TABLE V

REACTION OF EXCESS AsH₃ WITH LiNH₂

(Bracketted terms refer to millimoles)

Run	[AsH₃] (initial)	[AsH₃] (reacted)	]LiNH₂]	[NH₃] ~25°	~80°	~300°	[H₂] ~25°	~80°	~300°
10	2.41	2.41	8.7	2.943	0.024	...	0.175	0	...
11	2.335	2.335	4.65	4.52	...	...	.647	...	0.606
12	1.36	1.33	~2.4	2.332	0.054	0.032	.560	0.134	0.146
13ᵃ	1.750	0.462	0.908	0.885	0.015	...	.092	0.090	...
14	2.000	0.920	1.772	1.741	...	0.030	.205	...	0.280

ᵃ AsD₃ used.

TABLE VI

REACTION OF AsD₃ WITH LiNH₂

		D/H ratios		
Run	AsH₃	H₂ evolved at 25°	H₂ evolved at 90°	NH₃ evolved at 25°	NH₃ evolved at 80°
2	24.0	0.53	..	0.53	0.19
7	5.85	0.83	..	0.38	0.16
13	24.0	2.10	2.15	..	..

The decreasing tendency toward elimination of arsine on going from the lithium salt to the potassium salt may be explained in terms of the increasing cation size. If we postulate that the mechanism of arsine evolution involves migration of a proton from one AsH_2^- ion to another, then we would expect this process to occur more readily when the AsH_2^- ions are next to smaller, more polarizing ions. The first step in the decomposition of $LiAsH_2$ is presumably
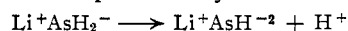
$$Li^+AsH_2^- \longrightarrow Li^+AsH^{-2} + H^+$$

The proton may re-unite with the AsH^{-2} ion or it may unite with some other AsH_2^- ion to form arsine, which may escape. The stability of $LiAsH_2 \cdot 4NH_3$

at room temperature bears out this polarization concept. In this compound, the ammoniated lithium ion is relatively large and weakly polarizing; hence no decomposition of the AsH_2^- ion occurs.

The hydrogens in Li_2AsH, Na_2AsH and $KAsH_2$ have very little protonic character; therefore little or no arsine is evolved when these compounds are heated. Another type reaction takes place, probably involving hydrogen atom or hydride ion transfer. The behavior of $NaAsH_2$ is between that of $LiAsH_2$ and that of $KAsH_2$. Arsine is lost until the remaining hydrogens have lost their protonic character; this occurs before the composition Na_2AsH is reached. However, the protonic character of the hydrogen in Li_2AsH is manifested in its implied reaction with lithium amide to form Li_3As. The corresponding sodium salt, Na_2AsH, does not react with sodium amide at room temperature.

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[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Stability of Metal Chelates of 8-Quinolinol-5-sulfonate[1]

BY C. F. RICHARD, R. L. GUSTAFSON AND A. E. MARTELL

The interaction of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Mg(II), Fe(III), UO₂(VI) and Th(IV) ions with 8-hydroxy-quinoline-5-sulfonate has been investigated by potentiometric and spectrophotometric methods. Formation constants have been calculated for chelates containing 1:1, 2:1 and in some cases 3:1 and 4:1 ratios of ligand to metal ion. Comparison of these stability constants with those obtained for 8-quinolinol itself shows that the observed differences are essentially the result of the lower basicity of the sulfonated ligand. The hydrolytic behavior of Fe(III), UO₂(VI) and Th(IV) chelates containing two unfilled coördination positions has been investigated quantitatively. The hydrolysis and olation tendencies of the 3:1 thorium and 2:1 uranyl and ferric chelates were found to follow the order Fe(III) > Th(IV) > UO₂(VI).

In view of the relatively high stabilities of the uranyl(VI) and thorium(IV) chelates of pyrocatechol-3,5-disulfonate (Tiron), it was decided to investigate the interaction of these and other metal ions with 8-quinolinol-5-sulfonate. Both of these ligands form five-membered rings with metals, the essential difference between the two being that the Tiron contains two phenolic groups as donors, while the latter ligand contains one phenolic group and one heterocyclic nitrogen atom. Both ligands would be expected to form chelates solubilized by sulfonate groups. The soluble 8-hydroxyquinoline-5-sulfonate is of further interest as a ligand

because of the well-known affinity of the parent compound, 8-hydroxyquinoline itself, for the thorium(IV) ion and for many other metal ions.

The stabilities of the chelate compounds formed by this ligand and some of the metals studied in the present investigation have been reported by Näsänen[2] and others[3-5] for somewhat different reaction conditions. A more important difference between the present and previous work, however, is a study of the interactions between metal and ligand under conditions such that the maximum

(2) R. Näsänen and E. Uisatalo, Acta Chem. Scand., 8, 112 (1954).

(3) A. Albert, Biochem. J., 54, 646 (1953).

(4) L. E. Maley and D. P. Mellor, Austral. J. Sci. Res., 2, A, 579 (1949).

(5) A. Albert and A. Hampton, J. Chem. Soc., 505 (1954).

coördination number of the metal ion is not attained. These interactions lead to disproportionation reactions or the formation of hydroxo complexes which are in equilibrium with polynuclear complexes.

Experimental

The experimental method consisted of potentiometric titration of monopotassium 8-quinolinol-5-sulfonate in the absence of and in the presence of the metal ion being investigated. The ionic strength was maintained relatively constant by using a medium containing 0.10 M potassium nitrate and low concentrations of ligand and metal ion. Presaturated nitrogen was passed through the solution throughout the course of a titration and the temperature was maintained at $25.0 \pm 0.1°$.
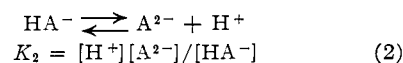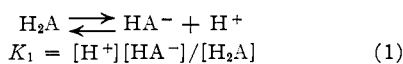
The Beckman Model G pH meter used to determine the hydrogen ion concentration was calibrated by direct titration of acetic acid, the observed pH meter reading being compared with the actual hydrogen ion concentration, determined from the data tabulated by Harned and Owen.[6] The pH regions below 3.5 and above 10.5 were calibrated by measurements in HCl and KOH solutions, respectively.

