

Synthesis, characterisation and polynuclearisation reaction of *trans*(S)-[Co(aminothiolate-*N,S*)₂(en)]-type cobalt(III) complexes with 2-aminoethanethiolate, L-cysteinate and D-penicillamate

Toshiaki Yonemura,^{*a} Zhi-Ping Bai,^b Ken-ichi Okamoto,^c Tomoharu Ama,^a Hiroshi Kawaguchi,^a Takaji Yasui^a and Jinsai Hidaka^d

^a Department of Material Science, Kochi University, Akebono-cho, Kochi 780-8520, Japan.
E-mail: yonemura@cc.kochi-u.ac.jp

^b Co-ordination Chemistry Institute, Nanjing University; State Key Laboratory of Co-ordination Chemistry of Nanjing University, Nanjing, 210093, China

^c Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

^d Department of Industrial Chemistry, Kinki University in Kyushu, Iizuka, Fukuoka 820-8555, Japan

Received 15th December 1998, Accepted 30th April 1999

The *trans*(S)-[Co(N)₄(S)₂]-type mononuclear complexes [Co(L)₂(en)]^{+ or -} (L = 2-aminoethanethiolate (aet) **1**, L-cysteinate (L-cys) **3** or D-penicillamate (3-sulfanyl-D-valinate) (D-pen) **5**) were newly prepared by the reaction of *trans*-[CoCl₂(en)₂]⁺ with L at pH 8.5 and 25 °C. The crystal structure of **1** was determined by X-ray diffraction analysis. The geometry around the cobalt atom is approximately octahedral and two thiolate donor atoms in the aet ligands occupy *trans* positions to each other. Two Co–S bonds are lengthened by the double sulfur *trans* influence across the cobalt centre attributable to two thiolato sulfur donor atoms. The diastereomers of **3** and **5** were separated by the column chromatographic technique and characterised on the basis of their UV/Vis, CD and ¹³C NMR spectra. The Λ_{DD} isomer of **5** ($5\Lambda_{DD}$) is preferably formed by attractive (COO...H–N–H) interactions. Though *cis*(S)-[Co(L)₂(en)]^{+ or -} (L = aet **2**, L-cys **4** or D-pen **6**) were also produced by the same preparative reaction, they could not be separated into the geometrical isomers because of very rapid isomerisation and/or polynuclearisation reaction during elution from the column. It is clear that all *trans*(S) complexes also show drastic and characteristic UV/Vis spectral changes with time in aqueous solutions and tend to isomerise to the *cis*(S) isomer, followed by the formation of S-bridged polynuclear complexes owing to both the double sulfur *trans* influence and high nucleophilicity of the thiolate donor atoms. The polynuclearisation reactions of the three *trans*(S) isomers proceed according to different processes depending on their ligands. In the polynuclearisation reaction of **3**, especially, the novel dinuclear complex Λ_{LLL} -[Co{Co(L-cys-*N,S*)₃}(L-cys-*N,O,S*)₂]²⁻ **7**, which has not so far been identified in usual dinuclearisation reactions, was newly obtained.

Introduction

Metal thiolate co-ordination chemistry has experienced explosive development during the past two decades as a consequence of growing awareness of the occurrence of cysteine ligation in a variety of electron-transfer proteins, metalloenzymes and so on. However, only a few systematic studies have been reported for the properties of these complexes, because their syntheses are not generally trivial but complicated by difficulties inherent to thiolate co-ordination chemistry.^{1–3} Cobalt(III) complexes are appropriate to the investigation of the stereochemistry and spectroscopic properties of complexes with sulfur-containing aminocarboxylate ligands because cobalt(III) ions produce stable complexes with sulfur-containing ligands.^{2–8} So far, although a lot of cobalt(III) complexes with thiolate ligands have been reported with biochemical or structural interests, only one isomer has ever been preferentially isolated in many cases. The presence of two or more thiolate donor atoms in the co-ordination sphere induces an extreme specificity concerned with the formation of geometrical isomers. In general, cobalt(III) complexes containing two or three thiolate donor atoms take the *cis*(S) geometry as found in *fac*-[Co(L-*N,S*)₃] [L = 2-aminoethanethiolate (aet), L-cysteinate (L-cys) or D-penicillamate (3-sulfanyl-D-valinate) (D-pen)] or bridge easily to other metal ions to form S-bridged polynuclear structures, which are stable enough in aqueous solution thus hampering the isolation of mononuclear species.^{2,3,9} However, the *trans*(S)

isomers of [Co(N)₄(S)₂] and [Co(N)₂(O)₂(S)₂] type were isolated by using a multidentate thiolate ligand such as endet = {–S(CH₂)₂N(CH₃)CH₂}₂ in [Co(endet)(en)]⁺,¹⁰ an aromatic thiolate ligand such as 2-pyrimidinethiolate in [Co(pymt)₂(en)]⁺,¹¹ a thioether and/or sulfinate ligand, such as L-methioninate in [Co(L-met)₂],⁵ S-methyl-D-penicillamate (smp) in [Co(D-smp)(D-psi)] (D-psi = 3-sulfino-D-valinate).¹² It is difficult to isolate the *trans*(S) isomer of the cobalt(III) complexes with two or three L-cysteine like aliphatic aminothiolate ligands.

The first partial report of the crystal structure of the *trans*(S)-type cobalt(III) thiolato complex [Co(aet)₂(en)]⁺ **1** has been published as a preliminary communication.¹³ We report here the correct crystal structure of *trans*(S)-[Co(aet-*N,S*)₂(en)]ClO₄, and complete descriptions of the syntheses, separation of the diastereomers, structural characterisation and specific properties of *trans*(S)-[Co(aminothiolate-*N,S*)₂(en)]-type complexes. The detailed investigations of these complexes will contribute significantly not only to our understanding of the mononuclear thiolato complexes but also to those of S-bridged di- and tri-nuclear complexes.

Experimental

Synthesis

trans(S)- **1** and *cis*(S)-[Co(aet-*N,S*)₂(en)]⁺ **2**. A solution of 2-aminoethanethiol hydrochloride (5.68 g, 50 mmol) in 20 cm³

of water was added to a solution of *trans*-[CoCl₂(en)₂]Cl¹⁴ (7.27 g, 25 mmol) in 50 cm³ of water. The mixed solution was adjusted to pH 8.5 and stirred at 25 °C for 1 h, whereupon it immediately turned from green to reddish brown. The reaction mixture was poured onto an SP-Sephadex C-25 column and separated into three bands, brownish violet (A-1), yellow (A-2) and greenish brown (A-3), in this elution order, by development with a 0.2 mol dm⁻³ KCl aqueous solution. The formation ratio A-1:A-2:A-3 was about 4:1:2. It was confirmed on the basis of the UV/Vis spectral data that the A-2 and A-3 bands contained [Co(aet)(en)₂]²⁺¹⁵ and trinuclear complex [Co₃(aet-*N,S*)₆]³⁺⁹, respectively. The A-1 band containing the desired complexes was circulated several times with the same eluent. It was separated into two bands, violet (**1**) and brown (**2**).

The early violet eluate (**1**) was concentrated to a small volume with a rotary evaporator below 25 °C, and a large amount of methanol added to the concentrated solution to eliminate KCl. After the filtrate had again been concentrated to a small volume, a large amount of methanol was added to the concentrated solution to deposit a violet complex. The complex obtained as its chloride salt was dissolved in water and the resulting solution passed through a QAE-Sephadex column (ClO₄⁻ form) by elution with water in order to replace the Cl⁻ ion by ClO₄⁻. The eluate was concentrated to a small volume and allowed to stand in a refrigerator for a week. The resulting violet crystals were collected by filtration and dried in a silica gel desiccator. Yield: 0.2 g {Found: C, 19.57; H, 5.20; N, 15.14. Calc. for *trans*(S)-[Co(aet-*N,S*)₂(en)]ClO₄, C₆H₂₀ClCoN₄O₄S₂: C, 19.44; H, 5.44; N, 15.11%. NMR(¹³C, D₂O): δ 54.51 (CH₂S), 47.63 (CH₂NH₂ of (en) and 30.15 (CH₂NH₂ of (aet). UV/Vis (H₂O): λ/nm (ε/dm³ mol⁻¹ cm⁻¹) 548 (230), 448 (sh) (160), 324 (23000), 244 (sh) (2800) and 216 (sh) (13000).

