

Diaqua(2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)copper(II) Nitrate

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(Received 12 June 1981; accepted 15 September 1981)

Abstract. $C_{14}H_{28}CuN_4O_2^{+} \cdot 2NO_3^{-}$, $[Cu(C_{14}H_{24}N_4)(H_2O)_2](NO_3)_2$, orthorhombic, *Cmca*, $a = 12.007$ (2), $b = 15.690$ (4), $c = 10.869$ (5) Å, $Z = 4$, $V = 2047.6$ Å³, $d_m = 1.533$ (8), $d_c = 1.531$ Mg m⁻³. The structure was refined to $R = 0.041$ for 985 observed reflections. The structure consists of six-coordinate complex cations and nitrate ions. The coordination sphere of Cu is defined by the four N atoms of the macrocyclic ligand in a planar arrangement with O atoms of water molecules lying above and below this plane.

Introduction. The chemistry of 14-membered tetraazamacrocyclic ligands and their transition-metal complexes has been studied extensively in recent years. The syntheses and properties of metal complexes of variously saturated 14-membered tetraazamacrocyclics have been described (Busch, 1967; Curtis, 1968; Christensen, Eatough & Izatt, 1974; Melsom, 1979). Most published studies have involved saturated 14-membered macrocycles ([14]aneN₄) and partially unsaturated macrocycles ([14]eneN₄ and [14]dieneN₄). Only a few complexes of [14]tetraeneN₄ have been reported (Martin, Sperati & Busch, 1977).

The title compound was prepared by metal-ion template reaction of bis(1,3-propanediamine)copper(II) nitrate (Näsänen, Virtamo & Stedt, 1966) with 2,3-butanedione in water–ethanol mixture. After one week of reaction red-violet crystals of the compound were obtained. Cell parameters and the intensities of 1216 reflections were measured with a Syntex P2₁ diffractometer (graphite monochromator, Mo K α radiation, $\lambda = 0.7107$ Å, ω -scan method $3 < 2\theta < 55^\circ$). Of the recorded reflections, those 985 with $I > 3\sigma(I)$ were used in the calculations. Systematic absences yielded two possible space groups: *Cmca* and *C2ca*, which with $Z = 4$ require point symmetries of the complex $2/m$ and 2 respectively. The refinement of the structure confirmed the centrosymmetric space group *Cmca*.

The phase problem was solved by the Patterson function. The carbon atom C(2) of the macrocyclic ligand is positionally disordered, being divided between two positions with occupancy factors of 0.5. Most of

the H atoms were visible in the difference map, but because of the disorder the H atoms bonded to C(1) and C(2) were placed at calculated positions. The H atoms were included in the refinement with fixed isotropic temperature parameters ($U = 0.06$ Å²) and fixed positional coordinates. Refinement by full-matrix least squares with anisotropic temperature factors for the non-H atoms converged to $R = 0.041$. Calculations were performed on a Univac 1108 computer with the XRAY system (Stewart, 1976). The final

Table 1. Fractional atomic coordinates ($\times 10^4$) and U_{eq} (Å² $\times 10^2$) for the non-H atoms

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cu	0	0	0	3.48 (4)
O(1)	0	−401 (3)	2279 (4)	7.1 (3)
O(2)	2500	−723 (2)	2500	7.1 (2)
O(3)	1677 (3)	−1908 (2)	2171 (3)	10.0 (2)
N(1)	1246 (2)	768 (1)	397 (2)	3.6 (1)
N(2)	2500	−1517 (3)	2500	4.9 (2)
C(1)	1069 (3)	1635 (2)	865 (3)	5.0 (2)
C(2A)*	0	2036 (4)	405 (7)	3.2 (4)
C(2B)*	0	1706 (7)	1598 (14)	7.8 (8)
C(3)	2204 (2)	450 (2)	252 (2)	3.5 (1)
C(4)	3293 (3)	862 (2)	534 (4)	5.6 (2)

* Occupancy factor 0.5.

