The Crystal Structures of a Dicopper(II) Complex Containing Two *N*₄-Macrocyclic Rings Connected with an Ethylene Chain

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Synopsis. The crystal structure of diaqua {7,7′-ethylenebis[2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17),2,11,13,15-pentaene]}dicopper(II) perchlorate dihydrate was determined by a single-crystal X-ray diffraction method. The complex assumes an extended conformation with the intramolecular Cu···Cu separation 7.081(2) or 6.985(2) Å.

Recently, Murase *et al.* reported the synthesis and characterization of a binuclear copper(II) complex with bis(macrocycle), $Cu_2(dap)(ClO_4)_4$ (dap=7,7′-ethylenebis[2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17),2,11,13,15-pentaene]), as shown in Fig. 1.[1] Molecular models showed many structural possibilities between two extremes of open(extended) conformation and closed(bent) conformation. The ESR spectra in DMF frozen solution suggested that the two copper(II) ions are located in a proximity and the two coordination planes are of a face-to-face or half-opened clam shell structure. The present X-ray study was undertaken to reveal the structure of this complex in crystal.

Experimental

The $Cu_2(dap)(ClO_4)_4$ complex was prepared by the method previously reported.[1] Crystals suitable for an X-ray study were obtained from a dilute aqueous solution after standing one year. The unit-cell parameters and intensities were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo*Kα* radiation (λ=0.71069 Å) at 21±1 °C.

Crystal Data: $Cu_2(C_{32}H_{46}N_8)(ClO_4)_4 \cdot 4H_2O$, FW=1139.72; triclinic; $P\bar{1}$; a=14.894(2), b=15.144(2), c=10.734(1) Å; α=91.04(1), β=108.80(1), γ=87.22(1)°; D_m=1.64, D_c=1.65 g cm^{-3}; Z=2; μ(Mo*Kα*)=12.4 cm^{-1}, crystal dimensions: 0.23×0.28×0.50 mm³.

The intensity data were collected by the 2θ—ω scan technique with a scan rate of 2° min^{-1}. A total of 15954 reflections with $2\theta<62°$ were collected. The intensity data were corrected for the Lorentz and the polarization effects, but not for absorption. Independent 6564 reflections with $|F_o|>3\sigma(|F_o|)$ were considered as "observed" and were used for the structure analysis. The structure was solved by the direct methods and refined by the block-diagonal least-squares method. In the course of refinement, it became apparent that the oxygen atom of the perchlorate ion, O(4A), is subjected to disorder. The oxygen atom was divided between two positions with an occupancy factor 0.5 on the basis of a difference Fourier map. Hydrogen atoms were inserted in their calculated positions and included in the refinement. In the least-squares refinement the weighting scheme, $w=(8.82+|F_o|+0.0086|F_o|^2)^{-1}$ was employed. The final discrepancy factors were $R_1=\sum||F_o|-|F_c||/\sum|F_o|$=0.081 and $R_2=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$=0.123.

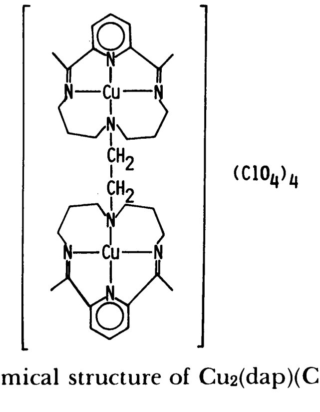

Fig. 1. Chemical structure of $Cu_2(dap)(ClO_4)_4$.

The atomic scattering factors and the anomalous dispersion corrections were taken from the International Tables for X-Ray Crystallography.[2] All the calculations were carried out on the FACOM M-200 computer at the Computer Center of Kyushu University by the use of a local version of the UNICS-III programs.[3] The final positional and thermal parameter with their estimated standard deviations are given in Table 1. The atomic coordinates, the thermal parameters and the F_o-F_c tables have been deposited as a Document No. 8531 at the Office of the Editor.

