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Article

Octanuclear Zinc(II) and Cobalt(II) Clusters Produced by Cooperative Tetrameric Assembling of Oxime Chelate Ligands

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We have synthesized an octanuclear zinc(II) cluster [$L_4Zn_8(H_2O)_3$] by the complexation of 3-hydroxysalamo (H_4L) with zinc(II) acetate. The complex crystallizes in the triclinic system, space group $P\bar{1}$, with unit cell parameters $a = 18.233(10)$ Å, $b = 20.518(11)$ Å, $c = 21.366(11)$ Å, $\alpha = 98.7557(2)°$, $\beta = 99.191(11)°$, $\gamma = 108.309(10)°$, and $Z = 4$. The crystallographic analysis revealed the S_4 symmetrical assembling of four ligands and that the tetrameric complex has three water molecules in an unsymmetrical fashion. Spectroscopic analysis of the complex strongly suggests that the octanuclear cluster also exists in solution and maintains a conformation similar to that in the crystal structure, although exchange of the coordinating water molecules presumably takes place. In addition, the formation process of the octanuclear complex is highly cooperative. A high coordinating ability of the [(salamo)-Zn] unit as well as the catecholato^{2-} moieties probably stabilizes the octanuclear assembly and makes the complexation process cooperative. The corresponding octanuclear cobalt(II) cluster [$L_4Co_8(EtOH)_3$] was prepared in a similar manner. Complex [$L_4Co_8(H_2O)_2X$] (X = H_2O or EtOH) was obtained by the recrystallization from chloroform/hexane. The complex crystallizes in the triclinic system, space group $P\bar{1}$, with unit cell parameters $a = 15.2359(10)$ Å, $b = 16.9625(12)$ Å, $c = 18.9325(13)$ Å, $\alpha = 101.9710(10)°$, $\beta = 105.5410(10)°$, $\gamma = 97.1290(10)°$, and $Z = 2$. Temperature dependence of magnetic susceptibility showed a continuous decrease in the $\chi_M T$ value with decreasing temperature, suggesting antiferromagnetic interaction among cobalt(II) ions. The magnetic susceptibility above 40 K obeys the Curie–Weiss law with a Weiss constant θ of –39 K and a Curie constant C of 19.7 cm^3 K mol^{-1}.

Introduction

N_2O_2 type ligands such as salen, which are easily obtained by the reaction of salicylaldehyde with diamines, coordinate to d-block transition metals in a tetradentate fashion to afford stable mononuclear complexes.[1] In addition to the mononuclear species, there are a number of reports on the synthesis of d-block homometallic tri- and tetranuclear complexes consisting of two molecules of parent salen[2] or saltn[3] ligands. In these complexes, μ_2-phenoxo bridging plays an important role in assembling metal ions and two ligands. When alkoxy groups are introduced at the 3 position of salicylidene moieties, an O_4 coordination site consisting of the alkoxy groups and phenoxo oxygen atoms is produced in addition to the N_2O_2 site. The O_4 site of this type of ligands is particularly suitable for lanthanides to afford 3d−4f heterodinuclear complexes,[4−6] some of which exhibit interesting magnetic[4] and photochemical properties.[5]

We have recently found that salamo (1,2-bis(salicylideneaminooxy)ethane) ligands,[7] an oxime analogue of salen, resist C=N exchange reaction and that they are useful as a

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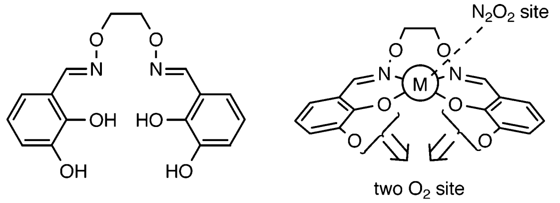
building block for larger supramolecules.[8] We obtained dimeric homotrinuclear complexes $[Zn_3(salamo)_2(OAc)_2]$ and $[Zn_3(3\text{-}MeOsalamo)_2(OAc)_2]$ on the complexation of the corresponding ligands with zinc(II) acetate.[9] We have demonstrated that the complexation of 3-MeOsalamo ligand with zinc(II) acetate takes place highly cooperatively, unlike in the case of the corresponding Schiff-base ligand, such as 3-MeOsalen.

If hydroxyl groups are introduced to the 3 position of salicylidene moieties of salen type ligands, highly versatile coordination ability is expected. This versatility is due to the two neighboring hydroxyl groups at the 2 and 3 positions, which can act as a catecholato^{2-} ligand when they are deprotonated. Indeed, 3-hydroxysalen derivatives form a variety of metal complexes such as mononuclear,[10−12] dinuclear,[11] trinuclear,[13] and heterometallic 3d−4f or 3d−5f complexes.[12] Furthermore, coordination of 3-hydroxysalen type ligands to metals in a divergent fashion leads to serendipitous[14] formation of interesting Zn_8[15] and uranium[16] clusters. In addition to the salen-based Zn_8 cluster, there are a number of reports on self-assembling clusters that have a Zn_x core.[17] In most cases, however, the structure and properties in solution were not thoroughly investigated because of low solubility or instability. To obtain stable self-assembling supramolecular clusters, combination of the high cooperativity of salamo complexes with the coordination ability of catecholato^{2-} moieties would be useful. We herein report the synthesis and crystal structure of octanuclear zinc(II) and cobalt(II) clusters that can be obtained by the cooperative tetrameric assembling of the 3-hydroxysalamo ligand (see Chart 1). Structural analysis of the zinc(II) complex in solution revealed the significant stability

Chart 1



3-hydroxysalamo (= H_4L)

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of the octanuclear core, indicating that the tetrameric self-assembly took place highly cooperatively.

