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Crystal Structure of Dehydrated Cesium and Silver Exchanged Zeolite A, Cs_{7.3}Ag_{4.7}-A

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The structure of Cs_{7.3}Ag_{4.7}Si₁₂Al₁₂O₄₈, vacuum dehydrated zeolite A with all Na⁺ ions replaced by Cs⁺ and Ag⁺ as indicated, has been determined by single-crystal x-ray diffraction techniques in the cubic space group, *Pm3m* (*a* = 12.282 (1) Å). The structure was refined to the final error indices *R*₁ = 0.089 and *R*₂ (weighted) = 0.099 using 347 independent reflections for which *I*₀ > 3σ(*I*₀). Although dehydration occurred at 360°C, no silver atoms or clusters have been observed. The 8-ring sites are occupied only by Cs⁺ ion, and the 4-ring sites only by a single Ag⁺ ion. The 6-ring sites contain Ag⁺ and Cs⁺ ions with Ag⁺ nearly in 6-ring planes and Cs⁺ well off them, one on the sodalite unit side. With regard to the 6-rings, the structure can be represented as a superposition of two types of unit cells: about 70% have 4Ag⁺ and 4Cs⁺ ions, and the remaining 30% have 3Ag⁺ and 5Cs⁺. In all unit cells, 3 Cs⁺ ions lie at the centers of the 8-rings at sites of *D*_{4h} symmetry; these ions are approximately 0.3 Å further from their nearest framework-oxygen neighbors than the sum of the appropriate ionic radii would indicate. To minimize electrostatic repulsions, the Cs⁺ ions at Cs(1) are not likely to occupy adjacent 6-rings in the large cavity; they are likely to be tetrahedrally arranged when there are 4.

Introduction

If completely Cs⁺-exchanged zeolite A could be prepared, the total volume of exchangeable cations would be maximized (ignoring Fr⁺). These ions would be extremely crowded on the inner surfaces of the zeolite, their arrangement might be novel, and the zeolite might have some unique physical properties. Unfortunately, only incomplete exchange of Cs⁺ into Na₁₂-A (zeolite 4A),^{1,2} K₁₂-A (zeolite 3A),³ Tl₁₂-A⁴, and Ca₆-A (zeolite 5A)⁵ has been achieved so far.

This work was undertaken with the hope that complete exchange of Cs⁺ for Ag⁺ could be accomplished by using aqueous CsCN. It was hoped that the large formation constant⁶ of Ag(CN)₂⁻, *K*_f ≈ 10²¹, would greatly promote the removal of Ag⁺ from the zeolite, thereby facilitating the exchange process and allowing it to go to completion.

Even though the complete exchange of Cs⁺ for Ag⁺ was not achieved, other results have been learned, such as the structural basis for a lesser exchange limit and the relative preference of Cs⁺ and Ag⁺ for the coordination sites available within the zeolite. In future experiments, treatment with H₂ might lead to cluster formation, and the Cs⁺ ions, by blocking 8-rings, might prevent these clusters from migrating out of the structure.

Experimental

Crystals of zeolite 4A were prepared by a modification of Charnell's method,⁷ including crystallization using seed crystals from a first synthesis. A single crystal 0.08 mm on an edge was lodged in a fine glass capillary. AgNO₃ (0.05*M*) was allowed to flow past the crystal at about 1 cm/sec for two days; since the exchange of Ag⁺ for Na⁺ has been shown to be facile and complete after mild treatment, complete exchange was assured in this case.^{8,9,10} This clear colorless crystal was further ion-exchanged by the flow method with 0.05*M* Cs⁺ solution, a mixture of CsCN and CsOH with pH = 11.4. It was then rinsed lightly with 0.05*M* CsOH solution, and dehydrated for 1 day at 360°C and 2 × 10⁻⁶ Torr. While still under vacuum, the crystal was allowed to cool quickly to room temperature and was sealed in its capillary by torch. Microscopic examination showed it to be brownish-yellow in color. Subsequent diffraction experiments were performed at 24 (1) °C.

