for a given mode. In our calculations $g(\nu_i - \bar{\nu}_i)$ was assumed to be a Gaussian function of width γ (HWHM) for every mode. The excited-state displacements are related to the FC factors through the relationships[64]

$$\langle v_i|0_i\rangle^2 = \frac{\Delta_i^{2v}}{2^v v!}e^{-\Delta_i^2/2} \qquad \text{(B-2a)}$$

$$\langle 1_i|v_i\rangle\langle v_i|0_i\rangle = \frac{\Delta_i^{2v+1} - 2v\Delta_i^{2v-1}}{2^v 2^{1/2} v!}e^{-\Delta_i^2/2} \qquad \text{(B-2b)}$$

where Δ_s is the shift in the excited state relative to the ground state along the normal coordinate s. The Cartesian displacements, δr, of the atoms for the excited state can be extracted from the origin shifts via the transformation[15,61]

$$\delta r_i = (m_i)^{-1/2}\sum_s L_{si}\Delta_s/0.17\nu_s^{1/2} \qquad \text{(B-3)}$$

where L_{si} is the eigenvector element that connects atom i having mass m_i with the normal mode s (this assumes that the normal modes have the same form in the ground and excited states).

Registry No. [(OEP)Fe(py)$_2$], 19496-63-0; [(OEP)Ru(py)$_2$], 54762-60-6; [(OEP)Os(py)$_2$], 51286-87-4; deuterium, 7782-39-0.

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[64] Inagaki, F.; Tasumi, M.; Miyazawa, T. *J. Mol. Spectrosc.* **1974**, *50*, 286–303.

Positive Halogen Cryptates[1]

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Abstract: Interactions of molecular bromine or iodine with [2.2.2], [2.2.1], and [2.1.1] cryptands were examined in chloroform. NMR measurements evidence a 1:1 complex in each case and allow the determination of the kinetic parameters for the decomplexation process. UV spectroscopy permits the determination of the equilibria constants. The complexes are destroyed (displacement of "X$^+$") by addition of either a protic acid or an alkaline metal salt. The results taken as a whole strongly suggest the conclusion that the complexes are positive halogen cryptates.

The formation of charge-transfer complexes between diatomic halogens and amines or ethers has been extensively investigated.[2] In these complexes a linear orientation of the halogen molecule with the donor atom is observed in the solid state. In solution, in the case of amines, the occurrence of ionic species has been considered.

Cationic species X_2^+ and X_3^+ were shown to be present in superacid media, but no direct evidence has been found for the occurrence of the cations X$^+$ either in solution or in the solid state,[3] although their intervention in the course of electrophilic halogenation reactions seems to be accepted.

Macrocyclic polyethers exhibit remarkable complexing properties toward metallic ions whose size fits their cavity's diameter.[4] It seemed interesting to us to investigate the potential complexing ability of these macrocycles toward positive halogen ions formed by induced dissociation of halogen molecules.[5]

Crown ethers do not seem to effect this transformation. Indeed Short[6] and Pannell[7] have shown that bromine forms the same type of charge-transfer complexes with crown ethers and single ethers. Although the presence of ionic species had been postulated, Hopkins[8] obtained, for the complexes of iodine with crown ethers, stability constants of the same order of magnitude as those obtained with simple ethers. Table I summarizes some results reported in the literature.

Table I. 1:1 Complexes

complex	solvent	K_S, L M^{-1} at 25 °C	ref
1,4-dioxane-Br$_2$	CCl$_4$-EtBr (3:1)	1.2	7
18-6-crown-Br$_2$	CCl$_4$-EtBr (3:1)	1.0	7
THF-I$_2$	cyclohexane	2.54	8
18-6-crown-I$_2$	cyclohexane	4.93	8
Et$_3$N-I$_2$	heptane	4690	2
18-6-crown-K$^+$	MeOH	$10^{6.1}$	4
[2.2.2] cryptand-K$^+$	MeOH (95%)	$10^{9.75}$	4

Table II. 100-MHz NMR Spectra of 10^{-1} M Solutions in CDCl$_3$ at −15 °C for the [2.2.2] Cryptand-I$_2$ 1:1 Complex (δ in ppm)

complex	-OCH$_2$CH$_2$O- (s)	-OC*H*$_2$CH$_2$N (t)	-C*H*$_2$N (t)
[2.2.2]	3.69	3.60	2.65
[2.2.2]-I$_2$	3.65	3.70	3.23
[2.2.2]-Br$_2$	3.65	3.80	3.30
[2.2.1]	3.69	3.60	2.68
[2.2.1]-I$_2$	3.71	3.65	3.25
[2.2.1]-Br$_2$	3.70	~3.70	3.35
[2.1.1]	3.66	3.51	2.71
[2.1.1]-I$_2$	3.65	3.73	3.35
[2.1.1]-Br$_2$	3.65	3.70	3.35

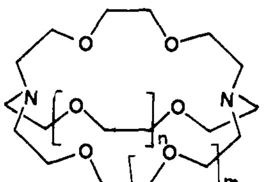

Figure 1. Cavity diameters of cryptands: [2.2.2], $m = n = 1$, 2.8 Å; [2.2.1], $m = 1$ and $n = 0$, 2.3 Å; [2.1.1], $m = n = 0$, 1.6 Å.

