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Synthesis, Crystal Structures, Electronic Spectra, and Magnetic Properties of Bis(μ-Thiolato)-Bridged Trinuclear Co^{II} Complexes with Tridentate-*N*, *N*, *S*-Thiolates

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Abstract. New trinuclear Co^{II} complexes, $[\{Co(apaet)_2\}_2Co]X_2$ (apaet$^-$ = 2-[(3-aminopropyl)amino]ethanethiolato; X = SCN (**1**), ClO_4 (**2**), NO_3 (**3**), Cl (**4**), Br (**5**), I (**6**)) and $[\{Co(apampt)_2\}_2Co]X_2$ (apampt$^-$ = 1-[(3-aminopropyl)amino]-2-methylpropane-2-thiolato; X = NO_3(**7**), ClO_4 (**8**), Cl (**9**), Br (**10**), I (**11**)), and mononuclear Co^{III} complexes, $[Co(apaet)_2]X$ (X = ClO_4 (**12**), NO_3 (**13**)), were synthesized. Single-crystal X-ray crystallography of **1** and **7** confirmed that the trinuclear complexes have a linear arrangement of octahedral $Co^{II}S_2N_4$-tetrahedral $Co^{II}S_4$-octahedral $Co^{II}S_2N_4$ chromophores where two thiolate ligands are coordinated to each terminal Co atom in a *mer* coordination mode and the two thiolato S atoms are further bound to the central Co atom, which is consistent with the electronic spectra and antiferromagnetic properties.

Keywords: thiolato complex, cobalt complex, mononuclear Co(III) complex, trinuclear Co(II) complex

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1. Introduction

The synthesis and crystal structures of a great number of metal thiolates have appeared in the literature over the past fifty years, since there have been their diverse coordination compounds of many kinds of metal atoms with redox reactions in metal-assembling [1-8]. The growing interests in metal thiolates have stimulated research efforts for the efficient synthesis and synthetic methods of thiolate ligands have been developed [8,9,23]. Metal thiolates are also of interest from a point of view that their metal complexes have similar functionalities to those of active sites of metallo-enzymes containing cysteine residue in catalyzing organic oxidation or electron-transfer reactions. We are interested in using organic thiolate ligands containing nitrogen atoms besides thiolate sulfur atom, because synthesis of metal thiolates may be controlled by the formation of chelate rings by the combination of donor set [9-32]. Reactions of metal ions and tridentate-*N*, *N*, *S*-thiolates (Figure 1) such as 2-[(3-aminopropyl)amino]ethanethiol (abbreviated as Hapaet), we isolated trinuclear thiolates of homonuclear $[\{M(apaet)_2\}_2M](ClO_4)_2$ (M = Mn^{II} [17], Fe^{II} [18], Cd^{II} [24]) as well as heterometal $[\{M(apaet)_2\}_2M'](ClO_4)_2$ (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}; M' = Zn^{II}, Cd^{II}, Hg^{II}) [19], which have a linearly arranged trinuclear metal ions with octahedral S_2N_4, tetrahedral S_4, and octahedral S_2N_4 coordination environments. The linear trinuclear structure seems to be most favorable for metal thiolates with apaet. In addition to the trinuclear species, dinuclear nickel(II) [12], dinuclear iron(II) [18], dinuclear molybdenum(V) [30], cyclic trinuclear zinc(II) [22], mixed-valent trinuclear molybdenum(V,VI) [31], tetranuclear palladium(II) [20,21], adamantane-like teranuclear manganese(II) and iron(II) [23], mixed-valent hexanuclear and octanuclear copper(I,II) [25,26,28], infinite polynuclear manganese(II) [14,17] and zinc(II) [22] species also have been isolated in these systems. In the case of 2-[(2-pyridylmethyl)amino]ethanethiol, a mononuclear rhenium thiolate was isolated [29]. It is well known that cobalt(III) ion favours an octahedral geometry because of the crystal field stabilization energy, resulting in the mononuclear octahedral Co(III) species, $[Co(apaet)_2](ClO_4)$, and dinuclear octahedral cobalt(III) species, $[Co_2\{SCH(CH_2CH_2NH_2)_2\}_3](ClO_4)_3$, for Hapaet and Hdpet (Hdpet = 1,5-diamino-3-pentanethiol), respectively [10,27,32].

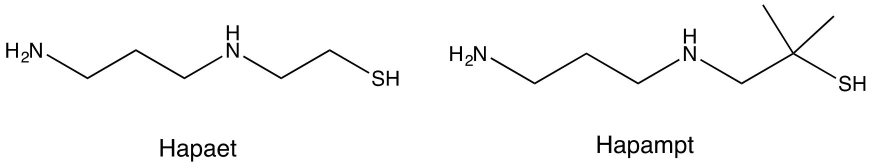

Figure 1. Tridentate-*N*, *N*, *S*-thiolates

In this study, we made an effort to extend cobalt thiolate chemistry by synthesizing new cobalt thiolates in addition to the mononuclear thiolates, because the isolated compounds may have relevance to model compounds of metallo-enzymes in bacteria, Co-nitrile hydratases, which have non-corrinoid Co atom with N and S donor-atoms and catalyze the hydration of nitriles to the corresponding amides [33-35]. Crystallographic study of the Co-nitrile hydratases has revealed that the metal is coordinated by two deprotonated carboxamide-N and three cysteine-S atoms which can be converted to cysteine-sufenic and -sulfinic group as like those of Fe-nitrile hydratases [36,37]. We synthesized a series of cobalt thiolates with $apaet^-$, using a variety of cobalt salts, and further, synthesized 1-[(3-aminopropyl)amino]-2-methylpropane-2-thiol (Hapampt), which corresponds to an analogous tridentate-*N*, *N*, *S*-thiol substituted the α-methylene hydrogens by methyl groups, and performed synthesis of cobalt thiolates with $apampt^-$. We report herein the synthesis, crystal structures, electronic spectral and magnetic properties of the isolated cobalt thiolates.

