sure effect on the ligands appears to give a spectrum similar to that of the complex. (4) Three types of behavior are noted for internal vibrations under pressure: (a) broadening and diminishing in intensity; (b) doubling of bands; (c) blue shifts of bands.

Further studies are under way with other ligand systems to determine to what extent the above conclusions are general. The necessity to study a ligand whose vibrations are properly assigned limits the choices that one can make for these studies.

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Metal Derivatives of Arylazopyrazolone Compounds. VIII. Molarity Quotients of the Sulfonic Acid Derivatives of Azo-3- and Azo-5-pyrazolones

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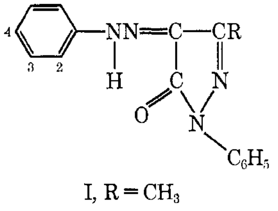
The formation constants of divalent metal ions with sulfonic acid derivatives of benzeneazo-3- and benzeneazo-5-pyrazolone have been measured in 75 vol % dioxane. With the sulfonic acid group in the chelate position (*ortho* to the azo linkage), the ligands are terdentate, and 1:1 complexes are formed. The decreasing order of stability for the divalent metal derivatives of 5-methyl-1-phenyl-4-(2-sulfophenylazo)-3-pyrazolone is Cu > UO_2 > Ni > Co > Zn > Cd > Mg > Ca > Sr > Ba. The *m*- and *p*-sulfo-substituted azo compounds behave like other bidentate azopyrazolone derivatives and form 2:1 compounds.

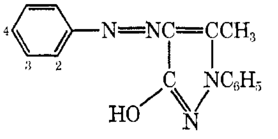
Introduction

Arylazo compounds which contain acidic or basic groups in one or more of the *ortho* positions are strong coordinating ligands.[2] In the dye industry such molecules generally contain one or more sulfonic acid groups which act as solubilizing centers. Drew[3] and coworkers have prepared metal derivatives with a few of the sulfonic acid compounds. Shetty[4] has stated that a sulfonic acid group in the chelate position *ortho* to a hydroxy group in *o,o'*-dihydroxyazo compounds causes dyes to be difficultly water soluble and difficult to chrome. He suggested that the sulfonic acid group is involved in the coordination although not directly attached to the metal ion. However, no work has been reported on azo compounds which contain sulfonic acid groups *ortho* to the azo linkage.

We have prepared and studied the chelating ability of a series of azo-3- and azo-5-pyrazolones which contain sulfonic acid groups in either the 2 or 4 position.



I, R = CH_3
II, R = $COOC_2H_5$



III

Experimental Section

Preparation of Azo Compounds.—The azo derivatives were prepared by coupling the appropriate diazotized amines to the pyrazolones in aqueous solution containing enough sodium hydroxide to dissolve the pyrazolones and sodium carbonate to serve as a buffer. The coupling bath was just neutralized with hydrochloric acid, and the crude product was isolated as the sodium salt of the sulfonic acid group. The III-3-SO_3H and the III-4-SO_3H were isolated as the free acids. The sodium salts and the free acids were recrystallized from 50% ethanol and dried in an oven at 110°. Purity was determined by measuring the neutral equivalents which gave values within 0.2% of those calculated.

Potentiometric Titrations.—The titrations were performed at 30.0 ± 0.1° in 75% dioxane as described previously.[5] The solutions were so adjusted that in 100 ml of solution there were 0.9568 mmol of azo compound, 0.9568 mmol of nitric acid, and 0.200 mmol of metal nitrate. The solution of the azo compound was thus equivalent to the free sulfonic acid. To those compounds which had been isolated as the free acid, no nitric acid was added, but 0.9568 mmol of sodium nitrate was added. A 1.0405 *N* solution of carbonate-free sodium hydroxide was used. The meter reading correction factor (log U_H)[6] was 0.47 for the calculation of the first acid dissociation constant and 0.41 for the calculation of the formation constants and the second dissociation constant. The acid dissociation constants of the chelating agents were obtained by titrating the azo compound in the absence of divalent metal ions.

Calculations.—The stability constants were calculated by curve fitting[7] by the method of least-squares using an IBM 1130 computer (eq 1). β_n is the product of the first n stability con-

$$-\beta_1 + \frac{(\bar{n} - 2)a}{1 - \bar{n}}\beta_2 + \frac{\bar{n}}{(1 - \bar{n})a} = 0 \qquad (1)$$

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stants, a is the concentration of the chelating agent anion, and $\bar{n}$ is the average number of chelating agent groups attached to each metal ion. The experimentally observed independent variables are $\bar{n}$ and a. We chose to omit points having $\bar{n}$ within 0.1 of 0, 0.15 of 1, or 0.11 of 2 and minimized the absolute deviations of eq 1. It was found that minimizing the relative deviations of eq 1 gives essentially the same results. The range of the third term in eq 1 is such that either method is valid.[8]

The standard deviation of the residuals of eq 1 was computed for each titration. This is a measure of the curve-fitting uncertainty in β_1 and β_2. We chose, however, to ascribe the standard deviation largely to uncertainty in β_1, because different titrations invariably yield the same value for β_2 with only β_1 varying appreciably. The value of β_2 from the computer output is almost always identical with the value taken from the formation curves where $\bar{n} = 1$. The errors listed below for β_1 values are equal to log $[(\beta_1 + v)/\beta_1]$, where v is the standard deviation of the residuals of eq 1. It is important to note that this error is a measure of the extent to which eq 1 is violated and is by no means intended to reflect the maximum possible experimental error.