Experimental Section

General. All experiments were carried out under aerobic conditions. Ligand H_4L was prepared according to the literature.[7b] Zinc(II) acetate dihydrate and cobalt(II) acetate tetrahydrate were purchased from Kishida Chemical Co., Ltd., and were used without further purification. Ethanol (>99.5%, Japan Alcohol Trading Co., Ltd.) and chloroform (>99%, Wako Pure Chemical Industries, Ltd.) were used without further purification. ^1H NMR spectra were recorded on a Bruker ARX400 spectrometer. 2D-COSY and ROESY spectra were recorded on a Bruker AVANCE600 spectrometer. Mass spectra (ESI-TOF, positive mode) were recorded on an Applied Biosystems QStar Pulsar *i* spectrometer.

Preparation of Octanuclear Complex $[L_4Zn_8(H_2O)_3]$. A hot solution of zinc(II) acetate dihydrate (44 mg, 0.20 mmol) in ethanol (4 mL) was added to a solution of H_4L (33 mg, 0.10 mmol) in ethanol (4 mL). Chloroform was added to the mixture until the precipitate dissolved, and the resulting solution was concentrated to one-third of the initial volume. After the mixture was kept at room temperature, yellow microcrystals were collected on a suction filter and washed with diethyl ether to give $[L_4Zn_8(H_2O)_3]$ (42.5 mg, 84%). ^1H NMR (400 MHz, DMSO-d_6, 330 K): δ 3.97 (d, J = 12.4 Hz, 1H), 4.07 (dd, J = 14.4, 3.1 Hz, 1H), 4.34 (td, J = 12.4, 3.1 Hz, 1H), 5.02 (dd, J = 14.4, 12.4 Hz, 1H), 5.95 (t, J = 7.8 Hz, 1H), 6.11 (dd, J = 7.8, 1.5 Hz, 1H), 6.32 (dd, J = 7.8, 1.5 Hz, 1H), 6.44 (dd, J = 7.6, 2.2 Hz, 1H), 6.47 (t, J = 7.6 Hz, 1H), 6.59 (dd, J = 7.6, 2.2 Hz, 1H), 8.22 (s, 1H), 8.33 (s, 1H). Anal. Calcd for $C_{64}H_{54}N_8O_{27}Zn_8{\cdot}7H_2O$: C, 38.12; H, 3.40; N, 5.56. Found: C, 37.99; H, 3.39; N, 5.33.

Preparation of Octanuclear Complex $[L_4Co_8(EtOH)_3]$. A hot solution of cobalt(II) acetate tetrahydrate (100 mg, 0.40 mmol) in ethanol (20 mL) was added to a solution of H_4L (66 mg, 0.20 mmol) in chloroform (20 mL). The mixture was gently heated for 10 min, and the resulting brown solution was concentrated to one-third of the initial volume. After the mixture was kept at room temperature, reddish-brown microcrystals were collected on a suction filter and washed with diethyl ether to give $[L_4Co_8(EtOH)_3]$ (60.7 mg, 59%). Anal. Calcd for $C_{70}H_{66}Co_8N_8O_{27}{\cdot}2EtOH{\cdot}0.5CHCl_3$: C, 43.13; H, 3.81; N, 5.40; Cl, 2.56. Found: C, 43.20; H, 3.99; N, 5.66; Cl, 2.24.

NMR Titration. Sample solutions containing H_4L (4.0 mM) and varying amounts of zinc(II) acetate dihydrate (0−12.0 mM) in DMSO-d_6 were prepared. ^1H NMR spectra (400 MHz) were recorded at 330 K.

X-ray Crystallographic Analysis of H_4L, $[L_4Zn_8(H_2O)_3]$, and $[L_4Co_8(H_2O)_2X]$ (X = H_2O or EtOH). Single crystals of H_4L, $[L_4Zn_8(H_2O)_3]$, and $[L_4Co_8(H_2O)_2X]$ (X = H_2O or EtOH) were obtained from ethanol, chloroform/ethanol, and chloroform/hexane solutions, respectively. Intensity data were collected on a Rigaku RAXIS Rapid (H_4L), a Rigaku Mercury CCD ($[L_4Zn_8(H_2O)_3]$), or a Bruker SMART APEX II ($[L_4Co_8(H_2O)_2X]$) diffractometer with Mo Kα radiation (λ = 0.71069 Å). Reflection data were corrected for Lorentz and polarization factors and for absorption using the multiscan method. Crystallographic data are summarized in Table 1. The structure was solved by a direct method (SHELXS 97)[18] and refined by full-matrix least squares on F^2 using SHELXL 97.[19]

Table 1. Crystallographic Data for H_4L, $[L_4Zn_8(H_2O)_3]$, and $[L_4Co_8(H_2O)_2X]$ (X = H_2O or EtOH)[a]

	$H_4L{\cdot}H_2O$	$[L_4Zn_8(H_2O)_3]{\cdot}4.5H_2O$	$[L_4Co_8(H_2O)_2X]{\cdot}2H_2O{\cdot}1.5CHCl_3{\cdot}0.5$hexane (X = H_2O or EtOH)
formula	$C_{16}H_{18}N_2O_7$	$C_{64}H_{63}N_8O_{31.5}Zn_8$	$C_{72.5}H_{75.5}Cl_{4.5}Co_8N_8O_{29}$
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	4.6664(8)	18.233(10)	15.2359(10)
b (Å)	24.167(5)	20.518(11)	16.9625(12)
c (Å)	14.220(3)	21.366(11)	18.9325(13)
α (deg)		98.7557(2)	101.9710(10)
β (deg)	95.926(8)	99.191(11)	105.5410(10)
γ (deg)		108.309(10)	97.1290(10)
V (Å^3)	1595.0(5)	7314(7)	4526.9(5)
Z	4	4	2
D_{calcd} (g cm^{-3})	1.459	1.790	1.580
R1[a] ($I > 2\sigma(I)$)	0.0910	0.0890	0.0602
wR2[a] (all data)	0.2425	0.2354	0.1945

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

The non-hydrogen atoms were refined anisotropically except for the disordered solvent molecules of $[L_4Zn_8(H_2O)_3]$ and $[L_4Co_8(H_2O)_2X]$ (X = H_2O or EtOH). Hydrogen atoms were included at idealized positions refined by use of the riding models.

