Heterometallic Complexes **Hot Paper**

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Overcoming Statistical Complexity: Selective Coordination of Three Different Metal Ions to a Ligand with Three Different Coordination Sites

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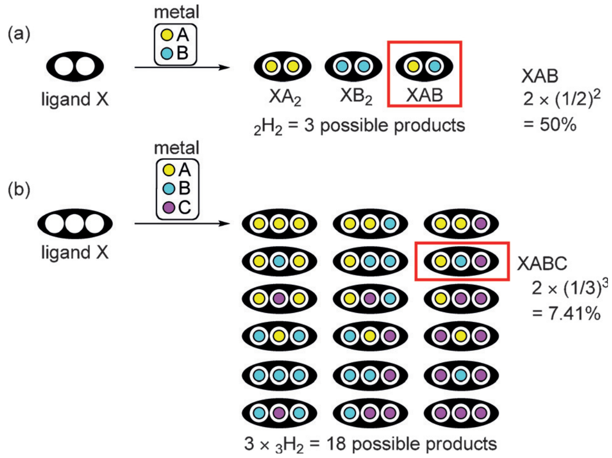
Abstract: *In general, it is difficult to selectively introduce different metal ions at specific positions of a cluster-like structure. This is mainly due to statistical problems as well as the reversibility of the formation of coordination bonds. To overcome this statistical problem, we used a carefully designed ligand, H_6L, which can accommodate three different kinds of metal ions in three types of coordination sites. The complex $[LNiZn_2La]^{3+}$, which contains three different metals, was quantitatively obtained by a stepwise procedure, but different products were obtained when the metal ions were added in a different order. However, equilibration studies indicated that this complex was almost solely formed among 54 ($=3\times3\times{}_3H_2$) possible products upon heating; the formation efficiency (ca. 100 %) was significantly higher than the statistical probability (2.47 %). Such carefully designed ligands should be useful for the synthesis multimetallic systems, which are of interest because of the interplay between the different metals.*

Selectivity is one of the most important issues in multicomponent chemical reactions.[1] By making use of chemoselective and regioselective reactions we can synthesize organic compounds basically at will. For metal-containing structures, however, it is rather difficult to selectively introduce different kinds of metal ions into appropriate positions in a cluster-like structure. Nevertheless, such heterometallic complexes[2] are of interest when designing multifunctional catalysts[3] or magnetic materials,[4] for example. The interplay between three or more kinds of metals is known to be important in highly functional materials, such as the superconducting material $YBa_2Cu_3O_7$,[5] but few multimetallic systems with discrete structures have been developed. The difficulty is due to statistical complexity.

As the simplest case, we consider a ligand X with two binding sites, each of which can accommodate two different kinds of metals, A or B (Scheme 1 a). If a homodinuclear species XA_2 (or XB_2) is needed, it can be obtained simply by reacting X with 2 equiv of A (or B). However, if a heteronuclear species XAB is needed, it is not always obtained as the sole product in the reaction of X with a mixture of A and B. The reaction could give three (${}_2H_2 = 3$)[17] products, XA_2, XB_2, and XAB. If there is no preference in reactivity between A and B, the yield of the XAB species is governed by statistics: $2\times(1/2)^2 = 50\,\%$. Nevertheless, we might isolate the XAB species from the mixture because separation of only three products is not particularly difficult in many cases.



Scheme 1. Statistical complexity of the formation of multiple-metal-containing species. a) XAB species from a two-site ligand. b) XABC species from a three-site ligand.

However, as the number of binding sites increases and a greater variation of metals are used, the one-step synthesis of multi-metal structures becomes more and more difficult. We here consider a ligand X with three binding sites, each of which can accommodate three different kinds of metals, A, B, and C, with equal probability (Scheme 1 b). The reaction could give 18 ($3\times{}_3H_2 = 18$) kinds of products. This situation is considered as a problem of “permutation with repetition”; there are 18 different ways in which three balls could be arranged when three different kinds of balls are available and the same kinds of balls can be chosen more than once. As the expected yield of heterospecies XABC is less than 10 % ($2\times(1/3)^3 = 0.0741$), most of the substrates (more than 90 %) will be lost as undesired side products. As the target compound XABC has to be separated from the 17 side products, the separation would be terribly difficult. Even if the XABC species can be isolated, the yield should be impractically low.

