A Linear Polymer of Copper(II) with Water and the Carboxy Group of L-alanine as Bridges

Hywel O. Davies, Robert D. Gillard,* Michael B. Hursthouse* and Alice Lehmann

School of Chemistry and Applied Chemistry, University of Wales, PO Box 912, Cardiff CF1 3TB

Copper(II) (L-alanine) (sulfate)dihydrate is described; the natural amino acid L-alanine behaves unusually as a carboxylic acid.

Compounds of amino acids with cupric ions are well known.[1] They have provided metabolic intermediates, the prototypes of chelated structures, chromophores in early Cotton effect studies of relative configurations, and transformations of geometric isomers in the solid state. Similarly, carboxylate compounds of copper(II) have been widely studied,[2] being invariably oligomeric or polymeric [e.g. dimeric copper(II) ethanoate and hexameric copper(II) phenoxyethanoate].

We report the nature of the new compound copper(II) (L-alanine)(sulfate)dihydrate in which the natural amino acid
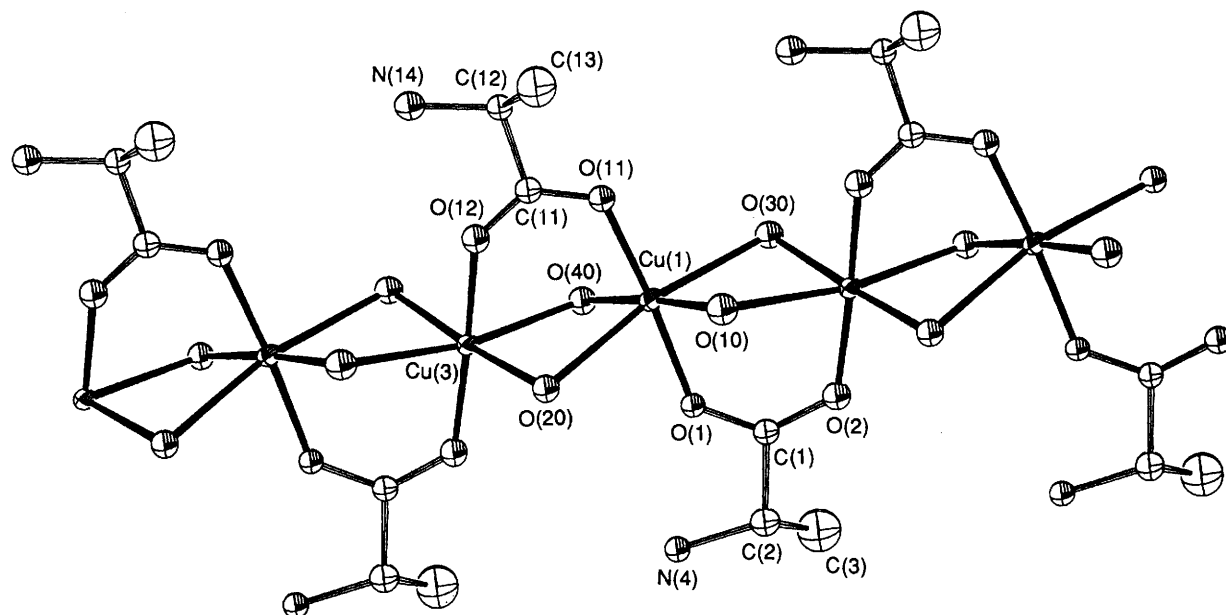
Fig. 1 The atom numbering and relative arrangements of one of the $[Cu_2(\mu-H_2O)_2(\mu-L-AlaH^+)]_n$ units, each consisting of two independent copper centres. Sulfate ions are not shown. Bond length ranges: Cu–Cu 3.149–3.156 Å, Cu–O (carboxylate) 1.933–1.934 Å, Cu–O (water, short) 1.969–1.986 Å, Cu–O (water, long) 2.415–2.538 Å.