Magnetic Measurements. Magnetic susceptibility data were collected on a powdered sample of $[L_4Co_8(EtOH)_3]$ using a Quantum Design model MPMS XL5 SQUID magnetometer. Data were collected at a magnetic field of 0.05 T between 300 and 1.8 K. Data were corrected for diamagnetism for the ligands estimated from Pascal's constants.[20]

Results and Discussion

Synthesis and Structure of Ligand H_4L. The ligand 3-hydroxysalamo (H_4L) was prepared by the reaction of 1,2-bis(aminooxy)ethane with 2 equiv. of 2,3-dihydroxybenzaldehyde.[7b] The crystal structure of the ligand H_4L was determined by X-ray crystallography (Figure 1a). The molecule adopts an extended conformation where the two salicylaldoxime moieties are apart from each other. The oxime groups have anti conformation, and there are hydrogen bonds between O1−H···N1 (2.626(5) Å) and O5−H···N2 (2.632(5) Å). In addition, there is an intermolecular hydrogen-bond network involving four hydroxyl groups of H_4L (O1, O2, O5, O6) and cocrystallized water O7 (Figure 1b).

Preparation of Octanuclear Zinc(II) Complex. When the ligand was mixed with zinc(II) acetate in ethanol, yellow precipitate was obtained from the reaction mixture. The product was analyzed to be $LZn_2{\cdot}2.5H_2O$ (84% yield) by elemental analysis. In the ESI mass spectrum of the complex in chloroform/methanol solution, peaks at m/z = 919 $[L_4Zn_8H_2]^{2+}$, 1837 $[L_4Zn_8H]^+$, 1869 $[L_4Zn_8(MeOH)H]^+$, and 1901 $[L_4Zn_8(MeOH)_2H]^+$, which support formation of the tetrameric octanuclear complex in solution, appeared without fragmentation; this is unlike the Schiff-base analogue (Figure 2).[15a,b]

Crystal Structure of $[L_4Zn_8(H_2O)_3]$. Single crystals suitable for X-ray crystallographic analysis were obtained from the chloroform/ethanol solution. The complex crystallizes in the triclinic system, space group $P\bar{1}$, and the unit

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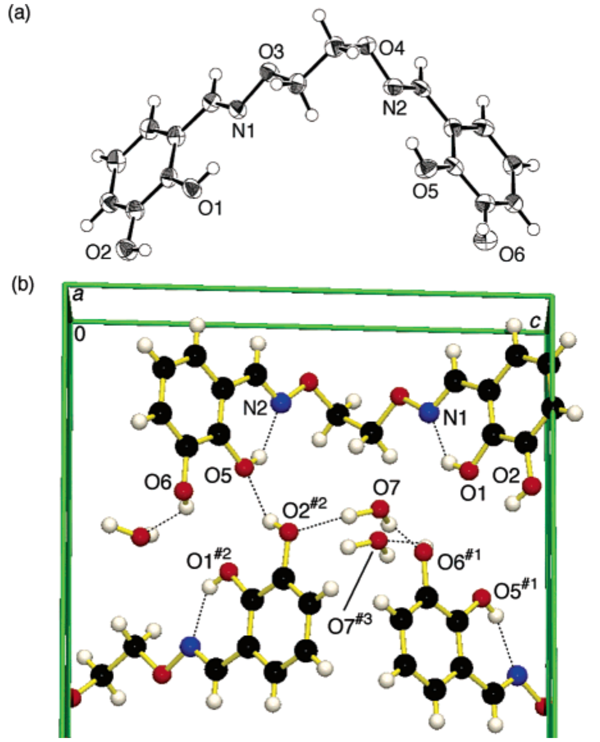

Figure 1. (a) Crystal structure of H_4L with thermal ellipsoids plotted at the 50% probability level. The cocrystallizing water molecule is omitted. (b) Part of the packing diagram of the crystal structure of H_4L showing intra- and intermolecular hydrogen bonds. Selected interatomic distances (Å): O1−N1, 2.626(5); O5−N2, 2.632(5); O5−O2$^{\#2}$, 2.837(5); O2$^{\#2}$−O7, 2.823(5); O7−O6$^{\#1}$, 2.682(5); O6$^{\#1}$−O7$^{\#3}$, 2.952(5). Symmetry transformation used to generate equivalent atoms: $\#1 = -^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; $\#2 = -^1/_2 + x, {}^1/_2 - y, -^1/_2 + z$; $\#3 = -1 + x, y, z$.

cell contains two independent octanuclear complexes (molecules 1 and 2, see the Supporting Information) that have similar structures. The assembly of four ligand units L^{4-} and eight zinc(II) ions results in a discrete octanuclear complex $[L_4Zn_8(H_2O)_3]$ (Figure 3), similar to the corresponding Schiff-base complex.[15] One benzene ring of each of the salamo moieties (A2, B2, C2, D2; see Figure 3c for label numbering) directs inward from the complex and the other (A1, B1, C1, D1) outward. $\pi-\pi$ stacking interactions were observed between A2−C2 and B2−D2. The four ligands assemble in an S_4 symmetrical fashion, but three water molecules coordinate to the metal centers in an unsymmetrical manner to distort the symmetry.

