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# Synthesis and Chelation Studies of 2,2-Dialkyl-1,3-propanediamines[1]

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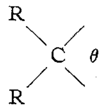
2,2-Dimethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 1,1-di(hydroxymethyl)cyclopropane, 1,1-di(hydroxymethyl)-cyclobutane, 1,1-di(hydroxymethyl)cyclopentane, and 1,1-di(hydroxymethyl)cyclohexane were converted *via* the corresponding methanesulfonates into the bisazides which were reduced to 2,2-dimethyl-1,3-diaminopropane, 2,2-diethyl-1,3-diaminopropane, 1,1-di(aminomethyl)cyclopropane, 1,1-di(aminomethyl)cyclobutane, 1,1-di(aminomethyl)cyclopentane, and 1,1-di(aminomethyl)cyclohexane by lithium aluminum hydride. The first and second acid dissociation constants are listed in Table I. The Cu(II) formation constants in Table II and the Ni(II) formation constants in Table III show that the *gem*-dialkyl-1,3-diamines form more stable complexes than does trimethylenediamine but less stable complexes than ethylenediamine. The lack of an appreciable *gem*-dialkyl effect as compared to other examples involving covalent ring bonds in which the *gem*-dialkyl effect is large is explained by the longer bonds between Cu(II) and Ni(II).

The rates of formation of five- and six-membered ring compounds from acyclic precursors and the stabilities of the cyclic compounds produced are markedly affected by the substitution of alkyl groups on the carbon skeleton involved. When the substituents are on different carbons, effects are observed which depend not only on the alkyl groups but also on the stereochemistry. However, in this paper we will be concerned only with geminal substitution of like groups.

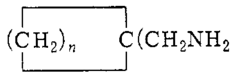
The *gem*-dialkyl effect[4] (in most cases methyl groups are involved) has been attributed to the effect of the size of the groups on the angle $\theta$ included by the two bonds of the carbon atom not attached to the *gem*-dialkyl groups.[5,6] Alternately, the *gem*-dialkyl effect has been attributed, in part, to differences in entropy of the open chain and cyclic structures.[7,8]



In several studies, the magnitude of the *gem*-dialkyl effect has been increased by increasing the size of the *gem*-alkyl groups.[9] In work from our laboratory we have been particularly interested in kinetic studies on hydrolysis of acetals and ketals of 2,2-disubstituted 1,3-propanediols and in the equilibrium constants for formation of acetals and ketals from a number of diols.[9c,10]

In most of the examples cited in the above references cyclization and ring opening involved covalent bond formation and bond cleavage. We thought it of interest to study the *gem*-dialkyl effect in reactions which involve complexing of Cu(II) and Ni(II) with diamines because a different type of bond is involved in formation of these chelates. The formation constants of Cu(II) and Ni(II) with ethylenediamine, 1,2-propylenediamine, and other methyl- and phenyl-substituted ethylenediamines have been reported.[11] The only example of the *gem*-dialkyl effect has been provided by the demonstration that the Cu(II) and Ni(II) complexes of 2,2-dimethyl-1,3-propanediamine are more stable than the corresponding complexes of 1,3-propanediamine,[12] whereas the Cu(II) and Ni(II) complexes of 1,3-propanediamine are less stable than those of ethylenediamine.[13]

In this paper we report on the complexes formed from Cu(II) and Ni(II) with the ethylenediamine (**1**), 1,3-propanediamine (**2**), 2,2-dimethyl-1,3-propanediamine (**3**), 2,2-diethyl-1,3-propanediamine (**4**), 1,1-di(aminomethyl)cyclobutane (**6**), 1,1-di(aminomethyl)cyclopentane (**7**), and 1,1-di(aminomethyl)cyclohexane (**8**).



$(CH_2)_n\,C(CH_2NH_2)_2$

**5**, $n = 2$, **6**, $n = 3$, **7**, $n = 4$, **8**, $n = 5$

The preparation of the desired diamines caused much difficulty as several conventional approaches proved impractical.[14] The successful route is shown in Scheme I and is described in the Experimental Section.

