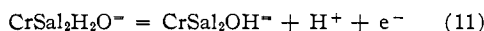


in a qualitative sense. The independence of half-wave potential on salicylate concentration and the dependence on pH show that the number of salicylate ions is the same in both the chromous and chromic complexes and that one hydrogen ion is released (or one hydroxide consumed) in the oxidation. It is reasonable to think that, if a water molecule were coordinated to the chromous ion, when this ion is oxidized the increased central positive charge would promote the ionization of one of the water protons. Such a reaction is proposed to account for the observed behavior. Chromous ion is characteristically four-coordinated but like cupric ion can accept another ligand.¹³ It is thought that two salicylate ions occupy four of the coordination positions in a square-planar arrangement and the fifth position above the plane holds a water molecule bound more loosely. Then, at the d.m.e., the reaction proposed is



The anodic limiting current was shown to be diffusion controlled and was found to be precisely linear with concentration in the range from 0.04

(13) R. L. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, **11**, 1419 (1957).

to 0.28 mF chromium(II). The diffusion current constant, I , of the complex in 3 F sodium perchlorate at pH 12 is -1.05 .

It was mentioned earlier that the very negative anodic half-wave potential of the chromous salicylate complex showed it to be one of the most powerful reductants known in aqueous solution. It was thought that this property could lead to certain practical applications and for that reason the present study was initiated. In the course of this investigation, a very brief study of the ethylenediaminetetraacetate complex of chromous ion was made, and it was found that above pH 12, this complex has an anodic half-wave potential of -1.48 v. *vs.* s.c.e. The wave was apparently reversible and the half-wave potential was not a function of pH or of EDTA concentration in this region. Between pH 12 and 8, the half-wave potential decreased to -1.24 v., indicating that one hydrogen ion per electron is involved in the oxidation in this region. Below pH 8 no studies were made; the solutions turn purple and begin evolving hydrogen gas when they are made too acid. However, it seems clear that the chromous EDTA complex in basic media is an even more powerful reducing agent than the salicylate complex.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

Mononuclear and Polynuclear Complex Formation by Manganese(II) and Zinc(II) Ions with 2,3-Dimercapto-1-propanol: The Behavior of the E_r Function with Mercaptide^{1a}

BY D. L. LEUSSING^{1b} AND T. N. TISCHER

RECEIVED MAY 26, 1960

Manganese(II) and zinc(II) ions react with 2,3-dimercapto-1-propanol to form complexes of the type MDMP and MDMP₂⁻. The formation constants of these species are $1.7 \times 10^{+6}$ and $2.7 \times 10^{+10}$, respectively with manganese(II) and are $3 \times 10^{+13}$ and $2 \times 10^{+23}$ with zinc(II) at 30° and at an ionic strength of 0.10 M . For the bis DMP complexes the difference in the free energies of complex formation corrected for the hydration energies of the aqua ions, the George E_r function, has the largest value of any that can be calculated from data found in literature. This seems to be the result of a larger increase in the strength of σ bonds in the series Mn(II) through Zn(II) with mercaptide than with the more common ligands having oxygen or nitrogen donor groups. The value of E_r is roughly proportional to the number of mercaptide groups coordinated to the metal ions. Polynuclear complexes are also formed by zinc(II) and DMP. The data indicate that a "core plus links" series, $(\text{ZnDMP}_2)_n$, is formed. The stability of the dimer (the first member of this series) is less than that for the corresponding dimeric nickel(II) DMP complex. This appears to be due to the greater importance of π bonding in the nickel(II)-polynuclear complexes.

The ligand field stabilization energies for a number of complexes of the divalent metal ions of the first transition series have been shown²⁻⁴ to be related to the difference in the free energies of formation of the corresponding Mn(II) and Zn(II) complexes. This difference after correction for the hydration energies of the aqua metal ions is designated E_r .⁵ Its value gives direct evidence of the course of the almost linear⁴ monotonic function in the series Mn(II)-Zn(II) that would describe the stabilities

of the intervening ions in the absence of ligand field stabilization. A comprehensive examination of the stabilities of a large number of complexes with different ligands reveals that E_r increases with the coordination $O < N < S$ and its use, together with ligand field stabilization energies, as a tool diagnostic of the number and kind of coordinated groups has been demonstrated.⁴

The value of E_r represents essentially the free energy for the reaction $\text{Zn}_g^{++} + \text{MnL}_{naq} \rightarrow \text{ZnL}_{naq} + \text{Mn}^{++}$ and is almost entirely determined by the difference in the heats of formation of the solvated complexes. Because the effect of the ligand activity is absent, or at least minimized, and the activities of the metal ions are the same, changes in E_r with different ligands are more significant of changes in the metal ion-donor atom bond strengths than are changes in just the formation constants, the reason being that changes

(1a) Financial support for this work was made available by a grant from the National Science Foundation. Presented before the 138th National American Chemical Society Meeting, New York, N. Y., 1960.

(1b) To whom inquiries should be addressed at National Bureau of Standards, Washington, D. C.

