($k_f = (CdA_2)/(Cd^{++})(A)^2$ are 5.4, 5.3, 5.2, 5.2 for the Cd(II) complexes of glycylglycine, glycylglycylglycine, tetraglycine and glycine amide, respectively. As an example of the precision obtained in calculating the values of k_f, polarographic results for the Cd(II) complex of glycylglycinate are given in Table V.

TABLE V

POLAROGRAPHIC RESULTS FOR CD(II) COMPLEX OF GLYCYLGLYCINE, 25°, $u = 0.15$

Total concn., of glycylglycine	pH	$-E_{1/2}$	log k_f
0		0.585	
0.02	7.80	.616	5.42
.02	8.20	.630	5.44
.02	8.76	.639	5.40
.04	8.13	.645	5.41
.08	8.16	.663	5.39

Discussion

Ahrland,[5] *et al.*, have shown that the complex formation curve is dependent on concentration of metal ion, if polynuclear complexes exist; while if the complex formation curve is independent of metal ion concentration, the complex is mononuclear. The difference in the metal ion concentration used in sections (A) and (B) is 5-fold, and the agreement in the formation constant values listed in Tables II and IV must mean therefore that the peptide complexes are mononuclear.

The pH data of Tables II, IV and our polarographic data show that with each of the three metal cations (Cd(II), Zn(II) and Ni(II)), the glycylglycine, glycylglycylglycine, tetraglycine and glycine amide complexes are about equally stable. With Mg(II), the glycylglycine and tetraglycine complexes are equally stable. Li, Doody and White[3] found that the Co(II) complexes of the three glycine peptides are also about equally stable, and inferred from this and from infrared data that the three glycine peptides probably have common coördination sites, namely, the terminal amino group and the immediately adjacent peptide group. The same conclusion about the coördination sites of the three glycine peptides toward Cd(II), Zn(II), Ni(II) and Mg(II) therefore may be made. With regard to the Zn(II) complexes, it is interesting to note that Li, *et al.*,[3] already have inferred from infrared data that in glycine amide and in glycylglycine, the preferable site of binding in the amide group toward Zn(II) is the carbonyl oxygen.

Acknowledgment.—The authors are indebted to Mr. Richard Brane for carrying out the polarographic experiments on the Cd(II) complexes of glycine amide.

PITTSBURGH, PENNA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL COLLEGE]

Studies of Complexes of the Transition Metals. I. Nickel Complexes with Sulfur Containing Ligands

BY WILLIAM A. DESKIN

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The formation constants for complexes of nickel(II) with the sulfur containing ligands (thiocarbonate, dithioloxalate and dithiolmalonate) have been determined from spectrophotometric measurements in the visible region of the spectrum. The formulas for these complexes were confirmed to be 1:2 complexes, that is, one nickel ion per two ions of the ligand, by the methods of continuous variation and varying mole ratio. These complexes were studied in aqueous solution of total ionic strength of 0.1. The formation constants (k_1k_2) indicated the order of stability for the complexes to be: dithioloxalate > dithiolmalonate > thiocarbonate. These ligands form complexes with nickel(II) which contain four-membered rings with thiocarbonate, five-membered rings with dithioloxalate and six-membered rings with dithiolmalonate. The order of stability is what one might predict since five- and six-membered rings are known to be more stable. It is also interesting to compare the stability of these complexes with the corresponding oxygen containing complexes. The sulfur-containing ligands form complexes which are more stable than the corresponding oxygen complexes.

Introduction

Nickel(II) forms many coördination compounds with various chelating agents. Three of these reagents are the dithioloxalate, dithiolmalonate and thiocarbonate ions. These ions have been proposed as reagents for the detection of nickel.[1] It has been shown that many of the transition metal ions form colored solutions with dithioloxalate[2] and dithiolmalonate[3] ions, and a colorimetric method for the determination of nickel with dithioloxalic acid dipotassium salt has been studied.[4] X-Ray studies[5] have indicated that dipotassium bisdithioloxalato nickelate(II) exists in a planar configuration.

