Crystal Structure of a Copper Complex of 2-Carboxypentonic Acid;† a Decomposition Product of Dehydroascorbic Acid

Richard E. Norman and Norman J. Rose *
Department of Chemistry, University of Washington, Seattle, WA 98195, U.S.A.
Ronald E. Stenkamp
Department of Biological Structure, University of Washington, Seattle, WA 98195, U.S.A.

In acidic aqueous solution and in the presence of copper(II), ascorbic acid is rapidly oxidized to dehydroascorbic acid, which rearranges to give the branched-chain dicarboxylic acid 2-carboxypentonic acid (1,2,3,4-tetrahydroxybutane-1,1-dicarboxylic acid) (H_3cpa). The ion cpa^{3-} is sequestered by copper(II) to produce the insoluble crystalline product $[Cu_9Cl_2(cpa)_6(H_2O)_3]^{2-}\cdot xH_2O$. Characterization of the crystals by *X*-ray diffraction indicates that copper exists in two distinct environments, one of which is five-co-ordinate and the other six-co-ordinate, and that cpa^{3-} makes seven bonds to copper. Channels of disordered solvent occupy 40% of the cell volume and pass completely through the crystals.

Ascorbic acid (**1**) and its metabolic products [including dehydroascorbic acid (**2**)] are known to interact with copper in biological systems. They are linked in tumour inhibition,[1] the induced haemolysis of rat erythrocytes,[2] and the induction of DNA lesions in bacterial cells.[3] Also, dietary absorption of copper is inhibited by ascorbic acid.[4] These observations, along with the lack of structural information for transition-metal complexes of dehydroascorbate,‡ or its derivatives, stimulated exploratory synthetic studies which led to the discovery of an insoluble blue crystalline complex (**5**). The empirical formula of the complex, derived from the structural analysis, is $[Cu_9Cl_2(cpa)_6(H_2O)_3]^{2-}\cdot xH_2O$, where H_3cpa is 2-carboxypentonic acid (1,2,3,4-tetrahydroxybutane-1,1-dicarboxylic acid) (**3**). Compound (**3**) can be derived from diketogulonic acid (4,5,6-trihydroxy-2,3-dioxohexanoic acid) (**4**), a hydrolysis product of (**2**). The synthesis and structure of complex (**5**) are of potential relevance to investigations of the role of copper(II) and the metabolic products of ascorbic acid,[1–4] solid-state studies of substances containing two different complexes of the same metal (two distinct co-ordination geometries for copper found in the same crystal),[6] and studies of materials containing regular channels or cavities of specific sizes.[7]

Experimental

Synthesis of $[Cu_9Cl_2(cpa)_6(H_2O)_3]^{2-}\cdot xH_2O$ (**5**).—Copper(II) chloride hydrate (0.3410 g, 2.00 mmol) was dissolved in water (20 cm^3). Addition of ascorbic acid (0.1762 g, 1.00 mmol) resulted in the precipitation of white copper(I) chloride. This mixture was stirred for 1 h and the CuCl was filtered off. Copper(II) chloride hydrate (0.1704 g, 1.00 mmol) was then added to the filtrate, followed by the addition of a freshly prepared 1.00 mol dm^{-3} NaOH solution (4.5 cm^3). After 3 d, blue crystalline trapezoidal prisms of the product were collected (0.2364 g, 68%).

Compound (**5**) is insoluble in water and organic solvents, and decomposes in concentrated acids or bases. It has not been recrystallized. Consequently, given that the crystals contain large channels of mother-liquor (see below), elemental analyses are of very limited utility.

Table 1. Positional parameters for compound (**5**)

