Crystal-to-crystal interconversion of open and closed dicopper(II) paddle-wheels in a heterotrimetallic coordination polymer

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Crystal-to-crystal interconversion of open and closed dicopper(II) paddle-wheels in a heterotrimetallic coordination polymer

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Treatment of [Au_2Pd(dppm)(D-pen)$_2$] ([1]) with $Cu(NO_3)_2$ gave a 1D ($Au^{I}_2Pd^{II}Cu^{II}_2$)$_n$ coordination polymer, [Cu_2(1)$_2$(H_2O)$_4$](NO_3)$_4$ ([2](NO_3)$_4$), which was reversibly converted to its dehydrated species, [Cu_2(1)$_2$(H_2O)$_2$](NO_3)$_4$ ([3](NO_3)$_4$), with retention of crystallinity. The magnetic feature of [2](NO_3)$_4$ differs dramatically from that of [3](NO_3)$_4$, showing an unusual loop in the course of the magnetic susceptibility measurements due to the reversible openning and closing motions of dicopper(II) paddlewheels in the solid state.

Polymetallic coordination polymers containing metal clusters as a substructure have received considerable attraction because this class of compounds is expected to exhibit unique physical properties and/or chemical reactivities that are not observed for the constituent metal clusters.[1] One of the most attractive performances of this class of compounds is the stimuli-responsible transformation of cluster units with concomitant changes in their properties and functionalities, which makes them applicable for chemical and/or physical sensors.[2] However, such a dynamic system often leads to a loss of crystallinity, and thus reports on the structurally characterized transformation of metal cluster units in polymetallic coordination polymers are still highly limited in number.[3] The paddle-wheel clusters, [$M_2(RCOO)_4(L^1)_2$] (Figure 1a), composed of two metal ions, four equatorial bridging carboxylate ligands, and two axial ligands, are one of the most ubiquitous classes of metal clusters incorporated in coordination polymers,[4,5] serving as an orthogonal 4-directional subunit using four equatorial $RCOO^-$ ligands. In particular, paddle-wheels containing Cu^{II} ions as a metal component are a target of many years of research due to their efficient magnetic super-exchanges between the two Cu^{II} centers, which leads to a quite large magnetic interaction.[6,7] In addition to this regular 'closed' paddle-wheel structure in [$Cu_2(RCOO)_4(L^1)_2$], a unique 'open' paddle-wheel structure in [$Cu_2(RCOO)_3(L^1)_2(L^2)_2$] (Figure 1b), in which one of the four bridging carboxylate groups is replaced by two monodentate ligands, has also been found in coordination polymers. However, there are only five coordination polymers showing an 'open' paddle-wheel structure reported thus far.[8-12] Furthermore, examples that report both the open and closed paddle-wheel structures in one coordination system have not appeared to date, presumably due to the thermodynamic instability of the open paddle-wheel structure. Thus, the inherent differences in the properties between open and closed paddle-wheels remains unknown, although a weaker magnetic interaction has been reported for an open dicopper(II) paddle-wheel structure in [Cu_2(dpda)$_2$(H_2O)$_2$(4,4'-dpdo)$_{0.5}$]$_n$ ($2J = -120$ cm^{-1}).[8] In this paper, we report on an unprecedented dicopper(II) paddle-wheel system created from [Au_2Pd(dppm)(D-pen)$_2$] ([**1**]; dppm = bis(diphenylphosphino)methane, D-H_2pen = D-penicillamine) and $Cu(NO_3)_2$ (Scheme 1). This system involves both the open and closed paddle-wheel structures, which are crystal-to-crystal interconvertible with each other in response to the removal/incorporation of water molecules. The change in the paddle-wheel structures is accompanied by a dramatic change in magnetic interaction between the two Cu^{II} centers, showing

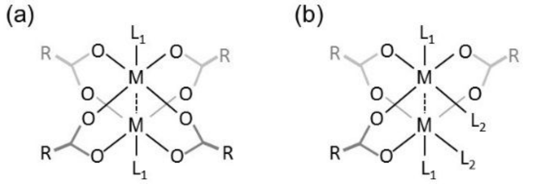

Figure 1. (a) Closed and (b) open paddle-wheel structures.

