figure. The points of intersection of generalized helices with equidistant planes always form regular polygons in parallel planes with each polygon being rotated by a constant angle with respect to the preceding polygon.

An interesting feature of this structure is that the molecules are almost centrosymmetric[5] but are arranged in a noncentrosymmetric space group. This is, apparently, a rare situation; Herbstein and Schoening[21] were able to find only five examples of such an occurrence. Kitajgorodskij[22] maintains on the basis of his theory of close packing that it is impossible for centrosymmetric molecules to form a noncentrosymmetric structure. This view received support when van Niekerk and Boonstra[23] showed that the molecules of 4,4′-dinitrodiphenyl (which had been one of the more reliable of the five examples of Herbstein and Schoening[21]) are in fact noncentrosymmetric in the crystal. They were inclined, from this discovery, to infer that possibly the remaining known exceptions to the rule would be found, on further study, to conform. However, the present work establishes the structure of bis(acetylacetonato)-nickel(II) as a definite exception to Kitajgorodskij's rule and therefore calls this rule to question.

Acknowledgments.—We are grateful to Mrs. J. Dollimore, Mr. O. S. Mills, Drs. J. S. Rollett, and R. Sparks for providing copies of their programs for the University of London "Mercury" Computer.

[21] F. H. Herbstein and F. R. L. Schoening, *Acta Cryst.*, **10**, 657 (1957).

[22] A. I. Kitajgorodskij, *Kristallografiya*, **3**, 391 (1958); "Organicheskaya Kristallokhimiya," Izd. Akad. Nauk S.S.S.R., 1955, Chapter 3.

[23] J. N. van Niekerk and E. G. Boonstra, *Acta Cryst.*, **14**, 1186 (1961).

Contribution from the Department of Chemistry,
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Equilibrium Studies of Uranyl Complexes. III. Interaction of Uranyl Ion with Citric Acid[1-3]

By K. S. RAJAN and A. E. MARTELL

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A potentiometric study of complex formation between citric acid (H_3L) and the uranyl ion at 25° and ionic strengths of 0.1 and 1.0 (KNO_3) is reported. From the concentration dependence of the formation constant, it is concluded that polynuclear complexes are formed in which bridging between metal ions occurs through carboxylate and hydroxyl groups of the ligand. The values of the logarithms of the formation constant of the metal chelate $[UO_2L^-]/[UO_2^{2+}][L^{3-}]$ and of the dimerization constant $[(UO_2)_2L_2^{2-}]/[UO_2L^-]^2$ are found to be 7.40 and 4.07, respectively, at $\mu = 0.10$, and 6.87 and 3.96 at $\mu = 1.0$. Infrared absorption measurements of protonated and dissociated carboxyl groups in aqueous uranyl citrate system indicate the presence of both carboxylate and hydroxide bridging in the polynuclear complex. On the basis of the "core plus links" treatment of polynuclear complexes, the polymeric species in solution in the buffer region between 3 and $4^2/_3$ moles of base per mole of metal complex appears to be predominantly $(UO_2)_2L_2((OH)_5(UO_2)_2L_2)_2^{16-}$.

Introduction

As a part of a general investigation of olation reactions of uranyl complexes,[4,5] a study of the nature of the uranyl citrate complexes formed in aqueous solutions and the conditions under which polynuclear complexes may be formed was undertaken. The probable formation of binuclear and ternuclear uranyl citrate chelates in the pH range 2–8 was reported by Feldman and coworkers[6,7] on the basis of polarographic, potentiometric, and spectrophotometric determinations. Subsequent potentiometric work by Feldman, *et al.*,[8] was given as confirmation of the original suggestion that a binuclear diolated uranyl citrate complex is formed at low pH and that a ternuclear species is formed as the pH is increased. A formation constant for the binuclear complex was reported. On the basis of nonequilibrium ultracentrifugation measurements of the 1:1 uranyl citrate system, Gustafson and Martell[9] have reported the formation of a dimer and a probable mixture of trimers and hexamers at 3 and $4^2/_3$ moles of base per mole of total metal species, respectively.

However, on the basis of potentiometric measurements, Li and co-workers[10] reported that equimolar concentrations of uranyl ion and citric acid react at low

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[1] This work was supported by the U. S. Atomic Energy Commission under contract No. AT(11-1)-1020 and by the U. S. Public Health Service under research grant GM 10834.

[2] (a) Abstracted in part from material submitted to the faculty of Illinois Institute of Technology in partial fulfillment of the requirements of the Degree of Doctor of Philosophy. (b) Presented before the Division of Inorganic Chemistry at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962.

[3] An appendix giving the experimental data has been deposited as Document No. 8265 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[4] K. S. Rajan and A. E. Martell, *J. Inorg. Nucl. Chem.*, **26**, 789 (1964).

[5] K. S. Rajan and A. E. Martell, *ibid.*, **26**, 1927 (1964).

[6] I. Feldman, J. R. Havill, and W. F. Newman, *J. Am. Chem. Soc.*, **76**, 4726 (1954).

[7] W. F. Newman, J. R. Havill, and I. Feldman, *ibid.*, **73**, 3593 (1951).

[8] I. Feldman, C. A. North, and H. B. Hunter, *J. Phys. Chem.*, **64**, 1224 (1960).

[9] R. L. Gustafson and A. E. Martell, *J. Am. Chem. Soc.*, **85**, 2571 (1963).

[10] N. C. Li, A. Lindenbaum, and J. M. White, *J. Inorg. Nucl. Chem.*, **12**, 122 (1959).

pH to form only a mononuclear chelate having a composition which corresponds to the interaction of uranyl ion with the three carboxylic acid groups of citric acid. They have also reported stability constants for the mononuclear complex.

Heitner and Bobtelsky[11] have demonstrated the existence of uranyl citrate chelates in alkaline solution having 1:1 and 2:3 molar ratios of uranyl to citrate ions.

In view of the contradictory nature of the published reports on the uranyl citrate chelates, a detailed quantitative study of the equilibria involved in the interaction of uranyl ion with citric acid over a wide range of concentration and pH is presented in this paper.

