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# The nitrate dihydrate of an aquadicopper(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 $\left[\mu\right.$-( $N^{1}$-carboxylatomethylguanidino) oxidoacetato] ( $\mu$-guanidinoacetic acid)dicopper(II) nitrate dihydrate, $\left[\mathrm{Cu}_{2}\left(\mathrm{C}_{5} \mathrm{H}_{6} \mathrm{~N}_{3} \mathrm{O}_{5}\right)\left(\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{~N}_{3} \mathrm{O}_{2}\right)\right.$ $\left.\left(\mathrm{H}_{2} \mathrm{O}\right)\right] \mathrm{NO}_{3} \cdot 2 \mathrm{H}_{2} \mathrm{O}$, 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 $\mathrm{Cu}^{\mathrm{II}}$ complexes with amino acids (Felcman \& de Miranda, 1997; de Miranda \& Felcman, 2001), we previously reported the structure of $\left[\mathrm{Cu}_{2}\left(\mathrm{NO}_{3}\right)_{2^{-}}\right.$ (gaa) $)_{4}$ ], (I) [gaa is guanidinoacetic acid, $\mathrm{H}_{2} \mathrm{NC}\left(=\mathrm{NH}_{2}\right) \mathrm{NH}-$ $\mathrm{CH}_{2} \mathrm{CO}_{2}$; de Miranda et al., 2002]. Green crystalline (I) was isolated from a reaction mixture containing $\mathrm{Cu}^{\mathrm{II}}\left(\mathrm{NO}_{3}\right)_{2}$, 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
$\mathrm{C}_{8} \mathrm{H}_{19} \mathrm{Cu}_{2} \mathrm{~N}_{7} \mathrm{O}_{10}$, where this formula corresponds to an aquadicopper complex cation of formula $\left(\mathrm{C}_{8} \mathrm{H}_{15} \mathrm{Cu}_{2} \mathrm{~N}_{6} \mathrm{O}_{8}\right)^{+}$, a nitrate counter-anion and two hydrate water molecules (see Scheme below and Fig. 1). Only the complex cation merits further detailed discussion.

(I)

Three ligand species contribute to the variously distorted approximately square-planar cooordinaton 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 $\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{~N}_{3} \mathrm{O}_{2}$, comprising atoms $\mathrm{O} 1, \mathrm{O} 2, \mathrm{C} 1-\mathrm{C} 3$ and $\mathrm{N} 1-\mathrm{N} 3$ ). Previous examples of complexes containing zwitterionic gaa are (I) (de Miranda et al., 2002) and $\left[\mathrm{CuCl}_{2}(\mathrm{gaa})_{2}\right]$ (Silva et al., 2001). The third and most interesting ligand is the tetradentate bis-chelate species, oag ${ }^{3-}$, formulated $\left(\mathrm{C}_{5} \mathrm{H}_{6} \mathrm{~N}_{3} \mathrm{O}_{5}\right)^{3-}$, which comprises atoms C4$\mathrm{C} 8, \mathrm{~N} 4-\mathrm{N} 6$ and O3-O7 and corresponds to the trianion of the previously unknown ( $N^{1}$-carboxymethylguanidino)hydroxyacetic acid. In this last case, atoms O 3 and N 4 form bonds with Cu 2 , thus creating a five-membered chelate ring, and O5 and O6 form bonds with Cu 1 in a similar manner. However, O5 forms a further bond with Cu 2 and therefore has an additional bridging function, which allows the creation of a further sixmembered ring.

The chemical identities of the individual atoms within the oag $^{3-}$ 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 N 6 , 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 $\mathrm{C} 7, v i z . R$ at C7A (subunit $A$ ) and $S$ at $\mathrm{C} 7 B$ (subunit $B$ ). The differing configurations at $\mathrm{C} 7 A$ and $\mathrm{C} 7 B$ are, however, compatible with the formation of oag ${ }^{3-}$ 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
given in Table 2 correspond to hydrogen bonds within the layer and once again demonstrate the similarity of the structural subunits. The most obvious and inevitable exceptions are when interlayer hydrogen bonds (not shown in Fig. 2) are considered (e.g. the marked differences for pairs of donor atoms such as $\mathrm{N} 6 A / \mathrm{N} 6 B$ and $\mathrm{O} 9 A / \mathrm{O} 9 B$ ), because the layers occur centred on $y=\frac{1}{8}$ and at intervals of $y=\frac{1}{4}$ thereafter. Thus, any one layer is related to any other layer with a different $y$ coordinate by only one of the crystallographic symmetry elements of the space group $P 2_{1} / c$. Furthermore, for any one layer, while it is related to its immediate neighbour on one side by a crystallographic centre of symmetry, the relationship to the layer on the other side must be that of the $c$-glide plane, and the interlayer hydrogen bonds must reflect this fact.