2. Research Methods

2.1. Synthesis of Complexes

All commercial chemicals and solvents were used without further purification. Methanol was dried using standard laboratory techniques. The thiolate ligands, Hapaet and Hapampt, were synthesized according to literature procedure [12,25]. All manipulations were performed under an argon atmosphere using Schlenk techniques.

Safety Notes. *Warning!* Cobalt(II) perchlorate hexahydrate are potentially explosive and should only be handled in small quantities with great care.

$[\{Co(apaet)_2\}_2Co](SCN)_2\cdot CH_3OH\cdot 2H_2O$ (**1**·$CH_3OH\cdot 2H_2O$)

To a mixed solution of 4 mL of methanol and 2 mL of *N*,*N*-dimethylacetamide containing Hapaet (34 mg, 0.25 mmol) and triethylamine (two drops) was added 4 mL of methanol solution of cobalt(II) thiocyanate (44 mg, 0.25 mmol). The solution was stirred for 5 min at room temperature and was left standing without disturbance for several days. The deposited crystals were filtered off, washed with methanol, and dried. Yield 26 mg (49%). Anal. Calcd for $C_{23}H_{60}N_{10}O_3S_6Co_3$: C, 30.98; H, 6.48; N, 15.67%. Found: C, 31.44; H, 6.50; N, 15.64%. IR (KBr, pellet) ν/cm^{-1} ν(N-H) 3288(m), 3239(m); ν(C-H) 2930(m), 2866(m), 2840(m); ν(SCN) 2051(s). Diffused reflectance spectra λ_{max}/nm 264, 326, 636, 732, 784, 1360, 1598, 1700. μ_{eff}(300 K)/μ_B 6.95, μ_{eff}(4.5 K)/μ_B 4.58.

$[\{Co(apaet)_2\}_2Co](ClO_4)_2\cdot H_2O$ (**2**·H_2O)

To a mixed solution of 4 mL of methanol and 2 mL of *N*,*N*-dimethylacetamide containing Hapaet (34 mg, 0.25 mmol) and triethylamine (two drops) was added 4 mL of methanol solution of cobalt(II) perchlorate hexahydrate (93 mg, 0.25 mmol). The solution was left standing without disturbance at room temperature for several days. The deposited crystals were filtered off, washed with methanol, and dried. Yield 12 mg (21%). Anal. Calcd for $C_{20}H_{54}N_8O_9S_4Cl_2Co_3$: C, 25.92; H, 5.87; N, 12.09%. Found: C, 25.84; H, 5.80; N, 11.97%. IR (KBr, pellet) ν/cm^{-1} ν(N-H) 3327(m), 3282(m); ν(C-H) 2930(m), 2823(m); ν(Cl-O) 1145(s), 1100(s), 1080(s), 623(s). Diffused reflectance spectra λ_{max}/nm 272, 342(sh), 458(sh), 666, 730, 782, 1368, 1630. Electronic absorption spectra in dmf (*N*,*N*-dimethylformamide) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}) 673 (300), 731 (370), 786 (870), 1355 (94). μ_{eff}(300 K)/μ_B 5.11, μ_{eff}(4.5 K)/μ_B 3.55.

$[\{Co(apaet)_2\}_2Co](NO_3)_2\cdot 3H_2O$ (**3**·$3H_2O$)

To a mixed solution of 4 mL of methanol and 2 mL of *N*,*N*-dimethylacetamide containing Hapaet (34 mg, 0.25 mmol) and triethylamine (two drops) was added 4 mL of methanol solution of cobalt(II) nitrate hexahydrate (73 mg, 0.25 mmol). The solution was left standing without disturbance at room temperature for several days. The deposited crystals were filtered off, washed with methanol, and dried. Yield 38 mg (69%). Anal. Calcd for $C_{20}H_{56}N_{10}O_7S_4Co_3$: C, 27.06; H, 6.58; N, 15.18%. Found: C, 27.37; H, 6.25; N, 15.33%. IR (KBr, pellet) ν/cm^{-1} ν(N-H) 3301(m), 3265(m); ν(C-H) 2931(m), 2882(m); ν(N-O) 1382(s), 1336(s). Diffused reflectance spectra λ_{max}/nm 276, 342(sh), 486(sh), 636, 726, 782, 1358, 1642.

