Secondary Hypervalent I(III)···O Interactions: Synthesis and Structure of Hypervalent Complexes of Diphenyl-λ³-iodanes with 18-Crown-6

Masahito Ochiai,*,[†] Takashi Suefuji,[†] Kazunori Miyamoto,[†] Norihiro Tada,[†] Satoru Goto,[†] Motoo Shiro,[‡] Shigeru Sakamoto,[§] and Kentaro Yamaguchi[§]

Contribution from the Faculty of Pharmaceutical Sciences, University of Tokushima, 1-78 Shomachi, Tokushima 770-8505, Japan, Rigaku Corporation, 3-9-12 Matsubara, Akishima, Tokyo 196-8666, Japan, and Chemical Analysis Center, Chiba University, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Received August 23, 2002 ; E-mail: mochiai@ph2.tokushima-u.ac.jp

Abstract: Reported here for the first time are the synthesis and characterization of supramolecular complexes between diaryl-λ³-iodanes and 18-crown-6 (18C6). Slow evaporation of solvents afforded 1:1 and 2:1 complexes between Ph_2IBF_4 and 18C6 as stable crystals, depending on the conditions. X-ray crystal structures of these complexes indicated that each iodine atom contacts with the three adjacent oxygen atoms of 18C6 through two hypervalent secondary bonding and a weak interaction. ^{1}H NMR analyses and CSI-MS spectra showed that, in dichloromethane solution, Ph_2IBF_4 exclusively forms the 1:1 complex with 18C6 (binding constant K_a, 1.02×10^3 M^{-1}). The binding constants decrease with the increased solvent donor ability (Gutmann's DN). Changing the heteroatom ligand from BF_4 to the less nucleophilic PF_6 and AsF_6 increased the binding constant by about six times. Substitution of an electron-withdrawing group onto the *para* position of Ph_2IBF_4 tends to increase in the complex stability. A linear Hammett relationship ($\rho = 0.59$) between log K_a and σ_p^+ values of substituents indicates that the diaryl-λ³-iodanes with electropositive iodine(III) interact more efficiently with 18C6. Decreased binding magnitude was measured with 15C5, dibenzo-18C6, dibenzo-21C7, and dibenzo-30C10.

Introduction

Metal ions form crystalline complexes with crown ethers through ion—dipole electrostatic interactions, the oxygen lone pairs being attracted to the cation positive charge.[1] A variety of organic molecules with acidic hydrogens bind to crown ethers via hydrogen bonding.[2] For instance, alkylonium ions such as alkylammonium,[3a] alkylsulfonium,[3b] and alkylphosphonium ions[3c] as well as hydronium ion[2a] with acidic hydrogens bind crown ether hosts via X—H···O (X = C, N, and O) hydrogen bonding in a perching arrangement. Solid complexes of certain neutral molecules such as MeCN, $MeNO_2$, Me_2SO_2, and DMSO with polar C—H bonds with 18-crown-6 (18C6) showed C—H···O interactions. In this paper, we show that intermolecular hypervalent I(III)···O interactions,[4] secondary bonding,[5] play an essential role in complexation of diaryl-λ³-iodanes with crown ethers. The result provides us with a new class of interaction in supramolecular chemistry of crown ethers.

Molecular iodine forms 1:1 complexes with crown ethers, but the interaction is moderate.[6,7] The binding of iodine does not involve the cavity of the macrocyclic polyethers but rather involves a single oxygen—iodine interaction with a linear orientation of the halogen molecule with the donor atom. Diaryl-λ³-iodanes (diaryliodonium salts) are generally tetra- or penta-coordinated in the solid states,[8] which suggested to us that these λ³-iodanes might form discrete complexes with crown ethers through cooperative interactions between iodine(III) and oxygen atoms of crown ethers, in marked contrast to a simple interaction in iodine·crown ether complexes.[9]

[†] University of Tokushima.

[‡] Rigaku Corporation.

[§] Chiba University.

(1) (a) Pedersen, C. J.; Frensdorff, H. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 16. (b) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: New York, 2000. (c) Inoue, Y.; Gokel, G. W. *Cation Binding by Macrocycles*; Marcel Dekker: New York, 1990.

(2) (a) Cram, D. J.; Trueblood K. N. *Top. Curr. Chem.* **1981**, *98*, 43. (b) Vogtle, F.; Sieger, H.; Muller, W. *Top. Curr. Chem.* **1981**, *98*, 107.

(3) (a) Kyba, E. P.; Helgeson, R. C.; Madan, K.; Gokel, G. W.; Tarnowski, T. L.; Moore, S. S.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 2564. (b) Allwood, B. L.; Crosby, J.; Pears, D. A.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 977. (c) Allwood, B. L.; Colquhoun, H. M.; Crosby, J.; Pears, D. A.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 824.

