

Synthesis of Novel S-Bridged Heterotrinuclear Complexes Containing Six-Membered Chelate Rings: Structural, Spectroscopic, and Electrochemical Properties of $[\text{Co}\{\text{Rh}(\text{apt})_3\}_2]^{3+}$ (apt = 3-Aminopropanethiolate)

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A bidentate ligand, 3-aminopropanethiolate (apt), was synthesized and treated with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in basic water to yield a novel mononuclear complex, *fac*(S)- $[\text{Rh}(\text{apt})_3]$ (**1**), which was characterized by spectroscopic methods. Furthermore, the reaction of **1** with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in water formed the linear-type, S-bridged trinuclear complexes $\Delta\Delta\text{-}[\text{Co}\{\text{Rh}(\text{apt})_3\}_2]^{3+}$ (**2a**) and $\Delta\Delta/\Delta\Delta\text{-}[\text{Co}\{\text{Rh}(\text{apt})_3\}_2]^{3+}$ (**2b**), which were characterized by stereochemical, spectrochemical, and electrochemical methods. **2a** and **2b** are stable and exhibit trivalency in water. X-ray crystallographic analysis of **2a** and **2b** showed that all of the bridging sulfur atoms are fixed in the *R* configuration for the Δ unit and in the *S* configuration for the Λ unit, and each complex has six six-membered chelate rings, all of which are in the chair conformation. The crystal structure of the corresponding 2-aminoethanethiolate (aet) trinuclear complex $\Delta\Delta\text{-}[\text{Co}\{\text{Rh}(\text{aet})_3\}_2]^{3+}$ (**4a**) was also deter-

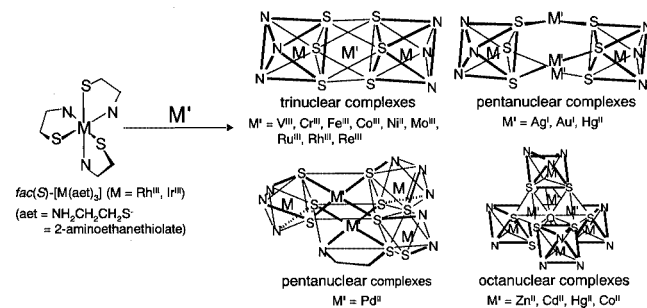
mined. The structures of **2a** and **2b** have some differences from that of **4a** as a result of the six-membered chelate rings. The Co...Rh distances in **2a** and **2b** [3.0490(4) and 3.063(1) Å] are significantly longer than this distance in the aet complex **4a** [2.9139(2) Å]. The UV/Vis absorption spectra of **2a** and **2b** indicate a shift to higher energies as compared with **4a** and $\Delta\Delta/\Delta\Delta\text{-}[\text{Co}\{\text{Rh}(\text{aet})_3\}_2]^{3+}$ (**4b**). The chemical shifts for the NCH_2 and SCH_2 carbon atoms in **2a** and **2b** are shifted to higher fields than those for **4a** and **4b** in the NMR spectra. The $\text{Co}^{\text{III/II}}$ redox potential values are -0.56 V (**2a**) and -0.57 V (**2b**) compared with -0.35 V (**4a**) and -0.36 V (**4b**). This shows that the Co^{III} state is more stable in **2a** and **2b** than it is in **4a** and **4b**.

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Introduction

The chemistry of sulfur-bridged metal complexes has attracted much interest because of the importance of coordinated thiolato groups in a variety of systems ranging from inorganic to organic and biological chemistry. It has been recognized that, because of their high Lewis basicity, coordinated thiolato groups have an affinity to form S-bridged polynuclear structures with transition-metal ions. Therefore, mononuclear complexes, *fac*(S)- $[\text{M}(\text{aet})_3]$ ($\text{M} = \text{Co}^{\text{III}}$, Rh^{III} , Ir^{III} ; aet = 2-aminoethanethiolate), could function as metalloligands to other transition-metal ions, using sulfur atoms.^[1] The polynuclear complexes obtained so far have shown unique stereochemical, spectrochemical, and electrochemical properties, depending highly upon the nature of

the central metal ions and the metal ions in the terminal building blocks (Scheme 1).^[1–5]



Scheme 1.

The complex $[\text{Co}(\text{tn})_3]^{3+}$ (tn = 1,3-propanediamine) containing an additional methylene group shows some interesting differences in properties when compared with the corresponding complex $[\text{Co}(\text{en})_3]^{3+}$ (en = ethylenediamine).^[6–13] For example, six-membered chelate rings give rise to a larger bite angle ($\text{N}\cdots\text{N}$ distances in chelates) than five-membered rings.^[6–9] It was reported that both the conformational flexibility and the structural bulkiness are larger in $[\text{M}(\text{tn})_3]^{3+}$ than in $[\text{M}(\text{en})_3]^{3+}$ ($\text{M} = \text{Co}^{\text{III}}$ or Cr^{III}

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ion).^[10,11] It was also observed that the ring–ring interactions, which give rise to the energy differences between conformations, are more severe and more numerous in the six-membered chelate ring complexes than in five-membered systems.^[10] Moreover, the absorption maxima in the first d–d transition region in the tn complexes shift to lower energies than those in the corresponding en complexes.^[12,13]

Similar to the complexes $[\text{Co}(\text{tn})_3]^{3+}$ and $[\text{Co}(\text{en})_3]^{3+}$ with N–N donor ligands, complexes containing five- and six-membered chelate rings with N–S donor ligands also show interesting differences in properties. For example, an additional methylene group led to differences in reactivity: all the attempts to synthesize $[\text{Co}(\text{apt})_3]$ (apt = 3-aminopropanethiolate) were unsuccessful, unlike the corresponding complex $[\text{Co}(\text{aet})_3]$, which was obtained easily.^[14] Similarly, $[\text{Ni}(\text{apt})_2]$ was obtained under more drastic conditions than $[\text{Ni}(\text{aet})_2]$. Moreover, differences in chemical properties were also observed: $[\text{Ni}(\text{apt})_2]$ gave $[\text{Ni}\{\text{Ni}(\text{apt})_2\}_2]^{2+}$ when dissolved in polar solvents, whereas $[\text{Ni}(\text{aet})_2]$ remained practically insoluble. The aqueous solutions of $[\text{Ni}\{\text{Ni}(\text{apt})_2\}_2]^{2+}$ were less stable than those of the homologous trinuclear complex $[\text{Ni}\{\text{Ni}(\text{aet})_2\}_2]^{2+}$.^[15] The solubility of complexes with six-membered chelate rings, e.g. $[\text{Ni}\{\text{Ni}(\text{apt})_2\}_2]^{2+}$, was lower than that of complexes with five-membered chelate rings, e.g. $[\text{Ni}\{\text{Ni}(\text{aet})_2\}_2]^{2+}$.^[16] As far as structure was concerned, the most striking difference resulting from the presence of an additional methylene group was found to be the opening of the dihedral angle by 30°. This can be attributed to the steric requirements of the enlargement of the chelate ring. The electronic properties are also influenced by the additional methylene group, which could be explained in terms of different bond lengths and angles of the chromophores in these complexes.^[15]

