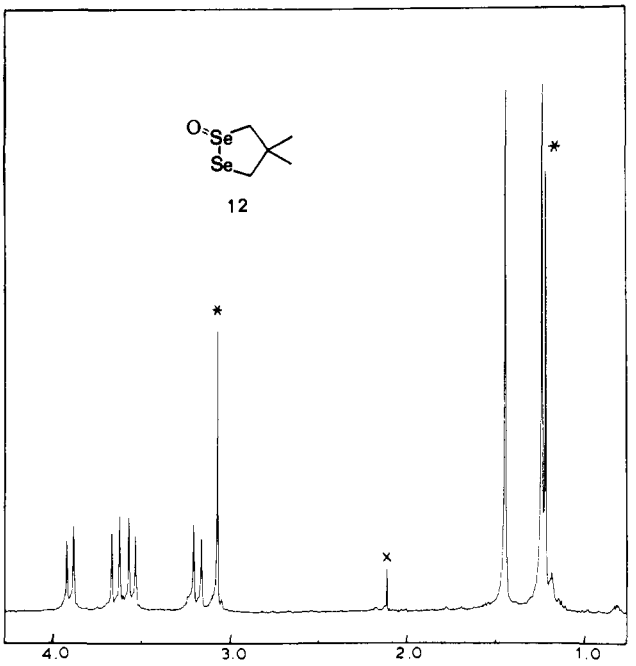
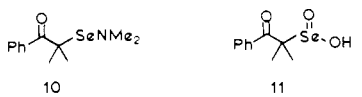


Figure 1. ^1H NMR spectrum (270 MHz, −50 °C, CD_2Cl_2) of **12**. The singlets at δ 1.22 and 3.08 marked with an asterisk are those of **13**.

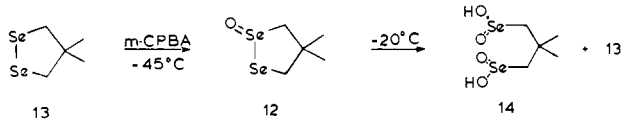
NMR signals assignable to the selenenic acid **6** were observed during these studies.



10 11

Compound **8** is moderately stable at −50 °C ($t_{1/2} \approx 1$ h), decomposing to several products including enone **3** (57%), seleninic acid **11** (8%), diselenide **9** (18%), and two other products thought to be polyselenides (25%, 4%). These products account for 80% of the selenoxide **5** used. The formation of the enone **3** can be considered diagnostic of the Se–oxide grouping in **8**, which should share with selenoxides,[1] seleninic acids, seleninate esters,[16] and their sulfur analogues[17a] the capability for pericyclic syn elimination. Compound **8** is the first example of an observable selenolseleninate ester, although a thiolseleninate ester has been detected during a study of the reaction of thiols with benzeneseleninic acids.[18] Thiolsulfinates are much more stable, and a number have been isolated.[12,17]

Further support for the assignment of structure **8** is provided by the spectroscopic properties of the cyclic selenolseleninate **12**, which is formed by oxidation of 4,4-dimethyl-1,2-diselenolane (**13**)



13 12 14

with 1 equiv of *m*-chloroperbenzoic acid at −45 °C. The proton NMR spectrum (Figure 1) is particularly characteristic, showing two AB quartets for the methylene protons and two singlets for the diastereotopic methyl groups.[19] The ^{77}Se NMR spectrum (CD_2Cl_2, −56 °C) has resonances at 273 and 693 ppm.[10,13] The strong downfield shift of one of the selenium resonances is expected from other comparisons[11a] and was also observed for selenolseleninate **8**.[20] Compound **12** decomposes at −20 °C to give ~65% yield of diselenide **13** and a precipitate of the seleninic acid **14**, the expected disproportionation products.[21]

Summary. The selenoxide syn elimination occurs at temperatures below −50 °C in certain carbonyl derivatives. Under these conditions normally unstable species such as selenenic acids or their dimeric dehydration products, the selenolseleninates, can be observed and characterized spectroscopically (^1H, ^{13}C, ^{77}Se NMR) and chemically. A cyclic selenolseleninate has also been prepared by partial oxidation of a diselenide.

Acknowledgment. We thank the National Institutes of Health for a research grant (AM 23042) in support of this work.

Registry No. **1**, 81360-85-2; **2**, 81360-86-3; **3**, 769-60-8; **4**, 81360-87-4; **5**, 81360-88-5; **7**, 4335-90-4; **8**, 81360-89-6; **9**, 81360-90-9; **10**, 81360-91-0; **11**, 81360-92-1; **12**, 81360-93-2; **13**, 81360-94-3; **14**, 81360-95-4; 1-phenyl-1-trimethylsilyloxy-1-isobutene, 39158-85-5; 2-chloroselenyl-2-methylpropiophenone, 81360-96-5; 3-benzyl-2,4-pentanedione, 1134-87-8.