(4) (a) Oae, S. *Phosphorus Sulfur* **1986**, *27*, 13. (b) Ochiai, M.; Iwaki, S.; Ukita, T.; Matsuura, Y.; Shiro, M.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4606.

(5) (a) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1. (b) Alcock, N. W. *Bonding and Structure*; Ellis Horwood: Chichester, 1990. (c) Starbuck, J.; Norman, N. C.; Orpen, A. G. *New J. Chem.* **1999**, *23*, 969. (d) Macikenas, D.; Skrzypczak-Jankun, E.; Protasiewicz, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2007. (e) Landrum, G. A.; Hoffmann, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1887.

(6) Binding constants of iodine in cyclohexane at 25 °C are 4.93 M^{-1} for 18C6, 4.78 for 15C5, 5.36 for 12C4, and 2.54 for THF. See: Hopkins, H. P.; Jahagirdar, D. V.; Windler, F. J. *J. Phys. Chem.* **1978**, *82*, 1254.

(7) For donor—acceptor complexes between alkyl iodides with oxygen atoms, see: (a) Chu, Q.; Wang, Z.; Huang, Q.; Yan, C.; Zhu, S. *J. Am. Chem. Soc.* **2001**, *123*, 11069. (b) Rege, P. D.; Malkina, O. L.; Goroff, N. S. *J. Am. Chem. Soc.* **2002**, *124*, 370.

(8) (a) Koser, G. F. *The Chemistry of Functional Groups, Supplement D*; Wiley: New York, 1983; Chapter 18. (b) Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH: New York, 1992. (c) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123.
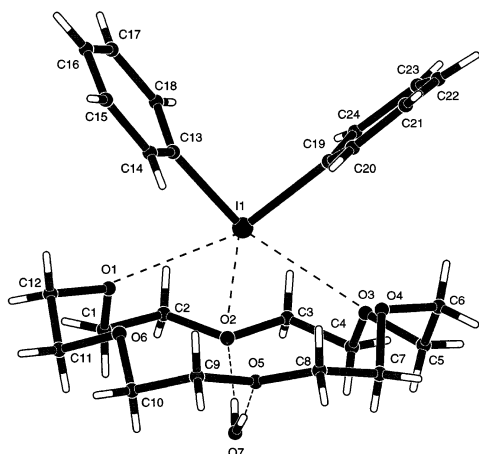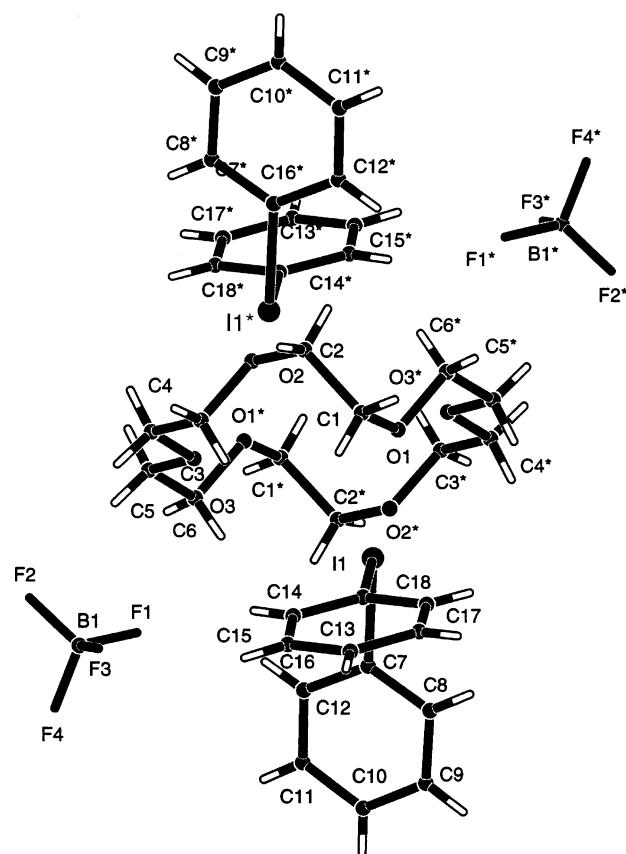
Figure 1. X-ray crystal structure of Ph$_2$IBF$_4$·18C6·1.5 H$_2$O complex **2a**. Secondary interactions are shown in dashed lines. The O8, iodine with lower probability, and BF$_4$ were omitted for clarity. Selected bond lengths (Å) and angles (deg): I(1)−C(13), 2.101(3); I(1)−C(19), 2.107(3); I(1)−O(1), 2.949(2); I(1)−O(2), 3.201(2); I(1)−O(3), 3.143(2); O(5)−H(7O), 2.045; O(2)−H(7O′), 2.116; C(13)−I(1)-C(19), 91.6(1); C(19)−I(1)-O(1), 163.7-(1); C(13)−I(1)-O(3), 167.6(1).

