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A cryptand containing three diiminopyridyl units; aromatic-aromatic interaction and the stability of the complexes

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The solution properties of a hexaimino cryptand containing 2,6-diiminopyridyl units have been investigated by NMR, UV-VIS absorption and luminescence spectroscopy. The difference in the NMR and UV spectra of the Ba^{2+} complex and the cryptand is attributed to the conformational change of the diiminopyridyl group. The luminescence spectra of the compounds show near-UV bands and unexpected low-energy bands. The former is attributed to the normal π-π^* transition, while the origin of the low-energy bands is discussed in terms of *inter*- and *intra*-molecular aromatic-aromatic interactions. The *inter*-molecular interaction is important in the free ligand, however, *intra*-molecular interaction is suggested in the Ba^{2+} complex. Further, the specific conformational change of the Ba^{2+} complex in DMSO-acetonitrile solution is investigated by the measurements of the stability constant of the Ba^{2+} complex in various DMSO concentrations. The large decrease over 4.0 in logK is found only for the Ba^{2+} complex. The behavior is explained by the factors brought about the nature of DMSO and the interactions among the diiminopyridyl units, DMSO and the Ba^{2+} ion.

INTRODUCTION

A variety of hexaimino cryptands containing aromatic rings have been well studied owing to the easiness of the preparation *via* a condensation of tri-amine and di-aldehyde.[1] These studies also contribute to the development of supramolecular chemistry.[2] We previously reported the electronic properties of a 18-membered tetraimino macrocyclic complexes of lanthanides.[3] As an extension of the work, we have also reported the structure and properties of tripyridyl hexaimino cryptand, pytren.[4,5]

A mononuclear Ba^{2+} complex of pytren was prepared by the [2 + 3] condensation of tris(2-aminoethyl)amine (tren) with 2,6-pyridinedicarboxaldehyde (pdca) in the presence of Ba^{2+} as a template.[5a] The structure is shown in Figure 1.[5a] The Ba^{2+} complex has a convergent (C-type) structure in which all the lone pairs on the imino nitrogen atoms point toward the center of the cavity. On the other hand, the free ligand, pytren, can be prepared by the [2 + 3] condensation without any template. As shown in Figure 2, the ligand shows divergent (D-type) structure in which all the lone pairs on the imino nitrogen atoms point toward the outside of the cavity.[5b] Thus the conformation around the $C_{imino} - C_{2\text{-}pyridyl}$ bond in the Ba^{2+} cryptate is quite different from that in the free ligand. The Ba^{2+} cryptate of pytren has a 'propeller-like' structure with regard to the three diiminopyridyl moieties (see Figure 1), and therefore intramolecular π-stacking interactions are expected in the Ba^{2+} cryptate. Whereas, no intramolecular π-π interactions are found in the crystal of the free pytren (see Figure 2). The dinuclear Ag^+ complexes were also reported,[1a,d] although the structure remains unclarified. The dinuclear Ag^+ complex is expected to have a C-type structure which can be deduced from the fact that a Cu^+ cryptate of an analogous cryptand has a C-type structure.[1h] Each Ag^+ ion must be bound to four nitrogen atoms of each tren moiety.

The present study shows that the diiminopyridyl group introduced in the cryptands provides many interesting features both for the cryptands and for its cryptates; *i.e.* electronic absorption and luminescence properties related to the $\pi - \pi^*$ transitions, and *inter*- and *intra*-molecular $\pi - \pi$ interactions. We have obtained a new crystal of the free pytren from an acetonitrile solution,

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*To whom correspondence should be addressed.

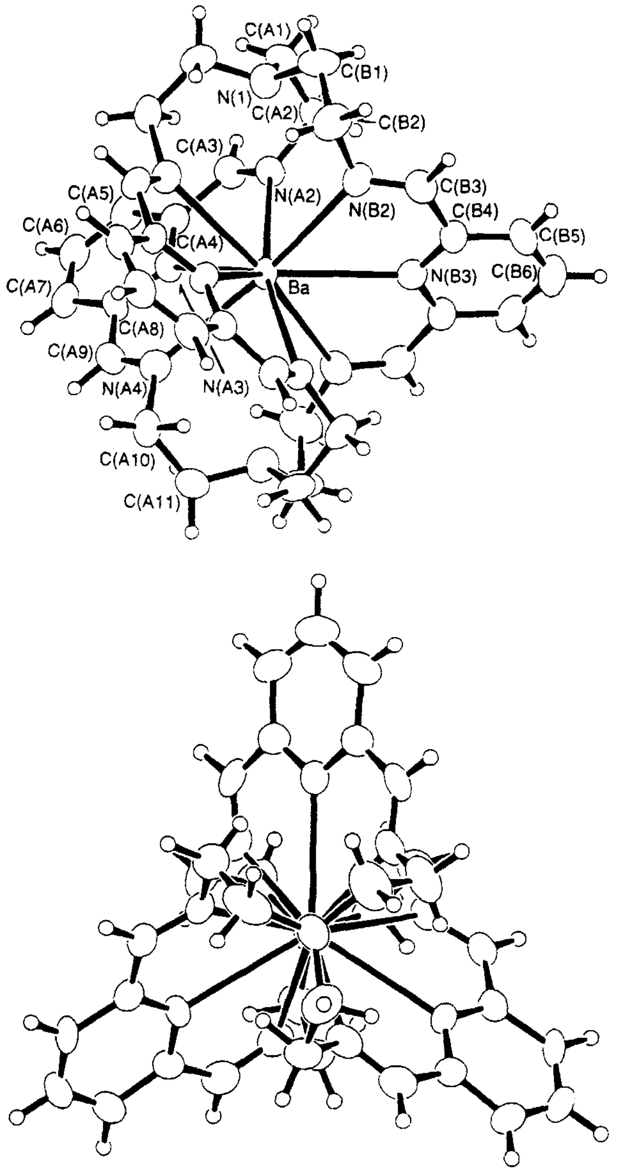
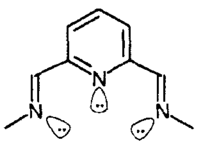
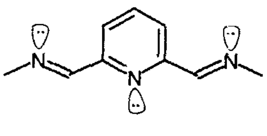


