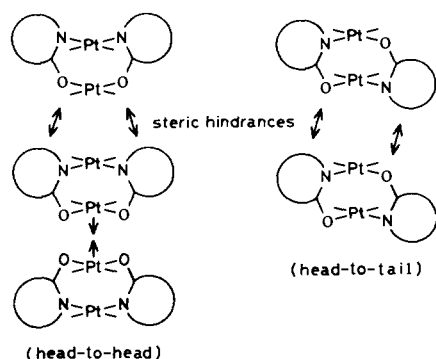


**Figure 1.** ORTEP view of the  $[\text{Pt}_6(\text{NH}_3)_{16}(\text{C}_2\text{H}_4\text{NO})_8]^{10+}$  cation. Selected Pt-Pt distances ( $\text{\AA}$ ) and angles (deg) are as follows: Pt(1)-Pt(2), 2.880 (2); Pt(2)-Pt(3), 2.900 (1); Pt(3)-Pt(4), 2.778 (1); Pt(4)-Pt(4'), 2.934 (1); Pt(1)-Pt(2)-Pt(3), 163.77 (5); Pt(2)-Pt(3)-Pt(4), 165.51 (4); Pt(3)-Pt(4)-Pt(4'), 168.78 (5), where a symmetry operation for Pt(4') is  $-X, -Y + 1, -Z + 1$ .

#### Scheme I



$\text{\AA}$ ). Each outer interdimer interaction of Pt(2)-Pt(3) = 2.900 (1)  $\text{\AA}$  is also reinforced by two chemically nonequivalent hydrogen bonds ( $\text{O}(1)-\text{N}(10) = 2.98$  (3)  $\text{\AA}$  and  $\text{O}(2)-\text{N}(4) = 2.83$  (3)  $\text{\AA}$ ), where a new type of interdimer interaction is achieved between the outer O,O-coordination and the inner N,N-coordination spheres. The close contacts of non-hydrogen-bonding nitrogens between Pt(2) and Pt(3) planes,  $\text{N}(8)-\text{N}(3) = 3.26$  (4)  $\text{\AA}$  and  $\text{N}(7)-\text{N}(9) = 3.45$  (4)  $\text{\AA}$ , and the large torsional angle of  $37.9^\circ$  about the Pt(2)-Pt(3) axis suggest an attractive interaction of the two planes. Both of the interdimer Pt-Pt distances are a little longer than the values of 2.866 (2)-2.9158 (6)  $\text{\AA}$  for the tetra-

**Table I.** Geometric Features around the Pt-Pt Spheres

Pt-Pt	$\tau^a$ deg	$\omega^b$ deg	repulsion distances, <sup>c</sup> $\text{\AA}$ (esd)
Pt(1)-Pt(2)	28.4	3.7	$\text{N}(5)-\text{N}(7) = 3.66$ (4), $\text{N}(6)-\text{N}(8) = 3.68$ (4)
Pt(2)-Pt(3)	10.7	37.9	$\text{N}(7)-\text{N}(9) = 3.45$ (4), $\text{N}(8)-\text{N}(3) = 3.26$ (4)
Pt(3)-Pt(4)	25.6	5.6	$\text{N}(9)-\text{N}(11) = 3.57$ (4), $\text{N}(10)-\text{N}(12) = 3.47$ (3)

<sup>a</sup> Tilt angles between adjacent platinum coordination planes. <sup>b</sup> Average torsional angles about the Pt-Pt axes. <sup>c</sup> Repulsion distances between non-bridged amines, including a non-hydrogen-bonded nitrogen of acetamidate, N(3).

nuclear platinum (2.25+) blues,<sup>1,2</sup> but still much shorter than the values of 3.129 (1)-3.2355 (5)  $\text{\AA}$  for the tetranuclear Pt(II)<sub>4</sub> complexes.<sup>5</sup> Table I summarizes geometric features around Pt-Pt vectors.

As the unit cell contains ten nitrate anions, the average platinum oxidation state is 2.25, Pt<sup>II</sup><sub>6</sub>Pt<sup>III</sup><sub>2</sub>. The complex shows no ESR signal and seems to be diamagnetic. The intradimer Pt-Pt distances are different between the inner (2.778 (1)  $\text{\AA}$ ) and the outer (2.880 (2)  $\text{\AA}$ ) dimers. The former, 2.778 (1)  $\text{\AA}$ , is comparable to the values of 2.7745 (4)<sup>1b</sup> to 2.8296 (5)<sup>2</sup>  $\text{\AA}$  for the tetranuclear platinum (2.25+) blues, suggesting the average oxidation state for the inner units is close to 2.25, and, therefore, the outer two units would also be partially oxidized. Since there are no distinctively short distances ascribable to Pt(II)-Pt(III)<sup>4</sup> or Pt(III)-Pt(III),<sup>6</sup> all seven Pt-Pt distances would be rather equivalent except for the existence or the absence of the bridging ligands. Therefore, it seems probable that the two Pt(III) states delocalize over several Pt atoms as in the previous platinum blues.