The late brown eluate (**2**) was treated with the same procedure. The separation of the geometrical isomer of **2** was attempted by the same column chromatographic method as that used for **1**. However, it was not successful because of the formation of [Co₃(aet-*N,S*)₆]³⁺⁹ during the elution. The ¹³C NMR spectral measurements of the brown eluate **2** indicated that the complex contained two isomers (C₁-*cis*(S) and C₂-*cis*(S) were distinguished by the peak intensities). Yield: 0.9 g {Found: C, 19.33; H, 5.23; N, 14.92. Calc. for *cis*(S)-[Co(aet-*N,S*)₂(en)]ClO₄, C₆H₂₀ClCoN₄O₄S₂: C, 19.44; H, 5.44; N, 15.11%. NMR(¹³C, D₂O): δ 52.85, 51.48 (CH₂S), 48.38, 46.09 (CH₂NH₂ of en), 33.11, 30.73 (CH₂NH₂ of aet) for C₁ isomer and 52.94 (CH₂S), 47.61 (CH₂NH₂ of en) and 30.61 (CH₂NH₂ of aet) for C₂ isomer. UV/Vis (H₂O): λ/nm (ε/dm³ mol⁻¹ cm⁻¹) 574 (190), 444 (sh) (310), 380 (sh) (750), 334 (sh) (2800), 284 (15500), 266 (sh) (15000) and 216 (sh) (11000).

trans(S)- **3** and **cis**(S)-[Co(L-cys-*N,S*)₂(en)]⁻ **4**. These complexes were prepared by a method similar to that used for the aet complex, using 3.02 g (25 mmol) of L-cysteine. The reaction was carried out at 25 °C for 20 min. The reaction mixture was poured onto a QAE-Sephadex A-25 column and then separated into two bands, brownish violet (B-1) and greenish brown (B-2), in this elution order, by development with a 0.2 mol dm⁻³ KCl aqueous solution. The formation ratio B-1 : B-2 was about 1 : 3. It was confirmed on the basis of the UV/Vis spectral data that the B-2 band contained trinuclear complexes, Δ_{LLL}Δ_{LLL}⁻, Δ_{LLL}-Λ_{LLL}⁻ and Λ_{LLL}Λ_{LLL}⁻[Co₃(L-cys-*N,S*)₆]³⁻.² The B-1 band containing the desired complexes was circulated several times. It was separated into two bands, violet (**3**) and brown (**4**). The resolution of the diastereomers of **3** was carried out by the column chromatographic method. As the band of **3** was circulated more than two times, it was separated into two bands, brownish violet (+)₅₅₅^{CD}-**3**Δ_{LL}, which showed a positive CD sign at 555 nm, and violet (-)₅₅₅^{CD}-**3**Δ_{LL}, which showed a negative one, in this order. The formation ratio of (+)₅₅₅^{CD}-**3**Δ_{LL} and (-)₅₅₅^{CD}-**3**Δ_{LL} was 27 : 73.

The early eluate ((+)₅₅₅^{CD}-**3**Δ_{LL}) was concentrated to a small volume with a rotary evaporator below 25 °C, and a large amount of methanol added to the concentrated solution to eliminate KCl. After the filtrate was again concentrated to a small volume, a large amount of methanol was added. The brownish violet complex was deposited from the solution and collected by filtration. The complex obtained as its chloride salt was dissolved in water and the resulting solution passed through a SP-Sephadex C-25 column (Cs⁺ form) by elution with water in order to replace the K⁺ ion by Cs⁺. The eluate was concentrated to a small volume and methanol-ethanol (1 : 1) added till crystals deposited. The resulting brownish violet complex was collected by filtration and dried in a silica gel desiccator. The late eluate ((-)₅₅₅^{CD}-**3**Δ_{LL}) was treated in the same manner except that the complex was obtained as its potassium salt. Yield: 0.1 (+)₅₅₅^{CD}-**3**Δ_{LL} and 0.4 g (-)₅₅₅^{CD}-**3**Δ_{LL}. Found for (+)₅₅₅^{CD}-Cs**3**Δ_{LL}: C, 18.81; H, 4.81; N, 10.77. Calc. for (+)₅₅₅^{CD}-Λ_{LL}-*trans*(S)-Cs[Co(L-cys-*N,S*)₂(en)], C₈H₁₈CoCsN₄O₄S₂·2.5H₂O: C, 17.95; H, 4.33; N, 10.47%. NMR(¹³C, D₂O): δ 179.67 (COO), 69.00 (CH₂S), 47.46 (CH₂NH₂ of en) and 34.26 (CH₂NH₂ of L-cys). UV/Vis (H₂O): λ/nm (ε/dm³ mol⁻¹ cm⁻¹) 543 (190), 446 (sh) (230) and 326 (21900). CD (H₂O): λ/nm (Δε/dm³ mol⁻¹ cm⁻¹) 595 (+1.50), 515 (+1.85), 440 (sh) (+0.5), 324 (-21.20) and 214 (+18.20). Found for (-)₅₅₅^{CD}-K**3**Δ_{LL}: C, 21.72; H, 5.41; N, 12.55. Calc. for (-)₅₅₅^{CD}-Δ_{LL}-*trans*(S)-K[Co(L-cys-*N,S*)₂(en)], C₈H₁₈CoKN₄O₄S₂·3H₂O: C, 21.33; H, 5.37; N, 12.44%. NMR(¹³C, D₂O): δ 69.28 (CH₂S), 47.79 (CH₂NH₂ of en) and 34.05 (CH₂NH₂ of L-cys). UV/Vis (H₂O): λ/nm (ε/dm³ mol⁻¹ cm⁻¹) 543 (190), 446 (sh) (190) and 326 (20000). CD (H₂O): λ/nm (Δε/dm³ mol⁻¹ cm⁻¹) 555 (-2.50), 377 (+2.60), 307 (+1.80), 260 (sh) (+2.0) and 234 (+6.00).

The late brown eluate (**4**) by treated with the same procedure as that used for the early eluate. However, the desired complex could not be isolated as crystals because it was thermally unstable and readily isomerised to the *fac*-[Co(L-cys-*N,S*)₃]³⁻ and polynuclear complexes during the repeated elution. Thus, the brown eluate (**4**) was used intact for measurements of the UV/Vis, CD and ¹³C NMR spectra and the plasma emission spectral analysis.

