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Structure of Aqua[*N*,*N*'-ethylenebis(*N*-carbamoylmethylglycinato)]copper(II) Dihydrate

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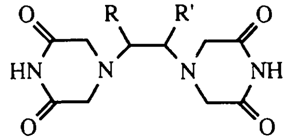
Abstract

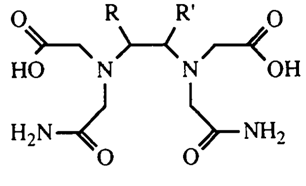
The structure consists of a copper(II) cation octahedrally coordinated to the polyaminocarboxylate ligand through five ligating atoms: one N atom of the ethylenediamine ring, two carboxylate O atoms and a molecule of water form a square plane, while one amide O and the other ethylenediamine-ring N atom are above and below the plane. The latter two atoms display tetragonal distortion. Eight intermolecular hydrogen bonds involve H, N and O atoms of the complex as well as the two water molecules of crystallization.

Comment

DL-[1,2-Bis(3,5-dioxo-1-piperazinyl)ethane (1) is a well known anti-tumor agent (Camerman, Hempel & Camerman, 1984; Creighton, Hellmann & Whitecross, 1969). Methyl substitution on the ethylenediamine backbone also yields an immunoreactive agent (2); however, the ethyl-substituted derivative (3) shows no such effect. The biological activity of these compounds is thought to be due to the role of their hydrolysis products, (4), (5) and (6), respectively, which act as intracellular chelators for biologically essential metals such as copper(II), iron(III) and zinc(II). To gain insight into the mechanism of activity, structure–function relationships have been probed (Hasinoff, 1990; Huang, May, Quinlan, Williams & Creighton, 1982). Copper(II) complexes, in particular, have received considerable attention. Relatively high thermodynamic stability constants (Smith & Martell, 1989; Huang, May, Quinlan, Williams & Creighton, 1982) and crystal structures (Prout, Sanderson & Couldwell, 1979) for the copper(II) complexes of ligands (5) and (6) have been reported. Also, Houghton & Williams (1982) have shown that copper(II) promotes the rapid hydrolysis of (1) to form the stable metal–(4) complex, Cu(EDTA-BA). In this paper we report the coordination geometry for copper(II) chelated to (4), and compare the structure with those determined for (5), (6) and structurally related EDTA ligands.



(1) R = H, R' = H
(2) R = CH$_3$, R' = H
(3) R = C$_2$H$_5$, R' = H



(4) R = H, R' = H
(5) R = CH$_3$, R' = H
(6) R = C$_2$H$_5$, R' = H

Atomic coordinates and equivalent isotropic displacement coefficients for [Cu(EDTA-BA)(H_2O)].2H_2O are listed in Table 1. A stereoview of the asymmetric unit and the atom-numbering scheme are shown in Fig. 1 and selected bond distances and angles are given in Table 2. Ligand (4) acts as a pentadentate ligand, binding a single copper(II) cation, with the sixth coordination site occupied by a molecule of water. Amido O-atom

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coordination obtained at near neutral pH is consistent with spectroscopic results reported for similar copper(II) complexes (Hay, Nolan & Shuaib, 1979). The octahedral environment is tetragonally distorted with two elongated axial bonds, Cu—N(2) 2.356 (5) and Cu—O(4) 2.379 (4) Å, and four equatorial bonds, Cu—N(3) 2.084 (4), Cu—O(6) 1.935 (3), Cu—O(7) 1.987 (3) and Cu—O(3) 1.947 (3) Å. The chelate restricts the amount of tetragonal distortion. For example, a difference between the equatorial and axial Cu—N bond lengths of 0.27 Å for Cu$^{\rm II}$–(4) compares to *ca* 0.6 Å for complexes with monodentate ligands (Hathaway & Billing, 1969). The equatorial carboxylato O—Cu distances [1.935 (3) and 1.947 (3) Å] and the axial amide carbonyl O—Cu distance [2.379 (4) Å] in Cu$^{\rm II}$–(4) are not unusual and agree with previously reported values (Prout, Sanderson & Couldwell, 1979; Bulman, Jobanputra, Kuroda, McKinnon & Sadler, 1987).

