Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 156–165
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

# Rational synthesis of hexanuclear metallacycles by alkylation reactions of an S-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear complex containing non-binding thiolato groups

Yu Chikamoto, Nobuto Yoshinari, Tatsuya Kawamoto, Takumi Konno *

*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*

Received 28 February 2006; received in revised form 8 April 2006; accepted 18 April 2006
Available online 30 August 2006

**Abstract**

The reaction of an S-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear complex containing two non-bridging thiolato groups, $[Pd\{Co(aet)_3\}_2]^{2+}$ (aet = 2-aminoethanethiolate), with *o*-dibromoxylene (*o*-xyl$Br_2$) in water produced a cyclic $Co^{III}{}_4Pd^{II}{}_2$ hexanuclear complex, $[\{Co_2Pd(aet)_4\}_2(o\text{-}L)_2]^{8+}$ ($[\mathbf{1}]^{8+}$; *o*-L = *o*-bis(2-aminoethylthiomethyl)benzene), in which two $Co^{III}Pd^{II}Co^{III}$ trinuclear units are linked by two *o*-$xyl^{2+}$ moieties through C–S bonds. A similar cyclic $Co^{III}{}_4Pd^{II}{}_2$ complex, $[\{Co_2Pd(aet)_4\}_2(m\text{-}L)_2]^{8+}$ ($[\mathbf{2}]^{8+}$; *m*-L = *m*-bis(2-aminoethylthiomethyl)benzene), bearing a relatively large cavity that accommodates water molecule(s), was synthesized by the reaction of $[Pd\{Co(aet)_3\}_2]^{2+}$ with *m*-dibromoxylene (*m*-xyl$Br_2$) in water. While $[\mathbf{1}]^{8+}$ afforded only the *racemic* ($\Delta_4/\Lambda_4$) isomer, both the *racemic* ($[\mathbf{2a}]^{8+}$; $\Delta_4/\Lambda_4$) and the *meso* ($[\mathbf{2b}]^{8+}$; $\Delta_2\Lambda_2$) isomers were formed for $[\mathbf{2}]^{8+}$. In addition, the *meso* $[\mathbf{2b}]^{8+}$ was found to exist as a mixture of two diastereomers, $(\Delta_S)_2(\Lambda_R)_2$ and $(\Delta_S\Delta_R)(\Lambda_R\Lambda_S)$, which arise from the difference in chiral configurations (*R* and *S*) of asymmetric sulfide S atoms, while the *racemic* $[\mathbf{1}]^{8+}$ and $[\mathbf{2a}]^{8+}$ existed as a pair of enantiomers, $(\Delta_S)_4$ and$(\Lambda_R)_4$, which were optically resolved. The complexes obtained were characterized on the basis of electronic absorption, CD, and NMR spectroscopies, along with single crystal X-ray analyses.


*Keywords:* Palladium(II); Cobalt(III); Alkylation reaction; Sulfur-containing ligand; C–S bond formation

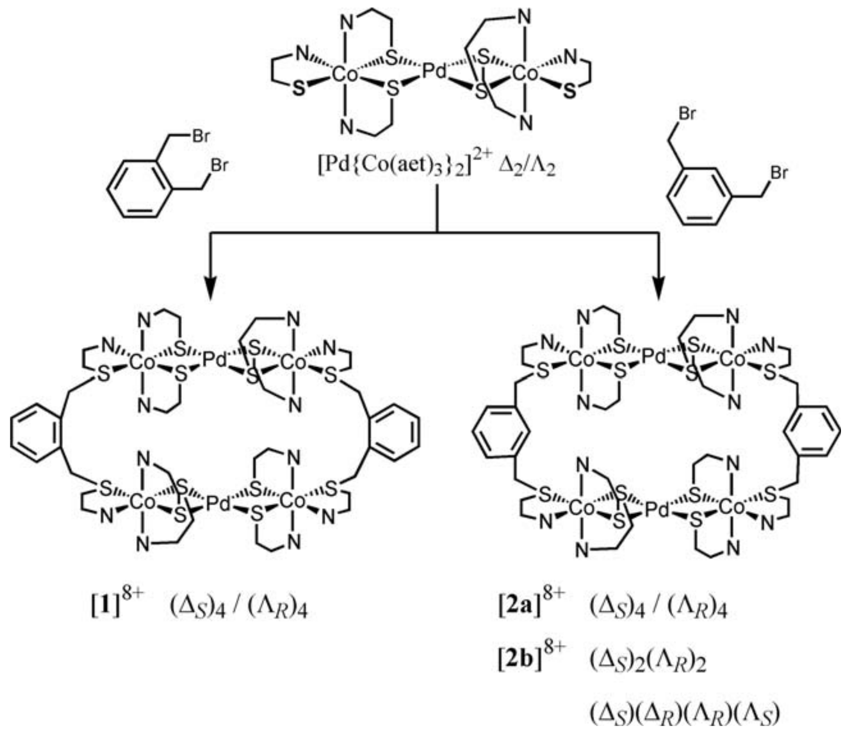
## 1. Introduction

The design and synthesis of molecular assembled compounds have received intense attention, because of the structural diversity, stereoselective aggregation, and characteristic properties based on their unique frameworks [1–12]. In particular, current interest has been devoted to the creation of ring- or cage-shaped metalloaggregates in relation to the development of supramolecular chemistry and host–guest chemistry [5–12]. In most cases, ring- or cage-shaped structures have been constructed from the self-assembly of well-designed organic compounds in combination with transition metal ions through coordination bonds. On the other hand, the use of covalent bonds, such as C–C and C–S, for the construction of ring- or cage-shaped metalloaggregates is little investigated, despite its advantage in forming rigid frameworks that are resistant to external influences.

It has been recognized that thiolato groups coordinated to a transition metal center possess a relatively high nucleophilicity, which results in the formation of C–S bonds by alkylation reactions [13–15]. In fact, a number of metal complexes with sulfide ligands have been derived from thiolato complexes by treatment with alkyl halides or alkyl sulfate [13–20]. Recently, we have shown that two non-bridging thiolato groups in an S-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear complex, $[Pd\{Co(aet)_3\}_2]^{2+}$, which selectively forms a *racemic*-*syn* isomer [21,22], are readily alkylated by benzyl bromide to produce $[Pd\{Co(aet)_2(bztea)\}_2]^{4+}$

* Corresponding author.
*E-mail address:* konno@ch.wani.osaka-u.ac.jp (T. Konno).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.08.059




Scheme 1.

(bztea = benzyl-2-thioethylamine), retaining the *racemic-syn* configuration of the trinuclear structure, although the corresponding reaction with methyl iodide or dimethyl sulfate is accompanied by the *syn*-to-*anti* isomerization [23]. Thus, it is expected that the use of dibromoxylene, instead of benzyl bromide, would lead to the production of some cyclic metalloaggregates, in which the $[Pd\{Co(aet)_3\}_2]^{2+}$ cations are linked by xylene fragments through C–S bonds.

In this paper, we report on the synthesis and characterization of a new class of cyclic metalloaggregates, which are formed by the reactions of $[Pd\{Co(aet)_3\}_2]^{2+}$ with dibromoxylene in aqueous media (Scheme 1). Notable differences in the cavity size and the stereochemistry of cyclic metalloaggregates, which is caused by the change of geometrical isomerism (*ortho* vs. *meta*) of dibromoxylene, is also reported, along with their molecular structures determined by single-crystal X-ray analyses.

## 2. Results and discussion

### 2.1. Synthesis and characterization of $[\{Co_2Pd(aet)_4\}_2(\textbf{o}\text{-}L)_2]^{8+}$ ($[\mathbf{1}]^{8+}$)

Treatment of a dark brown aqueous solution of $[Pd\{Co(aet)_3\}_2]^{2+}$, which has two non-bridging thiolato groups at the terminal [22], with *o*-dibromoxylene (*o*-xylBr$_2$) in a 1:1 ratio gave a dark-red solution. When the reaction solution was chromatographed on an SP-Sephadex C-25 column, only one red-brown band was eluted with a 1.0 mol dm$^{-3}$ NaCl aqueous solution. From the red-brown eluate, a red-brown compound ($[\mathbf{1}]^{8+}$) was isolated as the chloride salt. As expected, X-ray fluorescence spectrometry of $[\mathbf{1}]Cl_8$ revealed the presence of Co and Pd atoms in a 2:1, and its elemental analytical result is consistent with the formula for a 1:1 adduct of $[Pd\{Co(aet)_3\}_2]^{2+}$ and *o*-xyl$^{2+}$. The electronic absorption spectrum of $[\mathbf{1}]Cl_8$ in water is characterized by a visible band at ca. $20 \times 10^3$ cm$^{-1}$ with a shoulder at the lower energy side and an intense near-UV band at *ca.* $30 \times 10^3$ cm$^{-1}$ with shoulders at the lower and higher energy sides (Fig. 1 and Table 1). This absorption spectrum coincides well with that of 2 mol of $[Pd\{Co(aet)_2(bztea)\}_2]^{4+}$ (bztea = benzyl-2-thioethylamine), in which two non-bridging S atoms for $[Pd\{Co(aet)_3\}_2]^{2+}$ is bound by benzyl groups [23]. Furthermore, the $^{13}$C NMR spectrum of $[\mathbf{1}]^{8+}$ in $D_2O$ showed aromatic carbon signals in the region $\delta$ 132–137, besides methylene carbon signals in the region $\delta$ 35–58. These results indicate that $[Pd\{Co(aet)_3\}_2]^{2+}$ and *o*-xyl$^{2+}$ are connected through C–S bonds in a 1:1 ratio in $[\mathbf{1}]^{8+}$. The cyclic $Co^{III}{}_4Pd^{II}{}_2$ hexanuclear structure of $[\mathbf{1}]^{8+}$ ($[\{Co_2Pd(aet)_4\}_2(o\text{-}L)_2]^{8+}$) that is composed of two $Co^{III}Pd^{II}Co^{III}$ trinuclear units and two *o*-xyl$^{2+}$ moieties was established by X-ray analysis for $[\mathbf{1}](ClO_4)(NO_3)_7$ (vide infra).