**Acknowledgment.** The present work is financially supported by Toray Science Foundation, Japanese Ministry of Health and Welfare, and Japanese Ministry of Education, Science and Culture (Grant-in-Aid for Scientific Research on Priority Area).

**Supplementary Material Available:** Tables giving crystallographic data, positional parameters, mean square displacement tensors, symmetry operations, bond distances and angles, torsion angles, shifts of Pt atoms from the least-squares planes, dihedral angles between Pt coordination planes, and repulsion distances (14 pages); listing of structure factors (26 pages). Ordering information is given on any current masthead page.

#### A Remarkable Effect of Solvent Size on the Stability of a Molecular Complex

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The thermodynamic stability of molecular complexes depends in part upon attractive forces between the binding partners and upon changes in entropy which occur on binding. It also depends upon solvation. For organic molecules dissolved in organic solvents, solvation energies are usually negative, and the decreases in solvation which often accompany binding inhibit molecular complex formation. An example of such a phenomenon is provided by the solvent-dependent dimerization of the five-membered lactam 2-pyrrolidinone. In  $\text{CCl}_4$ , the lactam forms a hydrogen-bonded dimer with a dissociation energy of  $\sim 3$  kcal/mol which falls to 0.0-0.6 kcal/mol in the more polar, hydrogen bond donor solvent  $\text{CHCl}_3$ .<sup>1,2</sup> The decrease in dissociation energy which occurs on

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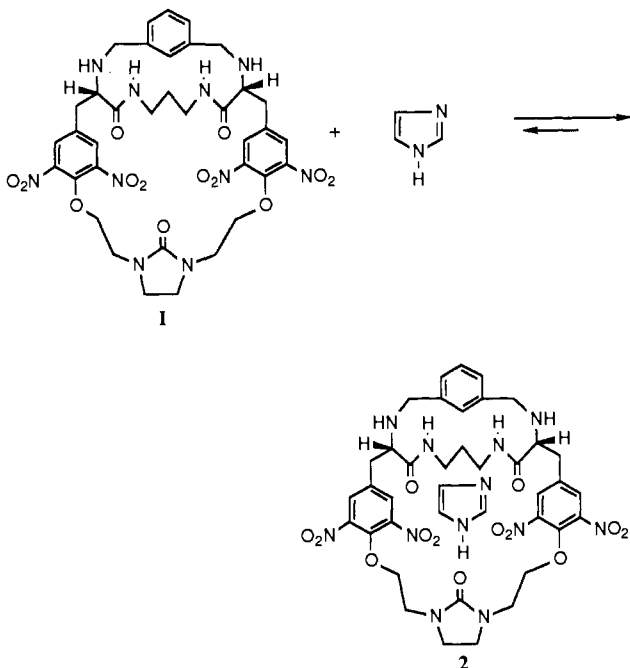
**Table I.** Solvent Dependence of Association between **1** and Imidazole

