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S-Bridged Polynuclear Complexes. I. Selective Formation and Crystal Structure of $(+)^{\mathrm{CD}}_{600}$-Bis[tris(L-cysteinato-*N*,*S*)cobaltate(III)-μ-*S*,μ-*S′*,μ-*S″*]cobalt(III) Nitrate Pentahydrate

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The crystal structure and the absolute configuration of the selectively formed title isomer, $(+)^{\mathrm{CD}}_{600}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$](NO$_3$)$_2$·5H$_2$O,[2] have been determined by X-ray diffraction. In the $(+)^{\mathrm{CD}}_{600}$ isomer, the six L-cysteinates coordinate through the nitrogen and sulfur atoms to give two terminal [Co(L-cys-*N*,*S*)$_3$] moieties. The central cobalt atom spans the six sulfur atoms in these terminals to form a trinuclear structure. The $(+)^{\mathrm{CD}}_{600}$ isomer takes selectively a $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ configuration, in which both of the two terminals have a Λ_{LLL}-fac(S) configuration, and the six sulfur donor atoms take an *R* one. The L-cysteinate chelate rings take a lel conformation along the C$_3$ axis and the carboxyl or carboxylato groups take the axial orientations forming the intramolecular hydrogen bonds. The $(-)^{\mathrm{CD}}_{600}$ isomer is assigned to the $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$ configuration on the basis of the electronic absorption, CD, and ^{13}C NMR spectral behaviors. The selective formation for each of the $(+)^{\mathrm{CD}}_{600}$ and $(-)^{\mathrm{CD}}_{600}$ isomers is discussed in relation to their reaction conditions.

2-Aminoethanetholate, aet, has a propensity to form the S-bridged polynuclear metal complexes, which have been investigated by the stereochemical and spectrochemical interests,[3–9] or by the relevance to the catalytic and biological systems.[7,8] The trinuclear cobalt(III) complexes with 2-aminoethanethiolate, [Co{Co(aet)$_3$}$_2$]$^{3+}$, have been prepared by the reaction of *fac*(*S*)-[Co(aet)$_3$] with Co(II) or Co(III),[4] and resolved into the optically active isomers, ΛΛ and ΔΔ.[5] In this work, the reaction of Δ_{LLL}-*fac*(*S*)-tris(L-cysteinato-*N*,*S*)cobaltate(III), Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$,[10–12] which has a similar framework to *fac*(*S*)-[Co(aet)$_3$], with Co(II) or Co(III) was investigated. This starting Δ_{LLL}-*fac*(*S*) complex has been selectively formed because of the preferred lel conformation of the L-cysteinate chelate rings with the equatorial carboxylato groups.[11,12] This paper deals with the stereochemistry of the $(+)^{\mathrm{CD}}_{600}$ and $(-)^{\mathrm{CD}}_{600}$ isomers formed selectively by the reaction mentioned above, and with the X-ray crystal analysis of the $(+)^{\mathrm{CD}}_{600}$ isomer. Namely, each of the $(+)^{\mathrm{CD}}_{600}$- and $(-)^{\mathrm{CD}}_{600}$-bis[tris(L-cysteinato-*N*,*S*)cobaltate(III)-μ-*S*,μ-*S′*,μ-*S″*]cobaltate(III) isomers, $(+)^{\mathrm{CD}}_{600}$- and $(-)^{\mathrm{CD}}_{600}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$,[2] was selectively prepared. The crystal structure of $(+)^{\mathrm{CD}}_{600}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$](NO$_3$)$_2$·5H$_2$O,[2] which is crystallized from a 4 mol dm^{-3} nitric acid, is established by the X-ray diffraction study. The absolute configurations of the two terminal [Co(L-cys-*N*,*S*)$_3$] moieties and the six sulfur donor atoms were also determined. The electronic absorption, CD, and ^{13}C NMR spectral behaviors of the $(+)^{\mathrm{CD}}_{600}$ and $(-)^{\mathrm{CD}}_{600}$ isomers are discussed in relation to their geometrical and absolute configurations.

Experimental

1) Preparation of Complexes. **a) Δ_{LLL}-*fac*(*S*)-Potassium Tris(L-cysteinato-*N*,*S*)cobaltate(III): Δ_{LLL}-*fac*(*S*)-K$_3$[Co(L-cys-*N*,*S*)$_3$]·9H$_2$O·0.5KCl.** This complex was prepared by the method of Schubert,[10] and the Δ_{LLL}-*fac*(*S*) isomer formed selectively.[11,12] Found: C, 14.77; H, 4.50; N, 5.74%. Calcd for C$_9$H$_{33}$N$_3$O$_{15}$Cl$_{0.5}$S$_3$K$_{3.5}$Co: C, 14.75; H, 4.54; N, 5.73%.