Figure 1 ORTEP drawings of $[Ba(pytren)]^{2+}$.[5a] (a) A side view (b) A view down the N(bridgehead) ... N(bridgehead) axis.

and found intermolecular aromatic interactions in the crystal. The purpose of this study is to clarify the electronic and structural properties of the pytren complexes including the interactions between the aromatic groups. We will also show that the specific interaction between DMSO molecules and $[Ba(pytren)]^{2+}$ largely affects the thermodynamic stability of the cryptate.



C-type



D-type

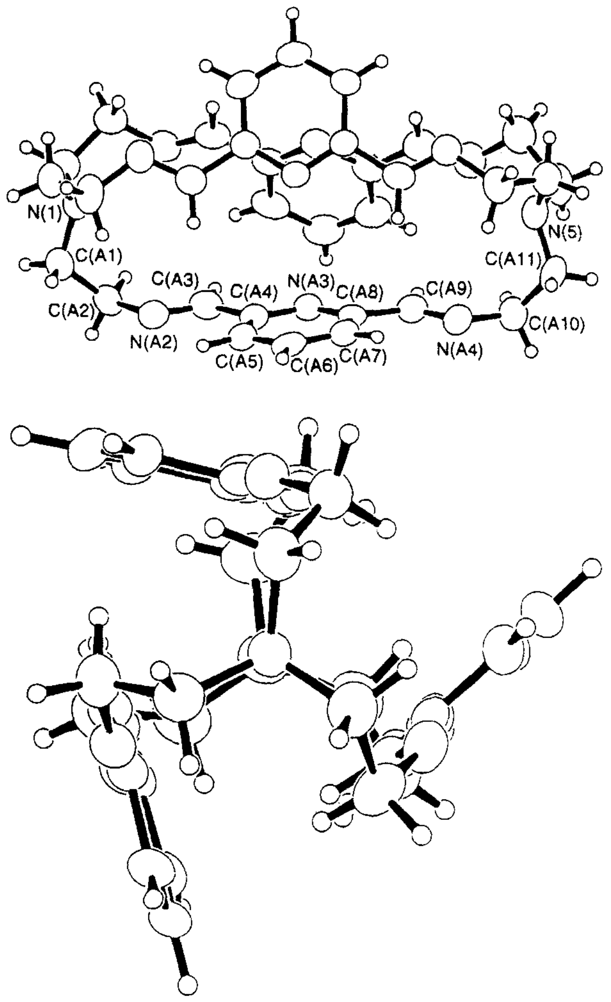


Figure 2 ORTEP drawings of free pytren ligand.[5b] (a) A side view (b) A view down the N(bridgehead) ... N(bridgehead) axis.

RESULTS AND DISCUSSION

Conformations of the macrobicyclic ligand in solution.

^{1}H-NMR spectra of the free ligand and the Ba^{2+} complex consist of two or three sets of peaks at 2.4–3.5 ppm corresponding to the methylene protons of tren, and three sets of peaks for the imino and pyridyl moieties at 7.8–8.5 ppm.[5b] Further, only six ^{13}C-NMR peaks are observed for both the compounds. Therefore both the complex and the free ligand have D_3 symmetry in solution on the NMR time scale. However, their signal patterns of the conjugated groups are different with each other, *i.e.*, the order of three sets of peaks is different between them. This fact suggests that these compounds possess different structures around the diiminopyridiyl moiety. It is known for usual cryptands having oxygen donor atoms that the free cryptands show the D-type conformation in solution.[6] Our previous X-ray studies have shown that the free pytren and Ba^{2+} complex takes D-type and C-type conformations, respectively. Therefore, it is reasonable to consider that they possess D-type and C-type conformation also in solution respectively, and the spectral difference between the two compounds is attributable to the structural difference. In the ^{1}H-NMR spectra of the free ligand, the two broad methylene peaks observed at room temperature show splitting at −40°C, but the sharp peaks of the conjugated moieties remains unchanged. Therefore the conformations of the conjugated moieties are rigid even at room temperature, but the conformations around the tren moieties of the free ligand are fluxional at room temperature but becomes rigid at −40°C. In contrast with this dynamic behavior, the ^{1}H-NMR spectrum of the Ba^{2+} cryptate shows no temperature dependence down to −40°C and represents the presence of four independent methylene protons. This fact indicates that the propeller-like structure of the Ba^{2+} cryptate observed in the X-ray study (Figure 1) is rigid and preserved in solution even at these temperatures. In addition, since the NMR peaks of the Ag^+ complex show the same order as that of the Ba^{2+} complex, it is concluded that the Ag^+ complex has a C-type conformation.

