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Transfer of 2-Aminoethanethiolate (aet) from Nickel(II) to Cobalt(III) Coordination Sphere.
Synthesis, Crystal Structure, and Some Properties of an S-Bridged Trinuclear Complex $[Ni\{Co(aet)_2(en)\}_2]^{4+}$

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The reaction of $[CoCl_2(en)_2]^+$ with $[Ni(aet)_2]$ in water gave an S-bridged $Co^{III}Ni^{II}Co^{III}$ trinuclear complex, $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ (**1**), which indicates that the bidentate-N,S ligand aet transfers from the Ni^{II} to the Co^{III} coordination sphere. **1** formed only the racemic compound of Δ(C_2-*cis*(S))Δ(C_2-*cis*(S)) and Λ(C_2-*cis*(S))Λ(C_2-*cis*(S)) isomers, and its crystal structure was analyzed by X-ray diffraction. $[Ni\{Co(aet)_2(en)\}_2]Cl_4\cdot 6H_2O$, chemical formula $C_{12}H_{52}N_8O_6S_4Cl_4Co_2Ni$, crystallizes in the monoclinic space group $C2/c$ with $a=14.987(4)$, $b=19.480(3)$, $c=12.916(4)$ Å, $\beta=113.67(1)°$, $V=3454(1)$ Å^3, $Z=4$, and $R=0.046$. The central Ni^{II} atom is situated in an environment markedly distorted from a square-planar to a tetrahedral geometry, coordinated by four thiolato sulfur atoms from two octahedral C_2-*cis*(S)-$[Co(aet)_2(en)]^+$ units. The H_2O_2 oxidation of **1** caused the cleavage of the Ni–S bonds to afford the mononuclear sulfinato complex, $[Co(NH_2CH_2CH_2SO_2\text{-}N,S)_2(en)]^+$ (**2**), retaining the C_2-*cis*(S) geometry of **1**. **1** and **2** were optically resolved and their absorption, CD, and NMR spectral behavior are reported.

The binding ability of coordinated thiolato sulfur atoms to other metal ions has led to the development of the stereochemistry of S-bridged polynuclear complexes containing aminothiolate ligands such as 2-aminoethanethiolate (aet=$NH_2CH_2CH_2S^-$) and L-cysteinate (L-cys=$NH_2CH(COO^-)CH_2S^-$).[1—6] While a number of S-bridged polynuclear complexes with aet have been prepared by reacting octahedral $[M(aet)_3]$ (M=Co^{III}, Rh^{III}, Ir^{III}) with a variety of metal ions,[1,2] the number of the polynuclear complexes derived from square-planar $[M'(aet)_2]$ (M'=Ni^{II}, Pd^{II}) has been limited.[4] In fact, the linear-type S-bridged $Ni^{II}Ni^{II}Ni^{II}$ complex, $[Ni\{Ni(aet)_2\}_2]^{2+}$, in which the two *cis*(S)-$[Ni(aet)_2]$ units bind to one square-planar Ni^{II} ion, has long been the only S-bridged structure which has been well characterized.[4,7] We have found that the *cis*(S)-$[M'(aet)_2]$ unit can bind to two square-planar Pd^{II} ions to produce a new class of S-bridged hexanuclear complexes, $[Pd_2\{M'(aet)_2\}_4]^{4+}$.[5] The diversity of S-bridged polynuclear structures composed of *cis*(S)-$[M'(aet)_2]$ units encouraged us to investigate the reaction of $[Ni(aet)_2]$ with the octahedral $[CoCl_2(en)_2]^+$. To our surprise, it was found that this reaction does not give an expected $Co^{III}Ni^{II}$ dinuclear complex, $[Co\{Ni(aet)_2\}(en)_2]^{3+}$, but a novel Co^{III} $Ni^{II}Co^{III}$ trinuclear complex, $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ (**1**), in which the bidentate-*N,S* ligand aet chelates to Co^{III} ion.

A partial report of the crystal structure of **1** has been published as a preliminary communication.[8] We report here the complete description of synthesis, optical resolution, structural characterization, and some properties of this complex. Since the properties of the mononuclear $[Co(aet)_2(en)]^+$ complex have been little studied because of its preparative difficulty,[9,10] detailed investigations of **1** composed of *cis*(S)-$[Co(aet)_2(en)]^+$ units will contribute significantly to our understanding of the chemistry of mononuclear thiolato complexes in addition to that of the S-bridged polynuclear complexes with aminothiolate ligands.