Results and Discussion

Synthesis and Solid-State Structure of Crown Ether Complexes of Diphenyl-λ^3-iodane. Slow evaporation of a dichloromethane−diethyl ether (5:3) solution of a 1:2 mixture of diphenyl-λ^3-iodane Ph$_2$IBF$_4$ (**1a**) and 18C6 in a refrigerator (ca. 4 °C) afforded a 92% yield of colorless single crystals of 1:1 Ph$_2$IBF$_4$·18C6 complex **2a** that were suitable for X-ray crystallography (Figure 1). The iodine atom of **2a** is disordered at the two locations in a probability of 0.756:0.244. On the other hand, when the solvent was changed to dichloromethane−hexane (1:2) and twice as much **1a** relative to 18C6 was used, colorless single crystals of the 2:1 Ph$_2$IBF$_4$·18C6 complex **2b** were obtained in an 86% yield (Figure 2). These crystals are highly stable, and no decomposition was observed on standing at room temperature for over 2 months. This is the first example of complexation between λ^3-iodanes and crown ethers.

Figures 1 and 2 indicate that for both complexes **2** the diphenyl-λ^3-iodanyl groups protrude above one face (for **2a**) and both faces (for **2b**) of the host to provide a perching type of host−guest relationship.[2a] As observed in the crystal structure of (diacetoxyiodo)benzene,[10] both complexes **2** adopt a distorted pentagonal planar coordination about the iodines, in which each iodine atom contacts with the three adjacent oxygen atoms of 18C6: O1−O3 for I1 of **2a**; O1, O2*, and O3* for I1 of **2b**. The average deviations of the six atoms (iodine, two *ipso* carbons of phenyl groups, and three oxygens) from their least squares planes are 0.256(1) (**2a**) and 0.244(2) Å (**2b**), with the sums of the iodine-centered bond angles $\Sigma°I = 359.2(1)°$ for **2a** and 362.0(2)° for **2b**.

The I1···O1 and I1···O3 distances in **2a** are 2.949(2) and 3.143(2) Å, respectively, being considerably longer than the average covalent bond between O and I (2.14 Å)[11] but definitely shorter than the sum of the van der Waal's radii of O (1.52 Å) and I (1.98 Å). Because both the C19−I1···O1 and

(9) For supramolecular chemistry of diaryl-λ^3-iodanes, see: Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502.

(10) Alcock, N. W.; Countryman, R. M.; Esperas, S.; Sawyer, J. F. *J. Chem. Soc., Dalton Trans.* **1979**, 854.

(11) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

Figure 2. X-ray crystal structure of (Ph$_2$IBF$_4$)$_2$·18C6 complex **2b**. Selected bond lengths (Å) and angles (deg): I(1)−C(7), 2.119(2); I(1)−C(13), 2.096-(2); I(1)−O(2*), 2.949(2); I(1)−O(1), 3.042(2); I(1)−O(3*), 3.088(2); C(7)−I(1)-C(13), 92.18(7); C(7)−I(1)-O(1), 162.4(1); C(13)−I(1)-O(2*), 177.9(1).