The N_2O_2 site of salamo ligands was occupied by the zinc atom (Zn1, Zn2, Zn3, Zn4; outer zinc atoms hereafter). In addition, four zinc atoms (Zn5, Zn6, Zn7, Zn8; inner zinc atoms hereafter) connect the salamo−zinc unit [LZn] to the adjacent one in such a way that it binds two catecholato moieties (O5−O6 and O7−O8 for Zn5; O11−O12 and O13−O14 for Zn6; O17−O18 and O19−O20 for Zn7; O23−O24 and O1−O2 for Zn8). Phenolate oxygen atoms of the catechol moieties (O6, O12, O18, O24) also coordinate in a μ_2 fashion to Zn6, Zn7, Zn8, and Zn5, respectively. The two types of salamo−salamo linkage with four inner zinc atoms (Zn5, Zn6, Zn7, Zn8) resulted in the formation of a cyclic tetramer. Each of the inner zinc atoms is pentacoordinate, with catechol phenolate oxygen donors occupying all five sites. Interestingly, the geometry of Zn6 is different from the other three inner zinc atoms (Zn5, Zn7, and Zn8). Zn6 adopts a trigonal bipyramidal geometry with axial donors of O11 and O13 ($\tau = 0.792$,[21] Table 2), whereas Zn5, Zn7, and Zn8 have a square pyramidal structure in which the axial sites are occupied by O24, O12, and O18, respectively ($\tau = 0.053$ (Zn5), 0.180 (Zn7), and 0.232 (Zn8)). In the center of the octanuclear cluster, there is an eight-membered ring Zn5−O6−Zn6−O12−Zn7−O18−Zn8−O24. The ring adopts a chair−chair conformation and the four metal−metal distances (Zn5−Zn6, Zn6−Zn7, Zn7−Zn8, and Zn8−Zn5) are in the range of 3.32−3.45 Å.

Outer zinc atoms Zn1, Zn2, Zn3, and Zn4 sit in the N_2O_2 salamo tetradentate chelate moieties. Each zinc atom has a similar trigonal bipyramidal geometry ($\tau = 0.70-0.79$) in which the axial positions are occupied by N1−O5, N3−O11, N5−O17, and N7−O23, respectively, of N_2O_2 sites. In addition, three of the four zinc atoms (Zn2, Zn3, and Zn4) have a water ligand (O25, O26, and O27, respectively). These water molecules are hydrogen bonded to phenolate oxygen atoms of the neighboring salamo moiety (O25−O14, 2.582 Å; O26−O20, 2.585 Å; O27−O2, 2.542 Å). However, there is no water molecule coordinating to Zn1. Instead, a direct coordination bond is formed between Zn1 and the neighboring phenolate O8 (Zn1−O8, 1.965 Å). The four outer zinc atoms contribute to the formation of six-membered rings (Zn1−O1−Zn8−O24−Zn5−O8, Zn2−O7−Zn5−O6−Zn6−O11, Zn3−O13−Zn6−O12−Zn7−O17, and Zn4−O19−Zn7−O18−Zn8−O23) outside of the inner eight-membered Zn_4O_4 ring. In addition, there is a four-membered ring, Zn1−O5−Zn5−O8, that results from the coordination of O8 to Zn1.

Because of the absence of a water molecule coordinating to Zn1, the structure of the octanuclear core distorts from the ideal S_4 symmetry. The interatomic distance Zn1−Zn2 is 6.180 Å, which is considerably shorter than those of Zn2−Zn3 (7.161 Å), Zn3−Zn4 (7.328 Å), and Zn4−Zn1 (7.294 Å).

The two independent molecules (1 and 2) in the asymmetric unit have an almost-similar structure (see the Supporting Information). The four outer zinc atoms of molecule 2 (Zn9, Zn10, Zn11, and Zn12) are trigonal bipyramidal ($\tau = 0.77-0.85$), as seen in molecule 1. Interestingly, the τ values of Zn14 and Zn15 are 0.590 and 0.443, respectively, which are best described as an intermediate geometry between trigonal bipyramidal and square pyramidal. The structure of the octanuclear complex $[L_4Zn_8(H_2O)_3]$ is essentially similar to that of Schiff-base analogue $[L'_4Zn_8(H_2O)_3]$ (Table 2).[15]

Structure of Octanuclear Zinc(II) Complex in Solution. Because the complex is soluble in chloroform and DMSO, we can investigate the structure in solution by using spectroscopic methods. The ^1H NMR spectra of the free ligand H_4L and its zinc(II) complex $[L_4Zn_8(H_2O)_3]$ in DMSO-

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[21] The trigonality index τ ($\tau = 0$ denotes ideal square pyramidal; $\tau = 1$ denotes ideal trigonal bipyramidal) was calculated according to the literature. See: Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.