Experimental

Preparation of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ (1). To a green suspension containing 1.0 g (4.7 mmol) of $[Ni(aet)_2]$[4,11] in 20 cm^3 of water was added 2.7 g (9.4 mmol) of *trans*-$[CoCl_2(en)_2]Cl$.[12,13] After the mixture had been stirred at room temperature for 2 h, the resulting red-brown complex (**1**Cl_4) was collected by filtration. Recrystallization of **1**Cl_4 from water gave dark red crystals, one of which was used for X-ray structural analysis. Yield: 0.42 g. Anal. Found: C, 16.93; H, 6.15; N, 12.97; Co, 13.54; Ni, 6.56%. Calcd for $[Ni\{Co(C_2H_6NS)_2(C_2H_8N_2)\}_2]Cl_4\cdot 6H_2O$: C, 16.93; H, 6.16; N, 13.16; Co, 13.85; Ni, 6.89%. NMR (500 MHz, D_2O, ppm from DSS): ^1H NMR $\delta=1.78$ (td, $J=14$ and

5 Hz, $-CH_2S$), 2.50 (dd, $J=14$ and 4 Hz, $-CH_2S$), 2.54 (d, $J=9$ Hz, $-CH_2N$ of en), 2.77 (d, $J=9$ Hz, $-CH_2N$ of en), 3.67 (dd, $J=13$ and 4 Hz, $-CH_2N$), 4.31 (td, $J=13$ and 4 Hz, $-CH_2N$); ^{13}C NMR $\delta=34.76$ ($-CH_2S$), 46.65 ($-CH_2NH_2$ of en), and 56.00 ($-CH_2NH_2$). **1**Cl_4 was also obtained using *cis*-$[CoCl_2(en)_2]Cl$[12] instead of *trans*-$[CoCl_2(en)_2]Cl$.

Optical Resolution of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$. To a solution containing 0.5 g (0.6 mmol) of **1**$Cl_4\cdot 6H_2O$ and 0.2 g (0.7 mmol) of $Ni(NO_3)_2\cdot 6H_2O$[14] in 25 cm^3 of water was added 0.8 g (1.2 mmol) of $Na_2[Sb_2(R,R\text{-tartrato})_2]\cdot 5H_2O$ dissolved in a small amount of water. The mixture was stored in a refrigerator for 1 d and the resulting brown powder ($(+)^{\rm CD}_{520}$ diastereomer, 0.31 g), which showed a positive CD value at 520 nm, was collected by filtration.

To the reddish brown filtrate, which showed a negative CD value at 520 nm, was added 8 cm^3 of a saturated NaCl aqueous solution. When the mixture was left in a refrigerator for 1 d, racemic crystals of **1**Cl_4 (0.28 g) appeared, which were removed by filtration. The remaining filtrate was concentrated to a small volume with a rotary evaporator until dark red microcrystals appeared. After cooling in a refrigerator for several hours, the resulting microcrystals ($(-)^{\rm CD}_{520}$-**1**Cl_4) were collected by filtration. Yield: 0.05 g. Anal. Found: C, 16.29; H, 5.91; N, 12.40%. Calcd for $[Ni\{Co(C_2H_6NS)_2(C_2H_8N_2)\}_2]Cl_4\cdot 6H_2O\cdot 0.75NaCl$: C, 16.10; H, 5.86; N, 12.52%.

To a solution containing 0.3 g of the $(+)^{\rm CD}_{520}$ diastereomer and 0.1 g of $NiCl_2\cdot 6H_2O$[14] in 20 cm^3 of water was added 5 cm^3 of a saturated NaCl aqueous solution. The mixture was stirred at room temperature for several minutes, followed by storing in a refrigerator for 1 d. The resulting racemic crystals of **1**Cl_4 (0.08 g) were filtered off and the remaining filtrate was concentrated to a small volume until dark red microcrystals appeared. After cooling in a refrigerator for several hours, the resulting microcrystals ($(+)^{\rm CD}_{520}$-**1**Cl_4) were collected by filtration. Yield: 0.08 g. Anal. Found: C, 16.85; H, 6.07; N, 12.95%. Calcd for $[Ni\{Co(C_2H_6NS)_2(C_2H_8N_2)\}_2]Cl_4\cdot 6H_2O$: C, 16.93; H, 6.16; N, 13.16%.

When an aqueous solution of **1**Cl_4 was chromatographed on a SP-Sephadex C-25 column (Na^+ form, 4 cm × 120 cm), two reddish brown bands, which partially overlapped each other, were eluted with a 0.2 mol dm^{-3} aqueous solution of $Na_2[Sb_2(R,R\text{-tartrato})_2]\cdot 5H_2O$. It was found from the absorption and CD spectral measurements that the earlier and later moving bands contained $(-)^{\rm CD}_{520}$-**1** and $(+)^{\rm CD}_{520}$-**1**, respectively.

Preparation of $[Co(NH_2CH_2CH_2SO_2\text{-}N,S)_2(en)]^+$ (2). To a reddish brown solution containing 0.2 g of **1**$Cl_4\cdot 6H_2O$ in 10 cm^3 of water was added 5 cm^3 of 10% H_2O_2. The mixture was stirred at 50 °C for 1 h, during which time the solution color turned dark yellow. After adding 2 cm^3 of 15% HBr, the dark yellow solution was concentrated almost to dryness. The residue was then dissolved in 8 cm^3 of water. To this was added a large amount of ethanol (ca. 100 cm^3), followed by cooling in a refrigerator for 1 d. The resulting brown-yellow microcrystals were collected by filtration. Yield: 0.10 g. Anal. Found: C, 17.30; H, 4.94; N, 13.32%. Calcd for $[Co(C_2H_6NO_2S)_2(C_2H_8N_2)]Br$: C, 17.36; H, 4.86; N, 13.32%. NMR (500 MHz, D_2O, ppm from DSS): ^1H NMR $\delta=2.75$ (td, $J=13$ and 5 Hz, $-CH_2S$), 2.90 (br, $-CH_2N$ of en), 2.91 (dt, $J=13$ and 5 Hz, $-CH_2S$), 3.00 (br, $-CH_2N$ of en), 3.14 (dt, $J=12$ and 5 Hz, $-CH_2N$), and 3.78 (td, $J=12$ and 5 Hz, $-CH_2N$); ^{13}C NMR $\delta=41.09$ ($-CH_2N$), 46.74 ($-CH_2N$ of en), and 64.15 ($-CH_2S$).