$[\{Co(apaet)_2\}_2Co]Cl_2\cdot 2CH_3OH\cdot 2H_2O$ (**4**·$2CH_3OH\cdot 2H_2O$)

To a mixed solution of 4 mL of methanol and 2 mL of *N*,*N*-dimethylacetamide containing Hapaet (34 mg, 0.25 mmol) and triethylamine (two drops) was added 4 mL of methanol solution of cobalt(II) chloride hexahydrate (60 mg, 0.25 mmol). The solution was left standing without disturbance at room temperature for several days. The deposited crystals were filtered off, washed with methanol, and dried. Yield 34 mg (61%). Anal. Calcd for $C_{22}H_{64}N_8O_4S_4Cl_2Co_3$: C, 30.00; H, 7.32; N, 12.72%. Found: C, 30.42; H, 7.44; N, 12.70%. IR (KBr, pellet) ν/cm^{-1} ν(N-H) 3204(m), 3148(m); ν(C-H) 2925(m), 2875(m), 2820(m). Diffused reflectance spectra λ_{max}/nm 266, 316, 626, 724, 778, 1366, 1644. μ_{eff}(300 K)/μ_B 6.45, μ_{eff}(4.5 K)/μ_B 3.67.

$[\{Co(apaet)_2\}_2Co]Br_2\cdot 2CH_3OH\cdot 4H_2O$ (**5**·$2CH_3OH\cdot 4H_2O$)

This complex was prepared in the same manner as complex **4**·$2CH_3OH\cdot 2H_2O$ using cobalt(II) bromide hexahydrate. Yield 20 mg (32%). Anal. Calcd for $C_{22}H_{68}N_8O_6S_4Br_2Co_3$: C, 26.27; H, 6.82; N, 11.14%. Found: C, 26.30; H, 6.51; N, 11.06%. IR (KBr, pellet) ν/cm^{-1} ν(N-H) 3194(m), 3147(m); ν(C-H) 2926(m), 2866(m), 2842(m). Diffused reflectance spectra λ_{max}/nm 274, 350, 380, 664(sh), 778, 1364, 1650.

$[\{Co(apaet)_2\}_2Co]I_2\cdot 2CH_3OH\cdot 2H_2O$ (**6**·$2CH_3OH\cdot 2H_2O$)

This complex was prepared in the same manner as complex **4**·$2CH_3OH\cdot 2H_2O$ using cobalt(II) iodide. Yield 26 mg (38%). Anal. Calcd for $C_{22}H_{64}N_8O_3S_4I_2Co_3$: C, 24.84; H, 6.06; N, 10.53%. Found: C, 24.57; H, 5.85; N, 10.30%. IR (KBr, pellet) ν/cm^{-1} ν(N-H) 3186(m), 3129(m); ν(C-H) 2926(m), 2866(m), 2798(m). Diffused reflectance spectra λ_{max}/nm 348, 728, 664(sh), 782, 1352, 1658. μ_{eff}(300 K)/μ_B 4.86, μ_{eff}(4.5 K)/μ_B 2.60.

$[\{Co(apampt)_2\}_2Co](NO_3)_2\cdot 2CH_3OH$ (**7**$\cdot 2CH_3OH$)

To a mixed solution of 5 mL of methanol and 2 mL of *N*,*N*-dimethylacetamide containing Hapampt (41 mg, 0.25 mmol) and triethylamine (two drops) was added 5 mL of methanol solution of cobalt(II) nitrate hexahydrate (73 mg, 0.25 mmol). The solution was stirred for 5 min at room temperature and was left standing without disturbance for several days. The deposited crystals were filtered off, washed with methanol, and dried. Yield 39 mg (64%). Anal. Calcd for $C_{30}H_{76}N_{10}O_8S_4Co_3$: C, 35.67; H, 7.58; N, 13.87%. Found**:** C, 35.84; H, 7.79; N, 14.22%. IR (KBr, pellet) ν/cm^{-1} ν(N-H) 3324(m), 3238(m); ν(C-H) 2947(m), 2839(m); ν(N-O) 1402(s), 1384(s), 1325(s). Diffused reflectance spectra λ_{max}/nm 288, 336, 434(sh), 696, 754(sh), 796, 1392, 1744. μ_{eff}(300 K)/μ_B 6.60, μ_{eff}(4.5 K)/μ_B 4.52.

$[\{Co(apampt)_2\}_2Co](ClO_4)_2\cdot dmac\cdot H_2O$ (dmac = *N*,*N*-dimethylacetamide) (**8**$\cdot dmac\cdot H_2O$)

This complex was prepared in the same manner as complex **7**$\cdot 2CH_3OH$ using cobalt(II) perchlorate hexahydrate. Yield 12 mg (16%). Anal. Calcd for $C_{32}H_{79}N_9O_{10}S_4Cl_2Co_3$: C, 33.60; H, 7.14; N, 11.02%. Found**:** C, 33.75; H, 7.01; N, 10.81%. IR (KBr, pellet) ν/cm^{-1} ν(N-H) 3331(m), 3285(m), 3264(m); ν(C-H) 2928(m), 2843(m); ν(Cl-O) 1106(s), 1058(s), 1014(s), 626(s). Diffused reflectance spectra λ_{max}/nm 290, 348(sh), 694, 754(sh), 798, 1384, 1730. Electronic absorption spectra in dmf λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}) 687 (390), 742 (540), 794 (1140), 1389 (130). μ_{eff}(300 K)/μ_B 6.84, μ_{eff}(4.5 K)/μ_B 4.57.