trans(S)- **5** and **cis**(S)-[Co(D-pen-*N,S*)₂(en)]⁻ **6**. These complexes were prepared by a method similar to that used for the L-cys complex, using 3.78 g (25 mmol) of D-penicillamine. The reaction was carried out at 25 °C for 2 h. On QAE-Sephadex the mixture was separated into three bands, brownish violet (C-1), green (C-2) and brownish green (C-3), in this elution order, by development with a 0.2 mol dm⁻³ KCl aqueous solution. The formation ratio C-1 : C-2 : C-3, was about 4 : 1 : 1. It was confirmed on the basis of the UV/Vis spectral data that the C-2 and C-3 bands contained mono- and tri-nuclear complexes, [Co(D-pen-*N,S*)₃]³⁻ and [Co₃(D-pen-*N,S*)₆]³⁻, respectively.³ The C-1 band containing the desired complexes was circulated several times. It was separated into three bands, violet (**5**), brown and dark brown (**6**). The second brown eluate showed an identical UV/Vis spectrum to that of *trans*(N)-[Co(D-pen-*N,O,S*)₂]⁻.⁶ The resolution of the diastereomers of **5** was carried out by the column chromatographic method. The band containing **5** was separated into two bands, violet (-)₅₃₅^{CD}-**5**Δ_{DD} and brownish violet (+)₅₃₅^{CD}-**5**Δ_{DD}, in this order, by circulation more than two times. The formation ratio of (-)₅₃₅^{CD}-**5**Δ_{DD} and (+)₅₃₅^{CD}-**5**Δ_{DD} was 20 : 80. The cesium salts of those complexes were obtained by the same method as that used for the L-cys complex. Yield: 0.2 g (-)₅₃₅^{CD}-**5**Δ_{DD} and 1.1 g (+)₅₃₅^{CD}-**5**Δ_{DD}. Found for (-)₅₃₅^{CD}-Cs**5**Δ_{DD}: C, 24.41; H, 5.62; N, 9.32. Calc. for (-)₅₃₅^{CD}-Δ_{DD}-*trans*(S)-Cs[Co(D-pen-*N,S*)₂(en)], C₁₂H₂₆CoCsN₄O₄S₂·3H₂O: C, 24.01; H, 5.37; N, 9.33%. NMR(¹³C, D₂O): δ 177.76 (COO), 76.12 (CH), 50.31 (CS), 48.5 (CH₂ of en), 34.25, 31.53 (CH₃). UV/Vis (H₂O): λ/nm (ε/dm³ mol⁻¹ cm⁻¹) 552(220), 392 (sh) (1600), 327 (22400) and 248 (sh) (6300). CD (H₂O): λ/nm (Δε/dm³ mol⁻¹ cm⁻¹) 535 (-6.22), 420 (sh) (+1.3), 322 (+29.83), 270 (sh) (+2.5), 240 (sh)

(−9.1) and 212 (−25.22). Found for (+)₅₃₅^{CD}-Cs5 Λ_{DD} : C, 23.63; H, 5.82; N, 9.03. Calc. for (+)₅₃₅^{CD}- Λ_{DD} -*trans*(S)-Cs[Co(D-pen-*N,S*)₂(en)], C₁₂H₂₆CoCsN₄O₄S₂·4H₂O: C, 23.31; H, 5.54; N, 9.06%. NMR(¹³C, D₂O): δ 177.85 (COO), 77.89 (CH), 50.18 (CS), 47.7 (CH₂ of en), 34.30, 31.93 (CH₃). UV/Vis (H₂O): λ /nm (ϵ /dm³ mol^{−1} cm^{−1}) 550 (280), 423 (sh) (320) and 326 (21400), 244 (sh) (7900). CD (H₂O): λ /nm ($\Delta\epsilon$ /dm³ mol^{−1} cm^{−1}) 570 (+2.69), 540 (sh) (+2.3), 470 (sh) (−0.5), 378 (−2.55), 314 (−3.79) and 236 (−20.31).

The late eluate containing complex **6** was concentrated to a small volume with a rotary evaporator below 20 °C. After the deposited KCl had been filtered off, a small amount of ethanol and a large amount of acetone were added to the filtrate in an ice-bath. The resulting dark brown complex was collected by filtration, washed with acetone and diethyl ether, and then dried in a vacuum desiccator. The separation of the geometrical isomer of **6** was attempted by the same column chromatographic method as that used for **5**. However, it was not successful because of the isomerisation to *trans*(N)-[Co(D-pen-*N,O,S*)₂]^{−6} during the repeated elution. The ¹H and ¹³C NMR spectral measurements of the eluate (**6**) indicated that **6** contained two isomers (Λ_{DD} -C₁ and Λ_{DD} -C₂) of the four possible (Λ_{DD} -C₁, Δ_{DD} -C₁, Λ_{DD} -C₂ and Δ_{DD} -C₂). Yield: 0.7 g. Found for **K6**: C, 28.57; H, 6.37; N, 10.43. Calc. for *cis*(S)-K[Co(D-pen-*N,S*)₂(en)], C₁₂H₂₆CoKN₄O₄S₂·3H₂O·0.2C₄H₁₀O·0.2KCl: C, 28.53; H, 6.39; N, 10.44%. NMR(¹³C, D₂O): δ 179.04, 178.11 (COO), 76.59, 75.14 (CH), 52.51, 49.12 (CS), 48.78, 46.38 (CH₂ of en), 33.61, 33.58, 31.22, 30.71 (CH₃) for Λ_{DD} -C₁ isomer and 177.78 (COO), 77.65 (CH), 50.23 (CS), 47.72 (CH₂ of en), 34.31, 31.98 (CH₃) for Λ_{DD} -C₂ isomer.

Isomerisation and polynuclearisation reactions of *trans*(S)-type complexes in the solution

Each solution of *trans*(S)-[Co(aminothiolate-*N,S*)₂(en)]⁺ or [−] (aminothiolate-*N,S* = aet, L-cys or D-pen) was allowed to stand at 22 or 50 °C under a nitrogen atmosphere, and its change with time was monitored by UV/Vis and CD spectral measurements. After 2 weeks the solution was diluted 10 times with deoxygenated water and poured onto a QAE-Sephadex A-25 (Cl[−] form, 4 × 100 cm) or an SP-Sephadex C-25 (K⁺ form, 4 × 100 cm) column. The adsorbed band was eluted with a degassed 0.05 mol dm^{−3} KCl aqueous solution. The chromatographic behaviours and UV/Vis and CD spectral data of the resulting eluates corresponded to those of the eluates obtained in the preparation of the complexes. Namely, four bands for the aet complex, *trans*(S)-**1**, *cis*(S)-**2**, [Co(aet)(en)₂]²⁺ and [Co₃(aet-*N,S*)₆]³⁺, and five bands for the D-pen complex, *trans*(S)-**5**, *cis*(S)-**6**, [Co(D-pen-*N,O,S*)₂][−], Λ_{DDD} -[Co(D-pen-*N,S*)₃]^{3−} and $\Lambda_{DDD}\Delta_{DDD}$ -[Co₃(D-pen-*N,S*)₆]^{3−}, were obtained. On column chromatography of the L-cys complex, especially, besides the three eluates *trans*(S)-**3**, *cis*(S)-**4** and $\Lambda_{LLL}\Lambda_{LLL}$ - and $\Lambda_{LLL}\Delta_{LLL}$ -[Co₃(L-cys-*N,S*)₆]^{3−} obtained in the preparation of the complexes, a new brown band appeared between the B-1 and B-2 bands. The UV/Vis, CD and ¹³C NMR spectral behaviours indicated that the brown band contained a dinuclear complex, Λ_{LLL} -[Co{Co(L-cys-*N,S*)₃}(L-cys-*N,O,S*)₂]^{2−} **7**. The eluate from the brown band was concentrated to a small volume and filtered to remove KCl. The brown complex **7** was obtained on addition of acetone to the filtrate. Yield: 0.3 g. Found for **K27**: C, 19.53; H, 4.18; N, 7.43. Calc. for K₂[Co{Co(L-cys-*N,S*)₃}(L-cys-*N,O,S*)₂], C₁₂H₂₀Co₂K₂N₄O₈S₄·5H₂O·0.2C₃H₆O: C, 19.55; H, 4.06; N, 7.24%. NMR(¹³C, D₂O): δ 186.27, 179.7–179.4 (COO), 66.90, 64.53, 63.54, 63.31 (CH), 40.04, 37.88, 37.79, 30.46 (CH₂S). UV/Vis (H₂O): λ /nm (ϵ /dm³ mol^{−1} cm^{−1}) 617 (sh) (630), 495 (sh) (2500), 448 (4200), 348 (sh) (10000), 316 (14100) and 262 (19500). CD (H₂O): λ /nm ($\Delta\epsilon$ /dm³ mol^{−1} cm^{−1}) 642 (+4.35), 552 (−11.36), 482 (+5.70), 460 (sh) (+4.7), 398 (+5.55), 356 (+9.91), 320 (sh) (−0.5), 268 (−29.86) and 232 (−17.96).

