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Structure of the Copper(II) Complex of (S)-β-(2-Pyridylethyl)-L-cysteine

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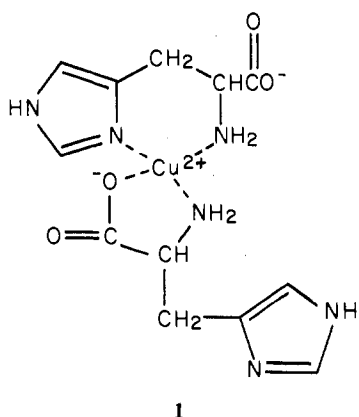
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The structure of the copper(II) 1:2 complex of (S)-β-(2-pyridylethyl)-L-cysteine (2-PEC), 3, has been ascertained by nmr, esr, mid- and far-infrared, and Raman spectroscopy, as well as circular dichroism (CD). The results in solution (nmr, esr, CD) show that the 2:1 complex, 3, involves coordination of copper(II) to the amino and carboxylate groups of 2-PEC in glycine-like fashion. The solid 2:1 complex, 3, can be isolated and mid- and far-infrared as well as CD data confirm that 3, in the solid state, is also coordinating in glycine-like fashion. The esr spectra on frozen solutions of 3 indicate that 3 has approximately square-planar D_{2h} symmetry and that tentatively the configuration of the amino and the carboxylate groups around the copper(II) ion is trans.

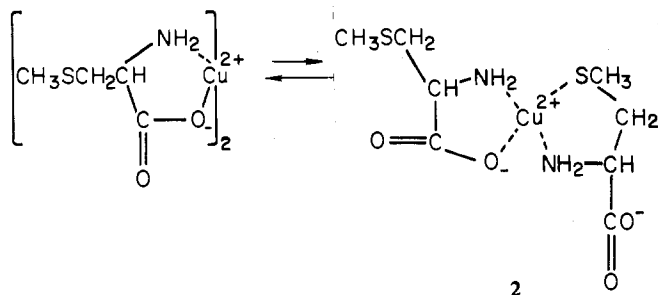
Introduction

The structures of naturally occurring amino acid complexes of copper(II) have been extensively studied.¹ The 2:1 complexes of multidentate amino acids and copper(II) are of particular interest, since the copper(II) ion usually forms square-planar complexes that for steric reasons involve only two of the possible binding sites per ligand.

Recently Sigel and McCormick² reported on the structure of the 1:2 copper(II) complex of histidine, a tridentate amino acid, and verified by nmr that this was a mixed complex binding both histamine- and glycine-like, 1.



McCormick, *et al.*,³ also reported that (S)-methylcysteine, another tridentate amino acid, coordinates predominantly in glycine-like fashion but that the thioether and the amino groups coordinate in a mixed complex 2, however, in small concentration.

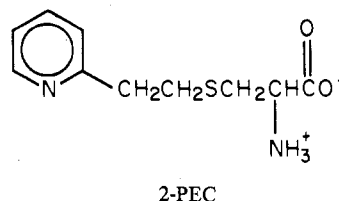


(1) K. Nakamoto and P. J. McCarthy, "Spectroscopy and Structure of Metal Chelate Compounds," Wiley, New York, N. Y., 1968.

(2) H. Sigel and D. B. McCormick, *J. Amer. Chem. Soc.*, 93, 2041 (1971).

(3) D. B. McCormick, H. Sigel, and L. D. Wright, *Biochim. Biophys. Acta*, 184, 318 (1969).

We have been interested in the interaction of metals with synthetic amino acids that have multicoordinating sites.⁴ Specifically, we have been interested in (S)-β-(2-pyridylethyl)-L-cysteine (2-PEC), a tetradentate amino acid, and in this paper we describe the interaction of copper(II) with 2-PEC utilizing spectroscopic techniques in order to ascertain what functional groups are involved in binding the copper(II) ion.



