direction for the third step than for the other two), consistent with the fact that Cu(sal–his) already has built in the potential for strong axial ligation once the equatorial plane becomes an N_2O_2 coordination sphere. The large difference between parameters with dry dioxane and aqueous dioxane solutions with *N*-MeIm suggests an important role for axial solvation by water, in addition to *N*-MeIm in the mixed-solvent system. Thus this system most nearly approaches that of a six-coordinate tetragonal geometry.

The EPR spectra of the Cu(sal–his) and Cu(sal–hm) complexes with *N*-MeIm in aqueous dioxane, though they have rather different values of $g_{\parallel}$ and $|A_{\parallel}|$ (Table II, Figure 3, and Figure 5, triangle I), are unique among all of those seen in this study in that they are axial and yet have no extra absorption peak. They also have well-resolved nitrogen shfs from up to three and what appears to be equal numbers of coordinated nitrogens. The absence of these features in the case of Cu(sal–gly) and Cu(sal–lysAc) with *N*-MeIm in aqueous dioxane solutions suggests a difference in the coordination sphere of Cu(II) from that in the solutions of Cu(sal–his) and Cu(sal–hm). Possible differences include (a) deprotonation of the histidine imidazole nitrogens of these two multidentate ligands in the presence of *N*-MeIm, a stronger Lewis base ($pK_a(BH^+) = 7.33$[73]) than pyridine, (b) a change in magnetic axis system so as to place three nitrogens in the x–y plane of Cu(sal–his) + *N*-MeIm to interact with the unpaired electrons in the $d_{x^2-y^2}$ orbital, thus placing the phenolate and carboxylate oxygens on the z magnetic axis, and (c) the interchange of imidazole and carboxylate groups in Cu(sal–his) in the presence of *N*-MeIm to provide a "histamine-like" coordination mode of the sal–his ligand, thus placing the carboxylate oxygen on the z axis. The last case should reverse the sense of the CD spectra. Although such reversal was not observed in the CD spectrum of Cu(sal–his) + *N*-MeIm at room temperature, the lability of the coordination sphere of Cu(II) could permit switching of the coordination mode of the sal–his ligand as the solution is frozen, if thermodynamic factors favor the "histamine-like" mode in the presence of *N*-MeIm at low temperatures. Each of these possibilities provides a plausible explanation for the similarity in the appearance of the EPR spectra of Cu(sal–his) and Cu(sal–hm) in the presence of *N*-MeIm, while not requiring them to have identical values of $g_{\parallel}$ and $|A_{\parallel}|$. In the absence of other physical data obtained in the same solvent system at the same low temperature, it is not possible to differentiate among these possibilities.

In any case, it appears from these results that the branched tetradentate nature of the sal–his ligand, together with the unique coordinating properties of its imidazole nitrogen, confers special reactivity upon its complex with Cu(II) and the further adducts formed with Lewis bases such as pyridine and *N*-methylimidazole. These spectral features are different from those present in tridentate vitamin B_6 model complexes, those either lacking the imidazole (Cu(sal–gly)) or containing it in place of the carboxylate (Cu(sal–hm)), and therefore must be considered in further studies of these models.

Acknowledgment. The support of the NSF (Grant No. CHE-79-18217) and NIH RCDA (Grant No. 5 KO4 GM 00227) is gratefully acknowledged. We wish to thank Dr. N. D. Chasteen for providing the program EPRPOW and for helpful comments concerning its use, Ronald D. Guiles for adapting the program to the CDC computer at San Francisco State and for carrying out the EPR spectra simulations, and Dr. Rollie J. Myers for providing access to the Calcomp plotter at the University of California, Berkeley, CA.

Registry No. Cu(sal–gly), 18534-56-0; Cu(sal–lysAc), 86994-30-1; Cu(sal–his), 64254-72-4; Cu(sal–hm)(OH), 86994-31-2; Cu(sal–hm$^-$), 86994-32-3.

Contribution from the Department of Macromolecular Science, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan, and Chemical Research Institute of Nonaqueous Solutions,
Tohoku University, Sendai, Miyagi 980, Japan

Circular Dichroism and Magnetic Circular Dichroism Spectra of Tetrahedral Cobalt(II) Complexes of Thiophenolate, *o*-Xylene-α,α'-dithiolate, and L-Cysteine-Containing Oligopeptides

MICHIO NAKATA,[1a] NORIKAZU UEYAMA,[1a] AKIRA NAKAMURA,*[1a] TSUNENORI NOZAWA,[1b]
and MASAHIRO HATANO[1b]

Received December 10, 1982

Mononuclear Co(II) complexes of *o*-xylene-α,α'-dithiolate and thiophenolate, $[Co(S_2\text{-}o\text{-}xyl)_2]^{2-}$ and $[Co(SPh)_4]^{2-}$, which possess *terminal* thiolate to Co(II) bonds only, have been compared with a tetranuclear thiophenolate complex, $[(CoSPh)_4(\mu\text{-}SPh)_6]^{2-}$, possessing *bridging* as well as *terminal* thiolate ligations, by absorption and MCD spectra in order to elucidate the core structure of Co(II)–thiolate complexes. The cluster complex has shown a characteristic MCD spectrum for the $^4A_2(F) \rightarrow {}^1T_1(P)$ transition having weak negative Faraday effects at 600–900 nm in addition to a strong absorption due to the charge-transfer transition from *bridging* thiolates to the Co(II) ion at 500–600 nm. The CD and MCD spectra of Co(II) complexes of Z-Cys-Ala-Ala-Cys-OMe and Z-Ala-Cys-OMe (Z = benzyloxycarbonyl and OMe = methoxy) have been interpreted to indicate the presence of *terminal* and *bridging* cysteine thiolate ligands. The results have been compared to the CD and MCD spectra of Co(II)-substituted metallothionein, which has been known to have polynuclear clusters with *bridging* cysteine thiolates.

Introduction

The spectroscopic properties of Co(II) have been utilized as a spectroscopic probe for metal-binding sites in Co(II)-reconstituted metalloenzymes.[2] Among many spectroscopic methods, circular dichroism (CD) and magnetic circular dichroism (MCD) spectroscopies are powerful techniques for this purpose because they reflect electronic and chiroptical properties and, hence, the coordination geometry around the metal ion more sensitively than other methods.[3] Several authors have investigated CD and MCD spectra of Co(II)-

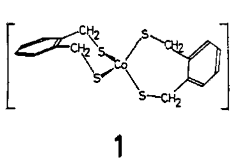
---

(1) (a) Osaka University. (b) Tohoku University.

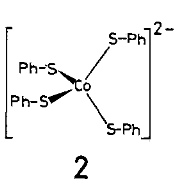
(2) (a) Sigel, H., Ed. *Met. Ions Biol. Syst.* **1974**, *4*. (b) Darral, D. W., Wilkins, R. G., Eds. *Adv. Inorg. Biochem.* **1980**, *2*.

(3) Vallee, B. L.; Holmquist, B. *Adv. Inorg. Biochem.* **1980**, *2*, Chapter 2.