$[\{Co(apampt)_2\}_2Co]Cl_2\cdot CH_3OH\cdot H_2O$ (**9**$\cdot CH_3OH\cdot H_2O$)

To a mixed solution of 5 mL of methanol and 2 mL of *N*,*N*-dimethylacetamide containing Hapampt (41 mg, 0.25 mmol) and triethylamine (two drops) was added 5 mL of methanol solution of cobalt(II) chloride hexahydrate (60 mg, 0.25 mmol). The solution was stirred for 5 min at room temperature and was left standing without disturbance for several days. The deposited crystals were filtered off, washed with methanol, and dried. Yield 15 mg (26%). Anal. Calcd for $C_{29}H_{74}N_8O_2S_4Cl_2Co_3$: C, 36.94; H, 7.91; N, 11.88%. Found**:** C, 36.86; H, 7.77; N, 11.79%. IR (KBr, pellet) ν/cm^{-1} ν(N-H) 3244(m), 3204(m); ν(C-H) 2954(m), 2921(m), 2865(m). Diffused reflectance spectra λ_{max}/nm 216, 260, 294(sh), 340(sh), 506(sh), 694, 754(sh), 794, 1504, 1580, 1758.

$[\{Co(apampt)_2\}_2Co]Br_2\cdot CH_3OH$ (**10**$\cdot CH_3OH$)

This complex was prepared in the same manner as complex **9**$\cdot CH_3OH\cdot H_2O$ using cobalt(II) bromide hexahydrate. Yield 14 mg (22%). Anal. Calcd for $C_{29}H_{72}N_8OS_4Br_2Co_3$: C, 34.36; H, 7.16; N, 11.05%. Found**:** C, 34.28; H, 7.01; N, 10.96%. IR (KBr, pellet) ν/cm^{-1} ν(N-H) 3244(m), 3204(m); ν(C-H) 2954(m), 2921(m), 2865(m). Diffused reflectance spectra λ_{max}/nm 280, 338, 442(sh), 694, 754(sh), 794, 1394, 1502(sh), 1730. μ_{eff} (300 K)/μ_B 6.02, μ_{eff}(4.5 K)/μ_B 2.93.

$[\{Co(apampt)_2\}_2Co]I_2\cdot CH_3OH$ (**11**$\cdot CH_3OH$)

This complex was prepared in the same manner as complex **9**$\cdot CH_3OH\cdot H_2O$ using cobalt(II) iodide. Yield 16 mg (22%). Anal. Calcd for $C_{29}H_{72}N_8OS_4I_2Co_3$: C, 30.96; H, 6.63; N, 9.95%. Found**:** C, 31.04; H, 6.62; N, 9.96%. IR (KBr, pellet) ν/cm^{-1} ν(N-H) 3205(m), 3147(m); ν(C-H) 2945(m), 2839(m). Diffused reflectance spectra λ_{max}/nm 288, 340(sh), 696, 754(sh), 796, 1386, 1732, 1782. μ_{eff}(300 K)/μ_B 5.71, μ_{eff}(4.5 K)/μ_B 3.24.

$[Co(apaet)_2]ClO_4\cdot CH_3OH$ (**12**$\cdot CH_3OH$)

This complex was prepared according to the method reported recently [32].

$[Co(apaet)_2]NO_3\cdot H_2O$ (**13**$\cdot H_2O$)

To 3 mL of methanol containing Hapaet (34 mg, 0.25 mmol) and triethylamine (two drops) was added 3 mL of methanol solution of cobalt(II) nitrate hexahydrate (36 mg, 0.18 mmol). The solution was left standing without disturbance at room temperature for several days. The deposited crystals were filtered off, washed with methanol, and dried.-Yield 45 mg (70%). Anal. Calcd for $C_{10}H_{54}N_5O_4S_2Co$: C, 29.63; H, 6.96; N, 17.27%. Found**:** C, 29.66; H, 6.56; N, 17.40%. IR (KBr, pellet) ν/cm^{-1} ν(N-H) 3252(m), 3213(m), 3142(m); ν(C-H) 2969(m), 2928(m); ν(N-O) 1372(s), 1348(s). Diffused reflectance spectra λ_{max}/nm 272, 348(sh), 492, 838, 916, 1370, 1584, 1712, 1748, 1782, 1928.

2.2 Measurements

C, H, and N elemental analyses were carried out by the use of a Perkin-Elmer 2400 Series II CHNS/O Analyzer. IR spectra (4000—600 cm^{-1}) were recorded on a JASCO MFT-2000 FT-IR Spectrometer with the samples prepared as KBr pellets. Electronic spectra (200—2000 nm) were recorded on a Shimadzu UV-3100 Spectrophotometer. Magnetic susceptibility measurements in the temperature range 4.5—300 K were performed with a Quantum Design MPMS-5S SQUID magnetometer at an applied field of 0.5 T. The data were corrected for diamagnetic contributions calculated from Pascal's constants for all constituent atoms [38].

The X-ray data were collected at room temperature with a Bruker CCD diffractometer (SMART APEX) with Mo-$K\alpha$ radiation. The data collection and refinement processes are summarized in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares method, using the SHELXTL program package [39]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located on calculated positions.

Table 1. Crystal data and structure refinement details for **1** and **7**.

