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# Copper(II) Complexes with an Apically Coordinated Thioether Group

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*Five coordinate copper(II) complexes have been prepared from non-linear pentadentate ligands derived from pyridine-2-carbaldehyde and 1,2-diamino-5-thiahexane. The thioether group in the side chain interacts with copper(II) through an apical coordination position, which was revealed by systematic comparison of the absorption, circular dichroism and electron spin resonance spectra of the thioether-containing complexes and those of the reference complexes. Displacement of pyridine-2-carbaldehyde by salicylaldehyde affords complexes having stronger character of planarity because of the absence of the interaction between sulfur and copper(II).*

## Introduction

Little is known about the structure and function of 'non-blue' (type II) copper(II), which is believed to be present in galactose oxidase and amine oxidase and also in multi-copper oxidases in contrast to those of 'blue' (type I) copper(II) found in the blue oxidase [1]. However, it seems noteworthy that the coordination geometry of non-blue copper(II) contained in galactose oxidase [2] and amine oxidase [3] might be square-pyramid with an apically coordinated sulfur group. In a previous paper we reported the syntheses and spectral properties of several pentadentate copper(II) complexes of ligands prepared by the condensation of 1,6-diamino-3-thiahexane or 1,5-diamino-3-thiapentane and pyridine-2-carbaldehyde or salicylaldehyde as type II copper models [4]. The ligand consisted of the linearly arranged NNSNN or ONSNO donor set. Here we present syntheses and spectral properties of copper(II) complexes of non-linear pentadentate ligands derived from S-1,2-diamino-5-thiahexane and pyridine-2-carbaldehyde or salicylaldehyde.

## Experimental

### *Materials*

Copper(II) perchlorate hexahydrate and salicylaldehyde (abbreviated as sal) were purchased from Nakarai Chemicals Ltd., pyridine-2-carbaldehyde-(pyal) from Merck AG, S-methionine amide hydrochloride from Sigme Chem. Co., and S-leucine amide hydrochloride from Tokyo Kasei. All other reagents used were of the highest grade commercially available. S-1,2-diamino-5-thiahexane(dath) was made from S-methionine amide according to Amundsen *et al.* [5] and S-1,2-diamino-4-methylhexane(damh) from S-leucine amide by the similar method.

### *Cu(pyal=dath=pyal)*

To thioether-containing diamine, dath, was added twice amounts of pyal in aqueous ethanol to give 2: 1 pyal: dath Schiff base (abbreviated as pyal=dath=pyal), which was treated with $Cu(ClO_4)_2 \cdot 6H_2O$ and was allowed to stand at room temperature. Blue crystals were isolated as perchlorate, and were recrystallized from aqueous ethanol. *Anal.* Found: C, 35.50; H, 3.43; N, 9.74%. Calcd for $C_{17}H_{20}N_4SCu(ClO_4)_2$: C, 35.52; H, 3.51; N, 9.74%.

### *Cu(pyal=damh=pyal(H₂O))*

Synthesis of the reference complex, Cu(pyal=damh=pyal) was carried out by the similar method as that of Cu(pyal=dath=pyal). The result of elemental analysis indicated that the complex was isolated as monohydrate. *Anal.* Found: C, 37.62; H, 4.16; N, 9.88%. Calcd for $C_{18}H_{22}N_4Cu(H_2O)(ClO_4)_2$: C, 37.61; H, 4.21; N, 9.75%. However, the water of crystallization was not removed even *in vacuo* over $P_2O_5$ at an elevated temperature. Accordingly, it was reasonably considered that an addition reaction of one water molecule occurred at one of the azomethine groups.

### *Cu(pyal–dath–pyal)*

The condensed product of pyal and dath, pyal=dath=pyal was reduced with $NaBH_4$ until the yellow color of the Shiff base faded out, and the excess of $NaBH_4$ was treated with HCl. The reduced ligand was represented as pyal-dath-pyal instead of pyal=dath=pyal. After filtration, the filtrate was mixed with $Cu(ClO_4)_2 \cdot 6H_2O$ to give blue crystals. Recrystallization was performed from aqueous ethanol. *Anal.* Found: C, 35.16; H, 4.73; N, 9.25%. Calcd for $C_{17}H_{24}N_4SCu(ClO_4)_2$: C, 35.27; H, 4.18; N, 9.68%.