Complex $[\mathbf{1}]^{8+}$ was optically resolved into the $(+)^{CD}_{520}$ and $(-)^{CD}_{520}$ isomers, which show CD spectra enantiomeric to each other, by an SP-Sephadex C-25 column chromatography using a 0.5 mol dm$^{-3}$ $[Sb_2(R,R\text{-tartrato})_2]^{2-}$ aqueous solution as an eluent. This is consistent with the X-ray analytical result of $[\mathbf{1}]^{8+}$, which indicated the presence of a pair of enantiomers, $\Delta_4$ and $\Lambda_4$. The entire CD spectral pattern of the $(+)^{CD}_{520}$ isomer of $[\mathbf{1}]^{8+}$ resembles that of the $\Lambda_2$ isomer of $[Pd\{Co(aet)_2(bztea)\}_2]^{4+}$ (Fig. 1). This suggests

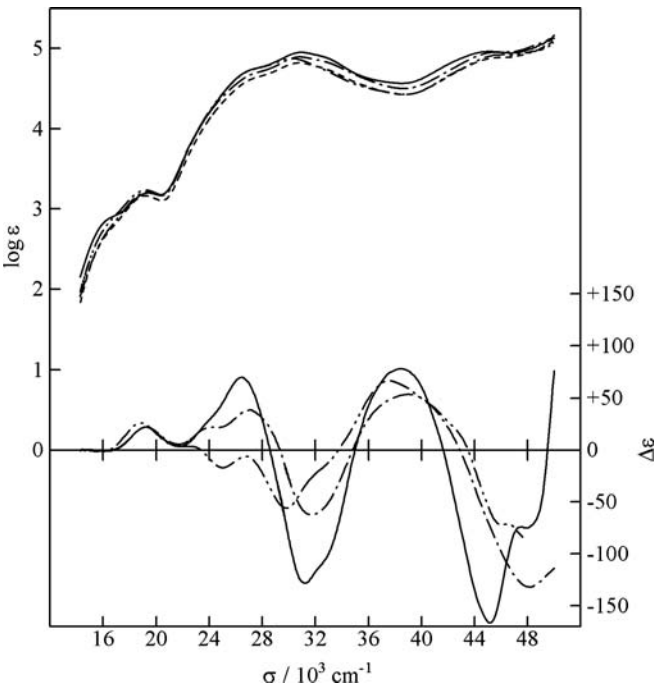



Fig. 1. Absorption and CD spectra of $(+)^{CD}_{520}$-$\Lambda_4$-[**1**]$^{8+}$ (—), $(+)^{CD}_{520}$-$\Lambda_4$-[**2a**]$^{8+}$ (-·-), [**2b**]$^{8+}$ (---), and $(+)^{CD}_{560}$-[Pd{Co(aet)$_2$(bztea)}$_2$]$^{4+}$ × 2 (-···-) in $H_2O$.

that $(+)^{CD}_{520}$-[**1**]$^{8+}$ has the $\Lambda_4$ configuration, while its $(-)^{CD}_{520}$ isomer has the $\Delta_4$ configuration. It is interesting to noted that the CD spectral curve of $(+)^{CD}_{520}$-$\Lambda_4$-[**1**]$^{8+}$ considerably deviates from the curve of two moles of ΛΛ-[Pd{Co(aet)$_2$(bztea)}$_2$]$^{4+}$ in the region of *ca.* 22–28 × $10^3$ cm$^{-1}$. The asymmetric sulfide S atoms in $\Lambda_4$-[**1**]$^{8+}$, which would be fixed to the *R* configuration more tightly than those in $\Lambda_2$-[Pd{Co(aet)$_2$(bztea)}$_2$]$^{4+}$, together with the skew cyclic structure of [**1**]$^{8+}$, seems to be responsible for this deviation.

Table 1
Absorption and CD spectral data of [**1**]$^{8+}$, [**2a**]$^{8+}$, and [**2b**]$^{8+}$ in $H_2O$[a]

| Abs max: $\sigma/10^3$ cm$^{-1}$ (log$\varepsilon$/mol$^{-1}$ dm$^3$ cm$^{-1}$) | | CD extrema: $\sigma/10^3$ cm$^{-1}$ ($\Delta\varepsilon$/mol$^{-1}$ dm$^3$ cm$^{-1}$) | |
|---|---|---|---|
| $\Lambda_4$-[{PdCo$_2$(aet)$_4$}$_2$(*o*-L)$_2$]$^{8+}$ ([**1**]$^{8+}$) | | | |
| 16.2 | (2.9)$^{sh}$ | 16.17 | (−1.3) |
| 19.41 | (3.20) | 19.19 | (+22.2) |
| 23.0 | (4.0)$^{sh}$ | 26.46 | (+70.1) |
| 26.7 | (4.7)$^{sh}$ | 31.64 | (−128.2) |
| 30.90 | (4.95) | 38.46 | (+78.3) |
| 33.5 | (4.8)$^{sh}$ | 45.15 | (−166.4) |
| 45.17 | (4.96) | 48.19 | (−75.0) |
| $\Lambda_4$-[{PdCo$_2$(aet)$_4$}$_2$(*m*-L)$_2$]$^{8+}$ ([**2a**]$^{8+}$) | | | |
| 16.1 | (2.7)$^{sh}$ | 16.10 | (−0.5) |
| 19.26 | (3.21) | 19.25 | (+22.2) |
| 23.5 | (4.1)$^{sh}$ | 24.27 | (+22.0) |
| 26.9 | (4.7)$^{sh}$ | 27.06 | (+38.7) |
| 30.81 | (4.89) | 31.70 | (−62.3) |
| 33.1 | (4.8)$^{sh}$ | 38.99 | (+53.7) |
| 45.1 | (5.0)$^{sh}$ | 48.19 | (−132.0) |
| $\Delta_2\Lambda_2$- [{PdCo$_2$(aet)$_4$}$_2$(*m*-L)$_2$]$^{8+}$ ([**2b**]$^{8+}$) | | | |
| 16.0 | (2.6)$^{sh}$ | | |
| 19.21 | (3.16) | | |
| 24.0 | (4.1)$^{sh}$ | | |
| 27.2 | (4.6)$^{sh}$ | | |
| 30.81 | (4.82) | | |
| 36.1 | (4.5)$^{sh}$ | | |
| 45.5 | (4.9)$^{sh}$ | | |

[a] The sh label denotes a shoulder.

## 2.2. Synthesis and characterization of [{Co$_2$Pd(aet)$_4$}$_2$-(m-L)$_2$]$^{8+}$ ([2]$^{8+}$)

The 1:1 reaction of [Pd{Co(aet)$_3$}$_2$]$^{2+}$ with *m*-dibromoxylene (*m*-xylBr$_2$) in water also gave a dark-red solution, like the reaction with *o*-dibromoxylene. When the reaction solution was chromatographed on an SP-Sephadex C-25 column, however, two red-brown bands were eluted with a 1.0 mol dm$^{-3}$ NaCl aqueous solution. From the two red-brown eluates, red-brown compounds ([**2a**]$^{8+}$ and [**2b**]$^{8+}$) were isolated as the chloride salts. The X-ray fluorescence and elemental analyses of [**2a**]Cl$_8$ and [**2b**]Cl$_8$ are in agreement with the formula for a 1:1 adduct of [Pd{Co(aet)$_3$}$_2$]$^{2+}$ and *m*-xyl$^{2+}$. Furthermore, the absorption spectra of [**2a**]$^{8+}$ and [**2b**]$^{8+}$ in water are very similar to that of [**1**]$^{8+}$ over the whole region (Fig. 1 and Table 1). Based on these results, together with their NMR spectra, it is considered that [**2a**]$^{8+}$ and [**2b**]$^{8+}$ are isomers of a cyclic Co$^{III}_4$Pd$^{II}_2$ hexanuclear complex composed of two Co$^{III}$Pd$^{II}$Co$^{III}$ trinuclear units and two *m*-xyl$^{2+}$ moieties, the structure of which is analogous to the cyclic structure in [**1**]$^{8+}$. Indeed, X-ray analyses demonstrated that [**2a**]$^{8+}$ and [**2b**]$^{8+}$ are the *racemic* ($\Delta_4/\Lambda_4$) and *meso* ($\Delta_2\Lambda_2$) isomers of [{Co$_2$Pd(aet)$_4$}$_2$(*m*-L)$_2$]$^{8+}$, respectively, in which two Co$^{III}$Pd$^{II}$Co$^{III}$ trinuclear units are linked by two *m*-xyl$^{2+}$ moieties in a cyclic form (vide infra). This is compatible with the fact that [**2a**]$^{8+}$ was optically resolved into the $(+)^{CD}_{520}$ and $(-)^{CD}_{520}$ isomers, which show CD spectra enantiomeric to each other, while [**2b**]$^{8+}$ was not optically resolved. The entire CD spectral feature of the $(+)^{CD}_{520}$ isomer of [**2a**]$^{8+}$ is similar to that of $\Lambda_4$-[**1**]$^{8+}$. Thus, the $(+)^{CD}_{520}$ and $(-)^{CD}_{520}$ isomers of [**2a**]$^{8+}$ are assignable to have the $\Lambda_4$ and $\Delta_4$ configurations, respectively (Fig. 1 and Table 1). Consistent with this assignment, only the $(+)^{CD}_{520}$ isomer of [**2a**]$^{8+}$ was formed when the $\Lambda_2$ isomer of [Pd{Co(aet)$_3$}$_2$]$^{2+}$ was used as the starting complex.