Atom	*x*	*y*	*z*
Cu(1)	0.561 94(7)	0.280 09(13)	−0.017 7(2)
Cu(2)	0.498 82(2)	0.498 82	0.0000
Cl	0.333 33	0.666 67	0.294 7(6)
O(1)	0.688 2(5)	0.508 2(5)	−0.069(2)
O(2)	0.600 8(5)	0.529 9(5)	−0.052(1)
O(3)	0.620 5(6)	0.379 1(5)	0.060 0(9)
O(4)	0.525 7(7)	0.464 9(7)	0.250(1)
O(5)	0.468 5(8)	0.313 2(7)	0.287(2)
O(6)	0.589(1)	0.423(1)	0.616(1)
O(7)	0.496 8(6)	0.310 8(6)	−0.084(1)
O(8)	0.471 3(5)	0.402 4(6)	−0.069(1)
C(1)	0.623 3(7)	0.488 7(7)	−0.036(2)
C(2)	0.584 6(9)	0.421(1)	0.057(1)
C(3)	0.574(1)	0.436(1)	0.247(1)
C(4)	0.540(1)	0.365(1)	0.353(2)
C(5)	0.527(1)	0.378(1)	0.528(2)
C(6)	0.508 5(9)	0.370 2(9)	−0.031(2)
O(10)	0.570(1)	0.570	0.5000
O(20)	0.200(4)	0.359(3)	0.205(7)
O(21)	0.110(5)	0.376(5)	0.35(1)
O(22)	0.002(3)	0.329(2)	0.233(5)
O(23)	0.359(2)	0.351(2)	0.280(4)
O(24)	0.000	0.308(5)	0.000
O(25)	0.361(6)	0.155(8)	0.01(1)
O(26)	0.420(2)	0.171(2)	0.316(6)
O(27)	0.115(2)	0.413(3)	0.421(5)
O(28)	0.235(4)	0.410(4)	0.40(1)
O(29)	0.274(4)	0.308(4)	0.06(1)

Ion Exchange.—The ion exchange of complex (**5**) and a strongly acidic cation-exchange resin were compared by monitoring the pH of salt solutions added to each. The resin (Dowex 50W-X12, rated as 1 g = 5.1 mequiv. H$^+$; 0.3396 g) was soaked in concentrated HCl for 30 min and then washed in deionized water (in 10-cm^3 increments) until constant pH was attained. To eliminate Na$^+$ from complex (**5**), copper(II) acetate hydrate was substituted for the copper(II) chloride and NaOH in the synthesis described above. The reaction yield was greatly reduced by this substitution. The resulting material (2.7053 g) was washed until a constant pH was achieved. A 1.00 mol dm^{-3} NaCl solution (10 cm^3) was then added to each. For the ion-exchange resin, the pH dropped to 1.9, while for

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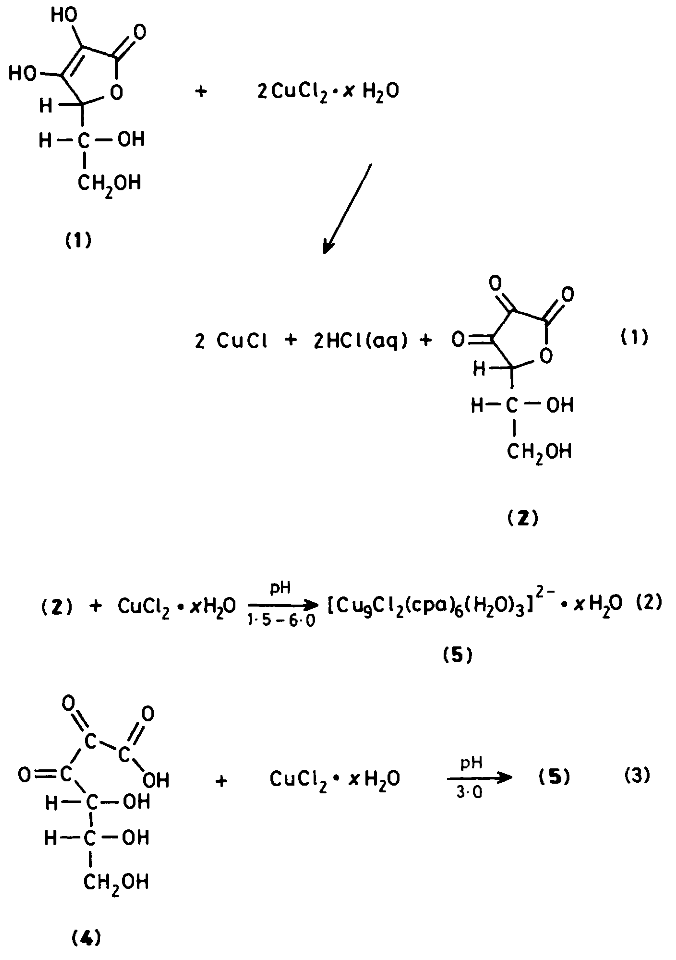
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

‡ After solving the structure described in this paper, we became aware of one transition-metal ascorbate structure, see ref. 5.