Results and Discussion

Nuclear Magnetic Resonance (Nmr). The use of nmr spectroscopy for the elucidation of binding sites of metals on amino acids is a well-established technique.¹ The copper(II) ion, being paramagnetic, causes proton relaxation effects and selectively broadens the signals of protons near the binding sites. Since there is rapid exchange between complexed and free ligand, then we only use a trace of paramagnetic copper(II) ions to cause the broadening of signals of proton in proximity to the binding sites. Figure 1 shows the results as we add increasing amounts of copper(II) at pD 10.3. The signal for the methine proton at 3.53 ppm (quartet, X portion of ABX spin system) is broadened dramatically with the initial line width for the quartet, measured at half-height, going from 14 Hz at zero copper(II) concentration to 27 Hz at 2 × 10⁻⁴ M copper(II), and 38 Hz at 1 × 10⁻³ M copper(II). The signal for the methylene protons adjacent to the methine which are a pair of overlapping quartets at 2.88 ppm (AB portion of ABX spin system) are also broadened, however slightly, and we attribute this to a proximity effect. This is analogous to L-α-amino-n-butyric acid where the signal for the α-methylene group is broadened in the presence of 2 × 10⁻⁴ M copper(II) at pD 7.6.³ The signal for the other methylene group of 2-PEC adjacent to the sulfur, which overlaps the signals for the methylene group adjacent to the pyridyl group, at 2.98 ppm does not appear to be influenced by the copper(II) ions. Thus we feel that if sulfur is participating in a mixed complex, as in 2, it is very weak. The signals for the pyridyl protons (Figure 1) at all the copper(II) concentrations are not affected and, thus, the pyridyl nitrogen is eliminated as a site of binding. The dramatic broadening of the signal for the methine pro-

(4) R. H. Fish and M. Friedman, *J. Chem. Soc., Chem. Commun.*, 812 (1972).

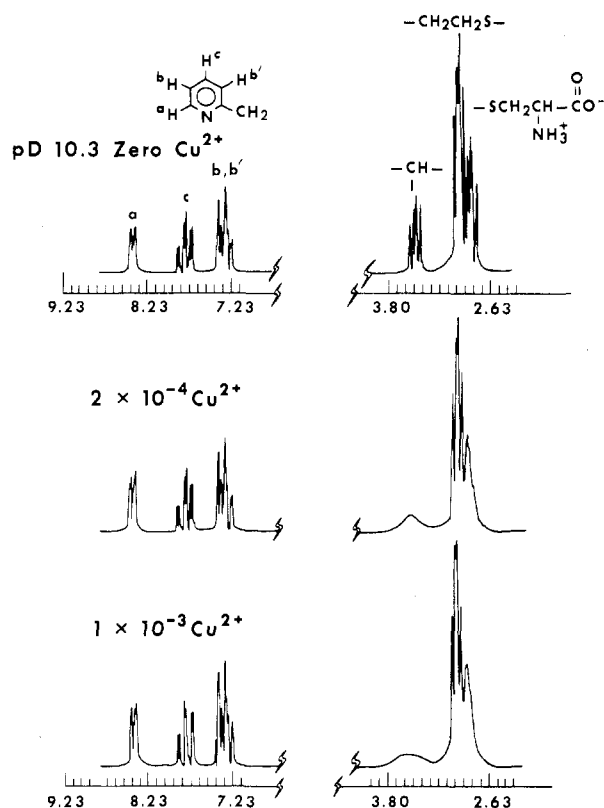
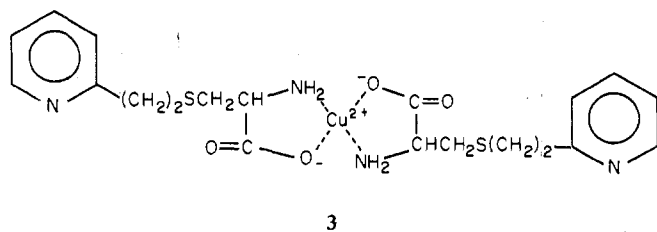