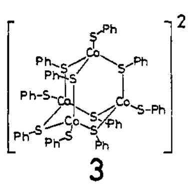
substituted metalloenzymes containing cysteine thiolate groups at metal-binding sites such as liver alcohol dehydrogenase,[3] rubredoxin,[4] blue copper proteins,[5] and metallothionein,[6] some of which possess amino acid sequences such as Cys-X-Y-Cys (X, Y = amino acid residues) to ligate the metal ion. Cobalt(II) complexes with simple thiolate ligands, e.g. *o*-xylene-α,α'-dithiolate (*o*-xyl-S_2^{2-})[7] and thiophenolate (PhS^-),[8,9] have been synthesized as inorganic models for these reconstituted enzymes. X-ray structural analyses and spectral studies of these complexes have revealed structures such as **1**–**3**.[7–9] Two of them, $[Co(S_2\text{-}o\text{-xyl})_2]^{2-}$ (**1**) and $[Co(SPh)_4]^{2-}$ (**2**), are mononuclear and the other, $[(CoSPh)_4(\mu\text{-}SPh)_6]^{2-}$ (**3**), is an adamantane-type cluster with bridging thiophenolates, all of which have approximately tetrahedral geometry around the Co(II) ion. MCD spectroscopy is expected to definitely reveal their structural differences, i.e., mononuclear from polynuclear. We have measured MCD spectra of **1**–**3** and compared their spectral features in relation to their structural characteristics.



1



2



3

From the viewpoint of bioinorganic chemistry, model studies of the peptide comlexes having active-site sequences such as Cys-X-Y-Cys are very important to clarify metal ion environment surrounded by protein ligands. We also report here MCD and CD spectral studies of Co(II) complexes of benzyloxycarbonyl-L-cysteinyl-L-alanyl-L-alanyl-L-cysteine methyl ester (Z-Cys-Ala-Ala-Cys-OMe) and benzyloxycarbonyl-L-alanyl-L-cysteine methyl ester (Z-Ala-Cys-OMe) as models for Co(II)-substituted metallothiolate proteins and discuss their structures in solution on the basis of absorption and MCD spectral features of the structurally known Co(II) thiolate complexes such as **1**–**3**. The results have been compared to the CD and MCD spectra of Co(II)-substituted metallothionein,[6] and their structural relationship have been discussed.

Experimental Section

All operations were carried out under argon or nitrogen atmosphere. *N,N*-Dimethylformamide (DMF) as a solvent for spectroscopic measurements and triethylamine were degassed and distilled before use. Cobalt(II) perchlorate hexahydrate was of commercial grade.

Preparation of Complexes. The Co(II) complexes $[Et_4N]_2[Co(S_2\text{-}o\text{-xyl})_2]$[7] (**1**), $[Me_4N]_2[Co(SPh)_4]$[8] (**2**), and $[Me_4N]_2[(CoSPh)_4(\mu\text{-}SPh)_6]$[8] (**3**) were prepared according to the literature methods. The cysteine-containing peptides Z-Ala-Cys-OMe and Z-Cys-Ala-Ala-Cys-OMe were prepared as previously described.[10] All amino acid residues used in this study were of the L configuration. Preparation of Co(II)/Cys-containing peptide complexes was carried out as follows: $Co(ClO_4)_2\cdot 6H_2O$ and 4 molar equiv of SH groups based on cysteine content of the corresponding peptide were dissolved in DMF. The addition of triethylamine to the solution gave a deep green solution, which was used for the spectroscopic measurement without further purification.

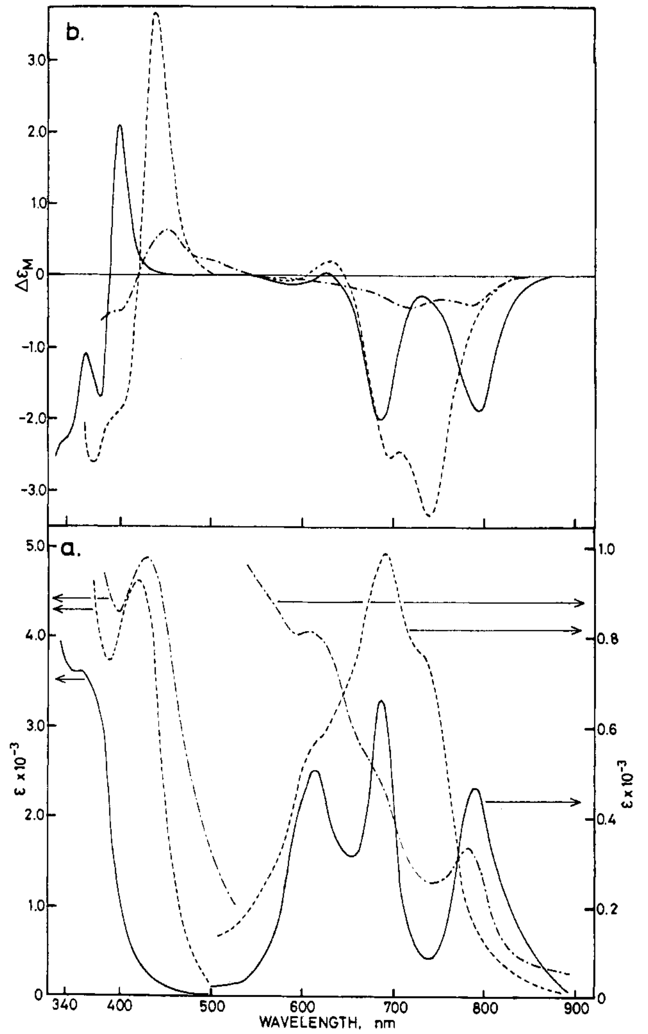


Figure 1. Near-UV-visible absorption (a) and MCD (b) spectra of Co(II) complexes of simple thiolate ligands in DMF and at room temperature: —, **1**; ---, **2**; –·–, **3**.

Physical Measurements. All spectra were measured in DMF solution. Absorption spectra at room temperature were recorded on a JASCO UVIDEC-5A and a Hitachi 323 spectrophotometer in the near-UV–visible and near-infrared regions, respectively. The CD and MCD spectra were measured with JASCO J-500C and J-200 spectropolarimeters[11] equipped with electromagnets in the near-UV–visible and near-IR regions, respectively. The magnetic field was calibrated by using aqueous $K_3[Fe(CN)_6]$ solution, $\Delta\epsilon_M$ (420 nm) 3.0.[12] Calibration of the spectropolarimeter was performed with an aqueous solution of (+)-camphor-10-sulfonic acid, $[\theta]$(290 nm) 7.8×10^3.[13]

The values of ϵ and $\Delta\epsilon$ are given in units of $M^{-1}\ cm^{-1}$, and $\Delta\epsilon_M$ is given in $M^{-1}\ cm^{-1}\ T^{-1}$ where M is the molar concentration of Co(II). In the case of Co(II)/Cys-containing peptide complexes, the MCD spectra were corrected for the zero-field circular dichroism.

Results

MCD spectra of a series of structurally known Co(II)–thiolate complexes, **1**–**3**, were examined. All of the complexes adopt approximately tetrahedral geometry around the Co(II) ion.[7–9]

Room-temperature absorption and MCD spectra of the Co(II)–thiolate complexes are presented in Figure 1 in the range 340–900 nm. The value of $\Delta\epsilon_M$ of **3** was about one-

---

(4) May, S. W.; Kuo, J.-Y. *Biochemistry* **1978**, *17*, 3333.

(5) (a) Solomon, E. I.; Rawlings, J. W.; McMillin, D. R.; Stephens, P. J.; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 8046. (b) McMillin, D. R. *Bioinorg. Chem.* **1978**, *8*, 179. (c) Tennent, D. T.; McMillin, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 2307.