C13−I1···O3 triads are near-linear (163.7(1)° and 167.6(1)°), these close contacts are indicative of hypervalent interactions, in which the oxygen donates an electron pair into a I−C σ* orbital. The other I1···O2 contact is weak (3.201(2) Å) and considerably deviates from the linearity of 3c-4e σ bonding.[5] The symmetry of the crown ether approximates to C_2. In the crystalline complex, a molecule of water appears to be hydrogen bonded via H7O···O5 (2.045 Å) and H7O′···O2 (2.116 Å) to 18C6 from the side opposite the λ^3-iodane and helps to fill voids in the structure. The structure of **2a** reminds us of a free and easy scene in which a butterfly with wings spread is resting on a leaf and drinking water.
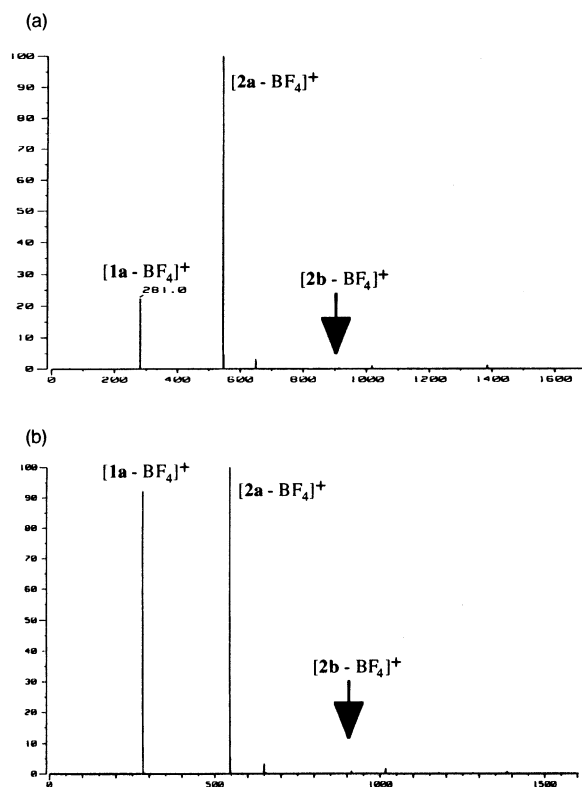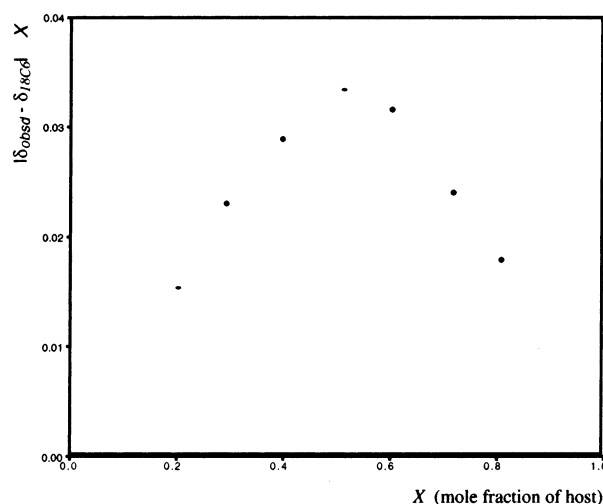
Coordination at the I1 of the 2:1 complex **2b** similarly includes two hypervalent secondary bonding (I1−O2* 2.949-(2) Å and I1−O1 3.042(2) Å) with a near-linear C−I···O triad (177.9(1)° and 162.4(1)°) and a weak contact (I1−O3*, 3.088-(2) Å). The second iodine I1* is bound to the three other adjacent oxygen atoms at the other side of the crown plane so that a centrosymmetric complex results.

Solution Structure of Crown Ether Complexes of Diaryl-λ^3-iodanes. In solution, the complex formation between **1a** and 18C6 is clearly evident in ^{1}H NMR experiments: a methylene singlet of 18C6 in CD$_2$Cl$_2$ (0.04 M) exhibits an upfield shift of 0.07 ppm by the addition of 1 equiv of **1a**, probably because of the shielding effects of the phenyl groups.[12] The ^{13}C resonance of 18C6 at δ 70.7 ppm is shifted to higher field (δ 70.2 ppm) during the addition of **1a**. In addition, irradiation of the

(a)

(b)

Figure 3. CSI-MS spectra in CH$_2$Cl$_2$. (a) [(Ph$_2$IBF$_4$)$_2$·18C6] **2b** [0.04 M]. (b) A 10:1 mixture of **1a** and 18C6.

Figure 4. Job plot for complexation between Ph$_2$IBF$_4$ **1a** and 18C6 in CD$_2$Cl$_2$ at 24 °C. Concentration: [**1a**] + [18C6] = 0.04 M.

Figure 5. Observed ^{1}H NMR chemical shifts of 18C6 (0.04 M) when titrated with **1a** in CD$_2$Cl$_2$ at 24 °C. The solid line is calculated as described in text.
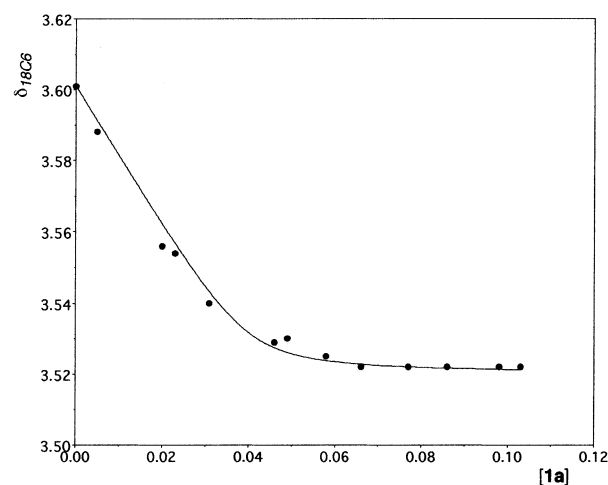
methylene protons of 18C6 gives rise to nuclear Overhauser effects (NOEs) for the *ortho* protons of **1a**, but not for the *meta* and *para* protons. These data can only be rationalized by the formation of a stable complex in solution, which is similar to the solid-state structure.

