

suggest the presence of a tetragonal ligand field around the nickel ion essentially similar to that in the olive-yellow form of $[(C_6H_5)_4As]_2Ni(NCS)_4$ discussed earlier. In agreement with this, the infrared spectra of these two compounds in the range $400\text{--}200\text{ cm.}^{-1}$ are rather similar. The spectrum of $NiHg(SCN)_4$ shows one relatively sharp band at 303 cm.^{-1} and broad, ill-resolved absorption from ~ 280 to 200 cm.^{-1} with a maximum at $\sim 250\text{ cm.}^{-1}$.

Conclusions.—The results of our studies suggest that a distinction between N- and S-bonded thiocyanate groups can be made from their infrared spectra in the

region $400\text{--}200\text{ cm.}^{-1}$. Isothiocyanate complexes give rise to strong bands at values slightly above the M–Cl stretches of the corresponding chloro complexes (assuming the same symmetry). Thiocyanato complexes, on the other hand, give bands of medium intensity which, in the cases studied here, fall approximately midway between the metal–halogen stretches of the corresponding chloro and bromo complexes.

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Thermodynamics of Metal Cyanide Coordination. IV. Log β_i° , ΔH_i° , and ΔS_i° Values for the Zinc(II)–Cyanide System at 25° ^{1a}

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A pH titration study of the $Zn^{2+}\text{--}CN^-$ system at 25° in dilute aqueous solution provides positive evidence for only $Zn(CN)_2$ (aq), $Zn(CN)_3^-$, and $Zn(CN)_4^{2-}$ up to an 8:1 total cyanide to zinc ratio. Use of an IBM 7040 digital computer has allowed extensive analysis of the pH titration data to be carried out with the only major assumption being that of the species present. The absence of the $ZnCN^+$ species is substantiated by a polarographic study of the system. Equilibrium constants valid at ionic strength values of 0, 3.5×10^{-3} , and 7×10^{-3} are reported for the formation at 25° of each of the above species from Zn^{2+} and CN^- . Calorimetric ΔH_i° values are also reported together with ΔS_i° values. Preferential occurrence of certain complexes is discussed in the light of these thermodynamic quantities.

Introduction

Metal–cyanide complexes have occupied an important place in the development of our understanding of transition metal chemistry. One interesting, although as yet little understood, fact about these complexes is that some, *e.g.*, $Hg(CN)_4^{2-}$,^{2,3} are formed in a stepwise fashion by interaction of CN^- with the metal ion while others are not. For example, in the $Ni(CN)_4^{2-}$ system⁴ measurable concentrations of intermediate metal–cyanide species apparently do not exist even at low CN^- to Ni^{2+} ratios. Because of the opposite behavior of CN^- toward Ni^{2+} and Hg^{2+} , it seemed to us that the next logical step would be a study of the $Zn^{2+}\text{--}CN^-$ system. In common with nickel and mercury, zinc has the oxidation state +2. In addition, both Zn^{2+} and Ni^{2+} are in the same period differing in that they are d^{10} and d^8 ions, respectively. Also, Zn^{2+} resembles Hg^{2+} in being a d^{10} ion; however, the

underlying energy levels of these metal ions differ considerably. In view of these similarities and differences it appeared to be of interest to learn which, if either, of these $M^{2+}\text{--}CN^-$ systems the $Zn^{2+}\text{--}CN^-$ system resembled. Also, thermodynamic data for a large number of metal– CN^- systems should provide the basis for a better understanding of the nature of the bonding forces and, consequently, of stepwise and nonstepwise behavior in these systems.

Published data for the $Zn^{2+}\text{--}CN^-$ system are not consistent either with respect to which cyanide complexes intermediate between Zn^{2+} and $Zn(CN)_4^{2-}$ exist, or to the magnitude of β_4^5 for the formation of $Zn(CN)_4^{2-}$. Log β_4 values ranging from 16 to 21.4 have been reported,^{6–9} while the values reported for log $\beta_3^{7–10}$ and log β_5^8 lie within the range of these reported log β_4 values. Kunschert¹⁰ and Ferrell, Ridgion, and Riley¹¹ report that both Zn and Zn–Hg electrodes are attacked by aqueous CN^- solutions. Since most previous work on the $Zn^{2+}\text{--}CN^-$ system has been done

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(5) $\beta_i = [Zn(CN)_i^{2-i}]/[Zn^{2+}][CN^-]^i$; corresponding equilibrium constants valid at zero ionic strength are designated β_i° .