Results

In order to investigate the possible effects of cavity size[5] (Figure 1) three different cryptands were used in this study, namely [2.2.2], [2.2.1], and [2.1.1]. The halogens used were molecular iodine

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[1] Preliminary communication: Pierre, J. L.; Handel, H.; Labbe, P.; Le Goaller, R. *J. Am. Chem. Soc.* **1980**, *102*, 6574.

[2] Foster, R. "Organic Charge-Transfer Complexes"; Academic Press: New York, 1969.

[3] Effenberger, F. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 151.

[4] "Synthetic Multidentate Macrocyclic Compounds"; Izatt, R. M., Christensen, J. J., Eds.; Academic Press: New York, 1979.

[5] The evaluation of ionic radius by the Sanderson method allows one to consider the cryptation of X$^+$ species: rI$^+$ 0.6–0.8 Å; rBr$^+$ 0.45–0.72 Å (the first value corresponds to the cation in a gaseous phase; the second to the coordinated cation).

[6] Schori, E.; Jagur-Grodzenski, J. *Israel J. Chem.* **1972**, *10*, 935.

[7] Pannell, K. H.; Mayr, A. *J. Chem. Soc., Chem. Commun.* **1979**, 132.

[8] Hopkins, H. P.; Jahagirdar, D. V.; Winder, F. J. *J. Phys. Chem.* **1978**, *82*, 1254.

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Table III. Exchange Parameters between Free and Complexed Cryptand

complex[a]	T_c, °C (-CH_2-N)	k_c, s^{-1}	$\Delta G_c^{\ddagger}$, kcal mol^{-1}
[2.2.2]-I_2	30	129	14.9
[2.2.1]-I_2	37	97.7	15.4
[2.1.1]-I_2	67	142	16.7
[2.2.2]-Br_2	30	146	14.8
[2.2.1]-Br_2	25	126	14.7
[2.1.1]-Br_2	65	142	16.6

[a] Results are the same with ICl instead of I_2.

and bromine and the interhalogen species ICl. Measurements were carried out in chloroform, since protic solvents can transform halogens into reactive halogenites. We also excluded acidic solvents such as Me_2SO to avoid possible reactions involving this solvent and the activated halide ions. Some complementary measurements were carried out in nitromethane.

Proton Magnetic Resonance Study. Measurements were performed with 10^{-1} M cryptand solutions. As an example, we describe the experiments run with iodine and [2.2.2] cryptand since similar observations were obtained with the other cryptands and the other substrates.

Lehn showed that the ^1H NMR spectra of the free cryptands[9] were almost unaffected by temperature changes between -40 and 90 °C.

When 0.5 equiv of I_2 in chloroform is added to the cryptand solution at 24 °C, two broad triplets with approximately equal intensities appear at 2.65 and 3.23 ppm. At -40 °C, these signals become two well-resolved triplets corresponding, respectively, to the NCH_2 protons of the free [2.2.2] cryptand and to the same protons in the complex. Signals of the other protons of the cryptands are also shifted upon complexation (Table II), but they will not be discussed since the NCH_2 protons are more informative. Upon heating to 40 °C, a singlet is observed at 2.97 ppm. At the coalescence temperature (T_c = 30 °C), the corresponding exchange rate (k_c) and free energy of activation can be calculated in the usual way from spectral parameters by using the Eyring rate equation (Table III). When 1 equiv of I_2 is added to a solution of the cryptand at 24 °C, a signal is observed at 3.23 ppm. At the concentrations used for NMR spectroscopy, the solution becomes turbid when more than 1.3 equiv of halogen is added. The NMR data of the 1:1 complexes are given in Table II (at -15 °C, to minimize the exchange). Exchange parameters between free and complexed cryptands are listed in Table III. When the interhalogen compound ICl is used instead of iodine, the NMR spectra of the complexes formed with the three cryptands are identical with those observed for the I_2 complexes. The same is true for the exchange parameters between free and complexed cryptands.

In order to avoid any confusion with a possible secondary reaction, we briefly examined the reaction of the [2.2.2] cryptand with trifluoroacetic acid. Species obtained by addition of 0.5 equiv of acid exhibit a different NMR spectrum than the iodine and ICl complex: δ CH_2N appeared at 3.15 at -15 °C and the coalescence temperature was +5 °C (free and protonated cryptand exchange).