The new ligand oag ${ }^{3-}$ is considered to be derived from two gaa molecules. Nakai et al. (1979) have reported that gaa in the presence of $\mathrm{Ag}_{2} \mathrm{CO}_{3}$ supported on Celite generates guanidine


Figure 1
Subunit $A$ of (II), showing the labelling scheme (the suffix $A$ has been deliberately suppressed), which applies equally to subunit $B$. Displacement ellipsoids for non-H atoms are shown at the $50 \%$ probability level, and H atoms are shown as spheres of arbitrary radius. Dashed lines represent hydrogen bonds.


Figure 2
A portion of the layer at $y=\frac{1}{8}$ in the structure of (II), viewed along $b$. Displacement ellipsoids for non-H atoms are shown at the $50 \%$ probability level, and H atoms are shown as spheres of arbitrary radius. H atoms other than those involved in hydrogen-bond (dashed lines) formation have been omitted for clarity, and only selected atoms are labelled.
by the loss of a two-C-atom moiety, either hydroxyacetic acid, $\mathrm{HOCH}_{2} \mathrm{CO}_{2} \mathrm{H}$, (III), or the oxidized species $\mathrm{HC}(\mathrm{O}) \mathrm{CO}_{2} \mathrm{H}$, (IV). If (IV) is not directly formed it will be readily generated via the oxidation of (III) by the Ag salt in air. In our reaction media, $\mathrm{Cu}^{\mathrm{II}}$ is available to bring about the oxidation of (III) to (IV), which then permits the reaction with another molecule of gaa to provide the new ligand (see reaction scheme above). There is partial and somewhat circumstantial evidence for this process as follows. Consideration of the stoichiometry and charge balance of the formula, $\left[\mathrm{Cu}_{2}\left(\mathrm{NO}_{3}\right)_{2}(\mathrm{gaa})_{4}\right]$ (de Miranda et al., 2002), of the overall neutral complex in green (I) now suggests that Cu is present there in the +1 oxidation state, because gaa is once again present in its uncharged zwitterionic form and nitrate is the only anion present. This assumption would be consistant with both the involvement of $\mathrm{Cu}^{\mathrm{II}}$ in the genesis of oag ${ }^{3-}$ and the recovery of crystals of blue (II) in admixture with green (I) from our reaction mixtures.

## Experimental

To a solution of gaa ( $1.171 \mathrm{~g}, 10 \mathrm{mmol}$ ) in $50 \%$ aqueous ethanol $(50 \mathrm{ml})$ were successively added, with stirring, nitric acid ( $0.1 \mathrm{~mol} \mathrm{l}^{-1}$, until $\mathrm{pH}<7)$, aspartic acid ( $1.331 \mathrm{~g}, 10 \mathrm{mmol}$ ) and copper nitrate trihydrate $(2.462 \mathrm{~g}, 10 \mathrm{mmol})$. After stirring the solution for 1 h at 303 K , KOH solution ( 0.1 M ) was added slowly until precipitation occurred. The mixture was filtered, and ethanol $(25 \mathrm{ml})$ was added to the filtrate. On standing at room temperature, green crystals of (I) and blue crystals of (II) were slowly deposited from the solution. The two types of crystal were separated manually. The crystal used in the
structure analysis reported here was obtained in essentially this manner, except that aspartic acid was not present in the reaction mixture.

## Crystal data

$\left[\mathrm{Cu}_{2}\left(\mathrm{C}_{5} \mathrm{H}_{6} \mathrm{~N}_{3} \mathrm{O}_{5}\right)\left(\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{~N}_{3} \mathrm{O}_{2}\right)\right.$ -
$\left.\left(\mathrm{H}_{2} \mathrm{O}\right)\right] \mathrm{NO}_{3} \cdot 2 \mathrm{H}_{2} \mathrm{O}$
$M_{r}=548.38$
Monoclinic, $P 2_{1} / c$
$a=15.2979$ (2) $\AA$
$b=13.0020$ (2) $\AA$
$c=17.7821$ (2) $\AA$
$\beta=90.0302$ (7) ${ }^{\circ}$
$V=3536.92$ (8) $\AA^{3}$
$Z=8$
Data collection
Nonius KappaCCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997) $T_{\text {min }}=0.890, T_{\text {max }}=0.923$
33782 measured reflections

