

TABLE I
FORMATION CONSTANTS OF $(\text{H}_2\text{NCH}_2)_2\text{CHOH}$ WITH VARIOUS METALS IN 1.0 M KNO_3 SOLUTION
Values for $(\text{H}_2\text{NCH}_2)_2\text{CH}_2$ and $(\text{H}_2\text{NCH}_2)_2\text{C}(\text{CH}_3)_2$ included for comparison.

	$(\text{H}_2\text{NCH}_2)_2\text{CHOH}$		$(\text{H}_2\text{NCH}_2)_2\text{CH}_2^6$		$(\text{H}_2\text{NCH}_2)_2\text{C}(\text{CH}_3)_2^6$	
	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2
H^+ , 0°	10.65	9.14	11.60	9.95	11.22	9.07
30°	9.68	8.23	10.54	8.95	10.22	8.18
50°	9.11	7.69	9.92	8.38	9.65	7.55
Ag^{++} , 30°	5.80				4.66	
Co^{++} , 30°	3.90	3.24			4.88	3.07
Ni^{++} , 0°	6.19	4.88	7.00	4.92	7.22	4.99
30°	5.64	4.38			6.59	4.41
50°	5.37	4.01			6.23	4.15
Zn^{++} , 30°	4.60	4.42			5.21	5.20

stants are those given by Carlson, McReynolds and Verhoek.⁵ The calculated constants are given in Table I.

1,3-Diamino-2-propanol is a somewhat weaker base than either 1,3-diaminopropane or 2,2-dimethyl-1,3-propanediamine. The complete agreement in the N values for all three amines (except for Cu^{++}) indicates that the $-\text{OH}$ group is not active in coordination. The complexes of 1,3-diamino-2-propanol with Co^{++} , Ni^{++} and Zn^{++} are less stable than those of 2,2-dimethyl-1,3-diaminopropane with the same ions. Similarly, the Ni^{++} complexes are less stable than those of 1,3-diaminopropane. The system Cu^{++} -1,3-diamino-2-propanol is anomalous in that \bar{n} reaches a maximum value of 1.5.

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

(6) G. B. Hares, W. C. Fernelius and B. E. Douglas, *ibid.*, accepted.

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The Preparation of *cis*- and of *trans*-Dichloro-bis-*l*-propylenediaminecobalt(III) Chloride^{1,2}

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The preparation of *cis*- and of *trans*-dichloro-bis-*l*-propylenediaminecobalt(III) chloride was first reported by Werner and Fröhlich.³ This method was later modified by Bailar and co-workers.⁴ We wish to report a semi-micro preparation which is a further modification of the original procedure. By making a careful study of the acidity requirements and of the procedure for oxidizing cobalt(II) to cobalt(III) the time required has been greatly diminished and the product is obtained without difficulty. The original method often yielded a product which could not readily be converted from *trans* to *cis*, possibly because of a residual acid condition; consequently the product was of questionable purity. The ready conversion from *trans* to *cis* has been considered a good index of purity. Use of 30% H_2O_2 cuts down the original 16 hours of aera-

(1) From the B.S. theses of Misses Joan Busch and Milda Gulbinkas.

(2) Aided by a grant from Research Corporation.

(3) A. Werner and A. Fröhlich, *Ber.*, **40**, 2225 (1907).

(4) J. C. Bailar, Jr., C. A. Stiegman, J. H. Balthis, Jr., and E. H. Huffman, *THIS JOURNAL*, **61**, 2402 (1939).

tion time to about 10 minutes. The original method gave yields from 35 to 45%. This method gives yields of from 45 to 55%.

Experimental

Preparation of the *trans* Form.—A flask containing 3.8 ml. of *l*-propylenediamine (resolved by the method of Baumann⁵ as modified by Bailar and co-workers⁴ and further modified by Jonassen⁶) and 4.76 g. of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was immersed in an ice-bath. While swirling the solution in the reaction vessel 3 ml. of 30% H_2O_2 was added cautiously. On removal from the ice-bath, 25 ml. of concd. HCl (sp. gr. 1.18, 34% HCl) was added slowly. The resulting solution was concentrated to one-third of its original volume by passing a stream of air over it, keeping the temperature below 80°. The green crystals formed, *trans*- $[\text{Co-}l\text{-pn}_2\text{Cl}_2]\text{Cl}$, were separated from the solution by filtration, washed with ether and dried in an oven below 80°.

Conversion to the *cis* Form.—The dried crystals of the *trans* salt were dissolved in a minimum of water and the solution carefully neutralized with dilute (1:4) NH_4OH to a pH of approximately 7. On evaporation of this solution on a steam-cone, purple *cis*- $[\text{Co-}l\text{-pn}_2\text{Cl}_2]\text{Cl}$ formed as a glassy solid. The extreme solubility of the compound in water and the fact that it must be converted to the *cis* form in a neutral solution seems to make the preparation as a glassy solid imperative. Solubility studies made in this Laboratory have failed to yield any solvent from which it may be crystallized. This entire preparation was carried out in less than 4 hours.

(5) G. Baumann, *Ber.*, **28**, 1180 (1895).

(6) H. B. Jonassen, Thesis, University of Illinois, 1946.

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Basic Equilibrium Constants of Nitroguanidine and Nitroaminoguanidine

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The basic equilibrium constants of nitroguanidine and nitroaminoguanidine are extremely small. Consequently accurate determination of these values has not been possible by the usual titrimetric procedures. In connection with a study of the reactions of nitroguanidine in strongly acidic solutions,¹ it was observed that the small peak at 220–225 $m\mu$ increased with increasing acidity. The family of curves obtained showed a sharp isobestic point at 240 $m\mu$ between the minor (225 $m\mu$) and major (265 $m\mu$) absorption peaks, Fig. 1. The 265 $m\mu$ peak did not shift appreciably

(1) W. W. Brandt, J. E. De Vries and E. St. C. Gantz, *Anal. Chem.* **27**, 392 (1955).