April, 1989] © *1989 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* **62**, *1057—1060 (1989)* 1057

Structure and Properties of Chloro(*N,N*-diethylglycinato)copper(II)

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(Received August 18, 1988)

An X-ray diffraction study of the title complex has been carried out, along with spectroscopic measurements and thermal analyses. The crystal is orthorhombic, space group $P2_12_12_1$, Z=4, a=9.978(2), b=12.624(3), c=7.129(1) Å, U=898.0(3) Å^3. Block-diagonal least-squares refinements have led to the final R value of 0.032. The structure consists of a one-dimensional polymer chain bridged by a carboxylato group of an *N,N*-diethylglycinato ligand. One oxygen atom in the carboxylato group is coordinated to two copper atoms, and the other is coordinated to one of these two copper atoms. This is the same bridging form as in aquachloro(4-hydroxy-L-prolinato)copper(II). The copper atom reveals a distorted five-coordination: the copper atom is surrounded by three carboxylato oxygen atoms, one nitrogen atom, and one chlorine atom. The infrared spectra of the title complex and of aquachloro(4-hydroxy-L-prolinato)copper(II) both show the characteristic pattern at the peaks assigned to the vibrations of the carboxylato group. The peaks can be an indicator of the bridging form.

The amino acids with a pyrrolidine ring, 4-hydroxy-L-proline (Hhpro) and L-proline (Hpro) (their anion ligands abbreviate to hpro and pro, respectively), have slightly different structural features from other α-amino acids. Some interesting properties of their metal complexes are reported. To give an example, the solution of Cu$^{\mathrm{II}}$ complex with an L-amino acid, in general, exhibits a negative circular dichroism (CD) band at near 600 nm, and that of a D-amino acid has a positive one. But those of L-pro and L-hpro both exhibit a positive CD band at near 600 nm.[1,2] Another example is as follows. The four possible isomers, *Δ-fac, Λ-fac, Δ-mer,* and *Λ-mer,* are all obtained in the tris amino acid complexes of Co$^{\mathrm{III}}$ with L-alanine, L-valine and L-leucine. However, in the L-pro complex only three isomers can be isolated, and *Λ*-mer isomer can not be obtained.[3] These facts are based on the characteristic structures of Hhpro and Hpro. Therefore studies about syntheses, properties, and structures of some metal complexes with Hhpro and Hpro have been carried out in our group.[4–8]

A complex was prepared from $CuCl_2$ and Hhpro ([CuCl(hpro)(H_2O)]),[5] and its crystal structure was discussed.[8] In this work, a complex was prepared from $CuCl_2$ and *N,N*-diethylglycine (Hdeg; the anion ligand abbreviates to deg); its structure was determined and its spectroscopic data and thermal behavior were investigated, in order to compare the results with those of [CuCl(hpro)(H_2O)]. The aim of this study is to confirm whether the interesting bridging form existing in [CuCl(hpro)(H_2O)] is characteristic for amino acid ligands having a pyrrolidine ring (e.g. hpro), or whether it can also be formed by other *N*-substituted amino acids like Hdeg.

Experimental

Preparation of Chloro(*N,N*-diethylglycinato)copper(II). To an ethanol solution (100 cm^3) of 1.53 g (0.01 mol) of sodium *N,N*-diethylglycinate, 1.34 g (0.01 mol) of dichlorocopper(II) was added. As $CuCl_2$ was dissolved, sodium chloride was precipitated. As soon as $CuCl_2$ was dissolved completely, centrifugation of the solution was carried out until NaCl was removed. Dark blue crystals were obtained from the solution by keeping it at room temperature for several days. The crystals were recrystallized from methanol. Found: C, 31.53; N, 5.97; H, 5.22%. Calcd for $CuCl(C_6H_{12}NO_2)$: C, 31.44; N, 5.97; H, 5.28%.

