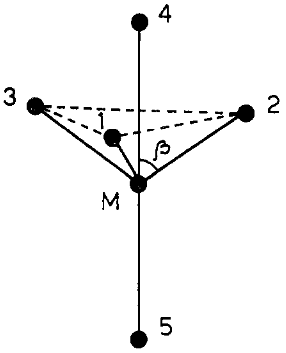

Figure 2.—A sketch of the coordinates used in thec rystal-field calculation.

Ancmon tables.[26] In every case it has been put $\mu_1 = \mu_2 = \mu_3 = \mu_4$ (see Figure 2 for numbering of the dipoles). The energy of the Cr^{2+} and Fe^{2+} levels, split in fields of C_{3v} symmetry, are reported in Table IV for several values of the parameters β and μ_5.

Table IV

Energy Levels of the Terms ^5D ($3d^4$ and $3d^6$) in Crystalline Fields of C_{3v} Symmetry[a]

β, deg	μ_5/μ_1		$E[^5A_1]/\mu_1$, cm^{-1} $D.^{-1}$	$E[^5E(1)]/\mu_1$, cm^{-1} $D.^{-1}$	$E[^5E(2)]/\mu_1$, cm^{-1} $D.^{-1}$
90	1.0	Cr	−3960	+200	+1780
		Fe	+2620	−230	−1080
	0.8	Cr	−3460	−60	+1790
		Fe	+2260	−20	−1110
85	1.0	Cr	−3920	+170	+1790
		Fe	+2620	−210	−1100
	0.8	Cr	−3420	−80	+1790
		Fe	+2260	−20	−1110
80	1.0	Cr	−3840	+60	+1860
		Fe	+2590	−120	−1170
	0.8	Cr	−3340	−150	+1820
		Fe	+2220	+30	−1140

[a] The baricenter of these levels has been taken as the zero of the energy.

(26) C. J. Ballhausen and E. M. Ancmon, *Kgl. Danske Videnskab. Selskab, Mat Fys. Medd.*, **29**, 4 (1954).

Contribution from Argonne National Laboratory,
Argonne, Illinois

Coordination in Solutions. IV. Association Constants for 1:1 Complexes of Cu(II), Zn(II), Ca(II), La(III), and Y(III) with Anions of Salicylaldehydes[1,2]

By C. POSTMUS, JR., L. B. MAGNUSSON, and C. A. CRAIG

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Association constants for 1:1 complexes of Cu(II), Zn(II), Ca(II), La(III), and Y(III) are reported at 25° and an ionic strength of 0.1 *M* in aqueous solution. The ligands were the anions of the parent and of the 3-, 4-, 5-, 6-chloro, 3-, 5-nitro, and 3,5-dinitro derivatives of salicylaldehyde. Constants are reported for the association of La(III) with the anions of phenol, *o*-nitrophenol, and *o,p*-dinitrophenol and for Y(III) with phenol anion. π bonding, if it occurs in the Cu(II) complexes, has no detectable effect on trends in stability. Generalized and special case treatments are presented to obtain complex constants from spectrophotometric data where three absorbing species change concentration.

Irregularities in the relative stability of 1:1 Cu(II) complexes with anions of salicylaldehyde and derivatives in aqueous–dioxane solutions have been attributed to variations in π bonding involving d electrons from the Cu(II).[3-5] This proposal is examined in the present work by comparison of the Cu(II) complex stabilities in aqueous solution with those of noble gas structure cations. Two of the monochloro derivatives of salicylaldehyde have been reassigned as 4- and 6-chloro isomers,[6] invalidating some of the previous observations.[3,4] Generalized and special case treatments of spectrophotometric data for systems of three absorbing species are presented. The acid dissociation constants have been reported previously.[6,7]

Experimental Section

Materials.—The preparation and purification of the chelating acids and the inorganic reagents have been reported previously.[2,6-8] Perchlorate stock solutions of Cu^{2+}, Zn^{2+}, Y^{3+}, and La^{3+} were prepared by reaction of the oxides with excess perchloric acid. Perchlorate stock solutions of Ca^{2+} were prepared by the reaction of perchloric acid with three calcium salts: (1) reagent grade carbonate, (2) carbonate prepared from reagent grade chloride (the latter contained a smaller concentration of interfering metals than reagent grade carbonate), and (3) reagent grade chloride. In method 3, a chloride-free solution was obtained by repeated evaporation of excess perchloric acid. The Cu^{2+} stock was analyzed by electrodeposition. The other metal stocks were analyzed in two ways: gravimetrically as sulfate by evaporation and ignition at 400° of an aliquot to which an excess of sulfuric acid had been added, and by titration of the hydrogen ion liberated from a cation-exchange column (Dowex

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Part III: L. B. Magnusson, C. A. Craig, and C. Postmus, Jr., *J. Am. Chem. Soc.*, **86**, 3958 (1964).

