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Formation of 1D and 3D Coordination Polymers in the Solid State Induced by Mechanochemical and Annealing Treatments: Bis(3-cyano-pentane-2,4-dionato) Metal Complexes

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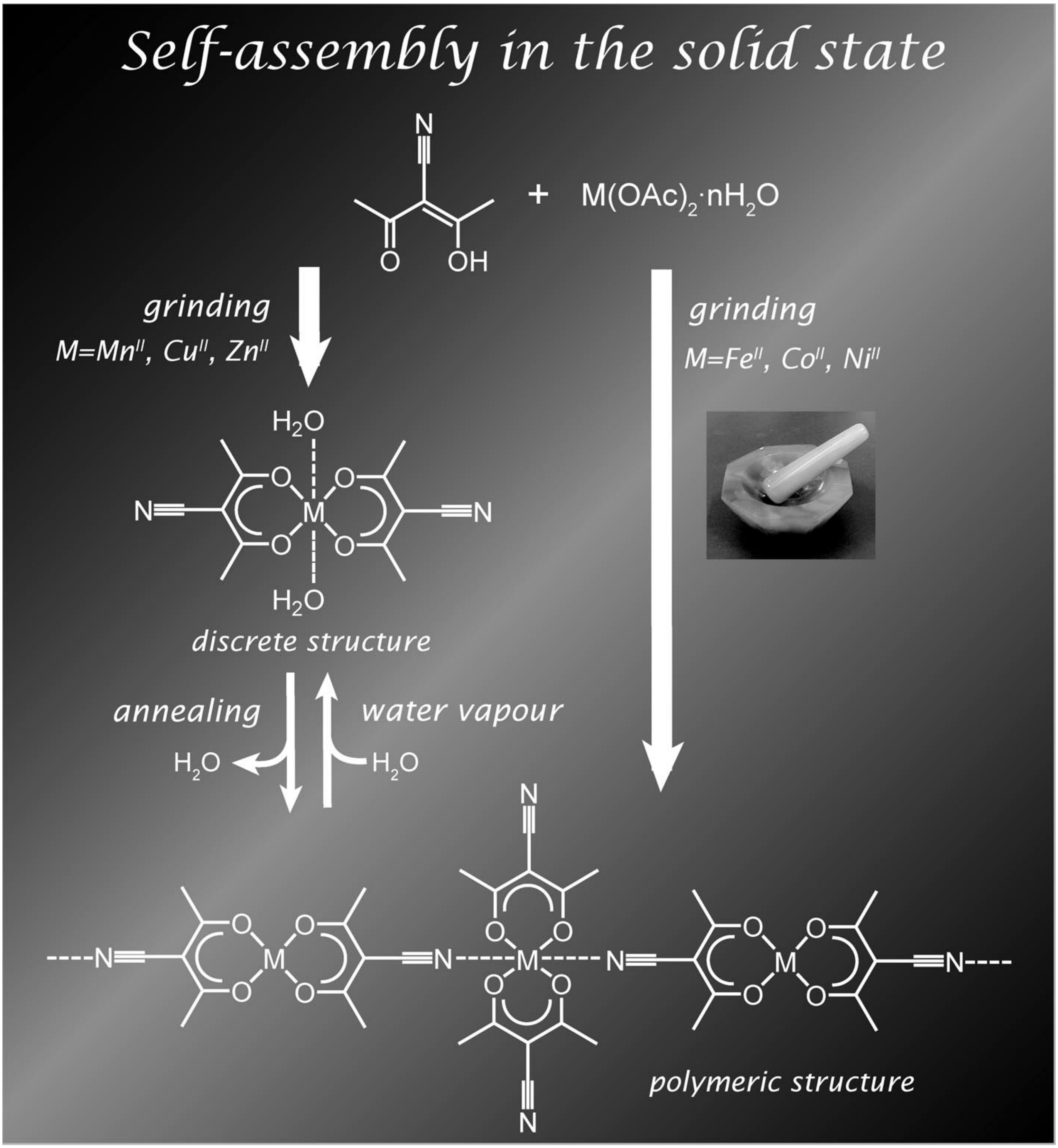

Abstract: Bis(3-cyano-pentane-2,4-dionato) (CNacac) metal complex, [M(CNacac)$_2$], which acts as both a metal-ion-like and a ligand-like building unit, forms supramolecular structures by self-assembly. Co-grinding of the metal acetates of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} with CNacacH formed a CNacac complex in all cases: mononuclear complex was formed in the cases of Mn^{II}, Cu^{II} and Zn^{II}, whereas polymeric ones were formed in the cases of Fe^{II}, Co^{II} and Ni^{II}. Subsequent annealing converted the mononuclear complexes of Mn^{II}, Cu^{II} and Zn^{II} to their corresponding polymers as a result of dehydration of the mononuclear complexes. The resultant Mn^{II}, Fe^{II}, Co^{II}, Ni^{II} and Zn^{II} polymeric complexes had a common 3D structure with high thermal stability. In the case of Cu^{II}, a 1D polymer was obtained. The Mn^{II}, Cu^{II} and Zn^{II} polymeric complexes returned to their original mononuclear complexes on exposure to water vapour but they reverted to the polymeric complexes by re-annealing. Co-grinding of metal chlorides with CNacacH and annealing of the mononuclear CNacac complexes prepared from solution reactions were also examined for comparison. [Mn(CNacac)$_2$(H$_2$O)$_2$], [M(CNacac)$_2$(H$_2$O)] (M = Cu^{II} and Zn^{II}) and [M(CNacac)$_2$]$_\infty$ (M = Mn^{II}, Fe^{II} and Zn^{II}) are new compounds, which clearly indicated the power of the combined mechanochemical/annealing method for the synthesis of varied metal coordination complexes.

