

# Structures and Properties of (L-Prolinato)copper(II) Complexes prepared from Different Solvents\*

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Two amino acid complexes, aquachloro(L-prolinato)copper(II) **1** and chloro(methanol)(L-prolinato)-copper(II) **2**, were prepared from aqueous and methanol solutions. Complex **1** crystallized in the monoclinic system, space group  $P2_1$ , with  $a = 9.509(2)$ ,  $b = 5.206(2)$ ,  $c = 8.189(2)$  Å,  $\beta = 109.40(2)^\circ$ ,  $Z = 2$ ;  $R = 0.030$  ( $R' = 0.043$ ). The structure consists of a one-dimensional polymer chain bridged by a carboxylate group of a L-prolinato (pro) ligand: two carboxylate oxygen atoms in the pro are co-ordinated to different copper atoms, thus forming a carboxylate *syn-anti* bridge. Each copper atom is surrounded by five atoms, thus forming a square pyramid. Complex **2** also crystallized in the monoclinic system, space group  $P2_1$ , with  $a = 9.038(3)$ ,  $b = 5.980(1)$ ,  $c = 8.567(2)$  Å,  $\beta = 101.62(2)^\circ$ ,  $Z = 2$ ;  $R = 0.039$  ( $R' = 0.051$ ). Although the structure also consists of a one-dimensional polymer chain bridged by a carboxylate group of a pro ligand, the bridging form is different from that in **1**: one carboxylate oxygen atom is co-ordinated to two copper atoms and the other is co-ordinated to one of these copper atoms, thus forming a four-membered chelate ring. Each copper atom in the complex is surrounded by six atoms, thus forming an extremely distorted octahedron. The infrared and electronic spectra, magnetic moments, and simultaneous thermogravimetric and differential thermal analyses of complexes **1** and **2** are described.

For amino acid complexes to be helpful as part of models for metal-binding sites on metalloproteins, or as subjects for stereochemistry, it is important to investigate many complexes obtained under different conditions, e.g. in various solvents or at different pH values. Unfortunately, most typical amino acids which form proteins dissolve in either water or alcohols. This places limits on the control of the preparation of the amino acid complexes. As an exception, L-proline (Hpro; the anion ligand is abbreviated to pro) easily dissolves in both water and alcohols. Therefore investigations under different conditions can be carried out using Hpro complexes.

The preparation of Hpro complexes under an unusual condition (slightly low pH) has been reported:<sup>1</sup>  $[\text{CdCl}_2(\text{Hpro})_2] \cdot \text{H}_2\text{O}$  consists of a one-dimensional polymer bridged by chlorine atoms and carboxyl oxygen atoms of Hpro. The Hpro is a zwitterion, and is co-ordinated to cadmium only by carboxyl oxygen atoms.<sup>1a</sup> In contrast,  $[\text{ZnCl}_2(\text{Hpro})_2]$  is a monomer and Hpro is co-ordinated as a monodentate ligand. The zinc atom is in a tetrahedral geometry, co-ordinated to two chlorine atoms and two carboxyl oxygen atoms from the two Hpro ligands.<sup>1b</sup>

In this paper the preparation of copper(II) complexes with L-proline in different solvents (water and methanol) will be described. From an aqueous solution  $[\text{CuCl}(\text{pro})(\text{H}_2\text{O})]$  was obtained, and  $[\text{CuCl}(\text{pro})(\text{CH}_3\text{OH})]$  from a methanol solution. The crystal structures of these complexes as well as their characteristics were determined.

## Experimental

**Preparations.**— $[\text{CuCl}(\text{pro})(\text{H}_2\text{O})]$  **1**. To an aqueous solution (40 cm<sup>3</sup>) of copper(II) chloride (1.34 g, 0.01 mol) was added L-proline (1.15 g, 0.01 mol). Blue crystals were obtained from the solution by keeping it in a desiccator containing acetone for 1 week (Found: C, 25.90; H, 4.30; N, 5.85. Calc. for  $\text{C}_5\text{H}_{10}\text{ClCuNO}_3$ : C, 26.00; H, 4.35; N, 6.0%).

