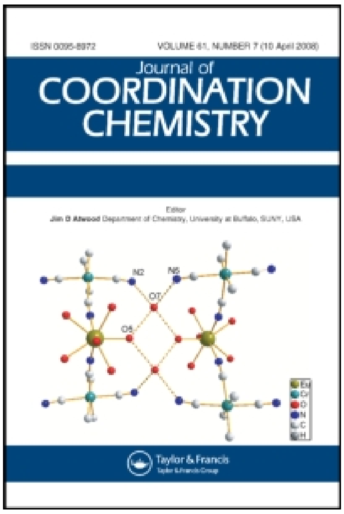

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Stereospecific dimerization through π-conjugated systems of sulfur-bridged dinuclear cobalt(III)-platinum(II) complexes of 1,2-propanediamine

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Reaction of Λ,Λ-$[Ni\{Co(aet)_2(S\text{-}pn)\}_2]^{4+}$ (aet = 2-aminoethanethiolate pn = 1,2-propanediamine) in which Λ-cis(S)-$[Co(aet)_2(S\text{-}pn)]^+$ units act as bidentate metalloligands with $[PtCl_2(bpy)]$ (bpy = 2,2′-bipyridine) gave an optically active S-bridged dinuclear complex Λ-$[Pt(bpy)\{Co(aet)_2(S\text{-}pn)\}](ClO_4)_3$ (**2**) whose structure is enantiomeric to that previously reported for Δ-$[Pt(bpy)\{Co(aet)_2(S\text{-}pn)\}]$ $(ClO_4)_3$ (**1**). A mixture of equimolar amounts of **1**$(ClO_4)_3$ and **2**$(ClO_4)_3$ in H2O crystallizes as Δ-$[Pt(bpy)\{Co(aet)_2(R\text{-}pn)\}]_{0.5}\Lambda$-$[Pt(bpy)\{Co(aet)_2(S\text{-}pn)\}]_{0.5}(ClO_4)_3 \cdot 2H_2O$ $({}_3(ClO_4)_3 \cdot 2H2O)$ in which the enantiomeric complex cations **1** and **2** are included at a ratio of 1 : 1. The structure of **2** is consistent with that for **1** except for the absolute configuration at Co(III). The optically active cation in 2 exists as a monomer accompanied by no intermolecular π interactions with bpy moieties. However in crystals of **3**$(ClO_4)_3 \cdot 2H_2O$ the enantiomeric complex cations Δ-$[Pt(bpy)\{Co(aet)_2(R\text{-}pn)\}]^{3+}$ and Λ-$[Pt(bpy)\{Co(aet)_2(S\text{-}pn)\}]^{3+}$ interact stereospecifically with each other through π-conjugated systems to form dimeric structures.

Keywords: Co(III)–Pt(II) complexes; 2,2′-Bipyridine; 2-Aminoethanethiolate; 1,2-Propanediamine; Crystal structure; Dimer

1. Introduction

It is well known that the mononuclear metal complexes ligated by β-aminoalkylthiolates such as 2-aminoethanethiolate (aet), L-cysteinate (L-cys), and D-penicillaminate (D-pen), in which the coordinated sulfur atoms possess further nucleophilicity, can bridge various metal species to form S-bridged polynuclear structures [1–11]. Among such mononuclear β-aminoalkylthiolate complexes, octahedral species are particularly diversified in terms of reactivity and stereochemistry, and hence make possible construction of a wide variety of S-bridged polynuclear complexes [1–5, 7–11].

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In cases where additional ligands with π electronic systems, such as 2,2′-bipyridine (bpy), are introduced, structural and functional variation is introduced in resulting S-bridged polynuclear complexes [12–15]. Recently, we have shown that octahedral mononuclear complexes ligated by β-aminoalkylthiolates react with $[MX_2(bpy)]$ (M = Pd(II), Pt(II); X = Cl, NO_3), to form simple dinuclear complexes composed of $[M(\mu\text{-}S)_2(bpy)]$ frameworks and octahedral d^6 metal units [16]. For instance, *fac*-(S)-$[Co(aet)_3]$ reacts with $[PtCl_2(bpy)]$ (bpy = 2,2′-bipyridine) to afford dinuclear $[Pt(bpy)\{Co(aet)_3\}]^{2+}$ [16]. A similar reaction of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ (en = ethylenediamine), in which the two terminal *cis*-(S)-$[Co(aet)_2(en)]^+$ units can be regarded as bidentate S-donating metalloligands, with $[PtCl_2(bpy)]$ gives $[Pt(bpy)\{Co(aet)_2(en)\}]^{3+}$ [16]. On the other hand, an optically active dinuclear analogue, Δ-$[M(bpy)\{Co(aet)(R\text{-}pn)\}]^{3+}$ (M = Pd(II) or Pt(II), pn = 1,2-propanediamine), is stereoselectively obtained by the reaction of Δ,Δ-$[Ni\{Co(aet)_2(R\text{-}pn)\}_2]^{4+}$ with $[MX_2(bpy)]$ (X = Cl or NO_3) [17, 18]. Furthermore, analogous reaction of *trans*-(N)-$[Co(\text{D-pen-}N,O,S)_2]^-$ with $[MCl_2(bpy)]$ (M = Pd(II) or Pt(II)) also leads to the formation of optically active $[M(bpy)\{Co(\text{D-pen})\}_2]^+$ [18]. While these optically active dinuclear complexes exist as monomers in the solid state, the racemic dinuclear complexes afford dimeric or higher dimensional linear-chain structures due to π–π stacking interactions between bpy groups in the dinuclear units [16–18]. This suggests some stereospecific interaction between the π frameworks, which are rather remote from the chiral octahedral centre. In order to obtain more detailed information on the stereospecific π–π interactions, we have the assembly of optically active Δ-$[Pt(bpy)\{Co(aet)(R\text{-}pn)\}]^{3+}$ and Λ-$[Pt(bpy)\{Co(aet)(S\text{-}pn)\}]^{3+}$ from stereo- and spectrochemical viewpoints.

