Circular Dichroism Spectrophotometric Determination of Metal Ions by Using Optically Resolved Sparingly Soluble *fac(S)*-[Rh(aet)$_3$] (aet = 2-Aminoethanethiolate)

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Sparingly soluble neutral *fac(S)*-[Rh(aet)$_3$] (aet = 2-aminoethanethiolate) was optically resolved completely. The *S*-bridged complex formation of the optically active isomer of *fac(S)*-[Rh(aet)$_3$] was utilized for the selective determination of metal ions by using circular dichroism spectra.

Circular dichroism (CD) spectra usually exhibit positive and negative Cotton effects. Consequently, we can obtain several wavelengths where molar CD coefficient ($\Delta\varepsilon$) is equal to zero ($\lambda_{\Delta\varepsilon=0}$) and can observe a large difference in CD intensity at a fixed wavelength by a small structural difference of the compound with a slight shift of the absorption maximum. Such characteristics of CD spectra are quite advantageous to selective spectrophotometric determination for a mixed solution because we can detect a change in concentration of one species at $\lambda_{\Delta\varepsilon=0}$ for the other species. However, the advantage of CD spectra has not been utilized in the field of analytical chemistry so far.

Recently, it has been revealed that tris(thiolato)-type cobalt(III) and rhodium(III) complexes, *fac(S)*-[M(aet)$_3$] and *fac(S)*-[M(L-cys-*N*,*S*)$_3$]$^{3-}$ (M = Co(III) and Rh(III), aet = 2-aminoethanethiolate, and L-cys = L-cysteinate), readily form the *S*-bridged linear-type trinuclear complexes with various transition metal ions such as Fe(III), Co(II), Co(III), and Ni(II).[1] The *S*-bridged complexes are usually considerably stable in a solution and their optically active isomers exhibit quite strong CD bands attributed to the μ-thiolato sulfur-to-metal charge-transfer. In addition, while the neutral *fac(S)*-[M(aet)$_3$] are sparingly soluble, their *S*-bridged complexes positively charged are mostly water-soluble. Such properties of *fac(S)*-[M(aet)$_3$] and the *S*-bridged complexes are extremely suitable for the CD spectrophotometric determination if optically active *fac(S)*-[M(aet)$_3$] are available. Nevertheless, so far neutral *fac(S)*-[M(aet)$_3$] has not been optically resolved mainly due to the low solubility in any solvents. Under these circumstances, we have attained the optical resolution of the sparingly soluble *fac(S)*-[Rh(aet)$_3$] and the application of the enantiomer to the selective spectrophotometric determination of metal ions. The reason for preference for the Rh(III) complex to the corresponding Co(III) complex are that the configurational inversion by the redox reaction of the *S*-bridged metal ion[1b,c,2] and the self-rearrangement in a solution[3] is observed for the Co(III) complex, while neither of them is observed for the Rh(III) complex at all.[1d]

The water-soluble heptanuclear complex [{Rh(aet)$_3$}$_4$Zn$_3$-OH]Br$_5$ was optically resolved by using K$_2$[Sb$_2$(*R*,*R*-tartrate)$_2$].[4] After conversion of the $\Lambda\Lambda\Lambda\Lambda$ isomer to the bromide salt, an excess of EDTA disodium salt was reacted with the 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)$_3$}$_4$Zn$_{3.7}$Co$_{0.3}$O]Br$_6$[5] obtained from $\Lambda\Lambda$-[Co{Rh(aet)$_3$}$_2$](NO$_3$)$_3$[1d] was also used to give Λ-*fac(S)*-[Rh(aet)$_3$] by the capture reaction of Zn(II) with EDTA. The optical purity of Λ isomer was 99%, which was estimated by the absorption and CD spectral measurements of [Co{Rh(aet)$_3$}$_2$]$^{3+}$ formed by the reaction of the optically resolved *fac(S)*-[Rh(aet)$_3$] with [CoCl(NH$_3$)$_5$]Cl$_2$.[1d] It was also found from the SP-Sephadex column chromatography that the only $\Lambda\Lambda$-[Co{Rh(aet)$_3$}$_2$]$^{3+}$ was formed by the above reaction. The Δ-*fac(S)*-[Rh(aet)$_3$] was also obtained by procedures similar to those for the Λ isomer. These results confirmed that the sparingly soluble *fac(S)*-[Rh(aet)$_3$] was optically resolved completely.

The dependence of the absorption and CD intensity on the metal ion concentration was examined for aqueous solutions of Co(NO$_3$)$_2$·6H$_2$O (C_{Co} = 2.00, 4.00, 6.00, 8.00, 10.01, and 12.01 × 10^{-5} mol dm^{-3}), Ni(NO$_3$)$_2$·6H$_2$O (C_{Ni} = 5.01, 10.01, 15.02, 20.03, 25.04, and 30.04 × 10^{-5} mol dm^{-3}), and both of the two salts (C_{Co} = 0.00, 2.00, 4.00, 6.00, 8.00, 10.01, and 12.01 × 10^{-5} mol dm^{-3}, C_{Ni} = 5.01 × 10^{-5} mol dm^{-3}; C_{Co} = 2.00 × 10^{-5} mol dm^{-3}, C_{Ni} = 0.00, 5.01, 10.01, 15.02, 20.03, 25.04, and 30.04 × 10^{-5} mol dm^{-3}). The sample solutions were stood at room temperature for at least 1h in the presence of an excess amount of powdery Λ-*fac(S)*-[Rh(aet)$_3$].[6] Absorption and CD spectra of the supernatant solutions or the filtrates were recorded on a Shimadzu UV-3100 spectrophotometer and a JASCO J-720WL spectropolarimeter, respectively.

