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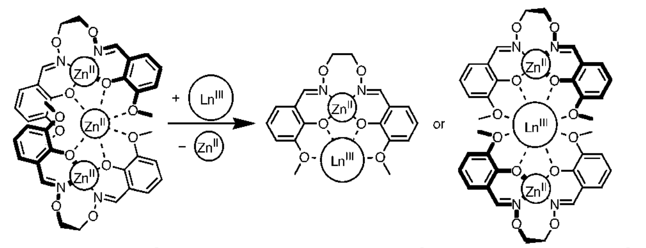
Heterometallic Zn_2La and ZnLu Complexes Formed by Site-selective Transmetalation of a Dimeric Homotrinuclear Zinc(II) Complex

Shigehisa Akine, Takanori Taniguchi, and Tatsuya Nabeshima*
Department of Chemistry, University of Tsukuba, Tsukuba 305-8571

(Received March 7, 2006; CL-060277; E-mail: nabesima@chem.tsukuba.ac.jp)

Transmetalation of a dimeric homotrinuclear zinc(II) complex $[(3\text{-MeOsalamo})_2Zn_3]$ with Lu^{3+} and La^{3+} afforded heterometallic dinuclear $[(3\text{-MeOsalamo})ZnLu]^{3+}$ and trinuclear $[(3\text{-MeOsalamo})_2Zn_2La]^{3+}$ complexes, respectively, whose structures were determined by X-ray crystallography. The transmetalation process was investigated by ^1H NMR titrations.

Heteronuclear complexes containing d- and f-block transition metals have been extensively studied because they exhibit interesting magnetic and photochemical properties.[1] Such complexes are generally prepared by stepwise introduction of two different metals via intermediary mononuclear complexes.[2] Recent advances in a series of macrocyclic compartmental ligands facilitate the synthesis of various dinuclear systems, particularly in the case of ligands consisting of two different types of coordination sites.[3] Using such types of ligands, simple one-pot metalation with two kinds of metals selectively gives the desired heterometallic complexes having different metals in appropriate sites. Recently, we have developed a new strategy for the synthesis of 3d–4f heterotrimetallic complexes by utilizing site-selective transmetalation of a homotrimetallic complex.[4a,5] In this system, one zinc atom in a homotrinuclear zinc(II) complex of a linear tetraoxime ligand was selectively replaced by a guest metal such as lanthanide(III) or calcium.[4] We have already shown that self-assembled L_2Zn_3-type homotrinuclear complexes[6] can also be synthesized by using simpler N_2O_2 ligands, salamo and 3-MeOsalamo.[7] It is important to investigate whether transmetalation occurs without decomposition of the self-assembled dimeric form or the assembly dissociates, because some salen-type ligands give (3d)(4f) and/or $(3d)_2(4f)$ complexes depending on the conditions.[2,8,9] Here, we report the transmetalation of $[(3\text{-MeOsalamo})_2Zn_3(OAc)_2]$ (**1**) on the addition of lanthanide ions by spectroscopic methods (Scheme 1). Structures of the resulting zinc(II)–lanthanide(III) complexes were determined by X-ray crystallography.



Scheme 1.

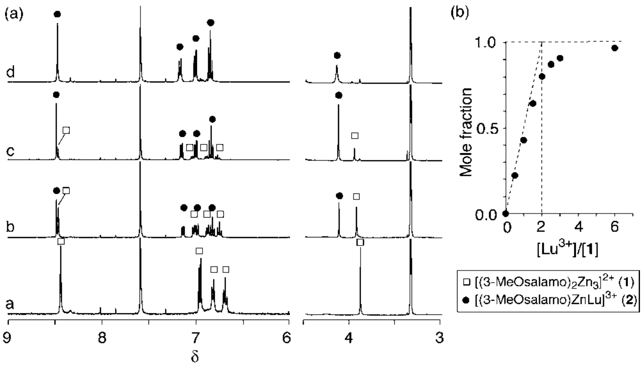


Figure 1. (a) ^1H NMR spectra (400 MHz) of **1** in the presence of $Lu(NO_3)_3$ (a, 0 equiv.; b, 1 equiv.; c, 2 equiv.; d, 6 equiv.) in $CDCl_3/CD_3OD$ (1:1). (b) Mole fraction of Lu^{3+} complex plotted against $[Lu^{3+}]/[\mathbf{1}]$.