It was the purpose of this research to study these complexes in dilute solution and to determine the formulas as well as the formation constants. Since each of these complexes is highly colored a spectrophotometric method seemed advantageous.

Experimental Part

Materials.—A 0.0200 *M* standard nickel solution was prepared by dissolving the proper amount of nickel(II) sulfate hexahydrate (Mallinckrodt Analytical reagent) in water at 25°. The concentration of nickel was deter-

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(1) F. J. Welcher, "Organic Analytical Reagents," Vol. IV, D. Van Nostrand Co., New York, N. Y., 1948, p. 142, 146.

(2) C. S. Robinson and H. O. Jones, *J. Chem. Soc. Trans.*, **101**, 62 (1912).

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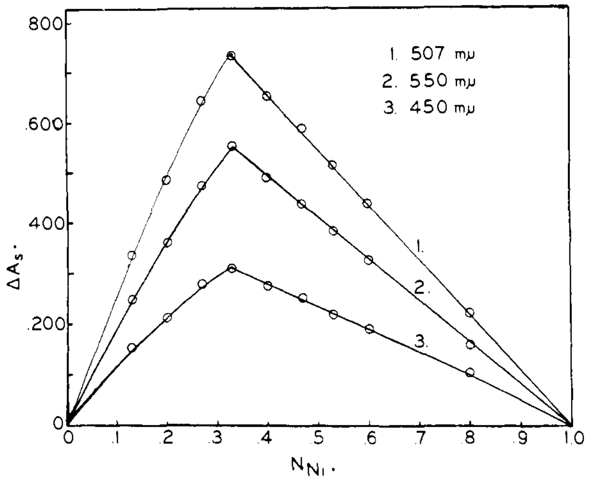

Fig. 1.—Continuous variation plot for the nickel-dithioloxalate complex.

mined by a gravimetric method using dimethylglyoxime and the above value was confirmed.

The dithioloxalic acid dipotassium salt was Eastman Kodak Co. white label which was dried and used without further purification.

Potassium thiocarbonate was prepared by saturating an absolute alcohol solution of potassium hydroxide with hydrogen sulfide and adding carbon disulfide dissolved in absolute alcohol. The precipitate was washed and dried. The sample was analyzed by dissolving a portion in distilled water and boiling to hydrolyze the salt to the hydroxide. A potentiometric titration indicated the original material to be about 99.5% K_2CS_3. Analysis for potassium as the sulfate yielded a value of 41.45%, calculated value is 41.95%.

The dithiolmalonic acid dipotassium salt was prepared by adding malonyl chloride to ethanethiol and heating the mixture to remove hydrogen chloride and any excess of either reagent. The resulting dithiolmalonic acid diethyl ester was added to potassium hydrosulfide in alcohol. The precipitate which was formed was filtered and washed with cold alcohol and dried in a vacuum desiccator. Analyses of the compound were carried out: potassium by the sulfate method, 36.87%, sulfur as barium sulfate, 29.89%. Calculated for $K_2C_3H_2O_2S_2$ gives potassium as 36.82% and sulfur as 30.20%.

Solutions.—Solutions of the above compounds were prepared with freshly boiled distilled water at 25°. Potassium sulfate was added to adjust the total ionic strength to 0.1.

The *p*H measurements were made with a Beckman model H-2 *p*H meter. This was calibrated against a standard buffer.

Absorption Spectra.—Measurements of absorption were made with a Beckman model DU Quartz Spectrophotometer, using a tungsten lamp and Corex cells of 10 ± 0.01 mm. light path. The measurements were made at room temperature of approximately 25°.

Experimental Results

Composition of Complexes.—The compositions of the complexes were determined by Job's method of continuous variation[6] and by the method of varying mole ratio.[7] In the method of continuous variation a series of solutions were prepared in which the concentrations of nickel and the ligand were varied, but the sum of the concentrations was constant. The difference between the observed absorption and the calculated absorption (ΔA_s) was then plotted *vs.* the mole fraction of nickel and a maximum was observed at the composition of the complex. A typical plot obtained for the nickel–dithioloxalate complex is shown in Fig. 1. In each case a 1:2 complex was observed, that is, one nickel ion to two ions of ligand.

