working currently to explore these factors further.

Acknowledgments.—The authors gratefully acknowledge the assistance of Mrs. Elisabeth C. Colthup in the preparation of the complexes and Mr. Norman B. Colthup in the design of the high temperature infrared cell and in the interpretation of spectra. The authors also are indebted to Dr. G. Warren Kennerly for helpful discussions.

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

The Reactions of Nickel(II) with 2,3-Dimercapto-1-propanol[1]

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A spectrophotometric investigation of the reactions in alkaline solutions of 2,3-dimercapto-1-propanol with nickel(II) ions has revealed the existence of two complexes, $Ni_2(DMP)_3OH^{=}$ and $Ni(DMP)_2^{=}$. The first of these complexes is brown and the second is green. The constants for the reactions $2Ni^{++} + OH^- + 3DMP^{=} \rightleftarrows Ni_2(DMP)_3OH^{=}$ and $Ni^{++} + 2DMP^{=} \rightleftarrows Ni(DMP)_2^{=}$ are calculated to be $4 \times 10^{+45}$ and $6 \times 10^{+22}$. The absorption spectra of the complexes have been determined and are discussed. The Ni–S bond appears to be predominantly σ.

The high stability of complexes of heavy metals with 2,3-dimercapto-1-propanol (British Anti Lewisite, BAL) has been recognized since its preparation. Little, however, is known quantitatively of the nature and stabilities of the complexes that are formed in solution. As one of a series of investigations into the nature of metal ion–mercaptide complexes a study was undertaken of the nickel(II)–2,3-dimercapto-1-propanol reactions. Hereafter, in this paper the latter will be referred to as DMP.

Zuman and Zumanova[2] have investigated by means of polarometric titrations the nature of the compounds formed by many heavy metal ions with DMP. They report that with nickel(II) an insoluble compound with a 1:1 ratio of metal to DMP is formed in slightly acid and alkaline solutions. They state also that in ammoniacal solutions a soluble complex is formed which is indicated to have a ratio of 1:1.5. Pribil and Roubal[3] report that nickel(II) reacts in alkaline solutions containing excess DMP to form an olive green complex.

The formation of the insoluble compound prevents the use of the conventional *p*H-titration method of determining stability constants. In the present work, the equilibria involving the soluble complexes which exist in alkaline solutions were investigated spectrophotometrically. It was found that the olive-green solutions are mixtures of two complexes, a brown one and a green one. Their absolute stabilities were obtained from the results of experiments in which DMP and ethylenediaminetetraacetate ions were allowed to compete for limited amounts of nickel ions.

In this connection, Pribil and Roubal[3] who have proposed the use of DMP in chelatometric titrations of mixtures of metal ions report that DMP does not replace EDTA bound to Ni(II), although the EDTA is replaced readily by DMP with the other divalent transition metal complexes. This seeming anomaly has been demonstrated in the present investigation to be due to the effect of rates of reaction. The soluble Ni(II)–DMP complexes were found to have very great stability, presumably, in line with those of the other transition metals.

Experimental

2,3-Dimercapto-1-propanol, J. T. Baker Chemical Company, was vacuum distilled. During the distillation dry, high purity nitrogen was bled into the system to prevent bumping. The fraction distilling at 74–76° (1 mm.) was collected and stored under nitrogen at −10°. Air-free aqueous solutions of DMP were prepared by weight from the redistilled reagent. Solutions which were 0.02 *M* or less in DMP were prepared by dissolution of the reagent in air-free water. Solutions which were 0.05 to 0.10 *M* were prepared by adding an equimolar amount of air-free sodium hydroxide solution to the weighed reagent and diluting with the necessary amount of de-aerated water.

Nickel nitrate solution, 0.516 *M*, was prepared from the reagent-grade material and standardized by the cyanide method.[4] Solutions for use in the experiments were prepared by dilution of this stock solution.

Disodium dihydrogenethylenediaminetetraacetate$\cdot 2H_2O$ solution, 0.1000 *M*, was prepared by weight from the Fisher reagent. Analysis[5] against a standard zinc solution showed this product to have a purity of 100 ± 0.5%.

Ammonia stock solutions were prepared from the redistilled reagent.

Redistilled water was used throughout.

Solutions of DMP, especially those which are alkaline, are extremely air-sensitive. For this reason rigorous precautions were taken to exclude air during the preparation and equilibration of all DMP solutions. The sealed bottle-syringe technique described previously[6] was employed in preparing solutions of the complexes.

