tal rotation result in *d* and *l* forms of the molecule. The thermodynamic functions are tabulated in Table IX. Some entries in the table are given to more significant figures than is justified by their absolute accuracy, in order to retain internal consistency among the different functions.

TABLE IX

THERMODYNAMIC FUNCTIONS OF 2,3-DITHIABUTANE

T, °K.	$(H_0^0 - F_T^0)$ cal./deg./mole	$H_T^0 - H_0^0$ kcal./mole	S cal./deg./mole	C_p^0 cal./deg./mole
298.16	64.64	4.732	80.51	21.97
300	64.72	4.769	80.62	22.04
400	69.58	7.164	87.49	25.81
500	73.81	9.915	93.64	29.23
600	77.56	13.00	99.22	32.20
700	81.02	16.35	104.37	34.75
800	84.25	19.93	109.16	36.96
900	87.27	23.73	113.63	38.86
1000	90.13	27.71	117.84	40.53

Summary

The heat capacity of 2,3-dithiabutane has been measured over the temperature range 13 to 350°K. The triple point (188.44°K.) and heat of fusion (2197.1 ± 0.1 cal./mole) were determined. The vapor pressure has been measured over the temperature range 0 to 130° and the following equation was found to fit the vapor pressure data: $\log_{10} p$ (mm.) = 6.97792 − 1346.342/(t + 218.863). The normal boiling point is 109.75°; the heat of vaporization calculated from the vapor pressure data is 9,181 ± 75 cal./mole at 298.16°K. The entropy of the liquid is 56.26 ± 0.10 cal./deg./mole and the entropy of the ideal gas at one atmosphere pressure is 80.54 ± 0.30 cal./deg./mole, both at 298.16°K.

A vibrational assignment has been made for 2,3-dithiabutane with the aid of normal coördinate calculations. Internal rotation about the S–S bond is highly restricted; a 9500 cal./mole two-fold potential barrier was used for thermodynamic calculations. The barrier height for methyl rotation was found to be 1140 cal./mole. Values of the free energy function, heat content, entropy, and heat capacity were calculated by the methods of statistical mechanics for selected temperatures up to 1000°K.

BARTLESVILLE, OKLA. RECEIVED OCTOBER 14, 1949

[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY OF THE TULANE UNIVERSITY OF LOUISIANA]

Dissociation Constants of Polyethyleneamines[1,2]

BY HANS B. JONASSEN, R. BRUCE LEBLANC, A. W. MEIBOHM AND RUTH M. ROGAN

The acid–base dissociation constants of ethylenediamine (abbreviated to en) and the complexity constants of some of its complexes with metal ions have been measured.[3,4]

The three next higher, straight chain members of this polyethyleneamine series are now available in a technical grade,[5] and this paper reports the determination of their acid–base dissociation constants by the method of Bjerrum.[3]

Calculation of Constants

The dissociation constants or "hydrolysis" constants for diethylenetriamine (abbreviated di en) are determined by the following equilibria present in aqueous solution:

$$\text{di enH}_3^{+3} \rightleftarrows \text{di enH}_2^{+2} + \text{H}^+$$

$$K_1 = [\text{di enH}_2^{+2}][\text{H}^+]/[\text{di enH}_3^{+3}] \quad (1)$$

$$\text{di enH}_2^{+2} \rightleftarrows \text{di enH}^+ + \text{H}^+$$

$$K_2 = [\text{di enH}^+][\text{H}^+]/[\text{di enH}_2^{+2}] \quad (2)$$

$$\text{di enH}^+ \rightleftarrows \text{di en} + \text{H}^+$$

$$K_3 = [\text{di en}][\text{H}^+]/[\text{di enH}^+] \quad (3)$$

These constants can be calculated from pH measurements of solutions containing known amounts of di en and a mineral acid.

Throughout this discussion, activity and concentration are used interchangeably. Since the ionic strength of all solutions is very high and is maintained constant, the activity coefficients will be assumed to be constant.

