

**Syntheses, Structures and Magnetic Properties of Mixed-valence
Pentanuclear $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$ and Hexanuclear $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$ Complexes
Derived from 3-formylsalicylic acid**

Takuya Shiga and Hiroki Oshio*

*Graduate School of Pure and Applied Sciences, University of Tsukuba, Tennodai
1-1-1, Tsukuba 305-8571, Japan*

Abstract

Mixed-valence pentanuclear manganese complex,
 $[\{\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(\text{fsatren})\}_2\text{Mn}^{\text{II}}(\text{H}_2\text{O})_4] \cdot n(\text{sol})$ ($[\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_3]$, $\text{H}_6\text{fsatren} =$
tris[(2-hydroxy-3-carboxybenzylidene)aminoethyl]amine, $\text{sol} = \text{H}_2\text{O}$ or MeOH),
and hexanuclear cobalt complex, $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2(\text{fsaea})_2(\text{OMe})_4(\text{NO}_3)_2(\text{OAc})_2$
 $(\text{MeOH})_2]$ ($[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$, $\text{H}_3\text{fsaea} = 3$ -[*N*-(2-hydroxyethyl)formimidoyl]-salicyl
aldehyde) were prepared and their magnetic properties were studied.
 $[\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_3]$ has a linear tetranuclear core, whereas $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$ has a face
shared incomplete tetra cubane core.

1. Introduction

Extensive research has been devoted to synthesize large metal clusters with unique magnetic properties such as quantum effects and spin frustrations.^[1-3] Reaction of bridging ligands and metal salts yields unexpected multinuclear core structures with oxo and hydroxo bridges. We have focused on preparing large molecules by using multidentate Schiff-base type ligands^[4] derived from 3-formylsalicylic acid^[5] with phenoxo and carboxyl groups. In this work, a mixed-valence pentanuclear manganese complex with a tripod type Schiff-base ligand and a hexanuclear cobalt complex with a Schiff-base ligand including alkoxy group were prepared, and their crystal structures and magnetic properties of the complexes were presented.

2. Experimental

2.1. *Materials*

All chemicals were purchased from commercial sources and used without further purification. 3-Formylsalicylic acid was prepared according to the literature method.^[5]

2.2. *Synthesis of* $[\{Mn^{II}Mn^{III}(fsatren)\}_2Mn^{II}(H_2O)_4] \cdot n(sol)$ ($[Mn^{II}_3Mn^{III}_2]$)

To a solution of 3-formylsalicylic acid (84 mg, 0.5 mmol), triethylamine (202 mg, 2.0 mmol) and tris(2-aminoethyl)amine (25 mg, 0.17 mmol) in methanol (20 ml) was added a solution of $Mn(OAc)_2 \cdot 4H_2O$ (612 mg, 2.5 mmol) in methanol (20 ml), and the mixture was stirred for several minutes. The resulting solution was allowed to stand for several days to give brown lozenge crystals ($[\{Mn^{II}Mn^{III}(fsatren)\}_2Mn^{II}(H_2O)_4] \cdot 2MeOH \cdot 3H_2O$), suitable for X-ray structure analysis. They were collected by suction filtration and dried in vacuo.

Anal. Calcd. for $C_{60}H_{78}N_8O_{33}Mn_5$: C, 42.04; H, 4.59; N, 6.54. Found: C, 41.92; H, 4.46; N, 6.45. IR (KBr disk): $\nu = 1625.9, 1591.2 \text{ cm}^{-1}$.

2.3. *Synthesis of* $[Co^{II}_4Co^{III}_2(fsaea)_2(OMe)_4(NO_3)_2(OAc)_2(MeOH)_2]$
($[Co^{II}_4Co^{III}_2]$)