Preliminary experiments revealed no essential differences in the equilibrium properties of Ni(II)–DMP mixtures in either sodium hydroxide solutions or ammonia buffers. Equilibrium was slow to be attained but appeared to be reached faster in the less alkaline solutions. For this reason most of the final measurements were made in ammoniacal buffers, 0.100 *M* in NH_4Cl and at *p*H 9.27, 9.88 or 10.14. The total nickel(II) concentration, Ni_t, was varied from 0.00052 to 0.00206 *M* and the total DMP concentration, DMP_t, was varied from 0.00050 to 0.0103 *M*. All solutions were equilibrated in a water-bath at 30.0 ± 0.5°. Twenty-

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[1] Presented at the 135th National Meeting of the American Chemical Society, Boston, Massachusetts, April, 1959. Financial assistance for this work was made available by a grant from the National Science Foundation.

[2] P. Zuman and R. Zumanova, *Tetrahedron*, **1**, 289 (1957), and references cited therein.

[3] R. Pribil and Z. Roubal, *Coll. Czech. Chem. Communs.*, **19**, 1162 1954); *Chem. Listy*, **48**, 818 (1954).

[4] I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, 2nd Rev. Ed., Interscience Publishers, Inc., New York, N. Y., 1947.

[5] G. Schwarzenbach, "Die Komplexometrische Titrationen," Ferdinand Enke, Stuttgart, 1955.

[6] D. L. Leussing and I. M. Kolthoff, THIS JOURNAL, **75**, 3904 (1953).

four to thirty-six hours were required for equilibration. The ionic strength in these solutions was about 0.12 ± 0.01.

The Ni(II)–DMP–EDTA mixtures also were prepared in ammonia buffers. Two sets of experiments were run, one in which $\mathrm{Ni_t}$ was 0.00103 M at pH 9.20 and the other in which $\mathrm{Ni_t}$ was 0.00206 at pH 9.85. In both sets the total EDTA concentration was held at 0.0100 M and $\mathrm{DMP_t}$ was varied. A period of seven to eight days was required for equilibration at 30°. About the same period of time was required when either the Ni(II)–EDTA complex was decomposed by DMP or when the Ni–DMP complex was decomposed by EDTA. The ionic strength in the solutions at pH 9.20 was about 0.14 and at pH 9.85 was about 0.18.

The pH measurements were made with a Beckman Model G pH meter with glass and saturated calomel electrodes. The electrode system was standardized at 30° against National Bureau of Standards Borax, 0.010 M, pH 9.14.

The usual fiber type reference electrode gives reproducible results when measurements are made on DMP solutions in ammonia buffers. However, when measurements are made on solutions in which the DMP system is the principal buffering agent, readings which change erratically are observed. This condition is cured when a salt bridge with ground glass terminal plugs making connection to an external reference electrode is used.

The proton dissociation constants of DMP were evaluated by the pH-titration method. DMP behaves as a dibasic acid in the pH range investigated. Titration with 1.00 M KOH of 50.0 ml. of 0.01136 M DMP to which was added 2.08 ml. of 2.5 M KCl yielded results from which Q_{1a} and Q_{2a} were calculated in terms of hydrogen ion activity to be 2.4×10^{-9} and 2.6×10^{-11} at 30°. Correction was made for unreacted hydroxide in computing the quotients. The undissociated, mono-, and di-ionized forms of DMP will henceforth be referred to as $\mathrm{DMPH_2}$, $\mathrm{DMPH^-}$ and $\mathrm{DMP^{=}}$ when it is necessary to distinguish between these in the text.

Spectrophotometric measurements were made with a Cary Model 14 Spectrophotometer which was equipped with a thermostated cell block. The absorption spectra were determined under air-free conditions. To do this, the necks of the usual cylindrical cells were fitted with gum rubber tubing which was closed on the outer end. The cells were flushed with nitrogen passed through by means of hypodermic needles inserted in the tubing. After flushing, solutions were introduced into the cells by means of syringes. The spectra of solutions obtained in this way showed no changes after several hours. Spectra of solutions in contact with air become more brown with time.