Compounds	**1**	**7**
Empirical Formula	$C_{24}H_{60}Co_3N_{10}O_2S_6$	$C_{30}H_{60}Co_3N_{10}O_7S_4$
Formula weight	889.97	977.91
Temperature / K	293	293
Crystal dimensions / mm	0.31×0.30×0.14	0.40×0.39×0.20
Crystal system	Monoclinic	Tetragonal
Space group	*C*2/*c*	*I*4/*m*
a / Å	24.728(6)	12.9269(11)
b / Å	9.415(2)	
c / Å	18.336(5)	28.238(4)
β / °	104.178(3)	
V / Å^3	4138.8(18)	4718.7(8)
Z	4	4
d_{calcd}	1.428	1.377
μ / mm^{-1}	1.527	1.268
F(000)	1868	2044
Reflections collected	10932	10567
Independent reflections	4533	1751
θ range for data collection	1.70 to 28.27°	1.73 to 23.23°
Data / Restraints / Parameters	4533/0/206	1751/0/129
$R1$, $wR2[I>2\sigma(I)]$$^{a)}$	0.1008, 0.2823	0.0387, 0.1340
$R1$, $wR2$[all data]$^{a)}$	0.1182, 0.3160	0.0503, 0.1387
Goodness-of-fit on F^2	1.218	1.122
CCDC number	1953679	2073611

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

3. Results and Discussion

3.1 Synthesis and Structural Characterization of Co Thiolates

Our previous studies showed that the reactions of Hapaet with Mn(II) [17], Fe(II) [18], and Cd(II) [24] afforded trinuclear thiolate complexes, $[\{M(apaet)_2\}_2M]X_2$, where the three metal atoms are arranged linearly with *Oh-Td-Oh* geometries. In this study, we isolated analogous trinuclear Co(II) complexes with apaet$^-$ and apampt$^-$, $[\{Co(apaet)_2\}Co]X_2$ (X = SCN (**1**), ClO_4 (**2**), NO_3 (**3**), Cl (**4**), Br (**5**), I (**6**)) and $[\{Co(apampt)_2\}_2Co]X_2$ (X = NO_3(**7**), ClO_4 (**8**), Cl (**9**), Br (**10**), I (**11**), under the similar condition with equivalent molar ratio of the thiolate ligand : metal salt.

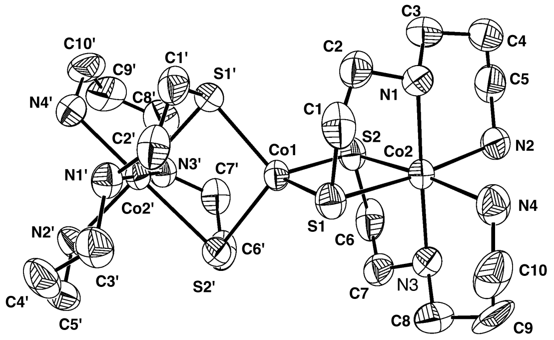

Figure 2. ORTEP Diagram of Trinuclear Complex Cation in **1**

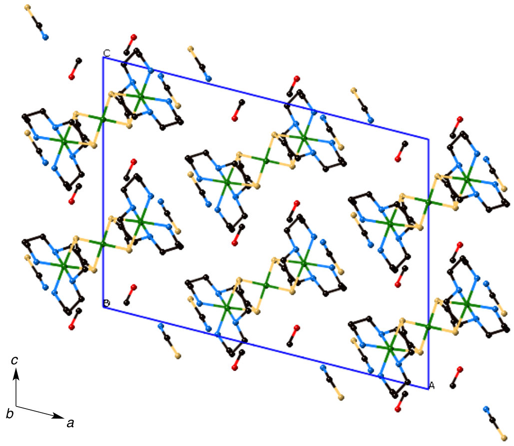

Figure 3. Packing Diagram of **1**

The results of the elemental analyses suggest that the cations of these complexes should consist of three cobalt atoms and four thiolato ligands, apaet$^-$ or apampt$^-$. The infrared spectra of these complexes are essentially the same except for the bands due to the counter anion X, showing the characteristic bands of apaet$^-$ and apampt$^-$ deprotonated ligands with the ν(N-H) bands at 3327—3129 cm^{-1} and the ν(C-H) bands at 2969–2798 cm^{-1} and without the ν(S-H) band around 2500 cm^{-1} [40,41]. If we use an excess amount of thiolate ligand to metal salt with 1.4:1 molar ratio, mononuclear cobalt(III) thiolates, [Co(apaet)$_2$]X$_2$ (X = ClO$_4$ (**12**) and NO$_3$ (**13**)) were isolated as described in the previous paper [32]. X-ray structure analysis was performed for the single crystals of **1** and **7**. The crystal structure of **1** contains trinuclear complexes, [Co{Co(apaet)$_2$}$_2$]$^{2+}$, thiocyanate anions, and methanol molecules in a 1:2:2 molar ratio. An ORTEP diagram of [Co{Co(apaet)$_2$}$_2$]$^{2+}$ is depicted in Figure 2. The three cobalt atoms are arranged almost linearly (Co2-Co1-Co2' = 179.57(3)°). The cation has a C_2-symmetry, where the crystallographic C_2 axis passes through the Co1 atom and the midpoint of S1 and S1' atoms. The Co1 atom is bonded to four thiolato-sulfur atoms of apaet$^-$ in a distorted tetrahedral geometry, while each of the Co2 and Co2' atoms is coordinated by two thiolato-sulfur atoms and four amino-nitrogen atoms of apaet$^-$ in a distorted octahedral geometry. Each apaet$^-$ ligand is coordinated to the terminal cobalt atom in a meridional mode to form a fused chelate with six- and five-membered rings. The bond distances of the terminal octahedral cobalt atoms [Co2-S 2.524(2)—2.526(2) Å] are longer than those of the central tetrahedral cobalt atom [Co1-S 2.331(2)—2.340(2) Å]. The bond distances of Co2-S and Co1-S are similar to the Co-S bonds of octahedral and tetrahedral thiolato Co(II) complexes, respectively [19,27]. The Co2-N distances [2.203(5)—2.224(5)Å] are also similar to the Co-N bonds of octahedral Co(II) complexes [19,27]. The Co2-S1-C1-C2-N1 and Co2-S2-C6-C7-N3 chelate rings are in a gauche form which is common for five-membered chelate ring, whereas the Co2-N1-C3-C4-C5-N2 and Co2-N3-C8-C9-C10-N4 chelate rings are in a chair form. The complex cation structure is similar to that of