(3) J. G. Jones, J. B. Poole, J. G. Tomkinson, and R. J. P. Williams, *J. Chem. Soc.*, 2001 (1958).

(4) K. Clarke, R. A. Cowen, G. W. Gray, and E. H. Osborne, *ibid.*, 245 (1963).

(5) B. R. James, M. Parris, and R. J. P. Williams, *ibid.*, 4630 (1961).

(6) Part II: C. Postmus, Jr., I. A. Kaye, C. A. Craig, and R. S. Matthews, *J. Org. Chem.*, **29**, 2693 (1964).

(7) Part I: L. B. Magnusson, C. Postmus, Jr., and C. A. Craig, *J. Am. Chem. Soc.*, **85**, 1711 (1963).

(8) I. A. Kaye, R. S. Matthews, and A. A. Scala, *J. Chem. Soc.*, 2816 (1964).

50). Correction for the free acid in the stock solution was made in the latter method. Free acid in the stock solutions was determined by pH measurement with the pH scale calibrated for hydrogen ion concentration.[7] In the Cu^{2+}, Zn^{2+}, and Ca^{2+} stocks the free acid was *ca.* 10^{-2} *M*. In the La^{3+} and Y^{3+} stocks the free acid was 10^{-4} *M* or greater. The analyses agreed to within 1% with the concentrations calculated from the starting weight of the metal salt. The metal purities were 99.7%, or better, by spectroscopic analysis.

Measurements and Calculations.—The association constants were evaluated from the optical absorbance of aqueous solutions using procedures and instruments described previously.[7] The spectra were recorded on chart paper which was periodically calibrated for absorbance by readings taken from the slide wire scale of the spectrophotometer. In the equilibrium solutions the range of concentration of chelating agent was 3×10^{-5} to 2×10^{-4} *M*. The ranges of metal ion concentrations in runs in which the pH was varied were: Cu(II), 3×10^{-3} to 3.3×10^{-2} *M;* La(III), 7×10^{-3} to 1.6×10^{-2} *M;* Y(III), 3×10^{-3} to 1.67×10^{-2} *M;* Ca(II), 3.3×10^{-2} *M;* Zn(II), 1.6×10^{-2} to 3.2×10^{-2} *M*. In runs in which the metal ion concentration was varied, the range was 2×10^{-4} to 3.3×10^{-2} *M*.

The concentration constant for the 1:1 metal complexing reaction, $M + L \rightleftharpoons ML$, is defined by

$$K_1 = [ML]/[M][L] \qquad (1)$$

and the acid dissociation constant for the reaction $HL \rightleftharpoons H + L$ is given by

$$K' = a'_H[L]/[HL] \qquad (2)$$

where [S] is the molar concentration of species S, a'_H is antilog (−pH), and M, L, ML, and HL are the free metal ion, free organic anion, 1:1 metal complex ion, and the organic acid species, respectively.[9] The latter three species absorb light in the 3000–5000-A region. There appears to be no general method in the literature for the evaluation of K_1 from spectrophotometric data when all three species contribute significantly to the absorbance.[10]

The formation of complexes containing more than one ligand per metal ion was suppressed by using concentrations of metal ion which were 20 to 100 times the concentration of complexing agent, $[L]_T$, the latter being defined as

$$[L]_T = [HL] + [L] + [ML] \qquad (3)$$

The solution absorbance, corrected for absorbance by all metal ion species other than ML, is

$$A = \epsilon_{HL}[HL] + \epsilon_L[L] + \epsilon_{ML}[ML] \qquad (4)$$

for a 1-cm cell, where ϵ_S is the molar absorptivity of species S. The metal ions other than ML which absorbed were hydrolyzed species in the short-wavelength region and Cu^{2+} at the longer wavelengths. When hydrolysis or Cu^{2+} concentration was significant, the spectrum of a duplicate solution of metal ion without ligand but at the same pH as the complexing solution was recorded. The absorbance in the metal ion solution was subtracted from the absorbance in the complexing solution to give the *A* of eq 4.

