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Metal Complexes of "Squaric Acid" (Diketocyclobutenediol) in Aqueous Solution

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Formation constants of complexes of diketocyclobutenediol (squaric acid) with several metal ions have been measured in aqueous solution at 25° and ionic strength 0.5 and found to be as follows: Fe(III), 41,000; U(VI), 1200; Al(III), 680; Cu(II), 160; Mn(II), 32; Co(II), 42; Ni(II), 30. A few measurements were made at other temperatures and ionic strengths. Spectrophotometric, polarographic, potentiometric, and paper-chromatographic techniques were used. In every case, 1:1 complexes predominated over a wide concentration range. The complexes of Fe, U, and Cu are strongly colored; yellow and brown solutions were also observed with Ti(IV) and Ti(III). Sparingly soluble solid yellow complexes of U(VI) and Ti(IV) were prepared and analyzed, and the solubility of copper(II) squarate was redetermined. K_2 for squaric acid was found to be 1.3×10^{-3} at 25° and ionic strength 0.5. The complexes are of special interest because of the simple aromatic character of the ligand ion.

The compound diketocyclobutenediol, $C_4H_2O_4$, also known as "squaric acid," was first prepared by Cohen, Lacher, and Park.[1] They noted that it was a fairly strong acid and that it formed colored complexes with certain metal ions. In our laboratory[2] we found its second ionization constant K_2 to be 6.2×10^{-4} at 25° in 0.1 M KCl. We were unable to measure K_1, but we estimated it to be about 2×10^{-2} or more. We noted the formation of strongly colored, sparingly soluble complexes with Fe(III) and Cu(II) and made preliminary measurements of their solubilities. There were indications that anionic complexes were formed at high ligand concentrations.

Structurally, diketocyclobutenediol somewhat resembles oxalic acid. It is a stronger acid than oxalic, and while it is oxidized by such reagents as permanganate and ceric sulfate, the rate of reaction is slower than with oxalic acid. It forms complex ions with metals, but we find them to be less stable than the corresponding oxalate complexes, and we find that the association tends to stop at a ratio 1:1. In general the "squarate" ion, $C_4O_4^{2-}$, seems to be a stable entity with relatively little tendency to associate with other ions. This is in keeping with its aromatic character.

We have investigated the interaction of certain metal ions with the "squarate" ion in aqueous solutions, measuring formation constants by several methods and in some cases studying the absorption spectra and other properties of the complexes. Two new complexes, those of titanium(IV) and uranium(VI), were prepared in solid form. Many of the studies were made at ionic strengths of 0.5 and higher, and it was therefore necessary to redetermine K_2 at ionic strength 0.5.

Experimental Section

Materials. Diketocyclobutenediol.—The first batches were made from perfluorocyclobutene, C_4F_6, obtained from Peninsular ChemResearch Inc. This gas was bubbled through alcoholic potassium hydroxide to give the ether $C_4F_4(OC_2H_5)_2$, which was then hydrolyzed with 50% sulfuric acid at 100° to give diketocyclobutenediol.[3] This was purified as we described earlier.[2] Later batches were purchased from Aldrich Chemical Co. and purified by a single recrystallization from water. The solubility is about 2.5 g/100 ml of water at 25°. The purity was checked by titration with standard base and by measurement of the absorption spectrum at pH 6–7; see ref 2.

Ion-Exchange Resins.—The cation-exchange resin AG 50W-X8 was obtained from the Bio-Rad Corp., and resin-impregnated paper SA-2 was from Reeve Angel Co.

Other chemicals were obtained in reagent grades from regular commercial sources. The stock sodium perchlorate solutions used to adjust the ionic strength were standardized by passing them through cation-exchange resin columns in the hydrogen form and titrating the acid liberated.

Equipment.—Absorbance measurements were made with Beckman DB-G and Cary Model 14 spectrophotometers, pH and electrode potential measurements were made with Leeds and Northrup and Beckman Model GS pH meters, and polarographic measurements were made with a Sargent Model III manual polarograph. Analyses by atomic absorption were made with a Beckman attachment.

Titration of Diketocyclobutenediol.—Solutions of the acid, about 0.02 M in 0.5 M sodium chloride or perchlorate, were titrated with 0.53 N sodium hydroxide as previously described.[2] The initial pH of 0.047 M squaric acid was 1.67, showing that the first ionization constant is high. The second ionization constant, $K_2 = a_{H^+}[C_4O_4^{2-}]/[HC_4O_4^-]$, was calculated from the pH values found between 1.25 and 1.75 mol of sodium hydroxide per mol of squaric acid. The method of calculation was described previously.[2] In making the calculations it would have been desirable to titrate higher concentrations of squaric acid, but this could not be done as the acid is "salted out" by the 0.5 M electrolyte.