Because the diamines are very hygroscopic and absorb carbon dioxide rapidly on exposure to the atmosphere, all were isolated and stored as dihydrochlorides.

The acid dissociation constants for the diamines were determined and are given in Table I. The formation constants for the nickel(II) and copper(II) complexes were determined by the Calvin–Bjerrum method.[15,16] The average number of ligands bound per metal ion, $\bar{n}$, and the negative log of the concentration of the che-

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[1] This work was supported by Grant 5552X of the National Science Foundation.

[2] To whom correspondence should be addressed.

[3] This work was taken from the M.S. (1967) and Ph.D. (1968) theses of C. R. G. Many studies on the *gem*-dialkyl effect are reviewed in the Ph.D. thesis.

[4] For a discussion see G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956.

[5] R. M. Beesley, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, **107**, 1080 (1915).

[6] C. K. Ingold, *ibid.*, **119**, 305 (1921).

[7] Reference 4, pp 462–470.

[8] N. L. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, 701 (1960).

[9] (a) Rates of hydrolysis of $\beta,\beta$-dialkylglutaric anhydrides: T. C. Bruice and W. C. Bradbury, *J. Amer. Chem. Soc.*, **87**, 4838 (1965). (b) Formation of pyrrolidines from 4-bromo-2,2-dialkylbutylamines: R. F. Brown and N. von Gulick, *J. Org. Chem.*, **21**, 1046 (1956). (c) Rates of hydrolysis of ketals: M. S. Newman and R. J. Harper, Jr., *J. Amer. Chem. Soc.*, **80**, 6350 (1958). (d) Intramolecular hydrogen bonding in 2,2-disubstituted 1,3-propanediols: P. von R. Schleyer, *ibid.*, **83**, 1368 (1961). This article discusses the hypothesis of valency deviation and gives numerous references to the *gem*-dialkyl effect.

[10] (a) M. S. Newman and R. E. Dickson, *ibid.*, **92**, 6880 (1970); (b) S. W. Smith and M. S. Newman, *ibid.*, **90**, 1249, 1253 (1968).

[11] F. Basolo, Y. T. Chen, and K. R. Murmann, *ibid.*, **76**, 956 (1954).

[12] G. B. Hares, W. C. Fernelius, and B. E. Douglas, *ibid.*, **78**, 1816 (1956).

[13] C. R. Bertsch, W. C. Fernelius, and B. P. Block, *J. Phys. Chem.*, **62**, 444 (1958).

[14] Consult the M.S. (1967) and Ph.D. (1968) theses of C. R. Gustafson, The Ohio State University, for details.

[15] M. Calvin and A. B. Martell, "Chemistry of Metal Chelate Compounds," Prentice-Hall, New York, N. Y., 1953, p 179.

[16] J. Bjerrum, "Metal Amine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

SCHEME I

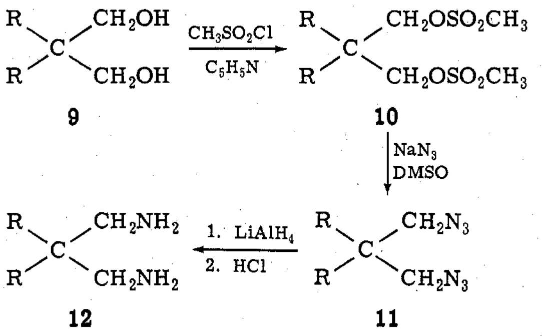

TABLE I

ACID DISSOCIATION CONSTANTS OF AMINES AT 25°

| Amine | $pK_{a_1}$ | $pK_{a_2}$ |
|---|---|---|
| 2,2-dimethyl-1,3-propanediamine | 7.82 | 10.18 |
| 2,2-diethyl-1,3-propanediamine | 7.59 | 10.23 |
| 1,1-di(aminomethyl)cyclopropane | 8.11 | 10.28 |
| 1,1-di(aminomethyl)cyclobutane | 7.80 | 10.05 |
| 1,1-di(aminomethyl)cyclopentane | 7.77 | 10.39 |
| 1,1-di(aminomethyl)cyclohexane | 7.69 | 10.32 |
| ethylenediamine | 6.96 | 9.86 |
| 1,3-propanediamine | 8.36 | 10.52 |

lating species, pR, were calculated for each point in the titration. A graph of $\bar{n}$ *vs.* pR was made for each diamine.