2. Experimental

2.1. *Materials*

$CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, K_2PtCl_4, 2-aminoethanethiol hydrochloride, 2,2′-bipyridine, $AgNO_3$, $AgClO_4$ and 1,2-propanediamine were commercially available and used as received. $[Ni\{Co(aet)_2(R\text{-}pn)\}_2]Cl_4 \cdot 6H_2O$, $[Ni\{Co(aet)_2(S\text{-}pn)\}_2]Cl_4 \cdot 6H_2O$, and $[PtCl_2(bpy)]$ were prepared using modified literature methods [3, 17–19]. $[Pt(bpy)\{Co(aet)_2(R\text{-}pn)\}](ClO_4)_3$ (**1**$(ClO_4)_3$) was synthesized by a previously reported procedure [18].

2.2. *Preparation of $[Pt(bpy)\{Co(aet)_2(R\text{-}pn)\}](NO_3)_3 \cdot 7H_2O$ ($1(NO_3)_3 \cdot 7H_2O$)*

To a reddish brown solution of $[Ni\{Co(aet)_2(R\text{-}pn)\}_2]Cl_4 \cdot 6H_2O$ (0.22 g, 0.25 mmol) in 50 cm^3 of H_2O was added $[PtCl_2(bpy)]$ (0.21 g, 0.5 mmol). The mixture was stirred at 55°C for 1 h, whereupon it became dark red. The solution was cooled to room temperature followed and $AgNO_3$ (0.34 g, 2 mmol) in 5 cm^3 of H_2O was added. After removing precipitated AgCl by filtration, the filtrate was evaporated to one tenth of its original volume under reduced pressure. After ca 20 cm^3 of acetone was added, the whole was allowed to stand at 25°C for several days. The resulting dark red microcrystalline powder was collected by filtration. Yield: 0.33 g (70% based on Co).

Anal. Calcd for $C_{17}H_{44}N_9O_{16}S_2CoPt$ (**1**$(NO_3)_3 \cdot 7H_2O$) (%): C, 21.52; H, 4.67; N, 13.29. Found: C, 21.50; H, 4.70; N, 13.18. Electronic spectrum in H_2O [ν_{max}, $10^3\,cm^{-1}$ (log $\varepsilon/M^{-1}\,cm^{-1}$)]: 20.00 (2.49), 25.3 (3.1sh), 29.3 (3.9sh), 31.35 (4.38), 32.57 (4.37), 38.3 (4.4sh), 41.8 (4.3sh). CD spectrum in H_2O [ν_{max}, $10^3\,cm^{-1}$ ($\Delta\varepsilon/M^{-1}\,cm^{-1}$)]: 19.49 (−7.12), 25.25 (−7.75), 30.7 (+12.5 sh), 34.25 (+26.85), 37.0 (+11.0sh), 39.8 (−9.2sh), 45.66 (−54.95). Diffuse reflectance spectrum [ν_{max}, $10^3\,cm^{-1}$]: 19.82, 25.1sh, 28.4sh, 30.77, 32.1sh, 37.2sh, 40.1sh.

2.3. *Preparation of [Pt(bpy){Co(aet)$_2$(S-pn)}](ClO$_4$)$_3$ (2(ClO$_4$)$_3$)*

To a reddish brown solution of $[Ni\{Co(aet)_2(S\text{-}pn)\}_2]Cl_4 \cdot 6H_2O$ (0.22 g, 0.25 mmol) in 50 cm^3 of H_2O was added $[PtCl_2(bpy)]$ (0.21 g, 0.5 mmol). The mixture was stirred at 55°C for 1 h, whereupon it became red. The red solution was cooled to room temperature and $AgClO_4$ (0.41 g, 2 mmol) in 5 cm^3 of H_2O was added. After removing precipitated AgCl by filtration, the dark red filtrate was evaporated to one-fifth of its original volume under reduced pressure. After ca 10 cm^3 of saturated aqueous $NaClO_4$ solution was added, the whole was allowed to stand at 4°C for several days. The resulting dark red microcrystalline powder was collected by filtration, and recrystallized by vapor diffusion of diethylether into a CH_3CN solution. Yield: 0.35 g (75% based on Co). Anal. Calcd for $C_{17}H_{30}N_6O_{12}S_2Cl_3CoPt$ (**2**$(ClO_4)_3$) (%): C, 21.84; H, 3.23; N, 9.99. Found: C, 21.88; H, 3.25; N, 9.8. Electronic spectrum in H_2O [ν_{max}, $10^3\,cm^{-1}$ (log $\varepsilon/M^{-1}\,cm^{-1}$)]: 20.00 (2.46), 25.6 (3.1sh), 29.5 (3.8sh), 31.35 (4.32), 32.57 (4.30), 38.2 (4.3sh), 42.0 (4.5sh). CD spectrum in H_2O [ν_{max}, $10^3\,cm^{-1}$ ($\Delta\varepsilon/M^{-1}\,cm^{-1}$)]: 19.57 (+6.47), 25.25 (+6.19), 30.5 (−11.0sh), 34.25 (−24.85), 37.0 (−11.4sh), 39.5 (+7.8sh), 45.66 (+49.07). Diffuse reflectance spectrum [ν_{max}, $10^3\,cm^{-1}$]: 19.84, 25.3sh, 28.4sh, 30.77, 32.1sh 37.3sh, 40.0sh.

