splitting is the largest for DMP, 4600 cm.$^{-1}$, intermediate for mercaptoacetate, 4000 cm.$^{-1}$, and the smallest for cysteine, 3000 cm.$^{-1}$. The stabilities of both the mercaptoacetate and DMP complexes[15,35,37,38] are found to be lower with nickel(II) than with zinc(II), but the stability of the nickel(II)–cysteine complex is 1.1 log Q_2 units greater than that of the zinc complex.[39] This last difference is still less than expected, although the order conforms to the usual Irving–Williams sequence. Thus, both the spectral and stability data are consistent with what is expected from the operation of dπ–pπ antibonding effects and not with what is expected from either σ or dπ–dπ effects.

In further support of these views, in the polynuclear nickel(II)–mercaptides, where dπ–dπ bonding results in the donation of metal ion electrons to *empty* sulfur d orbitals,[15,40] the normal order of stabilities results.

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Stabilities of Chelates of Certain Substituted 8-Quinolinols

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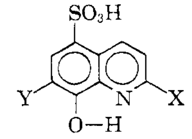
The acid dissociation constants of 8-quinolinol-5-sulfonic acid, 2-methyl-8-quinolinol-5-sulfonic acid, 2-methyl-7-bromo-8-quinolinol-5-sulfonic acid, 2-methyl-7-nitro-8-quinolinol-5-sulfonic acid, and 7-nitro-8-quinolinol-5-sulfonic acid have been determined. The stability constants of the corresponding chelates with copper(II), nickel(II), cobalt(II), and zinc(II) were determined potentiometrically at 25° by the Bjerrum method. The complexes of the methyl-substituted ligands are less stable then the corresponding complexes of the unsubstituted ligands. The stability decrease arises from steric repulsions of the 2-methyl groups.

Studies of the thermodynamics of formation of divalent metal chelates of substituted 8-quinolinols have indicated how variations in the structure of 8-quinolinol influence the stability of the corresponding chelates. For example, comparisons of the free energies and enthalpies of formation of the chelates of 8-quinolinol, 2-methyl-8-quinolinol, and 4-methyl-8-quinolinol have provided evidence for reduced chelate stability from a sterically hindering substituent.[1,2] It is of interest to note that the differences in the stabilities of corresponding metal complexes of 8-quinolinol[3–5] and 8-quinolinol-5-sulfonic acid[3,6] are not great, whereas the corresponding pK values differ by one log unit. This may reflect, first, enhanced resonance stabilization of the chelate by conjugation with the sulfonate group and, second, a greater degree of charge neutralization between the metal ion and the doubly-charged anion of 8-quinolinol-5-sulfonic acid in the first formation step, at least. In the present investigation, the formation constants of the metal chelates of these polysubstituted 8-quinolinols are compared: 2-methyl-8-quinolinol-5-sulfonic acid, 2-methyl-7-bromo-8-quinolinol-5-sulfonic acid, 2-methyl-7-nitro-8-quinolinol-5-sulfonic acid, 7-nitro-8-quinolinol-5-sulfonic acid, and 8-quinolinol-5-sulfonic acid.



X = H or CH_3
Y = H, NO_2, or Br

Substituted 8-quinolinol-5-sulfonic acids

Experimental

Preparation of Compounds.—8-Quinolinol-5-sulfonic acid was prepared by the sulfonation of 8-quinolinol according to the procedure of Matsumura.[7] After three recrystallizations from boiling water, the compound was dried at 105°. The equivalent weight determined by titration with standard sodium hydroxide was found to be 238 (theoretical for the monohydrate: 243). 2-Methyl-8-quinolinol-5-sulfonic acid was prepared by the sulfonation of 2-methyl-8-quinolinol according to the procedure of Matsumura recommended by Phillips.[8] After three recrystallizations from boiling water the compound was dried at 105°. The equivalent weight determined by titration with standard sodium hydroxide was found to be 257 (theoretical for the monohydrate: 257). 2-Methyl-7-nitro-8-quinolinol-5-sulfonic acid was prepared by dissolving 5 g. of 2-methyl-8-quinolinol in 50 ml. of 15% fuming sulfuric acid with gentle heating. After cooling

