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Self-Assembling Synthesis of Cyclic Tri- and Tetranuclear Cobalt(III) Complexes Bridged by Purine-6-thione and Their Characterization by Electrospray Mass Spectrometry and X-ray Crystal Analysis

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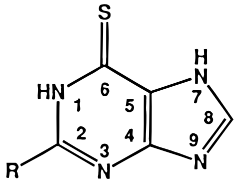
The cyclic multinuclear complexes $[Co_n(L\text{-}N,S,N')_n(tacn)_n]^{n+}$ (L = purine-6-thiones; tacn = 1,4,7-triazacyclononane) were synthesized through self-assembly of the mononuclear complex $[Co(HL\text{-}N,S)Cl(tacn)]^{+}$ based on the multidentate bridging ability of purine-6-thione. Three kinds of purine-6-thione ligands were used: 9*H*-purine-6(1*H*)-thione (H_2put), 2-amino-9*H*-purine-6(1*H*)-thione (H_2aput), and 3,6-dihydro-6-thioxo-9*H*-purin-2(1*H*)-one (H_3tpuo). The complexes $[Co_n(L\text{-}N,S,N')_n(tacn)_n]^{n+}$, $n = 3$ and 4 for put and $n = 4$ for aput and Htpuo, were characterized by NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and X-ray crystal structure analysis. ESI-MS proved to be a very powerful tool for determining the nuclearity (n value) unambiguously. X-ray crystal structure analyses of $[Co_4(put)_4(tacn)_4](CF_3SO_3)_4\cdot 12H_2O$ [triclinic, $P\bar{1}$ (No. 2)] and $[Co_4(aput)_4(tacn)_4]Cl_4\cdot 16H_2O$ [monoclinic, $C2/c$ (No. 15)] reveal that all purinethione ligands act as tridentate ligands via S^6/N(7) chelation and the N(9) bridge and both tetranuclear complexes adopt the cyclic S_4 structure which is stabilized by four intramolecular hydrogen bonds between N(3) and H−N(tacn). The trinuclear complex $[Co_3(put)_3(tacn)_3]^{3+}$ having the C_1 structure was optically resolved. Stereochemistry for the cyclic molecular boxes containing chiral octahedral ions is developed.

Introduction

A number of the synthetic strategies based on self-assembly reactions have been developed to synthesize supramolecular compounds.[1] Molecular squares (or boxes) are one of the simplest but interesting members of such supramolecular compounds.[2] Most molecular squares contain square planar d^8 metals as the components, such as Pd(II) and Pt(II), and hence their chemistry is relatively simple.[3] The use of an inherently chiral octahedral metal complex leads to stereochemical diversities due to the chiralities, and its chemistry is very challenging. We reveal here that the stereochemistry in a cyclic multinuclear complex containing octahedral cobalt(III) is quite different from that of complexes containing square planar d^8 metals.[4]

Purine-6-thione (H_2put) has multiple binding sites such as N(1), N(3), S^6, N(7), and N(9).[5] In the metal complex with a N,S-chelating purine-6-thione ligand, linkage isomerism is possible due to N(1)/S^6 four- or S^6/N(7) five-membered chelation. Recently, our studies showed that only S^6/N(7) five-membered chelation is found in $[Co(put\ or\ Hput)(en)_2]^{n+}$ (en = ethane-1,2-diamine)[6] and $[Ru(H_2put)(bipy)_2]^{2+}$ (bipy = 2,2′-bipyridine).[7] It is quite interesting that such a S^6/N(7) chelated put ligand still has coordination ability at N(1), N(3), and/or N(9).



	R
H_2put	H
H_2aput	NH_2
H_3tpuo	OH

Our strategy is based on the utilization of this multidentate bridging ability of put and related ligands. Three kinds of ligands were used: 9*H*-purine-6(1*H*)-thione (H_2put), 2-amino-9*H*-purine-6(1*H*)-thione (H_2aput), and 3,6-dihydro-6-thioxo-9*H*-purin-2(1*H*)-one (H_3tpuo). As shown in Scheme 1, the reaction of *fac*-$[CoCl_3(tacn)]$ (tacn = 1,4,7-triazacyclononane) and H_2put in the presence of an equimolar amount of NaOH will initially produce $[Co(Hput\text{-}N,S)Cl(tacn)]^{+}$. Then the resultant mononuclear complex $[Co(Hput\text{-}N,S)Cl(tacn)]^{+}$ will self-assemble mutually to form cyclic polynuclear complexes $[Co_n(put\text{-}N,S,N')_n(tacn)_n]Cl_n$. Here we report the synthesis of cyclic tri- and tetranuclear cobalt(III) complexes $[Co_n(L\text{-}N,S,N')_n(tacn)_n]$-

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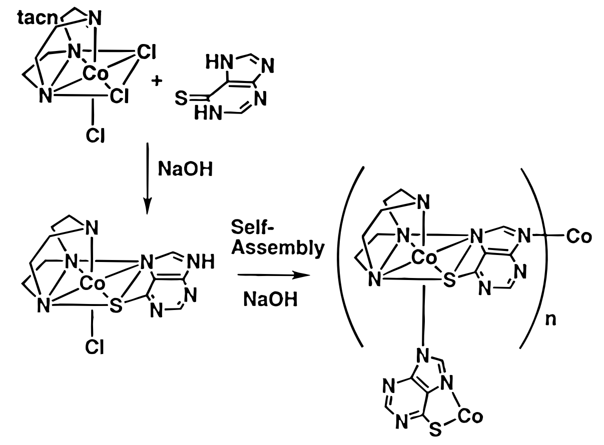
10.1021/ic9802146 CCC: $15.00

Scheme 1



X_n ($n = 3$ and 4 for L = put and $n = 4$ for L = aput and Htpou) and their characterization by NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and X-ray crystal structure analysis. Similar cyclic complexes containing purine ligands have been reported: $[Pt^{IV}_6(CH_3)_{18}$(theophyllinate-*O,N,N*)$_6]\cdot 12CHCl_3$,[8] $[Rh^{III}_3Cp^*_3$(9-methyladeninate-*N,N,N*)$_3](CF_3SO_3)_3\cdot 6H_2O$ (Cp* = η^5-pentamethylcyclopentadienyl),[9] $[Ru_4(\eta^6$-*p*-cymene)$_4$(adeninate-*N,N,N*)$_4](CF_3SO_3)_4$,[10] and $[Ru_3(\eta^6$-*p*-cymene)$_3$(9-ethyladeninate-*N,N,N*)$_3](CF_3SO_3)_3$.[10]

Experimental Section

Syntheses. Three purine-6-thione ligands were purchased from Aldrich, and tacn·3HCl was purchased from Tokyo Kasei Kogyou Co., Ltd., and these were used without further purification. The starting complex *fac*-$[CoCl_3(tacn)]$ was prepared according to the literature.[11]