Equations can be derived relating the concentration of the amine, the concentration of HNO_3, and the pH to the dissociation constants of the amines. The following symbols are used in the derivation of these equations:

C_{HNO_3} = total concentration of nitric acid in the solution

C_{dien} = total concentration of di en in the solution

$$C_{dien} = [\text{di en}] + [\text{di enH}^+] + [\text{di enH}_2^{+2}] + [\text{di enH}_3^{+3}] \quad (4)$$

$$C_s = C_{HNO_3} - [\text{H}^+] + [\text{OH}^-] \quad (5)$$

$$C_s = [\text{di enH}^+] + 2[\text{di enH}_2^{+2}] + 3[\text{di enH}_3^{+3}] \quad (6)$$

$$n = C_s/C_{dien} \quad (7)$$

Substituting the values of C_s and C_{dien} into (7), the following equation is obtained

$$\bar{n} = \frac{[\text{di enH}^+] + 2[\text{di enH}_2^{+2}] + 3[\text{di enH}_3^{+3}]}{[\text{di en}] + [\text{di enH}^+] + [\text{di enH}_2^{+2}] + [\text{di enH}_3^{+3}]} \quad (8)$$

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[1] In part from the thesis submitted by R. Bruce LeBlanc to the Graduate School of the Tulane University of Louisiana in February, 1949, in partial fulfillment of the requirements for the degree of Master of Science.

[2] Presented, in part, before the General Technical Session of the Fourth Annual Southwest Regional meeting of the American Chemical Society in December, 1948, at Shreveport, Louisiana.

[3] J. Bjerrum and P. Anderson, *K. Danske Vidensk. Selsk. Math-Fys. Medd.*, **22**, No. 7, 1945.

[4] G. A. Carlson, *et al.*, THIS JOURNAL, **67**, 1334 (1945).

[5] Carbide and Carbon Chemicals Corporation, *Synthetic Organic Chemicals*, 12th edition, 74 (1945).

A combination of (1), (2), (3) and (8) gives

$$\bar{n} = \frac{K_1K_2[\mathrm{H}^+] + 2K_1[\mathrm{H}^+]^2 + 3[\mathrm{H}^+]^3}{K_1K_2K_3 + K_1K_2[\mathrm{H}^+] + K_1[\mathrm{H}^+]^2 + [\mathrm{H}^+]^3} \qquad (9)$$

Solving (9) for K_1 and converting to negative logarithms

$$pK_1 = p\mathrm{H} + \log\frac{\bar{n} - 2}{3 - \bar{n}} + \log\left(1 + \frac{K_2[\mathrm{H}^+](\bar{n} - 1) + K_2K_3\bar{n}}{[\mathrm{H}^+]^2(\bar{n} - 2)}\right) \qquad (10)$$

If $K_2 \ll [\mathrm{H}^+]$ and $\bar{n}$ is appreciably greater than two, the last term is negligible and (10) becomes

$$pK_1 = p\mathrm{H} + \log\frac{\bar{n} - 2}{3 - \bar{n}} \qquad (11)$$

Solving (9) for K_2

$$K_2 = \frac{[\mathrm{H}^+]^2(2 - \bar{n})}{[\mathrm{H}^+](\bar{n} - 1) + \bar{n}K_3} + \frac{[\mathrm{H}^+]^3(3 - \bar{n})}{K_1[\mathrm{H}^+](\bar{n} - 1) + \bar{n}K_1K_3} \qquad (12)$$

If $[\mathrm{H}^+]^2/K_1 \ll K_2$ and if $\bar{n}$ is appreciably greater than one, the last term is negligible. Equation (12) becomes

$$pK_2 = p\mathrm{H} + \log\frac{\bar{n} - 1}{2 - \bar{n}} + \log\left(1 + \frac{\bar{n}K_3}{[\mathrm{H}^+](\bar{n} - 1)}\right) \qquad (13)$$

Solving (9) for K_3

$$K_3 = \frac{[\mathrm{H}^+](1 - \bar{n})}{\bar{n}} \times \frac{K_2(1 - \bar{n}) + (2 - \bar{n})[\mathrm{H}^+]}{(1 - \bar{n})K_2} + \frac{[\mathrm{H}^+]^3(3 - \bar{n})}{K_1K_2\bar{n}} \qquad (14)$$

If $[\mathrm{H}^+]/K_1K_2 \ll K_3$ and if $\bar{n}$ is appreciably. greater than zero, the last term of the equation is negligible. On conversion to negative logarithms

$$pK_3 = p\mathrm{H} + \log\frac{\bar{n}}{1 - \bar{n}} - \log\left(1 + \frac{(2 - \bar{n})[\mathrm{H}^+]}{(1 - \bar{n})K_2}\right) \qquad (15)$$

It is seen that for measurement of pK_1, $\bar{n}$ must be less than three and greater than two; for pK_2, less than two and greater than one; for pK_3, less than one.

