[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FRANKLIN AND MARSHALL COLLEGE]

Metal Derivatives of Azo Pyrazolone Dyes. II. Molarity Quotients of Azo Pyrazolone Dyes Containing *o*-Methoxy and *o*-Thiomethoxy Groups[1a,b]

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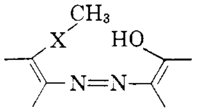
The relative stabilities of the metal derivatives of azo pyrazolone dyes containing an *ortho*-OCH_3 or $-SCH_3$ group have been measured potentiometrically in 75 volume % dioxane. The order of decreasing stability of the metal derivatives, Cu > Ni > Co > Zn > Cd, agrees with orders already reported for other terdentate dye groups.[2] The sulfur of the thiomethoxy group is found to be a much stronger donor atom than the oxygen of the methoxy group. Also the log Q_1 values are generally greater than log Q_2 values, a reversal of the simple bidentate azo pyrazolone dyes.

Introduction

Although thioethers are known to be much stronger coördinating agents than ethers, little quantitative information is available as to the relative strength of coördination of a methoxy or a thiomethoxy group. Quite recently Ahrland[3] and coworkers reported that silver(I)[3a,b] and cadmium(II)[3c] form more stable derivatives with aromatic sulfides than with aromatic ethers.

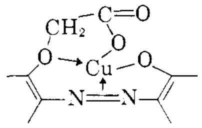
It is reported[4] that azo compounds containing the nucleus



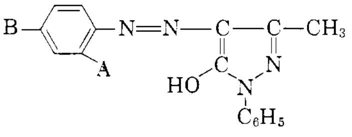
(where X = O) form 2:1, dye to metal, derivatives with such ions as copper(II) and nickel(II) with apparently no contribution from the ether oxygen. Wittenberger[5] reports that the methyl group of an *ortho*-OCH_3 as in the above structure is readily lost under certain conditions upon complexing with either copper(II) or chromium(III), suggesting a rather strong contribution from the ether oxygen.

Specklin and Meybeck[6] on the other hand have found that with dyes where X = sulfur there is no loss of the methyl group upon coördination with copper(II) even at elevated temperatures. They also found that chromium(III) does not form a complex as noted with the *o*-methoxy dyes. On this basis they argue that the thiomethoxy group is apparently not bonded to the metal ion.

H. Pfitzner[7] reports the coördination of an ether-like oxygen to copper(II) where the *ortho*-substituted group to the azo linkage is carboxymethoxy.



The work reported here is part of a general study to determine the relative contributions of methoxy, thiomethoxy and tertiary amine groups to the stability of the metal derivatives of azo pyrazolone dyes. Three azo compounds in which



(I) A is $-OCH_3$ and B is H; (II) A is $-SCH_3$ and B is H; and (III) A is H and B is $-OCH_3$ were prepared and studied.

Experimental

Preparation of the Azo Compounds.—The azo compounds were prepared by senior honor students[8] by coupling appropriate diazotized amines to 1-phenyl-3-methyl-5-pyrazolone; they were recrystallized from hot dioxane. (I) 1-phenyl-3-methyl-4-(2-methoxyphenylazo)-5-pyrazolone, tiny orange crystals, m.p. 165–167°; (II) 1-phenyl-3-methyl-4-(2-thiomethoxyphenylazo)-5-pyrazolone, orange powder, m.p. 149–150°; (III) 1-phenyl-3-methyl-4-(4-methoxyphenylazo)-5-pyrazolone, orange powder, m.p. 139–140°.

Each of the azo compounds was tested for purity as previously reported.[9]

Determination of neutral equivalents gave values within 0.1% of calculated values.

Potentiometric Titrations.—The titrations were performed at 30.0 ± 0.1° in 75% dioxane as described previously.[2,9] The solutions were so adjusted that in 100 ml. of solution there was 1.00 mmole of dye, 0.913 mmole of nitric acid and 0.200 mmole of the metal nitrate. A 0.9982 *N* solution of sodium hydroxide was used. The meter reading correction factor (log U_H) equals 0.45.[10]

Calculations.—The molarity quotients were calculated by the method of Block and McIntyre.[11]

Results and Discussion

Dye III, the *p*-methoxy compound, a simple bidentate pyrazolone, gives results completely analogous to those previously reported.[9] That is, a fairly stable 2:1, dye to metal, compound is formed with copper(II), nickel(II) and cobalt(II). A much weaker 3:1 derivative forms with nickel and cobalt. The zinc derivative is poorly defined and cadmium does not coördinate.

However, compound I, the *ortho*-methoxy derivative, forms 2:1 derivatives which are considerably more stable than those of compound III. In addition, there is no evidence for 3:1 complex formation and zinc and cadmium form well-defined compounds. The behavior of the thiomethoxy compound is similar.

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[1] (a) From a portion of a thesis presented by Bruce D. Krecker in partial fulfillment of the requirements for the degree of Master of Science, June, 1957; (b) from a portion of a thesis presented by Charles G. Clark in partial fulfillment of the requirements for graduation with Honors in Chemistry, B.Sc., June, 1957.

[2] F. A. Snavely, W. C. Fernelius and B. E. Douglas, *J. Soc. Dyers Colourists*, **73**, 492 (1957).

[3] (a) S. Ahrland, J. Chatt, N. R. Davies and A. A. Williams, *J. Chem. Soc.*, 264 (1958); (b) 276 (1958); (c) 1403 (1958).

[4] G. B. Crippa, *Gazz. chim. ital.*, **57**, 497 (1927).

[5] W. Wittenberger, *Meilliand Textileber.*, **32**, 456, 458 (1951).

[6] R. Specklin and J. Meybeck, *Bull. soc. chim.*, **18**, 621 (1951).

