

The nitrate dihydrate of an aqua-dicopper(II) complex cation with guanidinoacetic acid and a novel trianionic disubstituted guanidine as ligands at 120 K

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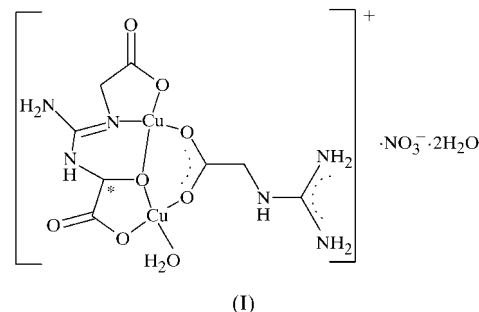
The structure of the title compound, aqua[μ -(*N*¹-carboxylato-methylguanidino)oxidoacetato](μ -guanidinoacetic acid)dicopper(II) nitrate dihydrate, [Cu₂(C₅H₆N₃O₅)(C₃H₇N₃O₂)(H₂O)]NO₃·2H₂O, contains two enantiomers of the dicopper(II) complex cation that comprise water, neutral zwitterionic guanidinoacetic acid and the trianion of (*N*¹-carboxymethylguanidino)hydroxyacetic acid as ligands. Extensive hydrogen bonding creates three-dimensional connectivity but is largely confined to layers that each contain both cation enantiomers. These layers are related to one another by crystallographic symmetry and are therefore identical in composition and connectivity.

Comment

As part of a continuing study of Cu^{II} complexes with amino acids (Felcman & de Miranda, 1997; de Miranda & Felcman, 2001), we previously reported the structure of [Cu₂(NO₃)₂(gaa)₄], (I) [gaa is guanidinoacetic acid, H₂NC(=NH₂)NH-CH₂CO₂; de Miranda *et al.*, 2002]. Green crystalline (I) was isolated from a reaction mixture containing Cu^{II}(NO₃)₂, guanidinoacetic acid and aspartic acid. Obtained along with (I) from this reaction mixture were blue crystals of the title compound, (II), whose structure we now report. The sample crystal used for the analysis presented here came, in fact, from a subsequent preparation of (II), again accompanied by (I), but in the absence of aspartic acid, which must therefore, when present, be merely a spectator species.

For convenience, the asymmetric unit in the structure of (II) is described in terms of two subunits (labelled identically and distinguished by the suffixes *A* and *B*) of formula

C₈H₁₉Cu₂N₇O₁₀, where this formula corresponds to an aqua-dicopper complex cation of formula (C₈H₁₅Cu₂N₆O₈)⁺, a nitrate counter-anion and two hydrate water molecules (see *Scheme* below and Fig. 1). Only the complex cation merits further detailed discussion.



Three ligand species contribute to the variously distorted approximately square-planar coordination of Cu (Table 1) in the complex cation of (II). The first and simplest of these is the water molecule, O8. The second is the bis-monodentate bridging guanidinoacetic acid species, gaa, in its zwitterionic and therefore neutral form (formula C₃H₇N₃O₂, comprising atoms O1, O2, C1–C3 and N1–N3). Previous examples of complexes containing zwitterionic gaa are (I) (de Miranda *et al.*, 2002) and [CuCl₂(gaa)₂] (Silva *et al.*, 2001). The third and most interesting ligand is the tetradentate bis-chelate species, oag³⁻, formulated (C₅H₆N₃O₅)³⁻, which comprises atoms C4–C8, N4–N6 and O3–O7 and corresponds to the trianion of the previously unknown (*N*¹-carboxymethylguanidino)hydroxyacetic acid. In this last case, atoms O3 and N4 form bonds with Cu2, thus creating a five-membered chelate ring, and O5 and O6 form bonds with Cu1 in a similar manner. However, O5 forms a further bond with Cu2 and therefore has an additional bridging function, which allows the creation of a further six-membered ring.

The chemical identities of the individual atoms within the oag³⁻ species were determined initially by consideration of the atomic displacement parameters but were supported by the comparison of these parameters with those found for atoms of a corresponding type in gaa. Further support for the correctness of the atom designations comes from the positions of the H atoms determined by difference synthesis and their satisfactory contribution to the hydrogen-bonding scheme discussed below.