$[\text{CuCl}(\text{pro})(\text{CH}_3\text{OH})]$  **2**. The above method was employed,

**Table 1** Crystal data for complexes **1** and **2**

Complex	<b>1</b>	<b>2</b>
Formula	$\text{C}_5\text{H}_{10}\text{ClCuNO}_3$	$\text{C}_6\text{H}_{12}\text{ClCuNO}_3$
$M$	231.14	245.16
$a/\text{Å}$	9.509(2)	9.038(3)
$b/\text{Å}$	5.206(2)	5.980(1)
$c/\text{Å}$	8.189(2)	8.567(2)
$\beta/^\circ$	109.40(2)	101.62(2)
$U/\text{Å}^3$	382.4(2)	453.5(2)
$D_m/\text{g cm}^{-3}$	1.96	1.78
$D_c/\text{g cm}^{-3}$	2.01	1.80
$F(000)$	234	250
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	30.8	27.6
$2\theta$ range/ $^\circ$	< 80	< 70
$N(I \geq 3.0\sigma(I))$	2196	1582
$R$	0.030	0.039
$R'$	0.043	0.051
Weighting scheme, $w$	$1/[\sigma^2(F) + 0.040F^2]$	$1/[\sigma^2(F) + 0.045F^2]$

Details in common: monoclinic, space group  $P2_1$ ,  $Z = 2$ .

but using methanol instead of water. Pale blue crystals were obtained by keeping the methanol solution in a desiccator containing diethyl ether for several days (Found: C, 28.50; H, 4.75; N, 5.95. Calc. for  $\text{C}_6\text{H}_{12}\text{ClCuNO}_3$ : C, 29.40; H, 4.95; N, 5.70%).

An almost quantitative yield of each complex was obtained.

**X-Ray Measurements and Structure Determination.**—X-Ray diffraction measurements were performed on a Rigaku AFC-6A automated four-circle diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  0.7107 Å). Intensities were collected by the  $\omega$ - $2\theta$  scan technique, and corrected for Lorentz and polarization factors. The crystal data are given in Table 1.

The structures of complexes **1** and **2** were solved by the heavy-atom method. The positions of the heavy atoms (Cu and Cl) were deduced from a three-dimensional Patterson map; other atoms were located by successive Fourier syntheses. The hydrogen atoms were detected by Fourier difference syntheses

\* Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx-xxv.

**Table 2** Positional ( $\times 10^4$ ) parameters and their estimated standard deviations (e.s.d.s) for complexes **1** and **2**

Atom	<i>x</i>	<i>y</i>	<i>z</i>
<b>Complex 1</b>			
Cu	2488.3(3)	2500	1435.2(3)
Cl	4512.4(7)	4848(2)	2909.6(8)
O(w)	2864(3)	6(5)	3371(3)
O(1)	1120(2)	-16(4)	-18(2)
O(2)	-870(2)	-193(6)	-2393(2)
N	2013(2)	4565(4)	-731(2)
C(1)	296(3)	852(5)	-1491(3)
C(2)	814(2)	3251(5)	-2147(3)
C(3)	1521(3)	2667(8)	-3540(3)
C(4)	2603(3)	4866(7)	-3353(3)
C(5)	3256(3)	5171(9)	-1404(4)
<b>Complex 2</b>			
Cu	852.9(5)	2500	1997.8(5)
Cl	1990(2)	4578(3)	4129(2)
O(1)	-2226(4)	-1441(6)	-594(4)
O(2)	-184(4)	588(7)	262(4)
N	-1098(4)	2774(8)	2763(4)
C(1)	-1496(5)	-36(7)	345(5)
C(2)	-2220(5)	983(8)	160(5)
C(3)	-3451(5)	2690(16)	910(6)
C(4)	-3419(7)	4327(13)	2252(8)
C(5)	-1768(6)	4532(10)	2948(7)
O(Me)	2348(5)	-558(8)	2816(6)
C(Me)	3927(7)	-324(14)	3408(8)

