described above was repeated a total of eight times. After the eighth treatment the solvent dichloromethane was distilled out under vacuum. The solid remaining in the tube was dissolved in a fresh portion of dichloromethane, and the solution was transferred into an NMR sample tube for the NMR measurements.

When a solution of tetrahydrofuran–triborane(7) was treated with DCl in a manner similar to that described above, similar results were obtained; the recovered DCl was of lower enrichment in deuterium, and the total recovery of the DCl–HCl mixture was quantitative.

Similar runs were made using tetrahydrofuran as solvent. Since the separation of DCl–HCl gas from the reaction mixture cannot be effected by the ordinary distillation method, the reaction mixture was allowed to warm to higher temperature (not above 0 °C) and all volatile components were distilled out. The deuterated triborane adduct which remained in the tube was dissolved in dichloromethane and its ^{11}B NMR spectrum was examined.

Stability of Trimethylamine–Triborane(7) toward HCl in Tetrahydrofuran and Dichloromethane. A solution of $(CH_3)_3N\cdot B_3H_7$ (0.65 mmol) in about 2 mL of tetrahydrofuran was prepared in a 10-mm o.d. NMR sample tube. The tube was cooled to −196 °C, and a measured amount of HCl (0.62 mmol) was condensed in the tube. The tube was then allowed to slowly warm to room temperature. The ^{11}B NMR spectrum of the mixture was identical with that of an authentic sample of $(CH_3)_3N\cdot B_3H_7$, and no evidence of any reaction between the triborane(7) adduct and HCl was observed, even after 50 h at room temperature.

A solution of $(CH_3)_3N\cdot B_3H_7$ (0.58 mmol) in about 2 mL of dichloromethane was prepared in a 22-mm o.d. reaction tube. A 1.16-mmol quantity of HCl was condensed in the tube and the mixture was allowed to warm to room temperature and kept at this temperature for 24 h. Slow continuous evolution of hydrogen gas proceeded during this period. The solution was transferred to a 10-mm o.d. NMR sample tube and its ^{11}B NMR spectrum was examined. Trimethylamine–chlorotriborane(7), trimethyl–dichloroborane(3), and minor quantities of other borane compounds were identified in the spectrum.

Registry No. Trimethylamine–triborane(7), 12076-72-1; tetrahydrofuran–triborane(7), 12544-89-7; B-deuterated trimethylamine–triborane(7), 64282-97-9; B-deuterated tetrahydrofuran–triborane(7), 64282-96-8.

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A Novel Metal Ion–Porphyrin Equilibrium

Adegboye Adeyemo and M. Krishnamurthy*

The normal metal-complex formation equilibria have not been observed for metalloporphyrins by virtue of their extreme thermodynamic stability. Though some equilibrium constants for such reactions of metalloporphyrins have been reported,[1] there has been no evidence of a truly labile equilibrium under the conditions of those studies. Results of our studies on an instance of a truly dynamic equilibrium observed in the case of a water-soluble porphyrin, tetrakis(p-sulfonatophenyl)-porphine (H₂TPPS), are reported here.

Experimental Section

Tetraphenylporphine was synthesized by the literature methods[2] and sulfonated.[3] A stock solution of mercury(II) nitrate (J. T. Baker) was made and standardized complexometrically with EDTA. Other standard chemicals such as NaNO₃ (Alfa Products), THAM (tris(hydroxymethyl)aminomethane) (Fisher Scientific), etc., were used as obtained.

A Beckman Model Acta CIII spectrophotometer with thermostated cell compartment and a Radiometer PHM 64 Research pH meter were used for titration studies. A typical titration was carried out as follows. A 4.12×10^{-5} M solution of H_2TPPS (500 mL), which was 0.20 M in NaNO₃ and 0.02 M in THAM, was constantly stirred in a thermostated (30 °C) vessel. Initially, the pH was adjusted to 7.0, and the pH was found to remain constant by intermittent monitoring. Constant volumes of mercury(II) nitrate solution (1.556×10^{-2} M) were added to the porphyrin solution using a semimicro buret at 5-min intervals. Earlier it was established that longer waiting periods do not effect any further changes in the spectrum. A visible spectrum of the porphyrin solution between 700 and 450 nm was recorded by drawing a sample just before every addition of mercury(II) nitrate solution. By returning the sample to the reaction vessel, the volume of the bulk solution remained essentially constant.