Solution structures of the complex were further analyzed by coldspray ionization (CSI) MS,[13] a variant of electrospray (ESI) MS[14] operating at low temperature, which allows facile and precise characterization of labile organic species in solution. The CSI-MS spectrum for 2:1 complex **2b** [0.04 M] in dichloromethane showed the most prominent ion peak of 1:1 complex [**2a**−BF$_4$]$^+$ at m/z 545 but, interestingly, a peak corresponding to 2:1 complex [**2b**−BF$_4$]$^+$ was not detected to a discernible extent (Figure 3a). Even in the presence of large amounts of λ^3-iodane **1a** (10-fold excess to 18C6), the most intensive peak (taken as the base peak) detected is assigned to 1:1 complex **2a** and the peak extent of 2:1 complex **2b** is found to be less than 1% (Figure 3b). These results suggest that in dichloromethane solution λ^3-iodane **1a** exclusively forms the 1:1 complex **2a** and the contribution of **2b** is negligibly small.

The 1:1 stoichiometry between **1a** and 18C6 in CD$_2$Cl$_2$ solution was further confirmed from the Job plots by the ^{1}H NMR experiments.[15] The complexation-induced shifts of a methylene singlet of 18C6 were small but distinct and reproducible. A plot of complex concentration versus [**1a**]/([**1a**] + [18C6]) shows a maximum at near 0.5 (Figure 4). Thus, the facile formation of

the 2:1 crystalline complex **2b** from a dichloromethane−hexane (1:2) solution is probably due to the limited solubility.

The binding efficacy of 18C6 to **1a** was evaluated by analyzing the ^{1}H NMR spectral changes that occur upon titrating CD$_2$Cl$_2$ solutions of 18C6 (0.04 M) with **1a** at 24 °C (Figure 5). The resulting binding curve gave an excellent fit with a 1:1 binding isotherm and was analyzed by a nonlinear least-squares method to give a binding constant (K_a) value of 1.02 × 10^3 M^{-1} (correlation coefficient 0.99).

Solvent and Ligand Effects on Complexation. Solvents have a large effect on the complexation (Table 1): use of CDCl$_3$ as a solvent decreased the binding constant to one-half of the value in CD$_2$Cl$_2$, probably because of a competing hydrogen bonding between CDCl$_3$ and 18C6 (compare entries 1 and 2 in Table 1).[16,17] Table 1 indicates that the solvent donor ability presumably affects the binding efficacy of 18C6 to **1a** and the binding constants decrease with the increased donor ability.[18]

(12) A similar upfield shift of 0.04 ppm in CDCl$_3$ was reported in the complexation of 18C6 with *p*-toluenediazonium tetrafluoroborate, in which the diazonium group deeply penetrates the hole. See ref 3a.

(13) Sakamoto, S.; Fujita, M.; Kim, K.; Yamaguchi, K. *Tetrahedron* **2000**, *56*, 955.

(14) Fenn, J. B.; Mann, M.; Meng, K.; Wong, S. F.; Whitehouse, C. M. *Science* **1989**, *246*, 64.

(15) Job, A. *Ann. Chim. (Paris)* **1928**, *9*, 113.

(16) For hydrogen bonding between CHCl$_3$ and 18C6, see ref 2b.

(17) Solvent acceptor numbers: CHCl$_3$ (23.1), CH$_2$Cl$_2$ (20.4). See: Gutmann, V. *The Donor−Acceptor Approach to Molecular Interactions*; Plenum: New York, 1978.

(18) For DN, see: (a) Gutmann, V. *Chemtech* **1977**, 255. (b) Reichardt, C. *Solvent Effects in Organic Chemistry;* Verlag Chemie: Weinheim, 1979.

Table 1. Solvent Effects on Binding Constants (K_a) Resulting from ^{1}H NMR Titration between Diphenyl-λ^3-iodane **1a** and 18C6 at 24 °C

entry	solvent	DN^a	K_a (M^{-1})
1	CD$_2$Cl$_2$	0^b	1.02×10^3
2	CDCl$_3$	0^b	5.45×10^2
3	CD$_3$COCD$_3$	17.0	6.33×10
4	THF-d_8	20.0	3.30×10
5	CD$_3$CN	14.1	1.92×10
6	CD$_3$OD	25.7^c	5.55
7	D$_2$O	33.0^c	2.30

^{a} Donor numbers of Gutmann.[18] ^{b} Estimated values. ^{c} Bulk donor numbers.

Table 2. Substituent Effects on Binding Constants (K_a) between λ^3-Iodanes **1** and 18C6 in CD$_2$Cl$_2$ at 24 °C

| entry	ArAr′IBF$_4$ **1** Ar	Ar′		K_a (M^{-1})
1	Ph	o-MeC$_6$H$_4$	**1b**	4.79×10^2
2	Ph	p-MeC$_6$H$_4$	**1c**	6.70×10^2
3	Ph	p-ClC$_6$H$_4$	**1d**	1.30×10^3
4	Ph	p-CF$_3$C$_6$H$_4$	**1e**	2.58×10^3
5	p-MeC$_6$H$_4$	p-MeC$_6$H$_4$	**1f**	5.07×10^2

The logarithm of the binding constants correlates well with Gutmann's donor number (DN) of solvents with a correlation coefficient r of 0.96. DN expects a greater binding in CD$_3$CN than in THF-d_8, but not the case (Table 1, entries 4 and 5). This is probably due to a competing hydrogen bonding between CD$_3$CN and 18C6.[19] In DMSO (DN, 29.8), an efficient ligand to iodine(III),[20] no evidence for complex formation was observed.