Absorption Spectrum of Diketocyclobutenediol.—In an effort to measure K_1, the absorption spectrum of 2×10^{-4} M acid was recorded with 2-mm cells in a series of sodium perchlorate–perchloric acid mixtures of ionic strengths 0.1, 0.5, and 1.0, with perchloric acid concentrations ranging from 0.01 to 1.0 M. Between 0.01 and 0.10 M acid concentrations the spectra showed very little change. There were two absorbance maxima at 242 and 256 mμ with a shallow minimum between; the 242-mμ peak was slightly more intense. Between 0.10 and 1.0 M there was a gradual change to a single maximum, at 245 mμ. The absorbance diminished slightly with increase of ionic strength; for 0.10 M

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[1] S. Cohen, J. R. Lacher, and J. D. Park, *J. Am. Chem. Soc.*, **81**, 3480 (1959).

[2] D. T. Ireland and H. F. Walton, *J. Phys. Chem.*, **71**, 751 (1967).

[3] J. D. Park, S. Cohen, and J. R. Lacher, *J. Am. Chem. Soc.*, **84**, 2919 (1962).

$HClO_4$–0.4 *M* $NaClO_4$ the molar absorptivity was 2.10×10^4 at 242 mμ and 2.05×10^4 at 256 mμ. It was concluded that the concentration of H_2Sq (Sq^{2-} = the "squarate" ion, $C_4O_4^{2-}$) is not significant below 0.1 *M* acid and that K_1 is of the order 0.5 at an ionic strength of 1.

The Copper–Squarate System.—When squaric acid is mixed with a copper(II) solution and the pH is adjusted to 3–5, a yellow color appears, and at higher concentrations a yellow precipitate forms. Previous work[2] showed this precipitate to have the formula $CuC_4O_4 \cdot 2H_2O$. The present investigation was aimed at studying the complex in solution. Perchlorate solutions were used, and the ionic strength was regulated by adding sodium perchlorate. The adjustment of pH was made by carefully adding dilute sodium hydroxide and in some experiments by adding sodium bicarbonate. All experiments were made at pH 4.0–4.5. In this range the pH adjustment is not critical, as the squaric acid is more than 90% converted to the doubly charged anion and the hydrolysis of Cu^{2+} does not become appreciable until the pH exceeds 6.

The yellow complex has a flat absorption maximum at 385 mμ. A solution 2.6×10^{-3} *M* in Cu(II) and 4.0×10^{-4} *M* in squaric acid (these are total or stoichiometric concentrations) had absorbance 0.31 in a 5-cm cell, which gives a molar absorptivity of 400 for the CuSq complex, using the value of the formation constant that is given below. The spectrum of this solution was also measured in the ultraviolet region, using 1-mm cells. It was identical with that of 4.0×10^{-4} *M* squaric acid containing no copper, even though 40% of the acid had been converted to squarate complex. It seems that association with copper does not affect the ultraviolet absorption of the squarate ion.

Using the absorption at 385 mμ, the method of continuous variations indicated that copper and squarate ions combine in the ratio 1:1. The stability constant of this complex was evaluated spectrophotometrically, polarographically, potentiometrically, and chromatographically on ion-exchange resin-impregnated paper.

(a) Spectrophotometric Method.—Solutions were prepared which had the same squaric acid concentration (6×10^{-4} *M*) and copper concentrations ranging from 1.0×10^{-3} to 5.0×10^{-3} *M*. The ionic strength was 0.5 and the pH 4.0. The cell compartment of the spectrophotometer was maintained at 25 ± 0.2°. The absorbances were read in 5-cm cells at 400 mμ, and the quantity AB/A_s was plotted against $(A + B)$, where A_s is the absorbance, and A and B are the total concentrations of ligand and metal ion, following the method of McConnell and Davidson.[4,5] The graph is shown in Figure 1. It follows the equation

$$\frac{AB}{A_s} = \frac{1}{K'\epsilon} + \frac{A + B}{\epsilon} \tag{1}$$

where ϵ is the molar absorptivity of the complex and K' is its conditional formation constant. This simplified treatment presumes that only one complex is formed, that only the complex absorbs light at the wavelength chosen, and that $AB >> [\text{complex}]^2$.

(b) Polarographic Method.—Half-wave potentials and diffusion currents were measured at a dropping mercury electrode in 0.5 *M* sodium perchlorate solutions which contained Cu(II) and squaric acid in varying concentrations. The ratio of squarate ion to Cu(II) concentrations varied from zero to 60. Normal experimental precautions were taken[6] and the formation constant of the 1:1 complex was calculated by the method of DeFord and Hume.[7] (The calculated value is given in Table IV.)