### *Cu(pyal–damh–pyal)*

This complex was prepared according to a similar procedure as mentioned above using damh in place of dath. *Anal.* Found: C, 38.59; H, 4.74; N, 10.13%. Calcd for $C_{18}H_{26}N_4CuClO_4)_2$: C, 38.54; H, 4.67; N, 9.99%.

### *Cu(sal=dath=sal) and Cu(sal=damh=sal)*

These complexes were prepared by the same method as described above using sal instead of pyal. *Anal.* Found: C, 51.06; H, 4.50: N, 6.31%. Calcd for $C_{19}H_{20}N_2O_2SCu \cdot 1/3NaClO_4$(Cu(sal=dath=sal)): C, 51.30; H, 4.53; N, 6.30%. Although the complex was accompanied by a coprecipitation of $NaClO_4$, it afforded no fear of serious effect for spectral measurements. *Anal.* Found: C, 61.54; H, 5.87; N, 6.96%. Calcd for $C_{20}H_{22}N_2O_2Cu \cdot 1/4H_2O$(Cu(sal=damh=sal)): C, 61.52; H, 5.80; N, 7.18%.

### *Spectral Measurements*

Absorption spectra were recorded in 1 cm or 1 mm path length cell in the range 300–800 nm with a Union Giken SM-401 high sensitivity spectrophotometer. Electron spin resonance (ESR) spectra of copper(II) complexes were measured using a JEOL JES-FEIX instrument at 77 K. Magnetic field was calculated by the splitting of Mn(II) in MnO($\Delta H_{3-4}$ = 86.9 G) and g values were determined by taking Li·TCNQ (g = 2.0026) as a standard. Dimethylformamide (DMF) was used as solvent.

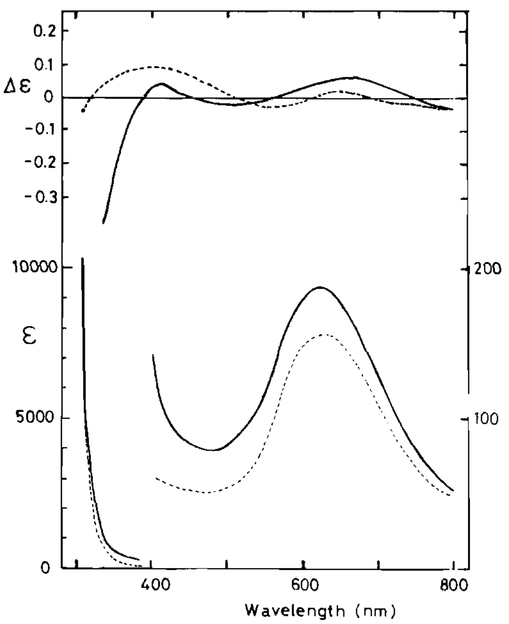
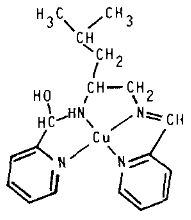


Fig. 1. Absorption and circular dichroism spectra of Cu(pyal=dath=pyal) (——) and Cu(pyal=damh=pyal($H_2O$)) (– – –).