(16) Both **11** and its methyl ester decompose at room temperature to give **3**, **9**, and other products. See also: Sharpless, K. B.; Gordon, K. M. *J. Am. Chem. Soc.* **1976**, *98*, 300.

(17) (a) Block, E.; O'Connor, J. *J. Am. Chem. Soc.* **1974**, *96*, 3929. (b) Kice, J. L.; Large, G. B. *Ibid.* **1968**, *90*, 4069. (c) Takata, T.; Kim, Y. H.; Oae, S. *Tetrahedron Lett.* **1978**, 4303.

(18) Kice, J. L.; Lee, T. W. S. *J. Am. Chem. Soc.* **1978**, *100*, 5094.

(19) The ^{13}C NMR spectrum also supports the assigned structure: δ (CD_2Cl_2, −56 °C) 25.8 (q), 27.0 (q), 47.4 (t), 50.6 (s), 71.4 (t).

(20) Oxidation of diselenide **9** with either ozone or peracid has not given selenolseleninate **8** as a major product. 4,4'-Difluorodiphenyl diselenide also gave no intermediates during oxidation with *tert*-butylhydroperoxide.[4c]

(21) Bergson, G. (*Acta Chem. Scand.* **1961**, *15*, 1611) has suggested that 1,2-diselenolane-4-carboxylic acid is oxidized to a marginally stable ($t_{1/2}$ = 5–10 min at room temperature) selenolseleninate.

Remarkably Enhanced Charge-Transfer Interaction in Stable Single-Compartment Vesicles

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Received December 1, 1981

The characterization and chemical application of synthetic bilayer membranes constitute a rapidly growing research area in recent years.[2-7] Several recent studies are concerned with the extent of spatial organization of surfactant molecules when they are assembled into bilayer aggregates.[8,9] We have recently shown that amphiphiles involving an amino acid residue (L-Ala or L-His) interposed between a polar head group and an aliphatic double chain form *stable single-compartment vesicles* in aqueous media.[10,11] We have also successfully identified for these bilayer

(1) To whom correspondence should be addressed.

(2) (a) Kunitake, T.; Okahata, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3860–3861. (b) Kunitake, T.; Okahata, Y.; Tamaki, K.; Kumamaru, F.; Takayanagi, M. *Chem. Lett.* **1977**, 387–390. (c) Kunitake, T.; Okahata, Y. *Ibid.* **1977**, 1337–1340. (d) Kunitake, T.; Nakashima, N.; Shimomura, M.; Okahata, Y.; Kano, K.; Ogawa, T. *J. Am. Chem. Soc.* **1980**, *102*, 6642–6644.

(3) (a) Lim, Y. Y.; Fendler, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 4023–4029. (b) Kano, K.; Romero, A.; Djermouni, B.; Ache, H. J.; Fendler, J. H. *Ibid.* **1979**, *101*, 4030–4037. (c) Infelta, P. P.; Grätzel, M.; Fendler, J. H. *Ibid.* **1980**, *102*, 1479–1483. (d) Nomura, T.; Escabi-Perez, J. R.; Sunamoto, J.; Fendler, J. H. *Ibid.* **1980**, *102*, 1484–1488.

(4) Sunamoto, J.; Kondo, H.; Nomura, T.; Okamoto, H. *J. Am. Chem. Soc.* **1980**, *102*, 1146–1152.

(5) Mortara, R. A.; Quina, F. H.; Chaimovich, H. *Biochem. Biophys. Res. Commun.* **1978**, *81*, 1080–1086.

(6) Sudhölter, E. J. R.; Engberts, J. B. F. N.; Hoekstra, D. *J. Am. Chem. Soc.* **1980**, *102*, 2467–2469.

(7) Moriarty, R. M.; Schwartz, R. N.; Lee, C.; Curtis, V. *J. Am. Chem. Soc.* **1980**, *102*, 4257–4259.

(8) Czarniecki, M. F.; Breslow, R. *J. Am. Chem. Soc.* **1979**, *101*, 3675–3676.

(9) Russell, J. C.; Costa, S. B.; Seiders, R. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 5678–5679.

(10) Murakami, Y.; Nakano, A.; Fukuya, K. *J. Am. Chem. Soc.* **1980**, *102*, 4253–4254.

(11) Murakami, Y.; Nakano, A.; Yoshimatsu, A.; Fukuya, K. *J. Am. Chem. Soc.* **1981**, *103*, 728–730.