b) $(+)^{\mathrm{CD}}_{600}$-Potassium Bis[tris(L-cysteinato-*N*,*S*)cobaltate(III)-μ-S,μ-S′,μ-S″]cobaltate(III): $(+)^{\mathrm{CD}}_{600}$-K$_3$[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]·9H$_2$O.[2] To a solution containing an excess amount (0.9g, 3.78 mmol) of CoCl$_2$·6H$_2$O in 25 cm^3 of water was added a solution containing 1.0 g (1.36 mmol) of Δ_{LLL}-*fac*(*S*)-K$_3$[Co(L-cys-*N*,*S*)$_3$]·9H$_2$O·0.5KCl in 10 cm^3 of water. The color of the solution turned immediately from deep green to deep brownish green. The solution (ca. pH 9) was stirred at room temperature for 10 min. To this was added a large amount of ethanol in an ice bath. The resultant complex was recrystallized twice from water by adding ethanol in an ice bath, and washed with ethanol and ether. It was found, from the QAE-Sephadex A-25 column chromatographic technique and the absorption and CD spectral measurements, that the reaction solution contained only $(+)^{\mathrm{CD}}_{600}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$. Found: C, 18.25; H, 4.04; N, 7.29%. Calcd for C$_{18}$H$_{48}$N$_6$O$_{21}$S$_6$K$_3$Co$_3$: C, 18.46; H, 4.13; N, 7.17%.

This isomer was also prepared by the following procedure. To a solution containing 0.01 g of $(-)^{\mathrm{CD}}_{600}$-K$_3$[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]·6.5H$_2$O described in **1c**) (vide infra) in 10 cm^3 of water was added 1.0 g of zinc powder. After the solution was allowed to stand at room temperature for a week, the reaction solution was filtered to remove the zinc powder. The filtrate showed the identical absorption and CD spectra to $(+)^{\mathrm{CD}}_{600}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$.

The single crystal of the $(+)^{\mathrm{CD}}_{600}$ isomer, which was used for the X-ray crystal structure analysis, was obtained as follows. $(+)^{\mathrm{CD}}_{600}$-K$_3$[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]·9H$_2$O was recrystallized from an 1 mol dm^{-3} warm nitric acid (ca. 40 °C). Then the crystals obtained were dissolved in a 4 mol dm^{-3} warm nitric acid (ca. 40 °C) again, and stood at room temperature for 3 d. The crystals which appeared as nitrate salt, $(+)^{\mathrm{CD}}_{600}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$](NO$_3$)$_2$·5H$_2$O,[2] were collected by filtration.

c) $(-)^{\mathrm{CD}}_{600}$-Potassium Bis[tris(L-cysteinato-*N*,*S*)cobaltate(III)-μ-S,μ-S′,μ-S″]cobaltate(III): $(-)^{\mathrm{CD}}_{600}$-K$_3$[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]·6.5H$_2$O. This complex was prepared selectively by a procedure similar to that used for the $(+)^{\mathrm{CD}}_{600}$ isomer described in **1b**), using [CoCl(NH$_3$)$_5$]Cl$_2$ (0.2 g, 0.80 mmol) instead of an excess amount of CoCl$_2$·6H$_2$O. It was found, from the same manner as in **1b**), that the reaction solution contained only $(-)^{\mathrm{CD}}_{600}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$. Found: C, 19.12; H, 3.91; N, 7.49%. Calcd for C$_{18}$H$_{43}$N$_6$O$_{18.5}$S$_6$K$_3$Co$_3$: C, 19.20; H, 3.85; N,