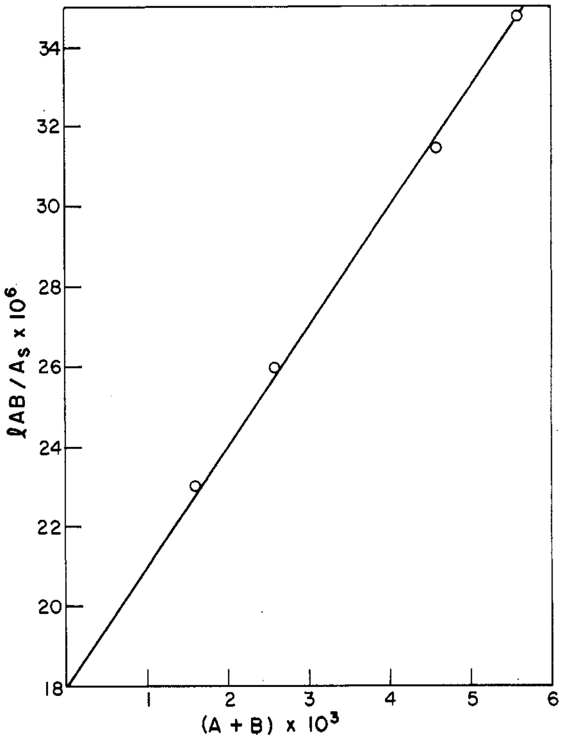

Figure 1.—Spectrophotometric determination of the formation constant of copper(II) squarate. A and B are total concentrations of ligand and metal, respectively, A_s is absorbance, and l is light path of cell (5 cm in these experiments). The line is the least-squares fit.

(c) Potentiometric Method.—An H-shaped cell was used with solutions 1.0×10^{-3} *M* in copper(II) perchlorate on each side. One compartment contained squaric acid; the other did not. Sodium perchlorate was added to maintain an ionic strength of 0.50, and the pH was adjusted to 4.0. Copper rods were placed in each solution, and the potential between them was measured to 0.4 mV. Experiments were made at three temperatures—25, 38, and 50°. (The calculated constants are given in Table IV.)

(d) Chromatographic Method.—This rough but rapid method for the measurement of stability constants was introduced by Grimaldi.[8] The migration of a spot of the metal salt on paper impregnated with a cation-exchange resin is observed in the absence and presence of complexing agent, while a high and constant concentration of displacing cation (sodium ion in our experiments) was maintained. The migration rate of the metal ions depends on their distribution ratio between the resin and the moving solution, which in turn depends on the metal ion–complex ion equilibrium. We used 0.5 *M* sodium perchlorate at pH 4 containing varying concentrations of squaric acid and let this solution advance up the paper for 1–2 cm before placing the copper spot behind the solvent front. After the solvent had advanced an additional 19.0 cm, the paper was sprayed with ferrocyanide to make the copper spot visible. The temperature was 24 ± 0.5°. The stability constants are calculated from

$$\frac{1}{D} = \frac{R_F}{1 - R_F} = \frac{1}{D_0}(1 + K'A) \tag{2}$$

where K' is the conditional stability constant of the complex, A is the total ligand concentration, D and D_0 are the distribution ratios, with and without ligand, per unit area of paper. It is assumed that only one complex is formed and that the water content of the paper remains constant. The latter assumption was found experimentally to be valid.

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[4] H. McConnell and N. Davidson, *J. Am. Chem. Soc.*, **72**, 3164 (1950).

[5] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

[6] L. Meites, "Polarographic Techniques," 2nd ed, Interscience Division, John Wiley & Sons, Inc., New York, N. Y., 1965, p 70.

[7] D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951); see also ref 6, Chapters 4 and 5.

[8] M. Grimaldi, A. Liberti, and M. Vicedomini, *J. Chromatog.*, **11**, 101 (1963).

Figure 2 shows $R_F/(1 - R_F)$ plotted against ligand concentration. The straight line shown in the figure is the least-squares line of best fit. (The value of D_0 found by extrapolation was used to calculate the formation constant given in Table IV.)

(e) The Solubility of Copper Squarate.—Solutions were prepared with known ionic strengths, controlled pH, and enough $Cu(ClO_4)_2$ and squaric acid that precipitates formed. They were left for 20 days at room temperature (23 ± 1°). At the end of this period the copper concentrations were determined by titration with EDTA and the total squaric acid concentrations by direct ultraviolet spectrophotometry. Taking the formation constant of the complex as 150, we calculated the concentrations of undissociated copper squarate and subtracted them from the total Cu(II) and squarate concentrations in order to calculate the solubility product; see Table I.

The Iron–Squarate System.—When squaric acid is mixed with a solution of Fe(III) at pH 1–2, a deep violet color is formed, and at higher concentrations violet-black crystals separate whose formula is $FeOHC_4O_4 \cdot 3H_2O$.[9] The method of continuous variations shows that the principal complex in solution is 1:1.

