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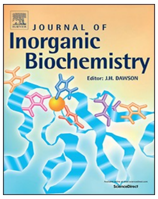

Artificial bioinorganic clusters of dinuclear 3d-transition metal ions coordinated by an inorganic coordination ligand

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ABSTRACT

A new biologically relevant cubane-type artificial inorganic ligand was developed to support 3d-transition metal ions of Mn(II), Co(II), Ni(II), Zn(II), Fe(III), and also In(III). All of the reactions produce dinuclear cationic clusters of $[(\{Co(tacn)\}_2HMo_3O_{13}{\cdot}H_2O)\{M(H_2O)_2\}]_2{}^{n+}$ (M = Mn^{2+} (**4Mn**), Co^{2+} (**4Co**), Ni^{2+} (**4Ni**), Zn^{2+} (**4Zn**), n = 2; M = Fe^{3+} (**5**), In^{3+} (**6**), n = 4), where tacn is the abbreviation of 1,4,7-triazacyclononane ligand. Clusters **4** do not dissolve in any solvents at all to prevent the recrystallization or the further characterization whereas the high solubility of clusters **5** and **6** allowed us to characterize the solution state properties. The dinuclear cores are separated at a fixed-distance in the range of 5.66–5.77 Å for M(II) complexes and 5.45–5.65 Å for M(III) complexes. Each 3d-transition metal ion is supported by two pairs of *cis*-oxido groups from a cubane unit formed by $CoMo_3O_3(OH)$ group, and remaining two sites on the 3d-transition metal centers are occupied by two water molecules. The hydroxido group on the cubane unit provides an interaction route through bifurcated hydrogen bondings between dinuclear centers. Three consecutive stepwise reduction waves were observed at −0.73, −0.91, and −1.16 mV *vs* Fc^+/Fc for **5** in cyclic voltammetry and the comparison with the redox inactive In^{3+} complex revealed that two iron centers are interacted each other through the inorganic ligand which gave a reduction wave observed at −0.91 mv *vs* Fc^+/Fc.

1. Introduction

Molybdenum is one of the essential trace elements in biological system for growing processes in all organisms [1]. Redox enzymes bearing molybdenum active centers can be classified into two groups: (1) FeMo protein in nitrogenase [2] and (2) molybdopterin [3,4] as a molybdenum dithiolene complex in various enzymes such as formate dehydrogenase [5], sulfite oxidase [6], DMSO (dimethyl sulfoxide) reductase [7], xanthine oxidase [8], and so on. In both type of enzymes, their reaction processes are always involved by the concerted effects from molybdenum and iron clusters [9].

In nitrogenase, P cluster [8Fe-7S] and FeMo cofactor are one of the essential inorganic cluster structures to perform an electron transfer and the catalytic reduction of nitrogen molecule to synthesize ammonia. The inorganic clusters are biologically synthesized by a conection of two cubane-type [4Fe-4S] clusters [2]. Interestingly, the presence of two cubane-units is a significant characteristic for the catalytic activity of the nitrogen molecule reduction [10]. Moreover, a cubane-type structure can be often found in biological systems such as a catalytic center of photosystem II (PSII) as a manganese-oxido-cluster [11,12]. Thus, the artificial construction of a cubane-type core is necessary to understand the biological role of the cluster systems. In this study, we developed a synthetic method to construct a metal cluster system that allows an interaction between various 3d-transition metal ions through the support of two cubane-units to evaluate how the electronic states of the 3d-transition metal centers are affected by the connection of two cubane-units which may mimic biologically relevant cubane units.

Previously, we have reported a Co(tacn) coordinated cluster system (tacn, 1,4,7-triazacyclononane), in which a fragment of metal-oxido clusters are isolated with a coordination of Co(tacn) groups which caps the peripheral of the oxido-cluster units to prevent a further condensation [13,14]. We discovered that $\{Co(tacn)\}_2Mo_3O_{12}$ unit is a useful key intermediate species for the isolation of cubane-type metal-oxido fragments. The cubane-type inorganic coordination unit has several advantages to construct biologically relevant systems. The first advantage of this new cluster systems is a role of Co(tacn) group as a terminal protecting group to prevent a formation of hydroxides or oxides by further condensation. The second advantage is the formation of hydrogen bonding networks from NH groups on tacn ligands to stabilize the cluster structures at a wide pH range in water. The hydrogen bondings allow the cluster to maintain the structure even in a

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solution state. The diamagnetic nature of Co(tacn) capping systems is additional advantage because ^{59}Co NMR spectroscopy is available. Even though the capping group is an inorganic complex, it can be considered as a compact protecting group with hydrogen bonding capability. Our aim of the terminal protecting group is to substitute a protein chain that is supporting a cubane unit in biological system.

