Nuclearity Control of a Trisaloph Zinc Cluster Complex Dependent on Minute Structural Differences in the Bridging Anions

Masaki Yamamura,[†,‡] Hayato Miyazaki,[†] Masaya Iida,[†] Shigehisa Akine,[†] and Tatsuya Nabeshima*[,†,‡]

[†]Graduate School of Pure and Applied Sciences and [‡]Tsukuba Research Center for Interdisciplinary Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan

Ⓢ Supporting Information

ABSTRACT: The Zn_6 cluster complex **2** of the trisaloph ligand was synthesized using $EtCO_2^-$ anions as bridging ligands. Complex **2** has a dimeric structure in the crystalline state, while two monomeric isomers were in equilibrium in solution. The anion-exchange reaction successfully resulted in nuclearity control from Zn_7 to Zn_6.

Recently, the design and synthesis of multimetallocluster complexes has been actively investigated because of not only their unique and attractive structures but also their diverse applications such as optical materials,[1] magnetic materials,[2] catalysts for organic reactions,[3] and multimetalloreceptors.[4] Among the various metal clusters, zinc clusters have been most studied because they are suitable models and alternative species as multimetalloenzymes.[5] For example, a tetranuclear zinc cluster is an efficient Lewis acid catalyst for ester hydrolysis inspired by metalloenzymes.[6] Bridging ligands, such as carboxylate, phosphate, and other multidentate ligands, were required for construction of the zinc clusters. Recently, salen and its analogues have been utilized as ligands to form multizinc complexes because they are multidentate ligands having an O_2 coordination site besides an N_2O_2 site.[7] We first reported a macrocyclic trisaloph ligand ($L'H_6$) composed of three N_2O_2 coordination sites (Chart 1a).[8] When the three N_2O_2 ligation units of the trisaloph analogues bind to metal ions, their homo- and heteromultinuclear complexes were formed because of ligation on the N_2O_2 and central O_6 sites.[9,10] The heptanuclear Zn_7 complexes of the trisaloph ligands were synthesized; they have three zinc atoms at the N_2O_2 sites, and the other four zinc atoms accumulated on the O_6 site (Chart 1b).[10a,b,f] The other zinc cluster complexes with lower nuclearity should be intermediates of the Zn_7 complex **1**, but isolation was difficult because of the formation of several intermediates. Only the tetranuclear Zn_4 complexes were obtained by reaction with 4 equiv of the zinc salt.[10f] The carboxylates as counteranions bridge the zinc atoms, and the bridging ligands should play an important role in maintaining the cluster structure. Thus, we intended to change the acetate ligands into other bridging carboxylate ligands to construct a different cluster structure. Two types of zinc carboxylates, i.e., acetate and methacrylate, have been reported for the zinc cluster complexes of the trisaloph ligands, and the structures of these complexes resemble each other. We now report the synthesis of a trisaloph hexanuclear complex with a slightly more bulky $EtCO_2$ ligand than the $MeCO_2$ ligand and also demonstrate its different

Chart 1

LH$_6$: R = OC$_4$H$_9$
L'H$_6$: R = H

LZn$_7$(MeCO$_2$)$_8$(O) (1)
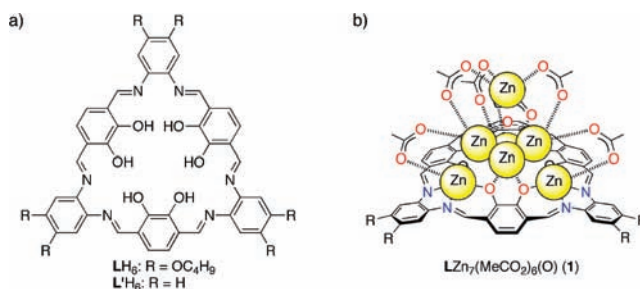
nuclearity and the unique dynamic structural behavior of the zinc complex in solution.

