Preparation and Crystal Structure of Aqua(ethanol)tetrakis(μ-salicylato-O,O')dicopper(II)–Ethanol–Water (1/1/1)

Kimio Yoneda,† Khoichi Uchiyama,† Barry Boettcher,†† and Yoshinobu Inouye*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305
†Ina Research Inc., Nishiminowa 8047, Ina, Nagano 399-45
††Department of Biological Sciences, University of Newcastle, New South Wales, Australia

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Synopsis. A new dinuclear copper(II) salicylate, $[Cu_2(C_7H_5O_2)_4]\cdot 2C_2H_5OH\cdot 2H_2O$, was prepared from copper(II) hydroxide and excess salicyclic acid in 80% ethanol. The structure was clarified by a single crystal X-ray analysis.

Copper(II) complexes of salicyclic acid are of continuous interest from both structural and biological viewpoints.[1)] With respect to the chemical structures, a number have been reported in the literature. Three types of the complex have been studied in some detail. These are a pale-blue mononuclear copper(II) complex, $[Cu(C_7H_5O_2)_2]$,[2)] a dark-green dinuclear copper(II), $[Cu_2(C_7H_5O_2)_4]$,[3)] and a yellow-brown polymeric copper(II), $[Cu(C_7H_4O_2)]_n$,[4)] with or without solvents of crystallization. The formation of the respective complex is dependent on the reaction solvent, the ionic species present in the reaction-system, and/or the purification procedure. Concerning the above compounds, the dinuclear copper(II) salicylates are biologically interesting because they have anti-inflammatory activity.[5)] The initial method for preparing the dinuclear copper(II) salicylate involved a mononuclear copper(II) salicylate and an equimolar amount of salicylic acid.[3)] However, the mononuclear copper(II) complex was a contaminant, and it was difficult to purify the dinuclear copper(II) complex by recrystallization, because of the instability of the dinuclear copper(II) complex in solution. It is thus necessary to find conditions for the selective preparation of a dinuclear copper(II) complex. One of us (B. B.) has found that the dinuclear copper(II) salicylate selectively separated as crystals when copper(II) hydroxide and salicylic acid were heated in absolute ethanol, though the reaction time was long due to the poor solubility of copper(II) hydroxide.[6)]

In this note, we wish to report on the facile preparation and the crystal structure of a new dinuclear copper(II) salicylate, compound **1** (Fig. 1).

A mixture of copper(II) hydroxide and 5 molar excess of salicyclic acid was heated in 80% (w/w) ethanol at 65 °C for 5 min. The dark-green solution was cooled to room temperature to give dark-green crystals **1** in 30% yield. No other products and/or contaminants of the starting reagents were found under these conditions. When the ratio of salicyclic acid to copper(II) hydroxide was lowered to 1 : 4, polymeric copper(II) salicylates contaminated the product. The amount of water was also significant and the successful formation of **1** was found to be dependent on the concentration of water between 10 and 30%. Either copper(II) hydroxide or salicylic acid remained undissolved at water concentrations lower than 10% or higher than 30%, respectively. When water exceeded 70%, a yellow polymeric complex contaminated the preparation.

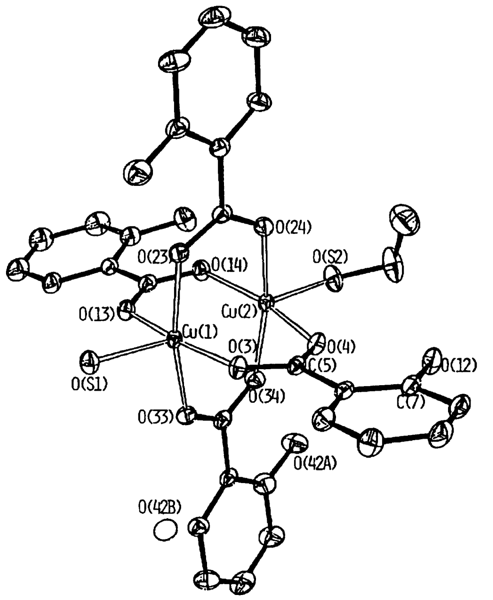

Fig. 1. ORTEP drawing[11)] of **1** with thermal ellipsoids scaled at the 20% probability level and numbering scheme for copper and oxygen atoms. H_2O and EtOH molecules uncoordinated to the copper are omitted.