Results and Discussion

On first adding an air-free Ni(II) solution to an air-free alkaline DMP solution an intense brown color is assumed by the mixture. This slowly fades and the solution becomes more or less green depending on the conditions. The color of the brown complex predominates in the equilibrium mixture at ratios of $\mathrm{DMP_t}$ to $\mathrm{Ni_t}$ less than two to one. At ratios greater than two to one a sharp change occurs in the character of the absorption with the green color becoming dominant. Vestiges of the brown color disappear as the ratio of $\mathrm{DMP_t}$ to $\mathrm{Ni_t}$ becomes even greater. The brown complex has an absorption maximum in the visible region at 452 mμ and the green complex has maxima at 475 and 610 mμ.

A precipitate, either NiDMP or $\mathrm{Ni(OH)_2}$, is obtained in the ammonia–ammonium chloride buffers and potassium hydroxide solutions when the ratio of $\mathrm{DMP_t}$ to $\mathrm{Ni_t}$ drops below about 1.5:1. No precipitate is obtained when the ammonium salt is omitted from solutions at least 0.5 M or greater in ammonia.

In complexes in which at least two mercaptide groups are coördinated, nickel(II) assumes the square-planar configuration of coördination number four.[7-9] An upper limit of two molecules of DMP per Ni(II) is thus set if each thiol in the DMP molecule ionizes and coördinates. This consideration coupled with the above qualitative observations suggests that the green complex has the formula, $\mathrm{Ni(DMP)_2^{=}}$ and that the brown complex has a lower ratio of DMP to Ni(II).

The lower complex is indicated to be a hydroxy complex. Compelling evidence in favor of this is the observed effect of ammonium salts on the stability of the lower complex is ammoniacal solutions. A solution of 0.00206 M Ni(II), 0.00272 M DMP in 0.60 M ammonia assumes a deep brown color which is stable. The absorbance at 452 mμ is measured to be 3.02 cm.$^{-1}$. In a similar solution which also contains 0.10 M ammonium chloride, the brown complex disproportionates forming insoluble NiDMP and green $\mathrm{Ni(DMP)_2^{=}}$ in the supernate.

Anticipating the conclusions in order to facilitate the presentation, the formulation of the lower complex which best fits the data is $\mathrm{Ni_2(DMP)_3OH^{\equiv}}$. The evidence for this is discussed further below.

On the basis of $\mathrm{Ni_2(DMP)_3OH^{\equiv}}$ and $\mathrm{Ni(DMP)_2^{=}}$ the equations (1), (2) and (3) may be set up in terms of the known and measured quantities for each solution.[10]

$$[\mathrm{Ni}]_\mathrm{t} = 2[\mathrm{Ni_2(DMP)_3OH^{\equiv}}] + [\mathrm{Ni(DMP)_2^{=}}] \quad (1)$$

$$[\mathrm{DMP}]_\mathrm{t} = [\mathrm{DMP}]_\Sigma + 3[\mathrm{Ni_2(DMP)_3OH^{\equiv}}] + 2[\mathrm{Ni(DMP)_2^{=}}] \quad (2)$$

$$A_\lambda = \epsilon_{\mathrm{d},\lambda}[\mathrm{Ni_2(DMP)_3OH^{\equiv}}] + \epsilon_{2,\lambda}[\mathrm{Ni(DMP)_2^{=}}] \quad (3)$$

The subscript Σ in the above equations and those below indicates the sum of the concentrations of the variously ionized uncomplexed forms of the species so designated.

Another equation is obtained from the equilibrium quotient, $Q_{\mathrm{d},2}$, equal to $[\mathrm{Ni(DMP)_2^{=}}]^2/[\mathrm{Ni_2(DMP)_3OH^{\equiv}}][\mathrm{DMPH^-}]$ for the reaction

$$\mathrm{Ni_2(DMP)_3OH^{\equiv}} + \mathrm{DMPH^-} \rightleftarrows 2\mathrm{Ni(DMP)_2^{=}} + \mathrm{H_2O}$$

From these relationships, the equation can be derived that

$$A_\lambda/[\mathrm{Ni(DMP)_2^{=}}] = \epsilon_{2,\lambda} + \epsilon_{\mathrm{d},\lambda}[\mathrm{Ni(DMP)_2^{=}}]/Q_{\mathrm{d},2}[\mathrm{DMPH^-}]$$