The cubic space group *Pm3m* (no systematic absences) was used instead of *Fm3c* for reasons described previously.^{11,12} A Syntex 4-circle computer-controlled diffractometer with a graphite monochromator and a pulse-height analyzer was used throughout for preliminary experiments and

for the collection of diffraction intensities. Molybdenum radiation ($K\alpha_1$, $\lambda=0.70930 \text{ \AA}$; $K\alpha_2$, $\lambda=0.71359 \text{ \AA}$) was used. The cell constant, $a=12.282(1) \text{ \AA}$, was determined by a least-squares treatment of 15 intense reflections for which $20^\circ < 2\theta < 24^\circ$ using $K\alpha$, $\lambda=0.71073 \text{ \AA}$. The $\theta-2\theta$ scan technique was used. Each reflection was scanned at a constant rate of 1.0 deg min^{-1} from 1.0° (in 2θ) below the calculated $K\alpha_1$ peak to 1.0° above the $K\alpha_2$ maximum. Background intensity was counted at each end of the scan range for a time equal to half the scan time. The intensities of 3 reflections in diverse regions of reciprocal space were recorded after every 100 reflections to monitor crystal and instrument stability. Only small, random fluctuations of these reflections were noted during the course of data collection.

The intensities of all lattice points for which $2\theta < 70^\circ$ were recorded. Although few reflections were significantly greater than background for high 2θ values, this limit was selected to allow the data set to be more complete.

Standard deviations were assigned to individual reflections according to the formula,

$$\sigma(I) = [\omega^2(CT + B_1 + B_2) + (pI)^2]^{1/2}$$

where CT is the total integrated count, B_1 and B_2 are the background counts, and I is the intensity. The value of $p=0.02$ was found to be appropriate for the instrumentation used.¹³ Of the 884 symmetry independent reflections measured, 347 had intensities greater than three times their standard deviations, and only these were used in subsequent structure determinations. The intensities were corrected for Lorentz and polarization effects;¹⁴ the contribution of the monochromator crystal was calculated assuming it to be half-perfect and half-mosaic in character. An absorption correction ($\mu=4.0 \text{ mm}^{-1}$) was judged to be negligible^{15,16} and was not applied.

Structure Determination

Full-matrix least-squares refinement¹⁴ was initiated using the atomic parameters of the framework atoms ((Si, Al), O(1), O(2), and O(3)) and Cs^+ ions at Cs(1) and Cs(2) of de-

hydrated $\text{Cs}_7\text{K}_5\text{-A}$.³ Anisotropic refinement of the framework atoms and isotropic refinement of the Cs^+ ions converged to an R_1 index, $(\sum |F_o - |F_c|| / \sum F_o)$, of 0.32 and a weighted R_2 index, $(\sum w(F_o - |F_c|)^2 / \sum wF_o^2)^{1/2}$ of 0.38. A subsequent difference Fourier function revealed the Ag^+ ions at Ag(1). Anisotropic refinements of the framework atoms, Cs(1), Cs(2), and Ag(1) converged to $R_1=0.16$ and $R_2=0.20$.

It is easy to distinguish Ag^+ from Cs^+ ions because their ionic radii are quite different, 1.26 \AA and 1.67 \AA ,¹⁷ respectively. Therefore, their approach distances to zeolite oxygens are indicative, as has been observed in $\text{K}_5\text{Cs}_7\text{-A}$,³ $\text{Na}_5\text{Cs}_7\text{-A}$,² $\text{Cs}_9\text{Ti}_3\text{-A}$,⁴ and partially decomposed $\text{Ag}_{12}\text{-A}$.^{9,10}

A subsequent Fourier function revealed a broad peak $4.5(2) \text{ e\AA}^{-3}$ in height at Cs(3). Simultaneous positional, thermal, and occupancy refinement including this position converged with $R_1=0.096$ and $R_2=0.118$.

The occupancy numbers of these ions per unit cell refined to Cs(1)=3.43(9), Cs(2)=3.27(7), Cs(3)=1.13(8), and Ag(1)=3.82(11). The ions at Cs(2) are associated with 8-rings, and because these rings can accommodate no more than 3 ions per unit cell, the occupancy at Cs(2) was thereafter held fixed at 3. A subsequent difference function had a peak of height $1.4(2) \text{ e\AA}^{-3}$ at Ag(2), and its inclusion in refinement led to $R_1=0.083$ and $R_2=0.091$.

The ions at Cs(1), Ag(1), and Cs(3) are associated with 6-rings and lie on threefold axes. The number of ions per unit cell at these positions cannot sum to more than 8: otherwise unacceptably close interactionic distances would occur. The Cs^+ ions at Cs(3) are located deep inside the sodalite cavity. At this position, the occupancy number of Cs(3) cannot be more than 1: otherwise a prohibitively close Cs(1) to Cs(3) distance would exist. Therefore the occupancy at Cs(3), 1.13(8), was fixed at 1. With the constraint that the sum of the occupancies at Ag(1) and Cs(1) be 7 per unit cell, full-matrix least-squares refinement converged to Cs(1)=3.32 and Ag(1)=3.68 (see Table 1). The final R values are $R_1=0.089$ and $R_2=0.099$.