The Cu$^{\rm II}$–(4) complex contains four five-membered chelate rings. Two rings Cu–N(2)–C(5)–C(6)–O(3) and Cu–N(3)–C(9)–C(10)–O(6) are nearly planar. Deviations from the least-squares plane are 0.0470, −0.0775, 0.0886, −0.0308 and −0.0272 Å and 0.0470, −0.0991, 0.1324, −0.0946 and 0.0206 Å for the atoms in each plane, respectively. One other ring, Cu–N(3)–C(7)–C(8)—O(4), displays an envelope conformation showing corresponding deviations of 0.1902, −0.2778, 0.2039, 0.0672 and −0.1835 Å. The atoms C(3) and C(4) of the ethylenediamine ring, Cu–N(2)–C(3)–C(4)–N(3), are positioned −0.2862 below and 0.2928 Å above the Cu–N(2)–N(3) plane, respectively. This zigzag conformation is consistent with those observed in similar EDTA-type copper(II) complexes (Prout, Sanderson & Couldwell, 1979).

The above data allow comparison of the Cu$^{\rm II}$–(4) structure with those of other copper(II) complexes containing EDTA-type ligands. Selected bond distances and angles for the copper(II) complexes of ligands (4), (5), (6), EDTA and H_2EDTA are presented in Table 2. The copper(II) complex geometry for ligand (4) is significantly different from that determined for the similar alkyl-substituted-EDTA bis(amide)ligands, (5) and (6) (Prout, Sanderson & Couldwell, 1979). While both amido O atoms are coordinated to the metal center in Cu$^{\rm II}$–(5), and Cu$^{\rm II}$–(6), only one amide arm is bound in Cu$^{\rm II}$–(4). A solvent water molecule occupies this equatorial site. Distinction between Cu$^{\rm II}$–(4) and its alkyl derivatives is also found in the atom-type ligation comprising the two distorted axial positions. These coordination sites in Cu$^{\rm II}$–(5), and Cu$^{\rm II}$–(6) are filled by weakly bound amide donors [Cu—O(5), 2.298 (6) and 2.328 (9) Å; Cu—O(6), 2.387 (6) and 2.407 (10) Å], while the elongated bonds in Cu$^{\rm II}$–(4) contain one amido O linkage [Cu—O(4), 2.379 (4) Å] and one N donor [Cu—N(2), 2.356 (5) Å] from the ethylenediamine ring. Cu$^{\rm II}$–(5), and Cu$^{\rm II}$–(6) resemble the Cu$^{\rm II}$(EDTA) structure reported by Solans, Font-Altaba, Oliva & Herrera (1982) while the structure of Cu$^{\rm II}$–(4) is nearly isostructural with that of Cu(H_2EDTA) (Stephens, 1969). The C[O(4)]NH_2 of (4) is positioned analogously to the protonated carboxylate arm, C[O(4)OH, of H_2EDTA. Comparison of axial bond lengths, however, shows that the distortion with ligand (4) is more tetragonal in nature than that in H_2EDTA, which distorts towards a square pyramid (Stephens, 1969).

A view of the crystal packing and the hydrogen-bonding network for Cu$^{\rm II}$–(4) is shown in Fig. 2. Each copper complex interacts with four others and with four water molecules, producing a continuous structure interconnected through hydrogen bonding. In general, hydrogen-bond lengths vary from 1.80 to 2.23 Å and angles are between 125 and 172°. Hydrogen-bond distances and angles are given in Table 2. Water molecules of crystallization form hydrogen bonds with metal-bound carboxylate O atoms [O(9)···O(6) 2.85 and O(8)···O(3) 2.88 Å] with lengths comparable to those reported for Cu$^{\rm II}$–(5), and Cu$^{\rm II}$–(6) (2.80–2.85 Å) (Prout, Sanderson & Couldwell, 1979). The N atom of the non-coordinating amide arm forms longer hydrogen bonds with both a water molecule of crystallization [N(1)···O(8) 2.96 Å], and with a ligating O atom of a neighboring

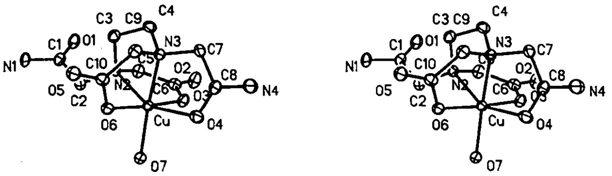

Fig. 1. Stereoview showing the thermal ellipsoids at 50% probability level and atom-numbering scheme.