Table 1. Position and Thermal Parameters

Atom	x	y	z	$B_{\mathrm{eq}}/\mathrm{Å}^2$[a)]	Atom	x	y	z	$B_{\mathrm{eq}}/\mathrm{Å}^2$[a)]
Co1	0.7500	0.5000	0.5000	1.61	C3	0.6760(8)	0.7241(10)	0.2879(11)	2.30
Co2	0.5181(2)	0.5888(2)	0.4850(2)	1.66	C4	0.8760(8)	0.5905(10)	0.8353(11)	2.75
Co3	0.2875(1)	0.6698(1)	0.4791(2)	1.70	C5	0.9047(7)	0.4649(12)	0.9222(12)	3.04
S1	0.6718(2)	0.7159(3)	0.4816(3)	1.85	C6	0.7497(8)	0.6306(10)	0.8177(11)	2.79
S2	0.6566(2)	0.4935(3)	0.6685(3)	2.06	C7	0.7070(8)	0.1907(9)	0.3855(11)	2.47
S3	0.5786(2)	0.4263(3)	0.3210(3)	1.99	C8	0.7310(8)	0.1645(9)	0.2332(11)	2.69
S4	0.3744(2)	0.4628(3)	0.5102(4)	2.20	C9	0.5849(8)	0.2462(9)	0.3704(12)	2.74
S5	0.3683(2)	0.6700(3)	0.2905(3)	1.85	C10	0.1559(8)	0.4068(9)	0.3032(12)	2.48
S6	0.4598(2)	0.7621(3)	0.6379(3)	2.22	C11	0.1080(7)	0.3434(9)	0.4148(12)	2.61
N1	0.8220(7)	0.5356(8)	0.3393(10)	1.94	C12	0.2855(8)	0.3652(10)	0.3237(13)	3.04
N2	0.8925(6)	0.5674(8)	0.6825(9)	2.15	C13	0.2449(7)	0.9125(9)	0.3050(11)	2.35
N3	0.7964(7)	0.2974(9)	0.4968(11)	2.43	C14	0.1462(9)	0.8685(11)	0.1520(13)	2.77
N4	0.1445(6)	0.5632(8)	0.3295(10)	2.13	C15	0.3677(8)	0.8630(9)	0.2958(11)	2.30
N5	0.2198(7)	0.8605(9)	0.4329(10)	2.33	C16	0.3226(9)	0.7405(13)	0.8120(11)	3.54
N6	0.2367(8)	0.6751(11)	0.6641(11)	2.98	C17	0.3044(10)	0.9031(14)	0.8346(13)	3.98
O1	0.9876(6)	0.7413(8)	0.4818(9)	3.02	C18	0.4494(9)	0.7017(14)	0.8127(12)	3.78
O2	0.8696(6)	0.9140(7)	0.3927(10)	3.92	NA	0.7074(10)	0.0562(11)	0.7847(14)	4.65
O3	0.9224(8)	0.3423(8)	0.8405(9)	3.63	NB	0.2022(12)	0.4353(18)	0.8983(21)	7.49
O4	0.9103(7)	0.4756(9)	1.0567(9)	4.41	OA1	0.7659(12)	0.0542(13)	0.6950(13)	7.93
O5	0.8145(8)	0.2154(10)	0.2102(11)	4.57	OA2	0.7388(11)	0.9859(10)	0.8815(12)	6.67
O6	0.6548(7)	0.0734(8)	0.1293(9)	3.89	OA3	0.6216(13)	0.1384(17)	0.7613(26)	13.04
O7	0.0520(7)	0.4129(8)	0.4864(10)	3.44	OB1	0.2682(13)	0.4112(19)	0.8103(17)	11.36
O8	0.1269(7)	0.2107(8)	0.4168(13)	5.11	OB2	0.2046(21)	0.3300(25)	0.9622(20)	17.02
O9	0.1607(6)	0.9103(9)	0.0346(9)	4.21	OB3	0.1406(13)	0.5423(25)	0.8983(23)	13.37
O10	0.0570(7)	0.8099(9)	0.1490(9)	3.98	OW1	0.9662(7)	0.1533(9)	0.0328(10)	4.67
O11	0.2208(9)	0.9547(9)	0.7505(10)	4.17	OW2	0.9744(7)	0.8813(8)	0.7793(9)	4.05
O12	0.3896(8)	0.9633(13)	0.9532(11)	6.89	OW3	0.3743(10)	0.1261(11)	0.6080(14)	7.55
C1	0.7984(8)	0.6797(9)	0.2905(11)	2.36	OW4	0.0251(7)	0.1082(9)	0.5696(11)	4.65
C2	0.8921(8)	0.7883(9)	0.3981(10)	2.13	OW5	0.3753(17)	0.2264(19)	−0.0003(20)	14.75

a) B_{eq} is the equivalent isotropic temperature factors defined by Hamilton.[20)]

7.49%.

2) General Data. The electronic absorption spectra were recorded with JASCO UVIDEC-1 and UVIDEC-610 spectrophotometers, and the CD spectra with a JASCO J-20 spectropolarimeter. The infrared spectra were recorded with a JASCO IRA-2 infrared spectrophotometer using the KBr disk method. The ^{13}C NMR spectra were recorded on a JEOL JNM-FX-100 or -FX-90Q NMR spectrometer at the probe temperature in $\mathrm{D_2O}$. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate was used as an internal reference. The pH of the aqueous solution was measured with a Hitachi-Horiba pH meter, model F7-SS, equipped with a glass and saturated calomel electrodes. The X-ray analysis calculations were carried out on a FACOM M-380 computer at the University of Tsukuba.

3) X-Ray Characterization. Unit cell parameters and intensity data for the single crystal (ca. $0.10\times0.15\times0.40$ mm^3) were measured on a Rigaku-denki four-circle diffractometer (AFC-5) with graphite-monochromatized Mo $K\alpha$ radiation. The unit cell parameters were determined by least-squares refinement based on 19 reflections. Crystal data: $[\mathrm{Co}\{\mathrm{Co}(\text{L-cys})_3\}_2](\mathrm{NO}_3)_2\cdot5\mathrm{H}_2\mathrm{O}=\mathrm{Co}_3\mathrm{S}_6\mathrm{O}_{23}\mathrm{N}_8\mathrm{C}_{18}\mathrm{H}_{45}$, triclinic, space group $P1$, M.W.=1110.76, $a=12.087(8)$, $b=9.541(4)$, $c=9.214(4)$ Å, $\alpha=99.09(5)$, $\beta=109.32(4)$, $\gamma=87.86(5)°$, $V=990(1)$ Å^3, $D_\mathrm{m}=1.86$ g cm^{-3} (by the flotation), $D_\mathrm{x}=1.863$ g cm^{-3}, $Z=1$, and $\mu(\mathrm{Mo}\,K\alpha)=1.692$ mm^{-1}.