Experimental

Reagents.—Aqueous uranyl nitrate solutions were prepared from Baker and Adamson analyzed reagent and were standardized gravimetrically by ignition of suitable aliquots to U_3O_8. Aqueous stock solutions of citric acid (Fisher certified reagent) were freshly prepared for each series of experiments and were standardized potentiometrically with standard carbonate-free NaOH.

The experimental method consisted of making potentiometric measurements of the hydrogen ion concentrations of the ligand citric acid in the presence of and in the absence of uranyl ion. A Radiometer pH meter (Type PHM4) fitted with glass and calomel extension electrodes was used for measuring hydrogen ion concentrations. The electrode system was calibrated as described previously.[4] Potentiometric measurements were made at a temperature of 25.0 ± 0.05° and at ionic strengths of 0.1 and 1.0, maintained constant by the addition of potassium nitrate.

Since the uranyl citrate system is light-sensitive and the equilibrium was reached slowly, the titration of the uranyl chelate was carried out in the dark on a series of individual solutions containing equimolar amounts of uranyl nitrate and citric acid, and to which varying amounts of base were added. The pH values were recorded at 24-hr. intervals until equilibrium was reached, as indicated by the fact that no further change in pH occurred.

Spectral Measurements.—Infrared spectral measurements were made with a Perkin-Elmer Model 21 infrared spectrophotometer fitted with sodium chloride optics. For measurements in "aqueous" solutions, 0.1-ml. cells of 0.0021-cm. thickness, with silver chloride windows, were employed. "Aqueous" solutions were made with 99.5% D_2O purchased from New England Nuclear Corporation, Boston, Mass. The concentrations of the solutions employed were in the range of 5–6 wt. % of uranyl citrate.

Results

A typical set of potentiometric titration curves of citric acid and uranyl citrate systems containing one mole of ligand per mole of metal salt is shown in Figure 1. The titration curve of citric acid (Figure 1) gives an inflection at 3 moles of base per mole of the ligand indicating that the dissociation of all three carboxylic acid groups takes place in overlapping steps. Calculation of the acid dissociation constants of the ligand was carried out by means of a modification of the method outlined by Carlson, *et al.*[12] The values of the dissociation constants obtained are presented in Table I.

TABLE I

FORMATION CONSTANTS OF 1:1 URANYL CITRATE CHELATES AT VARIOUS CONCENTRATIONS AT 25°

Ionic strength	Ligand dissociation constants	T_L or T_M, M	log K_{ML}
0.1	$K_1 = 10^{-2.79}$	1.70×10^{-2}	8.60 ± 0.01
	$K_2 = 10^{-4.30}$	8.50×10^{-3}	8.47 ± 0.03
	$K_3 = 10^{-5.65}$	3.40×10^{-3}	8.30 ± 0.02
		1.70×10^{-3}	8.14 ± 0.03
		6.80×10^{-4}	7.93 ± 0.02
1.0	$K_1 = 10^{-2.63}$	1.61×10^{-2}	8.03 ± 0.03
	$K_2 = 10^{-4.11}$	4.36×10^{-3}	7.79 ± 0.02
	$K_3 = 10^{-5.34}$	8.13×10^{-4}	7.41 ± 0.04

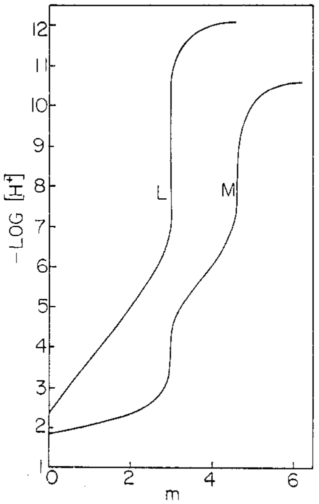

Figure 1.—Potentiometric titration of L, 4.1×10^{-3} M citric acid solution, and M, 4.0×10^{-3} M citric acid solution containing an equivalent concentration of uranyl nitrate; $t = 25.0°$; $\mu = 0.1$ (KNO_3); m = moles of sodium hydroxide added per mole of uranyl salt present in the solution.

Potentiometric titration of solutions containing equimolar amounts of uranyl ion and citric acid (Figure 1) gives inflections at 3 and $4^2/_3$ moles of base per mole of uranyl salt, respectively. The first inflection at three equivalents of base ($m = 3$) is in accord with the assumption that the metal ion combines through the dissociation of the three hydrogens from the carboxylic acid groups of the ligand. If it is assumed that the metal ion does not hydrolyze in this pH range, the reaction which may be taking place in the first buffer region involving the addition of up to three equivalents of base per mole of metal chelate compound can be represented by the equations

$$UO_2^{2+} + H_3L \rightleftharpoons UO_2L^- + 3H^+$$

$$K_{eq} = \frac{[UO_2L^-][H^+]^3}{[UO_2^{2+}][H_3L]} \quad (1)$$

$$K_{eq} = \frac{(T_M - [L^{3-}]X)K_1K_2K_3}{[L^{3-}]^2X} \quad (2)$$

where

$$[L^{3-}] = \frac{3T_L - T_{OH} - [H^+]}{\dfrac{3[H^+]^3}{K_1K_2K_3} + \dfrac{2[H^+]^2}{K_2K_3} + \dfrac{[H^+]}{K_3}}$$

and

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[11] C. Heitner and M. Bobtelsky, *Bull. soc. chim. France,* 356 (1954).

[12] G. A. Carlson, J. P. McReynolds, and F. H. Verhoek, *J. Am. Chem. Soc.,* **67**, 1335 (1945).

$$X = \frac{[H^+]^3}{K_1K_2K_3} + \frac{[H^+]^2}{K_2K_3} + \frac{[H^+]}{K_3} + 1$$

T_M and T_L represent the total concentration of uranyl ion and ligand species, respectively, T_{OH} is the total molar concentration of the hydroxide ion added to the solution, and H_3L is the acid form of the ligand. The dissociation constants K_1, K_2, and K_3 represent the dissociation of the carboxylic acid groups of the citric acid.

The value of K_{eq} which was calculated from six equilibrium measurements at $T_M = 3.40 \times 10^{-3}$ *M* is $10^{-4.44\pm0.02}$. This corresponds to a value of

$$K_{ML} = \frac{[UO_2L^-]}{[UO_2^{2+}][L^{3-}]} = \frac{K_{eq}}{K_1K_2K_3} = 10^{8.30\pm0.02} \quad (3)$$

These measurements were then extended by varying the concentrations of the chelate to test for the possibility of polynuclear complex formation. The data thus obtained at an ionic strength of 0.1 (KNO_3) are given in Table I.