(6) (a) Vašák, M. *J. Am. Chem. Soc.* **1980**, *102*, 3953. (b) Vašák, M.; Kägi, J. H. R.; Holmquist, B.; Vallee, B. L. *Biochemistry* **1981**, *20*, 6659.

(7) Lane, R. L.; Ibers, J. A.; Frankel, R. B.; Papaefthymiou, G. C.; Holm, R. H. *J. A. Chem. Soc.* **1977**, *99*, 84.

(8) Dance, I. G. *J. Am. Chem. Soc.* **1979**, *101*, 6264.

(9) Swenson, D.; Baenziger, N. C.; Coucouvanis, D. *J. Am. Chem. Soc.* **1978**, *100*, 1932.

(10) Ueyama, N.; Nakata, M.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1727.

(11) Nozawa, T.; Yamamoto, T.; Hatano, M. *Biochim. Biophys. Acta* **1976**, *427*, 28.

(12) Vickerly, L. E.; Nozawa, T.; Sauer, K. *J. Am. Chem. Soc.* **1976**, *98*, 351.

(13) Tuzimura, K.; Konno, T.; Megro, H.; Hatano, M.; Murakami, T.; Kashiwabara, K.; Saito, K.; Kondo, Y.; Suzuki, T. *Anal. Biochem.* **1977**, *81*, 167.

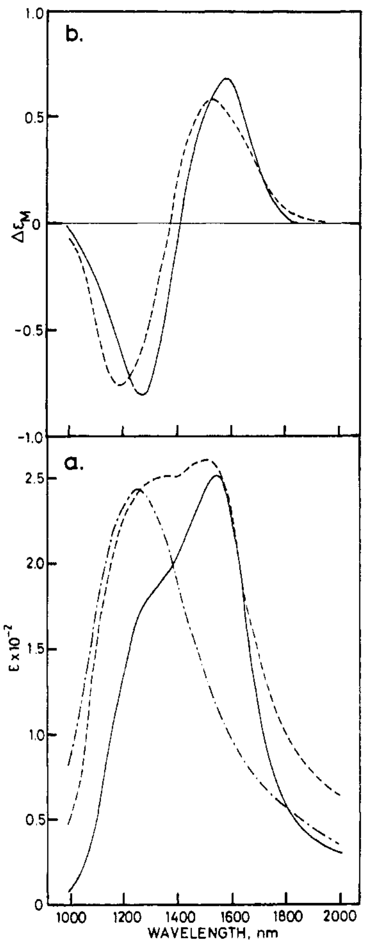


Figure 2. Near-IR absorption (a) and MCD (b) spectra of Co(II) complexes of simple thiolate ligands in DMF at room temperature: —, **1**; - - -, **2**; —·—, **3**.

fourth of that from the MCD spectrum of **2** whereas the ϵ vales were comparable in each case. Near-IR spectra of the Co(II) complexes are shown in Figure 2. In the case of a polynuclear complex, **3**, the MCD spectrum could not be observed with a reliable signal-to-noise ratio although the same experimental conditions used for the other two were employed ([Co(II)] ~2 $\times 10^{-2}$ M, cell length 0.1 cm, magnetic field strength 1.4 T, room temperature). The absorption and MCD spectral data of these Co(II) complexes are summarized in Table I. Figures 3 and 4 show absorption, MCD, and CD spectra of Co(II)/Cys-containing peptide complexes in the near-UV–visible and the near-IR regions, respectively, and these spectral data are also listed in Table II. Ligand field parameters[14] and optical electronegativities[5b,15] of various thiolate ligands for these Co(II) complexes were calculated according to literature methods and are listed in Tables III and IV, respectively.

Discussion

MCD Spectra of Co(II) Complexes of Simple Thiolate Ligands. We have measured absorption and MCD spectra of structurally known Co(II) complexes of *o*-xylene-α,α'-dithiolate and thiophenolate (**1–3**) for diagnostic purposes in determining the structures of Co(II) complexes of L-cysteine-containing peptides as discussed later.

Figures 1 and 2 show absorption and MCD spectra of **1–3** in DMF in the ranges 340–900 and 1000–2000 nm, respectively. Tetrahedral Co(II) complexes with the $^4A_2(F)$ ground state are expected to have ν_2 ($^4A_2(F) \rightarrow {}^4T_1(F)$) and ν_3($^4A_2(F)$

Table I. Absorption and MCD Spectral Data for Co(II) Complexes of Simple Thiolate Ligands[a]

complexes		$^4A_2(F) \rightarrow {}^4T_1(F)$		$^4A_2(F) \rightarrow {}^4T_1(P)$				$^4A_2(F) \rightarrow {}^2T_1$	S → Co(II) charge transfer				
$[Co(S_2\text{-}o\text{-xyl})_2]^{2-}$ (1)	abs	1550 (253)	1300 sh (182)	788 (468)	695 (663)		613 (505)						355 (3610)
	MCD	1580 (+0.68)	1270 (−0.80)	793 (−1.87)	686 (−2.00)	627 (+0.02)	616 (0)	588 (−0.11)			397 (+2.08)	378 (−1.69)	345 sh (−2.17)
$[Co(SPh)_4]^{2-}$ (2)	abs	1500 (260)	1350 (252)	730 sh (757)	690 (986)		615 sh (572)			420 (4620)			
	MCD	1530 (+0.57)	1180 (−0.76)	739 (−3.33)	695 (−2.52)	630 (+0.21)		585 (−0.05)		438 (+3.65)	400 sh (−1.35)	370 (−2.60)	
$[(CoSPh)_4(\mu\text{-SPh})_6]^{2-}$ (3)	abs		1265 (241)	782 (331)	690 sh (460)		610 (812)			428 (4880)			
	MCD			785 (−0.38)	715 (−0.43)	660 (−0.18)			500 (+0.21)	450 (+0.63)	400 (−0.49)		

[a] Data are expressed in units of nm in DMF at room temperature. The values in parentheses indicate ϵ and $\Delta\epsilon_M$ for absorption and MCD spectra, respectively.

---

(14) Cotton, F. A.; Goodgame, M. *J. Am. Chem. Soc.* **1961**, *83*, 1777.
(15) Jørgensen, C. K. *Prog. Inorg. Chem.* **1970**, *12*, 101.

Table II. Absorption, MCD, and CD Spectral Data for Co(II) Complexes of Cysteine-Containing Peptides[a]

complexes		$^4A_2(F) \to {}^4T_1(F)$			$^4A_2(F) \to {}^4T_1(P)$			S → Co(II) charge transfer				
Co(II)/Z-Cys-Ala-Ala-Cys-OMe	abs	1400 (163)	1200 (153)		750 (385)	690 (425)	610 (432)			386 (3450)		314 (4270)
	MCD	1540 (+0.15)	1140 (−0.17)		750 (−0.60)		615 (+0.01)	560 sh (+0.06)		425 (0.38)	330 (−0.78)	
	CD	1590 (+0.14)	1310 (−0.18)	825 (−0.23)	750 (+0.05)	710 (+0.04)	610 (+0.16)	530 sh (−0.08)	460 (−0.29)	376 (+0.83)	355 sh (+0.70)	315 (−0.49)
Co(II)/Z-Ala-Cys-OMe	abs	1400 (149)	1200 (164)		740 (505)	680 (475)	610 (440)				386 (3600)	326 (4450)
	MCD	1440 (+0.16)	1160 (−0.21)		730 (−0.66)	680 sh (−0.37)	615 (+0.03)		510 sh (0.09)	434 (0.19)		
	CD	1540 (−0.46)	1350 (+0.10)	850 (+0.04)	780 (+0.03)	700 (−0.13)	600 (+0.13)	550 sh (+0.06)	520 (+0.03)	445 (+0.08)	390 (−0.05)	350 (+0.13)

[a] Data are expressed in units of nm in DMF at room temperature. The values in parentheses indicate ϵ, $\Delta\epsilon_M$, and $\Delta\epsilon$ for absorption, MCD, and CD spectra, respectively.