Table 2. Bond lengths (Å) and angles (°)

Cu–N(1)	1.969 (2)	N(1)–C(3)	1.264 (3)
Cu–O(1)	2.556 (5)	C(3)–C(3)	1.516 (4)
N(1)–C(1)	1.468 (4)	C(3)–C(4)	1.491 (4)
C(1)–C(2A)	1.514 (5)	N(2)–O(2)	1.246 (6)
C(1)–C(2B)	1.515 (9)	N(2)–O(3)	1.217 (4)
N(1)–Cu–N(1 ⁱ)	81.1 (1)	C(1)–C(2A)–C(1 ⁱⁱ)	115.9 (5)
N(1)–Cu–N(1 ⁱⁱ)	98.9 (1)	C(1)–C(2B)–C(1 ⁱⁱ)	115.8 (10)
N(1)–Cu–O(1)	86.5 (1)	N(1)–C(3)–C(3 ⁱ)	114.4 (2)
Cu–N(1)–C(1)	122.2 (2)	N(1)–C(3)–C(4)	127.0 (3)
Cu–N(1)–C(3)	115.0 (2)	C(3 ⁱ)–C(3)–C(4)	118.6 (2)
C(1)–N(1)–C(3)	122.7 (3)	O(2)–N(2)–O(3)	120.3 (2)
N(1)–C(1)–C(2A)	113.2 (3)	O(3)–N(2)–O(3 ⁱⁱⁱ)	119.5 (4)
N(1)–C(1)–C(2B)	111.9 (5)		

Symmetry code: (i) $x, -y, -z$; (ii) $-x, y, z$; (iii) $\frac{1}{2} - x, y, \frac{1}{2} - z$.

atomic coordinates are given in Table 1* and the bond lengths and angles in Table 2.

Discussion. The structure consists of six-coordinate monomeric [(Cu[14]tetraeneN₄)(H₂O)₂]²⁺ units and NO₃⁻ ions. The complex cation is shown in Fig. 1. Cu has tetragonally distorted octahedral coordination geometry. The Cu atom lies at a center of symmetry, and the complex cation has point symmetry 2/m. The four N atoms which are coordinated to Cu are necessarily planar. Their arrangement is a rectangle with sides N(1)—N(1)(x, -y, -z) and N(1)—N(1)(-x, y, z) equal to 2.560 (2) and 2.992 (3) Å respectively. The angles subtended by the N atoms at Cu

show significant deviations from 90°: N(1)—Cu—N(1)(x, -y, -z) in the five-membered chelate ring is 81.1 (1)° and N(1)—Cu—N(1)(-x, y, z) in the six-membered chelate ring is 98.9 (1)°. The coordination is completed by O atoms from each of the two water molecules at a distance of 2.556 (5) Å. The Cu—O(1) bond is slightly tilted [5.4 (1)°] relative to the normal to the equatorial plane.

Because of the symmetry the five-membered chelate ring is planar, and, also, the whole macrocycle ligand, except for C(2), is almost planar. The C(2) atom is positionally disordered above and below this plane and therefore the six-membered chelate ring exists in the structure in two conformations.

The O atoms of the nitrate ions have large temperature factors, but no disorder was observed in the nitrate ions. Their point symmetry is 2.

There are no contacts shorter than the sums of van der Waals radii between adjacent molecules.

* Lists of observed and calculated structure factors, anisotropic thermal parameters for non-H atoms and positional parameters for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36397 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

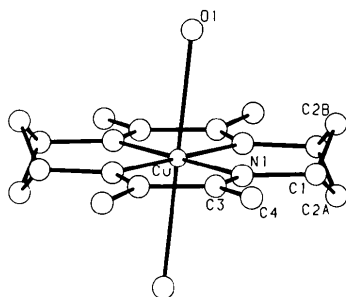


Fig. 1. View of the cation showing the atom numbering.

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Acta Cryst. (1982). **B38**, 929–932

Structure of Carfecillin (Sodium Salt)

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(Received 27 April 1981; accepted 21 September 1981)

Abstract. C₂₃H₂₁N₂NaO₆S, monoclinic, space group *P*2₁, *a* = 8.77 (3), *b* = 6.20 (3), *c* = 21.40 (3) Å, β =

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0567-7408/82/030929-04\$01.00

99.5 (1)°, *V* = 1147.6 Å³, *Z* = 2, *D*_c = 1.378 Mg m⁻³, μ(Cu *K*α) = 1.476 mm⁻¹. The final *R* = 0.095 for 1198 reflexions. The title compound is the α-phenyl ester of carbenicillin. The configuration of the asymmetric carbon to which the phenyl ester group is attached is *R*.

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