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Oligonuclear Cobalt Assembly with Schiff-base Ligands

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Abstract. In order to develop molecular magnetic compounds, oligonuclear cobalt complexes with Schiff-base ligands, 1,3-bis(salicylideneamino)-2-propanol (H_3salpr), 1,3-bis(5-chlorosalicylideneamino)-2-propanol (H_3clsalpr), 1,3-bis(5-bromosalicylideneamino)-2-propanol (H_3brsalpr), and 1,3-bis(5-nitrosalicylideneamino)-2-propanol (H_3pnsalpr), were synthesized by reaction of cobalt(II) acetate and Schiff-base ligand in organic solvent. The molecular structures of $[Co^{II}\{Co^{III}(\mu\text{-HL})(\mu\text{-}CH_3COO)(CH_3COO)\}_2]$ (HL = Hsalpr and Hbrsalpr), $[Co^{II}\{Co^{II}(\mu\text{-Hsalpr})(\mu\text{-}CH_3COO)\}_2]$, and $[Co^{III}_2Co^{II}_4(\mu\text{-L})_2(\mu_3\text{-}CH_3O)_2(\mu\text{-}CH_3O)_6(CH_3OH)_2]$ (L = salpr, clsalpr, brsalpr, and pnsalpr) were elucidated by the single-crystal X-ray crystallography. The electronic spectra and magnetic susceptibilities with variable-temperature are in accordance with the trinuclear and hexanuclear molecular structures. The cyclic voltammograms are basically featureless, giving a clue to isolate reduced complexes $[Co^{II}\{Co^{II}(\mu\text{-Hsalpr})(\mu\text{-}CH_3COO)\}_2]$ and $[Co^{II}_2(Hpnsalpr)_2(CH_3OH)]$. These findings may guide future design of molecular magnet materials.

Keywords: crystal structures, coordination chemistry, cobalt complexes, oligonuclear complexes, Schiff base

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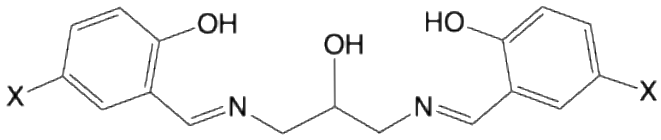
1. Introduction

Schiff-base compounds have been one of most popular organic ligands as easily available chelates to most of metal ions which belong to metallic elements of main group and transition elements including lanthanoid and actinoid metals [1-13], and thus a large number of metal complexes of Schiff-base ligands have been reported in both of the basic and applied chemistry fields. For example, bis(salicylidene)ethylenediamine (H_2salen) comprised of two imino-nitrogen and two phenol-oxygen donor atoms gives a tetradentate chelate with many kinds of metal ions, forming a planar reaction field. The H_2salen ligand was used to prepare a representative functional cobalt complex, [Co(salen)], known as a famous oxygen carrier [14-16] and salen type of manganese complexes have been used as homogenous or heterogeneous catalysts in many organic reactions [5-9]. Similar Schiff-base ligands with hydroxymethyl group, 1,3-bis(salicylideneamino)-2-propanol (H_3salpr) and its substituted derivatives with X-groups at the benzene rings, 1,3-bis(X-salicylideneamino)-2-propanol (H_3Xsalpr), are interesting pentadentate ligands, which were designed to make dinuclear metal complexes by introduction of the potential bridging alkoxy group [17-29]. In the solid state, these Schiff base ligands

are not coplanar, twisting the two salicylideneamino moieties at the central hydroxymethyl carbon atom in some degree [30-35]. The deprotonation of the central alkoxy group is a key factor to conform the alkoxido-bridged dinuclear metal system with an exogenous donor atom, forming dinuclear Mn^{III}_2 [21-27], Fe^{III}_2 [28], Co^{III}_2 [29,36], Ni^{II}_2 [20], and Cu^{II}_2 complexes [17-19], otherwise these ligands behave a tetradentate chelate with two phenolic-*O* and two imino-*N* donor atoms for one metal atom, forming mononuclear Mn^{III} [37,38], Ni^{II} [39], Cu^{II} [39-41], and Pd^{II} complexes [42]. In rare cases, different mononuclear species $[Mn^{III}(salen)]^+$ [22] and $[Co^{III}(Hdcsalapr)_2]^+$ (Hdcsalapr = 1-(3,5-dichlorosalicylideneamino)-3-amino-2-propanol) [43] were isolated during reactions of these Schiff bases and metal ions. When further reactions of mononuclear complexes with other linking ligands occurred, oligonuclear and polynuclear metal complexes could be synthesized: trinuclear $Co^{III}_2Co^{II}$ [44,45], Cu^{II}_3 [46], Zn^{II}_3 [47], and Cd^{II}_3 [48], tetranuclear Mn^{III}_4 [49], $Mn^{III}_2Mn^{II}_2$ [28,50,51], $Co^{III}_2Co^{II}_2$ [36], Co^{II}_4 [48,52], Ni^{II}_4 [36,48], and Zn^{II}_4 [48,53], hexanuclear $Co^{III}_2Co^{II}_4$ [54] and Cu^{II}_6 [28,54], octanuclear $Mn^{II}_2Mn^{III}_6$ [55], and polynuclear Mn^{III} complexes [25,38,46] have been reported. As for cobalt system, there are interesting points of cobalt for molecular magnetic materials [56-58]. Therefore, we have continued synthesis on the cobalt system by utilizing 1,3-bis(salicylidenamino)-2-propanol (H_3salpr), 1,3-bis(5-chlorosalicylideneamino)-2-propanol (H_3clsalpr), 1,3-bis(5-bromosalicylideneamino)-2-propanol (H_3brsalpr), and 1,3-bis(5-nitrosalicylideneamino)-2-propanol (H_3pnsalpr) as depicted in Figure 1. In this paper, we report on the synthesis and crystal structures, and spectral, magnetic, and electrochemical properties of the isolated trinuclear and hexanuclear cobalt complexes.



