

catena-Poly { [bis(2-amino-2-methyl-1-propanol)copper(II)]- μ -[salicylato(2-)-O : O', O'']-copper(II)- μ -[salicylato(2-)-O', O''] : O } Tetrakis(2-propanol)

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Abstract. $[\text{Cu}_2(\text{C}_4\text{H}_{11}\text{NO})_2(\text{C}_7\text{H}_4\text{O}_3)_2] \cdot 4\text{C}_3\text{H}_8\text{O}$, $\text{C}_{22}\text{H}_{30}\text{Cu}_2\text{N}_2\text{O}_8 \cdot 4\text{C}_3\text{H}_8\text{O}$, triclinic, $P1$, $a = 10.085$ (7), $b = 8.663$ (4), $c = 13.522$ (8) Å, $\alpha = 102.78$ (4), $\beta = 72.65$ (5), $\gamma = 108.32$ (5)°, $V = 1060$ (1) Å³, $Z = 1$, $D_c = 1.28$ Mg m⁻³, $R = 0.046$, 2480 observed reflections. Two centrosymmetric Cu^{II} complexes alternate along a with Cu atoms at the centres of symmetry. One Cu is dichelated by two divalent salicylato groups each through one of the carboxylate O atoms and the phenolic O atom in a slightly distorted square-planar arrangement. The other Cu has a stereochemistry intermediate between four- and six-coordinate with the aminoalcohol N and O atoms in the coordination plane and the second carboxylate O atoms at a distance of 2.658 (4) Å from the Cu. Complexes are joined together by the very weak carboxylate bridge, hydrogen bonds between ligands, and hydrogen bonds through one of the two symmetry-independent solvate molecules. The other symmetry-independent solvate molecule is linked into the chain by a single hydrogen bond.

Introduction. The salicylic acid anion is a ligand able to coordinate to metal ions through a variety of dentation modes in which both the carboxylate and the phenolic O atoms participate. Especially with ions of heavy elements such as lanthanides and actinides, which possess high coordination numbers, there are several coordination modes in the same complex (Burns & Baldwin, 1977). In the few structures that have been described for Cu^{II} complexes containing the salicylato ligand, the following coordination modes occur: monodentate through a carboxylate O atom (Hanic & Michalov, 1960; Jagner, Hazell & Larsen, 1976); bidentate chelating (Muhonen & Hämäläinen, 1978a) and bidentate bridging (Ablov, Kiosse, Dimitrova, Malinowski & Popovich, 1974) through both carboxylate O atoms; bidentate bridging through one of the carboxylate O atoms and the phenolic O atom (Jagner, Hazell & Larsen, 1976). The aim of the present investigation was to study the effect of a bulky multidentate ligand on the Cu^{II} aminoalcohol complex.

The powdered crude product was prepared by the reaction of copper(II) salicylate with 2-amino-2-methyl-1-propanol in methanol. Recrystallization in 2-propanol yielded green crystals, which were shown by Weissenberg photographs to be triclinic. Intensities and unit-cell dimensions were measured on a Syntex P2₁ diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.7107$ Å) and a crystal 0.60 × 0.32 × 0.18 mm coated with epoxy glue. With the ω -scan technique and a variable scan rate from 2.2 to 29.3° min⁻¹, 3722 unique reflections with $4 < 2\theta < 50^\circ$ were collected. Of these, 2480 with $|F_o| > 5\sigma(|F_o|)$ were used for the structure determination and refinement. Two test reflections checked after every 98 intensity

Table 1. *Fractional coordinates ($\times 10^4$) and U_{eq} values ($\times 10^2$) for non-H atoms*

