[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Optical Activity of Some *l*-Propylenediamine–Metal Complexes

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RECEIVED MAY 20, 1954

The dissociation constants of the acid salts of propylenediamine have been redetermined. The rotatory power of complexes of *l*-propylenediamine with Zn^{+2}, Cd^{+2}, Hg^{+2} and Ag^{+} have been measured as a function of the number of propylenediamine molecules in the complex. With Zn^{+2} and Cd^{+2} complexes the rotation of a complex bound *l*-propylenediamine molecule reaches a minimum with the formation of the bis complex. The optical activity of *l*-propylenediamine is unaffected by the presence of barium and magnesium ions, indicating no formation of even very weak complexes in solution.

Introduction

When an optically active ligand coördinates with a metal ion, optical rotations are observed which are different from those of the optically active ligand. In some cases the sign of rotation is reversed. These changes have been ascribed to "partial induced asymmetry" in the complex ion itself, and also to a change in the contribution of the optically active ligand by the coördination.

Generally those metal ions which form inert octahedral amine complexes are colored, Co^{+3}, Cr^{+3}, etc., so they exhibit a strong Cotton effect, making interpretations very difficult if not impossible. The relatively stable colorless ions are Pt^{+2}, Zn^{+2}, Hg^{+2}, Cd^{+2} and Ag^{+}, and their complex propylenediamine (pn) ions have been examined in order to try to find whether partial induced asymmetry occurs or whether the optical activity is changed by coördination.

Optically active propylenediamine–Pt^{+2} complexes have been investigated by Tschugaeff and Sokoloff[1] who concluded that each active propylenediamine contributed ±96° to the total activity. Since there is no possibility of optical activity arising from asymmetry about the central metal ion itself, this should be a true measure of the effect of coördination on the optical activity of propylenediamine.

Experimental

All optical rotations were measured at 25° on a Schmidt and Haensch polarimeter at the sodium D line. Unless otherwise specified two-decimeter (2 dm.) tubes were used. All the rotations reported are the average of at least eight observations and have an average deviation of ±0.01° unless otherwise noted.

Eastman yellow label 85% propylenediamine was resolved according to the method of Hurliman,[2] in which 710 g. of *d*-tartaric acid is dissolved in 950 cc. of water at 95°. To this is added 210 g. of *rac*-propylenediamine with stirring. The precipitate is filtered and dissolved in 1610 cc. of water at 80°, allowed to cool and filtered. These crystallizations are continued until the *l*-propylenediamine *d*-tartrate is separated from the dextro form (7 times). The product melts sharply at 142°. The filtrates are combined and the levo salt recrystallized; 252 g. was obtained from first crystallization.

This salt is then mixed with 102 g. of KCl, both substances being dissolved in the smallest volume of hot water. The resulting insoluble potassium acid tartrate is filtered, and the filtrate is evaporated to dryness to recover the *l*-propylenediamine hydrochloride. The solid hydrochloride is then mixed with a slight excess of solid KOH and the liberated *l*-propylenediamine distilled from a copper flask.

The *p*H measurements were made at 25° on a model "M" Beckman *p*H meter, which was frequently standardized against buffer solutions of known *p*H.

The zinc solutions were prepared from stock solutions of 0.4647 *M* $ZnCl_2$ (0.2532 *M* in HCl) and 63.35% *l*-propylenediamine. The stock solution was made by dissolving a weighed amount of zinc metal (analytical reagent, arsenic free) in a slight excess of concentrated hydrochloric acid. The free acid was determined by titration with standard base. The concentration of the stock solution of *l*-propylenediamine was determined by titration with standard acid.

The cadmium, mercury, silver, barium and magnesium solutions were prepared in a similar manner from stock solutions made from reagent grade salts of the respective metals.

Results

Dissociation Constants of Propylenediamine.—In order to calculate the concentrations of all species present in solution, the acid dissociation constants of propylenediamine must be known. Carlson, McReynolds and Verhoek[3] reported for the HCl salts $pK_{pn\cdot H_2^{+2}} = 7.07$ and $pK_{pn\cdot H^+} = 9.83$, and for the HNO_3 salts $pK_{pn\cdot H_2^{+2}} = 7.00$ and $pK_{pn\cdot H^+} = 9.78$. These constants were redetermined so that conditions for determination would be the same as those for which the constants are applied.

The average of 17 values obtained for $pK_{pn\cdot H^+}$ was 10.00 ± 0.04 and the average of 6 values obtained for $pK_{pn\cdot H_2^{+2}}$ was 7.05 ± 0.02. There is no indication of any substantial difference in the constants for the HCl and HNO_3 salts as previously reported.[3]

Zinc-*l*-Propylenediamine Complexes.—Optical rotations were measured for a series of solutions, all 0.0465 *M* in $ZnCl_2$, 0.0253 *M* in HCl and 0.50 *M* in KCl. The concentration of *l*-propylenediamine was varied in order to obtain optically active complex species comprising a full range of metal–ligand compositions.