For the L-cys complex, the concentration of each eluate

Table 1 Crystallographic data for *trans*(S)-[Co(aet)₂(en)]ClO₄ **1**

Chemical formula	C ₆ H ₂₀ ClCoN ₄ O ₄ S ₂
<i>M</i>	370.75
Crystal colour	Purple
Crystal system	Orthorhombic
Space group	<i>Fdd2</i> (no. 43)
<i>a</i> /Å	10.5077(6)
<i>b</i> /Å	17.108(1)
<i>c</i> /Å	15.7022(6)
<i>V</i> /Å ³	2822.7(2)
<i>Z</i>	8
<i>F</i> (000)	768
<i>D</i> _x /g cm ^{−3}	1.744
μ (Mo-K α)/cm ^{−1}	8.56
Reflections collected	4312
Observed reflections [<i>I</i> > 3 σ <i>I</i>]	3878
<i>R</i>	0.040
<i>R</i> '	0.064

obtained from the chromatographic separation was determined by plasma emission spectral analysis. The amounts of the four isomers, *trans*(S)-**3**, *cis*(S)-[Co(L-cys-*N,S*)₂(en)][−] **4**, [Co{Co(L-cys-*N,S*)₃}(L-cys-*N,O,S*)₂]^{2−} **7** and [Co₃(L-cys-*N,S*)₆]^{3−} in the eluate were estimated from curve analyses of the UV/Vis spectra. The concentration of each component in solution was determined at given times by calculation using a NEC PC-9801 VM computer using a least-squares linear method. In the curve analyses the spectral data at 81 points in the region of 400–240 nm (intervals of 2 nm) were used.

Measurements

The UV/Vis spectra of the complexes were recorded on a JASCO UVDEC-610C or 670 spectrophotometer and the CD spectra on a JASCO J-600 or 720 spectropolarimeter. All the measurements were carried out in aqueous solutions at room temperature. The elemental analyses were performed by the Analysis Centre of the University of Tsukuba. The concentrations of cobalt in the complexes were determined by plasma emission spectral analysis with a Nippon Jarrel-Ash ICAP-575 ICP spectrophotometer. The ¹H and ¹³C NMR spectra were recorded on a Bruker AM-500 spectrometer at the probe temperature in D₂O. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as an internal reference.

Crystal structure determination

Single-crystal X-ray diffraction experiments were performed on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo-K α radiation (λ = 0.71073 Å). Crystallographic data for *trans*(S)-[Co(aet)₂(en)]⁺ **1** are summarised in Table 1. Unit cell parameters for a single crystal (0.38 × 0.40 × 0.45 mm) of **1** were determined by a least-squares refinement of 25 reflections in the range of 20 < 2 θ < 22.

The structure was solved by direct methods and refined by full-matrix least-squares treatment on *F*. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined as riding atoms (C–H = N–H 0.95 Å and B = 1.20 × value of riding atom). All the calculations were performed using the TEXSAN crystallographic software package.¹⁶ The largest parameter shifts were 0.02 times e.s.d. and $|\Delta\rho|_{\max}$ in the final Fourier-difference maps were 0.38 e^{−2}, and 15 e^{−3}.

CCDC reference number 186/1447.

See <http://www.rsc.org/suppdata/dt/1999/2151/> for crystallographic files in .cif format.

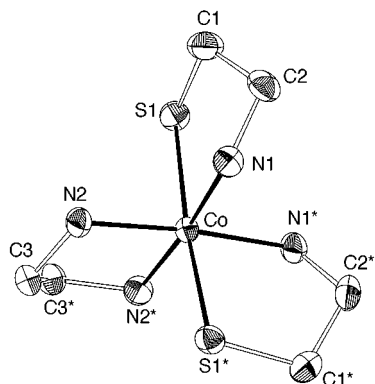
Results and discussion

Molecular structure

Although we first considered the possibility of a monoclinic symmetry for complex **1** in the preliminary communication,

Table 2 Selected bond distances (Å) and angles (°) for *trans*(S)-[Co(aet)₂(en)]ClO₄ **1**

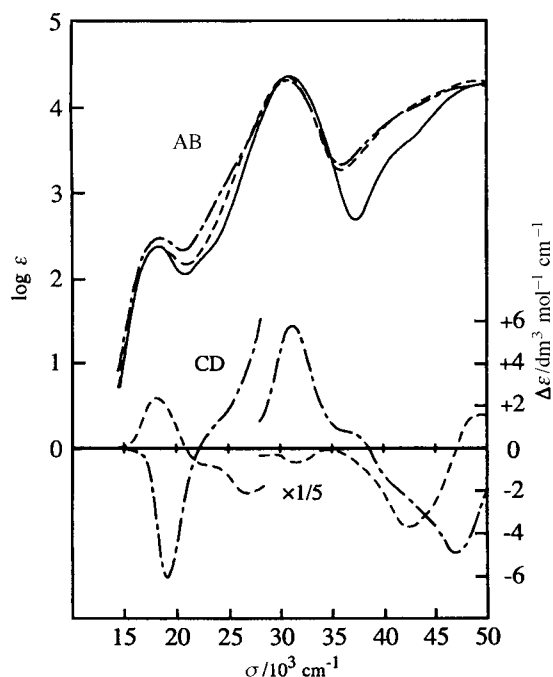
Co–S(1)	2.2871(4)	N(2)–C(3)	1.484(2)
Co–N(1)	1.975(2)	C(3)–C(3*)	1.509(4)
Co–N(2)	1.979(2)	N(1)–C(2)	1.492(2)
S(1)–C(1)	1.817(2)	C(1)–C(2)	1.508(3)
S(1)–Co–S(1*)	175.09(3)	N(1)–Co–N(2*)	174.82(7)
S(1)–Co–N(1)	90.77(4)	N(2)–Co–N(2*)	84.98(10)
S(1)–Co–N(2)	90.37(5)	Co–N(1)–C(2)	114.9(1)
S(1)–Co–N(1*)	85.81(4)	N(1)–Co–N(1*)	91.8(1)
S(1)–Co–N(2*)	93.25(5)	Co–S(1)–C(1)	98.70(6)
N(1)–Co–N(2)	91.73(7)	Co–N(2)–C(3)	109.3(1)

**Fig. 1** Molecular structure of *trans*(S)-[Co(aet)₂(en)]ClO₄ **1**. Hydrogen atoms have been omitted for clarity.

further refinement showed that the orthorhombic space group *Fdd2* fits much better to all observed reflections. A perspective drawing of the complex cation is given in Fig. 1, together with a numbering scheme. Selected bond distances and angles are listed in Table 2. The present complex adopts a six-co-ordinate structure and the co-ordination geometry around the Co atom is approximately octahedral CoN₄S₂. Two thiolato sulfur atoms of the aet ligands occupy *trans* positions to each other. Therefore, **1** is assigned to *trans*(S)-[Co(aet)₂(en)]⁺. The Co–S1 distances (2.2871(4) Å) are longer than the Co–S distances of other complexes containing a co-ordinating aliphatic thiolate or thioether sulfur atom, such as 2.226 Å in [Co(aet)(en)₂]²⁺,¹⁵ 2.267(10) Å in [Co(CH₃S(CH₂)₂NH₂)(en)₂]³⁺,¹⁷ 2.239(1) Å in *trans*-[Co{CH₃SCH(CH₃)CO₂}(tren)]²⁺ (tren = tris(2-aminoethyl)amine),¹⁸ and 2.232(1)–2.244(2) Å in *trans*-[Co(ma or mta)(tren)]²⁺ (ma = 2-sulfanyl-acetate and mta = 2-(methylsulfanyl)acetate).^{7,9} This indicates that the Co–S bonds are lengthened by the double sulfur *trans* influence due to two aliphatic thiolato-type sulfur donor atoms. As the other striking structural characters are almost the same as described previously, further detailed descriptions are omitted here.