Dividing eq 4 by eq 3, after expressing [ML] and [L] in terms of [HL] by eq 1 and 2, gives

$$A = A_{ML} - \{a'_H(A - A_{HL}) - K'(A_L - A)\}/K'K_1[M] \qquad (5)$$

where A_S is the absorbance the solution would have if all of the chelating agent were present as species S, *i.e.*, $[S] = [L]_T$.[11] The total concentration of chelating agent was constant for any series of measurements and, to eliminate any dependence upon the accuracy of the concentration of the stock solution, A_{HL} and A_L were measured on an identical aliquot of the stock solution. By changing the variables a'_H or [M] (eq 5), six to eight values of *A* were determined. The rates of reaction were too rapid to detect and no change in absorbance or pH could be observed with time. A plot of *A* against the coefficient of $1/K_1$ in the second term on the right of eq 5 should be a straight line with A_{ML} as the intercept and $-1/K_1$ as the slope.[12]

Similar equations may be derived for conditions in which a variable is eliminated from eq 3 and 4. For complex formation in the pH region well below the p*K* value of the acid, where the anion absorbance and concentration are negligible

$$A = A_{ML} - a'_H(A - A_{HL})/K'K_1[M] \qquad (6)$$

In the pH region well above the p*K* value of the acid, where the acid can be neglected[13,14]

$$A = A_{ML} + (A_L - A)/K_1[M] \qquad (7)$$

Further simplification proved to be worthwhile. When the concentration of the metal ion is held essentially constant, the ratio of [ML] to [L] is a constant. Defining [X] by

$$[X] = [ML] + [L] = [L](K_1[M] + 1) \qquad (8)$$

and multiplying both sides of eq 2 by $(K_1[M] + 1)$, one obtains

$$K'(K_1[M] + 1) = K_X = a'_H[X]/[HL] \qquad (9)$$

By a derivation similar to that for eq 5, the absorbance may be expressed as

$$A = A_X - a'_H(A - A_{HL})/K_X \qquad (10)$$

where A_X is the absorbance if all of the chelating agent is present as the species [ML] and [L]. The intercept, A_X, and the slope, $-1/K_X$, are obtained from a plot of the absorbance against the numerator of the second term on the right. There is no need to measure A_L.

When the concentration of the metal ion is varied but the pH is held constant, the ratio of [HL] to [L] is constant. Defining [Y] by

$$[Y] = [HL] + [L] = [L](K' + a'_H)/K' \qquad (11)$$

and multiplying both sides of eq 1 by $K'/(a'_H + K')$, one obtains

$$K_1K'/(a'_H + K') = K_Y = [ML]/[M][Y] \qquad (12)$$

The derived absorbancy equation

$$A = A_{ML} - (A - A_Y)/K_Y[M] \qquad (13)$$

again simplifies the calculations. A_Y is the absorbance of an identical aliquot of the chelating stock solution in the absence of the complexing metal at the same pH used for the complexing measurements. A_L and A_{HL} need not be measured. When a'_H is negligible with respect to K', eq 12 simplifies to $K_Y = K_1$.

Since eq 10 and 13 are easy to use, the measurement of K_1 was based on one of these equations whenever possible. When the pH was altered at constant metal concentrations (eq 10), the techniques were identical with those in the measurement of acid dissociation constants.[7] A series of samples was prepared for variation of the metal concentration (eq 13).

Calculations were carried out at three wavelengths near that at which maximum change occurred in the absorbance. The decrease in metal ion concentration caused by complexing was generally negligible since $[M] >> [L]_T$, but a correction was applied when necessary. The Cu^{2+} and Zn^{2+} metal concentrations were corrected for hydrolysis, never more than 10%, by using the data

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(9) K' is an apparent acid dissociation constant which differs from K_c, the concentration acid constant, in that a'_H rather than [H] is used. See ref 7.

(10) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 276.

(11) Since the measurements of K_1 were made using a'_H, it was convenient to use K' rather than K_c (see ref 7) in the calculations. The K' was measured at the same ionic strength as that for K_1.