Table III. Ligand Field Spectral Parameters (cm^{-1})[a]

complexes	ν_2	ν_3	Δ_t	B	ref
$[Co(S_2\text{-}o\text{-}xyl)_2]^{2-}$ (1)	6980[b]	14570[c]	4090	619	7
$[Co(SPh)_4]^{2-}$ (2)	6900[d]	14800[c]	4030	643	7
$[(CoSPh)_4(\mu\text{-}SPh)_6]^{2-}$ (3)	7910[d]	14540	4740	549	this work
Co(II)/Z-Cys-Ala-Ala-Cys-OMe	7630	14800	4520	591	this work
Co(II)/Z-Ala-Cys-OMe	7780	14890	4620	587	this work
Co(II)/Boc-(Gly-Cys-Gly)$_4$NH$_2$	7330[b]	15100[b]	4300	636	33

[a] Data calculated by averaging the position of MCD bands of $\nu_2(^4A_2(F) \to {}^4T_1(F))$ and $\nu_3(^4A_2(F) \to {}^4T_1(P))$ transitions. [b] Data calculated by using intensity-weighted $\nu_{2,max}$ or $\nu_{3,max}$ bands of absorption spectra. [c] Data calculated by averaging ν_3 bands of absorption spectra. [d] Data for single $\nu_{2,max}$ bands.

Table IV. Calculated Data for Charge-Transfer Spectra[a]

complexes	ν_{obsd}[b]	Δ(SPE)[b]	ν_{cor}[b]	χ_L
$[Co(S_2\text{-}o\text{-}xyl)_2]^{2-}$ (1)	25190[c]	5780	15320	2.4
$[Co(SPh)_4]^{2-}$ (2)	22830[c]	6000	12800	2.3
$[(CoSPh)_4(\mu\text{-}SPh)_6]^{2-}$ (3)	20000[c]	5120	10140	2.2
Co(II)/Z-Cys-Ala-Ala-Cys-OMe	17860[c]	5520	7820	2.2
Co(II)/Z-Ala-Cys-OMe	18180[c]	5490	8070	2.2
	19610[d]	5490	9500	2.2

[a] The values of Δ_t and B are in Table III. χ_M for the Co(II) ion is 1.9.[15] [b] These values are expressed in units of cm^{-1}. [c] Data from the lowest charge-transfer bands of MCD spectra. [d] Data from the lowest charge-transfer bands of CD spectra.

→ $^1T_1(P)$) in the near-infrared and visible regions, respectively. These bands are usually separated into several components by not only the spin–orbit coupling but also the dynamic Jahn–Teller effects.

The mononuclear Co(II) complexes, **1** and **2**, each have a pair of positive and a negative MCD bands in the near-infrared region. The MCD peaks of the cluster complex were not obtained in this region (see Results). It is noteworthy that well-defined MCD spectra in the near-infrared region cannot be obtained for this type of cluster complex under the experimental conditions used. Such a characteristic is important to identify core structures in solutions of Co(II)/Cys-containing peptides (see later).

Spin-allowed $^4A_2(F) \to {}^4T_1(P)$ transitions for tetrahedral Co(II) compexes were observed at 600–900 nm (Figure 1). Ligand field theory tells us that the $^4T_1(P)$ state splits into four sublevels (E′, $U_{3/2}'$, E″, and $U_{5/2}'$) by first- and second-order spin–orbit interactions.[16] Thus, four transitions are expected at 600–900 nm. In this region, we found three or four splittings in the absorption and MCD spectra of Co(II) complexes with simple thiolate ligands at room temperature (Figure 2 and Table I). The MCD spectra show these splittings more clearly.

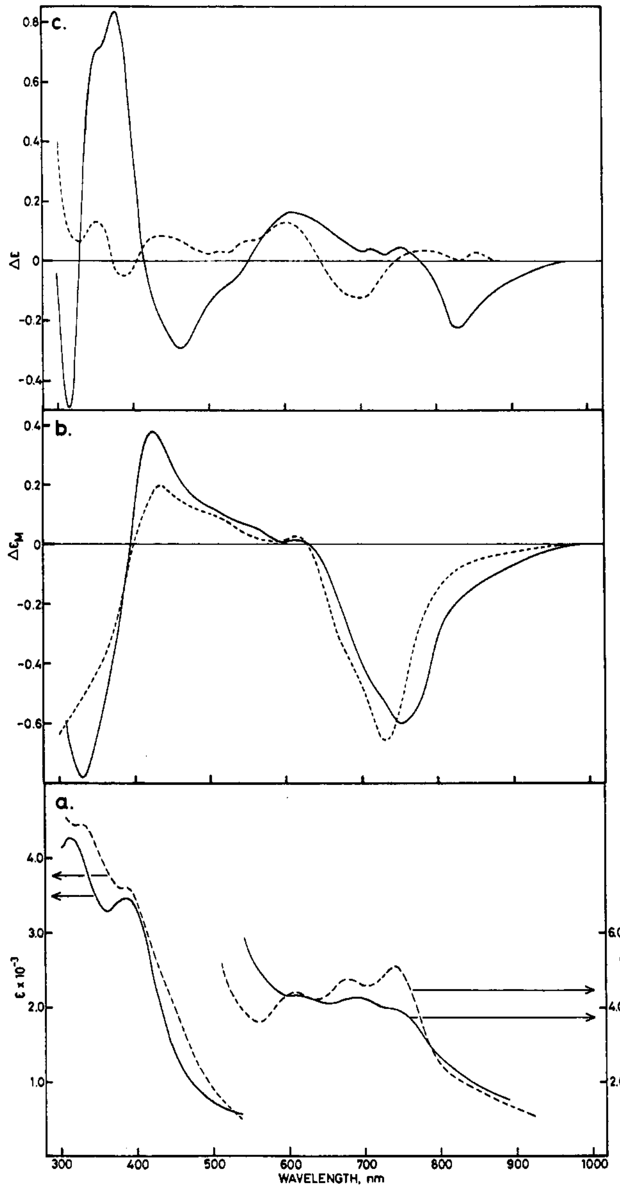


Figure 3. Near-UV–visible absorption (a), MCD (b), and CD (c) spectra of Co(II) complexes of cysteine-containing peptides in DMF at room temperature: —, Co(II)/Z-Cys-Ala-Ala-Cys-OMe complex; - - -, Co(II)/Z-Ala-Cys-OMe complex.

Much attention has been paid to this area of spectra (600–900 nm) of many Co(II) complexes having various ge-

---

(16) Weakliem, H. A. *J. Chem. Phys.* **1962**, *36*, 2117.

