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Positive Halogen Cryptate: Complexation of Iodine with [2.2.2]Cryptand

Sir:

Many cationic species (e.g., metal cations and ammonium, guanidinium, imidazolidium, and diazonium cations) are known to form inclusion complexes with macrocyclic ligands.[1] We report in this communication *the first example of a positive halogen ion cryptation*, formed by complexation of molecular iodine with the [2.2.2]cryptand ([2.2.2]) (Figure 1).[2]

The formation of charge-transfer complexes between diatomic halogens and amines or ethers has been extensively investigated.[3] In these complexes, a linear orientation of the halogen molecule with the donor atom is generally observed in the solid state.[4] Recently, Schori[5] and Pannell[6] have investigated the interaction between bromine and several crown ethers. They have concluded that the binding of the bromine to the polyether does not involve the cavity of the crown but rather that the bonding is essentially the same as in tetrahydrofuran or dioxan complexes, which involves a single oxygen–bromine interaction. The same conclusion was reached by Hopkins[7] for crown ether–iodine complexes.

The NMR spectrum of a solution of [2.2.2] in $CDCl_3$ shows a cleanly resolved triplet at 2.65 ppm for the CH_2N protons, with no significant alteration between −40 and +50 °C. When 1 equiv of I_2 is added to this solution, a new triplet appears at 3.22 ppm for the CH_2N protons, and the signal at 2.65 ppm nearly disappears.[5] The same spectra are obtained from +24 to −40 °C. This new spectrum must be due to the formation of a 1:1 complex between [2.2.2] and iodine. On the other hand, when 0.5 equiv of I_2 is added to the solution at 24 °C, two broad singlets of approximately equal intensity appear at 2.65 and 3.23 ppm. When the solution is cooled to −40 °C, triplets at 2.65 and 3.23 ppm are obtained which correspond to the free [2.2.2] and the [2.2.2]–iodine complex, respectively. When the solution is heated to 50 °C, a singlet is obtained 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 the spectral parameters by using the Eyring rate equation ($k_c = 129\ s^{-1}$, $\Delta G_c^{\ddagger} = 14.9$ kcal·mol^{-1}) (Figure 2).[8]

Figure 1. [2.2.2]Cryptand

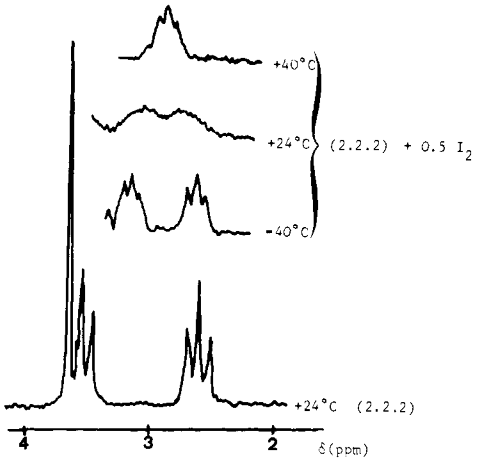

Figure 2. 100-MHz NMR spectra of $CDCl_3$ solutions.

Similar experiments were performed with triethylamine instead of [2.2.2]. The methylene protons of free triethylamine and triethylamine–iodine complex are observed at 2.55 and 3.55 ppm, respectively. When 0.5 equiv of I_2 is added, the quartet is displaced to 3.07 ppm, corresponding to a fast exchange rate between the complexed and noncomplexed species; at −40 °C, the exchange remains rapid, normally indicating a less stable complex.

In the present case, NMR spectroscopy is not a convenient method for estimating the equilibrium constant (K_s) of the complex formation since the Benesi–Hildebrand method requires a large excess of I_2.[9]

When iodine is added to chloroform solutions of [2.2.2], conductance measurements reveal an *ionic character* for the resulting complex: the conductance of a 2×10^{-2} M solution of [2.2.2] and I_2 (1:1 stoichiometry) was found to be $6 \times 10^{-2}\ \Omega^{-1}\cdot M^{-1}\cdot cm^{-2}$ ([2.2.2]cryptand or I_2 alone is not conducting). This value is similar to that obtained for a 2×10^{-2} M solution of N^+Bu_4, I^- ($3.45 \times 10^{-3}\ \Omega^{-1}\cdot M^{-1}\cdot cm^{-2}$).