For purposes of comparison, an identical experiment was carried out with iodine and triethylamine in place of the cryptand. The methylene protons that appear at 2.55 ppm in the free base are shifted to 3.35 ppm when 1 equiv of the amine is in the presence of 1 equiv of iodine. When the concentration of iodine was reduced to 0.5 equiv the quartet was observed at 3.05 ppm. *The exchange remains rapid even at -90 °C in $CHFCl_2$.* A complete study of the triethylamine-iodine interaction has been previously described.[12]

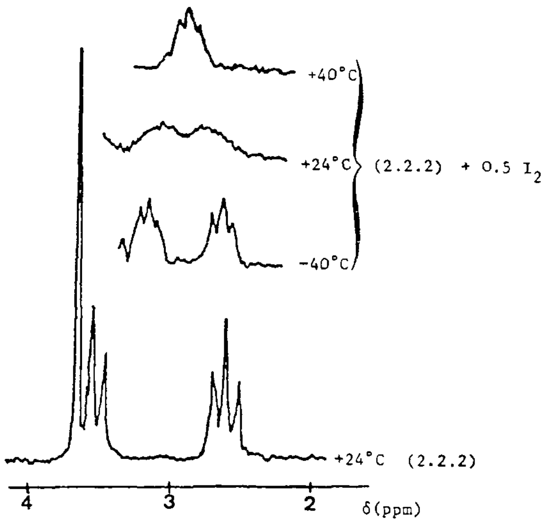

Figure 2. ^1H NMR spectra of [2.2.2] cryptand-I_2 system (100 MHz, $CDCl_3$).

In addition, the following reactions were studied by NMR spectroscopy.

(a) Upon addition of $NaBPh_4$ to the 1:1 solution of iodine and [2.2.2] cryptand, the spectrum of the iodine complex is progressively replaced by the known spectrum of sodium cryptate, while a precipitate slowly appears.

(b) Addition of [2.2.2] cryptand to the known iodopyridinium complex[3] $(Py_2I)^+NO_3^-$ leads to the formation of free pyridine and of a complex whose ^1H NMR spectrum is identical with that of iodine-cryptand complex. Additional experiments were run in nitromethane, which appears to be a more favorable solvent than chloroform due to its higher solubilizing properties. In this solvent, addition of iodine to the [2.2.2] cryptand leads to the same qualitative observations as in chloroform solution: δ NCH_2 = 3.04 for the complex and 2.58 for the free cryptand at 20 °C with T_c = +17 °C.

(c) In this solvent, addition of a soluble potassium salt (iodide or nitrate) to the complex results in the formation of the potassium cryptate and the release of iodine.

(d) Conversely, addition of tetrabutylammonium iodide did not release iodine, and the spectrum remained unmodified.

(e) When the complex is treated with an excess of trifluoroacetic acid, release of iodine is observed.

(f) Addition of cryptand to a nitromethane solution of iodine nitrate results in the formation of a complex with the same NMR pattern as the iodine-cryptand complex.

(g) When potassium iodide is added to this complex, the formation of potassium cryptate is observed together with iodine release.

(h) As it is the case for the $CHCl_3$ solution, addition of tetrabutylammonium iodide to this complex gives no reaction, whereas trifluoroacetic acid gives an iodine release.

Electrochemical Studies. The studies carried out for bromine and iodine with the three cryptands in chloroform are described in ref 13 in which the ionic character for the halogen-cryptands solution is demonstrated. The 1:1 stoichiometry of the complexes was evidenced by conductance measurements. Voltamperometry was used for detecting and determining the amounts of I^-, I_3^-, and I_2 species in the iodine-cryptand complexes.

Ultraviolet and Visible Spectroscopy. Preliminary Study of the Equilibrium

$$X^- + X_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X_3^-$$

As far as we know these equilibria have not been studied in

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[9] Dietrich, B.; Lehn, J. M.; Sauvage, J. P.; *Tetrahedron* **1973**, *29*, 1647.

[10] These observations as quite similar to those of Lehn and co-workers with alkaline cation cryptate studies.

[11] Lehn, J. M.; Sauvage, J. P.; Dietrich, B.; *J. Am. Chem. Soc.* **1970**, *92*, 2916.

[12] Handel, H.; Labbé, P.; Le Goaller, R.; Pierre, J. L. *J. Chem. Phys.* **1981**, *78*, 421.

[13] Labbe, P.; Le Goaller, R.; Handel, H.; Pierre, G.; Pierre, J. L. *Electrochim. Acta.* **1982**, *27* (*2*), 257.