H_3salpr (X = H); H_3clsalpr (X = Cl); H_3brsalpr (X = Br); H_3pnsalpr (X = NO_2)

Figure 1. Schiff-base ligands

2. **Methods**

2.1. Synthesis of Complexes

Reagents and solvents with pure grade were purchased from Kishida and used as received. The Schiff-base ligands, H_3salpr, H_3clsalpr, H_3brsalpr, and H_3pnsalpr, were synthesized according to literature procedures [20,32,33,35]. The reproducibility and yield consistency of synthesis of the following complexes were confirmed by the repeated experiments for each complex.

$[Co_3(Hsalpr)_2(CH_3COO)_4]$ (**1**)

To an acetonitrile solution (4 cm^3) of H_3salpr (149.2 mg, 0.5 mmol) was added cobalt(II) acetate tetrahydrate (186.6 mg, 0.75 mmol). After the mixture was stirred for 3 min, ten drops of triethylamine was added to the solution, and placed for a week in a refrigerator. Black plates deposited were collected by filtration. Yield 46.3 mg (18% based on H_3salpr). Found: C, 50.03; H, 4.75; N, 5.66%. Calcd for $C_{42}H_{44}Co_3N_4O_{14}$: C, 50.16; H, 4.41; N, 5.57%. IR(KBr) ν/cm^{-1} ν(Ar-H) 3050(m), ν(CH) 2922(m), ν(C=N) 1635(s), ν_{as}(COO) 1558(s), ν_s(COO) 1421(s). Diffuse reflectance spectrum λ_{max}/nm 358, 568, 640, 1264.

$[Co_3(Hclsalpr)_2(CH_3COO)_4]$ (**2**)

This complex was synthesized as described in the previous paper [45].

$[Co_3(Hbrsalpr)_2(CH_3COO)_4]$ (**3**)

To a solution of H_3brsalpr (45.6 mg, 0.1 mmol) in acetonitrile (1 cm^3) was added cobalt(II) acetate tetrahydrate (74.7 mg, 0.3 mmol) dissolved in methanol (3 cm^3). The solution was placed for a week in a refrigerator to give gray precipitate. The precipitate was recrystallized from tetrahydrofuran. The deposited crystals were collected by filtration. Yield 15.9 mg (24% based on H_3brsalpr). Found: C, 37.28; H, 3.29; N, 4.22%. Calcd for $C_{42}H_{44}Br_4Co_3N_4O_{16}$: C, 37.17; H, 3.27; N, 4.13%. IR(KBr) ν/cm^{-1} ν(Ar-H) 3050(m), ν(CH) 2925(m), ν(C=N) 1631(s), ν_{as}(COO) 1561(s), ν_s(COO) 1412(s). Diffuse reflectance spectrum λ_{max}/nm 358, 550, 652, 1246.

$[Co_3(Hsalpr)_2(CH_3COO)_2]$ (**4**)

The synthesis was performed under argon utilizing the Schlenk techniques. A methanol solution of H_3salpr (118.4 mg, 0.4 mmol) was connected with a methanol solution of cobalt(II) acetate tetrahydrate (149.1 mg, 0.6 mmol) in an H tube. The solution was placed for a week at room temperature to give black crystals, which were collected by filtration. Yield 51.6 mg (30% based on H_3salpr). Found: C, 50.44; H, 4.78; N, 6.04%. Calcd for $C_{38}H_{40}Co_3N_4O_{11}$: C, 50.40; H, 4.45; N, 6.19%. IR(KBr) ν/cm^{-1} ν(Ar-H) 3020(m), ν(CH) 2937(m), ν(C=N) 1633(s), ν_{as}(COO) 1565(s), ν_s(COO) 1440(s). Diffuse reflectance spectrum λ_{max}/nm 414, 546, 644, 1004.

$[Co_6(salpr)_2(CH_3O)_8(CH_3OH)_2]$ (**5**)

The complex was prepared by a similar process to the complex **6**. The analytical data could not be obtained because of the low yield.

Yield 3.2 mg (5% based on H_3salpr). IR(KBr) ν/cm^{-1} ν(Ar-H) 2930(m), ν(C=N) 1621(s). Diffuse reflectance spectrum λ_{max}/nm 358, 546, 668, 1324.

$[Co_6(clsalpr)_2(CH_3O)_8(CH_3OH)_2]$ (**6**)

To a solution of H_3clsalpr (36.7 mg, 0.1 mmol) in acetonitrile (1 cm^3) was added cobalt(II) acetate tetrahydrate (74.7 mg, 0.3 mmol) dissolved in methanol (3 cm^3). Five drops of triethylamine was added to the mixed solution. The solution was placed for a week in a refrigerator to give reddish-brown crystals. Yield 13.0 mg (20% based on H_3clsalpr). Found: C, 37.42; H, 4.28; N, 3.97%. Calcd for $C_{44}H_{60}Cl_4Co_6N_4O_{17}$: C, 36.98; H, 3.80; N, 4.32%. IR(KBr) ν/cm^{-1} ν(Ar-H) 2913(m), ν(C=N) 1625(s). Diffuse reflectance spectrum λ_{max}/nm 344, 568, 650, 1320.

$[Co_6(brsalpr)_2(CH_3O)_8(CH_3OH)_2]$ (**7**)

This complex was prepared by a similar process to the complex **6**. Yield 17.2 mg (22% based on H_3brsalpr). Found: C, 31.44; H, 3.90; N, 3.58%. Calcd for $C_{44}H_{70}Br_4Co_6N_4O_{22}$: C, 31.45; H, 4.20; N, 3.33%. IR(KBr) ν/cm^{-1} ν(Ar-H) 2914(m), ν(C=N) 1622(s). Diffuse reflectance spectrum λ_{max}/nm 352, 568, 670, 1324.

$[Co_6(pnsalpr)_2(CH_3O)_8(CH_3OH)_2]$ (**8**)

This complex was prepared by a similar process to the complex **6**. Yield 8.7 mg (24% based on H_3pnsalpr). Found: C, 33.82; H, 4.43; N, 7.70%. Calcd for $C_{46}H_{77}Co_6N_9O_{32}$: C, 34.07; H, 4.79; N, 7.77%. IR(KBr) ν/cm^{-1} ν(Ar-H) 2917(m), ν(C=N) 1632(s). Diffuse reflectance spectrum λ_{max}/nm 354, 418, 540, 1320.