In this study, we tried to isolate biologically relevant 3d-transition dinuclear complexes of Mn(II), Fe(III), Co(II), Ni(II), Zn(II), and In(III) bridged by two inorganic cubane-type coordination ligands. Although the dinuclear complexes of Mn(II), Co(II), Ni(II), and Zn(II) have very low solubility that hinders further purification and solution state chracterization, we successfully isolated highly soluble Fe(III) and In (III) clusters. From the X-ray analysis results, the clusters, $[(\{Co(tacn)\}_2HMo_3O_{12}\cdot H_2O)_2\{M(H_2O)_2\}]_2{}^{n+}$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Zn^{2+}, $n = 2$; $M = Fe^{3+}$, In^{3+}, n = 4), have a dinuclear center supported by two cubane-units that is parallel to the nitrogenase active center. In these cluster systems, the overall cluster framework is supported by hydrogen bonding networks from hydroxido groups on the cubane-units and the hydrogen bondings mediate an interaction between 3d transition metal centers. The iron(III) cluster shows two consecutive quasi-reversible reduction waves. The redox waves are assigned by synthesizing an In^{3+} derivative that is redox inactive, and it reveals the stepwise reductions of two Fe centers mediated by the redox from the cubane-type coordination ligand system.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from commercial sources and used without further purifications. $Fe(ClO_4)_2\cdot 6H_2O$ (99%) and $Co(ClO_4)_2\cdot 6H_2O$ (99%) were purchased from Sigma. $Fe(ClO_4)_3\cdot xH_2O$ (70%), $Co(ClO_4)_2\cdot 3H_2O$ (99%), and $Na_2MoO_4\cdot 2H_2O$ (99%) were purchased from FUJIFILM Wako Pure Chemical Corporation. $Ni(ClO_4)\cdot 6H_2O$ (95%) was purchased from KANTO KAGAKU. $Mn(ClO_4)_2\cdot 6H_2O$ was synthesized by the reaction of $MnCO_3$ (purchased from FUJIFILM Wako Pure Chemical Corporation, 90%) with 70% $HClO_4$ according to a literature [15]. The organic ligand of 1,4,7-triazacyclonone (tacn) and $[Co(tacn)(H_2O)_3](CF_3SO_3)_3$ were prepared using literature methods [16,17]. The starting materials of $[\{Co(tacn)\}_2Mo_3O_{12}](\mathbf{1})\cdot 2NaI\cdot 7H_2O$ and $[\{Co(tacn)\}_2Mo_3O_{12}](\mathbf{1})\cdot 2NaClO_4\cdot 7H_2O$ were obtained by our original synthetic procedure which was previously reported [13]. The syntheses of $[(\{Co(tacn)\}_2HMo_3O_{13}\cdot H_2O)\{M(H_2O)_2\}]_2(ClO_4)_2\cdot 26H_2O$ (M = Mn(II), Co(II), Ni(II), and Zn(II) for **4Mn**, **4Co**, **4Ni**, and **4Zn**, respectively) are shown in supporting information. Concerning clusters **4**, we only report their single crystal X-ray analysis results because the solubility is not enough for the characterization in solution states. FT-IR spectra were recorded using a Jasco FT/IR-4100 in KBr pellets. ^{59}Co NMR spectra were measured using a JEOL spectrometer (94.44 MHz) in dimethyl sulfoxide (DMSO). Electrochemical analyses were performed on SP-50 potentiostat of Bio-Logic Science Instruments with a scan rate of 100 mVs^{-1}. The working and the counter electrodes were a glassy carbon and a Pt wire, respectively. All the cyclic voltammetry measurements were measured using a 0.5 mM solution in DMSO with 0.1 M tetra-*n*-butylammonium hexafluorophosphate supporting electrolyte. The potential values monitored by an Ag^+/Ag reference electrode were corrected using the Fc^+/Fc redox couple.