For the copper(II) ion a nearly constant value of $\bar{n} = 2$ was obtained toward the end of each titration. This indicates that a maximum of two bidentate ligands coordinate. The only exception is the 1,3-propanediamine plot, in which a maximum of $\bar{n} = 1.5$ was obtained, which shows that the stability of the bis diamine complex of this ligand is low.

Nickel(II) showed a maximum of $\bar{n} = 2$ for all 2,2-disubstituted 1,3-propanediamines. The ethylenediamine plot showed a maximum of $\bar{n} = 3$. Table II contains the stepwise formation constants for copper(II) and Table III the same for nickel(II) chelates. (The values of pR at $\bar{n} = 0.5$, 1.0, and 1.5 are equal to log $K_1$, log $K_{av}$, and log $K_2$, respectively, and 2.5 and 3.0 are equal to log $K_{av}$ and log $K_3$ for the ethylenediamine plot.)

TABLE II

COPPER(II) FORMATION CONSTANTS AT 25°

| Diamine | Log $K_1$ | Log $K_{av}$ | Log $K_2$ |
|---|---|---|---|
| 2,2-dimethyl-1,3-propanediamine | 9.92 | 8.55 | 7.30 |
| 2,2-diethyl-1,3-propanediamine | 9.94 | 8.60 | 7.36 |
| 1,1-di(aminomethyl)cyclopropane | 10.12 | 8.78 | 7.64 |
| 1,1-di(aminomethyl)cyclobutane | 9.76 | 8.43 | 7.22 |
| 1,1-di(aminomethyl)cyclopentane | 10.15 | 8.70 | 7.56 |
| 1,1-di(aminomethyl)cyclohexane | 10.12 | 8.67 | 7.42 |
| ethylenediamine | 10.50 | 9.72 | 9.02 |
| 1,3-propanediamine | 9.18 | 7.40 | 5.66 |

TABLE III

NICKEL(II) FORMATION CONSTANTS AT 25°

| Diamine | Log $K_1$ | Log $K_{av}$ | Log $K_2$ | Log $K_{av}$ | Log $K_3$ |
|---|---|---|---|---|---|
| 1,1-dimethyl-1,3-propanediamine | 6.28 | 5.20 | 4.16 | | |
| 1,1-diethyl-1,3-propanediamine | 6.54 | 4.30 | 4.06 | | |
| 1,1-di(aminomethyl)-cyclopropane | 6.42 | 5.00 | 4.00 | | |
| 1,1-di(aminomethyl)-cyclobutane | 6.36 | 4.80 | 4.07 | | |
| 1,1-di(aminomethyl)-cyclopentane | 6.60 | 5.40 | 4.30 | | |
| 1,1-di(aminomethyl)-cyclohexane | 6.61 | 5.16 | 3.90 | | |
| ethylenediamine | 7.30 | 6.60 | 5.95 | 5.09 | 4.08 |
| 1,3-propanediamine | 6.18 | | 4.28 | | |

In general the five-membered chelate rings are the most stable in systems with unsubstituted saturated rings.[12,13] A quantitative comparison is possible for the chelation of both nickel(II) and copper(II) ions with 1,3-propanediamine and ethylenediamine. The chelates with the former diamine are approximately 10 times less stable than those with the latter. The enthalpy values favor chelation by 1,3-propanediamine over ethylenediamine, in agreement with the greater basicity of the former diamine. Therefore, the large difference in stability of the chelates of these two diamines must arise from a less-favorable entropy change in the formation of the six-membered ring.[12,13]

