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Cooperative Formation of Trinuclear Zinc(II) Complexes via Complexation of a Tetradentate Oxime Chelate Ligand, Salamo, and Zinc(II) Acetate

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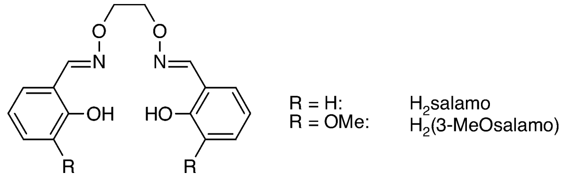
Novel trinuclear zinc(II) complexes $[Zn_3L_2(OAc)_2]$ (L = salamo, 3-MeOsalamo) were synthesized, and their structures were determined by X-ray crystallography. Ligation of methoxy groups in the salamo ligand causes a significantly different coordination mode of the central zinc atom in the trinuclear system. The complexes between the salamo ligands and zinc(II) in methanol formed exclusively and very cooperatively. In contrast to other imine ligands, the mononuclear [ZnL] and other complexes are not observed at all.

Transition metal complexes bearing an *N*,*N*′-disalicylidene-ethylenediamine (salen) ligand or its derivatives are extensively studied because these complexes are used as catalysts for organic reactions,[1,2] models of reaction centers of metalloenzymes,[3,4] and nonlinear optical materials.[5,6] Some of these complexes possess interesting magnetic properties.[7−11] To tune or improve such functions, chemical modifications of the ligand, e.g., introduction of some functional groups or substitution of some parts with appropriate ones, are effective and inevitable. In particular, replacement of some atoms of the ligands with other elements often changes its properties drastically.[12,13] We have recently reported an *O*-alkyloxime analogue of salen, 1,2-bis(salicylideneaminooxy)ethane (=H_2salamo), which shows high stability under the conditions where the imine analogues suffer metathesis reaction of the C=N bonds.[14] The higher electronegativity of the oxime oxygen considerably changes the properties of the copper(II) complex [Cu(salamo)]. In a similar way, we synthesized and characterized the corresponding zinc(II) complex, which is a candidate for a model of di- or trinuclear metalloenzymes such as leucine aminopeptidase and phospholipase P1.[15,16] Here we report unexpected and exclusive formation of trinuclear complexes $[Zn_3L_2(OAc)_2]$ (L = salamo, 3-MeOsalamo), which is in significant contrast to the parent salen ligand that gives a monomeric pentacoordinate zinc(II) complex [Zn(salen)X] (X = H_2O,[17] py[18]).



The reaction of H_2salamo with zinc(II) acetate resulted in the formation of a zinc(II) complex. The absorption spectrum in methanol shows a new band at 350 nm characteristic of a $\pi-\pi^*$ transition.[19] Job plots for the mixture at 350 nm clearly show a maximum at [ligand]/([ligand] + [metal]) = 0.4, which indicates the formation of a 2:3 (or 2*n*:3*n*) complex (Figure 1a). A similar result was obtained for the methoxy derivative, H_2(3-MeOsalamo) (Figure 1b).

From a 2:3 mixture of H_2salamo and zinc(II) acetate, pale yellow microcrystals of $[Zn_3(salamo)_2(OAc)_2]$ were obtained in 61% yield.[20] X-ray crystallographic analysis[21,22] reveals formation of a trinuclear structure $[Zn_3(salamo)_2(OAc)_2]$

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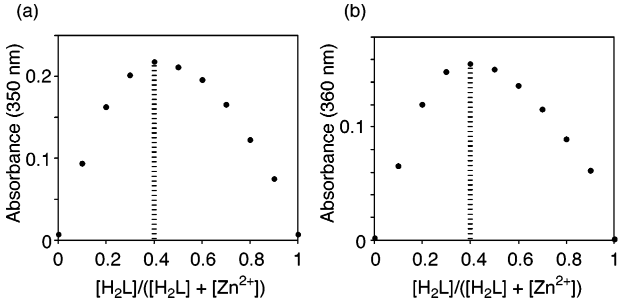

Figure 1. Job plots for the mixture of H_2L and zinc(II) acetate in methanol, $[H_2L] + [Zn^{2+}] = 1.0 \times 10^{-4}$ M: (a) L = salamo, (b) L = 3-MeOsalamo.

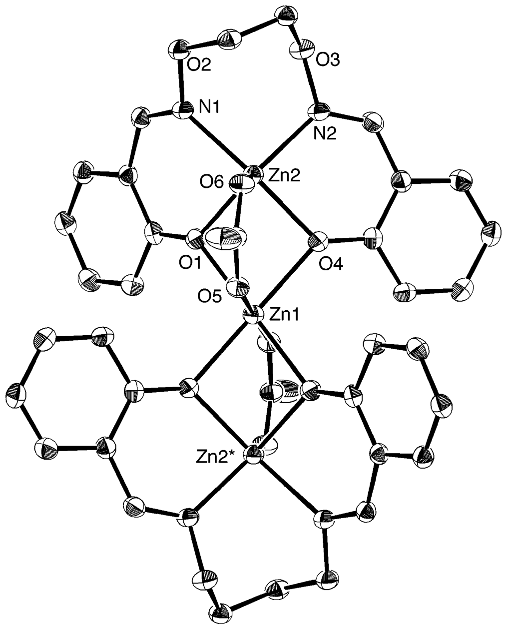

Figure 2. Crystal structure of $[Zn_3(salamo)_2(OAc)_2]$. Thermal ellipsoids are plotted at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Zn1−O1 2.149(3), Zn1−O4 2.129(3), Zn1−O5 2.079(3), Zn2−O1 2.003(3), Zn2−O4 2.045(3), Zn2−O6 1.961(4), Zn2−N1 2.123(4), Zn2−N2 2.062(4).

