with a Perkin-Elmer 202 spectrophotometer; infrared spectra were measured with a Perkin-Elmer 237B grating spectrophotometer, using the KBr-disk technique. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill., and Triangle Chemical Laboratories, Inc., Chapel Hill, N. C.

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Transition Metal Complexes of 3,3′-Diaminodipropylamine: Stability Constants

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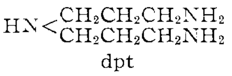
The basicity constants of 3,3′-diaminodipropylamine (dpt) were determined in 0.1 *M* KCl at 25.0° and were found to be greater than those of 2,2′-diaminodiethylamine (den). The equilibria between dpt and the bivalent transition metal ions from Mn(II) to Zn(II) were investigated under the same conditions. In the case of Mn(II) and Fe(II) the precipitation of hydroxides prevented the measurement of the complex formation constants. Co(II), Ni(II), and Zn(II) form 1:1 complexes for which the formation constants were measured. In the case of Ni(II) the existence of 1:2 complex was demonstrated spectrophotometrically and its formation constant was measured potentiometrically. The reflectance spectrum of the octahedral complex $[Ni(dpt)_2](ClO_4)_2$ was recorded. In the presence of excess ligand, the ions Cu(II) and Zn(II) do not form 1:2 complexes, but hydroxo complexes of formulas $[Cu(dpt)(OH)]^+$ and $[Zn(dpt)(OH)]^+$ for which the stability constants were determined. The formation of $[Cu(dpt)(OH)]^+$ was also confirmed by conductometric titrations. The metal complexes of dpt are less stable than the corresponding complexes of den, and this is consistent with the strain energies in the chelate rings.

Introduction

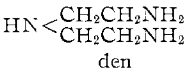
It is known that six-membered chelate rings are less stable than the analogous five-membered rings.[1] For example, the formation constants of the complexes formed by nickel and copper with 1,3-diaminopropane or β-aminoethylpyridine are smaller than the corresponding values for the complexes with ethylenediamine and picolylamine.[2] 3,3′-Diaminodipropylamine (dpt) is a triacid base which can form metal complexes having six-membered chelate rings.

The purpose of the present investigation was to measure the three basicity constants of dpt and the formation constants of its complexes with the bivalent metal ions from Mn(II) to Zn(II), at 25.0° in 0.1 *M* KCl. This enabled us to make a comparison with the corresponding values, under the same conditions of temperature and ionic medium, for 2,2′-diaminodiethylamine (den).[3,4] Some of the den complexes such as $[Cu(den)]^{2+}$ and perhaps $[Zn(den)]^{2+}$ form monohydroxo complexes.[4] We therefore attempted to find out if the complexes $[M(dpt)]^{2+}$ are also able to bind hydroxide ions and if such ability is related to the stability of the simple polyamine complex.



$HN{<}\begin{matrix}CH_2CH_2CH_2NH_2\\CH_2CH_2CH_2NH_2\end{matrix}$

dpt



$HN{<}\begin{matrix}CH_2CH_2NH_2\\CH_2CH_2NH_2\end{matrix}$

den

Fernelius and others[5] have confirmed the existence of 1:1 complexes with the ions Co(II), Ni(II), and Cu(II) for which they have measured the stability constants at 30° in 1 *M* KNO_3. Furthermore, the solid complexes $[Ni(dpt)_2](NO_3)_2$,[6] $[Ni(dpt)_2](ClO_4)_2$, and $[Ni(dpt)_2](BF_4)_2$[7] have been isolated, showing that dpt, in spite of considerable steric hindrance, is capable of forming a 2:1 complex with the Ni(II) ion, at least in the solid state. It appeared therefore of some interest to extend the investigation of the equilibria in aqueous solution between dpt and the bivalent transition metal ions, in order to ascertain whether other complexes existed than those found by Fernelius.

Experimental Section

Materials.—Reagent grade metal chlorides were used for the preparation of approximately 0.4 *M* stock solutions. The solution of ferrous chloride was made *ca.* 0.01 *M* in hydrochloric acid and reduced with hydrogen in the presence of indigo tetrasulfonate as indicator and of several drops of 2% suspension of colloidal palladium. This solution was kept under hydrogen. The solutions of the other metal chlorides were slightly acidified with HCl in order to prevent hydrolysis. The concentrations of the metal ions in the different solutions were determined using conventional methods. The concentration of the hydrochloric acid was determined potentiometrically.

Nitrogen was purified by passing over pyrophoric copper at 100°. An alcoholic solution of commercial 3,3′-diaminodipropylamine (Fluka) was treated with an excess of concentrated

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[1] G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 2344 (1952); H. Irving, R. J. P. Williams, D. J. Ferret, and A. E. Williams, *J. Chem. Soc.*, 3494 (1954); P. Teyssié, G. Anderegg, and G. Schwarzenbach, *Bull. Soc. Chim. Belges*, **71**, 177 (1962).

[2] L. G. Sillén and A. E. Martell, "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964.

[3] M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 2994 (1961).

[4] J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 985 (1950).