Table I

Acid Dissociation Constants[a] of the Azo Compounds in 75 Vol % Dioxane at 30°

Azo compound	pK_{D_1}	pK_{D_2}
I-2-SO_3H	1.41	11.06
I-4-SO_3H	1.46	10.96
II-4-SO_3H	1.53	9.49
III-2-SO_3H	1.62	9.65
III-3-SO_3H	1.90	9.81
III-4-SO_3H	1.45	9.82

[a] For the method of calculation see ref 11b.

Table II

Formation Constants for the 2-SO_3H Derivatives in 75 Vol % Dioxane at 30°

	Log β_1	
	I-2-SO_3H	III-2-SO_3H
Cu	>11.00	9.92 ± 0.14
UO_2	Hydrolysis	9.71 ± 0.09
Ni	9.95 ± 0.06	9.40 ± 0.08
Co	9.08 ± 0.11	9.11 ± 0.06
Zn	8.42 ± 0.03	8.69 ± 0.08
Cd	6.79 ± 0.10	7.24 ± 0.05
Mg	5.10 ± 0.02	5.37 ± 0.02
Ca	4.38 ± 0.12	4.64 ± 0.07
Sr	Hydrolysis	4.07 ± 0.03
Ba	Hydrolysis	3.69 ± 0.07

Many of the titrations were performed several times and were found to be almost exactly reproducible. Many of the stability constants reported below were also calculated by the method of Block and McIntyre[9] and by graphically solving eq 1. Agreement among the three methods is excellent. It is felt, however, that the least-squares method is by far the best since it in effect allows simultaneous consideration of data and eliminates the error in finding the best visual fit by the graphical method. All stability constants reported below were obtained by the least-squares method.[10]

Results

The pK_D values of the chelating agents for the reactions $H_2Ch = H^+ + HCh^-$ and $HCh^- = H^+ + Ch^{2-}$ are recorded in Table I. The log of the formation constants of the divalent metals with the *o*-sulfo derivatives are recorded in Table II; values for the *meta*- and *para*-substituted acids are given in Table III.

The chelating agents having the sulfonic acid group *ortho* to the azo linkage are terdentate ligands and 1:1 (ligand to metal) compounds are formed. The decreasing order of stability for III-2-SO_3H, Cu > UO_2 Ni > Co > Zn > Cd > Mg > Ca > Sr > Ba, follows the order reported for *o,o'*-dihydroxyazo compounds. The *meta*- and *para*-substituted compounds behave as other benzeneazo-3- and benzeneazo-5-pyrazolones in which 2:1 derivatives are formed with little or no evidence for 3:1 compound formation.[11] Beryllium ion did not coordinate with the *o*-sulfonic acid derivatives. Barium and strontium hydrolyzed with I-2-SO_3H; the calcium derivative gave no evidence of hydroxide formation, but the titration was within the buffer zone of hydroxide formation, and thus the constant is not as reliable as the others which are reported. In all cases, reported data are in agreement with the stoichiometry of the titrations.

Discussion

The azopyrazolones containing sulfonic acid groups in the chelate position yield surprisingly good ligands. The alkaline earths and the 2-SO_3H derivative of azo-3-pyrazolone coordinate almost as strongly as the *o*-carboxy derivative[12] even though the sulfonic acid derivative is a considerably stronger acid. Schwarzenbach,[13] *et al.*, have studied the coordination of a sulfonic acid group as part of a chelate moiety with alkaline earths and found the same relationship.

Table III

Formation Constants of the 4-SO_3H and 3-SO_3H Derivatives in 75 Vol % Dioxane at 30°

	Cu		Ni		Co		Zn		Cd	
Azo compound	Log β_1	Log β_2	Log β_1	Log β_2	Log β_1	Log β_2	Log β_1	Log β_2	Log β_1	Log β_2
I-4-SO_3H	9.08 ± 0.16	17.71	6.84 ± 0.04	13.24	6.36 ± 0.10	12.36	*a*		*a*	
II-4-SO_3H	8.13 ± 0.04	15.87	6.25 ± 0.05	12.10	5.81 ± 0.05	11.25	*a*		*a*	
III-3-SO_3H	9.84 ± 0.11	16.85	7.78 ± 0.17	13.62	7.36 ± 0.08	13.15	6.71 ± 0.08	11.84	6.37 ± 0.07	11.01
III-4-SO_3H	9.63 ± 0.04	17.71	7.68 ± 0.19	13.67	6.95 ± 0.03	12.61	6.55 ± 0.08	12.26	6.21 ± 0.10	11.15

[a] Metal ion hydrolysis within the buffer zone of compound formation.