Table 2. Selected interatomic distances (Å) and angles (°) for compound (5). Primes denote symmetry-related atoms

Cu(1)–O(1)	1.94(2)	Cu(2)–O(2)	1.97(1)
Cu(1)–O(7)	1.88(2)	Cu(2)–O(8)	1.91(2)
Cu(1)–O(3)	1.94(2)	Cu(2)–O(4)	2.29(2)
Cu(1)–O(3′)	1.92(2)	Cu(1) • • • Cu(1′)	3.342(4)
Cu(1)–Cl	2.93(2)		
O(1)–Cu(1)–O(7)	91.4(6)	O(2)–Cu(2)–O(8)	89.7(5)
O(1)–Cu(1)–O(3)	170.7(6)	O(2)–Cu(2)–O(4)	83.3(5)
O(1)–Cu(1)–O(3′)	84.6(7)	O(2)–Cu(2)–O(2′)	88.2(5)
O(7)–Cu(1)–O(3)	84.1(5)	O(2)–Cu(2)–O(8′)	175.3(5)
O(7)–Cu(1)–O(3′)	174.7(4)	O(2)–Cu(2)–O(4′)	99.4(5)
O(3)–Cu(1)–O(3′)	99.3(6)	O(8)–Cu(2)–O(4)	84.4(5)
Cl–Cu(1)–O(1)	106.5(4)	O(8)–Cu(2)–O(8′)	92.8(5)
Cl–Cu(1)–O(7)	101.7(5)	O(8)–Cu(2)–O(4′)	93.0(5)
Cl–Cu(1)–O(3)	82.5(3)	O(4)–Cu(2)–O(4′)	176.3(4)
Cl–Cu(1)–O(3′)	82.9(3)		
		Cu(1)–O(3)–Cu(1′)	120.4(6)
		Cu(1)–Cl–Cu(1′)	69.4(1)



Scheme.

complex (5) the pH was virtually unchanged. Crushing the crystals with a glass stirring rod did not significantly alter the pH. Similar experiments were conducted with LiCl, KCl, RbCl, CsCl, NH_4Cl, $MgCl_2$, and $CaCl_2$ with similar results.

