are used. The inactive meso form has a dispersion ratio of 2.06 and λ_0 of approximately 3200 Å.

In Table I the available data are summarized. Previously published data were used in calculating the dispersion ratio at 4705 and 5880 Å. for some of the compounds.

TABLE I

DISPERSION RATIO OF METAL–DIAMINE COMPLEXES

Complex	$\alpha_{4705}/\alpha_{5880}$	Reference
(1) Complexes containing more than two molecules of an optically active diamine		
$[Rh(l\text{-chxn})_3]Cl_3$	1.75	(6)
$[Rh(l\text{-cptdin})_3]Cl_3$	1.74	(7)
$[Rh(d\text{-ptn})_3]I_3$	1.75	(12)
$[Pt(l\text{-pn})_3]Br_4$	1.74	This work
$[Pt\text{-}(d\text{-pn})_2]Cl_2$	1.74	(11)
$[Zn(l\text{-pn})_{2-3}]Cl_2$	1.74	This work (av. of 3 results)
$[Cd(l\text{-pn})_{2-3}](NO_3)_2$	1.75	This work (av. of 3 results)
(2) Complexes containing less than two molecules of an optically active diamine		
$[Pt(l\text{-phenen})(en)]I_2$	1.80	(13)
$[Pt(Htapn)Cl_4]Cl$	1.88	(14)
$[Pt(l\text{-pn})(NH_3)_2]Cl_2$	1.83	This work
$[Cd(l\text{-pn})_{1.57}](NO_3)_2$	1.86	This work
$[Zn(l\text{-pn})_{1.95}]Cl_2$	1.85	This work
$[Ag(l\text{-pn})_{1.56}](NO_3)$	1.85	This work
(3) Complexes with inactive diamines		
$[Rh(en)_3]I_3$	1.44	(15)
$[Ir(en)_3]Br_3$	1.56	(15)
$[Pt(en)_3]Cl_4$	1.68	(16)
$[Rh(m\text{-ptn})_3]I_3$	2.08	(12)
$[Pt(m\text{-stien})(buten)]Cl_2$	1.66	(17)

Conclusions

From the results reported here the following conclusions seem justified:

1. The source of optical activity in metal complexes with optically active diamines is different than for the resolved metal complexes with inactive diamines.

2. For the complexes with optically active diamines: A. The dispersive power seems independent of the nature of the metal atom even when the metal atom itself may become a center of asymmetry. B. The dispersive power seems independent of the nature of the optically active diamine. C. The dispersive power appears dependent on the formation function $\bar{n}$. The ratio $\alpha_{4705}/\alpha_{5880}$ is 1.74–1.75 when $\bar{n} > 2$ and 1.85 when $\bar{n} < 2$.

Finally because of the constant dispersion ratio for the optically active amines and for the metal complexes with these amines, it seems fair to presume that the optical activity of the complex arises only from the ligands, and not from any induced asymmetry around the central atom.

MINNEAPOLIS, MINNESOTA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE COLLEGE OF WASHINGTON[1]]

Complex Ions of Zinc and Hydroxylamine

BY C. J. NYMAN

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The complex ions formed between zinc ion and hydroxylamine have been investigated by the polarographic method, and two species, $[Zn(NH_2OH)]^{++}$ and $[Zn(NH_2OH)_2]^{++}$, were found to exist in aqueous solution. In solutions of ionic strength 1.0, the formation constants of the ions were found to be 2.5 ± 1 and 10.2 ± 2, respectively. No evidence was found to indicate the presence of any higher species of complex ions up to 1 *M* hydroxylamine concentration.

Introduction

Early reports in the literature by Crismer[2] and by Antonoff[3] indicated the preparation of the solid coördination compound $ZnCl_2 \cdot 2NH_2OH$. Goldschmidt and Syngros[4] reported the preparation of $ZnCO_3 \cdot 2NH_2OH$. These authors also reported the presence of the ion $[Zn(NH_2OH)_2]^{++}$ in aqueous solutions of zinc salts and hydroxylamine, but made no attempt to determine stability constants.