2.4. *Preparation of [Pt(bpy){Co(aet)$_2$(S-pn)}](NO$_3$)$_3$ · 7H$_2$O (2(NO$_3$)$_3$ · 7H$_2$O)*

This complex was prepared by a similar method to that used for **1**$(NO_3)_3 \cdot 7H_2O$, using $[Ni\{Co(aet)_2(S\text{-}pn)\}_2]Cl_4 \cdot 6H_2O$ instead of $[Ni\{Co(aet)_2(R\text{-}pn)\}_2]Cl_4 \cdot 6H_2O$. Yield: 0.30 g (63% based on Co). Anal. Calcd for $C_{17}H_{44}N_9O_{16}S_2CoPt$ (**2**$(NO_3)_3 \cdot 7H_2O$) (%): C, 21.52; H, 4.67; N, 13.29. Found: C, 21.54; H, 4.69; N, 13.20. Electronic spectrum in H_2O [ν_{max}, $10^3\,cm^{-1}$ (log $\varepsilon/M^{-1}\,cm^{-1}$)]: 19.96 (2.49), 25.3 (3.1sh), 29.3 (3.9sh), 31.35 (4.36), 32.57 (4.34), 38.3 (4.4sh), 41.8 (4.5sh). CD spectrum in H_2O [ν_{max}, $10^3\,cm^{-1}$ ($\Delta\varepsilon/M^{-1}\,cm^{-1}$)]: 19.53 (+7.28), 25.25 (+6.97), 30.7 (−13.0sh), 34.25 (−27.88), 37.0 (−11.8sh), 39.8 (+9.1sh), 45.46 (+55.92). Diffuse reflectance spectrum [ν_{max}, $10^3\,cm^{-1}$]: 19.67, 25.2sh, 28.4sh, 30.77, 32.1sh, 37.2sh, 40.0sh.

2.5. *Preparation of [Pt(bpy){Co(aet)$_2$(R-pn)}]$_{0.5}$ [Pt(bpy){Co(aet)$_2$(S-pn)}]$_{0.5}$(ClO$_4$)$_3$ · 2H$_2$O (3(ClO$_4$)$_3$ · 2H$_2$O)*

To a red solution of **1**$(ClO_4)_3$ (0.10 g, 0.11 mmol) in 10 cm^3 of H_2O was added **2**$(ClO_4)_3$ (0.10 g, 0.11 mmol) in 10 cm^3 of H_2O. After the mixture was allowed to stand at 25°C for several days, dark red crystals were collected by filtration. Yield: 0.18 g (84% based on Co). Anal. Calcd for $C_{17}H_{34}N_6O_{14}S_2Cl_3CoPt$ (**3**$(ClO_4)_3 \cdot 2H_2O$) (%): C, 21.03;

H, 3.53; N, 8.66. Found: C, 21.05; H, 3.55; N, 8.59. Electronic spectrum in H_2O [ν_{max}, $10^3\,cm^{-1}$ ($\log\varepsilon/M^{-1}\,cm^{-1}$)]: 20.00 (2.46), 25.3 (3.0sh), 29.4 (3.8sh), 31.35 (4.33), 32.57 (4.32), 38.2 (4.3sh), 41.7 (4.5sh). Diffuse reflectance spectrum [ν_{max}, $10^3\,cm^{-1}$]: 19.72, 25.4sh, 28.0sh, 30.91, 32.3sh, 37.1sh, 39.8sh.

2.6. *Preparation of [Pt(bpy){Co(aet)$_2$(R-pn)}]$_{0.5}$ [Pt(bpy){Co(aet)$_2$(S-pn)}]$_{0.5}$(NO$_3$)$_3$ · 2H$_2$O (3(NO$_3$)$_3$ · 2H$_2$O)*

To a red solution of **1**$(NO_3)_3 \cdot 7H_2O$ (0.11 g, 0.11 mmol) in $10\,cm^3$ of H_2O was added **2**$(NO_3)_3 \cdot 7H_2O$ (0.11 g, 0.11 mmol) in $10\,cm^3$ of H_2O. After the mixture was allowed to stand at 25°C for several days, the resulting dark red crystals were collected by filtration. Yield: 0.16 g (85% based on Co). Anal. Calcd for $C_{17}H_{34}N_9O_{11}S_2CoPt$ (**3**$(NO_3)_3 \cdot 2H_2O$) (%): C, 23.78; H, 3.99; N, 14.68. Found: C, 23.81; H, 4.01; N, 14.65. Electronic spectrum in H_2O [ν_{max}, $10^3\,cm^{-1}$ ($\log\varepsilon/M^{-1}\,cm^{-1}$)]: 19.96 (2.74), 25.4 (3.3sh), 29.2 (4.1sh), 31.35 (4.62), 32.57 (4.60), 38.3 (4.6sh), 41.7 (4.8sh). Diffuse reflectance spectrum [ν_{max}, $10^3\,cm^{-1}$]: 19.76, 27.0sh, 30.72, 31.9sh, 37.0sh, 39.8sh.