2.2 Measurements

Elemental analytic data of CHN were found by a Thermo Finnigan FLASH EA1112series CHNO-S analyzer. Infrared spectra were recorded with a JASCO MFT-2000 FT-IR Spectrometer in the 4000—600 cm^{-1} region. Diffused reflectance spectra were recorded with a Shimadzu UV-vis-NIR Recording Spectrophotometer (Model UV-3100) equipped with an integrating sphere in the 200—2000 nm region. Magnetic susceptibilities were measured with a Quantum Design MPMS-XL7 SQUID susceptometer with a magnetic field of 0.5 T over a temperature range of 4.5—300 K. The susceptibilities were corrected for the diamagnetic contribution using Pascal's constants [59]. 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 or hexanuclear molecule. Cyclic voltammograms were obtained in THF containing 0.1 M $^nBu_4NClO_4$ on a BAS 100BW Electrochemical Workstation with a glassy carbon disk, a platinum wire and a Ag/Ag^+ electrode.

X-Ray Crystallography.

After a preliminary examination on crystal data, diffraction data were collected at 90±1 K using a Bruker CCD X-ray diffractometer (SMART APEX) with graphite-monochromated Mo-$K\alpha$ radiation. Crystal data and details on data collection are listed in Table 1. The structures were solved by direct methods and refined by full-matrix least-square methods utilizing the SHELXTL programs [60]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in their calculated positions and fixed at their positions.

Table 1. Crystallographic data for **1**, **3**-**8**.

Complexes	$[Co_3(Hsalpr)_2(CH_3COO)_4]\cdot 5CH_3CN$ (**1**·5CH$_3$CN)	$[Co_3(Hbrsalpr)_2(CH_3COO)_4]\cdot 8THF$ (**3**·8THF)	$[Co_3(Hsalpr)_2(CH_3COO)_2]$ (**4**)	$[Co_6(salpr)_2(CH_3O)_8(CH_3OH)_2]\cdot CH_3OH$ (**5**·CH$_3$OH)
Empirical Formula	$C_{52}H_{59}Co_3N_9O_{14}$	$C_{74}H_{104}Br_4Co_3N_4O_{22}$	$C_{38}H_{38}Co_3N_4O_{10}$	$C_{47}H_{74}Co_6N_4O_{19}$
Formula weight	1210.87	1898.04	887.51	1352.68
Temperature / K	90(1)	90(1)	90(1)	90(1)
Crystal dimensions / mm	060×0.40×0.24	0.50×0.34×0.15	0.70×0.22×0.05	0.18×0.15×0.06
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$C2/c$
a / Å	11.261(2)	20.309(5)	9.4324(15)	29.913(5)
b / Å	14.251(3)	14.040(4)	9.9151(16)	12.4794(19)
c / Å	18.343(4)	27.502(7)	9.9606(16)	16.540(3)
α / °	100.364(4)		90.730(3)	
β / °	102.965(4)	98.935(5)	102.028(3)	117.406(2)
γ / °	105.364(3)		90.685(3)	
V / Å^3	2674.7(10)	7747(3)	910.9(3)	5481.5(14)
Z	2	4	1	4
d_{calcd}	1.503	1.627	1.618	1.639
μ / mm^{-1}	0.994	2.775	1.416	1.849
F(000)	1254	3892	455	2792
Reflections collected	15906	22650	5338	16778
Independent reflections	11591	8936	3904	6444
θ range for data collection	1.53 to 28.39°	1.50 to 28.52°	2.05 to 28.20°	1.53 to 28.58°
Data / Restraints / Parameters	11591/0/703	8936/0/484	3904/0/260	6444/0/352
$R1$, $wR2[I>2\sigma(I)]$[a)]	0.0389, 0.1090	0.1040, 0.2063	0.0394, 0.1052	0.0319, 0.0670
$R1$, $wR2$[all data][a)]	0.0506, 0.1131	0.1617, 0.2229	0.0488, 0.1096	0.0498, 0.0695
Goodness-of-fit on F^2	1.007	1.147	1.017	0.867
CCDC number	2475459	2475607	2475460	2475463

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

Table 1. Crystallographic data for **1**, **3**-**7**. (continued)

Complexes	$[Co_6(clsalpr)_2(CH_3O)_8(CH_3OH)_2]\cdot 2CH_3OH$ (**6**·2CH_3OH)	$[Co_6(brsalpr)_2(CH_3O)_8(CH_3OH)_2]\cdot 5H_2O$ (**7**·5H_2O)	$[Co_6(pnsalpr)_2(CH_3O)_8(CH_3OH)_2]\cdot 4H_2O$ (**8**·4H_2O)
Empirical Formula	$C_{46}H_{66}Cl_4Co_6N_4O_{18}$	$C_{44}H_{68}Br_4Co_6N_4O_{21}$	$C_{44}H_{66}Co_6N_8O_{28}$
Formula weight	1458.41	1662.24	1508.63
Temperature / K	90(1)	90(1)	90(1)
Crystal dimensions / mm	0.55×0.26×0.05	0.40×0.20×0.10	0.30×0.20×0.06
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a / Å	32.120(5)	32.610(18)	33.298(6)
b / Å	13.003(2)	12.953(7)	13.052(2)
c / Å	16.177(3)	16.305(9)	16.454(3)
α / °			
β / °	118.244(3)	117.403(9)	119.258(3)
γ / °			
V / Å^3	5952.1(17)	6115(6)	6239(2)
Z	4	4	4
d_{calcd}	1.627	1.806	1.606
μ / mm^{-1}	1.882	4.276	1.646
F(000)	2976	3320	3088
Reflections collected	17850	18211	18586
Independent reflections	6894	6981	7220
θ range for data collection	1.72 to 28.49°	1.72 to 28.41°	1.40 to 28.45°
Data / Restraints / Parameters	6894/0/371	6981/0/357	7220/0/398
*R*1, *wR*2[$I>2\sigma(I)$][a)]	0.0511, 0.1638	0.0866, 0.2151	0.0598, 0.1864
*R*1, *wR*2[all data][a)]	0.0788, 0.1736	0.1236, 0.2333	0.0935, 0.2027
Goodness-of-fit on F^2	1.016	0.943	1.011
CCDC number	2475462	2475461	2475466

