Synthesis and Stereochemistry of Homoleptic Cobalt(III) Complexes Containing Pyrimidine-2-thionate and Its Derivatives

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A room-temperature reaction of $Co(CH_3CO_2)_2 \cdot 4H_2O$ with pyrimidine-2-thione (Hpymt), or eight kinds of their derivatives (mole ratio=1 : 2.8—3.0) in methanol, was carried out in air. It was found that the substituent group at a 4-position in the pymt skeleton governs the product. The pymt and its derivatives, having an alkyl or an amino group as the 4-substituent, gave tris-type cobalt(III) complexes *mer*-$[Co(N\text{-}S)_3]$ in good yields. On the other hand, the 2-thiouracil derivatives, having an oxygen or a sulfur atom as the 4-substituent, produced only bis-type cobalt(II) complexes $[Co(N\text{-}S)_2]$. Such different ligand behavior concerns the different electronic structures of the pyrimidine rings. The presence of three linkage isomers in *mer*-[Co(4-methyl-pymt)$_3$] has been confirmed by ^{59}Co NMR spectroscopy, and an important role of the CH$\cdots\pi$ attractive interaction has been found.

We are interested in the coordination chemistry of cobalt(III) and rhodium(III) complexes containing more than one sulfur atom as donors, because of stereochemical diversity. However, relatively little work has been carried out with heterocyclic thione ligands, such as pyridine-2-thione (Hpyt), pyrimidine-2-thione (Hpymt), and 2-thiouracil derivatives.[1] The coordination of these ligands generates four-membered chelate rings. Particularly tris-type complexes become highly strained, since all chelate rings are four-membered. In a homoleptic tris-type $[M(N\text{-}S)_3]$, six crystal structures have been known so far (Chart 1). The two cobalt(III)[2,3] and the two rhodium(III)[4,5] complexes containing Hpyt or 3-trimethylsilyl-pyridine-2-thione (Hsipyt) adopt a meridional geometrical form, whereas a facial form has been reported for $[Co(dmpyt)_3]$ (Hdmpymt= 4,6-dimethylpyrimidine-2-thione)[6] and $[Rh(6mpyt)_3]$ (H6mpyt=6-methylpyridine-2-thione).[7] Since there are many ligand derivatives having a pyrimidine-2-thione skeleton,[1] it is very intriguing to prepare new homoleptic tris-type complexes and to compare these structures to the known ones.

In this paper we discuss our attempted preparation of cobalt(III) complexes $[Co(N\text{-}S)_3]$ from a room-temperature reaction between $Co(CH_3CO_2)_2 \cdot 4H_2O$ and a pyrimidine-2-thione ligand in the presence of air. Nine kinds of pyrimidine-2-thionato ligands were used (Fig. 1): pyrimidine-2-thione (Hpymt), 4-methylpyrimidine-2-thione (Hmpymt), 4-aminopyrimidine-2-thione (Hapymt), 4,6-diaminopyrimidine-2-thione (Hdapymt), 6-methyl-2-thiouracil ($H_2$6mtuc), 6-amino-2-thiouracil ($H_2$6atuc), 5,6-diamino-2-thiouracil (H_2datuc), 6-amino-5-nitroso-2-thiouracil (H_2antuc), and 2,4-dithiouracil (H_2dtuc). The complexes were characterized based on elemental analysis, UV-vis absorption spectra as well as ^{1}H, ^{13}C, and ^{59}Co NMR spectroscopy.

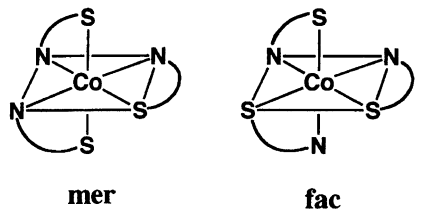
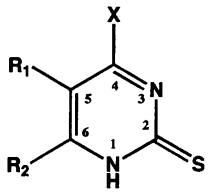
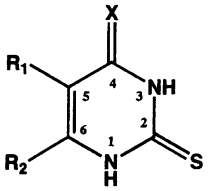


Chart 1.