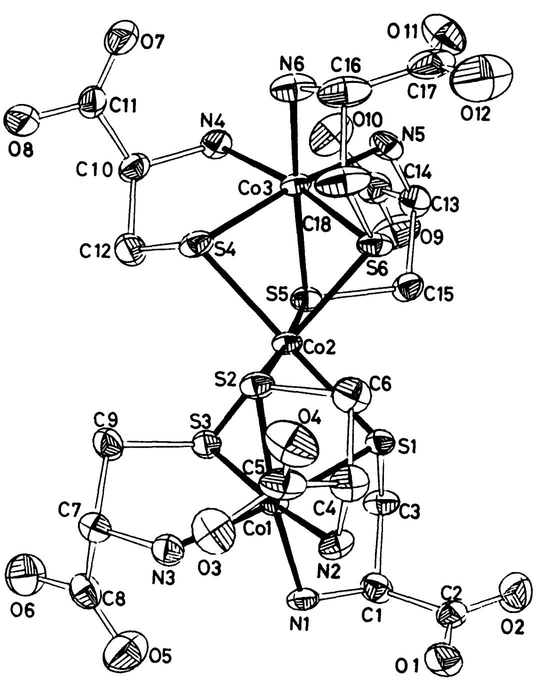

Fig. 1. Perspective view of $(+)^{\mathrm{CD}}_{600}$-$[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{2+}$ ion,[2)] with the numbering scheme.

Intensity data were collected by a $\omega-2\theta$ scan technique up to $2\theta=50°$ with a scan rate of 3° min^{-1}. The intensity data were converted to F_o data in the usual manner. Absorption corrections were not applied. A total of 3677 independent reflections with $|F_\mathrm{o}|>3\sigma(|F_\mathrm{o}|)$ of the measured 3741 reflections were considered as 'observed' and used for the structure analysis.

4) Determination of the Crystal Structure. The positions of three cobalt atoms were obtained from a three-

Table 2. Interatomic Distances and Bond Angles (with e.s.d.'s)

(a) Bond distances (l/Å)

Co1-S1	2.242(3)	Co1-S2	2.210(4)
Co1-S3	2.234(3)	Co1-N1	2.024(10)
Co1-N2	2.008(7)	Co1-N3	1.991(8)
Co2-S1	2.267(4)	Co2-S2	2.233(4)
Co2-S3	2.265(4)	Co2-S4	2.242(4)
Co2-S5	2.296(3)	Co2-S6	2.246(4)
Co3-S4	2.216(3)	Co3-S5	2.257(4)
Co3-S6	2.229(3)	Co3-N4	2.008(7)
Co3-N5	2.017(9)	Co3-N6	1.987(11)
S1-C3	1.816(11)	S2-C6	1.840(9)
S3-C9	1.838(10)	S4-C12	1.823(10)
S5-C15	1.834(9)	S6-C18	1.837(13)
N1-C1	1.502(13)	N2-C4	1.468(14)
N3-C7	1.508(11)	N4-C10	1.482(12)
N5-C13	1.469(15)	N6-C16	1.472(12)
O1-C2	1.269(11)	O2-C2	1.225(11)
O3-C5	1.338(13)	O4-C5	1.207(14)
O5-C8	1.228(16)	O6-C8	1.317(11)
O7-C11	1.207(14)	O8-C11	1.281(12)
O9-C14	1.275(16)	O10-C14	1.224(15)
O11-C17	1.195(14)	O12-C17	1.299(13)
C1-C2	1.536(11)	C1-C3	1.517(13)
C4-C5	1.512(16)	C4-C6	1.521(14)
C7-C8	1.507(16)	C7-C9	1.519(13)
C10-C11	1.540(17)	C10-C12	1.559(13)
C13-C14	1.524(12)	C13-C15	1.566(13)
C16-C17	1.550(18)	C16-C18	1.562(15)
NA-OA1	1.251(21)	NA-OA2	1.156(16)
NA-OA3	1.257(19)	NB-OB1	1.306(26)
NB-OB2	1.237(30)	NB-OB3	1.241(26)

(b) Bond angles (ϕ/°)

