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Redetermination of bis(L-asparaginato)-copper(II)

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Key indicators

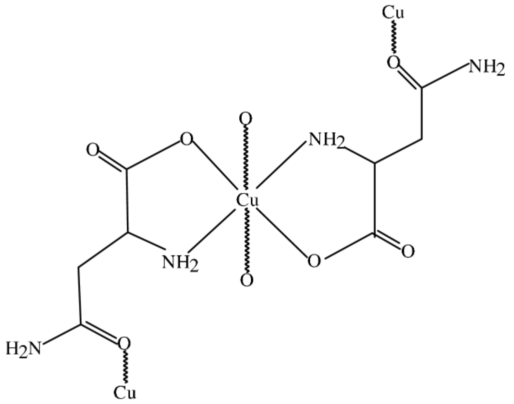
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.034
wR factor = 0.092
Data-to-parameter ratio = 6.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The Cu atom of the title compound, $[Cu(C_4H_7N_2O_3)_2]$, is in a tetragonally distorted octahedral environment. A carboxyl O atom and the α-amino N atom from each ligand coordinate to Cu in a *trans* square-planar configuration [Cu—O = 2.003 (3) and 2.020 (3) Å, and Cu—N = 2.029 (4) and 2.049 (4) Å]. The octahedron is completed by bridging amide O atoms from adjacent molecules [Cu—O = 2.229 (4) Å and Cu—O = 2.885 (4) Å] separated by *c* translations. This arrangement creates infinite chains linked in the [001] direction, stabilized by intra- and intermolecular N—H···O bonds. The structure has already been published [Stephens, Vagg & Williams (1975). *Acta Cryst*. B**31**, 841–845]; this redetermination reports the structure with higher precision.

Comment

Electron paramagnetic resonance (EPR) and single-crystal X-ray diffraction (XRD) techniques are usually employed to study structural, electronic and magnetic properties of biologically important metal–amino acid complexes which are useful for modelling the bonding and properties of metal ions in metalloproteins. Good quality royal-blue prismatic crystals of bis(L-asparaginato)copper(II), Cu(L-asn)$_2$ were obtained in an effort by our group to grow these crystals and crystals of bis(L-asparaginato)zinc(II) doped with Cu^{2+} ions for EPR studies.



(I)

A search of the November 2003 release of the Cambridge Structural Database (Allen, 2002) showed that the structure of bis-(L-asparaginato)copper(II), (I), has been reported by Stephens *et al.* (1975), based on film data collection and visually estimated intensities. The final discrepancy *R* factor they obtained was 0.107 for 636 data and the H atoms were not located. As we had grown good quality Cu(L-asn)$_2$ single crystals and we had an X-ray diffractometer data collection

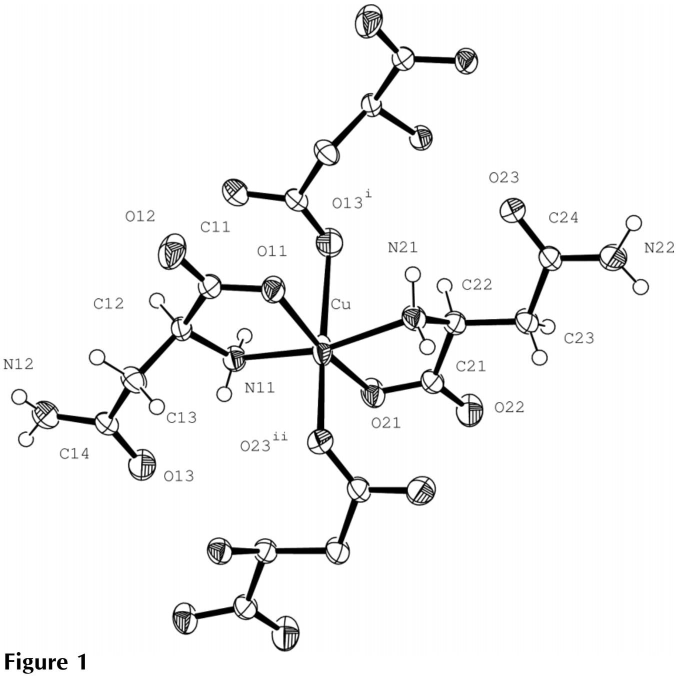


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) *x*, *y*, $z + 1$; (ii) *x*, *y*, $z - 1$.] The H atoms of the asparaginate residues have been omitted for clarity.