The largest peak on the final difference function, whose estimated standard deviation at a general position was 0.14 e\AA^{-3} , was 3.6 e\AA^{-3} in height and was at (0.20, 0.20, 0.20).

TABLE 1: Positional, Thermal,^a and Occupancy Parameters for Dehydrated $\text{Cs}_{7.3}\text{Ag}_{4.7}\text{-A}$

	Wyckoff Position	x	y	z	β_{11}^b or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy factor ^c
(Si, Al)	24(k)	0	1837(4)	3729(4)	14(3)	12(3)	12(3)	0	0	8(5)	24.0 ^d
O(1)	12(h)	0	2252(14)	5000	98(22)	15(13)	14(13)	0	0	0	12.0
O(2)	12(i)	0	2943(11)	2943(11)	38(10)	32(10)	32(10)	0	0	33(25)	12.0
O(3)	24(m)	1134(7)	1134(7)	3425(11)	18(6)	18(6)	80(15)	3(14)	10(12)	10(12)	24.0
Cs(1)	8(g)	2714(3)	2714(3)	2714(3)	39(2)	39(2)	39(2)	18(4)	18(4)	18(4)	3.32(5)
Cs(2)	3(c)	0	5000	5000	115(7)	71(3)	71(3)	0	0	0	3.0
Cs(3)	8(g)	893(15)	893(15)	893(15)	116(13)	116(13)	116(13)	-45(29)	-45(29)	-45(29)	1.0
Ag(1)	8(g)	1938(6)	1938(6)	1938(6)	98(5)	98(5)	98(5)	103(12)	103(12)	103(12)	3.68(5)
Ag(2)	12(j)	1674(52)	1674(52)	5000	331(88)	331(88)	206(95)	-123(216)	0	0	1.0

^a Positional and anisotropic parameters are given $\times 10^4$. Numbers in parentheses are the estimated standard deviations in the units of the least significant figure for the corresponding parameter. The anisotropic temperature is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

^b R.m.s. displacements can be calculated from β_{ii} values using the formula, $\mu_i = 0.225 a (\beta_{ii})^{1/2}$, where $a = 12.282 \text{ \AA}$; ^c Occupancy factors are given as the number of ions per unit cell; ^d Occupancy for (Si) = 12; occupancy (Al) = 12.

This peak represents density residual at Ag(1). The goodness-of-fit, $(\sum w(F_0 - |F_c|)^2 / (m-s))^{1/2}$ is 4.3; m (347) is the number of observations, and s (37) is the number of variables in least-squares.

The final structural parameters are presented in Table 1. Interatomic distances and angles are given in Table 2. A listing of observed and calculated structure factors is available. A likely atomic arrangement in a particular unit cell is shown in Figure 1.

The quantity minimized in least-squares is $(\sum w(F_0 - |F_c|)^2)$ and the weights (w) are the reciprocal squares of $\sigma(F_0)$, the standard deviation of each observed structure factor. Atomic scattering factors^{18,19} for O⁻ and (Si, Al)^{1.75+} (the average of Si⁰, Si⁴⁺, Al⁰, and Al³⁺), Ag⁺, and Cs⁺ were used. All scattering factors were modified to account for the real components ($\Delta f'$) of the anomalous dispersion correction.^{20,21}

Discussion

Each 8-oxygen ring²² in the structure contains a Cs⁺ ion at its center, Cs(2), a site of C_{4h} (D_{4h} in $Pm3m$) symmetry. Each such ion is 3.38 Å from 4 O(1) oxygens and 3.57 Å from 4 O(2)'s. As has been observed before in other zeolite A structures,^{2,3,4} these distances are substantially longer than the sum of the ionic radii,¹⁷ 1.67 + 1.32 = 2.99 Å.

