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Tetrakis(μ-guanidinoacetic acid-κ²O:O′)bis[(nitrato-κO)copper(II)]

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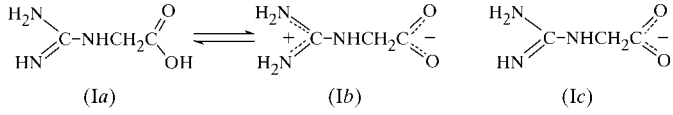
The title compound, $[Cu_2(NO_3)_2(C_3H_7N_3O_2)_4]$, forms a centrosymmetric dimer, with the two Cu^{2+} ions separated by 2.6525 (6) Å. The asymmetric unit contains a Cu atom coordinated to two guanidinoacetic acid ligands (*via* one carboxylate O atom from each ligand) and to a nitrate group. The inversion centre in $P\overline{1}$ generates the entire molecule, in which each Cu atom is coordinated to four carboxylate and to one nitrate O atom; ignoring the Cu—Cu separation, the geometry about each Cu atom is square pyramidal. The amino acid ligand is in the zwitterionic form. Strong N—H···O hydrogen bonds lead to a three-dimensional supramolecular structure, in which the N···O distances are in the range 2.931 (4)–3.278 (3) Å, with N—H···O angles ranging from 128 to 170°.

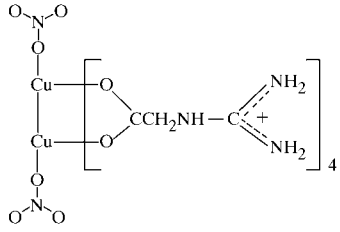
Comment

Guanidinoacetic acid, (I), alternatively called glycocyamine or *N*-(aminoiminomethyl)glycine, is a very significant amino acid as it is the precursor of creatine and is involved in many biological processes. It is synthesized in the kidneys (Borsook & Dubnoff, 1941; Takeda *et al.*, 1992) and measurement of its urinary levels is considered a sensitive tool for the early diagnosis of renal failures (Tanaka *et al.*, 1999), such as nephrotoxicity (Nakayama *et al.*, 1989), hypertensive renal diseases (Takano *et al.*, 1989) and rejection crises in kidney transplantation (Ishizaki *et al.*, 1985). In addition, (I) is important in creatine deficiency (Ilas *et al.*, 2000), cholesterol production (Sugiyama *et al.*, 1989), thyroid dysfunction (Verhelst *et al.*, 1997), hepatic encephalopathy (De Deyn *et al.*, 1995) and insulin regulation (Kuroda, 1993). Accumulation of (I) has been detected in patients both with guanidinoacetate methyltransferase deficiency (Stockler *et al.*, 1996) and with urinary tract neoplasm on treatment with cisplatin (Yasuda *et al.*, 2000).

Studies of the interaction of (I) with biologically active metals are limited. Previously, we reported the dissociation constants of (I)–metal ion complexes determined by potentiometric methods in solution (Felcman & Miranda, 1997), as well as the spectra of complexes in the solid state (IR) and in solution (UV and EPR) (Miranda & Felcman, 2001). Recently, the first crystal structure of a metal–guanidinoacetic acid complex, namely dichlorobis(glycocyamine-*O*)copper, (II), formed from $CuCl_2$ and (I) in aqueous solution, has been reported (Ramos Silva *et al.*, 2001).



(I*a*) (I*b*) (I*c*)



(III)

We have now isolated a dinuclear copper complex of (I), namely tetrakis(μ-guanidinoacetic acid)bis[nitratocopper(II)], (III), from a dilute aqueous nitric acid solution of $Cu(NO_3)_2$ and (I). The centrosymmetric core of the green-coloured compound is made up of two Cu^{2+} ions bridged by four carboxylate anions, with Cu—O bond lengths ranging from 1.9520 (19) to 1.9814 (19) Å (Table 1). Each Cu^{2+} ion in (III) is further coordinated to a nitrate O atom, with a Cu1—$O5^{ii}$ distance of 2.1500 (18) Å [symmetry code: (ii) $x-1$, $y-1$, z]. The carboxylate O atoms are in equatorial positions about the Cu atoms, with the nitrate O atom in an apical site.