Optical Resolution of $[Co(NH_2CH_2CH_2SO_2\text{-}N,S)_2(en)]^+$. An aqueous solution of **2**Br was poured onto a SP-Sephadex C-25 column (Na^+ form, 2.5 cm × 100 cm). After the column had been swept with water, the adsorbed band was eluted with a 0.025 mol dm^{-3} aqueous solution of $Na_2[Sb_2(R,R\text{-tartrato})_2]\cdot 5H_2O$. When the adsorbed band was circulated in the same column three times, the band was completely separated into two yellow bands. After complete separation into two bands, each band was eluted with a 0.05 mol aqueous solution of NaCl. It was found from the absorption and CD spectral measurements that the earlier and later moving bands contained $(-)^{\rm CD}_{440}$-**2** and $(+)^{\rm CD}_{440}$-**2**, respectively. The concentration of each isomer was evaluated on the basis of the absorption spectral datum of the racemic bromide salt.

When the $(+)^{\rm CD}_{520}$ diastereomer of **1** was treated with 10% H_2O_2 in the manner described above, the resulting solution showed the same absorption and CD spectral patterns as those of $(+)^{\rm CD}_{440}$-**2**.

Measurements. The electronic absorption spectra were recorded with a JASCO Uvidec-505 or JASCO Ubest-55 spectrophotometer, and the CD spectra with a JASCO J-600 spectropolarimeter at room temperature. The ^1H and ^{13}C NMR spectra were recorded with a Bruker-AM-500 NMR spectrometer at a probe temperature in D_2O.[15] Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference. The elemental analyses (C, H, N) were done by the Analysis Center of the University of Tsukuba. The concentrations of Co and Ni in **1**Cl_4 were measured with a Nippon Jarrel-Ash ICPA-575 ICP spectrophotometer. The molar conductivity of **1**Cl_4 was measured with a Horiba DS-14 conductivity meter at 23 °C in water.

X-Ray Structure Analysis. A dark red crystal (ca. 0.23×0.20×0.15 mm) of **1**Cl_4 was used for data collection on an Enraf–Nonius CAD4 diffractometer with a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.71073$ Å). Unit cell dimensions were measured by least-squares refinement of 25 reflections with $15° < 2\theta < 21°$. Crystal data: $[Ni\{Co(aet)_2(en)\}_2]Cl_4\cdot 6H_2O=C_{12}H_{52}N_8O_6S_4Cl_4Co_2Ni$, M=851.2, monoclinic, space group $C2/c$ (No. 15), $a=14.987(4)$, $b=19.480(3)$, $c=12.916(4)$ Å, $\beta=113.67(1)°$, $V=3454(1)$ Å^3, $Z=4$, $D_x=1.64$ g cm^{-3}, $F(000)=1768$, $\mu(\text{Mo}\,K\alpha)=20.75$ cm^{-1}, and room temperature.

The intensity data were collected by the ω–2θ scan mode up to $2\theta=50°$ ($-18\leqq h\leqq 18$, $0\leqq k\leqq 24$, $0\leqq l\leqq 15$) with the scan width $(1.20+0.35\tan\theta)°$ and the scan rate varied from 1 to $5°$ min^{-1} (on ω). The intensities were corrected for Lorentz and polarization. An empirical absorption correction based on a series of ψ scans was applied (max. and min. transmission factors, 1.00 and 0.91). A total of 2875 independent reflections with $F_o>3\sigma(F_o)$ of the measured 7129 reflections were considered as 'observed' and used for the structure analysis.

The position of the nickel atom was obtained from a three-dimensional Patterson function. The remaining non-hydrogen atoms were found by conventional difference Fourier techniques to give a trial structure. The structure was refined by full-matrix least-squares techniques using SHELX76.[16] The Col, Ni, and Co2 atoms were constrained to the special positions of point symmetry 2 (0, y, 0.25) with a site occupancy factor of 0.5. Two of three water oxygen atoms (Ow2 and Ow3) had positional disorder and were best modeled with two positions for each atom. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were not included in the calculations. Neutral atomic scattering factors for cobalt and nickel atoms were taken from the literature,[17] while all others were supplied in SHELX76. The final refinement gave R=0.046 and R_w=0.065 (w=0.3313/($\sigma^2(F_o)$+0.015673$|F_o|^2$). The final atomic coordinates for non-hydrogen atoms are given in Table 1.[18]

Results and Discussion

Crystal Structure of [Ni{Co(aet)$_2$(en)}$_2$]Cl$_4$ (1Cl$_4$). X-Ray structural analysis showed the presence of a discrete complex cation, chloride anions, and water molecules. The total number of chloride anions implies that the entire complex cation is tetravalent. This is compatible with the observed molar conductivity in water of 507 Ω^{-1} cm^2 mol^{-1}, which is in agreement with those of the 1 : 4 electrolytes, [Pd{Ni(aet)$_2$}$_x${Pd(aet)$_2$}$_{4-x}$]Br$_4$ (527—540 Ω^{-1} cm^2 mol^{-1}).[5] A perspective drawing of the entire complex cation (**1**) is given in Fig. 1. The bond distances and angles are listed in Table 2.