Since the concentration of the uranyl salts at $\mu \approx 0.1$ (KNO_3) in Table I constitutes a considerable fraction of the total ionic atmosphere, there must be an appreciable change in the ionic atmosphere resulting from the substitution of alkali metal ions by uranyl ions, as the result of the dependence of interionic forces on the nature of the electrolyte. In order to achieve a more constant ionic atmosphere in the comparison of solutions containing widely differing concentrations of uranyl ion and uranyl citrate, it was decided to carry out a series of determinations at an ionic strength of 1.0 (KNO_3). The values of log K_{ML} obtained under these conditions are also given in Table I.

The formation constants listed in Table I show an increase of log K_{ML} with increase in concentration of total metal salt. Such a trend indicates that polymerization reactions may be taking place in solution. As a basis for the mathematical treatment of the data in the range of neutralization values between 0 and 3 equivalents of base per mole of ligand or per gram-ion of metal, the formation of dimer may be tentatively assumed. On this basis the reactions taking place in solution may be represented by eq. 3 and the relationship

$$2UO_2^{2+} + 2L^{3-} \rightleftharpoons (UO_2)_2L_2^{2-}$$

$$K_D = \frac{[(UO_2)_2L_2^{2-}]}{[UO_2^{2+}]^2[L^{3-}]^2} \quad (4)$$

When T_M equals T_L, the usual material balance expressions may be employed to give the relationships

$$K_{ML} = \frac{[UO_2L^-]}{[L^{3-}]^2X} \quad (5)$$

$$K_D = \frac{T_M - [L^{3-}]X - [UO_2L^-]}{2[L^{3-}]^2X^2} \quad (6)$$

and $[L^{3-}]$ and X are evaluated as indicated above.

Equations 5 and 6 may be rearranged to give

$$\frac{T_M - [L^{3-}]X}{[L^{3-}]^2X} = 2K_D[L^{3-}]^2X + K_{ML} \quad (7)$$

A plot of the left-hand term of eq. 7 *vs.* $[L^{3-}]^2X$ would give a straight line with a slope equal to $2K_D$ and an intercept equal to K_{ML}, if the predominating species in solution is the dimer $[(UO_2)_2L_2^{2-}]$. Potentiometric data obtained in 0.1 and 1.0 *M* KNO_3 media are treated in accordance with eq. 7 and the linear plots obtained with the method of least squares are shown in Figures 2 and 3. The values of the equilibrium constants taken from the lines in Figures 2 and 3 are presented in Table II.

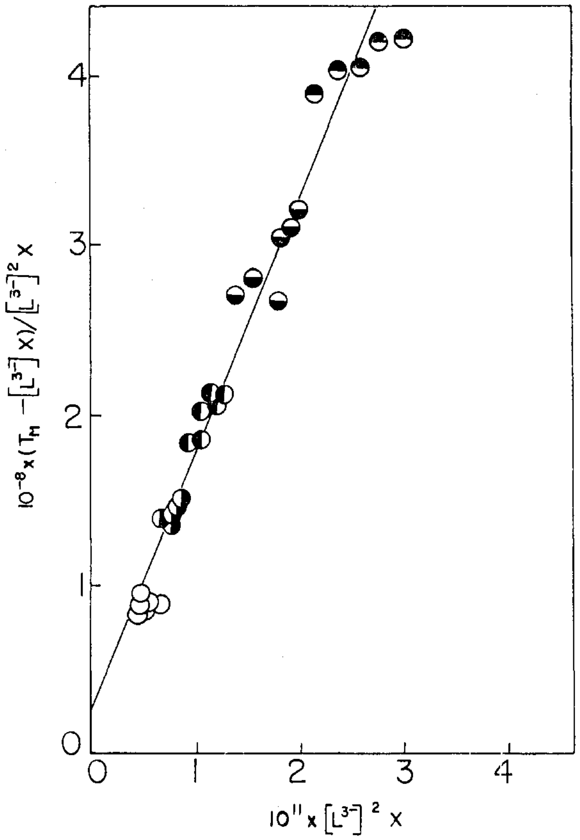

Figure 2.—Demonstration of formation of a binuclear complex from uranyl and citrate ions in accordance with eq. 7; $T_M = T_L$ = total concentration of metal or ligand species; H_3L represents the neutral ligand; $X = [H^+]^3/K_1K_2K_3 + [H^+]^2/K_2K_3 + [H^+]/K_3 + 1$ where K_n represents the acid dissociation constants of citric acid: ◓, $[UO_2L^-] = 1.70 \times 10^{-2}$ *M*; ◒, $[UO_2L^-] = 8.50 \times 10^{-3}$ *M*; ◐, $[UO_2L^-] = 3.40 \times 10^{-3}$ *M*; ◑, $[UO_2L^-] = 1.70 \times 10^{-3}$ *M*; ○, $[UO_2L^-] = 6.80 \times 10^{-4}$ *M*; $\mu = 0.1$ (KNO_3); $t = 25°$.

Table II

Interaction of Uranyl ion with Citric Acid at 25°

Equil. quotient[a]	Ionic strength (KNO_3 medium)	log of equil. constant
$K_{ML} = \frac{[ML^-]}{[M^{2+}][L^{3-}]}$	0.1	7.40 ± 0.21
	1.0	6.87 ± 0.11
$K_D = \frac{[M_2L_2^{2-}]}{[M^{2+}]^2[L^{3-}]^2}$	0.1	18.87 ± 0.06
	1.0	17.70 ± 0.04
$K_d = \frac{[M_2L_2^{2-}]}{[ML^-]^2}$	0.1	4.07 ± 0.35
	1.0	3.96 ± 0.18