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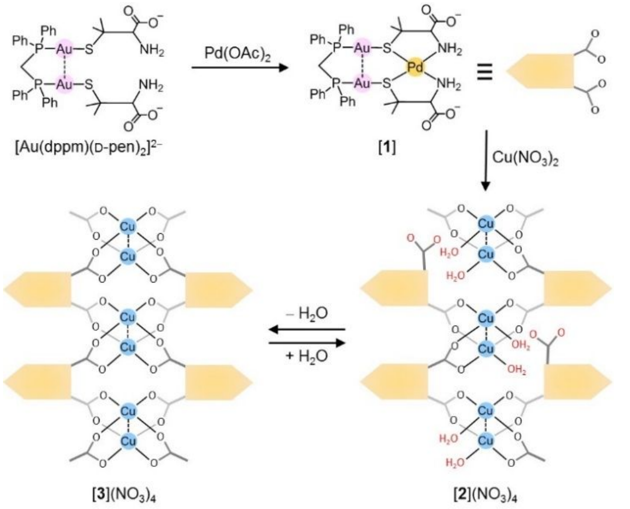
a quite unique loop during the magnetic susceptibility measurements.



Scheme 1. Synthetic routes to [**1**], [**2**](NO_3)$_4$, and [**3**](NO_3)$_4$.

The starting $Au^I_2Pd^{II}$ trinuclear complex, [Au_2Pd(dppm)(D-pen)$_2$] ([**1**]), was newly prepared by the 1:1 reaction of the digold(I) metalloligand [Au_2(dppm)(D-Hpen)$_2$] [13] with Pd(OAc)$_2$ in EtOH, and it was isolated as yellow block crystals.† Based on the IR and NMR spectra, together with the X-ray fluorescence and elemental analyses, [**1**] was assigned to a C_2 symmetrical $Au^I_2Pd^{II}$ trinuclear complex having two deprotonated carboxylate groups (Figures S1, S2, and S3).† The structure of [**1**] was confirmed by single-crystal X-ray crystallography.† In [**1**], the digold(I) metalloligand chelates to a square-planar Pd^{II} center in a tetradentate-N_2S_2 mode to form an $Au^I_2Pd^{II}$ trinuclear structure in [Au_2Pd(dppm)(D-pen)$_2$] (Figure S4).† The average intramolecular Au···Au distance is 3.05 Å, suggestive of the presence of an aurophilic interaction.[14] In [**1**], two D-pen carboxylate groups are not involved in the coordination and have an orientation almost parallel to the *cis*-[Pd(N)$_2$(S)$_2$] square-plane.

The subsequent reaction of [**1**] with excess Cu(NO_3)$_2$ in EtOH/water (4:1) gave a blue-green solution, from which green block crystals ([**2**](NO_3)) were isolated.†,‡ The X-ray fluorescence spectrometry of [**2**](NO_3)$_4$ indicated the presence of Au, Pd, and Cu as metal components, and its elemental analytical data agreed well with the formula for a 1:1 adduct of [**1**] and Cu(NO_3)$_2$.§ The coordination of a carboxylate group of [**1**] was suggested by the IR spectrum, which exhibited an additional ν_{CO} band at 1650 cm^{-1}, in addition to a ν_{CO} band at 1605 cm^{-1} found in [**1**] (Figure S5).†[15] Single-crystal X-ray analysis of [**2**](NO_3)$_4$ revealed the presence of two independent molecules of [**1**] ([$\mathbf{1_A}$] and [$\mathbf{1_B}$]), one {$Cu_2(H_2O)_4$}$^{4+}$ unit (av. Cu–O_{H2O} = 2.03 Å), and four nitrate anions, in addition to four solvated water molecules, in the asymmetric unit.† As shown in Figure 2a, [$\mathbf{1_A}$] spans two {$Cu_2(H_2O)_4$}$^{4+}$ units through the coordination of two carboxylate groups to the dicopper(II) cores (av. Cu–O_{COO} = 1.96 Å). Molecule [$\mathbf{1_B}$] also spans two {$Cu_2(H_2O)_4$}$^{4+}$ units, but only one of two carboxylate groups coordinates to a dicopper(II) core (av. Cu–O_{COO} = 1.95 Å). The other carboxylate group in [$\mathbf{1_B}$] forms O-H···O hydrogen bonds with two aqua ligands of a {$Cu_2(H_2O)_4$}$^{4+}$ unit (av. O_{COO}···O_{H2O} = 2.65 Å). As a result, [**2**](NO_3)$_4$ constructs a cationic 1D coordination polymer {[$Cu_2(H_2O)_4(\mathbf{1})_2$]$^{4+}$}$_n$ (Figure 2a), in which each {$Cu_2(H_2O)_4$}$^{4+}$ unit is coordinated by three carboxylate groups from three different $Au^I_2Pd^{II}$ molecules (av. Cu–O_{COO} = 1.96 Å), forming an open paddle-wheel structure with the intramolecular Cu···Cu distance of 3.17 Å (Figure 2b). It should be noted that the 1D chain possesses cavities surrounded by two [**1**] molecules and two {$Cu_2(H_2O)_4$}$^{4+}$ units. In each cavity, a nitrate ion is fixed by forming rigid N-H···O hydrogen bonds with the amine groups of [**1**], which appears to stabilize the open paddle-wheel structure in [**2**](NO_3)$_4$ (Figure S6a, Table S1).†

