A portion of this oil yielded a blood-red solid on treatment with ammonia. This solid, unlike XII, was alcohol-soluble and water-insoluble. It was basic, dissolving in dilute hydrochloric acid. This material was purified by Soxhlet extraction with water, then dried *in vacuo.*

Anal. Found[14]: N, 15.17; Ni, 16.46; S, 19.12.

A final portion of the oil was diluted with ethanol and treated with VI and triethylamine, whereupon a purple solid precipitated. This product was alcohol-insoluble, and so was Soxhlet extracted for a day with ethanol, then dried *in vacuo*. This product is believed to be XII.

Anal. Found[14]: N,15.62; Ni, 15.09; S, 19.19.

N,N'-Dimethyldithiooxamidoethylenediaminenickel(II) (XIII).—A solution of trisethylenediaminenickel(II) ion was prepared from the reaction of nickel nitrate hexahydrate (392.3 g., 1.35 moles) and ethylenediamine (405.7 g., 6.75 moles) in 80% ethanol (5 l.). To this well-stirred solution was added slowly a hot (65°) alcoholic solution (2720 cc.) of I[13] (200.0 g., 1.35 moles). The brown mixture was diluted with an equal volume of water, whereupon the bulk of the product precipitated. After standing overnight, the product was filtered and Soxhlet extracted with water for a day. The bulk of the water was removed from the wet, extracted XIII as a benzene azeotrope. The brown product was obtained in 58% yield.

Anal. Found[14]: C, 28.22; H, 4.72; N, (Dumas) 17.44; (Kjeldahl) 9.83; Ni, 23.58; S, 25.83.

XIII does not melt or decompose below 300°. It was shown to be non-crystalline by X-ray analysis. The magnetic susceptibility of XIII was measured in the same manner as that of VII.[9,17]

The Kjeldahl or Dumas nitrogen determinations gave comparable results for complexes VII–XII. Complex XIII, however, consistently gave low values by the Kjeldahl method.

N,N'-Di-*n*-butyldithiooxamide from N,N'-Dimethyldithiooxamide.—A solution of I[13] (7.41 g., 0.05 mole) and *n*-butylamine (21.94 g., 0.30 mole) in 80% ethanol (600 cc.) was refluxed overnight. The mixture was then poured over cracked ice, and the solid which formed was collected and recrystallized from ethanol to give yellow-orange needles of N,N'-di-*n*-butyldithiooxamide[17], m.p. 36.0–36.3°.

Anal. Calcd. for $C_{10}H_{20}N_2S_2$: N, 12.05; S, 27.55. Found: N, 11.64; S, 27.73.

When cyclohexylamine was substituted for *n*-butylamine in the above experiment, only I was recovered.

Acknowledgments.—We are indebted to Prof. John C. Bailar, Jr., of the University of Illinois, for his continued interest and for the magnetic measurements, and to Dr. W. J. Larson, Dr. T. J. Kneip and Miss Wilma Anderson, Department of Chemical Control, Mallinckrodt Chemical Works, for the development of analytical procedures and analyses of the complexes.

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

The Reactions of Nickel(II) with 1,2-Ethanedithiol[1]

BY D. L. LEUSSING AND G. S. ALBERTS

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Ethanedithiol reacts with nickel(II) under alkaline conditions to give the extremely stable complexes $Ni_2es_3^{=}$ and $Nies_2^{=}$. The formation constants for these complexes are about $2 \times 10^{+47}$ and $4 \times 10^{+26}$, respectively, at 30° and at an ionic strength of 0.1. A comparison of the spectra of these complexes with those of the analogous 2,3-dimercapto-1-propanol (DMP) complexes of nickel(II) shows that in these latter complexes coördination takes place only through the sulfur atoms. Relative activities of DMP and ethanedithiol at a given concentration in solution have been determined, and these are shown to have quite a large effect on the relative values of the molar formation constants of $Ni(DMP)_2^{=}$ and $Nies_2^{=}$. The combination of ligand activity effects and complex ion solvation energies obscures conclusions drawn from the relative values of molar formation constants regarding the nature of either bonding or steric factors in a series of complexes.

