The Crystal Structure of Dimeric Copper(II) Complex with Chiral Tetradentate N_4 Bis Amide Ligand, 1,6-Bis(*S*)-pyrrolidinyl-1,6-dioxo-2,5-diazahexane(*S,S*-proenH_2)

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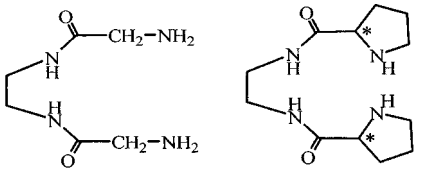
The chemistry of interaction between the biological molecules and metal complexes with amino acids, peptides, and their derivatives is well known.[1] Amides (peptides), which are essential components constituting living organisms, have strong coordinating ability to various transition metal ions such as Cu(II), Ni(II), Pt(II), Ru(III) and Co(III).[2] Generally, ligands containing an amide group coordinate to metal through a terminal amino nitrogen and the oxygen of amide moiety. After amide ligands lose an amide proton in alkaline solution, metal ion complexation have mainly occurred at the amide nitrogen, the most basic site.[3] Therefore, amide ligands can act as a chelating ligand to yield monomeric, dimeric, and polymeric complexes with transition metal ions.[4] In particular, coordinating properties of the metal complexes with tetradentate N_4 mono or bis amide ligands have been widely studied by potentiometric and spectrophotometric measurements, and a crystal structure analysis during the last thirty years.[5] The Cu(II) complexes of bispicolinamide ligands such as *N,N'*-bis(2′-pyridinecarboxamide)-*cis*-1,2-cyclohexane(*cis*-bpch),[6a] *N,N'*-bis(2′-pyridinecarboxamide)-*trans*-1,2-cyclohexane(*trans*-bpch),[6b] *N,N'*-bis(2′-pyridinecarboxamide)-1,2-benzene(bpbH_2)[6c] and *N,N'*-bis(6′-methylpyridine-2′-carboxamido)-1,2-benzene(6-mebpbH_2)[6d] have been shown to exhibit a distorted square-pyramidal structure owing to a planar preferential tendency of an amide ligands containing pyridine ring.

On the other hand, Martell *et al*.[7] suggested possible structures of the dimeric Cu(II) complex formed by *N,N'*-Diglycylethylenediamine (DGEN) on the basis of an electron spin resonance (ESR) study and potentiometric measurements. However, X-ray crystal structure was not yet reported. In this study, we report X-ray crystal structure of the dimeric Cu(II) complex formed by 1,6-bis(*S*)-pyrrolidinyl-1,6-dioxo-2,5-diazahexane(*S,S*-proenH_2) as related ligand with DGEN. The *S,S*-proenH_2 is a linear chiral tetradentate bisamide ligand that has not only two chiral center in *S*-proline moiety but also two pyrrolidinyl ring instead of pyridine. The circular dichroism(CD) spectra of Cu(II) complexes with *S,S*-proenH_2 in aqueous solution was also investigated.



DGEN *S,S*-proenH_2

Experimental Section

Electronic and CD spectra were measured using a HP 8452 spectrophotometer and Jasco J-715 spectropolarimeter, respectively. ^{13}C NMR spectra were recorded with a Bruker (300) in D_2O, using DSS (sodium 2,2-dimethyl-2-silapentane sulfonate) as internal standard. Elemental analysis was carried out by Perkin Elmer 240-C. All material was of reagent grade and was used without further purification.

Preparation of *S,S*-proenH_2 Ligand. Carbobenzoxy-(*S*)-proline was prepared from (*S*)-proline (0.2 mol, 23.0 g) and carbobenzoxy chloride(cbz-Cl) (0.24 mol, 40.9 g) according to the method of Corey *et al*.[8] and then, *N,N'-bis*(carbobenzoxy-(*S*)-prolyl)ethylenediamine was prepared from the Carbobenzoxy-(*S*)-proline (0.24 mol, 60.0 g) and en (0.12 mol, 7.2 g) by using dicyclohexylcarbodiimide (DCC) as coupling agent in dichloromethane. The *S,S*-proenH_2 was obtained from decarbobenzoxylation[9] of *N,N'-bis*(carbobenzoxy-(*S*)-prolyl)ethylenediamine in methanol. Yield; 60%. ^{13}C NMR (D_2O), δ = 28.09, 33.38, 41.19, 49.87 (CH_2 of en backbone and pyrrolidinyl ring), 63.88 (chiral carbon of *S*-proline moiety), 179.80 (C=O).