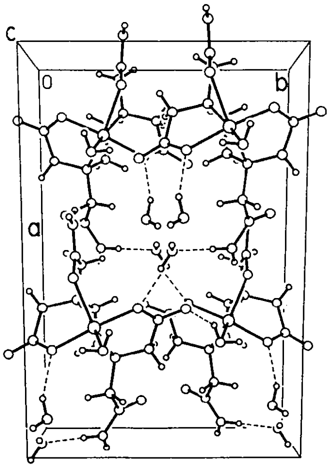

Fig. 2. View of the crystal packing and the hydrogen-bonding network.

complex [N(1)···O(4) 3.05 Å]. The shortest hydrogen bond in the structure is between the coordinated water molecule and the O atom of a neighboring metal-bound carboxylate linkage [O(7)···O(2) 2.65 Å]. A nearly identical interaction is observed in the packing of Cu(H_2EDTA) with a reported distance of 2.627 Å (Stephens, 1969).

Experimental

Crystal data

[Cu($C_{10}H_{16}N_4O_6$)(H_2O)].2H_2O
M_r = 405.9
Monoclinic
Cc
a = 16.495 (7) Å
b = 10.841 (6) Å
c = 9.118 (4) Å
β = 104.03 (3)°
Cell parameters from 9 reflections

θ = 6–12.5°
V = 1581.8 (13) $Å^3$
Z = 4
D_x = 1.704 Mg m^{-3}
Mo *Kα*
λ = 0.71069 Å
μ = 1.435 mm^{-1}
T = 130 K
Block
0.84 × 0.56 × 0.52 mm
Blue

Data collection

Nicolet *R*3*m*/V diffractometer
Absorption correction: empirical
T_{min} = 0.10, T_{max} = 0.34
1439 measured reflections
1439 independent reflections
1418 observed reflections [$F > 4.0\sigma(F)$]

θ_{max} = 50.0°
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 12$
$l = -10 \rightarrow 9$
2 standard reflections monitored every 198 reflections
intensity variation: 3%

Refinement

Refinement on *F*
Final *R* = 0.0293
wR = 0.0352
S = 1.65
1418 reflections

229 parameters
$w = 1/[\sigma^2(F)+0.0003F^2]$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.40 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.46 e $Å^{-3}$

Compound (4) was prepared using a modification of a procedure reported by Konings, Dow, Love, Raymond, Quay & Rocklage (1990). 1,2-Bis(2,6-dioxo-4-morphyl)ethane (Aldrich) (1.0 g, 3.9 mmol) was added slowly (over 45 min) to cold (≤ 278 K) 30% aqueous NH_4OH (3 mL, 42 mmol) and the mixture stirred for 8 h at room temperature. The yellow solution was filtered and the filtrate evaporated to dryness under reduced pressure. The solid was redissolved in a minimum amount of water and concentrated HCl added dropwise to bring the pH to 2. The white precipitate was filtered, washed with 95% EtOH, ether and air dried to yield 1.1 g (98%) of (4). The spectral parameters for this ligand are identical to those reported by Houghton & Williams (1982). The copper(II) complex was prepared by adding dropwise (4) (0.25 g, 0.86 mmol), dissolved in a minimum amount of hot water, to a hot MeOH solution of $Cu(ClO_4)_2.6H_2O$ (0.32 g, 0.86 mmol). The pH was adjusted to 5.5 with aqueous NaOH. Crystals suitable for X-ray analysis were obtained upon slow evaporation at 277 K.