Keywords: annealing treatment · coordination polymers · mechanochemical reactions · self-assembly · solid-state reactions

Introduction

Self-assembly of simple building units is a general and useful approach for constructing supramolecular materials. For example, careful selection and combination of metal ions and ligands can produce coordination polymers with an infinite multidimensional structure[1] or discrete large assemblies with an fascinating structure, such as a cage and a circle.[2] In many cases, such self-assembly processes are realized in solution. In contrast, solid-state reactions are currently attracting attention as novel and unique synthetic techniques. A representative example is the mechanochemical method, a direct co-grinding of solid-state reactants. This method has several advantages over the conventional solution methods: 1) there is no waste solvent generated, 2) the method is easily manipulated, 3) there are usually high yields and 4) the method sometimes gives products that are different from those produced by solution reactions.[3] However, the application of such a mechanochemical method to the synthesis of supramolecular materials, especially coordination polymers, is still limited and its versatility is unknown.[4] Thus, it is worth the challenge to investigate the applicability of the mechanochemical method to the synthesis of coordination polymers and to seek auxiliary methods that cover the insufficient nature of the synthetic technique. In this study, we investigated mechanochemical reactions with the help of annealing treatment. Annealing treatment, a method to keep compounds at high temperature for a while, is often effective in encouraging crystallization and in obtaining thermodynamically stable compounds.[3i,4d,5]

In this study, we chose [M(CNacac)$_2$]$_\infty$ as the target coordination polymer, which has a multidimensional continuous structure with a building unit of bis(3-cyano-pentane-2,4-dionato) (CNacac) metal complex, [M(CNacac)$_2$] (Figure 1). [M(CNacac)$_2$] is known as a useful precursor for the formation of supramolecular assemblies in solution. This complex can work as a linear ligand by using its two cyano groups. For example, [Cu(CNacac)$_2$] forms a 1D coordination polymer with Ag^{I} ions.[6] On the other hand, [M(CNacac)$_2$] can accept additional ligands at the axial sites of the metal centre so that it also works as a metal-ion-like unit.[7] Therefore, [M(CNacac)$_2$], which has both ligand-like and metal-ion-like connection abilities, must form supramolecular structures by self-assembly. In fact, [Co(CNacac)$_2$] and [Cu(CNacac)$_2$] assemble in solution to form 3D and a 1D continuous supramolecular structures, [Co(CNacac)$_2$]$_\infty$ (**Co-3D**)[8] and [Cu(CNacac)$_2$]$_\infty$ (**Cu-1D**),[9] respectively (Figure 1). In **Co-3D**, the two axial sites of [Co(CNacac)$_2$] are linked by the CN groups of the two adjacent [Co(CNacac)$_2$] units, whereas only one axial site is used in the case of **Cu-1D**. [Ni(CNacac)$_2$]$_\infty$ (**Ni-3D**), which has the same 3D structure as that of **Co-3D**, was also reported. However, it was obtained as a mixture with Na[Ni(CNacac)$_3$]·EtOH in ethanol.[8] In contrast, formation of [M(CNacac)$_2$]$_\infty$ (M = Mn^{II}, Fe^{II} and Zn^{II}) in solution was not known. We have applied, for the first time, the solid-state reaction methods and have succeeded in synthesizing new coordination polymers, [M(CNacac)$_2$]$_\infty$ (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}). In the case of Ni^{II}, **Ni-3D** was solely ob-

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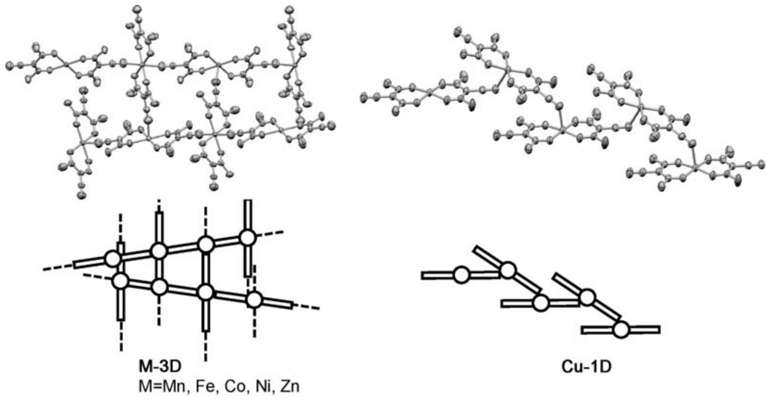


Figure 1. Crystal structures and schematic structural models of **Co-3D** and **Cu-1D** composed of [M(CNacac)$_2$] (M = Co^{II}, Cu^{II}).

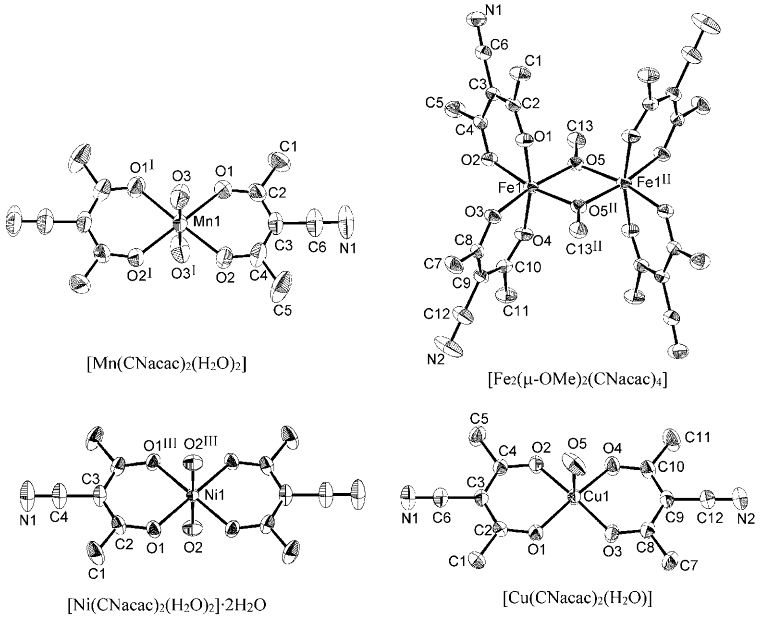
tained from our solid-state reaction. The role of grinding and annealing treatments will be discussed.