**Table 3** Selected bond distances (Å) in complexes **1** and **2**

<b>Complex 1</b>		<b>Complex 2</b>	
Cu-Cl	2.261(2)	Cu-Cl	2.276(3)
Cu-O(w)	1.987(5)	Cu-O(1 <sup>l</sup> )	1.998(5)
Cu-O(1)	1.948(3)	Cu-O(2)	1.958(6)
Cu-N	1.994(4)	Cu-N	2.006(6)
Cu-O(2 <sup>l</sup> )	2.286(5)	Cu-O(2 <sup>l</sup> )	2.656(6)
		Cu-O(Me)	2.297(6)
O(1)-C(1)	1.282(5)	O(1)-C(1)	1.254(7)
O(2)-C(1)	1.236(4)	O(2)-C(1)	1.259(6)
C(1)-C(2)	1.506(5)	C(1)-C(2)	1.497(10)
C(2)-C(3)	1.534(8)	C(2)-C(3)	1.538(9)
C(3)-C(4)	1.512(6)	C(3)-C(4)	1.506(17)
C(4)-C(5)	1.516(9)	C(4)-C(5)	1.497(9)
N-C(2)	1.494(4)	N-C(2)	1.486(8)
N-C(5)	1.495(6)	N-C(5)	1.502(8)
		O(Me) ... Cl <sup>III</sup>	3.158(7)
		Cl <sup>III</sup> ... H(OMe)	2.40(6)

Key to symmetry operations: I  $-x, \frac{1}{2} + y, -z$ ; III  $x, -1.0 + y, z$ .

Their positional, isotropic and then anisotropic thermal parameters (except for hydrogen atoms) were refined by the block-diagonal least-squares method. The final *R* values were 0.030 (*R'* = 0.043) for **1** and 0.039 (*R'* = 0.051) for **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.<sup>2</sup> Atomic scattering factors were taken from ref. 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

**Other Measurements.**—The infrared spectra of the samples were obtained by means of a Hitachi 295 spectrophotometer, using Nujol mull and KBr disks. Magnetic moments for the solid samples were obtained by the Gouy method at room temperature, using Hg[Co(SCN)<sub>4</sub>] as a calibration standard. The simultaneous thermogravimetric (TGA) and differential thermal (DTA) analyses were carried out with a Rigaku

**Table 4** Selected bond angles (°) in complexes **1** and **2**

<b>Complex 1</b>			
Cl-CuO(w)	91.8(1)	Cu-O(1)-C(1)	114.4(2)
Cl-Cu-N	94.9(1)	Cu-O(2 <sup>l</sup> )-C(1)	126.8(4)
Cl-Cu-O(2 <sup>l</sup> )	94.8(1)	O(1)-C(1)-O(2)	123.6(3)
O(w)-Cu-O(1)	87.4(1)	O(1)-C(1)-C(2)	117.2(3)
O(w)-Cu-O(2 <sup>l</sup> )	91.9(2)	O(2)-C(1)-C(2)	119.2(4)
O(1)-Cu-O(2 <sup>l</sup> )	100.0(1)	C(1)-C(2)-C(3)	112.2(3)
O(1)-Cu-N	84.9(1)	C(2)-C(3)-C(4)	103.1(4)
N-Cu-O(2 <sup>l</sup> )	92.4(1)	C(3)-C(4)-C(5)	102.3(5)
Cl-Cu-O(1)	165.23(7)	C(4)-C(5)-N	105.5(3)
O(w)-Cu-N	171.7(2)	C(5)-N-C(2)	107.7(4)
<b>Complex 2</b>			
Cl-Cu-O(2)	176.2(2)	Cu <sup>II</sup> -O(1)-C(1)	106.7(3)
Cl-Cu-N	93.4(2)	Cu-O(2)-C(1)	116.3(5)
Cl-Cu-O(Me)	92.7(1)	O(1)-C(1)-O(2)	122.9(6)
Cl-Cu-O(1 <sup>l</sup> )	94.3(2)	O(1)-C(1)-C(2)	118.9(5)
Cl-Cu-O(2 <sup>l</sup> )	101.8(1)	O(2)-C(1)-C(2)	118.2(5)
O(2)-Cu-N	83.8(2)	C(1)-C(2)-C(3)	112.4(6)
O(2)-Cu-O(Me)	85.9(2)	C(2)-C(3)-C(4)	103.7(8)
O(2)-Cu-O(1 <sup>l</sup> )	89.3(2)	C(3)-C(4)-C(5)	102.8(7)
O(2)-Cu-O(2 <sup>l</sup> )	81.3(2)	C(4)-C(5)-N	106.0(5)
N-Cu-O(Me)	110.4(2)	C(5)-N-C(2)	107.6(4)
N-Cu-O(1 <sup>l</sup> )	155.8(2)	Cu-N-C(2)	110.0(5)
N-Cu-O(2 <sup>l</sup> )	101.5(2)	Cu-N-C(5)	111.9(4)
O(Me)-Cu-O(1 <sup>l</sup> )	92.2(2)		
O(Me)-Cu-O(2 <sup>l</sup> )	144.1(2)	Cu-O(Me)-C(Me)	121.2(4)
O(1)-Cu <sup>II</sup> -O(2)	54.4(2)		
		O(Me)-H(OMe) ... Cl <sup>III</sup>	166(6)