	X	R_1	R_2
Hpymt	H	H	H
Hmpymt	CH_3	H	H
(Hdmpymt	CH_3	H	CH_3)
Hapymt	NH_2	H	H
Hdapymt	NH_2	H	NH_2



	X	R_1	R_2
$H_2$6mtuc	O	H	CH_3
$H_2$6atuc	O	H	NH_2
H_2datuc	O	NH_2	NH_2
H_2antuc	O	NO	NH_2
H_2dtuc	S	H	H

Fig. 1. Used thio-ligands and their abbreviations.

Results and Discussion

Preparation of Complexes. The complexes were prepared by a room-temperature reaction between $Co(CH_3CO_2)_2 \cdot 4H_2O$ and a pyrimidine-2-thione ligand (mole ratio=1 : 2.8—3.0) in methanol in the presence of atmospheric oxygen. The deprotonation of Hpymt has been known to easily occur under the above-mentioned condition; auto-redox reactions would then lead to the formation of cobalt(III) complexes.[3] A similar method was used to prepare *fac*-$[Co(dmpymt)_3]$.[6] The use of cobalt(II) halides instead of cobalt(II) acetate is not appropriate because the halides often coordinate to metal ions.[8]

The isolated complexes are shown in Table 1. They are classified into two groups based on an elemental

Table 1. Elemental Analyses of the Complexes

Complex	Color	Found (Calcd) / %		
		C	H	N
mer-[Co(pymt)$_3$]	Brown	36.85 (36.73)	2.47 (2.31)	20.92 (21.42)
mer-[Co(mpymt)$_3$]·2H$_2$O	Brown	38.26 (38.29)	4.12 (4.07)	17.90 (17.86)
fac-[Co(dmpymt)$_3$]	Green	45.37 (45.37)	4.42 (4.44)	17.82 (17.64)
mer-[Co(apymt)$_3$]·0.5H$_2$O	Dark green	32.80 (32.29)	2.84 (2.94)	28.49 (28.24)
mer-[Co(dapymt)$_3$]·H$_2$O	Brown	28.96 (28.80)	3.27 (3.42)	33.72 (33.58)
[Co(dapymt)$_2$]·0.5H$_2$O [a]	Green	27.64 (27.43)	3.17 (3.17)	32.07 (31.99)
[Co(H6mtuc)$_2$]·2CH$_3$OH	Pink	35.47 (35.56)	4.52 (4.48)	13.82 (13.84)
[Co(H6mtuc)$_2$]·2H$_2$O [a]	Pink	31.91 (31.83)	3.77 (3.74)	14.81 (14.85)
[Co(H6atuc)$_2$]·CH$_3$OH·H$_2$O	Violet	27.43 (27.48)	3.45 (3.59)	21.81 (21.37)
[Co(H6atuc)$_2$]·2H$_2$O [a]	Violet	24.47 (24.19)	3.63 (3.55)	21.27 (21.15)
[Co(Hdatuc)$_2$]·4H$_2$O [a]	Brown	21.58 (21.58)	4.08 (4.07)	24.81 (25.16)
[Co(Hantuc)$_2$]·0.5CH$_3$OH·3.5H$_2$O [a]	Brown	20.93 (21.26)	2.80 (3.15)	23.26 (23.33)
[Co(Hdtuc)$_2$]·H$_2$O [a]	Brown	26.20 (26.44)	2.03 (2.22)	15.34 (15.42)

a) The ligand was neutralized by an equimolar of N $(CH_2CH_3)_3$.