Voltamperometric measurements in $CHCl_3$ (2.9×10^{-4} M) unambiguously confirm the ionic character of the complex. I_2, I^- and I_3^- are the only species detected (I_3^- is also detected by UV analysis). The quantities present of these species add up to less than the initial I_2 concentration; thus, from the law of conservation of both charge and mass, one can state that there is necessarily present additional, positively charged iodine species. I_3^- is formed in the well-known equilibrium (eq 2). The results favor a mechanism corresponding to eq 1 and 2.

$$[2.2.2] + I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ([2.2.2]\text{–}I^+), I^- \quad K_s = \frac{k_1}{k_{-1}} = \frac{[2.2.2\text{–}I]^+[I^-]}{[2.2.2][I_2]} \qquad (1)$$

$$I^- + I_2 \rightleftarrows I_3^- \quad K_2 = \frac{[I_3^-]}{[I^-][I_2]} \qquad (2)$$

The equilibrium constant K_s is estimated to be $\geq 10^7$ (for the $Et_3N\text{–}I_2$ complex, the K_s value is only 4.6×10^3 M). K_2 is obtained (3.12×10^6 M) in a manner similar to that used by Guidelli and Piccardi[10] for CH_3CN solutions. The relative values of K_s and K_2 are in agreement with the stoichiometry determined from NMR measurements (vide supra).

As the complex is more stable than the dissociated state ($K_s > 1$), the k_c and $\Delta G_c^{\ddagger}$ values correspond to the rate (k_{-1}) of the I^+ leaving the [2.2.2]–I^+ complex. Attention must be focused on the fact that the spectrum remains symmetrical at −40 °C (one

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(1) Izatt, R. M.; Christensen, J. J., Eds. "Synthetic Multidentate Macrocyclic Compounds", Academic Press: 1979.

(2) The cavity of [2.2.2] is approximately 2.8 Å. The diameter of I^+ is approximately 1.6 Å (calculated value).

(3) Foster, R. "Organic Charge-Transfer Complexes"; Academic Press: 1969.

(4) In solution, the ionic character of the amine–I_2 complexes increases with the polarity of the solvent. The formation of conducting species occurs, possibly arising from an electron transfer in which the complex $Et_3N\cdots I\text{–}I$ turns to the ion pair $Et_3N^+\text{–}I$, I^-.

(5) Schori, E.; Jagur-Grodzinsky, J. *Isr. J. Chem.* **1972**, *10*, 935.

(6) Pannell, K. H.; Mayr, A. *J. Chem. Soc., Chem. Commun.* **1979**, 132.

(7) Hopkins, H. P.; Jahagirdal, D. V.; Windler, F. J. *J. Phys. Chem.* **1978**, *82*, 1254.

(8) The spectrum of [2.2.2] shows a triplet at 3.60 ppm (CH_2O protons) and a singlet at 3.70 ppm (OCH_2CH_2O protons). Modifications of these resonances upon complexation with iodine (3.70 ppm for the triplet and 3.65 ppm for the singlet) have not been considered since the CH_2N proton shift is more significant.

(9) Near 1.3:1 stoichiometry, the solutions became turbid; more dilute solutions (2×10^{-4} M) remain homogeneous.

(10) Guidelli, R.; Piccardi, G. *Electrochim. Acta* **1967**, *12*, 1085.

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triplet for all CH_2N protons). In an outside complexation, the spectrum would display a lack of symmetry under the coalescence temperature of the exchange (30 °C).

In summary, the ionic character of the solution, the large value for K_s (which can be attributed to the "cryptate effect"), and the symmetry of the spectrum under the coalescence temperature strongly suggest that $[2.2.2]\text{-I}^+$ is an inside complex. A more detailed discussion will appear in a full paper.

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Metal-Metal Distances in a Platinum Acetamide Blue

Sir:

We report here the determination of some Pt-Pt distances in a platinum acetamide blue (PAB) from a Fourier analysis of its X-ray diffraction pattern. Platinum blues have elicited much interest recently not only because of their reported antitumor activity[1,2] but also because of their intense color which stands out against the paleness of most mononuclear platinum compounds. This intense color has been postulated to arise from the presence of Pt-Pt bonds and chains. Therefore, it is of particular importance to ascertain the presence or absence of a strong Pt-Pt interaction. However, it appears that the overwhelming majority of blues isolated so far are amorphous or very difficult to crystallize, and for this reason their structures have, with few exceptions, eluded direct determination. To date, we are aware of only two studies that have given significant structural information on blues: first, the crystal and molecular structure determination of *cis*-diammineplatinum α-pyridone blue[4] (α-PB) which established that this blue is composed of tetranuclear platinum chains, and second, an extended X-ray absorption fine structure study[5] of two uridine blues in which it was concluded that platinum atoms ~2.9 Å apart are present in these blues.

The PAB was prepared by the method of Hofmann and Bugge.[6] The products obtained from this synthesis vary from batch to batch.[3] The particular PAB sample used in this study has been described previously.[3] It was chosen because it exhibits the interesting average oxidation state of 3+ for platinum as determined by ceric ion titration, it is paramagnetic, and it has an average molecular weight of only 372 in water despite the intense blue ($\epsilon = 3560\ \text{cm}^{-1}$ L/mol of Pt at 6740 Å) of the solution.

