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Conformational Change of a Macrobicyclic Complex. Structure of Free Ligand and Interactions with DMSO

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An X-ray crystal structure determination has been carried out on a free macrobicyclic ligand pytren (1,4,12,15,18,26,31,39,42,43,44,-undeca-azapentacyclo-[13.13.13.$1^{6,10}$.$1^{20,24}$.$1^{33,37}$]-tetratetraconta-4,6(42),7,9,11,18,20(43),21,23,25,31,33(44),34,36,38-pentadecane). It shows a different conformation from its Ba complex for direction of lone pairs of the six imine nitrogen atoms. Addition of dimethylsulfoxide (DMSO) to the acetonitrile solution of the Ba complex causes the conformational change of pytren ligand and driving out of the Ba ion from the cavity due to interactions of the complex with DMSO.

Conformational changes of macrocyclic ligands upon complexation are of current considerable interest.[1] Particularly for macrobicyclic ligands in which two imino groups connected with both sides of aromatic rings, there are several possible arrangements, i. e. lone pairs on the imine nitrogens direct inward to the center of the cavity or outward.[2] We have been studying the structure of a macrobicyclic ligand, pytren,[3] and previously reported the structure of the Ba-pytren complex.[4] The Ba complex has a "convergent"[2] structure in which all lone pairs on the imino nitrogen atoms point toward the center of its cavity. While it was reported [5] for the Na complex of pytren that the conformation of the ligand is a "half convergent" type in which the three lone pairs in one of the tren moiety turn toward the inside of the cavity, the rest toward outside of the cavity. We now report that the free ligand has a divergent conformation. Furthermore, we found an interesting effect of aprotic solvents.

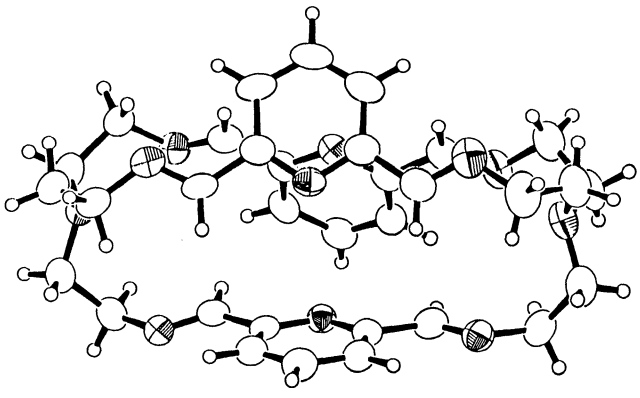

Fig. 1. ORTEP drawing of pytren ligand.
Nitrogen atoms are shown as cross-hatched.

Free pytren was obtained by condensation of tris(2-aminoethyl)amine (1.0 mmol) with 2,6-pyridinedicarboxaldehyde (1.5 mmol) in methanol (20 ml) for 3 h at 40 °C without template.[4] After evaporation under reduced pressure, DMSO (1 ml) was added to the syrup, free pytren crystals was isolated. The crystals of pytren can only be obtained by a recrystallization from methanol containing a small amount of DMSO. Figure 1 shows an ORTEP drawing of pytren.[6] We expected that the structure of the free ligand would be unsymmetrical half convergent type since the IR spectrum of the compound shows more splitting bands than that of the Ba com-

plex.[4] However, the X-ray analysis shows that free pytren has a divergent structure. Although the Ba complex of the convergent structure has a spherical cavity, the cavity of free pytren seems to be as a column. The three nitrogens in pyridine rings are located nearly in a circumference, the radius of which is 2.26 Å (2.99 Å in the Ba complex). Therefore the cavity seems to be too small for its complexation. In spite of necessity of DMSO for the crystallization, no solvent molecules are found around the pytren or in the cavity. The X-ray analyses of all the possible three conformers around a conjugated moiety of pytren are completed by the present work.

These two different conformers, convergent and divergent, can be distinguished clearly by the spectral data. The order of ^{1}H-NMR peaks for the pyridine and imine moieties of the free ligand is different from that for the Ba complex (see Fig. 2a and 2d).[7] It is reasonable that the spectra of the Ba complex and the free ligand are ascribed to those of the convergent type and the divergent type, respectively. The Na complex gives different broad ^{1}H-NMR peaks from the spectra of the Ba complex and the free ligand.[8] The UV-VIS spectrum of the Ba complex is different from that of the free ligand.[9] The difference may be ascribed to the conformational difference of the N=C-C_5H_3N-C=N chromophore.