Takaishi and Hosoi²³ carried out a theoretical calculation of the potential experienced by a Cs⁺ ion in an idealized Cs₃Na₉-A structure. Using electrostatic and Lennard-Jones 6-12 potentials, they found that the potential minima are locally exactly at the centers of 8-ring, in agreement with these and previous crystallographic results.^{2,3,4}

The Cs⁺ ions at Cs(1) and Cs(3) are on threefold axes and associated with 6-rings.²² The 3.3 ions at Cs(1) are recessed 1.74 Å into the large cavity from the (111) plane at O(3) (see Table 3), and the ion at Cs(3) is correspondingly recessed 2.14 Å into the sodalite cavity. These ions are each associated with three O(3) oxygens, at 2.88(1) Å for Cs(1) and 3.14(2) Å for Cs(3).

The 3.7 Ag⁺ ions at Ag(1) are on threefold axes and lie close to the 6-ring planes at O(3). These positions are familiar, having been found in previous work.^{9,10} Ag(1) is 2.30(1) Å from three O(3)'s, less than the sum of the conventional ionic radii¹⁷ of Ag⁺ and O²⁻, 2.58 Å.

The Ag⁺ ion at Ag(2) is statistically distributed over a 12-fold equipoint. This position is in the large cavity and lies on a twofold axis opposite a 4-ring. It approaches 4 zeolite framework oxide ions at approximately equal distances, 2.15(3) Å to 2 at O(3) and 2.18(6) Å to 2 at O(1). The large thermal parameters at Ag(2) agree with its low partial occupancy to indicate that this is the least favorable cation site. One cation must occupy this position because the more favorable sites cannot accommodate more than 11 monovalent cations per $Pm3m$ unit cell.

Various Ag-O distances are found in oxygen-containing silver salts.²⁴ Some are 2.06 Å in Ag₂O (quite a short bond with considerable covalent character), 2.34 Å in Ag₃PO₄ and 2.51 Å in AgClO₃ (long and less covalent interactions).

TABLE 2: Selected Interatomic Distances (Å) and Angles (deg) *

(Si, Al)-O(1)	1.642(7)	O(1)-(Si, Al)-O(2)	107.4(8)
(Si, Al)-O(2)	1.666(15)	O(1)-(Si, Al)-O(3)	111.7(6)
(Si, Al)-O(3)	1.680(9)	O(2)-(Si, Al)-O(3)	106.8(5)
		O(3)-(Si, Al)-O(3)	112.0(9)
Cs(1)-O(3)	2.880(9)	(Si, Al)-O(1)-(Si, Al)	143.9(12)
Cs(2)-O(1)	3.375(17)	(Si, Al)-O(2)-(Si, Al)	160.9(10)
Cs(2)-O(2)	3.573(14)	(Si, Al)-O(3)-(Si, Al)	143.4(9)
Cs(3)-O(3)	3.137(22)		
Ag(1)-O(3)	2.299(13)	O(3)-Cs(1)-O(3)	87.4(5)
Ag(2)-O(1)	2.175(64)	O(3)-Cs(3)-O(3)	78.2(5)
Ag(2)-O(3)	2.148(30)	O(1)-Cs(2)-O(2)	45.0(2)
		O(3)-Ag(1)-O(3)	119.9(6)
		O(1)-Ag(2)-O(3)	79.0(11)

* Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding value.

TABLE 3: Deviations of Atoms (Å) from the (111) Plane at O(3) *

Cs(1)	1.74
Cs(3)	-2.14
Ag(1)	0.09
O(2)	0.14

* A negative deviation indicates that the atom lies on the same side of the plane as the origin.

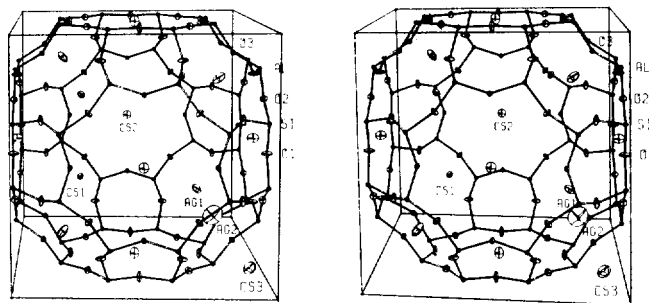


Figure 1. A stereoview of the structure of dehydrated Cs_{7.3}Ag_{4.7}-A is shown using ellipsoids of 20% probability. The Cs⁺ and Ag⁺ ions are distributed within their equipoints of partial occupancy in a plausible manner as discussed in the text. This arrangement is seen in about 70% of the unit cells. The remainder have 4 Cs⁺ ions at Cs(1) and 3 Ag⁺ ions at Ag(1), not 3 and 4, respectively, as shown here.

