Excellent chiralselectivity in sulfur-bridged Co^{III}MCo^{III} (M = Ni^{II} and Pd^{II}) trinuclear complexes containing 1,2-cyclohexanediamine†

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The reaction of [Ni(aet)$_2$] with [CoCl$_2$(R,R-chxn)$_2$]$^+$ (aet = 2-aminoethanethiolate, R,R-chxn = 1R,2R-cyclohexanediamine) in water gave a Co^{III}Ni^{II}Co^{III} trinuclear complex, $\Delta_{RR}\Delta_{RR}$-[Ni{Co(aet)$_2$-(R,R-chxn)}$_2$]$^{4+}$ ([1a]$^{4+}$), in which two cis(S)-[Co(aet)$_2$(R,R-chxn)]$^+$ units are linked by a central Ni^{II} ion through sulfur bridges. The two Co^{III} units in [1a]$^{4+}$ uniformly adopt the Δ configuration, which is induced by the chirality of the terminal R,R-chxn ligands. The central Ni^{II} ion in [1a]$^{4+}$ was replaced by a Pd^{II} ion to produce an analogous Co^{III}Pd^{II}Co^{III} trinuclear complex, $\Delta_{RR}\Delta_{RR}$-[Pd{Co(aet)$_2$(R,R-chxn)}$_2$]$^{4+}$ ([2a]$^{4+}$), with retention of the Δ configuration. When racemic R,R/S,S-chxn was employed instead of R,R-chxn, not only the chirality about two Co^{III} centers but also the chirality about two chxn ligands was unified in the S-bridged trinuclear structure, leading to the selective formation of a pair of enantiomers, $\Delta_{RR}\Delta_{RR}$/$\Lambda_{SS}\Lambda_{SS}$-[M{Co(aet)$_2$(chxn)}$_2$]$^{4+}$ (M = Ni^{II} ([1b]$^{4+}$) and Pd^{II} ([2b]$^{4+}$)). The stereochemical and spectroscopic features of these complexes are discussed on the basis of the electronic absorption, CD, and NMR spectroscopies, along with the crystal structures of [1a]$^{4+}$ and [2a]$^{4+}$.

Introduction

The chiralselective synthesis of transition metal complexes has been a subject of considerable interest not only due to their significance in fundamental co-ordination chemistry but also due to their potential applications such as asymmetric catalysts and nonlinear optical materials.[1] Recent growing interest in this subject has been stimulated by the development of metallosupramolecular chemistry, in which chiral components existed in their building units play an important role in the creation of metallosupramolecular species with predetermined chiral structures.[2] We have been interested in this subject, focusing on the chiralselective construction of multinuclear and metallosupramolecular structures based on chiral octahedral complex-units with simple aminothiolate ligands such as 2-aminoethanethiolate (aet), L-cysteinate (L-cys), and D-penicillaminate (D-pen).[3] Previously, we showed that the reaction of [Ni(aet)$_2$] with [CoCl$_2$(en)$_2$]Cl (en = ethylenediamine) gives an S-bridged Co^{III}Ni^{II}Co^{III} trinuclear complex, [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$, which is converted to the corresponding Co^{III}Pd^{II}Co^{III} complex, [Pd{Co(aet)$_2$(en)}$_2$]$^{4+}$, by treatment with [PdCl$_4$]$^{2-}$.[4] In these trinuclear structures, two cis(S)-[Co(aet)$_2$(en)]$^+$ octahedral units that are linked by a square-planar Ni^{II} or Pd^{II} ion adopt the same chiral configuration (Δ or Λ) to form a pair of enantiomers ($\Delta\Delta$ and $\Lambda\Lambda$). Analogous S-bridged Co^{III}MCo^{III} trinuclear complexes,

[M{Co(aet)$_2$(R-pn)}$_2$]$^{4+}$ (R-pn = (R)-1,2-propanediamine), which contain (R)-1,2-propanediamine as the terminal non-bridging ligands, have also been synthesized by using [CoCl$_2$(R-pn)$_2$]Cl instead of [CoCl$_2$(en)$_2$]Cl.[5] Interestingly, X-ray analysis indicated that the isolated crystals for these R-pn Co^{III}MCo^{III} complexes have the $\Delta\Delta$ configuration. In this R-pn system, however, there exists syn-$anti$ geometrical isomerism, which arises from the relative arrangement of two terminal asymmetrical R-pn ligands, besides Δ-Λ enantio isomerism, and thus it remained unclear whether a single isomer with the $\Delta\Delta$ configuration is exclusively formed for [M{Co(aet)$_2$(R-pn)}$_2$]$^{4+}$. In this context, we further investigated the chiral behavior of this S-bridged Co^{III}MCo^{III} trinuclear system, introducing symmetrical R,R- or S,S-chxn ligands at the terminal. Herein we report on the synthesis, characterization and stereochemical properties of S-bridged Co^{III}MCo^{III} trinuclear complexes with R,R-chxn ligands, [M{Co(aet)$_2$(R,R-chxn)}$_2$]$^{4+}$ (M = Ni^{II}, Pd^{II}), along with their molecular structures (Scheme 1). The corresponding Co^{III}MCo^{III} complexes formed by the use of racemic R,R/S,S-chxn, which exhibit a remarkable chiralselectivity, are also reported.

Experimental

Preparation of the complexes

Starting complexes. The starting complexes, [Ni(aet)$_2$],[6] $trans$-[CoCl$_2$(R,R-chxn)$_2$]Cl,[7] and $trans$-[CoCl$_2$(rac-chxn)$_2$]Cl,[8] were prepared according to the methods described in the literature.

