TABLE VII

GEOMETRIES OF SYSTEMS CONTAINING OXO-BRIDGED METAL ATOMS

Complex	M–O, A	M–O–M, deg	No. of π electrons[a]	Ref
$[PyPcMn^{III}]_2O$[b]	1.71	178	12	3c
$\{[(H_2O)BFe^{III}]_2O\}^{2+}$[c]	1.8	. . .	14	4
$\{[(HEDTA)Fe^{III}]_2O\}^{2-}$	1.79	165	14	This work
$\{[Cl_5Ru^{IV}]_2O\}^{4-}$	1.80	180	12	6
$\{[Cl_5Re^{IV}]_2O\}^{4-}$	1.86	180	10	7

[a] Referred to the Dunitz–Orgel molecular orbital scheme.[15] [b] Py = pyridine; Pc = phthalocyanato. [c] B = macrocyclic, pentadentate ligand.[4]

which describe complexes containing linear Mo–O–Mo bonds, because the presence of nonbridging oxo ligands in these compounds requires the Dunitz–Orgel molecular orbital treatment to be significantly modified.[18] From the table, the M–O distances in $[PyPcMn^{III}]_2O$ and $\{[(HEDTA)Fe]_2O\}^{2-}$ are found to be 1.71 and 1.79 A, respectively, a result which cannot be explained on the basis of the relevant covalent radii ($r_{Mn(III)} \geqslant r_{Fe(III)}$). A satisfactory explanation is provided by the molecular orbital treatment described above, however, since there is more π-bonding character in the M–O–M group for manganese than for iron, the latter having the . . . $E_u{}^{*2}$ configuration.

Another geometric manifestation of the difference in electronic structure between the manganese and iron dimers is the M–O–M angle, being 178° for Mn and 165° for Fe. Apparently, the lesser amount of π-bonding character in the Fe–O–Fe systems makes it more susceptible to intramolecular strains (*e.g.*, those imposed by the chelating HEDTA ligands) and to intermolecular crystal-packing forces (Table III).

Direct comparisons of the $\{[(HEDTA)Fe]_2O\}^{2-}$ structure with the remaining compounds of Table VII are not as meaningful. Of interest, however, is that, in those cases where the number of π electrons is 12 or less, the M–O–M systems retain the maximum M–O bond orders of 2 and are linear. The seven-coordinate iron complex will probably require a separate molecular orbital treatment although, from the observed Fe–O bond distance of 1.8 A, it is likely that its electronic structure will not be too different from that of the HEDTA dimer.

Finally, we wish to emphasize that the success of the Dunitz–Orgel scheme in accounting for certain structural differences in oxo-bridged systems has been the main justification for its adoption. Clearly, there are several other electronic and steric factors present in these complexes which have not been taken into account. While more detailed calculations on these systems can (and should) be carried out, it seems likely that, in any more sophisticated treatment, extensive M–O–M π bonding will be a dominant feature.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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A Study of the Effect of Steric Hindrance in Metal Coordination with Azo-3-pyrazolones

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The formation constants of divalent metal ions with azo derivatives of 1-phenyl-5-methyl-3-pyrazolone have been measured in 75 vol. % dioxane. These azo derivatives are both stronger acids and stronger coordinating ligands than the analogous azo derivatives of 1-phenyl-3-methyl-5-pyrazolone. A steric effect is found with the *ortho*-substituted derivatives which decreases in the order: I > Br > Cl > F > H and $C_2H_5 > CH_3$. A possible explanation given is that the *ortho* groups hinder the retention of water molecules to form $MCh_2 \cdot 2H_2O$ in solution (Ch = chelate).

Introduction

Considering the wide use of the azo derivatives of 5-pyrazolones in the dye industry,[2] the sparcity of data on the azo derivatives of 3-pyrazolones is rather surprising. The difficulty of preparation of the latter probably has been the major deterrent to an extensive investigation of their properties. The commercial availability of diketene makes the preparation of 1-phenyl-5-methyl-3-pyrazolone and its azo derivatives relatively easy. We have prepared a series of azo derivatives of 1-phenyl-5-methyl-3-pyrazolone and measured their formation constants with divalent metal cations in dioxane–water solutions. It was also pos-

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[1] Participants, NSF Undergraduate Research Participation Program, 1963 (A. T.) and 1966 (D. A. S.).

[2] K. Venkataramen, "The Chemistry of Synthetic Dyes," Vol. I, Academic Press Inc., New York, N. Y., 1952, pp 607–622.

sible to prepare *ortho* derivatives and study any possible steric effects, which had not been successful with the 5-pyrazolone *ortho* derivatives due to their relative insolubility.

