

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

## Thermodynamics of Chelation. II. Bond Energy Effects in Chelate Ring Formation

BY C. G. SPIKE AND R. W. PARRY

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The relative contributions of enthalpy and entropy terms to the stability of chelate complexes of Zn(II) and Cu(II) have been determined by comparing the thermodynamic functions for the ammonia and ethylenediamine complex ions of Cu(II) and Zn(II) over the temperature range of 10 to 40°. In complexes of Zn<sup>++</sup>, as in the preceding case of Cd<sup>++</sup>, the increase in stability resulting from chelation is purely an entropy effect; however, in the case of the transition type copper(II) ion the increase in stability resulting from chelation is distributed about equally between entropy and enthalpy terms.

In an earlier paper<sup>1</sup> the thermodynamic functions  $\Delta F$ ,  $\Delta H$  and  $\Delta S$  for methylamine complexes of cadmium were compared with the corresponding functions for the ethylenediamine and ammonia complexes of cadmium. It was found that the increase in stability which results from chelate ring formation is largely an entropy effect. It seemed desirable to examine other metal-ammine and metal-ethylenediamine systems to determine the generality of the phenomenon observed with cadmium.

In studying the methylamine complexes of metals other than cadmium, it was impossible to get the very important first formation constants because of precipitation of the hydroxides which occurred during the titration with methylamine. This made impossible a comparison of the type carried out for cadmium. The use of ammonia, a somewhat weaker base than methylamine, as the monodentate group obviated this difficulty but introduced other uncertainties which could be only partially resolved. For instance the secondary effects which might arise from replacement of the methyl group on the amine by a hydrogen atom should be considered. Data of the preceding paper show only a slight difference between the thermodynamic functions for the methylamine and ammonia complexes of cadmium. On the basis of these data, it seemed reasonable that a comparison of the thermodynamic data for the M(en)<sup>++</sup> and M(NH<sub>3</sub>)<sub>2</sub><sup>++</sup> complexes of other metal ions should provide the desired information. The Zn<sup>++</sup> ion was selected because of its similarity to the Cd<sup>++</sup> ion, and the Cu<sup>++</sup> ion was selected as the ion of a typical transition metal with available *d*-orbitals.

## Experimental

**Reagents.**—Ammonia and ethylenediamine solutions as described in the preceding paper were used. Reagent grade Zn(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>, KNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> were used without further purification.

The stock solution of copper nitrate was standardized by converting an aliquot to the sulfate through evaporation with sulfuric acid followed by electrolytic deposition of the copper.

The stock solution of zinc nitrate was standardized by determining zinc gravimetrically with 8-hydroxyquinoline according to the method of Welcher.<sup>2</sup>

**Procedure.**—Equilibrium constants were determined at 5° intervals from 10 to 40°, using the method of Bjerrum described previously.<sup>1</sup> Solutions had an ionic strength of 2.1 as described for cadmium. The equilibrium constants calculated are concentration constants and not true thermodynamic constants. They were calculated as described previously and from them the values of  $\Delta F$ ,  $\Delta H$  and  $\Delta S$  were calculated.

(1) C. G. Spike and R. W. Parry, *THIS JOURNAL*, **75**, 2726 (1953).

(2) F. J. Welcher, "Organic Analytical Reagents," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1947.

**Results.**—Figure 1 shows  $\ln K$  vs.  $1/T$  for each of the systems investigated, where  $K$  is the dissociation constant for the M(en)<sup>++</sup> or M(A)<sub>2</sub><sup>++</sup> complex. The thermodynamic data are summarized in Table IA. In Table II the differences in thermodynamic functions for chelate and non-chelate systems are summarized.