Preparation of [Cu_2(*S,S*-proen$H$)$_2$](ClO_4)$_2$·2H_2O. *S,S*-proenH_2 (10 mmol, 2.54 g) and $Cu(ClO_4)_2$·6H_2O (8 mmol, 2.96 g) was dissolved in 50 mL water and then the mixture was stirred for 4 h. at room temperature. The solution was diluted to 500 mL and then loaded onto a cation exchange resin (SP Sephadex C25) column. After the column was washed thoroughly with water, the adsorption band was separated with 1.0 M $NaClO_4$. The solution was evaporated to a volume of *ca*. 50 mL and left overnight in a refrigerator; blue crude crystals of [Cu_2(*S,S*-proen$H$)$_2$](ClO_4)$_2$·2H_2O were precipitated, which (1.15 g) was collected by filtration. A crystal, suitable for single-crystal X-ray diffraction, was recrystallised by dissolving in the minimum volume of hot water. ***Calc.*** for $Cu_2C_{24}H_{46}N_8O_{14}Cl_2$**:** C, 33.18; H, 5.34; N, 12.90. ***Found*****:** C, 33.21; H, 4.91; N, 13.26.

X-ray Diffraction Measurements. Single crystal of [Cu_2(*S,S*-proen$H$)$_2$](ClO_4)$_2$·2H_2O was mounted on an Enraf-Nonius CAD-4 diffractometer. Unit cell parameters were determined from automatically centered of 25 reflections ($22.68 \le 2\theta \le 24.70$) and refined by least-squares methods. Intensities were collected with graphite-monochromated Mo Kα radiation, using the ω-2θ scan. For [Cu_2(*S,S*-proen$H$)$_2$]

$(ClO_4)_2 \cdot 2H_2O$, among 3259 reflections measured in the range $4.30 \le 2\theta \le 49.94$, 2640 were assumed to be observed ($F > 4\sigma(F)$). Three standard reflections were measured every 2 h as orientation and intensity control and no significant intensity decay was observed. Lorentz and polarization corrections were made but no absorption correction was made. The crystal structure was solved by direct method[10] for $[Cu_2(S,S\text{-proenH})_2](ClO_4)_2 \cdot 2H_2O$ and refined by full-matrix least-squares methods using the SHELXL93 computer program.[11] For $[Cu_2(S,S\text{-proenH})_2](ClO_4)_2 \cdot 2H_2O$, the positions of all non-hydrogen atoms were refined with anisotropic displacement factors. H3 and H7 were located and refined with isotropic thermal parameters whereas the remaining hydrogen atoms were allowed to ride on their bonded atoms with the isotropic displacement factors fixed with values 1.2 times those of the bonded atoms.

Results and Discussion

The dimeric Cu(II) complex was prepared by the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ and *S,S*-proenH_2 in aqueous solution. Elemental analysis indicated that the blue product was $[Cu_2(S,S\text{-proenH})_2](ClO_4)_2 \cdot 2H_2O$. An ORTEP drawing of the complex is shown in Figure 1. Its crystallographic data, and selected bond lengths and angles are listed in Table 1 and Table 2, respectively. In the $[Cu_2(S,S\text{-proenH})_2]^{2+}$ complex, two Cu(II) ions bridged by an amide nitrogen of deprotonated *S,S*-proenH^- ligand; Cu(1) is bound to the nitrogen of pyrrolidinyl ring and amide nitrogen and Cu(2) is chelated by the amide oxygen and nitrogen of pyrrolidinyl ring. Each copper atom of distorted square planar is surrounded by three nitrogen atoms and one oxygen atom such as one of the possible structure of the dimeric Cu(II) complex with DGEN