Similarly equations for the constants of tri en can be derived. The following are the simplified equations

$$pK_1 = p\mathrm{H} + \log\frac{\bar{n} - 3}{4 - n} \qquad (16)$$

$$pK_2 = p\mathrm{H} + \log\frac{\bar{n} - 2}{3 - \bar{n}} + \log\left(1 + \frac{K_3(\bar{n} - 1)}{[\mathrm{H}^+](\bar{n} - 2)}\right) \qquad (17)$$

$$pK_3 = p\mathrm{H} + \log\frac{\bar{n} - 1}{2 - \bar{n}} + \log\left(1 + \frac{K_4\bar{n}}{[\mathrm{H}^+](\bar{n} - 1)}\right) \qquad (18)$$

$$pK_4 = p\mathrm{H} + \log\frac{\bar{n}}{1 - \bar{n}} - \log\left(1 + \frac{(2 - \bar{n})[\mathrm{H}^+]}{(1 - \bar{n})K_3}\right) \qquad (19)$$

The limits of $\bar{n}$ are similar to those for dien and are obvious from the equations.

Experimental

Technical grade amines purchased from Carbide and Carbon Chemicals Corporation were redistilled *in vacuo* from metallic sodium. Di en distilled at 65–67° under 1 mm. of pressure; tri en at 108–110° under 1 mm. of pressure. It was found that this treatment did not sufficiently purify the amines. However, their acid salts, fractionally crystallized from cold 95% alcohol, gave pure products.

I. **Purification of Diethylenetriamine.**—About 300 g. of distilled amine was dissolved in about 750 ml. of 95% ethanol. One hundred and fifty ml. of 8.5 *M* hydrochloric acid in ethanol was added and the mixture was cooled to 0° in an ice-bath. The white precipitate formed was removed and discarded. Again 150 ml. of 8.5 *M* hydrochloric acid in ethanol was added. On cooling to 0° a white crystalline precipitate formed. This precipitate was washed with ether and dried by suction. This precipitate proved to be di en monohydrochloride. Aqueous stock solutions, about 1 molar in concentration of di en monohydrochloride, were prepared and standardized potentiometrically against standard 1 molar nitric acid.

The di en monohydrochloride is so extremely hygroscopic that chloride determinations or other analyses were not considered feasible, but the titration data indicated that the di en monohydrochloride was better than 99.5% pure.

Attempts to prepare and purify the mononitrate salt of di en met with failure.

II. **Purification of Triethylenetetramine.**—A solution of 160 g. of distilled triethylenetetramine in 500 ml. of 95% ethanol maintained at 0–10° was treated by dropwise addition of 60 ml. of concentrated nitric acid. The white precipitate was removed. A second fraction was precipitated by addition of 55 ml. of concentrated nitric acid.

Four recrystallizations of the second fraction from ethanol afforded white plates. Potentiometric titration showed that the compound consists of 2 moles of nitric acid per mole of amine.

III. **Preparation of Solutions.**—The di en monohydrochloride and the tri en di-nitrate were neutralized with standard potassium hydroxide solution for the preparation of solutions for the measurement of the acid–base constants. These solutions, of approximately constant ionic strength, were 0.1 molar in barium chloride, 0.1 molar in nitric acid, and of varying concentration in amine. Standard potassium nitrate solution was added to make the sum of the potassium nitrate concentration and the potassium chloride concentration (since the di en solution contained potassium chloride) 1 molar. The concentration of di en varied from about 0.033 to 0.050 for measurement of *p* 0.050 to 0.100 for pK_2; and 0.10 to 0.20 for pK_3.

The molarity of tri en varied from about 0.0025 to 0.0033 for measurement of pK_1; 0.033 to 0.050 for pK_2; and 0.050 to 0.100 for pK_3; and 0.10 to 0.14 for pK_4.

The required range of $\bar{n}$ was obtained by keeping the concentration of nitric acid constant and varying the concentration of amine. An approximate calculation of n can be made from the concentrations of the acid and the amine since: $\bar{n}$ = (approx.) $C_{\mathrm{HNO_3}}/C_{\mathrm{amine}}$.

The concentration of nitric acid was 0.1 molar in all cases except in the measurement of pK_1 for tri en. Because tri en decomposes in very acid solution, 0.01 *M* nitric acid was used for these measurements.