In Fig. 2 the natural logs of less precise constants for the systems Cu(en)<sub>2</sub><sup>++</sup>, Cu(NH<sub>3</sub>)<sub>4</sub><sup>++</sup>, Zn(en)<sub>2</sub><sup>++</sup> and Zn(NH<sub>3</sub>)<sub>4</sub><sup>++</sup> are plotted against  $1/T$ . Thermodynamic data for the bis-ethylenediamine complexes and tetramine complexes are summarized in Table IB. In Table III the uncorrected constants which are plotted in Figs. 1 and 2 are summarized.

## Discussion

Data summarized in Tables I and II indicate conclusively that Zn<sup>++</sup> is behaving in a manner very closely analogous to the Cd<sup>++</sup> ion. The  $\Delta H$  value for the Cd(NH<sub>3</sub>)<sub>2</sub><sup>++</sup> complex is only 0.1 kcal. above the value for the Cd(en)<sup>++</sup> complex. In an exactly analogous manner the Zn(NH<sub>3</sub>)<sub>2</sub><sup>++</sup> complex is only 0.1 kcal. above the Zn(en)<sup>++</sup> complex. In both cases this small difference is only slightly greater than the experimental uncertainty in measuring  $\Delta H$ . It is apparent that the increase in stability due to chelation is an entropy effect in the case of the Zn<sup>++</sup> complexes just as with Cd<sup>++</sup>. It is of interest to see in Table II that the difference in entropy between chelate and non-chelate structures is approximately the same for

TABLE I

SUMMARY OF THERMODYNAMIC FUNCTIONS FOR THE M(en)<sup>++</sup>, M(A)<sub>2</sub><sup>++</sup>, M(en)<sub>2</sub><sup>++</sup> AND M(A)<sub>4</sub><sup>++</sup> COMPLEXES OF Cu<sup>++</sup> AND Zn<sup>++</sup> AT 25°

Complex	$\rho K^{\circ}$ (cor.)	$\Delta H^{\circ}$ , kcal.	$\Delta F^{\circ}$ , kcal.	$T\Delta S$ , kcal.
A Zn(NH <sub>3</sub> ) <sub>2</sub> <sup>++</sup>	5.010	6.7	6.84	-0.1
Zn(en) <sup>++</sup>	6.148	6.6	8.39	-1.8
Cu(NH <sub>3</sub> ) <sub>2</sub> <sup>++</sup>	7.865	12.0	10.7	1.3
Cu(en) <sup>++</sup>	11.023	14.6	15.0	-0.4
B Zn(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup>	9.80	14.1	13.35	0.8
Zn(en) <sub>2</sub> <sup>++</sup>	11.49	12.5	15.67	-3.2
Cu(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup>	13.05	23.6	17.8	5.9
Cu(en) <sub>2</sub> <sup>++</sup>	20.61	28.4	28.2	0.2

<sup>a</sup> In this table,  $\rho K$  is equal to  $\rho K_1 + \rho K_2 + \dots + \rho K_n$  for dissociation of the complexes M(A)<sub>n</sub><sup>++</sup> and M(en)<sub>n</sub><sup>++</sup> listed in column 1. The calculated thermodynamic quantities are for the process of dissociation.

TABLE II

DIFFERENCES IN THERMODYNAMIC PROPERTIES OF CHELATE AND NON-CHELATE COMPLEXES AT 25°

Complexes compared	$\Delta(\Delta F^{\circ})$ , kcal.	$\Delta(\Delta H^{\circ})$ , kcal.	$\Delta(T\Delta S^{\circ})$ , kcal.
Cd(en) <sup>++</sup> -Cd(NH <sub>3</sub> ) <sub>2</sub> <sup>++</sup>	1.40 ± 0.02	0.0 ± 0.1	-1.4 ± 0.1
Cd(en) <sup>++</sup> -Cd(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup>	1.20 ± .02	-0.1 ± .1	-1.3 ± .1
Zn(en) <sup>++</sup> -Zn(NH <sub>3</sub> ) <sub>2</sub> <sup>++</sup>	1.55 ± .02	-0.1 ± .1	-1.6 ± .1
Cu(en) <sup>++</sup> -Cu(NH <sub>3</sub> ) <sub>2</sub> <sup>++</sup>	4.30 ± .02	2.6 ± .1	-1.7 ± .1