(12) There are similar treatments of spectrophotometric data, but K_1 is obtained by dividing the slope by the intercept; *cf.*, *e.g.*, H. McConnell and N. Davidson, *J. Am. Chem. Soc.*, **72**, 3164 (1950); P. S. Farrington, *ibid.*, **74**, 966 (1952); H. S. Frank and R. L. Ostwalt, *ibid.*, **69**, 1321 (1947).

(13) T. W. Newton and G. M. Arcand, *ibid.*, **75**, 2449 (1953).

(14) Reference 10, p 275, contains a minor confusion in nomenclature since the symbol ϵ is defined as the corrected absorbance divided by the total concentration of one of the reactants, yet is treated as an absorbance in some of the discussion.

of Berecki-Biedermann[15] and Perrin.[16] To avoid excessive hydrolysis with the formation of species not in rapid equilibrium with the metal ion, the base was added slowly with vigorous agitation.

The criteria for accepting any set of data as reliable were: (1) the standardization of the pH meter (ref 7) was the same before and after the series of spectrophotometric measurements; (2) an isosbestic point was obtained; and (3) the plot to evaluate K_1 was a straight line within experimental error.

Results

As long as the ratio $a'_H/[H]$ is constant in the solution used to evaluate K' and K_1, the value of K_1 is independent of this ratio. Since the ionic strength was held constant at 0.100 M, usually with sodium perchlorate as the predominant electrolyte, a constant ratio is to be expected. The ratio was measured over a range of 10^{-2} to 10^{-4} M [H] at a μ of 0.100 M for solutions of Na^+, Ca^{2+}, Cu^{2+}, La^{3+}, and Y^{3+} perchlorates and found constant. The constancy of the ratio is confirmed by the agreement of K_1 values for different metal concentrations and the agreement of values from eq 7 and those from equations involving K'. Since potassium ion solutions remain anomalous (see ref 7), values of K' measured in potassium perchlorate (high pH range) were corrected to those for sodium perchlorate.

A compilation of the metal complexing constants, as log K_1 values, and the acid dissociation constants, as pK_c values, is given in Table I. The results are the average of at least two separate determinations, generally under different concentration conditions. Only a few complex constants for Zn^{2+} were measurable owing to the limitations imposed by the ionic strength and hydrolysis of the Zn^{2+} ion.

Discussion

In the previous work[3,4,17] with the salicylaldehyde complexes, data were compared by means of the empirical relation

$$\log K_1 = a\mathrm{p}K_c + b \qquad (14)$$

where a and b are constants.

Although there are no reasons for expecting better than a rough correlation of the data with eq 14,[18-20] the log–log display, given in Figure 1, is useful for comparison. The curvature noted previously[3,4] in the log–log plots for the water–dioxane systems resulted mainly from the positions of the points for 3,5-dinitrosalicylaldehyde and 6-chlorosalicylaldehyde. A plot of the constants (log K_1 and pK_c) in the various media $vs.$ the reciprocal of the dielectric constant shows a medium effect which increases with decreasing acid strength.[21]

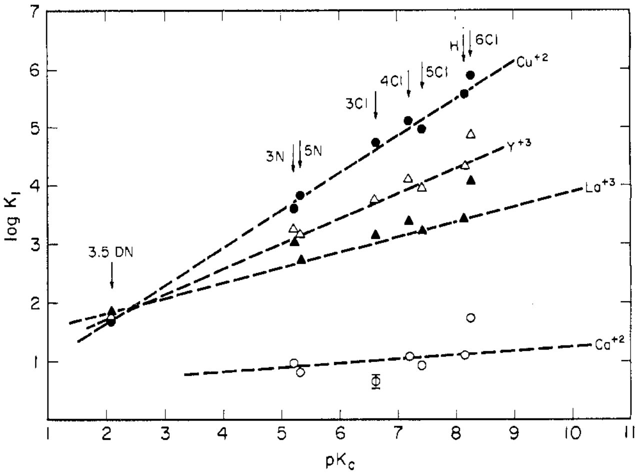

Figure 1.—The log K_1 values $vs.$ pK_c values for salicylaldehyde and its derivatives with different metal ions. Arrows are drawn at the respective pK_c values for each derivative: H, parent; Cl, chloro; N, nitro; DN, dinitro. Salicylaldehyde is numbered with the carbonyl group in the 1 position and the hydroxyl group in the 2 position.