It has been well explained in the literature that the variations in the bridging ligands provide remarkable control over the electronic structures and photophysics of complexes. In one of the reports it was found that bpa dimers [bpa = 1,2-bis(4-pyridyl)ethane] exhibit a broad, low-energy emission from a metal-centered ³LF excited state, whereas the bpe and bpy dimers [bpe = *trans*-1,2-bis(4-pyridyl)ethylene, bpy = 4,4'-bipyridyl] exhibit structured emission from the lowest pyridyl-centered $3(\pi-\pi^*)$ excited state.^[17] In another report, complexes of 4-pyridine thiolate with Co^{II} , Ni^{II} , Zn^{II} , Cd^{II} , Pt^{II} , Sn^{IV} , and Bi^{III} involve bonding through sulfur rather than nitrogen,^[18] while complexes of 2-(2-mercaptoethyl)pyridine with Co^{II} , Ni^{II} , Pd^{II} , and Pt^{II} involve bonding through sulfur as well as nitrogen.^[19] It can therefore be demonstrated that the modifications of the bridging ligand provide exquisite control over the electronic structures and photophysics of the compounds, including the orbital character of the lowest emissive state. It is also assumed that the complexes using apt, which has an additional methylene group as compared with aet, can lead to somewhat different structural, spectrochemical, or electrochemical properties, which might be quite interesting.

No doubt metal complexes of aet ligands have been widely studied, many of them form stable chelates, but those of apt have received little attention up to now. Only

a few Co^{III} , Ni^{II} , Zn^{II} , Cd^{II} , Hg^{II} , and Fe^{III} complexes have been reported.^[14,15,20,21] The polynuclear complexes obtained were homopolynuclear complexes only, and to the best of our knowledge, there is no report of heteropolynuclear complexes. The choice of apt is based on the simplicity of the ligand and the fact that the ligand had been poorly studied. Turning to six-membered rings in the mononuclear unit, we are interested in the effects of changes in the three-dimensional structure on the metal, spectroscopic, and electrochemical properties.

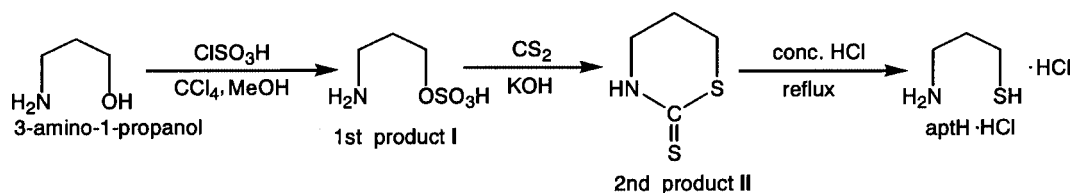
In this paper, we report on the stepwise synthesis of aptH·HCl from 3-aminopropanol following literature methods with some modifications.^[22–24] After synthesis, aptH·HCl was treated with the Rh^{III} ion to obtain a mononuclear complex *fac*(S)-[Rh(apt)₃] (**1**), which reacts with the Co^{II} ion to form heterotrinuclear complexes $[\text{Co}\{\text{Rh}(\text{apt})_3\}_2]^{3+}$ in *meso* (**2a**) and *racemic* (**2b**) forms. Crystal structural analysis and spectrochemical characterization have been described comparatively for the corresponding aet complexes. Electrochemical measurements were also performed.

Results and Discussion

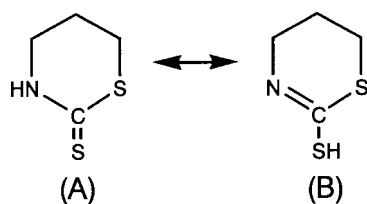
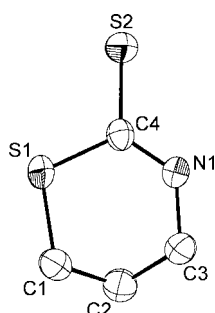
Synthesis of Ligand

The ligand aptH·HCl was prepared by modified literature methods.^[22–24] There was only a very simple description for the synthesis of the aminoalkanethiol series in the literature. Therefore, the synthesis of aptH·HCl was examined in detail and improved. The ligand was obtained by the three-step reaction shown in Scheme 2. Each compound was characterized by elemental analysis and NMR spectroscopy.

The first step of the reaction was vigorous and was therefore carried out in an ice bath. From this step, the compound 1-amino-3-propylsulfate (**I**) was obtained. The second step gave tetrahydro-1,3-thiazine-2-thione (**II**) with the ring-formation reaction of **I** and carbon disulfide. Compound **II** is a thione-thiol tautomer that consists of tetrahydro-1,3-thiazine-2-thione and 5,6-dihydro-1,3-thiazine-2-thiol (Figure 1). The X-ray crystal structure of **II** is shown in Figure 2, and bond lengths and angles are listed in Table 1. The six-membered ring is not a planar structure because of the sp^3 carbon atoms C1 and C2, and the sp^3 sulfur atom S1, although the C1, S1, C4, N1, C3, and S2 atoms are almost on the same plane. The S2–C4 distance [1.692(3) Å] is shorter than the length of the single bond S1–C1 [1.814(4)] and S1–C4 [1.729(3) Å]. It is reported that the length of the single bond S–C of typical thiol compounds is 1.82 Å, and that of typical thione compounds is 1.56 Å.^[25–28] Similarly, the N1–C4 distance [1.321(4) Å] is shorter than the length of the single bond N1–C3 [1.471(5) Å], which suggests multibonding. Thus, the C4 atom is in an sp^2 hybridized state. The S1–C4 distance in **II** is similar to the corresponding S–C distance [1.722(7) Å] in *N,N'*-trimethylenethiourea.^[29]



Scheme 2.

Figure 1. Two tautomers of **II**.Figure 2. Crystal structure of **II**.Table 1. Bond lengths [Å] and angles [°] of **II**.