[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 the Complexes with the Electrochemical Feature

It is known that reactions of Schiff-base ligands having 1,3-bis(salicylideneamino)-2-propanol moiety reacted with cobalt salts afforded mononuclear cobalt(III) complex $[Co^{III}(Hdcsalapr)_2]Cl$ [43], dinuclear cobalt(III) complexes $[Co^{III}_2(L)_2(CH_3OH)]$ (L = H_3pnsalpr and H_3mnsalpr) [29], trinuclear complexes $[Co^{III}_2Co^{II}(L)_2(CH_3COO)_4]$ (L = Hsalpr [44] and Hclsalpr [45]), tetranuclear complexes $[Co^{II}_4(L)_2(CH_3O)_2(H_2O)_2]$ (H_3L = 1,3-bis(3-methoxysalicylideneamino)-2-propanol) [48],

$[Co^{III}_2Co^{II}_2(L)_2(CH_3CH_2O)_4]$ (H_3L =1,3-bis(3,5-*tert*-butylsalicylideneamino)-2-propanol) [52] and hexanuclear complex $[Co^{III}_2Co^{II}_4(msalpr)_2(N_3)_4(CH_3O)_4(CH_3OH)_2]$ ($H_3msalpr$ = 1,3-bis(5-methylsalicylideneamine)-2-propanol) [54]. In this study, we performed reactions of H_3salpr, $H_3clsalpr$, $H_3brsalpr$), and $H_3pnsalpr$ with cobalt(II) acetate tetrahydrate in organic solvents. The reaction of the Schiff-base ligands and cobalt(II) acetate in acetonitrile afforded trinuclear complexes $[Co_3(HL)_2(CH_3COO)_4]$ (HL = Hsalpr (**1**), Hclsalpr (**2**), and Hbrsalpr (**3**)), where the molecular structures elucidated by the single-crystal X-ray crystal analyses are depicted in Figure 2 and compared with the reported crystal structures of **1** [44] and **2** [45]. All of these complexes have a similar trinuclear structure. The central OH group of each Schiff base is not deprotonated nor does not participate in coordination, but forms a hydrogen bond with the uncoordinate-oxygen atom of the monodentate carboxylato ligand. Each Schiff base ligand binds the terminal cobalt atom with a tetradentate fashion, giving an equatorial plane. The axial positions of the cobalt atom are occupied by the *syn-syn* bridging acetato ligand and the monodentate acetato ligand [61] to complete a distorted octahedral geometry for the terminal cobalt atoms. The two terminal $Co(HL)(CH_3COO)$ moieties are linked to the central Co1 atom by two μ-phenolato-oxygen atoms of each Schiff base ligand and *syn-syn* bridging acetato ligand to form a distorted octahedral geometry for the central Co atom and a trinuclear complex with linear *Oh-Oh-Oh* cobalt array. This is in contrast with the cases of thiolato-bridged trinuclear cobalt(II) complexes with linear *Oh-Td-Oh* cobalt array [62]. The Co-O and Co-N bond lengths around the terminal cobalt atoms of **1**-**3** are 1.876(2)—1.925(2) Å, corresponding to those of low-spin Co(III) oxidation state, whereas the central Co-O distances are 2.045(2)—2.161(2) Å which are within the observed for high-spin Co(II) complexes [63]. The IR spectra of these complexes exhibit ν(C=N) band of the Schiff base at 1631-1635 cm^{-1} [64], the $\nu(COO)_{as}$ and $\nu(COO)_s$ bands at 1558-1562 cm^{-1} and 1412-1421 cm^{-1}, respectively, with the separation between these bands of 137-149 cm^{-1}, corresponding to the *syn-syn*-bridging and hydrogen-bonded monodentate acetate ions [65]. Cyclic voltammogram of **1** is depicted in Figure 3. As for oxidation, irreversible oxidation waves were observed and attributable to Schiff-base ligand oxidation. On the other hand, a reduction wave was found at –1.01 V (vs. Ag/Ag^+), suggesting the existence of a reduced species. In the cases of **2** and **3** which have electron-withdrawing Cl or Br groups, the reduction wave was observed at –1.10 V, meaning the substituent group's effect. Considering these features, we performed the reaction of H_3salpr and cobalt(II) acetate under argon by utilizing the Schlenk technique and obtained a trinuclear Co^{II}_3 complex, $[Co_3(Hsalpr)_2(CH_3COO)_2]$ (**4**). The X-ray crystal structure of **4** revealed a similar trinuclear complex to the mixed-valent trinuclear complexes **1**-**3**, but without the monodentate acetato ligands, as depicted in Figure 4, resulting in distorted square pyramidal geometries for the two terminal cobalt atoms (τ value = 0.049 [65]). The Co-O and Co-N

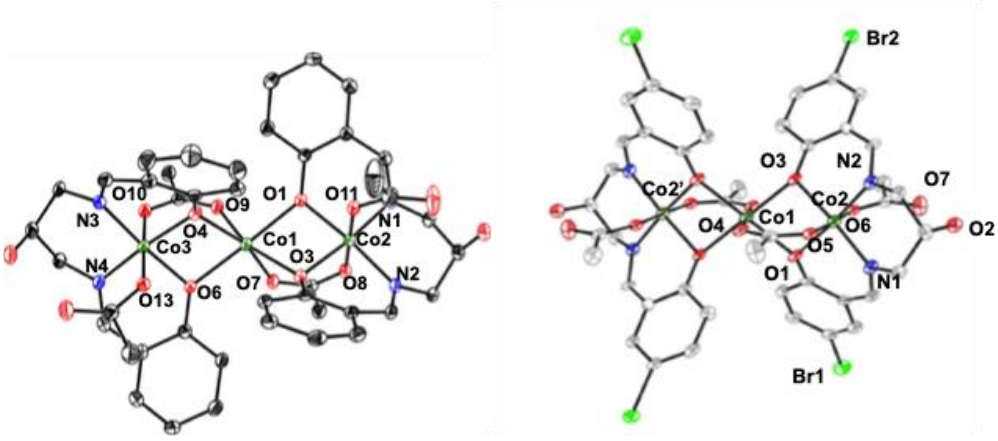


Figure 2. ORTEP drawings of $[Co_3(Hsalpr)_2(CH_3COO)_4]\cdot 5CH_3CN$ (**1**·$5CH_3CN$) (left) and $[Co_3(Hbrsalpr)_2(CH_3COO)_4]\cdot 8THF$ (**3**·8THF) (right). The crystal solvent molecules and hydrogen atoms are omitted for clarity.

