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Metal Derivatives of Arylazopyrazolone Compounds. V. Molarity Quotients of an Azopyrazolone Containing an *o*-Dimethylamine Group

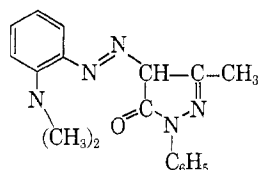
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The relative stabilities of the metal derivatives of azopyrazolone compounds containing an *o*- or *p*-dimethylamine group have been measured potentiometrically in 75 volume % dioxane. The decreasing stability order for bivalent cations with the *ortho* derivative is Cu > Ni > Co > Zn > Cd, Pb > Mn. A comparison with analogous compounds containing *o*-OCH₃ or -SCH₃ groups shows the following decreasing order of stability for nickel, cobalt, and cadmium ions N > S > O; for zinc N > O > S. Metal derivatives have been prepared and characterized.

Introduction

This is a continuation of the study of the relative bonding of oxygen, sulfur, and nitrogen to metal ions. The stabilities of the metal derivatives of azopyrazolone compounds containing an *o*-methoxy or -thiomethoxy group have been reported.² The present study in which a dimethylamine group is either *ortho* (I) or *para* substituted (II) completes this series.



I, N(CH₃)₂ *ortho* to N
II, N(CH₃)₂ *para* to N

Experimental³

Preparation of Azo Compounds.—The N,N-dimethyl-2-nitroaniline was prepared from 2-chloronitrobenzene and dimethylamine as described by Campbell.⁴ The above product (19 g.), a dark red liquid, was added to 600 ml. of a 5% ammonium chloride solution. To this solution under reflux was added 40 g. of zinc dust over a period of 2 hr. The solution was steam distilled and the distillate extracted with ethyl ether. The extract was dried over anhydrous magnesium sulfate and distilled under reduced pressure. The N,N-dimethyl-*o*-phenylenediamine, a colorless liquid, distilled at 113–114° (32–36 mm.), lit.⁵ 99.5–101° (20–25 mm.).

The N,N-dimethyl-*o*-phenylenediamine was diazotized by the direct method and coupled to 1-phenyl-3-methyl-5-pyrazolone dissolved in dilute aqueous sodium hydroxide. The coupling bath was adjusted to pH 7 by the addition of sodium acetate. After 2 hr. the solution was acidified with hydrochloric acid and filtered. The crude 1-phenyl-3-methyl-4-(2-N,N-dimethylaminobenzeneazo)-5-pyrazolone (I) was digested in hot water and recrystallized from 95% ethanol in orange fibers, m.p. 143°.

Anal. Calcd. for C₁₈H₁₉N₅O: C, 67.26; H, 5.85; N, 21.78. Found: C, 67.27; H, 5.96; N, 21.79.

The 1-phenyl-3-methyl-4-(4-N,N-dimethylaminobenzeneazo)-5-pyrazolone (II) was prepared in an analogous manner. The

crude product was recrystallized from 95% ethanol in dark red crystals, m.p. 144°.

Anal. Calcd. for C₁₈H₁₉N₅O: C, 67.26; H, 5.85; N, 21.78. Found: C, 67.48; H, 5.98; N, 21.92.

Preparation of Metal Derivatives.—All metal derivatives, except the 1:1 copper compound, were isolated after the coordination titrations by adding enough metal nitrate to give a ratio of azo compound to metal ion of 2:1. The solutions then were adjusted to the pH at which the formation of the complex occurred. In most cases the metal derivatives precipitated out of solution after a few days. Nickel and zinc solutions were evaporated to half volume before precipitation occurred. All the precipitates were recrystallized from chlorobenzene.

The 1:1 copper complex of 1-phenyl-3-methyl-4-(2-N,N-dimethylaminobenzeneazo)-5-pyrazolone: A 0.50-mmol sample

TABLE I
CHELATE FORMATION CONSTANTS OF SOME *o*-SUBSTITUTED
4-BENZENEAZO-5-PYRAZOLONES IN 75 VOLUME % DIOXANE AT
30°.

Metal ion	log K ₁	log K ₂	log K _{av} at $\bar{n} = 1$
1-Phenyl-3-methyl-4-(2-N,N-dimethylaminobenzeneazo)-5-pyrazolone			
Cu(II)	>13.0	7.6	...
Ni(II)	12.37 ^a	10.34	11.36
	12.55 ^b	10.35	
Co(II)	11.02 ^a	9.88	10.45
	10.99 ^b	9.92	
Zn(II)	10.14 ^a	8.88	9.50
	10.11 ^b	8.88	
Cd(II)	8.95 ^a	9.34	9.12
	8.94 ^b	9.33	
Pb(II)	~8.9	~8.3	~8.6
Mn(II)	~7.2
1-Phenyl-3-methyl-4-(2-thiomethoxybenzeneazo)-5-pyrazolone ^c			
Cu	>13.0	8.7	9.9
Ni ^d	11.08	9.83	10.40
Co	8.6	9.3	8.95
Zn	7.2	7.4	7.3
Cd	6.7	7.3	7.0
1-Phenyl-3-methyl-4-(2-methoxybenzeneazo)-5-pyrazolone ^c			
Cu	10.9	10.3	10.6
Ni	8.8	8.0	8.5
Co	8.2	8.0	8.1
Zn	7.8	7.6	7.7
Cd	6.0	6.7	6.35

^a Calculated by the method of Block and McIntyre.⁷ ^b Calculated by the method of Irving and Rossotti.⁸ ^c Data from ref. 2. ^d Calculated from new titration data.