Results and Discussion

The crystal contains two crystallographically inde-

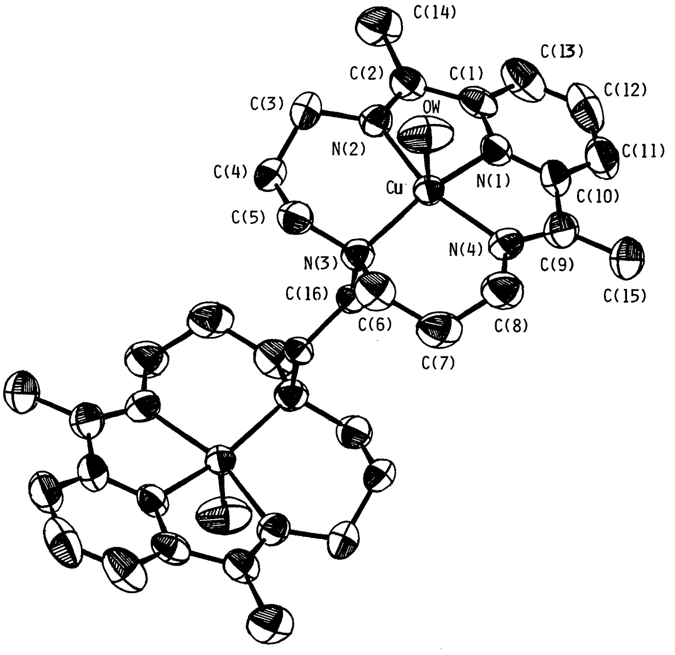

Fig. 2. Molecular structure of $[(Cu_2(dap)(H_2O)_2]^{4+}$ with thermal ellipsoids. Distances (l/Å): Cu-N(1) 1.915(6), 1.904(7); Cu-N(2) 2.013(6), 2.023(10); Cu-N(3) 2.010(7), 1.988(6); Cu-N(4) 2.003(8), 2.001(7); Cu-OW 2.255(8), 2.237(8). Angles (ϕ/°): N(1)-Cu-N(2) 79.7(3), 80.3(4); N(1)-Cu-N(4) 80.2(3), 79.7(3); N(2)-Cu-N(3) 100.4(3), 99.1(3); N(3)-Cu-N(4) 98.1(3), 99.0(3) for molecules A and B, respectively.

pendent binuclear molecules; they are denoted by A and B. Their structures are essentially the same. Both molecules are centrosymmetric about the mid-point of the central ethylene group connecting the two macrocyclic rings. The molecular structure is shown in Fig. 2. The coordination geometry of each copper atom is a distorted square pyramid. Each basal plane is formed by four nitrogen atoms, which are coordinated to Cu with Cu–N bond lengths, 1.904—2.023 Å, of the macrocyclic ring. The fifth coordination site is occupied by a water oxygen atom with Cu–O distance of 2.255(8) or 2.237(8) Å. The basal atoms around each copper atom deviate from the mean plane within ±0.2 Å and Cu(A) and Cu(B) are displaced by 0.23 Å and 0.24 Å, respectively, from the basal-mean planes toward water molecules.

The structures of the macrocyclic moieties are similar to that of the analogous mononuclear copper(II) complex, $Cu(CR)Cl(NO_3)\cdot 2H_2O$ (CR=2,7,12-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,-13,15-pentaene).[4]

Both binuclear molecules assume an extended conformation and the intramolecular Cu···Cu distances are 7.081(2) Å and 6.985(2) Å for molecules A and B, respectively. The shortest intermolecular Cu···Cu distance is 8.059(2) Å (Cu(A)···Cu(B)($x, y-1, z$)). The water molecules (two per complex molecule) are trapped in the space of the crystal lattice. The perchlorate ions are hydrogen bonded with the coordinated or crystal water molecules.

This structure dose not accord with that presumed from the ESR spectra. But, this is not surprising, because in solution, free rotation about the central ethylene group is possible and may give rise to the closed conformation allowing the two copper atoms to array close to each other.

References

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