The nickel(II) and copper(II) formation constants of the 2,2-dialkylated 1,3-propanediamine and the 1,1-di(aminomethyl)cycloalkanes are slightly greater than those of 1,3-propanediamine and slightly less than those of ethylenediamine. Therefore, the introduction of *gem*-dialkyl groups into 1,3-propanediamine increases the stability of the resulting chelates. This greater stability of the chelates of the dialkylated diamines may be attributed to the entropy change.[12,13]

It was anticipated that the formation constants would vary with substituents on 1,3-propanediamine. The *gem*-dialkyl effect of small rings in acetal and ketal formation and hydrolysis showed[10] that the equilibrium constant is largest for the acetal of 1,1-di(hydroxymethyl)cyclohexane and 1-naphthaldehyde and the smallest for the acetal of 1,1-di(hydroxymethyl)cyclopropane and 1-naphthaldehyde. If the relief of angle strain is an important factor in the stability of the acetals, and the hydrolysis thereof, the most stable ones would be the spirocyclohexyl acetals, and the least stable would be the cyclopropyl one. This order proved correct with the change in equilibrium constants occurring between the cyclopropyl and cyclobutyl acetals and smaller changes progressively involved in the cyclopentyl and cyclohexyl acetals.

No comparative analogies of substituent effect can be made concerning the formation constants of the disubstituted diamine chelates studied. The formation constants of the disubstituted diamines did not vary greatly within the series; that is, increasing the size of the substituent from dimethyl to diethyl and varying the ring size from cyclopropyl to cyclohexyl showed no measurable difference in the stability of the chelates. A possible explanation for the small variations in the values of the formation constants for the disubstituted diamine chelates compared to the corresponding equilibrium constants for cyclic acetal formation from disubstituted 1,3-propanediols lies in the large radius of nickel and copper. The metal–nitrogen bond distance is greater than the carbon–oxygen distance in the cyclic acetals. The nickel–nitrogen (ammonia) bond distance in octahedral $Ni(NH_3)_4(NCS)_2$ has been determined by X-ray crystallographic studies to be 2.15 Å,[17] and the carbon–oxygen bond distance in compar-

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(17) E. K. Iukhno and M. W. Porai-Koshits, *Kristallografiya*, **2**, 239 (1957).

able 1,4-dioxane has been determined by electron diffraction to be 1.42 Å.[18]

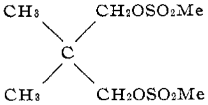
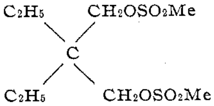
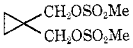
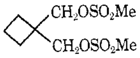
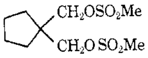
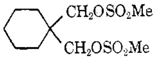
This greater bond distance in the metal complexes may accommodate better any strain that may be introduced into the six-membered ring system by the varying of the C–C–C bond angle due to substitution at the 2 position and hence the *gem*-dialkyl effect is about constant in this series of complexes.

## Experimental Section[19]

**Preparation of Bis(methanesulfonates) (10).**—To a stirred solution at ~5° of 0.30 mol of 2,2-dialkyl-1,3-propanediol (9)[20] in 75 ml of pyridine was added 0.66 mol (75 g) of methanesulfonyl chloride during 30 min (temperature at 5° throughout). After 3 hr at 5° the mixture was poured on ice and the mixture acidified with cold HCl. The crystals were collected, washed with water, and recrystallized from ethanol to give the results shown in Table IV.