Structural assignment and properties

Three geometrical isomers, *trans*(S), *C*₂-*cis*(S) and *C*₁-*cis*(S), are possible for [Co(aminothiolate-*N,S*)₂(en)]-type complexes. The ¹³C NMR spectrum of **1** exhibits three peaks [δ 54.51, 30.15 (aet) and 47.63 (en)] due to methylene carbons of each ligand. This indicates that **1** has a *C*₂ symmetry. The UV/Vis spectral behaviour resembled those of other *trans*(S)-[Co(N₂S₂)(en)]-type complexes with pymt or endet ligands,^{10,11} giving a sharp d–d absorption band at (17–18) × 10³ cm⁻¹ and a characteristic sulfur-to-cobalt charge transfer (SCCT) band at 31 × 10³ cm⁻¹ (Fig. 2). These spectral behaviours provide useful information for structural assignment of the other *trans*(S)-type complexes. The UV/Vis spectra of **3** and **5** also show the d–d transition and intense SCCT bands in the same region as **1** does. The ¹³C NMR spectra revealed that **3** and **5** have *C*₂ symmetry, because (–)₅₅₅^{CD}-3 Δ_{LL} and (+)₅₅₅^{CD}-3 Δ_{LL} exhibited four resonance lines due to the eight carbons, and (–)₅₃₅^{CD}-5 Δ_{DD} and (+)₅₃₅^{CD}-5 Δ_{DD} exhibited six

**Fig. 2** The UV/Vis and CD spectra of *trans*(S)-[Co(aet)₂(en)]⁺ **1** (—), Δ_{DD} -*trans*(S)-[Co(D-pen-*N,S*)₂(en)]⁻ 5 Δ_{DD} (---) and Λ_{DD} -*trans*(S)-[Co(D-pen-*N,S*)₂(en)]⁻ 5 Δ_{DD} (----).

resonance lines due to the twelve carbons. Therefore, these four complexes are assignable to *trans*(S)-[Co(aminothiolate-*N,S*)₂(en)]-type (aminothiolate = L-cys or D-pen) complexes. Two diastereomers, Δ_{LL} (Δ_{DD}) and Λ_{LL} (Λ_{DD}), are possible for each of **3** and **5**. The CD spectrum of (–)₅₃₅^{CD}-5 Δ_{DD} exhibits a negative band in the first absorption band region, while that of the (+)₅₃₅^{CD}-5 Δ_{DD} has a positive band in that region (Fig. 2). Accordingly, (–)₅₃₅^{CD}-5 Δ_{DD} and (+)₅₃₅^{CD}-5 Δ_{DD} are assigned to (–)₅₃₅^{CD}- Δ_{DD} and (+)₅₃₅^{CD}- Λ_{DD} -*trans*(S)-[Co(D-pen)₂(en)]⁻, respectively. In a similar manner, (+)₅₅₅^{CD}-3 Δ_{LL} and (–)₅₅₅^{CD}-3 Δ_{LL} are assigned to (+)₅₅₅^{CD}- Λ_{LL} - and (–)₅₅₅^{CD}- Δ_{LL} -*trans*(S)-[Co(L-cys)₂(en)]⁻, respectively. In the first absorption band region of (–)₅₅₅^{CD}-3 Δ_{LL} , two CD bands of the same + sign appeared. This agrees well with the pattern predicted from the CD spectra of the *trans*(N)-[Co(L-aminocarboxylate)₂(ox)]⁻ and *trans*(O)-[Co(L-aminocarboxylate)₂(en)]⁺ complexes.²⁰ On the contrary, (+)₅₃₅^{CD}-5 Δ_{DD} shows only one CD band in the first absorption band region. This difference may be related to the UV/Vis spectral behaviour, which does not have the splitting in the first absorption band region, and attributed to the peculiar transition of the thiolate sulfur donor atom.

The resonance peaks due to the methine and methylene carbons in isomers (–)₅₅₅^{CD}-3 Δ_{LL} and (+)₅₅₅^{CD}-3 Δ_{LL} showed almost the same chemical shift patterns. For the en moiety the resonance peaks due to the methylene carbons in (–)₅₅₅^{CD}-3 Δ_{LL} and (+)₅₅₅^{CD}-3 Δ_{LL} have almost the same chemical shifts as those in **1**. These facts suggest that (–)₅₅₅^{CD}-3 Δ_{LL} and (+)₅₅₅^{CD}-3 Δ_{LL} do not form any hydrogen bond in the solution. Thus the difference in the amounts between (–)₅₅₅^{CD}-3 Δ_{LL} and (+)₅₅₅^{CD}-3 Δ_{LL} (73:27) reflects the favourable equatorial orientation of the carboxylate and the steric repulsion between the methine and methylene groups on the L-cys ligands. The resonance peaks due to the methylene carbons in the en ligand in (–)₅₃₅^{CD}-5 Δ_{DD} are shifted to lower magnetic field (*ca.* 1 ppm) compared to those in (+)₅₃₅^{CD}-5 Δ_{DD} and the resonance peaks due to the methine carbons in (–)₅₃₅^{CD}-5 Δ_{DD} are shifted to higher magnetic field (*ca.* 2 ppm) compared to those in (+)₅₃₅^{CD}-5 Δ_{DD} . Similar trends are observed for the di- and trinuclear complexes [Co{Co(aminothiolate-*N,S*)₃}(D-pen-*N,O,S* or dien)]^{0 or 2-} and [Co₂(aminothiolate-*N,S*)₃]³⁻ (aminothiolate-*N,S* = L-cys or D-pen).^{2,3} It is reasonable to consider that these shifts are affected by the formation of the intramolecular hydrogen bond COO⋯H–N–H. Molecular models of these

complexes suggest the formation of hydrogen bonds due to steric repulsion between the methyl protons on the D-pen ligands and the amine protons on the D-pen or en ligand. The formation ratio of (+)₅₃₅^{CD}-5 Λ_{DD} :(-)₅₃₅^{CD}-5 Δ_{DD} (80:20) slightly increased compared with (-)₅₅₅^{CD}-3 Δ_{LL} :(+)₅₅₅^{CD}-3 Λ_{LL} (73:27) because of such structural stabilisation.

On the other hand, the UV/Vis spectral pattern of complex **6** is quite similar to that of other *cis(S)*-[Co(N)₂(S)₂(en)]-type complexes, giving a characteristic broad SCCT band at 34×10^3 cm⁻¹.¹⁰ Further, the ¹³C NMR spectrum exhibits twelve intense resonance lines (δ 30.71, 31.22, 33.58, 33.61, 46.38, 48.78, 49.12, 52.51, 75.14, 76.59, 178.11 and 179.04) and six weak ones (δ 31.98, 34.31, 47.72, 50.23, 77.65 and 177.78). This suggests that **6** is a mixture of the C₁-*cis(S)* (major) and C₂-*cis(S)* (minor) isomers. The *cis(S)* isomers seem to take preferentially the absolute configuration Λ_{DD} or Δ_{DD} . The absolute configurations of the C₁- and C₂-*cis(S)* isomers containing **6** are more favourable to Λ_{DD} configurations than Δ_{DD} ones because of similar steric repulsion attributable to the methyl group in **5** and the repulsion between the unshared electron pairs on the sulfur donor atoms located in *cis* positions.³ The CD spectrum of **6** shows a relatively intense positive peak in the first absorption band region, suggesting that the configurations of the *cis(S)* isomers containing **6** are assignable to Λ_{DD} . The C₁-*cis(S)* isomer was formed in larger amount than the C₂-*cis(S)* one. This fact may be explained as follows: in the C₂-*cis(S)* isomer, the two sulfur donor atoms occupy *trans* positions to the two nitrogen atoms of the en ligand, so that the en ligand seems to become labilised by the structural *trans* effect due to the sulfur donor atoms. This interpretation is consistent with the fact that cobalt(III) complexes with thiolate ligands prefer to the *cis(S)* geometry. The UV/Vis spectra of **2** and **4** are quite similar to that of *cis(S)*-[Co(D-pen-N,S)₂(en)]⁻ **6** over the whole region. They exhibit a broad SCCT band at 35×10^3 cm⁻¹ characteristic of *cis(S)*-[Co(N)₂(S)₂(en)]-type complexes.¹⁰ This suggests that **2** and **4** also adopt the *cis(S)* geometries of [Co(aet-N,S)₂(en)]⁺ and [Co(L-cys-N,S)₂(en)]⁻, respectively, contain two geometrical isomers, C₁- and C₂-*cis(S)*, and each of the geometrical isomers in **4** consists of two diastereomers, Λ_{LL} and Δ_{LL} . Actually, the ¹³C NMR spectral measurements indicated that **2** and **4** contained two and four possible isomers, respectively. However, the desired complex could not be separated because it was thermally unstable and readily isomerised to the *fac*-[Co(L-cys-N,S)₃]³⁻ and polynuclear complexes during repeated elution.

