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# $^1$H NMR and Visible Spectroscopic Studies on the Complexation of Paraquat Dication with Cyclotetrachromotropylene in Water

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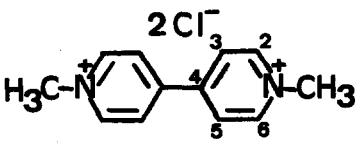
**Abstract:** Cyclotetrachromotropylene forms a 1:1 complex with paraquat dication in water. The stability constant of the complex is $1.1 \times 10^4$ $M^{-1}$ at 25°C.

The electron relaying efficiency of paraquat dication(1) has made it a very potent herbicide and a popular choice as an electron relay in the study of photochemically produced solar energy. The possibility of improving the electron relaying efficiency of paraquat dication by complexing it within a host molecule has attracted the attention of some researchers.[1-3] Their studies have revealed that a good host is one that can provide strong electrostatic interaction with paraquat dication.[1,2] Since cyclotetrachromotropylene(2), the macrocycle reported earlier,[4,5] appears to be a potential good host (the negative charges on the sulfonic groups can provide electrostatic interactions with paraquat dication and its cavity is big enough to accommodate the guest dication) we undertook to study its complexing ability with paraquat dication in water, using $^1$H nmr and visible spectroscopic methods. This paper reports our results.

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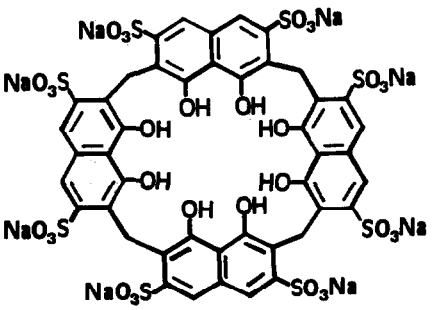


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**Results and Discussion**

That paraquat dication is enclosed in the cavity of 2 in water is indicated by the large upfield shifts of its protons in the presence of 2 (Table 1). Both CPK model examinations of 2 and paraquat dication and the $^1H$ nmr titration data (Figure 1 shows the titration data of $H_{3,5}$ ) indicate that the complex is of 1:1 stoichiometry.

Table 1. Complexation-Induced $^1H$ NMR Chemical Shifts (ppm) of Paraquat Dication with 2 in Water

| Paraquat | $H_{2,6}$ | $H_{3,5}$ | $CH_3$ |
|---|---|---|---|
| Free, $\delta_u$ | 9.02 | 8.49 | 4.47 |
| Complexed, $\delta_c$ | 8.17 | 7.30 | 3.99 |