A recent publication from these Laboratories[2] describes the reactions of nickel(II) with 2,3-dimercapto-1-propanol (DMP). Exceptionally stable complexes having the composition $Ni_2(DMP)_3OH^{=}$ and $Ni(DMP)_2^{=}$ are reported to form through the displacement of the sulfhydryl protons. The present study was undertaken with 1,2-ethanedithiol to ascertain what changes in the nature of the complexes are brought about by using this simpler ligand. In this way it was hoped to determine the role in the DMP complexes played by the DMP alcohol group. Of particular interest also is the nature of the OH^- term which appears in the Ni(II)–DMP dimer.

In addition, the DMP and ethanedithiol system are well suited for determining the effect of ligand activities on the relative values of the molar formation constants which have been obtained in systems of a given metal ion with different ligands. It is quite common to compare formation constants in such systems and attribute the differences to factors such as steric effects, differences in inductive effects in ligand substituents or to different degrees of σ and π bonding between the metal ion and the various ligands. However, the formation constants usually are calculated using concentration units and the different ligands at any given reference concentration need not have the same activity in solution. Therefore, in any comparison the values of the various formation constants also reflect the differences in the activities of the ligands in addition to reflecting those other factors which contribute to complex stability. Because of their relatively low solubilities and high vapor pressures it is a simple matter to obtain the activities of ethanedithiol and DMP in solution. This effect on the relative molar formation constants of $Nies_2^{=}$ and $Ni(DMP)_2^{=}$ is described below.

Experimental

The symbols esH_2, esH^- and $es^{=}$ shall refer to ethanedithiol in its various stages of ionization. Where it is not necessary to distinguish between these in the text just the designation ethanedithiol will be used regardless of its actual state of ionization under the described conditions.

1,2-Ethanedithiol obtained from the Aldrich Chemical Co. was redistilled. The fraction boiling between 65–66° at 43 mm. was used. Air-free stock solutions were prepared by weight and were stored in bottles sealed with

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[1] Financial assistance for this work was made available by a grant from the National Science Foundation.

[2] D. L. Leussing, THIS JOURNAL, **81**, 4208 (1959).

self-sealing Buna-N caps. Dissolution of the ethanedithiol was hastened by adding an equimolar amount of potassium hydroxide in air-free solution.

Analyses by titration with a standard solution of iodine of either aliquots of the stock solutions or weighed amounts of the ethanedithiol were attempted in 1 *M* hydrochloric acid solutions. Erratic results were obtained in which the indicated purity ranged from 93 to 97.8%. A possible source of these variations might arise with the precipitation of polymeric disulfides which cause the formation of a heterogeneous system as the titration proceeds. Analyses in homogeneous systems can be carried out by the spectrophotometric titration of known amounts of nickel(II) in approximately 1.5 *M* ammonia with ethanedithiol solutions. The results of such a titration are presented in Fig. 1 as a plot of the apparent extinction coefficient based on total nickel(II) at 452 mμ *versus* the mole ratio of ethanedithiol to nickel(II). For the original plots in Fig. 1, the points of intersection were found to lie at values of 1.60 and 2.10 for the mole ratio. As is shown below, the first break lies at a somewhat higher value than that corresponding to the stoichiometry for the formation of the first complex because of appreciable dissociation. No dissociation occurs in the region of the sharp second break, however, and in accordance with the quantitative formation of $Ni es_2^=$ at this point the ethanedithiol was assigned a purity of 95%.