Crystal structure of the free ligand obtained from acetonitrile.

The free pytren ligand crystallized from methanol has a monoclinic system as previously reported.[5b] The second crystal form of pytren obtained from acetonitrile possesses the trigonal crystal system. Although the basic structure of the molecule is similar to that of the crystal obtained from methanol, the arrangement of the molecules in the crystal is quite different. No distinct intermolecular interactions are observed in the previous crystal except a weak hydrogen bond between the imino nitrogen atom and the 4-pyridyl hydrogen atom (the distance between the nitrogen atom and the 4-carbon atom is 3.43 Å). On the other hand, strong intermolecular aromatic interactions are found in the new crystal (Figure 3a, b and c). One of the conjugated planes is associated with that of the next molecule through an inversion center. These two molecules are stacked with each other with a face-to-face interaction. The distance between the conjugated planes is 3.4 Å.

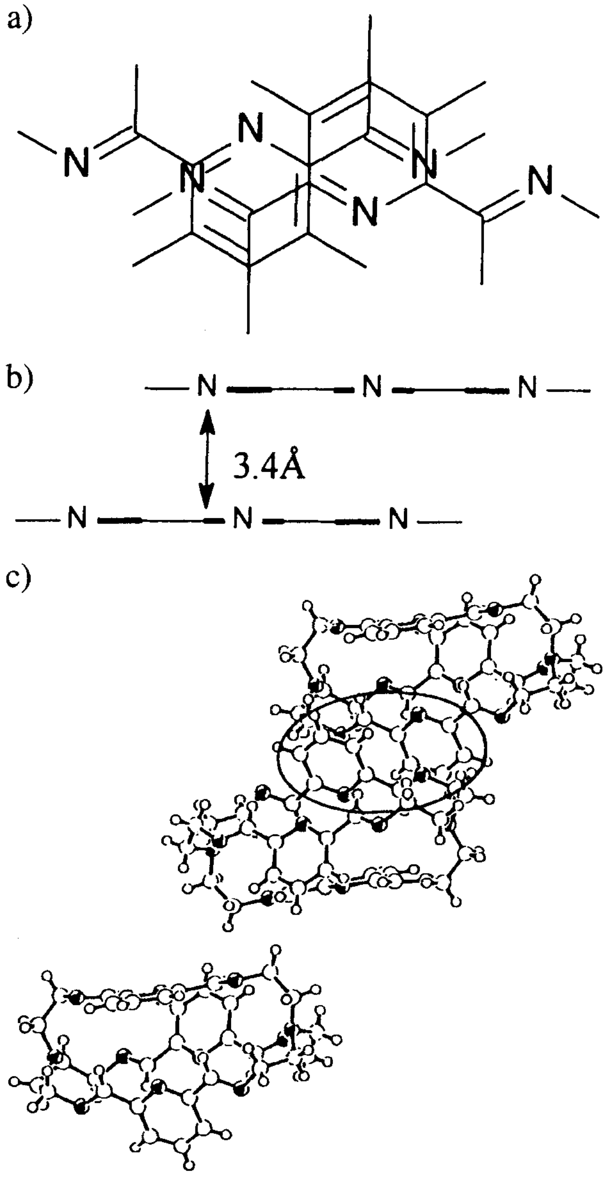


Figure 3 The structural models of diimino-pyridyl units in crystals obtained from acetonitrile. (a) The enlarged view of the oval area shown in (c). The overlapping of parallelly oriented diimino-pyridyl planes. The distance of them is 3.4 Å. (b) A side view of (a). (c) A part of the crystal packing in the crystal obtained from acetonitrile.

Aggregation of a tetraimino macrocyclic complex.

Before examining the intermolecular interactions between the diiminopyridyl groups of pytren, we first examine the aggregate properties of an 18-membered macrocyclic Ca^{2+} complex which has a simplified structure containing the same conjugated units (pyen, see Figure 4). The absorption intensity around 300 nm obeys Beer's law but that in the 360–380 nm region does not. In the latter region, increase in the molar absorption coefficient is observed at high molarities (> 10^{-4} M). Therefore, this behavior must arise from the oligomerization reactions via face-to-face interactions between the aromatic systems. On the other hand, excitation of the complex at 360 nm results in a luminescence band at 500 nm in addition to an expected $\pi^* \rightarrow \pi$ luminescence band at 400 nm (Figure 4). The luminescence intensity at 500 nm has been confirmed to exhibit a non-linear dependence on the complex concentration (10^{-3}–10^{-5} M), and considerably increases at high concentration. Therefore the low-energy luminescence would be originated from the aggregated species linked by the aromatic-aromatic interaction between the diiminopyridyl moieties.

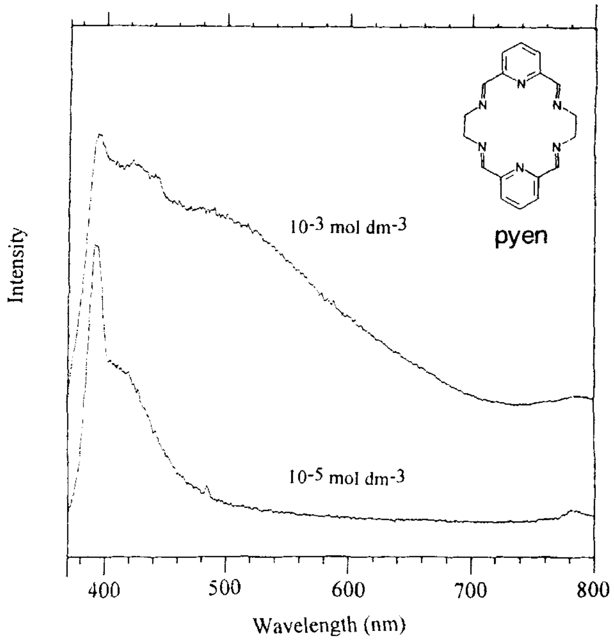


Figure 4 Emission spectra of $[Ca(pyen)]^{2+}$ in acetonitrile. (a) 1.00 × 10^{-3} M (b) 1.00 × 10^{-5} M.