## Results and Discussion

Condensed product of pyal and ethylenediamine or its derivatives in 2:1 ratio has been known to be inadaptable to copper(II) ion since addition reaction of one or two water or ethanol molecules to the azomethine group occurs with the procedure for the isolation of copper(II) complexes [6]. In line with this, the copper(II) complex of pyal=damh=pyal($H_2O$) (1) but not that of pyal=damh=pyal was isolated, although it remained unknown to which azomethine group the addition of one water molecule occurred. Contrary to this, Cu(pyal=dath=pyal) (2) with a thioether group in the side chain was successfully isolated without being accompanied by further reaction, indicating that donation of the thioether group contributes in stabilizing the formation of this complex. This would be understood by assuming that the central metal ion might be somewhat raised from the equatorial plane through the apical donation of the thioether group to make the skeletal structure of the small 5-5-5 membered ring system adaptable to copper(II) ion.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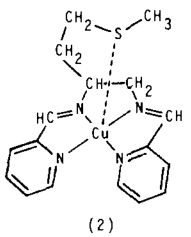
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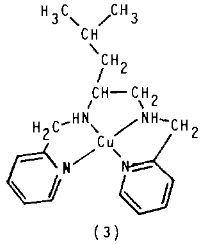
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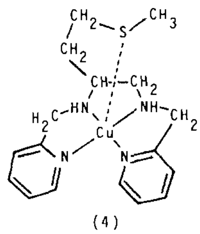
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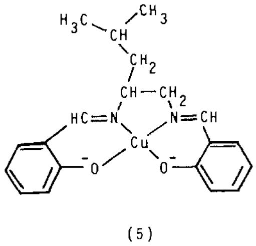
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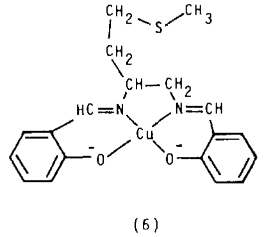
(6)

Absorptions of 1 and 2 complexes are shown in Fig. 1. These spectra are similar to each other in the d–d band region. However, the sulfur does interact with copper(II) ion as shown in the increase of absorptivity of 2 over 1 in the 300–400 nm region where S → Cu charge transfer band always appeared regardless of the donated position of the sulfur group [4]. The strong charge transfer is not expected when a sulfur group interacts with copper(II) ion at an apical position, because tetragonal copper(II) is in the $d_{x^2-y^2}$ ground state. The sulfur to copper(II) charge transfer band affords a negative CD peak at *ca.* 330 nm, although this band does not appear as a notable peak. The same is true for the reduced Schiff base complexes, Cu(pyal–damh–pyal) (3) and Cu(pyal–dath–pyal) (4). The sulfur-containing complex, 4, afforded the d–d absorption peak at a longer wavelength than the reference complex, 3 as shown in Fig. 2, suggesting that the apical coordination became stronger with the reduction of the ligand. Here again, the charge transfer band, although it does not appear as an apparent peak, exists in the 300–400 nm region as is illustrated in the increase in absorptivity of 4 over 3 in the region. This band is completely obscured in CD spectrum because of the masking by another charge transfer band.

The sulfur ligation is confirmed also by ESR spectra. The $A_{\parallel}$ value of Cu(pyal–dath–pyal), 18.7 mK is apparently reduced from that of Cu(pyal–damh–pyal), 19.1 mK (Table I). The slight decrease in the $A_{\parallel}$ value is characteristic of pentadentate copper(II) complexes [4]. The $A_{\parallel}$ values of Cu(pyal=dath=pyal) and Cu(pyal=damh=pyal($H_2O$)) were 18.3 mK and 18.5 mK, respectively. The lesser decrease in the $A_{\parallel}$ value for the Schiff base complex can be related to the weaker sulfur interaction with copper(II) ion due to the rigid structure in the equatorial plane of the central copper(II) ion.

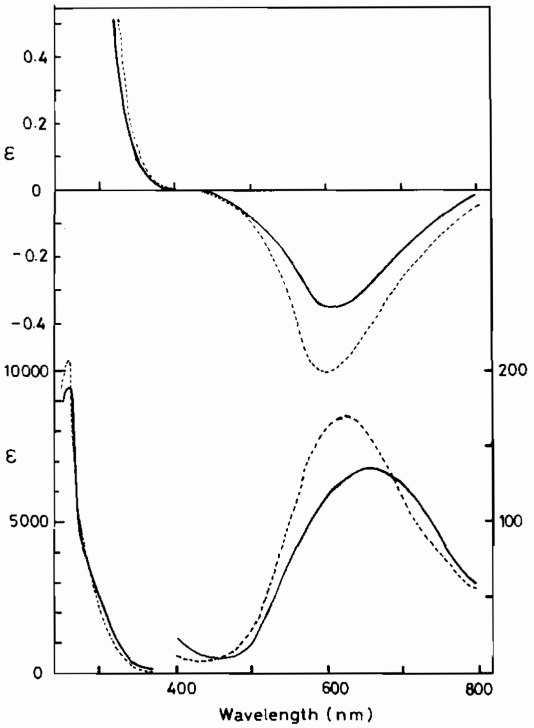

Fig. 2. Absorption and circular dichroism spectra of Cu(pyal–dath–pyal) (——) and Cu(pyal–damh–pyal) (– – –).