After the *p*H of the solution is measured C_s can be calculated using equation (5). In all cases $[\mathrm{OH}^-]$ was negligible as was $[\mathrm{H}^+]$ in most cases. After C_s is calculated, $\bar{n}$ can be calculated accurately using equation (6).

All *p*H measurements were made with a Beckman Model G *p*H meter and a glass electrode. Beckman buffer solutions, *p*H's of 4, 7 and 10, were used to standardize the instrument. The solutions were maintained in a constant temperature bath at 30 ± 0.2° and 40 ± 0.2°.

Discussion

Ethylenediamine can be standardized with methyl orange as the indicator. For the higher members of the series no indicator is suitable. Only electrometric titrations give reproducible results.

All the assumptions previously made in deriving the equations for di en and tri en were found to be valid within the limits of the precision and accuracy of the results. The terms of the equations which were neglected affect the values of the pK's in the third decimal place or beyond.

Equations (11), (13) and (15) were used for calculations of the constants of di en; equations (16), (17), (18) and (19) for the constants of tri en.

Table I

Dissociation Constants of Di en at 30°

In all cases: $C_{BaCl_2} = 0.100\ M$ $C_{KNO_3} + C_{KCl} = 1.00\ M$

A. Determination of pK_1

C_{dien}	C_s	$\bar{n}$	pH	$\log\frac{\bar{n}-2}{3-\bar{n}}$	pK_1
0.03572	0.1001	2.802	4.18	+0.61	4.79
.03605	.1000	2.774	4.26	+ .53	4.79
.03709	.0999	2.693	4.41	+ .35	4.76
.03824	.1002	2.620	4.55	+ .21	4.76
.03851	.0999	2.594	4.60	+ .17	4.77
.03974	.1001	2.519	4.73	+ .03	4.76
.04009	.1001	2.497	4.78	− .01	4.77
.04172	.1001	2.399	4.96	− .18	4.78
.04194	.1003	2.392	4.97	− .19	4.78
.04538	.1051	2.316	5.11	− .34	4.77
.04397	.1001	2.277	5.19	− .42	4.77
.04354	.0950	2.182	5.45	− .65	4.80
				Av.	4.78

B. Determination of pK_2

$$\Delta_1 = \log\left(1 + \frac{\bar{n}K_3}{(\bar{n}-1)[\text{H}^+]}\right)$$

C_{dien}	C_s	$\bar{n}$	pH	$\log\frac{\bar{n}-1}{2-\bar{n}}$	Δ_1	pK_2
0.0557	0.1001	1.797	8.60	+0.59	+0.04	9.23
.0580	.1000	1.723	8.73	+ .42	+ .06	9.21
.0589	.1000	1.699	8.78	+ .37	+ .07	9.22
.0632	.1007	1.594	8.95	+ .17	+ .11	9.23
.0644	.1001	1.555	9.00	+ .10	+ .12	9.22
.0667	.1000	1.500	9.09	.00	+ .15	9.24
.0684	.1001	1.463	9.11	− .06	+ .17	9.22
.0715	.1001	1.399	9.19	− .18	+ .21	9.22
.0728	.1001	1.375	9.21	− .22	+ .22	9.21
.0769	.1000	1.301	9.30	− .37	+ .30	9.23
.0834	.1001	1.200	9.40	− .60	+ .44	9.24
.0837	.1002	1.198	9.40	− .61	+ .44	9.23
					Av.	9.23

C. Determination of pK_3

$$\Delta_2 = \log\left(1 + \frac{(2-\bar{n})[\text{H}^+]}{(1-\bar{n})K_2}\right)$$

C_{dien}	C_s	$\bar{n}$	pH	$\log\frac{\bar{n}}{1-\bar{n}}$	Δ_2	pK_3
0.1114	0.1003	0.900	9.68	+0.95	−0.67	9.96
.1142	.1000	.876	9.70	+ .85	− .61	9.94
.1191	.1001	.840	9.72	+ .72	− .52	9.92
.1283	.1001	.780	9.79	+ .55	− .40	9.94
.1348	.1022	.758	9.83	+ .50	− .36	9.97
.1390	.1001	.720	9.84	+ .41	− .33	9.92
.1521	.1004	.660	9.90	+ .29	− .27	9.92
.1554	.0999	.643	9.92	+ .26	− .25	9.93
.1668	.1001	.600	9.97	+ .18	− .21	9.94
.1764	.0997	.565	10.01	+ .11	− .19	9.93
.1855	.1001	.540	10.02	+ .07	− .18	9.91
.1972	.0998	.506	10.10	+ .01	− .15	9.96
					Av.	9.94

Table I shows the values obtained for pK_1, pK_2, and pK_3 of di en. The simplified equations were used in calculations of these constants. Calculations of pK_1 are independent of pK_2 and pK_3 because pK_1 differs from pK_2 and pK_3 by more than four pK units. Since pK_2 and pK_3 differ from each other by less than one pK unit, equations used to calculate either one must involve the value of the other.