The data were collected using a Nicolet *R*3*m*/V diffractometer equipped with a locally modified Enraf–Nonius low-temperature apparatus.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* ($Å^2$)

Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Cu	0.6812	0.2375 (1)	0.7116	0.015 (1)
O(1)	0.8897 (2)	0.4086 (3)	0.4153 (4)	0.026 (1)
O(2)	0.6380 (2)	0.5834 (3)	0.5606 (4)	0.029 (1)
O(3)	0.6331 (2)	0.4015 (3)	0.6692 (3)	0.020 (1)
O(4)	0.5535 (2)	0.1649 (3)	0.7574 (4)	0.026 (1)
O(5)	0.7548 (3)	−0.0935 (3)	0.6234 (4)	0.027 (1)
O(6)	0.7385 (2)	0.0804 (3)	0.7414 (3)	0.019 (1)
O(7)	0.7316 (2)	0.2779 (3)	0.9270 (4)	0.019 (1)
O(8)	0.9857 (3)	0.0308 (3)	0.7023 (4)	0.030 (1)
O(9)	0.9052 (3)	0.0692 (4)	0.9231 (4)	0.034 (1)
N(1)	0.9806 (3)	0.2588 (3)	0.5214 (5)	0.025 (1)
N(2)	0.7669 (3)	0.3115 (3)	0.5583 (4)	0.017 (1)
N(3)	0.6147 (2)	0.1647 (3)	0.5060 (4)	0.018 (1)
N(4)	0.4187 (3)	0.1597 (5)	0.6298 (5)	0.034 (2)
C(1)	0.9108 (3)	0.3241 (4)	0.5094 (5)	0.020 (1)
C(2)	0.8573 (3)	0.2927 (4)	0.6196 (5)	0.021 (1)
C(3)	0.7364 (3)	0.2402 (4)	0.4192 (6)	0.022 (2)
C(4)	0.6418 (3)	0.2273 (4)	0.3815 (5)	0.022 (2)
C(5)	0.7439 (3)	0.4424 (4)	0.5419 (5)	0.021 (1)
C(6)	0.6656 (3)	0.4787 (4)	0.5924 (5)	0.019 (1)
C(7)	0.5229 (3)	0.1813 (4)	0.4870 (5)	0.021 (1)
C(8)	0.4996 (3)	0.1672 (4)	0.6368 (5)	0.021 (1)
C(9)	0.6363 (3)	0.0309 (4)	0.5134 (5)	0.021 (1)
C(10)	0.7171 (3)	0.0025 (4)	0.6331 (5)	0.019 (1)

Table 2. *Selected bond and hydrogen-bond distances* (Å) *and angles* (°) *for copper*(II) *complexes of* (4), (5), (6), *EDTA and* H_2*EDTA*

	(4)	(5)[a]	(6)[a]	EDTA[b]	H_2EDTA[c]
Cu—N(3)	2.084 (4)	2.036 (7)	2.046 (12)	2.043 (5)	2.066 (2)
Cu—N(2)	2.356 (5)	2.005 (6)	2.017 (11)	2.042 (5)	2.291 (2)
Cu—O(4)	2.379 (4)[d]	1.954 (5)[e]	1.931 (9)[e]	1.965 (5)	2.467 (2)
Cu—O(6)	1.935 (3)[3]	2.387 (6)[d]	2.407 (10)[d]	2.215 (4)	1.929 (2)
Cu—O(7)	1.987 (3)[f]	1.972 (6)[e]	1.977 (8)[e]	2.016 (4)	1.978 (3)[f]
Cu—O(3)	1.947 (3)[e]	2.298 (6)[d]	2.328 (9)[d]	2.289 (4)	1.970 (2)
O(4)—Cu—O(7)	94.3 (1)	108.0 (3)	106.7 (4)	108.6 (2)	99.0 (1)
N(2)—Cu—N(3)	81.7 (1)	86.8 (3)	87.0 (4)	—	84.6 (1)
N(2)—Cu—O(4)	154.3 (1)	164.9 (2)	166.0 (4)	—	154.6 (1)