Figure 1. Nmr spectra of 2-PEC in the presence of 0, 2×10^{-4} , and 1×10^{-3} M copper(II) ions at pD 10.3.

ton of 2-PEC at 3.53 ppm in the presence of copper(II) at pD 10.3 is not evident at pD 2.4 and verifies the fact that when copper(II) is not binding to 2-PEC there is no effect on the line width. The *N*-acetyl derivative of 2-PEC, **4**, which selectively blocks the amino group, was prepared and the signals in its nmr spectrum were not affected at pD 8.3 by copper(II) ions, which further supports the necessity of the amino group in a glycine-like complex **3** or if present in a mixed complex with sulfur participation as in **2**. The nmr data are therefore consistent with the glycine-like complex **3**.



Electron Spin Resonance (Esr) and Circular Dichroism (CD). The esr spectra of **3** (10^{-3} M) in dimethyl sulfoxide (DMSO) at 77 and 328°K are shown in Figure 2. The main features of the 77°K spectrum can be described by an axially symmetric Hamiltonian and are summarized in Table I. The solution spectrum at 328°K consists of four copper hyperfine lines centered at an average g value, $\langle g \rangle = 1/3(g_{\parallel} + 2g_{\perp})$, with an average copper hyperfine splitting, $\langle A \rangle = 1/3(A_{\parallel} + 2A_{\perp})$, given in Table I. The g_{\perp} line of the 77°K spectrum and the high-field line of the 328°K spectrum show additional hyperfine splitting of at least five lines attributed to nitrogen coupling. This supports the nmr conclusion that the copper is complexed to two nitrogen atoms since coupling to two

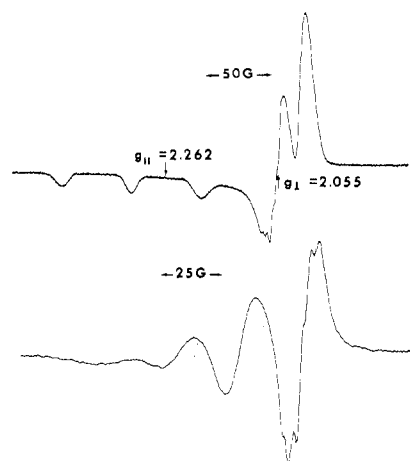


Figure 2. ESR spectra of **3** at 77°K (top spectrum) and 328°K (bottom spectrum). The magnetic field increases from left to right.

Table I. ESR Parameters of **3**

Parameter	328°K	77°K
$\langle g \rangle$	2.124 ± 0.002	
g_{\parallel}		2.262 ± 0.002
g_{\perp}		$2.055^a \pm 0.002$
$\langle A \rangle$, G	75.5	
A_{\parallel} , G		173
A_{\perp} , G		30^b
$\langle A^N \rangle$, G	8.8	
A^N_{\parallel} , G		18.4^c
A^N_{\perp} , G		4.0

^a $g_{\perp} = 1/2(3\langle g \rangle - g_{\parallel})$. ^b $A_{\perp} = 1/2(3\langle A \rangle - A_{\parallel})$. ^c $A^N_{\parallel} = (3\langle A^N \rangle - 2A^N_{\perp})$; A^N is the nitrogen hyperfine coupling constant.

equivalent nitrogens will give a five-line esr spectrum with intensity ratios of 1:2:3:2:1. The esr parameters (Table I) are consistent with other 1:2 copper-amino acid complexes of tetragonal or square-planar D_{2h} symmetry whether studied in water^{5,6} or DMSO.⁷ The g -tensor values are given by

$$g_{\parallel} = 2 \left(1 + \frac{4k^2 \lambda}{\Delta_1} \right); \quad g_{\perp} = 2 \left(1 + \frac{k^2 \lambda}{\Delta_2} \right)$$

where λ is the spin-orbit coupling constant (-828 cm^{-1} for free copper(II)) and k is the orbital reduction factor ($k = 1$ for ionic bonding and 0.5 for covalent bonding).⁸ The Δ_1 and Δ_2 values are the energy separations between $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{xz, yz}$ orbital levels, respectively. The value of 173 G for A_{\parallel} (Table I) is consistent with values reported for other copper complexes of amino acids^{6,7} which have been shown to contain the amino and carboxylate group in a trans configuration around copper. We tentatively assign a trans configuration for the amino and carboxylate groups around the copper(II) ion in **3**.