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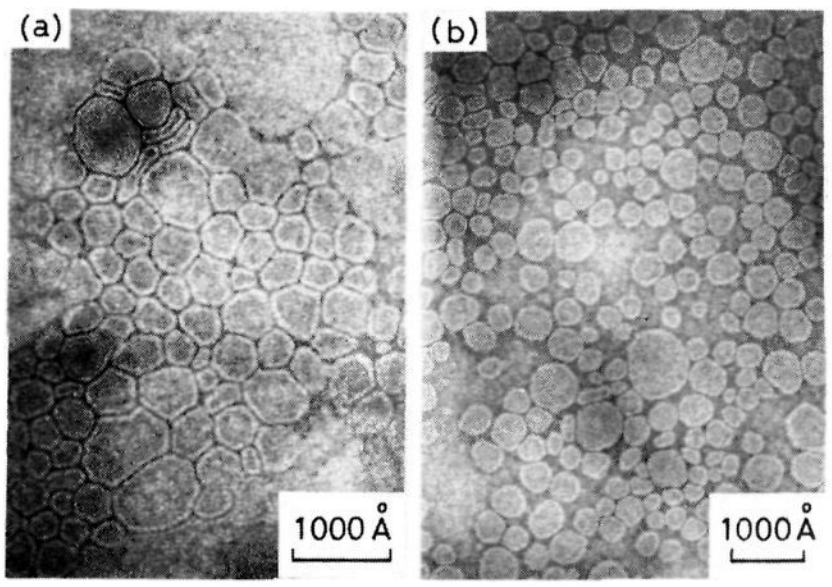
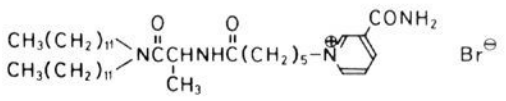


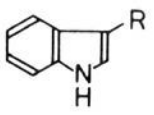
Figure 1. Electron micrographs of single-compartment vesicles of $(NA)^+C_5Ala2C_{12}$ negatively stained with uranyl acetate: (a) 5.0×10^{-3} M aqueous solution sonicated for 3 min with a probe-type sonicator at 30 W (W-220F, Heat Systems-Ultrasonics) and allowed to stand for 10 min at 5 °C (magnification, ×96 000); (b) 5.0×10^{-3} M aqueous solution containing **1** (1.0×10^{-3} M) sonicated as above (magnification, ×70 000).

assemblies two different binding sites, which are separated by the so-called hydrogen belt, in the intramembrane region. One binding site is located near the polar head group and the other at the hydrophobic double-chain interior.[12] In order to get further insight into the specific amphiphile–substrate interaction in the microenvironment provided by such single-walled vesicles in consequence of the highly orientational arrangement of amphiphile molecules, we prepared in the present work an amphiphile involving a nicotinamide head group as an electron acceptor, $[(NA)^+C_5Ala2C_{12}]$.



$(NA)^+C_5Ala2C_{12}$

The charge-transfer interaction of $(NA)^+C_5Ala2C_{12}$ with an aromatic π donor, indolyl-3-acetic acid (**1**),[13] was investigated in the vesicular phase.



1 : R = CH_2CO_2H
2 : R = H

Sonication of an aqueous dispersion of $(NA)^+C_5Ala2C_{12}$[14] resulted in a clear solution of single-compartment vesicles with relatively uniform size (200–900 Å, Figure 1a).[15] Addition of indolyl-3-acetic acid (**1**) to the sonicated solution led to the formation of a charge-transfer (CT) complex characterized by a broad CT transition band in the 300–450-nm range without noticeable change in the morphology of vesicles (size distribution 200–900 Å, Figure 1b). Figure 2 shows a biphasic feature of correlation between optical density at 380 nm and total concentration of **1** ($[\mathbf{1}]_t$) when a total concentration of the amphiphile ($[(NA)^+C_5Ala2C_{12}]_t$) was fixed at 1.0×10^{-4} M; a break point at $[(NA)^+C_5Ala2C_{12}]_t \simeq [\mathbf{1}]_t$. The spectral data under conditions of $[(NA)^+C_5Ala2C_{12}]_t \gg [\mathbf{1}]_t$ were analyzed in terms of an ordinary solution equilibrium (eq 1), giving $K_1 = 1.9 \times 10^4$ M^{-1} at

$$(NA)^+C_5Ala2C_{12} + \mathbf{1} \overset{K_1}{\rightleftharpoons} \text{CT complex} \qquad (1)$$

25.0 °C and $\epsilon_{CT} = 270$ at 380 nm.[16] The correlation curve at lower concentrations of **1** in Figure 2 was reproduced, as shown in Figure 3, upon converting the optical density data into the corresponding amounts of the CT complex by using the ϵ_{CT} value obtained above. Quantity K_1 defined by eq 2 was again evaluated

$$K_1 = \frac{[\text{CT}]}{([(NA)^+C_5Ala2C_{12}]_t - [\text{CT}])([\mathbf{1}]_t - [\text{CT}])} \qquad (2)$$

from the data in Figure 3, and the value $[(1.8 \pm 0.3) \times 10^4$ $M^{-1}]$ is in good agreement with the above value derived under conditions of $[(NA)^+C_5Ala2C_{12}]_t \gg [\mathbf{1}]_t$.