L-alanine behaves not as an amino acid but as a carboxylic acid. Two views are given in Figs. 1 and 2. Fig. 1 shows the polymeric chain of copper ions bridged by water molecules and by the carboxylate functions of the alanine molecule, in its zwitterionic form. The chains have the composition $[Cu(OH_2)_2(L-alanine)]^{2+}$. Each copper ion has an environment of six ligated oxygen atoms. Four are essentially in plane (xy) giving a unique polymeric unit $[Cu(OH_2)_2]_n^{2n+}$. The bridging water molecules with their four-coordinated oxygen atoms are most unusual.†

Aqueous copper(II) ions hydrolyse[3] to oligomeric $[Cu(\mu-OH)]_n^{n+}$, best established for $n = 2$. However, the conjugate acids, *i.e.* $[Cu(\mu-OH_2)]_n^{2n+}$ {and the related $[Cu(\mu-OH_2)_2]_n^{2n+}$ stabilized here} are novel: the cation with $n = 2$ is known,[4] in $[Cu_2(OH_2)_{10}][Cu(OH_2)_6](ZrF_7)_2$. Water is often said to be a poor bridging ligand, but in the solutions typically used for syntheses (*e.g.* 1 mol dm^{-3}, as here), such oligomers may actually be significant.

The coordination sphere about each cupric ion is completed (on the z-axis) by a *trans*-pair of bridging carboxylates. The magnetic moment at room temperature per copper ion is in the normal range.

In a sense, the molecule of uncharged alanine in the present remarkable compound is acting as a betaine. The normal
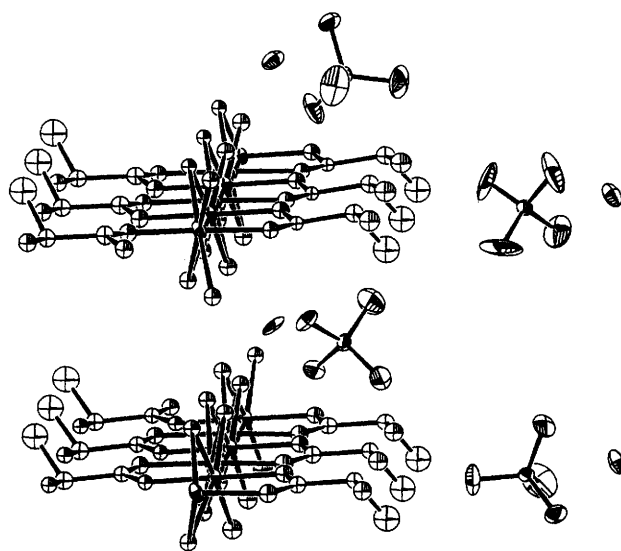

Fig. 2 The linearity and similarity of the two independent chains. Sulfates and waters of crystallisation shown. Labelling omitted for clarity.

expectation, based on the potential operation of a chelate effect, would be for the nitrogen atom of the amino acid, quaternized by a proton, to become quaternized by a cupric ion instead, yielding a five-membered chelate ring. This does not happen.

Like Boussingault's compound[5] $[Cu(gly-O)(NO_3)(OH_2)]$, the present simple compound forms from aqueous solutions of its constituents. Copper(II) sulfate pentahydrate and L-alanine were dissolved in water in a 1:1 molar ratio, typically 0.5 mol dm^{-3}, and allowed to crystallize by slow evaporation. Crystals were dried over P_2O_5.

We note that the new compound crystallizes better in the presence of phenolic compounds, and attribute this to catalytic selective nucleation, a phenomenon likely to be of great utility.

Such observations reinforce the need to incorporate all

possible species into discussions of equilibria (whether heterogeneous or homogeneous) in labile aqueous systems.

Received, 22nd March 1993; Com. 3/01660I

References

1 J. P. Greenstein and M. Winitz, *The Chemistry of the Amino Acids*, vol. 1–3, John Wiley, Chichester, 1961.

2 M.-Y. Chow, Z.-Y. Zhou and T. C. W. Mak, *Inorg. Chem.*, 1992, **31**, 4900 and references cited therein.

3 J. Burgess, *Metal Ions in Solution*, Ellis Harwood, Chichester, 1978, p. 299; C. F. Baes and R. E. Mesmer, *The Hydrolysis of Cations*, John Wiley NY, 1976, p. 268ff; J. Burgess, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 2, p. 298.

4 J. Fisher and R. Weiss, *Acta Crystallogr., Sect. B*, 1973, **29**, 1963.

5 H. O. Davies, R. D. Gillard, M. B. Hursthouse, M. A. Mazid and P. A. Williams, *J. Chem. Soc., Chem. Commun.*, 1992, 226.