Results

Changes in the spectrum of H_2TPPS during a titration with mercury(II) nitrate are presented in Figure 1. The initial spectrum indicates the porphyrin species in the solution to be dimeric, as expected from earlier studies.[4] As mercury(II) nitrate solution was added, the spectrum changed with a clear set of isosbestic points at 492 and 571 nm. The close resemblance between the spectrum of the novel mercury porphyrin reported recently[5] and the final spectrum of this titration suggests the composition of the complex species to be two mercury(II) ions to one porphyrin. The presence of a set of isosbestic points in the spectra would mean that either the 2:1 mercury–porphyrin is formed in a single step or the intermediate 1:1 mercury–porphyrin exists in only negligible quantities in the solution at any instance during the titration. A plot of the absorbance at 518 and 616 nm as a function of the concentration of mercury(II) ion is shown in Figure 2. Assuming an equilibrium[6] such as

$$(H_2TPPS)_2 + 4Hg^{2+} \overset{K_1}{\rightleftharpoons} 2Hg_2TPPS + 4H^+ \tag{1}$$
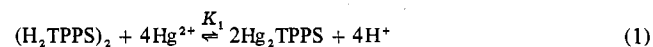
the following equation for the equilibrium constant, K_1, can be derived as

$$K_1 = \frac{2(A - A_i)^2 C_p (H^+)^4}{(A_f - A)(A_f - A_i)(Hg^{2+})_{eq}{}^4}$$

$$(Hg^{2+})_{eq} = (Hg^{2+})_{total} - 2\left(\frac{A - A_i}{A_f - A_i}\right) C_p$$

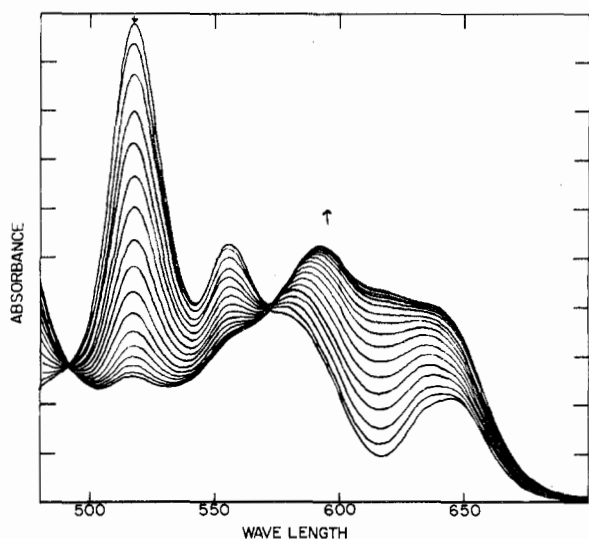where A_i, A and A_f are absorbances of the solution initially

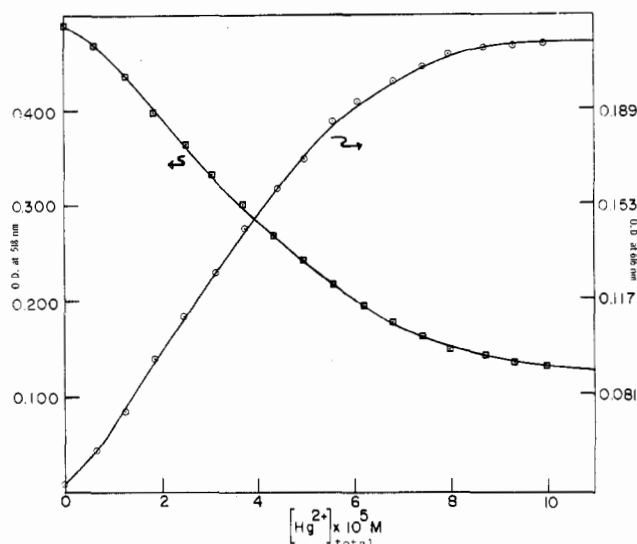**Figure 1.** Changes in the spectrum of the porphyrin solution (water) during the titration with Hg^{2+}.

Figure 2. Changes in the absorbance of the porphyrin solution (water) at 518 and 616 nm with the addition of varying amounts of Hg^{2+}.