The structural subunits *A* and *B* and the complex cations within them are identical in their connectivity. It is clear from Table 2 that with few exceptions, *e.g.* the angles at N6, the bond distances and angles of the two complex cations within the asymmetric unit are very similar. However, the cations differ in their configuration at the asymmetric centre *C7*, *viz.* *R* at *C7A* (subunit *A*) and *S* at *C7B* (subunit *B*). The differing configurations at *C7A* and *C7B* are, however, compatible with the formation of oag³⁻ from non-chiral components in the manner suggested below.

Extensive hydrogen bonding (Table 2 and Fig. 2) is mainly to be found within layers parallel to (010). Most of the values

structure analysis reported here was obtained in essentially this manner, except that aspartic acid was not present in the reaction mixture.

Crystal data

[Cu₂(C₅H₆N₃O₅)(C₃H₇N₃O₂)(H₂O)]NO₃·2H₂O
M_r = 548.38
 Monoclinic, *P*2₁/*c*
a = 15.2979 (2) Å
b = 13.0020 (2) Å
c = 17.7821 (2) Å
 β = 90.0302 (7)°
V = 3536.92 (8) Å³
Z = 8

D_x = 2.060 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 17 990 reflections
 θ = 2.9–27.5°
 μ = 2.49 mm⁻¹
T = 120 (2) K
 Block, blue
 0.20 × 0.15 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
T_{min} = 0.890, *T_{max}* = 0.923
 33 782 measured reflections

7933 independent reflections
 7112 reflections with *I* > 2σ(*I*)
R_{int} = 0.034
 θ_{max} = 27.5°
h = -19 → 19
k = -16 → 16
l = -23 → 22

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.035
wR(*F*²) = 0.084
S = 1.14
 7933 reflections
 589 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 6.7574P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.93 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -1.03 \text{ e \AA}^{-3}$

Table 1 Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1A—H1A...O11A	0.872 (18)	2.07 (2)	2.921 (3)	164 (3)
N1B—H1E...O11B	0.847 (18)	2.098 (19)	2.933 (3)	169 (3)
N2A—H2C...O4B	0.88	1.95	2.804 (3)	164
N2A—H2D...O12B ⁱ	0.88	2.20	3.076 (3)	172
N2B—H2G...O4A ⁱⁱ	0.88	2.00	2.866 (3)	166
N2B—H2H...O12A	0.88	2.11	2.980 (3)	169
N3A—H3A...O3B	0.88	2.19	3.061 (3)	172
N3A—H3B...O12A	0.88	2.21	3.072 (3)	166
N3B—H3E...O3A ⁱⁱⁱ	0.88	2.22	3.099 (3)	176
N3B—H3F...O12B	0.88	2.19	3.056 (3)	168
N5A—H5C...O7B ⁱⁱⁱ	0.88	2.15	2.991 (3)	159
N5A—H5D...O9B ⁱⁱⁱ	0.88	2.15	2.942 (3)	150
N5B—H5G...O7A ^{iv}	0.88	2.21	3.055 (3)	162
N5B—H5H...O9A ^{iv}	0.88	2.04	2.901 (3)	166
N6A—H6A...N6B ^v	0.849 (18)	2.52 (3)	3.158 (4)	132 (3)
N6B—H6E...O9A ^{iv}	0.872 (18)	2.57 (2)	3.328 (3)	146 (3)
O8A—H8A...O9A	0.812 (17)	1.861 (19)	2.664 (3)	170 (4)
O8A—H8B...O11A	0.800 (17)	1.855 (18)	2.653 (3)	175 (4)
O8B—H8E...O9B	0.809 (17)	1.871 (18)	2.673 (3)	172 (4)
O8B—H8F...O11B	0.809 (17)	1.867 (17)	2.669 (3)	172 (3)
O9A—H9A...O10A	0.815 (17)	1.854 (18)	2.663 (3)	172 (4)
O9A—H9B...O10B ^{vi}	0.810 (17)	2.19 (2)	2.896 (3)	146 (3)
O9A—H9B...O13B ^{vi}	0.810 (17)	2.63 (3)	3.212 (3)	131 (3)
O9B—H9E...O10B	0.807 (17)	1.848 (18)	2.651 (3)	173 (4)
O9B—H9F...O3A ^{vii}	0.808 (17)	2.18 (2)	2.930 (3)	155 (3)
O10A—H10A...O7B ^{viii}	0.801 (17)	2.10 (2)	2.870 (3)	161 (4)
O10A—H10B...O4A ⁱⁱ	0.801 (17)	2.16 (2)	2.926 (3)	160 (4)
O10B—H10E...O7A ^{ix}	0.804 (17)	2.047 (18)	2.840 (3)	169 (4)
O10B—H10F...O4B ⁱⁱ	0.808 (17)	2.011 (19)	2.802 (3)	166 (4)