[5] G. B. Hares, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **78**, 1816 (1956).

[6] O. Bostrup and C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 1223 (1957).

[7] N. F. Curtis and D. A. House, *J. Chem. Soc.*, 5502 (1965).

hydrochloric acid. The hydrochloride dpt·3HCl was obtained as a white precipitate. This product, recrystallized three times from alcohol–water mixtures, had mp 253–253.5°.[8] *Anal.* Calcd for $C_6H_{20}N_3Cl_3$: Cl, 44.21. Found: Cl, 44.27. Attempts to prepare the hydrochloride starting with the products supplied by two other firms were unsatisfactory, giving noncrystallizable oils. Furthermore, acidometric titration curves of these crude products were different from those expected for a polyamine of this type. The refractive index and density were not in agreement with the values in the literature.[9]

Preparation of $[Ni(dpt)_2](ClO_4)_2$.—A 50% (10 g) alcoholic solution of dpt was added to 1 g of $Ni(ClO_4)_2 \cdot 6H_2O$ dissolved in 2 g of water. On cooling the solution, a violet crystalline precipitate was obtained, easily soluble in hot water. The product obtained after three recrystallizations from water was washed with cold water and with methanol and then dried at 110° to constant weight. *Anal.* Calcd for $C_{12}H_{34}O_8N_6Cl_2Ni$: Ni, 11.29; N, 16.16; equiv wt, 86.67. Found: Ni, 11.13; N, 16.00; equiv wt, 86.81.

Emf Measurements.—The apparatus for the potentiometric titrations was as described previously.[10] During the measurements nitrogen was bubbled through the solutions. The hydrogen ion concentrations were calculated from the experimental emf values, using the formula $[H^+] = \text{antilog}\,[(E - E_0)/59.154]$. The standard electrode potential E_0 was determined from the experimental emf values obtained from the curve for the titration of a 0.001 *M* solution of hydrochloric acid (0.1 *M* in KCl) with 0.1 *M* KOH, over a wide range of pH. The dissociation constant for water ($pK_w = 13.79$) measured by us under these conditions is in excellent agreement with the values reported in the literature.[11]

For the measurements of the basicity constants *ca.* 100 ml of a solution 10^{-3} *M* in dpt·3HCl were titrated with varying volumes of 0.1 *M* KOH added by a piston buret graduated to 0.01 ml. For the measurements of the formation constants of the metal complexes, the solution in the cell contained a known amount of the metal salt and was 0.001–0.010 *M* in dpt·3HCl. The strength of the KOH solution was checked daily against a standard solution of hydrochloric acid. The KOH solution was stored in a neutral Jena glass flask.

Conductivity Measurements.—The conductometric titrations were carried out using a WTW (Model LBR/B) conductivity bridge. The temperature of the cell was held constant at 25.0 ± 0.1°. The solution of potassium hydroxide was added from the piston buret. The concentration of complex in the solution was 0.01 *M*.

Spectrophotometric Measurements.—The absorption spectra were measured between 8000 and 30,000 cm^{-1} with a Beckman DK 2 spectrophotometer using stoppered silica cells. The reflectance spectra were measured using the standard Beckman reflectance attachment. Magnesium oxide was used as the reference.

Results

The determination of the basicity constants for dpt and the formation constants for the metal complexes was carried out using the experimental method due to Schwarzenbach.[12] dpt·3HCl and mixtures of dpt 3HCl with metal salts were titrated with a standard solution of KOH. The concentration conditions (metal ion and ligand concentrations, the range of $-\log [H^+]$ and of $\bar{n}$) of all experiments are summarized in Table I. Some titration curves are shown in Figure 1. Only in the case of Ni(II) was it possible to obtain a complete titration curve with an excess of metal ion (molar ratio of metal to ligand, 10:1). For all of the other metals this was not possible owing to the precipitation of the hydroxides. For Fe(II) and Mn(II)

TABLE I

EXPERIMENTAL DETAILS OF THE POTENTIOMETRIC MEASUREMENTS

	Initial concn, m*M*		Range	
Ion	MCl_2	dpt·3HCl	$-\log [H]$	$\bar{n}$
H^+		1.133	7.4–10.9	
		1.071	7.5–10.9	
		1.019	7.5–10.8	
Co^{2+}	0.962	1.016	7.1–9.3	0.00–0.93
	11.571	29.910	7.2–8.5	0.06–0.98
	11.520	32.600	7.1–9.0	0.05–1.00
	11.480	31.980	7.4–9.6	0.21–1.00
Ni^{2+}	1.123	1.111	6.7–8.3	0.03–0.94
	1.142	1.131	6.7–8.1	0.03–0.91
	11.310	1.107	6.4–7.1	0.00–0.07
	0.538	1.074	6.8–10.4	0.04–1.30
	0.531	1.028	6.8–10.4	0.05–1.30
	1.159	5.865	6.6–10.7	0.12–1.88
Cu^{2+}	1.127	1.035	5.2–6.3	0.06–0.86
	1.132	1.052	5.2–6.2	0.06–0.85
	1.103	1.101	5.3–10.9	0.12–1.00
	1.049	2.112	5.1–9.9	0.06–1.00
	0.638	4.512	5.2–9.9	0.20–1.00
Zn^{2+}	1.173	1.040	6.6–8.0	0.00–0.65
	0.596	1.109	6.9–9.0	0.01–1.00
	0.546	1.086	7.0–9.3	0.01–1.00
	1.100	5.409	6.9–11.0	0.03–1.00