analysis. The first group contains the ligands of pymt, mpymt, apymt, and dapymt as well as dmpymt. In these systems auto-oxidation easily occurred with stirring in air, and deep-colored tris-chelate cobalt(III) complexes [Co(N-S)$_3$] were formed. On the other hand, all of the derivatives of 2-thiouracil belong to the second group. Most ligands of this group gave the bis-chelate cobalt(II) species [Co(N-S)$_2$], which could not be auto-oxidized to the corresponding cobalt(III) species even in the presence of an excess amount of ligands. Although the bis-type complex [Co(pymt)$_2$] has been reported for the pymt ligand of the first group, the used mole ratio of cobalt(II) acetate and Hpymt was 1 : 1.6—1.75.[9] It should be noted that the present condition (mole ratio=1 : 2.8—3.0) gave only the tris-type complex [Co(pymt)$_3$]. The ligand behavior of the second group is thus different from that of the first group.

We recently revealed that a 4-substituent group (X) in the pyrimidine ring plays an essential role in the stereochemistry of pyrimidine-2-thionato and its related complexes. The stereochemistry of mpymt (X=CH$_3$)[10] is similar to that apymt (X=NH$_2$).[11] The behavior of tuc (X=O)[12] and dtuc (X=S)[13] systems is similar to each other. However, the former group is quite different from the latter one concerning the ligand reactivity, product distribution, linkage isomerism, and pyrimidine ring structure. The situation is extremely analogous to the present one.

The different ligand behavior between the present two groups seems to concern different electronic structures of the pyrimidine ring. A single-crystal structure analysis has revealed that the first-group complexes with mpymt and apymt adopt a delocalized electronic structure of the pyrimidine ring,[10,11] and, consequently, resonance may be possible over the entire molecule even in the strained tris-type complexes. On the other hand, tuc[12] and dtuc complexes[13] with the second-group ligands adopt a localized structure of the pyrimidine ring; stabilization by resonance can not be expected for these complexes. This may be the reason why those complexes with second-group ligands are not auto-oxidized to the strained cobalt(III) species.

Characterization of Complexes. UV-vis absorption spectral data are listed in Table 2 and the representative spectrum of [Co(mpymt)$_3$] is shown in Fig. 2 as well as that of *fac*-[Co(dmpymt)$_3$]. The four absorption spectra of [Co(pymt)$_3$], [Co(mpymt)$_3$], [Co(apymt)$_3$], and [Co(dapymt)$_3$] are very similar to each other; there are many shoulders and inflections, and the band intensities are considerably high in the region of 700—300 nm. Their spectra are clearly different from that of *fac*-[Co(dmpymt)$_3$], whose structure was determined by an X-ray crystal analysis.[6]

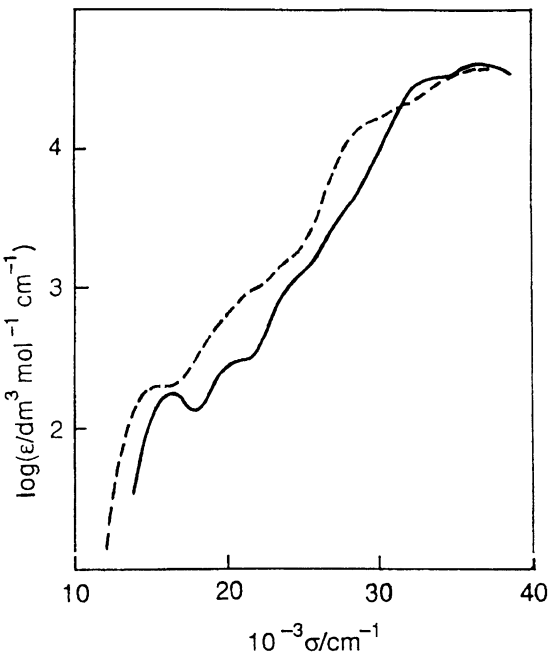


Fig. 2. UV-vis absorption spectra of *mer*-[Co(mpymt)$_3$] (dotted line) and *fac*-[Co(dmpymt)$_3$] (solid line) in CHCl$_3$.