[a] M^{2+} represents uranyl ion

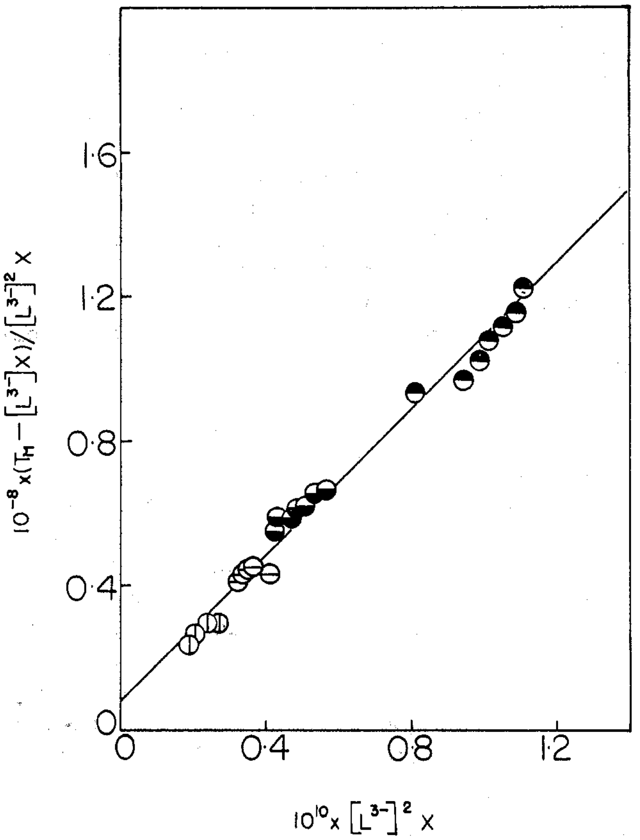

Figure 3.—Demonstration of formation of a binuclear complex from uranyl and citrate ions in accordance with eq. 7 at $\mu = 1.0$ (KNO_3) and $t = 25°$: ◓, $[UO_2L^-] = 1.61 \times 10^{-2}$ *M*; ◒, $[UO_2L^-] = 4.36 \times 10^{-3}$ *M*; ⊖, $[UO_2L^-] = 2.18 \times 10^{-3}$ *M*; ⦶, $[UO_2L^-] = 8.13 \times 10^{-4}$ *M*.

Alternately, if it is assumed that a trimer is formed the expression

$$\frac{(T_M - [L^{3-}]X)}{[L^{3-}]^2X} = 3K_T[L^{3-}]^4X^2 + K_{ML} \qquad (8)$$

is obtained. A plot of the left-hand term of eq. 8 *vs.* $[L^{3-}]^4X^2$ would give a straight line, if trimers predominate, with a slope equal to $3K_T$ and an intercept equal to K_{ML}.

Aqueous Infrared Spectra.—Preliminary infrared absorption measurements were made on "aqueous" (*i.e.*, D_2O) solutions of citric acid (0.3 *M*) and 1:1 UO_2–citrate (0.1 *M*) solutions as a function of pH. The spectra are shown in Figures 4 and 5. Ratios of $[COOD]/([COOD] + [COO^-])$ are obtained from the spectra by using the values of extinction coefficients of COOD and COO^- in D_2O (ϵ_{COOD} 240 mole^{-1} cm.$^{-1}$ l.; ϵ_{COO^-} 700 mole^{-1} cm.$^{-1}$ l.) reported by Nakamoto, *et al.*[13] These "observed" ratios are plotted against pH in Figure 6. In the same figure are also plotted the ratios of $[\text{–COOH}]/([\text{–COOH}] + [\text{–COO}^-])$[14] calculated from potentiometric equilibrium data according to the two possible reactions

$$2UO_2^{2+} + 2HL^{2-} + 2H_2O \rightleftharpoons (UO_2HLOH)_2^{2-} \qquad (A)$$

$$2UO_2^{2+} + 2L^{3-} \rightleftharpoons (UO_2L)_2^{2-} \qquad (B)$$

(The error in the measurement of $-\log [H^+]$ is <0.01, and in the evaluation of the ratio $[COOD]/([COOD] + [COO^-])$ it is <0.02.) In the above reactions, H_3L represents the neutral ligand, HL^{2-} represents the ligand containing one neutral (protonated) carboxyl group, and L^{3-} is the fully dissociated ligand. Thus the binuclear complex $(UO_2HLOH)_2^{2-}$ would contain two neutral carboxyl (–COOH) groups not bound to the metal ion and two hydroxyl ions presumably acting as bridges between the uranyl ions. The other binuclear complex would not contain hydroxyl ions, so that bridging would occur through the ligand.

Reactions at High pH.—The buffer region of the potentiometric curve (Figure 1) between 3 and $4^2/_3$ moles of base per mole of the uranyl chelate can be accounted for by assuming that the dimer $((UO_2)_2L_2)^{2-}$ hydrolyzes and polymerizes further. As a basis for the quantitative treatment of the potentiometric data, the hydrolysis of the dimer followed by the formation of the "core plus links" type of polynuclear complex of the general form $M_2L_2((OH)_tM_2L_2)_n$ in solution was used. This model is based on the mathematical treatment given by Sillén[15a] and Sillén and Hietanen[15b] for

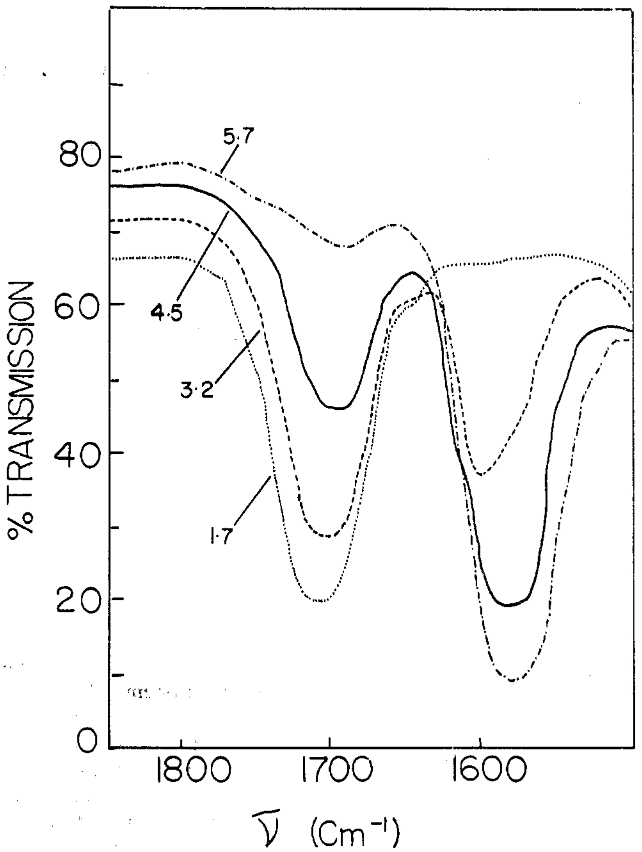

Figure 4.—Infrared spectra of "aqueous" solutions (0.3 *M*) of citric acid in 99.5% D_2O as a function of hydrogen ion concentration; $\mu = 1.0$ (KCl); $t = 25°$; numbers on the graph represent $-\log [H^+]$.