In the method of varying mole ratio a constant concentration of nickel ion was used and to this increasing amounts of ligand were added. When the measured absorbance was plotted *vs.* moles of ligand per mole of nickel, a curve was obtained which rises to a constant value. Figure 2 is a typical plot obtained for the nickel–dithioloxalate complex. One also obtains a 1:2 complex by this method as indicated by the intersection of the extrapolated straight lines.

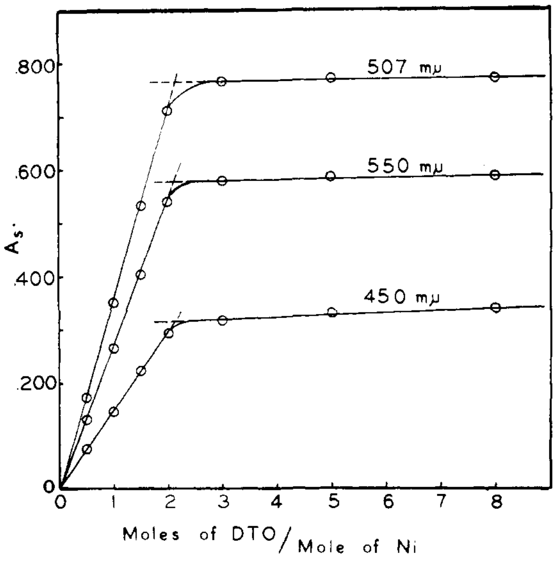

Fig. 2.—Varying mole ratio plot for the nickel–dithioloxalate complex.

Formation Constants.—The formation constant[8] for the complex may be evaluated from the data obtained for the varying mole ratio plots.[9] In the solutions containing a large excess of ligand, *e.g.*, dithioloxalate ion, one may assume that association is complete. If one chooses a wave length at which the ligand does not absorb, then the molar absorptivity for the complex may be evaluated. From this value one may calculate the equilibrium concentrations of the complex in the other solutions and thus the formation constant.

Another method[10] for evaluating the formation constant also was used. A mixture containing 2.0 $\times 10^{-4}$ *M* nickel(II) and 4.0 $\times 10^{-4}$ *M* dithioloxalate (corresponding to the peak of the curves in Fig. 1) was diluted in successive stages—adding potassium sulfate as needed to keep the ionic strength constant. The absorbance was obtained at the various wave lengths for this series of diluted solutions. From these data and the data of Fig. 1 a series of pairs of solutions could be selected, having equal absorbance (and thus essentially equal concentrations of complex) but different concentra-

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[6] (a) P. Job, *Ann. chim.*, **9**, 113 (1928); **11**, 97 (1936); (b) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941); (c) R. K. Gould and W. C. Vosburgh, *ibid.*, **64**, 1630 (1942).

[7] (a) J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944); (b) R. M. Rush and J. H. Yoe, *Anal. Chem.*, **26**, 1345 (1954).

[8] Note: this is the concentration formation constant.

[9] A. E. Harvey, Jr., and D. L. Manning, THIS JOURNAL, **72**, 4488 (1950).

[10] (a) S. E. Turner and R. C. Anderson, *ibid.*, **71**, 913 (1949); (b) R. T. Foley and R. C. Anderson, *ibid.*, **71**, 909 (1949).

tions of reagents. Then from the equation

$$K_f = \frac{X}{[\mathrm{Ni}_1 - X][\mathrm{L}_1 - 2X]^2} = \frac{X}{[\mathrm{Ni}_2 - X][\mathrm{L}_2 - 2X]^2}$$

X, the concentration of the complex, and then K_f could be calculated since the values for [Ni] and [L] (the ligand) were known.