Experimental Section

Preparation of 1-Phenyl-5-methyl-3-pyrazolone.—To a well-stirred solution of 144 g of phenylhydrazine in 400 ml of benzene cooled in an ice bath, 56 g of diketene was added dropwise at such a rate that the temperature did not exceed 20°. Additional benzene was added as the mixture became too thick. After the addition, the dirty white hydrazone was suction filtered (yield, 155 g), added to 1850 ml of concentrated HCl, and boiled for 15 min. Water was carefully added until the precipitate dissolved, and the solution was boiled for 15 min. After cooling to room temperature, the solution was made basic by the careful addition of 5 *M* NaOH and then just neutralized with acetic acid to produce a yellow-white precipitate which was filtered, washed with water, then with very small amounts of 95% ethanol, and finally with ether. Recrystallization from 95% ethanol yielded 80 g (69%) of white crystals; mp 167–169°, lit.[3] mp 166°.

Preparation of Azo Compounds.—The azo derivatives were prepared by coupling the appropriate diazotized amines to the 1-phenyl-5-methyl-3-pyrazolone in aqueous solution containing enough sodium hydroxide to dissolve the pyrazolone and sodium carbonate to serve as a buffer. After 4 hr the coupling bath was carefully neutralized with HCl and the crude product, washed with boiling water, was finally recrystallized from 95% ethanol. The carbon, hydrogen, and nitrogen analyses are given in Table I.

Potentiometric Titrations.—The titrations were performed at 30.0° (±0.1°) in 75 vol. % dioxane as described previously.[4] The solutions were so adjusted that in 100 ml of solution there were 1.000 mmole of azo compound, 1.040 mmoles of nitric acid, and 0.200 mmole of metal nitrate. A 1.001 *N* solution of carbonate-free sodium hydroxide was used. The meter reading correction factor (log U_H)[5] equals 0.47. The acid dissociation constants of the chelating agents were obtained by titrating the azo compound in the absence of divalent metal ions.

Calculations.—The negative logarithms of the acid dissociation constants were found by adding the meter reading correction factor to the meter reading at the stoichiometric midpoint of the neutralization titration curves.

The stability constants were calculated by curve fitting[6]

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

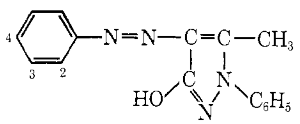
by the method of least squares using an IBM 1130 computer. β_n is the product of the first n stability constants, a is the concentration of the chelating agent anion, and $\bar{n}$ is the average number of chelating agent groups attached to each metal ion. Because of the nature of eq 1, $\bar{n}$ values within 0.15 of 1 or 0.11 of 2 were automatically rejected for curve fitting.

In this least-squares treatment each point was given equal weight because there is no reason to believe that a point with, *e.g.*, $\bar{n} = 0.5$ is significantly more or less reliable than a point with $\bar{n} = 1.5$. Values of $\bar{n}$ close to 1 or 2 were rejected not because they are less reliable than other values but because the experimental error is of greater relative importance with $\bar{n}$ values close to 1 or 2 if eq 1 is to be used.

Equation 1 is not identically equal to zero over the entire titration; *i.e.*, there is a residual for each titration point. Thus β_1 and β_2 were allowed to vary until the requirements of the method of least squares were fulfilled. The standard deviation of the residuals of eq 1 was computed for each titration. Since the absolute value of the coefficient of β_1 in eq 1 is unity, the standard deviation of the residuals can be correlated to the curve-fitting uncertainty in β_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.

TABLE I

ELEMENTAL ANALYSIS OF THE AZO-3-PYRAZOLONES[a]