The UV/Vis spectrum of brown complex **7** shows d-d transition bands in the region $(16\text{--}24) \times 10^3$ cm⁻¹ and intense bands due to the SCCT transition at *ca.* 38×10^3 cm⁻¹. Such spectral behaviour is quite similar to those of [Co{Co(aminothiolate-N,S)₃}(D-pen-N,O,S or dien)]-type (aminothiolate = aet, L-cys or D-pen) dinuclear complexes.³ The ¹³C NMR shift pattern of **7** also resembles that of the latter complexes. Four resonance peaks due to the carboxylate carbon atoms of the L-cys ligands were observed in the δ 186–179 region. The carbon resonance peaks appeared at δ 186.27 and 179.7–179.4 for the co-ordinated and unco-ordinated carboxyl groups, respectively. A single resonance peak due to the methylene carbon atom is located relatively upfield (δ 30.46) compared with those of the corresponding carbon atoms in the [Co(aminothiolate-N,S)₃] moiety (δ 40.04–37.79). These results suggest that three sulfur atoms in the L-cys ligands bridge two cobalt(III) ions, but a sulfur atom in one tridentate L-cys-N,O,S does not. The results from UV/Vis and NMR spectral measurements indicate that **7** is the dinuclear complex [Co{Co(L-cys-N,S)₃}(L-cys-N,O,S)]²⁻, having C₁ symmetry. The CD spectral behaviour of **7** is similar to those of Λ_{LLL} -[Co{Co(L-cys-N,S)₃}(D-pen-N,O,S or dien)]^{2- or 0} and Λ -[Co{Co(aet-N,S)₃}(D-pen-N,O,S)]⁺.³ The IR spectral measurement also supports this. Accordingly, it is suggested that **7** adopts a Λ_{LLL} configuration. This complex containing L-cys-N,O,S as a tridentate ligand was not obtainable by the usual preparative method for the dinuclear complexes.

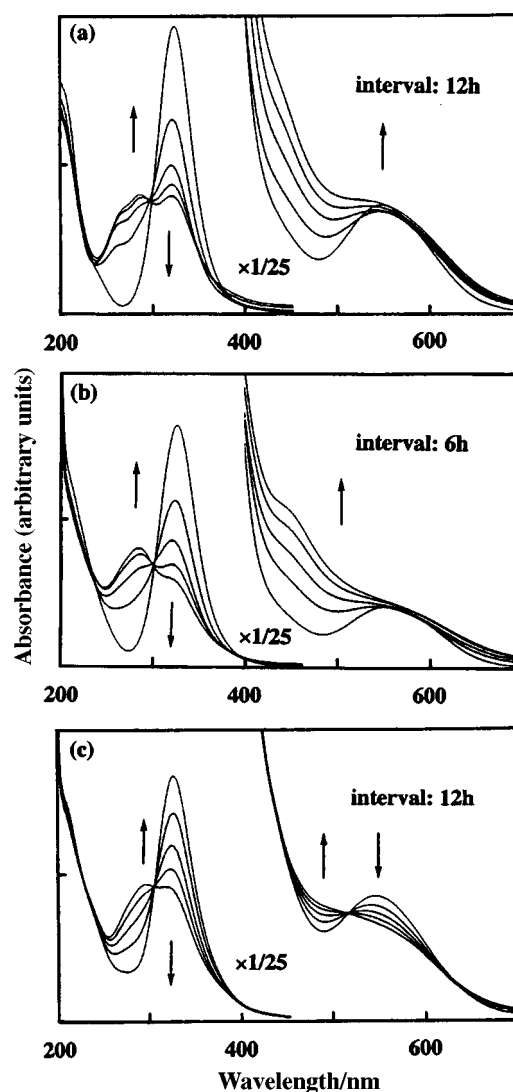


Fig. 3 The UV/Vis spectral changes of the complexes in 0.1 mol dm⁻³ KCl solution at 50 °C measured at 12 or 6 h intervals: (a) *trans(S)*-[Co(aet)₂(en)]⁺ **1**, (b) Δ_{LL} -*trans(S)*-[Co(L-cys-N,S)₂(en)]⁻ **3** Δ_{LL} and (c) Λ_{DD} -*trans(S)*-[Co(D-pen-N,S)₂(en)]⁻ **5** Λ_{DD} .

Structural change of *trans(S)*-type complexes

Fig. 3 shows the UV/Vis spectral changes of the *trans(S)* isomers in 0.1 mol dm⁻³ KCl solution at 50 °C. The UV/Vis and CD spectra became approximately constant after 2 weeks. During this time course, clear-cut isosbestic and isodichroic points were not observed. The change in the absorption curve, in which the maximum of the SCCT band shifted to higher energy (from 327–324 to 291–284 nm), suggests that the *cis(S)* type isomers were formed. Moreover, Fig. 3 (a) and (b) show that the absorption intensities in the d-d transition region increased with time, accompanied by the production of di- and trinuclear complexes. These imply that the *trans(S)* isomer in the solution changes to several species, which were confirmed by the spectral data of the eluate from the column chromatographic separation [four eluates showing four different spectra for aet and L-cys complexes and five eluates with five different spectra for the D-pen complex] as described in the Experimental section.

The observed and calculated curves of *trans(S)*-[Co(L-cys-N,S)₂(en)]⁻ **3** at 22 °C after 2 weeks were in good agreement. The calculated concentration–time dependencies are plotted in Fig. 4. The starting *trans(S)* isomer decreased during the monitored timescale, while the *cis(S)* isomer increased in concentration for the initial period and then (after *ca.* 250 h) the dinuclear and trinuclear complexes were formed. With time (after *ca.* 800 h)

the *cis*(S) isomer began to decrease and simultaneously the dinuclear and trinuclear complexes increased. The dinuclear complexes, $\Lambda_{LLL}[\text{Co}\{\text{Co}(\text{L-cys-N,S})_3\}(\text{L-cys-N,O,S})]^{2-}$ **7**, finally became major species. In this case, the dinuclear complex **7** was selectively formed with only the Λ_{LLL} configuration and the trinuclear complexes were formed with $\Lambda_{LLL}\Lambda_{LLL}$ and $\Lambda_{LLL}\Delta_{LLL}$ (ca. 1:1) configurations; the reason for these selectivities is not clear at present. The isomerisation and polynuclearisation reactions of **3** are explained in Scheme 1. In the initial stage of the reaction (i), (ii) mononuclear complexes are formed. Path (i) is an equilibrium reaction because a small amount of *trans*(S) isomer was also obtained from the isomerisation reaction of the *cis*(S) one. The tris(L-cysteinato)cobalt(III) complex, *fac*-[Co(L-cys-N,S)₃]³⁻, produced in path (ii) has high nucleophilicity, so in the final stage of the reaction the S-bridged di- and trinuclear complexes are mainly formed (iii), (iv). That is a reason why the pure *trans*(S) and *cis*(S) isomers were not isolated up to now. This is supported by a previous report that the S-bridged trinuclear complex [Co₃(L-cys-N,S)₆]³⁻ was easily formed from *fac*-[Co(L-cys-N,S)₃]³⁻.² Path (v) (the change between the di- and tri-nuclear complexes) did not occur under the present conditions. For the *trans*(S)-aet complex **1** a similar spectral change and column chromatographic separation were observed except that only trinuclear complex was formed in the polynuclearisation stage (of course the dinuclear complex is not formed because the aet ligand functions only as a didentate-N,S ligand).