(2) P. George, *Rec. trav. chim.*, **75**, 671 (1956)

(3) D. L. Leussing, *THIS JOURNAL*, **80**, 4180 (1958).

(4) P. George and D. S. McClure, *Progress in Inorganic Chemistry*, Vol. I, F. A. Cotton, ed., Interscience Publishing Co., New York, N. Y., 1959.

(5) This has been designated as Δ in ref. 3.

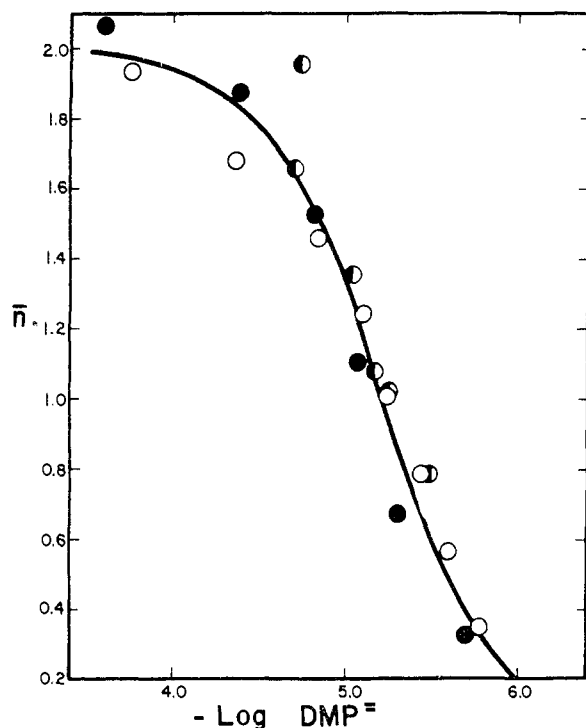


Fig. 1.—The formation curve for the Mn(II)-DMP complexes: O, $4.19 \times 10^{-3} M$ MnCl₂; ●, $1.01 \times 10^{-3} M$ MnCl₂; ○, $4.19 \times 10^{-4} M$ MnCl₂.

in the formation constants with different ligands also reflect changes in the ligand activity in addition to reflecting differences in bond strengths. The large effect that the differences in the ligand activities can have on the relative values of formation constants has been demonstrated with the nickel(II) complexes of 2,3-dimercapto-1-propanol and 1,2-ethanedithiol.⁶

A study with mercaptoacetate⁸ has shown that the value of E_r for this complexing agent is unusually large compared to the values obtained with the complexors having oxygen and nitrogen donor groups. In order to obtain more information about the nature of the sulfur-metal ion bond, it is desirable to examine the behavior of E_r in complexes with a ligand having a higher proportion of coordinatable mercaptide groups. The ligand, 2,3-dimercapto-1-propanol (DMP) was chosen for this purpose.

Of further interest, studies of the nickel(II)-mercaptide systems have revealed that polynuclear species are formed in addition to mononuclear complexes. With β -mercaptoethylamine the complex $Ni_3(SCH_2CH_2NH_2)_4Cl_2$ has been isolated⁷ and with mercaptoacetate a "core plus links" series, $Ni_{n+1}(SCH_2CO_2)_{2n}^{(2n-2)-}$, has been found.⁸ The dithiols, 2,3-dimercapto-1-propanol⁹ and 1,2-ethanedithiol,⁶ form dimeric complexes having a metal ion to ligand ratio of 2:3. It is another goal of the present study to learn more about the nature

(6) D. L. Leussing and G. S. Alberts, *THIS JOURNAL*, **82**, 4458 (1960).

(7) D. C. Jicha and D. H. Busch, 135th National Meeting of the American Chemical Society, Boston, Massachusetts, April 1959.

(8) D. L. Leussing, R. C. Laramy and G. S. Alberts, *THIS JOURNAL*, **82**, 4826 (1960).

(9) D. L. Leussing, *ibid.*, **81**, 4208 (1959).

of these polymeric species by determining the effect that a variation of the metal ion has on their composition and stabilities.

Experimental

Stock solutions of manganous chloride and zinc chloride were prepared and standardized as previously described,³ as were also those of DMP.⁹ The pH-titration technique was essentially used.¹⁰ Because of either extreme sensitivity to oxygen, in the case of manganese(II), or slowness to equilibrate, in the case of zinc(II), the points along the titration curve were not obtained as in the usual manner with successive additions of base but rather individual points were obtained in batchwise experiments. Specific details are given below for each system but certain experimental features are common and these will be described first.