The dark-green crystals were obtained from the solution as a plate and a crystal structure analysis was performed using freshly filtered crystals. The elementary analysis of these crystals agreed with $[Cu_2(C_7H_5O_2)_4]\cdot 2C_2H_5OH\cdot 2H_2O$.

The dimeric structure was unambiguously determined by a single-crystal X-ray analysis. The crystallographic data are summarized as follows: monoclinic, $P2_1/n$; $a=14.761(4)$, $b=15.979(2)$, $c=15.038(4)$ Å, $\beta=90.711(12)°$, $Z=4$; $D_c=1.39\ \mathrm{g\,cm^{-3}}$.

The structure was solved by the direct method (SHELX76).[7)] The first E-map revealed the position of two copper atoms; a difference Fourier synthesis revealed the position of 8 oxygen atoms coordinated with the coppers. By subsequent difference Fourier syntheses the remaining non-hydrogen atoms were found along with one molecule of water and one of ethanol, which are not coordinated with the copper atoms. An OH group in one of four salicylate groups was found in disorder with an occupancy of 0.6 and 0.4. The final refinement with anisotropic for non-hydrogen atoms converged the R factor to 0.059 (wR=0.071, S=1.04). The final weighting scheme was $\omega=1.0/[\sigma^2(F_o)+0.00698F^2]$. The ratio of the maximum least-squared shift to the error was less than 0.1.

The atomic parameters of **1** are listed in Table 1 and the molecular structure with an atomic numbering scheme is shown in Fig. 1.

The structure was a dinuclear copper(II) complex, similar to other copper(II) carboxylates,[8] with 4 molecules of salicylate in a basal plane, and with H_2O and EtOH molecules in apical positions. The geometries around te copper atoms (in Fig. 1 and Table 2) are similar to those in diaquatetrakis(μ-2-methoxybenzoato-O,O')dicopper(II)[9] or diaquatetrakis(μ-salicylato-O,O')dicopper(II)-dioxane.[10] The presence of two different ligands at the apical position is, as far as we know, the first example in dinuclear copper(II) carboxylates. A streoview of the crystal packing is shown in Fig. 2. One water molecule [O(S5)] exist between two dimers by forming two hydrogen bonds: O(S5)···O(S1) (x,y,z), 2.894(4) Å and O(S5)···O(S2) ($0.5-x$, $0.5+y$, $0.5-z$), 2.677(4) Å, while the remaining ethanol molecule [O(S6)] hydrogen-bonds only to O(S1) ($0.5-x$, $-0.5+y$, $1.5-z$), 2.655(5) Å. The large thermal parameters along with the abnormal bond lengths of this ethanol molecule show that the position is still disordered, though no further refinement was attempted. The solvents of crystallization were easily lost when the crystals were left in a desiccator over silica-gel; an elementary analysis at this stage fitted $[Cu_2(C_7H_5O_2)_4]\cdot C_2H_5OH\cdot H_2O$.

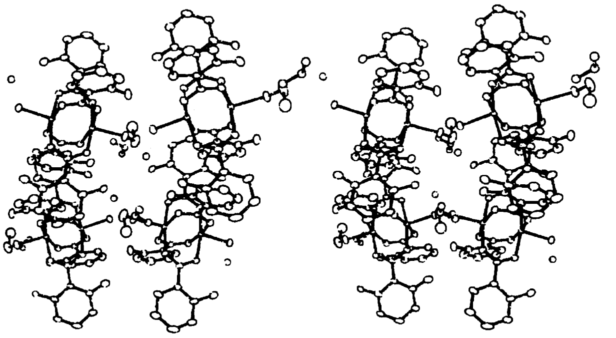

Fig. 2. Stereoview of the crystal packing of **1** viewed down the c^*-axis (b is horizontal).