X-Ray Measurements and Structure Determination. The crystal data are as follows. The crystal is orthorhombic, space group $P2_12_12_1$, Z=4, a=9.978(2), b=12.624(3), c=7.129 (1) Å, U=898.0(3) Å^3, D_m=1.67 g cm^{-3}, D_m=1.70 g cm^{-3}, μ(Mo $K\alpha$)=27.7 cm^{-1}. The size of the crystal used for the measurement was 0.15×0.16×0.14 mm^3. The reflection intensities were collected by the ω-2θ scan technique (measured range 3—60° (2θ); scan width 1.30° (θ); scan speed 4° min^{-1} (θ)) on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The measured reflections were 1598, of which 1255 ($|F_o|>3\sigma(|F_o|)$) were used for the structure refinement. The intensities were corrected for Lorentz and polarization factors, but not for absorption and extinction.

The structure was solved by a heavy-atom method. The positions of the copper and chlorine atoms were deduced on a three-dimensional Patterson map; other atoms were located by successive Fourier syntheses. Their positional, isotropic and then anisotropic thermal parameters (except for hydrogen atoms) were refined by the block-diagonal least-squares method. Isotropic temperature factors for hydrogen atoms of $-CH_3$ in $-CH_2CH_3$ were assumed to be 4.0 Å^2. All the calculations were carried out on a HITAC M-680H computer at the Computer Center of The University of Tokyo, using the local version of the UNICS program.[9] The atomic scattering factors were taken from Ref. 10. The final R value was 0.032 and R_w was 0.038.[11]

The Other Measurements. The simultaneous thermogravimetric (TG) and differential thermal (DTA) analyses were carried out with a Rigaku Denki "Thermoflex" M-8075 using a sample weighing about 7.8 mg; the heating rate was 5 °C min^{-1} in air; α-alumina was used as the reference.

The infrared spectra of the sample were obtained by means of a Hitachi 295 type infrared spectrophotometer, using Nujol mull and KBr disks.

Visible and ultraviolet spectra were measured on a Hitachi U-3200 Spectrophotometer.

The magnetic moment was obtained for the solid sample by the Gouy method at room temperature, using Hg[Co-$(SCN)_4$] as a calibration standard.

Results and Discussion

The final atomic parameters are listed in Table 1, the interatomic distances in Table 2, and the bond angles in Table 3.[12] The perspective drawing of the complex and the numbering scheme of the atoms are shown in Fig. 1.

Table 1. Final Positional Parameters ($\times 10^5$ for Cu and $\times 10^4$ for the Other Non-Hydrogen Atoms) and Equivalent Isotropic Temperature Factors ($B_{eq}/Å^2$), with the Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq} a)
Cu	19430(5)	38573(4)	28463(7)	2.02
Cl	1828(1)	2325(1)	1390(2)	3.46
O(1)	2239(3)	4935(3)	4756(4)	2.73
O(2)	1230(3)	5844(2)	6984(4)	2.63
N	1(3)	3908(3)	3755(5)	2.11
C(1)	1209(4)	5244(3)	5605(6)	2.14
C(2)	−136(4)	4882(4)	4855(6)	2.60
C(3)	−978(4)	3874(4)	2170(7)	2.91
C(4)	−739(5)	4713(4)	710(8)	3.94
C(5)	−244(5)	2968(4)	4972(7)	3.20
C(6)	748(5)	2837(4)	6528(8)	4.08

a) The equivalent isotropic temperature factors were computed using the following expression: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2)$.

Table 2. Interatomic Distances (l/Å) with the Estimated Standard Deviations in Parentheses

Cu-Cl	2.199(1)	C(1)-C(2)	1.515(6)
Cu-O(1)	1.947(4)	C(3)-C(4)	1.504(8)
Cu-O(1)^{I}	2.801(4)	C(5)-C(6)	1.496(8)
Cu-O(2)^{I}	1.961(3)	N-C(2)	1.465(6)
Cu-N	2.044(3)	N-C(3)	1.494(6)
C(1)-O(1)	1.254(5)	N-C(5)	1.490(6)
C(1)-O(2)	1.241(6)		

Key to symmetry operation: I. 0.5−x, 1.0−y, −0.5+z.