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using these electrodes and since the reported results vary widely, the validity of the reported equilibrium constant values is questionable. No evidence has been reported for or against the existence of $\text{Zn}(\text{CN})^+$. Østerud and Prytz¹² have presented evidence, based on polarographic studies, for $\text{Zn}(\text{CN})_2$, $\text{Zn}(\text{CN})_3^-$, and $\text{Zn}(\text{CN})_4^{2-}$. These authors also state that a wave, probably corresponding to the formation of $\text{Zn}(\text{CN})_5^{3-}$, appears when the total cyanide to zinc ratio exceeds 8:1. They observed another wave at a total cyanide to zinc ratio of 60:1 which was assigned to $\text{Zn}(\text{CN})_6^{4-}$.

Few calorimetric ΔH determinations for the Zn^{2+} - CN^- system have been reported. Joannis¹³ in 1882 reported a calorimetrically determined value for the heat of solution of $\text{Zn}(\text{CN})_2(\text{s})$ in HCl at 12° and high ionic strength, μ . Berthelot¹⁴ in 1899 measured the heat of precipitation of $\text{Zn}(\text{CN})_2$ as well as the heat of solution of $\text{Zn}(\text{CN})_2(\text{s})$ in aqueous KCN . A ΔH_4 value of 26 kcal./mole for the reaction $\text{Zn}^{2+} + 4\text{CN}^- = \text{Zn}(\text{CN})_4^{2-}$ is estimated from these data assuming stoichiometric formation of $\text{Zn}(\text{CN})_4^{2-}$. More recently, Guzzetta and Hadley¹⁵ reported a ΔH value of 27.7 kcal./mole for the formation of $\text{Zn}(\text{CN})_4^{2-}$ from Zn^{2+} and 4CN^- in a 1 *F* KCN solution.

In the present paper data are reported which establish the Zn^{2+} - CN^- species present in dilute aqueous solution up to a CN^- to Zn^{2+} ratio of 8:1 together with the corresponding β_i° , ΔH_i° , and ΔS_i° values for their formation from Zn^{2+} and CN^- at 25°.

Experimental

Materials.—Reagent grade NaCN (Baker Analyzed), NaOH (Baker Analyzed), Zn (Baker Analyzed), HClO_4 (Baker and Adamson), and NaClO_4 (Baker and Adamson) were used in the study. A stock $\text{Zn}(\text{ClO}_4)_2$ solution was prepared by dissolving Zn in a small excess of HClO_4 . The NaCN solutions were freshly prepared before each titration (to avoid errors due to decomposition) and standardized by the Liebig method. All solutions were prepared from freshly boiled distilled water kept in a N_2 atmosphere and were standardized by conventional procedures. Buffer solutions were prepared using reagents and directions furnished by the National Bureau of Standards (NBS Standard Samples No. 187a and 186b.)

Equilibrium Constant Determinations.—Zinc-cyanide solutions were prepared for titration by mixing known quantities of standard $\text{Zn}(\text{ClO}_4)_2$ and NaCN solutions, together with sufficient NaOH to just neutralize the HClO_4 present in the $\text{Zn}(\text{ClO}_4)_2$ solution. The resultant solutions were of the compositions (1) 0.000849 *F* $\text{Zn}(\text{ClO}_4)_2$, 0.00674 *F* NaCN , 0.0001322 *F* NaClO_4 , and (2) 0.000424 *F* $\text{Zn}(\text{ClO}_4)_2$, 0.00337 *F* NaCN , 0.0000660 *F* NaClO_4 . These solutions were then titrated in a N_2 atmosphere with 0.3161 *F* HClO_4 and pH readings made with a Leeds and Northrup No. 7401 pH meter equipped with Beckman glass and saturated calomel electrodes. A helipot and microdial were used with the pH indicator, giving a tenfold sensitivity increase. A check showed that the pH readings of the solutions being titrated remained constant over a period of several hours. The μ range covered by the study¹⁶ was 3.5×10^{-3} to 7×10^{-3} .

Polarographic Determinations.—Polarographic data were obtained using a Sargent Model XXI polarograph for zinc-cyanide solutions having a total zinc concentration of 0.000813 *F*. These solutions contained NaClO_4 as a supporting electrolyte, gelatin,

and sufficient NaCN to give cyanide to zinc ratios of 0, 1, 2, 3, 4, 6, and 8. Oxygen was removed by bubbling pure N_2 saturated with water vapor through the solutions for at least 6 hr. prior to the polarographic determinations. The measurements were made using dropping mercury and saturated calomel electrodes.