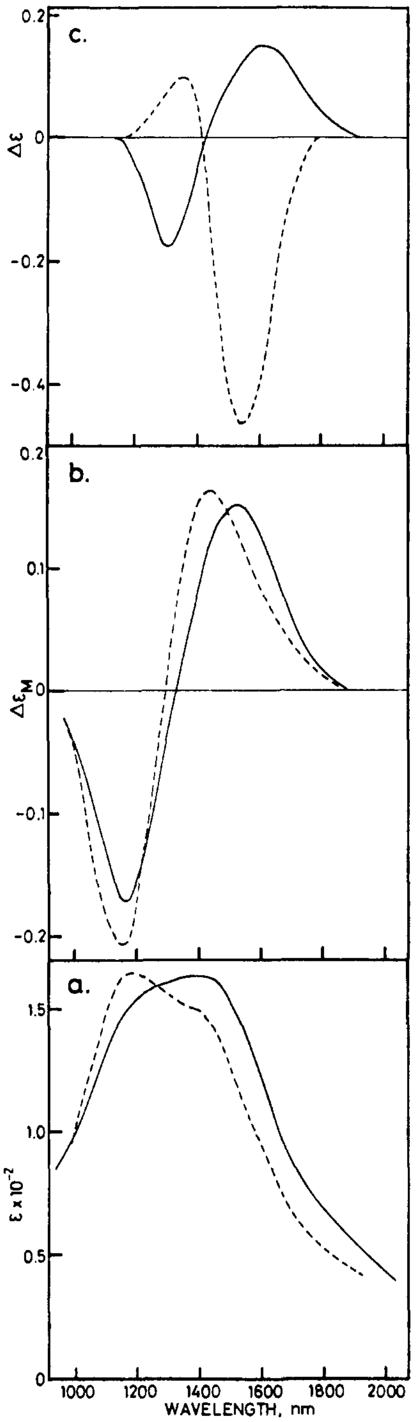


Figure 4. Near-IR absorption (a), MCD (b), and CD (c) spectra of Co(II) complexes of cysteine-containing peptides in DMF at room temperature: —, Co(II)/Z-Cys-Ala-Ala-Cys-OMe complex; ---, Co(II)/Z-Ala-Cys-OMe complex.

ometries and to Co(II)-substituted metalloenzymes by inorganic and biological chemists since the spectra in this area show characteristic features for Co(II) complexes having diverse coordination geometries. Vallee and Holmquist examined MCD as well as absorption spectra of a series of tetra-, penta-, and hexacoordinated Co(II) complexes in order to elucidate the relationships between MCD spectral characteristics and structures of Co(II) complexes in solution, and the results were utilized to infer coordination environment of Co(II)-reconstituted metalloproteins.[3,17] For diagnostic purposes, the band shapes of MCD spectra and sometimes their magnitudes are compared with those of reference samples.

The MCD spectra of the mononuclear complexes, **1** and **2**, exhibited two well-separated negative MCD bands in the 680–800-nm region and a much smaller positive one at ca. 620 nm as shown in Figure 1b. On the other hand, the cluster complex, **3**, did not show a positive one at 600–650 nm at room temperature. Most of the mononuclear Co(II) tetrahedral complexes so far examined exhibit positive MCD bands at the highest energy end of $^4A_2(F) \rightarrow {}^4T_1(P)$ transition.[17-20] This definitive difference between mononuclear and polynuclear complexes may also serve as a diagnostic for the solution structures of cysteine-containing peptide complexes of Co(II)(see later).

Using the transition energies estimated from the MCD spectra of **3** (Table I), we calculated the ligand field parameter Δ_t, and Racah's parameter B according to literature methods[14] where tetrahedral ligand field was assumed and spin–orbit interactions were neglected. The parameters are shown in Table III together with those of **1** and **2** calculated previously. The value of Δ_t for **3** is significantly larger than that of **2**. The smaller B value for **3** than for **2** indicates larger "nephelauxetic effect" in the cluster complex.

The weak negative MCD bands at 588 and 585 nm for **1** and **2**, respectively, are very likely to arise from the spin-forbidden transitions from the ground state to lower sublevels of the $^2T_1$ state.[18,21] In the case of **3**, these bands were obscured by the intense charge-transfer transitions.

The absorption at energy higher than that of the $^4A_2(F) \rightarrow {}^4T_1(P)$ transitions contains S → Co(II) charge-transfer transitions.[3-5,7,8] The polynuclear complex, **3**, exhibited broad intense absorption betwen 500 and 600 nm whereas the mononucler complexes did not have any substantial absorption in this region. This was also confirmed by the MCD spectra. Thus, the broad band in the range between 500 and 600 nm is attributed to the charge-transfer transition from *bridging* thiolates to Co(II) ion. Then, higher energy charge-transfer transitions below 500 nm may arise from charge transfer from the *terminal* thiolates to Co(II) whose MCD spectra indicate that they contain several components accompanying the charge-transfer transitions as shown in Figure 1b.

We have analyzed the charge-transfer spectra in terms of "optical electronegativities"[15] in order to estimate the difference in the ligand properties between *terminal* and *bridging* thiolates by using the lowest charge-transfer transition energies, the change in the spin-pairing energies accompanying the ligand-to-metal charge-transfer transition, and the ligand field parameter for a tetrahedral field.[5b,15] The calculated values of optical electronegativities of thiolate ligands, χ_L, are summarized in Table IV. The χ_L value of 2.4 for o-xyl-S_2^{2-} is in excellent agreement with the value of 2.40 for cysteine thiolate in Co(II)-substituted azurin.[5b,c] A slightly smaller value of χ_L for **3** (2.0) than for **2** (2.3) was obtained, which suggests stronger electron-donor ability of the *bridging* thiolate than that of the terminal one.

Detailed analyses of the MCD spectra of tetrahalide Co(II) complexes having tetrahedral geometry around the Co(II) ion have been done by several authors. Gale et al. have concluded that the Faraday effects of $^4A_2(F) \rightarrow {}^4T_1(F)$ transitions of several tetrahalide Co(II) complexes are attributable to the C term.[22] Denning and Spencer have studied MCD spectra of $[CoCl_4]^{2-}$ as a function of temperature and have revealed

---

(17) Kaden, T. A.; Holmquist, B.; Vallee, B. L. *Inorg. Chem.* **1974**, *13*, 2585.

(18) Kato, H.; Akimoto, K. *J. Am. Chem. Soc.* **1974**, *96*, 1351.

(19) Denning, R. G. *J. Chem. Phys.* **1966**, *45*, 1307.

(20) Denning, R. G.; Spencer, J. A. *Symp. Faraday Soc.* **1969**, *No. 3*, 84.

(21) Lomenzo, J. A.; Bird, B. D.; Osborne, G. A.; Stephens, P. J. *Chem. Phys. Lett.* **1971**, *9*, 332.

(22) Gale, R.; Godfrey, R. E.; Mason, S. F. *Chem. Phys. Lett.* **1976**, *38*, 446.

that the major contribution to the Faraday effect on $^4A_2(F) \rightarrow {}^4T_1(P)$ transitions is the *C* term.[20] Detailed studies on the $^4A_2(F) \rightarrow {}^4T_1(P)$ transitions in MCD spectra of tetrahedral Co(II) complexes other than tetrahalide complexes by Kaden et al.[17] and Kato and Akimoto[18] have also revealed that the major contribution to the Faraday effects is derived from the *C* term. From the temperature-dependent MCD study on $[CoI_4]^{2-}$ in the charge-transfer region by Bird et al., it has been also suggested that the major contribution to the Faraday effects in the charge-transfer transition is derived from the *C* term.[23] Considering the tetrahedral geometry of the Co(II) complexes of simple thiolates, **1** and **2**, and similarity of MCD spectral patterns among the Co(II) thiolate complexes and the well-defined tetrahedral Co(II) complexes,[17-20,22,23] we presume that the major contribution of the Faraday effects of the mononuclear complexes, **1** and **2**, in the whole region probably arises from the *C* term. In order to obtain precise information on the origin of the Faraday effects, however, the measurement of temperature-dependent MCD spectra will have to be done. In the case of the cluster complex, **3**, intramolecular spin coupling makes the assignment of the origin of Faraday effects more difficult.