Reagents.—The potassium chloride and metal nitrate solutions were prepared from J. T. Baker Analyzed materials. The metal ion solutions except for those of UO_2^{2+} and Th^{4+} were standardized volumetrically by titration with the disodium salt of ethylenediaminetetraacetic acid in the presence of suitable indicators as outlined by Schwarzenbach.[7] The latter were standardized gravimetrically by ignition of aliquots to U_3O_8 and ThO_2, respectively. Carbonate-free potassium hydroxide was prepared by the method of Schwarzenbach and Biedermann[8] and was standardized by titration with potassium hydrogen phthalate. A sample of 8-quinolinol-5-sulfonic acid was recrystallized twice from water and then converted in solution to the monopotassium salt. An aqueous stock solution of the ligand was standardized potentiometrically.

Procedure.—Solutions containing 1:1, 2:1, 3:1 or 4:1 molar ratios of ligand to metal ion were introduced into the titration cell, so that 150 ml. of the final solution contained approximately 0.1–0.5 millimole of metal ion. After thermal equilibrium was reached, the hydrogen ion concentration was determined by a number of successive readings after each addition of small increments of standard 0.1 M KOH.

Calculations

A. Acid Dissociation Constants.—The acid dissociation constants for 8-quinolinol-5-sulfonate were calculated by a direct algebraic method. The equilibria and the dissociation constants involved are

$$H_2A \rightleftharpoons HA^- + H^+$$
$$K_1 = [H^+][HA^-]/[H_2A] \qquad (1)$$
$$HA^- \rightleftharpoons A^{2-} + H^+$$
$$K_2 = [H^+][A^{2-}]/[HA^-] \qquad (2)$$

If T_A represents the total concentration of ligand species and a represents the number of moles of base added per mole of ligand, it follows that for the lower buffer region, assuming that no $[A^{2-}]$ is present

$$T_A = [H_2A] + [HA^-] \qquad (3)$$
and
$$aT_A + [H^+] = [HA^-] \qquad (4)$$
and for the upper buffer region
$$T_A = [HA^-] + [A^{2-}] \qquad (5)$$

(6) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 523.

(7) G. Schwarzenbach, "Die komplexometrische Titration," Ferdinand Enke, Stuttgart, 1955.

(8) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 331 (1948).
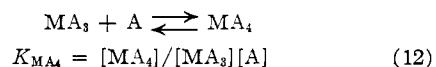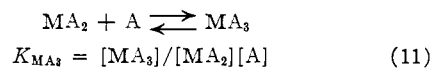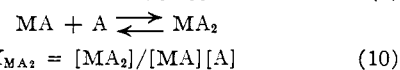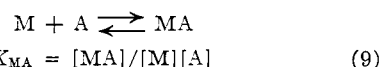
and

$$(a - 1)T_A + [H^+] - [OH^-] = [A^{2-}] \qquad (6)$$

Substitution and solving for K_1 and K_2 gives

$$K_1 = \frac{[H^+](aT_A + [H^+] - [OH^-])}{T_A - (aT_A + [H^+] - [OH^-])} \qquad (7)$$

$$K_2 = \frac{[H^+]((a - 1)T_A + [H^+] - [OH^-])}{T_A - ((a - 1)T_A + [H^+] - [OH^-])} \qquad (8)$$

B. Chelate Stability Constants.—The equilibria involved in metal chelate formation may be expressed as

$$M + A \rightleftharpoons MA$$
$$K_{MA} = [MA]/[M][A] \qquad (9)$$
$$MA + A \rightleftharpoons MA_2$$
$$K_{MA_2} = [MA_2]/[MA][A] \qquad (10)$$
$$MA_2 + A \rightleftharpoons MA_3$$
$$K_{MA_3} = [MA_3]/[MA_2][A] \qquad (11)$$
$$MA_3 + A \rightleftharpoons MA_4$$
$$K_{MA_4} = [MA_4]/[MA_3][A] \qquad (12)$$

Since T_A represents the total concentration of the various ligand species and T_M that of all the metal species

$$T_A = [H_2A] + [HA^-] + [A^{2-}] + [MA] + $$
$$2[MA_2] + 3[MA_3] + 4[MA_4] \qquad (13)$$
and
$$T_M = [M] + [MA] + [MA_2] + [MA_3] + [MA_4] \qquad (14)$$

Also the total amount of titratable hydrogen is

$$(2 - a)T_A = 2[H_2A] + [HA] + [H^+] - [OH^-] \qquad (15)$$

Combination of equations 15, 1 and 2 gives an expression for $[A^{2-}]$

$$[A^{2-}] = \frac{(2 - a)T_A - [H^+] + [OH^-]}{\frac{2[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2}} \qquad (16)$$

Combination of equations 10, 12 and 13, with the added assumption that $[MA_2]$, $[MA_3]$ and $[MA_4]$ are negligible when the ratio of ligand to metal ion is 1:1, gives an equation for K_{MA}

$$K_{MA} = \frac{T_A - [A^{2-}]X}{[A^{2-}]^2} \qquad (17)$$

where

$$X = \frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1$$

Similarly, the data obtained from the titrations involving a 2:1 ratio of ligand to metal ion may be used to solve for K_{MA_2} by the relationship

$$K_{MA_2} = \frac{K_{MA}[A^{2-}](T_M - X[A^{2-}]) - X[A^{2-}] + T_A}{K_{MA}[A^{2-}]^3X} \qquad (18)$$

Under conditions where the difference between successive formation constants is small, the assumptions used in deriving equation 16 are not valid, and it becomes more practical to use the method of Bjerrum.[9] The average number of moles of ligand bound per mole of metal ion is designated by $\bar{n}$ and may be calculated by the expression

$$n = \frac{1}{T_M}(T_A - X[A^{2-}]) \qquad (19)$$

(9) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

Values of $\bar{n}$ obtained from equation 18 were plotted against pA, the negative logarithm of $[A^{2-}]$. As a first approximation, the values of pA at $\bar{n}$ = 0.5, 1.5, 2.5 and 3.5 are equal to log K_{MA}, log K_{MA_2}, log K_{MA_3} and log K_{MA_4} respectively. These temporary constants then were corrected by a method of successive approximations described by Carlson, et al.[10]

Discussion of Results

8-Quinolinol-5-sulfonic Acid.—Potentiometric titration of 8-quinolinol-5-sulfonic acid produces two sharp inflections which probably correspond to the separate neutralization reactions
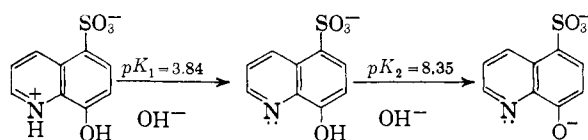
The pK values of 3.84 and 8.35 may be compared to the corresponding values of 5.02 and 9.81 obtained for 8-quinolinol by Näsänen, et al.[11] The lower basicity of the sulfonate derivative may be considered as the result of electronic interaction of the sulfonate group with the aromatic ring. Although the group is itself negative, the nature of the interaction is such that negative charge is withdrawn from the ring.

