Stereoselective Formation and Some Properties of Polynuclear Cobalt(III) Complexes with D-Penicillaminate

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The novel mononuclear, dinuclear, and trinuclear cobalt(III) complexes with D-penicillaminate(D-pen), Λ_{DDD}-*fac*(*S*)-[Co(D-pen-*N*,*S*)$_3$]$^{3-}$, Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$}(dien)], Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$}(D-pen-*N*,*O*,*S*)]$^{2-}$, and $\Lambda_{DDD}\Lambda_{DDD}$-[Co{Co(D-pen-*N*,*S*)$_3$}$_2$]$^{3-}$ were prepared. These complexes were characterized from their electronic absorption, CD, and ^{13}C NMR spectra. These complexes formed selectively each one isomer. The stereoselectivity for the D-pen complexes is discussed in comparison with that of the corresponding L-cys ones. The D-pen polynuclear complexes exhibited characteristic absorption spectral behaviors in the visible region. The ^{13}C NMR spectral behaviors for the D-pen complexes are connected with those of the corresponding L-cys ones.

The mononuclear and polynuclear cobalt(III) complexes with L-cysteinate (L-cys) have been extensively investigated for their spectrochemical and stereochemical interests.[1-8] It has been pointed out that [Co(L-cys-*N*,*S*)$_3$]$^{3-}$ forms selectively the Λ_{LLL}-*fac*(*S*) isomer because of the preferred lel conformation[9] of the L-cysteinate chelate rings with the equatorial carboxylate groups. This was confirmed by the fact that the reaction of Λ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ with Co(III) forms only $\Lambda_{LLL}\Lambda_{LLL}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$, although the reaction with Co(II) is accompanied by the inversion of unitary complex to form $\Lambda_{LLL}\Lambda_{LLL}$-and $\Delta_{LLL}\Lambda_{LLL}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$.[5-7] Recently, Arnold and Jackson[10] have reported on the basis of the NMR spectral study that [Co(L-cys-*N*,*S*)$_3$]$^{3-}$ forms a 1 : 1 mixture of the diastereomeric *fac*(*S*) isomers, Δ_{LLL} and Λ_{LLL}. However, this 1 : 1 mixture is questionable in relation to the formation of polynuclear complexes which are successively formed in the reaction. In this viewpoint, it is worthwhile to investigate the stereochemical behavior of the corresponding D-penicillaminato (D-pen) complex, which is quite similar in framework to the corresponding L-cys ones (Fig. 1).[11] This report deals with the preparation and stereochemical properties of the mononuclear complex, Λ_{DDD}-*fac*(*S*)-[Co(D-pen-*N*,*S*)$_3$]$^{3-}$, together with those of the dinuclear and trinuclear complexes, which were obtained by the reaction of Λ_{DDD}-*fac*(*S*)-[Co(D-pen-*N*,*S*)$_3$]$^{3-}$ with Co(II) or Co(III) (Fig. 1).

