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Synthesis, Crystal Structure, and Some Spectrochemical Properties of Optically Active *S*-Bridged Trinuclear Complex $\Delta\Delta$-[Ni{Co(aet)$_2$(*R*-pn)}$_2$]$^{4+}$ (aet = 2-Aminoethanethiolate, *R*-pn = (*R*)-1,2-Propanediamine)

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The reaction of *cis*-[CoCl$_2$(*R*-pn)$_2$]$^+$ (*R*-pn = (*R*)-1,2-propanediamine) with [Ni(aet)$_2$] (aet = 2-aminoethanethiolate) in water stereoselectively gave an *S*-bridged trinuclear complex, [Ni{Co(aet)$_2$(*R*-pn)}$_2$]$^{4+}$, accompanied by the ligand-transfer of aet from Ni^{2+} to Co^{3+}. The $\Delta\Delta$ isomer of the trinuclear complex was selectively formed. The spectrochemical properties of the$\Delta\Delta$ isomer are also discussed in relation to the stereochemical behavior.

It has been shown that the *S*-bridged trinuclear Co$^{\mathrm{III}}$Ni$^{\mathrm{II}}$Co$^{\mathrm{III}}$ complex, [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ (aet = 2-aminoethanethiolate, en = ethylenediamine), is derived from the reaction between [Ni(aet)$_2$] and [CoCl$_2$(en)$_2$]$^+$ accompanied by the ligand-transfer of aet from Ni^{2+} to Co^{3+}.[1] For this trinuclear complex, three isomers ($\Delta\Delta$, $\Lambda\Lambda$, and $\Delta\Lambda$) are possible by considering the absolute configurations (Δ and Λ) of the two *cis*(*S*)-[Co(aet)$_2$(en)]$^+$ units; the crystals have consisted of the $\Delta\Delta$ and $\Lambda\Lambda$ isomers to form the racemic compound. However, the mechanisms for ligand-transfer and the absolute configuration of the optically active isomer have been unclear. It is expected that a similar trinuclear Co$^{\mathrm{III}}$Ni$^{\mathrm{II}}$Co$^{\mathrm{III}}$ complex can be stereoselectively obtained by a reaction between [Ni(aet)$_2$] and the mononuclear Co(III) complex with an optically active diamine ligand, such as (*R*)-1,2-propanediamine (*R*-pn), which is known to play an important role in the emergence of stereoselectivity for the complexes with octahedral geometry.[2] In the present paper, we report on the stereo- and spectrochemical properties of the *S*-bridged trinuclear complex, $\Delta\Delta$-[Ni{Co(aet)$_2$(*R*-pn)}$_2$]$^{4+}$.

An X-ray structural analysis[3] for the optically active trinuclear complex revealed the presence of a discrete tetravalent complex cation, four perchlorate anions, and one water molecule, $(-)^{\mathrm{CD}}_{500}$-[Ni{Co(aet)$_2$(*R*-pn)}$_2$](ClO$_4$)$_4$·H$_2$O. The complex cation exhibits a quite similar trinuclear structure to [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ (Fig. 1).[1] The central NiS$_4$ sphere is somewhat distorted from a square-planar to a tetrahedral geometry, in which the NiS$_1$S$_2$ and NiS$_3$S$_4$ planes intersect to form a dihedral angel of 13.94°, but less distorted than that of [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$.[1] Taking the absolute configurations (Δ and Λ) of the two *cis*(*S*)-[Co(aet)$_2$(*R*-pn)]$^+$ units into consideration, three isomers ($\Delta\Delta$, $\Lambda\Lambda$, and $\Delta\Lambda$) are possible for [Ni{Co(aet)$_2$(*R*-pn)}$_2$]$^{4+}$. However, an X-ray structural analysis indicates that all of the crystals of the *R*-pn complex consist of only the $\Delta\Delta$ isomer to show the negative CD sign at 500 nm in solution. This is contrary to the case of [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$, whose crystal consists of the $\Delta\Delta$ and $\Lambda\Lambda$ isomers to form a racemic compound.[1] Furthermore, all of the two aet and one *R*-pn chelate rings in each *cis*(*S*)-[Co(aet)$_2$(*R*-pn)]$^+$ units take λ conformations. These may be attributed to the fact that the methyl groups of the *R*-pn ligands take equatorial conformations.[2] It is noted that the methyl groups of two *R*-pn ligands are situated in *trans* position with respect to the C_2 axis passing through the central Ni atom, although two geometrical isomers, *cis* and *trans*, are possible for the methyl groups in the trinuclear complex. This may suggest the pathway of the selective formation to give the $\Delta\Delta$ trinuclear complex accompanied by the ligand transfer reaction of the Δ-*cis* starting complex. The selective formation of the $\Delta\Delta$ isomer was confirmed by SP-Sephadex column chromatography for the reaction mixture.