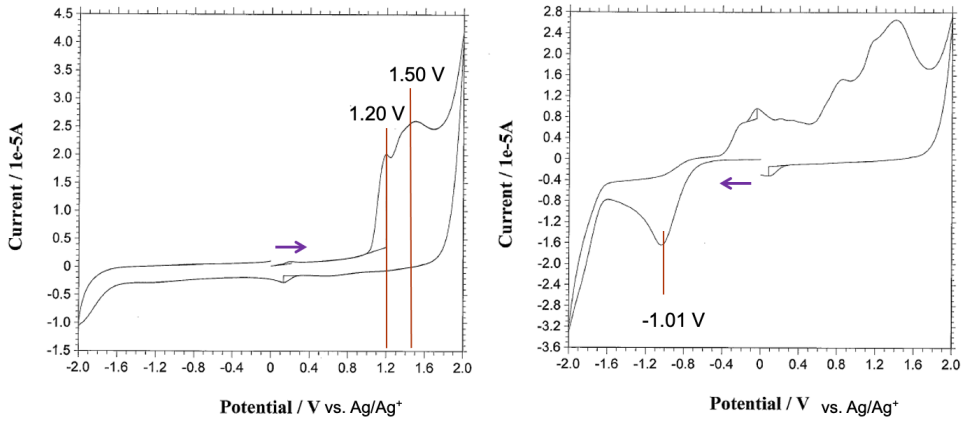


Figure 3. Cyclic voltammograms of $[Co_3(Hsalpr)_2(CH_3COO)_4]\cdot 5CH_3CN$ (**1**·$5CH_3CN$).

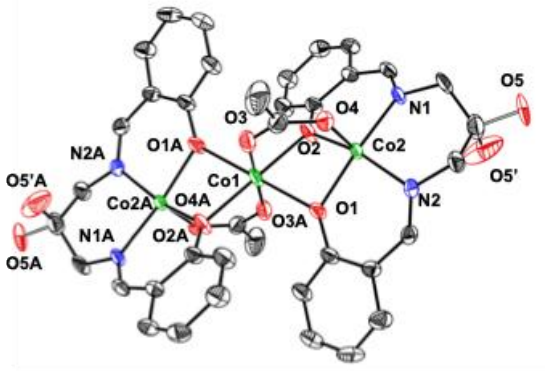


Figure 4. ORTEP drawing of $[Co_3(Hsalpr)_2(CH_3COO)_2]$ (**4**). The central OH group of Hsalpr is disordered in two positions. The crystal solvent molecules and hydrogen atoms are omitted for clarity.

bond lengths around the terminal cobalt atoms are 2.012(2)—2.062(2) Å, being definitely longer than those of **1**-**3**, whereas the central Co-O distances are 2.084(2)—2.100(2) Å with octahedral geometry. All of these bond lengths are within the observed range for high-spin Co(II)complexes [63], supporting the three cobalt(II) oxidation state with linear C_{4v}-*Oh*-C_{4v} cobalt array. When the reactions with cobalt(II) acetate were performed in methanol-containing acetonitrile, methoxido-bridged hexanuclear cobalt complexes $[Co_6(L)_2(CH_3O)_8(CH_3OH)_2]$ (L = salpr (**5**), clsalpr (**6**), brsalpr (**7**), and pnsalpr (**8**) were isolated. The X-ray crystal structure analysis revealed that all of the molecular structures of **5**-**8** are crystallographically centrosymmetric and similar to each other (Figure 5), where each twisted Schiff-base ligand binds trigonal bipyramidal Co(II) atom (τ value = 0.639 (**5**), 0.699 (**6**), 0.698 (**7**), 0.695 (**8**)) and octahedral Co(III) atom, forming a mixed-valent $Co^{III}Co^{II}$ dinuclear unit. The two $Co^{III}Co^{II}(\mu\text{-L})(\mu\text{-}CH_3O)$ dinuclear units are further bound to the central $Co^{II}_2(\mu_3\text{-}CH_3O)_2(CH_3OH)_2$ dinuclear unit by four $\mu\text{-}CH_3O$ bridges to form a hexanuclear defective tetracubane core made up of two trigonal-bipyramidal Co(II), two octahedral Co(II), and two octahedral Co(III) atoms. The Co-O and Co-N bond lengths around the trigonal bipyramidal and octahedral cobalt atoms are 1.931(3)—2.234(2) Å, corresponding to those of high-spin Co(II) state, whereas the other hexa-coordinated Co-O and Co-N distances are 1.859(2)—1.944(5) Å which are within the observed for low-spin Co(III) complexes [63]. The cyclic voltammograms of **5**-**8** are featureless, lacking any reduction wave. Concerning to this, we previously obtained dinuclear cobalt(III) complex of $[Co^{III}_2(pnsalpr)_2(CH_3OH)]$ which showed a reduction wave at –0.61 V vs. Ag/Ag^+ [29], suggesting possible isolation of a reduced species. Thus, we examined the reaction of H_3pnsalpr with cobalt(II) acetate under argon utilizing the Schlenk technique, resulting successfully isolating dinuclear