The entire complex cation consists of two *cis*(S)-[Co(aet)$_2$(en)]$^+$ units and one nickel atom. The two thiolato sulfur atoms in each *cis*(S)-[Co(aet)$_2$(en)]$^+$ unit coordinate to the central nickel atom, forming a linear-type S-bridged Co$^{\rm III}$Ni$^{\rm II}$Co$^{\rm III}$ trinuclear structure. The crystallographic 2-fold axis passing through the Col, Ni, and Co2 atoms requires that the three metals are arranged to be exactly linear. The central NiS$_4$ sphere is markedly distorted from a square-planar to a tetrahedral geometry, in which the NiS1S1′ and NiS2S2′ planes intersect to form a dihedral angle of 16.2°. This is inconsistent with the square-planar geometry of the central NiS$_4$ sphere observed in the related S-bridged trinuclear complex [Ni{Ni(aet)$_2$}$_2$]$^{2+}$.[7] Molecular model examinations showed that in **1** this distortion allows the C12 and C22 methylene protons not to be located at the apical position of the central nickel atom. The S–Ni–S "bite" angles in **1** (86.86(4)° and 86.80(5)°) are larger than those found in [Ni{Ni(aet)$_2$}$_2$]$^{2+}$ (81.4(2)°) and closer to the S–Ni–S "bite" angles of 90°—92° observed in the mononulcear

Table 1. Final Atomic Coordinates, Equivalent Isotropic Thermal Parameters ($B_{\rm eq}$/Å^2), and Occupancy Factors (Occ) for **1**Cl$_4$·6H$_2$O

Atom	x	y	z	$B_{\rm eq}$$^{\rm a)}$	Occ
Col	0.0	0.07767(4)	0.25	1.84(3)	0.5
Ni	0.0	0.24404(3)	0.25	1.95(4)	0.5
Co2	0.0	0.41110(4)	0.25	1.92(3)	0.5
S1	0.1082(1)	0.1518(1)	0.3247(1)	2.26(4)	
S2	0.1098(1)	0.3261(1)	0.2925(1)	2.38(4)	
N11	0.0356(3)	0.0792(2)	0.1189(3)	2.70(14)	
N12	0.0942(2)	0.0025(2)	0.3219(3)	2.55(13)	
N21	0.0173(2)	0.4094(2)	0.4107(3)	2.53(13)	
N22	0.0978(2)	0.4867(2)	0.2796(3)	2.52(13)	
C11	0.1719(3)	0.1535(2)	0.2303(5)	3.89(21)	
C12	0.0972(4)	0.1393(2)	0.1123(4)	3.92(20)	
C13	0.0415(3)	−0.0631(2)	0.3077(4)	2.99(17)	
C21	0.1534(3)	0.3316(2)	0.4445(4)	2.94(18)	
C22	0.0680(3)	0.3478(2)	0.4755(4)	2.98(17)	
C23	0.0452(3)	0.5522(2)	0.2374(4)	3.19(18)	
CL1	0.1645(1)	−0.0490(1)	0.1027(1)	3.49(5)	
CL2	0.1703(1)	0.4758(1)	0.0612(1)	4.40(6)	
Owl	0.3651(7)	0.2940(3)	0.3341(9)	15.0(7)	
Ow2a	0.2237(16)	0.3209(7)	0.0808(15)	14.5(11)	0.6
Ow2b	0.1662(24)	0.3098(21)	−0.0400(29)	17.1(24)	0.4
Ow3a	0.5132(24)	0.2404(10)	0.3162(22)	17.4(19)	0.6
Ow3b	0.0951(29)	0.2440(11)	−0.0965(27)	14.0(21)	0.4

a) $B_{\rm eq}$ is the arithmetic mean of the principal axes of the thermal ellipsoid.

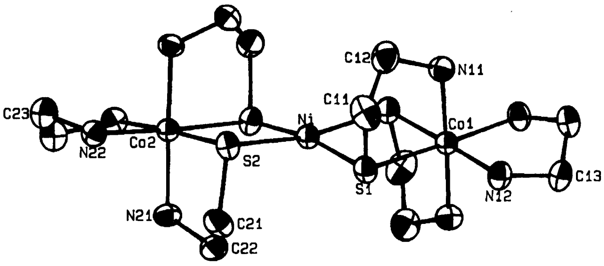

Fig. 1. A perspective view of the ΔΔ isomer of [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ (**1**) with the atomic labeling scheme. Unlabeled atoms are related to labeled atoms by the 2-fold axis through the Col, Ni, and Co2 atoms. Ellipsoids represent 50% probability.