Results and Discussion

Preparation of CNacac metal complexes in solution: To obtain information on the molecular structure, the following CNacac complexes were prepared by solution methods and their thermogravimetry (TG), IR and X-ray powder diffraction (XRPD) spectra were measured. The known compounds, [Co^{II}(CNacac)$_2$]$_\infty$ (**Co-3D**), [Cu^{II}(CNacac)$_2$]$_\infty$ (**Cu-1D**) and [Zn^{II}(CNacac)$_2$(H$_2$O)$_2$]·2 H$_2$O, were synthesized according to the reported procedures.[8,9,10] Unknown CNacac complexes of Mn^{II}, Fe^{II}, Ni^{II} and Cu^{II}, synthesized from the reaction of respective metal acetates with CNacacH in a methanol/water mixed solution were found to be new complexes, [Mn(CNacac)$_2$(H$_2$O)$_2$], [Fe$_2$(μ-OMe)$_2$(CNacac)$_4$], [Ni(CNacac)$_2$(H$_2$O)$_2$]·2 H$_2$O and [Cu(CNacac)$_2$(H$_2$O)]. In the case of Fe^{II}, Fe^{II} in Mohr's salt was oxidized to form a dinuclear Fe^{III} complex [Fe$_2$(μ-OMe)$_2$(CNacac)$_4$]. Neither [Fe(CNacac)$_2$]$_\infty$ nor [Fe(CNacac)$_2$(H$_2$O)$_n$] (n = 1, 2) were obtained. For Ni^{II} and Cu^{II}, although their polymeric structures were already known, new mononuclear hydrated complexes were obtained in our preparation. We also obtained [Mn(CNacac)$_2$(H$_2$O)$_2$], [Ni(CNacac)$_2$(H$_2$O)$_2$]·2 H$_2$O, [Cu(CNacac)$_2$(H$_2$O)] and [Zn^{II}(CNacac)$_2$(H$_2$O)$_2$]·2 H$_2$O from the reaction of respective metal chlorides and CNacacH in a methanol/water mixed solution.

The molecular structures of the new complexes determined by the single-crystal X-ray diffraction are shown in Figure 2. From solution reactions, mononuclear structures were obtained in the cases of Mn^{II}, Fe^{III}, Ni^{II}, Cu^{II} and Zn^{II}, whereas polymeric structures were obtained in the cases of Co^{II} and Cu^{II}. The formation of the hydrated mononuclear complexes, in which aquo ligands occupy the axial coordination sites, appears to compete with the formation of a polymeric structure. The results of their TG measurements are shown in Figure S1 (Supporting Information). In all hydrated complexes, one-step decomposition was observed, which must correspond to the release of one or two aquo ligand(s) and lattice water.

Solid-state reactions of metal acetates with CNacacH: We performed mechanochemical reactions of metal (Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}) acetates with CNacacH by using a pestle and mortar (Scheme 1). After five minutes of grinding the mixture, which contained metal acetate and CNacacH in the ratio of 1:2, the smell of acetic acid was detected in all



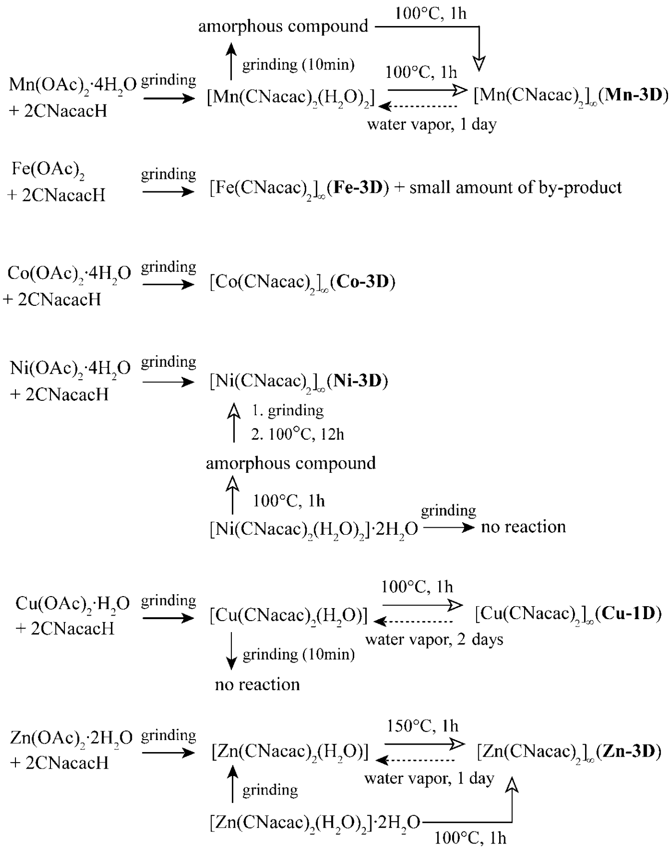
[Mn(CNacac)$_2$(H$_2$O)$_2$]

[Fe$_2$(μ-OMe)$_2$(CNacac)$_4$]

[Ni(CNacac)$_2$(H$_2$O)$_2$]·2H$_2$O

[Cu(CNacac)$_2$(H$_2$O)]

Figure 2. ORTEP representations of new complexes synthesized by solution methods. Hydrogen atoms are omitted for clarity and displacement ellipsoids are drawn at the 50 % probability level. The Mn^{II}, Fe^{III} and Ni^{II} complexes reside in a special position and the molecules are respectively related by the symmetry code; I: $1-x, y, 3/2-z$; II: $1-x, -y, 2-z$; III: $2-x, 1-y, 2-z$.



Scheme 1. Summary of the solid-state reactions investigated in this report. Grinding was done for 5 min unless otherwise noted.

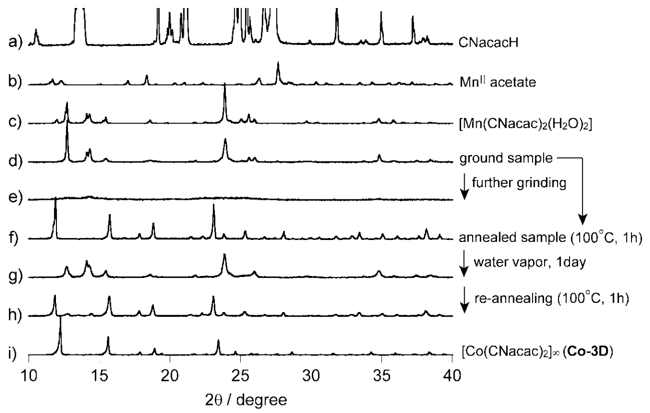


Figure 3. XRPD patterns of a) CNacacH; b) $Mn(OAc)_2$•4 H_2O; c) [Mn-$(CNacac)_2(H_2O)_2$] prepared in a solution; d) a mixture of Mn-$(OAc)_2$•4 H_2O and CNacacH after 5 min grinding; e) sample (d) after 10 min more grinding; f) sample (d) after annealing; g) sample (f) exposed to water vapour for 1 day; h) sample (g) after re-annealing at 100 °C for 1 h; i) **Co-3D** prepared by a solution method.