Table 2. UV-vis Absorption, ^1H and ^{13}C NMR Spectral Data

	UV-vis	^{13}C[a]	^1H[b]
	Solv. λ/nm (ε /dm^3 mol^{-1}cm^{-1})	Solv.[c] δ	Solv. δ
mer-[Co(pymt)$_3$]	$CHCl_3$ 620 (240) 530sh (480) 460sh (1000) 420sh (1700) 340sh (16000) 310 (22000) 273 (40700)	$CDCl_3$ 159.2 158.6 158.4 158.2 157.4 155.3 (C^4 and C^6) 115.2 114.9 144.4 (C^5)	
mer-[Co(mpymt)$_3$] Main isomer	$CHCl_3$ 620 (200) 530sh (430) 460sh (960) 420sh (1500) 340sh (15500) 310sh (21000) 272 (37000)	$CDCl_3$ 170.3 169.6 169.2 (C^4) 157.1 156.1 154.2 (C^6) 115.1 114.8 114.4 (C^5) 24.5 24.4 24.3 (CH_3)	
Second dominant isomer		170.4 169.7 168.9 (C^4) 157.3 156.0 155.9 (C^6) 115.3 115.0 114.8 (C^5) 21.2 (CH_3)[d]	
fac-[Co(dmpymt)$_3$]	$CHCl_3$ 618 (179) 486 (300) 410sh (1100) 303 (32000) 275 (42000)	$(CD_3)_2CO$ 169.2 168.3 (C^4 and C^6) 116.2 (C^5) 23.6 19.8 (CH_3)	CD_3Cl 7.26 (s, 1H, H^5) 2.43 (s, 3H, CH_3) 1.55 (s, 3H, CH_3)
mer-[Co(apymt)$_3$]	CH_3OH 625 (244) 425 (1810) 340 sh (18200) 315sh (23400) 266sh (48000) 246 (53000) 225sh (43000)	$(CD_3)_2SO$ 182.8 181.7 181.3 (C^2) 163.4 163.2 163.1 (C^4) 152.9 152.3 151.1 (C^6) 101.0 100.7 100.5 (C^5)	$(CD_3)_2SO$ 7.66 (d, 2H, H^6) 7.67 (s, 2H, NH_2) 7.20 (s, 4H, NH_2) 6.96 (d, 1H, H^6) 6.16 (d, 1H, H^5) 6.05 (t, 2H, H^5)
mer-[Co(dapymt)$_3$]	CH_3OH 630sh (170) 460sh (990) 335sh (10000) 310sh (14000) 260sh (42000) 220 (75000)	$(CD_3)_2SO$ 180.3 179.9 178.1 (C_2) 165.4 164.6 162.7* 162.4 161.5 (C^4 and C^6) 79.6 78.9 78.5 (C^5)	$(CD_3)_2SO$ 7.12 (s, 2H, NH_2) 6.93 (s, 2H, NH_2) 6.48 (s, 2H, NH_2) 6.30 (s, 4H, NH_2) 5.34 (s, 2H, NH_2) 5.11 4.94 4.91; (s, 1H, H^5)

a) Referenced to 1,4-dioxane (δ=67.40) in $CDCl_3$ and $(CD_3)_2CO$ or $SiMe_4$ in $(CD_3)_2SO$. b) Downfield relative to $SiMe_4$. c) The C^2 signal were not observed in $CDCl_3$ and $(CD_3)_2CO$. d) The other two methyl signals are overlapped in the region of δ=24.2—24.6.

The ^{13}C NMR spectrum of *fac*-[Co(dmpymt)$_3$] showed only five signals because of the lack of a C^2 signal (Table 2). This signal pattern is consistent with the *fac* form of C_3 symmetry. The two complexes [Co(apymt)$_3$] and [Co(dapymt)$_3$], however, showed twelve ^{13}C NMR signals, which means that both complexes belong to a *mer* form with C_1 symmetry. In [Co(pymt)$_3$] and [Co(mpymt)$_3$] three signals were also observed for each carbon atom. Four complexes ([Co(pymt)$_3$], [Co(mpymt)$_3$], [Co(apymt)$_3$], and [Co(dapymt)$_3$]) can hence be assignable to a *mer* form.