[7] H. Pfitzner, *Angew. Chem.*, **62**, 245 (1950).

[8] M. M. Chamberlain and C. E. Glassick, Senior Honor Dissertation, 1953.

[9] F. A. Snavely, W. C. Fernelius and B. P. Block, THIS JOURNAL, **79**, 1028 (1957).

[10] L. G. Van Uitert and C. G. Haas, Jr., *ibid.*, **75**, 451 (1953).

[11] B. P. Block and G. H. McIntyre, Jr., *ibid.*, **75**, 5667 (1953).

Manganese(II), iron(II) and (III), lead(II) and the uranyl ions were tried without success. Manganese(II) and iron(II) appeared to coördinate but oxidation was so rapid even in the presence of a nitrogen atmosphere that no definite results were obtained.

As previously reported,[9] the successive formation quotients listed in Table I are an average of those evaluated by using at least four sets of $\bar{n}$ and $p\mathrm{Ch}^-$ values. Note that $pQ_1 > pQ_2$ for the copper and nickel derivatives with dyes I and II while dye III follows the pattern of other simple pyrazolones with $pQ_2 > pQ_1$. Indeed, the first formation quotients for the copper and the nickel derivatives of the thiomethoxy compound are much greater than the second, so that two distinct formation buffer zones are present. It is interesting to point out that Irving and Fernelius[12] found $\log K_2 > \log K_1$ for alkyl mercapto carboxylic acids.

TABLE I

Dye	pQ_D	Metal		Log Qn		Log Qav
			$n = 1$	$n = 2$	$n = 3$	at $\bar{n} = 1$
I	11.60[a]	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
II	11.58[a]	Cu	>13	8.7[b]		9.9
		Ni	>11	9.8[b]		10.15
		Co	8.6	9.3		8.95
		Zn	7.2	7.4		7.3
		Cd	6.7	7.3		7.0
III	11.19[a]	Cu	9.7	10.0		9.8
		Ni	6.6	7.7	4.2[c]	7.2
		Co	6.4	7.3	3.6[c]	6.9
		Zn	6.1	≈7		≈6.5

[a] The color of the dyes in solution in either the dissociated or the undissociated form was the same, a light orange.

[b] Values taken from the formation curves at $\bar{n} = 1.5$.

[c] Values taken from the formation curves at $\bar{n} = 2.5$.

The much greater stability of the metal derivatives and the lack of 3:1 compounds argues in favor of a strong contribution from the ether oxygen and the ether sulfur to bond formation. The well defined zinc and cadmium compounds also support this view.

Sidgwick[13] states that in general the relative tendencies for complex formation is oxygen > sulfur for most of the metal ions. He also points out that the tendency for oxygen to act as a donor group decreases with increasing substitution in the order $H_2O > ROH > R_2O$, while the reverse appears to be true for sulfur $R_2S > RSH > H_2S$. Although the acid dissociation constants for dyes I and II are practically the same, pQ_1 values for the metal derivatives of the thiomethoxy dye are considerably greater (with the exception of zinc) than pQ_1 values with the o-methoxy compound. It is quite apparent that in this case the ether sulfur is a much stronger donor than the ether oxygen. This probably is due to the dative π-bonding of the metal to the sulfur. It would appear from the above data that zinc, the end member of the first transition series, does not show this effect. Ahrland[3] and co-workers interpreted the increased stability of the organic sulfides of silver(I) and cadmium(II) to be due to π-bonding. They also report that the ability of a metal to dative π-bond to a ligand falls sharply at the end of a transition series.

With the exception of the copper and the nickel titrations of dyes I and II, equilibrium was achieved rapidly and the average time per titration was about 1.5 hours. The copper titrations with I and II required about 3 hours, the nickel titrations 12 to 15 hours. The slowness of the copper titrations probably can be explained by the necessity of breaking the metal bond to the ether oxygen before a second chelate group can be added. That is, the dye is acting as a terdentate group in the 1:1 complex and a bidentate group in the 2:1 derivative. The significant difference between the stability of the 1:1 derivative of the sulfur dye and the 2:1 derivative may be due to the strong sulfur bond. The possibility of sp^3d^2 hybridization with copper being 6-coördinate must not be overlooked.

The case for the nickel derivatives is hardly this simple. It is possible that the first dye molecule forms a penetration complex in which a 3d orbital is used, the fourth coördination position being occupied by a water molecule. Upon the addition of the second dye molecule a rearrangement occurs to form a 6-coördinate outer-complex. The fact that cobalt(II) reaches rapid equilibrium is in harmony with this view since two 3d orbitals are available for d^2sp^3 hybridization and no rearrangement is necessary upon the addition of the second dye molecule. The terdentate chelate ion and its charge satisfy both the coördination number and the charge of the cobalt(II) ion in the 2:1 derivative. There was no evidence of oxidation to cobalt(III) as noted with the *o,o'*-dihydroxy azo compounds.[2]

The reported ease with which the methyl group of the methoxy linkage undergoes hydrolysis is apparently in error. Under the conditions of these titrations there is no evidence of loss of the methyl group with either dye I or II. Iron(III) and chromium(III) which would form strong derivatives with the resulting *o,o'*-dihydroxy structures gave no indication of complex formation with either dye I or II. Indeed, by the addition of nitric acid to the solutions of the metal derivatives the azo compounds were recovered intact.

Studies now in progress with *ortho*-carboxymethoxy groups and *o*-carboxythiomethoxy groups also show a strong contribution from the ether oxygen and the ether sulfur, with sulfur a stronger donor atom than the oxygen.

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(12) R. J. Irving and W. C. Fernelius, *J. Phys. Chem.*, **60**, 1427 (1956).

(13) N. V. Sidgwick, *J. Chem. Soc.*, 433 (1941).