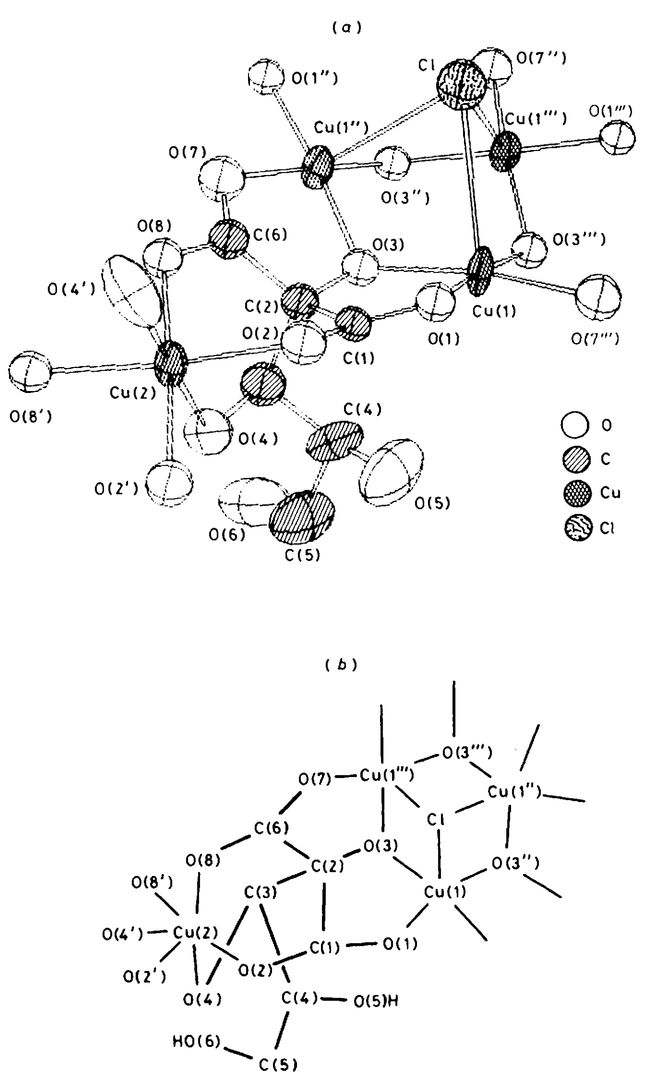


Figure 1. A view of one portion of $[Cu_9Cl_2(cpa)_6(H_2O)_3]^{2-}\cdot xH_2O$ (5) containing a single cpa^{3-} ligand, showing its bonds to copper and including ligating atoms of all the copper atoms. Single primes indicate atoms related by a two-fold axis passing through Cu(2), double and triple primes denote atoms related by a three-fold axis passing through Cl. The ligand in this view is shown with the same configuration as that of L-ascorbic acid. (*a*) ORTEP view; (*b*) schematic representation

Crystallography.—A blue, trapezoidal prismatic crystal measuring approximately 0.1 × 0.2 × 0.3 mm was mounted in a glass capillary with a drop of mother-liquor and sealed for *X*-ray studies. The crystals gave unsuitable diffraction patterns if allowed to dry. The unit-cell parameters were obtained from a least-squares fit of 18 centred reflections on a Picker FACS1 four-circle diffractometer.

Crystal data. $C_{36}H_{50}Cl_2Cu_9O_{51}\cdot xH_2O$ (the contents of the unit cell), trigonal, $a = b = 21.274(5)$ Å, $c = 7.976\,6(7)$ Å, $U = 3\,126.4$ Å^3, Cu-K_α radiation, $\lambda = 1.5418$ Å, space group *P*321.

Data collection was carried out using ω—2θ scans with a scan speed of 2° min^{-1} in 2θ, with nickel-filtered Cu-K_α radiation. Of the 1 446 reflections measured in the range ($2 < 2\theta < 90°$), there were 1 227 with $(F_o)^2 > 2\sigma(F_o)^2$. An absorption correction[8] (maximum value 1.350) and a deterioration correction (based on the behaviour of six standard reflections monitored throughout the data collection) were also applied.

Structure analysis and refinement. Direct methods[9,10] were

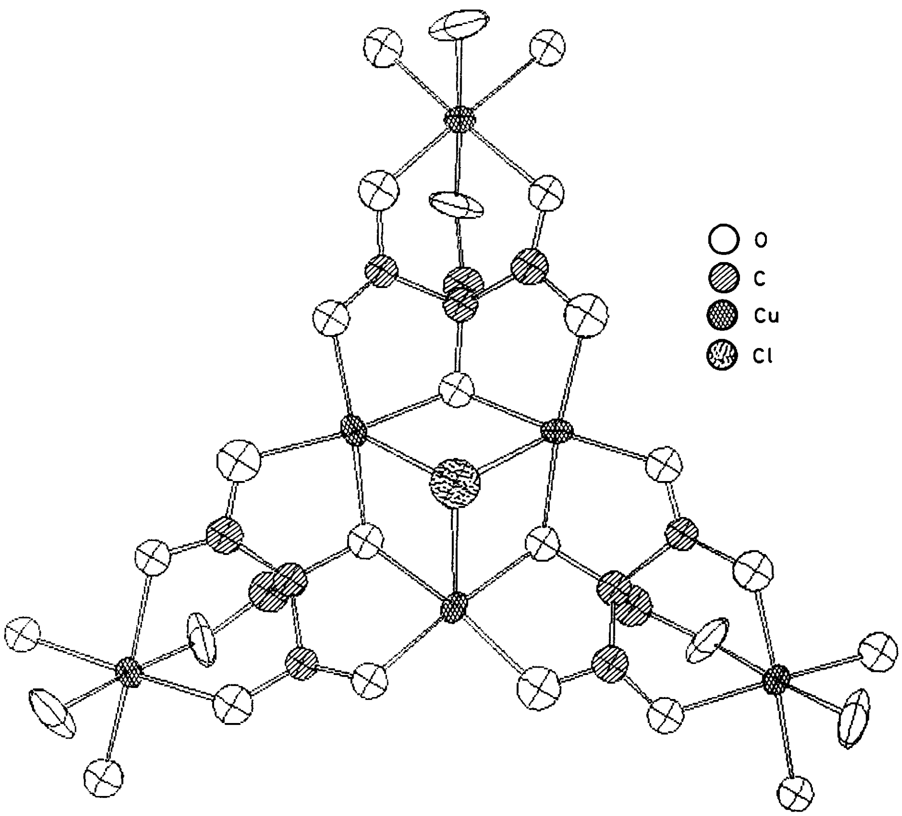


Figure 2. A larger view of compound (**5**) looking down the three-fold axis, emphasizing the two different copper sites. This view contains a $Cu_6Cl(cpa)_3$ sub-section with the copper ligating atoms included, but omitting the two terminal alcohol units of each cpa^{3-}