Table 1. Final Atomic Coordinates of the Non-Hydrogen Atoms ($\times10^4$) and Equivalent Isotropic Temperature Factors with esd's in Parentheses

Atom	x	y	z	B_{eq}[a)]
Cu(1)	2422.0(2)	1952.3(2)	3916.9(2)	2.57(2)
Cu(2)	2818.4(2)	3525.6(2)	4223.7(2)	2.72(2)
O(3)	2994 (2)	1721 (2)	5072 (2)	3.6(1)
O(4)	3454 (2)	3039 (1)	5272 (2)	3.7(1)
C(5)	3400 (2)	2280 (2)	5515 (2)	3.2(1)
C(6)	3825 (2)	2038 (2)	6377 (2)	3.2(1)
C(7)	4232 (2)	2639 (2)	6934 (2)	3.8(1)
C(8)	4575 (3)	2406 (3)	7775 (3)	4.7(2)
C(9)	4520 (3)	1582 (3)	8041 (3)	5.5(2)
C(10)	4151 (3)	969 (3)	7476 (3)	5.3(2)
C(11)	3797 (3)	1205 (3)	6654 (3)	4.3(2)
O(12)	4295 (2)	3455 (2)	6708 (2)	5.2(1)
O(13)	1934 (2)	2375 (1)	2778 (2)	3.5(1)
O(14)	2105 (2)	3711 (1)	3119 (2)	3.7(1)
C(15)	1872 (2)	3130 (2)	2592 (2)	3.2(1)
C(16)	1507 (2)	3376 (2)	1704 (2)	3.1(1)
C(17)	1378 (3)	4218 (2)	1475 (2)	4.1(2)
C(18)	1065 (3)	4451 (3)	641 (3)	6.0(2)
C(19)	847 (4)	3817 (4)	24 (3)	6.1(2)
C(20)	980 (3)	2987 (3)	225 (3)	5.5(2)
C(21)	1299 (3)	2768 (3)	1068 (2)	4.3(2)
O(22)	1570 (2)	4848 (2)	2071 (2)	5.3(1)
O(23)	1293 (2)	2235 (1)	4536 (2)	3.6(1)
O(24)	1683 (2)	3552 (1)	4876 (2)	3.7(1)
C(25)	1139 (2)	2955 (2)	4882 (2)	3.2(1)
C(26)	251 (2)	3090 (2)	5304 (2)	3.5(1)
C(27)	−360 (2)	2441 (3)	5442 (3)	4.4(2)
C(28)	−1203 (3)	2582 (4)	5818 (4)	6.3(2)
C(29)	−1432 (3)	3366 (5)	6066 (3)	7.0(3)
C(30)	−852 (3)	4049 (4)	5918 (3)	6.1(2)
C(31)	−2 (3)	3907 (3)	5553 (3)	4.9(2)
O(32)	−147 (2)	1627 (2)	5241 (3)	6.3(2)
O(33)	3630 (2)	1914 (1)	3394 (2)	3.6(1)
O(34)	3884 (2)	3286 (2)	3506 (2)	3.9(1)
C(35)	4115 (2)	2554 (2)	3287 (2)	3.3(1)
C(36)	5036 (2)	2427 (2)	2922 (2)	3.3(1)
C(37)	5606 (3)	3113 (3)	2765 (3)	5.2(2)
C(38)	6489 (3)	2983 (3)	2472 (4)	6.0(2)
C(39)	6782 (3)	2176 (4)	2317 (4)	6.4(2)
C(40)	6230 (3)	1490 (3)	2480 (3)	5.3(2)
C(41)	5359 (2)	1620 (3)	2763 (3)	4.1(2)
O(42A)	5394 (3)	3916 (3)	2914 (4)	6.0(3)
O(42B)	4954 (5)	947 (6)	2919 (6)	6.1(4)
O(S1)	1975 (2)	711 (1)	3585 (2)	4.0(1)
O(S2)	3188 (2)	4814 (2)	4377 (2)	5.2(1)
C(S3)	3389 (5)	5267 (3)	5165 (4)	8.0(3)
C(S4)	2726 (5)	5184 (4)	5838 (5)	9.5(4)
O(S5)	930 (2)	556 (2)	1952 (2)	6.6(2)
O(S6)	3861 (3)	4907 (3)	10116 (3)	8.7(2)
C(S7)	3579 (9)	5011 (7)	9168 (7)	16.9(8)
C(S8)	3291 (11)	4500 (7)	8686 (7)	19.5(10)

a) B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

Experimental

Aqua(ethanol)tetrakis(μ-salicylato-O,O')dicopper(II)–Ethanol–Water (1/1/1) (1). Copper(II) hydroxide (20 g) and salicylic acid (140 g) were stirred in 500 ml of 80% (w/w) ethanol at 65 °C until the solids dissolved (5 min). The dark-green solution was left to stand at room temperature (ca. 20 °C) overnight and blue-green crystals were collected by filtration and washed with 50 ml of 80% ethanol, then air-dried to give 45 g of compound **1**. Found: C, 47.49; H, 4.51; Cu, 15.9%. Calcd