To a solution of 3-formylsalicylic acid (498 mg, 3.0 mmol), triethylamine (1212 mg, 12.0 mmol) and 2-ethanolamine (183 mg, 3.0 mmol) in methanol (100 ml) was added a $Mn(OAc)_2 \cdot 4H_2O$ (1471 mg, 6.0 mmol), and the mixture was stirred for several minutes. The resulting solution was diffused with diethyl ether to give brown solid. The brown solid was dissolved in methanol (100 ml), and $Co(NO_3)_2 \cdot 6H_2O$ (1746 mg, 6.0 mmol) was added to the solution. The resulting

solution was allowed to stand for several days to give red lozenge crystals of $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$. Anal. Calcd. for $\text{C}_{30}\text{H}_{42}\text{N}_4\text{O}_{24}\text{Co}_6$: C, 30.12; H, 3.54; N, 4.68; Mn, 0.00, Co, 29.56. Found: C, 30.32; H, 3.56; N, 4.71; Mn, 1.13; Co, 28.72. IR (KBr disk): $\nu = 1651.0, 1598.9, 1384.8 \text{ cm}^{-1}$.

2.4. X-ray crystallography

A brown lozenge crystal ($0.30 \times 0.18 \times 0.07 \text{ mm}^3$) of $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$, and a red lozenge crystal ($0.17 \times 0.16 \times 0.06 \text{ mm}^3$) of $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$ were mounted with epoxy resin on the tip of a glass fiber. Diffraction data were collected at $-70 \text{ }^\circ\text{C}$ on a Bruker SMART APEX diffractometer fitted with a CCD type area detector, and a full sphere of data were collected using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). At the end of data collection, the first 50 frames of data were recollected to establish that the crystal had not deteriorated during the data collection. The data frames were integrated using SAINT and were merged to give a unique data set for structure determination. Total reflections collected were 7939 and 25546 for $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$ and $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$, respectively, of which independent reflections were 6665 ($R(\text{int}) = 0.0597$) and 9326 ($R(\text{int}) = 0.0487$). The structures were solved by direct methods and refined by the full-matrix least-squares method on all F^2 data using the SHELXTL 5.1 package (Bruker

Analytical X-ray Systems). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms.

Crystallographic data for $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$ and $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$ have been deposited at the Cambridge Crystallographic Data Centre as the publication citation and deposition numbers CCDC 617363 ($[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$) and 617364 ($[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$).

Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK, fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

Crystal data for $[\{\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(\text{fsatren})\}_2\text{Mn}^{\text{II}}(\text{H}_2\text{O})_4]\cdot 2\text{MeOH}\cdot 3\text{H}_2\text{O}$ ($[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$): $\text{C}_{32}\text{H}_{32}\text{N}_4\text{O}_{15}\text{Mn}_{2.5}$, F. W. = 849.97; brown lozenge, triclinic, space group $P\bar{1}$, $a = 12.345(2)$, $b = 13.142(2)$, $c = 13.862(3)$ Å, $\alpha = 77.451(4)^\circ$, $\beta = 82.671(4)^\circ$, $\gamma = 65.767(4)^\circ$, $V = 2000.0(6)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.411$ Mg m⁻³, μ (Mo-K α) = 0.850 mm⁻¹, $R1 = 0.0808$, $wR2 = 0.2269$ ($I > 2\text{sigma}(I)$).

Crystal data for $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2(\text{fsaea})_2(\text{OMe})_4(\text{NO}_3)_2(\text{OAc})_2(\text{MeOH})_2]$ ($[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$): $\text{C}_{30}\text{H}_{42}\text{N}_4\text{O}_{24}\text{Co}_6$, F. W. = 1196.26; red lozenge, orthorhombic, space group $P2_12_12_1$, $a = 15.097(3)$, $b = 16.137(3)$, $c = 17.164(3)$ Å, $V = 4181.7(13)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.900$ Mg m⁻³, μ (Mo-K α) = 2.419 mm⁻¹, $R1 = 0.0696$, $wR2 = 0.1711$ ($I > 2\text{sigma}(I)$).