Interaction of Metal Ions with 8-Quinolinol-5-sulfonate.—Titration curves are illustrated in Figs. 1–4 for the 8-quinolinol-5-sulfonate chelates of Mn(II), Fe(III), Co(II), Ni(II) Cu(II), Zn(II), Mg(II), UO$_2$(VI) and Th(IV) for 1:1, 2:1, and in some cases 3:1 and 4:1 ratios of ligand to metal ion. The concentration of metal chelate was varied from 2–5 millimoles per liter.

Copper(II).—Titration of equimolar amounts of ligand and cupric ion (Fig. 1) resulted in a steep inflection at m = 1 corresponding to the initial formation of CuA. A precipitate was observed at a pH value of approximately 6. A buffer region was found in the region m = 1–2, probably corresponding to the disproportionation of the 1:1 chelate

$$2CuA + 2OH^- \rightleftharpoons CuA_2^{2-} + Cu(OH)_2$$
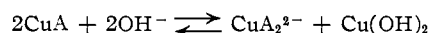
Preparation of a solution containing a 2:1 molar ratio of ligand to cupric ion results in immediate precipitation at a $-\log[H^+]$ value of 2.3. This probably corresponds to the formation of a chelate of the type
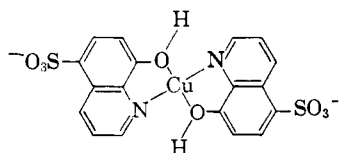
Addition of base to this neutral chelate species would result in neutralization of the phenolic hydrogens and should produce a soluble, negatively-charged chelate. Indeed complete solubility is reached at an m value of approximately 1.5. A

(10) G. A. Carlson, J. P. McReynolds and F. H. Verhoek, THIS JOURNAL, **67**, 1335 (1945).

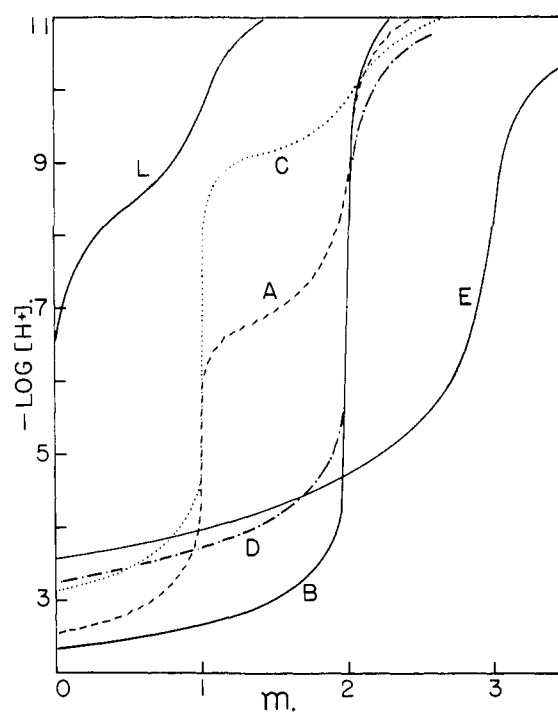(11) R. Näsänen, P. Lumme and A. Mukula, *Acta Chem. Scand.*, **5**, 1199 (1951).

Fig. 1.—Potentiometric titration of Cu(II) and Ni(II) chelates of 5-sulfo-8-quinolinol in 0.1 M KNO$_3$ at 25°, with these molar ratios of ligand to metal ion: A, Cu (1:1); B, Cu (2:1); C, Ni (1:1); D, Ni (2:1); E, Ni (3:1); L, ligand alone; m = moles of base added per mole of metal ion.
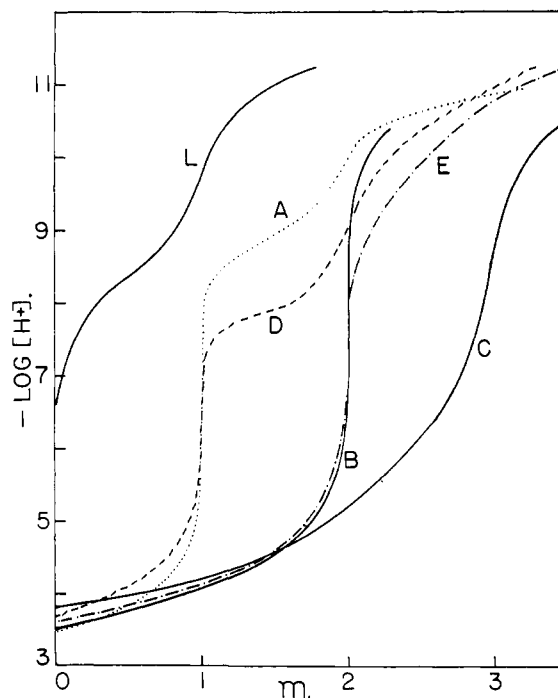

Fig. 2.—Potentiometric titration of Co(II) and Zn(II) chelates of 5-sulfo-8-quinolinol in 0.1 M KNO$_3$ at 25°, with these molar ratios of ligand to metal ion: A, Co (1:1); B, Co (2:1); C, Co (3:1); D, Zn (1:1); E, Zn (2:1); L, ligand alone; m = moles of base added per mole of metal ion.

steep inflection is observed at m = 2, corresponding to the formation of the completely coördinated
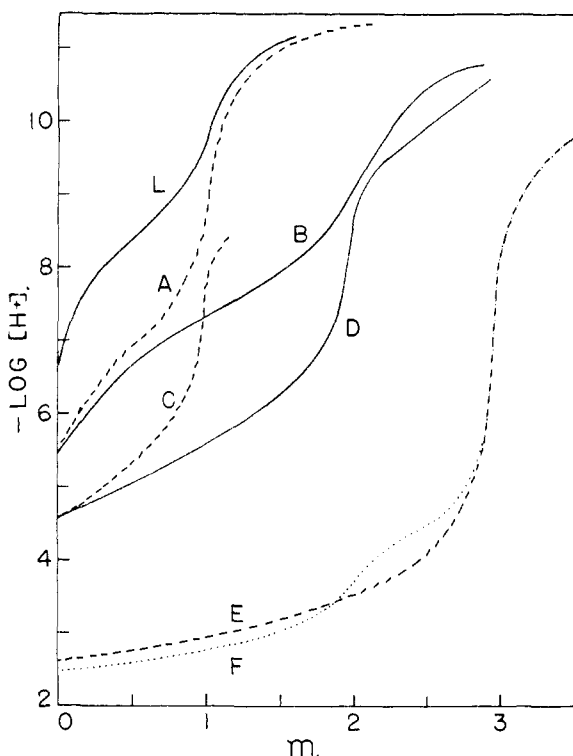
Fig. 3.—Potentiometric titration of Mg(II), Mn(II) and Fe(III) chelates of 5-sulfo-8-quinolinol in 0.1 M KNO$_3$ at 25°, with these molar ratios of ligand to metal ion; A, Mg (1:1); B, Mg (2:1); C, Mn (1:1); D, Mn (2:1); E, Fe (1:1); F, Fe (2:1); L, ligand alone; m = moles of base added per mole of metal ion.

copper chelate CuA$_2{}^{2-}$. No precipitation of Cu-(OH)$_2$ was observed, even at pH values greater than 11.

