

971. *Thermochemical Studies. Part XIII.*¹ *Heats and Entropies of Reaction of Tetraethylenepentamine with Protons and Bivalent Transition-metal Ions.*

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The basicity constants of tetraethylenepentamine (tetren) have been determined in 0.1M potassium chloride at 25°. The formation constants of the complexes of the bivalent metal ions, manganese to zinc, with tetraethylenepentamine have been determined under the same conditions: the heats of stepwise neutralization of tetraethylenepentamine and the heats of formation of the complexes $[M \text{ tetren}]^{2+}$ have been measured calorimetrically, and the relevant entropy changes have been calculated from the combined results. The values obtained of the enthalpies of formation of the complexes $[M \text{ tetren}]^{2+}$ are compared with the corresponding values for the complexes $[M \text{ trien}]^{2+}$ and $[M \text{ pentenH}]^{2+}$. The zinc complex $[Zn \text{ tetren}]^{2+}$ is shown to be weakly hydrated. The absorption spectra of the coloured complexes have been measured.

TETRAETHYLENEPENTAMINE $(NH_2CH_2CH_2NHCH_2CH_2)_2NH$ can accept five protons and forms 1 : 1 complexes with transition metal ions with ease. Some of these systems have been investigated by potentiometric means in divers ionic media.²⁻⁸ In the present study,

¹ Part XII, Sacconi, Paoletti, and Ciampolini, preceding Paper.

² Reilley and Holloway, *J. Amer. Chem. Soc.*, 1958, **80**, 2917.

³ Holloway, Diss., Univ. of North Carolina, 1959.

⁴ Jonassen, Frey, and Schaafsma, *J. Phys. Chem.*, 1957, **61**, 504.

⁵ Jonassen and Westerman, *J. Amer. Chem. Soc.*, 1957, **79**, 4275.

⁶ Jonassen, Bertrand, and Groves, *J. Amer. Chem. Soc.*, 1957, **79**, 4279.

⁷ Jonassen, Schaafsma, and Westerman, *J. Phys. Chem.*, 1958, **62**, 1022.

⁸ Westerman, Thesis, Tulane Univ., 1959.

the five basicity constants of tetraethylenepentamine have been measured potentiometrically in 0.1M potassium chloride and the stability constants of the complexes $[M \text{ tetren}]^{2+}$ and some protonated complexes of the type $[M \text{ tetrenH}]^{3+}$ and $[M \text{ tetrenH}_2]^{4+}$ ($M = \text{Mn, Fe, Co, Ni, Cu, Zn}$) have been measured under the same conditions. The enthalpies of successive neutralization of tetraethylenepentamine and the enthalpies of complex formation have been measured in a solution calorimeter.

The relevant entropy changes were obtained by combining the results collected. Values of the crystal field parameter have been obtained from the visible absorption spectra of the coloured complexes.

The present information concerning the equilibria between tetraethylenepentamine and metal ions is compared with results previously recorded for other polyethylenepolyamine systems.^{1,9}

EXPERIMENTAL

Materials.—Commercial tetraethylenepentamine (Bender, Hobein A.G.) was purified as follows: 100 g. of crude material were dissolved in 200 ml. of water and cooled in an ice-bath; 400 ml. of 30% nitric acid were then added to it dropwise, while the temperature was maintained below 10°. The precipitate of tetren, 5HNO_3 , which appeared near the end of the addition, was collected by filtration and recrystallized five times from aqueous 5% nitric acid solution. The free base was obtained by passing an aqueous solution of the pentahydrate salt through a column filled with Amberlite-IRA 400 ion-exchange resin. Water was removed from aqueous solution by simple distillation; afterwards the base was distilled *in vacuo*. Two samples of the tetraethylenepentamine so obtained were titrated against standard hydrochloric acid and proved to be 99.2, 99.5% pure. The hydrochloric acid was standardized as silver chloride and the same solution was used in the measurements of the heats of neutralization. An approximately 1M solution of tetraethylenepentamine was standardized by potentiometric titration.

Tetren hydrochloride (tetren, 5HCl) was prepared and purified according to Jonassen *et al.*⁴

The solutions of metal chlorides were prepared and standardized, as described previously.¹⁰ All experiments with the oxidizable metal(II) salts were carried out under nitrogen and, where convenient, the nitrogen was actually bubbled through the solution. All tetraethylenepentamine solutions were made up in carbon-dioxide-free water.

Hydrogen and nitrogen were purified by passage over copper gauze at 400°.