Table 2. Selected Bond Distances (Å) and Angles (°) around Dinuclear Copper Atoms

(a) Bond distances			
Cu(1)–Cu(2)	2.621(0)		
Cu(1)–O(3)	1.958(2)	Cu(2)–O(4)	1.984(2)
Cu(1)–O(13)	1.970(2)	Cu(2)–O(14)	1.979(2)
Cu(1)–O(23)	1.971(2)	Cu(2)–O(24)	1.952(2)
Cu(1)–O(33)	1.958(2)	Cu(2)–O(34)	1.957(2)
Cu(1)–O(S1)	2.147(2)	Cu(2)–O(S2)	2.141(2)
(b) Bond angles			
O(3)–Cu(1)–O(13)	170.4(1)	O(4)–Cu(2)–O(14)	165.5(1)
O(3)–Cu(1)–O(23)	89.0(1)	O(4)–Cu(2)–O(24)	90.6(1)
O(3)–Cu(1)–O(33)	88.0(1)	O(4)–Cu(2)–O(34)	89.2(1)
O(13)–Cu(1)–O(23)	91.7(1)	O(14)–Cu(2)–O(24)	88.1(1)
O(13)–Cu(1)–O(33)	89.2(1)	O(14)–Cu(2)–O(34)	89.4(1)
O(23)–Cu(1)–O(33)	167.4(1)	O(24)–Cu(2)–O(34)	169.2(1)
Cu(2)–Cu(1)–O(3)	86.1(1)	Cu(1)–Cu(2)–O(4)	82.3(1)
Cu(2)–Cu(1)–O(13)	84.4(1)	Cu(1)–Cu(2)–O(14)	83.1(1)
Cu(2)–Cu(1)–O(23)	83.4(1)	Cu(1)–Cu(2)–O(24)	85.3(1)
Cu(2)–Cu(1)–O(33)	84.1(1)	Cu(1)–Cu(2)–O(34)	83.9(1)
Cu(2)–Cu(1)–O(S1)	173.9(1)	Cu(1)–Cu(2)–O(S2)	175.7(1)

for $[Cu_2(C_7H_5O_2)_4]\cdot 2C_2H_6O\cdot 2H_2O$: C, 47.82; H, 4.52; Cu, 15.8%.

Aqua(ethanol)tetrakis(μ-salicylato-*O*,*O′*)dicopper(II) (2). Pulverized **1** was dried over silica-gel in a desiccator for two weeks to give **2**. Found: C, 48.71; H, 3.52; Cu, 17.3%. Calcd for $[Cu_2(C_7H_5O_2)_4]\cdot C_2H_6O\cdot H_2O$: C, 48.72; H, 3.82; Cu, 17.2%.

Crystallographic and Diffraction Data Collection of 1. The unit-cell dimensions were refined by a least-squares refinement from 25 reflections with $11° < \theta < 13°$ on an Enraf–Nonius Cad4 automated kappa-axis diffractometer with graphite-monochromated Mo $K\alpha$ radiation (50 kV and 26 mA). The diffraction intensities were measured for a single crystal of about $0.3\times 0.3\times 0.1$ mm^3 on the diffractometer up to $2\theta=60°$; 2θ–ω scan, the scan rate was 4 min^{-1} in θ, the scan width$=0.40+0.35\tan\theta$. Three standard reflections were measured after every 2 h. The intensities were corrected for Lorentz, polarization, and decay (−20% in intensity) but not for absorption. Systematic absences ($h=2n$, $k=2n$, $l=2n$, and $h+l=2n$) indicated unambiguously the space group $P2_1/n$. Of 9446 unique reflections, 8283 of the independent structure factors with $|F_o|>3\sigma(F_o)$ were used for a structure determination. The complete F_o-F_c data are deposited as Document No. 66052 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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