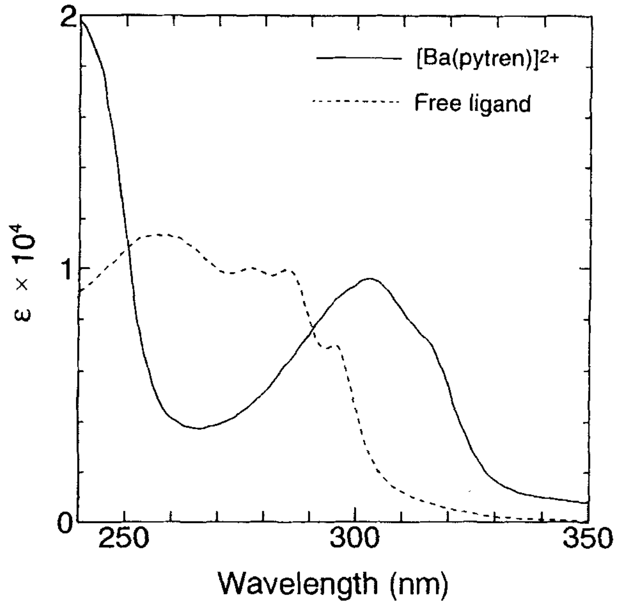


Figure 5 UV absorption spectra of $[Ba(pytren)]^{2+}$ (——) and the free pytren ligand (-----) in acetonitrile. The concentrations of the compounds are 1.00 × 10^{-4} M.

Absorption and luminescence of the free pytren.

The absorption band of the free ligand seen in the UV region can be assigned to a singlet $\pi - \pi^*$ transition in the $N{=}C{-}C_5H_3N{-}C{=}N$ chromophore.[3] There is a distinct difference in the spectra between the Ba^{2+} complex and the free ligand, as shown in Figure 5. The spectrum of the free ligand shifts to higher energy site. As described in the former section, the conformation around the chromophores in solution is D-type for the free pytren and C-type for the Ba^{2+} complex, which must be responsible for the spectral difference.

The free ligand exhibits luminescence upon the irradiation with UV light (Figure 6) whose band shape strongly depends on the excitation energy. Two emission bands of the free ligand centered at 370 nm and 530 nm are found upon the irradiation with 300 nm, however the irradiation at 400 nm gives an emission band at 480 nm. The life times of the luminescence bands are short ($\tau <$ 10 ns) to be measured. The excitation spectrum monitored at 370 nm shows a band maximum at 315 nm. The relatively small Stokes-shift and the short life-time suggest that the band at 370 nm corresponds to a $\pi^* \rightarrow \pi$ fluorescence of the diiminopyridyl moiety of the ligand. The intensity of the low-energy luminescence band (530 nm) shows a non-linear dependence on the concentration of the free ligand and the observation is strongly dependent on the solvent. The intensity ratio of the low-energy band to the high-energy band increases as the pytren concentration is increased in acetonitrile. The intensity of the low-energy band is small in methanol and disappears in cyclohexane. The excitation spectra monitored at 530 nm shows a 500 nm band as well as a 300 nm band (Figure 7). Further, we have confirmed that excitation with 500 nm light gives the emission band at 530 nm. The enhancement of the molar absorption coefficient (ϵ) at 500 nm is observed with increase of the concentration (10^{-5}–10^{-3} M), while ϵ in the UV region is constant in the range. The crystallographic result indicates that the three diiminopyridyl planes are exposed at surface of the molecule in the free ligand (Figure 2b), and intermolecular interactions are observed between the planes. These facts suggest that the absorption and luminescence in the low-energy region are originated by the *inter*-molecular aromatic-aromatic interactions of the diiminopyridyl chromophores.

The origin of the luminescence band at 480 nm remains ambiguous. The excitation spectrum of the free ligand monitored at 480 nm shows a band at 350 nm. Since both the absorption intensity at 350 nm and the emission intensity at 480 nm nearly show a linear dependence on the concentration of pytren, the bands should not be related to the aggregation phenomena.

Absorption and luminescence of $[Ba(pytren)]^{2+}$.

The UV absorption band (304 nm) of the Ba^{2+} complex shows a bathochromic shift by only 4 nm compared to the 18-membered macrocyclic $[Ba(pyen)]^{2+}$ complex (Figure 5). The band (300–304 nm) is characteristic of the C-type diiminopyridyl group. Further, a weak and broad absorption band, which is not found in the $[Ba(pyen)]^{2+}$ complex, is observed as a long tail of the UV band until 530 nm in the spectrum of $[Ba(pytren)]^{2+}$.