The linear concentration dependence of the absorption and CD intensities was observed in the whole spectral region with the isodichroic points at 321.5, 347.0, 385.5, and 526.5 nm for the Co(II) solutions and at 308.0, 328.5, 355.5, 390.0, and 487.5 nm for the Ni(II) solutions. These facts indicate that the concentration of Λ-*fac(S)*-[Rh(aet)$_3$] slightly dissolved is constant in each sample solution. The linearity and sensitivity for the CD spectra are comparable or better than those for the absorption spectra.[7]

Assuming that the Co(II) and Ni(II) ions independently form the *S*-bridged complexes in the mixed solution, the CD intensity (θ_{obs}) of the solution containing Co(II) and Ni(II) ions is expressed as $\theta_{\mathrm{obs}} = [\mathrm{Rh}][\theta]_{\mathrm{Rh}} + [\mathrm{Co}][\theta]_{\mathrm{Co}} + [\mathrm{Ni}][\theta]_{\mathrm{Ni}}$, where [Rh], [Co], and [Ni] are the concentrations of Λ-*fac(S)*-[Rh(aet)$_3$] dissolved, $\Lambda\Lambda$-[Co{Rh(aet)$_3$}$_2$]$^{3+}$,[1d] and $\Lambda\Lambda$-[Ni{Rh(aet)$_3$}$_2$]$^{2+}$,[1e] respectively, and $[\theta]_{\mathrm{Rh}}$, $[\theta]_{\mathrm{Co}}$, and $[\theta]_{\mathrm{Ni}}$ are the molar CD intensity of the corresponding complexes. Because it is confirmed from the linearity between the metal ion concentration and the absorption and CD intensity that the Co(II) and Ni(II) ions quantitatively form the corresponding *S*-bridged complexes, [Co] and [Ni] are regarded as the total concentrations of the respective metal(II) ions. The linear concentration dependence of Co(II) and Ni(II) ions for the mixed solution is expected to be observed at the wavelength of the isodichroic points given above for the Ni(II) and Co(II) solutions where $[\theta]_{\mathrm{Ni}} = 0$ and $[\theta]_{\mathrm{Co}} = 0$, respectively, since [Rh] is constant as above described. As shown in Figure 1(A), the isodichroic points for the mixed solutions with variation of the Ni(II) concentration were observed at the same wavelengths as those for the Ni(II) solution. Consequently, it is indicated that only the Co(II) concentrations are detectable at these wavelengths. In fact, good linearity between the Co(II) concentration and CD intensity for the mixed solution was observed at 487.5 and 308.0 nm with variation of the Co(II) concentration (Figure 1B),[8] where the change in CD intensity is relatively large. Similarly, the wavelengths of the isodichroic points for the mixed solutions with variation of the Co(II) concentration agree with those for the Co(II) solution (Figure 1B), and fairly good linearity of the Ni(II) concentration dependence of the CD intensity for the mixed solution was also observed at 526.5 and 347.0 nm (Figure 1A).[8] Accordingly, it is confirmed that the selective or simultaneous determination of Co(II) and Ni(II) ions in the mixed solution is possible. Because the two ions are classified into the same category with similar chemical properties from an analytical point of view, they can be often the interfering ions with each other in the quantitative analyses.[9] Hence, it is notable that such an independent determination for the mixed solution is feasible by using only one reagent without any adjustment of the solution conditions.