Reaction of the trisaloph ligand LH_6 with $Zn(EtCO_2)_2$ at a 1:7 ratio in $CH_3CN/CHCl_3$ followed by recrystallization from $CHCl_3$ and hexane gave red crystals of the hexanuclear zinc complex $LZn_6(EtCO_2)_5(OH)(H_2O)$ (**2**) in 95% yield instead of the heptanuclear complex. The structure of **2** in the crystalline state was determined by X-ray diffraction (Figure 1).[11] Three zinc atoms, Zn1, Zn2, and Zn3, located in the N_2O_2 sites and the other three zinc atoms, Zn4, Zn5, and Zn6, which are bridged by μ_3-OH, sit on each O_2 site of the catecholato moieties (Figure 1b). Three $EtCO_2$ ligands, **A**, **B**, and **C**, bridge Zn1, Zn2, and Zn3 in the N_2O_2 sites with Zn4, Zn5, and Zn6 in the O_2 sites, respectively (Figure 1b). The $EtCO_2$ ligand **D** binds to Zn5 in a bidentate fashion and **E** binds to Zn1 and Zn6* (Zn6* is an inversion-symmetry equivalent of Zn6). One aqua ligand is bound to Zn6. The Zn_6 cluster **2** has a dimeric structure with an inversion center in which two $EtCO_2$ ligands bridge Zn1 and Zn1* with Zn6* and Zn6, respectively (Figure 2). Overall, Zn1, Zn5, and Zn6 are octahedral, Zn2 and Zn3 are square-pyramidal, and Zn4 is tetrahedral. The dimer **2**$_2$ having a total of 12 zinc atoms is the highest-nuclearity cluster complex among all of the reported trisaloph-based complexes. The matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) of **2** supported the dimer formation because fragment peaks $[\mathbf{2}_2 - (Zn_3(EtCO_2)_6) + H]^+$, $[\mathbf{2}_2 - (Zn_3(EtCO_2)_8H)]^+$, and $[\mathbf{2}_2 - (Zn_4(EtCO_2)_8) + H]^+$ were observed. A similar hexanuclear zinc cluster was synthesized using a macrocyclic hexaoxime ligand, but it remains as a monomer in the crystalline state.[12]
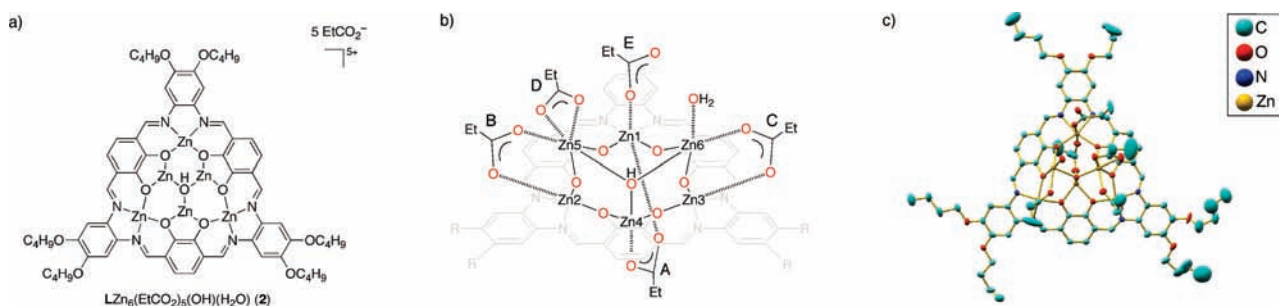
Figure 1. Structure of **2**: (a) Schematic representation and (b) emphasized illustration of the metal cluster core. (c) X-ray crystal structure of **2**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.
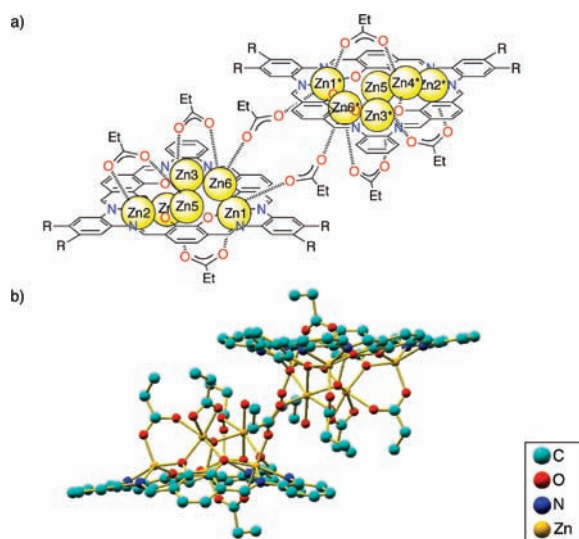
Figure 2. Dimeric structure 2_2 in the crystalline state. (a) Schematic representation and (b) X-ray crystal structure drawn with a ball-and-stick representation. Hydrogen atoms are omitted for clarity.