Solutions of iron(III) perchlorate and squaric acid mixed in a wide range of proportions at pH 1.0–1.5 give solutions of similar color, with a broad, flat absorption band whose maximum is at 545 mμ. Above 225 mμ the ultraviolet spectrum of such solutions is identical with that of squaric acid of the same total concentrations and pH.

When we began to investigate this complex spectrophotometrically, we found that the intensity of absorption at 545 mμ decreased significantly just after the solutions were mixed. The drop was about 10% in the first 3 min. The rate depended on experimental conditions. It was slightly higher at pH 2 than at pH 1.5 and was higher if squaric acid was in excess than if iron was in excess (over the 1:1 ratio). The curve of absorbance *vs.* time at constant wavelength followed no obvious rate law; its slope decreased very rapidly, and the change after 15–30 min was extremely slow. Light did not seem to affect it; a sample left in a closed tube by the window retained a discernible color for 2 months.

The implication is that iron(III) oxidizes squaric acid and that the reaction is inhibited by the product, Fe(II). To test this hypothesis a solution of iron(II) perchlorate was made by placing iron wire in a solution of the Fe(III) salt, and this solution was mixed in various proportions, up to 1:1 by moles, with iron(III) perchlorate just before this was mixed with the squaric acid. The color was now essentially stable; the absorbance dropped by only 1% over 20–30 min. Furthermore, the absorbances obtained for a given Fe(III) concentration were independent of the proportion of Fe(II), extrapolated to the time of mixing.

Two techniques were therefore followed in the spectrophotometric studies of the iron(III)–squarate association. Either the absorbance at 545 mμ was extrapolated to zero time after mixing, or Fe(II) was mixed with the Fe(III) solutions beforehand. We were unable to find any evidence that Fe(II) associated with squaric acid, and in view of the very weak association of other divalent ions with squaric acid (see below) we have no reason to expect any measurable association at the pH values used (1.0–1.5).

The redox reaction between Fe(III) and squaric acid prevented us from studying the complex ion association potentiometrically. A platinum wire placed in a Fe(III)–Fe(II)–squaric acid solution had a potential which drifted rapidly to more negative values on standing and became more positive again when the platinum wire was moved or the solution stirred. Evidently the reduction of Fe(III) to Fe(II) was occurring rapidly at the surface of the platinum.

Separate experiments showed that the stoichiometric ratio of Fe(III) to squaric acid was 10:1 for the redox reaction and that the squaric acid was oxidized to CO_2 and water with no detectable intermediate formation of oxalic acid.

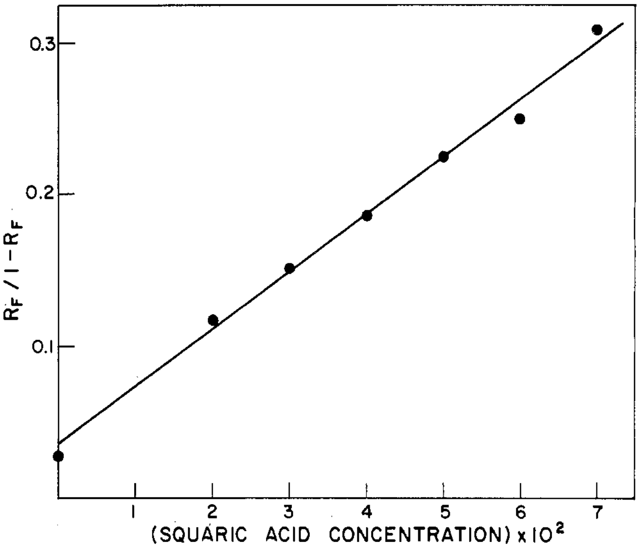

Figure 2.—Formation constant of copper(II) squarate by ion-exchange paper chromatography.

The complex ion association was investigated by the spectrophotometric method and by this method only. Except for the steps needed to suppress the redox reaction, the method was the same as that used for the copper–squarate system.

Representative plots of absorbance against ligand and metal concentrations according to eq 1 are shown in Figure 3, and the calculated values of K are summarized in Table II.

The Aluminum–Squarate System.—Ion-exchange paper chromatographic tests with 0.5 M sodium perchlorate solutions were inconclusive, probably owing to hydrolysis of Al(III). Experiments were then made in which 20-ml portions of 0.30 M sodium perchlorate solution containing 1–2 μmol of aluminum perchlorate, with and without squaric acid, were shaken with 0.6-g portions of a cation-exchange resin in the sodium form, and the distribution of aluminum ions between the resin and the solution was measured. The solutions were adjusted to pH 3.0 by adding perchloric acid; the pH was checked after the solution and resin had been shaken together for several hours and was found to be within 0.1 unit of its original value. Shaking was continued for 3 days in a water bath at 25°, though tests showed that there were no concentration changes after 24 hr. Samples of solution were withdrawn and acidified, the squaric acid was destroyed by boiling for 10–15 min with ammonium persulfate, and the aluminum was determined photometrically with 8-hydroxyquinoline in chloroform.[10] From this measurement the distribution ratio was evaluated and the formation constant was evaluated by the method of Fronaeus.[11] The distribution ratios are interpolated to a constant resin loading, in this case 1.5×10^{-3} mmol/g. If the simplifying assumptions are now made that only the 1:1 complex is formed and that this complex is not absorbed by the resin, values for the formation constant of $AlSq^+$ are easily calculated, and the fact that they show no "drift" with squaric acid concentration suggests that the assumptions are valid. The calculations are summarized in Table III.