ΔH Determinations.— ΔH_i° values were determined for the Zn^{2+} - CN^- system using a thermometric titration procedure involving the titration of a $\text{Zn}(\text{ClO}_4)_2$ solution with a NaCN solution.¹⁶ The equipment and procedure used in these determinations have been described¹⁷ as well as more recent refinements.¹⁸ Independently, calorimetric ΔH_4 determinations were made for the formation of $\text{Zn}(\text{CN})_4^{2-}$ from Zn^{2+} and 4CN^- using a classical solution calorimeter.^{16,19}

Calculations.—The ion product of water,²⁰ $K_w = 1.008 \times 10^{-14}$, the dissociation constant of HCN ,¹⁸ $K_d = 6.15 \times 10^{-10}$, and the measured pH were corrected to the corresponding quantities at the experimental μ values used at each point in the study by means of an expanded form of the Debye-Hückel equation.¹⁶

Calculation of the β_i values required a knowledge of $[\text{CN}^-]$ and \bar{n} values. $[\text{CN}^-]$ was calculated from $[\text{H}^+]$, K_w , K_d , and the charge balance relationship of the solution components as shown in eq. 1 where $[\text{H}^+]_a$ is the product of the titrant concentration

$$[\text{CN}^-] = ([\text{H}^+]_a + K_w[\text{H}^+]^{-1} - [\text{H}^+])K_d[\text{H}^+]^{-1} \quad (1)$$

and the volume of the titrant added at the point of measurement divided by the volume of the solution. Using the results of (1) and measured quantities, \bar{n} was obtained from eq. 2. However, \bar{n}

$$\bar{n} = \frac{\text{CN}_{\text{bound to Zn}}}{\text{Zn}_{\text{total}}} = \frac{[\text{CN}_{\text{total}}] - [\text{CN}^-] - [\text{H}^+][\text{CN}^-]K_d^{-1}}{[\text{Zn}_{\text{total}}]} \quad (2)$$

may also be expressed in terms of β_i and $[\text{CN}^-]$ using appropriate zinc and cyanide mass balance expressions, in which case eq. 3 results, the values of β_i being the only unknowns, where j refers to

$$\bar{n}_j = \sum_i (i - \bar{n}_j)[\text{CN}^-]_j^i \beta_i \quad (3)$$

a particular data point.

Thus, using an appropriate number of experimental data points, one can calculate $[\text{CN}^-]$ and \bar{n} values and obtain the values of β_i . The calculations were recycled on an IBM 7040 digital computer until β_i and μ values of the desired self-consistency were obtained. The experimental error was minimized by using all possible combinations (approximately 85) of points in half-integral $\pm 0.25\bar{n}$ regions to calculate the β_i values. These β_i values were then averaged and a 90% confidence limit calculated. β_i° values were determined from the corresponding β_i values using appropriate activity coefficient values calculated from the Debye-Hückel equation.¹⁶

The methods used to calculate the heats of formation from the classical calorimetric¹⁹ and thermometric titration^{16,21} data have

(16) Material supplementary to this paper in the form of pH titration data, Debye-Hückel expressions, equation derivations, thermometric titration data, and classical calorimetric data has been deposited as Document No. 8261 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$8.25 for photoprints or \$2.50 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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TABLE I
 SUMMARY OF THERMODYNAMIC QUANTITIES FOR THE Zn^{2+} - CN^- SYSTEM^a

Reaction	log K^b	ΔG° , kcal./mole	ΔH° , kcal./mole	$T\Delta S^\circ$, kcal./mole
$Zn^{2+} + 2CN^- = Zn(CN)_2(aq)$	11.067 ± 0.017	-15.10	-10.8 ± 0.5	4.3
$Zn^{2+} + 3CN^- = Zn(CN)_3^-$	16.050 ± 0.023	-21.90	-19.2 ± 0.5	2.7
$Zn^{2+} + 4CN^- = Zn(CN)_4^{2-}$	19.62 ± 0.06	-26.77	-27.8 ± 0.5	-1.0
			$(-27.9 \pm 0.1)^{16}$	
$Zn(CN)_2(aq) + CN^- = Zn(CN)_3^-$	4.98	-6.80	-8.4	-1.6
$Zn(CN)_3^- + CN^- = Zn(CN)_4^{2-}$	3.57	-4.87	-8.6	-3.7

^a The log K values are valid at $\mu = 0$. The ΔH° value in parentheses was determined by classical calorimetry.¹⁶ Temperature 25°. ^b The uncertainties of the log K values are 90% confidence limits computed from the average results of three runs made at $[Zn^{2+}] = 0.000849 F$ and two runs made at $[Zn^{2+}] = 0.000424 F$.

been described. Corrections were made in both calculations for HCN^{18} and H_2O^{19} formation.