S1-Co1-S2	84.1(1)	S1-Co1-S3	83.8(1)
S1-Co1-N1	86.7(2)	S1-Co1-N2	94.9(2)
S1-Co1-N3	171.7(2)	S2-Co1-S3	84.6(1)
S2-Co1-N1	170.8(2)	S2-Co1-N2	87.5(3)
S2-Co1-N3	94.0(3)	S3-Co1-N1	93.4(2)
S3-Co1-N2	172.1(3)	S3-Co1-N3	87.9(2)
N1-Co1-N2	94.4(3)	N1-Co1-N3	94.9(4)
N2-Co1-N3	93.1(3)	S1-Co2-S2	83.0(1)
S1-Co2-S3	82.5(1)	S1-Co2-S4	175.1(1)
S1-Co2-S5	100.7(1)	S1-Co2-S6	94.5(1)
S2-Co2-S3	83.4(1)	S2-Co2-S4	92.7(1)
S2-Co2-S5	175.6(1)	S2-Co2-S6	99.2(1)
S3-Co2-S4	99.6(1)	S3-Co2-S5	94.6(1)
S3-Co2-S6	175.8(2)	S4-Co2-S5	83.7(1)
S4-Co2-S6	83.7(1)	S5-Co2-S6	83.1(1)
S4-Co3-S5	85.2(1)	S4-Co3-S6	84.7(1)
S4-Co3-N4	88.1(2)	S4-Co3-N5	172.9(3)
S4-Co3-N6	92.8(3)	S5-Co3-S6	84.4(1)
S5-Co3-N4	92.0(3)	S5-Co3-N5	87.8(3)
S5-Co3-N6	172.7(2)	S6-Co3-N4	172.2(2)
S6-Co3-N5	93.6(2)	S6-Co3-N6	88.5(3)
N4-Co3-N5	93.2(3)	N4-Co3-N6	94.9(4)
N5-Co3-N6	94.1(4)	Co1-S1-Co2	78.8(1)
Co1-S1-C3	96.3(3)	Co2-S1-C3	114.3(3)
Co1-S2-Co2	80.3(1)	Co1-S2-C6	95.0(4)
Co2-S2-C6	111.7(3)	Co1-S3-Co2	79.1(1)
Co1-S3-C9	95.4(3)	Co2-S3-C9	112.7(4)
Co2-S4-Co3	79.5(1)	Co2-S4-C12	111.5(4)
Co3-S4-C12	96.6(3)	Co2-S5-Co3	77.5(1)
Co2-S5-C15	114.8(3)	Co3-S5-C15	96.4(4)
Co2-S6-Co3	79.1(1)	Co2-S6-C18	112.1(4)
Co3-S6-C18	95.6(3)	Co1-N1-C1	114.5(6)
Co1-N2-C4	115.8(6)	Co1-N3-C7	115.9(6)
Co3-N4-C10	115.2(5)	Co3-N5-C13	115.1(6)
Co3-N6-C16	114.6(8)	N1-C1-C2	110.9(7)
N1-C1-C3	109.1(8)	C2-C1-C3	111.9(7)
O1-C2-O2	125.2(8)	O1-C2-C1	117.8(8)
O2-C2-C1	116.9(7)	S1-C3-C1	105.9(6)
N2-C4-C5	114.9(8)	N2-C4-C6	110.1(7)
C5-C4-C6	107.8(9)	O3-C5-O4	122.6(11)
O3-C5-C4	115.9(9)	O4-C5-C4	121.5(10)
S2-C6-C4	106.4(6)	N3-C7-C8	108.2(9)
N3-C7-C9	109.0(7)	C8-C7-C9	113.3(8)
O5-C8-O6	123.8(10)	O5-C8-C7	124.7(8)
O6-C8-C7	111.5(9)	S3-C9-C7	107.5(7)
N4-C10-C11	108.6(8)	N4-C10-C12	110.8(7)
C11-C10-C12	112.4(8)	O7-C11-O8	123.8(12)
O7-C11-C10	121.9(9)	O8-C11-C10	114.2(10)
S4-C12-C10	106.3(7)	N5-C13-C14	110.2(8)
N5-C13-C15	111.5(7)	C14-C13-C15	112.3(8)
O9-C14-O10	124.3(9)	O9-C14-C13	114.3(9)
O10-C14-C13	121.0(11)	S5-C15-C13	105.8(6)
N6-C16-C17	109.2(8)	N6-C16-C18	109.7(9)
C17-C16-C18	112.2(10)	O11-C17-O12	129.7(12)
O11-C17-C16	120.9(9)	O12-C17-C16	109.4(10)
S6-C18-C16	104.6(7)	OA1-NA-OA2	117.3(13)
OA1-NA-OA3	115.6(16)	OA2-NA-OA3	127.1(18)
OB1-NB-OB2	108.3(18)	OB1-NB-OB3	122.1(21)
OB2-NB-OB3	129.1(23)		

dimensional Patterson function. Difference Fourier maps, based on the three cobalt positions, revealed all the non-hydrogen atoms. The structure was refined by a full-matrix least-squares refinement of the positional and anisotropic thermal parameters of all the non-hydrogen atoms (program RFINE by L. W. Finger was used). The neutral atomic scattering factors for all the non-hydrogen atoms were taken from the literature.[13] The final *R* and R_w values were 0.044 and 0.057, respectively. The absolute configuration was determined on the basis of the known configuration of L-cysteinates.[14]

The final atomic parameters are given in Table 1. A list of structure factors (Table A) and anisotropic thermal parameters of non-hydrogen atoms (Table B) are kept at the Chemical Society of Japan as Document No. 8704.

Results and Discussion

Description of the Structure. A perspective drawing of the complex cation, $(+)^{\mathrm{CD}}_{600}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{2+}$,[2] is given in Fig. 1, together with a numbering scheme. The bond lengths and angles (with their standard deviations) in the complex cation and the nitrate anions are summarized in Table 2. Three cobalt atoms are aligned at short intervals (Co1-Co2=2.863(3) and Co2-Co3=2.849(3) Å, Co1-Co2-Co3=177.66(9)°); thus the complex cation takes a trinuclear structure. The coordination geometries around each cobalt atom are approximately octahedral. All the six L-cysteinates coordinate to two cobalt atoms (Co1 and Co3) through the nitrogen and sulfur atoms, and they form two terminal [Co(L-cys-*N*,*S*)$_3$] moieties. The Co1 and Co2 atoms or the Co2 and Co3 ones are bridged by the sulfur atoms in the L-cysteinates, namely, the central cobalt atom, Co2, is surrounded by the six sulfur atoms.