The ^{13}C NMR spectrum of [Ni{Co(aet)$_2$(*R*-pn)}$_2$]$^{4+}$ in D$_2$O exhibits six signals at δ = 19.58, 34.50, 34.60, 52.24, 55.65, and 55.91. Among these signals, the signals at 34.50 and 34.60 are due to the carbon atoms of –CH$_2$S groups, and the signal at 55.65 to –CH$_2$N groups in aet.[1,4,5] Further, the signals at 19.58, 52.24, and 55.91 are assigned to the carbon atoms of –CH$_3$, –CH$_2$N, and –CH groups in *R*-pn, respectively. These imply that two aet and one *R*-pn ligands in each *cis*(*S*)-[Co(aet)$_2$(*R*-pn)]$^+$ units indicate C_1 symmetry.

The electronic absorption and CD spectra of $(-)^{\mathrm{CD}}_{500}$-[Ni{Co(aet)$_2$(*R*-pn)}$_2$]$^{4+}$ in water are shown in Fig. 2. These absorption spectral patterns are almost identical with those of[Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$.[1] Furthermore, $(-)^{\mathrm{CD}}_{500}$-[Ni{Co(aet)$_2$(*R*-pn)}$_2$]$^{4+}$, whose absolute configuration has

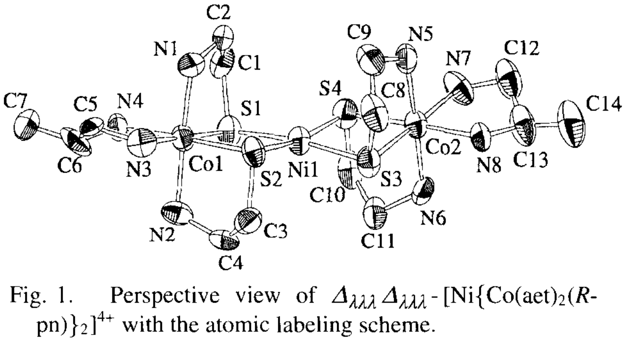

Fig. 1. Perspective view of $\Delta_{\lambda\lambda\lambda}\Delta_{\lambda\lambda\lambda}$-[Ni{Co(aet)$_2$(*R*-pn)}$_2$]$^{4+}$ with the atomic labeling scheme.

been determined to be $\Delta\Delta$ configuration by an X-ray study, also exhibits similar CD bands over the whole region to $(-)^{CD}_{500}$-[Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$.[1] This supports the results of the assignment of the optically active en complex, which are determined from the empirical relationship between the absolute configuration and the CD spectral sign in the first d–d absorption regions.[6]

Experimental

Preparation. To a suspension containing 1.05 g (5.0 mmol) of [Ni(aet)$_2$][7] in 20 cm^3 of water was added 3.14 g (10 mmol) of *cis*-[CoCl$_2$(*R*-pn)$_2$]Cl.[8] After the mixture was stirred at room temperature for 2 h, the resulting reddish-brown product was collected by filtration. The product was dissolved in 20 cm^3 of water, and then any undissolved materials were filtered off. To the reddish-brown filtrate 20 cm^3 of a saturated NaClO$_4$ solution was added. The mixture was allowed to stand at 4 °C for several days, and the resulting reddish-brown fine crystals were collected by filtration. The crystals were recrystallized from a small amount of water. Well-formed crystal was used for the X-ray structural analysis.[3] Yeild: 0.536 g (16.0%). Calcd for [Ni{Co(aet)$_2$(*R*-pn)}$_2$](ClO$_4$)$_4$·H$_2$O = C$_{14}$H$_{46}$N$_8$O$_{17}$S$_4$Cl$_4$Co$_2$Ni: C, 16.09; H, 4.44; N, 10.72%. Found: C, 15.85; H, 4.48; N, 10.42%.

Measurement. The electronic absorption spectra were recorded with a JASCO Ubest V-560 spectrophotometer, and the CD spectra with a JASCO J-600 spectropolarimeter. The ^{13}C NMR spectra were recorded with a Bruker AM-500 NMR spectrometer in D$_2$O. The sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as an internal reference. The elemental analyses (C, H, N) were performed by the Analysis Center of the University of Tsukuba.

