A Molecular Structure of Bis(*N*-octylethylenediamine)zinc(II) Nitrate in Crystal and the Aggregations in Wet Chloroform and Benzene Solutions

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Zinc complex with *N*-octylethylenediamine(= OE), $Zn(OE)_2(NO_3)_2$, was prepared and its molecular structure was determined on the basis of an X-ray crystallographic analysis. It was revealed that in the octahedral molecular structure the nitrato groups are *trans* and the octyl chains are *transoid*. Extensive aggregations of this complex in wet chloroform and wet benzene systems were also studied using ^1H NMR self-diffusions for the solvents and the zinc complex.

Surfactants of metal complex ions are expected as components of synthetic assemblies having highly organized functions.[1] The metal complexes are furthermore able to provide particular insight into the delicate balance between hydrophobic and electrostatic interactions existing for amphiphilic ions. One (M.I.) of the present authors has found unique solubility and aggregation behavior of $Zn(OE)_2Cl_2$ using multinuclear NMR spectroscopies and vapor pressure osmometry;[2] the characteristic aggregation behavior is due to the unique structure arising from the metal complex moiety. More recently, double-chain(bis(*N*-*n*-alkylethylenediamine)) surfactant Co(III) complexes have been shown to have a unique character that the *cisoid/transoid* diastereomer ratio in solution depends on the water/ethanol molar ratios because of the hydrophobic interactions between the alkyl chains of the ligands in water.[3] Surfactants of bis(long-chain carboxylate) transition metals, so-called metallosoaps, have been extensively used for industrial purposes; they are almost non-electrolytes having strong metal-ligand ionic bonds and it has not been established whether the geometry of the alkyl chains in the crystal is *cisoid* or *transoid* since it is difficult to get their single crystals. Structurally characterized examples for metallosoaps are limited only for a few cases.[4,5]

In the present study, we have obtained single crystals of $Zn(OE)_2(NO_3)_2$ which can be regarded as a kind of metallosoaps, and could be subject to an X-ray crystallographic analysis. The $Zn(OE)_2$ complex was prepared by mixing aqueous $Zn(NO_3)_2$(0.2 mol dm^{-3}) and OE(0.6 mol dm^{-3}) solutions in 3 : 2(v/v) ethanol-water for one day. The solution was evaporated to dryness. The residual water and the free OE were removed furthermore from coevaporation with benzene for 4-5 times. The crystals obtained from benzene were recrystallized 3-4 times from ethanol to give single crystals suitable for an X-ray diffraction study.[6] An ORTEP drawing of the nitrato complex is given in Figure 1. The coordination geometry around a zinc(II) atom is octahedral and the octyl chains are *transoid* in contrast to the *cisoid* for dinitrobis(*N*-*n*-alkylethylenediamine)cobalt(III) nitrate in the crystal.[3] Figure 2 shows a packing diagram of the Zn(II) complex, indicating unique respective hydrophobic and hydrophilic stackings of the octyl and zinc-nitrate parts along an *a* axis.

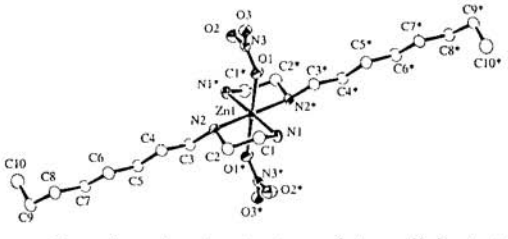

Figure 1. A molecular structure of *trans*-dinitrato-*transoid*-bis(*N*-octylethylenediamine)zinc(II) complex. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°); Zn(1)-O(1)= 2.280(2), Zn(1)-N(1)= 2.068(2), Zn(1)-N(2)= 2.184(2), O(1)-Zn(1)-O(1)= 180.0, N(1)-Zn(1)-N(2)= 82.60(7).