The fluorescence of **1** is known to be quenched upon CT complex formation with nicotinamide.[17] In fact, the fluorescence intensity of **1** (<1×10^{-4} M) at 360 nm (excitation at 280 nm)

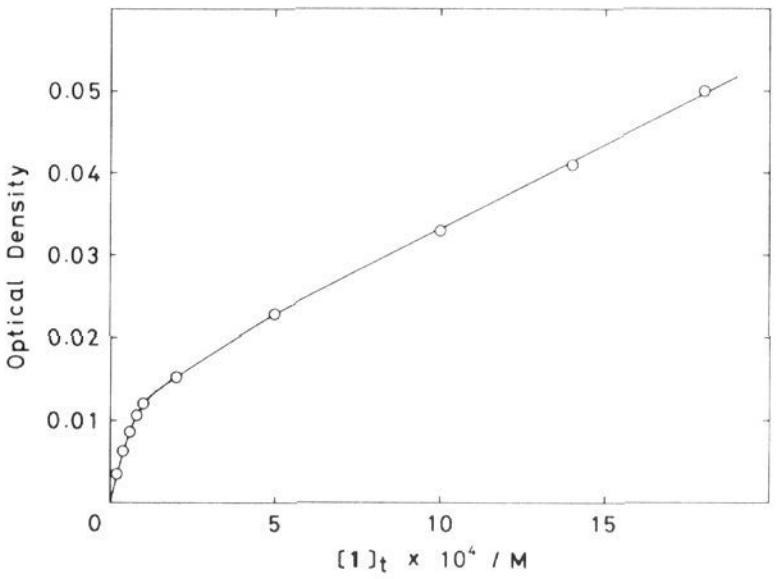


Figure 2. Correlation between total concentration of **1** ($[\mathbf{1}]_t$) and optical density at 380 nm as observed for the system of single-compartment vesicles of $(NA)^+C_5Ala2C_{12}$ (1.0×10^{-4} M) in water at 25.0 °C.

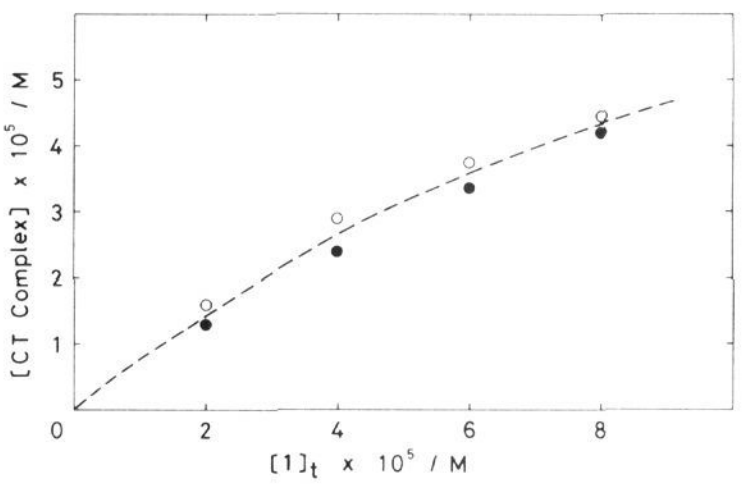


Figure 3. Correlations between total concentration of **1** ($[\mathbf{1}]_t$) and concentration of the corresponding CT complex as evaluated from absorption (●) and fluorescence (○) spectra; the total concentration of $(NA)^+C_5Ala2C_{12}$ being 1.0×10^{-4} M.

(12) Murakami, Y.; Aoyama, Y.; Nakano, A.; Tada, T.; Fukuya, K. *J. Am. Chem. Soc.* **1981**, *103*, 3951–3953.

(13) The CT interaction between 1-alkylnicotinamides and indolyl-3-acetic acid is well documented: (a) Cilento, G.; Tedeschi, P. *J. Biol. Chem.* **1961**, *236*, 907–910. (b) Shinkai, S.; Tamaki, K.; Kunitake, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1918–1921.