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in a rock salt–ice mixture, 7 ml. of cold concentrated nitric acid was added dropwise with constant stirring. The solution then was poured over an excess of shaved ice. The yellow crystals which formed were filtered and recrystallized from boiling water three times and dried at 105°. The equivalent weight determined by titration with standard sodium hydroxide was found to be 294 (theoretical for the monohydrate: 302). 7-Nitro-8-quinolinol-5-sulfonic acid was prepared from 8-quinolinol in the manner previously described for 2-methyl-7-nitro-8-quinolinol-5-sulfonic acid. After three recrystallizations from water the compound was dried at 105°. The equivalent weight determined by titration with standard sodium hydroxide was found to be 283 (theoretical for the monohydrate: 288). 2-Methyl-7-bromo-8-quinolinol-5-sulfonic acid was prepared by the dropwise addition of an ethanol solution of 0.350 g. of bromine to a stirred aqueous solution containing 0.50 g. of 2-methyl-8-quinolinol-5-sulfonic acid. After evaporation of the solution to a fraction of the original volume and cooling, crystallization occurred slowly. The product was filtered and recrystallized twice from hot water and then dried at 110°. The equivalent weight as determined by titration with standard sodium hydroxide was found to be 318 (theoretical for the monohydrate is 320).

Apparatus and Materials.—The titration apparatus and standardization of sodium hydroxide, perchloric acid, and metal perchlorate solutions have been described previously.[9]

Potentiometric measurements of pH values were made with a Beckman Model G pH meter equipped with an external glass-saturated calomel electrode pair and standardized at 25° by titration of standard 0.0050 M perchloric acid with standard sodium hydroxide. The analytical concentration of unneutralized perchloric acid and the hydrogen ion concentration were assumed to be the same.

Procedure.—The procedure was similar to that employed in previous determinations of chelate formation constants.[9] A 50-ml. volume of 0.01 M perchloric acid, 2 or 3 ml. of 0.01 M metal perchlorate solution, and sufficient water for a final volume of 110 ml. were delivered to a weighed quantity of reagent. In the case of the nitrated 8-quinolinol-5-sulfonic acids, dissolution was slow and stirring times up to 1 hr. were required to effect complete solution. After outgassing the solution with nitrogen, standard base (0.1 N) was added in small increments to the stirred solution while an atmosphere of nitrogen was maintained in the titration vessel. For the titration of reagent alone, water was substituted for the metal perchlorate solution.

Acid Dissociation Constants.—Values of K_2 and K_3, the dissociation constants of the protonated heterocyclic nitrogen and the hydroxyl group, respectively, were calculated from potentiometric titration data. The expressions employed were $K_2 = \mathrm{H}^+(T_\mathrm{R} - S)/S$ and $K_3 = -\mathrm{H}^+S/S + T_\mathrm{R}$, where T_R is the analytical concentration of the ligand and $S = T_\mathrm{R} + \mathrm{ClO_4}^- + \mathrm{OH}^- - \mathrm{H}^+ - \mathrm{Na}^+$. The reported values of the dissociation constants are an average of about ten values obtained over a range from 20 to 80% neutralization. Standard deviations expressed as $-\log K$ values did not exceed 0.02.

K_2 values for 7-nitro-8-quinolinol-5-sulfonic acid and 2-methyl-7-nitro-8-quinolinol-5-sulfonic acid were estimated from the dependence of absorbance on pH near 286, 295, and 379 mμ for the former compound and 288, 301, and 372 mμ for the latter. Solutions which were 5×10^{-5} M with respect to these quinolinolsulfonic acids were measured over a range of hydrochloric acid concentrations from 2 to 0.001 M at 28 ± 1°. These measurements were performed with a Cary Model 11 recording spectrophotometer and 1-cm. quartz cells.

Chelate Formation Constants.—For the quinolinolsulfonic acids, $\bar{n}$, the average number of anionic ligands bound to a divalent metal ion, may be expressed as

$$\bar{n} = \frac{1}{T_\mathrm{M}}\left[T - \frac{S(K_2 + \mathrm{H}^+)}{K_2 + 2\mathrm{H}^+} - \frac{SK_2K_3}{\mathrm{H}^+(K_2 + 2\mathrm{H}^+)}\right]$$

where T_M is the analytical concentration of metal ion, T is the analytical ligand concentration, and S is the sum, $2T + \mathrm{ClO_4}^- + \mathrm{OH}^- - 2T_\mathrm{M} - \mathrm{Na}^+ - \mathrm{H}^+$. From a graph of $\bar{n}$ *vs.* $-\log R$, where R, the reagent anion concentration, is given by $SK_2K_3/[\mathrm{H}^+(K_2 + 2\mathrm{H}^+)]$, values of $-\log R$ corresponding to $\bar{n} = 0.5$, 1.5, and 2.5 were reported as $\log k_1$, $\log k_2$, and $\log k_3$. In the case of zinc and 2-methyl-8-quinolinol-5-sulfonic acid, the formation constants were obtained from the slope and intercept of the linear plot of the function[10]

$$\frac{(2 - \bar{n})}{\bar{n}}R^2 = \frac{1}{k_1k_2} + \frac{1}{k_2}\,\frac{(\bar{n} - 1)R}{\bar{n}}$$