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

Table 2 Geometric parameters (Å, °).

	Cation A	Cation B
Cu1—O1	1.9259 (19)	1.9344 (18)
Cu1—O5	1.9207 (19)	1.9066 (18)
Cu1—O6	1.9161 (19)	1.9126 (18)
Cu1—O8	1.911 (2)	1.939 (2)
Cu2—O2	1.9308 (18)	1.9486 (18)
Cu2—O3	1.9832 (19)	1.9825 (19)
Cu2—O5	1.920 (2)	1.9179 (18)
Cu2—N4	1.927 (2)	1.928 (2)
O1—C1	1.259 (3)	1.255 (3)
O2—C1	1.253 (3)	1.260 (3)
C1—C2	1.511 (3)	1.515 (3)
C2—N1	1.450 (3)	1.457 (3)
N1—C3	1.341 (3)	1.335 (3)
C3—N2	1.319 (4)	1.321 (3)
C3—N3	1.337 (3)	1.341 (3)
O3—C4	1.290 (3)	1.279 (3)
O4—C4	1.245 (3)	1.253 (3)
C4—C5	1.509 (3)	1.505 (4)
C5—N4	1.457 (3)	1.458 (3)
N4—C6	1.315 (3)	1.315 (3)
C6—N5	1.333 (3)	1.326 (4)
C6—N6	1.355 (3)	1.380 (3)
N6—C7	1.416 (3)	1.449 (4)
C7—O5	1.414 (3)	1.406 (3)
C7—C8	1.537 (4)	1.539 (3)
C8—O6	1.276 (3)	1.275 (3)
C8—O7	1.236 (3)	1.236 (3)
O1—Cu1—O5	99.27 (8)	98.03 (8)
O1—Cu1—O6	175.94 (8)	174.81 (8)
O1—Cu1—O8	87.43 (9)	86.98 (8)
O5—Cu1—O6	84.65 (8)	86.17 (8)
O5—Cu1—O8	167.85 (11)	163.10 (9)
O6—Cu1—O8	88.91 (9)	89.85 (8)
O2—Cu2—O3	84.83 (8)	89.00 (8)
O2—Cu2—O5	97.26 (8)	94.40 (8)
O2—Cu2—N4	168.59 (9)	171.34 (8)
O3—Cu2—O5	177.90 (7)	170.99 (9)
O3—Cu2—N4	83.90 (8)	83.79 (9)

Intensity data were taken over the full Ewald sphere. Only the monoclinic crystal system permitted the solution and refinement of the structure, and this system was confirmed as appropriate by *checkCIF*. The maximum residual electron density was 0.85 Å from atom Cu2B. H atoms attached to C atoms were placed geometrically, with C—H distances of 0.99 and 1.00 Å for methylene (C2 and C5) and tertiary (C7) H atoms, respectively. H atoms attached to N and water O atoms were initially found in sensible, if approximate, positions by difference synthesis and thereafter idealized as follows. The *SHELXL97* command AFIX 93 with N—H distances of 0.88 Å was used for the H atoms of terminal NH₂ groups (N2, N3 and N5). For the remaining H atoms, the coordinates were allowed to refine but with DFIX used to constrain the N—H distance in the case of secondary amine atoms N1 and N6 and SADI used to restrain the O—H distances for water atoms O8, O9 and O10. For all H atoms, *U_{iso}* was set at 1.2*U_{eq}* of the non-H atom to which the H atom is attached.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hoof, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1052). Services for accessing these data are described at the back of the journal.

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