(14) Prepared from reaction of nicotinamide with *N*,*N*-didodecyl-N^{α}-(6-bromohexanoyl)-L-alaninamide bromide:[10] liquid crystal with final mp 221 °C, $[\alpha]^{25}_D$ −15.0° (*c* 1.00, EtOH); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.88 [6 H, t, $(CH_2)_{11}CH_3$], 1.25 [40 H, s, $CH_2(CH_2)_{10}CH_3$], 1.35 [3 H, s, $CH(CH_3)$], 1.80 [6 H, m, $N^+CH_2(CH_2)_3CH_2$], 2.20 [2 H, br t, $N^+(CH_2)_4CH_2CO$], 3.30 [4 H, m, $NCH_2(CH_2)_{10}CH_3$], 4.80 [3 H, m, N^+CH_2 and $CH(CH_3)$], 8.15 (1 H, m, Py-5H), 9.24 (2 H, m, Py-4H and -6H), and 10.05 (1 H, br s, Py-2H). Anal. Calcd for $C_{39}H_{71}BrN_4O_3 \cdot H_2O$: C, 63.13; H, 9.92; N, 7.55. Found: C, 62.77; H, 9.71; N, 7.58. A critical aggregate concentration was found by the surface-tension method (Wilhelmy principle), 6.0×10^{-6} M, T_c by the differential scanning calorimetry, −24.5 °C.

(15) Electron micrographs were taken on a JEOL JEM-200B electron microscope installed at the Research Laboratory of High Voltage Electron Microscopy, Kyushu University.

(16) At the increased limit of $(NA)^+C_5Ala2C_{12}$ concentration, which is in a large excess relative to $[\mathbf{1}]_t$ fixed at 1.0×10^{-4} M, an absorbance leveled off. Consequently, ϵ_{CT} was directly determined from the absorbance change in such a saturation range. The variation of $[\mathbf{1}]_t$ [(1.0–5.0) × 10^{-5} M] under conditions of $[\mathbf{1}]_t \ll [(NA)^+C_5Ala2C_{12}]_t = 1.0 \times 10^{-3}$ M led to a linear correlation of $[\mathbf{1}]_t$ vs. absorbance; the slope, which corresponds to $(\epsilon_{CT})^{-1} \cdot (K_1^{-1}[(NA)^+C_5Ala2C_{12}]_t^{-1} + 1)$ on the basis of eq 1, being 3.9×10^{-3}.

(17) Velick, S. F. *J. Biol. Chem.* **1958**, *233*, 1455–1467.

Table I. Formation Constants for CT Complexes of Nicotinamides with Indoles 1 and 2

nicotinamide[a]	state	medium	temp, °C	$K_1(1)$, M^{-1}	ϵ_{CT}[b]	$K_1(2)$, M^{-1}	$K_1(1)/K_1(2)$	ref
$(NA)^+C_5Ala2C_{12}$	vesicle	water	25.0	1.9×10^4	270	1.1×10^2	1.7×10^2	this work
$(NA)^+C_5Ala2C_{12}$	vesicle	bb[d]	25.0	4.5×10^3	280	1.1×10^2	4.1×10	this work
BNA	hs[c]	pb[e]	25	4.09	1060	2.21	1.85	13a
NLaN	micelle	bb[f]	30	41	690	14	2.9	13b
PVCC	polymer	bb[g]	30	271	440	72	3.8	13b
$(N\text{-Et})BNA^+$	hs[c]	water	25.0	8.2	500	4.1	2.0	this work
$Bis(N\text{-Et})XNA^+$	hs[c]	water	25.0	21	340	11	1.9	this work
$BisC_6BNA^+$	hs[c]	water	25.0	28	250	9.0	3.1	this work

[a] BNA, 1-benzylnicotinamide chloride; NLaN, 1-laurylnicotinamide bromide; PVCC, poly-1-(*p*-vinylbenzyl)nicotinamide chloride. [b] Molar absorption coefficient at 380 nm for a CT complex formed with 1. [c] Homogeneous solution. [d] Borate buffer (0.01 M, pH 7.6). [e] Phosphate buffer (0.017 M, pH 6.7). [f] Borate buffer (0.02 M, pH 9.30) containing 8% (v/v) ethanol. [g] Borate buffer (0.02 M, pH 9.30).

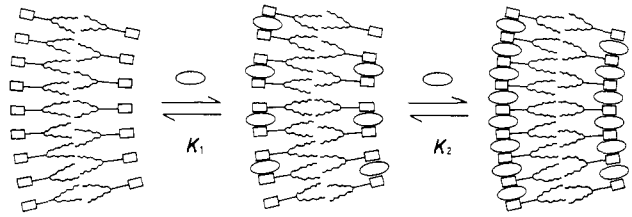


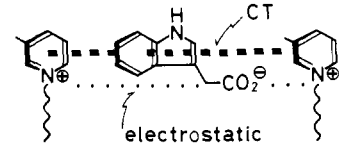
Figure 4. Schematic representation of the biphasic behavior for CT complex formation between vesicular $(NA)^+C_5Ala2C_{12}$ (□ stands for the nicotinamide head group) and **1** (⬭).

underwent significant reduction in the presence of $(NA)^+C_5Ala2C_{12}$ (1.0×10^{-4} M).[18] This allows ready evaluation of the uncomplexed fraction of **1** and hence the amount of CT complex (Figure 3).[19] The data from absorption spectroscopy are in reasonable agreement with those from the fluorescence measurements.