The magnitude of the interactions with 18C6 depends on the nature of heteroatom ligands X in Ph$_2$IX. Changing the ligand from BF$_4$ to the less nucleophilic PF$_6$ and AsF$_6$ resulted in a binding constant about six times larger: binding constants (M^{-1}) in CD$_2$Cl$_2$ at 24 °C (X); 6.65×10^3 (PF$_6$), 5.84×10^3 (AsF$_6$), 8.13×10^2 (ClO$_4$), 2.83×10^2 (OTf), and 1.47×10^2 (BPh$_4$). In marked contrast, diphenyl-λ^3-iodanes with highly nucleophilic ligands such as Br and I did not show any evidence of complexation with 18C6.

Substituent Effects on Complexation. Substitution of a methyl group onto the *ortho* and *para* position(s) of diphenyl-λ^3-iodane **1a** tends to decrease the complex stability, to a slightly greater extent in o-methyl **1b** than in p-methyl iodane **1c** (Table 2). In the case of arenediazonium salts, the presence of sterically demanding *ortho* methyl group inhibits the complexation with 18C6, because the diazonium group must deeply penetrate the hole to complex well.[3a] Thus, the observed small *ortho* methyl effect in **1b** probably reflects a perching type of host−guest relationship in solution. Electron-withdrawing *p*-chloro and *p*-trifluoromethyl groups increase the binding constants. These results illustrate that the stabilities of λ^3-iodane·18C6 complexes are dependent on both the electronic and steric effects of the substituents. A linear Hammett relationship ($\rho = 0.59$) for the substituent effects with a correlation coefficient r of 0.99 was found between log K_a and σ_p^+ values associated with the *para* substituents. Thus, the λ^3-iodanes with electropositive iodine-(III) interact more efficiently with 18C6.

(19) Gokel, G. W.; Cram, D. J.; Liotta, C. L.; Harris, H. P.; Cook, F. L. *J. Org. Chem.* **1974**, *39*, 2445.
(20) (a) Zhu, S.-Z. *Heteroatom Chem.* **1994**, *5*, 9. (b) Ochiai, M.; Kitagawa, Y. *J. Org. Chem.* **1999**, *64*, 3181.
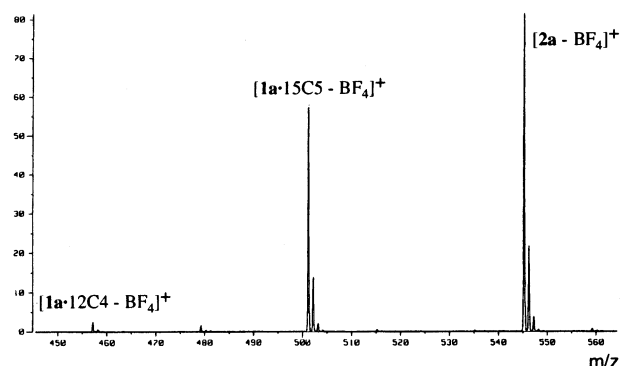
Figure 6. CSI-MS spectrum of a mixture of 18C6, 15C5, 12C4, and **1a** (each 0.001 M) in CH$_2$Cl$_2$.

Effects of Ring Size in Crown Ethers. ^{1}H NMR titration showed that the binding magnitude of λ^3-iodane **1a** is dependent on the ring size of crown ethers. The binding constant with 15C5 decreased to 1.58×10^2 M^{-1} (in CD$_2$Cl$_2$ at 24 °C), while that with 12C4 was very small. These differences in binding efficacy were clearly confirmed by the measurements of the CSI-MS spectrum for a mixture of an equal amount of 18C6, 15C5, and 12C4 in the presence of **1a**, as shown in Figure 6. The ion peak intensities of 1:1 complexes [**2a**−BF$_4$]$^+$, [**1a**·15C5−BF$_4$]$^+$, and [**1a**·12C4−BF$_4$]$^+$ decrease in this order. Dibenzo-18C6 showed a slightly decreased interaction ($K_a = 7.48 \times 10^2$ M^{-1}) compared to 18C6, owing to the decreased basicity of the oxygen atoms. Decreased binding magnitude was measured with larger crown ethers, dibenzo-21C7 ($K_a = 2.44 \times 10^2$ M^{-1}) and dibenzo-30C10 ($K_a = 9.27 \times 10$ M^{-1}).