In a typical experiment the desired volume of the metal chloride solution was pipetted into a Pyrex bottle and sufficient volumes of water and a potassium chloride solution were added so that after all the solutions were added, the final volume would be either 50.0 or 100.0 ml. and the solution would be 0.100 M in potassium chloride. The bottle was then sealed with a self-sealing Firestone K-1410 Buna N cap and the contents were purged thoroughly with nitrogen introduced by means of a six inch hypodermic needle which pierced the cap. The desired air free volumes of the DMP solution and a 1.000 M potassium hydroxide solution were then added by means of syringes. After equilibrating at 30° the pH of the solution was determined while the system was kept under nitrogen. The electrode system was calibrated as previously described.⁸

To determine the pH of a solution in the Mn(II) experiments, the cap of the bottle was removed and a nitrogen inlet tube was immediately inserted so that nitrogen flowed through the gas space over the solution. Another cap in which were fitted a Beckman probe electrode and small fritted glass potassium chloride salt bridge was then placed on the bottle, the nitrogen tube being removed at the last instant. By carrying out these processes rapidly it was found possible to put the glass electrode and salt bridge in place without oxidation as manifested by the appearance of a yellow color in the solution (see below). An external calomel reference electrode completed the system.

The pH of a solution in the Zn(II) experiments was determined by transferring a sample with a syringe to a partially closed flask containing the electrodes and through which nitrogen was rapidly passed.

In initial experiments it was observed in those solutions where no precipitate was obtained that the pH remained constant after equilibration over the period from 18 hr. to at least 24 hr., so this interval was used for equilibration in subsequent runs.

Values of \bar{n} , the average number of ligand molecules bound per metal ion, were calculated in the usual way.¹⁰ In making this calculation and in obtaining the concentration of the DMP⁻ ions, values of 2.4×10^{-9} and 2.6×10^{-11} were used for the proton dissociation constants of DMP at 30° in solution, at an ionic strength of about 0.10 M.⁹

Manganese(II) System.—The manganous chloride concentration was varied over a ten-fold range from $4.20 \times 10^{-4} M$ to $4.20 \times 10^{-3} M$ and, except for one run at the lower manganese concentration where the DMP was 0.00300 M, the DMP-concentration was maintained at a value two to three times that of the manganese.

Contrary to the results given below with zinc(II), no precipitate formed and only soluble complexes were obtained. These complexes are extremely air-sensitive and under the present conditions are oxidized rapidly by oxygen to a yellow complex which slowly goes over to a green complex of manganese(III).¹¹ Because of this extreme sensitivity, the deviations caused by the accidental admittance of traces of air during some of the pH determinations are somewhat greater than are usually obtained in complex ion studies. However, a sufficient number of good points were obtained to allow a satisfactory interpretation of the results to be made. The results are given in Fig. 1 as a plot of \bar{n} versus the logarithm of the concentration of uncombined DMP⁻ ions. These results show that \bar{n} is a function only

(10) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice Hall, New York, N. Y., 1952.

(11) D. H. Rosenblatt and G. N. Jean, *Anal. Chem.*, **27**, 951 (1955).

TABLE I
THE SOLUBILITY PRODUCT OF ZnDMP
0.100 M KCl, 30°

Initial concentration of ZnCl₂ equals $5.00 \times 10^{-3} M$

Initial concn. DMP, mole/l. $\times 10^{+3}$	Initial concn. KOH, ^a mole/l. $\times 10^{+3}$	pH	Total equil. concn. Zn, mole/l. $\times 10^{+3}$	Total equil. concn. DMP, moles/l. $\times 10^{+3}$	Mn ⁺⁺ $\times 10^{+3}$	Zn in precip. mole/l. $\times 10^{-3}$	DMP in precip. mole/l. $\times 10^{+3}$	K _{sp} $\times 10^{18}$
4.64	0.290	3.02	4.40	4.10	1.17	0.60	0.54	1.19
4.80	0.794	3.09	4.25	3.95	1.02	0.75	.85	1.51
4.64	1.30	3.11	4.00	3.71	0.98	1.00	.93	1.47
5.79	1.80	3.11	3.73	4.46	.98	1.27	1.33	1.65
4.80	1.80	3.21	3.84	3.55	.77	1.16	1.25	2.13
4.64	2.31	3.20	3.51	3.28	.79	1.49	1.36	1.71
5.79	2.81	3.19	3.32	4.08	.80	1.68	1.71	1.93
4.80	2.81	3.30	3.40	3.17	.62	1.60	1.63	2.54
5.41	5.82	3.54	1.98	2.28	.35	3.02	3.13	3.12
5.97	6.82	3.52	1.47	2.43	.36	3.53	3.54	2.22
9.82	7.39	3.41	1.12	6.00	.48	3.88	3.82	2.50
5.97	7.83	3.69	1.02	1.98	.26	3.98	3.99	2.64
9.82	8.41	3.57	0.64	5.41	.33	4.36	4.41	2.52
5.97	8.84	3.88	.58	1.50	.17	4.42	4.47	2.47
9.82	9.42	3.78	.31	4.95	.21	4.69	4.87	2.42

^a Corrected for the amount of hydrochloric acid in the zinc chloride solution.

of the DMP⁻ concentration and is independent of the total Mn(II) and DMP concentrations in the system. This signifies that only mononuclear species which are neither protonated nor hydroxylated are formed. A maximum of only two DMP⁻ ions are indicated to be coordinated. Values of DMP⁻ were estimated from a smoothed curve at \bar{n} equals 0.50 and 1.50, and these were used in simultaneous equations to obtain the formation constants. Values of $1.7 \times 10^{+5}$ and $2.7 \times 10^{+10}$ were found for the constants for the equilibria $Mn^{++} + DMP \rightleftharpoons MnDMP$ and $Mn^{++} + 2DMP \rightleftharpoons MnDMP_2^-$. The solid line in Fig. 1 is a theoretical curve which was computed from these results. A curve drawn to pass through the lower points in Fig. 1 gives values of Q_1 and Q_2 equal to $1.3 \times 10^{+5}$ and $1.5 \times 10^{+10}$ while a curve passing through the higher points gives values equal to $1.9 \times 10^{+5}$ and $4.3 \times 10^{+10}$. Thus, the relative range of Q_1 is about 10–20% and that of Q_2 is of the order of 50%.