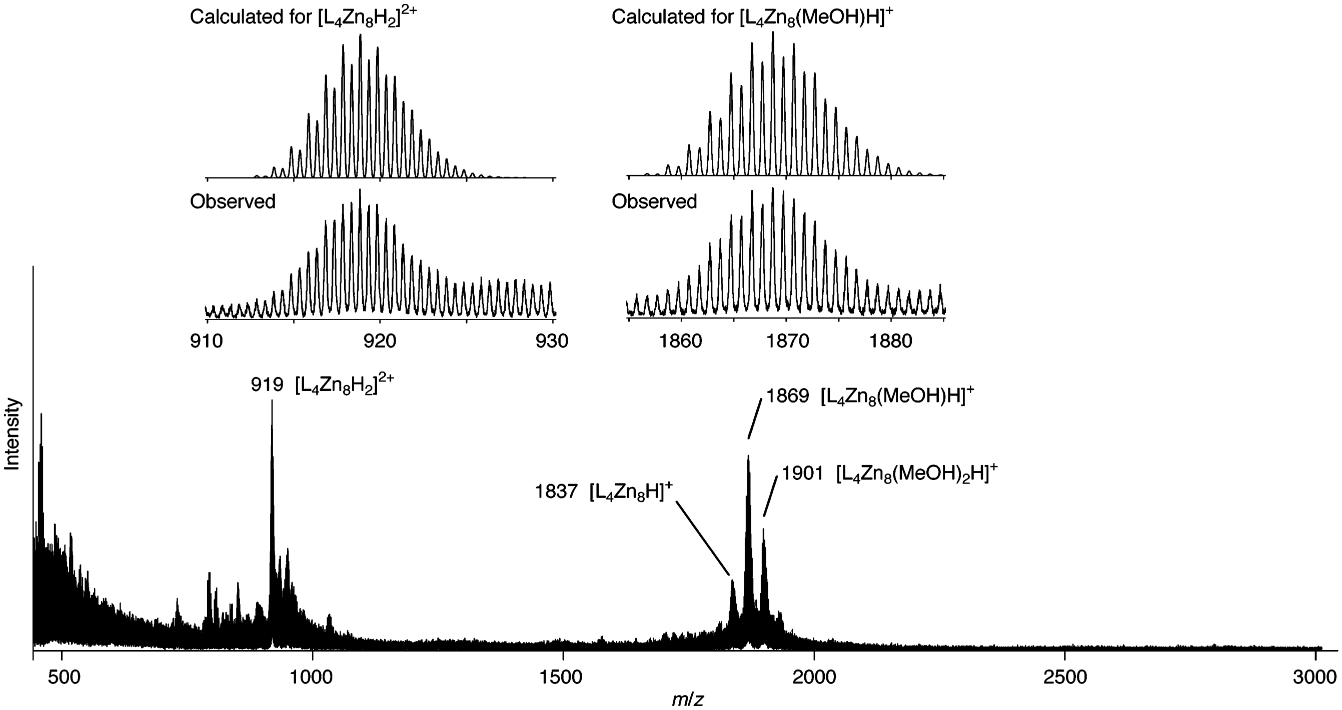

Figure 2. ESI mass spectrum of $[L_4Zn_8]$ in methanol/chloroform.

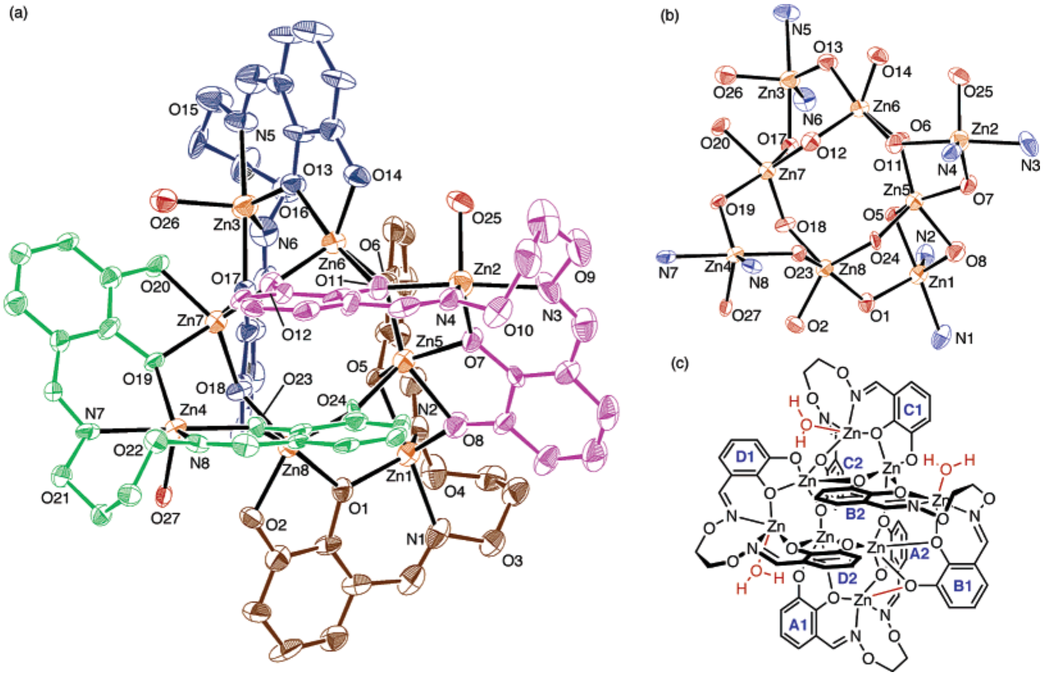

Figure 3. (a) Crystal structure of $[L_4Zn_8(H_2O)_3]$ projected along the apparent S_4 axis. Thermal ellipsoids are plotted at the 30% probability level. Only molecule 1 of the two crystallographically independent molecules 1 and 2 is shown (see the Supporting Information). Hydrogen atoms are omitted for clarity. (b) View of the inorganic core of the octanuclear cluster $[L_4Zn_8(H_2O)_3]$. (c) Schematic drawing of octanuclear complex $[L_4Zn_8(H_2O)_3]$ showing the structural asymmetry arising from the three water molecules. Outer and inner benzene rings are indicated as A1−D1 and A2−D2, respectively.