$\Delta_{RR}\Delta_{RR}$-[Ni{Co(aet)$_2$(R,R-chxn)}$_2$]X$_4$ ([1a]X$_4$; X = Cl, ClO$_4$). To a green suspension containing 5.4 g (0.026 mol) of [Ni(aet)$_2$] in 90 cm^3 of water was added 20.1 g (0.051 mol) of $trans$-[CoCl$_2$(R,R-chxn)$_2$]Cl. The mixture was stirred at room temperature for 2 h, during which time a red-brown powder ([1a]Cl$_4$) was precipitated.

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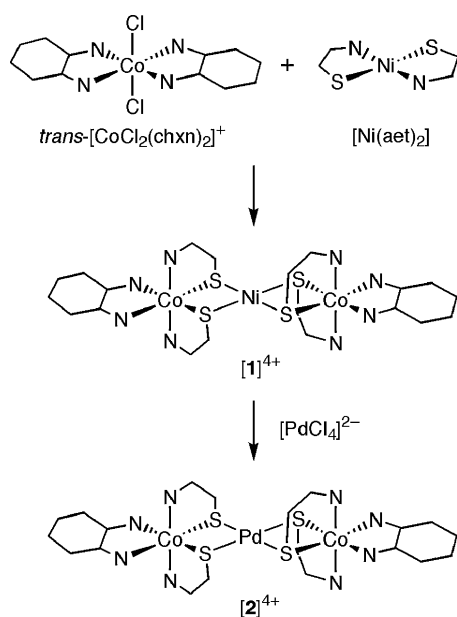
Scheme 1

This product was collected by filtration and recrystallized from water by adding a saturated aqueous solution of NaCl. Yield: 1.86 g (15%). Anal. Calcd. for [Ni{Co(aet)$_2$(R,R-chxn)}$_2$]Cl$_4$·6.5H$_2$O: C, 24.81; H, 6.77; N, 11.57%. Found: C, 24.79; H, 6.51; N, 11.46%. Molecular conductivity: 504.8 Ω^{-1} cm^2 mol^{-1}. δ_H (270 MHz, D$_2$O) 1.14 (CH_2 (chxn)), 1.35 (CH_2 (chxn)), 1.67 (CH_2 (chxn)), 1.73 (CH_2S (aet)), 2.12 (CH_2 (chxn)), 2.20 (CH_2 (chxn)), 2.47 (CH_2S (aet)), 3.70 (CH_2N (aet)), 4.34 (CH_2N (aet)); δ_C (270 MHz, D$_2$O) 26.30 (CH_2 (chxn)), 34.63 (CH_2S (aet)), 35.63 (CH_2 (chxn)), 55.76 (CH_2N (aet)), 62.13 (CH_2 (chxn)).

To a solution containing 0.50 g of [**1a**]Cl$_4$·6.5H$_2$O in 40 cm^3 of water was added 2.0 cm^3 of a saturated aqueous solution of NaClO$_4$, followed by allowing to stand in a refrigerator for 1 day. The resulting red-brown powder was collected by filtration and recrystallized from water by adding a saturated aqueous solution of NaClO$_4$. Yield: 0.37 g (63%). Anal. Calcd. for [Ni{Co(aet)$_2$(R,R-chxn)}$_2$](ClO$_4$)$_4$·1.5H$_2$O: C, 21.18; H, 4.89; N, 9.88%. Found: C, 21.09; H, 4.78; N, 9.70%.

$\Delta_{RR}\Delta_{RR}$/$\Lambda_{SS}\Lambda_{SS}$-[Ni{Co(aet)$_2$(*rac*-chxn)}$_2$]Cl$_4$ ([1b]Cl$_4$). To a green suspension containing 0.54 g (2.6 mmol) of [Ni(aet)$_2$] in 15 cm^3 of water was added 2.0 g (5.1 mmol) of *trans*-[CoCl$_2$(*rac*-chxn)$_2$]Cl. The mixture was stirred at room temperature for 2 h, during which time a brown powder ([**1b**]Cl$_4$) was precipitated. This product was collected by filtration and recrystallized from water by adding a saturated aqueous solution of NaCl. Yield: 0.13 g (10%). Anal. Calcd. for [Ni{Co(aet)$_2$(*rac*-chxn)}$_2$]Cl$_4$·5.5H$_2$O: C, 25.28; H, 6.68; N, 11.79%. Found: C, 25.28; H, 6.43; N, 11.91%. Molecular conductivity: 502.3 Ω^{-1} cm^2 mol^{-1}.