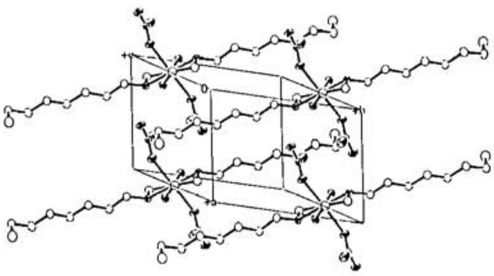

Figure 2. A crystal packing diagram for the Zn(II) complex.

The complex of *trans*-dinitrato-*transoid*-bis(*N*-octylethylenediamine)zinc(II) is readily soluble in methanol and ethanol, and is significantly soluble in chloroform. The solubility to chloroform was increased with an addition of water. Although this complex is sparingly soluble in water and benzene, the solubility becomes appreciable in some ratios of water-benzene mixed solvents. The aggregation behavior of this complex in dry(or wet) chloroform and wet benzene was also studied by measurements of self-diffusion coefficients using pulsed-gradient spin-echo (PGSE) technique[7] with ^1H NMR on a JEOL FX 90 NMR spectrometer operating at 90 MHz for protons. The spectrometer was equipped with an apparatus producing a field gradient in the range of 0.6-1 T m^{-1}. The attenuation of the spin-echo amplitude after Fourier transformation was sampled as a function of the duration, δ, of the applied gradient pulses ($0.2 \le \delta \le 7.5$ ms). We followed ^1H NMR signals for the H_2O, $CHCl_3$, and C_6H_6 solvents, and for the methylene protons of the zinc(II) complex. In order to obtain more clear H_2O ^1H spin-echo signals, we used $CDCl_3$ and C_6D_6 solvents, except for the measurements of diffusion coefficients of $CHCl_3$ and C_6H_6 solvents. The differences in the chemical shifts between H_2O and the methylene protons of the zinc(II) complex were 2.8

and 3.1 ppm in the chloroform and benzene systems, respectively. The ^1H spin-echo signal of H_2O was disappeared in the chloroform system at the concentrations above 1.9 mol kg^{-1} by being covered with that of the methylene protons of the zinc(II) complex. Temperature was controlled 27±0.5 ℃ with a JEOL GVT2 temperature control unit. The accuracy of the measured diffusion coefficients is estimated to be better than ±5%.

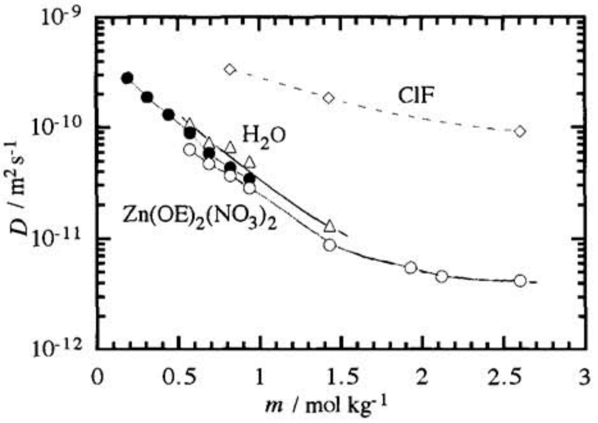

Figure 3. Diffusion coefficients for the Zn(II) complex(●) in the dry chloroform, and those for the Zn(II) complex(○), water(△), and chloroform(◇) in the wet chloroform systems(27 ℃). The concentrations of the complex are expressed for chloroform in the wet system. In the wet system, the [water]/[complex] ratios are 1-2 and 3.1-3.3 at concentrations below and above 1 mol kg^{-1}, respectively.[9] The ^1H spin-echo signals of water were not observed by being covered with those for the methylene protons of the complex above 1.9 mol kg^{-1}.