Experimental

The procedures and equipment employed in this investigation were the same as those employed in another study.[5]

All chemicals were of reagent grade and were used without further purification with the exception of hydroxylamine hydrochloride. This salt was purified by recrystallization from 95% ethanol. Stock solutions of 1.920 *M* hydroxylamine hydrochloride, 4.02×10^{-2} *M* zinc chloride, 1.9 *M* potassium hydroxide and 4.0 *M* potassium chloride were prepared. All solutions used in the polarographic runs had a zinc ion concentration of 4×10^{-4} mole per liter, and 1.0 *M* potassium chloride in addition to varying amounts of hydroxylamine. The solutions were prepared from the stock solutions by converting hydroxylamine hydrochloride to free hydroxylamine just prior to use by the addition of potassium hydroxide in such quantity that there was still a small amount of hydroxylammonium ion present. Sufficient potassium chloride was added so that on the final dilution to volume, the ionic strength of the solution was 1.0. The *p*H of the diluted solution was measured with a Beckman Model G *p*H meter, and the free hydroxylamine was calculated by consideration of the equilibrium

$$NH_2OH \cdot H^+ \rightleftharpoons NH_2OH + H^+$$

with equilibrium constant 1.04×10^{-6}.[6] It was assumed

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[1] This project was carried out under support of the Office of Ordnance Research, U. S. Army, Project No. DA-04-200-ORD-65, and the State College of Washington Committee on Research.

[2] L. Crismer, *Bull. soc. chim.*, **3**, 114 (1890).

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that this value for the equilibrium constant was valid at ionic strength 1.0, and that the activity coefficients were unity. Data presented by Hagisawa[6] and Winkelblech[7] indicated that the value of the dissociation constant did not change markedly with increase in ionic strength of the solutions. At the *p*H of these solutions, practically all of the hydroxylamine is present as the free amine. In view of the small variation of half-wave potential with hydroxylamine concentration, and the possible error involved therein, this estimation of hydroxylamine concentration is acceptable.

Data and Discussion

In Table I are recorded half-wave potentials and the diffusion currents of zinc ion with various concentrations of hydroxylamine and the *p*H of the various solutions.

TABLE I

VARIATION OF $E_{1/2}$ FOR ZINC ION WITH INCREASING CONCENTRATION OF HYDROXYLAMINE IN 1.0 *M* POTASSIUM CHLORIDE SOLUTION AT 25°

Hydroxylamine, moles/l.	*p*H	i_d, μ-amperes	$-E_{1/2}$ v. *vs.* S.C.E.
0.00	..	2.10	1.0127
.093	7.10	2.10	1.0164
.187	7.51	2.11	1.0207
.280	7.52	2.11	1.0248
.373	7.57	2.10	1.0282
.466	7.57	2.05	1.0317
.653	7.58	1.98	1.0368
.913	7.01	1.94	1.043

The method of DeFord and Hume[8] was used to determine the species of complex ions in solution and their formation constants. In view of the small values of the formation constants obtained, it was thought necessary to consider the hydrolysis of zinc ion. The formation constant of $[ZnOH]^+$ has been determined by Kolthoff and Kameda.[9] Recently, Fulton and Swinehart[10] have reported equilibrium constants from which the formation constants of the other hydroxide complexes of zinc may be calculated. These are summarized below.