Results

Attempted calculation of formation constants for $ZnCN^+$, $Zn(CN)_2$, $Zn(CN)_3^-$, and $Zn(CN)_4^{2-}$ showed only the latter three to be present under the conditions of the present study. The β_1° value calculated for $ZnCN^+$ formation was either negative or varied widely from point to point; however, in all cases the β_i° values for the formation of the other species remained constant between determinations. Setting $\beta_1 = 0$, the absence of $ZnCN^+$ was verified by the fact that constant β_2° values were calculated over the entire \bar{n} range 0 to 2 including values calculated at and near $\bar{n} = 1$. If the monocyano species were present, our experience has shown that a constant β_2° value could not be calculated in the \bar{n} region from 0 to 1. Similar results are observed in the nonstepwise formation of $Ni(CN)_4^{2-}$ where log β_4° is constant regardless of the \bar{n} region from which it is calculated.⁴

Polarographic support of the absence of $Zn(CN)^+$ was also obtained. In $Zn(ClO_4)_2$ solutions containing $NaClO_4$ as the supporting electrolyte only two waves are observed. These waves at -1.0 and -1.8 v. are assigned to reduction of Zn^{2+} and $NaClO_4$, respectively. Upon addition of varying amounts of $NaCN$ to the $Zn(ClO_4)_2$ solutions two new waves are observed, presumably due to the formation of Zn^{2+} - CN^- complexes. Assignment of these waves to $Zn(CN)_2$ and $Zn(CN)_3^-$ is based on the fact that the first wave reaches a peak between a total cyanide to total zinc ratio, R , of 2 and 3, while the second reaches a maximum between $R = 3$ and $R = 4$. Since zinc cyanide complexes are very stable, these waves may be assigned to the $Zn(CN)_2$ and $Zn(CN)_3^-$ species, respectively. No wave corresponding to lower Zn^{2+} - CN^- species is observed. Waves for higher Zn^{2+} - CN^- complexes were not seen because of reduction of the supporting electrolyte at -1.8 v.

Values of \bar{n} calculated from the pH titration data approached 4 at the beginning of each titration. This fact together with the coincidence as \bar{n} approached 4 of the actual titration curve with the curve calculated from the theoretical pH titration of the cyanide ion in excess of that necessary to form $Zn(CN)_4^{2-}$ led us to conclude that $Zn(CN)_4^{2-}$ was the principal species in regions of high pH under our experimental conditions. This conclusion agrees with earlier work¹² where evi-

dence for complexes higher than $Zn(CN)_4^{2-}$ was found only in solutions having cyanide to zinc ratios greater than eight.

A summary of the thermodynamic quantities determined in the present study is given in Table I.

The validity of the equilibrium constants reported in Table I and of the equations with which they were determined was established by using these constants to calculate the pH titration curve from which they were derived.¹⁶ These calculations resulted in a fit within experimental error of the entire pH titration curve.

The relatively high estimated uncertainties of the ΔH° values in Table I are a result primarily of the inaccuracies inherent in the calculation of the concentrations of the species in solution. Equilibrium constants were also used in the classical calorimetric determinations to correct for incomplete reactions between Zn^{2+} and CN^- to form $Zn(CN)_4^{2-}$. The estimated uncertainty of the ΔS° values is ± 1 e.u.

It is seen in Table I that the ΔH° values for the stepwise addition of the third and fourth CN^- to Zn^{2+} are approximately equal, and either value is nearly as large as the value for the addition of $2CN^-$ to Zn^{2+} . This result is observed qualitatively in the curvature of the thermometric titration curve for this system.¹⁶ This curvature is a result of the greater rate of heat production with continued addition of $NaCN$ after the $Zn(CN)_2(aq)$ species reaches its maximum concentration, indicating that the third and fourth stepwise ΔH° values are larger than is ΔH_2° per ligand added.

Further evidence for the validity of the β_i values is provided by the constant ΔH_i values which were obtained at different points along the thermometric titration curve despite the fact that the relative species concentrations (as calculated using the β_i values in Table I) differ along the curve.

Discussion

Earlier studies of the Zn^{2+} - CN^- system⁶⁻¹⁵ were not carried out under the conditions of the present work; therefore, no comparisons are attempted between the results presented here and those of previous investigations. As seen in Table I, the ΔH_4° values determined in the present study by the two calorimetric procedures are in excellent agreement.