$[Co_3(put)_3(tacn)_3]Cl_3\cdot 11H_2O$ (1) and $[Co_4(put)_4(tacn)_4]^{4+}$ (2). The ligand H_2put (0.29 g, 1.7 mmol) was suspended in water (50 cm^3), and the solution pH was adjusted to 8−9 by adding aqueous NaOH. To the above solution was added *fac*-$[CoCl_3(tacn)]$ (0.5 g, 1.7 mmol), and the mixture was stirred at 60 °C to dryness. After the solid was dissolved in water, the solution was concentrated at 60 °C to dryness again. The resulting solid was dissolved in 50 cm^3 of water, and the solution was evaporated at room temperature to give a brown precipitate (**1**: 160 mg). The filtrate was poured onto a column of SP-Sephadex C-25 resin and eluted with a 0.5 mol dm^{-3} solution of NaCl. The first brown band was concentrated with a vacuum evaporator, and the white precipitate of NaCl deposited by adding methanol to the filtrate was filtered off. This desalting process was repeated three times. The filtrate was poured onto a column of QAE-Sephadex A-25 resin (ClO_4^- form) and eluted with water. During this operation, separation of the complexes occurred: a part of the complex was precipitated in the column, and the remaining portion was eluted with water. The precipitated perchlorate **2a** was eluted only with hot water, and the solution was evaporated to a small volume to give the perchlorate salt. The eluted portion **2b** was collected, and the solution was evaporated to a small volume to give the perchlorate salt. The yields were 20% for **1** and 36% for **2** (**2a** + **2b**). These complexes were converted into other kinds of counterions using a QAE-Sephadex A-25 column. Complex **1** {Anal. Found: C, 29.74; H, 5.41; N, 22.26. Calc for $[Co_3(put)_3(tacn)_3]Cl_3\cdot 11H_2O$ ($C_{33}H_{73}Cl_3Co_3N_{21}O_{11}S_3$): C, 30.04; H, 5.58, N, 22.29}: UV/vis (water), λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}) 570 sh (300), 475 sh (640), 412 sh (1300), 324 (63 300), 268 sh (68 800), 244 sh (97 600), 228 (113 000). Complex **2a** {Anal. Found: C, 28.37; H, 4.35; N, 21.22. Calc for $[Co_4(put)_4(tacn)_4](ClO_4)_4\cdot 6H_2O$ ($C_{44}H_{80}Cl_{14}Co_4N_{28}O_{22}S_4$): C, 28.43; H, 4.34; N, 21.10. Found: C, 26.54; H, 3.86; N, 18.02. Calc for $[Co_4(put)_4(tacn)_4](CF_3SO_3)_4\cdot 12H_2O$ ($C_{48}H_{92}Co_4F_{12}N_{28}O_{24}S_8$): C, 26.62; H, 4.28, N, 18.11}: UV/vis (water), λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}) 513 (530), 402 (1800), 328 (49 900), 307 (45 300), 273 sh (45 200), 253 sh (58 500), 212 (115 000); ^{13}C NMR $[(CD_3)_2SO]$ δ 52.8, 51.7, 51.1, 50.7, 49.2 (tacn), 167.7 (C^6), 153.5 (C^4), 152.6 (C^2, C^8), 139.5 (C^5). Anal. Found for complex **2b**: C, 26.74; H, 4.19; N, 18.43. Calc for $[Co_4(put)_4(tacn)_4](CF_3SO_3)_4\cdot 11H_2O$ ($C_{48}H_{90}Co_4F_{12}N_{28}O_{23}S_8$): C, 26.84; H, 4.22, N, 18.26.

Optical Resolution of $[Co_3(put)_3(tacn)_3]^{3+}$. A column of 12 mm diameter was packed with 15 g of SP-Sephadex C-25 swollen in H_2O. A 30 mg sample of $[Co_3(put)_3(tacn)_3]Cl_3\cdot 11H_2O$, dissolved in 5 cm^3 of H_2O, was loaded onto the column and eluted with a 0.2 mol dm^{-3} solution of $Na_2[Sb_2$(D-tart)$_2]\cdot 2H_2O$ [D-tart = (*R,R*)-$C_4H_2O_6^{4-}$]. The complex completely separated into two enantiomers. Each band was concentrated with a vacuum evaporator, and the white precipitate of $Na_2[Sb_2$(D-tart)$_2]\cdot 2H_2O$ deposited by adding methanol to the filtrate was filtered off. The filtrate was poured onto a column of QAE-Sephadex A-25 resin (Cl^- form) and analyzed by circular dichroism (CD) measurements. The concentration of the solution was determined by referring to the molar absorption coefficient at 324 nm (ϵ/dm^3 mol^{-1} cm^{-1} = 63 300). The $(-)_{425}$-enantiomer (CD) was eluted first.

$[Co_4(aput)_4(tacn)_4]^{4+}$ (3). Complex **3** was prepared and isolated in a manner similar to that the above except for the use of H_2aput instead of H_2put. The chloride salt of complex **3** was obtained from the first brown band. The yield was ca. 50%. Complex **3** {Anal. Found: C, 28.58; H, 5.54; N, 24.47. Calc for $[Co_4(aput)_4(tacn)_4]Cl_4\cdot 16H_2O$ ($C_{44}H_{104}Cl_4Co_4N_{32}O_{16}S_4$): C, 28.67; H, 5.69; N, 24.32. Found: C, 25.23; H, 4.02; N, 19.52. Calc for $[Co_4(aput)_4(tacn)_4](CF_3SO_3)_4\cdot 15H_2O$ ($C_{48}H_{102}Co_4F_{12}N_{32}O_{27}S_8$): C, 25.29; H, 4.51, N, 19.66}: UV/vis (water), λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}) 536 sh (490), 394 sh (1720), 328 (41 500), 308 (38 000), 265 (56 100), 233 (104 000), 208 (127 000); ^{13}C NMR $[(CD_3)_2SO]$ δ 52.2, 52.1, 51.4, 50.9, 50.3, 50.1 (tacn), 165.3 (C^6), 157.1, 155.3, 153.2 (C^2, C^8 C^4), 133.2 (C^5).

$[Co_4(Htpuo)_4(tacn)_4]^{4+}$ (4). Complex **4** was prepared in a manner similar to the above except for the use of H_3tpuo instead of H_2put. The chloride salt of complex **4** was easily precipitated by concentrating the reaction mixture. This complex was converted into a CF_3SO_3 salt using a QAE-Sephadex A-25 column. The yield was ca. 50%. Complex **4** {Anal. Found: C, 25.91; H, 5.48; N, 19.42. Calc for $[Co_4(Htpuo)_4(tacn)_4]Cl_4\cdot 2NaCl\cdot 20H_2O$ ($C_{44}H_{108}Cl_6Co_4N_{28}Na_2O_{24}S_4$): C, 25.95; H, 5.35; N, 19.26. Found: C, 25.47; H, 4.46; N, 17.56. Calc for $[Co_4(Htpuo)_4(tacn)_4](CF_3SO_3)_4\cdot 14H_2O$ ($C_{48}H_{92}Co_4F_{12}N_{28}O_{30}S_8$): C, 25.45; H, 4.27; N, 17.31}: UV/vis (water), λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}) 541 sh (530), 426 sh (1360), 362 sh (46 600), 351 (59 000), 311 sh (22 900), 280 sh (33 700), 234 (107 000), 219 (116 000).