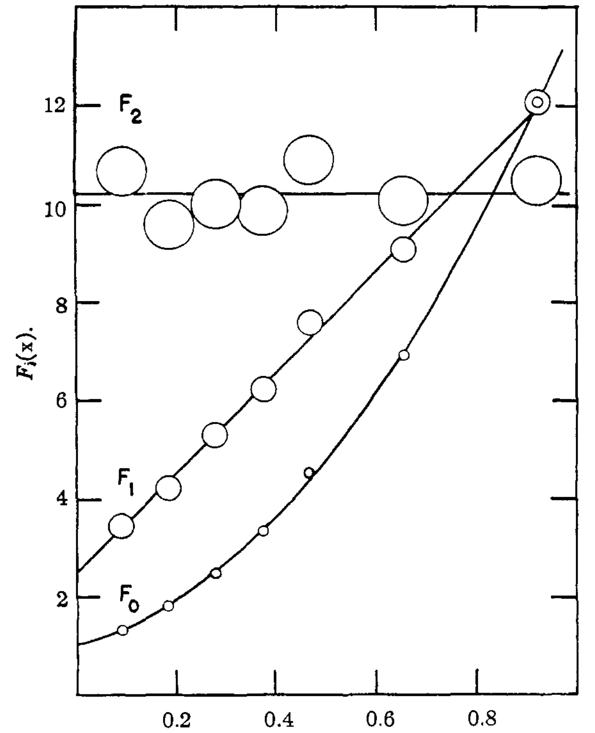

Fig. 1.—Values of $F_0(X)$, $F_1(X)$ and $F_2(X)$ for zinc ion in hydroxylamine solution

$$Zn^{++} + OH^- \rightleftarrows [ZnOH]^+;\ B_1 = 2.45 \times 10^4$$

$$Zn^{++} + 2OH^- \rightleftarrows [Zn(OH)_2];\ B_2 = 5.72 \times 10^{11}$$

$$Zn^{++} + 3OH^- \rightleftarrows [Zn(OH)_3]^-;\ B_3 = 1.71 \times 10^{14}$$

$$Zn^{++} + 4OH^- \rightleftarrows [ZnOH)_4]^{--};\ B_4 = 3.14 \times 10^{15}$$

DeFord and Hume related the shift in half-wave potential to the concentration of the complexing agent by the equation

$$\sum_j K_j(C_x)^j = \text{antilog}\left(0.435\frac{nF}{RT}[(E^0{}_{1/2})_s - (E_{1/2})_c] + \log\frac{I_s}{I_c}\right) \quad (1)$$

In this expression, K_j is the formation constant for the reaction

$$Zn^{++} + jNH_2OH \rightleftarrows [Zn(NH_2OH)_j]^{++}$$

C_x is the concentration of hydroxylamine in moles per liter; $(E^0{}_{1/2})_s$ and $(E_{1/2})_c$ are the half-wave potentials of the simple and complex zinc ions, respectively; and I_s and I_c are the diffusion current constants of the simple and complex zinc ions, respectively.

In order to take into account the hydrolysis of zinc ion, one must revise equation (1) to the following

$$\sum_j K_j(C_x)^j = \text{antilog}\left(0.435\frac{nF}{RT}[(E^0{}_{1/2})_s - (E_{1/2})_c] + \log I_s/I_c\right) - [B_1(OH) + B_2(OH)^2 + B_3(OH)^3 + B_4(OH)^4] \quad (2)$$

where B_1 through B_4 have the values given above and (OH) represents the concentration of hydroxide ion in the solutions.

Setting the right-hand side of equation 2 equal to $F_0(X)$, the subsequent operations as outlined by DeFord and Hume can then be carried out. The quantity $F_1(X)$ is defined as equal to $[F_0(X) - 1]/C_x$, and $F_j(X) = [F_{(j-1)}(X) - K_{(j-1)}]/C_x$. If $F_j(X)$ plotted against C_x and extrapolated to $C_x = 0$, the value of $F_j(X)$ at the intercept is K_j.

It was found that the two species $[ZnOH]^+$ and $[Zn(OH)_2]$ are present in concentration sufficiently great to make a slight correction to the value of $F_0(X)$, while the concentration of $[Zn(OH)_3]^-$ and $[Zn(OH)_4]^{--}$ is so small that their effect is negligible.

Plots of $F_j(X)$ for the zinc–hydroxylamine complexes in a supporting electrolyte of potassium chloride are shown in Fig. 1. It is apparent from these plots that the two ions which exist in solution under the conditions of this investigation are $[Zn(NH_2OH)]^{++}$ and $[Zn(NH_2OH)_2]^{++}$ with formation constants $K_1 = 2.5 \pm 1$ and $K_2 = 10.2 \pm 2$. The fact that the plot of $F_2(X)$ is a straight line with a slope of zero indicates that the species

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$[Zn(NH_2OH)_2]^{++}$ is the most complex which exists in the solutions under investigation here. The finding that this ion is capable of existence is in agreement with the reports of the formulas for the solid coördination compounds and with the previous report of the existence of this ion in aqueous solution.