2.2. Synthesis of $[(\{Co(tacn)\}_2HMo_3O_{13}\cdot H_2O)\{Fe(H_2O)_2\}]_2(ClO_4)_4\cdot 16H_2O$: (5)

To an aqueous solution of $[\{Co(tacn)\}_2Mo_3O_{12}](\mathbf{1})\cdot 2NaClO_4\cdot 7H_2O$ (61 mg, 0.05 mmol) in distilled water (1 mL) was added $Fe(ClO_4)_3\cdot H_2O$ (59 mg, 0.15 mmol). A clear red solution was immediately obtained, then the pH value of the solution was 3.1. Single-crystals of **5** suitable for X-ray analysis were obtained directly from the solutions by slow evaporation. Yield: 40 mg (60% based on Co(III)). Anal. Found (calcd for $[(\{Co(tacn)\}_2HMo_3O_{13}\cdot H_2O)\{Fe(H_2O)_2\}]_2(ClO_4)_4\cdot 16H_2O$) C, 10.52 (10.87); H, 3.91 (4.03); N, 6.20 (6.34). FT-IR spectrum (KBr disk, 1200–500 cm^{-1}): 1145 (m), 1120 (s, sh), 1108 (s), 1089 (s), 1059 (m, sh), 1027 (w), 984 (w), 884 (m), 866 (m), 846 (m), 821 (s), 810 (s), 772 (s), 635 (m), 626 (m), 598 (w), 562 (w), 555 (m), 541 (m). ^{59}Co NMR spectrum (DMSO, 94.44 MHz): 9806 ppm ($\nu_{1/2}$ = 19,432 Hz), 10,258 ppm ($\nu_{1/2}$ = 26,334 Hz).

2.3. Synthesis of $[(\{Co(tacn)\}_2HMo_3O_{13}\cdot H_2O)\{In(H_2O)_2\}]_2(ClO_4)_4\cdot 16H_2O$: (6)

To an aqueous solution of $[\{Co(tacn)\}_2Mo_3O_{12}](\mathbf{1})\cdot 2NaClO_4\cdot 7H_2O$ (61 mg, 0.05 mmol) in distilled water (1 mL) was added $In(NO_3)_3\cdot 3H_2O$ (71 mg, 0.2 mmol). After obtaining a purple color solution, $[(\{Co(tacn)\}_2HMo_3O_{12}\cdot H_2O)_2\{In(H_2O)_2\}]_2(NO_3)_4\cdot xH_2O$ was rapidly crystallized (58 mg, ~90% based on Co assuming $x = 16$). To obtain high quality single crystals, the nitrate salt was dissolved in warm water and filtered. To the clear purple solution was added $NaClO_4$ until turbid solution formed. Standing this solution overnight afforded suitable single crystals for X-ray analysis. Anal. Found (calcd for $[(\{Co(tacn)\}_2HMo_3O_{13}\cdot H_2O)\{In(H_2O)_2\}]_2(ClO_4)_4\cdot 16H_2O$) C, 10.38 (10.41); H, 3.83 (3.86); N, 6.06 (6.07). FT-IR spectrum (KBr disk, 1200–500 cm^{-1}): 1145 (m), 1120 (s, sh), 1108 (s), 1089 (s), 1059 (m, sh), 1027 (w), 984 (w), 888 (m), 863 (m), 845 (m, sh), 814 (s), 635 (m), 626 (m), 598 (w), 562 (w), 555 (m), 541 (m). ^{59}Co NMR spectrum (DMSO, 94.44 MHz): 9835 ppm ($\nu_{1/2}$ = 21,856 Hz), 11,079 ppm ($\nu_{1/2}$ = 22,623 Hz).