Hydrogen-bond data for Cu^{II}–(4)

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
N(1)—H(1C)···O(8^i)	2.07 (8)	2.96	172 (3)
O(9)—H(9C)···O(6^i)	2.09 (5)	2.85	149 (4)
O(8)—H(8B)···O(3^{iii})	2.08 (6)	2.88	158 (6)
O(7)—H(7D)···O(2^{iii})	1.93 (6)	2.65	142 (4)
O(7)—H(7C)···O(5^{iv})	1.88 (6)	2.65	150 (4)
N(4)—H(4D)···O(1^v)	1.99 (7)	2.86	162 (3)
N(1)—H(1D)···O(4^{vi})	2.23 (6)	3.05	153 (4)

Symmetry operations for hydrogen-bonding data: (i) x, y, z; (ii) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $x, 1 - y, \frac{1}{2} + z$; (iv) $x, -y, \frac{1}{2} + z$; (v) $x - \frac{1}{2}, \frac{1}{2} + y, \frac{1}{2} + z$; (vi) $x + \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

Notes: (*a*) values from Prout, Sanderson & Couldwell (1979); (*b*) values from Solans, Font-Altaba, Oliva & Herrera (1982); (*c*) values from Stephens (1969); (*d*) amido O donor atom; (*e*) carboxylato O donor atom; (*f*) solvent water O donor atom.

H atoms were located from a difference Fourier map and subsequently modeled at ideal geometry with fixed isotropic thermal parameters, $U = 0.030$ $Å^2$, and fixed bond lengths, C—H = 0.96, N—H = 0.90, O—H = 0.85 Å. The two uncoordinated water molecules were additionally constrained with a fixed H···H distance of 1.35 Å. Hydrogen bonding was considered for intermolecular H···H distances approximating 1.8 Å. Non-H distances near 2.8 Å and angles near 180° were used to reinforce the proposed scheme.

The data were corrected for absorption using *XABS*, a program which provides an empirical correction based on F_o and F_c differences (Hope & Moezzi, 1988).

The absolute configuration was determined by a routine in *SHELXTL-Plus* (Sheldrick, 1989). The method is similar to that suggested by Rogers (1981).

We thank Marilyn M. Olmstead for her helpful assistance. Generous support from the National Cancer Institute, NIH [Public Health Service, National Research Service Award 1 F32 CA09024-01 (RAM)], and from Claude F. Meares [NCI, NIH (grant No. CA 47829)] is gratefully acknowledged.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54914 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1000]

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SHORT COMMUNICATION

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Acta Cryst. (1992). C**48**, 972

Structure of $MgCl_2.NH_4Cl.6H_2O$: amplification and apology.

By Richard E. Marsh, *The Beckman Institute, California Institute of Technology, Pasadena, California* 91125, *USA*

(*Received* 27 *February* 1992)

In a recent paper [Marsh (1992). *Acta Cryst.* C**48**, 218–219] correcting the reported structure of $MgCl_2.RbCl.6H_2O$, I noted that the structure of the corresponding ammonium compound $MgCl_2.NH_4Cl.6H_2O$ should also be corrected from triclinic, space group *P*1 [Nakayasu, Suzukawa & Kobayashi (1983). *Denki Kagaku*, **51**, 419–422], to monoclinic, *C*2/*c*. In fact, the correct *C*2/*c* structure had been reported in that same year by Solans, Font-Altaba, Aguiló, Solans & Domenech [*Acta Cryst.* (1983), C**39**, 1488–1490]. Also in that year, *Structure Reports* [(1983), Vol. A, edited by Ferguson & Trotter, pp. 120–121. Dordrecht: Kluwer Academic Publishers] had already noted that the triclinic structure reported by Nakayasu *et al.* (1983) could be transformed to *C*2/*c*, so as to agree with the results of Solans *et al.* I apologize both to Solans *et al.* and to the editors of *Structure Reports* for the oversights. They were brought to my attention by Professor J. Trotter, to whom I am much indebted.

All relevant information is given in the *Abstract*.