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NOTES

Determination of *n*- or *p*-Type Conductivity by the Effect Produced by Hydrogen Adsorption on Electrical Conductivity

By Louis F. Heckelsberg, Grant C. Bailey and Alfred Clark

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Introduction.—In the investigation of the electrical and catalytic properties of semi-conductors the determination of the mode of conduction—whether it is *n*-type or *p*-type—is of interest. At the present time the mode of conduction is determined quantitatively by measuring the Hall effect or qualitatively by the thermoelectric effect. As a result of observations made during an investigation of the electrical and catalytic properties of powdered metal oxides and sulfides, we have found another method which can be used for the qualitative determination of the mode of conduction of these materials.

This method involves the effect produced by adsorbed hydrogen on the electrical conductivity of these materials. We have observed in the case of the *p*-type semi-conductor chromium sesquioxide that its conductivity is drastically reduced as rapidly as hydrogen can come in contact with it. The converse effect was observed for the *n*-type semiconductor zinc oxide where the conductivity was drastically increased when hydrogen came into contact with it. As a result of these observations it was decided to check several additional semiconductors to see if this effect was of a general nature.

Experimental Details.—As an example of this method we shall describe the procedure followed for nickel oxide. The sample of nickel oxide was pretreated with oxygen at 500° for 12 hours in an apparatus previously described by the authors.[1] With prepurified nitrogen flowing over the nickel oxide its conductivity was measured as a function of temperature. At 300° hydrogen was introduced over the nickel oxide. This resulted in a rapid decrease in the conductivity of the nickel oxide of the order of about 10^{-3}. After approximately one minute the conductivity began to increase as the nickel oxide was being reduced. This may mean that the nickel oxide on contact with hydrogen underwent a transition from *p*-type to *n*-type and ultimately to a metallic conductor. In the case of chromium sesquioxide where hydrogen does not materially reduce the oxide at 500° the conductivity decreases and remains extremely low.

Results.—The results for semi-conductors which we have tested or were tested by others and that exhibit this behavior are as follows: nickel oxide, chromium sesquioxide, stannous sulfide and chromia–alumina were classified as *p*-type semiconductors while titanium dioxide, zinc oxide, zinc sulfide, calcium oxide and tungsten sulfide were classified as *n*-type semi-conductors. The change produced by hydrogen on conductivity has been reported previously for stannous sulfide,[2] chromia–alumina[3] and for zinc oxide.[4] These results agree with the classification of these materials by Hall effect as reported in the literature.

In the case of insulators such as silica this effect was not observed.

The magnitude of change observed was found to vary from a ten-thousand-fold change for titanium dioxide to a threefold change for zinc sulfide.

The effect produced by hydrogen was found to be reversible. After the hydrogen contacted the semi-conductor the material's original conductivity could be restored by flushing the hydrogen out with nitrogen. The change produced on the electrical conductivity by the nitrogen flushing was much slower than the change produced when hydrogen contacted the semi-conductor.

Discussion

Pretreatment of *n*-type semi-conductors, such as zinc oxide, with hydrogen results in an increase of electrical conductivity caused by an increase in lattice defect concentration. These defects are formed by the oxygen or sulfur combining chemically with the hydrogen leaving a cation-excess material. The increase observed by reduction with hydrogen is slow compared to the rate of increase observed when hydrogen is adsorbed on a semiconductor in an inert atmosphere.

A plausible explanation of the mechanism involved in reducing the current flow in *p*-type semiconductors is as follows. When the hydrogen comes into contact with a *p*-type semi-conductor it dissociates and ionizes. The protons are adsorbed on the surface while the electrons enter the lattice and combine with positive holes. Filling the positive holes—which are considered to be the current carriers in *p*-type semi-conductors—reduces the current flow.

The mechanism involved in the increase in current flow observed when hydrogen comes into con-

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[1] Heckelsberg, Clark and Bailey, "A Correlation between Lattice Defects and Catalytic Activity of Zinc Oxide" presented before a Symposium on Mechanisms of Homogeneous and Heterogeneous Hydrocarbon Reactions at the Kansas City Meeting of the American Chemical Society, March 29 to April 1, 1954.

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