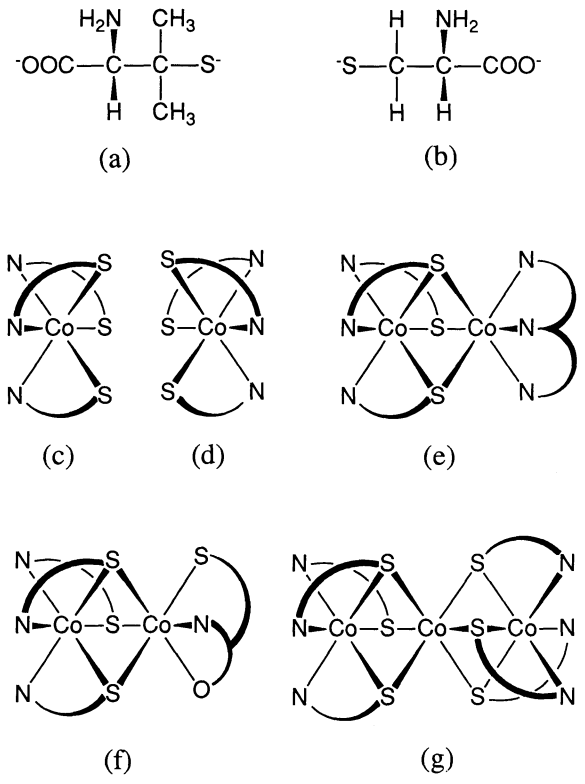

Fig. 1. Structures of (a) D-penicillaminate, (b) L-cysteinate, (c) Λ_{DDD}-, and (d) Λ_{DDD}-*fac*(*S*)-[Co(D-pen-*N*,*S*)$_3$]$^{3-}$, (e) Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$}(dien)], (f) Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$}(D-pen-*N*,*O*,*S*)]$^{2-}$, and (g) $\Lambda_{DDD}\Lambda_{DDD}$-[Co{Co(D-pen-*N*,*S*)$_3$}$_2$]$^{3-}$.

Experimental

Preparation of Complexes. 1) Λ_{DDD}-*fac*(*S*)-Na$_3$[Co(D-pen-*N*,*S*)$_3$]·6H$_2$O·0.25(CH$_3$)$_2$CO (A): To a suspension containing 10.0 g (0.03 mol) of Na$_3$[Co(CO$_3$)$_3$]·3H$_2$O[12] in 55 cm^3 of water was added 15.0 g (0.1 mol) of D-penicillamine. The color of the solution immediately turned from deep green to dark brown and a little while later turned to deep green. The mixture was stirred at 60 °C for 20 min and then cooled to room temperature. A part of the reaction mixture was poured onto a column of QAE-Sephadex A-25 (Cl^- form), in order to determine the coexisting species. When the column was swept with water, no band was eluted. By eluting with a 0.05 mol dm^{-3} NaCl aqueous solution, a small amount of the brown band was eluted. This brown eluate showed the identical absorption and CD spectra with *trans*(*N*)-[Co(D-pen-*N*,*O*,*S*)$_2$]$^-$.[13] Then, the adsorbed band was eluted with a 0.1 mol dm^{-3} NaCl aqueous solution. Only green band was eluted and fractionated. From the absorption and CD spectral measurements, it was found that all of the fractions contained only one species, complex **A**. Therefore, to the reaction mixture mentioned above was added 400 cm^3 of ethanol in an ice bath.

The resultant crude complex was collected by filtration and recrystallized from water by adding ethanol in an ice bath. The deep green **A** was collected by filtration, washed with ethanol, acetone, and ether, and then dried in a vacuum desiccator. It was found from the ^{1}H NMR spectral measurement that the complex contained 0.25 mol of acetone. Found: C, 27.27; H, 5.82; N, 6.01%. Calcd for $C_{15}H_{27}N_3O_6S_3Na_3Co\cdot 6H_2O\cdot 0.25C_3H_6O$: C, 27.34 ;H, 5.90; N, 6.07%.

2) Λ_{DDD}-[Co{Co(D-pen-*N,S*)$_3$}(dien)]·7H$_2$O·0.25C$_2$H$_5$OH (B): To a suspension containing 0.41 g (1.5 mmol) of $[CoCl_3(dien)]$[14] in 5 cm^3 of water was added a solution containing 0.77 g (4.5 mmol) of $AgNO_3$ in 5 cm^3 of water. The mixture was stirred at room temperature for 30 min, and then filtered to remove the deposited AgCl. To a red filtrate was added 1.05 g (1.5 mmol) of **A** in 1). The mixture was stirred at room temperature for 20 min, whereupon the deep green complex was gradually dissolved and the color of the solution turned to brownish black. The solution was filtered, and the filtrate was passed through the columns of SP-Sephadex C-25 (Na^+ form, 4.5×42 cm) and QAE-Sephadex A-25 (Cl^- form, 5×40 cm). The uncharged grayish black band was eluted with water. The eluate was concentrated to a small volume with a rotary evaporator below 20 °C, and to this was added a large amount of ethanol in an ice bath. The resulting brownish black complex **B** was collected by filtration, washed with ethanol and ether, and then dried in a vacuum desiccator. Found: C, 29.28; H, 7.03; N, 10.44%. Calcd for $C_{19}H_{40}N_6O_6S_3Co_2\cdot 7H_2O\cdot 0.25C_2H_6O$: C, 29.27; H, 6.99; N, 10.50%.