Metal-to-ligand ratios were 1:5 and 1:6. The constants are accurate to one-tenth in the log.

TABLE I

ACID DISSOCIATION CONSTANTS OF SUBSTITUTED 8-QUINOLINOL-5-SULFONIC ACIDS AT 25°

Compounds	pK_1	pK_2	pK_3
8-Quinolinol-5-sulfonic acid	<0[a]	4.09	8.66
2-Methyl-8-quinolinol-5-sulfonic acid	<0[a]	4.73	8.99
2-Methyl-7-bromo-8-quinolinol-5-sulfonic acid	<2.0	3.32	7.96
2-Methyl-7-nitro-8-quinolinol-5-sulfonic acid	...	0.7[a]	6.24
7-Nitro-8-quinolinol-5-sulfonic acid	...	0.4[a]	5.62

[a] Spectrophotometric value, 28 ± 1°.

TABLE II

CHELATE FORMATION CONSTANTS OF SUBSTITUTED 8-QUINOLINOL-5-SULFONIC ACIDS AT 25°

Metal ion	log k_1	log k_2	log k_3
	8-Quinolinol-5-sulfonic acid		
Ni(II)	9.57	8.58	7.42
Co(II)	8.54	7.22	5.39
	2-Methyl-8-quinolinol-5-sulfonic acid		
Cu(II)	9.86	8.70	<3.5
Ni(II)	7.69	6.45	4.48
Co(II)	7.54	6.52	<3.5
Zn(II)	7.50	7.14	<3.5
	2-Methyl-7-bromo-8-quinolinol-5-sulfonic acid		
Cu(II)	...	8.53	<3.5
Ni(II)	6.80	5.50	<3.5
Co(II)	6.56	5.48	<3.5
Zn(II)	6.61	5.68	<3.5
	2-Methyl-7-nitro-8-quinolinol-5-sulfonic acid		
Cu(II)	...	∽6.4	<3.5
Ni(II)	5.92	4.85	<3.5
Co(II)	5.50	4.34	<3.5
Zn(II)	5.31	4.32	<3.5
	7-Nitro-8-quinolinol-5-sulfonic acid		
Cu(II)	...	>6.4	<3.8
Ni(II)	...	∽6.2	4.74
Co(II)	...	5.41	<3.8
Zn(II)	5.90	4.90	<3.8

Results

The acid dissociation constants of the 8-quinolinol-5-sulfonic acids have been summarized in Table I. In Table II the chelate formation constants have been collected. Since concentrations rather than activities

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have been considered, the equilibrium constants are concentration quotients.

Discussion

Values for the first dissociation constant of 8-quinolinol-5-sulfonic acid, $pK_1 = 2.04^{11,12}$ and 1.3,[3] have been reported by several investigators but not by others.[4,13] In the present investigation, this pK was found to be less than 2.0, which is the approximate lower limit of reliability of the potentiometric method. Ultraviolet absorption spectra recorded for solutions of 8-quinolinol-5-sulfonic acid and 2-methyl-8-quinolinol-5-sulfonic acid were not affected by changes in hydrogen ion concentration within the range 1.0 to 0.001 M. This behavior is consistent with the strong acid properties previously reported for other sulfonic acids.[14,15] The second and third dissociation constants of 8-quinolinol-5-sulfonic acid[3,6] and 2-methyl-8-quinolinol-5-sulfonic acid[16] are in reasonable agreement with other values for these compounds obtained under somewhat altered conditions. Comparable acid dissociation constants are smaller for 2-methyl-8-quinolinol-5-sulfonic acid than for 8-quinolinol-5-sulfonic acid. The difference is in accord with the inductive and hyperconjugative effects of the methyl group. The reduction in base strength of the bromine derivative of 2-methyl-8-quinolinol-5-sulfonic acid is consistent with the electron-withdrawing ability of a bromine substituent.