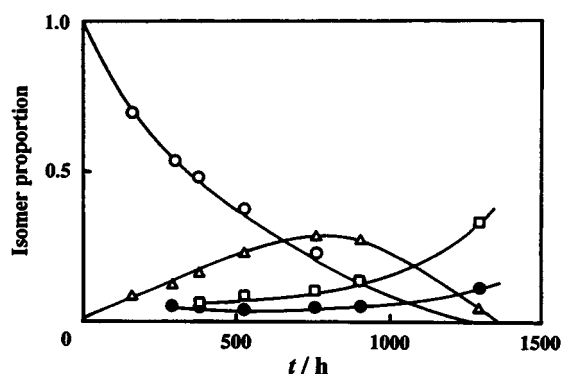


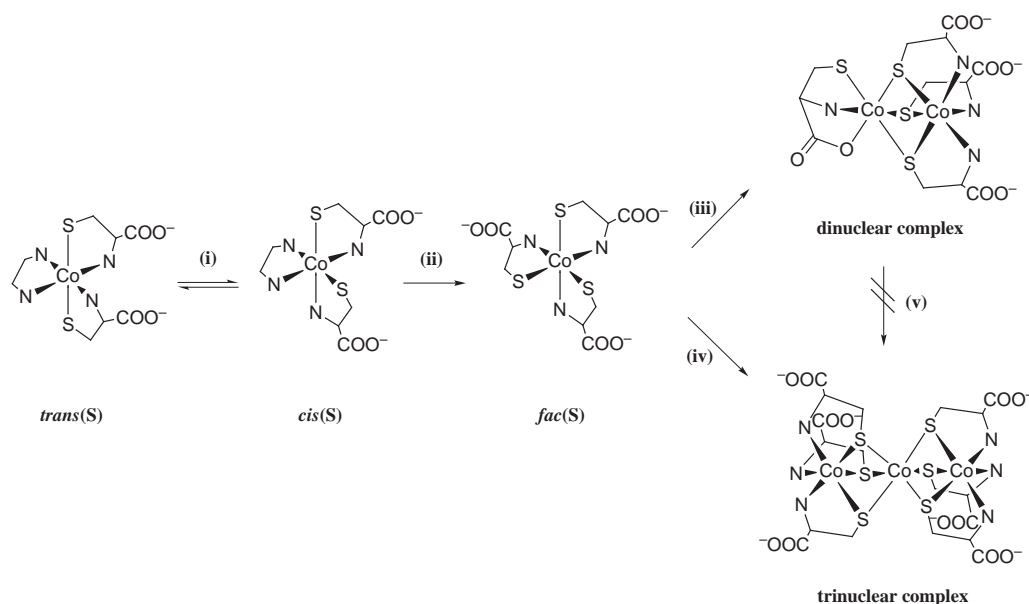
Fig. 4 The changes of the isomer proportions in the isomerisation and polynuclearisation reactions of *trans*(S)-[Co(L-cys-N,S)₂(en)]⁻ **3** (0.05 mol dm⁻³ KCl, 22 °C): *trans*(S)-[Co(L-cys-N,S)₂(en)]⁻ (○), *cis*(S)-[Co(L-cys-N,S)₂(en)]⁻ (△), [Co{Co(L-cys-N,S)₃} (L-cys-N,O,S)]²⁻ (□), [Co₃(L-cys-N,S)₆]³⁻ (●).

and). In the isomerisation and polynuclearisation of *trans*(S)-D-pen complex **5**, although the SCCT band shifts to higher energy, a drastic increase of the absorption intensities in the d-d transition region was not observed. These results suggest that the S-bridged di- and tri-nuclear complexes are difficult to form, since the six methyl groups attached to the neighbouring carbon atoms of the co-ordinated sulfur atoms in the [Co(D-pen-N,S)₃] moiety are sterically bulky. Therefore, the mononuclear *trans*(N)-[Co(D-pen-N,O,S)₂]⁻ complex, which has the minimum steric hindrance of all products, is produced as major species, and small amounts of $\Lambda_{DDD}\text{-fac}$ -[Co(D-pen-N,S)₃]³⁻ and $\Lambda_{DDD}\Delta_{DDD}$ -[Co₃(D-pen-N,S)₆]³⁻ are formed in the final stage of this reaction. The result of the column chromatographic separation also supports this. Consequently, the isomerisation reactions of *trans*(S)-[Co(D-pen-N,S)₂(en)]⁻ proceed through the paths shown in Scheme 2.

UV/Vis Spectral behaviours of [Co(S)_n(N)_{6-n}]-type (n = 1, 2 or 3) complexes

Fig. 5 shows the UV/Vis spectra of mononuclear complexes, [Co(D-pen-N,S)(en)₂]⁺,⁸ *trans*(S)-[Co(D-pen-N,S)₂(en)]⁻ **3**, *cis*(S)-[Co(D-pen-N,S)₂(en)]⁻ **4** and *fac*-[Co(D-pen-N,S)₃]³⁻,³ which are of [Co(S)_n(N)_{6-n}]-type (n = 1, 2 or 3). As the UV/Vis spectral patterns of the L-cys and D-pen complexes, *trans*(S)- or *cis*(S)-[Co(L-cys- or D-pen-N,S)₂(en)]⁻ **3-6**, are also similar to one another, these can be compared with the same *trans*(S)- or *cis*(S)-[Co(N)₄(S)₂] system.

It is known that the first absorption band (¹A_{1g} → ¹T_{1g} transition of the complex for the O_h symmetry) splits clearly into two components for the *trans*(O)-[Co(N)₄(O)₂]- or *trans*(N)-[Co(N)₂(O)₄]-type complexes. This is the so-called Yamatera semiempirical rule which states that the position and shape of the d-d absorption band can be predicted from semiempirical calculation on the basis of molecular orbital theory.² According to this treatment, the complexes adopting the same geometry are expected to show similar UV/Vis spectral behaviour. However, the present sulfur-atom containing *trans*(S)-[Co(D-pen- or L-cys-N,S)₂(en)]⁻ complexes indicate a deviation from the rule, that is no clearly explicit splitting is observed for those complexes. The reason is that the splitting is so small because the ligand field strengths of nitrogen and sulfur are similar, and further it has not been clarified how the ligand field strength of thiolato sulfur compares with those of nitrogen and oxygen (N > S > O or S > N > O).³⁻¹⁰ Consequently, the geometrical structures of the complexes with thio-