Table I. The Equilibrium Constants for Reaction 1 Computed at 518 and 616 nm

$(Hg^{2+})_{total}$, 10^{-5} M	Log K_1	
	616 nm	518 nm
3.11	−15.17	−14.56
3.73	−15.68	−14.33
4.36	−15.09	−14.18
4.98	−15.12	−14.06
5.60	−15.12	−14.07
6.22	−15.16	−13.94
6.85	−15.15	−13.88
7.47	−15.19	−13.84
8.09	−15.22	−13.86
8.71	−15.23	−13.88
9.34	−15.27	−13.94
10.58	−15.44	−14.03
11.20	−15.51	−14.06
11.83	−15.48	−14.14
12.45	−15.55	−14.17
13.07	−15.49	−14.27
13.69	−15.51	−14.34
Av	−15.32 ± 0.18	−14.09 ± 0.19
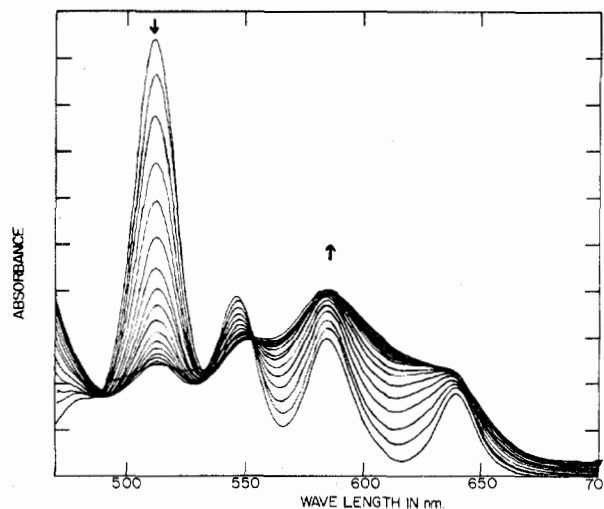
Figure 3. Changes in the spectrum of the porphyrin solution (50% methanol) during the titration with Hg^{2+}.

when varying amounts of Hg^{2+} are added and when Hg_2TPPS is the only light-absorbing species in the solution, respectively. C_p is the total concentration of the porphyrin, if it were monomeric. The equilibrium constants thus computed employing the above equation are presented in Table I. Considering the complexity of the equation, the difference between the equilibrium constants computed at 518 and at 616 nm is not unreasonable.

To determine the effect of hydrogen ion concentration on this equilibrium, titrations were carried out using the same buffer (THAM) at pH 7.5 and at pH 8.0. At lower hydrogen ion concentrations, the equilibrium shifted far to the right. The plot of absorbance vs. mercury(II) ion concentration is essentially made up of two intersecting straight lines, resembling a mole-ratio plot,[7] and at the point of intersection the ratio of mercury(II) ion to porphyrin dimer concentration is 4:1. Titrations at pH 6.5 confirmed the involvement of the hydrogen ions in the equilibrium, though calculations could not be made as the buffers, morpholinoethanesulfonic acid (Mes) and piperazinebis(2-ethanesulfonic acid) (Pipes), used precipitated out during the latter stages of the titration, being less soluble in the zwitterion form. These titrations also indicated that independent of the type of buffer used the results were the same as far as the equilibrium is concerned. This rules

out any interaction of the buffer in the system, for structurally these buffers are dissimilar. In all the titrations using THAM, no Tyndall effect was observed, indicating the absence of any larger aggregates. Though these titrations indicated the lack of interaction of sulfonic acid groups with mercury(II) ions, titrations were carried out using a water-soluble peripherally positively charged porphyrin of different basicity. The same equilibrium was observed in this case also. Details of this study will be published later along with kinetic studies. Though this titration with positively charged porphyrin indicated the presence of a 2:1 mercury(II)–porphyrin equilibrium even when the reacting porphyrin is in the monomeric form, another set of experiments was carried out with H_2TPPS.

The spectrophotometric titration was repeated, but now the solution was made up of 50% methanol and the ionic strength was made to be 0.1 μ (NaNO$_3$). The resulting spectra are shown in Figure 3. Under these conditions the porphyrin exists in the form of monomer, as indicated by the spectra. Results indicate that the same complex is formed under these conditions, even though the free-base porphyrin is monomeric initially. Here again, a set of isosbestic points are observed at 554 and 491 nm, suggesting the absence of, or insignificantly low concentrations of, any intermediate 1:1 Hg^{2+}–porphyrin species. Assuming the reaction as

$$H_2TPPS + 2Hg^{2+} \overset{K_2}{\rightleftharpoons} Hg_2TPPS + 2H^+ \qquad (2)$$
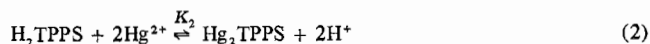
the following equation can be derived.

$$K_2 = \left(\frac{A_i - A}{A - A_f}\right) \frac{1}{(\text{Hg}^{2+})_{\text{eq}}^2} (\text{H}^+)^2$$

$$(\text{Hg}^{2+})_{\text{eq}} = (\text{Hg}^{2+})_{\text{total}} - 2\left(\frac{A_i - A}{A_i - A_f}\right) C_p$$

The equilibrium constants (log K_2) computed employing the above equation for this system at 512 and 616 nm are -6.57 ± 0.03 and -6.51 ± 0.05, respectively.