The absolute configuration of the $(+)^{\mathrm{CD}}_{600}$ isomer in the crystal could be confirmed on the basis of the known configuration, *R*, of the asymmetric carbon atom in the coordinated L-cysteinate.[14] Both of the two terminal [Co(L-cys-*N*,*S*)$_3$] moieties in the $(+)^{\mathrm{CD}}_{600}$ isomer have Λ configuration and all the six sulfur donor atoms, which become chiral by coordination, have *R* one. This indicates that the reaction with $CoCl_2 \cdot 6H_2O$ causes an inversion of the absolute configuration of the starting complex, Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$, to give selectively two terminal Λ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$] moieties.

The average bond lengths of [Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{2+}$ are quite similar to those of [Co{Co(aet)$_3$}$_2$]$^{3+}$;[9] Co1-S and Co3-S (2.226(3) Å), Co2-S (2.258(4) Å), Co-N (2.006(9) Å), S-C (1.831(10) Å), N-C (1.484(13) Å), and C-C (1.534(14) Å). A similar trend was also observed for the bond angles; Co1-S-Co2 and Co3-S-Co2 (79.0 (1)°), S-Co1-S and S-Co3-S (84.5(1)°), S-Co2-S (83.2 (1)°), N-Co1-N and N-Co3-N (94.1(4)°), S-Co1-N and S-Co3-N (87.8(3)°), Co1-S-C and Co3-S-C (95.9 (3)°), Co2-S-C (112.9(4)°), S-C-C (106.1(7)°), and C-C-N (110.2(8)°).[9] The acute S-Co2-S angle and the Co2-S distance indicate that the central cobalt atom, Co2, is trigonally distorted from regular octahedron and its distortion has the effect of lengthening the molecule along the C_3 axis through the Co1, Co2, and Co3 atoms. In the terminal [Co(L-cys-*N*,*S*)$_3$] moieties, the average bond lengths and angles (given above) indicate the compressions of the S1-S2-S3 and S4-S5-S6 faces and the concomitant expansions of the N1-N2-N3 and N4-N5-N6 ones. The average bond lengths of Co1-N and Co3-N in the present complex seem to be longer than those of the cobalt(III) complexes with the amino carboxylate ligands.[15–17]

The crystal structure consists of the complex cation, two nitrate anions, and five water molecules, as shown in Fig. 2. In the crystal, the hydrogen bonds are recognized between the carboxyl or carboxylato groups and water molecules: e.g., OW1-O3 (2.644(13) Å), OW1-O5 (2.825(15) Å), OW2-O1 (2.905(12) Å), OW2-O9 (2.649(9) Å), OW3-O8 (3.079(13) Å), OW4-O2 (2.627(10) Å), OW4-O8 (2.475(16) Å), and OW5-O12 (2.488(22) Å). Similar O-O bond distances to the short hydrogen bonds in this work (2.475—2.649 Å) have also been observed for the hydrogen bis(*p*-methylbenzoate) anions.[18] Taking account of the facts that only two nitrate anions exist in the unit cell and the five carboxyl groups are connected strongly to the water molecules (2.475—2.649 Å), it may be considered that the five carboxyl groups in the L-cysteinates are protonated and the one carboxylato group is not. This is supported from the result that the IR spectrum of the present $(+)^{\mathrm{CD}}_{600}$-$\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ isomer exhibits a strong band at ca. 1720 cm^{-1} due to the COOH group and a week band at ca. 1625 cm^{-1} due to the COO$^-$ group.[19]

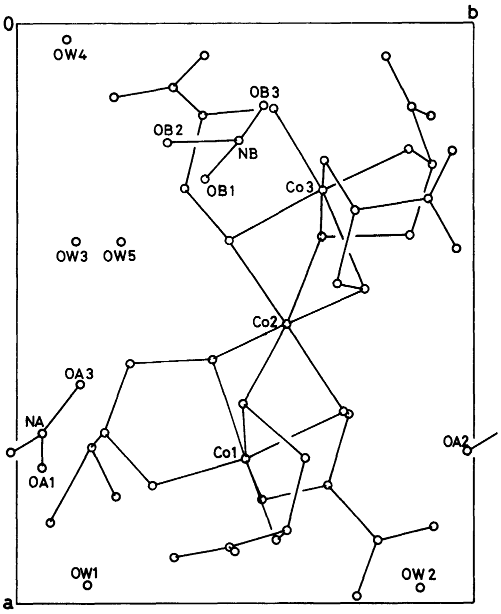

Fig. 2. The crystal packing diagram of the complex.