$\Delta_{RR}\Delta_{RR}$-[Pd{Co(aet)$_2$(R,R-chxn)}$_2$]X$_4$ ([2a]X$_4$; X = Cl, ClO$_4$). To a solution containing 0.10 g (0.10 mmol) of [**1a**]Cl$_4$·6.5H$_2$O in 25 cm^3 of water was added 0.030 g (0.10 mmol) of Na$_2$[PdCl$_4$] in 5 cm^3 of water. The mixture was stirred at 60 °C for 30 min. After cooling to room temperature, a saturated aqueous solution of NaCl was added to the red-brown reaction solution, followed

by allowing to stand in a refrigerator for 1 day. The resulting red-brown powder was collected by filtration and recrystallized from water by adding a saturated aqueous solution of NaCl. Yield: 0.04 g (35%). Anal. Calcd. for [Pd{Co(aet)$_2$(R,R-chxn)}$_2$]Cl$_4$·6H$_2$O: C, 23.85; H, 6.41; N, 11.13%. Found: C, 23.64; H, 6.32; N, 11.06%. Molecular conductivity: 492.6 Ω^{-1} cm^2 mol^{-1}. δ_H (270 MHz, D$_2$O) 1.15 (CH_2 (chxn)), 1.38 (CH_2 (chxn)), 1.68 (CH_2 (chxn)), 2.07 (CH_2S (aet)), 2.14 (CH_2 (chxn)), 2.24 (CH_2 (chxn)), 2.54 (CH_2S (aet)), 3.59 (CH_2N (aet)); δ_C (270 MHz, D$_2$O) 26.25 (CH_2 (chxn)), 35.50 (CH_2S (aet), CH_2 (chxn)), 56.01 (CH_2N (aet)), 62.11 (CH_2 (chxn)).

To a solution containing 0.50 g of [**1a**]Cl$_4$·6.5H$_2$O in 80 cm^3 of water was added 0.15 g (0.53 mmol) of (NH$_4$)$_2$[PdCl$_4$] in 20 cm^3 of water. The mixture solution was stirred at 60 °C for 30 min. After cooling to room temperature, a saturated aqueous solution of NaClO$_4$ was added to the red-brown reaction solution, followed by allowing to stand in a refrigerator for 1 day. The resulting red-brown powder was collected by filtration and recrystallized from water by adding a saturated aqueous solution of NaClO$_4$. Yield: 0.41 g (61%). Anal. Calcd for [Pd{Co(aet)$_2$(R,R-chxn)}$_2$](ClO$_4$)$_4$·H$_2$O: C, 20.48; H, 4.64; N, 9.55%. Found: C, 20.54; H, 4.57; N, 9.56%.

$\Delta_{RR}\Delta_{RR}$/$\Lambda_{SS}\Lambda_{SS}$-[Pd{Co(aet)$_2$(*rac*-chxn)}$_2$]Cl$_4$ ([2b]Cl$_4$). To a solution containing 0.10 g (0.10 mmol) of [**1b**]Cl$_4$·5.5H$_2$O in 25 cm^3 of water was added 0.030 g (0.10 mmol) of Na$_2$[PdCl$_4$] in 5 cm^3 of water. The mixture solution was stirred at 60 °C for 30 min. After cooling to room temperature, a saturated aqueous solution of NaCl was added to the red-brown reaction solution, followed by allowing to stand in a refrigerator for 1 day. The resulting red-brown powder was collected by filtration and recrystallized from water by adding a saturated aqueous solution of NaCl. Yield: 0.055 g (50%). Anal. Calcd. for [Pd{Co(aet)$_2$(*rac*-chxn)}$_2$]Cl$_4$·6H$_2$O: C, 23.85; H, 6.41; N, 11.13%. Found: C, 23.64; H, 6.32; N, 11.06%. Molecular conductivity: 518.3 Ω^{-1} cm^2 mol^{-1}.

Caution. Perchlorate salts are potentially explosive and should be carefully treated.

Physical measurements

The electronic absorption spectra were recorded with a JASCO Ubest-55 spectrophotometer, and the CD spectra with a JASCO J-700 spectropolarimeter at room temperature. The ^{13}C and ^{1}H NMR spectra were recorded with a JEOL EX-A270 NMR spectrometer at the probe temperature in D$_2$O. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference. The IR spectra were recorded with a JASCO FT/IR-5000 infrared spectrophotometer using KBr disks. The elemental analyses (C, H, N) were performed at Osaka University.

X-Ray structure determination

Crystallographic data for [**1a**](ClO$_4$)$_4$ and [**2a**](ClO$_4$)$_4$ are given in Table 1.

$\Delta_{RR}\Delta_{RR}$-[Ni{Co(aet)$_2$(R,R-chxn)}$_2$](ClO$_4$)$_4$·1.33H$_2$O ([1a]-(ClO$_4$)$_4$·1.33H$_2$O). A single-crystal X-ray diffraction experiment for $\Delta_{RR}\Delta_{RR}$-[Ni{Co(aet)$_2$(R,R-chxn)}$_2$](ClO$_4$)$_4$·1.33H$_2$O was preformed on a Bruker SMART APEX diffractometer with a graphite-monochromated Mo-Kα radiation. The intensity data

Table 1 Crystallographic data for [1a](ClO$_4$)$_4$ and [2a](ClO$_4$)$_4$

	[1a](ClO$_4$)$_4$·1.33H$_2$O	[2a](ClO$_4$)$_4$·1.33H$_2$O
Formula	C$_{20}$H$_{54.67}$Cl$_4$Co$_2$-N$_8$NiO$_{17.33}$S$_4$	C$_{20}$H$_{54.67}$Cl$_4$Co$_2$-N$_8$O$_{17.33}$PdS$_4$
M_r	1131.28	1179.02
Crystal system	Hexagonal	Hexagonal
Space group	$P6_3$	$P6_3$
a/Å	14.815(2)	14.936(4)
c/Å	34.618(7)	35.317(5)
V/Å^3	6580(2)	6824(2)
Z	6	6
T/K	100(2)	296(2)
D_c/g cm^{-3}	1.713	1.722
μ(Mo-Kα)/mm^{-1}	1.679	1.601
Refl. collected	30948	6236
Indep. refl.	5740	5470
R_{int}	0.1017	0.0676
Flack parameter	0.00(5)	0.05(5)
R1 ($I > 2\sigma(I)$)^a	0.0684	0.0562
wR2 (all data)^b	0.1663	0.1891

