most significant intermolecular distances (Å).

$O2-O1_I$	2.706(11)	$C1-O1_I$	3.051(14)
$O4-O3_{II}$	2.729(14)	$Cu-O3_{III}$	3.141(10)
$O2-O4_I$	2.828(11)	$O3-O2_{IV}$	3.150(14)
$O1-O3_{III}$	2.995(11)	$Cu-Cu_I$	4.358(2)
$O1-O1_I$	3.041(11)		

I $= -x, \frac{1}{2}+y, \frac{1}{2}-z$ III $= \frac{1}{2}-x, 1-y, \frac{1}{2}+z$

II $= \frac{1}{2}-x, -y, \frac{1}{2}+z$ IV $= \frac{1}{2}+x, \frac{3}{2}-y, -z$

(1.47 – 1.49 Å), and the bond B between the nitrogen atom and the carbon atom of the aldehyde or ketone part has the usual C = N bond dimensions. In Type II, on the other hand, the bond A is normal, wherease the bond B is clearly shorter than normal (1.29 – 1.30 Å). Because in both types one bond, A or B, is shorter than normal, it can be concluded that the nitrogen atom carries more electrons than usual and that one of the bonds is electron-rich. In Type I the mean value expected for bond A is 1.453 Å and for bond B 1.285 Å; in Type II the corresponding values are 1.480 Å and 1.247 Å. The values 1.446 Å for bond A and 1.280 Å for bond B in the present compound agree well with the bond values of Type I.

Table 4 presents some selected intermolecular distances. The H – C and H – O bond lengths vary from 0.60(19) to 1.26(12) Å. It is interesting to note that the hydroxyl oxygen atom O3 in the tyrosine group has not been able to take a sixth place in the coordination sphere of the copper(II) atom but is situated at hydrogen bond distance from the oxygen atoms of the adjacent carboxylate and salicylidene groups ($O1-O3_{III} = 2.995$ Å and $O4-O3_{II} = 2.729$ Å). Thus the hydroxyl oxygen atom lies aside from the axial position and the distance between the copper ion and the hydroxyl oxygen is relatively long ($Cu-O3_{III} = 3.141$ Å).

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