Complexes with Nickel, Cobalt, and Manganese.—These were studied by paper chromatography, and the stability of the nickel complex was also measured by equilibration with an ion-exchange resin in the same way that the aluminum complex was studied. In all cases 0.5 M sodium perchlorate was used as the supporting electrolyte, and the pH was adjusted to 3.5–4. No atmospheric oxidation of Mn(II) or Co(II) was noted.

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[9] R. West and H. Y. Niu, *J. Am. Chem. Soc.*, **85,** 2589 (1963).

[10] S. E. Wiberley and L. G. Bassett, *Anal. Chem.*, **20,** 279 (1948); **21,** 609 (1951).

[11] S. Fronaeus, *Acta Chem. Scand.*, **5,** 859 (1951); **6,** 1200 (1952).

TABLE I

SOLUBILITY OF COPPER SQUARATE

pH	Molar concentrations at equilibrium: Total Cu	Total squarate	CuSq	Cu^{2+}	Sq^{2-}	K_{sp}, M^2
2.0	2.5×10^{-3}	1.28×10^{-2}	4×10^{-4}	2.1×10^{-3}	1.3×10^{-3}	2.7×10^{-6}
2.5	1.2×10^{-3}	6.08×10^{-3}	2.3×10^{-4}	1.0×10^{-3}	1.6×10^{-3}	1.6×10^{-6}
3.0	6.0×10^{-4}	6.4×10^{-3}	2.8×10^{-4}	5.7×10^{-4}	3.3×10^{-3}	1.9×10^{-6}
3.5	4.2×10^{-4}	6.0×10^{-3}	2.7×10^{-4}	3.9×10^{-4}	4.6×10^{-3}	1.8×10^{-6}

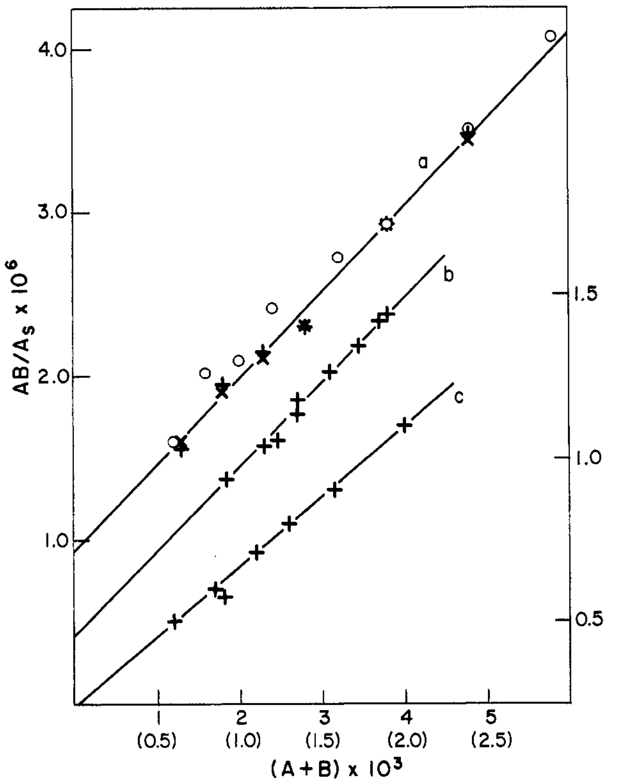

Figure 3.—Spectrophotometric determination of the formation constant of iron(III) squarate: curve a: ionic strength 0.50, pH 1.10, 8×10^{-4} *M* squaric acid; circles, no Fe(II); +, 0.2×10^{-3} *M* Fe(II); ×, 5×10^{-4} *M* Fe(II); the line is the least-squares fit of the points with Fe(II); $K' = 580$; curve b: ionic strength 0.5, pH 1.50, $K' = 1150$; curve c: ionic strength 0.1, pH 1.55, $K' = 1720$. For curve a, the ordinate scale is on the left and the abscissa values are 1–5. For curves b and c, the ordinate scale is on the right and the abscissa values are 0.5–2.5.

