

Study of Metal-1,10-Phenanthroline Complex Equilibria by Potentiometric Measurement^{1,2}

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The silver-1,10-phenanthroline system has been studied and the stability constants determined for the 1:1 and 2:1 complexes using the silver electrode. This known system then was used to study the complexes of 1,10-phenanthroline with other metals. The $\log \beta_n$ values found for the over-all stoichiometric stability constants are: Ag, 5.02, 12.07; Mn, 3.88, 7.04, 10.11; Cd, 5.93, 10.52, 14.30; Zn, 6.83, 12.05, 16.92. The stoichiometric stability constants determined for copper are $\log k_2 = 6.42$ and $\log k_2k_3 = 11.05$.

Introduction

The silver electrode has been used in the past to study complexes of metal ions by competitive means.^{3,4} The 1:1 complexes of some transition metals with 1,10-phenanthroline have been investigated using the mercury electrode.⁵

The purpose of the present work was to investigate the complexes of silver with 1,10-phenanthroline using the silver electrode and to apply this known system to the study of complexes of 1,10-phenanthroline with some transition metals. The method depends upon the competition between the ions of silver and of a second metal to form complexes with 1,10-phenanthroline. The theory of competitive systems has been discussed previously.⁶

Sullivan, *et al.*,⁷ have developed a program for the least squares treatment of potentiometric titration data using the IBM 704 electronic computer. This program was used to evaluate the stability constants and their standard deviations for the transition metals investigated in this work.

Experimental

Titration were performed in a three-compartment cell. The center compartment, containing a saturated solution of potassium sulfate, was separated from the outer compartments by ultrafine porosity Pyrex disks. Salt diffusion through the Pyrex disks was shown to be negligible compared to that already in the solution by a conductometric time study. The construction of the cell permitted thorough cleaning of the frits after each titration. During the titrations, the potential difference between two Beckman silver billet electrodes in each of the outer two compartments was followed. Potentiometric measurements were made with a Leeds and Northrup No. 7552 Type K-2 potentiometer coupled with a No. 2430-C Type E galvanometer having a sensitivity of 0.005 $\mu\text{a./mm}$. The temperature was controlled at $25 \pm 0.05^\circ$.

(1) Abstracted from a dissertation submitted by John M. Dale to graduate faculty of Iowa State University in partial fulfillment of requirements for the degree of Doctor of Philosophy, 1962.

(2) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(3) I. Leden, *Acta Chem. Scand.*, **6**, 971 (1952).

(4) S. Cabani and E. Scrocco, *Ann. chim.* (Rome), **48**, 99 (1958).

(5) G. Anderegg, *Helv. Chim. Acta*, **42**, 344 (1959).

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

(7) J. C. Sullivan, J. Rydberg, and W. F. Miller, *Acta Chem. Scand.*, **13**, 2023 (1959).

At the beginning of each titration, the two outer compartments of the cell contained identical solutions. One solution which was not altered served as a reference while the other solution was titrated. The titrant, except for the 1,10-phenanthroline concentration, was identical with the solution to be titrated with respect to ionic strength and total concentrations of sulfate, acetate, acetic acid, and metal ions. Thus, the over-all composition of the solution to be titrated was not altered during titration except for the addition of the 1,10-phenanthroline. Metal sulfates were used in this work because nitrate and perchlorate ions form insoluble salts with the bis-(1,10-phenanthroline)-Ag(I) complex ion.

After each addition of titrant, the system came to equilibrium in approximately 3 to 5 min. in most cases. Equilibrium was assumed to have been attained when two consecutive readings, 1 min. apart, did not differ by more than 0.01 or 0.02 mv. Equilibrium was very slowly established in the titration of nickel, an hour being required for certain experimental points.

Evaluation of the System

In order to evaluate the response of the concentration cell, potentiometric measurements were made for several dilute solutions of silver. The ionic strength in both the reference and experimental solutions was 0.1 and the pH was 4.80. The concentrations of silver were calculated from the e.m.f. values of the concentration cell and compared to the concentration of silver known to be present.