At equilibrium the initial acid concentration $C_H = [pn\cdot H^+] + 2[pn\cdot H_2^{+2}] + [H^+]$. For all the solutions studied, the initial acid concentration and the observed *p*H were of such values that the last term $[H^+]$ could be neglected. However, in solutions where the $pH \geqq 9$, additional hydrogen ion is furnished by the water as $pn + H_2O = pn\cdot H^+ + OH^-$, so the expression becomes $C_H + [OH^-] = [pn\cdot H^+] + 2[pn\cdot H_2^{+2}]$. This relation and the expression for the dissociation constant $K_{pn.H_2^{+2}} = [pn\cdot H^+][H^+]/[pn\cdot H_2^{+2}] = 10^{-7.05}$ allows the calculation of the concentration of the acid salts when the *p*H is measured. The concentration of free amine can then be obtained from the second dissociation constant expression $K_{pn\cdot H^+} = [pn][H^+]/[pn\cdot H^+] = 10^{-10.00}$.

The optical rotation of the complex bound amine is obtained by subtracting from the observed rotation, $\alpha_{obs.}$, the rotation due to the free amine and to

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(1) L. Tschugaeff and V. Sokoloff, *Ber.*, **40**, 3461 (1907); **42**, 55 (1909).

(2) Hurliman, Thesis, Zurich, 1918.

(3) G. A. Carlson, J. P. McReynolds and F. H. Verhoek, THIS JOURNAL, **67**, 1334 (1945).

the two acid salts at the concentrations calculated for these species in each solution. Table I shows the experimental data from which these values were obtained.

TABLE I

OPTICAL ROTATIONS OF *l*-PROPYLENEDIAMINE–HCl SOLUTIONS

Initial concn., l-pn	Initial concn., HCl	Molar ratio, acid/base	Obsd. rotation α	Mol. rotation $[M_D]$
0.7975	....	..	−1.30	−8.15
.3724	0.1862	0.50	−0.65	−8.74
.3103	.2172	0.70	− .55	−8.87
.2482	.2483	1.00	− .46	−9.25
.2172	.2638	1.21	− .245	−5.64
.1862	.2793	1.50	− .07	−1.88
.1689	.2879	1.70	+ .04	+1.19
.7140	1.4280	2.0	+ .85	+5.95
.1206	0.2412	2.0	+ .072	+5.97

The molecular rotation $[M]_D$ is given by $10\alpha/lm$ when molar concentrations are used. Since 2-dm. tubes have been used except where noted, the rotation of any species is given by $\alpha = {}^1/_5\, m[M]_D$. The following calculations for a zinc chloride–*l*-propylenediamine solution illustrate the method used to obtain the results illustrated in Table II.

TABLE II

C_{pn}	pH	$\alpha_{obsd.}$	[pn]	$[pn \cdot H^+]$	$[pn \cdot H_2^{+2}]$	$[pn]_c$	α_{pn}	$\alpha_{pn \cdot H^+}$	$\alpha_{pn \cdot H_2^{+2}}$	α_c	$[M]_D$	$\bar{n}$
0.1233	8.53	−0.75	0.0008	0.0237	0.0008	0.0980	−0.001	−0.044	+0.001	−0.71	−36.2	2.11[a]
.1185	8.49	− .72	.0006	.0207	.0008	.0964	− .001	− .043	+ .001	− .68	−35.3	2.18[b]
.0658	8.06	− .08	.0002	.0183	.0020	.0453	.....	− .038	+ .002	− .044	− 4.9	0.95[c]
.2302	10.85	− .24	.1117	.0185	....	.1000	− .182	− .038	.....	− .02	− 1.0	..[d]

[a] $ZnCl_2$ solution [b] $Cd(NO_3)_2$ solution. [c] $AgNO_3$ solution. [d] $Hg(NO_3)_2$ solution.

Initial molar concn. of $ZnCl_2$ (C_M) = 0.0465
Initial molar concn. of HCl (C_H) = 0.0253
Initial molar concn. of *l*-pn (C_{pn}) = 0.1233
Measured *p*H 8.53 Obsd. rotation = −0.75°

$$\frac{[pn \cdot H^+]}{[pn \cdot H_2^{+2}]} = \frac{K_{pn \cdot H^+}}{[H^+]} = \frac{10^{-7.05}}{10^{-8.53}} = 30.2$$

$$[pn \cdot H^+] + 2[pn \cdot H_2^{+2}] = C_H + [OH^-]\ 0.0253$$

So

$$[pn \cdot H^+] = 2.37 \times 10^{-2} \text{ and } [pn \cdot H_2^{+2}] = 7.85 \times 10^{-4}$$