At each pH, the data for the points where $[\mathrm{DMP}]_\mathrm{t} > 2[\mathrm{Ni}]_\mathrm{t}$ give essentially a straight line for a plot of $\mathrm{A}_{452}/[\mathrm{Ni}]_\mathrm{t}$ *versus* $[\mathrm{Ni}]_\mathrm{t}/([\mathrm{DMP}]_\mathrm{t} - 2[\mathrm{Ni}]_\mathrm{t})$. The plots for each buffer are illustrated in Fig. 1. The lines for the three buffers converge to a value on the intercept of $\epsilon_{2,452}$ equal to 104 ± 1 M^{-1}cm.$^{-1}$. Values of the slopes are 8, 5 and 3 at pH 9.28, 9.88 and 10.14. The estimated uncertainty is about ± 1 unit in the slope. For such plots to be linear indicates that in the region $[\mathrm{DMP}]_\mathrm{t} > 2[\mathrm{Ni}]_\mathrm{t}$, $[\mathrm{Ni(DMP)_2^{=}}] \sim [\mathrm{Ni}]_\mathrm{t}$ and $[\mathrm{DMP}]_\Sigma \sim [\mathrm{DMP}]_\mathrm{t} - 2[\mathrm{Ni}]_\mathrm{t}$.

Similar plots for the measurements at 550 and 610 mμ also yield straight lines but because of smaller spectral changes give less precise slopes.

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(7) J. J. Draney and M. Cefola, THIS JOURNAL, **76**, 1975 (1954).

(8) J. M. White, T. J. Weismann and N. C. Li, *J. Phys. Chem.*, **61**, 126 (1957).

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

(10) These equations assume that the concentrations of the ammino nickel(II) complexes are negligible. The formation constants given below verify the validity of this assumption in solutions when the ratio of $\mathrm{DMP_t}$ to $\mathrm{Ni_t}$ is greater than 1:1.

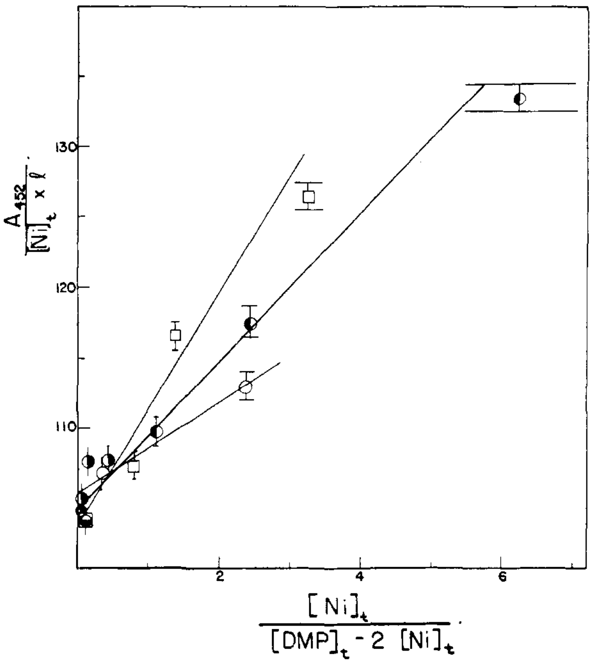

Fig. 1.—The absorbance of Ni(II) solutions as a function of the concentration of excess DMP: □, *p*H 9.27, 0.00206 *M* $\mathrm{Ni_t}$ (except lowest point which was 0.00103 *M*): ◑, *p*H 9.88, 0.00052 *M* $\mathrm{Ni_t}$; ◒, *p*H 9.88, 0.00103 *M* $\mathrm{Ni_t}$; ◐, *p*H 9.88, 0.00206 *M* $\mathrm{Ni_t}$; ○, *p*H 10.14, 0.00206 *M* $\mathrm{Ni_t}$. The error limits were drawn on the basis of ±1% uncertainty in A_{452} and $\mathrm{DMP_t}$.

For the data in the region $[\mathrm{DMP}]_t<2[\mathrm{Ni}]_t$ the approximation can be made that $[\mathrm{DMP}]_\Sigma$ is negligible compared with the concentrations of $\mathrm{Ni_2(DMP)_3OH^{\equiv}}$ and $\mathrm{Ni(DMP)_2^{=}}$. This assumption is shown to be valid by the value of $Q_{d,2}$ which is obtained below. This assumption allows equations 1 and 2 to be solved simultaneously for the concentrations of the complexes in each solution. The value of $\epsilon_{d,452}$ then can be obtained from equation 3 using the measured absorbance at 452 mμ and a value of $\epsilon_{2,452}$ equal to 104. The experimental details and results of such calculations are presented in Table I.