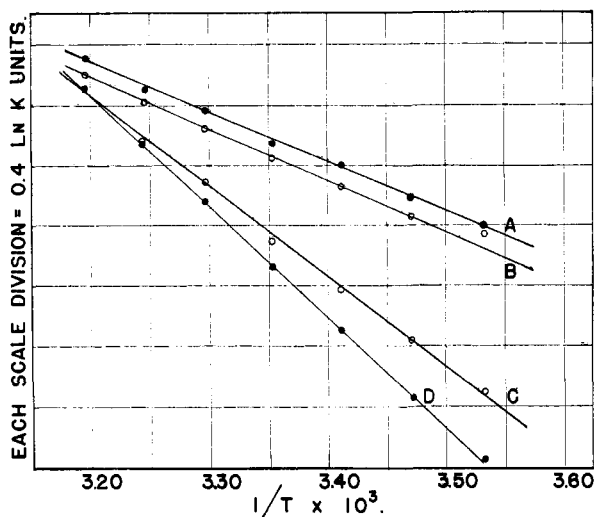


Fig. 1.— $\ln K$  plotted against  $1/T$  for: A,  $Zn(en)_2^{++}$ ; B,  $Zn(NH_3)_2^{++}$ ; C,  $Cu(NH_3)_2^{++}$ ; D,  $Cu(en)_2^{++}$ .  $K$  for  $M(NH_3)_2^{++}$  complexes =  $k_1k_2$ .

all metal ions tested. (See  $\Delta(T\Delta S)$  values in Table II.)

TABLE III

SUMMARY OF UNCORRECTED DISSOCIATION CONSTANTS FOR THE COMPLEXES OF  $Zn^{++}-NH_3$ ,  $Zn^{++}-en$ ,  $Cu^{++}-NH_3$  AND  $Cu^{++}-en$  AT TEMPERATURES BETWEEN 10 AND 40°

$t$ , °C.	$1/T$	$-\ln K$			
		$Cu(NH_3)_2^{++}$	$Zn(NH_3)_2^{++}$	$Cu(en)_2^{++}$	$Zn(en)_2^{++}$
		A.			
9.9	3.533	19.295	13.050	26.737	14.955
14.9	3.472	18.954	12.940	26.336	14.805
20.0	3.412	18.627	12.733	25.892	14.598
25.1	3.353	18.314	12.549	25.475	14.455
30.2	3.297	17.913	12.351	25.040	14.229
35.0	3.246	17.637	12.180	24.660	14.096
39.8	3.196	17.296	11.996	24.289	13.891

$K = k_1k_2$  for ammonia complexes.

B. Tetrammine and bis-ethylenediamine complexes

$t$ , °C.	$1/T$	$-\ln K$			
		$Cu(NH_3)_4^{++}$	$Zn(NH_3)_4^{++}$	$Cu(en)_2^{++}$	$Zn(en)_2^{++}$
9.9	3.533	32.10	23.90	50.01	27.44
14.9	3.472	31.36	23.55	49.09	27.10
20.0	3.412	30.81	23.05	48.26	26.78
25.1	3.353	30.16	22.66	47.52	26.46
30.2	3.297	29.43	22.38	46.65	26.04
35.0	3.246	28.80	21.87	46.10	25.72
39.8	3.196	28.21	21.41	45.18	25.37

In the case of the  $Cu^{++}$  complexes the increase in stability of the complex due to chelate ring formation is much greater than the increase observed with  $Zn^{++}$  and  $Cd^{++}$ . (See  $\Delta(\Delta F)$  values in Table II). Examination of  $\Delta(\Delta H)$  values for the cupric ion complexes indicates, in direct contrast to the complexes of  $Zn^{++}$  and  $Cd^{++}$ , that the bonds between  $Cu^{++}$  and ethylenediamine appear to be noticeably stronger than the bonds between  $Cu^{++}$  and ammonia. (In Table II the  $\Delta(\Delta H)$  value is 2.6 kcal. as compared to 0.1 for both  $Zn^{++}$  and  $Cd^{++}$ ).