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq} (Å ²) |
|-------|------------|-----------|----------|----------------------------|
| Cu(1) | 0 | 0 | 0 | 5.07 (5) |
| Cu(2) | 5000 | 0 | 0 | 4.54 (5) |
| O(1) | -361 (3) | 1919 (3) | 1088 (2) | 5.3 (2) |
| O(2) | 2950 (3) | -669 (4) | 332 (2) | 5.6 (2) |
| O(3) | 741 (3) | -1270 (4) | 1308 (2) | 6.6 (2) |
| O(4) | 5107 (3) | -647 (4) | 1222 (2) | 5.5 (2) |
| O(5) | -1799 (4) | -1513 (5) | 2818 (3) | 9.1 (2) |
| O(6) | 6972 (3) | 2128 (4) | 2035 (3) | 8.2 (2) |
| N | 1855 (3) | 1586 (4) | -490 (2) | 4.0 (2) |
| C(1) | 502 (5) | 3420 (5) | 665 (4) | 5.4 (3) |
| C(2) | 2015 (4) | 3218 (4) | 184 (3) | 4.4 (2) |
| C(3) | 2904 (5) | 4607 (6) | -469 (4) | 7.5 (3) |
| C(4) | 2747 (5) | 3242 (6) | 1028 (4) | 6.9 (3) |
| C(5) | 2037 (4) | -1216 (5) | 1151 (3) | 4.9 (2) |
| C(6) | 2527 (4) | -1806 (5) | 1906 (3) | 4.5 (2) |
| C(7) | 4008 (4) | -1508 (5) | 1890 (3) | 4.7 (2) |
| C(8) | 4323 (5) | -2143 (6) | 2632 (4) | 5.9 (3) |
| C(9) | 3263 (6) | -3036 (6) | 3356 (4) | 6.7 (3) |
| C(10) | 1830 (5) | -3326 (6) | 3363 (4) | 6.7 (3) |
| C(11) | 1477 (5) | -2720 (5) | 2658 (4) | 5.6 (3) |
| C(12) | -2966 (10) | -964 (12) | 4533 (6) | 17.5 (7) |
| C(13) | -1803 (9) | -580 (11) | 3766 (6) | 16.7 (6) |
| C(14) | -492 (9) | 766 (10) | 3848 (6) | 12.8 (6) |
| C(15) | 4944 (7) | 3140 (8) | 3021 (5) | 10.5 (5) |
| C(16) | 6283 (6) | 2736 (6) | 3048 (4) | 7.5 (3) |
| C(17) | 7339 (9) | 4114 (8) | 3469 (5) | 12.0 (5) |

measurements showed no decomposition of the crystal during the data collection. Lorentz, polarization and empirical absorption corrections [$\mu(\text{Mo } K\alpha) = 1.10 \text{ mm}^{-1}$] were applied. ψ scans over eight reflections, evenly distributed over the 2θ range used, showed slight absorption. The intensities decreased by 12–18%, when the crystal was rotated from the least to the most absorbing position.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques using programs of the XRAY 76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The atomic scattering factors were those contained in the program system and the anomalous-dispersion correction for the scattering factor for Cu was taken from *International Tables for X-ray Crystallography* (1974). The coordinates of the H atoms were obtained from the difference map and were allowed to vary initially. Because of the presence of loosely bound solvate molecules with methyl C atoms of high thermal motion, the H atoms were included in the last few cycles with fixed coordinates obtained from the previous refinement and with fixed U_{iso} of 0.05 \AA^2 . The final conventional R was 0.046 with unit weights for reflections and anisotropic temperature factors for all non-hydrogen atoms. The validity of unit weights was demonstrated by analysing the variation of $\langle w\Delta^2 \rangle$

in terms of batches of increasing $|F_o|$ and $\sin \theta$. Final atomic parameters are given in Table 1, and bond lengths and angles in Table 2.*

Discussion. The compound reveals two interesting features. Firstly, instead of the formation of some mixed-ligand complex as in the reaction of copper(II) salicylate with a diamine (Muhonen & Hämäläinen, 1978*a*), basically two different complexes result: an aminoalcohol and a salicylate complex are taken into the same structure (Fig. 1). Earlier the monohydrate of bis(2-amino-2-methyl-1-propanolato)copper(II) (Muhonen, 1981) and the di- and tetrahydrates of bis(salicylate)copper(II) (Jagner, Hazell & Larsen, 1976; Hanic & Michalov, 1960) had been synthesized as separate stable compounds. Secondly, the salicylate ligand coordinates to one of the Cu^{II} ions through one of the carboxylate O atoms and the phenolic O atom. No previously reported Cu^{II} complex has contained the salicylate ligand coordinated in this way. Such binding is common for ions of heavy elements with high coordination numbers (Burns & Baldwin, 1977; Nassimbeni, Rodgers & Haigh, 1976), and has also been reported for a Co^{III} complex with coordination number six (Kushi, Hosoo & Kuroya, 1970). The coordination geometry of the salicylate complex is square planar with $\text{Cu}(2)\text{—O}(2)$ and $\text{Cu}(2)\text{—O}(4)$ bonds of 1.903 (3) and 1.900 (3) Å. The Cu—salicylate six-membered ring is roughly planar. The deviations of the atoms from the least-squares plane are $\text{Cu}(2) - 0.029$ (4), $\text{O}(2) - 0.049$ (3), $\text{O}(4) - 0.082$ (3), $\text{C}(5) - 0.089$ (4), $\text{C}(6) - 0.041$ (4) and $\text{C}(7) - 0.052$ (4) Å.