Table I

Values of Absorbance and Calculated Extinction Coefficients of $\mathrm{Ni_2(DMP)_3OH^{\equiv}}$ for the Region $[\mathrm{DMP}]_t$ $<2[\mathrm{Ni}]_t$

*p*H	$\mathrm{Ni_t}$	$\mathrm{DMP_t}$	A_{452}, cm.$^{-1}$	$\epsilon_d \times 10^{-3}$
9.27	0.00206	0.00382	1.098	3.4
9.88	.000516	.000883	0.464	3.0
9.88	.00103	.00155	1.357	2.7
9.88	.00103	.00181	1.073	4.1
9.88	.00206	.00387	0.945	3.1
9.88	.00206	.00398	0.649	3.3
10.14	.00206	.00398	0.638	3.2
			Avg.	3.1 ± 0.2

It can be seen in the data of Table I that with the exception of one point the calculated values of $\epsilon_{d,452}$ are reasonably constant and independent of *p*H. Omitting the value $4.1 \times 10^{+3}$, an average value of $3.1 \times 10^{+3}\ M^{-1}\mathrm{cm.}^{-1}$ is calculated. Using this value and those for the slopes of Fig. 1 and, also, correcting for the ratio $[\mathrm{DMPH^-}]/[\mathrm{DMP}]_\Sigma$, values of $Q_{d,2}$ are calculated to be $5 \pm 0.7 \times 10^{+2}$, $8 \pm 1.7 \times 10^{+2}$ and $14 \pm 4 \times 10^{+2}$ at *p*H 9.28, 9.88 and 10.14.

One solution was made up to contain 0.00103 *M* Ni(II), 0.00904 *M* DMP in 0.10 *M* KOH (A_{452} equaled 0.135 cm.$^{-1}$ after 68 hours). A value of $Q_{d,2}$ equal to $19 \pm 3 \times 10^{+2}$ was calculated from this result ($p\mathrm{H_{calcd}}$ equals 12.70).[11]

A plot similar to that in Fig. 1 was made based on the postulated composition, $\mathrm{NiDMPOH^-}$, for the lower complex. For a 1:1 complex, a plot of $A/[\mathrm{Ni}]_t$ *versus* $1/[\mathrm{DMP}]_t - 2[\mathrm{Ni}]_t$ should yield a straight line. Thus, only by considering the effect of $\mathrm{Ni_t}$ on the slope is it possible to distinguish the monomer from the dimer. Because of experimental variations a clearcut distinction between the two models is not had with the present data. However, the points in Fig. 1 do give less deviation from a straight line than when plotted for the 1:1 case. Also, for the 1:1 plot the points at the two lower nickel concentrations show a definite tendency to fall below the straight line passed through points at the highest nickel concentration. In Fig. 1, on the other hand, the points for the low nickel concentrations scatter about equally between high and low deviations.

Evidence which more clearly favors the dimer is obtained from the absorption spectra of ammoniacal solutions from which the ammonium chloride was omitted. In these solutions it is possible to achieve an excess of nickel ions over DMP without precipitation. The formation constant for $\mathrm{Ni_2(DMP)_3OH^{\equiv}}$ given below (or that calculated for $\mathrm{NiDMPOH^-}$) shows that the DMP should be quantitatively combined as the lower complex even when high concentrations of ammonia are present to compete for the nickel ions. The concentration of the lower complex then can be calculated directly from the amount of DMP present. The dotted curve in Fig. 2 gives the absorption spectrum calculated on the basis of $\mathrm{Ni_2(DMP)_3OH^{\equiv}}$ from the absorption of a solution in which the ratio of Ni(II) to DMP was very close to 2:3 (*p*H 9.88). The circles are values calculated from the spectrum of 0.00206 *M* Ni(II), 0.00050 *M* DMP in 1.08 *M* ammonia. The agreement between the two sets of data is very good. Calculations assuming the formula NiDMPOH leave the dotted curve of Fig. 2 almost unchanged in shape and position throughout the visible region. However, the extinction coefficients calculated from the data obtained from the excess nickel solution are only one-third the value calculated on the basis of $\mathrm{Ni_2(DMP)_3OH^{\equiv}}$. A very great discrepancy thus results when a 1:1 complex is assumed.