Solutions for the spectral measurements were prepared in three different ways: (a) **1** was added to a presonicated solution of the amphiphile; (b) solution a was sonicated subsequently; and (c) a dichloromethane solution of the amphiphile and **1** was evaporated to dryness, followed by addition of water and sonication. Each sonication was performed for 3 min with a probe-type sonicator at 30 W (W-220F, Heat Systems-Ultrasonics). It is interesting to note, however, that there are no differences in absorbance and fluorescence intensities among these solutions under identical stoichiometric concentrations of species concerned. This indicates that the present single-compartment vesicles provide sufficient substrate permeability,[20] which allows the CT complex formation with **1** to take place at both inner and outer surface regions of the vesicle.

As shown in Figure 3, an amount of the CT complex approaches 0.5×10^{-4} M (half of the total amount of the amphiphile) as the total amount of **1** increases under conditions of $[\mathbf{1}]_t < [(NA)^+C_5Ala2C_{12}]_t$, indicating that two nicotinamide moieties interact with one molecule of **1**. Thus, the CT interaction is so effective that an equimolar mixture of the amphiphile and **1** exhibits nearly complete formation of the CT complex, having remarkable stability (vide infra) and novel stoichiometry (2:1, nicotinamide/**1**) indicating construction of a sandwichlike ternary structure. The CT complex thus formed on a 2:1 stoichiometry basis underwent further interaction with free indolyl-3-acetic acid, which was present in a large excess, but less effectively, as indicated by a moderate rate of absorbance increase in the higher concentration range of **1** (Figure 2). A plausible scheme for the biphasic CT complex formation is shown in Figure 4. The CT interaction in the K_2 step seems to disturb the ternary structure initially formed, and such complexity as arising from the second-step interaction allows evaluation of only an approximate value for K_2 on the basis of the Benesi–Hildebrand-type treatment; $K_2 = 4 \times 10^2$ M^{-1}. A significantly lower value for K_2 relative to K_1 seems to be reasonable.

When the medium was changed from water without any additive to 0.01 M aqueous borate buffer (pH 7.6), the K_1 value was somewhat reduced. Table I summarizes the formation constants for the vesicular system along with those for various nicotinamide derivatives in homogeneous solution as well as for micellar (with a nicotinamide moiety at the head portion of a surfactant molecule) and polymer (with a nicotinamide moiety placed at the side chain of a vinyl polymer) systems. The formation constant increases in the following order when **1** was used as a donor species: homogeneous solution ($\sim 10^0$) < micelle ($\sim 10^1$) < polymer ($\sim 10^2$) < vesicle (10^3–10^4 M^{-1}). This sequence seems to reflect the extent of static organization of nicotinamide groups in each system. The remarkably large formation constant (K_1) for the present vesicular system, as compared with those for the micellar and polymer systems (Table I), is not simply due to high local nicotinamide concentrations but reflects the tight side-by-side arrangement of the amphiphile molecules provided by their hydrophobic and hydrogen-belt interactions[10-12] as well as by an electrostatic interaction among anionic carboxyl groups of the incorporated CT donor molecules (**1**) and cationic nicotinamide moieties of the vesicle (see **3**). The high orientation



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of nicotinamide head groups in the present *tight* vesicles of $(NA)^+C_5Ala2C_{12}$ must be in favor of forming the 2:1 ternary complex with effective contact among interacting species upon desolvation of **1**. Importance of the electrostatic interaction becomes clearer when the K_1 values are compared with those for another CT donor, indole (**2**), which lacks a carboxylate group; there is a 40–170-fold reduction upon changing from **1** to **2** for the present vesicular system. On the other hand, the corresponding values of $K_1(\mathbf{1})/K_1(\mathbf{2})$ for homogeneous solutions, micellar system, and polymer are in the range 2–4 (Table I).

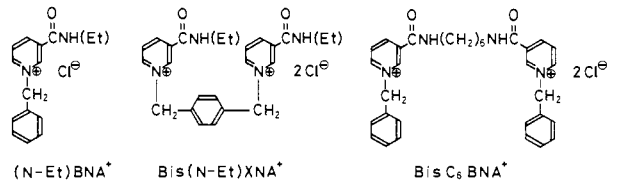
In view of the ternary CT complex formation, it is instructive to refer to simple bis(nicotinamide) systems, $Bis(N\text{-Et})XNA^+$ and $BisC_6BNA^+$,[21] whose CT interactions with **1** are enhanced by 2.6–3.5-fold as compared with the CT affinity of their mono-

(18) Examination of vesicles formed with an amphiphile analogous to $(NA)^+C_5Ala2C_{12}$, but having a trimethylammonium group in place of a nicotinamide moiety as the head group, showed such vesicles practically have no effect on the fluorescence phenomena. Thus, the reduction of fluorescence intensity in the present study is not due to a simple vesicular effect. The fluorescence of **1** was also measured in a homogeneous aqueous phase in the presence of NaBr, but we failed to observe any detectable effect of Br^- ion on the fluorescence phenomenon. Thus, Br^- ion has no effect on the fluorescence in both homogeneous aqueous solution and vesicular assembly.

