Bull. Chem. Soc. Jpn., *73*, 2043—2050 (2000) 2043

Circular Dichroism Spectrophotometric Determination of Metal Ions Using Optically Active Tris(thiolato) Type Rhodium(III) Complexes

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(Received March 24, 2000)

Sparingly soluble neutral *fac*(*S*)-$[\mathrm{Rh(aet)_3}]$ was newly optically resolved in order to apply the optically active isomer as a CD-inducing reagent to the circular dichroism (CD) spectrophotometric determination of the transition metal ions. Simple determinations of cobalt(II) and nickel(II) and a simultaneous determination for the binary solution were successful by using an excess of powdery Λ-*fac*(*S*)-$[\mathrm{Rh(aet)_3}]$ with the dissolution equilibrium. A more sensitive determination of the transition metal ions, such as iron(III), iron(II), cobalt(III), cobalt(II), and nickel(II), was possible by using a homogeneous solution of Δ_{LLL}-*fac*(*S*)-$[\mathrm{Rh(L\text{-}cys\text{-}}N,S)_3]^{3-}$ without the dissolution equilibrium. The latter CD spectrophotometric determination is quite effective for a simultaneous determination of the transition metal ions in binary and ternary solutions of metal ions, such as iron(III)–cobalt(III), cobalt(III)–cobalt(II), and cobalt(II)–nickel(II)–zinc(II).

Spectrophotometric and fluorometric methods have been widely applied to various kinds of quantitative analysis so far.[1] However, because the absorption and emission transitions for polyatomic molecules are usually observed as a broad transition band which arises from the electronic transition with a number of vibrational or rotational modes, the application of the electronic spectra is not convenient for simultaneous or selective determinations for a mixed solution due to an overlapping of the broad absorption and emission bands. In order to compensate for the inconvenience, derivative spectrophotometry has been utilized in recent years.[2] Considering the sensitivity of this method, the sharpness of the electronic transition bands is of importance, because the intensity of the derivative spectra is directly dependent on the steepness of the observed spectra. From this point of view, derivative spectrophotometry is not very advantageous for the determination of metal ions by using complexation, because metal complexes usually exhibit relatively broad electronic transition bands due to the overlapping of a large number of components of the electronic transition, even in the ligand-to-metal or metal-to-ligand charge-transfer bands, which is often applicable to the determination because of their strong intensity. Consequently, the selective determination of metal ions is usually achieved by the selectivity of the complexation of the reagent used.

The circular dichroism (CD) spectra of optically active compounds usually exhibit positive and negative Cotton effects for each component of the electronic transition. Consequently, several wavelengths where the molar CD coefficient ($\Delta\varepsilon$) is equal to zero ($\lambda_{\Delta\varepsilon=0}$) can be obtained for each compound. Furthermore, since the CD intensity is drastically changed depending on the wavelength, some isodichroic points are inevitably observed for respective reactions. Such characteristics of the CD spectra are quite advantageous to a selective or simultaneous determination for a mixed solution, especially of metal ions exhibiting broad absorption bands, because a change in the concentration of one species can be detected at $\lambda_{\Delta\varepsilon=0}$ or at isodichroic wavelengths (λ_{iso}) for the other species. However, the advantage of the CD spectra has so far not been utilized in the field of analytical chemistry.

Recently, it has been revealed that tris(thiolato)-type cobalt(III) and rhodium(III) complexes, *fac*(*S*)-$[\mathrm{M(aet\ or\ L\text{-}cys\text{-}}N,S)_3]^{n-}$ (M = Co(III) and Rh(III); aet = 2-aminoethanethiolate, $n = 0$; L-cys = L-cysteinate, $n = 3$), readily form *S*-bridged linear-type trinuclear complexes with various transition metal ions, such as Cr(III),[3] Fe(III),[4—6] Co(III),[6—13] Co(II),[7] and Ni(II).[14—16] The *S*-bridged complexes are usually considerably stable in a solution and their optically active isomers exhibit quite strong CD bands attributed to μ-thiolato sulfur-to-metal charge-transfer. While these *S*-bridged trinuclear complexes exhibit broad intense absorption bands in the whole spectral region characteristic of the *S*-bridged structure, several $\lambda_{\Delta\varepsilon=0}$ of the trinuclear complexes and λ_{iso} for their formation reactions are observed at different wavelengths, depending on the *S*-bridged metal ions. Such reactivity and spectrochemical properties of *fac*(*S*)-$[\mathrm{M(aet\ or\ L\text{-}cys\text{-}}N,S)_3]^{0\ \mathrm{or}\ 3-}$ and their *S*-bridged complexes are particularly suitable for the simultaneous CD spectrophotometric determination of metal ions. Accordingly, we have applied *fac*(*S*)-$[\mathrm{Rh(aet)}]$ newly optically resolved[17] and Δ_{LLL}-*fac*(*S*)-$[\mathrm{Rh(L\text{-}cys\text{-}}N,S)_3]^{3-}$ to the determination of metal ions, because the configurational inversion or decomposition of the rhodium(III) complexes is not observed at all at room temperature.[7]

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Experimental

Materials. Rhodium(III) complexes, *fac*(*S*)-$[Rh(aet)_3]$[18] and Δ_{LLL}-*fac*(*S*)-$H_3[Rh(L\text{-cys-}N,S)_3]$,[7,19] were prepared by a reported procedure. The metal salts (Wako, Special Gr. or 99.9%), $Fe(SO_4)\cdot 7H_2O$, $Fe(NO_3)_2\cdot 9H_2O$, $Co(NO_3)_2\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, and $Zn(NO_3)_2\cdot 6H_2O$ were used without further purification.

Optical Resolution of *fac*(*S*)-[Rh(aet)₃]. The water-soluble heptanuclear complex $[\{Rh(aet)_3\}_4Zn_3OH]Br_5$ was optically resolved by using $K_2[Sb_2(R,R\text{-tartrate})_2]\cdot 3H_2O$.[20] After conversion of the $\Lambda\Lambda\Lambda\Lambda$ isomer to the bromide salt with NaBr, an excess of disodium dihydrogen ethylenediaminetetraacetate was reacted with the $\Lambda\Lambda\Lambda\Lambda$ isomer in a basic solution (pH = 9) to give the precipitate of Λ-*fac*(*S*)-$[Rh(aet)_3]$. The $\Lambda\Lambda\Lambda\Lambda$ isomer of the water-soluble mixed octanuclear complex $[\{Rh(aet)_3\}_4Zn_{3.7}Co_{0.3}O]Br_6$,[19,21] obtained from $\Lambda\Lambda$-$[Co\{Rh(aet)_3\}_2](NO_3)_3$,[7] was also used to give Λ-*fac*(*S*)-$[Rh(aet)_3]$ by the capture reaction of Zn(II) and Co(II) ions with ethylenediaminetetraacetate ion. The Δ-*fac*(*S*)-$[Rh(aet)_3]$ was also obtained by procedures similar to those for the Λ isomer.

