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Synthesis, Crystal Structures, Electronic Spectra, and Magnetic Properties of Thiolato-Bridged Trinuclear Cobalt(II) Complexes with N, N, S-Tridentate Thiolate Ligands

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Abstract. Trinuclear cobalt(II) complexes with 2-[(3-aminopropyl)amino]ethanethiol (Hapaet) and 1-[(3-aminopropyl)amino]-2-methylpropane-2-thiol (Hapampt), $[\{Co(apaet)_2\}_2Co]X_2$ (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**)), and mononuclear cobalt(III) complexes with Hapaet, $[Co(apaet)_2]X$ (X = ClO_4 (**12**), NO_3 (**13**)), were synthesized and characterized by measurements of the elemental analysis, infrared and electronic spectra (UV-vis-NIR), and temperature dependence of magnetic susceptibilities (4.5—300 K). X-Ray crystal structure analysis of **1** and **7** revealed 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 meridional fashion and the thiolato S atoms are further bridged 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

Chemistry of metal thiolates has attached much attention over the past five decades, because of 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

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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 have been engaged in study on metal complexes with thiolate ligands containing nitrogen donor atoms besides thiolate sulfur atom, because formation of discrete metal thiolates can be expected to be feasible by virtue of chelating effect of the donor set of this combination [9-32]. By the use of *N*, *N*, *S*-tridentate ligands containing two amino-nitrogen and one thiolate-sulfur atoms as donor atoms, such as 2-[(3-aminopropyl)amino]ethanethiol (abbreviated as Hapaet), we isolated trinuclear species 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 linear arrangement of the three metal ions with octahedral-tetrahedral-octahedral 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,

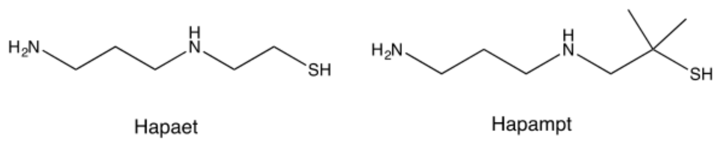

Figure 1. N,N,S-tridentate thiolate ligands

$[Co(apaet)_2](ClO_4)$, 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]. In this study, we made an effort to extend cobalt thiolate chemistry by synthesizing new cobalt thiolates in addition to the mononuclear species, because the isolated compounds may be relevant to models for bacterial enzymes, nitrile hydratases (NHase), which catalyze the partial hydration of nitriles to give amides and have non-corrinoid cobalt(III) or low-spin non-heme iron(III) center with nitrogen and thiolato-sulfur donors [33-35]. Crystallographic study of the Co-containing NHase, *Pseudonocardia thermophila* JCM 3095 has revealed that the metal environment in the Co-NHase is similar to those of iron(III)-containing NHases [36,37], containing two deprotonated carboxamide nitrogens and three cysteine-S centers two of which are modified to cysteine-sufenic and –sulfinic group [33]. We synthesized a series of cobalt thiolates with $apaet^-$, using a variety of cobalt salts, and further, synthesized an analogous N, N, S-donor tridentate thiolate ligand, 1-[(3-aminopropyl)amino]-2-methylpropane-2-thiol (Hapampt), which has two methyl groups at the alpha positions of the thiolate-sulfur, and performed reaction of Hapampt with cobalt salts in order to synthesize new cobalt thiolates. Herein we report on the synthesis and characterization of isolated cobalt complexes with $apaet^-$ and $apampt^-$.

2. Research Methods

2.1. Synthesis of Complexes

Unless otherwise specified, commercial chemicals were used as supplied. Methanol was dried using standard laboratory techniques. The thiolate ligands, Hapaet and Hapampt, were synthesized by

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applying a method described in the literature [12,25]. All reactions were performed under an atmosphere of argon using standard Schlenk techniques.

Safety Notes. *Caution!* Although no problems were encountered handling cobalt(II) perchlorate hexahydrate, perchlorate salts are potentially explosive when heated. Only small amounts of materials should be prepared, and these should be handled with great caution.