2.7. *Measurements*

Electronic spectra were recorded with a Perkin Elmer Lambda 19 spectrophotometer, and CD spectra with a JASCO J-600 spectropolarimeter. These measurements were carried out using aqueous solutions at room temperature. Diffuse reflectance spectra were measured with a Jasco Ubest V-570 spectrophotometer equipped with an integrating sphere apparatus. ^1H and 13C NMR spectra were recorded with a Bruker AVANCE-600 NMR spectrometer in a 1 : 1 mixed solvent of CD_3CN and D_2O for **2**$(ClO_4)_3$ and **3**$(ClO_4)_3 \cdot 2H_2O$, or in D_2O for **1**$(NO_3)_3 \cdot 7H_2O$, **2**$(NO_3)_3 \cdot 7H_2O$, and **3**$(NO_3)_3 \cdot 2H_2O$, using sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) as internal reference. Elemental analyses (C,H,N) were performed with a Perkin-Elmer 2400 system.

2.8. *X-ray crystallography*

Single crystals of **2**$(ClO_4)_3$, **3**$(ClO_4)_3 \cdot 2H_2O$, and **3**$(NO_3)_3 \cdot 2H_2O$ were used for data collection on a Rigaku AFC5S automated four-circle diffractometer with graphite-monochromatized Mo-Kα ($\lambda = 0.71069$ Å) radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections in the range $10° < \theta < 15°$ for **2**$(ClO_4)_3$, **3**$(ClO_4)_3 \cdot 2H_2O$, and **3**$(NO_3)_3 \cdot 2H_2O$. Data were collected at 296 ± 1 K using the $\omega - 2\theta$ (for **2**$(ClO_4)_3$ and **3**$(NO_3)_3 \cdot 2H_2O$) or ω scan technique (for **3**$(ClO_4)_3 \cdot 2H_2O$) to a maximum 2θ value of 55°. Weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 5 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2 : 1. Intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards changed by −2.4 to +1.1%. Polynomial correction factors were applied to the data to account for this phenomenon. Empirical absorption corrections based on

Table 1. Crystallographic data for **2**$(ClO_4)_3$, **3**$(ClO_4)_3 \cdot 2H_2O$, and **3**$(NO_3)_3 \cdot 2H_2O$.

	2$(ClO_4)_3$	**3**$(ClO_4)_3 \cdot 2H_2O$	**3**$(NO_3)_3 \cdot 2H_2O$
Formula	$C_{17}H_{30}N_6O_{12}S_2Cl_3CoPt$	$C_{17}H_{34}N_6O_{14}S_2Cl_3CoPt$	$C_{17}H_{34}N_9O_{11}S_2CoPt$
Formula weight	934.96	970.99	858.65
Crystal size (mm)	0.50 × 0.50 × 0.60	0.20 × 0.20 × 0.50	0.20 × 0.20 × 0.50
Space group	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$
a (Å)	14.142(4)	9.201(5)	
b (Å)	16.966(2)	26.117(6)	
c (Å)	12.909(2)	14.076(6)	
α (°)			91.69(1)
β (°)		108.49(4)	97.89(2)
γ (°)			104.52(2)
V (Å^3)	3097(1)	3207(2)	1444.9(5)
Z	4	4	2
D_c (g cm^{-3})	2.005	2.010	1.974
μ (cm^{-1})	54.87	53.06	56.04
Trans. factors	0.48–1.00	0.70–1.00	0.54–1.00
Tot. reflections	7980	8021	14314
Refl. $I > 2\sigma(I)$	2367	3713	4456
No. of variables	421	427	411
R (R_w)	0.044 (0.055)	0.052 (0.070)	0.047 (0.068)
Goodness-of fit on F^2	1.01	1.00	1.0

azimuthal scans of several reflections were applied. The data were corrected for Lorentz and polarization effects. Crystal data and experimental parameters are summarized in table 1.

The structures were solved by direct methods for **2**$(ClO_4)_3$ and **3**$(ClO_4)_3 \cdot 2H_2O$, and Patterson methods for **3**$(NO_3)_3 \cdot 2H_2O$, and expanded using Fourier techniques [20–22]. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined using the riding model. The final cycles of full-matrix least-squares refinement on F was based on observed reflections ($I > 2.00\sigma(I)$) and variable parameters, and converged smoothly. Neutral atom scattering factors were taken from Cromer and Waber [23]. Anomalous dispersion effects were included in Fc; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [24–26]. The absolute configuration for **2**$(ClO_4)_3$ was determined on the basis of the known S configuration of the asymmetric carbon atom in the S-pn ligand, and the structure was supported by the Flack parameter (0.03(2) for **2**$(ClO_4)_3$) [27]. All calculations were performed using the Crystal Structure crystallographic software package of Molecular Structure Corporation [28].