Potentiometric Measurements.—A Radiometer model 4 pH-meter equipped with 0.1M calomel and glass electrodes was employed. All the titrations were carried out in a 150 ml. 7-necked vessel; the solution was stirred continuously by means of a magnetic stirrer. The temperature was kept constant at $25.0 \pm 0.1^\circ$. The pH-meter was calibrated against phthalate buffer (pH = 4.01) and checked against borax buffer (pH = 9.18) before each determination. The potassium hydroxide solution (0.1M) was always added from a piston burette (graduated to 0.01 ml.). The titration vessel contained either tetren, 5HCl (in 0.1M potassium chloride) or various mixtures of tetren, 5HCl and metal(II) chloride. For copper, a competitive method was also used: the vessel contained tetren, 5HCl , cupric chloride, disodium salt of ethylenediamine-tetra-acetic acid and calcium chloride. The equilibrium potential was reached almost instantaneously in all the cases, except for nickel, when about 20 min. after each addition of potassium hydroxide solution were required for equilibration.

Calorimetric Measurements.—The calorimeter and the experimental procedure used have been described previously.¹⁰⁻¹² For each run, the bottle was filled with either a weighed amount of *ca.* 0.5M metal chloride solution or 1.5M hydrochloric acid solution for the neutralisation experiments. A weighed amount of tetraethylenepentamine was placed in the Dewar flask and 0.1M potassium chloride solution was then added to give a final weight of 920 g. With the nickel system, however, an indirect method had to be employed, owing to the slow formation of the metal complex: a solution containing nickel chloride and tetraethylenepentamine in equivalent molar amounts was left overnight to *ca.* 45°. The heat evolved when

⁹ Sacconi, Paoletti, and Ciampolini, *J.*, 1961, 5115.

¹⁰ Ciampolini, Paoletti, and Sacconi, *J.*, 1960, 4553.

¹¹ Ciampolini and Paoletti, *J. Phys. Chem.*, 1961, 65, 1224.

¹² Sacconi, Paoletti, and Ciampolini, *Ricerca sci.*, 1959, 11, 2412.

the complex contained in this solution was decomposed with *ca.* 25 ml. of 3·3M hydrochloric acid was measured. A blank experiment was performed under the same conditions.

Spectrophotometric Measurements.—Spectra of the complexes $[\text{Fe}(\text{den})_3]^{2+}$, $[\text{Fe tetren}]^{2+}$, $[\text{Co tetren}]^{2+}$, $[\text{Ni tetren}]^{2+}$, and $[\text{Cu tetren}]^{2+}$ in water were recorded on a Beckmann DK2 spectrophotometer fitted with 1 cm. stoppered silica cells. The solutions containing the oxidizable iron complexes were prepared and transferred to the cell as described for the $[\text{Fe}(\text{en})_3]^{2+}$ complex;¹⁰ about a 10% excess of tetraethylenepentamine was used and a slight pale green precipitate, which appeared after the mixing of the solutions, was removed by filtration.

RESULTS

The determination of the acid dissociation constants of a polyamine and the formation constants of metal complexes (including protonated complexes) by the potentiometric method has been developed by Schwarzenbach¹³ and applied by him to other polyamine

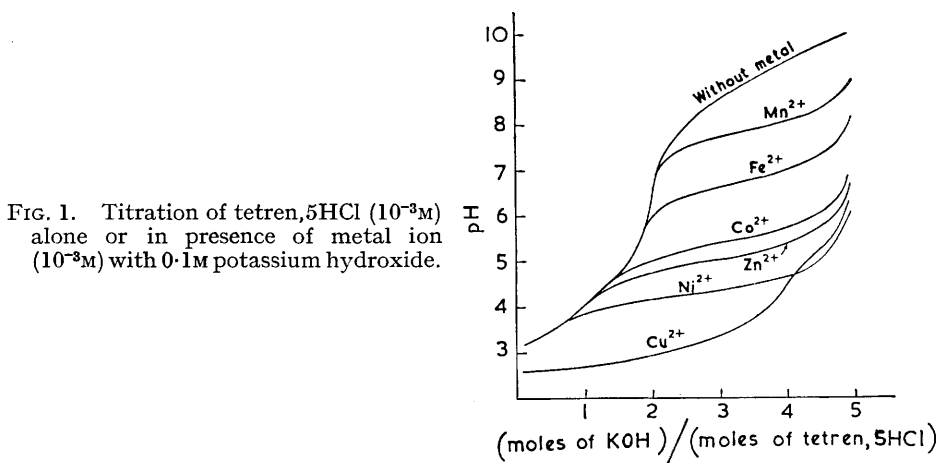


FIG. 1. Titration of tetren,5HCl (10^{-3}M) alone or in presence of metal ion (10^{-3}M) with 0·1M potassium hydroxide.

systems. Following Schwarzenbach's method, mixtures of tetren,5HCl and metal ion (mole ratio 10 : 1 and 1 : 1) and tetren,5HCl alone were titrated with standard 0·1M potassium hydroxide solution. Some of the titration curves are shown in Fig. 1.