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

To a solution of Hapaet (34 mg, 0.25 mmol) and two drops of triethylamine in methanol (4 cm^3)/*N*,*N*-dimethylacetamide (2 cm^3), was added a methanol solution (4 cm^3) of cobalt(II) thiocyanate (44 mg, 0.25 mmol). After the mixture was stirred for 5 min, the solution was allowed to stand for several days at room temperature to give black plates. These were collected by filtration. Yield 26 mg (49% based on the thiolate ligand). Found: C, 31.44; H, 6.50; N, 15.64%. Calcd for $C_{23}H_{60}N_{10}O_3S_6Co_3$: C, 30.98; H, 6.48; N, 15.67%. IR(KBr) ν/cm^{-1} ν(NH) 3288(m), 3239(m); ν(CH) 2930(m), 2866(m), 2840(m); ν(SCN) 2051(s). Diffuse reflectance spectrum 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)$_2$}$_2$Co](ClO_4)$_2$·H_2O (**2**·H_2O)

To a solution of Hapaet (34 mg, 0.25 mmol) and two drops of triethylamine in methanol (4 cm^3)/*N*,*N*-dimethylacetamide (2 cm^3), was added a methanol solution (4 cm^3) of cobalt(II) perchlorate hexahydrate (93 mg, 0.25 mmol). After the mixture was allowed to stand for several days at room temperature, black plates deposited, which were collected by filtration. Yield 12 mg (21%). Found: C, 25.84; H, 5.80; N, 11.97%. Calcd for $C_{20}H_{54}N_8O_9S_4Cl_2Co_3$: C, 25.92; H, 5.87; N, 12.09%. IR(KBr) ν/cm^{-1} ν(NH) 3327(m), 3282(m); ν(CH) 2930(m), 2823(m); ν(ClO) 1145(s), 1100(s), 1080(s), 623(s). Diffuse reflectance spectrum λ_{max}/nm 272, 342(sh), 458(sh), 666, 730, 782, 1368, 1630. Electronic absorption spectrum in dmf (*N*,*N*-dimethylformamide) λ_{max}/nm (ε/$dm^3mol^{-1}cm^{-1}$) 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)$_2$}$_2$Co](NO_3)$_2$·3H_2O (**3**·3H_2O)

To a solution of Hapaet (34 mg, 0.25 mmol) and two drops of triethylamine in methanol (4 cm^3)/*N*,*N*-dimethylacetamide (2 cm^3) was added a methanol solution (4 cm^3) of cobalt(II) nitrate hexahydrate (73 mg, 0.25 mmol). The mixture was allowed to stand for several days at room temperature to give black plates. These were collected by filtration. Yield 38 mg (69%). Found: C, 27.37; H, 6.25; N, 15.33%. Calcd for $C_{20}H_{56}N_{10}O_7S_4Co_3$: C, 27.06; H, 6.58; N, 15.18%. IR(KBr) ν/cm^{-1} ν(NH) 3301(m), 3265(m); ν(CH) 2931(m), 2882(m); ν(NO) 1382(s), 1336(s). Diffuse reflectance spectrum λ_{max}/nm 276, 342(sh), 486(sh), 636, 726, 782, 1358, 1642.

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

To a solution of Hapaet (34 mg, 0.25 mmol) and two drops of triethylamine in methanol (4 cm^3)/*N*,*N*-dimethylacetamide (2 cm^3), was added a methanol solution (4 cm^3) of cobalt(II) chloride hexahydrate (60 mg, 0.25 mmol). After the mixture was allowed to stand for several days at room temperature, dark brown plates resulted, which were collected by filtration. Yield 34 mg (61%). Found: C, 30.42; H, 7.44; N, 12.70%. Calcd for $C_{22}H_{64}N_8O_4S_4Cl_2Co_3$: C, 30.00; H, 7.32; N, 12.72%. IR(KBr) ν/cm^{-1} ν(NH) 3204(m), 3148(m); ν(CH) 2925(m), 2875(m), 2820(m). Diffuse reflectance spectrum 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)$_2$}$_2$Co]Br_2·2CH_3OH·4H_2O (**5**·2CH_3OH·4H_2O)

This was prepared as dark brown plates by a method similar to that of **4**·2CH_3OH·2H_2O using cobalt(II) bromide hexahydrate instead of cobalt(II) chloride hexahydrate. Yield 20 mg (32%). Found: C, 26.30; H, 6.51; N, 11.06%. Calcd for $C_{22}H_{68}N_8O_6S_4Br_2Co_3$: C, 26.27; H, 6.82; N, 11.14%. IR(KBr) ν/cm^{-1} ν(NH) 3194(m), 3147(m); ν(CH) 2926(m), 2866(m), 2842(m). Diffuse reflectance spectrum λ_{max}/nm 274, 350, 380, 664(sh), 778, 1364, 1650.