Table 1. Cell parameters of **M-3D** calculated from their XRPD patterns.

M-3D	*a* [Å]	*c* [Å]	*V* [Å^3]
Mn-3D	14.913 (6)	6.640 (6)	1477 (2)
Fe-3D	14.684 (6)	6.769 (7)	1459 (2)
Co-3D	14.445 (3)	6.808 (4)	1420 (1)
Co-3D[a]	14.444 (1)	6.832 (2)	1423.9 (7)
Ni-3D	14.39 (3)	6.78 (6)	1403 (15)
Zn-3D	14.508 (3)	6.838 (5)	1439 (1)

[a] Cited from the single-crystal X-ray diffraction study.[8]

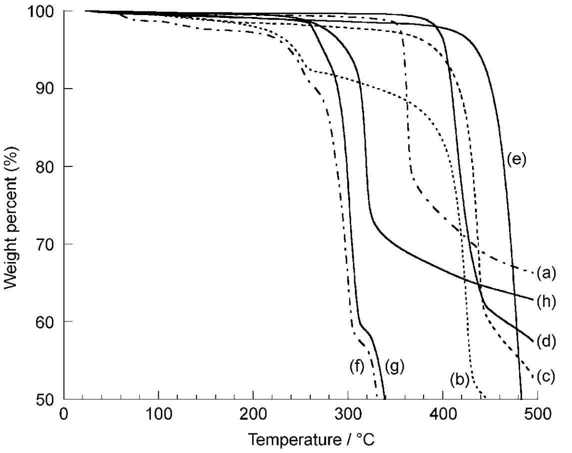


Figure 4. TG curves of a) **Mn-3D**, b) **Fe-3D**, c) **Co-3D** (mechanochemical), d) **Co-3D** (solution), e) **Ni-3D**, f) **Cu-1D** (mechanochemical), g) **Cu-1D** (solution) and h) **Zn-3D**.

cases and a colour change was observed in all cases except for the case of Zn^{II}.

During the grinding of the mixture of $Mn(OAc)_2$•4 H_2O and CNacacH, the colour of the reactant changed from pale pink to pale yellow. The XRPD patterns of the ground sample together with that of CNacacH, $Mn(OAc)_2$•4 H_2O and [$Mn(CNacac)_2(H_2O)_2$] are shown in Figure 3. The pattern of the ground sample agreed with that of [Mn-$(CNacac)_2(H_2O)_2$] prepared from solution. The TG curves of the ground sample and [$Mn(CNacac)_2(H_2O)_2$] were very similar to each other (see Figure S1 in the Supporting Information). These findings indicate the ground sample to be [$Mn(CNacac)_2(H_2O)_2$]. Ten minutes of further grinding of [$Mn(CNacac)_2(H_2O)_2$] made the sample amorphous. In contrast, annealing of [$Mn(CNacac)_2(H_2O)_2$] at 100 °C for 1 h exhibited a XRPD pattern very similar to that of **Co-3D** (Figure 3f). The assignment of its diffraction peaks based on the Miller indices of **Co-3D** was possible and the cell parameters thus calculated are listed in Table 1. The TG curve of the annealed sample was also similar to that of **Co-3D**, though its thermal decomposition temperature was somewhat lower (Figure 4a). This must be due to the absence of the crystal-field stabilization energy in the d^5 high-spin state of Mn^{II}. These results indicate that [$Mn(CNacac)_2$]$_\infty$ (**Mn-3D**), isomorphic to **Co-3D**, was formed from [Mn-$(CNacac)_2(H_2O)_2$] by the annealing treatment. The annealing treatment of the amorphous sample that was obtained from the further grinding of [$Mn(CNacac)_2(H_2O)_2$] also afforded **Mn-3D**.

During this investigation, we found that **Mn-3D**, which has a polymeric structure, gradually returned to [Mn-$(CNacac)_2(H_2O)_2$], which has a mononuclear structure, on exposure to water vapour in one day. The XRPD pattern of the sample exposed to water vapour matched with that of $[Mn(CNacac)_2(H_2O)_2]$ (Figure 3g,c). Moreover, the decomposed sample $[Mn(CNacac)_2(H_2O)_2]$ returned to the polymeric structure **Mn-3D** by re-annealing at 100 °C for 1 h (Figure 3h).

Grinding of brown $Fe(OAc)_2$ with CNacacH afforded a light-brown powder. XRPD patterns of the ground sample, $Fe(OAc)_2$ and **Co-3D** are shown in Figure 5. Most peaks of the ground sample reasonably agreed with the main peaks of **Co-3D.** Cell parameters calculated are listed in Table 1. The TG curve of the ground sample showed a two-step weight loss: approximately 7 % of loss around 250 °C and approximately 40 % of loss around 400 °C (Figure 4b). The small weight loss around 250 °C may come from a byproduct attributed to a Fe^{III} species, which was not detectable in the XRPD pattern. In contrast, the large weight loss around 400 °C is very similar to that of **Co-3D**. These results indicate the formation of $[Fe(CNacac)_2]_\infty$ (**Fe-3D**).

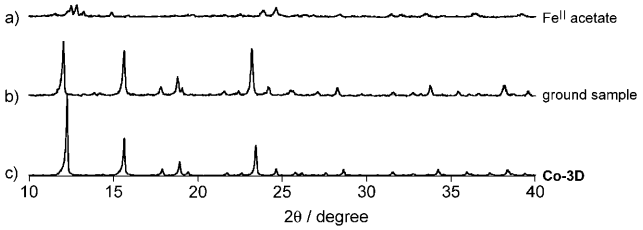


Figure 5. XRPD patterns of a) $Fe(OAc)_2$, b) a mixture of $Fe(OAc)_2$ and CNacacH after 5 min grinding and c) **Co-3D**.