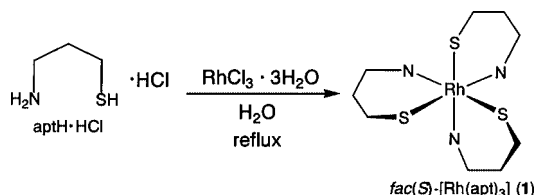
S1–C1	1.814(4)	S1–C4	1.729(3)
S2–C4	1.692(3)	N1–C3	1.471(5)
N1–C4	1.321(4)	C1–C2	1.502(5)
C2–C3	1.513(5)		
C1–S1–C4	105.2(2)	C3–N1–C4	127.0(3)
S1–C1–C2	110.9(2)	C1–C2–C3	111.7(3)
N1–C3–C2	112.1(3)	S1–C4–S2	115.1(2)
S1–C4–N1	122.2(2)	S2–C4–N1	122.7(2)

The third step in the reaction of **II** gave aptH·HCl as a result of ring opening. This ligand is hygroscopic and soluble in water, methanol, ethanol, and acetone, and less soluble in other solvents. The overall process was carried out in a manner similar to that of the synthesis of 1-Meapt (1-Meapt = 1-amino-2-propanethiolate).^[30]

Syntheses of Complexes

Preparation of the apt mononuclear complex *fac*(S)-[Rh(apt)₃] (**1**) (Scheme 3) was carried out by a modified method of the synthesis of the aet mononuclear complex, *fac*(S)-[Rh(aet)₃] (**3**).^[31,32] The difference between the syntheses was the order in which the starting materials were added. For the synthesis of the aet mononuclear complex, RhCl₃·3H₂O was added to a basic aqueous solution containing the ligand, and the mixture was heated to reflux

under nitrogen. However, in this work, the apt was added at the end and gave a higher yield than a similar method for synthesizing the aet mononuclear complex. The resulting yellow powder was found to be **1**. This neutral complex is not soluble in general solvents, but soluble in acidic water following the protonation of the sulfur atoms of the coordinated thiolato group. Complex **1** was obtained more easily and in a purer form than the complexes *fac*(S)-[Co(apt)₃] and *trans*(S)-[Ni(apt)₂], which were obtained under more drastic conditions.^[15]

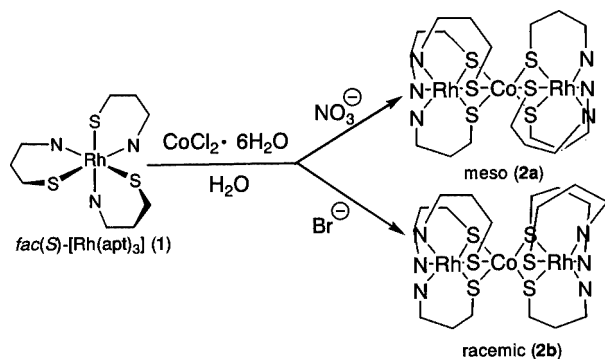


Scheme 3.

The trinuclear complexes $\Delta\Delta$ -[Co{Rh(apt)₃}₂](NO₃)₃ [**2a**(NO₃)₃] and $\Delta\Delta/\Delta\Delta$ -[Co{Rh(apt)₃}₂]Br₃ (**2b**Br₃) were synthesized by the reported procedure, but using aptH instead of aetH.^[33] It was found that, in the case of **2a**(NO₃)₃ and **2b**Br₃, the reaction gave the trivalent Co^{III} complexes under nitrogen or air. This result is different from the case of $\Delta\Delta$ -[Co{Rh(aet)₃}₂](NO₃)₃ [**4a**(NO₃)₃] and $\Delta\Delta/\Delta\Delta$ -[Co{Rh(aet)₃}₂]Br₃ (**4b**Br₃), which gave divalent Co^{II} complexes under such conditions, in which case H₂O₂ was used for oxidation.^[33] This difference in reactivity can be related to the difference in the redox potential of the Co^{III} ion in trinuclear structures (vide infra). Complexes **2a** and **2b** (Scheme 4) were obtained both in *meso* and *racemic* forms similar to **4a** and **4b**. Selective crystallization using suitable counter anions was achieved. This is different from the case of the Co^{III} complexes in which [Co{Co(aet)₃}₂]Cl₃ gave both *meso* and *racemic* forms while [Co{Co(apt)₃}₂]Cl₃ gave only the *meso* form.^[14,21]

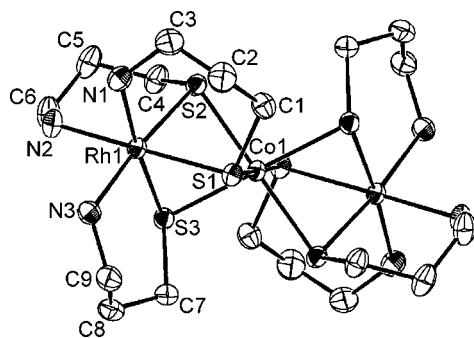
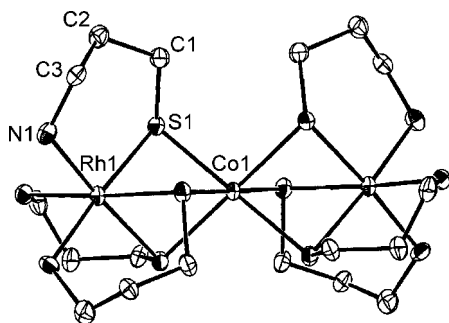
Crystal Structures of Complexes **2a**, **2b**, and **4a**

The results of the ICP analysis and elemental analysis confirmed that the ratio of Co to Rh was 1:2 in **2a** and **2b**. The values obtained for the molar conductivity in aqueous solution for the apt complexes **2a** and **2b** (329 and 363 S·cm²·mol⁻¹, respectively) are comparable to the values of the aet complexes **4a** and **4b** (384 and 401 S·cm²·mol⁻¹, respectively). These values are also within the range normally observed for other trivalent trinuclear complexes containing *fac*(S)-[Rh(aet)₃] units (323–404 S·cm²·

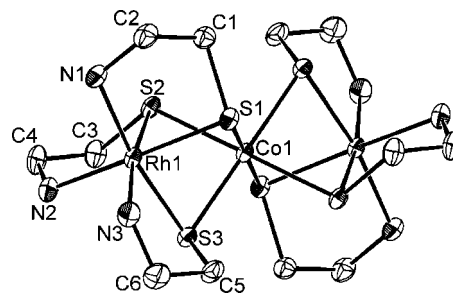


Scheme 4.