Table 3. Bond Angles (ϕ/°) with the Estimated Standard Deviations in Parentheses

Cl-Cu-O(1)	162.4(1)	O(1)-C(1)-O(2)	124.0(4)
Cl-Cu-O(1)^{I}	97.05(8)	O(1)-C(1)-C(2)	117.5(4)
Cl-Cu-O(2)^{I}	94.00(9)	O(2)-C(1)-C(2)	118.6(4)
Cl-Cu-N	97.3(1)	C(1)-C(2)-N	111.1(3)
O(1)-Cu-O(1)^{I}	97.2(1)	C(2)-N-Cu	106.5(3)
O(1)-Cu-O(2)^{I}	86.8(1)	C(3)-N-Cu	112.3(3)
O(1)-Cu-N	84.3(1)	C(5)-N-Cu	108.4(3)
N-Cu-O(1)^{I}	120.6(1)	C(4)-C(3)-N	113.6(4)
N-Cu-O(2)^{I}	167.1(1)	C(6)-C(5)-N	114.2(4)
O(1)^{I}-Cu-O(2)^{I}	51.5(1)	Cu-O(1)-Cu^{II}	167.0(2)
Cu-O(1)-C(1)	115.5(3)		

Key to symmetry operations: I. 0.5−x, 1.0−y, −0.5+z; II. 0.5−x, 1.0−y, 0.5+z.

The structure of the complex consists of a one-dimensional polymer chain bridged by only one carboxylato group of deg. One carboxylato oxygen atom of the deg is coordinated to two copper atoms to form an oxygen bridge, and the other is coordinated to one of these two copper atoms. Therefore the carboxylato group forms a four-membered chelate ring. It is the same bridging form as that of the hpro in [CuCl-(hpro)(H_2O)] forms.[8]

The copper atom is surrounded by five atoms: three carboxylato oxygen atoms, one nitrogen atom, and one chlorine atom. The coordination type can not be assigned to a typical five-coordination polyhedron, a trigonal-bipyramid or a square-pyramid. It may be an extremely distorted tetrahedron, if the whole of the carboxylato group (forming the four-membered chelate ring) is regarded as an unidentate ligand.

The bond length of Cu-Cl, 2.199(1) Å, is a common value as a bond of Cu-Cl(terminal), which is different from Cu-Cl in [CuCl(hpro)(H_2O)]. The other bond lengths are common values except for Cu-O(1)^{I}, 2.801(4) Å. The rather long distance of Cu-O(1)^{I}, however, is not very surprising as discussed previously.[8]

In this complex, one of the two types of the chelate rings, the four-membered ring formed by Cu, O(1)^{I}, C(1)^{I}, and O(2)^{I}, is a fairly flat plane: the deviations from the least-squares plane are: Cu^{II} (0.007 Å), O(1)^{I}

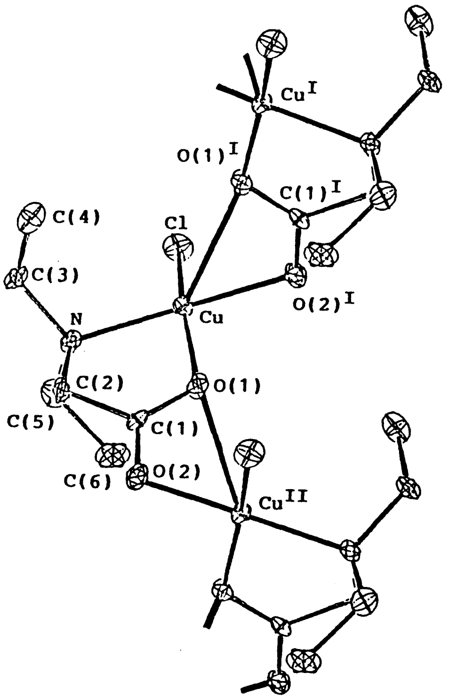

Fig. 1. The perspective drawing of [CoCl(deg)] and the numbering scheme of the atoms. Thermal ellipsoids are drawn at 30% probability level.
Key to symmetry operations: I. 0.5−x, 1.0−y, −0.5+z; II. 0.5−x, 1.0−y, 0.5+z.