TABLE I. ESR Parameters of Copper(II) Complexes.

| Complex | $g_{\parallel}$ | $g_{\perp}$ | $-A_{\parallel}$(mK) |
|---|---|---|---|
| Cu(pyal=dath=pyal) | 2.22 | 2.06 | 18.3 |
| Cu(pyal=damh=pyal($H_2O$)) | 2.22 | 2.06 | 18.5 |
| Cu(pyal–dath–pyal) | 2.22 | 2.04 | 18.7 |
| Cu(pyal–damh–pyal) | 2.22 | 2.05 | 19.1 |
| Cu(sal=dath=sal) | 2.22 | 2.06 | 20.0 |
| Cu(sal=damh=sal) | 2.22 | 2.06 | 19.9 |

The displacement of pyal by sal led to the complete loss of the expected interaction between copper(II) ion with the thioether group. The absorption spectra of Cu(sal=damh=sal) (5) and Cu(sal=dath=sal) (6) are almost identical not only in the d–d band region but also in the charge transfer band region (Fig. 3). A similar behavior has also been pointed out by Amundsen *et al.* [5]. Furthermore the CD and ESR spectra also indicated that the sulfur group departs from coordination sphere, affording very similar spectra for the couple. The difference in pyal- and sal-containing complexes stems from the different structure of the respective equatorial plane. The sal-containing complexes with 6-5-6 fused chelate ring structure have a strong character of square-planar geometry, which weakens the interaction of the sulfur in the side chain with copper(II) ion. On the other hand, present pyal-containing complexes with 5-5-5 chelate ring structure are strained in the equatorial plane to a considerable extent as clearly shown in the lowering of the $A_{\parallel}$ values comparing with those of sal-containing complexes in spite of similar $g_{\parallel}$ values for both the systems (see Table I). Adjacent

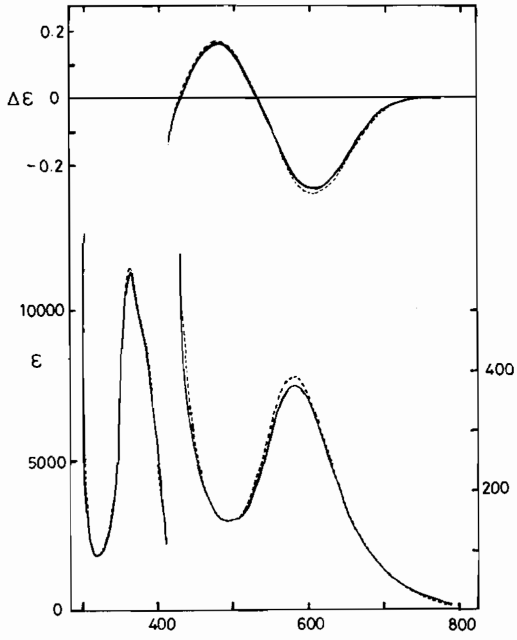

Fig. 3. Absorption and circular dichroism spectra of Cu(sal=dath=sal) (——) and Cu(sal=damh=sal) (– – –).

five-membered chelate rings seem to distort the copper(II) to a considerable extent. For example, $g_{/\!/}$ and $A_{/\!/}$ values of glycylglycinatocopper(II) and glycl-β-alaninatocopper(II) are 2.24, 15.7 mK and 2.25, 19.2 mK, respectively [7]. In conclusion, the slight distortion imposed to copper on its equatorial plane generally favors an approach of the fifth ligand to an apical position.

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