2.4. X-ray analysis

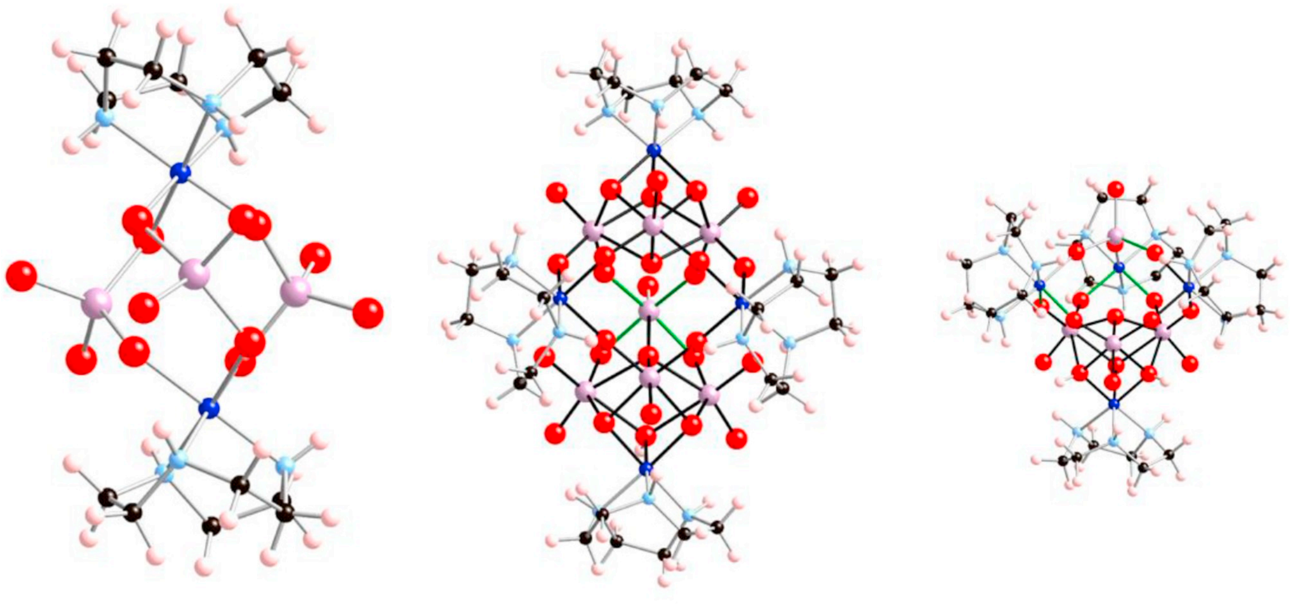
Single crystal X-ray analyses of all obtained clusters were measured at 90 K using a Bruker D8 VENTURE diffractometer with graphite monochromated Cu Kα radiation (λ = 1.54178 Å). The data reduction and absorption correction were performed using the APEX3 program [18]. The initial structures were also obtained using APEX3 software (SHELXT) [19], and then their refinements were performed using shelxle software (SHELXL-2014) [20,21]. To analyze the perchlorate anion in clusters **4**, DELU, SIMU, ISOR, and SADI restraints were utilized. In the refinements of clusters **4**, the electron densities of the bulk water regions were fitted by the SQUEEZE procedure on the PLATON program [22]. The calculated void spaces of **4Mn**, **4Co**, **4Ni**, and **4Zn** in a unit cell are 780, 761, 775, and 776 $Å^3$, respectively. Their values are consistent with a presence of 26 water molecules, per unit cell which is consistent with the number of water molecules estimated from elemental analyses in the all cases. CCDC reference numbers 1911518, 1911527, 1911526, 1911525, 1911524, and 1911516.

3. Results & discussion

3.1. Synthetic strategy

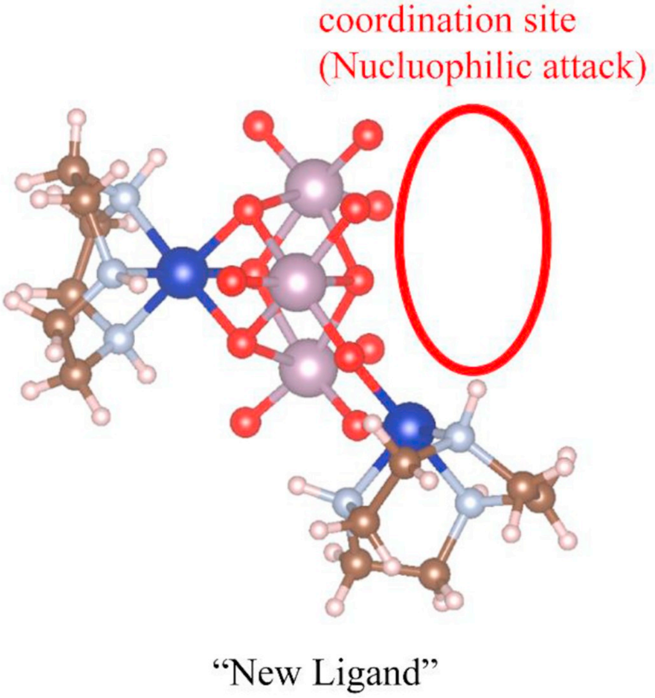
To establish a new ligand system based on a cubane-type core, we designed a polyoxometalate modified system as an inorganic coordination ligand. In an acidic condition, a mononuclear molybdate grows into a larger cluster to form polyoxometalates by an acid condensation reaction. The small intermediate clusters such as a cubane-type species are thermodynamically unstable and typical polyoxomolybdate species are rather larger such as heptamolybdates and octamolybdates [23]. We have tried to isolate an intermediate species by terminating the condensation in an earlier stage by using $Co(tacn)^{3+}$ as a terminal ligand. It allows us to isolate several new clusters such as clusters **1**, **2**, and **3** (The structures and the chemical formulas are shown in Scheme 1).