## Refinement

Refinement on $F^{2}$
$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.035$
$w R\left(F^{2}\right)=0.084$
$S=1.14$
7933 reflections
589 parameters
H atoms treated by a mixture of independent and constrained refinement

Table 1
Hydrogen-bonding geometry ( $\AA \AA^{\circ}$ ).

| $D-\mathrm{H} \cdots A$ | $D-\mathrm{H}$ | H $\cdots$ A | $D \cdots A$ | $D-\mathrm{H} \cdots A$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{N} 1 A-\mathrm{H} 1 A \cdots \mathrm{O} 11 A$ | 0.872 (18) | 2.07 (2) | 2.921 (3) | 164 (3) |
| $\mathrm{N} 1 B-\mathrm{H} 1 E \cdots \mathrm{O} 11 B$ | 0.847 (18) | 2.098 (19) | 2.933 (3) | 169 (3) |
| $\mathrm{N} 2 A-\mathrm{H} 2 C \cdots \mathrm{O} 4 B$ | 0.88 | 1.95 | 2.804 (3) | 164 |
| $\mathrm{N} 2 A-\mathrm{H} 2 D \cdots \mathrm{O} 12 B^{\mathrm{i}}$ | 0.88 | 2.20 | 3.076 (3) | 172 |
| $\mathrm{N} 2 B-\mathrm{H} 2 G \cdot \cdots \mathrm{O} 4 A^{\text {ii }}$ | 0.88 | 2.00 | 2.866 (3) | 166 |
| $\mathrm{N} 2 B-\mathrm{H} 2 H \cdots \mathrm{O} 12 A$ | 0.88 | 2.11 | 2.980 (3) | 169 |
| $\mathrm{N} 3 A-\mathrm{H} 3 A \cdots \mathrm{O} 3 B$ | 0.88 | 2.19 | 3.061 (3) | 172 |
| $\mathrm{N} 3 A-\mathrm{H} 3 B \cdots \mathrm{O} 12 A$ | 0.88 | 2.21 | 3.072 (3) | 166 |
| $\mathrm{N} 3 B-\mathrm{H} 3 E \cdots \mathrm{O} 3 A^{\text {ii }}$ | 0.88 | 2.22 | 3.099 (3) | 176 |
| $\mathrm{N} 3 B-\mathrm{H} 3 F \ldots \mathrm{O} 12 B$ | 0.88 | 2.19 | 3.056 (3) | 168 |
| N5 $A-\mathrm{H} 5 C \cdots \mathrm{O} 7 B^{\text {iii }}$ | 0.88 | 2.15 | 2.991 (3) | 159 |
| N5A-H5D . O99 $B^{\text {iii }}$ | 0.88 | 2.15 | 2.942 (3) | 150 |
| $\mathrm{N} 5 B-\mathrm{H} 5 \mathrm{G} \cdot \cdots \mathrm{O} A^{\text {iv }}$ | 0.88 | 2.21 | 3.055 (3) | 162 |
| $\mathrm{N} 5 B-\mathrm{H} 5 H \cdots \mathrm{O} 9 A^{\text {iv }}$ | 0.88 | 2.04 | 2.901 (3) | 166 |
| $\mathrm{N} 6 A-\mathrm{H} 6 A \cdots \mathrm{~N} 6 B^{\mathrm{v}}$ | 0.849 (18) | 2.52 (3) | 3.158 (4) | 132 (3) |
| $\mathrm{N} 6 B-\mathrm{H} 6 E \cdots \mathrm{O} 9 A^{\text {iv }}$ | 0.872 (18) | 2.57 (2) | 3.328 (3) | 146 (3) |
| $\mathrm{O} 8 A-\mathrm{H} 8 A \cdots \mathrm{O} 9 A$ | 0.812 (17) | 1.861 (19) | 2.664 (3) | 170 (4) |
| $\mathrm{O} 8 A-\mathrm{H} 8 B \cdots \mathrm{O} 11 A$ | 0.800 (17) | 1.855 (18) | 2.653 (3) | 175 (4) |
| $\mathrm{O} 8 B-\mathrm{H} 8 E \cdots \mathrm{O} 9 B$ | 0.809 (17) | 1.871 (18) | 2.673 (3) | 172 (4) |
| $\mathrm{O} 8 B-\mathrm{H} 8 F \cdots \mathrm{O} 11 B$ | 0.809 (17) | 1.867 (17) | 2.669 (3) | 172 (3) |
| $\mathrm{O} 9 A-\mathrm{H} 9 A \cdots \mathrm{O} 10 A$ | 0.815 (17) | 1.854 (18) | 2.663 (3) | 172 (4) |
| $\mathrm{O} 9 A-\mathrm{H} 9 B \cdots \mathrm{O} 10 B^{\text {vi }}$ | 0.810 (17) | 2.19 (2) | 2.896 (3) | 146 (3) |
| $\mathrm{O} 9 A-\mathrm{H} 9 B \cdots \mathrm{O} 13 B^{\text {vi }}$ | 0.810 (17) | 2.63 (3) | 3.212 (3) | 131 (3) |
| $\mathrm{O} 9 B-\mathrm{H} 9 E \cdots \mathrm{O} 10 B$ | 0.807 (17) | 1.848 (18) | 2.651 (3) | 173 (4) |
| $\mathrm{O} 9 B-\mathrm{H} 9 F \cdots \mathrm{O} 3 A^{\text {vii }}$ | 0.808 (17) | 2.18 (2) | 2.930 (3) | 155 (3) |
| $\mathrm{O} 10 A-\mathrm{H} 10 A \cdots \mathrm{O} 7 B^{\text {viii }}$ | 0.801 (17) | 2.10 (2) | 2.870 (3) | 161 (4) |
| $\mathrm{O} 10 A-\mathrm{H} 10 B \cdots \mathrm{O} 4 A^{\mathrm{ii}}$ | 0.801 (17) | 2.16 (2) | 2.926 (3) | 160 (4) |
| $\mathrm{O} 10 B-\mathrm{H} 10 E \cdots \mathrm{O} 7 A^{\mathrm{ix}}$ | 0.804 (17) | 2.047 (18) | 2.840 (3) | 169 (4) |
| $\mathrm{O} 10 B-\mathrm{H} 10 F \cdots \mathrm{O} 4 B^{\text {ii }}$ | 0.808 (17) | 2.011 (19) | 2.802 (3) | 166 (4) |