TABLE II

CONDITIONAL FORMATION CONSTANTS OF IRON(III) SQUARATE[a]

Ionic strength	pH	Concn $\times 10^{-4}$, *M*: Fe(III)	Squarate	Molar absorbance $\times 10^3$	K'
0.064	1.50	5–10	8	1.9	2100
0.10	1.50	4–20	4	2.3	2000
0.10	1.55	2–12	4–8	2.3	1720
0.50	1.00	6	20–140	1.91	500
0.50	1.00	4–50	8	1.89	545
0.50	1.10	5–40	8	1.90	580
0.50	1.15	5–50	8	1.80	695
0.50	1.35	5–50	8	1.86	1080
0.50	1.50	1–10	2–12	1.92	1150
0.50	1.50	5–50	8	1.90	1600
0.50	1.55	5–15	4	1.82	1260
0.50	1.55	4–12	8	1.96	1350
0.50 (40°)	1.00	. 4–50	8	1.93	395

[a] At 25° except the last. Each line in the table represents a set of at least 7 data points; the last line, for 40°, represents 16 points.

TABLE III

DISTRIBUTION OF Al(III) BETWEEN A CATION-EXCHANGE RESIN AND 0.3 *M* $NaClO_4$ PLUS SQUARIC ACID AT pH 3.0[a]

Squaric acid concn $\times 10^{-3}$, *M*	Distribution ratio, ml/g, for total Al (μmol): 2.0	1.6	1.0	Ratio for 1.0-μmol loading	Ratio of complexed to free Al	K' (conditional)
0	300	295	290	295	0	...
3.0	260	240	167	177	0.65	220
7.0	90	80	...	82	2.6	370
12	86	74	45	60	3.9	320
18	51	42	29	42	6.0	330
24	35	...	17	30	8.8	370
30	25	19	11	25	10.8	360

[a] Average of 5 highest values for $K' = 340$; taking K_2 for H_2Sq as 1.0×10^{-3} (see text), true formation constant = 680.

The Uranium–Squarate System.—When squaric acid is mixed with a uranyl salt solution at pH 1.5 or higher, an intense yellow color results, and if the concentration is sufficient, a yellow precipitate forms. Two portions of this precipitate were prepared—the first by mixing equal volumes of 0.2 *M* squaric acid and 0.4 *M* uranyl perchlorate and adjusting to pH 2.5 with sodium hydroxide and the second by pouring a solution of 2.50 g (5.0 mmol) of uranyl nitrate in 25 ml of water into a hot solution of 0.60 g (5.2 mmol) of squaric acid in 30 ml of water and then adding sodium hydroxide to pH 1.7. The precipitates were filtered (with some difficulty as they were very fine), washed with small portions of water and 95% ethanol, and dried at 115° for several hours. Constant weight was obtained after 1 or 2 hr. The precipitates were analyzed as follows.

Uranium was determined by ignition in a platinum crucible, with free access of air, to form U_3O_8. To confirm that this compound was formed, the residues were dissolved in a few drops of concentrated nitric acid, giving yellow solutions of uranyl nitrate, which were evaporated and reignited. The weights were the same after this treatment as before.

Squarate ion was determined by placing 75–100-mg portions in an erlenmeyer flask, adding about 20 ml of 2 *M* sulfuric or hydrochloric acid and a slight excess of ceric sulfate, heating to 60° for 15–20 min, cooling, and back-titrating the excess ceric sulfate with standardized ferrous sulfate solution.

The squaric acid is oxidized to carbon dioxide by this treatment, consuming nearly 10 equiv of oxidant per mole. Tests with pure squaric acid showed that the oxidation is not quite stoichiometric; some 5% less ceric sulfate is consumed than the theoretical amount. Therefore, elemental carbon and hydrogen determinations were also run.

The results were as follows: U, 56.5%; C_4O_4 by ceric sulfate, uncorrected for incomplete oxidation, 26.7%, equivalent to 11.4% C; C and H by combustion, 12.0 and 0.63%. (Each value is the mean of at least two closely agreeing analyses.) The compound $UO_2C_4O_4 \cdot H_2O$ would contain 59.5% U, 12.0% C, and 0.5% H; $UO_2C_4O_4 \cdot 2H_2O$ would contain 56.9% U, 11.45% C, and 0.96% H. Our product was evidently not a pure compound, which is not surprising considering that it was a fine precipitate, but the ratio U:C_4O_4 is very close to 1:1.