The five dissociation constants of tetraethylenepentamine, computed from the pH values of the simple neutralization curve (upper curve in Fig. 1) are listed in Table 1 and

TABLE 1.

Acid dissociation constants of tetren and stability constants of metal-tetren complexes in 0·1M potassium chloride at 25°.

Ion	$\text{p}K_1$	$\text{p}K_2$	$\text{p}K_3$	$\text{p}K_4$	$\text{p}K_5$
H^+	9·68	9·10	8·08	4·72	2·98
	$\log K_{\text{Mtetren}}$		$\log K_{\text{MHtetren}}$		$\log \bar{K}_{\text{MH}_2\text{tetren}}$
Mn^{2+}	6·55		—		—
Fe^{2+}	9·85		4·2		—
Co^{2+}	13·30		—		4·9
Ni^{2+}	17·43		11·80		6·7
Cu^{2+}	22·80		18·30		13·0
Zn^{2+}	15·10		—		5·7

are in satisfactory agreement with the values already reported in the literature,²⁻⁵ remembering that they were determined in a different ionic medium. From an analysis of the titration curves obtained in the presence of metal ions and from a knowledge of the acid

¹³ Schwarzenbach, *Helv. Chim. Acta*, 1950, **33**, 947.

dissociation constants of the ligand, the stability constants of the metal complexes, except for the copper system, were calculated and are reported in Table 1. It was also shown that no polynuclear complexes are formed under the condition studied. The stability constants of the copper complexes $[\text{Cu tetren}]^{2+}$, $[\text{Cu tetrenH}]^{3+}$, and $[\text{Cu tetrenH}_2]^{4+}$ cannot be determined by the general method, because complex formation is virtually complete even in the very low pH region, as is shown by the lowest curve in Fig. 1. In this case, the constants reported in Table 1 were obtained by the EDTA competition method.¹⁴

TABLE 2.

Calorimetric data for the system tetren + HCl in 0.1M potassium chloride at 25°.

Tetren (10 ⁻⁵ mole)	HCl (10 ⁻⁵ mole)	Q (cal.)	Q _{cz.} (cal.)	Tetren (10 ⁻⁵ mole)	HCl (10 ⁻⁵ mole)	Q (cal.)	Q _{cz.} (cal.)
1989	1990	219.2	12.3	631	1891	206.3	7.0
2001	2001	220.9	12.3	485	1944	197.0	6.1
2004	2001	221.0	12.3	476	1903	193.2	5.8
1067	2136	236.1	9.1	480	1920	194.5	5.8
952	1904	210.9	8.6	389	1942	175.5	5.5
982	1965	217.8	8.7	385	1925	173.0	5.1
717	2148	236.8	7.5	383	1916	172.6	5.1
648	1944	214.3	7.1				

The heats evolved during the reaction of varying proportions of hydrochloric acid with tetraethylenepentamine were measured. The results are shown in Table 2. Knowing the exact concentrations of each protonated form of the amine both before and after the reaction, the heats of stepwise neutralization were obtained, by solving a system of five equations of the type

$$(Q - Q_{cz.})/b = -[(\alpha_1 \text{ after} - \alpha_1 \text{ before})\Delta H_1 + (\alpha_2 \text{ after} - \alpha_2 \text{ before})\Delta H^{1-2} \dots]$$

where α_1 , α_2 , etc. are the degrees of formation of the monoammonium, diammonium, etc. ions, respectively, and b is the number of moles of amine used. The third column of Table 2, headed Q , lists the heat evolved in each experiment, corrected for the heat of dilution of hydrochloric acid. In the last column, $Q_{cz.}$ is the calculated correction for the

TABLE 3.

Calorimetric data for the systems $\text{MCl}_2 + \text{tetren}$ in 0.1M potassium chloride at 25°.