Nickel(II).—A steep inflection at m = 1 was observed for the 1:1 titration (Fig. 1) corresponding to the formation of NiA. Precipitation of what seemed to be Ni(OH)$_2$ was observed at a pH value above 9. A steep inflection indicating the formation of NiA$_2{}^{2-}$ also was observed for the 2:1 titration, but in this case no precipitation occurred. The coördination of a third mole of ligand was indicated by a sloping inflection at m = 3 for the case in which a ligand to metal ratio of 3/1 was employed. Again, in the case of Ni(II) no indication of the formation of hydroxo chelates was apparent, and the 1:1 mixture disproportionated to the 2:1 chelate and the metal hydroxide.

Cobalt(II).—Titration of solutions containing 1:1, 2:1 and 3:1 ratios of ligand to metal ion, (Fig. 2) results in pronounced inflections at m = 1, 2 and 3, corresponding to the formation of chelates having the compositions CoA, CoA$_2{}^{2-}$ and CoA$_3{}^{4-}$, respectively. In the first (1:1) case, a very steep inflection is observed but precipitation of what appears to be cobaltous hydroxide begins at a pH value of approximately 9. A steep inflection is also observed in the case of the 2:1 titration with precipitation appearing above pH 10. The lack of a steep inflection at m = 3 in the 3:1 titration indicates only slight affinity of the metal ion for the donor groups of the third ligand molecule, and precipitation of Co(OH)$_2$ is again
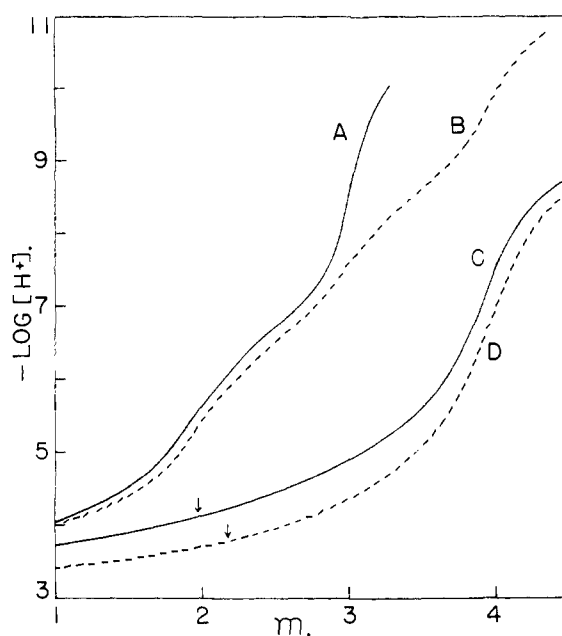
observed at a $-\log[\mathrm{H}^+]$ value of greater than 10. No indications of hydroxo chelate formation are apparent in any of the titrations involving cobalt-(II) ion. The high pH buffer region in the 1:1 curve seems to be due to disproportionation to the 2:1 chelate and cobalt hydroxide.

Zinc(II).—Preparation of a solution containing equimolar amounts of 8-quinolinol-5-sulfonate and zinc ion resulted in an immediate precipitate at a pH of 3.6. Titration of this mixture (Fig. 2) resulted in increased precipitation and a steep inflection at m = 1. The observed precipitate was probably the neutral chelate species ZnA, since zinc hydroxide would not be expected to precipitate below pH 8. (Solubility product of Zn(OH)$_2$ = 1.8 × 10^{-14} at 20°.)

Titration of a 2:1 molar ratio of ligand to metal ion resulted in a steep inflection at m = 2 corresponding to the formation of a chelate of type ZnA$_2{}^{2-}$. A faint turbidity appeared at about pH 7, and further titration produced a buffer region beyond m = 2, accompanied by increased precipitation of Zn(OH)$_2$.

Magnesium(II).—Titration of a 1:1 molar ratio of 8-quinolinol-5-sulfonate to magnesium ion (Fig. 3) resulted in a sloping buffer region and a steep inflection at m = 1, indicating the formation of a chelate of the type MgA. No precipitation of Mg(OH)$_2$ was observed until a pH of 11.5 was reached. Titration of a solution with a 10:1 molar ratio of metal ion to ligand resulted in a greater depression of the first buffer region (m = 0–1), corresponding to more complete formation of the 1:1 chelate. Again a steep inflection was observed at m = 1 and precipitation of Mg(OH)$_2$ was observed at a $-\log(\mathrm{H}^+)$ value of 9.7.

Fig. 4.—Potentiometric titration of UO$_2$(VI) and Th(IV) chelates of 5-sulfo-8-quinolinol in 0.1 M KNO$_3$ at 25°, with these molar ratios of ligand to metal ion: A, UO$_2$ (2:1); B, UO$_2$ (3:1); C, Th (4:1); D, Th (3:1); m = moles of base added per mole of metal ion. Arrows indicate point at which disappearance of a solid phase occurred.

Titration of a solution containing two moles of ligand per mole of magnesium ion resulted in a sloping buffer region followed by an inflection at $m = 2$, corresponding to the formation of a chelate of the type MgA_2^{2-}. No precipitation was observed during the titration.