The proton dissociation constants of ethanedithiol were determined by measuring the *p*H of partially neutralized air-free solutions at 30°. The beakers containing the solutions were capped with rubber stoppers which had close fitting holes for the electrodes and a nitrogen inlet tube. The *p*H of a solution which contained 2.36 millimoles of es, 1.37 millimoles of potassium hydroxide and 2.33 millimoles of potassium chloride in 65.7 ml. was measured to be 9.06. That of a solution containing 2.36 millimoles of es and 3.70 millimoles of potassium hydroxide in 53.7 ml. was measured to be 10.65. From these results, values of K_{1a} and K_{2a} are calculated to be 1.1×10^{-9} and 2.9×10^{-11}. A correction was made for unreacted hydroxide using a value of the activity product of water equal to 1.4×10^{-14} at 30°[3] and an activity coefficient of hydroxide equal to 0.79.

Nickel chloride solution, 0.488 *M*, was prepared from the reagent grade material and was standardized using the ethylenediaminetetraacetate method.[4] This solution was also made 0.0060 *M* in hydrochloric acid to stabilize it. The acid in the final solution was checked by passing an aliquot through a cation exchange column in the acid form. The total acidity of the effluent was determined by titration with standard base and the number of milliequivalents of nickel present was subtracted to obtain the initial acidity.

Air-free solutions of the complexes were prepared from the nickel chloride and ethanedithiol solutions using the sealed bottle-syringe technique previously described.[5] Most of the experiments were carried out in ammonia buffers, 0.10 *M* in ammonium chloride. When a different medium was used the ionic strength was adjusted to 0.10 *M* with potassium chloride. All solutions were thermostated at 30°.

The reaction rates of ethanedithiol with nickel(II) are much faster than are those with dimercaptopropanol.[2] No spectral changes were observed one-half hour after mixing the reactants. However, all nickel-ethanedithiol solutions were allowed to equilibrate 16–24 hours before measurements were made on them.

Results

Spectrophotometric Measurements.—Spectrophotometric measurements were made under air-free conditions as previously described.[2] Two concentration levels of nickel chloride were run in the titrations illustrated in Fig. 1. Each point was determined from the result of a single experiment in order to avoid the cumulative effects of the small amounts of oxygen which would be introduced each time reagents were added in a conventional titration. It is necessary to have a high concentration of ammonia which prevents the precipitation of Nies to obtain points in the region where the mole ratio of ethanedithiol to nickel is less than 1.50. A medium 1.45 *M* in ammonia and 0.10 *M* ammonium chloride (*p*H 10.38) was ordinarily used, but variations were made. The details are given in the legend of Fig. 1.