Thus, MCD spectral differences between mononuclear and polynuclear Co(II) complexes of simple thiolate ligands have been clarified although more detailed studies such as quantitative evaluation of the Faraday parameters are to be done. The differences are related to differences in the number of *terminal* thiolate–Co(II) and *bridging* thiolate–Co(II) bonds involved in the Co(II) complexes. These MCD spectral characteristics will provide a diagnostic to identify the structures of Co(I) complexes of cysteine-containing peptides in solution as discussed in the next section.

Co(II) Complexes of Cysteine-Containing Peptides. The tetrapeptide sequences Cys-X-Y-Cys are frequently found for most metal thiolate proteins: Fe protein, *Clostridium pasteurianum* rubredoxin, Cys(6)-Thr-Val-Cys(9) and Cys(39)-Pro-Leu-Cys(42);[24] Zn protein, horse liver alcohol dehydrogenase (E chain), Cys(97)-Gly-Lys-Cys-Arg-Val-Cys(103),[25] and *Escherichia coli* aspartate carbamoyltransferase, Cys(137)-Lys-Tyr-Cys(140).[26] Conformational restriction due to the steric effects caused by side chains of two amino acid residues interposed between the two cysteine residues may contribute to the formation of chelate rings and determination of geometry around the metal ion. Previously, we reported spectral studies of Fe(III) complexes of Z-Cys-X-Y-Cys-OMe (X = Y = Ala, X = Pro, and Y = Leu) as rubredoxin models to obtain the basic information.[10,27]

For the model studies of isomorphous Co(II) replacement for metalloenzymes containing cysteine thiolate coordination, we have studied absorption, MCD, and CD spectra of Co(II) complexes of Z-Cys-Ala-Ala-Cys-OMe and Z-Ala-Cys-OMe over the range from 300 to 2000 nm where d–d transitions within the Co(II) ion and $S^- \rightarrow$ Co(II) charge-transfer bands are expected.

First, we discuss the absorption and MCD spectral characteristics of the Co(II) complexes of Z-Cys-Ala-Ala-Cys-OMe and Z-Ala-Cys-OMe. The absorption and MCD exhibited those of typical tetrahedral Co(II) complexes with four thiolate groups as shown in Figures 3 and 4. Similar spectral patterns were observed for Co(II) complexes of Z-Cys-Ala-Ala-Cys-OMe and Z-Ala-Cys-OMe in DMF. In the near-IR region (Figure 4), the distinct MCD bands attributable to the $^4A_2(F) \rightarrow {}^4T_1(F)$ transition, which resembled those of model complexes **1** and **2**, could be observed with a reliable signal-to-noise ratio under the conditions ([Co(II)] 2.0×10^{-2} M, cell length 0.1 cm, magnetic field strength 1.4 T, room temperature). This result suggests that a substantial amount of mononuclear Co(II) complexes or *terminal* thiolate–Co(II) bonds in the Co(II)/Cys-containing peptide systems exists even under the conditions of thiolate-to-metal ratio of 4. Thiolate ligands such as the thiophenolate anion have been known to form polynuclear complexes with *bridging* thiolate.[8] The formation of polynuclear complexes for a system containing Co(II) and cysteine with *bridging* thiolates was also reported by Garbett et al.[28] For the case of Z-Cys-Ala-Ala-Cys-OMe and Z-Ala-Cys-OMe as ligands, mononuclear Co(II) complexes were found to form in thiolate-to-metal ratio of 4. This is presumably caused by the steric hindrance of the peptide side chains. Positive Faraday effects at 615 nm (see Figure 3b) corresponding to an absorption maximum at 610 nm for the peptide complexes also support the presence of mononuclear species.

On the other hand, in the charge-transfer region (300–600 nm), the absorption and MCD spectra of the Co(II)/Cys-containing peptide complexes are similar to those of polynuclear complex **3**. Presence of a broad absorption tailing between 500 and 600 nm is indicative of coexistence of *terminal* and *bridging* thiolates from the similarities of absorption and MCD spectra between the peptide complexes and **3** in the charge-transfer region (Figures 1 and 3a,b). The higher energy S → Co(II) charge-transfer bands at 314 nm of the Co(II) complex of Z-Cys-Ala-Ala-Cys-OMe and at 326 nm of that of Z-Ala-Cys-OMe have molar extinction coefficients ϵ of 4270 and 4470 $M^{-1}\ cm^{-1}$, respectively. The S → Co(II) charge-transfer bands due to the Co(II)–SCH_2–moiety have been known to have molar extinction coefficients in the range of 900–1300 $M^{-1}\ cm^{-1}$ per Co(II)–S bonding.[4,6a,29,30] The presence of the $[Co^{II}(Cys\text{-}S)_4]^{2-}$ core is apparent according to the above criteria while the presence of a small amount of polynuclear cluster with *bridging* thiolate cannot be ruled out. The absorption maxima at 386 nm are due to a charge-transfer transition from thiolate to Co(II). The MCD bands between 400 and 500 nm also arise from the charge-transfer transitions from *bridging* thiolate to Co(II).

As mentioned above, the Co(II) complexes of Z-Ala-cys-OMe and Z-Cys-Ala-Ala-Cys-OMe seem to have rather complicated core structures. To our disappointment, despite close examination of absorption and MCD spectra, we could not state definitely the core structures of Co(IIe complexes of cyteine-containing peptides. However, at least, some spectral evidence, especially MCD spectra in the near-IR region and positive MCD bands at 615 nm, allows us to infer the peptide complexes have a substantial amount of Co(II)–*terminal* thiolate bonds, probably more than in the case of **3**.

In Table IV are also listed the optical electronegativities of cysteine-containing peptides, from the lowest energy charge-transfer bands and ligand field parameters (see later). The χ_L value of 2.2 for both peptides is smaller than that of 2.40 for cysteine thiolate,[5b,c] which indicates the presence of *bridging* thiolates.

Next, let us consider the CD spectra of the Co(II) complexes of Z-Cys-Ala-Ala-Cys-OMe and Z-Ala-Cys-OMe. Although

---

[23] Bird, B. D.; Briat, B.; Day, P.; Rivoal, J. C. *Symp. Faraday Soc.* **1969**, *No. 3*, 70.

[24] Orme-Johnson, W. H. *Annu. Rev. Biochem.* **1973**, *42*, 159.

[25] Eklund, H.; Nordström, B.; Zeppezauer, E.; Söderlund, G.; Ohlsson, I.; Boiwe, T.; Söderberg, B.-O.; Tapia, O.; Brändén, C.-I.; Åkeson, Å. *J. Mol. Biol.* **1976**, *102*, 27.

[26] Monaco, H. L.; Crawford, J. L.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 5276.

[27] Nakata, M.; Ueyama, N.; Nakamura, A. *Pept. Chem. 18th* **1981**, 195.