3. Results and discussion

X-ray structural analysis of **2**$(ClO_4)_3$ revealed the presence of a discrete trivalent complex cation and three perchlorate anions. A perspective drawing of the cation is given in figure 1, and selected bond distances and angles are listed in table 2. As shown in figure 1, **2** has an S-bridged dinuclear structure. The Co atom is surrounded by two N and S atoms of two aet ligands, and two N atoms of one S-pn. Equatorial coordination sites of Co atom are occupied by two N and S atoms, and axial sites by two N atoms to form an octahedral *cis*-(S)-$[Co(aet)_2(S\text{-}pn)]^+$ unit. The flack parameter indicates that all

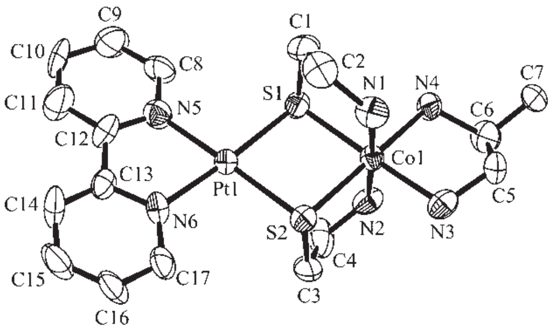

Figure 1. Perspective view of **2** with the atom labelling scheme.

of the crystals of **2**$(ClO_4)_3$ contain of only the Λ isomer [27]. Furthermore, the absolute configuration of **2**$(ClO_4)_3$ was supported by e known *S* configuration of the asymmetric carbon atom in the S-pn ligand. It is concluded that the geometry of octahedral Co(III) unit in the starting material, Λ,Λ-$[Ni\{Co(aet)_2(S\text{-}pn)\}_2]^{4+}$, is retained during the formation of **2**$(ClO_4)_3$. The Pt atom in **2** is coordinated by two N atoms of bpy and bridged by two S atoms from the Λ-*cis*-(S)-$[Co(aet)_2(S\text{-}pn)]^+$ units to adopt square planar geometry. The Co(III) equatorial plane and PtS_2N_2 plane in **2** are almost coplanar (dihedral angle 3.4°) and the Pt atom in **2** is almost perfectly square planar geometry (dihedral angle between the PtS1S2 and PtN5N6 planes 3.8°). Although two chiral configurations, *R* and *S*, are possible for each of the two bridging S atoms in **2**, both S atoms are stereoselectively of *S* configuration, in contrast to the S atoms with *R* configurations in Δ-*cis*-(S)-$[Co(aet)_2(R\text{-}pn)]^+$ unit of **1**$(ClO_4)_3$. In crystals of **2**$(ClO_4)_3$, as shown in figure 2, two perchlorate anions are located in the vicinity of the Pt(II) centre of complex cation **2**. The shortest contact of Pt(II) with a perchlorate oxygen atom (O1) is 3.89(3) Å. Another perchlorate anion (symmetry operators: $x+1/2$, $-y+1/2$, $-z+1$) lies close the Pt(II) centre (Pt1-O4′ = 4.06(2) Å). It seems that such arrangements result in no π–π stacking between bpy frameworks of neighboring cations.

The mixture of equimolar amounts of **1**$(ClO_4)_3$ and **2**$(ClO_4)_3$ in H_2O crystallizes as **3**$(ClO_4)_3 \cdot 2H_2O$ in the centric space group $P2_1/c$, in contrast with the acentric space group $P2_12_12_1$ for **1**$(ClO_4)_3$ or **2**$(ClO_4)_3$ (table 1) [18]. Although the enantiomeric complex cations, Δ-$[Pt(bpy)\{Co(aet)_2(R\text{-}pn)\}]^{3+}$ and Λ-$[Pt(bpy)\{Co(aet)_2(S\text{-}pn)\}]^{3+}$, are included at a ratio of 1 : 1 in crystals of **3**$(ClO_4)_3 \cdot 2H_2O$, only one monovalent complex cation is a crystallographically independent component. As shown in table 2, there are no significant distinctions in bond distances and angles around the Co(III) and Pt(II) atoms between **3**$(ClO_4)_3 \cdot 2H_2O$ and **2**$(ClO_4)_3$ (or **1**$(ClO_4)_3$) [18]. However, the Co(III) equatorial plane and PtS_2N_2 plane in **3**$(ClO_4)_3 \cdot 2H_2O$ are somewhat bent in comparison with **2**$(ClO_4)_3$ (dihedral angle for **3**$(ClO_4)_3 \cdot 2H_2O$:, 4.9°). This indicates some intermolecular interactions alternative to those in the crystals of **2**$(ClO_4)_3$. In fact, as shown in figure 3, a pair of enantiomeric complex cations, Δ-$[Pt(bpy)\{Co(aet)_2(R\text{-}pn)\}]^{3+}$ (***R***) and Λ-$[Pt(bpy)\{Co(aet)_2(S\text{-}pn)\}]^{3+}$ (***S***), forms a dimeric unit through π–π stacking of the bpy framework; the interplanar distance between bpy ligands in the dimeric unit is 3.58 Å. The opposite side of the bpy plane in Δ-$[Pt(bpy)\{Co(aet)_2(R\text{-}pn)\}]^{3+}$ or Λ-$[Pt(bpy)\{Co(aet)_2(S\text{-}pn)\}]^{3+}$ is occupied by

Table 2. Selected bond distances (Å) and angles (°) for **2**$(ClO_4)_3$, **3**$(ClO_4)_3 \cdot 2H_2O$, and **3**$(NO_3)_3 \cdot 2H_2O$.