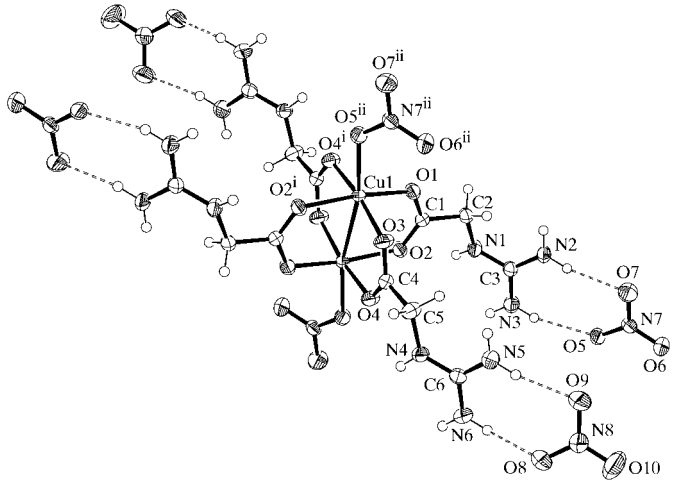


Figure 1
A view of (III), showing the copper coordination within the centrosymmetric dimer [symmetry codes: (i) $-x, 1-y, -z$; (ii) $x-1, y-1, z$]. The intramolecular hydrogen bonding to the NO_3 groups is shown by the dashed lines. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres.

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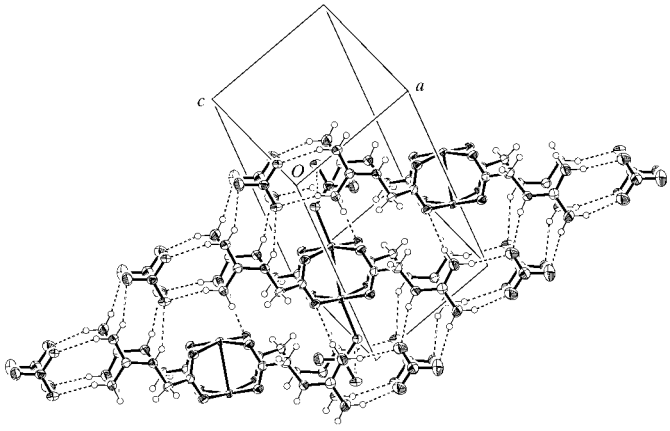

Figure 2
Part of the crystal structure of (III), showing the co-operation of the strong hydrogen bonds to form a chain along (100), including the hydrogen bonds N1—H1···O7^{iii}, N3—H3*B*···O6^{iii}, N4—H4···O9^{iii}, N6—H6*A*···O10^{iii} and N5—H5*C*···O1^{vi} [symmetry codes: (iii) $x-1$, y, z; (vi) $1-x$, $1-y$, $-z$].

Bond-valence sums (BVS; Brown, 1981) around the copper confirm this fivefold coordination, giving a BVS of 2.02, whereas if the long Cu1—O5 bond is omitted, the BVS is 1.76, well short of the expected value of 2 for copper(II). In addition, the intramolecular Cu1—Cu1^{i} separation is 2.6525 (6) Å, with a Cu1^{i}—Cu1—O5^{ii} angle of 168.10 (5)° [symmetry code: (i) $-x$, $1-y$, $-z$]. Ignoring the Cu—Cu separation, the geometry about each Cu atom is square pyramidal.

The main molecule is shown in Fig. 1, together with the atom-numbering scheme and the intramolecular hydrogen bonding to the nitrate groups. The core of (III) is similar to those generally found in dimeric copper(II)–carboxylate species, $[Cu_2(RCO_2)_4L_2]$, (IV), in which the ligands, *L*, are situated in apical positions [*e.g.* as in *L* = EtOH and *R* = 1-Ph-cyclopropyl (Agterberg *et al.*, 1997), *L* = H_2O and *R* = 4-HO-3-$MeOC_6H_3$ (Zhu *et al.*, 2000), *L* = H_2O and *R* = Me_2PhSi (Steward *et al.*, 1986), *L* = Me_2CO and *R* = 2,4-Cl_2-5-$MeC_6H_2SCH_2$ (Smith, O'Reilly, Kennard & White, 1985), *L* = pyridine and *R* = PhCO (Harada *et al.*, 1997), and *L* = C_nH_{2n+1} (*n* = 9, 11, 13, 15, 17 and 19) and *R* = $C_{12}H_{25}$-pyridine (Rusjan *et al.*, 2000)], and also in $[Cu_2(RCO_2)_4]$, (V), in which an intermolecular axial Cu–carboxylate coordination also occurs to each Cu centre [*e.g.* as in *R* = *n*-C_5H_{11} (Doyle *et al.*, 2000), *R* = PhSCHMe (Chen *et al.*, 1987) and *R* = 2-$ClC_6H_4OCH_2CH_2$ (Smith, O'Reilly, Kennard & White, 1985)].