The values for the log K_f as obtained by each of the above methods are given in Table I. The mean values of log K_f for each of the methods are in reasonable agreement. The wave lengths at which these measurements were made were chosen at the peak or as near to the peak as possible in order that the absorbance of the free ligand would be a minimum. The complexes were studied at other wave lengths as well and values of log K_f were determined. The variations in log K_f were greater at the other wave lengths due to the corrections necessary for the absorption of the free ligand; however, satisfactory agreement was obtained.

The molar absorptivity is given for each complex at the wave length studied in Table I.

TABLE I

CONCENTRATION FORMATION CONSTANTS AT 25°

Ligand	Total concn. of Nickel(II)	Total concn. of Ligand	Log K_f Soln. of equal A_s	Log K_f Mole ratio[a]
Dithioloxalate	1.32×10^{-4}	2.64×10^{-4}	9.77	
	3.20×10^{-4}	2.80×10^{-4}	9.10	
a_M = 3840 at 507 mμ		Mean	9.43	9.72
Dithiolmalonate	1.30×10^{-3}	2.60×10^{-3}	8.62	
	1.42×10^{-3}	2.84×10^{-3}	8.64	
a_M = 167 at 575 mμ		Mean	8.63	8.64
Thiocarbonate	1.6×10^{-4}	4.4×10^{-4}	8.43	8.79
a_M = 1600 at 510 mμ				

[a] Value given for mole ratio method is the mean value of four measurements.

Discussion

Oxygen and sulfur resemble one another in many ways; however, their ability to form complexes with metal ions is greatly different.[11] In general, the donor properties of sulfur are somewhat more restricted as regards the nature of the acceptor atom, but in some types of compounds they are exceptionally strong. The thioethers, for example, form much more stable compounds than the corresponding oxyethers.[12]

A rough comparison may be made on the basis of the relative insolubilities of the sulfides of the metals. Those which form insoluble sulfides seem to be the same metals which form complexes containing a metal–sulfur bond, while those forming water-soluble sulfides (in which oxygen replaces sulfur in the coördination sphere about the metal) form much stronger complexes when oxygen rather than sulfur is the donor.[13]

The formation constants determined in this research are for the over-all reaction

$$\mathrm{Ni^{II}} + 2\mathrm{L}^{--} \rightleftarrows \mathrm{NiL_2}^{--}$$

and thus are k_1k_2 where k_1 is the formation constant for the addition of one ligand ion to Ni(II) and k_2 for the subsequent reaction in forming the 1:2 complex. Sufficient data are not available in the literature to make a complete comparison of the formation constants of the above complexes containing the sulfur–metal linkages with other complexes in which oxygen or nitrogen metal linkages occur, but some comparisons are interesting.

The complex anion formed between nickel(II) and the oxalate ion has been studied[14] and the formation constant (k_1k_2) was evaluated by solubility measurements. A value for log K_f of 6.51 was obtained and this indicates that for nickel(II) the oxalate ion is a weaker coördinating ligand than the dithioloxalate ion (log K_f = 9.43).

Stock and Davies[15] have determined the first stepwise formation constant (k_1) for the complex anion between nickel(II) and the malonate ion and have reported a value for log k_1 of 4.00. It is difficult if not impossible to compare k_1 with the over-all formation constant (k_1k_2); however, one would expect that for the above complex, log k_1k_2 would be less than 8. Thus it may be stated that the coördinating ability of the malonate ion is about the same as the dithiolmalonate ion (log K_f = 8.63), but it is also probable that it is not a stronger coördinating ligand and may perhaps be a weaker one.

Other ligands which may be compared are not of a similar type of structure. Some ligands which form complexes with nickel(II) and have the same number and kinds of atoms in the ring are glycine[16] (log K_f = 11.14), α-alanine[16] (log K_f = 10.66), and ethylenediamine[17] (log K_f = 14.06). These are different in that they contain only one or no carbonyl oxygen on the carbon atom adjacent to the donor atom. It is interesting to note that all of these ligands form stronger complexes with nickel(II) than the ligands studied in this research.

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MOUNT VERNON, IOWA

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