Manganese(II).—Addition of base to a solution containing equimolar amounts of ligand and Mn(II) ion (Fig. 3, curve C) results in a pronounced inflection at $m = 1$ (where $m =$ moles of base added per gram-ion of metal), corresponding to the reaction
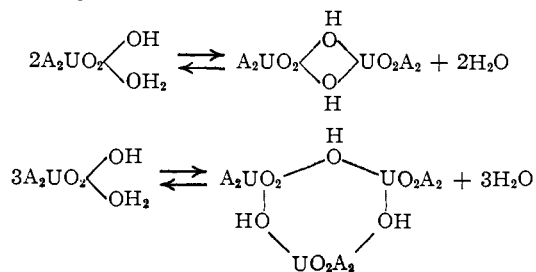
$$Mn^{2+} + HA^{1-} \rightleftharpoons MnA + H^+$$
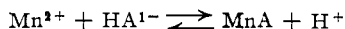
Precipitation which occurs at a $-\log[H^+]$ value of approximately 7.5 probably is due to the insolubility of the hydroxide. The addition of a second mole of ligand results in an inflection at $m = 2$, curve D, corresponding to the reaction

$$Mn^{2+} + 2HA^{1-} \rightleftharpoons MnA_2^{2-} + 2H^+$$
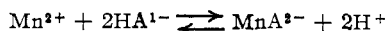
Precipitation of manganese(II) hydroxide was observed at pH 10.

Uranyl(VI).—Titration of a 1:1 ratio of ligand to uranyl ion (Fig. 4) resulted in precipitation at about pH 5.5. The 2:1 curve exhibits a weak inflection at $m = 2$ probably corresponding to the formation of a 2:1 chelate, and a steeper inflection at $m = 3$ indicating the presence of a monohydroxo species and possibly polynuclear chelates formed by condensation of the monohydroxo compound, according to the reactions

$$2A_2UO_2{\bigg\langle}{\overset{OH}{\underset{OH_2}{}}} \rightleftharpoons A_2UO_2{\bigg\langle}{\overset{\overset{H}{O}}{\underset{\underset{H}{O}}{}}}{\bigg\rangle}UO_2A_2 + 2H_2O$$

$$3A_2UO_2{\bigg\langle}{\overset{OH}{\underset{OH_2}{}}} \rightleftharpoons A_2UO_2{\overset{\overset{H}{O}}{\underset{HO}{}}}\cdots UO_2A_2 + 3H_2O$$

The 3:1 curve may be obtained by the addition of the abscissas of the 2:1 and free ligand curves, thus indicating little or no formation of a chelate containing 3 moles of ligand per mole of uranyl ion. Continuous variations measurements (Fig. 5) were carried out at a pH of 5.6, which is the mid-point of the inflection of the titration curves, where $T_A/T_M = 2$. In each case the total concentration of metal ion plus ligand was $3 \times 10^{-4}\ M$. The pH was adjusted by use of 0.10 M pyridine buffer. Because of the danger of oxidation of the ligand, the absorption measurements were made within ten minutes of the preparation of the sample. At wave lengths higher than 340 mμ, a definite peak was observed at $T_A/(T_A + T_M)$ values of 0.67 corresponding to the formation of a chelate compound containing two moles of ligand per gram-ion of metal.

Similar measurements at pH 8.6 were inconclusive since at this point the extinction coefficient of the ligand was nearly equal to those of the chelates. However, the potentiometric data indicate that no further interaction of ligand with a 2:1 chelate occurs, since in the range of $m = 2$-3, both 2:1 and 3:1 titration curves contain similar buffer regions.
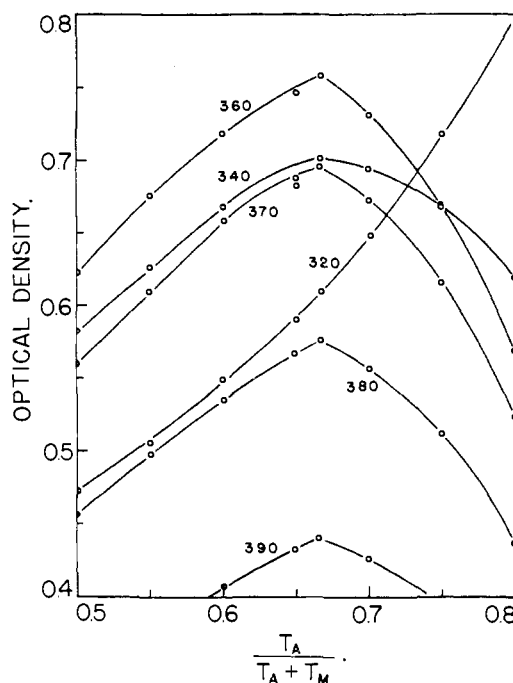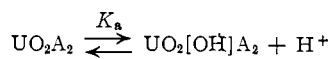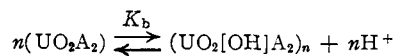

Fig. 5.—Continuous variations measurements of the uranyl-8-hydroxyquinoline-5-sulfonate system at $-\log$ [H$^+$] 5.62. $T_M + T_A = 3.01 \times 10^{-4}\ M$; solutions prepared in medium 0.05 M in KNO$_3$ and 0.010 M in pyridine giving final value of ionic strength approximately equal to 0.10 M. Numbers refer to wave lengths measured in mμ.
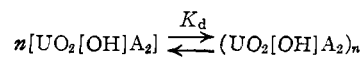
In order to investigate the presence of polynuclear chelates above $m = 2$, a series of 2:1 titrations were carried out over approximately a twelvefold range of concentration. The curves shown in Fig. 6 have a slight spread of pH in the region $m = 2$-3 indicating a small degree of polymerization of 2:1 hydroxo chelate species. The data of Fig. 6 were treated mathematically by the method outlined by Courtney, $et\ al.,$[12] and by Bogucki and Martell,[13] in order to obtain equilibrium constants for the reactions

$$UO_2A_2 \overset{K_a}{\rightleftharpoons} UO_2[OH]A_2 + H^+$$

and

$$n(UO_2A_2) \overset{K_b}{\rightleftharpoons} (UO_2[OH]A_2)_n + nH^+$$

or

$$n[UO_2[OH]A_2] \overset{K_d}{\rightleftharpoons} (UO_2[OH]A_2)_n$$

where A represents the ligand, and [OH] represents a coördinated hydroxyl ion. Ionic charges are omitted for clarity. If a binuclear chelate is formed as indicated above, a plot of $[H^+]^{(n-1)}$ $(T_{OH} + [H^+] - [OH^-])/[UO_2A_2]$ as ordinate $vs.$ $[UO_2-A_2]/[H^+]^{(n-1)}$ as abscissa should give a straight line of slope nK_b and intercept K_a according to equation 20

$$[H^+]^{(n-1)}\,(T_{OH} + [H^+] - [OH^-])/[UO_2A_2] =$$
$$K_a + nK_b([UO_2A_2]/[H^+])^{(n-1)} \quad (20)$$

(12) R. C. Courtney, R. L. Gustafson, S. Chaberek, Jr., and A. E. Martell, THIS JOURNAL, **81**, 519 (1959).