Five cobalt(II) complexes of a [Co(N-S)$_2$] were obtained from the 2-thiouracil derivatives. They are all insoluble in any solvents. Abbot et al. assigned the red complex [Co(pymt)$_2$] to a tetrahedral structure based on its reflectance spectrum.[9] The colors of the present cobalt(II) complexes are pale pink, pale violet and brown. We think that although co-ordination commonly occurs through the nitrogen and the sulfur donors, such color deviation may mean the existence of several structures, including polymeric types.

Linkage Isomerism in *mer*-[Co(mpymt)$_3$] and *mer*-[Co(apymt)$_3$]. Since such ligands as mpymt and apymt are unsymmetrical, linkage isomerism is possible: a remote form with a C^4 substituent group away from the other two chelates and an adjacent form with this group near them (Chart 2). For *mer*-[Co(N-S)$_3$] (C_1 symmetry) eight linkage isomers, one (remote, remote, remote), three (remote, remote, adjacent), three (remote, adjacent, adjacent), and one (adjacent, adjacent, adjacent), exist in total.

Cobalt-59 NMR spectroscopy is very sensitive to sub-

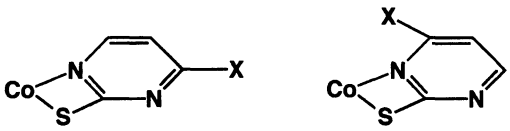


Chart 2.

tle changes in the environment of a central cobalt nucleus, and is expected to be a useful tool to distinguish these linkage isomers. Yajima et al. have successfully applied it to distinguish *mer*–*fac* isomerism due to the orientation of the methyl groups of Δ-$[Co(R\text{-pn})_3]^{3+}$ (*R*-pn=*R*-propane-1,2-diamine).[14] Figure 3 shows the ^{59}Co NMR spectrum of *mer*-$[Co(mpymt)_3]$. Three signals appear at δ=12820, 12670, and 12480 in addition to the reference peak at δ=12600. The formation ratio based on the signal intensity is 24 : 160 : 1 from the lower magnetic field side. The second dominant isomer at δ=12820 was also confirmed by the ^{13}C NMR spectrum: Relatively weak three signals in addition to three strong signals of the main linkage isomer are observed in each of the C^4, C^5, and C^6 chemical shift regions (Table 2). Since only a remote form is found in the mpymt complexes of $[Co(mpymt)(en)_2]^{2+}$ (remote) and *trans*-$[Co(mpymt)_2(en)]^+$ (remote, remote),[10] we conclude that the major isomer at δ=12670 is (remote, remote, remote) and the two minor isomers at δ=12820 and 12480 are (remote, remote, adjacent). The various attempts to separate these linkage isomers by column chromatography [alumina or cosmosil (nacalai tesque corp.)] have been unsuccessful.

The ^{59}Co NMR spectrum of *mer*-$[Co(apymt)_3]$ showed one signal at δ=12930. Only remote forms