Another factor that makes it difficult to obtain multimetal structures is the reversibility of the coordination bonds between metals and organic ligands. When a coordination bond is formed in a reversible process, a heterospecies such as

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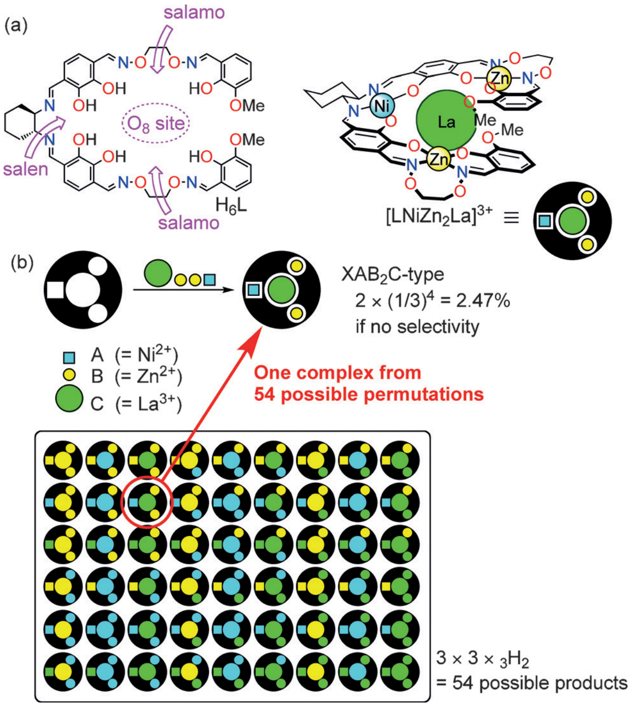
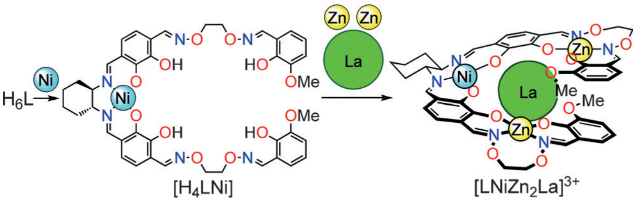
XABC may be in equilibrium with other competing species such as XABA or XBCA. In this case, we cannot obtain the XABC species in pure form owing to the metal exchange equilibrium. We often encounter such problems in obtaining complexes containing several different kinds of metal ions. Therefore, an ingenious strategy is needed to efficiently obtain mixed-metal species such as XABC. To date, metal complexes containing three different kinds of metal ions are limited to those that can be prepared by stepwise metal introduction,[6] whereas the programmed introduction of different kinds of metal ions has now been recognized as an important topic in functional molecular chemistry.[7]

This paper reports the first efficient and selective introduction of three different kinds of metals in a four-site ligand under thermodynamic control, overcoming the above-mentioned statistical complexity with an equilibrium process. A tetranucleating ligand H_6L[8–10] (Scheme 2a) is a promising candidate for selectively introducing three different kinds of metal ions in close proximity. It has one imine-based N_2O_2 site (salen), two oxime-based N_2O_2 sites (salamo),[11] and one O_8 site, which are separated from each other by phenoxo groups. If there is no preference in the introduction of the three different kinds of metal ions, ligand H_6L could give 54 ($=3\times 3\times {}_3H_2$) possible products (Scheme 2b). The expected yield of the XAB_2C species is less than 3% ($2\times(1/3)^4=0.0247$) if equal amounts of the three kinds of metal ions are present. Surprisingly, the complexation of the ligand H_6L with Ni^{2+}, Zn^{2+}, and La^{3+} ions selectively gave $[LNiZn_2La]^{3+}$ among the 54 possible complexes as the thermodynamically most stable product.