Calculations also were made assuming the lower complex to have the composition $\mathrm{Ni_2(DMP)_3^{=}}$ or $\mathrm{Ni_2(DMP)_3(OH)_2^{\equiv}}$. Both of these models give

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[11] The value of γ_{OH} was taken equal to 0.79 and that of K_w equal to 1.4×10^{-14} in making the calculation. The DMP was added as the monosodium salt and the concentration of hydroxide was corrected for the amount required to neutralize the second hydrogen ion. Equations 1 and 3 were used to obtain the concentrations of the complexes with ϵ_d set equal to 3.1×10^{-3}.

a considerable variation in the calculated apparent constants over the pH range investigated. Thus, the best description of the behavior of the system is given by $Ni_2(DMP)_3OH^{=}$.

The values of $Q_{d,2}$ reported above show an increase with increasing pH. The rate of increase is not very great being about fourfold for a twenty-five hundred-fold decrease in pH.[12] The effect may be real or it may be caused by a slight systematic error. If real, this can be explained readily by the ionization of one of the OH groups of DMP. The absence of changes in the absorption spectra does not rule out the possibility that the effect is real but indicates that the group which is being affected is not coördinated to the central metal ion. This is analogous to the negligible spectral effects which occur with the ionization of the proton on the uncoördinated carboxylic acid group of Cr(III)(H_2O)EDTAH.[13] Because of uncertainty about the nature of the effect an average value of $12 \times 10^{+2}$ is assumed for $Q_{d,2}$ in calculations below.

The details and results of the competition experiments with EDTA are presented in Table II. The DMP concentration in the solutions was sufficiently high so that the amount of $Ni_2(DMP)_3OH^{=}$ in the equilibrium solutions can be neglected as far as the mass relationships are concerned. However, sufficient $Ni_2(DMP)_3OH^{=}$ was present to affect the absorbance measurements. To minimize this effect calculations were made from the absorbance values at 610 mμ. The equations used to calculate the results are

$$[Ni]_t = [Ni(DMP)_2^{=}] + [NiY^{=}]$$
$$[DMP]_t = [DMP)_\Sigma + 2[Ni(DMP)_2^{=}]$$
$$[Y]_t = [Y]_\Sigma + [NiY^{=}]$$
$$A_{610} = \epsilon_{d\ 610}[Ni_2(DMP)_3OH^{=}] + \epsilon_{2\cdot 610}[Ni(DMP)_2^{=}] + \epsilon_{NiY^{=}\ 610}[NiY^{=}]$$

Values of the extinction coefficients at 610 mμ are 670, 78 and 9.5 M^{-1}cm.$^{-1}$ for $\epsilon_{d\text{-}610}$, $\epsilon_{2\text{-}610}$ and $\epsilon_{NiY^{=}\text{-}610}$. The correction for the effect of $Ni_2(DMP)_3OH^{=}$ was made by successive approximations: first its contribution was neglected in order to evaluate approximately the concentrations of $NiY^{=}$, $Ni(DMP)_2^{=}$, Y_Σ and DMP_Σ in the above equations, then from $Q_{d,2}$ and $\epsilon_{d\text{-}610}$ the approximate concentration and absorbance of $Ni_2(DMP)_3OH^{=}$ were calculated. The observed absorbance at 610 mμ was corrected for this latter and better values of the concentrations of the other four components then were obtained. Only two or three cycles were sufficient to attain constant values.

Calculated values of $Q'_{y,2}$ for the equilibrium

$$NiY^{=} + 22DMP_\Sigma \rightleftarrows Ni(DMP)_2^{=} + Y_\Sigma$$

also are given in Table II. The invariance of the values at each pH further supports the conclusions reached above that the green complex has the composition $Ni(DMP)_2^{=}$. Values of $Q_{y,2}$ for the equi-

$$NiY^{=} + 2DMP^{=} \rightleftarrows Ni(DMP)_2^{=} + Y^{-4}$$

librium are then calculated to be $2.4 \times 10^{+5}$ at pH 9.20 and $1.4 \times 10^{+5}$ at pH 9.82 using the values given above for the proton dissociation of DMP and 10.24 for pK_{4a} of EDTA.[14] The difference in ionic strengths between the solutions has an effect on the constants which is smaller than the observed differences. For this reason, corrections for ionic strength are neglected and a value of $1.9 \times 10^{+5}$ is chosen as the average for equilibrium 3.