Interestingly, clusters **2** and **3** have a common structural building block composed of $\{Co(tacn)\}_2Mo_3O_{13}$ unit. In cluster **2**, two {Co



1 2 3

Scheme 1. Structures of clusters [{Co(tacn)}$_2$Mo$_3$O$_{12}$] (**1**), [{Co(tacn)}$_4$H$_2$Mo$_7$O$_{27}$]$^{2+}$ (**2**), and [{Co(tacn)}$_4$H$_3$Mo$_4$O$_{17}$]$^{5+}$ (**3**). Pink, blue, red, light blue, black, and white balls show molybdenum, cobalt, oxygen, nitrogen, carbon, and hydrogen atoms. The common structural building blocks of {Co(tacn)}$_2$Mo$_3$O$_{13}$ in clusters **2** and **3** are highlighted as black lines. The green lines show coordination bonds by the common structural building blocks which are utilized as an inorganic ligand in this study. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Scheme 2. Structure of our proposed inorganic ligand of {Co(tacn)}$_2$Mo$_3$O$_{13}$.

(tacn)}$_2$Mo$_3$O$_{13}$ units supported a heptamolybdate core, whereas cluster **3** also has {Co(tacn)}$_2$Mo$_3$O$_{13}$ unit. In these clusters, {Co (tacn)}$_2$Mo$_3$O$_{13}$ can be regarded as a common ligand (nucleophile) against the other cobalt or molybdenum metal centers. The key point of the stabilization mechanism of these clusters is a hydrogen bond formation on a Co(tacn) group to bind trinuclear molybdenum unit: it reinforces the intermediate cluster units through a hydrogen bonds between a terminal oxido-group on each of the molybdate. As a result, CoMo$_3$ group works as a rigid and bulky inorganic coordination ligand. In this research, we utilize this hybrid cubane-type inorganic ligand to support 3d-transition dinuclear metal centers (Scheme 2) that are able to electronically communicate through the redox active inorganic ligand system. The precursor of the {Co(tacn)}$_2$Mo$_3$O$_{13}$ was synthesized from cluster **1** and the Lewis acidity of 3d-transtion metal ions allows to spontaneously produce {Co(tacn)}$_2$Mo$_3$O$_{13}$ group.

3.2. Syntheses and characterizations

As described in the above section, the cubane type {Co (tacn)}$_2$Mo$_3$O$_{13}$ unit can be regarded as an inorganic ligand (Scheme 2). Therefore, we generated {Co(tacn)}$_2$Mo$_3$O$_{13}$ moiety from cluster **1** *in situ*. In these reactions, we added ten equivalents of 3d-transition metal ions such as manganese(II), iron(II), cobalt(II), nickel(II), or zinc(II) to the aqueous solution of cluster **1** (see Experimental section). The Lewis acidity of the metal ions facilitates the reaction to form the cubane-type structure of {Co(tacn)}$_2$Mo$_3$O$_{13}$ in solution. All obtained complexes (**4**) have two 3d-transition metal ions and two {Co(tacn)}$_2$Mo$_3$O$_{13}$ units which is arranged as if it sandwiched the dinuclear complex. Although manganese(II), cobalt(II), nickel(II), or zinc(II) ion is coordinated without changing the oxidation state of 3d-transition metal ions, the reaction with iron(II) gave an oxidation product under air. Therefore, the iron sandwiched cluster (**5**) was obtained from iron(III) perchlorate instead of iron(II) perchlorate. In addition, an indium(III) analogue (**6**) was also synthesized for comparison with the redox properties of the iron(III) cluster (**5**). The IR spectra of **5** and **6** clusters have almost identical patterns because it has the same molybdenum-oxido framework which gives characteristic stretching vibration within the region of 750–900 cm^{-1} as shown in Fig. 1.

The clusters **4** bearing divalent 3d-transition metal ions do not dissolve in any solvents at all. Therefore, it is difficult to recrystallize their samples leading to the high purities (see supporting information). In this paper, the low-solubility problem was resolved by the changes of the cluster charges, that is the syntheses of clusters **5** and **6**. Moreover, the high solubility allows us to elucidate the properties in solution.