Preparation of $[Fe\{Rh(aet)_3\}_2]^{3+}$ (1). To a solution containing 0.146 g (0.54 mmol) of $FeCl_3\cdot 6H_2O$ in 20 cm^3 of water was added 0.339 g (1.02 mmol) of *fac*(*S*)-$[Rh(aet)_3]$.[18] The solution was stirred at room temperature for 10 min and then filtered. A solution containing 3 g of NaI in 5 cm^3 of water was added to the filtrate, which was then kept in a refrigerator for 1 h. The resultant greenish-brown microcrystals were collected by filtration and then chromatographed on an SP Sephadex C-25 column (Na^+ form, 3.5 cm×90 cm) with a 0.2 $mol\,dm^{-3}$ aqueous solution of NaCl as an eluent. Greenish-brown (**1a**) and brownish-green (**1b**) bands were eluted in this order, and each eluate was concentrated to a small volume with a rotary evaporator below 30 °C, followed by the addition of a solution containing 5 g of NaI in 8 cm^3 of water. Each solution was allowed to stand at room temperature, and the resultant crystals were collected by filtration and washed with ethanol and ether. Found for **1a**: C, 13.17; H, 3.33; N, 7.70% and for **1b**: C, 13.01; H, 3.40; N, 7.66%. Calcd for $[Fe\{Rh(C_2H_6NS)_3\}_2]I_3$: C, 13.11; H, 3.30; N, 7.65%. Each isomer of the iodide salt was converted into a chloride salt with an anion exchange column of QAE Sephadex A-25 (Cl^- form) to give the absorption spectrum in the absence of iodide ion.

An aqueous solution of $\mathbf{1b}I_3$ was chromatographed on an SP Sephadex C-25 column (Na^+ form, 3.5×90 cm). Two greenish-brown bands, $(-)^{CD}_{600}$-**1b** and $(+)^{CD}_{600}$-**1b**, were eluted in this order with a 0.075 M aqueous solution of $K_2[Sb_2(R,R\text{-tartrate})_2]\cdot 3H_2O$, and succeedingly with a 0.2 M NaCl (1 M = 1 $mol\,dm^3$) aqueous solution to give the CD spectra unaffected by the chirality of $[Sb_2(R,R\text{-tartrate})_2]^{2-}$. The $\Delta\varepsilon$ values were estimated by using the concentration calculated from the absorbance.

Preparation of $\Delta_{LLL}\Delta_{LLL}$-$[Fe\{Rh(L\text{-cys-}N,S)_3\}_2]^{3-}$ (2). This complex was prepared by a procedure similar to that reported for the corresponding trinuclear complex with cobalt(III) center $\Delta_{LLL}\Delta_{LLL}$-$[Co\{Rh(L\text{-cys-}N,S)_3\}_2]^{3-}$.[7] The reaction of 0.29 g (0.63 mmol) of Δ_{LLL}-*fac*(*S*)-$H_3[Rh(L\text{-cys-}N,S)_3]$ with 0.086 g (0.32 mmol) of $FeCl_3\cdot 6H_2O$ instead of $[CoCl(NH_3)_5]Cl_2$ was carried out at room temperature for 30 min. Found: C, 17.21; H, 3.90; N, 6.79%. Calcd for $Na_3[Fe\{Rh(C_3H_5NO_2S)_3\}_2]\cdot H_2O\cdot 0.5NaCl$: C, 17.48; H, 3.91; N, 6.79%.

Sample Preparation and Measurements. An excess amount of powdery Λ-*fac*(*S*)-$[Rh(aet)_3]$ was suspended in aqueous solutions of metal ions. Each suspension was allowed to stand at room temperature for at least 1 h, and the filtrate or supernatant solution was used for measurements. The dependence of the absorption and CD spectra on the metal ion concentration was checked by using aqueous solutions of $Fe(NO_3)_3\cdot 9H_2O$ ($4.00-24.0\times10^{-5}$ M), $Co(NO_3)_2\cdot 6H_2O$ (2.00—12.0×10^{-5} M), $Ni(NO_3)_2\cdot 6H_2O$ (5.01—30.0×10^{-5} M), and $Zn(NO_3)_2\cdot 6H_2O$ (3.00—18.0×10^{-5} M). The concentration dependence of the CD spectra for binary solutions of $Co(NO_3)_2\cdot 6H_2O$ and $Ni(NO_3)_2\cdot 6H_2O$ ($C_{Co(II)} = 0.00$—12.0×10^{-5} M and $C_{Ni(II)} = 5.01\times10^{-5}$ M; $C_{Co(II)} = 2.00\times10^{-5}$ M and $C_{Ni(II)} = 0.00$—30.0×10^{-5} M) was examined.

A stock solution of Λ_{LLL}-*fac*(*S*)-$[Rh(L\text{-cys-}N,S)_3]^{3-}$ was prepared by adding a 0.1 M NaOH solution to a suspension of a known amount of Λ_{LLL}-*fac*(*S*)-$H_3[Rh(L\text{-cys-}N,S)_3]$[7,19] until the pH of the solution was raised to 5—6 to dissolve the protonated rhodium(III) complex. Solutions with a constant concentration of Λ_{LLL}-*fac*(*S*)-$[Rh(L\text{-cys-}N,S)_3]^{3-}$ and various concentrations of metal ions were prepared by using the stock solution. The dependence of the absorption and CD spectra on the metal ion concentration was checked by using aqueous solutions of Λ_{LLL}-*fac*(*S*)-$[Rh(L\text{-cys-}N,S)_3]^{3-}$ containing $Fe(NO_3)_3\cdot 9H_2O$ ($C_{Rh} = 6.71\times10^{-5}$ and 3.29×10^{-4} M and $C_{Fe(III)} = 6.09$—22.3×10^{-6} and 2.19—10.95×10^{-6} M for absorption and CD spectra, respectively), $FeSO_4\cdot 7H_2O$ ($C_{Rh} = 3.29\times10^{-4}$ M and $C_{Fe(II)} = 2.19$—13.14×10^{-5} and 2.20—11.00×10^{-6} M for absorption and CD spectra, respectively), $[CoCl(NH_3)_5]Cl_2$ ($C_{Rh} = 4.67\times10^{-4}$ M and $C_{Co(III)} = 1.12$—8.96×10^{-5} M), $Co(NO_3)_2\cdot 6H_2O$ ($C_{Rh} = 4.67\times10^{-4}$ M and $C_{Co(II)} = 1.02$—8.13×10^{-5} M), $Ni(NO_3)_2\cdot 6H_2O$ ($C_{Rh} = 1.32\times10^{-3}$ M and $C_{Ni(II)} = 4.24$—33.9×10^{-5} M), and $Zn(NO_3)_2\cdot 6H_2O$ ($C_{Rh} = 2.43\times10^{-4}$ M and $C_{Zn(II)} = 4.36$—26.2×10^{-5} M for CD spectra). In order to accelerate the oxidation reaction of the cobalt(II) and iron(II) ions, a small amount (1—5×10^{-4} M) of H_2O_2 was used. The concentration dependence of the CD spectra was examined for binary solutions of $Fe(NO_3)_3\cdot 9H_2O$ and $[CoCl(NH_3)_5]Cl_2$ ($C_{Rh} = 8.02\times10^{-4}$ M, $C_{Fe(III)} = 0.00$—14.00×10^{-5} M, and $C_{Co(III)} = 2.00\times10^{-5}$ M; $C_{Rh} = 5.00\times10^{-4}$ M, $C_{Fe(III)} = 2.00\times10^{-5}$ M, and $C_{Co(III)} = 0.00$—7.00×10^{-5} M) and $[CoCl(NH_3)_5]Cl_2$ and $Co(NO_3)_2\cdot 6H_2O$ ($C_{Rh} = 1.78\times10^{-3}$ M, $C_{Co(III)} = 4.17\times10^{-5}$ M, and $C_{Co(II)} = 0.00$—28.1×10^{-5} M) and ternary solutions of $Co(NO_3)_2\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, and $Zn(NO_3)_2\cdot 6H_2O$ ($C_{Rh} = 4.16\times10^{-4}$ M, $C_{Co(II)} = 0.00$—4.60×10^{-5} M, $C_{Ni(II)} = 2.50\times10^{-5}$ M, and $C_{Zn(II)} = 2.18\times10^{-5}$ M; $C_{Rh} = 6.24\times10^{-4}$ M, $C_{Co(II)} = 2.30\times10^{-5}$ M, $C_{Ni(II)} = 0.00$—12.5×10^{-5} M, and $C_{Zn(II)} = 2.18\times10^{-5}$ M; $C_{Rh} = 4.16\times10^{-4}$ M, $C_{Co(II)} = 2.30\times10^{-5}$ M, $C_{Ni(II)} = 2.50\times10^{-5}$ M, and $C_{Zn(II)} = 0.00$—21.8×10^{-5} M). Each solution was reacted at room temperature for at least 1 h. The preparation of the binary system of $[CoCl(NH_3)_5]Cl_2$ and $Co(NO_3)_2\cdot 6H_2O$ was carried out under a nitrogen atmosphere in a glove box by using water deoxygenated by bubbling nitrogen. The CD spectra of the mixed solution were measured using a quartz cuvette with a Teflon® cap to prevent the oxidation of cobalt(II). After the CD measurements, the solution was exposed to air and the CD spectra of the oxidized solutions were measured again.[7]