Zinc(II) System.—In preliminary experiments it was found that solutions of zinc chloride and DMP produce a white precipitate on mixing. This precipitate is shown from the results in Table I to be ZnDMP. The problem then was divided into two phases: one, to find the solubility product of ZnDMP from experiments in moderately acid solutions where ZnDMP dissolves to give aquo zinc(II) ions and DMPH₂ molecules and, two, to use this value of the solubility product and determine the stabilities of the species found in more alkaline solutions where in the presence of excess DMP, ZnDMP dissolves as complex ions. In principle it is possible to meet both of these objectives with the pH-titration method by modifying the procedure only slightly. This is done by determining the total amount of dissolved zinc(II) and DMP in those experiments where a precipitate results.

The details of the experiments in which the solubility product of ZnDMP is determined are given in Table I. After preparation as described above the solutions were equilibrated with frequent shaking at 30°. After 24–48 hr. they were centrifuged and aliquots of the supernatant liquid were withdrawn for analyses. The pH was determined on one aliquot and on others the zinc and DMP concentrations were determined. The zinc analysis was carried out by titration with EDTA¹² after the mercaptan was destroyed by hydrogen peroxide. The DMP was obtained in another aliquot by titration with a standard iodine solution after acidification. The amounts of zinc(II) and DMP which precipitated were obtained by difference. By this process the result for the composition of the solid phase reflects all errors. Even so, the average of the ratio Zn/DMP in the solid phase is calculated from the results of Table I to be

1.00:1.01. This is in good agreement with the theoretical value predicted for the neutral species.

The molar concentrations of the hydrogen ion in Table I were obtained from the measured pH values by means of a calibration curve which was derived from an experiment in which increments of a standard hydrochloric acid solution were added to 0.100 M potassium chloride. In this way the pH meter readings can be converted directly to concentration units, and the necessity of estimating activity coefficients and liquid junction potentials is eliminated.

For the case where no soluble complexes are formed, the number of mmoles per ml. of ZnDMP which should precipitate is equal to one-half the sum of the hydrogen ion concentration plus the total concentration of added base. The data show, however, that one-half this sum is greater than the amount of zinc precipitated by an amount which is approximately constant and is independent of the DMP⁻ concentration. This means that an appreciable quantity of the neutral species, ZnDMP, remains dissolved. An average value of $8.8 \times 10^{-6} M$ is calculated from the data for the solubility of this species. Values of K_{sp} were calculated after correcting the observed solution zinc(II) and DMP concentrations for this concentration of ZnDMP and are given in the last column of Table I.

The calculated K_{sp} values are reasonably constant in the pH range 3.30 to 3.78. Below this range, however, they show a tendency to become smaller. We have not been able to account for this behavior but the less acid, values, which are more pertinent to the present study, yield an average of 2.6×10^{-18} . This will be taken for the value of K_{sp} in further calculations.

The formation constant of ZnDMP, computed at $8.8 \times 10^{-3} / K_{sp}$, is found to have a value of $3 \times 10^{+13}$.

In the more alkaline region the DMP concentration was kept at a level two to three times that of the zinc. Here where the ZnDMP redissolves in the form of anionic complexes, it was found that a partial colloidal dispersion of the solid phase occurs to give a milky solution, and it was not possible to effect a complete separation of the supernatant liquid by centrifuging. Thus, the data in this region of heterogeneous equilibria were not useful for calculations. However, in those solutions where the precipitate has entirely redissolved the data can be treated in the usual way and relative formation constants can be calculated for the species which are indicated. These formation constants can be put on an absolute basis by locating as closely as possible the point where the precipitate just disappears so that at this one point the restriction (Zn^{++}) (DMP^-) equals K_{sp} can be invoked. We therefore attempted to locate this point as closely as possible. This point was ascertained by visually determining whether, or

(12) G. Schwarzenbach, "Die Komplexometrische Titraktionen," Ferdinand Enke, Stuttgart, 1955.