^{a} $R1 = \sum ||F_o| - |F_c||/\sum(|F_o|)$. ^{b} $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

were collected by the ω–2θ scan mode up to $2\theta = 46°$. The data integration and reduction were undertaken with SAINT and XPREP. An empirical absorption correction determined with SADABS was applied to each data set. The 5740 independent reflections with $I > 2\sigma(I)$ of the measured 30948 reflections were considered as observed and used for structure determination. [1a](ClO$_4$)$_4$·1.33H$_2$O occurred as twin crystals to contain two microdomains, and the twin law was 0 1 0, 1 0 0, 0 0 −1. One major component was contained, as indicated by the batch scale factor (BASF) of 0.23. The structure was solved by a direct method using SIR97[9] and refined on F^2 with all independent reflections by full-matrix least-squares method as using SHELXL-97 program.[10] The Ni, Co and S atoms were refined anisotropically, while the other atoms were refined isotropically. Some perchlorate anions were refined with the restrained geometrical parameters (Cl–O = 1.4 Å and O–O = 2.29 Å). H atoms were included in calculated positions except those of water molecules.

$\Delta_{RR}\Delta_{RR}$-[Pd{Co(aet)$_2$(R,R-chxn)}$_2$](ClO$_4$)$_4$·1.33H$_2$O ([2a]-(ClO$_4$)$_4$·1.33H$_2$O). A single-crystal X-ray diffraction experiment for $\Delta_{RR}\Delta_{RR}$-[Pd{Co(aet)$_2$(R,R-chxn)}$_2$](ClO$_4$)$_4$·1.33H$_2$O was preformed on Rigaku AFC7R four-circle diffractometer with a graphite-monochromated Mo-Kα radiation. The intensity data were collected by the ω–2θ scan mode up to $2\theta = 55°$. An empirical absorption correction based on a series of ψ scans was also applied. The 5470 independent reflections with $I > 2\sigma(I)$ of the measured 6236 reflections were considered as observed and used for structure determination. The structure was solved by a Patterson method using DIRDIF99 (PATTY) program[11] and refined on F^2 with all independent reflections by full-matrix least-squares methods as using SHELXL-97 program.[10] All non-hydrogen atoms except for the oxygen atoms of the disordered perchlorate anions were refined anisotropically. Some perchlorate anions were refined with the restrained geometrical parameters (Cl–O = 1.4 Å and O–O = 2.29 Å). H atoms were included in calculated positions except those of water molecules.

Results and discussion

Synthesis and characterization

Treatment of [Ni(aet)$_2$] with 2 molar equiv. of *trans*-[CoCl$_2$(R,R-chxn)$_2$]Cl in water under a mild condition gave a dark brown solution, from which a dark brown complex, [1a]X$_4$(X = Cl, ClO$_4$), was isolated by adding an aqueous solution of NaX.[12] X-Ray fluorescence spectrometry indicated the presence of Ni and Co atoms in [1a]X$_4$, and its elemental analysis was in good agreement with the formula for [Ni{Co(aet)$_2$(chxn)}$_2$]X$_4$. Single-crystal X-ray analysis of [1a](ClO$_4$)$_4$ demonstrated that [1a]$^{4+}$ has an expected S-bridged Co^{III}Ni^{II}Co^{III} trinuclear structure consisting of two *cis*(S)-[Co(aet)$_2$(R,R-chxn)]$^+$ units that are linked by a Ni^{II} ion (*vide infra*). Considering the Δ and Λ chiral configurations of each Co^{III} center bound by a R,R-chxn ligand, three isomers ($\Delta_{RR}\Delta_{RR}$, $\Delta_{RR}\Lambda_{RR}$ and $\Lambda_{RR}\Lambda_{RR}$) are possible for [Ni{Co(aet)$_2$(R,R-chxn)}$_2$]$^{4+}$. In the crystal structure of [1a]$^{4+}$, both the two units adopt the Δ_{RR} configuration to give only the $\Delta_{RR}\Delta_{RR}$ isomer. The ^{13}C NMR spectrum of a bulk sample of [1a]$^{4+}$ exhibits a single set of signals due to four aet and two R,R-chxn ligands in the complex (Fig. 1(a)). From these results, it is considered that only the $\Delta_{RR}\Delta_{RR}$ isomer with a molecular D_2 symmetry is formed for [1a]$^{4+}$, although the selective formation of the $\Delta_{RR}\Delta_{RR}$ isomer was not confirmed by a cation-exchange SP-Sephadex C-25 column chromatography due to its decomposition in the column. As shown in Fig. 2, the electronic absorption spectrum of [1a]$^{4+}$ in water is characterized by three intense bands at 27.62×10^3, 36.83×10^3 and 41.49×10^3 cm^{-1}. This absorption spectral feature is the same as that of the corresponding S-bridged Co^{III}Ni^{II}Co^{III} trinuclear complex with en ligands, [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ (Fig. S1, ESI†).[4a] In addition, the CD spectrum of [1a]$^{4+}$ is very similar to that of $\Delta\Delta$-[Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$, which is indicative of the minor CD contribution from the terminal R,R-chxn ligands.
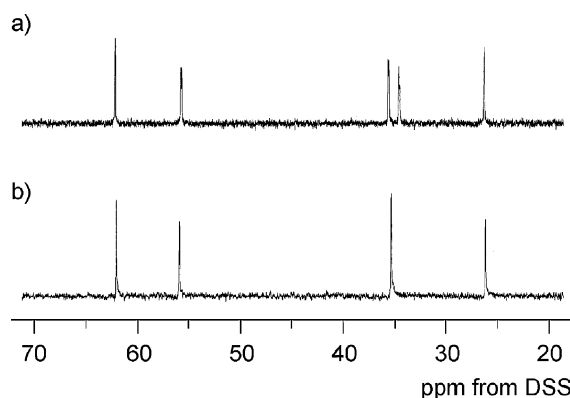
Fig. 1 ^{13}C NMR spectra of (a) [1a]$^{4+}$ and (b) [2a]$^{4+}$ in D$_2$O.