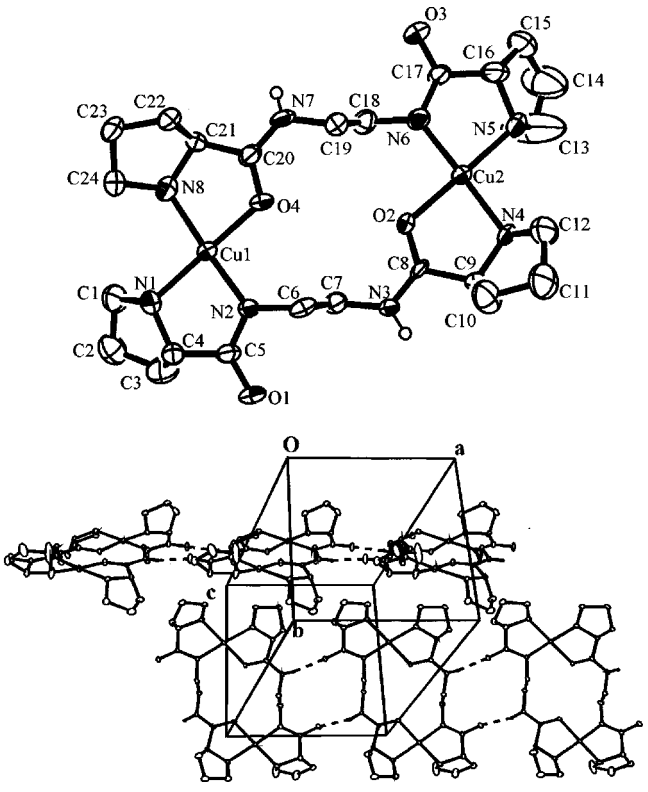


Figure 1. An ORTEP drawing and crystal packing of the $[Cu_2(S,S\text{-proenH})_2](ClO_4)_2 \cdot 2H_2O$ with the labeling of the atoms. Thermal ellipsoids are drawn to include 50% probability. Two of each hydrate and ClO_4^- ion is omitted for clarity.

Table 1. Crystallographic Data for $[Cu_2(S,S\text{-proenH})_2](ClO_4)_2 \cdot 2H_2O$

formula	$Cu_2C_{24}H_{46}N_8Cl_2O_{14}$
fw	868.67
λ, Å	0.71069
crystal system	monoclinic
space group	P_{21} (#4)
Unit cell dimensions	a=9.7820(13) Å
	b=12.8244(8) Å, β=104.033(10) deg
	c= 14.519(2) Å
V	1767.1(3) Å^3
Z	2
D_{calc}	1.633 g/cm^3
crystal size	0.3×0.4×0.3 mm^3
absorption coeff.	1.430 mm^{-1}
F(000)	900
index ranges	-3≤h≤11, -6≤k≤15, -17≤l≤16
2θ range	4.30-49.94 deg
no. of unique data	3259 [R_{int} = 0.0302]
no. of obsd data (F>4σ(F))	2640
R^a	0.0512 (4σ data)
$wR(F^2)^b$	0.1268 (4σ data)
R^a	0.0703(all data)
$wR(F^2)^b$	0.1520(all data)
goodness of fit	1.046
largest diff. peak and hole	0.677 and -0.807 e/Å^3

$^aR = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bwR(F^2) = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2)+(0.0894P)^2+0.0950P]$, $P=(F_o^2+2F_c^2)/3$