The e.m.f. of the working electrode with respect to the reference electrode may be expressed as

$$E = -\frac{RT}{F} \ln \frac{[\text{Ag}^+]_r}{[\text{Ag}^+]_x} \quad (1)$$

where the subscripts r and x refer to the reference and experimental solutions, respectively. The term $[\text{Ag}^+]$ represents the total concentration of silver not bound to 1,10-phenanthroline. Because the ionic strength in both half-cells was held constant, the activity coefficients of silver cancel. In a like manner, it can be shown that the consideration of the sulfate and acetate complexes of silver introduces a constant term which also cancels in the ratio of the silver concentrations. Table I shows the comparison of the silver concentration known to be present and that calculated from eq. 1.

A comparison at lower concentrations of silver was made by means of a titration with chloride. At the beginning of the titration, the reference and experi-

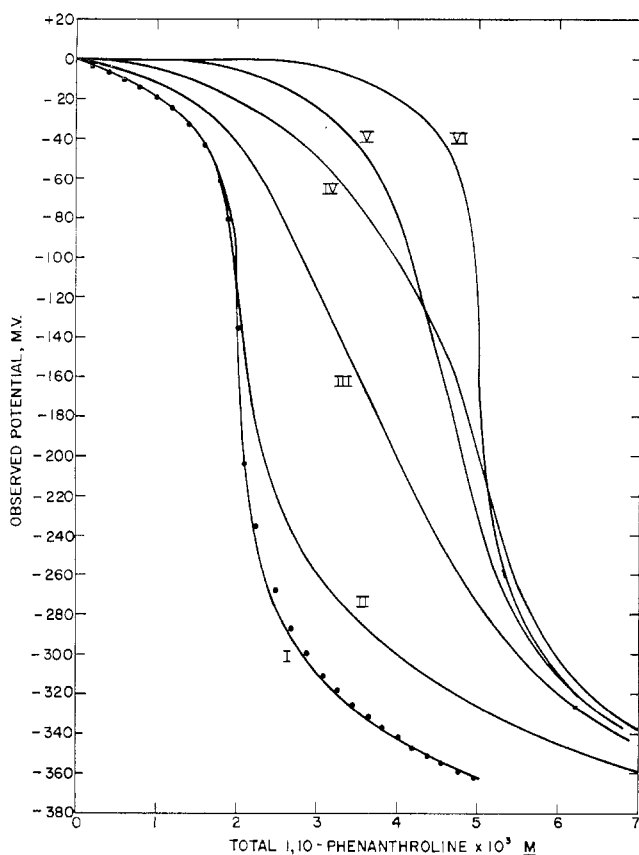


Fig. 1.—Titration of metal solutions with 1,10-phenanthroline: I, silver; II, manganese + silver; III, cadmium + silver; IV, zinc + silver; V, copper + silver; VI, nickel + silver.

TABLE I

POTENTIAL MEASUREMENTS OF DILUTE SILVER SOLUTIONS^a

pAg' _x			pAg' _x		
E, mv.	Taken	e.m.f.	E, mv.	Taken	e.m.f.
-17.8	2.90	2.90	-94.8	4.20	4.20
-28.2	3.08	3.08	-118.0	4.60	4.60
-35.8	3.20	3.21	-135.5	4.90	4.89
-59.1	3.60	3.60	-145.6	5.08	5.06
-76.8	3.90	3.90	-152.6	5.20	5.18
-87.2	4.08	4.08			

^a Reference solution: $\text{Ag}_2\text{SO}_4 = 1.25 \times 10^{-3} M$; $\text{K}_2\text{SO}_4 = 2.21 \times 10^{-2} M$; $\text{KOAc} = 3.00 \times 10^{-2} M$; $\text{HOAc} = 3.01 \times 10^{-2} M$. Experimental solution: $\text{Ag}_2\text{SO}_4 < 1.25 \times 10^{-3} M$; $\text{K}_2\text{SO}_4 + \text{Ag}_2\text{SO}_4 = 2.34 \times 10^{-2} M$; $\text{KOAc} = 3.00 \times 10^{-2} M$; $\text{HOAc} = 3.01 \times 10^{-2} M$.