Table I

Complexing Constants at 25.0° with μ = 0.10 M

Anion	pK_c[a]	Log K_1[b] Cu^{2+}	Zn^{2+}	Ca^{2+}	La^{3+}	Y^{3+}
6-Chlorosalicylaldehyde	8.26	5.88		1.74	4.08	4.87
Salicylaldehyde	8.14	5.56		1.10	3.40	4.34
5-Chlorosalicylaldehyde	7.41	4.96		0.94	3.20	3.94
4-Chlorosalicylaldehyde	7.18	5.11		1.07	3.38	4.09
3-Chlorosalicylaldehyde	6.61	4.74	2.39	0.67	3.16	3.77
5-Nitrosalicylaldehyde	5.32	3.83	2.01	0.80	2.73	3.17
3-Nitrosalicylaldehyde	5.21	3.61		0.98	3.03	3.27
3,5-Dinitrosalicylaldehyde	2.09	1.68	0.75		1.84	1.75
Phenol	9.78				1.51	2.40
o-Nitrophenol	7.06				2.20	
o,p-Dinitrophenol	3.93				1.01	

[a] pK_c = −log K_c where K_c = [H][L]/[HL] from ref 2, 6, and 7. [b] K_1 = [ML]/[M][L]. The estimated uncertainty in the log values is 0.02 except for the smaller log values for Ca^{2+} and Zn^{2+} where the error could be as large as 0.1.

The exceptional behavior of the 6-chlorosalicylaldehyde complexes will be discussed later.

Deviations from a single linear relationship (eq 14) have been attributed to the donation of d_ϵ electrons from the Cu(II) to the π orbitals of the ligand making the ratio of substituent effects, Δ log K_1/ΔpK, dependent on both the electron donor–acceptor properties of the substituent and its ring position.[3-5] According to this hypothesis, a nitro group, a σ and π acceptor, would give a smaller value of the slope, Δ log K_1/ΔpK, in the 3 or 5 positions than a chloro group, a σ acceptor and π donor. Hence, the 3- and 5-chloro points should fall below a line connecting the points for parent and the 3- or 5-nitro derivative. Since they do not (Figure 1, 3-chloro above and 5-chloro slightly below), it would appear that changes in d_ϵ electron donation are not important in determining log K_1 values. Comparison of the effects for chloro substitution in different ring positions in the Cu(II) complexes gives no information regarding d_ϵ electron donation because the same pattern of scatter of the points appears for the complexes of

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[15] C. Berecki-Biedermann, *Arkiv Kemi*, **9**, 175 (1956).

[16] D. D. Perrin, *J. Chem. Soc.*, 4500 (1962).

[17] M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).

[18] J. E. Duncan, *Analyst*, **77**, 830 (1952).

[19] H. Irving and F. J. C. Rossotti, *J. Chem. Soc.*, 2904, 2910 (1954); *Acta Chem. Scand.*, **10**, 72 (1956).

[20] F. J. C. Rossotti in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 52.

[21] The pK_c value for 3,5-dinitrosalicylaldehyde in 50% dioxane (ref 4) and the log K_1 value for salicylaldehyde in 75% dioxane (ref 3) appear to be too small by about 0.5.

the noble gas type of cations in which there can be no electron donation. The position of chloro substitution does have a specificity which, however, must apply mainly to the acid and anion, not to the metal complex.

The most stable complexes reported here are those with the anion of 6-chlorosalicylaldehyde. The behavior of this ligand is unique by reason of proximity and/or steric interactions of the chloro and carbonyl groups.[6] A normal pK_0 for this acid would be that of the other isomer with the chloro substituent in the position *meta* to the hydroxyl group, 4-chlorosalicylaldehyde. The difference in pK_0 values, 1.08, is caused by the stronger hydrogen bond and a reduction in the energy of the flip effect, the rotation of the carbonyl oxygen away from the negative oxygen in the anion.[2] The reduced flip energy is a specific property of the anion and will be a constant contribution to the bonding of hydrogen ion or any metal ion. In support, we note that the difference in the log K_1 values for 6- and 4-chlorosalicylaldehyde with any of the cations falls in the range 0.67–0.78.