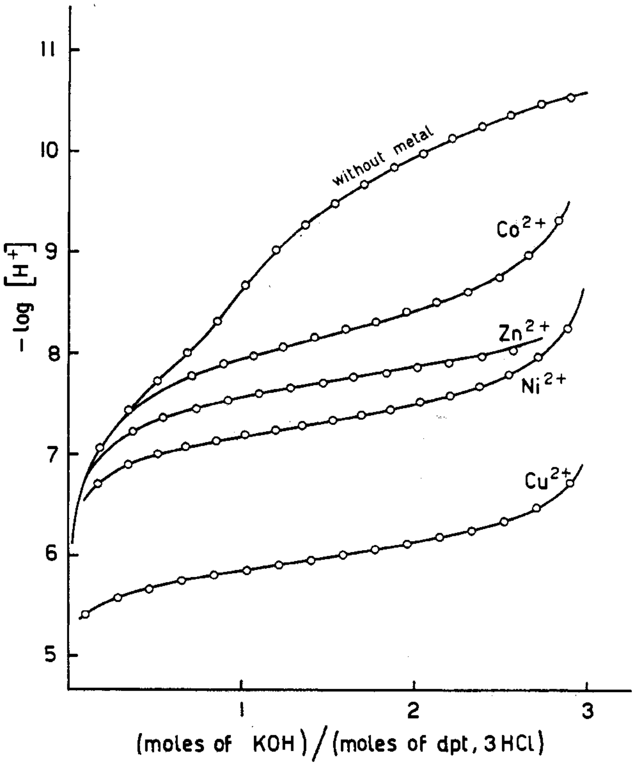

Figure 1.—Titration of dpt·3HCl ($10^{-3}M$) alone or in presence of metal ion (10^{-3} *M*) with 0.1 *M* KOH. The curves are drawn using the data of Table II: open circles, experimental points; solid lines, calculated from the equilibrium constants reported in Table III.

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[8] Mp 250°: J. von Braun and W. Pinkernelle, *Ber.*, **70B**, 1230 (1937).

[9] O. F. Wiedeman and W. H. Montgomery, *J. Am. Chem. Soc.*, **67**, 1994 (1945).

[10] P. Paoletti, J. H. Stern, and A. Vacca, *J. Phys. Chem.*, **69**, 3759 (1965).

[11] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, p 634.

[12] G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 947 (1950).

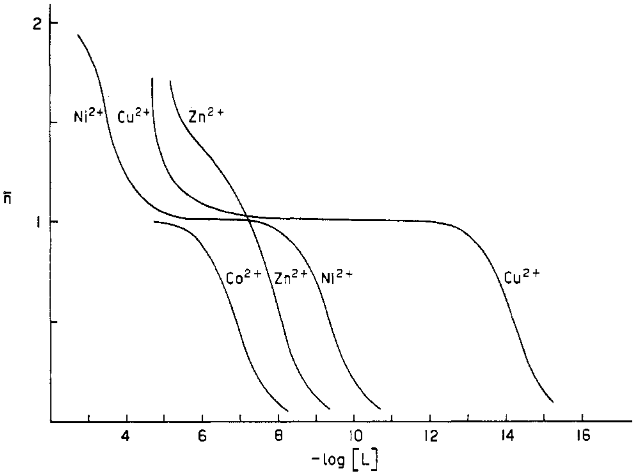

Figure 2.—Formation curves of dpt–metal complexes. The $\bar{n}$ values are calculated from the formula $\bar{n} = \{T_L - [L](1 + \Sigma\beta_{p,0,1} \cdot [H]^p)\}/T_M$, where [H] is the experimental value and [L] is calculated from eq 3b.

all attempts to obtain a titration curve failed, even in the presence of a considerable excess of the ligand, owing to the precipitation of the hydroxides before an appreciable amount of the complex was formed. The formation curves for the ions Co(II), Ni(II), Cu(II), and Zn(II) were calculated by Bjerrum's method[13] and are shown in Figure 2.

The results of the spectrophotometric measurements are as follows: $[Ni(dpt)_2](ClO_4)_2$ solid, λ_{max} 915 mμ, λ_{max} 565 mμ; $[Ni(dpt)]^{2+}$, λ_{max} 920 mμ (ϵ 3.0), λ_{max} 605 mμ (ϵ 7.1); $[Ni(dpt)_2]^{2+}$, λ_{max} 910 mμ (ϵ 4.5), λ_{max} 565 mμ (ϵ 6.3).

The agreement with the spectrum reported for the complex $[Ni(dpt)_2](NC_3)_2$[6] is not very satisfactory.

Calculations

All of the equilibrium constants reported in this paper were calculated from at least 15 data points for each system.