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TABLE II
 METAL DERIVATIVES OF THE AZO COMPOUNDS^a

Metal	Color of crystals	M.p., °C.	Calcd.			Found		
			C	H	N	C	H	N
Compound I (<i>o</i> -N(CH ₃) ₂)								
Cu	Brown	205-206	61.38	5.16	19.88	61.53	5.16	19.81
Ni	Brown	263-265	61.81	5.21	20.02	61.71	5.27	20.12
Co	Brown	264-266	61.79	5.20	20.01	63.61	5.54	^b
Zn	Yellow-orange	240-242	61.22	5.15	19.83	61.23	5.34	20.16
Cd	Orange	262-264	57.40	4.83	18.59	57.44	5.06	18.82
Compound II (<i>p</i> -N(CH ₃) ₂)								
Cu	Purple	>300	61.38	5.16	19.88	61.46	5.43	19.60
Co	Purple	>300	61.79	5.20	20.01	62.31	5.15	19.68

^a The metal derivatives are 2:1, azo compound to metal ion, of general formula M(C₁₃H₁₈N₂O)₂. ^b Insufficient material for a nitrogen determination.

of the azo compound was dissolved in 40 ml. of purified dioxane. A solution of 0.70 mmole of copper(II) chloride and 0.70 mmole of potassium chloride in 10 ml. of water was added to the dioxane solution of the azo compound. The green precipitate which slowly formed over a period of 12 hr. was recrystallized from chlorobenzene to give a green microcrystalline powder, m.p. >300°.

Anal. Calcd. for CuCl(C₁₃H₁₈N₂O): C, 51.55; H, 4.34; N, 16.70. Found: C, 51.80; H, 4.56; N, 16.80.

Potentiometric Titrations.—The titrations were performed at 30.0 ± 0.1° in 75% dioxane as described previously.⁶ The solutions were so adjusted that in 100 ml. of solution there were 1.00 mmole of azo compound, 0.996 mmole of nitric acid, and 0.200 mmole of the metal nitrate. The titrant was a 1.001 *N* solution of carbonate-free sodium hydroxide. The meter reading correction factor (log *U*₁) equals 0.47. Titration time was about 2 hr.; nickel(II) titrations required about 15 hr.

Calculations.—The molarity quotients were calculated by the method of Block and McIntyre.⁷ The constants also were calculated graphically by plotting $\bar{n}/(1 - \bar{n})a$ against $(2 - \bar{n})a/(1 - \bar{n})$ in which the intercept of the straight line is *k*, and the slope is *k*₁*k*₂ (*a* is the free chelate ion concentration at the \bar{n} value used).⁸

Results

No values are recorded for the metal formation constants of the *p*-N(CH₃)₂ compound. The dimethylamine group in this position was considerably more basic than in the *ortho* position, and the stoichiometry of the titration curves was not well defined. Approximate values argue in favor of a 2:1 dye to metal complex in which the compound behaves similarly to other bidentate arylazopyrazolones.

The dissociation constant, *K*_D, for the *o*-N(CH₃)₂ derivative is 3.72 × 10⁻¹³. The *o*-N(CH₃)₂ group is too weakly basic to affect the pH of the solution and the stoichiometry of the titration is quite exact. The log of the formation constants recorded in Table I are the average of at least four sets of calculations from experimentally determined points. Standard deviations expressed as log *K* values do not exceed 0.10 except with zinc(II), where it is 0.21.

The two different methods of calculating the constants give results that are in good agreement. The

values recorded for lead(II) and manganese(II) are more approximate; hydrolysis probably occurred near the end of the titrations. Magnesium and the uranyl ion did not coordinate but precipitated as hydroxides.

The 2:1 metal derivatives and their elemental analyses are listed in Table II. Compounds isolated for lead and manganese were not of constant composition.

Discussion

A comparison of the coordination of an *o*-N(CH₃)₂ group with an *o*-OCH₃ or -SCH₃ group (Table I) shows that all of them follow the same order of decreasing stability (*K*₁) Cu > Ni > Co > Zn > Cd. It also can be shown that for a given metal ion (Ni, Co, Cd) the relative stabilities for *K*₁ of the three compounds are N > S > O, but for zinc(II) they are N > O > S and for copper(II), N, S > O.

It was suggested previously² that the oxygen-sulfur difference could perhaps be explained on the basis of π-bonding from the metal to the sulfur and that zinc(II) showed little tendency for forming π-bonds.⁹ It would seem that the greater stability with the -N(CH₃)₂ compound shows that the basicity of the tertiary amine is more significant than the possible π-bonding occurring with the sulfur.

The significant decrease between log *K*₁ and log *K*₂ for the copper(II) compound (log *K*₁ - log *K*₂ ≈ 6) shows the strong terdentate character of this chelating agent. Log *K*₁ is greater than log *K*₂ for all of the metal derivatives except cadmium. Arylazopyrazolone compounds^{6, 10} which are simple bidentate groups generally show log *K*₁ < log *K*₂. The *o*-OCH₃ and -SCH₃ compounds showed log *K*₁ > log *K*₂ only for the copper and nickel derivatives. The ease of preparation of the 1:1 dye to metal compound also argues in favor of a strong contribution from the *o*-N(CH₃)₂ group.

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