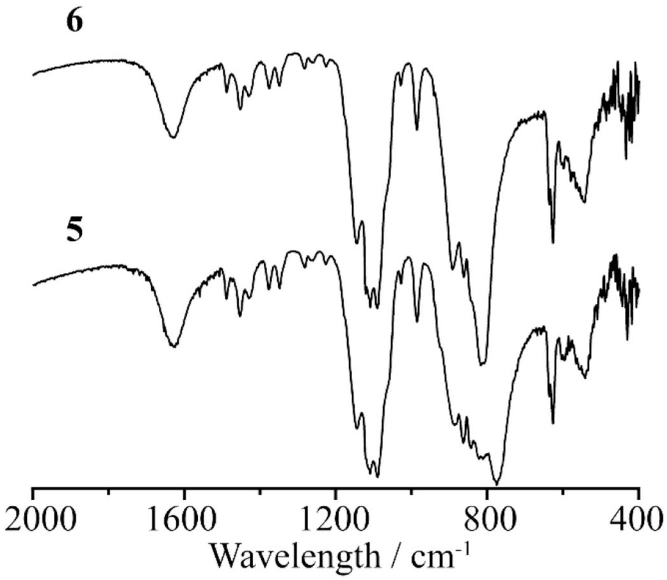


Fig. 1. IR spectra of clusters **5** and **6** (KBr disk).

3.3. X-ray structures

The structures of the obtained clusters, **4Mn**, **4Co**, **4Ni**, **4Zn**, **5**, and **6**, were obtained using single crystal X-ray analysis. The crystals of **4Mn**, **4Co**, **4Ni**, and **4Zn** clusters have isomorphous structures (Table S1). In addition, the cell volume values of their crystals are gradually shifted depending on the ionic radius of the respective 3d-transition metal ions. The cell constants of iron(III) cluster (**5**) are isomorphous to that of indium(III) one (**6**) (Table 1) and it was different from M(II) clusters because of a different oxidation state.

The overall structure of these clusters can be described that the 3d-transition dinuclear units is sandwiched by the inorganic ligands which is composed by Co(tacn)Mo_3O_3(OH) cubane-unit (Fig. 2). The Co(tacn) group sits on one apex of the cubane core, and hydroxido group sits at the opposite site. At the apex of the hydroxido group, the adjacent three faces of the cubane unit have three sets of two oxido ligands which arranges in a *cis* position. Those *cis*-oxido groups act as a ligand to a metal center, and two *cis*-oxido groups are coordinated to the 3d-transition metal ions as a bidentate ligand, and one *cis*-oxido group is coordinated to another Co(tacn) group. Thus, there are two chemically different Co(tacn) groups. One is incorporated in the cubane-unit, and the other is coordinated to the side of a cubane-unit though *cis*-oxido group.

As shown in Fig. 2, two 3d-transition metal ions are separated in the distances of 5.449(2) Å in **5** which is comparable to that of pyrazine bridged dinuclear iron(III) complex bearing a relatively strong electronic communication between the iron(III) centers [4]. The distances between the transition metal ions in **4Co**, **4Ni**, **4Zn**, and **6** are 5.659(7), 5.692(8), 5.682(7), and 5.645(1) Å, respectively. Therefore, the distance in **5** is significantly shorter than those of M(II) clusters, and it may be suitable for an electronic communication between the iron(III) centers. Their 3d-transition metal ions have two coordinated water ligands, respectively. The coordinated water ligands interact with NH groups of tacn ligands though the crystallization water molecules by forming a hydrogen bonding network.

Table 1
Crystallographic data for **5** and **6**.

	5	6
Crystal system	*Orthorhombic*	*Orthorhombic*
Space group	*P*bca	*P*bca
a/Å	23.6282(6)	23.8580(6)
b/Å	13.2867(3)	13.2867(3)
c/Å	25.7806(6)	25.7806(6)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
V, Å^3	8079.4(3)	8172.3(3)

The oxidation numbers of the incorporated 3d-transition metal ions are estimated by bond valence sum (BVS) calculations based on the bond distances obtained from the X-ray analyses. As shown in supporting information, the incorporated manganese, cobalt, nickel, and zinc ions in **4Mn**, **4Co**, **4Ni**, and **4Zn** clusters are confirmed as divalent states, whereas the indium and iron centers in **5** and **6** are obtained as trivalent oxidation states. In addition, the BVS calculations show one bridging oxygen ligand (O5) is protonated to form hydroxido-bridging ligand as shown in Fig. 2. The hydroxido ligand (OH) is directed to the interior of the cluster to form a hydrogen bonding interaction with another $\{Co(tacn)\}_2HMo_3O_{13}$ unit at an opposite side of the molecule. As shown in Fig. 2, the intramolecular hydrogen bonds have bifurcated three-centered form as one of important structural features in biological systems [24,25], and the pointing direction of hydroxide group may be rearranged by an external stimuli such as an electron injection. The two sets of intramolecular hydrogen bonds from one donor (O5) to two accepter oxygen atoms (O13 and O14) in cluster **5** have moderate distances (2.765(7) and 2.812(7) Å). Thus, the hydrogen bonding interactions stabilize the cluster structures and provide a route for an electronic interaction between 3d transition metal ions.