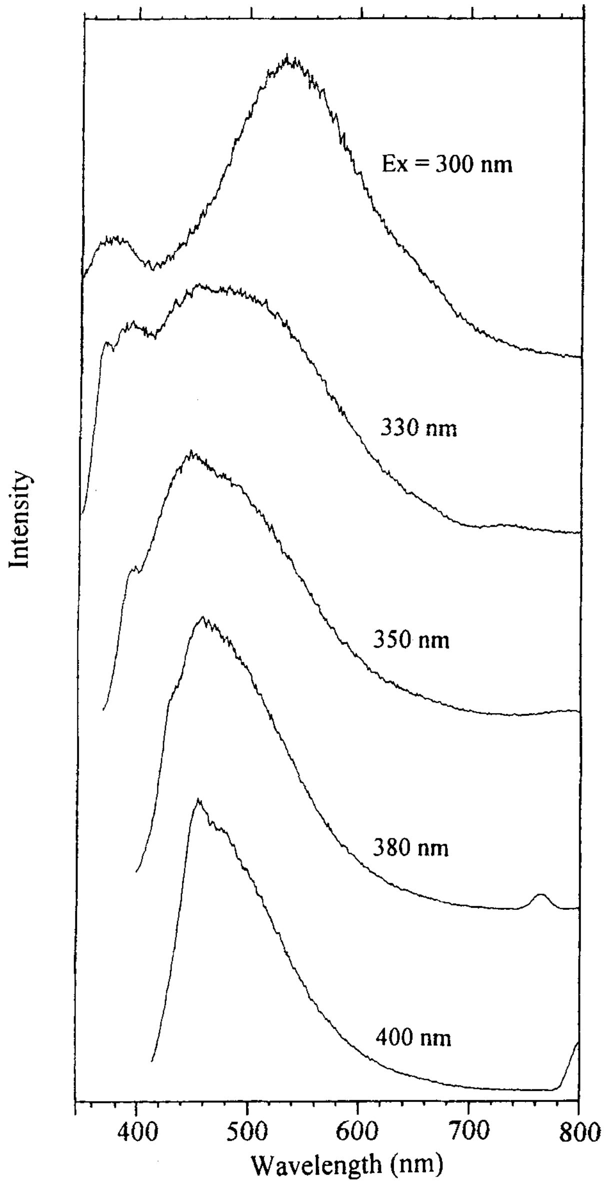


Figure 6 Emission spectra of the free ligand in acetonitrile (1.00 × 10^{-4} M).

The absorption intensity at the broad band follows Beer's law.

The Ba^{2+} complex shows an emission band centered at 500 nm with a shoulder at 390 nm with excitation at 300 nm (Figure 8). The shoulder (390 nm) would be assigned to $^1\pi^* \rightarrow \pi$ transition of the diiminopyridyl moiety, as discussed for the 370 nm band of the free ligand. The 20-nm red shift compared to that of the free ligand agrees with the corresponding shift observed in their UV absorption band. The main band of the luminescence in the low-energy region (500 nm) is characteristic of the Ba^{2+} complex. Although the free pytren and the macrocyclic $[Ca(pyen)]^{2+}$ complex show a concentration-dependent luminescence in the low-energy region, the luminescence intensity at 500 nm for the Ba^{2+} cryptate is linearly changed with the complex concentration. The results of the absorption and emission intensity in low-energy region indicates that no aggregation occurs for the Ba^{2+} complex. It is not likely that this low-energy luminescence (500 nm) corresponds to the normal $\pi - \pi^*$ transition of the diiminopyridyl chromophore having no aromatic-aromatic interactions. Therefore, we rather suggest that this low-energy band must arise from the *intra*-molecular aromatic-aromatic interactions formed between the diiminopyridyl moieties which are located in a propeller-like arrangement (Figure 2).

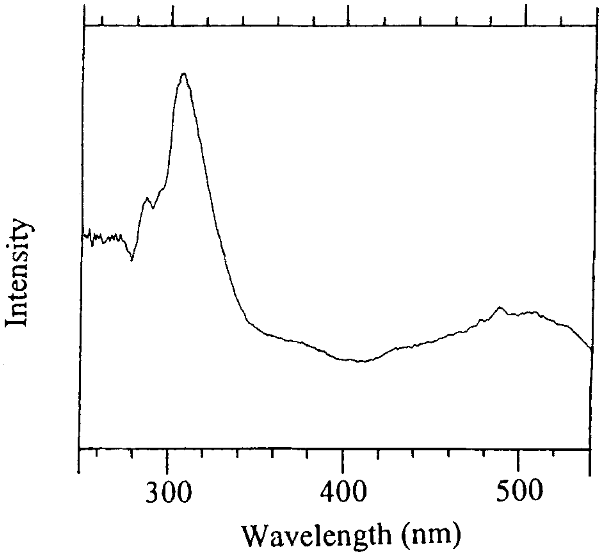


Figure 7 Excitation spectra of the free ligand in acetonitrile (1.00 × 10^{-4} M).

Stability of the Complexes and Complex-Solvent Interaction.