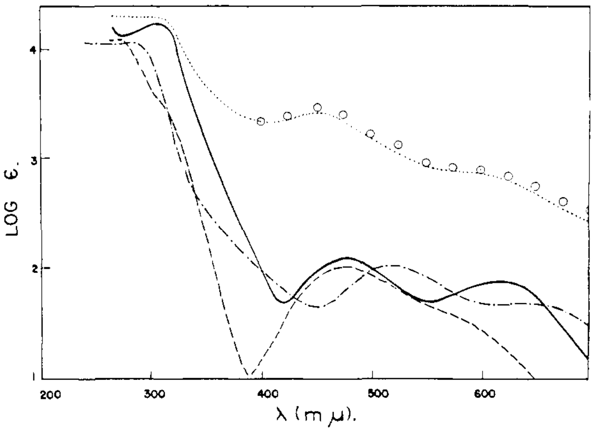

Fig. 2.—The absorption spectra of some Ni(II)–mercaptides: ———, $Ni(DMP)_2^{=}$; ----, $Ni(cysteinate)_2^{=}$; – · – ·, $Ni(thioglycolate)_2^{=}$; . . . ., $Ni_2DMP_3OH^{=}$ (0.00103 M Ni_t, 0.00155 M DMP_t, pH 9.95); O, 0.00206 M Ni_t, 0.00050 M DMP_t, 1.08 M NH_3.

TABLE II

THE COMPETITION OF ETHYLENEDIAMINETETRAACETATE IONS AND 2,3-DIMERCAPTO-1-PROPANOL FOR NICKEL(II)

Total Na_2H_2EDTA = 0.0100 M; t = 30°; all concentrations are expressed in moles per liter

Ni_t	DMP_t	NH_4Cl_t	NH_{3t}	pH	A_{610}, cm.$^{-1}$	$Q'_{y,2}$
0.00103	0.00818	0.060	0.100	9.20	0.0760	$2 \times 10^{+3}$
.00103	.00614	.060	.100	9.20	.0728	$4.0 \times 10^{+3}$
.00103	.00511	.060	.100	9.20	.0680	$3.4 \times 10^{+3}$
.00206	.00766	.100	.60	9.82	.154	$1.0 \times 10^{+4}$
.00206	.00565	.100	.60	9.82	.143	$1.2 \times 10^{+4}$
.00206	.00479	.100	.60	9.82	.131	$1.2 \times 10^{+4}$
.00206	.00383	.100	.60	9.82	.115	$1.3 \times 10^{+4}$

The formation constant Q_2 for the reaction is

$$Ni^{++} + 2DMP^{=} \rightleftarrows Ni(DMP)_2^{=}$$

calculated to be $6 \times 10^{+22}$ using $3.2 \times 10^{+17}$ for the formation constant of $NiY^{=}$ at 30°, $\mu = 0.10$.[15]

The formation constant Q_d for the reaction

$$2Ni^{++} + 3DMP^{=} + OH^{-} \rightleftarrows Ni_2(DMP)_3OH^{=}$$

then is calculated to be $4 \times 10^{+45}$ using γ_{OH} equal to 0.8 in order to express the constant purely on a molarity basis.

The value of Q_2 is about the largest tabulated[16] for the formation of a nickel(II) complex in which the change in the number of particles for reaction is minus two (neglecting water). Comparable values are given for the formation of bis-dimethylglyoxime nickel(II) and bis-(8-hydroxyquinoline)-nickel(II), but these are neutral complexes and their stabilities were determined in dioxane rich–water

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[12] With the model $NiDMPOH^{-}$ the drift with pH is even greater. The apparent constants which are calculated using a value of $\epsilon_{1\text{-}452}$ equal to 2.5×10^{-3} M^{-1} cm.$^{-1}$, are $2.0 \times 10^{+5}$, $3.3 \times 10^{+5}$, $4.7 \times 10^{+5}$, $16 \times 10^{+5}$ at pH 9.28, 9.88, 10.14 and 12.70.

[13] Chr. K. Jorgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

[14] F. F. Carini and A. E. Martell, THIS JOURNAL, **75**, 4810 (1953).

[15] V. L. Hughes and A. E. Martell, *J. Phys. Chem.*, **57**, 694 (1953).

[16] J. Bjerrum, G. Schwarzenbach and L. G. Sillen, "Stability Constants," Part 1, The Chemical Society, London, 1957.

mixtures where the low dielectric constant of the solvent promotes the formation of neutral from ionic species. The data reported for various solvent mixtures indicate that in pure water the stabilities of these latter complexes would be less than that of the DMP complex.