Table IV. Equilibrium Study of $X^- + X_2 \rightleftarrows X_3^-$

$I^- + I_2 \rightleftarrows I_3^-$; $K_2 = [I_3^-]/[I^-][I_2]$	$Br^- + Br_2 \rightleftarrows Br_3^-$; $K_2 = [Br_3^-]/[Br^-][Br_2]$
I_2: λ_{max} 520 nm	Br_2: λ_{max} 407 nm
I_3^-: λ_{max} 363 nm (ϵ 27 000) and 295 nm (ϵ 44 300)	Br_3^-: λ_{max} 273 nm (ϵ 51 000)
$K_2(I_3^-) = 0.7 \times 10^6$ L mol^{-1} [a]	$K_2(Br_3^-) = 1.2 \times 10^5$ L mol^{-1} [a]

[a] Values obtained by voltamperometry:[13] $K_2(I_3^-) = 3 \times 10^6$ L mol^{-1}; $K_2(Br_3^-) = 10^6$ L mol^{-1}.

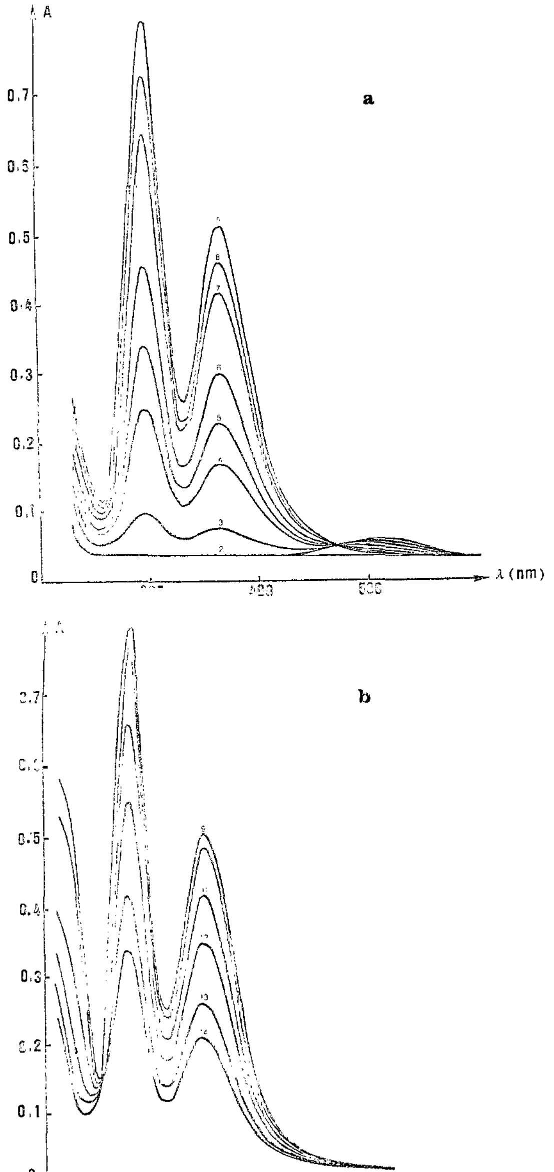

Figure 3. UV spectral results upon addition of [2.2.2] to I_2: (a) 1, $CHCl_3$; 2, I_2 (3.5×10^{-4} M); 3, I_2 (3.5×10^{-4} M) + 0.05 equiv of [2.2.2]; 4, I_2 (3.5×10^{-4} M) + 0.15 equiv of [2.2.2]; 5, I_2 (3.5×10^{-4} M) + 0.20 equiv of [2.2.2]; 6, I_2 (3.5×10^{-4} M) + 0.30 equiv of [2.2.2]; 7, I_2 (3.5×10^{-4} M) + 0.40 equiv of [2.2.2]; 8, I_2 (3.5×10^{-4} M) + 0.45 equiv of [2.2.2]; 9, I_2 (3.5×10^{-4} M) + 0.50 equiv of [2.2.2]; (b) 9, I_2 (3.5×10^{-4} M) + 0.5 equiv of [2.2.2]; 10, I_2 (3.5×10^{-4} M) + 0.7 equiv of [2.2.2]; 11, I_2 (3.5×10^{-4} M) + 1.0 equiv of [2.2.2]; 12, I_2 (3.5×10^{-4} M) + 1.45 equiv of [2.2.2]; 13, I_2 (3.5×10^{-4} M) + 2.0 equiv of [2.2.2]; 14, I_2 (3.5×10^{-4} M) + 2.85 equiv of [2.2.2].

chloroform. We examined the spectra of iodine and bromine solutions in the presence of increasing amounts of tetrabutylamonium iodide and bromide. The dilution method and the Benesi–Hildebrand method[2] led to consistent results as shown in Table IV.