Table II shows the values obtained for the four constants of tri en. Again the simplified equations were used for calculations since the terms neglected are too small to affect the value

Table II

Dissociation Constants of Tri en at 30°

In all cases $C_{KNO_3} = 1.00\ M$ and $C_{BaCl_2} = 0.100\ M$

A. Determination of pK_1

C_{trien}	C_s	$\bar{n}$	pH	$\log\frac{\bar{n}-3}{4-\bar{n}}$	pK_1
0.002415	0.00917	3.798	3.27	+0.60	3.87
.002508	.00937	3.736	3.47	+ .45	3.92
.002601	.00948	3.644	3.63	+ .26	3.89
.002693	.00956	3.550	3.81	+ .09	3.90
.002879	.00964	3.348	4.16	− .27	3.89
				Av.	3.89

B. Determination of pK_2

$C_{HNO_3} = C_s = 0.0991$ $\quad \Delta_3 = \log\left(1 + \frac{K_3(\bar{n}-1)}{[\text{H}^+](\bar{n}-2)}\right)$

C_{trien}	$\bar{n}$	pH	$\log\frac{\bar{n}-2}{3-\bar{n}}$	Δ_3	pK_2
0.03715	2.666	6.67	+0.30	0.00	6.97
.03901	2.541	6.94	+ .07	.00	7.01
.03994	2.481	7.06	− .03	.00	7.03
.04086	2.425	7.15	− .13	+ .01	7.03
.04273	2.319	7.32	− .33	+ .02	7.01
.04366	2.270	7.42	− .43	+ .02	7.01
				Av.	7.01

C. Determination of pK_3

$C_{HNO_3} = C_s = 0.0991$ $\quad \Delta_4 = \log\left(1 + \frac{K_4\bar{n}}{[\text{H}^+](\bar{n}-1)}\right)$

C_{trien}	$\bar{n}$	pH	$\log\frac{\bar{n}-1}{2-\bar{n}}$	Δ_4	pK_3
0.0650	1.524	9.17	+0.04	+0.16	9.37
.0697	1.423	9.27	− .14	+ .22	9.35
.0743	1.333	9.36	− .30	+ .29	9.35
.0790	1.255	9.44	− .47	+ .38	9.35
.0836	1.185	9.51	− .64	+ .50	9.37
.0882	1.123	9.56	− .85	+ .65	9.36
				Av.	9.36

D. Determination of pK_4

$C_{HNO_3} = C_s = 0.0991$ $\quad \Delta_5 = -\log\left(1 + \frac{(2-\bar{n})[\text{H}^+]}{(1-\bar{n})K_3}\right)$

C_{trien}	$\bar{n}$	pH	$\log\frac{\bar{n}}{1-\bar{n}}$	Δ_5	pK_4
0.1115	0.889	9.77	+0.90	−0.69	9.98
.1161	.854	9.81	+ .77	− .57	10.01
.1208	.821	9.83	+ .66	− .51	9.98
.1254	.790	9.85	+ .58	− .46	9.97
.1301	.762	9.89	+ .51	− .40	10.00
.1347	.736	9.91	+ .45	− .37	9.99
				Av.	9.99

of the pK's. Calculations of pK_1 are independent of pK_2, pK_3 and pK_4 because pK_1 differs from pK_2 by over three pK units. Only in the solutions in which $\bar{n}$ is less than 2.5 is the calculation of pK_2 affected very slightly by the value of pK_3, because pK_2 differs from pK_3 by approximately 2.4 units. Since pK_3 and pK_4 differ by only 0.6 pK unit, equations used to calculate either one must involve the value of the other.

Tri en decomposes in very acid solutions. The solutions turn brown and the pH varies. Measurements of pK_1, therefore, were made in solutions 0.01 molar in nitric acid instead of 0.1 molar. Determinations of pK_2, pK_3, and pK_4 were obtained from solutions 0.1 molar in nitric acid.