The X-ray data were obtained with a General Electric powder diffractometer by using a copper target tube and an argon flow proportional counter with a pulse height selector. The balanced filter technique (nickel and cobalt filters) was used so that the resulting diffraction data are essentially due to the copper Kα lines alone ($\lambda = 1.542$ Å). The sample consisted of a paste of 131 mg of PAB and 24 mg of mineral oil formed into a rectangular slab 3 cm × 1 cm. For measurements with 2θ less than 20°, a 0.5° entrance slit was used while a 3° slit was used for angles greater than 20°. The quantity 2θ is defined as the angle between the incident and diffracted beams. A 1° receiving slit was used throughout. Data were recorded for $k = 0.3\text{-}8.0$ at intervals of 0.1 ($k = 4\pi \sin \theta/\lambda$). After correction for air scattering and polarization, the intensity curve was normalized and the Compton scattering subtracted.[8a,b] For this purpose the sample composition was taken to be Pt, 1; O, 3.61; N, 1.99; C, 7.51; H, 14.94, based on the elemental analysis of the PAB, and the mineral oil was assumed to have the formula CH_2.

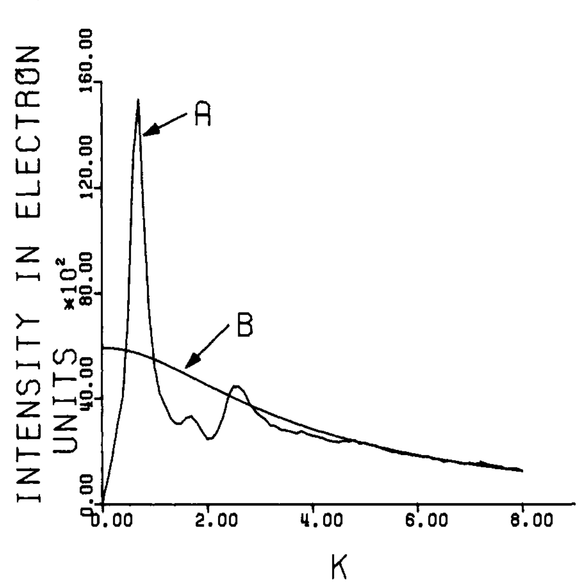

Figure 1. Scattering curves for PAB. Curve A is the normalized experimental intensity curve corrected for polarization and Compton scattering. Curve B is the total calculated independent scattering calculated from tabulated values of the atomic scattering factors [*Int. Tables X-Ray Crystallogr.*, 99 (1974)].

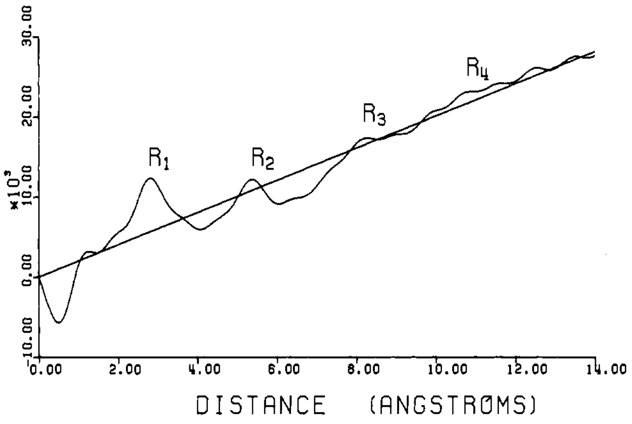

Figure 2. Pair function distribution curve of platinum acetamide blue. Only peaks due to platinum-platinum pairs will be expected to appear because the scattering power of X-rays is so much greater for platinum than for the other atoms of this compound.

The corrected scattering curves for our sample and the pair function distribution derived[8a] from it are shown in Figures 1 and 2, respectively. The very negative peak below 1 Å in the distribution curve is due in part to the fact that points were not collected for $k > 8$. Otherwise, the distribution curve shows prominent maxima at 2.76 (R_1), 5.36 (R_2), 8.02 (R_3), and 10.58 (R_4) Å.[9] The first distance is assigned to the Pt-Pt bond length in the PAB sample. It compares well with the average Pt-Pt separation in the metal (2.775 Å[10] with bond number 0.5). It is also comparable to the Pt-Pt separation in catenated partial oxidation complexes such as α-PB (2.78, 2.88 Å; $Pt^{2.25}\text{-}Pt^{2.25}$ tetranuclear chain)[4] and $K_2Pt(CN)_4Br_{0.3}\cdot 2.3H_2O$ (2.887 Å;

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[8] (a) The relations used to derive the radial distribution are from B. E. Warren, "X-Ray Diffraction", Addison-Wesley, Reading, MA, 1969, Chapter 10. (b) Compton scattering factors were obtained from D. T. Cramer and J. B. Mann, *J. Chem. Phys.*, **47**, 1892 (1969).

[9] Error bars for these numbers have not been evaluated as there is no simple or direct way of accomplishing this.

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