mental solutions were both $1.0 \times 10^{-3} M$ in total silver. The sodium chloride titrant contained the same amounts of sulfate, acetate, and acetic acid as the reference solution, and as the experimental solution to be titrated. Due to the increasing amount of sodium chloride, the ionic strength of the solution being titrated varied from 0.1 to approximately 0.14 during the titration. The concentrations of silver calculated from the e.m.f. measurements were compared to those calculated from the known concentrations of chloride and the solubility product constant of silver chloride.⁸ Even though the ionic strength was not exactly 0.1 throughout the titration, the solubility product constant was adjusted for $\mu = 0.1$, using the ion activity co-

(8) J. H. Jonte and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **74**, 2052 (1952).

TABLE II

POTENTIAL MEASUREMENTS OF SILVER SOLUTIONS^a CONTAINING CHLORIDE

[Cl ⁻] × 10 ³	E, mv.	Calcd. pAg' _x K _{sp}	e.m.f.	[Cl ⁻] × 10 ³	E, mv.	Calcd. pAg' _x K _{sp}	e.m.f.
2.885	-230.0	6.97	6.99	18.56	-277.4	7.78	7.79
4.720	-242.3	7.18	7.20	22.32	-282.1	7.86	7.88
8.186	-256.2	7.42	7.44	27.87	-287.8	7.95	7.97
11.41	-264.8	7.57	7.58	36.89	-295.0	8.08	8.09
15.84	-273.3	7.71	7.73	43.91	-299.6	8.15	8.17

^a Reference solution: $\text{Ag}_2\text{SO}_4 = 5.00 \times 10^{-4} M$; $\text{K}_2\text{SO}_4 = 2.28 \times 10^{-2} M$; $\text{KOAc} = 3.00 \times 10^{-2} M$; $\text{HOAc} = 3.01 \times 10^{-2} M$.

efficients of Kielland.⁹ Because only the free silver ion is involved in the solubility product constant, it was necessary, in this case, to account for the sulfate¹⁰ and acetate¹¹ complexes of silver. The values of the formation constants for these complexes also were adjusted for $\mu = 0.1$. All potentiometric measurements were taken beyond the equivalence point. It was shown that a negligible amount of the excess chloride ion was present as AgCl_2^- .⁸ Table II shows the results from the titration with chloride.

In view of the assumptions and adjustments made in order to make the comparisons in Table II, it was felt that the results were satisfactory. Equation 1 therefore was used for the calculation of silver concentrations from e.m.f. data in the titrations with 1,10-phenanthroline.

Silver(I)-1,10-Phenanthroline System.—Titrations of silver with 1,10-phenanthroline were performed as described previously. The ionic strength was controlled at 0.1 and the pH at 4.80. The composition of the reference solution was the same as that indicated by the footnote to Table II. The titration curve is shown in Fig. 1.

Values for the logarithm of the over-all conditional formation constant, $\log \beta_2'$, were calculated from the measured silver concentration, $[\text{Ag}']$, and the known concentration of the excess 1,10-phenanthroline, $[\text{P}']$, for several experimental points beyond the stoichiometric point. The term $[\text{P}']$ represents the total concentration of 1,10-phenanthroline not bound to a metal. The average value of $\log \beta_2'$ and the standard deviation are given in Table III.

TABLE III

OVER-ALL CONDITIONAL FORMATION CONSTANTS^a

Metal	$\log \beta_1'$	$\log \beta_2'$	$\log \beta_3'$
Ag	4.525 ± 0.027	11.186 ± 0.018	
Mn	3.230 ± 0.011	6.004 ± 0.031	8.685 ± 0.031
Cd	5.028 ± 0.016	9.225 ± 0.024	12.624 ± 0.033
Zn	6.081 ± 0.036	10.906 ± 0.036	15.388 ± 0.036
Cu		6.030 ± 0.024^b	10.274 ± 0.030^b

^a Values not corrected for acetate and sulfate complexes or for the presence of phenanthrolium ion, $\mu = 0.1$ and $t = 25 \pm 0.05^\circ$.

^b Values reported are $\log k_2'$ and $\log k_2'k_3'$, respectively, where k_n' indicates the stepwise conditional formation constant.