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(13) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **85**, 309 (1963).

(14) For a meaningful interpretation of the results and for comparison with potentiometric data, it is assumed that differences between the ratios $[COOD]/([COOD] + [COO^-])$ and $[COOH]/([COOH] + [COO^-])$ are within the limits of tolerances at any given pH of interest in the present study.

(15) (a) L. G. Sillén, *Acta Chem. Scand.*, **8**, 299, 318 (1954); (b) S. Hietanen and L. G. Sillén, *ibid.*, **8**, 1607 (1954).

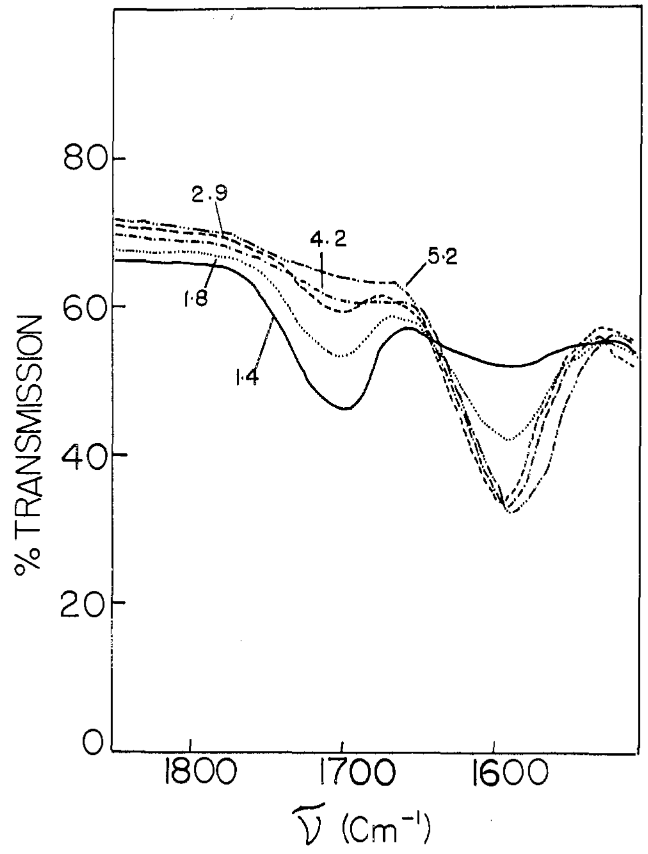


Figure 5.—Infrared spectra of "aqueous" solutions (0.07 *M*) of 1:1 uranyl citrate compound in 99.5% D_2O as a function of $-\log [H^+]$; μ = 1.0 (KCl); t = 25°; numbers on the graph represent $-\log [H^+]$.

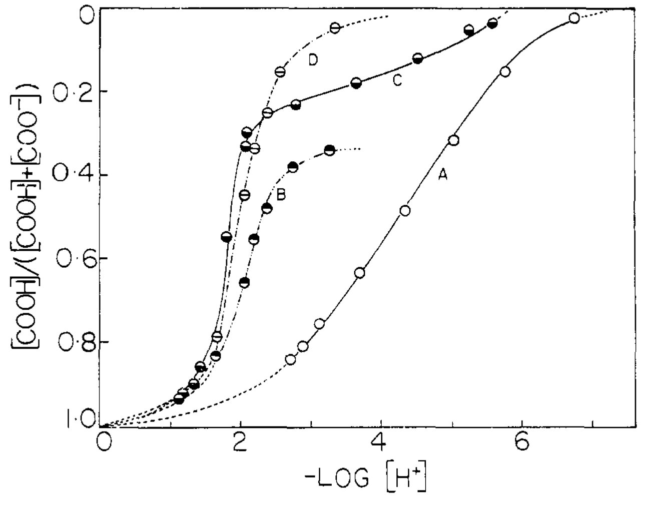


Figure 6.—Correlation of infrared measurements with potentiometric data on the polynuclear uranyl citrate system: A, "calculated" values based on potentiometric equilibrium measurements for the free ligand; B, "calculated" from potentiometric data under the assumption that two hydroxo bridges are present (*i.e.*, $(UO_2HLOH)_2{}^{2-}$ is formed); C, "observed" plot based on infrared measurements; D, "calculated" from potentiometric data under the assumption that no hydroxo bridges are present (*i.e.*, $(UO_2L)_2{}^{2-}$ is formed); μ = 1.0 (KCl).

the hydrolysis and polymerization of metal ions. They have shown that if the curves obtained by plotting Z, the average number of equivalents of protons which are dissociated or hydroxyl ions which react per mole of metal ion, *vs.* $-\log [H^+]$, for different constant values of total metal ion concentration, are found to be parallel, then the complexes in solution can be written in the "core plus links" form $M((OH)_tM)_n$ where t represents the number of hydroxo bridges per link in the polynuclear complex and n represents the number of links attached to the core. It is found that at a constant Z value, the horizontal spacing between two lines, $\Delta(-\log [H^+])$, is proportional to the difference between the logarithm of the two different total metal concentrations (T_M) represented by the lines. Stated differently

$$\left(\frac{\partial \log T_M}{\partial \log [H^+]}\right)_Z = t \tag{9}$$

This constant value t has been shown by Sillén and coworkers[15] to correspond to the number of hydroxo groups per link in the polymeric complex $M((OH)_tM)_n$.