Table 2. Bond Distances (Å) and Angles (deg) for **1**

Co1–S1	2.233(1)	S1–C11	1.833(5)
Co1–N11	1.969(3)	S2–C21	1.806(5)
Co1–N12	1.987(3)	N11–C12	1.514(5)
Ni–S1	2.208(1)	N12–C13	1.474(5)
Ni–S2	2.199(1)	N21–C22	1.485(5)
Co2–S2	2.242(1)	N22–C23	1.484(6)
Co2–N21	1.987(3)	C11–C12	1.512(7)
Co2–N22	2.003(3)	C21–C22	1.519(7)
S1–Co1–N11	87.7(1)	Co2–S2–C21	97.6(1)
S1–Co1–N12	94.8(1)	S2–Ni–S2′	86.80(5)
N11–Co1–N12	91.5(1)	S2–Co2–S2′	84.74(4)
Sl–Ni–S2	94.24(4)	Co1–N11–C12	116.2(3)
S2–Co2–N21	87.5(1)	Co1–N12–C13	109.7(3)
S2–Co2–N22	95.0(1)	N12–Co1–N12′	85.0(2)
N21–Co2–N22	91.9(1)	Co2–N21–C22	115.1(3)
Co1–S1–Ni	93.75(4)	Co2–N22–C23	108.8(3)
Co1–S1–C11	97.5(1)	N22–Co2–N22′	85.4(2)
Ni–S1–C11	105.1(2)	S1–C11–C12	108.3(3)
S1–Co1–S1′	85.64(5)	N11–C12–C11	107.9(4)
S1–Ni–S1′	86.86(4)	S2–C21–C22	108.9(3)
Ni–S2–Co2	94.23(4)	N21–C22–C21	108.3(3)
Ni–S2–C21	102.9(2)		

$[Ni^{II}(thiolato)_4]^{2-}$ complexes.[19] The Ni-S bond distances (2.208(1) and 2.199(1) Å) are within the range of 2.16—2.23 Å normally observed for four-coordinated Ni(II) complexes.[5,7,19,20]

The geometry about each terminal cobalt atom is approximately octahedral, coordinated by two sulfur, two aet nitrogen, and two en nitrogen atoms. As shown in Fig. 1, the two sulfur and the two en nitrogen atoms lie almost on the same plane, forming a C_2 symmetrical *cis*(*S*)-$[Co(aet)_2(en)]^+$ unit. The Col–S1 and Co2–S2 bond distances are 2.233(1) and 2.242(1) Å, respectively, which are slightly longer than the Co–S distance (2.226(2) Å) in the mononuclear $[Co(aet)(en)_2]^{2+}$ complex.[21] One may assume that the longer Co–S bonds in **1** are due to the μ_2-thiolato structure (Co^{III}–S–Ni^{II}). However, it has been shown that the Co–S distance (2.247(1) Å) in the S-bridged $Co^{III}Ag^{I}Co^{III}$ complex, $[Ag\{Co(SCH_2COO)(en)_2\}_2]^{3+}$, is in good agreement with that in the parental mononuclear $[Co(SCH_2COO)(en)_2]^{2+}$ complex (2.243(2) Å).[22] Thus, it is likely that the monocationic environment of the $[Co(aet)_2(en)]^+$ unit is mainly responsible for the longer Co–S bonds than the Co–S bond in the dication of $[Co(aet)(en)_2]^{2+}$, since the complex cation that bears a net charge of 1+ is expected to bind its ligands more weakly than the complex cation with a net charge of 2+.[21] Consistent with this estimation, the Co–$N_{cis(S)}$ distances in **1** (1.969(2) and 1.987(3) Å) are longer than the Co–$N_{cis(S)}$ ones in $[Co(aet)(en)_2]^{2+}$ (average 1.955 Å).[23] On the other hand, the Co–$N_{trans(S)}$ distances (1.987(3) and 2.003(3) Å) in **1** are comparable to the Co–$N_{trans(S)}$ distance in $[Co(aet)(en)_2]^{2+}$ (2.001(5) Å).[23] As a result, the difference between the averaged Co–$N_{trans(S)}$ distance and the averaged Co–$N_{cis(S)}$ one in **1** (0.017 Å) is much smaller than the corresponding difference in $[Co(aet)(en)_2]^{2+}$ (0.046 Å). This result indicates that the structural trans effect[21] due to the coordinated thiolato sulfur atom is decreased on making a sulfur bridge with the Ni^{II} atom. A similar trend has been found in $[Ag\{Co(SCH_2COO)(en)_2\}_2]^{3+}$, in which the structural trans effect is decreased from 0.043 Å observed for $[Co(SCH_2COO)(en)_2]^{2+}$ to 0.017 Å.[22]

Considering the absolute configurations (Δ and Λ) of the two C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units, three isomers ($\Delta\Delta$, $\Lambda\Lambda$, and $\Delta\Lambda$) are possible for $[Ni\{Co(aet)_2(en)\}_2]^{4+}$. Crystal **1** consists of the $\Delta\Delta$ and $\Lambda\Lambda$ isomers, which combine to form the racemic compound (Fig. 1). This is consistent with the fact that **1** was optically resolved with use of $[Sb_2(R,R\text{-tartrato})_2]^{2-}$ as the resolving agent. All the aet and en chelate rings have a distinct gauche form with the λ conformation for the $\Delta\Delta$ isomer and the δ one for the $\Lambda\Lambda$ isomer, and therefore all the four bridging sulfur atoms are fixed to the *R* configuration for the $\Delta\Delta$ isomer and the *S* one for the $\Lambda\Lambda$ isomer.