mol^{−1}).^[2,3,34,35] The structures of **2a**, **2b**, and **4a**, determined by X-ray structural analysis, are shown in Figures 3, 4, and 5, respectively. The crystal structure of **4a** was determined for purposes of comparison. The selected bond lengths and angles are summarized in Table 2 and Table 3. Compounds **2a** and **2b** consist of two approximately octahedral *fac*(S)-[Rh(apt)₃] units and one Co atom, forming the completely linear-type, S-bridged trinuclear structures, ΔΛ-[Co{Rh(apt)₃}₂]³⁺ (for **2a**) and ΔΔ/ΛΛ-[Co{Rh(apt)₃}₂]³⁺ (for **2b**). Only the ΛΛ configuration of **2b** is shown in Figure 4. All of the bridging sulfur atoms in **2a** and **2b** have the *R* configuration for the Δ unit and the *S* configuration for the Λ unit, which corresponds to the results in all of the reported trinuclear structures. Each complex has six six-membered chelate rings in a molecule, and all of the rings are in the chair conformation.

Figure 3. Crystal structure of **2a**.Figure 4. Crystal structure of **2b**.

The Co···Rh distances in apt complexes **2a** and **2b** [3.0490(4) and 3.063(1) Å] are significantly longer than that

Figure 5. Crystal structure of **4a**.

in the aet complex **4a** [2.9139(2) Å]. The Rh–S [av. 2.322(1) Å], Rh–N [av. 2.133(5) Å], and Co–S [av. 2.291(1) Å] distances in **2a** are slightly longer than those in **4a** [av. 2.306(8), av. 2.121(3), and av. 2.290(9) Å]. The S–Rh–S (av. 80.43(4)°), N–Rh–N [av. 88.2(2)°], and S–Co–S [av. 81.71(4)°] angles in **2a** are more acute than those in **4a** [av. 83.75(3), av. 96.2(1), and av. 84.45(3)°] while Co–S–Rh angles [av. 82.73(4)°] in **2a** are more obtuse than those in **4a** [av. 78.67(3)°]. These differences in the bond lengths and angles are attributed to the presence of six-membered chelate rings that are formed between the metal and ligands in the case of apt complexes **2a** and **2b** compared with the five-membered chelate rings found in the case of aet complex **4a**. It can be concluded that increasing the number of methylene groups in the chelate rings influences the stereochemistry of the complexes. Six-membered chelate rings give rise to a larger bite angle than five-membered rings, which is very clearly observed in the present case. The S–Rh–N bite angles in **2a** [av. 96.0(1)°] and **2b** [98.5(3)°] are significantly larger than those in **4a** [av. 87.0(1)°].

Spectroscopic Properties

UV/Visible Spectra

Diffuse reflectance (DR) spectra of **1** and **3** were measured in the solid state, since the neutral mononuclear complexes are sparingly soluble in water. Both complexes exhibit the characteristic intense bands at ca. 40×10^3 cm^{−1}. These bands may be due to charge transfer (CT) transitions from the sulfur atoms to the Rh^{III} ion. This suggests that **1** is the apt mononuclear complex *fac*(S)-[Rh(apt)₃] with the same geometry as **3**.

UV/Vis absorption (AB), DR, and circular dichroism (CD) spectra of **2a** and **2b** are shown in Figure 6. It was found that **2a** and **2b** exhibit characteristic AB and CD spectra of the trinuclear structure just as for complexes **4a** and **4b** with some shift towards the higher energy side.^[33] The observed AB peaks arise from d–d transitions and CT transitions from the sulfur atoms to the metal ions. The peaks observed at about 40 – 50×10^3 cm^{−1} are due to CT transitions from the sulfur atoms to the Rh^{III} ion. DR and AB spectra show similar patterns, and therefore it is believed that the symmetry of **2a** and **2b** is not altered in solution. Furthermore, AB did not change with time. This means that **2a** and **2b** are stable for a long time in solution.

Table 2. Selected bond lengths [Å] and angles [°] of **2a** and **4a**.

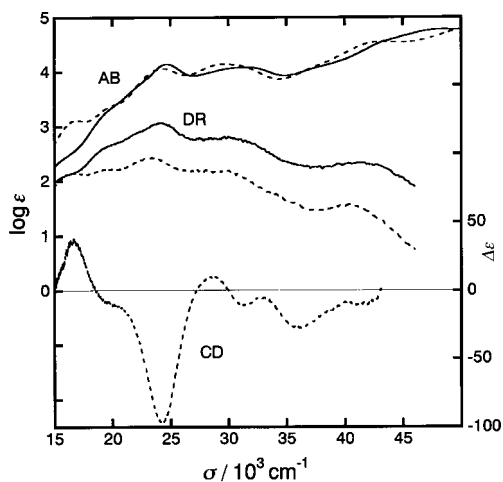
	2a	4a		2a	4a
Rh1–S1	2.316(1)	2.3121(9)	Rh1–S2	2.330(1)	2.3077(9)
Rh1–S3	2.320(1)	2.2993(7)	Rh1–N1	2.138(5)	2.122(3)
Rh1–N2	2.127(4)	2.123(4)	Rh1–N3	2.136(5)	2.120(3)
Co1–S1	2.291(1)	2.2853(9)	Co1–S2	2.294(1)	2.3069(9)
Co1–S3	2.290(1)	2.2796(7)	Rh1...Co1	3.0490(4)	2.9139(2)
Rh1–S1–Co1	82.87(4)	78.66(3)	Rh1–S2–Co1	82.51(4)	78.31(3)
Rh1–S3–Co1	82.82(5)	79.04(2)	S1–Rh1–S2	80.74(4)	83.29(3)
S1–Rh1–S3	80.77(4)	84.32(3)	S2–Rh1–S3	79.83(5)	83.63(3)
N1–Rh1–N2	87.0(2)	96.0(1)	N1–Rh1–N3	88.2(2)	96.4(1)
N2–Rh1–N3	89.4(2)	96.2(1)	S1–Co1–S2	81.99(4)	83.90(3)
S1–Co1–S3	81.94(4)	85.38(3)	S2–Co1–S3	81.20(5)	84.08(3)
S1–Rh1–N1	96.3(1)	87.04(9)	S2–Rh–N2	95.2(1)	87.0(1)
S3–Rh1–N3	96.5(1)	87.06(8)			

Table 3. Selected bond lengths [Å] and angles [°] of **2b**.