2·2dmac·2CH$_3$OH (dmac = *N*,*N*-dimethylacetamide) [27]. In the crystal, thiocyanate ions and methanol molecules are arranged among the trinuclear cations as like separating these molecules (Figure 3). The crystal structure of **7** contains trinuclear complexes, [Co{Co(apampt)$_2$}$_2$]$^{2+}$, nitrate anions, methanol molecules, and water molecules in a 1:2:0.5:0.5 molar ratio. An ORTEP diagram of [Co{Co(apampt)$_2$}$_2$]$^{2+}$ is depicted in Figure 4. The trinuclear structure of the complex cation is similar to those for **1**·2CH$_3$OH and **2**·2dmac·2CH$_3$OH [27]. However, the three cobalt atoms are arranged in a crystallographical line (Co2-Co1-Co2" = 180°). The cation has a *C*$_2$-symmetry, where the crystallographic *C*$_2$ axis passes through the Co1 atom and the midpoint of S1 and S1' atoms. The Co1 atom is bonded to four thiolato-sulfur atoms of apampt$^-$ in a distorted tetrahedral geometry, while each of the Co2 and Co2" atoms is coordinated by two thiolato-sulfur atoms and four amino-nitrogen atoms of apampt$^-$ in a distorted octahedral geometry. Each apampt$^-$ ligand is coordinated to the terminal cobalt atom in a meridional mode to form a fused chelate with six- and five-membered rings. The bond distances of the terminal octahedral Co2-S [2.477(1) Å] are significantly shorter than those of **1**·2CH$_3$OH and **2**·2dmac·2CH$_3$OH [2.509(4)-2.526(2) Å]. As the electron density of the sulfur atom is increased, compared with that of apaet$^-$, by the methyl groups which are attached at the alpha position of the sulfur atom, bond lengths between the octahedral Co and the sulfur atoms would be appreciably shortened. The bond distances of the Co2-N [2.204(3)-2.232(3) Å] are comparable to those of **1**·2CH$_3$OH and **2**·2dmac·2CH$_3$OH [27], which are normal as the Co-N bond lengths of octahedral Co(II) complexes [42]. On the other hand, the bond distances of the central Co1-S [2.334(1) Å] are significantly longer than those of **1**·2CH$_3$OH and **2**·2dmac·2CH$_3$OH [Co1-S 2.305(4)—2.340(2) Å] [27], reflecting the steric hindrance with the methyl groups attached to the alpha carbon atom of the thiolato sulfur atom.

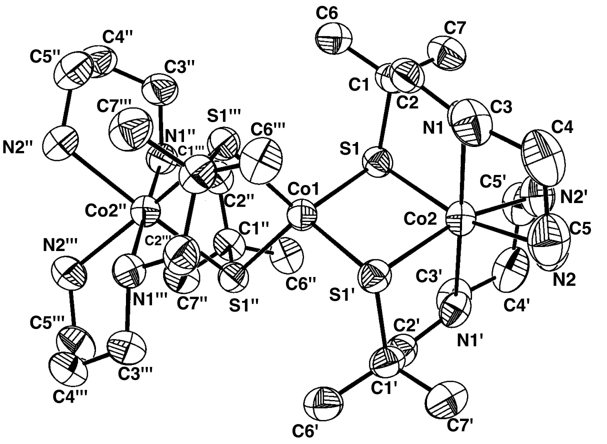

Figure 4. ORTEP Diagram of Trinuclear Complex Cation in **7.**

The Co2-S1-C1-C2-N1 five-membered chelate ring is in a gauche form, whereas the Co2-N1-C3-C4-C5-N2 six-membered chelate ring is in a chair form. The nitrate anion is considered to be hydrogen-bonded to the nitrogen atoms of the thiolate ligand as indicated by the distances O1(NO$_3$)···N2 3.052(6) Å, O1(NO$_3$)···N2' 3.057(6) Å, and O1(NO$_3$)···N1' 3.171(6) Å (Figure 5).