Acyclic podand, pentaglyme, exhibited a significantly lower affinity for **1a** ($K_a = 2.07 \times 10$ M^{-1}) than that of 18C6, which is presumably due to the macrocyclic effect.[1b] Acyclic diglyme offered similar binding with $K_a = 1.49 \times 10$ M^{-1}. On the other hand, a sulfur analogue of 18C6, [18]aneS$_6$, gave no evidence of interaction with **1a**, probably because of the decreased apicophilicity of sulfur ligands relative to oxygen ligands and of the conformational restriction.[21]

Conclusion

Diphenyl-λ^3-iodane·crown ether complexes were synthesized as stable crystals. X-ray crystal structure analysis of these complexes indicated that cooperative hypervalent interactions between iodine(III) and oxygen atoms of crown ethers is critical to the formation. Further works are required to establish that occurrence of the secondary bonding involving crown ether oxygens provides a new tool for forming supramolecular synthons in the field of crystal engineering.

In solution, it was determined by ^{1}H NMR analyses and/or CSI-MS spectra that diphenyl-λ^3-iodanes (Ph$_2$IX: X = BF$_4$, PF$_6$, AsF$_6$, ClO$_4$, OTf, and BPh$_4$) exclusively form a 1:1 complex with 18C6. The magnitude of the interactions with 18C6 depends on the solvent donor ability (Gutmann's DN) and the differences in nucleophilicity of the heteroatom ligands X. Substitution of electron-withdrawing *p*-chloro and *p*-trifluoromethyl groups onto the *para* position of Ph$_2$IBF$_4$ tends to increase in the complex stability. Hammett analysis for the substituent effects clearly indicates that the λ^3-iodanes with

(21) For apicophilicity, see: Thatcher, G. R.; Campbell, A. S. *J. Org. Chem.* **1993**, *58*, 2272.

electropositive iodine(III) interact more efficiently with 18C6. Decreased binding magnitude was measured with 15C5, dibenzo-18C6, dibenzo-21C7, and dibenzo-30C10. Acyclic podand, pentaglyme, exhibited only a very weak interaction with Ph₂-IBF₄. The sulfur analogue of 18C6, [18]aneS₆, gave no evidence of the interaction.

Experimental Section

General Methods. For general experimental details, see ref 22. CSI-MS measurements were performed with a four-sector (BE/BE) tandem mass spectrometer (JMS-700T, JEOL) equipped with the CSI source. Diaryl-λ^3-iodanes **1a**−**1f** and Ph₂IBPh₄ were prepared by the silicon-[23] or boron−iodine(III) exchange reaction.[24] Diphenyl-λ^3-iodanes Ph₂IX (X = PF₆, AsF₆, ClO₄, and I) were purchased from Tokyo Kasei Kogyo Co.

Preparation of Ph₂IBF₄·18-Crown-6 Complex (2a). Diphenyl-(tetrafluoroborato)-λ^3-iodane (**1a**) (118 mg, 0.32 mmol) and 18-crown-6 (170 mg, 0.64 mmol) were dissolved in dichloromethane (2.5 mL), and the solution was stirred for 1 h at room temperature. After addition of diethyl ether (1.5 mL), a slow evaporation at 4 °C of the solvent with exposure to the atmosphere yielded Ph₂IBF₄·18-crown-6 **2a** (192 mg, 92%) as colorless plates: mp 143.5−144 °C; IR (KBr) 3576, 3058, 2893, 1631, 1472, 1353, 1150−1000, 837, 741 cm⁻¹; ¹H NMR (400 MHz, CD₂Cl₂, 0.04 M) δ 8.09 (d, J = 7.3 Hz, 4H), 7.65 (t, J = 7.3 Hz, 2H), 7.49 (t, J = 7.3 Hz, 4H), 3.53 (s, 24H); ¹³C NMR (75 MHz, CD₂Cl₂, 0.04 M) δ 136.2, 132.9, 132.4, 113.8, 70.2. Anal. Calcd for C₂₄H₃₄BF₄IO₆·3/2 H₂O: C, 43.72; H, 5.66. Found: C, 43.71; H, 5.52.