The absorption and CD spectra were recorded on a Shimadzu UV-3100 and a JASCO V-570 spectrophotometer and a JASCO J-720WL spectropolarimeter, respectively.

Results and Discussion

Characterization of Complexes. The rhodium(III) complexes with three thiolato sulfur atoms in the facial position, *fac*(*S*)-$[Rh(aet\text{ or }L\text{-cys-}N,S)_3]^{0\text{ or }3-}$, readily forms trinuclear complexes with the first-row transition metal ions, such as chromium(III),[3] cobalt(III),[7] cobalt(II),[7] and nickel(II),[16] $[M\{Rh(aet\text{ or }L\text{-cys-}N,S)_3\}_2]^{n+\text{ or }(6-n)-}$ (M = Cr(III), Co(III), Co(II), and Ni(II), n = oxidation number of M) with a retention of the absolute configuration of the rhodium(III) complexes (Figure 1), except for the reaction of cobalt(II) at a high temperature (ca., 90 °C).[7] Therefore, the optical purity of newly optically resolved *fac*(*S*)-[Rh(aet)$_3$] can be estimated by that of a trinuclear complex, [Co{Rh(aet)$_3$}$_2$]$^{3+}$, prepared from the optically resolved *fac*(*S*)-[Rh(aet)$_3$] by a reaction with [CoCl(NH$_3$)$_5$]$^{2+}$ as the cobalt(III) source. The optical purity of Δ- and Λ-*fac*(*S*)-[Rh(aet)$_3$] resolved in this work was calculated to be 99% by using the CD intensity and the absorbance of [Co{Rh(aet)$_3$}$_2$]$^{3+}$, respectively, formed. It was also found from the SP-Sephadex column chromatography that only $\Delta\Delta$ - and $\Lambda\Lambda$ - [Co{Rh(aet)$_3$}$_2$]$^{3+}$ were formed by the reaction of optically resolved Δ - and Λ - *fac*(*S*)-[Rh(aet)$_3$] with cobalt(III), respectively. These results confirmed that the sparingly soluble *fac*(*S*)-[Rh(aet)$_3$] was completely optically resolved.

The cobalt(III) complexes, *fac*(*S*)-[Co(aet or L-cys-*N*,*S*)$_3$]$^{0\text{ or }3-}$, were known to form trinuclear complexes with an iron(III) center.[4—6] Considering the potential bridging ability of the sulfur atoms in the facial position and the steric and chemical compatibility between cobalt(III) and rhodium(III) complexes, it is reasonably expected that the rhodium(III) complexes also form trinuclear complexes with an iron(III) center as do the cobalt(III) complexes. The reaction of the *fac*(*S*)-[Rh(aet or L-cys-*N*,*S*)$_3$]$^{0\text{ or }3-}$ and iron(III) in a 2 : 1 molar ratio gave complexes showing absorption spectra quite similar to each other. Their intense absorption bands in the visible spectral region are characteristic of the *S*-bridged structure with the first-row transition metal ions, and the intensity is comparable with that of [Co{Rh-(aet or L-cys-*N*,*S*)$_3$}$_2$]$^{3+\text{ or }3-}$ [7] (Fig. S1 as supporting data), as observed for the corresponding trinuclear complexes with cobalt(III) terminals, [M{Co(aet or L-cys-*N*,*S*)$_3$}$_2$]$^{3+\text{ or }3-}$ (M = Fe(III)[5,6] and Co(III)[6,9,12]). Only one isomer, $\Delta_{LLL}\Delta_{LLL}$-[M{Rh(L-cys-*N*,*S*)$_3$}$_2$]$^{n-6}$, is invariably formed by the reaction of Δ_{LLL}-*fac*(*S*)-[Rh(L-cys-*N*,*S*)$_3$]$^{3-}$ with metal ion (M^{n+}) at room temperature, as described above. On the other hand, the three isomers $\Delta\Delta$ -, $\Delta\Lambda$ -, and $\Lambda\Lambda$ -[M{Rh(aet)$_3$}$_2$]$^{n+}$ are inevitably formed by the reaction of *rac*-*fac*(*S*)-[Rh(aet)$_3$]. The experimental results in this work are consistent with the above facts; that is, complex **2**, showing a quite intense CD spectrum with a pattern similar to that of $\Delta_{LLL}\Delta_{LLL}$-[Co{Rh-(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$, is assigned to $\Delta_{LLL}\Delta_{LLL}$-[Fe{Rh(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ (Fig. S1A), and **1a** without optical activity and **1b**, which was optically resolved into $(-)^{CD}_{600}$- and $(+)^{CD}_{600}$-**1b**, are assignable to *meso*-($\Delta\Lambda$-) and *rac*-[Fe{Rh(aet)$_3$}$_2$]$^{3+}$, respectively. Since $(-)^{CD}_{600}$-**1b** shows a CD spectrum quite similar to that of **2** (Fig. S1B) and $(+)^{CD}_{600}$-**1b** shows a CD spectrum completely enantiomeric to $(-)^{CD}_{600}$-**1b**, $(-)^{CD}_{600}$- and $(+)^{CD}_{600}$-**1b** are assigned to $\Delta\Delta$- and $\Lambda\Lambda$ -[Fe{Rh(aet)$_3$}$_2$]$^{3+}$, respectively.