The calculation of the equilibrium constants was carried out using Sillén's procedure of "pit mapping."[14]

At each point of the titration there is an equilibrium among the various species of general formula $H_pM_qL_r$ (M = metal, L = ligand). The concentration of the general species $H_pM_qL_r$, using the symbolism introduced by Sillén,[14] is given by

$$[H_pM_qL_r] = \beta_{p,q,r}[H]^p[M]^q[L]^r$$

where $\beta_{p,q,r}$ is the formation constant of the species being considered and [H], [M], and [L] are, respectively, the concentrations of the hydrogen ion, the metal ion, and the free ligand at the equilibrium.

Using this symbolism, the first basicity constant of the ligand, K_1, will be written as $\beta_{1,0,1}$, the hydroxyl ion will be written H_{-1}, with a formation constant $\beta_{-1,0,0} = K_w$, and the formation constant for a hydroxo complex, having formula ML(OH), will be $\beta_{-1,1,1}$ and so on.

The mass balance relationship will then be

$$T_M = [M] + \sum q\beta_{p,q,r}[H]^p[M]^q[L]^r \quad (1a)$$
$$T_L = [L] + \sum r\beta_{p,q,r}[H]^p[M]^q[L]^r \quad (1b)$$
$$T_H = [H] + \sum p\beta_{p,q,r}[H]^p[M]^q[L]^r \quad (1c)$$

where T_M, T_L, and T_H are the total concentrations of metal ion, ligand, and hydrogen ion present, respectively.

Given the values of the constants $\beta_{p,q,r}$, we can write a system of three nonlinear equations in the three unknowns [H], [M], and [L] which can be solved, at least in principle, by trial and error using the method of successive approximations. From the values of [H] thus obtained for each point of the titration curve, the values of E_{calcd} are then calculated

$$E_{calcd} = E_0 + 59.154 \log[H]$$

If the agreement between the experimental values E_{exptl} and the calculated ones E_{calcd} is not satisfactory, the values of the constants $\beta_{p,q,r}$ are varied in turn, in such a way as to minimize the error-square sum U

$$U = \sum_{i=1}^{m} (E_{calcd} - E_{exptl})_i^2$$

where m is the number of points.

According to Sillén,[14] near its minimum U approximates to a function of second degree in the variables $\beta_{p,q,r}$ and can be represented by a paraboloid. The minimum of this paraboloid is found by the method described by Sillén.[14] The standard deviations are obtained as a by-product of the calculation procedure.[14]

The numerical calculations necessary for the reconstruction of the titration curve (E_{calcd} *vs.* volume of titrant) vary with the type of species present in the solution. In the present work a distinction has been drawn between three possible cases.

(a) **Absence of Metal Ions (Basicity Constant Determinations).**—The species present are HL, H_2L, H_3L (p = 1, 2, 3; q = 0; r = 1) and OH (p = −1; q = 0; r = 0).

The mass balance equations become

$$T_L = [L] + \beta_{1,0,1}[H][L] + \beta_{2,0,1}[H]^2[L] + \beta_{3,0,1}[H]^3[L] = [L] + \sum r\beta_{p,q,r}[H]^p[L]^r \quad (2b)$$

$$T_H = [H] - \beta_{-1,0,0}[H]^{-1} + \beta_{1,0,1}[H][L] + 2\beta_{2,0,1}[H]^2[L] + 3\beta_{3,0,1}[H]^3[L] = [H] + \sum p\beta_{p,q,r}[H]^p[L]^r \quad (2c)$$

From eq 2b

$$[L] = T_L/\{1 + \beta_{1,0,1}[H] + \beta_{2,0,1}[H]^2 + \beta_{3,0,1}[H]^3\} = T_L/\{1 + \sum r\beta_{p,q,r}[H]^p\}$$

Substituting this value into eq 2c we obtain a nonlinear equation with a single unknown, [H], that can be solved by trial and error. A suitable Fortran program (LGSN)[15] for an IBM 1620 computer has been written.

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[13] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1957.

[14] L. G. Sillén, *Acta Chem. Scand.*, **16**, 159 (1962); **18**, 1085 (1965); N. Ingri and L. G. Sillén, *Arkiv Kemi*, **23**, 97 (1964).

[15] The maximum number of constants $\beta_{p,q,r}$ anticipated is 10. A list of the Fortran programs can be obtained on request from the authors.