	2$(ClO_4)_3$	**3**$(ClO_4)_3 \cdot 2H_2O$	**3**$(NO_3)_3 \cdot 2H_2O$
Pt(1)–S(1)	2.290(5)	2.276(3)	2.278(3)
Pt(1)–S(2)	2.288(5)	2.288(4)	2.298(3)
Pt(1)–N(5)	2.02(2)	2.02(1)	2.041(9)
Pt(1)–N(6)	2.03(2)	2.060(9)	2.05(1)
Co(1)–S(1)	2.239(5)	2.233(4)	2.231(3)
Co(1)–S(2)	2.252(6)	2.236(4)	2.250(3)
Co(1)–N(1)	1.98(2)	1.98(1)	1.97(1)
Co(1)–N(2)	1.96(2)	1.98(1)	1.99(1)
Co(1)–N(3)	2.02(2)	2.00(1)	1.997(9)
Co(1)–N(4)	1.98(1)	1.98(1)	1.965(9)
Pt(1)–S(1)–Co(1)	96.1(2)	96.2(1)	95.9(1)
S(2)–Pt(1)–S(1)	83.0(2)	82.8(1)	83.5(1)
N(5)–Pt(1)–S(1)	99.0(5)	97.3(3)	96.8(3)
N(6)–Pt(1)–S(1)	175.2(5)	177.6(4)	177.5(3)
Pt(1)–S(2)–Co(1)	95.8(2)	95.8(1)	94.8(1)
N(5)–Pt(1)–S(2)	177.9(5)	176.8(4)	178.9(3)
N(6)–Pt(1)–S(2)	99.9(5)	98.9(3)	98.8(3)
N(6)–Pt(1)–N(5)	78.0(7)	80.9(4)	80.9(4)
S(2)–Co(1)–S(1)	85.0(2)	84.9(1)	85.7(1)
N(1)–Co(1)–S(1)	88.0(5)	88.5(4)	87.8(3)
N(2)–Co(1)–S(1)	90.5(5)	91.2(4)	89.7(3)
N(3)–Co(1)–S(1)	177.4(5)	177.5(4)	178.7(3)
N(4)–Co(1)–S(1)	94.1(5)	94.4(4)	93.8(3)
N(1)–Co(1)–S(2)	88.9(5)	89.3(3)	90.1(3)
N(2)–Co(1)–S(2)	88.2(5)	88.0(4)	87.5(3)
N(3)–Co(1)–S(2)	96.0(5)	95.2(3)	95.4(3)
N(4)–Co(1)–S(2)	177.9(5)	178.3(3)	179.0(3)
N(2)–Co(1)–N(1)	176.9(7)	177.3(5)	176.7(4)
N(3)–Co(1)–N(1)	89.6(6)	89.0(5)	91.5(4)
N(4)–Co(1)–N(1)	93.0(6)	92.2(5)	90.7(4)
N(3)–Co(1)–N(2)	92.0(6)	91.2(6)	91.0(4)
N(4)–Co(1)–N(2)	89.9(7)	90.5(5)	91.6(4)
N(4)–Co(1)–N(3)	85.0(6)	85.6(5)	85.1(4)

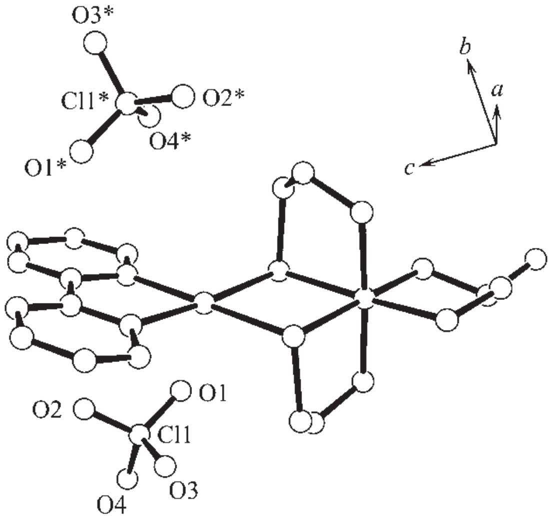

Figure 2. Monomeric structure of the optically active complex cation in **2**$(ClO_4)_3$ with neighbouring perchlorate anions.

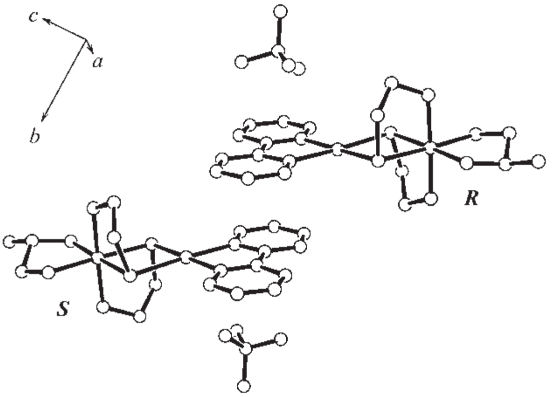

Figure 3. Dimeric structures comprised of enantiomeric complex cations, Δ-[Pt(bpy){Co(aet)$_2$(R-pn)}]$^{3+}$ (***R***) and Λ-[Pt(bpy){Co(aet)$_2$(S-pn)}]$^{3+}$ (***S***), in **3**(ClO$_4$)$_3$ · 2H$_2$O with neighbouring counter anions.