Cotton effects for square-planar complexes such as **3** arise from absorption bands attributed to $d \rightarrow d$ transitions of the metal chromophore which is in an asymmetric environment due to its proximity to the asymmetric carbon atom of the L-amino acid. CD spectra were obtained on **3** in DMSO and in the solid state (KBr) as shown in Figure 3. The absorption maximum at 617 nm ($E = 71$) in DMSO and the negative Cotton effect at 604 nm ($[\theta] = -900$) in DMSO are similar to visible and CD curves found for other complexes

(5) See ref 1, Chapter 5, p 286.

(6) G. Rotilio and L. Calabrese, *Arch. Biochem. Biophys.*, **143**, 218 (1971).

(7) R. Zand and G. Palmer, *Biochemistry*, **6**, 999 (1967).

(8) B. G. Malmstrom and T. Vanngard, *J. Mol. Biol.*, **2**, 118 (1960).

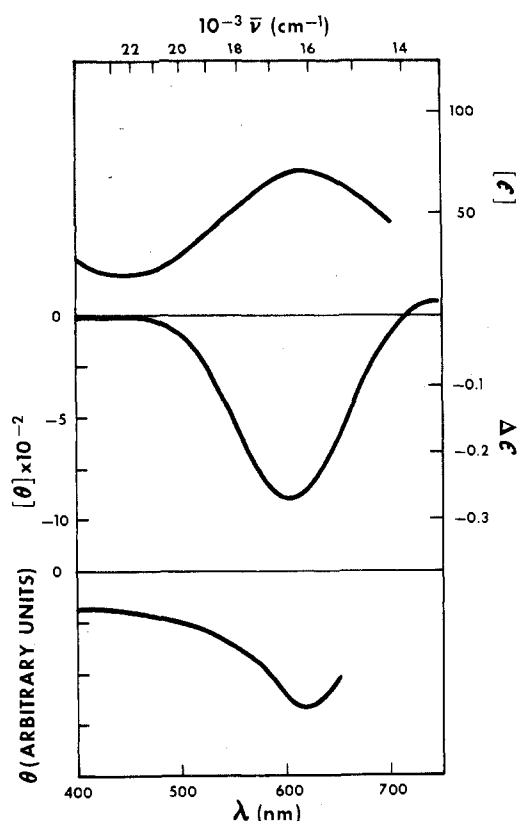


Figure 3. From top to bottom the visible, solution CD (DMSO), and solid CD (KBr) spectra of **3** are shown.

in which only glycine-like coordination is possible.⁹ These complexes are usually characterized in the $d \rightarrow d$ absorption region by a relatively large negative CD maximum at 600–630 nm and a weak positive CD maximum at higher wavelengths. A digital-curve resolving program has resolved the experimental CD curve into two gaussian bands, a negative CD band at 604 nm ($[\theta] = -900$) and a positive CD band at 713 nm ($[\theta] = +240$). If we assign these maxima to the two allowed $d \rightarrow d$ transitions, $d_{xy} \rightarrow d_{xz,yz}$ and $d_{xy} \rightarrow d_{x^2-y^2}$, respectively, then $\Delta_1 = 14,025 \text{ cm}^{-1}$ and $\Delta_2 = 16,550 \text{ cm}^{-1}$ which are consistent with the esr g_{\parallel} and g_{\perp} values for a value of the orbital reduction factor $k = 0.75$. Hawkins and Wong¹⁰ have suggested that when three CD bands are observed between 800 and 400 nm they are probably due to the magnetic dipole allowed transitions $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{xz}$, d_{yz} , respectively. If this is correct, the presence of only two CD bands for **3** indicates that this complex does not deviate appreciably from D_{2h} symmetry in agreement with the esr results. Finally the similarity of the solid-state CD spectrum (KBr) to that of the solution spectrum (DMSO) suggests the same glycine-like coordination of **3** in both solid and solution.