TABLE II

POTENTIOMETRIC DATA[a]

Run DPT–H/A,[b] $U = 2.827$ mv^2

KOH, ml	E_{exptl}, mv	E_{calcd}, mv	g	$-\log$ [H]
0.40[c]	−151.3	−150.5	2.657	7.427
0.60[c]	−168.3	−168.0	2.487	7.722
0.80[c]	−184.8	−184.7	2.316	8.005
1.00	−203.2	−203.4	2.147	8.321
1.20	−225.0	−224.7	1.980	8.682
1.40[c]	−245.0	−244.5	1.818	9.016
1.60[c]	−260.5	−260.1	1.659	9.280
1.80[c]	−273.1	−272.8	1.507	9.495
2.00	−284.0	−283.8	1.361	9.680
2.20[c]	−293.6	−293.7	1.224	9.847
2.40	−302.1	−302.6	1.097	9.998
2.60	−310.1	−310.7	0.981	10.134
2.80	−317.3	−317.9	0.878	10.257
3.00	−324.1	−324.4	0.786	10.367
3.20[c]	−329.9	−330.3	0.706	10.466
3.40	−335.2	−335.5	0.636	10.554
3.60[c]	−340.1	−340.2	0.575	10.633
3.80	−344.5	−344.4	0.522	10.704
4.00[c]	−348.6	−348.2	0.476	10.769
4.20	−351.9	−351.7	0.436	10.827
4.40	−355.0	−354.8	0.401	10.881

Run DPT–CO/A,[b] $U = 10.420$ mv^2

KOH, ml	E_{exptl}, mv	E_{calcd}, mv	$\bar{n}$	$-\log$ [L]
0.20	−101.2	−99.2	0.001	9.889
0.40	−120.1	−120.5	0.010	8.902
0.60[c]	−132.6	−133.0	0.034	8.359
0.70[c]	−137.5	−137.7	0.052	8.168
0.80[c]	−141.7	−141.7	0.074	8.011
0.90[c]	−145.0	−145.2	0.098	7.878
1.00[c]	−148.3	−148.3	0.124	7.763
1.10[c]	−151.2	−151.2	0.152	7.661
1.20[c]	−154.0	−153.9	0.182	7.568
1.30[c]	−156.7	−156.4	0.213	7.484
1.40[c]	−158.9	−158.9	0.244	7.405
1.50[c]	−161.8	−161.3	0.278	7.330
1.60[c]	−164.2	−163.7	0.312	7.259
1.70[c]	−166.8	−166.1	0.346	7.191
1.80[c]	−169.2	−168.4	0.382	7.124
1.90[c]	−171.7	−170.9	0.418	7.059
2.00[c]	−174.1	−173.4	0.455	6.993
2.10	−176.7	−176.0	0.493	6.928
2.20	−179.3	−178.7	0.531	6.861
2.30	−182.0	−181.5	0.570	6.793
2.40	−184.8	−184.6	0.609	6.722
2.60	−191.2	−191.6	0.690	6.569
2.80	−200.2	−200.3	0.772	6.386
3.20	−233.9	−232.3	0.932	5.772

Run DPT–NI/A,[b] $U = 6.489$ mv^2

KOH, ml	E_{exptl}, mv	E_{calcd}, mv	$\bar{n}$	$-\log$ [L]
0.20	−109.0	−110.1	0.026	10.758
0.40	−120.0	−119.9	0.071	10.299
0.60	−126.0	−125.7	0.122	10.046
0.80	−130.6	−130.1	0.174	9.865
1.00[c]	−134.6	−133.8	0.227	9.720
1.20[c]	−138.0	−137.1	0.282	9.595
1.40[c]	−141.0	−140.3	0.337	9.483
1.60[c]	−143.8	−143.5	0.393	9.378
1.80[c]	−147.0	−146.6	0.449	9.277
2.00[c]	−150.1	−149.9	0.506	9.177
2.20[c]	−153.9	−153.4	0.564	9.076
2.40[c]	−157.5	−157.3	0.623	8.971
2.60[c]	−161.7	−161.7	0.682	8.856
2.80[c]	−166.9	−166.9	0.743	8.728
3.00	−173.6	−173.6	0.804	8.574
3.20	−183.5	−183.3	0.868	8.368
3.40	−200.1	−201.7	0.936	8.023

Run DPT–CU/A,[b] $U = 1.672$ mv^2

KOH, ml	E_{exptl}, mv	E_{calcd}, mv	$\bar{n}$	$-\log$ [L]
0.20	−17.5	−18.3	0.061	15.383
0.40	−24.5	−25.0	0.118	15.083
0.60	−29.0	−29.6	0.174	14.873
0.80	−33.1	−33.3	0.231	14.720
1.00[c]	−36.6	−36.6	0.288	14.591
1.20[c]	−39.6	−39.7	0.345	14.476
1.40[c]	−42.6	−42.7	0.403	14.370
1.60[c]	−45.7	−45.8	0.460	14.269
1.80[c]	−48.8	−48.9	0.517	14.169
2.00[c]	−52.0	−52.0	0.574	14.069
2.20	−55.8	−55.8	0.631	13.965
2.40	−59.9	−60.0	0.688	13.854
2.60	−64.8	−64.9	0.745	13.732
2.80	−71.2	−71.2	0.803	13.589
3.00	−81.0	−80.8	0.860	13.409