used to obtain the positions of the two copper atoms (one in a general position, the other on a two-fold axis) and the chlorine atom (located on the three-fold axis). Normal heavy-atom procedures then revealed the positions of the atoms of the ligand and an oxygen atom located on the other two-fold axis half a unit cell from the copper position on the two-fold axis. A model of the disordered solvent occupying 40% of the cell volume was generated using difference syntheses. Full-matrix least-squares refinement was not well behaved. Thermal parameters for some of the solvent and two of the ligand atoms became non-positive definite during the refinement, which did not converge. The model finally adopted had anisotropic thermal parameters for the copper atoms, the chlorine atom, five of the six carbon atoms of the ligand, seven of the eight oxygen atoms of the ligand, and three of the nine disordered oxygen atoms of the solvent. The $(\sin\theta)/\lambda$ cut-off was 0.100 (which excludes 15 low-lying reflections) to account for extinction. The refinement included anomalous dispersion terms for copper and chlorine[11] and gave $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.062$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}} = 0.105$. Calculations were carried out using the *X*-RAY system[12] on a VAX 11-780 computer. Atomic scattering factors were taken from ref. 13.

Table 1 lists the fractional atomic co-ordinates with their estimated standard deviations, Table 2 selected distances and angles.

Results and Discussion

Syntheses.—Compound (**5**) can be prepared in acidic aqueous solution at approximately 25 °C by starting with ascorbic acid (**1**), dehydroascorbic acid (**2**), or diketogulonic acid (**4**)[14] according to reactions (1) and (2) together, (2) alone, or (3) alone (Scheme).* Given that the lactone ring of (**2**) readily opens to give (**4**),[14] we surmise that all of the routes have in common the rearrangement of the straight-chain (**4**) to the branched-chain cpa^{3-}. Compound (**3**) has previously been prepared under basic conditions (including pH 7.4) from (**2**) with (**4**) as a proposed intermediate.[15] This conversion from a straight-chain to a branched-chain carbon compound has now apparently been demonstrated over the range pH 1.0—14.0. The ion cpa^{3-} is sequestered by copper in the range pH 1.0—7.0.

Description of the Structure.—Two environments for copper were found in the structure. The copper atom in site one, located near a crystallographic three-fold axis, has a square-pyramidal co-ordination polyhedron of four oxygen atoms in the basal plane, and a more distant, axial chlorine atom (located on the three-fold axis). The copper atom in site two is located on a crystallographic two-fold axis and has four relatively short equatorial bonds and two longer axial bonds all to oxygen, see Figures 1 and 2. The copper in site one binds to two symmetry-related (by the three-fold axis) oxygen atoms forming a part of an alternating copper–oxygen six-membered ring above which the chlorine atom is centred. This ring is quite similar to the copper–oxygen ring reported[16] for the complex of tartronic acid (H_3tart), $[Cu_3(tart)_3]^{3-}$, with comparable bond lengths. The co-ordination polyhedron of this site is completed by two carboxylate oxygen atoms of symmetry-related ligands. The four Cu(1)–O distances range from 1.88(2) to 1.94(2) Å and are similar to those reported (1.89—1.94 Å) for a series of copper complexes of 2-alkoxycarboxylates.[17] The Cu(1)–Cl distance is

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* The compounds prepared by these various routes have been shown to be identical by *X*-ray powder diffraction patterns.