Key to symmetry operations: I  $-x, \frac{1}{2} + y, -z$ ; II  $-x, -\frac{1}{2} + y, -z$ ; III  $x, -1.0 + y, z$ .

Thermoflex M-8057 using a sample weighing about 10 mg; the heating rate was 5 °C min<sup>-1</sup> in air and  $\alpha$ -alumina was used as the reference. The powder diffuse reflectance spectra were measured on a Hitachi U-3200 spectrophotometer, using a standard Hitachi reflection attachment with a magnesium oxide reference. Visible spectra were recorded on a Hitachi U-3400 spectrophotometer.

## Results and Discussion

**Description of the Structures.**—[CuCl(pro)(H<sub>2</sub>O)] **1**. The final atomic parameters are listed in Table 2, interatomic distances in Table 3, and bond angles in Table 4. A stereoscopic view of the complex and the atom numbering scheme are shown in Fig. 1. The structure consists of a one-dimensional polymer chain bridged by a carboxylate group of pro: two carboxylate oxygen atoms in the pro are co-ordinated to different copper atoms, thus forming a *syn-anti* bridge. For one copper atom the pro ligand functions as a bidentate chelate, and the metal is surrounded by five atoms: one carboxylate oxygen and one amino nitrogen atom of the pro, one carboxylate oxygen atom from the different pro, one water oxygen atom, and one chlorine atom. The bond lengths are as usual except for a slightly longer Cu-O(2<sup>l</sup>): [2.286(5) Å]. The bond angles around the copper atom are near 90° (84.9–100.0°) as shown in Table 4. Therefore the co-ordination is of the square-pyramidal type: Cl, N, O(1) and O(w) lie in equatorial and O(2<sup>l</sup>) in axial position. The four equatorial atoms form a plane (deviations from which are within 0.11 Å), and the copper atom deviates from this plane by 0.18 Å.

Some square-pyramidal copper(II) complexes had been studied.<sup>4,5</sup> Recently, however, many more with new types of ligands have been reported.<sup>6–8</sup> Therefore five-co-ordinated copper(II) complexes of square-pyramidal geometry are no longer novel. In peptide complexes this kind of co-ordination can also be detected.<sup>9</sup> In simple amino acid complexes, however, a co-ordination geometry such as that in **1** is not common. The copper in amino acid complexes usually has