In the ^{1}H NMR spectra of **2** in CDCl$_3$, two isomers of monomeric **2** bearing five EtCO$_2^-$ anions were independently observed (Figure 3).[11] The ^{1}H NMR spectral patterns suggest that one is a C_{3v}-symmetric isomer with only one kind of imine proton and the other is a C_s-symmetric isomer with three different kinds of imine protons (Scheme 1). The arrangement of the three ligands bridging between the zinc atoms in the N$_2$O$_2$ sites and in the O$_2$ sites should cause this symmetry difference observable by ^{1}H NMR because of the slow anion exchange on the NMR time scale, which was supported by observing the several signals of the anions (vide infra). The EtCO$_2$ ligands were considered to locate on the up or down sides of the trisaloph plane, as seen in the X-ray structure. We called the C_{3v} isomer the *uuu* isomer having three bridging propionates at the up side and the other the *uud* isomer having two EtCO$_2$ ligands at the up side and one at the down side. We have recently reported a similar isomerization of a trisaloph·Zn$_3$La complex bearing three MeCO$_2^-$ anions.[12] It is worth noting that such an isomerization was not observed in the case of the heptanuclear Zn$_7$ complex **1**, which existed as a monomeric compound in the solid state and solution. The isomer *uuu*-**2** showed an ABX$_2$ pattern for the methylene protons of the side chains (OCH$_2$) at 330 K, supporting the C_{3v} symmetry. In this spectrum, two nonequivalent EtCO$_2$ ligands were observed. The signals of *uud*-**2** in the
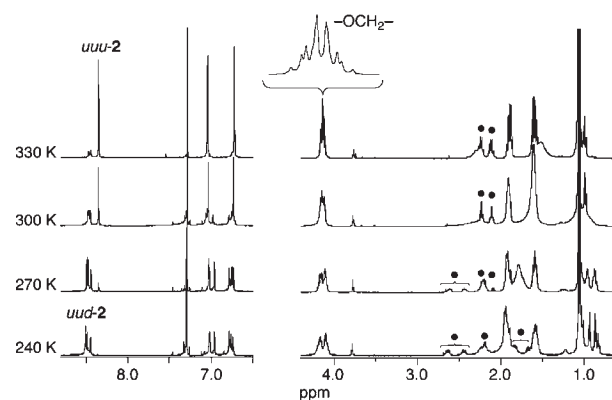

Figure 3. Variable-temperature ^{1}H NMR spectra of **2** (600 MHz, CDCl$_3$, 1 mM). Black circles represent methylene protons of the EtCO$_2$ ligands.

aliphatic region were more complicated because of the lower symmetry. The COSY and NOESY spectra at 240 K allowed identification of the signals of all of the EtCO$_2$ ligands of *uud*-**2**.[11] The five EtCO$_2$ ligands were observed as three kinds of EtCO$_2$ ligands at a 2:2:1 ratio. The methylene protons of the four EtCO$_2$ ligands out of the five anions are diastereotopically different, while the methylene protons of one of the anions are equivalent. The ^{1}H NMR signals were not assigned to the dimeric complex 2_2 that was seen in the crystalline state because the ratios of the signal integrals were not dependent on the complex concentrations. The DOSY experiment also supported no involvement of dimerization.[14] Furthermore, a monomeric species [**2** − EtCO$_2$]$^+$ was observed in the electrospray ionization mass spectrometry (ESI-MS) without any dimeric species.

The variable-temperature NMR spectra of **2** (1 mM, CDCl$_3$) provided insight into the dynamics of interconversion between the two isomers (Figure 3). The two isomers of **2** in solution are in equilibrium, and the ratio of the two isomers was determined by the integrals of the relevant signals. The ratio of *uuu*-**2** to *uud*-**2** decreased as the temperature decreased. The signals of *uuu*-**2** diminished at 240 K, and only the *uud*-**2** isomer was observed. The equilibrium constants for isomerization (K_{eq} = [*uud*-**2**]/ [*uuu*-**2**]) at several temperatures allowed the van't Hoff plots to provide the thermodynamic parameters estimated at ΔH° = -47 ± 1 kJ/mol and $\Delta S^\circ = -152 \pm 4$ J/mol·K. No coalescence was observed up to 60 °C in CDCl$_3$, but the exchange spectroscopy (EXSY) correlation peaks between the two isomers established a pseudo-first-order kinetics for the isomerization