Rh1–S1	2.327(3)	Rh1–N1	2.13(1)
Co1–S1	2.304(3)	Rh1...Co1	3.063(1)
Rh1–S1–Co1	82.82(9)	S1–Rh1–S1 ^[a]	80.5(1)
N1–Rh1–N1 ^[a]	86.7(5)	S1–Co1–S1 ^[a]	81.5(1)
S1–Rh1–N1	98.5(3)		

[a] Symmetry code: 1 – y, x – y, z.

When comparative studies were performed, it was found that there was no significant difference between the electronic spectra of the aqueous solutions of **2a**, **2b** and **4a**, **4b**. This trend is similar to that of $[\text{Co}\{\text{Co}(\text{aet or apt})_3\}_2]^{3+}$ [14,21], whereas it is different from that of $[\text{Ni}\{\text{Ni}(\text{aet or apt})_2\}_2]^{2+}$, in which important differences were observed.^[15] The AB peaks in **2a** and **2b** were observed at higher energy levels compared with those in the corresponding Co^{III} and Ni^{II} complexes. It is therefore concluded that the addition of another methylene group to the chelate ring in octahedral trinnuclear complexes does not cause important modifications in the chromophores, and the structures are very similar in both cases.

Figure 6. UV/Vis AB (log ϵ), DR (arbitrary scale), and CD ($\Delta\epsilon$) spectra of **2a** (—) and $(-)\text{412-2b}$ (----).

The CD spectrum of **2b**, which was optically resolved with an SP-Sephadex C-25 column, shows bands in the region $15\text{--}40 \times 10^3 \text{ cm}^{-1}$. These CD bands correspond well to the d–d and CT bands for $[\text{Co}\{\text{Rh}(\text{apt})_3\}_2]^{3+}$ in the AB spectra. It seems that $(-)\text{412-2b}$ is the $\Lambda\Lambda$ isomer and $(+)\text{412-2b}$ is the $\Delta\Delta$ isomer. The CD spectrum of **2b** is also in agreement with that of **4b**. In the CD spectra, no significant changes were observed with time over several hours. This illustrates that the trinnuclear structures are fairly stable, retaining their oxidation state even under aerobic conditions.

IR and Far-IR Spectra

The IR and far-IR spectra of **I**, **II**, and $\text{aptH}\cdot\text{HCl}$ show all the characteristic bands for the vibration and bending modes of the NH_2 and CH_2 groups (Figure S1). The overall IR spectral pattern of **1** is in good agreement with that of **3**.^[35] The IR spectral patterns of **2a**(NO_3)₃ and **2b**Br₃ are similar to each other, reflecting the similarity between the isomers (Figure S2). Moreover, these spectral patterns are typical for linear-type, S-bridged trinnuclear complexes in the range $4000\text{--}400 \text{ cm}^{-1}$.^[2,3,35–38] The IR spectra of **1**, **2a**(NO_3)₃, and **2b**Br₃ show characteristic bands in the range $3500\text{--}2800 \text{ cm}^{-1}$, corresponding to the vibration modes of the NH_2 and CH_2 groups. The bands for the bending mode of the NH_2 and CH_2 groups are observed at $1700\text{--}1000 \text{ cm}^{-1}$. The IR spectra show similar patterns in the range $3500\text{--}2800 \text{ cm}^{-1}$, but in the range $1700\text{--}1000 \text{ cm}^{-1}$, there are small differences between the spectrum of the mononuclear complex **1** and those of the trinnuclear complexes **2a**(NO_3)₃ and **2b**Br₃. The bands at ca. 1100 cm^{-1} in **1** are shifted to higher energies in **2a**(NO_3)₃ and **2b**Br₃, which reflects the change from mononuclear to trinnuclear geometry. The same trend is observed in the case of Co^{II} , Ni^{II} , Zn^{II} , Cd^{II} , and Hg^{II} complexes with apt.^[14,15,20,21] The similarity between the IR spectral patterns of **1** and those of the trinnuclear **2a**(NO_3)₃ and **2b**Br₃ shows that the terminal units retain their structure during the formation of S-bridged complexes. The absence of bands in the range $2550\text{--}2600 \text{ cm}^{-1}$ ($\nu\text{S-H}$) is characteristic of coordinated sulfur. The far-IR spectra of **1**, **2a**(NO_3)₃, and **2b**Br₃ are quite complicated, but show little difference in the region $500\text{--}420 \text{ cm}^{-1}$ be-

Table 4. ^1H - and ^{13}C NMR spectral data (coupling constants/Hz).^[a]

	NH	NCH ₂	CH ₂	SCH ₂
I	— ^[c]	4.17 (t, 2 H, 5.7)	2.07 (2 H, quint, 6.4)	3.15(t, 2 H, 7.2) ^[d]
II ^[b]	9.02 (s, 1 H)	3.48 (t, 2 H, 4.1)	2.18 (2 H, quint, 5.7)	3.00 (t, 2 H, 5.9)
aptH·HCl	— ^[c]	3.12 (t, 2 H, 7.6)	2.10 (2 H, quint, 7.3)	2.82 (t, 2 H, 7.1)
2a	4.15 ^[c]	2.98 (m, 2 H)	2.15 (d, 1 H, 15.6)	2.45 (dd, 1 H, 5.1, 4.9)
	3.41 ^[c]		1.83 (dd, 1 H, 11.6, 13.3)	2.08 (t, 1 H, 13.5)
2b	4.14 ^[c]	2.98 (dd, 1 H, 5.5, 5.2)	2.18 (d, 1 H, 15.7)	2.46 (dd, 1 H, 5.2, 5.1)
	3.33 ^[c]	2.92 (dd, 1 H, 10.6, 12.9)	1.74 (dd, 1 H, 6.0, 12.7)	1.89 (t, 1 H, 12.5)
4a	— ^[c]	3.15 (d, 1 H, 11.2)		2.49 (d, 1 H, 13.2)
	— ^[c]	2.73 (dd, 1 H, 22.5, 13.9)		1.86 (td, 1 H, 13.5, 3.3)
4b	— ^[c]	3.16 (d, 1 H, 12.9)		2.39 (d, 1 H, 11.2)
	— ^[c]	2.73 (dd, 1 H, 23.7, 10.5)		1.73 (td, 1 H, 13.5, 3.6)
	C=S	NCH ₂	CH ₂	SCH ₂
I		68.92	29.19	39.61 ^[e]
II ^[b]	194.61	44.30	20.46	30.02
aptH·HCl		40.72	28.60	36.39
2a		44.04	29.82	30.72
2b		43.82	30.84	31.18
4a		49.89		34.40
4b		50.11		34.62

[a] ppm from D₂O containing DSS. [b] ppm from CHCl₃ containing TMS. [c] NH₂ signals were broad or missing due to H–D exchange. [d] OCH₂. [e] OCH₂.

tween the mononuclear complex **1** and the two trinuclear complexes **2a**(NO₃)₃ and **2b**Br₃ (Figure S2). Because the far-IR spectra were complicated, it was difficult to assign the bands for the shifts resulting from the vibrations of the Co–S bonds.