Metal		Tetren	Q	Q _{cz.}	Metal		Tetren	Q	Q _{cz.}
(10 ⁻⁵ mole)		(10 ⁻⁵ mole)	(cal.)	(cal.)	(10 ⁻⁵ mole)		(10 ⁻⁵ mole)	(cal.)	(cal.)
Manganese	811	811	31.6	1.7	Nickel	698	698	267.6	—
	817	818	31.7	1.7		—	698	401.0	1.6
Iron	807	808	71.7	1.7	Copper ...	700	700	269.0	—
	797	799	71.3	1.7		—	700	402.7	1.6
Cobalt	739	739	104.2	1.6	Zinc	707	709	178.5	1.6
	742	743	104.5	1.6		693	693	174.4	1.6
						704	711	99.0	1.6
						696	706	97.9	1.5

heat effect due to the neutralization of hydroxyl ions which arise by the reaction of water with the free base. For the heat of ionization of water we have chosen the value of 13.65 kcal. mole⁻¹.¹⁵

The calorimetric data for the tetraethylenepentamine/metal ion systems are recorded in Table 3. The value of the heat evolved in each run, corrected for the heat of dilution of the metal chloride, is given in the third column, and must be further corrected for the heat effect due to the neutralization reaction that takes place on complex formation; these

¹⁴ Schwarzenbach, *Helv. Chim. Acta*, 1953, **36**, 581.

¹⁵ Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd edn., Reinhold, New York, p. 754.

corrections are listed in the last column. Under the conditions used, the complex formation was complete, on account of the high values of the stability constants. The molar heats of formation were therefore calculated by using the formula

$$-\Delta H = (Q - Q_{cz.})/(\text{moles of metal})$$

For nickel the formula was modified to

$$-\Delta H = (Q_{blank} - Q + Q_{cz.})/(\text{moles of metal})$$

The results of the spectrophotometric measurements were: [Fe den₂]²⁺, λ_{sh.} 790 (ε 1.8), λ_{max.} 870 (ε 2.4), λ_{max.} 1060 mμ (ε 2.6). [Fe tetren]²⁺, λ_{max.} 890 (ε 2.6), λ_{max.} 1045 (ε 2.6), λ_{sh.} 1140 mμ (ε 2.1). [Co tetren]²⁺, λ_{sh.} 476 (ε 3.2), λ_{max.} 485 (ε 4.4), λ_{max.} 990 mμ (ε 2.2). [Ni tetren]²⁺, λ_{max.} 547 (ε 6.7), λ_{sh.} 790 (ε 8.7), λ_{max.} 895 mμ (ε 12.2). [Cu tetren]²⁺, λ_{max.} 670 mμ (ε 191).

DISCUSSION

The values of the thermodynamic functions for the stepwise neutralization of tetraethylenepentamine are given in Table 4. It has been shown¹⁶ that the entropy and enthalpy of monoprotonation of polyethylenepolyamines are linear functions of the proportion of secondary amine groups present in the molecule relative to the total number of amine groups. The values for tetraethylenepentamine calculated by interpolation between previous results are: $-\Delta H_1 = 10.82 \text{ kcal. mole}^{-1}$ and $\Delta S_1 = 8.4 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, in excellent agreement with the measured values.

TABLE 4.

Thermodynamic functions for the successive neutralization stages of tetraethylenepentamine at 25° in 0.1M potassium chloride.

Reaction	$-\Delta H$ (kcal. mole ⁻¹)	$-\Delta G$ (kcal. mole ⁻¹)	ΔS (cal. deg. ⁻¹ mole ⁻¹)
Tetren + H ⁺ → tetrenH ⁺	10.76	13.20	8.2
TetrenH ⁺ + H ⁺ → tetrenH ₂ ²⁺	11.32	12.41	3.7
TetrenH ₂ ²⁺ + H ⁺ → tetrenH ₃ ³⁺	10.71	11.02	1.0
TetrenH ₃ ³⁺ + H ⁺ → tetrenH ₄ ⁴⁺	7.89	6.44	-4.9
TetrenH ₄ ⁴⁺ + H ⁺ → tetrenH ₅ ⁵⁺	6.83	4.06	-9.3

For both diethylenetriamine¹¹ and triethylenetetramine,¹⁶ the first heat of neutralization, $-\Delta H_1$, is less than the second, $-\Delta H_2$. The same is found with tetraethylenepentamine. The ion [tetrenH]⁺ in solution may be assumed to exist in two tautomeric forms in equilibrium with each other; in one, the proton is bound to a secondary amine group and, in the other, to a primary amine group. As the second and third protons are attached, these protons bound to secondary amine groups tend to pass over to the primary amine groups, on account of electrostatic repulsion, and this process is accompanied by an evolution of heat. The fourth and fifth stages of neutralization are accompanied by a much smaller enthalpy change, attributed to the fact that exclusively secondary nitrogen atoms are involved, and to the repulsion between the two positive charges. The fact that the value of ΔH_5 for tetraethylenepentamine is exactly equal to that of ΔH_4 for triethylenetetramine¹⁶ indicates that charges beyond the nearest have no influence on the heat evolved in the last protonation.