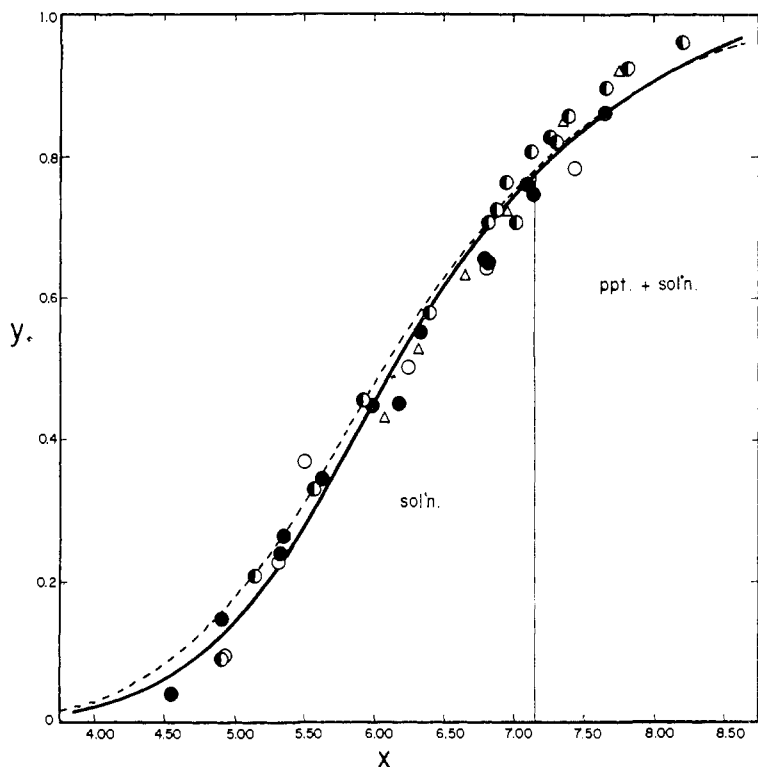


Fig. 2.—The formation function for the Zn(II)–DMP complexes: ●, $5.00 \times 10^{-3} M$ ZnCl₂; ●, $4.00 \times 10^{-3} M$ ZnCl₂; ○, $3.00 \times 10^{-3} M$ ZnCl₂; △, $1.00 \times 10^{-3} M$ ZnCl₂; $y = 2 - \bar{n}$, $x = -\log(\text{DMP}^-) + \log(\text{Zn})_t$.

not, a Tyndall effect was exhibited by each of the solutions in this region. At \bar{n} values below the point of solubility the solutions show a pronounced Tyndall effect, whereas above this point, no Tyndall effect occurs. This latter observation shows that the species are in true solution. That the solutions are not merely supersaturated is demonstrated by the observation that a precipitate forms very rapidly on mixing all solutions lying near the phase change. The solid disappears as equilibrium is approached by those solutions which have a value of \bar{n} greater than a certain minimum value.

The question arises as to whether, or not, an error is introduced into the results because of the possibly higher solubility of colloidal particles relative to massive particles. We feel that no significant error is introduced because (1) the opaque nature of the solutions indicates a relatively large particle size, (2) the massive and colloidal particles coexist at equilibrium indicating that their solubilities are the same and (3) up to a point which is close to that at which the Tyndall effect ceases, it is always possible to bring down some solid by centrifuging. Thus, at worst, any error is small.

The results when plotted as \bar{n} versus $\log \text{DMP}^-$, exhibited a dependence not only on the DMP^- concentration but also on total zinc(II) concentration, Zn_t . This dependence is implied in Fig. 2 where the results are presented in a plot of y equals $2 - \bar{n}$ versus x equals $-\log(\text{DMP}^-) + \log(\text{Zn})_t$ is given. The reason for plotting the data in this manner is discussed below.

It was found that the precipitate disappears in the region \bar{n} equals 1.22 to 1.26. With smaller \bar{n} values a precipitate is always present, with larger \bar{n} values only a clear solution is obtained. This fact, and the observed dependence of \bar{n} on Zn_t , indicates that polynuclear species are formed. Even allowing for the solubility of ZnDMP (which is small), the value of \bar{n} in the region where the precipitate disappears does not correspond to a value which is expected for the formation of only mononuclear complexes. For this latter case an integral value of \bar{n} would be obtained.

The "core plus links" treatment proposed by Sillen¹³ for the case $A_r(A_tB)_n$ was applied to the present data. The requirement that the concentration of the aquo zinc(II)

ions be negligible is fulfilled at \bar{n} values greater than one. The species $A_{r+t}B$ is the highest complex in the system and here corresponds to ZnDMP_2^- . The value t is taken equal to unity since \bar{n} for the system approaches one as \bar{n} approaches infinity. These considerations give a series of polynuclear complexes of the general formula $\text{DMP}(\text{DMPZn})_n^-$ or, as written differently, $\text{ZnDMP}_2^-(\text{ZnDMP})_n^-$. The plot shown in Fig. 2 verifies these expectations since for the $A_r(A_tB)_n$ case the experimental points should fall along a single curve when the quantity y equals $(r + t - \bar{n})/r$ is plotted versus x equals $-\log(\text{DMP}^-) + \log(\text{Zn})_t$.¹³