3) Λ_{DDD}-Cs$_2$[Co{Co(D-pen-*N,S*)$_3$}(D-pen-*N,O,S*)]·4.5H$_2$O·0.33C$_4$H$_{10}$O·0.1C$_3$H$_6$O (C): To a solution containing 3.00 g (12.5 mmol) of $CoCl_2\cdot 6H_2O$ in 10 cm^3 of water was added a solution containing 8.25 g (12 mmol) of **A** in 1) in 90 cm^3 of water. The color of the solution turned immediately from deep green to deep brown. The solution was stirred at room temperature for 1 h. The reaction mixture was filtered to remove insoluble materials. The filtrate was poured onto a column of QAE-Sephadex A-25 (Cl^- form, 5×40 cm). After sweeping the column with water, the adsorbed band was eluted with a 0.1 mol dm^{-3} KCl aqueous solution. Two bands, brown (F-1) and reddish brown (F-2), were eluted in this order. Further, two bands, green (F-3) and dark green (F-4), were eluted with a 0.2 mol dm^{-3} KCl aqueous solution. From the absorption and CD spectral measurements, it was found that the F-2 and F-3 eluates contained [Co{Co(D-pen-*N,S*)$_3$}(D-pen-*N,O,S*)]$^{2-}$ and [Co{Co(D-pen-*N,S*)$_3$}$_2$]$^{3-}$ respectively. The F-1 and F-4 eluates showed the identical absorption and CD spectra with *trans*(*N*)-[Co(D-pen-*N,O,S*)$_2$]$^-$ [13] and Λ_{DDD}-*fac*(*S*)-[Co(D-pen-*N,S*)$_3$]$^{3-}$ respectively. The F-2 eluate was concentrated to a small volume with a rotary evaporator below 20 °C. The deposited KCl was filtered off. The filtrate was passed through a column of Sephadex G-10 (3.5×90 cm) by eluting with water, in order to remove completely KCl. The potassium salt converted to the cesium one using a column of SP-Sephadex C-25 (Cs^+ form, 2.5×35 cm). The eluate was concentrated to a small volume again. To this was added a large amount of acetone in an ice bath and kept in a freezer overnight. The resulting dark brown complex **C** was collected by filtration, washed with acetone and ether, and then dried in a vacuum desiccator. From the ^{1}H NMR and ^{13}C NMR spectral measurements, it was found that **C** contained 0.33 mol of ether and 0.1 mol of acetone. Found: C, 23.87; H, 4.55; N, 5.16%. Calcd for $C_{20}H_{36}N_4O_8S_4Cs_2Co_2\cdot 4.5H_2O\cdot 0.33C_4H_{10}O\cdot 0.1C_3H_6O$: C, 23.93; H, 4.56; N, 5.17%.

4) $\Lambda_{DDD}\Delta_{DDD}$-K$_3$[Co{Co(D-pen-*N,S*)$_3$}$_2$]·8H$_2$O(D): The F-3 eluate in 3) was concentrated to a small volume with a rotary evaporator below 25 °C. The deposited KCl was filtered off, and the filtrate was passed throuth a column of Sephadex G-10 (3.5×90 cm) by eluting with water, in ordre to remove completely KCl. The eluate was concentrated to a small volume again. To this was added a large amount of ethanol in an ice bath. The resulting green complex **D** was collected by filtration, washed with ethanol and ether, and then dried in a vacuum desiccator. Found: C, 28.08; H, 5.49; N, 6.52%. Calcd for $C_{30}H_{54}N_6O_{12}S_6K_3Co_3\cdot 8H_2O$: C, 28.11; H, 5.50; N, 6.56%.

Measurements. The electronic absorption spectra were recorded on a JASCO UVIDEC-505 or UVIDEC-610C spectrophotometer, and the CD spectra on a JASCO J-600 spectropolarimeter. All the measurements were carried out in aqueous solution at room temperature. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-FX-100 or -FX-90Q NMR and BRUKER-AM-500 NMR spectrometers at the probe temperature in D_2O. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as an internal reference.