Ag-O is 2.25 Å in dehydrated Ag₁₂-A.^{9,10} It appears that the relatively short bonds between the Ag⁺ ions at Ag(2) and oxide ions of the zeolite framework, 2.16(3) Å are quite covalent.

The Cs⁺ ions at Cs(1) are also somewhat closer, 2.88 Å, to 3 O(3) oxygens than the sum of the conventional ionic radii, 2.99 Å. Such short bonds are common in dehydrated zeolite A structures which contain large monovalent cations, perhaps because of their unusually low association numbers within the zeolite. Examples include Ag₁₂-A,^{9,10} Rb₁₁Na₁-A,²⁵ Cs₇Na₅-A,² Cs₇K₅-A,³ and Tl₁₂-A.²⁶

The fractional occupancies observed at Cs(1) and Ag(1) indicate the existence of 2 types of unit cells in dehydrated Cs_{7.3}Ag_{4.7}-A. About 70% of the unit cells have 4 ions at

Ag(1) and 3 at Cs(1) on the threefold axes, and the remainder have 3 ions at Ag(1) and 4 at Cs(1). All unit cells have 3 ions at Cs(2), 1 at Cs(3), and 1 at Ag(2).

The Cs(1)–O(3) distance appears to be about 0.1 Å shorter than the corresponding distance in Cs₇Na₅–A.² This might be virtual, a result of the change in average O(3) position due to the replacement of 4 6–ring Na⁺ ions by 3.7 Ag⁺ (and 0.3 Cs⁺) ions. Because of the disorder implicit in the structure,¹¹ only an average O(3) position was determined and could be used to calculate interatomic distances, although one would expect the conformation of a particular 6–ring to depend upon the identity and position of the cation associated with it. In Cs_{7.3}Ag_{4.7}–A, at least 4 chemically nonequivalent 6–rings exist, but only the average conformation over 8 such rings has been determined.

Something can be said about the relative sizes of the 6–ring apertures in Cs⁺–containing M₁₂–A by comparing the meta O(3)–O(3) distances. Those in Cs_{7.3}Ag_{4.7}–A and Cs₇K₅–A³ are about the same, 3.98 Å and 3.96 Å respectively, somewhat longer than that in Cs₇Na₅–A, 3.82 Å.² This indicates that the average 6–ring apertures are larger when the 8 6–ring cations are larger (4.3 Cs⁺, 3.7 Ag⁺ and 4 Cs⁺, 4 K⁺ respectively), and smaller when those ions are on the average smaller (4 Cs⁺, 4 Na⁺). Combined with the result that Cs(1)–O(3) is about 0.1 Å shorter (possibly virtual) in Cs_{7.3}Ag_{4.7}–A than in Cs₇Na₅–A, it follows that the threefold-axis Cs⁺ position is 0.28 Å closer to its O(3) plane in Cs_{7.3}Ag_{4.7}–A.

All 8–rings contain a Cs⁺ ion at Cs(2). However, only about half of the 6–rings are occupied by Cs⁺ ions. This is consistent with the general observation that larger cations occupy 8–ring sites and smaller ones 6–rings; this is the rule in Tl_{5.5}Ag_{6.5}–A,²⁷ Na₅Cs₇–A,² and K₅Cs₇–A,³ all fully dehydrated.

In contrast to Ag₁₂–A dehydrated at 350 °C,⁸ in which 3 residual water molecules were found bridging between Ag⁺ ions in the sodalite unit, Cs_{7.3}Ag_{4.7}–A is found to be fully dehydrated at 360 °C. Not only are H₂O molecules not found, but the Ag⁺ ions are not near the positions they occupied when coordinated to H₂O in Ag₁₂–A evacuated at 350 °C.

During this work, another crystal was prepared by an identical procedure, except for the final wash step which was done with distilled water instead of 0.05M CsOH. The structure was determined and refined to $R_1 = R_2 = 0.063$ using 297 independent reflections for which $I_0 \geq 3\sigma(I_0)$. This structure has the formula Cs₇Ag₄–A with no cation at Ag(2), the 4–ring site. Otherwise, the structure was approximately the same, with 4 Ag⁺ in 6–rings, 3 Cs⁺ at 8–ring centers, and 4 Cs⁺ ions on threefold axes near 6–rings (3 deep in the large cavity and 1 inside the sodalite unit). Apparently the twelfth cation, the one at the 4–ring site, readily exchanged for a H⁺ from the distilled water. Simultaneously, stoichiometry was achieved as the occupancy at Cs(1) decreased from 3.3 to 3.0 ions per unit cell, and that at Ag(1) increased from 3.7 to 4.0 by accepting some of the formerly 4–ring Ag⁺ ions. Altogether it appears that 0.7 Ag⁺ and 0.3 Cs⁺ were replaced by a H⁺ ion (unlocated), that the least favorable site for a large cation was emptied, and that stoichiometry, with all unit cells

equivalent, was achieved.