TABLE IV

YIELDS AND PHYSICAL CONSTANTS OF DIMETHYLSULFONATES

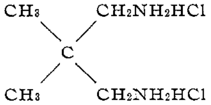
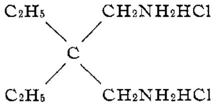
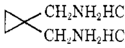
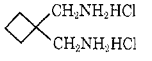
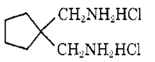
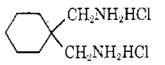
| Product | Yield, % | Mp, °C | Analysis |
|---|---|---|---|
|  | 95 | 70–71 | $C_7H_{16}S_2O_6$<br>Calcd C, 32.3; H, 6.2; S, 24.6<br>Found C, 32.1; H, 6.3; S, 24.4 |
|  | 91 | 94–95 | $C_9H_{20}S_2O_6$<br>Calcd C, 37.5; H, 7.0; S, 22.2<br>Found C, 37.7; H, 7.1; S, 22.0 |
|  | 90 | 58–60 | $C_7H_{14}S_2O_6$<br>Calcd C, 32.6; H, 5.4; S, 24.8<br>Found C, 32.7; H, 5.4; S, 24.6 |
|  | 86 | 72–73 | $C_8H_{16}S_2O_6$<br>Calcd C, 35.3; H, 5.9; S, 23.5<br>Found C, 35.2; H, 5.8; S, 23.5 |
|  | 99 | 91–92 | $C_9H_{18}S_2O_6$<br>Calcd C, 37.8; H, 6.3; S, 22.4<br>Found C, 37.8; H, 6.4; S, 22.3 |
|  | 93 | 67–70 | $C_{10}H_{20}S_2O_6$<br>Calcd C, 40.0; H, 6.7; S, 20.1<br>Found C, 40.1; H, 6.8; S, 20.0 |

**Preparation of 2,2-Dialkyl-1,3-diazidopropanes (11).**—A mixture of 0.10 mol of **10**, 19.5 g (0.3 mol) of sodium azide, and 400 ml of dimethyl sulfoxide was heated with stirring at 65° for 16 hr. The cooled mixture was diluted with 400 ml of water and the crude diazide taken into petroleum ether, bp 30–60°. After washing with water and drying there were obtained (% yield) the following diazides (11) by vacuum distillation (this is a hazardous operation; see footnote 21): 2,2-dimethyl-1,3-diazidopropane (70%), bp 76–78° at 5 mm, 2,2-diethyl- (87%), bp 68–72° at 1 mm, 1,1-di(azidomethyl)cyclopropane (81%), bp 73–74° at 4.8 mm, 1,1-di(azidomethyl)cyclobutane (94%), bp 64–67° at 1.4 mm, 1,1-di(azidomethyl)cyclopentane (94%), bp 72–73° at 0.9 mm, 1,1-di(azidomethyl)cyclohexane (93%), bp 85–87° at 0.8 mm. The infrared and nmr spectra of these compounds were consistent with the proposed structure.

**Preparation of 2,2-Dialkyl-1,3-propanediamine (12).**—After heating a stirred slurry of 11.4 g of lithium aluminum hydride in 500 ml of dry ether for 1 hr a solution of 0.084 mol of diazide (11) in 100 ml of dry ether was added during 3 hr. Gas was evolved copiously on each addition of diazide. The reaction appeared to be over 15 min after the last addition of **11**. After heating 1 hr more, no more gas was evolved. After careful addition of moist ether and 50 ml of water, the solids were filtered and the filtrate was dried over $MgSO_4$. On distillation, the following yields of diamines, **12**, were obtained: 2,2-dimethyl-1,3-propanediamine (65%), bp 75–77° at 8 mm, 2,2-diethyl-1,3-propanediamine (47%), bp 78–80° at 8 mm, 1,1-di(aminomethyl)cyclopropane (64%), bp 77–79° at 15 mm, 1,1-di(aminomethyl)cyclopentane (62%), bp 77–80° at 2 mm, 1,1-di(aminomethyl)cyclohexane (51%), bp 90–93° at 4.8 mm. Since these amines react immediately with carbon dioxide, the vacuum was broken through a KOH tower. The amines were converted quantitatively to the dihydrochlorides by treatment of benzene solutions with dry HCl (Table V). The analyses of these for C, H, N, and Cl were within 0.3% of the theoretical values.[3]