Mid- and Far-Infrared and Raman Spectroscopy. The solid 2:1 complex **3** was examined in the mid- and far-infrared regions as well as in the Raman. Table II summarizes the data for 2-PEC and **3**. Our data show that the pyridyl nitrogen is not involved in binding to the copper(II) ion, since the ring breathing vibration (992 cm^{-1}) in **3** is not shifted from its value in 2-PEC (995 cm^{-1}). When the pyridyl ring nitrogen is complexed with a metal, we have observed that the ring breathing mode shifts to 1015 cm^{-1} .⁴ This finding for **3** is also consistent with our nmr data. The

(9) B. C. Varma and Y. P. Myer, *Bioinorg. Chem.*, **1**, 141 (1972).

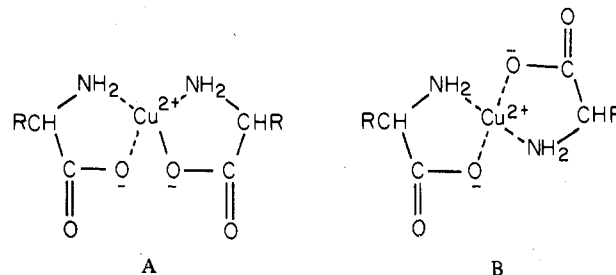
(10) C. J. Hawkins and C. L. Wong, *Aust. J. Chem.*, **23**, 2237 (1970).

Table II. Infrared and Raman Data for 2-PEC and Complex **3**

2-PEC ^a	Complex 3 ^b	Assignment
	3290 vw ^c	NH str
	3240 w	
3000 s, br	1620	NH ₃ ⁺ str
	1595 m (R)	C=O str
1580 s, br	1565 m (R)	Pyridyl ring str
		Antisym COO ⁻ str
1490 s		Pyridyl ring str
1472 sh	1472 m	NH ₃ ⁺ def
1442 m	1442 m	} Pyridyl ring str, C-H bend
1410 s		
1050 w	1050 w (R)	Sym COO ⁻ str
995 w	992 s (R)	Disubst ring def C-H bend
540 m		Monosubst ring breathing
458		COO ⁻ rock
410	410	
396		
	380	} Antisym str M-N (?)
	335	
	325	
324	265	vw (ir)
292	258	m (R); w (ir), sym M-N str (?)
250	234	
210	210	
	196	

^a Measured in KBr (mid). ^b Measured in KBr (mid) and in Nujol with polyethylene plates (far). Raman were run as solids. ^c Key: s, strong; m, medium; w, weak; br, broad; ir, infrared; R, Raman; ?, questionable assignment (see text).

antisymmetric carboxylate stretch in 2-PEC (1580 cm^{-1}) disappears upon chelation and a new band appears at 1620 cm^{-1} which we attribute to the carbonyl stretch of the chelated carboxylate group.^{11–13} Nakagawa and coworkers¹¹ assigned an infrared band at 394 cm^{-1} to a copper–nitrogen antisymmetric stretching mode for a copper–valine (1:2) complex using an approximate normal-coordinate analysis to support their conclusion. Their calculation shows that this mode is not pure (*ca.* 37% M–N stretch in the potential energy distribution). These metal–nitrogen antisymmetric and symmetric stretching modes have been used to determine the configuration of amino and carboxylate groups around various metal atoms. For instance, the M–N stretching modes (antisymmetric and symmetric) have been assigned to bands at 332 and 275 cm^{-1} for a cis copper–glycine complex (chelate A) and 332 cm^{-1} for the corresponding trans complex^{14a} (chelate B). Also the copper complex of iso-



leucine^{14b} had bands at 431 and 357 cm^{-1} which were assigned to the antisymmetric and symmetric M–N stretching modes. This complex was then assigned a cis configuration

(11) I. Nakagawa, R. J. Hooper, J. L. Walter, and T. J. Lane, *Spectrochim. Acta*, **21**, 1 (1965).