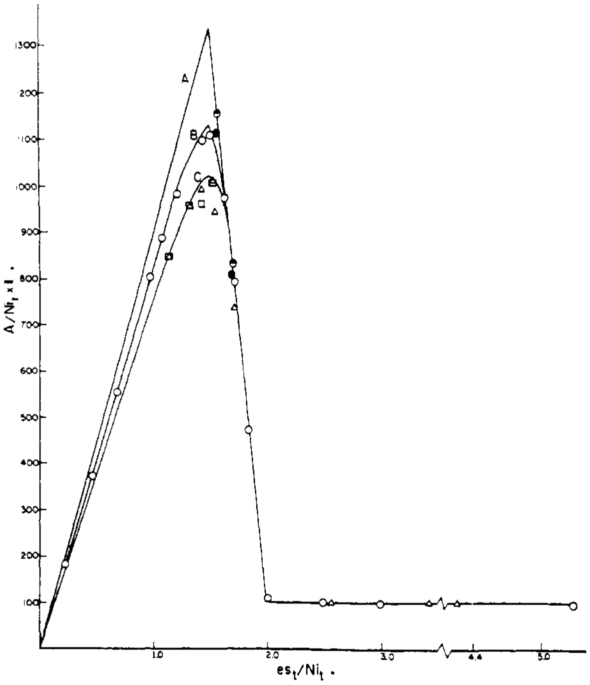

Fig. 1.—The spectrophotometric titration of nickel(II) with ethanedithiol: ○, 0.00244 *M* $NiCl_2$, 1.45 *M* NH_3, 0.10 *M* NH_4Cl; △, 0.00097_7 *M* $NiCl_2$, 1.45 *M* NH_3, 0.10 *M* NH_4Cl; □, 0.00097_7 *M* $NiCl_2$, 1.45 *M* NH_3, 0.010 *M* KOH, 0.090 *M* KCl; ◓, 0.00244 *M* $NiCl_2$, 0.29 *M* NH_3, 0.10 *M* NH_4Cl; ●, 0.00244 *M* $NiCl_2$, 0.010 *M* KOH, 0.090 *M* KCl.

The results of Fig. 1 indicate the formation of both an intensely colored complex having the general composition $Ni_p es_{1.5p}$ and a less intensely colored complex having the composition $Ni es_2^=$. The intensely colored complex is indicated to be somewhat dissociated because the apparent extinction coefficients at the maximum and at points to the left of it depend upon the concentration level of nickel. The degree of dissociation at a given value of the mole ratio is seen practically not to change when a potassium hydroxide–potassium chloride mixture replaces the ammonium chloride in the ammoniacal solution. This independence of the degree of dissociation on changes in *p*H rules out the existence of appreciable amounts of hydroxy complexes.

The apparent extinction coefficients depend only on the value of the mole ratio in the region to the right of the maximum. This indicates no dissociation of the species. Also, no effect of the medium is observed here so long as the solution is sufficiently alkaline to form the complexes. In fact, a potassium hydroxide, potassium chloride solution can be completely substituted for the am-

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[3] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

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

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

monia buffer without effect on the apparent extinction coefficients. This result indicates no significant formation of mixed ethanedithiol–ammonia complexes.

The value of p is indicated to be two for reasons given below and the dissociation of the intensely colored complex takes place

$$\mathrm{Ni_2es_3^=} \rightleftarrows \mathrm{Ni^{++}} + 3\mathrm{Nies_2^=} \qquad (1)$$

The nickel ions which appear on the right hand side are, of course, present as ammonia complexes under the present experimental conditions. Equation 1 is shifted quantitatively to the left by a slight excess of $\mathrm{Nies_2^=}$. In the presence of a slight excess of ethanedithiol in alkaline solutions, $\mathrm{Ni_2es_3^=}$ is quantitatively converted to $\mathrm{Nies_2^=}$.

The absorption spectrum of $\mathrm{Nies_2^=}$ is almost identical with that of $\mathrm{Ni(DMP)_2^=}$. The ethanedithiol complex has two absorption maxima in the visible at 608 and 477 mμ corresponding to singlet–singlet transitions. The extinction coefficients are 70.2 and 123 l. mole^{-1}cm.$^{-1}$, respectively. The absorption spectrum of $\mathrm{Ni_2es_3^=}$ is also almost identical with that of its DMP counterpart. A shallow maximum appears in the visible at 452 mμ with an extinction coefficient of $2.67 \times 10^{+3}$ l. mole^{-1}cm.$^{-1}$.

The conditional constant, Q'_1, for equilibrium 1 was calculated from the results in Fig. 1 obtained in the 1.45 M ammonia solutions where $\mathrm{Ni_2es_3^=}$ is partially dissociated. Using a value of 100 for the extinction coefficient of $\mathrm{Nies_2^=}$ at 452 mμ and that given above for $\mathrm{Ni_2es_3^=}$, concentrations of the solution species were calculated from the equations

$$A_{452}/\mathrm{l.} = 2670\,(\mathrm{Ni_2es_3^=}) + 100\,(\mathrm{Nies_2^=})$$
$$\mathrm{Ni_t} = (\mathrm{Ni_\Sigma^{++}}) + 2(\mathrm{Ni_2es_3^=}) + (\mathrm{Nies_2^=})$$
$$\mathrm{es_t} = 3(\mathrm{Ni_2es_3^=}) + 2(\mathrm{Nies_2^=})$$