Crystallography. The unit-cell parameters and intensity data for [Ni{Co(aet)$_2$(*R*-pn)}$_2$](ClO$_4$)$_4$·H$_2$O were used for data collection on a Rigaku RASA-7S four-circle diffractometer with graphite-monochromatized Mo *Kα* radiation. The unit-cell parameters were determined by a least-square refinement of 19 reflections (8.5° < θ < 18.8°). The intensity data were collected by the ω–2θ scan technique, and the intensities were corrected for Lorentz and polarization. An empirical absorption correction based on a series of Ψ scans was applied. The independent reflections with $I_0 > 2\sigma(I_0)$ were used for structure determinations. The positions of the Co and Ni atoms were determined by a direct method. Difference Fourier maps based on these atomic positions revealed some remaining non-hydrogen atoms. The structures were refined by a full-matrix least-squares refinement on F of the positional parameters and the anisotropic thermal parameters of the non-hydrogen atoms in [Ni{Co(aet)$_2$(*R*-pn)}$_2$](ClO$_4$)$_4$·H$_2$O. The hydrogen atoms on the ligands were fixed by the geometrical and thermal constrains (C–H = N–H = 0.95 Å and $U = 1.3U$ (C, N). For $(-)^{CD}_{500}$-[Ni{Co(aet)$_2$(*R*-pn)}$_2$]$^{4+}$, when the refinements were carried out using a set of non-H atoms parameters containing the $\Delta\Delta$ configuration of the complex cation, the residual values converged in $R = 0.057$ and $R_w = 0.065$, and the Flack parameter[9] gives 0.13(4). A refinement using the enantiomeric atomic parameters (the $\Lambda\Lambda$ configuration) resulted in residual values of $R = 0.060$ and $R_w = 0.068$, and Flack parameter gives 0.84(4). Further, the asymmetric carbon atom of 1,2-propanediamine in the $\Delta\Delta$ configuration shows the *R* configuration, which is expected for the used ligand. It was thus assumed that the former is most likely to be the correct choice, namely, the $(-)^{CD}_{500}$ complex cation with the $\Delta\Delta$ configuration. All of the calculations were performed on an Indigo II computer using teXsan.[10] The final atomic positional parameters are deposited in Tables S1—S3.[11] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 141263.

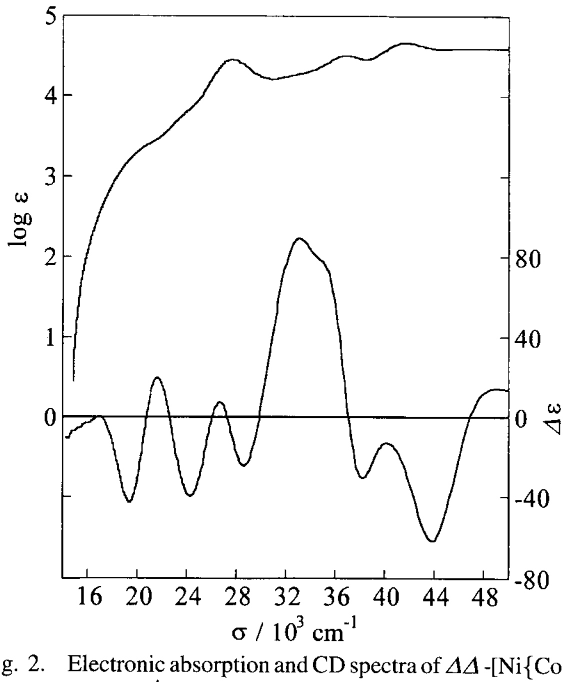

Fig. 2. Electronic absorption and CD spectra of $\Delta\Delta$-[Ni{Co(aet)$_2$(*R*-pn)}$_2$]$^{4+}$ in H$_2$O.

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3 Crystal data for [Ni{Co(aet)$_2$(*R*- pn)}$_2$](ClO$_4$)$_4$·H$_2$O: F.W. = 1380.61, Cryst dimens = 0.10×0.20×0.30 mm, Orthorhombic, $P2_12_12_1$ (#19), $Z = 4$, $a = 13.56(1)$, $b = 30.790(9)$, $c = 9.319(9)$ Å, $V = 3889(4)$ Å^3, $D_{\text{calc}} = 1.785$ g cm^{-3}, $\mu = 18.85$ cm^{-1}.

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11 Lists of final atomic coordinates and equivalent isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, and bond distances and angles are deposited as Document No. 73032 at the Office of the Editor of Bull. Chem. Soc. Jpn.