NMR Spectra

The ^1H - and ^{13}C NMR spectra were measured for each product during the synthesis of ligands **2a** and **2b**. The ligand aptH·HCl as well as **I** and **II** show three sharp signals for the CH₂ protons and three sharp signals for the CH₂ carbons. The proton signals in the ^{13}C - ^1H heteronuclear multiple-bond correlation spectrum (HMBC) of aptH·HCl show coupling with the corresponding carbon signals (Figure S3). Moreover, the proton signals in the ^1H - ^1H correlation spectroscopy (COSY) indicate coupling between the corresponding proton signals. Both **2a** and **2b** also exhibit three sets of sharp proton signals and three carbon signals resulting from the six apt ligands (Figure S4). This means that the *S*₆ or *D*₃ symmetrical, S-bridged, trinuclear structures observed in the crystals are retained in aqueous solution. The details of the NMR spectroscopic data are shown in Table 4. In **2a** and **2b**, the chemical resonances in the ^1H NMR spectra show shifts to lower fields for the NCH₂ protons and to higher fields for the SCH₂ protons. Moreover, the splitting pattern for the protons is also different from that observed in **4a** and **4b**.^[35] It is worth noting that the chemical shifts for the NCH₂ and SCH₂ carbon atoms in **2a** and **2b** show shifts to higher fields than those for **4a** and **4b**.

Electrochemical Properties

Cyclic voltammetry experiments were performed for **2a** and **2b**. The cyclic voltammogram obtained for **2b** is shown

in Figure 7. For the already reported complexes of apt with Co^{III}, Ni^{II}, Zn^{II}, Cd^{II}, and Hg^{II}, there is no information about the electrochemical properties.^[14,15,20,21] Therefore, to the best of our knowledge, this is the first report on the electrochemistry of S-bridged complexes containing apt. Each of the voltammograms displays a quasi-reversible redox couple in the negative potential region. In analogy to the characterized electrochemistry of the [Co{M(aet)₃}₂]³⁺ (M = Rh^{III}, Co^{III}) system,^[33,39–41] this redox process is assigned as the redox couple corresponding to Co^{III/II}. The redox couples of the apt complexes **2a** (–0.56 V) and **2b** (–0.57 V) are more negative than those of the aet complexes **4a** (–0.35 V) and **4b** (–0.36 V).^[33,39] This means that the Co^{III} state in apt complexes is more stable than that in **4a** and **4b**. A possible reason for this might be the difference in nucleophilicity of sulfur or structural differences of the Co^{III} ion resulting from the additional methylene group in apt, which forms six-membered chelates rather than five-membered ones, as is the case for aet. Since the difference in reduction potential resulting from the difference in the configuration of complexes is very slight, the *E*_{1/2} value for the *meso* isomer **2a** is only 0.01 V more positive than that for the corresponding *racemic* isomer **2b**. A profound difference was observed when the ligand was changed from *fac*(S)-[Rh(aet)₃] to *fac*(S)-[Rh(apt)₃], where **2b** is reduced (0.21 V) more easily than **4b**. The redox process of **2b** is reversible, as with **4a** and **4b**. However, in the case of **2a**, the observed peak separation was too broad to establish whether the redox process is reversible. The difference in electrochemical properties of **2a**, **2b** and **4a**, **4b** could be related to the difference of reactivity explained in the synthetic part, where it was found that, in the case of **2a** and **2b**, the reaction under nitrogen or air gave the trivalent Co^{III} complexes as compared with the case of **4a** and **4b**, where H₂O₂ was used for oxidation.

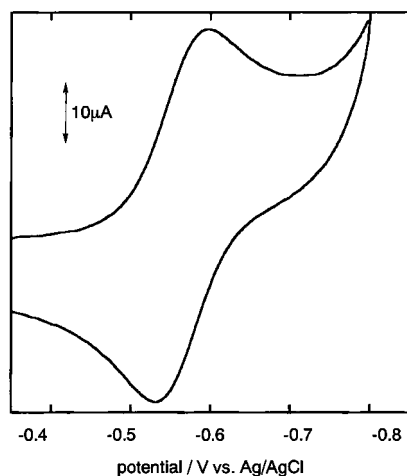


Figure 7. Cyclic voltammogram of **2b**.

Conclusions

A novel mononuclear complex *fac*(S)-[Rh(*apt*)₃] (**1**) was synthesized and characterized by spectroscopic methods. The reaction of **1** with CoCl₂·6H₂O in water formed linear-type, S-bridged trinuclear complexes ΔΔ-[Co{Rh(*apt*)₃}₂]³⁺ (**2a**) and ΔΔ/ΔΔ-[Co{Rh(*apt*)₃}₂]³⁺ (**2b**), unlike ΔΔ-[Co{Rh(*aet*)₃}₂]³⁺ (**4a**) and ΔΔ/ΔΔ-[Co{Rh(*aet*)₃}₂]³⁺ (**4b**) where an oxidizing agent was required. The complexes were characterized by stereochemical, spectrochemical, and electrochemical techniques. The Co···Rh, Rh–S, and Rh–N distances in **2a** and **2b** are longer than those of **4a**. The differences in bond lengths and angles are due to the presence of six-membered chelate rings in **2a** and **2b**, rather than the five-membered chelate rings in **4a**. The absorption bands in **2a** and **2b** are shifted to higher energies than those of **4a**. The results of IR and far-IR spectra indicate that the terminal units retain their structure during the formation of S-bridged complexes. NMR spectra of **2a** and **2b** show that the chemical shift values in ¹³C NMR are shifted to higher fields as compared to **4a** and **4b**. In addition, the Co^{III} oxidation state in **2a** and **2b** is more stable than that in **4a** and **4b**. It can be concluded that the properties of complexes are greatly influenced by increasing the number of methylene groups in the chelate rings.