d_6 are shown in Figure 4a and b, respectively. Although two salicylaldoxime moieties of H_4L are observed as equivalent signals, those of $[L_4Zn_8(H_2O)_3]$ were observed as unequivalent signals; the oxime protons were observed at 8.22 and 8.33 ppm (d, i), and two sets of aromatic protons were also observed (a−c, j−l). In addition, protons of the salamo OCH_2CH_2O moiety were observed as four separate signals (e−h). This characteristic pattern is consistent with the S_4 symmetric structure, although an asymmetric feature, which was seen in the crystal structure, was not observed. The S_4 symmetrical spectral pattern can be explained by assuming that the water molecules coordinating to outer zinc atoms dissociate to some extent and are replaced by another coordinating solvent. This is why a series of peaks corresponding to $[L_4Zn_8(MeOH)_nH]^+$ ($n = 0, 1, 2$) was observed in the ESI mass spectrum in methanol/chloroform. It is noteworthy that the ^1H NMR as well as mass spectra suggest that the octanuclear core is maintained in solution. No signals

Table 2. Trigonality Index τ around Metal Centers in the Octanuclear Complex[a]

$[L_4Zn_8(H_2O)_3]$						$[L_4Co_8(H_2O)_2X]$	
molecule 1	τ	molecule 2	τ	$[L'_4Zn_8(H_2O)_3]$[b]	τ	(X = H_2O or EtOH)	τ
Zn1	0.717	Zn9	0.848	Zn1	0.775	Co1	0.825
Zn2	0.788	Zn10	0.812	Zn2	0.888	Co2	0.788
Zn3	0.765	Zn11	0.817	Zn3	0.948	Co3	0.862
Zn4	0.708	Zn12	0.772	Zn4	0.793	Co4	0.837
Zn5	0.053	Zn13	0.162	Zn5	0.018	Co5	0.274
Zn6	0.792	Zn14	0.590	Zn6	0.718	Co6	0.521
Zn7	0.180	Zn15	0.443	Zn7	0.327	Co7	0.308
Zn8	0.232	Zn16	0.017	Zn8	0.032	Co8	0.083

[a] The trigonality index τ is calculated according to ref 21. [b] From ref 15 (H_4L' = *N*,*N*′-bis(2,3-dihydroxybenzylidene)-1,4-diaminobutane).

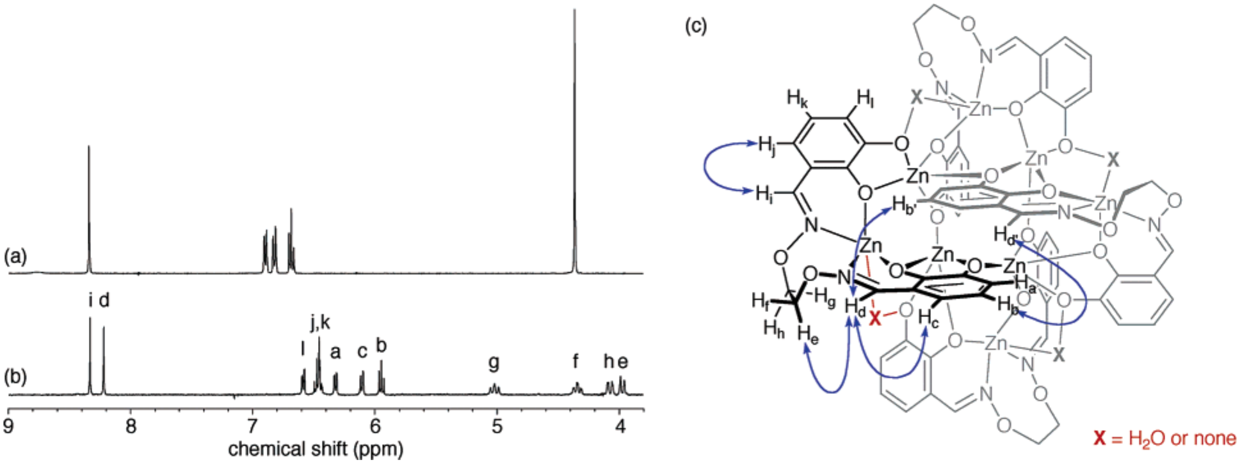

Figure 4. ^1H NMR spectra of (a) H_4L and (b) $[L_4Zn_8]$ in DMSO-d_6 at 400 MHz and 330 K. (c) Assignment of ^1H NMR signals on the basis of 2D-COSY and ROESY spectra. Selected ROEs are indicated as blue arrows.

that are ascribed to the dissociation products were observed in the ^1H NMR spectra.

^1H NMR analysis supported that the octanuclear complex in solution has a conformation similar to that in the crystalline state. Stacking of the inner benzene rings found in the X-ray structure is also apparent in solution from ROE (rotational nuclear Overhauser effect) correlation between $H_b-H_{d'}$ and $H_{b'}-H_d$. Considerable upfield shift of the signals of the inner benzene ring (H_a, 6.32 ppm; H_b, 5.95 ppm; H_c, 6.11 ppm) is ascribed to the stacking of benzene rings. Furthermore, ROEs between H_c-H_d, H_d-H_e, and H_i-H_j are consistent with the conformation found in the crystal structure (Figure 4c). It is noteworthy that one of the OCH_2CH_2O protons (H_g) resonates at considerably low field (5.02 ppm). This large difference ($\Delta\delta = \delta(H_g) - \delta(H_h) = 0.95$ ppm) is presumably attributed to C−H⋯O interaction[22] between H_g and the coordinating oxygen from solvent (X in Figure 4c).