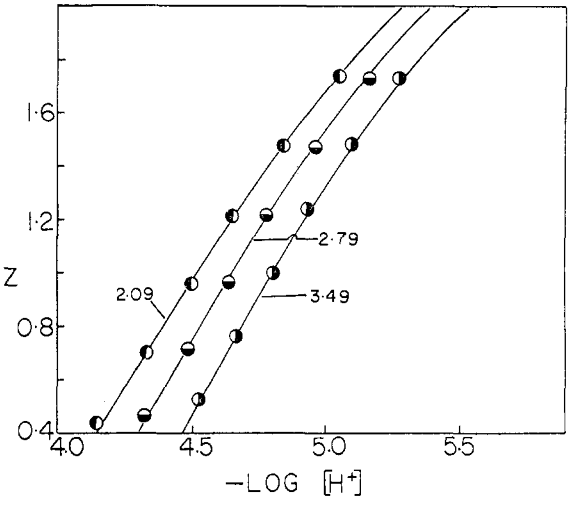


Figure 7.—Plot of Z, average number of equivalents of protons dissociated per molecule of uranyl citrate dimer, as a function of $-\log [H^+]$; μ = 1.0 (KNO_3); t = 25°; the numbers on the graph represent values for $-\log T_D$, where T_D = the total initial concentration of dimer.

This method was applied to the potentiometric data obtained in the present investigation. In the uranyl citrate system, the species at the beginning of the buffer region (*i.e.*, 3 moles of base per mole of uranyl salt) is assumed to be dimeric and T_D represents total concentration of dimer. In Figure 7 are shown the curves of Z *vs.* log $[H^+]$ for three different constant values of total dimer concentration (T_D). The quantity Z, the average number of equivalents of protons dissociated per mole of dimer species, is given by

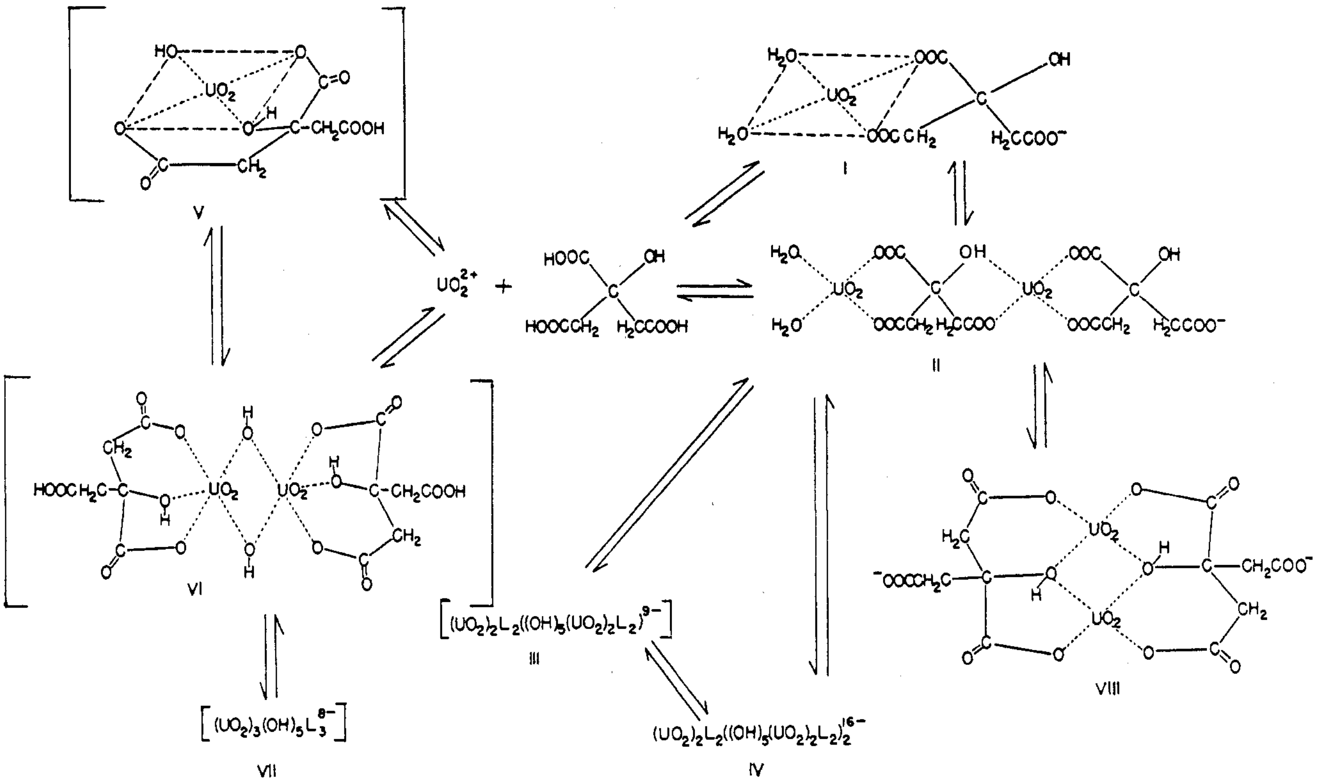
$$Z = \frac{T_{OH} + [H^+] - [OH^-]}{T_D} \tag{10}$$

The curves obtained (Figure 7) are essentially parallel. The quantity t, the number of hydroxo bridges per link in the polymeric complex, is given by the derivative

$$\left(\frac{\partial \log T_D}{\partial \log [H^+]}\right)_Z = t \tag{11}$$

CHART I

PROPOSED PRODUCTS AND INTERMEDIATES IN THE POLYMERIZATION OF URANYL CITRATE



To determine the quantity *t*, plots of $-\log T_D$ *vs.* $-\log [H^+]$ at different *Z* values (0.6, 0.8, 1.0, 1.2, 1.4, and 1.6) were constructed in Figure 8. From the plots in Figure 8 an average value of 5.08 ± 0.26 was obtained for the slope *t* (which can be approximated to $t = 5$). If the derivative in eq. 11 is constant and is equal to 5 this means that *Z* should be a function of $X = \log T_D - 5 \log [H^+]$. To check whether this is so, the data were recalculated and a plot of $y = Z/5$ as a function of $X = \log T_D - 5 \log [H^+]$ is drawn in Figure 9.