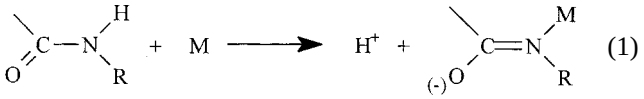
Table 2. Selected Bond Lengths (Å) and Angles(°) for $[Cu_2(S,S\text{-proenH})_2](ClO_4)_2 \cdot 2H_2O$

bond lengths (Å)		bond angles (°)	
Cu1-N2	1.892(7)	N2-Cu1-O4	94.0(3)
Cu1-O4	1.966(6)	N2-Cu1-N1	84.8(3)
Cu1-N1	2.022(7)	O4-Cu1-N1	176.0(3)
Cu1-N8	2.023(8)	N2-Cu1-N8	176.4(3)
Cu2-N6	1.927(7)	O4-Cu1-N8	83.2(3)
Cu2-O2	1.963(6)	N1-Cu1-N8	98.1(3)
Cu2-N5	1.981(9)	N6-Cu2-O2	94.4(3)
Cu2-N4	2.007(7)	N6-Cu2-N5	83.8(4)
O1-C5	1.265(11)	O2-Cu2-N5	175.4(5)
O2-C8	1.256(9)	N6-Cu2-N4	175.5(3)
O3-C17	1.264(11)	O2-Cu2-N4	84.7(3)
O4-C20	1.273(10)	N5-Cu2-N4	96.7(3)
N2-C5	1.323(11)	C5-N2-C6	116.3(7)
N3-C8	1.292(11)	C5-N2-Cu1	116.7(6)
N6-C17	1.285(12)	C6-N2-Cu1	126.7(5)
N7-C20	1.293(12)	C17-N6-C18	118.3(8)
		C17-N6-Cu2	114.6(7)
		C18-N6-Cu2	125.9(6)

was suggested by potentiometric measurements and ESR study. The least-square plane through the four donor atoms of Cu(1)[N(1), N(2), N(8), O(4)] forms a dihedral angle of 10.09° with the Cu(2)[N(4), N(5), N(6), O(2)] plane.

Bond distances between each copper atom and donor (N, O) atoms are Cu(1)-N(1); 2.022(7) Å, Cu(1)-N(2); 1.892(7) Å, Cu(1)-N(8); 2.023(8) Å, Cu(1)-O(4); 1.966(6) Å, Cu(2)-N(4); 2.007(7) Å, Cu(2)-N(5); 1.981(9) Å, Cu(2)-N(6); 1.927(7) Å, Cu(2)-O(2); 1.963(6) Å. The shortening of the Cu(1)-N(2) and Cu(2)-N(6) bond lengths agree with the stronger basicity of the deprotonated amide nitrogen atoms.[5,12] The N(1)-Cu(1)-O(4), N(2)-Cu(1)-N(8), N(5)-Cu(2)-O(2), and N(4)-Cu(2)-N(6) angles are 176.0(3)° and 176.4(3)°, respectively. Distortion of the complex is also evident from the values found for the N(2)-Cu(1)-O(4), N(8)-Cu(1)-O(4), N(4)-Cu(2)-O(2), and N(6)-Cu(2)-O(2) angles [94.0(3)°, 83.2(3)°, 84.7(3)° and 94.4(3)°, respectively].

The bond lengths within the amide portion of the ligands in $[Cu_2(S,S\text{-proenH})_2]^{2+}$ are unusual. The bond lengths of four amide portion are N(2)-C(5); 1.323(11), O(1)-C(5); 1.265(11), N(6)-C(17); 1.285(12), O(3)-C(17); 1.264(11), N(7)-C(20); 1.293(12), O(4)-C(20); 1.273(10), N(3)-C(8); 1.292(11), O(2)-C(8); 1.256(9) Å, respectively. It should be noted that the C-N distance is shorter and C=O is longer compared to those found from free amide (C-N; 1.330 Å, C=O; 1.240 Å). This result agrees with many investigations which reveal that complexation of the deprotonated amide nitrogen shortens the peptide C-N and lengthens the C-O bond.[3] These observations have been attributed to that the substitution of an amide proton by a metal ion results in the bond length change to the direction of double bond character in the C-N and single bond character in the C-O (eq 1).[3] However, the shortening of the bond lengths in $[Cu_2(S,S\text{-proenH})_2]^{2+}$ crystal for two C-N bonds were different. The decrease in the bond lengths of 0.007 Å and 0.045 Å for the N(2)-C(5) and N(6)-C(17) were found, indicating that the



(1)

character of N(2)-C(5) bond is close to that of the single bond. It can also be seen that the structure of the $[Cu_2(S,S\text{-proenH})_2]^{2+}$ allows an intermolecular one dimensional hydrogen bonding [C(5)=O(1) ⋯ H-N(7) (2.737 Å) and C(17)=O(3) ⋯ H-N(3) (2.728 Å)] interaction between the amide oxygen and the hydrogen on the unbounded nitrogen to Cu(II) ion.