Azo compd	Mp, °C	Analyses, %					
		C		H		N	
		Calcd	Found	Calcd	Found	Calcd	Found
H	96	69.06	69.07	5.03	5.25	20.14	20.01
2-CH_3	96–97	69.86	69.30	5.48	5.38	19.17	18.55
3-CH_3	111–113	69.86	69.62	5.48	5.69	19.17	19.20
4-CH_3	139–140	69.86	69.38	5.48	5.55	19.17	19.18
2-F	126–128	64.86	65.10	4.39	4.28	18.92	18.68
3-F	129–130	64.86	64.69	4.39	4.43	18.92	18.90
4-F	145–147	64.86	64.17	4.39	4.53	18.92	18.20
2-Cl	154–155	61.44	62.26	4.19	4.43	17.92	17.99
3-Cl	118–120	61.44	61.44	4.19	3.92	17.92	18.00
4-Cl	158–160	61.44	61.13	4.19	4.29	17.92	17.95
2-Br	156–157	53.78	53.94	3.64	3.80	15.69	15.66
3-Br	123–125	53.78	53.89	3.64	3.58	15.69	15.59
4-Br	160–162	53.78	53.68	3.64	3.72	15.69	15.52
2-I	124–126	47.52	47.69	3.22	3.34	13.83	13.40
4-I	153–155	47.52	47.64	3.22	3.36	13.83	13.65
2-NO_2	141–142	59.44	59.77	4.05	4.63	21.66	21.30
3-NO_2	161–163	59.44	59.59	4.05	3.96	21.66	21.45
4-NO_2	206–209	59.44	59.25	4.05	4.01	21.66	21.51
2-OCH_3	137–138	66.22	66.32	5.19	5.13	18.77	18.33
3-OCH_3	109–110	66.22	65.97	5.19	5.19	18.77	18.41
4-OCH_3	122–124	66.22	66.05	5.19	5.05	18.77	18.01
2-SCH_3	162–163	62.96	62.97	4.93	5.07	17.28	17.02
3-SCH_3	144–145	62.96	62.21	4.93	4.81	17.28	16.68
2,6-$(CH_3)_2$	136–138	70.59	70.49	5.88	5.73	18.30	18.40
2-C_2H_5	71–73	Neutral equiv: calcd, 306; found, 304					

[a] Analytical data of G. Weiler and F. B. Strauss, Oxford, England.

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.

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[7] 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. The log β_2 values given by the computer are in close agreement with 2 log K_{av} values obtained from $\bar{n}$ curves.

The computer output for the nickel(II) derivatives of 1-phenyl-5-methyl-4-(2-chlorophenylazo)-3-pyrazolone is given in Table II. Note that the residuals of the points are random, meaning that the constants are determined by all of the points, not just a few in a particular range of $\bar{n}$.

Results

The pK_D values of the chelating agents for the reaction HCh = $H^+ + Ch^-$ are recorded in Table III along with the logarithms of the formation constants for the copper(II) derivatives. A typical Hammett σ-function plot shows a nice linear relationship for the *para*-substituted azo compounds with decreasing acid

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TABLE II

SAMPLE COMPUTER OUTPUT OF THE LEAST-SQUARES TREATMENT[a]

NaOH, ml	Meter reading	pCh$^-$	$\bar{n}$	Residual × 10^{-6}
1.040	4.77	7.14	0.213	−1.20
1.080	4.99	6.94	0.413	−0.435
1.120	5.16	6.79	0.615	+0.214
1.180	5.38	6.60	0.917	Rejected
1.240	5.62	6.39	1.22	−0.935
1.280	5.80	6.23	1.42	−0.126
1.340	6.21	5.86	1.72	+0.899
1.370	6.62	5.47	1.87	+1.58

[a] $\beta_1 = 3.12 \times 10^6$; $\beta_2 = 1.09 \times 10^{13}$. Standard deviation of residuals = 9.90×10^5.

TABLE III

FORMATION CONSTANTS OF COPPER(II) DERIVATIVES

Azo compd	pK_D	Log β_1	Log β_2	Log K_2
H	10.38	9.65 ± 0.11	18.62	8.97
2-C_2H_5	10.62	9.29 ± 0.05	17.83	8.54
2-CH_3	10.54	9.50 ± 0.09	18.31	8.81
3-CH_3	10.54	9.88 ± 0.07	19.16	9.28
4-CH_3	10.47	9.56 ± 0.14	18.28	8.72
2-F	10.02	9.31 ± 0.04	18.48	9.17
3-F	10.10	9.35 ± 0.05	17.97	8.62
4-F	10.30	9.57 ± 0.06	18.52	8.95
2-Cl	10.36	9.48 ± 0.08	18.72	8.97
3-Cl	10.12	9.31 ± 0.04	18.22	8.91
4-Cl	10.12	9.39 ± 0.13	18.33	8.94
2-Br	10.40	9.31 ± 0.12	18.70	9.39
3-Br	10.05	9.29 ± 0.13	18.15	8.86
4-Br	10.12	9.28 ± 0.04	18.23	8.95
2-I	10.22	8.87 ± 0.16	18.03	9.16
4-I	10.09	9.40 ± 0.01	18.20	8.80
2-NO_2	9.73	8.76 ± 0.11	17.93	9.17
3-NO_2	9.77	8.98 ± 0.06	17.56	8.58
4-NO_2	9.45	8.44 ± 0.17	16.67	8.23
2,6-$(CH_3)_2$	10.72	10.80 ± 0.04	20.54	9.74
2-OCH_3	9.82	10.26 ± 0.20	19.01	8.75
3-OCH_3	10.42	9.36 ± 0.23	17.90	8.54
4-OCH_3	10.61	9.60 ± 0.26	17.93	8.33
2-SCH_3	10.64	>14.00[a]		
3-SCH_3	10.35	9.57 ± 0.06	18.96	9.39