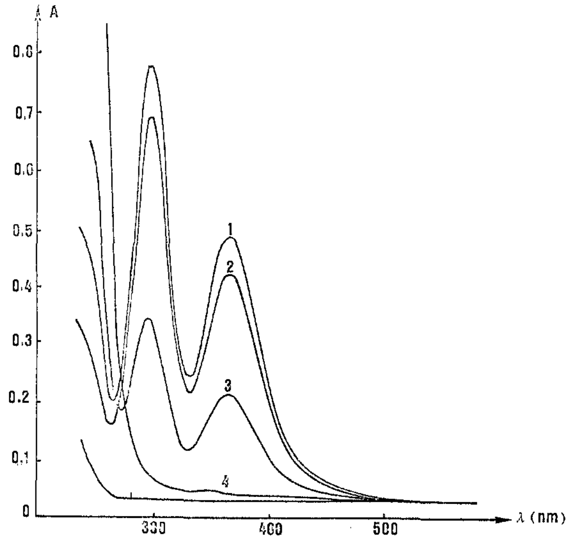

Figure 4. Cryptand–I_3^- interaction: 1, $[I^-] = 6 \times 10^{-4}$ M + $[I_2] = 3.39 \times 10^{-4}$ M; 2, $[I^-] = 6 \times 10^{-4}$ M + $[I_2] = 3.39 \times 10^{-4}$ M + $[2.2.2] = 6 \times 10^{-4}$ M; 3, $[I^-] = 6 \times 10^{-4}$ M + $[I_2] = 3.39 \times 10^{-4}$ M + $[2.2.1] = 6 \times 10^{-4}$ M; 4, $[I^-] = 6 \times 10^{-4}$ M + $[I_2] = 3.39 \times 10^{-4}$ M + $[2.1.1] = 6 \times 10^{-4}$ M.

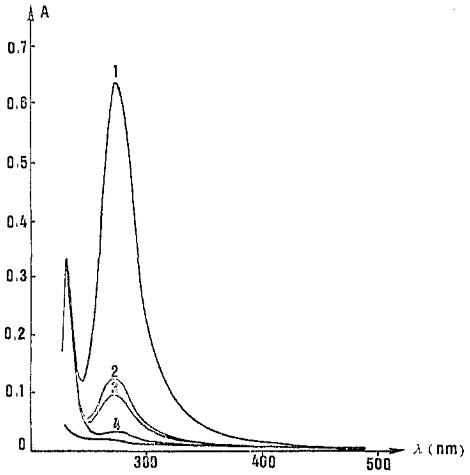

Figure 5. Cryptand–Br_3^- interaction: 1, $[Br^-] = 2.5 \times 10^{-3}$ M + $[Br_2] = 2.5 \times 10^{-4}$ M; 2, $[Br^-] = 2.5 \times 10^{-3}$ M + $[Br_2] = 2.5 \times 10^{-4}$ M + $[2.2.2] = 2.5 \times 10^{-4}$ M; 3, $[Br^-] = 2.5 \times 10^{-3}$ M + $[Br_2] = 2.5 \times 10^{-4}$ M + $[2.2.1] = 2.5 \times 10^{-4}$ M; 4, $[Br^-] = 2.5 \times 10^{-3}$ M + $[Br_2] = 2.5 \times 10^{-4}$ M + $[2.1.1] = 2.5 \times 10^{-4}$ M.

Study of the Halogen–Cryptand Interaction. We titrated a 2.5 10^{-4} M solution of iodine in chloroform with a solution of each of the cryptands. First of all, the disappearance of the iodine band (λ_{max} 520 nm) is observed together with the appearance of two bands at 363 and 295 nm corresponding to the I_3^- species. These two bands are also present in the spectrum of tetrabutylammonium triiodide under the same conditions. An isosbestic point present at 472 nm indicates a single transformation of I_2 into I_3^- (Figure 3). The amount of I_3^- formed reaches a maximum when 0.5 equiv of cryptand is added. By further addition of the cryptand the I_3^- absorption band diminishes while a new one appears at the limit of the solvent absorption. This band can be attributed to the absorption of iodide ion by comparison with the spectrum of tetrabutylammonium iodide in chloroform solution. The presence of a second isosbestic point at 267 nm confirms a single transformation of triiodide to iodide ion.

The action of a cryptand on molecular bromide only allows the obervation of the tribromide ion in the presence of an excess of bromine, but in this case a precipitation forecludes any measurement.

The complexation equilibria between halogens and cryptands were studied in every case by addition of the cryptand into a

Table V. Complex Stability Constants

$K_1 = [([2.i.i']X)^+][X^-]/([2.i.i'][X_2])$, $K_1' = [([2.i.i']X)^+]/([2.i.i'][X_2])$

complex	K_1' from UV, L mol^{-1}	K_1' from voltamperometry, L mol^{-1}
[2.2.2] + I_2	3.2×10^6	2.3×10^6
[2.2.1] + I_2	8.7×10^6	5.4×10^6
[2.1.1] + I_2	1.4×10^8	3×10^7
[2.2.2] + Br_2	3.5×10^7	
[2.2.1] + Br_2	6.11×10^7	
[2.1.1] + Br_2	2.16×10^9	