(9) J. Kielland, *ibid.*, **59**, 1675 (1937).

(10) E. C. Righelato and C. W. Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

(11) F. H. MacDougall and L. E. Topel, *J. Phys. Chem.*, **56**, 1090 (1952).

Once β_2' is known, it is possible to calculate β_1' using experimental points prior to the end point. Equation 2 results from subtracting the expression for the total concentration of silver, Ag_T , from that representing the total concentration of 1,10-phenanthroline, P_T , and substituting for $[AgP_2]$.

$$[Ag']\beta_2'[P']^2 + [P'] + Ag_T - [Ag'] - P_T = 0 \quad (2)$$

The values of $[P']$ may be determined from eq. 2 using the values of $[Ag']$ calculated from the experimental e.m.f. values. The concentration of AgP_2 may now be calculated and the concentration of AgP found by difference. All quantities necessary for the calculation of β_1' are now known and the average value is given in Table III.

Using the values for β_1' and β_2' , the concentration of total 1,10-phenanthroline, P_T , was calculated for each experimental point. The calculated values (dots) are plotted in Fig. 1 as a comparison to the experimental curve.

Metal(II)-1,10-Phenanthroline Systems.—In this study, titrations were performed which were identical with those with silver alone except that a known amount of a second metal was present. As before, the reference solution, the solution to be titrated, and the titrant were of identical composition except for the 1,10-phenanthroline in the titrant.

The metals studied were cadmium(II), zinc(II), copper(II), nickel(II), and manganese(II). No attempt was made to study iron because iron(II) reduced silver(I) in the initial solutions. An attempt was made to study cobalt(II) with no success. This was due to the reduction of the free silver by the cobalt(II) complex.

Figure 1 illustrates the titration data obtained for manganese, cadmium, zinc, copper, and nickel. In each case the total silver concentration was $1.000 \times 10^{-3} M$ while the total concentration of the second metal was: manganese, $1.004 \times 10^{-3} M$; cadmium, $1.004 \times 10^{-3} M$; zinc, $1.062 \times 10^{-3} M$; copper, $1.003 \times 10^{-3} M$; nickel, $1.003 \times 10^{-3} M$. Because the concentrations of the second metal were almost the same, comparison of the titration curves gives an indication of the relative strength of the complexes which, in general, increases from left to right.

The values of β_1' and β_2' for the silver-1,10-phenanthroline complexes combined with the measured silver concentration, $[Ag']$, permitted the calculation of the concentration of the uncomplexed 1,10-phenanthroline, $[P']$, for each experimental point on these titration curves.

The logarithms of the conditional stability constants, $\log \beta_n'$, obtained from the least squares treatment of the data are shown in Table III. The adjusted constants wherein the concentrations of the sulfate¹² and acetate¹³ complexes of the metals and the phenanthro-

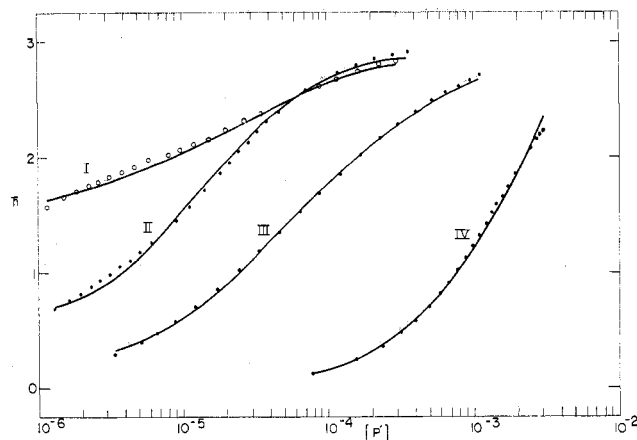


Fig. 2.—Formation functions: I, copper; II, zinc; III, cadmium; IV, manganese.