We have reported that a reversible conformational change between the C-type and D-type structures occurs in DMSO-CH_3CN mixed solvent system.[5b] The similar conformational change is known for many crown ethers and cryptands.[6] However some specific characteristics have been found in the present system; *e.g.* a distinct ligand-DMSO interaction has been found,[5b] and the conformational change observed in the Ba^{2+} complex does not occur in the Ag^+ complex. In order to study the details of the interaction, the stability constants of both the complexes have been determined at various DMSO concentrations. Those of $[Ba([2,2,2])]^{2+}$ and $[Ag([2,2,2])]^+$ have also been measured for comparison.[7] The stability constants are summarized in Table 1 and are plotted in Figure 9. For the Ag-pytren system, only the first formation constant is calculated because the second encapsulation process could not be observed

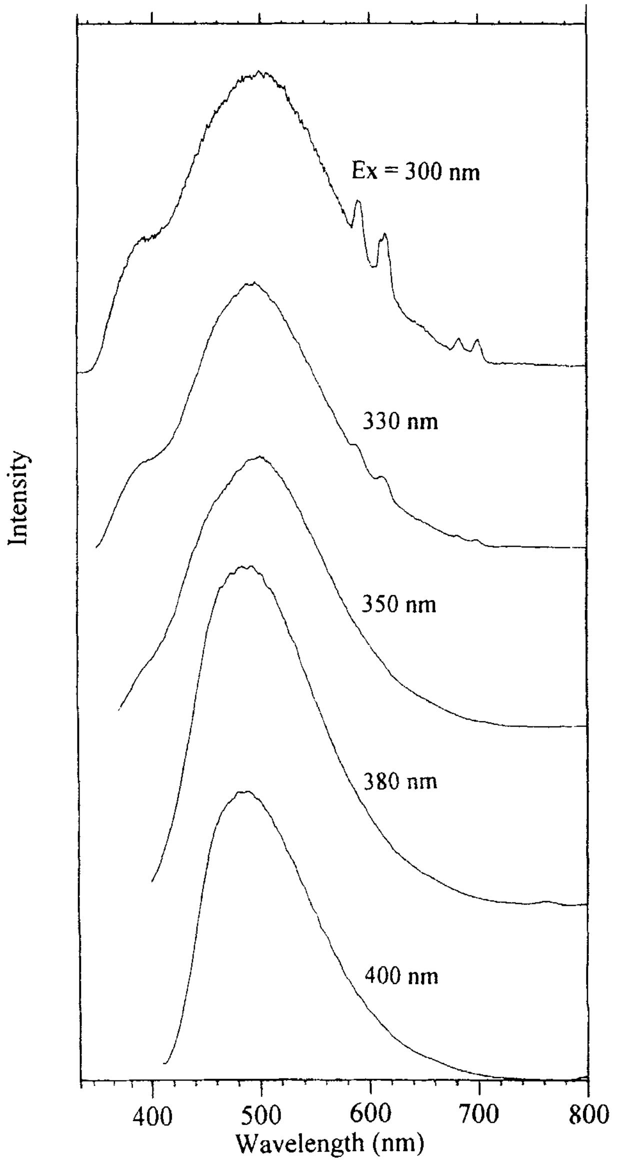


Figure 8 Emission spectra of $[Ba(pytren)]^{2+}$ in acetonitrile (1.00×10^{-4} M).

under the conditions of our titration, although the formula of the solid sample was reported as $[Ag_2(pytren)](PF_6)_2$.[1a]

As shown in Figure 9, all the cryptates except the Ba^{2+}-pytren cryptate show a very similar [DMSO]-dependence of logK with a minimum at [DMSO] = *ca.* 2.5 M. Only the Ba^{2+}-pytren cryptate exhibits an exceptionally large decrease in logK at [DMSO] = 1–2 M, and the logK value shows no augmentation up to pure DMSO. The decrease in high [DMSO] region for the Ba^{2+}-pytren complex agrees with our previous NMR and UV data.[5b] The fact that the stability of the Ag^+-pytren complex does not decrease in the region is also ascertained by UV and NMR studies.

The association properties of DMSO molecules have been extensively studied.[8] The DMSO molecule has a trigonal pyramidal structure, in which the dipole moment at the S=O bond locates along the edge of the pyramid,[8d] *i.e.*, the electric dipole is exposed at the surface of the molecule in contrast to the embedded dipole of acetonitrile.[9] Thus, associations between the DMSO molecules easily occur *via* the dipole-dipole interactions. The associations occurs at 5–10% molar fraction of DMSO in organic solvent,[10] and the donicity of DMSO is enhanced with the associations.[10b,11] Plots of the stability constants of $[Ba(pytren)]^{2+}$ are curved around this region. Further, the structural conversion of the pytren ligand in the Ba^{2+} complex always begins at 1 M (*ca.* 5% molar fraction), regardless of the concentration of the complex in the range 10^{-5}–10^{-3} M.[5b] Therefore the intrinsic association properties of DMSO must be connected with the change in the stability constants.

The change in the stability constants of the [2,2,2] complexes may also be correlated with the change in the donicity of DMSO. The solvation of DMSO molecules toward the Ba^{2+} ions must predominantly decrease the stability constant. On the other hand, preorganization effect may also exist; (1) electrostatic repulsion between O-donor atoms of [2,2,2] may be eliminated by the solvation of DMSO molecules,[6b] or (2) the hydrogen bonds may be formed between the methylene groups of [2,2,2] and associated DMSO molecules.[8b,c] These two effect which would force the conformation more suitable for complexation, increase the stability constant occurs. Therefore the decrease and increase in the apparent stability constants for $[Ba(2,2,2)]^{2+}$ with increasing DMSO concentrations would be interpreted by the two opposite actions.