Grindings of $Co(OAc)_2{\cdot}4H_2O$ and $Ni(OAc)_2{\cdot}4H_2O$ with CNacacH were also examined, and a colour change from bright pink to dark pink and that from green to blue were observed, respectively. XRPD patterns of both ground samples were similar to each other and they were consistent with that of **Co-3D** prepared by the solution method (Figure 6). Cell parameters calculated from the XRPD patterns are listed in Table 1. TG curves of both samples and **Co-3D** were also similar to each other and they were thermally very stable up to approximately 400 °C (Figure 4c,e). These results indicate that **Co-3D** and **Ni-3D** were formed in the mechanochemical reaction. In our mechanochemical reaction, **Ni-3D** was solely obtained, whereas it was reported that a mixture of **Ni-3D** and $Na[Ni(CNacac)_3]{\cdot}EtOH$ was obtained from an ethanol solution.[8] Five minutes grinding of $[Ni(CNacac)_2(H_2O)_2]{\cdot}2H_2O$, which was obtained in our preparation by using a methanol/water mixed solution, induced no reaction, and resulted in broadened XRPD peaks.

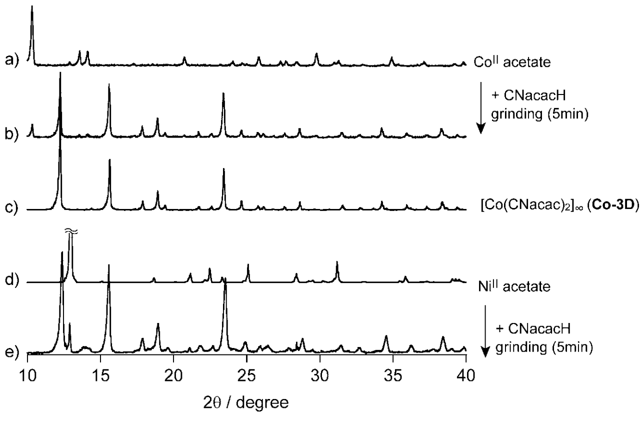


Figure 6. XRPD patterns of a) $Co(OAc)_2{\cdot}4H_2O$, b) a mixture of $Co(OAc)_2{\cdot}4H_2O$ and CNacacH after 5 min grinding c) **Co-3D** obtained by the solution method, d) $Ni(OAc)_2{\cdot}4H_2O$ and e) a mixture of $Ni(OAc)_2{\cdot}4H_2O$ and CNacacH after 5 min grinding.

Grinding of $Cu(OAc)_2{\cdot}H_2O$ with CNacacH afforded a blue powder. Its XRPD pattern matched with that of $[Cu(CNacac)_2(H_2O)]$ prepared by the solution method (Figure 7b,d). Ten minutes more grinding induced no reaction to broaden the XRPD peaks somewhat. In contrast, the annealing treatment of the ground sample at 100 °C for 1 h afforded a bright blue powder. The XRPD pattern of the annealed sample was consistent with that of **Cu-1D** obtained from the solution reaction (Figure 7e). TG curves of both samples were also similar to each other (Figure 4f,g). Moreover, we found that polymeric **Cu-1D** gradually returned to $[Cu(CNacac)_2(H_2O)]$, which has a mononuclear structure, on exposure to water vapour in two days as shown in the case of **Mn-3D**. The XRPD pattern of the sample exposed to water vapour well matched with that of $[Cu(CNacac)_2(H_2O)]$ (Figure 7f). This structural change is probably induced by the coordination of a water molecule to an axial site of **Cu-1D**, and this coordination decomposes the polymeric structure. The decomposed sample $[Cu(CNacac)_2(H_2O)]$ returned to the polymeric **Cu-1D** by re-annealing at 100 °C for 1 h (Figure 7g). Thus, the process is reversible.

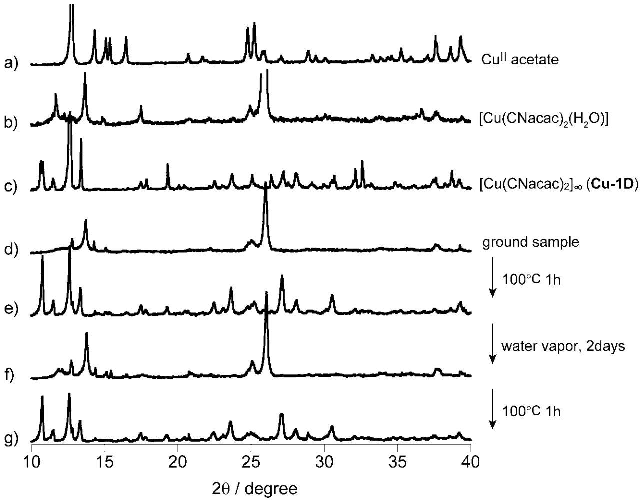


Figure 7. XRPD patterns of a) $Cu(OAc)_2{\cdot}H_2O$; b) $[Cu(CNacac)_2(H_2O)]$; c) **Cu-1D**; d) a mixture of $Cu(OAc)_2{\cdot}H_2O$ and CNacacH after 5 min grinding; e) sample (d) after annealing at 100 °C for 1 h; f) sample (e) exposed to water vapour for 2 days; g) sample (e) after re-annealing at 100 °C for 1 h.

From the grinding of $Zn(OAc)_2{\cdot}2H_2O$ with CNacacH, a white powder was obtained. Its XRPD pattern was different from that of $[Zn(CNacac)_2(H_2O)_2]{\cdot}2H_2O$ prepared by the solution method and that of **Co-3D** (Figure 8c,f). We succeeded in obtaining single crystals of the white powder by slowly evaporating the solution of the white powder in methanol and in determining its crystal structure by the single-crystal X-ray diffraction method. The crystal contains $[Zn(CNacac)_2(H_2O)]$ in which Zn^{II} has a trigonal bipyramidal form coordinated by two twisted CNacacs and a water molecule as shown in Figure 9. The XRPD pattern simulated based on the crystal structure matched with that of the ground sample (Figure 8b,c). The TG measurement of this ground sample showed about 5% weight loss around 100 °C, which is consistent with the release of one water molecule from $[Zn(CNacac)_2(H_2O)]$ (see Figure S1 in the Supporting Information). Grinding of $[Zn(CNacac)_2(H_2O)_2]{\cdot}2H_2O$, which was obtained by the solution method, also afforded a XRPD pattern similar to that of $[Zn(CNacac)_2(H_2O)]$ (Figure 8g).