Results and Discussion

Characterization. The deep green complex **A** was obtained from the reaction of $Na_3[Co(CO_3)_3]$ with D-pen. The absorption spectrum of **A** exhibits the d–d transition

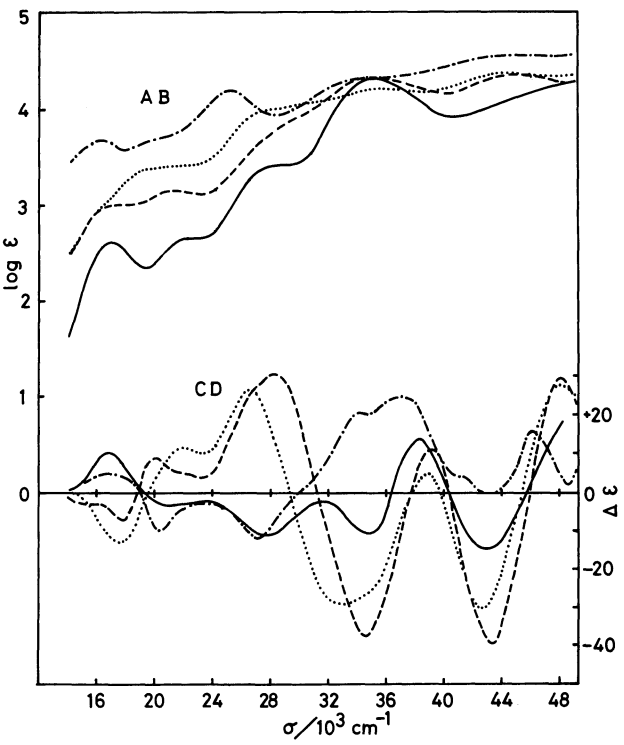

Fig. 2. Absorption and CD spectra of the complexes: Λ_{DDD}-*fac*(*S*)-[Co(D-pen-*N,S*)$_3$]$^{3-}$ (——), Λ_{DDD}-[Co{Co(D-pen-*N,S*)$_3$}(dien)] (------), Λ_{DDD}-[Co{Co(D-pen-*N,S*)$_3$}(D-pen-*N,O,S*)]$^{2-}$ (·····), and $\Lambda_{DDD}\Delta_{DDD}$-[Co{Co(D-pen-*N,S*)$_3$}$_2$]$^{3-}$ (-·-·-·-).

Table 1. Absorption and CD Spectral Data of Polynuclear Complexes

Complex ion	Absorption maxima $\sigma/10^3$ cm^{-1} ($\log \varepsilon$/mol^{-1} dm^3 cm^{-1})	CD extrema $\sigma/10^3$ cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
Λ_{DDD}-*fac*(*S*)-[Co(D-pen-*N*,*S*)$_3$]$^{3-}$ (**A**)	17.09 (2.60) 22.7 (2.7sh) 28.57 (3.4sh) 35.21 (4.32)	16.93 (+10.7) 20.60 (−2.90) 27.93 (−11.1) 35.40 (−11.1) 38.40 (+13.7) 43.07 (−14.1)
Λ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ [a]	17.18 (2.54) 22.62 (2.68) 28.9 (3.3sh) 37.03 (4.39)	16.72 (−7.53) 20.83 (+2.06) 28.17 (+8.60) 34.96 (+28.3) 38.61 (−9.43) 44.44 (+14.7)
Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$}(dien)] (**B**)	17.5 (3.0sh) 20.93 (3.14) 28.7 (3.9sh) 34.93 (4.34) 44.93 (4.37)	17.80 (−7.03) 20.00 (+8.82) 28.02 (+30.3) 34.53 (−37.7) 39.07 (+10.3) 43.47 (−40.0) 48.01 (+29.0)
Λ_{LLL}-[Co{Co(L-cys-*N*,*S*)$_3$}(dien)] [b]	18.48 (2.83) 23.17 (3.34) 32.0 (4.1sh) 37.59 (4.45) 46.40 (4.37)	18.66 (+4.33) 20.79 (−8.74) 22.73 (−1.24) 25.0 (−1.4sh) 27.9 (−7.4sh) 31.23 (−32.8) 36.76 (+38.6) 45.25 (+48.0)
Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$}(D-pen-*N*,*O*,*S*)]$^{2-}$ (**C**)	16.8 (3.1sh) 19.0 (3.4sh) 27.6 (4.0sh) 35.71 (4.23) 44.45 (4.39)	17.70 (−12.6) 21.98 (+11.6) 26.55 (+26.8) 33.15 (−28.4) 35.7 (−21.2sh) 38.76 (+43.8) 42.74 (−28.8)
$\Lambda_{DDD}\Lambda_{DDD}$-[Co{Co(D-pen-*N*,*S*)$_3$}$_2$]$^{3-}$ (**D**)	16.40 (3.67) 20.2 (3.7sh) 25.27 (4.20) 33.4 (4.3sh) 45.87 (4.58)	16.87 (+4.95) 20.43 (−9.80) 27.27 (−12.0) 30.5 (−1.4sh) 34.07 (+21.3) 37.20 (+25.1) 41.32 (+3.27) 43.48 (−0.47) 46.20 (+15.8)
$\Lambda_{LLL}\Lambda_{LLL}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ [c]	18.0 (3.4sh) 22.83 (3.85) 28.41 (4.31) 35.46 (4.39) 48.08 (4.43)	16.77 (−2.10) 18.79 (+5.52) 21.55 (+1.25) 24.21 (−1.72) 26.9 (+3.2sh) 30.30 (+19.4) 30.76 (−22.3) 40.3 (+5.7sh) 43.85 (+13.2) 47.39 (−16.2)