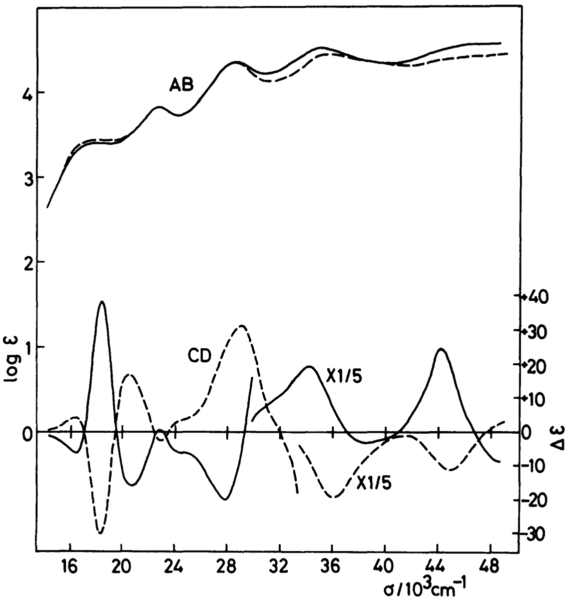

Fig. 3. Absorption and CD spectra of [Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$;[2] the $(-)^{\mathrm{CD}}_{600}$ isomer (——) and the $(+)^{\mathrm{CD}}_{600}$ one (---).

In [Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{2+}$,[2] all of the bond distances between the oxygen atoms in the carboxyl or carboxylato groups and the nitrogen atoms in the adjacent amine groups range from 2.919 to 3.260 Å (average 3.080 Å). This indicates that they are also hydrogen bonds and incidentally, all the six L-cysteinate chelate rings take the lel conformations along the C_3 axis, which is accompanied by the axial orientations of the carboxyl or carboxylato groups.

Formation of Isomers. Three isomers, $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$, $\Lambda_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$, and $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$, are possible for the trinuclear

Table 3. Absorption and CD Data of $(+)^{\rm CD}_{600}$- and $(-)^{\rm CD}_{600}$-[Co{Co(L-cys-N,S)$_3$}$_2$]$^{3-}$

Complex	Absorption maxima $\sigma/10^3\,\mathrm{cm^{-1}}$ ($\log\varepsilon/\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$)	CD extrema $\sigma/10^3\,\mathrm{cm^{-1}}$ ($\Delta\varepsilon/\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$)
$(+)^{\rm CD}_{600}$-[Co{Co(L-cys-N,S)$_3$}$_2$]$^{3-}$	17.80 (3.43)	16.23 (+4.4)
	22.53 (3.83)	18.40 (−30.0)
	28.60 (4.35)	20.43 (+17.1)
	35.53 (4.44)	23.00 (−2.8)
	45.5 (4.41 sh)	24.5 (+3.8 sh)
		29.07 (+31.8)
		36.13 (−96.5)
		44.93 (−60.5)
$(-)^{\rm CD}_{600}$-[Co{Co(L-cys-N,S)$_3$}$_2$]$^{3-}$	17.70 (3.40)	16.39 (−6.3)
	22.62 (3.83)	18.45 (+38.7)
	28.57 (4.35)	20.62 (−15.9)
	35.09 (4.51)	22.78 (+0.7)
	47.39 (4.57)	24.09 (−6.3)
		27.86 (−19.7)
		34.25 (+94.0)
		38.53 (−15.0)
		44.05 (+95.9)

Sh denotes a shoulder.

complex, [Co{Co(L-cys-N,S)$_3$}$_2$]$^{3-}$,[2] with respect to the absolute configuration of two terminal [Co(L-cys-N,S)$_3$] moieties. The $(-)^{\rm CD}_{600}$ isomer exhibits a quite similar absorption spectral behavior over the whole region to the $(+)^{\rm CD}_{600}$-$\Lambda_{\rm LLL}\Lambda_{\rm LLL}$ isomer as shown in Fig. 3 and Table 3. Furthermore, each of the present two isomers exhibits three ^{13}C NMR resonance lines (39.0, 64.1, and 179.3 ppm for the $(+)^{\rm CD}_{600}$-$\Lambda_{\rm LLL}\Lambda_{\rm LLL}$ isomer and 38.6, 67.1, and 178.3 ppm for the $(-)^{\rm CD}_{600}$ isomer) due to the methylene, methine, and carboxylato carbon atoms in each of the six L-cysteinate ligands (Fig. 4). The ^{13}C NMR spectral behaviors point out that the present $(-)^{\rm CD}_{600}$ isomer takes $\Delta_{\rm LLL}\Delta_{\rm LLL}$ configuration having D_3 symmetry, because the $(+)^{\rm CD}_{600}$-$\Lambda_{\rm LLL}\Lambda_{\rm LLL}$ isomer has approximately D$_3$ symmetry in the crystal (Fig. 1) but the $\Lambda_{\rm LLL}\Delta_{\rm LLL}$ isomer has lower than or equal to a C_3 symmetry. This assignment is supported by the fact that the $(-)^{\rm CD}_{600}$ isomer exhibits almost enantiomeric CD spectrum over the whole region to that of $(+)^{\rm CD}_{600}$-$\mathit{\Delta}_{\rm LLL}\mathit{\Delta}_{\rm LLL}$-[Co{Co(L-cys-$N$,$S$)$_3$}$_2$]$^{3-}$ (Fig. 3 and Table 3). Accordingly, the $(-)^{\rm CD}_{600}$ isomer can be assigned to $\mathit{\Delta}_{\rm LLL}\mathit{\Delta}_{\rm LLL}$-[Co{Co(L-cys-$N$,$S$)$_3$}$_2$]$^{3-}$. The absorption and CD spectra of the $(-)^{\rm CD}_{600}$-$\Delta_{\rm LLL}\Delta_{\rm LLL}$ isomer are also in good agreement with those of $\mathit{\Delta\Delta}$-[Co{Co(aet)$_3$}$_2$]$^{3+}$ whose absolute configuration was assigned on the basis of the CD spectral behavior by Brubaker and Douglas.[5] The similarity between these CD spectra suggests that the CD contribution due to the chiral carbon atom, $R(C)$, of the coordinated L-cysteinate is minor.

