Acta Crystallographica Section C Crystal Structure Communications

ISSN 0108-2701

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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Received 17 January 2003 Accepted 11 February 2003 Online 28 February 2003

The structure of the title compound, $aqua[\mu-(N^1-carboxylato$ $methylguanidino)oxidoacetato](\mu-guanidinoacetic acid)di$ copper(II) nitrate dihydrate, [Cu₂(C₅H₆N₃O₅)(C₃H₇N₃O₂)-(H₂O)]NO₃·2H₂O, contains two enantiomers of the dicopper(II) complex cation that comprise water, neutralzwitterionic guanidinoacetic acid and the trianion of(N¹-carboxymethylguanidino)hydroxyacetic acid as ligands.Extensive hydrogen bonding creates three-dimensionalconnectivity but is largely confined to layers that each containboth cation enantiomers. These layers are related to oneanother by crystallographic symmetry and are thereforeidentical 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 $[Cu_2(NO_3)_2-(gaa)_4]$, (I) [gaa is guanidinoacetic acid, $H_2NC(=NH_2)NH-CH_2CO_2$; 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

 $C_8H_{19}Cu_2N_7O_{10}$, where this formula corresponds to an aquadicopper complex cation of formula $(C_8H_{15}Cu_2N_6O_8)^+$, 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 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 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, oag^{3-} , formulated $(C_5H_6N_3O_5)^{3-}$, 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 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 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.* Rat 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

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 N6A/N6B and O9A/O9B), 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 $P2_1/c$. 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 Ag₂CO₃ 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, HOCH₂CO₂H, (III), or the oxidized species $HC(O)CO_2H$, (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, Cu^{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, $[Cu_2(NO_3)_2(gaa)_4]$ (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 Cu^{II} in the genesis of oag³⁻ 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 g, 10 mmol) in 50% aqueous ethanol (50 ml) were successively added, with stirring, nitric acid (0.1 mol l^{-1} , until pH < 7), aspartic acid (1.331 g, 10 mmol) and copper nitrate trihydrate (2.462 g, 10 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 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

$\begin{split} & [\mathrm{Cu}_2(\mathrm{C}_3\mathrm{H}_6\mathrm{N}_3\mathrm{O}_5)(\mathrm{C}_3\mathrm{H}_7\mathrm{N}_3\mathrm{O}_2)-\\ & (\mathrm{H}_2\mathrm{O})]\mathrm{NO}_3\cdot 2\mathrm{H}_2\mathrm{O}\\ & M_r = 548.38\\ & \mathrm{Monoclinic}, \ P_2_1/c\\ & a = 15.2979\ (2) \ \mathrm{\mathring{A}}\\ & b = 13.0020\ (2) \ \mathrm{\mathring{A}}\\ & c = 17.7821\ (2) \ \mathrm{\mathring{A}}\\ & \beta = 90.0302\ (7)^\circ\\ & V = 3536.92\ (8) \ \mathrm{\mathring{A}}^3\\ & Z = 8 \end{split}$	$D_x = 2.060 \text{ Mg m}^{-3}$ Mo K\alpha radiation Cell parameters from 17 990 reflections $\theta = 2.9-27.5^{\circ}$ $\mu = 2.49 \text{ mm}^{-1}$ T = 120 (2) K Block, blue $0.20 \times 0.15 \times 0.15 \text{ mm}$
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 $I > 2\sigma(I)$ $R_{int} = 0.034$ $\theta_{max} = 27.5^{\circ}$ $h = -19 \rightarrow 19$ $k = -16 \rightarrow 16$ $l = -23 \rightarrow 22$
Refinement	
Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.035$ $wR(F^2) = 0.084$ S = 1.14 7933 reflections 589 parameters	$w = 1/[\sigma^{2}(F_{o}^{2}) + (0.0253P)^{2} + 6.7574P]$ where $P = (F_{o}^{2} + 2F_{c}^{2})/3$ $(\Delta/\sigma)_{max} = 0.001$ $\Delta\rho_{max} = 0.93 \text{ e} \text{ Å}^{-3}$ $\Delta\rho_{min} = -1.03 \text{ e} \text{ Å}^{-3}$

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Table 1	
Hydrogen-bonding geo	metry (Å, °).

