

Boussingault's Mixed Copper(II) Glycinate Nitrate

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The mixed compound of nitrate and glycinate with copper(II) is readily made; its crystal structure reveals an unusual helix and that each copper ion carries both unidentate nitrate and chelated glycinate as ligands.

Compounds CuX_2 of copper(II) with anions X^- abound. The nitrate, where $\text{X}^- = \text{NO}_3^-$, is well-known since its discovery as a readily volatile compound.¹ Bis(glycinato)copper(II), $\text{X}^- = \text{H}_2\text{NCHRCO}_2^-$, with $\text{R} = \text{H}$, has been much studied. It was first made² by Boussingault, the father of food chemistry. He used it to isolate glycine from protein hydrolysates. It provided an early example³ of *cis-trans* isomers: the *cis*- is converted into the *trans*-isomer in a unique solid-state reaction.⁴ Its homologues and analogues were used⁵ to establish the relative configurations of natural α -amino acids ($\text{R} = \text{Me}$, etc.), via their ORD (optical rotatory dispersion) and have been implicated in the supposed mode of action of anti-arthritis copper bracelets.

For the copper-glycinate system the stepwise stability constants are:⁶ $\log K_1$ (8.00); larger than $\log K_2$ (7.00); very much larger than $\log K_3$ (about⁷ -1). Despite this stability in solution of the 1:1 moiety, mixed solid compounds are hardly known. The sole example, $[\text{Cu}(\text{glycinate})(\text{NO}_3)(\text{OH}_2)]$, has not been studied for 150 years, since Boussingault first isolated it² from aqueous solutions.

Structural reports on the very stable bis(amino acid) complexes are plentiful, and are currently extending. For example,⁸ the copper ion in its cationic bis-complex with the neutral neurotoxic *R,S*- α -aminomethylaminopropionic acid (from *Cycas spp*) is at a centre of symmetry. *cis*-[Bis(L-hydroxyprolinato)copper(II)] and *trans*-[bis(D-allohydroxyprolinato)copper(II)] water (2/5) are⁹ likewise bis-chelated. However, for the very stable 1:1 systems and for the very unstable 1:3 systems, the only structural report seems to be that¹⁰ of Ozutsumi and Ohtaki, using X-ray diffraction (XRD) on extremely concentrated solutions. Their results for the single chelated glycinate in their $[\text{Cu}(\text{glyO})(\text{OH}_2)_4]^+$ are compared with ours in Table 1.

We now report the preparation and properties of $[\text{Cu}(\text{glyO})(\text{NO}_3)(\text{OH}_2)]$, including its X-ray crystal structure[†] shown in Fig. 1. Several solutions (ca. 0.1 mol dm^{-3}) containing Cu^{II} ions, glycine-glycinate and nitrate, at values of pH where the bis-complex has not precipitated, readily give the mixed compound. As Boussingault said,² these may be derived from $\text{Cu}(\text{NO}_3)_2$ by adding glycine or from $\text{Cu}(\text{glycinate})_2$ (either form) by adding nitric acid or aqueous copper nitrate. The royal-blue crystals contain magnetically dilute copper(II), $\mu_{\text{eff}} = 1.86 \text{ BM}$ ($1 \text{ BM} = 1 \text{ J T}^{-1}$) at 20°C , and decompose explosively at $167\text{--}169^\circ\text{C}$, the water molecule having been lost first on heating.

The present structure shows several unusual features. The elegant helical polymerization *via* carboxylate bridging is

noteworthy. The α -aminoacidate is chelated to one copper ion *via* the N atom and O(5) oxygen atom of carboxylate, and bridges to the next copper *via* the other oxygen atom, O(4), of its carboxylate. The remaining positions in the plane at the copper ion are occupied by the water molecule and by a unidentate and unbridged nitrate ion. This is an unusual mode of ligation. Indeed, in the present structure, the angle at the ligated oxygen of NO_3^- , $\text{N}(1)\text{--O}(1)\text{--Cu}$, is 108.9° and the distance from the copper atom to the other oxygen of nitrate, $\text{O}(3)\text{--Cu}$, is 262.4 pm . These dimensions would, in less simple structures, be regarded as indicating bonding from O(3) to Cu. However, the coordination sphere of the copper ion is already very full, so this position of O(3) relative to copper arises simply from the fact that it has to go somewhere. A similar case arose in a recent structure of another complex containing unidentate nitrate ligands, $[\text{Ag}(\text{ONO}_2)_2]^-$.

The most striking feature of this work is that, once again, the solid, which actually crystallizes from an aqueous solution, albeit fairly concentrated, contains a complex species that has never been considered among those proposed to account for the thermodynamic properties of that homogeneous solution.