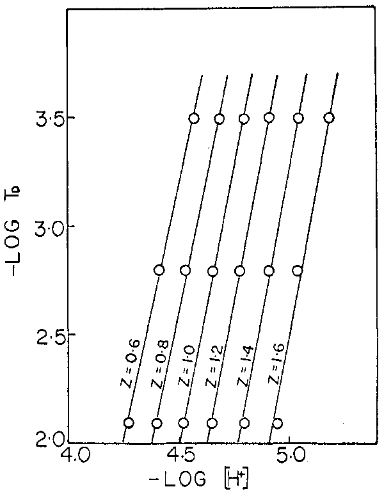


Figure 8.—Variation of $-\log T_D$, the total initial concentration of dimer, as a function of $-\log [H^+]$ at constant *Z*; $\mu = 1.0$ (KNO_3); $t = 25°$.

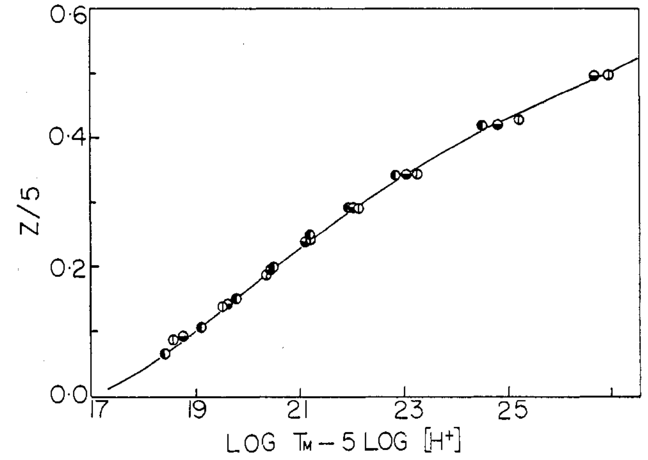


Figure 9.—Plot of $Z/5$ *vs.* $\log T_D - 5 \log [H^+]$; data in Figure 8 recalculated on the basis of the assumption that *t*, the number of hydroxo groups per link, is equal to 5; $\mu = 1.0$ (KNO_3); $t = 25°$.

Discussion

A complete scheme of the possible equilibria involved in the interaction of uranyl ion with citric acid in the pH range 2–8 is shown in Chart I. Uranyl ion is in equilibrium with mononuclear (I) and binuclear citrate (II, VIII) chelates in the pH range 2–4. The mononuclear complex (I) is shown to be formed through the dissociation of three protons from three carboxylic acid groups of the ligand. Feldman[8] and co-workers have visualized structure V for the mononuclear species. Their interpretation is based on the assumption that a hydroxo uranyl complex containing a monoprotonated ligand anion is formed and was made to account for the inflection in the titration curve at 3 moles of base per mole of uranyl salt. It is obvious that the equilibrium constant is the same whether the initial mononuclear complex is formulated as UO_2L^- or UO_2HLOH^-, since it is impossible to distinguish between these species by potentiometric (thermodynamic) measurements. The most reasonable assumption would be that the polarizing power of the uranyl ion on coordinated water molecules would be reduced by coordination with the citrate anion. Therefore, since the uncomplexed uranyl ion itself does not hydrolyze appreciably below pH 3, the uranyl group in the uranyl citrate chelate would not be expected to be coordinated directly to the hydroxyl ion at pH 2.8. Feldman, *et al.*,[8] have suggested that the tendency of UO_2^{2+} ion to hydrolyze after complexing by a potentially terdentate ligand is the result of the deformation of the collinear dioxouranium entity, as the result of mutual repulsion between the uranyl oxygen atoms and the coordinating oxygens of the terdentate ligand. This process is presumably accompanied by rehybridization of the coordinate bonds of the uranyl ion. They also contend that complexes in which the uranyl ion is coordinated to mono- and bidentate ligands tend to hydrolyze less readily. However, recent studies by Rajan and Martell[4] indicated that uranyl ion interacts with the terdentate ligands iminodiacetic acid and hydroxyethyliminodiacetic acid in the pH range 2–4 to form mononuclear chelates with stability constants (log K_{ML}) equal to 8.93 and 8.32, respectively. There was no hydrolysis of the chelates or polymerization through olate bridging. On the basis of the considerations given above, it is suggested that the mononuclear uranyl chelate species formed in acid solution is indicated by structure I.

The formation constants listed in Table I show an increase of log K_{ML} with increase in the concentration of the total metal ion and of the ligand. This variation indicates that polynuclear complex formation may be occurring in solution. The degree of correlation shown in Figure 3 for the formation of dimer is not found for a similar treatment of the data for a trimer. It is therefore concluded that the complex species formed in solution in the buffer region (pH 2–4) is predominantly binuclear. The concentration dependence of log K_{ML} (Table I) is probably not due to polymerization of the uranyl citrate through hydroxyl ion bridges (olation), since the attachment of the ligand to the metal ion reduces its tendency to hydrolyze. Feldman and coworkers[8] have proposed the formation of a diolated binuclear uranyl citrate chelate (structure VI, Chart I). However, in view of the above conclusions concerning the nature of the mononuclear complex, it is necessary to look for another mechanism to explain the polymerization reaction. The formation of polynuclear complexes in the absence of hydroxyl ion bridging may conceivably occur through the ligand in two possible alternate ways which are indicated by structures II and VIII, Chart I. Since increasing the total concentration would shift the equilibrium to the right, it is seen that such a reaction would account for the increasing values of log K_{ML} in Table I. The selection of II, which is favored by us at present, would imply the formation of trimers or even higher polymers at very high concentration.

The graphical comparison of the variation of $[\text{-COOD}]/([\text{-COOD}] + [\text{COO}^-])$ with hydrogen ion concentration, illustrated in Figure 6, indicates that the "observed" values (curve C) based on infrared absorption measurements lie between the two "calculated" plots (curves B and D) which are both based on potentiometric equilibrium data, but calculated according to the formation of two different postulated species, *viz.*, $(UO_2)_2L_2^{2-}$ (curve D) and $(UO_2(OH)HL)_2^{2-}$ (curve B). The fact that curve C lies closer to D than to B up to pH 2.8 (Figure 6) can be considered as an indication that dimerization takes place primarily by bridging through the ligand groups (structures II and VIII, Chart I). However, the possibility of a small but appreciable amount of dissociation of a proton from either the alcoholic (OH) group of the ligand or a coordinated water molecule above pH 2.8–3.0 cannot be ruled out.