Scheme 2. A system for overcoming statistical complexity in the introduction of different metal ions at different sites. a) Ligand H_6L with three types of coordination sites and the XAB_2C-type tetranuclear complex $[LNiZn_2La]^{3+}$. b) The 54 possible products that can be formed upon complexation of H_6L with three different kinds of metal ions.

Initially, we intended to synthesize heteronuclear complexes of ligand H_6L by using a partially stepwise procedure (Scheme 3). We have already demonstrated that La^{3+}, which has a larger ionic radius than Ni^{2+} and Zn^{2+}, prefers to occupy the O_8 site.[12] Consequently, the synthesis of an XAB_2C-type complex mainly relies on the selectivity in the introduction of the d block metals (Ni^{2+} and Zn^{2+}) in the salen and salamo sites.



Scheme 3. Stepwise synthesis of $[LNiZn_2La]^{3+}$.

In the case of Zn^{2+}, selective complexation at either the salen or salamo site did not occur, judging from the complicated ^1H NMR spectra of H_6L in the presence of 1, 2, or 3 equiv of zinc(II) acetate. On the other hand, the complexation with 1 equiv of nickel(II) acetate quantitatively gave a single mononuclear species $[H_4LNi]$, which was isolated as brown crystals. Its structure was revealed by X-ray crystallographic analysis: Ni^{2+} was introduced at the salen N_2O_2 site with a square-planar arrangement (Figure 1). Thus, we can selectively introduce a Ni^{2+} ion into the salen coordination site of H_6L.

We expected that this $[H_4LNi]$ complex would be a good precursor for an XAB_2C-type tetranuclear complex. We investigated the selective introduction of Zn^{2+} and La^{3+} in

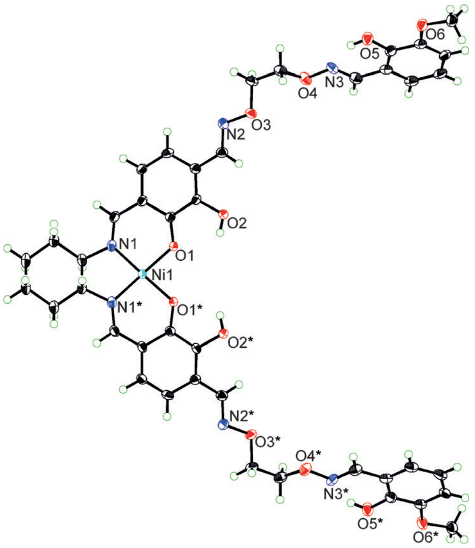


Figure 1. Crystal structure of $[H_4LNi]$. Thermal ellipsoids set at 50% probability. Only one of the crystallographically independent molecules is shown.

the remaining salamo and O_8 sites of [H_4LNi] while keeping the Ni^{2+} in the salen site. As expected, the complex [$LNiZn_2La$]$^{3+}$ was formed as a single product by reaction of [H_4LNi] with zinc(II) acetate (2 equiv) and lanthanum(III) acetate (1 equiv; Scheme 3). The formation of the tetranuclear complex [$LNiZn_2La$]$^{3+}$, which simultaneously has three kinds of metal ions, was supported by mass-spectrometric analysis (m/z 383.0 for [$LNiZn_2La$]$^{3+}$, m/z 604.0 for [$LNiZn_2La(OAc)$]$^{2+}$, m/z 1267.0 for [$LNiZn_2La(OAc)_2$]$^{+}$), and the uniformity of the product was confirmed by ^{1}H NMR spectroscopy.[13] X-ray crystallographic analysis (Figure 2) revealed the positions and geometries of the metal ions. The Ni^{2+} ion was located at the salen coordination site with square-planar geometry. The two Zn^{2+} ions were located in the salamo coordination sites with square-pyramidal geometry in which the apical position was occupied by a monodentate acetato ligand. The La^{3+} ion was found in the central O_8 site and surrounded by eight oxygen donor atoms (six phenoxo and two methoxy groups).