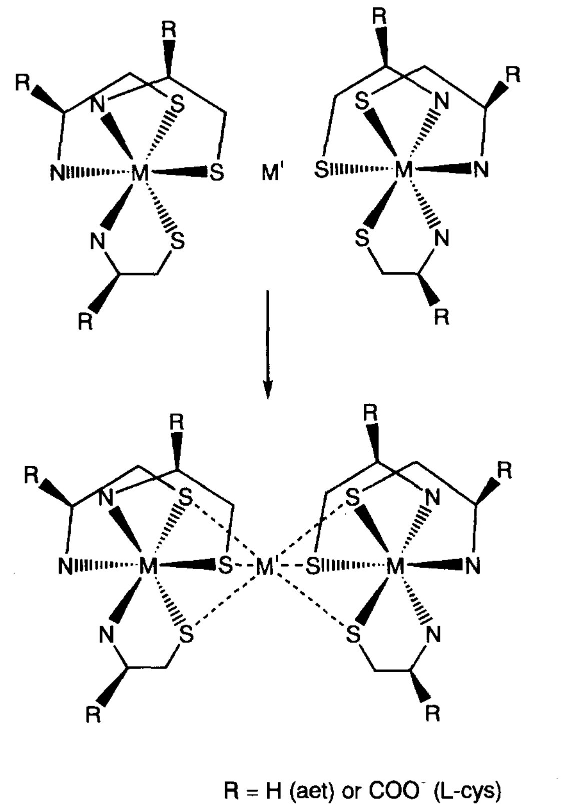

Fig. 1. *S*-Bridged trinuclear complex formation reaction of *fac*(*S*)-[M(aet or L-cys-*N*,*S*)$_3$]$^{0\text{ or }3-}$ with M′; M′ = Cr(III), Co(III), Co(II), and Ni(II) for M = Rh(III) and M′ = Fe(III), Co(III), and Ni(II) for M = Co(III).

Determination with Λ-*fac*(*S*)-[Rh(aet)$_3$]. The almost colorless or pale pink solutions of the cobalt(II) ion (2.0—12.0×10^{-5} M) are gradually colored dark brown in the presence of excess Λ-*fac*(*S*)-[Rh(aet)$_3$]. The absorption and CD spectral patterns of each supernatant solution become similar to those of $\Lambda\Lambda$-[Co{Rh(aet)$_3$}$_2$]$^{3+}$ [7] as the cobalt(II) concentration is increased (Fig. S2). The colorless solutions of the nickel(II) ion (5.01—30.0×10^{-5} M) immediately turned red in the presence of excess Λ-*fac*(*S*)-[Rh(aet)$_3$], and each supernatant solution began to exhibit absorption and CD spectral patterns similar to those for $\Lambda\Lambda$-[Ni{Rh(aet)$_3$}$_2$]$^{2+}$ [16] along with an increase in the nickel(II) concentration (Fig. S3). The linear dependence of the absorbance and CD intensity on the cobalt(II) or nickel(II) concentration was observed over the whole spectral region with no isosbestic point, but isodichroic points at 321, 341, 385, and 526.5 nm for the cobalt(II) solution (Fig. S2B) and at 308, 328.5, 355.5, 390, and 487.5 nm for the nickel(II) solution (Fig. S3B), which correspond to $\lambda_{\Delta\varepsilon=0}$ for $\Lambda\Lambda$-[M{Rh(aet)$_3$}$_2$]$^{3+\text{ or }2+}$ (M = Co(III)[7] or Ni(II)[16]), respectively. These facts indicated that the cobalt(II) and nickel(II) ions are quantitatively incorporated in linear-type trinuclear complexes as the central metal ion and that the cobalt(II) ion surrounded by the μ-thiolato sulfur atoms is quantitatively oxidized. The linearity and sensitivity obtained by using six data points in the above concentration range for the CD spectra (R = 0.9997, D = 0.14 at 361 nm for cobalt(II) and R = 0.9996 and D = 0.41 at 422 nm for nickel(II)) are comparable or better than those for the absorption spectra (R = 0.9997, D = 0.15 at 415 nm for cobalt(II) and R = 0.9918 and D = 1.9 at 320 nm for nickel(II)), where R is the correlation coefficient and D (μg ml^{-1}) is the detection limit calculated as three-times the standard deviation of the intercept divided by the slope of the linear regression equation.

Contrary to the results for the cobalt(II) and nickel(II) ions, a good linear dependence of the absorbance or CD intensity on the metal ion concentration was not observed in the case of iron(III) or zinc(II) ions, though a spectral pattern similar to $\Lambda\Lambda$-[Fe{Rh(aet)$_3$}$_2$]$^{3+}$ (vide supra) was shown for the iron(III) solution. Because Λ-*fac*(*S*)-[Rh(aet)$_3$] is sparingly soluble, it is probable that the concentration of the rhodium(III) complex is not sufficient to form the trinuclear complex $\Lambda\Lambda$-[Fe{Rh(aet)$_3$}$_2$]$^{3+}$ quantitatively, and some by-products with a higher iron(III) content are formed. On the other hand, zinc(II) ion is expected to form some types of sulfur-bridged polynuclear complexes with different proportion of zinc(II) to rhodium(III) by changing the concentration of zinc(II) ion (vide infra).

Considering that the cobalt(II) and nickel(II) ions quantitatively form the trinuclear complexes [Co$^{\mathrm{III}}$ or Ni$^{\mathrm{II}}${Rh(aet)$_3$}$_2$]$^{3+\text{ or }2+}$, it is assumed that each ion is independently incorporated in the trinuclear complex in a mixture of these two ions. In this case, the observed CD intensity (θ_{obs}) of the binary solution of the cobalt(II) and nickel(II) ions is expressed as

$$\theta_{\mathrm{obs}} = [\mathrm{Rh}][\theta]_{\mathrm{Rh}} + [\mathrm{Co}][\theta]_{\mathrm{Co}} + [\mathrm{Ni}][\theta]_{\mathrm{Ni}}, \qquad (1)$$

where [Rh], [Co], and [Ni] are the concentrations of Λ-*fac*(*S*)-[Rh(aet)$_3$] slightly dissolved, $\Lambda\Lambda$-[Co{Rh(aet)$_3$}$_2$]$^{3+}$, and $\Lambda\Lambda$-[Ni{Rh(aet)$_3$}$_2$]$^{2+}$, respectively, and $[\theta]_{\mathrm{Rh}}$, $[\theta]_{\mathrm{Co}}$, and $[\theta]_{\mathrm{Ni}}$ are the molar CD intensity of the corresponding complexes. Furthermore, [Co] and [Ni] are regarded as being the total concentrations of the respective metal(II) ions, because of the quantitative formation of each trinuclear complex, and [Rh] is considered to be a constant, which corresponds to the solubility of the rhodium(III) complex. Accordingly, if Eq. 1 is applied, the isodichroic points for the binary mixtures with a variation of one metal ion concentration, [Co] or [Ni], are expected to be observed at $\lambda_{\Delta\varepsilon=0}$ for $\Lambda\Lambda$-[Co or Ni{Rh(aet)$_3$}$_2$]$^{3+\text{ or }2+}$ where $[\theta]_{\mathrm{Co}} = 0$ or $[\theta]_{\mathrm{Ni}} = 0$, respectively, and only the concentration of the other metal ion can be detectable at those wavelengths. In fact, λ_{iso} for a binary mixture with a variation of the nickel(II) concentration was observed at $\lambda_{\Delta\varepsilon=0}$ for $\Lambda\Lambda$-[Ni{Rh(aet)$_3$}$_2$]$^{2+}$ (Fig. 2A), and a good linearity between the cobalt(II) concentration and the CD intensity was observed at 308 and 487.5 nm, where the change in the CD intensity with a variation of the cobalt(II) concentration is relatively large among $\lambda_{\Delta\varepsilon=0}$ for $\Lambda\Lambda$-[Ni{Rh(aet)$_3$}$_2$]$^{2+}$ (Fig. 2B). Similarly, λ_{iso} for the binary mixture with a variation of the cobalt(II) concentration agrees with $\lambda_{\Delta\varepsilon=0}$ for $\Lambda\Lambda$-[Co{Rh(aet)$_3$}$_2$]$^{3+}$ (Fig. 2B), and a fairly good linearity of the nickel(II) concentration dependence of the CD intensity was also observed at 341 and 526.5 nm (Fig. 2A). Consequently, it is confirmed that the simultaneous determination of cobalt(II) and nickel(II) ions in a binary solution is possible by taking advantage of the CD spectra with the sensitivity comparable to the reported colorimetric determinations.[1] These two ions are classified into the same category with similar chemical properties from an analytical point of view, because they can often be the interfering ions with each other in quantitative analyses.[1] Hence, it is notable that such a simple simultaneous determination is achieved by just adding only one reagent to the mixed solution.