Caution! In general, perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great care. Our perchlorate salts ignited in a Bunsen-burner flame but presented no hazard in solutions and in normal treatment of the solids.

ESI Mass Spectral Measurements. ESI mass spectra were obtained on a sector-type mass spectrometer (JEOL-D300) connected to a laboratory-made ESI interface.[12] A sample solution was sprayed from the tip of a needle by applying a voltage 3.5 kV higher than that of a counter electrode. The distance between the needle and the counter electrode was 1 cm. The counter electrode consisted of a 12 cm long stainless steel capillary tube (0.5 mm i.d.). A stream of heated N_2 gas (70 °C) was used to aid desolvation of sprayed charged droplets. The flow rate of the sample solution was 2 μL/min and the corn voltage was 50 eV. For measurements of ESI mass spectra, the trifluoromethanesulfonate salts were used because of their higher solubilities in organic solvents. The samples were dissolved in freshly distilled acetonitrile or methanol, and nothing was added to promote ionization. The concentrations of samples were kept at ca. 10^{-4} mol dm^{-3}.

X-ray Crystal Structure Determinations of $[Co_4(put)_4(tacn)_4](CF_3SO_3)_4\cdot 12H_2O$ (2a: CR2) and $[Co_4(aput)_4(tacn)_4]Cl_4\cdot 16H_2O$ (3). The perchlorate salt of complex **2a** formed distorted octahedral crystals [CR**1**: tetragonal, $P\bar{4}2_1c$ (No. 114)]. The trifluoromethanesulfonate of complex **2a** crystallized as brown distorted trigonal prisms [CR**2**:

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Table 1. Crystallographic Data for $[Co_4(put)_4(tacn)_4](CF_3SO_3)_4{\cdot}12H_2O$ (Complex **2a**) and $[Co_4(aput)_4(tacn)_4]Cl_4{\cdot}16H_2O$ (Complex **3**)

	complex **2a** (CR**2**)	complex **3**
empirical formula	$C_{48}H_{92}Co_4F_{12}N_{28}O_{24}S_8$	$C_{44}H_{104}Cl_4Co_4N_{32}O_{16}S_4$
fw	2165.67	1843.32
crystal system	triclinic	monoclinic
a, Å	18.410(8)	23.423(5)
b, Å	18.772(8)	14.630(4)
c, Å	15.667(6)	22.914(4)
α, deg	97.37(4)	
β, deg	106.76(4)	90.70(2)
γ, deg	112.78(3)	
V, Å^3	4603(4)	7851(2)
Z	2	4
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
T, °C	23	23
ρ_c, g cm^{-3}	1.562	1.559
μ(Mo Kα), cm^{-1}	9.76	11.51
R^a	0.077	0.042
$R_w{}^b$	0.1055	0.045

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)]^{1/2}$; $w = 1/\sigma^2(F_o)$.

triclinic, $P\bar{1}$ (No. 2)]. On the other hand, the trifluoromethanesulfonate of complex **2b** gave two kinds of crystals: hexagonal plates [CR**3**: triclinic, $P\bar{1}$ (No. 2)] and distorted square prisms [CR**4**: monoclinic, $P2_1/a$ (No. 14)]. The last three crystals have the same composition, $[Co_4(put)_4(tacn)_4](CF_3SO_3)_4{\cdot}nH_2O$, but belong to the distinct crystal systems with different lattice constants. X-ray crystal analyses revealed that the complex cations $[Co_4(put)_4(tacn)_4]^{4+}$ have the same structure in all cases, though the data qualities for CR**1**, CR**3**, and CR**4** are not so good.[13] Hence we show only the structure determination for CR**2** ($[Co_4(put)_4(tacn)_4](CF_3SO_3)_4{\cdot}12H_2O$). A brown prismatic 0.35 × 0.25 × 0.45 mm crystal of CR**2** was obtained from aqueous solution at room temperature. For complex **3** ($[Co_4(aput)_4(tacn)_4]Cl_4{\cdot}16H_2O$), red-brown columnar 0.25 × 0.25 × 0.40 mm crystal was obtained from an aqueous solution at room temperature.

Diffraction data were collected on a Rigaku AFC7R or AFC5R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Crystallographic data for the complexes are listed in Table 1. Structures were solved using direct methods, and parameters were refined by full-matrix least-squares methods. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Significant disorder was observed in the structure of complex **2a**. Three of the four CF_3SO_3 anions and most crystal waters were disordered, and their exact positions could not been determined. Some hydrogen atoms were included but not refined. The final cycles of full-matrix least-squares refinement were based on 9748 observed reflections ($I > 3\sigma_I$) and 856 variable parameters for complex **2a** and on 6410 observed reflections ($I > 3\sigma_I$) and 485 variable parameters for complex **3**. Refinement was carried out on F. The final values of R and R_w were 0.077 and 0.1055, respectively, for complex **2a** and 0.042 and 0.045, respectively, for complex **3**. The weighting scheme was based on counting statistics. Maximum and minimum peaks in the final Fourier-difference map were 0.84 and −0.64 e Å^{-3} for complex **2a** and 0.83 and −0.56 e Å^{-3} for complex **3**. Neutral-atom scattering factors were taken from ref 14, anomalous dispersion coefficients from ref 15, and $\Delta f\,'$ and $\Delta f\,''$ values from ref 16. All calculations were performed using the TEXSAN[17] crystallographic software package.

Measurements. UV/vis absorption spectra were recorded on a Hitachi 330 spectrophotometer, CD spectra on a JASCO J-500 spectrophotometer, and proton and ^{13}C NMR spectra on a JEOL JNM-GSX-270 spectrometer in $(CD_3)_2SO$ at 30 °C. X-ray crystal analyses were performed by the X-ray Diffraction Service of the Department of Chemistry, Osaka University.

Results and Discussion

Preparation of the Complexes. The reaction of *fac*-$[CoCl_3(tacn)]$ and H_2put in the presence of an equimolar amount of NaOH will initially produce $[Co(Hput\text{-}N,S)Cl(tacn)]^+$. Subsequent deprotonation of the put ligand will result in the formation of cyclic polynuclear complexes $[Co_n(put\text{-}N,S,N')_n(tacn)_n]Cl_n$ via self-assembly of the mononuclear complex $[Co(Hput)Cl(tacn)]^+$. The synthetic strategy as shown in Scheme 1 has been effectively realized in the present systems.

In the case of the put ligand, two complexes, **1** and **2**, were obtained by fractional crystallization. Because of its low solubility, complex **1** was easily isolated by concentrating the reaction mixture, and complex **2** was obtained after column purification. The column separation of the two complexes using SP-Sephadex C-25 was unsuccessful because of the coprecipitation of the complexes in the column. There were some bands with the higher complex charge in the column, but they were minor products and could not be isolated. Only one complex was obtained for aput (**3**) and for Htpuo (**4**). There was no evidence for the presence of the isomers from the fractional crystallization or the column separation of these systems.