3. Result and discussion

3.1. Crystal structures

An ORTEP drawing of $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$ is shown in Figure 1. X-ray structure analyses for $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$ reveals that a $[\text{Mn}^{\text{II}}(\text{H}_2\text{O})_4]$ unit bridges two $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(\text{fsatren})]^-$ units to form a linear pentanuclear manganese core. In the $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(\text{fsatren})]^-$ unit, a Mn(II) ion has seven-coordinated geometry (monocapped trigonal prism environment) and locates at an N_4O_3 site of fsatren^{3-} ligand, whereas a Mn(III) ion has a distorted octahedral environment and locates an O_6 site of fsatren^{3-} ligand. The terminal carboxyl group of $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(\text{fsatren})]^-$ unit connects to additional Mn(II) ion with syn-anti manner bridge to form a linear pentanuclear manganese core. Coordination bond lengths about Mn1, Mn2 and Mn3 are in the range of 2.245(6)–2.561(7) Å, 1.861(7)–2.059(6) Å and 2.130(7)–2.220(7) Å, respectively. On the bases of bond valence sum calculations and coordination bond lengths, Mn1 and Mn3 ions are Mn^{II} ions, and Mn2 ions are Mn^{III} ions. Interatomic Mn1 \cdots Mn2 and Mn2 \cdots Mn3 separations are 3.144(2) Å and 5.237(2) Å, respectively. The bridging angles of Mn1–O1–Mn2, Mn1–O4–Mn2, and Mn1–O7–Mn2 are 90.9(3), 95.2(3), and 94.1(3) $^\circ$, respectively.

[Insert Figure 1]

An ORTEP drawing for $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$ with atom numbering scheme is shown in Figure 2. The structure of $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$ is composed of a face shared incomplete tetra cubane core with four cobalt(II) ions (Co2, Co3, Co5, Co6) and two cobalt(III) ions (Co1, Co4) bridged by $\mu_3\text{-MeO}^-$, phenoxo, alkoxo and carboxyl groups. Co1 and Co4 ions have an octahedral coordination geometry and locate at an N_1O_2 site of fsaea^{3-} ligand. Co2 and Co5 ions have an octahedral coordination and locate at an O_2 site of fsaea^{3-} ligand. Co3 and Co6 ions have a distorted octahedral geometry and are coordinated by the oxygen atom of carboxyl group of fsaea^{3-} ligand. Coordination bond lengths are in the range of 1.881(6)–1.942(5), 2.022(5)–2.136(5), 2.009(5)–2.228(6), 1.863(7)–1.950(5), 2.032(5)–2.116(5), 1.995(5)–2.179(6) Å for Co1–Co6, respectively. The assignment of oxidation number was confirmed by the bond distances.

[Insert Figure 2]

3.2. Magnetic property

Magnetic susceptibilities for $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$ and $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$ were measured in the temperature range of 1.8 – 300 K. $\chi_m T$ vs. T and M vs. H plots are given in

Figures 3 and 4, respectively. In the case of $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$, the $\chi_m T$ value at 300 K is $17.809 \text{ emu mol}^{-1} \text{ K}$, which is smaller than the expected spin-only value for uncorrelated three Mn(II) ions and two Mn(III) ions ($19.125 \text{ emu mol}^{-1} \text{ K}$, $g = 2$). The $\chi_m T$ value gradually decreased as the temperature was lowered, and reached the value of $6.655 \text{ emu mol}^{-1} \text{ K}$, which suggests that $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$ has spin ground states $S = 7/2$ ($g_{\text{ave}} = 1.84$). The Curie-Weiss plot gave a negative Weiss constant ($C = 18.939 \text{ emu mol}^{-1} \text{ K}$, $\theta = -15.284 \text{ K}$), which suggested antiferromagnetic interaction between the Mn ions. A magnetization measurement performed at 1.8 K yielded a value of $8.73 N\beta$ at 5 T, which is still unsaturated. This magnetization behavior suggests the existence of near excited state above a ground spin state $S = 7/2$. In the case of $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$, the $\chi_m T$ value at 300 K is $11.978 \text{ emu mol}^{-1} \text{ K}$, which is larger than the value expected for uncorrelated four Co(II) ions ($7.5 \text{ emu mol}^{-1} \text{ K}$, $g = 2$). As the temperature decreased, the $\chi_m T$ value slightly decreased, reaching a minimum value of $11.573 \text{ emu mol}^{-1} \text{ K}$ at 58 K followed by steep increase to $22.877 \text{ emu mol}^{-1} \text{ K}$ at 2.2 K. This magnetic behavior is indicative of ferromagnetic interactions between the Co(II) ions, giving rise to an $S = 6$ ground state. A magnetization measurement performed at 1.8 K yielded a value of $8.80 N\beta$ at 5 T, which is still unsaturated. The observed magnetization is smaller than the

value expected for $S = 6$ ground spin state. This deviation will be brought about by T term contribution of high-spin Co(II). The ferromagnetic behavior can be understood by the accidental orthogonality of magnetic orbitals of Co(II) ions derived from a face shared incomplete tetra cubane core. It is noted that out-of-phase signals in ac magnetic susceptibility measurements were not observed.