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

This was prepared as dark brown plates by a method similar to that of **4**·2CH_3OH·2H_2O using cobalt(II) iodide instead of cobalt(II) chloride hexahydrate. Yield 26 mg (38%). Found: C, 24.57; H, 5.85; N, 10.30%. Calcd for $C_{22}H_{64}N_8O_3S_4I_2Co_3$: C, 24.84; H, 6.06; N, 10.53%. IR(KBr) ν/cm^{-1} ν(NH)

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3186(m), 3129(m); ν(CH) 2926(m), 2866(m), 2798(m). Diffuse reflectance spectrum 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 solution of Hapampt (41 mg, 0.25 mmol) and two drops of triethylamine in methanol (5 cm^3)/*N,N*-dimethylacetamide (2 cm^3) was added a methanol solution (5 cm^3) of cobalt(II) nitrate hexahydrate (73 mg, 0.25 mmol). The mixture was allowed to stand for several days at room temperature to give black plates. These were collected by filtration. Yield 39 mg (64% based on the thiolate ligand). Found: C, 35.84; H, 7.79; N, 14.22%. Calcd for $C_{30}H_{76}N_{10}O_8S_4Co_3$: C, 35.67; H, 7.58; N, 13.87%. IR(KBr) ν/cm^{-1} ν(NH) 3324(m), 3238(m); ν(CH) 2947(m), 2839(m); ν(NO) 1402(s), 1384(s), 1325(s). Diffuse reflectance spectrum 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 was prepared as black plates by a method similar to that of **7**$\cdot 2CH_3OH$ using cobalt(II) perchlorate hexahydrate instead of cobalt(II) nitrate hexahydrate. Yield 12 mg (16%). Found: C, 33.75; H, 7.01; N, 10.81%. Calcd for $C_{32}H_{79}N_9O_{10}S_4Cl_2Co_3$: C, 33.60; H, 7.14; N, 11.02%. IR(KBr) ν/cm^{-1} ν(NH) 3331(m), 3285(m), 3264(m); ν(CH) 2928(m), 2843(m); ν(ClO) 1106(s), 1058(s), 1014(s), 626(s). Diffuse reflectance spectrum λ_{max}/nm 290, 348(sh), 694, 754(sh), 798, 1384, 1730. Electronic absorption spectrum 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 solution of Hpampt (41 mg, 0.25 mmol) and two drops of triethylamine in methanol (5 cm^3)/*N,N*-dimethylacetamide (2 cm^3) was added a methanol solution (5 cm^3) of cobalt(II) chloride hexahydrate (60 mg, 0.25 mmol). The mixture was allowed to stand for several days at room temperature to give black plates. These were collected by filtration. Yield 15 mg (26%). Found: C, 36.86; H, 7.77; N, 11.79%. Calcd for $C_{29}H_{74}N_8O_2S_4Cl_2Co_3$: C, 36.94; H, 7.91; N, 11.88%. IR(KBr) ν/cm^{-1} ν(NH) 3244(m), 3204(m); ν(CH) 2954(m), 2921(m), 2865(m). Diffuse reflectance spectrum 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 was prepared as dark brown plates by a method similar to that of **9**$\cdot CH_3OH\cdot H_2O$ using cobalt(II) bromide hexahydrate instead of cobalt(II) chloride hexahydrate. Yield 14 mg (22%). Found: C, 34.28; H, 7.01; N, 10.96%. Calcd for $C_{29}H_{72}N_8OS_4Br_2Co_3$: C, 34.36; H, 7.16; N, 11.05%. IR(KBr) ν/cm^{-1} ν(NH) 3244(m), 3204(m); ν(CH) 2954(m), 2921(m), 2865(m). Diffuse reflectance spectrum 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 was prepared as dark brown plates by a method similar to that of **9**$\cdot CH_3OH\cdot H_2O$ using cobalt(II) iodide instead of cobalt(II) chloride hexahydrate. Yield 16 mg (22%). Found: C, 31.04; H, 6.62; N, 9.96%. Calcd for $C_{29}H_{72}N_8OS_4I_2Co_3$: C, 30.96; H, 6.63; N, 9.95%. IR(KBr) ν/cm^{-1} ν(NH) 3205(m), 3147(m); ν(CH) 2945(m), 2839(m). Diffuse reflectance spectrum 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 a methanol solution (3 cm^3) of Hapaet (34 mg, 0.25 mmol) and two drops of triethylamine was added a methanol solution (3 cm^3) of cobalt(II) nitrate hexahydrate (36 mg, 0.18 mmol). The mixture was allowed to stand for several days at room temperature to give dark red-purple crystals. These were collected by filtration. Yield 45 mg (70%). Found: C, 29.66; H, 6.56; N, 17.40%. Calcd for $C_{10}H_{54}N_5O_4S_2Co$: C, 29.63; H, 6.96; N, 17.27%. IR(KBr) ν/cm^{-1} ν(NH) 3252(m), 3213(m), 3142(m); ν(CH) 2969(m), 2928(m); ν(NO) 1372(s), 1348(s). Diffuse reflectance spectrum λ_{max}/nm 272, 348(sh), 492, 838, 916, 1370, 1584, 1712, 1748, 1782, 1928.