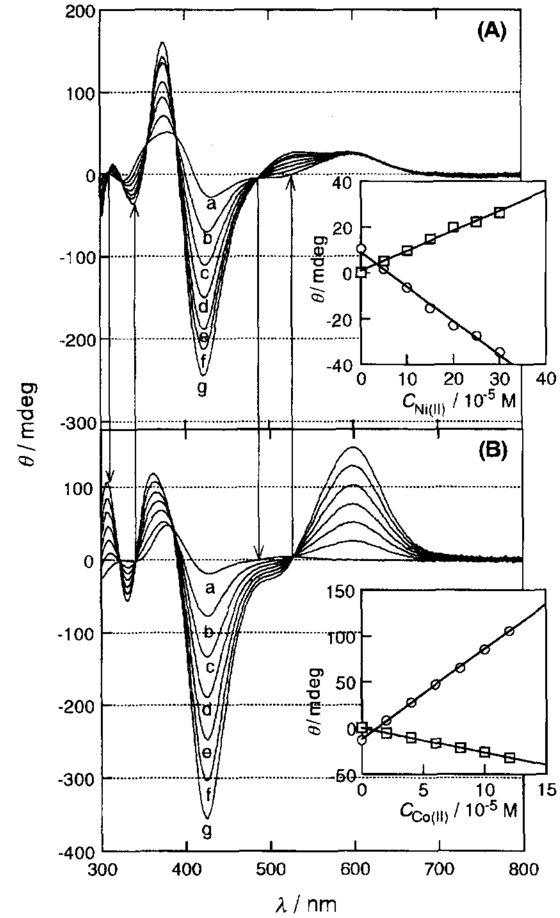

Fig. 2. Dependence of CD spectra on the concentration of nickel(II) (A) and cobalt(II) (B) ions in the binary mixture; (A) $C_{\mathrm{Co(II)}} = 2.00\times10^{-5}$ M, $C_{\mathrm{Ni(II)}} = 0.00$ (a), 5.01 (b), 10.01 (c), 15.02 (d), 20.03 (e), 25.04 (f), and 30.04 (g)$\times10^{-5}$ M; (B) $C_{\mathrm{Co(II)}} = 0.00$ (a), 2.00 (b), 4.00 (c), 6.00 (d), 8.00 (e), 10.01 (f), and 12.01 (g)$\times10^{-5}$ M, $C_{\mathrm{Ni(II)}} = 5.01\times10^{-5}$ M. The linear regression equations were expressed as $\theta = -1.50\times10^{5}C_{\mathrm{Ni(II)}}+8.99$ at 341 nm (○) ($R = -0.9961$ and $D = 1.6$) and $\theta = 8.78\times10^{4}C_{\mathrm{Ni(II)}}+0.82$ at 526.5 nm (□) ($R = 0.9929$ and $D = 1.6$) (inset in A) and $\theta = 9.79\times10^{5}C_{\mathrm{Co(II)}} - 12.22$ at 308 nm (○) ($R = 0.9999$ and $D = 0.11$) and $\theta = -2.68\times10^{5}C_{\mathrm{Co(II)}}+0.24$ at 487.5 nm (□) ($R = -0.9997$ and $D = 0.17$) (inset in B).

Determination with Δ_{LLL}-*fac*(*S*)-[Rh(L-cys-*N*,*S*)$_3$]$^{3-}$. As mentioned above, the method of determination with optically active *fac*(*S*)-[Rh(aet)$_3$] is quite simple, because an excess of sparingly soluble rhodium(III) complex is merely added to sample solutions, which are allowed to stand at room temperature. However, unless the trinuclear complex is quantitatively formed in such a low concentration of the rhodium(III) complex, satisfactory linearity of the concentration dependence of the CD intensity is not obtained, as in the case of iron(III). In such a case, Δ_{LLL}-*fac*(*S*)-H_3[Rh(L-cys-*N*,*S*)$_3$] can be used instead of Λ-*fac*(*S*)-[Rh(aet)$_3$], which is quite soluble in a neutral or alkaline solution as a deprotonated form, though it is necessary to keep the total concentration of the rhodium(III) complex constant during the calibration and sample analysis. Actually, the linear concentration dependence of the absorption and CD intensity was observed for a solution of the iron(III)[22] and iron(II)[23] almost over the entire spectral region, showing no isosbestic point, but isodichroic points at 506 and 493 nm, respectively (Figs. S4 and S5). The absorption and CD spectral patterns for the iron(III) and iron(II) solutions are almost the same and coincide with those of the trinuclear complex with an iron(III) center $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Fe{Rh(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ (Fig. S1A) overlapped by the spectra of Δ_{LLL}-*fac*(*S*)-[Rh(L-cys-*N*,*S*)$_3$]$^{3-}$.[7] In the case of the iron(II), a small amount of H_2O_2 is required as an oxidant (see Experimental) in order to prevent a side reaction. Consequently, it is probable that an excess of the thiolatorhodium(III) complex is partially oxidized to form a sulfenato complex, as reported for *fac*(*S*)-[Rh(aet)$_3$];[18] this may cause the slight difference in λ_{iso} between the iron(II) and iron(III) solutions.

As described for a determination with Λ-*fac*(*S*)-[Rh(aet)$_3$], the cobalt(III), cobalt(II), and nickel(II) ions form the trinuclear complex $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Co or Ni{Rh(L-cys-*N*,*S*)$_3$}$_2$]$^{3-\text{ or }4-}$ quantitatively, where cobalt(II) is also oxidized. The metal concentration dependences of the absorption and CD spectra exhibit no isosbestic point, but isodichroic points at 304.5, 316, 342, 384, and 529 nm for the cobalt(III) and cobalt(II) solution and at 326, 356, 386, and 491 nm for the nickel(II) solution. The linearity and sensitivity for this determination in a homogeneous solution appear to be better than those in a two-phase system with Λ-*fac*(*S*)-[Rh(aet)$_3$][24] (Figs. S6, S7, and S8). In the case of the L-cys system, Eq. 2 holds at λ_{iso} for the M_1 concentration dependence, where the CD intensity for the consumed rhodium(III) complex is compensated in the trinuclear complex formation of M_1.