Run DPT–ZN/A,[b] $U = 31.271$ mv^2

KOH, ml	E_{exptl}, mv	E_{calcd}, mv	$\bar{n}$	$-\log$ [L]
0.10	−102.2	−105.4	0.001	10.886
0.20	−121.2	−122.8	0.007	10.042
0.40	−137.2	−137.5	0.036	9.358
0.60	−145.7	−145.2	0.076	9.026
0.80	−151.2	−150.7	0.122	8.807
1.00	−155.6	−155.0	0.170	8.644
1.20[c]	−159.4	−158.8	0.221	8.510
1.40[c]	−163.0	−162.3	0.273	8.395
1.60[c]	−166.2	−165.7	0.325	8.292
1.80[c]	−169.5	−169.0	0.379	8.197
2.00[c]	−172.5	−172.4	0.433	8.108
2.20[c]	−175.4	−175.9	0.487	8.023
2.40	−178.3	−179.5	0.541	7.940
2.60	−181.5	−183.5	0.595	7.858
2.80	−185.0	−187.8	0.648	7.777

[a] For the data of all potentiometric curves performed, see ref 16. [b] Composition of solutions: DPT–H/A: dpt·3HCl = 0.1122 mmole, initial volume 99.0 ml, E_0 = 288.8 mv, [KOH] = 0.0959 *M*. DPT–CO/A: dpt·3HCl = 0.1110 mmole, Co(II) = 0.1051 mmole, initial volume 109.2 ml, E_0 = 317.4 mv, [KOH] = 0.0985 *M*. DPT–NI/A: dpt·3HCl = 0.1110 mmole, Ni(II) = 0.1122 mmole, initial volume 99.9 ml, E_0 = 288.0 mv, [KOH] = 0.0942 *M*. DPT–CU/A: dpt·3HCl = 0.1027 mmole, Cu(II) = 0.1118 mmole, initial volume 99.2 ml, E_0 = 288.8 mv, [KOH] = 0.0959 *M*. DPT–ZN/A: dpt·3HCl = 0.1045 mmole, Zn(II) = 0.1178 mmole, initial volume 100.4 ml, E_0 = 290.5 mv, [KOH] = 0.0960 *M*. [c] This value was used in the "pit mapping" procedure.

(b) **Simple Mononuclear Complexes.**—The species present are ML and ML$_2$ ($p = 0$; $q = 1$; $r = 1, 2$) as well as the species in case a.

Equations 1a and 2c can be written

$$T_{\text{M}} = [\text{M}] + \beta_{0,1,1}[\text{M}][\text{L}] + \beta_{0,1,2}[\text{M}][\text{L}]^2$$

$$T_{\text{H}} = [\text{H}] - \beta_{-1,0,0}[\text{H}]^{-1} + \sum p\beta_{p,q,r}[\text{H}]^p[\text{L}]$$

from which

$$[\text{M}] = T_{\text{M}}/\{1 + \beta_{0,1,1}[\text{L}] + \beta_{0,1,2}[\text{L}]^2\} = T_{\text{M}}/\{1 + \sum q\beta_{p,q,r}[\text{H}]^p[\text{L}]^r\} \quad (3a)$$

$$[\text{L}] = \{T_{\text{H}} - [\text{H}] + \beta_{-1,0,0}[\text{H}]^{-1}\}/\sum p\beta_{p,0,1}[\text{H}]^p \quad (3b)$$

Substituting the values of [M] and [L] in eq 1b, a relationship containing only one unknown, [H], is

TABLE III

BASICITY CONSTANTS OF dpt AND STABILITY CONSTANTS OF ITS METAL COMPLEXES IN 0.1 *M* KCl AT 25.0°[a]

Ion	Reaction		
H^+	$H^+ + dpt \rightleftarrows H(dpt)^+$	10.65 ± 0.02	K_1
	$H^+ + H(dpt)^+ \rightleftarrows H_2(dpt)^{2+}$	9.57 ± 0.03	K_{12}
	$H^+ + H_2(dpt)^{2+} \rightleftarrows H_3(dpt)^{3+}$	7.72 ± 0.03	K_{13}
Co^{2+}	$Co^{2+} + dpt \rightleftarrows [Co(dpt)]^{2+}$	6.92 ± 0.01	K_1
Ni^{2+}	$Ni^{2+} + dpt \rightleftarrows [Ni(dpt)]^{2+}$	9.19 ± 0.02	K_1
	$[Ni(dpt)]^{2+} + dpt \rightleftarrows [Ni(dpt)_2]^{2+}$	3.55 ± 0.08	K_2
Cu^{2+}	$Cu^{2+} + dpt \rightleftarrows [Cu(dpt)]^{2+}$	14.20 ± 0.06	K_1
	$[Cu(dpt)]^{2+} + OH^- \rightleftarrows [Cu(dpt)(OH)]^+$	4.14 ± 0.16	$K_{[Cu(dpt)(OH)]^+}$
Zn^{2+}	$Zn^{2+} + dpt \rightleftarrows [Zn(dpt)]^{2+}$	7.92 ± 0.03	K_1
	$[Zn(dpt)]^{2+} + OH^- \rightleftarrows [Zn(dpt)(OH)]^+$	5.23 ± 0.10	$K_{[Zn(dpt)(OH)]^+}$

[a] Uncertainty intervals associated with all values are twice the standard deviations. The symbolism used for the equilibrium constants is that used in ref 2.

obtained. This equation can be solved by successive approximations. A suitable Fortran program (LGS)[15] for the IBM 1620 computer has been written.