Equilibrium constants can be defined by

$$q_n = \frac{(\text{Zn}_{n+1}\text{DMP}_{n+2}^-)(\text{DMP}^-)^n}{(\text{ZnDMP}_2^-)^{n+1}}$$

for the reactions, $(\bar{n} + 1)\text{ZnDMP}_2^- \rightleftharpoons \text{Zn}_{\bar{n}+1}\text{DMP}_{\bar{n}+2}^- + \bar{n}\text{DMP}^-$. In terms of these constants and making the substitution u equals $(\text{ZnDMP}_2^-)/(\text{DMP}^-)$ it can be shown that

$$y = \frac{q_1u + 2q_2u^2 + 3q_3u^3 + \dots}{1 + 2q_1u + 3q_2u^2 + 4q_3u^3 + \dots} \quad (1)$$

$$x = \log(u + 2q_1u^2 + 3q_2u^3 + \dots) \quad (2)$$

Methods are given¹³ for solving for the q_n . Only when the data are highly precise is it feasible to obtain n values of u (by graphical integration) corresponding to n chosen values of y and solve simultaneous equations of type 1 for the constants. Even for the relatively simpler case of mononuclear complexes the equations have been termed "ill-conditioned"¹⁴ because of the disparity in the range of the dependent variable (\bar{n}) and the independent variable (the concentration of uncombined ligand). This means that there are a number of nearly correct solutions to the equations. The equations for the polynuclear case certainly are "ill-conditioned" to a higher degree. Because of this, a solution to the problem was obtained using the Sillen curve fitting method.¹³ In this method only two parameters, q_0 and q , need be evaluated. For the present case it was found possible to fit the data using the relationship $q_n = q_0 q^n$. This assumes a constant change given by $q_{n+1}/q_n = q$ and allows the function which gives the sum of a geometric series to be used in place of the terms for the polynuclear complexes in equations 1 and 2. Making this substitution and also making the substitution v equals qu it can be shown that

$$y = \frac{q_0v}{(1-v)^2} \frac{1 - (1-v)^2}{1 + q_0 \frac{1 - (1-v)^2}{(1-v)^2}} \quad (3)$$

Then using the procedure of Sillen, values of q_0 and q equal to 1.5 and 1.4×10^{-8} respectively were found. The solid line in Fig. 2 is the theoretical curve calculated using this value of q_0 . Except in the region where precipitate exists and the equations no longer apply, a good fit is had. For comparison purposes the dotted curve has been calculated using a value of q_0 equal to 2.0. It is seen that a discrimination between these two values can be made.

The formation constant of ZnDMP_2^- can be evaluated from the data at the point where the solid phase just disappears. For solutions in equilibrium with the solid ZnDMP it can be shown that

$$Q_2 = \frac{(\text{ZnDMP}_2^-)}{(\text{Zn}^{++})(\text{DMP}^-)^2} = \frac{u_{\text{sol}}}{K_{\text{sp}}} = \frac{v_{\text{sol}}}{qK_{\text{sp}}}$$

where u_{sol} and v_{sol} represent values of these quantities for solutions which are in equilibrium with the solid. The value of v which gives a value of y equal to 0.78 (\bar{n} equals

(13) L. G. Sillen, *Acta Chem. Scand.*, **8**, 299, 318 (1954).

(14) J. C. Sullivan, J. Rydberg and W. F. Miller, *ibid.*, **13**, 2023 (1959).

1.22) in equation 3 is 0.77. Choosing this to be equal to v_{sol} , and using those values given above for q and K_{sp} , a value of Q_2 equal to $2 \times 10^{+23}$ is calculated.

The value of q for the dotted curve in Fig. 2 is 1.8×10^{-8} and the value of v corresponding to \bar{n} equals 1.22 is 0.76. These give a value of Q_2 equal to $1.6 \times 10^{+23}$. This represents a relative change of only 20% in Q_2 and gives some indication of the precision of this quantity.

It should be noted at this point that although q and a value of v obtained from equation 3 are used to calculate Q_2 , the resulting value of Q_2 is entirely independent of any arbitrary relationship which is assumed between the q_n just as long as the assumed relationship allows the data to be reproduced. It is possible to obtain the same value of v_{sol} (i.e., v_{sol}/q) at n equals 1.22 directly from the data by a graphical integration. The use of equation 3 is merely a convenience in attaining this goal.