solvent	$K_a^e$ ( $M^{-1}$ )	$\Delta G_a$ (kcal/mol)	% saturation <sup>f</sup>	$\epsilon^g$
CH <sub>2</sub> Cl <sub>2</sub>	240 ± 24 <sup>h</sup>	-3.25 ± 0.06 <sup>h</sup>	79	9.08 <sup>a</sup>
CHCl <sub>3</sub>	490 ± 70 <sup>h</sup>	-3.67 ± 0.09 <sup>h</sup>	80	4.81 <sup>a</sup>
CH <sub>2</sub> CCl <sub>3</sub>	8161 ± 370 <sup>h</sup>	-5.33 ± 0.03 <sup>h</sup>	90	7.20 <sup>b</sup>
CHCl <sub>2</sub> CHCl <sub>2</sub>	128 000 ± 9000 <sup>h</sup>	-6.96 ± 0.10 <sup>h</sup>	88	8.20 <sup>c</sup>
THF	29.0 ± 4.0 <sup>h</sup>	-2.00 ± 0.08 <sup>h</sup>	65	8.20 <sup>b</sup>
2-Me-THF	77.0 ± 9.0 <sup>h</sup>	-2.57 ± 0.07 <sup>h</sup>	83	6.97 <sup>d</sup>
2,5-Me <sub>2</sub> -THF	185 ± 27 <sup>h</sup>	-3.09 ± 0.10 <sup>h</sup>	85	
2,2-Me <sub>2</sub> -THF	156 ± 19 <sup>h</sup>	-2.99 ± 0.08 <sup>h</sup>	85	
2,2,5,5-Me <sub>4</sub> -THF	1067 ± 110 <sup>h</sup>	-4.13 ± 0.30 <sup>h</sup>	76	
tetrahydropyran	104 ± 18 <sup>h</sup>	-2.75 ± 0.10 <sup>h</sup>	86	5.61 <sup>c</sup>
1,4-dioxane	87 ± 10 <sup>h</sup>	-2.65 ± 0.08 <sup>h</sup>	74	2.21 <sup>c</sup>
<i>tert</i> -butyl methyl ether	566 ± 80 <sup>h</sup>	-3.75 ± 0.10 <sup>h</sup>	83	
<i>i</i> -propanol	13 ± 2 <sup>h</sup>	-1.53 ± 0.06 <sup>h</sup>	82	18.3 <sup>a</sup>
<i>tert</i> -butyl alcohol	66 ± 13 <sup>h</sup>	-2.48 ± 0.13 <sup>h</sup>	82	10.9 <sup>a</sup>
acetonitrile	no association	>-1.5		37.5 <sup>a</sup>

<sup>a</sup> *Handbook of Chemistry and Physics*, 62nd ed.; Weast, R. C., Ed.; Chemical Rubber Co.: 1981. <sup>b</sup> *Industrial Solvents Handbook*; Flick, E. W., Ed.; Noyes Data Corp.: Parkridge, NJ, 1985. <sup>c</sup> Mashuhara, H.; Hino, T.; Mataga, N. *J. Phys. Chem.* **1975**, *79*(10), 994. <sup>d</sup> Furutsaka, T.; Imura, T.; Kojima, T.; Kawabe, K. *Technol. Rep. Osaka Univ.* **1974**, *24*, 367. <sup>e</sup> By UV titration of imidazole (0.03–0.3 M depending on the solvent) to **1** ( $\sim 1 \times 10^{-4}$  M) at 25.0 ( $\pm 0.1$ ) °C. <sup>f</sup> Percentage of saturation achieved in titration binding assay. <sup>g</sup> Dielectric constant. <sup>h</sup> Errors follow from error propagation analysis given a UV machine error of 0.0002 AU and uncertainties in solution volume of 5%.

changing the solvent from CCl<sub>4</sub> to CHCl<sub>3</sub> results from a selective increase in the extent of solvation of the unbound lactam (i.e., its solvation energy becomes more negative). In this communication, we show that relative solvation energies of host, guest, and complex may be varied by subtle changes in solvent structure and that these changes give rise to major variations in the association constant of a simple host-guest system.

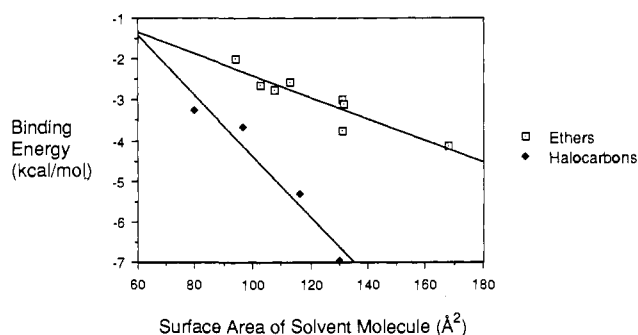
The equilibrium we have studied is shown below. Compound **1** is closely related to a host we described previously which uses the formation of hydrogen bonds as a driving force for association in organic solvents with donor/acceptor guests such as imidazole.<sup>3</sup>



In the current system we replace the previously described aryl iodide substituents with chromophoric nitro groups. This substitution facilitates binding measurements using UV difference spectroscopy due to the large changes in the long wavelength absorptions ( $\lambda \cong 350$  nm) of **1** which occur upon binding.

(2) For other reports of organic solvation effects upon molecular complex stability, see: Schneider, H.-J.; Kramer, R.; Simova, S.; Schneider, U. *J. Am. Chem. Soc.* **1988**, *110*, 6442. Diederich, F.; Dick, K.; Griebel, D. *J. Am. Chem. Soc.* **1986**, *108*, 2273. Canceill, J.; Lacombe, L.; Collet, A. *J. Am. Chem. Soc.* **1986**, *108*, 4230. Sheridan, R. E.; Whitlock, H. W., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 7120.