## 2.3. Molecular structure of $\Delta_4/\Lambda_4$-[{Co$_2$Pd(aet)$_4$}$_2$-(o-L)$_2$]$^{8+}$ ([1]$^{8+}$)

X-ray structural analysis of [**1**](ClO$_4$)(NO$_3$)$_7$ · 13H$_2$O revealed the presence of a discrete complex cation, $ClO_4^-$ and $NO_3^-$ anions, besides water molecules. The number of the counter anions implies that the complex cation is octavalent. The structure of the complex cation [**1**]$^{8+}$ is shown in Fig. 2, and its selected bond distances and angles are listed in Table 3.

The complex cation [**1**]$^{8+}$ contains two linear-type Co$^{III}$Pd$^{II}$Co$^{III}$ trinuclear units (average Pd–Co = 3.347(2)

Table 2
Crystallographic data of complexes

| | [**1**]$(ClO_4)(NO_3)_7 \cdot 13H_2O$ | [**2a**]$Cl_8 \cdot 17H_2O$ | [**2b**]$Cl_8 \cdot 17H_2O$ |
|---|---|---|---|
| Empirical formula | $C_{40}H_{114}Cl_1Co_4N_{19}O_{38}Pd_2S_{12}$ | $C_{40}H_{122}Cl_8Co_4N_{12}O_{17}Pd_2S_{12}$ | $C_{40}H_{122}Cl_8Co_4N_{12}O_{17}Pd_2S_{12}$ |
| Fw | 2338.19 | 2160.34 | 2160.34 |
| $T$ (K) | 200 | 296 | 296 |
| Radiation $\lambda$ (Å) | 0.7107 | 0.7107 | 0.7107 |
| Crystal system | Monoclinic | Monoclinic | Triclinic |
| Space group | $P2_1/n$ | $P2_1/c$ | $P\bar{1}$ |
| $a$ (Å) | 20.85(2) | 15.463(3) | 15.722(2) |
| $b$ (Å) | 17.48(1) | 34.444(6) | 17.485(2) |
| $c$ (Å) | 23.94(2) | 18.066(4) | 18.351(3) |
| $\alpha$ (°) | | | 71.32(1) |
| $\beta$ (°) | 90.83(7) | 107.11(2) | 91.87(1) |
| $\gamma$ (°) | | | 112.43(1) |
| $V$ (Å$^3$) | 8729(12) | 9196(3) | 4395(1) |
| $Z$ | 4 | 4 | 2 |
| $\rho_{calc}$ (cm$^{-3}$) | 1.779 | 1.560 | 1.633 |
| $\mu$(Mo-K$\alpha$) (cm$^{-1}$) | 1.556 | 1.648 | 1.725 |
| $R$ ($I > 2\sigma(I)$) | 0.086 | 0.104 | 0.059 |
| $R_w$ (all data) | 0.224 | 0.318 | 0.219 |

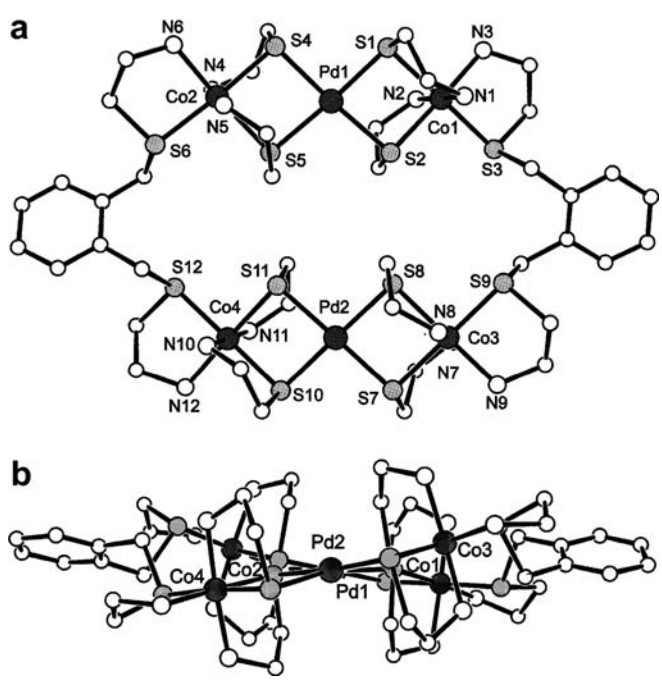



Fig. 2. Top (a) and side (b) views of $\Delta_4/\Lambda_4$-[{$Co_2Pd(aet)_4$}$_2$($o$-L)$_2$]$^{8+}$ ([**1**]$^{8+}$) with the atomic labeling scheme. The $\Lambda_4$ isomer is selected. Hydrogen atoms are omitted for clarity.

Å, Co–Pd–Co = 174.92(5)°), in which two *mer*-(*S*)-[$Co(N)_3(S)_3$] octahedra are bridged by a square-planar $Pd^{II}$ atom through four thiolato S atoms. The two terminal S atoms in each $Co^{III}Pd^{II}Co^{III}$ trinuclear unit are bound by two methylene carbon atoms from two $o$-xyl$^{2+}$ moieties so as to form a cyclic $Co^{III}{}_4Pd^{II}{}_2$ hexanuclear structure in [{$Co_2Pd(aet)_4$}$_2$($o$-L)$_2$]$^{8+}$ (Pd···Pd = 7.016(1) Å). Two chiral configurations ($\Delta$ and $\Lambda$) are possible for each *mer*-(*S*)-[$Co(N)_3(S)_3$] octahedron. The two *mer*-(*S*)-[$Co(N)_3(S)_3$] octahedra in each $Co^{III}Pd^{II}Co^{III}$ trinuclear unit have the same chiral configuration to give the $\Delta_2$ or $\Lambda_2$ form, like the parental [Pd{$Co(aet)_3$}$_2$]$^{2+}$ [22]. Furthermore, the same configurational $Co^{III}Pd^{II}Co^{III}$ trinuclear units are connected by $o$-xyl$^{2+}$ moieties to afford only the $\Delta_4$ and $\Lambda_4$ isomers. All the four sulfide S atoms bound by $o$-xyl$^{2+}$ moieties are fixed to the *S* configuration for the $\Delta_4$ isomer and to the *R* configuration for the $\Lambda_4$ isomer. Thus, only a pair of enantiomers, $(\Delta_S)_4$ and $(\Lambda_R)_4$, exist in [**1**]$^{8+}$; the latter isomer is selected in Fig. 2. In [**1**]$^{8+}$, there is no crystallographically imposed symmetry, but three quasi $C_2$ axes that are orthogonal to one another pass through the center of the cyclic structure to have an idealized $D_2$ symmetry. This $D_2$ symmetrical cyclic structure in [**1**]$^{8+}$ resembles that found in an S-bridged $Co^{III}{}_4Pd^{II}{}_2Au^{I}{}_2$ octanuclear complex, [$Au_2${Pd[$Co(aet)_3$]$_3$}$_2$]$^{6+}$ (Pd···Pd = 6.991(1) Å), in which two [Pd{$Co(aet)_3$}$_2$]$^{2+}$ units are linked by two linear $Au^I$ atoms through thiolato groups [21]. However, in [**1**]$^{8+}$ the two Co–Pd–Co lines are not parallel to each other with a skew angle of 22.4°, which is distinct from the nearly parallel Co–Pd–Co lines in [$Au_2${Pd[$Co(aet)_3$]$_3$}$_2$]$^{6+}$.

The bond distances and angles about the S-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear units in [**1**]$^{8+}$ are essentially the same as those in [Pd{$Co(aet)_2$(bztea)}$_2$]$^{4+}$ [23]. In particular, the Pd–$S_{thiolato}$ (average 2.332(4) Å) and Co–$S_{thiolato}$ (average 2.262(3) Å) distances are very similar to those in [Pd{$Co(aet)_2$(bztea)}$_2$]$^{4+}$ (average Pd–S = 2.324(2) Å and Co–$S_{aet}$ = 2.251(2) Å), although the Co–$S_{sulfide}$ (average 2.299(4) Å) bonds are somewhat longer than the Co–$S_{sulfide}$ (2.277(2) Å) bonds in [Pd{$Co(aet)_2$(bztea)}$_2$]$^{4+}$, presumably due to the steric congestion between the two $Co^{III}Pd^{II}Co^{III}$ trinuclear units in [**1**]$^{8+}$.