Preparation of (Ph₂IBF₄)₂·18-Crown-6 Complex (2b). Diphenyl-λ^3-iodane **1a** (22 mg, 0.06 mmol) and 18-crown-6 (8 mg, 0.03 mmol) were dissolved in dichloromethane (1 mL), and the solution was stirred for 1 h at room temperature. After addition of hexane (2 mL), a slow evaporation at 4 °C of the solvent with exposure to the atmosphere yielded (Ph₂IBF₄)₂·18-crown-6 **2b** (26 mg, 86%) as colorless plates: mp 143.5−144.5 °C; IR (KBr) 3054, 2908, 1562, 1473, 1150−1000, 819, 738, 681 cm⁻¹; ¹H NMR (400 MHz, CD₂Cl₂, 0.04 M) δ 8.07 (d, J = 8.1 Hz, 8H), 7.67 (t, J = 7.4 Hz, 4H), 7.51 (dd, J = 8.1, 7.4 Hz, 8H), 3.52 (s, 24H); ¹³C NMR (75 MHz, CD₂Cl₂, 0.04 M) δ 136.0, 133.3, 132.8, 113.1, 70.0; CSI-MS (CH₂Cl₂, 0.04 M) m/z (relative intensity) 913 [0.3%, (M − BF₄)⁺], 545 [100, (**2a** − BF₄)⁺], 281 [22, (**1a** − BF₄)⁺]. Anal. Calcd for C₃₆H₄₄B₂F₈I₂O₆: C, 43.23; H, 4.43. Found: C, 43.59; H, 4.35.

Job Plot. Equimolar solutions (0.04 M) of diphenyl-λ^3-iodane **1a** and 18-crown-6 were prepared and mixed in various amounts. ¹H NMR spectra of the mixtures were recorded at 24 °C, and the complexation-induced chemical shifts of a methylene singlet of 18C6 were analyzed by the method developed by Newcomb and co-workers.[25]

¹H NMR Titration. A solution of 18-crown-6 (0.01 or 0.04 M) was prepared. Ten to fifteen NMR tubes were each filled with the solution and with an adequate amount of diaryl-λ^3-iodanes **1** (i.e., 0−2.5 or 0−5 equiv). ¹H NMR spectra of the mixtures were recorded at 24 °C. The curve fittings of the chemical shift data of a methylene singlet of 18C6 were carried out by a nonlinear least-squares method (Marquardt−Levenberg Algorithm) according to the reported equation[26] with use of SigmaPlot (Jandel Scientific, San Rafael, CA).

Crystallographic Data. Crystallographic data were recorded on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by the direct methods[27] and expanded using Fourier techniques.[28] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[29] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[30] All calculations were performed using the teXsan[31] crystallographic software package of Molecular Structure Corp. For **2a**, the iodine atom is disordered at the two locations represented by the corresponding unprimed and primed numbers. One of the two water molecules, O8, is disordered around an inversion center.

2a (Ph₂IBF₄·18C6·3/2 H₂O): C₂₄H₃₇BF₄IO₇.₅, M = 659.26, T = 113 K, monoclinic space group $P2_1/n$ (No. 14), a = 9.544(1) Å, b = 21.210-(2) Å, c = 14.297(2) Å, β = 101.446(4)°, V = 2836.7(6) Å³, Z = 4, D_c = 1.544 g cm⁻³, μ(Mo Kα) = 11.97 cm⁻¹. A total of 25918 reflections were collected; 8141 were unique. R = 0.076, R_w = 0.110.

2b [(Ph₂IBF₄)₂·18C6]: C₃₆H₄₄B₂F₈I₂O₆, M = 1000.16, T = 123 K, monoclinic space group $P2_1/c$ (No. 14), a = 9.5023(4) Å, b = 24.527-(1) Å, c = 9.5248(5) Å, β = 117.567(2)°, V = 1967.8(2) Å³, Z = 2, D_c = 1.688 g cm⁻³, μ(Mo Kα) = 16.80 cm⁻¹. A total of 17524 reflections were collected; 5620 were unique. R = 0.043, R_w = 0.077.

Supporting Information Available: Details of crystal structure determination, solution, and refinement in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0211205

(22) Okuyama, T.; Takino, T.; Sueda, T.; Ochiai, M. *J. Am. Chem. Soc.* **1995**, *117*, 3360.
(23) (a) Ochiai, M.; Sumi, K.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron Lett.* **1985**, *26*, 2351. (b) Ochiai, M.; Sumi, K.; Takaoka, Y.; Kunishima, M.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, *44*, 4095.
(24) Ochiai, M.; Toyonari, M.; Nagaoka, T.; Chen, D.-W.; Kida, M. *Tetrahedron Lett.* **1997**, *38*, 6709.
(25) Blanda, M. T.; Horner, J. T.; Newcomb, M. *J. Org. Chem.* **1989**, *54*, 4626.
(26) Funasaki, N.; Ishikawa, S.; Neya, S. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 719.
(27) SIR92: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.
(28) DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-94 program system;* Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands. 1994.
(29) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography;* The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2 A.
(30) Creagh, D. C.; Hubbell, J. H. *International Tables for Crystallography;* Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, 1992; Vol C, Table 4.2.4.3, pp 200−206.
(31) teXsan: *Crystal Structure Analysis Package*; Molecular Structure Corp: The Woodlands, TX, 1985, 1999.