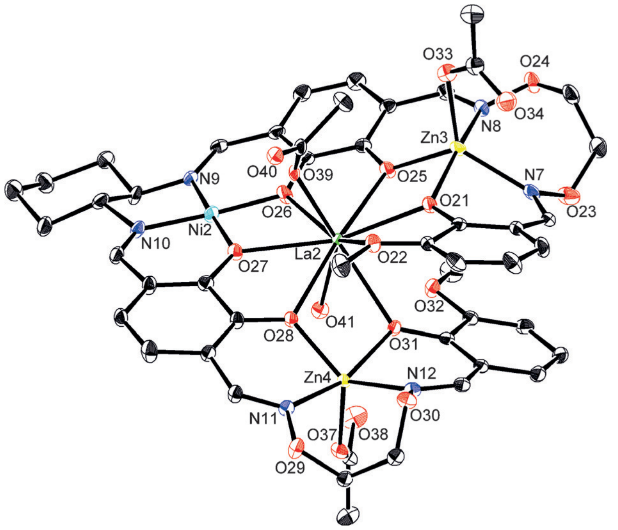
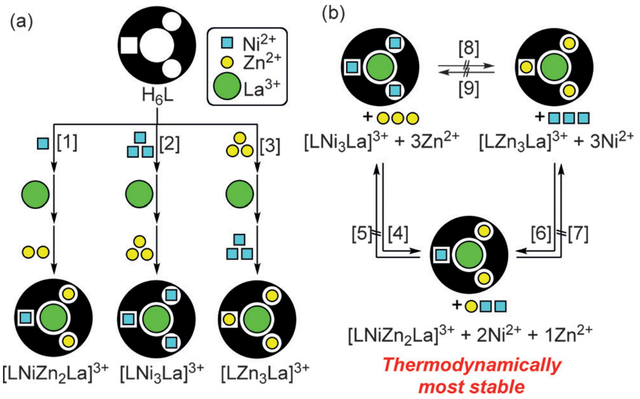


Figure 2. Crystal structure of [$LNiZn_2La(OAc)_3(H_2O)_n$] (n = 1, 2). Thermal ellipsoids set at 30% probability. Hydrogen atoms and the minor disorder components are omitted for clarity. Only one of the crystallographically independent molecules is shown.

As a result, the XAB_2C-type complex [$LNiZn_2La$]$^{3+}$ was efficiently obtained by the complexation of H_6L with Ni^{2+} and then La^{3+} and Zn^{2+} (Scheme 4 a, [1]). However, it was unclear whether it could be formed irrespective of the order of addition of the three kinds of metal ions. If the formation equilibrium is fast enough to give an equilibrated mixture, [$LNiZn_2La$]$^{3+}$ should always be the sole product, even when the metal ions are added in a different order. On the other hand, if the formation equilibrium is slow, the order of addition and the reaction temperature will be crucial for product formation. Thus we investigated the products of the complexation upon the addition of Zn^{2+} and Ni^{2+} in different orders.

When we first added 3 equiv of Ni^{2+} to the ligand and then La^{3+} and Zn^{2+}, only [LNi_3La]$^{3+}$ was formed (Scheme 4 a, [2]).



Scheme 4. Complexation of H_6L with three different metal ions, Ni^{2+}, Zn^{2+}, and La^{3+}. a) The product depends on the order of addition at room temperature. b) Thermodynamic equilibration between three different tetranuclear complexes, [$LNiZn_2La$]$^{3+}$, [LNi_3La]$^{3+}$, and [LZn_3La]$^{3+}$, upon heating.