When Lu^{3+} was added to a solution of **1**, a new set of signals appeared in the ^1H NMR spectrum (Figure 1a). About 80% of **1** was converted to a new species in the presence of 2 equiv. of Lu^{3+} and the addition of 6 equiv. of Lu^{3+} resulted in the almost complete conversion (>97%). On the basis of the titration curve showing 1:2 ($\mathbf{1}$:Lu^{3+}) stoichiometry, the resulting complex consists of the ligand (3-MeOsalamo) and Lu^{3+} in a 1:1 ratio (Figure 1b). ESI mass spectrum confirmed the formation of a dinuclear species $[(3\text{-MeOsalamo})ZnLu(OAc)_3]$ (**2**) (m/z 715.0 for $[\mathbf{2} - OAc]^+$ and 328.0 for $[\mathbf{2} - 2OAc]^{2+}$). It is noteworthy that the complexation gave only one species. No other complexes having different stoichiometry were detected in the NMR spectra.

$[(3\text{-MeOsalamo})ZnLu(OAc)_3]$ (**2**) was isolated (58% yield) and the structure was determined by X-ray crystallography (Figure 2a).[10,11] As expected, the zinc atom sits in the N_2O_2 salamo site and has pentacoordinate square-pyramidal geometry. In addition, the phenolate (O1, O5) and the methoxy oxygen (O2, O6) donors coordinate to the lutetium as a tetradentate ligand. An acetate ion bridges the Zn–Lu metal centers and the other two coordinate to the lutetium in an η^2-fashion. Thus, the central zinc in the initial trinuclear zinc(II) complex is liberated and is replaced with lutetium(III), and the dimeric assembly simultaneously dissociates.

In contrast, complexation of **1** with La^{3+} gave a different type complex. In this case, addition of La^{3+} (1.0 equiv.) resulted in quantitative conversion of **1** to a new complex (Figure 3a). This indicates that the new complex has the ratio (3-MeOsalamo)/La = 2. The intense peak at m/z 1103.0 in the ESI mass spectrum corresponds to the heterotrinuclear species $[(3\text{-MeOsalamo})_2Zn_2La(OAc)_2]^+$. Thus, transmetalation of **1** took place to give similar dimeric heterotrinuclear complex $[(3\text{-MeOsalamo})_2Zn_2La]^{3+}$. The trinuclear complex exhibits an unsymmetrical ^1H spectral pattern. Protons of two salicylaldoxime moieties were observed as two unequivalent signals; δ 3.38 and 3.40 for methoxy protons, 8.45 and 8.77 for oxime protons, and

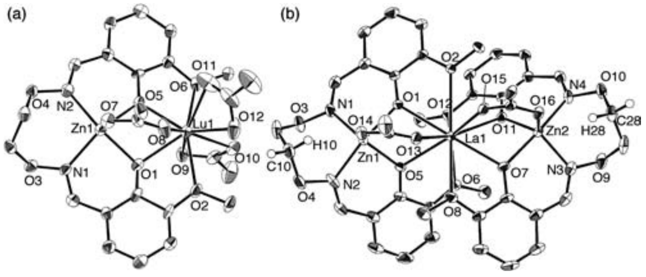


Figure 2. X-ray structures of (a) [(3-MeOsalamo)ZnLu(OAc)$_3$] (**2**) and (b) [(3-MeOsalamo)$_2$Zn$_2$La(OAc)$_2$]$^+$ (**3**).