5316

dx.doi.org/10.1021/ic2002833 |*Inorg. Chem.* 2011, 50, 5315–5317

Scheme 1
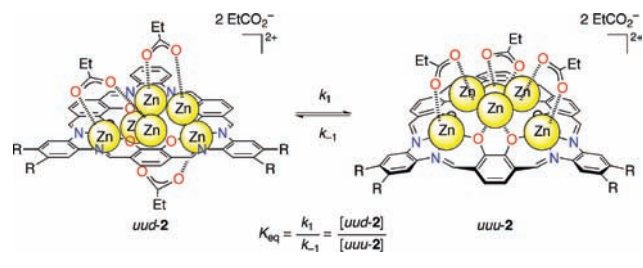
(k_1: isomerization rate from *uud*-**2** to *uuu*-**2**).[15] The Eyring plots for the rate constants k_1 afforded the kinetic parameters of $\Delta H^{\ddagger}$ = 80 ± 6 kJ/mol and $\Delta S^{\ddagger}$ = 3 ± 20 J/mol·K. The small contribution of $\Delta S^{\ddagger}$ suggested that the structure of the complex at the transition state was not significantly different from that of *uud*-**2**. Cleavage of the Zn—O bond between zinc and the bridging $EtCO_2^-$ anion in *uud*-**2** should contribute to the rate-determining step in the ligand exchange because this process is predominantly driven by the enthalpic factor. Above 250 K, EXSY correlation peaks were observed among the protons of the $EtCO_2$ ligands, indicating that the anion-exchange reaction contributes to isomerization.

The hexanuclear cluster complex **2** was obtained as the sole product from LH_6 and an excess of $Zn(EtCO_2)_2$, although the synthetic conditions for **2** were similar to those for the heptanuclear cluster complex **1**. The ^1H NMR spectroscopy indicated that the hexanuclear complex **2** was formed in solution in high efficiency even upon the addition of 7 equiv of $Zn(EtCO_2)_2$. A small amount of the heptanuclear complex might be involved in the reaction mixture of LH_6 with an excess of $Zn(EtCO_2)_2$ because the ion peaks assigned to $[LZn_7(EtCO_2)_5(O)]^+$ in the ESI-MS were observed, but the formation ratio was not determined. On the other hand, the reaction of LH_6 with 7 equiv of $Zn(MeCO_2)_2$ quantitatively afforded the heptanuclear complex **1** in solution.[10b,c,f] The anion effect on the nuclearity encouraged us to examine the structural control of the zinc cluster by the anion-exchange reaction. The reaction of **1** with an excess of $EtCO_2H$ and successive recrystallization yielded **2**. This fact demonstrated that one zinc atom of **1** was removed just by the addition of excess $EtCO_2H$ and recrystallization. Namely, the nuclearity of the cluster was easily controlled by changing the anionic ligand with a slightly different structure.

In conclusion, the trisaloph Zn_6 complex was first synthesized using $EtCO_2^-$ anions as bridging ligands. Surprisingly, only minute structural differences in the bridging ligands significantly affects the zinc cluster structure and enabled isolation of the Zn_6 complex, which is an intermediate of the zinc heptanuclear complex. Conversion from Zn_7 to the less nuclear Zn_6 cluster was achieved by a simple ligand-exchange reaction. Hence, trisaloph zinc cluster complexes would be applicable as an anion-responsive control of the structure and properties of supramolecular assemblies based on the unique metal cluster structures. We are now investigating complex structures with other anions to clarify the anion effect and to apply the anion-exchange strategy to other metal cluster complexes.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Synthetic procedure, compound data, NMR, ESI-MS, MALDI-TOF-MS, and X-ray crystallographic data for **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: nabesima@chem.tsukuba.ac.jp.

■ ACKNOWLEDGMENT

■ REFERENCES

(1) Balzani, V., Campagna, S., Eds. *Photochemistry and Photophysics of Coordination Compounds II*; Springer: Berlin, 2007.

(2) (a) Bagai, R.; Christou, G. *Chem. Soc. Rev.* **2009**, *38*, 1011–1029. (b) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268–297.