Similarly, when we first added 3 equiv of Zn^{2+} and then La^{3+} and Ni^{2+}, only [LZn_3La]$^{3+}$ was formed (Scheme 4 a, [3]). These results clearly indicate that the product of the complexation depends on the order of addition of Ni^{2+} and Zn^{2+}. This also suggests that interconversion among the three complexes [LZn_3La]$^{3+}$, [LNi_3La]$^{3+}$, and [$LNiZn_2La$]$^{3+}$ is slow under the synthesis conditions for these metal complexes even if the solution contains a sufficient amount of Ni^{2+} and Zn^{2+} ions to replace those in the tetranuclear complexes.

Under the conditions described above, the complex [$LNiZn_2La$]$^{3+}$ containing three kinds of metal ions was formed only when the intermediate mononuclear complex [H_4LNi] was mixed with a solution of Zn^{2+} and La^{3+}. [$LNiZn_2La$]$^{3+}$ was not formed when 3 equiv of Ni^{2+} or Zn^{2+} were present initially. At first, we expected that the complexation/decomplexation rates of L^{6-} with Ni^{2+}, Zn^{2+}, and La^{3+} would be fast enough that the most thermodynamically stable species could be formed under the reaction conditions because all three of the metal ions generally form labile metal complexes. However, the studied complexes, [LNi_3La]$^{3+}$, [LZn_3La]$^{3+}$, and [$LNiZn_2La$]$^{3+}$, behaved as inert complexes under the reaction conditions, and each of the three complexes was obtained in a manner dependent on the order of addition of the metal ions.

Each of the three complexes, [$LNiZn_2La$]$^{3+}$, [LNi_3La]$^{3+}$, and [LZn_3La]$^{3+}$, was heated to 60 °C in $CDCl_3/CD_3OD$ (1:1) in the presence of a sufficient amount (3 equiv in total) of Ni^{2+} and Zn^{2+} ions to see whether the complexes could undergo metal exchange to give the other two complexes. As expected, a mixture of [LNi_3La]$^{3+}$ and 3 equiv of Zn^{2+} underwent a metal exchange reaction to give [$LNiZn_2La$]$^{3+}$ after heating for 30 days (Scheme 4 b, [4]). In this reaction mixture, [LZn_3La]$^{3+}$ was not observed ([8]). Similarly, a mixture of [LZn_3La]$^{3+}$ and 3 equiv of Ni^{2+} gave the same complex, [$LNiZn_2La$]$^{3+}$ ([6]), but [LNi_3La]$^{3+}$ was not observed ([9]). On the other hand, [$LNiZn_2La$]$^{3+}$ remained intact in the presence of Ni^{2+} and Zn^{2+} (2 and 1 equiv, respectively; [5], [7]); [LZn_3La]$^{3+}$ and [LNi_3La]$^{3+}$ were not observed in the ^{1}H NMR spectrum.

It can thus be concluded that the complex $[LNiZn_2La]^{3+}$ is the most thermodynamically stable in the presence of uncomplexed Ni^{2+} and Zn^{2+}.[14] The different characteristics of the three kinds of metal coordination sites (salen, salamo, and the central O_8 site) resulted in the excellent selectivity in the introduction of the three metal ions Ni^{2+}, Zn^{2+}, and La^{3+}. The formation efficiency of the XAB_2C-type species was significantly higher than the statistical probability of 2.47%. It is easy to understand that the central O_8 site, which is larger than the N_2O_2 tetradentate sites, preferred the larger La^{3+} ion. It is also worth noting that the salen and salamo sites, both of which have similar N_2O_2 coordination environments (two sp^2 nitrogen atoms and two phenoxo groups), can completely discriminate between the two kinds of d block metal ions, Ni^{2+} and Zn^{2+}, which have similar ionic radii. The imine-based salen site preferred square-planar Ni^{2+} coordination, while the oxime-based salamo site preferred pentacoordinate Zn^{2+}. This preference seems to be one of the reasons for the spontaneous metal selection in $[LNiZn_2La]^{3+}$.