The question of whether or not the increased bond strength of the copper chelates arises entirely

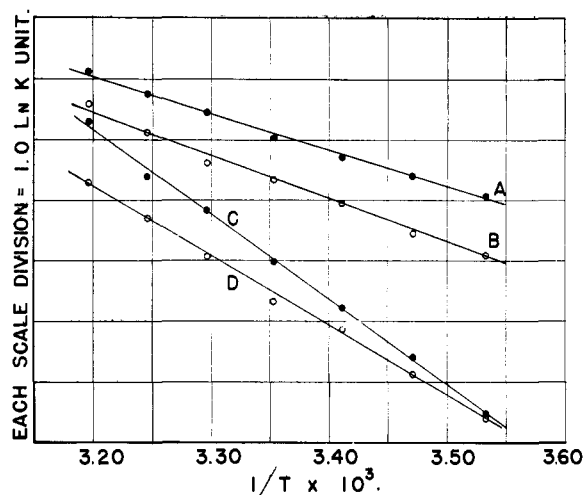


Fig. 2.— $\ln K$  plotted against  $1/T$  for: A,  $Zn(en)_2^{++}$ ; B,  $Zn(NH_3)_4^{++}$ ; C,  $Cu(en)_2^{++}$ ; D,  $Cu(NH_3)_4^{++}$ .  $K$  for  $M(NH_3)_4^{++} = k_1k_2k_3k_4$ ;  $K$  for  $M(en)_2^{++} = k_1k_2$ .

from electronic effects due to the formation of the chelate ring, or from the inductive effects due to the methylene groups in the ethylenediamine, makes it worthwhile to re-evaluate the differences between ammonia and methylamine. If it is assumed with Brown<sup>3</sup> and others that the methyl group serves as an electron donor to the nitrogen, then the larger bond strength in the ethylenediamine complex could arise in part from the effect of the methylene group. It is significant, however, that the donor effect of the methylene or methyl group was not apparent in complexes of  $Zn^{++}$  and  $Cd^{++}$ . Still, extrapolation of data from the palladium type<sup>4</sup> zinc and cadmium ions to the transition type cupric ion is hazardous.

A more direct basis for comparison is found in the very recently available thermodynamic data of Basolo and Merman<sup>5</sup> for the complexes of  $Cu^{++}$  and  $Ni^{++}$  with ethylenediamine and N-alkyl substituted ethylenediamine. In this case the addition of a methyl group to the nitrogen of the ethylenediamine had no detectable effect upon the strength of the  $Cu^{++}$ -nitrogen bond.

Bjerrum and Lamm<sup>6</sup> report measurements in concentrated methylamine solution which give an approximation of the fourth consecutive dissociation constant of  $Cu(NH_2CH_3)_4^{++}$ . This dissociation constant of the methylamine complex is approximately 20 times the constant for the corresponding ammonia complex, indicating greater stability of the ammonia compound. This fact also argues against attributing the greater bond strength in the ethylenediamine complex of  $Cu^{++}$  to the inductive effect of the methylene groups.

In view of the above facts the most reasonable conclusion to be drawn from the available data is that in the case of the transition type  $Cu^{++}$  ion

(3) H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, *THIS JOURNAL*, **66**, 435 (1944).

(4) Ions such as  $Cd^{++}$  which are isoelectronic with the palladium atom and ions such as  $Zn^{++}$  with a complete outer d-level (i.e., 18 electron ions) are referred to as palladium type ions in the same sense that  $Na^+$  and  $Cl^-$  are called inert gas type ions.