Synthesis and Properties. In water, $[Ni(aet)_2]$ reacts with $[CoCl_2(en)_2]^+$ at room temperature to yield the S-bridged Co^{III} $Ni^{II}Co^{III}$ complex, $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ (**1**), of which the formulation agrees with the elemental and plasma emission analytical results. The formation of the expected $Co^{III}Ni^{II}$ complex, $[Co\{Ni(aet)_2\}(en)_2]^{3+}$, was not detected by the SP-Sephadex column chromatography of the reaction solution. This result obviously implies that the bidentate-*N*,*S* ligand aet readily transfers from the Ni(II) to the Co(III) coordination sphere, probably because of the lower stability of the Ni–N_{aet} bonds. Considering two absolute configurations (Δ and Λ) and two geometries (C_1-*cis*(*S*) and C_2-*cis*(*S*)) for the two *cis*(*S*)-$[Co(aet)_2(en)]^+$ units, ten isomers are possible for **1**.[24] However, it was found from the X-ray analysis and the SP-Sephadex column chromatography that **1** gives only two isomers, $\Delta(C_2$-*cis*(*S*)$)\Delta(C_2$-*cis*(*S*)$)$ and $\Lambda(C_2$-*cis*(*S*)$)\Lambda(C_2$-*cis*(*S*)$)$. Model examinations point out that significant non-bonding interactions exist in the other isomers. That is, in the isomers having the C_1-*cis*(*S*) geometry one of the amino groups is placed at the apical position of the central Ni^{II} atom, and in the isomers having the $\Delta\Lambda$ configuration the cross-plane interaction between the aet chelate rings of the two *cis*(*S*)-$[Co(aet)_2(en)]^+$ units are serious, as illustrated in Fig. 2.

The ^{13}C NMR spectrum of **1** in D_2O gives only two signals due to methylene carbons of the four aet ligands and one signal due to methylene carbons of the two en ligands. In the ^{1}H NMR spectrum, methylene protons of the four aet ligands appear as two sets of double–doublet and two sets of triple–doublet and

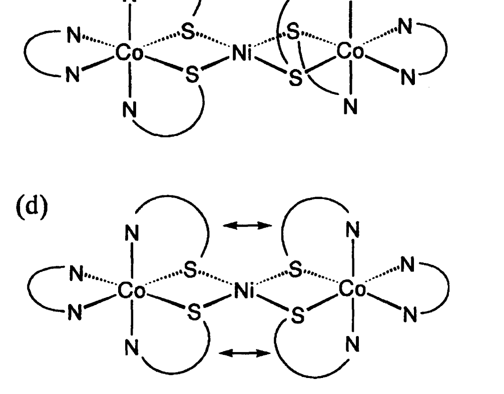

Fig. 2. Model structures of the isomers for $[Ni\{Co(aet)_2(en)\}_2]^{4+}$; C_2-*cis*(*S*) (a) and C_1-*cis*(*S*) (b) geometries and $\Delta\Delta$ (c) and $\Delta\Lambda$ (d) configurations.

those of the two en ligands appear as two sets of doublet. These NMR spectral behavior suggests that the D_2 symmetrical structure of **1** observed in crystal is retained in relatively concentrated solution (complex concentration=ca. 0.05 mol dm^{-3}).

As shown in Fig. 3 and Table 3, the electronic absorption spectrum of **1** in water is characterized by the three intense absorption bands at 27.70, 37.04, and 41.67×10^3 cm^{-1}. When **1** is treated with H_2O_2 in water, the solution color changed from red-brown to yellow, from which the yellow complex (**2**) was isolated in a reasonable yield. The absorption spectrum of **2** is quite similar to those of *cis*(*S*)-[Co(sulfinato-*S*)$_2$(amine)$_4$]$^+$ type complexes over the whole region,[25,26] showing the first d–d absorption band at 23.20×10^3 cm^{-1} and the intense sulfur-to-cobalt charge transfer band, which is composed of two absorption components at 32.89 and 34.70×10^3 cm^{-1} (Fig. 3). In the ^{13}C NMR spectrum **2** gives only three sharp signals at $\delta=41.09$, 46.74, and 64.15. From these facts and elemental analysis, it is confidently assigned that **2** is C_2-*cis*(*S*)-[Co(NH$_2$CH$_2$CH$_2$SO$_2$-*N*,*S*)$_2$(en)]$^+$, that is, the H_2O_2 oxidation of **1** effectively causes the cleavage of Ni–S bonds to form the mononuclear sulfinato Co(III) complex, retaining the C_2-*cis*(*S*) geometry of the [Co(aet)$_2$(en)]$^+$ unit.