The buffer region of the titration curve between 3 and $4^2/_3$ moles of base per mole of the uranyl chelate can be accounted for by assuming that hydrolysis of the dimer $(UO_2)_2L_2^{2-}$ is accompanied by polymerization. On the basis of a number of different mathematical treatments of the potentiometric data it is concluded that polynuclear complexes of the "core plus links" type may be present in solution in this region. Two plausible interpretations used for the treatment of the equilibrium data which failed to show correlation with the experimental results are conversion of the dimer to a trimer (structure VII, Chart I) and to a hexamer, according to the reactions

$$3(UO_2)_2L_2^{2-} \rightleftharpoons 2(UO_2)_3L_3(OH)_5^{8-} + 10H^+ \qquad (C)$$

$$3(UO_2)_2L_2^{2-} \rightleftharpoons (UO_2)_6L_6(OH)_{10}^{16-} + 10H^+ \qquad (D)$$

The model which gave successful correlation is the hydrolysis of the dimer followed by the formation of the "core plus links" type of polynuclear complex (structure IV, Chart I). The fact that essentially parallel curves of Z *vs.* $-\log [H^+]$ (Figure 7) at three different total concentrations of the dimer $(UO_2)_2L_2^{2-}$ are obtained indicates that the polynuclear species in solution can be represented by the "core plus links" type of formula and that the reaction occurring in solution can be represented by the equation

$$(n + 1)((UO_2)_2L_2)^{2-} + nt\text{H}_2\text{O} \rightleftharpoons (UO_2)_2L_2((OH)_t(UO_2)_2L_2)_n{}^{(n2+2+nt)-} + nt\text{H}^+$$

The quantity t, the number of hydroxo bridges per link, is obtained from the derivative $(\partial \log T_D/\partial \log [H^+])_Z = t$ (*i.e.*, the slope of the plot of $-\log T_D$ *vs.* $-\log [H^+]$ in Figure 8). An approximate value of 5 was obtained for t. The constancy of the value of 5 for the derivative is nicely indicated by the fact that a single curve is obtained when $y = Z/5$ is plotted as a function of $X = \log T_{\bar{D}} - 5 \log [H^+]$ (Figure 9). The complexes formed in appreciable amounts in solution can therefore be written in the form $(UO_2)_2L_2((OH)_5(UO_2)_2L_2)_n^{-7n-2}$.

In view of the fixed stoichiometry (1:1) of the uranyl citrate system under investigation and on the basis of the fact that a definite inflection of the titration curve occurs at $4^2/_3$ moles of base per mole of uranyl chelate, the value of n in the "core plus links" formula should be equal to 2. Thus, the polynuclear species present in the buffer region of the titration curve between 3 and $4^2/_3$ moles of base per mole of uranyl chelate appears to be predominantly hexameric and has the formula $(UO_2)_2L_2((OH)_5(UO_2)_2L_2)_2^{16-}$ (structure IV, Chart I). The hexameric chelate may be formed either directly or through the formation of a tetranuclear chelate intermediate (structure III, Chart I). By applying the method of calculation reported by Sillén and Hietanen[15] and Hietanen,[16] the equilibrium constant (K_2) for the formation of the hexanuclear chelate was determined.

$$K_2 = \frac{[(UO_2)_2L_2((OH)_5(UO_2)_2L_2)_2^{16-}][H^+]^{10}}{[(UO_2)_2L_2^{2-}]^3} = 10^{-47.9}$$

A consideration of the results of the uranyl citrate, uranyl malate, and uranyl tartrate[5] systems brings out a striking similarity, *viz.*, in each of these systems the complex species formed in solution in the buffer range (pH 2–4) is predominantly binuclear. Above pH 4, each of these binuclear chelates reacts with hydroxide ions and polymerizes further. The dimerization constants (K_d) follow the order citrate > malate > tartrate. However, the differences in stability constants do not exceed 0.6 log K unit. Consideration of the nature of the equilibria involved in the formation of these binuclear chelates and a comparison of the dimerization constant (K_d) would strongly suggest the involvement of the α-hydroxyl group of the ligands in bridging. In the light of this observation it is of interest to reconsider the data thus far reported on the polynuclear uranyl complexes. The hydrolysis of the uranyl–Tiron chelate (pyrocatechol-3,5-disodium sulfonate) and formation of a ternuclear species at pH 5 has been reported by Gustafson, *et al.*[17] They have visualized a possible structure for the polynuclear uranyl complex which involves both the hydroxo groups and the ligand groups containing oxygen donors in the bridging of the uranyl ions. Richard, *et al.*,[18] have reported the formation of a binuclear uranyl chelate with 8-quinolinol-5-sulfonate which would presumably involve the phenoxide ion of the ligand in the bridging. In the polymerization of the uranyl–HIMDA chelate[4] (N-hydroxyethyliminodiacetic acid), it could be suggested that the bridging between the uranyl ions may take place through the alkoxide group of the ligand. It should thus be noted that all the polynuclear uranyl complexes thus far reported have ligands with hydroxyalkyl or phenolic groups. Of course, the reverse is not true; many ligands with these functional groups do not form polynuclear uranyl complexes. This interesting observation leaves open a fundamental question for future investigations, *viz.*, how fundamental or how essential are hydroxyorganic groups in the polymerization reactions of uranyl complexes?

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Complexes Derived from Strong Field Ligands. XIX. Magnetic Properties of Transition Metal Derivatives of 4,4′,4′′,4′′′-Tetrasulfophthalocyanine

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The tetrasulfophthalocyanine complexes of manganese, iron, cobalt, nickel, and copper have been prepared in high purity and the magnetic moments of these substances have been determined both in the solid state and in solution. Solid state determinations are complicated by cooperative interactions. The iron(II) complex is a reversible oxygen carrier in the solid state. In aqueous solution, Mn(II), Co(II), Ni(II), and Fe(III) are spin paired. The ligand field strength of tetrasulfophthalocyanine is comparable to that of cyanide ion.

Introduction

Although a number of investigations[1–5] have been devoted to the magnetic properties of unsubstituted metal phthalocyanines, magnetic susceptibilities have

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