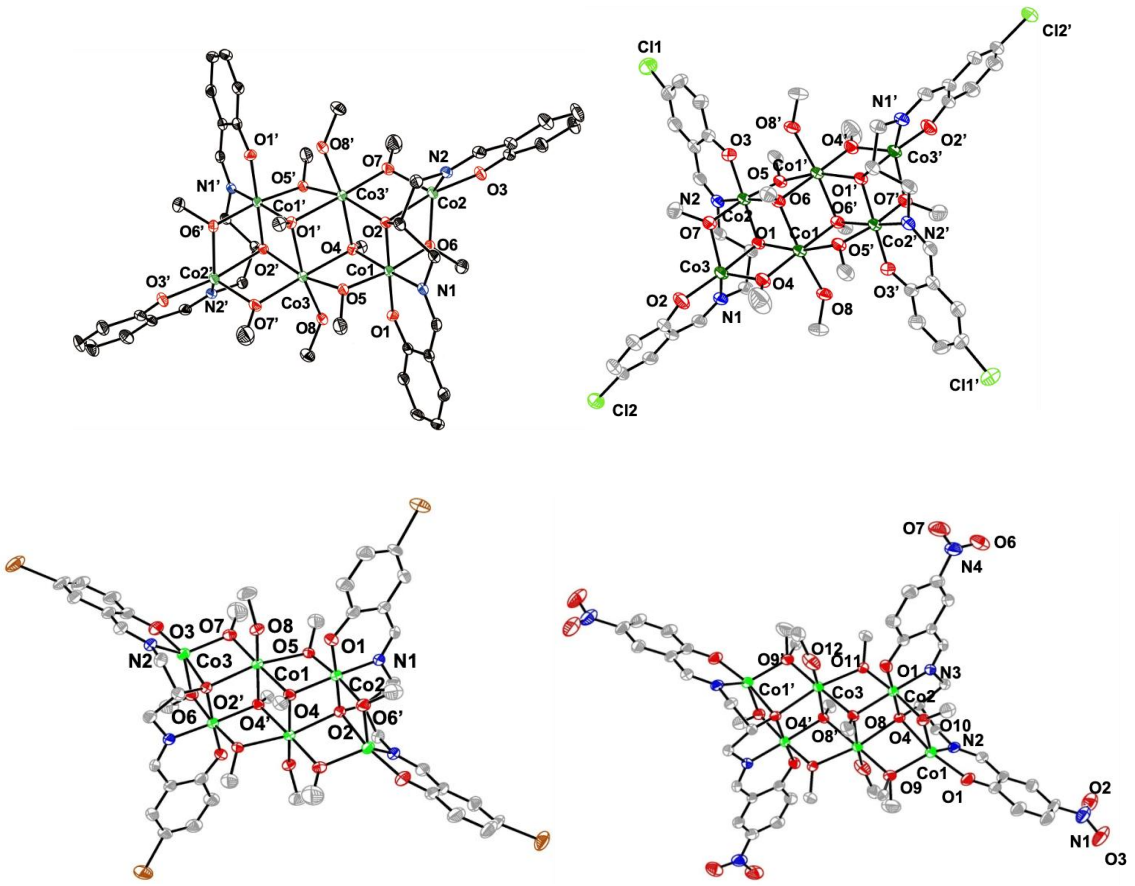


Figure 5. ORTEP drawings of $[Co_6L_2(CH_3O)_8(CH_3OH)_2]$ (L = salpr (**5**) (upper left), clsalpr (**6**) (upper right), brsalpr (**7**) (lower left), and pnsalpr (**8**) (lower right).

cobalt(II) complex $[Co^{II}_2(Hpnsalpr)_2(CH_3OH)]$. The analytical data and diffused reflectance spectra of this complex supported the dinuclear cobalt(II) formulation.

3.2. Electronic Spectra of the Complexes

The diffused reflectance spectra of $[Co_3(HL)_2(CH_3COO)_4]$ (HL = Hsalpr (**1**), Hclsalpr (**2**), and Hbrsalpr (**3**)) are depicted in Figure 6. The spectra are similar to each other, having the $^1T_{1g} \leftarrow ^1A_{1g}$ transition due to octahedral Co(III) and $^4T_{1g}(P) \leftarrow ^4T_{1g}$, $^4T_{2g} \leftarrow ^4T_{1g}$ transitions of octahedral Co(II), demonstrating the coexistence of the low-spin Co(III) and high-spin Co(II) states [66]. The diffuse reflectance spectrum of $[Co_3(Hsalpr)_2(CH_3COO)_2]$ (**4**) is different from those of **1**-**3**, with appearance of $^4T_{1g}(P) \leftarrow ^4T_{1g}$ and $^4T_{2g} \leftarrow ^4T_{1g}$ transitions of octahedral Co(II) and $^4A_2(P) \leftarrow ^4A_2$, $^4E(P) \leftarrow ^4A_2$, and $^4B_1(F) \leftarrow ^4A_2$ transitions of square pyramidal Co(II) in the visible and NIR regions as depicted in Figure 7. The diffused reflectance spectra of $[Co_6(L)_2(CH_3O)_8(CH_3OH)_2]$ (L = salpr (**5**), clsalpr (**6**), brsalpr (**7**), and pnsalpr (**8**) (Figure 8) are similar to each other, having the $^1T_{1g} \leftarrow ^1A_{1g}$ transition due to octahedral Co(III), $^4E' \leftarrow ^4A_2'$ and $^4E'' \leftarrow ^4A_2'$ transitions of trigonal bipyramidal Co(II), and $^4T_{1g}(P) \leftarrow ^4T_{1g}$, $^4T_{2g} \leftarrow ^4T_{1g}$ transitions of octahedral Co(II), demonstrating the coexistence of the low-spin Co(III) and high-spin Co(II) states [66]. The electronic spectral features of the present complexes are consistent with the presence of the octahedral Co(III) and Co(II) in **1**-**3**, octahedral and square-pyramidal Co(II) in **4**, and octahedral Co(III) and octahedral and trigonal bipyramidal Co(II) in **5**-**8**.