In solution the complex absorbed light below 500 $m\mu$; the absorbance rose rapidly below 450 $m\mu$. Uranyl ions in equimolar concentration are virtually nonabsorbing above 400 $m\mu$, and a wavelength of 400 $m\mu$ was therefore selected for spectrophotometric determination of the formation constant. A series of tests was made in 0.5 M sodium perchlorate with 1.0×10^{-3} M squaric acid, 4.0×10^{-3} M uranyl perchlorate, and the pH adjusted by addition of perchloric acid or sodium hydroxide. The following pH values and absorbances were found in 1-cm cells: 1.30, 0.08; 1.50, 0.21; 1.85, 0.42; 2.95, 0.95; 4.00, 1.00. These values (except for the first, where A is too low) suggest that the principal complex in solution is UO_2Sq, and the 1:1 ratio was confirmed by the method of continuous variations. A pH value of 2.50 was chosen for the stability constant measurements. Uranyl concentrations ranged from 5×10^{-4} to 2×10^{-3} M and squaric acid concentrations ranged from 2×10^{-3} to 1.5×10^{-2} M.

The data are shown graphically in Figure 4. The graph is linear over a wide range, indicating that only the 1:1 complex is formed.

The Titanium–Squarate System.—Twenty milliliters of a freshly prepared solution, 0.11 M in titanium tetrachloride and 1 M in hydrochloric acid, was slowly stirred into 22 ml of 0.10 M squaric acid to which 2 ml of 1 M hydrochloric acid and 10 ml of water had been added. The temperature was 75–80°. A deep yellow solution was formed which soon began to deposit a yellow precipitate. After a couple hours of digestion the precipitate was filtered, washed with hot 0.5 M hydrochloric acid and water, and then dried at 155°. The solid was a darker yellow than the uranium complex.

It was analyzed for titanium by heating in a platinum crucible. It charred and burned vigorously, leaving a white residue of titanium dioxide which was weighed. The squarate content could not be determined by ceric sulfate oxidation as the titanium complex, once formed, was virtually insoluble in 1 M sulfuric or 2 M hydrochloric acid. Only a carbon–hydrogen analysis was performed, therefore. *Anal.* Calcd for $TiOC_4O_4$: Ti, 27.3; C, 27.3. Found: Ti, 27.2; C, 19.0; H, 0.92. The titanium content agrees precisely with that expected in $TiOC_4O_4$, but we are at a loss to explain the carbon and hydrogen analyses.

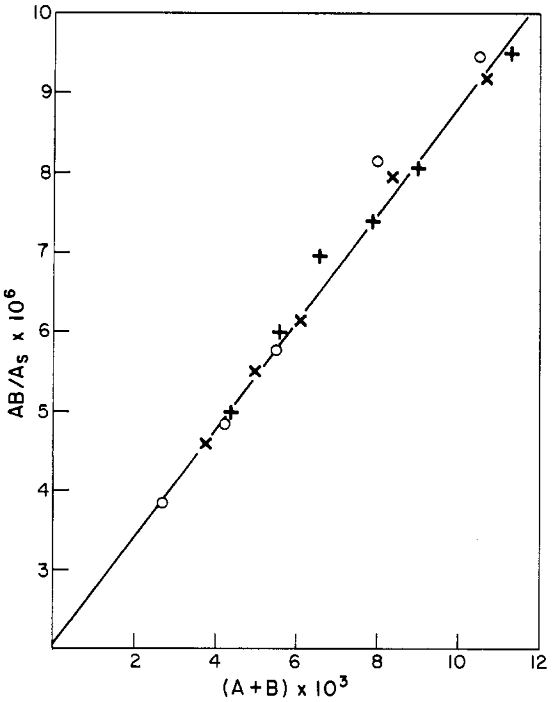

Figure 4—Spectrophotometric determination of the formation constant of uranium(VI) squarate at ionic strength 0.5 and pH 2.50: circles, 5×10^{-4} M U; ×, 1.5×10^{-3} M U; +, 2.1×10^{-3} M U. The least-squares line gives $K' = 340$ and $\epsilon = 1460$.

Experiments were made in which quantities of titanium of about 10 μmol were added to 25 ml of solutions 0.02 M in Na_2SO_4, 0.02 M in $NaHSO_4$, and up to 0.016 M in squaric acid. Sodium hydroxide was added to maintain a constant pH of about 1.90. Yellow solutions formed which darkened very slowly on standing at room temperature; the more dilute squaric acid solutions were still increasing in absorbance after 5 weeks. The change was accelerated by heating to 80°, and the intensity appeared to become constant within 4 hr. The slowness of reaction did not seem to be due to hydrolysis of Ti(IV), but rather to the actual combination of Ti(IV) with squaric acid.

The yellow titanium(IV)–squarate solutions absorbed appreciably below 450 $m\mu$. At 400 $m\mu$ the molar absorptivity exceeded that of the titanium(IV) peroxide complex and continued to increase rapidly with decreasing wavelength, unlike that of the peroxide complex, which shows a peak of absorption at 405 $m\mu$.

A solution of titanium(III) chloride gave a deep mustard yellow color with squaric acid; the absorbance rose steeply below 600 $m\mu$.

The association of titanium with squaric acid is more complicated than the other associations and will be the subject of a future communication.