[^0]Table 2
Geometric parameters ( $\mathrm{A},{ }^{\circ}$ ).

|  | Cation $A$ | Cation B |
| :---: | :---: | :---: |
| Cu1-O1 | 1.9259 (19) | 1.9344 (18) |
| $\mathrm{Cu} 1-\mathrm{O} 5$ | 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) |
| $\mathrm{O} 2-\mathrm{C} 1$ | 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) |
| $\mathrm{O} 1-\mathrm{Cu} 1-\mathrm{O} 8$ | 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) |
| $\mathrm{O} 2-\mathrm{Cu} 2-\mathrm{O} 3$ | 84.83 (8) | 89.00 (8) |
| $\mathrm{O} 2-\mathrm{Cu} 2-\mathrm{O} 5$ | 97.26 (8) | 94.40 (8) |
| $\mathrm{O} 2-\mathrm{Cu} 2-\mathrm{N} 4$ | 168.59 (9) | 171.34 (8) |
| $\mathrm{O} 3-\mathrm{Cu} 2-\mathrm{O} 5$ | 177.90 (7) | 170.99 (9) |
| $\mathrm{O} 3-\mathrm{Cu} 2-\mathrm{N} 4$ | 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 $0.85 \AA$ from atom $\mathrm{Cu} 2 B . \mathrm{H}$ atoms attached to C atoms were placed geometrically, with $\mathrm{C}-\mathrm{H}$ distances of 0.99 and $1.00 \AA$ for methylene ( C 2 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 SHELXL 97 command AFIX 93 with $\mathrm{N}-\mathrm{H}$ distances of $0.88 \AA$ was used for the H atoms of terminal $\mathrm{NH}_{2}$ groups ( $\mathrm{N} 2, \mathrm{~N} 3$ and N 5 ). For the remaining H atoms, the coordinates were allowed to refine but with DFIX used to constrain the $\mathrm{N}-\mathrm{H}$ distance in the case of secondary amine atoms N 1 and N6 and SADI used to restrain the $\mathrm{O}-\mathrm{H}$ distances for water atoms $\mathrm{O} 8, \mathrm{O} 9$ and O 10 . For all H atoms, $U_{\text {iso }}$ was set at $1.2 U_{\text {eq }}$ of the non- H atom to which the H atom is attached.

Data collection: DENZO (Otwinowski \& Minor, 1997) and COLLECT (Hooft, 1998); cell refinement: DENZO and COLLECT; data reduction: $D E N Z O$ 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).

## metal-organic compounds

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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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[^0]:    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) $1+x, \frac{1}{2}-y, z-\frac{1}{2}$; (viii) $x, y, 1+z$; (ix) $1+x, y, z-1$.