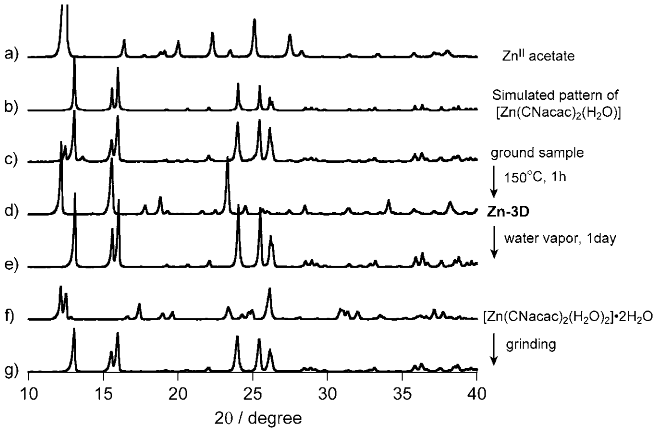


Figure 8. XRPD patterns of a) $Zn(OAc)_2{\cdot}2H_2O$, b) simulated pattern of $[Zn(CNacac)_2(H_2O)]$, c) a mixture of $Zn(OAc)_2{\cdot}2H_2O$ and CNacacH after 5 min grinding, d) **Zn-3D** obtained by annealing, e) **Zn-3D** exposed to water vapour for 1 day, f) $[Zn(CNacac)_2(H_2O)_2]{\cdot}2H_2O$ and g) $[Zn(CNacac)_2(H_2O)_2]{\cdot}2H_2O$ after 5 min grinding.

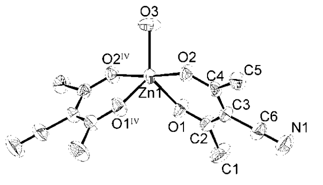


Figure 9. ORTEP representation of $[Zn(CNacac)_2(H_2O)]$ with displace ellipsoids drawn at the 50% probability level (symmetry code; IV: $1/2-x$, $1/2-y$,z).

Annealing treatment of $[Zn(CNacac)_2(H_2O)]$ was examined. Although no reaction was induced by annealing at 100 °C for 1 h, annealing at 150 °C for 1 h afforded a compound with a very sharp XRPD pattern similar to that of **Co-3D** (Figure 8d). This finding suggests that $[Zn(CNacac)_2]_\infty$ (**Zn-3D**), isomorphic to **Co-3D**, was formed in the solid-state reaction. Cell parameters calculated from this XRPD pattern are listed in Table 1. The TG curve of this sample has features similar to those of other 3D complexes, whereas the thermal decomposition temperature is lower (Figure 4h). It is likely that the low thermal stability comes from the absence of the crystal field stabilization due to the d^{10} electronic configuration of Zn^{II}. As shown in the case of **Mn-3D** and **Cu-1D**, $[Zn(CNacac)_2]_\infty$ (**Zn-3D**) also responded to water vapour. After exposure to water vapour for one day, $[Zn(CNacac)_2]_\infty$ (**Zn-3D**) was converted to $[Zn(CNacac)_2(H_2O)]$ (Figure 8e). This mononuclear compound returned to the polymeric structure by re-annealing at 150 °C for 1 h.

On the whole, the mechanochemical method in combination with the annealing treatment was effective in the formation of the coordination polymers. The role of the mechanochemical reaction and that of the annealing treatment were different. CNacac complexes were obtained from the mechanochemical method but they did not always form polymeric structures. Many of them were mononuclear hydrated complexes. These results were similar to those obtained in the solution reaction. The annealing treatment following the mechanochemical reaction changed the mononuclear complexes to polymeric ones. In this process, the dehydration from the mononuclear complexes occurs and the structural conversion proceeds as shown below.

Annealing treatments of mononuclear complexes: The annealing treatments changed the mononuclear structures of $[Mn(CNacac)_2(H_2O)_2]$, $[Cu(CNacac)_2(H_2O)]$ and $[Zn(CNacac)_2(H_2O)]$, which were mechanochemically obtained, to the polymeric structures of **Mn-3D**, **Cu-1D** and **Zn-3D**, respectively. The annealing process was clearly effective for the conversion from the mononuclear to the polymeric structures. To confirm the effect of the annealing, we annealed microcrystalline mononuclear complexes prepared by the solution methods, $[Mn(CNacac)_2(H_2O)_2]$, $[Ni(CNacac)_2(H_2O)_2]{\cdot}2H_2O$, $[Cu(CNacac)_2(H_2O)]$ and $[Zn(CNacac)_2(H_2O)_2]{\cdot}2H_2O$, at 100 °C for 1 h without grinding. In the annealing processes, dehydration was observed around 100 °C for all the samples, as confirmed by TG and IR (see Figures S1 and S2 in the Supporting Information). XRPD patterns of the samples annealed are shown in Figure 10. In the cases of Mn^{II}, Cu^{II} and Zn^{II}, the XRPD patterns changed to those of the respective polymeric structures.

In the case of Ni^{II}, the observations were complicated. The annealing treatment of $[Ni(CNacac)_2(H_2O)_2]{\cdot}2H_2O$, which was blue, afforded an unknown green amorphous compound. The green powder turned to an unknown blue amorphous powder after 5 min of grinding, and subsequent annealing of the blue powder at 100 °C for 12 h finally provided **Ni-3D**, the crystallinity of which was low. The details

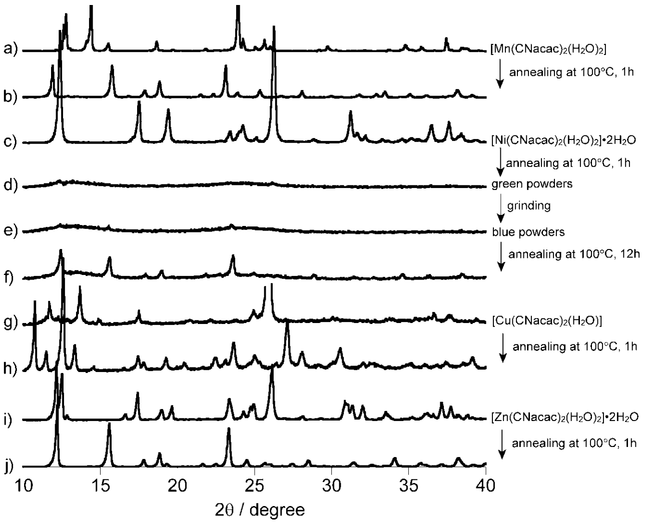


Figure 10. XRPD patterns of a) $[Mn(CNacac)_2(H_2O)_2]$; b) sample (a) after annealing at 100 °C for 1 h; c) $[Ni(CNacac)_2(H_2O)_2]\cdot 2H_2O$; d) sample (c) after annealing at 100 °C for 1 h; e) sample (d) after 5 min grinding; f) sample (e) after annealing at 100 °C for 12 h; g) $[Cu(CNacac)_2(H_2O)]$; h) sample (g) after annealing at 100 °C for 1 h; i) $[Zn(CNacac)_2(H_2O)_2]\cdot 2H_2O$; j) sample (i) after annealing at 100 °C 1 h.