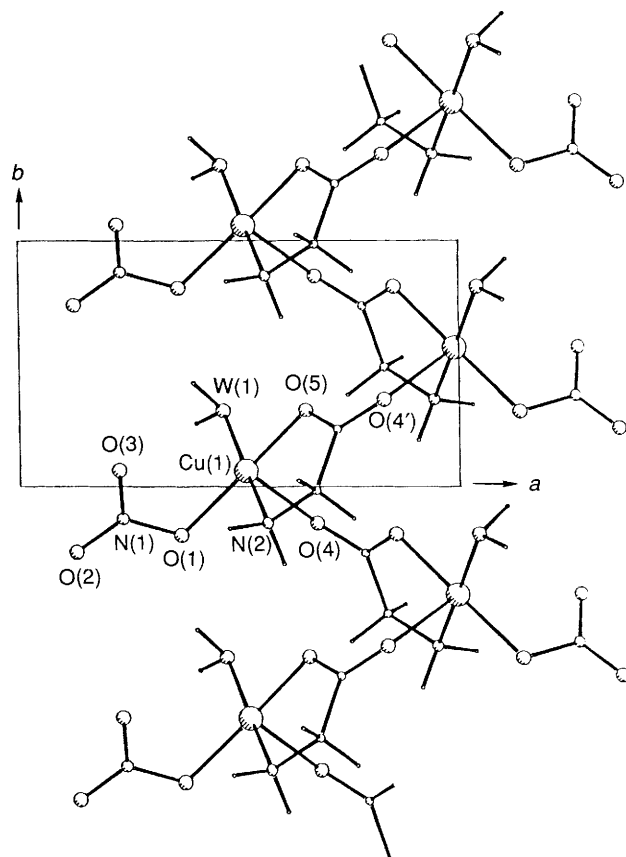


Fig. 1 The structure of $[\text{Cu}(\text{gly-O})(\text{NO}_3)(\text{OH}_2)]$ showing the formation of the helical chains. Selected bond lengths are (pm): $\text{Cu}(1)\text{--O}(1)$ 199.5(5), $\text{Cu}(1)\text{--O}(3)$ 262.4(7), $\text{Cu}(1)\text{--N}(2)$ 198.2(6), $\text{Cu}(1)\text{--O}(4)$ 237.3(5), $\text{Cu}(1)\text{--O}(5)$ 194.3(5), $\text{Cu}(1)\text{--W}(1)$ 196.5(5). [W(1) denotes the water molecule].

[†] Crystal data: $\text{C}_2\text{H}_6\text{N}_2\text{O}_6\text{Cu}$, $M_r = 217.63$, monoclinic, $a = 9.278(1)$, $b = 5.183(1)$, $c = 13.982(1) \text{ \AA}$, $\beta = 103.26(1)^\circ$, $V = 654.4 \text{ \AA}^3$, space group $P2_1/n$, $Z = 4$, $D_c = 2.21 \text{ g cm}^{-3}$, $F(000) = 436$, $\mu(\text{Mo-K}\alpha) = 33.32 \text{ cm}^{-1}$. Data were collected on a FAST TV Area detector diffractometer following previously described procedures.¹¹ From the ranges scanned, 2962 data were recorded and merged to give 1131 unique ($R_{\text{int}} = 0.036$) and 1002 observed [$F_o > 3\sigma(F_o)$]. The structure was solved *via* direct methods and refined by least-squares analysis. A correction for absorption was made using DIFABS.¹² The final R , R_w , values were 0.032, 0.036 for 110 parameters (hydrogens in riding mode). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1 Copper(II)-ligand bond distances (pm) in glycinate complexes

Complex	Cu-O	Cu-N	Cu-X ^a	X	Y ^b	Ref.
Cu(gly-O)(NO ₃)H ₂ O	194.3	198.3	199.9 196.55	O of NO ₃ ⁻ O of H ₂ O		<i>c</i>
[Cu(gly-O)(OH ₂) ₄] ⁺	199	199	198	H ₂ O (equ)	227	H ₂ O(ax) <i>d</i>
<i>cis</i> -[Cu(gly-O) ₂]OH ₂	194.6	198.4			240.4	H ₂ O(ax) <i>e</i>
<i>trans</i> -[Cu(gly-O) ₂] ^f	~200	~200			~280	O of CO ₂ ⁻ <i>g</i>
[Cu(gly-O) ₃] ^{-h}	202	202	—			<i>d</i>

^a X Denotes an in-plane ligand. ^b Y Denotes an out-of-plane distance; ^c This work. ^d Ref. 10; ^e H. C. Freeman, M. R. Snow, I. Nitta and K. Tomita, *Acta Crystallogr.*, 1964, **17**, 1463. ^f By electron diffraction. ^g B. K. Vainstein, I. A. Dyakon and A. V. Ablov, *Sov. Phys. Crystallogr.*, 1967, **12**, 299. ^h Of unknown isomeric (*fac*:*mer*) character.

The 'non-complexing' anions, X⁻, of the salts CuX₂ (X = ClO₄⁻, NO₃⁻, Cl⁻, SO₄²⁻ and the like) often used in such solution studies may compete effectively with the chelating ligands. This remark applies to other metal ions and ligands. We have certainly been able to crystallize a number of mixed compounds of amino acids [CuX(H₂NCHRCO₂)] analogous to Boussingault's prototype described here.

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References

- B. Hathaway, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 2, p. 413 and references cited therein.
- J. B. Boussingault, *Ann. Chim. Phys.*, 1841, 257.
- H. Ley and G. Wiegner, *Z. Elektrochem.*, 1905, **2**, 585 and references cited therein.
- B. W. Delf, R. D. Gillard and P. O'Brien, *J. Chem. Soc., Dalton Trans.*, 1979, 1301.
- J. P. Greenstein and M. Winitz, *Chemistry of The Amino Acids*, Wiley, New York, 1961, p. 119 and references cited therein including P. Pfeiffer and W. Christeleit, *Z. Physiol. Chem.*, 1937, **245**, 197.
- Critical Stability Constants*. Volume 1: Amino Acids, ed. A. E. Martell and R. M. Smith, Plenum, New York and London, 1974.
- R. M. Keefer, *J. Am. Chem. Soc.*, 1946, **68**, 2329.
- M. B. Hursthouse, M. Motevalli, P. O'Brien and P. B. Nunn, *J. Chem. Soc., Dalton Trans.*, 1990, 1985.
- M. A. A. F. C. T. Carrondo, M. T. L. S. Duarte, M. L. S. Simoes Goncalves, P. O'Brien and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1990, 213.
- K. Ozutsumi and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2605.
- A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1991, 1855.
- N. P. C. Walker and D. Stuart, *Acta Crystallogr. Sect. A*, 1983, **39**, 158.