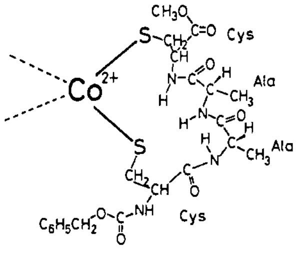
[28] Garbett, K.; Partridge, G. W.; Williams, P. J. *Bioinorg. Chem.* **1972**, *1*, 309.

[29] Drum, D. E.; Vallee, B. L. *Biochem. Biophys. Res. Commun.* **1970**, *41*, 33.

[30] McMillin, D. R.; Holwerda, R. A.; Gray, H. B. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 1339.

the absorption and MCD spectra of Co(II) complexes of the peptides did not show significant differences between the dipeptide and the tetrapeptide complexes, the CD spectra exhibited very different spectral patterns (Figures 3 and 4). The CD spectra of these Co(II) peptide compexes are more highly structured than the absorption and the MCD spectra. Therefore, the CD spectra have more structural information about the orientation of the asymmetric carbons in the peptide ligands among probabilities of the conformers of the peptide ligands around the central metal ion. In the charge-transfer region, the tetrapeptide complex shows much stronger Cotton effects than the dipeptide complex.

From the comparison of di- and tetrapeptide complexes, a macroring chelate structure is proposed for Co(II) complexes of Z-Cys-Ala-Ala-Cys-OMe:



The Z-Cys-Ala-Ala-Cys-OMe and Z-Ala-Cys-OMe complexes should have the same intrinsic chiralities, that is, L configuration around the α-carbons. The Cotton effects in the charge-transfer region originate from the chiral charge transfer from thiolate to Co(II) induced by the asymmetric carbons and are crucial for determining the CD spectral features. Monodentate coordination through cysteine thiolate is reflected in the CD spectra by the chiral effects averaged by thermal motion of the asymmetric center. Thus, the Z-Ala-Cys-OMe complex exhibits only weak Cotton effects. On the other hand, chelate ring formation with a bidentate ligand as Z-Cys-Ala-Ala-Cys-OMe restricts the thermal motion and, therefore, the orientations of the chiral centers are fixed in space. In such a case, large Cotton effects are expected. The chelate ring formation with Z-Cys-Ala-Ala-Cys-OMe is also supported by the fact that the tetrapeptide complexes of Fe(II) and Fe(III) exhibit CD spectra similar to that of native rubredoxin, in which two tetrapeptide Cys-X-Y-Cys units serve as bidentate chelates with cysteine thiolate coordination to the metal ion.[24,31]

The CD spectra of Co(II) complexes of the tetra- and dipeptide in the region of the ligand field transition, ${}^4A_2(F) \rightarrow {}^4T_1(F)$ and ${}^4A_2(F) \rightarrow {}^4T_1(P)$, were significantly different (Figures 3c and 4c). The intensities of the Cotton effects in these regions, however, did not exhibit the differences shown in the charge-transfer transition regions. Very interestingly, the CD pattern of the Co(II) complex of Z-Cys-Ala-Ala-Cys-OMe is entirely opposite in sign when compared with that of Z-Ala-Cys-OMe in the near-IR region. The different CD spectral propertie of Co(II) complexes of cysteine-containing peptides are explained by the difference of the orientations of dipole moments toward the central Co(II) ion between the tetra- and dipeptides. These CD differences also may be caused by subtle distortion of geometry around the Co(II) ion resulting from different coordination environments due to the peptide ligands.

For theoretical models of iron sulfur proteins, Bair and Goddard have studied the electronic properties of the active site of rubredoxin by ab initio methods.[32] They have used $[Fe(SH)_4]^{-/2-}$ as a model complex for the rubredoxin active site and examined several different sets of S–Fe–S–H dihedral angles and have found that the energy separation of the d–d transitions is sensitive to the dihedral angle of the Fe–S and S–H bonds. Their calculations have revealed that the changes of the dihedral angles altered ${}^5E \rightarrow {}^5T_2$ transition energies within 6% for their reduced rubredoxin models. Therefore, the Co(II) complexes of cysteine-containing peptides may have different ligand field parameters from each other.

For the purpose of meaningful comparison, the ligand field parameters Δ_t and B for Co(II) complexes of cysteine-containing peptides were calculated from the estimated values of $\nu_2({}^4A_2(F) \rightarrow {}^4T_1(F))$ and $\nu_3({}^4A_2(F) \rightarrow {}^4T_1(P))$. The data are presented in Table III. The calculated values for Δ_t of 4520 and 4620 cm^{-1} of the Co(II) complexes of Z-Cys-Ala-Ala-Cys-OMe and Z-Ala-Cys-OMe, respectively, indicate the presence of the weak ligand field of the cysteine thiolate groups and agree with the values found for Co(II) complexes with simple thiolate ligands.[7] When we consider the case of Co(II) complexes of Boc-(Gly-Cys-Gly)$_4$-NH_2[33] (Table III), the differences among them are roughly consistent with the results of the calculation by Bair and Goddard.[32] Thus, the identity of the amino acid residues interposed between two cysteine residues is important in regulating the electronic state of the central ion.

Core Structures in the Co(II) Complexes of Cysteine-Containing Peptides and Co(II) Metallothioneins. Interest lies in the striking similarities of the absorption and MCD spectral features between Co(II) complexes of cysteine-containing peptides and Co(II)-substituted metalloproteins. Native metallothioneins contain seven Zn(II) and/or Cd(II) ions per molecule. It has been postulated that the minimum metal-binding unit generally consists of three cysteine thiolate ligands per metal ion.[34] The ${}^{113}Cd$ NMR studies have given strong evidence that these units are forming polynuclear metal clusters, with some thiolates serving as *bridging* ligands.[35] Recently Vašák and his co-workers have reported spectroscopic studies of Co(II)-substituted metallothioneins including MCD and CD spectra and revealed that Co(II) ions are organized in clusters.[6,36]

The MCD spectra of Co(II) metallothioneins are as follows: Co(II)-substituted horse kidney metallothionein exhibited positive Faraday effects at 615, 420, and 253 nm and negative ones at 762, 687, 330, and 280 nm;[6a] (Co(II) rabbit liver metallothionein, positive ones at 628, 425, and 250 nm and negative ones at 757, 690, 373, 342, and 300 nm.[6b] From the comparison with the Co(II) complexes of cysteine-containing peptides (Table II), close similarities between them are apparent. These facts suggest strongly that similar core structures of Co(II)–cysteine thiolate complexes are present in Co(II)-reconstituted metallothioneins and Co(II) complexes of cysteine-containing peptides and that a substantial number of Co(II)–*terminal* cysteine thiolate bonds exist in the Co(II) metallothioneins. Further, the appearance of positive MCD bands at 615 and 628 nm of both Co(II) metallothioneins suggests that the Co(II)–thiolate clusters organized in Co(II) metallothionein have more Co(II)–*terminal* thiolate bonds than the cluster complex, **3**, has. This speculation is consistent with a recent finding by ${}^{113}Cd$ NMR techniques that rabbit metallothionein possesses two types of clusters.[35b]

---

[31] Ueyama, N.; Nakata, M.; Terakawa, T.; Nakamura, A., to be submitted for publication.

[32] Bair, R. A.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1977**, *99*, 3505.

