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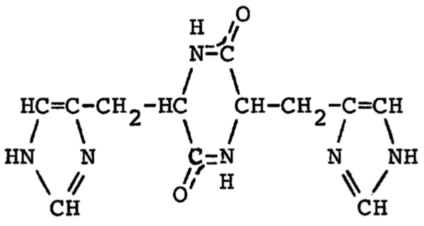
STRUCTURE OF AQUOBISCYCLO(L-HISTIDYL-L-HISTIDYL)DICOPPER(II) PERCHLORATE COMPLEX

Yoshitane KOJIMA, Ken HIROTSU, and Keiji MATSUMOTO
Department of Chemistry, Faculty of Science, Osaka
City University, Sumiyoshi-ku, Osaka 558

The crystal structure of the title complex, $[H_2O\ Cu_2(C_{12}H_{13}N_6O_2)_2](ClO_4)_2 \cdot 3.5H_2O$, was determined from X-ray diffraction data. The unit cell contains two independent complex cations which have similar structures. The complex cation consists of a dimer in which one Cu atom is pseudo tetrahedral and the other one distorted square pyramidal.

There has been considerable interest in the structure of the complexes of amino acid anhydride as a simple model compound for the biomolecule.$^{1)}$ Although some IR studies were reported on such complexes,$^{2)}$ no X-ray work has been done. Therefore, we prepared the title complex and performed single crystal X-ray structure analysis.



$HISH_2$

Cyclo(L-histidyl-L-histidyl)($HISH_2$) was prepared following the procedure of Abderhalden et al.$^{3)}$ A suspension of equimolar amounts of $HISH_2$ and copper(II) perchlorate in hot aqueous solution was stirred until they were completely dissolved. An equimolar amount of lithium hydroxide was then added and the resultant solution was allowed to stand for several days at room temperature. The blue crystals were separated out. They were recrystallized from hot aqueous solution.

Crystal data: $Cu_2(C_{12}H_{13}N_6O_2)_2(H_2O)(ClO_4)_2 \cdot 3.5H_2O$, M. W. = 953.6, monoclinic, a = 22.97(2), b = 15.89(1), c = 10.00(1)Å, β = 100.1(1)°, Z = 4, D_m = 1.74(by flotation), $D_X = 1.76 g \cdot cm^{-3}$, space group $P2_1$.

The intensities of 4563 non-zero reflections($3° \leq 2\theta \leq 50°$) were measured with a Philips PW1100 four-circle diffractometer using graphite-monochramated MoKα radiation (λ = 0.71069Å). The structure was solved by Patterson and Fourier methods and refined by anisotropic block-diagonal least-squares method to an R value of 0.061. However, the isotropic temperature factors were assigned to 15 O atoms of perchlorate ions and water of crystallization throughout the refinement because they were somewhat disordered.

There are two crystallographically independent complex cations in the unit cell, but their structures are similar. The Figure gives a perspective view of the complex cation, the coordination geometry, and the numbering of the atoms. The complex consists of a dimeric $[H_2O\ Cu_2(C_{12}H_{13}N_6O_2)_2]^{2+}$ unit: the two Cu atoms have different coordinations. The Cu(B)[or Cu'(B)] atom has a pseudo tetrahedral coordination by the

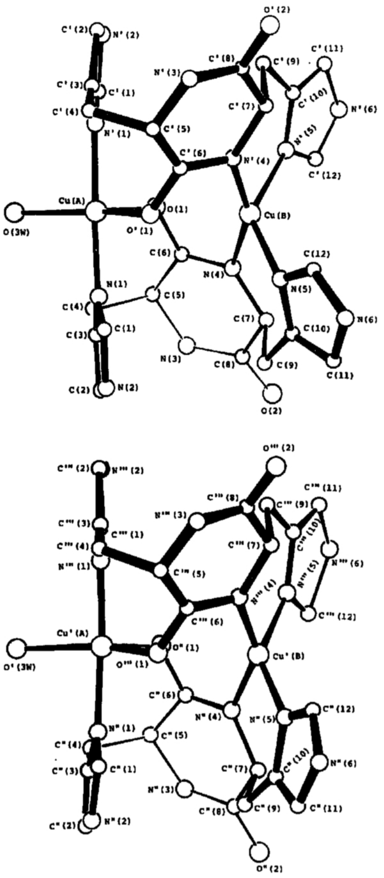


Fig. A perspective view of the complex cations. The atom numbering scheme is the same for the four ligands and primes(') are used in order to identify them.

imidazole N(5)[or N''(5)] atom and the anionic N(4)[or N''(4)] atom of the cyclic dipeptide group of one ligand, and the chemically equivalent N'(5)[or N'''(5)] and N'(4)[or N'''(4)] atoms of the other ligand [Cu-N = 1.97(1)Å on the average]. The dihedral angles between the N(4)-Cu(B)-N(5) and N'(4)-Cu(B)-N'(5) planes and the N''(4)-Cu'(B)-N''(5) and N'''(4)-Cu'(B)-N'''(5) planes are 51.2° and 48.8°, respectively.

The geometry around the Cu(A)[or Cu'(A)] atom is described as distorted square pyramidal with the O(3W)[or O'(3W); W, water molecule], N(1)[or N''(1)], O'(1) [or O'''(1)], and N'(1)[or N'''(1)] atoms forming the base and the O(1)[or O''(1)] atom occupying the apical position. The Cu(A)-O(1)[or Cu'(A)-O''(1)] apical bond length of 2.21(1)Å[or 2.20(1)Å] is about 10% longer than the four bonds in the basal plane [Cu-O = 2.04(1) and Cu-N = 1.97(1)Å on the average]. The two Cu atoms in each dimeric cation are separated by 3.539(3)Å [Cu(A) and Cu(B)] and 3.600(3)Å[Cu'(A) and Cu'(B)].

No appreciable differences were observed in the chemically equivalent bond lengths and angles of four independent ligands. The average bond lengths and angles of the eight imidazole rings agree with the values found for those in bis(L-histidinato)Zn(II).[4] The imidazole group is planar (within 0.02Å). The diketopiperadine ring is nearly planar. The α carbons, C(5), C(7), C'(5), C'(7), C''(5), C''(7), C'''(5), and C'''(7), deviate about 0.2Å from each least-squares plane defined by two peptide bonds.

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