When an aqueous solution of [1a]Cl$_4$ was treated with 1 molar equiv. of Na$_2$[PdCl$_4$], a red-brown powder of [2a]X$_4$ (X = Cl, ClO$_4$) that contains Pd and Co atoms was obtained from the reaction solution by adding an aqueous solution of NaX. The elemental analysis of [2a]X$_4$ was consistent with the formula of [Pd{Co(aet)$_2$(chxn)}$_2$]X$_4$, and its S-bridged Co^{III}Pd^{II}Co^{III} trinuclear structure composed of two *cis*(S)-[Co(aet)$_2$-(R,R-chxn)]$^+$ units with the Δ_{RR} configuration was established by X-ray analysis (*vide infra*). As in the case of the parental [1a]$^{4+}$,

Fig. 2 Electronic absorption and CD spectra of [**1a**]$^{4+}$ (—) and [**2a**]$^{4+}$ (---) in water.

the ^{13}C NMR spectrum of [**2a**]$^{4+}$ exhibits a single set of signals due to four aet and two R,R-chxn ligands in the complex (Fig. 1(b)). This is ind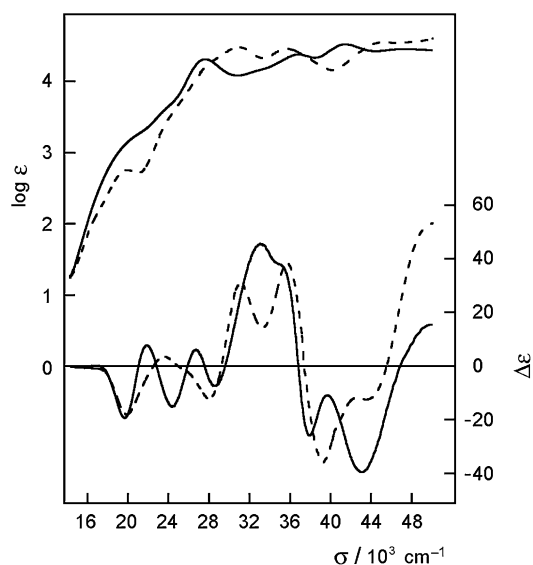icative of the selective formation of the $\Delta_{RR}\Delta_{RR}$ isomer having a molecular D_2 symmetry. The selective formation is confirmed by an SP-Sephadex C-25 column chromatography of the reaction solution; a single brown band was eluted with a 0.5 M NaCl aqueous solution and all the fractions of the eluate showed absorption and CD spectra identical with those of [**2a**]$^{4+}$. The absorption and CD spectra of [**2a**]$^{4+}$ in water are very similar to those of the corresponding trinuclear complex with en ligands, $\Delta\Delta$-[Pd{Co(aet)$_2$(en)}$_2$]$^{4+}$, over the whole region (Fig. S2, ESI†),[4b] which supports the Co^{III}Pd^{II}Co^{III} trinuclear structure with the $\Delta_{RR}\Delta_{RR}$ configuration.

As expected, similar treatment of [Ni(aet)$_2$] with *trans*-[CoCl$_2$($R,R/S,S$-chxn)$_2$]$^+$, instead of *trans*-[CoCl$_2$(R,R-chxn)$_2$]$^+$, followed by the addition of an aqueous solution of NaCl, also gave a red-brown powder ([**1b**]Cl$_4$), X-ray fluorescence and elemental analyses of which were consistent with the formula of [Ni{Co(aet)$_2$(chxn)}$_2$]Cl$_4$. The electronic absorption spectrum of [**1b**]Cl$_4$ is identical with that of [**1a**]Cl$_4$ over the whole region. This indicates that [**1b**]$^{4+}$ has the same S-bridged Co^{III}Ni^{II}Co^{III} trinuclear structure as that found in [**1a**]$^{4+}$. Considering the R,R and S,S configurations of each chxn ligand and the Δ and Λ configurations of each Co^{III} center, 10 isomers ($\Delta_{RR}\Delta_{RR}$, $\Delta_{RR}\Delta_{SS}$, $\Delta_{SS}\Delta_{SS}$, $\Delta_{RR}\Lambda_{RR}$, $\Delta_{RR}\Lambda_{SS}$, $\Delta_{SS}\Lambda_{RR}$, $\Delta_{SS}\Lambda_{SS}$, $\Lambda_{RR}\Lambda_{RR}$, $\Lambda_{RR}\Lambda_{SS}$, $\Lambda_{SS}\Lambda_{SS}$) are possible for [Ni{Co(aet)$_2$($R,R/S,S$-chxn)}$_2$]$^{4+}$. Notably, the ^{13}C NMR spectrum of [**1b**]$^{4+}$ exhibits only a single set of five signals, and furthermore the chemical shifts of the signals for [**1b**]$^{4+}$ are the same as those for [**1a**]$^{4+}$. Thus, it is considered that [**1b**]$^{4+}$ contains only a pair of enantiomers, $\Delta_{RR}\Delta_{RR}$ and $\Lambda_{SS}\Lambda_{SS}$. Unfortunately, the selective formation of the $\Delta_{RR}\Delta_{RR}$ and $\Lambda_{SS}\Lambda_{SS}$ isomers was not determined by an SP-Sephadex C-25 column chromatography due to the decomposition in the column.