### 2.4. Molecular structure of $\Delta_4/\Lambda_4$-[{$Co_2Pd(aet)_4$}$_2$-($m$-L)$_2$]$^{8+}$ ([**2a**]$^{8+}$)

X-ray structural analysis of [**2a**]$Cl_8 \cdot 17H_2O$ showed the presence of a discrete complex cation, $Cl^-$ anions and water molecules. The number of $Cl^-$ anions implies that

Table 3
Selected bond distances (Å) and angles (°) of $[\{Co_2Pd(aet)_4\}_2(o\text{-}L_2)](ClO_4)(NO_3)_7 \cdot 13H_2O$ ($[\mathbf{1}](ClO_4)(NO_3)_7 \cdot 13H_2O$)

| | | | | | |
|---|---|---|---|---|---|
| Pd1–S1 | 2.318(2) | Co1–N1 | 1.977(4) | Co3–S9 | 2.286(2) |
| Pd1–S2 | 2.354(2) | Co1–N2 | 2.004(4) | Co3–N7 | 1.982(4) |
| Pd1–S4 | 2.315(2) | Co1–N3 | 2.006(4) | Co3–N8 | 1.989(4) |
| Pd1–S5 | 2.352(2) | Co2–S4 | 2.271(2) | Co3–N9 | 2.001(4) |
| Pd2–S7 | 2.319(2) | Co2–S5 | 2.273(2) | Co4–S10 | 2.246(2) |
| Pd2–S8 | 2.344(2) | Co2–S6 | 2.323(2) | Co4–S11 | 2.266(2) |
| Pd2–S10 | 2.325(2) | Co2–N4 | 1.994(4) | Co4–S12 | 2.284(2) |
| Pd2–S11 | 2.324(2) | Co2–N5 | 2.009(4) | Co4–N10 | 1.973(4) |
| Co1–S1 | 2.253(2) | Co2–N6 | 2.013(4) | Co4–N11 | 1.992(4) |
| Co1–S2 | 2.276(2) | Co3–S7 | 2.257(2) | Co4–N12 | 2.002(4) |
| Co1–S3 | 2.301(2) | Co3–S8 | 2.248(2) | | |
| S1–Pd1–S2 | 84.28(5) | S4–Co2–S5 | 87.02(5) | S10–Co4–S12 | 176.44(5) |
| S2–Pd1–S4 | 175.22(4) | S4–Co2–S6 | 178.84(5) | S10–Co4–N10 | 87.7(1) |
| S1–Pd1–S5 | 176.99(4) | S4–Co2–N4 | 87.0(1) | S11–Co4–N11 | 87.9(1) |
| S4–Pd1–S5 | 84.17(5) | S5–Co2–N5 | 87.7(1) | S11–Co4–N12 | 178.5(1) |
| S7–Pd2–S8 | 84.94(6) | S5–Co2–N6 | 175.9(1) | S12–Co4–N12 | 87.6(1) |
| S7–Pd2–S11 | 175.63(5) | S6–Co2–N6 | 87.3(1) | N10–Co4–N11 | 175.6(2) |
| S8–Pd2–S10 | 174.30(5) | N4–Co2–N5 | 177.1(1) | Pd1–S1–Co1 | 94.78(5) |
| S10–Pd2–S11 | 85.10(6) | S7–Co3–S8 | 88.67(6) | Pd1–S2–Co1 | 93.22(5) |
| S1–Co1–S2 | 87.59(5) | S7–Co3–S9 | 177.62(5) | Pd1–S4–Co2 | 93.41(5) |
| S1–Co1–S3 | 176.08(5) | S7–Co3–N7 | 87.5(1) | Pd1–S5–Co2 | 94.39(5) |
| S1–Co1–N1 | 88.6(1) | S8–Co3–N8 | 87.8(1) | Pd2–S7–Co3 | 93.23(6) |
| S2–Co1–N2 | 87.7(1) | S8–Co3–N9 | 177.9(1) | Pd2–S8–Co3 | 92.81(6) |
| S2–Co1–N3 | 176.4(1) | S9–Co3–N9 | 87.5(1) | Pd2–S10–Co4 | 93.48(6) |
| S3–Co1–N3 | 86.4(1) | N7–Co3–N8 | 177.2(4) | Pd2–S11–Co4 | 93.00(6) |
| N1–Co1–N2 | 178.3(2) | S10–Co4–S11 | 88.31(6) | | |

the complex cation is octavalent. The structure of the complex cation $[\mathbf{2a}]^{8+}$ is shown in Fig. 3, and its selected bond distances and angles are listed in Table 4.

The complex cation $[\mathbf{2a}]^{8+}$ contains two linear-type $Co^{III}Pd^{II}Co^{III}$ trinuclear units (average Pd–Co = 3.325(6) Å, Co–Pd–Co = 176.5(1)°) that are linked by two $m$-xyl$^{2+}$ moieties through the terminal non-bridging S atoms, forming a cyclic $Co^{III}_4Pd^{II}_2$ hexanuclear structure in $[\{Co_2Pd(aet)_4\}_2(m\text{-}L)_2]^{8+}$ (Pd···Pd = 7.016(1) Å). The two *mer*-(*S*)-$[Co(N)_3(S)_3]$ octahedra in each $Co^{III}Pd^{II}Co^{III}$ trinuclear unit have the same chiral configuration to give the $\Delta_2$ or $\Lambda_2$ form, and furthermore, the same configurational $Co^{III}Pd^{II}Co^{III}$ trinuclear units are connected by $m$-xyl$^{2+}$ moieties to give only the $\Delta_4$ and $\Lambda_4$ isomers. All the four sulfide S atoms bound by $m$-xyl$^{2+}$ moieties are restricted to have the *S* configuration for the $\Delta_4$ isomer and the *R* configuration for the $\Lambda_4$ isomer. Thus, only a pair of enantiomers with an idealized $D_2$ symmetry, $(\Delta_S)_4$ and $(\Lambda_R)_4$, is formed in $[\mathbf{2a}]^{8+}$; the former isomer is selected in Fig. 3. This $Co^{III}_4Pd^{II}_2$ cyclic structure in $[\mathbf{2a}]^{8+}$ resembles that in $[\mathbf{1}]^{8+}$, featuring a skew arrangement of two Co–Pd–Co lines with an angle of 19.0°. However, $[\mathbf{2a}]^{8+}$ possesses a relatively larger cavity inside the ring (Pd···Pd = 10.155(3) Å), which accommodates a water molecule, because of the steric demand of the $m$-xyl$^{2+}$ connector (Fig. S1). The bond distances around each metal center in $[\mathbf{2a}]^{8+}$ (average $Pd–S_{thiolato}$ = 2.315(10) Å, $Co–S_{thiolato}$ = 2.243(10) Å, $Co–S_{sulfide}$ = 2.268(10) Å) are comparable with those in $[\mathbf{1}]^{8+}$.

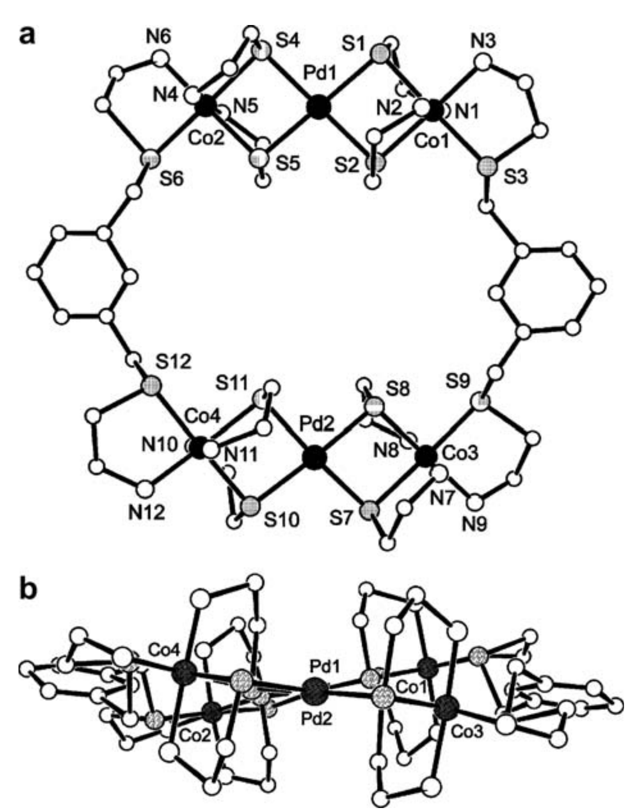



Fig. 3. Top (a) and side (b) views of $\Delta_4/\Lambda_4$-$[\{PdCo_2(aet)_4\}_2(m\text{-}L)_2]^{8+}$ ($[\mathbf{2a}]^{8+}$) with the atomic labeling scheme. The $\Delta_4$ isomer is selected. Hydrogen atoms are omitted for clarity.