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2.2 Measurements

Elemental analyses for carbon, hydrogen, and nitrogen were done using a Perkin-Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JASCO MFT-2000 FT-IR Spectrometer in the 4000—600 cm^{-1} region. Electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer (Model UV-3100) equipped with an integrating sphere in the 200—2000 nm region. Variable-temperature magnetic susceptibilities were measured with a Quantum Design MPMS-5S SQUID susceptometer operating at a magnetic field of 0.5 T over a range of 4.5—300 K. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants [38]. The effective magnetic moments were calculated from the equation $\mu_{eff} = 2.828\sqrt{\chi_M T}$, where χ_M is the magnetic susceptibility per trinuclear molecule.

X-Ray Crystallography.

A preliminary examination was made and data were collected on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo-*Kα* radiation at 20±1 °C. Crystal data and details concerning data collection are given in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were inserted at their calculated positions and fixed at their positions. All of the calculations were carried out on a Pentium III Windows NT computer utilizing the SHELXTL software package [39].

Table 1. Crystallographic data for **1** and **7**.

Compounds	[{Co(apaet)$_2$}$_2$Co](SCN)$_2$·2CH$_3$OH (**1**·2CH$_3$OH)	[{Co(apampt)$_2$}$_2$Co](NO$_3$)$_2$·0.5CH$_3$OH·0.5H$_2$O (**7**·0.5CH$_3$OH·0.5H$_2$O)
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] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

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3. Results and Discussion

3.1 Synthesis and Crystal Structures of The Complexes

Our previous studies showed that the reactions of Hapaet with Mn(II) [17], Fe(II) [18], and Cd(II) [24] afforded trinuclear thiolate complexes, $[\{M(apaet)_2\}_2M]X_2$, which have a linear arrangement of the three metal atoms with *Oh-Td-Oh* geometries. In this study, we isolated analogous trinuclear Co(II) complexes with apaet$^-$ and apampt$^-$, $[\{Co(apaet)_2\}_2Co]X_2$ (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. 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 absorption bands due to apaet$^-$ and apampt$^-$ ligands appear as a set of distinctive bands in a similar region such as ν(NH) bands at 3327—3129 cm^{-1} and ν(CH) bands at 2969–2798 cm^{-1} to those of the free thiolate ligands, with lacking the ν(SH) 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].

Crystals suitable for single-crystal X-ray studies were obtained for **1**, **2**, and **7**. Single-crystal X-ray analysis revealed that **1**·$2CH_3OH$ crystallizes in the space group *C*2/*c* and the crystal structure consists of trinuclear cations, $[Co\{Co(apaet)_2\}_2]^{2+}$, thiocyanate ions, and methanol molecules in a 1:2:2 molar ratio. A perspective view of $[Co\{Co(apaet)_2\}_2]^{2+}$ is shown in Figure 2. The three cobalt atoms are

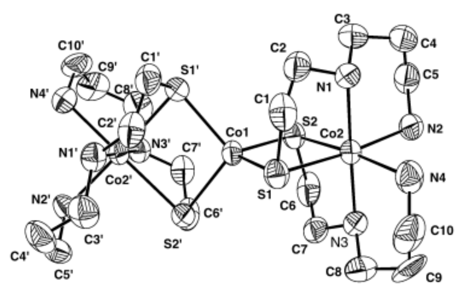

Figure 2. ORTEP Diagram of Trinuclear Cation in $[\{Co(apaet)_2\}_2Co](SCN)_2 \cdot 2CH_3OH$ (**1**·$2CH_3OH$)

arranged almost linearly (Co2-Co1-Co2' = 179.57(3)°). The cation has a C_2-symmetry with the crystallographic two-fold axis passing through Co1 and the midpoint of S1 and S1'. The central cobalt ion, Co1, has a distorted tetrahedral geometry with four thiolato-sulfur atoms of apaet$^-$, while the terminal cobalt atoms, Co2 and Co2', have a distorted octahedral geometry, where each octahedral cobalt atom is coordinated by two thiolato-sulfur atoms and four amino-nitrogen atoms of apaet$^-$.