Table III

Dissociation Constants at 40° and Heats of Neutralization of Di en and Tri en

	pK	ΔH, kcal.
	Di en	
pK_1	4.59	− 8.2
pK_2	8.94	−12.6
pK_3	9.68	−11.7
	Tri en	
pK_1	3.76	− 5.6
pK_2	6.79	− 9.6
pK_3	9.14	− 9.6
pK_4	9.76	−10.0

Table III gives the values for the pK's of di en and tri en at 40°, and heats of neutralization calculated from the equation

$$d \ln K/dT = \Delta H/RT^2$$

Undoubtedly, the values for the heats of neutralization are no better than the accuracy to which the change in pK with temperature is known.

The above values, however, are of the right order of magnitude, which indicates that the pK values are correct within the limits of the accuracy of the pH determination.

Work is being continued in this Laboratory on the purification of tetraethylenepentamine and the determination of its acid-base constants.

Summary

1. A method of purification of diethylenetriamine and triethylenetetramine is described.
2. Acid-base dissociation constants of diethylenetriamine and triethylenetetramine have been determined at 30 and 40°.
3. Approximate heats of neutralization of these bases have been calculated from the acid-base constants at 30 and 40°.

New Orleans 15, La. Received April 9, 1949

[Contribution from the Noyes Laboratory of Chemistry of the University of Illinois and from the Chemical Laboratory of Northwestern University]

The Stereochemistry of Complex Inorganic Compounds. X. The Stereoisomers of Dichlorobis-(ethylenediamine)-platinum(IV) Chloride[1]

By Fred Basolo, John C. Bailar, Jr., and Betty Rapp Tarr[2]

Dichlorobis-(ethylenediamine)-platinum (IV) chloride has been reported by several investigators, all of whom obtained it by oxidation of bis-(ethylenediamine)-platinum(II) ion. Tschugajeff and Chlopin[3] used ozone and hydrochloric acid, while Grinberg and Ptitsuin[4] employed potassium permanganate. The latter work is open to question, as the product was not analyzed. Kurnakow[5] reported that $[Pt\,en_2Cl_2]\,Cl_2$[6] is formed as an orange-yellow, insoluble crystalline material when $[Pt\,en_2]Cl_2$ is treated with chlorine. However, he did not analyze the product. Schleicher, Henkel and Spies[7] got no orange salt when they chlorinated $[Pt\,en_2]Cl_2$, but obtained several pale yellow hydrates of $[Pt\,en_2Cl_2]\,Cl_2$. We have been able to repeat Kurnakow's experiment without difficulty, and to show that the orange product is $[Pt\,enCl_4]$. If care is taken to avoid prolonged action of an excess of chlorine, the bis-ethylenediamine compound described by Schleicher is obtained.

Schleicher and his co-workers believed that the $[Pt\,en_2Cl_2]\,Cl_2$ obtained in their chlorination experiments had the *trans* configuration. They based this conclusion upon the similarity of the material with $[Pt\,en\,py_2Cl_2]\,Cl_2$, the configuration of which they deduced from its reactions with ethylenediamine. This conclusion has been attacked by Chernyaev and Rubinshtein.[8] They argue that the compound which Schleicher used in his proof of structure was not $[Pt\,en\,py_2Cl_2]\,Cl_2$ but was instead $[Pt\,enCl_4]\cdot 2py$.

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[1] Presented before the Physical and Inorganic Division at the 116th meeting of the American Chemical Society, Atlantic City, N. J., September 18-23, 1949.

[2] Most of the work reported in this article was taken from the doctorate theses of Betty Rapp (1941) and Fred Basolo (1943). The remainder was done by Mr. Basolo at Northwestern University.

[3] Tschugajeff and Chlopin, *Z. anorg. allgem. Chem.*, **151**, 264 (1926).

[4] Grinberg and Ptitsuin, *Ann. inst. platine*, **11**, 77 (1933).

[5] Kurnakow, *Z. anorg. Chem.*, **17**, 226 (1898).

[6] The following symbols are used: en = ethylenediamine and py = pyridine.

[7] Schleicher, Henkel and Spies, *J. prakt. Chem.*, **105B**, 31 (1922).

[8] Chernyaev and Rubinshtein, *Ann. inst. platine*, **11**, 63 (1933).