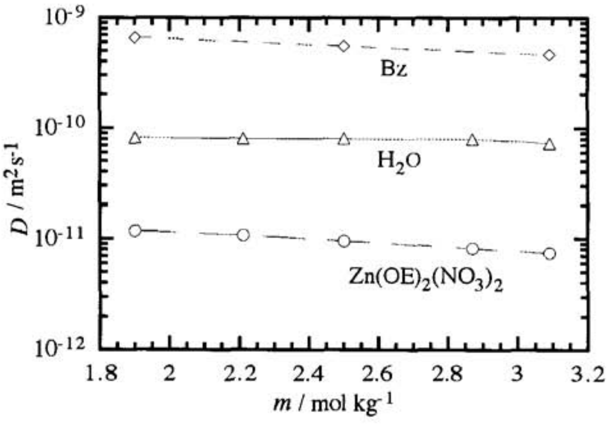

Figure 4. Diffusion coefficients for the Zn(II) complex, water, and benzene(Bz) in the wet benzene systems(27 ℃). The concentrations of the complex are expressed for the benzene. The [water]/[complex] ratios are almost kept constant as 4.6-4.7.

Figure 3 shows the result for water and the Zn(II) complex in the chloroform system as a function of the complex concentrations. Appreciable decrease in the water diffusion coefficients compared to that for pure water (2.32×10^{-9} m^2s^{-1}) means that the motions of water molecules are largely restricted in the presence of the zinc(II) complex. Figure 3 furthermore shows that an addition of water slightly (20-30%) retards the diffusion of the Zn(II) complex in the concentration ranges of 0.5-1.0 mol kg^{-1}. On the basis of the two-state(free and aggregated) model for the diffusion processes of the surfactants,[7,8] this result suggests that the ratio of the aggregated surfactants may increase with an addition of water at the same concentrations of the zinc(II) complex for chloroform. The appreciable increase in the solubility of the zinc(II) complex to chloroform with an addition of water would be due to water-assisted aggregations and is consistent with the present result. The differences in the diffusion coefficients between the Zn(II) complex and water are significantly smaller in the chloroform system compared to the benzene system(Figure 4); this trend means that the Zn(II) complex and water tend to move together to a larger extent in the former system. Figure 4 shows the similar plot for the benzene system. In order to form homogeneous and transparent phase(L_2 phase), larger amounts of water are necessary and the concentration range of the Zn(II) complex for the L_2 phase is much narrower in the benzene system than in the chloroform system. In both systems the diffusion coefficients for organic solvents were much larger than those for water and therefore we can presume that reverse micelles may be largely formed in the higher concentration ranges(above 1 mol kg^{-1}).

At the present stage, we cannot clearly say whether the *transoid* geometry in the crystal state is retained or is changed to the *cisoid* isomer in the solutions. However, it is possible that the *transoid* geometry in the crystal state will make this complex sparingly soluble both in water and in hydrocarbons, since the *cisoid* geometry may be more favorable for dissolving in water or hydrocarbons.[3]

References and Notes

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4 Cambridge Crystallographic Structure Database (~1997).

5 For examples, see: (a) M. Petric, I. Leben, and P. Segedin, *Polyhedron*, **14**, 983(1995). (b) M. Petric, I. Leben, and P. Segedin, *Polyhedron*, **15**, 4277(1996).

6 Crystal data : $C_{20}H_{48}N_6O_6Zn$, M=534.02, triclinic, space group $P1$ (No. 2), a=7.172(6) Å, b=14.339(4) Å, c=6.900(6) Å, α = 94.70(5)°, β= 109.35(5)°, γ =84.30(5)°, V =665.3(8) $Å^3$, Z=1, and D_{calcd}=1.333 g cm^{-3}. A colorless block-shaped crystal (0.48 x 0.43 x 0.20 mm) was fixed on the top of a glass fiber with Paraton N oil, and 2336 reflections ($4<2\theta<50°$) were measured on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation at -118 ℃. An absorption correction by Ψ-scan method was applied (μ=9.67 cm^{-1}). The structure was solved by direct methods using the program SIR92 and was refined with full-matrix least-squares techniques to R=0.028 and R_w=0.035 for 2108 independent reflections with $I>3\sigma(I)$. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located from difference Fourier syntheses and were refined isotropically. All calculations were carried out on a Silicon Graphics O2 Station with teXsan program system.

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9 Water content of the dry chloroform is below 0.1% and therefore the [water]/[zinc complex] ratios are below 0.5 in this system.