When ^{1}H-NMR of the Ba complex is measured in CD_3CN with increase of DMSO concentration, peaks for the Ba complex are disappearing gradually, and new peaks appear which have the same chemical shifts as the free ligand (Fig. 2). The UV-VIS spectrum of the Ba complex also changes into that of the free ligand. When an excess amount of $Ba(ClO_4)_2$ was added to the solution containing DMSO, both of the NMR and UV-VIS spectra again returned to those of the convergent conformation. We conclude that adding DMSO to the solution of the Ba complex causes the change of the conformation from convergent into divergent and that Ba^{2+} which should be encapsulated tightly is driven out. Furthermore, the ligand encapsulates Ba^{2+} again with increase of the Ba^{2+} concentration (Fig. 3). The similar effect is also observed for other dipolar aprotic solvents, the dipole of which is

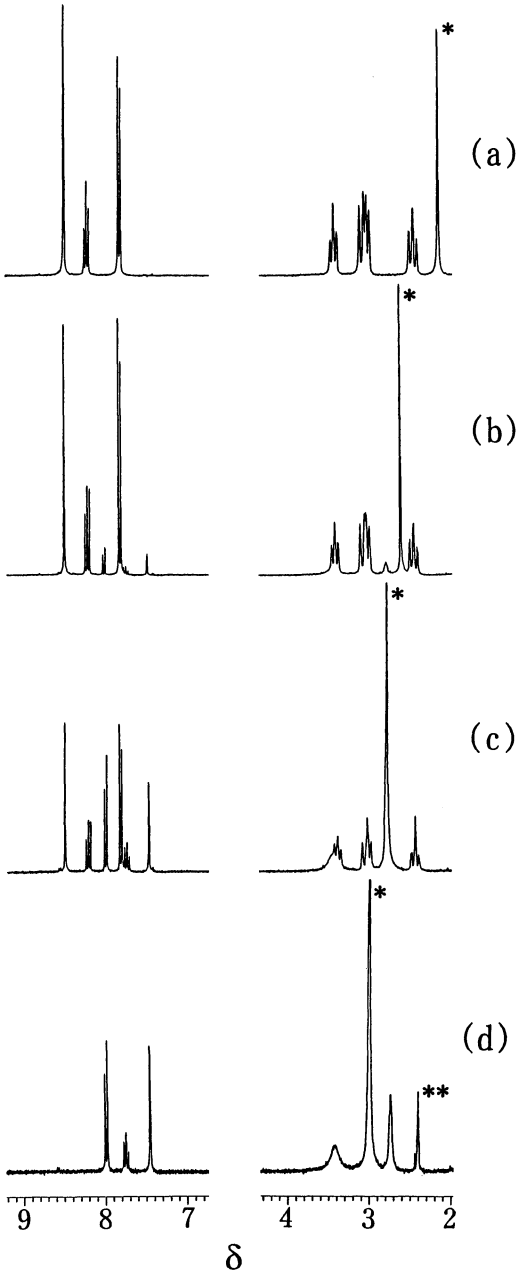

Fig. 2. The change of ^{1}H-NMR for [Ba(pytren)]$(ClO_4)_2$ in CD_3CN solution with addition of DMSO. The quantity of DMSO added is (a), 0 equiv.; (b), 64 equiv. (1.50 mol dm^{-3}); (c), 117 equiv. (2.74 mol dm^{-3}); (d), 300 equiv. (7.02 mol dm^{-3}) with respect to Ba complex. The molar concentration of DMSO is shown in parenthesis. Peaks * and ** indicate water and DMSO in the solution, respectively. (d) is the same spectrum as that of the free ligsnd.

exposed at the surface of the molecule, such as HMPA, DMF, and DMA in contrast to the embedded dipole of acetonitrile.[10] It is expected that this effect occurs by solvation of metal ions with polar solvents generally seen for many cryptands. However, in pytren complex, DMSO-ligand interaction is also important, because DMSO was reported to interact with nitrogen atoms of the pyridine rings and imino groups via dipole interactions.[11,12] Actually, ^{1}H-NMR of the free ligand which was measured with increase of DMSO concentration showed that only the peaks

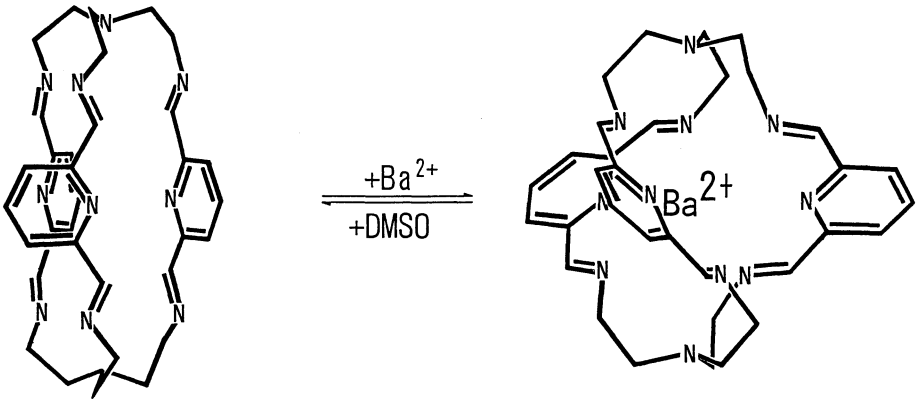

Fig. 3. Scheme for reversible conformational change of pytren.

of the imine proton and the proton on the meta-position of the pyridine rings shifted although the peak of the para-proton hardly shifted.