consisting of two salamo ligands and three zinc atoms as expected from the analytical data (Figure 2). Two of the three zinc atoms (Zn2 and Zn2*) are located in the salamo chelate moieties with a square pyramidal geometry. The μ-phenoxo oxygen atoms (O1 and O4) of the [Zn(salamo)] chelates further coordinate to Zn1 at the inversion center to form octahedral geometry. The trinuclear structure is probably stabilized by the two μ-acetato ligands bridging Zn1−Zn2 and Zn1−Zn2*, which neutralize the whole charge of the complex. Similar trinuclear structures supported by two acetato ligands are also found in salicylideneimine complexes containing zinc(II),[18,23] cadmium(II),[24] and copper(II).[25]

A trinuclear complex, $[Zn_3(3\text{-MeOsalamo})_2(OAc)_2]$, was similarly prepared as pale yellow crystals in 59% yield,[26] whose structure was also determined by X-ray crystallography (Figure 3).[22,27] Noteworthy is that one of the two methoxy groups of each 3-MeOsalamo ligand (O6 and O7) as well as the phenoxo oxygen atoms (O2, O5, O8, and O11) coordinate to the central Zn2. Thus, the geometry around Zn2 is distorted octahedral with six O-ligands. The acetato ligand did not bridge the two metal centers, probably because there is no space around Zn2 for coordination of the acetate ions. On the other hand, the geometry of Zn1 and Zn3 is distorted trigonal bipyramidal; four coordination sites are occupied by a tetradentate salamo ligand and one of the oxygen atoms of an acetato ligand. Furthermore, there is weak interaction between the other oxygen atom of the acetato ligand and zinc (Zn1−O14, 2.630(4) Å, Zn3−O16, 2.625(6) Å).

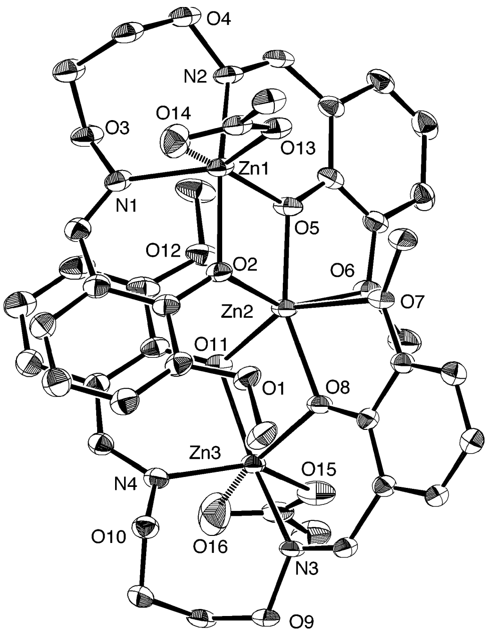

Figure 3. Crystal structure of $[Zn_3(3\text{-MeOsalamo})_2(OAc)_2]$. Thermal ellipsoids are plotted at 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å): Zn1−O2 2.074(3), Zn1−O5 2.012(3), Zn1−O13 1.969(3), Zn1−O14 2.625(6), Zn1−N1 2.044(4), Zn1−N2 2.171(4), Zn2−O2 2.039(3), Zn2−O5 1.988(3), Zn2−O6 2.298(3), Zn2−O7 2.330(3), Zn2−O8 1.998(3), Zn2−O11 2.047(3), Zn3−O8 2.013(3), Zn3−O11 2.073(3), Zn3−O15 2.027(4), Zn3−O16 2.630(4), Zn3−N3 2.178(4), Zn3−N4 2.043(4).

Consequently, the coordination mode of the trinuclear complex of 3-MeOsalamo ligand is completely different from that of the salamo complex, although they have the same formula, $[Zn_3L_2(OAc)_2]$. This contribution of the methoxy group to the ligation is very interesting. The methoxy group

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(20) $[Zn_3(salamo)_2(OAc)_2]$: pale yellow crystals, mp > 300 °C. Anal. Calcd for $C_{36}H_{34}N_4O_{12}Zn_3$: C, 47.47; H, 3.76; N, 6.15. Found: C, 47.35; H, 3.99; N, 6.03.