3.4. ^{59}Co NMR spectra

All of the obtained clusters are stabilized by $\{Co(tacn)\}^{3+}$ capping units. Therefore, ^{59}Co NMR spectroscopy is useful to consider their structures in solution state. Unfortunately, **4Mn**, **4Co**, **4Ni**, and **4Zn** clusters have poor solubility to measure the spectra in solution. On the other hand, **5** and **6** dissolve well in water or DMSO solvent, probably due to the differences of the crystal packings compared to those of **4Mn**, **4Co**, **4Ni**, and **4Zn** clusters. In particular, the ^{59}Co NMR signal of **6** is easy to detect because it is a diamagnetic species. The ^{59}Co NMR signals of **6** in DMSO are observed at 9835 and 11079 ppm (Fig. 3). Interestingly, **5** also showed a similar ^{59}Co NMR signal pattern (9806 and 10258 ppm, Fig. 3), even though it is paramagnetic species. This is because the paramagnetic iron(III) centers are separated far enough from cobalt(III) centers. These observations of two signals are consistent with the crystal structure analysis of one Co(tacn) group constructing cubane-unit and the other Co(tacn) group which is coordinated at the side of the cubane-unit. No signal from a dissociated Co (tacn) group was observed. These results from the ^{59}Co NMR measurements indicate the retention of the structures in DMSO solvent. The solution state stabilities of **5** and **6** allow us to measure their cyclic voltammograms in DMSO described in the next section.

3.5. Redox properties

As shown in the above section, the structures of **5** and **6** in solid state are maintained even in DMSO. Therefore, we measured the cyclic voltammograms in DMSO solution by using glassy carbon electrode as a working electrode. The measurements were performed with tetra-*n*-butylammonium hexafluorophosphate as a supporting electrolyte by using an Ag^+/Ag reference electrode. The cyclic voltammogram of iron (III) cluster (**5**) in DMSO shows two quasi-reversible reduction waves at -0.73 V and -1.16 V *vs* Fc^+/Fc and two irreversible reduction waves at -0.91 V and -1.39 V *vs* Fc^+/Fc (Fig. 4). In CV measurement of **6**, the later irreversible reduction waves are also observed at -0.98 V and -1.82 V *vs* Fc^+/Fc in DMSO solution. Thus, the irreversible reduction wave at –0.98V is related to a reduction of $\{Co(tacn)\}_2HMo_3O_{13}$ cubane units, because the indium(III) centers are redox inactive. Therefore, the former two quasi reversible reduction waves of **5** are assigned to the

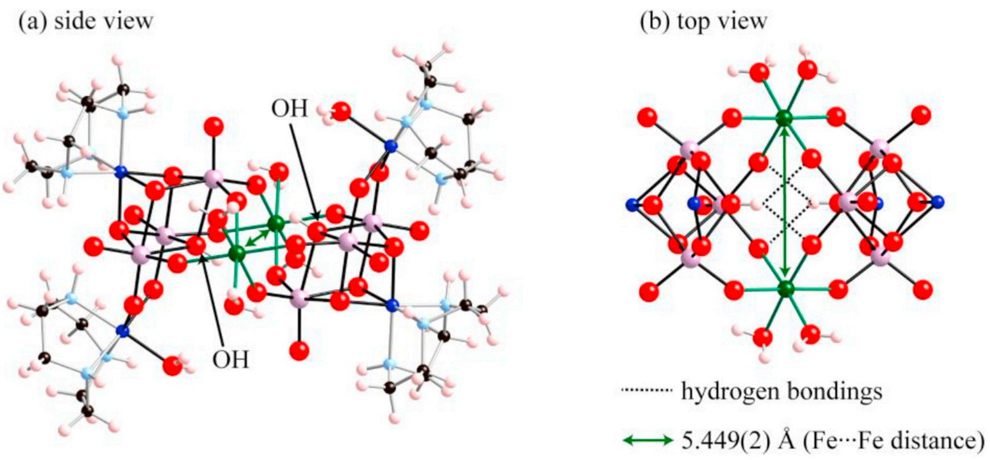


Fig. 2. X-ray structure of cluster **5**. Blue, pink, green, red, black, and white balls show cobalt, molybdenum, iron, oxygen, carbon, and hydrogen atoms, respectively. In the top view (b), the tacn and water ligands on Co(III) centers are omitted for clarity. All the obtained clusters composed of common frameworks. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