$D - H \cdots A$	D-H	$H \cdots A$	$D \cdots A$	$D - H \cdots A$
$N1A - H1A \cdots O11A$	0.872 (18)	2.07 (2)	2.921 (3)	164 (3)
$N1B - H1E \cdots O11B$	0.847 (18)	2.098 (19)	2.933 (3)	169 (3)
$N2A - H2C \cdots O4B$	0.88	1.95	2.804 (3)	164
$N2A - H2D \cdots O12B^{i}$	0.88	2.20	3.076 (3)	172
$N2B - H2G \cdots O4A^{ii}$	0.88	2.00	2.866 (3)	166
$N2B - H2H \cdot \cdot \cdot O12A$	0.88	2.11	2.980 (3)	169
$N3A - H3A \cdots O3B$	0.88	2.19	3.061 (3)	172
$N3A - H3B \cdots O12A$	0.88	2.21	3.072 (3)	166
$N3B-H3E\cdots O3A^{ii}$	0.88	2.22	3.099 (3)	176
$N3B - H3F \cdot \cdot \cdot O12B$	0.88	2.19	3.056 (3)	168
$N5A - H5C \cdots O7B^{iii}$	0.88	2.15	2.991 (3)	159
$N5A - H5D \cdots O9B^{iii}$	0.88	2.15	2.942 (3)	150
$N5B-H5G\cdots O7A^{iv}$	0.88	2.21	3.055 (3)	162
$N5B-H5H\cdots O9A^{iv}$	0.88	2.04	2.901 (3)	166
$N6A - H6A \cdot \cdot \cdot N6B^{v}$	0.849 (18)	2.52 (3)	3.158 (4)	132 (3)
$N6B - H6E \cdots O9A^{iv}$	0.872 (18)	2.57 (2)	3.328 (3)	146 (3)
$O8A - H8A \cdots O9A$	0.812 (17)	1.861 (19)	2.664 (3)	170 (4)
$O8A - H8B \cdot \cdot \cdot O11A$	0.800 (17)	1.855 (18)	2.653 (3)	175 (4)
$O8B - H8E \cdots O9B$	0.809 (17)	1.871 (18)	2.673 (3)	172 (4)
$O8B - H8F \cdot \cdot \cdot O11B$	0.809 (17)	1.867 (17)	2.669 (3)	172 (3)
$O9A - H9A \cdot \cdot \cdot O10A$	0.815 (17)	1.854 (18)	2.663 (3)	172 (4)
$O9A - H9B \cdots O10B^{vi}$	0.810 (17)	2.19 (2)	2.896 (3)	146 (3)
$O9A - H9B \cdots O13B^{vi}$	0.810 (17)	2.63 (3)	3.212 (3)	131 (3)
$O9B - H9E \cdots O10B$	0.807 (17)	1.848 (18)	2.651 (3)	173 (4)
$O9B - H9F \cdot \cdot \cdot O3A^{vii}$	0.808 (17)	2.18 (2)	2.930 (3)	155 (3)
$O10A - H10A \cdot \cdot \cdot O7B^{viii}$	0.801 (17)	2.10 (2)	2.870 (3)	161 (4)
$O10A - H10B \cdots O4A^{ii}$	0.801 (17)	2.16 (2)	2.926 (3)	160 (4)
$O10B - H10E \cdot \cdot \cdot O7A^{ix}$	0.804 (17)	2.047 (18)	2.840 (3)	169 (4)
$O10B - H10F \cdots O4B^{ii}$	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) $1 + x, \frac{1}{2} - y, z - \frac{1}{2}$; (viii) x, y, 1 + z; (ix) 1 + x, y, z - 1.

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, $U_{\rm iso}$ was set at $1.2U_{\rm eq}$ 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: *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).

metal-organic compounds

The use of the EPSRC X-ray crystallographic service at Southampton and the valuable assistance of the staff there is gratefully acknowledged. We thank CPNq and FAPERJ, Brazil, for financial support.

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.

References

Blessing, R. H. (1995). Acta Cryst. A51, 33–37.
Blessing, R. H. (1997). J. Appl. Cryst. 30, 421–426.
Farrugia, L. J. (1997). J. Appl. Cryst. 30, 565.

Felcman, J. & de Miranda, J. L. (1997). J. Braz. Chem. Soc. 8, 575-580.

Hooft, R. (1998). COLLECT. Nonius BV, Delft, The Netherlands.

- Miranda, J. L. de & Felcman, J. (2001). Synth. React. Inorg. Met. Org. Chem. 31, 873–894.
- Miranda, J. L. de, Felcman, J., Wardell, J. L. & Skakle, J. M. S. (2002). Acta Cryst. C58, m471–m474.
- Nakai, T., Ohta, T., Fujita, Y. & Horiuchi, K. (1979). Agric. Biol. Chem. 43, 2623–2624.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Silva, M. R., Paixao, J. A., Beja, A. M. & da Veiga, L. A. (2001). Acta Cryst. C57, 7–8.
- Spek, A. L. (2003). J. Appl. Cryst. 36, 7-13.