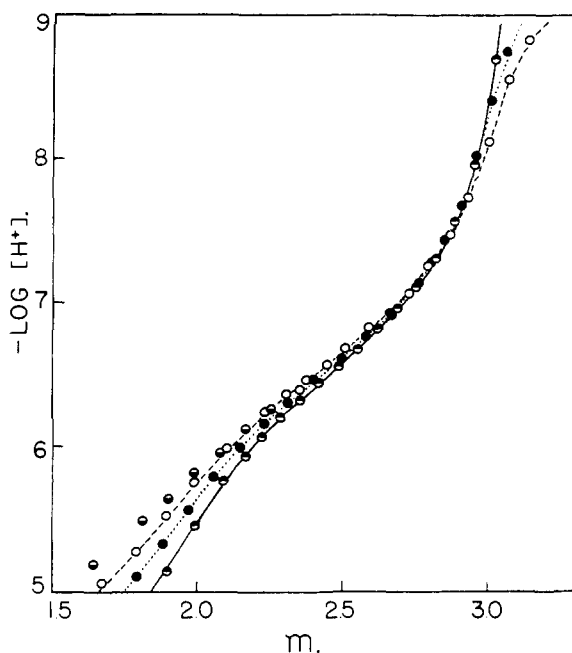(13) R. Bogucki and A. E. Martell, $ibid.$, **80**, 4170 (1958).

Fig. 6.—Potentiometric titrations of solutions containing 2:1 ratios of 8-hydroxyquinoline-5-sulfonate to uranyl ion. Concentrations: ⊖, 5×10^{-3} M; ●, 2×10^{-3} M; O, 1×10^{-3} M; ⊖, 4×10^{-4} M; $t = 25.0°$; $\mu = 0.10$ (KNO₃); m = number of moles of KOH added per mole of metal ion.

where T_{OH} is the total concentration of added base. Here [UO₂A₂] is the stoichiometric concentration of the 2:1 chelate which was assumed to be equal to T_M at $m = 2.00$. Straight lines were not obtained for calculations based on any arbitrary integral value for n. However, since investigations of cupric[12,14] and thorium[13] chelates, in which all but two coördination sites have been occupied by organic ligands, have shown that dimeric species exist, it seems that the 2:1 8-hydroxyquinoline-5-sulfonate–uranyl chelate also forms a dimer. Seven points each from titration curves at $T_M = 5 \times 10^{-3}$, 2×10^{-3} and 1×10^{-3} were taken in the range $m = 2.3$–2.7 and were used to calculate the data illustrated in Fig. 7. A least squares analysis of the data indicated a value of $K_a = 10^{-6.63}$ and $K_b = 10^{-11.7}$. Thus the value of the dimerization constant, K_d, is $10^{1.7}$. This result is much lower than values of $10^{4.3}$ obtained for EDTA and CDTA (cyclohexanediaminetetraacetate) chelates of unsubstituted diamines.[13]

The scatter of experimental points in Fig. 7 represents an average deviation corresponding to only 0.02 pH unit, a quantity which is within experimental error. Since only a small amount of dimer is present (Fig. 9), resulting in only a slight spreading of the curves of Fig. 6 in the region $m = 2$–3, the calculated data are extremely sensitive to slight errors in pH.

Iron(III).—Interaction of equimolar amounts of ligand and ferric ion (Fig. 3) results in a large pH depression and a single steep inflection at $m = 3$, which corresponds to the formation of di-
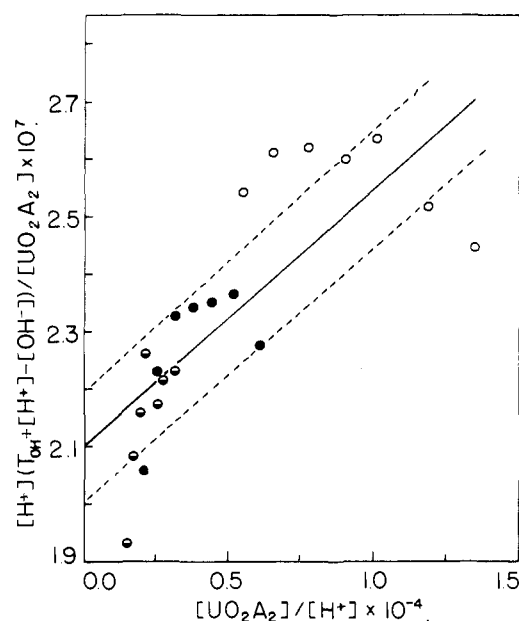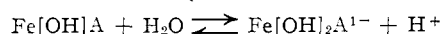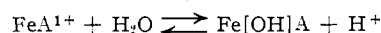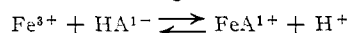
(14) R. L. Gustafson and A. E. Martell, THIS JOURNAL, **81**, 525 (1959).

Fig. 7.—Plot of data of Fig. 6 for a binuclear chelate [UO₂A₂[OH]₂UO₂A₂], in the region $m = 2$–3. Points are calculated from data at the concentrations: O, 5×10^{-3} M; ●, 2×10^{-3} M; ⊖, 1×10^{-3} M. Dotted lines indicate deviation from average plot produced by a change of ± 0.02 pH unit.

hydroxo chelate according to the reactions

$$Fe^{3+} + HA^{1-} \rightleftharpoons FeA^{1+} + H^+$$

$$FeA^{1+} + H_2O \rightleftharpoons Fe[OH]A + H^+$$

$$Fe[OH]A + H_2O \rightleftharpoons Fe[OH]_2A^{1-} + H^+$$

The increasing slope of the titration curve in the region $m = 1$–3 indicates that the formation of the dihydroxo chelate does not take place in one step but that it is formed by the series of overlapping reactions indicated above. At the start of the titration the solution was deep green but changed to dark brownish red in the region $m = 2$–3. This reddish color seems to be typical of many iron-phenolate compounds. A buffer region at m values greater than 3 suggests the possibility of further hydroxo chelate formation at higher pH. No precipitate was observed at any time during the titration.

Titration of a solution containing a 2:1 molar ratio of ligand to metal ion results in a slight inflection at $m = 2$ and a steep inflection at $m = 3$ corresponding to the formation of chelates having the formulas FeA₂¹⁻ and Fe[OH]A₂²⁻, respectively. Here also a color change from dark green to deep red was observed in the region $m = 2$–3. A buffer region in the pH range 8–10 probably corresponds to the coördination of an additional hydroxo group to form a chelate having the composition Fe[OH]₂A₂³⁻.