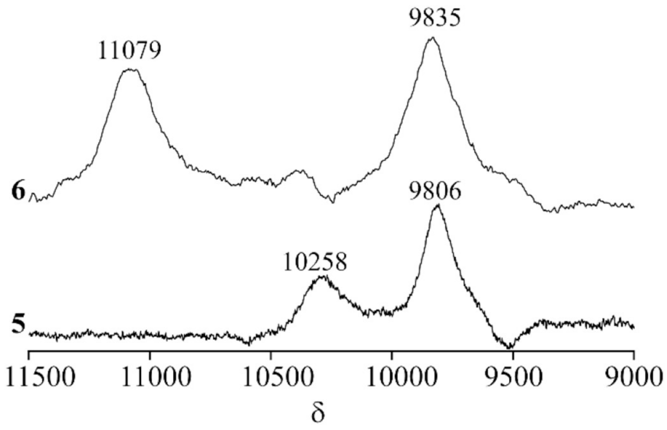


Fig. 3. ^{59}Co NMR spectra of clusters **5** and **6** in DMSO.

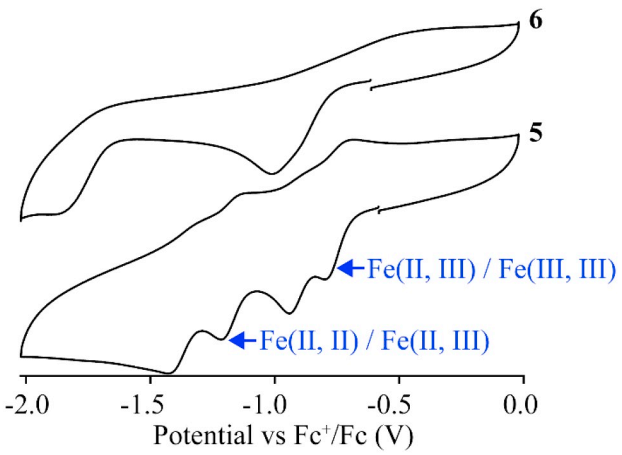


Fig. 4. Cyclic voltammograms of clusters **5** and **6** in DMSO with 0.1 M $TBAPF_6$. The working electrode used is a glassy carbon.

reductions of iron(III) to iron(II). Although the iron(III) centers are centrosymmetric and quite far each other, two consecutive reduction reactions from iron(III) to iron(II) are observed. These experimental results imply that the iron(III) centers have electronic interaction through the hydrogen bonding networks by OH bridging ligands on the $\{Co(tacn)\}_2HMo_3O_{13}$ cubane frameworks.

Such long-distance electronic communication between transition metal centers has been usually studied using organic conjugated ligands. For example, as reported by Taube and Creutz groups, transition metal centers can interact each other *via* π electron organic ligands such as bipyridine or pyrazine [26]. Very recently, Kubiak et al. reported a hydrogen bonding assisted electronic communication on π electron organic ligands between ruthenium centers [27,28]. Our hydrogen-bond-assisted electronic communication on $\{Co(tacn)\}_2HMo_3O_{13}$ cubane inorganic frameworks is a new possibility to construct a long-distance interaction.

4. Conclusion

We have designed a new artificial system to support 3d-transition dinuclear complexes by a redox active coordination ligands to afford a series of complexes, $[(\{Co(tacn)\}_2HMo_3O_{13}{\cdot}H_2O)\{M(H_2O)_2\}]_2^{n+}$ (M = Mn^{2+} (**4Mn**), Co^{2+} (**4Co**), Ni^{2+} (**4Ni**), Zn^{2+} (**4Zn**), n = 2; M = Fe^{3+} (**5**), In^{3+} (**6**), n = 4). Although clusters **4** do not have enough solubility to consider the solution state properties, the high solubility of **5** and **6** allowed us to perform their characterization in solution state. The dinuclear units are sandwiched by $CoMo_3O_3(OH)$ cubane ligands and each of which provides two sets of *cis*-oxido ligands to occupy coordination sites of the 3d-transition ions leaving two coordination sites for the coordination of water. The unique features of these complexes are an interesting separation distance of a dinuclear center with hydrogen bondings and redox active ligands. The electrochemical study of the iron complex (**5**) reveals consecutive three step reduction waves. The stepwise reductions are assisted by the bifurcated hydrogen bonding networks based on the redox active inorganic cubane ligand $CoMo_3O_3(OH)$ as one of biologically relevant cluster frameworks. This study suggests the new way to study the role of biologically important cubane cluster that is generated from water soluble precursor $[\{Co(tacn)\}_2Mo_3O_{12}]$(**1**) by using our Co(tacn) capping strategy. An interaction path through the two cubane cores is interesting in terms of constructing a redox active scaffold that is reminiscent of the FeMo cofactor.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jinorgbio.2019.110821.

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