[a] Coordination too strong to obtain accurate constants.

strength as: $NO_2 > I > Br, Cl > F > H > CH_3 > OCH_3$. Such a simple relationship was not found with the azo derivatives of 1-phenyl-3-methyl-5-pyrazolone.[8] It is also to be noted that azo derivatives of the 3-pyrazolone are stronger acids than the azo derivatives of 5-pyrazolone whereas Veibel,[9] *et al.*, report that 3-pyrazolones are weaker acids than 5-pyrazolones. At the same time the copper(II) chelates of the azo-3-pyrazolones are more stable than the copper(II) analogs of the azo-5-pyrazolones.[4,8]

The formation constants of divalent nickel, cobalt, zinc, and cadmium with the 2-substituted derivatives are reported in Table IV. A rather surprising steric effect is found here which causes the formation constants to decrease in the order: $H > F > Cl > Br > I$ and $CH_3 > C_2H_5$. An inspection of the data for the copper(II) derivatives indicates that they are relatively insensitive to this effect.

In Table V are listed the nickel, cobalt, zinc, and cadmium formation constants with the nitro derivatives and several other compounds studied. Again a steric effect is found for the 2-nitro derivatives compared to the 3- and 4-nitro derivatives. A comparison of the log β_2 values shows the order of decreasing stability as *meta* > *para* > *ortho*, while acid strength decreases *para* > *meta*, *ortho*.

Discussion

The azo-3-pyrazolone derivatives show a much smaller tendency for 3:1 (azo compound to metal) complex formation than do the analogous azo-5-pyrazolones. The very weak 3:1 coordination vanishes completely with the *ortho* derivatives. When the *ortho* substituent is a coordinating group, OCH_3 or SCH_3, the stability increases and the ligand becomes terdentate as reported previously for the azo-5-pyrazolones.[10] Log K_1 is significantly greater than log K_2. Although the 2-OCH_3 derivative is a stronger acid than the 2-SCH_3 compound, the log β_2 value for the 2-OCH_3 zinc(II) derivative is about 2 log units greater than the log β_2 value for the 2-SCH_3 complex. This is consistent with past reports in which divalent copper, nickel, and cobalt are stated to bond more strongly to sulfur while zinc bonds more strongly to oxygen.

Values for cobalt(II) with these two derivatives are about equal. Results with cobalt(II) and the 2-SCH_3 derivative are in some doubt. Although titration data could be reproduced, stoichiometry was not exact for the formation of $CoCh_2$. Either oxidation to cobalt(III) occurred or the methyl group of the SCH_3 group was lost by hydrolysis.

The rather surprising steric effect can be rationalized with the aid of various data on analogous 5-pyrazolone complexes. Present work with these 5-pyrazolone chelates shows that water of coordination is found with the 2:1 (azo compound to metal) compounds and that magnetic measurements give results in agreement with octahedral high-spin nickel(II) and cobalt(II). If the derivatives are prepared with excess ammonia, compounds containing ammonia, $MCH_2(NH_3)_2$, are formed. Apparently the solution species in the absence of an *ortho* group is $MCH_2(H_2O)_2$ in which the metal ion is six coordinate.

Attempts to prepare metal derivatives of the 2-CH_3 and 2-Cl derivatives of azo-5-pyrazolone which contain either water or ammonia have not been successful. The nickel(II) complex of the 2-I derivative of azo 5-pyrazolone does not contain water. Thus it would seem that the *ortho* groups hinder the retention of water molecules and that the iodo group is large enough to prevent the formation of $MCH_2(H_2O)_2$ giving instead a four-coordinate species MCH_2.