The apparent colors of all complexes are dark brown. The UV/vis absorption spectra of complexes **1** and **2** are shown with that of $[Co(put)(en)_2]^+$ in the Supporting Information (Figure S1). The first and second d−d bands of the present complexes are broad and obscure compared with those of $[Co(put)(en)_2]^+$. It is noteworthy that the molar absorption coefficients of the present complexes are especially large in the second d−d absorption region. The absorption patterns in the region 28 000−50 000 cm^{-1} are very similar, which indicates the coordination of the put ligand. Thus, the absorption spectral similarities show that complexes **1** and **2** have the same CoN_5S chromophore as that of $[Co(put)(en)_2]^+$.[6] The situation was the same for the systems of aput and Htpuo. The elemental analyses of all complexes agreed well with the composition of $[Co_n(L\text{-}N,S,N')_n(tacn)_n]X_n$. The determination of n, however, was very difficult except for the use of X-ray crystal analysis. Then, ESI mass spectral measurements were attempted.

ESI Mass Spectra. Figure 1 shows positive ESI mass spectra of complexes **1** and **2** in methanol, which are very simple. The m/z values given, unless noted otherwise, refer to calculated masses. The dominant peaks of $m/z = 338$ and 582 for complex **1** in Figure 1a correspond to the ions $[M - 3X]^{3+}$ and $[M - 2X]^{2+}$, respectively. The peak of $m/z = 506$ corresponds to the ion $[M - 3X - H]^{2+}$. The peak of $[M - X]^+$ ($m/z = 1312$) could not be observed because our apparatus can measure up to only $m/z = 1200$. These multiply charged ions are produced from loss of negative counterions, which is denoted by $[M - nX]^{n+}$, where M and X represent the complex and $CF_3SO_3^-$, respectively. These results indicate that complex **1** has a cyclic trinuclear structure. Similarly, the values of $m/z = 338$, 500, and 825 for complex **2** in Figure 1b correspond to the ions $[M - 4X]^{4+}$, $[M - 3X]^{3+}$, and $[M - 2X]^{2+}$, respectively, and agree

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(13) Crystal data are as follows. CR**1**: $C_{44}H_{80}Cl_4Co_4N_{28}O_{22}S_4$, tetragonal, space group $P\bar{4}2_1c$ (No. 114), $a = 15.659(2)$ Å, $c = 14.274(3)$ Å, $Z = 2$, $V = 3500.2(6)$ Å^3, $R = 0.113$, $R_w = 0.138$. CR**3**: $C_{48}H_{86}Co_4F_{12}N_{28}O_{12}S_8{\cdot}nH_2O$, triclinic, space group $P\bar{1}$ (No. 2), $a = 17.55(1)$ Å, $b = 20.223(9)$ Å, $c = 15.509(7)$ Å, $\alpha = 104.16(4)°$, $\beta = 119.17(5)°$, $\gamma = 99.20(4)°$, $Z = 2$, $V = 4400(5)$ Å^3, $R = 0.157$, $R_w = 0.172$. CR**4**: $C_{48}H_{86}Co_4F_{12}N_{28}O_{12}S_8{\cdot}nH_2O$, monoclinic, space group $P2_1/a$ (No. 14), $a = 19.568(6)$ Å, $b = 20.958(5)$ Å, $c = 22.056(5)$ Å, $\beta = 115.25(2)°$, $Z = 4$, $V = 8181(4)$ Å^3, $R = 0.091$, $R_w = 0.118$.

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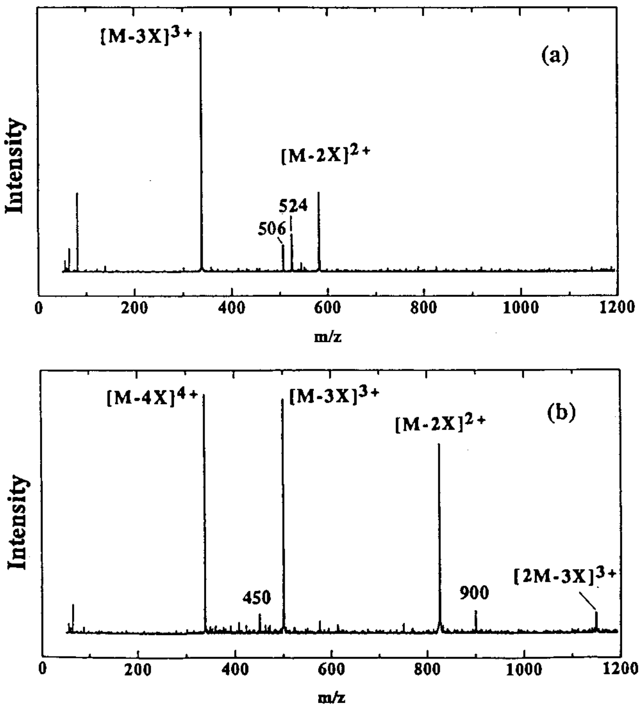

Figure 1. Positive ESI mass spectra of complexes **1** (a; $n = 3$) and **2** (b; $n = 4$) measured in methanol. M = $[Co_n(put\text{-}N,S,N')_n(tacn)_n](CF_3SO_3)_n$. A few mass peaks in the Figure could not be identified.

well with the calculated values. The peaks of *m/z* = 450 and 900 correspond to the ions $[M - 4X - H]^{3+}$ and $[M - X + H]^{2+}$, respectively. The peak of $[M - X]^+$ (*m/z* = 1799) is beyond our apparatus capability. These results confirm that complex **2** has a cyclic tetranuclear structure.

ESI mass spectra were also recorded for complexes **3** and **4** (Figure S2, Supporting Information). Both complexes show the peaks of $[M - 4X]^{4+}$, $[M - 3X]^{3+}$, and $[M - 2X]^{2+}$. The peaks of *m/z* = 470, 570, and 930 for complex **3** correspond to the ions $[M - 4X - H]^{3+}$, $[M - 2X + H]^{3+}$, and $[M - X + H]^{2+}$, respectively, and the peaks of *m/z* = 472 and 782 for complex **4** to the ions $[M - 4X - H]^{3+}$ and $[M - 3X - H]^{2+}$, respectively. The peaks of $[M - X]^+$ (*m/z* = 1859 for aput and 1863 for Htpuo) are beyond our apparatus capability. The other peaks agree well with the values expected for a cyclic tetranuclear structure.

ESI mass spectrometry has proved to be a very powerful tool for determining the nuclearity (*n* value) unambiguously for the present cyclic multinuclear complexes of $[Co_n(L\text{-}N,S,N')_n(tacn)_n](CF_3SO_3)_n$. All spectra are very simple and contain almost only the desired peaks. This is partly because the present complexes have very robust cyclic structures.[18]

Possible Geometrical Isomers and NMR Spectra. When we consider the geometrical isomers of the present complexes, the unit complex is expressed as an arrow because it has a head and a tail as shown in Figure 2. The head denotes the N,S-chelated moiety having further coordinating ability and the tail means that the moiety is bridged by the neighboring put ligand. The arrows must be arrayed in the same direction to form cyclic polynuclear complexes. It should be noted that the structures where two arrows converge on one Co(III) unit never become cyclic. Each unit cobalt(III) complex has a chirality of C (clockwise) or A (anticlockwise)[19] because it belongs to a $[Co(N_3)(AB)C]$ structure type.[20]

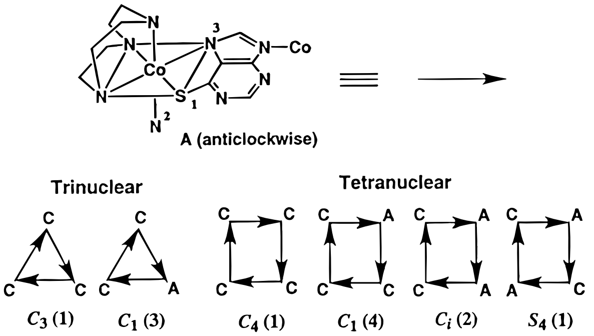

Figure 2. Possible geometrical isomers for the cyclic tri- and tetranuclear complexes. The characters C (clockwise) and A (anticlockwise) denote the chirality of the unit Co(III) complex. Each isomer is denoted by its complex symmetry, and the numbers in parentheses show the expected NMR sets.