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Each apaet⁻ ligand forms a fused 6-5 membered chelate ring for the terminal cobalt atom in a meridional fashion. 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 comparable to those of octahedral and tetrahedral thiolato Co(II) complexes, respectively [19,27]. The Co2-N distances [2.203(5)—2.224(5)Å] are also comparable to those of octahedral Co(II) complexes [19,27]. The five-membered chelate rings, Co2-S1-C1-C2-N1 and Co2-S2-C6-C7-N3, take a gauche form which is common for five-membered ring, whereas the six-membered chelate rings, Co2-N1-C3-C4-C5-N2 and Co2-N3-C8-C9-C10-N4, take a chair form. The molecule structure of the complex cation is similar to that of **2**·2dmac·2CH_3OH (dmac = *N*,*N*-dimethylacetamide) [27]. In the crystal, thiocyanate ions and methanol molecules are arranged

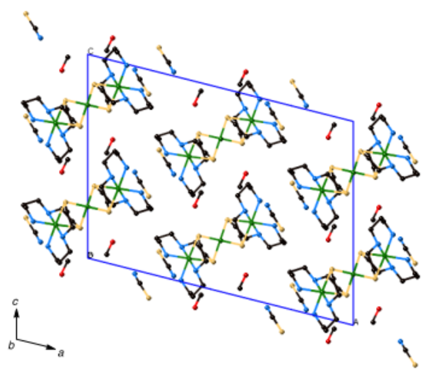

Figure 3. Packing Diagram of $\{Co(apaet)_2\}_2Co](SCN)_2$·2$CH_3OH$ (**1**·2CH_3OH)

among the trinuclear cations as like separating these molecules (Figure 3). Trinuclear Co(II) complex with apampt⁻, **7**·0.5CH_3OH·0.5H_2O, crystallizes in the space group *I*4/*m* and the crystal structure

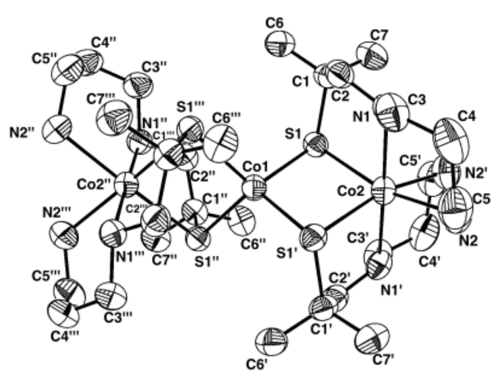

Figure 4. ORTEP Diagram of Trinuclear Cation in
$[\{Co(apampt)_2\}_2Co](NO_3)_2$·0.5$CH_3OH$·0.5$H_2O$ (**7**·0.5CH_3OH·0.5H_2O)

consists of trinuclear cations, $[Co\{Co(apampt)_2\}_2]^{2+}$, nitrate ions, methanol molecules, and water molecules in a 1:2:0.5:0.5 molar ratio. A perspective view of $[Co\{Co(apampt)_2\}_2]^{2+}$ is shown in Figure