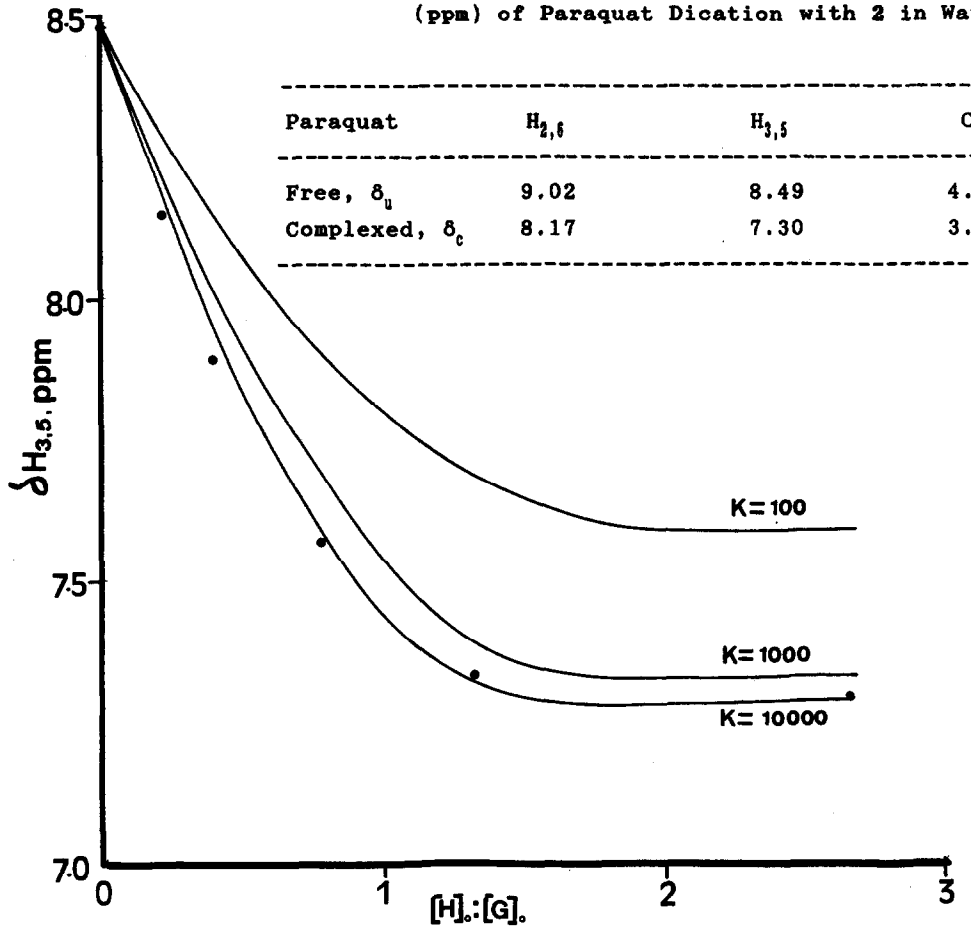


Figure 1. Variation of the chemical shift of $H_{3,5}$ of paraquat dication with the molar ratio of host to guest in $D_2O$ for several stability constants, calculated for a 1:1 complex stoichiometry and using 8.49 and 7.30 ppm for the free and complexed guest forms respectively. Host concentration is 0.012 M. Solid dots are experimental points.

The shielding effects experienced by the paraquat dication protons are larger than those reported for the bismetaphenylene-32-crown-10 and bisparaphenylene-34-crown-10 hosts.[1,2] However, the trend in the upfield shifts of the protons, $H_{3,5} > H_{2,6} > CH_3$, is the same, indicating the paraquat dication is enclosed in the cavity of 2 with the pyridinium rings of the former sandwiched between the two vertical naphthalene rings of the latter.[1,2]

Using the values of 8.49 and 7.30 ppm for the $H_{3,5}$ chemical shifts of the free and complexed paraquat dication respectively, we calculated the $H_{3,5}$ chemical shift titration curves for the 1:1 host to guest stoichiometry for various values of the stability constant K (Figure 1). From K>10,000 $M^{-1}$ the chemical shift is insensitive to changes in K. Since the calculated curve for K = 10,000 $M^{-1}$ gives the best fit to the experimental points, this value of K is the estimated lower limit (a more exact value is obtained from the visible spectroscopic data). The same lower limit of K is also obtained from the chemical shift titration curves of $H_{2,6}$ and $CH_3$.

The visible spectra of 2 in water at 30 $^0$C in the presence of various concentrations of paraquat dication were recorded (Figure 2). The titration curve for the absorbance at 535 nm indicates the complex formed is of 1:1 stoichiometry (Figure 3). This stoichiometry is supported by the consistency in the calculated values of K for the various ratios of host to guest used (Table 2). The average value of K obtained is $1.2 \times 10^4$ $M^{-1}$. It is smaller than that for a tetracarboxylic macrocycle host (about $10^5$ $M^{-1}$ in aqueous solution at pH 7.0 at 23$^0$C).[3] Two other reported K values were measured in acetone; 760 and 730 $M^{-1}$ for bismetaphenylene-32-crown-10 and bisparaphenylene-34-crown-10 as hosts respectively.[1,2]