Two racemic isomers, (CCC + AAA) and (CCA + AAC), are possible for the cyclic trinuclear structure. The complex symmetries C_3 and C_1 are used to denote the isomers. The numbers in parentheses following the symmetries indicate the expected NMR set. One set of NMR signals is composed of three NH(tacn) signals and two proton signals in the case of put (H^2 and H^9). It should be noted that the two C sites in the C_1 isomer are chemically different because both the heads and tails at two sites are different from each other, and hence three NMR sets are expected for this isomer. Similarly there are four isomers for the cyclic tetranuclear structure as shown in Figure 2. These isomeric symmetries are C_4 (CCCC + AAAA), C_1 (CCCA + AAAC), C_i (CCAA), and S_4 (CACA) for the cyclic tetranuclear complex. The latter two isomers are achiral.

Figure 3a shows the ^1H NMR spectrum of complex **1**: three sets of NMR signals appear. This complex is determined to have the cyclic trinuclear structure by ESI mass spectrometry. For the cyclic trinuclear structure, two isomers, C_3 and C_1, are possible as shown in Figure 2. The presence of three NMR sets indicates that complex **1** has the C_1 structure whose cyclic isomeric array is CCA (or AAC).

Figure 3b shows the ^1H NMR spectrum of complex **2**. This complex has the cyclic tetranuclear structure as determined by ESI mass spectrometry. Complex **2** showed one NMR set, which is expected for the C_4 or S_4 isomer. The S_4 structure was determined by X-ray crystal analysis as described below. One of broad NH signals appears at δ 10.55 whose chemical shift is very low compared with those of the other tacn complexes.[21] Such a low magnetic field shift indicates the existence of an intramolecular hydrogen bond.[22] The hydrogen bond is only possible for the S_4 isomer. Complexes **3** and **4** also showed one NMR set and the presence of a low magnetic NH signal (δ 10.89 for **3** and 11.40 for **4**); see Table 2. Since both have the cyclic tetranuclear structure, the S_4 structure is also assigned to these complexes. The fact that only the S_4 isomer exists stereoselectively in all the systems is rather surprising but can be explained by the presence of intramolecular hydrogen bondings in this isomer as described below.

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Table 2. Proton NMR Spectral Data (δ)[a] for the Cyclic Purine-6-thione Complexes [Solvent: $(CD_3)_2SO$]

compound	H^2 and/or H^8	NH(tacn)	NH_2(aput)	NH(Htpuo)
$[Co_3(put)_3(tacn)_3](ClO_4)_3$ (**1**)	8.29 (s, 2H), 8.37 (s, 1H) 8.73 (s, 1H), 8.95 (s, 1H) 9.19 (s, 1H)	6.54 (s, 1H), 7.40 (s, 1H), 7.49 (s, 1H) 7.62 (s, 1H), 7.75 (s, 1H), 7.83 (s, 1H) 8.54 (s, 1H), 9.60 (s, 1H), 10.55 (s, 1H)		
$[Co_4(put)_4(tacn)_4](ClO_4)_4$ (**2**)	8.28 (s, 1H), 8.44 (s, 1H)	6.95 (s, 1H), 7.56 (s, 1H), 10.64 (s, 1H)		
$[Co_4(aput)_4(tacn)_4](ClO_4)_4$ (**3**)	8.50 (s, 1H)	6.64 (s, 1H), 7.75 (s, 1H), 10.89 (s, 1H)	5.69 (s, 2H)	
$[Co_4(Htpuo)_4(tacn)_4](CF_3SO_3)_4$ (**4**)	8.10 (s, 1H)	7.10 (s, 1H), 7.71 (s, 1H), 11.40 (s, 1H)		10.74 (s, 1H)

[a] Downfield relative to $SiMe_4$ in $(CD_3)_2SO$.

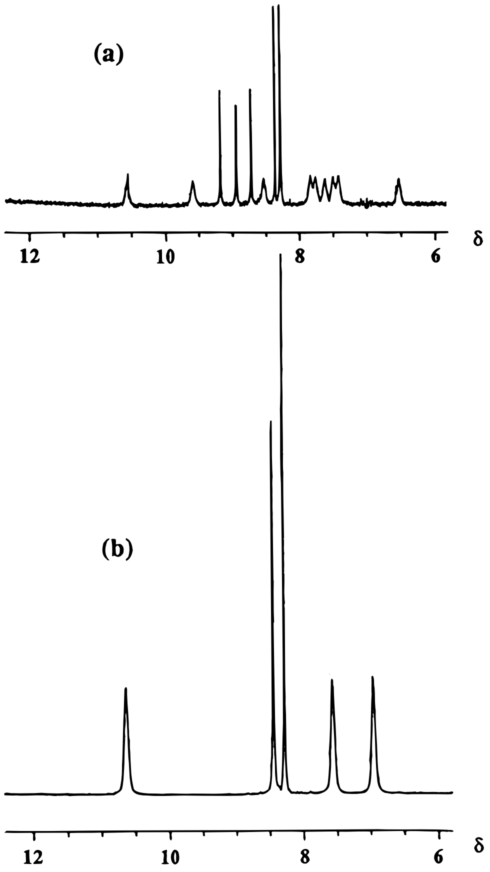

Figure 3. Proton NMR spectra of $[Co_3(put)_3(tacn)_3](ClO_4)_3$ (complex **1**: a) and $[Co_4(put)_4(tacn)_4](ClO_4)_4$ (complex **2**: b) in $(CD_3)_2SO$.