$$\frac{[pn]}{[pn \cdot H^+]} = \frac{K_{pn \cdot H^+}}{[H^+]} = \frac{10^{-10.00}}{10^{-8.53}} = 3.39 \times 10^{-2} \text{ from which}$$

$$[pn] = 8.03 \times 10^{-4}$$

The concentration of complex bound propylenediamine $[pn]_C$ =

$$C_{pn} - [pn] - [pn \cdot H^+] - [pn \cdot H_2^{+2}] = 0.0980$$

The rotations due to the various uncomplexed species of propylenediamine are then

$$\alpha_{pn} = 1/5\,(8.03 \times 10^{-4})(-8.15°) = -0.001°$$
$$\alpha_{pn \cdot H^+} = 1/5\,(2.37 \times 10^{-2})(-9.25°) = -0.044°$$
$$\alpha_{pn \cdot H_2^{+2}} = 1/5\,(7.85 \times 10^{-4})(+5.96°) = +0.001°$$

The rotation due only to complexed amine, α_C, is then $-0.75° + 0.044 = -0.71°$.

The molecular rotation $[M]_D$ calculated per mole of complex bound amine is then $5\alpha_C/[pn]_C = -36.2°$.

The formation function $\bar{n}$ which defines the average number of complex bound ligands per total moles of metal ion is given by

$$\bar{n} = \frac{[pn]_C}{C_M} \text{ or } = \bar{n}\ \frac{0.0980}{0.0465} = 2.11.$$

The results are given in Table II.

Cadmium–Propylenediamine Complexes.—Optical rotations were measured for a series of solutions all 0.0441 *M* in $Cd(NO_3)_2$, 0.0222 *M* in HNO_3 and 0.50 *M* in KNO_3.

Mercury–*l*-Propylenediamine Complexes.—Optical rotations were measured for solutions of mercury(II) nitrate containing *l*-propylenediamine in excess of that required for the complete formation of the bis complex. Lower ratios resulted in the formation of insoluble mercury salts. Apparently these solutions contain only the bis complex because of the constant values of $pK_{pn \cdot H^+}$ and $[M]_D$. The solutions were 0.0500 *M* in $Hg(NO_3)_2$, 0.0178 *M* in HNO_3 and 0.50 *M* in KNO_3.

Silver–*l*-Propylenediamine Complexes.—Optical rotations were measured for a series of solutions all 0.0479 *M* in $AgNO_3$, 0.0222 *M* in HNO_3 and 0.50 *M* in KNO_3.

Non-complex Forming Metals with *l*-Propylenediamine.—It has been suggested by Balfe[4] that optical rotatory power might be utilized to determine very minor changes in chemical constitution

A solution 0.0336 *M* in $MgCl_2$, 0.5000 *M* in HCl, 0.50 *M* in KCl and 0.4279 *M* in *l*-propylenediamine had a *p*H of 7.62 and an observed rotation of −0.44 ± 0.01°. From the dissociation constants the calculated concentrations and rotations are

$$[pn \cdot H^+] = 0.228 \qquad \alpha_{pn \cdot H^+} = -0.533°$$
$$[pn \cdot H_2^{+2}] = 0.106 \qquad \alpha_{pn \cdot H_2^{+2}} = +0.122°$$
$$[pn] = 0.017 \qquad \alpha_{pn} = -0.028°$$
$$\text{Total } \alpha_{calcd.} = -0.439°$$

A solution 0.0542 *M* in $BaCl_2$, 0.0252 *M* in HCl, 0.50 *M* in KCl and 0.4279 *M* in *l*-propylenediamine had a *p*H of 11.62 and an observed rotation of −0.66 ± 0.02°. The calculated concentrations and rotations are

$$[pn \cdot H_2^{+2}] < 10^{-5} \text{ or negligible} \qquad \alpha_{pn \cdot H_2^{+2}} = \text{negligible}$$
$$[pn \cdot H^+] = 0.0265 \qquad \alpha_{pn \cdot H^+} = -0.049°$$
$$[pn] = 0.3844 \qquad \alpha_{pn} = -0.625°$$
$$\text{Total } \alpha_{calcd.} = -0.674°$$

The agreement between observed and calculated rotations indicates no complex formation occurs with these metals.