TABLE V

ANALYSES OF DIAMINE DIHYDROCHLORIDES

| Compound | Formula | Analysis |
|---|---|---|
|  | $C_5H_{16}N_2Cl_2$ | Calcd C, 34.3; H, 9.2;<br>N, 16.0; Cl, 40.5<br>Found C, 34.5; H, 9.2;<br>N, 16.1; Cl, 40.5 |
|  | $C_7H_{20}N_2Cl_2$ | Calcd C, 41.4; H, 9.9;<br>N, 13.8; Cl, 34.9<br>Found C, 41.3; H, 10.0;<br>N, 13.8; Cl, 34.8 |
|  | $C_5H_{14}N_2Cl_2$ | Calcd C, 34.7; H, 8.1;<br>N, 16.2; Cl, 40.9<br>Found C, 34.6; H, 8.0;<br>N, 16.2; Cl, 40.6 |
|  | $C_6H_{16}N_2Cl_2$ | Calcd C, 38.5; H, 8.6;<br>N, 14.9; Cl, 37.9<br>Found C, 38.4; H, 8.4;<br>N, 15.0; Cl, 38.0 |
|  | $C_7H_{18}N_2Cl_2$ | Calcd C, 41.8; H, 9.0;<br>N, 13.9; Cl, 35.3<br>Found C, 41.9; H, 9.0;<br>N, 13.7; Cl, 35.4 |
|  | $C_8H_{20}N_2Cl_2$ | Calcd C, 44.6; H, 9.4;<br>N, 13.0; Cl, 32.9<br>Found C, 44.8; H, 9.6;<br>N, 13.1; Cl, 32.9 |

**Potentiometric Titrations.**—The potentiometric titration technique employed was that developed by Bjerrum,[16] and later extended by Calvin and Wilson,[22] and Sen.[23]

The chelation reaction involving the diamine and a divalent metal ion may be represented by the equation

$$M^{2+} + 2RH_2^{2+} \rightleftharpoons M(R)_2 + 4H^+$$

This equation involves the stepwise formation constants of the chelate

$$M^{2+} + RH_2^{2+} \overset{K_1}{\rightleftharpoons} M(R)^{2+} + 2H^+$$

$$M(R)^{2+} + RH_2^{2+} \overset{K_2}{\rightleftharpoons} M(R)_2^{2+} + 2H^+$$

and the acid dissociation constant of the conjugate acid of the complexing species.

$$RH_2^{2+} \overset{K_{a_1}}{\rightleftharpoons} H^+ + RH^+$$

$$RH^+ \overset{K_{a_2}}{\rightleftharpoons} H^+ + R$$

The determination of the formation constants of the chelates was performed experimentally by titrating a known initial concentration of chelating agent and metal ion with standard alkali and following the change in pH potentiometrically. The determinations of the acid dissociation constants of the diamines were performed similarly.

The titrations were made using a Beckman Model "G" pH

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[18] *Chem. Soc., Spec. Publ.*, **No. 11**, M162 (1958).

[19] All melting points were taken on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Elemental analyses by Galbraith Laboratories, Inc., Knoxville, Tenn.

[20] The known diols were prepared essentially as described by S. Searles, Jr., R. G. Nickerson, and W. K. Witsiepe, *J. Org. Chem.*, **24**, 1839 (1959), and had approximately the same properties.

[21] All of the vacuum distillations were done on small portions behind safety glass. Each of the diazides evolved nitrogen slowly on heating at 45–55°. Because of this, no attempts were made to fractionate the azides carefully and no elemental analyses were attempted since G. Swift and D. Swern, *J. Org. Chem.*, **32**, 511 (1967) report that one diazide exploded on attempted analysis for N.

[22] M. Calvin and K. W. Wilson, *J. Amer. Chem. Soc.*, **67**, 2003 (1945).

[23] B. Sen, *Anal. Chim. Acta*, **27**, 515 (1962).

meter equipped with a Beckman E-2 glass and saturated calomel electrode pair. A Pyrex vessel with an outer jacket was used for the titrations. The temperature of the solvent system was kept constant to within 0.1° by circulating water from a constant-temperature bath through the outer jacket of the titration vessel.

A known excess of perchloric acid was added initially to be certain that all the diamine was present as a diammonium ion, and also to repress the extent of initial chelate formation.

The standard sodium hydroxide was stored in polyethylene bottle and standardized against potassium acid phthalate.