Table 4
Selected bond distances (Å) and angles (°) of $\Delta_4/\Lambda_4$-[{$PdCo_2(aet)_4$}$_2$(*m*-L)$_2$]$Cl_8 \cdot 17H_2O$ ([**2a**]$Cl_8 \cdot 17H_2O$)

| | | | | | |
|---|---|---|---|---|---|
| Pd1–S1 | 2.322(8) | Co1–N1 | 2.00(2) | Co3–S9 | 2.292(9) |
| Pd1–S2 | 2.284(8) | Co1–N2 | 2.01(2) | Co3–N7 | 2.00(2) |
| Pd1–S4 | 2.325(8) | Co1–N3 | 1.95(2) | Co3–N8 | 1.95(2) |
| Pd1–S5 | 2.303(9) | Co2–S4 | 2.259(9) | Co3–N9 | 1.97(2) |
| Pd2–S7 | 2.366(8) | Co2–S5 | 2.220(9) | Co4–S10 | 2.268(9) |
| Pd2–S8 | 2.292(8) | Co2–S6 | 2.262(9) | Co4–S11 | 2.210(9) |
| Pd2–S10 | 2.325(8) | Co2–N4 | 2.00(2) | Co4–S12 | 2.262(9) |
| Pd2–S11 | 2.288(8) | Co2–N5 | 1.98(2) | Co4–N10 | 1.94(2) |
| Co1–S1 | 2.268(9) | Co2–N6 | 2.00(2) | Co4–N11 | 1.97(2) |
| Co1–S2 | 2.227(9) | Co3–S7 | 2.231(9) | Co4–N12 | 2.06(3) |
| Co1–S3 | 2.287(9) | Co3–S8 | 2.236(9) | | |
| S1–Pd1–S2 | 85.3(3) | S4–Co2–S5 | 88.2(3) | S10–Co4–S12 | 176.7(4) |
| S1–Pd1–S5 | 178.7(3) | S4–Co2–S6 | 177.3(4) | S10–Co4–N10 | 88.0(6) |
| S1–Pd1–S4 | 176.8(3) | S4–Co2–N4 | 88.5(6) | S11–Co4–N11 | 87.1(7) |
| S4–Pd1–S5 | 84.7(3) | S5–Co2–N5 | 87.4(7) | S11–Co4–N12 | 176.9(8) |
| S7–Pd2–S8 | 83.8(3) | S5–Co2–N6 | 177.8(7) | S12–Co4–N12 | 85.8(8) |
| S7–Pd2–S11 | 173.7(3) | S6–Co2–N6 | 87.3(7) | N10–Co4–N11 | 174.5(9) |
| S8–Pd2–S10 | 172.5(3) | N4–Co2–N5 | 175.7(9) | Pd1–S1–Co1 | 92.2(3) |
| S10–Pd2–S11 | 84.2(3) | S7–Co3–S8 | 88.3(3) | Pd1–S2–Co1 | 94.3(3) |
| S1–Co1–S2 | 87.9(3) | S7–Co3–S9 | 178.4(4) | Pd1–S4–Co2 | 92.6(3) |
| S1–Co1–S3 | 176.3(4) | S7–Co3–N7 | 84.7(6) | Pd1–S5–Co2 | 94.3(3) |
| S1–Co1–N1 | 86.5(7) | S8–Co3–N8 | 87.6(6) | Pd2–S7–Co3 | 93.0(3) |
| S2–Co1–N2 | 89.9(7) | S8–Co3–N9 | 176.5(7) | Pd2–S8–Co3 | 94.9(3) |
| S2–Co1–N3 | 177.0(7) | S9–Co3–N9 | 88.8(7) | Pd2–S10–Co4 | 92.9(3) |
| S3–Co1–N3 | 84.8(7) | N7–Co3–N8 | 176.5(9) | Pd2–S11–Co4 | 95.5(3) |
| N1–Co1–N2 | 178(1) | S10–Co4–S11 | 87.4(3) | | |

### 2.5. Molecular structures of $\Delta_2\Lambda_2$-[{$Co_2Pd(aet)_4$}$_2$-(*m*-L)$_2$]$^{8+}$ ([**2b**]$^{8+}$)

X-ray analysis revealed that the asymmetric unit of [**2b**]$^{8+}$ contains two crystallographically independent complex cations ([**2b**$_\alpha$]$^{8+}$ and [**2b**$_\beta$]$^{8+}$), besides $Cl^-$ anions and water molecules. The number of $Cl^-$ anions implies that each complex cation is octavalent. The structures of the two complex cations are shown in Fig. 4, and their selected bond distances and angles are listed in Table 5.

The two complex cations have a similar cyclic $Co^{III}{}_4Pd^{II}{}_2$ structure ([{$Co_2Pd(aet)_4$}$_2$(*m*-L)$_2$]$^{8+}$), in which two linear-type $Co^{III}Pd^{II}Co^{III}$ trinuclear units (average Pd–Co = 3.318(2) Å, Co–Pd–Co = 176.57(5)°) are linked by two *m*-xyl$^{2+}$ moieties through the terminal non-bridging S atoms. The two *mer*-(*S*)-[Co(N)$_3$(S)$_3$] octahedra in each $Co^{III}Pd^{II}Co^{III}$ trinuclear unit have the same chiral configuration to give the $\Delta_2$ or $\Lambda_2$ form, like the two $Co^{III}$ octahedra in [**1**]$^{8+}$ or [**2a**]$^{8+}$. However, in each of [**2b**$_\alpha$]$^{8+}$ and [**2b**$_\beta$]$^{8+}$ the $\Delta_2$ and $\Lambda_2$ configurations are selected for the two $Co^{III}Pd^{II}Co^{III}$ units, constructing a *meso* ($\Delta_2\Lambda_2$) structure. The structures of [**2b**$_\alpha$]$^{8+}$ and [**2b**$_\beta$]$^{8+}$ can be discriminated in terms of the *R* and *S* configurations for the four sulfide S atoms. That is, [**2b**$_\alpha$]$^{8+}$ adopts the $(\Delta_S)_2(\Lambda_R)_2$ configuration with an averaged $C_{2h}$ symmetry, while [**2b**$_\beta$]$^{8+}$ has the $(\Delta_S\Delta_R)(\Lambda_R\Lambda_S)$ configuration with a $C_i$ symmetry (Fig. 4).

The bond distances around each metal center in [**2b**$_\alpha$]$^{8+}$ (average Pd–S = 2.317(3) Å, Co–$S_{bridging\text{-}Pd}$ = 2.243(3) Å, Co–$S_{thioether}$ = 2.275(3) Å) and [**2b**$_\beta$]$^{8+}$ (average Pd–S = 2.323(3) Å, Co–$S_{bridging\text{-}Pd}$ = 2.254(3), Co–$S_{thioether}$ = 2.289(3) Å) are very similar to each other, and these distances are comparable with the corresponding distances in [**2a**]$^{8+}$. Furthermore, the intramolecular Pd···Pd distances between the two $Co^{III}Pd^{II}Co^{III}$ trinuclear units (9.921(1) Å for [**2b**$_\alpha$]$^{8+}$ and 10.033(1) Å for [**2b**$_\beta$]$^{8+}$) are similar to the distances in [**2a**]$^{8+}$ (10.155(3) Å). It is worth to mention that [**2b**$_\alpha$]$^{8+}$ and [**2b**$_\beta$]$^{8+}$ accommodate water molecules in their cavity, as does [**2a**]$^{8+}$ (Fig. S1).

### 2.6. Stereochemistry of the $Co^{III}{}_4Pd^{II}{}_2$ metallacycles

In the $Co^{III}{}_4Pd^{II}{}_2$ hexanuclear complexes, [{$Co_2Pd(aet)_4$}$_2$(*o*-L)$_2$]$^{8+}$ ([**1**]$^{8+}$) and [{$Co_2Pd(aet)_4$}$_2$(*m*-L)$_2$]$^{8+}$ ([**2**]$^{8+}$), the two *mer*-(*S*)-[Co(N)$_3$(S)$_3$] octahedra in each $Co^{III}Pd^{II}Co^{III}$ trinuclear unit commonly have the same chiral configuration to give the $\Delta_2$ or $\Lambda_2$ form. Thus, it is seen that the chiral configuration ($\Delta_2$ or $\Lambda_2$) of the parental [Pd{$Co(aet)_3$}$_2$]$^{2+}$ is retained in the course of the reactions with *o*- or *m*-xyl$Br_2$ This is supported by the fact that only the $\Lambda_4$ isomer was formed for [**2**]$^{8+}$ when the $\Lambda_2$ isomer of [Pd{$Co(aet)_3$}$_2$]$^{2+}$ was reacted with *m*-xyl$Br_2$.

Considering the combination of the $\Delta_2$ and $\Lambda_2$ configurations for the two $Co^{III}Pd^{II}Co^{III}$ units, *racemic* ($\Delta_4/\Lambda_4$) and *meso* ($\Delta_2\Lambda_2$) forms are possible for [**1**]$^{8+}$ and [**2**]$^{8+}$. However, [**1**]$^{8+}$ afforded only the *racemic* form, which was shown by the column chromatographic behavior, together with the single-crystal X-ray analysis. Molecular model examinations reveal that there exists an unfavorable steric interaction between the two $Co^{III}Pd^{II}Co^{III}$ units when [{$Co_2Pd(aet)_4$}$_2$(*o*-L)$_2$]$^{8+}$ adopts the *meso* form. The selective formation of the *racemic* form has also been