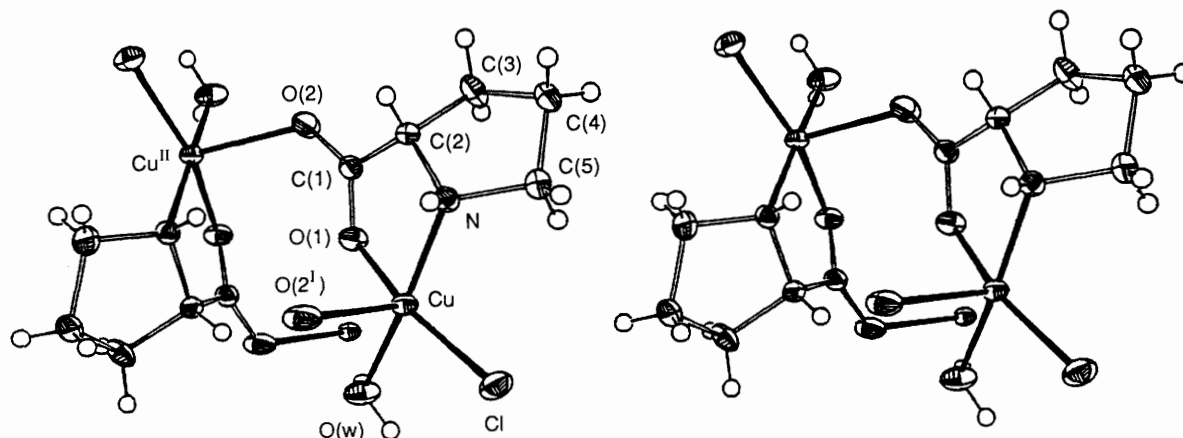


Fig. 1 Stereoscopic view of complex 1 and the atom numbering scheme. Key to symmetry operations: I  $-x, \frac{1}{2} + y, -z$ ; II  $-x, -\frac{1}{2} + y, -z$

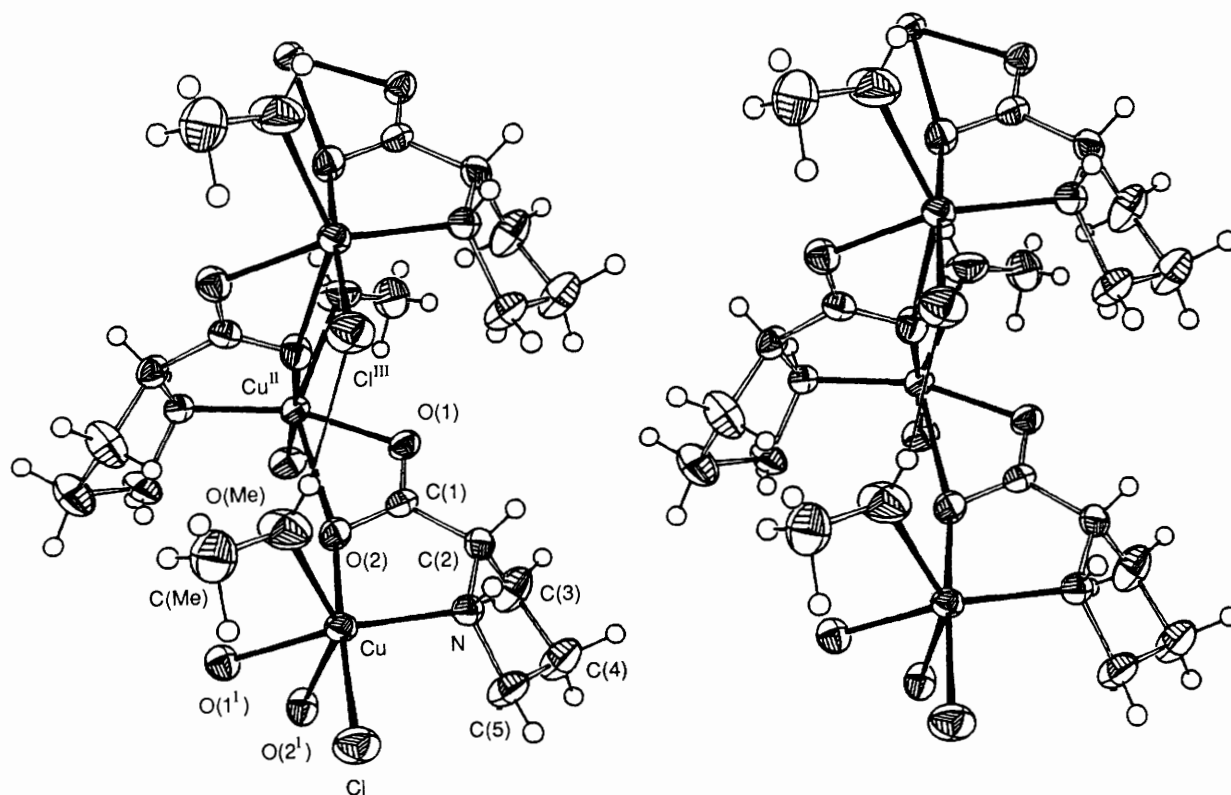


Fig. 2 Stereoscopic view of complex 2 and the atom numbering scheme. Key to symmetry operations: I  $-x, \frac{1}{2} + y, -z$ ; II  $-x, -\frac{1}{2} + y, -z$ ; III  $x, -1 + y, z$

distorted-tetrahedral, trigonal-bipyramidal or octahedral coordination geometries. Most recently, square-pyramidal distorted towards trigonal-bipyramidal geometry was reported in chloro(glycinato)(1-methylimidazole)copper(II).<sup>10</sup>

The polymer chains are arranged parallel to the *b* axis. The copper atoms in the chain, which are bridged by carboxylates, are related by a  $2_1$  axis. There is no inter- nor intra-chain hydrogen bonding.