It is important to consider that the apparent stability constant may be affected by the thermodynamical stabilization of the free metal ion by solvent molecules. As for the pytren cryptates, the Ba^{2+}-DMSO interaction must be considered to account for the remarkable decrease in the stability constant of the Ba^{2+} cryptate. The first formation constants for M-DMSO complexes were determined as $K_{Ba\text{-}DMSO} = 42$ and $K_{Ag\text{-}DMSO} = 7.5\ M^{-1}$ (only the first formation constant can be reliably calculated by the spectrophotometric method employed in these experiments). Although the successive formation constants K_n may be changed in the series $n = 1,2, \cdots$, *on* $= 1,2, \cdots$, $xn = 1,2, \cdots$, the $K_{Ba\text{-}DMSO}/K_{Ag\text{-}DMSO}$ ratio of 5.6 is not enough to explain the 10^4 times of difference between the stability constants of Ag^+-pytren and Ba^{2+}-pytren complexes at high [DMSO]. Further, such remarkable decrease is not observed for $[Ba(2,2,2)]^{2+}$. The unusual behavior of the Ba^{2+}-pytren complex can not be satisfactory explained by the Metal-DMSO interaction.

The interaction between DMSO and pytren ligand *via* dipole-dipole interactions has already been studied by NMR spectroscopy including NOE technique. The study reveals that the aromatic nitrogen atoms as behave

Table 1 Stability constants of 2,2,2 and pytren complexes at various DMSO concentration.

[DMSO]	$[Ag(2,2,2)]^+$	$[Ba(2,2,2)]^{2+}$	$[Ag(pytren)]^+$	$[Ba(pytren)]^{2+}$
0M (pure AN)	8.67(1) 8.9[a,b] 9.3[c]	10.30(2)	8.16(5)	7.86(7)
1M	7.8(3)	8.9(6)	7.5(2)	7.3(5)
2M	7.5(4)	7.9(9)	7.1(2)	4.6(5)
3M	7.64(4)	8.0(1)	7.19(2)	3.78(2)
5M	8.15(2)	9.74(3)	7.60(8)	3.6(1)

[a]ref 17b, [b]ref17a, [c]M. Lejaille, M. Livertoux, C. Guidon, J. Bessiere, *Bull. Soc. Chim. Fr.*, 1978, I-373.

donors and the sulfur atoms as acceptors.[5b] The stabilization effect of the free pytren ligand by this interaction is another factor which must be taken into consideration. However, the stabilization effect on the released free pytren ligand should be achieved regardless of the metal species and may not cause a large difference between the stability constants of the Ba^{2+} and Ag^+ cryptates of pytren.

We want to discuss the low stability of Ba^{2+}-pytren complex in DMSO in connection with the specific structure of Ba^{2+}-pytren complex itself. It should be noted that the Ba^{2+} ion is located at the center of the cryptand, while the Ag^+ ion is fit in a tren moiety. The DMSO molecules electrostatically attracted would be present around the pyridyl rings of the cryptate due to the positive charge of the central Ba^{2+} ion. When the O atom of the DMSO molecule approaches the central Ba^{2+} ion, the S atom of the DMSO must be close to the coordinated pyridyl N atom (N_{py}). The DMSO-metal interactions are reported to become strong when the S atom has aninteraction with a pyridyl nitrogen donor.[10,11] Since theDMSO molecule has interactions with both the Ba^{2+} ion and the N atom, which are bonded with each other, it is reasonable that the Ba-N_{py} bonds in the Ba^{2+}(pytren) complex are weakened by the pyridine-DMSO-Ba^{2+} interaction. This interaction may cause considerable destabilization of the Ba^{2+} complex. On the other hand, in the Ag^+ complex, the Ag^+ ion would be bonded to the four amino-nitrogen atoms of a tren moiety.[1g,12] If the S atom forms a dipole-dipole interaction with the non-coordinated N_{py} atom, such an interaction is not expected to give a strong influence on the coordination of the Ag^+ ion. In conclusion, we suggest that the thermodynamic destabilization of the Ba^{2+}-pytren complex due to the DMSO-complex interaction is the main reason for the large decrease in the stability of the Ba-pytren complex at higher [DMSO].

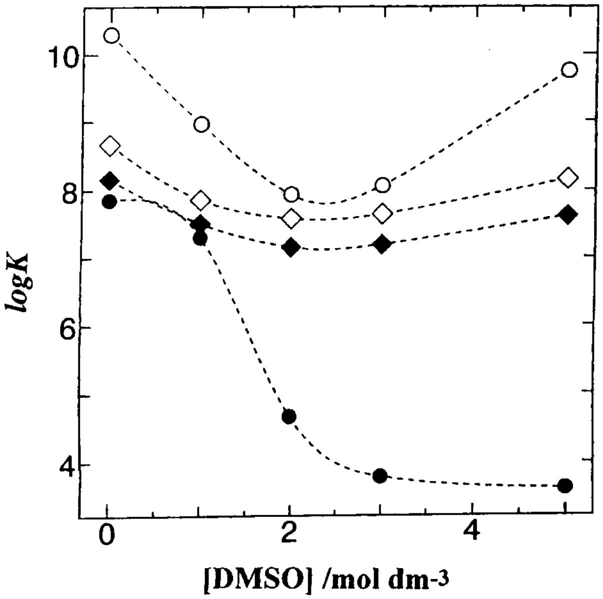


Figure 9 The stability constants obtained at various DMSO concentrations; $[Ba(pytren)]^{2+}$ (●); $[Ag(pytren)]^+$ (●); $[Ba(2,2,2)]^{2+}$ (○); $[Ag(2,2,2)]^+$ (◇).