of the reactions are not clear but the coordination form of Ni^{II} might have changed from an octahedral to a square-planar form in the dehydration of the first annealing process.[11]

These findings indicate that the dehydration is a key process. The generation of vacant axial coordinating sites is a prerequisite for the structural conversion from the hydrated bis-CNacac complexes to the polymeric ones. It is known that heating is effective to release the aquo ligands at axial sites of bis(β-diketonato) metal complexes and to generate vacant axial sites.[11] This heating effect works well in our case and helps the formation of polymeric structures. Note that annealing of a mixture of metal acetate and CNacacH without grinding generates neither CNacac complexes nor polymeric structures because the sublimation of CNacacH occurs around 40 °C.

Mechanochemical reactions of metal chlorides with CNacacH: In the solution reaction, the formation of a CNacac complex starts with a solvated metal ion. The influence of the counter anion in the metal salt used as a starting material is not expected to be so large in the reaction. In fact, solution reactions with metal chlorides produced the same mononuclear Mn^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes that were prepared by using the metal acetates. In contrast, in the solid-state reactions described above, formation of acetic acid is always detected on top of the CNacac complexes, and hence a direct interaction between the acetate ion and CNacacH must be involved. Therefore, the counter anion is considered to play an important part. To examine this point, we investigated the mechanochemical reactions of metal chloride with CNacacH in each case of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}. Similar to the cases of the metal acetates, XRPD measurements of the ground samples following five minutes grinding and their original metal chlorides were carried out. As shown in Figure S3 (Supporting Information), no reaction proceeded except for the case of Cu^{II} chloride in which an unknown green powder different from blue Cu^{II} chloride was obtained. In all cases, ten more minutes grinding was also performed, which only resulted in a broadening of the XRPD peaks. These findings indicate that the selection of the counter anion in the starting metal salt is an important factor for the mechanochemical reaction. In fact, most preceded works on mechanochemical syntheses were carried out by using metal acetates.[4a–d] Although the mechanism of these mechanochemical reactions is still unknown and detailed discussion is difficult, it is clear that there is a large difference between the standard Gibbs energy of formation ($\Delta_f G^\circ_{298}$) of acetic acid ($-389.9\,kJ\,mol^{-1}$) and that of hydrochloric acid ($-95.3\,kJ\,mol^{-1}$). These values suggest that the formation of acetic acid is more advantageous than that of hydrochloric acid. The formation of such a conjugated acid is a part of the whole reaction process so that the thermodynamic factor may contribute to the superiority of the acetates observed here.

Conclusion

Co-grinding of the metal acetates of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} with CNacacH afforded mononuclear hydrated CNacac complexes, $[Mn(CNacac)_2(H_2O)_2]$, $[Cu(CNacac)_2(H_2O)]$ and $[Zn(CNacac)_2(H_2O)]$, and polymeric CNacac complexes, $[Fe(CNacac)_2]_\infty$ (**Fe-3D**), $[Co(CNacac)_2]_\infty$ (**Co-3D**) and $[Ni(CNacac)_2]_\infty$ (**Ni-3D**). Remarkably, annealing treatment of the hydrated complexes of Mn^{II}, Cu^{II} and Zn^{II} converted the mononuclear structures to polymeric ones by removing the aquo ligands at the axial sites. The resultant polymeric complexes, **Fe-3D**, **Co-3D**, **Ni-3D**, $[Mn(CNacac)_2]_\infty$ (**Mn-3D**) and $[Zn(CNacac)_2]_\infty$ (**Zn-3D**), have a common 3D network structure, whereas the Cu^{II} polymer $[Cu(CNacac)_2]_\infty$ (**Cu-1D**) has a 1D structure. $[Mn(CNacac)_2(H_2O)_2]$, $[Cu(CNacac)_2(H_2O)]$, $[Zn(CNacac)_2(H_2O)]$, **Fe-3D**, **Mn-3D** and **Zn-3D** are first reported in this study, which clearly indicates the usefulness of the mechanochemical method in combination with the annealing treatment as a synthetic method for mononuclear and polymeric complexes. **Mn-3D**, **Cu-1D** and **Zn-3D** polymeric complexes decomposed to their respective mononuclear complexes on exposure to water vapour, but returned to their original polymeric structures by re-annealing. This reversible behaviour indicates that the control of the water content of these CNacac complexes is the key to activate self-assembly and, therefore, that the annealing treatment is an effective method.

Experimental Section

Materials and physical measurements: CNacacH was synthesized according to a literature procedure.[12] X-ray powder diffraction patterns were measured by using a Rigaku MultiFlex diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.5406$ Å). The TG study was performed by using a TA Instruments TGA-2950 thermobalance under N_2 flow.

[Mn(CNacac)$_2$(H$_2$O)$_2$]: $Mn(OAc)_2{\cdot}4H_2O$ (1.00 g, 4.1 mmol), CNacacH (1.00 g, 8.1 mmol) and $CH_3COONa{\cdot}3H_2O$ (1.30 g, 9.6 mmol) were dissolved into water (20 mL), methanol (10 mL) and water (20 mL), respectively. The solutions were successively mixed and additional water (20 mL) was finally added. After 5 min stirring, the resultant pale-yellow solution was left at 4°C. After a week, yellow crystals were obtained (0.51 g, 37% yield). Elemental analysis calcd (%) for $C_{12}H_{16}O_6N_2Mn$: C 42.49; H 4.75, N 8.26; found: C 41.98, H 4.86; N 8.17.