The values of the entropy changes show a decreasing trend with the number of protons bound, as is generally found in systems of this type.

¹⁶ Paoletti, Ciampolini, and Vacca, *J. Phys. Chem.*, 1963, **67**, 1065.

The values of the thermodynamic functions relevant to the formation of the metal complexes with tetraethylenepentamine are given in Table 5. The enthalpies of formation of the complexes, ΔH , are plotted against the atomic number of the metal in Fig. 2. The curve rises very regularly from manganese to copper and then drops for the zinc complex.

TABLE 5.

Thermodynamic functions and spectral data for metal(II)-tetraethylenepentamine systems in 0.1M potassium chloride at 25°.

	Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺
$-\Delta G$ (kcal. mole ⁻¹)	8.95	13.45	18.15	23.80	31.10	20.60
$-\Delta H^a$ (kcal. mole ⁻¹)	3.70	8.70	13.85	18.90	24.95	13.85
ΔS (cal. deg. ⁻¹ mole ⁻¹)	17.5	16.0	14.5	16.5	20.5	22.5
$Dq[M(H_2O)_6]^{2+}$ (cm. ⁻¹)	—	1040 ^b	900 ^c	850 ^b	—	—
$Dq[Mtetren]^{2+}$ (cm. ⁻¹)	—	1125	1180	1120	—	—
$-\Delta H_{C.F.S.E.}$ (kcal. mole ⁻¹)	0	0.90	6.40	9.25	—	0
$-\Delta H_{corr.}$ (kcal. mole ⁻¹)	3.70	7.80	7.45	9.65	—	13.85

^a Holloway's values (ref. 3) for $-\Delta H$, in kcal. mole⁻¹ are: Ni, 18.4; Cu, 24.0; Zn, 14.0 and the Jonassen's values (ref. 5, 7) are: Mn, 5.16; Fe, 9.36; Ni, 11.3. ^b Jørgensen, Reports Tenth Solvay Conf., Brussels, 1956. ^c Ballhausen and Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 397.

The correction, $\Delta H_{C.F.S.E.}$ (Table 5), which expresses the crystal field stabilization energy, was calculated for the complexes of iron, cobalt and nickel, according to the formula

$$\Delta H_{C.F.S.E.} = (4n_e - 6n_v)(Dq_{M(H_2O)_6} - Dq_{Mtetren})$$

The values of $Dq_{Mtetren}$ (reported in Table 5) were obtained from the spectra of the metal complexes, shown in Fig. 3, by assuming an octahedral field, the sixth co-ordinating entity being water. The corrected heats of formation, $-\Delta H_{corr} = -\Delta H + \Delta H_{C.F.S.E.}$, are given in

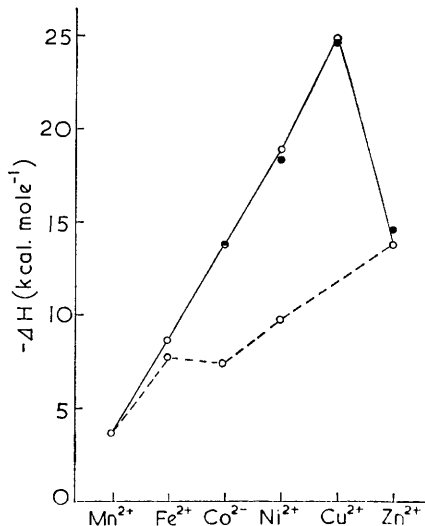


FIG. 2. Experimental (—○—) and corrected (crystal field stabilization energy) --○-- heats of formation of $[Mtetren]^{2+}$ ions. Experimental (●) heats of formation of $[MpentenH]^{3+}$ ions.¹

the last row of Table 5 and also in Fig. 2. These values, with the exception of that for the iron complex, lie exactly on the straight line drawn between those of manganese and zinc. The anomalous position of the iron complex is usual in the polyamine complexes.¹⁷