In order to investigate more completely the second buffer region of the 2:1 Fe(III)-8-quinolinol-5-sulfonate chelate, potentiometric titrations were carried out over a tenfold range of metal ion concentration. Mathematical treatment of the data yielded the plot shown in Fig. 8, which is similar to that of Fig. 7 except that much
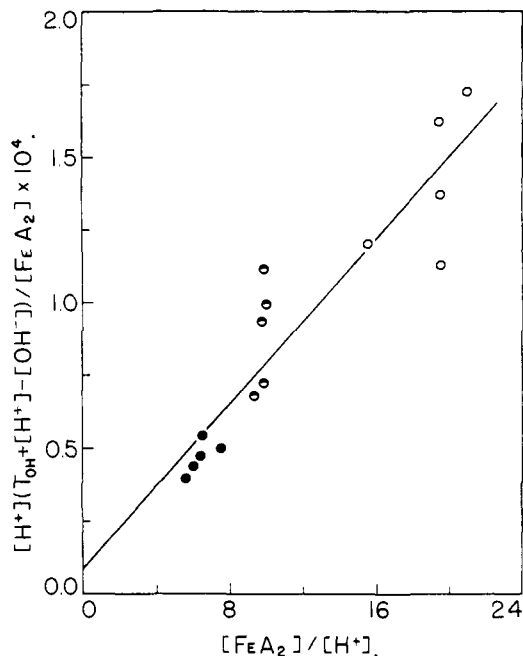
Fig. 8.—Graphical demonstration of binuclear diolate 2:1, 8-hydroxyquinoline–5-sulfonate–Fe(III) chelate. Points are calculated from data at the concentrations: O, 5 × 10⁻³ M; ●, 2 × 10⁻³ M; ◓, 1 × 10⁻³ M.
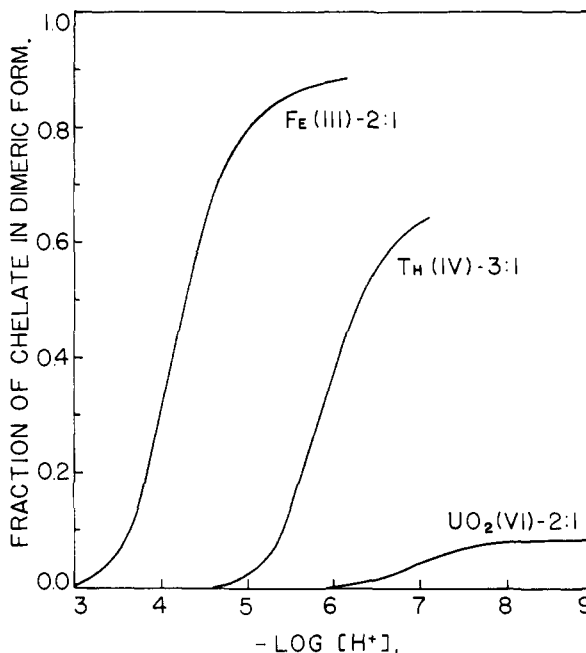

Fig. 9.—Plot showing fraction of metal chelate present in binuclear form as a function of $-\log[H^+]$ for 8-hydroxyquinoline-5-sulfonate chelates containing ligand to metal ratios as shown: $T_M = 1 \times 10^{-3}\ M$; $t = 25.0°$.

better conformity with a straight line was obtained. The high value ($10^{4.58}$) calculated for the dimerization constant, K_d, indicates a very strong tendency for polymerization of the monohydroxo chelate, $Fe[OH]A_2$.

Thorium(IV).—In Fig. 4 are shown titration curves for solutions containing 3:1 and 4:1 ratios of ligand to metal ion. In a solution containing a 1:1 ratio of ligand to metal ion, precipitation of what appeared to be thorium hydroxo chelate complexes occurred at pH 3.5. Precipitation was observed almost immediately in solutions containing 3:1 and 4:1 ratios of ligand to Th(IV), although clear solutions were obtained in both cases by adding sufficient quantities of acid or base. Presumably the precipitate observed in the latter cases is that of the neutral chelate, ThA_2.

The 4:1 curve of Fig. 4 indicates normal stepwise combination of four moles of ligand with the Th(IV) ion. The second and third formation constants were determined by graphical extrapolation of the formation function since $\bar{n}$ values in the range 1.4–2.7 correspond to regions where a solid phase was present. The 3:1 curve exhibits a steep inflection at $m = 4$ indicating formation of the monohydroxo chelate species, $Th[OH]A_3{}^{3-}$.

Solutions containing 3:1 ratios of ligand to thorium ion plus varying concentrations of KOH in the range $m = 3.3$–3.7 were equilibrated for 36 hr. in a thermostated bath, after which time the hydrogen ion concentrations were measured. The data were treated mathematically in a manner analogous to that employed in studying the polymerization of the 2:1 uranyl–8-quinolinol-5-sulfonate chelate. As in the case of the uranyl chelate, a considerable spread of the data was obtained. However, analysis indicated values of $K_a = 10^{-6.2}$, $K_b = 10^{-8.9}$

and $K_d = 10^{3.5}$. Comparison of the latter value with $10^{1.7}$ obtained for K_d of the 2:1 uranyl chelate, indicates a considerably greater tendency of the thorium chelate toward polymerization.

Equilibrium Constants.—The acid dissociation constants and chelate stability constants for 8-quinolinol-5-sulfonate as well as those of the parent unsulfonated compound are listed in Tables I and II. Acid dissociation constants and the initial formation constants of the chelates of Cu(II),

TABLE I

EQUILIBRIUM CONSTANTS FOR THE INTERACTION OF 8-QUINOLINOL-5-SULFONATE WITH VARIOUS METAL IONS

$t = 25.0°$; $\mu = 0.10$; $pK_1 = 3.84$; $pK_2 = 8.35$

M^{n+}	log K_{MA}	log K_{MA_2}	log K_{MA_3}	log K_{MA_4}
Mn^{2+}	5.67	5.05	..	..
Fe^{3+}	11.6	11.2	..	..
Co^{2+}	8.11	6.95	5.36	..
Ni^{2+}	9.02	7.75	6.16	..
Cu^{2+}	11.92	9.95	..	..
Zn^{2+}	7.54	6.78	..	..
Mg^{2+}	4.06	3.57	..	..
Th^{4+}	9.56	8.73	7.62	6.12
$UO_2{}^{2+}$	8.52	7.16	..	..