(19) The complete quenching of emission originated from the indole moiety of 1-(β-indolylethyl)-3-carbamoylpyridinium chloride has been observed upon CT complex formation: Shifrin, S. *Biochim. Biophys. Acta* **1964**, *81*, 205–213. On this basis, the present CT complexes were assumed to undertake no emission process.

(20) Permeability of 8-anilino-1-naphthalenesulfonate in a similar manner through dimyristoyl-L-α-lecithin liposomes has been reported: Tsong, T. Y. *Biochemistry* **1975**, *14*, 5409–5414.

(21) Murakami, Y.; Aoyama, Y.; Kikuchi, J. *J. Chem. Soc., Chem. Commun.* **1981**, 444–446. K_1 values were evaluated for the interaction between the nicotinamide unit and the indole moiety (**1** or **2**) on a 1:1 molar basis in reference to eq 1.



nicotinamide analogue, (N-Et)BNA$^+$ (Table I). The bis(nicotinamide) complexes are presumably constrained to a limited number of conformations by their linkages, decreasing the possibility of an optimal side-by-side interaction.

In conclusion, the present work reveals the importance of side-by-side coherent arrangement of CT donor and acceptor for enhancement of their mutual interaction, which is otherwise not effective in aqueous systems. Even though bis(nicotinamide)-type CT acceptors undergo somewhat enhanced interaction with π donors relative to the corresponding mononicotinamide through intramolecular cooperation of two nicotinamide moieties, such ternary CT complex formation is remarkably enhanced in single-compartment vesicles that lead to the formation of CT complex aggregates. The tight side-by-side arrangement of amphiphile molecules due to their hydrophobic and hydrogen-belt interactions forces CT donor molecules to be placed in the proximity sites of acceptor moieties and to come into close contact with them upon desolvation when donor molecules are incorporated. Such molecular organization favorable to CT interaction is further advanced by additional electrostatic interaction among donor and acceptor molecules on the vesicular surface. Such highly organized molecular assemblies can be utilized as effective reaction fields that are able to enhance various reactions due to so-called proximity effects. Single-compartment vesicles involving amino acid residues as molecular components are quite promising molecular assemblies for this purpose.

Registry No. 1, 87-51-4; **2**, 120-72-9; (NA)$^+C_5Ala2C_{12}$, 81388-56-9; (*N*-Et)BNA$^+$, 81388-57-0; bis(*N*-Et)BNA$^+$, 81388-58-1; bis(C_6BNA$^+$), 81408-01-7.

Complexity in the Reductive Reaction of $CoCl_2$ in the Presence of Phosphites. Isolation of Stable, Noninterconvertible $Co[P(OCH_3)_3]_4$ and $Co_2[P(OCH_3)_3]_8$ Molecules

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Received December 10, 1981

We have found that the reduction of cobalt(II) chloride by sodium amalgam in the presence of triisopropyl phosphite in tetrahydrofuran solution yielded $HCo[P(O\text{-}i\text{-}C_3H_7)_3]_4$ and $Co_2[P(O\text{-}i\text{-}C_3H_7)_3]_8$ in an approximate molar ratio of 2:1. This result was initially interpreted by us, in partial analogy to cobalt carbonyl chemistry, as a primary generation of a $Co[P(O\text{-}i\text{-}C_3H_7)_3]_4$ radical, which then either dimerized or abstracted a hydrogen atom from a solution-state species. However, this seemingly plausible mechanistic rationale is untenable. In the analogous trimethyl phosphite system, we have now isolated and fully characterized the monomer $Co[P(OCH_3)_3]_4$ and the dimer $Co_2[P(OCH_3)_3]_8$ and have further shown that they do not interconvert. Neither monomer nor dimer abstracts hydrogen atoms from organic solvents