(21) Crystallographic data for $[Zn_3(salamo)_2(OAc)_2]$: $C_{36}H_{34}N_4O_{12}Zn_3$ (910.78), monoclinic, $P2_1/a$, $a = 8.3320(18)$ Å, $b = 20.420(4)$ Å, $c = 10.320(3)$ Å, $\beta = 95.253(16)°$, $V = 1748.5(6)$ Å^3, $Z = 2$, $D_{calcd} = 1.730$, μ(Mo Kα) = 2.114 mm^{-1}, R1 = 0.0587 ($I > 2\sigma(I)$), wR2 = 0.1474 (all data).

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(26) $[Zn_3(3\text{-MeOsalamo})_2(OAc)_2]$: pale yellow crystals, mp > 300 °C. Anal. Calcd for $C_{40}H_{42}N_4O_{16}Zn_3 \cdot CH_2Cl_2$: C, 44.13; H, 3.97; N, 5.02. Found: C, 43.94; H, 4.25; N, 4.80.

(27) Crystallographic data for $[Zn_3(3\text{-MeOsalamo})_2(OAc)_2] \cdot 3CH_2Cl_2$: $C_{43}H_{48}Cl_6N_4O_{16}Zn_3$ (1285.66), monoclinic, $P2_1/c$, $a = 9.4964(5)$ Å, $b = 21.386(3)$ Å, $c = 25.994(2)$ Å, $\beta = 101.0566(9)°$, $V = 5181.1(8)$ Å^3, $Z = 4$, $D_{calcd} = 1.648$, μ(Mo Kα) = 1.758 mm^{-1}, R1 = 0.0528 ($I > 2\sigma(I)$), wR2 = 0.1462 (all data).

of salen analogues perturbs electronic structure and donor ability, but the oxygen atom of the methoxy groups does not coordinate to transition metals in almost all the examples reported except one.[28]

As discussed, the [Zn(salamo)] and [Zn(3-MeOsalamo)] units are apt to assemble to give the crystalline 2:3 complexes in high yield. In contrast, salicylideneimine ligands (salen, saltn, and salbn) give mononuclear or dinuclear complexes depending on the substituents on the ligand or the reaction conditions.[18,29] In the case of the salamo ligand, however, only the trinuclear complex $[Zn_3L_2(OAc)_2]$ was observed in the ^{1}H NMR spectra of salamo solutions in the presence of varying amounts of zinc(II) in $CDCl_3/CD_3OD$ (1:1), while no other signal attributed to mononulcear [ZnL] was observed (Figure 4).[19,30−32] The result clearly indicates that $[Zn_3L_2(OAc)_2]$ is formed very cooperatively without forming any stable intermediates including mononuclear [ZnL].

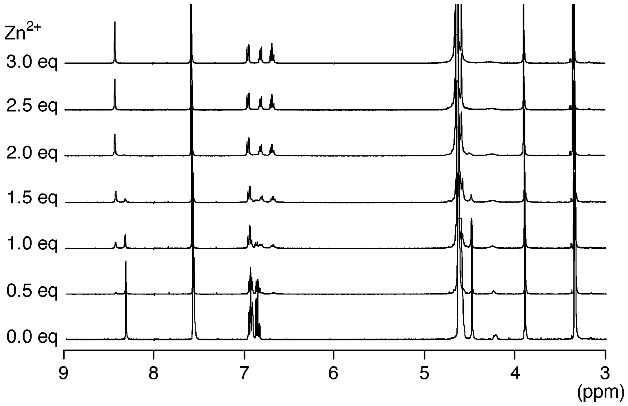

Figure 4. ^{1}H NMR (400 MHz) titration for the complexation between H_2(3-MeOsalamo) and zinc(II) acetate in $CDCl_3/CD_3OD$ (1:1). Concentration of H_2(3-MeOsalamo) is 2.0 mM.

In conclusion, the complexation between the ligand and zinc(II) acetate gave trinuclear zinc(II) complexes $[Zn_3L_2(OAc)_2]$ (L = salamo, 3-MeOsalamo). The methoxy group of 3-MeOsalamo surprisingly affects the coordination geometry around the central zinc atom of the trinuclear system. Spectroscopic studies showed that the trinuclear complexes formed highly cooperatively. Such a highly cooperative effect on the formation of $[Zn_3(salamo)_2(OAc)_2]$ should be useful for the molecular assembling which is driven by coordination of several metal ions. The oxime framework of the salamo ligands has sufficient stability under protic conditions to construct a more complicated, higher-order supramolecular structure containing multiple imine chelate units.[33] Furthermore, investigation of the structure and properties of this kind of trinuclear zinc(II) complex seems to be important because a multinuclear zinc(II) core bridged by alkoxo and carboxylato ligands frequently appears in metalloenzymes.[15,16] Thus, we believe that the trinuclear salamo−zinc(II) complex is a useful building block to construct metal-containing functional supramolecules.

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Supporting Information Available: Crystallographic data for $[Zn_3(salamo)_2(OAc)_2]$ and $[Zn_3(3\text{-MeOsalamo})_2(OAc)_2]\cdot 3CH_2Cl_2$ in CIF formats and ^{1}H NMR titration experiments for the complexation between the imine ligand (salbn and salen) and zinc(II) acetate. This material is available free of charge via the Internet at http://pubs.acs.org.

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