In conclusion, we have developed the first molecular system that can selectively accommodate three kinds of metal ions in specified positions under thermodynamic conditions. The XAB_2C-type complex $[LNiZn_2La]^{3+}$, which contains three different metal ions (Ni^{2+}, Zn^{2+}, and La^{3+}), was solely and spontaneously formed among 54 ($=3\times3\times{}_3H_2$) possible products upon heating; the formation efficiency (ca. 100%) was significantly higher than the statistical probability (2.47%). The different characteristics of the three kinds of coordination sites in H_6L allowed the selective introduction of three different metals and thereby allowed us to overcome the statistical complexity. To date, studies on multimetallic systems containing three or more kinds of metal ions have been limited to inert metal systems mainly owing to the lack of versatile synthetic strategies, despite the interest in such complexes because of the interplay that occurs between the different metals. Multicoordination strategies based on finely designed ligands such as H_6L could pave the way for the development of a wide range of multimetallic functional systems with different kinds of metal ions.

Experimental Section

Crystallographic data for $[H_4LNi]\cdot1.67\,MeOH$:[15] $C_{43.67}H_{50.67}N_6NiO_{13.67}$ (936.94), monoclinic, space group $C2$, $a=25.537(10)$, $b=13.344(4)$, $c=13.752(4)$ Å, $\beta=111.577(15)°$, $V=4358(3)$ Å^3, $Z=4$, $T=120$ K, $D_{calcd}=1.428\,g\,cm^{-1}$, $\mu(Mo\ K\alpha)=0.520\,mm^{-1}$, 21473 reflections, 9697 unique ($R_{int}=0.0212$), $R1=0.0329$ ($I>2\sigma(I)$), $wR2=0.0890$ (all data), Flack $\chi=-0.006(6)$. Crystallographic data for $[LNiZn_2La(OAc)_3(H_2O)_{1.16}]\cdot0.5\,CHCl_3$:[15,16] $C_{48.5}H_{51.82}Cl_{1.5}LaN_6NiO_{19.16}Zn_2$ (1406.87), triclinic, space group $P1$, $a=9.2394(7)$, $b=15.0435(12)$, $c=21.2617(16)$ Å, $\alpha=73.1120(10)$, $\beta=78.7850(10)$, $\gamma=76.0430(10)°$, $V=2719.6(4)$ Å^3, $Z=2$, $T=90$ K, $D_{calcd}=1.718\,g\,cm^{-1}$, $\mu(Mo\ K\alpha)=2.135\,mm^{-1}$, 14100 reflections, 11940 unique ($R_{int}=0.0160$), $R1=0.0405$ ($I>2\sigma(I)$), $wR2=0.1058$ (all data), Flack $\chi=0.115(17)$. CCDC 1412883 ($[H_4LNi]\cdot1.67\,MeOH$) and 1412884 ($[LNiZn_2La(OAc)_3(H_2O)_{1.16}]\cdot0.5\,CHCl_3$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgements

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[13] The left-handed isomer of $[LNiZn_2La]^{3+}$ was formed almost exclusively in this reaction thanks to the chiral cyclohexane group whereas the crystallization of this product gave quasi-racemic crystals; for related observations, see Ref. [8].

[14] $[LNiZn_2La]^{3+}$ was found to be stable against metal scrambling in the absence of free Ni^{2+} and Zn^{2+}; $[LNiZn_2La]^{3+}$ remained intact upon heating at 60 °C for one month while a 1:2 mixture of $[LNi_3La]^{3+}$ and $[LZn_3La]^{3+}$ gradually produced $[LNiZn_2La]^{3+}$, as determined by ^{1}H NMR spectroscopy.

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[17] The ${}_nH_r$ notation denotes the number of combinations of n distinct objects taking r at a time when objects may occur with repetitions. This can be calculated as $(n+r-1)!/((n-1)!r!)$.

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