Crystal Structure of $[Co_4(put)_4(tacn)_4](CF_3SO_3)_4$. Figure 4 shows an ORTEP drawing[23] of the cation in complex **2**, $[Co_4(put)_4(tacn)_4](CF_3SO_3)_4$. The selected mean bond distances and angles are listed in Table 3. Complex **2** has a tetranuclear structure. The orientations of the put ligands are alternately up and down. The Co(1) and Co(3) complexes have chirality C and the Co(2) and Co(4) complexes chirality A; hence complex **2** adopts the S_4 structure. Since space group is $P\bar{1}$ and Z is 2, the four unit Co(III) complexes are crystallographically independent. The put ligand acts as a tridentate ligand: it coordinates to one cobalt(III) ion in a bidentate manner via the S^6 and N(7) donors, which form a five-membered chelate ring, and bridges to another cobalt(III) ion via the N(9) donor. The mean bite angle S−Co−N(7) is 88.1(3)°, which is comparable to 88.6(1)° in $[Co(put\text{-}N,S)(en)_2]Cl$[6] and much larger than 84.7(2)° in $[Ru(H_2put\text{-}N,S)(bipy)_2]ClO_4$.[7]

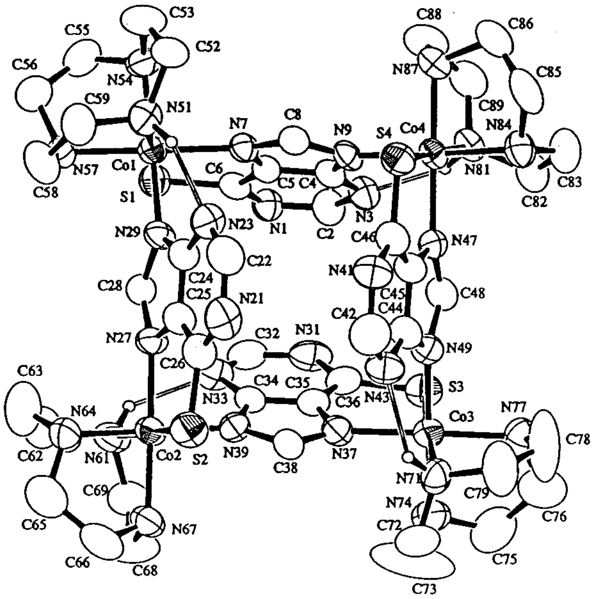

Figure 4. ORTEP drawing of the cation of $[Co_4(put)_4(tacn)_4](CF_3SO_3)_4{\cdot}12H_2O$ (complex **2a**: CR**2**).

The mean Co−S and Co−N(7) lengths [2.342(3) and 1.962(8) Å] of the present complex are similar to 2.331(1) and 1.953(3) Å in $[Co(put\text{-}N,S)(en)_2]Cl$.[6] Similarly, the mean C(6)−S bond length 1.73(1) Å is analogous to 1.732(4) Å in $[Co(put\text{-}N,S)(en)_2]^{2+}$ and also to values for other cobalt(III) complexes: 1.732(4) Å in $[Co(mpymt\text{-}N,S)(en)_2](ClO_4)_2$,[24] 1.738(7) Å in $[Co(tuc\text{-}N,S)(en)_2]ClO_4$,[22a] and 1.742(7) Å in $[Co(apymt\text{-}N,S)(en)_2](ClO_4)_2$.[22b] Interestingly, the bond lengths and angles of the present put ligand are quite analogous to those in $[Co(put\text{-}N,S)(en)_2]Cl$ irrespective of the bridging of the N(9) donor.

Each unit Co(III) complex has chirality C (clockwise) or A (anticlockwise). The S_4 structure has the alternate array of CACA, and this tetranuclear S_4 complex cannot be optically resolved. It is important that four intramolecular hydrogen bonds between N(3) and H−N(tacn) become possible only in the S_4 structure: N(51)- - -N(23) 2.80(1) Å [N(51)−H(9)- - -N(23) 150.01°]; N(61)- - -N(33) 2.80(1) Å [N(61)−H(12)- - -N(33) 137.34°]; N(71)- - -N(43) 2.91(1) Å [N(71)−H(15)- - -N(43) 140.17°]; N(81)- - -N(3) 2.78(1) Å [N(81)−H(18)- - -N(3) 148.86°]. These hydrogen bonds, in addition to the N(9)−Co bridges, stabilize the S_4 cyclic structure. The intramolecular hydrogen bonds exist in solution: the low-field NH(tacn) signal at δ 10.55 corresponds to this interaction.

Crystal Structure of $[Co_4(aput)_4(tacn)_4]Cl_4{\cdot}16H_2O$. Figure 5 shows an ORTEP drawing[23] of the cation in complex **3**, $[Co_4(aput)_4(tacn)_4]Cl_4$. The selected mean bond distances and angles are listed in Table 3. Since the space group is $C2/c$ (Z = 4) and complex **3** has a C_2 axis, the two unit complexes become crystallographically independent. The Co(1) and Co(1*) complexes have chirality C and the Co(2) and Co(2*) complexes chirality A; hence complex **3** adopts the same S_4 structure as complex **2**. The aput ligand acts as a tridentate ligand through the S^6, N(7), and N(9) donors. The mean bite

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Table 3. Selected Mean Bond Distances (Å) and Bond Angles (deg) of $[Co_4(put)_4(tacn)_4](CF_3SO_3)_4{\cdot}12H_2O$ (**2a**: CR**2**) and $[Co_4(aput)_4(tacn)_4]Cl_4{\cdot}16H_2O$ (**3**)

complex **2a**[a]		complex **3**[a]	
	Bond Distances		
Co−S	2.342(3)	Co−S	2.335(1)
Co−N(7)	1.962(9)	Co−N(7)	1.967(3)
Co−N(29)	1.961(9)	Co−N(29)	1.956(3)
Co−N(51)	1.958(9)	Co−N(51)	1.981(3)
Co−N(54)	1.95(1)	Co−N(54)	1.955(3)
Co−N(57)	1.95(1)	Co−N(57)	1.944(3)
S−C(6)	1.73(1)	S−C(6)	1.736(4)
N(1)−C(2)	1.37(1)	N(1)−C(2)	1.370(5)
N(1)−C(6)	1.35(1)	N(1)−C(6)	1.341(5)
N(3)−C(2)	1.33(1)	N(3)−C(2)	1.346(5)
N(3)−C(4)	1.35(1)	N(3)−C(4)	1.355(5)
C(4)−C(5)	1.39(1)	C(4)−C(5)	1.365(5)
C(5)−C(6)	1.37(1)	C(5)−C(6)	1.380(5)
N(7)−C(5)	1.36(1)	N(7)−C(5)	1.371(4)
N(7)−C(8)	1.34(1)	N(7)−C(8)	1.335(4)
N(9)−C(4)	1.38(1)	N(9)−C(4)	1.376(4)
N(9)−C(8)	1.37(1)	N(9)−C(8)	1.367(5)
		C(2)−N(2)	1.368(5)
	Bond Angles		
S−Co−N(7)	88.1(3)	S−Co−N(7)	88.3(1)
Co−S−C(6)	95.5(4)	Co−S−C(6)	96.2(1)
S−C(6)−C(5)	115.8(9)	S−C(6)−C(5)	115.1(3)
C(6)−C(5)−N(7)	128(1)	C(6)−C(5)−N(7)	128.4(4)
C(5)−N(7)−Co	111.8(7)	C(5)−N(7)−Co	112.0(2)
C(5)−C(6)−N(1)	118(1)	C(5)−C(6)−N(1)	118.6(4)
C(2)−N(1)−C(6)	116(1)	C(2)−N(1)−C(6)	116.6(3)
N(1)−C(2)−N(3)	130(1)	N(1)−C(2)−N(3)	128.4(4)
C(2)−N(3)−C(4)	112(1)	C(2)−N(3)−C(4)	112.8(3)
N(3)−C(4)−C(5)	123(1)	N(3)−C(4)−C(5)	122.8(3)
C(4)−C(5)−C(6)	121(1)	C(4)−C(5)−C(6)	120.9(3)
C(5)−N(7)−C(8)	103.9(9)	C(5)−N(7)−C(8)	103.3(3)
N(7)−C(8)−N(9)	114(1)	N(7)−C(8)−N(9)	114.3(3)
C(4)−N(9)−C(8)	104.0(9)	C(4)−N(9)−C(8)	104.0(3)
N(9)−C(4)−C(5)	108(1)	N(9)−C(4)−C(5)	107.8(3)
C(4)−C(5)−N(7)	111(1)	C(4)−C(5)−N(7)	110.8(3)
S−Co−N(51)	174.4(3)	S−Co−N(51)	173.9(1)
N(7)−Co−N(57)	179.0(4)	N(7)−Co−N(57)	177.1(1)
N(54)−Co−N(29)	177.6(4)	N(54)−Co−N(29)	177.2(1)

[a] Each value is the mean of four values for complex **2a** and two values for complex **3**, and the smallest number is used as the representative.