2 was optically resolved into the $(+)^{\rm CD}_{440}$ and $(-)^{\rm CD}_{440}$ isomers, which show CD spectra enantiomeric to each other, by the SP-Sephadex C-25 column chromatography. The CD spectrum of $(+)^{\rm CD}_{440}$-**2** gives a positive CD band in the first d–d transition band region (Fig. 3). This CD spectral pattern is consistent with that of the corresponding [Co(sulfinato-*S*)$_2$ (amine)$_4$]$^+$ type complex having the Λ configuration, Λ-[Co{(O$_2$SC(CH$_3$)$_2$CH$_2$NHCH$_2$–)$_2$}(*R*,*R*-chxn)]$^+$.[25] Taking this fact and the empirical relationship between the absolute configuration and the CD spectral sign in the first d–d region,[27] the $(+)^{\rm CD}_{440}$ and $(-)^{\rm CD}_{440}$ isomers are assignable to have the Λ and Δ configurations, respectively. **1** was partially resolved by the SP-Sephadex column chromatography and the optical resolution was effectively achieved by the fractional crystallization of the diastereomeric salt of [Sb$_2$(*R*,*R*-tartrato)$_2$]$^{2-}$. As shown in Fig. 3, the CD spectrum of $(+)^{\rm CD}_{520}$-**1** gives several negative and positive CD bands in the visible region, from which the absolute configuration can not be identified. When the $(+)^{\rm CD}_{520}$ isomer of **1** was oxidized with H_2O_2, the Λ-$(+)^{\rm CD}_{440}$ isomer of **2** was formed. This result suggests that the $(+)^{\rm CD}_{520}$-**1** isomer of **1** has the $\Lambda\Lambda$ configuration, while $(-)^{\rm CD}_{520}$-**1** has the $\Delta\Delta$ one. The similarity of the CD patterns of $(+)^{\rm CD}_{520}$-**1** and Λ-$(+)^{\rm CD}_{440}$-**2** in the energy region higher than 30×10^3 cm^{-1} may support this assignment.

Table 3. Absorption and CD Spectral Data of Complexes in Water

Complex	Absorption maxima $\sigma/10^3$ cm^{-1} (log ε/mol^{-1} dm^3 cm^{-1})	CD extrema $\sigma/10^3$ cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
$\Lambda\Lambda$-$(+)^{\rm CD}_{520}$-[Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$		
	21.3 (3.3 sh)	19.34(+13.84)
	24.6 (3.8 sh)	21.55 (−6.58)
	27.70 (4.30)	24.21 (+13.47)
	37.04 (4.31)	26.53 (−1.29)
	41.67 (4.50)	28.57 (+9.69)
		33.11 (−30.34)
		35.0 (−25.6 sh)
		38.02 (+24.92)
		43.48 (+27.09)
		48.08 (−7.36)
Λ-$(+)^{\rm CD}_{440}$-[Co(NH$_2$CH$_2$CH$_2$SO$_2$-*N*,*S*)$_2$(en)]$^+$		
	23.30 (2.45)	22.78 (+1.73)
	32.89 (4.17)	32.47 (−3.99)
	34.72 (4.19)	36.10 (−4.10)
	46.7 (4.0 sh)	43.86 (+4.67)
		48.31 (−5.67)

The sh label denotes a shoulder.

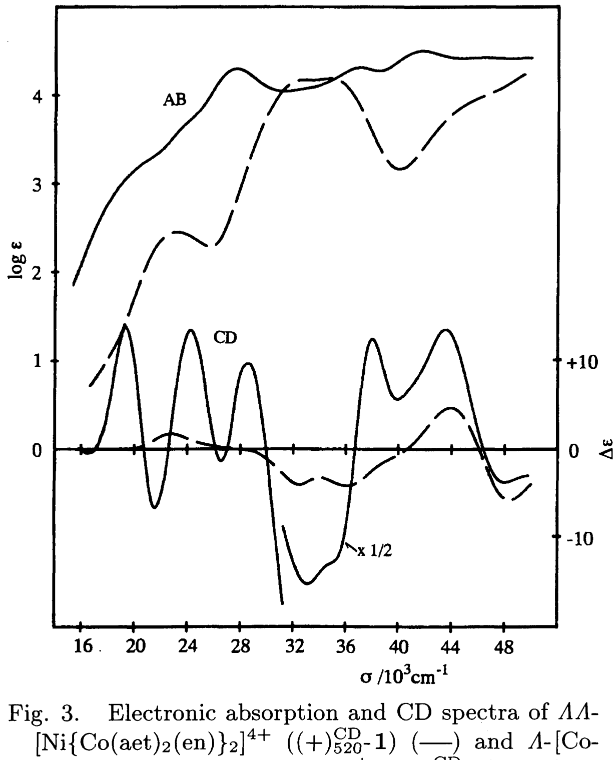

Fig. 3. Electronic absorption and CD spectra of $\Lambda\Lambda$-[Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ ($(+)^{\rm CD}_{520}$-**1**) (—) and Λ-[Co(NH$_2$CH$_2$CH$_2$SO$_2$-*N*,*S*)$_2$(en)]$^+$ ($(+)^{\rm CD}_{440}$-**2**) (---) in water.

