

Stability Constants of Transition Ion Tetramines¹

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Formation constants have been determined for a wide variety of amines with transition metal ions,² as for example 1,3-propanediamine³ and its derivatives.^{4,5}

In the present study data have been extended to include *N,N'*-bis(2-aminoethyl)-1,3-propanediamine and *N,N'*-bis(3-aminopropyl)-1,3-propanediamine.

Experimental

Reagents

N,N'-bis(2-aminoethyl)-1,3-propanediamine (Eastman Organic Chemicals, Rochester, N.Y.), AETH, $n_D = 1.4935$ at 25 °C; reported $n_D = 1.4953$ at 20 °C,⁶ was purified by generating the tetrahydrochloride as described by Walton⁷ (Calc: C, 27.47; H, 7.90; N, 18.30. Found:⁸ C, 28.53; H, 8.04; N, 18.19) and passing a solution of the tetrahydrochloride through a column packed with Fisher Analytical Grade Amberlite IRA-40 ion exchange resin converted to the basic form with 1*N* NaOH solution; 88% of the tetrahydrochloride was converted to the amine.

N,N'-bis(3-aminopropyl)-1,3-propanediamine (Eastman Organic Chemicals, Rochester, N.Y.), APRO, $n_D = 1.4890$ at 25 °C; reported⁶ $n_D = 1.4907$ at 20 °C was purified by the same procedure used for AETH. The tetrahydrochloride (Calc: C, 32.35; H, 8.44; N, 16.77. Found:⁸ C, 33.06; H, 8.32; N, 16.42) was passed through a Fisher Analytical Grade Amberlite IRA-40 ion exchange column converted to the basic form as described above; 98% of the tetrahydrochloride was converted to the amine.

The metal perchlorate solutions used were prepared without further purification from reagent grade salts from G. Frederick Smith Co., Columbus, Ohio, and were analyzed by standard analytical techniques using EDTA.

The perchloric acid used was prepared from perchloric acid supplied by J. T. Baker Chemical Co., Phillipsburg, N.J. and standardized against tris(hydroxymethyl)aminomethane.

Procedure and Calculation Methods

The titration procedure was essentially that described by Goldberg⁹ except that an Instrumentation Delta Matic pH meter, model 135A, was employed and no Ba(ClO₄)₂ was used in the protonation

TABLE I. Logarithms of Formation Constants.

	n of logK _n	AETH	APRO
H ⁺	1	10.02 ± 0.02	10.54 ± 0.02
	2	9.16 ± 0.03	9.60 ± 0.02
	3	6.86 ± 0.11	8.06 ± 0.02
	4	5.22 ± 0.03	6.34 ± 0.05
Cu ²⁺	1	23.05 ± 0.06	16.48 ± 0.01
Ni ²⁺	1	16.15 ± 0.02	10.11 ± 0.01
Zn ²⁺	1	12.38 ± 0.02	9.12 ± 0.01
Co ²⁺	1	12.36 ± 0.03	7.42 ± 0.01
	2	3.34 ± 0.11	2.74 ± 0.05

reactions. The calculation procedure was described previously.⁹ It was necessary to employ subroutine SIMQ in computing solutions to $N = 4$ in the IBM-360 program used in calculating the values of the various K 's. The 95% confidence intervals were determined by the method of Youden.¹⁰

Results

The results are tabulated in Table I. The ninety-five percent confidence intervals are given.

Discussion

The protonation constants of APRO are greater than those for AETH because of the greater separation of the four nitrogen atoms in the former. The general trend is consistent for the comparison of AETH with triethylenetetramine, trien, which has still smaller protonation constants.¹¹

The formation constants of APRO are uniformly lower than those of AETH. This effect is in full agreement with the higher stability with divalent metal ions of saturated five-membered chelate rings over six-membered chelate rings.¹²⁻¹⁴ The AETH complex has two five-membered chelate rings; the APRO complex has none. The same trends in protonation constants and stepwise formation constants of linear tetramines with transition metal ions can be seen in the recent work done by Paoletti *et al.*¹⁵ The stability of the complexes follows the so-called "natural order".¹⁶ The formation constants follow the order $Co < Ni < Cu > Zn$ with AETH and APRO.

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References

- 1 A portion of a thesis presented by Harold C. Nelson for the degree of Master of Arts, March, 1972.
- 2 L. G. Sillen, "Stability Constants of Metal-Ion Complexes," 2nd ed., London, Chemical Society, 1964, Special Publications no. 17; Supplement no. 1, London, Chemical Society, 1971, Special Publications no. 25.
- 3 C. Bertsch, *J. Am. Chem. Soc.*, **77**, 5605 (1955).
- 4 G. B. Hares, W. C. Fernelius and B. E. Douglas, *J. Am. Chem. Soc.*, **78**, 1816 (1956).
- 5 E. Gonick, W. C. Fernelius and B. E. Douglas, *J. Am. Chem. Soc.*, **77**, 6506 (1955).
- 6 Eastman Organic Chemicals, Quality Control Center, Rochester, N.Y., Private Communication.
- 7 H. F. Walton, "Inorganic Preparations; A Laboratory Manual," Prentice-Hall, New Jersey, 1948, p. 71.
- 8 Alfred Bernhardt, Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen, Fritz-Pregl-Strasse 14-16, West Germany.
- 9 D. E. Goldberg, *J. Chem. Ed.*, **39**, 328 (1962).
- 10 W. J. Youden, "Statistical Methods for Chemists," D. Van Nostrand, New York, 1953, p. 512.
- 11 G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 974 (1950).
- 12 G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **31**, 1029 (1948).
- 13 S. Chabarek and A. E. Martell, "Organic Sequestering Agents." Wiley, N.Y., 1959, p. 129.
- 14 D. C. Weatherburn, E. J. Billo, J. P. Jones and D. W. Margcrum, *Inorg. Chem.*, **9** 1557 (1970).
- 15 P. Paoletti, L. Fabbri and R. Barbucci, *Inorg. Chem.*, **12**, 1861 (1973).
- 16 J. Irving and H. Williams, *Nature*, **162**, 746 (1948).