(5) F. Basolo and R. K. Merman, *THIS JOURNAL*, **74**, 5243 (1952).

(6) J. Bjerrum and C. Lamm, *Acta Chem. Scand.*, **4**, 997 (1950).

complexes the formation of the chelate ring is accompanied by an increase in bond strength. This contrasts sharply with the palladium type  $Zn^{++}$  and  $Cd^{++}$  ion complexes in which chelate ring formation has no influence on the bond strength.

It is possible (though not yet established with certainty) that transition ions generally form a stronger bond as a result of chelate ring formation and involvement of  $d$ -orbitals. Calvin and Bailes<sup>7</sup> reported approximate  $\Delta H$  and  $\Delta S$  values for the dissociation of  $Ni(en)_3^{++}$  and  $Ni(NH_3)_6^{++}$  in which increased bond strength due to chelation was indicated for the transition type  $Ni^{++}$  ion; how-

(7) M. Calvin and R. N. Bailes, *THIS JOURNAL*, **68**, 953 (1946).

ever, since their comparison was for the triethylenediamine and hexammine complexes, the data are not strictly comparable to those given above. In addition the previously published data on the cadmium complexes<sup>1</sup> of methylamine and ethylenediamine indicated that data for the simplest species such as  $MA_2^{++}$  and  $Men^{++}$  are more easily interpreted than data for the higher complexes such as  $MA_4^{++}$  and  $Men_2^{++}$ . It is still probable, however, that the generalizations reported for  $Ni(en)_3^{++}$  and  $Ni(NH_3)_6^{++}$  would be qualitatively applicable to a comparison between  $Ni en^{++}$  and  $Ni(NH_3)_2^{++}$ .

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

## Spectrophotometric Study of Np(V) Oxalate Complexes<sup>1</sup>

BY D. M. GRUEN AND J. J. KATZ

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A spectrophotometric study has shown that the complexes  $NpO_2C_2O_4^-$  and  $NpO_2(C_2O_4)_2^{=}$  exist in aqueous solution. Their association constants have been estimated in solutions having an ionic strength of 0.5. The heat of formation for the first complex is  $0.0 \pm 0.3$  kcal.

Although the absorption spectrum of  $NpO_2^+$  was extensively studied in aqueous solutions,<sup>2,3</sup> there has been so far no spectrophotometric indication of complex formation. Thus the  $NpO_2^+$  spectrum is the same, in 1  $M$   $HClO_4$ ,  $10^{-5}$   $M$   $HClO_4$ , 1  $M$   $HCl$ , 1  $M$   $H_2SO_4$ , 0.5  $M$   $HNO_3$ -1.5  $M$   $H_2O_2$  and 1  $M$   $HNO_3$ .<sup>2,3</sup> The behavior of  $NpO_2^+$  appears to be radically different from  $UO_2^{++}$ ,  $NpO_2^{++}$  and  $PuO_2^{++}$  which complex strongly with a large variety of anions.<sup>4-6</sup> It was therefore of some interest to study in more detail the recent observation that the maximum of the main Np(V) absorption peak, which had always been found at 983  $m\mu$  was displaced to 990  $m\mu$  in the presence of oxalate ion.<sup>7</sup> The present investigation concerns itself with a quantitative study of this shift as a function of oxalate concentration and of  $pH$  over the temperature range 10-47°.

### Experimental

**Procedure.**—Preliminary experiments carried out in 0.1 and 1.0  $M$  acetate buffers showed that  $NpO_2^+$  forms weak acetate complexes. The 983  $m\mu$  band is measurably broader in 1  $M$  acetate than in 1  $M$  perchlorate for example. A similar broadening effect was observed with citrate and phthalate, the other two common acid buffer substances. All the data presented here were, therefore, obtained in an unbuffered, 0.50  $M$   $NaClO_4$  solution.