The reaction of $\mathit{\Delta}_{\rm LLL}$-$fac(S)$-[Co(L-cys-$N$,$S$)$_3$]$^{3-}$ with [CoCl(NH$_3$)$_5$]Cl$_2$ gave only $(-)^{\rm CD}_{600}$-$\mathit{\Delta}_{\rm LLL}\mathit{\Delta}_{\rm LLL}$-[Co{Co(L-cys-$N$,$S$)$_3$}$_2$]$^{3-}$. Namely, the reaction with Co(III) proceeds with retention of the absolute configuration of the starting $\mathit{\Delta}_{\rm LLL}$-$fac(S)$ complex to give two terminal $\mathit{\Delta}_{\rm LLL}$-$fac(S)$-[Co(L-cys-$N$,$S$)$_3$] moieties. In contrast with this reaction, the reaction (pH≈9) with an excess amount of CoCl$_2$ was accompanied by the inversion of the starting complex to give $(+)^{\rm CD}_{600}$-$\mathit{\Delta}_{\rm LLL}\mathit{\Delta}_{\rm LLL}$-[Co{Co(L-cys-$N$,$S$)$_3$}$_2$]$^{3-}$. Moreover, the inversion of the two terminals in the $(-)^{\rm CD}_{600}$-$\Delta_{\rm LLL}\Delta_{\rm LLL}$ isomer was also observed for its reaction solution with zinc powder. These facts suggest that the Co(II) ion relates catalytically to the inversion of the starting $\mathit{\Delta}_{\rm LLL}$-$fac(S)$ complex and accelerates the formation of the $(+)^{\rm CD}_{600}$-$\Lambda_{\rm LLL}\Lambda_{\rm LLL}$ isomer, i.e., bridging the sulfur donor atoms of the starting complex to Co(II) ion is favorable to the labilization and inversion of the terminals. Here, an intramolecular hydrogen bonding is accompanied by the inversion. Considering from the result of the X-ray analysis of the $(+)^{\rm CD}_{600}$-$\Lambda_{\rm LLL}\Lambda_{\rm LLL}$ isomer (Fig. 1), it is probable for the $\Lambda_{\rm LLL}\Lambda_{\rm LLL}$ isomer that in the above reaction conditions (pH≈9), the hydrogen bonds are formed between the axial carboxylato groups regulated by the lel conformation of the N–S chelate rings and the adjacent amine protons. While, the model construction of the $\Lambda_{\rm LLL}\Lambda_{\rm LLL}$ isomer reveals that this isomer prefers to the lel conformation with the equa-

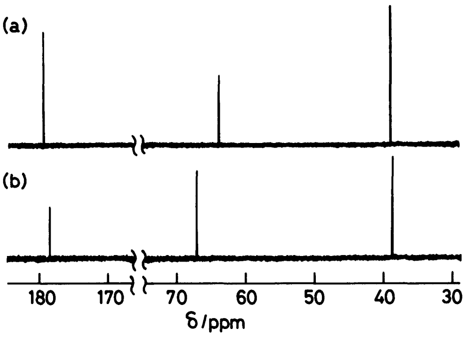

Fig. 4. ^{13}C NMR spectra of [Co{Co(L-cys-N,S)$_3$}$_2$]$^{3-}$;[2] (a) the $(+)^{\rm CD}_{600}$ isomer and (b) the $(-)^{\rm CD}_{600}$ one.

torial carboxylato groups (unfavorable orientation for the hydrogen bond formation) because of the repulsion between the carboxylato groups and the lone pairs of the adjacent sulfur donor atoms. The difference in the hydrogen bond formation is probably related to the selective formation of the $(+)^{\mathrm{CD}}_{600}$-$\Lambda_{\mathrm{L.L.L.}}\Lambda_{\mathrm{L.L.L.}}$ isomer.

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2) In this paper, we showed with the superscript of the chemical formula whether the L-cysteinates in the trinuclear complex take the carboxyl or carboxylato groups (they are protonated or not); that is, the five carboxyl groups are protonated in case the superscript is 2+, and all the carboxylato groups are deprotonated in case it is 3−.

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