The steric effect observed with the *o*-3-pyrazolone complexes might be attributed, then, to changes in the stereochemistry and composition (and resulting changes in thermodynamic stability) of the solution species produced by the size of the *ortho* group. This hypothe-

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TABLE IV

FORMATION CONSTANTS FOR THE 2-SUBSTITUTED DERIVATIVES

Azo compd	pK_D	Cu		Ni		Co		Zn		Cd	
		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
H	10.38	9.65 ± 0.11	18.62	7.18 ± 0.19	14.62	6.90 ± 0.05	14.00	6.73 ± 0.10	13.67	6.12 ± 0.23	12.47
F	10.02	9.31 ± 0.04	18.48	7.02 ± 0.14	13.76	6.09 ± 0.28	13.09	6.19 ± 0.11	12.70	5.40 ± 0.12	10.84
Cl	10.36	9.48 ± 0.08	18.72	6.49 ± 0.12	13.04	5.87 ± 0.22	12.07	5.31 ± 0.10	11.59	5.01 ± 0.17	10.60
Br	10.40	9.31 ± 0.12	18.70	6.20 ± 0.04	12.53	5.56 ± 0.11	11.45	Neg[b]	11.25	4.84 ± 0.26	10.32
I	10.22	8.87 ± 0.16	18.03	5.74 ± 0.11	11.39	5.24 ± 0.17	10.87	Neg[b]	10.68	4.18 ± 0.16	9.44
CH_3	10.54	9.50 ± 0.09	18.31	6.56 ± 0.05	12.60	6.15 ± 0.07	12.34[a]	5.62 ± 0.43	11.74	5.11 ± 0.13	10.77
C_2H_5	10.62	9.29 ± 0.05	17.83	6.48 ± 0.04	12.45	5.98 ± 0.04	12.01	Hydrolysis[c]		5.03 ± 0.07	10.33

[a] Value is probably too high. Buffer zone of formation is in region of hydroxide coordination. [b] Negative values were obtained for β_1. The log β_2 value reported is within ±0.05 of 2 log K obtained from the $\bar{n}$ formation curve. Hydrolysis and buffer zones of complex formation are fairly close. [c] Hydrolysis and buffer zones of complex formation are too close to calculate a value.

TABLE V

FORMATION CONSTANTS OF THE NITRO AND COORDINATION *ortho* DERIVATIVES

Azo compd	Log β_1	Log β_2	Log β_2	Log K_2
2-NO_2	Ni	6.62 ± 0.08	13.02	6.40
	Co	6.12 ± 0.12	12.57	6.45
	Zn	5.81 ± 0.20	11.61	5.80
	Cd	4.96 ± 0.09	10.26	5.30
3-NO_2	Ni	7.02 ± 0.24	14.65	7.63
	Co	6.99 ± 0.25	14.08	7.39
	Zn	6.16 ± 0.19	12.91	6.75
	Cd	5.54 ± 0.24	12.31	6.77
4-NO_2	Ni	6.77 ± 0.20	13.66	6.89
	Co	6.47 ± 0.13	13.35	6.88
	Zn	5.77 ± 0.15	11.87	6.10
	Cd	5.57 ± 0.18	11.63	6.06
2-OCH_3	Ni	9.54 ± 0.10	17.11	7.57
	Co	8.80 ± 0.10	16.16	7.36
	Zn	8.37 ± 0.07	15.20	6.83
	Cd	6.58 ± 0.11	12.26	5.68
2-SCH_3	Ni	9.91 ± 0.04	18.65	8.74
	Co	8.67 ± 0.12	16.02	7.35
	Zn	7.08 ± 0.01	13.39	6.31
	Cd	6.39 ± 0.07	12.56	6.17

sis, that the steric effect is involved with the water of hydration, is strengthened by the fact that the effect is not observed with the copper derivatives.

Derivatives of copper(II) which have been isolated for either the azo compounds of 3- or 5-pyrazolone have not contained water. Even if the copper(II) derivatives were prepared in the presence of a large excess of ammonia, no ammonia was found in the complexes. In none of the rather extensive titration studies has copper(II) ever given any indication of 3:1 (azo compound to metal) coördination. Because the copper(II) complexes were relatively insensitive to the observed effect, it is not unreasonable to assume that the steric effect is not concerned with one chelate group bumping into the other.

Preliminary work with the hydrated nickel(II) complexes of the non-*ortho*-substituted compounds of azo-5-pyrazolone shows that the water is lost at about 105° and that the anhydrous nickel(II) complexes are diamagnetic. Work is continuing in collecting magnetic data for compounds with and without *ortho* blocking groups.[11]

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(11) Material supplementary to this article (titration data) has been deposited as Document No. 9549 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $3.75 for photoprints, or $2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.