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**Figure 1.** Correlation between **1**/imidazole association and surface area of solvent molecules listed in Table I.

To investigate the effect of solvent structure on binding, we measured the association constant of **1** and imidazole in a range of organic solvents differing both in functionality and dimensions. As shown in Table I, the extent of binding is strongly dependent upon the nature of the solvent. Significant variations are found even within the same functional class. For example, the chlorinated hydrocarbon solvents methylene chloride, chloroform, 1,1,1-trichloroethane, and 1,1,2,2-tetrachloroethane give binding constants for **1** and imidazole of 240, 490, 8161, and 128 000  $M^{-1}$ , respectively. This span of association constants corresponds to an increase in binding energy of >3.5 kcal/mol upon changing the solvent from methylene chloride to tetrachloroethane. Analogous increases in binding were observed in the series of ethereal solvents.

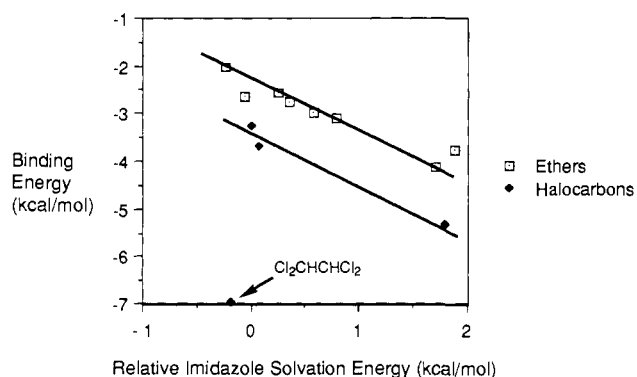
Among solvents of a single class, there is no apparent connection between binding energy and solvent properties such as bulk dielectric constant or molecular dipole moment. However, there is a good correlation with solvent size. Figure 1 shows our host/guest binding energies in chlorinated hydrocarbon and ethereal solvents plotted against the van der Waals surface areas of the solvent molecules. The plot indicates that binding increases roughly in proportion to the surface area of the solvent molecule. Decreases in extent of solvation with increasing size of solvent molecules have been reported previously in simple systems and generally reflect decreases in solute coordination number.<sup>4</sup> While the size of solvent molecules may thus be one determinant of binding affinity, the relative ability of the solvent molecules to develop specific associative interactions with the solutes is another.

(4) The solvation of inert gas solutes decreases as the size of inert gas and hydrocarbon solvent molecules increases: Davies, R. H.; Duncan, A. G.; Saville, G.; Staveley, L. A. K. *Trans. Faraday Soc.* **1967**, *63*, 855. Chui, C. H.; Canfield, F. B. *Trans. Faraday Soc.* **1971**, *67*, 2933. Pollack, G. L. *J. Chem. Phys.* **1981**, *75*, 5874. Pollack, G. L.; Himm, J. F. *J. Chem. Phys.* **1982**, *77*, 3221.

**Table II.** Relative Solubility of Imidazole in Chlorinated Hydrocarbon and Tetrahydrofuran Solvents

solvent	solubility <sup>a</sup> (mg/mL)	partition coeff <sup>b</sup>	$\Delta G^c$ (kcal/mol)
CH <sub>2</sub> Cl <sub>2</sub>	27.5	$1.5 \times 10^{-2}$	0.0
CHCl <sub>3</sub>	25.8	$1.3 \times 10^{-2}$	+0.04, <sup>c</sup> +0.08 <sup>d</sup>
CH <sub>3</sub> CCl <sub>3</sub>	0.08	$7.1 \times 10^{-4}$	+3.5, <sup>c</sup> +1.8 <sup>d</sup>
CHCl <sub>2</sub> CHCl <sub>2</sub>	37.4	$2.2 \times 10^{-2}$	-0.2, <sup>c</sup> -0.2 <sup>d</sup>
THF	41.3		-0.3 <sup>c</sup>
2-MeTHF	18.0		+0.3 <sup>c</sup>
2,5-Me <sub>2</sub> THF	7.3		+0.8 <sup>c</sup>
2,2-Me <sub>2</sub> THF	10.5		+0.6 <sup>c</sup>
2,2,5,5-Me <sub>4</sub> THF	1.58		+1.7 <sup>c</sup>
tetrahydropyran	16.1		+0.3 <sup>c</sup>
dioxane	30.5		-0.1 <sup>c</sup>
<i>t</i> -BuOMe	1.18		+1.9 <sup>c</sup>

<sup>a</sup> [Imidazole] in a saturated solution of the solvent shown. <sup>b</sup> [Imidazole]<sub>organic solvent</sub>/[imidazole]<sub>water</sub> by weight after vigorously stirring 1 M imidazole in water with an equal volume of organic solvent (25 °C). <sup>c</sup> From solubility. <sup>d</sup> From partition coefficient. <sup>e</sup> Solvation energies of imidazole in various solvents relative to methylene chloride.