A reversal in the stability of the complexes with the 3- and 5-nitro derivatives is observed between Cu(II) and the noble gas type of ions. Insofar as the dashed lines in Figure 1 can be considered to define a normal relation between substituent effects, the reversal in stability appears to be caused by a specific effect in the 3-nitro derivative. The results for the complexing of La(III) with the phenols (Table I) show that La(III) forms a chelate complex with the anion of *o*-nitrophenol, but it is unlikely that the difference between the log K_1 values for La(III) with 3- and 5-nitrosalicylaldehyde can be accounted for entirely by the formation of species in which the La(III) is chelated by nitro oxygen and phenoxy oxygen. If one assumes the log K_1 value for 5-nitrosalicylaldehyde to be the normal value for chelation between the carbonyl and phenoxy oxygens and adds the concentration of species with nitro–phenoxy chelation given by the log K_1 value for *o*-nitrophenol, one obtains 2.84 for the log K value for the formation of both species. This value is smaller than that for 3-nitrosalicylaldehyde and, furthermore, is probably an upper limit because the nitro–phenoxy chelation would be weakened by the substitution of a formyl group *ortho* to the phenoxy oxygen.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Transition Metal Dithiolate Complexes. I. π-Cyclopentadienyl Maleonitrile Dithiolate Compounds[1]

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New complexes of Co, Mo, W, and Ti containing the π-cyclopentadienyl and the maleonitrile dithiolate ($[S_2C_2(CN)_2]^{2-}$) ligands have been prepared. These complexes are compared with the π-cyclopentadienyl bis(perfluoromethyl)dithiete ($S_2C_2(CF_3)_2$) derivatives of Cr, Mo, and Co, and their further reactions with excess $Na_2S_2C_2(CN)_2$ to give simple unsubstituted maleonitrile dithiolate complexes are described.

Introduction

The reactions of sulfur ligands related to ethylene *cis*-dithiol with metal carbonyl and π-cyclopentadienyl carbonyl derivatives are well documented.[3,4] For example, bis(perfluoromethyl)dithiete, $S_2C_2(CF_3)_2$, reacts with the carbonyls and π-cyclopentadienyl carbonyls of V, Cr, Mo, Co, and Ni, generally causing displacement of CO and forming simple dithiolate derivatives, *e.g.*, $MoS_6C_6(CF_3)_6$, or π-cyclopentadienyl compounds, *e.g.*, $[\pi\text{-}C_5H_5MoS_2C_2(CF_3)_2]_2$. Few reactions of carbonyl derivatives with $Na_2S_2C_2(CN)_2$ have been described, but it has been reported[5] that this ligand displaces only one CO group from $Mn(CO)_5Br$ forming $[Mn(CO)_4S_2C_2(CN)_2]^-$ and, in the hope of obtaining anionic carbonyl derivatives of the type $[\pi\text{-}C_5H_5M(CO)_nS_2C_2(CN)_2]^-$ (where M = Fe and $n = 1$ or M = Mo or W and $n = 2$, etc.), the reaction of the appropriate π-cyclopentadienyl metal carbonyl halide with $Na_2S_2C_2(CN)_2$ was investigated.

Experimental Section

All melting points are uncorrected and all solvents were degassed before use. All analyses were carried out by the Microanalytical Laboratory of this department or by Alfred Bernhardt Mikroanalytisches Laboratorium im Max-Planck Institut für Kohlenforschung, Mülheim (Ruhr), Germany.

Physical Measurements.—Infrared spectra were recorded using a Unicam SP 100 spectrophotometer, and proton magnetic resonance spectra were obtained using a Varian A-60 spectrometer.

Disodium Maleonitrile Dithiolate.—Initially this salt was prepared from $NaS_2C\cdot CN\cdot 3DMF$ by the standard methods[6]

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[1] Submitted, in part, as a paper presented to the 2nd International Symposium on Organometallic Chemistry, Madison, Wis., 1965.

[2] Supported by the Scientific Research Council.

[3] (a) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963); **4**, 55 (1965); G. N. Schrauzer and V. P. Mayweg, *Z. Naturforsch.*, **19b**, 192 (1964); (b) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **86**, 2799 (1964); *Inorg. Chem.*, **3**, 814 (1964); R. B. King, *ibid.*, **2**, 641 (1963).

[4] R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

[5] J. Locke and J. A. McCleverty, *Chem. Commun.*, 102 (1965).

[6] G. Bahr and G. Schleitzer, *Chem. Ber.*, **90**, 438 (1954); A. Davison and R. H. Holm, *Inorg. Syn.*, submitted for publication.