sh denotes a shoulder. a) Ref. 16. b) Ref. 8. c) Ref. 7.

bands in the region of 16—28×10³ cm⁻¹ and the intense band at ca. 35×10³ cm⁻¹ due to the sulfur-to-metal charge transfer (SMCT) transition (Fig.2 and Table 1).[3-8,10,13] This spectral behavior is quite similar to that of the mononuclear L-cys complex, *fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$.[3,7] The ^{13}C NMR spectrum of **A** exhibits five resonance lines due to two methyl, quaternary, methine, and carboxylate carbon atoms in each of three D-pen ligands (Table 2). These suggest that **A** is the Λ_{DDD} or Δ_{DDD} isomer of *fac*(*S*)-[Co(D-pen-*N*,*S*)$_3$]$^{3-}$ having a C_3 symmetry (Fig. 1(a) and (b)). The CD spectral pattern of **A** is almost enantiomeric to that of Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$.[8,11] Accordingly, **A** is assignable to Λ_{DDD}-*fac*(*S*)-[Co(D-pen-*N*,*S*)$_3$]$^{3-}$ (Fig. 1(a)).

The brownish black complex B exhibits quite similar d–d and SMCT transition to the L-cys dinuclear complex, Δ_{LLL}-[Co{Co(L-cys-*N*,*S*)$_3$}(dien)], and further, the CD spectral pattern is almost enantiomeric to that of the Δ_{LLL}-L-cys dinuclear complex (Fig. 2 and Table 1).[8] The ^{13}C NMR spectrum of **B** exhibits four resonance lines due to four methylene carbon atoms of the dien ligand, and three sets of the resonance lines due to each carbon atom in three D-pen ligands (Table 2). These results indicate that **B** is Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$}(dien)] (Fig. 1(c)) having a C_1 symmetry.

The green complex **D** exhibits a quite similar absorption spectral behavior to the trinuclear L-cys complex, [Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ (Fig. 2 and Table 1),[5-7] whose structure has been determined by X-ray crystal structure analysis.[5,6] The CD intensity of **D** is comparable to that of $\Lambda_{LLL}\Lambda_{LLL}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ over the whole region.[7] Further, the ^{13}C NMR spectrum of **D** exhibits two sets of the resonance lines due to each carbon atom in six D-pen ligands (Table 2). Accordingly, **D** is $\Lambda_{DDD}\Lambda_{DDD}$-[Co{Co(D-pen-*N*,*S*)$_3$}$_2$]$^{3-}$ (Fig. 1(e)) having a C_3 symmetry, and not the $\Lambda_{DDD}\Lambda_{DDD}$ or $\Delta_{DDD}\Delta_{DDD}$ isomer having a D_3 symmetry.