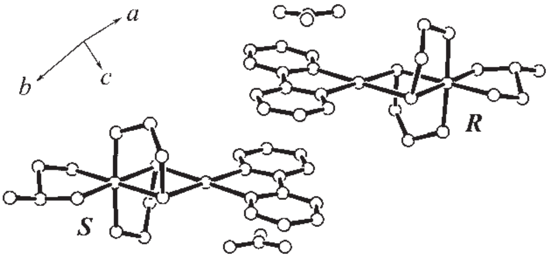

Figure 4. Dimeric structures comprised of enantiomeric complex cations, Δ-[Pt(bpy){Co(aet)$_2$(R-pn)}]$^{3+}$ (***R***) and Λ-[Pt(bpy){Co(aet)$_2$(S-pn)}]$^{3+}$ (***S***), in **3**(NO$_3$)$_3$ · 2H$_2$O with neighbouring counter anions.

a perchlorate anion. In crystals of **3**(NO$_3$)$_3$ · 2H$_2$O, as shown in figure 4, Δ-[Pt(bpy){Co(aet)$_2$(R-pn)}]$^{3+}$ (***R***) and Λ-[Pt(bpy){Co(aet)$_2$(S-pn)}]$^{3+}$ (***S***) cations build a similar dimeric structure with π–π stacking between bpy ligands (interplanar distance, 3.47 Å). In addition, one of the nitrate anions occupies the other side of the bpy plane and the interplanar distance and dihedral angle between the NO$_3$ ion and bpy are 3.31 Å and 12.3°, respectively. This implies that the arrangement of counter anions affects the dimeric structure. In the crystal a linear-chain structure due to π–π stacking is formed [16]. It is clear therefore that the dimeric structure is also influenced by the terminal diamine ligand in the octahedral unit.

In CD$_3$CN/D$_2$O (1 : 1), the ^{13}C NMR spectrum of **2**(ClO$_4$)$_3$ shows six signals due to the ligands in the octahedral Co(III) unit and five signals characteristic of the coordinated bpy ligand [3, 8, 17, 18] (table 3). Although two kinds of the complex cations, Δ-[Pt(bpy){Co(aet)$_2$(R-pn)}]$^{3+}$ and Λ-[Pt(bpy){Co(aet)$_2$(S-pn)}]$^{3+}$, exist in **3**(ClO$_4$)$_3$ · 2H$_2$O, the ^{13}C NMR spectrum exhibits eleven signals due to one S-pn, two aet, and one bpy ligands. Furthermore, the pattern of **3**(ClO$_4$)$_3$ · 2H$_2$O is quite similar to those of **1**(ClO$_4$)$_3$ and **2**(ClO$_4$)$_3$. A similar trend is also observed for the hydrogen atoms of bpy in ^{1}H NMR spectra of **1**(ClO$_4$)$_3$, **2**(ClO$_4$)$_3$, and **3**(ClO$_4$)$_3$ · 2H$_2$O [18]. These facts indicate no detectable intermolecular interactions at the chosen concentration of 10^{-2} mol dm^{-3}.

Table 3. ^{1}H and ^{13}C NMR chemical shifts[a] for **2**$(ClO_4)_3$ and **3**$(ClO_4)_3 \cdot 2H_2O$ in a 1 : 1 mixed solvent of CD_3CN and D_2O, and **1**$(NO_3)_3 \cdot 7H_2O$, **2**$(NO_3)_3 \cdot 7H_2O$, and **3**$(NO_3)_3 \cdot 2H_2O$ in D_2O.

	2$(ClO_4)_3$	**3**$(ClO_4)_3 \cdot 2H_2O$	**1**$(NO_3)_3 \cdot 7H_2O$	**2**$(NO_3)_3 \cdot 7H_2O$	**3**$(NO_3)_3 \cdot 2H_2O$
^{1}H NMR					
$–CH_2N$ (aet)	3.67, 3.29	3.68, 3.30	3.81, 3.37	3.81, 3.37	3.80, 3.35
$–CH_2S$ (aet)	2.67, 2.22	2.68, 2.23	2.79, 2.30	2.78, 2.30	2.78, 2.29
$–CH_2N$ (pn)	2.94	2.94	3.05	3.05	3.04
$–CHN$ (pn)	2.36	2.37	2.47	2.47	2.46
$–CH_3$ (pn)	1.37	1.37	1.43	1.43	1.42
bpy framework	9.08	9.08	9.12	9.12	9.12
	8.48	8.48	8.47	8.47	8.47
	8.44	8.44	8.43	8.43	8.43
	7.93	7.93	7.91	7.92	7.91
^{13}C NMR					
$–CH_2N$ (aet)	53.70	53.67	53.79	53.79	53.78
$–CH_2S$ (aet)	37.28, 37.16	37.24, 37.12	37.28, 37.15	37.28, 37.15	37.27, 37.14
$–CHN$ (pn)	56.27	56.25	56.39	56.39	56.38
$–CH_2N$ (pn)	52.26	52.25	52.50	52.50	52.50
$–CH_3$ (pn)	19.36	19.36	19.59	19.60	19.60
bpy framework	158.59	158.57	158.93	158.93	158.96
	149.29	149.25	149.10	149.10	149.09
	144.88	144.85	144.70	144.70	144.70
	131.20	131.15	130.87	130.87	130.86
	126.99	126.95	126.79	126.79	126.79

[a] In ppm from DSS.