The stability constants for the bis complexes with nickel(II) of thioglycolate,[9] β-mercaptoethylamine,[17] cysteine[18] and DMP (log Q_2 equal to 13.53, 19.81, 19.3 and 22.78) increase markedly in the order $-COO_2^-NH_2$, $-S^-$. For the same order in the complexes, oxalate, ethylenediamine, DMP (log Q_2 = 6.51, 13.34, 22.78) a similar large increase is observed. Slight differences exist in the conditions under which these various constants have been determined, but the effects of these differences are small compared with the large effect that is shown by the mercaptide group.

In some of the experiments (not described above) either slight precipitation of NiDMP or a pronounced Tyndall effect was observed. An approximate value of the solubility product of NiDMP can be calculated from these solutions. The minimum values obtained for the product $[Ni^{++}][DMP^=]$ lies in the range $1\text{–}5 \times 10^{-20}$. This is in fair agreement with the observation that partial precipitation of NiDMP was obtained in fairly acid solutions, *e.g.*, a solution of, 0.05 *M* HCl, 0.01 *M* DMP and 0.002 *M* $Ni(NO_3)_2$ ($K_{sp} \sim 10^{-21}$). Precipitation in this solution was very slow, requiring about a week.

The absorption spectra of $Ni_2(DMP)_3OH^=$ and $Ni(DMP)_2^=$ are illustrated in Fig. 2. The spectrum of $Ni(DMP)_2^=$ has features similar to those shown by the chloro and ammino square-planar Pt(II) complexes in which σ-bonding is predominant.[19] Both Ni(II) and Pt(II) in the square-planar complexes have the outer electron configuration $(d_z)^2(d_{xz},d_{yz})^4(d_{xy})^2(d_{x^2-y^2})^0$. The absorption bands in the Pt(II) complexes have been described[19] in terms of one electron transition from this configuration. The two long wave length maxima in $Ni(DMP)_2^=$ most likely are singlet–singlet transitions corresponding to the two singlet–singlet transitions in $PtCl_4^=$. Two singlet–triplet transitions also are observed in $PtCl_4^=$ at longer wave lengths than the singlet–singlet transitions; singlet–triplet transitions are not expected to appear with the first row transition elements because of lower spin-orbit coupling.[19]

The close resemblance of the spectrum of Ni$(DMP)_2^=$ to those of the chloro- and ammino-Pt(II) complexes and the very slight resemblance to that of $Ni(CN)_4^{=}$[20] indicates that σ-bonding is predominant in the Ni–S bond.

The absorption spectra of bis-thioglycolato-nickel(II) and bis-cysteinato-nickel(II) are also presented in Fig. 2. In the bis-thioglycolato complex, the two singlet–singlet transitions are clearly discernible, although the first band has shifted slightly into the second. Both maxima lie at much longer wave lengths than with $Ni(DMP)_2^=$. The shift to longer wave lengths is in accordance with the positions of $-CO_2^-$ and $-S^-$ in the spectrochemical series.[9]

In the bis-cysteinato complex, the second band lies at about the same position as the second band in $Ni(DMP)_2^=$. The first band has shifted markedly into the second. In the Pt(II) complexes, successive replacement of Cl^- by NH_3 causes a progressive shift of the absorption bands toward shorter wave lengths. The shift, in the case of *cis*-Pt$(NH_3)_2Cl_2$, of the second singlet–singlet band is much greater than with the *trans* isomer. Also, with the *cis* isomer a pronounced shift of the first singlet–singlet band into the second occurs. These effects which appear with the bis-cysteinato-nickel(II) complex suggest that this latter also has the *cis*-configuration. It would appear, in addition, that the thioglycolato complex has the *cis* configuration or is a mixture of the *cis* and *trans* isomers.

The charge-transfer bands in the bis complexes also are presented in Fig. 2. They are somewhat complicated and consist of more than one transition. An unresolved band at a longer wave length than the maximum appears to be present in each case. This is most evident in the cysteinato complex where a shoulder exists at about 310 mμ. No regular progression is apparent in the order $S < N < COO_2^-$ as with the d-d transitions, but it is clear that in $Ni(DMP^=)_2$ the excited state is separated from the lower by less energy than in the other complexes where the field about the nickel ion is less symmetrical.

The spectrum of $Ni_2(DMP)_3OH^=$ is radically different from those of the other complexes. This attests to its different structure. Little more can be said about the spectrum until the nature of the dimer is more fully understood.

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