It is well known that association of DMSO molecules easily occurs at 5-10% molar fraction in organic solvent,[11a] and the donicity of DMSO is enhanced by this association.[11b] Figure 4 shows the conversion ratio of the divergent form against the total pytren quantity calculated from the ratio of the ^{1}H-NMR peak area at various concentrations of DMSO in CD_3CN. The conversion begins when the concentration of DMSO is beyond 1 mol dm^{-3} (ca. 5% molar fraction). In UV-VIS spectral measurements, the conversion occurs at the same region although the concentration of the complex is only $1/10^3$ as compared with the condition of NMR. Moreover, DMSO-ligand interaction studied by ^{1}H-NMR also begins at the same region. Therefore, associated DMSO would be concerned in the conversion of pytren ligand. It was also reported that the donicity of DMSO is also enhanced by interaction with nitrogen atoms of pyridine and imine.[12] The conformational change may be given by tripartite co-operative interactions among pytren, DMSO, and Ba^{2+}. Attempts to determine the equilibrium constants have been unsuccessful.

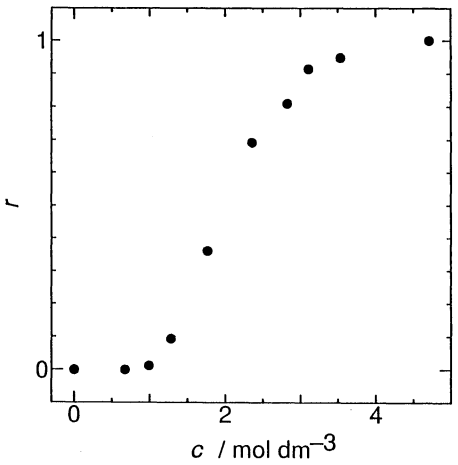

Fig. 4. The ratios (r) of divergent conformation to sum of both conformers are plotted against the concentration (c) of DMSO. A concentration of the Ba^{2+} complex is 2.34×10^{-2} mol dm^{-3}.

In conclusion, the conformation and metal complexation can be controlled by using the interaction between ligand and DMSO. By utilizing the interaction, we may design a molecular system which draws out metal ions as the

system demands. Detailed studies of the interaction are in progress.

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6) Crystal data: $C_{33}H_{39}N_{11}$, M=583.70, monoclinic, space group $P2_1/c$, a = 9.619(3), b = 19.041(5), c = 18.173(2) Å, β = 94.48(2)°, V = 3318(1) $Å^3$, Z = 4, D_{calcd} = 1.168 g cm^{-3}, F(000) = 1232, Data collected with Cu-Kα (λ=1.54178Å) radiation on a Rigaku AFC5S diffractomater; scan speed: 4° min^{-1}; Scan width: $3° < 2\theta < 120°$; 5454 measured intensities, 1637 with $I > 3\sigma(I)$. The structure was solved by direct method using a program package, TEXSAN. R=0.044, Rw=0.022.

7) NMR Data for pytren in CD_3CN at room temperature: ^{1}H-NMR δ 8.04 (d, 6, CH), 7.75 (t, 3, CH), 7.51 (s, 6, CH), 3.47 (br, 12, CH_2), 2.80 (br, 12, CH_2). For $[Ba(pytren)]^{2+}$ in CD_3CN at room temperature: ^{1}H-NMR δ 8.50 (s, 6, CH), 8.22 (t, 3, CH), 7.81 (d, 6, CH), 3.41 (m, 6, CH_2), 3.04 (m, 12, CH_2), 2.45 (m, 6, CH_2). At -40 °C, the peaks of 3.47 and 2.80 of pytren are sharpened with splitting and a multiplet peak appears at 3.19, however, the peaks of the Ba complex have no change.

8) NMR Data for $[Na(pytren)]^+$ in CD_3CN at room temperature: ^{1}H-NMR δ 8.28 (br, 6, CH), 7.80 (br, 9, CH), 3.36 (br, 12, CH_2), 2.80 (br, 12, CH_2). The exchange of the Na^+ between complexed and uncomplexed positions is reported in ref 3. The broad peaks would be given by a conformational change of pytren with the exchange.

9) UV-VIS spectra data for pytren in CH_3CN at 20 °C: 259 (ε 1.90×10^4), 277 (1.67×10^4), 285 (1.66×10^4) and 295 nm (1.17×10^4 dm^3 mol^{-1} cm^{-1}). For $[Ba(pytren)]^{2+}$ in CH_3CN at 20 °C: 303 (2.00×10^4) and 315 nm (sh, 1.51×10^4 dm^3 mol^{-1} cm^{-1}).

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