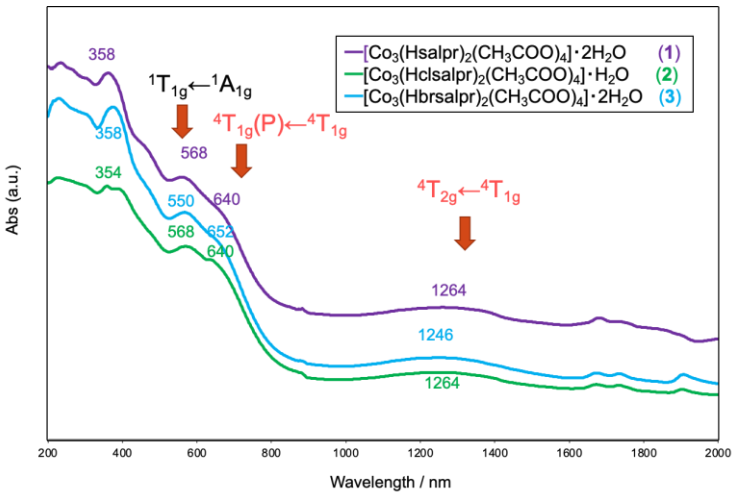


Figure 6. Diffused reflectance spectra of $[Co_3(HL)_2(CH_3COO)_4]$ (HL = Hsalpr (**1**), Hclsalpr (**2**), and Hbrsalpr (**3**).

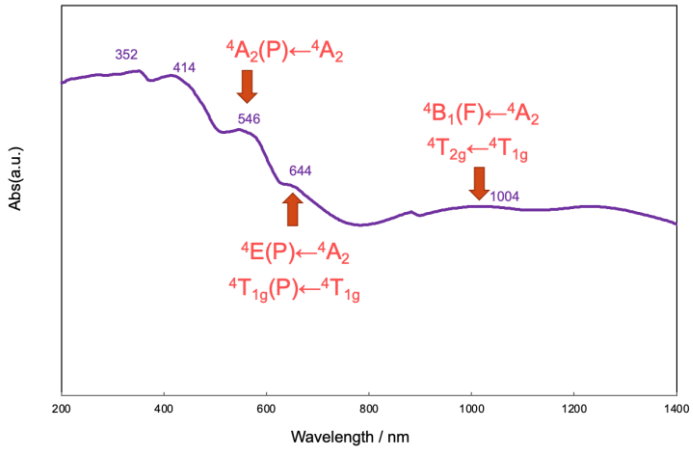


Figure 7. Diffused reflectance spectra of $[Co_3(Hsalpr)_2(CH_3COO)_2]$ (**4**).

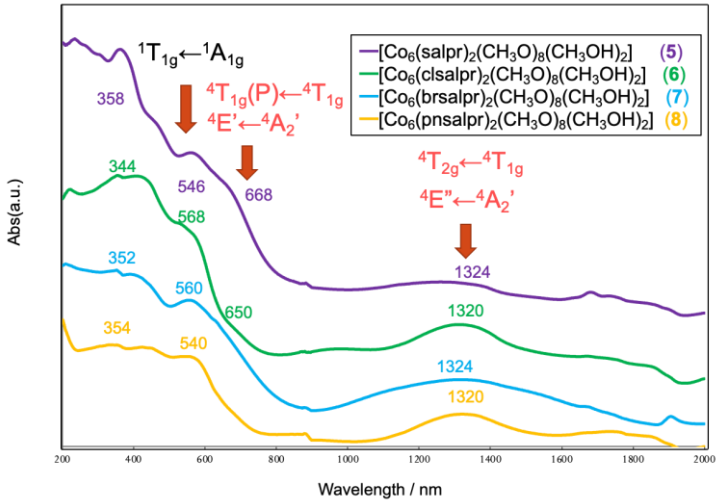


Figure 8. Diffused reflectance spectra of $[Co_6L_2(CH_3O)_8(CH_3OH)_2]$ (L = salpr (**5**), clsalpr (**6**), brsalpr (**7**), and pnsalpr (**8**).

3.3. Magnetic Data of the Complexes

Magnetic susceptibility data of $[Co_3(HL)_2(CH_3COO)_4]$ (HL = Hsalpr (**1**), Hclsalpr (**2**), and Hbrsalpr (**3**)) are shown as magnetic moments in Figure 9. The magnetic moments of $[Co_3(HL)_2(CH_3COO)_2]$ (HL = Hsalpr (**1**), Hclsalpr (**2**), and Hbrsalpr (**3**)) are 5.16, 5.73, and 5.13 μ_B, respectively, at 300 K, which are significantly higher than the spin-only value of high-spin Co(II), 3.87 μ_B, rather corresponding to the spin-orbit coupling value of high-spin Co(II), 5.20 μ_B. The magnetic moments gradually decrease with lowering of temperature and reached at 4.09, 3.82, and 4.17 μ_B, respectively, at 4.5 K. These magnetic behavior can be explained by the anisotropic character due to the spin-orbit coupling of the central Co(II)

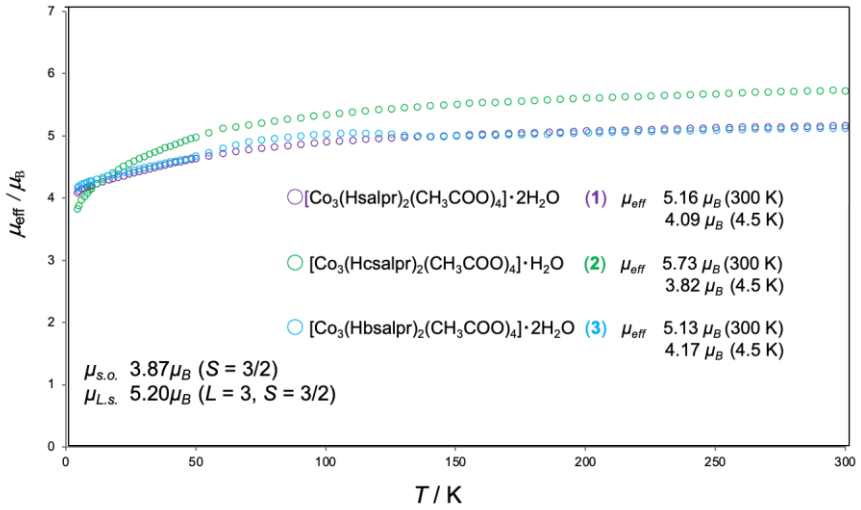


Figure 9. Magnetic moment data of $[Co_3(HL)_2(CH_3COO)_4]$ (HL = Hsalpr (**1**), Hclsalpr (**2**), and Hbrsalpr (**3**).