The lack of coordination of uranyl ion with the 3-methyl-1-phenyl-4-(2-sulfophenylazo)-5-pyrazolone is not understood. Differences in the coordination of the

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azo derivatives of 3- and 5-pyrazolones have been noted before,[11b] and the cause is probably a steric one.

The ratio of log β_2 to log β_1 for the *para* and *meta* derivatives is less than 2. This is in agreement with expected behavior but differs from that found for other *para*- and *meta*-substituted benzeneazo-5-pyrazolones in which the ratio is greater than 2. The extra charge on the chelate ion for the sulfonic acid derivatives probably accounts for this difference. The extra charge on the chelate ion would also account for the lack of 3:1 (azo compound to metal ion) coordination found with the sulfonic acid derivatives.

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The Crystal Structure of Diiodobis(*o*-phenylenebis(dimethylarsine))gold(III) Iodide—a Discrete Six-Coordinate Cationic Complex of Gold(III)

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The crystal structure of diiodobis(*o*-phenylenebis(dimethylarsine))gold(III) iodide, abbreviated as $Au(diars)_2I_3$, has been determined from three-dimensional, photographically recorded X-ray data. The compound crystallizes in the monoclinic system with $a = 21.6 \pm 0.2$ Å, $b = 8.92 \pm 0.04$ Å, $c = 16.10 \pm 0.08$ Å, $\beta = 107 \pm 1°$, $Z = 4$, and space group C2/c. The structure, refined by least-squares methods to a final conventional R factor for nonzero data of 0.14, consists of layers of $Au(diars)_2I_2^+$ cations interspersed with iodide ions. The cations have $\bar{1}$-C_i symmetry and the gold(III) atom is coordinated to two diarsine ligands, approximately in a square plane, with iodine atoms in octahedral positions. The Au–As bond distances are shorter than normal, indicating a degree of π bonding. The Au–I distances are longer than normal but nevertheless are indicative of strong interactions between the gold and iodine atoms. The latter atoms are each cushioned on four methyl groups which prevent any closer approach.

Introduction

Tervalent gold compounds are invariably diamagnetic and early investigations[1-3] established the occurrence of four-coordinate square-planar structures in which the $5d6s6p^2$ hybrid orbitals of the gold atom were used for bonding.

Coordination numbers greater than 4 have been reported recently for gold(III) complexes. Charlton, Harris, Patil, and Stephenson[4] determined the crystal structure of trichlorobiquinolylgold(III) and found the metal atom to be five-coordinate. Solution studies have lead to postulated five-coordinate gold(III) species and in some cases[5-7] the coordination number is claimed to be 6.

The cationic complex $Au(diars)_2I_2^+$, where diars represents the bidentate ligand *o*-phenylenebis(dimethylarsine), has been investigated using conductometric and spectroscopic methods[5] and a six-coordinate species was postulated to exist in solution. In view of the high coordination numbers induced by this diarsine ligand[8-11] the crystal structure of diiodobis(*o*-phenylenebis(dimethylarsine))gold(III) iodide was undertaken to establish whether a six-coordinate cation of gold(III) exists in the solid state.

Experimental Section

The substance was provided by Professor C. M. Harris. It is obtained as a dark red solid by the addition of the *o*-phenylenebis(dimethylarsine) ligand and sodium iodide to a solution of sodium tetrachloroaurate (all in ethanol). Recrystallization was carried out by taking up the solid in nitromethane, near its boiling point, in a test tube and allowing the solution to cool very slowly by immersing the test tube in a large reservoir of boiling water. The irregularly shaped crystals which formed were invariable multiple crystals and the resulting X-ray data were of extremely poor quality. Nevertheless these data were considered suitable enough to aid in attempting the crystal structure determination. Efforts to find more suitable solvents for recrystallization resulted in a change in crystal structure. This will be discussed later. The unit cell dimensions were obtained from zero-level precession photographs taken with Mo Kα radiation.

Diiodobis(*o*-phenylenebis(dimethylarsine))gold(III) Iodide, $AuI_3As_4C_{20}H_{32}$.—The formula weight of this compound is 1149.8. It crystallizes in a monoclinic system with $a = 21.6 \pm 0.2$ Å, $b = 8.92 \pm 0.04$ Å, $c = 16.10 \pm 0.08$ Å, $\beta = 107 \pm 1°$, $V = 296.8$ Å^3, $D_m = 2.63$ g cm^{-1} (by flotation), $D_o = 2.57$ g cm^{-1}, $Z = 4$, $F(000) = 2088$, and space group Cc or C2/c from systematic absences (visually absent).

The intensity data $h0l$–$k7l$ were collected on multiple-film packs of five. Equiinclination Weissenberg geometry was used together with Cu Kα radiation.

Correlation data were obtained from zero-level precession photographs and were adequate during the initial stages of the structure determination. Interlayer scale factors were introduced as variables during the final refinement stages.

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