2 is fairly stable in water at room temperature; no significant absorption and CD spectral changes were noticed for several hours. On the other hand, **1** undergoes drastic and complicated absorption and CD spectral changes with time in dilute aqueous solution. As shown in Fig. 4, at a complex concentration of 5.3×10^{-5} mol dm^{-3} the characteristic intense absorption bands at 361 and 240 nm decreased with time, and the spectrum after 24 h is very similar to that observed for the mononuclear *cis*(*S*)-[Co(thiolato-*S*)$_2$(amine)$_4$]$^+$ type complexes,[25,26] giving one intense absorption band

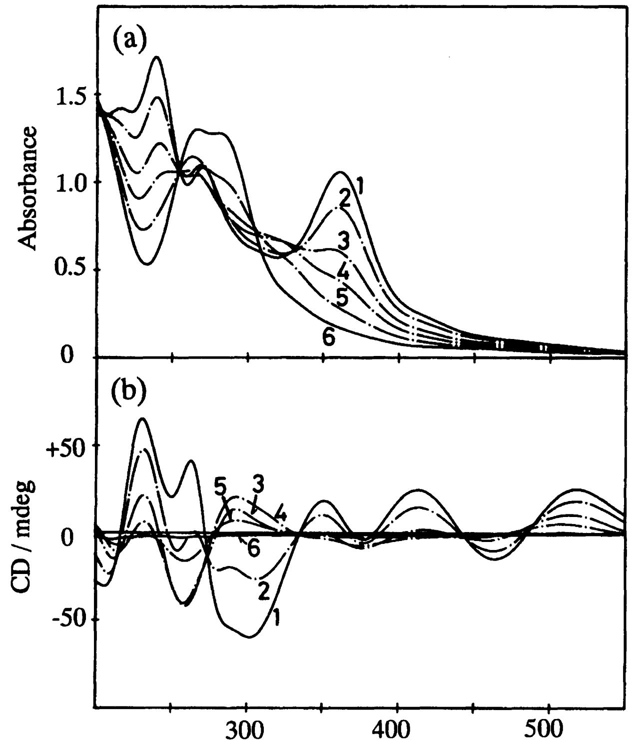

Fig. 4. Absorption (a) and CD (b) spectral changes with time for $\Lambda\Lambda$-(+)$^{\rm CD}_{520}$-**1** in water at 23 °C; Curves 1—6 were measured at 0, 1, 3, 5, 10, and 24 h, respectively.

composed of two component at around 275 nm. In the CD spectrum, $\Lambda\Lambda$-(+)$^{\rm CD}_{520}$-**1** has little CD over the whole region after 24 h (Fig. 4). These spectral changes suggest that in dilute aqueous solution the cleavage of the Ni–S bonds occurs for **1** to afford the mononuclear *cis*(*S*)-[Co(aet)$_2$(en)]$^+$species, followed by the racemization at the $\rm Co^{III}$ chiral center. Since **1** is substantially stable in concentrated solution, as shown by the NMR spectra, it is reasonable to assume that the cleavage of the Ni–S bonds is promoted by the contact of water molecules with the vacant apical positions of the central $\rm Ni^{II}$ atom.

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14) The nickel(II) salt (Ni(NO$_3$)$_2$·6H$_2$O or NiCl$_2$·6H$_2$O) was added in order to minimize the decomposition and racemization of **1**. When the nickel(II) salt was not added, no significant amount of optically active **1**Cl$_4$ could not be isolated.

15) The pH of D$_2$O was adjusted to ca. 4 with use of HNO$_3$, in order to avoid the deuteration of amino groups in the complexes.

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23) $\mathrm{N}_{cis(S)}$ and $\mathrm{N}_{trans(S)}$ denote the nitrogen donor atoms which locate at the *cis* and *trans* positions relative to the sulfur donor atoms, respectively.

24) The possible isomers are $\Delta(\mathrm{C_1}\text{-}cis(S))\Delta(\mathrm{C_1}\text{-}cis(S))$, $\Delta(\mathrm{C_1}\text{-}cis(S))\Delta(\mathrm{C_2}\text{-}cis(S))$, $\Delta(\mathrm{C_2}\text{-}cis(S))\Delta(\mathrm{C_2}\text{-}cis(S))$, $\Delta(\mathrm{C_1}\text{-}cis(S))\Lambda(\mathrm{C_1}\text{-}cis(S))$, $\Delta(\mathrm{C_1}\text{-}cis(S))\Lambda(\mathrm{C_2}\text{-}cis(S))$, $\Delta(\mathrm{C_2}\text{-}cis(S))\Lambda(\mathrm{C_1}\text{-}cis(S))$, $\Delta(\mathrm{C_2}\text{-}cis(S))\Lambda(\mathrm{C_2}\text{-}cis(S))$, $\Lambda(\mathrm{C_1}\text{-}cis(S))\Lambda(\mathrm{C_1}\text{-}cis(S))$, $\Lambda(\mathrm{C_1}\text{-}cis(S))\Lambda(\mathrm{C_2}\text{-}cis(S))$, and $\Lambda(\mathrm{C_2}\text{-}cis(S))\Lambda(\mathrm{C_2}\text{-}cis(S))$. The prefixes $\mathrm{C_1}$ and $\mathrm{C_2}$ denote that the $cis(S)$-$[\mathrm{Co(aet)_2(en)}]^+$ subunit has a $\mathrm{C_1}$ or $\mathrm{C_2}$ axis.

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