Most importantly, the octanuclear complex is formed in a cooperative fashion just by mixing H_4L and zinc(II) acetate in DMSO-d_6 solution. When 0.5 equiv. of zinc(II) acetate was mixed with H_4L, about 25% of H_4L was converted to the zinc(II) complex (Figure 5b). The conversion to the zinc(II) complex was proportional to the amount of added zinc(II), and the octanuclear zinc(II) complex was quantitatively formed in the presence of 2 equiv. of zinc(II) acetate (Figure 5e). When the corresponding Schiff-base ligand is used for electrochemical synthesis, mononuclear and octanuclear complexes are obtained.[15a,b] Because the product ratio depends on the synthetic conditions, the formation process is not cooperative but stepwise. In the case of the 3-hydroxy-

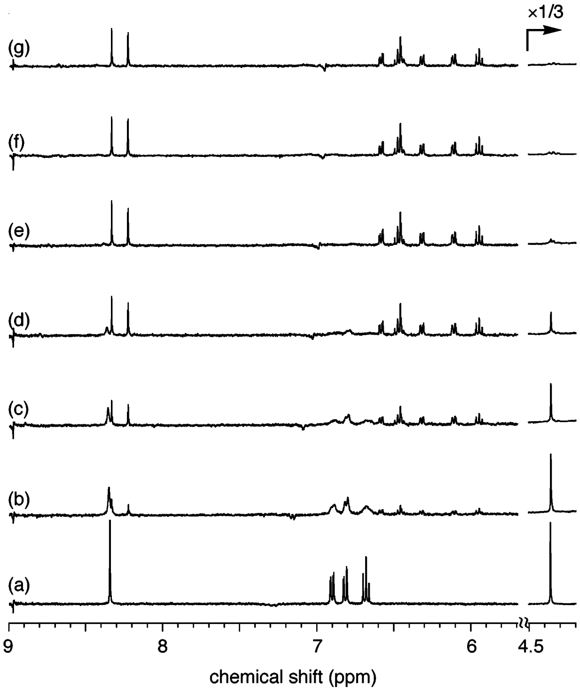

Figure 5. ^1H NMR spectra of H_4L (4.0 mM) in DMSO-d_6 in the presence of zinc(II) acetate at 400 MHz and 330 K: (a) 0, (b) 0.5, (c) 1.0, (d) 1.5, (e) 2.0, (f) 2.5, and (g) 3.0 equiv.

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(22) Intramolecular C−H⋯O contact causes a significant downfield shift of the ^1H NMR signal. See: Bourne, S. A.; Mbianda, X. Y.; Wan, H.; Modro, T. A. *J. Mol. Struct.* **1999**, *475*, 161−165.

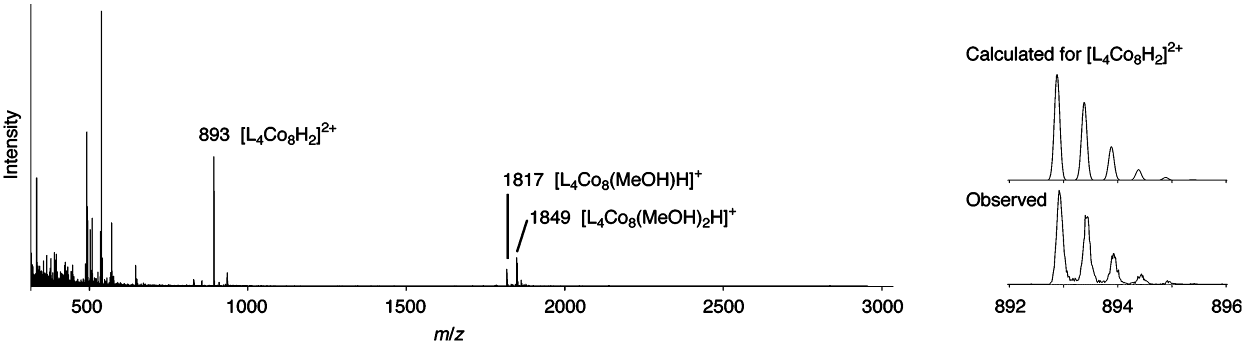

Figure 6. ESI mass spectrum of $[L_4Co_8]$ in methanol/chloroform.

salamo ligand H_4L, however, intermediary complexes were not observed, even when zinc(II) is less than 2 equiv. Moreover, excess zinc(II) (3 equiv.) did not affect the spectrum of $[L_4Zn_8(H_2O)_3]$ (Figure 5g). Thus, stable tetrameric assembly containing eight zinc(II) ions was generated in a highly cooperative fashion.

Octanuclear Cobalt(II) Cluster and Its Magnetic Property. Chelate ligand H_4L is also useful for the synthesis of a metal cluster containing cobalt(II). Recently, cobalt(II) clusters are attracting much attention because they show interesting magnetic properties.[23,24] Reaction of H_4L with cobalt(II) acetate in ethanol/chloroform gave the cobalt(II) complex as reddish-brown crystalline precipitates, which were analyzed to be $[L_4Co_8(EtOH)_3]\cdot 2EtOH\cdot 0.5CHCl_3$ (yield: 59%). The discrete octanuclear structure in solution was confirmed by ESI mass spectrum (m/z = 893 $[L_4Co_8H_2]^{2+}$; Figure 6).

A single crystal suitable for crystallographic analysis was obtained by recrystallization from chloroform/hexane. The X-ray crystallography revealed the octanuclear cobalt(II) complex $[L_4Co_8(H_2O)_2X]$ (X = H_2O or EtOH) (Figure 7). Probably, the ethanol molecules in the sample obtained initially are replaced by water in the recrystallization process. The cobalt(II) complex was the tetrameric assembly of the ligand L^{4-} similar to the zinc(II) analogue. All eight cobalt atoms are pentacoordinate. The geometries around four outer cobalt atoms (Co1, Co2, Co3, Co4) are trigonal bipyramidal ($\tau = 0.788-0.862$, Table 2). Three of the four outer cobalt atoms have coordinating solvent molecules (H_2O or EtOH), as in the case of the zinc(II) complex. One of the inner cobalt atoms (Co6) has an intermediate geometry between trigonal bipyramidal and square pyramidal ($\tau = 0.521$), whereas Co8 is square pyramidal ($\tau = 0.083$) and Co5 and Co7 are distorted one ($\tau = 0.274, 0.308$).