(c) **The General Case for Mononuclear Complexes.**—The species present are ML(OH) ($p = -1$; $q = 1$; $r = 1$) as well as the species present in case b.

Substituting the value of [M] obtained from eq 3a in eq 1b and 1c, two nonlinear equations in the two unknowns [H] and [L] are obtained. Starting with two arbitrary values for these quantities, it is possible by successive approximations to find two values which satisfy both equations. The calculations were carried out on an IBM 1620 computer for which a suitable Fortran program (LG)[15] has been written.

As examples of the application of these methods of calculation, Table II contains some data relating to five neutralization curves for dpt·3HCl, the first in the absence of metal ions, and the others in the presence of Co(II), Ni(II), Cu(II), and Zn(II) ions, respectively.[16] The first column shows the volume of KOH solution added, while the second and third contain the value of E_{exptl} (the measured emf) and E_{calcd} (the emf calculated using the equilibrium constants shown in Table III). The last two columns contain the degree of protonation, g, and $-\log$ [H] for the first curve and the formation function, $\bar{n}$, and $-\log$ [L] for the other curves.

Discussion

Basicity Constants.—The basicity constants for 3,3′-diaminodipropylamine are shown in Table III. The agreement with the values obtained by Fernelius at 30° in 1 *M* KNO_3 ($\log K_1 = 10.70$, $\log K_{12} = 9.70$, $\log K_{13} = 8.02$)[5] is satisfactory, allowing for the different experimental conditions. Comparison with the corresponding constants for den, determined by Schwarzenbach[4] in 0.1 *M* KCl at 20° and later corrected[17] at 25° ($\log K_1 = 9.70$, $\log K_{12} = 8.98$, $\log K_{13} = 4.25$) leads to two conclusions: (a) All of the amine groups of dpt are more basic than the corresponding groups of den. This can be attributed to the inductive effect due to the greater number of methylene groups in the chain. (b) The third constant K_{13} is very much greater (*ca.* 3000 times) for dpt; this is due not only to an increased inductive effect but also to a decreased electrostatic repulsion by the NH_3^+ groups.

Complexes of Mn(II) and Fe(II).—It was impossible, by the potentiometric method, to demonstrate the existence of any complex formed by dpt with the ions Mn(II) and Fe(II), owing to the precipitation of their hydroxides. It is reasonable to suppose that the complexes would not be very stable and that complex formation could occur only in the presence of appreciable amounts of the free amine. However under these conditions the solution would be so alkaline that the hydroxides would precipitate.

Complexes of Co(II).—The formation curve (Figure 2) for the system Co(II)–dpt reaches a maximum at the value $\bar{n} = 1.0$. In this region only one complex, $[Co(dpt)]^{2+}$, is present, whose calculated formation constant is in agreement with that calculated by Fernelius[5] in 1 *M* KNO_3 at 30° ($\log K = 6.63$).

While the complex $[Co(den)_2]^{2+}$ exists,[4] no evidence for the existence of the corresponding complex $[Co(dpt)_2]^{2+}$ was found. The formation constant for $[Co(dpt)]^{2+}$ is smaller by 1.1 logarithmic units than the corresponding constant for the den complex.[3]

Complexes of Ni(II).—The values of $\bar{n}$ (Figure 2) rise above 1 and reach a maximum of 1.9. This leads to the conclusion that the Ni(II) complex containing two molecules of ligand is formed. This hypothesis is supported by spectrophotometric evidence: (a) the visible absorption spectra of solutions containing Ni(II) and dpt have maxima which move to higher frequencies with an increase in the concentration of the ligand (Figure 3); (b) a solid complex of formula $[Ni(dpt)_2](ClO_4)_2$ has been isolated and the absorption maxima of its reflectance spectrum (Figure 3) coincide with those of a solution containing Ni(II) in the presence of an excess of ligand (about three times the concentration of metal ion).

Fernelius[5] detected only the 1:1 complex ($\log K = 9.09$). The complex $[Ni(dpt)]^{2+}$ has a stability constant 1.4 logarithmic units smaller than the corresponding den complex.[3] This difference is slightly higher than that found in the case of Co(II). The stability

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[16] The data relating to all the 22 potentiometric curves performed (402 data points) have been deposited as Document No. 8914 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 $2.50 for photoprints, or $1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[17] M. Ciampolini and P. Paoletti, *J. Phys. Chem.*, **65**, 1224 (1961).

constant of the complex $[Ni(dpt)_2]^{2+}$ (Table III) is relatively small; this shows that the second molecule of dpt enters the coordination sphere of Ni(II) only with difficulty, probably because of the greater bulkiness of the dpt molecule. An examination of the spectra leads us to believe that both $[Ni(dpt)]^{2+}$ and $[Ni(dpt)_2]^{2+}$ have an octahedral environment, completed, in the first case, by molecules of water.