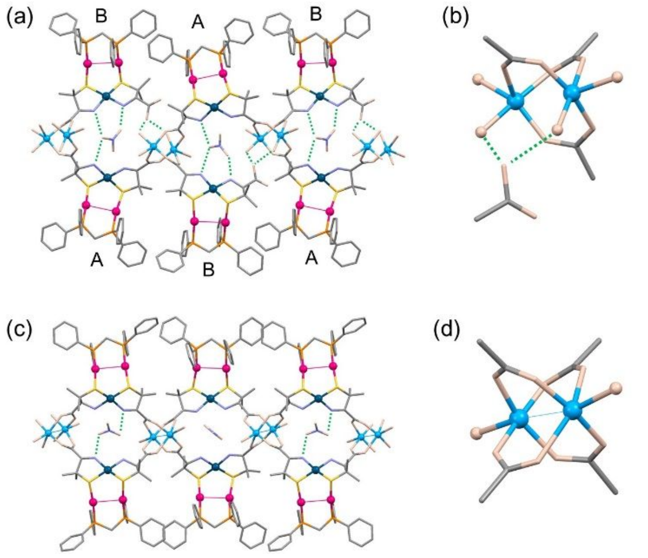


Figure 2. Perspective views of (a) the 1D chain and (b) open paddle-wheel structures in [**2**](NO_3)$_4$. Perspective views of (c) the 1D chain and (d) closed paddle-wheel structures in [**3**](NO_3)$_4$. Color codes: Au, pink; Pd, blue-green; Cu, sky-blue; S, yellow; O, pink; N, blue; and C, gray. H atoms, solvated water molecules and several nitrate anions were omitted for clarity. The coordinated water molecules are illustrated as a small ball in (b) and (d). Green dashed lines indicate OH···O hydrogen bonds.

The magnetic properties of [**2**](NO_3)$_4$ were investigated by the SQUID measurements in the temperature range of 2-300 K under a direct current (dc) magnetic field of 0.5 T. As illustrated in Figure 3a, the $\chi_M T$ values of [**2**](NO_3)$_4$ gradually increase from 0.02 cm^3 K mol^{-1} at 2 K to 0.73 cm^3 K mol^{-1} at 270 K (Figure 3a-i), indicativeof the presence of an antiferromagnetic interaction between the two Cu^{II} centers in each open paddle-wheel. By fitting the data to the Van Vleck model, the magnetic interaction between the two copper(II) centers (2J) was evaluated to be –114 cm^{-1} (Table S2).† Unexpectedly, a further increase of the temperature over 270 K caused an abrupt decrease of the $\chi_M T$ values (Figure 3a-ii). When the susceptibilities were measured upon cooling down from 300 K to 2 K, the $\chi_M T$ vs T plots (Figure 3a-iii) were largely deviated from that of the heating process. This suggests that [**2**](NO_3)$_4$ was transformed to another species ([**3**](NO_3)$_4$) at high temperature. The 2*J* value of this species was evaluated to be –308 cm^{-1} (Table S2),† which is about three times larger than that of [**2**](NO_3)$_4$.

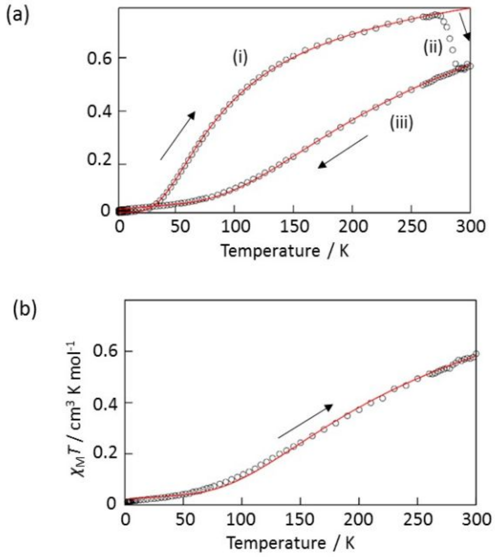


Figure 3. $\chi_M T$ vs T plots of (a) [**2**](NO_3)$_4$ and (b) [**3**](NO_3)$_4$ (T = 2-300 K, H = 0.5 T). Black circles indicate the observed data. Red lines indicate the fitting curves. For [**2**](NO_3)$_4$, the measurements with increasing temperature from 2 K to 300 K showed an anomaly at approximately 270-300 K, which corresponds the transformation from [**2**](NO_3)$_4$ to [**3**](NO_3)$_4$.