[CuCl(pro)(CH<sub>3</sub>OH)] 2. The final atomic parameters are listed in Table 2, interatomic distances in Table 3, and bond angles in Table 4. A stereoscopic view of the complex and the atom numbering scheme are shown in Fig. 2. Although the structure consists of a one-dimensional polymer chain bridged by a carboxylate group of pro, the bridging form is different from that in 1. One carboxylate oxygen atom is co-ordinated to two copper atoms to form a bridge, and the other is co-ordinated to one of these two copper atoms. Therefore the carboxylate group forms a four-membered chelate ring. The bridging form is the same as those of 4-hydroxy-L-proline

(hpro) in [CuCl(hpro)(H<sub>2</sub>O)]<sup>11</sup> and of the *N,N*-diethylglycinate group (degly) in [CuCl(degly)]<sup>12</sup>.

The copper atom in complex 2 is surrounded by six atoms: one carboxylate oxygen and one amino nitrogen atom of the pro ligand, which form a chelate ring, two carboxylate oxygen atoms of the different pro, one chlorine atom, and one methanol oxygen atom. Among them, O(2') and O(Me) are at a longer distance from the copper atom than the others. Especially the distance Cu–O(2') [2.656(6) Å] is rather longer than usual, but this is not very surprising as discussed previously.<sup>11,12</sup> The angle O(1)–Cu–O(2) is 54.4(2)°. Therefore the octahedron surrounding the copper atom is extremely distorted.

The polymer chains are also arranged parallel to the *b* axis, as in structure 1, and the copper atoms are related by the  $2_1$  axis. There are no interchain hydrogen bonds, but there is an intrachain hydrogen bond between a chlorine atom and an oxygen atom of a methanol ligand.

Although it is difficult for methanol to co-ordinate to metals, it is not very unusual since many copper(II) or other metal

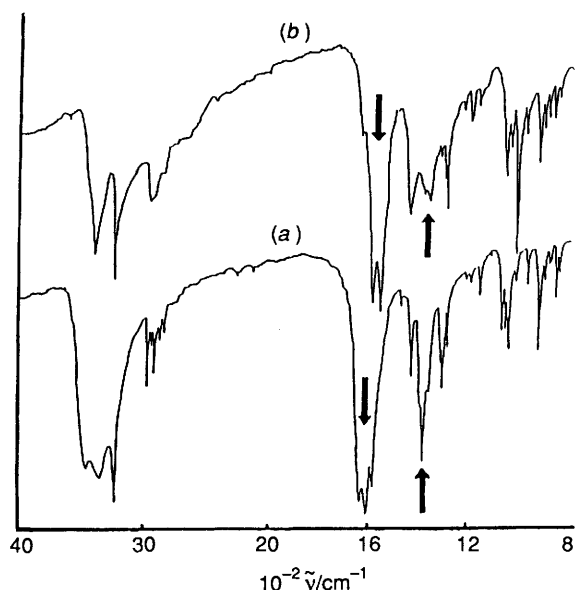


Fig. 3 Infrared spectra of complexes 1 (a) and 2 (b). Arrows represent antisymmetric and symmetric stretching vibrations of  $\text{CO}_2^-$

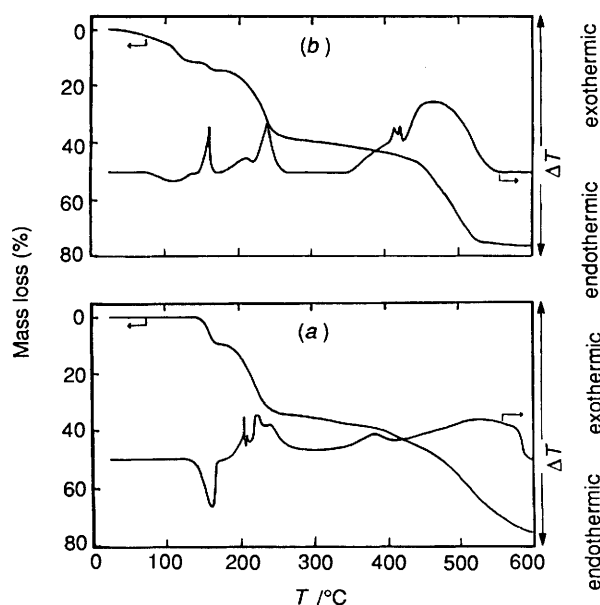


Fig. 4 Thermogravimetric and differential thermal analysis curves of complexes 1 and 2