CONCLUSIONS

The second crystal structure of free pytren has been characterized by X-ray diffraction, in which the free pytren is found to form a dimer in the crystal by a face-to-face interaction between the diiminopyridyl moieties. The spectroscopic studies indicate the presence of the aromatic-aromatic interactions between diiminopyridyl moieties. There are intermolecular interactions between the free ligands, and intramolecular π-π interactions in the Ba^{2+} complex.

The remarkable decrease is observed in the stability constant for $[Ba(pytren)]^{2+}$ at higher [DMSO] region, while the similar decrease is not observed for $[Ag(pytren)]^+$ and [2,2,2] complexes. It is suggested that the dipole-dipole interactions of DMSO molecules towards the pyridyl nitrogen donors bound to the Ba^{2+} ion play major roles in the unusual destabilization of $[Ba(pytren)]^{2+}$ in the presence of DMSO.

EXPERIMENTAL SECTION

Preparation of the cryptand and the complex.

The free pytren ligand and the Ba^{2+} complex are prepared by the method reported in ref. 5b and 5a, respectively.

Spectroscopic measurements.

^{1}H, and ^{13}C NMR spectra were acquired out on a JEOL JNM-GX270 spectrometer. Each spectrum was obtained without additional internal standard, and was referenced to the solvent itself. Hitachi 340 was used as spectrometer in the UV-VIS spectral measurement. Emission spectra was recorded on a Shimadzu RF-5000 fluorometer.

Structure Determination of the free pytren.

Atomic coordinates and tables of bond angles and distances are given in supplementary materials. A colorless prismatic crystal of the pytren was obtained from an acetonitrile solution containing a small amount of DMSO.

Crystal Data. $C_{33}H_{39}N_{11}$, $M = 584.70$, trigonal, $a = 30.234(6)$, $c = 18.593(3)$ Å, $V = 14719(6)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centered reflections in the range $45.2 < 2\theta < 48.4°$, $\lambda = 1.54178$ Å), space group R$\bar{3}$ (no. 148), $Z = 18$, $Dc = 1.197$ g cm^{-3}, $F(000) = 5652$. Colorless, prismatic. Crystal dimensions: $0.6 \times 0.6 \times 0.6$ mm, $\mu = 5.99$ cm^{-1}.

Data Collection and Processing. Rigaku AFC5S diffractomter, ω-2θ scan with ω scan width $= 1.52 + 0.30 \tan\theta$, ω scan speed 8.0° min^{-1}, graphite monochromated Cu-Kα radiation; 15062 reflections measured ($6.0 < \theta < 120°$), 14242 unique after absorption correction (max., min. transmission factors = 0.9730, 1.0171)], giving 4509 with $I > 4.0\sigma(I)$. Linear and approx. isotropic crystal decay, 1.89%, were corrected during processing.

Structure Analysis and Refinement. The structure was solved by direct methods[13] and expanded using Fourier techniques.[14] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms located in calculated positions (C-H = 0.95 Å) were included but not refined in the final cycle of full-matrix least-squares refinement[15], $p = 0.004$. Final R and R_w values are 0.082, 0.068. All the calculations were performed using the teXsan[16] crystallographic software package of Molecular Structure Corporation.

Measurements of Stability Constants.

Materials. Cryptand (2,2,2) (Merck) was used without further purification. $AgClO_4$ was dried under vacuum at 80°C for 24h. High purity grade $Ba(ClO_4)_2$ were used as received. Acetonitrile and DMSO were dried over Molecular Sieves, type 5A. Tetrabutylammonium perchlorate (TBAP) was recrystallized twice from methanol, washed with ether, and dried under vacuum at 60°C.

Measurements of Formation Constants of Metal-DMSO. The first formation constants in the complexations of Ag^+ and Ba^{2+} ions with DMSO molecule were spectrophtometrically determined by equilibrium shift method at 20°C. The concentrations of Ag^+ and Ba^{2+} were varied from 0 to 0.36 M and from 0 to 0.12 M, respectively. The DMSO concentration was kept at 1.5×10^{-3} M in each measurements. The first formation constants were obtained as 7.49(4) M^{-1} for Ag(DMSO) and 42(6) M^{-1} for Ba(DMSO).

Measurements of Stability Constants with an Ag^+ Selective Electrode. Spectrophotometric technique cannot be used for the determination of the constants in DMSO containing solvents due to the intense absorption of DMSO. We adopted the Ag^+-selective electrode method because this appears to be the most popular and reliable method for the measurements of the stability constants of cryptates. The stability constants of the Ag^+ complexes were determined from the direct potentiometric titration of Ag^+. The concentration of the free silver ion was measured with the silver selective electrode (DKK, type 7080), whose potential being measured with a digital multimeter (ADVANTEST, TR 6846) at 23°C. Each constant was determined from a least-squares fitting of the titration data. The stability constants of other metal complexes were determined by disproportionative reaction of the metal ions with the corresponding Ag^+ cryptates.[17] The total Ag^+ and Ba^{2+} concentrations were in the range $1 \times 10^{-3} - 3 \times 10^{-3}$ M and the concentrations of cryptand were always 10^{-3}M. Total metal concentration is maintained in excess of that of the free ligand to assure the absence of the free ligand. In all the measurements the ionic strength was kept constant at $I = 0.1$ M with TBAP, and the experiments were performed under nitrogen.

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