Discussion

Mononuclear Complexes.—As was also found for the nickel(II) complexes, the formation constants of the manganese(II) and zinc(II)-DMP complexes are unusually large relative to those constants found for the complexes with ligands possessing only oxygen or nitrogen donor atoms. For example, the formation constants of the bis ethylenediamine complexes are of the order of 10^{+5} and 10^{+11} for Mn(II) and Zn(II), respectively,¹⁵ compared to the values of 10^{+10} and 10^{+23} for the analogous DMP complexes found here. The value of E_r for the bis DMP complexes is calculated to be -65.3 kcal./mole. This represents a difference in the free energies of formation of MnDMP₂⁼ and ZnDMP₂⁼ which is much greater than that for any other ligand so far investigated. For the mono DMP complexes E_r is about -59 kcal./mole. This is comparable to the value for the tris 1,10-phenanthroline complexes.⁴ For the bis mercaptoacetato complexes E_r has a value of -57.8 kcal.³ The proximity of this latter value to that found for the mono DMP complexes suggests that E_r is diagnostic of the number of coordinated sulfur atoms. Using also the value -52.4 kcal. for the mono mercaptoacetato complexes,³ a plot of E_r versus the number of coordinated sulfur atoms gives a shallow curve which closely approximates a straight line. The slope of this line is approximately -5 kcal./mole of sulfur and can be compared to a value of -2.6 kcal./mole of aliphatic nitrogen.⁴ The increase of E_r in the order O<N<S is also in the same order of increasing polarizability of these donor atoms. The increase in the bond strength of the zinc(II) complex relative to that for the manganese(II) complex in the order given is probably due to the induction of a greater polarization of the donor atoms in this same order under the influence of the greater effective charge of the zinc(II) ion.¹⁶ In the limit this would represent a greater degree of σ bonding in zinc(II) complexes relative to those of manganese(II) in the order O<N<S. Some evidence that π bonding has little influence in bringing about this increase is given by the absorption spectrum of NiDMP₂⁼⁹ which shows that at least in this case σ bonding is predominant.

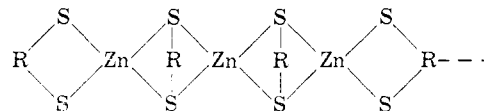
(15) J. Bjerrum, G. Schwarzenbach and L. G. Sillen, "Stability Constants," Part I, Special Publication No. 6, The Chemical Society, London, 1957.

(16) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," J. Wiley and Sons, Inc., New York, N. Y., 1958.

The formation constant of NiDMP₂⁼ (Q_2 equals $6 \times 10^{+22}$)⁹ is smaller than that of ZnDMP₂⁼. This inversion in the usually observed order of stabilities has been noted with other mercapto-Ni(II) complexes.^{3,17-19} The explanation for this behavior lies in the fact that in a tetragonal field the spin-free nickel(II) ion can lose up to one-third of the ligand field stabilization energy which would be obtained in the octahedral field.¹⁶ A gain in stabilization energy is had by going over to the spin-coupled configuration but much of this is off-set by the electron pairing energy. Thus, only with a most highly polarizable ligand (or when π bonding contributes appreciably) will the stability of a diamagnetic square planar nickel(II) complex occupy a position relative to the stability of the corresponding zinc(II) complex that is obtained with the usual paramagnetic complexes.

Polynuclear Complexes.—The relationship $q_n + 1/q_n = q$ which was used to fit a curve to the Zn(II)-DMP data describes a series which converges the slowest of any which have been proposed for these purposes.^{3,13} This means that a relatively large number of species coexist and calculations show that complexes with up to seven and eight zinc(II) ions are present in appreciable concentration at the point where the solid phase forms. This calculation is in accordance with the low value of \bar{n} (1.22) which is observed at this point. The relatively slow decrease in stability with an increasing number of zinc ions is probably a consequence of the fact that the core, ZnDMP₂⁼, is charged but the link, ZnDMP, is neutral. Thus, charge does not build up with increasing complexity to bring about a rapid decrease in stability as was found with the nickel(II)-mercaptoacetato system. In this latter case the link is NiRS₂⁼ and the complexes above Ni₄RS₆⁼ were found to exist only in minor concentrations.⁸

Analogous to the structures proposed for the polymeric nickel(II)-mercapto complexes,⁶⁻⁸ the polynuclear zinc(II) complexes likely have the sulfur bridged structure represented by



In the nickel(II)-DMP system only the lowest polynuclear complex of this series (the dimer) is observed, and apparently higher complexes with additional "links" of NiDMP are unstable with respect to disproportionation to NiDMP₂⁼ and the highly insoluble NiDMP.

Polynuclear complex formation with mercaptoide occurs more readily with nickel(II) ions than with zinc(II) ions. The constant for the equilibrium $2\text{Ni}^{++} + 3\text{DMP}^- \rightarrow \text{Ni}_2\text{DMP}_3^-$ most likely²⁰

(17) G. E. Cheney, H. Freiser and Q. Fernando, THIS JOURNAL, **81**, 2611 (1959).

(18) Q. Fernando and H. Freiser, *ibid.*, **80**, 4928 (1958).

(19) G. E. Cheney, Q. Fernando and H. Freiser, *J. Phys. Chem.*, **63**, 2055 (1959).