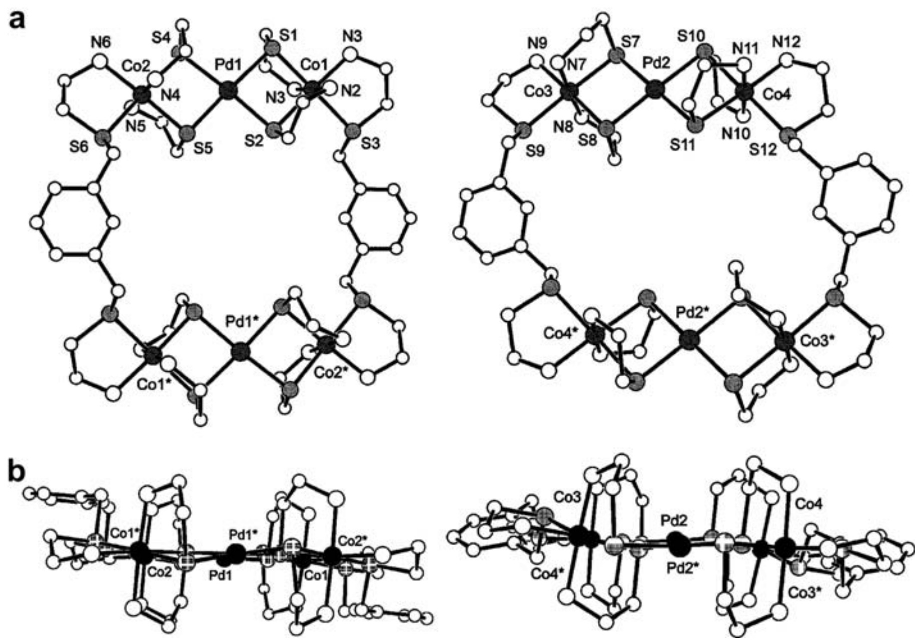



Fig. 4. Top (a) and side (b) views of two isomers of $\Delta_2\Lambda_2$-[{$Co_2Pd(aet)_4$}$_2$(*m*-L)$_2$]$^{8+}$ ([**2b**]$^{8+}$) with the atomic labeling scheme (left for [$\mathbf{2b}_\alpha$]$^{8+}$ and right for [$\mathbf{2b}_\beta$]$^{8+}$). Hydrogen atoms are omitted for clarity.

Table 5
Selected bond distances (Å) and angles (°) of $\Delta_2\Lambda_2$-[{$PdCo_2(aet)_4$}$_2$(*m*-L)$_2$]$Cl_8 \cdot 17H_2O$ ([**2b**]$Cl_8 \cdot 17H_2O$)

| | | | | | |
|---|---|---|---|---|---|
| Pd1–S2 | 2.305(2) | Co1–N1 | 1.980(6) | Co3–S9 | 2.266(3) |
| Pd1–S1 | 2.331(2) | Co1–N2 | 1.973(7) | Co3–N7 | 1.978(7) |
| Pd1–S4 | 2.328(2) | Co1–N3 | 2.011(7) | Co3–N8 | 1.984(7) |
| Pd1–S5 | 2.305(2) | Co2–S4 | 2.255(2) | Co3–N9 | 1.998(7) |
| Pd2–S7 | 2.330(2) | Co2–S5 | 2.237(3) | Co4–S10 | 2.254(2) |
| Pd2–S8 | 2.318(3) | Co2–S6 | 2.282(3) | Co4–S11 | 2.258(3) |
| Pd2–S10 | 2.321(3) | Co2–N4 | 1.987(7) | Co4–S12 | 2.313(3) |
| Pd2–S11 | 2.322(2) | Co2–N5 | 1.972(7) | Co4–N10 | 1.980(7) |
| Co1–S1 | 2.252(2) | Co2–N6 | 1.987(7) | Co4–N11 | 1.966(7) |
| Co1–S2 | 2.239(2) | Co3–S7 | 2.260(3) | Co4–N12 | 1.995(8) |
| Co1–S3 | 2.272(3) | Co3–S8 | 2.244(2) | | |
| S1–Pd1–S2 | 84.74(8) | S4–Co2–S5 | 88.03(9) | S10–Co4–S12 | 171.0(1) |
| S2–Pd1–S4 | 172.9(1) | S4–Co2–S6 | 179.7(1) | S10–Co4–N10 | 86.9(2) |
| S1–Pd1–S5 | 173.08(8) | S4–Co2–N4 | 86.5(2) | S11–Co4–N11 | 87.2(3) |
| S4–Pd1–S5 | 84.69(8) | S5–Co2–N5 | 86.9(2) | S11–Co4–N12 | 178.1(3) |
| S7–Pd2–S8 | 84.72(9) | S5–Co2–N6 | 175.5(2) | S12–Co4–N12 | 85.7(2) |
| S7–Pd2–S11 | 179.7(1) | S6–Co2–N6 | 86.5(2) | N10–Co4–N11 | 176.6(3) |
| S8–Pd2–S10 | 177.89(9) | N4–Co2–N5 | 175.4(3) | Pd1–S1–Co1 | 92.46(8) |
| S10–Pd2–S11 | 84.40(9) | S7–Co3–S8 | 88.09(9) | Pd1–S2–Co1 | 93.48(8) |
| S1–Co1–S2 | 88.16(9) | S7–Co3–S9 | 176.8(1) | Pd1–S4–Co2 | 92.56(9) |
| S1–Co1–S3 | 178.3(1) | S7–Co3–N7 | 87.4(2) | Pd1–S5–Co2 | 93.64(9) |
| S1–Co1–N1 | 86.5(2) | S8–Co3–N8 | 88.4(2) | Pd2–S7–Co3 | 92.96(8) |
| S2–Co1–N2 | 87.2(2) | S8–Co3–N9 | 176.9(2) | Pd2–S8–Co3 | 93.72(9) |
| S2–Co1–N3 | 175.4(2) | S9–Co3–N9 | 87.1(2) | Pd2–S10–Co4 | 93.29(9) |
| S3–Co1–N3 | 86.8(2) | N7–Co3–N8 | 176.5(3) | Pd2–S11–Co4 | 93.16(8) |
| N1–Co1–N2 | 176.0(3) | S10–Co4–S11 | 87.45(9) | | |

recognized for the S-bridged $Co^{III}{}_4Pd^{II}{}_2Au^{I}{}_2$ metallacycle, [$Au_2${Pd[Co(aet)$_3$]$_3$}$_2$]$^{6+}$, the Pd···Pd distance (6.991(1) Å) of which is quite similar to that in [**1**]$^{8+}$ (7.016(1) Å) [21]. On the other hand, both the *racemic* and *meso* forms were generated for [**2**]$^{8+}$. This is understood by the larger separation between the two $Co^{III}Pd^{II}Co^{III}$ units due to the linkage with *m*-xyl$^{2+}$ moieties, which can avoid an unfavorable interaction. It should be noted that the *meso* form of [**2**]$^{8+}$ ([**2b**]$^{8+}$) was found to contain two diastereomers, $(\Delta_S)_2(\Lambda_R)_2$ and $(\Delta_S\Delta_R)(\Lambda_R\Lambda_S)$, which are discriminated by the difference in the *R* and *S* configurations of the asymmetric sulfide S atoms, while the *racemic* form of [**2**]$^{8+}$ ([**2a**]$^{8+}$) exists as a pair of enantiomers having the unified chiral configurations, $(\Delta_S)_4$ and $(\Lambda_R)_4$, as does [**1**]$^{8+}$.

Recently, we have shown that the two terminal thiolato groups in $\Delta_2$- and $\Lambda_2$-[Pd{Co(aet)$_3$}$_2$]$^{2+}$ are bound by benzyl groups so as to give the *S* and *R* configurational sulfide S atoms, respectively [23]. Thus, the selective formation of the $(\Delta_S)_4$ and $(\Lambda_R)_4$ isomers for [**1**]$^{8+}$ and [**2a**]$^{8+}$ can be explained by the stability of the $\Delta_S$ or $\Lambda_R$ configuration for each Co$^{III}$ octahedron, which does not involve a serious non-bonding interaction between an attached alkyl group and an aet chelate ring in each Co$^{III}$ octahedron. The formation of the $\Delta_R$ and $\Lambda_S$ configurational Co$^{III}$ octahedra in [**2b**]$^{8+}$, besides the $\Delta_S$ and $\Lambda_R$ configurational ones, is most likely due to an additional steric factor between the *m*-xyl$^{2+}$ methylene groups and the adjacent aet ligands, which is caused by the linkage of the two Co$^{III}$Pd$^{II}$Co$^{III}$ units having the opposite chiral configurations.

The $^{13}$C NMR spectrum of [**1**]$^{8+}$ in $D_2O$ exhibits only three aromatic and seven methylene carbon signals for 12 aromatic and 28 methylene carbon atoms in the complex (Fig. S2). Furthermore, only two *o*-xyl$^{2+}$ methylene doublets are recognized at $\delta$ 4.21 and 3.97 in the $^{1}$H NMR spectrum of [**1**]$^{8+}$ (Fig. S3). These NMR spectral features imply that the symmetrical cyclic structure of [**1**]$^{8+}$ found in crystal is retained in solution. A similar $^{13}$C and $^{1}$H NMR spectral behavior is also observed for [**2a**]$^{8+}$, indicative of the retention of its symmetrical cyclic structure in solution. However, two *m*-xyl$^{2+}$ methylene doublets appear at much closer positions ($\delta$ 4.12 and 4.08) in the $^{1}$H NMR spectrum of [**2a**]$^{8+}$, reflecting the more flexible cyclic structure of [**2a**]$^{8+}$ compared with that of [**1**]$^{8+}$. The overall NMR spectral behavior of [**2b**]$^{8+}$ resemble that of [**1**]$^{8+}$ and [**2a**]$^{8+}$, but a characteristic difference is noticed in more minute detail, which results from the presence of two diastereomers, $(\Delta_S)_2(\Lambda_R)_2$ and $(\Delta_S\Delta_R)(\Lambda_R\Lambda_S)$. That is, all proton signals, including *m*-xyl$^{2+}$ methylene signals ($\delta$ 4.19 and 4.08), are broadened in the $^{1}$H NMR spectrum of [**2b**]$^{8+}$ (Fig. S3). In addition, the $^{13}$C NMR spectrum of [**2b**]$^{8+}$ exhibits rather broad *m*-xyl$^{2+}$ methylene signals at $\delta$ 39.41 and 39.82 (Fig. S2).