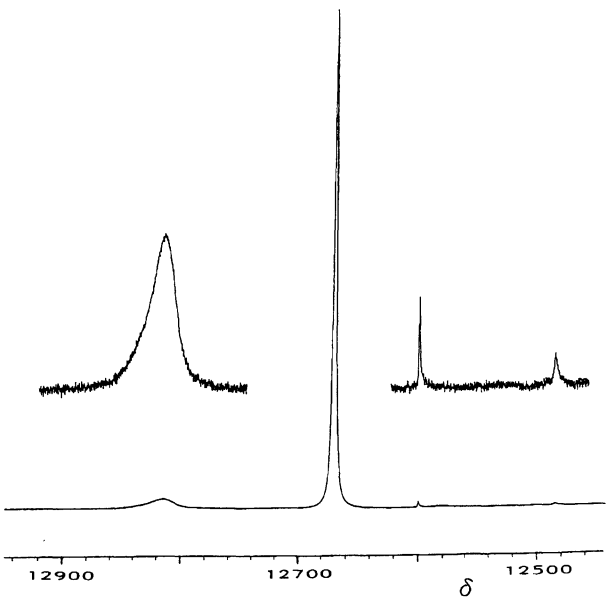


Fig. 3. Cobalt-59 NMR spectrum (90.46 MHz) of *mer*-$[Co(mpymt)_3]$ in $CDCl_3$. $[Co(acac)_3]$ (δ=12600) is used as an external standard.

are also found in the apymt complexes of $[Co(apymt)(en)_2]^{2+}$ (remote) and *trans*-$[Co(apymt)_2(en)]^+$ (remote, remote),[11] and, hence, we assign *mer*-$[Co(apymt)_3]$ to a (remote, remote, remote) form.

Preferable Geometry in $[M(N\text{-}S)_3]$ (M=Co and Rh). We can now compare the structure of seven $[Co(N\text{-}S)_3]$ complexes {*mer*-$[Co(pyt)_3]$,[2] *mer*-$[Co(sipyt)_3]$,[3] *mer*-$[Co(pymt)_3]$, *mer*-$[Co(mpymt)_3]$, *fac*-$[Co(dmpymt)_3]$,[6] *mer*-$[Co(apymt)_3]$, and *mer*-$[Co(dapymt)_3]$} and three $[Rh(N\text{-}S)_3]$ complexes {*mer*-$[Rh(pyt)_3]$,[4] *mer*-$[Rh(sipyt)_3]$,[5] and *fac*-$[Rh(6mpyt)_3]$[7]}. In these complexes the preferable geometry seems to be meridional, because the facial geometry is found only in *fac*-$[Co(dmpymt)_3]$ and *fac*-$[Rh(6mpyt)_3]$. It is noteworthy that only a *trans*(*S*) form exists even in the bis type complexes $[Co(mpymt)_2(en)]^+$, $[Co(dmpymt)_2(en)]^+$, $[Co(apymt)_2(en)]^+$, and $[Co(dapymt)_2(en)]^+$.[10,11] The addition of a third N-S ligand to *trans*(*S*)-$[Co(N\text{-}S)_2(en)]$ would produce only a *mer* isomer if there is no ligand scrambling. The preference of the *trans*(*S*) geometry may be related to a small *trans*-influence of the present ligands. The situation is quite different from that of aliphatic N-S ligands. For example, only *fac* isomers have been reported for the 2-aminothanethiolato (aet) and L-cysteinato (L-Hcyt) complexes $[Co(aet)_3]$,[15] $[Rh(aet)_3]$,[16] $[Co(L\text{-}cyst)_3]$,[15,17] and $[Rh(L\text{-}cyst)_3]$.[18] Aliphatic thiolates commonly have a large *trans*-influence,[10] and, hence, *cis*(*S*)- and *fac*-(*S*) isomers become favorable in $[M(S)_2(N)_4]$ and $[M(S)_3(N)_3]$, respectively.

The facial geometry in *fac*-$[Co(dmpymt)_3]$ and *fac*-$[Rh(6mpyt)_3]$ is rather exceptional. In these complexes we emphasize that the CH$\cdots\pi$ attractive interaction between each methyl group and a pyrimidine ring of an other ligand plays an important role.[19] The common structural feature concerns a 6-methyl group in both complexes. The two complexes are forced to adopt a sterically crowded structure, such that each 6-methyl group is positioned neat to one of the other ligands irrespective of the *mer* or *fac* geometry. The structures apparently resemble an (adjacent, adjacent, adjacent) linkage form. Figure 4 shows the structures of *mer*- and *fac*-$[Co(dmpyt)_3]$. In the *fac* geometry all three 6-meth-