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4. The molecular structure of the complex cation is similar to those of **1**·$2CH_3OH$ and **2**·2dmac·$2CH_3OH$ [27]. However, the three cobalt atoms are arranged in a crystallographical line (Co2-Co1-Co2" = 180°). The cation has a C_2-symmetry with the crystallographic two-fold axis passing through Co1 and the midpoint of S1 and S1'. The central cobalt ion, Co1, has a distorted tetrahedral geometry, while the terminal cobalt atoms, Co2 and Co2'', have a distorted octahedral geometry. Each of the octahedral Co2 and Co2'' atoms is coordinated by two thiolato apampt$^-$ ligands with four amino-nitrogen atoms and two thiolato-sulfur atoms. Each thiolato ligand forms a fused 6-5 membered chelate ring in a meridional fashion. The two thiolato-sulfur atoms of apampt$^-$ ligand are further bonded to the central Co1 atom. The bond distances of the terminal octahedral Co2-S [2.477(1) Å] are significantly shorter than those of **1**·$2CH_3OH$ and **2**·2dmac·$2CH_3OH$ [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**·$2CH_3OH$ and **2**·2dmac·$2CH_3OH$ [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**·$2CH_3OH$ and **2**·2dmac·$2CH_3OH$ [Co1-S 2.305(4)—2.340(2) Å] [27]. This may be due to the steric hindrance between the methyl groups attached to the alpha carbon atom of the thiolato sulfur atoms. The five-membered chelate ring, Co2-S1-C1-C2-N1 takes a gauche form, which is common for five-membered ring, whereas the six-membered chelate ring, Co2-N1-C3-C4-C5-N2 takes a chair form. The nitrate ion is in the vicinity of the nitrogen atoms of the thiolate ligand as indicated by the distances

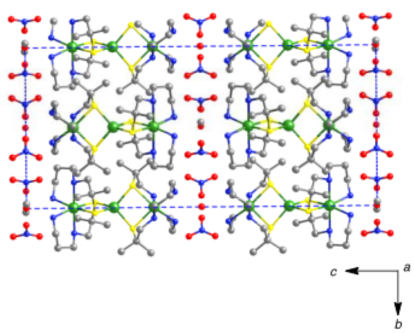

Figure 5. Packing Diagram of [{Co(apampt)$_2$}$_2$Co]$(NO_3)_2$·$0.5CH_3OH$·$0.5H_2O$ (**7**·$0.5CH_3OH$·$0.5H_2O$)

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, suggesting the hydrogen bonding (Figure 5).

3.2 Electronic Spectra of the Complexes

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 around 350 nm which can be attributed to thiolato-sulfur-to-cobalt(II) charge transfer transition, three bands around 670, 730, and 780 nm, and two broad bands around 1370 and 1630 nm, which can be assigned to d-d transitions of

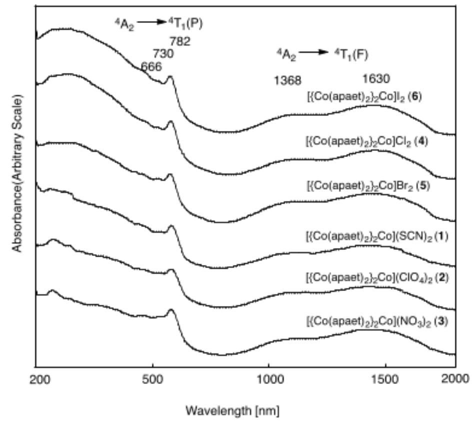

Figure 6. Diffuse Reflectance Spectra of Trinuclear Co(II) Complexes with apaet⁻

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 around 350 nm which can be attributed to thiolato-sulfur-to-cobalt(II) charge transfer transition, three bands around 690, 750, and 790 nm, and two broad bands around 1390

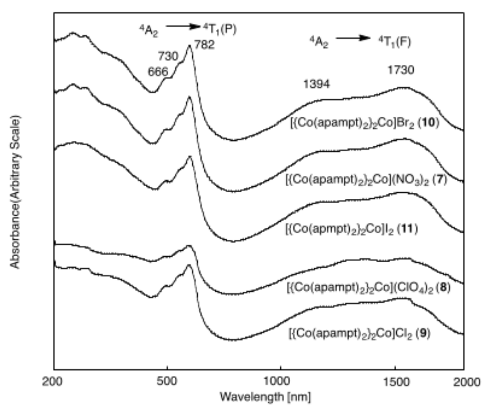

Figure 7. Diffuse Reflectance Spectra of Trinuclear Co(II) Complexes with apampt⁻

and 1730 nm, which can be assigned to d-d transitions 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 shifted to a little lower frequencies compared with those of the unmethylated thiolato complexes **1**—**6**. We can ascribe

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this weak coordination field of the methylated thiolato complexes **7**—**11** may be occurred to the steric hindrance between the methyl groups as indicated in the bond lengthening of the central Co-S bonds. The electronic absorption spectra in *N,N*-dimethylformamide (dmf) are shown in Figure 8. The