(−0.013 Å), C(1)^{I} (0.028 Å), O(1)^{I} (−0.022 Å). The other, five-membered ring formed by Cu, O(1), C(1), C(2), and N, is slightly distorted; C(2) and N deviate from the plane formed by the five atoms in opposite directions. The distortion is not found in [CuCl(hpro)(H_2O)].[8] The difference of the five-membered chelate ring between [CuCl(hpro)(H_2O)] and [CuCl(deg)] is likely to be based on the difference of the positions of N and C(2) in each amino acid ligand. In hpro, N and C(2) belong to a pyrrolidine ring. On the other hand, N and C(2) in deg can be shifted more easily than those of hpro. The N and C(2) in deg, may deviate from the above mean plane in order to avoid the steric hindrance by ethyl groups connected to the nitrogen atom. The ethyl groups may also play a role of preventing coordination of a solvent molecule.

The projection of the structure along the c axis is given in Fig. 2. The polymer chains arrange in parallel with the c axis. There is no hydrogen bond, since the complex does not have any hydrogen donors, different from [CuCl(hpro)(H_2O)]: in [CuCl(hpro)(H_2O)], there are two types of hydrogen bonds, inter- and intrachain hydrogen bonds, between the water oxygen and chlorine atoms.

The structure of [CuCl(deg)] has the same bridging form as that of [CuCl(hpro)(H_2O)], though the coordination environment of the copper atom and the formation of the hydrogen bonds are different, as mentioned above. The bond lengths of Cu-N in [CuCl(deg)] and in [CuCl(hpro)(H_2O)] are 2.044(3) Å and 2.024(5) Å, respectively. Both of them are slightly longer than that common for Cu-N. It is suggested that the interesting bridge is formed when the nitrogen atom in an amino acid ligand makes the longer bond to the metal, because of steric hyndrance due to *N*-substituted groups. The coordination number of a metal or hydrogen bonding is not a principal cause of the formation of the bridging.

The magnetic moment of [CuCl(deg)] is 1.86 B.M. This is close to the value of [CuCl(hpro)(H_2O)], 1.89 B.M. The value is a little lower than those of the common octahedral copper(II) complexes, but the apparent Cu-Cu interaction is not considered. The result is supported by Cu-Cu atomic distances: 4.72 Å in [CuCl(deg)], and 4.46 Å in [CuCl(hpro)(H_2O)].

Infrared spectra of [CuCl(deg)] and [CuCl(hpro)(H_2O)] are shown in Fig. 3. There is a characteristic large split peak around 1600 cm^{-1} in both complexes, and near 1400 cm^{-1} a slightly split peak (in [CuCl(hpro)(H_2O)]) or a peak with a shoulder (in [CuCl(deg)]). These peaks are assigned to COO^- antisymmetric and symmetric stretching vibrations, respectively. The shapes of the peaks reflect the coordination form of the carboxylato group. Therefore the peaks can be an indicator of this coordination type, without reference to whether the amino acids have a pyrrolidine ring or not. The bis-chelate complex, [Cu(deg)$_2$(H_2O)$_2$], has the peak at 1617 cm^{-1} (COO^- antisymmetric). This agrees well with the higher frequency peak of the COO^- antisymmetric split peaks of [CuCl(deg)]. Moreover, the COO^- symmetric vibration of [Cu(deg)$_2$(H_2O)$_2$] has the same frequency (1381 cm^{-1}) as that of [CuCl(deg)].[13] These similarities are also found for [Cu(hpro)$_2$] and [CuCl(hpro)(H_2O)]: [Cu(hpro)$_2$] has the peaks at 1592 cm^{-1} and 1407 cm^{-1} and they agree with the higher frequency peaks between the respective corresponding split peaks of [CuCl(hpro)(H_2O)]. Therefore, in the interesting carboxylato bridging, the COO^- anti- and symmetric vibrations which are also shown in the normal amino acid chelate are kept and the new vibrations are added.