$$2[\theta]_{\mathrm{Rh}} = [\theta]_{\mathrm{M1}}, \tag{2}$$

where $[\theta]_{\mathrm{Rh}}$ and $[\theta]_{\mathrm{M1}}$ are the molar CD intensity of Δ_{LLL}-*fac*(*S*)-[Rh(L-cys-*N*,*S*)$_3$]$^{3-}$ and a trinuclear complex with the M_1 center, respectively. As described above for the determination with Λ-*fac*(*S*)-[Rh(aet)$_3$], assuming that the trinuclear complexes are independently formed with different metal ions, M_1 and M_2, the observed CD intensity is expressed as

$$\begin{aligned}\theta_{\mathrm{obs}} = C_{\mathrm{Rh}}[\theta]_{\mathrm{Rh}} - 2[\mathrm{M_1}][\theta]_{\mathrm{Rh}} - 2[\mathrm{M_2}][\theta]_{\mathrm{Rh}}\\ +[\mathrm{M_1}][\theta]_{\mathrm{M1}} + [\mathrm{M_2}][\theta]_{\mathrm{M2}},\end{aligned} \tag{3}$$

where C_{Rh} is the initial concentration of Δ_{LLL}-*fac*(*S*)-[Rh(L-cys-*N*,*S*)$_3$]^3, and $[\mathrm{M_1}]$ and $[\mathrm{M_2}]$ are the total concentration of the metal ion if the trinuclear complex formation of each metal ion is quantitative. By substitution for $2[\theta]_{\mathrm{Rh}}$ in Eq. 3 by using Eq. 2, θ_{obs} at λ_{iso} for the M_1 concentration dependence is given by

$$\begin{aligned}\theta_{\mathrm{obs}} &= C_{\mathrm{Rh}}[\theta]_{\mathrm{Rh}} - 2[\mathrm{M_2}][\theta]_{\mathrm{Rh}} + [\mathrm{M_2}][\theta]_{\mathrm{M2}}\\ &= C_{\mathrm{Rh}}[\theta]_{\mathrm{Rh}} + [\mathrm{M_2}]([\theta]_{\mathrm{M2}} - 2[\theta]_{\mathrm{Rh}}),\end{aligned} \tag{4}$$

where θ_{obs} is linearly dependent on $[\mathrm{M_2}]$ because C_{Rh}, $[\theta]_{\mathrm{Rh}}$, and $[\theta]_{\mathrm{M2}}$ are constant. Similarly, the linear dependence of the CD intensity on $[\mathrm{M_1}]$ can be observed at λ_{iso} for the M_2 concentration dependence. For the binary solution of iron(III) and Co(III), the isodichroic points for iron(III) and cobalt(III) concentration dependence were observed at 506 nm for the former and 384 and 529 nm for the latter, which were in agreement with λ_{iso} for a solution containing only iron(III) or cobalt(III), respectively (vide supra). As shown in Fig. 3, relatively good linearity between the CD intensity and each metal ion concentration was observed at λ_{iso} for the other metal ion.

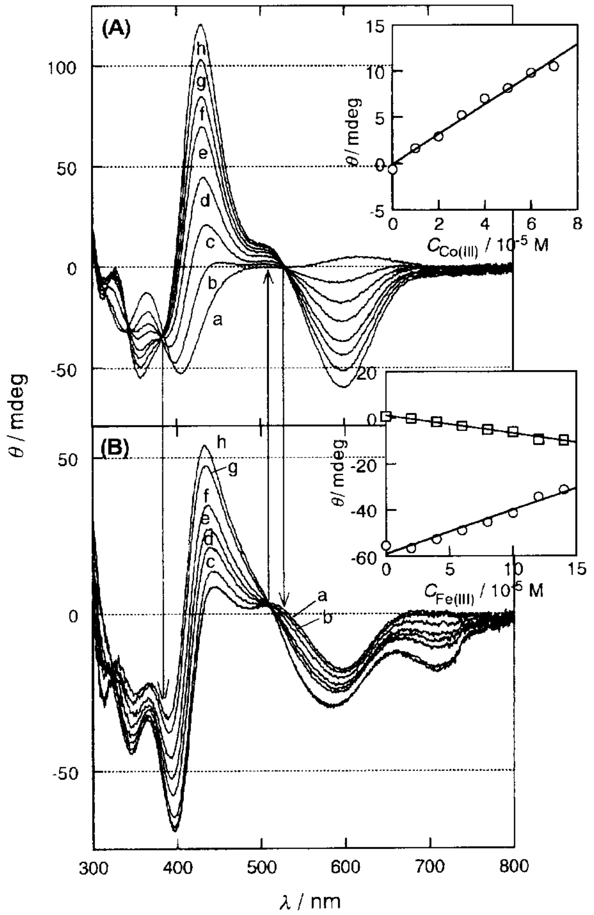

Fig. 3. Dependence of CD spectra on the concentration of cobalt(III) (A) and iron(III) (B) ions in the binary solutions; (A) $C_{\mathrm{Rh(III)}} = 5.00\times10^{-4}$ M, $C_{\mathrm{Fe(III)}} = 2.00\times10^{-5}$ M, and $C_{\mathrm{Co(III)}} = 0.00$ (a), 1.00 (b), 2.00 (c), 3.00 (d), 4.00 (e), 5.00 (f), 6.00 (g) and 7.00 (h)$\times10^{-5}$ M; (B) $C_{\mathrm{Rh(III)}} = 8.02\times10^{-4}$ M, $C_{\mathrm{Fe(III)}} = 0.00$ (a), 2.00 (b), 4.00 (c), 6.00 (d), 8.00 (e), 10.00 (f), 12.00 (g) and 14.00 (h)$\times10^{-5}$ M and,$C_{\mathrm{Co(III)}} = 2.00\times10^{-5}$ M. The linear regression equations were expressed as $\theta = 1.62\times10^5 C_{\mathrm{Co(III)}} - 0.10$ at 506 nm ($R = 0.9929$ and $D = 0.48$) (inset in A) and $\theta = 1.89\times10^5 C_{\mathrm{Fe(III)}} - 59.02$ at 384 nm (○) ($R = 0.9771$ and $D = 1.7$) and $\theta = -8.00\times10^4 C_{\mathrm{Fe(III)}} + 1.07$ at 529 nm (□) ($R = -0.9914$ and $D = 1.0$) and (inset in B).

Because the cobalt(II) ion bridged with thiolato sulfur atoms is oxidized by oxygen or other oxidants, it seems to be possible that only the cobalt(II) is selectively determined in the binary solution of cobalt(III) and cobalt(II) under a nitrogen atmosphere. Considering the high oxygen sensitivity of the *S*-bridged cobalt(II), water-soluble Δ_{LLL}-*fac*(*S*)-[Rh(L-cys-*N*,*S*)$_3$]$^{3-}$ is preferred rather than Λ-*fac*(*S*)-[Rh(aet)$_3$] as a sulfur bridging reagent because the reaction time can be cut short by the time consumed in the dissolution equilibrium of *fac*(*S*)-[Rh(aet)$_3$]. The determination of the cobalt(III) may be possible simultaneously under anaerobic conditions in the same manner as described above for the binary solution of iron(III) and cobalt(III), but it is experimentally easier to determine the total cobalt concentration after complete oxidation followed by subtracting the cobalt(II) concentration because it is not necessary to keep the anaerobic condition.