TABLE IV
STOICHIOMETRIC FORMATION CONSTANTS^a

Metal	$\log k_1$	$\log k_2$	$\log k_3$	$\log \beta_3$
Ag	5.02	7.05		
Mn	3.88	3.16	3.07	10.11
	4.8 ^b	4.1 ^b	5.4 ^b	14.3 ^b
				7.35 ^c
Cd	5.93	4.59	3.78	14.30
	5.17 ^b	4.83 ^b	4.26 ^b	14.26 ^b
	5.75 ^d	5.09 ^d	3.07 ^d	13.91 ^d
	6.01 ^k		2.04 ^e	15.19 ^e
Zn	6.83	5.22	4.87	16.92
	6.5 ^f	5.45 ^f	5.10 ^f	17.05 ^f
	6.4 ^b	5.63 ^b	4.97 ^b	17.00 ^b
	6.36 ^g	5.64 ^g	5.00 ^g	17.00 ^g
	6.6 ^h	5.72 ^h	4.85 ^h	17.17 ^h
	6.31 ^d	6.09 ^d	4.77 ^d	17.17 ^d
	6.47 ⁱ	5.53 ⁱ	1.1 ⁱ	13.1 ⁱ
	6.40 ^k			
Cu		6.42	4.63	
	8.82 ^b	6.57 ^b	5.02 ^b	20.41 ^b
	9.15 ^g	6.65 ^g	5.25 ^g	21.05 ^g
	6.3 ^j	6.15 ^j	5.50 ^j	17.95 ^j
	7.53 ^d	6.07 ^d	5.00 ^d	18.60 ^d
	9.30 ^k	6.84 ^k		

^a Values stated without reference are from this work in which $\mu = 0.1$ and $t = 25^\circ \pm 0.05^\circ$. ^b H. Irving and D. H. Mellor, private communication. ^c R. R. Miller and W. W. Brandt, *J. Am. Chem. Soc.*, **77**, 1384 (1955). ^d R. Fullerton, Ph.D. Thesis, Iowa State University, 1959. ^e B. E. Douglas, H. A. Laitinen, and J. C. Bailar, *J. Am. Chem. Soc.*, **72**, 2484 (1950). ^f H. Irving and D. H. Mellor, *J. Chem. Soc.*, 3457 (1955). ^g C. V. Banks and R. I. Byströf, *J. Am. Chem. Soc.*, **81**, 6153 (1959). ^h I. M. Kolthoff, D. L. Leussing, and T. S. Lee, *ibid.*, **73**, 390 (1951). ⁱ J. H. McClure, Ph.D. Thesis, Iowa State University, 1961. ^j R. T. Pflaum and W. W. Brandt, *J. Am. Chem. Soc.*, **76**, 6215 (1954). ^k Reference 5.

lium¹⁴ ion have been taken into account are given in Table IV. These values are compared to those obtained by other workers.

The stabilities of the nickel complexes were too great for silver to be an effective competitor and no constants could be calculated for this system. This also was true for the 1:1 complex of copper.

Figure 2 compares the experimentally determined

(12) J. C. James, Thesis, London, 1947; C. W. Davies, *J. Chem. Soc.*, 2093 (1938); P. A. H. Wyatt, *Trans. Faraday Soc.*, **47**, 656 (1951).

(13) R. S. Kolat and J. E. Powell, *Inorg. Chem.*, **1**, 293 (1962); S. K. Siddhanta and S. N. Banerjee, *J. Indian Chem. Soc.*, **85**, 419 (1958).

(14) T. S. Lee, I. M. Kolthoff, and D. L. Leussing, *J. Am. Chem. Soc.*, **70**, 2348 (1948).

formation function for each metal with values of \bar{n} calculated (circles and dots) from experimental values of $[P']$ and the over-all conditional formation constants.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MINNESOTA AT DULUTH, DULUTH 18, MINNESOTA

Complexes of the Rare Earths. VI. N-Hydroxyethyliminodiacetic Acid

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The formation constants of the complexes between the rare earth ions and N-hydroxyethyliminodiacetic acid (HIMDA) have been investigated at 25° and $\mu = 0.1$ (KNO₃). Both 1:1 and 2:1 chelates of unusually large stability were found. Trends in the formation constants are discussed and it is shown that the data can be explained by assuming that the hydroxyethyl group is coordinated in both the 1:1 and 2:1 chelates. The data also indicate that the rare earth ions have a coordination number larger than six in these species.