The Cu···Cu distances in (V) are generally shorter (2.55–2.59 Å) than those in (IV), which can be as great as 2.9 Å. Of interest, the Cu—Cu distance in (III) [2.6525 (6) Å] is comparable with those generally found for (IV) (*L* = *O*-ligand), *e.g.* the value in $[Cu_2(2,4\text{-}Cl_2\text{-}5\text{-}MeC_6H_2SCH_2CO_2)_4(Me_2CO)_2]$ is 2.646 (1) Å (Smith, O'Reilly, Kennard, Mak & Yip, 1985). The Cu—O(equatorial) and Cu—O(apical) bond lengths in (III) are similar to the distances found in related compounds.

As in the mononuclear complex (II) (Ramos Silva *et al.*, 2001), the guanidinoacetic acid ligand in (III) is present in the zwitterionic form, (I*b*), rather than in either the neutral form, (I*a*), or the mono-anionic form, (I*c*) (see *Scheme*). As with other complexes, *e.g.* (IV), having carboxylate ligands with additional functionality, it is only the carboxylate group of (I) which coordinates to copper in (III). The nitrogen centres in the guanidinoacetic acid ligand, while not involved in the complexation to the metal, are however extensively involved in hydrogen bonding.

A number of strong intermolecular hydrogen bonds form (*PLATON*; Spek, 2002) in addition to the intramolecular N—H···O$_{nitrate}$ bonds shown in Fig. 1. These are supported by three C—H···O hydrogen bonds (Table 2). The first set of strong hydrogen bonds form between the molecule at (x, y, z) and those at ($x-1$, y, z) (symmetry code iii) and ($1-x$, $1-y$, $-z$) (symmetry code vi); this involves N1—H1···O7^{iii}, N3—H3*B*···O6^{iii}, N4—H4···O9^{iii}, N6—H6*A*···O10^{iii} and N5—H5*C*···O1^{vi} (Fig. 2), which combine to form a chain along (100). Fig. 3 shows the chain resulting from the N2—H2*D*···O8^{iv} hydrogen bond [symmetry code: (iv) x, y, $1+z$]

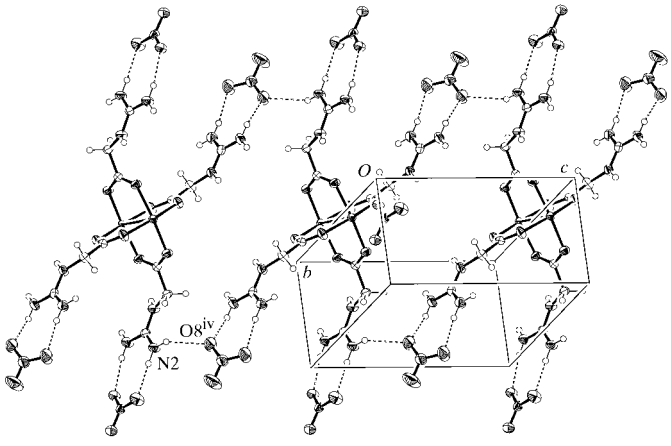

Figure 3
Part of the crystal structure of (III), showing the formation of chains along (001) *via* $R_2^2(32)$ dimers [N2—H2*D*···O8^{iv}; symmetry code: (iv) x, y, $1+z$].

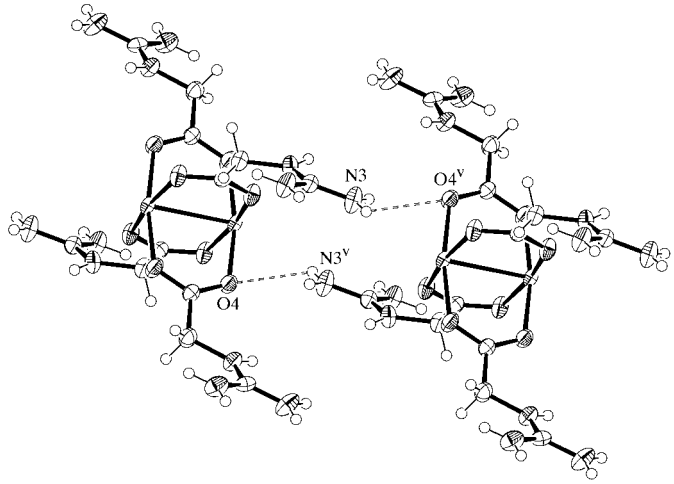

Figure 4
Part of the crystal structure of (III), showing the $R_2^2(18)$ dimer formed from N3—H3*A*···O4^{v} [symmetry code: (v) $1-x$, $2-y$, $-z$].

propagating along (001) and formed from $R_2^2(32)$ dimers. Finally, N3—H3A···O4^{v} [symmetry code: (v) $1-x$, $2-y$, $-z$] gives an $R_2^2(18)$ dimer centred on ($\frac{1}{2}$, 1, 0) (Fig. 4). These hydrogen bonds combine to form a three-dimensional framework.