(12) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 4528 (1961).

(13) See ref 1, Chapter 4, p 216.

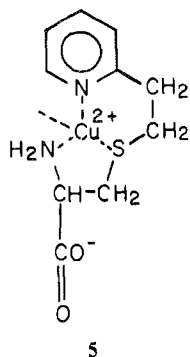
(14) (a) T. J. Lane, J. A. Durkin, and R. J. Hooper, *Spectrochim. Acta*, **20**, 1013 (1964); (b) R. J. Hooper, T. J. Lane, and J. L. Walter, *Inorg. Chem.*, **3**, 1568 (1964).

based on the above-mentioned M-N stretching modes.

The far-infrared spectrum of 2-PEC shows many bands in the region below 500 cm^{-1} (see Table II) and it is quite clear that this region has undergone dramatic changes upon chelation. However, we hesitate to assign any single band to the copper-nitrogen stretching modes in view of the probable extensive mixing of this coordinate with other skeletal vibrations of the five-membered ring chelate of **3**. We therefore cannot assign **3** a cis or trans configuration based upon the tenuous data we have for the copper-nitrogen stretching modes.¹⁵

Conclusions

It is evident from this study that the sites which participate in metal binding, in ligands with multicoordination sites, depend upon the geometry of the ligands around the metal, *i.e.*, square planar as with copper(II). Thus for steric reasons usually only two binding sites can coordinate with copper(II) in multidentate ligands such as histidine² or (*S*)-methylcysteine³ in order to maintain a square-planar D_{2h} configuration. However, 2-PEC is unusual in that it has the possibility of coordinating as a tridentate ligand with the pyridyl nitrogen, sulfur, and amino groups participating in a square-planar configuration **5**.¹⁶



Our results concerning this type of configuration are negative, since the solution spectra (nmr, esr, CD) do not indicate participation of the pyridyl nitrogen or the thioether group in binding to copper(II). A configuration such as **5** would result in a 1:1 Cu(II)-2-PEC complex, since sterically a second ligand would find only one coordination site available. This would be an unfavorable situation and could be the reason that 2-PEC binds in a glycine manner and does not form mixed complexes as in the case of histidine² or (*S*)-methylcysteine.³

It is noteworthy to mention that 2-PEC does form a nine-membered ring chelate with mercuric chloride, which involves the pyridyl nitrogen and the amino group but does not include the thioether group.⁴ In this instance, changing the geometry of the chelate (presumably tetrahedral) dramatically changes sites which bind the metal.

We are continuing our studies of 2-PEC with other metals and hope to clarify further the relationship between the ligand configuration and the metals involved in chelation.

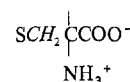
Experimental Section

Instrumentation. The nmr spectra were recorded on a Varian HA-100. The solutions 2-PEC (0.2 *M* in D_2O) were adjusted to the appropriate pD (pD = pH + 0.4) with 0.3 *N* sodium deuterioxide using a Beckman Model G pH meter. Thus 0.9 ml of the ligand (pD 2.4, 8.3, 10.3) and 0.4 ml of a copper chloride dihydrate solu-

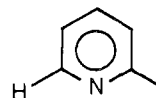
tion at concentrations of 2×10^{-4} and 1×10^{-3} *M* were placed in an nmr tube along with *tert*-butyl alcohol as an nmr internal standard, and the spectra were recorded at 31° . The sample preparation, including pD adjustments, were carried out in a drybox. The infrared spectra (mid and far) were recorded on a Cary White 90 (KBr) and a Beckman IR-11 (Nujol with polyethylene plates). The Raman spectra (solid) were recorded on a Spex 1401 equipped with a Coherent Radiation argon ion laser operating at 4880 and 5145 Å. The visible spectra were recorded on a Cary 15 in dimethyl sulfoxide, while the circular dichroism spectra were recorded on a Cary 60 modified for CD. The curve fitting for CD spectrum of **3** was done on an IBM 1800 computer using an IBAL program written by J. R. S. The esr were recorded on a Varian E3 spectrometer in dimethyl sulfoxide at 328 and 77°K .