As shown in Fig. 2 and Table 1, Λ_{DDD}-*fac*(*S*)-[Co(D-pen-*N*,*S*)$_3$]$^{3-}$ (**A**), Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$}(dien)] (**B**), and $\Lambda_{DDD}\Lambda_{DDD}$-[Co{Co(D-pen-*N*,*S*)$_3$}$_2$]$^{3-}$ (**D**) show quite similar SMCT band at ca. 35×10³ cm⁻¹, while their absorption intensities in the region of 16—28×10³ cm⁻¹ differ significantly from each other, namely, the intensities increase in the order of **A** (mononuclear) < **B**(dinuclear)< **D** (trinuclear). Applying the empirical criterion to the absorption spectrum of **C**, it is probable that **C** has a similar dinuclear structure to **B**. This suggestion is supported by the fact that **C** shows a quite similar CD spectrum to Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$}(dien)] (**B**) over the whole region. The ^{13}C NMR spectrum of **C** exhibits three resonance lines due to the carboxylate carbon atoms in the D-pen ligands, one resonance line locates at δ=184.28, while two lines locate at δ=176.90 and 176.91. Taking into consideration that the resonance lines of the coordinated carboxylate group appear to lower magnetic field than those of the free one,[15] it is probable that of the four D-pen ligands of **C**, three carboxylate groups do not coordinate to the Co(III) ion, and one carboxylate group does. One resonance line due to the quaternary carbon atoms locates at δ=48.90, while two resonance lines locate at δ=58.49 and 58.77. The resonance lines (δ=60.13—60.95) of the S-bridged polynuclear complexes, Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$}(dien)] and $\Lambda_{DDD}\Lambda_{DDD}$-[Co{Co(D-pen-*N*,*S*)$_3$}$_2$]$^{3-}$, shift to lower magnetic field than that (δ=50.27) of the non-S-bridged **A**, Λ_{DDD}-*fac*(*S*)-[Co(D-pen-*N*,*S*)$_3$]$^{3-}$, reflecting that the bridged sulfur atoms in the polynuclear complexes are more crowded by the methyl groups than those in the non-bridged one. This suggests that three sulfur atoms in **C** bridge to two Co(III) ions, and one sulfur atom does not. These facts indicate that **C** is a new-type dinuclear complex, Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$}(D-pen-*N*,*O*,*S*)]$^{2-}$, in which the D-pen ligands coordinate to the Co(III) ion by two different coordination modes.

Properties. The reaction of Λ_{DDD}-*fac*(*S*)-[Co(D-pen-*N*,*S*)$_3$]$^{3-}$ with Co(II) gave only Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$}(D-pen-*N*,*O*,*S*)]$^{2-}$ and $\Lambda_{DDD}\Lambda_{DDD}$-[Co{Co(D-pen-*N*,*S*)$_3$}$_2$]$^{3-}$. This result differs significantly from the fact that the reaction of Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ with Co (II) was accompanied by the inversion of the absolute configuration to give the $\Lambda_{LLL}\Lambda_{LLL}$- and $\Delta_{LLL}\Lambda_{LLL}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$.[5-7] According to model constructions, Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$}(D-pen-*N*,*O*,*S*)]$^{2-}$ is

Table 2. ^{13}C NMR Chemical Shifts[a]

Compound	COO	N–CH	S–C	S–CH$_3$	dien
D-H$_2$pen	181.97	71.67	49.19	30.93 37.11	
Λ_{DDD}-*fac*(*S*)-[Co(D-pen-*N*,*S*)$_3$]$^{3-}$ (**A**)	179.86	75.52	50.27	30.72 33.75	
Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$}(dien)] (**B**)	175.96	74.06	60.13	23.24 33.36	44.48 54.01
		74.31	60.30	24.16 33.48	49.62 58.18
		74.44	60.73	33.86	
Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$}(D-pen-*N*,*O*,*S*)]$^{2-}$ (**C**)	176.90	75.73	48.90	23.54 32.44	
	176.91		58.69	23.63 33.51	
	184.28		58.77	24.16 33.68	
				34.00	
$\Lambda_{DDD}\Lambda_{DDD}$-[Co{Co(D-pen-*N*,*S*)$_3$}$_2$]$^{3-}$ (**D**)	176.66	73.46	60.62	24.65 32.18	
	177.85	76.12	60.95	30.72 33.48	

a) ppm from DSS in D_2O.