The antiferromagnetic properties of many of the dicopper compounds have been studied [*e.g.* (IV) (Rusjan *et al.*, 2000; Agterberg *et al.*, 1997; Harada *et al.*, 1997) and (V) (Doyle *et al.*, 2000)]. While the biological aspects of (III) and related complexes are our dominant interest, the magnetic properties of (III) have not been neglected and will be reported in due course.

Experimental

Hydrated copper nitrate (0.5 mmol) was added slowly over a period of 6 h to a stirred aqueous solution of (I) (1 mmol), acidified with HNO_3 (0.1 mol l^{-1}). The reaction mixture was concentrated to half its original volume, and ethanol and acetone were added. After a period of 7 months at room temperature, small green crystals were collected from the reaction mixture, washed with acetone and air-dried.

Crystal data

$[Cu_2(NO_3)_2(C_3H_7N_3O_2)_4]$
M_r = 843.58
Triclinic, $P\overline{1}$
a = 7.2535 (8) Å
b = 10.3652 (12) Å
c = 10.5626 (12) Å
α = 99.262 (2)°
β = 94.862 (2)°
γ = 105.844 (2)°
V = 747.05 (15) Å^3
Z = 1
D_x = 1.875 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3425 reflections
θ = 3.7–29.9°
μ = 1.54 mm^{-1}
T = 298 (2) K
Block, green
0.58 × 0.22 × 0.18 mm

Data collection

Bruker SMART 1000 area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.596, T_{max} = 0.928
6444 measured reflections
4202 independent reflections
3433 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 30.0°
$h = -9 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.115
S = 1.03
4202 reflections
226 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0744P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.82 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9696 (17)	Cu1—O4^{i}	1.9814 (19)
Cu1—O2^{i}	1.9766 (17)	Cu1—O5^{ii}	2.1500 (18)
Cu1—O3	1.9520 (19)	Cu1—Cu1^{i}	2.6525 (6)
O1—Cu1—O3	91.26 (8)	O2^{i}—Cu1—O5^{ii}	88.27 (7)
O1—Cu1—O2^{i}	167.60 (7)	O4^{i}—Cu1—O5^{ii}	85.44 (8)
O3—Cu1—O2^{i}	90.80 (8)	O1—Cu1—Cu1^{i}	85.12 (5)
O1—Cu1—O4^{i}	88.53 (8)	O2^{i}—Cu1—Cu1^{i}	83.05 (5)
O2^{i}—Cu1—O4^{i}	86.96 (8)	O3—Cu1—Cu1^{i}	82.21 (5)
O3—Cu1—O4^{i}	168.16 (7)	O4^{i}—Cu1—Cu1^{i}	85.98 (5)
O3—Cu1—O5^{ii}	106.12 (8)	O5^{ii}—Cu1—Cu1^{i}	168.10 (5)
O1—Cu1—O5^{ii}	102.88 (7)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O7^{iii}	0.86	2.35	3.114 (3)	147
N2—H2D···O8^{iv}	0.87	2.28	2.966 (3)	136
N2—H2C···O7	0.87	2.15	2.983 (3)	160
N3—H3A···O5	0.86	2.21	3.021 (3)	158
N3—H3A···O4^{v}	0.86	2.54	3.142 (3)	128
N3—H3B···O6^{iii}	0.86	2.27	3.063 (3)	154
N3—H3B···O7^{iii}	0.86	2.36	3.137 (3)	151
N4—H4···O9^{iii}	0.86	2.12	2.960 (3)	165
N5—H5C···O1^{vi}	0.87	2.49	3.278 (3)	151
N5—H5D···O9	0.87	2.07	2.931 (4)	170
N6—H6A···O10^{iii}	0.86	2.19	3.005 (4)	158
N6—H6B···O8	0.86	2.24	3.017 (4)	151
C2—H2A···N6^{iv}	0.97	2.60	3.553 (4)	166
C2—H2B···O3^{vi}	0.97	2.56	3.491 (3)	162
C5—H5A···O1^{vi}	0.97	2.39	3.352 (3)	172
C5—H5B···O8^{vii}	0.97	2.55	3.444 (4)	154

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

All H atoms were placed in geometrically calculated positions and refined using a riding model (see Table 2 for distances involving H atoms). Both nitrate groups were located in positions with the centre of gravity outside the unit cell so as to emphasis the hydrogen bonding from the amino groups. Two high residual electron densities were located close to the Cu1 atom as follows: 1.48 e Å^{-3} at a distance of 0.90 Å and 1.42 e Å^{-3} at a distance of 0.88 Å.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* in *OSCAIL* (McArdle, 1994, 2000) and *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1121). Services for accessing these data are described at the back of the journal.

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