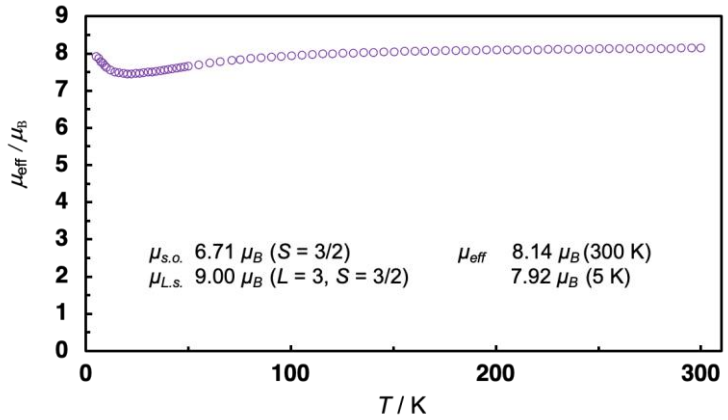


Figure 10. Magnetic moment data of $[Co_3(Hsalpr)_2(CH_3COO)_2]$ (**4**).

atom [45]. On the other hand, the magnetic moment of **4** is 8.14 μ_B at 300 K, being much higher than those of **1**-**3**, as depicted in Figure 10. The magnetic moment stays constant from 300 K to 100 K and slightly decreases below 100 K and then increases with further lowering of temperature and reached at 7.92 μ_B at 5 K. The observed magnetic moment is higher than the spin-only value of three 3/2 spins and lower than the spin-orbit coupling value of three high-spin Co(II), 9.00 μ_B. The magnetic behavior may be due to a ferromagnetc or ferrimagnetic interaction between the three 3/2 spins. As depicted in Figure 11, the magnetic moments of **5**, **6**, **7**, and **8** are 9.00, 9.60, 9.42 and 10.06 μ_B, respectively, at 300 K, which are significantly higher than the spin-only value of four high-spin Co(II), 7.75 μ_B, rather close to

the spin-orbit coupling value of four high-spin Co(II), 10.39 μ_B. The magnetic moments of **5**, **6**, and **8** gradually increase with lowering of temperature, reaching at 10.67, 10.26, and 14.68 μ_B, respectively, at 4.5 K, whereas the magnetic moment of **7** slightly decreases with lowering of temperature and reached at 8.14 μ_B at 4.5 K. These magnetic behaviors may be occurred by a ferromagnetic interaction between the two octahedral and two trigonal bipyamidal Co(II) atoms with anisotropic character due to the spin-orbit coupling [45]. Although the magnetic behavior of **7** at low temperature region is a little different from those of **5**, **6**, and **8**, the magnetic moments between 80-300 K are similar to each other in these complexes. As a whole, we can consider that the substitution groups on the benzene rings of the Schiff-base ligands do not give significant effect on the magnetic properties in these complexes.

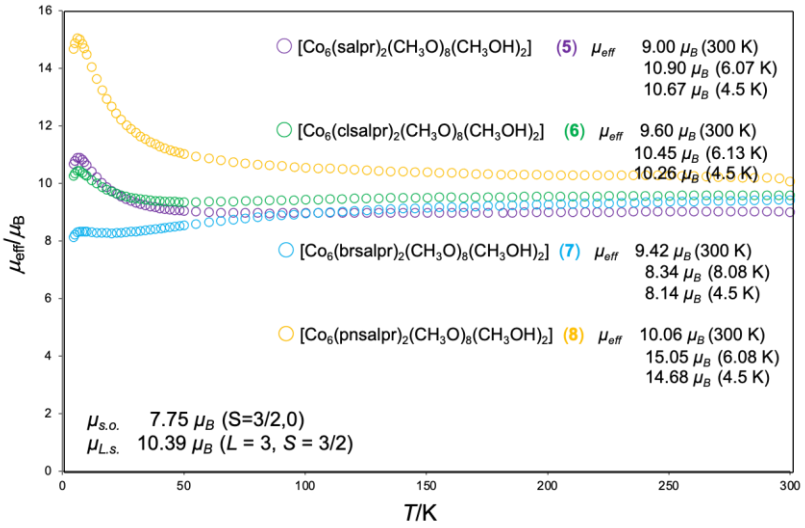


Figure 11. Magnetic moment data of $[Co_6L_2(CH_3O)_8(CH_3OH)_2]$ (L = salpr (**5**), clsalpr (**6**), brsalpr (**7**), and pnsalpr (**8**).

4. Conclusion

This study revealed that the Schiff-base ligands made up of 1,3-bis(salicylideneamino)-2-propanolato framework, H_3salpr, H_3clsalpr, H_3brsalpr, and H_3pnsalpr, are useful ligands to synthesize trinuclear complexes $[Co^{III}_2Co^{II}(HL)_2(CH_3COO)_4]$ and hexanuclear complexes $[Co^{III}_2Co^{II}_4(L)_2(CH_3O)_8(CH_3OH)_2]$ as well as dinuclear and tetranuclear cobalt complexes. Cyclic voltammograms can be used as a clue to synthesize the reduced complexes $[Co^{II}\{Co^{II}(\mu\text{-Hsalpr})(\mu\text{-}CH_3COO)\}_2]$ and $[Co^{II}_2(Hpnsalpr)_2(CH_3OH)]$. Although the effect of substituent groups on the benzene rings of the Schiff base ligands seems to be negligible for the electronic spectra and magnetic properties of the cobalt complexes, the redox properties seem to be affected by the substituent groups of the Schiff base ligands as found in the trinuclear complexes. Our previous result that only H_3pnsalpr and H_3mnsalpr ligands having strong electron-withdrawing NO_2 groups which prefer low oxidation state, afforded the Co^{III}_2 complexes with higher oxidation states unexpectedly [29], also support this trend. These trends may be complicated feature as the substituting group effect. Further studies for more assembled cobalt atoms are desired to develop cobalt-based molecular magnetic materials.

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