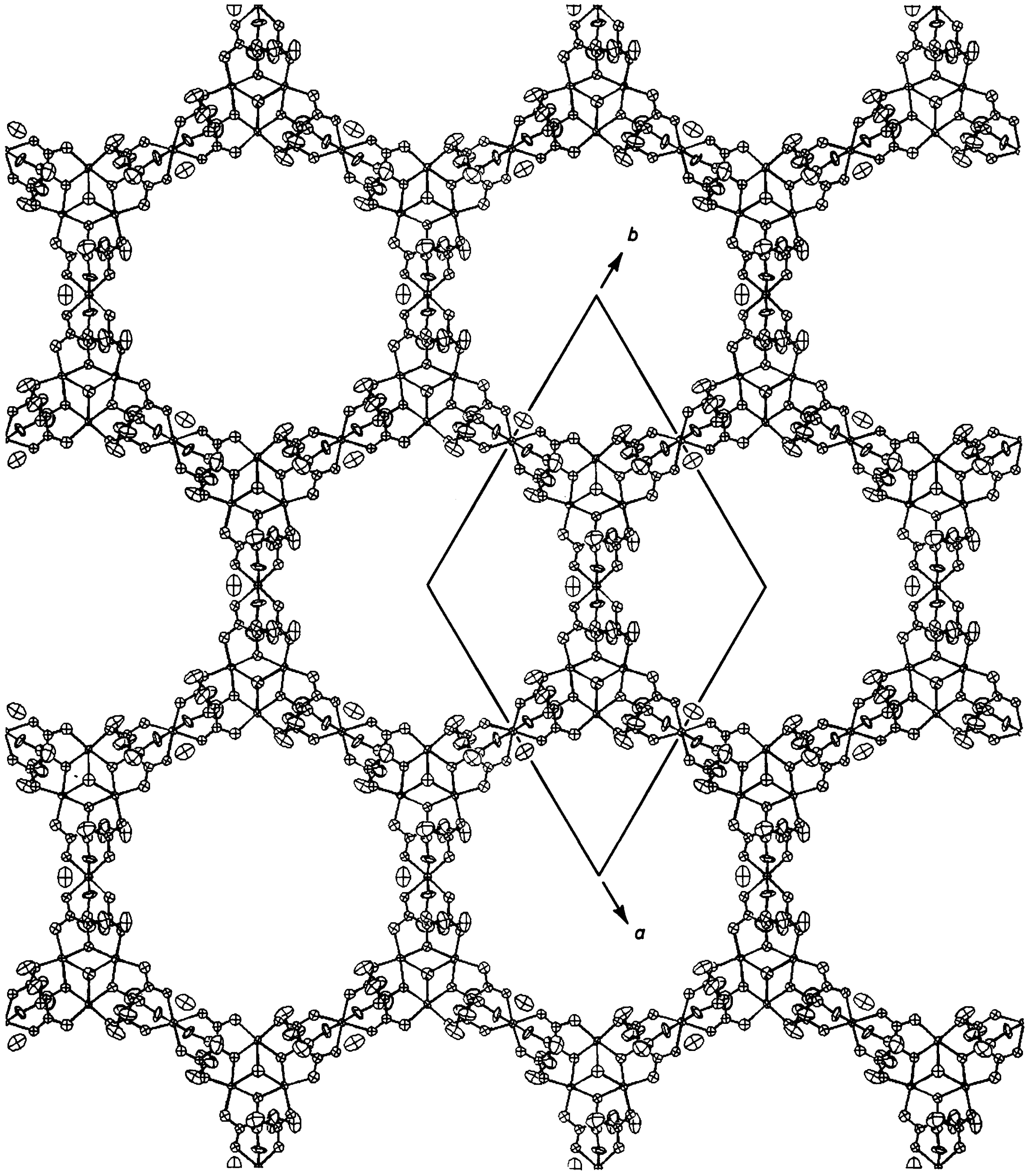

Figure 3. A view of a small portion of one polymeric layer emphasizing the regions of disordered solvent. The unit cell {containing the $[Cu_9Cl_2(cpa)_6(H_2O)_3]^{2-}$ repeating unit} is indicated

2.93(2) Å, which is longer than typical values for such distances when the chlorine is in an axial position[18] [2.411(7)—2.635(2) Å], but the copper atom is displaced from the plane of its four oxygen ligating atoms towards the chlorine atom by 0.10 Å, suggesting that the copper–chlorine interaction is significant. Although μ_3 chlorides are a known structural feature for copper(I) complexes,[19] such as the cubane-type clusters $[\{CuCl(PR_3)\}_4]$ and their analogues with typical Cu^I–Cl distances ranging from 2.363 to 2.505 Å, to our knowledge this is the first example of a symmetrical μ_3-chloride bridge in a copper(II) complex. Similar bridges with one long (2.95—3.185 Å) and two relatively short (2.264—2.322 Å) Cu–Cl distances are found in some Cu_nCl_m-containing complexes.[20]