Electronic and CD spectroscopic data are given in the Experimental section. **2**$(ClO_4)_3$ shows two d–d bands due to the Co^{3+} at 20.0 and $25.6 \times 10^3\,cm^{-1}$, two sulfur-to-cobalt CT bands at 38.2 and $42.0 \times 10^3\,cm^{-1}$, and two localized electronic bands on bpy at 31.4 and $32.6 \times 10^3\,cm^{-1}$. By analogy to absorption spectra of **1**$(ClO_4)_3$ and Δ,Δ-$[Pt\{Co(aet)_2(R\text{-}pn)\}_2]^{4+}$, the remaining intense band at $29.5 \times 10^3\,cm^{-1}$ is related to the Pt^{2+} ion [8, 18]. Naturally, these absorption features are also found in optically active **1**$(NO_3)_3 \cdot 7H_2O$ and **2**$(NO_3)_3 \cdot 7H_2O$. Although **3**$(ClO_4)_3 \cdot 2H_2O$ or **3**$(NO_3)_3 \cdot 2H_2O$ involves two complex cationic components, the spectroscopic pattern is quite similar to those of **1** and **2**. This also seems to support there being no significant interaction between the π electronic systems in solutions of **3**$(ClO_4)_3 \cdot 2H_2O$ or **3**$(NO_3)_3 \cdot 2H_2O$ in H_2O. The CD spectrum of **2**$(ClO_4)_3$ in H_2O is composed of four positive bands at 19.57, 25.25, 39.5, and $45.66 \times 10^3\,cm^{-1}$, and three negative bands at 30.5, 34.25, and $37.0 \times 10^3\,cm^{-1}$. In contrast, **3**$(ClO_4)_3 \cdot 2H_2O$ and **3**$(NO_3)_3 \cdot 2H_2O$ show no CD signals at all. This emphasizes the fact that t crystals of **3**$(ClO_4)_3 \cdot 2H_2O$ or **3**$(NO_3)_3 \cdot 2H_2O$ contain exactly equimolecular amounts of **1** and **2**.

Diffuse reflectance spectra of **2**$(ClO_4)_3$ and **3**$(ClO_4)_3 \cdot 2H_2O$ are essentially consistent with those of **2**$(NO_3)_3 \cdot 7H_2O$ and **3**$(NO_3)_3 \cdot 2H_2O$, respectively. In addition, spectra of **1**$(NO_3)_3 \cdot 7H_2O$ and **2**$(NO_3)_3 \cdot 7H_2O$ are quite similar, and correspond with absorption spectra in H_2O. On the other hand, the reflectance features for **3**$(NO_3)_3 \cdot 2H_2O$ are somewhat different from those for **1**$(NO_3)_3 \cdot 7H_2O$ or **2**$(NO_3)_3 \cdot 7H_2O$. In the $24–30 \times 10^3\,cm^{-1}$ region, **1**$(NO_3)_3 \cdot 7H_2O$ and **2**$(NO_3)_3 \cdot 7H_2O$ show two well-resolved shoulders, while **3**$(NO_3)_3 \cdot 7H_2O$ has one broad shoulder. Furthermore, the bands of the $30.77 \times 10^3\,cm^{-1}$ peak and $32.1 \times 10^3\,cm^{-1}$ shoulder for **1**$(NO_3)_3 \cdot 7H_2O$ or **2**$(NO_3)_3 \cdot 7H_2O$, which are assigned as localized electronic transitions on bpy, shift toward slightly lower energies for **3**$(NO_3)_3 \cdot 2H_2O$. These reflects some difference in the electronic natures of dimeric **3**$(NO_3)_3 \cdot 2H_2O$ and monomeric **1**$(NO_3)_3 \cdot 7H_2O$ or **2**$(NO_3)_3 \cdot 7H_2O$. For the reflectance spectrum of **3**$(ClO_4)_3 \cdot 2H_2O$, however, two well-resolved shoulders are also observed in the $24–30 \times 10^3\,cm^{-1}$ region and bands localized on bpy shift toward higher energies side than those in **3**$(NO_3)_3 \cdot 2H_2O$. In both of **3**$(ClO_4)_3 \cdot 2H_2O$ and **3**$(NO_3)_3 \cdot 2H_2O$, a pair of enantiomeric complex cations, Δ-[Pt(bpy){Co(aet)$_2$(R-pn)}]$^{3+}$ (***R***) and Λ-[Pt(bpy){Co(aet)$_2$(S-pn)}]$^{3+}$ (***S***), forms a dimer through π–π stacking of bpy ligands. This would provide an explanation for the spectroscopic differences mentioned above.

Supplementary material

CCDC 298071 for **2**$(ClO_4)_3$, CCDC 298072 for **3**$(ClO_4)_3 \cdot 2H_2O$, and CCDC 298073 for **3**$(NO_3)_3 \cdot 2H_2O$ contain the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.jk).

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