Table VI. Dilution Method

A_{363}, nm	0.862	0.418	0.197	0.092
ν	1	2	4	8
r		2.0622	4.3756	9.369
F		0.928	0.914	0.9169
pK		5.95	5.81	5.84

Table VII. Benesi-Hildebrandt Method,[a] $X = I_2$

$[I_2]_0$	3×10^{-4}	3×10^{-4}	3×10^{-4}	3×10^{-4}
$[I_3^-]$	2.82×10^{-4}	2.92×10^{-4}	2.95×10^{-4}	2.98×10^{-4}
$[I^-]_0$	3×10^{-4}	3.6×10^{-4}	4.5×10^{-4}	7.5×10^{-4}
$[I_2]$	0.184×10^{-4}	0.078×10^{-4}	0.049×10^{-4}	0.016×10^{-4}
$[I^-]$	0.184×10^{-4}	0.678×10^{-4}	1.549×10^{-4}	4.516×10^{-4}
pK	5.92	5.7	5.6	5.6

[a] All concentrations are given in mol L^{-1}.

Table VIII. Benesi-Hildebrandt Method,[a] $X = Br_2$

$[Br_2]_0$	2.5×10^{-4}	2.5×10^{-4}	2.5×10^{-4}	2.5×10^{-4}
$[Br^-]_0$	2.5×10^{-4}	12.5×10^{-4}	5×10^{-4}	2.5×10^{-4}
$[Br_3^-]$	2.49×10^{-4}	2.476×10^{-4}	2.426×10^{-4}	2.148×10^{-4}
$[Br^-]$	22.51×10^{-4}	10.024×10^{-4}	2.574×10^{-4}	0.352×10^{-4}
$[Br_2]$	0.01×10^{-4}	0.0249×10^{-4}	0.074×10^{-4}	0.352×10^{-4}
pK	5.05	5	5.1	5.24

[a] All concentrations are given in mol L^{-1}.

tetrabutylammonium trihalogenide solution and by observation of the disappearance of the trihalogenide ions (Figures 4 and 5).

It should be noted that when the cryptand reacts with X_3^-, no detectable X_2 appears as it is instantaneously complexed.

In the case of the [2.2.2]–iodine and [2.2.2]–bromine complexes some measurements were carried out in nitromethane. The absorption band of the trihalogenide ions is masked by the solvent absorption, but the disappearance of iodine and of bromine as well as their reappearance can be followed by addition of trifluoroacetic acid or potassium salt, respectively.

Discussion

Stability Constants of the Complexes. NMR studies provide evidence for the stoichiometric formation of 1:1 complexes. These complexes exhibit an increased stability as compared to the iodine–triethylamine complex and indicated by the coalescence temperatures of complexed and uncomplexed species. This agrees with Lehn's observation[11] that the higher the temperature and the corresponding ΔG_c^* the more stable the complex.

UV spectroscopy measurements indicate the formation of ionic species, thus confirming the conclusions of the electrochemical study. Complementary studies, particularly in nitromethane, demonstrate that iodine can be "displaced" from the complex by H^+, Na^+, and K^+ but not by NBu_4^+.

All the experimental observations favor the formation of the complex according to equilibrium 1, the halide ion reacting with excess halogen according to (2). Reaction 3 has also been followed by UV spectroscopy.

$$[2.i.i'] + X_2 \overset{K_1}{\rightleftharpoons} [[2.i.i']X]^+ + X^- \qquad (1)$$

$$X_2 + X^- \overset{K_2}{\rightleftharpoons} X_3^- \qquad (2)$$

$$[2.i.i'] + X_3^- + NBu_4^+ \overset{K_3}{\rightleftharpoons} [[2.i.i']]^+ + 2X^- + NBu_4^+ \qquad (3)$$

Reactions 4–11 interpret experiments a–h; the presence of the counteranion I_3^-, which is not represented, does not alter the conclusions.

$$[2.2.2\text{–}I]^+I^- + Na^+BPh_4^- \rightarrow [2.2.2\text{–}Na]^+BPh_4^- \qquad (4)$$

$$(C_5H_5N\text{–}I\text{–}C_5H_5N)^+, NO_3^- + [2.2.2] \rightarrow [2.2.2.\text{–}I]^+NO_3^- + 2C_5H_5N \qquad (5)$$

$$C_5H_5N = \text{1-pyridyl}$$

$$[2.2.2\text{–}I]^+I^- + K^+I^-(\text{or } NO_3^-) \rightarrow [2.2.2\text{–}K]^+I^-(\text{or } NO_3^-) + I_2 \qquad (6)$$

$$[2.2.2\text{–}I]^+I^- + NBu_4^+I^- \rightarrow \text{no reaction} \qquad (7)$$

$$[2.2.2\text{–}I]^+I^- + xH^+ \rightarrow [2.2.2\text{–}H_x]^{x+} + I_2 \qquad (8)$$

$$[2.2.2] + INO_3 \rightarrow [2.2.2\text{–}I]^+NO_3^- \qquad (9)$$

$$[2.2.2\text{–}I]^+NO_3^- + K^+I^- \rightarrow [2.2.2\text{–}K]^+NO_3^- + I_2 \qquad (10)$$

$$[2.2.2\text{–}I]^+NO_3^- + NBu_4^+I^- \rightarrow \text{no reaction} \xrightarrow{xH^+} [2.2.2\text{–}H_x]^{x+} + I_2 + NBu_4^+ + NO_3^- \qquad (11)$$