[Fe$_2$(μ-OMe)$_2$(CNacac)$_4$]: A solution of CNacacH (0.52 g, 4.2 mmol) in methanol (10 mL) and an aqueous solution (10 mL) of $CH_3COONa{\cdot}3H_2O$ (0.53 g, 3.9 mmol) were successively added to an aqueous solution (20 mL) containing $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ (0.82 g, 2.1 mmol). After stirring for 5 min, the resultant green precipitate was filtered and washed with water. The green powder was dissolved into a small amount of methanol. The colour of the solution gradually turned from yellow to orange. After slow evaporation at ambient temperature for a week, red crystals were obtained. Elemental analysis calcd (%) for $C_{26}H_{30}O_{10}N_4Fe_2$: C 46.59, H 4.51, N, 8.36; found: C 46.49, H 4.51, N 8.30.

[Ni(CNacac)$_2$(H$_2$O)$_2$]·2H$_2$O: A solution of CNacacH (1.01 g, 8.1 mmol) in methanol (5 mL) and an aqueous solution (10 mL) of $CH_3COONa{\cdot}3H_2O$ (1.36 g, 10 mmol) were successively added to an aqueous solution (20 mL) containing $Ni(OAc)_2{\cdot}4H_2O$ (1.00 g, 4.0 mmol). The resultant blue precipitate was filtered and washed with water (1.26 g, 83% yield). Single crystals were obtained by dissolving the blue powder into a small amount of methanol and leaving the solution at 4°C for a few weeks. Elemental analysis calcd (%) for $C_{12}H_{20}O_8N_2Ni$: C 38.03, H 5.32, N 7.39; found: C 37.87, H 5.45, N 7.39.

[Cu(CNacac)$_2$(H$_2$O)]: A solution of CNacacH (0.497 g, 4.0 mmol) in methanol (5 mL) and an aqueous solution (10 mL) of $CH_3COONa{\cdot}3H_2O$ (0.552 g, 4.1 mmol) were successively added to an aqueous solution (20 mL) containing $Cu(OAc)_2{\cdot}H_2O$ (0.398 g, 2.0 mmol). The resultant blue precipitate was filtered and washed with water (0.63 g, 95% yield). The powder obtained was dissolved into a small amount of methanol. After slow evaporation at ambient temperature for a week, blue crystals were obtained. Elemental analysis calcd (%) for $C_{12}H_{14}O_5N_2Cu$: C 43.70, H 4.28, N 8.49; found: C 43.49, H 4.26, N 8.48.

[Zn(CNacac)$_2$(H$_2$O)]: A mixture of $[Zn(OAc)_2]{\cdot}2H_2O$ (0.335 g, 1.5 mmol) and CNacacH (0.384 g, 3.1 mmol) was ground for 5 min, then dissolved into methanol (15 mL). After slow evaporation for 3 days, colourless crystals were obtained (0.35 g, 69% yield). Elemental analysis calcd (%) for $C_{12}H_{14}O_5N_2Zn$: C 43.46, H 4.25, N 8.45; found: C 43.18, H 4.29, N 8.32.

Syntheses of mononuclear complexes by using metal chlorides: [Mn(CNacac)$_2$(H$_2$O)$_2$], [Ni(CNacac)$_2$(H$_2$O)$_2$]·2H$_2$O, [Cu(CNacac)$_2$(H$_2$O)] and [Zn(CNacac)$_2$(H$_2$O)$_2$]·2H$_2$O were obtained by the above methods in which respective metal chlorides were used instead of the metal acetates. Their XRPD patterns were identical to those of the complexes prepared from the metal acetates (41% yield for [Mn(CNacac)$_2$(H$_2$O)$_2$], 83% yield for [Ni(CNacac)$_2$(H$_2$O)$_2$]·2H$_2$O, 17% yield for [Cu(CNacac)$_2$(H$_2$O)] and 20% yield for [Zn(CNacac)$_2$(H$_2$O)$_2$]·2H$_2$O).

Mechanochemical reactions of metal acetates with CNacacH: Grinding of a mixture of metal acetate and CNacacH in the ratio of 1:2 was carried out for 5 min by using a pestle and mortar made of agate. During the grinding, the smell of acetic acid was detected and the mixture became slightly sticky in all cases.

Annealing treatments: Mononuclear complexes obtained by grinding or solution reactions were set into a round three-necked flask. The flask was heated by using an oil bath set at 100°C with a thermal controller (± 0.3°C, OHB-2000G, TOKYO RIKAKIKAI, Japan) except for the case of [Zn(CNacac)$_2$(H$_2$O)]. The annealing temperature for [Zn(CNacac)$_2$(H$_2$O)] was 150°C.

Crystal structure determination: The crystal structures of new complexes, [Mn(CNacac)$_2$(H$_2$O)$_2$], [Fe$_2$(μ-OMe)$_2$(CNacac)$_4$], [Ni(CNacac)$_2$(H$_2$O)$_2$]·2H$_2$O, [Cu(CNacac)$_2$(H$_2$O)] and [Zn(CNacac)$_2$(H$_2$O)] were determined by the single-crystal X-ray diffraction method. Their crystallographic and experimental data are summarized in Table S1 in the Supporting Information. For the collection of the diffraction data, a Rigaku R-AXIS RAPID imaging plate diffractometer was used. Measurements were carried out at room temperature in the cases of [Mn(CNacac)$_2$(H$_2$O)$_2$], [Ni(CNacac)$_2$(H$_2$O)$_2$]·2H$_2$O and [Zn(CNacac)$_2$(H$_2$O)], whereas at 153 K in the cases of [Fe$_2$(μ-OMe)$_2$(CNacac)$_4$] and [Cu(CNacac)$_2$(H$_2$O)]. The structures were solved by the direct method using the program SHELXS-97[13] The refinement and all further calculations were carried out by using the program SHELXL-97[14] All non-H atoms were refined anisotropically by using weighted full-matrix least-squares on F^2. Hydrogen atoms were generated geometrically. CCDC-697691, 697692, 697693, 697694 and CCDC-697695 contain the supplementary crystallographic data of [Mn(CNacac)$_2$(H$_2$O)$_2$], [Fe$_2$(μ-OMe)$_2$(CNacac)$_4$], [Ni(CNacac)$_2$(H$_2$O)$_2$]·2H$_2$O, [Cu(CNacac)$_2$(H$_2$O)] and [Zn(CNacac)$_2$(H$_2$O)], respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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