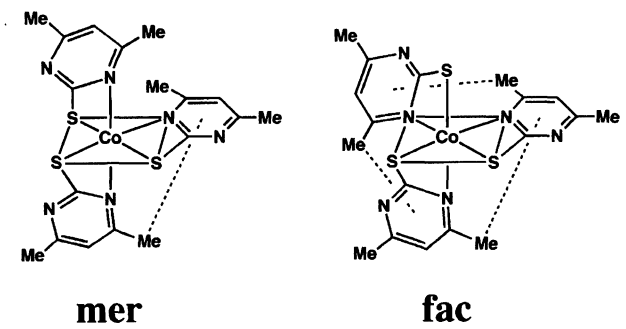


Fig. 4. Proposed CH$\cdots\pi$ interactions in *mer*- and *fac*-$[Co(dmpymt)_3]$.

yl groups participate in this interaction, whereas in the *mer* form only one 6-methyl group does. Proton NMR spectroscopy provides evidence. Two methyl groups of $[Co(dmpymt)(en)_2]^{2+}$ appear at the same region (δ= 2.51 and 2.35)[10] because there is no CH$\cdots\pi$ interaction in this complex. However, half of the methyl groups of *fac*-$[Co(dmpymt)_3]$ appear at δ=2.42 and the other half at a high magnetic field (δ=1.55) due to the ring current of the pyrimidine ring. In *mer*-$[Co(dapymt)_3]$ instead of *mer*-$[Co(dmpymt)_3]$, only one NH_2 signal locates at a high magnetic field (δ=5.34) compared with the other five NH_2 signals (δ=6.30—7.12). Thus, the CH$\cdots\pi$ attractive interaction in a *fac* form is more favorable than that in a *mer* one. Such a CH$\cdots\pi$ interaction may be a driving force to the *fac* geometry in $[Co(dmpymt)_3]$ and $[Rh(6mpyt)_3]$.

As described above, one (remote, remote, remote) and two (remote, remote, adjacent) linkage isomers are confirmed in *mer*-$[Co(mpymt)_3]$. The (remote, remote, adjacent) isomer at δ=12820 has one CH$\cdots\pi$ interaction in the adjacent site, a fact that is supported by an upfield shift of one methyl carbon signal (δ=21.2) compared with the others (δ=24.2—24.6). The relatively high yield of this isomer concerns the CH$\cdots\pi$ interaction. Such an interaction is possible only for one isomer out of three (remote, remote, adjacent) isomers. The complex *mer*-$[Co(apymt)_3]$ has no CH$\cdots\pi$ interaction and, hence, only one (remote, remote, remote) linkage isomer exists. The importance of intramolecular interligand interactions in stereoselectivities has been known regarding many complexes.[19]

Experimental

Preparation of Complexes. All of the ligands (Aldrich) were used without further purification. The general method of preparation was as follows: To a methanol solution (100 cm^3) of cobalt(II) acetate (2 mmol) was added a deficit of pyrimidine-2-thione (5.6—6.0 mmol) and the mixture was stirred for 8—12 h at room temperature. The resulting precipitate was filtered by suction and washed with methanol. Although the crude cobalt(III) complexes were recrystallized from methanol or $CHCl_3$, the cobalt(II) species could not be recrystallized because of their poor solubilities. When a ligand was completely insoluble in methanol the reaction was carried out after neutralizing it with an equimolar of $N(CH_2CH_3)_3$. In cases of 2-thiouracil, 5-methyl-2-thiouracil, and thiobarbituric acid, no complex with a definite composition was isolated. The elemental analyses of the complexes are shown in Table 1.

Measurements. UV-vis absoption spectra were measured with a Hitachi 330 spectrophotometer. Proton, ^{13}C and ^{59}Co NMR spectra were recorded with JEOL JNM-GSX-270 and GSX-400 spectrometers in $CDCl_3$, $(CD_3)_2CO$, and/or $(CD_3)_2SO$.

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