The electronic spectrum of the methanol solution

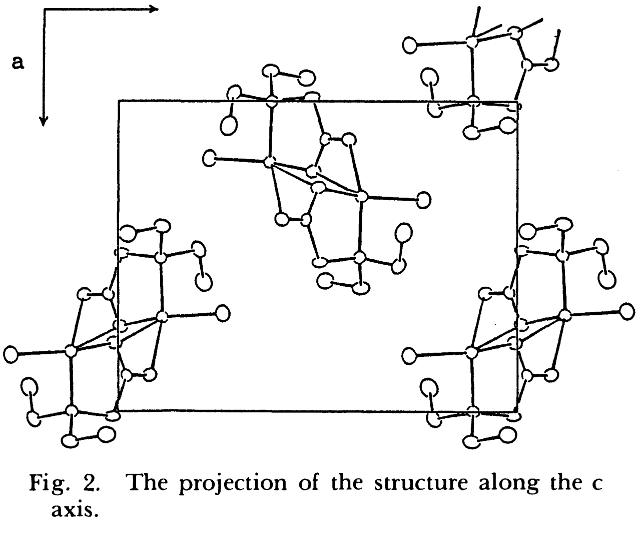

Fig. 2. The projection of the structure along the c axis.

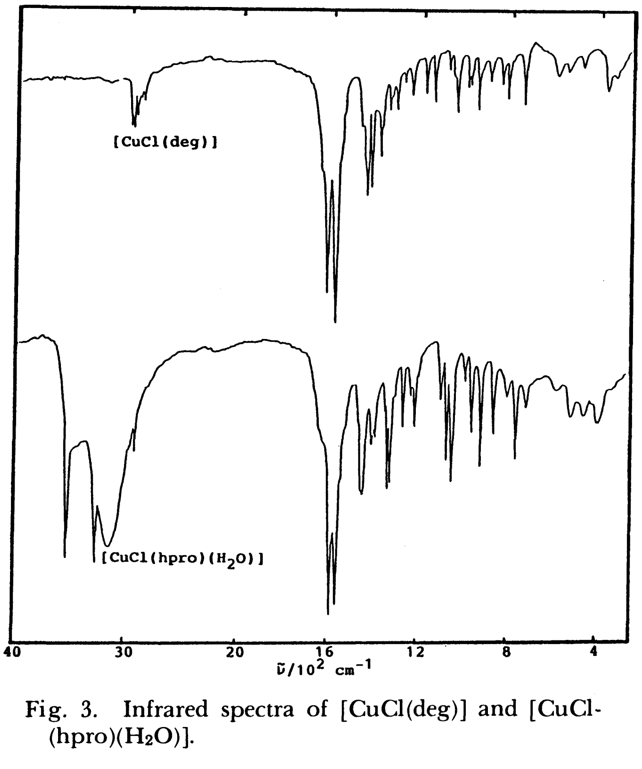

Fig. 3. Infrared spectra of [CuCl(deg)] and [CuCl(hpro)(H_2O)].

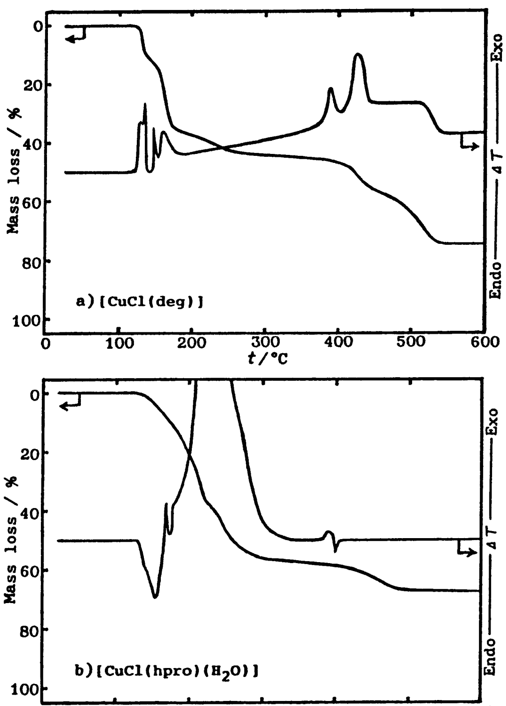

Fig. 4. The thermogravimetric and differential thermal analysis curves of [CoCl(deg)] and [CuCl(hpro)(H_2O)].