(20) The formula Ni₂DMP₃OH⁻ has been assigned to the dimeric nickel(II) complex on the basis of the pH behavior of the system.⁹ However, comparison with the ethanedithiol system¹ indicates that the OH⁻ term probably arises from the ionization of one of the alcohol groups of a coordinated DMP molecule. Most likely this group is not ionized in the solution at the lowest pH studied in the earlier work,⁹

has a value of $4 \times 10^{+41}$. The analogous constant for the formation of $Zn_2DMP_3^-$ is equal to the product $q_0qQ_2^2ZnDMP_3^-$ and calculation yields a value of $4 \times 10^{+40}$ for this constant. Although this latter value can be considered to be only an estimate, the relative difference between it and the value for the nickel(II) complex is sufficiently great to be significant. Further evidence that the polynuclear nickel(II) complexes are more stable is suggested by the relative solubilities of the neutral species. The solid phase can be considered to be a polynuclear complex with an infinite value of n . The species $ZnDMP$ has a solubility product of about 10^{-18} and even dissolves to a slight extent as the undissociated species. With $NiDMP$, on the other hand, the solubility product is of the order 10^{-20} – 10^{-21} , and there is no evidence that the undissociated species is soluble to an appreciable extent under equilibrium conditions. And finally, mercaptoacetate ions form a "core plus links" polynuclear series with nickel(II), but there is no evidence that this ligand forms polynuclear complexes with zinc(II).

Spectral evidence^{3,6,8,9} indicates that $dd-\pi$ bonding is important in the polynuclear nickel(II) complexes. The π bonding acts to reduce the positive charge that would otherwise exist on the multiply bonded sulfur atoms and apparently has and the complex is probably present as $Ni_2DMP_3^-$. Recalculating the data on this basis gives a value of $4 \times 10^{+41}$ for the formation constant of this species.

a greater effect on the square planar nickel(II) complexes than in the (presumably) tetrahedral zinc(II) complexes. Both platinum(II) and palladium(II) ions, which like nickel(II) also have the d^8 electron configuration, form sulfur bridged complexes and π bonding has been suggested to be important in these complexes.^{21,22} Indeed, the MS_2M ring is probably an "inorganic aromatic ring".²²

The manganese(II)-DMP system does not form polynuclear complexes, at least under the present experimental conditions. Also, it was found that the neutral species, $MnDMP$, has quite high solubility. These observations give further support to the suggestion that π bonding is important in the polynuclear species. With the manganese(II) ion, the d shell is only half filled and the tendency for dative π bonding is much less.

It is interesting that complexes with such a large number of zinc ions are stable in solution. Preliminary experiments indicate that the alcohol group of the DMP molecule is important in bringing about the solution stability of these polynuclear zinc(II) species. With ethanedithiol as the ligand the benefit of the solvation of the OH group is not had and the solid phase remains dissolved to much higher n values than are observed with DMP.

(21) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 2363 (1953).

(22) J. Chatt and F. A. Hart, *ibid.*, 2807 (1960).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK, AND STATE UNIVERSITY OF NEW YORK, LONG ISLAND CENTER, OYSTER BAY, NEW YORK]

The Kinetics of the Oxidation of the Iron(II) Ion by the Tris-(1,10-phenanthroline)-iron(III) Ion¹

BY N. SUTIN AND B. M. GORDON

RECEIVED JUNE 17, 1960

The kinetics of the oxidation of the iron(II) ion by tris-(1,10-phenanthroline)-iron(III) ion in 0.50 F $HClO_4$ has been studied using a rapid-mixing and flow technique. The reaction was shown to be first order with respect to each reagent and the specific rate constant determined to be $3.70 \times 10^4 F^{-1} \text{sec.}^{-1}$ at 25.0°. The rate constant increased slightly with decreasing acid concentration. The activation energy calculated from the temperature dependence of the rate constant is 0.8 ± 0.2 kcal./mole and the entropy of activation is -37.2 cal./mole deg. The oxidation of ferrous ion by the tris-(1,10-phenanthroline)-iron(III) ion is compared with other ferrous ion oxidations and the existence of a linear relation between the free energies of activation and the standard free energy changes of the oxidation-reduction reactions is shown.

Introduction

The iron(II)-iron(III) exchange reaction has been studied extensively in an attempt to elucidate some of the features of electron transfer in aqueous solution. Silverman and Dodson² studied the reaction between the uncomplexed cations and found the bimolecular rate constant to be $4.0 F^{-1} \text{sec.}^{-1}$ at 25.0°. The complexing of the ferric ion by halides^{2,3} increases the specific rate of exchange by a factor of ten, while complexing by hydroxide ion increases the specific rate a thousandfold. The results do not yield a satisfactory interpretation of the reaction mechanism. There is also some

doubt as to whether the ferric halides are inner or outer sphere complexes.

Eichler and Wahl⁴ used both radioactive tracers and optical activity methods in a study of the tris-(1,10-phenanthroline)-iron(II)-tris-(1,10-phenanthroline)-iron(III) electron transfer reaction. Both ions of this system are definitely inner sphere complexes in which the ligands are not readily substituted. The optical activity method resulted in a lower limit of $k = 10^2 F^{-1} \text{sec.}^{-1}$ for the exchange at 25°. The tracer experiments are more ambiguous because of the possibility of separation-induced exchange. Assuming 50% separation-induced exchange, Eichler and Wahl placed a lower limit of $k = 10^6 F^{-1} \text{sec.}^{-1}$ on the bimolecular rate constant at 0°.

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

(3) J. Hudis and A. C. Wahl, *THIS JOURNAL*, **75**, 4153 (1953).

(4) E. Eichler and A. C. Wahl, *ibid.*, **80**, 4145 (1958).