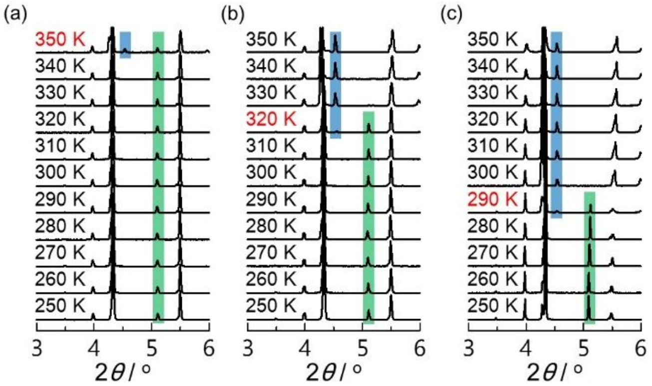


Figure 4. VT-PXRD patterns of [**2**](NO_3)$_4$ under (a) 100 kPa (1 atm), (b) 1.3 kPa, and (c) 0.6 kPa. The temperature increased from 250 K to 350 K. Blue and green colors indicate the diffraction from [**2**](NO_3)$_4$ and [**3**](NO_3)$_4$, respectively.

To check the transformation behavior from [**2**](NO_3)$_4$ to [**3**](NO_3)$_4$ by heating, variable temperature powder X-ray diffraction (VT-PXRD, 250-350 K) experiments were carried out. As shown in Figure 4a, the diffraction pattern of [**2**](NO_3)$_4$ at 250 K was consistent with the pattern simulated from the single-crystal X-ray data of [**2**](NO_3)$_4$. While the pattern remained unchanged until 340 K, a new diffraction pattern appeared at 350 K, indicative of the structural transformation of [**2**](NO_3)$_4$ to a new crystalline phase. However, this transformation temperature (350 K) is much higher than the temperature that showed an abrupt decrease of the $\chi_M T$ values (270-290 K). We speculated that this difference is due to the difference in the pressure between the two kinds of measurements; the pressure in the SQUID instrument was set to 0.6 kPa during the measurements, while the PXRD measurements were carried out under ambient pressure (100 kPa). Thus, we carried out pressure-dependent VT-PXRD experiments (Figures 4b, 4c), which revealed the significant decrease of the transformation temperature under reduced pressure (320 K for 1.3 kPa and 290 K for 0.6 kPa). The pressure dependency of the transformation temperature suggests the removal of volatile solvent molecules, such as water, from [**2**](NO_3)$_4$ in the solid state.[16]

The structure of the new phase ([**3**](NO_3)$_4$) was successfully determined by X-ray analysis using a single-crystal that was obtained by heating a crystal of [**2**](NO_3)$_4$ at 380 K under ambient pressure.†,‡ As shown in Figure 2c, the overall structure of [**3**](NO_3)$_4$ is very similar to that of [**2**](NO_3)$_4$, showing a 1D chain polymeric structure made up of [**1**] molecules and dicopper(II) units (Figure 2d). The relationship between the structures of [**2**](NO_3)$_4$ and [**3**](NO_3)$_4$ is clear from comparing their unit cells (Table S3) and the packing plots in Figure S12.† However, in [**3**](NO_3)$_4$, each dicopper(II) core is chelated by four carboxylate groups from four different [**1**] molecules, completing a closed paddle-wheel structure in {[$Cu_2(H_2O)_2$(**1**)$_2$]$^{4+}$}$_n$ having two aqua ligands at the apical positions (Figure 2d). Thus, two of the four aqua ligands of each {$Cu_2(H_2O)_4$}$^{4+}$ unit in [**2**](NO_3)$_4$ are eliminated at high temperature, with the concomitant coordination of a carboxylate group that forms hydrogen bonds with two aqua ligands in [**2**](NO_3)$_4$. The Cu···Cu distance of the {$Cu_2(H_2O)_2$}$^{4+}$ unit in [**3**](NO_3)$_4$ is 2.71 Å, which is significantly shorter than that of the {$Cu_2(H_2O)_4$}$^{4+}$ unit in [**2**](NO_3)$_4$ (3.17 Å). Due to the contraction of the paddle-wheel structure, each cavity became narrower, with the Pd^{II}···Pd^{II} distance changing from 7.89 Å in [**2**](NO_3)$_4$ to 7.02 Å in [**3**](NO_3)$_4$. This caused the rotation of a nitrate ion in each cavity so as to form less effective N-H···O hydrogen bonding interactions in [**3**](NO_3)$_4$ (Figure S6b, Table S1).†