(3) (a) Shibasaki, M., Yamamoto, Y., Eds. *Multimetallic Catalysts in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2004. (b) Jacobsen, E. N. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993.

(4) (a) Robertson, A.; Shinkai, S. *Coord. Chem. Rev.* **2000**, *205*, 157–199. (b) Beer, P. D.; Hayes, E. J. *Coord. Chem. Rev.* **2003**, *240*, 167–189.

(5) (a) Weston, J. *Chem. Rev.* **2005**, *105*, 2151–2174. (b) Molenveld, P.; Engbertsen, J. F. J.; Reinhoudt, D. N. *Chem. Soc. Rev.* **2000**, *29*, 75–86. (c) Lipscomb, W. N.; Sträter, N. *Chem. Rev.* **1996**, *96*, 2375–2433.

(6) (a) Iwasaki, T.; Agura, K.; Maegawa, Y.; Hayashi, Y.; Ohshima, T.; Mashima, K. *Chem.—Eur. J.* **2010**, *16*, 11567–11571. (b) Ohshima, T.; Iwasaki, T.; Mashima, K. *Chem. Commun.* **2006**, 2711–2713 and references cited therein.

(7) (a) Wezenberg, S. J.; Kleij, A. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 2354–2364. (b) Kleij, A. W. *Chem.—Eur. J.* **2008**, *14*, 10520–10529. (c) Feltham, H. L. C.; Brooker, S. *Coord. Chem. Rev.* **2009**, *253*, 1458–1475. (d) Kleij, A. W. *Dalton Trans.* **2009**, 4635–4639. (e) Akine, S.; Nabeshima, T. *Dalton Trans.* **2009**, 10395–10408.

(8) Akine, S.; Taniguchi, T.; Nabeshima, T. *Tetrahedron Lett.* **2001**, *42*, 8861–8864.

(9) Nabeshima, T. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 969–991.

(10) (a) Miyazaki, H.; Iwasaki, A.; Akine, S.; Nabeshima, T. *Book of abstracts, Congress of Heterocyclic Chemistry*, Osaka, Japan, Oct 10, 2005; Vol 35, pp 5 and 6. (b) Nabeshima, T.; Miyazaki, H.; Iwasaki, A.; Akine, S.; Saiki, T.; Ikeda, C.; Sato, S. *Chem. Lett.* **2006**, *35*, 1070–1071. (c) Gallant, A. J.; Chong, J. H.; MacLachlan, M. J. *Inorg. Chem.* **2006**, *45*, 5248–5250. (d) Nabeshima, T.; Miyazaki, H.; Iwasaki, A.; Akine, S. *Tetrahedron* **2007**, *63*, 3328–3333. (e) Frischmann, P. D.; MacLachlan, M. J. *Chem. Commun.* **2007**, 4480–4482. (f) Frischmann, P. D.; Gallant, A. J.; Chong, J. H.; MacLachlan, M. J. *Inorg. Chem.* **2008**, *47*, 101–112. (g) Frischmann, P. D.; Facey, G. A.; Ghi, P. Y.; Gallant, A. J.; Bryce, D. L.; Lelj, F.; MacLachlan, M. J. *J. Am. Chem. Soc.* **2010**, *132*, 3893–3908.

(11) See the Supporting Information.

(12) (a) Akine, S.; Sunaga, S.; Taniguchi, T.; Miyazaki, H.; Nabeshima, T. *Inorg. Chem.* **2007**, *46*, 2959–2961. (b) Akine, S.; Sunaga, S.; Nabeshima, T. *Chem.—Eur. J.* **2011** in press.

(13) Yamamura, M.; Sasaki, M.; Kyotani, M.; Orita, H.; Nabeshima, T. *Chem.—Eur. J.* **2010**, *16*, 10638–10643.

(14) The diffusion coefficients of *uud*-**2** and *uuu*-**2** were almost the same (1.261×10^{-9} and 1.228×10^{-9} m²/s, respectively). In this case, the apparent diffusion coefficients of the two exchangeable components were not averaged because the mean lifetimes, τ_1 ($1/k_1$) = 12 s and τ_{-1} ($1/k_{-1}$) = 20 s, are much longer than the diffusion time parameter, $\Delta = 0.040$ s. See: Cabrita, E. J.; Berger, S. *Magn. Reson. Chem.* **2002**, *40*, S122–S127.

(15) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935–967.