## 3. Concluding remarks

It was shown in this study that in aqueous media the S-bridged Co$^{III}$Pd$^{II}$Co$^{III}$ trinuclear [Pd{Co(aet)$_3$}$_2$]$^{2+}$ reacts readily with dibromoxylene (xylBr$_2$) to form the Co$^{III}_4$Pd$^{II}_2$ hexanuclear metallacycles that are composed of two Co$^{III}$Pd$^{II}$Co$^{III}$ units and two xyl$^{2+}$ moieties ([**1**]$^{8+}$ and [**2**]$^{8+}$), thanks to the high nucleophilicity of two terminal thiolato groups in [Pd{Co(aet)$_3$}$_2$]$^{2+}$. The chiral configuration ($\Delta_2$ or $\Lambda_2$) of [Pd{Co(aet)$_3$}$_2$]$^{2+}$ was found to be retained in the course of the dialkylation reactions. The linkage of the two Co$^{III}$Pd$^{II}$Co$^{III}$ units with *o*-xyl$^{2+}$ moieties selected the $\Delta_2$ or $\Lambda_2$ configuration for the Co$^{III}$Pd$^{II}$Co$^{III}$ units and the *R* or *S* configuration for the sulfide S atoms, generating only a racemic compound with the unified chiral centers, $(\Delta_S)_4$ and $(\Lambda_R)_4$, which were successfully optically resolved. On the other hand, not only a racemic compound containing the $(\Delta_S)_4$ and $(\Lambda_R)_4$ enantiomers ([**2a**]$^{8+}$), but also a *meso* compound containing the $(\Delta_S)_2(\Lambda_R)_2$ and $(\Delta_S\Delta_R)(\Lambda_R\Lambda_S)$ diastereomers ([**2b**]$^{8+}$) was produced by the linkage with *m*-xyl$^{2+}$ groups. Note that the cyclic structures in [**2a**]$^{8+}$ and [**2b**]$^{8+}$ possesses a relatively large cavity enough to accommodate water molecule(s), while no appreciable cavity exists in [**1**]$^{8+}$. Thus, the slight modification of the geometrical isomerism of the xyl$^{2+}$ linkers (*ortho* vs. *meta*) results in a marked difference not only in the cavity size but also in the stereoisomerism of the generated Co$^{III}_4$Pd$^{II}_2$ metallacycles.

## 4. Experimental

### 4.1. Synthesis of complexes

#### 4.1.1. Preparation and optical resolution of $\Delta_4/\Lambda_4$-[{Co$_2$Pd(aet)$_4$}$_2$(**o-L**)$_2$]Cl$_8$ ([**1**]Cl$_8$)

To a brown solution containing [Pd{Co(aet)$_3$}$_2$]-Cl$_2 \cdot 5H_2O$ [22] (0.50 g, 0.61 mmol) in 100 cm$^3$ of water was added *o*-dibromoxylene (0.20 g, 0.67 mmol). The mixture was stirred at room temperature for 2 days, during which time the brown suspension turned to a dark red solution. The insoluble materials were filtered off, and the filtrate was chromatographed on an SP-Sephadex C-25 column (Na$^+$ form, 4 cm × 45 cm). After the column had been swept with water and with a 0.5 mol dm$^{-3}$ aqueous solution of NaCl, a red-brown band of [**1**]$^{8+}$ was eluted with a 1.0 mol dm$^{-3}$ aqueous solution of NaCl. The eluate was concentrated to a small volume with a rotary evaporator. After removal of deposited NaCl by filtration, the filtrate was allowed to stand at room temperature overnight. The resulting red-brown powder was collected by filtration, and then recrystallized from water at room temperature. Yield for [**1**]Cl$_8 \cdot 13H_2O$: 0.24 g (38%). Anal. Calc. for [Pd$_2$Co$_4$(C$_2$H$_6$NS)$_4$(C$_{12}$H$_{20}$N$_2$S$_2$)$_2$]Cl$_8 \cdot 13H_2O$: C, 23.01; H, 5.50; N, 8.05. Found: C, 22.87; H, 5.22; N, 8.18%. $^{1}$H NMR (D$_2$O): $\delta$ 7.55 (4H, m), 7.40 (4H, m), 4.21 (4H, d, $J = 13.4$ Hz), 3.97 (4H, d, $J = 13.4$ Hz), 3.82–3.72 (12H, m), 3.61 (4H, dd, $J = 11.9$, 3.4 Hz), 3.03–2.98 (4H, m), 2.83–2.81 (4H, m), 2.70 (4H, dd, $J = 13.4$, 3.1 Hz), 2.61–2.53 (16H, m) 2.39 (4H, td, $J = 13.4$, 6.7 Hz). $^{13}$C NMR (D$_2$O): $\delta$ 35.95 (CH$_2$S), 36.21 (CH$_2$S), 37.17 (CH$_2$S), 37.85 (CH$_2$S), 45.95 (CH$_2$NH$_2$), 56.61 (CH$_2$NH$_2$), 57.15 (CH$_2$NH$_2$), 132.59 (Ph), 132.89 (Ph), 136.05 (Ph). Dark red crystals of [**1**](ClO$_4$)(NO$_3$)$_7 \cdot 13H_2O$ suitable for X-ray analysis were obtained by the metathesis of [**1**]Cl$_8$ with NaClO$_4$ in water, followed by recrystallization from water by adding an aqueous solution of NaNO$_3$.

An aqueous solution of [**1**]Cl$_8 \cdot 13H_2O$ was chromatographed on an SP-Sephadex C-25 column (Na$^+$ form, 2 cm × 30 cm), using a 0.50 mol dm$^{-3}$ aqueous solution of Na$_2$[Sb$_2$(*R*,*R*-tartrato)$_2$] $\cdot 5H_2O$ as an eluent. When the developed band was completely separated into two bands in the column, the eluent was changed to a 1.0 mol dm$^{-3}$ aqueous solution of NaCl. Each eluate of the two bands was concentrated to a small volume, and the concentrated solution was used for the CD spectral measurement.

The concentration of each solution was evaluated on the basis of the absorption spectral data of the *racemic* chloride salt. It was found from the absorption and CD spectral measurements that the earlier and the later moving bands in the column contained the $(+)^{CD}_{520}$ and $(-)^{CD}_{520}$ isomers of $[\mathbf{1}]^{8+}$, respectively.

### 4.1.2. Preparation and optical resolution of $\Delta_4/\Lambda_4$- and $\Delta_2\Lambda_2$-$[\{Co_2Pd(aet)_4\}_2(m\text{-}L)_2]Cl_8$ ($[\mathbf{2a}]Cl_8$ and $[\mathbf{2b}]Cl_8$)

To a brown solution containing $[Pd\{Co(aet)_3\}_2]Cl_2 \cdot 5H_2O$ (0.50 g, 0.61 mmol) in 100 $cm^3$ of water was added *m*-dibromoxylene (0.20 g, 0.67 mmol). The mixture was stirred at room temperature for 2 days, during which time the brown suspension turned to a dark red solution. The insoluble materials were filtered off, and the filtrate was chromatographed on an SP-Sephadex C-25 column ($Na^+$ form, 4 cm × 45 cm). After the column had been swept with water and with a 0.5 mol $dm^{-3}$ aqueous solution of NaCl, two red-brown bands of $[\mathbf{2b}]^{8+}$ ($\Delta_2\Lambda_2$-$[\mathbf{2}]^{8+}$) and $[\mathbf{2a}]^{8+}$ ($\Delta_4/\Lambda_4$-$[\mathbf{2}]^{8+}$) were eluted in this order with a 1.0 mol $dm^{-3}$ aqueous solution of NaCl. The formation ratio for this reaction was estimated to be ca. $[\mathbf{2a}]^{8+}$:$[\mathbf{2b}]^{8+}$ = 1.4:1, based on the absorption spectral measurements. Each eluate of the two bands was concentrated to a small volume with a rotary evaporator. After removal of deposited NaCl by filtration, the filtrate was allowed to stand at room temperature overnight. The resulting red-brown microcrystals were collected by filtration, and then recrystallized from water at room temperature. One of the dark red crystals thus obtained for each of $[\mathbf{2a}]Cl_8$ and $[\mathbf{2b}]Cl_8$ was used for X-ray analysis. Yield for $[\mathbf{2a}]Cl_8 \cdot 13H_2O$:0.10 g (16%). Anal. Calc. for $[Pd_2Co_4(C_2H_6NS)_4(C_{12}H_{20}N_2S_2)_2]Cl_8 \cdot 17H_2O$: C, 23.01; H, 5.50; N, 8.05. Found: C, 22.83; H, 5.22; N, 8.04%. $^1H$ NMR ($D_2O$): $\delta$ 7.54 (6H, s), 7.38 (2H, s), 4.12 (4H, d, $J$ = 13.4 Hz), 4.08 (4H, d, $J$ = 13.4 Hz), 3.83 (4H, td, $J$ = 13.1, 4.3 Hz), 3.70–3.67 (8H, m), 3.57 (4H, dd, $J$ = 12.2, 4.3 Hz), 3.26–3.18 (8H, m), 2.99 (4H, td, $J$ = 11.8, 4.1 Hz), 2.84 (4H, dd, $J$ = 13.7, 2.1 Hz), 2.90–2.60 (8H, m), 2.32–2.29 (8H, m). $^{13}C$ NMR ($D_2O$): $\delta$ 35.77 ($CH_2S$), 37.64 ($CH_2S$), 40.16 ($CH_2S$), 40.19 ($CH_2S$), 46.69 ($CH_2NH_2$), 55.72 ($CH_2NH_2$), 57.24 ($CH_2NH_2$), 132.07 (Ph), 132.97 (Ph), 138.29 (Ph). Yield for $[\mathbf{2b}]Cl_8 \cdot 17H_2O$: 0.18 g (30%). Anal. Calc. for $[Pd_2Co_4(C_2H_6NS)_4(C_{12}H_{20}N_2S_2)_2]Cl_8 \cdot 17H_2O$: C, 22.24; H, 5.69; N, 7.78. Found: C, 21.97; H, 5.37; N, 7.77%. $^1H$ NMR ($D_2O$): $\delta$ 7.59 (2H, br s), 7.55 (6H, br s), 4.19 (4H, d, $J$ = 13.4 Hz), 4.08 (4H, br d, $J$ = 13.0 Hz), 3.80–3.63 (16H, m), 3.15 (8H, br s), 2.92 (4H, br s), 2.74 (8H, br s), 2.64 (4H, d, $J$ = 12.2 Hz), 2.30 (4H, br s), 2.12 (4H, br s). $^{13}C$ NMR ($D_2O$): $\delta$ 35.87 ($CH_2S$), 37.04 ($CH_2S$), 39.41 ($CH_2S$), 39.82 ($CH_2S$), 46.30 ($CH_2NH_2$), 55.96 ($CH_2NH_2$), 56.98 ($CH_2NH_2$), 132.28 (Ph), 132.79 (Ph), 132.92 (Ph), 137.56 (Ph).