K_1 has been determined by UV and voltamperometry in the case of iodine complexes and by UV only in other cases. It appears that the K_1 value (for which concentrations and activities have been assimilated) varies with the concentrations. Indeed the observations are satisfactorily interpreted by considering the K_1' values, which appear remarkably constant, particularly in the case of a complex. This fact implies a slow monomolecular decomplexation step of the halonium ion followed by its rapid reaction with the halide anion.

$$[2.i.i\ X]^+ \overset{\text{slow}}{\rightleftharpoons} [2.i.i'] + X^+$$

$$X^+ + X^- \underset{\text{very fast}}{\rightleftharpoons} X_2$$

Nature of the Complex (Cryptand X)$^+$. A charge-transfer complex is ruled out by the presence of ionic species and the far higher stability of these complexes compared to amine–halogens charge-transfer complexes.[2] An external ionic complex (Figure 6a) can also be ruled out by the following arguments.

Below the coalescence temperature the NMR spectrum displays a single signal for the NCH_2 protons compatible with a symmetric species. A fast intramolecular exchange, i.e., the jump of X^+ from one nitrogen to another, is highly improbable.

Iodine and triethylamine form a 1:2 complex; it should be the same in the case of the cryptand if external complexation were operative as in triethylendiamine. In this case, as in the case of quinuclidine, a 1:2 stoichiometry is observed.[15]

The cryptand complexes are always formed with the 1:1 stoichiometry, even in the presence of an excess of halogens as observed in nitromethane. An external complex should also be of 1:2 stoichiometry under such condition (one halogen for two cryptands).

The stability of an external complex should not be influenced by the size of the cryptand.

All the results and arguments lead consistently to the conclusion that a positive halogen cryptate (Figure 6b) is formed. Particularly interesting are the high values of the K_1' constant, implying a "cryptate effect" comparable to the one observed with the alkaline cations and the cavity effect (also shown by the ΔG^* values).

Indeed, comparison of the respective diameters of the three cryptands' cavities justifies this interpretation since the size of

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Table IX. Stability Constant of Cryptand Complexes from the Benesi-Hildebrandt Method

complex	$a = [X^-]_0$	$b = [X_2]_0$	$c = [2.i.i']_0$	$x = [X_3^-]$	$K_1' = [2.i.i' - X^+]/([2.i.i'][X_2])$
$[2.2.2] + I_3^-$	6×10^{-4}	3.39×10^{-4}	6×10^{-4}	3×10^{-4}	3.2×10^6
$[2.2.1] + I_3^-$	6×10^{-4}	3.39×10^{-4}	6×10^{-4}	1.40×10^{-4}	8.7×10^6
$[2.1.1] + I_3^-$	6×10^{-3}	3.39×10^{-4}	6×10^{-4}	2.25×10^{-5}	1.4×10^8
$[2.2.2] + Br_3^-$	2.5×10^{-3}	2.5×10^{-4}	2.5×10^{-4}	0.442×10^{-4}	3.5×10^7
$[2.2.1] + Br_3^-$	2.5×10^{-3}	2.5×10^{-4}	2.5×10^{-4}	0.345×10^{-4}	6.1×10^7
$[2.2.1] + Br_3^-$	2.5×10^{-3}	2.5×10^{-4}	2.5×10^{-4}	0.0625×10^{-4}	2×10^9

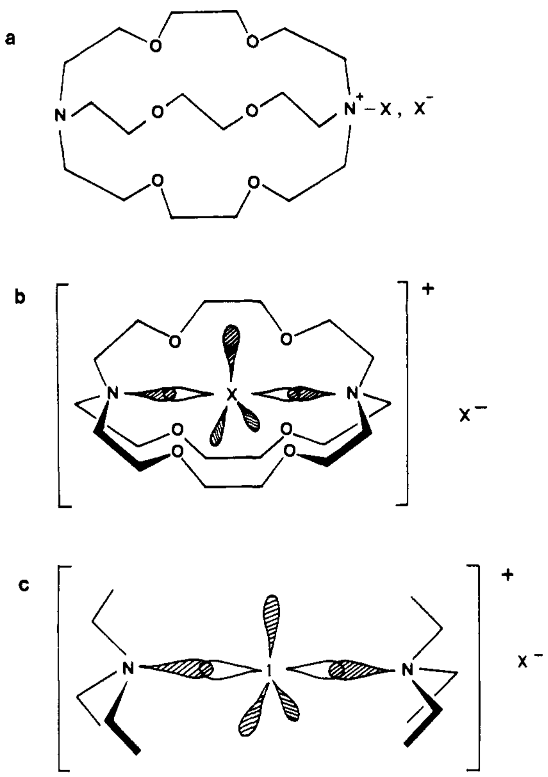

Figure 6. [2.2.2]–I_2 complexes: (a) 1:1 external complex; (b) 1:1 internal complex, (c) 2:1 $Et_3N–I_2$ complex.