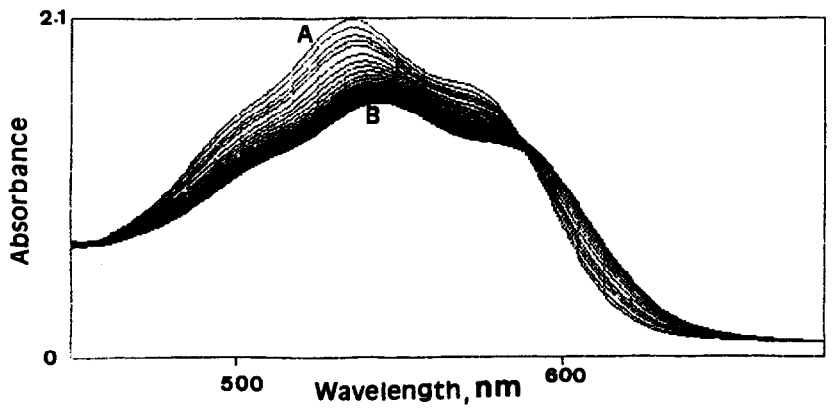


Figure 2. Visible spectra of 2 in water in the presence of various concentrations of paraquat dication. [2] = $3.02 \times 10^{-4}$ M; [paraquat] = 0 (A) to $1.43 \times 10^{-3}$ M(B).

**Table 2. Complexing of Paraquat Dication with 2 in Water at 30°C, [2] =3.02x10$^{-4}$ M**

| [Paraquat],M | $A_{535}$ | K,M$^{-1}$ | Log K |
|---|---|---|---|
| 1.27x10$^{-4}$ | 1.964 | 1.38x10$^{4}$ | 4.14 |
| 1.69x10$^{-4}$ | 1.935 | 1.17x10$^{4}$ | 4.07 |
| 2.53x10$^{-4}$ | 1.882 | 1.10x10$^{4}$ | 4.04 |
| 3.36x10$^{-4}$ | 1.842 | 1.07x10$^{4}$ | 4.03 |
| 4.18x10$^{-4}$ | 1.815 | 1.02x10$^{4}$ | 4.01 |
| 5.00x10$^{-4}$ | 1.786 | 1.13x10$^{4}$ | 4.05 |
| 5.81x10$^{-4}$ | 1.762 | 1.31x10$^{4}$ | 4.12 |
| $\epsilon_H$ = 6607 | | ------- | ---------- |
| $\epsilon_{HG}$ = 5580 | Average | 1.2x10$^{4}$ | 4.07±0.04 |