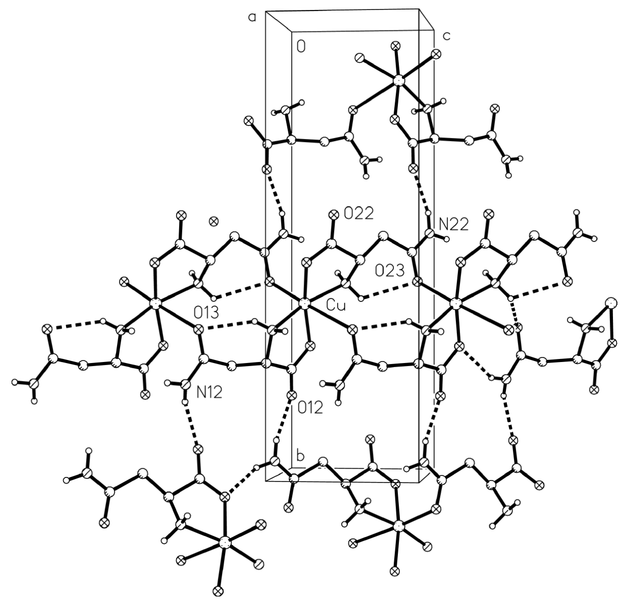


Figure 2
Packing diagram, viewed down the *a* axis. Intra- and intermolecular hydrogen bonds are shown as dashed lines. Only the H atoms involved in hydrogen bonds are shown.

facility, a more precise crystal structure determination was performed and is reported here. The *R* factor was reduced to 0.034 using 1228 unique reflections, the absolute configuration was determined and the hydrogen-bonding geometry is presented. Another motivation for this work is the EPR studies that are in progress, the results of which are analysed in terms of bonding structure around the metal ion and require accurate structural data.

An *ORTEP*III (Farrugia, 1997) plot of (I) with the same atomic numbering scheme of Stephens *et al.* (1975) is shown in Fig. 1. Selected bond distances and angles are given in Table 1. Each of the two L-asparagine ligands coordinates to the Cu atom *via* a carboxyl O and the α-amino N atom, forming a *trans* square-planar configuration. A distorted octahedral coordination about the Cu atom is completed *via* amide O atoms from neighbouring molecules linked in the [001] direction. This arrangement produces infinite chains parallel to **c**.

A detailed discussion was given by Stephens *et al.* (1975). The main differences between the former and the new structure of (I) are the bond lengths Cu—O13^{i} = 2.774 (25)/2.885 (4) Å and Cu—O23^{ii} = 2.529 (20)/2.229 (4) Å, respectively [symmetry codes: (i) *x*, *y*, $1 + z$; (ii) *x*, *y*, $z - 1$]. Some angles also differ markedly: O11—Cu—O21 = 176.2 (10)/168.86 (15)° and N11—Cu—N21 = 175.3 (10)/164.02 (16)°, respectively. The Cu atom lies 0.238 (2) Å out of the ligand-atom square plane, towards O23^{ii}. The directions of these axial Cu—O bonds are almost collinear with the normal to the mean plane defined by the square-plane ligand atoms, the angles between the normal and Cu—O bonds being 1.17 (Cu—O13^{i}) and 2.24° (Cu—O23^{ii}). The ring Cu→O11→ . . . →N11 exhibits an envelope conformation with the flap at N11, and the ring Cu→O21→ . . . →N21 is twisted about C22—N21; the Cremer & Pople (1975) parameters for the two rings are $Q = 0.126$ (4) and 0.338 (4) Å and $\varphi = 151$ (2) and 302.8 (6)°, respectively.

The molecular packing of (I) is stabilized through a hydrogen-bonded network, as can be seen in Fig. 2. The geometric parameters of the intra- and intermolecular hydrogen bonds are given in Table 2. The chains are held together in the [001] direction mainly through the N—H···O intramolecular hydrogen bonds between the α-amino N atoms and the amide O atoms, while in the [010] direction the intermolecular hydrogen bonding is between the β-amino N atoms and the carbonyl O atoms from neighbouring molecules.

Experimental

The crystals of Cu(L-asn)$_2$ were obtained from aqueous solutions of L-asparagine (37.0 mmol) and copper sulfate ($CuSO_4{\cdot}5H_2O$, 18.5 mmol) in water (100 ml). A neutralization reaction of L-asparagine with NaOH in equimolar ratio was performed before addition of the metal salt. After approximately one week of slow solvent evaporation, some good quality royal-blue elongated crystals of Cu(L-asn)$_2$ were obtained.

Crystal data

$[Cu(C_4H_7N_2O_3)_2]$
$M_r = 325.77$
Monoclinic, $P2_1$
$a = 5.036$ (2) Å
$b = 18.915$ (2) Å
$c = 6.152$ (1) Å
$\beta = 96.21$ (2)°
$V = 582.6$ (3) Å^3
$Z = 2$

$D_x = 1.857$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 14.4$–58.3°
$\mu = 2.99$ mm^{-1}
$T = 293$ (2) K
Prism, blue
0.21 × 0.20 × 0.08 mm

Acta Cryst. (2004). E**60**, m1428–m1430 Ivo Vencato *et al.* • $[Cu(C_4H_7N_2O_3)_2]$ **m1429**

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*; 1968)
$T_{\min} = 0.572$, $T_{\max} = 0.796$
2230 measured reflections
1228 independent reflections
1226 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\max} = 73.9°$
$h = -6 \rightarrow 6$
$k = 0 \rightarrow 23$
$l = -4 \rightarrow 7$
2 standard reflections frequency: 120 min intensity decay: <1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.092$
$S = 1.23$
1228 reflections
197 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.3521P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.58$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.058 (3)
Absolute structure: Flack (1983)
Flack parameter = 0.05 (5)

Table 1
Selected geometric parameters (Å, °).