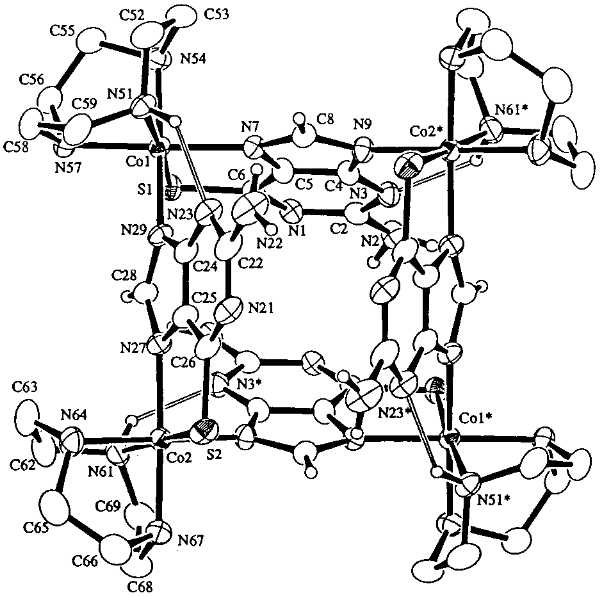

Figure 5. ORTEP drawing of the cation of $[Co_4(aput)_4(tacn)_4]Cl_4{\cdot}16H_2O$ (complex **3**).

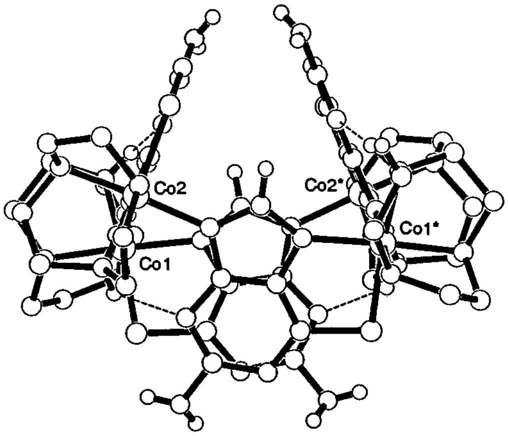

Figure 6. Side view of the cation of $[Co_4(aput)_4(tacn)_4]Cl_4{\cdot}16H_2O$ (**3**).

angle S−Co−N(7) [88.3(1)°], the mean Co−S and Co−N(7) lengths [2.335(1) and 1.967(3) Å] and the mean C(6)−S bond length [1.736(4) Å] are very similar to those of complex **2**. Three Co−N(tacn) bond lengths are different: the Co−N(51) bond length trans to sulfur is 1.981(3) Å, and the average of Co−N(54) and Co−N(57) cis to sulfur is 1.950(3) Å. The difference between the trans and cis bond lengths is 0.031 Å. This trans influence is slightly less than 0.039 Å of purine-6-thionate[5] and 0.041 Å of 2-aminoethanethiolate[25] but larger than 0.023 Å of the 2-pyridinethiolate[26] in the corresponding $[Co(N,S)(en)_2]^{n+}$ type complexes. Interestingly, the bond lengths and angles of the aput ligand are quite analogous to those of the put ligand in complex **2**, as shown in Table 2. The introduction of the amino group at the 2-position of the purine-6-thione results in no significant effect on the structure of the present cyclic complexes.

There are also four intramolecular hydrogen bonds between N(3) and H−N(tacn) of the neighboring complex in the S_4 structure: N(3)- - -N(61) 2.796(4) Å [N(61)−H(61)- - -N(3) 136.7°] and N(23)- - -N(51) 2.823(4) Å [N(51)−H(51)- - -N(23) 135.5°]. Both the N(9)−Co bridge and the N(3)- - -H−N(tacn) hydrogen bond resemble a bidentate chelation and stabilize the S_4 cyclic structure. The low-field NH(tacn) signal appears at δ 10.89 for complex **3**, which indicates that the intramolecular hydrogen bonds exist even in solution.

Figure 6 shows the side view of complex **3**. The four cobalt(III) ions form a square plane but are not in the same plane. The mean Co- -Co distance is 6.118 Å and the mean Co- -Co- -Co angle 87.53°. There are $\pi-\pi$ stacking interactions at two sites between the opposite two aput ligands. The mean distances N(1)- -N(1)*, N(1)- -N(2)*, and N(1)- -C(2)* are 3.174(6), 3.209(5), and 3.251(5) Å, respectively. The central cavity becomes narrow at the terminal position of aput due to these interactions. The side view and cavity size of complex **2** [mean Co- -Co = 6.113 Å and mean Co- -Co- -Co = 88.83°] quite resemble those of complex **3**.

Optical Resolution and Characterization of $[Co_3(put)_3(tacn)_3]^{3+}$. We prepared many kinds of counterions for complex **1**, but all crystals were fluffy needles and were not adequate for crystal analysis. It is reasonable that the put ligand coordinates via the S^6 and N(7) donors in this complex, but the bridging sites are not clear. Three bridging sites N(1), N(3),

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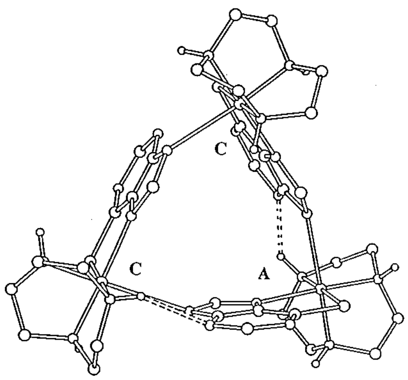

Figure 7. Proposed C_1 structure for $[Co_3(put)_3(tacn)_3]^{3+}$.