To determine the selective formation of the isomers, an aqueous solution of [**1b**]$^{4+}$ was treated with one molar equiv. of Na$_2$[PdCl$_4$] to obtain the corresponding Co^{III}Pd^{II}Co^{III} trinuclear complex ([**2b**]$^{4+}$), which is expected to be stable enough for column

chromatographic separation. When the reaction solution was poured onto an SP-Sephadex C-25 column, only one brown band was eluted with a 0.50 M aqueous solution of NaCl, and the electronic absorption spectrum of its eluate was identical with that of [**2a**]$^{4+}$. In addition, the brown band was separated into two bands, which show CD spectra enantiomeric to each other, on eluting with a 0.25 M aqueous solution of Na$_2$[Sb$_2$(R,R-tartrato)$_2$]. From these results and that the CD spectrum of the first moving band is identical with that of [**2a**]$^{4+}$, it is evidenced that only a pair of enantiomers, $\Delta_{RR}\Delta_{RR}$ and $\Lambda_{SS}\Lambda_{SS}$, is formed for [**2b**]$^{4+}$. An analytical pure solid sample of [**2b**]$^{4+}$ was successfully isolated from the reaction solution as the chloride salt by adding an aqueous NaCl solution. The ^{13}C NMR spectrum of [**2b**]$^{4+}$ is identical with that of [**2a**]$^{4+}$, which also supports the selective formation of a pair of enantiomers, $\Delta_{RR}\Delta_{RR}$ and $\Lambda_{SS}\Lambda_{SS}$.

Crystal structures of [1a](ClO$_4$)$_4$ and [2a](ClO$_4$)$_4$

Single-crystal X-ray analysis of [**1a**](ClO$_4$)$_4$ revealed the presence of a discrete complex cation, perchlorate anions, and water molecules. The number of perchlorate anions implies that the entire complex cation is tetravalent. A perspective drawing of the complex cation [**1a**]$^{4+}$ is shown in Fig. 3(a), and its selected bond distances and angles are listed in Table 2. The entire complex cation [**1a**]$^{4+}$ consists of two [Co(aet)$_2$(R,R-chxn)]$^+$ units and one Ni^{II} atom. The two S atoms of each *cis*(S)-[Co(aet)$_2$(R,R-chxn)]$^+$ unit are bound to the central Ni^{II} atom to form a linear-type S-bridged Co^{III}Ni^{II}Co^{III} trinuclear structure in [Ni{Co(aet)$_2$(R,R-chxn)}$_2$]$^{4+}$ (Co1–Ni1–Co2 = 178.60(11)°, Co1–Ni1 = 3.249(4), Co2–Ni1 = 3.228(4) Å). Each Co^{III} atom is octahedrally coordinated by two aet S and two R,R-chxn N atoms at the equatorial positions and two aet N atoms at the apical positions to have a C_2 symmetrical *cis*(S) geometry (av. Co–N$_{aet}$ = 1.976(13), Co–N$_{chxn}$ = 1.996(14) and Co–S = 2.235(5) Å). The chiral configuration about each Co^{III} center bound by R,R-chxn ligand is Δ, and only the $\Delta_{RR}\Delta_{RR}$ isomer exists in crystal [**1a**]$^{4+}$. All three chelate rings in each *cis*(S)-[Co(aet)$_2$(R,R-chxn)]$^+$ unit adopt the λ conformation to give a thermodynamically stable (*lel*)$_3$ form.[13] In addition, all the four bridging S atoms in [**1a**]$^{4+}$ are fixed to have the R configuration to give only the $(\Delta_{RR})_2(R)_4$ isomer. The central NiS$_4$ sphere is
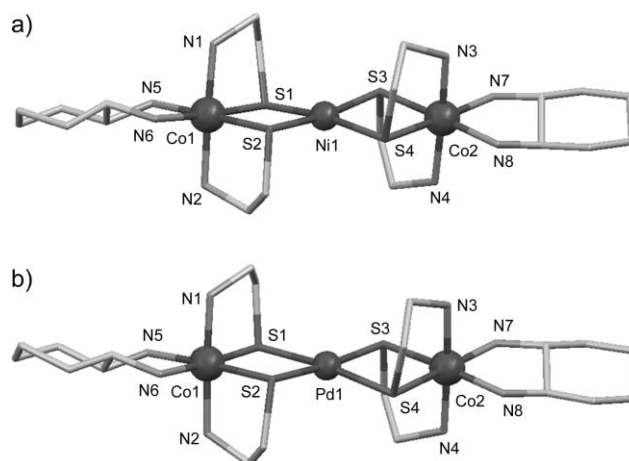