[Insert Figure 3]

[Insert Figure 4]

4. Conclusion

Mixed-valence pentanuclear manganese complex, $[\{\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(\text{fsatren})\}_2\text{Mn}(\text{H}_2\text{O})_4] \cdot n(\text{sol})$, and hexanuclear cobalt complex, $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2(\text{fsaea})_2(\text{OMe})_4(\text{NO}_3)_2(\text{OAc})_2(\text{MeOH})_2]$, with Schiff-base ligand derived from 3-formylsalicylic acid have been synthesized. $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$ complex has a linear pentanuclear core bridged by phenoxo and carboxyl groups, whereas $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$ complex has a face shared incomplete tetra cubane core bridged by $\mu_3\text{-MeO}^-$, phenoxo, alkoxo and carboxyl groups. $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$ complex shows an antiferromagnetic interaction between the Mn(II) ions, while $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$ complex shows a ferromagnetic interaction between Co(II) ions.

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Figure captions

Figure 1. ORTEP drawing of $[\{\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(\text{fsatren})\}_2\text{Mn}^{\text{II}}(\text{H}_2\text{O})_4]\cdot 2\text{MeOH}\cdot 3\text{H}_2\text{O}$ ($[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$).

Figure 2. ORTEP drawing of $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2(\text{fsaea})_2(\text{OMe})_4(\text{NO}_3)_2(\text{OAc})_2(\text{MeOH})_2]$ ($[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$).

Figure 3. Plots of $\chi_M T$ vs. T for $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$ (\square), and $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$ (\circ).

Figure 4. Plots of M vs. H for $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_2]$ (\square), and $[\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2]$ (\circ).