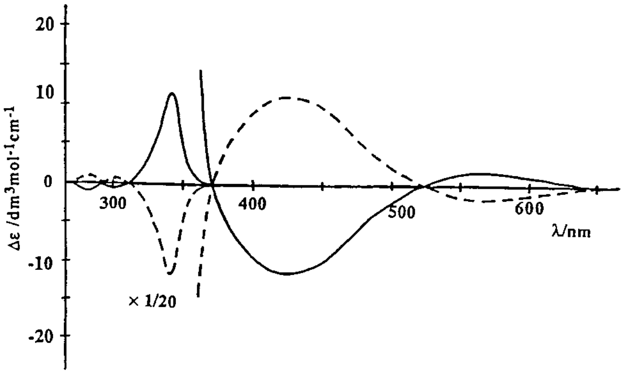

Figure 8. CD spectra of $[Co_3(put)_3(tacn)_3]^{3+}$: solid line, the first $(-)_{425}$-band; dotted line, the second $(+)_{425}$-band.

and N(9) are possible. The N(1) site is possible only for the isomeric array of CCC (or AAA) as exemplified in $[Rh_3Cp^*_3$(9-methyladeninate-*N*,*N*,*N*)$_3](CF_3SO_3)_3\cdot 6H_2O$[9] and $[Ru_3(\eta^6$-*p*-cymene)$_3$(9-ethyladeninate)$_3](CF_3SO_3)_3$[10] and impossible for the present CCA isomer. One low magnetic field NH(tacn) signal at δ 10.55 indicates the existence of a strong intramolecular hydrogen bond as found in complexes **2** and **3**. Such an intramolecular hydrogen bond is only possible for the N(9) bridging structure. Hence we conclude that the cyclic trinuclear complex **1** has the C_1 structure and the put coordination mode, with S^6 and N(7) chelation and N(9) bridging, is the same as that found in complex **2**. The proposed structure is shown in Figure 7, where one strong and one weak intramolecular hydrogen bond exist. There is increased strain in such a cyclic trinuclear structure compared with a tetranuclear structure, and hence even the flat plane of purinethione is distorted significantly. The fact that the molar absorption coefficients of complex **1** are somewhat larger than those of complex **2** reveals the strained feature of the trinuclear complex.

Complex **1** was optically resolved using a column of SP-Sephadex C-25 with a 0.2 mol dm^{-3} solution of $Na_2[Sb_2$(D-tart)$_2]\cdot 2H_2O$. The complex completely separated into two bands, and the $(-)_{425}$-enantiomer(CD) was eluted first. The CD spectra are shown in Figure 8. The first band exhibits two CD components, (+) and (−), from the lower energy side of the d−d band region. The main peak at 425 nm seems to be composite peaks of the first and the second components, judging from its peak position. It is noteworthy that the CD intensities [$\Delta\epsilon_{570} = +1.6$ and $\Delta\epsilon_{425} = -11.3$] are very much higher than those of [Co(N$_3$)(AB)C] type complexes such as $(-)_{488}$-[Co(gly)(NH$_3$)(tame)]$^{2+}$ [$\Delta\epsilon_{538} = +0.016$ and $\Delta\epsilon_{488} = -0.44$][20] and $(-)_{455}$-[Co(gly)(NH$_3$)(tacn)]$^{2+}$ [$\Delta\epsilon_{543} = -0.02$, $\Delta\epsilon_{505} = +0.06$, and $\Delta\epsilon_{455} = -0.42$],[27] where tame and gly denote 1,1,1-tris(aminomethyl)ethane and glycinate(1−), respectively. These results also indicate the distorted structure of the present complex. The CD pattern of complex **1** is very similar to those of the above mononuclear complexes. The absolute configuration of $(-)_{455}$-[Co(gly)(NH$_3$)(tacn)]$^{2+}$ is determined to be C (clockwise) by X-ray crystal analysis.[28] Since chirality A of complex **1** corresponds to chirality C of [Co(gly)(NH$_3$)(tacn)]$^{2+}$ due to the apparent reversal of the notation,[19] the first band of complex **1** can be assigned to A (anticlockwise).

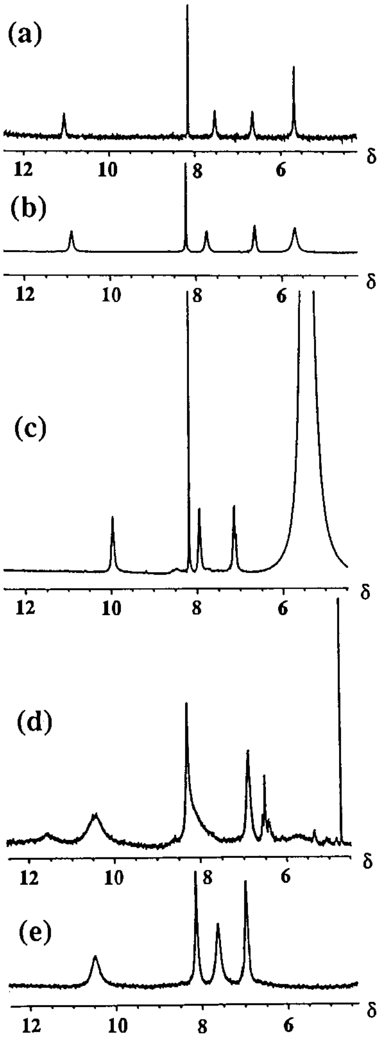

Figure 9. Counterion-dependent proton NMR spectral behaviors of $[Co_4(aput)_4(tacn)_4]X_4$: (a) X = Cl$^-$; (b) X = ClO$_4^-$; (c) X = BF$_4^-$; (d) X = PF$_6^-$; (e) X = CF$_3SO_3^-$. All spectra were obtained in (CD$_3$)$_2$SO.

Counterion Dependence of ^{1}H NMR Spectra. As described in the crystal analysis section, three kinds of crystals were obtained for the trifluoromethanesulfonate of complex **2**, $[Co_4(put)_4(tacn)_4](CF_3SO_3)_4\cdot n H_2O$: distorted octahedra (CR**2**), hexagonal plates (CR**3**), and octahedral prisms (CR**4**). X-ray crystal analyses show that they belong to the different crystal systems as shown in ref 13 but the complex cations $[Co_4(put)_4(tacn)_4]^{4+}$ adopt the same S_4 structure in all cases even though the proton NMR spectrum of complex **2a** is a little different from that of complex **2b**. Such polymorphism is characteristic of the present cyclic complexes.

Figure 9 shows the ^{1}H NMR spectra of several counterions for $[Co_4(aput)_4(tacn)_4]X_4$. All samples were prepared from the

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same chloride and measured in $(CD_3)_2SO$. The C(8)−H signal appears at the constant position δ 8.1. However, the chemical shifts of the other signals, three N−H(tacn) and NH_2, are variable depending on their counterions. The situation is common for all the cyclic complexes. The present cyclic complex has a large cavity in the central position which is surrounded by the aromatic rings of the purinethiones. Partial encapsulation and/or insertion of counterions into the cavity may be responsible for the variations of proton NMR chemical shifts. However, there is no concrete evidence of such encapsulation or insertion of counterions so far.

Supporting Information Available: Figure S1 (UV/vis absorption spectra of complexes **1** and **2** and $[Co(put\text{-}N,S)(en)_2]^+$) and Figure S2 (positive ESI mass spectra of complexes **3** and **4**) (2 pages). X-ray crystallographic files, in CIF format, for **2a** (CR**2**) and **3** are available on the Internet only. Ordering and access information is given on any current masthead page.

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