prevented by the comparatively steric bulk of the methyl groups of the D-pen-*N,S* and D-pen-*N,O,S* ligands. Similarly, the $\Delta_{DDD}\Delta_{DDD}$ and $\Lambda_{DDD}\Lambda_{DDD}$ isomers of $[Co\{Co(D\text{-pen-}N,S)_3\}_2]^{3-}$ show drastic steric interaction due to the methyl groups of two Λ_{DDD}- or Δ_{DDD}-*fac*(*S*)-$[Co(D\text{-pen-}N,S)_3]$ terminals, while the $\Lambda_{DDD}\Delta_{DDD}$ isomer does not. These steric interactions seem to be responsible for the result that Λ_{DDD}-$[Co\{Co(D\text{-pen-}N,S)_3\}(D\text{-pen-}N,O,S)]^{2-}$ and $\Lambda_{DDD}\Delta_{DDD}$-$[Co\{Co(D\text{-pen-}N,S)_3\}_2]^{3-}$ are formed retentively in the reaction of Λ_{DDD}-*fac*(*S*)-$[Co(D\text{-pen-}N,S)_3]^{3-}$ with Co(II).

In $\Lambda_{DDD}\Delta_{DDD}$-$[Co\{Co(D\text{-pen-}N,S)_3\}_2]^{3-}$, two ^{13}C NMR resonance lines due to the methine carbon atoms exhibit the difference in chemical shifts of about 3 ppm (Table 2). The carboxylate groups bound to the methine carbon atoms take the equatrial orientations for the Λ_{DDD}-$[Co(D\text{-pen-}N,S)_3]$ terminal and the axial orientations for the Δ_{DDD} one. The arrangement around the methine carbon atoms is reflected in the chemical shifts of the methine carbon signals, although the resonance lines of the carboxylate groups or the quaternary carbon atoms in the Λ_{DDD} and Δ_{DDD} terminals resemble each other. A similar spectral difference in chemical shifts was also observed for the signals due to the methine carbon atoms of the trinuclear L-cys complexes, $[Co\{Co(L\text{-cys-}N,S)_3\}_2]^{3-}$ (δ=63.3 and 66.4 for the $\Lambda_{LLL}\Lambda_{LLL}$ isomer, δ=64.1 for the $\Lambda_{LLL}\Delta_{LLL}$ isomer, and δ=67.1 for the $\Delta_{LLL}\Delta_{LLL}$ isomer).[6,7] In this region, the resonance line (δ=75.5) of Λ_{DDD}-*fac*(*S*)-$[Co(D\text{-pen-}N,S)_3]^{3-}$ is quite similar to the lower one (δ=76.1) of the trinuclear D-pen complex (Table 2). The other resonance lines due to each carbon atom of the mononuclear complex appear in similar region to those of the trinuclear one, except that the resonance lines due to the quaternary carbon atoms of the S-bridged polynuclear D-pen complexes shift fairly to lower magnetic field (ca. 10 ppm) than those of the mononuclear one. Arnold and Jackson have reported the existence of Λ_{LLL}-*fac*(*S*)-$[Co(L\text{-cys-}N,S)_3]^{3-}$ in an aqueous solution based on the NMR spectral study;[10] the Λ_{LLL}-*fac*(*S*) isomer isomerizes to the Λ_{LLL}-*fac*(*S*) isomer to give the 1:1 mixture by heating in an aqueous solution, while the reverse reaction does not occur. Judging from the present results for the D-pen complexes, however, it seems to be difficult to distinguish the mononuclear L-cys 1:1 mixture from the successively formed trinuclear L-cys complexes based on the NMR spectral behavior. For the presence of Λ_{LLL}-*fac*(*S*)-$[Co(L\text{-cys-}N,S)_3]^{3-}$, the absorption and CD spectral studies have to be expected.

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