Experimental Section

Materials

The *aet* complexes *fac*(S)-[Rh(*aet*)₃] (**3**), ΔΔ-[Co{Rh(*aet*)₃}₂](NO₃)₃ [**4a**(NO₃)₃], and ΔΔ/ΔΔ-[Co{Rh(*aet*)₃}₂](Br₃) (**4b**Br₃) were prepared by procedures similar to those in the literature.^[31–33] All reagents were purchased from Wako Pure Chemical Ind. Ltd. All chemicals were of reagent grade and were used without further purification.

Preparation of Ligand

The ligand was prepared by literature methods with some modifications as follows.^[22–24]

1-Amino-3-propylsulfate (I): A mixture of 3-amino-1-propanol (75.1 g, 1.0 mol) and carbon tetrachloride (200 cm³) was cooled in

an ice bath. Chlorosulfonic acid (116.5 g, 1.0 mol) was slowly added to the mixture. The reaction mixture was kept overnight, and carbon tetrachloride was removed in vacuo. The crude solid was crushed with methanol (400 cm³), and isolated by filtration. A pure white powder of 1-amino-3-propylsulfate was obtained by recrystallization from water/methanol. Yield: 123.5 g, 79%. C₃H₉NO₄S (155.17): calcd. C 23.35, H 5.66, N 9.15; found C 22.87, H 5.57, N 8.88.

Tetrahydro-1,3-thiazine-2-thione (II): To a suspension containing 1-amino-3-propylsulfate (252.2 g, 1.62 mol) and carbon disulfide (150.0 g, 1.94 mol) in ethanol (50%, 700 cm³) was added slowly in an ice bath NaOH (141.8 g, 3.56 mol) in ethanol (50%, 300 cm³). After the reaction mixture was heated to reflux for 30–40 min the ethanol was removed by evaporation. Colorless crystals of tetrahydro-1,3-thiazine-2-thione were obtained by recrystallization from hot water. Yield: 149.0 g, 70%. C₄H₇NS₂ (133.22): calcd. C 36.06, H 5.30, N 10.51; found C 35.40, H 5.06, N 10.34.

3-Aminopropanethiol Hydrochloride (aptH·HCl): A suspension of tetrahydro-1,3-thiazine-2-thione (149.0 g, 1.12 mol) in conc. HCl (800 cm³) was heated to reflux for 3 weeks. After evaporating until an oil remained, a white precipitate of aptH·HCl was obtained by the addition of ethanol/ether. Yield 133.0 g, 95%. C₃H₁₀CINS (127.63): calcd. C 28.23, H 7.89, N 10.97; found C 29.05, H 6.67, N 10.30.

Preparation of Complexes

***fac*(S)-[Rh(*apt*)₃] (**1**):** To a solution containing NaOH (0.61 g, 15 mmol) in water (10 cm³) was added RhCl₃·3H₂O (0.10 g, 0.38 mmol). A solution of aptH·HCl (1.10 g, 8.6 mmol) in water (40 cm³) was then added to this mixture. The mixture gave a yellow precipitate after slight heating and was then heated to reflux for a further 1–1.5 h. The yellow precipitate was collected by filtration and washed with water, methanol, and acetone. Yield of **1**·2H₂O: 0.075 g, 53%. C₉H₂₈N₃O₂RhS₃ (409.42): calcd. C 28.05, H 6.63, N 10.90; found C 28.02, H 6.11, N 10.34. Reflectance maxima (σ/10³ cm⁻¹): 13.5, 28.5, 34.1 sh, 40.4.

ΔΔ-[Co{Rh(*apt*)₃}₂](NO₃)₃ [2a**(NO₃)₃] and ΔΔ/ΔΔ-[Co{Rh(*apt*)₃}₂](Br₃) (**2b**Br₃):** To a suspension containing **1** (0.20 g, 0.55 mmol) in water (10 cm³) was added a solution containing CoCl₂·6H₂O (0.65 g, 2.7 mmol) in water (5 cm³). The mixture was stirred at room temperature for 30 min and filtered. A saturated aqueous solution of NaNO₃ (5 cm³) was added to the dark brown filtrate, and the resulting dark red crystals [**2a**(NO₃)₃·2H₂O] were collected by filtration. A saturated aqueous solution of NaBr (5 cm³) was added to the filtrate, and the resulting dark red crystals (**2b**Br₃·3.5H₂O) were collected by filtration. Crystals suitable for X-ray crystallography were obtained by recrystallization of **2a**(NO₃)₃·2H₂O and **2b**Br₃·3.5H₂O from the aqueous solutions containing NaNO₃ and NaCl. Yield of **2a**(NO₃)₃·2H₂O: 0.065 g, 12%. C₁₈H₅₂CoN₉O₁₁Rh₂S₆ (1027.77): calcd. C 21.04, H 5.10, N 12.27; found C 21.19, H 4.98, N 11.89. Absorption maxima [σ/10³ cm⁻¹ (log ε/mol⁻¹·dm³·cm⁻¹): 14.5 (2.11), 20.9 (3.49), 24.7 (4.14), 31.5 (4.08 sh), 38.6 (4.13 sh), 48.7 (4.78). Reflectance maxima (σ/10³ cm⁻¹): 15.3, 19.0, 24.2, 29.6 sh, 41.1. Yield of **2b**Br₃·3.5H₂O: 0.045 g, 7.9%. C₁₈H₅₅Br₃CoN₆O_{3.5}Rh₂S₆ (1100.49): calcd. C 19.50, H 5.00, N 7.58; found C 19.73, H 5.08, N 7.96. Absorption maxima [σ/10³ cm⁻¹ (log ε/mol⁻¹·dm³·cm⁻¹): 16.7 (3.11), 18.3 (3.14), 24.3 (4.06), 29.7 (4.14 sh), 40.2 (4.35 sh), 51.0 (4.80). Reflectance maxima (σ/10³ cm⁻¹): 16.5, 19.1, 23.4, 29.5 sh, 40.3.

Column Chromatography

Column chromatography was also performed with an SP-Sephadex C-25 column (Na⁺ form). When the reddish brown filtrate was

eluted with a NaCl solution (0.5 M), two bands were obtained: a reddish brown band followed by a greenish brown band. The UV/Vis absorption spectra of the bands showed that the reddish brown band contains **2a** and the greenish brown band contains **2b**. The purity of the isomers that had been obtained by fractional precipitation, was confirmed by column chromatography [SP-Sephadex C-25 column (Na⁺ form)].