**Figure 2.** Correlation between 1/imidazole association and imidazole solvation in solvents listed in Table II.

Such interactions might include, for example, solute hydrogen bonding to the ethereal oxygen of the tetrahydrofuranoid solvents in inverse proportion to the extent of hindering methylation.

Considering the effect of specific solvent/solute interactions upon the position of the binding equilibrium above, we note that imidazole must undergo substantial desolvation as it is encapsulated by **1** during binding. Other effects being comparable, we would therefore expect a decrease in the extent of solvation of the free substrate imidazole to favor its binding to **1**. To measure the relative solvation free energy of imidazole in various solvents, we carried out the solubility and partition experiments summarized in Table II. Upon plotting the relative free energies of imidazole solvation against the association energies of **1** and imidazole (Figure 2), we find a strong inverse correlation ( $R > 0.95$ , slope  $\approx -1.0$ ) for many of the solvents examined. The unitary relation of binding and imidazole solvation shows that the relative solvation energies of **1** and **2** are similar for most solvents of the same class and that it is differential imidazole solvation which is primarily responsible for shifting of the binding equilibrium.<sup>5</sup>

Some solvents, most notably 1,1,2,2-tetrachloroethane, lie well off the correlation lines in Figure 2. Such deviations imply differential solvation not of the substrate but of either the host **1** or the complex **2**.<sup>6</sup> We believe the best explanation of the 1,1,2,2-tetrachloroethane result lies in an especially poor solvation

(5) Using imidazole solvation energy as a standard, the somewhat tighter association of **1** and imidazole (Figure 2) in the chlorocarbon solvents implies an enhanced solvation of **2** or diminished solvation of **1** relative to the ethereal solvents.

(6) No chemical change to **1** (e.g., formation of ammonium salts) seems to occur in tetrachloroethane: the same binding constants were found in methylene chloride solution whether or not **1** had been previously treated with 1,1,2,2-tetrachloroethane.

(7) This work was supported by Grant CHE86-05891 from the National Science Foundation and an American Cancer Society fellowship to K.T.C.

of **1**. In particular, we suggest that the binding cavity is sensitive to the size and shape of the solvent molecules and that large solvents do not penetrate and solvate it as well as smaller ones. By using solvents which do not interact favorably with internal binding cavities, a binding site need not be extensively desolvated to accept and bind a smaller or more appropriately shaped substrate. Complex formation should thus be favored in solvents whose molecular dimensions are large relative to those of the binding site.

In conclusion, the stability of our molecular complex is highly dependent upon the detailed structure of the solvent molecules employed. Binding is favored by solvents which selectively provide weak solvation of uncomplexed components or strong solvation of the molecular complex. Our results provide examples of the former mechanism of complexation enhancement. If our hypothesis of differential solvation of the substrate binding site as a function of solvent molecule size is correct, then other host molecules with preorganized three-dimensional cavities should exhibit increases in association constant in media composed of increasingly bulky solvent molecules. The solvent effects described here should facilitate the study of many molecular complexes which are not stable enough to be readily observed in more traditional organic solvents.<sup>7</sup>

### Glycidyl Derivatives as Chiral C<sub>3</sub> Synthons. Ring Opening Catalyzed by BF<sub>3</sub> Etherate

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Derivatives of glycidol such as the 4-nitrobenzoate<sup>1</sup> and arenesulfonates<sup>2</sup> possess widespread synthetic utility as chiral building blocks because of their stability and convenience in preparation. Since some glycidyl derivatives can be obtained in high optical purity,<sup>3</sup> we have sought to prepare some monoprotected 1,2-diols via nucleophilic opening reactions. Although a variety of Lewis acids have been found to be effective mediators of regio- and stereoselective epoxide openings,<sup>4</sup> no reports of Lewis acid mediated opening of glycidyl derivatives have appeared.<sup>5</sup> The well-known Ti(OPr-*i*)<sub>4</sub>-mediated epoxy alcohol opening process<sup>6a,b</sup> failed to afford the desired opening of glycidyl derivatives **1-3** when benzyl alcohol, thiophenol, and various long-chain alcohols

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