Results

Ionization of Diketocyclobutenediol.—The second ionization constant was found to be $(1.30 \pm 0.05) \times 10^{-3}$ at ionic strength 0.5 and at 25°. This value was used to convert conditional formation constants to true formation constants. The formation constant of aluminum squarate was measured at ionic strength 0.3; here, K_2 was estimated to be 1.0×10^{-3}. The first ionization constant, K_1, was estimated from spectroscopic data to be about 0.5.

Formation Constants.—The formation constants found in this work are summarized in Table IV. All of them were measured over concentration ranges sufficiently wide to leave little doubt that 1:1 complexes predominate. Comments concerning individual complexes follow.

(a) **Copper.**—From the potentiometric data at three temperatures one can estimate the enthalpy of formation of aqueous CuC_4O_4; it is -9.5 ± 1.0 kcal mol^{-1}. The solubility product of $CuC_4O_4 \cdot 2H_2O$ was found to be 1.8×10^{-6}; a value of 10^{-9} was reported previously,[2]

Table IV

Summary of Formation Constants
(Ionic Strength 0.5)

Metal	Temp, °C	pH	Method	K'	K
Cu(II)	25	4.0	Spectrophotometric	167	180
	25	4.0	Polarographic	130	140
	25	4.0	Potentiometric	150	160
	38	4.0	Potentiometric	78	84
	50	4.0	Potentiometric	40	43
	25	4.0	Paper chromatographic	107	115
Fe(III)	25	1.0	Spectrophotometric	525	41,000
	40	1.0	Spectrophotometric	395	31,000
Al(III)	25	3.0	Cation exchange in 0.3 M $NaClO_4$	340	680
U(VI)	25	2.5	Spectrophotometric	340	1,200
Mn(II)	25	3.5	Paper chromatographic	26	32
Co(II)	25	4.0	Paper chromatographic	39	42
Ni(II)	25	4.0	Paper chromatographic	29	31

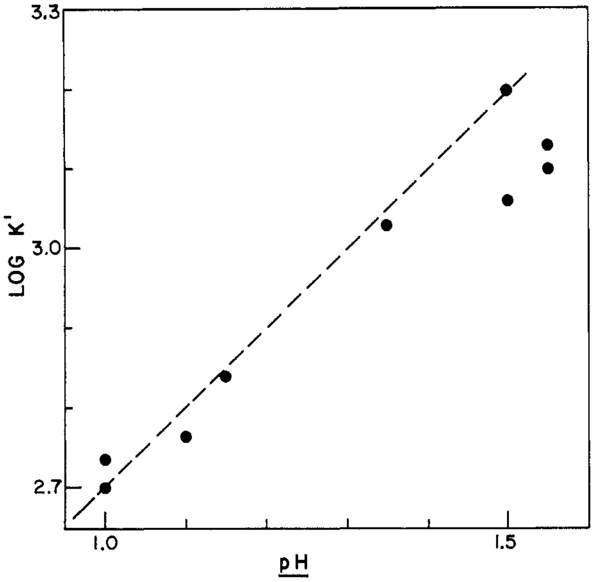

Figure 5—For iron(III) squarate, log (conditional constant) *vs.* pH at ionic strength 0.5. Data are from Table V. The dashed line shows the theoretical slope of 1.

but there was an arithmetical error in the earlier calculation.

(b) **Iron.**—The dependence of the conditional formation constant on pH, shown in Figure 5, indicates that the complex formed in this range is simply $FeC_4O_4^+$. This contrasts with the formula of the violet-black precipitate, which is $Fe(OH)C_4O_4 \cdot 3H_2O$.[9] However, we noticed that above pH 1.55 the absorption spectrum of the solution changes. The maximum absorption, which occurs at 545 mμ between pH 1.0 and 1.55, falls to 515 mμ at pH 2.08, indicating that a different complex, presumably $Fe(OH)C_4O_4$, forms at higher pH values. From the constants at 25 and 40° (Table II) the enthalpy of the reaction $Fe^{3+} + HC_4O_4^- \rightarrow FeC_4O_4^+ + H^+$ is -4 ± 1 kcal mol^{-1}.

(c) **Uranium.**—From Figure 4 the molar absorptivity of the complex at 400 mμ is 1450. This compares favorably with the absorptivity of 1050 for the peroxide complex of uranium(VI) and suggests that squaric acid might be used as an analytical reagent for uranium.

Discussion

As a ligand the squarate ion appears to associate primarily with reducible ions of high charge, forming 1:1 complexes that are often colored. The color seems to be due to charge transfer. The squarate ion is an unusual ligand, combining aromatic character with solubility in water. One might have expected it to act as the oxalate ion in forming metal complexes, but it does not; the aromatic character seems to be much more important than the carbon–oxygen configuration.

The solution chemistry of the metal complexes merits further study and so do their absorption spectra, in both ultraviolet and infrared spectra.

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