Approximately 0.01 *M* stock solutions of metal ions were prepared by dissolving the metal perchlorate, obtained from G. F. Smith Co., in water. The copper(II) solution was standardized by titration with a standard solution of disodium ethylenediaminetetraacetic acid (EDTA) using 1-(2-pyridylazo)-2-naphthol (PAN) as indicator.[24] The nickel(II) solution was standardized by back-titration of its EDTA complex with standard copper solution and PAN as indicator.[24]

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[24] H. A. Flaschka, "EDTA Titrations," Pergamon Press, New York, N. Y., 1959, p 81.

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# Some Tetragonal Cobalt(III) Complexes Containing Tetradentate Macrocyclic Amine Ligands with Different Degrees of Unsaturation

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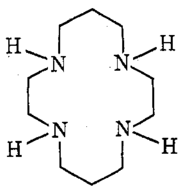
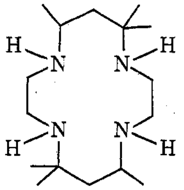
Condensation reactions under highly specific conditions have yielded series of cobalt complexes with two new macrocyclic ligands that vary in the extent of their unsaturation, and hydrogenation has given a related series of derivatives of a fully saturated ligand. All are 14-membered macrocycles containing four nitrogen donors; TIM has 4 imine groups; DIM, 2 imines and 2 secondary amines; and DMC, 4 amines. The syntheses, structures, and properties of the resulting series of cobalt(III) complexes, *trans*-[Co(TIM)$X_2$]Y, *trans*-[Co(DIM)$X_2$]Y, and *trans*-[Co(DMC)$X_2$]Y, are reported for $X^- =$ halide or $NO_2^-$ and $Y^- =$ halide, $ClO_4^-$, or $PF_6^-$. Infrared and pmr spectral studies provide proof of the structures of the macrocyclic ligands in these compounds and the latter has given insight into stereochemical relationships among these complexes. Spectrochemical studies reveal that the ligand field strengths of the macrocycles increase as the degree of unsaturation of the ligand increases. Comparisons with other macrocycles show the relative effect on ligand field strengths of such groups as –N(H)–, N=C, –N=C—C=N–, and py. Voltametric data show clearly that the lower oxidation states of cobalt are stabilized by greater degrees of ligand unsaturation.

## Introduction

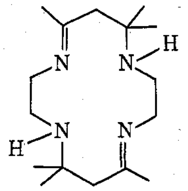
Because of their physical and chemical properties, cobalt(III) complexes are convenient vehicles for the study of the various subtle stereochemical and electronic relationships that accompany the formation of macrocyclic complexes.[1,2] These include formation of cis and trans isomers by the same macrocycle in octahedral complexes (cis and trans referring to the positions of the fifth and sixth ligating groups), the optical activity of coordinated amine functions, possible enhanced ligand field strength because of mechanical constrictive effects, the relationship between ligand field strength and extent and arrangement of ligand unsaturation, special rate effects, and the energetics and consequences of various chelate ring conformations. Early stereochemical studies suggest that most macrocyclic ligands, especially 14-membered ones, favor formation of either the *cis*- or *trans*-diacidotetramine isomers. While the majority of the ligands, *e.g.*, those of structures I–III, appear to favor the trans structure with monodentate extracyclic ligands,[3–6] all can be forced into folded forms to produce cis structures with bidentate extracyclic ligands ($C_2O_4^{2-}$, acac). Perhaps the general preference for the planar structure is related to the action of such restrictive factors as steric interactions of methyl groups in the folded form[7] or inflexibility of unsaturated structures (1,7-CT and others). The fact that the unsubstituted 14-membered ring cyclam will form the cis structure[4] with monodentate ligands supports this point of view. *meso*-CRH (structure IV) readily forms cis and trans isomers.[7] If a flexible ring is too small to encompass


cyclam

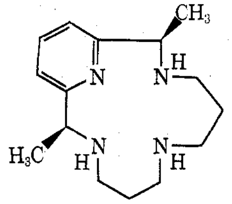
I


1,7-CTH

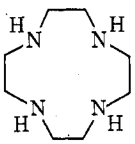
II


1,7-CT

III


meso-CRH

IV


cyclen

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