where $(\mathrm{Ni_\Sigma^{++}})$ refers to the sum of the concentrations of the nickel–ammonia complexes and the subscript t refers to the total concentration of the species designated. The results at both values of $\mathrm{Ni_t}$ yield a value of Q_1' equal to 2.8×10^{-9}. In Fig. 1 the solid lines are theoretical curves. Curve A is drawn on the basis of no dissociation and curves B and C are calculated using this value of Q_1' and the appropriate value of $\mathrm{Ni_t}$. It is seen that with the exception of two points at the lower $\mathrm{Ni_t}$ where slight oxidation has occurred, good agreement is obtained between the observed points and theoretical curves. Also, the correct change in the degree of dissociation with changing $\mathrm{Ni_t}$ is given by the theoretical curves.

Calculations of extinction coefficients and conditional constants also were made assuming the polymeric complex to be either $\mathrm{Ni_4es_6^{-4}}$ or $\mathrm{Ni_6es_9^{-6}}$. In each case the calculated conditional constants showed large drifts with increasing $\mathrm{es_t}$ so these models were rejected.

The concentration of the aquonickel(II) ions in 1.45 M ammonia at 30° at an ionic strength of 0.1 is calculated to be 5×10^{-10} times $(\mathrm{Ni_\Sigma^{++}})$ using the constants given by Bjerrum.[6] Multiplying Q_1' by this fraction gives a value of 1.4×10^{-18} for Q_1 which is defined as $(\mathrm{Ni^{++}aq})(\mathrm{Nies_2^=})^3/(\mathrm{Ni_2es_3^=})^2$.

EDTA Competition.—An attempt was made to determine the formation constants of the ethanedithiol complexes as was possible with DMP.[2] Experiments were performed in which ethylenediaminetetraacetate and ethanedithiolate ions were allowed to compete for limited amounts of nickel (II) ions. Two series of solutions were prepared, one at pH 9.10 and the other at pH 10.27 and up to an eight-fold excess EDTA (0.020 M) over ethanedithiol (0.0025 M) was used. No more than 2–3% of the nickel(II) appeared to be complexed by the EDTA at equilibrium under these conditions. As this is the level of the experimental error, the results are not suitable for calculations.

Solubility of Nies.—In a different approach to determine the formation constants, the solubility of Nies was determined in solutions containing an excess of ethanedithiol. The highly insoluble Nies dissolves in slightly acid or alkaline solutions of ethanedithiol according to the reaction

$$2\mathrm{Nies_s} + \mathrm{esH_2} \rightleftarrows \mathrm{Ni_2es_3^=} + 2\mathrm{H^+} \qquad (2)$$

Knowing the solubility product of Nies and the proton dissociation constants of $\mathrm{esH_2}$, it is possible to calculate the formation constant of $\mathrm{Ni_2es_3^=}$ from the equilibrium constant measured for reaction 2.

To determine K_{sp} for Nies a series of 50 ml. volumes of air-free solutions were prepared. They were 0.10 M in hydrochloric acid and contained the amounts of nickel chloride and ethanedithiol given in Table I. After three days at 30° no precipitation had occurred so the pH was lowered by injecting 2.5 ml. of approximately 2 M air-free sodium acetate into each solution. This was sufficient to bring about precipitation. After equilibration at 30° for eleven days with frequent shaking, the solutions were centrifuged and the pH and nickel concentration of aliquots was determined. The nickel was determined by first destroying the ethanedithiol with hydrogen peroxide and then titrating with a standard EDTA solution. The results are given in Table I together with the calculated values of K_{sp}. For the calculations below we shall use a value of 2×10^{-21} for the product $(\mathrm{Ni^{++}})(\mathrm{es^=})$.