In a typical experiment, a known volume ( $\approx 0.05$   $cm^3$ ) of Np(V) stock solution was added to a known volume ( $\approx 3.00$   $cm^3$ ) of 0.50  $M$   $NaClO_4$  solution in a 1-cm. silica absorption cell to give a fixed Np concentration  $\approx 10^{-3}$   $M$ .

(1) Presented in part at the Fall, 1952, Meeting of the American Chemical Society.

(2) R. Sjoblom and J. C. Hindman, *THIS JOURNAL*, **73**, 1744 (1951).

(3) J. C. Hindman, L. B. Magnusson, T. J. La Chapelle, Paper 15.2 of Vol. 14B of the NNES, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(4) R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, *ibid.*, Paper 4.20.

(5) G. E. Moore and K. A. Kraus, *ibid.*, Paper 4.22.

(6) R. T. Foley and R. C. Anderson, *THIS JOURNAL*, **71**, 909 (1949).

(7) G. Gibson, D. M. Gruen and J. J. Katz, *ibid.*, **74**, 2103 (1952).

A blank cell was filled only with the 0.50  $M$   $NaClO_4$  solution. Optical density readings were obtained on a Beckman Model D spectrophotometer in the region 970-1030  $m\mu$  at intervals of 2.5  $m\mu$ , the maxima of the absorption bands being obtained by slowly rotating the wave length drum and finding the point of maximum deflection of the galvanometer. Small increments (10-100 microliters) of a standardized oxalate solution ( $10^{-1}$ - $10^{-2}$   $M$  Sørensen oxalate in 0.50  $M$   $NaClO_4$  solution) were added by means of a Greiner microburet directly to the absorption cell containing the neptunium solution and optical density readings were obtained after each addition of oxalate. The microburet had been calibrated with mercury. During these runs water was circulated through the cell compartment from a constant temperature bath. The  $pH$ 's of the solution were determined spectrophotometrically at the same time in the following way. Approximately  $10^{-5}$  mole of a suitable indicator was dissolved in a liter of 0.50  $M$   $NaClO_4$  solution and it was this solution to which the neptunium and oxalate were added. Methyl orange was chosen for the  $pH$  range 3.1-4.4 and methyl red for the range 4.2-6.3. These indicators<sup>8</sup> absorb strongly in the region 400-600  $m\mu$  where  $NpO_2^+$  and its complexes have virtually no absorption but they do not absorb at all in the region 970-1030  $m\mu$ . The optical densities of the end forms of the indicator solutions were determined at 520 and 400  $m\mu$  where the acid and base forms, respectively, absorb strongly. From the known dissociation constants of the indicators and optical density readings at 400 and 520  $m\mu$ , it was then possible to calculate the  $pH$  of the solutions in the transition region of the indicators by well-established methods.<sup>9</sup> Methyl orange and methyl red were chosen because they exhibit very small salt errors<sup>9,10</sup> and their use in  $pH$  determinations has received intensive study.<sup>8</sup> Before each run, the neptunium and oxalate solutions were brought approximately to the same desired  $pH$  by the addition of small amounts of  $HClO_4$  or  $NH_4OH$ . When this was done the  $pH$  could be maintained constant to within  $\pm 0.1$   $pH$  unit during the entire course of a run.

For the runs in the  $pH$  range 1-2, no indicators were used. The  $pH$  was measured directly at the beginning and end of a run by means of a  $pH$  meter. A standardized oxalic acid solution was used instead of sodium oxalate. The  $pH$  of this solution had been adjusted to that of the neptunium

(8) W. B. Fortune and M. G. Mellon, *ibid.*, **60**, 2607 (1938).

(9) I. M. Kolthoff, "The Colorimetric and Potentiometric Determination of  $pH$ ," John Wiley and Sons, Inc., New York, N. Y., 1931.

(10) I. M. Klotz, Ph.D. Thesis, University of Chicago, 1940.