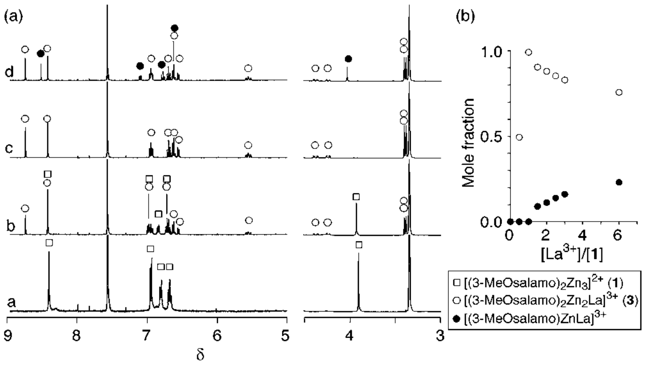


Figure 3. (a) ^{1}H NMR spectra (400 MHz) of **1** in the presence of La(NO$_3$)$_3$ (a, 0 equiv.; b, 0.5 equiv.; c, 1 equiv.; d, 6 equiv.) in CDCl$_3$/CD$_3$OD (1:1). (b) Mole fraction of La^{3+} complexes plotted against [La^{3+}]/[**1**].

two sets of aromatic protons. When an excess amount of La^{3+} ([La^{3+}]/[**1**] $>$ 1) was added, another set of signals appeared in the ^{1}H NMR spectra. The second complex is considered to be a heterodinuclear complex [(3-MeOsalamo)ZnLa]$^{3+}$, judging from the peak in the ESI-mass spectrum (m/z 679.0, [3-MeOsalamo)ZnLa(OAc)$_2$]$^+$) and a symmetrical ^{1}H NMR pattern similar to that of the lutetium(III) complex. However, the formation of the dinuclear complex took place with low efficiency. The mole fraction was 23% even in the presence of 6 equiv. of La^{3+} (Figure 3b).

[(3-MeOsalamo)$_2$Zn$_2$La(OAc)$_2$](NO$_3$) (**3**) was isolated (90% yield) and the structure was determined by X-ray crystallography (Figure 2b).[10,11] Two zinc atoms sit in the N$_2$O$_2$ chelate moieties and the resulting [(3-MeOsalamo)Zn] units further coordinate to decacoordinate La^{3+} in an η^4-fashion. Two acetate ions coordinate to the trinuclear Zn–La–Zn core from the same side of the complex. Thus, two salicylaldoxime moieties of each [(3-MeOsalamo)Zn] unit are unequivalent, one is close to the acetate ion and the other is remote. Probably, the structure of the complex in solution is essentially the same as that in the crystalline state because the unsymmetrical feature found in the crystalline state is consistent with the unsymmetrical ^{1}H NMR spectral pattern. The methoxy groups of one [(3-MeOsalamo)Zn] moiety is close to the benzene ring of the other [(3-MeOsalamo)-Zn] moiety, which can explain the significant upfield shift of the methoxy protons (δ 3.37 and 3.40) compared to those of [(3-MeOsalamo)ZnLa]$^{3+}$ (δ 4.02). In addition, the considerable downfield shift of one of the OCH$_2$CH$_2$O protons (δ 5.55) can be attributed to the C–H···O contact (2.322 Å for C10–*H10*···*O14*; 2.333 Å for C28–*H28*···*O16*) between the proton and the acetate oxygen found in the crystal structure.[12]

Heterometallic ZnLu and Zn$_2$La complexes reported here were also obtained by one-pot procedure. This fact indicates that these complexes are thermodynamically stable. The selectivity presumably attributed to the difference of ionic radius of lanthanide metals. This result implies the possibility of the trinuclear [L$_2$Zn$_3$] unit that can regulate aggregation depending on the external stimuli. Further investigation on the synthesis and function of paramagnetic 3d–4f systems is now in progress.

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