The temperature dependence of the magnetic susceptibility of the cobalt(II) complex $[L_4Co_8(EtOH)_3]$ is shown in Figure 8, in which χ_M is the molar magnetic susceptibility corrected for diamagnetism. The $\chi_M T$ of the complex is 17.6 cm^3 K mol^{-1} at 300 K, corresponding to an effective magnetic moment $\mu_{eff} = 11.9\ \mu_B$ (4.21 μ_B per Co^{II}). The μ_{eff} value is larger than the spin-only value of 3.87 μ_B expected for an isolated high-spin cobalt(II) ion with the assumption of $S = 3/2$ and $g = 2$. The μ_B value per Co^{II} of $[L_4Co_8(EtOH)_3]$ is nearly within the range of 4.26−5.03 μ_B for typical trigonal bipyramidal cobalt(II) complexes under the influence of the orbital contribution.[25] The $\chi_M T$ decreases continuously with decreasing temperature, as in the case of most cobalt(II)

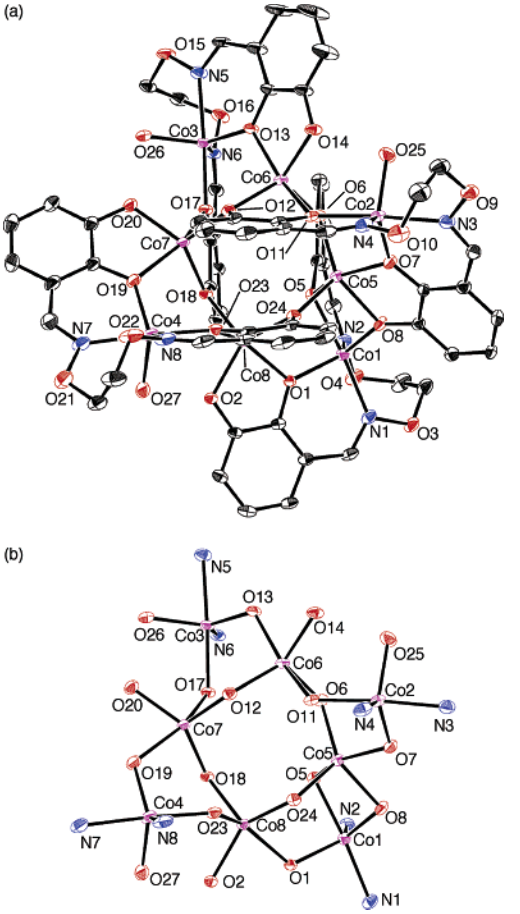

Figure 7. (a) Crystal structure of $[L_4Co_8(H_2O)_2X]$ (X = H_2O or EtOH) with thermal ellipsoids plotted at the 30% probability level. Hydrogen atoms are omitted for clarity. (b) View of the inorganic core of the octanuclear cluster $[L_4Co_8(H_2O)_2X]$.

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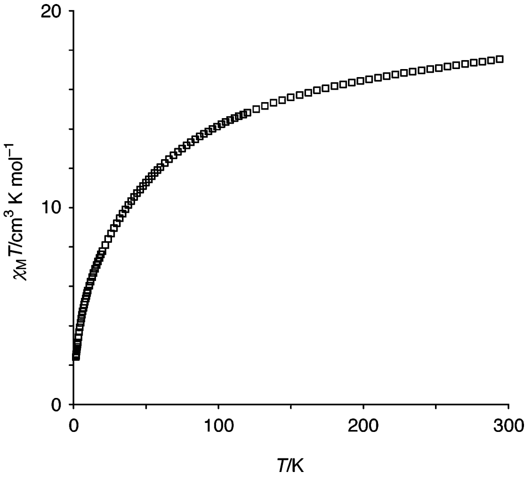

Figure 8. Temperature dependence of the magnetic susceptibility of $[L_4Co_8(EtOH)_3]$ in the range of 1.8−300 K.

clusters reported so far.[23,24] The $\chi_M T$ reaches 2.41 cm^3 K mol^{-1} at 1.8 K. The magnetic susceptibility above 40 K obeys the Curie−Weiss law, with a Weiss constant θ of −39 K and a Curie constant C of 19.7 cm^3 K mol^{-1}. These results suggest that there is antiferromagnetic interaction among cobalt(II) ions and that the ground state of the octanuclear core is $S = 0$.

Conclusion

An octanuclear zinc(II) cluster $[L_4Zn_8(H_2O)_3]$ was obtained by the complexation between 3-hydroxysalamo (H_4L) and zinc(II) acetate. Crystallographic analysis revealed the seeming S_4 symmetrical structure that has three water molecules in an unsymmetrical fashion. Spectroscopic analysis of the complex strongly suggests that the octanuclear cluster also exists in solution and maintains a conformation similar to that in the crystal structure, although exchange of the coordinating water molecules presumably takes place. In addition, it is demonstrated that the formation process of the octanuclear complex is highly cooperative. Probably, a high coordinating ability of the [(salamo)Zn] unit[9] as well as the catecholato^{2-} moieties stabilizes the octanuclear assembly and makes the complexation process cooperative. The strategy was also applied to the synthesis of an octanuclear cobalt(II) cluster in which antiferromagnetic coupling was observed. The ligand H_4L described here is a promising and useful building block for the cooperative synthesis of various kinds of clusters that can also exist in solution.

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Supporting Information Available: X-ray crystallographic data for H_4L, $[L_4Zn_8(H_2O)_3]$, and $[L_4Co_8(H_2O)_2X]$ (X = H_2O or EtOH) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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