The OH substituent in the *ortho* position in the benzene ring does not alter the coordination mode of the aminoalcohol from that in the benzoate compound

* Lists of structure factors, anisotropic thermal parameters and hydrogen atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36768 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances (Å) and angles (°)*

| | | | |
|-----------------|-----------|-------------------|------------|
| Cu(1)—N | 1.968 (3) | C(6)—C(7) | 1.428 (6) |
| Cu(1)—O(1) | 2.010 (3) | C(7)—C(8) | 1.398 (8) |
| Cu(1)—O(3) | 2.658 (4) | C(8)—C(9) | 1.375 (7) |
| C(1)—O(1) | 1.448 (5) | C(9)—C(10) | 1.384 (8) |
| C(1)—C(2) | 1.519 (6) | C(10)—C(11) | 1.361 (9) |
| C(2)—N | 1.493 (4) | C(11)—C(6) | 1.403 (6) |
| C(2)—C(3) | 1.533 (6) | | |
| C(2)—C(4) | 1.526 (8) | C(13)—O(5) | 1.355 (8) |
| | | C(13)—C(12) | 1.320 (10) |
| Cu(2)—O(2) | 1.903 (3) | C(13)—C(14) | 1.477 (11) |
| Cu(2)—O(4) | 1.900 (3) | | |
| C(5)—O(2) | 1.284 (4) | C(16)—O(6) | 1.407 (6) |
| C(5)—O(3) | 1.247 (5) | C(16)—C(15) | 1.510 (11) |
| C(7)—O(4) | 1.335 (4) | C(16)—C(17) | 1.465 (9) |
| C(5)—C(6) | 1.496 (7) | | |
| N—Cu(1)—O(1) | 82.8 (1) | O(3)—C(5)—C(6) | 120.2 (3) |
| N—Cu(1)—O(3) | 99.0 (1) | C(5)—C(6)—C(7) | 123.4 (3) |
| O(1)—Cu(1)—O(3) | 91.8 (1) | C(5)—C(6)—C(11) | 118.2 (4) |
| Cu(1)—N—C(2) | 112.9 (2) | O(4)—C(7)—C(6) | 124.3 (4) |
| Cu(1)—O(1)—C(1) | 108.6 (2) | O(4)—C(7)—C(8) | 118.0 (4) |
| O(1)—C(1)—C(2) | 106.7 (4) | C(6)—C(7)—C(8) | 117.7 (3) |
| N—C(2)—C(1) | 106.4 (3) | C(7)—C(8)—C(9) | 122.2 (5) |
| N—C(2)—C(3) | 110.9 (3) | C(8)—C(9)—C(10) | 119.7 (6) |
| N—C(2)—C(4) | 109.3 (4) | C(9)—C(10)—C(11) | 119.9 (4) |
| C(1)—C(2)—C(3) | 109.2 (4) | C(10)—C(11)—C(6) | 122.1 (5) |
| C(1)—C(2)—C(4) | 111.1 (3) | C(11)—C(6)—C(7) | 118.4 (5) |
| C(3)—C(2)—C(4) | 109.8 (3) | | |
| Cu(1)—O(3)—C(5) | 118.1 (3) | C(12)—C(13)—O(5) | 117.3 (7) |
| O(2)—Cu(2)—O(4) | 93.8 (1) | C(14)—C(13)—O(5) | 116.7 (6) |
| Cu(2)—O(2)—C(5) | 130.4 (3) | C(12)—C(13)—C(14) | 125.9 (7) |
| Cu(2)—O(4)—C(7) | 125.9 (3) | | |
| O(2)—C(5)—O(3) | 119.8 (4) | C(15)—C(16)—O(6) | 110.0 (5) |
| O(2)—C(5)—C(6) | 119.9 (4) | C(17)—C(16)—O(6) | 108.1 (4) |
| | | C(15)—C(16)—C(17) | 114.8 (5) |

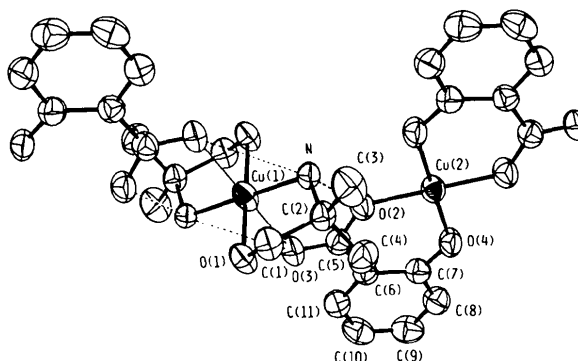


Fig. 1. View of the two complex units. Atoms are drawn with 50% probability thermal ellipsoids.