Discussion

Among the divalent ions of group 2B, mercury is unique in that it forms thermodynamically very stable complexes with N-donor ligands.[8] The preferred coordination of these mercury(II) complexes appears to be two with a linear configuration.[10,11] On comparing the formation constants of N-donor complexes of mercury(II) ion, there is a big gap in these constants after the addition of two monodentate ligands. For example, the successive formation constants of ammonia complexes[12] of Hg^{2+} are 6.0×10^8, 5.0×10^8, 10, and 6. Similarly, the successive formation constants of pyridine complexes[12] are 1.2×10^5, 8.0×10^4, and 2. Even the common bidentate ligand ethylenediamine coordinates[10] at only one position, indicating that chelate effects of N-donor ligands for Hg^{2+} are minimal, if any. On the basis of this information, one would expect that Hg^{2+} would prefer a linear configuration with the porphyrin ligand also. Among the porphyrins, synthetic porphyrins such as tetraphenylporphyrin (TPP) exhibit a remarkable ability to deform.[13] This deformation, with alternative pyrrole rings pointing above or below the mean plane of porphyrin, has been observed in crystals of the diacid form of TPP.[14] Such a buckling of the ring system has been proposed in solution studies of water-soluble porphyins.[15,16] If there is a dynamic equilibrium between the deformed and undeformed forms, the deformed form would provide the necessary configuration for binding with mercury(II) ions, though the two N–Hg bonds would still be under strain to attain a bond angle of 180°. This probably accounts for the relatively low formation constants observed in this case in comparison to that of pyridine or aniline complexes.[11]

A consequence of such a labile equilibrium is that it was found to be impractical to isolate this compound in the pure crystalline form and study its solution properties. Currently, work is in progress on kinetic aspects of this system.

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equilibrium constants. The exact nature of the mercury(II) ion species does not affect the fact that there is a complex ion equilibrium in this system. Though the magnitude of the constants would be affected depending upon the number of hydrogen or hydroxide ions in reactions 1 and 2, the change can be computed from the data presented herein.

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Contribution from the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and the Department of Chemistry, University of California, Berkeley, California 94720

Structure of Uranyl Nitrate–Bis(tetrahydrofuran)[1]

John G. Reynolds, Allan Zalkin,* and David H. Templeton*

Uranyl nitrate is soluble in a variety of organic solvents and forms various crystalline phases with them.[2,3] Extraction into ether was the classical method of purification of this salt, and today extraction with various nonaqueous solvents remains an important industrial technique. To extend our knowledge of the molecular basis for this solubility, we prepared the tetrahydrofuran complex $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{C}_4\text{H}_8\text{O}$ and determined its crystal structure. Feder, Ross, and Vogel[3] have reported a 1:1 addition compound of $\text{UO}_2(\text{NO}_3)_2$ with tetrahydrofuran.

Experimental Section

Uranyl nitrate hexahydrate was dissolved in tetrahydrofuran at room temperature to form a saturated solution. As the nitrate salt dissolved, the formation of an aqueous layer was evident. Upon saturation, the layers were separated and the ether layer was dried over anhydrous MgSO_4. After ~30 min, the solution was filtered into an Erlenmeyer flask equipped with an airtight seal. It was placed in a quiet place for crystal formation, and after 2 days large platelike yellow crystals had formed. Due to the high ether vapor pressure, the crystals had to be loaded in a glovebag with an atmosphere saturated with THF. The large crystals were fragmented with a pestle and loaded into 0.3-mm quartz capillaries. These were sealed temporarily with stopcock grease and then fire-sealed outside the glovebag.

After considerable effort, a crystal suitable for data collection was found that was irregularly shaped with poorly defined facets and had dimensions approximately $0.25 \times 0.25 \times 0.20$ mm. It was examined with a Picker FACS-I automatic diffractometer equipped with a graphite monochromator and a Mo x-ray tube ($\lambda(\text{K}\alpha_1)$ 0.709 26 Å). ω scans of several low-angle reflections showed peaks with half-widths of 0.1–0.2°. A unit cell was found that fit the space group $P2_1/a$. The setting angles of 12 manually centered reflections ($42° < 2\theta < 45°$) were used to determine by least squares the cell parameters $a = 9.412$ (7) Å, $b = 12.649$ (9) Å, $c = 7.237$ (5) Å, $\beta = 117.12$ (6)°, and $V = 766.8$ Å^3. For $Z = 2$ and a molecular weight of 538.25 the calculated density is 2.33 g cm^{-3}.

Intensity data were collected using the θ–2θ scan technique with a scan speed of 2°/min on 2θ. Each reflection was scanned from 1° before the Kα_1 peak to 1° after the Kα_2 peak, and backgrounds were counted for 10 s at each end of the scan range, offset by 0.5°. The temperature during data collection was 23 ± 1 °C. Preliminary investigations of the intensities showed a very pronounced pseudo-C-centering which was indicative of the uranium atom on a special