complexes with a methanol ligand have been reported.<sup>10,13</sup> However, there are no amino acid complexes, except for chloro-(glycinato)(methanol)copper(II)<sup>10</sup> prepared by adding a slurry of glycine and sodium methoxide to a methanol solution of copper(II) chloride. Therefore, **2** is the first case, to my knowledge, of an amino acid complex having a methanol ligand prepared from purely metal ion and amino acid methanol solutions, as compared with the complexes prepared from aqueous solutions.

**Properties of Complexes 1 and 2.**—The infrared spectra of the complexes are shown in Fig. 3. There are characteristic peaks which reflect the difference of the structures at 1600 and 1400  $\text{cm}^{-1}$  (as shown by arrows). These peaks are assigned to  $\text{CO}_2^-$  antisymmetric and symmetric stretching vibrations, respectively. The shapes of the peaks reflect the co-ordination of the carboxylate group. Complex **2** has a large split peak around 1600  $\text{cm}^{-1}$  and a slightly split peak near 1400  $\text{cm}^{-1}$ . The difference in the shapes of the peaks is caused by the difference in

the surroundings of the carboxylate oxygen atoms. In **1** each carboxylate oxygen atom forms only one bond, whereas in **2** one of the two carboxylate oxygen atoms is co-ordinated to two copper atoms. Owing to the additional bonding in **2** the vibrations of the carboxylate group are restrained. Therefore the antisymmetric and symmetric stretching frequencies are lower than those of **1**, and the peak shapes are also different.

The magnetic moments of **1** and **2** are 1.89 and 1.84, respectively, indicating that there is no  $\text{Cu} \cdots \text{Cu}$  interaction. This is supported by the metal-metal distances (5.32 Å for **1** and 4.57 Å for **2**) and unsuitable directions of the carboxylate orbital and the d orbital of the copper(II) for superexchange interaction between the copper atoms.

The results of the simultaneous TGA and DTA of the complexes are shown in Fig. 4. For **1** there is an endothermic peak on the DTA curve with a mass loss corresponding to one water molecule at 162 °C. It indicates that the water molecule is rather strongly co-ordinated to the copper atom; by contrast, the  $\text{H}_2\text{O}$  in  $[\text{CuCl}(\text{hpro})(\text{H}_2\text{O})]$  was eliminated at 154 °C.<sup>12</sup> On the other hand, **2** began to lose the methanol molecule at an earlier stage. It has a rather sharp exothermic peak on the DTA at 159 °C. Probably the complex recrystallised after losing the volatile methanol molecule. For **1** the thermal decomposition began without recrystallization at around 200 °C, corresponding to the decomposition temperature of L-proline, 220–222 °C. The DTA curve of this region is disordered. The thermal decomposition (endothermic reaction) and the oxidation (exothermic reaction) seem to have occurred almost simultaneously. For **2** similar reactions also occurred in this region, following the recrystallization. In each case a black ash ( $\text{CuO}$ ) was obtained at the final stage.

In the powder diffuse reflectance spectra there is a peak at 749 nm for complex **1** and at 757 nm for **2**. However, the electronic spectra of the aqueous solutions of these complexes accord with each other, as do those of the methanol solutions:  $\lambda_{\text{max}} = 696.6 \text{ nm}$ ,  $\epsilon = 34.9 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  for aqueous solutions and  $\lambda_{\text{max}} = 728.0 \text{ nm}$ ,  $\epsilon = 59.7 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  for methanol solutions. These facts indicate that the complexes have different co-ordination types in the solid state, and in aqueous solutions and in methanol solutions, but that in aqueous or in methanol solutions the two complexes have the same co-ordination type.

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