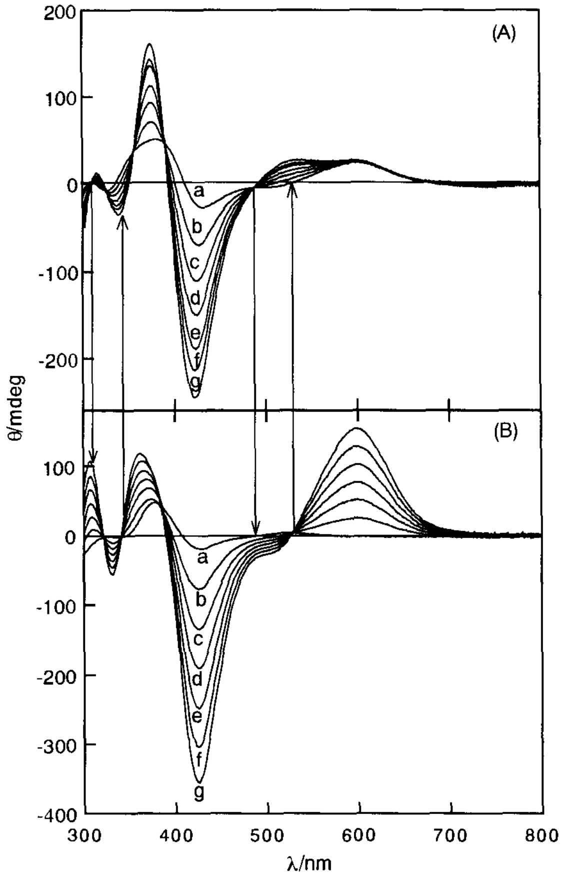

Figure 1. Dependence of CD spectra on the concentration of metal(II) ions in the mixed solutions; (A) C_{Co} = 2.00 ×10^{-5} mol dm^{-3}, C_{Ni} = 0.00(a), 5.01(b), 10.01(c), 15.02(d), 20.03(e), 25.04(f), and 30.04(g)×10^{-5} mol dm^{-3}; (B) C_{Co} = 0.00(a), 2.00(b), 4.00(c), 6.00(d), 8.00(e), 10.01(f), and 12.01 (g)×10^{-5} mol dm^{-3}, C_{Ni} = 5.01×10^{-5} mol dm^{-3}.

The present CD spectrophotometric determination of metal ions is expected to be applied to various metal ions potentially *S*-bridged. Furthermore, coexistence of Zn(II) and Cd(II) ions is allowable for the determination at the longer wavelength (λ > 480 nm) where Cotton effect attributed to Zn(II)[10] or Cd(II)[11] ion is not observed because of absence of *d-d* transition for the *S*-bridged metal ions.

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References and Notes

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[2] T. Konno, S. Aizawa, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **62**, 585 (1989).

[3] The Co(III) complex is gradually dissolved in an aqueous solution containing no metal ion to form *S*-bridged trinuclear complex $[Co\{Co(aet)_3\}_2]^{3+}$.

[4] T. Konno, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **67**, 101 (1994).

[5] T. Konno, K. Okamoto, and J. Hidaka, *Inorg. Chem.*, **33**, 538 (1994).

[6] The Ni (II) ion was reacted immediately. The reaction of the Co(II) ion was accelerated when a small amount (1−5×10^{-4} mol dm^{-3}) of H_2O_2 was contained, because the *S*-bridged Co(II) ion is quantitatively oxidized by O_2 or H_2O_2 in the solution to complete the formation reaction of $[Co\{Rh(aet)_3\}_2]^{3+}$ as reported in reference 1d.

[7] The linear regression equations were expressed as $A = 1.11 \times 10^4 C_{Co} + 0.011$ (at 415.0 nm, $r = 0.9997$, $D = 0.15$), $\theta = 7.06 \times 10^5 C_{Co} + 5.11$ (at 355.5 nm, $r = 0.9998$, $D = 0.13$), $A = 3.46 \times 10^3 C_{Ni} + 0.286$ (at 320.0 nm, $r = 0.9918$, $D = 1.9$), and $\theta = -6.87 \times 10^5 C_{Ni} + 30.87$ (at 422.0 nm, $r = -0.9997$, $D = 0.41$), where A and θ are the absorbance and CD intensity (mdeg) at the given wavelength, C is the total concentration (mol dm^{-3}) of the respective metal ions, r is the correlation coefficient, and D is the detection limit (mg dm^{-3}) calculated as the ratio of 3σ at $C = 0$ and the slop of the regression equation.

[8] The linear regression equations were expressed as $\theta = -2.68 \times 10^5 C_{Co} + 0.24$ (at 487.5 nm, $r = -0.9997$, $D = 0.17$), $\theta = 9.78 \times 10^5 C_{Co} - 12.10$ (at 308.0 nm, $r = 0.9999$, $D = 0.12$), $\theta = 8.78 \times 10^4 C_{Ni} + 0.82$ (at 526.5 nm, $r = 0.9957$, $D = 1.6$), and $\theta = -1.39 \times 10^5 C_{Ni} + 21.52$ (at 347.0 nm, $r = -0.9962$, $D = 1.5$), where meanings of the symbols are the same as in note 7.

[9] F. D. Snell, "Photometric and Fluorometric methods of analysis, Metals," John Wiley & Sons, New York (1978), Part 1, Chaps. 19 and 20.

[10] Our preliminary experiments revealed that the Zn(II) concentration dependence of CD intensity is observed especially in the wavelength region of 330−400 nm. Coexistence of the Zn(II) ion does not inhibit the formation of the respective *S*-bridged complexes $[M\{Rh(aet)_3\}_2]^{n+}$ (M = Co(III), Ni(II)) in the presence of an excess of *fac(S)*-$[Rh(aet)_3]$ probably due to the thermodynamic stability of $[M[Rh(aet)_3\}_2]^{n+}$ over the mixed metal complexes such as $[\{Rh(aet)_3\}_4Zn_{4-x}Co_xO]^{6+}$ (reference 5).

[11] T. Konno, Y. Kageyama, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **67**, 1957 (1994).