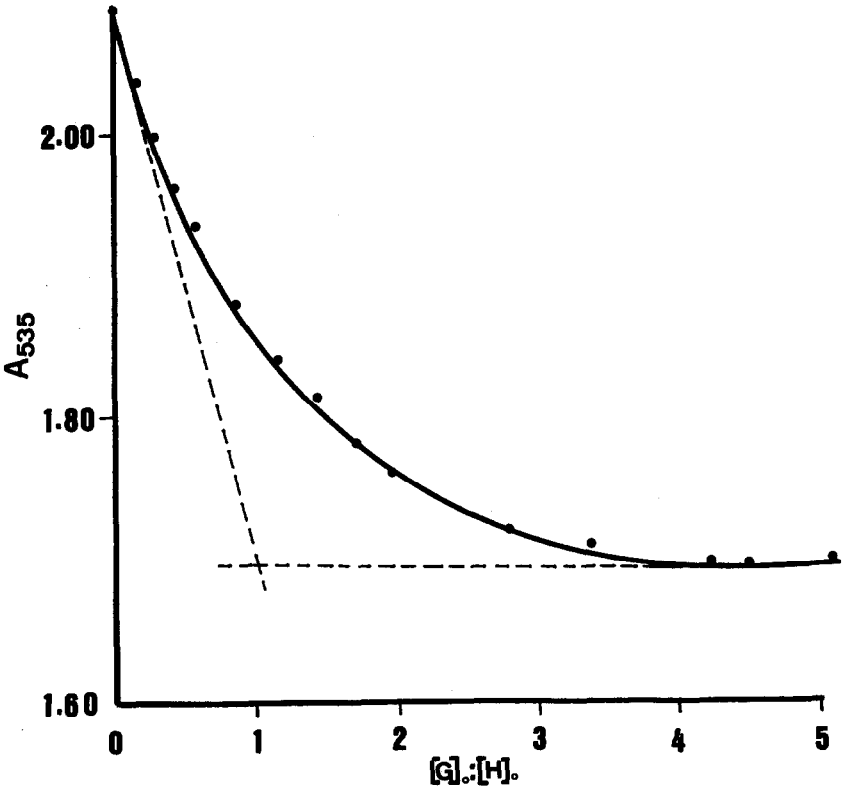


**Figure 3.** Variation of the absorbance at 535 nm of host 2 (3.02x10$^{-4}$ M) with the molar ratio of host to guest(paraquat) in water at 30 °C.

From the temperature dependence of log K plot[6] (Figure 4), the calculated enthalpy (from the slope) for the complexation equilibrium is 2.5 Kcal $mol^{-1}$ and the entropy (from the intercept) is 27.0 cal $mol^{-1}$ $deg^{-1}$. From these thermodynamic parameters, a K value of $1.1 \times 10^4$ $M^{-1}$ at 25 $^0C$ was obtained, giving a free energy, $\Delta G^0$, value of -5.5 Kcal $mol^{-1}$.The large positive entropy shows that the driving force for the complexation comes from the gain in entropy. This gain in entropy comes from the changes in solvations of the paraquat dication and 2 on complexation, analogous to the complexations of divalent metal cations with 2 reported earlier.[6]

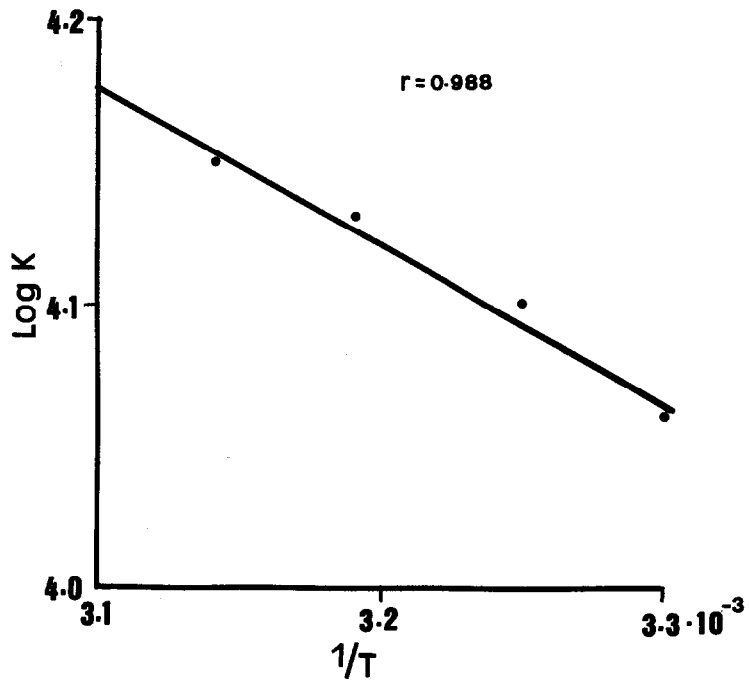


Figure 4. Temperature dependence of the stability constant of 2-paraquat dication complex.

**Experimental**

**Materials.** Paraquat (from BDH) was dried at 70°C for an hour before use. Since our earlier report[5] on the synthesis of 2, we encountered the difficulty of reproducing 2 with the same high purity even when the same procedure was repeated. We investigated the various conditions of synthesising 2 , such as the ratio of the reactants, temperature and reaction time used, and found the following procedure produces consistently crude 2 of high purity.