Table I

The Solubility of Nies in Acid Solutions

Volume, 52.5 ml.; 30°, 0.09 M NaCl

Initial es, mmole	Equil. Ni, mmole	Equil. pH	K_{sp} $(\mathrm{Ni^{++}})(\mathrm{es^=}) \times 10^{+21}$
0.0347[a]	0.0637, 0.0566	2.24	0.7, 0.5
.0694[a]	.0529, .0513	2.38	2.0, 1.9
.1040[a]	.0404, .0459	2.39	2.2, 2.7
.1040[b]	.0797	2.29	1.2

[a] Initially, 0.0652 millimole of $\mathrm{NiCl_2}$. [b] Initially, 0.1304 millimole of $\mathrm{NiCl_2}$.

To determine the solubility of Nies under complexing conditions a solution was made up to contain initially 0.00196 M nickel chloride, 0.00379 M ethanedithiol and 0.00600 M potassium hydroxide in 0.10 M potassium chloride. A small amount of Nies precipitated within a few hours. At equi-

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[6] J. Bjerrum, "Metal-Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

librium the *p*H of the solution was measured to be 6.80 and the concentration of nickel was found to be 0.00188 *M*. Since the *uncomplexed* ethanedithiol is present as esH_2 at the equilibrium *p*H, the concentration of *complexed* ethanedithiol is equal to one-half the amount of base added, *i.e.*, is 0.00300 *M*. This amount is only very slightly greater than that required to complex all the nickel in the system as $Ni_2es_3^{=}$. To preserve the mass balance an amount of $Ni_2es_3^{=}$ must therefore have been formed equal to the amount of Nies which had precipitated. This is about 1×10^{-4} and, thus, the concentration of $Nies_2$ in the equilibrium solution is calculated to be 0.0009 *M*. The concentration of *uncomplexed* esH_2 is 0.00079 *M*. The formation constant of $Ni_2es_3^{=}$ which is equal to $(Ni_2es_3^{=})/(Ni^{++})^2(es^{=})^3$ is then calculated to be $2 \times 10^{+47}$ from the relationship

$$Q_{Ni_2es_3^{=}} = \frac{(Ni_2es_3^{=})(H^+)^2}{K^2_{sp}K_{1a}K_{2a}(esH_2)}$$

An approximate value of the formation constant of $Nies_2^{=}$ is also calculated to be $5 \times 10^{+25}$ from the relationship

$$Q_{Nies_2^{=}} = \frac{(Nies_2^{=})(H^+)^2}{K_{sp}K_{1a}K_{2a}(esH_2)}$$

An alternate calculation also can be made which is independent of the experimentally determined solubility of Nies in this latter run. From the mass balance it results that

$$es_t - (esH_2) - Ni_t = (Ni_2es_3^{=}) + (Nies_2)$$

Making use of Q_1 and the fact that the solution species are in equilibrium with solid Nies, it can be shown that

$$es_t - (esH_2) - Ni_t = K_{1u}K_{2a}K_{sp}(Q_{Ni_2es_3^{=}}K_{sp} + (Q_{Ni_2es_3^{=}})^{2/3}Q_1^{1/3})\,\frac{(esH_2)}{(H^+)_2}$$

From the equilibrium concentration of esH_2 and the values of K_{1a}, K_{2a} and K_{sp} given earlier, $Q_{Ni_2es_3^{=}}$ is calculated to be $2.5 \times 10^{+47}$. A value of $Q_{Nies_2^{=}}$ equal to $4 \times 10^{+25}$ then results from the equation

$$Q_{Nies_2^{=}} = \sqrt[3]{Q^2_{Ni_2es_3^{=}}\,Q_1}$$

Close agreement is seen to be obtained between the two sets of calculations. Considering that the latter value of $Q_{Nies_2^{=}}$ depends directly on the cumulative constants reported for the nickel(II)-ammonia system[7] and that appreciable experimental uncertainties exist in the present work this close agreement is fortuitous. However, a high degree of consistency in the data is shown.