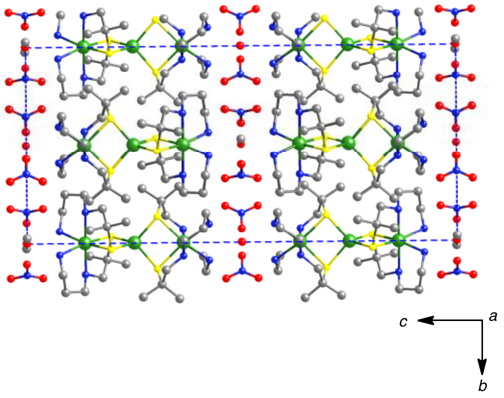

Figure 5. Packing Diagram of **7**

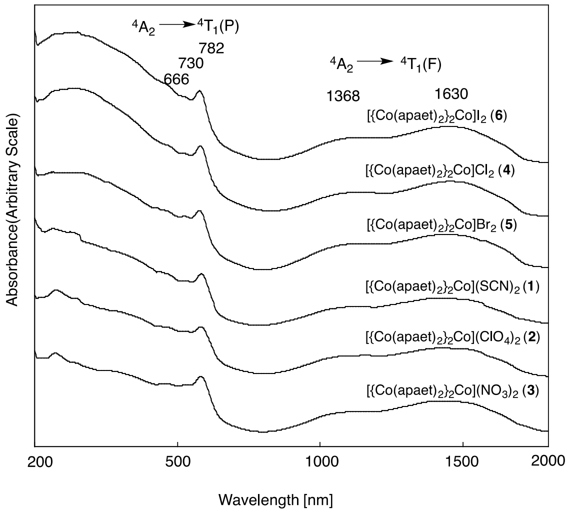

Figure 6. Diffuse Reflectance Spectra of Trinuclear Co(II) Complexes with apaet$^-$

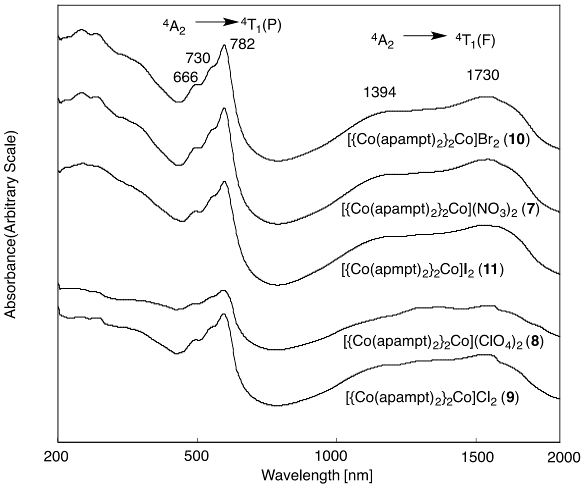

Figure 7. Diffuse Reflectance Spectra of Trinuclear Co(II) Complexes with apampt$^-$

3.2 Electronic Spectra of Co Thiolates

Diffuse reflectance spectra of the trinuclear cobalt complexes with apaet$^-$ **1**—**6** are shown in Figure 6. These spectra show essentially the same feature, having a broad band attributable to thiolato-sulfur-to-cobalt(II) charge transfer transition at around 350 nm, three bands at around 670, 730, and 780 nm, and two broad bands at around 1370 and 1630 nm, which may be attributed to d-d transition bands of high-spin tetrahedral cobalt(II) [43]. D-d transitions of octahedral cobalt(II) can be considered to be obscured by the stronger tetrahedral d-d transition bands [43]. As shown in Figure 7, diffuse reflectance spectra of the trinuclear cobalt(II) complexes with apampt$^-$ **7**—**11** are similar to those of **1**—**6**, exhibiting a broad band attributable to thiolato-sulfur-to-cobalt(II) charge transfer transition at around 350 nm, three bands at around 690, 750, and 790 nm, and two broad bands at around 1390 and 1730 nm, which may be attributed to d-d transition bands of high-spin tetrahedral cobalt(II) species ($^4A_2 \rightarrow {}^4T_1(P)$ and $^4A_2 \rightarrow {}^4T_1(F)$, respectively) [43]. These d-d transition bands are located at a little lower frequency side compared with those of the unmethylated thiolato complexes **1**—**6**. We can ascribe this weak coordination field of the methylated thiolato complexes **7**—**11** to the steric crowdedness with the methyl groups as indicated in the bond lengthening of the central Co-S bonds. The electronic absorption spectra of **2** and **8** in dmf are essentially the same as those in the solid state (Figure 8). The three absorption band at visible and near infra-red region can be attributed to ligand field absorptions for high-spin tetrahedral Co(II). The ligand field absorptions for **8** show red-shift features and molar absorption coefficients are slightly large compared with those of **2**. This result suggests that the crystal field of the central cobalt atom is weaker than that of **2** and the deviation from the tetrahedral arrangement may be smaller by adding methyl groups to the alpha-carbon atom of the thiolato sulfur atom. The differences between the bond distances and angles around the central cobalt atoms of **1**, **2**, and **7** [Co1-S 2.305(4)—2.322(2) Å, S-Co1-S 100.60(5)—119.9(2)° for **1** and **2**; Co1-S 2.334(1) Å, S-Co1-S 99.35(5), 114.76(3)° for **7**] are consistent with this result. The diffuse reflectance spectra of the mononuclear cobalt (III) complexes with apaet$^-$ are shown in Figure 9. The three ligand field absorptions at around 480—930 nm can be ascribed as octahedral d-d transitions of low-spin cobalt (III) $^1A_{1g} \rightarrow {}^1T_{2g}, {}^1T_{1g}, {}^3T_{2g})$ [43].