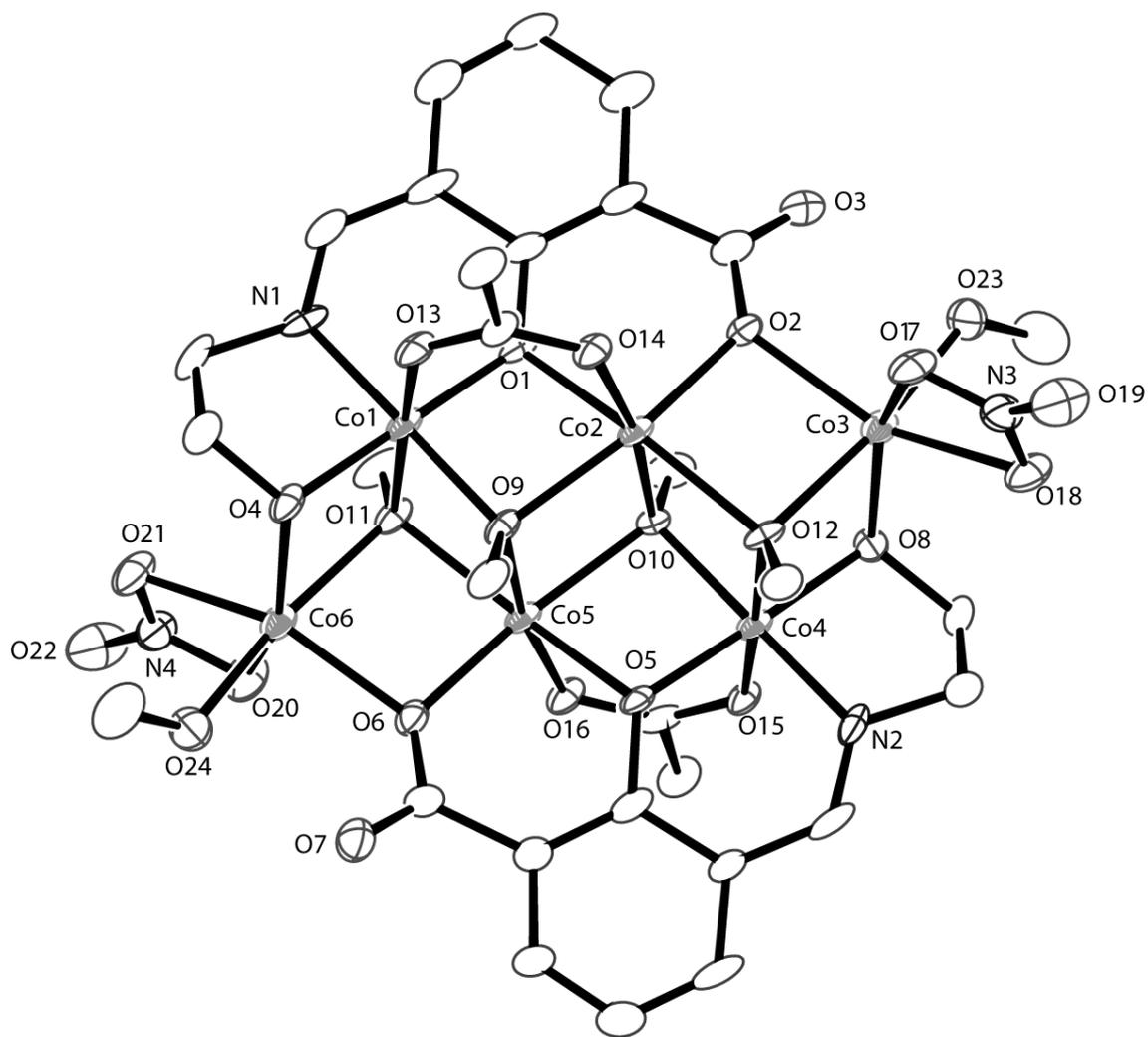


Figure 2.