Discussions of Results

The negative rotations found for the complexes of *l*-propylenediamine with Zn^{+2}, Cd^{+2}, Hg^{+2} and Ag^{+} show that the reversal in sign of rotation when an optically active base is complexed with a metal is not a general phenomenon as some assume from the behavior of complexes of the trivalent metals. The fact that this reversal of sign occurs with the "inert" complexes of Co^{+3}, Pt^{+4}, Cr^{+3}, Rh^{+3}, Ir^{+3}, etc., and is absent in the "labile" complexes studied, suggests a dependence on the type of bond-

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(4) M. P. Balfe, *J. Chem. Soc.*, 1871 (1950).

ing in the complex. A theoretical model[5] describing the optical activity of propylenediamine would be in accord with these facts if the base were monodentate in the "labile" complexes. The existence of these monodentates for some silver–amine salts has been reported by Schwartzenbach.[6]

Figure 1 shows the change in rotatory power of complex bound *l*-propylenediamine as the number of amine ligands about the central metal ion increases. The zinc and cadmium curves are quite similar in shape. The rotatory power of a complexed *l*-propylenediamine molecule appears to decrease as additional molecules of active base are coördinated, until a minimum is reached, when two molecules are bound to the zinc or cadmium ion. Coördination of additional molecules of the base then causes an increase in the rotatory power of each ligand. The effect of coördination geometry on the rotatory power of an active ligand appears more prominent in the case of the zinc complex. It is interesting to note in this connection that the four-coördinate (tetrahedral) complexes of zinc are much more stable than those of cadmium. With the zinc–ammonia complexes a coördination of four seems to be a maximum and even with ethylenediamine and propylenediamine this tendency is observed in the formation constant curves.[3] The change from one to two ligands about a cadmium ion appears to have only a small effect on the rotatory power of the base, an effect no greater than that observed with the planar platinum complexes.[1]

With silver as the central metal ion, the rotation of the base increases with the number of bound ligands until the formation function $\bar{n}$ is about 1.5. Here the rotation is the same as for the fully coördinated ($\bar{n} = 2$) metal.

In an attempt to explain the effect of the metal ion on the rotation of the complex bound *l*-propylenediamine molecule, the rotations are compared with the strength of the corresponding ethylenediamine complexes in Table III. For comparison, the rotations shown are those for the bis ($n = 2$) complex. The constant $1/N \log K_N$ is a measure of the average tendency of a ligand to be removed from the complex, when $K_N = [M]^{+n}[en]^N/[M(en)_N]^{+n}$(en = ethylenediamine).

It appears that the rotation of a complex bound propylenediamine molecule increases with the weakness of the metal–nitrogen bond.

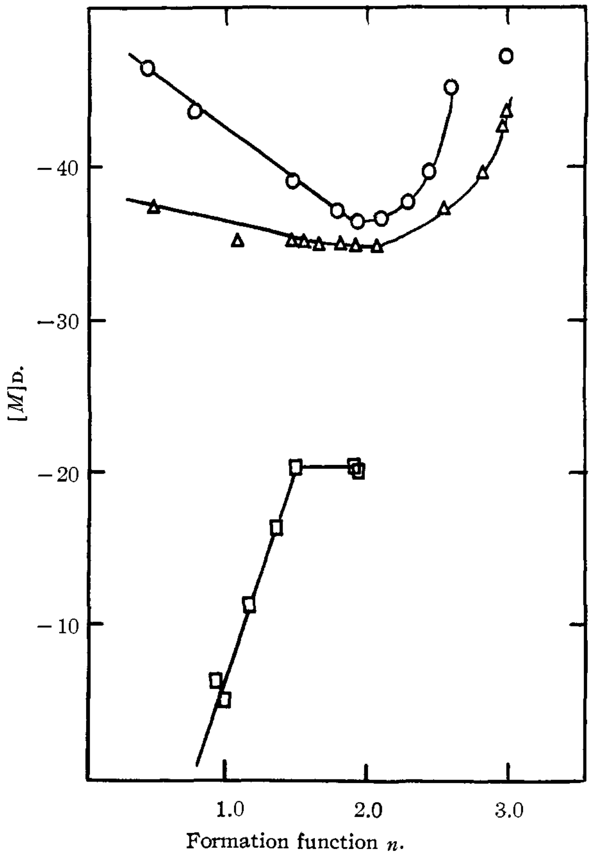

Fig. 1.—○-$ZnCl_2$ and *l*-propylenediamine: Δ, $Cd(NO_3)_2$ and *l*-propylenediamine; □, $AgNO_3$ and *l*-propylenediamine.

TABLE III

Metal	$[M]_D$	$1/N \log K_N$	Reference
Hg	−1.0°	−11.7	7
Ag	−20.9	−7.7	6
Cd	−35.1	−4.0	3
Zn	−36.0	−4.0	3

Results soon to be published show the striking effect of *n* on some rotatory dispersion curves.

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[5] W. C. G. Baldwin, *Proc. Roy. Soc. (London)*, **A167**, 539 (1938).

[6] G. Schwartzenbach, *Helv. Chim. Acta*, **35**, 2337 (1952); **36**, 23 (1953).

[7] J. Bjerrum, unpublished results; see J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).