(Muhonen & Hämäläinen, 1978*b*). In both complexes the aminoalcohol is a non-oxygen-bridged protonated ligand. A much more common oxygen-bridged aminoalcohol ligand is found for an aryl carboxylate compound in the complex formed between copper(II) benzoate and 2-dibutylaminoethanol (Muhonen, Pajunen & Hämäläinen, 1980). In the present complex the bidentate aminoalcohol ligands are attached to a second Cu^{II} ion in a planar arrangement with $\text{Cu}(1)\text{—N}$ and $\text{Cu}(1)\text{—O}(1)$ bond lengths of 1.968 (3) and 2.010 (3) Å. The five-membered ring has unsymmetrical *gauche* conformation: the ring atoms C(1) and C(2) deviate -0.597 (6) and 0.056 (5) Å from the $\text{N—Cu}(1)\text{—O}(1)$ plane, and the dihedral angle between the planes $\text{O}(1)\text{—C}(1)\text{—C}(2)$ and $\text{N—C}(2)\text{—C}(1)$ is 48.9 (3)°. The second carboxylate O atoms are at a distance of 2.658 (4) Å from the Cu of the aminoalcohol complex, and the angle between the axial direction and the normal of the coordination plane is 9.0 (1)°. The stereochemistry around the Cu^{II} ion is planar or extremely elongated octahedral, depending on whether or not the second carboxylate O atoms are considered to be involved in semi-coordinate bonding to the Cu^{II} ion. This interpretation consequently determines the extent to which the compound can be described as ionic. The benzoate compound of the same aminoalcohol is clearly ionic with the out-of-plane

Table 3. *Hydrogen-bond distances and angles*

| $D\text{—H}\cdots A$ | Angle (°)* | $D\cdots A$ (Å) | $H\cdots A$ (Å)* | $D\text{—H}$ (Å)* |
|--|------------|-----------------|------------------|-------------------|
| $\text{N—H}(11)\cdots\text{O}(2)$ | 138 | 3.053 (6) | 2.46 | 0.74 |
| $\text{N—H}(10)\cdots\text{O}(3^{\text{ii}})$ | 112 | 3.049 (5) | 2.66 | 0.79 |
| $\text{O}(1)\text{—H}(1)\cdots\text{O}(6^{\text{ii}})$ | 173 | 2.656 (4) | 2.00 | 0.66 |
| $\text{O}(5)\text{—H}(16)\cdots\text{O}(3)$ | 164 | 2.740 (5) | 2.01 | 0.75 |
| $\text{O}(6)\text{—H}(24)\cdots\text{O}(4)$ | 170 | 2.783 (4) | 2.14 | 0.65 |

Symmetry codes: (i) $-x, -y, -z$; (ii) $x - 1, y, z$.

* No estimated standard deviation is given for these data since H-atom parameters were not varied in the last few cycles.

Cu—O distance of 3.184 (6) Å (Muhonen & Hämäläinen, 1978*b*).

The complexes are joined into a one-dimensional polymeric chain (Fig. 2) by the very weak carboxylate bridge, the hydrogen bonds from the aminoalcohol N atom to the carboxylate O atoms, and the $\text{O}(6)\cdots\text{O}(4)$ and the $\text{O}(1)\cdots\text{O}(6^{\text{ii}})$ hydrogen bonds between one of the solvate molecules and the different ligands. The other symmetry-independent solvate molecule is hydrogen bonded to the axial carboxylate O(3) atom. Hydrogen-bonding parameters are given in Table 3.

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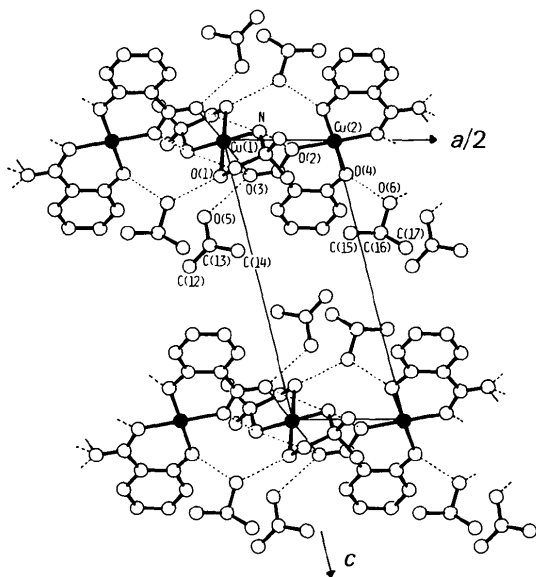


Fig. 2. Projection of the structure roughly along the b^* axis. Hydrogen bonds are shown by broken lines.