The *g* values were determined by comparison with samples of known *g* value and are estimated to be good to ± 0.002 .

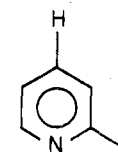
Preparation of (*S*)- β -(2-Pyridylethyl)-L-cysteine (2-PEC).¹⁷ In a 100-ml round-bottom flask equipped with a magnetic stirring bar was placed 5.0 g (0.048 mol) of 2-vinylpyridine (Aldrich) and 5.8 g (0.048 mol) of *L*-cysteine (Cyclo) along with 4.85 g (0.048 mol) of triethylamine dissolved in 50 ml of distilled, deionized water that was saturated with nitrogen gas. The reaction mixture was stirred for 24 hr at room temperature. The water was then removed on a rotary evaporator (50°) and the residue was recrystallized from 95% ethanol to give 8.0 g (75%) of white needles, mp $199\text{--}201^\circ$ (lit.¹⁷ mp $165\text{--}166^\circ$). The nmr spectrum at pD 7.5 (D_2O , 2,2,3,3-tetradeuterio-3-trimethylsilylpropionic acid sodium salt as the internal standard) is as follows: -CH-, 3.89 ppm (quartet);



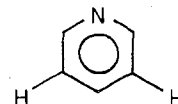
3.03 ppm (multiplet); -CH₂CH₂S-, 3.03 ppm (multiplet);



8.45 ppm (doublet, $J_{\text{ortho}} = 6.0\text{ Hz}$);



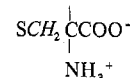
7.82 ppm (triplet, $J_{\text{ortho}} = 7.0\text{ Hz}$, $J_{\text{meta}} = 2.0\text{ Hz}$);



7.33 ppm (multiplet) with integrated areas of 1:6:1:1:2.

Anal. Calcd for $C_{10}H_{14}N_2OS$: C, 53.08; H, 6.24. Found: C, 53.0; H, 6.28.

Preparation of *N*-Acetyl-(*S*)- β -(2-pyridylethyl)-L-cysteine. In a flask was placed 0.626 g (6.1×10^{-3} mol) of 2-vinylpyridine, 1.0 g (6.1×10^{-3} mol) of *N*-acetylcysteine, and 0.6 g (6.1×10^{-3} mol) of triethylamine in 20 ml of distilled, deionized water that was saturated with nitrogen gas. The reaction mixture was stirred at room temperature for 48 hr, after which the water was removed on a rotary evaporator. A thick oil remained, which, when placed in acetone and refrigerated, yielded white crystals, which were filtered and washed with cold acetone to give 0.8 g (50%), mp $121\text{--}123^\circ$, of product. By repeating this procedure of refrigerating the oil and removing the crystals yields to 80% were obtained. The 100-MHz nmr spectrum (in D_2O with 2,2,3,3-tetradeuterio-3-trimethylsilylpropionic acid sodium salt as the internal standard) is as follows: -CH-, 4.35 ppm (quartet);

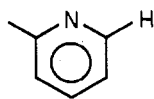


(17) M. Friedman and A. Noma, *Textile Res. J.*, **40**, 1073 (1970).

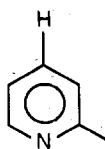
(15) D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968, p 281.

(16) We wish to acknowledge a referee for helpful comments concerning several points in our conclusions.

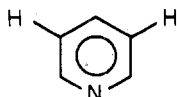
3.0 ppm (multiplet); $-\text{CH}_2\text{CH}_2\text{S}$, 3.0 ppm (multiplet);



8.50 ppm (doublet, $J_{\text{ortho}} = 8.0$ Hz, $J_{\text{meta}} = 2.0$ Hz);



8.04 ppm (triplet, $J_{\text{ortho}} = 8.0$ Hz, $J_{\text{meta}} = 2.0$ Hz);



7.50 ppm (multiplet);



2.02 ppm (singlet).

Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{SO}_3$: C, 53.73; H, 5.97; N, 10.45. Found: C, 53.90; H, 6.04; N, 10.41.

Preparation of the Copper(II) Complex of 2-PEC (1:2), 3.¹⁸

Procedure A. In a flask was placed 0.9 g (4 mmol) of 2-PEC dissolved in 3 ml of distilled deionized water. To this was added 0.170 g (1 mmol) of copper(II) chloride dihydrate. The blue-green 2:1 complex, 3, immediately precipitated out of solution and was filtered and dried under vacuum to give 0.5 g in 97% yield.

Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{N}_4\text{O}_4\text{S}_2\text{Cu}$: C, 46.7; H, 5.05; N, 10.9; Cu, 12.4. Found: C, 46.6; H, 4.93; N, 10.8; Cu, 12.1.

Procedure B. A procedure similar to A was used, except that 2 mmol of 2-PEC was allowed to react with 1 mmol of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The complex 3 was precipitated out of solution at pH 8 using 0.1 *N* sodium hydroxide. The yield was 95% and the complex was similar to that formed in procedure A.¹⁹

Registry No. 2-PEC, 29567-83-7; *N*-acetyl-(*S*)- β -(2-pyridylethyl)-L-cysteine, 38402-54-9; 2-vinylpyridine, 100-69-6; *N*-acetylcysteine, 616-91-1; triethylamine, 121-44-8; 3, 38402-55-0.

(18) We wish to acknowledge G. Secor, M. Long, and E. Ducaj for elemental analyses.

(19) Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

Contribution from the Department of Industrial Chemistry, Ehime University, Matsuyama, Japan, and the Department of Chemistry, Osaka University, Osaka, Japan

Stereochemistry and Circular Dichroism of Cobalt(III) Complexes with a Tripod-Like Ligand Having Nonidentical Feet. Geometrical and Optical Isomers of Potassium (*N,N*- β -Alaninadiacetato)(α -aminocarboxylato)cobaltate(III)

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Fourteen new *trans*(*N*)- and *cis*(*N*)-(*N,N*- β -alaninadiacetato)(α -aminocarboxylato)cobaltate(III) ions have been prepared and isolated as their potassium salts, where the α -aminocarboxylate is glycinate, *S*-alaninate, or *S*-proline. The isomers with respect to the arrangement of three feet of a tripod-like *N,N*- β -alaninadiacetato ligand have been separated by optical resolution, fractional crystallization, or ion-exchange column chromatography and characterized by electronic absorption, proton nuclear magnetic resonance, and circular dichroism spectra. The additivity of two kinds of circular dichroism contributions, the one from the arrangement chirality of *N,N*- β -alaninadiacetato ligand and the other from the vicinal chirality of optically active α -aminocarboxylato ligand, has been discussed.

Introduction

There have been many studies concerning the circular dichroism (CD) spectra in the region of first and second d-d spin-allowed absorption bands of optically active Co(III) complexes, which have "configurational" contribution due to a chiral configuration of the tris-chelate¹ or bis-chelate² type around the central Co(III) ion and which have "vicinal" contribution due to optically active ligands, *i.e.*, unidentate³ or bidentate⁴⁻⁶ amino acids or diamines,⁷ or

which have both the contributions operating additive.^{8,9}

In a previous paper,¹⁰ we reported the CD spectra of *trans*(*N*)- and *cis*(*N*)-((*S*)- or (*R*)-*N,N*-alaninadiacetato)-((*S*)- α -aminocarboxylato)cobaltate(III) ion, which had two kinds of vicinal and no configurational chirality, and recognized a good additivity between the two vicinal CD contributions.

In a similar complex containing a tripod-like quadridentate ligand which has nonidentical feet, *N,N*- β -alaninadiacetato ion, three kinds of structure are possible for the arrangement of chelate rings of the tripod-like ligand as shown in Figure 1.

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