Although the second and third dissociation constants of 7-nitro-8-quinolinol-5-sulfonic acid had been reported previously,[17] it was possible to determine only the third constant for 7-nitro-8-quinolinol-5-sulfonic acid and 2-methyl-7-nitro-8-quinolinol-5-sulfonic acid by the potentiometric method. In comparable solution conditions, the value of pK_3 would be 5.61 and is in close agreement with that obtained in the present study. The dissociation constant of the sulfonic acid group which corresponded to $pK_1 < 0$ for 8-quinolinol-5-sulfonic acid and 2-methyl-8-quinolinol-5-sulfonic acid probably is reduced even further by the powerful electron-withdrawing effect of the nitro substituent. On this basis, the spectrophotometrically derived pK values, 0.7 and 0.4, for 2-methyl-7-nitro-8-quinolinol-5-sulfonic acid and 7-nitro-8-quinolinol-5-sulfonic acid, respectively, have been assigned as pK_2 values. Comparisons of spectra of solutions of these compounds recorded at pH values of 1, 2, and 3 do not support the existence of a pK value slightly less than 2 as previously reported for 7-nitro-8-quinolinol-5-sulfonic acid, which illustrates the difficulty of obtaining reliable pK values in this pH range by the potentiometric method.

For the complexes of almost all ligands, the stability varies as Zn(II) < Cu(II) > Ni(II) > Co(II) > Fe(II) > Mn(II).[18,19] The order of chelate stability for 8-quinolinol and 8-quinolinol-5-sulfonic acid on the basis of k_1k_2 values decreases as Cu(II) > Ni(II) > Co(II) > Zn(II) > Mn(II) and is consistent with the usual order. The stability order observed for 2-methyl-8-quinolinol was Cu(II) > Zn(II) > Co(II) > Ni(II) > Mn(II).[1] The order of stabilities of Zn(II) and Ni(II) are interchanged as compared to the 8-quinolinols without substitution on the number two position. This decrease in nickel chelate stability in cases where steric hindrance to chelate formation is possible has been described previously.[1,20] The stability order of the chelates of 2-methyl-8-quinolinol-5-sulfonic acid as determined in the present study was Cu(II) > Zn(II) > Ni(II), Co(II). The order is the same as the 2-methyl-8-quinolinol order except for the similar stabilities of Ni(II) and Co(II). For the same metal ion, the chelates of 2-methyl-8-quinolinol-5-sulfonic acid are less stable than those of 8-quinolinol-5-sulfonic acid. The stability decrease is in accord with the steric hindrance imposed by the 2-methyl group.

In agreement with another investigation,[13] the addition of a third 8-quinolinol-5-sulfonic acid molecule to cobalt(II) and nickel(II) was indicated from an analysis of their titration data. Only in the case of nickel(II) was the addition of a third molecule of 2-methyl-8-quinolinol-5-sulfonic acid so demonstrable. Since gallium(III) possesses a smaller ionic radius than nickel(II) and forms a well characterized tris-2-methyl-8-quinolinol chelate,[21] the formation of the corresponding chelate of nickel(II) is not unprecedented.

The stabilities of the chelates of 2-methyl-7-bromo-8-quinolinol-5-sulfonic acid were two orders of magnitude less than the corresponding chelates of 2-methyl-8-quinolinol-5-sulfonic acid. This difference is of the same order as that reported for the chelates of α-bromotropolone and tropolone.[22] For Ni(II) and Zn(II), the chelate stabilities of α-bromotropolone were 1/50 and 1/20 times as stable, respectively, as the corresponding chelates with tropolone. Appreciable formation of the copper chelate prior to the start of the titration precluded the determination of the first formation constant of this complex. The order of chelate stabilities may be considered to be Cu(II) > Zn(II) > Ni(II) > Co(II). The comparatively low stabilities of these chelates did not allow their formation functions to be extended into the region where the addition of a third ligand might be observed.

The chelate stabilities of 7-nitro-8-quinolinol-5-sulfonic acid and 2-methyl-7-nitro-8-quinolinol-5-sulfonic acid were in the range of three to five orders of magnitude less than the corresponding stabilities with

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the compounds not containing the nitro group. The decreased stability arises from the electron-withdrawing influence of the nitro group. The extent of destabilization of the chelates of 2-methyl-7-nitro-8-quinolinol-5-sulfonic acid appears to differ markedly among the several metal ions studied. The order of destabilization as measured by the stability decrease on the introduction of the nitro group is Zn(II) > Co(II) > Ni(II), which is reflected in the stability order as Cu(II) > Ni(II) > Zn(II), Co(II). This stability order is in better agreement with the order observed for 8-quinolinol and 8-quinolinol-5-sulfonic acid than any other 2-methyl derivative thus far studied.