Optical Resolution of **2b**

Compound **2b** was optically resolved with an SP-Sephadex C-25 column (K⁺ form). An aqueous solution of **2b** was charged onto the column and adsorbed. The column was first eluted with an aqueous solution of K₂[Sb₂(R,R-tartrato)₂]·5H₂O (0.15 M), whereupon two distinct greenish brown bands were separated. The bands were finally eluted and collected by an aqueous solution of KCl (0.5 M). The CD spectra of the two bands were measured, which had a positive or negative CD sign at 412 nm. The CD spectra of two bands were just opposite to each other. The Δε values of each eluent containing the (+)₄₁₂^{CD} and (−)₄₁₂^{CD}-**2b** isomers were evaluated on the basis of the absorption spectroscopic data of **2bBr**₃·3.5H₂O. CD extrema [$\sigma/10^3$ cm^{−1} (Δε/mol^{−1}·dm³·cm^{−1}): **2b** (lower) 16.73 (−41.06), 24.26 (+99.62), 28.62 (−11.27), 31.38 (+10.65), 35.94 (+28.10), 42.05 (+10.96); **2b** (upper) 16.62 (+38.24), 24.19 (−96.92), 28.80 (+10.45), 31.46 (−11.07), 36.23 (−27.98), 41.87 (−10.12).

Measurements

Elemental analysis (C, H, and N) was performed by the Department of Chemistry in the University of Tsukuba. The concentrations of Co and Rh in the complexes were determined with a NIP-PON Jarrell-Ash ICPA-575 spectrometer. UV/Vis absorption spectra were recorded with a JASCO V-560 spectrophotometer and solid-state diffuse reflectance spectra were recorded with a JASCO V-570 spectrophotometer equipped with an integrating sphere apparatus (JASCO ISN-470) using powder samples diluted with MgO. IR and far-IR spectra were recorded with a JASCO FT/IR-550 spectrometer using KBr disks in the range 4000–400 cm^{−1} and Nu-jol mulls between polyethylene pellets in the range 650–50 cm^{−1}. ¹H and ¹³C NMR spectra were recorded with a BRUKER AM500 and

AM600 NMR spectrometer in D₂O using sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) as an internal reference or CDCl₃ using tetramethylsilane (TMS) as an internal reference. The molar conductance of the complexes was measured with a HORIBA conductivity meter (DS-14). Electrochemical experiments were performed with a CV-50W voltammetry analyzer, Bioanalytical Systems, Inc. (BAS) with a platinum-working electrode (BAS, Pt). In the electrochemical experiments an aqueous Ag/AgCl/NaCl (3 mol·dm^{−3}) (BAS, RE-1B) and platinum wire were used as the reference and auxiliary electrodes, respectively. All the measurements were carried out at room temperature in an aqueous solution, which was bubbled with N₂ gas, and contained Na₂SO₄ (0.1 mol·dm^{−3}) as a supporting electrolyte.

X-ray Crystal Structure Determinations

Single-crystal X-ray data collections were performed with a Rigaku AFC-7S Mercury CCD area detector with a graphite monochromatized Mo-*K*_α (0.71070 Å) radiation using the CrystalClear (Rigaku) program package. Crystallographic data of **II** and complexes **2a**(NO₃)₃·2H₂O, **2b**Cl₃, and **4a**(NO₃)₃·3H₂O are listed in Table 5. The positions of Rh, Co, and non-hydrogen atoms were determined by direct methods (SHELX 97 **2a**, **4a**)^[42] or (SIR97 **II**, **2b**)^[43] and some remaining atom positions were found by successive difference Fourier techniques (DIRDIFF-99).^[44] The structures were refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-hydrogen atoms. All hydrogen atoms except for those of **II** were included in calculated positions but not refined. The CrystalStructure (Rigaku) program package was used for the calculations.^[45]

CCDC-279990–CCDC-279993 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): IR and far-IR spectra of **I**, **II**, and aptH·HCl (Figure S1); IR and far-IR spectra of complexes **1**, **2a**, and **2b** (Figure S2); ¹H-¹H

Table 5. Crystallographic Data for **II**, **2a**(NO₃)₃·2H₂O, **2b**Cl₃, and **4a**(NO₃)₃·3H₂O.

	II	2a (NO ₃) ₃ ·2H ₂ O	2b Cl ₃	4a (NO ₃) ₃ ·3H ₂ O
Empirical formula	C ₄ H ₇ NS ₂	C ₁₈ H ₅₂ CoN ₉ O ₁₁ Rh ₂ S ₆	C ₁₈ H ₄₈ Cl ₃ CoN ₆ Rh ₂ S ₆	C ₁₂ H ₄₂ CoN ₉ O ₁₂ Rh ₂ S ₆
Formula weight	133.23	1027.77	912.08	961.62
Dimensions [mm]	0.55 × 0.30 × 0.10	0.27 × 0.20 × 0.05	0.15 × 0.13 × 0.10	0.25 × 0.25 × 0.10
Crystal system	monoclinic	monoclinic	hexagonal	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>C</i> 2/ <i>c</i> (#15)	<i>P</i> 6/ <i>mcc</i> (#192)	<i>P</i> 1̄ (#2)
<i>a</i> [Å]	4.9986(5)	17.2186(7)	12.8060(2)	8.8570(1)
<i>b</i> [Å]	6.2381(7)	9.3370(2)		8.9760(1)
<i>c</i> [Å]	19.717(2)	23.2258(10)	26.3105(5)	12.0893(1)
<i>α</i> [°]				70.854(8)
<i>β</i> [°]	93.486(2)	98.1420(5)		69.761(8)
<i>γ</i> [°]				77.198(9)
Volume [Å ³]	613.69(11)	3696.4(2)	3736.69(11)	845.52(2)
<i>Z</i>	4	4	4	1
<i>D</i> _{calcd.} [g·cm ^{−3}]	1.442	1.847	1.621	1.888
<i>μ</i> [cm ^{−1}]	7.39	17.25	18.79	18.80
Total reflections	9380	29146	31160	13730
Unique reflections	1444	4413	1771	3820
<i>R</i> _{int}	0.020	0.030	0.073	0.016
Used [<i>I</i> > 3σ(<i>I</i>)]	1113	2701	699	3482
No. Variables	64	239	65	250
Used/ Variables	17.39	11.30	10.75	13.93
Final <i>R</i> [<i>I</i> > 3σ(<i>I</i>)]	0.062	0.036	0.074	0.039
Final <i>R</i> _w [<i>I</i> > 3σ(<i>I</i>)]	0.194	0.092	0.195	0.126
Goodness of fit	1.000	1.019	1.002	1.002

COSY and ^1H - ^{13}C HMQC NMR spectra of aptH-HCl (Figure S3); ^1H - ^1H COSY of **2a** and **2b** (Figure S4).

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