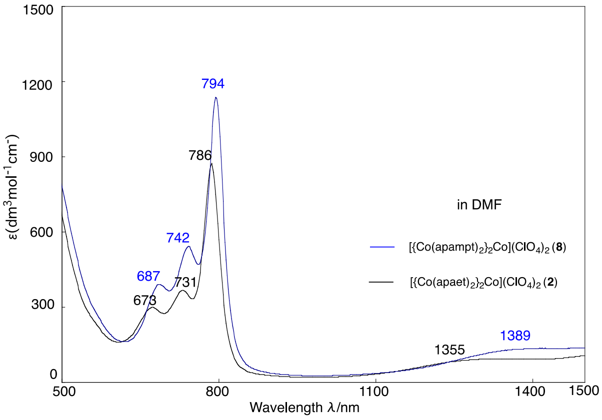

Figure 8. Electronic Absorption Spectra of **2** and **8**

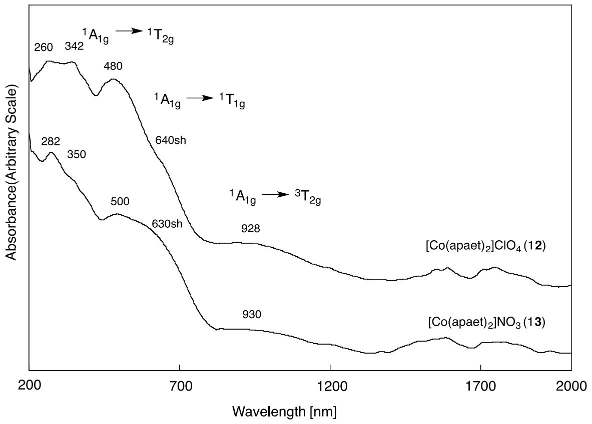

Figure 9. Diffuse Reflectance Spectra of Mononuclear Co(III) complexes **12** and **13**

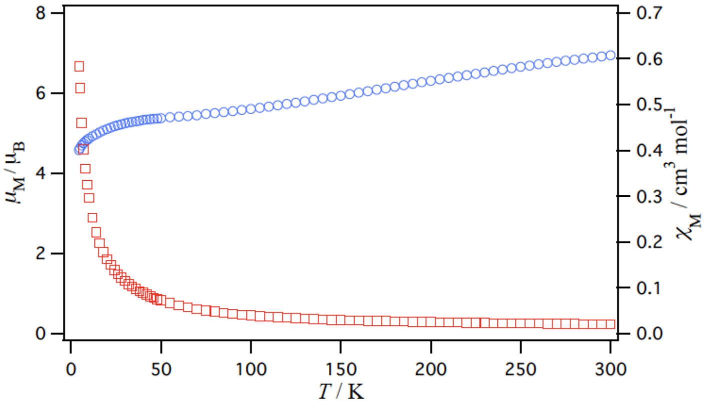

Figure 10. Magnetic Data of **1** (Blue Circle: Magnetic Moment; Red Square: Magnetic Susceptibility)

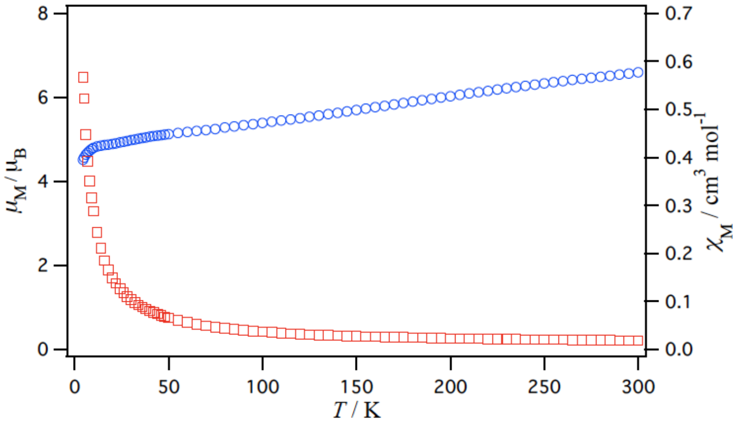

Figure 11. Magnetic Data of **7** (Blue Circle: Magnetic Moment; Red Square: Magnetic Susceptibility)

3.3 Magnetic Properties of Co Thiolates

Variable-temperature magnetic data were measured for the complexes **1**, **2**, **4**, **6**, **7**, **8**, **10**, and **11** in the temperature range of 4.5—300 K (Figures 10 and 11). The effective magnetic moments at 300 K of **1**, **2**, **4**, **6**, **7**, **8**, **10**, and **11** are 6.95, 5.11, 6.45, 4.86, 6.60, 6.84, 6.02, and 5.71 μ_B, per trinuclear molecule, respectively, showing generally lower values, compared with the spin-only magnetic moment (6.71 μ_B) for a non-interacted spin system of high-spin octahedral d^7-tetrahedral d^7-octahedral d^7. The magnetic moments decrease upon cooling from room temperature to 4.58, 3.55, 3.67, 2.60, 4.52, 4.57, 2.93, and 3.24 μ_B, respectively, at 4.5 K, suggesting an overall antiferromagnetic interaction in these systems.

4. Conclusions

In this study, we synthesized and characterized a series of thiolato-bridged trinuclear cobalt (II) complexes by the use of two kinds of tridentate thiolate ligands, 2-[(3-aminopropyl) amino] ethanethiol and 1-[(3-aminopropyl) amino]-2-methylpropane-2-thiol. Although no large structural, spectral, and magnetochemical changes were found in this series of trinuclear complexes, whether or not for the existence of the added methyl groups at the alpha position of the sulfur atom, some minor differences were observed. We also isolated mononuclear cobalt (III) complexes for the former thiolate ligand by changing the reaction condition, but not for the latter thiolate ligand. The mononuclear thiolate complexes may react with hydrogen peroxide, resulting in the sulfinato species [32].

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