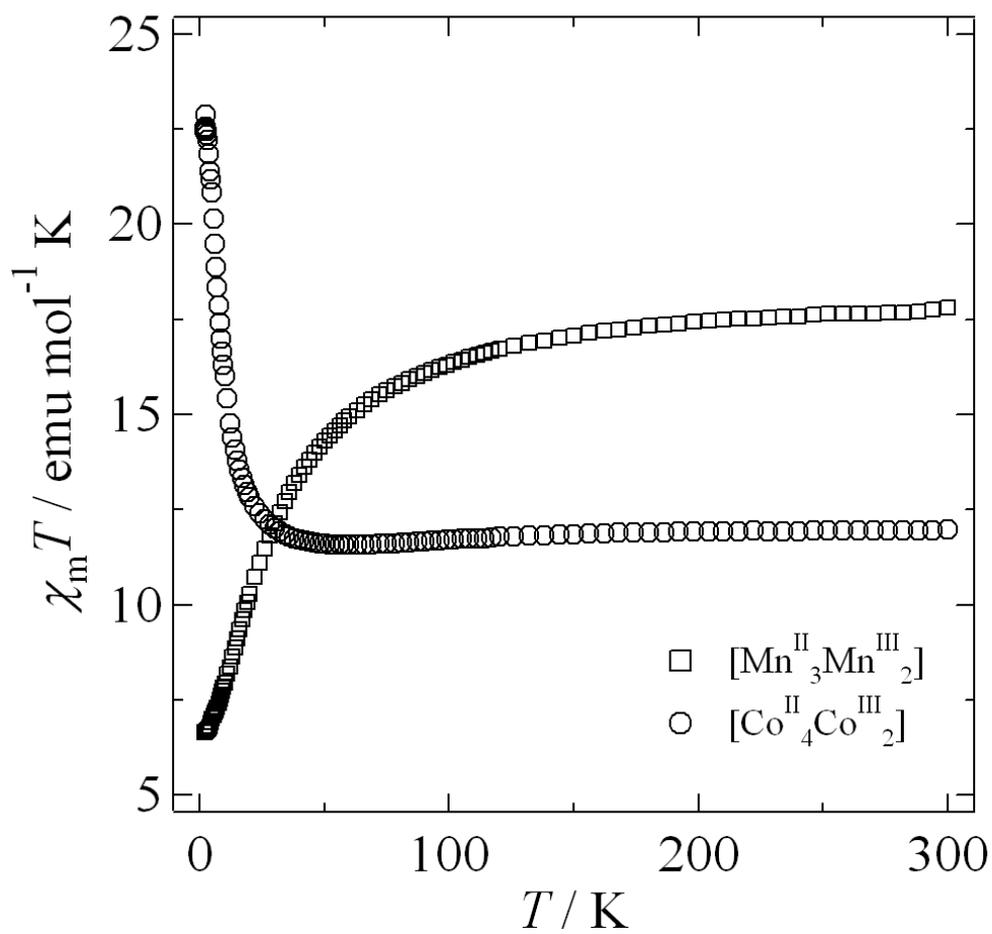


Figure 3.

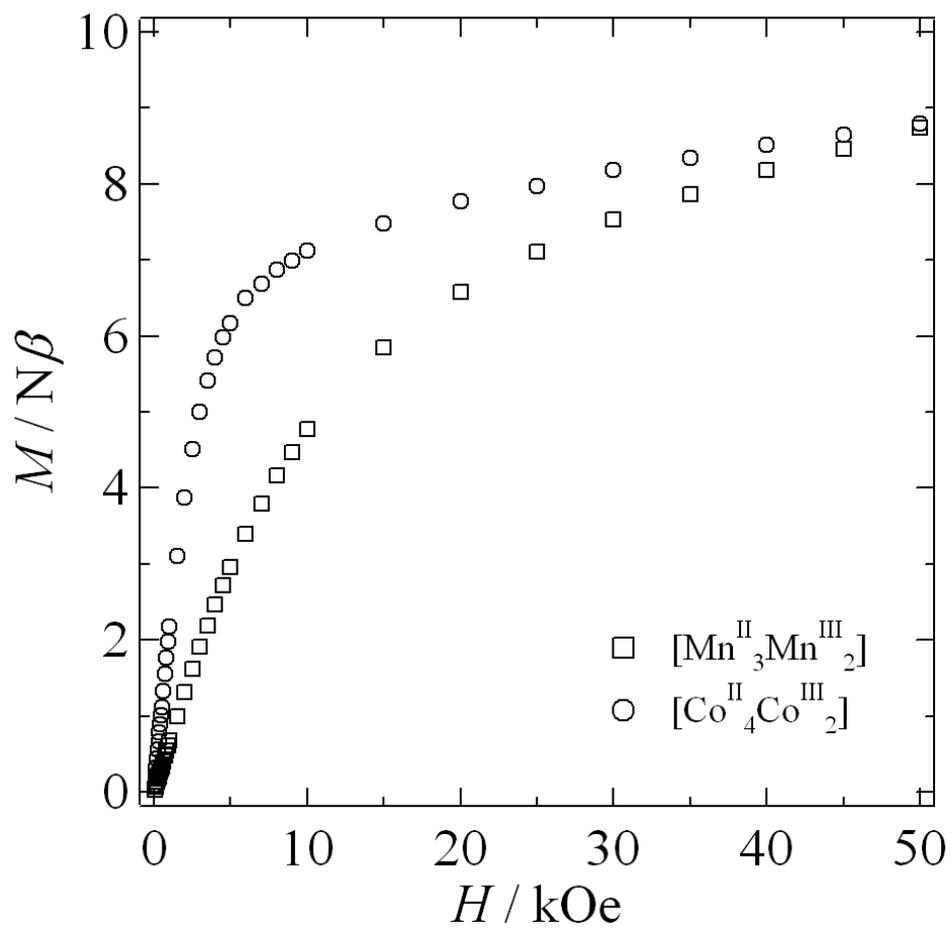


Figure 4.

Contents

Mixed-valence pentanuclear manganese complex and hexanuclear cobalt complex with Schiff-base ligand derived from 3-formylsalicylic acid have been prepared. Structures and magnetic properties of these compounds are reported.