Cu—O11	2.003 (3)	C11—C12	1.543 (6)
Cu—O21	2.020 (3)	C12—C13	1.543 (5)
Cu—N11	2.029 (4)	C13—C14	1.522 (6)
Cu—N21	2.049 (4)	O21—C21	1.273 (6)
Cu—O13^{i}	2.885 (4)	O22—C21	1.222 (6)
Cu—O23^{ii}	2.229 (4)	O23—C24	1.249 (6)
O11—C11	1.282 (6)	N21—C22	1.493 (6)
O12—C11	1.219 (6)	N22—C24	1.313 (7)
O13—C14	1.244 (6)	C21—C22	1.533 (6)
N11—C12	1.483 (5)	C22—C23	1.501 (6)
N12—C14	1.317 (7)	C23—C24	1.511 (6)
O11—Cu—O21	168.86 (15)	N11—C12—C11	110.4 (3)
O11—Cu—N11	82.75 (14)	N11—C12—C13	112.8 (3)
O21—Cu—N11	97.44 (15)	C11—C12—C13	108.0 (3)
O11—Cu—N21	94.70 (14)	C14—C13—C12	111.9 (4)
O21—Cu—N21	82.04 (14)	O13—C14—N12	123.3 (5)
N11—Cu—N21	164.02 (16)	O13—C14—C13	119.2 (4)
O11—Cu—O23^{ii}	97.81 (14)	N12—C14—C13	117.5 (4)
O21—Cu—O23^{ii}	93.18 (15)	C21—O21—Cu	115.4 (3)
N11—Cu—O23^{ii}	98.80 (14)	C24—O23—Cu^{i}	125.3 (3)
N21—Cu—O23^{ii}	97.18 (15)	C22—N21—Cu	107.5 (3)
O23^{ii}—Cu—O13^{i}	176.61 (13)	O22—C21—O21	124.0 (4)
O11—Cu—O13^{i}	85.56 (12)	O22—C21—C22	120.3 (4)
O21—Cu—O13^{i}	83.45 (13)	O21—C21—C22	115.5 (4)
N11—Cu—O13^{i}	81.82 (14)	N21—C22—C23	114.3 (4)
N21—Cu—O13^{i}	82.26 (14)	N21—C22—C21	107.9 (3)
C11—O11—Cu	116.7 (3)	C23—C22—C21	113.9 (4)
C12—N11—Cu	111.6 (3)	C22—C23—C24	113.0 (4)
O12—C11—O11	123.1 (4)	O23—C24—N22	123.0 (4)
O12—C11—C12	119.5 (4)	O23—C24—C23	121.6 (4)
O11—C11—C12	117.4 (4)	N22—C24—C23	115.4 (4)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N11—H1N···O11^{iii}	0.92 (4)	2.20 (5)	2.987 (5)	143 (5)
N11—H2N···O13	0.81 (4)	2.26 (5)	2.944 (5)	143 (6)
N12—H3N···O22^{iv}	0.84 (4)	2.11 (5)	2.908 (7)	158 (7)
N12—H4N···O11^{v}	0.82 (4)	2.49 (5)	3.235 (5)	151 (6)
N21—H5N···O13^{vi}	0.90 (4)	2.54 (5)	3.135 (5)	125 (4)
N21—H5N···O23	0.90 (4)	2.44 (5)	2.975 (5)	119 (5)
N21—H6N···O21^{vii}	0.90 (4)	2.30 (5)	3.141 (6)	156 (6)
N22—H7N···O12^{viii}	0.86 (5)	1.97 (5)	2.805 (6)	165 (8)
N22—H8N···O21^{vi}	0.85 (5)	2.03 (5)	2.830 (6)	157 (7)

Symmetry codes: (iii) $1 + x, y, z$; (iv) $2 - x, \frac{1}{2} + y, -z$; (v) $1 + x, y, z - 1$; (vi) $x - 1, y, 1 + z$; (vii) $x - 1, y, z$; (viii) $1 - x, y - \frac{1}{2}, 1 - z$.

H atoms bonded to C atoms were placed in calculated positions (C—H = 0.97–0.98 Å) and refined as riding, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. H atoms bonded to N atoms were found in difference Fourier maps and were refined with restraints N—H = 0.87 (5) Å and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm N})$. Owing to the original poor data/parameter ratio, the intensity measurements were extended to $\theta_{\max} = 73.9°$, resulting in a ratio of 6.23 with little improvement. The absolute configuration was determined although no Friedel pairs had been measured.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1993); cell refinement: *CAD*-4-*PC*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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