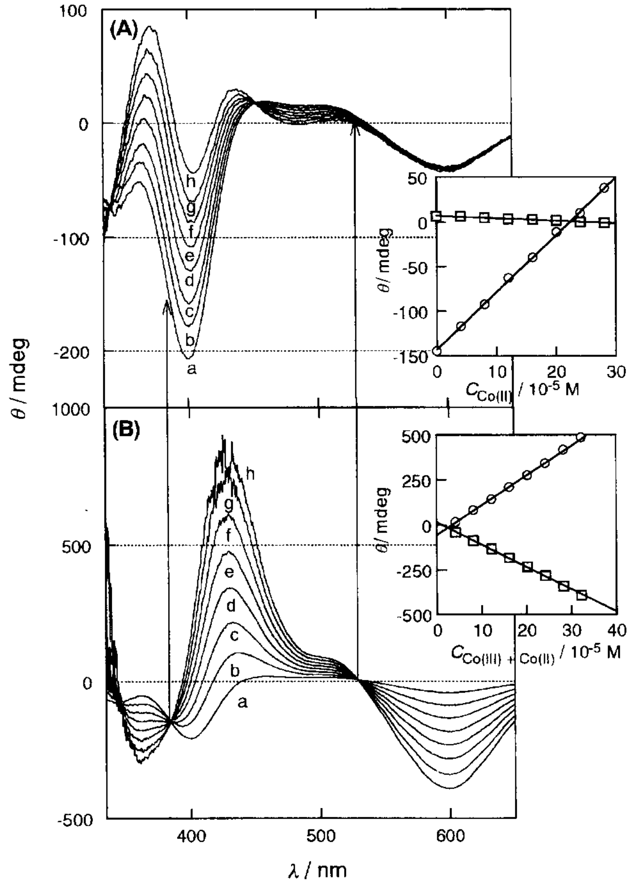

Fig. 4. Dependence of CD spectra on the concentration of cobalt(II) in the binary solutions of caobalt(III) and cobalt(II) before (A) and after (B) oxidation; $C_{\mathrm{Rh(III)}} = 1.78\times10^{-3}$ M, $C_{\mathrm{Co(III)}} = 4.17\times10^{-5}$ M, and $C_{\mathrm{Co(II)}} = 0.00$ (a), 4.02 (b), 8.03 (c), 12.05 (d), 16.06 (e), 20.08 (f), 24.10 (g) and 28.11 (h)$\times10^{-5}$ M. The linear regression equations were expressed as $\theta = 6.54\times10^{5}C_{\mathrm{Co(II)}} - 143.13$ at 384 nm (○) ($R = 0.9996$ and $D = 0.45$) and $\theta = -2.65\times10^{4}C_{\mathrm{Co(II)}}+6.88$ at 529 nm (□) ($R = -0.9873$ and $D = 2.6$) (inset in A) and $\theta = 1.68\times10^{6}C_{\mathrm{Co(III)+Co(II)}}-57.32$ at 452 nm (○) ($R = 0.9997$ and $D = 0.40$) and $\theta = -1.25\times10^{6}C_{\mathrm{Co(III)+Co(II)}}+17.22$ at 600 nm (□) ($R = 0.9994$ and $D = 0.55$) (inset in B).

As shown in Fig. 4A, a change in the cobalt(II) concentration can be detected in the binary solution of cobalt(III) and cobalt(II) under a nitrogen atmosphere at λ_{iso} for the cobalt(III) solution, i. e., 384 nm. After the oxidation of cobalt(II), good linearity was observed for the dependence of the CD intensity on the total cobalt concentration over the whole spectral region (Fig. 4B).

The sulfur bridged Rh–Zn heptanuclear complex [{Rh(aet)$_3$}$_4$Zn$_3$OH]$^{5+}$ and octanuclear complex [{Rh(aet or L-cys-*N*,*S*)$_3$}$_4$Zn$_4$O]$^{6+\text{ or }6-}$ have been reported so far.[19—21,25] In such polynuclear complex formations, only a slight absorption and CD spectral shifts to the shorter wavelength have been observed due to absence of the transition caused by zinc(II). Because the octanuclear complexes are formed only under a quite high concentration of zinc(II) ion, a slight CD spectral shift and a small change in the CD intensity, depending on the zinc(II) concentration, is attributed to the formation of the heptanuclear complex (Fig. 5). However, in order to explain the apparently constant CD spectra at a lower zinc(II) concentration, as shown in Fig. 5, it is necessary to consider another equilibrium with little change in the CD spectra forming the species with a lower zinc(II) proportion, such as trinuclear complex [Zn{Rh(L-cys-*N*,*S*)$_3$}$_2$]$^{4-}$. Taking these equilibria into account, the CD spectrophotometric method is not suitable for the determination of zinc(II), but the determination of the transition metal ion is expected not to be affected by the existence of the zinc(II) ion if the forma-

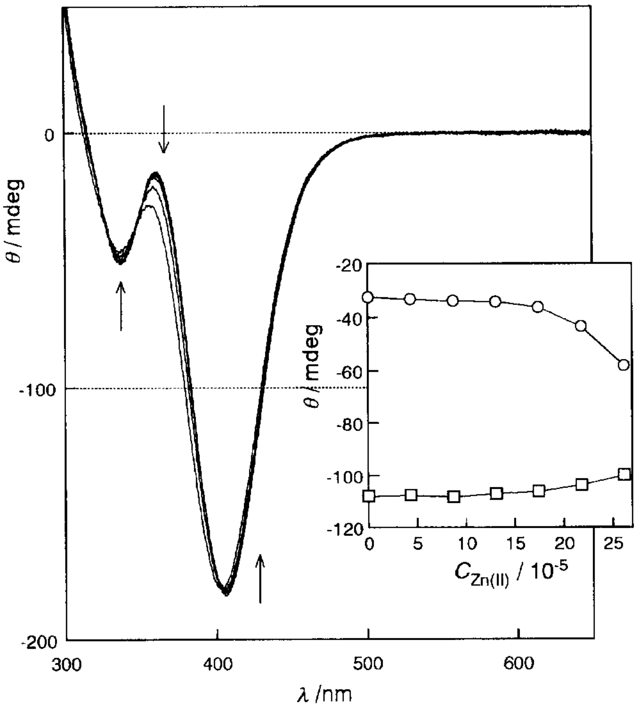

Fig. 5. Dependence of CD spectra on the concentration of zinc(II); $C_{\mathrm{Rh}} = 2.43\times10^{-3}$ M and $C_{\mathrm{Zn(II)}} = 0.00$, 4.36, 8.72, 13.08, 17.44, 21.80, and 26.16$\times10^{-5}$ M. Arrows denote the direction of increase in zinc(II) concentration. Inset shows the variation of CD intensity at 370 (○) and 430 (◇) nm with $C_{\mathrm{Zn(II)}}$.