An aqueous solution of $[\mathbf{2a}]Cl_8 \cdot 13H_2O$ was chromatographed on an SP-Sephadex C-25 column ($Na^+$ form, 2 cm × 40 cm), using a 0.50 mol $dm^{-3}$ aqueous solution of $Na_2[Sb_2(R,R\text{-tartrato})_2] \cdot 5H_2O$ as an eluent. When the developed band was completely separated into two bands in the column, the eluent was changed to a 1.0 mol $dm^{-3}$ aqueous solution of NaCl. Each eluate of the two bands was concentrated to a small volume, and the concentrated solution was used for the CD spectral measurement. The concentration of each solution was evaluated on the basis of the absorption spectral data of the *racemic* chloride salt. It was found from the absorption and CD spectral measurements that the earlier and the later moving bands in the column contained the $(+)^{CD}_{520}$ and $(-)^{CD}_{520}$ isomers, respectively.

## 4.2. Physical measurements

The electronic absorption spectra were recorded on a Ubest-55 spectrophotometer and the CD spectra on a JASCO J-700 spectropolarimeter at room temperature. The elemental analyses (C, H, N) were performed at Osaka University. The $^1H$ and $^{13}C$ NMR spectra were recorded on a JEOL JNM-A500 NMR spectrometer at the probe temperature in $D_2O$, using sodium 4,4-dimetyl-4-silapentane-1-sulfonate (DSS) as the internal reference.

## 4.3. X-ray structural determination

Single crystal X-ray diffraction measurements for $[\mathbf{1}](ClO_4)(NO_3)_7 \cdot 13H_2O$ was made on a Rigaku RAXIS-RAPID imaging plate area detector, while those for $[\mathbf{2a}]Cl_8 \cdot 17H_2O$ and $[\mathbf{2b}]Cl_8 \cdot 17H_2O$ were made on a Rigaku AFC5R four-cycle diffractometer with a graphite monochromated Mo-K$\alpha$ radiation. Crystallographic data are summarized in Table 2. Unit cell parameters were determined by a least-squares refinement. The intensity data were collected by the $\omega$ scan mode up to $2\theta_{max} = 55.0°$ for $[\mathbf{1}](ClO_4)(NO_3)_7 \cdot 13H_2O$ and by the $\omega$-$2\theta$ scan mode up to $2\theta = 40.1°$ for $[\mathbf{2a}]Cl_8 \cdot 17H_2O$ and up to $2\theta = 55.0°$ for $[\mathbf{2b}]Cl_8 \cdot 17H_2O$ [24]. The intensities were corrected for Lorentz and polarization. The 6594, 2959, and 8189 independent reflections with $I > 2\sigma(I)$ of the measured 15948, 8598, and 20180 reflections were considered as "observed" and used for the structure determinations of $[\mathbf{1}](ClO_4)(NO_3)_7 \cdot 13H_2O$, $[\mathbf{2a}]Cl_8 \cdot 17H_2O$, and $[\mathbf{2b}]Cl_8 \cdot 17H_2O$, respectively.

Each structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms except some disordered anions and water molecules were refined anisotropically by full-matrix least-squares methods for $[\mathbf{1}](ClO_4)(NO_3)_7 \cdot 13H_2O$. For $[\mathbf{2a}]Cl_8 \cdot 17H_2O$, only Pd, Co, S, and Cl atoms were refined anisotropically, while the other non-hydrogen atoms were refined isotropically. For $[\mathbf{2b}]Cl_8 \cdot 17H_2O$, all the non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms except those of water molecules were placed at calculated positions but were not refined. All calculations were performed using the CrystalStructure crystallographic software package [25].

## Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 16033235) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

## Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 299775, 299776, and 299777. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing to data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033. Figures of molecular structures of [**2a**]$^{8+}$ and [**2b**]$^{8+}$ involving accommodated water molecule(s) and $^{13}$C and $^{1}$H NMR spectra of [**1**]$^{8+}$, [**2a**]$^{8+}$, and [**2b**]$^{8+}$ are available (Figs. S1–S3). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.059.

## References

[1] J.M. Lehn, Science 295 (2002) 2400.
[2] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi, Science 295 (2002) 469.
[3] R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R.V. Belosludov, T.C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, Nature 436 (2005) 238.
[4] T. Konno, Bull. Chem. Soc. Jpn. 77 (2004) 627.
[5] P.J. Stang, B. Olenyuk, Acc. Chem. Res. 30 (1997) 502.
[6] S. Leininger, B. Olenyuk, P.J. Stang, Chem. Rev. 100 (2000) 853.
[7] D. Fiedler, D.H. Leung, R.G. Bergman, K.N. Raymond, Acc. Chem. Res. 38 (2005) 351.
[8] S. Hiraoka, K. Harano, M. Shiro, M. Shionoya, Angew. Chem., Int. Ed. 44 (2005) 2727.
[9] C.S. Campos-Femández, B.L. Schottel, H.T. Chifotides, J.K. Bera, J. Bacsa, J.M. Koomen, D.H. Russel, K.R. Dunbar, J. Am. Chem. Soc. 127 (2005) 12909.
[10] A. Hori, T. Sawada, K. Yamashita, M. Fujita, Angew. Chem., Int. Ed. 44 (2005) 4896.
[11] S.P. Argent, H. Adams, T. Riis-Johannessen, J.C. Jeffery, L.P. Harding, M.D. Ward, J. Am. Chem. Soc. 128 (2006) 72.
[12] A. Toyota, T. Yamaguchi, A. Igashira-kamiyama, T. Kawamoto, T. Konno, Angew. Chem., Int. Ed. 44 (2005) 1088.
[13] R.C. Elder, G.J. Kennard, M.D. Payne, E. Deutsch, Inorg. Chem. 17 (1978) 1296.
[14] S.G. Murray, F.R. Hartley, Chem. Rev. 81 (1981) 365.
[15] B. Krebs, G. Henkel, Angew. Chem., Int. Ed. Engl. 30 (1991) 769.
[16] K. Yamanari, Y. Shimura, Bull. Chem. Soc. Jpn. 56 (1983) 2283.
[17] M.Y. Darensbourg, I. Font, D.K. Mills, M. Pala, J.H. Reibenspies, Inorg. Chem. 31 (1992) 4965.
[18] D.C. Goodman, R.M. Buonomo, P.J. Farmer, J.H. Reibenspies, M.Y. Darensbourg, Inorg. Chem. 35 (1996) 4029.
[19] G. Musie, J.H. Reibenspies, M.Y. Darensbourg, Inorg. Chem. 37 (1998) 302.
[20] M. Hirotsu, A. Kobayashi, T. Yoshimura, T. Konno, J. Chem. Soc., Dalton Trans. (2002) 878.
[21] T. Konno, Y. Chikamoto, K. Okamoto, T. Yamaguchi, T. Ito, M. Hirotsu, Angew. Chem., Int. Ed. 39 (2000) 4098.
[22] Y. Chikamoto, M. Hirotsu, T. Yoshimura, T. Yamaguchi, T. Ito, T. Kawamoto, T. Konno, Dalton Trans. (2004) 3654.
[23] Y. Chikamoto, M. Hirotsu, T. Kawamoto, T. Konno, Chem. Lett. (2005) 362.
[24] Due to a rapid, significant decay of the crystal, only a part of the complete data set (up to $2\theta = 40.1°$) was collected for [**2a**]$Cl_8 \cdot 17H_2O$, and thus empirical absorption correction could not be applied.
[25] Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.