hypothetical I^+ or Br^+ species has been estimated to be the closest to the one corresponding to the [2.1.1].[5] In such a cryptate, the positive charge is thought to be shared by the two nitrogens. Furthermore, a sp^{3}d-type hybridization of the X^+ species, with two vacant orbitals, is compatible with the collinearity of the N···X···N atoms, a structure similar to that observed in the 1:2 amine–halogen complexes (Figure 6c).

Experimental Section

NMR spectra were recorded on a Brucker WP 100, Fourier transform spectrometer with tetramethylsilane as internal standard. UV spectra were run on an Acta 3C Beckman apparatus. Conductivities were measured on a Taccussel CD 6N conductometer with a CM 02/566 electrode. Voltamperometry apparatus have been described in ref 13.

Chemicals were of commercial origin. Cryptands, $NaBPh_4$, KNO_3, KI, KBr, and Bu_4NI were dried in vacuo on P_2O_5. Solvents were dried and purified before use. Iodine nitrate was prepared from I_2 and $AgNO_3$ in nitromethane. Iodopyridinium nitrate was prepared from pyridine (2 equiv) and $AgNO_3$ (1 equiv) in $CHCl_3$: addition of iodine (1 equiv) resulted in the precipitation of AgI. After filtration, the complex was precipitated by addition of anhydrous ether.

Experimental descriptions of conductometric and voltamperometric measurements were described previously.[13]

Measurement of Stability Constants by UV Spectroscopy: $X^- + X_2 \rightarrow X_3^-$. This equilibrium was studied in $CHCl_3$, both by the dilution[16] method and by the Benesi–Hildebrandt[17] method. The dilution method was carried out on a 1.90×10^{-4} M triiodide solution. The dilution factor $V = C_1/C_2$ led to the nondissociated complex fraction in the more concentrated solution.

$$F = \frac{1}{V(r-1)}\left[(V-1) - (V-1)^2 - (r-1)\left(\frac{V^2}{r} - 1\right)\right]^{1/2}$$

r is the ratio between the concentration of the dissociation complex in the more concentrated solution and the more diluted one. This ratio was measured spectrophotometrically. Results are given in Table VI.

$$K = \frac{[I_2][I^-]}{[I_3^-]} = \frac{C(1-F)^2}{F}$$

The Benesi–Hildebrandt method was monitored by adding halide anion to a standardized solution of halogen, the X_3^- was measured spectrophotometrically. Results are given in Tables VII and VIII.

Stability Constants of Complexes. These constants were obtained from

$$[2.i.i'] + I_3^- + N^+Bu_4 \rightleftarrows [2.i.i'–I]^+ + 2I^- + NBu_4^+$$

The disappearance of X_3^- upon cryptand addition was followed by UV spectroscopy. If $K_1 = [[2.i.i'\ I]^+]/([2.i.i][X_2])$ and $K_2 = [X_3]/([X_2][X^-])$ and if $[X^-]_0 = a$, $[X_2]_0 = b$, $[2.i.i']_0 = c$, the measured concentration of $[X_3^-] = x$, $[X_2] << [X^-]$ and $[X_3^-]$, then we obtain $[X^-] = a = b - 2x$; $[X_2] = x/[K_2(a + b - 2x)]$; $[(2.i.i'–I)^+] = b - a$; and $[2.i.i'] = c - b + x$. Thus, the stability constant becomes $K_1 = [(b - x).K_2.(a + b - 2x)]/[(c - b + x)x]$. Results are given in Table IX.

Registry No. [29292]-I_2, 74734-71-7; [2.2.1]-I_2, 88442-13-1; [2.1.1]-I_2, 88442-14-2; [2.2.2]-Br_2, 88442-15-3; [2.2.1]-Br_2, 88442-16-4; [2.1.1]-Br_2, 88442-17-5; $[2.2.2\text{-}I]^+I_3^-$, 88442-18-6; $[2.2.1\text{-}I]^+I_3^-$, 88442-19-7; $[2.1.1HI]^+I_3^-$, 88442-20-0; $[2.2.2\text{-}Br]^+Br_3^-$, 88442-21-1; $[2.2.1\text{-}Br]^+Br_3^-$, 88442-22-2; $[2.1.1\text{-}Br]^+Br_3^-$, 88442-23-3.

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