The absorption and CD spectra of $[Cu_2(S,S\text{-proenH})_2]^{2+}$ in aqueous solutions are shown in Figure 2. Before addition of base, the complex exhibited an absorption band at 572 nm (ε = 115 $dm^3mol^{-1}cm^{-1}$) and a weak CD band at 516 nm (Δ_ε = -0.26) (curve 1). A weakness of CD spectrum in d-d region indicates that the vicinal effect was derived from the stereospecifity of the *S,S*-proenH_2 ligand. As the concentration of base is increased, the band maximum shifts to shorter wavelength and increases in intensity of the absorption and CD spectrum. The color gradually changes from blue to red-violet. In strong base, the absorption spectral data is similar to those of Cu(II) complex with the deprotonated DGEN ligand.[7,13] It is clear that the substitution of amide oxygen atoms by deprotonated amide nitrogen atoms moves the absorption maximum to shorter wavelengths. By using ion exchange chromatography, it was identified that the Cu(II) complex with deprotonated *S,S*-proenH_2 is neutral. Therefore, complex I is considered to be the most probable structure for [Cu(*S,S*-proen)], which has two deprotonated amide

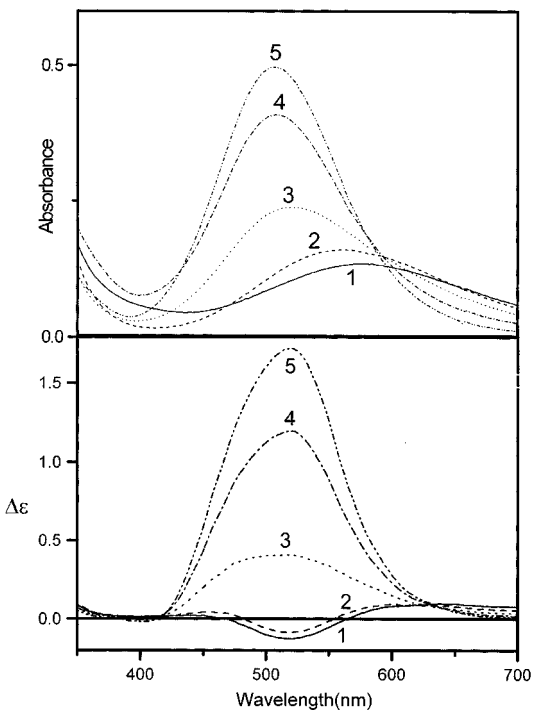
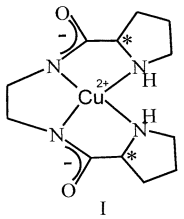


Figure 2. Absorption(top) and CD spectra(bottom) of $[Cu_2(S,S\text{-proenH})_2]^{2+}$ (1.2×10^{-3} mol·dm^{-3}) at various OH^- molar ratio. The molar ratios are (1) aqueous solution, (2) 1 : 1, (3) 1 : 2, (4) 1 : 3 and (5) 1 : 4, respectively.



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groups. In addition to the red-shift and increases in the absorption intensity, the CD spectra gradually changes from negative band to positive as the basicity of the solution increases (Figure 2). These observations can be explained by increases in the number of the nitrogen atom in complex I which has an *S* orientation (from three nitrogens in $[Cu_2(S,S\text{-proenH})_2]^{2+}$ to four nitrogens in basic solution). It suggests that the vicinal effect of complex I becomes larger compared to that of $[Cu_2(S,S\text{-proenH})_2]^{2+}$.

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