This study has shown the Zn^{2+} - CN^- system to be similar in certain respects to both the Ni^{2+} and Hg^{2+} -

CN⁻ systems; like Ni²⁺, Zn²⁺ shows nonstepwise complex formation (Zn(CN)₂(aq)), while, like Hg²⁺, stepwise complex ion formation is also observed (Zn(CN)₃⁻, Zn(CN)₄²⁻).

The trends in the ΔG° , ΔH° , and $T\Delta S^\circ$ values as a function of i for the Ni²⁺-CN and Zn²⁺-CN⁻ systems are shown in Table II. The values in Table II were obtained by dividing the total quantity in each case by i , e.g., ΔH_4° for each system ($M^{2+} + 4CN^- = M(CN)_4^{2-}$) was divided by 4.

TABLE II
 $\Delta G^\circ/i$, $\Delta H^\circ/i$, and $T\Delta S^\circ/i$ VALUES (KCAL./MOLE)
CALCULATED FOR THE REACTION $M^{2+} + iCN^- = M(CN)_i^{2-i}$

i	$\Delta G^\circ/i$	$\Delta H^\circ/i$	$-T\Delta S^\circ/i$
M = Zn			
2	-7.55	-5.4	-2.2
3	-7.30	-6.4	-0.9
4	-6.69	-7.0	0.3
M = Ni			
4	-10.3	-10.8	0.5

Since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, it is interesting that the $\Delta H^\circ/i$ and $-T\Delta S^\circ/i$ values diverge with increasing i in the Zn²⁺-CN⁻ system and, since the change of $-T\Delta S^\circ$ with i is greater than is that of ΔH_i° , ΔG_i° values become more positive with increasing i , resulting in stepwise formation of Zn(CN)₃⁻ and Zn(CN)₄²⁻. Our understanding of nonstepwise complex formation where it occurs in these M²⁺-CN⁻ systems is severely hampered by the fact that no data are available in aqueous solution for the formation of the obviously less stable intermediate complexes. Statistically, it is

hardly conceivable that these intermediate species do not form; however, if they do, it must be in heretofore undetectable concentrations. Thus, one can only estimate the thermodynamic properties of these species. The absence of the ZnCN⁺ species, for example, must be explained by the ΔG_1° value being sufficiently more positive than the ΔG_2° value to cause the Zn(CN)₂(aq) species to predominate in the n region 0 to 2. No data indicating Ni²⁺-CN⁻ complexes lower than Ni(CN)₄²⁻ have been reported, and available equilibrium constant values²² for the formation of the Ni(CN)₅³⁻ and Ni(CN)₆⁴⁻ species show that ΔG_4° is more negative than ΔG_5° or ΔG_6° by approximately 41 kcal./mole. Thus, the Ni(CN)₄²⁻ species shows maximum stability in this system. As seen in Table II, the magnitude of ΔG_4° in the Ni²⁺-CN⁻ system is determined by that of ΔH_4° ; the $T\Delta S_4^\circ$ term being small and of the same order of magnitude as that for the corresponding Zn²⁺ complex. The larger ΔH_4° value of Ni²⁺ compared to that of Zn²⁺ is undoubtedly a result of the ligand field stabilization of the Ni(CN)₄²⁻ species by CN⁻. Such stabilization does not occur with the d¹⁰ metal ion Zn²⁺, and this fact parallels the marked ΔH_4° difference in the formation of their respective tetracyano complex ions.

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Studies of Nitro and Nitrito Complexes. II. Complexes Containing Chelating NO₂ Groups

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The preparations of CoL₂(NO₂)₂ (L = (C₆H₅)₃PO, (C₆H₅)₃AsO), Ni{(CH₃)₂NCH₂CH₂N(CH₃)₂}(NO₂)₂, and NiL₂(NO₂)₂ (L = quinoline, α -picoline) are described. The first three compounds are monomeric in acetone or chloroform. The magnetic moments at room temperature and the electronic and infrared spectra of the complexes are reported. The results of the physical measurements suggest that the anions in these compounds are coordinated as bidentate, chelating groups.

Introduction

The nitrite ion is known to coordinate to metal ions in a variety of ways. As a monodentate ligand it may bond either through nitrogen, forming the well-known nitro complexes, or through one of the oxygen atoms to give the less-common nitrito complexes. It may also function as a bridging group, as in $\{(n-C_4H_9)_3P\}_2Pd_2-$

(NO₂)₄,¹ with nitrogen and one of the oxygen atoms acting as the donor atoms.^{1,2} During studies carried out to investigate the factors influencing the mode of coordination of the nitrite ion we recently prepared

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