Scheme 1

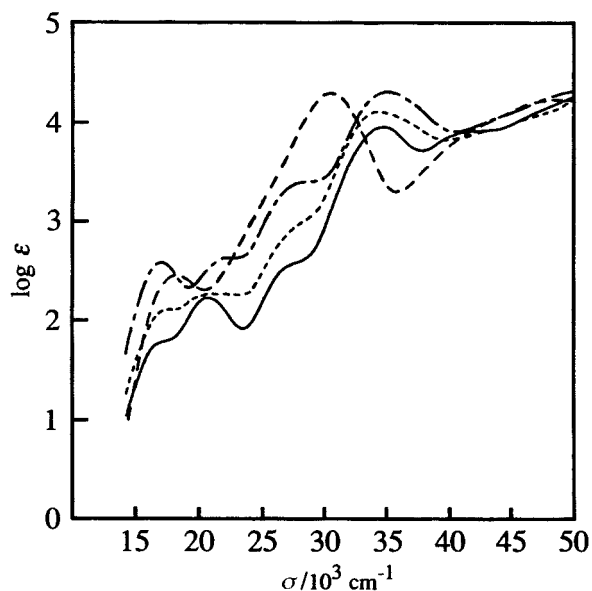
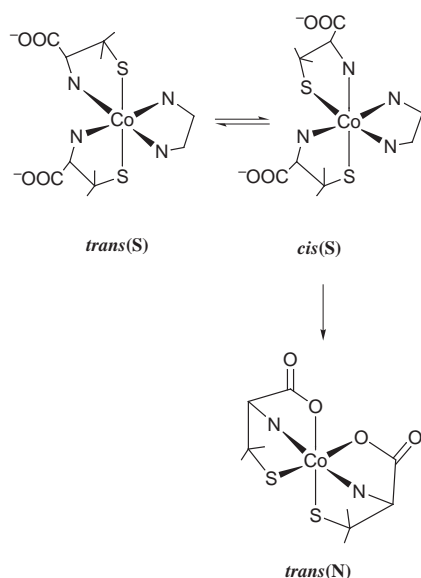


Fig. 5 The UV/Vis spectra of $[\text{Co}(\text{S})_n(\text{N})_{6-n}]$ -type ($n = 1-3$) complexes: $[\text{Co}(\text{D-pen-N,S})(\text{en})_2]^+$ (—), $\text{trans}(\text{S})$ - $[\text{Co}(\text{D-pen-N,S})_2(\text{en})]^-$ (5) (---), $\text{cis}(\text{S})$ - $[\text{Co}(\text{D-pen-N,S})_2(\text{en})]^-$ (6) (....) and fac - $[\text{Co}(\text{D-pen-N,S})_3]^{3-}$ (— · —).



Scheme 2

late sulfur-containing ligands cannot be determined from only the splitting patterns in their d-d absorption band region. The position and pattern of the SCCT bands commonly reflect the geometries such as *cis*(S) and *trans*(S) for cobalt(III) complexes containing two thiolate or thioether sulfur atoms. The *cis*(S) isomers of thiolato and thioether complexes exhibit intense broad SCCT bands in the region of $(32-38) \times 10^3 \text{ cm}^{-1}$ which are composed of more than two components. The *trans*(S) isomers exhibit an intense sharp band at lower energy (*ca.* $31 \times 10^3 \text{ cm}^{-1}$). Of course, the present *trans*(S)- $[\text{Co}(\text{aet-}, \text{L-cys-}$ or $\text{D-pen-N,S})_2(\text{en})]^-$ is also distinguishable from the *cis*(S) isomer on the basis of the UV/Vis spectral patterns in the SCCT band region (Fig. 5). Further, for the $[\text{Co}(\text{S})_n(\text{N})_{6-n}]$ -type ($n = 1-3$) complexes (except the *trans*(S) isomer), we found that the SCCT band broadens (no explicit splitting), shifts to higher energy, and

increases in intensity with n (1 to 3). This seems to depend on the number of the sulfur atoms co-ordinating to Co^{III} . Such spectral behaviours were also observed for all cobalt(III) complexes with the other thiolate ligands. Therefore, these facts suggest that the structures of the $[\text{Co}(\text{S})_n(\text{N})_{6-n}]$ -type ($n = 1-3$) complexes are characterised by the position and intensity of the SCCT band in their UV/Vis spectra.

Acknowledgements

This work was supported by a Grant-in-Aid for Encouragement of Young Scientists (No. 08740522) from the Ministry of Education, Science, Sports and Culture, Japan.

References

- J. J. Mayerle, S. E. Denmark, B. V. DePamphilis, J. A. Ibers and R. H. Holm, *J. Am. Chem. Soc.*, 1975, **97**, 1032; R. W. Lane, J. A. Ibers, R. B. Frankel, G. C. Papaefthymiou and R. H. Holm, *J. Am. Chem. Soc.*, 1977, **99**, 84; P. de Meester and D. J. Hodgson, *J. Am. Chem. Soc.*, 1977, **99**, 101; H. M. Helis, P. de Meester and D. J. Hodgson, *J. Am. Chem. Soc.*, 1977, **99**, 3309; G. J. Gainsford, W. G. Jackson and A. M. Sargeson, *J. Am. Chem. Soc.*, 1977, **99**, 2383; 1979, **101**, 3966; N. Baidya, M. M. Olmstead and P. K. Mascharak, *Inorg. Chem.*, 1989, **28**, 3426; N. Baidya, D. Ndreu, M. M. Olmstead and P. K. Mascharak, *Inorg. Chem.*, 1991, **30**, 2448; I. E. Burgeson and N. M. Kostic, *Inorg. Chem.*, 1991, **30**, 4299; L. Zhu and N. M. Kostic, *Inorg. Chem.*, 1992, **31**, 3994.
- K. Okamoto, S. Aizawa, T. Konno, H. Einaga and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 3859; S. Aizawa, K. Okamoto, H. Einaga and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 1601.
- K. Okamoto, T. Yonemura, T. Konno and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 794; T. Yonemura, S. Nakahira, T. Ama, H. Kawaguchi, T. Yasui, K. Okamoto and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2859.
- V. M. Kothari and D. H. Busch, *Inorg. Chem.*, 1969, **8**, 2276; P. de Meester and D. J. Hodgson, *J. Chem. Soc. Dalton Trans.*, 1976, 618; K. Wakayama, K. Okamoto, H. Einaga and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1995; K. Okamoto, M. Takaki, T. Yonemura, T. Konno and J. Hidaka, *Inorg. Chim. Acta*, 1990, **175**, 31.
- J. Hidaka, S. Yamada and Y. Shimura, *Chem. Lett.*, 1974, 1487.
- K. Okamoto, K. Wakayama, H. Einaga, S. Yamada and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 165.
- T. Yonemura, K. Shibuya, K. Okamoto, T. Ama, H. Kawaguchi and T. Yasui, *Inorg. Chim. Acta*, 1997, **260**, 119.
- H. C. Freeman, C. J. Moore and A. M. Sargeson, *Inorg. Chem.*, 1978, **17**, 3513.
- G. R. Brubaker and B. E. Douglas, *Inorg. Chem.*, 1967, **6**, 1562.
- K. Yamanari, N. Takeshita and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 1227, 2852.
- K. Yamanari, K. Okusako and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, 1992, 1615.
- T. Yonemura, T. Yasui, K. Okamoto and J. Hidaka, *Acta Crystallogr., Sect. C*, 1996, **52**, 1390.
- T. Yonemura, K. Okamoto, T. Ama, H. Kawaguchi and T. Yasui, *Chem. Lett.*, 1993, 1123.
- J. C. Bailar, Jr., *Inorg. Synth.*, 1946, **2**, 222.
- R. C. Elder, L. R. Florian, R. E. Lake and A. M. Yacynych, *Inorg. Chem.*, 1973, **12**, 2690.
- TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corp., The Woodlands, TX, 1985 and 1992.
- R. C. Elder, G. J. Kennard, M. D. Payne and E. Deutsch, *Inorg. Chem.*, 1978, **17**, 1296.
- S. Ohba and Y. Saito, *Acta Crystallogr., Sect. C*, 1984, **40**, 398.
- The *t*-isomer has the S atom at the *trans* position to the tertiary amine of the tren ligand.
- N. Matsuoka, J. Hidaka and Y. Shimura, *Inorg. Chem.*, 1970, **9**, 719; *Bull. Chem. Soc. Jpn.*, 1972, **45**, 2491, 1975, **48**, 458.
- H. Yamatera, *Bull. Chem. Soc. Jpn.*, 1958, **31**, 95; N. Matsuoka, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 1868.

Paper 8/09753D