Fig. 3 Perspective view of (a) [**1a**]$^{4+}$ and (b) [**2a**]$^{4+}$ with the atomic labeling scheme. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond distances (Å) and angles (°) for [**1a**](ClO₄)₄ and [**2a**](ClO₄)₄

	[**1a**](ClO₄)₄	[**2a**](ClO₄)₄
M1–S1[a]	2.201(5)	2.317(5)
M1–S2[a]	2.200(6)	2.338(4)
M1–S3[a]	2.186(5)	2.315(4)
M1–S4[a]	2.193(5)	2.318(4)
Co1–S1	2.214(5)	2.256(5)
Co1–S2	2.245(5)	2.254(5)
Co1–N1	1.989(11)	1.983(12)
Co1–N2	1.954(12)	1.964(12)
Co1–N5	2.003(11)	1.995(13)
Co1–N6	1.968(11)	2.031(12)
Co2–S3	2.230(5)	2.234(4)
Co2–S4	2.251(5)	2.266(4)
Co2–N3	1.961(13)	1.992(11)
Co2–N4	1.999(13)	1.983(12)
Co2–N7	1.998(12)	1.974(11)
Co2–N8	2.015(14)	1.968(10)
S1–M1–S2[a]	86.3(2)	84.46(16)
S3–M1–S4[a]	87.6(2)	84.20(15)
S1–Co1–S2	84.87(18)	87.84(17)
S1–Co1–N1	88.3(4)	87.2(4)
S2–Co1–N2	86.4(4)	87.6(4)
N5–Co1–N6	84.1(5)	84.4(5)
S3–Co2–S4	85.14(18)	87.30(15)
S3–Co2–N3	91.0(4)	87.1(4)
S4–Co2–N4	89.5(4)	86.8(4)
N7–Co2–N8	84.8(6)	84.4(4)
M1–S1–Co1[a]	94.75(17)	94.07(15)
M1–S2–Co1[a]	93.93(18)	93.56(15)
M1–S3–Co2[a]	93.93(17)	94.60(14)
M1–S4–Co2[a]	93.17(18)	93.66(15)

[a] M = Ni ([**1a**](ClO₄)₄) and Pd ([**2a**](ClO₄)₄).

slightly distorted from square-planar to tetrahedral geometry, in which the dihedral angle between the S1–Ni1–S2 and S3–Ni1–S4 planes is 13.2(3)°. A similar distortion has been observed for [Ni{Co(aet)₂(en)}₂]Cl₄ (dihedral angle 16.2°),[4a] and it has been pointed out that this distortion allows the methylene protons of the aet chelate rings not to be located at the apical positions of the central metal atom. The averaged Ni–S bond distance in [**1a**]⁴⁺ is 2.195(6) Å, which is comparable well with that in [Ni{Co(aet)₂(en)}₂]Cl₄ (2.204(1) Å).

The crystal structure of [**2a**](ClO₄)₄ was also determined by X-ray analysis, which revealed that [**2a**](ClO₄)₄ is isostructural with [**1a**](ClO₄)₄. Thus, the overall structure of [**2a**]⁴⁺ is essentially the same as that of [**1a**]⁴⁺ (Fig. 3(b)), except the presence of Pd^II atom in place of Ni^II atom (Co1–Pd1–Co2 = 178.68(7)°, Co1–Pd1 = 3.347(3), Co2–Pd1 = 3.344(3) Å). As in the case of [**1a**]⁴⁺, [**2a**]⁴⁺ contains only a single isomer with the $\Delta_{RR}\Delta_{RR}$ configuration, in which all the chelate rings and the bridging S atoms have the λ conformation and the R configuration, respectively. The averaged Co–N_aet (1.981(12) Å), Co–N_chxn (1.992(13) Å) and Co–S (2.253(5) Å) bond distances in [**2a**]⁴⁺ are very similar to those in [**1a**]⁴⁺. The Pd–S bonds (av. 2.322(5) Å) in [**2a**]⁴⁺ are longer than those of the Ni–S bonds in [**1a**]⁴⁺, and the dihedral angle of the central PdS₄ sphere in [**2a**]⁴⁺ (9.6(2)°) is smaller than that of the NiS₄ sphere in [**1a**]⁴⁺. A similar trend has been found in the analogous Co^IIIMCo^III trinuclear system with en ligands, [M{Co(aet)₂(en)}₂]⁴⁺ (M = Ni^II, Pd^II).[4]