A stock solution of formaldehyde ($4.99 \times 10^{-3}$ mole) was prepared by diluting 0.40 mL of a commercial sample of 37% w/w formaldehyde solution to 5 mL with distilled water. 1 mL of it was added to 18 mL of distilled water containing 2.0 g of chromotropic acid, disodium salt ($4.99 \times 10^{-3}$ mole). The mixture was gently refluxed for an hour. Then a further 1 mL of the stock formaldehyde solution was added and the mixture continued to be refluxed. This was repeated after every hour until all the 5 mL of the stock formaldehyde solution was used. The mixture was refluxed for another hour after the last addition of formaldehyde (a total of 6 hours of reflux). Then it was evaporated to dryness on a hot plate, giving 2 as a dark red solid in high yield. Normally the 300 MHz $^1$H nmr spectrum of the crude 2 showed little impurity. If some little peaks appeared around δ 8 ppm, the crude 2, was redissolved in 18 mL of distilled water and refluxed for another hour with another 0.25 mL of the stock solution of formaldehyde to give purer 2. The crude product was further purified as follows: it was dissolved in a minimum of boiling water. Ethanol was then added until the solution became cloudy. The cloudy solution was reheated until it became clear. It was then left to cool overnight in a refrigerator. The solution was then decanted leaving behind a sticky mass. Acetone was added to it and stirred. It was then

a few times until 2 was in a dry solid form. Any acetone trapped in the solid 2 was removed by dissolving 2 in water and then evaporating the solution to dryness.

Anal. Found: C 27.72; H 3.50; Na 9.45; $H_2O$ 21.0. Cald. for $(C_{11}H_6O_8S_2Na_2)_4.22H_2O$: C 27.79; H 3.58; Na 9.68; $H_2O$ 20.8. $^1$H nmr ($D_2O$, 25 °C, solvent peak at δ 4.80 ppm as internal reference) δ 4.85($CH_2$, s), 8.01 (ArH, s); $^{13}$C nmr ($D_2O$, 25 °C, TMS external reference) δ 26.8($CH_2$), 117.4, 119.2, 119.9, 130.3, 139.9 and 151.4 (aromatic carbons). The negative ion FAB mass spectrum (KRATOS II HQ mass spectrometer) in 3-nitrobenzyl alcohol matrix of the acidic form of 2 ($Na^+$ replaced by $H^+$ by passing an aqueous solution of 2 through a column of Dowex 50W-X8 hydrogen ion exchange resin and then

evaporating the solution to dryness) showed the [M - H] ion peak at m/z 1327.

Karl-Fischer titrations for water content of 2 were carried out with a Metrohm Karl-Fischer automaat E547 titrator.

Sodium determinations were carried out with a Corning-Eel 100 flame photometer.

Visible spectra of 2 ($3.02 \times 10^{-4}$ M) in the presence of various concentrations of paraquat were recorded with a Hitachi U-2000 spectrophotometer.

75 MHz $^{13}C$ and 100 MHz $^{1}H$ nmr spectra were recorded in $D_2O$ with a Bruker AC300 Superconducting nmr spectrometer at $25^0$C. The solvent peak at $\delta$ 4.80 was used as the internal reference for all $^{1}H$ spectra. In all the nmr titrations the host concentration was kept constant at about $1.2 \times 10^{-2}$ M while the paraquat concentration was varied.

The stability constant $k_1$ at each temperature was calculated from the absorbance at 535 nm according to the reported method.[6] The average of several calculated values was taken as the stability constant (Table 2).

The $^{1}H$ nmr titration curves for the various values of K were calculated from the following equations. From equations 1 to 3 the concentration of the complex, [HG], could be expressed in terms of K and the original concentrations of the host, $[H]_0$, and guest, $[G]_0$, and calculated from their values. The value of $f_c$ was then obtained from equation 4 and used to calculate the chemical shift $\delta_{cald}$ in equation 5 (the $\delta_u$ and $\delta_c$ values taken from Table 1).

$$K = [HG]/[H][G] \qquad (1)$$

$$[H]_0 = [H] + [HG] \qquad (2)$$

$$[G]_0 = [G] + [HG] \qquad (3)$$

$$f_c = [HG]/[G]_0 \qquad (4)$$

$$\delta_{cald} = f_c\delta_c + (1-f_c)\delta_u \qquad (5)$$

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