The six oxygen atoms bound to the copper atom of site two are the remaining carboxylate oxygen atoms (those not bound to the copper atom in site one), a hydroxy oxygen atom, and their symmetry-related equivalents (by the two-fold axis). The copper–carboxylate oxygen distances are similar to the Cu–O distances in the 2-alkoxycarboxylates previously mentioned.[17] The copper–hydroxy oxygen distance is typical of the range reported [2.159(7)—2.477(2) Å] for copper–methanol complexes.[21]

The ligand cpa^{3-}, which has no crystallographically imposed symmetry, binds to three copper atoms (two from site one and one from site two) through six oxygen atoms with a total of seven bonds. The hydroxy group of the terminal carbon participates in hydrogen bonding with the chlorine atom of a neighbouring cell. The chlorine–oxygen distance is in the range reported (2.86—3.21 Å) for such hydrogen bonds.[22]

It is readily seen in Figure 3 that $[Cu_9(cpa)_6]_n$ is a polymeric sheet or layer held together by a combination of copper–oxygen, oxygen–carbon, and carbon–carbon bonds. The crystal consists of stacks of these layers which are held together by interactions involving chlorine atoms and water molecules located between the layers. The water molecules (located on the second crystallographic two-fold axis above and below copper site two) are hydrogen bonded to both the axial oxygen atoms in copper site two, one from a layer above and the other from a layer below. The oxygen–oxygen distance is typical of this type of interaction.[22] The chlorine atom interacts with three copper atoms of one layer and hydrogen bonds to three terminal alcohol groups of three ligands of an adjacent layer.

The stacking of these layers gives rise to cylindrical channels of diameter *ca.* 20 Å. These pass completely through the crystal and occupy 40% of the unit cell, see Figures 2 and 3. Channels similar to these are observed in the copper complexes of pyridine-2-carbaldehyde oxime[23] and 2-methylamino-1-phenylpropan-1-ol.[24] As the crystals dry, they bend along the *c* axis (the axis perpendicular to the trapezoidal face), and we speculate that water leaves the solvent channels first which then allows the loss of the water molecules located on the two-fold axis, the ones critical for holding adjacent polymer layers together. However, it should be noted that in the copper complex of pyridine-2-carbaldehyde oxime,[23] which also contains similar channels of water, there is no specific hydrogen bonding as in compound (**5**), yet loss of the solvent leads to a 'collapse' of the crystals.

Ion Exchange.—If each copper ion is assumed to be bivalent, and if the ligand has a charge of −3 (arising from the deprotonation of the two carboxylate units and the hydroxy group giving rise to the ring oxygen atom), then electrical neutrality of the compound can only be achieved if two positive charges are added for each $[Cu_9Cl_2(cpa)_6]^{2-}$ unit. Given that the compound can be synthesized in an acidic medium with no other cations present besides Cu^{II}, we assume that the positive charges are protons. We conducted parallel experiments with compound (**5**) and a strongly acidic cation-exchange resin on the hydrogen cycle (see Experimental section for details). No evidence for cation exchange was observed. Based on these experiments, we conclude that H_3O^+ is probably not present in the channels of disordered solvent. Although an alternative for the extra positive charge is the presence of Cu^{2+}(aq) in the channels in a disordered fashion, variability in elemental analyses of two samples (Cu:Cl:C = 8.02:1.85:36.0 and 8.35:1.63:36.0) does not allow a resolution of this issue. We surmise that protons are involved in a trifurcated hydrogen bond which holds the layers together (one proton per Cl^-), hence a possible formulation is $[Cu_9(HCl)_2(cpa)_6(H_2O)_3]\cdot xH_2O$.

We must stress that, due to the channels of disordered solvent, compound (**5**) changes upon separation from the mother-liquor. Consequently, studies of it must be performed in the presence of the mother-liquor. Otherwise one cannot be sure if it is compound (**5**) which is being studied or some other solid phase.

We offer two speculations concerning compound (**5**). (1) Given the stability of these crystals when maintained in contact with aqueous solution, if some method of supporting these crystals were devised which would maintain the proper orientation of the solvent channels, this material might serve as a molecular filter or membrane. (2) The facile rearrangement of dehydroascorbic acid in the presence of copper(II) occurs in water under moderate conditions of pH and temperature, suggesting that such processes may be important in the context of biological studies such as those mentioned above.[1–4]

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