Chiralselectivity for [M{Co(aet)₂(chxn)}₂]⁴⁺

In a previous study, it was shown that the racemic ($\Delta\Delta/\Lambda\Lambda$) isomer is exclusively formed for the S-bridged trinuclear complexes with en ligands, [M{Co(aet)₂(en)}₂]⁴⁺ (M = Ni^II, Pd^II), which has been ascribed to an unfavorable non-bonding interaction between aet chelate rings from two $cis(S)$-[Co(aet)₂(en)]⁺ units existed in the meso ($\Delta\Lambda$) isomer.[4] Taking account of this fact, the formation of the $\Delta_{RR}\Delta_{RR}$ and $\Lambda_{RR}\Lambda_{RR}$ isomers is anticipated for [Ni{Co(aet)₂(R,R-chxn)}₂]⁴⁺. However, [**1a**]⁴⁺ was found to contain only the $\Delta_{RR}\Delta_{RR}$ isomer. Furthermore, the metal replacement reaction of [**1a**]⁴⁺ with Pd^II produced [**2a**]⁴⁺ that contains only the $\Delta_{RR}\Delta_{RR}$ isomer of [Pd{Co(aet)₂(R,R-chxn)}₂]⁴⁺. A similar replacement reaction of $\Delta\Delta$-[Ni{Co(aet)₂(en)}₂]⁴⁺ with Pd^II has been shown to give a mixture of the $\Delta\Delta$ and $\Lambda\Lambda$ isomers, accompanied by the racemization of $cis(S)$-[Co(aet)₂(en)]⁺ units.[4b] Thus, the introduction of R,R-chxn ligands at the terminal of the trinuclear structure, in place of en ligands, resulted in the selective formation and the stabilization of the Δ configurational $cis(S)$-[Co(aet)₂(R,R-chxn)]⁺ units. It has been recognized that the R,R-chxn ligand forms a rigid five-membered chelate ring with the λ conformation, which induces the preferential formation of the Δ isomer so as to adopt the thermodynamically favorable lel conformation.[13] However, the selective formation of the Δ isomer has rarely been recognized for mononuclear cobalt(III) complexes even when they possess two or three R,R-chxn ligands.[14] Unlike in the mononuclear system, the conformation of the aet ligands are locked in the present trinuclear system, because each S atom bridges two metal centers to fix its tetrahedral orientation. Molecular model examinations reveal that there exists an unfavorable non-bonding interaction between methylene protons of aet ligand and amine protons of R,R-chxn ligand in [M{Co(aet)₂(R,R-chxn)}₂]⁴⁺ when each aet ligand adopts the δ conformation. For this reason, two bridging aet ligands are forced to have the λ conformation, as well as the R,R-chxn ligand, leading to the selective formation of the Δ configurational $cis(S)$-[Co(aet)₂(R,R-chxn)]⁺ units with a substantially stable $(lel)_3$ form.

More interestingly, only a pair of enantiomers, $\Delta_{RR}\Delta_{RR}$ and $\Lambda_{SS}\Lambda_{SS}$, was produced for [Ni{Co(aet)₂(chxn)}₂]⁴⁺ and [Pd{Co(aet)₂(chxn)}₂]⁴⁺ when racemic $R,R/S,S$-chxn was employed instead of R,R-chxn. This result clearly indicates that not only the chirality of two $cis(S)$-[Co(aet)₂(chxn)]⁺ units, but also the chirality of two chxn ligands located at the terminal of the structure is unified in this S-bridged trinuclear system. Of ten isomers possible for [M{Co(aet)₂(chxn)}₂]⁴⁺ ($\Delta_{RR}\Delta_{RR}$, $\Delta_{RR}\Delta_{SS}$, $\Delta_{SS}\Delta_{SS}$, $\Delta_{RR}\Lambda_{RR}$, $\Delta_{RR}\Lambda_{SS}$, $\Delta_{SS}\Lambda_{RR}$, $\Delta_{SS}\Lambda_{SS}$, $\Lambda_{RR}\Lambda_{RR}$, $\Lambda_{RR}\Lambda_{SS}$, $\Lambda_{SS}\Lambda_{SS}$), the isomers with Δ_{SS} or Λ_{RR} configurational Co^III unit is excluded to be formed due to the Δ_{RR}/Λ_{SS} selectivity as described above. In addition, the $\Delta\Lambda$-type isomers are also excluded in this trinuclear system due to the unfavorable non-bonding interaction between two Co^III units with the opposite configurations. Thus, the Δ_{RR}/Λ_{SS} selectivity in combination with the $\Delta\Delta/\Lambda\Lambda$ selectivity leads to the selective formation of the $\Delta_{RR}\Delta_{RR}$ and $\Lambda_{SS}\Lambda_{SS}$ isomers for [M{Co(aet)₂(chxn)}₂]⁴⁺.

Conclusion

In this study, we have prepared the S-bridged Co^IIINi^IICo^III trinuclear complex having R,R-chxn ligands at the terminal,

$[Ni\{Co(aet)_2(R,R\text{-chxn})\}_2]^{4+}$, by the reaction of $[Ni(aet)_2]$ and *trans*-$[CoCl_2(R,R\text{-chxn})_2]^+$, which were converted to the corresponding $Co^{III}Pd^{II}Co^{III}$ trinuclear complex, $[Pd\{Co(aet)_2(R,R\text{-chxn})\}_2]^{4+}$, by the metal replacement reaction with Pd^{II}. Notably, both the trinuclear complexes gave only a single optically active isomer with the $\Delta_{RR}\Delta_{RR}$ configuration. This result indicates that the chirality of two terminal coligands, which are not involved in the S-bridged core structure, could regulate the chirality of the whole structure. Furthermore, only a pair of enantiomers, $\Delta_{RR}\Delta_{RR}/\Lambda_{SS}\Lambda_{SS}$, was selectively produced for $[Ni\{Co(aet)_2(chxn)\}_2]^{4+}$ and $[Pd\{Co(aet)_2(chxn)\}_2]^{4+}$ when racemic $R,R/S,S$-chxn was employed instead of R,R-chxn. Thus, the chirality of terminal coligands is in reverse regulated by the S-bridged structure so as to adopt the same chiral configuration. The conformational locking of aet ligands in the S-bridged structure and the conformational rigidity of chxn ligands, together with the homochiral linkage of two octahedral units, are key to the excellent chiral selectivity of this trinuclear system. Finally, the present results would provide valuable insight into the design and creation of polynuclear systems that selectively produce a single optically active isomer.

Acknowledgements

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