A similar comparison of the chelates of 7-nitro-8-quinolinol-5-sulfonic acid was not possible because the chelates were significantly formed prior to titration, in most cases. However, sufficient stability data were obtained to establish that steric hindrance was still a factor in the formation of the chelates of 2-methyl-7-nitro-8-quinolinol-5-sulfonic acid. The stability order obtained for 7-nitro-8-quinolinol-5-sulfonic acid is Cu(II) > Ni(II) > Co(II) > Zn(II). The formation constant of the zinc chelate was in satisfactory agreement with the previous study.[17] The formation of a 3:1 nickel chelate was indicated for the first time in the present study.

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Metal-Containing Compounds of the Anion $(C_2H_5)_2NN_2O_2^-$

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The following compounds of the anion $(C_2H_5)_2NN_2O_2^-$ have been prepared: $K(C_2H_5)_2NN_2O_2$, $Ca((C_2H_5)_2NN_2O_2)_2 \cdot 2H_2O$, and $Cu((C_2H_5)_2NN_2O_2)_2 \cdot CH_3OH$. Evidence is presented to indicate that the anion is a bidentate, chelate ligand in the copper compound. Complexes with Co^{+2}, Ni^{+2}, Mn^{+2}, Fe^{+3}, and Cr^{+3} form in solution. The infrared spectrum of the ethylated product $(C_2H_5)_2NN_2O_2C_2H_5$ is compared with those of the metal derivatives.

Introduction

Reactions of nitrogen(II) oxide with various primary and secondary amines are reported[2,3] to form compounds of the type $R_2NH_2{}^+R_2NN_2O_2^-$. It is suggested that the structure of $(C_2H_5)_2NN_2O_2^-$ is similar to that for the anion $SO_3N_2O_2^{-2}$, which is established by an X-ray study.[4] The two oxygens would then be *cis* to one another and $(C_2H_5)_2NN_2O_2^-$ should be capable of forming neutral chelate complexes with metal ions, similar to those formed by acetylacetonate. These considerations led us to study some metallic derivatives of the ligand $(C_2H_5)_2NN_2O_2^-$. Ionic sodium, potassium, and calcium compounds are formed.

Spectroscopic and conductometric studies demonstrate the existence of the neutral copper and cobalt complexes in solution. The neutral complexes appear to be solvent-stabilized, forming readily in solution but decomposing upon removal of solvent; however, a solvated copper complex can be isolated. Elemental analysis, infrared spectra, and molecular weight data are presented for the copper complex to indicate that the $(C_2H_5)_2NN_2O_2^-$ ion behaves as a bidentate ligand.

Experimental

Instrumentation.—Infrared spectra were obtained with a Perkin-Elmer Model 21 infrared spectrophotometer with sodium chloride optics. The instrument was frequency calibrated using the absorptions of ammonia, water vapor, and polystyrene, and the appropriate corrections were applied to the spectral data reported.

Nuclear magnetic resonance spectra were obtained at room temperature in carbon tetrachloride solution (with 1% tetramethyl silane) with a Varian Model A-60 spectrophotometer employing a 60 Mc. probe.

Conductivity data were obtained with an Industrial Instruments, Inc., conductivity bridge, Model RC 16 B2.

Molecular weights were determined in toluene with a Mechrolab, Inc., Model 301A vapor pressure osmometer.

Ultraviolet and visible spectra were obtained with a recording Bausch and Lomb Spectronic 505 spectrophotometer employing hydrogen and tungsten lamp sources.

Preparative Techniques.—Unless otherwise indicated, commercial, reagent grade materials were used.

Diethylammonium Salt.—This compound was prepared by the high pressure technique and purified as previously described.[3]

Sodium and Potassium Salts.—The synthesis of the sodium salt has been reported.[2] An analogous procedure (except for the use of KOC_2H_5) yields the potassium salt. Purification was effected by washing the crude material with cold ethanol, chloroform, and anhydrous diethyl ether. Both compounds were very hygroscopic, and were dried in a vacuum desiccator

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