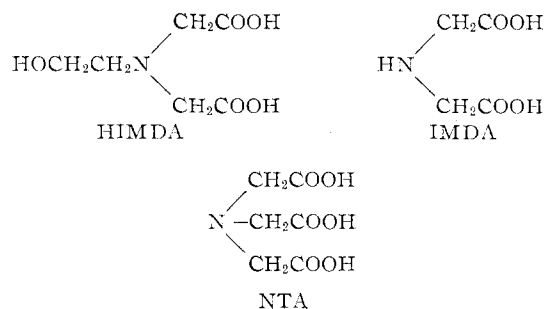
In connection with the project underway in this Laboratory in which the basic complexing tendencies of the rare earths are being investigated, the formation constants for the rare earth-N-hydroxyethyliminodiacetic acid (HIMDA) chelates have been measured and are reported herein. This ligand is of particular interest for several reasons. First of all, it has been rather extensively and carefully studied and the formation constants for a large number of HIMDA-metal chelates have been determined.^{2,3} Comparison of these data with the corresponding formation constants for the rare earth chelates should be useful in obtaining information relative to the factors influencing the coordination of the rare earth ions.

A second reason for investigating this ligand is the opportunity to compare these complexes with the corresponding complexes of iminodiacetic acid (IMDA).⁴ Of primary interest here is the inductive effect of the N-hydroxyethyl group and the possibility of coordination through the hydroxy group. In addition, since HIMDA contains four potential donor sites, it is possible that in the 2:1 complexes the central rare earth ion has a coordination number larger than six.

The only previous studies with the rare earth complexes of HIMDA appear to be an investigation of some mixed complexes with N-hydroxyethylethylenediaminetriacetic acid,⁵ a study of the hydrolysis of the lanthanum chelate,⁶ and a study of the ligand as an eluent in the ion-exchange separation of the rare earths.⁷

The structural formulas of HIMDA and the other

ligands which are mentioned in this paper are given below.



Experimental

Solutions.—The HIMDA was obtained from the Dow Chemical Company and was purified by two recrystallizations from water. An approximately 0.005 M solution was prepared by dissolving the required amount of acid in de-ionized water and was standardized by potentiometric titration both in the presence and absence of copper(II) ions. The preparation and standardization of the 0.005 M rare earth nitrate⁸ and 1.000 M potassium nitrate solutions have been described previously.⁴ A solution 0.005 M in tren·3HCl (tren is 2,2',2''-triaminotriethylamine) was prepared by dissolving the required amount in de-ionized water and was standardized by potentiometric titration in the presence of copper(II) nitrate. All other metal ion solutions were prepared from the analytical reagents and standardized complexometrically. For the measurements using the copper amalgam electrode a 0.05 M HIMDA solution was prepared so that the total ionic strength was 0.1 using potassium nitrate as the inert salt.

Copper(II) Amalgam.—The liquid copper amalgam, 2.00% by weight, was prepared by electrolyzing a solution of copper(II) sulfate with pure mercury as the cathode. The amalgam was stored under dilute nitric acid and an atmosphere of nitrogen.

Experimental Procedures.—(a) pH method: In those cases where the 1:1 complex was not too stable ($\log K_1 < 9$), the direct titration procedure described previously⁴ was used with solutions containing HIMDA and the rare earth ion in the ratio 1:1, 2:1,

(1) National Science Foundation Undergraduate Research Participant, 1961–1962.

(2) G. Schwarzenbach, G. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955).

(3) S. Chaberek, Jr., R. C. Courtney, and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5057 (1952).

(4) L. C. Thompson, *Inorg. Chem.*, **1**, 490 (1962).

(5) L. C. Thompson and J. A. Loraas, *ibid.*, **2**, 89 (1963).

(6) R. C. Courtney, R. L. Gustafson, S. Chaberek, Jr., and A. E. Martell, *J. Am. Chem. Soc.*, **80**, 2121 (1958).

(7) L. Wolf and J. Massone, *J. Prakt. Chem.*, **5**, 288 (1958), and references therein.

(8) The rare earth materials were generously supplied by Lindsay Chemical Division, American Potash and Chemical Corporation, West Chicago, Illinois.