Complexes of Cu(II).—As in the case of Ni(II) the values of $\bar{n}$ rise above 1. However, the shape of the formation curve in this region leads us to believe that at the equilibrium hydroxo species are present rather than 1:2 complex species. Elaboration of the potentiometric data has confirmed this hypothesis and two complexes have been characterized: $[Cu(dpt)]^{2+}$ and $[Cu(dpt)(OH)]^{+}$.

The maximum extent of formation obtained for the complex $[Cu(dpt)(OH)]^{+}$ was 94.7% (curve DPT–CU/D).[16] This complex is sufficiently stable for its existence to be shown by a conductometric method. The appropriate curve is shown in Figure 4. The complex $[Cu(dpt)]^{2+}$ is also less stable than the corresponding den complex[4] and the difference between the stability constants (1.6 logarithmic units) is only just greater than the corresponding differences for Co(II) and Ni(II).

Complexes of Zn(II).—The equivalent titration curve for Zn(II) has a slope, in the buffer region, different from those of the other metals (Figure 1). The values of $\bar{n}$ (Figure 2) rise considerably above 1, and no point of inflection is found. Elaboration of the potentiometric data leads us to the conclusion that two complexes are formed in this system: $[Zn(dpt)]^{2+}$ and $[Zn(dpt)(OH)]^{+}$.

Because of their similar stability constants these two complexes are always present together, and the maximum percentage of the hydroxo complex was 99.7% (curve DPT–Zn/D).[16]

The stability constants are shown in Table III. The formation constant of the complex $[Zn(dpt)]^{2+}$ is smaller than that of the complex $[Zn(den)]^{2+}$ by about 0.9 logarithmic unit.[3] In the case of the Zn(II)–den system too, Schwarzenbach[4] was able to show that a hydroxo complex is formed, but he did not measure its formation constant.

The stability constant for the complex $[Zn(dpt)(OH)]^{+}$ is high and it is greater (by 1.1 logarithmic units) than the corresponding constant for the complex $[Cu(dpt)(OH)]^{+}$. Unfortunately, it is not possible to make a general comparison since there are few values available of the stability constants for polyamine complexes of Zn(II) containing also the hydroxide ion.[18]

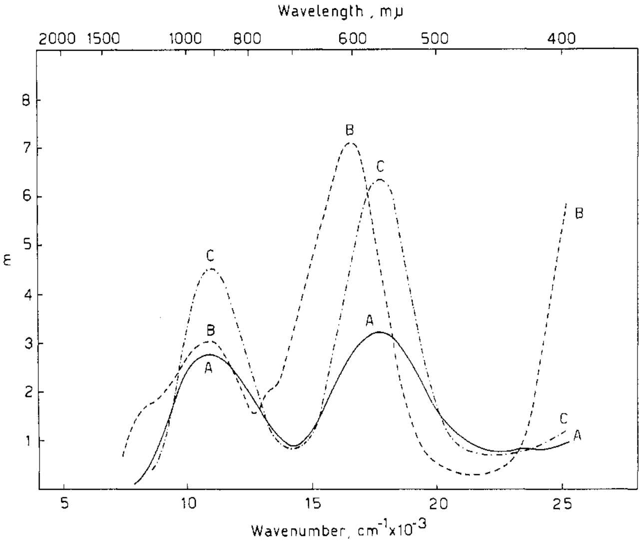

Figure 3.—Absorption spectra of: (A) $[Ni(dpt)_2](ClO_4)_2$ solid, (B) $[Ni(dpt)]^{2+}$, and (C) $[Ni(dpt)_2]^{2+}$ in aqueous solution.

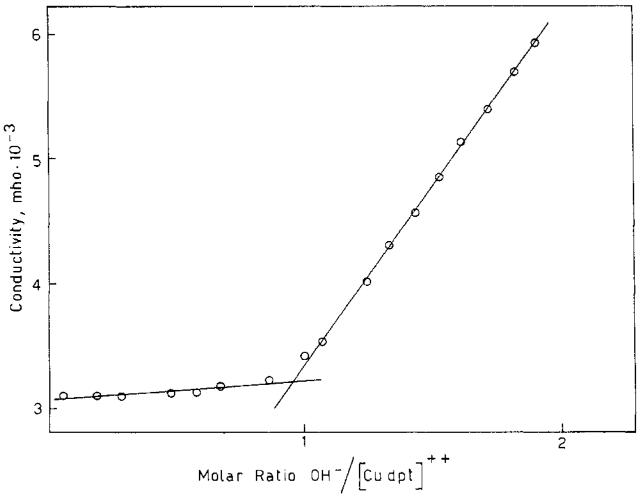

Figure 4.—Conductivity titration curve.

Conclusions

dpt is an amine with an over-all basicity greater than that of den, but for steric reasons it forms less stable complexes. In particular, because of its considerable size, only with Ni(II) is it possible to fit two molecules of ligand around a metal ion.

In the case of its complexes with Cu(II) and Zn(II), the combined effect of the increased basicity and the considerable steric hindrance favors the formation of hydroxo complexes.

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(18) G. Schwarzenbach and R. Bauer, *Helv. Chim. Acta*, **39**, 722 (1956).