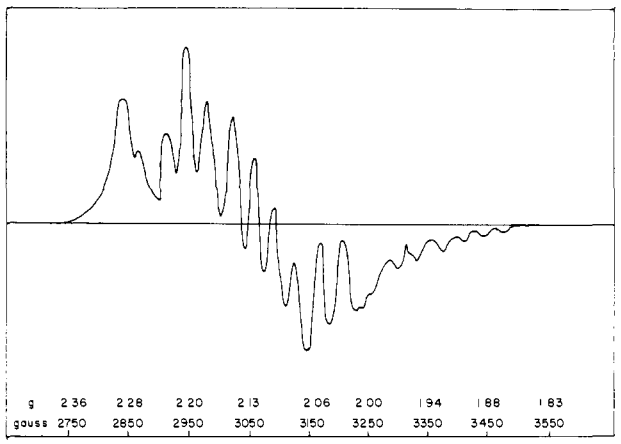
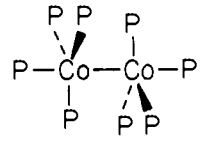


Figure 1. The electron spin resonance spectrum of $Co[P(OCH_3)_3]_4$ in a toluene glass at −196 °C shows a $g_\perp = 2.099$ and $g_\parallel = 2.149$ with hyperfine coupling constants (cm^{-1}) of $|A_\parallel(Co)| = 0.0072$, $|A_\perp(Co)| = 0.0037$, $|A_\perp(P_1)| = 0.08$, $|A_\parallel(P_1)| = 0.0104$, and $|A_\parallel(P_2\text{-}P_4)| \simeq 0.00055$. This spectrum was originally observed and analyzed by F. J. Hirsekorn and K. Zamaraev in our laboratories at Cornell Univeristy in 1975, but the composition of the complex was not defined at that time nor were single crystals obtained. The analysis of the spectral details presented here is based on the earlier studies with slightly better resolved spectra obtained at −196 and −160 °C in toluene and toluene-d_8 glasses.

or reacts with hydrogen (H_2) until temperatures of 50–90 °C. There are, in fact, rather striking differences between the phosphite and the carbonyl chemistry of zerovalent or monovalent cobalt complexes as established by our studies described herein.

Reduction of cobalt(II) chloride by 2 equiv of sodium amalgam in the presence of excess triisopropyl phosphite in tetrahydrofuran at 25 °C produced $HCo[P(O\text{-}i\text{-}C_3H_7)_3]_4$[2] and $Co_2[P(O\text{-}i\text{-}C_3H_7)_3]_8$ in respective yields of 54% and 46% (based on cobalt equivalents).[4] The dimer is a novel, remarkable species, with eight bulky isopropyl phosphite ligands, which has an axially bridged bi(trigonal bipyramidal) form, **1**, as established by the solution-state NMR



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studies.[5] In sharp contrast, the analogous reduction[6] in the presence of excess trimethyl phosphite produced as major products the new trigonal-bipyramidal $Co[P(O)(OCH_3)_2][P(OCH_3)_3]_4$ complex,[7] the mercurial $Hg\{Co[P(OCH_3)_3]_4\}_2$,[8,10] and an unusual salt, $\{Co[P(OCH_3)_3]_5^+\}\{Co[P(OCH_3)_3]_4Na[(CH_3O)_3P]_4Co^-\}$[13] in respective yields[4] of ~20%, 20%, and 50%. Only small amounts of $HCo[P(OCH_3)_3]_4$[8] and $CH_3Co[P(OCH_3)_3]_4$[8] and none of the

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(2) For original synthesis and characterization data, see ref 3.

(3) (a) Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 6978. (b) Rakowski, M. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 739.

(4) All yields reported here are in terms of cobalt atom equivalents.

(5) $^{31}P\{^1H\}$ NMR (toluene-d_8, −70 °C) δ 183.3 (eq P, d, J_{PP} = 73 Hz, 3), 245 (ax P, q, J_{PP} = 73 Hz, 1). All ^{31}P data are referenced to 85% H_3PO_4.

(6) See Supplementary Material for synthesis procedure.

(7) Anal. Calcd for $CoC_{14}H_{42}O_{15}P_5$: C, 25.31; H, 6.39; P, 23.31. Found: C, 25.68; H, 6.29; P, 23.04. ^1H NMR ($CD_3C_6D_5$, 35 °C) δ 3.55 (complex m); $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, −70 °C; A = ax $P(OCH_3)_3$, B = eq $P(OCH_3)_3$, C = ax $P(O)(OCH_3)_2$) δ 169.09 (A, second-order d of quar, J_{AB} = 137.6 Hz, J_{AC} = 275.2 Hz, 1), 154.09 (B, t, J_{AB} = 137.6 Hz, J_{BC} = 137.6 Hz, 3), 109.87 (C, overlapping d of quar, J_{AC} = 275.2 Hz, J_{BC} = 137.6 Hz, 1); $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 27 °C) δ 155.9 (A and B, br, s, 4), 107.5 (C, br, s, 1).

(8) For the original synthesis and characterization of this complex see ref 9.

(9) Muetterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 7920.

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