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Charge Transfer Complexing Between Indole Derivatives and Methylviologen and Effects of Sodium Dodecyl Sulfate on It

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The charge transfer complex formations between indole derivatives and methylviologen were investigated spectroscopically. In aqueous solutions near room temperature, the order of complex stability was tryptamine < tryptophan < indole < indole acetate, which is the reverse order of the magnitude of molar absorptivities. This was interpreted as involvement of contact charge transfer. The decrease of enthalpy of complex formation ($-\Delta H$) was highest in tryptamine, and lowest in indole acetate. ΔH and entropy of complex formation (ΔS) varied nearly in a linear fashion with isokinetic temperature 242°K. These results were attributed to the hydration-dehydration properties of the side chains in indole derivatives. Except indole acetate, the complex formations were greatly enhanced by the addition of sodium dodecyl sulfate (SDS). However, the direct relationship between the enhanced complex formation and SDS micelle formation was not found. The enhanced charge transfer interaction in SDS solutions was attributed to the increased ΔS by interaction between methylviologen and SDS in pre-micellar level. The order of complex stability in SDS solutions was indole acetate < tryptophan < tryptamine < indole, which reflects the hydrophobicity of indole derivatives as well as electrostatic interaction between indole derivatives and methylviologen associated with SDS.

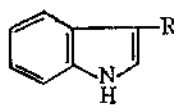
Introduction

Since Mulliken's suggestion of importance of charge transfer complexes in biological systems¹, studies have demonstrated that the complexes are indeed directly involved in various biochemical reactions, such as photosynthesis, phosphorylation and redox chains with flavin-nicotinamide chains.² One of the most important electron donor moieties in biologically active molecules is indole ring. Thus, the charge transfer complex formation of indole and/or its derivatives with various electron acceptors including pyridinium salts (mainly nicotinamide dinucleotide (NAD) or its analogs)³⁻⁷, tetracyanoethylene (TCNE)⁸, methylviologen⁹⁻¹¹, etc, has been investigated. The charge transfer interaction properties of indole ring with pyridinium salts were attributed to the coenzyme activity of NAD,⁵⁻⁷ and were also utilized as a conformational probe^{9,12} in the systems of biological interests.

Methylviologen (MV²⁺), commonly known as paraquat, is a dication, N,N'-dimethyl-4,4'-bipyridinium, and its salts are used widely as a weed killer.¹³ It has been found that the compound inhibits electron transfer in both the cytochrome chain of mitochondria and electron transfer chain of chloroplast.¹³ Recently, MV²⁺ and viologen polymers have attracted much attention as an electron catalyst in the hydrogen fuel production through the splitting of water by sunlight.¹⁴ The potential uses and biological properties of MV²⁺ are based on the high electron-accepting ability of the

dication: the estimated electron affinity of MV²⁺ is 1.24eV.¹⁵ In view of these interesting properties of MV²⁺, several investigators have reported the charge transfer complex formation of MV²⁺ with various electron donors.^{10, 11, 15, 16}

Despite the extensive uses of MV²⁺ in many biological systems as one-electron transfer agent and as redox indicators,¹⁷ studies on effects of neighboring charge and micro-environment on the interaction between donor moieties of biological molecules and MV²⁺ are scarce. For this reason, we considered it interesting to examine the charge transfer complex formation between indole derivatives and MV²⁺ systematically. To evaluate the contribution of electrostatic interaction to the complex formation and simulate the local environment of the indole ring in biological systems, the following indole derivatives with different charges in the side chain were chosen.



Indole (In) : R=H

3-Indole acetate (In. Ac) : R=CH₂COO⁻

Tryptamine-HCl (TA) : R=CH₂CH₂NH₃⁺Cl⁻

L-Tryptophan (Try) : R=CH₂CH(COO⁻)NH₃⁺

We have also studied the effects of sodium dodecyl sulfate (SDS), because reactions in micellar media are simple model systems for chemical processes occurring at interfaces in a living cell, and an anionic surfactant, SDS, is expected to have strong influence on the interaction properties of the