(756 nm (log{ε/mol^{-1} dm^3 cm^{-1}}=1.87), 266 nm (3.74)) is different from the powder diffuse reflection spectrum (609 nm (shoulder ca. 750 nm))[14] in [CuCl(deg)], which is similar to that observed in [CuCl(hpro)(H_2O)]. The deg complex is also likely to change into a six-coordinated Cu^{II} complex cation in the solution. The peak in the methanol solution, 756 nm, is closer to that in the powder diffuse reflection spectrum in [CuCl(hpro)(H_2O)] rather than to the corresponding peak of the electronic spectrum in [CuCl(hpro)(H_2O)]. The fact may indicate that the coordination polyhedron is not a typical shape, i.e. an elongate-octahedral symmetry due to coordination of solvent molecules along the axis normal to the molecular plane, but a widely different shape from an octahedron. The effect of the difference in solvent could not be checked, because the deg complex is hydrolyzed in the aqueous solution.

The results of the simultaneous TG and DTA of [CuCl(deg)] and of [CuCl(hpro)(H_2O)] are shown in Fig. 4. In the former, the decomposition began at about 130 °C, with some exothermic peaks on the DTA, and beyond 540 °C, black ash was obtained. In [CuCl(hpro)(H_2O)], after the elimination of water molecules (endothermic reaction), the decomposition began immediately and the black ash was obtained at the final stage. Both complexes change into CuO in the last place, but the process of the decomposition of each amino acid is different. It appears that the deg in [CuCl(deg)] decomposes through some steps, but in [CuCl(hpro)(H_2O)] the hpro decomposes at once. The difference may be based on the difference of the structure of the amino acid: the deg has two flexible ethyl groups, while the hpro has a rigid pyrrolidine ring.

The authors wish to express their thanks to Professor Akira Ouchi of The University of Tokyo and Associate Professor Mamoru Shimoi of Tohoku University for X-ray diffractometer measurements. They gratefully acknowledge the assistance on the structure-analysis calculations given by Mr. Kimitake Aoyagi of Sophia University. Thanks are due to Associate Professor Yoshio Masuda of Niigata University for TG and DTA measurements. They would also like to thank Dr. F. S. Howell of Sophia University for correcting this manuscript.

References

1) T. Yasui, J. Hidaka, and Y. Shimura, *J. Am. Chem. Soc.*, **87**, 2762 (1965).

2) T. Yasui, *Bull. Chem. Soc. Jpn.*, **38**, 1746 (1965).

3) R. G. Denning and T. S. Piper, *Inorg. Chem.*, **5**, 1056 (1966).

4) Y. Yukawa, Y. Inomata, T. Takeuchi, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **55**, 3135 (1982).

5) Y. Inomata, T. Takeuchi, and T. Moriwaki, *Inorg. Chim. Acta*, **68**, 187 (1983).

6) Y. Yukawa, Y. Inomata, and T. Takeuchi, *Bull. Chem. Soc. Jpn.*, **56**, 2125 (1983).

7) Y. Yukawa, N. Yasukawa, Y. Inomata, and T. Takeuchi, *Bull. Chem. Soc. Jpn.*, **58**, 1591 (1985).

8) S. Itoh, Y. Yukawa, Y. Inomata, and T. Takeuchi, *Bull. Chem. Soc. Jpn.*, **60**, 899 (1987).

9) "Universal Crystallographic Computation Program System (UNICS)," ed by T. Sakurai, Crystallographic Society of Japan, Tokyo (1967).

10) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.

11) $R=\sum||F_o|-|F_c||/\sum|F_o|$; $R_w=[\sum\omega(|F_o|-|F_c|)^2/\sum\omega|F_o|^2]^{1/2}$, where $\omega=1/[\{\sigma(|F_o|)\}^2+(F_{weight}\times|F_o|)^2]$, $F_{weight}=0.025$.

12) The final thermal parameters, the final positional parameters including hydrogen atoms, the final F_o-F_c table, some bond lengths for hydrogen atoms, and several least-squares planes are deposited as Document No. 8863 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

13) Y. Inomata, Y. Kato, Y. Yukawa, and T. Takeuchi, the 50th National Meeting of the Chemical Society of Japan, Tokyo, April 1985, Abstr. 1K03.

14) The reflection spectrum data reported at the 52th National Meeting of the Chemical Society of Japan, Kyoto, April 1986, Abstr. 4K27, was 626 nm, as measured by a Hitachi 624 digital spectrophotometer. In this work, the data were remeasured.