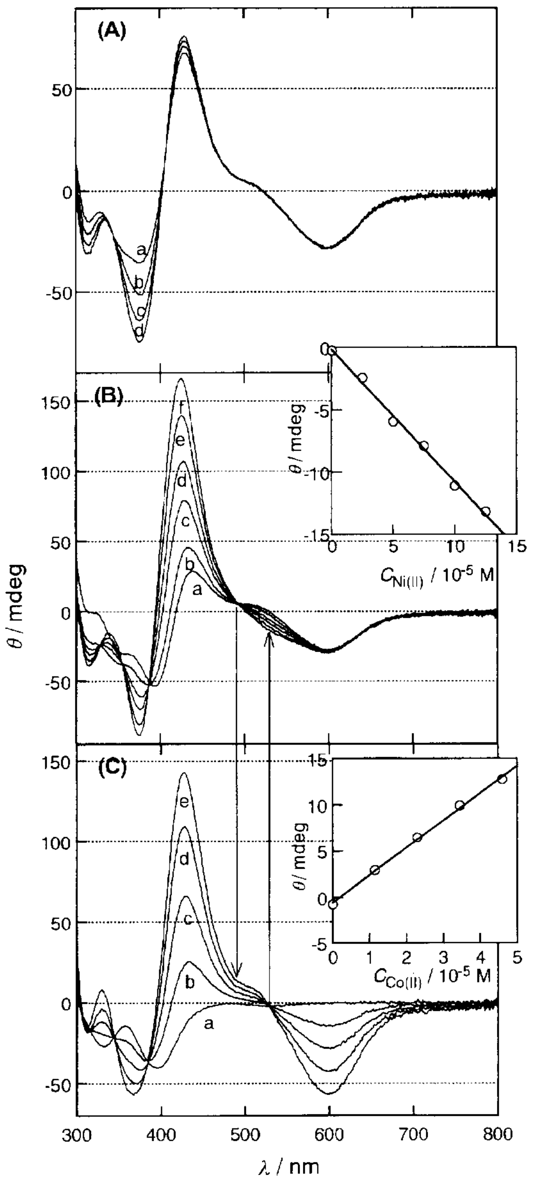

Fig. 6. Dependence of CD spectra on the concentration of zinc(II) (A), nickel(II) (B), and cobalt(II) (C) ions in the ternary solutions; (A) $C_{Rh} = 2.08 \times 10^{-4}$ M, $C_{Zn(II)} = 0.00$ (a), 5.45 (b), 10.90 (c), and 16.35 (d)$\times 10^{-5}$ M, $C_{Ni(II)} = 2.50 \times 10^{-5}$ M, and $C_{Co(II)} = 1.15 \times 10^{-5}$ M; (B) $C_{Rh} = 2.08 \times 10^{-4}$ M, $C_{Zn(II)} = 2.18 \times 10^{-5}$ M, $C_{Ni(II)} = 0.00$ (a), 2.50 (b), 5.00 (c), 7.50 (d), 10.00 (e), and 12.50 (f)$\times 10^{-5}$ M, and $C_{Co(II)} = 2.30 \times 10^{-5}$ M; (C) $C_{Rh} = 4.16 \times 10^{-4}$ M, $C_{Zn(II)} = 2.18 \times 10^{-5}$ M, $C_{Ni(II)} = 2.50 \times 10^{-5}$ M, and $C_{Co(II)} = 0.00$ (a), 1.15 (b), 2.30 (c), 3.45 (d), and 4.60 (e)$\times 10^{-5}$ M. The linear regression equations were expressed as $\theta = -1.06 \times 10^5 C_{Ni(II)} - 0.18$ at 529 nm ($R = 0.9974$ and $D = 0.55$) (inset in B) and $\theta = 2.95 \times 10^5 C_{Co(II)} - 0.53$ at 491 nm (○) ($R = 0.9989$ and $D = 0.14$) (inset in C).

tion of the sulfur bridged zinc(II) complexes is independent of the sulfur bridging reaction of the other metal ions, and if we apply λ_{iso} for the zinc(II) solution or $\lambda_{\Delta\varepsilon = 0}$ for both the *S*-bridged zinc(II) complexes and Δ_{LLL}-*fac*(*S*)-[Rh(L-cys-*N*,*S*)$_3$]$^{3-}$.

As shown in Fig. 5, the above requirements of wavelength are satisfied in the region of wavelengths longer than ca. 470 nm, where the CD intensity of each solution is almost the same, or equal to zero. As an example, each metal concentration dependence of the CD spectra for a ternary mixed solution containing cobalt(II), nickel(II), and zinc(II) is shown in Fig. 6. The isodichroic points are observed at 334, 344, and 405 nm in the zinc(II) concentration dependence for the ternary solution (Fig. 6A) which coincide with λ_{iso} for a zinc(II) solution shown in Fig. 5. The values of λ_{iso} observed in the concentration dependence for the other metal ion, cobalt(II) and nickel(II), also agree with those for the respective metal ion solution. These facts indicate that an *S*-bridged complex with each metal ion is formed independently. It is possible that an octanuclear complex with mixed metal ions is formed in the presence of an excess of zinc(II), as reported for *fac*(*S*)-[Rh(aet)$_3$], to give [{Rh(aet)$_3$}$_4$Zn$_{3.7}$Co$_{0.3}$O]$^{6+}$.[19,21] However, under the present condition that the rhodium(III) complex is in large excess of zinc(II), which is quite diluted, the formation of an octanuclear complex is thermodynamically unfavorable (vide supra) and the trinuclear complexes, [Co or Ni{Rh(L-cys-*N*,*S*)$_3$}$_2$]$^{3- \text{ or } 4-}$, are selectively formed. Consequently, each concentration of cobalt(II) and nickel(II) is expected to be determined at 491 and 529 nm, which are λ_{iso} for the nickel(II) and cobalt(II) concentration dependence, respectively. In fact, satisfactory linearity was obtained for each calibration curve (Fig. 6). It has been confirmed that a simultaneous determination of the transition metal ions is possible for a ternary solution containing zinc(II).

Supporting Data.

The absorption and CD spectra of trinuclear complexes with rhodium(III) terminals (Fig. S1), the dependence of the absorption and CD spectra on the concentration of cobalt(III) (Fig. S2) and nickel(II) (Fig. S3) in the presence of excess Λ-*fac*(*S*)-[Rh(aet)$_3$], the dependence of the absorption and/or CD spectra on the concentration of iron(III) (Fig. S4), iron(II) (Fig. S5), cobalt(III) (Fig. S6), cobalt(II) (Fig. S7), and nickel(II) (Fig. S8) in solutions containing excess Λ_{LLL}-*fac*(*S*)-[Rh(L-cys-*N*,*S*)$_3$]$^{3-}$ (in total 8 pages) are deposited as Document No. 73044 at the Office of the Editor of Bull. Chem. Soc. Jpn. and are also available from the author upon request.

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22 The values, $R = 0.9975$ and $D = 0.056$ for absorbance at 428 nm and $R = 0.9984$ and $D = 0.29$ for CD intensity at 420 nm, were obtained from eight data points ($C_{\mathrm{Fe(III)}} = 6.09$—$20.30\times10^{-6}$ M) and five data points ($C_{\mathrm{Fe(III)}} = 2.19$—$10.95\times10^{-5}$ M), respectively.

23 The values, $R = 0.9968$ and $D = 0.50$ for absorbance at 428 nm and $R = 0.9993$ and $D = 0.20$ for CD intensity at 447 nm, were obtained from six data points ($C_{\mathrm{Fe(II)}} = 2.19$—$13.14\times10^{-5}$ M) and five data points ($C_{\mathrm{Fe(II)}} = 2.20$—$11.00\times10^{-5}$ M), respectively.

24 The representative R and D value are follows: $R = 0.9998$ and $D = 0.096$ for absorbance at 416 nm and $R = 0.9999$ and $D = 0.061$ for CD intensity at 361.5 nm obtained from nine data points for cobalt(III) ($C_{\mathrm{Co(III)}} = 0$—8.96×10^{-5} M); $R = 1.0000$ and $D = 0.028$ for absorbance at 425 nm and $R = 1.0000$ and $D = 0.030$ for CD intensity at 434 nm obtained from nine data points for cobalt(II) ($C_{\mathrm{Co(II)}} = 0$—8.13×10^{-5} M); $R = 0.9999$ and $D = 0.029$ for absorbance at 555 nm and $R = 0.9999$ and $D = 0.030$ for CD intensity at 450 nm obtained from eight data points for nickel (II) ($C_{\mathrm{Ni(II)}} = 0$—3.39×10^{-4} M).

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