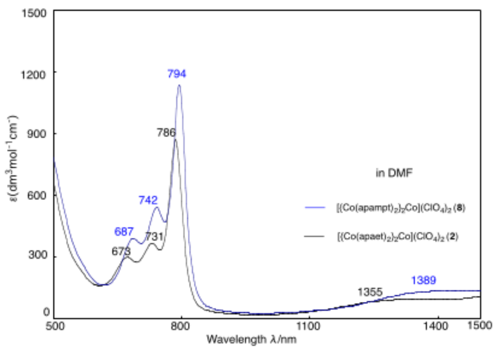

Figure 8. Electronic Absorption Spectra of $[\{Co(apaet)_2\}_2Co](ClO_4)_2$ (**2**) and $[\{Co(apampt)_2\}_2Co](ClO_4)_2$ (**8**)

electronic absorption spectra of **2** and **8** in dmf are essentially the same as those in the solid state. 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

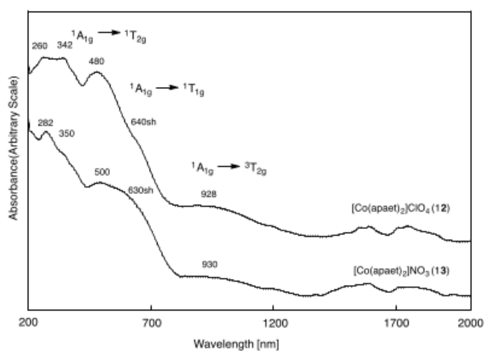

Figure 9. Diffuse Reflectance Spectra of Mononuclear Co(III) complexes, $[Co(apaet)_2]ClO_4 \cdot CH_3OH$ (**12**$\cdot CH_3OH$) and $[Co(apaet)_2]NO_3 \cdot H_2O$ (**13**$\cdot H_2O$)

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

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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].

3.3 Magnetic Properties of the Complexes

Magnetic susceptibility data for complexes **1**, **2**, **4**, **6**, **7**, **8**, **10**, and **11** were measured over the 4.5—300 K temperature range (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 values lower than the spin-only magnetic moment (6.71 μ_B) for a non-

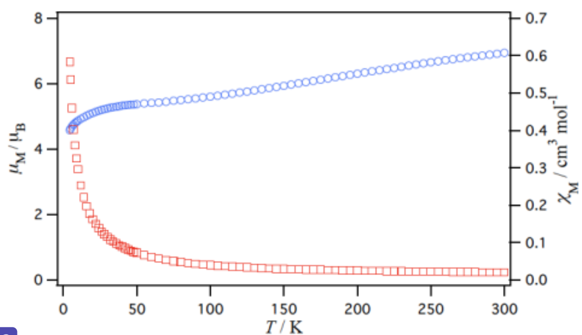

Figure 10. Temperature Dependence of Magnetic Moment (Blue Circle) and Magnetic Susceptibility (Red Square) of [{Co(apaet)$_2$}$_2$Co](NCS)$_2$ (**1**)

interacting high-spin octahedral d^7-tetrahedral d^7-octahedral d^7 system. The magnetic moments gradually decrease with lowering of 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.

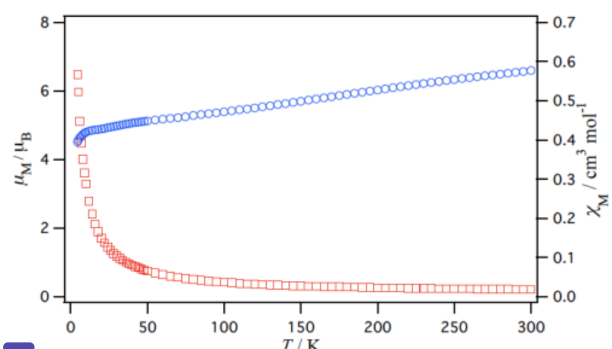

Figure 11. Temperature Dependence of Magnetic Moment (Blue Circle) and Magnetic Susceptibility (Red Square) of [{Co(apmpt)$_2$}$_2$Co](NO$_3$)$_2$ (**7**)

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

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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, which is relevant to models for bacterial enzymes, nitrile hydratase (NHase) [32].

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References

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with a Tripod-Like Tetradentate Ligand, Nâ€², Nâ€²-Bis(2-hydroxy-3,5-dimethylbenzyl)-N, N-dimethylethylenediamine", Bulletin of the Chemical Society of Japan, 2002.
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Publication

---

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