The heats of formation of the complexes $[Mtetren]^{2+}$ are all clearly greater than those

¹⁷ Ciampolini, Paoletti, and Sacconi, in "Advances in the Chemistry of Coordination Compounds," Kirschner edn., Macmillan Co., New York, p. 303.

of the corresponding triethylenetetramine complexes,⁹ the differences being: Mn, 1.40; Fe, 2.65; Co, 3.20; Ni, 4.90; Cu, 3.40; Zn, 5.00 kcal. mole⁻¹. This confirms that tetraethylenepentamine behaves as a pentadentate ligand with all these metallic ions. The values of the difference rise regularly from manganese to nickel, but for copper the difference is rather small, due to the fact that the complex [Cu tetren]²⁺ is probably less distorted than the triethylenetetramine complex. The tetragonality factors, as defined by Jørgensen,¹⁸ of the complexes [Cu trien]²⁺ and [Cu tetren]²⁺, 1.66¹⁹ and 1.40, respectively, are calculated from the spectra.

The difference $\Delta H_{\text{Zn tetren}} - \Delta H_{\text{Zn trien}}$ is exceptionally large, and this confirms the hypothesis previously advanced that the zinc complexes can be less hydrated. Thus it is reasonable to suppose that the complex [Zn tetren]²⁺ does not contain a molecule of water in the primary co-ordination sphere.

It is interesting to compare the heats of formation of the tetraethylenepentamine complexes of cobalt, nickel, copper, and zinc with the corresponding values of the complexes with the monoprotonated ligand [pentenH]⁺¹.¹ The values are very similar, the greatest

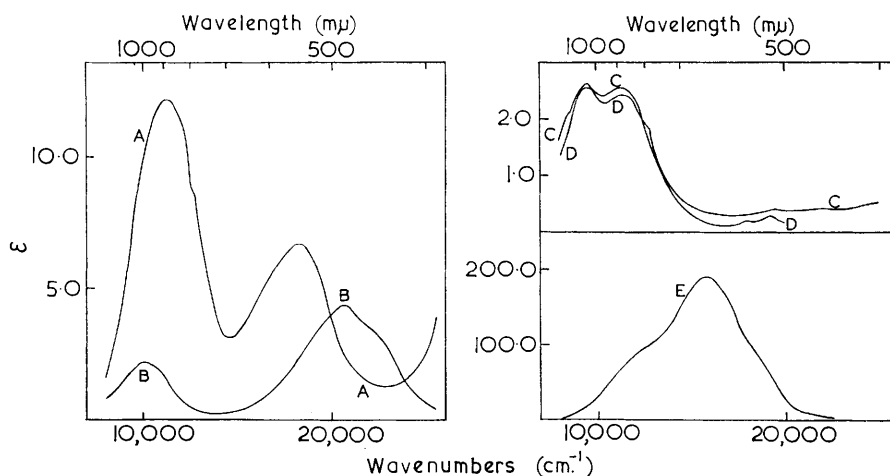


FIG. 3. Absorption spectra of: (A) [Ni tetren]²⁺, (B) [Co tetren]²⁺, (C) [Fe tetren]²⁺, (D) [Fe den₂]²⁺, (E) [Cu tetren]²⁺ in aqueous solution.

difference being only 0.8 kcal. mole⁻¹ (with nickel) in spite of differences in the nature of the amine groups in the two ligands and of the presence of a positive charge in one of them.

The heat of formation of [Fe tetren]²⁺ is 4.25 kcal. mole⁻¹ less than that of the hexa-co-ordinate [Fe den₂]²⁺ but, on the other hand, the spectra of the two complexes are similar (Fig. 3). The small shift of the frequency of the first absorption band towards that of the hexa-aquo ion follows the rule of the average environment.²⁰

The entropies of formation of the tetraethylenepentamine complexes are all positive, varying from a minimum of 14.5 cal. deg.⁻¹ mole⁻¹ for the cobalt complex to a maximum of 22.5 cal. deg.⁻¹ mole⁻¹, for the zinc complex. The high value for the zinc complex further confirms the hypothesis already mentioned that the complex [Zn tetren]²⁺ is not hydrated very much.

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¹⁸ Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 1362.

¹⁹ Paoletti, Ciampolini, and Sacconi, *J.*, 1963, 3589.

²⁰ Tsuchida, *Bull. Chem. Soc. Japan*, 1938, **13**, 388, 436; Tsuchida and Kobayashi, *ibid.*, 471.