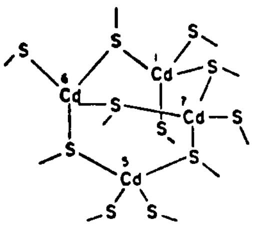
[33] Anglin, J. R.; Davison, A. *Inorg. Chem.* **1975**, *14*, 234.

[34] Kojima, Y.; Berger, C.; Vallee, B. L.; Kägi, J. H. R. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 3413.

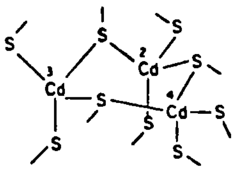
[35] (a) Salder, P. J.; Bekka, A.; Beyon, P. J. *FEBS Lett.* **1978**, *94*, 315. (b) Otvos, J. D.; Armitage, I. M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 7094.

[36] Vašák, M.; Kägi, J. H. R. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 6709.

Cluster A



Cluster B



Similarities of the absorption and MCD spectra between Co(II) complexes of cysteine-containing peptides and Co(II) metallothioneins suggest the presence of a similar type of cluster, postulated by Otvos and Armitage[35b] for the Co(II) complexes of cysteine-containing peptides.

The calculated ligand field parameter Δ_t (4780 cm^{-1}) for Co(II)-substituted rabbit metallothionein[65] is comparable to those of 3 and Co(II) complexes of cysteine-containing peptides, indicating cluster formation (Table III). Using the ligand field parameters ($\Delta_t = 4780$ cm^{-1} and $B = 624$ cm^{-1}) and the lowest charge-transfer energy ($\nu_{obsd} = 17\,240$ cm^{-1}) estimated from the MCD band at 580 nm for rabbit metallothionein,[6b] we obtained the optical electronegativity, χ_L, of cysteine thiolate (*terminal* and *bridging*) for the metallothionein as 2.1. This value is in agreement with those of 3 and Co(II) complexes of Z-Cys-Ala-Ala-Cys-OMe and Z-Ala-Cys-OMe (Table IV) and is significantly smaller than the χ_L value, 2.40, for *terminal* cysteine thiolate previously reported.[5b] This fact also indicates the presence of *bridging* thiolates.

Next, let us consider CD spectra of Co(II) metallothioneins in comparison with those of Co(II) complexes of cysteine-containing peptides. Much stronger Cotton effects have been observed in the *charge-transfer transition region* for Co(II) metallothionein than in the $^1A_2(F) \rightarrow {}^4T_1(P)$ transition region.[6b] This is consistent with the CD spectral feature found for the Co(II) complex of Z-Cys-Ala-Ala-Cys-OMe shown in Figure 3c. These are presumably due to the chelating effects of Cys-X-Cys and/or Cys-X-Y-Cys units on the metal ion since the Co(II) complex of Z-Ala-Cys-OMe exhibited weak Cotton effects at the charge-transfer region.

Finally, we have demonstrated through this work that the combination of CD and MCD spectroscopies is superior to sole utilization of absorption spectroscopy for elucidation of the geometry around the metal ion and that CD spectra provide interesting information about the dynamic contribution of ligand conformations to the electronic states of metal ions. The model studies using optically active peptide ligands are important to the understanding of active site structures of metalloenzymes.

Registry No. 1, 61896-95-5; 2, 47610-67-3; 3, 57659-25-3.

Contribution from the Department of Chemistry,
University of Southern California, Los Angeles, California 90089-1062

Synthesis, Kinetics, and Photochemistry of the Chromium(III) Dicyano-Aquo-Ethylenediaminetetraacetate Complex

ZHONG CHEN,[1] MARC CIMOLINO, and ARTHUR W. ADAMSON*

Received February 11, 1983

A new EDTA complex of Cr(III) is described, $Na_3[Cr(Y)(CN)_2(H_2O)]\cdot 4H_2O$, where Y denotes ethylenediaminetetraacetate or EDTA. The EDTA ligand is terdentate in this complex, three of the carboxyl groups being uncoordinated. The complex undergoes pH-dependent aquation of the cyano groups, the rate-determining step being the reaction of $Cr(YH)(CN)_2(H_2O)^{2-}$, followed by rapid loss of the second cyano group. The acid dissociation constant of the YH complex is 2.55×10^{-6} M at 20 °C and 1 M ionic strength, and the rate constant at 20 °C and activation parameters for the slow step are 2.55×10^{-2} M^{-1} s^{-1}, $\Delta H^{\circ\ddagger} = 18.9$ kcal mol^{-1}, and $\Delta S^{\circ\ddagger} = -1.4$ cal mol^{-1} K^{-1}. It is suggested that internal hydrogen bonding of the protonated carboxyl group in $Cr(YH)(CN)_2(H_2O)^{2-}$ may assist the aquation. The complex $Cr(Y)(CN)_2(H_2O)^{3-}$ undergoes photoaquation of cyanide with a quantum yield of 0.018 at 20 °C and pH 7.6, with 514-nm excitation. The pH dependence of ϕ indicates that the protonated form cannot be significantly more photoactive than the unprotonated one. Emission from aqueous solution is weak and of lifetime less than 15 ns at 10 °C. The photochemical and emission behavior is compared with expectations from the photochemistry and emission rules for Cr(III) complexes.

Introduction

A complex of Cr(III) and EDTA, ethylenediaminetetraacetate or Y^{4-}, was first reported by Brintzinger et al.[2] in 1943. The complex was later shown not to be sexidentate but rather to have the formula $Cr(YH)(H_2O)$,[3] YH denoting the EDTA ligand with one of the carboxyl groups unattached and protonated. Later, Hamm[4] studied the acid-base equilibrium $Cr(YH)(H_2O) = Cr(Y)(H_2O)^-$. That the water in $Cr(YH)(H_2O)$ is indeed coordinated has been confirmed by a crystal structure determination.[5] Although the existence of the sexidentate complex has been proposed, Thorneley et al.,[6] in an extensive study of acid-base and related equilibria, were unable to find evidence for the CrY^- species.

The EDTA complexes of Cr(III) are interesting because of the several states of partial coordination that are found. Some of the associated equilibrium constants are given as follows:

$$Cr(YH)(H_2O) = CrY(H_2O)^- + H^+ \qquad pK_a = 3.1 \qquad (1)^4$$

$$Cr(Y)(H_2O)^- = CrY(OH)^{2-} + H^+ \qquad pK_a = 7.5 \qquad (2)^{3,4}$$

$$Cr(YH_2)(H_2O)_2^+ = Cr(YH)(H_2O)_2 + H^+ \quad pK_a = 2.49 \qquad (3)^5$$

$$Cr(YH)(H_2O)_2 = Cr(Y)(H_2O)_2^- + H^+ \quad pK_a = 2.92 \qquad (4)^5$$

---

[1] Permanent address: Shandong University, Jinan, Shandong, China.

[2] Britzinger, H.; Thiele, H.; Müller, U. *Z. Anorg. Allg. Chem.* **1943**, *251*, 285.

[3] Schwarzenbach, G.; Biedermann, W. *Helv. Chim. Acta* **1948**, *31*, 459.

[4] Hamm, R. E. *J. Am. Chem. Soc.* **1953**, *75*, 5670.

[5] Gerdom, L. E.; Baenziger, N. A.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 1606.

[6] Thorneley, R. N. F.; Sykes, A. G.; Gans, P. *J. Chem. Soc. A* **1971**, 1494.

0020-1669/83/1322-3035$01.50/0 © 1983 American Chemical Society