We confirmed, based on the PXRD measurements, that the reverse conversion from [**3**](NO_3)$_4$ to [**2**](NO_3)$_4$ occurs within 10 min by just exposing [**3**](NO_3)$_4$ to air at ambient conditions (Figure S7).† Compatible with this, the $\chi_M T$ vs T plot recovered to that for [**2**](NO_3)$_4$ during the heating process when [**3**](NO_3)$_4$ was exposed to air, while a sample of [**3**](NO_3)$_4$ without exposure to air gave plots (Figure 3b) identical with those observed in the cooling process (Figure 3a-iii).

It is well known that dicopper(II) complexes with a regular closed paddle-wheel structure have a strong antiferromagnetic interaction between the two Cu^{II} centers. This is explained by the SPY (square-pyramidal) geometry for both of the Cu^{II} centers, which allows an efficient super-exchange between their d_{x2-y2} magnetic orbitals through the carboxylate coordination.[7] In [**3**](NO_3)$_4$, the two Cu^{II} centers both adopt a

SPY geometry (τ = 0.27, 0.33),[17] and thus, they show a strong antiferromagnetic interaction with a 2J value of –308 cm^{-1}, which is within the range normally observed for this class of dicopper(II) complexes (–200 ~ –400 cm^{-1}).[7] On the other hand, the 2J value for [**2**](NO$_3$)$_4$ (2J = –114 cm^{-1}) is much smaller. In [**2**](NO$_3$)$_4$, one Cu^{II} atom in the dicopper(II) core has a SPY geometry (τ = 0.11) [17] with a magnetic orbital of d$_{x2-y2}$, while the geometry of the other Cu^{II} atom is highly distorted from the SPY geometry and approaches a TBP (trigonal-bipyramidal) geometry (τ = 0.49) [17] with a magnetic orbital of d$_{z2}$. This mismatch of the two magnetic orbitals as well as the decrease of the super-exchange pathway due to the three bridging carboxylate groups is responsible for the much weaker antiferromagnetic interaction found in the open paddle-wheel structure in [**2**](NO$_3$)$_4$. As for the stability of the paddle-wheel structures, a closed paddle-wheel structure is assumed to be more stable than the corresponding open structure, considering the very limited examples of open paddle-wheel structures in the literature.[8-12] In the present system, however, the open paddle-wheel structure is more stable than the closed paddle-wheel structure, showing the quick conversion of [**3**](NO$_3$)$_4$ to [**2**](NO$_3$)$_4$ in the solid state. This is most likely due to an unfavorable strain brought in the 1D polymeric structure in [**3**](NO$_3$)$_4$, resulting in the loss of effective hydrogen bonding interactions between nitrate anions and amine groups in its cavities.

In summary, we showed that the Pd^{II}Au$^{I}_2$ complex ([**1**]) acts as a carboxylate-donating metalloligand to give the Au^{I}Pd^{II}Cu^{II} heterotrimetallic coordination polymer with a rare open paddle-wheel structure ([**2**](NO$_3$)$_4$). It was found that [**2**](NO$_3$)$_4$ is convertible to the closed paddle-wheel structure in [**3**](NO$_3$)$_4$ by heating, which is easily reverted back to [**2**](NO$_3$)$_4$ by exposure to air in a crystal-to-crystal interconversion manner; the processes involve the removal/binding of two water molecules in each dicopper(II) paddle-wheel with the concomitant binding/removal of an adjacent carboxylate group of [**1**]. Importantly, this novel paddle-wheel interconversion event led to the generation of an enormous magnetic loop due to the very large difference in magnetic interactions between [**2**](NO$_3$)$_4$ and [**3**](NO$_3$)$_4$. The present results should provide new insight into the design and creation of dynamic paddle-wheel systems as well as the basic understanding of the correlation between the structure and magnetism in dicopper(II) paddle-wheel systems.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ The phase purity of [**2**](NO$_3$)$_4$ and [**3**](NO$_3$)$_4$ was confirmed by powder X-ray diffraction patterns that match well with the patterns simulated from the single-crystal X-ray data (Figures S8, S9).†

§ TG-DTA analysis showed 2 step dehydration at 47 °C and 134 °C (Figure S10).†

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A dicopper(II) paddle-wheel system that shows a unique magnetic loop induced by crystal-to-crystal structural transformation is reported.