Equilibrium quotient	log K
$[FeA]/[Fe[OH]A][H^+]$	3.06
$[Fe[OH]A]/[Fe[OH]_2A][H^+]$	3.94
$[FeA_2]/[Fe[OH]A_2][H^+]$	5.02
$[FeA_2]^2/[(Fe[OH]A_2)_2][H^+]^2$	5.45
$[(Fe[OH]A_2)_2]/[Fe[OH]A_2]^2$	4.6
$[UO_2A_2]/[UO_2[OH]A_2][H^+]$	6.68
$[UO_2A_2]^2/[(UO_2[OH]A_2)_2][H^+]$	11.7
$[(UO_2[OH]A_2)_2]/[UO_2[OH]A_2]^2$	1.7
$[ThA_3]/[Th[OH]A_3][H^+]$	6.2
$[ThA_3]^2/[(Th[OH]A_3)_2][H^+]^2$	8.9
$[(Th[OH]A_3)_2]/[Th[OH]A_3]^2$	3.5

TABLE II

COMPARISON OF EQUILIBRIUM CONSTANTS OF 8-QUINO-
LINOL[15] AND 8-QUINOLINOL-5-SULFONATE

	8-Quinolinol		8-Quinolinol-5-sulfonate		Δ log	Δ log
M_n^+	log K_{MA}	log K_{MA_2}	log K_{MA}	log K_{MA_2}	K_{MA}	K_{MA_2}
Co^{2+}	10.91	9.9	8.11	6.95	2.8	3.0
Ni^{2+}	11.65	10.4	9.02	7.75	2.6	2.6
Cu^{2+}	15.0	14.0	11.92	9.95	3.1	4.1
Zn^{2+}	10.91	9.9	7.54	6.78	3.4	3.1

Acid dissociation constants[11]: $pK_1 = 5.02$; $pK_2 = 9.81$

Ni(II) and Co(II) were calculated by the algebraic method described above. All of the other formation constants were determined by the method of Bjerrum.[9]

In Table II the relative stabilities of the Co(II), Ni(II), Cu(II) and Zn(II) chelates of 8-quinolinol-5-sulfonate are compared with the corresponding stabilities of 8-quinolinol chelates reported by Irving (Table II).[15] The lower basicity of the sulfonated ligand is reflected in a correspondingly lower stability of the metal chelates of 8-hydroxy-quinoline (average Δ log K_1 = 3.0 and average Δ log K_2 = 3.2).

It is of interest to compare the dimerization tendencies of the 3:1 thorium, 2:1 uranyl and 2:1 ferric chelates as listed in Table I. The more posi-

(15) H. Irving, Paper No. 4, "A Discussion on Coördination Chemistry," Butterwick Research Laboratory, I. C. I., Sept. 21–22, 1950.

tive charge (−1) of the ferric chelate relative to that of the chelate of uranyl or thorium (−2) plus the smaller radius of the ferric ion combine to produce an iron(III) chelate which is less resistant to hydrolysis ($pK_a[FeA_2^{1-}] = 5.02$; $pK_a[ThA_3^{2-}] = 6.2$; $pK_a[UO_2A_2^{2-}] = 6.68$). Because of the greater affinity of the ferric hydroxo chelate for additional donor groups, polymerization takes place more readily than in the cases of the chelates of uranyl or thorium ions. In addition the coulombic barrier is less for the polymerization of two binegatively charged ferric hydroxo complexes than for that of the trinegatively charged hydroxo chelate species of uranyl or thorium. In Fig. 9 are plotted the fractions of chelate present in the binuclear form as a function of $-\log[H^+]$ for a solution which is 1×10^{-3} molar in metal chelate. It may be seen that the uranyl chelate polymerizes only to a maximum extent of about 8%, whereas nearly 70 and 90% of the thorium and ferric chelates, respectively, are ultimately present in the binuclear form.

It should be pointed out that the hydrolysis reactions observed for the 8-quinolinol-5-sulfonate chelates have no counterpart in the reactions of the unsulfonated compound, since the metal chelates formed from the latter are insoluble and do not react further with water.

WORCESTER, MASS.

The Nature of the Chromium(VI)–1,5-Diphenylcarbohydrazide Reaction. I. Extraction Studies[1]

BY IVAN E. LICHTENSTEIN AND THOMAS L. ALLEN

The magenta-colored product of the chromium(VI)–1,5-diphenylcarbohydrazide reaction was extracted into isoamyl alcohol. Analysis of the isoamyl alcohol extract revealed that chromium was present. The amount of color left in the aqueous extract agreed closely with the amount of chromium found in that extract. The results of this and other pertinent extraction experiments show that the colored product of the chromium(VI)–1,5-diphenylcarbohydrazide reaction contains chromium.

The reaction of 1,5-diphenylcarbohydrazide (diphenylcarbazide) with an acidified chromate solution yields an intense magenta color. This reaction has been known and used for many years, although the nature of the colored substance is not clear. There is even a difference of opinion in the literature as to whether it contains chromium. Cazeneuve[2] first proposed that the colored substance is an organometallic derivative of chromium. Babko and Paliĭ[3] then found that it contains no chromium and is rather an oxidation product of 1,5-diphenylcarbohydrazide. The most recent investigators have sided with Cazeneuve's proposal. Bose[4] concluded that the colored substance is a complex of chromium(II) and diphenylcarbazone, while Das Sarma and Ray[5] and Pflaum

and Howick[6] postulate that the colored species is a complex of chromium(III) and diphenylcarbazone.

When the experimental evidence adduced by the various investigators is examined, the most direct proof is found to be that of Babko and Paliĭ. They extracted the magenta-colored substance with isoamyl alcohol. On oxidation of the organic extract with sodium peroxide and subsequent determination of chromate ion, no chromium was found. All of the chromium was found to be retained in the colorless aqueous layer. It was therefore concluded by these workers that no organometallic complex is formed in the reaction and that the colored substance is an oxidation product of 1,5-diphenylcarbohydrazide.

Evidence supporting the majority opinion may be summarized as follows.

(a) Pflaum and Howick found that it was possible to detect chromium in an isoamyl alcohol extract of the colored substance; chromium was not

(1) This work was assisted by a research grant from the National Science Foundation.

(2) P. Cazeneuve, Bull. soc. chim. France, 25, 758 (1901).

(3) A. K. Babko and L. A. Paliĭ, Zhur. Anal. Khim., 5, 272 (1950).

(4) M. Bose, Anal. Chim. Acta, 10, 201, 209 (1954).

(5) B. Das Sarma and J. N. Ray, Sci. and Culture (India), 21, 477 (1956).

(6) R. T. Pflaum and L. C. Howick, THIS JOURNAL, 78, 4862 (1956).