Solubilities and Vapor Pressures of 1,2-Ethanedithiol and 1,3-Dimercapto-1-propanol.—The solubilities of these ligands were determined in air-free media of 0.010 *M* hydrochloric acid, 0.090 *M* potassium chloride at 30°. An excess of the reagent was shaken with the solvent for 24 hr. and the mixture then was centrifuged. An aliquot of the supernate was titrated with a standard iodine solution to determine the dithiol content. After an additional 24 hr. shaking no significant differences were obtained. The solubility of ethanedithiol was found to be 0.066 *M* and that of DMP was found to be 0.35 *M*.

The boiling points of these ligands are given at various pressures.[7] By extrapolating a plot of $1/T$ *versus* log *p*, the vapor pressure is found to be 1.9 mm. for ethanedithiol and about 0.010 mm. for DMP at 303°K.

Discussion

The virtually identical absorption spectra of the pairs $Ni_2es_3^{=}$ and $Ni_2(DMP)_3OH^{=}$ and $Nies_2^{=}$ and $Ni(DMP)_2^{=}$ verify the original conclusion[2] that in DMP the sulfur-nickel(II) bond is sufficiently strong to over-ride any competing effect of the alcohol group. Therefore, only sulfur is bound, at least at the square planar positions, to the nickel(II) ion in these complexes. In the dimeric complex, $Ni_2(DMP)_3OH^{=}$, the OH^- term probably arises from the ionization of the alcohol group in one of the coördinated DMP molecules.

The complex $Ni(DMP)_2^{=}$ has an exceptionally large formation constant[2] and that found here for $Nies_2^{=}$ (about $4 \times 10^{+25}$) is about one thousand times greater. The relative intrinsic stabilities of $Ni(DMP)_2^{=}$ and $Nies_2^{=}$ in solution can be obtained by comparing the ratio of their concentrations in a (hypothetical) solution in which the ligands have the same activity, *i.e.*, have the same partial pressure. Using Henry's law it can be shown that

$$\frac{(Ni(DMP)_2^{=})}{(Nies_2^{=})} = \frac{(p_{DMPH_2}S_{DMPH_2}K_{1aDMPH_2}K_{2aDMPH_2}p^0_{esH_2})^2\ Q_{Ni(DMP)_2^{=}}}{(p_{esH_2}S_{esH_2}K_{1aesH_2}K_{2aesH_2}p^0_{DMPH_2})^2\ Q_{Niei_2^{=}}}$$

where p^0 is the vapor pressure of the pure ligand, S is its solubility and p is its partial pressure over the solution. The values of $Q_{Ni(DMP)_2^{=}}$ and of the product K_{1aDMPH_2} times K_{2aDMPH_2} are $6 \times 10^{+22}$ and 6.2×10^{-20}. Using these and the values reported above for the other quantities, the ratio $(Ni(DMP)_2^{=})/(Nies_2^{=})$ is calculated to be about 1000 when p_{esH_2} and p_{DMPH_2} are equal.

It is seen from this result that the difference in the activities of ethanedithiol and DMP has a very large effect (about a million-fold) on the relative values of the molar formation constants of $Ni(DMP)_2^{=}$ and $Nies_2^{=}$. Intrinsically $Ni(DMP)_2^{=}$ is a much more stable species in solution than is $Nies_2^{=}$ although, a comparison of the molar formation constants leads to the opposite conclusion. Apparently, the same forces which reduce the activity of DMP in solution are also operative in the complex, *i.e.*, the alcohol group which is highly solvated in *uncomplexed* DMP must also be solvated to a considerable extent in *complexed* DMP.

In other systems similar large effects may also be present. What remains after correcting for ligand activities are such factors as steric effects, bond energies and solvation energies. These latter are largely an unknown quantity for complexes at present and this prevents an accurate evaluation of the first two from only formation constant data.

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(7) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Chemical Pub. Co., New York, N. Y., 1958.